

Understanding Correlations in Vanadium Dioxide from First Principles

Matteo Gatti,^{1,2} Fabien Bruneval,^{3,1,2} Valerio Olevano,^{4,2} and Lucia Reining^{1,2}

¹Laboratoire des Solides Irradiés, École Polytechnique, CNRS-CEA/DSM, F-91128 Palaiseau, France

²European Theoretical Spectroscopy Facility (ETSF)

³Department of Chemistry and Applied Biosciences, ETH Zurich c/o USI Campus,
Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland

⁴Institut Néel, CNRS, F-38042 Grenoble, France

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Vanadium dioxide is a prototype material for the discussion of correlation effects in solids. First-principles density-functional theory does not describe the metal-insulator transition, whereas strongly correlated models reproduce the main features. Here we present a parameter-free *GW* calculation of VO₂ and show that the correlation effects in the band structure of both the metallic and the insulating phases are correctly reproduced, provided that quasiparticle energies and wave functions are calculated self-consistently. Our calculations explain the satellite in the photoemission spectrum of the metal as due to a plasmon resonance in the energy-loss function and show that this feature disappears in the insulator.

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Understanding and describing electronic correlations is one of the major challenges in solid state physics. With progress in experimental techniques such as hard x-ray photoemission [1] a wealth of new data are available that provide insight, but also benchmarks and questions to theory. *Ab initio* density-functional theory (DFT) [2], often used in simple approximations like the local-density approximation (LDA), can yield ground-state properties correctly, but the interpretation of Kohn-Sham (KS) eigenvalues as band structures is not appropriate and leads to a systematic underestimate or even closing of photoemission band gaps [3]. Approaches like the LDA+*U* [4] and, more recently, dynamical mean-field theory (DMFT) [5] have put forward new points of view that are able to overcome these limitations. The drawback of most LDA+*U* and DMFT calculations, on the other hand, is their dependence on one or more parameters, and the fact that the more advanced description of correlations is usually limited to a reduced number of electronic states around the Fermi level. Therefore, the nature of many correlated materials is still very much debated.

A prototype for such a material is vanadium dioxide (VO₂). At high temperature it is in a rutile metallic phase. At 340 K it undergoes a transition to a monoclinic insulator [6], where the V atoms dimerize and the V pairs tilt around the rutile *c* axis. It has long been debated whether the electronic correlation is strong enough to localize the electrons and form a Mott-Hubbard insulator [7] or whether structural distortions alone can induce the insulating phase (Peierls model) [8]. Very recently, the need to go beyond standard single-band Hubbard and Peierls transition models has been put forward by both experimental [9,10] and theoretical [11] works. They indicate as the most relevant effect for the transition the orbital switching of the V 3*d* states from the isotropic metal to the insulator: in the latter mainly the so-called *d*_{||} states oriented along the rutile *c* axis should be occupied.

KS-LDA [8,12] as well as single-site DMFT [13,14] wrongly predict both phases to be metallic. In LDA+*U* instead even the metallic rutile structure becomes an insulator [13,15]. So far only a cluster DMFT [11] and a simplified *GW* calculation [16] have been able to reproduce the correct character of both phases. The latter approach is an efficient model for Hedin's *GW* approximation [17] to many-body perturbation theory. In *GW* the self-energy Σ is the product of the one-electron Green's function *G* and the dynamically screened Coulomb interaction *W*. In *ab initio GW* [3] screening is calculated at the random-phase approximation (RPA) level. In the simplified approach of Ref. [16] a model screened interaction *W* is instead used. In particular, the static dielectric constant is a parameter taken from experiment. In this way, a good description of the quasiparticle density of states (DOS) has been obtained in Ref. [16], but the satellite at 1.3 eV in the photoemission spectrum (PES) [10] of the metallic phase was not addressed. Cluster DMFT *does* describe that peak, but the method is limited to the *t*_{2g} *d*-bands around the Fermi level so that the other parts of the photoemission spectrum cannot be described, and the effect of the remaining electrons on the phase transition, which may be important, is not accounted for. Moreover, correlations are introduced by an adjustable Hubbard-model on-site parameter *U*. For these reasons, no final conclusion could be drawn *from first principles* concerning the metal-insulator transition in VO₂ and the corresponding nature of its electronic structure.

