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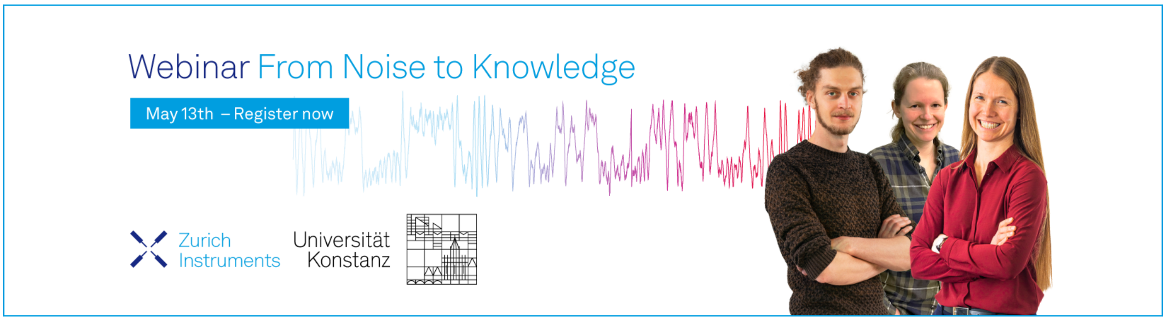

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# The self-energy beyond *GW*: Local and nonlocal vertex corrections

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It is commonly accepted that the *GW* approximation for the electron self-energy is successful for the description of the band structure of weakly to moderately correlated systems, whereas it will fail for strongly correlated materials. In the present work, we discuss two important aspects of this approximation: first, the "self-screening error," which is due to an incorrect treatment of induced exchange, and second, the atomic limit, in which, instead, correlation is directly responsible for the observed problem. Using the example of the removal of a particle from a box, we show that the self-screening error stems from the use of test charge-test charge screening and that it can be corrected by a two-point vertex contribution to the self-energy derived from time-dependent density functional theory (TDDFT). We explain why the addition of a particle, instead, requires the use of a different approximate vertex. This illustrates why the general vertex function, valid both for valence and conduction states, must be a three-point function. Moreover, we show that also the bad performance of *GW* in the atomic limit is due to the neglect of the vertex in the self-energy; in that case, the TDDFT-derived vertex correction is not sufficient in order to remove the error even qualitatively. We discuss the effects of the self-screening error as well as the atomic limit using *GW* for the exactly solvable two-site Hubbard model. © *2009 American Institute of Physics*. [doi:10.1063/1.3249965]

## I. INTRODUCTION

In many-body perturbation theory (MBPT) the self-energy plays a key role since it contains all the many-body effects of the system. In Hedin's equations,[1] the exchange-correlation (xc) part of this quantity is expressed as

$$\Sigma_{\text{xc}}(12) = iG(14)W(31^+)\Gamma(42;3), \tag{1}$$

where $G$ is the one-particle Green's function, $W$ is the screened Coulomb potential, and $\Gamma$ a three-point vertex. Here, the set of variables (1) comprises position, spin, and time coordinates: $(1)=(x_1,t_1)=(\mathbf{r}_1,\sigma_1,t_1)$ (integration or summation on the right-hand side over indices not present on the left is implicit throughout the paper). The exact self-energy is not known. As first approximation, one could neglect the vertex and arrive at the well known *GW* approximation (GWA), $\Sigma_{\text{xc}}(12)=iG(12)W(21^+)$.[1] The use of Hedin's GWA in realistic calculations of band structures has led to a breakthrough: in general, *GW* corrections to the Kohn–Sham (KS) eigenvalue gap remove most of the underestimate of the latter with respect to experimental photoemission gaps.[2–8] This success is not fortuitous but stems from the fact that the GWA captures most of the important physics for the electron addition and removal. In fact, in its static, so-called COHSEX,[9] approximation, one finds the bare Fock operator for the exact description of exchange, as well as the screening of all interactions stemming from the rearrangement of charge responding to the addition of a point charge to the system (hence the name—Coulomb hole plus screened exchange). A full *GW* calculation includes the frequency dependence of the response of the system. However, as in the COHSEX case, the response of the system (the screened Coulomb interaction $W$) is evaluated in the random phase approximation (RPA), neglecting the so-called vertex corrections. The latter appears in two ways in Hedin's equations: first, as a correction to the irreducible polarizability, which simply reads as $P=-iGG$ (instead of $P=-iGG\Gamma$) in RPA. This vertex is today approximately evaluated in *ab initio* calculations, especially in the framework of optical absorption spectra, because $\Gamma$ contains the electron-hole interaction leading to excitonic effects. $P$ is hence obtained from the Bethe–Salpeter equation with an effective electron-hole attraction kernel derived from $\Gamma$. Calculations are cumbersome but feasible for reasonably simple systems, and the results are usually in excellent agreement with experiment.[10] Second, $\Gamma$ appears as a correction to the GWA in the full expression for the xc self-energy $\Sigma_{\text{xc}}=iGW\Gamma$. This contribution is less frequently included.[2,3] Cancellation effects on quasiparticle energies between the vertices in $P$ and $\Sigma$ have been discussed mostly for selected cases, like, e.g., for the homogeneous electron gas,[11–16] where the two contributions are found to cancel to some extent. Studies on Hubbard clusters[17,18] have emphasized that including vertex corrections in $P$ only does not even qualitatively improve the problematic description of satellite spectra in *GW*. A few investigations in real materials also exist. Shirley and Martin[19] reported calculations on atoms using a generalized *GW*, in which an exchange-only vertex is included. Calculations for bulk silicon, performed using an approximate vertex derived from time-dependent adiabatic local density approximation

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(TDLDA) (Ref. 20) or from second-order corrections,[21] have showed that the inclusion of vertex corrections in $P$ alone should be avoided. Recently, in a work on the lifetimes in LiF, it has been proved that, contrary to previous results for electron gas, the inclusion of a time-dependent density functional theory (TDDFT)-based nonlocal vertex in the self-energy and in the polarization do not compensate each other. Besides *GW*, other approaches have been used to explore vertex corrections, as, e.g., the *T*-matrix,[22–25] the cumulant expansion approximations,[26–30] and the Parquet theory.[31]

More recently, another way has been sketched to make an *ab initio* calculation of the vertex correction to $\Sigma$ feasible.[32,33] Though still requiring further simplifications in realistic applications, the so-called $\rho/G$-approach introduced by Bruneval *et al.*[32] has the advantage to replace the cumbersome four-point Bethe–Salpeter integral equation by an explicit expression for $\Gamma$,

$$\Gamma(12;3) = \delta(13)\delta(23) + \frac{\delta\Sigma_{\rm xc}(12)}{\delta\rho(4)}P(43). \tag{2}$$

Since $P$ is the two-point irreducible polarizability, it can often be calculated quite precisely in approximate schemes such as the TDLDA and compared to experiments.[34] The difficult term is the functional derivative $\delta\Sigma_{\rm xc}/\delta\rho$. In Ref. 32, a local ($\delta(12)$) approximation has been proposed; this approximation has been applied to the calculation of the bandgaps of some semiconductors.[32,35] However, a systematic study and a detailed discussion of the related physics are still missing. In particular, clear benchmark results for limiting cases are needed.

This is the scope of the present work: using simple models, we illustrate the role of vertex corrections in $\Sigma_{\rm xc}$ in relation to two major shortcomings of the GWA, namely, the self-screening error and the incorrect atomic limit. In Sec. II we introduce the concepts of self-screening and atomic limit. The model problem that we deal with is, as a first step, the addition/removal of one particle to/from a box, and, as a second step, the addition of a second particle into a second, distinct, box. In this way we are able to (i) illustrate that the GWA suffers from a self-screening error due to the neglect of induced exchange, (ii) show that a two-point vertex derived from TDDFT, but different from the one proposed in Ref. 32, should be a good approximation for the necessary correction to valence band energies, (iii) explain why, instead, a three-point vertex is needed for a correct simultaneous description of both valence and conduction, and (iv) suggest a simple way to correct *GW* results for systems that may be interpreted by the model. In Sec. III, we apply the GWA and corrections to the two-site Hubbard model.[36,37] This system allows us to compare the *GW* and the exact results, hence to illustrate the consequences of self-screening and the improvements due to vertex corrections.

We also discuss the problem of the atomic limit: while *GW* is exact for one isolated site, it yields the wrong vanishing-hopping limit for the two-site model. We show that this failure stems from the interpretation of the density as a classical charge distribution, i.e., a bad treatment of correlation. It can therefore be understood that the approximate three-point vertex function, which cures the self-screening problem, is not sufficient to correct the atomic limit. Finally, we draw our conclusions and future perspectives.

## II. THEORY

In this paper, we want to go beyond the GWA. We start from the results of the $\rho/G$-approach of Bruneval *et al.*,[32] where Eq. (2) was derived. In that reference, it is suggested that $\Gamma$ can be divided into three contributions according to

$$\Gamma(12;3) = \delta(13)\delta(23) + \delta(12)f_{\rm xc}^{\rm eff}(14)P(43) + \Delta\Gamma(12;3), \tag{3}$$

where

$$\Delta\Gamma(12;3) = \left[\frac{\delta\Sigma_{\rm xc}(12)}{\delta\rho(4)} - \delta(12)f_{\rm xc}^{\rm eff}(14)\right]P(43) \tag{4}$$

and

$$f_{\rm xc}^{\rm eff}(14) = -iP_0^{-1}(16)G(65)G(76)\frac{\delta\Sigma_{\rm xc}(57)}{\delta\rho(4)}, \tag{5}$$

with $P_0(12)=-iG(12)G(21)$. The present separation of the three-point vertex in a two-point part and a three-point part is, of course, arbitrary, and it could be done differently. However, choices (4) and (5) are well motivated. Indeed, only the two-point term $\delta(1,2)f_{\rm xc}^{\rm eff}(14)P(43)$ contributes to the polarizability $P=-iGG\Gamma$, as it has been pointed out in Ref. 32; moreover, the xc contribution to the total energy $E_{\rm xc}=-iG(12)\Sigma_{\rm xc}(21)$ is exclusively determined by that term. Indeed, it is immediate to verify that $-G(12)G(24)W(32)\Delta\Gamma(41;3)=0$.

