Mott gapping in 3d ABO₃ perovskites without Mott-Hubbard interelectronic U

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Abstract

The existence of band gaps in Mott insulators such as perovskite oxides with partially filled 3d shells has been traditionally explained in terms of strong, dynamic inter-electronic repulsion codified by the on-site repulsion energy U in the Hubbard Hamiltonian. The success of the “DFT+U approach” where an empirical on-site potential term U is added to the exchange-and correlation Density Functional Theory (DFT) raised questions on whether U in DFT+U represents interelectronic correlation in the same way as it does in the Hubbard Hamiltonian, and if empiricism in selecting U can be avoided. Here we illustrate that ab-initio DFT without any U is able to predict gapping trends and structural symmetry breaking (octahedra rotations, Jahn-Teller modes, bond disproportionation) for all ABO₃ 3d perovskites from titanates to nickelates in both spin-ordered and spin disordered paramagnetic phases. We describe the paramagnetic phases as a supercell where individual sites can have different local environments thereby allowing DFT to develop finite moments on different sites as long as the total cell has zero moment. We use a recently developed exchange and correlation functional (“SCAN”) that is sanctioned by the usual single-determinant, mean-field DFT paradigm, but has a more precise rendering of self-interaction cancelation. Our results suggest that strong dynamic electronic correlations are not playing a universal role in gapping of 3d ABO₃ Mott insulators, and opens the way for future applications of DFT for studying a plethora of complexity effects that depend on the existence of gaps, such as doping, defects, and band alignment in ABO₃ oxides.
Transition metal oxide perovskites $\text{ABO}_3$ with a $3d$ transition metal atom substituting the B site exhibit intriguing metal vs insulator characteristics as well as different forms of magnetism across the series both in their high-temperature (HT) spin-disordered paramagnetic (PM) phases and/or in the low-temperature (LT) spin-ordered phases [1]. Some of the compounds are metallic ($\text{CaVO}_3$, $\text{SrVO}_3$ or $\text{LaNiO}_3$ for instance), while others are insulating, such as titanates $\text{RTiO}_3$ ($d^1$), vanadates $\text{RVO}_3$ ($d^2$), manganites $\text{CaMnO}_3$ ($d^3$) and $\text{RMnO}_3$ ($d^4$), ferrites $\text{CaFeO}_3$ ($d^4$) and $\text{RFeO}_3$ ($d^5$), cobaltites $\text{RCO}_3$ ($d^6$), nickelates $\text{RNiO}_3$ ($d^7$) or possibly cuprates $\text{RCuO}_3$ ($d^8$), where R is a rare-earth element or yttrium. Concomitantly with opening of band gap, one observes a variety of systematic symmetry-breaking modes, such as the Jahn-Teller (JT) distortions in $\text{RVO}_3$ [2] or $\text{RMnO}_3$ [3] compounds, propagating either in-phase ($Q_2^+$ mode) or in anti-phase ($Q_2^-$ mode), or the B-O bond disproportionation $B_{oc}$ observed in the insulating phase of $\text{RNiO}_3$ [4] and $\text{CaFeO}_3$ [5] (see sketches in Figure 1). Understanding and controlling such band gaps and the associated lattice distortions and forms of magnetism is central to the ability to dope these oxides, just as is designing specific band offsets in oxide heterojunctions, to the benefit of future oxide electronics. The crucial question here is what minimum theoretical framework is needed to explain and therefore design such gapping-related phenomena.

![Figure 1](https://example.com/figure1.png)

**Figure 1:** Sketches of Jahn-Teller motions (a and b) and bond disproportionation (c) distortions appearing in some $\text{ABO}_3$ materials.

The standard explanation of gapping of these compounds despite the presence of partially filled $d$ shells and the ensuing expected orbital degeneracy is generally formulated in terms of strong inter-electronic repulsions appearing in the celebrated Mott-Hubbard model [6–9]. This leads to a uniform explanation of gapping for all $d$-electron $\text{ABO}_3$ compounds and degrees of spin order or disorder, based on the symmetry-conserving interelectronic repulsion, and ensuing localization. Within this framework, the experimental observations of a variety of
different symmetry-breaking modes, such as those presented in Fig.1, or magnetic moments is not related to the gapping mechanism but can appear afterwards as an additional effect.

