Limitations of the hybrid functional approach to electronic structure of transition metal oxides

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During the last decade, *ab initio* methods to calculate electronic structure of materials based on hybrid functionals are increasingly becoming widely popular. In this Letter, we show that, in the case of small gap transition metal oxides, such as VO_2, with rather subtle physics in the vicinity of the Fermi-surface, such hybrid functional schemes without the inclusion of "expensive" fully self-consistent GW corrections fail to yield this physics and incorrectly describe the features of the wave function of states near the Fermi-surface. While a fully self-consistent GW on top of hybrid functional approach does correct these wave functions as expected, and is found to be in general agreement with the results of a fully self-consistent GW approach based on semilocal functionals, it is much more computationally demanding as compared to the latter approach for the benefit of essentially the same results.

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During the last few decades, new materials based on transition metal oxides (TMOs) as the key parent component have surprised us with their novel and unexpected behaviors. These include high temperature superconductivity in the cuprates, giant magnetoresistance in magnanites and a plethora of fascinating new phenomena which has been recently reported on oxide heterostructures of TMOs and devices [1–3]. For example, an interface between two insulators behaves as a metal [2] which becomes superconducting at sufficiently low temperatures, while an interface between two antiferromagnets becomes ferromagnetic [4]. These new structures not only create a playground for unexpected physical phenomena to be observed, but, in addition, they open up the possibility for new applications based on radically different foundations. The complex, unusual, and as yet not fully discovered or understood behavior of small-gap TMOs can be manipulated in a variety of fundamentally new applications [5].

While in the late 80's, immediately after the discovery of the cuprate superconductors, electronic structure calculations could not predict the correct ground state of TMO based materials, during the following decades significant progress has been made which has restored some of the faith in the newly developed *ab initio* computational schemes.

The room temperature M_1 phase of VO_2, a prototypical material[6] in the family of TMOs, is such a small gap system of correlated d-electrons. Small-gap TMOs have a very rich, complex and interesting phase diagram, where understanding their electronic structure and wave functions is of high importance. As a result these TMOs have been widely studied with sophisticated *ab initio* methods. A recent *Letter* reported [7] that HSE06 nonlocal range-separated hybrid density functional theory (DFT) [8] is able to correctly describe the ground state wave functions of VO_2, and produces a reasonable though larger gap than the experimental one. HSE is a slower method than traditional (semi)local DFT functionals but much faster than many-body perturbation methods, such as the GW-method or the dynamical mean field theory; thus, it has been assumed with a growing number of followers [9–12] that HSE06 may be a very practical method to explore the properties of small-gap TMOs.

Here we show by a fully dynamical self-consistent GW (scGW) calculation [13, 14] that HSE06 does not provide accurate wave functions and a semi-local DFT functional is as good a starting point for the scGW calculation as the computationally demanding HSE06 method. Furthermore, we demonstrate that even if the admixture of the Fock-exchange in the hybrid functional is tuned to reproduce the scGW fundamental gap, still, the resulting wave functions deviate from those obtained by scGW close to the Fermi-level. We conclude that (semi)local functionals are as good starting points for the scGW procedure as the hybrid functionals for small-gap TMOs. The former, however, is much less computationally demanding.

We carried out DFT calculations on the M_1 phase of VO_2 as implemented within the VASP package [15–17]. We used small core projectors for vanadium ions, so we explicitly included $3s$ and $3p$ electrons as valence. The valence electron states were expressed as linear combinations of plane waves. We found that the plane wave

cutoff of 400 eV provided convergent single particle levels. As we applied various functionals and GW schemes for calculating the quasi-particle energies, we used the experimental geometry[18]. The Brillouin-zone integration was approximated by a weighted sum on a special k-point set. We found that the required size of the Monkhorst-Pack [19] k-point set depends strongly on the existence of a gap. Convergent charge density could be achieved with a $5 \times 5 \times 5$ Monkhorst-Pack k-point set when there is a gap, while an $18 \times 18 \times 18$ k-point set was required without a gap. We applied 146 conduction bands in the GW calculations.

The ground state electronic structure and wave functions were calculated by the standard semi-local Perdew-Burke-Ernzerhof (PBE) functional [20] as well as non-local, range separated hybrid functionals as proposed by Heyd-Scuseria-Ernzerhof (HSE) [8, 21]. The HSE functional for the exchange-correlation part of the energy involves a parameter α which mixes the contribution of the short-range parts of the Fock-exchange and the PBE expression for the exchange energy [8]. It also involves a second parameter ω which defines what is meant by the short and long ranged part of the Coulomb potential.

