**Ab Initio Wavefunction Analysis of Electron Removal Quasi-Particle State of NdNiO$_2$ With Fully Correlated Quantum Chemical Methods**

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The discovery of superconductivity in hole-doped infinite-layer NdNiO$_2$ — a transition metal (TM) oxide that is both isostructural and isoelectronic to cuprate superconductors—has led to renewed enthusiasm in the hope of understanding the origin of unconventional superconductivity. Here, we investigate the electron-removal states in finite-layered Ni$_{1+}$ oxide, NdNiO$_2$, which mimics hole doping, with the state-of-the-art many-body multireference quantum chemistry methods. From the analysis of the many-body wavefunction we find that the hole-doped $d^8$ ground state of NdNiO$_2$ is very different from the $d^8$ ground state in isostructural cuprate analog CaCuO$_2$, although the parent $d^9$ ground states are for the most part identical. We show that the doped hole in NdNiO$_2$ mainly localizes on the Ni $3d_{x^2−y^2}$ orbital to form a closed-shell singlet, and this singlet configuration contributes to ~40% of the wavefunction. In contrast, in CaCuO$_2$, the Zhang-Rice singlet configurations contribute to ~65% of the wavefunction. With the help of the quantum information concept of entanglement entropy, we quantify the different types of electronic correlations in the nickelate and cuprate compounds, and find that the dynamic radial-type correlations within the Ni $d$ manifold are persistent in hole-doped NdNiO$_2$. As a result, the $d^8$ multiplet effects are stronger and the additional hole foot-print is more three-dimensional in NdNiO$_2$. Our analysis shows that the most commonly used three-band Hubbard model employed to express the doped scenario in cuprates represents ~90% of the $d^8$ wavefunction for CaCuO$_2$, but such a model grossly approximates the $d^8$ wavefunction for NdNiO$_2$ as it only stands for ~60% of the wavefunction.

**Keywords:** nickelates, superconductors, wavefunction quantum chemistry, doped-holes, ab initio

1 **INTRODUCTION**

For more than 3 decades, understanding the mechanism of superconductivity observed at high critical temperature (HTC) in strongly correlated cuprates [1] has been the “holy grail” of many theoretical and experimental condensed matter researchers. In this context, the observation of superconductivity in nickelates $LnNiO_2$, $Ln = \{La, Nd and Pr\}$ [2–4] upon doping with holes is
remarkable. These superconducting nickelates are isostructural as well as isoelectronic to HTC cuprate superconductors and thus enable the comparison of the essential physical features that may be playing a crucial role in the mechanism driving superconductivity.

LnNiO$_2$ family of compounds are synthesized in the so-called infinite-layer structure, where NiO$_2$ and Ln layers are stacked alternatively [2]. The NiO$_2$ planes are identical to the CuO$_2$ planes in HTC cuprates which host much of the physics leading to superconductivity [5]. A simple valence counting of the three nickelates reveals a $1+$ oxidation state for Ni (2- for O and 3+ for Ln) with nine electrons in the 3$d$ manifold. In the cuprates, the Cu$^{2+}$ oxidation state gives rise to the same 3$d^9$ electronic configuration. Contrary to many nickel oxides where the Ni atom sits in an octahedral cage of oxygens, in the infinite-layered structure, square planar NiO$_2$ plaques are formed without the apical oxygens. The crystal field due to square-planar oxygen coordination stabilizes the $d_{x^2-y^2}$ orbital of the $e_g$ manifold, making its energy close to the $t_{2g}$ orbitals (the 3$d$ orbitals split to 3-fold $t_{2g}$ and 2-fold $e_g$ sub-shells in an octahedral environment). With $d^9$ occupation, a half-filled $d_{x^2-y^2}$-orbital system is realized as in cuprates. In fact, recent resonant inelastic X-ray scattering (RIXS) experiments [6] as well as the ab initio correlated multiplet calculations [7] confirm that the Ni$^{1+}$ $d$-$d$ excitations in NdNiO$_2$ are similar to the Cu$^{2+}$ ions in cuprates [8].

