DFT+DMFT study of spin-charge-lattice coupling in covalent LaCoO$_3$

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We study the energetics of both homogeneous and mixed spin-states incorporating structural changes of the crystal volume expansion and the Co-O bond-disproportionation (BD) in LaCoO$_3$ using the density functional theory plus dynamical mean field theory (DFT+DMFT) method. Within DFT+DMFT, the multi-configurational nature of excited spin-states exhibits smooth crossover from the low spin state during the spin-state transition and both excited spin-states are energetically almost the same while the DFT+U calculation of the same structure produces various meta-stable solutions with energetics depending sensitively on spin-states. The homogeneous spin-state has non-negligible occupancy probabilities of both high spin (HS) and low spin (LS) states along with $d^6$ and $d^7$ charges indicating the dynamically fluctuating nature of spin and charge states due to the Co-O covalency. We find that the energetics depend on the $d$-occupancy, $N_d$ tuned by the double counting potential, and $N_d$ close to 6.7 is consistent with the nature of the spin-state transition. The mixed spin-state under the BD structure shows that Co sites with long Co-O bonds favors HS with $d^6$ states while covalent Co sites with short bonds occupies more LS with $d^7$ states, therefore charge ordering is also induced from spin-state ordering.

Transition metal oxides exhibit complex and rich phase diagrams arising from the strongly correlated nature of spin, charge, orbital, and lattice degrees of freedom $^{[1]}$. LaCoO$_3$ has been known for the spin-state transition of partially filled $d$ orbitals in a Co ion. At very low temperatures, LaCoO$_3$ is a non-magnetic insulator with the low spin (LS) state. As the temperature is elevated above 90K, the magnetic susceptibility changes to a Curie-Weiss form indicating that paramagnetism dominates with higher spin states while retaining an insulating behavior $^{[2]}$. The spin-state transition can be explained based on the atomic multiplet structure of the Co $d$ orbital, namely from the $|S_z|=0$ LS ground state to $|S_z|=1$ intermediate spin (IS) or $|S_z|=2$ high spin (HS) state. Various experimental results have been used to interpret the higher spin state as either IS $^{[3, 4]}$ or HS $^{[5, 6]}$. The mixed spin-state of LS and HS has been also suggested to explain other experimental measurements $^{[6, 7]}$. Despite extensive experimental works, the nature of excited spin-states has not been clarified yet.

The spin-state transition in LaCoO$_3$ occurs since the Hund’s coupling tends to maximize the spin and excite electrons from $t_{2g}$ to $e_g$ orbitals by overcoming the crystal field splitting between them. Here, the interplay between electron and lattice degrees of freedom plays an important role as the $e_g$ orbital occupation increases the Co-O bond-length to reduce the repulsive Coulomb interaction of electrons between Co and O ions. This structural change also gives the positive feedback since the reduction of the crystal-field splitting can favor the spin-state transition. This strong electron-lattice coupling has been measured experimentally by the anomalous lattice expansion arising due to the Co-O bond-length elongation at the spin-state transition $^{[14, 17]}$. Several scenarios of local structural distortions due to the spin excitation have been proposed although clear experimental evidences have not been given yet. The Co-O bond-disproportionation (BD) with alternating the long bond (LB) site and the short bond (SB) site $^{[9, 18]}$ was suggested to accommodate mixed spins with HS and LS. The Jahn-Teller distortion $^{[6, 19]}$ was also discussed possibly due to the IS state. The strong electron-lattice coupling has been also shown in the tensile-strained LaCoO$_3$ film promoting various competing orders including spin $^{[20-22]}$, charge $^{[23]}$, and orbital orderings $^{[24]}$.

