Effective Hamiltonian for transition-metal compounds. Application to Na$_3$CoO$_2$

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We describe a simple scheme to construct a low-energy effective Hamiltonian $H_{\text{eff}}$ for highly correlated systems containing non-metals like O, P or As (O in what follows) and a transition-metal (M) as the active part in the electronic structure, eliminating the O degrees of freedom from a starting Hamiltonian that contains all M d orbitals and all non-metal p orbitals. We calculate all interaction terms between d electrons originating from Coulomb repulsion, as a function of three parameters ($F_0$, $F_2$ and $F_4$) and write them in a basis of orbitals appropriate for cubic, tetragonal, tetrahedral or hexagonal symmetry around M. The approach is based on solving exactly (numerically if necessary) a $MO_6$ cluster containing the transition-metal atom and its $n$ nearest O atoms (for example a Co$_4$O$_8$ cluster in the case of the cobaltates, or a Cu$_4$O$_8$ cluster in the case of the cuprates, in which $n$ depends on the number of apical O atoms), and mapping them into many-body states of the same symmetry containing d holes only. We illustrate the procedure for the case of Na$_3$CoO$_2$. The resulting $H_{\text{eff}}$, including a trigonal distortion $D$, has been studied recently and its electronic structure agrees well with angle-resolved photoemission spectra [A. Bourgeois, A. A. Aligia, and M. J. Rozenberg, Phys. Rev. Lett. 102, 066402 (2009)]. Although $H_{\text{eff}}$ contains only 3d $t_{2g}$ holes, the highly correlated states that they represent contain an important amount not only of O 2p holes but also of 3d $e_g$ holes. When more holes are added, a significant redistribution of charge takes place. As a consequence of these facts, the resulting values of the effective interactions between $t_{2g}$ states are smaller than previously assumed, rendering more important the effect of $D$ in obtaining only one sheet around the center of the Brillouin zone for the Fermi surface (without additional pockets).

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I. INTRODUCTION

In condensed matter physics, several materials containing transition metal atoms (M) and oxygen have attracted great interest, for example the superconducting cuprates, manganites with high magnetoresistance, and more recently cobaltates and Fe pnictides. In the latter, the role of O in the electronic structure is replaced by either P or As. The electronic structure of these systems near the Fermi energy is determined essentially by some d orbitals of M and some 2p orbitals of O (or 3p, 4p for P, As in the pnictides), while the rest of the orbitals and elements play the role of reservoirs of charge. In most of these systems, strong correlations at M play an essential role. For example, while first-principles calculations predict that the undoped cuprates like La$_2$CuO$_4$ are non-magnetic metals, they are in fact antiferromagnetic insulators. In the cobaltates Na$_3$CoO$_2$, first-principles calculations predicted a Fermi surface with six prominent hole pockets along the $\Gamma - K$ direction, which are absent in measured angle-resolved photoemission spectra.

Because of the presence of strong correlations, numerical methods which treat exactly the interactions in a small cluster of the system have led to a considerable advance in the understanding of these materials. Due to the exponential increase of the size of the Hilbert space, it is highly desirable that the set of relevant orbitals included in these numerical studies is the smallest possible. For the cuprates, low-energy reduction procedures that eliminate the O degrees of freedom, simplifying the problem to an effective one-band one, have been very successful, in spite of the fact that doped holes enter mainly at O atoms (optical properties related with O atoms were calculated using these one-band models). Approximate treatments of the problem are also expected to lead to more accurate results when applied to the effective model, because the construction of the latter begins with an exact treatment of the local interactions at M. For example a slave-boson mean-field treatment applied to the three-band model (with Cu and O orbitals) for the cuprates predicts a metal for the most accepted parameters, whereas the same treatment on the one-band effective model gives a gap that agrees with experiment.

The main idea behind the construction of an effective one-band model for the cuprates, proposed by Zhang and Rice starts from the exact solution of a CuO$_4$ cluster with one and two holes added to the vacuum in which the Cu atoms are in the 3d$^{10}$ configuration and the O atoms in the 2p$^6$ one. For two holes, the ground state is a singlet formed essentially by one hole in the 3d$x^2-y^2$ orbital of Cu and one hole in the linear combination of 2p orbitals of the nearest-neighbor O sites, with
the same symmetry. Mapping this singlet state onto the corresponding state of a one-band model leads to the usual Hubbard or $t-J$ models. Using a mapping involving non-orthogonal singlets, Zhang has shown that in a particular case, the mapping is exact. More systematic derivations lead to additional terms of smaller magnitude like three-site terms, which might be important for superconductivity. Three-site terms play also an important role in effective models for vanadates or other systems with $t_{2g}$ electrons. Triplet states can be included perturbatively.

Second-order perturbation theory in the Cu-O hopping applied to the three-band model for the cuprates leads to an interaction between Cu spins and O holes. Adding to it the superexchange interaction between Cu spins one has the so-called spin-fermion model. Similar derivations have been made for NiO, doped Y$_2$BaNiO$_5$, and other perovskites. An important point is that the parameters of the model are improved if instead of taking the values that result from perturbation theory, they are obtained fitting the energy levels of a CuO$_2$ cluster in the case of the cuprates or a NiO$_6$ cluster in the case of the nickelates. The Cu and O photoemission spectra for the cuprates obtained from the resulting spin-fermion model are practically identical to those of the three-band Hubbard model but required a much less computational effort for the same cluster.