Several electronic structure calculations based on density-functional theory (DFT) have shown that in monovalent nickelates the Ni 3$d_{x^2-y^2}$ states sit at the Fermi energy level [9–11]. These calculations further show that the nickelates are more close to the Mott-Hubbard insulating limit with a decreased Ni 3$d$-O 2$p$ hybridization compared to cuprates. The latter are considered to be charge transfer insulators [12] where excitations across the electronic band gap involves O 2$p$ to Cu 3$d$ electron transfer. Correlated wavefunction-based calculations [7] indeed find that the contribution from the O 2$p$ hole configuration to the ground state wavefunction in NdNiO$_2$ is four times smaller than in the cuprate analogue CaCuO$_2$. X-ray absorption and photoemission spectroscopy experiments [13, 14] confirm the Mott behavior of nickelates.

In the cuprate charge-transfer insulators, the strong hybridization of the Cu 3$d_{x^2-y^2}$ and O 2$p$ orbitals result in O 2$p$ dominated bonding and Cu 3$d_{x^2-y^2}$-like antibonding orbitals. As a consequence, the doped holes primarily reside on the bonding O 2$p$ orbitals, making them singly occupied. The unpaired electrons on the Cu 3$d_{x^2-y^2}$ and the O 2$p$ are coupled antiferromagnetically resulting in the famous Zhang-Rice (ZR) spin singlet state [15]. In the monovalent nickelates, it is unclear where the doped-holes reside. Do they form a ZR singlet as in cuprates? Instead, if the holes reside on the Ni site, do they form a high-spin local triplet with two singly occupied Ni 3$d$ orbitals and aligned ferromagnetically or a low-spin singlet with either both the holes residing in the Ni 3$d_{x^2-y^2}$ orbital or two singly occupied Ni 3$d$ orbitals but aligned anti-parallel. While Ni L-edge XAS and RIXS measurements [6] conclude that an orbitally polarized singlet state is predominant, where doped holes reside on the Ni 3$d_{x^2-y^2}$ orbital, O K-edge electron energy loss spectroscopy [14] reveal that some of the holes also reside on the O 2$p$ orbitals.

On the other hand, calculations based on multi-band $d$–$p$ Hubbard models show that the fate of the doped holes is determined by a subtle interplay of Ni onsite ($U_{dd}$), Ni $d$–O 2$p$ inter-site ($U_{dp}$) Coulomb interactions and the Hund’s coupling along with the charge-transfer gap [16, 17]. However, with the lack of extensive experimental data, it is difficult to identify the appropriate interaction parameters for a model Hamiltonian study, let alone identifying the model that best describes the physics of superconducting nickelates.

Despite the efforts to discern the similarities and differences between the monovalent nickelates and superconducting cuprates, there is no clear understanding on the nature of doped holes in NdNiO$_2$. Particularly, there is no reliable parameter-free ab initio analysis of the hole-doped situation. In this work, we investigate the hole-doped ground state in NdNiO$_2$ and draw parallels to the hole-doped ground state of cuprate analogue CaCuO$_2$. We use fully ab initio many-body wavefunction-based quantum chemistry methodology to compute the ground state wavefunctions for the hole-doped NdNiO$_2$ and CaCuO$_2$. We find that the doped hole in NdNiO$_2$ mainly localizes on the Ni 3$d_{x^2-y^2}$ orbital to form a closed-shell singlet, and this singlet configuration contributes to ~40% of the wavefunction. In contrast, in CaCuO$_2$ the Zhang-Rice singlet configurations contribute to ~65% of the wavefunction. The persistent dynamic radial-type correlations within the Ni $d$ manifold result in stronger $d^9$ multiplet effects than in CaCuO$_2$, and consequently the additional hole foot-print is more three-dimensional in NdNiO$_2$. Our analysis shows that the most commonly used three-band Hubbard model to express the doped scenario in cuprates represents 90% of the $d^8$ wavefunction for CaCuO$_2$, but such a model grossly approximates the $d^8$ wavefunction for the NdNiO$_2$ as it only stands for ~60% of the wavefunction.

In what follows, we first describe the computational methodology we use in this work where we highlight the novel features of the methods and provide all the computational details. We then present the results of our calculations and conclude with a discussion.

