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Band-gap energy in the random-phase approximation to density-functional theory

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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 $E_g = E^{\mathrm{RPA}}(N+1) + E^{\mathrm{RPA}}(N-1) - 2E^{\mathrm{RPA}}(N)$, where $E^{\mathrm{RPA}}(N)$ 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[1–3] (DFT) is widely used today to calculate the ground-state properties of solids and molecules. The local density approximation[2] (LDA) and the generalized gradient approximation[4] (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.[5] These shortcomings have stimulated the need for fully nonlocal 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,[6,7] Kohn-Sham perturbation theory,[8,9] and the adiabatic-connection fluctuation-dissipation (ACFD) theorem[10,11] within time-dependent DFT.[12–14] 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,[15–17] then to jellium slabs and surfaces;[18–21] the calculation of the ground-state energy surface of simple diatomic molecules[22–25] ($\mathrm{H}_2, \mathrm{N}_2, \ldots$) and solids[26] (Si, Na, …), which 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,[27–29] but misses important short-range correlations.[30] This deficiency can, however, be cured with LDA-like corrections[21,31] or using refined time-dependent DFT kernels.[23,32]

The DFT-RPA exchange-correlation potential $v_{xc}^{\mathrm{RPA}}(\mathbf{r})$ satisfies a complex integral equation known as the linear-response Sham-Schlüter equation.[6,33,34] In Refs. 35–37, we have investigated the asymptotic behavior of the DFT-RPA potential, and we have notably shown that $v_{xc}^{\mathrm{RPA}}(\mathbf{r}) \sim -1/r + Q/r^3 - \alpha/(2r^4)$ (in finite, closed shell systems with spherical symmetry), where Q is a screened quadrupole moment and α is the RPA polarizability of the system. This is in much better agreement with the expected behavior[38] than the LDA and GGA (and to a lesser extent, exact exchange[39]). As for (semi)extended systems, the linear-response Sham-Schlüter equation has been solved by Eguiluz *et al.* for a jellium surface[40] and by Godby *et al.* in bulk silicon,[41,42] 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.[43]

One of the main limitations of DFT in solids is the well-known "bandgap problem." Indeed, the Kohn-Sham (KS) bandgap energy E_g^{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.[33,44–46] In practice, the bandgap energy and quasiparticle band structure are thus computed with many-body Green function techniques[47] such as the GW method.[48,49] In principle, the Green function G should be updated with Dyson equation until self-consistency is achieved.[50–53] In most cases, however, the GW self-energy is calculated using KS orbitals and energies as input, thus leaving out self-consistency. This "G_0W_0" approach has been successfully applied to a wide variety of materials.[14,42,54–56] 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.[57–62]

In this paper, we calculate the DFT-RPA interacting bandgap energy $E_g = E(N+1) + E(N-1) - 2E(N)$ in solids. We show that E_g-E_g^{KS} is equal to the above-mentioned G_0W_0 self-energy correction, up to the so-called renormalization factors. This definitely provides a clear rationale behind G_0W_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_0W_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.[10,11] The adiabatic connection formula indeed yields the sum of the Hartree (E_h), KS exchange (E_x), and correlation (E_c) energies of a N-electron system:

$$E_{hxc} = \int_0^1 d\lambda \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle . \tag{1}$$

V_{ee} 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 λV_{ee} between electrons and with a one-body potential $v_\lambda(\mathbf{r})$ such that the ground-state density $n_\lambda(\mathbf{r})$ equals the physical density $n_1(\mathbf{r})$ [hence $v_1(\mathbf{r})=v_{ext}(\mathbf{r})$ is the external (ionic) potential, while $v_0(\mathbf{r})=v_{\mathrm{KS}}(\mathbf{r})$ is the KS potential]. The ground-state expectation value of the Coulomb interaction operator can then be calculated with the fluctuation-dissipation theorem

$$\langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle = E_h + E_x - \frac{1}{2}\int \frac{du}{2\pi}\,\mathrm{Tr}\{\nu[\chi_\lambda(iu) - \chi_0(iu)]\}. \tag{2}$$

The symbol Tr stands for the trace over spatial coordinates $\mathrm{Tr}\{A(iu)B(iu)\}=\int d^3\mathbf{r}d^3\mathbf{r}' A(\mathbf{r},\mathbf{r}';iu)B(\mathbf{r}',\mathbf{r};iu)$, $\nu(\mathbf{r},\mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'|$ is the bare Coulomb interaction, and $\chi_\lambda(\mathbf{r},\mathbf{r}';iu)$ is the imaginary-frequency density-density response function at coupling constant λ. The KS density-density response function $\chi_0(\mathbf{r},\mathbf{r}';iu)$ reads, as a function of the KS orbitals $\varphi_i(\mathbf{r})$ and KS energies ε_i (we assume a spin-compensated N-electron ground state):

$$\chi_0(\mathbf{r},\mathbf{r}';iu) = 2\sum_{j=1}^{N/2}\sum_k \frac{\varphi_j^\star(\mathbf{r})\varphi_k(\mathbf{r})\varphi_k^\star(\mathbf{r}')\varphi_j(\mathbf{r}')}{iu+\varepsilon_j-\varepsilon_k} + \mathrm{c.c.} \tag{3}$$

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

$$\chi_\lambda^{\mathrm{RPA}}(iu) = [1 - \lambda\chi_0(iu)\nu]^{-1}\chi_0(iu). \tag{4}$$

Refined approximations for $\chi_\lambda(iu)$, based on various time-dependent DFT kernels, can also be considered.[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 λ finally yield the following expression for the DFT-RPA correlation energy:

$$E_c^{\mathrm{RPA}}[n] = \frac{1}{2}\int \frac{du}{2\pi}\,\mathrm{Tr}\{\ln[1-\nu\chi_0(iu)] + \nu\chi_0(iu)\}. \tag{5}$$

