Effect of the electron-lattice coupling on the charge and magnetic order in rare-earth nickelates

Stepan Fomichev,1,2,* Giniyat Khaliullin,3 and Mona Berciu1,2

1Department of Physics and Astronomy, University of British Columbia, Vancouver B.C. V6T 1Z1, Canada
2Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver B.C. V6T 1Z4, Canada
3Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany

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We investigate the impact of electron-lattice coupling on the stability of various magnetic orders in rare-earth nickelates. We use the Hartree-Fock approximation, at zero temperature, to study an effective, two-band model with correlations characterized by a Hubbard $U$ and a Hund’s $J$. This is coupled to breathing-mode distortions of the octahedral oxygen cages, described semi-classically, with a Holstein term. We analyze the effect of the various parameters on the resulting phase diagram, in particular on the charge disproportionation and on the magnetic order. We confirm that the coupling to the lattice cooperates with Hund’s coupling and thus encourages charge disproportionation. We also find that it favors the fully disproportionated, 4-site periodic magnetic order of type $\uparrow 0 \downarrow 0$. Other convergent magnetic phases, such as the collinear $\uparrow\uparrow\downarrow\downarrow$ and non-collinear $\uparrow\downarrow\downarrow\uparrow$ states, do not couple to the lattice because of their lack of charge disproportionation. Novel phases, e.g. with charge disproportionation but no magnetic order, are also found to be stabilized in specific conditions.

I. INTRODUCTION

The rare-earth nickelates RNiO$_3$, $R$ being any rare-earth element from La to Lu, are a class of materials that have generated considerable interest because of their complex phase diagram, where both a metal-insulator transition (MIT) and a magnetic ordering transition can be tuned via pressure, strain, and/or variations in the size of the $R$ ion (except for $R$=La, which is a metal at all temperatures).$^{1,2}$ Understanding the features of this phase diagram is of significant interest for the advancement of our basic knowledge of strongly correlated systems, but also because of their potential for applications, especially in heterostructures$^3$ and memory storage.$^4-6$

The perovskite RNiO$_3$ consists of Ni ions arranged on a simple cubic lattice with lattice constant $a$, and connected through ligand O, such that each Ni ion is inside an octahedral cage of oxygen atoms.$^7$ Standard valence counting suggests the starting configuration to be Ni:3$d^7$. Crystal fields split the 3$d$ levels into well-separated $e_g$ and $t_{2g}$ manifolds, suggesting a doubly-degenerate $t_{2g}e_{g}$ configuration that should be unstable to Jahn-Teller distortions.$^8$ Such distortions are not observed experimentally,$^9$ so the $e_g$ degeneracy must be resolved in some other way. Many scenarios have been proposed, including, most notably, (i) charge disproportionation (CD),$^{1,10}$ and (ii) a negative charge transfer (NCT) energy.$^{11-15}$

The CD scenario posits that below the MIT there are two inequivalent Ni sites with different charge, $3d^0 3d^7 \rightarrow 3d^2 3d^5$; this is then thought to drive the experimentally observed distortion$^{16}$ of the O octahedra into small/large ones around the two inequivalent Ni sites. As typical for strongly correlated insulators, magnetic order also develops at or below the MIT phase line.

In contrast, the NCT scenario has all the Ni in the 3$d^8$ ($S=1$) configuration, with each releasing a ligand hole into the O band. The resulting 1/6 filled (with holes) O band is metallic at high temperatures. In this view, the MIT is primarily due to electron-phonon coupling which distorts the O octahedra into small and large ones ($pp$ and $pd$ hopping are enhanced on the shorter bonds), resulting in pairs of ligand holes localized on the small octahedra and locked into a singlet with their central Ni. The spins of the Ni ions located in the large cages, on the other hand, order magnetically at or below the MIT temperature.

The electron-phonon coupling is obviously important for the MIT transition in both scenarios (even if in rather different ways), but its impact on the magnetic order is not well understood. Neutron scattering experiments on powders$^{17,18}$ indicate a magnetic ordering wavevector $Q_m = \begin{pmatrix} \pi/3a \\ \pi/3a \\ \pi/3a \end{pmatrix}$ in perovskite notation, which is half of the value associated with the lattice distortion ordering (and charge modulation, in the CD scenario) of $Q_c = \begin{pmatrix} \pi/3a \\ \pi/3a \\ \pi/3a \end{pmatrix}$. The orientations and magnitudes of the local magnetic moments in the 4-site (counting Ni only) magnetic unit cell are still under debate. Three leading contenders are the fully-disproportionated antiferromagnetic state $\uparrow 0 \downarrow 0,^{19}$ and two partially disproportionated orders: the collinear$^{20}$ order $\uparrow\uparrow\downarrow\downarrow$, and the non-collinear$^{21}$ order $\uparrow\downarrow\downarrow\uparrow$. (Throughout this work we use fat arrows to indicate larger spin magnitudes).

While the preferred magnetic order is likely to be
primarily decided by the electron-electron interactions, as is generally the case in strongly-correlated systems, it is possible that the strong coupling to the lattice also plays an important role by favoring or hindering some of these possible candidates. We study this possibility here using an effective two-orbital Hamiltonian that, within the appropriate framework (discussed below), can be used to model both the CD and the NCT scenarios. Our work builds on that of Lee et al.\textsuperscript{20} who studied magnetic orders possible in similar multi-orbital models. The main novelty is that our model also includes coupling to the lattice, at the semi-classical level.

We verify that the electron-lattice coupling favors insulating charge order, as noticed by earlier investigators. While a number of 4-site magnetic orders, insulating charge order, as noticed by earlier investigations, as is generally the case in strongly-correlated systems, are found to be self-consistent within our model, we find that only one of these candidates is strongly favored by the electron-lattice coupling. The other magnetic orders are active, and as a result do not couple to the lattice in our model. As the strength of the electron-lattice interaction increases, we also find that a novel phase is stabilized, wherein charge modulation occurs in the absence of magnetic order.

The paper is organized as follows: In section II, we describe our effective model Hamiltonian. Section III reviews the Hartree-Fock calculation used to study it, as well as its numerical implementation. In Section IV we present and discuss our results. Finally, Section V contains our conclusions.

II. THE MODEL

We consider a simple cubic lattice, with lattice constant \(a\), which we set to 1. At each site \(i\), two \(e_g\) “effective” orbitals \(|z\rangle \equiv |3z^2 - r^2\rangle\) and \(|\bar{z}\rangle \equiv |x^2 - y^2\rangle\) are active, and \(d^\dagger_{i z\sigma}, d_{i \bar{z}\sigma}\) are the electronic creation operators associated with them. The physical connection to the actual material of these and the other “effective” degrees of freedom that we introduce below is discussed after the Hamiltonian is fully defined.