Alongside experimental measurements, various theoretical scenarios based on first-principle calculations have been proposed to address this long-standing problem of the spin-state transition in LaCoO$_3$. Density functional theory (DFT)+U calculations have been predicting that excited spin-states including IS $^{[25, 26]}$ and mixed spin $^{[27, 28]}$ states can be energetically stable. Dynamical mean field theory (DMFT) can capture the multi-configurational nature of a paramagnetic state fluctuating dynamically beyond DFT+U $^{[29, 30]}$. Early DFT+DMFT studies computed the single-particle spectra with spin-state crossover $^{[31]}$ comparable to the experimental X-ray absorption spectra $^{[4]}$ and also studied effects of the pressure $^{[32]}$ and the Co-O covalency $^{[32]}$ on the spin-state transition. Both the homogeneous spin excitation including the electronic entropy $^{[34]}$ and the mixed LS and HS solution without any structural distortions $^{[35, 36]}$ have been discussed as the possible origin of the spin-state transition within DFT+DMFT. However, no DFT+DMFT studies have addressed yet both the nature and energetics of paramagnetic states with possible structural changes in this material. In this paper, we adopt the DFT+DMFT method to study both homogeneous and mixed spin-states incorporating the structural distortions and will show that the DFT+DMFT energet-
ics treating the multi-configurational nature of a paramagnetic state can be noticeably different from static DFT+U solutions. We also find that both the structural change and the Co-O covalency effect tuned by the double counting potential can strongly affect the nature of spin-states in LaCoO$_3$.

To study possible structural distortions during the spin-state transition, we first perform the structural relaxation by adopting the DFT+U method as implemented in the VASP code using different spin-states as initial guess. LaCoO$_3$ is a rhombohedral structure with the $R3c$ symmetry containing two Co ions per unit cell. The experimental crystal volume $V$ is 56.0Å$^3$ per formula unit at low temperatures [17]. We find that the DFT+U relaxation calculation with the PBE functional converging to LS produces the volume $V$ ∼ 56.40Å$^3$ per formula unit with the Co-O bond-length, $a$ ∼ 1.95Å while the IS state results in the 2.7% volume expansion resulting $V$ ∼ 57.98Å$^3$ per formula unit and $a$ ∼ 1.97Å. The HS structure converged to a more expanded volume but the total energy is much higher than either LS or IS one. Interestingly, the mixed spin-state imposing HS to one Co ion and LS to the other Co ion within the unit-cell produces the BD structure by lowering the crystal symmetry from $R3c$ to $R3$. The crystal volume $V$ is similar to the IS volume ($V$ ∼ 57.98Å$^3$) and the HS site is a Co-O long-bond (LB) with $a$ ∼ 1.99Å and the LS site is a short-bond (SB) with $a$ ∼ 1.94Å, resulting in the bond-length difference $\delta a$ ∼ 0.05Å.

Using LS, IS, and mixed spin structures obtained from DFT+U relaxations, we employ a charge-self-consistent DFT+DMFT method [12] to study the nature and energetics of the spin-state transition. The DFT+DMFT method is implemented using the maximally localized Wannier functions (MLWFs) [43,44] as localized orbitals. The DMFT impurity problem is solved using the continuous time quantum Monte Carlo (CTQMC) [45,46] solver. The on-site Hubbard interaction $U$=6eV, which is obtained using the constraint DFT method [35], and the Hund’s coupling $J$=0.9eV are used for both DFT+DMFT and DFT+U calculations. Temperature used in DMFT is 300K. The details of our calculations used in this paper and the charge-self-consistency effect on results are given in the Appendix.

The double counting (DC) energy, $E^{DC}$, needs to be defined for beyond-DFT methods including DFT+DMFT and DFT+U since the potential energy treated in the correlated subspace is already accounted as the part of the DFT energy and it needs to be subtracted from the total energy formula. Various DFT+DMFT calculations suggest that the DC potential, $V^{DC}(=\partial E^{DC}/\partial N_d)$ smaller than the frequently used fully localized limit (FLL) form [47] can produce better agreements of energetics [42,48], the metal-insulator transition [49,51], and the $p-d$ orbital splitting [49,51,52] of oxides compared to experiments. Here, we propose an $E^{DC}$ form which can be modified from the FLL form by replacing $N_d$ to $\tilde{N}_d$:

$$E^{DC} = \frac{U}{2} \cdot (\tilde{N}_d - \alpha) \cdot (\tilde{N}_d - 1) - \frac{J}{4} \cdot \tilde{N}_d \cdot (\tilde{N}_d - 2)$$  (1)
$$V^{DC} = U \cdot (\tilde{N}_d - \frac{1}{2}) - \frac{J}{2} \cdot (\tilde{N}_d - 1)$$  (2)

