Reduced Density-Matrix Functional Theory: correlation and spectroscopy

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In this work we explore the performance of approximations to electron correlation in reduced density-matrix functional theory (RDMFT) and of approximations to the observables calculated within this theory. Our analysis focuses on the calculation of total energies, occupation numbers, removal/addition energies, and spectral functions. We use the exactly solvable Hubbard molecule at 1/4 and 1/2 filling as test systems. This allows us to analyze the underlying physics and to elucidate the origin of the observed trends. For comparison we also report the results of the GW approximation, where the self-energy functional is approximated, but no further hypothesis are made concerning the approximations of the observables. In particular we focus on the atomic limit, where the two sites of the molecule are pulled apart and electrons localize on either site with equal probability: this is the regime of strong electron correlation. In this limit, using the Hubbard molecule at 1/2 filling with or without a spin-symmetry-broken ground state, we can get insights into, respectively, an antiferromagnetic or a paramagnetic spin structure. We find that, within the used approximations, neither in RDMFT nor in GW the signature of strong correlation are present in the paramagnetic case, whereas both give the exact result for the antiferromagnetic case. Moreover we show how the spectroscopic properties change from one spin structure to the other, but that this change cannot be straightforwardly detected in the experiment.

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I. INTRODUCTION

Strongly correlated electron systems exhibit remarkable and magnetic properties, such as metal-insulator transitions, half-metallicity, or unconventional superconductivity, which make them among the most attractive and versatile materials. Typically these materials have incompletely filled d- or f-electron shells with narrow energy bands. In this case a theoretical description based on current mean-field or perturbation approaches is not enough and a more accurate treatment of electron correlation is required. This represents one of the greatest challenges in condensed-matter physics today.

One of the most popular approaches in condensed-matter physics is many-body perturbation theory (MBPT) based on Green’s functions. Within the so called GW approximation electron correlation, MBPT has become, over the last two decades, the tool of choice for the calculations of quasiparticle (QP) band structures and direct and inverse photo emission spectra of many materials improving substantially over the results provided by static mean-field electronic structure methods. However GW suffers from some fundamental shortcomings, and, in particular, it is not expected to describe strong correlation. More refined levels of approximations are hence needed and much effort is devoted to this goal both by going beyond standard methods and also by exploring completely novel routes to calculate Green’s functions. In this context, promising results for solids have been reported using reduced density-matrix functional theory (RDMFT). Within RDMFT the ground-state properties of a physical system are functionals of the ground-state density matrix, since there exists a one-to-one mapping between the (non-degenerate) ground-state wavefunction of the system and the corresponding density matrix. In particular the ground-state total energy is a functional of the one-body density matrix and it can be written as where is the kinetic energy, the energy due to the coupling to an external potential, and the Hartree and exchange-correlation energies, respectively. Energy minimization under the constraint that determines, for example, removal energies can be approximated differently and occupation numbers . Once the density matrix of the system is known, all the observables of the system can be calculated, provided that their expression as functional of the density matrix is known.

This is not the case for the one-body spectral function, which determines, for example, photoemission spectra. Various ways to calculate removal/addition energies have been proposed. For example, removal energies can be calculated by using extended Koopmans’ theorem (EKT) as proposed by Pernal and Cioslowski. The method has been so far used only for finite systems. In Ref. an approximate procedure to calculate quasiparticle ener-
gies and photoemission spectra within RDMFT has been proposed, which is also inspired by Koopmans’ theorem. When applied to a series of transition-metal oxides, the method seems to capture the essential physics of strong electron correlations. Several approximations are, however, involved: i) an approximate exchange-correlation energy functional, ii) an approximate expression for the removal and addition energies, iii) an approximate expression for the spectral function. It then becomes important to explore more in detail this approach, in order to elucidate the underlying physics, the origin of its success, and its capability to capture strong correlation. In order to achieve this we use the exactly solvable two-site Hubbard model at 1/4 and 1/2 filling as a test case. Besides the exact solution at hand, a big advantage of the Hubbard molecule is that the natural orbitals have a simple link the molecular orbitals. The model can also offer insights into some fundamental questions that occur in extended systems. Let us in particular show some aspects that are analogous to the homogeneous electron gas (HEG). The HEG is one of the most important model system in condensed-matter physics. At high densities the electron gas behaves as a free-particle system, since the electron-electron interaction is a perturbation to the dominant kinetic energy; in this case the ground state is translationally invariant and has a paramagnetic phase. At low densities, instead, it forms a Wigner crystal to minimize the electron-electron interaction; in the crystal the translational symmetry is spontaneously broken. Moreover the system can be already in some kind of broken symmetry state, such as, for example, an antiferromagnetic state, when it crystallizes. The HEG displays hence a complex phase diagram. The Hubbard molecule can capture certain aspects of this physics, such as symmetry breaking. In the atomic limit, when the two sites are pulled apart, electrons localize on either site with equal probability: this is the regime of strong electron correlation. In this limit the molecule at 1/2 filling can give insights into a paramagnetic or an antiferromagnetic spin structure, depending on whether or not the spin symmetry is broken. In the following we will hence put particular focus on this limit to see if MBPT and RDMFT can capture strong correlation and, if so, for which spin structure (paramagnetic or antiferromagnetic). Moreover this will also show how the spectroscopic properties change between the paramagnetic and antiferromagnetic case and whether they can be distinguished in an experiment.

The paper is organized as follows. In Sec. II we will report the key equations of MBPT and RDMFT. In Sec. III MBPT and RDMFT results for occupation numbers, total energies, removal/addition energies, and spectral function are compared to exact results and analyzed. Conclusions are given in Sec. IV.

