

Effective Hamiltonian for transition-metal compounds: Application to Na_xCoO_2

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We describe a simple scheme to construct a low-energy effective Hamiltonian H_{eff} for highly correlated systems containing nonmetals such as 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 nonmetal 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_n cluster containing the transition-metal atom and its n nearest O atoms (for example, a CoO_6 cluster in the case of the cobaltates, or a CuO_n 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_xCoO_2 . The resulting H_{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_{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_2CuO_4 are nonmagnetic metals,¹ they are, in fact, antiferromagnetic insulators. In the cobaltates Na_xCoO_2 , first-principles calculations² predicted a Fermi surface with six prominent hole pockets along the Γ - K direction, which are absent in measured angle-resolved photoemission spectra.^{3,4}

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.⁵⁻⁹ Due to the exponential increase in 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,¹⁰⁻¹⁶ have been very successful, in spite of the fact that

doped holes enter mainly at O atoms¹⁷⁻¹⁹ (optical properties related with O atoms were calculated using these one-band models^{16,20}). 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,²¹ whereas the same treatment on the one-band effective model gives a gap that agrees with experiment.¹²

The main idea behind the construction of an effective one-band model for the cuprates, proposed by Zhang and Rice,²² 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 nonorthogonal singlets, Zhang has shown that in a particular case, the mapping is exact.²³ More systematic derivations lead to additional terms of smaller magnitude,^{14,15,24} like three-site terms, which might be important for superconductivity.^{6,25-27} Three-site terms play also an important role in effective models for vanadates or other systems with t_{2g} electrons.²⁸ Triplet states can be included perturbatively.²⁹

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.³⁰ Adding to it the superexchange interaction between Cu spins one has the so-called spin-fermion model. Similar derivations have been made for NiO,³¹ doped Y_2BaNiO_5 ,^{32,33} and other perovskites.³⁴ 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_4 cluster in the case of the cuprates³⁰ or a NiO_6 cluster in the case of the nickelates.³² 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.³⁰

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 method¹⁰ used extensively in the cuprates^{10,12,13,15,16,35} exploits this idea: it divides the system into orthogonal cells containing one M 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_{eff} (the effect of this overlap in the cuprates was calculated in Ref. 14). A discussion of the effect of the overlap in the cobaltates is contained in Sec. III E. 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_{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,³⁶ a simplified expression derived previously³⁷ was used. While the form of H_I is well known when either only e_g orbitals³² or only t_{2g} orbitals^{38,39} are important, the correct expressions were not always used.^{33,38} 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_{eff} as described above. While for the sake of clarity we consider that the

relevant nonmetal 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_xCoO_2 . A brief description of this case together with a dynamical-mean-field treatment of H_{eff} to study the electronic structure and Fermi surface of the system was published before.⁴⁰

In Sec. II, we describe the construction of the multiband model containing both M $3d$ (or $4d$) and O $2p$ (or P $3p$, As $4p$) electrons, including all the d - d interaction terms. In Sec. III, we derive the effective Hamiltonian H_{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_xCoO_2 . Section IV is a summary and discussion.

II. 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 nonmetal) atoms. An example in which only one d orbital is relevant is the three-band Hubbard model for the cuprates^{41,42} with parameters determined by constrained-density-functional theory.^{43,44} The Hamiltonian contains d - p hopping terms and interactions. The most important of the latter are the interaction terms among the d electrons.

A. 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 ten d spin orbitals is⁴⁵

$$H_I = \frac{1}{2} \sum_{\lambda\mu\nu\rho} V_{\lambda\mu\nu\rho} d_{\lambda}^{\dagger} d_{\mu}^{\dagger} d_{\nu} d_{\rho}, \quad (1)$$

where d_{λ}^{\dagger} creates an electron or a hole at the spin-orbital λ (H_I is invariant under an electron-hole transformation) and

$$V_{\lambda\mu\nu\rho} = \int d\mathbf{r}_1 d\mathbf{r}_2 \bar{\varphi}_{\lambda}(\mathbf{r}_1) \bar{\varphi}_{\mu}(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_{\nu}(\mathbf{r}_1) \varphi_{\rho}(\mathbf{r}_2), \quad (2)$$

