A DFT+DMFT calculation for $SrVO_3$

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In this report, we will study the electron properties of $SrVO_3$ by using DFT+DMFT algorithm. Firstly we use LDA method to sketch the rough band structure and then carry on the DFT+DMFT method. From the calculation, it can be seen that correlation between electrons plays an important role in system like $SrVO_3$ and DFT+DMFT is a suitable numerical method for this transition metal oxide composition.

I. BASIC THEORY OF DFT+DMFT

Dynamical mean-field theory (DMFT) was first introduced by Antoine Georges and Gabriel Kotliar[2]. In order to simplify the Hubbard model, they considered each site in the lattice was coupled with a reservoir which represented rest of the crystal and electron on the single site could create or annihlate by coupling with the reservoir. With energy of single atom, the Hamiltonian can be written as

$$\begin{aligned} H_{AIM} = H_{atom} + \sum_{\nu,\sigma} \epsilon_{v}^{bath} n_{\nu,\sigma}^{bath} \\ + \sum_{\nu,\sigma} (V_\nu c_{0,\sigma}^{\dagger} a_{\nu,\sigma}^{bath} + h.c) \end{aligned} \tag{1}$$

which is called the Anderson impurity model. Here, H_{atom} includes all the single site interaction and ϵ_{ν}^{bath} represents the energy level of bath electrons. These two terms can be regarded as the non-interaction energy while the last term describes the dynamics of coupling effect. V_ν is the coupling strength of bath electron and atom on site electron, $c_{0,\sigma}^{\dagger}$ is the creation operator of atom electron and $a_{\nu,\sigma}^{bath}$ is the annihlation operator of bath electron. Treating the hopping term with second-order perturbation, we can have an energy shift of

$$\Delta(\omega) = \sum_{\nu} \frac{|V_\nu|^2}{\omega - \epsilon_{\nu}^{bath}} \tag{2}$$

And the Green's function of $\Delta(\omega)$ can be written as

$$G[\Delta(\omega)] = \sum_{k} \{\omega - \Sigma[\Delta(\omega)] - t_k\}^{-1} \tag{3}$$

Here, t_k is the Fourier transform of the hopping strength t_{ij} in lattice. With the discussion above, we can write the functional of charge density and Green's function as

$$\begin{aligned} \Gamma[\rho(\boldsymbol{r}), G] = T[\rho(\boldsymbol{r}), G] + \int V(\boldsymbol{r})\rho(\boldsymbol{r}) d^3\boldsymbol{r} \\ + \frac{1}{2} \int \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r'})}{|\boldsymbol{r} - \boldsymbol{r'}|} d^3\boldsymbol{r} d^3\boldsymbol{r'} + E_{xc}[\rho(\boldsymbol{r}), G] \end{aligned} \tag{4}$$

which is similar with DFT functional except that the $T[\rho, G]$ contains the local Green's function and $E_{xc}[\rho(\boldsymbol{r}), G]$ can be calculated with an explicit approximation.

In real practice, we first use DFT to diagnolize the Kohn-Sham Hamiltonian and obtain the Kohn-Sham(KS) wave functions. Based on those KS wave functions, we calculate the local Green's function and bath Green's function. In order to study the coupling term in Anderson impurity model, we use Quantum Monte Carlo method(QMC) to solve the self-energy. Since the bath also changes while self-energy changes, a self-consistent calculation is needed. Within several loops, a self-energy solution can be obtained. Meanwhile, electron density is also modified by the new self-energy. To achieve full consistency, Kohn-Sham Hamiltonian should be updated which is called the outer loop. Using the method mentioned above, we can practically complete the DMFT calculation.

II. NUMERICAL CALCULATION OF SRVO$_3$

In this part, we first use the LDA method to calculate the band structure of $SrVO_3$. The fat band of V with $l = 2$ is shown in FIG.1 and fant band of O with $l = 1$ is shown in FIG.2. We can see that bands 21 to 25 are mainly d orbitals from vanadium while 12 to 20 bands are from oxygen p orbital. Meanwhile, an obvious hybridization of d orbitals and p orbitals is near the Fermi surface, which are bands 21-23. According to the structure of $SrVO_3$, the vanadium atom is in the center of an octahedron of oxygen atoms and classical crystal field theory tells us that this perovskite structure will split d orbitals into three t_{2g} orbitals and two e_g orbitals. Thus the single unpaired electron occupies t_{2g} orbitals and the Wannier function need to be established on these t_{2g} like bands.

