Compositional phase stability of correlated electron materials within DFT+DMFT

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Predicting the compositional phase stability of strongly correlated electron materials is an outstanding challenge in condensed matter physics, requiring precise computations of total energies. In this work, we employ the density functional theory plus dynamical mean-field theory (DFT+DMFT) formalism to address local correlations due to transition metal $d$ electrons on compositional phase stability in the prototype rechargeable battery cathode material Li$_2$CoO$_2$, and detailed comparisons are made with the simpler DFT+$U$ approach (i.e., the Hartree-Fock solution of the DMFT impurity problem). Local interactions are found to strongly impact the energetics of the band insulator LiCoO$_2$, most significantly via the $E_g$ orbitals, which are partially occupied via hybridization with O $p$ states. We find CoO$_2$ and Li$_{1/2}$CoO$_2$ to be moderately correlated Fermi liquids with quasiparticle weights of 0.6–0.8 for the $T_2g$ states, which are most impacted by the interactions. As compared to DFT+$U$, DFT+DMFT considerably dampens the increase in total energy as $U$ is increased, which indicates that dynamical correlations are important to describe this class of materials despite the relatively modest quasiparticle weights. Unlike DFT+$U$, which can incorrectly drive Li$_2$CoO$_2$ towards spurious phase separating or charge ordered states, DFT+DMFT correctly captures the system’s simultaneous phase stability and lack of charge ordering. Most importantly, the error within DFT+$U$ varies strongly as the composition changes, challenging the common practice of artificially tuning $U$ within DFT+$U$ to compensate the errors of Hartree-Fock. DFT+DMFT predicts the average intercalation voltage decreases relative to DFT, opposite to the result of DFT+$U$, which would yield favorable agreement with experiment in conjunction with the overprediction of the voltage by the strongly constrained and appropriately normed (SCAN) DFT functional.

I. INTRODUCTION

Strongly correlated materials, for which density functional theory (DFT) calculations often break down due to strong electron-electron interactions, are a challenging class of condensed matter systems relevant to several important technologies [1, 2]. One example is Li ion rechargeable batteries. These electrochemical cells rely critically on a cathode material that can reversibly intercalate Li ions [3]. Since cathode materials typically are based on transition metal oxides to accommodate intercalate Li ions [3]. Since cathode materials typically are based on transition metal oxides to accommodate intercalation voltage decreases relative to DFT, opposite to the result of DFT+$U$, which would yield favorable agreement with experiment in conjunction with the overprediction of the voltage by the strongly constrained and appropriately normed (SCAN) DFT functional.

While DFT in many ways reliably characterizes LCO, there are deficiencies in its description. DFT underestimates the intercalation voltage by around 0.8 V [11]. In addition, using a plane-wave basis set and ultrasoft pseudopotentials, Van der Ven et al. found that LDA overestimates the order-disorder transition temperature for $x = 1/2$ by 100 °C [8]. We note that the LDA linear augmented plane wave results of Wolverton and Zunger [7] do not show the same overestimation, though this study uses only roughly one third as many DFT calculations to parameterize the cluster expansion, in addition to performing slightly restricted structural relaxations.

One widely utilized approach to go beyond DFT is the DFT+$U$ method [12], in which an explicit on-site Coulomb interaction $U$ is added to account for the strong interactions in the $d$ shell along with a simple mean-field ansatz for the energy functional. However, DFT+$U$ does not fully remedy the shortcomings of DFT and in some cases hurts the description more than it helps. DFT+$U$ still underestimates the voltage by 0.3 V, and it can overestimate the order-disorder transition temperature by as much as several hundred degrees [13]. DFT+$U$ drives LiCoO$_2$ towards a high-spin transition [14] not observed in experiments [15-17] and, unless spurious charge ordering is permitted to occur, incorrectly predicts phase separation [13, 15]. Moreover, DFT+$U$ finds CoO$_2$ to be an insulator in disagreement with experiment [19]. DFT+$U$ clearly is problematic in the context of LCO.