The same is not true for quasiparticle addition and removal energies and their differences (bandgaps): there is no indication for $\Delta\Gamma$ to be negligible. Of course, one may, as a first attempt, suppose that the main contribution to vertex corrections is given by the above defined two-point term, which leads to a physically intuitive test charge-test electron (TC-TE)-like screening; this approximation has been used in Ref. 32 in order to discuss the influence of a long-range kernel on the gap corrections in simple semiconductors and insulators. However, the physical interpretation and importance of the neglected contribution $\Delta\Gamma$ had not been explored in that work.

There are therefore two important aspects of this problem we want to elucidate, namely, the choice of the local part of the vertex and the role of the remaining nonlocality correction. We will discuss this in relation to two main deficiencies of the GWA: the self-screening error, which essentially stems from a bad description of induced exchange, and the incorrect atomic limit, which stems from a bad description of correlation.

### A. Self-screening error and vertex corrections

The self-screening problem has been numerically studied for one electron in Refs. 38 and 39 (called there self-interaction). Here, we discuss the main source of error and an approximate remedy.

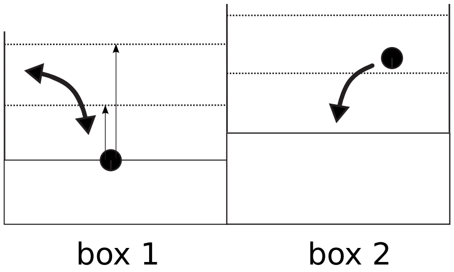

FIG. 1. Model system for removal and addition energies: first an electron is added to/removed from box 1 occupied by zero/one electron; in the second step, an electron is added to box 2 in the presence of the electron in box 1 (see text).

### *1. Self-screening*

In order to illustrate the problem of self-screening, we first consider an empty box with potential $V_0$ and introduce a particle (see Fig. 1, left box). This problem is of course solved exactly by the independent-particle Schrödinger equation,

$$\left(-\frac{\nabla^2}{2}+V_0(x_1)\right)\phi_1(x_1)=\epsilon_1\phi_1(x_1). \tag{6}$$

The total energy difference between the system with $N=0$ and $N+1=1$ particles is given by the eigenvalue $\epsilon_1$. If one dealt with this problem using the KS equation of DFT, one would get the same equation and result since the density of the system is zero. The same holds, of course, for any other commonly used approach, such as Hartree–Fock (HF) or *GW*.

One can now instead think of solving the reverse problem, namely, to extract the particle from the box. Again, Eq. (6) correctly describes the total energy difference between $N=1$ and $N-1=0$ particles. The description in the KS framework is now less trivial since there is a nonvanishing charge density in the box. The KS equation reads as

$$\left(-\frac{\nabla^2}{2}+V_0(x_1)+v_H(x_1)+v_{\mathrm{xc}}(x_1)\right)\phi_1(x_1)=\epsilon_1\phi_1(x_1), \tag{7}$$

where the exact KS xc potential $v_{\mathrm{xc}}$ is nothing else than the Hartree potential $v_H$, but with opposite sign.[40] Therefore, the KS approach yields the same, exact result (as it should since Koopmans' theorem applies to the highest occupied state).

Also HF is exact, as one can easily verify: the HF equation

$$\left(-\frac{\nabla^2}{2}+V_0(x_1)+v_H(x_1)\right)\phi_1(x_1) - \int dx_2\frac{\phi_1(x_1)\phi_1^*(x_2)}{|x_1-x_2|}\phi_1(x_2)=\epsilon_1\phi_1(x_1) \tag{8}$$

has the exact cancellation between the Hartree and the Fock terms because the density is built with just the state $\phi_1$ one is looking at.

Let us now look at the COHSEX quasiparticle equation,

$$\left(-\frac{\nabla^2}{2}+V_0(x_1)+v_H(x_1)\right)\phi_1(x_1) - \int dx_2\left(\phi_1(x_1)\phi_1^*(x_2)W(x_1x_2) + \delta(x_1-x_2)\frac{1}{2}W_p(x_1x_2)\right)\phi_1(x_2)=\epsilon_1\phi_1(x_1), \tag{9}$$

where $W$ is the statically screened Coulomb potential and $W_p=W-v$, with $v$ as the bare Coulomb potential. The exchange term that previously cancelled the Hartree self-interaction is now screened, and the cancellation is no longer perfect. This problem is not cured, or at least not completely, by the last term (the Coulomb hole). If we had $W=v$ (no screening), we would be back to the exact HF result. However, RPA screening (which is the one that is used in COHSEX) is calculated by summing independent transitions from occupied states (vertical arrows in Fig. 1), and the box containing one particle has, in fact, one occupied state—there is no reason to think that one would find vanishing RPA screening. The same holds for full GW, where dynamical screening and (sometimes) self-consistency is considered. Therefore, it is obvious that *GW suffers from a self-screening problem*: the particle that is extracted from the system screens itself, which makes the approach nonsymmetric with respect to the case where the particle is added to the empty box. In other words, when the quasiparticle eigenvalue is used to represent a total energy difference, the energy of the system has changed after one has first added and then extracted one electron! The source of this error comes from the fact that direct and exchange interactions are not treated on equal footing in *GW*. One can overcome this problem in various ways, e.g., considering nonlocal vertex corrections (see, for example, Ref. 19) or trying to keep Hartree and exchange terms together by using a spin-dependent Coulomb potential[18,41,42] or the Parquet theory.[31] Here, we make suggestions for approximate vertex corrections.

### *2. Vertex corrections*

*a. Valence state* Let us now see how vertex corrections remove the self-screening error and which is the important contribution. First, we evaluate the effect of the vertex in $P=-iGG\Gamma$ on the test charge-test charge (TC-TC) screened Coulomb interaction defined by $W=v+vPW$. The easiest way to calculate the exact polarizability is to use TDDFT, with $P=\chi_0+\chi_0 f_{\mathrm{xc}}P$ (where $\chi_0$ is the KS independent-particle polarizability).[43] Since $v_{\mathrm{xc}}$ is minus the Hartree potential, the exact xc kernel $f_{\mathrm{xc}}$ is minus the bare Coulomb interaction, $f_{\mathrm{xc}}=-v$. Therefore, the reducible polarizability $\chi=\chi_0+\chi_0(v+f_{\mathrm{xc}})\chi$ equals the independent-particle $\chi_0$ and we find $W=v+v\chi_0 v$. This is what one would expect: it simply expresses the fact that one electron alone is always independent. This exact TC-TC screening, however, does not cure the self-screening error since $W\neq v$.

In order to show the effect of the explicit vertex in $\Sigma_{\mathrm{xc}}=iGW\Gamma$, we evaluate the self-energy using Eq. (2) for the vertex, which yields

$$\Sigma_{\mathrm{xc}}(12) = iG(12)v(21^+) + iG(12)v(23)\chi_0(34)v(41^+) + iG(14)\frac{\delta\Sigma_{\mathrm{xc}}(42)}{\delta\rho(5)}\chi_0(53)v(31^+), \qquad (10)$$

where we used that $PW=\chi v$ and the fact that here $\chi=\chi_0$. The difficulty in Eq. (10) is the unknown term $\delta\Sigma_{\mathrm{xc}}/\delta\rho$. However, being interested in the occupied state $\phi_v(x_2)$, here it is reasonable to approximate $\delta\Sigma_{\mathrm{xc}}/\delta\rho$ by $\delta v_{\mathrm{xc}}/\delta\rho$ since the exact $v_{\mathrm{xc}}$ should act correctly on the highest occupied state. Indeed, with $\delta\Sigma_{\mathrm{xc}}/\delta\rho \approx f_{\mathrm{xc}} = -v$ for one electron, the last two terms in Eq. (10) cancel each other: the exact solution for the valence state is obtained. This suggests approximating the self-energy for the top valence band as

$$\Sigma_{\mathrm{xc}}(12) \approx iG(12)W(21^+) + iG(12)W(31^+)f_{\mathrm{xc}}(24)P(43) = iG(12)W(31^+)\Gamma(23), \qquad (11)$$

with $\Gamma(23)=\delta(23)+f_{\mathrm{xc}}(24)P(43)$. This result puts into evidence several interesting facts. First, it demonstrates that the vertex in $P$ alone is not sufficient to correct the self-screening problem of *GW*. Second, it suggests that one can indeed neglect a nonlocal part of the vertex corrections; it should be similar, but not identical, to $\Delta\Gamma$ in Eq. (4) since the full $f_{\mathrm{xc}}$ instead of $f_{\mathrm{xc}}^{\mathrm{eff}}$ is to be used. The difference $f_{\mathrm{xc}}^{(1)} = f_{\mathrm{xc}} - f_{\mathrm{xc}}^{\mathrm{eff}}$ is essentially the quasiparticle gap correction.

*b. Conduction state* One might now hope that $\Gamma$ could always be reasonably approximated by a two-point function. In order to understand the necessity of a three-point vertex, it is instructive to look at the addition of a second electron. This electron could be localized in the same region as the first electron, but also elsewhere: the latter choice represents, e.g., the case of ionic insulators. To model this, the second electron is added to a second separate box (see Fig. 1), and therefore it does not feel induced exchange, but only an induced Hartree potential (this applies also to the case of opposite spin since the latter situation equally suppresses exchange effects).

