Full Orbital Scheme for Computation of Properties of Materials with Strongly Correlated Electrons[1]

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Abstract—We propose a method in which the Wannier functions (WFs) are calculated explicitly and the *ab initio* full-orbital Hamiltonian is projected onto the WF subspace defined for the partially filled bands of interest. The (Wannier-basis) Hamiltonian calculated in this way together with the Coulomb-interaction term between Wannier orbitals could be used as *ab initio* setup of the correlation problem which can then be solved within the Dynamical Mean-Field Theory (DMFT) in the framework of the LDA (Local Density Approximation) + DMFT computational scheme. The DMFT results can be used for the calculation of the full-orbital interacting Green's function. This Green's function contains spectral, magnetic and electronic properties of the system. Results obtained with this method for $SrVO_3$ are reported and compared with new bulk-sensitive photoemission spectra.

1. INTRODUCTION

Let us consider the general case of the electronic-structure problem. For the LDA Hamiltonian, we have a Hilbert space of eigenfunctions (Bloch states $|\psi_{ik}\rangle$) with the basis $|\varphi_\mu\rangle$ defined by some particular methods (e.g., LMTO, LAPW, etc.). In this basis the Hamiltonian operator is defined as

$$\hat{H} = \sum_{\mu v} |\varphi_\mu\rangle H_{\mu v} \langle \varphi_v| \qquad (1)$$

(hereinafter, greek indices are used for full-orbital matrices).

If we consider a certain subset of the Hamiltonian eigenfunctions, e.g., Bloch states of partially filled bands $|\psi_{nk}\rangle$, we can define a corresponding subspace in the total Hilbert space. Although the Hamiltonian matrix is diagonal in the basis of Bloch states, a basis that has the form of site-centered atomic orbitals is physically more attractive. Such is a set of Wannier functions (WFs) $|W_n^T\rangle$ [1] defined as the Fourier transform of a certain linear combination of Bloch functions from this subspace (see Eq. (5) below). The Hamiltonian operator $\hat{H}^{WF}$ defined in this basis is

$$\hat{H}^{WF} = \sum_{nn'T} |W_n^0\rangle H_{nn'}(T) \langle W_{n'}^T| . \qquad (2)$$

Practically, this means that the correlation problem is solved with a noninteracting few-orbital Hamiltonian $\hat{H}^{WF}$ (2) instead of the full Hilbert-space Hamiltonian $\hat{H}$ (1). The interaction term of the model Hamiltonian can be determined with constrained LDA calculations for the specific WF basis set [2].

Projecting the full-orbital Hilbert-space Hamiltonian $\hat{H}$ (1) on the subspace of partially filled bands gives us a few-orbital Hamiltonian $\hat{H}^{WF}$ (2) and, so, significantly decreases the complexity of the correlation problem allowing for its practical solution. However, in this way one loses information about the states corresponding to the bands that lie below and above the chosen ones. It would be also useful to be able to calculate the interacting Green's function in the full-orbital Hilbert space.

This problem can be solved in the following way. The effect of the Coulomb interaction on the system is usually expressed in the form of the local self-energy operator $\hat{\Sigma}(\varepsilon)$

$$\hat{\Sigma}(\varepsilon) = \sum_{nn'} |W_n\rangle \Sigma_{nn'}(\varepsilon) \langle W_{n'}| . \qquad (3)$$

It is possible to convert this local operator back to the full Hilbert-space basis

$$\hat{\Sigma}(\varepsilon) = \sum_{\mu v} |\varphi_\mu\rangle \Sigma_{\mu v}(\varepsilon) \langle \varphi_v| \qquad (4)$$

(for example, LMTO) and to calculate the full-orbital interacting Green's function with it.

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2. METHOD

In this work, we define a set of trial orbitals $|\varphi_n\rangle$ and choose Bloch bands which will be used in the projection procedure for the construction of WFs. The latter can be defined either by the band numbers from N_1 to N_2 or by the energy interval (E_1, E_2).

Nonorthogonal WFs in reciprocal space $|\tilde{W}_{n\mathbf{k}}\rangle$ are defined as the projection of the set of site-centered atomic-like trial orbitals $|\varphi_n\rangle$ on the subspace defined by the Bloch functions $|\psi_{i\mathbf{k}}\rangle$ from the chosen bands (the bands are defined by either their numbers from N_1 to N_2 or by the energy interval (E_1, E_2) [2]

$$|\tilde{W}_{n\mathbf{k}}\rangle = \sum_{i=N_1}^{N_2} |\psi_{i\mathbf{k}}\rangle\langle\psi_{i\mathbf{k}}|\varphi_n\rangle$$

$$= \sum_{i(E_1 \le \varepsilon_i(\mathbf{k}) \le E_2)} |\psi_{i\mathbf{k}}\rangle\langle\psi_{i\mathbf{k}}|\varphi_n\rangle. \tag{5}$$