The total DFT-RPA energy of the system can thus be written $E^{\mathrm{RPA}}[n]=E_0[n]+E_x[n]+E_c^{\mathrm{RPA}}[n]$, where $E_0[n]$ is the sum of the noninteracting kinetic energy, Hartree energy, electron-ion, and ion-ion interaction energies, and where

$$E_x[n] = -\sum_{j=1}^{N/2}\sum_{k=1}^{N/2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\,\varphi_j^\star(\mathbf{r})\varphi_k(\mathbf{r})\nu(\mathbf{r},\mathbf{r}')\varphi_k^\star(\mathbf{r}')\varphi_j(\mathbf{r}'). \tag{6}$$

Note that $E_x[n]$ and $E_c^{\mathrm{RPA}}[n]$ are *implicit* functionals of the density through the KS orbitals and energies. The RPA exchange-correlation potential $v_{xc}^{\mathrm{RPA}}(\mathbf{r})=\delta E_{xc}^{\mathrm{RPA}}[n]/\delta n(\mathbf{r})$ hence satisfies an integral equation known as the linear-response Sham-Schlüter equation.[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 $E_g^{\mathrm{KS}}=\varepsilon_c-\varepsilon_v$, where ε_v and ε_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 $\Omega\to\infty$ (the average density being kept fixed).

The interacting bandgap energy of a N-electron system is the difference $E_g=I-A$ between its first ionization potential I and its electron affinity A. These are defined as total energy differences between the N- and $(N\pm1)$-electron systems

$$I = E[n_{N-1,N-1}] - E[n_{N,N}] \approx E[n_{N-1,N}] - E[n_{N,N}], \tag{7a}$$

$$A = E[n_{N,N}] - E[n_{N+1,N+1}] \approx E[n_{N,N}] - E[n_{N+1,N}]. \tag{7b}$$

$n_{N,M}(\mathbf{r})$ 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,[63] the rightmost (approximate) equality in both equations holds up to a $O(\Omega^{-1})$ correction thanks to the variational principle of DFT.[2,46] The interacting bandgap energy of a solid can thus be calculated at constant (N-electron) KS potential $v_{\mathrm{KS}}(\mathbf{r})$.

We first focus on the electron affinity A. We get from Eq. (7b)

$$A = A_0 + A_x + A_c, \tag{8}$$

where $A_0 = E_0[n_{N,N}] - E_0[n_{N+1,N}]$ (with similar definitions for A_x and A_c). A_0 is easily calculated

$$\begin{aligned} -A_0 &= \langle \varphi_c | -\tfrac{1}{2}\nabla^2 + v_{ext} + v_h | \varphi_c \rangle + U_{cc} \\ &= \varepsilon_c + U_{cc} - \langle \varphi_c | v_{xc}^{\mathrm{RPA}} | \varphi_c \rangle. \end{aligned} \tag{9}$$

$\varphi_c(\mathbf{r})$ is the lowest unoccupied KS orbital, $v_h(\mathbf{r})$ is the Hartree potential, and U_{cc} is the self-interaction integral for orbital φ_c. A_x moreover reads.[39]

$$-A_x = \langle \varphi_c | \Sigma_x | \varphi_c \rangle - U_{cc}, \tag{10}$$

where $\Sigma_x(\mathbf{r},\mathbf{r}')$ is the KS exchange-only self-energy:

$$\Sigma_x(\mathbf{r},\mathbf{r}') = -\sum_{j=1}^{N/2} \varphi_j(\mathbf{r})\nu(\mathbf{r},\mathbf{r}')\varphi_j^{\star}(\mathbf{r}'). \tag{11}$$

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

$$\begin{aligned} -A_c = \frac{1}{2}\int \frac{du}{2\pi} \mathrm{Tr}\{&\ln[1-\nu\chi_0(iu) - \nu\delta\chi_0(iu)] \\ &- \ln[1-\nu\chi_0(iu)] + \nu\delta\chi_0(iu)\}. \end{aligned} \tag{12}$$

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

$$\delta\chi_0(\mathbf{r},\mathbf{r}';iu) = \varphi_c^{\star}(\mathbf{r})G_0(\mathbf{r},\mathbf{r}';\varepsilon_c + iu)\varphi_c(\mathbf{r}') + \text{c.c.}, \tag{13}$$

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

$$G_0(\mathbf{r},\mathbf{r}';z) = \sum_j \frac{\varphi_j(\mathbf{r})\varphi_j^{\star}(\mathbf{r}')}{z - \varepsilon_j}. \tag{14}$$

Using the identity $\mathrm{Tr}\{\ln A(iu) - \ln B(iu)\} = \mathrm{Tr}\{\ln[A(iu) \times B^{-1}(iu)]\} = \mathrm{Tr}\{\ln[B^{-1}(iu)A(iu)]\}$, we further get

$$-A_c = \frac{1}{2}\int \frac{du}{2\pi} \mathrm{Tr}\{\ln[1 - W(iu)\delta\chi_0(iu)] + \nu\delta\chi_0(iu)\}, \tag{15}$$

where $W(iu) = [1-\nu\chi_0(iu)]^{-1}\nu$ 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 trace of the logarithm $\mathrm{Tr}\{\ln[1-F(iu)]\} = -\mathrm{Tr}\{F(iu)\} + \cdots$, we can indeed split $A_c = A_c^{\mathrm{qp}} + A_c'$ in two parts, where

$$-A_c^{\mathrm{qp}} = -\frac{1}{2}\int \frac{du}{2\pi} \mathrm{Tr}\{[W(iu) - \nu]\delta\chi_0(iu)\} \tag{16a}$$

$$-A_c' = +\frac{1}{2}\int \frac{du}{2\pi} \mathrm{Tr}\{\ln[1 - W(iu)\delta\chi_0(iu)] + W(iu)\delta\chi_0(iu)\}. \tag{16b}$$

As we will next show, A_c^{qp} is a GW-like self-energy correction,[48,49] while A_c' vanishes in solids.