In order to describe in a simple way the conduction quasiparticle energy, we have to resort to further approximations: we use a static screening $W(x_2x_1)\delta(t_{1^+}-t_2)$ to approximate the self-energy in the functional derivative in Eq. (2). Keeping $W$ fixed as an externally given interaction, this yields

$$\frac{\delta\Sigma_{\mathrm{xc}}(42)}{\delta\rho(5)} = i\frac{\delta G_{\mathrm{KS}}(42)}{\delta\rho(5)}W(x_2x_4)\delta(t_{4^+}-t_2) = iG_{\mathrm{KS}}(46)G_{\mathrm{KS}}(62)\chi_0^{-1}(65)W(x_2x_4)\delta(t_{4^+}-t_2), \qquad (12)$$

where we used $\delta G_{\mathrm{KS}}/\delta\rho = -G_{\mathrm{KS}}(\delta G_{\mathrm{KS}}^{-1}/\delta\rho)G_{\mathrm{KS}} = G_{\mathrm{KS}}\chi_0^{-1}G_{\mathrm{KS}}$. The self-energy then becomes

$$\Sigma_{\mathrm{xc}}(12) = iG(12)W(21^+) + G(14)W(31^+)G_{\mathrm{KS}}(46)G_{\mathrm{KS}}(62) \times\chi_0^{-1}(65)W(x_2x_4)P(53)\delta(t_{4^+}-t_2). \qquad (13)$$

When this self-energy acts on the conduction state $\phi_c(x_2)$ in box 2, because of the vanishing overlap between conduction and valence states, the two KS Green's functions in the last term on the right-hand side of Eq. (13) contribute with their electron part only. Hence, $t_6$ is integrated from $t_4$ to $t_2$. On the other hand, the static approximation implies that $t_2=t_{4^+}$: the correction to the GW approximation vanishes! Note that in order to obtain this simple result, it was crucial to take a static approximation for $\Sigma$ (the same conclusion is reached if COHSEX instead of statically screened exchange is used). The constraint of a non-self-consistent $G_{\mathrm{KS}}$ is, instead, just for the sake of simplicity, in the spirit of the so-called $G_0W_0$ calculations in which the KS Green's function is usually used to build the self-energy.

The interpretation of this finding is as follows: adding the second particle in the empty box 2 leads to an induced charge in box 1 (created by the virtual transitions), where charge is already present. The second charge has no overlap, hence no exchange interaction, with this induced charge. There should be a further correlation correction, but this is evidently neglected when one chooses a static approximation for the self-energy (the screening expresses then merely static relaxation).

It seems reasonable to generalize these intuitive findings for the case of more bands. In fact, we know that the KS potential yields often a quite good description for all valence bands, not only the highest occupied one. In these cases, one should expect that the TC-TE approximation for the self-energy derived above is the method of choice to describe valence bands. Of course, the exact KS potential and kernel are not known, but one can express the TC-TE screened interaction $W^{\mathrm{TC\text{-}TE}} = v + (v+f_{\mathrm{xc}})\chi v$ as $\chi_0^{-1}\chi v$ [here we use that $\chi_0(v+f_{\mathrm{xc}})\chi = \chi - \chi_0$ from TDDFT]. Since TDLDA often yields a good description of $\chi$ (Ref. 10) and since $\chi_0$ should be quite close to the LDA result because the LDA bandgap resembles the exact KS one,[44,45] one might use TDLDA as a first approximation. For conduction states that are spatially distinct from valence states or with different spin, the above discussions suggest that one should, instead, rather stick to the TC-TC approximation (i.e., *GW*).

## B. Atomic limit

Another very important diagnostic tool is the study of the atomic limit. This limit corresponds to pulling apart the atoms of a system so that the overlap between wave functions on different atoms is negligible. In particular, $H_2^+$ and $H_2$ dissociations have been extensively studied in order to trace errors in the approximations used in DFT and MBPT.[46–49] The study of the $H_2$ dissociation within *GW* shows that this approximation is not size consistent, i.e., the total energy in the atomic limit is not equal to the sum of the total energies of the two isolated atoms.[48,49] Also the description of the spectrum can be expected problematic, and this can be understood as follows: the GWA takes into account only the Hartree and exchange and the induced Hartree potentials to describe an interacting system and its response to an additional electron or hole, i.e., besides exchange it gives a classical description of the system and of its response. This means, e.g. for $H_2^+$, that an additional electron sees half an electron on each atom at any distance of the two atoms; this results in only one type of addition energy. In reality, instead, one has the same probability of finding the electron on one or the other atom, resulting in two types of addition energies depending if the additional electron is added to an empty or to an occupied atom. In Sec. III, using the exactly solvable two-site Hubbard model, we will show that *GW* indeed yields the wrong vanishing-hopping limit for the spectral function of this model, that the approximate vertex, which cures the self-screening error, does not correct the atomic limit, and that the fundamental origin of this failure lies in the bad description of correlation.

## III. ILLUSTRATION: THE TWO-SITE HUBBARD MOLECULE

The Hubbard model[36,37] is widely used to deal with the physics of strongly correlated materials. Since the model can be solved exactly for small cluster sizes, it is very useful for theoretical investigations, as, for example, for scrutinizing the performance of the GWA.[18,41,50–53] Here we use the two-site Hubbard molecule to show the effects of the self-screening problem on the removal and addition energies, the performance of *GW* in the atomic limit and the impact of vertex corrections on the observed problems. To be precise, our "Hubbard molecule" is a two-site system with one orbital per site and an on-site electron-electron interaction, described by the following Hamiltonian:

$$H=-t\sum_{\substack{i,j=1,2\\ i\neq j}}\sum_{\sigma}c^{\dagger}_{i\sigma}c_{j\sigma}+\frac{U}{2}\sum_{i=1,2}\sum_{\sigma\sigma'}c^{\dagger}_{i\sigma}c^{\dagger}_{i\sigma'}c_{i\sigma'}c_{i\sigma}+\epsilon_0\sum_{\sigma,i=1,2}n_{i\sigma}+V_0. \qquad (14)$$

Here, $n_{i\sigma}=c^{\dagger}_{i\sigma}c_{i\sigma}$, $c^{\dagger}_{i\sigma}$ and $c_{i\sigma}$ are the creation and annihilation operators for an electron at site $i$ with spin $\sigma$, $U$ is the on-site (spin-independent) interaction, $-t$ is the hopping kinetic energy, and $\epsilon_0$ is the orbital energy. The Hamiltonian further contains a potential $V_0$ that can be chosen to fix the zero energy scale. The eigenstates of the system will be linear combinations of Slater determinants, which are denoted by the kets $|12\rangle$, with occupations of the sites 1, 2 given by 0, ↑, ↓, ↑↓. We consider only one electron in this system and we choose $V_0=0$ so that the vacuum state $|\zeta^{N=0}\rangle=|00\rangle$ has zero energy.[54]

### A. One-particle Green's function: Exact solution

Using the Lehmann representation, the one-particle time-ordered Green's function for our system reads as

$$G_{ij\sigma}(\omega)=\sum_{\phi}\frac{\langle\phi^{N=2}|c^{\dagger}_{i\sigma}|\psi_0^{N=1}\rangle\langle\psi_0^{N=1}|c_{j\sigma}|\phi^{N=2}\rangle}{\omega-(E_{\phi}-E_0)+i\eta}+\sum_{\zeta}\frac{\langle\zeta^{N=0}|c_{j\sigma}|\psi_0^{N=1}\rangle\langle\psi_0^{N=1}|c^{\dagger}_{i\sigma}|\zeta^{N=0}\rangle}{\omega+(E_{\zeta}-E_0)-i\eta}, \qquad (15)$$

where the indices $i,j$ run on the model sites. Here, $|\psi_0^{N=1}\rangle$ and $E_0$ are the ground-state wave function and energy, respectively, $|\phi^{N=2}\rangle$ and $E_{\phi}$ are the wave functions and energies of the system with a particle added, and $|\zeta^{N=0}\rangle$ and $E_{\zeta}$ are the wave functions and energies of the system with a particle removed. These quantities can be obtained by diagonalizing the Hamiltonian for $N=0$, $N=1$, and $N=2$ electrons, separately (as shown in Appendix A). In particular, the ground state is $|\psi_0^{N=1}\rangle=1/\sqrt{2}[|\uparrow 0\rangle+|0\uparrow\rangle]$ with $E_0=(\epsilon_0-t)$ (equivalently, the spin-down situation could be chosen). Note that, since we consider a spin-independent Hamiltonian, the Green's function in Eq. (15) is diagonal in spin. The one-particle Green's function has the following components:

$$G_{ij\uparrow}(\omega)=\frac{(-1)^{(i-j)}}{2}\left[\frac{1}{\omega-(\epsilon_0+t)+i\eta}+\frac{(-1)^{(i-j)}}{\omega-(\epsilon_0-t)-i\eta}\right], \qquad (16)$$

$$\begin{aligned}G_{ij\downarrow}(\omega)=\frac{(-1)^{(i-j)}}{4}\Bigg[&\frac{1}{\omega-(\epsilon_0+t)+i\eta}+\frac{1}{\omega-(\epsilon_0+t+U)+i\eta}\Bigg]\\&+\frac{1}{2}\left[\frac{\frac{1}{a^2}\left(1+\frac{4t}{(c-U)}\right)^2}{\omega-(\epsilon_0+t-(c-U)/2)+i\eta}+\frac{\frac{1}{b^2}\left(1-\frac{4t}{(c+U)}\right)^2}{\omega-(\epsilon_0+t+(c+U)/2)+i\eta}\right],\end{aligned} \qquad (17)$$

where $c=\sqrt{16t^2+U^2}$, $a=\sqrt{2((16t^2/(c-U)^2)+1)}$, and $b=\sqrt{2((16t^2/(c+U)^2)+1)}$. The one-particle Green's function is spin diagonal; the spin-down block has only the electron part, whereas the spin-up block has both electron and hole parts. This is consistent with the fact that with a spin-up electron in the ground state one can have only spin-up holes. Note also that $G_{11\uparrow}=G^{U=0}_{11\uparrow}$ and $G_{12\uparrow}=G^{U=0}_{12\uparrow}$, whereas

$$G^{U=0}_{ij\downarrow}(\omega)=\frac{(-1)^{(i-j)}}{2}\left[\frac{1}{\omega-(\epsilon_0+t)+i\eta}+\frac{(-1)^{(i-j)}}{\omega-(\epsilon_0-t)+i\eta}\right]. \qquad (18)$$

The Green's function at $U=0$ represents the noninteracting Green's function $G_0$. The self-energy $\Sigma(\omega)=G_0^{-1}(\omega)-G^{-1}(\omega)$ has, therefore, the following structure:

$$\Sigma(\omega)=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&\Sigma_{11\downarrow}&\Sigma_{12\downarrow}\\0&0&\Sigma_{12\downarrow}&\Sigma_{11\downarrow}\end{pmatrix}. \qquad (19)$$

Note that here the Hartree term is included in the self-energy, which contains hence the full electron-electron interaction, contrary to the xc $\Sigma_{\mathrm{xc}}$ defined in Sec. II. The self-energy has only a spin-down part, i.e., the electron in the system interacts only with spin-down electrons. This is in line with the fact that our system consists of one electron with spin up. When we add a second electron to the system, it can have spin up or spin down. If the second electron has spin up, the two electrons are locked in a configuration where two different sites are occupied, and therefore, there is no interaction.