where $\tilde{N}_d = N_d - \alpha$, $N_d$ is the d–occupancy obtained self-consistently at each correlated site, and $\alpha$ is a parameter which can be tuned for different $E^{DC}$ and $V^{DC}$ values from the FLL form. Recently, it has been also shown that the exact form of $V^{DC}$ should be close to the nominal DC form, where $N_d$ in the FLL form is replaced to the nominal d–occupancy, $N_d^0$ in the atomic limit [52]. Our modified $V^{DC}$ form can also recover this nominal $V^{DC}$ value as $\tilde{N}_d$ becomes $N_d^0$ by increasing $\alpha$. One should note that changing $V^{DC}$ with different $\alpha$ values can also tune the $p-d$ covalency effect by effectively shifting the $d$ orbital level. For example, the smaller $V^{DC}$ than the FLL potential will make the $d$ orbital level higher and the covalency effect weaker, resulting in a reduced $N_d$ value.

![FIG. 1. Total energy differences between excited spin-states and LS in LaCoO$_3$ computed using DFT+DMFT (top panel) and DFT+U (bottom panel) as a function of $N_d$ tuned by different $\alpha$ values in $V^{DC}$ (Eq.2). The excited spin-states incorporate the volume expansion with or without the Co-O BD ($\delta a$=0.05Å or 0Å). The left vertical dashed line represents the $N_d$ value obtained from the nominal DC formulae while the right one shows $N_d$ obtained using the FLL formulae. Both DFT+DMFT and DFT+U methods use the same correlated orbitals (MLWFs) with the same interaction parameters ($U$=6eV and $J$=0.9eV). Temperature is 300K within DMFT.](image)
Here, we begin by showing the effect of different $V^{DC}$ values on the energetics of spin-states in LaCoO$_3$ computed using DFT+DMFT (Fig. 2 top panel) and DFT+U (Fig. 3 bottom panel). The $x$-axis shows $N_d$ values obtained by changing $V^{dc}$ in Eq. 2 using different $\alpha$ values, namely $\alpha=0$, $0.2$, $0.4$, $0.6$, and $0.7$. Two vertical dashed lines indicate the $N_d$ values obtained using the FLL DC formulae (the right line) and the nominal DC formulae (the left line). The calculations with the FLL DC ($\alpha=0$) converge to $N_d \sim 7.2$ for DFT+DMFT and $7.1$ for DFT+U while those with the nominal DC result in $N_d \sim 6.68$ for DFT+DMFT and $6.65$ for DFT+U. The $y$-axis indicates the total energy difference between the expanded volume ($V \sim 57.98 \text{Å}^3$) accompanying excited spin-states and the LS volume ($V \sim 56.4 \text{Å}^3$). Here, DFT+U energies are computed by adopting the MLWFs as correlated orbitals consistently with DFT+DMFT calculations, therefore the difference between DFT+DMFT and DFT+U results is attributed purely to the dynamical correlation effect beyond DFT+U.

The energetics obtained using two methods show noticeable differences depending on $N_d$ (the Co-O covalency effect). The DFT+DMFT energy difference between two expanded volume structures ($\delta a=0$Å and 0.05Å) is much smaller (maximally 20meV) than the DFT+U energy difference while DFT+U solutions converge to various meta-stable states for a given structure (LS, IS, and HS for $\delta a=0$Å and LS-HS and LS-IS for $\delta a=0.05$Å) and the energy depends sensitively on $N_d$ and spin-states. This difference in energetics arises since the spin-state within DFT+DMFT is described as a multi-configurational state with a mixture of various spin states showing smooth crossover (see Fig. 3) while DFT+U can produce meta-stable states based on a single-determinant form even when the structure and $N_d$ change.

