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Effects of low-energy excitations on spectral properties at higher binding energy: the metal-insulator transition of VO₂

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The effects of electron interaction on spectral properties can be understood in terms of coupling between excitations. In transition metal oxides the spectral function close to the Fermi level and low-energy excitations between d states have attracted particular attention. In this work we focus on photoemission spectra of vanadium dioxide over a wide (10 eV) range of binding energies. We show that there are clear signatures of the metal-insulator transition over the whole range due to a cross coupling of the delocalized s and p states with low-energy excitations between the localized d states. This coupling can be understood by advanced calculations based on many-body perturbation theory in the GW approximation. We also advocate the fact that tuning the photon energy up to the hard X-ray range can help to distinguish fingerprints of correlation from pure bandstructure effects.

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The study of metal-insulator transitions (MIT)[1] is important for both fundamental and practical reasons. Concerning applications, materials undergoing a MIT are characterised by a great sensitivity to external parameters, which may give rise to huge variations in their properties, like resistivity changes by several orders of magnitude [2]. On the fundamental side, strong electronic correlations are often put forward as intriguing source of new phenomena, but much remains to be understood, in particular the distinction between intrinsic correlation effects and other contributions, such as modifications due to the surface. Therefore, theorists and experimentalists continue to add pieces to the puzzle. In this work we concentrate on vanadium dioxide VO₂. It is a prototype system for the study of MITs, at the center of new experimental achievements to reveal the dynamics of the ultrafast first-order transition [3–7], and for the design of new technological applications [8].

Concerning theory, the most prominent method to treat the effects of interaction involving strongly localized states is dynamical mean-field theory (DMFT) [9]. It has shown to be a powerful tool for understanding signatures of correlation close to the Fermi level. DMFT is based on a separation between low-energy and high-energy degrees of freedom. It focuses on the former, by introducing a Hubbard hamiltonian for localized $3d$ or $4f$ orbitals, while the remaining states are most often described at the level of the local-density approximation (LDA) of density-functional theory (DFT). Despite the strong approximations involved in this model, DMFT has successfully contributed to elucidate long-standing questions.

In VO₂ the origin of the MIT and the nature of the gap

opening have caused much discussion [10], and a combination of correlation and Peierls distortion has been evoked to reconcile theory [11] and experiment [12]. Recently, however, the observation of multiple transition paths and of the coexistence of competing phases has led to the discovery of a complex phase diagram [13–21]. The gap opening is in fact not the only signature of the MIT, and the long standing discussions concerning this topic illustrate the fact that one should consider more spectral features than just the gap in order to get a clear picture. The study of the spectra over a wide range of binding energies, possibly as a function of tunable parameters, is therefore an important goal.

On the experimental side the possibility to tune the photon energy, up to the recent development of hard X-ray photoemission spectroscopy (HAXPES) [22], offers such a playground. In HAXPES one has a drastic enhancement of bulk sensitivity due to the increase of the photoelectron escape depth at higher energies, which makes it possible to disentangle volume and surface contributions, a particularly important feature since correlation manifests differently at the surface than in the bulk [23]. Recent HAXPES measurements on VO₂ [24, 25] show important transfer of spectral weight that occurs with the MIT both in core level and valence band spectra. For the valence band the metallic phase develops incoherent structures around -2 eV [see S₁ in Fig. 1(a)] that are well studied and interpreted as a lower Hubbard band in DMFT [11, 26]. However, changes occur over a much larger energy range. In particular, when going from the insulator to the metal, in addition a shoulder appears at ~ -9 eV at the bottom of the O $2p$ valence band region [see S₂ in Fig. 1(a)], that has to our knowl-

edge never been addressed by theory.

