Electronic structure of Co doped ZnO from the \textit{GW} perspective

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In transition metal doped ZnO, the energy position of dopant 3d states relative to host conduction and valence bands is crucial in determining the possibility of long range ferromagnetism. Density functional theory based estimates of the energy position of Co-3d states in Co doped ZnO differ substantially depending upon the choice of exchange-correlation functional. In this work we investigate many-body GW corrections on top of DFT+\textit{U} and hybrid-DFT groundstates to provide a theoretical benchmark for the quasiparticle energies in wurtzite ZnO:Co. Both single shot \textit{G}_0\textit{W}_0 as well as partially self-consistent \textit{GW} wherein the wavefunctions are held fixed at the DFT level but the eigenvalues in \textit{G} are iterated, are considered. The predicted energy position of the minority spin Co-t\textsubscript{2} states is 3.0-3.6 eV above the ZnO conduction band minimum which is closer to hybrid-DFT based estimates.

\textbf{INTRODUCTION}

The quest for oxide dilute magnetic semi-conductors (DMS) exhibiting high Curie temperature has been ongoing for nearly a decade driven by the prospect of realizing future spintronic materials incorporating both semi-conducting and ferromagnetic properties\textsuperscript{5}. ZnO, already of great technological relevance as a transparent conducting and ferromagnetic properties, has been widely studied as a potential DMS material following initial reports of room-temperature ferromagnetism (RTF) in ZnO thin-films\textsuperscript{6}. Stabilizing high-T\textsubscript{c} ferromagnetism in ZnO in conjunction with its direct and wide band gap, large exciton binding energies, and large piezoelectric constants would lead to a truly multifunctional DMS\textsuperscript{5}. However, after several years of experimental and theoretical investigations a complete explanation of the ferromagnetism in Co doped ZnO (ZnO:Co) remains elusive\textsuperscript{5}. Recent experiments suggest a picture wherein ferromagnetism is absent in uniformly doped single-crystal ZnO:Co but emerges in highly defective poly-crystalline samples with extended defects such as grain-boundaries playing a role\textsuperscript{7,8}.

Numerous theoretical efforts based on density functional theory (DFT) have also investigated the microscopic origins of magnetic interactions between Co ions in ZnO:Co\textsuperscript{9–12}. In particular, a variety of beyond-LDA/GGA methodologies (indicated collectively as \textit{b-LDA}) such as DFT+\textit{U}\textsuperscript{11,12}, NLEP\textsuperscript{13}, ASIC\textsuperscript{14} and hybrid-DFT\textsuperscript{12} have been employed, to mitigate the severe band-gap underestimation in ZnO by semi-local functionals. The description of the ground-state electronic structure of ZnO:Co in the absence of additional charge doping defects is similar in the different \textit{b-LDA} approaches: Co\textsuperscript{2+} ions doping the Zn site (Co\textsubscript{Zn}) in wurtzite ZnO are nominally in a \textit{d}\textsuperscript{2} valence state and the approximately tetrahedral crystal field splits the Co-3d states into a set of lower \textit{e} and higher \textit{t}\textsubscript{2} like levels. The majority-spin \textit{e} and \textit{t}\textsubscript{2} as well as the minority-spin \textit{e} states are filled while the minority spin \textit{t}\textsubscript{2} (\textit{t}\textsubscript{2}) states are empty leading to a net magnetic moment of 3\mu\textsubscript{B} per Co\textsubscript{Zn}. The energy position of the \textit{t}\textsubscript{2} states relative to the host conduction band (CB) is however crucial for ferromagnetism in ZnO:Co. Theoretical works in the literature\textsuperscript{10–12} employing a variety of \textit{b-LDA} approximations indicate that partial occupancy of the \textit{t}\textsubscript{2} states under extraneous electron doping is a minimum requirement for long-range FM interactions between Co ions in ZnO:Co. Unfortunately, the different approaches differ substantially in their estimates for the position of the \textit{t}\textsubscript{2} states relative to the conduction band minimum (CBM), leading to different predictions for the feasibility of RTF in ZnO:Co\textsuperscript{10–12}. A scenario where the Co-\textit{t}\textsubscript{2} states are located at or below the CBM\textsuperscript{12,13} would be conducive for ferromagnetism in ZnO:Co at modest n-doping and without the need for structural defects where as if the \textit{t}\textsubscript{2} states were resonant well inside the conduction band, either larger n-doping\textsuperscript{12} or additional structural defects that lower the position of the \textit{t}\textsubscript{2} states towards the CBM\textsuperscript{12} would be necessary to drive a FM state. The assumption underlying these predictions based on DFT is the interpretation of Kohn-Sham (KS) eigenvalues as approximate addition and removal energies that correspond to photoemission spectra (PES). While no formal justification exists for such an interpretation, \textit{b-LDA} approaches are generally designed to improve the agreement with experimental PES of either all or a subset of KS eigenvalues. In the absence to-date of direct observation of the empty Co-\textit{t}\textsubscript{2} states by inverse photoemission experiments, we seek to resolve the ambiguity in the theoretical description by directly calculating the quasiparticle (QP) spectrum of ZnO:Co within the \textit{GW} approximation (\textit{GWA})\textsuperscript{15–18}.

