

Supplemental Material for “Electronic correlations and magnetic interactions in NdNiO₂”

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A. Ni¹⁺ and Cu²⁺ *d*-orbital excitations

As mentioned in the main text, a cluster-in-an-embedding methodology was employed. We used a single NiO₄ (CuO₄) square plaque (central reference unit) along with the nearest neighbor (NN) Ni (Cu) and Nd (Ca) ions in the quantum cluster. The NN Ni¹⁺ (Cu²⁺) ions were approximated with closed shell Cu¹⁺ (Zn²⁺) ions to avoid spin-couplings with the central Ni¹⁺ (Cu²⁺) ion. Such procedure is often used in quantum chemistry calculations for systems involving transition-metal or lanthanide ions, see Refs.^{1–3}. The solid-state matrix was modeled as a finite array of point charges fitted to reproduce the Madelung crystal field in the cluster region⁴.

We used all-electron atomic natural orbital (ANO)-L basis sets of tripple- ζ quality with additional polarization functions – $[7s6p4d2f1g]$ for Ni (Cu)⁵ and $[4s3p2d1f]$ for oxygens⁶ of the reference unit. For the eight Nd (Ca) atoms large core effective potentials^{7–9} and associated $[3s2p2d]$ basis functions were used. In the case of Nd, the *f*-electrons were incorporated in the core. Cu¹⁺ (Zn²⁺) total ion potentials (TIPs) with $[2s1p]$ functions were used for the NN Ni¹⁰¹¹ (Cu¹²) ions. We found that basis functions on top of the TIPs were essential for representing the charge redistribution on these ions to reproduce correctly the crystal field splittings. Test calculations were performed to estimate the scalar relativistic effects within Douglas-Kroll-Hess integral correction and no significant deviations were found and hence they were not included in the data reported.

Due to the constraints in the PYSCF and OPENMOLCAS programs D_{2h} symmetry was imposed in the calculations, even though the crystal structures imply D_{4h} point-group symmetry at the Ni (Cu) sites. As mentioned in the main text, multiconfiguration reference wave functions were first generated by complete active space self-consistent field CAS(35,36)SCF calculations. DMRG active space CI solver from BLOCK program¹³ was used with 3000 renormalized states (M). We found that $M = 2000$ was sufficient to converge the CASSCF energy. Nevertheless, we used $M = 3000$ to ensure good quality of the higher-order electron RDMs used for perturbation theory calculations. The five states shown in Fig. 1 in the main text belong to the following irreducible representations: A_g ($x^2 - y^2, z^2$); B_{1g} (xy); B_{2g} (xz) and B_{3g} (yz).

In the NEVPT2 calculations all Ni (Cu) $3s, 3p, 3d$ and O $2s, 2p$ electrons were correlated starting from the reference wavefunctions generated in the CAS(35,36)CI space.

B. FCIQMC calculations

The GS wavefunctions shown in the main text are in the basis of CASSCF natural orbitals and were obtained from spin-adapted FCIQMC calculations. For the population dynamics in FCIQMC, the initiator approximation¹⁴ has been used with a threshold value of 3.0 together with the semistochastic method¹⁵ using a deterministic subspace consisting of 8000 most populated CSFs. Further, adaptive shift approach¹⁶ was employed to speed up calculations. We used 100 million walkers to converge the total energies to within 0.5 mHa of the DMRG energies with stochastic noise less than 0.02 mHa, see Fig. S1.