In fact, this phenomenon that requires a coupling of localized and delocalized electrons falls into a sort of no-man’s land for theory. Delocalized s and p electrons are often successfully treated by first-principle calculations based on Kohn-Sham (KS) DFT or using many-body perturbation theory in the GW approximation for the self-energy [27]. The GW self-energy is given by a product of the one-particle Green’s function G and the screened Coulomb interaction W , that contains electron-hole and plasmon excitations evaluated in the random phase approximation (RPA). The resulting dynamical screening of the photoemission hole is a crucial ingredient for understanding electron addition and removal spectra of many materials. Importantly, all orbital degrees of freedom are treated on equal footing in this approach. Indeed, GW calculations for VO_2 yield a reasonable overall description of the photoemission spectra, including the gap opening in the insulating phase [28, 29]. However, most often GW calculations are carried out in the quasiparticle (QP) approximation, where dynamical effects only lead to renormalization of energies, but by definition, right as in DFT, no satellite structure can be obtained. This was also the case for the work in [28]. The authors of [29] calculated spectral functions beyond the QP approximation in GW, but no satellites were detected, although, as pointed out in [28], $\text{Im}W(\omega)$ does show a peak around 1.5 eV. This structure could in principle cause the satellite in the 0-2 eV binding energy range. On the other side, it has been shown that, even when W is well described, GW often fails to reproduce satellites, because it creates spurious “plasmaron” satellites (i.e. coupled plasmon-hole excitations), even for materials as “simple” as the homogeneous electron gas or bulk silicon [30–32]. One has then to admit that the study of correlations effects in the MIT further away from the Fermi level seems to be completely out of reach for today’s prominent electronic structure methods.

The present work closes this gap. It shows that VO_2 does not suffer from the existence of spurious plasmaron excitations. Moreover, we demonstrate that, and why, the absence of satellites noticed in [29] for VO_2 can be overcome by calculations with a sufficient level of self-consistency. Because GW treats all orbitals on the same footing, the method is then able to reproduce incoherent structure *over the whole spectral range*. Therefore it can explain also the shoulder at 9 eV binding energy: it turns out to be an effect of cross-coupling between the s and p states and the strongly localized $d-d$ excitations.

Photoemission spectra depend on the energy of the incoming photon through the dipole transition matrix elements, that weight the contributions of the different states. This is clearly visible going from $h\nu = 700$ eV (XPS) [12] to $h\nu = 8$ KeV (HAXPES) [24, 25] [see Fig. 1(a)], where the spectral weight of the V $3d$ region (between -2 eV and the Fermi energy) is strongly reduced

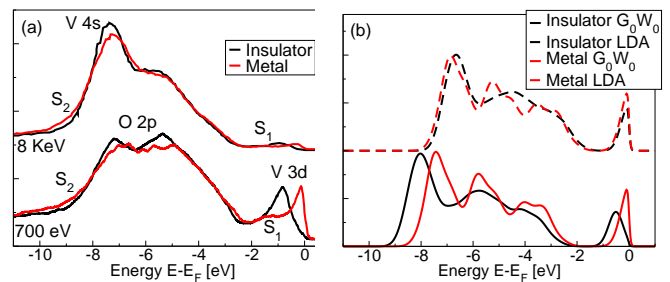


FIG. 1. (Color online) (a) Experimental HAXPES spectra at $h\nu = 8$ KeV [24] (similar results have been obtained in Ref. [25]) and XPS spectra at $h\nu = 700$ eV [12]. (b) LDA (dashed lines) and GW (solid lines) PDOS for metallic and insulating VO_2 , weighted by photoionization cross sections at 8 KeV.

with respect to the O $2p$ region (between -10 and -2 eV). The prominent peak that appears at the bottom of the O $2p$ band is linked to a V $4s$ contribution, which is strongly enhanced in HAXPES (similarly to V_2O_3 [33]).