In this Letter we go beyond modelistic approaches, without recurring to adjustable parameters. On the basis of a fully *ab initio GW* calculation [3,17,18], we show that correlation effects in the electronic structure of both the metallic and the insulating phases are correctly reproduced *provided that* quasiparticle energies and wave functions are calculated self-consistently. Our RPA result for the energy-loss function that enters the *GW* dynamically screened

self-energy is itself in good agreement with experimental electron energy-loss (EELS) spectra [19]. In particular, in the rutile phase it shows the plasmon resonance above 1 eV, which is characteristic for the metal, and correctly suppresses it in the insulator. This explains the difference in the satellite structure between the photoemission spectra of the two phases.

We start with a DFT-LDA calculation to determine the ground state of the system. Our results for the lattice parameters of both phases confirm previous calculations [8] and are in good agreement (within 1%–2%) with experiment [20]. Also our KS band structure agrees with previous results [12,16,21]: in the insulator the bottom-conduction band overlaps the top valence band, with a negative gap of -0.2 eV. In Fig. 1 the LDA DOS for the insulator is compared with PES measurements [10], showing a V $3d$ peak at -0.9 eV and an O $2p$ band between around -2 and -9 eV (see the inset of Fig. 1 for the angular momentum analysis of the calculated DOS). The LDA DOS is metallic because the V $3d$ peak around the Fermi level lacks the correct splitting of the $d_{||}$ states.

By definition, a KS DOS is not meant to reproduce the excitation energies measured in photoemission, whereas GW is an approximation designed to describe electron addition and removal. Since *ab initio* GW calculations are cumbersome, however, most often [3] G and W are constructed using LDA eigenvalues and orbitals instead of a self-consistent treatment (this approach is called G_0W_0), and self-energy corrections are evaluated to first order in the difference between Σ and the KS potential [18].

We have applied this perturbative G_0W_0 approach to the monoclinic phase of VO_2 . In seeming support of the hy-

pothesis of “strong correlation,” G_0W_0 (that works very well for a wide range of materials [3]) fails to open the gap (see Fig. 1) of VO_2 . However, a better GW calculation should get rid of the DFT KS starting point, a fact that has been shown to be potentially important in materials containing d electrons [23–25]. We have therefore performed self-consistent quasiparticle calculations, along the scheme of Ref. [26]. In this approach, self-consistency is obtained on the so-called COHSEX level [17]. COHSEX is a *static* approximation to GW with an instantaneous screened interaction W . It consists of a statically screened exchange (SEX) and a Coulomb hole (COH), which represents the induced classical potential due to an extra point charge. The result of the COHSEX calculations is then used as input for a one-step, perturbative, but fully dynamical G_0W_0 . The procedure yields results close to quasiparticle self-consistent GW [24], at a lower computational cost.

Already the self-consistent COHSEX calculation alone *does* succeed in opening a gap (0.78 eV, quite close to the experimental value of 0.6 eV) in the density of states of the insulating VO_2 . To identify the origin of this result we have also done a COHSEX calculation where the wave functions are constrained to be the LDA ones and only the energies are updated self-consistently. In this case, on the contrary, an almost zero gap (0.02 eV) is found: the change of the wave functions with respect to the LDA ones is of utmost importance. Finally, a one-step perturbative G_0W_0 starting from the self-consistent COHSEX structure leads to a gap of 0.65 eV, in quantitative agreement with experiments [10]. At this level, also our 2.5 eV estimate of the $d_{||}$ bonding-antibonding splitting matches well the experimental results.

In order to elucidate the role of wave functions, we have plotted in Fig. 2 the top valence (left) and bottom-conduction (right) LDA wave functions (upper panels), and the difference (lower panels) with respect to the COHSEX quasiparticle ones. One finds confirmation of the $d_{||}$ character of the top valence state, with a strong polarization (V–V bonding) along the c axis (vertical direction in the picture). The differences induced by self-consistency shown in the lower panels display the enhancement of this anisotropy, a consequence of a specular mixing between top valence and bottom-conduction wave functions. The angular momentum projected DOS (inset of Fig. 1) shows that the total amount of V $3d$ –O $2p$ hybridization remains pretty unchanged, as found also by the model GW calculations [16]. The main change of the wave functions is instead a mixing among the different V $3d$ states around the Fermi level, which induces a stronger $d_{||}$ character of the top valence wave functions.