The Hamiltonian we study is defined as:

\[
\hat{H} = \hat{T} + \hat{H}_{e-e} + \hat{H}_{lat} + \hat{H}_{e-lat}.
\] (1)

The kinetic energy \(\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3\) includes up to 4\textsuperscript{th} nearest-neighbor hopping. The hopping term \(\hat{T}_1\) includes hopping between nearest-neighbor \(|z\rangle\) orbitals along the \(z\)-axis, and between \(|x\rangle \equiv |3x^2 - r^2\rangle\) and \(|y\rangle \equiv |3y^2 - r^2\rangle\) orbitals along the \(x\)- and \(y\)-axes, respectively. There is no nearest-neighbor hopping in the \(z\)-direction between \(|\bar{z}\rangle\) orbitals, etc., because these orbitals are orthogonal to their corresponding ligand \(O\). As a result:

\[
\hat{T}_1 = -t_1 \sum_{i\sigma} \sum_{\eta=x,y,z} (d^\dagger_{i\eta\sigma} d_{i+\eta,\eta\sigma} + \text{h.c.}).
\] (2)

This can be easily expressed in terms of the \(d^\dagger_{i z\sigma}, d^\dagger_{i \bar{z}\sigma}\) operators using the identities:

\[
\begin{align*}
\hat{d}_{i z\sigma}^\dagger &= \frac{1}{2} \hat{d}_{i z\sigma}^\dagger + \frac{\sqrt{3}}{2} \hat{d}_{i \bar{z}\sigma}^\dagger, \\
\hat{d}_{i y\sigma}^\dagger &= -\frac{1}{2} \hat{d}_{i z\sigma}^\dagger - \frac{\sqrt{3}}{2} \hat{d}_{i \bar{z}\sigma}^\dagger.
\end{align*}
\] (3)

Similarly, we define 2\textsuperscript{nd} nearest-neighbor and 4\textsuperscript{th} nearest-neighbor hopping terms \(\hat{T}_2\) and \(\hat{T}_4\), respectively.

The coefficients \(t_{ab}(k)\) are listed in the Appendix.

The on-site electron-electron interactions are described by the Kanamori Hamiltonian:\textsuperscript{22-24}

\[
\begin{align*}
\hat{H}_{e-e} &= U \sum_{i a} \hat{n}_{i\sigma a} \hat{n}_{i\sigma a} + U' \sum_{i \sigma} \hat{n}_{i z\sigma} \hat{n}_{i \bar{z}\sigma} \\
&\quad + (U' - J) \sum_{i \sigma} \hat{n}_{i z\sigma} \hat{n}_{i \bar{z}\sigma} - J \sum_{i \sigma} \hat{d}_{i z\sigma}^\dagger \hat{d}_{i \bar{z}\sigma} \hat{d}_{i \bar{z}\sigma}^\dagger \hat{d}_{i z\sigma} \\
&\quad + J \sum_{i a} \hat{d}_{i\sigma a}^\dagger \hat{d}_{i\sigma a} \hat{d}_{i\sigma a}^\dagger \hat{d}_{i\sigma a}.
\end{align*}
\] (6)

with the spherically symmetric choice \(U' = U - 2J\).\textsuperscript{25}

Here, \(\hat{n}_{i\sigma a} = \hat{d}_{i\sigma a}^\dagger \hat{d}_{i\sigma a}\) counts the electrons with spin \(\sigma\) in the \(a = z, \bar{z}\) orbital at site \(i\), and \(\hat{n}_i = \sum_{a \sigma} \hat{n}_{i\sigma a}\).

We use this full form of \(\hat{H}_{e-e}\) as opposed to the simpler one used in Lee et al.\textsuperscript{20} because it leads only to minor complications in the mean-field treatment and has a formal derivation based on allowed Coulomb intraionic interactions.\textsuperscript{21-23} This change explains the quantitative differences between our results – in the absence of coupling to the lattice – and those of Lee et al.
Next, $H_{lat}$ describes, at the semi-classical level, the breathing-mode distortion resulting in contracted and expanded octahedra:

$$H_{lat} = \sum_i \left( \frac{k}{2} (\delta U_i)^2 + \frac{A}{4} (\delta U_i)^4 \right)$$

where $\delta U_i$ is the (isotropic) change in the Ni-O bond length of the octahedral cage surrounding site $i$, and we include quartic anharmonicity to ensure reasonable values for these distortions.

The octahedral distortions affect the on-site electron energies, hence the electron-lattice interaction term:

$$\hat{H}_{el-lat} = -g \sum_i \delta U_i (\hat{n}_i - 1).$$

It is convenient to use dimensionless variables $u_i = (\delta U_i)k/g$, in terms of which we rewrite:

$$H_{lat} + \hat{H}_{el-lat} = 2\epsilon_k \sum_i \left( \frac{1}{2} u_i^2 + \alpha \frac{1}{4} u_i^4 \right) -2\epsilon_b \sum_i u_i (\hat{n}_i - 1). \quad (7)$$

where $\epsilon_k = g^2/2k$ is the energy gain from the breathing-mode distortion for $u_i = 1$, $\alpha = 0$, and $\alpha \sim A$ is the dimensionless parameter characterizing the anharmonicity.

To summarize, there are 7 parameters characterizing this Hamiltonian: the three hoppings $t_1, t_2, t_4$; the on-site Coulomb repulsion $U$ and Hund’s exchange $J$; the electron-lattice coupling strength $\epsilon_b$ and the dimensionless anharmonicity parameter $\alpha$.

Before concluding this section, we comment on how this Hamiltonian describes the two scenarios discussed above. Within the CD scenario, only the Ni $e_g$ orbitals are relevant as valence orbitals, so they should be directly identified with the $e_g$ orbitals of this model. In this view, the O are electronically inert, and serve only to modulate the on-site energy at the Ni sites when the cages are distorted. Even though the octahedra are known to tilt and rotate, the Ni-O distances stay equal inside each cage, so it is reasonable to use a single distortion $u_i$ to characterize each octahedron. Note that while our model does not explicitly impose constraints between distortions on neighboring cages, the mean-field solution will turn out to satisfy them, as discussed below.

The relevance to the NCT scenario is less obvious. Here, a full description of the electronic degrees of freedom include the Ni $e_g$ orbitals but also the ligand O $2p$ ones, as discussed in Ref. [26]. Of course, in principle one could do a mean-field treatment on the Hamiltonian used there to discuss the MIT, to find what magnetic order it favors and how (or if) it is affected by the fact that the O displacements modulate the hopping amplitudes. The difficulty is that the magnetic unit cell contains 4 Ni together with their 12 O, i.e. 20 distinct orbitals (counting spins as well). Needless to say, when combined with the multitude of possible mean-field parameters in such a large basis, the problem becomes rather unwieldy.

On the other hand, when considering a single Ni plus its O octahedron, one finds that the relevant eigenstates on the O sites are linear combinations with the same $e_g$ symmetries like the atomic Ni orbitals. This is because in order for an electron from the O band to move in the $e_g$ Ni manifold (and thus leave behind a ligand hole), it has to come from an O state that will hybridize (via $t_{pd}$ hopping) with the Ni orbital, and that only occurs if they have the same point symmetry. This is what allows us to identify the two $e_g$ “effective” orbitals as being these O-based linear combinations with the correct $e_g$ symmetry, surrounding various Ni sites, and into which the ligand hole can go. The complication here is that such orbitals centred about nearest-neighbour Ni ions are not orthogonal, so the true “effective” orbitals must correct for that and are therefore somewhat more extended and more complicated than simple linear combinations of O orbitals from each octahedral cage. As a result, all hoppings and electronic parameters are now likely strongly renormalized from their atomic values. We do not attempt to estimate their realistic values; instead, we will treat them as free parameters. This allows us to investigate what kind of magnetic orders arise in different regions of this large parameter space, and thus cover simultaneously both the CD and the NCT scenarios (their parameters are likely to be quite different).