Within DFT+DMFT, the $\delta a=0$Å structure (triangular dot) is more stable when $N_d > 7.0$ and the LS state is dominant while the $\delta a=0.05$Å BD structure (circular dot) becomes stable when the spin-state transition to LS-HS occurs ($N_d < 7.0$). Two structures become energetically almost the same when $N_d$ is further reduced ($N_d \sim 6.7$) since the energy of the $\delta a=0$Å structure becomes even lowered as HS is more excited. The dependence of DFT+U energetics on $N_d$ behaves qualitatively similar as LS with the $\delta a=0$Å structure is stable when $N_d > 6.8$ and LS-HS with the $\delta a=0.05$Å BD structure becomes rapidly stable when $N_d$ is further reduced. The energy of HS with the $\delta a=0$Å structure is also rapidly decreasing at smaller $N_d$ as the Hund’s coupling lowers the energy in the HS state. Within DFT+U, energetics of other meta-stable states including LS and LS-IS do not depend much on $N_d$ while IS is not favored as $N_d$ is reduced. Our calculations show that the spin-state transition from the LS volume structure to excited spin-states with the expanded volume ($E - E(\text{LSvol.}) < 0$) occurs when $N_d$ becomes smaller ($< 6.9$ for DFT+DMFT and $< 6.8$ for DFT+U). This is consistent with the nominal $V^{DC}$ result (the left vertical dashed lines; $N_d \sim 6.8$ for DFT+DMFT) and the fact that higher spin states are more excited at smaller $N_d$.

Now we turn to the nature of paramagnetic states in LaCoO$_3$ obtained within DFT+DMFT. Fig. 2 displays the spin $|S_z|$ probabilities sampled using CTQMC as a function of $N_d$ for different structures. The multi-configurational nature of the paramagnetic state treated in DFT+DMFT means that various $|S_z|$ states ($S_z = 0.0 \sim 2.0$) contribute to the solution. When $N_d > 7.0$, LS with $|S_z| = 0$ and 0.5 has the highest probability for all structures, consistently with the fact that the LS structure ($V = 56.40 \text{Å}^3$) is energetically stable. As $N_d$ is reduced, LS is still dominant for the LS structure while HS with $|S_z| = 1.5$ and 2 becomes more excited for the expanded structure ($V = 57.98 \text{Å}^3$). The nature of paramagnetic state in this expanded structure, which is energetically stable when $N_d < 6.7$, is characterized by a mixture of both LS and HS, fluctuating dynamically with non-negligible probabilities. The IS state ($|S_z| = 1.0$) is strongly suppressed for all structures. In the BD structure, HS becomes rapidly favored in the LB site as $N_d$ is reduced while LS is always dominant in the SB site. The covalent nature of Co $d$ and O $p$ orbitals means that the charge $d^\delta$ state with $|S_z|=0.5$ and 1.5 is also strongly populated in addition to the nominal $d^\delta$ state, therefore both spin and charge states are coupled and strongly fluctuating.

The strongly coupled spin and charge degrees of freedom also produce an intriguing charge ordering state induced from the mixed spin-state in the BD structure. Fig. 3 shows that the DFT+DMFT charge in the LB site
FIG. 3. The $d-$occupancy, $N_d$ computed for both LB and SB sites in the BD structure computed using DFT+DMFT as a function of the average $\langle N_d \rangle$ between two sites.

(angular dots) gets smaller more rapidly than the SB charge (circular dots) as the average $\langle N_d \rangle$ becomes reduced (the overall Co-O covalency is reduced). This is because HS in the LB site favors the $|S_z| = 2$ with $d^0$ state while the $|S_z| = 0.5$ with $d^2$ state is dominant in the SB site as the Co-O covalency remains strong. This enhancement of charge ordering when $N_d < 6.9$ is also consistent with the rapid increase of the HS probability in the LB site as shown in Fig. 3. The experimental evidence of charge ordering with the concomitant spin-state ordering in LaCoO$_3$ has been reported in the tensile-strained film [23]. This mixed spin-state with the BD structure is somewhat reminiscent of the site-selective Mott physics occurring in nickelates in which the LB site is Mott insulating with the $d^0$ state while the SB site is a covalent insulator hybridized with O hole states as $d^6 L^2$. Although charge ordering between two Ni sites is not necessary to induce the insulating state in nickelates, the mixed spin-state with the Co-O breathing distortion induces charge ordering ($\sim 0.2$) in LaCoO$_3$. Also, nickelates are negative charge-transfer insulators meaning that almost one electron is donated to each Ni ion from surrounding O ions while the Co ion in LaCoO$_3$ favors a mixed-valence state with $N_d = 6.6 \sim 6.7$.