Once the Wannier function is obtained, we use DFT+DMFT to study the electron structure of $SrVO_3$. Since we choose Wannier function to be build on the 21-23 bands, we define parameters $dmftbandi = 21$ and $dmftbandf = 23$. To simplify the calculation, we restrict electron interaction on t_{2g} orbitals, so we set $lpawu = 2$ and $dmft\_t2g = 1$. In addition, density-density continuous time quantum monte carlo(CTQMC) is used to solve the self-energy with parameter $dmft\_solv = 5$.

In the output file, we can see that occupation on three

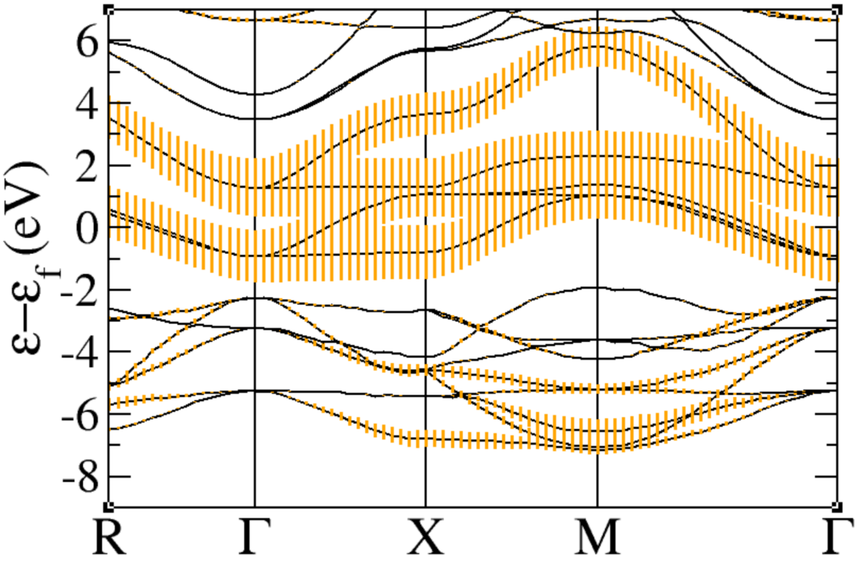

FIG. 1. Fat band of vanadium

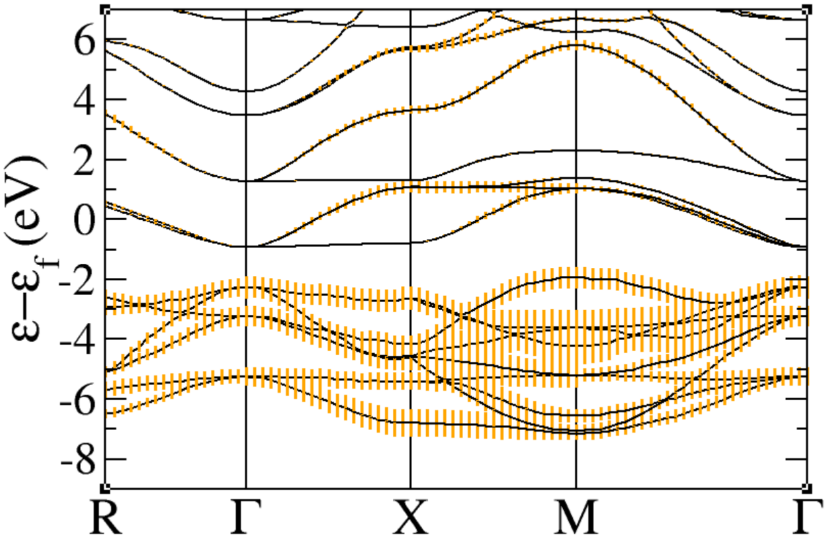

FIG. 2. Fat band of oxygen

t_{2g} orbitals are symmetric, which means that this three orbitals are degenerate. The occupation is 0.11142 and normalization of this orbital basis is 0.65790. We notice that the norm is smaller than one. Several reasons contribute to this issue. First, we only consider three Kohn-Sham wave functions which is not the real case in which infinite bands should be included. Moreover, atom orbitals are truncated at the PAW radius during the projection process. Thus according to tutorial file, the upper limit of norm is 0.86852 rather than 1.

