Multi-orbital cluster perturbation theory for transition metal oxides

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Abstract

We present an extension of cluster perturbation theory to include many-body correlations associated with local e–e repulsion in real materials. We show that this approach can describe the physics of complex correlated materials where different atomic species and different orbitals coexist. The prototypical case of MnO is considered.

The competition between inter-site hopping and on-site electron–electron repulsion dominates the physics of transition metal oxides [1]. Standard band theory based on the independent particle approach predicts these large gap insulators to be metallic in the paramagnetic phase and fails in reproducing the band width and satellite structures observed in the experiments. Only approaches that augment band theory with true many-body effects such as 3-body scattering theory (3BS) [2–4] and dynamical mean field theory (DMFT) [5, 6] have been able to reproduce the band gap in the paramagnetic state and to describe photoemission data. However, the agreement between experiments and many-body calculations is still far from being fully quantitative [7–9] and different theoretical methods are constantly explored.

In this paper we show that a multi-orbital extension of cluster perturbation theory (CPT) [10, 11] can be applied to the study of quasi-particle excitations in transition metal monoxides. CPT solves the problem of many interacting electrons in an extended lattice by first approaching the many-body problem in a subsystem of finite size—a cluster—and then embedding it within the infinite medium. CPT shares this strategy with other approaches such as the variational cluster approach (VCA) [12, 13] and cellular dynamical mean field theory [14] where the embedding procedure is variationally optimized.

Up to now CPT has been mainly applied to simplified models with one orbital per site and the goal of this paper is to present a general scheme to extend it to multi-orbital systems in order to study the effect of e–e correlations in real complex materials where different atomic species and different orbitals coexist. Here we use MnO as a test case. We restrict ourselves to the paramagnetic phase at zero pressure where, according to single-particle band structure, MnO is metallic with half occupied d-orbitals—a paradigmatic case to study the Mott–Hubbard metal-to-insulator transition. The paper is organized as follows: in section 1 we recall the CPT theory and outline its extension to the many-orbital case; in section 2 we describe how the cluster Green function is calculated in a complex lattice with more than one atomic species and many orbitals per site; section 3 discusses the results obtained for MnO.

1. Multi-orbital CPT

In CPT the lattice is seen as a periodic repetition of identical clusters (figure 1) and the Hubbard Hamiltonian can be partitioned into two terms, an intra-cluster term ($\hat{H}_c$) and an inter-cluster term ($\hat{V}$)

$$\hat{H} = \hat{H}_c + \hat{V}$$

where

$$\hat{H}_c = \sum_{i \alpha} \epsilon_{i \alpha} \hat{n}_{i \alpha} + \sum_{ \beta} \sum_{j \beta} t_{i \alpha j \beta} \hat{c}_{i \alpha}^\dagger \hat{c}_{j \beta} + \sum_{i \alpha \beta} U_{i \alpha \beta} \hat{n}_{i \alpha} \hat{n}_{i \beta}$$

$$\hat{V} = \sum_{ \alpha \beta} \sum_{i \alpha j \beta} t_{i \alpha j \beta} \hat{c}_{i \alpha}^\dagger \hat{c}_{j \beta}$$

Here $\alpha, \beta$ are orbital indices, $\epsilon_{i \alpha}$ are intra-atomic orbital parameters and $t_{i \alpha j \beta}$ hopping terms connecting orbitals centered on different sites. Each atom is identified by the cluster it belongs to (index $l$) and by its position inside the cluster.

#1 For an account of the rich phase diagrams of MnO as a function of temperature and pressure see [21, 25, 26].
Cluster (index \(i\)). The lattice is a collection of \(L \rightarrow \infty\) clusters, each of them containing \(M\) atoms whose position is identified by the vector \(\mathbf{R}_i + \mathbf{r}_c\). Each atom in the cluster is characterized by a set of orbitals \(n_i^{\text{orb}}\) and \(K = \sum_i n_i^{\text{orb}}\) is the total number of sites/orbitals per cluster.

