Spin-state transition and spin-polaron physics in cobalt oxide perovskites: ab initio approach based on quantum chemical methods

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\textbf{Abstract.} A fully \textit{ab initio} scheme based on quantum chemical wavefunction methods is used to investigate the correlated multiorbital electronic structure of a 3d-metal compound, LaCoO\textsubscript{3}. The strong short-range electron correlations, involving both Co and O orbitals, are treated by multireference techniques. The use of effective parameters such as the Hubbard $U$ and interorbital $U'$, $J$ terms and the problems associated with their explicit calculation are avoided with this approach. We compute the ordering of the lowest $N$-particle states in the parent compound and provide new insight into the nature of charge carriers in the hole-doped material. Our results suggest that the transition to a magnetically active state at about 90 K in LaCoO\textsubscript{3} involves a high-spin, $t^4_{2g} e^2_{g}$ configuration. Additionally, we explain the paramagnetic phase in the low-temperature lightly doped compound through the formation of Zhang–Rice-like oxygen hole states and ferromagnetic clusters.

An accurate description of correlated electrons is one of the central problems of condensed-matter theory. The commonly used approach for the computation of electronic structures is based on the density functional theory and various approximations to it, the most applied being the local density approximation (LDA). This approach has led to unprecedented progress in computational condensed-matter physics and surprisingly good results for numerous compounds. However, it is also known and well documented that the LDA has problems

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with describing strongly correlated systems that usually involve d and f electrons. For that reason, extensions such as the LDA + U [1] and LDA plus dynamical mean-field theory (LDA + DMFT) [2] were developed. In the latter approach, the strong local correlations are described by effective interactions such as the Hubbard $U$, the interorbital Coulomb repulsion $U'$ and on-site exchange coupling $J$. Even so, the correlation treatment is limited to on-site effects, despite the fact that intersite correlations are known to be sizeable. To deal with the latter, the DMFT scheme has been generalized to a cluster DMFT [2, 3]. But a self-consistent computation of the Coulomb repulsion parameters $U$, $U'$ (and intersite $V$) is particularly difficult [4] in this context. It is fair to state that the main virtue of LDA, namely its simplicity, has got more and more lost.

This suggests the use of a different approach, based on the computation of many-body wavefunctions [5] by means of quantum chemical techniques [6]. It has the advantage that all approximations are well controlled and that it is not necessary to introduce effective interactions such as $U$, $U'$ or $J$. Here, we demonstrate this for the case of a 3d oxide compound, LaCoO$_3$. Our analysis is based on a local Hamiltonian approach [5], [7]–[11] and performed on large fragments including several CoO$_6$ octahedra. Localized Wannier functions and embedding potentials are obtained for these fragments from prior periodic Hartree–Fock (HF) calculations for the infinite crystal [10, 12]. Since our scheme is parameter-free, variational and multiconfigurational (or multireference, see below), it has great predictive power. It can, for example, predict the basic ingredients required in effective impurity models such as DMFT. For late transition-metal oxides, in particular, it is important to anticipate whether (and which of) the transition-metal d orbitals are sufficient for constructing a minimal effective orbital space or whether both transition-metal d and oxygen p functions must be considered as active. That such questions can be reliably addressed with quantum chemical methods was shown before for the layered copper oxides [13] and ladder vanadates [14]. However, simple point-charge embeddings were used in our previous work for representing the surroundings of the region where the correlation treatment is carried out. A newly developed, rigorous embedding technique [10, 12] is applied here for the first time to a 3d-metal compound.

LaCoO$_3$ has attracted considerable attention due to a number of puzzling phase transitions induced by changes in temperature [15, 16], doping [16, 17] and/or strain [18, 19]. Up to now, most of the experimental work was aimed at understanding the nature of the phase transitions in the undoped compound, from a nonmagnetic insulator at low temperatures to a paramagnetic semiconductor above 90 K and to a metal for $T > 500 \text{ K}$. The low-temperature ground state was assigned to a closed-shell $t_{2g}^6e_g^0$ configuration (low-spin (LS), $S = 0$) of the Co ions [15]. For $T \gtrsim 90 \text{ K}$, however, the available experimental results are rather contradictory. While recent x-ray absorption spectroscopy (XAS) [20] and inelastic neutron scattering (INS) [21] measurements indicate a gradual transition into an $S = 2$ ($t_{2g}^5e_g^2$) high-spin (HS) configuration of the Co 3d electrons with increasing $T$, electron energy-loss spectroscopy data [22] and the observation of Co–O bond-length alternation [23, 24] suggest the formation of an $S = 1$ ($t_{2g}^5e_g^1$) intermediate-spin (IS) state for $T > 90 \text{ K}$, susceptible to Jahn–Teller distortions. On the theoretical side, the transition to a HS state around 90 K is favored by many-body model Hamiltonian calculations [20]. The IS electron configuration is supported by LDA + $U$ calculations [22, 25]. A wavefunction-based quantum chemical analysis is not yet available for this system.