The many-body perturbation theory based \textit{GWA} is a popular approach for calculating the quasiparticle energies of solid-state systems\textsuperscript{19}. Many-body effects in the electron-electron interaction that go beyond the mean-field picture are incorporated into the \textit{GWA} via the energy-dependent electron self-energy operator \textit{\Sigma} which
is approximated as a product of the Green’s function $G$ and the dynamically screened Coulomb interaction $W$. $W$ is in turn obtained by screening the bare-Coulomb interaction with the inverse frequency-dependent dielectric matrix. $GW$ self-energy corrections are generally calculated on top of DFT independent-particle wavefunctions and eigenvalues and the resulting QP spectra are systematically improved towards direct/inverse photoemission spectra (PES). Different levels of self-consistency are possible within a perturbative GW scheme and in this work, we consider both single-shot $G_0W_0$ as well as partially self-consistent $GW_0$ wherein one iterates the eigenvalues in $G$ while keeping $W$ and the wavefunctions fixed at the DFT estimate. We find that irrespective of the specific $b$-LDA starting point, quasi-particle energies of the $Co-t_2^e$ states are located well above the CBM of ZnO. Thus partial occupancy of these states is difficult to achieve for low electron doping concentrations.

**METHODS**

All the calculations presented in this work were carried out within the planewave based DFT framework as implemented in the standard VASP package. A plane-wave kinetic energy cutoff of 300 eV and projector-augmented wave (PAW) pseudopotentials with the following valence-electron configurations were employed: $3d^{10}4s^2$ for Zn, $2s^22p^4$ for O and $3d^84s^1$ for Co. The pseudopotentials as well as pure DFT calculations in this work employed the PBE exchange-correlation functional. Two different $b$-LDA approaches viz., PBE+$U_{\text{SDM}}$ and hybrid-DFT were considered to provide starting points for subsequent GW calculations. The PBE+$U$ calculations employed Hubbard parameters of $U_{\text{Zn}}=7$ eV, $U_{\text{Co}}=3$ eV and $J_{\text{Co}}=1$ eV, for the 3$d$ states of Zn and Co respectively. The bigger $U$ for Zn is attributed to a deeper and more localized semicore $d^{10}$ shell in Zn compared to Co. Hybrid-DFT calculations employed the HSE06 functional.