Here, we revisit the electronic structure, voltage, and phase stability of LCO using more sophisticated DFT plus dynamical mean-field theory (DFT+DMFT) calculations [20] based on GGA. In this framework, the many-body DMFT approach captures the dynamical local correlations of Co $d$ electrons embedded in the crys-
functional. Similar to the voltage behavior, the predicted voltage for DFT+DMFT based on the SCAN functional strongly constrained and appropriately normed the qualitatively opposite behavior. Given the more acute impact of $U$ than $p$ states, $\text{CoO}_2$ and $\text{Li}_{1/2}\text{CoO}_2$ are Fermi liquids whose $T_{2g}$ states are most strongly affected by the interactions, with quasiparticle weight of around 0.6–0.7. DFT+DMFT, unlike DFT+U, does not spuriously predict charge ordering in $\text{Li}_{1/2}\text{CoO}_2$, nor does it predict insulating behavior for $\text{CoO}_2$ or $\text{Li}_{1/2}\text{CoO}_2$; in other words, DFT+DMFT substantially improves the description of the electronic structure. Dynamical correlations significantly dampen the impact of $U$ on the total energy of LCO, but more substantially for $\text{CoO}_2$ than $\text{LiCoO}_2$, leading to a reduction in voltage as compared to DFT, whereas DFT+U yields the qualitatively opposite behavior. Given the more accurate strongly constrained and appropriately normed (SCAN) DFT functional overestimates the experimental voltage, such a decrease in the predicted voltage is expected to lead to agreement between experimental and predicted voltage for DFT+DMFT based on the SCAN functional. Similar to the voltage behavior, the $x = 1/2$ formation energy prediction is significantly affected by dynamical correlations: while DFT+DMFT only weakly influences the formation energy of $x = 1/2$ compared to DFT, DFT+U strongly decreases its magnitude. Our results demonstrate the importance of dynamical correlations, missing in DFT+U, to accurately describe the electronic structure and energetics of correlated electron materials.

II. COMPUTATIONAL DETAILS

We perform single-site paramagnetic DFT+DMFT total energy calculations using the formalism of Ref. [30] based on the spin-independent GGA [44] and the projector augmented wave method [45, 46] as implemented in the VASP code [47–50]. Select calculations are also performed using the SCAN functional [51]. Given that LCO exhibits no long range magnetic order in experiment [52], the paramagnetic state is justified and we do not search for long-range magnetic order. The structures are fixed to the fully relaxed spin-dependent DFT ground state structures with O3 layer stacking [8], corresponding to a band insulator for $x = 1$ and ferromagnetic low-spin metals for $x = 0$ and $x = 1/2$. Except where otherwise noted, calculations are performed using the fixed non-spin-polarized DFT charge density, i.e., they are noncharge-self-consistent (NCSC); this is done for reasons of computational efficiency. We characterize the magnitude of the error associated with charge self-consistency by directly comparing NCSC and charge-self-consistent (CSC) calculations within DFT+U, demonstrating that the error is sufficiently small for the trends we are studying in this paper. A 500 eV energy cutoff and $k$-point meshes of $k$-point density corresponding to $9 \times 9 \times 9$ for the rhombohedral LiCoO$_2$ primitive cell and $19 \times 19 \times 19$ for the bulk Li primitive cell are employed. The ionic forces and total energy are converged to 0.01 eV/Å and $10^{-6}$ eV, respectively.

To define the correlated subspace, we utilize the maximally-localized Wannier function (MLWF) basis [53] for the full $p$-$d$ manifold and perform a unitary rotation of the $d$ orbitals to minimize the off-diagonal hoppings [34]. The Slater-Kanamori (SK) interaction with $J_{SK}$ set to 0.7 eV is employed, and we use the numerically exact hybridization expansion continuous-time quantum Monte Carlo (CTQMC) solver for the 5-orbital impurity problem [54, 55] at temperature $T = 290$ K. For DMFT, we perform calculations (1) using density-density interactions and (2) augmenting the density-density interactions with the off-diagonal $J$ terms within the $E_g$ manifold. For comparison, we also perform DFT+U calculations in the projector basis in VASP (LDATYPE=4) and present all our results in terms of the $U$ and $J$ corresponding to this interaction model via $U = U_{SK} - 8J_{SK}/5$ and $J = 7J_{SK}/5$ [56]. It should be noted that $J$ is fixed in all calculations, even though a range of different $U$ is explored. We employ the fully-localized-limit (FLL) form of the double counting [57].

III. RESULTS AND DISCUSSION

A. Electronic structure of CoO$_2$ and LiCoO$_2$

We begin by studying the basic electronic structure of LiCoO$_2$ and CoO$_2$ as a function of $U$, allowing for a direct comparison between DFT+DMFT and DFT+U. Corresponding results for Li$_{1/2}$CoO$_2$ are included, but these are not directly discussed until Section III C. In LCO, the ability of the oxygens to relax in the out-of-plane direction slightly distorts the CoO$_6$ octahedra and results in a symmetry lineage of $T_{2g} \rightarrow A_{1g} + E'_g$ relative to cubic symmetry, though we will still sometimes refer to this manifold as $T_{2g}$ for brevity. The DFT density of states is shown in Fig. 1(a) and 1(c) for CoO$_2$ and LiCoO$_2$, respectively. Within DFT, LiCoO$_2$ is a band insulator with nominally filled $T_{2g}$ and empty $E_g$ states, whereas CoO$_2$ is metallic with a hole in the $T_{2g}$ manifold. The density of states from the Wannier basis for the full $p$-$d$ manifold, shown in the dashed red lines, is numerically identical to that of DFT by construction. The Wannier functions are well localized with values for the spread $\langle \mathbf{r} - \mathbf{r}' \rangle^2$ of around 0.42 and 0.45 Å$^2$ for the individual Co $d$ orbitals of CoO$_2$ and LiCoO$_2$, respectively.