Our analysis uses the fact that the correlation hole of an electron in the ground-state of a system is rather a local object. It extends to a good approximation over a few lattice
sites only. Therefore, when we want to construct the correlation hole of an electron in a given orbital, we can limit its description to a finite cluster. The cluster must be properly embedded though in order to avoid unwanted charge flow. In our approach, the basis set for the correlation treatment is a set of localized Wannier orbitals. They are obtained from an HF calculation for the infinite crystal. If electron correlations are strong, a single Slater determinant is a poor starting point for the ground-state wavefunction. In this case, one must start from a self-consistent calculation which includes all possible configurations of strongly correlated electrons in Wannier orbitals centered within a certain neighborhood. Such multiconfiguration wavefunctions can be constructed with the complete-active-space self-consistent-field (CASSCF) method [6]. One might ask the question how is it possible to write down a ground-state wavefunction of this type for an infinite system. That is indeed a problem which can be solved only via a cumulant formulation, see [5]. However, since we calculate here the ground-state energy the problem does not show up if we use the method of computing energy increments [7], which includes correlation-energy contributions step by step. Having dealt with the strong correlation effects from the start, we may compute the energy contributions of the remaining weak correlations by any standard method. Here, we chose a multireference configuration-interaction (MRCI) method with single and double excitations [6].

For electron-removal and electron-addition states, the correlation hole is no longer short-ranged, due to the long-ranged polarization cloud of the added electron or hole. When comparing energies of different electron-removal (or electron-addition) states, the long-range polarization cloud drops out. Thus it is again the short-ranged part which is responsible for these energy differences. If the dielectric constant of the system is known, it is also possible to treat the long-range polarization contribution to the correlation energy by a continuum approximation [8]–[11]. This allows for calculating, e.g., ionization energies, although the accuracy for such quantities does not match the accuracy for ground-state properties.

The first step in our investigation is an \textit{ab initio} closed-shell restricted HF (RHF) calculation for the periodic solid. The \textsc{crystal} code [26] is employed for this purpose. We use all-electron Gaussian-type basis sets of triple-zeta quality\(^5\) and a cubic perovskite crystal structure. The Co–O distance is taken to be \(d = 1.92\ \text{Å}\), as reported for low temperatures in [29].

It is well known that the HF approximation strongly overestimates the fundamental band gap in insulators. For LaCoO\(_3\), the RHF gap is 13.3 eV, where the upper valence bands have O 2\(p\) character and the lowest conduction bands are related to the Co 3\(d\)-e\(_{g}\) levels.

On-site and intersite correlation effects are investigated in direct space by multiconfiguration CASSCF and MRCI calculations [6]. The orbital basis entering the correlation treatment is provided by the localization module of the \textsc{crystal} program. These functions are the Wannier orbitals associated with the RHF bands [30]. The CASSCF and MRCI calculations are carried out with the \textsc{molpro} quantum chemical package [31]. Although these electronic-structure calculations are performed at zero temperature, the energy splittings computed between the different \(N\)-particle states allow us to draw a more complete picture for the spin-state transition at about 90 K in LaCoO\(_3\).

Several sites are included in the correlation treatment. These sites are partitioned into two groups: an ‘active’ region \(C_A\), which here consists of one CoO\(_6\) octahedron, and a ‘buffer’ zone \(C_B\), including the Co and all other O ions of the six nearest-neighbor (NN) octahedra.

\(^{5}\) For O, we used the basis set (BS) of Corá [27], without d functions. For La, Towler’s BS was applied, see http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html. For Co, we used Towler’s s and p functions (see above) and the d functions of Seijo \textit{et al.} [28].
The role of $C_B$ is to ensure an accurate representation of the tails of the Wannier orbitals centered in the active region $C_A$. While the occupied orbitals in the buffer zone are frozen, orbitals centered at sites in the $C_A$ region (and their tails in $C_B$) are allowed to relax and polarize in the quantum chemical calculation. We denote $C_A + C_B$ as $C$. The surroundings of this group of ions (i.e. the crystalline environment) are modeled as an effective one-electron potential. This potential is obtained from the periodic RHF calculation and incorporated in the one-electron Hamiltonian in the CASSCF/MRCI treatment via the crystal–molpro interface [10, 12]. A ground-state closed-shell self-consistent-field calculation for $C$ leads to changes of only a few meV ($\approx 3$ meV) in the total energy, which shows that our embedding potential was properly constructed and the projection of the original crystal Wannier orbitals centered at sites of the $C_A$ region onto the set of basis functions associated with $C = C_A + C_B$ leads to insignificant changes of the longer-ranged ‘tails’, see also [10, 11].