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

$$-A_c^{\mathrm{qp}} = \langle \varphi_c | \Sigma_c(\varepsilon_c) | \varphi_c \rangle, \tag{17}$$

where $\Sigma_c(\mathbf{r},\mathbf{r}';\varepsilon)$ is the correlation part of the "G_0W_0" self-energy (i.e., the GW self-energy[48,49] calculated with KS orbitals and energies):

$$\Sigma_c(\mathbf{r},\mathbf{r}';\varepsilon) = -\,\mathrm{PV}\int \frac{du}{2\pi} G_0(\mathbf{r},\mathbf{r}';\varepsilon + iu)W_s(\mathbf{r},\mathbf{r}';iu). \tag{18}$$

$W_s(\mathbf{r},\mathbf{r}';iu) = W(\mathbf{r},\mathbf{r}';iu) - \nu(\mathbf{r},\mathbf{r}')$ 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 GW self-energy is equal to the usual (real-frequency) expression[48,49] as long as ε is in the KS bandgap (including $\varepsilon = \varepsilon_c$ and $\varepsilon = \varepsilon_v$). 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_c^{RPA} [Eq. (5)], but with $\chi_0(iu)$ replaced by $\delta\chi_0(iu)$ and ν 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 DFT-RPA correlation energy per particle in the homogeneous electron gas[64] $\varepsilon_c^{\mathrm{RPA}}(n) \propto n^{1/4}$ (which yields $\varepsilon_c^{\mathrm{RPA}} \propto \Omega^{-1/4}$ 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

$$-A = \varepsilon_c + \langle \varphi_c | \Sigma_{xc}(\varepsilon_c) - v_{xc}^{\mathrm{RPA}} | \varphi_c \rangle + O(\Omega^{-1/4}), \tag{19}$$

where

$$\Sigma_{xc}(\mathbf{r},\mathbf{r}';\varepsilon) = -\,\mathrm{PV}\int \frac{du}{2\pi} e^{iu\delta} G_0(\mathbf{r},\mathbf{r}';\varepsilon + iu)W(\mathbf{r},\mathbf{r}';iu), \tag{20}$$

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

$$-I = \varepsilon_v + \langle \varphi_v | \Sigma_{xc}(\varepsilon_v) - v_{xc}^{\mathrm{RPA}} | \varphi_v \rangle + O(\Omega^{-1/4}), \tag{21}$$

where $\varphi_v(\mathbf{r})$ is the highest occupied KS orbital. Let us recall that the relation $-I = \varepsilon_v$ holds[38,65] for the exact exchange-correlation functional provided $v_{ext}(\mathbf{r}) \to 0$ when $r \to \infty$. As for the DFT-RPA, one may show[35] that $\langle \varphi_v | \Sigma_{xc}(\varepsilon_v)$

$-v_{xc}^{\mathrm{RPA}}|\varphi_v\rangle = 0$ if $v_{\mathrm{KS}}(\mathbf{r})$ has been shifted so that $v_{\mathrm{KS}}(\mathbf{r}) \to 0$ when $r \to \infty$, which yields $I = -\varepsilon_v + O(\Omega^{-1/4})$: the highest occupied KS energy tends to the negative of the DFT-RPA first ionization potential in a large system with a delocalized $\varphi_v(\mathbf{r})$. This result only holds if ε_v 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-like self-energy correction. We further discuss the implications of this result in the next section.

IV. LINKS WITH G_0W_0 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 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 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 band structures. Even the bandgap energy, a linear combination of ground-state total energies, may not be correctly given by the KS band structure.[33,44–46] The quasiparticle band structure of a solid is thus usually computed with the *GW* method.[48,49] In principle, the Dyson equation should be solved iteratively to find the self-consistent Green function *G* and the self-consistent *GW* self-energy Σ_{xc}. 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 are thus usually computed from the G_0W_0 self-energy using a first-order-like approximation. The conduction band edge $E_c \equiv -A$, for example, is obtained as the solution of

$$E_c = \varepsilon_c + \langle \varphi_c|\Sigma_{xc}(E_c) - v_{xc}|\varphi_c\rangle. \tag{22}$$

Σ_{xc} is the G_0W_0 self-energy and $v_{xc}(\mathbf{r})$ is the exchange-correlation potential used to calculate the KS orbitals and energies. $\Sigma_{xc}(\mathbf{r},\mathbf{r}';E_c)$ is then further expanded in powers of $E_c - \varepsilon_c$, which yields at first order

$$E_c = \varepsilon_c + Z_c\langle \varphi_c|\Sigma_{xc}(\varepsilon_c) - v_{xc}|\varphi_c\rangle, \tag{23}$$

where $Z_c = [1 - \langle \varphi_c|(\partial\Sigma_c/\partial\varepsilon)(\varepsilon_c)|\varphi_c\rangle]^{-1}$ is the quasiparticle renormalization factor. A similar equation holds for $E_v \equiv -I$. We will refer to these equations for E_c and E_v as the $r-G_0W_0$ bandgap. The renormalization factors Z_c and Z_v are worth around 0.75–0.90 in most semiconductors.[54,55] They will thus lower the self-energy correction by about 10–25 %. The G_0W_0 approach has been successfully applied to many materials.[14,42,54,55] In most cases it shifts the KS conduction bands with respect to the KS valence bands in a nearly rigid way. It has long been thought that self-consistency would degrade the quality of the *GW* quasiparticle band structure (i.e., that the effects of self-consistency and those of vertex corrections nearly cancel[66–70]). The first self-consistent *GW* calculations in real materials[61,62] have, however, revived this debate and questioned the rationale behind G_0W_0 calculations.

Equations (19) and (21) provide such a rationale, at least as regards the calculation of bandgap energies in solids. They show that the G_0W_0 approach is not a mere "practical recipe," and that it has a well-defined and meaningful interpretation within DFT. Indeed, the unrenormalized G_0W_0 bandgap energy, calculated in the DFT-RPA exchange-correlation potential, is precisely the DFT-RPA interacting bandgap energy. This physically motivates the use of KS orbitals and energies as a starting point for *GW* calculations. This does not, however, settle the debate about the need or effects of many-body self-consistency.

