Materials design using correlated oxides: 
Optical properties of vanadium dioxide

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Abstract – Materials with strong electronic Coulomb interactions play an increasing role in modern materials applications. “Thermochromic” systems, that exhibit thermally induced changes in their optical response, provide a particularly interesting case. The optical switching associated with the metal-insulator transition of vanadium dioxide (VO\textsubscript{2}), for example, has been proposed for use in “intelligent” windows that selectively filter radiative heat in hot weather conditions. In this work, we develop the theoretical tools for describing such a behaviour. Using a novel scheme for the calculation of the optical conductivity of correlated materials, we obtain quantitative agreement with experiments for both phases of VO\textsubscript{2}. On the example of an optimized energy-saving window setup, we further demonstrate that theoretical materials design has now come into reach, even for the particularly challenging class of correlated electron systems.

The concerted behaviour of electrons in materials with strong electronic Coulomb interactions causes an extreme sensitivity to external stimuli such as temperature, pressure or external fields. Heating insulating SmNiO\textsubscript{3} beyond 400 K or applying a pressure of just a few kbar to the Mott insulator (V\textsubscript{1-x}Cr\textsubscript{x})\textsubscript{2}O\textsubscript{3} (x = 0.01), for example, makes the materials undergo transitions to metallic states [1]. This tuneability of fundamental properties is both a harbinger for diverse technological applications and a challenge for a theoretical description. Indeed, many materials used in modern applications fall in this class of strongly correlated materials where electron-electron interactions profoundly modify (if not invalidate) a pure band picture. State-of-the-art first principles methods, such as density functional theory, are then no longer sufficient to predict physical properties of these compounds.

An increasing role is nowadays played by artificial structures, ranging from spintronic multilayers [2,3] to functional surfaces, where appropriate coatings, for example, provide a self-cleaning mechanism [4]. However, the huge freedom in the design, which concerns not only the chemical composition, the doping and the growth conditions, but also the geometry of the setup (e.g., the layer thicknesses), makes the search for devices with specific electronic properties a tedious task. Ideally, the quest for promising materials and setups should therefore be seconded by theoretical predictions, in order to minimize expensive experimental surveys and prototyping. Yet, the abundance of fruitful experimental work on tailoring, for example, materials with specific optical absorption profiles is met with only scarce contributions from theoretical investigations [5].

Here, we demonstrate that even for the particularly challenging class of correlated materials a quantitative description, and thus predictions, are possible. We present a novel scheme for the calculation of optical properties, by introducing an accurate, yet handy way to compute transition matrix elements, which can in principle be employed in conjunction with any electronic structure technique that uses localized basis functions. It is thus especially useful for calculations for correlated materials, where Wannier-like basis sets provide a particularly suitable starting point. We demonstrate the power of the approach within the framework of the combined density functional dynamical mean-field method “LDA + DMFT” [6], on the example of the optical conductivity of vanadium dioxide, VO\textsubscript{2}. We further investigate VO\textsubscript{2}-based heterostructures to show that theoretical materials design of correlated material-derived devices is coming into reach.
Within dynamical mean-field theory, emphasis is commonly put on spectral properties, and the evaluation of observables other than spectral functions is a rather new advancement in the realistic context. Yet, as explained above, it is the response behaviour of correlated systems [7] that is promising for applications. In this vein, recent pioneering work [8–12] has successfully described qualitative features of the optical response of several correlated materials. The calculation of absolute values in theoretical response functions — a prerequisite for quantitative theoretical materials design — has, however, turned out to be a formidable challenge [10]. This is mainly due to the sensitivity of the obtained results on the accuracy of the transition matrix elements [13].

