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Quasiparticle band structure of vanadium dioxide

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Abstract

Vanadium dioxide is insulating below 340 K in experiments, whereas the band structure calculated in the local density approximation (LDA) is gapless. We study the self-energy effects using the *ab initio* *GW* method. We found that the self-energy depends strongly on the energy, and proper treatment of the dynamical effect is essential for getting precise quasiparticle energies. Off-diagonal matrix elements in the Kohn–Sham basis are also important for disentangling bands. Inclusion of the two effects opens up a direct gap. Our results also suggest that one-shot *GW* on top of LDA is not enough, and the impact of self-consistency is significant.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Vanadium dioxide is a material that has been under debate over years. It exhibits a metal–insulator transition at 340 K [1]. The high temperature phase is metallic with rutile structure, while it transforms to the monoclinic (M1) structure and becomes insulating below the transition temperature. There has long been discussion about the transition, with particular interest in the role of electron correlations in forming a charge gap.

From the band picture viewpoint, the electronic states are understood as follows (figure 1) [2]. The low energy states near the Fermi level are of strong vanadium 3d character. Each vanadium atom is surrounded by an oxygen octahedron, and the crystal field makes the d states split into t_{2g} and e_g . Since the structure is not cubic, the t_{2g} states are lifted further into e_g^π and a_{1g} states. The atomic number of vanadium is 23. There are three 3d and two 4s valence electrons. Four of them transfer to oxygen 2p orbitals in VO_2 ; thereby VO_2 is a d^1 system. The remaining d electron partially occupies the a_{1g} band and the system is metallic in the rutile phase. In the M1 phase, two vanadium atoms form a dimer. This Peierls distortion causes strong hybridization between the a_{1g} orbitals of the two vanadium atoms. Then the bonding state is fully filled, which opens a gap between the bonding a_{1g} and the unoccupied e_g^π band.

The overall feature above was confirmed by first-principles calculations [5, 6] in the local density approximation

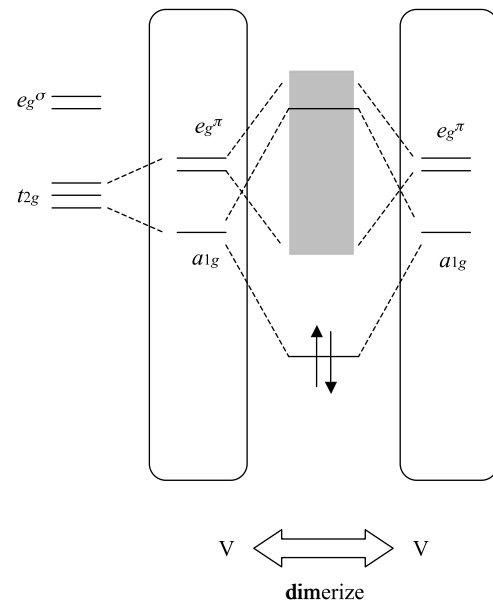


Figure 1. Schematic picture of the energy levels. The a_{1g} level is half-filled in the rutile phase. In the monoclinic phase, two vanadium atoms form a dimer and the a_{1g} orbital splits into bonding a_{1g} and anti-bonding a_{1g} . The former is fully occupied and a gap is formed.

(LDA) [3] of density functional theory [4]. However, it was also found that the bonding a_{1g} band overlapped with the e_g^π band, yielding metallic behavior, in contrast with the

experimental finding. This may be ascribed to the band gap problem that the gap of semiconductors and insulators is significantly underestimated in the LDA. If we include many-body effects, the e_g^π may shift up and then a gap would open. This is one interpretation of the insulating state.

On the other hand, some authors claimed that electron correlations play a major role [7, 8]. In fact, another monoclinic phase (M2) is observed under chromium doping [9, 10]. Half of the vanadium atoms are not dimerized in this structure, so the Peierls picture alone cannot provide an explanation of the insulating behavior.

In this work, we present a band structure of the M1 structure. We include the self-energy correction in the GW approximation [11, 12] and study the many-body effects beyond LDA. Such a calculation was done before in a model treatment [13]. Very recently, a first-principles GW calculation has also been carried out [14]. These works reported a gapful state for the M1 structure in agreement with measurements. Here, we perform another GW calculation. In our calculation, the dynamical effect of the self-energy is fully taken into account. We find that the self-energy is highly energy dependent and it is essential to take into account nonlinearity of the self-energy.

2. Method

The calculations start with the LDA using the full-potential LMTO method [15]. The Kohn–Sham wavefunctions $\{\psi_{\mathbf{k}n}\}$ and eigenvalues $\{\epsilon_{\mathbf{k}n}\}$ obtained are used to construct the one-particle Green’s function, from which polarization, screened interaction, and the self-energy are computed. The plasmon-pole approximation [16] for the dielectric function is not adopted in our calculation and full frequency dependence is taken into account. More technical details are found elsewhere [17, 18].