An essential quantity in Green function based approaches is the self-energy, which is central to computing the total energy and determining the low-energy proper-
FIG. 1. Density of states for DFT (black solid lines) and using the Wannier basis (dotted red lines) for (a) metallic CoO, (b) metallic Li$_{1/2}$CoO$_2$, and (c) band insulator LiCoO$_2$. The Fermi level (valence band maximum for $x = 1$) is indicated by the vertical dotted black line. (d) Crystal structure of LCO with O3 layer stacking with all the Li shown ($x = 1$). The large green, medium blue, and small red spheres represent ionic positions of Li, Co, and O, respectively. The image of the crystal structure is generated using VESTA [55].

densities. The electronic self-energy $\Sigma$ on the imaginary (Matsubara) frequency axis obtained via the CTQMC solver is shown for CoO$_2$ and LiCoO$_2$ in Fig. 2 for density-density interactions. The noise in the self-energy stems from the stochastic nature of the CTQMC solver, and for frequencies above 20 eV there is no noise since we utilize the analytic form of $\Sigma$ in the high-frequency limit. We note that the self-energy is well converged, particularly for low frequency.

For both CoO$_2$ and LiCoO$_2$, Im$(\Sigma)$ goes to 0 at low frequency, consistent with well-defined quasiparticles and a band insulator, respectively. This indicates that CoO$_2$ can be described as a Fermi liquid and is not a Mott insulator, consistent with experiments on CoO$_2$ [59–61], whereas past DFT+$U$ studies incorrectly predict an insulating state [19]. Therefore, DFT+DMFT is providing an improved description of the electronic structure of LCO. As a function of $U$, the magnitude of Im$(\Sigma)$ increases. The imaginary part of the self-energy is essentially identical for the $E'_{g}$ and $A_{1g}$ states, which indicates the symmetry breaking within the $T_{2g}$ manifold is small. The overall magnitude of Im$(\Sigma)$ is moderately larger for CoO$_2$ than for LiCoO$_2$. For CoO$_2$, the imaginary part of the self-energy of the $E'_{g}$ and $A_{1g}$ states are larger in magnitude than those of the $E_{g}$ states below $i\omega \approx 10$ eV. The impact of correlations is stronger for these states since $E'_{g}$ and $A_{1g}$ are partially filled. The opposite trend is found for LiCoO$_2$ with a larger magnitude of Im$(\Sigma)$ for the $E_{g}$ states for the full range of frequency shown. This suggests that for LiCoO$_2$ the correlations have a larger impact on the nominally-unoccupied $E_{g}$ states since they are partially occupied via hybridization with O $p$ states, whereas the $E'_{g}$ and $A_{1g}$ are filled.

For LiCoO$_2$, in the high-frequency limit, Re$(\Sigma)$ is typically negative for $E'_{g}$ and $A_{1g}$ and positive for $E_{g}$. This indicates that the static part of the correlations tend to push $E_{g}$ and $A_{1g}$ down in energy and $E'_{g}$ up in energy as is observed using DFT+$U$. The $U=1.9$ eV case is an exception as $J$ is likely too large relative to $U$ in this case. The real part of the self-energy increases at lower frequency for $E'_{g}$ and $A_{1g}$, whereas it decreases for $E_{g}$. This leads to a higher Re$(\Sigma)$ for $E'_{g}$ and $A_{1g}$ than $E_{g}$ towards zero frequency. Overall, the magnitude of the changes in Re$(\Sigma)$ with $U$ are significantly larger for $E'_{g}$ and $A_{1g}$ than for $E_{g}$.

For CoO$_2$, the self-energy of the $E_{g}$ states has a small real part (at most 0.21 eV), which decreases and becomes negative at low frequency. The magnitude is substantially larger for $E'_{g}$ and $A_{1g}$ than $E_{g}$ with a maximum magnitude of 1.2 eV for $U=5.9$ eV. For these states, like in the LiCoO$_2$ case, the values are negative at high frequency (except for very low $U$) and become positive at low frequency. As opposed to the imaginary part, the real part of the self-energy has smaller magnitude for CoO$_2$ than for LiCoO$_2$.