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

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 $R(r)Y_2^m(\theta, \phi)$, where R is the radial part and Y_l^m is a normalized spherical harmonic. Using standard methods of atomic physics^{38,46} one obtains

$$V_{\lambda\mu\nu\rho} = \delta(\sigma^{\lambda}, \sigma^{\nu}) \delta(\sigma^{\mu}, \sigma^{\rho}) \delta(m^{\lambda} + m^{\mu}, m^{\nu} + m^{\rho}) \times \sum_{k=0}^{\infty} c^k(2m^{\lambda}, 2m^{\nu}) c^k(2m^{\rho}, 2m^{\mu}) R^k \quad (3)$$

with

$$c^k(lm, l'm') = \sqrt{\frac{2}{2k+1}} \times \int_0^{\pi} P_k^{m-m'}(\cos \theta) P_l^m(\cos \theta) P_{l'}^{m'}(\cos \theta) \sin \theta d\theta,$$

$$R^k = e^2 \int_0^\infty \int_0^\infty \frac{r_{<}^k}{r_{>}^{k+1}} R^2(r_1) R^2(r_2) r_1^2 r_2^2 dr_1 dr_2, \quad (4)$$

where $P_l^m[\cos(\theta)]$ is a normalized Legendre function and $r_{<}(r_{>})$ 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 $F_4=R^4/441$.^{38,46}

In the presence of a cubic crystal field (point group O_h) or some other local symmetry (for example, point groups D_{6h} , D_{4h} , C_{4v} , and T_d), it is more convenient to change from the basis of operators with definite angular-momentum projection $d_{m\sigma}^\dagger$ to that of irreducible representations of the point group (e_g and t_{2g} for O_h) orbitals using

$$\begin{aligned} d_{\pm 2\sigma}^\dagger &= \frac{1}{\sqrt{2}}(d_{x^2-y^2,\sigma}^\dagger \pm id_{xy,\sigma_1}^\dagger), \\ d_{\pm 1\sigma}^\dagger &= \frac{-1}{\sqrt{2}}(d_{zx,\sigma}^\dagger \pm id_{yz,\sigma}^\dagger), \\ d_{0\sigma}^\dagger &= d_{3z^2-r^2,\sigma}^\dagger. \end{aligned} \quad (5)$$

In cubic symmetry, $d_{x^2-y^2,\sigma}^\dagger$ and $d_{3z^2-r^2,\sigma}^\dagger$ correspond to e_g symmetry and the remaining creation operators transform as the t_{2g} irreducible representation. Each term of the resulting H_I contains two creation and two annihilation operators. H_I 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,³² while H_0 contains the relevant interaction terms for early transition metals with a few t_{2g} electrons, such as titanates³⁸ or rutenates.³⁹ The sums over α (β, γ) below run over the indices of e_g (t_{2g}) operators. The interaction can be written as

$$H_I = H_4 + H_0 + H_1 + H_2 \quad (6)$$

with

$$\begin{aligned} H_4 &= U \sum_{\alpha} n_{\alpha,\uparrow} n_{\alpha,\downarrow} + (U - 2J_e) \sum_{\sigma_1, \sigma_2} n_{x^2-y^2, \sigma_1} n_{3z^2-r^2, \sigma_2} \\ &+ J_e \sum_{\sigma_1, \sigma_2} d_{x^2-y^2, \sigma_1}^\dagger d_{3z^2-r^2, \sigma_2}^\dagger d_{x^2-y^2, \sigma_2} d_{3z^2-r^2, \sigma_1} \\ &+ J_e (d_{x^2-y^2, \uparrow}^\dagger d_{x^2-y^2, \downarrow}^\dagger d_{3z^2-r^2, \downarrow} d_{3z^2-r^2, \uparrow} + \text{H.c.}), \end{aligned} \quad (7)$$

$$\begin{aligned} H_0 &= U \sum_{\beta} n_{\beta, \uparrow} n_{\beta, \downarrow} + \frac{U - 2J_t}{2} \sum_{\beta \neq \gamma} \sum_{\sigma_1, \sigma_2} n_{\beta, \sigma_1} n_{\gamma, \sigma_2} \\ &+ \frac{J_t}{2} \sum_{\sigma_1, \sigma_2} \sum_{\beta \neq \gamma} d_{\beta, \sigma_1}^\dagger d_{\gamma, \sigma_2}^\dagger d_{\beta, \sigma_2} d_{\gamma, \sigma_1} + J_t \sum_{\beta \neq \gamma} d_{\beta, \uparrow}^\dagger d_{\beta, \downarrow}^\dagger d_{\gamma, \downarrow} d_{\gamma, \uparrow}, \end{aligned} \quad (8)$$

$$\begin{aligned} H_1 &= \lambda \sum_{\sigma_1, \sigma_2} [\sqrt{3}(d_{x^2-y^2, \sigma_1}^\dagger d_{zx, \sigma_1} + \text{H.c.}) \times (d_{xy, \sigma_2}^\dagger d_{yz, \sigma_2} + \text{H.c.}) \\ &- \sqrt{3}(d_{x^2-y^2, \sigma_1}^\dagger d_{yz, \sigma_1} + \text{H.c.})(d_{xy, \sigma_2}^\dagger d_{zx, \sigma_2} + \text{H.c.}) \\ &- 2(d_{3z^2-r^2, \sigma_1}^\dagger d_{xy, \sigma_1} + \text{H.c.})(d_{zx, \sigma_2}^\dagger d_{yz, \sigma_2} + \text{H.c.}) \\ &+ (d_{3z^2-r^2, \sigma_1}^\dagger d_{zx, \sigma_1} + \text{H.c.})(d_{xy, \sigma_2}^\dagger d_{yz, \sigma_2} + \text{H.c.}) \\ &+ (d_{3z^2-r^2, \sigma_1}^\dagger d_{yz, \sigma_1} + \text{H.c.}) \times (d_{xy, \sigma_2}^\dagger d_{zx, \sigma_2} + \text{H.c.})], \end{aligned} \quad (9)$$