II. THEORETICAL FRAMEWORK

In the following we will give the key equations used in many-body perturbation theory and reduced density-matrix functional theory, and in particular we will discuss how one can calculate ground- and excited-state properties, namely total energies, occupation numbers, removal and addition energies, and spectral function in the two approaches. We will use atomic units $\hbar = m = e = 1$ and work at zero temperature throughout the paper.

A. MBPT

Within MBPT the leading role is played by the one-body Green’s function. At zero temperature the time-ordered Green’s function\textsuperscript{31} reads

$$G(1, 2) \equiv -i \langle \Psi_0 | \hat{T} \hat{\psi}^\dagger (2) | \hat{\psi} (1) \rangle | \Psi_0 \rangle,$$

(1)

where \(\hat{T}\) is the time-ordering operator, \(\Psi_0\) is the ground-state many-body wavefunction, \(\hat{\psi}\) and \(\hat{\psi}^\dagger\) are field operators in the Heisenberg picture. Here (1) \(\equiv (x_1, t_1) \equiv (r_1, s_1, t_1), (1^+) \equiv (x_1, t_1^+)\) with \(t^+_1 \equiv t_1 + \delta (\delta \to 0^+)\) describe space, spin and time coordinates. \(G\) contains a wealth of information about a physical system. In particular the ground-state total energy can be obtained using the Galitskii-Migdal formula

$$E_0 = -\frac{i}{2} \int dx_1 \lim_{2 \to 1^+} \left( i \frac{\partial}{\partial t_1} + h_0(r_1) \right) G(1, 2)$$

(2)

where \(h_0(r_1) = -\nabla r_1/2 + v_{\text{ext}}(r_1)\) is the one-body hamiltonian. Moreover we are also interested in the density matrix \(\gamma(x_1, x_2) = -i G(1, x_2 t_1^+) = -i \int d\omega/(2\pi \Gamma) G(\omega)e^{i\omega t_1}\) and the spectral function \(A(\omega) = \langle |\beta G(\omega)|/\pi\rangle\), which is closely related to photoemission spectra\textsuperscript{32}.

Equation (1) is not practical to determine \(G\), since it requires the knowledge of the many-body wavefunction. In MBPT one uses instead the Dyson equation \(G = G_0 + G_0 \Sigma G\), where \(G_0\) is the non-interacting one-body Green’s function and \(\Sigma\) is the self-energy, which describes all the many-body effects of the system. Approximations to the self-energy are needed, and a very popular one is \(\Sigma = v_H + iGW\), where \(v_H\) is the Hartree potential and \(W = \epsilon^{-1} v_c\) is the dynamically screened Coulomb interaction, with \(\epsilon^{-1}\) the inverse dielectric function and \(v_c\) the Coulomb interaction\textsuperscript{33}. In Sec. III we will compare the exact results obtained using (1) with those obtained from the GW approximation. The GW equations should, in principle, be solved self-consistently, since the self-energy is a functional of the one-body Green’s function. Here, instead, we solve the GW equations without self-consistency, which is often the case in practice.
B. RDMFT

The reduced $p$-body density matrix is defined as

$$\Gamma^{(p)}(x_1...x_p, x'_{1}...x'_{p}) \equiv \binom{N}{p} \int dx_{p+1}...dx_N \Psi^*(x'_{1}...x'_{p}, x_{p+1}...x_N) \times \Psi(x_1...x_p, x_{p+1}...x_N)$$

Within RDMFT\textsuperscript{29} the total energy is a unique functional of the one-body density matrix $\gamma \equiv \Gamma^{(1)}$. It reads

$$E_{tot}[\gamma] = E_{kin}[\gamma] + E_{ext}[\gamma] + \int dx dx' \nu_{c}(x, x') \Gamma^{(2)}[\gamma](x, x'; x, x')$$

The first and second terms on the right-hand side of (\ref{eq:1}) are the Hartree and exchange-correlation contributions, respectively. The latter is not known and needs to be approximated. Various approximations have been proposed in literature\textsuperscript{33-39}. Many of them, however, can be traced back to the work of Müller\textsuperscript{40}, and are based on the factorization

$$\Gamma^{(2)}[\gamma](x, x'; x, x') = -\gamma^\alpha(x, x') \gamma^\alpha(x', x')$$

where

$$\gamma^\alpha(x, x') = \sum_j n_j^\alpha \phi_j(x) \phi_j^*(x')$$

with $\phi_j(x)$ and $n_i$ being the natural orbitals and the occupation numbers, respectively. Note that with $\alpha = \alpha' = 1$ in (\ref{eq:4}) one gets the Hartree-Fock approximation to $\Gamma^{(2)}$. The total energy can then be expressed as functional of $\phi_i$ and $n_i$, $E_{tot}[\{n_i\}, \{\phi_i\}]$: functional minimization with respect to the natural orbitals, under orthonormality constraints, and occupation numbers, under total particle conservation and $N$-representability constraints ($0 \leq n_i \leq 1$), leads to the ground-state total energy. In this work we concentrate only on exchange-correlation functionals with $\alpha = \alpha'$ in (\ref{eq:4}), which have been applied both to extended\textsuperscript{30,41} as well as to finite systems\textsuperscript{41}. From the natural orbitals and occupation numbers which minimize the total energy one can build the one-body density matrix which corresponds to a given approximation for $\Gamma^{(2)}$. The procedure to determine the one-body density matrix is then different from the standard one used for the Green’s function, for which one solves a Dyson equation for a given approximation to the self-energy. Moreover, whereas one can easily extract information about photoemission spectra directly from the imaginary part of $G$, this is not the case in RDMFT. We do not know $G$ nor its imaginary part.