From the low-frequency behavior of Im$(\Sigma)$, we compute the quasiparticle weight $Z = [1 - \partial \text{Im}(\Sigma)/\partial i\omega|_{i\omega \rightarrow 0}]^{-1}$, shown in Fig. 3. This quantity is unity for $U=J=0$ [Im$(\Sigma) = 0$] and is inversely proportional to the effective mass arising from electron interactions. All the values decrease with $U$, as expected, in a roughly linear fashion. $Z$ is always larger for LiCoO$_2$ than CoO$_2$, consistent with the fact that LiCoO$_2$ is a band insulator. This effect is pronounced in the $E'_{g}$ and $A_{1g}$ states, for which the CoO$_2$ values are 0.14–0.20 lower than those of LiCoO$_2$. For the $E_{g}$ states, the disparity is smaller, with differences of only 0.01–0.04. For CoO$_2$, $Z$ is larger and decreases less rapidly for the $E'_{g}$ orbitals compared to the $E_{g}$ and $A_{1g}$
orbitals. From $U = 1.9$ to $5.9$ eV, $Z$ of the $E_g'$ and $A_{1g}$ orbitals of CoO$_2$ goes from 0.79 to 0.57 and that of the $E_g$ orbitals goes from 0.88 to 0.73. For LiCoO$_2$, over the same range of $U$, $Z$ of the $E_g'$ and $A_{1g}$ orbitals goes from 0.93 to 0.77 and that of the $E_g$ orbitals goes from 0.89 to 0.77. Here, $Z$ is smaller and decreases less rapidly for the $E_g$ states such that $Z$ is the same for all the orbitals at $U = 5.9$ eV.

### B. Atomic configurations and $d$ occupancies

To further understand the detailed electronic configuration of CoO$_2$ and LiCoO$_2$, in Fig. 3 we plot the probabilities of the different atomic configurations sampled by the CTQMC solver in terms of the number of $d$ electrons ($N_d$) and the spin projection $S_z$. The results for $U = 4.9$ eV are shown as a representative example. We note that the probability distribution is symmetric about $S_z = 0$ since our DFT+DMFT calculations are paramagnetic (i.e., there is no long-range magnetic order).

Although CoO$_2$ and LiCoO$_2$ are nominally $d^8$ and $d^7$, respectively, the probability distribution is centered at higher values of $N_d$ for both cases due to the appreciable hybridization with O $p$ states. For example, for LiCoO$_2$ there is substantial time in the Monte Carlo simulation in which an electron from an O $p$ state has hopped into an $E_g$ orbital, leading to a $d^7$ state. There are substantial fluctuations in $N$ as well as $S_z$ for the Co site in both systems. For CoO$_2$ the spin fluctuations are moderately larger than in LiCoO$_2$; there is even probability of $S_z = 3/2$ states. We note that these fluctuations of the Co site highlight why both DFT and DFT+$U$ struggle to capture all the physics in this system.

It is also useful to examine the behavior of $N_d$ versus $U$ for all the methodologies employed in this work in Fig. 5, giving insight into the behavior and impact of the double counting correction [36, 62, 63]. Within DFT, one can observe that $N_d$ is larger for the projector correlated subspace than the Wannier correlated subspace. The difference is moderate for LiCoO$_2$ (0.09), but significantly larger for CoO$_2$ (0.26). LiCoO$_2$ has 0.08 (0.26) more $d$ electrons than CoO$_2$ in the projector (Wannier) correlated subspace. These values are much smaller than the nominal value of unity, which is indicative of the strong $p$–$d$ rehybridization in this system [7, 64].

For LiCoO$_2$, $N_d$ generally decreases with $U$. For DFT+$U$ in the projector correlated subspace, the decrease is small in magnitude (around 0.03 electrons) and including charge self-consistency leads to even smaller changes on the order of 0.006 electrons. In the Wannier correlated subspace, the decrease in $N_d$ with $U$ for DFT+$U$ is more substantial with a change of 0.25 electrons. The inclusion of dynamical correlations (DFT+DMFT) substantially dampens the decrease in $N_d$ versus $U$ to around 0.06 electrons.

DFT+DMFT also gives a similar decrease, of 0.04 electrons, in $N_d$ of CoO$_2$ with $U$. In contrast, DFT+$U$ show
starkly different behavior. Here, $N_d$ increases dramatically with $U$, by 0.39 electrons for the projector correlated subspace and 0.19 electrons for the Wannier case. This increase in $N_d$ is dampened by the metal-insulator transition that occurs using the projector correlated subspace including charge self-consistency, in which case the overall magnitude of the $N_d$ variation is only 0.02 electrons. The very large increase in $N_d$ for CoO$_2$ within DFT+$U$ to values even greater than those of LiCoO$_2$ strongly suggests the Hartree-Fock treatment of the impurity problem is problematic for CoO$_2$. This suggests DFT+DMFT is more reliable to describe CoO$_2$.

The behavior of $N_d$ versus $U$ can further be understood by decomposing $N_d$ into the components from the $T_{2g}$ ($E_g'$ and $A_{1g}$) and $E_g$ orbitals, as shown in Fig. 6. Within DFT, the Wannier correlated subspace leads to higher (lower) occupancy of $T_{2g}$ ($E_g$) by 0.13–0.23 (0.32–0.39) electrons compared to the projector case. In DFT+$U$, the LiCoO$_2$ $T_{2g}$ occupancy increases with $U$, whereas the
$E_g$ occupancy decreases more rapidly; this leads to the overall decrease in $N_d$. For the Wannier case, the $T_{2g}$ occupancy increases more rapidly with $U$ at lower $U$ compared to the projector case; for larger $U$, the occupancy begins to saturate close to the nominal value of 6. Similarly, the decrease in $E_g$ occupancy is more substantial in the Wannier case compared to the projector case. Including charge self-consistency has a negligible effect on the occupancies of LiCoO$_2$ in the projector case. The trends in the occupancies are the same for DFT+DMFT as in DFT+$U$, but the magnitude of the changes in occupancy are much smaller.