2 THE WAVEFUNCTION QUANTUM CHEMISTRY METHOD

Ab initio configuration interaction (CI) wavefunction-based quantum chemistry methods, particularly the post Hartree-Fock (HF) complete active space self-consistent field (CASSCF) and the multireference perturbation theory (MRPT), are employed. These methods not only facilitate systematic inclusion of electron correlations, but also enable to quantify different types of correlations, static vs. dynamic [18]. These calculations do not use any ad hoc parameters to incorporate electron-electron interactions unlike other many-body methods, instead, they are computed fully ab initio from the kinetic and Coulomb integrals. Such ab initio calculations provide techniques to systematically analyze electron correlation effects and offer insights into the electronic structure of correlated solids that go substantially beyond standard DFT approaches,
e.g., see Refs. [7, 19–22] for the 3d TM oxides and Refs. [23–27] for 5d compounds.

### 2.1 Embedded Cluster Approach

Since strong electronic correlations are short-ranged in nature [28], a local approach for the calculation of the $N$ and $N \pm 1$ -electron wavefunction is a very attractive option for transition metal compounds. In the embedded cluster approach, a finite set of atoms, we call quantum cluster (QC), is cut out from the infinite solid and many-body quantum chemistry methods are used to calculate the electronic structure of the atoms within the QC. The cluster is “embedded” in a potential that accounts for the part of the crystal that is not treated explicitly. In this work, we represent the embedding potential with an array of point charges (PCs) at the lattice positions that are fitted to reproduce the Madelung crystal field in the cluster region [29]. Such procedure enables the use of quantum chemistry calculations for solids involving transition-metal or lanthanide ions, see Refs. [23, 30, 31].

### 2.2 Complete Active Space Self-Consistent Field

CASSCF method [18] is a specific type of multi-configurational (MC) self-consistent field technique in which a complete set of Slater determinants or configuration state functions (CSFs) that is used in the expansion of the CI wavefunction is defined in a constrained orbital space, called the active space. In the CASSCF(n,m) approach, a subset of $n$ active electrons are fully correlated among an active set of $m$ orbitals, leading to a highly multi-configurational (CAS) reference wavefunction. CASSCF method with a properly chosen active space guarantees a qualitatively correct wavefunction for strongly correlated systems where static correlation [18] effects are taken into account.

We consider active spaces as large as CAS(24,30) in this work. Because the conventional CASSCF implementations based on deterministic CI space (the Hilbert space of all possible configurations within the active space) solvers are limited to active spaces of 18 active electrons in 18 orbitals, we use the full configuration interaction quantum Monte Carlo (FCIQMC) [32–34] and density matrix renormalization group (DMRG) theory [35, 36] algorithms to solve the eigenvalue problem defined within the active space.

### 2.3 Multireference Perturbation Theory

While the CASSCF calculation provides a qualitatively correct wavefunction, for a quantitative description of a strongly correlated system, dynamic correlations [18] (contributions to the wavefunction from those configurations related to excitations from inactive to active and virtual, and active to virtual orbitals) are also important and must be accounted for. A natural choice is variational multireference CI (MRCI) approach where the CI wavefunction is extended with excitations involving orbitals that are doubly occupied and empty in the reference CASSCF wavefunction [18]. An alternative and computationally less demanding approach to take into account the dynamic correlations is based on perturbation theory in second- and higher-orders. In multireference perturbation theory (MRPT) MC zeroth-order wavefunction is employed and excitations to the virtual space are accounted by means of perturbation theory. If the initial choice of the MC wavefunction is good enough to capture the large part of the correlation energy, then the perturbation corrections are typically small. The most common variations of MRPT are the complete active space second-order perturbation theory (CASPT2) [37] and the n-electron valence second-order perturbation theory (NEVPT2) [38] which differ in the type of zeroth-order Hamiltonian $H_0$ employed.