The value of the parameter $\omega = 0.2a_0^{-1}$ is determined to give a balanced description that provides good accuracy and speed for both molecules and solids [21]. The Fock-exchange part is calculated using the short-range part of the Coulomb interaction. The PBE [20] expression for the exchange energy functional is modified to use the short and long range parts of the Coulomb interaction [8]. The choice of ω and α may depend on the actual system. We fixed the parameter ω at $0.2a_0^{-1}$ while we varied the parameter α. This parameter is often tuned to agree with experimental data, such as the band gap [22–24] or the dielectric constant [25] of a given crystal. α=0.25 corresponds to the HSE06 functional [21] that we call now HSE-0.250. We note that α=0.25 was rationalized in Ref. 26 where they showed that a smaller value is needed for systems with nearly-degenerate ground-states. VO_2 may fall into this category, thus we applied α=0.125 and α=0.172 (HSE-0.125 and HSE-0.172 functionals, respectively).

As HSE functionals contain external parameters they are not truly *ab initio* methods. Nevertheless, HSE DFT functionals may provide a good starting point for many-body perturbation methods, such as the GW-method which may result in quasi-particle energies and wave functions that are ideally *independent* from the starting point. We applied several levels of approximations within the GW quasi-particle scheme as implemented in VASP [27–30]. (i) First, we applied the simplest single-shot GW approach, i.e., the G_0W_0 approximation. This means that we have used the Kohn-Sham eigenvalues and orbitals in G_0 and W_0. For W we took $W_0 = \epsilon^{-1}V$, where the dielectric matrix $\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q},\omega)$, with $\mathbf{G}$ and $\mathbf{G}'$ denoting reciprocal lattice vectors, were calculated in the

TABLE I: We list the direct gaps in the M_1 phase of VO_2 calculated using different methods and compare with the results of other work and experimental values. Abbreviations of functionals are explained in the text. We note that PBE results in a metallic state (no gap).

Source	Gap
PBE (GGA)	N/A
HSE-0.250	1.01 eV
HSE-0.125	0.26 eV
HSE-0.172	0.55 eV
HSE-0.250+G_0W_0	1.01 eV
HSE-0.125+G_0W_0	0.69 eV
HSE-0.250+G_4W_0	1.01 eV
HSE-0.125+G_4W_0	0.69 eV
HSE-0.250+scGW	0.54 eV
HSE-0.125+scGW	0.54 eV
PBE+scGW	0.54 eV
LDA+COHSEX+G_0W_0 [a]	0.6 eV
LDA+empirical correction+G_0W_0 [b]	0.6 eV
Experiment [c]	~0.6 eV

[a]Ref. 33 (with LDA lattice constant)
[b]Ref. 34 (empirical correction on d-orbitals)
[c]Ref. 35

random phase approximation and the self-energy corrections were evaluated to first order in the difference between the self-energy Σ and the Kohn-Sham potential [31, 32]. (ii) As a higher level approximation, we solved for G self-consistently within the GW approximation following the procedure described in Ref. 30. Typically, four iterations in G were sufficient to achieve convergence of the self-consistent quasi-particle energies within 0.02 eV, and we denote this procedure by G_4W_0. (iii) Last, we applied a fully self-consistent dynamical GW correction as proposed by van Schilfgaarde *et al.* [14] and implemented in VASP [30]. In this case, the G and W are updated *together* with the wave functions by means of the following equation:

$$[T + V + \Sigma(E_n)]\,|\psi_n\rangle = E_n|\psi_n\rangle, \qquad (1)$$

where T is the kinetic energy operator, V is the electrostatic potential, and, $\Sigma(E_n)$ is the energy-dependent Hermitian part of the self-energy as calculated from the GW approximation. E_n and ψ_n are the quasi-particle energies and wave functions. Formally, Eq. 1 looks like an ordinary Kohn-Sham DFT equation. Thus, the resulting wave functions and energies can be used to recalculate G and W of the system, and, the (Hermitian) part of $\Sigma(E_n)$, until self-consistency has been reached. We found that typically 13-18 iterations were sufficient to obtain self-consistent quasi-particle energies *and* wave functions.

First, we discuss our results for the quasi-particle en-

ergies close to the Fermi-level obtained with DFT and quasi-particle correction calculations on the M_1 phase of VO_2. The M_1 phase of VO_2 has a small gap of ~0.6 eV [35]. PBE falsely predicts a metallic state while HSE-0.250 (HSE06) yields too large a gap of 1.01 eV, in agreement with a previous work [7]. If we apply HSE-0.125 then the gap becomes too low at 0.26 eV. One may assume that HSE functionals are a much better starting point for GW-calculation as they provide a gap, thus G_0W_0 may result in good results on top of HSE functionals. However, G_0W_0 did not improve the results on HSE-0.250. The calculated gap did not change, (Table I) which might imply that HSE-0.250 produces very good quasi-particle energies and wave functions. However, the G_0W_0 correction on top of HSE-0.125 gave a very different result, yielding a gap of 0.69 eV . When G was self-consistently updated, the quasi-particle energies did not change (see HSE-0.250+G_4W_0 and HSE-0.125+G_4W_0 results in Table I). We conclude that G_0W_0 and G_4W_0 corrections do not supply a ground state in close agreement with experiment near the Fermi-level. A more complete calculation is needed to approach the experimental situation.