TABLE I. Two-site Hubbard model: eigenvalues and coefficients for the one-electron sector.

| $E_i$ | $\lvert\uparrow 0\rangle$ | $\lvert\downarrow 0\rangle$ | $\lvert 0\uparrow\rangle$ | $\lvert 0\downarrow\rangle$ |
|---|---|---|---|---|
| $\epsilon_0-t$ | 0 | $1/\sqrt{2}$ | 0 | $1/\sqrt{2}$ |
| $\epsilon_0-t$ | $1/\sqrt{2}$ | 0 | $1/\sqrt{2}$ | 0 |
| $\epsilon_0+t$ | 0 | $1/\sqrt{2}$ | 0 | $-1/\sqrt{2}$ |
| $\epsilon_0+t$ | $1/\sqrt{2}$ | 0 | $-1/\sqrt{2}$ | 0 |

If the second electron has spin down, the two electrons can interact.

One can interpret the poles of the Green's function using a simple molecular picture with bonding and antibonding orbitals at energies $\epsilon_0-t$ and $\epsilon_0+t$, respectively, and a spin-up electron in the bonding orbital. If $U=0$, one can remove (add) a spin-up (spin-down) electron from (to) the bonding orbital ($\omega=\epsilon_0-t$), and one can add a spin-up/spin-down electron to the antibonding orbital ($\omega=\epsilon_0+t$). When the on-site electron-electron interaction $U$ is switched on, the energy for the addition of a spin-down electron to the bonding state evolves to $\omega=\epsilon_0+t+U/2-c/2$, and the addition energy to the antibonding state is split into $\omega=\epsilon_0+t$ and $\omega=\epsilon_0+t+U$. The addition of a spin-down electron, furthermore, can excite the system, giving rise to the satellite $\omega=\epsilon_0+t+U/2+c/2$.

### *1. Limiting cases*

We now discuss two limiting cases, which are directly related to the importance of correlation: the noninteracting limit and the atomic limit.

- *Noninteracting limit:* $U\rightarrow 0$ . Of course, in this limit one retrieves the noninteracting Green's function. The spectral weight of the pole $\omega=\epsilon_0+t+(c+U)/2$, which becomes $\omega=\epsilon_0+3t$, is suppressed. Note that $\omega=\epsilon_0+3t$ deviates from the antibonding peak by an energy $\Delta=2t$, which is a pole of the polarizability $P$: this pole of the Green's function involves hence an excitation of the system, which justifies the identification of the related peak as a satellite.
- *Atomic limit:* $t\rightarrow 0$ . In this limit one get, in particular, $a(c-U)\approx U/\sqrt{2}t(1+2t^2/U^2)8t^2/U=8t/\sqrt{2}(1+2t^2/U^2)$. Note that for $t=0$ the ground-state energy goes to $E_0=\epsilon_0$ so that it approaches degeneracy with the other doublet state in the $N=1$ spin-up subspace (see Table I). However for any small but finite $t$ this degeneracy is lifted. In this limit the poles of the Green's function reduce to the addition and removal energies of two isolated atoms, one with one electron and the other one empty.[36,37] Indeed the spin-up poles retain the same equal weight ($\pm 1/2$) and go toward $\omega=\epsilon_0$, which can be interpreted as the removal energy of an atom with a spin-up electron and the addition energy of an empty atom, respectively. The spin-down poles $\omega=\epsilon_0+t$ and $\omega=\epsilon_0+t-(c-U)/2$, and $\omega=\epsilon_0+t+U$ and $\omega=\epsilon_0+t+(c+U)/2$ (satellite) merge at $\omega=\epsilon_0$ and $\omega=\epsilon_0+U$, respectively, each of the four with equal weight ($\pm 1/4$). These two energies can be interpreted as the energy for the addition of a spin-down electron to an empty atom and to an atom with a spin-up electron, respectively.

## B. One-particle Green's function: *GW* solution

We now compare this exact result with the GWA. First, we derive the RPA polarizability $P=-iGG$, which is given by

$$P_{ij\uparrow}(\omega)=\frac{(-1)^{(i-j)}}{4}\left[\frac{1}{\omega-2t+i\eta}-\frac{1}{\omega+2t-i\eta}\right]. \tag{20}$$

Note that since we have only one electron with spin up in the ground state, the polarizability is not zero only for the spin-up block. Moreover, the same result is obtained whether the noninteracting or exact $G$ is used since they are equal for the spin-up block. The RPA screened interaction $W=[1-UP(\omega)]^{-1}U$ becomes

$$W_{ij}(\omega)=U\delta_{ij}+(-1)^{(i-j)}\frac{U^2t}{\omega^2-h^2}, \tag{21}$$

with $h^2=4t^2+2Ut$. Remember that the Coulomb interaction $U$ is spin independent.

The self-energy $\Sigma(\omega)=v_H+i/2\pi\int d\omega' G(\omega+\omega')W(\omega')e^{i\omega'\eta}$, with $v_H$ as the Hartree potential and $G=G_0$, has the following structure:

$$\Sigma(\omega)=\begin{pmatrix}\Sigma_{11\uparrow} & \Sigma_{12\uparrow} & 0 & 0\\ \Sigma_{12\uparrow} & \Sigma_{11\uparrow} & 0 & 0\\ 0 & 0 & \Sigma_{11\downarrow} & \Sigma_{12\downarrow}\\ 0 & 0 & \Sigma_{12\downarrow} & \Sigma_{22\downarrow}\end{pmatrix}, \tag{22}$$

with

$$\Sigma_{ij\uparrow}(\omega)=\frac{U^2t}{4h}\left[\frac{1}{\omega-(\epsilon_0+t+h)+i\eta}+\frac{(-1)^{(i-j)}}{\omega-(\epsilon_0-t-h)-i\eta}\right], \tag{23}$$

$$\Sigma_{ij\downarrow}(\omega)=\frac{U}{2}\delta_{ij}+\frac{U^2t}{4h}\left[\frac{1}{\omega-(\epsilon_0+t+h)+i\eta}+\frac{(-1)^{(i-j)}}{\omega-(\epsilon_0-t+h)+i\eta}\right]. \tag{24}$$

The one-particle Green's function can be obtained from

$$G^{GW}(\omega)=[G_0^{-1}(\omega)-\Sigma(\omega)]^{-1}. \tag{25}$$

This equation should, in principle, be solved self-consistently, i.e., the interacting Green's function obtained from Eq. (27) should be used in the self-energy until convergence is achieved. However, a self-consistent procedure is computationally demanding, specially for big systems and, furthermore, the neglect of vertex corrections together with self-consistency has been found to be problematic for the calculation of spectra.[55,56] Therefore, in practice, Eq. (27) is used only once to obtain an updated Green's function [however, $G_0$ already contains part of the interaction through a suitable single-particle Hamiltonian, such as KS, HF, or quasiparticle self-consistent *GW* (Ref. 57)]. In this way, the interacting Green's function inherits the chemical potential of the noninteracting Green's function, which can result in a violation of the particle number conservation and a poor description of the satellite spectrum.[50,51] This problem can be in part corrected by shifting the energy zero in the noninteracting Green's function in such a way as to align its chemical potential to that of the interacting Green's function.[9] This results in a shift in the self-energy. We will come back to this issue later in the paper. For the moment we will not shift the chemical potential. The *GW* Green's function is given by

$$G^{GW}_{ij\uparrow}(\omega) = (-1)^{(i-j)}\left[\frac{\left(\frac{1}{4}+\frac{2t+h}{4A}\right)}{\omega-\omega_1+i\eta}+\frac{\left(\frac{1}{4}-\frac{2t+h}{4A}\right)}{\omega-\omega_2-i\eta}\right] + \frac{\left(\frac{1}{4}-\frac{2t+h}{4A}\right)}{\omega-\omega_3+i\eta}+\frac{\left(\frac{1}{4}+\frac{2t+h}{4A}\right)}{\omega-\omega_4-i\eta}, \tag{26}$$

$$G^{GW}_{ij\downarrow}(\omega) = (-1)^{(i-j)}\left[\frac{\left(\frac{1}{4}+\frac{2t-h+U/2}{4B}\right)}{\omega-\omega_5+i\eta} + \frac{\left(\frac{1}{4}-\frac{2t-h+U/2}{4B}\right)}{\omega-\omega_6+i\eta}\right] + \frac{\left(\frac{1}{4}-\frac{2t+h-U/2}{4C}\right)}{\omega-\omega_7+i\eta} + \frac{\left(\frac{1}{4}+\frac{2t+h-U/2}{4C}\right)}{\omega-\omega_8+i\eta}, \tag{27}$$

where $A=\sqrt{(h+2t)^2+2U^2t/h}$, $B=\sqrt{(h-2t-U/2)^2+2U^2t/h}$, $C=\sqrt{(h+2t-U/2)^2+2U^2t/h}$, and the poles are $\omega_{1,2}=(2\epsilon_0-h\pm A)/2$, $\omega_{3,4}=(2\epsilon_0+h\pm A)/2$, $\omega_{5,6}=(2\epsilon_0+h+U/2\pm B)/2$, and $\omega_{7,8}=(2\epsilon_0+h+U/2\pm C)/2$.