The optical properties of a solid are determined by its response to the external perturbation due to a light field. They thus involve electronic states, and transitions between them. If excitonic effects can be neglected, the knowledge of the one-particle spectra, as well as of the dipole matrix transition elements (Fermi velocities) that couple different states, is sufficient to assess the optical response. Indeed, in the framework of linear response theory, the optical conductivity can be expressed as (for reviews see [13,14])

$$\text{Re } \sigma^{\alpha\beta}(\omega) = \frac{2\pi e^2}{V} \sum_k \int \frac{d\omega'}{2\pi} \frac{f(\omega') - f(\omega' + \omega)}{\omega'} \times \text{tr} \left\{ A_k(\omega' + \omega) v_{k,\alpha} A_k(\omega') v_{k,\beta} \right\}.$$  (1)

Here, $\alpha$ and $\beta$ denote Cartesian coordinates, and $\text{Re } \sigma^{\alpha\beta}$ is the response in $\alpha$-direction for a light polarization along $\beta$. Correlation effects enter the calculation via the spectral functions $A_k(\omega)$, while the Fermi velocities $v_{k,\alpha} = \frac{1}{\hbar} \langle kL'|\mathcal{P}_\alpha|kL \rangle$, matrix elements of the momentum operator $\mathcal{P}$, are determined by the one-particle wave functions of the band-structure. Both, spectral functions and velocities are matrices in orbital space. If a localized basis set is used, these quantities are indexed by $L = (n,l,m,\gamma)$, with the usual quantum numbers $(n,l,m)$, while $\gamma$ denotes the atoms in the unit cell. $|kL \rangle$ corresponds to the Fourier transform of the Wannier function $\chi_{RL}(r)$ that is localized at atom $\gamma$ in the unit cell located at $R$, $f(\omega)$ is the fermionic occupation function, and $V$ is the unit-cell volume. Approaches such as LDA + DMFT [6] require the use of localized, Wannier-like, basis sets. This, however, renders the evaluation of the full transition matrix element $v_{k,\alpha}$ formidable.

To this end, we have generalized the Peierls formalism for lattice models [14] to the realistic case of multi-atomic unit cells [13]. In this framework, the Fermi velocities are approximated as

$$v_{k,\alpha}^{L,L'} = \frac{1}{\hbar} \left( \partial_{\rho_{k,\alpha}} H_{k}^{L,L'} - t (\rho_{k,\alpha}^L - \rho_{k,\alpha}^L) H_{k}^{L,L'} \right).$$

Here, $\rho_{k,\alpha}^L$ denotes the projection of the position of an atom within the unit cell onto the $\alpha$-direction. While the derivative term is the common Fermi velocity [14], the hitherto neglected term proportional to the Hamiltonian originates from the different phases that the coupling to the light field acquires for the individual atoms in a multi-atomic unit cell. The “generalized Peierls” velocity is a handy and versatile approximation, since no matrix elements (integrals involving the wave functions) other than the Hamiltonian need to be evaluated.

From the optical conductivity, other quantities become accessible, such as the specular reflectivity and transmittance, and, ultimately, also the seemingly most basic one of optical properties: the (specular) colour of the material [15].

Our focus material, VO$_2$, has attracted a lot of attention recently [13,16–20]. It is among those materials in which correlation effects play a decisive role, to the extent that standard band-structure approaches fail to capture even most basic experimental facts: In metallic VO$_2$, important incoherent spectral features (lower Hubbard band) witnessed by photoemission experiments are absent in band theory. At $T_c = 340$ K, VO$_2$ undergoes a metal-insulator transition. This property, which will be extensively made use of in the following, is also not reproducible by band theory. Hence, any description of the thermochromic properties of this material must foot on an electronic structure approach that goes beyond band-theory and masters the many-body effects at work. Indeed, LDA + DMFT results for the spectral properties of VO$_2$ agree well with experimental findings in both, the metallic [21–23] and the insulating phase [23]. They yield an ab initio confirmation of Goodenough’s picture [24] of the metal-insulator transition in VO$_2$: Vanadium atoms pair up in the monoclinic insulator to form tilted dimers along the $c$-axis, which causes the 3d orbitals that point along this axis (“$a_{1g}$” orbitals) to split into bonding and antibonding states. While within band-structure approaches this is not enough to open a gap, beyond mean-field correlations induce both, an increase in the splitting, and a further pushing up of the other low-lying 3d orbitals (“$e_g$” orbitals), thus completely filling the $a_{1g}$-bonding states and opening the gap [25,26].