Natural occupation numbers are strictly related to the multi-determinant nature of the wavefunction of a physical system. Let us expand the many-body wavefunction in terms of Slater determinants constructed from the eigenvectors of the one-body density matrix $\{\phi_i\}$, $\Psi_0(x_1...x_N) = \sum_i C_i \Phi_i(x_1...x_N)$. The one-body density-matrix then reads\textsuperscript{42}

$$\gamma(x, x') = \sum_i |C_i|^2 \gamma_i(x, x')$$

where $\gamma_i(x, x') = \sum_{k} \phi_k^i(x) \phi_{k}^i(x')$ is the density matrix associated to the $i$th Slater determinant. If the wavefunction of the system is described by a single Slater determinant, as in the case of a single (spin-polarized) electron (see Hubbard molecule at 1/4 filling), then the natural occupation numbers are either 1 or 0. If instead more determinants are involved, the natural occupation numbers, in general, take fractional values between 0 and 1. This can be nicely illustrated by considering a two-electron system with a singlet wavefunction $\Psi_0(x_1, x_2) = \sum_{i=1,2} C_i \Phi_i(x_1, x_2)$, where $\Phi_1 = |b \uparrow, b \downarrow\rangle$ and $\Phi_2 = |a \uparrow, a \downarrow\rangle$ are Slater determinants constructed from bonding and antibonding orbitals, respectively (see Hubbard molecule at 1/2 filling). The one-body density matrix reads:

$$\gamma(x, x') = |C_1|^2 \sum_{i=b \uparrow, b \downarrow} \phi_i(x) \phi_i^*(x') + |C_2|^2 \sum_{i=a \uparrow, a \downarrow} \phi_i(x) \phi_i^*(x')$$

where $n_{b\uparrow} = |C_1|^2$ and $n_{a\uparrow} = |C_2|^2$, and $|C_1|^2 + |C_2|^2 = \chi$ since the wavefunction $\Psi_0$ is normalized. In general the relation between $C_i$ and natural occupation numbers is more complicated than in this example, but the fact that fractional occupation numbers reflect the multideterminant nature of the wavefunction, and hence the degree of correlation in a system, remains still valid.

Recently Sharma at al.\textsuperscript{27} proposed the following approximate expression for the spectral function within RDMFT

$$A(\omega) \approx \sum_i \left[ n_i(\delta(\omega - \epsilon_i^\uparrow) + (1 - n_i) \delta(\omega + \epsilon_i^\uparrow) \right]$$

where $\epsilon_i^\uparrow = E_i^N - E_i^{N+\uparrow}$, with $E_i^N$ and $E_i^{N+\uparrow}$ the $N$-electron system ground-state and the $N \pm 1$-electron system $i$th-state, respectively. To arrive at Eq. (\ref{eq:7}) one starts from the exact expression $A(\omega) = |3G(\omega)/\pi$ and approximates the ground and excited states of the
and for the occupation numbers one gets
\[ n_i = -i \int \frac{\omega}{2\pi} G_i(\omega)e^{i\omega t}. \] (11)

If \( G_i \) has more than one pole, then the total number of removal/addition energies that one should find is larger than the number of occupation numbers. Therefore, equation (8), in general, describes a mixture of quasiparticle and satellite energies, as will be illustrated in Sec. III.

The total energy difference, Eq. (8), can be further approximated as
\[ E([[n_i], \{\phi_i\}]]_{n_k=1} - E([[n_i], \{\phi_i\}]]_{n_k=0}) \approx \frac{\partial E}{\partial n_k} \bigg|_{n_k=1/2} \] (12)
which is justified if the total energy is linear in the occupation number \( n_k \). This method will be referred to as DER. Using Eqs (7) and (12) the spectral function of several transition metal oxides has been calculated, showing that some experimental features are captured.

As an alternative to Eq. (8) (or (12)) removal energies can be calculated by using extended Koopmans’ theorem (EKT) as proposed by Pernal and Cioslowski. The method is based on the diagonalization of the Lagrangian matrix:
\[ \Lambda_{ij} = \frac{1}{\sqrt{n_{ij}n_{ji}}} \left[ n_{ij}h_{0,ji} + 2 \sum_{klm} \Gamma^{(2)}_{sklm}v_{c,ijklm} \right] \] (13)
with \( h_{0,ji} = \int dx \phi_j^*(x)h_0(x)\phi_i(x), \)
\[ \Gamma^{(2)}_{sklm} = \int dx_1 dx_2 dx_3 dx_4 \Gamma^{(2)}(x_1', x_2', x_1, x_2) \times \phi_m^*(x_2)\phi_i^*(x_1)\phi_k(x_4')\phi_l(x_3'), \]
and
\[ v_{c,ijklm} = \int dx_1 dx_2 dx_3 dx_4 \phi_j^*(x_1)\phi_i^*(x_2)v_c(x_1, x_2)\phi_m(x_3')\phi_l(x_4'). \]

The eigenvalues of \( \Lambda \) are the removal energies. The underlying physics of this method is similar to that of Eq.(7), although more advanced: in the EKT the \( N - 1 \)-electron states are obtained as linear combination of states obtained by removing an electron from the ground state of the \( N \)-electron system, \( |\Psi^{N-1}\rangle = \sum_i B_i c_i|\Psi^0_i\rangle \); the energy of the so obtained \( N - 1 \)-electron states is minimized with respect to the coefficients \( C_i \), unlike in the DIF/DER method. In practice the EKT has only been applied to finite systems. In this work we will use it to test the approximation to the \( x \)-energy functional. Indeed, although it is an approximate method for the calculation of removal energies, for the Hubbard molecule at 1/4 and 1/2 filling it delivers the exact results when combined with the exact exchange-correlation energy functional. Note that the lowest addition energy can be obtained from the highest removal energy of the \( N + 1 \)-system (if the latter is stable).