Since in the Hubbard model the e-e Coulomb interaction is on-site, the inter-cluster Hamiltonian \(\hat{V}\) contains only single-particle terms, the many-body part being present in the intra-cluster Hamiltonian \(\hat{H}_L\) only, a key feature for the practical implementation of the method. Having partitioned the Hamiltonian in this way an exact expression involving the resolvent operator \(\hat{G}\) is obtained

\[
\hat{G}^{-1} = z - \hat{H}_c - \hat{V} = \hat{G}_c^{-1} - \hat{V}
\]

and from this

\[
\hat{G} = \hat{G}_c + \hat{G}_c \hat{V} \hat{G}_c.
\]

The one-particle propagator

\[
\mathcal{G}(\mathbf{k}\omega) = \langle \Psi_0 | \hat{c}_{\mathbf{k}\alpha} \hat{G}_{ck}\mathbf{k}\alpha | \Psi_0 \rangle + \langle \Psi_0 | \hat{c}_{\mathbf{k}\alpha} \hat{G}_{ck}\mathbf{k}\alpha | \Psi_0 \rangle
\]

(4)

is obtained by exploiting the transformation from the Bloch to a localized basis

\[
\hat{c}_{\mathbf{k}\alpha} = \frac{1}{\sqrt{M}} \sum_{i,\alpha} C_{i\alpha}^{\mathbf{n}}(\mathbf{k}) e^{-i \mathbf{k} \cdot (\mathbf{R}_i + \mathbf{r}_c)} \hat{c}_{i\alpha}^\dagger
\]

and similarly for \(\hat{c}_{\mathbf{k}\alpha}^\dagger\). Here \(n\) is a band index, \(C_{i\alpha}^{\mathbf{n}}(\mathbf{k})\) are the eigenstate coefficients obtained by a band calculation for a superlattice of \(L\) identical clusters and the summation is over \(M \times L \times K\). We get

\[
\mathcal{G}(\mathbf{k}\omega) = \frac{1}{K} \sum_{i,\alpha,\beta} e^{-i \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} e_{i\alpha}^{\mathbf{n}}(\mathbf{k})^* e_{j\beta}^{\mathbf{n}}(\mathbf{k}) \mathcal{G}_{\text{int}}^{\alpha\beta}(\mathbf{k}\omega)
\]

where \(\mathcal{G}_{\text{int}}^{\alpha\beta}(\mathbf{k}\omega)\) is the superlattice Green function, namely the Fourier transform of the Green function in the local basis

\[
\mathcal{G}_{\text{int}}^{\alpha\beta}(\mathbf{k}\omega) = \frac{1}{L} \sum_{i'} e^{-i \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_{i'})} \mathcal{G}_{\text{int}}^{\alpha\beta}(\omega).
\]

This is the quantity that can be calculated by equation (3), which explicitly becomes:

\[
\mathcal{G}_{\text{int}}^{\alpha\beta}(\mathbf{k}\omega) = \mathcal{G}_{\text{int}}^{\alpha\beta}(\omega) + \sum_{jj'} B_{\text{int}}^{jj'}(\mathbf{k}\omega) \mathcal{G}_{jj'}^{\alpha\beta}(\mathbf{k}\omega)
\]

(7)

where the \(K \times K\) matrix \(B_{\text{int}}^{jj'}(\mathbf{k}\omega)\) is the Fourier transform of \(\mathcal{G} \hat{V}\) involving neighboring sites that belong to different clusters. Its calculation is the key point in the ‘periodization’ process that allows one to go from the cluster Green function to the lattice function. This periodization is conceptually the same as has been described in the original papers where CPT is applied to model systems with one orbital per site [10]; in section 2 we will describe in detail how it is actually calculated in the many-orbital case.

Once the cluster Green function in the local basis \(\mathcal{G}_{\text{int}}^{\alpha\beta}(\omega)\) has been obtained by exact diagonalization, equation (7) is solved by a \(K \times K\) matrix inversion at each \(\mathbf{k}\) and \(\omega\). The quasi-particle spectrum is then obtained in terms of the spectral function \(A(\mathbf{k}\omega)\)

\[
A(\mathbf{k}\omega) = \frac{1}{\pi} \sum_n \text{Im} \mathcal{G}(\mathbf{k}\omega).
\]

(8)

2. Cluster calculation for TM oxides

The valence and first conduction states of TM oxides are described by TM spd and oxygen sp orbitals. The dimer with \(M = 2\) TM atoms and \(K = 10\) d orbitals (figure 1(a)) is the basic unit where we will perform the exact diagonalization.