The above mentioned results suggest that in general the key for constructing a low-energy Hamiltonian is to solve exactly a cluster $MO_n$ containing the transition metal atom and the O atoms of its neighborhood. In fact, the cell-perturbation method used extensively in the cuprates exploits this idea: it divides the system into orthogonal cells containing one atom each, using appropriate O Wannier functions centered at $M$, solves exactly each cell, writes the Hamiltonian in the basis of the resulting eigenstates, retains only the relevant low-energy eigenstates, and includes the rest perturbatively. However, while in the cuprates the O Wannier functions can be easily constructed and the Hilbert space of the cluster involves only a few eigenstates, in the general case, as we show below, at least ten d and p orbitals are involved. In this case, the size of the Hilbert space of the $MO_n$ cluster is $4^{10}$ and (except for favorable cases) the matrices should be solved numerically. For O rich systems, we propose to neglect the overlap between different O clusters and retain only the most important terms in the resulting effective model $H_{\text{eff}}$ (the effect of this overlap in the cuprates was calculated in Ref. [12]). A discussion of the effect of the overlap in the cobaltates is contained in Section. Similarly to the above mentioned ideas, the most relevant parameters are obtained from a fit of the low-energy levels of the original $M-O$ multiband model $H$ (obtained numerically) and those of $H_{\text{eff}}$ in the $MO_n$ cluster. An additional calculation is required to obtain effective hoppings between clusters.

An essential ingredient of the original multiband model $H$ is the part of it which contains the interactions between 3d electrons $H_I$. While it is straightforward to obtain it using known results of atomic physics, the derivation is lengthy and it seems that only simplified forms were used so far for research in these systems. For example in a recent study of Fe pnictides, a simplified expression derived previously was used. While the form of $H_I$ is well known when either only $e_g$ orbitals or only $t_{2g}$ orbitals are important, the correct expressions were not always used. In the general case, new terms appear which were not discussed before. One of the goals of this work is to present the complete $H_I$. We believe that this will be useful for future theoretical work on strongly correlated systems of transition metals, when the relevant orbitals cannot be restricted to either $e_g$ or $t_{2g}$ only.

In this work, we outline the derivation of $H_{\text{eff}}$ as described above. While for the sake of clarity we consider that the relevant non-metal orbitals are the 2p of O atoms, they could also be the 3p of P or 4p of As in the case of the Fe pnictides. We consider in detail the specific example of the cobaltates Na$_x$CoO$_2$. A brief description of this case, together with a dynamical-mean field treatment of $H_{\text{eff}}$ to study the electronic structure and Fermi surface of the system was published before.

In Section II, we describe the construction of the multiband model containing both M 3d (or 4d) and O 2p (or 4p) electrons, including all the d-d interaction terms. In Section III, we derive the effective Hamiltonian $H_{\text{eff}}$, which contains only effective d operators but no O ones. While some considerations are valid for the general case, the explicit construction is done for the case of Na$_x$CoO$_2$. Section IV is a summary and discussion.

II. THE STARTING HAMILTONIAN

As in many transition-metal compounds, we assume that the essential part of the electronic structure consists of the d electrons of the transition-metal atoms and the p electrons of the O (or other non-metal) atoms. An example in which only one d orbital is relevant is the three-band Hubbard model for the cuprates with parameters determined by constrained-density-functional theory. The Hamiltonian contains d-p hopping terms and interactions. The most important of the latter are the interaction terms among the d electrons.

A. The interactions inside the d shell

Here we can consider only one transition-metal atom and drop the site index for simplicity. The part of the Hamiltonian that contains the interaction among the 10 d spin-orbitals is:

$$H_I = \frac{1}{2} \sum_{\lambda\mu\nu\rho} V_{\lambda\mu\nu\rho} t^d_\lambda d^+_\mu d_\rho d^d_\nu,$$  \hspace{1cm} (1)
where \( d_{\pm} \) creates an electron or a hole at the spin-orbital \( \lambda \) (\( H \) is invariant under an electron-hole transformation) and

\[
V_{\lambda \mu \nu \rho} = \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi(\mathbf{r}_1) \varphi(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi(\mathbf{r}_1) \varphi(\mathbf{r}_2),
\]

(2)

where \( \varphi(\mathbf{r}_1) \) is the wave function of the spin-orbital \( \lambda \).

In the basis of given angular momentum and spin projections (\( \lambda \equiv m\lambda, \sigma \lambda \)), the orbital part of the wave functions can be written as \( R(r)Y_{\ell m}^{m}(\theta, \varphi) \), where \( R \) is the radial part and \( Y_{\ell m}^{m} \) is a normalized spherical harmonic. Using standard methods of atomic physics, one obtains

\[
V_{\lambda \mu \nu \rho} = \delta(\sigma \lambda, \sigma \mu) \delta(\sigma \rho, \sigma \nu) \delta(m \lambda + m \mu, m \nu + m \rho) \\
\times \sum_{k=0}^{\infty} c^k(2m \lambda, 2m \mu)c^k(2m \rho, 2m \nu) \cdot R^k,
\]

(3)

with

\[
c^k(lm, l'm') = \sqrt{\frac{2}{2k+1}} \\
\times \int_{0}^{\pi} P_{km-m'}(\cos \theta)P_{k'm'}(\cos \theta)\sin \theta d\theta \\
R^k = e^2 \int_{0}^{r_1} \int_{r_2}^{r_1} R(r_1)R(r_2) r_1^2 r_2^2 d\mathbf{r}_1 d\mathbf{r}_2,
\]

(4)

where \( P_{k}(\cos(\theta)) \) is a normalized Legendre function and \( r_\mu (r_\sigma) \) is the smaller (larger) between \( r_1 \) and \( r_2 \). The values of \( c^k \) that are needed are tabulated in Ref. \( 46 \).

To remove uncomfortable denominators, one defines the three free parameters as \( F_0 = R^0 \), \( F_2 = R^2 / 49 \) and \( F_1 = R^5 / 441^{38,46} \).