### 1. Limiting cases

We can now study the noninteracting limit and the atomic limit.

- *Noninteracting limit:* $U\to 0$ . In this limit the interacting *GW* Green's function reduces, of course, to the noninteracting one, with the poles $\omega_1$ ("+" combination), $\omega_4$ ("−" combination), $\omega_5$ (+ combination), $\omega_6$ (− combination), and $\omega_8$ (− combination) collapsing to the bonding and antibonding energies $\omega=\epsilon_0-t$ and $\omega=\epsilon_0+t$, respectively. The poles $\omega_2$, $\omega_3$, and $\omega_7$, instead, collapse to $\omega=\epsilon_0-3t$ and $\omega=\epsilon_0+3t$ with zero intensity. Note also that the energies $\omega=\epsilon_0-3t$ and $\omega=\epsilon_0+3t$ deviate from the bonding and antibonding peaks, respectively, by $\pm 2t$, which are the poles of the RPA polarizability $P$. This means that these energies arise from excitations of the system. The poles $\omega_2$, $\omega_3$, and $\omega_7$ can be, therefore, identified as satellites. In Fig. 2 we compare the *GW* and exact addition/removal energies. The GWA yields two satellites more than the exact solution, namely, $\omega_2$ and $\omega_3$. These satellites come from the poles of the spin-up Green's function and are produced by the frequency-dependent spin-up self-energy.

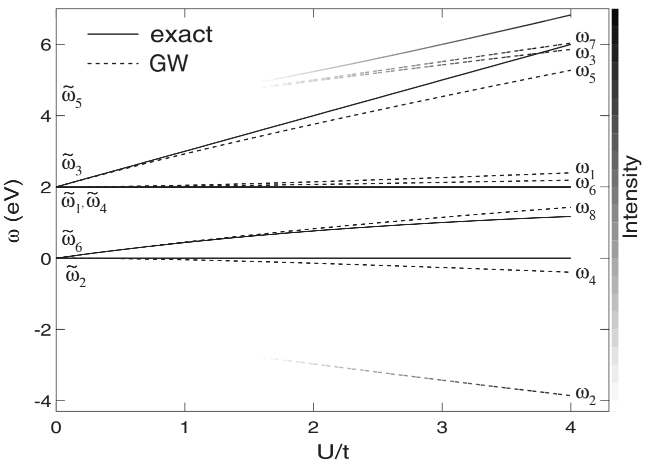

FIG. 2. Two-site Hubbard model at one-fourth filling: comparison between exact (solid lines) and *GW* excitation (dashed lines) energies as function of $U/t$, with $\epsilon_0=t=1$ eV and $\mu=0$. The thin lines represent weak satellites, which appear with increasing interaction $U$. The labels on the left of the figure refer to the exact energies, with $\tilde{\omega}_1=\tilde{\omega}_4=\epsilon_0+t$, $\tilde{\omega}_2=\epsilon_0-t$, $\tilde{\omega}_3=\epsilon_0+t+U$, $\tilde{\omega}_5=\epsilon_0+t+U/2+c/2$, and $\tilde{\omega}_6=\epsilon_0+t+U/2-c/2$, whereas the labels on the right refer to the *GW* energies.

- *Atomic limit:* $t\to 0$ . In this limit all the spin-up poles acquire an equal weight ($\pm 1/4$) and go toward $\omega=\epsilon_0$, in agreement with the exact solution. The unphysical poles, hence the self-screening problem, cannot be detected in the atomic limit because the excitation energy $2t\to 0$. The spin-down poles $\omega_5$ and $\omega_7$ (satellite) go toward $\omega=\epsilon_0+U/2$, each with weight ($\pm 1/2$), whereas $\omega_6$ and $\omega_8$ merge at $\omega=\epsilon_0$ with zero weight. This is in contrast to the exact solution where the four poles go toward $\omega=\epsilon_0$ and $\omega=\epsilon_0+U$ with equal weight ($\pm 1/4$). The total spectral weight is the same for *GW* and exact poles, as one can see from the spectral function $A(\omega)$

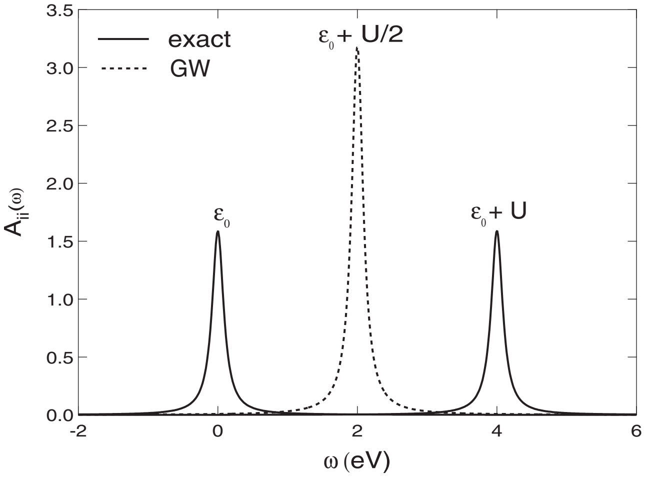

FIG. 3. Two-site Hubbard model at one-fourth filling: comparison between exact (solid line) and *GW* (dashed line) spin-down spectral function in the limit $t\to 0$, with $\epsilon_0=t$ and $U=4$ eV. Only the component $A_{11}$ appears in the plot, whereas $A_{12}$ is zero. For the addition of a spin-down electron the GWA yields only one peak at $\omega=\epsilon_0+U/2$ in the limit $t\to 0$, instead of two peaks at $\omega=\epsilon_0$ and $\omega=\epsilon_0+U$ as in the exact solution. However the spectral weight of the *GW* peak is equal to the sum of the spectral weight of the exact peaks.

$=\pi^{-1}\,\mathrm{sign}(\mu-\omega)\Im G(\omega)$ depicted in Fig. 3. It is very instructive to look at the total energy in the atomic limit. Using the Galitskii–Migdal-like formula (14) in Ref. 25, one finds that the total energy of the system depends on the hole part of $G_{\uparrow}^{GW}$. In the atomic limit $G_{\uparrow}^{GW}$ reduces to the exact one (no matter the level of self-consistency) and therefore also the GW total energy equals the exact one in this limit, i.e., $E_{\mathrm{tot}}=\epsilon_0$. This is an interesting example where $GW$ performs very well for the total energy, but badly for the quasiparticle spectrum.

As mentioned earlier in the paper, one can take into account the difference in the chemical potential between noninteracting and interacting Green's functions by shifting the self-energy as $\Sigma(\omega-\tilde{\omega})$ such that $\mu=\mu_0+\tilde{\omega}$, with $\mu_0=\epsilon_0-t$ as the chemical potential of the nointeracting Green's function.[9,50,51] We found that this shift does not yield a substantial overall improvement of the energies and, in particular, it leads to the same atomic limit solution as without shifting the chemical potential. Therefore we do not report the results in the article.

### C. Discussion

Comparing exact and $GW$ solution, we can now discuss the self-screening error and the atomic limit.

#### 1. Self-screening error

We start by analyzing the $GW$ self-energy in Eq. (22). First, this self-energy is not zero also for the spin-up block, unlike the exact one in Eq. (19), which is not zero only for the spin-down block: this means that in the GWA the electron of the system interacts also with itself! Second, since $G_{\uparrow}=G_{0\uparrow}$, $G_0W_0$, $G_0W$, $GW_0$, and $GW$ (with $G$ as the exact Green's function) give the same expression for the spin-up self-energy.

Direct consequence of the self-screening is the occurrence of unphysical satellites (namely, $\omega_2$ and $\omega_3$) in the $GW$ solution: the nonzero spin-up self-energy creates two extra poles in the spin-up one-particle Green's function. This is due to the fact that one and the same electron can be used twice—for example, once to be removed and at the same time to screen this perturbation. These findings are in line with the $GW$ results of Ref. 18, where the GWA is shown to overestimate the amplitude of the satellite spectrum, which deteriorates with the increase in correlation.

*a. Electron addition and removal symmetry* In Sec. II we showed that the self-screening error makes the removal and addition of an electron in a box nonequivalent within $GW$. Here, we illustrate this asymmetry by comparing the poles of the Green's function for the Hubbard molecule with one electron and two electrons. The exact and $GW$ one-particle Green's function for the half-filled Hubbard molecule are given in Appendix B.[52] The lowest addition energy in the one-electron system should be equal to the highest removal energy in the two-electron system. This is the case for the exact Green's function: indeed the lowest addition energy in the one-electron system is (spin-down pole) $\omega=\epsilon_0+t-(c-U)/2$, which corresponds to the highest removal energy in the two-electron system. The same is true for the noninteracting $G_0$.