There is nonetheless one major difference between Eqs. (19) and (23): the DFT-RPA obviously lacks the renormalization factors that appear in the r-G_0W_0 approximation. The DFT-RPA bandgap energy will thus be significantly higher (~0.2 eV in Si) than the r-G_0W_0 bandgap energy. Yet we stress that the physics behind those renormalization factors is questionable. First, Eq. (23) is not a genuine first-order approximation to the quasiparticle energy, since the renormalization factor Z_c involves terms of any power in Σ_c. This is so primarily because the quasiparticle energy $\varepsilon = E_c$ itself appears on the right-hand side of Eq. (22) instead of its zeroth-order approximation $\varepsilon = \varepsilon_c$. The actual first-order solution of the self-consistent quasiparticle equation is in fact the unrenormalized G_0W_0 quasiparticle energy [Eq. (19)], as shown in Appendix B. Secondly, Eq. (22) [from which Eq. (23) is derived] does not necessarily catch the right physics. Indeed, the quasiparticle energies E_c and E_v are expected to be real (i.e., the quasiparticle lifetime is expected to diverge at the edges of the gap[71]), while the *exact* solution of Eq. (22) may be complex, especially in semiconductors with small KS bandgaps.[72,73] This challenges the use of Eqs. (22) and (23) for the calculation of the G_0W_0 bandgap energy. We will further compare the values of the r-G_0W_0 and DFT-RPA bandgap energies with the experimental bandgap energy in Secs. IV B and V.

The choice of the exchange-correlation potential $v_{xc}(\mathbf{r})$ used throughout the calculation is another practical but important issue. Indeed, the unrenormalized G_0W_0 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 $v_{xc}^{\mathrm{RPA}}(\mathbf{r})$ as a starting point for the computation of the *whole* G_0W_0 quasiparticle band structure is further emphasized in Appendix B. The DFT-RPA potential satisfies the linear-response Sham-Schlüter equation[6,33,34] in the *GW* approximation for the self-energy, which is unfortunately very difficult to solve. The works of Godby *et al.*[41,42] and of Kotani,[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 Ref. 43 and Refs. 35–37, which are much simpler to compute while being likely of reasonnable 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 χ^{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 H_2 (Ref. 25) and in the homogeneous electron gas (HEG).[7,17,32,74] In the latter case, the total energy error per particle $\Delta\varepsilon_c(n)=\varepsilon_c^{\mathrm{RPA}}(n)-\varepsilon_c^{\mathrm{HEG}}(n)$ weakly increases (in absolute value) with the density[17,74] [$\varepsilon_c^{\mathrm{HEG}}(n)$ and $\varepsilon_c^{\mathrm{RPA}}(n)$ 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+ functional[21,31]) 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 calculations[42,54,55] 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 calculations[62,77–80] 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.[62,80,81] 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 $E_c^{\mathrm{RPA}}=E_c^{\mathrm{int}}+E_c^{\mathrm{kin}}$, where $E_c^{\mathrm{int}}=\langle\Psi_1|V_{ee}|\Psi_1\rangle-E_h-E_x$ is the Coulomb correlation energy and $E_c^{\mathrm{kin}}=T_c-T_s$ is the difference between the interacting kinetic energy T_c and the noninteracting KS kinetic energy $T_s=-\sum_{j=1}^{N/2}\langle\varphi_j|\nabla^2|\varphi_j\rangle$. E_c^{int} 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 ($E_c^{\mathrm{kin}}>0$). 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^{kin}) from Coulomb (A_c^{int}) contributions in A_c. A_c^{int} is easily calculated from Eqs. (2) and (4). To that end, we introduce $F(iu)=\nu[\chi_1^{\mathrm{RPA}}(iu)-\chi_0(iu)]=[W(iu)-\nu]\chi_0(iu)$ and write, upon addition of one electron to the lowest unoccupied orbital

$$\delta F(iu)=[W(iu)-\nu]\delta\chi_0(iu)+\delta W(iu)\chi_0(iu)+\delta W(iu)\delta\chi_0(iu), \qquad (24)$$

where $\delta F(iu)$ and $\delta W(iu)=[1-W(iu)\delta\chi_0(iu)]^{-1}W(iu)-W(iu)$ are, respectively, the changes in $F(iu)$ and $W(iu)$. The trace of $\delta F(iu)$ over spatial coordinates and frequency yields $-A_c^{\mathrm{int}}$ 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 nonvanishing contribution (beyond the first term) arises from the first-order variation of the screened Coulomb interaction $\delta W^{(1)}(iu)=W(iu)\delta\chi_0(iu)W(iu)$ in the second term. This contribution thus equals $A_c^{\mathrm{kin}}=A_c-A_c^{\mathrm{int}}$, which yields after straightforward algebra

$$-A_c^{\mathrm{kin}}=\langle\varphi_c|\Sigma_c^{\mathrm{kin}}(\varepsilon_c)|\varphi_c\rangle+O(\Omega^{-1/4}), \qquad (25)$$

where

$$\Sigma_c^{\mathrm{kin}}(\mathbf{r},\mathbf{r}';\varepsilon)=\mathrm{PV}\int\frac{du}{2\pi}G_0(\mathbf{r},\mathbf{r}';\varepsilon+iu)\widetilde{W}_s(\mathbf{r},\mathbf{r}';iu) \qquad (26)$$

and

$$\widetilde{W}_s(iu)=W(iu)\chi_0(iu)W(iu)=\varepsilon^{-1}(iu)W_s(iu), \qquad (27)$$

$\varepsilon(iu)=1-\nu\chi_0(iu)$ being the RPA dielectric function. A similar equation holds for the first ionization energy I, $|\varphi_c\rangle$ and ε_c being replaced with $|\varphi_v\rangle$ and ε_v. Note that Σ_c^{kin} has the same functional form as the correlation part of the G_0W_0 self-energy [Eq. (18)], but with a (re)screened $W_s(iu)$.