In a broader view, the CD and NCT scenarios are limiting cases in a continuum of possibilities. The $t_{pd}$ hopping always leads to some hybridization between the Ni $e_g$ states and O-based states of the same symmetry. If the O bands are well below the Ni levels (for a large, positive charge transfer energy compared to $|t_{pd}|$), then these hybridized states are predominantly located on the Ni; this is the CD scenario. On the other hand, if the charge transfer energy is very negative, then the hybridized states will live primarily on the O; this corresponds to the NCT scenario. The reality is likely to be somewhere in between, where the probability to be on the Ni is neither 1 nor 0. Our effective model describes this entire continuum of possibilities, for appropriate choices of the parameters.
III. HARTREE-FOCK CALCULATION

We study the Hamiltonian of Eq. (1) within the Hartree-Fock approximation. As usual, this implies finding the global minimum of the average energy

\[ E(\{u\}) = \langle \Psi_e | \hat{H}(\{u\}) | \Psi_e \rangle \]  

(8)

where the Slater determinant \( |\Psi_e\rangle \) describes the electronic part, and the set \( \{u\} = (u_1, u_2, \ldots) \) characterizes the semiclassical distortions of the lattice.

A. Lattice contributions

First, we minimize the energy with respect to the lattice distortions \( u_i \). This can be done easily using the Hellmann-Feynman theorem:28,29

\[ \frac{d}{du_j} E(\{u\}) = \langle \Psi_e | \frac{\partial \hat{H}(\{u\})}{\partial u_j} | \Psi_e \rangle . \]  

(9)

Note that Eq. (9) holds despite the fact that \( |\Psi_e\rangle \) is not an eigenstate of \( \hat{H}(\{u\}) \) (as assumed in the usual proof30). This is because a stronger proof is available, one that shows the theorem to hold for any sufficiently optimized variational state, not just for exact eigenstates31 (in our case, we also confirmed this numerically). An optimal variational state \( |\Psi_e\rangle \) satisfies the stationarity condition: \( \frac{\delta E}{\delta \Psi_e(u)} = 0 \) (this is a shorthand notation replacing all the derivatives with respect to all the one-particle orbitals defining \( |\Psi_e\rangle \)). This condition justifies why the second term vanishes in the identity \( \frac{d}{du_j} E(\{u\}) = \frac{\delta E(\{u\})}{\delta u_j} + \frac{\delta E(\{u\})}{\delta \Psi_e(u)} \frac{\partial \Psi_e(u)}{\partial u_j} \), which then leads to Eq. (9).

Thus, for our Hamiltonian we obtain the minimization condition, at each site \( j \):

\[ u_j + \alpha u_j^3 = (\hat{n}_j) - 1, \]  

(10)

where from now on we use the short-hand notation \( \langle \hat{O} \rangle = \langle \Psi_e | \hat{O} | \Psi_e \rangle \) for any electronic operator.

To make further progress, we use the experimentally well-established fact36 that the octahedra alternate between expanded and collapsed ones, so that \( u_j = u e^{iQ_c \cdot R_j} \), where \( Q_c = \pi (1, 1, 1) \). This immediately implies the appearance of a charge modulation \( \langle \hat{n}_j \rangle = 1 + \delta e^{iQ_c \cdot R_j} \), where the amplitude of the lattice distortion \( u \) is directly linked to the amplitude of the charge modulation \( \delta \) by:

\[ u + \alpha u^3 = \delta \]  

(11)

This equation shows that in our model, the existence of a charge modulation \( \delta \neq 0 \) forces the appearance of a lattice distortion \( u \neq 0 \), and vice versa. This depressed32 cubic equation admits the exact solution using Cardano’s formula (see Appendix B for details):

\[ u = \delta \frac{3}{2\beta^2} \left[ \left( \sqrt{1 + \frac{1}{\beta}} + 1 \right)^{\frac{1}{3}} - \left( \sqrt{1 + \frac{1}{\beta}} - 1 \right)^{\frac{1}{3}} \right], \]  

(12)

with \( \beta = \frac{4}{27} \alpha^2 \).

It is useful to consider this expression in some limiting cases: in the case of vanishing anharmonicity, \( \alpha \to 0 \), already from Eq. (11) we see that \( u = \delta \). For a fixed value of \( \delta \), increased anharmonicity \( \alpha \) will lead to a decrease of \( u \). Indeed, in the case of infinite anharmonicity, \( \beta \to \infty \) and we find

\[ u \approx \delta \frac{3}{2\beta^2} \left[ 2^{1/3} \right] \to 0. \]  

(13)

The exact solution listed in Eq. (12) is very convenient because it allows us to substitute for any \( u \) dependence in the Hartree-Fock equations (discussed next), and have them depend only on the electronic mean-fields.

B. Electronic contributions

We follow the usual steps, briefly summarized here for completeness, to derive the Hartree-Fock (HF) equations. Any Slater determinant has the general form:

\[ |\Psi_e\rangle = \prod_p a^\dagger_p |0\rangle , \]

where the appropriate number of electrons (here equal to the number of sites in our lattice) are created. The new states and old states are related by a unitary transformation

\[ a_n^\dagger = \sum_n \phi^*_n (ia\sigma) a_n^\dagger. \]

The goal is to determine the optimal \( \phi_n (ia\sigma) \) which minimize the total energy \( E(\{u\}) = \langle \hat{H}(\{u\}) \rangle \). The evaluation of this expectation value, and its minimization with respect to all properly normalized \( \phi_n (ia\sigma) \) proceeds in the usual way. As always, the resulting HF equations depend on various mean-field expectation values \( \langle a_i^\dagger a_j \rangle \) (because all interactions are local, terms with \( i \neq j \) do not appear).

We constrain these mean-fields to have the most general forms consistent with the 4-site unit cell found experimentally in the magnetically ordered state. Specifically, we set:
Equation (14) is consistent with the condition that
\[ \langle \hat{n}_z \rangle = \sum_{a,a'} \langle d_{i a a'}^{\dagger} d_{i a a} \rangle = 1 + \delta e^{iQ \cdot \mathbf{R}_i}. \]
The other terms in it allow for various possible magnetic orders with a non-vanishing z-axis spin expectation value:
\[ \langle \hat{S}_{i z} \rangle = \frac{1}{2} \sum_{a, \sigma} \sigma \langle d_{i a a}^{\dagger} d_{i a a} \rangle = S_{FM} + S_{AFM} e^{iQ \cdot \mathbf{R}_i}, \]
\[ + S_{1z} \cos(Q_m \cdot \mathbf{R}_i) + S_{2z} \sin(Q_m \cdot \mathbf{R}_i). \]

If only \( S_{FM} \neq 0 \), the order is ferromagnetic (FM), or \( \uparrow \uparrow \downarrow \downarrow \) (for simplicity, we only show the order inside one 4-site unit cell); if only \( S_{AFM} \neq 0 \), the order is antiferromagnetic (AFM) \( \uparrow \downarrow \downarrow \uparrow \); finally, having \( S_{1z} \neq 0 \) or \( S_{2z} \neq 0 \) further breaks translational symmetry, resulting in states with order like \( \uparrow 0 \downarrow 0 \) and \( 0 \uparrow 0 \downarrow \), respectively. Combinations of two or more finite expectation values lead to yet more possibilities, for example, having both \( S_{FM} \neq 0, S_{AFM} \neq 0 \) implies a ferrimagnetic order \( \uparrow \downarrow \downarrow \uparrow \) or \( \uparrow \uparrow \uparrow \downarrow \), depending on the relative magnitude of the parameters, etc.

Equation (15) allows for non-collinear magnetic orders, because a finite \( S_{1z} \) and/or \( S_{2z} \) imply non-vanishing \( \langle \hat{S}_{i z} \rangle \). In particular, a solution with finite \( S_{1z} = S_{2z} \) while all other values are set to zero implies the order \( \uparrow \rightarrow \downarrow \leftarrow \), which is one of the possible candidates. To conclude, Eqs. (14) and (15) allow the realization of any magnetic order with a 4-site unit cell consistent with the ordering vector \( Q_m = Q_{c}/2 \).