Within the GWA the two energies are different: the lowest addition energy in the one-electron system is (spin-down pole) $\omega_8=(2\epsilon_0+h+U/2-\sqrt{(2t+h-U/2)^2+2U^2t/h})/2$, whereas the highest removal energy in the two-electron system is $\omega_4=(2\epsilon_0+h'+U/2-\sqrt{(2t+h'-U/2)^2+4U^2t/h'})/2$, with $h'=4t^2+4tU$. The difference stems from the different polarizability $P$, which is used to build the screening for the $N=1$ and $N=2$ cases. This simply shows again that the problems arise from the use of a TC-TC screening, which depends only on the charge density of the system but not on the charge that is to be screened. Indeed, the removal of an electron from the $N=2$ system should be screened by one electron only—which can be expressed through the vertex correction.

*b. Vertex corrections* We now show the effect of vertex corrections on the $GW$ removal and addition energies. First, we consider the vertex corrections in $P$ by using the exact polarizability instead of RPA. One arrives at a self-energy with a structure similar to that in Eq. (19). For one electron, the screened Coulomb interaction is given as $W=v+v\chi_0v$ (see Sec. II). This expression yields a screened Coulomb interaction with the same structure as Eq. (21), but with poles at $2t$ (the pole of $P$) instead of at $h$. This will change only the poles of the self-energy but not its structure. This illustrates that the inclusion of vertex corrections only in the polarizability are not sufficient to correct the structure of the self-energy!

It is the inclusion of an explicit vertex in the self-energy, namely, a two-point $\Gamma=\delta+f_{\mathrm{xc}}P$ for valence bands and, e.g., $\Gamma=\delta$ for the well separated conduction bands, which removes the self-screening error. Indeed, using this vertex it is clear that the self-energy remains unchanged for the spin-down block, whereas for the spin-up block $\Sigma_{\mathrm{xc}}=-v_H$ (as we showed in the previous section). Therefore, we arrive at

$$\Sigma(\omega)=\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \Sigma_{11\downarrow} & \Sigma_{12\downarrow} \\ 0 & 0 & \Sigma_{12\downarrow} & \Sigma_{22\downarrow} \end{pmatrix}, \qquad (28)$$

with $\Sigma_{11\downarrow}$ and $\Sigma_{12\downarrow}$ given by Eq. (24). We now get a self-energy with the same structure as the correct one. It is clear that now the spin-up block of the one-particle Green's function equals the noninteracting Green's function, like the exact one. For the spin-down block we get four poles as in the exact case, although they still differ from the exact values by the $GW$ error.

We point out that it is essential to use a three-point vertex in order to get the correct number of poles. Indeed, by using the two-point vertex $\Gamma=\delta+f_{\mathrm{xc}}P$ both for valence and conduction bands, one would get a zero self-energy for the spin-down block. Therefore, the spin-down Green's function would equal the noninteracting one, which has only two poles instead of four as the exact interacting Green's function: there would be no satellites since there would be no screening.

This illustrates how (i) the two-point vertex $\Gamma=\delta+f_{\mathrm{xc}}P$ corrects the self-screening error and (ii) a three-point vertex ($\Gamma=\delta+f_{\mathrm{xc}}P$ for the valence band and, in this case, $\Gamma=\delta$ for the conduction band) is essential in order to get qualitatively correct results.

### 2. Atomic limit

We showed that in the atomic limit $t\rightarrow 0$ the GWA does not yield the exact solution (see Fig. 3). We also saw that the self-screening (unphysical poles) does not affect the atomic limit. The error stems from the fact that the self-energy [Eqs. (23) and (24)] is static in this limit (it consists of the Hartree potential $U/2$ only for the spin-down block). The exact atomic limit self-energy, instead, has an extra term that is frequency dependent, namely,

$$\Sigma_{ij\downarrow}(\omega)=\delta_{ij}\frac{U}{2}\left[1+\frac{U}{2(\omega-\varepsilon_0)-U+i\eta}\right].$$

This self-energy shows, in addition to the Hartree potential, a frequency-dependent term that creates the extra pole $\omega=\epsilon_0+U$ besides the only pole $\omega=\epsilon_0$ of the noninteracting Green's function (for $t\rightarrow 0$). The appearance of the peak $\omega=\epsilon_0+U$ is an effect of "strong correlation." One can understand that the problems of *GW* in the atomic limit arise from the interpretation of the charge density: in *GW*, it is treated as a classical charge distribution, namely, half electron on each atom in the limit that responds to the additional electron or hole. Instead, it should rather express the probability for an electron to be on one or the other atom so that the additional electron can meet an empty or occupied atom with equal probability, which leads to the peak splitting.

*a. One site-one electron* In the limit $t\rightarrow 0$ the two-site Hubbard model should represent two isolated atoms.[36,37] In order to compare this limiting case with the solution of an isolated atom, we calculate the exact and *GW* one-particle Green's function for the case of a one-site Hubbard model with one electron. We choose as ground state the spin-up configuration $|\uparrow\rangle$.

The exact one-particle Green's function is diagonal in spin space with

$$G_{\uparrow}=\frac{1}{\omega-\epsilon_0-i\eta},\qquad G_{\downarrow}=\frac{1}{\omega-U-\epsilon_0+i\eta}. \tag{29}$$

Therefore, there is only a removal energy, $\omega=\epsilon_0$, and an addition energy, $\omega=\epsilon_0+U$, for this system. The exact self-energy is given by

$$\Sigma(\omega)=\begin{pmatrix}0 & 0\\ 0 & U\end{pmatrix}, \tag{30}$$

which reflects the fact that the electron in the ground state can interact only with an additional spin-down electron.

The polarizability $P=-iGG$ is zero, consistent with the fact that the system has only one state in which it could be excited, which would, however, require a spin flip, which is not allowed. Therefore, there is no response of the system, and thus the screened potential equals the bare Coulomb potential, $W=U$. The self-energy, therefore, is equal to the exact one and, consequently, also the Green's function. Together with the fact that *GW* is also exact for the empty atom, it follows that for two separate one-site Hubbard models the GWA yields the exact solution, contrary to the $t\rightarrow 0$ limit of the two sites, as we showed above. This shows again the relation to the classical description of the system charge: for the one-site Hubbard model, where the electron is well confined, the classical description of the system works well (i.e., one knows where the electron is). For the two-site Hubbard model, where, instead, the electron shows its quantum nature, this classical picture fails! This is in line with the size-consistency problem *GW* suffers from[48,49] and it is analogous to what is observed in DFT.[47]

*b. Vertex corrections* We now show that the vertex corrections considered so far do not correct the atomic limit. First we consider the exact vertex corrections in $P$. The exact polarizability shifts only the poles of $\Sigma$ (see Sec. III C 1), and therefore one has again a zero self-energy for the spin-up block and only the Hartree term for the spin-down block in the limit $t\rightarrow 0$, as within *GW*.

Concerning the explicit vertex in $\Sigma$, if one considers the approximate three-point vertex correction ($\Gamma=\delta+f_{\mathrm{xc}}P$ for the valence state and $\Gamma=\delta$ for the conduction state), the spin-up self-energy is zero and the spin-down self-energy reduces to the Hartree term only in the limit $t\rightarrow 0$ (see Sec. III C 1), and one obtains again the *GW* solution. One might be tempted to explore the use of the two-point vertex $\Gamma=\delta+f_{\mathrm{xc}}P$ for both valence and conduction states, but then the self-energy is zero (see Sec. III C 1) and the spin-down Green's function has a pole at $\omega=\epsilon_0$ instead of at $\omega=\epsilon_0+U/2$ as within *GW*. This is, of course, completely wrong since neither exchange nor correlation are taken into account.

In conclusion, the vertex corrections that cure the self-screening problem are not sufficient to improve the description of the atomic limit. Indeed, we have shown that the two problems have a different nature; therefore, a more complex vertex, able to introduce an additional frequency dependence in $\Sigma$, is needed to fix both.

## IV. CONCLUSIONS

In this paper we discuss the importance of two-point and three-point parts of the vertex in relation to two major shortcomings of the GWA to the self-energy: the self-screening error and the incorrect atomic limit. Using the example of the removal of a particle from a box, we showed that the GWA to the self-energy suffers from a self-screening error, which stems from the use of a TC-TC screening. We showed that this error can be corrected by a two-point vertex contribution derived from TDDFT. The addition of a particle, instead, requires, in general, the use of a different approximate vertex, which illustrates why the general vertex function, valid both for valence and conduction states, must be a three-point function. We showed the consequences of the self-screening error and of the vertex corrections on the addition and removal energies of the two-site Hubbard model with one elec-

TABLE II. Two-site Hubbard model: eigenvalues and coefficients for the two-electron sector.

| $E_i$ | $\lvert\uparrow\downarrow\rangle$ | $\lvert\downarrow\uparrow\rangle$ | $\lvert\uparrow\uparrow\rangle$ | $\lvert\downarrow\downarrow\rangle$ | $\lvert\uparrow\downarrow 0\rangle$ | $\lvert 0\uparrow\downarrow\rangle$ |
|---|---|---|---|---|---|---|
| $2\epsilon_0+(U-c)/2$ | $\frac{4t}{a(c-U)}$ | $-\frac{4t}{a(c-U)}$ | 0 | 0 | 1/a | 1/a |
| $2\epsilon_0+(U+c)/2$ | $-\frac{4t}{b(c+U)}$ | $\frac{4t}{b(c+U)}$ | 0 | 0 | 1/b | 1/b |
| $2\epsilon_0+U$ | 0 | 0 | 0 | 0 | $-1/\sqrt{2}$ | $1/\sqrt{2}$ |
| $2\epsilon_0$ | 0 | 0 | 0 | 1 | 0 | 0 |
| $2\epsilon_0$ | 0 | 0 | 1 | 0 | 0 | 0 |
| $2\epsilon_0$ | $1/\sqrt{2}$ | $1/\sqrt{2}$ | 0 | 0 | 0 | 0 |

tron, for which we know the exact solution. Because of the self-screening, the GWA produces extra unphysical removal and addition energies. The two-point vertex $\Gamma=\delta+f_{\mathrm{xc}}P$ removes the extra energies, but it should be used only for the valence state, for which it produces exact results. For the conduction state, instead, this two-point vertex produces less poles than the exact solution. In fact, it seems to be more reasonable to stick to the TC-TC description of the screening for the conduction state, with $\Gamma=\delta$, which yields the correct number of energies, although the values are still different from the exact ones. One could extrapolate these findings for the case of more bands in the situation where the valence bands are similar and the conduction bands are localized elsewhere or with different spin.