Footling on the calculations of refs. [25,26] and an unfolding scheme [27] in order to include states down to $-8$ eV and up to $+6$ eV, we first employ our scheme to assess optical properties of bulk VO$_2$ both above and below its metal-insulator transition. Figure 1(a) shows our results for the optical conductivity of metallic VO$_2$ as a function of frequency and in comparison with experimental data [28–30], see also [17]). As can be expected from the rutile crystal structure, the optical response depends only weakly on the light polarization. The Drude-like metallic response is caused by transitions between narrow vanadium 3d excitations near the Fermi level, and thus affects only the low infrared regime — a crucial observation as seen in the following. The shoulder at 1.75 eV still stems from intra-vanadium 3d contributions, while transitions involving oxygen 2p orbitals set in at 2 eV, henceforth constituting the major spectral weight up to the highest
energies of the calculation. Also for insulating VO$_2$ (see fig. 1(b)) the results are in good agreement with experiments. This time, a slight polarization dependence is seen in both, experiment and theory, owing to the change in crystal symmetry, namely the aforementioned formation of $a_{1g}$ bonding-antibonding states in the insulator [24]. Optical transitions between these excitations result, in the corresponding energy range ($\omega = 1.5$–$2.5$ eV), in a higher amplitude of the conductivity for a light polarization parallel to the $c$-axis than for other directions [13].

Having established the theoretical optical response of VO$_2$ in the bulk, and thus verified that our scheme can quantitatively reproduce optical properties of correlated materials, we now investigate the possibilities of VO$_2$-based intelligent window coatings [31,32]. The effect to be exploited can already be seen in the above bulk responses: The conductivities of both phases (fig. 1(a) and (b)) exhibit a close similarity in the range of visible light ($\omega = 1.7$–$3.0$ eV), whereas in the infrared regime ($\omega < 1.7$ eV) a pronounced switching occurs across the transition. As a result, heat radiation can pass at low external temperatures, while its transmission is hindered above $T_c$. The insensitivity to temperature for visible light, in conjunction with the selectivity of the response to infrared illumination, is an essential feature of an intelligent window setup. Yet, for an applicable realization, other important requirements have to be met. First of all, the switching of the window has to occur at a relevant, that is ambient, temperature. Also, the total transmittance of VO$_2$ films in the visible range needs improvement [31], and the transmitted visible light should be uniform in order to provide a colourless vision. Experimentalists have addressed these issues and have proposed potential solutions [5]: Diverse dopings, $M_xV_{1-x}$O$_2$, were proved to influence $T_c$, with tungsten ($M = W$) being the most efficient: A doping of only 6% results in $T_c \approx 20^\circ$C [33]. However, this causes a deterioration of the infrared switching. Fluorine doping, on the other hand, improves on the switching properties, while also reducing $T_c$ [34,35]. An increase in the overall visible transmittance can also be achieved without modifying the intrinsic properties of the material itself, but by adding antireflection coatings, using, for example, TiO$_2$ [36].

Here, we address the optical properties of window coatings from the theoretical perspective. In doing so, we assume that the specular response of VO$_2$ layers is well described by the optical properties of the bulk, and we use geometrical optics to deduce the properties of layered structures. First, we consider the most simple of all setups, which consists of a single VO$_2$ layer (of thickness $d_{VO_2}$) on a glass substrate [37]. Such a window has been experimentally investigated by Tazawa et al. [38] and Jin et al. [36]. In fig. 2(a), we show their measured reflectivity data as a function of wavelength, in comparison with our theoretical results: At low temperatures (insulating VO$_2$), the calculated reflectivity is in quantitative agreement with the experimental data. In the visible range ($\lambda \approx 400$–$700$ nm), the reflectivity strongly depends on the wavelength. Therefore, the current window will filter certain wavelengths more than others, resulting in an illumination of a certain colour — an obvious drawback. Moreover, the reflectivity in this region is rather elevated, causing poor global transmission. In the infrared regime ($\lambda > 700$ nm) — and beyond — the reflectivity decreases, and radiation that causes greenhouse heating can pass the setup. At high temperatures, the infrared reflectivity switches to a rather elevated value, thus filtering heat radiation. The changes in the visible region are less pronounced, but still perceptible, and both, the degree of transparency and the colour change through the transition. The current setup is thus not yet suited for applications.

