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Momentum-resolved spectroscopy of correlated metals: A view from dynamical mean field theory

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Abstract

In this review we discuss how theoretical momentum-resolved many-body spectral functions can help understanding the physics underlying angular resolved photoemission spectra (ARPES). Special focus is set on phenomena induced by electronic Coulomb correlations. Among these effects are transfers of spectral weight, the loss of quasi-particle coherence, and the sensitivity of these phenomena on external parameters, such as temperature or pressure. For the examples of the metallic phases of VO₂ and V₂O₃ we review results obtained within dynamical mean-field theory, and assess the limits of band-structure approaches. Our discussion emphasizes the need for true many-body techniques even for certain metallic materials. *To cite this article: J.M. Tomczak et al., C. R. Physique 10 (2009).*

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Résumé

Fonctions spectrales résolues en moment des matériaux métalliques corrélés : Des résultats de la théorie de champ moyen dynamique. Dans ce rapport nous discutons comment les fonctions spectrales résolues en moment, déterminées dans le cadre des théories à plusieurs corps, peuvent nous aider à comprendre la physique sous-jacente aux spectres de photo émission résolue en angle (ARPES). Une attention particulière est portée aux phénomènes induits par les corrélations électroniques coulombiennes. Parmi ces effets on trouve les transferts de poids spectral, la perte de cohérence de quasi-particules, et la sensibilité de ces phénomènes aux paramètres externes tels que la température ou la pression. Prenant pour exemple les phases métalliques de VO₂ et V₂O₃ nous examinons des résultats obtenus dans le cadre de la théorie de champ moyen dynamique, et les limites des approches de structure de bandes. Notre discussion souligne le besoin de techniques véritablement à plusieurs corps, même pour la description de certains matériaux métalliques. *Pour citer cet article : J.M. Tomczak et al., C. R. Physique 10 (2009).*

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1. Introduction

The most prominent hallmarks of correlated metals are the occurrence of finite lifetimes of one-particle excitations, the appearance of incoherent spectral weight and the sensitivity on external parameters, such as temperature or pressure. Photoemission spectroscopy [1–3] has been a very valuable tool in assessing these effects by confronting many-body theories with experimental findings. Over the years, both theory and experiment, have thus enriched and stimulated each other, and reached nowadays a consensus on the basic incarnations of many-particle effects. Indeed, a sketch of the spectral function of a correlated metal, namely the paradigmatical three-peak-structure, consisting of occupied and unoccupied Hubbard satellites with the quasi-particle peak in between, has somewhat become the mascot of the field.

In recent years, photoemission has witnessed important progress, both conceptually and in precision. The latter concerns not only the improvement in detector technology, but also the rather recent use of either very high or very low photon energies, which both result in a better bulk-sensitivity by increasing the electron escape depth [1]. On the conceptual side, there are at least two branches that are pursued: assessing non-equilibrium states by pump-probe experiments (see e.g. [4]), and the momentum selective collection of electrons (for a review see [2]).

In this theoretical review, we shall be concerned with the latter, commonly known as angular resolved photoemission spectroscopy, or ARPES in short. Probably the most prominent examples of materials where ARPES data provide us with puzzles, the solutions of which are likely to yield key insights into the physics of the compounds, are the high- T_c superconductors. In fact, the momentum selective breakdown of the Fermi liquid regime (see e.g. the review [2]) has already called for serious refinements of theoretical approaches for models with electronic correlations. Beyond model considerations (see e.g. the examples [5–8]) however, the reliable description of momentum-resolved spectra in the realistic case is still a challenge, and yet bound to shed more light on intricate details of the excitation spectra and possibly on the physics of high- T_c superconductivity.