### 3 THE AB INITIO MODEL

Before we describe the ab initio model we consider, let us summarize the widely used and prominent model Hamiltonian to study the nature of doped hole in HTC cuprates and also employed for monovalent nickelates lately. It is the three-band Hubbard model [39] with three orbital degrees of freedom (bands) which include the $d$ orbital of Cu with $x^2-y^2$ symmetry and the in-plane oxygen $p$ orbitals aligned in the direction of the nearest Cu neighbours. These belong to the $b_1$ irreducible representation (irrep) of the $D_{4d}$ point group symmetry realized at the Cu site of the CuO$_4$ plaque, the other Cu $d$ orbitals belong to $a_1$ ($d_{xz, yz}$), $b_2$ ($d_{xy}$) and $e$ ($d_{x^2,y^2}$) irreps. The parameters in this Hamiltonian include the most relevant hopping and Coulomb interactions within this set of orbitals. More recently, the role of the Cu 3d multiplet structure on the hole-doped ground state is also studied [40]. While this model explains certain experimental observations, there is still a huge debate on what is the minimum model to describe the low-energy physics of doped cuprates. Nevertheless, this model has also been employed to investigate the character of the doped hole in monovalent nickelates [16, 17, 41].

Within the embedded cluster approach described earlier, we consider a QC of five NiO$_4$ (CuO$_4$) plaques that includes five Ni (Cu) atoms, 16 oxygens and 8 Nd (Ca) atoms, see Figure 1. The 10 Ni (Cu) ions neighbouring to the cluster are also included in the QC, however, these are considered as total ion potentials (TIPs). The QC is embedded in point charges that reproduce the electrostatic field of the solid environment. We used the crystal structure parameters for the thin film samples reported in Refs. [2, 42–44].

We used effective core potentials [45] and correlation consistent basis sets of triple-ζ quality with additional

| CAS | NEL | NORB |
|-----|-----|------|
| CAS-1 | 18 | 24 (1–24) |
| CAS-2 | 24 | 30 (1–30) |
| CAS-3$^a$ | 12 | 14 (1, 6, 11, 16 and 21–30) |

$^a$The four neighbouring Ni$^{3+}$ (Cu$^{2+}$) ions in the quantum cluster are treated as closed shell Cu$^{1+}$ (Zn$^{2+}$) ions.
polarization functions—\([4s3p3d1f]\)—for Ni (Cu) \([46]\) and double-\(\zeta\) quality—\([3s2p1d]\)—for oxygens \([47]\). For the eight Nd (Ca) atoms large core effective potentials \([48–50]\) and associated \([3s2p2d]\) basis functions were used. In the case of Nd, the \(f\)-electrons were incorporated in the core. Cu\(^{1+}\) (Zn\(^{2+}\)) total ion potentials (TIPs) with \([2s1p]\) functions were used for the 10 Ni\(^{1+}\) (Cu\(^{2+}\)) \([51, 52]\) peripheral ions of the QC.

To investigate the role of different interactions in the \(d^8\) ground state, two different active spaces were considered. In the first active space, CAS-1 in Table 1, only the orbitals in the \(b_1\) and \(a_1\) irreps are active. These are \(d_{x^2-y^2}\) and \(d_{z^2}\)-like orbitals respectively, and the corresponding double-shell 4\(d\) orbitals of each of the five Ni (Cu) atoms. CAS-1 also contains the symmetry-adapted ZR-like composite O 2\(p\) and the double-
shell 3p-like orbitals, numbers 1–20 and 21–24 in Figure 2. At the mean-field HF level of theory, there are 16 electrons within this set of orbitals, resulting in CAS(16,22) active space. In the second active space, CAS-2, orbitals of b$_2$ and the e irreps from the central Ni (Cu) d manifold are also included. These are the 3$d_{xy}$, 3$d_{x^2-y^2}$-like orbitals and the corresponding 4$d$ orbitals and the six electrons, numbers 25–30 in Figure 2, resulting in a CAS(24,30) active space. The latter active space takes into account the $d^8$ multiplet effects within the 3d manifold explicitly.

The two active spaces considered in this work not only describe all the physical effects included in the above mentioned three-band Hubbard model but go beyond. More importantly, we do not have any ad-hoc input parameters for the calculation as all the physical interactions are implicitly included in the ab initio Hamiltonian describing the actual scenario in the real materials. We employed openmolcas [53] quantum chemistry package for all the calculations.