Similarly, Eqs. (16) and (17) allow for various orbital and magnetic/orbital orders, respectively. To the best of our knowledge, there is no experimental signature of any orbital ordering in the rare-earth nickelates, and numerical calculations suggest that orbital order states are expected to be relatively high energy. Previous work found orbitally ordered ground states for \( U'/W \approx (U - 2J)/6 > 2 \). Here, \( W \sim 6 \) is the bandwidth of the non-interacting system for \( t_1 = 1 \) and \( t_2, t_4 < 0.3 \). For a realistic \( J/t_1 \sim 1 - 2 \), this implies \( U/t_1 > 14 - 16 \), which is enough to stabilize a conventional spin and orbital ordered Mott phase with no charge disproportionation. Our model is consistent with this, in the sense that the lowest energy self-consistent states for experimentally reasonable values of the charge modulation \( \delta \) always have vanishing \( O, X, Z \) values. However, we have also found regions of parameter space where orbital ordered states appear to have the lowest energy, as discussed below. For convenience, in the following we will still set \( \langle d_{i a a}^{\dagger} d_{i a a} \rangle = 0 \) so as to keep the equations shorter, with the full form available in the appendix. We emphasize that in the regions of parameter space relevant to us, i.e. the neighborhood of the region where \( \delta \sim 0.3-0.4 \) in agreement with experimental observations, we have tested explicitly that the ground states do not exhibit orbital order, by running self-consistency loops where these mean-fields \( O, X, Z \) had finite initial values. The resulting self-consistent solutions either converged to vanishing values for these orbital mean-fields, or had much higher total energy than self-consistent states without orbital order, in accord with earlier findings.

The corresponding HF equations are identical to those arising from a non-interacting Hamiltonian \( \hat{H}_{\text{eff}} \) (which can be thought of as being the properly factorized counterpart of the original \( \hat{H} \)).
This Hamiltonian has four more similar lines of terms involving various $O, Z, X$ mean-fields which we do not write here explicitly, as discussed above.

We remind the reader that the lattice parameter $u$ appearing in the second line is given by Eq. (12).

After Fourier transforming, $H_{\text{eff}} = \sum_{k} \psi_{k}(h(k))\psi_{k}$, where $\psi_{k} = (\psi_{k\uparrow}, \psi_{k\downarrow}, \psi_{k\uparrow\downarrow}, \psi_{k\downarrow\uparrow})$ and $\psi_{\kappa\sigma} = (\psi_{\kappa\sigma\uparrow}, \psi_{\kappa\sigma\downarrow}, \psi_{\kappa\uparrow\downarrow}, \psi_{\kappa\downarrow\uparrow})$. The $16 \times 16$ matrix $h(k)$ can be directly read from Eq. (19) and is trivial to diagonalize numerically.

The self-consistent HF ground state is then straightforward to find, at least in principle. We start with an initial guess for the mean-field parameters $w^{(0)} = (\delta^{(0)}, S_{\text{FM}}^{(0)}, S_{\text{AFM}}^{(0)}, ...)$. These can be chosen either so as to test if a certain state, e.g. $\uparrow \rightarrow \downarrow$, is self-consistent, or by choosing random values for all these fields. We have always checked all the “simple” magnetic orders to see if they are self-consistent and if yes, what is their corresponding energy. However, in all cases we have also run a multitude of searches starting with random initial conditions, to make sure we are not missing a better candidate.

Once the mean-field parameters are chosen, the Hamiltonian (19) is diagonalized at all allowed $k$-points in the Brillouin zone, and its ground state at quarter-filling is identified. Using it, we compute the new mean-field parameters $v^{(0)} = (\delta^{(0)}, S_{\text{FM}}^{(0)}, S_{\text{AFM}}^{(0)}, ...)$. For example, $\delta^{(0)} = \frac{1}{N} \sum_{i\alpha\sigma} \epsilon_{Q, R} \langle \hat{n}_{i\alpha\sigma} \rangle$. We then compute the residual $e^{(0)} = |v^{(0)} - w^{(0)}|^2$. If this is below the desired accuracy, then convergence has been reached. If not, we set new values for the mean-field parameters: $w^{(1)} = v^{(0)}$ (this is a simplification: in reality we use a better choice, discussed below), and iterate until either the desired accuracy is reached, or the maximum iteration count is surpassed and this search is abandoned.

Once self-consistency is reached, i.e. $w \approx v$, the total energy associated with the set $w$ of mean-field parameters is given by:

$$E = \frac{1}{N} \sum_{p} E_{p} - \frac{1}{N} \langle \hat{H}_{\text{c-\epsilon}} \rangle + 2\epsilon_{b} \left( \frac{u^{2}}{2} + \frac{a^{4}}{4} \right).$$

Here $E_{p}$ are the eigenenergies of the occupied states, and

$$\langle \hat{H}_{\text{c-\epsilon}} \rangle = \frac{3U - 5J}{8} (1 + \delta^{2}) - \frac{U + J}{2} \left( S_{\text{FM}}^{2} + S_{\text{AFM}}^{2} + S_{1x}^{2} + S_{1z}^{2} + S_{2x}^{2} + S_{2z}^{2} \right).$$

(again, terms proportional to the $O, Z, X$ fields are omitted here and are instead given in the appendix).

After multiple searches for various initial conditions, the set $w \approx v$ corresponding to the lowest total energy $E$ is declared as the HF ground state, and its magnetic (and charge, orbital, lattice...) order is read off from its mean-field parameters.

While all this seems straightforward, in reality the problem is complicated by the large number of mean-field parameters whose convergence is sought: 15 when the $O, Z, X$ fields are included explicitly, and 7 otherwise. Searching for a local minimum in this many-dimensional space is non-trivial, and for too simplistic update rules such as $w^{(n+1)} = v^{(n)}$, it can take extremely many iteration steps before self-consistency is reached, if it is reached at all.

Because of this, we briefly mention here a few strategies that we found very useful:

(a) A much better update is an interpolation of the type:

$$w^{(n+1)} = \alpha v^{(n)} + (1 - \alpha)w^{(n)}.$$

The literature on nonlinear iterative equation solution techniques suggests that the choice of the mixing parameter $\alpha$ is typically problem-specific.\textsuperscript{35} We find the smoothest and most reliable convergence over most of the parameter space of interest occurs for $\alpha = 0.3$. This type of update can avoid the iteration being stuck in a loop, or helplessly hopping on either side of a “flat minimum".
(b) However, we found that this approach works best in conjunction with Pulay mixing, or direct inversion in the iterative subspace (DIIS). The idea behind DIIS, originally developed for high-parameter Hartree-Fock quantum chemistry calculations by Pulay,\textsuperscript{36} is as follows: suppose that a sequence of solutions $v^{(n+1)}, v^{(n+2)}, ..., v^{(n+N)}$ to the nonlinear system has been generated, from some initial solution step $n$. Together, they span a linear subspace $W_{N,n} = \text{span}\{v^{(n+1)}, v^{(n+2)}, ..., v^{(n+N)}\}$ within the higher-dimensional (possibly nonlinear) parameter manifold $W$. It is then possible to pick the “best possible” vector $w^{(N)}$ within this linear subspace, by minimizing the error $\epsilon = \| \sum_{i=1}^{N} v^{(i)} - w^{(i)} \|^2$, which amounts to solving an $N + 1 \times N + 1$ system of linear equations (hence the “inversion of the iterative subspace” – for more details, see Ref. [36]).

