

On the Neglect of Local Coulomb Interaction on Oxygens in Perovskites Described by the Multiband d - p Model

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On the example of TiO_4 layer (such as realized in Sr_2TiO_4) we study electronic structure of multiband d - p models describing transition metal perovskites. As suggested by experiment, the studied system is predicted to be a robust nonmagnetic insulator. A realistic treatment of electronic structure requires one to introduce non-zero Coulomb local interactions at $2p$ oxygen orbitals. However, up till now majority of papers based upon multiband models made an approximation of neglecting such interactions. We show that this simplification does not lead to serious problems in predictions of the electronic structure provided the Coulomb interactions at titanium ions and charge transfer gap are suitably renormalized (so they become entirely different with respect to the true microscopic d - p model parameters).

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1. Introduction

Shortly after the discovery of high temperature superconductors, it was realized that both copper $3d$ and oxygen $2p$ orbitals contribute to the correlated states in the cuprates and should be thus included explicitly in the respective multi-band d - p model for CuO_2 planes [1, 2] or CuO_3 chains [3]. Nowadays a common approach is to use d - p model for the description of electronic structure of a correlated insulator for the analysis of charge and magnetization density distribution and electron correlations, exactly as was done in cuprates in the past [4]. The multi-band d - p model is richer and provides one with a much more wide physical picture than simpler models which feature only d -orbitals [5, 6]. Quite recently the multi-band d - p models featuring on-site interactions defined both on oxygens and on metal ions were investigated for ruthenium, iridium, and titanium oxides [7, 8]. We focused on the full description of Coulomb interactions including oxygen orbitals and showed that they cannot be neglected. In contrast to this many papers in the literature neglect such interactions on oxygens. We will show that this simplification does not lead to serious problems in prediction of the electronic structure provided Coulomb interactions at titanium ions and charge-transfer-gap are properly renormalized.

In the previous paper [8] the preliminary density functional theory computations were performed on quasi-two-dimensional Sr_2TiO_4 and it was found that the ionicity of Sr ions is exactly +2. Therefore for the description of the two-dimensional (2D) model for TiO_4 layer one must assume that the number of valence electrons per TiO_4 unit is exactly 24. This number is used as input to unrestricted HF computations within multi-band d - p

model featuring on-site Coulomb interactions both on titanium ions and oxygen ions. The result is that Sr_2TiO_4 is a robust non-magnetic insulator. The experimental band gap of 3.8 eV was recovered from the computations for: $U_d = 9.0$ eV, $U_p = 4.4$ eV and charge-transfer gap $\Delta = \varepsilon_d - \varepsilon_p = 6.5$ eV (defined for bare energy levels) [8]. The d -electron count on Ti ion is $n_d \simeq 1.2$, almost equally distributed over e_g and t_{2g} orbitals.

Following preliminary results from ref. [8] we provide definite prescription how to modify local Coulomb interaction on metal ions and charge-transfer-gap in simplified d - p models which neglect local interactions on oxygens.

2. Multi-band d - p model Hamiltonian

The multi-band d - p Hamiltonian for TiO_4 layer includes five $3d$ orbitals at each titanium ion and three $2p$ orbitals at each oxygen ion. It consists of the following parts:

$$\mathcal{H} = H_{\text{kin}} + H_{\text{diag}} + H_{\text{int}}, \quad (1)$$

where the different terms in Eq. (1) stand for the kinetic energy (H_{kin}), crystal-field splitting (H_{diag}), and the intraatomic Coulomb interactions (H_{int}).

The kinetic (hopping) part of the Hamiltonian is:

$$H_{\text{kin}} = \sum_{\{i,\mu;j,\nu\},\sigma} t_{i,\mu;j,\nu} c_{i,\mu,\sigma}^\dagger c_{j,\nu,\sigma} + \text{H.c.}, \quad (2)$$

where we employ notation with $c_{j,\nu,\sigma}^\dagger$ standing for the creation of an electron at site j in an orbital ν with up and down spin, $\sigma = \uparrow, \downarrow$. The model includes all d orbital states on titanium, $\nu \in \{xy, yz, zx, 3z^2 - r^2, x^2 - y^2\}$, and three $2p$ orbitals per oxygen atom, $\nu \in \{p_x, p_y, p_z\}$. Alternatively, i.e., choosing a more intuitive notation, we can write $d_{j,\nu,\sigma}^\dagger$ for d orbitals, while $p_{j,\nu,\sigma}^\dagger$ for p orbitals. The matrix elements $t_{i,\mu;j,\nu}$ are non-zero only for nearest-neighbor atoms; they are obtained using Slater-Koster rules [7, 9].