While for angle integrated photoemission there are many examples for which theoretical calculations, e.g. based on dynamical mean field theory (DMFT) [9,10] within its realistic extensions (in particular the so-called “LDA + DMFT” scheme [11,12]), are congruent with experiment, assessing the momentum-resolved electronic structure poses a further challenge to theoretical investigations. Nevertheless, in recent years ARPES modeling based on dynamical mean field theory has evolved into a tool that provides us with useful insights into the excitation spectra of materials such as transition metal oxides or rare-earth compounds. Early LDA + DMFT calculations for the ARPES spectra of γ -phase of manganese [13], e.g., have revealed the existence of Hubbard bands in this simple transition metal and have been confirmed by experiments. The seemingly simple transition metal oxide SrVO_3 was proposed to exhibit a kink structure much like in the high-temperature superconducting cuprates [14] (see also [15]). Finally, ARPES spectra have been calculated for heavy fermion compounds [16] and the new iron oxypnictide superconductors, revealing an intrinsically multi-band electronic structure [17].

In this review, we focus on the examples of VO_2 and V_2O_3 , two oxides that undergo metal-insulator transitions under changes of external parameters – as a function of temperature for VO_2 , and as a function of pressure or temperature for Cr-doped V_2O_3 . While it is well established that e.g. the charge gaps of strongly correlated insulators are not described by density functional theory (DFT) [18] within the local density approximation (LDA) [19], the limits of band theory for metallic phases have attracted less attention. Here, we shall put the emphasis on this point, and – using as examples the metallic phases of the mentioned vanadium oxides – discuss the influence of correlation effects onto the electronic structure, thus assessing the limits of band-structure approaches.

In this context we address two issues that are induced by electron–electron interactions: (a) the transfer of spectral weight to incoherent excitations; (b) the (orbital-dependent) coherence temperature of quasi-particle derived states.

When becoming of seizeable magnitude, both of these effects lead to the break-down of effective one-particle approaches such as DFT. One then has to go beyond the notion of a band-structure and employ a true many-body technique, examples of which are Hedin’s GW approximation (GWA, for reviews see e.g. [20,21], for recent works on vanadium oxides [22–26]), and DMFT.

This review is organized as follows: In Section 2 we summarize the main ideas of the DMFT method. Then we discuss – within the DMFT framework – the impact of correlation effects onto the electronic structure, elucidating energy shifts and life-time effects. In Section 4 we review results for momentum-resolved spectra of the vanadium oxides VO_2 and V_2O_3 . We close the article with some comments on temperature dependence within electronic structure calculations, and on perspectives of more detailed comparisons to ARPES experiments.

2. Dynamical mean field theory (DMFT) and electronic structure calculations

The basic idea of DMFT is to replace a lattice problem (or as in the realistic case, the correlated orbitals of an atom/a cluster of atoms, defined within a localized basis set) by an effective local system, coupled to a bath and subject to a self-consistency condition, in analogy to conventional Weiss mean field theory in statistical mechanics. Contrary to the latter however, the intervening mean field is energy-dependent, hence the notion of a dynamical MFT.

Let us illustrate the method on the example of a multi-band Hubbard model, defined by the Hamiltonian

$$\mathbf{H} = \sum_{\mathbf{k}, LL', \sigma} H_0^{LL'}(\mathbf{k}) c_{\mathbf{k}L\sigma}^\dagger c_{\mathbf{k}L'\sigma} + \sum_{\mathbf{R}, LL', \sigma\sigma'} U_{LL'}^{\sigma\sigma'} n_{\mathbf{R}L\sigma} n_{\mathbf{R}L'\sigma'} \quad (1)$$

The associated local problem is defined within the action formalism by

$$S^{imp} = - \int_0^\beta d\tau \int_0^\beta d\tau' \sum_{LL'\sigma} c_{L\sigma}^\dagger(\tau) [\mathcal{G}_0^{-1}]_{LL'\sigma}(\tau - \tau') c_{L'\sigma}(\tau') + \sum_{LL'\sigma\sigma'} U_{LL'}^{\sigma\sigma'} \int_0^\beta d\tau n_{L\sigma}(\tau) n_{L'\sigma'}(\tau) \quad (2)$$

where c^\dagger [c] are the Grassmann variables associated with the creation [annihilation] operators of the Hamiltonian of Eq. (1), n refers to the corresponding particle number operator, and \mathcal{G}_0 is the non-interacting propagator of the effective impurity problem. Alternatively, we can go back to a Hamiltonian formulation by parameterizing the bath Green's function by a set of auxiliary bath parameters:

$$[\mathcal{G}_0^{-1}]_{LL'\sigma}(\omega_n) = (\omega_n + \mu)\mathbf{I} - \sum_l \sum_{L''L'''} V_{LL''}^l [\omega_n \mathbf{I} - \hat{\epsilon}^l]_{L''L'''}^{-1} V_{L''L'}^l \quad (3)$$