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Fig. 1: (Colour on-line) Optical conductivity of (a) metallic and (b) insulating VO$_2$ for polarizations $E$. Theory (red) ($[aab]=[0.85$ $0.85$ $0.53]$) and experimental data (i) single crystals [28] (green), (ii) thin film [29] (solid blue) and (iii) polycrystalline film [30] (dashed blue).
We therefore now investigate a more complicated setup: An additional (rutile) TiO$_2$ coating is added on top of the VO$_2$ layer, with the objective of serving as an antireflection filter [36]. With the thicknesses $d_{\text{VO}_2}$ and $d_{\text{TiO}_2}$, the geometry of the current setup has two parameters that can be used to optimize the desired optical properties. Since, however, each variation of them requires the production of a new individual sample under comparable deposition conditions, along with a careful structural characterization in order to guarantee that differences in the optical behaviour are genuine and not related to variations of the sample quality, the experimental expenditure is tremendous. This led Jin et al. [36] to first estimate a highly transmitting setup by using tabulated refractive indices and to produce and measure only one such sample. Here, we shall use our theoretical results on VO$_2$ to not only optimize the geometry ($d_{\text{TiO}_2}$, $d_{\text{VO}_2}$) with respect to the total visible transmittance, but to also investigate the transmission colour. Figure 2 displays the normalized visible specular transmittance$^2$ for the window in its high (b) and low (c) temperature state, as a function of both film thicknesses. On the same graph the resulting transmission colours are shown. The evolution of the light interferences in the layers causes pronounced changes in both, the overall transmittance and the colour. The coating of VO$_2$ globally degrades the transparency of the bare glass window. An increase of the TiO$_2$ coating, on the other hand, has the potential to improve the total transmittance. This can be understood from the mechanism of common quarter-wave filters. The wavelength dependence of the real part of the TiO$_2$ refractive index, $n_{\text{TiO}_2}(\lambda)$, results in an optimal quarter-wave thickness,

\[\delta_{\text{TiO}_2}(\lambda) = \lambda/(4n_{\text{TiO}_2}(\lambda)),\]

which varies from blue to red light only slightly from $\delta_{\text{TiO}_2}(\lambda) = 40$ to 60 nm. This and the fact that the imaginary part of the refractive index, $k_{\text{TiO}_2}(\lambda)$, is negligible for visible light explain why the colour does not change significantly with $d_{\text{TiO}_2}$. While, as for TiO$_2$, the variation of the real part of the VO$_2$ refractive index yields a rather uniform ideal thickness $d_{\text{VO}_2}(\lambda)$, its imaginary part changes significantly (by a factor of 4) within the range of visible light. As a consequence, the colour is very sensitive to VO$_2$ deposition. At higher thickness $d_{\text{VO}_2}$, however, this dependence becomes smaller and the colour lighter. Our theoretical transmittance profiles suggest relatively thick windows to yield good visual properties. Indeed, at low temperatures (fig. 2(c)) the local maximum that gives the thinnest window is located at $(d_{\text{TiO}_2}, d_{\text{VO}_2}) \approx (40, 85 \text{ nm})$ within our calculation. However, this setup is still in the regime of important oscillations. Given the uncertainties in industrial deposition techniques, it seems cumbersome to consistently stabilize colourless samples. From this point of view, a thicker VO$_2$ film would be desirable. Indeed, while almost preserving the overall transmittance, a colourless window at low temperatures is realized for $(d_{\text{TiO}_2}, d_{\text{VO}_2}) \approx (50, 220 \text{ nm})$, or for $(d_{\text{TiO}_2}, d_{\text{VO}_2}) = (\geq 100, 220 \text{ nm})$. In the high-temperature state (fig. 2(b)) the transmittance is globally lower than that at low temperatures. Moreover, only $d_{\text{TiO}_2}$, $d_{\text{VO}_2}$ = $(\geq 100, 220 \text{ nm})$ yields a simultaneously high transmittance in both states of the window.