Finally, we show the density of states (DOS) computed using DFT+DMFT in Fig. 4 for different structures. The $\alpha$ in $V^{DC}$ (Eq. 2) is set to 0.7 resulting $N_d \sim 6.68$ for all structures. Different $V^{DC}$ values will change the relative position of the O $p$ peak from the Fermi energy as $N_d$ is also varied. Our O $p$ top peak position is located at -2eV when $N_d \sim 6.68$ and this peak position is consistent with the measured X-ray photo-emission spectra [4]. The DOS in the LS volume (Fig. 4a) shows that the band gap is almost 0.6eV, which is consistent with the optical gap measurement [5]. The $t_{2g}$ state is almost occupied while $e_g$ state is unoccupied, as expected. As the volume is expanded, the spin-state transition to higher spins occurs continuously and the $t_{2g}$ state begins to be unoccupied while more $e_g$ orbitals are occupied. Both $e_g$ and $t_{2g}$ orbitals are gapped and the gap size has increased from the LS gap. The nature of this paramagnetic insulating state is a mixture of fluctuating HS and LS states and it is distinct from the IS state which usually requires the large hybridization between Co and O. In the BD structure, the LB site becomes higher spin state with more unoccupied $t_{2g}$ states while the SB site remains as LS with a similar gap size as the homogeneous LS gap.

In conclusion, we adopt the charge-self-consistent DFT+DMFT method to study the nature and energetics of both homogeneous and mixed spin states in covalent LaCoO$_3$. As the crystal volume is expanded, the occupation probability of higher spin state increases and the paramagnetic insulating state exhibit a multi-configurational mixture of both HS and LS states with strong spin and charge fluctuations. The mixed spin-state accompanies the Co-O BD structure with HS in the LB Co sites and LS in the SB sites. Charge ordering is also induced from spin-state ordering since HS favors the $d^0$ charge state while LS occupies more $d^2$ states as covalently bonded with O ions. Changing $V^{DC}$ potentials in DFT+DMFT can lead to different $N_d$ values and also affect both the nature and energetics of spin-states. We find that both the energetics and the one-
particle spectra are more consistent with experiments when $N_d \sim 6.7$ (similarly obtained using the nominal $V^{\text{DC}}$ potential). Energetics of both homogeneous and mixed spin-states incorporating structural changes are very close in DFT+DMFT while DFT+U can suffer from the multiple meta-stable solutions and their energetics depend sensitively on the spin-state and $N_d$. Therefore, DFT+DMFT can be a promising method for describing the strong interplay among spin, charge, and lattice degrees of freedom in transition metal oxides.

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**APPENDIX A: DETAILS OF THE METHODS USED IN THE PAPER**

In this paper, we perform the structural relaxation of LaCoO$_3$ using the DFT+U method as implemented in the Vienna ab-initio simulation package (VASP) [37–40] code. The Perdew-Burke-Ernzerhof (PBE) functional [11] is used for the exchange-correlation functional within DFT. The DFT+U convergence is achieved using the plane-wave energy cut-off of 600eV and the $k$–point mesh of $8 \times 8 \times 8$. The convergence of the structural relaxation is achieved if the atomic forces of all ions are smaller than 0.01eV/Å. Within DFT+U, we use the onsite Hubbard interaction $U=6$eV, which is obtained using the constraint DFT method [33], and the Hund’s coupling $J=0.9$eV.

After we obtain relaxed structures, we employ a charge-self-consistent DFT+DMFT method [42] implemented using Wannier functions as localized basis sets to study correlated electronic structure of LaCoO$_3$. First, we solve the non-spin-polarized Kohn–Sham (KS) equation within DFT using the VASP code. Then, we use the maximally localized Wannier functions (MLWFs) [33, 14] as localized orbitals for the DFT+DMFT method. In the case of LaCoO$_3$, Co 3$d$ and O 2$p$ orbitals are constructed from MLWFs to represent the hybridization subspace for solving DMFT equations. The Co–O covalency effect can be treated within DMFT by including both $d$ and $p$ orbitals in the hybridization subspace. The DMFT self-consistent equations are solved using the continuous time quantum Monte Carlo (CTQMC) [43, 46] impurity solver. Once the DMFT loop is converged, the charge density can be recomputed from the DMFT local Green’s function and the KS equation is solved again using the updated charge density. The DFT+DMFT self-consistency loop is continued until both the DFT charge density and the DMFT self-energy $\Sigma^{\text{loc}}$ are converged. Within the DFT loop, the energy cut-off of 600eV and the $k$–point mesh of $8 \times 8 \times 8$ are used. The Hubbard U is 6eV, the Hund’s coupling J is 0.9eV, and the temperature is 300K within DMFT calculations. Within the DMFT loop, a dense $k$–point mesh of $30 \times 30 \times 30$ is used within the hybridization subspace of Wannier orbitals.

