Effect of Hubbard $U$ on the construction of low energy Hamiltonians for LaMnO$_3$ via maximally localized Wannier functions

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We use maximally localized Wannier functions to construct tight-binding (TB) parameterizations for the $e_g$ bands of LaMnO$_3$ based on first principles electronic structure calculations. We compare two different ways to represent the relevant bands around the Fermi level: i) a $d$-$p$ model that includes atomic-like orbitals corresponding to both Mn($d$) and O($p$) states in the TB basis, and ii) an effective $e_g$ model that includes only two $e_g$-like Wannier functions per Mn site. We first establish the effect of the Jahn-Teller distortion within the $d$-$p$ model, and then compare the TB representations for both models obtained from GGA+$U$ calculations with different values of the Hubbard parameter $U$. We find that in the case of the $d$-$p$ model the TB parameters are rather independent on the specific value of $U$, if compared with the mean-field approximation of an appropriate multi-band Hubbard Hamiltonian. In contrast, the $U$ dependence of the TB parameters for the effective $e_g$ model cannot easily be related to a corresponding mean-field Hubbard model, and therefore these parameters depend critically on the specific value of $U$, and more generally on the specific exchange-correlation functional, used in the electronic structure calculation.

I. INTRODUCTION

The construction of realistic low-energy Hamiltonians based on first principles electronic structure calculations is an important tool for the investigation of correlated electron systems, such as e.g. cuprates, manganites, or other complex transition metal (TM) oxides. While much of the general physics determining the diverse properties of these materials can be understood in terms of simplified models, the corresponding model parameters are generally unknown and have to be adjusted to fit experimental data. Alternatively, electronic structure calculations based on density functional theory (DFT) can be used to determine these parameters, which in turn allows for a quantitative evaluation of the underlying model assumptions and the construction of realistic model Hamiltonians with all parameters determined ab initio.

Model Hamiltonians for correlated electron systems are typically formulated within a tight-binding (TB) picture that involves only a small number of electronic states localized on certain atoms (e.g. the “$d$-states” of the TM atoms within a TM oxide). Ideally, these states give rise to an isolated group of bands around the Fermi energy, which then determines the low energy behavior of the system. A corresponding TB representation can in principle be obtained by constructing Wannier functions from the Kohn-Sham Bloch states calculated within DFT.

In the case of model Hamiltonians that contain an explicit electron-electron interaction, typically in the form of a local Hubbard term with interaction parameter $U$, the DFT band-structure can either be viewed as mean-field approximation to this interacting model, or as representative for the “non-interacting” case, i.e. corresponding to $U = 0$ in the model Hamiltonian. While it is often convenient to consider the electronic structure calculated within either the local density approximation (LDA) or the generalized gradient approximation (GGA) as essentially non-interacting, this is probably not a good assumption if the electronic structure is calculated using more advanced exchange correlation functionals such as (LDA/GGA)+$U$ or hybrid functionals.

In this work we use maximally localized Wannier functions (MLWFs) to obtain TB parameterizations for the important case of LaMnO$_3$, the parent material of the colossal magneto-resistive manganites, and a prototype system for correlated electron physics. We calculate the electronic structure of LaMnO$_3$ using the GGA+$U$ method and different values for the Hubbard parameter $U$. We then compare two different ways to represent the relevant bands around the Fermi level: i) a $d$-$p$ model that includes atomic-like orbitals corresponding to both Mn($d$) and O($p$) states in the TB basis, and ii) an effective $e_g$ model that includes only two $e_g$-like Wannier functions per Mn site. In particular, we analyze the $U$ dependence of the two different TB parameterizations and relate this to commonly used model Hamiltonians for manganites.

We find that for the $d$-$p$ parameterization, the effect of $U$ is mostly local, leading to $U$ dependent shifts of the on-site energies and an increase in the Jahn-Teller (JT) splitting, whereas the corresponding hopping amplitudes are only weakly affected by the value of $U$. Thus, the $U$ dependence of the $d$-$p$ parameters closely resembles the $U$ dependence of a corresponding multi-band Hubbard Hamiltonian in mean-field approximation. On the other hand, the change of on-site energies and JT splitting for the effective $e_g$ MLWFs, calculated for different values of $U$, are distinctly different from a corresponding mean-field model Hamiltonian. In addition, there is also a strong $U$ dependence of the effective $e_g$ hopping amplitudes, which is due to electronic degrees of freedom that are excluded from the TB basis. This indicates that while the TB parameterization for the $d$-$p$ model is fairly robust with respect to a variation of $U$, for the case of...
the effective $e_g$ basis an appropriate choice of $U$ in the GGA+$U$ calculation is crucial. Our results demonstrate the simple fact that the transferability of a specific TB parameterization is generally increased if more electronic degrees of freedom are included in the model description.

This paper is organized as follows. In the next section we first summarize the most important aspects of typical model Hamiltonians for manganites, emphasizing in particular the role of the JT distortion (Sec. II A), before introducing MLWFs (Sec. II B) and describing the technical details of our calculations (Sec. II C). In Secs. II A and II B we first present the main features of the $d$-$p$ model based on the MLWFs calculated for $U = 0$ eV, and then clarify the effect of the JT distortion on the corresponding TB parameterization. An analogous analysis for the effective $e_g$ model parameterization has recently been presented in Ref. 9. The effect of varying the Hubbard $U$ in the GGA+$U$ calculation on the MLWF parameters of the two different models is presented in Sec. II C for the $d$-$p$ model and in Sec. II D for the effective $e_g$ model. Finally, Sec. IV summarizes our main conclusions, while further details about the $d$-$p$ TB parameterization can be found in Appendix A.