### III. CORRELATION IN THE HUBBARD MOLECULE

In this section we will illustrate the physics behind different approximations to correlation as well as to observables in RDMFT and how it compares with the standard \( GW \) method used in MBPT. To this purpose we use the
Hubbard molecule, a simple prototype of a strongly correlated system that can be solved exactly. The Hamiltonian of the Hubbard molecule reads

\[
H = -t \sum_{i,j=1,2} \sum_{\sigma} c^\dagger_{i,\sigma} c_{j,\sigma} + \frac{U}{2} \sum_{i=1,2} \sum_{\sigma} c^\dagger_{i,\sigma} c^\dagger_{i,\sigma} c_{i,\sigma} c_{i,\sigma} + \epsilon_0 \sum_{\sigma,j=1,2} c^\dagger_{j,\sigma} c_{i,\sigma} + V_0.
\]  

(14)

Here \(c^\dagger_{i,\sigma}\) 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 physics of the Hubbard model arises from the competition between the hopping term, which prefers to delocalize electrons, and the on-site interaction, which favours localization. The ratio \(U/t\) is a measure for the relative contribution of both terms and is the intrinsic, dimensionless coupling constant of the Hubbard model, which will be used in the following.

We refer to Ref 14 for the exact results of the model at 1/4 and 1/2 filling. Here, however, instead of the site basis, which can be considered as an atomic-like basis set, we will use the bonding/antibonding basis set (see App. A), which is conceptually similar to a molecular-like basis set. The reason behind this choice is that within this basis set the density matrix is diagonal; in other words this basis set is the basis of natural orbitals. This is another advantage to use the Hubbard model: the natural orbitals have a simple link to the molecular orbitals.

A. Hubbard molecule and real systems

The choice to study the Hubbard molecule is also motivated by the insight it can give into other systems with partially filled shells or bands. Let us focus on the 1/2 filling. The molecule, with the electrons equally delocalized on its two sites, can, indeed, capture some of the physics underlying the complex phase diagram of the homogeneous electron gas, such as symmetry breaking. In the atomic limit \(t \to 0\), the two sites are stretched apart, and the two electrons localize one on each site: this is a low-density regime where strong correlation between electrons dominates. In this limit the ground-state wavefunction at 1/2 filling becomes \(|\Psi_0\rangle = (|\uparrow \downarrow\rangle - |\downarrow \uparrow\rangle)/\sqrt{2}\), with \([\ldots]\) Slater determinants in the site basis; per each site, hence, the spin has equal probability to be up or down. This scenario can describe some aspects of a paramagnetic spin structure. If, instead, one selects only one of the two Slater determinants, e.g. \(|\Psi_0\rangle = |\uparrow \downarrow\rangle\) (spin-symmetry breaking), then the Hubbard molecule can explain what happens in an antiferromagnetic spin structure. For these reasons, in the following, particular focus will be put in the study of the atomic limit.

B. Total energy and occupation numbers

1. 1/4 filling

In the case of the Hubbard molecule at 1/4 filling the ground-state wavefunction reads \(|\Psi_0\rangle = (|\uparrow \downarrow\rangle + |\downarrow \uparrow\rangle)/\sqrt{2}\) in the site basis. When projected in the bonding/antibonding basis one gets \(|\Psi_0\rangle = |b \uparrow\rangle\), i.e. one single Slater determinant with one electron in the bonding orbital. The exact density matrix is idempotent for any \(U/t\) value at zero temperature (see Fig. 1, upper panel), with the occupation number of the bonding (antibonding) orbital \(n_{b\uparrow} = 1\) and \(n_{b\downarrow} = 0\) \((n_{a\uparrow} = n_{a\downarrow} = 0)\). In particular in the atomic limit \(t \to 0\), for which \(U/t \to \infty\) for \(U\) fixed, the electron remains in the bonding orbital. Analyzed in the site basis this means that the electron has the same probability of being on either of the two sites. This means that when it comes to electron addition there are two addition energies: one at \(\epsilon_0\) when the addition electron goes to the unoccupied site, and one at \(\epsilon_0 + U\) when it goes to the occupied one. This is an example of strong correlation, since the added electron needs to see the electron in the system and not just an average charge distribution. The occupation numbers, instead,
being zero or one, indicate no correlation in the system!

When we use the Müller functional \((\alpha = 0.5 \text{ in Eq. } (4))\), the optimal occupation numbers \(n_{\alpha\beta}\) and \(n_{\alpha\dagger}\) tend to 0.5 with increasing \(U/t\) (see Fig. 1, upper panel). By increasing \(\alpha\) up to 1 (Hartree-Fock) one approaches the exact situation (without discontinuities). This is because exchange and Hartree energy completely cancel each other in case of one electron. Self-interaction corrections introduced by Goedecker and Umrigar (GU)\(^{36}\) to the Müller functional (Müller GU) slow down the eventual merging of bonding and antibonding occupation numbers at 1/2. Interestingly the occupation numbers calculated from the \(G_{GW}\) are almost on top of the self-interaction corrected Müller functional results. To obtain \(GW\) occupation numbers we use Eq. (11), with the \(GW\) one-body Green’s function on the right-hand side.