Whereas Density Functional Theory (DFT) has been shown to be able to address numerous physical effects in such oxides, including ferroelectricity [10], catalysis [11] and electrical battery voltage [12], its use of single Slater determinant and mean-field treatment of electron-electron interactions has disqualified it, according to numerous literature statements [13–15] for the study such “strongly correlated” oxides, requiring far more computationally costly dynamically correlated methodologies, such as Dynamical Mean Field Theory (DMFT).

However, the DFT calculations in such demonstrations of failure [13–15] often used non-spin polarized description and at times exchange correlation functionals that do not distinguish occupied from unoccupied orbitals (LDA or GGA functionals without U), and generally neglect sublattice displacements. For example, Ref. [14] demonstrated vanishing band gaps in LuNiO$_3$, in contradiction with experiment, and Ref. [15] demonstrated failure to stabilize JT distortions in LaMnO$_3$, again, in contradiction with both experiments and DMFT calculations. Such naïve (N-) DFT calculations, however, do not necessarily represent what proper DFT can do, as demonstrated in recent calculations for the binary 3$d$ oxides MnO, NiO, CoO and FeO [16] or ABO$_3$ materials [17–24]. In these calculations [16,24], the PM phase was represented by specially constructed supercells that has a total zero spin, but unlike the N-DFT implementations, there was no requirement that each transition metal ion have a zero spin. Such polymorphous representation lowered substantially the total energy relative to the N-DFT representations, while producing finite band gaps and local moments in all studied binary and ternary ABO$_3$ compounds, in general accord with experiment. The need for an exchange-correlation functional that distinguishes occupied from unoccupied orbitals was satisfied by using a simplified self-interaction corrected functional in the form of “DFT+U” [25]. The use of “U” created sometimes the false impression that this approach owes its success in explaining gaps to the interelectronic repulsion and localization, just as in the Mott-Hubbard view.

To examine if the explanation of gapping requires an explicit Hubbard U, we have performed DFT calculations on several popular ABO$_3$ perovskite oxides with $d$ fillings from 1
to 8 electrons, using (unlike previous DFT+U calculations of Ref. [24]) the recently developed SCAN meta GGA functional [26], \textit{without Mott-Hubbard interelectronic} U. \textit{We find that DFT without} U \textit{captures the experimentally observed trends in gapping and in key structural symmetry breaking} (JT motions, bond disproportionation), magnetic moments and relative B-d to O-p level position in both LT spin-ordered and HT PM phases. Since the static mean-field treatment of DFT is largely sufficient to produce insulation, our results suggest that whereas ABO$_3$ oxide perovskites may certainly be complicated, they are not necessarily strongly dynamically correlated, and gapping in such specific cases may not sweepingly obey the celebrated Mott-Hubbard explanation of formation of two electron sites.

\textbf{Method}: We have performed DFT [27,28] total energy minimization with respect to lattice parameters and cell-internal atomic positions of different perovskite oxides with $d$ fillings from 1 to 8 electrons. Structure types compared for their total energy included orthorhombic (Pbnm), monoclinic ($P2_1/b$ and $P2_1/n$) and rhombohedral (R-3c), whereas spin configurations examined included ferromagnetic (FM), as well as classical A, C and G-type antiferromagnetic (AFM) orders, and more complex S-type AFM order based on $\uparrow\uparrow\downarrow\downarrow$ spins chains in the (ab)-plane with different stackings along the c axis. The paramagnetic (PM) spin-disordered state has been modelled using the Special Quasirandom structures (SQS) method [29], following references [16,24], which represents a random “alloy” of up and down (collinear) spins with total spin zero, within the 2x2x2 orthorhombic or monoclinic cells (32 ABO$_3$ formula units containing 160 atoms). Convergence with SQS supercell size was tested and found adequate at 160 atoms [24]. All atomic displacements as well as breaking of degeneracies of partially occupies $e_g$ and $t_{2g}$ levels are allowed as long as they reduce the total energy. Amplitudes of the energy-minimizing distortions were determined by performing a symmetry adapted mode analysis [30,31] with a reference structure set to the ideal high symmetry cubic $Pm-3m$ structure of perovskites. The lattice parameter of this hypothetical cubic structure is fixed to the ground state pseudo-cubic lattice parameter.