Here, $V_{LL'}^l$ are the hybridization matrix elements of the l -th orbital in the discretized bath with the physical orbitals L, L' , and $\hat{\epsilon}^l$ is the corresponding local Hamiltonian of the l -th orbital of the bath. This form is a straightforward generalization of the usual Anderson impurity model [27] to the multi-orbital case.

The task consists in calculating the local Green's function $G_{LL'\sigma}^{imp} = -\langle T c_{L\sigma} c_{L'\sigma}^\dagger \rangle_{S^{imp}}$ of the above local impurity model. For its solution, a variety of techniques, ranging from Monte Carlo simulations to approximate schemes, are available.

In contrast to the original ideas of Anderson who wrote an impurity model in order to describe a physical impurity in a (given) host material, the impurity within the DMFT context is representative of a correlated orbital at a given site of a translationally invariant solid. One thus obtains a self-consistency condition by imposing that all equivalent sites behave in this same way. Mathematically, one imposes the local Green's function G of the solid to equal the impurity Green's function G^{imp} . To this effect, the self-energy of the impurity model $\Sigma_{imp} = \mathcal{G}_0^{-1} - G^{-1}$ is calculated and used as an approximation to the full self-energy of the lattice. Thus

$$G(\omega_n) = \sum_{\mathbf{k}} [\omega_n + \mu - H_0(\mathbf{k}) - \Sigma^{imp}(\omega_n)]^{-1} \quad (4)$$

In practice, this set of equations is solved iteratively, starting from a guess for the bath Green's function \mathcal{G}_0 , solving the impurity model, inserting the corresponding self-energy into the self-consistency equation (4), recalculating \mathcal{G}_0 from Dyson's equation, using the result to update the impurity model, and so forth.

The basic idea of constructing a local model for the purpose of calculating a local self-energy as an approximation to the full many-body self-energy of the system, carries directly over from the model context to the case of a real solid. The most basic version of the combined "LDA + DMFT" scheme [11,12] can be viewed as a DMFT solution of a multi-orbital Hubbard model, where the parameters are calculated from DFT-LDA. The impurity represents the correlated orbitals of a type of atoms in the solid, and the self-consistency condition attributes the same self-energy to all equivalent correlated atoms – up to rotations in orbital space.

Besides varying techniques for solving the impurity problem, implementations mainly differ in issues such as the orbitals used for defining the interaction terms and the notion of locality in the DMFT context [28], the basis set of the LDA implementation and the self-consistency condition, as well as the possibility of an update of the one-particle Hamiltonian [29–31].

From a conceptual point of view, LDA + DMFT in its general framework can be viewed as an approximation to a functional of both, the density and the spectral density of correlated orbitals, as formulated within spectral density functional theory [32].

3. Momentum-resolved spectral functions

3.1. The many-body spectrum

Band structure methods rely on effective one-particle theories: The Schrödinger equation becomes separable, and the Hilbert space therewith sufficiently small to render the time-independent problem of the Hamiltonian solvable. The eigenstates become Slater determinants of one-particle states, and the excitation energies are identified with the corresponding eigenvalues. These being real, the excitations are delta-distribution-like, with infinite lifetimes. The band picture is in this sense an idealisation of the normal Fermi liquid, with infinite lifetime on all energy scales. The decay of quasi-particles leaving the Fermi surface is already beyond the band-picture. Within many-body approaches, the impact of correlation effects is encoded in the electron self-energy $\Sigma(\omega)$, which is a complex non-Hermitian quantity, which is furthermore frequency-dependent.¹ While its real and imaginary parts are connected by a Kramers–Kronig transformation, we can separate their principle impacts on the electronic structure. The real parts of the self-energy are responsible for the shifting of spectral weight with respect to the non-interacting problem, in a way alike to an external potential, albeit a frequency and orbital dependent one. As we will discuss below, already this complication may lead to effects beyond a usual band-approach. The imaginary parts of the self-energy encode life-time effects and thus the loss of coherence. If these imaginary parts are seizable, band-structures and densities of states loose their meaning, and the only quantity that represents the one-particle excitations is the many-body spectral function