These observations show hence that (i) DFT-LDA reproduces VO_2 ground-state properties well. DFT is an exact theory for the ground state and LDA is, even for VO_2 , a good approximation. On the other hand, KS-LDA wave functions are not a sufficiently good approximation for the quasiparticle wave functions at the Fermi level. This

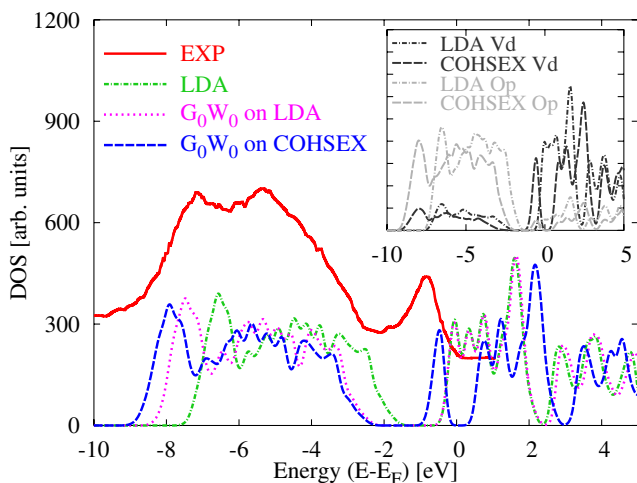


FIG. 1 (color online). Experimental PES from [10] [solid (red) line] for the insulating phase compared to theoretical densities of states in different approximations: LDA [dash-dotted (green) line], G_0W_0 on top of LDA [dotted (purple) line], G_0W_0 on top of COHSEX (see the text for the definition) [dashed (blue) line]. Inset: angular momentum analysis of the LDA and COHSEX DOS. Dark lines: V $3d$ components; light lines: O $2p$ components.

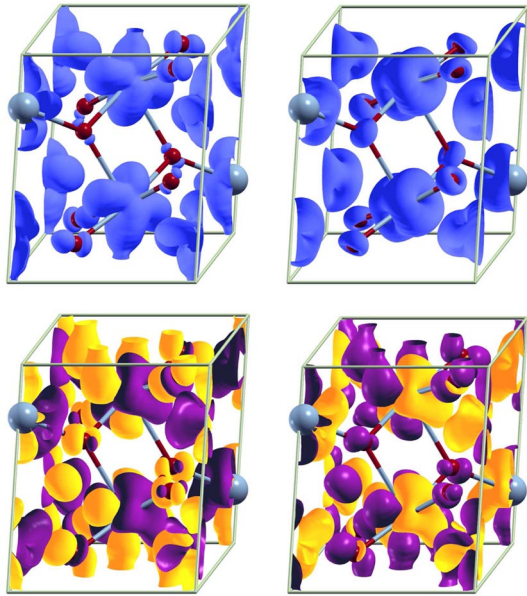


FIG. 2 (color online). LDA wave functions (upper panels) and the difference between COHSEX and LDA wave functions (bottom panels), for the top valence (left column) and bottom-conduction (right column) states. The value for the isosurfaces in the bottom panels [light (yellow) surfaces are for positive variations and dark (purple) for negative ones] is 10% of the value of the isosurfaces in the upper panels. In the ball and stick representation, O is always small (red) and V is large (cyan).

explains the failure of G_0W_0 starting from LDA to open the gap and reproduce PES spectra. (ii) The quasiparticle band paradigm is still valid for VO_2 . Importantly, in order to obtain quantitative agreement with experiments it is crucial to take into account self-consistency including the degrees of freedom beyond the t_{2g} orbital subset (which are instead neglected in the DMFT calculations [11]). A COHSEX calculation where the self-consistency is limited to the t_{2g} still opens a gap, but only to 0.36 eV. (iii) Electronic correlation has indeed to be adequately treated. A Hartree-Fock calculation, where no correlation at all is taken into account, yields an insulator with a huge gap (7.6 eV). The RPA screening of the Coulomb interaction W (which is the only difference to Hartree-Fock where the latter is unscreened) in the GW calculation turns out to be already sufficient in dealing with electronic correlation. (iv) The nonlocality of the self-energy is essential. The ability of the model calculations [11,16] to catch this feature of the self-energy has played a fundamental role in determining a good representation of the insulating VO_2 . On the other side, the frequency dependence of the self-energy is less important in this context, confirming the conjectures of Ref. [13]. As a matter of fact, the dynamical G_0W_0 corrections on top of the *static* COHSEX are small and do not change the results qualitatively. Our calculations, taking into account all those observations, finally show that in the insulating phase the system becomes more electronically one dimensional with a stronger polarization

along the c axis and that this leads to the gap opening, in agreement with the experimental evidence [9,10]. If this orbital redistribution is underestimated, as happens in LDA, the system remains metallic.