The Bloch functions in the LMTO basis (or any other atomic orbital-like basis) are defined as

$$|\psi_{i\mathbf{k}}\rangle = \sum_{\mu} c_{\mu i}(\mathbf{k})|\varphi_{\mu}^{\mathbf{k}}\rangle, \tag{6}$$

where μ is the combined index of the qlm (q is the atomic number in the unit cell and lm are the orbital and magnetic quantum numbers, respectively), $\varphi_{\mu}^{\mathbf{k}}(\mathbf{r})$ are the Bloch sums of the basis orbitals $\varphi_{\mu}(\mathbf{r} - \mathbf{T})$ and the $c_{\mu i}(\mathbf{k}) = \langle\varphi_{\mu}^{\mathbf{k}}|\psi_{i\mathbf{k}}\rangle$ are the corresponding coefficients.

Therefore, the nonorthogonal WFs are

$$|\tilde{W}_{n\mathbf{k}}\rangle = \sum_{i=N_1}^{N_2} |\psi_{i\mathbf{k}}\rangle c_{ni}^*(\mathbf{k})$$

$$= \sum_{i=N_1}^{N_2} \sum_{\mu} c_{\mu i}(\mathbf{k})c_{ni}^*(\mathbf{k})|\varphi_{\mu}^{\mathbf{k}}\rangle = \sum_{\mu} \tilde{b}_{\mu n}^{\mathbf{k}}(\mathbf{k})|\varphi_{\mu}^{\mathbf{k}}\rangle; \tag{7}$$

$$\tilde{b}_{\mu n}^{\mathbf{k}}(\mathbf{k}) \equiv \sum_{i=N_1}^{N_2} c_{\mu i}(\mathbf{k})c_{ni}^*(\mathbf{k}).$$

To orthonormalize the WFs (7), one needs to calculate the overlapping matrix $O_{nn'}(\mathbf{k}) \equiv \langle\tilde{W}_{n\mathbf{k}}|\tilde{W}_{n'\mathbf{k}}\rangle = \sum_{i=N_1}^{N_2} c_{ni}(\mathbf{k})c_{n'i}^*(\mathbf{k})$ and its inverse square root $S_{nn'}(\mathbf{k}) \equiv$

$Q_{nn'}^{-1/2}(\mathbf{k})$. Then, the orthonormalized WFs in the $\mathbf{k}$ space, $|W_{n\mathbf{k}}\rangle$, can be obtained as

$$|W_{n\mathbf{k}}\rangle = \sum_{n'} S_{nn'}(\mathbf{k})|\tilde{W}_{n\mathbf{k}}\rangle$$

$$= \sum_{i=N_1}^{N_2} |\psi_{i\mathbf{k}}\rangle\bar{c}_{ni}^*(\mathbf{k}) = \sum_{\mu} b_{\mu n}^{\mathbf{k}}(\mathbf{k})|\varphi_{\mu}^{\mathbf{k}}\rangle \tag{8}$$

with

$$\bar{c}_{ni}^*(\mathbf{k}) \equiv \langle\psi_{i\mathbf{k}}|W_{n'\mathbf{k}}\rangle = \sum_{n'} S_{nn'}(\mathbf{k})c_{n'i}^*(\mathbf{k})$$

$$\text{and } b_{\mu n}^{\mathbf{k}} \equiv \langle\varphi_{\mu}^{\mathbf{k}}|W_{n\mathbf{k}}\rangle = \sum_{i=N_1}^{N_2} c_{\mu i}(\mathbf{k})\bar{c}_{ni}^*(\mathbf{k}). \tag{9}$$

The matrix elements of the Hamiltonian $\hat{H}^{WF}$ in reciprocal space are

$$\hat{H}^{WF}(\mathbf{k}) = \langle W_{n\mathbf{k}}|\left(\sum_{i\mathbf{k}'}|\psi_{i\mathbf{k}'}\rangle\varepsilon_i(\mathbf{k}')\langle\psi_{i\mathbf{k}'}|\right)|W_{m\mathbf{k}}\rangle$$

$$= \sum_{i=N_1}^{N_2} \bar{c}_{ni}(\mathbf{k})\bar{c}_{mi}^*(\mathbf{k})\varepsilon_i(\mathbf{k}). \tag{10}$$

Using this projected Hamiltonian (10), one can set up LDA + DMFT-like calculations of the local Green's function $G_{nn'}^{loc}$ (ε) [3] with the lattice problem defined as an integral over the first Brillouin zone (BZ):

$$G_{nn'}^{loc}(\varepsilon)$$

$$= \frac{1}{V_{BZ}}\int d\mathbf{k}([(\varepsilon + E_f^{(N)})\hat{1} - \hat{H}^{WF}(\mathbf{k}) - \hat{\Sigma}(\varepsilon)]^{-1})_{nn'}. \tag{11}$$