### 4 RESULTS

#### 4.1 Ground State of the $d^8$ Configuration

Starting from the electronic structure of the parent compounds, where each Ni (Cu) is in the $d^8$ configuration, we compute the electron-removal (in the photoemission terminology) $d^7$ state to investigate the hole-doped quasiparticle state. Since the parent compounds in $d^8$ configuration have strong nearest neighbour antiferromagnetic (AF) correlations [7], the total spin of our QC in undoped case, with five Ni (Cu) sites, in the AF ground state is $S_{QC} = 3/2$. By introducing an additional hole (or removing an electron) from the central Ni (Cu) in our QC, the $S_{QC}$ values range from 0 to 3. To simplify the analysis of the distribution of the additional hole, we keep the spins on the four neighbouring Ni (Cu) sites parallelly aligned in all our calculations and from now on we only specify the spin multiplicity of the central Ni (Cu)O$_4$ plaque. The multiplet structure of the $d^7$ configuration thus consists of only spin singlet and triplet states, spanned by the four irreps of the 3d manifold. The active spaces we consider in this work allow us to compute accurately the excitations only within the $b_1$ and $a_1$ irreps [55] and we address the full multiplet structure elsewhere.

When computing the local excitations, a local singlet state on the central Ni (Cu) corresponds to a total spin on the cluster $S_{QC} = 2$. However, a local triplet state, with central spin aligned parallel to the neighboring spins, corresponds to $S_{QC} = 3$ and do not satisfy the AF correlations. To avoid the spin coupling between the central $d^8$ Ni (Cu) with the neighbouring $d^7$ Ni (Cu) ions, we replace the latter with closed shell, Cu (Zn) $d^{10}$, ions and freeze them at the mean-field HF level. Such a simplification is justified, as the local excitation energy we compute is an order of magnitude larger than the exchange interaction [7].

In Table 2, the relative energies of the lowest local spin singlets $^1A_{1g}$, $^1B_{1g}$ and spin triplet $^3B_{1g}$ states are shown. These are obtained from CASSCF + CASPT2 calculations with CAS(12,14) active space (CAS-3 in Table 1) which includes the 3d and 4d orbitals of the central Ni (Cu) ion and the in-plane O 2p and 3p orbitals in the $b_1$ irrep. In the CASPT2 calculation, the remaining doubly occupied O 2p, the central Ni (Cu) 3s and 3p orbitals and all the unoccupied virtual orbitals are correlated.

It can be seen that the ground state is of $^1A_{1g}$ symmetry and the lowest triplet excited state, with $^3B_{1g}$ symmetry, is around 1.88 and 2.5 eV for NdNiO$_2$ and CaCuO$_2$ respectively. The AF magnetic exchange in these two compounds is 76 and 208 meV respectively [7], and thus we expect that our simplification of making the neighbouring $d^7$ ions closed shell do not over/underestimate the excitation energies. At the CASSCF level, the $^1A_{1g}$-$^3B_{1g}$ excitation energy is 1.35 eV in NdNiO$_2$ while it is 2.26 eV in CaCuO$_2$. Interestingly, the inclusion of dynamical correlations via the CASPT2 calculation, the $^1A_{1g}$ in NdNiO$_2$ is stabilized by 0.53 eV compared to $^3B_{1g}$ state. However, in CaCuO$_2$, the $^1A_{1g}$ state is stabilized by only 0.24 eV. This indicates that the dynamical correlations are more active in the $^1A_{1g}$ state in NdNiO$_2$ than in CaCuO$_2$. We note that the hole excitations within the 3d orbitals in the irreps $b_2$ and $e$, calculated with this limited active space (CAS-3) results in energies lower than the $^3B_{1g}$ and $^1B_{1g}$ states. However, an accurate description of those states requires an enlarged active space that includes not only the same symmetry oxygen 2p and 3p orbitals from the central NiO$_4$ plaque but also the 3d, 4d manifold of the neighbouring Ni (Cu) ions, making the active space prohibitively large. Here, we concentrate on the analysis of the $^1A_{1g}$ ground state and address the complete $d^8$ multiplet spectrum elsewhere.