II. METHOD AND THEORETICAL BACKGROUND

A. Jahn-Teller distortion in LaMnO$_3$

LaMnO$_3$ crystallizes in an orthorhombically distorted perovskite structure with $Pbnm$ space group symmetry.\cite{24}

The distortion relative to the cubic perovskite structure can be decomposed into three components:\cite{23} a staggered JT distortion of the MnO$_6$ octahedra, alternating tilts and rotations of these octahedra around the cubic axes (GdFeO$_3$ distortion), and an orthorhombic strain of the unit cell. The electronic structure of LaMnO$_3$ around the Fermi energy is dominated by Mn 3d states, which are split by the octahedral crystal field into lower-lying $t_{2g}$ and higher-lying $e_g$ states.\cite{25,26}

The formal $d^4$ occupation of the Mn$^{3+}$ cation leads to a high spin configuration with filled majority spin $t_{2g}$ states, half-filled majority spin $e_g$ states, and empty minority spin states. The low energy behavior of LaMnO$_3$ is therefore governed by the partially filled majority spin bands with predominant $e_g$ character.

Motivated by this, the complex phenomenology observed in manganites is often modeled within an effective TB model that involves only two $e_g$ orbitals per Mn site. Electrons can then hop between the two $e_g$ levels on neighboring sites, and can interact with each other through a Hubbard-type electron-electron interaction, with the $t_{2g}$ “core-spins” through a Hund’s rule interaction, and with the local JT distortion through a crystal field splitting (see e.g. Ref. 3). It is usually understood that the corresponding “$e_g$ orbitals” are spatially extended Wannier orbitals that result from hybridization between atomic-like Mn($e_g$) orbitals and the $p$ orbitals of the surrounding oxygen ligands.

The effect of the JT distortion on this $e_g$ manifold is typically expressed via a local crystal-field splitting of the form:

$$\hat{H}_{JT} = -\lambda \sum_{R,\sigma,a,b,i} \hat{c}^\dagger_{aR\sigma} Q_i R \hat{c}_{bR\sigma},$$

(1)

Here, $\lambda$ is the JT coupling strength, $\tau_{ab}$ are the usual Pauli matrices, $\hat{c}_{aR\sigma}$ is the annihilation operator corresponding to orbital $b$ with spin $\sigma$ at site $R$, and the JT distortion of the oxygen octahedron surrounding site $R$ is described by specific modes $Q_i^R (i = x, y)$.\cite{9}

In the following we only consider a staggered JT distortion of the form $Q_i^R = -Q_i^{R'}$, where $R$ and $R'$ correspond to nearest neighbor sites within the $x$-$y$ plane (see Fig. 1). Thereby:

$$Q_i^R = \frac{1}{\sqrt{2}} (d_{R}^x - d_{R}^y),$$

(2)

with $d_{R}^x$ and $d_{R}^y$ being the Mn-O distances along the $x$ and $y$ directions, respectively, corresponding to the oxygen octahedron surrounding the Mn at site $R$. We note that it has been shown in Ref. 9 that this component of the JT distortion has the most pronounced effect on the electronic structure of LaMnO$_3$. Furthermore, in Ref. 9 we showed that the effect of the various structural distortions on the calculated model parameters can be analyzed separately, since they are to a great extent independent of each other.

B. Maximally localized Wannier functions

A set of $N$ localized Wannier functions $|w_{nR}\rangle$ corresponding to a group of $N$ bands that are described by delocalized Bloch states $|\psi_{mk}\rangle$, is defined by the follow-
ing transformation:

\[ |w_{nT}⟩ = \frac{V}{(2\pi)^3} \int_{\text{BZ}} \text{dk} \left( \sum_{m=1}^{N} U_{nm}^{(k)} |\psi_m⟩_{k} \right) e^{-i\mathbf{k} \cdot \mathbf{T}}. \]  

\( (3) \)

Thereby, \( \mathbf{T} \) is the lattice vector of the unit cell associated with the Wannier function, \( m \) is a band index, \( \mathbf{k} \) is the wave-vector of the Bloch function, and the integration is performed over the first Brillouin zone (BZ) of the lattice. Different choices for the unitary matrix \( U^{(k)} \) lead to different Wannier functions, which are thus not uniquely defined by Eq. (3). A unique set of maximally localized Wannier functions (MLWFs) can be generated by minimizing the total quadratic spread of the Wannier orbitals.

Once the transformation matrices \( U^{(k)} \) are determined, a TB representation of the Hamiltonian in the MLWF basis is obtained:

\[ \hat{H} = \sum_{\mathbf{T},\Delta\mathbf{T}} h_{nm}^{\mathbf{T}} T_{nT}^\dagger T_{mT}^\Delta + \text{h.c.}, \quad (4) \]

with

\[ h_{nm}^{\mathbf{T}} = \frac{V}{(2\pi)^3} \int_{\text{BZ}} \text{dk} \left( \sum_{l} \left( U_{ll}^{(k)} \right)^* \epsilon_{lk} U_{lm}^{(k)} \right) e^{-i\mathbf{k} \cdot \mathbf{T}}. \]

\( (5) \)

Here, \( \epsilon_{lk} \) is the eigenvalue corresponding to Bloch function \( |\psi_{lk}⟩ \). For cases where the bands of interest do not form an isolated set of bands but are entangled with other bands, a two step procedure for obtaining the unitary transformation matrices (which in this case are typically rectangular) is employed.

We note that \( \mathbf{T} \) and \( \Delta\mathbf{T} \) in Eqs. (3)-5 indicate lattice translations, whereas for crystal structures with more than one atom per unit cell \( n \) and \( m \) represent a combined orbital and site index, specifying the various orbitals at all sites within the primitive unit cell.

C. Computational details

All results presented in this work are obtained from spin-polarized first principles DFT calculations using the Quantum-ESPRESSO program package\(^{23}\) the GGA exchange-correlation functional of Perdew, Burke, and Ernzerhof\(^{23}\) and Vanderbilt ultrasoft pseudopotentials\(^{22}\) La (5s,5p) and Mn (3s,3p) semicore states are included in the valence. The Hubbard +U correction is applied using the simplified approach according to Dudarev et al.\(^{25}\) which corresponds to the case \( J = 0 \) in the more elaborate expression by Lichtenstein et al.\(^{17}\) Projections on orthogonalized atomic Mn(d) orbitals are used to evaluate the \( U \) dependent contributions to potential and energy.