The DIIS can quickly maximize the potential of the vectors within the subspace $W_{N,n}$, but if the true solution is outside the subspace by more than the allowed residual $\epsilon_0$, then no matter how many times the Pulay mixing is carried out, it will not result in improved convergence. The solution\textsuperscript{35} is to intersperse Pulay mixing with regular updates of the form (22), with a given periodicity $k$ (typically $k = 3$). The algorithm thus alternates between expanding its iterative subspace, and finding the lowest residual vector within it, resulting in optimal convergence for most parameter values. Our experience is that it can even arrest divergences from round-off error accumulation. Often even small errors (say, in mean-fields that should be zero for a particular type of converged solution) can lead to rapid divergence of the HF iterative trajectory away from a self-consistent point. Yet DIIS appears to nullify that tendency, firmly slashing those creeping mean-field magnitudes back to zero and guiding the trajectory towards the self-consistent point.

(c) Parallelization: While the iterative loop is not easy to parallelize efficiently, there are higher-level parallelization opportunities: (i) multiple initial guesses can be iterated in parallel, for a given set of parameter values $U, J, \epsilon_0, t_1, \ldots$; and (ii) ground states can be found at multiple parameter values, in parallel. We opted for option (ii) due to ease of implementation and data management, together with linear speed-up of the calculation (because ground states corresponding to different parameter values are independent from each other, there is no overhead to the parallelization).

(d) Boot-strapping: While calculations at neighbouring points in the parameter space are independent from each other, we expect small changes in the values of the various parameters $U, J, \epsilon_0, t_1, \ldots$ to normally lead to small changes in the nature of the ground state $w$. As such, an already converged solution from a neighbouring point can result in fast convergence to a similar kind of converged solution at the current point. Where available, we included this option in the set of initial mean-field guesses.

Finally, we found that there are two key parameters that need to be tested for convergence: the cutoff iteration count $n_{\text{max-iter}}$, and the number of points sampled in the Brillouin zone $n_{\text{num-k-pts}} = N^3$. The sampling of the momentum space slows down the calculation time $\sim O(N^3)$, so choosing too large an $N$ is costly while too low a value introduced finite-size effects. Similarly, the cutoff iteration count needs to be large enough to allow convergence for the interesting solutions, but not so large as to waste computation time on “dead-end” iterative trajectories that never converge. We found $N = 25$ and $n_{\text{max-iter}} = 500$ to be optimal for our purposes, taming the error in mean-fields to below $\epsilon_0 = 10^{-4}$ and in ground state energies to less than $10^{-3}$.

In total, to obtain a typical phase diagram, we carry out anywhere from 400 to 1,600 calculations (depending on the desired resolution), each of which starts from a pool of 20-30 initial guesses and proceeds through anywhere from 5 to 500 iterative steps (where each iterative step involves the diagonalization of roughly 15,000 $16 \times 16$ subblocks of the Hartree-Fock matrix, as well as the calculation of the density matrix and the order parameters $w$).

\textbf{IV. RESULTS}

The results shown here focus on areas of the phase diagram with essentially no orbital order. As mentioned, our searches for converged self-consistent states with non-trivial orbital order never produced

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{charge_modulation.png}
\caption{Charge modulation $\delta$ (see colour scale) in the HF ground-state in the $U$-$J$ plane. Other parameters are $t_1 = 1, t_2 = 0.15, t_4 = 0, \epsilon_0 = 0$. Resolution is $40 \times 40$.}
\end{figure}
FIG. 2. Representative density of states for the various phases in Fig. 1: (a) metallic phase, $U = 1.077, J = 0.538$; (b) itinerant magnetic phase (see the magnetic phase analysis below for more details about this phase), $U = 3.231, J = 0.385$; (c) charge modulated phase, with a clear gap at the Fermi level, $U = 2.0, J = 1.538$; (d) Mott insulating phase, $U = 5.846, J = 0.231$. Other parameters as in Fig. 1. Notice the van Hove singularity at the lower band edge in all the diagrams: its presence is due to the nonzero $t_2$ parameter, which introduces a strong asymmetry to the DOS. More on this below.

a viable candidate for an HF ground state in the region of the parameter space with finite charge modulation $\delta \sim 0.3-0.4$. However, we did find that sometimes orbitally ordered states were indeed the ground state configuration in other regions of the phase diagram, namely towards the large U Mott limit. Most notably, the antiferromagnetic ferroorbital order, $\uparrow \downarrow \uparrow \downarrow + X x X x$ (marked “afm-ferroorb” in the phase diagrams below), and other orbitally ordered possibilities (marked miscellaneous, or “misc”). Given that such orders are found outside the experimentally relevant parameter regime, from now on we focus only on the HF parameters $\delta, S_{FM}, S_{AFM}, S_{1z/x}, S_{2z/x}$ and leave the investigation of the regions with stable orbital order to future work. The lattice distortion $u$ is related to $\delta$ through Eq. (12).

To get a basic idea of the dependence of the charge modulation $\delta$ on the electronic interaction strengths $U$ and $J$, we start by showing in Fig. 1 a contour plot of the charge modulation in the $U$-$J$ plane, for $t_1 = 1, t_2 = 0.15, t_4 = 0, \epsilon_b = 0$. We set $t_1 = 1$ throughout this paper, so all energy scales are reported in units of $t_1$. Our results are in qualitative agreement with earlier findings at similar parameter values. Unsurprisingly, for small values of $U$ and $J$, we find $\delta = 0$ and the system is fully metallic, with no gaps in the band structure, as can be seen from typical (volume) densities of states (DOS) for the various phases, given in Fig. 2. The vertical scale in the DOS plots is normed to the total volume of the crystal, i.e., $1/N^3$ (the lattice constant is set to 1). For large $J$ and small $U$, in the spirit of Hund’s rule, the electrons find it preferable to occupy both orbitals at the same site, leading to ever-increasing charge modulation between neighboring sites and strong insulating behavior (this corresponds to the picture discussed in Ref. [37]).
the other extreme, for large Hubbard $U$ and small $J$, no charge modulation arises because of the prohibitive cost of double occupancy. As a result, the system remains itinerant up to fairly large values of $U$, where it switches to a Mott insulator.

Of course, the interesting question is how charge modulation is modified by the coupling to the lattice. To probe this, we fix various ratios of $J/U = 0.2, 0.3, 0.4, 0.5$ (they can be thought of as line slices of the phase diagram in Fig. 1 emanating from the origin) and tune the lattice coupling constant $\epsilon_b$, while keeping fixed the values of the other parameters $t_1 = 1, t_2 = 0.15, t_4 = 0.25, \alpha = 1$ (we added the 4th nearest neighbor hopping to watch the lattice interact with all the ingredients of the model – explicit results on its influence on the phase diagram will be discussed below). These results are shown in Fig. 3, while in Fig. 4 we indicate whether the HF ground state is metallic (blue) or insulating (yellow).

Clearly, for small values of $U$ the system is metallic and homogeneous, with $\delta = u = 0$. Even in the absence of coupling to the lattice, i.e. when $\epsilon_b = 0$, with increasing $J$ there is a transition to a state with a finite charge modulation $\delta$, which eventually becomes insulating if $J$ is large enough. This MIT occurs faster for larger $J/U$ ratios, as the tendency for two-orbital occupancy encouraged by $J$ grows faster than the drive toward single-site occupancy coming from increased $U$. If the coupling to the lattice is turned on, we find that $\delta$ increases with $\epsilon_b$ everywhere, and the system is more likely to become insulating; thus there is positive cooperation between $J$ and the lattice coupling $\epsilon_b$.