#### 4.2 Wavefunction of the $d^8$ Ground State

The $^1A_{1g}$ ground wavefunction in terms of the weights of the four leading Slater determinants (SD) (in the case of CaCuO$_2$) is
shown in Table 3. The wavefunctions corresponding to the CASSCF calculations with the active spaces CAS-1 and CAS-2 are shown. The basis in which the wavefunctions are represented is constructed in two steps: 1) A set of natural orbitals are generated by diagonalising the CASSCF one-body reduced density matrix. 2) To obtain a set of atomic-like symmetry-generated by diagonalising the CASSCF one-body reduced is constructed in two steps: 1) A set of natural orbitals are shown. The basis in which the wavefunctions are represented are visualy very close to the actual basis. The doubly occupied orbitals are shown as $\uparrow\uparrow$, the singly occupied ones with $\uparrow\downarrow$ for spin $\uparrow$ ($\downarrow$) and an empty box implies that the orbital is unoccupied. The red (electrons removed) and green (electrons added) colors indicate the orbitals involved in the excitation starting from the first configuration. The red box indicates that the orbital becomes empty in this particular excited configuration.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | Wt. (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ↓ | ↓ | ↓ | ↓ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 42.4 |
| 2 | ↓ | ↓ | ↓ | ↓ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 10.48 |
| 3 | ↑ | ↓ | ↓ | ↓ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 7.6 |
| 4 | ↓ | ↓ | ↓ | ↓ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 2.45 |
| 5 | ↓ | ↓ | ↓ | ↓ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 2.38 |
| 6 | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 0.61 |
| 7 | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 0.6 |
| 8 | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 0.48 |
| 9 | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 0.48 |
| 10 | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | ↑ | 0.23 |

We note that the four configurations shown in Table 3 encompass almost 90% of the $d^8$ wavefunction (with CAS-2 active space) in CaCuO$_2$. Thus, the use of a three-band Hubbard model [39, 40] to investigate the role of doped holes in CuO$_2$ planes is a reasonable choice. However, for NdNiO$_2$ these configurations cover only 60% of the $d^8$ wavefunction, hence a three-band Hubbard model is too simple to describe the hole-doped monovalent nickelates.

In Table 4 and Table 5, we show the first ten dominant SD configurations by weight in the $d^8$ wavefunction of NdNiO$_2$ and CaCuO$_2$ respectively. Interestingly, the configurations with two holes in the out-of-plane $d$-orbitals $d_{x^2-y^2}$ (configuration 6) and $d_{xz/yz}$ (9 and 10 configurations) is significant in NdNiO$_2$, while such configurations do not exist in the dominant ten for CaCuO$_2$. We also find the additional hole to be more delocalized on to the neighboring Ni ions in NdNiO$_2$ than it is in CaCuO$_2$, however, this observation should be taken with precaution as the oxygen environment around the neighboring Ni/Cu ions is only described at the mean-field level in our calculation setup.

A more intuitive and visual understanding of the distribution of the additional hole can be obtained by plotting the difference of the $d^8$ and the $d^9$ ground state electron densities as shown in Figure 3. Electron density of a multi-configurational state can be computed as a sum of densities arising from the natural orbitals and corresponding (well-defined) occupation numbers. We used Multiwfn program [56] to perform this summation. The negative values of the heat map of the electron density difference (blue color) and the positive values (in red) represent respectively the extra hole density and additional electron density in $d^9$ state compared to the $d^8$ state. From Figure 3A/Figure 3C that show the density difference in the NiO$_2$/CuO$_2$ planes (xy-plane), we conclude the following:

1. The hole density is concentrated on the Ni site (darker blue) with $b_1$ ($d_{x^2-y^2}$) symmetry in NdNiO$_2$ whereas it is distributed evenly on the four oxygen and the central Cu ions with $b_1$ symmetry in CaCuO$_2$, a result consistent with the wavefunction reported in Table 3.
2. In NdNiO$_2$, the hole density is spread out around the Ni ion with larger radius, and otherwise in CaCuO$_2$. This demonstrates that the 3$d$ manifold in Cu is much more localized than in Ni and therefore the onsite Coulomb repulsion $U$ is comparatively smaller for Ni.