To analyze the effect of the JT distortion on the electronic structure of LaMnO\(_3\), we perform GGA calculations with different degrees of distortion. Starting from the ideal cubic perovskite structure, we gradually increase the amplitude of the JT distortion \( |Q_0| \) from 0 to \( Q_0 = 0.151 \) Å. The latter value corresponds to the amount of distortion found in the experimentally observed crystal structure of LaMnO\(_3\). For the undistorted case we use a cubic perovskite structure with lattice constant \( a_0 = 3.9345 \) Å, which results in the same volume \( V = 60.91 \) Å\(^3\) per formula unit as in the experimentally observed \( Pbmn \) structure\(^{28}\).

After obtaining the DFT Bloch bands, we construct MLWFs using the wannier90 program integrated into the Quantum-ESPRESSO package\(^{22}\) Starting from an initial projection of atomic \( d \) and \( p \) basis functions centered on the Mn and O sites onto the Bloch bands within an appropriately chosen energy window, we obtain sets of either 14 atomic-like (\( d-p \) model) or 2 more extended \( e_g \)-like (effective \( e_g \) model) MLWFs per spin channel and unit cell. In both cases we will in the following refer to the MLWF Hamiltonian matrix elements \( h_{nm}^{\mathbf{T}} \) between the two different \( e_g \)-like MLWFs located on the same Mn site as on-site off-diagonal element \( q \), to any matrix element between the same orbital at a particular site as on-site energy \( \varepsilon \), and to matrix elements connecting two different sites as hopping amplitudes \( t \). To assess the effect of the “+U” correction on the two different MLWF parameterizations we then construct the corresponding MLWFs for the fully JT distorted structure from GGA+U calculations with different values for the Hubbard \( U \).

Convergence of the DFT total energy and total magnetization has been tested for the ideal cubic perovskite structure and ferromagnetic (FM) order. We find the total energy converged to an accuracy better than 1 mRy and the total magnetization converged to an accuracy of 0.05 \( \mu_B \) for a plane-wave energy cut-off of 35 Ry and a \( \Gamma \)-centered \( 10 \times 10 \times 10 \) k-point grid using a Gaussian broadening of 0.01 Ry. These values for plane-wave cut-off and Gaussian broadening are used throughout this work, whereas an appropriately reduced k-point grid of \( 7 \times 7 \times 10 \) is used for the JT distorted structure with doubled unit cell in the \( x-y \) plane. The MLWFs are considered to be converged if the fractional change of the quadratic spread (both gauge-invariant and non-gauge-invariant part) between two successive iterations is smaller than \( 10^{-10} \).

III. RESULTS AND DISCUSSION

A. \( d-p \) TB parameterization for cubic LaMnO\(_3\)

In this section we establish the general features of the extended \( d-p \) TB description of LaMnO\(_3\) within the ideal cubic perovskite structure, before we analyze the effect of the JT distortion in the next section. We are considering a FM arrangement of magnetic moments, but we have verified that the corresponding results for A-type antiferromagnetic (A-AFM) order do not exhibit any significant differences.
The Mn(eg) orbitals are pointing towards the Mn atom and hybridize in Fig. 3. Three of the O(pov) orbitals are located at slightly lower energies for minority spin, states with predominant Mn(eg) and Mn(t2g) character are located above the Fermi level. Strong hybridization between O(p) and Mn(d) orbitals is apparent from the various peaks in the DOS around 8 eV.

We construct 14 MLWFs per spin channel from the Kohn-Sham states located within an energy window of 3-17 eV and 3-20 eV for majority and minority spin, respectively. This corresponds to a TB representation of LaMnO₃ containing 5 Mn(d) orbitals and 9 O(p) orbitals per unit cell (three p orbitals corresponding to each of the three oxygen atoms within the simple cubic perovskite unit cell). The resulting MLWFs are depicted in Fig. 3. Three of the O(p) orbitals (one on each O atom) are pointing towards the Mn atom and hybridize with the Mn(eg) orbitals. We call them O(pσ) orbitals. The remaining 6 O(p) orbitals (two on each O atom) are oriented perpendicular to the Mn-O bond and hybridize with the Mn(t2g) orbitals. These will be called O(pτ) orbitals in the following.

The MLWF bands (shown as thick (red) lines in Fig. 2) are identical to the corresponding DFT bands for majority spin, whereas for minority spin the MLWF and DFT bands above the Fermi energy exhibit certain differences which are due to the strong entanglement with other bands in that energy region.

From the real-space Hamiltonian matrix elements in the MLWF basis, Eq. (5), we find that the most dominant hopping corresponds to the shortest Mn-O and O-O bonds (see Fig. 10), but that a variety of other hopping amplitudes are also non-negligible. In the following we will focus on the nearest neighbor Mn-O hopping amplitudes (t_{eg,σ} and t_{2g,σ}) and analyze how they are affected by the JT distortion and the inclusion of a Hubbard U in the DFT calculations. A more detailed discussion of the d-p TB parameterization for cubic LaMnO₃ can be found in Appendix A.

**B. Effect of JT distortion on the d-p TB parameterization**

We now analyze the effect of the JT distortion on the on-site energies and nearest neighbor hopping parameters of the d-p model. As in the previous section, we will discuss only results for FM order as we do not find significant differences for the case of A-AFM order.

Fig. 4 shows the diagonal on-site energies ε corresponding to Mn(eg), Mn(t2g), O(pσ), and O(pτ) MLWFs, as well as the on-site off-diagonal matrix elements q between the two Mn(eg) orbitals on the same site as function of the JT amplitude $Q^2/Q_0^2$. It can be seen that the on-site energies for the various orbitals are essentially unaffected by the JT distortion. The corresponding changes, which lead to small differences between formerly symmetry-equivalent orbitals (see below for the case of the two eg-like MLWFs), are of the order of a few tens of meV, and are thus negligible compared to the eg,t2g splitting or the d-p energy separation.

A more distinct effect of the JT distortion can be seen in the on-site off-diagonal matrix element q between the two majority spin Mn(eg) orbitals on the same site. This matrix element is zero for the undistorted
and minority spin, we note that in a partially covalent
field effect is identical for both spin projections, the hy-
bridization with the surrounding ligand orbitals is differ-
ent for majority and minority spin orbitals, due to their
large energy difference of about 3-4 eV.