$$A(\mathbf{k}, \omega) = (\omega + \mu - H_0(\mathbf{k}) - \Sigma(\omega + i0^+))^{-1} \quad (5)$$

which for $\omega > 0$ ($\omega < 0$) is understood as the probability of adding (removing) an electron with energy ω and momentum \mathbf{k} into the system. It thus represents the amplitudes for the transitions $N \rightarrow N \pm 1$ of the electron occupation. In principle, photoemission spectroscopy measures one of these processes, namely the removal of an electron by photo-excitation. The energy and momentum of the electron can be collected, thus giving information on $A(\mathbf{k}, \omega < 0)$. This alone would be a theorist's dream come true. Yet, there are several issues that complicate the occurring processes, but which are beyond the scope of the current review. Indeed the states of the ejected electron and the system of $N - 1$ electrons are assumed to factorize (sudden approximation). Further, the photo-electron will scatter on its escape path towards the surface, and transmit into the vacuum with only a certain probability. The casting of these effects into theory and approximative solutions go under the name of the one and three step model. Finally, the coupling of the electronic states to the light field modulates the momentum-resolved spectral function by matrix elements susceptible to suppress certain transitions and enhancing others [33].

Despite these complications, a comparison of theoretical spectral functions with photoemission signals has proved to be semi-quantitatively meaningful. For early examples of momentum-resolved spectra in the LDA + DMFT context, see e.g. [13,15].

3.2. Effective band-structures

As alluded to above, Fermi liquid theory provides us with a justification for the search of effective low energy band structures. In energy regions where the imaginary part of the self-energy is small (that is the quasi-particle life-time large), the k -resolved spectral function displays sharp peaks corresponding to one-particle band-like excitations. These quasi-particle excitations are given by the poles $\omega_{\mathbf{k}}$ of the momentum-resolved Green's function, i.e. by $\omega_{\mathbf{k}}$ verifying $\det(G[\Re\Sigma]^{-1}) = 0$, or

$$\det(H_0(\mathbf{k}) + \Re\Sigma(\omega_{\mathbf{k}} + i0^+) - \mu - \omega_{\mathbf{k}}) = 0 \quad (6)$$

¹ From now on we will be referring to DMFT results, thus the self-energy does not have any explicit momentum dependence.

This is closest in spirit to the band-picture, and simplifies to an eigenvalue problem in the limit of a static self-energy. Yet, in general, this equation is not a linear problem, which makes its numerical solution difficult.² In particular, the weight carried by the quasi-particle poles is $Z = (1 - \frac{\partial \Re \Sigma}{\partial \omega})^{-1}$, that is, unlike in the band case, it is in general smaller than one. Moreover, the number of poles is not limited to the orbital dimension. Indeed, when thinking of the atomic limit, for which in the case of a half-filled one-band Hubbard model $\Sigma = U^2/4\omega$, there are two solutions, corresponding to the Hubbard satellites, each having the weight 1/2. This means, only in weakly correlated materials can the above prescription be used for the construction of an effective one-particle Hamiltonian (for an example, see [34,35]). Yet, also for correlated materials, interesting insights can still be gained from assessing the energies of the (fictitiously coherent) quasi-particle dispersions (e.g. when assessing dispersion kinks near the Fermi surface [14], or symmetry breaking induced transitions [35,34]). The density of states of the resulting excitations can then sometimes be used as a guidance to the most coherent parts of the spectrum.³