Within DFT+$U$, the CoO$_2$ $T_{2g}$ occupancy increases substantially by 0.42 electrons with $U$ in the Wannier correlated subspace, whereas the $E_g$ occupancy only decreases by 0.23 electrons. Here, the $T_{2g}$ shell moves rapidly moving towards full filling. In the NCSC projector case, the $T_{2g}$ occupancy increases by a moderately smaller magnitude, whereas the $E_g$ occupancy is nearly constant as a function of $U$. Including charge self-consistency, once CoO$_2$ becomes insulating, the $T_{2g}$ occupancy sharply increases and the $E_g$ occupancy sharply decreases by a larger amount. As in the case of LiCoO$_2$, the changes in occupancy within DFT+DMFT are much smaller than those of NCSC DFT+$U$ with both $T_{2g}$ and $E_g$ occupancies slightly decreasing by 0.003 and 0.04, respectively, over the range of $U$. Dynamical correlations appear to dampen the changes in $N_d$ in the same fashion as charge self-consistency.
C. Electronic structure of Li$_{1/2}$CoO$_2$

Here, we discuss the electronic structure of Li$_{1/2}$CoO$_2$, which warrants extra attention due to the issue of spurious charge ordering which occurs in DFT$+U$. This known structure has an in-plane ordering of Li corresponding to a primitive unit cell with two formula units. We perform DFT$+$DMFT calculations in two different ways. First, we enforce the symmetry between the two structurally-equivalent Co sites, i.e., only a single impurity problem is solved. However, the aforementioned approach does not allow for charge ordering to spontaneously break point symmetry. Therefore, we also use a second approach where two impurity calculations are employed (i.e. one for each Co atom in the unit cell), and we only execute this at $U = 3.9$ eV due to computational expense. Using the second approach, we do find a stable charge-ordered state, with a difference in $N_d$ on the two sites of 0.4 electrons, but it is slightly higher in energy than the non-charge-ordered state (by 3 meV/f.u.). This indicates that DFT$+$DMFT removes the spurious charge ordering that is produced by DFT$+U$, and we proceed with our analysis of the symmetric solution.

Within DFT, Li$_{1/2}$CoO$_2$ is metallic with half a hole in the $T_{2g}$ manifold, as can be seen from the density of states in Fig. 1(b). Within NCSC DFT$+U$ in the projector basis, Li$_{1/2}$CoO$_2$ retains the metallic non-spin-polarized ground state. Including CSC, a metallic low-spin ground state at low $U$ transitions to a charge ordered insulating state at $U$ above $\sim 4$ eV. The DFT$+DMFT$ self-energy in Fig. 2 illustrates that Li$_{1/2}$CoO$_2$ is, like CoO$_2$, a Fermi liquid with correlations most significantly affecting the $T_{2g}$ manifold. We find a Fermi liquid up to the highest $U$ value considered, in agreement with the metallic behavior observed in experiment. The $T_{2g}$ quasiparticle weights, in Fig. 3 are significantly lower than those of LiCoO$_2$ and slightly larger than those of CoO$_2$. This reflects that the electronic structure of Li$_{1/2}$CoO$_2$ is closer to that of CoO$_2$ than LiCoO$_2$.

As for the endmembers ($x = 0$ and $x = 1$), for Li$_{1/2}$CoO$_2$, $N_d$ (Fig. 5) is larger in the projector correlated subspace. Within DFT$+DMFT$, $N_d$ decreases very mildly with $U$ similar to the endmember behavior. Here, dynamical correlations only slightly reduce $N_d$ (on the order of 0.02 electrons). As in CoO$_2$, within DFT$+U$ in the projector basis, $N_d$ increases with $U$, with a discontinuity in the CSC case when Li$_{1/2}$CoO$_2$ undergoes the metal-insulator transition. Unlike CoO$_2$, there is a smaller effect of charge self-consistency in the DFT$+U$ results in the projector correlated subspace. The individual $T_{2g}$ and $E_g$ occupancies are shown in Fig. 6. Here, as for the endmembers, the $T_{2g}$ occupancy fills more rapidly than $E_g$ empties. The decrease in $E_g$ occupancy across the metal-insulator transition is much smaller than that of CoO$_2$.

In summary, DFT$+DMFT$ can properly describe the electronic structure of Li$_{1/2}$CoO$_2$. Unlike DFT$+U$, which predicts a charge ordered insulator, DFT$+DMFT$ properly describes the electronic structure as a Fermi liquid.