The comparison with the exact solution for the two-site Hubbard model shed light on another feature of the GWA: in the atomic limit ($t\to 0$) the $GW$ solution for the two-site model does not reduce to the solution for two isolated sites; this is caused by the description of the system electrons as an average charge distribution, instead of a probability. The approximate three-point vertex, which cures the self-screening problem and yields the correct number of poles in the one-particle Green's function, is not sufficient to correct the atomic limit. Instead, the GWA gives the exact solution for two separate one-site Hubbard models (one site empty, one occupied): in this case the electron is well confined, it does not show its quantum nature, and a classical description works well.

## ACKNOWLEDGMENTS

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## APPENDIX A: DIAGONALIZATION OF THE TWO-SITE HUBBARD HAMILTONIAN WITH ONE ELECTRON

To construct the one-electron Green's function, we need the $N$-electron ground-state energy and wave function as well as the energies and wave functions for the system with $N+1$ and $N-1$ electrons. The Hamiltonian conserves particle number so we can diagonalize separately for $N-1$, $N$, and $N+1$ electrons. We denote the states of the system as linear combinations of Slater determinants $|12\rangle$ with occupations of the sites 1, 2 given by 0, ↑, ↓, ↑↓.[58] For the Hubbard molecule (14) with one electron, the system with $N-1$ electrons is the vacuum $|\zeta^{N=0}\rangle=|00\rangle$ with energy set to zero. For the $N=1$ system, the basis vectors are $|\uparrow 0\rangle$, $|\downarrow 0\rangle$, $|0\uparrow\rangle$, and $|0\downarrow\rangle$. In this basis the Hamiltonian matrix reads as

$$H=\begin{pmatrix} \epsilon_0 & 0 & -t & 0 \\ 0 & \epsilon_0 & 0 & -t \\ -t & 0 & \epsilon_0 & 0 \\ 0 & -t & 0 & \epsilon_0 \end{pmatrix}, \tag{A1}$$

with eigenvalues and eigenvectors given in Table I. We choose the ground state to be $|\psi_0^{N=1}\rangle=1/\sqrt{2}[|\uparrow 0\rangle+|0\uparrow\rangle]$ with $E_0=(\epsilon_0-t)$.[59]

The states $|N+1\rangle$ are found by diagonalizing the Hamiltonian matrix

$$H=\begin{pmatrix} 2\epsilon_0 & 0 & 0 & 0 & -t & -t \\ 0 & 2\epsilon_0 & 0 & 0 & t & t \\ 0 & 0 & 2\epsilon_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\epsilon_0 & 0 & 0 \\ -t & t & 0 & 0 & 2\epsilon_0+U & 0 \\ -t & t & 0 & 0 & 0 & 2\epsilon_0+U \end{pmatrix}, \tag{A2}$$

where the basis vectors are $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, $|\uparrow\downarrow 0\rangle$, and $|0\uparrow\downarrow\rangle$. The eigenvalues and eigenvectors are given in Table II, with $c=\sqrt{16t^2+U^2}$, $a=\sqrt{2((16t^2/(c-U)^2)+1)}$, and $b=\sqrt{2((16t^2/(c+U)^2)+1)}$.

Furthermore, to construct the one-particle Green's function, we need the action of the creation and annihilation operators on the ground state $|\psi_0^{N=1}\rangle=1/\sqrt{2}[|\uparrow 0\rangle+|0\uparrow\rangle]$,

$$c_{1\uparrow}^{\dagger}|\psi_0^{N=1}\rangle=c_{1\uparrow}^{\dagger}\frac{1}{\sqrt{2}}[|\uparrow 0\rangle+|0\uparrow\rangle]=-\frac{1}{\sqrt{2}}|\uparrow\uparrow\rangle,$$

$$c_{1\uparrow}|\psi_0^{N=1}\rangle=c_{1\uparrow}\frac{1}{\sqrt{2}}[|\uparrow 0\rangle+|0\uparrow\rangle]=\frac{1}{\sqrt{2}}|00\rangle,$$

$$c_{2\uparrow}^{\dagger}|\psi_0^{N=1}\rangle=c_{2\uparrow}^{\dagger}\frac{1}{\sqrt{2}}[|\uparrow 0\rangle+|0\uparrow\rangle]=\frac{1}{\sqrt{2}}|\uparrow\uparrow\rangle,$$

$$c_{2\uparrow}|\psi_0^{N=1}\rangle=c_{2\uparrow}\frac{1}{\sqrt{2}}[|\uparrow 0\rangle+|0\uparrow\rangle]=\frac{1}{\sqrt{2}}|00\rangle,$$

$$c_{1\downarrow}^{\dagger}|\psi_0^{N=1}\rangle=c_{1\downarrow}^{\dagger}\frac{1}{\sqrt{2}}[|\uparrow 0\rangle+|0\uparrow\rangle]=\frac{1}{\sqrt{2}}|\uparrow\downarrow 0\rangle-\frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle,$$

$$c_{1\downarrow}|\psi_0^{N=1}\rangle = 0,$$

$$c^{\dagger}_{2\downarrow}|\psi_0^{N=1}\rangle = c^{\dagger}_{2\downarrow}\frac{1}{\sqrt{2}}[|\uparrow 0\rangle + |0\uparrow\rangle] = \frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle + \frac{1}{\sqrt{2}}|0\uparrow\downarrow\rangle,$$

$$c_{2\downarrow}|\psi_0^{N=1}\rangle = 0.$$

We can immediately see from the expressions above that in the case of spin down the one-particle Green's function will have only the electron part, whereas for the spin-up case both electron and hole parts will be present. This is consistent with the fact that we have a spin-up electron in the ground state, and therefore we can have only a spin-up hole. The one-particle Green's function is given in Eqs. (16) and (17).

## APPENDIX B: EXACT AND *GW* ONE-ELECTRON GREEN'S FUNCTION FOR HALF-FILLED HUBBARD MOLECULE

On the same line as for the Hubbard molecule with one electron, one can construct the exact and *GW* one-electron Green's function also for the model with two electrons.[52] In this case the ground state is $|\psi_0\rangle = 4t/(a(c-U))(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) + 1/a(|\uparrow\downarrow 0\rangle + |0\uparrow\downarrow\rangle)$ with energy $E_0 = 2\epsilon_0 + (U-c)/2$.

### 1. Exact *G*

The symmetry of the system is such that $G_{11\uparrow} = G_{22\uparrow} = G_{11\downarrow} = G_{22\downarrow}$ and $G_{12\uparrow} = G_{21\uparrow} = G_{12\downarrow} = G_{21\downarrow}$, with

$$\begin{aligned} G_{ij\uparrow}(\omega) = \frac{(-1)^{(i-j)}}{2a^2}\Bigg[&\frac{\left(1+\frac{4t}{(c-U)}\right)^2}{\omega-(\epsilon_0 - t + (c+U)/2) + i\eta} \\ &+ \frac{(-1)^{(i-j)}\left(1-\frac{4t}{(c-U)}\right)^2}{\omega-(\epsilon_0 + t + (c+U)/2) + i\eta}\Bigg] \\ + \frac{1}{2a^2}\Bigg[&\frac{\left(1+\frac{4t}{(c-U)}\right)^2}{\omega-(\epsilon_0 + t - (c-U)/2) - i\eta} \\ &+ \frac{(-1)^{(i-j)}\left(1-\frac{4t}{(c-U)}\right)^2}{\omega-(\epsilon_0 - t - (c-U)/2) - i\eta}\Bigg], \end{aligned} \tag{B1}$$

with $\epsilon_0 - t + (c+U)/2$ and $\epsilon_0 + t - (c-U)/2$ being interpreted as quasiparticle peaks, and $\epsilon_0 + t + (c+U)/2$ and $\epsilon_0 - t - (c-U)/2$ as satellites. We can now study the two limits $U \to 0$ and $t \to 0$.

- $U \to 0$ . In this limit the ground state becomes $|\psi_0\rangle = \frac{1}{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle + |\uparrow\downarrow 0\rangle + |0\uparrow\downarrow\rangle)$ with energy $E_0 = 2(\epsilon_0 - t)$, and the one-particle Green's function reduces to the noninteracting one

$$\begin{aligned} G^{U=0}_{ij\uparrow}(\omega) = \frac{(-1)^{(i-j)}}{2}\Bigg[&\frac{1}{\omega-(\epsilon_0+t)+i\eta} \\ &+ \frac{(-1)^{(i-j)}}{\omega-(\epsilon_0-t)-i\eta}\Bigg]. \end{aligned} \tag{B2}$$

  Note that this is the same as the one we obtain for the spin-up block of the one-electron case.

- $t \to 0$ . In this limit the ground state becomes $|\psi_0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$; there are no double occupancies anymore (Heitler–London limit). The only peculiarity is the fact that for $t=0$ the ground-state energy goes to $2\epsilon_0$ so that it approaches degeneracy with the threefold degenerate triplet states. However, for any small but finite $t$ the ground state is the singlet $S=0$. In this limit all the poles of the dressed Green's function acquire equal weight ($\pm 1/4$), with the four poles collapsing into the two solutions $\epsilon_0 + U$ and $\varepsilon_0$, which represents the addition and removal energies, respectively, of an isolate atom with one electron.