In a Fermi liquid, however, close to the Fermi level, the imaginary part of the self-energy vanishes proportional to $\omega^2 + \pi^2 T^2$, and the low-energy excitation spectrum can safely be assimilated to an effective band structure. Indeed, expanding the self-energy to first order around the Fermi level $\Sigma(\omega) = \Re \Sigma(0) + \omega \partial_\omega \Re \Sigma(\omega)|_{\omega=0}$ and inserting the resulting expression into Eq. (6) shows that this band structure is given by the solutions $\omega_{\mathbf{k}}$ of

$$\det(\omega_{\mathbf{k}} - Z[H_0(\mathbf{k}) + \Re \Sigma(\omega = 0) - \mu]) = 0 \quad (7)$$

where $Z^{-1} = 1 - \partial_\omega \Re \Sigma(\omega)|_{\omega=0}$. Since $Z < 1$, this effective band-structure will in general have a smaller dispersion than within DFT, one speaks of “bandwidth narrowing”.

We close this paragraph with a remark on the description of this band-narrowing effect within single-site DMFT. Since this theory approximates the full non-local many-body self-energy by a purely local quantity it is sometimes argued that DMFT could not modify the form of the LDA band dispersion. This is, however, *not* correct. In fact, the energy and orbital dependence of the self-energy results very well in a k -dependent band renormalization, as can be seen from the above equation (6). In a one-band system, the renormalization at a given k -point depends on the energy ϵ_k of the band at that given k -point. In this situation, only LDA band states that have the same energy but correspond to different k -points would be renormalized in the same way. In the general multi-band case, even this is not true anymore, since differences in the orbital character can result in different band renormalizations even of bands that live at the same energy.

4. Momentum-resolved spectroscopy of vanadium oxides

4.1. VO₂

Our first example, vanadium dioxide (VO₂), has triggered much interest over decades, due to its metal-insulator transition as a function of temperature [36]. Metallic in its high temperature phase of rutile structure, cooling beneath 340 K provokes a phase transition to a monoclinic insulating phase. The nature of this transition – Peierls or Mott – has been the subject of a long-standing debate (for a review see e.g. [37]; recent works can be found e.g. in [38,34,35]).

Dynamical mean field calculations [39–42] for the local spectral function agree well with experimental findings as provided by (angle integrated) photoemission and X-ray absorption spectra [43–48]. In particular, the characteristic features of the metal, with a pronounced peak at the Fermi level, and a lower Hubbard band satellite have been experimentally confirmed [49]. Besides one-particle spectra, also the optical conductivity of experiments [50,47,51] and LDA + DMFT calculations [52–54] are in agreement.

While theoretical results thus received experimental validation as far as integrated quantities are concerned, the capturing of the precise structure in momentum space is evidently a much stricter demand. Early ARPES work [55] indeed evidenced that the vanadium 3d bandwidth is narrower than in band-structure calculations, but lacked sufficient

² Another view point (see e.g. [6]) identifies the effective band-structure with the *maxima* of the one-particle spectral function. Therewith the influence of the frequency dependence of the anti-hermitian parts of the self-energy are incorporated into the finding of the positions of prominent spectral features. This is motivated by the fact that experiments are measuring spectral weight and not pole positions. Yet, from a conceptual point, we prefer the notion of one-particle poles, which, especially in the multi-orbital case, are better suited to resolve individual excitations.

³ In general, it should however not be expected to reproduce the photoemission spectrum since spectral weight transfers and lifetime effects are missing.

