Ab initio many-body GW correlations in the electronic structure of LaNiO$_2$

Valerio Olevano,1,2 Fabio Bernardini,3 Xavier Blase,1,2 and Andrés Cano1,2

1CNRS, Institut Néel, 38042 Grenoble, France
2Université Grenobles Alpes (UGA), 38000 Grenoble, France
3Università di Cagliari, Dipartimento di Fisica, 09042 Monserrato, Italy

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We present an ab initio GW self-energy calculation of the electronic structure of LaNiO$_2$. With respect to density-functional theory (DFT) the GW band plot shows an important +2 eV shift of the La 4f bands away from the Fermi level region, and a −1.5 eV shift of the O 2p states which increases the charge-transfer ionic character. Unlike in cuprates, the d-like bands across the Fermi level and the Fermi surface topology are almost unaffected by correlations. We found only a small increase of the electron pocket at Γ making it more resistant to hole doping and, more interestingly, an avoided band-crossing which is present in DFT-LDA at -1 eV. This feature can play a role in the mechanism for superconductivity under hole doping.

The recent discovery of superconductivity in Sr-doped NdNiO$_2$/SrTiO$_3$ thin films [1] has attracted enormous interest [2–15]. Such discovery could represent the first successful extension of superconductivity from cuprates to isostructural/iselectronic nickelates. Indeed the bulk nickelates NdNiO$_2$ and LaNiO$_2$ share the same crystal structure with the cuprate superconductor CaCuO$_2$, and present also a very similar band structure at the level of density-functional theory (DFT) [2–5, 16, 17]. Thus, if the discovery will be confirmed [18, 19], these nickelates could provide an important workbench to check some key ideas put forward in relation to the microscopic mechanism of high-temperature unconventional superconductivity. In this respect, the most popular paradigm relies on the physics of strong correlations as described by the Hubbard model which provides the anti-ferromagnetic (AFM) parent phase of cuprates as a Mott insulator [20]. Thus, according to this picture, the emergence of superconductivity seems to require the presence of such an AFM Mott insulator state in first place. This point would be severely questioned if superconductivity in nickelates and cuprates is confirmed to have a common microscopic origin. Indeed nickelates are paramagnetic metals in their parent phase [20, 21]. Thus, it is important to carefully clarify the analogies and differences between cuprates and nickelates, and in particular to study their electronic structure. On nickelates most of the studies have been carried so far within the framework of density-functional theory (DFT) in the local-density approximation (LDA) or beyond [2–4, 6, 8, 9, 16, 17]. To make further progress it is therefore important to establish how these features are affected by electronic correlations. Attempts in this direction were carried on within dynamical mean-field theory (DMFT) [22–24].

In this work we calculate the electronic structure of LaNiO$_2$ within the framework of ab initio many-body perturbation theory taking into account correlations in the GW approximation for the self-energy [25]. We restrict ourselves to first-order perturbation theory one-iteration $G_0W_0$, starting from DFT-LDA as unperturbed zero-order. We find that the d bands around the Fermi surface are almost unaffected by correlations and that GW preserves the DFT-LDA Fermi surface topology, with only a moderate change in the size of hole and electron pockets. Noticeably, for the $d_{x^2−y^2}$ band across the Fermi level we observe a 0.3 eV bandwidth reduction and an avoided band crossing which instead is present in DFT-LDA. The O 2p states, in contrast, undergo a sizable shift down of ~1.5 eV due to correlations that increases considerably further the ionic charge-transfer character of this system. At the same time, the La 4f states are shifted upwards by as much as 2 eV, so that they are completely removed from the Fermi level region, seriously affecting the low-energy physics of this system.