In order to verify whether the large difference be-
tween majority and minority spin JT-splitting is indeed
due to a strong ligand-field contribution, we have con-
structed an alternative set of 20 MLWFs per formula unit
and spin channel, where we explicitly included also the
bands corresponding to O(s) and semi-core La(5p) states.
These states are energetically lower than the Mn(d) and
O(p) bands shown in Fig. 2, and are centered around
$E \approx -3\text{ eV (La}(5p))$ and $E \approx -5\text{ eV (O}(s))$. The
inclusion of these states in the MLWF basis reduces the
“tails” in the $e_g$-like MLWFs located at surrounding O
and La atoms, and should therefore decrease the ligand-
field contribution to the local JT splitting. Indeed, we
obtain $\Delta e_{\text{spin}} = 0.36/0.12\text{ eV}$ in this case, i.e., the spin-
dependent ligand-field contribution to the JT splitting
is indeed significantly reduced compared to the $d\text{-}p$ ML-
WFs. The remaining difference can be ascribed to fur-
ther contributions of orbitals that are not included in the
MLWF basis and to the remaining small O(s), O(p), and
La(p) contributions on the surrounding sites, which are
required to ensure orthogonality between the MLWFs.

We also note that the JT splitting corresponding to the
rather localized $e_g$ MLWFs of the $d\text{-}p$ TB model (0.50 eV
for majority spin) is a factor of two smaller than the
 JT-splitting for the more spatially extended MLWFs of the effective $e_g$ model which was reported in Ref. 2 (0.97 eV for majority spin). This demonstrates the much stronger ligand-field effect in the less localized effective $e_g$ MLWFs.

Next, we analyze the effect of the JT distortion on the
nearest neighbor hopping between Mn(d) and O(p) or-
bital. Fig. 5 shows the corresponding changes in the
structure, but exhibits a linear increase to a value of
about 0.25 eV for full JT distortion. This is consist-
ent with the usual crystal-field picture of $e_g$ orbitals in
an octahedral environment (see also Eq. (1)).

We thus define a total JT-induced orbital splitting within the “$e_g$” orbital subspace as the difference in eigenvalues of the corresponding $2\times2$ on-site Hamiltonian matrix, which is given by
$\delta = \sqrt{\Delta^2 + 4q^2}$. From the results presented
in Fig. 4 for full JT distortion, i.e. $Q^t/Q^0 = 1$, we ob-
tain $\delta_{\text{majority}} = 0.50\text{ eV}$ for majority spin and
$\delta_{\text{minority}} = 0.07\text{ eV}$ for minority spin.

To understand this large difference between majority
and minority spin, we note that in a partially covalent
system like LaMnO$_3$, the JT-induced orbital splitting
is caused by a superposition of two effects: i) the true
(\text{electro-static}) crystal-field effect, and ii) a “ligand-field”
effect due to changes in hybridization with the surround-

FIG. 4: On-site MLWF matrix elements of the $d\text{-}p$ model as function of the JT distortion. (a)/(b): On-site energies for majority/minority spin. (c): On-site off-diagonal element $q$. (d): Splitting $\Delta e$ between on-site energies of the two $e_g$-like MLWFs.
majority spin hopping amplitudes (the results for minority spin do not exhibit any qualitative differences).

We first discuss hopping between Mn($t_{2g}$) and O($p_\sigma$) orbitals (Fig. 5a). It can be seen that the hopping amplitude $t_{t2g,p\sigma}$ splits essentially according to the different Mn-O bond lengths in the JT distorted structure. The hopping amplitudes along the short (long) Mn-O bonds within the $x$-$y$ plane increase (decrease) with increasing JT distortion, while the hopping along the $z$-direction, i.e. corresponding to constant Mn-O bond distance, is only weakly affected.

In order to assess to what extent the $d$-$p$ hoppings in the JT distorted structure are simply determined by the corresponding Mn-O distances, we also calculate MLWFs for undistorted cubic LaMnO$_3$ with different lattice constants $a$. The Mn-O distances in the cubic structures with $a = a_0 \pm \Delta a$ are identical to the long/short Mn-O bond length in the JT distorted structure with $Q^x = \Delta a/\sqrt{2}$. The corresponding results for the nearest neighbor hopping amplitudes between Mn($d$) and O($p$) orbitals are also shown in Fig. 5.

It is apparent that the $t_{t2g,p\sigma}$-type hopping amplitudes in the JT distorted structures are nearly identical to the corresponding hopping amplitude in the undistorted cubic structure with the same Mn-O distance. The small deviations between these two cases as well as the weak effect of the JT distortion on the $t_{t2g,p\sigma}$ hopping along $z$ are due to changes in the orbital character of the MLWFs with increasing JT distortion. Thus, the magnitudes of the various hopping amplitudes are indeed determined mostly by the corresponding Mn-O bond lengths.

The case of the $t_{eg,p\sigma}$ hopping is only slightly different. The hopping (both in-plane and along $z$) between the Mn($3z^2-r^2$)-type orbital and the surrounding O($p_\sigma$) orbitals compares well with the hopping amplitude in the undistorted structure with the same Mn-O distance (even though the agreement for the short Mn-O distance is not as good as for $t_{t2g,p\sigma}$). On the other hand, the JT-induced splitting of the in-plane hopping between the Mn($x^2-y^2$)-type orbital and the surrounding O($p$) orbitals is significantly weaker than the corresponding bond-length dependence in the cubic structure. This indicates a strong change of the $|x^2-y^2|$-type orbital with increasing JT distortion. This change is due to different admixture of other orbitals that are not explicitly included in the MLWF construction, i.e. O($s$) and La($p$), which lead to a reduction/expansion of the lobes directed along the shorter/longer Mn-O bonds with increasing JT distortion. This partially compensates the effect of changing Mn-O distance and leads to the observed JT dependence of the hopping.

C. Effect of $U$ within the $d$-$p$ model

In order to investigate the influence of the Hubbard $U$ parameter on the TB parameterization obtained from the MLWFs, we now perform GGA+$U$ calculations for the fully JT distorted structure and FM order using different values for $U$. Figure 6 shows the resulting $U$ dependence of the on-site MLWF matrix elements. It can be seen that the diagonal elements (on-site energies $\varepsilon$) corresponding to O($p$)-type MLWFs are virtually unaffected by the value of $U$, while the corresponding matrix elements for Mn($t_{2g}$) and Mn($e_g$) orbitals exhibit a more or less linear dependence on $U$.