These results confirm the existence of the MIT, where the insulating state has a charge modulation $\delta \neq 0$ and a lattice distortion $u \neq 0$. Coupling to the lattice increases the likelihood of this insulating ground state with finite $u$, as expected.

We now discuss the magnetic order found in the HF ground state, and how it is influenced by the coupling to the lattice. Once again, it is useful to start with the $U$-$J$ plane picture. In Fig. 5 we show the magnetic order found in the HF ground state for various values of $U$ and $J$ both in the absence and in the presence of coupling to the lattice ($\epsilon_b = 0$ and $\epsilon_b = 0.8$, respectively). The black contours are kept fixed. The black contours indicate the corresponding value of $\delta$. If we fix $\delta$ at experimentally relevant values $\delta \approx 0.3 - 0.4$, we see that as a function of increasing $U$ (and $J$ adjusting accordingly), the system evolves through a variety of states. While charge modulation of the experimentally appropriate magnitude appears to originate just past the boundary of the metallic and insulating regimes at low $U$ and intermediate $J$, as we follow the contour line it quickly enters the bulk of the $\uparrow 0 \downarrow 0$ magnetic phase already at $U \approx 1$, before again falling on a phase line (this time between the ferromagnetic and aligned-ferrimagnetic phases) around $U \approx 4$ for what seems like the rest of the contour. The fact that the state $\uparrow 0 \downarrow 0$ is favored by larger $J$ and lies, for the most part, above these $\delta$ values, speaks...
in its favor as the preferred magnetic ground state. In addition, for a decently-sized range of $U$ and $J$ values ($U$ from 1 to 3 and $J$ from 1 to 1.5 – a range potentially consistent with experimental values for these parameters) the contour remains squarely in the $\uparrow 0 \downarrow 0$ phase, thus suggesting that this might be the most energetically favorable 4-site spin alignment. Our phase diagram agrees qualitatively with that of Ref. [20], although there are sizable quantitative differences, which we attribute to the different form of the on-site electronic Hamiltonian used.

We note that in between the magnetic phases there are often small regions wherein the energy of several different magnetic orders are indistinguishable to within our computational accuracy: such regions are designated “degenerate”. We emphasize that, compared to the picture of Ref. [20], these regions do not correspond to partially-disproportionated states of type $\uparrow\uparrow\downarrow\downarrow$ (in fact, such states are never convergent within our model: see below): instead, the states from neighboring phases (like, say, $\uparrow 0 \downarrow 0$ and $\uparrow\uparrow\downarrow\downarrow$ and $\uparrow\uparrow\downarrow\downarrow$ in the lower middle of the phase diagram) all have roughly the same energy, down to $\Delta E \sim 10^{-3}$.

When the coupling to the lattice is turned on, it acts to strongly reduce the energy of the charge modulated states, as one would expect. Not only does it lead to a significant shift of the $\uparrow 0 \downarrow 0$ magnetic order boundary, further increasing its likelihood to be the magnetic ground state; it also shifts the charge modulation contours, leading to an enhancement of the aligned ferrimagnetic phase for large $U$ and $J$, as well as the decoupling of the charge and magnetic order phase lines below $U = 1$, revealing a sizable metallic phase with partial charge modulation.

Given this large-scale picture of the magnetic order, we once again fix ratios $J/U$ and consider, in more detail, the impact of the lattice. The data, shown in Fig. 6, demonstrates clearly that an increase in coupling to the lattice leads to a creep of the $\uparrow 0 \downarrow 0$ phase boundary: the stronger the coupling to the lattice, the smaller the values of $U$ and $J$ that are required to stabilize the fully charge modulated magnetic order. A curious feature of this data, already noted in the previous paragraph, emerges in the upper-left corner of the diagrams: while typically the contours signaling the onset of charge modulation strongly follow the magnetic ordering phase lines, we see that with increased coupling to the lattice there is a decoupling of the onset of charge and magnetic order. In other words, we obtain a charge modulated phase without any magnetism. The lattice distortion acts to strongly gap out and flatten the band structure: however, the Fermi level is still well within the occupied band (a feature of the two-band Hubbard model), so the system stays metallic and magnetic order does not arise. Thus the coupling to the lattice acts to stabilize the charge order in the absence of magnetism and localization. This is strongly reminiscent of the decoupling of the MIT and the magnetic order transition for the 5m to Y members of the nickelate series, a well-known feature of the nickelates phase diagram, and could suggest that the strength of the lattice coupling is ultimately responsible for determining whether the charge and magnetic transitions are concurrent or not.

It is important to note that we usually find that many of the possible 4-site unit cell magnetic orders turn out to be self-consistent within HF at the same values of parameters, and that their HF energies can lie fairly close together. An example is shown in Fig. 7, where the energy corresponding to various self-consistent HF states is plotted vs. $\epsilon_b$, at fixed values of the other parameters. This is, in essence, a slice along the $U \approx 4$ line of the top left panel in Fig. 6.

At $\epsilon_b = 0$, we find that the states $\uparrow\uparrow\downarrow\downarrow$, $\uparrow\uparrow\downarrow\downarrow$, and $\uparrow\uparrow\downarrow\downarrow$ are all converged, with their HF energies per site being within $\sim 0.001t_1$ of each other. The $\uparrow\uparrow\downarrow\uparrow$ order has the lowest energy and thus is identified as the HF ground state. The close spacing between these energies suggests that changing any of the parameters and/or adding new ingredi-
FIG. 6. Magnetic order in the HF ground state, as a function of $U$ and $\epsilon_b$, for $J/U = 0.2, 0.3$ ((a) and (b), respectively) and $0.4, 0.5$, ((c) and (d), respectively). Other parameters are $t_1 = 1, t_2 = 0.15, t_4 = 0.25, \alpha = 1$.

ents – in particular coupling to the lattice – may favor another magnetic order as the ground state. Indeed, we see that as $\epsilon_b$ increases, the energy of the $\uparrow 0 \downarrow 0$ state decreases and it eventually becomes the new HF ground state. Note also that the energies of the other magnetic states are independent of $\epsilon_b$ – while this plot is made at a specific set of parameter values, this pattern seems to hold across various parameter regimes of $U, J, t_1$. There is a straightforward explanation to this: any state that includes no charge modulation also includes no lattice distortion, as $\delta \sim u$ through the lattice self-consistency equation (Eq. 12). The real question is: why are the states with partial charge modulation, e.g. $\uparrow \uparrow \downarrow \downarrow$ not convergent within this mean-field model? Such states could potentially compete with $\uparrow 0 \downarrow 0$ order for ground state status, as the coupling to the lattice is adjusted. We find, however, that such states fail to converge no matter the starting point, and in fact they are among the least stable, as can be seen most clearly from cuts in the 15-dimensional parameter space that show iterative trajectories of the Hartree-Fock calculation (such diagrams are called “Poincare sections” in the dynamical systems literature). In Fig. 8, we plot the evolution of the difference $S_{1z} - S_{2z}$ versus the charge disproportionation $\delta$. Note that the states $\uparrow \uparrow \downarrow \downarrow$ (central point) and $\uparrow 0 \downarrow 0$ (diagonal end points) are well-defined in this plane. Any solution not precisely on the $S_{1z} - S_{2z} = 0$ line converges to $\uparrow 0 \downarrow 0$ instead.

FIG. 7. Total energies of several converged self-consistent HF states as a function of $\epsilon_b$. The different colors correspond to different magnetic orders. The parameters are $U = 4.105, J = 0.2U, t_1 = 1, t_2 = 0.15, t_4 = 0.25, \alpha = 1$. 