In the presence of a cubic crystal field (point group \( O_h \)) or some other local symmetry (for example point groups \( D_{3d}, D_{4h}, C_{4v}, T_d \)), it is more convenient to change from the basis of operators with definite angular momentum projection \( d_{\pm \sigma} \) to that of irreducible representations of the point group (\( e_g \) and \( t_{2g} \) for \( O_h \)) orbitals using

\[
d_{\pm 2} = \frac{1}{\sqrt{2}} ( d_{x^2-y^2, \sigma} \pm id_{xy, \sigma} ), \\
d_{\pm 1} = \frac{1}{\sqrt{2}} ( d_{zx, \sigma} \pm id_{yz, \sigma} ), \\
d_{0 \sigma} = d_{3z^2-r^2, \sigma}.
\]

(5)

In cubic symmetry, \( d_{x^2-y^2, \sigma} \) and \( d_{3z^2-r^2, \sigma} \) correspond to \( e_g \) symmetry and the remaining creation operators transform as the \( t_{2g} \) irreducible representation. Each term of the resulting \( H_1 \) contains two creation and two annihilation operators. \( H_1 \) can be divided in four parts \( H_n \) according to the number \( n \) of \( e_g \) operators present in each term. There is no term with only one \( t_{2g} \) operator and therefore \( H_3 \) is absent. \( H_4 \) is usually enough to describe \( e_g \) holes in late transition metals, such as nickelates,\(^{33}\) while \( H_0 \) contains the relevant interaction terms for early transition metals with a few \( t_{2g} \) electrons, such as titanates\(^{35}\) or rutenates.\(^{32}\) The sums over \( \alpha (\beta, \gamma) \) below run over the indices of \( e_g (t_{2g}) \) operators. The interaction can be written as

\[
H_1 = H_4 + H_0 + H_1 + H_2,
\]

(6)

with

\[
H_0 = U \sum_{\alpha} n_{\alpha, \uparrow} n_{\alpha, \downarrow} \\
+ \frac{U - 2J_e}{2} \sum_{\alpha \neq \beta} \sum_{\gamma} n_{\alpha, \sigma} n_{\beta, \sigma} n_{\gamma, \sigma},
\]

(7)

\[
H_1 = \lambda \sum_{\alpha \neq \beta} \frac{3}{(d_{x^2-y^2, \sigma} d_{xx, \sigma} + H.c.)} \\
\times (d_{xy, \sigma} d_{yz, \sigma} + H.c.) \\
- \sqrt{3} (d_{x^2-y^2, \sigma} d_{xy, \sigma} + H.c.) (d_{xy, \sigma} d_{yz, \sigma} + H.c.) \\
- 2 (d_{x^2-y^2, \sigma} d_{xy, \sigma} + H.c.) (d_{xy, \sigma} d_{yz, \sigma} + H.c.) \\
+ (d_{3z^2-r^2, \sigma} d_{xx, \sigma} + H.c.) (d_{xy, \sigma} d_{yz, \sigma} + H.c.) \\
+ (d_{3z^2-r^2, \sigma} d_{yz, \sigma} + H.c.) \\
\times (d_{xy, \sigma} d_{xx, \sigma} + H.c.),
\]

(9)

\[
H_2 = (U - 2J_e) \sum_{\alpha \neq \beta} n_{x^2-y^2, \sigma} n_{xx, \sigma} + n_{yz, \sigma} \\
+ (U - 2J_e) \sum_{\alpha \neq \beta} n_{x^2-y^2, \sigma} n_{xy, \sigma} + n_{yz, \sigma}
\]

(8)
where $S_{\xi} = \sum_{\chi'} \sigma_{\chi \xi} \sigma_{\chi' \xi'} / 2$ is the spin of the orbital $\xi$. The interorbital repulsion between these orbitals is related to the former by $U' = U - 2J_e$, due to the spherical symmetry of $H_I$. For the same reason, $J'_I = J_I$, the energy for transfer of intraorbital pairs (like $d_{\chi \sigma} ^{\dagger} \rightarrow d_{\chi \sigma} ^{\dagger} \rightarrow d_{\chi \sigma} ^{\dagger}$). The remaining terms, with prefactor proportional to $\lambda$, involve more than two orbitals.

The parameters $F_2$ and $F_4$ related to the $J_e$ and $\lambda$ are expected to be very weakly screened in the solid as compared to the free atom and have little variation among the 3d series. For example, a fit of the lowest atomic energy levels (given in Ref 42) of $V^{+3}$ and Ni give nearly the same values $F_2 = 1300$ cm$^{-1}$ = 0.16 eV, and $F_4 = 88$ cm$^{-1}$ = 0.011 eV within 2%. This results in an exchange energy $J_e = 0.81$ eV for $e_g$ electrons and $J_e = 0.70$ eV for $t_{2g}$ ones. This implies for example that for two $e_g$ holes in cubic symmetry (as in Ni$^{+2}$), the triplet ground state is separated by the excited singlet by $2J_e \simeq 1.6$ eV if covalency can be neglected. Recent calculations in 3d metals suggest that the exchange interactions are reduced in $30\%$ in comparison with the atomic values. This reduction is also assumed in Ce compounds.

In contrast to $F_2$ and $F_4$, $F_0$ determines the intra-orbital repulsion $U$ is significantly screened in the solids and is difficult to determine theoretically. For the cuprates $U \simeq 10$ eV has been estimated by constrained-density-functional calculations and it decreases to the left of the periodic table inside the 3d series, because the 3d orbitals are more extended as a consequence of the smaller nuclear charge. The value of $U$ can be extracted from optical experiments.