The ground-state configuration and the nature of the lowest $N$-particle excited states are first studied at the CASSCF level. In CASSCF, a number of active electrons is allowed to be distributed in all possible ways over a given number of active orbitals. Both the orbitals and the coefficients in the multiconfiguration expansion are optimized [6]. In the present study, separate optimizations are performed for each particular spin state.

In the case of a single Co$^{3+}$ ion, a minimal active space is constructed with six electrons and five 3d orbitals, which we denote as CAS-5. Intriguingly, for such a minimal active space, CASSCF predicts a HS $t_{2g}^4e_{g}^2$ ($^3T_{2g}$) ground-state configuration. The LS state, $t_{2g}^6e_{g}^0$ ($^1A_g$), is 1.26 eV higher in energy. The IS state, $t_{2g}^5e_{g}^1$ ($^3T_{1g}$), is 0.21 eV above the LS state, see figure 1. Clearly, the minimal active orbital space is insufficient for this system.

A first guess is that the active space must be enlarged with O 2p orbitals. Indeed, the RHF band structure, with the O 2p bands located above the Co $t_{2g}$ levels, see above, suggests that O 2p to Co 3d charge-transfer (CT) effects are important. The two $\sigma$-like $e_g$ combinations of 2p orbitals at the NN O sites have the largest overlap with the Co 3d functions. When these two combinations of $e_g$ symmetry are added to the active space, which we denote as the CAS-7...
active orbital space, the CASSCF HS–LS splitting is reduced from 1.26 to 0.87 eV. This is related to the strong interaction between the ‘non-CT’ $t_{2g}^6e_g^0$ and the O 2p–e$_g$ to Co 3d–e$_g$ CT configurations in the LS CASSCF wavefunction. However, the HS state is still the lowest, see figure 1. Other types of charge fluctuations are taken into account by MRCI calculations. In a first step, we account for all single and double excitations from the Co 3d and O 2p–e$_g$ orbitals. The reference is the CAS-7 wavefunction. The HS–LS splitting is now reduced by an additional 0.70 eV to 0.17 eV, with the HS state remaining lower in energy. A switch in the energy order of these two states is only obtained when accounting for correlation effects (single and double excitations in the MRCI treatment) that involve the semi-core Co 3s and 3p electrons. These correlations are mainly related to the coupling between the O 2p–e$_g$ excitations in the MRCI treatment) that involve the semi-core Co 3s and 3p electrons. The reference is the CAS-7 wavefunction. The HS–LS splitting is now reduced by an additional 0.70 eV to 0.17 eV, with the HS state remaining lower in energy. A switch in the energy order of these two states is only obtained when accounting for correlation effects (single and double excitations in the MRCI treatment) that involve the semi-core Co 3s and 3p electrons. These correlations are mainly related to the coupling between the O 2p–e$_g$ to Co 3d–e$_g$ CT, on-site Co 3s, 3p → 3d, 4s, 4p and Co 3d → 4s, 4p excitations. For such MRCI wavefunctions, which are referred to as MRCI-11, the LS state is found indeed to be the lowest and the first N-particle excited state is the HS state, with an excitation energy of 6 meV (∼ 70 K, not visible in figure 1).

As compared with the IS state, we still find that the HS state is lower in energy, in agreement with the interpretation of recent XAS [20] and INS [21] experiments. For an undistorted lattice this energy difference is 0.60 eV, in contrast to LDA + $U$ calculations [25], which predict that the IS arrangement is lower in energy even when Jahn–Teller-type couplings are neglected. Additionally, the above quantum chemical study provides unique, detailed information about the importance of different correlation effects. In particular, our analysis demonstrates that inclusion of the O 2p orbitals in the correlation treatment is essential. In other many-body techniques such as DMFT, the ligand orbitals are usually excluded from the correlation treatment.