\textbf{Calculated structural and electronic properties}: Figure 2 summarizes the calculated band gap $\Delta E$ (in eV), magnetic moment $M_{3d}$ (in $\mu_B$) associated with the B cations and amplitudes of distortions (in Å) associated with JT and bond disproportionation motions, all done without Hubbard U, compared with experimental values available in literature. The
calculated energy-minimizing lattice type agrees with experiments with the exception of YVO$_3$ and LaVO$_3$ in the PM phase and CaFeO$_3$ in the AFM phase. In the two vanadates, the strongly entangled spin and orbital degrees of freedom induce small lattice distortions on each octahedra in the PM phase (where each transition metal element experiences a unique potential), thus releasing the symmetry from $P2_1/c$ to $P-1$ [32]. However, the lattice parameters, B-O-B angles and B-O bond lengths are very similar to the respective quantities observed in experimental structures. For CaFeO$_3$, the AFM-S magnetic order that we have used to approximate the experimentally observed AFM spiral [5] (similar to that in RNIo$_3$) breaks the inversion center and induce some small lattice distortions such as polar displacements [33], thus producing a polar $P2_1$ space group instead of a centrosymmetric $P2_1/n$ symmetry.
|         | d filling  | Sym. | Mag.  | Electronic properties | Structural distortions |
|---------|------------|------|-------|-----------------------|------------------------|
|         |            |      |       | Eₖ (eV) | M₃d (µ₀) | Q₂⁺ (Å) | Q₂⁻ (Å) | B₂c (Å) |
| YTiO₃  | t₂g⁰e⁰ | Pbnm | FM    | 0.08  | 0.92 (0.84³) | 0.03  | -            | -        |
|         |           | Pbnm | PM    | 0.33 (1.20³) | 0.84 | 0.02 (0.00³) | -            | -        |
| LaTiO₃ | t₂g⁰e⁰ | Pbnm | AFMG  | 0.05  | 0.67 (0.46³) | 0.06  | -            | -        |
|         |           | Pbnm | PM    | 0.14 (0.20³) | 0.78 | 0.04 (0.04³) | -            | -        |
| YVO₃   | t₂g⁰e⁰ | Pbnm | AFMG  | 0.89  | 1.77 (1.72³) | 0.19 (0.14³) | -            | -        |
|         |           | P-1  | PM    | 0.55 (1.60³) | 1.82 | NA            | NA        | -        |
| LaVO₃  | t₂g⁰e⁰ | Pbnm | AFMG  | 0.78  | 1.78 (1.30³) | 0.00 (0.01³) | 0.09 (0.08³) | -        |
|         |           | P-1  | PM    | 0.36 (1.10³) | 1.80 | NA            | NA        | -        |
| CaMnO₃ | t₂g⁰e⁰ | Pbnm | AFMG  | 0.79  | 2.62 (2.64³) | 0.01  | -            | -        |
|         |           | Pbnm | PM    | 1.46 (ins.) | 2.62 | 0.01 (0.04³) | -            | -        |
| LaMnO₃ | t₂g⁰e¹ | Pbnm | AFMA  | 0.52  | 3.65 (3.70³) | 0.28  | -            | -        |
|         |           | Pbnm | PM    | 0.30 (0.24³-1.70³) | 3.60 | 0.32 (0.30³) | -            | -        |
| CaFeO₃ | t₂g⁰e⁰ + t₂g⁰e³ | P₂₁ | AFMS  | 0.20  | 2.72-3.67 (2.48-3.48³) | 0.00  | -            | 0.13 |
|         |           | P₂₁/₂ | PM    | 0.07 (0.25³) | 2.66-3.72 | 0.00 (0.04³) | -            | 0.14 (0.18³) |
| LaFeO₃ | t₂g⁰e² | Pbnm | AFMG  | 1.67 (2.10³) | 3.94 (4.60³) | 0.01  | -            | -        |
|         |           | Pbnm | PM    | 0.52  | 4.04 | 0.01 (0.00³) | -            | -        |
| YCoO₃  | t₂g⁰e⁰ | Pbnm | NM    | 1.48 (ins.³) | - | 0.06 (0.05³) | -            | -        |
| YNiO₃  | t₂g⁰e² + t₂g⁰e⁶ | P₂₁/₂ | AFMS  | 0.92  | 1.41-0.00 (1.70-0.40³) | 0.05  | -            | 0.18 |
|         |           | P₂₁/₂ | PM    | 0.59 (0.20³-1.00³) | 1.38-0.28 | 0.05 (0.05³) | -            | 0.17 (0.13³) |
| LaCuO₃ | t₂g⁰e² | R-3c  | AFMG  | 0.48 (?) | 0.70 (7?) | - | -            | -        |