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-Martins[83] pseudopotentials and a plasmon-pole approximation for $\varepsilon^{-1}(iu)$. The wave functions were expanded in a plane-wave basis set with cutoff energy 12 Ha for Si and

TABLE I. The KS, r-G_0W_0 and DFT-RPA quasiparticle and bandgap energies of silicon and diamond, all in eV. The quasiparticle energies have been shifted so that the top of the valence band is at zero energy in the DFT-RPA. The total correlation (Σ_c), kinetic (Σ_c^{kin}), and Coulomb ($\Sigma_c^{\text{int}}=\Sigma_c-\Sigma_c^{\text{kin}}$) contributions to the DFT-RPA are also given.

		KS	r-G_0W_0	RPA	Σ_c	Σ_c^{kin}	Σ_c^{int}
Si	E_v	0.751	0.176	0.000	0.434	0.753	−0.318
	E_c (Ref. 86)	1.232	1.325	1.351	−3.555	1.294	−4.849
	E_g	0.481	1.149	1.351			
C	E_v	0.924	0.154	0.000	1.102	0.554	0.548
	E_c (Ref. 86)	5.074	5.757	5.884	−4.753	1.904	−6.656
	E_g	4.150	5.603	5.884			

30 Ha for diamond. Up to 200 bands and 256 k points (full Brillouin zone) were included in the computation of the 181×181 dielectric matrices and self-energies. The KS band structure was calculated in the LDA potential,[84] at the experimental lattice parameter[85] ($a=5.43$ Å for Si and $a=3.57$ Å for C). The quasiparticle energies E_c, E_v, and the bandgap energy E_g are reported in Table I. Both renormalized and unrenormalized (RPA) G_0W_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 (Σ_c), kinetic (Σ_c^{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 Σ_c^{kin} to be converged (from above and from below, respectively) within 0.05 eV. The values of Σ_c, Σ_c^{kin}, and Σ_c^{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_0W_0 bandgap energies of silicon and diamond are found in good agreement with the experiment[85] ($E_g=1.17$ 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_c^{int}, and E_c^{kin} to increase with the number of particles, i.e., $\Sigma_c<0$, $\Sigma_c^{\text{int}}<0$, and $\Sigma_c^{\text{kin}}>0$. This is clearly the case on the conduction band side. However, Σ_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 Σ_c^{int} itself is found positive. Σ_c^{kin} is a significant part of Σ_c but is much lower than the variations of the noninteracting kinetic energy $\Delta T_s=\langle\varphi_{v/c}|-\frac{1}{2}\nabla^2|\varphi_{v/c}\rangle$ (typically a few tens of eV). Again, Σ_c^{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_c^{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^{KS} and the interacting bandgap energy E_g can be related to the existence of a derivative discontinuity in the exchange-correlation functional.[33,44–46] 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.[44,45,87] It is basically the $T\to0$ limit of Mermin's DFT (Ref. 88) for finite temperature T and fixed chemical potential μ. In this approach, the $\tilde{N}=N+f$ electron system $(0\leqslant f\leqslant1)$ is described as a statistical mixture of the N and $(N+1)$-electron systems; the ground-state density and total energy thus read

$$\tilde{n}_{N+f}(\mathbf{r}) = f n_{N+1}(\mathbf{r}) + (1-f)n_N(\mathbf{r}), \tag{28a}$$

$$\tilde{E}[\tilde{n}_{N+f}] = fE[n_{N+1}] + (1-f)E[n_N], \tag{28b}$$

where $n_N(\mathbf{r})$ is the N-electron ground-state density. The exchange-correlation energy $\tilde{E}_{xc}[\tilde{n}_{N+f}]$ does not reduce to the weighted average of $E_{xc}[n_N]$ and $E_{xc}[n_{N+1}]$, but also includes nonlinear but straightforward kinetic and Hartree energy corrections.[87,89] By construction, we may expect derivative discontinuities in $\tilde{E}_{xc}$ for integer values of N. We thus define

$$\begin{aligned}\Delta_{xc}(\mathbf{r}) &= \lim_{\delta\to0^+}[v_{xc}^{N+\delta}(\mathbf{r}) - v_{xc}^{N-\delta}(\mathbf{r})]\\ &= \lim_{\delta\to0^+}\left[\left(\frac{\delta\tilde{E}_{xc}[\tilde{n}]}{\delta\tilde{n}(\mathbf{r})}\right)_{N+\delta} - \left(\frac{\delta\tilde{E}_{xc}[\tilde{n}]}{\delta\tilde{n}(\mathbf{r})}\right)_{N-\delta}\right],\end{aligned} \tag{29}$$

where $v_{xc}^{N+\delta}(\mathbf{r})$ and $v_{xc}^{N-\delta}(\mathbf{r})$ are the exchange-correlation potentials for the $\widetilde{N}=N+\delta$ and $\widetilde{N}=N-\delta$ electron systems, respectively. $\Delta_{xc}(\mathbf{r})$ happens to be a constant; a few formal considerations indeed yield[45]

$$\Delta_{xc}=(I-\varepsilon_c)-(A-\varepsilon_v)=E_g-E_g^{\mathrm{KS}}. \qquad (30)$$

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

$$\Delta_{xc}=\langle\varphi_c|\Sigma_{xc}(\varepsilon_c)-v_{xc}^{\mathrm{RPA}}|\varphi_c\rangle-\langle\varphi_v|\Sigma_{xc}(\varepsilon_v)-v_{xc}^{\mathrm{RPA}}|\varphi_v\rangle, \qquad (31)$$

where $\Sigma_{xc}(\mathbf{r},\mathbf{r}';\varepsilon)$ is the G_0W_0 self-energy. The DFT-RPA is one of the first known functionals that yields reasonnable 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 $\varphi_i(\mathbf{r})$ may be occupied with a fractional number of electrons f_i $(0\leqslant f_i\leqslant 1)$. This allows a straightforward extension of any *explicit* functional of the density such as the LDA and GGA to arbitrary densities $n(\mathbf{r})=\Sigma_i f_i|\varphi_i(\mathbf{r})|^2$. 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 developped 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' expression[95] for the total energy in many-body perturbation theory (Nozières' formula is a variant of the Luttinger Ward formula[96]). 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 [25,32] can be built upon the model of the RPA using a time-dependent exchange-correlation kernel in Eq. (4) (such as the adiabatic LDA kernel [97]). The extension of the results of Sec. III to these functionals is, however, intricate, notably because the integration over the coupling constant λ 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.