### 2. *GW* approximation

In order to calculate the poles of the Green's function within the GWA ($G_0W_0$), we need the following ingredients:

$$P_{ij\sigma\sigma'}(\omega) = \frac{(-1)^{(i-j)}}{4}\delta_{\sigma\sigma'}\left[\frac{1}{\omega - 2t + i\eta} - \frac{1}{\omega + 2t - i\eta}\right], \tag{B3}$$

$$W_{ij}(\omega) = U\delta_{ij} + (-1)^{(i-j)}\frac{2U^2 t}{\omega^2 - h'^2}, \tag{B4}$$

$$\begin{aligned} \Sigma_{ij\sigma\sigma'}(\omega) = \frac{U}{2}\delta_{ij}\delta_{\sigma\sigma'} + \frac{U^2 t}{2h'}\delta_{\sigma\sigma'}\Bigg[&\frac{1}{\omega - (\epsilon_0 + t + h') + i\eta} \\ &+ \frac{(-1)^{(i-j)}}{\omega - (\epsilon_0 - t - h') - i\eta}\Bigg], \end{aligned} \tag{B5}$$

with $h'^2 = 4t^2 + 4tU$. From $\det[G_0^{-1} - \Sigma] = 0$, we calculate the following poles for the Green's function:

$$\omega_{1,2} = \frac{2\epsilon_0 - h' + \frac{U}{2} \pm \sqrt{\left(2t + h' + \frac{U}{2}\right)^2 + 4U^2 t/h'}}{2}, \tag{B6}$$

$$\omega_{3,4} = \frac{2\epsilon_0 + h' + \frac{U}{2} \pm \sqrt{\left(2t + h' - \frac{U}{2}\right)^2 + 4U^2 t/h'}}{2}, \tag{B7}$$

each doubly degenerate (spin-up and spin-down poles). We can now study the two limits $U \to 0$ and $t \to 0$.

- $U \to 0$ . In this limit $h' \approx 2t$, therefore the poles $\omega_1$ (+ combination) and $\omega_4$ (− combination) collapse to the poles of $G_0$, $\omega = \epsilon_0 + 2t$ and $\omega = \epsilon_0 - 2t$, whereas $\omega_2$ and $\omega_3$ collapse to $\omega = \epsilon_0 - 3t$ and $\omega = \epsilon_0 + 3t$. These last two poles have zero intensity at $U=0$ and deviate from the bonding/antibonding energies by $\pm 2t$ (poles of $P$), which justify their identification as satellites.

- $t \rightarrow 0$ . In the limit $t \rightarrow 0$ we have $h' \approx 0$, from where it follows that the poles $\omega_1$ and $\omega_3$ merge at $\omega=\epsilon_0+U/2$, whereas the poles $\omega_2$ and $\omega_4$ go toward $\omega=\epsilon_0$. This in contrast to the exact solution where the poles go toward the poles of the isolated atom ($\omega=\epsilon_0$ and $\omega=\epsilon_0+U$).

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

[2] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998), and references therein.

[3] W. G. Aulbur, L. Jonsson, and J. W. Wilkins, *Solid State Physics* (Academic, New York, 2000), Vol. 54, p. 1, and references therein.

[4] G. Strinati, H. J. Mattausch, and W. Hanke, Phys. Rev. B **25**, 2867 (1982).

[5] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985).

[6] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).

[7] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **36**, 6497 (1987).

[8] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **37**, 10159 (1988).

[9] L. Hedin, J. Phys.: Condens. Matter **11**, R489 (1999).

[10] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002), and references therein.

[11] G. D. Mahan and B. E. Sernelius, Phys. Rev. Lett. **62**, 2718 (1989), and references therein.

[12] Y. Takada, Phys. Rev. Lett. **87**, 226402 (2001).

[13] M. Hindgren and C. O. Almbladh, Phys. Rev. B **56**, 12832 (1997).

[14] E. L. Shirley, Phys. Rev. B **54**, 7758 (1996).

[15] P. Minnhagen, J. Phys. C **7**, 3013 (1974).

[16] P. Minnhagen, J. Phys. C **8**, 1535 (1975).

[17] A. Schindlmayr and R. W. Godby, Phys. Rev. Lett. **80**, 1702 (1998).

[18] C. Verdozzi, R. W. Godby, and S. Holloway, Phys. Rev. Lett. **74**, 2327 (1995).

[19] E. L. Shirley and R. M. Martin, Phys. Rev. B **47**, 15404 (1993).

[20] R. Del Sole, L. Reining, and R. W. Godby, Phys. Rev. B **49**, 8024 (1994).

[21] R. T. M. Ummels, P. A. Bobbert, and W. van Haeringen, Phys. Rev. B **57**, 11962 (1998), and references therein.

[22] M. Springer, F. Aryasetiawan, and K. Karlsson, Phys. Rev. Lett. **80**, 2389 (1998).

[23] V. P. Zhukov, E. V. Chulkov, and P. M. Echenique, Phys. Rev. B **72**, 155109 (2005).

[24] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems*, (Benjamin, New York, 1964).

[25] A. Schindlmayr, T. J. Pollehn, and R. W. Godby, Phys. Rev. B **58**, 12684 (1998).

[26] P. Nozières and C. T. Dedominicis, Phys. Rev. **178**, 1097 (1969).

[27] D. C. Langreth, Phys. Rev. B **1**, 471 (1970).

[28] B. Bergersen, F. W. Kus, and C. Blomberg, Can. J. Phys. **51**, 102 (1973).

[29] L. Hedin, Phys. Scr. **21**, 477 (1980).

[30] A. S. Kheifets, V. A. Sashin, M. Vos, E. Weigold, and F. Aryasetiawan, Phys. Rev. B **68**, 233205 (2003).

[31] R. A. Smith, Phys. Rev. A **46**, 4586 (1992), and reference therein.

[32] F. Bruneval, F. Sottile, V. Olevano, R. Del Sole, and L. Reining, Phys. Rev. Lett. **94**, 186402 (2005).

[33] R. Stubner, I. V. Tokatly, and O. Pankratov, Phys. Rev. B **70**, 245119 (2004).

[34] TDLDA has turned out to cover a big part of $P$, namely, contributions for nonvanishing momentum transfer $\mathbf{q}$. We do not enter problems of time-ordering here, since, e.g., causal quantities can easily be obtained from time-ordered ones. We also use the fact that the relation between the measurable reducible polarizability $\chi$ and the irreducible $P$ is well established.

[35] M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. **99**, 246403 (2007).

[36] J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963).

[37] J. Hubbard, Proc. R. Soc. London, Ser. A **277**, 237 (1964).

[38] W. Nelson, P. Bokes, P. Rinke, and R. W. Godby, Phys. Rev. A **75**, 032505 (2007).

[39] J. J. Fernandez, Phys. Rev. A **79**, 052513 (2009).

[40] M. Taut, J. Phys. C **4**, 9595 (1992).

[41] X. Wang, C. D. Spataru, M. S. Hybertsen, and A. J. Mills, Phys. Rev. B **77**, 045119 (2008).

[42] K. S. Thygesen and A. Rubio, Phys. Rev. **77**, 11533 (2008).

[43] Note that the kernel $f_{xc}=\delta v_{xc}/\delta\rho$ is not the same as the many-body kernel $f_{xc}^{eff}$ [Eq. (5)]. The general relation between the two is $f_{xc}=f_{xc}^{eff}+f^{(1)}$, where $f^{(1)}=\chi_0^{-1}-P_0^{-1}$ represents essentially the quasiparticle shift. The two-point term $f^{(1)}$ contributes hence to the nonlocality correction $\Delta\Gamma=f^{(1)}+\Delta\tilde{\Gamma}$ defined in Eq. (3).

[44] R. W. Godby and M. Schlüter, Phys. Rev. Lett. **56**, 2415 (1986).

[45] M. Grüning, A. Marini, and A. Rubio, J. Chem. Phys. **124**, 154108 (2006).

[46] M. Grüning, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **118**, 7183 (2003).

[47] A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, Science **321**, 792 (2008).

[48] N. E. Dahlen, R. van Leeuwen, and U. von Barth, Phys. Rev. A **73**, 012511 (2006).

[49] A. Stan, N. E. Dahlen, and R. van Leeuwen, Europhys. Lett. **76**, 298 (2006).

[50] A. Schindlmayr, Phys. Rev. B **56**, 3528 (1997).

[51] T. J. Pollehn, A. Schindlmayr, and R. W. Godby, J. Phys.: Condens. Matter **10**, 1273 (1998).

[52] J. M. Tomczak, Ph.D. thesis, Ecole Polytechnique, 2007.

[53] M. Puig von Friesen, C. Verdozzi, and C.-O. Almbladh, e-print arXiv:0905.2061v1.

[54] We stress here that the electron-electron interaction $U$ is spin independent, contrary to $U_{\sigma\sigma'}=U(1-\delta_{\sigma\sigma'})$, which is often used in the Hubbard model (Refs. 41, 42, and 53). The constant $U$ in Eq. (14) corresponds to the localized limit of the many-body Hamiltonian as it is used in MBPT, hence it better reflects the approximations we want to examine. When acting on a Slater determinant, both choices yield the same result. This is not the case when the Hamiltonian acts on a generic state which is not antisymmetric. In this case, the spin-dependent interaction itself would take into account the Pauli principle, hence exchange-induced corrections.

[55] U. von Barth and B. Holm, Phys. Rev. B **54**, 8411 (1996); B. Holm and U. von Barth, *ibid.* **57**, 2108 (1998).

[56] A. Marini, R. Del Sole, A. Rubio, and G. Onida, Phys. Rev. B **66**, 161104(R) (2002).

[57] M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).

[58] We choose the following convention as fermionic ordering: $|\uparrow\downarrow\uparrow\rangle = c_{2\uparrow}^{\dagger}c_{1\downarrow}^{\dagger}c_{1\uparrow}^{\dagger}|00\rangle$.

[59] In order to lift the degeneracy between the states $|\uparrow\rangle$ and $|\downarrow\rangle$ we can apply a magnetic field which stabilizes, for example, the state $|\uparrow\rangle$.