$$\begin{aligned} H_2 &= (U - 2J_t) \sum_{\sigma_1, \sigma_2} n_{x^2-y^2, \sigma_1} (n_{zx, \sigma_2} + n_{yz, \sigma_2}) \\ &+ (U - 2J_a) \sum_{\sigma_1, \sigma_2} n_{x^2-y^2, \sigma_1} n_{xy, \sigma_2} \\ &+ (U - 2J_b) \sum_{\sigma_1, \sigma_2} n_{3z^2-r^2, \sigma_1} (n_{zx, \sigma_2} + n_{yz, \sigma_2}) \\ &+ (U - 2J_e) \sum_{\sigma_1, \sigma_2} n_{3z^2-r^2, \sigma_1} n_{xy, \sigma_2} \\ &+ J_t \sum_{\sigma_1, \sigma_2} (d_{x^2-y^2, \sigma_1}^\dagger d_{zx, \sigma_2}^\dagger d_{x^2-y^2, \sigma_2} d_{zx, \sigma_1} \\ &+ d_{x^2-y^2, \sigma_1}^\dagger d_{yz, \sigma_2}^\dagger d_{x^2-y^2, \sigma_2} d_{yz, \sigma_1}) \\ &+ J_a \sum_{\sigma_1, \sigma_2} d_{x^2-y^2, \sigma_1}^\dagger d_{xy, \sigma_2}^\dagger d_{x^2-y^2, \sigma_2} d_{xy, \sigma_1} \\ &+ J_b \sum_{\sigma_1, \sigma_2} (d_{3z^2-r^2, \sigma_1}^\dagger d_{zx, \sigma_2}^\dagger d_{3z^2-r^2, \sigma_2} d_{zx, \sigma_1} \\ &+ d_{3z^2-r^2, \sigma_1}^\dagger d_{yz, \sigma_2}^\dagger d_{3z^2-r^2, \sigma_2} d_{yz, \sigma_1}) \\ &+ J_e \sum_{\sigma_1, \sigma_2} d_{3z^2-r^2, \sigma_1}^\dagger d_{xy, \sigma_2}^\dagger d_{3z^2-r^2, \sigma_2} d_{xy, \sigma_1} \\ &+ J_t [d_{x^2-y^2, \uparrow}^\dagger d_{x^2-y^2, \downarrow}^\dagger (d_{zx, \downarrow} d_{zx, \uparrow} + d_{yz, \downarrow} d_{yz, \uparrow}) + \text{H.c.}] \\ &+ J_a [d_{x^2-y^2, \uparrow}^\dagger d_{x^2-y^2, \downarrow}^\dagger d_{xy, \downarrow} d_{xy, \uparrow} + \text{H.c.}] \\ &+ J_b [d_{3z^2-r^2, \uparrow}^\dagger d_{3z^2-r^2, \downarrow}^\dagger (d_{zx, \downarrow} d_{zx, \uparrow} + d_{yz, \downarrow} d_{yz, \uparrow}) + \text{H.c.}] \\ &+ J_e \sum_{\sigma_1, \sigma_2} [d_{3z^2-r^2, \uparrow}^\dagger d_{3z^2-r^2, \downarrow}^\dagger d_{xy, \downarrow} d_{xy, \uparrow} + \text{H.c.}] \\ &+ 2\lambda \sum_{\sigma_1, \sigma_2} (n_{yz, \sigma_1} - n_{zx, \sigma_1}) (d_{3z^2-r^2, \sigma_2}^\dagger d_{x^2-y^2, \sigma_2} + \text{H.c.}) \\ &+ \lambda \sum_{\sigma_1, \sigma_2} (d_{3z^2-r^2, \sigma_1}^\dagger d_{zx, \sigma_2}^\dagger d_{x^2-y^2, \sigma_2} d_{zx, \sigma_1} \\ &- d_{3z^2-r^2, \sigma_1}^\dagger d_{yz, \sigma_2}^\dagger d_{x^2-y^2, \sigma_2} d_{yz, \sigma_1} + \text{H.c.}) + \lambda [(d_{zx, \uparrow}^\dagger d_{zx, \downarrow}^\dagger \\ &- d_{yz, \uparrow}^\dagger d_{yz, \downarrow}^\dagger) \times (d_{x^2-y^2, \downarrow} d_{3z^2-r^2, \uparrow} - d_{x^2-y^2, \uparrow} d_{3z^2-r^2, \downarrow}) + \text{H.c.}], \end{aligned} \quad (10)$$

where $U=F_0+4F_2+36F_4$, $J_e=4F_2+15F_4$, $J_t=3F_2+20F_4$, $J_a=35F_4$, $J_b=F_2+30F_4$, and $\lambda=\sqrt{3}(F_2-5F_4)$.