B. The full M-O Hamiltonian

Since usually there are only a few O holes present, it turns out to be more convenient to write the Hamiltonian in terms of hole operators (which annihilate electrons) acting on the vacuum state in which all transition-metal (M) ions are in the $d^{10}$ configuration and the O (or P, As) ions are in the $p^6$ one. The most important of the remaining terms of the starting Hamiltonian are the Co-O ($t_0^{\delta}$ below) and O-O hopping ($\tau_{kij}^{\eta}$), parameterized as usual, in terms of the Slater-Koster parameters. We include a cubic crystal field splitting $\epsilon_{eg} - \epsilon_{eg} = 10Dq$ at the metal sites. Extension to tetragonal, tetrahedral or hexagonal crystal fields is straightforward, while other symmetries may require a change in the chosen basis for the d orbitals.

The Hamiltonian takes the form

$$H = \sum_{i,\alpha \neq \alpha} \epsilon_{\alpha \gamma} d_{i\alpha \sigma} ^{\dagger} d_{i\alpha \sigma} + \sum_{\beta < \beta} \epsilon_{\beta \gamma} d_{i\beta \sigma} ^{\dagger} d_{i\beta \sigma} + \sum_{j \neq \gamma} \epsilon_{\gamma j} ^{\dagger} P_{j\eta} \sigma P_{j\eta} \sigma + \sum_{j \neq \delta, \eta} t_{k\gamma} ^{\eta} \tau_{k\delta \eta} \sigma d_{i\delta \sigma} + H.c.)$$

Here $P_{j\eta} \sigma$ creates a hole on the O 2p orbital $\eta$ at site $j$ with spin $\sigma$. The operator $d_{i\xi \sigma} ^{\dagger}$ has an analogous meaning for the M d orbitals at site $i$. The interactions at this site $H_i$ has the form of Eqs. (5) to (11) with the site index $i$ added to the subscripts of the $d$ operators. The subscript $i + \delta$ in $P_{j+i\delta \eta}$ labels the different O atoms in the immediate neighborhood of the M atom at $i$ (their nearest neighbors in highly symmetric structures).

We have neglected here for simplicity the on-site Coulomb repulsion at O sites $U_p$ and the M-O interatomic repulsion $U_{pd}$. Experience in the cuprates indicates that this is not very important while it complicates the numerical treatment of the basic $MO_n$ cluster (see below). $U_{pd}$ can be incorporated easily and is
important in the formation of excitons\textsuperscript{14,15,16} and in charge-transfer instabilities\textsuperscript{22} which are beyond the scope of this work.

III. CONSTRUCTION OF THE EFFECTIVE HAMILTONIAN

A. Diagonalization of one cell

The solution of the basic MO\textsubscript{n} cluster containing a transition-metal atom and the O atoms in its neighborhood is greatly simplified for \( U_p = 0 \), since among the \( 3n \) O orbitals, only some linear (bonding) combinations with the same symmetry as the d orbitals hybridize with them, while the remaining (non-bonding) orbitals decouple. The presence of \( U_p \) would introduce scattering between the bonding orbitals and the non-bonding ones and does not modify the essential physics\textsuperscript{13} particularly for low or moderate number of O holes.

For a perfect MO\textsubscript{6} octahedra (point group \( O_h \)) with \( M \) at the origin of coordinates and the O atoms at \( \delta = \pm x, \pm y, \pm z \), there are 13 O 2p non-bonding orbitals and the 5 bonding O 2p orbitals are (spin indices and site index \( i \) are omitted for simplicity)

\[
\begin{align*}
p_{x^2-y^2} &= \frac{1}{2} (p_{x,x} - p_{-x,x} - p_{y,y} + p_{-y,y}), \\
p_{3z^2-r^2} &= \frac{1}{2\sqrt{3}} (2p_{z,z} - 2p_{-z,z} - p_{x,x} + p_{-x,x} - p_{y,y} + p_{-y,y}), \\
p_{xy} &= \frac{1}{2} (p_{x,y} - p_{-x,y} + p_{y,x} - p_{-y,x}), \\
p_{yz} &= \frac{1}{2} (p_{y,z} - p_{-y,z} + p_{z,y} - p_{z,y}), \\
p_{zx} &= \frac{1}{2} (p_{z,x} - p_{-z,x} + p_{x,z} - p_{x,z}) \quad (13)
\end{align*}
\]

Writing the hopping terms in this basis, and using the Slater-Koster formulas\textsuperscript{50} the bonding part of the Hamiltonian \( (12) \) in the MO\textsubscript{6} cluster takes the form

\[
H_b = \sum_{\alpha < \beta, \sigma} \{ \epsilon_{\alpha\beta} d^{\dagger}_{\alpha\sigma} d_{\beta\sigma} + |\epsilon_O - 2t_p| p^{\dagger}_{\alpha\sigma} p_{\beta\sigma} \\
- \sqrt{3} (pd\sigma) (d^{\dagger}_{\alpha\sigma} p_{\beta\sigma} + H.c.) \} \\
+ \sum_{\beta \in \ell_2 g, \sigma} \{ \epsilon_{\ell_2 g} d^{\dagger}_{\beta\sigma} d_{\beta\sigma} + |\epsilon_O + 2t_p| p^{\dagger}_{\beta\sigma} p_{\beta\sigma} \\
+ 2pd\sigma (d^{\dagger}_{\beta\sigma} p_{\beta\sigma} + H.c.) \} + H_1, \quad (14)
\]

where in terms of Slater-Koster parameters \( t_p = -[(pp\sigma) - (pp\pi)]/2 \).