The H_{diag} depends only on particle operator numbers and describes effects of crystal field and the difference of

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reference energies (i.e., charge-transfer-gap),

$$\Delta = \varepsilon_d - \varepsilon_p, \quad (3)$$

between empty d and empty p orbitals. In the following we fix reference energy at $\varepsilon_d = 0$, hence instead of Δ there is only ε_p present in H_{diag} :

$$H_{\text{diag}} = \sum_{i,\mu=x,y,z;\sigma} \varepsilon_p(i) p_{i,\mu,\sigma}^\dagger p_{i,\mu,\sigma} + \sum_{i,\mu=xy,yz,\dots;\sigma} f_{\mu,\sigma}^{cr} d_{i,\mu,\sigma}^\dagger d_{i,\mu,\sigma}. \quad (4)$$

Note that the first sum is restricted to oxygen sites, while the second one runs over titanium sites.

The local Coulomb interaction for titanium ions is

$$H_{\text{int}}(d) = U_d \sum_{m,\mu} n_{m,\mu,\uparrow} n_{m,\mu,\downarrow} + \frac{1}{2} \sum_{m,\mu \neq \nu} \left(U_d - \frac{5}{2} J_{d,\mu\nu} \right) n_{m,\mu} n_{m,\nu} - \sum_{m,\mu \neq \nu} J_{d,\mu\nu} \mathbf{S}_{m,\mu} \cdot \mathbf{S}_{m,\nu} + \sum_{m,\mu \neq \nu} J_{d,\mu\nu} d_{m,\mu,\uparrow}^\dagger d_{m,\mu,\downarrow}^\dagger d_{m,\nu,\downarrow} d_{m,\nu,\uparrow}, \quad (5)$$

where again μ, ν enumerate d -orbitals, and $J_{d,\mu\nu}$ is the tensor of on-site interorbital exchange elements [10]). In our computations the whole anisotropic tensor $J_{d,\mu\nu}$ is treated without any simplifications. The formula for local Coulomb interactions at oxygen sites (for $2p$ orbitals) is analogous.

The effective d - p model requires a number of parameters. The in-plane hopping elements were fixed as $(pd\sigma) = -2.4$ eV and $(pd\pi) = 1.3$ eV and also $(pp\sigma) = 0.6$ eV and $(pp\pi) = -0.15$ eV [11–13]. The choice of the Coulomb elements in d - p model is difficult. There are reliable estimates for U_d (~ 4 eV) but only in effective models featuring solely composite d -type Wannier orbitals (i.e., explicit treatment of p -orbitals is absent). The typical parameter $U_d \sim 4$ eV (for titanium ions) is different from that which should be used in the framework of the multiband d - p model. Namely, it is smaller in the d -orbital-only model from that used in the d - p model by $\sim 50\%$ due to a massive screening.

We decided to study several possibilities, namely $U_d = 4, 6, 8, 9$, and 10 eV according to the data in the literature [14]: ($U_d \in [7, 8]$ eV) [15–17]; ($U_d \sim 8$ eV); and $U_d \sim 6$ eV [18, 19]). The Hund exchange elements are less screened than intraorbital Coulomb elements and are closer to their atomic values. For the Hund exchange J_d (between two t_{2g} electrons) and for our computations we decided to select $J_d = 0.8$ eV according to refs. [19, 20] (also other possibilities were studied, namely $J_d = 0.9$ eV and $J_d = 1.0$ eV). The Coulomb repulsion U_p for oxygen p -orbitals was fixed as $U_p = 4.4$ eV like in refs. [7, 21, 22], while the Hund exchange was fixed as $J_p = 0.8$ eV [20]. Next the average t_{2g} to e_g crystal-field splitting (for bare levels) which we studied were either 2.0 eV or 3.0 eV [12, 23, 24]. Finally, very important parameter for the charge distribution in $(\text{TiO}_2)^{2-}$ planes is a charge-transfer gap Δ (3) which was examined as

a continuous parameter in the range from 1.0 eV up to 9.0 eV.