The largest energy in H_I is the intraorbital repulsion U . Most terms of H_I (in particular, all those of the pure e_g part H_4 and the pure t_{2g} part H_0) involve two and only two orbital

indices, like the (four different) ferromagnetic exchange interactions J_i , of the form

$$\sum_{\sigma_1, \sigma_2} d_{\xi, \sigma_1}^\dagger d_{\eta, \sigma_2}^\dagger d_{\xi, \sigma_2} d_{\eta, \sigma_1} = -(2\mathbf{S}_\xi \cdot \mathbf{S}_\eta + 1/2), \quad (11)$$

where $\mathbf{S}_\xi = \sum_{\chi\chi'} d_{\xi, \chi}^\dagger \boldsymbol{\sigma}_{\chi\chi'} d_{\xi, \chi'}/2$ is the spin of the orbital ξ . The interorbital repulsion between these orbitals is related to the former by $U' = U - 2J_i$ due to the spherical symmetry of H_I . For the same reason, $J'_i = J_i$, where J'_i is the energy for transfer of intraorbital pairs (like $d_{\beta, \uparrow}^\dagger d_{\beta, \downarrow}^\dagger d_{\gamma, \downarrow} d_{\gamma, \uparrow}$). The remaining terms, with prefactor proportional to λ , involve more than two orbitals.

The parameters F_2 and F_4 related to J_i and λ 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. 47) of V^{+3} and Ni gives nearly the same values $F_2 = 1300 \text{ cm}^{-1} = 0.16 \text{ eV}$ and $F_4 = 88 \text{ cm}^{-1} = 0.011 \text{ eV}$ within 2%. This results in an exchange energy $J_e = 0.81 \text{ eV}$ for e_g electrons and $J_e = 0.70 \text{ eV}$ 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 $2J_e \approx 1.6 \text{ eV}$ 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.⁴⁸ This reduction is also assumed in Ce compounds.⁴⁹

In contrast to F_2 and F_4 , F_0 which determines the intraorbital repulsion U is significantly screened in the solids and is difficult to determine theoretically. For the cuprates $U \approx 10 \text{ eV}$ has been estimated by constrained-density-functional calculations^{43,44} 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. 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 Co-O ($t_{\delta}^{\eta\xi}$ below) and O-O hopping ($\tau_{kj}^{\eta\theta}$), parameterized as usual, in terms of the Slater-Koster parameters.⁵⁰ We include a cubic crystal-field splitting $\epsilon_{t_{2g}} - \epsilon_{e_g} = 10 Dq$ 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

$$\begin{aligned} H = & \sum_{i, \alpha \in e_g, \sigma} \epsilon_{e_g} d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma} + \sum_{i, \beta \in t_{2g}, \sigma} \epsilon_{t_{2g}} d_{i\beta\sigma}^\dagger d_{i\beta\sigma} + \sum_{j\eta\sigma} \epsilon_j p_{j\eta\sigma}^\dagger p_{j\eta\sigma} \\ & + \sum_{i\delta\eta\xi\sigma} t_{\delta}^{\eta\xi} (p_{i+\delta, \eta\sigma}^\dagger d_{i\xi\sigma} + \text{H.c.}) + \sum_{j \neq k, \eta\theta\sigma} \tau_{kj}^{\eta\theta} p_{k\eta\sigma}^\dagger p_{j\theta\sigma} \\ & + \sum_i H_I^i. \end{aligned} \quad (12)$$

Here $p_{j\eta\sigma}^\dagger$ creates a hole on the O $2p$ orbital η at site j with spin σ . The operator $d_{i\xi\sigma}^\dagger$ has an analogous meaning for the Md orbitals at site i . The interactions at this site H_I^i has the form of Eqs. (6)–(10) with the site index i added to the subscripts of the d operators. The subscript $i+\delta$ in $p_{i+\delta, \eta\sigma}^\dagger$ 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 the former is not very important,¹³ 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^{35,51} and in charge-transfer instabilities⁵² 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_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 (nonbonding) orbitals decouple. The presence of U_p would introduce scattering between the bonding orbitals and the nonbonding ones and does not modify the essential physics,¹³ particularly for low or moderate number of O holes.