Computational methods — In all our calculations the crystal structure was that one of the space group 123 (P4/mmm or $D_{4h}$) with the lattice parameters $a = 3.96$ and $c = 3.37$ Å. DFT-LDA calculations have been carried on with norm-conserving pseudopotentials (PSP) on a plane-waves (PW) basis set by the ABINIT code [26]. For the PSP-PW calculation we used a Troullier-Martins pseudopotential for O with 6 electrons in valence ($2s^2$ $2p^4$), whereas for Ni we included 18 electrons in valence, that is $3d^8$ $4s^2$ plus all semicore electrons $3s^2$ $3p^6$, and finally a Hartwigsen-Goedecker-Hutter pseudopotential [27] for La with 11 electrons ($5d^1$ $6s^2$ plus the semicore $5s^2$ $5p^6$) in valence. While for DFT calculations the effect of including semicore electrons is negligible, this is not the case in GW calculations for semicore electrons having a large spatial overlap with valence electrons. The self-consistent DFT-LDA calculation was at convergence within 1 mHartree in the total energy with a cut off of 80 Hartree, a k-point sampling of the Brillouin zone of 4 × 4 × 5 shifted by 1/2 × 1/2 × 1/2, and a Gaussian smearing of 0.01 Hartree. Pseudopotentials and DFT-LDA PSP-PW calculations have been validated with an all-electron full-potential linear-augmented plane-wave (FP-LAPW) calculation by the WIEN2k code [28] (see Appendix). On top of the plane-waves DFT-LDA calculation we performed a one shot $G_0W_0$ calculation using a
We report the 3D GW quasiparticle energies has been achieved using a cutoff of 50 Hartree on the wavefunctions and on the exchange part \( \Sigma_x \) of the self-energy, 14 Hartree for the size of dielectric matrices to take into account local-field effects and for the correlation part \( \Sigma_c \) of the self-energy, 200 and 250 bands in the calculation of, respectively, the screening and the self-energy. For the GW calculation we used an unshifted k-point sampling of \( 4 \times 4 \times 4 \) which includes all high symmetry k-points. Both DFT-LDA and GW bands have been interpolated with maximally-localized Wannier functions by the Wannier90 code \cite{Marzari1997} separately considering the O 2p band manifold below the Fermi energy and separated by a band gap from one side, and all the rest (Ni 3d, La 6s, La 5d, La 4f Ni 4s and Ni 4p) of valence electrons for the other side.

Results — In Fig. 1 we report the \( G_0W_0 \) band plot compared to DFT-LDA. In the left panel the Fermi levels are not re-aligned and are indicated for both DFT and GW as dashed lines, so that we can appreciate the effect of the GW corrections to the zero-order DFT-LDA energies. We can clearly see that the manifold of the lower six valence bands of O 2p atomic character mainly (see e.g. Ref. [5] for the atomic-orbital character of the bands), are practically unaffected by GW corrections, apart from a flattening of an intermediate band at the \( M \) and the \( A \) points. On the other hand, we observe important GW corrections for the next manifold of the mainly Ni 3d character bands closer to the Fermi level, and a rather large shift upwards of almost 3 eV of the seven La 4f flat bands above the Fermi energy.

However, when the Fermi energies are realigned, as in the right panel of Fig. 1, we surprisingly discover that GW correlations do not induce qualitative modifications at the Fermi level and within a \( \pm 2 \) eV range (see also Fig. 3 left). In fact, the Fermi surface topology is exactly the same in DFT-LDA and in GW calculations as can be seen in Fig. 2. In both cases we observe a pocket of electrons at \( \Gamma \) and at the \( A \) points corners of the Brillouin zone, and a pocket of holes in the middle of the Brillouin zone half-way between \( \Gamma \) and the \( X \) and \( M \) points and almost dispersionless along the \( z \) direction. The most significant modification introduced by GW corrections is an increase in the size of the electron pocket at \( \Gamma \) (red surface) which becomes more than 0.3 eV deep in GW with respect to the less than 0.1 eV deep in DFT-LDA. This change makes the electron pocket more ‘resistant’ to hole doping and therefore can have a quantitative effect on the relative positions of the boundaries in the phase diagram of LaNiO\(_2\). Nevertheless, there are no qualitative changes since the bottom of the electron pocket at \( \Gamma \) and \(-0.35 \) eV remains 0.1 eV above the top of a pocket of holes at \( A \) and \(-0.45 \) eV that might open under doping (see Fig. 3).

Another apparently significant change can be observed around the \( R \) point (middle of the Brillouin zone sides in Fig. 2): the hole pocket Fermi surface branch closes in GW, whereas it keeps open in DFT-LDA. However, close inspection to the band plot (see the zoom in Fig. 3) reveals that this feature can be affected by a shift of the Fermi level of only 0.01 eV, a level of accuracy too high also for the DFT calculation. In fact our FP-LAPW and pseudopotential calculations differ around the \( R \) point: the FP-LAPW presents a topology with open branches more similar to GW and different from the pseudopotential DFT topology we show in Fig. 2. In any case, 0.01 eV is quite a tiny perturbation of the Fermi level also for the experiment.

On the other hand, despite GW corrections are negligible for them, the O 2p bands are shifted down by \( \sim 1 \) eV...
due to Fermi level re-alignment only. In GW they appear further away from the Fermi level. Also the band gap between these O 2$p$ band manifold and the topmost bands opens further. Consequently, correlations increase the ionic charge-transfer character.