If the cluster is elongated along the \( z \) direction or O atoms at \( \pm z \) are missing, in general one should consider two different 2p orbitals that hybridize with \( d_{3z^2-r^2} \). The first can be chosen as \((-p_{x,x} + p_{-x,x} - p_{y,y} + p_{-y,y})/2\), while the second is \((p_{z,z} - p_{-z,z})/\sqrt{2}\) for \( D_{4h} \) symmetry with obvious changes in absence of one or both O atoms at \( \pm z \). Similarly two independent states that hybridize with \( d_{yz} \) in \( D_{4h} \) symmetry are \((p_{y,y} - p_{-y,y})/\sqrt{2}\) and \((p_{x,y} - p_{x,y})/\sqrt{2}\) and the same changing \( y \) by \( x \). The hopping terms that involve these (at most 8) O orbitals can be easily constructed using Ref. 50.

In any case, the size of the Hilbert space of \( H_b \) with at most \( 13 \times 2 \) spin-orbitals is small enough to allow us to obtain its low-energy eigenstates numerically by the Lanczos method\textsuperscript{23}.

B. The cobaltates

For the case of Na\textsubscript{2}CoO\textsubscript{2}, we have solved numerically a CoO\textsubscript{6} cluster using the Hamiltonian \( H_b \) given by Eq. (11), mapped the corresponding states into those of an isolated Co atom with the corresponding charge to calculate effective on-site interactions, and calculated the hopping between effective Co sites mediated by O. The parameters of \( H_b \) were taken from fits to optical experiments\textsuperscript{24} as described below. We have neglected the trigonal distortion and assumed \( O_h \) symmetry in the cluster. As shown above, this assumption reduces the size of the relevant Hilbert space and in addition simplifies significantly the mapping between states of \( H \) and \( H_{\text{eff}} \), because as we shall see, the symmetry identifies unambiguously the correspondence between states of both Hamiltonians. The effective trigonal crystal-field splitting \( \Delta = 3D \sim 0.3 \text{ eV} \) was given by quantum-chemistry configuration-interaction calculations\textsuperscript{25} As we discuss in more detail below, this is one order of magnitude smaller than the effective cubic crystal-field splitting and does not affect our main findings.

Since Co\textsuperscript{3+} is in a 3d\textsuperscript{7} configuration (3 holes in the d shell), the states of the CoO\textsubscript{6} cluster with \( n + 1 \) holes are represented by a Co\textsuperscript{3+} ion in \( H_{\text{eff}} \). The most relevant values of \( n \) for Na\textsubscript{2}CoO\textsubscript{2} are 4 (the formal valence of Co for \( x = 0 \)) and 3 (formal valence for the fully doped compound), but it is important to consider also \( n = 5 \) to calculate the effective interactions, as we shall show. As the vacuum at one site for the effective Hamiltonian with only Co sites, it is convenient to chose the Co\textsuperscript{3+} 3d\textsuperscript{6} configuration, occupied with the four \( e_g \) states. Thus Co\textsuperscript{4+} has one \( t_{2g} \) hole and Co\textsuperscript{5+} has two \( t_{2g} \) holes. Therefore, one expects that the interacting part of \( H_{\text{eff}} \) at each site has the same form as \( H_b \) [Eq. (8)] but now \( U''_g \neq U - 2J_{eff} \), and \( J'_{g} \neq J_{eff} \) because the cubic crystal-field \( e_{t_{2g}} - e_{e_g} = 10Dq \) reduces the symmetry from that of the full rotational group to \( O_h \):

\[
H_{1g}^{\text{eff}} = U_{\text{eff}} \sum_{\beta} \tilde{n}_\beta \tilde{n}_\beta + \frac{1}{2} \sum_{\gamma \neq \beta, \sigma, \sigma'} (U_{\text{eff}}' \tilde{n}_\gamma \tilde{n}_\beta + J_{\text{eff}} \tilde{n}_\gamma \tilde{d}_\beta^{\dagger} \tilde{d}_\sigma \tilde{d}_\sigma^{\dagger} \tilde{d}_\beta)
\]
The resulting eigenstates and energies of the starting Hamiltonian corresponding eigenstates of the CoO cluster with 4, 5 and 6 holes are well represented by the low-energy eigenstates of the CoO cluster Hamiltonian. It turns out that the low-energy eigenstates of the CoO cluster Hamiltonian of Table I corresponds to the lowest energy levels of the core hole. In comparison with the present calculations,

| Symmetry | eigenstate | \( E - C + \mu_s N \) | \( E \) (eV) | \( d \) \( e_g \) | \( d \) \( t_{2g} \) | \( p \) \( e_g \) | \( p \) \( t_{2g} \) |
|----------|------------|----------------|-------------|----------------------------|
| \( A_{1g}^0 \) | \( 0 \) | 0 | 8.141 | 3.03 | 0.02 | 0.94 | 0 |
| \( T_{2g}^0 \) | \( \vec{d}_{x^2-y^2}|0\rangle \) | 0 | 17.271 | 2.67 | 0.91 | 1.29 | 0.14 |
| \( A_{1g}^0 \) | \( \sum_{\beta} \vec{d}_{\beta y}^\dagger \vec{d}_{\beta y}|0\rangle \) | \( U_{\text{eff}} + 2J'_\text{eff} \) | 28.609 | 2.41 | 1.46 | 1.48 | 0.66 |
| \( E^0 \) | \( \frac{1}{\sqrt{2}}(\vec{d}_{x^2-y^2}^\dagger \vec{d}_{x^2-y^2}^\dagger \vec{d}_{y^2-x^2}^\dagger \vec{d}_{y^2-x^2}^\dagger)|0\rangle \) | \( U_{\text{eff}} - J'_\text{eff} \) | 28.096 | 2.40 | 1.51 | 1.57 | 0.52 |
| \( T_{2g}^0 \) | \( \sum_{\beta} \vec{d}_{\beta y}^\dagger \vec{d}_{\beta y} \vec{d}_{\beta y}^\dagger \vec{d}_{\beta y}|0\rangle \) | \( U_{\text{eff}} + J_{\text{eff}} \) | 28.028 | 2.39 | 1.54 | 1.56 | 0.51 |
| \( T_{1g}^0 \) | \( \vec{d}_{x^2-y^2}^\dagger \vec{d}_{x^2-y^2}|0\rangle \) | \( U_{\text{eff}} - J_{\text{eff}} \) | 27.320 | 2.34 | 1.63 | 1.65 | 0.37 |