The result of the LDA + DMFT calculations is the self-energy operator $\hat{\Sigma}(\varepsilon)$ defined in the WF basis set (3). In order to compute the interacting Green's function in the full-orbital Hilbert space, one must convert it back to the full-orbital (LMTO) basis set (4). This can easily be done by using the linear expansion form of the WFs in terms of the full-orbital basis set (Eqs. (8) and (9))

$$\Sigma_{\mu\nu}^{\mathbf{k}}(\varepsilon) = \langle\varphi_{\mu}^{\mathbf{k}}|\hat{\Sigma}(\varepsilon)|\varphi_{\nu}^{\mathbf{k}}\rangle = \sum_{n} b_{\mu n}^{\mathbf{k}}\Sigma_{nn'}(\varepsilon)b_{\nu n'}^{\mathbf{k}*}. \tag{12}$$

To calculate the full-orbital Green's function matrix $G_{\mu\nu}^{\mathbf{k}}(\varepsilon)$, it is sufficient to use the matrix elements of the self-energy operator $\Sigma_{\mu\nu}^{\mathbf{k}}(\varepsilon)$. (12) together with the noninteracting Hamiltonian matrix $H_{\mu\nu}^{\mathbf{k}}$.
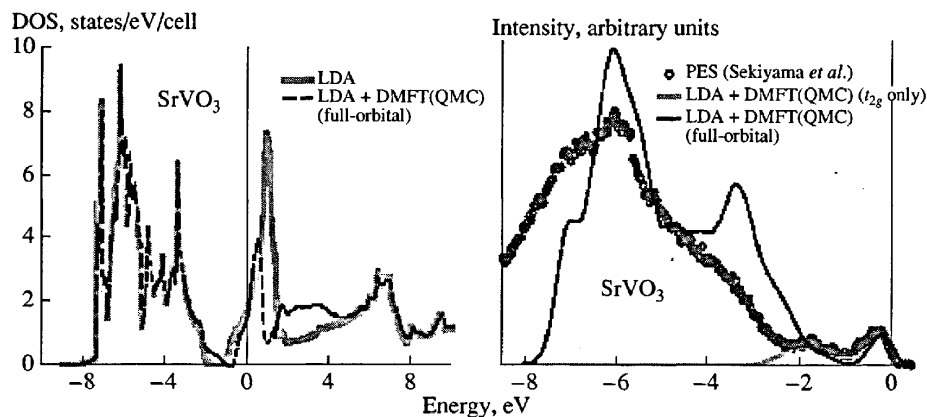
Left panel: comparison of the total densities of states of $SrVO_3$: (full light line) calculated in terms of the LDA and (dashed black line) full-orbital calculations. Right panel: comparison of the bulk-sensitive photoemission spectra of $SrVO_3$ with the total densities of states calculated via LDA + DMFT(QMC): (light line) calculation taking into account only t_{2g} orbitals and (black line) full-orbital calculations. The Fermi level corresponds to zero.

3. RESULTS FOR $SrVO_3$

In the figure (left panel), the total LDA and LDA + DMFT(QMC) densities of states (DOS) of $SrVO_3$ are presented [3]. The main differences between the LDA (full light line) and full-orbital LDA + DMFT(QMC) (dashed black line) spectral functions are observed near the Fermi level. The LDA spectral function has a more pronounced quasiparticle peak. The total DOS calculated using the self-energy converted to a full-orbital basis (see Eq. (12)) has a three-peak structure that are due to the lower Hubbard band (suppressed by oxygen states), quasiparticle peak, and upper Hubbard band located at about 3 eV.

Introduction of correlations between t_{2g} states significantly changes the total and partial LDA DOSs of $SrVO_3$. The main modification is a transfer of spectral weight from the energy region near the Fermi level to the lower and upper Hubbard bands and the reduction of the weight of the quasiparticle peak. Our calculations give a strongly correlated but still metallic ground state for $SrVO_3$.

To compare our results with the experimental photoemission spectrum, we calculated a weighted sum of V $3d$ and O $2p$ spectral functions according to the ratio of the photoemission cross sections (3 : 1), corresponding to an experimental photon energy 900 eV. The theoretical spectra were multiplied with the Fermi function corresponding to 20 K and broadened with a 0.2 eV Gaussian to simulate the instrumental resolution. In the figure (right panel) one can see that the calculated full-orbital spectra describe not only the quasiparticle peak

but also the peak at −6 eV and the shoulder at −3.5 eV of the PES spectra. Since the previous LDA + DMFT(QMC) results took into account only the t_{2g} states, they could not describe the PES spectra below −2 eV. It is very interesting to note that the previous experimental results do not show any states at −3.5 eV and only the new spectra show that feature.

REFERENCES

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