This linear dependence is a direct consequence of the $U$ dependent potential shift applied to the TM $d$ states within the DFT “$+U$” approach:

$$\Delta V_{nm'} = U\left(\frac{\delta_{nm'}}{2} - n_{mm'}^\sigma\right).$$

Here, $n_{mm'}^\sigma$ is the occupation matrix element between atomic orbitals $m$ and $m'$ for spin projection $\sigma$, which is calculated from the projection of the occupied Bloch states on fixed atomic orbitals.

In order to quantify, whether the $U$ dependence of the on-site MLWF matrix elements does indeed correspond to this potential shift, we explicitly evaluate Eq. (6) for each $U$, using the atomic occupation matrix elements obtained from the corresponding GGA+$U$ calculation, and add the so-obtained shifts to the on-site MLWF matrix elements for $U = 0$. The resulting data is shown as small open (red) symbols in Fig. 6c and is nearly identical to the MLWF matrix elements calculated for the corresponding values of $U$. Thus, the GGA+$U$ potential shifts
are directly reflected in the on-site matrix elements of the MLWFs.

The reason for this good correspondence between the GGA+$U$ potential shifts and the $U$ dependence of the on-site MLWF matrix elements is the fact that the MLWFs of the extended $d$-$p$ model are rather similar to the atomic orbitals used as projector functions within the GGA+$U$ approach. To further demonstrate this similarity, we also compare the occupation matrix elements used to evaluate the GGA+$U$ potential shifts with the occupation of the corresponding MLWFs.

$$n_{\sigma m'm}^{\text{MLWF}} = \int_{-\infty}^{E_F} \int_{\text{BZ}} d\epsilon \sum_k \left( U_{l_m}^{(k)} \right)^* \delta(\epsilon - \epsilon_{l_k}) U_{l_{m'}}^{(k)},$$

where $E_F$ is the Fermi energy. The corresponding values for $U = 0$ eV are listed in Table I. It is apparent that the occupations of the MLWFs are very similar to the occupations of the atomic orbitals used as GGA+$U$ projector functions. Furthermore, we note that due to the strong hybridization between the Mn($d$) and O($p$) states, the occupation of the atomic-like $d$ orbitals are quite different from a naive expectation based on the formal ionic configuration of the Mn$^{3+}$ cation.

The $U$ dependence of the on-site off-diagonal matrix element $q$ can be understood in the same way and is related to the off-diagonal occupation matrix element $n_{\sigma mm'}^{\text{off diagonal}}$, where $m \equiv |3z^2 - r^2|$ and $m' \equiv |x^2 - y^2|$. The nonlinearities that can be observed for large $U$ are due to changes in the corresponding $n_{\text{off diagonal}}$. Note that since $q$ is directly related to the JT splitting, increasing $U$ effectively amounts to increasing the strength of the JT coupling.

The $U$ dependence of the hopping amplitudes between O($p$) and Mn($d$)-like MLWFs for majority spin and FM order is shown in Fig. 7(a). All depicted hopping amplitudes exhibit a similar small increase in magnitude. The effect of $U$ on the hopping amplitudes for minority spin (not shown) is even weaker than for the majority spin orbitals. These small changes in the hopping amplitudes for both majority and minority spin can be attributed to changes in orbital character of the corresponding MLWFs. These changes in orbital character arise from a different admixture (hybridization) of orbitals centered at the surrounding ions, which results from the $U$ dependent shifts of the on-site energies of the Mn($d$) states relative to all other orbitals.

### TABLE I: Average occupations $n_{\sigma mm}$ corresponding to Mn($t_{2g}$) and Mn($e_g$) orbitals calculated for $U = 0$ in the fully JT distorted structure. Rows denoted “atomic” correspond to the fixed atomic orbitals used to evaluate the GGA+$U$ functional; rows denoted “MLWF” contain the occupation of the MLWFs calculated according to Eq. 7; rows denoted “formal” correspond to the formal occupation matrix elements used to evaluate the effective $U$ dependence of the on-site energies for the effective $U$ model presented in the previous section with the case of an effective $e_g$ model with only two $e_g$-like Wannier orbitals on each Mn site. This is probably the most common model used to describe the physics of manganites (see e.g. Ref. 33), and a detailed analysis of the effect of various distortions and different magnetic arrangements on the corresponding MLWF matrix elements for $U = 0$ eV has been presented in Ref. 9. Here we focus on changes in the MLWF parameterization due to the Hubbard $U$ correction for the purely JT distorted structure and FM order. The corresponding Wannier functions are constructed from the Kohn-Sham states located within an energy window of 12.0-17.0 eV and 15.9-20.0 eV for majority and minority spin, respectively. For further details see Ref. 9.

Fig. 8 shows the $U$ dependence of the on-site MLWF Hamiltonian matrix elements for the effective $e_g$ model. It can be seen that in particular the on-site energies exhibit a very similar trend as the on-site energies of the $e_g$-like MLWFs in the $d$-$p$ model, but that the $U$ dependence is weaker than in the latter case. The slope $dz/dU$ for both majority and minority spin is only about 66% compared to the $d$-$p$ model. This indicates that the $U$ dependence of the on-site energies for the effective model.
$e_g$ MLWFs is still determined by the GGA+$U$ potential shifts, Eq. (5), but is renormalized by the extent of overlap between the extended MLWF and the corresponding $e_g$ atomic orbital. In other words, the $U$ dependent energy shift experienced by the MLWF is determined by the projection of the MLWF on atomic orbitals and the occupation of these atomic orbitals.

In particular, this shows that the effect of $U$ on the on-site energies of the effective $e_g$ MLWFs are not determined by the occupation of the MLWFs themselves via a relation similar to Eq. (6). The occupation of the effective $e_g$ MLWFs are essentially identical to the “formal” occupations listed in Table 1 corresponding to the formal $3+$ charge state of the Mn cation in LaMnO$_3$ (0.5 for majority spin and 0.0 for minority spin). Therefore, the occupation-dependent potential shift following from a mean-field approximation to the Hubbard interaction similar to Eq. (6) would be zero for the majority spin $e_g$ states. The $U$ dependence of the corresponding on-site energies is thus notably different from a mean-field treatment of the electron-electron interaction in a two-orbital Hubbard-like model derived from the effective $e_g$ TB parameterization.