Then, we compare the occupation number above with Green's function calculation obtained by LDA method which turns out that the occupation is 0.11143 with relative error 10^{-5}. If the orthonormal Wannier functions are used, the occupation increases to 0.16937. After the DMFT loop, the polarization spin component occupation is 0.16843 and the whole occupation is 1.01058 which is close to unit.

Next, we focus on the local Green's function of $SrVO_3$. The relation between local Green's function and inverse temperature $\beta = \frac{1}{k_B T}$ is shown in FIG.3. From the calculated data, we conclude that the six t_{2g} orbitals for spin up and spin down electrons are degenerate and as temperature decreases, local Green's function increases.

Using imaginary time Green's function, we can calculate spectral function in real frequency. Here we use the Maximum Entropy Method[**?**]. The result is shown in FIG.4 and it is obvious that there exist two peaks in the

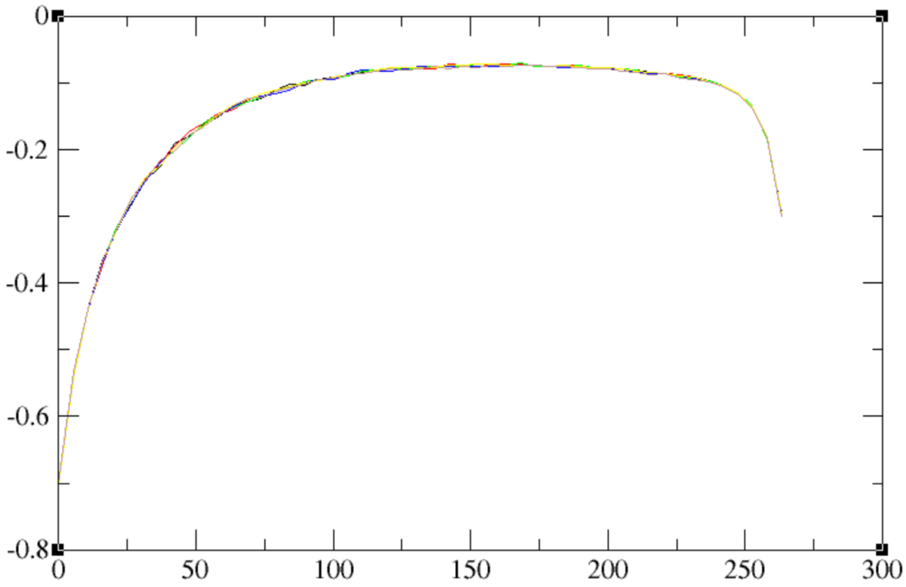

FIG. 3. Local Green's function versus imaginary time $\beta = \frac{1}{k_B T}$

spectral function and density of state near Fermi surface is finite which means $SrVO_3$ is under a metal insulator transition(MIT). In this calculation, parameter *tsmear* is chosen to be 1200K which is an order lower than Fermi temperature. Moreover, if we include t_{2g} like orbitals and p orbitals of oxygen, we can have sharper peaks in spectral function(FIG.5) and the second peak is higher than the prebious one. Thus we can conclude that insulator phase of $SrVO_3$ is not conventional Mott insulator but charge transfer Mott insulator.

III. DISCUSSION AND CONCLUSION

In this report, we first obtained Kohn-Sham wave functions by using LDA method. Based on this wave functions, we project orthonormal Wannier function onto three t_{2g} orbitals and conduct the DMFT calculation. During the process, we get occupation matrix, local Green's function of imaginary time($\beta = \frac{1}{k_B T}$) and spectral of real frequency. From those data, we conclude that $SrVO_3$ is under a metal insulator transition and the insulator phase is charge transfer Mott insulator under 1200K. Compared to common Mott insulator, p orbitals of oxygen reside in the neighbourhood of d orbitals of vanadium thus Fermi surface of this system crosses a hybridization of d and p orbitals. If we compare the numerical result with experimental phase diagram of perovskite metal-insulator obtained by Imada, Fujimori and Tokura[1], we will find that DFT+DMFT is a reliable method for correlated electron system.