Figure 2: Key properties of oxide perovskites with the SCAN meta-GGA functional without U using SQS for the PM phase. Band gap $E_g$ (in eV), magnetic moment $M_{3d}$ (in $\mu_0$) associated with the B cation and amplitudes of distortions (in Å) associated with Jahn-Teller and bond disproportionation motions [34]. Ins. stands for insulating phases. Experimental values are provided in parenthesis and are taken from: a: Ref. [35], b: Ref. [36], c: Ref. [37], d: Ref. [38], e: Ref. [39], f: Ref. [40], g: Ref. [41], h: Ref. [42], i: Ref. [43], j: Ref. [44], k: Ref. [45], l: Ref. [46], m: Ref. [47], n: Ref. [48], o: Ref. [49], p: Ref. [5], q: Ref. [50], r: Ref. [51], s: Ref. [52], t: Ref. [53], u: Ref. [4], v: Ref. [54], w: Ref. [55]
**Electronic structure as gleaned from DOS:** Figure 3 depicts the B-atom (grey) and Oxygen (red) projected density of states averaged on all sites in the low temperature phase. Several observations are apparent: (i) only the perovskites with light B atoms (LaTiO$_3$ and YVO$_3$, Fig3.a and b) have band edge states with dominant $d$ characters (as imagined in the original Mott- Hubbard model), while the O $p$ levels lie below the B $d$ levels in accord with Pavarini et al [56,57]; (ii) for heavier 3$d$ atoms the $d$ bands move deeper in energy, towards the oxygen bands and the electronic structure becomes strongly $p$-$d$ hybridized, yielding covalent charge transfer insulator behaviors (CaMnO$_3$ to YNiO$_3$ in accord with Bisogni et al [58]). (iii) A crossover between B $d$ and O $p$ level positions is likely reached for LaCuO$_3$ in which the top of valence band and the bottom of the conduction band are dominated by O $p$ levels, *i.e.* resembling a negative charge transfer insulator regime. Thus, our calculation reproduces the correct position of transition metal $d$ levels with respect to O $p$ levels as deduced from experiments and DMFT simulations on some perovskite compounds [1,56–58].

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**Band gaps without $U$:** All ABO$_3$ compounds tested here are insulators in both their spin-ordered and spin-disordered PM solutions (Figure 2). These results agree with the insulating character observed experimentally (some experimental values available in literature are reported in Figure 2) and also reproduce trends observed with DFT+$U$ and DMFT simulations on some of these materials (*e.g.* RTiO$_3$, RVO$_3$, RMnO$_3$ and RNiO$_3$, see references therein). For instance, we observe insulation in the rare-earth nickelates compounds in both AFM and PM phases, as DMFT does in PM phases [14,59]. Likewise, we also observe an increase in the band gap when going from rare-earth titanates ($d^1$) to rare-earth vanadates.
(d\(^2\)) in agreement with experimental observations [36,40]. We emphasize here that experimental data of structural and electronic properties on bulk and stoichiometric LaCuO\(_3\) crystals are scarce and diverging hindering confirmation of the SCAN-DFT calculation.