D. Total energy of LiCoO$_2$ and CoO$_2$

Having documented the basic electronic structure within DFT$+DMFT$ and DFT$+U$, we proceed to explore the total energy of LiCoO$_2$ and CoO$_2$ as a function of $U$, allowing for a direct comparison between DFT$+DMFT$ and DFT$+U$. The total energy of LiCoO$_2$ and CoO$_2$ are shown as a function of $U$ for several methodologies in Fig. 7. The two vertical dashed lines indicate the values of $U$ for CoO$_2$ and LiCoO$_2$ as computed from first principles via linear response. The total energies increase with $U$, as expected, for both LiCoO$_2$ and CoO$_2$. We note that for $U = 0$ the total energies within DFT$+U$ and DFT$+DMFT$ are not equal to those of DFT since we have chosen a fixed finite $J$. The magnitude of the increase in total energy with $U$ is generally greater for CoO$_2$ than LiCoO$_2$, which makes sense since the impact of the on-site interaction is expected to be larger for the system for which $T_{2g}$ is partially filled (namely). For NCSC DFT$+U$ in the Wannier correlated subspace, for example, over the full range of $U$ shown the increase in energy of CoO$_2$ is 5.7 eV as compared to only 3.6 eV for LiCoO$_2$. For the same set of calculations using the projector correlated subspace, we find the same trend with energy increases of roughly 4.9 eV for CoO$_2$ and 3.5 eV for LiCoO$_2$. We note that the individual total energies from methods utilizing these different correlated subspaces (projector and Wannier) are not directly comparable. LiCoO$_2$ is described as a band insulator within all of our DFT$+U$ results for the range of $U$ shown. In the Wannier correlated subspace, we find CoO$_2$ is a non-spin-polarized metal; only for $U$ above 6.9 eV does CoO$_2$ transition to a magnetic insulator. Similarly, we find CoO$_2$ is a non-spin-polarized metal in the projector correlated subspace. Ultimately, the behavior of the total energy with $U$ is relatively similar for these two choices of correlated subspaces within NCSC DFT$+U$.

For DFT$+U$ in the projector correlated subspace, we also perform CSC calculations in order to gauge the magnitude of the error associated with neglecting charge self-consistency. Here, LiCoO$_2$ is again a band insulator and we find only very small differences (at most 23 meV/f.u.) between the NCSC and CSC total energies. CoO$_2$ is a spin-polarized metal for smaller $U$ with differences in total energy of at most 22 meV/f.u. with respect to the NCSC calculations. However, for $U > 2.9$ eV, CoO$_2$ orbitally orders and opens up a band gap; in this regime the total energies are lowered by several hundreds of meV/f.u. compared to those of the NCSC calculations. The small impact of changes in charge density on the total energies for LiCoO$_2$ over the full $U$ range and in the metallic phase for CoO$_2$ suggest the fixed charge density should be a reasonable approxima-
FIG. 7. Total energy of (a) CoO\textsubscript{2}, (b) Li\textsubscript{1/2}CoO\textsubscript{2}, and (c) LiCoO\textsubscript{2}, respectively, as a function of \( U \) for several methodologies including DFT, DFT+\( U \), and DFT+DMFT. The dashed orange lines indicate the computed values of \( U \) for LiCoO\textsubscript{2} (lower value) and CoO\textsubscript{2} (higher value) within the linear response approach.

We find the general impact of dynamical correlations on the energetics is to dampen the magnitude of the increase in total energy with \( U \) as compared to the static Hartree-Fock treatment in DFT+\( U \). When \( U \) is increased from 1.9 to 5.9 eV, the total energy of LiCoO\textsubscript{2} increases by 2.3 eV within DFT+\( U \) as opposed to only 1.2 eV within DFT+DMFT. For CoO\textsubscript{2}, the magnitude of these energies is substantially larger with an increase of 3.9 eV for DFT+\( U \) and 1.6 eV for DFT+DMFT. By this measure, dynamical correlations decrease the energy penalty of \( U \) by a factor of 2 for LiCoO\textsubscript{2} and 2.5 for CoO\textsubscript{2}. Therefore, dynamical correlations have a larger impact on CoO\textsubscript{2} than LiCoO\textsubscript{2}. This corresponds to very large absolute differences in the energies predicted by DFT+\( U \) and DFT+DMFT. For CoO\textsubscript{2}, for example, around the linear response values of \( U \) the difference in energy is around 2 eV. This strongly suggests dynamical correlations, missing in the DFT+\( U \) approach, are important for accurate total energies.