For a perfect MO_6 octahedra (point group O_h) with M at the origin of coordinates and the O atoms at $\delta = \pm \mathbf{x}, \pm \mathbf{y}$, and $\pm \mathbf{z}$, there are 13 O $2p$ nonbonding orbitals and the five bonding O $2p$ orbitals are (spin indices and site index i are omitted for simplicity)

$$\begin{aligned} p_{x^2-y^2} &= \frac{1}{2}(p_{\mathbf{x},\mathbf{x}} - p_{-\mathbf{x},\mathbf{x}} - p_{\mathbf{y},\mathbf{y}} + p_{-\mathbf{y},\mathbf{y}}), \\ p_{3z^2-r^2} &= \frac{1}{2\sqrt{3}}(2p_{\mathbf{z},\mathbf{z}} - 2p_{-\mathbf{z},\mathbf{z}} - p_{\mathbf{x},\mathbf{x}} + p_{-\mathbf{x},\mathbf{x}} - p_{\mathbf{y},\mathbf{y}} + p_{-\mathbf{y},\mathbf{y}}), \\ p_{xy} &= \frac{1}{2}(p_{\mathbf{x},\mathbf{y}} - p_{-\mathbf{x},\mathbf{y}} + p_{\mathbf{y},\mathbf{x}} - p_{-\mathbf{y},\mathbf{x}}), \\ p_{yz} &= \frac{1}{2}(p_{\mathbf{y},\mathbf{z}} - p_{-\mathbf{y},\mathbf{z}} + p_{\mathbf{z},\mathbf{y}} - p_{-\mathbf{z},\mathbf{y}}), \\ p_{zx} &= \frac{1}{2}(p_{\mathbf{z},\mathbf{x}} - p_{-\mathbf{z},\mathbf{x}} + p_{\mathbf{x},\mathbf{z}} - p_{-\mathbf{x},\mathbf{z}}). \end{aligned} \quad (13)$$

Writing the hopping terms in this basis and using the Slater-Koster formulas,⁵⁰ the bonding part of Hamiltonian (12) in the MO_6 cluster takes the form

TABLE I. Eigenstates and energies of one site of H_{eff} , corresponding energies in the CoO_6 cluster and distribution of holes in the latter. For degenerate representations only one state is shown.

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\rangle$	0	8.141	3.03	0.02	0.94	0
T_{2g}^2	$\tilde{d}_{xy}^\dagger 0\rangle$	0	17.271	2.67	0.91	1.29	0.14
A_{1g}^0	$\frac{1}{\sqrt{3}} \sum_{\beta} \tilde{d}_{\beta 1}^\dagger \tilde{d}_{\beta 1}^\dagger 0\rangle$	$U_{\text{eff}} + 2J'_{\text{eff}}$	28.609	2.41	1.46	1.48	0.66
E^0	$\frac{1}{\sqrt{2}} (\tilde{d}_{zx}^\dagger \tilde{d}_{zx}^\dagger - \tilde{d}_{yz}^\dagger \tilde{d}_{yz}^\dagger) 0\rangle$	$U_{\text{eff}} - J'_{\text{eff}}$	28.096	2.40	1.51	1.57	0.52
T_{2g}^0	$\frac{1}{\sqrt{2}} (\tilde{d}_{yz}^\dagger \tilde{d}_{zx}^\dagger - \tilde{d}_{yz}^\dagger \tilde{d}_{zx}^\dagger) 0\rangle$	$U'_{\text{eff}} + J_{\text{eff}}$	28.028	2.39	1.54	1.56	0.51
T_{1g}^3	$\tilde{d}_{xy}^\dagger \tilde{d}_{yz}^\dagger 0\rangle$	$U'_{\text{eff}} - J_{\text{eff}}$	27.320	2.34	1.63	1.65	0.37

$$\begin{aligned}
H_b = & \sum_{\alpha \in e_g, \sigma} \{ \epsilon_e d_{\alpha\sigma}^\dagger d_{\alpha\sigma} + [\epsilon_0 - 2t_p] p_{\alpha\sigma}^\dagger p_{\alpha\sigma} \\
& - \sqrt{3} (pd\sigma) (d_{\alpha\sigma}^\dagger p_{\alpha\sigma} + \text{H.c.}) \} + \sum_{\beta \in t_{2g}, \sigma} \{ \epsilon_{t_{2g}} d_{\beta\sigma}^\dagger d_{\beta\sigma} \\
& + [\epsilon_0 + 2t_p] p_{\beta\sigma}^\dagger p_{\beta\sigma} + 2(pd\pi) (d_{\beta\sigma}^\dagger p_{\beta\sigma} + \text{H.c.}) \} + H_I,
\end{aligned} \quad (14)$$

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 $(p_{y,z} - p_{-y,z})/\sqrt{2}$ and $(p_{z,y} - p_{-z,y})/\sqrt{2}$ and the same changing y by x . The hopping terms that involve these (at most eight) O orbitals can be easily constructed using Ref. 50.