In the present work, we use a few techniques to go beyond the conventional GW scheme [19]. One is the use of the nonlinear dynamical effect of the self-energy. The GW quasiparticle energies $E_{\mathbf{k}n}$ are obtained from

$$E_{\mathbf{k}n} = \epsilon_{\mathbf{k}n} + \langle \psi_{\mathbf{k}n} | \Sigma(E_{\mathbf{k}n}) - v_{xc} | \psi_{\mathbf{k}n} \rangle, \quad (1)$$

where Σ is the self-energy in the GW approximation and v_{xc} is the LDA exchange–correlation potential. In weakly or moderately correlated semiconductors, $\Sigma_{\mathbf{k}n}(\omega) \equiv \langle \psi_{\mathbf{k}n} | \Sigma(\omega) | \psi_{\mathbf{k}n} \rangle$ is a smooth function of ω and it is a good approximation to expand the self-energy as

$$\Sigma_{\mathbf{k}n}(E_{\mathbf{k}n}) \simeq \Sigma_{\mathbf{k}n}(\epsilon_{\mathbf{k}n}) + C_{\mathbf{k}n}(E_{\mathbf{k}n} - \epsilon_{\mathbf{k}n}), \quad (2)$$

However, the validity of the linearization scheme is doubtful when electron correlation becomes strong. Hence we compute $\Sigma(\omega)$ for many frequency points and find the quasiparticle energy by solving the following equation:

$$\langle \psi_{\mathbf{k}n} | \omega - \epsilon_{\mathbf{k}n} - (\Sigma(\omega) - v_{xc}) | \psi_{\mathbf{k}n} \rangle = 0. \quad (3)$$

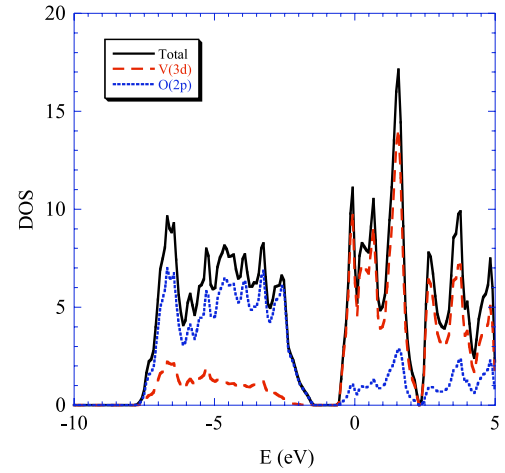


Figure 2. Density of states (DOS) of VO₂ (M1) obtained by LDA. The total DOS is shown by the solid line. The dashed line and dotted line are projected DOS of V 3d and O 2p contributions, respectively. Energy is measured from the Fermi level.

Another important technique is the use of the off-diagonal elements of the self-energy. The Kohn–Sham solution in the LDA is sometimes qualitatively wrong. In such cases, the self-energy correction changes the character of the wavefunctions; consequently the quasiparticle wavefunctions are very different from the LDA Kohn–Sham ones. This effect can be included by using the off-diagonal elements (in the Kohn–Sham basis) and solving equation (3) in matrix form.

The calculations are done for VO₂ in the M1 phase. The unit cell contains four formula units (12 atoms). Experimental lattice parameters are used [20, 21]. Vanadium 3s and 3p orbitals are treated as valence electrons and 302 unoccupied bands are included. Integration over the Brillouin zone is replaced by $4 \times 4 \times 4$ k point sampling.

3. Results and discussion

Figure 2 show the density of states (DOS) in the LDA. The peak between -8 and -1 eV is mainly of oxygen 2p character hybridized with vanadium 3d orbitals. Above that is dominated by vanadium 3d, with a little weight of oxygen 2p. There is a sharp peak just below the Fermi level. The peak comes from two bands shown by the solid line in figure 3. They are the bonding a_{1g} orbitals of vanadium 3d. Since four vanadium atoms are contained in the unit cell, there are four 3d electrons. Therefore, the two a_{1g} bands are almost fully occupied. However, they overlap with the e_g^π band that is located just above the a_{1g} . As a result, there is a small hole (electron) pocket in a_{1g} (e_g^π) band, and the system becomes metallic in the LDA.