For calculations on the wurtzite unit-cell of ZnO, the Brillouin zone was sampled using a $8 \times 8 \times 6$ $\Gamma$ centered $k$-point mesh. Cobalt doped ZnO was modeled with a 32 atom orthorhombic supercell of wurtzite ZnO, in which one Zn site was substituted by Co. This corresponds to a nominal Co doping concentration of $\sim 6.25\%$. In the supercell calculations, the Brillouin zone was sampled at 28 irreducible $k$-points in a $\Gamma$ centered mesh. Structures were optimized using the HSE06 functional until residual forces were smaller than 0.01 eV/Å (0.05 eV/Å) in the primitive-cell (supercell). This led to the following unit-cell parameters for wurtzite ZnO: $a=2.248$ Å, $c/a=1.61$, $u=0.380$. Within GW calculations, an energy cutoff of 150 eV was used for the response functions. A total of 240 and 1152 bands were employed in the primitive (wurtzite) cell and supercell calculations respectively. Both single-shot $G_0W_0$ as well as partially self-consistent $GW_0$ calculations were carried out on top of DFT based groundstate starting points. In the $GW_0$ calculations, the eigenvalues in $G$ were self-consistently updated four times while the orbitals were held fixed as obtained from DFT.

**RESULTS AND DISCUSSIONS**

**ZnO unitcell**

In order to set the framework for supercell defect calculations on Co doped ZnO, we first investigate the eigenvalue spectrum of pure ZnO obtained both from DFT as well as $GW$ quasi-particle corrections on top of DFT. In ZnO, the predominant character of the valence band maximum (VBM) and conduction band minimum (CBM) is $O_{2p}$ and $Zn_{4s}$ respectively. The $Zn_{3d}$ states meanwhile, are fully occupied and are located several eV below the VBM. The computed band gaps and $Zn_{3d}$ binding energies are reported in table I. ZnO is a prototypical case for extreme band-gap ($E_g$) underestimation by semi-local exchange-correlation (XC) functionals. The predicted band-gap from the PBE functional for instance is 0.78 eV while the experimental gap is 3.44 eV. Some part of this band gap underestimation by semi-local functionals can be traced to the too low binding energy of cation $3d$ states and their concomitant hybridization with anion $2p$ states in the valence band. The average $Zn_{3d}$ binding energy ($E_{3d}$) from PBE is $\sim 5.1$ eV compared to 7.5-8.81 eV in experiment. Given a bandwidth of $\sim 5.5$ eV for the $O_{2p}$ valence band, this leads to spurious $Zn_{3d}$-$O_{2p}$ hybridization which because of pd-repulsion, pushes the $O_{2p}$ states higher in energy reducing $E_g$. This effect which can be traced to self-interaction errors, is over and above the conventional DFT underestimation of band-gaps in semiconductors. A significant improvement in the value of $E_g$ can be obtained simply by correcting for the low binding energy of $Zn_{3d}$ states.