FIG. 8. Evolution of the difference $S_{1z} - S_{2z}$ versus the charge disproportionation $\delta$. Note the states $\uparrow \uparrow \downarrow \downarrow$ (central point) and $\uparrow 0 \downarrow 0$ (diagonal end points) are well-defined in this plane. Any solution not precisely on the $S_{1z} - S_{2z} = 0$ line converges to $\uparrow 0 \downarrow 0$ instead.
When it comes to the hopping amplitudes $t_2$ and $t_4$, given the spatial extent of the orbitals in the nickelates, it is unrealistic to expect them to be larger than $t_1$. Hoppings bounded by $t_2, t_4 < 0.3$ only renormalize the overall bandwidth in the non-interacting regime by at most 10%, which should not be enough to shift phase boundaries in the U-J to any appreciable degree. And yet even small adjustments to $t_2$ and $t_4$ can significantly alter the magnetic phase diagram, as can be seen for instance in Fig. 9 for changing $t_2$ and in Fig. 10 for changing $t_4$. We believe these changes to be a consequence of the shape of the DOS, which can change dramatically even for small perturbations of the hopping parameters.\(^{38}\) The way the introduction of a new hopping path affects the DOS can be predicted semianalytically and depends, in a hypercubic bipartite lattice, on whether the new hopping connects A-A and B-B sublattice sites, or the A-B sublattices.\(^{39}\)

In our case, $t_1$ and $t_4$ hopping appear to produce an entirely symmetrical (about band centre) DOS: meanwhile, $t_2$ leads to a strong asymmetry and the appearance of a van Hove singularity at the lower band edge. In the spirit of the Stoner criterion, an enhancement of the density of states near the Fermi level – an effective consequence of the introduction of a nonzero $t_2$ – lowers the value of $U$ required for ferromagnetism to arise, thus causing the metallic region near the origin to shrink significantly (Fig. 9). Meanwhile, introducing a nonzero $t_4$ in the presence of $t_2$ counteracts this tendency by boosting the density of states above the Fermi level, thus increasing the interaction strength $U$ required to exhibit magnetic order in the ground state (see Fig. 10).

At the same time, the effect of $t_2$ and $t_4$ on the magnetic order competition between the various 4-site contenders appears to be negligible. Figure 11 shows a typical form of the energy modulation with $t_2$ and $t_4$ for the chief contenders $\uparrow\uparrow\downarrow\downarrow$, $\uparrow\rightarrow\downarrow\leftarrow$ and $\uparrow\leftarrow\downarrow\rightarrow$ solely. The energies of the 4-site states are affected in a very similar way, with none of them being the clear favorite for the ground state. In the case of $t_4$, the explanation for this is that the frustration costs introduced by the 4th neighbor-hopping, which connects sites that are two lattice constants apart, are identical for all of these magnetic states, so they are all equally disfavored. The effect for $t_2$ is slightly different, as increasing it actually reduces the energy of all of the magnetic states, initially showing a slight preference for the non-collinear $\uparrow\rightarrow\downarrow\leftarrow$, then the collinear $\uparrow\uparrow\downarrow\downarrow$, and finally the FM state. This can be understood in the spirit of the Stoner effect, which is somewhat more general in this two-band Hubbard model: as the density of states at the Fermi level grows, most kinds of magnetic order benefit, but the FM state benefits the most. The strong response of the FM state to the hopping amplitude modulations can be readily seen in both Figs. 11 (a) and (b): the state suffers most strongly due to the added frustrations from $t_4$, and benefits the most from the Stoner effect with $t_2$. Notice that all of these effects occur with minimal bandwidth renormalization, as discussed — these are all purely consequences of the shape of the DOS.

Finally, we comment on the role played by the $\alpha$ anharmonicity parameter. Given the form of the lattice energy $E_{\text{latt}} = \epsilon_0(u_1^2 + \alpha u_4^4)/2$, and a typical value for lattice distortion $u_i \approx 0.5$, we see that the two terms compare numerically as $\epsilon_0(0.25 + 0.03\alpha)$. Thus for $\alpha = 1$ the quartic correction is merely 10% of the quadratic contribution, and serves only to modulate the bare magnitude of the lattice distortion $u$, as determined by Eq. (12), away from $u = \delta$, without affecting the basic physics of the problem. The results shown in Fig. 12 confirm as much: insofar as the charge modulation contours are displaced from their position at $\alpha = 0$, it is the ones closest to $\delta = 1$ and thus with the largest $u$ that are affected the most, whilst the rest of the phase diagram remains the same. In the interest of controlling the size of the lattice distortion, all the calculations in this paper were carried out at $\alpha = 1$, unless indicated otherwise.
FIG. 9. Magnetic order in the HF ground state, as a function of $U$ and $J$, for $t_2 = 0, 0.15, 0.25$ ((a) (b) and (c), respectively). Other parameters are $t_1 = 1, t_4 = 0, \epsilon_b = 0$. In (d), (e) and (f) we depict the non-interacting ($U = J = 0$) DOS that correspond to the systems (a) (b) and (c), respectively. Notice that increasing the bandwidth (even if just modestly by at most 15%), paradoxically, leads to more robust ferromagnetism at lower $U$ — a consequence of the van Hove singularity at the lower band edge. Also notice how when the next-nearest neighbor frustration is maximally reduced ($t_2 = 0$), the non-collinear 4-site magnetic order dominates the collinear one. Currently it is not clear to us why this would be the case, given how introducing $t_2, t_4$ seems to affect them equally based on pure lattice frustration arguments.

FIG. 10. Magnetic order in the HF ground state, as a function of $U$ and $J$, for $t_4 = 0, 0.15$ ((a) and (b), respectively), and $t_4 = 0.25, 0.35$ ((c) and (d), respectfully). The bandwidth is $W = 6.4$ in all cases. Other parameters are $t_1 = 1, t_2 = 0.15, \epsilon_b = 0$. The growth of the metallic region is clearly not the effect of a renormalized bandwidth, but rather is due to the changes of the shape of the DOS.
FIG. 11. Energies of several converged self-consistent HF states as a function of $t_4$, relative to the energy of the metallic state. The different colors correspond to different magnetic orders (see the legend). The parameters are $U = 4, J = 0.316, t_1 = 1, t_2 = 0, \epsilon_b = 0$ for (a) and $U = 5, J = 0.316, t_1 = 1, t_2 = 0.15, \epsilon_b = 0$ for (b). Notice how in (b) the relative energies of the chief magnetic ground state contenders are not affected by the change in the hopping rate $t_4$—except for ferromagnetism, which gets strongly frustrated with the additional $t_4$ hopping and, paradoxically, “unfrustrated” with the introduction of $t_2$ hopping due to DOS effects (see the text for details). Meanwhile, in (a) with tuning the $t_2$ rate away from 0 the non-collinear $\uparrow \rightarrow \downarrow \leftarrow$ gets briefly favored, but then quickly loses out to the collinear $\uparrow \uparrow \downarrow \downarrow$, before ferromagnetism begins to reign supreme.