We used the unrestricted HF approximation to investigate the TiO_4 cluster (4×4 TiO_4 units with cyclic boundary conditions) and with $N_e = 24$ electrons per single TiO_4 unit. The implementation of the model Hamiltonian (1) is the same as described in refs. [7, 11, 25, 26]. The possibilities of different types of order were taken into account: nonmagnetic phase, ferromagnetic and antiferromagnetic with spins aligned along: $(1,1,0)$ or $(1,0,0)$ or $(0,0,1)$ direction. We performed runs for all combinations of the Hamiltonian parameters. Any reasonable parameter set leads to nonmagnetic insulator as the ground state. The experimental band gap in Sr_2TiO_4 is 3.8 eV [27] and it is reproduced when the Hamiltonian parameters are properly tuned to $U_d = 9.0$ eV, $J_d = 0.8$ eV and $\Delta \simeq 6.5$ eV [8].

3. Consequences of the neglect of Coulomb repulsion on oxygens

Let us now study what happens when Coulomb repulsion on oxygens is neglected. We argue that in general it is not correct to set $U_p = J_p = 0$ but this approximation/simplification was used by almost all the authors up to now.

Thus, we performed multiple HF computations using Hamiltonian parameter sets with $U_p = J_p = 0$ and with numerous differently renormalized U_d and Δ . Much to our surprise we obtained quite normal electronic structure with nonmagnetic ground state as a generic solution. When studying various possibilities how to renormalize U_d and Δ so as the obtained results are physically sensible we obviously should look after such sets of U_d and Δ which reproduce experimental band gap of 3.8 eV. The results coming out from this approach are shown in Fig. 1.

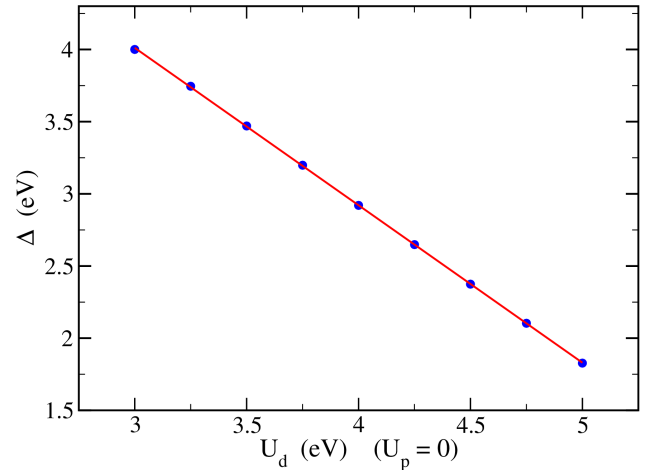


Fig. 1. Charge-transfer energy Δ (3) versus U_d for the parameters which reproduce experimental band gap of 3.8 eV. The extrapolated dependence is linear — $\Delta \approx 7.28 - 1.09 U_d$ (with U_d in eV). Fixed parameters of the d - p Hamiltonian are: $U_p = 0$, $J_0 = 0$; crystal field t_{2g} to e_g splitting is 2.0 eV and $J_d = 0.8$ eV.

4. Renormalization of U_d and Δ for $U_p = 0$ models

From Fig. 1 it follows that if one decides to model the titanium perovskite neglecting the local Coulomb repulsion on oxygen ($U_p = J_p = 0$) and in addition if one accepts $U_d = 4$ eV then the charge-transfer energy should be chosen as $\Delta \approx 3.0$ eV. Note that the usual parameters of the d - p multi-band model are by 50% larger, just to remind: $U_d = 9$ eV and $\Delta = 6.5$ eV.

If a different value of U_d is advocated in a particular paper one can pick out from the literature still we can predict the precise value of Δ which should be appropriate in such the context.

5. Summary

We have taken the number of electrons which follows from the ionic configuration of Sr^{2+} ions for a periodic 4×4 TiO_4 cluster, as suggested by *ab initio* electronic structure calculations and examined in electronic distribution within unrestricted HF computations performed using the multi-band d - p model. Several possibilities for Hamiltonian parameters were studied. For any reasonable choice of the parameters we find a good nonmagnetic insulator, with a gap reproduced for $U_d = 9.0$ eV, $U_p = 4.4$ eV, and a large charge-transfer gap $\Delta = 6.5$ eV.

We also considered a simplified set of parameters with $U_p = J_p = 0$ and find that this choice implies considerable reduction of the remaining parameters: (i) the value of U_d is smaller by $\sim 50\%$; (ii) the charge-transfer gap Δ is also reduced to ~ 3.0 eV. Only taking these renormalization one can reproduce the essential features of the electronic structure of Sr_2TiO_4 . We remark that while such a renormalization is possible for the bulk, the treatment of systems with non-equivalent oxygen and transition metal positions would require a complete parameter set with finite electron interactions at oxygen $2p$ orbitals.

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