| Method       | $E_g$ (eV) | $E_{3d}$ (eV) |
|--------------|------------|--------------|
| PBE          | 0.78       | 5.15         |
| PBE+$G_0W_0$ | 2.27       | 6.05         |
| PBE+$GW_0$   | 2.68       | 6.39         |
| PBE+$U$      | 1.58       | 6.98         |
| PBE+$U+G_0W_0$ | 2.62   | 6.69         |
| PBE+$U+GW_0$ | 2.85       | 6.63         |
| HSE          | 2.24       | 6.01         |
| HSE+$G_0W_0$ | 3.14       | 6.64         |
| HSE+$GW_0$   | 3.31       | 6.81         |
| Exp.         | 3.44       | 7.5-8.81     |
Accordingly, the inclusion of a Hubbard-\(U\) correction on the Zn\(3d\) states within PBE\(+U\) results in an E\(3d\) of \(\sim 7\) eV while also improving E\(g\) to 1.58 eV. This nevertheless still represents an almost 50\% underestimation of E\(g\). The description can be further improved by employing a hybrid-DFT functional such as HSE03. The inclusion of non-local Fock exchange not only leads to a reduction in the self interaction error but to a large extent also restores the derivative discontinuity in the XC functional within a generalized Kohn-Sham (GKS) scheme\(^{29}\), further improving the band-gap. Thus HSE03 predicts values of E\(g\) and E\(3d\) at 2.24 eV and 6 eV respectively. Perturbative \(G_0W_0\) corrections on top of DFT starting wavefunctions lead to systematic improvements in the resulting quasiparticle spectrum. We see from table I that irrespective of the starting DFT XC functional, both E\(g\) and E\(3d\) from \(G_0W_0\) are corrected towards the experimental values and including partial self-consistency through \(GW_0\) further improves the agreement. Nevertheless, the value of E\(g\) is seen to depend upon the DFT starting point\(^{30}\), \(G_0W_0\) on top of PBE (PBE\(+U\)) leads to a value of E\(g\) that is still underestimated by \(\sim 34\%\) (\(\sim 24\%\)). In contrast, E\(g\) from HSE\(+G_0W_0\) at 3.14 eV, is within \(\sim 9\%\) of experiment. At the \(GW_0\) level, E\(g\) is further increased relative to \(G_0W_0\) and is within 22\% of experiment irrespective of starting DFT functional. In particular, E\(g\) from HSE\(+GW_0\) at 3.31 eV matches well with experiment. Similarly, \(G_0W_0\) and \(GW_0\) QP shifts generally tend to increase E\(3d\) relative to the DFT starting point and towards PES. However, the PBE\(+U\) starting point which includes a large on-site U\(Zn=7\) eV to being with, seems to be an exception. Quasiparticle corrections in this case are seen to slightly reduce E\(3d\) from 6.98 eV in the DFT groundstate to 6.63 eV in PBE\(+U+GW_0\). Overall, the \(GWA\) leads to a \(\sim 1-1.5\) eV underestimation of the 3d band irrespective of the starting point as has been noted previously in the literature\(^{30}\). Our results for E\(g\) and E\(3d\) in table I are in good agreement with earlier benchmark calculations on zinc-blende ZnO\(^{20,30}\) taking into account that E\(g\) in wurtzite ZnO is expected to be \(\sim 0.2\) eV larger\(^{30}\).

**ZnO:Co supercell**

Co substituting Zn (Co\(2n\)) in ZnO is formally in a Co\(^{2+}\) oxidation state with 7 electrons in the occupied Co\(3d\) orbitals. The nearly tetrahedral crystal field around Co\(Zn\), splits the Co\(3d\) states into a set of lower \(e\) and higher \(t_2\) states. Furthermore, Co\(Zn\) assumes a high-spin configuration with \((e^\uparrow)^2\) \((t_2^\uparrow)^3\) majority spin and \((e^\downarrow)^2\) \((t_2^\downarrow)^0\) minority spin occupancies resulting in a local magnetic moment of 3\(\mu\)B per site. First we briefly discuss the electronic structure of ZnO:Co obtained from ground-state DFT calculations. LDA/GGA XC functionals yield a qualitatively incorrect groundstate for ZnO:Co\(^{10,13}\) by incorrectly placing the occupied \(e^\uparrow\) states in resonance with the CBM of ZnO resulting in spurious charge transfer to the host and fractional occupation of the \(e^\downarrow\) orbitals. This is due to a combination of underestimating both the host band-gap and the binding energy of the Co\(3d\) states. b-LDA approaches that either partially or fully rectify these shortcomings reproduce the correct occupancy of the \(e^\downarrow\) states\(^{9,11,13}\) and a magnetic moment of 3\(\mu\)B per Co\(Zn\). As a general feature common to the different b-LDA methods, the fully occupied majority spin Co\(3d\) states hybridize with the O\(2p\) valence band states of ZnO with some Co\(3d\) DOS at the top of the host VBM. Different approaches however differ substantially at a quantitative level in their description of the minority spin Co\(3d\) states. Considering the case of PBE\(+U\) with U\(Zn=7\) eV and U\(Co=3\) eV, J\(Co=1\) eV, we find that even though E\(g\) is still underestimated, the \(e^\downarrow\) orbitals are correctly occupied by two electrons and are located approximately 1.2 eV above the host VBM (see Fig. I and table I). Meanwhile, the empty \(t_2^\downarrow\) states are resonant in the conduction band with an onset at roughly 1.6 eV above the CBM and 3.3 eV above the host VBM. Note however that the CBM is still too low in energy as E\(g\) \(\approx 1.6\) eV. Within PBE\(+U+GW_0\) and related approaches, the positions of the minority spin \(e^\downarrow\), \(t_2^\downarrow\) states with respect to the host VBM (denoted by E\(c\), E\(t\) respectively) are largely determined by the choice of the parameter U\(Co\). These quantities E\(c\), E\(t\) are insensitive to additional on-site corrections employed on Zn\(3s\) orbitals, within a DFT\(+U\) approach to also rectify the host CBM position. Therefore if E\(g\) is restored to its full value of 3.44 eV within such a description\(^{11}\), the empty