Total energy results are reported in the lower panel of Fig. 1. All the approximations used underestimate the total energy, the exception being the Müller functional when fed with exact occupation numbers (obtained from \(G_0\) at 1/4 filling\(^{38}\)), which is on top of the exact result (“Müller+\(G_0\)” in Fig. 1). This finding is also observed at 1/2 filling. However, at one fourth filling, the exact occupation numbers being 1 or 0, any \(0 \leq \alpha \leq 1\) would give the exact total energy. For comparison we also reported the total energy obtained using the Galitskii-Migdal equation (2) with the \(GW\) Green’s function, which is similar to the results obtained using the Müller GU functional over the \(U/t\) range reported in Fig. 1. In the atomic limit, however, the \(GW\) total energy equals the exact one, i.e., \(E_{tot} = \epsilon_0\), as was already noticed in Ref.\(^{14}\), whereas the Müller GU gives a lower energy (see inset in the lower panel of Fig. 1).

In conclusion at one fourth filling we find that the Hartree-Fock approximation \((\alpha = 1 \text{ in } (4))\) gives the exact occupation numbers, whereas the Müller functional \((\alpha = 0.5 \text{ in } (4))\) gives results which quickly depart from the exact ones. Varying \(\alpha\) between 0.5 and 1 or using self-interaction corrected Müller functional gives results in between these two extremes for any \(U/t\); \(GW\) occupation numbers are almost on top of self-interaction corrected Müller functional results. Concerning the total energy all Müller-like functionals fed with exact occupation numbers give the exact results. All the other approximations tend to underestimate the total energy.

2. 1/2 filling

The wavefunction at 1/2 filling reads \(|\Psi_0\rangle = A (\uparrow \downarrow - \downarrow \uparrow) + B (\uparrow \downarrow | 0 \rangle - | 0 \downarrow \rangle)\) in the site basis, with \(A = 4t/\sqrt{a(c-U)}\), \(B = 1/a\), \(c = \sqrt{16t^2 + u^2}\), and \(a = \sqrt{2[16t^2/(c-U)^2 + 1]}\). When projected in the bonding/antibonding basis it reads \(|\Psi_0\rangle = \sqrt{\mu_2} (b \uparrow, b \downarrow) - \sqrt{\mu_1} (a \uparrow, a \downarrow)\) with \(\sqrt{\mu_2} = A + B\) and \(\sqrt{\mu_1} = A - B\). Note that the occupation numbers appear in the expression of \(|\Psi_0\rangle\) to the power 1/2; the success of the Müller functional with \(\alpha = 0.5\) at 1/2 filling is linked to this. At \(U/t = 0\) the wavefunction is the single Slater determinant \(|\Psi_0\rangle = |b \uparrow, b \downarrow\rangle\); increasing \(U/t\) also the antibonding orbital becomes important, and eventually the full wavefunction becomes a linear combination of bonding- and antibonding-orbital based Slater determinants with equal weight (see Fig. 2, upper panel). In terms of the site basis this means that for the noninteracting case each of the two electrons is equally distributed between the two sites, while increasing the interaction double occupancies become less probable. The optimal occupation numbers for the Müller functional are the exact ones. Clearly self-interaction corrections, as well as varying \(\alpha\) in the range 0.5-1, spoil this result. Again \(GW\) occupation numbers are very similar to self-interaction corrected Müller results. Note that \(GW\) produces fractional occupation numbers with increasing \(U/t\), eventually they go to 1/2 at \(t = 0\), but they go too slowly. In this limit \(t \to 0\) the molecule is stretched, the two atoms brought far apart, and the two electrons localize one on each site. In this limit \(GW\) does not manage to well localize the two electrons each on one site, and spurious double occupancies are still present at strong interaction.

Total energies are reported in the lower panel of Fig. 2. The total energy functional within the Müller approximation is not equal to the exact one, except at the exact occupation numbers. The Galitskii-Migdal result is similar to the result obtained using the self-interaction
corrected Müller functional, at least over the $U/t$ range reported in Fig. 2, and both overestimate the total energy.

In conclusion, at one half filling the Müller functional gives the exact occupation numbers, and varying $\alpha$ towards 1 increases the discrepancy with this exact result. GW and Müller GU give similar occupation numbers, which merge with the exact ones at $t = 0$, but at a lower speed than the exact values. This reflects the fact that these two approximations have difficulties to localize the two electrons one on each site, missing the atomic physics of strongly correlated electrons. Concerning the total energy both GW and Müller GU similarly overestimate the exact values, whereas the Müller functional gives the exact result. Varying $\alpha$ leads to higher total energies, with HF giving the worst agreement ($E_{\text{tot}}/t = -2 + U/(2t)$).

C. Removal/addition energies and Spectral function

Exact removal and addition energies are reported in Figs 3, 4, 6, and 7. We analyze various ways to compute removal/addition energies within RDMFT, which elucidate the role played by an approximate exchange-correlation energy functional and by an approximate expression for the removal/addition energies. First we test the Müller-like approximations to the xc functional by combining the latter with the method proposed by Pernal and Cioslowski (EKT) for the calculation of removal energies. The latter is based on the extended Koopman’s theorem, which is an approximation; however for the Hubbard molecule at 1/4 and 1/2 filling the method gives the exact removal energies when combined with the exact exchange-correlation energy functional. This allows us to study the accuracy of the xc functional approximations. Second we test the DIF/DER method for the calculation of removal/addition energies by combining it with the exact xc functional. We then test the combination of the DIF/DER method and of the Müller-like approximations to the xc functional.

Finally we combine the DIF/DER method and the Müller-like functionals with the approximate expression for the spectral function given in Eq. (7). In the following we refer to this combination of approximations as RDMFT spectral function. Exact, GW, and RDMFT spectral functions are compared in Figs 5 and 8.