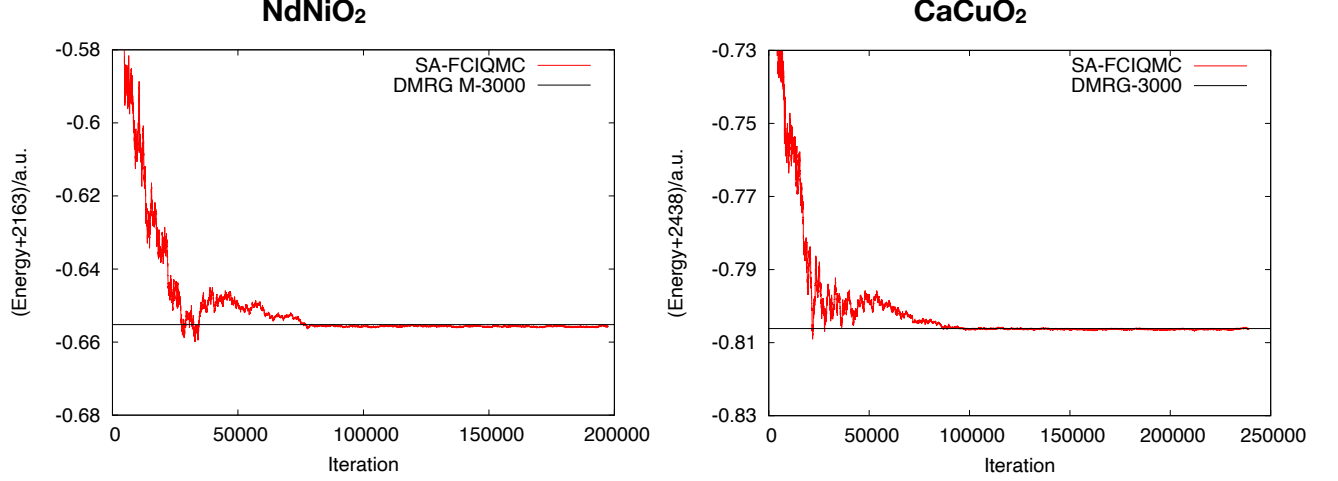


FIG. S1. Convergence of FCIQMC projected energy to DMRG ($M = 3000$) CASCI energies for IL-NdNiO₂ and IL-CaCuO₂.

C. Entanglement entropy

The single orbital entropy is given by

$$s(1)_i = - \sum_{\mu} w_{\mu,i} \ln w_{\mu,i}, \quad (\text{S1})$$

where $w_{\mu,i}$ are the eigenvalues of the one orbital RDM

$$\rho_{i_{\alpha}, i_{\beta}}^{(1)} = \sum_n \langle \mathbf{n} | \langle i_{\alpha} | \psi \rangle \langle \psi | i_{\beta} \rangle | \mathbf{n} \rangle. \quad (\text{S2})$$

It is constructed from conventional spin-dependent 1- and 2-particle RDMs¹⁷. The mutual information is

$$I_{i,j} = s(2)_{i,j} - s(1)_i - s(1)_j, \quad (\text{S3})$$

where

$$s(2)_{i,j} = - \sum_{\mu=1}^{16} w_{\mu,i,j} \ln w_{\mu,i,j} \quad (\text{S4})$$

is the two-orbital entropy between i and j with $w_{\mu,i,j}$ as the eigen values of two-orbital RDM $\rho_{i,j}^{(2)}$. Note that $\rho_{i,j}^{(2)}$ requires some diagonal elements of the 3- and 4-particle RDM, as well as a few off-diagonal elements of the 1-, 2-, and 3-particle RDM.

In Fig. S2, the single orbital entanglement entropy and mutual information for IL-NdNiO₂ and IL-CaCuO₂ computed in symmetry adapted localized orbital basis are shown. Comparing the entropy information with that computed in CASSCF natural orbital basis shown in Fig. S3 and S4, one can clearly see that the entanglement entropy encoded in the wavefunction represented in the more compact natural orbital basis is minimized. The total entanglement entropy I encoded in the wavefunction in localized orbital basis is 9.8 for IL-NdNiO₂ and 8.5 for IL-CaCuO₂. Where as for the wavefunction represented in the natural orbital basis it is 4.2 for IL-NdNiO₂ and 3.6 for IL-CaCuO₂. Interestingly the mutual entropy information computed in localized orbital basis also gives information about the orbital rotations during the CASSCF orbital optimization. For example, it can be clearly see that in the CASSCF procedure the Ni (Cu) 3s and 4s orbitals are strongly mixed, and more so in IL-NdNiO₂.