In conclusion, we have presented a novel scheme for the calculation of optical properties of correlated materials, and applied it to vanadium dioxide, VO$_2$. We find the bulk optical conductivity of both phases in quantitative agreement with experiments, and further validate our approach by comparing the transmittance of a VO$_2$ layer on SiO$_2$ to experimental data. Finally, we optimize the geometry of a multilayer setup of an intelligent window, which uses the metal-insulator transition of VO$_2$ to reduce the effect of greenhouse heating. This work can

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$^2$Given by $\int_{400 \text{ nm}}^{700 \text{ nm}} d\lambda S(\lambda) T(\lambda)/\int_{400 \text{ nm}}^{700 \text{ nm}} d\lambda S(\lambda)$, with the spectrum $S(\lambda)$ of the light source, and the transmittance $T = 1 - R$, $R$ being the specular reflection of Fresnel’s formulae. This neglects absorption by inhomogeneities that lead to diffuse reflection, as justified by our application to windows. Also, VO$_2$ looks glossy, and thus has a largely specular response.
be considered as a proof of principle of the feasibility of theoretical materials design, since our techniques can be applied to the general class of correlated materials.

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REFERENCES

[1] IMADA M., FUJIMORI A. and TOKURA Y., Rev. Mod. Phys., 70 (1998) 1039.
[2] BAIHICH N. M., BROTO J. M., FERT A., VAN DAU F. N., PETROFF F., ITTENNE P., CREUZET G., FRIEDRICH A. and CHAZELAS J., Phys. Rev. Lett., 61 (1988) 2472.
[3] BINASCH G., GRÖNBERG P., SAURENBACK F. and ZINN W., Phys. Rev. B, 39 (1989) 4828.
[4] PAX Y., LUO Z., RABENBERG L. and HELLER A., J. Mater. Res., 10 (1995) 2842.
[5] GRANQVIST C. G., Sol. Energy Mater. Sol. Cells, 91 (2007) 1529.
[6] KOTLIAR G. and VOLLHARDT D., Phys. Today, 57, issue no. 3 (2004) 53.
[7] PERLOV A., CHADOV S. and EBERT H., Phys. Rev. B, 68 (2003) 245112.
[8] BLÜMER N., Mott-Hubbard Metal-Insulator Transition and Optical Conductivity in High Dimensions, PhD Thesis, Universität Augsburg, Germany (2002).
[9] OUDOVENKO V. S., PALSSON G., SAVRASOV S. Y., HAULE K. and KOTLIAR G., Phys. Rev. B, 70 (2004) 125112.
[10] HAULE K., OUDOVENKO V., SAVRASOV S. Y. and KOTLIAR G., Phys. Rev. Lett., 94 (2005) 036401.
[11] PAVARINI E., YAMASAKI A., NUSJ J. and ANDERSEN O. K., New J. Phys., 7 (2005) 188.
[12] BALDASSARRE L., PERUCCHI A., NICOLETTI D., TOSCHI A., SANGIOVANNI G., HELD K., CAPONE M., ORTOLANI M., MALAVASI L., MARSIL M., METCALF P., POSTORINO P. and LUPI S., Phys. Rev. B, 77 (2008) 113107.
[13] TOMCZAK J. M., Spectral and Optical Properties of Correlated Materials, PhD Thesis, Ecole Polytechnique, France (2007).