Once the DFT+DMFT self-consistency loop is converged, the total energy $E$ is computed using the following formula:

$$E = E^{\text{DFT}}[\rho] + \frac{1}{N_{\kappa}} \sum_{\kappa \in W} \epsilon_{\kappa} (n_{\kappa} - n_{\kappa}^0) + E^{\text{POT}}[G^{\text{loc}}] - E^{\text{DC}}[N_d]$$

(3)

where $E^{\text{DFT}}$ is the DFT energy computed using the charge density $\rho$ obtained within DFT+DMFT, $\epsilon_{\kappa}$ is the DFT eigenvalues, $n_{\kappa}$ is the diagonal part of the DMFT occupancy matrix element with the KS band index $\kappa$ and the momentum $\kappa$, $W$ is the energy window for the hybridization subspace, and $n_{\kappa}^0$ is the DFT occupancy matrix element with the KS band $\kappa$ and the momentum $\kappa$. The potential energy $E^{\text{POT}}$ within DMFT is given by the Migdal-Galiski formula: $E^{\text{POT}} = \frac{1}{4} \text{Tr}[\Sigma^{\text{loc}}(i\omega) \cdot G^{\text{loc}}(i\omega)]$. More details of the DFT+DMFT implementation combining the projected augmented wave (PAW) method in the DFT part and including the formula for the charge update and the application of the total energy calculation to the rare-earth nickelates can be found in Ref. 12.

The double counting (DC) energy, $E^{\text{DC}}$ needs to be subtracted since the part of the DFT correlation energy already accounts the correlation energy treated within DMFT. A frequently used expression of $E^{\text{DC}}$ is the fully localized limit (FLL) form [17] which has been adopted mostly in DFT+U.

$$E^{\text{DC}} = \frac{U}{2} \cdot N_d \cdot (N_d - 1) - \frac{J}{4} \cdot N_d \cdot (N_d - 2)$$

(4)

$$V^{\text{DC}} = \frac{\partial E^{\text{DC}}}{\partial N_d} = U \cdot (N_d - \frac{1}{2}) - \frac{J}{2} \cdot (N_d - 1)$$

(5)

where $N_d$ is the occupancy of the correlated orbital and obtained as the result of self-consistent DFT+DMFT or DFT+U calculations. This $V^{\text{DC}}$ potential depends on the correlated site since $N_d$ is site-dependent. Recently, it has been shown that the exact form of $V^{\text{DC}}$ within DFT+DMFT [52] can be computed and the formulae should be close to the nominal DC form, where $N_d$ in Eq. 3 is replaced to the nominal $d$–occupancy, $N_d^0$ which...
is site-independent.

\[ V^{DC} = U \cdot (N_d^0 - \frac{1}{2}) - J \cdot (N_d^0 - 1) \]

The hybridization of \( d \) and \( p \) orbitals in transition metal oxides means that the resulting \( d \)-occupancy \( N_d \) will be larger than the nominal value \( N_d^0 \) (\( N_d > N_d^0 \)), therefore the nominal \( V^{DC} \) will be always smaller than the FLL \( V^{DC} \). Another modified form of \( V^{DC} \) for DFT+DMFT was suggested by reducing the \( U \) value used in the FLL form \((U' < U)\) to allow the smaller \( V^{DC} \) potential than the FLL one:

\[ E^{DC} = U' \cdot N_d \cdot (N_d - 1) - J \cdot (N_d - 2) \]

\[ V^{DC} = U' \cdot (N_d - \frac{1}{2}) - J \cdot (N_d - 1) \]