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

In this Appendix, we show that $A_c'=O(\Omega^{-1/4})$ when $\Omega\rightarrow\infty$. We also recover the low-density behavior of the DFT-

RPA correlation energy per particle in the homogeneous electron gas $\varepsilon_c^{\mathrm{RPA}}(n)\sim -0.574n^{1/4}$, a result found numerically by Wang and Perdew.[64] We consider a piece of crystalline solid with finite (but very large) volume Ω and periodic boundary conditions.[98] We thus now index the KS orbitals $\varphi_{n\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})/\sqrt{\Omega}$ and the KS energies $\varepsilon_{n\mathbf{k}}$ by their wave vector $\mathbf{k}$ in the first Brillouin zone (FBZ) and by their band index n. $u_{n\mathbf{k}}(\mathbf{r})$ has the periodicity of the underlying crystal lattice. We assume n_v occupied valence bands, a direct bandgap at $\mathbf{k}=\mathbf{0}$, and a nondegenerate conduction band minimum (though this is not restrictive). We let $c=n_v+1$ and take $\varepsilon_c\equiv\varepsilon_{c\mathbf{0}}$ as the reference of energies. We also assume (for simplicity) that $\varepsilon_{c\mathbf{k}}\sim k^2/(2m_c^*)$ around $\mathbf{k}=\mathbf{0}$. 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

$$\delta\chi_0(\mathbf{r},\mathbf{r}';iu)=\int\frac{d^3\mathbf{q}}{(2\pi)^3}\sum_{\mathbf{G},\mathbf{G}'}e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}\delta\chi_{0,\mathbf{GG}'}(\mathbf{q};iu)e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'},\tag{A1}$$

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

$$\delta\chi_{0,\mathbf{GG}'}(\mathbf{q};iu)=-\frac{2}{\Omega}\sum_{\varepsilon_{n\mathbf{q}}\neq 0}\Phi_{cn\mathbf{q}}(\mathbf{G})\Phi^{\star}_{cn\mathbf{q}}(\mathbf{G}')\frac{\varepsilon_{n\mathbf{q}}}{u^2+\varepsilon_{n\mathbf{q}}^2},\tag{A2}$$

where

$$\Phi_{cn\mathbf{q}}(\mathbf{G})=\frac{1}{\Omega_0}\int_{\Omega_0}d^3\mathbf{r}u^{\star}_{c\mathbf{0}}(\mathbf{r})u_{n\mathbf{q}}(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}\tag{A3}$$

and Ω_0 is the volume of the unit cell of the crystal lattice. The small q behavior of $\Phi_{cn\mathbf{q}}(\mathbf{G})$ [hence of $\delta\chi_{0,\mathbf{GG}'}(\mathbf{q};iu)$] follows from the orthogonality between KS orbitals

$$\Phi_{cn\mathbf{q}}(\mathbf{G}=\mathbf{0})\propto q\ (n\neq c),\tag{A4a}$$

$$\Phi_{cc\mathbf{q}}(\mathbf{G}=\mathbf{0})\to 1,\tag{A4b}$$

$$\Phi_{cn\mathbf{q}}(\mathbf{G}\neq\mathbf{0})\to\text{const}.\tag{A4c}$$

As for $W(iu)$, one typically gets[99] in a KS insulator, when $\mathbf{q}\to\mathbf{0}$:

$$W_{\mathbf{00}}(\mathbf{q};iu)\propto\frac{1}{q^2},\tag{A5a}$$

$$W_{\mathbf{0G}}(\mathbf{q};iu),\ W_{\mathbf{G0}}(\mathbf{q};iu)\propto\frac{1}{q}(\mathbf{G}\neq\mathbf{0}),\tag{A5b}$$

$$W_{\mathbf{GG}'}(\mathbf{q};iu)\to\text{const}\ (\mathbf{G}\neq\mathbf{0},\mathbf{G}'\neq\mathbf{0}).\tag{A5c}$$

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

$$-A_c'=\frac{\Omega}{2}\int\frac{du}{2\pi}\int\frac{d^3\mathbf{q}}{(2\pi)^3}\mathrm{Tr}\{\ln[1-W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)]+W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)\},\tag{A6}$$

where $\delta\chi_0(\mathbf{q};iu)$ and $W(\mathbf{q};iu)$ are the matrices with elements $\delta\chi_{0,\mathbf{GG}'}(\mathbf{q};iu)$ and $W_{\mathbf{GG}'}(\mathbf{q};iu)$ respectively. The trace of the logarithm can also be written

$$\mathrm{Tr}\{\ln[1-W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)]\}=\ln\det[1-W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)].\tag{A7}$$

Now, Eqs. (A4) and (A5) can be used to show that the integrand in Eq. (A6) is finite except around $\mathbf{q}=\mathbf{0}$, $u=0$. Moreover, $\delta\chi_0(\mathbf{q};iu)$ scales as $1/\Omega$. Hence, for any $q_0>0$ and any $u_0>0$, there exists Ω_0 large enough such that the power series expansion of $\mathrm{Tr}\{\ln[1-W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)]\}$ is convergent for $\Omega>\Omega_0$, $q>q_0$ and $|u|>u_0$. This yields

$$\mathrm{Tr}\{\ln[1-W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)]\}=-\mathrm{Tr}\{W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)\}+O\left(\frac{1}{\Omega^2}\right).\tag{A8}$$

The contribution to A_c' coming from the domain $q>q_0$, $|u|>u_0$ will thus vanish as $1/\Omega$ when $\Omega\to\infty$. We must last deal with the contribution $\delta A_c'(q_0,u_0)$ coming from the domain $q\leqslant q_0$, $|u|\leqslant u_0$.