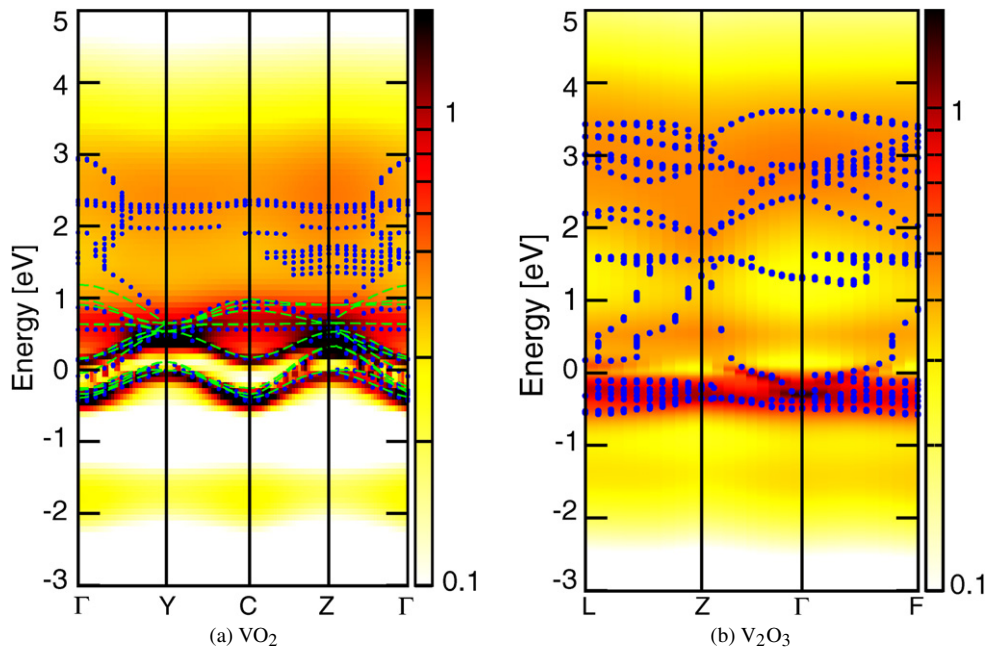


Fig. 1. Momentum-resolved spectra of (a) rutile VO_2 , (b) V_2O_3 . The (green) dotted lines in (a) show the renormalized band-structure according to Eq. (7). The (blue) dots in both figures indicate the solutions of the quasi-particle equation, Eq. (6). Both calculations use a low energy Hamiltonian for the t_{2g} orbitals of vanadium. The displayed energy window covers the entire range of the resulting t_{2g} many-body spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

bulk sensitivity to track in detail the dispersion of the low energy excitations. To the best of our knowledge, no further ARPES data on VO_2 are published at this stage. The momentum-resolved LDA + DMFT spectral function, shown along selected symmetry lines in Fig. 1(a) for the low energy t_{2g} subset of the vanadium 3d orbitals, is thus a theoretical prediction for future experiments. The current data is based on previous work [42,35], where the DMFT method was applied to the t_{2g} subset of the vanadium 3d orbitals, with a Hubbard–Hund type of interaction with $U = 4.0$ eV and $J = 0.68$ eV. The DMFT impurity problem was solved using a quantum Monte Carlo method at $T = 770$ K (see the original works [42,35] for further details). Of interest in the present context is the remark that the rutile phase of VO_2 is one of the few cases for which cluster DMFT calculations (using a dimer of vanadium atoms) have been performed in addition to single site calculations [42], with numerically identical results, thus giving additional confidence in the validity of the single site (i.e. momentum independent) DMFT approach in this case. As witnessed experimentally (in the momentum integrated spectra), the lower Hubbard band resides at about -1.75 eV, and our calculation suggests it to be almost dispersionless. Near the Fermi level, on the contrary, the quasi-particle derived excitations exhibit a notable dispersion. With respect to e.g. LDA band-structure calculations [37] the bandwidth in the many-body spectrum is considerably narrower. Yet, in the window of ± 0.5 eV, the LDA + DMFT self-energy is basically linear in energy, as well as almost orbital independent [35], with an average renormalization factor $Z \approx 0.6$. The spectral weight in this region is well described by a renormalized band-structure as provided by Eq. (7) and as indicated in Fig. 1(a). Consequently, in this region, also the solutions of the full quasi-particle equation, Eq. (6), follow the regions of high spectral intensity. However, according to the renormalization, the “band-like” features carry a weight less than one, with (around the Fermi level) $1 - Z$ being transferred to (Hubbard) satellite features. Besides this transfer, the life-time that is finite even on the Fermi surface (a non-vanishing imaginary part in the self-energy) causes the excitations in this area to visibly broaden.⁴

Beyond 0.5 eV, in the unoccupied spectrum, i.e. in the realm of *inverse* photoemission, coherence is quickly lost, and hence the pole structure can no longer be interpreted as representing the excitation spectrum. Clearly seen is

⁴ From optical experiments it was inferred that rutile VO_2 might be a “bad metal” in the sense that the Ioffe–Regel–Mott resistivity limit is surpassed [51].

moreover the discrepancy between the quasi-particle poles and the renormalized band-structure, which is a consequence of the non-linear frequency dependence of the electron self-energy above 0.5 eV [35]. Also, contrary to the lower Hubbard band, the upper Hubbard band, seen in the spectrum above 2 eV, is a solution to Eq. (6), i.e., in this case, dynamical correlations yield more “one-particle excitations” than the orbital dimension would allow in the band-picture.