[14] MILLIS A. J., Optical conductivity and correlated electron physics, in Proceedings of Strong Interactions in Low Dimensions, edited by D. BAERISWYL L. D. and DEGIORGI L., Phys. Chem. Mater. Low-Dimens. Struct. Ser., Vol. 25 (Springer) 2004, pp. 195ff.
[15] For this we will later employ the CIE 1964 conventions, along with the daylight illuminant D65, see, e.g., NASSAU K., The Physics and Chemistry of Color: The Fifteen Causes of Color, Pure Appl. Opt. Ser. (Wiley) 2001.
[16] BAUM P., YANG D.-S. and ZEWAIL A. H., Science, 318 (2007) 788.
[17] QAZILBASH M. M., BREHM M., CHAE B.-G., HO P.-C., ANDREEV G. O., KIM B.-J., YUN S. J., BALATSKY A. V., MAPLE M. B., KELLMANN F., KIM H.-T. and BASOV D. N., Science, 318 (2007) 1750.
[18] EYERT V., Ann. Phys. (Leipzig), 11 (2002) 650.
[19] MOSSANEK R. J. O. and ABBATE M., Phys. Rev. B, 74 (2006) 125112.
[20] MOSSANEK R. J. O. and ABBATE M., J. Phys.: Condens. Matter, 19 (2007) 346225.
[21] LAAD M. S., CRACO L. and MÜLLER-HARTMANN E., Europhys. Lett., 69 (2005) 984.
[22] LIEBSCH A., ISHIDA H. and BILHMAYER G., Phys. Rev. B, 71 (2005) 085109.
[23] BIERMANN S., POTERYAEV A., LICHTENSTEIN A. I. and GEORGES A., Phys. Rev. Lett., 94 (2005) 026404.
[24] GOODENOUGH J. B., J. Solid State Chem., 3 (1971) 490.
[25] TOMCZAK J. M. and BIERMANN S., J. Phys.: Condens. Matter, 19 (2007) 365206.
[26] TOMCZAK J. M., ARYASETTAWAN F. and BIERMANN S., Phys. Rev. B, 78 (2008) 115103.
[27] TOMCZAK J. M. and BIERMANN S., J. Phys.: Condens. Matter, 21 (2009).
[28] VERLEUR H. W., BARKER A. S. and BERGLUND C. N., Phys. Rev., 172 (1968) 788.
[29] OKAZAKI K., SUGAI S., MURAOKA Y. and HIROI Z., Phys. Rev. B, 73 (2006) 165116.
[30] QAZILBASH M. M., BURCH K. S., WHISLER D., BURKHARDT W., CHRISTMANN T., FRANKE S., KRIEGSEIS D., SHIRENHAMER D., CHAE B. G., KIM H. T. and BASOV D. N., Phys. Rev. B, 74 (2006) 205118.
[31] BABULANAM S. M., ERIKSSON T. S., NIKLAsson G. A. and GRANQVIST C. G., Sol. Energy Mater., 5 (1987) 347.
[32] GRANQVIST C. G., Thin Solid Films, 193–194 (1990) 730.
[33] SOBHA N A., KIVASI R. T., STJERNA B. and GRANQVIST C. G., Sol. Energy Mater. Sol. Cells, 44 (1996) 451.
[34] BURKHARDT W., CHRISTMAN T., FRANE S., KRIEGSEIS W., MEISTER D., MEYER B. K., NISSLER W., SCHALD D. and SCHARMANN A., Thin Solid Films, 402 (2002) 226.
[35] BURKHARDT W., CHRISTMAN T., MEYER B. K., NISSLER W., SCHALD D. and SCHARMANN A., Thin Solid Films, 345 (1999) 229.
[36] JIN P., XU G., TAZAWA M. and YOSHIMURA K., Appl. Phys. A, 77 (2003) 455.
[37] We suppose quartz glass, SiO2. All auxiliary refractive indices are taken from PALIK EDWARD K., Handbook of Optical Constants of Solids (Academic Press) 1985.
[38] TAZAWA M., JIN P. and TANEMURA S., Appl. Opt., 37 (1998) 1858.