We recall that the exact diagonalization corresponds to writing the many-body wavefunction as a superposition of Slater determinants that can be built by putting \(N\) electrons of spin up and \(N\) electrons of spin down in \(K\) boxes:

\[
| \Phi_N \rangle = \sum_l C_l | S_l \rangle
\]

(9)

with

\[
| S_l \rangle = e_{\uparrow 1}^\dagger e_{\uparrow 2}^\dagger \cdots e_{\uparrow N}^\dagger e_{\downarrow 1}^\dagger e_{\downarrow 2}^\dagger \cdots e_{\downarrow N}^\dagger | 0 \rangle.
\]

(10)

Each Mn atom brings to the dimer five d electrons (half occupation) and the dimension of the Hilbert space spanned by the Slater determinants is \(n_{\text{conf}} = \left(\frac{K^2}{\text{N}^{27N^2}}\right)^2 = 63504\). We separately solve the problem with \(N, N - 1\) and \(N + 1\) electrons and calculate the dimer Green function using the Lehmann representation, namely

\[
\mathcal{G}_{\text{d}}^{\alpha\beta}(\omega) = \sum_n \frac{\langle \Phi_N | e_{\alpha}^\dagger | \Phi_N^{n+1} \rangle \langle \Phi_{n+1} | e_{\beta} | \Phi_N \rangle}{\omega - (E_{n+1}^+ - E_n^-)} + \sum_n \frac{\langle \Phi_N | e_{\alpha}^\dagger | \Phi_N^{n+1} \rangle \langle \Phi_{n+1} | e_{\beta} | \Phi_N \rangle}{\omega - (E_{n+1}^- - E_n^+)}
\]

(11)

Due to the large dimensions of the matrix to be diagonalized the band-Lanczos algorithm [15] is used to obtain \(\sim 1000\) eigenvalues and eigenvectors \(E_n^{N\pm1}, \Phi_n^{N\pm1}\) for the system with \(N \pm 1\) electrons as well as the ground state \(E_N^0, \Phi_N^0\) for the \(N\) electron system.
The dimer problem that we have described accounts for both hopping and e–e repulsion on the d orbitals of TM atoms and therefore includes a large part of the relevant physics of the interacting system. In particular, since the system is half occupied, we expect the ground state $E_{\text{N}+1}^{\text{N}}$ to be larger than $E_{\text{N}}^{\text{N}}$, with an energy distance growing with $U$. This is promising in view of a gap opening in the extended system.

Notice, however, that this dimer does not represent a partition (in mathematical sense) of the 3D rocksalt lattice and therefore it is not the cluster to be used in the CPT procedure but a non-interacting. In the local basis equation (15) can be solved by performing a matrix inversion. 

$\hat{H}_{\text{c}} = \hat{H}_{\text{c}}^{\text{diag}} + \hat{V}_{\text{AB}}^{\text{AB}}$ (12)

with

$\hat{V}_{\text{AB}}^{\text{AB}} = \sum_{\alpha A\beta B} U_{\alpha A\beta B} \hat{n}_{\alpha A} \hat{c}_{\beta B} + \sum_{\alpha A\beta B} U_{\beta B\alpha A} \hat{c}_{\beta B} \hat{n}_{\alpha A}$

$\hat{H}_{\text{c}}^{\text{diag}} = \hat{H}_{\text{c}}^{\text{AA}} + \hat{H}_{\text{c}}^{\text{BB}}$ (13)

where

$\hat{H}_{\text{c}}^{\text{AA}} = \sum_{\alpha A} \epsilon_{\alpha A} \hat{n}_{\alpha A} + \sum_{\alpha A\beta B} U_{\alpha A\beta B} \hat{n}_{\alpha A} \hat{c}_{\beta B}$

$\hat{H}_{\text{c}}^{\text{BB}} = \sum_{\beta B} \epsilon_{\beta B} \hat{n}_{\beta B} + \sum_{\alpha A\beta B} U_{\beta B\alpha A} \hat{c}_{\beta B} \hat{n}_{\alpha A} + \sum_{\alpha A\beta B} U_{\alpha A\beta B} \hat{n}_{\alpha A} \hat{c}_{\beta B}$ (14)

and a similar expression for $\hat{H}_{\text{c}}^{\text{BB}}$.