| name          | \(E_{c\downarrow}\) | \(E_{t_2\downarrow}\) | \(E_{t_2\downarrow} - E_{g}\) | \(E_{t_2\downarrow} - E_{g}^{\exp}\) |
|---------------|------------------|------------------|------------------|------------------|
| ZnO:Co       |                  |                  |                  |                  |
| PBE\(+U\)    | 1.2              | 3.3              | 1.6              | -0.1             |
| PBE\(+U+G_0W_0\) | 1.3          | 5.2              | 2.4              | 1.8              |
| PBE\(+U+GW_0\) | 1.4          | 6.1              | 3.0              | 2.6              |
| HSE          | 0.6              | 5.0              | 2.7              | 1.6              |
| HSE\(+G_0W_0\) | 0.7          | 6.6              | 3.3              | 3.2              |
| HSE\(+GW_0\) | 0.8              | 7.1              | 3.6              | 3.7              |

| ZnO:Co + V\(O\) |                  |                  |                  |                  |
| PBE\(+U\)    | 0.6              | 2.5              | 0.2              | -1.0             |
| PBE\(+U+G_0W_0\) | 0.9          | 4.0              | 0.9              | 0.6              |
| PBE\(+U+GW_0\) | 1.0              | 4.4              | 1.3              | 0.9              |
$t^\text{↓}_2$ states would be approximately resonant with the host CBM suggesting that they could be partially occupied at relatively small electron doping concentrations.

The picture that emerges from the HSE functional while qualitatively similar to that of PBE+U is quantitatively rather different. We find that the $E_{g\downarrow}$ at $\sim$0.6 eV is slightly smaller than in PBE+U but $E_{t^\text{↓}_2}$ is substantially larger at $\sim$5.0 eV. The inclusion of a fraction of Fock-exchange generally pushes up unoccupied states higher in energy and so the increased value of $E_{t^\text{↓}_2}$ is expected. A similar result is found with other hybrid functionals. With an $E_g$ value of 2.3 eV, the onset of the $t^\text{↓}_2$ states is roughly 2.7 eV above the host CBM which renders partial occupancy of these states virtually impossible for reasonable electron doping levels. Even assuming the full experimental value for $E_g$ by rigidly shifting the Zn-4s CBM higher in energy while keeping the Co-3d states fixed leaves the $t^\text{↓}_2$ states about 1.6 eV above the CBM. Thus, starkly different implications emerge from PBE+U and HSE for carrier mediated ferromagnetism in ZnO:Co. A natural question then arises as to which of these two $b$-LDA descriptions is closer to the quasi-particle picture.