We note that size-consistency corrections on the relative energies are small, as shown by the influence of Davidson corrections to the variational MRCI results. These corrections reduce the HS–IS splitting by 0.05 eV and increase the LS–HS splitting by 0.07 eV in the MRCI-11 calculations. Small variations in the opposite directions are expected to arise for the LS–HS and HS–IS splittings from CT excitations involving the π-like O 2p and Co 3d orbitals of $t_{2g}$ symmetry because in the HS state the number of holes in the Co $t_{2g}$ orbitals is the largest. However, inclusion of these excitations in the MRCI wavefunctions is presently unfeasible (see footnote 7). We now proceed with the analysis of the lowest electron-removal and electron-addition states. It was argued that the largest interaction with the 2p → 3d CT configurations and the strongest stabilization effects occur for the $t_{2g}^6e_g^0$ IS hole state [32]. Therefore, the lowest (N − 1) states are often associated with an IS, $t_{2g}^6e_g^0$ ($^2T_g$) configuration of the Co ions. Our calculations show that the lowest-energy hole states are related to the LS, $t_{2g}^5e_g^0$ ($^2T_g$) configuration. Even by CASSCF, with a CAS-7 active space, the LS $t_{2g}^5e_g^0$ hole state is about half an electron volt lower than the IS (N − 1) state. MRCI calculations that include the Co 3s, 3p electrons yield an even larger splitting of 0.85 eV, see figure 1. The implication is that the strongest CT effects occur for reference configurations with completely empty 3d–e$_g$ levels, as also found in the N-electron system.

The lowest hole state in LaCoO$_3$ has strong O 2p character and resembles the lowest (N − 1) state in cuprates [33]. In cuprates, the dominant contribution to the ionized state is a superposition of two configurations, $|t_{2g}^6d_z^2b_z^2a_1^0\rangle$ and $|t_{2g}^6d_z^2b_z^2a_2^0\rangle$, where $b$ and $a$ are bonding

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7 In the present version of molpro [31], for an open-shell reference wavefunction, the virtual orbital space cannot be restricted only to the $C_A$ region. It thus includes virtual orbitals in both $C_A$ and $C_B$, which lead to very large expansions of the wavefunction, $\approx 10^9$ Slater determinants in the MRCI-11 calculations.

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Figure 2. Bonding and antibonding p–d orbitals for the LS hole state of (a) $(x^2 - y^2)$ and (b) $z^2$ symmetry. The $(x^2 - y^2)$ hybrids resemble the Zhang–Rice-like p–d orbitals \cite{33} in cuprates.

and antibonding combinations of the O 2p$_\sigma$ and Cu 3d orbitals of $(x^2 - y^2)$ symmetry on one CuO$_4$ plaquette. In the CASSCF wavefunction \cite{13}, the Cu 3d and O 2p$_\sigma$ $(x^2 - y^2)$ orbitals contribute with nearly equal weight to $b$ and $a$. The added hole has therefore predominant O 2p character \cite{13}. For cubic perovskites, the two 3d-e$_g$ components are degenerate. The dominant contributions to the first ionized state in LaCoO$_3$ then imply three configurations: $|t^5_2g b^2 x^2-y^2 b^0 a^0 y^2 a^0 z^2\rangle$, $|t^5_2g b^0 x^2-y^2 b^2 a^0 x^2-y^2 a^0 z^2\rangle$ and $|t^3_2g b^2 x^2-y^2 b^0 a^0 y^2 a^0 z^2\rangle$. The bonding and antibonding e$_g$ orbital combinations are again strong mixtures of transition-metal 3d and O 2p functions (see figure 2), such that the added hole has large weight at O sites. However, in contrast to the hole state in cuprates, all six ligands are involved, although in the presence of lattice distortions \cite{23, 24} the e$_g$ levels split and the hole does not have the same weight at each of the NN ligands. A study of the coupling between the charge and lattice degrees of freedom in LaCoO$_3$ is very demanding and therefore left for future work.

The strong O 2p hole character of the ionized state is expected to induce ferromagnetic (FM) correlations between the Co t$^4$-like ion and its six Co NNs, like for the 2p hole in cuprates\cite{8} or for the O 2p$^1$ configuration in NaV$_2$O$_5$ \cite{14}. The formation of FM spin-polaron clusters was indeed inferred from measurements of the magnetization in lightly doped samples, see, e.g., \cite{16}. For no or small distortions, the mixing with higher energy configurations related to intersite d–p excitations within the set of e$_g$ orbitals is expected to give rise to a HS t$^4_2$e$^2_\sigma$ configuration at each of the six NN Co sites and a total spin of $S = 1/2 + 6 \times 2 = 25/2$ for the seven-site spin cluster. If the coupling to the lattice is strong, an IS configuration t$^2_2$e$^1_\sigma$ at the NN Co sites \cite{23} can be energetically more favorable and the total spin is $S = 1/2 + 6 \times 1 = 13/2$. Obviously, the motion of the added hole is strongly renormalized by the NN FM correlations.