3. The darker red regions around the Ni site in NdNiO$_2$ indicate stronger $d^8$ multiplet effects that result in rearrangement of electron density compared to $d^9$ configuration.

4. In CaCuO$_2$, we see darker red regions on the oxygen ions instead, which shows that the significant presence of a hole on these ions results in noticeable electron redistribution.

The electron density difference in the xz-plane (which is perpendicular to the NiO$_2$/CuO$_2$ planes) is quite different in the two compounds. The hole density in NdNiO$_2$ is spread out up to 2 Å in the z-direction, unlike in CaCuO$_2$, where it is confined to within 1 Å. We attribute this to the strong radial-type correlations in NdNiO$_2$. With the creation of additional hole on the 3$d_{z^2}$ orbital, the electron density which is spread out in the $d_{x^2}$ symmetry via the dynamical correlation between 3$d_{x^2}$ and 4$d_{x^2}$ orbitals [7], becomes more compact in the $d_{z^2}$ symmetry through the reverse breathing. Thus, we see a strong red region with 3$d_{z^2}$ profile and a blue region with expanded 4$d_{z^2}$ profile.

To obtain a quantitative understanding of the charge density differences for the two compounds, in Figure 3E we plot the electron density difference integrated over a sphere centered on the central Ni(Cu) atom as a function of the radius $r$ shown in Figure 3A. Four features, which we marked A-D, clearly demonstrate the contrast in the charge density differences in the two compounds. From the feature A at $r$ close to Ni (Cu), it is evident that the extent of hole density around Ni in NdNiO$_2$ is larger than around Cu in CaCuO$_2$. The features B and C that are on either side of the position of oxygen ions show that the hole density is significantly larger on oxygen atoms in CaCuO$_2$ than in NdNiO$_2$. It is interesting to note that we see a jump (feature D) in the electron density above zero at $r$ close to the position of Nd ions in NdNiO$_2$, while in CaCuO$_2$ the curve is flat in the region of Ca ions. This shows that there is some electron redistribution happening around the Nd ions. The hole density within a solid sphere (SS) around the central Ni (Cu) atom obtained by additional integration over the radius $r$ is also shown in Figure 3E with dashed curves. It can be seen that the total hole density within the SS of $r$ ~4 Å, where the neighboring Ni (Cu) ions are located, is only ~0.5 in both the compounds, with slight differences related to the feature D. This is due to the screening of the hole with the electron density pulled in from the farther surroundings. As one would expect, a SS with $r$ of the size of the cluster, the total hole density is one in both the compounds.

### 4.3 Orbital Entanglement Entropy

To analyse the different type of correlations active in the two compounds in $d^9$ configuration, we compute the entanglement entropy [57–59]. While the single orbital entropy, $s(1)_i$, quantifies the correlation between $i$th orbital and the remaining set of orbitals, the mutual information, $I_{ij}$, is the two-orbital entropy between $i$ and $j$ [60, 61], and illustrates the correlation of an orbital with another, in the embedded environment comprising of all other orbitals. We used QCMAQUIS [63] embedded in openmolcas [54] package to compute the entropies.

In Figure 4, $s(1)_i$ and $I_{ij}$ extracted from the $d^8$ ground state CASSCF calculations with CAS-2 active space for NdNiO$_2$ and CaCuO$_2$ are shown. The orbital basis for which the entropy is computed is the same as the basis in which the wavefunction presented in Table 3 is expanded. As mentioned previously, this orbital basis is obtained from partial localization of the natural orbitals in a way that only the $3d_{z^2}$ and the O 2$p$ ZR-like orbitals are localized. Since a large part of electron correlation is compressed in natural orbitals, we see a tiny $s(1)_i$ for all orbitals except for the localized $3d_{z^2}$ and the O 2$p$ ZR-like orbitals where it is significant. This is consistent with the wavefunction in Table 3. The mutual orbital entanglement between pairs of orbitals shows strong entanglement between the $3d_{z^2}$ and the O 2$p$ ZR-like orbitals for both NdNiO$_2$ and CaCuO$_2$, a consequence of the dominant weight of the configurations spanned by these two orbitals in the wavefunction. The next strongest entanglement is between the Ni/Cu 3$d$ valence and their double-shell 4$d$ orbitals. Such strong entanglement also