We need therefore to embed the dimer into the plaquette, in other words we need to write the cluster Green function in terms of the dimer Green function. This can be done by noticing again that

$\hat{G}^{-1} = z - \hat{H}_c = (\hat{G}^{\text{diag}})^{-1} - \hat{V}_{\text{AB}}^{\text{AB}}$

which results as before in a Dyson-like equation

$\hat{G}^{\text{c}} = \hat{G}^{\text{diag}} + \hat{G}^{\text{diag}} \hat{V}_{\text{AB}}^{\text{AB}} \hat{G}^{\text{c}}$. (15)

In the local basis $\hat{G}^{\text{diag}}$ is block-diagonal and the non-zero elements $\hat{G}_{\text{AA}}^{\text{AA}}, \hat{G}_{\text{BB}}^{\text{BB}}$ are obtained by performing separate exact diagonalizations that include either A or B orbitals: $\hat{G}_{\text{AA}}^{\text{AA}} = \hat{G}_{\text{AA}}^{\text{d}}$ is the dimer Green function of equation (11) while $\hat{G}_{\text{BB}}^{\text{BB}}$ involves only sp orbitals and in the present case is non-interacting. In the local basis equation (15) can be solved by performing a matrix inversion.

$\hat{G}^{\text{c}} = \hat{G}^{\text{diag}} \times (\hat{G}^{\text{diag}} \hat{V}_{\text{AB}}^{\text{AB}})^{-1}$ (16)

or more explicitly

$\hat{G}_{\text{ABC}}^{\text{AB}}(\omega) = \sum_{j \Gamma} \hat{G}_{\text{ABC}}^{\text{AB}}(\omega) \times (\hat{G}^{\text{diag}} \hat{V}_{\text{AB}}^{\text{AB}})^{-1}$. (17)

with indices running over $K = 26$ sites/orbitals of the plaquette (nine spd orbitals on two TM atoms and four sp orbitals on two oxygens).

The knowledge of $\hat{G}_{\text{ABC}}^{\text{AB}}(\omega)$ for the plaquette is essential to obtain the full lattice Green function according to equation (7). In fact, as already mentioned, the 3D rocksalt lattice can be obtained by a periodic replication of $2 \times 2$ plaquettes, connecting them by single-particle hopping terms. In order to implement equation (7) one needs first of all to define for each site $r_J$ in the cluster the position of nearest neighbors $r_{J'}$ and the corresponding lattice vectors $R_{J'}$ connecting the cluster with the neighboring clusters. Then the matrix $B_{\text{abc}}(k\omega)$ is obtained as follows;

$B_{\text{abc}}(k\omega) = \sum_{j \Gamma} t_{\omega r_{J}r_{J'}} e^{-i\kappa J' R_{J} \omega} \hat{G}_{\text{ABC}}^{\text{AB}}(\omega) \delta_{J' \Gamma}$. (18)

Here $t_{\omega r_{J}r_{J'}}$ are the inter-site hopping terms previously defined (equation (2)), obtained in terms of Koster–Slater parameters in the usual way.

We want to stress again that the present formulation is nothing other than the extension of CPT to the case of more orbitals per site, when it is necessary to deal with exceedingly large dimensions of the configuration space. The CPT prescriptions in this case may be rephrased as follows: chose a partition of the lattice Hamiltonian into a collection of non-overlapping clusters connected by inter-cluster hopping; make a further partition inside each cluster defining a suitable collections of sites/orbitals; perform separate exact diagonalizations plus matrix inversion to calculate the cluster Green function in the local basis by equation (17) and, finally, obtain the full lattice Green function in a Bloch basis by adding the cluster–cluster hopping terms according to equation (7).

A final comment on the approximations involved: in the same way as in the standard single-orbital CPT, writing the lattice Green function in terms of Green functions of decoupled subunits amounts to identifying the many-electron states of the extended lattice as the product of cluster few-electron states. In the present case, in particular, choosing the TM dimer as the basic unit we have excluded from the few-electron eigenstates obtained by exact diagonalization the contribution of oxygen sp orbitals, treating the O sp—TM d hybridization by the embedding procedure (equation (17)) and by the periodization (equation (7)). This approximation can be improved by some kind of variational procedure [16, 17], but in any case it interesting to assess its validity per se, for instance by comparing theory and experiments in specific cases. This is what we do in section 3.

3. Application to MnO

The non-interacting contribution to the Hubbard Hamiltonian of equation (1) can be written as a standard tight-binding Hamiltonian in terms of Koster–Slater [18] parameters obtained by a least squares fitting of an ab initio band structure. The parameters obtained by fitting the band structure of MnO calculated in the DFT-LMTO scheme [19] are reported in tables 1 and 2 and give rise to the band structure of figure 2.