In figure 1b we also present DOS for ZnO:Co from $G_0W_0$ and $GW_0$ calculations applied on top of PBE+U and HSE. In general, the final QP spectrum both at the $G_0W_0$ and $GW_0$ levels depends to some extent on the DFT starting-point (SP). Note that in particular, perturbative $G_0W_0$ and $GW_0$ corrections applied on top of the qualitatively incorrect PBE groundstate of ZnO:Co (not shown), do not lead to any improvement and are therefore of little interest. $b$-LDA groundstate SPs on the other hand lead to more systematic results. We see that the QP shift on $E_{g\downarrow}$ is rather small irrespective of the SP. Accordingly $E_{g\downarrow}$ occurs at 1.3 eV (1.4 eV) for $G_0W_0$ ($GW_0$) on top of PBE+U and at 0.7 eV (0.8 eV) for $G_0W_0$ ($GW_0$) on top of HSE. In contrast, $E_{t^\text{↓}_2}$ not only shows a larger QP shift but the shift is also invariably towards higher energies compared to the $b$-LDA SP. On top of PBE+U, $G_0W_0$ ($GW_0$) leads to an $E_{t^\text{↓}_2}$ of 5.2 eV (6.1 eV) which places the onset of the empty $t^\text{↓}_2$ states $\sim$2.4 eV (3.0 eV) above the calculated host CBM. Thus the $t^\text{↓}_2$ quasiparticle levels are predicted to be much higher in the conduction band than suggested by PBE+U at the DFT level. Even assuming the full value of $E_g$ as above puts the $t^\text{↓}_2$ states about 1.8 eV (2.6 eV) higher than the CBM in $G_0W_0$ ($GW_0$). Similarly, $G_0W_0$ ($GW_0$) on top of HSE yields an $E_{t^\text{↓}_2}$ of 6.6 eV (7.1 eV) with the onset of the $t^\text{↓}_2$ states 3.3 eV (3.6 eV) above the corresponding calculated CBM. Based on these results for different DFT

FIG. 1. Calculated density of states (DOS) in ZnO:Co for a Co dopant concentration of 6.25 percent. The DOS from two groundstate DFT starting points PBE+U (left), HSE (right) and corresponding $G_0W_0$, $GW_0$ corrections on top of either are shown. Panels (d)-(f) in either case show a zoomed in view of the minority-spin DOS around the Fermi energy. Green arrows indicate the positions of the Co derived minority-spin $e$ and $t^\text{↓}_2$ states. Lower and higher dashed lines indicate the positions of the Fermi energy and of the conduction band minimum respectively. The Fermi energy in each case is aligned to 0 eV.
starting points, we estimate the onset of the $t_{2g}^\uparrow$ states to be 3.0-3.6 eV above the CBM of ZnO:Co. We find that the magnitude of the QP shifts relative to the DFT SP are smaller for HSE than PBE+U. The overall change in $E_{t_{2g}^\uparrow}$ going from the DFT SP to $GW_0$ is 2.1 eV and 2.8 eV in HSE and PBE+U respectively while the change in $E_{t_{2g}^\uparrow}$ with respect to the CBM (see $E_{t_{2g}^\uparrow}$-E$_g$ in table 11) also shows a similar trend at respectively 0.9 eV and 1.4 eV in HSE and PBE+U. A comprehensive study by Fuchs et al. indicated that for a wide range of materials, overall best agreement with experimental spectra was obtained at the HSE+$G_0W_0$ level. At this level, the Co $t_{2g}^\uparrow$ onset is predicted to be 3.3 eV above the CBM which we offer as a best compromise estimate. This precludes the possibility of FM interactions being mediated by partial occupancy of $t_{2g}^\uparrow$ states under electron doping in the absence of additional structural defects.