1. 1/4 filling

At 1/4 filling the Hubbard molecule shows five quasiparticle energies (one removal (labelled $\omega_1$ in Fig. 3) and 4 addition energies ($\omega_2 - \omega_5$)) and one addition satellite energy ($\omega_6$). Satellites are weak removal or addition energies which acquire spectral weight with increasing interaction. If the exact energy functional is used (which, for one-electron, is only $E_{\text{tot}} = E_{\text{kin}} + E_{\text{ext}}$), then the EKT method produces two energies: the exact removal energy ($\epsilon_0 - t$) and the exact second lowest addition energy ($\epsilon_0 + t$) ($\omega_1$ and $\omega_3$, respectively, in Fig. 3). Using the Müller functional, instead, the EKT produces four energies (see result “Müller+ EKT 1/4” in Fig. 3). This is due to the fact that within this functional the antibonding occupation number $n_{\alpha \uparrow}$ is not zero, and therefore more degrees of freedom are added to the problem. The energies do not match well with the exact results, the situation becoming dramatic when we increase $U/t$. In the limit $U/t \to \infty$ the four energies merge together at a value well off the exact one (see right panel of Fig. 3). In this limit the exact energies merge towards $\epsilon_0$ and $\epsilon_0 + U$: this reflects the fact that in this limit the electron has equal probability to localize on one site or the other of the molecule, therefore one can have removal and addition energies (for a spin-down or a spin-up electron added to the empty site) at $\epsilon_0$ and an addition energy at $\epsilon_0 + U$ (for a spin-down electron added to the site with one spin-up electron already). Improvements are obtained changing $\alpha$ from 0.5 to 1 (Hartree-Fock) as the exact functional is approached. Hartree-Fock, indeed, gives the exact total energy at 1/4 filling, due to an exact cancellation between Hartree and exchange energies. Note that if the lowest addition energy is calculated from the highest removal energy of the system at 1/2 filling the EKT yields the exact result (see result “Müller+ EKT 1/2” in Fig. 3), but only because the Müller functional gives the exact total energy and occupation numbers at 1/2 filling ($N + 1$-electron system).

The DIF/DER method (Eqs (8) and (12)) performs as the EKT if the exact xc functional is used: it produces the exact removal energy and the exact second lowest addition energy. With the Müller functional it gives four energies (see result “Müller+ DIF/DER” in Fig. 4): only two energies are in good agreement with the exact ones ($\epsilon_{\alpha \uparrow}$ and $\epsilon_{\alpha \downarrow}$, calculated from $n_{\alpha \uparrow}$ and $n_{\alpha \downarrow}$, respectively), whereas for the other two ($\epsilon_{\downarrow \uparrow}$ and $\epsilon_{\downarrow \downarrow}$) we observe that each is approximately an average of two exact ones, namely $\epsilon_{\downarrow \uparrow}$ is an average of $\omega_2$ and $\omega_5$ and $\epsilon_{\downarrow \downarrow}$ of $\omega_3$ (or, equivalently, $\omega_4$ and $\omega_5$). This can be understood considering that the $G_{\alpha \uparrow}$ and $G_{\alpha \downarrow}$ components of the one-body Green’s functions have only one pole, whereas $G_{\downarrow \uparrow}$ and $G_{\downarrow \downarrow}$ have two poles each; the corresponding occupation numbers (see Eq. (11)) reflect, hence, these features.

However, in general the spectral function profile is in overall good agreement with the exact one at moderately strong interaction $U/t$, although for the spin-down channel GW is slightly superior (Fig. 5). In the atomic limit ($t \to 0$) both DIF and DER methods show the same failure as GW: the spin-down spectral function the poles merge at $\epsilon_0 + U/2$, unlike the exact results which shows a gap of magnitude $U$. We observe the same scenario increasing the number of sites. Moreover self-interaction corrections to the Müller functional do not add any significant improvement to the picture. If the lowest addition energy (spin-down channel) is calculated from the highest removal energy of the $N + 1$-electron system (1/2
filling), the method produces a gap, unlike the exact result, where the lowest addition energy coincides with the highest removal energy \(e_0\). A similar error is found also in \(GW\) and it is a consequence of the self-screening error \(GW\) suffers from.

Nevertheless, combining the approximate Müller-like functionals with the DIF/DER method improves the bad performance of the former with respect to the case where it is used with the more advanced EKT. This indicates that there is a cancellation of errors between the approximate Müller functional and the DIF/DER method, at least at 1/4 filling.

2. 1/2 filling

At 1/2 filling there are four quasiparticle energies (labeled \(\omega_1, \omega_2, \omega_3, \omega_4\) in Fig. 6) and four satellites (\(\omega_1, \omega_2, \omega_3, \omega_4\)). Using the Müller functional, which, in this case, gives the exact total energy at the exact occupation numbers, the EKT gives two doubly-degenerate energies: these are the exact removal energies. To get the lowest addition energy one has to look at the \(N+1\)-electron system (3/4 filling); in this case the Müller functional does not reproduce the exact total energy and occupation numbers and, consequently, the EKT gives an addition energy that strongly departs from the exact one as \(U/t\) increases.

Both DIF and DER methods give only two energies per spin channel, but their nature is in fact a mixture of quasiparticle and satellite energies; for example, we found that the energy \(\epsilon_{\sigma i} \) in Fig. 6) is roughly a weighted average of the satellite and quasiparticle energies \(\omega_3 \) and \(\omega_7 \), respectively. This can be again understood by considering that the components \(G_{i\sigma} \) and \(G_{\sigma i} \) have two poles each, and therefore the corresponding occupation numbers reflect these features in the excitation energies \(\epsilon_{\sigma i} \) and \(\epsilon_{\sigma i} \). The results are quite different from the EKT, where one has both the removal quasiparticle and satellite energies. Since at 1/2 filling the Müller functional is exact, there is not the same cancellation of error as observed at 1/4 filling, and the DER/DIF method introduces, hence, quite a large error.