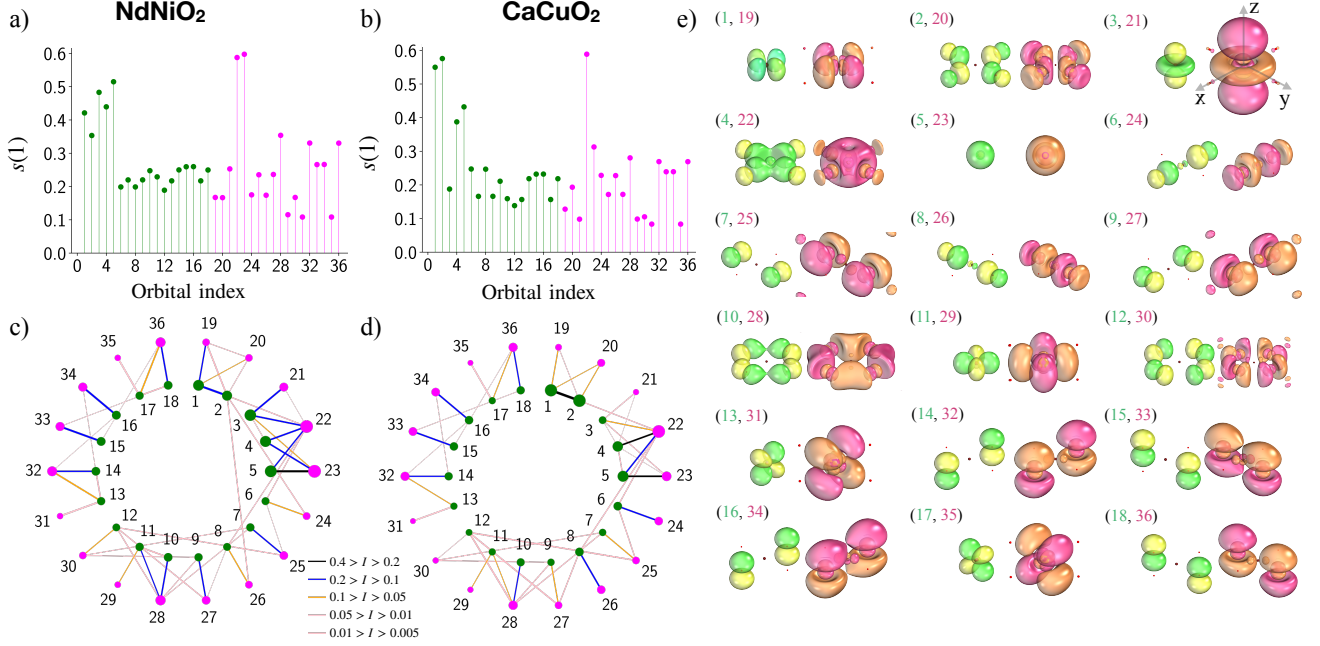


FIG. S2. (a) and (b) Single-orbital entropy, $s(1)_i$, (c) and (d) Mutual orbital information, $I_{i,j}$, from CAS(35,36)SCF calculation for IL-NdNiO₂ and IL-CaCuO₂, respectively, in **Symmetry-adapted (D_{2h}) localized orbital** basis. (e) Symmetry-adapted localized orbitals of IL-NdNiO₂ and their indices. The symmetry-adapted localized orbitals of IL-CaCuO₂ (not shown) look very similar. In (a) and (b) the green and magenta colors represent the two different type of orbitals, occupied and the corresponding double-shell (virtual), respectively. The thickness of the black, blue, purple and pink lines in (c) and (d) denote the strength of $I_{i,j}$, and the size of the dots is proportional to $s(1)_i$.