The divergence of the integrand in this region comes from the lowest conduction band contribution to $\delta\chi_{0,\mathbf{GG}'}(\mathbf{q};iu)$. We can discard the contribution from all the other bands for the purpose of our demonstration. $\delta\chi_0(\mathbf{q};iu)$ then reads

$$\delta\chi_0(\mathbf{q};iu)\simeq-\frac{1}{\Omega}\frac{q^2/m_c^*}{u^2+q^4/(2m_c^*)^2}|\Phi_{cc\mathbf{q}}\rangle\langle\Phi_{cc\mathbf{q}}|,\tag{A9}$$

where $|\Phi_{cc\mathbf{q}}\rangle$ is the vector with components $\Phi_{cc\mathbf{q}}(\mathbf{G})$. This yields

$$\mathrm{Tr}\{W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)\}=-\frac{1}{\Omega}\frac{q^2/m_c^*}{u^2+q^4/(2m_c^*)^2}\times\langle\Phi_{cc\mathbf{q}}|W(\mathbf{q};iu)|\Phi_{cc\mathbf{q}}\rangle\tag{A10a}$$

$$\det[1-W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)]=1-\mathrm{Tr}\{W(\mathbf{q};iu)\delta\chi_0(\mathbf{q};iu)\}.\tag{A10b}$$

The small q behavior of $\langle\Phi_{cc\mathbf{q}}|W(\mathbf{q};iu)|\Phi_{cc\mathbf{q}}\rangle$ is driven by $W_{\mathbf{00}}(\mathbf{q};iu)$; we thus get when both $\mathbf{q}\to\mathbf{0}$ and $u\to 0$

$$\langle\Phi_{cc\mathbf{q}}|W(\mathbf{q};iu)|\Phi_{cc\mathbf{q}}\rangle\sim\frac{4\pi}{\varepsilon_r q^2},\tag{A11}$$

where ε_r is the static dielectric constant.

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

$$u'=(\varepsilon_r m_c^*\Omega)^{1/2}u,\tag{A12a}$$

$$q' = \left(\frac{\varepsilon_r\Omega}{m_c^*}\right)^{1/4} q, \tag{A12b}$$

we get

$$-\delta A_c'(q_0,u_0) \sim \frac{1}{2\varepsilon_r}\left(\frac{m_c^*}{\varepsilon_r\Omega}\right)^{1/4}\int_{-u_0'}^{+u_0'}\frac{du'}{2\pi}\int_{B_{q_0'}}\frac{d^3\mathbf{q}'}{(2\pi)^3} \times \ln\left(1+\frac{4\pi}{u'^2+q'^4/4}\right)-\frac{4\pi}{u'^2+q'^4/4}, \tag{A13}$$

where $u_0'=(\varepsilon_r m_c^*\Omega)^{1/2}u_0$ and $B_{q_0'}$ is the domain $q\leqslant q_0'$ with $q_0'=(\varepsilon_r\Omega/m_c^*)^{1/4}q_0$. The above integral has a finite limit when $u_0'\to\infty$ and $q_0'\to\infty$, which finally yields the expected result

$$A_c' \sim \frac{K}{\varepsilon_r}\left(\frac{m_c^*}{\varepsilon_r\Omega}\right)^{1/4}, \tag{A14}$$

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

$$K = \frac{2}{\pi^{3/4}}\int_0^{+\infty} x^4\left[1-\sqrt{1+\frac{1}{x^4}}\right]^2 dx = 0.574(4). \tag{A15}$$

Equation (A14) is consistent with the low-density behavior of the RPA correlation energy per particle in the homogeneous electron gas $\varepsilon_c^{\text{RPA}}(n)$. Let us indeed add an electron to an otherwise empty box of large volume Ω. The RPA (self-) correlation energy of this electron will be given by $-A_c'$. If we now think of this system as a realization[100] of a spin-polarized homogeneous electron gas with (low) density $n=1/\Omega$, we get from Eq. (A14) $\varepsilon_c^{\text{RPA}}(n)\sim -0.574n^{1/4}$ [the low-density behavior of $\varepsilon_c^{\text{RPA}}(n)$ is independent[64] of the spin polarization]. This is precisely the result obtained numerically by Wang and Perdew.[64]

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 $n(\mathbf{r})$ yields $v_{ext}(\mathbf{r})$ up to an additive constant,[2] which then yields the interacting Green function G up to a 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:

$$-\frac{1}{2}\nabla^2\Psi_\alpha(\mathbf{r})+v_{ext}(\mathbf{r})\Psi_\alpha(\mathbf{r})+v_{h,\alpha}(\mathbf{r})\Psi_\alpha(\mathbf{r})+v_{xc,\alpha}(\mathbf{r})\Psi_\alpha(\mathbf{r}) + \alpha\int d^3\mathbf{r}'\Sigma_{xc}[G_\alpha](\mathbf{r},\mathbf{r}';E_\alpha)\Psi_\alpha(\mathbf{r}') = E_\alpha\Psi_\alpha(\mathbf{r}). \tag{B1}$$