V. CONCLUSIONS

The magnetic order of the rare-earth nickelate series, much like the metal-insulator behavior and charge order, can be expected to couple to the lattice degrees of freedom. Even the simplest semiclassical version of the Holstein coupling is sufficient to aid charge disproportionation and to turn the material into an insulator in much of the parameter space. While several magnetic orders are converge to self-consistency in our effective two-band Hubbard model for the nickelates, the $\uparrow 0 \downarrow 0$ antiferromagnetic order dominates, usually presenting hand-in-hand with charge disproportionation $\delta \neq 0$. In contrast, the non-disproportionated collinear $\uparrow \uparrow \downarrow \downarrow$ and non-collinear $\uparrow \rightarrow \downarrow \leftarrow$ orders only arise at intermediate/large $U$ and small $J$ and do not fare well when the coupling to the lattice is increased, quickly disappearing from the phase diagram entirely. This can be easily understood, as the non-disproportionated modes cannot couple to the lattice distortion, given that for them $\delta = 0$ and hence, via the self-consistency condition, also $u = 0$. Thus the main impact of the lattice on the magnetic order, in our model and at the HF level, is to make the $\uparrow 0 \downarrow 0$ order even more dominant, by decreasing its energy relative to that of the other states. Surprisingly, we find that self-consistency is never achieved for a state such as $\uparrow \rightarrow \downarrow \leftarrow$ or $\uparrow \uparrow \downarrow \downarrow$, that is, for $\delta \neq 0$. Such states are unstable in the iterative sequences, with the slightest deviations from their expected mean-field parameter structure leading to fast flow towards the stable solution $\uparrow 0 \downarrow 0$.

While usually the charge modulated phase $\delta \neq 0$ always occurs with $\uparrow 0 \downarrow 0$ for small $U$, we found that introducing a finite electron-lattice coupling $\epsilon_b$ also stabilizes a new phase, where the charge mod-
ulation persisted on its own, without any associated magnetic order. The magnetic order would then arise only at higher \( J \), leading to the effective decoupling of the charge modulation and magnetic transitions – a feature strongly reminiscent of the canonical nickelates phase diagram.

We therefore conclude that all else being equal, coupling to the lattice favors the \( \uparrow \uparrow \downarrow \downarrow \) 0 order. However, one must keep in mind that our simplified Hamiltonian may fail to capture properly some aspects of the actual physics of these materials, especially in the NCT scenario where the O sites should be included explicitly. Moreover, it is known that the accuracy of the Hartree-Fock approximation can be included explicitly. Moreover, it is known that the Hartree-Fock approach on the nickelate problem.

In the literature have had success using a Hartree-Fock approach on the nickelate problem.17,19,25,26 In addition to the question of the validity of the mean-field approach, other open questions remain. Specifically in the NCT scenario where the O sites should arise only at higher \( J \) and other orbital orders possible within the model, are not entirely clear and their investigation is left to future studies.

Overall, strong \( t_{pd} \) covalency places nickelates in the intermediate coupling regime of \( U/W \) (for instance, see Ref. [40]), wherein charge fluctuations coupled to lattice become an increasingly important factor in magnetic phase behavior of these materials.

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**Appendix A: Hopping operator**

The hopping operator is a sum of three terms

\[
\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_4, \tag{A1}
\]

where

\[
\hat{T}_1 = -t_1 \sum_{\sigma} \sum_{\eta,\mu \neq \sigma} \left( d_{i\eta\sigma}^\dagger d_{i+\eta,\mu \sigma} + \text{h.c.} \right), \tag{A2}
\]

\[
\hat{T}_2 = -t_2 \sum_{i,\eta,\mu, \eta, \mu \neq \sigma} \left( d_{i+\eta,\mu \sigma}^\dagger d_{i\eta\sigma} + \text{h.c.} \right), \tag{A3}
\]

\[
\hat{T}_4 = -t_4 \sum_{i,\eta,\mu \neq \sigma} \left( d_{i\eta\sigma}^\dagger d_{i,\mu,2\eta,\sigma} + \text{h.c.} \right). \tag{A4}
\]

**Appendix B: Minimizing lattice contributions**

In the text we were faced with the need to solve the cubic equation

\[
u^3 + \frac{1}{\alpha} u - \frac{\delta}{\alpha} = 0 \tag{B1}
\]

which arose during lattice energy minimization in the Hartree-Fock process. As we mentioned, it admits a closed form solution using Cardano’s formula.
More explicitly, write
\[ u^3 = (s - t)^3, \quad \frac{1}{\alpha} = 3st, \quad \frac{\delta}{\alpha} = s^3 - t^3 \]

Combining the latter two equations into one for \( t \), we find
\[ t^6 + t^3 \left( \frac{\delta}{\alpha} \right) - \left( \frac{1}{3\alpha} \right)^3 = 0 \]
which is easily solved as a quadratic
\[ t^3 = \frac{1}{2} \left( -\frac{\delta}{\alpha} \pm \sqrt{\left( \frac{\delta}{\alpha} \right)^2 + \frac{4}{27\alpha^3}} \right) \]

from which we can recover the expression for \( u \) in Eq. (12).

Appendix C: Full mean-field Hamiltonian

The full effective Hamiltonian is:

\[
\hat{H}_{\text{HF}} = \sum_{k,\alpha} t_{\alpha\beta}(k) \hat{d}^\dagger_{k\alpha\sigma} \hat{d}_{k\beta\sigma} + \sum_{k,\alpha} \left( \frac{3U - 5J}{4} - \frac{\sigma}{2}(U + J)S_{\text{FM}} \right) \hat{d}^\dagger_{k\alpha\sigma} \hat{d}_{k\alpha\sigma} + \left( \frac{3U - 5J}{4} \right) \delta - 2\epsilon_{k\alpha} - \frac{\sigma}{2}(U + J)S_{\text{AFM}} \right) \hat{d}^\dagger_{k+Q,\alpha\sigma} \hat{d}_{k\alpha\sigma} - \frac{\sigma}{4}(U + J) \left( (S_{1x} - iS_{2x}) \hat{d}^\dagger_{k+Q_{m},\alpha\sigma} \hat{d}_{k\alpha\sigma} + (S_{1x} + iS_{2x}) \hat{d}^\dagger_{k-Q_{m},\alpha\sigma} \hat{d}_{k\alpha\sigma} \right) - \frac{U + J}{4} \left( (S_{1x} - iS_{2x}) \hat{d}^\dagger_{k+Q_{m},\alpha\sigma} \hat{d}_{k\alpha\sigma} + (S_{1x} + iS_{2x}) \hat{d}^\dagger_{k-Q_{m},\alpha\sigma} \hat{d}_{k\alpha\sigma} \right) - \frac{U - J}{2} \left( (X_1 - iX_3) \hat{d}^\dagger_{k+Q_{m},\alpha\sigma} \hat{d}_{k\alpha\sigma} + (X_1 + iX_3) \hat{d}^\dagger_{k-Q_{m},\alpha\sigma} \hat{d}_{k\alpha\sigma} \right) + \frac{5}{4}(U - J)O_1 - \sigma(U - J)Z_1 \hat{d}^\dagger_{k\alpha\sigma} \hat{d}_{k\alpha\sigma} + \frac{1}{2}(S_{1x}^2 + S_{2x}^2) - 2(U - 5J)(O_1^2 + O_2^2) - 2(U - J)(Z_1^2 + Z_2^2) \]

Appendix D: Hartree-Fock energy

The full expression for the electron-electron interactions part of the Hamiltonian in a Hartree-Fock state \(|\Psi_e\rangle\) is given by

\[
\frac{1}{N} \langle \hat{H}_e \rangle = \frac{3U - 5J}{8} (1 + \delta^2) - \frac{U + J}{2} \left( S_{\text{FM}}^2 + S_{\text{AFM}}^2 + \frac{S_{1x}^2 + S_{2x}^2 + S_{2z}^2}{2} \right) - 2(U - 5J)(O_1^2 + O_2^2) - 2(U - J)(Z_1^2 + Z_2^2) - (U - J)(X_1^2 + X_2^2). \quad (D1)
\]

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