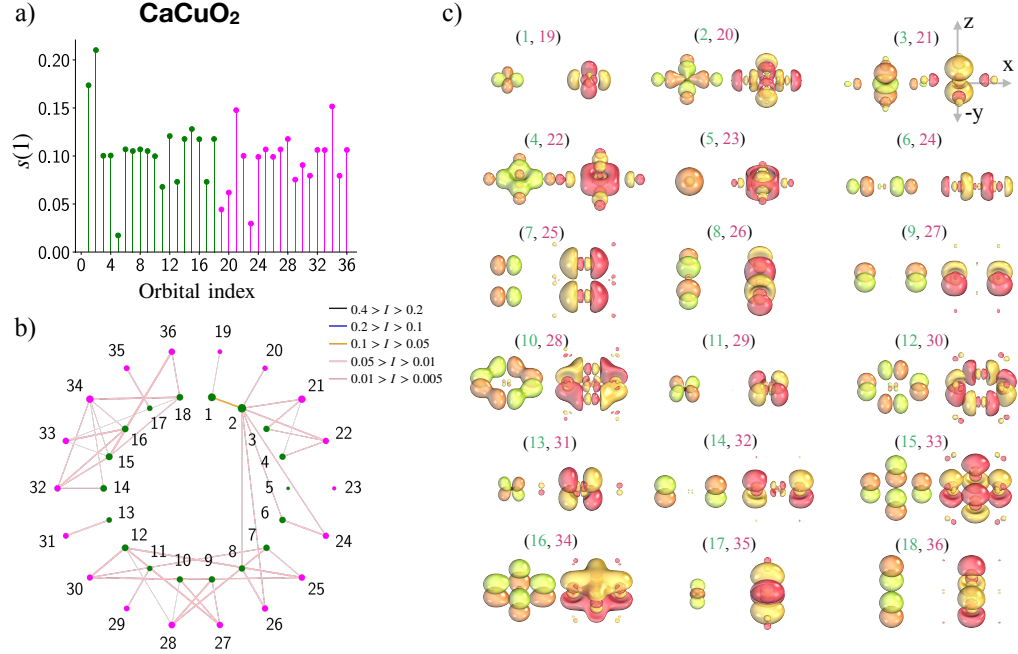


FIG. S3. (a) Single-orbital entropy, $s(1)_i$, (b) Mutual orbital information, $I_{i,j}$, from CAS(35,36)SCF calculation for IL-CaCuO₂. (c) **CASSCF natural orbitals**. In (a) and (b) the green and magenta colors represent the two different type of orbitals, occupied and the corresponding double-shell (virtual), respectively. The thickness of the black, blue, purple and pink lines in (b) denote the strength of $I_{i,j}$, and the size of the dots is proportional to $s(1)_i$.

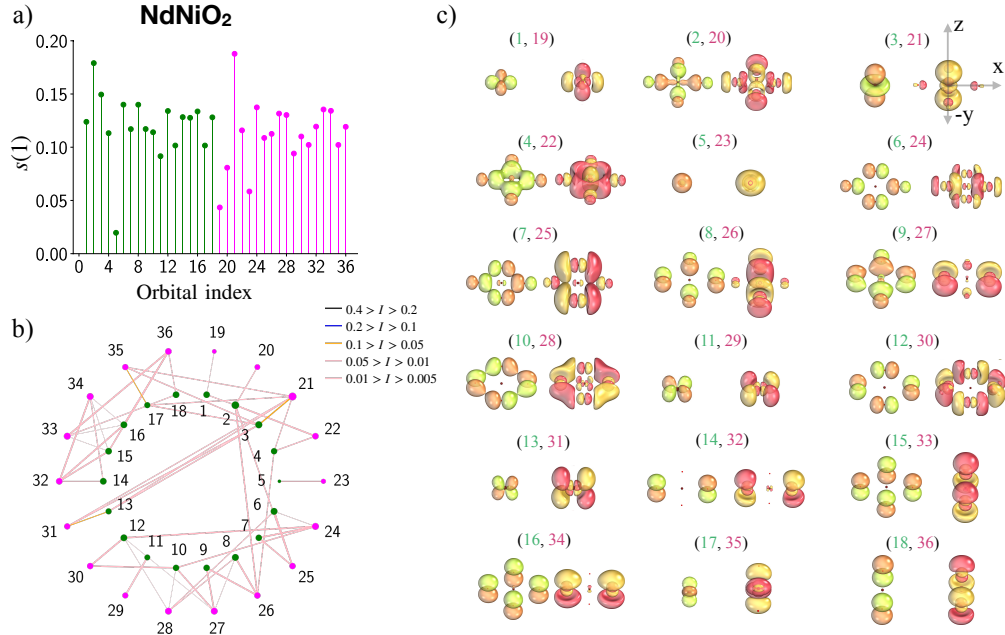


FIG. S4. (a) Single-orbital entropy, $s(1)_i$, (b) Mutual orbital information, $I_{i,j}$, from CAS(35,36)SCF calculation for IL-NdNiO₂. (c) **CASSCF natural orbitals**. In (a) and (b) the green and magenta colors represent the two different type of orbitals, occupied and the corresponding double-shell (virtual), respectively. The thickness of the black, blue, purple and pink lines in (b) denote the strength of $I_{i,j}$, and the size of the dots is proportional to $s(1)_i$.