In any case, the size of the Hilbert space of H_b with at most 13×2 spin orbitals is small enough to allow us to obtain its low-energy eigenstates numerically by the Lanczos method.⁵³

B. Cobaltates

For the case of Na_xCoO_2 , we have solved numerically a CoO_6 cluster using the Hamiltonian H_b given by Eq. (14), 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 experiments⁵⁴ 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_{eff} , because as we shall see, the symmetry identifies unambiguously the correspondence between states of both Hamiltonians. The effective trigonal crystal-field splitting $\Delta = 3D \sim 0.3$ eV was given by quantum-chemistry configuration-interaction calculations.⁵⁵ 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^{2+} is in a $3d^7$ configuration (three holes in the d shell), the states of the CoO_6 cluster with $n+1$ holes are represented by a Co^{n+} ion in H_{eff} . The most relevant values of n for Na_xCoO_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 choose the $\text{Co}^{3+}3d^6$ configuration, occupied with the four e_g holes. Thus Co^{4+} has one t_{2g} hole and Co^{5+} has two t_{2g} holes. Therefore, one expects that the interacting part of H_{eff} at each site has the same form as H_0 [Eq. (8)] but now $U'_{\text{eff}} \neq U_{\text{eff}} - 2J_{\text{eff}}$ and $J'_{\text{eff}} \neq J_{\text{eff}}$ because the cubic crystal field $\epsilon_{t_{2g}} - \epsilon_e = 10Dq$ reduces the symmetry from that of the full rotational group to O_h

$$\begin{aligned}
H_I^{\text{eff}} = & U_{\text{eff}} \sum_{\beta} \tilde{n}_{\beta 1} \tilde{n}_{\beta 1} + \frac{1}{2} \sum_{\gamma \neq \beta, \sigma \sigma'} (U'_{\text{eff}} \tilde{n}_{\gamma \sigma} \tilde{n}_{\beta \sigma'} \\
& + J_{\text{eff}} \tilde{d}_{\gamma \sigma}^\dagger \tilde{d}_{\beta \sigma'}^\dagger \tilde{d}_{\gamma \sigma'} \tilde{d}_{\beta \sigma}) + J'_{\text{eff}} \sum_{\gamma \neq \beta} \tilde{d}_{\gamma 1}^\dagger \tilde{d}_{\gamma 1}^\dagger \tilde{d}_{\beta 1} \tilde{d}_{\beta 1}.
\end{aligned} \quad (15)$$

This is the effective Hamiltonian at one site, except for an unimportant constant C and chemical potential term $-\mu N$ with $N = \sum_{\beta \sigma} \tilde{n}_{\beta \sigma}$. The tilde above the operators is to remind us that the effective operators $\tilde{d}_{\beta \sigma}^\dagger$ 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_{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_6 cluster with four, five, and six holes are well represented by the corresponding eigenstates of H_I^{eff} . 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 us⁵⁴ from a fit of polarized x-ray absorption spectra of Na_xCoO_2 to the results of a CoO_6 cluster with four and five holes including the core hole. In comparison with the present calculations, the previous ones were simplified neglecting the exchange, transfer of intraorbital pairs, and terms proportional to λ 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 $\gg F_2, F_4$.⁵⁴ The effect of the neglected terms is discussed in the next section. The parameters of H_b in electron volt are

$$\begin{aligned} F_0 &= 3.5, & F_2 &= 0.2, & F_4 &= 0.006, \\ (pd\pi) &= \frac{-\sqrt{3}}{4}(pd\sigma) = 1, & t_p &= 0.5, \\ \epsilon_0 &= 13, & \epsilon_{t_{2g}} &= 1.2, & \epsilon_{e_g} &= 0. \end{aligned} \quad (16)$$

The choice of the origin of on-site energies $\epsilon_e = 0$ is arbitrary. The resulting value of $U = 4.516$ eV and the charge-transfer⁵⁶ energy $\Delta_{CT} = 2.9$ 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_{eff} , like those containing nonbonding O orbitals or states with intermediate spin.⁵⁸ This energy difference is one order of magnitude larger than the corresponding hopping amplitude, assuring the validity of H^{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 Na_xCoO_2 ,^{57,59-61} 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_1^{eff} listed in the third column, we have determined the four parameters of Eq. (15) and the irrelevant constant C and shift in chemical potential μ_s . The result in electron volt is

$$U_{\text{eff}} = 1.865, \quad U'_{\text{eff}} = 1.272, \quad J_{\text{eff}} = 0.354, \quad J'_{\text{eff}} = 0.171. \quad (17)$$

These parameters are smaller than those assumed in different calculations of the electronic structure of Na_xCoO_2 near the Fermi surface which include the effect of correlations.⁶²⁻⁶⁷ For example, values of U_{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-principles value of the trigonal distortion D is assumed.^{65,66} Instead, using the value of D given by quantum-chemistry configuration-interaction calculations,⁵⁵ these pockets are absent and the electronic dispersion near the Fermi energy agrees with experiment.⁴⁰