We then applied a fully dynamical self-consistent GW-method where the wave functions were updated together with the G and W. The calculated HSE-0.250+scGW and HSE-0.125+scGW band gaps are the same (0.54 eV), which is quite close to the experimental one. In addition, the calculated density of states agrees well with the experimental photo-emission spectrum (see Fig. 1) [36].

A previous theoretical study indicated that the local-density-approximation (LDA) can be a good starting point for the self-consistent GW procedure for VO_2 [33]. Gatti *et al.* applied the self-consistent GW-method in the static COHSEX approximation first, which opened a band gap from the metallic solution. Then, they applied a fully dynamical G_0W_0 correction on the quasi-particle energies [33]. Here, we applied a fully dynamical self-consistent GW on top of a semi-local PBE functional. The calculated PBE+scGW band gap agrees well with HSE+scGW. From this, it is fairly clear that starting from the computationally "expensive" hybrid functional wave functions is not advantageous when a self-consistent GW calculation is required, as seems to be the case in many small-gap systems, such as the TMOs [34].

As the wave functions are updated in the scGW procedure, it is intriguing to study the change in the wave functions due to the scGW correction. This analysis was already carried out when starting from LDA wave functions [33]. Now, we analyze the case of HSE functionals. To show the change in wave functions, we present the projected density of states (PDOS) onto the spherical harmonics around one unique vanadium atom close to the Fermi-level where the change is the most significant. From these plots we observed several interesting issues: (i) starting with PBE [c.f., Figs. 2(a) and (b)], the scGW
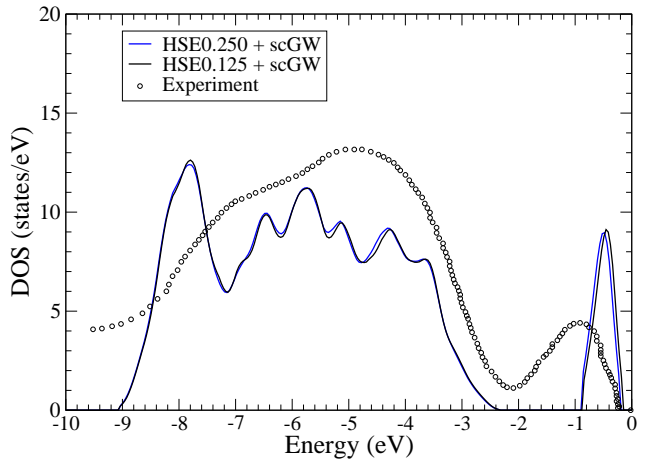

FIG. 1: (Color online) The photo-emission data taken from Ref. 36 is compared with the density of states (DOS) of the occupied states as calculated within scGW on top of different HSE functionals. The calculated data was smoothed using an exponentially weighted moving average with smoothing factor of 0.25. We averaged each data point with its seven neighbors using a decreasing weight $(1-\alpha)^n$, where n is the number of points to the central point.

procedure is needed to open the gap near the Fermi-level so that the contribution of d_z^2 and (d_{xz},d_{yz}) will be significantly smaller than that of d_{xy} and $d_{x^2-y^2}$ just below the Fermi-level and *vice versa* just above the Fermi-level, (ii) the unoccupied wave functions with energies of ~1 eV above the Fermi-level in PBE and PBE+scGW calculations are very similar, (iii) HSE naturally opens the gap [Figs. 2(c,e)], but the wave functions significantly differ from those obtained with HSE+scGW [c.f., Figs. 2(d) and (f)], particularly, at energies above the Fermi-level where HSE+scGW yields similar contributions from d_z^2 and $d_{x^2-y^2}$ orbitals at around 2 eV above the Fermi-level while they "split" in the HSE calculations. Apparently [Figs. 2(b,d,f)], the convergent scGW wave functions are the same *regardless* of the starting point. The semi-local PBE functional provides relatively good wave functions for states with energy 1 eV above the Fermi-level, *unlike* HSE-0.125 or HSE-0.250 functionals.

Recently, it has been claimed that for this material, the hybrid functional HSE-0.250 gives a good description of the ground state [7]. According to our analysis, this is questionable. Apart from close vicinity to the Fermi-level, the semi-local PBE wave functions are superior to the HSE-0.250 wave functions in the VO_2 crystal. Given the similar number of iterations required to achieve convergence in the scGW procedure, and the decreased workload, it seems that using the HSE family of functionals as a starting point for the more accurate scGW approximation does not provide an improved calculation at all.