In conclusion for the spectrum of rutile VO₂, two manifestations of correlation effects cause standard band-structure approaches to even qualitatively fail: The transfer of spectral weight to incoherent satellite features, and the finiteness of lifetimes of quasi-particle derived excitations.

4.2. V₂O₃

Vanadium sesquioxide (V₂O₃) has long been considered as the prototype of a Mott insulator [56]. Indeed, Cr-doped V₂O₃ undergoes under pressure – for temperatures above the antiferromagnetic ordering $T_N \sim 160$ K – a metal-insulator transition [57]. Probably this is also a reason why this compound has been studied extensively using different techniques, including photoemission and X-ray absorption spectroscopy [43,44,58–62].

While early theoretical work viewed this transition in complete analogy to the metal-insulator transition in the one-band Hubbard model (with which it indeed bears much resemblance, see e.g. the optical spectra in [63]), more recent calculations address the description of the transition within a first principles framework [64–70], stressing the importance of multi-orbital effects. The picture established in [69] views the transition as driven by a correlation-enhanced crystal field splitting. Unlike the traditional Mott transition in the one-band Hubbard model, in which quasi-particles are destroyed by a diverging effective mass [71], i.e. a vanishing lifetime, in V₂O₃, correlation effects disentangle overlapping bands to the extent to open a charge gap at the Fermi surface [69].

Besides the mechanism of the metal-insulator transition, already the metal phase is characterized by interesting multi-orbital correlation effects: The LDA + DMFT momentum-resolved spectrum of metallic V₂O₃ is displayed in Fig. 1(b). Also shown are the solutions of the quasi-particle Eq. (6). These results are based on a previous work [69], which used a downfolded vanadium t_{2g} setup, with a Hubbard–Hund interaction with $U = 4.2$ eV and $J = 0.7$ eV. The DMFT impurity problem was solved by a quantum Monte Carlo approach at a temperature $T \sim 390$ K.

The lower Hubbard band (better discernible in Fig. 5 of Ref. [69]) is independent of the momentum. The quasi-particle feature witnessed in angle integrated photoemission (see e.g. Ref. [58]) is resolved by the quasi-particle poles into several band-derived excitations. However, we note that the correlation induced lifetime effects broaden most of the occupied spectral weight to the extent that already at these low energies the notion of a band-structure becomes meaningless. Only around the Γ -point a well-defined structure crosses the Fermi level, accounting for the metallic character of the phase. Very recent ARPES experiments [62] confirm these findings.

In view of the limits of the band-picture, in this context, the effects of coherence are of particular interest. First, we note that owing to the octahedral oxygen coordination, the vanadium t_{2g} orbitals further split into e_g^π and a_{1g} components. The observation now is that when correlation effects are accounted for (here within DMFT), the broadening of excitations in the occupied spectrum is concentrated at around -0.5 eV, which corresponds to the e_g^π spectral weight, while the sharp feature that crosses the Fermi level is mainly of a_{1g} orbital character. This means that for the temperature $T \sim 390$ K of the calculation, the e_g^π electrons are out of their Fermi liquid regime (i.e. incoherent). The a_{1g} electrons, on the other hand, while also having a finite life-time at the Fermi level [69], they are still rather well defined (i.e. close to their coherence regime). In other words, the electronic coherence scale (the temperature limit T_{FL} of the Fermi liquid regime) is strongly orbital-dependent. We recall that any approach that assimilates the finite temperature electronic structure of a solid to a pure band structure tacitly assumes this coherence scale to be infinite by construction, irrespective of interactions and orbitals. While the existence of a Fermi liquid is limited to low energies ($\omega < \omega_{FL}$), it is also strictly defined only at $T = 0$. Yet, at reasonably low temperature, charge carriers still behave like quasi-particles, e.g. verifying Boltzmann’s transport theory and the Ioffe–Regel limit for resistivity. Beyond a temperature, T_{FL} , however, the quasi-particle picture is no longer applicable, and this is here the case for selected orbitals, namely the e_g^π ones, whereas the a_{1g} excitations are still close to their coherence regime.