We point out that in addition to the different dependence on orbital occupation, the magnitude of the screened Hubbard $U$ acting on the extended $e_g$-like Wannier orbitals will of course be significantly reduced compared to the magnitude of $U$ corresponding to more localized atomic-type orbitals. A comparison of the value of $U$ for “atomic-like” and “effective” Wannier orbitals in an Fe-pnictide system based on calculations using constrained random phase approximation has been presented recently in Ref. 33.

Similar to the case of the on-site energies, the $U$ dependence of the off-diagonal on-site matrix elements $q$, shown in Fig. 3b, resembles the $U$ dependence of the corresponding atomic-like MLWFs shown in Fig. 3a. The decrease of $q$ for majority spin observed for $U > 6$ eV can then be ascribed to changes in orbital character of the extended MLWFs, which lead to different projections between MLWFs and the corresponding atomic orbitals.

Finally, Fig. 9 shows the $U$ dependence of the nearest neighbor hopping parameters for the effective $e_g$ MLWFs. For majority spin, there is an overall increase in the magnitude of the hopping, whereas for minority spin there is an overall decrease. Compared to the $d$-$p$ model discussed in the previous section, the effect of $U$ on the hopping amplitudes of the effective $e_g$ model is strongly enhanced, with typical changes between 30% and 60% over the considered range of $U$ values. For the in-plane hopping between $[3z^2 - r^2]$ and $[x^2 - y^2]$-type orbitals the change can be even more than 100%.

This strong effect of $U$ on the hopping amplitudes of the effective $e_g$ MLWFs can be explained by the changes in the underlying $d$-$p$ model. The effective $e_g$ MLWFs are essentially linear combinations of an atomic-like Mn($e_g$) orbital and O($p_\sigma$) orbitals on the surrounding anions. As demonstrated in the previous section, the on-site energies of the atomic $d$ orbitals are strongly shifted relative to the oxygen $p$ orbitals as a function of $U$. This shift affects the hybridization between the atomic orbitals and thus changes the admixture of O($p_\sigma$) orbitals in the effective $e_g$ MLWF. For majority spin, increasing $U$ decreases the energy difference between atomic O($p$) and Mn($d$) orbitals and thus increases the hybridization, i.e. the admixture of O($p$) in the effective $e_g$ MLWF. This leads to an increase of the hopping amplitude due to the larger overlap between effective $e_g$ orbitals at neighboring Mn sites. For minority spin the trend is opposite to this, resulting in the decrease in magnitude seen in Fig. 9b.

Considering a simple $d$-$p$ nearest neighbor TB model for the cubic perovskite structure, one can show that in the limit of large energy separation between the $d$ and $p$ orbitals, the “antibonding” bands that result from the $d$-$p$ hybridization are formally equivalent to an effective “$d$-only” TB model with direct hopping between $d$-orbitals on adjacent TM sites. The amplitude of this “effective
d-d hopping is thereby given as:

$$t_{dd}^{\text{eff}} = \frac{t_{dp}^2}{\epsilon_d - \epsilon_p} . \tag{8}$$

Obviously, the overall trends discussed in the previous paragraph are consistent with this simple picture, but the limit for which Eq. (5) is valid is not fulfilled in the case of LaMnO$_3$. This is apparent from the on-site energies shown in Fig. [6], where it can be seen that for values of $U$ larger than 5-6 eV the Mn($e_g$) states become essentially degenerate with the O($p$) states. We also verified that Eq. (5) is not fulfilled quantitatively by the hoppings calculated from both sets of MLWFs ($d$-$p$ and effective $e_g$). Thus, even though it is possible to obtain a reasonable MLWF parametrization of the effective $e_g$ bands for all values of $U$, it is not obvious whether a low-energy description of LaMnO$_3$ based only on effective $e_g$ states is always physically reasonable.

The partial “breakdown” of the effective $e_g$ description of LaMnO$_3$ for values of $U$ larger than 5-6 eV also leads to a strong dependence of some MLWF parameters on subtle differences in the underlying Kohn-Sham bandstructure. For example the “crossing” of the mixed in-plane hopping amplitudes, i.e. corresponding to the in-plane hopping between $|3z^2-r^2\rangle$ and $|x^2-y^2\rangle$-type orbitals, that can be seen around $U = 5$ eV in Fig. [4], appears only if orthogonalized atomic orbital are used to evaluate the “+$U$” correction to the GGA energy functional. If instead a projection on non-orthogonal atomic orbitals is used (option “atomic” instead of “ortho-atomic” within QuantumESPRESSO), the resulting MLWF matrix elements do not exhibit this feature.

IV. SUMMARY AND CONCLUSIONS

In summary, we have discussed differences in the MLWF-derived TB parameterization of LaMnO$_3$ that result from different values of the Hubbard $U$ used in the GGA+$U$ calculation from which the MLWFs are obtained. Thereby, we have compared two different ways to represent the important bands around the Fermi energy. First, a $d$-$p$ TB model based on atomic-like Mn($d$) and O($p$) MLWFs, and second, an effective $e_g$ TB model involving only two $e_g$-like Wannier orbitals per Mn.

We have shown that the hopping amplitudes of the $d$-$p$ model are only weakly affected by a variation of $U$, and that the resulting changes in the on-site Hamiltonian matrix elements are consistent with a mean-field approximation to the electron-electron interaction for the corresponding TB Hubbard Hamiltonian. As a result, the TB parameters for the $d$-$p$ model of LaMnO$_3$ are fairly insensitive to variations of $U$ and can therefore be determined accurately without detailed knowledge about the precise value of $U$ for the corresponding $d$ orbitals.