It should be emphasized that the difference between DFT+DMFT and DFT+\( U \) changes substantially as a function of \( x \), and this error will therefore strongly affect observables. One strategy to correct errors within DFT+\( U \) calculations is to tune \( U \) to artificially low values, and this can be successful if \( U \) is first calibrated to some experimental observable. However, our work indicates that the errors vary strongly with composition, and therefore DFT+\( U \) studies of compositional phase stability would need to tune \( U \) as a function of doping, a far more challenging task. Below we explore the average battery voltage, where the composition dependent errors within DFT+\( U \) have severe consequences.
E. Average intercalation voltage

We turn our attention to the average intercalation voltage of LCO for \(0 \leq x \leq 1\), plotted in Fig. 8, which is a key observable for a rechargeable battery cathode. The average intercalation voltage \(V\) is computed via \(eV = E(Li) + E(CoO_2) - E(LiCoO_2)\), where \(e\) is the elementary charge and body-centered-cubic Li is the reference electrode [6]. As has been known, DFT tends to underpredict the experimental voltage [6], in this case by around 0.7 V. For DFT+U in the Wannier correlated subspace, the voltage increases roughly linearly with \(U\) at a rate of 0.28–0.33 V per eV. For \(U = 4.7\) eV, the voltage agrees with the experimental value of approximately 4.26 V [69]. For the projector correlated subspace, the computed voltage increases with \(U\) at a rate of 0.19–0.23 V per eV. For \(U = 4.2\) eV, in this case, the voltage agrees with experiment. The voltage curve using the Wannier correlated subspace is lower than that of the projector case by a few tenths of an eV until \(U = 5.6\) eV, at which point they intersect. In the projector correlated subspace, charge self-consistency serves to dampen the increase in voltage with \(U\) after CoO\(_2\) becomes insulating; in this case a voltage of 4.15 V is reached by \(U = 5.9\) eV. Within DFT+DMFT, the predicted intercalation voltage is decreased relative to the DFT value up to the highest computed value of \(U = 6\) eV. As compared to DFT+U, the voltage at fixed \(J\) increases much more slowly as a function of \(U\), with changes of around 0.08–0.13 V per eV. This mainly stems from the damped increase in energy for CoO\(_2\). For the computed values of \(U\), the predicted voltage is only 3.39–3.45 V, which is less than that of pure DFT.

The increase in \(V\) within DFT+U and general agreement with experiment was shown previously [68] and seemed to suggest that DFT+U is reliable for this class of materials. However, this viewpoint should be carefully scrutinized given that DFT+U is a rather crude theory, in that DFT+U is obtained from DFT+DMFT when the quantum impurity problem is solved within mean-field theory, neglecting dynamical correlations. Therefore, DFT+DMFT is superior in every respect. Since the voltage curve predicted by DFT+DMFT produces a result less than that of DFT, opposite to that of DFT+U, dynamical correlations are clearly essential to describe the energetics of LCO. The fact that DFT+U increases the voltage, relative to DFT, and provides more reasonable agreement with experiment appears to be fortuitous.

Given that DFT+DMFT actually worsens the predicted voltage as compared to DFT, we are left with the puzzling question as to why. We explore several possibilities. First and foremost, while DMFT should improve DFT with respect to local physics, it is possible that there are still substantial nonlocal errors within the density functional employed in the DFT+DMFT functional. Given the recent successes of the relatively new SCAN functional [70, 71], which contains nonlocal physics via a dependence on the orbital kinetic energy density, an obvious question is how the voltage would change if we replaced the GGA functional with SCAN; we pursue this idea at the level of DFT+U (see Fig. 8). The \(U = 0\) voltage predicted by SCAN is 4.58 V, which is already greater than the experimental voltage, in stark contrast to LDA and GGA. One expects the trends as a function of \(U\) for DFT(SCAN)+U and DFT(SCAN)+DMFT to be unchanged relative to GGA given that the SCAN electronic structure is very similar to that of GGA. As expected, increasing \(U\) within DFT(SCAN)+U causes the voltage to further increase, moving away from the experimental value. We do not compute the DFT(SCAN)+DMFT results due to the computational cost, but we anticipate that they should have the same \(U\)-dependence as DFT(GGA)+DMFT; just as DFT(SCAN)+U and DFT(GGA)+U have a very similar \(U\)-dependence. If so, the DFT(SCAN)+DMFT voltage should be mildly decreased compared to the DFT(SCAN) voltage, yielding reasonable agreement with experiment. Alternatively, DFT(SCAN)+U only worsens the voltage prediction, and suggests the reason why DFT(LDA/GGA)+U performs well is due to the cancellations of two large and distinct errors. Therefore, one cannot expect DFT+U to perform as a predictive tool in the context of compositional phase stability.