This distinction of orbital coherence scales manifests itself also in other experimental observables, and the current scenario is indeed confirmed by optical measurements [72,73] in conjunction with an analysis of multi-orbital effects in the theoretical conductivity [70]: As a matter of fact, optical transitions that involve the a_{1g} orbitals will be subjected

to greater changes upon heating beyond 390 K (i.e. approaching T_{FL} of the a_{1g} electrons) than the e_g^π contribution which are already incoherent.

This adds a third limitation of standard band-structure approaches: The effect of the physical temperature upon the electronic properties of the system.⁵

5. Discussion and perspectives

The above examples have demonstrated the limits of the band picture for the electronic structure of correlated materials in view of ARPES experiments.

For Mott insulating compounds the deficiencies of effective one-particle theories are well established. We stress that while in the one-band Hubbard model the Mott transition is driven by a vanishing quasi-particle life-time (i.e. a diverging self-energy) the multi-orbital nature of solids provides us with a variety of possibilities: gap opening by band shifts encoded in the real part of the self-energy, vanishing life-times as in the (half-filled) Hubbard model, or combinations of both mechanisms in an orbital-selective manner. Except for the pure band-insulating case, all of these effects are beyond band theory.

As we have discussed above, it is, however, not only the Mott insulating phase that can challenge the one-particle picture. As shown for our example compounds, spectral weight transfers and associated coherence and temperature related phenomena can be prominent also in metallic phases.

Indeed, already the seemingly canonical Fermi liquid exhibits correlation induced bandwidth narrowing, a loss of coherence upon leaving the Fermi surface, and a temperature contribution to low-energy scattering, none of which is included in effective one-particle theories that work at $T = 0$.

To mend the first issue, a true many-body technique should be applied. In the realistic context, well established approaches are e.g. the GW approximation to Hedin's equations, which meets tremendous success in describing weakly to moderately correlated materials [20,21],⁶ or realistic extensions of DMFT. For the latter, we have shown two applications taken from recent work on vanadium oxides.

Secondly, in order to account for the physical temperatures at which photoemission experiments are carried out, also the theoretical method should work at finite temperatures. Indeed, in dynamical mean field calculations, temperature is an input, and e.g. effects of orbital-dependent coherence are naturally obtained from the spectral functions, and open to interpretation in terms of the electronic self-energy.⁷

Once these prerequisites are met, the principle endeavor should be to further increase the realism of ARPES calculations by including effects that were not touched upon in this review, in particular by accounting for transition matrix elements [1,2,33] of the electron ejection process.

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⁵ See, however, the finite temperature generalization of DFT by Mermin [74]. Yet, like to the ordinary DFT at $T = 0$, this is an effective one-particle theory for ground-state properties, implying that excitations and effects of coherence are not obtainable in this framework.

⁶ As to the GWA, we remark however that calculations of the true spectral function with its full k -dependence are a numerical challenge, so that a “quasi-particle density of states”, calculated from perturbatively shifting the Kohn–Sham eigenvalues by the real part of the GW self-energy, is often given instead. While providing important information on band shifts, this approach however neglects coherence and spectral weight issues. For spectral functions obtained from GW calculations using a localized basis set, see e.g. [23,25].

⁷ Also the GW approach is in principle capable of dealing with finite temperatures. Given its perturbative nature, the GWA is expected to well describe phases that are well within the Fermi liquid regime. However, besides some pioneering work (see e.g. [75,76]), standard implementations of the GWA usually rely on the zero temperature formalism, thus impeding a potential merit of the approach to unfold.

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