**Magnetic moments:** Our calculations provide magnetic moment values that are comparable to experimental quantities available in literature (see Figure 2). For instance, we capture the decrease of the magnetic moment of Ti cations when going from YTiO\(_3\) to LaTiO\(_3\) [35,38]. Due to the presence of a DLE for Ni and Fe cations in YNiO\(_3\) and CaFeO\(_3\), respectively, two very different magnetic moments are extracted from our simulations. These quantities, compatible with experimental values and previous DFT+U studies of references [4,5,20–22,24,60], point towards a disproportionation of the unstable 3+ and 4+ formal oxidation states (FOS) of Ni and Fe cations, respectively, towards their more stable 2+/4+ and 3+/5+ FOS.

**Electronic Localization without U:** It is interesting to analyze the electronic localization of the \(d\) electrons in those perovskite oxides that are believed to be strongly correlated systems (\(d^1\), \(d^2\), \(d^4\) and \(d^7\) materials for instance). We report in Figure 4 the electronic charge density at the top of the valence band in the low temperature spin-ordered phase of LaTiO\(_3\) (\(d^1\)), YVO\(_3\) (\(d^2\)), LaMnO\(_3\) (\(d^4\)) and YNiO\(_3\) (\(d^7\)). In agreement with the pDOS reported in Fig.3, one notices increasing density on the O atoms when going from light to heavier transition metal atoms, underlining the progressive shift from “Mott insulators” (LaTiO\(_3\), YVO\(_3\), Fig. 4.a and b) to “charge transfer insulator” (YNiO\(_3\), Fig.4.d) behaviors as mentioned earlier. In LaTiO\(_3\) (Fig.4.a), the single Ti\(^{3+}\) \(d\) electron is localized in a linear combination of the three \(e_g\) levels, whose relative coefficients are alternating on neighboring Ti sites. In YVO\(_3\) (Fig.4.b), the additional \(d\) electron sits in a combination of the \(d_{xy}\) and \(d_{xz}\) or \(d_{yz}\) orbital, with alternating coefficients on neighboring sites due to the presence of an in-phase \(Q^+\) JT motions in the low-temperature phase (see Figure 2). We observe similar situation in LaMnO\(_3\) (Fig.4.c): the Mn\(^{3+}\) \(“e_g”\) electron is localized in a cigar shape orbital, corresponding to a mixing of the \(d_{x^2}\) and \(d_{y^2}\) orbitals, that is rotated by 90° between neighboring Mn sites in the \((ab)\)-plane but with parallel orientation between planes along the \(c\) axis. Finally, a “charge ordered” picture is observed in YNiO\(_3\) (Fig.4.d) with Ni cations sitting in an extended (compressed) octahedra bearing approximately 2 (0) electrons on the \(e_g\) levels. This is clearly proving a charge
disproportionated insulating state with Ni ions adopting their more stable 2+ and 4+ formal oxidation state (FOS) instead of the unstable 3+ FOS. Similar observations were obtained for other members such as YTiO₃, LaVO₃ or CaFeO₃, independently of the spin-order/disorder.

![Image](image.png)

**Figure 4: Partial charge density maps of levels at the top of the valence band in some selected “correlated oxide perovskites”.

**How displacements affect or create gapping:** To understand the role of JT and bond disproportionation motions on the gap opening, we use as a starting configuration a high symmetry *Pm-3m* phase and then apply to it successively all displacement modes appearing in the ground state AFM structure (*i.e.* O₆ rotations, antipolar displacements of ions). We then freeze the JT or Boc modes and compute the potential energy surface vs amplitude of the modes for NM, AFM and PM solutions in LaMnO₃ (Q⁺ mode), LaVO₃ (Q₋ mode) and YNiO₃ (Boc mode). This protocol has been used in Ref. [15] to demonstrate the inability of naïve DFT to stabilize JT motions in LaMnO₃ and the crucial role of strong correlation to obtain such displacements. Our results for the same NM ansatz are reported in Figure 5 where we confirm that this naïve model yields a single well potential whose energy minimum is located in zero amplitude, *i.e.* these structural distortions do not appear. Comparing with the full DFT calculation in Fig.5 clearly shows, however that N-DFT is not what DFT can actually do, the latter producing distortions where they appear experimentally. Moving to AFM and PM spin-polarized solutions, we observe that the energy minimum of the different potentials is located to non-zero amplitude of JT and Boc modes. We conclude that DFT without an interelectronic U can stabilize these previously believed to be “correlation-induced lattice distortions” [14,15] if minimal ingredients are provided to the simulations. It is evident that dynamical correlation
effects are not forcing these distortions whose role was previously hampered by a false initial hypothesis.