In a first approximation, we simulate the HAXPES spectra by considering the projected density of QP states (PDOS) deriving from band-structure calculations [28], where we weight each angular contribution by the tabulated values for the atomic photoionization cross sections at 8 KeV [34] [Fig. 1(b)]. The PDOS are obtained either in LDA (upper curves) or in the perturbative G_0W_0 scheme (lower curves), which is done on top of COHSEX and LDA for the insulator and the metal, respectively [35]. Even with the rough estimation of the matrix elements given by the tabulated cross sections, we find that the main experimental trends are reproduced by our GW band-structure calculations, in particular the prominent peak at the bottom of the O $2p$, which confirms its V $4s$ origin. With respect to LDA, G_0W_0 results, besides opening the band gap in the insulator [28], also improve the position of the O $2p$ states in both phases. The effect is overestimated in the insulator and leads to a too large $p-d$ gap, because the RPA W based on COHSEX is underscreened. One can estimate that vertex corrections in W taking into account excitonic effects would correct most of this overestimation [36], that is however not crucial for the topic of the present work. More importantly, this weighted-PDOS description, by definition, does not give satellites and is unable to explain the transfer of spectral weight across the MIT for the V $4s$ peak. In fact, the experiments show that the intensity of this peak is larger in the insulator than in the metal, while in the calculated weighted PDOS this is not found [Fig. 1(b)].

The origin of this discrepancy is dynamical correlation, that is not contained in a band-structure picture. We therefore determine the spectral function $A(\omega)$, with the

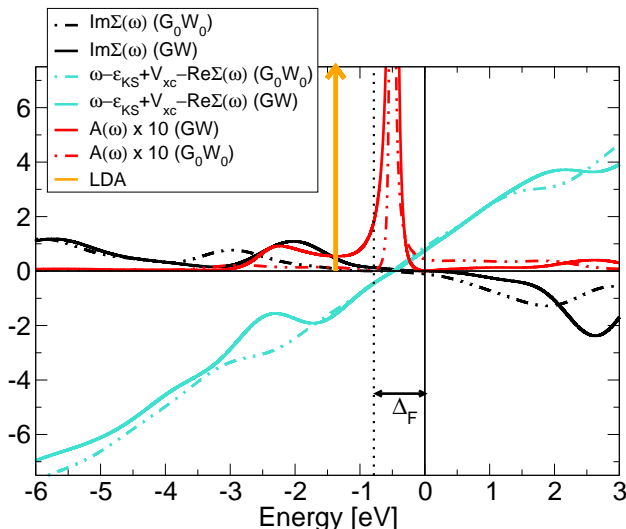


FIG. 2. (Color online) Spectral functions $A(\omega)$ and self-energy $\Sigma(\omega)$ for the top-valence state at Γ for the metallic phase, calculated in G_0W_0 (dashed lines) and energy self-consistent GW (solid lines). Vertical orange arrow: energy of the LDA KS state. Vertical dotted line: Fermi energy in LDA. The zero of the energy axis is at the Fermi energy calculated in the energy-self-consistent GW. Δ_F is the shift of the Fermi energy.

full frequency dependence of the GW self-energy Σ :

$$A(\omega) = \frac{1}{\pi} \sum_i \frac{|\text{Im}\Sigma_i(\omega)|}{(\omega - \epsilon_i - (\text{Re}\Sigma_i(\omega) - V_i^{xc}))^2 + (\text{Im}\Sigma_i(\omega))^2}. \quad (1)$$

Here ϵ_i are the LDA or COHSEX eigenvalues, and Σ_i and V_i^{xc} are matrix elements calculated on the LDA/COHSEX orbitals [35]. $\text{Im}\Sigma_i(\omega)$ induces a broadening of the various spectral features (e.g. providing a finite lifetime to QP excitations). Moreover, structures in its frequency dependence give rise to satellites in the spectral function. In the GWA they are linked to peaks in $\text{Im}W$, which for example are due to plasmon excitations [35]. One thus obtains plasmon satellites in $A(\omega)$. However, it has been shown that GW results can be deteriorated by spurious plasmaron satellites [30–32], due to additional zeroes of $\omega - \epsilon_i - (\text{Re}\Sigma_i(\omega) - V_i^{xc})$ in the denominator of (1) (besides the first one corresponding to the QP peak). This artifact of the GWA does not occur for the $d-d$ excitations in VO_2 .