Concerning the quasiparticle description of the metal, the task for KS-LDA is easier. The metal is electronically more isotropic than the insulator, and LDA and quasiparticle wave functions are more similar. In fact, as already found previously [12], the main quasiparticle features of the experimental PES [10] are already well described by the LDA DOS. Further GW calculations induce only small changes in the LDA DOS, maintaining good agreement with experiment. However, the experimental PES of the metallic phase shows a satellite at a binding energy of 1.3 eV. Such a satellite cannot be described by a quasiparticle DOS. In the DMFT model it is interpreted as a lower Hubbard band [11,13], a signature of strong correlation. In a GW calculation of the spectral function, satellites are due to the fact that screening is dynamic. In particular, features in the loss function (minus the imaginary part of the inverse dielectric function ϵ^{-1} , which screens the Coulomb interaction) can show up as satellites in the PES [27]. Is the RPA, employed to describe screening in GW , able to reproduce those features? Both EELS measurements [19] and thermorefectance spectra [28] show a noticeable peak in the energy range of interest (namely, at 1.2 eV) for the metallic phase. A clear peak is absent in the EELS of the insulating phase, consistent with the fact that also the PES does not exhibit significant structure in that range. This allows us to base our discussion directly on the loss function $-\text{Im}\epsilon^{-1}$.

We have carried out RPA calculations of the latter as a function of momentum transfer for both the metallic and the insulating phases. A calculated result for a small \mathbf{q} in the metallic phase is shown in Fig. 3 (continuous curve). In agreement with the experimental spectra [19], we find a sharp peak around 1.5 eV. This EELS peak has been interpreted in Ref. [19] as a $d-d$ interband transition on the basis of a Kramers-Kronig analysis of the experimental data. Our calculation, instead, clearly shows (see the Fig. 3 inset) that the peak is caused by a vanishing real part of the dielectric function ϵ_1 , i.e., a plasmon, as stated in Ref. [28]. This feature, in turn, is indeed due to a group of $d-d$ interband transitions visible in the imaginary part ϵ_2 at lower energy. A small \mathbf{q} average for the insulating phase is shown by the dashed curve in the main panel. Since the LDA band structure is qualitatively wrong for the insulator, we have adopted the GW -RPA approach, i.e., an RPA calculation using the GW band structure as calculated above. As expected, this corrects the main error of a pure LDA-RPA approach (dotted curve), and the result is in good agreement with experiment [19]. Most importantly, the sharp resonance is now strongly damped and shifted to higher energies. The phenomenon can be traced back to the fact that for the insulator the $d-d$ transitions give rise to a less pronounced peak in ϵ_2 . These findings for the loss function allow us to assign the 1.3 eV binding energy

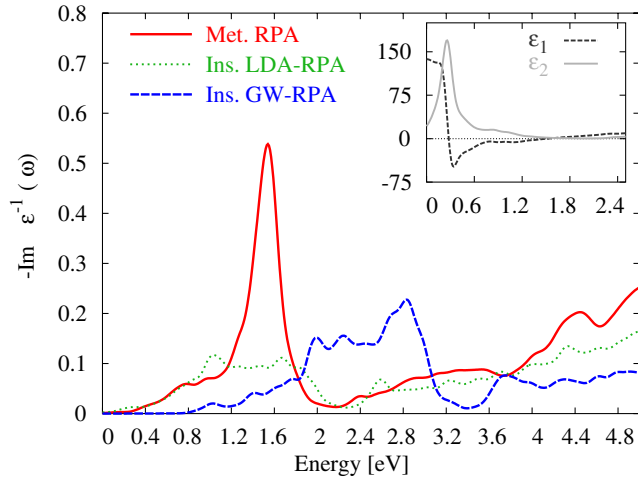


FIG. 3 (color online). Calculated EELS of the metallic (solid line) and insulating (dashed line) phases for a small value of the momentum transfer \mathbf{q} . For the insulator, also the LDA-RPA spectrum (see the text) is shown (dotted line). Inset: real and imaginary parts of ϵ (dashed and solid lines, respectively) for the metallic phase. For other \mathbf{q} values similar behaviors are found.

structure in the experimental PES of the metallic phase to a plasmon satellite, and to explain the difference to the insulator.

In conclusion, in this work we have analyzed the photoemission spectra of both the insulating and the metallic phase of vanadium dioxide. We have proved with a first-principles calculation that the main features of the spectra can be well interpreted in terms of a quasiparticle picture, even with a completely static description of correlation. We have found solid support to the experimental observations of the orbital switching of the V $3d$ states as the main responsible for the transition from the isotropic metal to the electronically more one-dimensional insulator. Moreover, we have shown that in VO_2 the treatment of electronic correlation is adequate already at the RPA level, both in the quasiparticle framework and for the interpretation of the satellite beyond the quasiparticle picture.

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