D. Exchange interactions

For estimating the exchange coupling, we used clusters that include two NiO_4 (CuO_4) units, six neighboring Ni^{1+} (Cu^{2+}) ions and all adjacent Nd^{3+} (Ca^{2+}) ions. The rest of the solid was modeled by an array of point charges fitted to reproduce the Madelung potential in the cluster region. The value of the NN exchange coupling parameter is extracted by mapping the energy spectrum of the two-magnetic-site cluster onto two-site Heisenberg model. To make this mapping straight-forward, the neighboring Ni^{1+} (Cu^{2+}) ions are represented by total-ion potentials with no associated electrons, such that exchange coupling parameter J can be extracted as the energy difference of lowest triplet and singlet states. We use all electron cc-pVTZ and cc-pVQZ basis sets for central Ni (Cu) and bridging O ion^{18,19}, while the other oxygens are represented with cc-pVDZ basis sets¹⁹. Large-core effective potentials were employed for other species as in the case of single Ni (Cu) site calculations.

E. Wavefunction methods

1. CASSCF

The complete active space self-consistent field (CASSCF) method²⁰ is a specific type of multiconfiguration (MC) self-consistent field technique in which the number of determinants or configuration state functions (CSFs) used in the expansion of the configuration interaction (CI) wavefunction are defined in a constrained orbital space. This is achieved by dividing the orbitals in a given system into three subspaces. In the first subspace, termed as inactive space, all orbitals are doubly occupied. The second subspace is known as the active space, and within this orbital space, a full-CI expansion is considered. The electrons and orbitals included in the active space are those that contribute most to the multireference character of the particular system of study. The occupation number of the orbitals in the active space will be a noninteger number between 0 and 2. Finally, the third subspace, known as the virtual space, consists of orbitals that are kept unoccupied. This method guarantees a qualitatively correct wavefunction for strongly correlated systems where static correlation²⁰ effects are taken into account. A single reference wavefunction based methods fail completely in this situation. CASSCF decreases the number of determinants or CSFs in the CI expansion of the wavefunction since it limits the MC wave function within a specific subset of electrons and orbitals rather than on all electrons in all orbitals as one would do in a full CI method. CASSCF method requires a priori knowledge of the system under investigation, i.e. a proper choice of the active orbitals and hence certain level of experience is required from the user. Since the CI expansion increases exponentially with respect to the number of electrons and orbitals, a limitation of CASSCF is that the number of electrons and orbitals that can be included in the active space. It should be noted that in the CASSCF method the orbital coefficients of all the orbitals are optimized variationally just like in the HF theory but based on minimization of the total energy constructed from the multireference CI wavefunction within the active space. The current limitations of the conventional CASSCF implementations (based on deterministic CI solvers) are 18 active electrons in 18 orbitals. Finally, it should be noted that the CAS concept is not the only approach for constructing the configuration space, but it is by far the most successful and widely applicable scheme.

In the last decade, there has been a steady development of several new and efficient algorithms for solving the CI problem (CI solvers). The full configuration interaction quantum Monte Carlo (FCIQMC)¹⁴ method and density matrix renormalization group theory²¹ algorithms are a few of them that allow CASSCF calculations with active spaces up to 40 electrons in 40 orbitals.