Now we add the self-energy correction to the LDA Kohn–Sham energies. Figure 4 shows the self-energy as a function of energy for selected states at the Γ point. The self-energy does not decrease monotonically, but has dips and peaks. This behavior is quite different from that of weakly correlated semiconductors, such as silicon. The peculiar energy dependence makes the linearization approximation

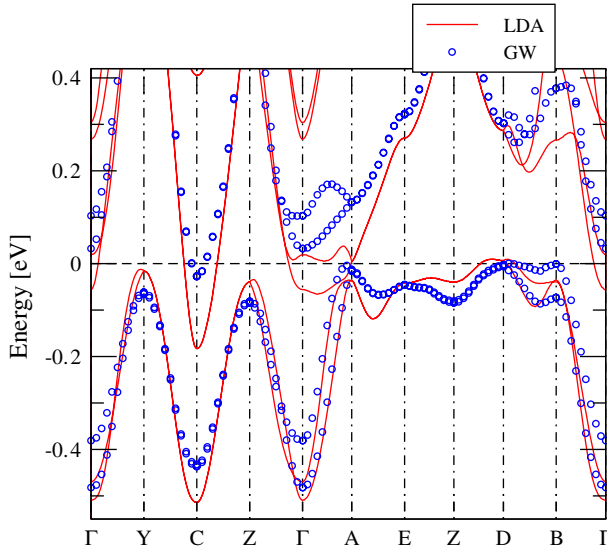


Figure 3. Quasiparticle band structure of vanadium dioxide in the monoclinic phase. The solid line is the LDA result and open circles are from the *GW* calculation.

break down. In fact, if we compute the quasiparticle band from the linearization scheme, the a_{1g} band gets too narrow. Another consequence of strong energy dependence is that equation (3) has multiple solutions in some cases, as can be seen in figure 4(c). Also the nonlinearity yields satellite structure in the one-electron spectral function.

The quasiparticle band structure is plotted in figure 3 (circles). We can see that band overlap between the a_{1g} and e_g^π is removed by the self-energy correction. It should be noted that the Kohn–Sham wavefunctions have too much hybridization between a_{1g} and e_g^π near the A point; therefore off-diagonal elements are essential to disentangle the bands. The quasiparticle a_{1g} band is now isolated and a direct gap opens.

However, the fundamental gap is almost zero and it is hard to tell whether the system is metallic or insulating. In any case, the value is much smaller than the experimental gap of 0.6 eV [22]. This implies that the one-shot scheme, which is used in almost all *ab initio GW* calculations, is not enough and self-consistency has a big impact. The starting Kohn–Sham solution is metallic in the present case. Thus, the screening effect is overestimated and so the self-energy correction may be underestimated. If we perform the *GW* calculation starting with a gapful state, the self-energy correction is larger and the quasiparticle gap will increase. Actually our preliminary calculation using a simplified self-consistent scheme suggests that the value of the gap increases significantly on updating initial wavefunctions and eigenvalues [19].

4. Concluding remarks

We have shown that the dynamical effect and off-diagonal matrix elements of the self-energy are important in VO_2 . Inclusion of the two effects opens up a direct gap. However, the value of the fundamental gap is too small. The

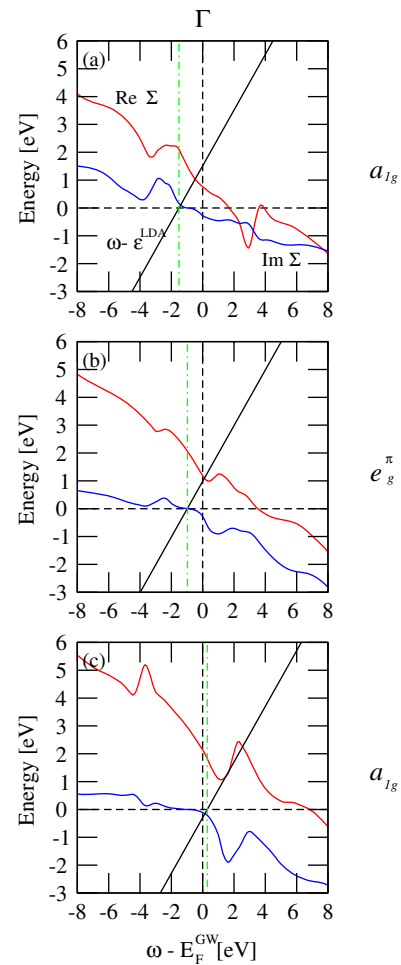


Figure 4. Self-energy in the Kohn–Sham basis as a function of energy. The vertical dash-dotted line indicates the Kohn–Sham eigenvalue ϵ_{kn} . The straight line with positive slope is $y = \omega - \epsilon_{kn}$. The point of intersection between this line and the real part of the self-energy gives the quasiparticle energy. Energy is measured from the *GW* Fermi level.

result suggests that self-consistent calculation is needed for getting accurate values of the band gap. This is a future problem. Another interesting problem is comparison with other many-body approaches. Recently, several authors reported calculations based on dynamical mean field theory combined with LDA [23–26]. These methods capture short range correlation more accurately than the *GW* approximation. On the other hand, long range screening effects and multi-band effects are lacking. Also, the Hubbard U parameter is not obtained from first principles. Comparison of these results with the *GW* result may be fruitful for a deeper understanding.

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