Next we investigate the effect of low oxygen coordination around Co$_{2n}$ on the $e^\downarrow$ and $t_{2g}^\downarrow$ QP energies. In an earlier work on ZnO:Co, based on a self-interaction corrected approach, we proposed that oxygen vacancies (V$_O$) next to Co$_{2n}$ could lower the energy of the $t_{2g}^\downarrow$ states enough to make partial occupancy of these states feasible at reasonable electron doping levels. In this context, we consider one Co$_{2n}$+V$_O$ pair in a nearest neighbour configuration within a 32 atom supercell of ZnO and calculate the QP energy levels for this system at the $G_0W_0$ and $GW_0$ level based on a PBE+U SP. The oxygen vacancy is created by removing one out of the three O atoms co-ordinating the Co$_{2n}$ in the $ab$ plane of wurtzite ZnO. The calculated DOS for this system is presented in figure 2 and relevant energy levels are reported in table 11. We find that the effect of V$_O$ next to Co$_{2n}$ is to lower both E$_{e^\downarrow}$ and E$_{t_{2g}^\downarrow}$. In fact the energy of all the occupied Co-3d manifold is lowered because of the smaller ligand field the Co$_{2n}$ is now subject to. Relative to the case of an isolated Co$_{2n}$, E$_{e^\downarrow}$ for the Co$_{2n}$+V$_O$ pair is lower by 0.6 eV in PBE+U and by 0.4 eV in both $G_0W_0$ and $GW_0$ on top of PBE+U. The effect on E$_{t_{2g}^\downarrow}$ is even larger as the crystal-field induced splitting between $e^\downarrow$ and $t_{2g}^\downarrow$ orbitals is also reduced. Thus at the PBE+U+$GW_0$ level E$_{t_{2g}^\downarrow}$ for a Co$_{2n}$+V$_O$ pair is lower by almost 1.7 eV relative to isolated Co$_{2n}$. The final alignment of the $t_{2g}^\downarrow$ states relative to the CBM, except in the case of PBE+U, is however still not favourable for driving carrier mediated FM. $G_0W_0$ ($GW_0$) places the onset of the $t_{2g}^\downarrow$ states $\sim$0.9 eV (1.3 eV) above the CBM even for Co$_{2n}$+V$_O$ pairs which sets a very high electron-doping threshold to achieve partial occupancy. Thus, at the level of the $GWA$ considered in this work, the perspective that emerges is decidedly more pessimistic for carrier mediated FM interactions between Co$_{2n}$ in ZnO:Co. We note that test calculations including self-consistency in the eigenvalues in both $G$ and $W$ also produce qualitatively similar results with the QP shifts being slightly larger in the same direction. These results are in line with the emerging consensus that ZnO:Co is not ferromagnetic in a conventional DMS sense but that the mechanisms responsible for the observed FM signatures are more exotic in nature and perhaps confined to extended defects such as grain-boundaries in poly-crystalline samples.

![Graph](image-url)

**FIG. 2.** Calculated density of states (DOS) from a ZnO:Co supercell containing a Co$_{2n}$ and oxygen vacancy (V$_O$) pair. The DOS from groundstate DFT starting point PBE+U (left) as well as corresponding $G_0W_0$, $GW_0$ corrections on top are shown. Panels (d)-(f) show a zoomed in view of the DOS around the Fermi energy. Green arrows indicate the positions of the Co derived minority-spin $e^\downarrow$ and $t_{2g}^\downarrow$ states. Lower and higher dashed lines indicate the positions of the Fermi energy and of the conduction band minimum respectively. The Fermi energy is aligned to 0 eV.

**CONCLUSION**

In conclusion, we investigated the quasiparticle (QP) spectrum of Co doped wurtzite ZnO (ZnO:Co) within a $GW$ framework with a focus on the minority-spin $e^\downarrow$ and $t_{2g}^\downarrow$ energy levels derived from Co substituting a Zn site (Co$_{2n}$). Single shot $G_0W_0$ and partially self-consistent $GW_0$ quasiparticle corrections were applied on top of two different ground-state DFT starting points (SPs) based on the PBE+U and HSE exchange-correlation functionals. We find in general, the magnitude of the QP shifts to be smaller in the case of HSE
compared to PBE+U. Irrespective of the DFT SP and the level of GW self-consistency, QP corrections are seen to shift the empty $t^\downarrow_2$ states on Co$_{\text{Zn}}$ higher in energy placing them roughly 3.3 eV above the conduction band minimum (CBM) of ZnO:Co. Low oxygen co-ordination around the Co$_{\text{Zn}}$ site lowers the QP energy position of the $t^\downarrow_2$ states to around 1 eV above the CBM. Our results therefore suggest that partial occupancy of the $t^\downarrow_2$ states by electron doping the host material is difficult to achieve making a conventional carrier mediated mechanism for ferromagnetism in ZnO:Co less likely.

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