It has been shown that using \( U' = U - 0.2eV \) can successfully reproduce the structural and electronic phase diagram of rare-earth nickelates \( 12 \, \text{RA} \). In this paper, we propose the following form of \( V^{DC} \) to allow the change between the FLL form and the nominal DC form:

\[ E^{DC} = U \cdot N_d \cdot (N_d - 1) - J \cdot N_d \cdot (N_d - 2) \]

\[ V^{DC} = U \cdot (N_d - \frac{1}{2}) - J \cdot (N_d - 1) \]

where \( \overline{N_d} = N_d - \alpha \). Setting \( \alpha = 0 \) makes this DC form same as the FLL DC form. By increasing \( \alpha \) one can approach the nominal DC form when \( \alpha = N_d - N_d^0 \). Our \( V^{DC} \) formulae can be derived from \( E^{DC} \) \((V^{DC} = \partial E^{DC} / \partial N_d)\) and allow the site-dependent potential. In this paper, We studied the effect of different \( V^{DC} \) values on the energetics and the nature of spin states in LaCoO\(_3\) by changing \( \alpha \) values.

### APPENDIX B: THE CHARGE-SELF-CONSISTENCY EFFECT IN DFT+DMFT

Fig. 5 shows the effect of the charge-self-consistency on the energetics of spin-state transition in LaCoO\(_3\) as a function of \( N_d \) for the charge-self-consistent (C.S.C) (top panel) and the non-charge-self-consistent (N.C.S.C) (bottom panel) DFT+DMFT calculations. Here, the N.C.S.C. calculation means that the charge density (\( \rho \) in Eq. 3) is fixed to the DFT one while the DMFT local Green’s function \((G^{loc} \text{ in Eq. 3})\) is obtained by converging DMFT self-consistent equations. The DC potential \( V^{DC} \) is computed using the Eq. 10 with the self-consistently determined \( N_d \) in the C.S.C. DFT+DMFT (top panel) while the fixed \( V^{DC} \) value \((V^{DC} \text{ is fixed during DFT+DMFT since the charge-density is not updated})\) is used for each data point and the constant shift of the \( V^{DC} \) potential converges to different \( N_d \) results within the N.C.S.C. DFT+DMFT (bottom panel). The homogeneous excited spin states without any Co-O bond-disproportionation (BD) show very similar energetics between C.S.C and N.C.S.C. calculations as a function of \( N_d \). In the case of the mixed spin state with the BD structure \((\delta a=0.05A)\), the N.C.S.C. DFT+DMFT energetics overestimate the tendency toward the spin-state transition as the energy difference between the excited spin-state and the low-spin state becomes much lower \((\sim150meV)\) than the C.S.C. energetics \((\sim30meV)\) when \( N_d \sim6.7 \). The energy dependence of the mixed spin state on \( N_d \) is also more sensitive for the N.C.S.C. case. Therefore, the effect of the charge-self-consistency within DFT+DMFT can be important for obtaining the energetics of inhomogeneous electronic phases in which spin-state or charge orderings can occur.
To further investigate the effect of the charge-self-consistency on charge ordering in the mixed spin state of LaCoO$_3$, we display the $d-$occupancy, $N_d$ in Fig. 6, computed for both LB and SB sites in the BD structure computed using C.S.C DFT+DMFT (solid lines) and N.C.S.C DFT+DMFT (dashed lines) as a function of the average $\langle N_d \rangle$ between two sites. Without the charge update as shown in N.C.S.C., the $N_d$ difference between two sites is more enhanced since the SB site occupies more $d-$orbitals while the LB site takes even less $N_d$ compared to the C.S.C. results across different $\langle N_d \rangle$ values. Therefore, the charge-self-consistency within DFT+DMFT reduces the tendency toward charge ordering between correlated Co sites and the energy difference between different spin-states is also much decreased within the C.S.C. calculation.

FIG. 6. The $d-$occupancy, $N_d$ computed for both LB and SB sites in the BD structure computed using C.S.C DFT+DMFT (solid lines) and N.C.S.C DFT+DMFT (dashed lines) as a function of the average $\langle N_d \rangle$ between two sites.

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