FCIQMC: is a stochastic method to compute the ground-state energy of extremely large many-body Hamiltonians in the context of FCI methods, i.e., electronic wave functions expanded in Slater determinant or CSF (Hilbert) spaces comprising all possible determinants/CSFs from a given spatial orbital basis. FCIQMC samples the Hilbert space by a number of walkers, whose population dynamics evolves according to a simple set of rules: spawning, death, and annihilation processes. The equation that guides the walkers population dynamics is

$$-\frac{dN_i}{d\tau} = (H_{ii} - S)N_i + \sum_{j \neq i} H_{ij}N_j \quad (\text{S5})$$

where N_i is the number of walkers on the determinant i , τ is the imaginary time, H_{ij} are the Hamiltonian matrix elements in the basis of Slater determinants/CSFs, and S is the shift parameter that controls the total walker number. A long time integration of the imaginary-time Schrödinger equation is performed with the propagator expanded to first order using a discrete time step $\Delta\tau$. In the limit of long imaginary-time propagation, the algorithm converges to the ground-state wave function when sufficient number of walkers are used to sample the Hilbert space. However, the number of walkers usually scales with the size of the Hilbert space itself. The initiator method (i-FCIQMC)¹⁴

makes it possible to get a stable convergence with a lower number of walkers while introducing a bias to the ground state which can get substantial in large systems. In the semistochastic approach¹⁵, where a number of the most populated determinants is selected and the imaginary-time propagation is performed deterministically in this space. This feature dramatically reduces the stochastic noise and is especially beneficial for our purposes of obtaining accurate CI coefficients from the FCIQMC calculation.

DMRG: is a wavefunction ansatz and the algorithm is an efficient variational optimization procedure for this ansatz. Unlike most wavefunctions in quantum chemistry, the DMRG wavefunction, called matrix product state (MPS), is not parameterized by excitations from a reference state. Rather, it is built as an ordered product of local variational objects (site functions) associated with the active orbitals of the system that describe how the orbitals are correlated with each other. The DMRG wavefunction can be written as

$$|\Psi_{\text{MPS}}\rangle = \sum_{|n_1 n_2 \dots n_k\rangle} \mathbf{A}^{n_1} \mathbf{A}^{n_2} \dots \mathbf{A}^{n_k} |n_1 n_2 \dots n_k\rangle \quad (\text{S6})$$

where, each site function $\mathbf{A}^i$ is a set of four matrices $\mathbf{A}^{n_i}$ correspond to four possible occupations of an orbital i , namely n_i in $\{|\square\rangle, |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle\}$. Matrices $\mathbf{A}^{n_i}$ in the middle have size $M \times M$, while the first and the last are $1 \times M$ and $M \times 1$ respectively. Thus the rank M measures the number of variational parameters, and as this rank increases to $4^{k/2}$, the MPS ansatz becomes exact. For an incomplete rank M , site functions are variationally optimized such that the weakest correlations are truncated.

2. MRPT (NEVPT2 and MRLCC)

While the CASSCF calculation provides a qualitatively correct wavefunction, for a quantitative description of a strongly correlated system dynamic correlations²⁰ are also important and must be accounted for. This amounts to adding the contributions to the wavefunction from those configurations related to excitations into virtual orbitals. A natural extension is variational multireference CI (MRCI-SD) approach where the CI wavefunction is expanded with excitations into the virtual orbital space as well. An alternative and computationally less demanding approach, which shares many similarities with MRCI is based on perturbation theory in second- and higher-orders. In multireference perturbation theory (MRPT) MC zeroth-order wave function is employed and excitations to the virtual space are accounted by means of perturbation theory. If the initial choice of the MC wave function is a good enough to capture the large part of the correlation energy, then the perturbation corrections are typically small. The most common variations used in MRPT are the complete active space second-order perturbation theory (CASPT2) and the n -electron valence second-order perturbation theory (NEVPT2) which differ in the type of zeroth-order Hamiltonian H_0 employed. While the CASPT2 uses effective one-electron Fock-type operator as H_0 ²², H_0 in the NEVPT2 includes two-electron operator restricted to the active space, as proposed by Dyal²³. A more recent variant multireference linearized coupled-cluster theory (MRLCC)²⁴ uses Fink's Hamiltonian²⁵ and is highly efficient when large active space reference wavefunctions are used. The latter two methods outperform CASPT2 method as they do not suffer from the intruder state problems associated with CASPT2²².

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