This is the effective Hamiltonian at one site, except for an unimportant constant \( C \) and chemical potential term \(-\mu N\), with \( N = \sum_{\beta \sigma} \bar{n}_{\beta \sigma} \). The tilde above the operators is to remind us that the effective operators \( \vec{d}_{\beta \sigma}^\dagger \) entering Eq. (15) are different from those entering the starting Hamiltonian \( H \), as discussed in more detail below. The resulting eigenstates and energies of \( H_{\text{eff}} \) at one site, are listed in the first three columns of Table I. It turns out that the low-energy eigenstates of the CoO cluster with 4, 5 and 6 holes are well represented by the corresponding eigenstates of \( H_{\text{eff}}^f \). The fourth column of Table I corresponds to the lowest energy levels of the cluster Hamiltonian \( H_b \) in each symmetry sector, using parameters determined previously by us\(^{54}\) from a fit of polarized x-ray absorption spectra of \( \text{Na}_x\text{CoO}_2 \) to the results of a CoO cluster with 4 and 5 holes including the core hole. In comparison with the present calculations, the previous ones were simplifying the exchange, transfer of intraorbital pairs, and terms proportional to \( \lambda \) of \( H_1 \) and \( H_2 \), because their magnitude is smaller than the energy of the crystal-field excitations related with these terms. The effect of hybridization increases the splitting between \( t_{2g} \) and \( e_g \) orbitals to more than 3 eV \( \gg F_2, F_4 \). The effect of the neglected terms is discussed in the next subsection. The parameters of \( H_b \) in eV are

\[
F_0 = 3.5, \quad F_2 = 0.2, \quad F_4 = 0.006, \\
(pd\pi) = -\sqrt{3}/4 (pd\sigma) = 1, \quad t_p = 0.5,
\]

These parameters are smaller than those assumed in different calculations of the electronic structure of

The choice of the origin of on-site energies \( \epsilon_{e_g} = 0 \) is arbitrary. The resulting value of \( U = 4.516 \) eV and the charge transfer energy \( \Delta_{\text{CT}} = 2.9 \) eV are similar to those derived from other x-ray absorption experiments.\(^{57}\)

The most relevant eigenstates of the cluster for the physics of the cobaltates are those corresponding to the first two rows of Table I, corresponding to formal Co\(^{3+} \) and Co\(^{4+} \) respectively. These states are separated by at least 2 eV from other eigenstates that cannot be represented by \( H_{\text{eff}} \), like those containing non-bonding O orbitals or states with intermediate spin.\(^{54}\) This energy difference is one order of magnitude larger than the corresponding hopping amplitude, assuring the validity of \( H_{\text{eff}} \) as representative of the low-energy physics of \( H \).

We note that while in Co compounds, intermediate or high spin states are usual, experiments show that the low spin states of Co are present in \( \text{Na}_x\text{CoO}_2 \)\(^{57,65,66}\) in agreement with our results. This is due to the fact mentioned above, that in this system the splitting between \( t_{2g} \) and \( e_g \) orbitals (due to \( 10Dq \) and Co-O hopping) is more than 3 eV, considerably larger than the exchange energies.

From the six energies listed in the fourth column of Table I and their corresponding expression for \( H_{\text{eff}}^f \) listed in the third column, we have determined the four parameters of Eq. (15) and the irrelevant constant \( C \) and shift in chemical potential \( \mu_s \). The result in eV is

\[
U_{\text{eff}} = 1.865, \quad U'_{\text{eff}} = 1.272, \quad J_{\text{eff}} = 0.354, \quad J'_{\text{eff}} = 0.171
\]
Na$_x$CoO$_2$ near the Fermi surface which include the effect of correlations. For example values of $U_{\text{eff}}$ between 3 eV and $+\infty$ were used. For our moderate values of the correlation energies, the hole pockets are still predicted in theory in contrast to experiment if the small first-principle value of the trigonal distortion $D$ is assumed. Instead, using the value of $D$ given by quantum-chemistry configuration-interaction calculations these pockets are absent and the electronic dispersion near the Fermi energy agrees with experiment.

The reduction in the effective value of $U_{\text{eff}}$ compared to the 3d value $U \sim 4.5$ eV is due to screening effects of the full model that are “hidden” in $H_{\text{eff}}$. Actually, the operators $\hat{d}^\dagger_{3g}$ of $H_{\text{eff}}$ do not correspond to pure 3d holes, but are complicated creation operators which involve 2p states. The detailed expression of these effective operators in terms of those of $H$ is beyond the scope of the present work. Examples of the construction of effective operators are given in Refs. 17,21,31. In this context, it is interesting to note that charge and current operators are given in Refs. 58–63. It is known that the cell-perturbation method allows us to obtain more accurate values of the effective hopping involving a calculation of only first order in the perturbation, using the eigenstates of the cell. Here we explain this procedure for Na$_x$CoO$_2$, using the eigenstates of the CoO$_6$ cluster with 5 holes (represented by one occupied $t_{2g}$ orbital in $H_{\text{eff}}$) and 4 holes (the vacuum state).