In contrast, the hopping amplitudes for the effective $e_g$ TB parameterization depend strongly on the value of $U$ used in the GGA+$U$ calculation. This is due to pronounced changes in the amount of admixture of O($p$) ligand orbital character in the effective $e_g$ MLWFs, which in turn is due to the large $U$ dependent shifts of the on-site energies of the corresponding atomic orbitals. Furthermore, the $U$ dependence within a mean-field Hubbard Hamiltonian derived from the effective $e_g$ MLWF parameters is distinctly different from the $U$ dependence of the MLWF parameters themselves. The former is determined by the occupations of the effective $e_g$ orbitals and the value of the screened Hubbard interaction in that basis, whereas the latter is determined by the occupations and the value of the screened Hubbard interaction corresponding to atomic-like $d$ states. A determination of suitable TB parameters for an effective $e_g$ model of LaMnO$_3$ therefore requires an accurate knowledge of $U$ in both basis sets. This is particularly important for the determination of the JT coupling strength, which is determined from the on-site splitting within the $e_g$ orbital manifold. This splitting on the other hand is critically affected by the value of $U$ in both the GGA+$U$ calculation and the mean-field Hubbard Hamiltonian.

In addition to the $U$ dependence, we have also analyzed the effect of the staggered JT distortion (“$Q^z$-type”) on the TB parameterization of the $d$-$p$ model. We have found that the JT distortion manifests itself both as a local ligand-/$\gamma$-crystal-field splitting within the $e_g$ orbital manifold, as well as via a pronounced bond-length dependence of the nearest neighbor $d$-$p$ hopping amplitudes. Our results demonstrate that even for the rather localized atomic-like $d$-$p$ MLWFs, the ligand-field effect dominates over the purely electro-static crystal-field effect. Furthermore, we have verified that the changes in the nearest neighbor hopping amplitudes due to the JT distortion are almost fully determined by the resulting change in Mn-O bond length.

A number of more general conclusions can be drawn from the results obtained in this work. It is reasonable to assume that the sensitivity/insensitivity of certain MLWF parameters from the specific value of $U$ used in the GGA+$U$ calculation can be generalized to a general sensitivity/insensitivity from the choice of exchange-correlation functional used in the electronic structure calculation. In the present study, we made use of the similarity between the “+$U$” correction to the GGA functional and the mean-field approximation to the electron-electron interaction in the corresponding model Hamiltonian (assuming of course that the latter is described via a local Hubbard interaction). Using this similarity, the observed trends in the MLWF TB parameters, and the difference between the two different TB models can be explained. The same similarity between DFT and mean-field Hubbard model is not present if the electronic structure is calculated using other “beyond LDA/GGA” methods such as for example self-interaction corrected methods$^{15}$ or the GW approach$^{36}$. In these cases the electronic band-structure should also be compared with the mean-field approximation of an
appropriate TB Hamiltonian. To extract the “bare” or “non-interacting” on-site energies and off-diagonal on-site matrix elements, one has to then subtract a $U$ dependent shift similar to Eq. 6. The corresponding value of $U$ has to be calculated by other means, for example via the recently proposed approach based on constrained random phase approximation.\textsuperscript{57,58}

While the so-obtained TB models will always give an essentially perfect representation of the Kohn-Sham bands for the given reference, it is still important to test whether the corresponding parameterization is also transferable to slightly different configurations, i.e. with different structural distortions and/or magnetic/orbital order. Of course, as shown through the comparison between the effective $e_g$ and the more elaborate $d$-$p$ model for LaMnO$_3$, transferability can always be improved by including more orbitals in the TB basis set.

Finally, we note that in the present work we have focused on how to obtain TB parameters using the DFT Kohn-Sham band-structure as (mean-field) reference. An entirely different, albeit at least equally important, question is whether these bands, calculated using a suitable exchange-correlation functional for a particular system, are indeed a good representation of the real material. However, this question is beyond the scope of the present study and will most likely be the topic of future research for a number of years to come.

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Appendix A: Further details on the $d$-$p$ TB parameterization for cubic LaMnO$_3$

In this appendix we give a more quantitative account of the $d$-$p$ TB parametrization obtained from the MLWFs for simple cubic LaMnO$_3$ and FM order.

There are 2 different hopping parameters between nearest neighbor Mn($d$) and O($p$) states ($t_{eg,p\sigma}$, $t_{t_{2g},p\pi}$) and 4 independent hopping parameters between closest neighbor O($p$) states ($t_{\parallel,p\sigma}$, $t_{\parallel,p\pi}$, $t_{\perp,p\sigma}$, $t_{\perp,p\pi}$) that are allowed by the symmetry of the system. All of these hopping parameters are illustrated in Fig. 10. The corresponding values together with the various on-site energies are summarized in Table II. It can be seen that the minority spin hopping amplitudes corresponding to nearest neighbor $d$-$p$ hopping are slightly larger than for major- ity spin, whereas the opposite is the case for the closest neighbor $p$-$p$ hoppings (except for $t_{\parallel,p\pi}$).

Within the two-center approximation to the linear combination of atomic orbitals (LCAO) method all closest neighbor O($p$)-O($p$) hoppings can be expressed as linear combination of purely $\sigma$- and $\pi$-type hopping parameters, $t(\parallel \sigma\pi)$ and $t(\parallel \pi\sigma)$\textsuperscript{59}. Thereby, $t(\parallel \pi\sigma)$ corresponds directly to $t_{\parallel,p\pi}$ in our notation. Calculating an estimate for $t(\parallel \pi\sigma)$ from each of the remaining MLWF hopping parameters as $(t_{\parallel,p\pi} - 2t_{\parallel,p\sigma})$, $(t_{\parallel,p\pi} - 2t_{\perp,p\pi})$, or

![Image](85x627 to 268x740)

**FIG. 10**: (Color online) Schematic depiction of all closest neighbor Mn-O and O-O hopping amplitudes within the extended $d$-$p$ model of LaMnO$_3$.

![Image](317x394 to 562x512)

**FIG. 11**: (Color online) Band dispersion calculated from the MLWFs (thick line) and from the truncated TB model described in the main text (dots and line); (a): majority spin, (b): minority spin.