In Fig. 8 we report the exact spectral function vs the \(GW\) and RDMFT spectral functions. As we see, only two peaks appear in the RDMFT spectra, which merge in the \(t \rightarrow 0\) limit both for the DIF and DER method. Self-interaction corrections tend to open the gap, but it is not enough at strong correlation. Changing \(\alpha\) does not improve the situation. DIF and DER, therefore, perform as bad as \(GW\) in the atomic limit, whereas \(GW\) is significantly superior at moderately strong interaction. We note that this conclusion is not restricted to the Hubbard molecule; we find the same scenario by increasing the number of sites up to 32. However, if the lowest addition energy is calculated from the highest removal energy of the \(N+1\)-electron system, the DIF/DER method yields a gap at best half of the exact one in the atomic limit.

In conclusion, using an exact xc functional, the method of Ref. 27 has a large deviation from the exact results, both in the values and nature of the removal and addition energies. For moderately strong interaction \(GW\) is clearly superior. In the atomic limit no gap is observed, like in \(GW\), unless the \(N+1\)-electron system is considered for the calculation of the lowest addition energy.

D. Occupation numbers and correlation

Occupation numbers are considered as a measurement of correlation. In Sec. III B.1 we looked at the Hubbard molecule at 1/4 filling for which the exact occupation numbers are either zero or one. This is a clear example in which the occupation numbers indicate no correlation in the system, but there are correlation effects when looking at the system using measurements of electron addition! In this case, indeed, we have a \(N+1\)-particle system (Hubbard molecule at 1/2 filling) whose density matrix indicates strong correlation. Therefore whether a system “is” correlated or not depends on how one looks at it.

How do we see correlation?

The Hubbard molecule at 1/2 filling can be considered, in the atomic limit, as a prototype system to highlight some characteristics of a paramagnetic (PM) or an antiferromagnetic (AF) spin structure, depending on whether one considers the spin-singlet or a spin-symmetry broken ground-state wavefunction. We note that in case of an AF spin structure both \(GW\) and RDMFT give exact result for total energy, occupation numbers, and spectral function. Let us first focus on the spectral function. From Fig. 8 we see that the exact spectral function of the spin singlet (lowest right panel) shows two peaks, one at \(e_0\) and one at \(e_0 + U\), both for spin-up and spin-down channels. For the antiferromagnetic case \((|\Psi_0\rangle = |\uparrow \downarrow\rangle\) the components of the one-body Green’s functions show the spin-symmetry breaking nature of the ground state, i.e. \(G_{0\uparrow\uparrow} \neq G_{0\downarrow\downarrow}\) and \(G_{1\uparrow\downarrow} = G_{2\downarrow\uparrow}\), \(G_{1\uparrow\downarrow} = G_{2\downarrow\uparrow}\), and hence are different from the ones of the singlet case (all diagonal components the same, all off diagonal components the same). However the spin-resolved total spectral function, i.e. \(A_{\sigma}(\omega) = \sum_i |3G_{i\sigma\sigma}(\omega)|/\pi\), is the same for the two spin structures: one can remove a spin-up or spin-down electron with energy \(e_0\), and can add a spin-up or spin-down electron with energy \(e_0 + U\). Extrapolating to real systems, this corresponds to the fact that photoemission experiments, even if spin-resolved, finds similar results for the two cases, although there are differences introduced by small changes in geometry, density etc...

What about the occupation numbers? The Compton profile can give information about the momentum distribution, i.e. the probability to observe a particle of momentum \(p\) (see, e.g. Refs 46,47). This can be expressed in terms of the Fourier transform in momentum space of the density matrix, as

\[
n(p) \propto \int d\mathbf{r} d\mathbf{r}' e^{-i \mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')} \gamma(\mathbf{r}, \mathbf{r}'),
\]  

(15)
where we defined $\gamma(\mathbf{r}, \mathbf{r}') = \sum_{\sigma} \int \! ds ds' \chi_{\sigma}^*(s) \gamma(x, x') \chi_{\sigma}(s')$, with $\chi_{\sigma}(s)$ the spin function. The Fourier transform (15) gives the matrix elements of the density matrix in a basis of plane waves $\phi_{\sigma\sigma}(\mathbf{r}, s) = 1/\sqrt{N} e^{i \mathbf{p} \cdot \mathbf{r}} \chi_{\sigma}(s)$, which are the exact one-electron eigenstates of the free electron gas, i.e. the perfectly translationally invariant system. In the Hubbard molecule this basis corresponds to the bonding/antibonding basis $\{ \phi_{\sigma\sigma} \}$, that reflects the symmetry of the system. Therefore, using this basis in analogy to the experiments, we have that the Compton profile for the spin-singlet system would give $n_{\uparrow\uparrow} = 1$ (with $n_{\uparrow\downarrow} = n_{\downarrow\uparrow} = 1/2$ and $n_{\downarrow\downarrow} = n_{\uparrow\uparrow} = 1/2$). What about the antiferromagnetic case? Antiferromagnetic systems are usually simple to treat by weakly correlated methods. One can hence think that there is little correlation in this spin structure. In reality the system is correlated, but part of the correlation is included in the spin-symmetry breaking. One can see that for this spin structure, characterized by a single Slater determinant, the natural orbitals are the site orbitals $\psi_{\sigma/2\sigma} = (\phi_{\sigma\sigma} \pm \phi_{\sigma\sigma})/\sqrt{2}$ with occupation numbers $n_{1\uparrow} = n_{2\downarrow} = 1$ and $n_{1\downarrow} = n_{2\uparrow} = 0$. Spin-resolved occupation numbers are, hence, different for the two spin structures. However to get the equivalent to the momentum distribution one has to project the density matrix in the symmetry-basis of the molecule, i.e. bonding/antibonding basis. For the AF case one then gets the same as for the PM case. In fact not even a spin-resolved Compton profile would distinguish between PM and AF spin structures, since for the latter $n_{\uparrow\uparrow}^A = \int \! dx dx' \phi_{\sigma\sigma}^*(x') \left[ \sum_{i=1\uparrow, 2\downarrow} \psi_i(x) \psi_i^*(x') \right] \phi_{\sigma\sigma}(x) = 1/2$, as for the paramagnetic case! To distinguish between the two cases one should carry out a spin- and space-resolved measurement of the occupation numbers. In this case the density matrix is projected in the site basis, which gives $n_{1\uparrow}^P = n_{2\downarrow}^P = n_{1\downarrow}^P = n_{2\uparrow}^P = 1$ and $n_{1\uparrow}^A = n_{2\downarrow}^A = 1, n_{1\downarrow}^A = n_{2\uparrow}^A = 0$.