However, there exist some issues to be improve. Such as the choice of orthonormal Wannier functions which influences the result of calcultaion dramatically. The trade-off of more bands with higher precision and reasonable calculation resource consuming is still a challenge. Further, DMFT uses the mean field method to approximate the coupling between each site and bath along with the interaction between bath electrons. If the coupling strength becomes larger and interaction between bath electrons is no longer negligible, we need to reconsider the feasibility of DMFT.

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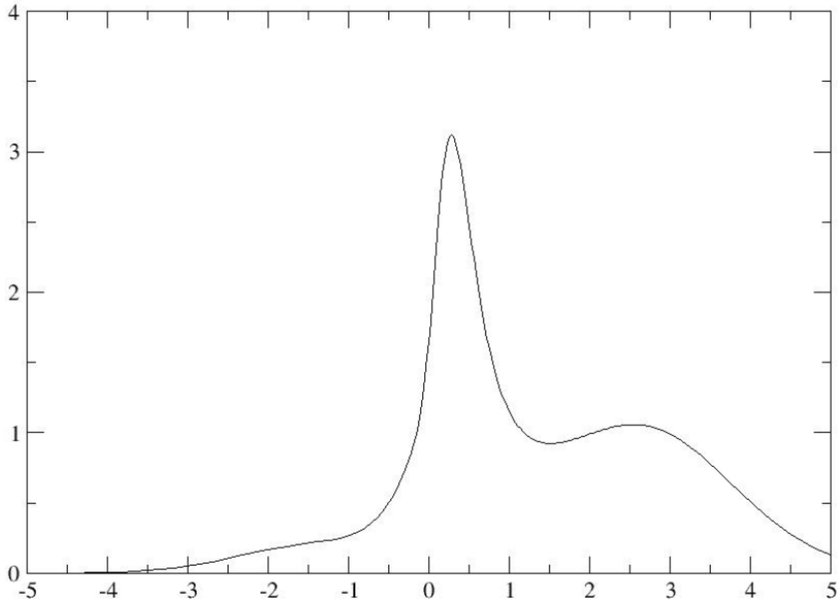

FIG. 4. Spectral with t_{2g} bands

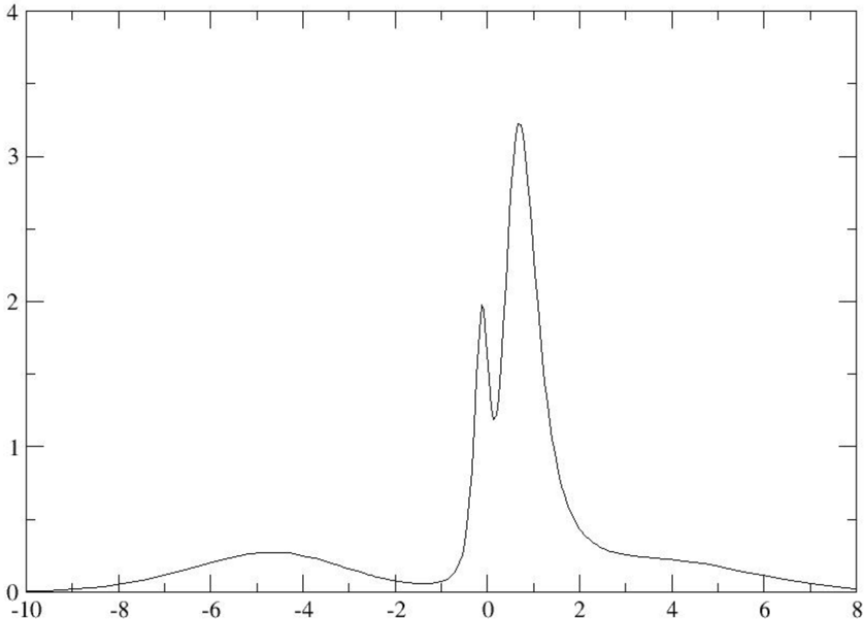

FIG. 5. Spectral with t_{2g} and p bands

ory. *Physics today*, 57(3):53–60, 2004.