The reduction in the effective value of U_{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_{eff} . Actually, the operators $\tilde{d}_{\beta\sigma}^\dagger$ of H_{eff} do not correspond to pure $3d$ holes, but are complicated creation operators which involve $2p$ states. The de-

tailed 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. 16, 20, and 30. In this context, it is interesting to note that charge and current operators are expressed as pure spin operators when Heisenberg-type models are used as effective Hamiltonians for Hubbard-type models.^{68,69} In any case, it is easy to understand that if the effective $3d$ operators $\tilde{d}_{\beta\sigma}^\dagger$ have an important component of O $2p$ orbitals distributed in the cluster, the effective repulsion between electrons occupying these states is smaller than that between the corresponding operators localized on the same Co ion.

In addition to covalency, another important point related with it and noticed before by Marianetti *et al.*,⁷⁰ is that the addition of a new effective hole causes a redistribution of the remaining charge. The distribution of charge among the different orbitals in the cluster for the different states is listed in the last four columns of Table I. The vacuum $|0\rangle$ of H_{eff} at one site, represents the CoO_6 cluster with four holes. Near three of them occupy the $3d e_g$ states and the remaining one occupies mainly linear combinations of $2p$ O orbitals with e_g symmetry [corresponding to the first two lines of Eq. (13)]. When an effective $3d t_{2g}$ hole is added, nearly 0.35 $3d e_g$ holes are promoted to the O states with the same symmetry. A similar effect is caused by the addition of the second effective $3d t_{2g}$ hole (with larger magnitude for the states of lowest energy). This is a combined effect of the interorbital Coulomb repulsion, which increases the energy of the e_g holes when t_{2g} holes are added, and the strong hopping between $3d e_g$ holes and linear combinations of O holes with the same symmetry.

The degree of covalency of the t_{2g} states is less than that of the e_g ones, due to the fact that the $3d$ - $2p$ hopping is a factor two larger for the latter [see Eqs. (14) and (16)].

C. 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.

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 ($10Dq$ plus effects of Co-O hopping)

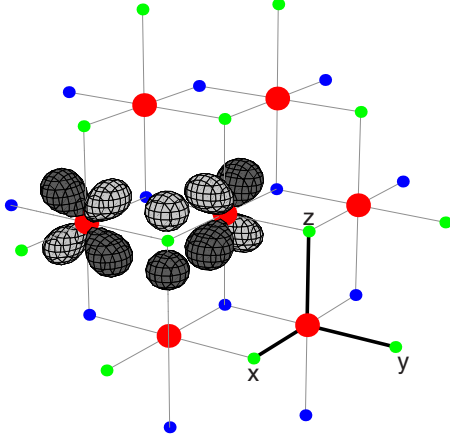


FIG. 1. (Color online) Scheme of the main orbitals involved in an effective hopping from a d_{yz} orbital at the left to a d_{zx} orbital at the right through an intermediate p_z orbital.

is smaller (like for other Co compounds), since for spherical symmetry all terms of exchange and transfer of intraorbital pairs are equally important.

D. Effective hopping

As shown first by Koshibae and Maekawa,⁷¹ the main hopping path from one Co site to a neighboring Co site in Na_xCoO_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 $t_{\text{eff}} = (pd\pi)^2 / \Delta_{\text{CT}}$. Using the parameters given in Eq. (16), $t_{\text{eff}} \cong 0.34$ 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 bandwidth obtained from first principles gives $t_{\text{eff}} \cong 0.1$ eV.⁷²

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.^{10,12,13,15,16,35} Here we explain this procedure for Na_xCoO_2 , using the eigenstates of the CoO_6 cluster with five holes (represented by one occupied t_{2g} orbital in H_{eff}) and four holes (the vacuum in H_{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 five holes and yz symmetry and a neighboring cluster j (whose center corresponds to the rightmost orbital represented in Fig. 1) is in its nondegenerate ground state $|g_j(4)\rangle$ with four 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 subscript is dropped for simplicity. This process is represented in H_{eff} by the hopping $\tilde{d}_{i,yz,\sigma}^\dagger \rightarrow \tilde{d}_{j,zx,\sigma}^\dagger$. By symmetry, only the hopping terms of Eq. (12) which annihilate a hole in the $2p_z$ orbital of the common O atom ($p_{i+y,z} = p_{j-x,z}$, middle orbital represented in Fig. 1) contribute to t_{eff} . Using Eq. (12) with Slater-Koster parameters, Eq. (13) and

symmetry one has, calling $t_{pd} = (pd\pi)$, $t_p = -[(pp\sigma) - (pp\pi)]/2$

$$\begin{aligned}
 -t_{\text{eff}} &= \langle g_i(4)g_j(5, zx) | t_{pd} d_{j,zx}^\dagger + t_p (p_{j+z,x}^\dagger - p_{j-z,x}^\dagger) \\
 &\quad \times p_{j-x,z} | g_i(5, yz)g_j(4) \rangle, \\
 &= \langle g_j(5, zx) | -t_{pd} d_{j,zx}^\dagger - t_p p_{j,zx}^\dagger | g_j(4) \rangle \langle g_i(4) | \frac{1}{2} p_{yz} | g_i(5, yz) \rangle
 \end{aligned} \tag{18}$$

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 Δ_{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 noninteracting part of the effective Hamiltonian contains the trigonal distortion $D \sim 0.1$ eV and a smaller direct hopping between Co ions t' .⁶⁴ 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 Eq. (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_{eff} , which were obtained assuming O_h symmetry.