**TABLE II**: On-site energies and nearest neighbor Mn-O and O-O hopping amplitudes obtained for the $d$-$p$ MLWFs in the cubic structure with FM order. In addition, the hopping between $t_{2g}$ orbitals along the shortest Mn-Mn distance is also listed. All values are given in eV.

|                        | majority spin | minority spin |
|------------------------|---------------|---------------|
| $\varepsilon[Mn(e_g)]$ | 12.459        | 16.074        |
| $\varepsilon[Mn(t_{2g})]$ | 11.031        | 15.104        |
| $\varepsilon[O(p\sigma)]$ | 9.400         | 9.603         |
| $\varepsilon[O(p\pi)]$ | 9.888         | 10.432        |
| $t_{eg,p\sigma}$ | 1.768         | 1.861         |
| $t_{t_{2g},p\pi}$ | -0.852        | -0.982        |
| $t_{p\sigma,p\sigma}$ | -0.444        | -0.409        |
| $t_{p\sigma,p\pi}$ | 0.306         | 0.265         |
| $t_{p\pi,p\pi}$ | -0.337        | -0.304        |
| $t_{p\pi,p\sigma}$ | -0.014        | -0.092        |
| $t_{2g,t_{2g}}$ | -0.069        | -0.105        |
The hopping integrals: $t_{pp\pi} = 0.873/0.725$ eV, $0.660/0.516$ eV, or $0.627/0.622$ eV, for majority/minority spin, respectively. The spread in these values shows to what extent the approximation of rigid atomic orbitals is not fulfilled within the $d$-$p$ set of MLWFs.

In a previous study, LCAO parameters for manganites were deduced based on a cluster-model analysis of photoemission spectra, leading to the following values for the hopping integrals: $t(p\alpha d) = 1.8$ eV, $t(p\alpha \pi) = 0.9$ eV, $t(p\pi p) = 0.60$ eV, $t(pp\pi) = -0.15$ eV. These values are in reasonable agreement with the values obtained from the MLWFs listed in Table II.

In Figure 10 we show a comparison of the dispersion between the MLWF bands and a 14-band TB model calculated using the parameters given in Table II.

For simplicity of notation we suppress the spin index $\sigma$ here. It should be understood that in general the eigenvalues $\epsilon_k$, the unitary matrices $U(k)$, and the occupation matrix of the MLWFs can be spin-dependent.

We point out that Eq. 6 corresponds to a simplified Hubbard interaction with exchange parameter $J = 0$. While for a more general interaction with $J \neq 0$ the potential shifts would be different, our general conclusion would be unaffected. For simplicity of presentation we therefore only discuss the case $J = 0$.

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* 1 E. Dagotto, Rev. Mod. Phys. 66, 763 (1994).
1 M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
1 E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. 344, 1 (2001).
1 P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
1 W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
1 O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B 39, 1708 (1989).
1 M. S. Hybertsen, Phys. Rev. B 9, 9462 (1974).
1 C. Ederer, C. Lin, and A. J. Millis, Phys. Rev. B 76, 155105 (2007).
1 R. Kováčik and C. Ederer, Phys. Rev. B 81, 245108 (2010).
1 T. F. A. Müller, V. Anisimov, T. M. Rice, I. Dasgupta, and T. Saha-Dasgupta, Phys. Rev. B 57, (1998).
1 W. Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, Phys. Rev. Lett. 89, 167204 (2002).
1 E. Zurek, O. Jepsen, and O. K. Andersen, ChemPhysChem 6, 1934 (2005).
1 F. Lechermann, A. Georges, A. Poteryaev, S. Biermann, M. Posternak, A. Yamashita, and O. K. Andersen, Phys. Rev. B 74, 125120 (2006).
1 I. V. Solovyev, Phys. Rev. B 73, 155117 (2006).
1 J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
1 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
1 A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B 52, (1995).
1 S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1506 (1998).
1 A. D. Becke, J. Chem. Phys. 98, 1372 (1993).
1 N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).
1 I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B 65, 035109 (2001).
1 A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comp. Phys. Comm. 178, 685 (2008).
1 J. M. D. Coey, M. Viret, and S. v. Molnár, Adv. Phys. 48, 167 (1999).
1 J. B. A. A. Elemans, B. V. Laar, K. R. V. d. Veen, and B. O. Loopstra, J. Solid State Chemistry 3, 238 (1971).
25 W. E. Pickett and D. J. Singh, Phys. Rev. B 53, 1146 (1996).
26 S. Satpathy, Z. S. Popović, and F. R. Vukajlović, 76, 960 (1996).
27 H. Sawada, Y. Morikawa, K. Terakura, and N. Hamada, Phys. Rev. B 56, 12154 (1997).
28 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cossoccioni, I. Dabo, et al., J. Phys.: Condens. Matter 21, 395502 (2009).
29 D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
30 P. Norby, I. K. Andersen, E. K. Andersen, and N. Andersen, J. Solid State Chem. 119, 191 (1995).
31 A. Kokalj, Comp. Mater. Sci. 28, 155 (2003), code available from http://www.xcrysden.org/.
32 J. Kanamori, J. Appl. Phys. (Suppl.) 31, 14 (1960).
33 For simplicity of notation we suppress the spin index $\sigma$ here. It should be understood that in general the eigenvalues $\epsilon_k$, the unitary matrices $U(k)$, and the occupation matrix of the MLWFs can be spin-dependent.
34 We point out that Eq. 6 corresponds to a simplified Hubbard interaction with exchange parameter $J = 0$. While for a more general interaction with $J \neq 0$ the potential shifts would be different, our general conclusion would be unaffected. For simplicity of presentation we therefore only discuss the case $J = 0$.
35 M. Aichhorn, L. Pourovskii, V. Vildosola, M. Ferrero, O. Parcollet, T. Miyake, A. Georges, and S. Biermann, Phys. Rev. B 80, 085101 (2009).
36 F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. 61, 237 (1998).
37 F. Aryasetiawan, M. Imada, A. Georges, G. Kotliar, S. Biermann, and A. I. Lichtenstein, Phys. Rev. B 70, 195104 (2004).
38 T. Miyake and F. Aryasetiawan, Phys. Rev. B 77, 085122 (2008).
39 J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).
40 T. Mizokawa and A. Fujimori, Phys. Rev. B 54, 5368 (1996).