A similarly large effect is observed for the La 4$f$ localized electrons flat bands which in GW end up 4 eV above the Fermi level. Consequently, they play a less important role in the physics at the Fermi level. More importantly, the raising of La 4$f$ bands exposes to the low-energy physics the other La 5$d$ and 6$s$ bands which in DFT-LDA were placed above and hidden by the La 4$f$ bands and in GW are almost unshifted or even downshifted (see bottom of the parabolic bands at +2 eV in Γ with respect to the Fermi level). The latter become the first completely empty bands above the Fermi level, replacing the place that in DFT-LDA was taken by the La 4$f$ bands. First direct optical transitions at Γ take place with these bands in GW, whereas in DFT-LDA La 4$f$ bands still have an important position. 4$f$ bands have been indicated to play an important role to understand differences in nickelates [30].

In Fig. 3 we point out another probably significant modification induced in the electronic structure when introducing correlations by a GW self-energy. As we can see, the DFT-LDA band structure displays a band crossing along the Γ-Z path at ~1 eV below the Fermi level, immediately followed by an avoided crossing along Z-R path. As a result of the latter, the large branch of the DFT-LDA Fermi surface emerges from two different bands (see also Fig. 1 and Ref. [6]). These bands swap their characters from Ni 3$d_{x^2−y^2}$ to Ni 3$d_{z^2}$ at the avoided crossing, with the result that the Fermi surface branch is of Ni 3$d_{x^2−y^2}$ character almost only. One can see in the figure, by looking at the points where the band-plot has been effectively calculated, that this band crossing is a real one and not an artifact of the MLWF interpolation, as for example is the case for the DFT-LDA band crossing around halfway between the Z and the R-point and at −1.3 eV.

The GW band plot, in contrast, does not show this feature (see Fig. 3 right). As a result, the entire hole-like pocket in the GW Fermi surface comes from the same band whose main character is Ni 3$d_{x^2−y^2}$ everywhere. On this point the GW electronic structure is closer to that of cuprates. We note that this feature is just only −0.8 eV from the Fermi energy and at −0.4 eV from the bottom of the electron pocket at Γ. Consequently it might play an important role under the physical doping that possibly leads to superconductivity.

We tried to reproduce our GW calculation using hybrid functionals, such as LDA0, PBE0, B3LYP, B3PW91, and also LDA+U. All these hybrids keep the same LDA/PBE Fermi surface topology, but none of them is able to reproduce the GW shifts of the La 4$f$ and O 2$p$ states. In LDA+U, in addition, the differences with GW are surprisingly very large on Ni 3$d$ states too. We will publish these data in a more technical paper of interest for a more specialized audience of theoreticians.

Finally, we compare our ab initio GW electronic structure (Fig. 3) with a recent dynamical mean-field theory calculation (DMFT) done on top of DFT-LDA (Ref. [22] Fig. 1b). Note that GW is an approximation to the exact solution, while DMFT relies on a Hubbard model (with the $U = 5$ eV term on the Ni 3$d$ electrons only in the case of [22]). Like GW, DMFT preserves the DFT-LDA Fermi surface topology, with little differences on the electron pocket at Γ (small stretch in GW, tiny shrink in DMFT). Both GW and DMFT reduce the bandwidth of the Ni 3$d_{x^2−y^2}$ band associated to the hole-like pocket of the Fermi surface (see the Γ-X-M and Γ-Z-R directions within the range [−1.0] eV). However, the GW reduction (0.3 eV) is half the DMFT one (0.6-0.7 eV). This bandwidth reduction is also present, and even larger, in a DMFT calculation on NdNiO$_2$ (see Fig. 4 of Ref. [24]). When it comes to the quasiparticle weight $Z$, we also find some differences. Specifically, GW yields an almost constant $Z_{GW} = 0.70 ± 0.02$ all along the BZ for this band while DMFT produces a noticeable reduction at Γ and along Γ-Z-R. In the DMFT calculation on NdNiO$_2$ (Fig. 4 of Ref. [24]) $Z$ appears constant, like in our GW, but there is an evident lower/upper Hubbard band split absent elsewhere. On the other, more La 5$d$-like, band crossing the FS the DMFT and GW $Z$ seem closer: we have found an almost constant $Z_{GW} = 0.79 ± 0.02$, apart at A where it reduces to $Z_{GW} = 0.71$. On the rest of the bandplot GW and DMFT differ more markedly. In DMFT there is no up shift of La 4$f$ states. O 2$p$ states down shift in GW whereas up shift by 0.5 eV in DMFT. The rest of Ni 3$d$ states are sensibly different in GW and DMFT.