When using TB parameters in the Hubbard Hamiltonian we must take care of the double-counting issue: ab initio band
structure, and the TB parameters deduced from it, contain the e–e Coulomb repulsion as a mean field that must be removed before including $U$ as a true many-body term. ‘Bare’ on-site parameters should be calculated by subtracting the mean field value of the Hubbard term, namely

$$E^*_{\alpha\sigma} = E_{\alpha} - \sum_i U_i \langle n_{i\sigma} \rangle.$$  \hspace{1cm} (19)

This definition involves the d occupation inside the cluster used in the exact diagonalization and cancels out the energy shift due to double-counting within each cluster. Notice that $\langle n_{i\sigma} \rangle = \langle n_{i\sigma-\sigma} \rangle$ and $E^*_{\alpha\sigma}$ is independent of spin.

We tested our approach using different $U$ values and we report the results obtained for $U = 9$ eV. This value optimizes the agreement between theory and experiments and is not far from the values reported in the literature, ranging from $U = 6.0$ up to $U = 8.8$ [5, 20–22]. Since we have ignored the orbital dependence of $U$ as well as the e–e repulsion among parallel spins the present value $U = 9$ should be considered as an effective one.

The quasi-particle band structure of MnO is shown in figure 3, where we plot the calculated $k$-resolved spectral function (equation (8)). We notice that the Mn d band that in the absence of correlation (figure 2) crosses the Fermi level is now split into lower and upper Hubbard bands.

It is interesting to look at the effects that the localized d–d interaction has on states of different orbital character. This is shown in figure 4, where the orbital contribution to the total density of quasi-particle states is compared with the results obtained in the single-particle scheme. It appears that not only d states are affected by e–e correlation but sp ones as well. This is particularly evident for oxygen sp states that in the single-particle case contribute to the metallic character and that after the inclusion of e–e correlation are removed from the energy region around the Fermi level and pushed to higher energies. The multi-orbital character of the present scheme then appears to be essential to obtain the correct insulating character.

Figure 5 shows a comparison between the quasi-particle density of states and the experimental results of [20]. We observe that the gap value is well reproduced as well as most of the spectroscopic structures. We do not find evidence of structures below the valence band bottom that are observed in photoemission experiments; this might be due to the reduced number of excited states that are obtained by the Lanczos procedure. We mention, however, that the origin of satellites features in MnO has been somewhat controversial in the literature, being attributed as either intrinsic [20] or extrinsic [23].

Apart from the satellite structure our results are comparable with what has been obtained by the variational cluster approximation [24], in spite of a different choice of the cluster, and by a recent DMFT calculation [5]. In both cases the basic unit contains a single TM atom: either a cluster containing one TM metal and two ligands [24] or a single TM atom embedded in a continuum [5]. Since these two approaches are either variationally optimized (VCA) or self-consistent (DMFT), we may identify in our scheme

### Table 1. On-site Koster–Slater parameters (in eV) for MnO.

|       | $E_{ss}$ (Mn) | $E_{sp}$ (Mn) | $E_{sd}$ (Mn) | $E_{pd}$ (Mn) | $E_{pp}$ (Mn) | $E_{pp}$ (O) | $E_{pd}$ (O) | $E_{sp}$ (O) |
|-------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Mn    | −0.514        | 1.435         | −0.137        | −0.353        | 0.028         | 0.047         | 0.486         | −0.285        |
| O     | 0.0           | 0.0           | 0.0           | 0.0           | 0.0           | 0.0           | −1.074        | −1.243        |

### Table 2. Inter-site Koster–Slater parameters (in eV) for MnO.

|       | $ss_{ss}$ | $pp_{ss}$ | $pp_{sp}$ | $dd_{dd}$ | $dd_{dp}$ | $sp_{sp}$ | $sp_{pd}$ | $pd_{dp}$ |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Mn    | −0.124    | 0.519     | −0.102    | 0.0       | 0.0       | 0.0       | −0.016    | 0.0       |
| O     | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       | 0.0       |
| O     | −0.081    | 0.209     | 0.632     | 0.209     | 0.209     | 0.632     | 0.209     | 0.632     |
the advantage of giving comparable results by a single-shot calculation, thanks, we believe, to our cluster choice. In fact we have assumed as the basic unit a dimer of two TM atoms, where both hopping and e–e repulsion coexist, including, already at the level of the cluster calculation, a large part of the relevant physics of the interacting system. Still we are convinced of the importance of variational optimization and our future goal will be to apply it to our CPT approach.