Fig. 2 shows that the weak satellite at ~ -2.5 eV in the G_0W_0 spectral function of the metal (red dashed line) for the top-valence $V d$ state at the Γ point is linked to a structure in $\text{Im}\Sigma_i$ (black dashed line): the real part contribution $\omega - \epsilon_i - (\text{Re}\Sigma_i(\omega) - V_i^{xc})$ (light blue dashed line) vanishes only at the QP energy. The peak in $\text{Im}\Sigma_i$ corresponds to a coherent oscillation of the d electrons that is visible in the loss function and hence in $\text{Im}W$: it may be called a localised $d-d$ plasmon at ~ 1.5 eV

[28, 37]. The absence of fictitious plasmarons in VO_2 is due to the fact that this plasmon peak in $\text{Im}\Sigma_i$ is weak (and hence, through Hilbert transform, the anomalous dispersion of $\text{Re}\Sigma_i$ is also weak). We expect a similar behavior in many transition-metal oxides where satellites derive from a coupling with weak $d-d$ excitations. However, this also implies that the resulting satellite is almost invisible in G_0W_0 , and, in agreement with the results of Ref. [29], located too far from the QP peak with respect to experiment.

At first sight, this might be interpreted as a failure of GW to describe strong correlation effects. However, the above results (as well those of [29]) have been obtained within the perturbative G_0W_0 scheme, where G and W are built with LDA ingredients. G_0W_0 on top of LDA has shown many shortcomings especially in transition metal oxides [28, 38–40]. In G_0W_0 the peaks of $\text{Im}\Sigma_i$ (for occupied states) are located approximately at $-\omega_s + \epsilon_i$, where ω_s are the energies of the neutral excitations of the system (like the localised $d-d$ plasmon at ~ 1.5 eV in the present case). In Fig. 2 the LDA ϵ_i is marked by the orange vertical arrow. G_0W_0 corrections induce a shift Δ of the QP energy with respect to the energy ϵ_i used to build Σ . Therefore, peaks of $\text{Im}\Sigma_i$ are located at a distance $\Delta + \omega_s$ from the QP peak. Since $\Delta > 0$, the satellite in G_0W_0 has then a too high binding energy.

We therefore move to a partially self-consistent GW scheme, in which we update the real quasiparticle energies entering the self-energy (solid lines in Fig. 2) [41]. In this energy-self-consistent GW the satellite gets closer to the QP peak, because at self-consistency $\Delta = 0$. Moreover, the intensity of the satellite is enhanced due to the fact that $|\omega - \epsilon_i - (\text{Re}\Sigma_i(\omega) - V_i^{xc})|$ is smaller and hence the satellite is less screened.

In the total spectral function calculated in energy-self-consistent GW (solid lines in Fig. 3) for this $V 3d$ satellite we obtain good agreement with the experiment [43]. The binding energy of the satellite (see S_1 in Fig. 3) remains only slightly overestimated, since also the plasmon peak in the RPA loss function is slightly overestimated with respect to electron energy loss (EELS) experiment [37]. Our $V 3d$ satellite compares well also with DMFT results [11, 26], although in DMFT the intensity and position of the satellite depend on the chosen value of the Hubbard U parameter. In DMFT the $V 3d$ satellite is interpreted as a lower Hubbard band. The parameter-free GW calculation gives a complementary interpretation, adding a level of explanation to DMFT, since it allows us to make a decomposition in terms of coupling of specific excitations. In fact, in GW all electron-hole excitations are explicitly calculated and the analysis shows that the $V 3d$ satellite is due to a $d-d$ coupling between a $V 3d$ hole and a localised plasmon deriving from $d-d$ transitions [35]. In DMFT excitations involving s and p electrons are summed in the screening of the Hubbard U , while $d-d$ excitations are only implicitly included, through