**Conclusions** — We have calculated the ab initio GW correlated electronic structure of LaNiO$_2$. GW correlations do not affect the DFT-LDA Fermi surface topology and only slightly renormalize the size of electron and hole pockets. La 4$f$ states undergo a 2 eV shift that place them faraway from the Fermi level. O 2$p$ states downshift so to increase the ionic charge-transfer character.

**FIG. 2.** LaNiO$_2$ Fermi surfaces for DFT LDA (left panel) and GW (right) as in a z-projection on a $xy$ plane.
FIG. 3. LaNiO$_2$ band plots near the Fermi level as calculated by DFT-LDA (red) and GW (black). The lines represent MLWF interpolations and the Fermi levels are all aligned to zero. Left: entire dispersion of $d$-like bands around the Fermi level. Right: zoom along the $\Gamma$-$Z$-$R$ path emphasizing the crossing and the avoided crossing that is obtained in DFT-LDA but not in GW due to correlations.

We observe also a missed band crossing just below the Fermi level and at a distance which can be relevant at the hole-doping levels at which superconductivity occurs. To date, there is no angle-resolved photoemission (ARPES) data reported in the literature on LaNiO$_2$. Thus our GW calculation provides a genuine prediction of the electronic structure of LaNiO$_2$. Future ARPES experiments will represent a check of the GW approximation validity.

Appendix — In this appendix we provide a validation of our norm-conserving pseudopotentials and of our PSP-PW calculation with respect to an all-electron full-potential linear-augmented plane-wave (FP-LAPW) calculation by the code WIEN2k [28]. We also discuss the validity of our MLWF set and interpolation.

For the FP-LAPW calculation we set muffin-tin radii to 2.5, 2.1 and 1.62 Bohr for La, Ni and O respectively, a cut off of $R_{MT}K_{\text{max}} = 7.0$, and a Brillouin zone sampling of $11 \times 11 \times 14$ for the self-consistent calculation of the density.

In Fig. 4 we compare the DFT-LDA band plots calculated using the FP-LAPW and the PSP-PW methods. Although the calculations have been carried out using very different methods and convergence parameters, we found a very good agreement between them. This is an important validation of the pseudopotentials as well as of the convergence parameters used in the plane-waves calculation which constitutes the starting point of our GW calculation. Our DFT band plot is also in very good agreement with previous calculations [2, 4].

In the same figure we report also the norm-conserving PSP-PW bands as interpolated using maximally-localized Wannier functions (MLWF). To build MLWF we used an unshifted $4 \times 4 \times 4$ k-point grid, different from the grid we used to calculate the self-consistent DFT-LDA density. One can see that the interpolation is satisfactory and starts to deviate on the highest energies, more than 10 eV bands above the Fermi level. There are however some fine details, not visible at the scale of Fig. 4, such as some band crossings, which are missed by the MLWF interpolation. For this reason, whenever a critical detail / band crossing was concerned, we referred to the real direct band plot calculations instead of the MLWF interpolation.

Since in $G_0W_0$ the wavefunctions are kept at the DFT-LDA level and not updated, the MLWF are not updated neither. So the quality of the GW band interpolation should be at the same level of DFT-LDA, and this can be checked in Fig. 1. Like DFT-LDA, GW energies are also reproduced remarkably well. However, there are two GW energies along the $\Gamma$-$Z$ direction not reproduced by the interpolated bands (at 11.3 eV and 11.8 eV). This $k$-point does not belong to the unshifted $4 \times 4 \times 4$ grid which was used to calculate the MLWF, and belongs to a grid which was introduced to check the MLWF and effective band crossings. Thus GW bands might look differently from what represented by the MLWF interpolation in that $\Gamma$-$Z$ $E = [11.3, 11.8]$ eV region. We recommend future ARPES experiments to keep into account this issue when comparing to our GW bands.

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FIG. 4. LaNiO$_2$ DFT-LDA band plot calculated in full-potential linear-augmented plane-waves (FP-LAPW, blue dots) by the WIEN2k code, as compared to norm-conserving pseudo-potential plane-waves bands (PSP-PW, orange dots) by the Abinit code. The PSP-PW bands have been interpolated by maximally-localized Wannier functions (MLWF, red lines) by the Wannier90 code. The Fermi level is set to zero.

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