\cite{8} In contrast to the original picture of Zhang and Rice \cite{33}, from the magnetic point of view, the two-hole p–d state is not decoupled from other Cu sites, see \cite{13}.
In cuprates, for example, the NN ‘bare’ hopping is reduced by a factor of 4 by short-range spin interactions [13]. The study of such correlations requires very involved calculations for LaCoO$_3$ because a number of five d orbitals is needed at each Co site. A computational approach like that used in cuprates, where all transition-metal neighbors of the two octahedra directly involved in the hopping process are included in CASSCF [13], is at present not feasible for LaCoO$_3$. The possibility of using an incremental scheme like that proposed in [7] will be investigated in future work.

The lowest ($N+1$) states are related to the HS $t_{2g}^4e_g^2$ ($^{4}T_{1g}$) configuration. MRCI calculations, which include in addition to the orbitals used in the CAS-7 reference the Co 3s, 3p, predict a splitting of 1.00 eV between the $t_{2g}^4e_g^2$ ($^{4}T_{1g}$) and $t_{2g}^5e_g^1$ ($^{2}E_g$) states.

The matrix elements associated with local electron-removal and electron-addition configurations such as those described above can be used to construct ‘correlated’ band structures within a quasiparticle picture [8]–[11], [13]. The $N \to (N+1)$ excitation energies correspond to the diagonal (‘on-site’) matrix elements in the $\vec{k}$-dependent secular problem while overlap and Hamiltonian integrals involving holes or added electrons at different lattice positions $R$ (i.e. $\langle \Psi_{\alpha_{1\sigma_{1}}}^{N+1} | H | \Psi_{\alpha_{2\sigma_{2}}}^{N+1} \rangle$ matrix elements, where $n$ is a band index and $\sigma$ denotes the spin) enter as off-diagonal (intersite) terms. As discussed above, accurate results for the intersite matrix elements cannot be obtained at this moment in LaCoO$_3$. Nevertheless, we can extract from our data estimates for the ionization potential (lowest $N \to (N-1)$ excitation energy) and electron affinity (lowest $(N+1)$ state). In our MRCI calculations, these values are $IP_0 = 4.47$ and $EA_0 = -4.24$ eV and incorporate the most important short-range correlations. Corrections due to long-range polarization effects can be estimated by applying the approximation of a dielectric continuum [8]–[11]. This gives $IP = IP_0 - C/R$ and $EA = EA_0 + C/R$, where $C = e^2(\varepsilon_0 - 1)/2\varepsilon_0$, $\varepsilon_0 \approx 23$ [34] is the static dielectric constant and $R$ defines a sphere around the extra hole or electron beyond which the dielectric response reaches its asymptotic value $\varepsilon_0$. $R$ is taken here as the average between the NN Co–O and Co–La distances, $R = 2.62$ Å, which leads to $IP = 1.84$ and $EA = -1.61$. Given the fact that we neglect the finite widths of the two bands, the energy difference $IP - EA = 3.45$ eV represents an overestimate of the actual band gap.

To summarize, a recently developed ab initio scheme is applied here to study many-body effects in LaCoO$_3$. The zero-temperature ground state involves a subtle interplay among Coulomb, exchange and ligand-field interactions plus on-site and CT fluctuations. The lowest $N$-particle excited state is predicted to be the HS $t_{2g}^4e_g^2$ state. In agreement with the interpretation of XAS [20] and INS [21] experiments, the IS $t_{2g}^5e_g^1$ state is found to be higher in energy. For an undistorted lattice, our calculations predict an energy difference of 0.60 eV between the HS and IS states. Whether this HS–IS splitting is sufficiently low to be compensated by the energy gain associated with a Jahn–Teller ordered configuration of the $e_g$ orbitals, as suggested in [23], will be the subject of future work. We also study the nature of the low-energy electron-removal and electron-addition states. The lowest $(N-1)$ excitation is related to a local $t^5$-like, $S = 1/2$ configuration. The added hole has large weight at the O sites, due to a strong mixing of the Co and O $e_g$ orbitals. A large hole density at the O sites causes FM correlations among the adjacent Co 3d electrons, which agrees with the observation of ‘giant’ FM polarons ($S = 10–16$) and paramagnetic behavior at small doping and low $T$ [16]. Our analysis offers new insight into the correlated electronic structure of LaCoO$_3$. Additionally, the ab initio results provide valuable information for models aiming at a realistic description of the finite-temperature properties of this system.

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