IV. CONCLUSIONS

We analyzed the results for total energy, natural occupation numbers, removal/addition energies, and spectral function for the Hubbard molecule at $1/4$ and $1/2$ filling by using reduced density-matrix functional theory and many-body perturbation theory within standard approximations to electron correlation, namely Müller-like functionals and $GW$, respectively. In general there is no Müller-like functional which works well at both one fourth and half filling: for the former the Hartree-Fock functional gives the exact total energy and occupation numbers, whereas for the latter the original Müller functional does the job. Other Müller-like functionals underestimate the total energy at $1/4$ filling and overestimate it at $1/2$ filling, like $GW$. The same behavior is found for the occupation numbers, which deviate in a similar way as $GW$ from the exact results.

We also analyzed various approximate methods to ob-
tain removal/addition energies and spectral functions from RDMFT. Our results for the removal/addition energies and spectral function obtained using the approximate method of Ref. 27 suggest a cancellation of errors between the latter and Müller-like approximations to electron correlations. Moreover the spectral peaks can have a mixed removal and addition nature as well as a mixed quasiparticle and satellite nature. At moderately strong interaction, GW is superior. In the strongly correlated electron regime, which is obtained stretching the molecule (atomic limit), we found that both RDMFT and GW fail for a spin-singlet ground state, whereas they give the exact results for the spin-symmetry-broken case.

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Figure 6: (Color online) Removal and addition energies $\omega/t$ as function of $U/t$ at 1/2 filling: exact vs EKT method used with the Müller functional. The labels $\omega_i$ indicate the exact energies.

Figure 7: (Color online) Removal and addition energies $\omega/t$ as function of $U/t$ at 1/2 filling: exact vs DIF and DER methods used with the Müller functional. The labels $\epsilon_i$ indicate the bonding/antibonding energies obtained using the DIF/DER methods.

Appendix A: Bonding-antibonding basis

The bonding/antibonding basis $\{\phi_i\}$ is defined as

$$
\phi_{b\sigma} = \frac{1}{\sqrt{2}} \psi_{1\sigma} + \frac{1}{\sqrt{2}} \psi_{2\sigma},
$$

(A1)

$$
\phi_{a\sigma} = \frac{1}{\sqrt{2}} \psi_{1\sigma} - \frac{1}{\sqrt{2}} \psi_{2\sigma},
$$

(A2)

where $\{\psi_i\}$ is the site basis.

In Ref 14 the results of the Hubbard molecule 1/4 and 1/2 filling are given using a basis of Slater determinants $|\ldots\rangle$ constructed using the site basis. In tables I and II we gives the transformation of this Slater determinants from the site basis to the bonding/antibonding basis.
The eigenstates of the Hamiltonian at 1/2 filling in the bonding/antibonding representation are given in table III. Here $c^2 = 16t^2 + U^2$ and $a^2 = 2 \left[16t^2/(c-U)^2 + 1\right]$, and $b^2 = 2 \left[16t^2/(c+U)^2 + 1\right]$.

2. 1/2 filling

The eigenstates of the Hamiltonian at 1/2 filling are $|b \uparrow\rangle$ (the ground state), $|b \downarrow\rangle$, $|a \uparrow\rangle$, $|a \downarrow\rangle$ with energies $\epsilon_0 - t$, $\epsilon_0 - t$, $\epsilon_0 + t$, $\epsilon_0 + t$.

1. 1/4 filling

The eigenstates of the Hamiltonian at 1/4 filling are $|b \uparrow\rangle$ (the ground state). $|b \downarrow\rangle$, $|a \uparrow\rangle$, $|a \downarrow\rangle$ with energies $\epsilon_0 - t$, $\epsilon_0 - t$, $\epsilon_0 + t$, $\epsilon_0 + t$.

Table I: Coefficients of the transformation from site to bonding/antibonding basis for 1 electron.

| | $|b \uparrow\rangle$ | $|b \downarrow\rangle$ | $|a \uparrow\rangle$ | $|a \downarrow\rangle$ |
|---|---|---|---|---|
|$|\uparrow,0\rangle$ | $1/\sqrt{2}$ | 0 | $1/\sqrt{2}$ | 0 |
|$|\downarrow,0\rangle$ | 0 | $1/\sqrt{2}$ | 0 | $1/\sqrt{2}$ |
|$|0,\uparrow\rangle$ | $1/\sqrt{2}$ | 0 | $1/\sqrt{2}$ | 0 |
|$|0,\downarrow\rangle$ | 0 | $1/\sqrt{2}$ | 0 | $-1/\sqrt{2}$ |

Table II: Coefficients of the transformation from site to bonding/antibonding basis for 2 electrons.

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

Table III: Eigenvalues and coefficients for the two electron system in bonding/antibonding basis.

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