### Table 5: Dominant ten SD configurations and their weights (in %) in the $d^9$ wavefunction for CaCuO$_2$. See the caption of Table 4 for details of the wavefunction representation.

|        |        |        |        |        |        |        |        |        |        |         |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|----------|
| 1      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | 1.0      |
| 2      | ↑      | ↑      | ↑      | ↑      | ↑      | ↑      | ↑      | ↑      | ↑      | 1.27     |
| 3      | □      | □      | □      | □      | □      | □      | □      | □      | □      | 0.24     |
| 4      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | 0.23     |
| 5      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | 0.13     |
| 6      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | 0.12     |
| 7      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | 0.10     |
| 8      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | 0.07     |
| 9      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | 0.06     |
| 10     | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | ↓      | 0.05     |
observed for the undoped $d^9$ ground state [7], is a result of dynamical radial correlation [18] and orbital breathing effects [63, 64]. Interestingly, the entanglement entropy in the range 0.001–0.01 (green lines) is quite similar in the two compounds, although one sees more entanglement connections in NdNiO$_2$. A comparison of the entropy information between NdNiO$_2$ and CaCuO$_2$ reveals that the Ni 3$d$ and 4$d$-like orbitals contribute rather significantly (thicker blue lines) to the total entropy, in contrast to the Cu 3$d$ and 4$d$-like orbitals, something that is also seen in the undoped compounds [7].

5 CONCLUSION AND DISCUSSION

In conclusion, our ab initio many-body quantum chemistry calculations for the electron removal ($d^8$) states find a low-spin closed-shell singlet ground state in NdNiO$_2$ and that the additional hole is mainly localized on the Ni 3$d_{x^2−y^2}$ orbital, unlike in CaCuO$_2$, where a Zhang-Rice singlet is predominant. We emphasise that the $d^8$ wavefunction is highly multi-configurational where the dominant closed-shell singlet configuration weight is only ~42%. This result is consistent with the experimental evidence [6, 14] of
orbitally polarized singlet state as well as the presence of holes on the O 2p orbitals. Importantly, the persistent dynamic radial-type correlations within the Ni d manifold result in stronger d8 multiplet effects in NdNiO2, and consequently the additional hole foot-print is more three dimensional. In CaCuO2, we find that the electron correlations within the dxy and dxz/yz orbitals changes the hole-doped wavefunction significantly. Specifically, the double hole occupation of Cu dx2−y2 is significantly increased and this can influence the transport properties.

It was recently proposed that nickelates could be a legitimate realization of the single-band Hubbard model [65]. However, our analysis shows that even the three-band Hubbard model [66], which successfully describes the hole-doped scenario in cuprates, falls short to describe hole-doped nickelates and additional orbital degrees of freedom are indeed necessary for the description of the strong multiplet effects we find. Much has been discussed about the importance of rare-earth atoms for the electronic structure of superconducting nickelates, e.g. see [67]. The three-dimensional nature of the hole density we find in NdNiO2 might also be hinting at the importance of out-of-plane Nd ions. It would be interesting to compare the hole density of NdNiO2 with other iso-structural nickelates such as LaNiO2 where La 5d states are far from the Fermi energy. Since the infinite-layered monovalent nickelates are thin films that are grown on substrates, one could ask the question of how the electronic structure of the undoped and doped compounds changes with varying Ni-O bond length. Would this influence the role of electronic correlations in d8 nickelates? We will address these in the near future.

DATA AVAILABILITY STATEMENT

The data supporting the conclusions of this study can be made available upon reasonable request.

AUTHOR CONTRIBUTIONS

VK and AA designed the project. VK and NB performed the calculations. All the authors analysed the data. VK wrote the paper with inputs from NB and AA.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fphy.2022.836784/full#supplementary-material
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