In conclusion, we have described a method based on a multi-orbital extension of the CPT approach to include on-site interactions in the description of quasi-particle states of real solid systems. The CPT strategy is applied twice, first to identify a partition of the lattice into non-overlapping clusters, and second to calculate the cluster Green function in terms of two local Green functions. This procedure has the advantage of replacing an unmanageable exact diagonalization by two separate diagonalizations followed by a matrix inversion. The non-interacting part of the lattice Hamiltonian is described in terms of tight-binding parameters deduced by least-squares fitting of an \textit{ab initio} single-particle band structure, including all the relevant orbitals (no minimal basis set is introduced). For our purposes, since we do not need any real-space expression of the single-particle wavefunctions, this tight-binding parametrization is fully equivalent to a representation in terms of maximally localized Wannier functions. We have applied this method to MnO as a test case and using a single value of Hubbard $U$ we have found a reasonable agreement with experimental data and with theoretical results obtained by different methods. The approach is well suited to treat local correlation in complex materials.

References

[1] Imada M, Fujimori A and Tokura Y 1998 Rev. Mod. Phys. \textbf{70} 1039
[2] Manghi F, Calandra C and Ossicini S 1994 Phys. Rev. Lett. \textbf{73} 3129
[3] Manghi F, Bellini V and Arcangeli C 1997 Phys. Rev. B \textbf{56} 7149
[4] Monasta S, Manghi F, Rozzi C A, Arcangeli C, Wetti E, Neff H-J, Greber T and Osterwalder J 2002 Phys. Rev. Lett. \textbf{88} 236402
[5] Thunström P, Di Marco I and Eriksson O 2012 Phys. Rev. Lett. \textbf{109} 186401
[6] Kuneš J, Anisimov V I, Skornyakov S L, Lukoyanov A V and Vollhardt D 2007 Phys. Rev. Lett. \textbf{99} 156404
[7] Sánchez-Barriga J \textit{et al} 2009 Phys. Rev. Lett. \textbf{103} 267203
[8] Sánchez-Barriga J \textit{et al} 2010 Phys. Rev. B \textbf{82} 104414
[9] Sánchez-Barriga J \textit{et al} 2012 Phys. Rev. B \textbf{85} 205109
[10] Sénéchal D 2012 Cluster Perturbation Theory (Springer Series in Solid-State Sciences vol 171) (Berlin: Springer) chapter 8, pp 237–69
[11] Gros C and Valentí R 1993 Phys. Rev. B \textbf{48} 418
[12] Potthoff M, Aichhorn M and Dahnken C 2003 Phys. Rev. Lett. \textbf{91} 206402
[13] Potthoff M 2003 \textit{Eur. Phys. J. B} \textbf{32} 245110
[14] Kanchcharla S S, Kyung B, Sénéchal D, Civelli M, Capone M, Kotliar G and Tremblay A-M S 2008 Phys. Rev. B \textbf{77} 184516
[15] Lehoucq R B, Sorensen D C and Yang C 1998 \textit{ARPACK Users’ Guide: Solution of Large-scale Eigenvalue Problems with Implicitly Restarted Arnoldi Methods} (Philadelphia, PA: SIAM)
[16] Daghofer M, Moreo A, Riera J A, Arrigoni E, Scalapino D J and Dagotto E 2008 Phys. Rev. Lett. \textbf{101} 237004
[17] Daghofer M, Nicholson A and Moreo A 2012 Phys. Rev. B 85 184515
[18] Slater J C and Koster G F 1954 Phys. Rev. 94 1498
[19] Andersen O K 1975 Phys. Rev. B 12 3060
[20] van Elp J, Potze R H, Eskes H, Berger R and Sawatzky G A 1991 Phys. Rev. B 44 1530
[21] Tomczak J M, Miyake T and Aryasetiawan F 2010 Phys. Rev. B 81 115116
[22] Sakuma R and Aryasetiawan F 2013 Phys. Rev. B 87 165118
[23] Fujimori A, Kimizuka N, Akahane T, Chiba T, Kimura S, Minami F, Siratori K, Taniguchi M, Ogawa S and Suga S 1990 Phys. Rev. B 42 7580
[24] Eder R 2008 Phys. Rev. B 78 115111
[25] Yoo C S et al 2005 Phys. Rev. Lett. 94 115502
[26] Kuneš J, Lukoyanov A V, Anisimov V I, Scalettar R T and Pickett W E 2008 Nature Mater. 7 198