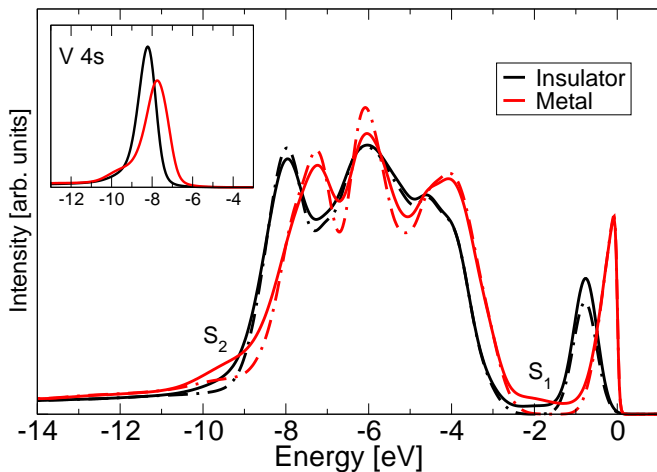


FIG. 3. (Color online) Total spectral functions in energy-self-consistent GW (solid lines). Spectral functions where the excitations of energy less than 2.7 eV have been suppressed in W (dashed lines). (Inset) Sum over states that have the largest V 4s contribution.

the solution of the impurity model, which does not allow the same kind of analysis.

Comparing the QP peak at the bottom of valence band, we now find that the intensity of the QP peak for the metal is *lower* than in the insulator, in agreement with experiment, which was not found with the weighted PDOS in Fig. 1(b). The difference between these two results is entirely due to dynamical correlations, beyond the band-structure picture of Fig. 1(b). In the metallic phase, the V 4s peak is more strongly renormalized than in the insulator: it has a larger broadening (i.e. the corresponding QP excitation has a shorter lifetime) and displays a long asymmetric tail at higher binding energies (see S_2 in Fig. 3). The inset of Fig. 3 shows the spectral functions summed over the states that have the largest V 4s contribution, i.e. the one that is enhanced in HAXPES, displaying this mechanism more clearly. A comparison with DMFT is not possible here, since the latter is limited to the d -electron region.

In order to confirm further our interpretation, we can use the fact that theory allows us to artificially suppress in the calculations the excitations ω_s of energy less than 2.7 eV [35], that correspond to the $d-d$ plasmon excitation seen in the loss function [28]. The result is reported in Fig. 3 (dashed lines). Now the V 3d satellite close to the Fermi energy is completely suppressed. Moreover, the renormalization of the V 4s peak is strongly reduced. Hence, the correlation effects around -9 eV are due to the cross-coupling of high binding energy s and p electrons with low-energy $d-d$ excitations. The transfer of spectral weight across the MIT for this peak at high binding energy is then a signature of the electronic correlations contained in the dynamical screening of the Coulomb po-

tential. Note that the shoulder at -9 eV (S_2) is a feature of the s and p projected spectral functions, not of a d projection. Therefore, when the d satellite (S_1) close to the Fermi level gets smaller because of cross section effects, the high binding energy shoulder (S_2) does not [see experiments in Fig. 1(a)], although it stems from the same $d-d$ excitation. GW provides the interpretation tool to access this binding energy range, where bulk sensitive HAXPES unambiguously displays intrinsic correlation effects.

In conclusion, we have explained the photoemission spectrum of VO_2 in function of the photon energy over a binding energy range of more than 10 eV. Even far from the Fermi level, in a previously unexplored range, correlation effects appear across the MIT. We have demonstrated that the GW approximation is able to provide a consistent interpretation of the effects due to dynamical correlations for both localized and delocalized states by treating them on equal footing. In particular the satellites at low and high binding energy are equally well described. Hence the shoulder around -9 eV in measured HAXPES spectra could be attributed to a cross coupling of V s states and localized $d-d$ excitations, which also explains its evolution in function of the photon energy. Several findings of this work are general, in particular the importance of cross-coupling between states of different character, and the fact that state-of-the-art GW will perform better for electron-hole like $d-d$ satellites than in “weakly correlated” materials like silicon. This suggests further studies on transition metal oxides combining photoemission experiments up to HAXPES, with loss spectroscopies, and GW calculations beyond the quasiparticle approximation.

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