![FIG. 8. Computed intercalation voltage of LCO via DFT, DFT+U, and DFT+DMFT as a function of \(U\). The dashed orange lines indicate the computed values of \(U\) for LiCoO\(_2\) (lower value) and CoO\(_2\) (higher value) within the linear response approach. The dotted black lines indicate the expected range of the experimental result [69].](image-url)
Of course, the precise value of the predicted voltage will depend on the precise values $U$ and $J$, perhaps allowing for small $U$ differences in the endmembers, in addition to details of the double counting correction, etc. We do not attempt to build a case for the most correct set of parameters in this work. It is worth noting that one early explanation for discrepancies in the DFT predicted voltages was the overestimated magnitude of the cohesive energy of body-centered-cubic Li within LDA [6]. However, we find the cohesive energy predicted by GGA ($−1.60$ eV) and SCAN ($−1.59$ eV) are in good agreement with experiment ($−1.63$ eV  [2]). Therefore, the discrepancy between theory and experiment should stem from the energetics of the cathode material itself.

**F. Phase stability of Li$_{1/2}$CoO$_2$**

As another test of the computed DFT+DMFT total energy, we compute the phase stability of Li$_{1/2}$CoO$_2$. The formation energy $\Delta E$, computed as $E(Li_{1/2}CoO_2) − \frac{1}{2}[E(CoO_2) + E(LiCoO_2)]$, is shown in Fig. 9. The DFT value is $−218$ meV/f.u.; the DFT+$U$ methodologies studied here drastically increase the predicted formation energy (destabilize Li$_{1/2}$CoO$_2$), by $\sim 100$–200 meV/f.u. While the formation energy remains negative (in agreement with the experimentally-known phase stability), we have shown previously that the more common DFT+$U$ methodology based on spin-dependent DFT incorrectly predicts phase separation of Li$_{1/2}$CoO$_2$ in the absence of charge ordering [13]. In stark contrast to DFT+$U$, DFT+DMFT shows only a mild increase in formation energy with $U$, on the order of tens of meV/f.u. The predicted value in the range of computed $U$ is similar to that of DFT. This results from the fact that dynamical correlations significantly lower the energy of Li$_{1/2}$CoO$_2$, as shown in Fig. 7 by an amount greater than the average of those of $x = 0$ and $x = 1$. This represents further evidence of the importance of dynamical correlations to describe the thermodynamics of LCO. In this case, such correlations serve to enhance the phase stability of $x = 1/2$. We use the difference in average experimental voltage values for $0 < x < 1/2$ ($V_-$) and $1/2 < x < 1$ ($V_+$) to estimate the experimental formation energy for $x = 1/2$, via $\Delta E = x(1−x)(eV_−−eV_+)$ [13]. Using the data of Ref. [69] we compute $\Delta E$ of $−114$ meV/f.u. for Li$_{1/2}$CoO$_2$. The predicted formation energy for NCSC DFT+$U$ agrees well with the experimental value for $U$ around the computed values for both the projector and Wannier correlated subspaces: for CSC DFT+$U$, agreement with experiment occurs for significantly smaller $U$. In contrast, both the DFT and DFT+DMFT results overestimate the formation energy magnitude by 80–100 meV/f.u. However, this error also may be associated with the DFT exchange-correlation functional. We also plot the formation energy the SCAN functional, which is approximately 50 meV/f.u. higher than GGA. Therefore, we would anticipate the DFT(SCAN)+DMFT results to be shifted by roughly the same amount, which would be much closer to the experimental range.

**IV. CONCLUSIONS**

We investigate the electronic structure, intercalation voltage, and phase stability of LCO with the many-body DFT+DMFT methodology and compare to DFT and DFT+$U$. In DFT+DMFT, LiCoO$_2$ is a band insulator, while we find that CoO$_2$ and Li$_{1/2}$CoO$_2$ are moderately correlated Fermi liquids, without any charge ordering in Li$_{1/2}$CoO$_2$, in agreement with experiments. Dynamical correlations (missing in DFT+$U$) substantially impact the energetics of LCO by dampening the changes in total energy and $N_d$ found via the DFT+$U$ approach, especially for CoO$_2$ and Li$_{1/2}$CoO$_2$. The intercalation voltage behavior of DFT+$U$ and DFT+DMFT are qualitatively different, with the latter decreasing the voltage with respect to DFT; the phase stability of Li$_{1/2}$CoO$_2$ within DFT+DMFT also differs starkly from DFT+$U$. DFT+DMFT calculations based on the GGA DFT functional underpredict the voltage and overestimate the stability of Li$_{1/2}$CoO$_2$ compared to experiment; we find evidence that DFT+DMFT based on the more accurate SCAN DFT functional will lead to significantly closer agreement to experiment.

We find that dynamical correlations are important to describe this class of materials despite the relatively modest quasiparticle weights. Our results suggest that the Hartree-Fock treatment of the impurity problem in DFT+$U$ is insufficient to accurately describe the elec-
tronics, our results challenge the common practice of artificially tuning \( U \) within DFT+U to compensate for the errors of Hartree-Fock. Given the significant computational expense of solving the impurity problem in DFT+DMFT, the development of less computationally expensive but still sufficiently accurate impurity solvers will be important future work to enable the study of compositional phase stability of strongly correlated electron materials.

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