D. The effective hopping

As shown first by Koshiba and Maekawa, the main hopping path from one Co site to a neighboring Co site in Na$_x$CoO$_2$ is via an intermediate O site. See Fig. 1. The expression of this effective hopping in second-order perturbation theory in the Co-O hopping is $t_{\text{eff}} = (p\delta n)^2/\Delta_{\text{CT}}$. Using the parameters given in Eq. 10, $t_{\text{eff}} \approx 0.34$ eV is obtained. Clearly, this value is an overestimation, expected in covalent systems for which the hopping term is not small enough compared to the charge-transfer energy. An estimation based on the band width obtained from first principles gives $t_{\text{eff}} \approx 0.1$ eV.22

Since most of the terms involved in Eqs. 9 and 10 are cumbersome, one might ask what happens if one neglects them. The first four terms of $H_2$ (the simplest ones), containing the Coulomb repulsion between d $e_g$ and $t_{2g}$ electrons are crucial to obtain the right distribution of particles and should be retained. Keeping the prefactors and neglecting the rest of the terms of $H_1$ and $H_2$, the cubic $O_h$ symmetry is lost. Therefore, to retain the $O_h$ symmetry, we have replaced these Coulomb repulsions by the average of all of them.

All energies increase with respect to those of the full Hamiltonian. In particular for the states corresponding to nominal Co$^4+$ (second row of Table I), the energy increases by 0.92 eV. However, the distribution of holes is not dramatically affected. There is a 10 % reduction in the amount of d $t_{2g}$ from 0.91 to 0.82 which distribute evenly among other orbitals. Similar effects take place for nominal Co$^5+$. The resulting effective repulsions are decreased considerably. Proceeding as indicated above we obtain $U_{\text{eff}} = 1.47$ eV, $U'_{\text{eff}} = 0.84$ eV (35% less than for the full Hamiltonian), $J_{\text{eff}} = 0.39$ eV, and $J'_{\text{eff}} = 0.25$ eV.

Of course, the changes should be more dramatic when the effective cubic splitting (10$Dq$ plus effects of Co-O hopping) is smaller (like for other Co compounds), since for spherical symmetry all terms of exchange and transfer of intraorbital pairs are equally important.

C. The effect of $H_1$ and $H_2$

Since most of the terms involved in Eqs. 9 and 10 are cumbersome, one might ask what happens if one neglects them. The first four terms of $H_2$ (the simplest ones), containing the Coulomb repulsion between d $e_g$ and $t_{2g}$ electrons are crucial to obtain the right distribution of particles and should be retained. Keeping the prefactors and neglecting the rest of the terms of $H_1$ and $H_2$, the cubic $O_h$ symmetry is lost. Therefore, to retain the $O_h$ symmetry, we have replaced these Coulomb repulsions by the average of all of them.

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It is known that the cell-perturbation method allows us to obtain more accurate values of the effective hopping involving a calculation of only first order in the perturbation, using the eigenstates of the cell. Here we explain this procedure for Na$_x$CoO$_2$, using the eigenstates of the CoO$_6$ cluster with 5 holes (represented by one occupied $t_{2g}$ orbital in $H_{\text{eff}}$) and 4 holes (the vacuum state $H_{\text{eff}}$).

To be specific, we start from a state in which the cluster $i$ (at the left in Fig. 1) is in its ground state $|g_i(5, yz)\rangle$ with 5 holes and $yz$ symmetry and a neighboring cluster $j$ (whose center corresponds to the rightmost orbital represented in Fig. 1) is in its non-degenerate ground state $|g_j(4)\rangle$ with 4 holes (symmetry $A_{1g}$). After the hopping the final state is $|g_i(4)g_j(5, zx)\rangle$. The initial and final states are not orthogonal, but as we show below, this does not affect significantly the resulting effective hopping. The spin is conserved and the corresponding others.
subscript is dropped for simplicity. This process is represented in $H_{\text{eff}}$ by the hopping $\tilde{d}_{i,xz} \rightarrow \tilde{d}_{j,xx,\sigma}$. By symmetry, only the hopping terms of Eq. (12) which annihilate a hole in the 2$p_z$ orbital of the common O atom $(p_{i+y,z} = p_{j-x,z})$, middle orbital represented in Fig. 1 contribute to $t_{\text{eff}}$. Using Eq. (12) with Slater-Koster parameters, Eq. (13) and symmetry one has (calling $t_{pd} = (pd\pi)$, $t_p = -(pp\sigma) - (pp\pi)/2$

\begin{equation}
-t_{\text{eff}} = \langle g_i(4)g_j(5,zz)|t_{pd}d_{j,xx}^{\dagger} + t_p(p_{j}^{\dagger}z, x - p_{j}^{\dagger}x, z)\times p_{j-x,z}|g_i(5,yz)g_j(4)\rangle
\end{equation}

In the equation above, the part of the Hamiltonian that leaves the initial state $|g_i(5,yz)g_j(4)\rangle$ unchanged is subtracted [see Eq. (22) below]. We have checked numerically that the perturbative expression $t_{\text{eff}} = (pd\pi)^2/\Delta_{\text{CT}}$ is recovered for large $\Delta_{\text{CT}}$.

To calculate the matrix elements, we have used the simplified Hamiltonian, neglecting some terms of $H_1$ and $H_2$ as described above. With the parameters derived from optical experiments [Eq. (16)], we obtain $t_{\text{eff}} = 0.101$ eV, which is in very good agreement with the estimate of Ref. 72.