We further note that HSE functionals have been used as a basis for investigating previously unknown materi-
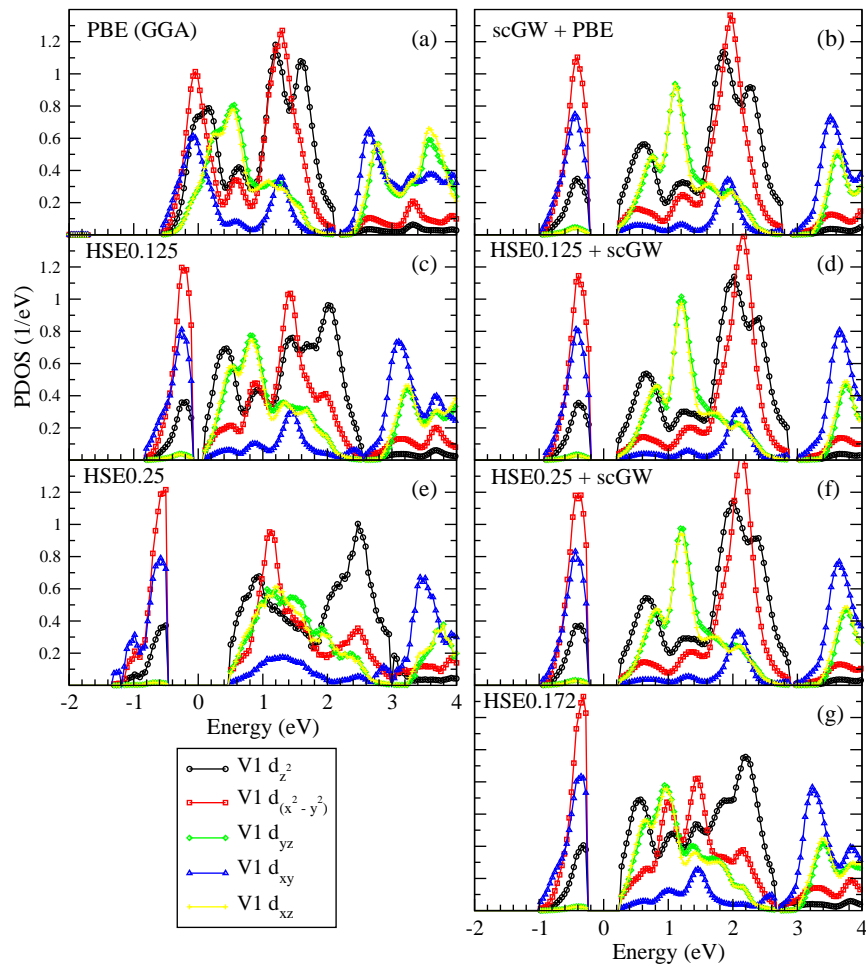
FIG. 2: (Color online) The partial density of states (PDOS) near the Fermi-level projected onto the spherical harmonics around one of the unique vanadium atoms (V1) in the M_1 phase of VO_2, for a variety of functionals. The $\vec{x}$ axis is parallel to the M_1 "a" axis, $\vec{y}$ is parallel to the M_1 "b" axis [18], and $\vec{z}$ is perpendicular to those, using a right-hand rule.

als [10], and to explore the complicated physics of phase transitions [9, 12]. In addition, the parameter α has been tuned to agree with experimental data such as the band gap [22–25]. In order to demonstrate the danger of fitting the α parameter to the band gap of M_1 phase of VO_2, we show that the "tuned" HSE functional does not produce the appropriate quasi-particle energies and wave functions. We found, by a simple linear interpolation of our HSE-0.250 and HSE-0.125 results, that the HSE functional with α=0.172 yields about the same gap of 0.55 eV as that found by the scGW approach. Comparing the wave functions of scGW and HSE-0.172 [c.f., Figs. 2(f) and (g)], it is clear that the tuned functional and scGW calculations significantly disagree for the wave functions with energies above the Fermi-level. Since the character of the wave functions is quite important for several properties such as optical excitations [5, 37, 38], it seems that using such tuned functionals as a starting point may be not appropriate for VO_2, and this "tuning" has to be carefully checked in small-gap TMOs.

In conclusion, we demonstrated that the HSE-type of functionals should be applied with great care on small-gap TMOs such as the M_1 phase of VO_2. We found that scGW calculations on top of semi-local PBE or the non-local HSE functionals provide the same results and they are in agreement with the experimental data. Furthermore, we have found that the PBE wave functions for states which have energy 1 eV above the Fermi-level are superior, thus, the PBE provides at least as good starting point as the HSE functionals for detailed scGW calculations.

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