E. Effect of the overlap

While in H_{eff} one assumes a basis with orthogonal states, the states of H involved in the calculation of t_{eff} above are nonorthogonal, due to the fact that some p orbitals belong to different clusters. In the cuprates,¹³ and in double perovskites,⁷³ the problem of nonorthogonality has been solved by a change in basis to orthogonal Wannier functions centered at transition-metal atoms. In the present case, in which five different $2p$ 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_{eff} in terms of S .¹⁴

Furthermore, a close examination of the structure of Na_xCoO_2 shows that in all nonzero elements of the overlap matrix between bonding combinations of O $2p$ orbitals [see Eq. (13)], at least one O t_{2g} 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

$$S = \langle g_i(4)g_j(5, zx) | g_i(5, yz)g_j(4) \rangle = \langle 1|2 \rangle = -0.0357, \quad (19)$$

where for simplicity, we denoted as $|1\rangle$ ($|2\rangle$), 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 five holes and symmetry $zx(yz)$. To first order in the overlaps $\langle l|m \rangle = S_{lm}$, $m \neq l$, orthonormal states can be obtained using

$$|\tilde{l}\rangle = |l\rangle - \frac{1}{2} \sum_{m, m \neq l} S_{ml} |m\rangle. \quad (20)$$

Then

$$t_{\text{eff}} = \langle \tilde{1} | H | \tilde{2} \rangle = H_{12} - \frac{1}{2} S_{12} (H_{11} + H_{22}), \quad (21)$$

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

$$t_{\text{eff}} = \langle 1 | (H - H_{22}) | 2 \rangle. \quad (22)$$

Except for the sign, the second member coincides with the second member of Eq. (18). Therefore the result previously obtained is not modified by terms linear in the overlap.

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_{eff} in which the O atoms are eliminated, using the cell-perturbation method.^{10,12,13,15,16,35} The Hamiltonian has the same form if O is replaced by other elements with p states near the Fermi energy, such as 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 H_I when all ten 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 in 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 make the physics of transition-metal compounds richer than that of the Hubbard model.^{28,31,32,37–39,74,75}

If all orbitals should be retained, more complicated terms appear [Eqs. (9) and (10)]. Our results suggest that because of the large M -O hopping for e_g holes in cubic or tetragonal symmetry, they should be retained, in general, even if the formal configuration of M contains six d electrons or less

(corresponding to only t_{2g} electrons in an ionic picture).

In the case of the cobaltates Na_xCoO_2 , where mainly $3d^6$ and $3d^5$ configurations play a role, our results as well as previous ones⁷⁰ show that addition or removal of electrons in the d shell causes a strong charge redistribution between metal e_g states and linear combination of $2p$ O states with the same symmetry. This has important consequences for the parameters of H_{eff} . In particular, the effective Coulomb repulsion U_{eff} is smaller than previously assumed in calculations of H_{eff} which include the effect of correlations.^{62–67} As a consequence if the hopping parameters and the trigonal distortion D are obtained from a fit of the bands obtained from first principles, six hole pockets appear along the Γ - K directions,^{65,66} which are not detected in photoemission experiments.^{3,4} Instead, using the values of the interactions and effective hopping obtained as described in the previous section, and the larger value of D given by quantum-chemistry configuration-interaction calculations,⁵⁵ these pockets are absent according to calculations which apply the dynamical mean-field theory to H_{eff} .⁴⁰ The resulting electronic dispersion near the Fermi energy agrees with experiment. Recent photoemission experiments in misfit cobaltates show results similar as previous ones with a significant band reduction due to correlations.⁷⁶

In general, the local-density approximation (LDA) underestimates gaps and one-particle excitations energies. Thus one might suspect that it underestimates the trigonal distortion energy D in the cobaltates. The above results suggest that taking the one-body parameters of the effective model H_{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,⁷⁴ 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.^{31,74} 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^{10–16,35} from a multiorbital Cu-O model^{41,42} with parameters obtained from constrained-density-functional theory.^{43,44}

For the cobaltates, we have determined the parameters of the original multiorbital model from a fit of polarized x-ray absorption spectra of Na_xCoO_2 .⁵⁴

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