Figure 5: Energy gains $\Delta E$ (in meV/f.u with respect to the 0-mode amplitude) associated with Jahn-Teller distortions (a and b) and the bond disproportionation (c) modes as obtained by the naive nonmagnetic N-DFT (black circles, upper panel), the PM described with a SQS supercell (blue triangles, middle panel) and AFM (red squares, lower panel). DMFT potential (orange diamonds) for the PM phase of LaMnO$_3$ extrapolated from Ref. [15] is also reported. Filled and unfilled symbols correspond to insulating (ins.) and metallic (met.) solutions. The reference structure at 0 amplitude of JT or B$_{oc}$ modes is set to a material displaying octahedra rotations and anti-polar motions of ions.

The role of atomic displacements on the gap opening. Opened and closed symbols in Fig.5 denote metallic or insulating solutions, respectively. Upon increasing the amplitude of the Q$_{2}^{+}$ and B$_{oc}$ modes in LaMnO$_3$ and YNiO$_3$, respectively, a band gap opens in the PM and AFM solutions. LaVO$_3$ is different where rotations plus antipolar displacements of ions are sufficient to produce an insulating state since the Q$_{2}^{-}$ JT mode is not important for the gap opening. The present SCAN-no-U results are consistent with DFT+U and DMFT simulations in LaMnO$_3$ [13,23,61] and RVO$_3$ [18,57], as well as the experimental observation of insulating states in RVO$_3$ irrespective of the presence of the JT Q$_{2}^{-}$ mode [62]. Surprisingly, even without any amplitude of the disproportionation B$_{oc}$ mode, YNiO$_3$ already exhibits a clear-cut of the Ni electronic structures with one Ni site bearing a magnetic moment of 1.06 (1.26) $\mu_B$ and the other one a value around 0.72 (0.00) $\mu_B$ in the PM (AFM) solution (Fig.5.c). It follows that YNiO$_3$ has a spontaneous tendency to undergo disproportionation effects through an electronic instability transforming the unstable 3+ formal oxidation state (FOS) of Ni cations to the more
stable 2+ and 4+ FOS in the insulating phase. Nevertheless, only the AFM order can render an insulating state without bond disproportionation $B_{oc}$ mode (Fig. 5c) – this is consistent with the fact that the PM phase of $\text{YNiO}_3$ without bond disproportionation is found metallic in experiments [4]. The observation of an electronic instability agrees with our recent DFT+U study [24] and with numerous DMFT calculations identifying a spontaneous tendency of $\text{Ni}^{3+}$ cations to undergo disproportionation effects [59, 63].

We have shown that a DFT using a functional without on-site correlation energy $U$ captures the basic properties of 3$d$ electron transition metal oxide perovskites namely band gap, magnetic moments, relative B$d$ to O$p$ levels positions and all structural features, by using a polymorphous representation allowing energy lowering formation of (i) magnetic moments, (ii) atomic displacements and octahedral rotations, and (iii) breaking of crystal field symmetry of partially occupied orbitals. We further show that lattice distortions including, Jahn-Teller and bond disproportionation modes, are well captured by single-determinant, mean field DFT without $U$ parameter suggesting that dynamic correlations are not the universal controlling factor here.

**Acknowledgments:** This work received support from the European Research Council (ERC) Consolidator grant MINT under the Contract No. 615759. Calculations took advantages of the Occigen machines through the DARI project EPOC A0020910084 and of the DECI resource FIONN in Ireland at ICHEC through the PRACE project FiPSCO. The work of AZ was supported by Department of Energy, Office of Science, Basic Energy Science, MSE division under Grant No. DE-FG02-13ER46959 to CU Boulder. JV acknowledges technical support from A. Ralph at ICHEC supercomputers.

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