The final form of the non-interacting part of the effective Hamiltonian contains the trigonal distortion $D \sim 0.1$ eV and a smaller direct hopping between Co ions $t_{60}^{\text{Co}}$. These terms are beyond our calculations based on the diagonalization of a CoO$_6$ cluster. The former because we assumed $O_h$ symmetry and the latter because direct Co-Co hopping cannot be included in the cluster. Nevertheless, the largest energies in the problem are the interactions given by Eqs. (17) within our approach. Note that the value of the trigonal splitting $3D$ is an order of magnitude smaller than the effective cubic crystal field (near 3 eV including the effects of Co-O hybridization) and therefore does not sensibly affect the derivation of the remaining parameters of $H_{\text{eff}}$, which were obtained assuming $O_h$ symmetry.

### E. The effect of the overlap

While in $H_{\text{eff}}$ one assumes a basis with orthogonal states, the states of $H$ involved in the calculation of $t_{\text{eff}}$ above are non-orthogonal, due to the fact that some $p$ orbitals belong to different clusters. In the cuprates,\textsuperscript{24} and in double perovskites,\textsuperscript{25} the problem of non-orthogonality has been solved by a change of basis to orthogonal Wannier functions centered at transition-metal atoms. In the present case, in which five different 2$p$ O Wannier functions centered at each Co site should be considered, this procedure cannot be handled analytically and becomes very awkward. Fortunately, the larger number of orbitals involved has also the consequence that the overlap between many-body states is considerably reduced with respect to those of the one-particle Wannier functions. This also takes place to a lesser extent in the cuprates, in which the overlap between Zhang-Rice states is $S = 1/8$, and leads to a rapidly convergent expansion of $H_{\text{eff}}$ in terms of $S$.

Furthermore, a close examination of the structure of Na$_2$CoO$_2$ shows that in all non-zero elements of the overlap matrix between bonding combinations of O 2$p$ orbitals [see Eq. (19)], at least one O $2p$ orbital is involved. Since the occupation of the latter is small in the relevant many-body eigenstates (see Table I), the overlap between the latter is reduced. In particular we find

\begin{equation}
S = \langle g_i(4)g_j(5,zx)|g_i(5,yz)g_j(4)\rangle = \langle 1|2 = -0.0357,
\end{equation}

where for simplicity, we denoted as $|\rangle$ $\langle |\rangle$, the many-body state in which all clusters except $j$ ($i$) are in the ground state for four holes and the remaining cluster is in the lowest lying state for 5 holes and symmetry $zx$ $(yz)$. To first order in the overlaps $|l|m = S_{lm}$, $m \neq l$, orthonormal states can be obtained using

\begin{equation}
|\tilde{l}\rangle = |l\rangle - \frac{1}{2} \sum_{m,m \neq l} S_{ml}|m\rangle.
\end{equation}

Then

\begin{equation}
t_{\text{eff}} = \langle 1|H|2\rangle = H_{12} - \frac{1}{2} S_{12}(H_{11} + H_{22}),
\end{equation}

where $H_{lm} = \langle l|H|m\rangle$. Since by symmetry $H_{11} = H_{22}$, the above result can be written as

\begin{equation}
t_{\text{eff}} = \langle 1|(H - H_{22})|2\rangle.
\end{equation}
IV. SUMMARY AND DISCUSSION

We have constructed the cell Hamiltonian $H_b$ that consists of a transition-metal atom $M$ and its neighboring O atoms. This Hamiltonian is the basis to construct a low-energy effective model $H_{\text{eff}}$ in which the O atoms are eliminated, using the cell-perturbation method.\textsuperscript{10,12–14,16,17} The Hamiltonian has the same form if O is replaced by other elements with p states near the Fermi energy, like P or As in the Fe pnictides. An essential part of the cell Hamiltonian and the full starting Hamiltonian $H$ is the interaction between electrons inside the d shell when all 10 spin-orbitals are important. We have constructed $H_I$ in a basis of orbitals appropriate for a cubic, hexagonal, tetragonal or tetrahedral environment of the M atoms. For other symmetries a change of basis may be required.

While $H_I$ has a trivial form $U \sum_i n_{i\uparrow} n_{i\downarrow}$ in the Hubbard model where only one orbital per site $i$ is relevant, the interaction contains interorbital Coulomb repulsion, exchange and pair hopping terms when only either $e_g$ [Eq. (7)] or $t_{2g}$ [Eq. (8)] are involved. These already makes the physics of transition-metal compounds richer than that of the Hubbard model.\textsuperscript{29,32,33,37–39,74,75}

If all orbitals should be retained, more complicated terms appear [Eqs. (9) and (10)]. Our results suggest that because of the large terms appear [Eqs. (9) and (10)]. Our results suggest that taking the one-body parameters of the effective model $H_{\text{eff}}$ with metal sites only from a fit of the bands obtained in LDA is not valid in general, or at least when the degree of covalency is important. This is also the case of NiO, for which agreement with experiment in LDA+DMFT calculations is only achieved once the O bands are explicitly included in the model.\textsuperscript{24} or when the O atoms have been integrated out using low-energy reduction procedures similar as ours, which take into account correlations from the beginning.\textsuperscript{24} The research in the superconducting cuprates also supports the above statement. In this case, the parameters of the effective one-band Hubbard or $t - J$ models are obtained accurately using systematic low-energy reduction procedures from a multi-orbital Cu-O model\textsuperscript{41,42} with parameters obtained from constrained-density-functional theory.\textsuperscript{43,44}

For the cobaltates, we have determined the parameters of the original multiorbital model form a fit of polarized x-ray absorption spectra of Na$_x$CoO$_2$.\textsuperscript{54}

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