$v_{ext}(\mathbf{r})$ is the external (ionic) potential and $\Sigma_{xc}[G_\alpha](\mathbf{r},\mathbf{r}';E)$ is the *GW* self-energy calculated with the self-consistent Green function G_α at coupling constant α. $v_{xc,\alpha}(\mathbf{r})$ is a local potential such that $v_{xc,1}(\mathbf{r})=0$ and such that the density $n_\alpha(\mathbf{r})=n_1(\mathbf{r})$ 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 $v_{xc,\alpha}(\mathbf{r})$ of the form $v_{xc,\alpha}(\mathbf{r})=\Sigma_k(1-\alpha^k)v_{xc}^{(k)}(\mathbf{r})$ and calculate $v_{xc}^{(k)}(\mathbf{r})$ so that the kth order variation of the density $\delta n^{(k)}(\mathbf{r})$ is zero. $\delta n^{(1)}(\mathbf{r})$ reads[6] (the limits $\mathbf{r}'\to\mathbf{r}$ and $\delta\to 0^+$ are understood)

$$\delta n^{(1)}(\mathbf{r}) = 0 = \int\frac{d\omega}{2i\pi}e^{i\omega\delta}\delta G^{(1)}(\mathbf{r},\mathbf{r}';\omega), \tag{B2}$$

where $\delta G^{(1)}(\omega)=G_0(\omega)\{\Sigma_{xc}[G_0](\omega)-v_{xc}^{(1)}\}G_0(\omega)$ is the first-order variation of the Green function. Equation (B2) is no more than the linear-response Sham-Schlüter equation,[6] meaning that $v_{xc}^{(1)}(\mathbf{r})$ is the DFT-RPA potential $v_{xc}^{\text{RPA}}(\mathbf{r})$.

Let $\Psi_0(\mathbf{r})=\varphi(\mathbf{r})$ be a zero-order KS orbital with KS energy $E_0=\varepsilon$. We then easily get

$$\left(\frac{dE_\alpha}{d\alpha}\right)_{\alpha=0} = \langle\varphi|\Sigma_{xc}[G_0](\varepsilon)-v_{xc}^{(1)}|\varphi\rangle, \tag{B3}$$

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

$$E = \varepsilon + \langle\varphi|\Sigma_{xc}[G_0](\varepsilon)-v_{xc}^{\text{RPA}}|\varphi\rangle. \tag{B4}$$

This result is valid in finite systems as well as solids, and for any KS orbital $\varphi(\mathbf{r})$. In particular, the first-order approximations to the conduction and valence band edges in the first-order potential $v_{xc}^{(1)}(\mathbf{r})=v_{xc}^{\text{RPA}}(\mathbf{r})$ are given by Eqs. (19) and (21), respectively. The DFT-RPA potential $v_{xc}^{\text{RPA}}(\mathbf{r})$ moreover appears as the adequate starting point for the computation of the whole G_0W_0 quasiparticle band structure. We acknowledge, though, that a higher-order expansion of E_α 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.[47] Indeed, the total energy of a system can be calculated from the interacting Green function G using the well-known Galitskii-Midgal[101] formula or variational functionals such as Luttinger-Ward's[96] or Nozières'[95] formula. The latter two formula 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 ν.[47] 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.[6,7] Evaluating Nozières' functional at the KS Green function G_0 yields[6] (we still work with spinless Green functions for the sake of simplicity)

$$E_{xc}[n] = \Phi[G_0] = 2\sum_{n=1}^{\infty}\frac{1}{2n}\int\frac{d\omega}{2i\pi}e^{i\omega\delta}\mathrm{Tr}\{\Sigma_{xc}^{(n)}[G_0](\omega)G_0(\omega)\}, \tag{C1}$$

where $\delta \to 0^+$ and $\Sigma_{xc}^{(n)}[G_0](\mathbf{r},\mathbf{r}';\omega)$ 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

$$G_0(\mathbf{r},\mathbf{r}';\omega) = \sum_j \frac{\varphi_j(\mathbf{r})\varphi_j^{\star}(\mathbf{r}')}{\omega - \varepsilon_j \pm i\eta}, \tag{C2}$$

where η 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.[6] This follows from a particular property[51,96] of the Φ functional defined in Eq. (C1):

$$\frac{\delta\Phi[G_0]}{\delta G_0(\mathbf{r},\mathbf{r}';\omega)} = \frac{1}{2i\pi}\Sigma_{xc}[G_0](\mathbf{r},\mathbf{r}';\omega). \tag{C3}$$

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.[24,25,102] Let us now consider any well-defined self-energy approximation in solids and calculate the electron affinity A with Eq. (7b) using 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)]

$$\delta G_0(\mathbf{r},\mathbf{r}';\omega) = \varphi_c(\mathbf{r})\left(\frac{1}{\omega - \varepsilon_c - i\eta} - \frac{1}{\omega - \varepsilon_c + i\eta}\right)\varphi_c^{\star}(\mathbf{r}') \underset{\eta\to 0}{\to} 2i\pi\varphi_c(\mathbf{r})\varphi_c^{\star}(\mathbf{r}')\,\delta(\omega - \varepsilon_c). \tag{C4}$$

Following the lines of Sec. III, we split A_{xc} in two parts $A_{xc} = \Phi[G_0] - \Phi[G_0 + \delta G_0] = A_{xc}^{\mathrm{qp}} + A_{xc}'$, where A_{xc}^{qp} is the contribution from the diagrams that contain only one δG_0 line, and A_{xc}' is the remainder. A_{xc}^{qp} is the first-order variation of the Φ functional

$$-A_{xc}^{\mathrm{qp}} = \int d^3\mathbf{r}\int d^3\mathbf{r}'\int\frac{d\omega}{2i\pi}e^{i\omega\delta}\frac{\delta\Phi[G_0]}{\delta G_0(\mathbf{r},\mathbf{r}';\omega)}\delta G_0(\mathbf{r},\mathbf{r}';\omega). \tag{C5}$$

Equations (C3) and (C4) thus yield

$$-A_{xc}^{\mathrm{qp}} = \langle\varphi_c|\Sigma_{xc}(\varepsilon_c)|\varphi_c\rangle. \tag{C6}$$

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

$$-A = \varepsilon_c + \langle\varphi_c|\Sigma_{xc}(\varepsilon_c) - v_{xc}|\varphi_c\rangle - A_{xc}' + O(\Omega^{-1}), \tag{C7}$$

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 $\Omega^{-1/4}$), 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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