

The f -electron challenge: localized and itinerant states in lanthanide oxides united by $GW@LDA+U$

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Many-body perturbation theory in the GW approach is applied to lanthanide oxides, using the local-density approximation plus a Hubbard U correction ($LDA+U$) as the starting point. Good agreement between the G_0W_0 density of states and experimental spectra is observed for CeO_2 and Ce_2O_3 . Unlike the $LDA+U$ method G_0W_0 exhibits only a weak dependence on U in a physically meaningful range of U values. For the whole lanthanide sesquioxide (Ln_2O_3) series $G_0W_0@LDA+U$ reproduces the main features found for the optical experimental band gaps. The relative positions of the occupied and unoccupied f -states predicted by G_0W_0 confirm the experimental conjecture derived from phenomenological arguments.

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The accurate first-principles description of the electronic structure of f -electron systems, i.e. materials containing lanthanide or actinide elements, is currently regarded as one of the great challenges in condensed matter physics. f -electron systems are characterized by the simultaneous presence of itinerant (delocalized) and highly localized f -states and interactions between them. Most computational methods are suited only to one type. Density-functional theory (DFT) – currently the standard approach for electronic structure calculations of extended systems – proves to be inadequate for f -electron systems in the most commonly applied local-density or generalized gradient approximation (LDA or GGA , respectively). One of the major deficiencies of LDA and GGA is the delocalization (or self-interaction) error [1], which is particularly severe for systems with partially occupied d or f -states and can even lead to qualitatively incorrect metallic ground states for many insulating systems. Hybrid functionals [2], on the other hand, partly correct the self-interaction error by incorporating a certain portion of exact exchange, which significantly improves the descriptions of d - or f -electron systems [3, 4]. The dependence on adjustable parameters, however, remains a concern. Conversely, correlation effects that govern the physics of localized f -electrons can in principle be treated systematically by dynamical mean field theory (DMFT) [5]. In practice these many-body corrections are only applied locally to an atomic site (e.g. the Anderson impurity model) and the impurity solvers require input parameters (such as the Hubbard U) for the interaction strength. Moreover, most existing DMFT schemes are coupled (non self-consistently) to local or semilocal DFT calculations and the description of the itinerant electrons therefore remains on the level of LDA and GGA .

As a first step towards a systematic *ab initio* understanding of f -electron systems, we apply many-body perturbation theory (MBPT) in the GW approach to a selected set of lanthanide oxides (CeO_2 and Ln_2O_3 (Ln =lanthanide series)) [6] in this Letter. These compounds have important technological applications [7, 8, 9, 10, 11, 12], in particular in catalysis, where CeO_2 -based compounds have attracted considerable interest from both experiment and theory [3, 13, 14, 15,

16, 17, 18, 19, 20]. Unlike in most previous studies, the GW calculations in this work are based on LDA ground state calculations including a Hubbard U correction (henceforth denoted $G_0W_0@LDA+U$). Our $G_0W_0@LDA+U$ calculations provide a qualitative understanding of the general trend observed for the band gaps of the Ln_2O_3 series and reproduce the characteristic features of the series, in particular the four dips observed in the experimental curve.

The GW approach corresponds to the first order term of a systematic expansion in MBPT [21] and has become the method of choice for the description of quasiparticle band structures in weakly correlated solids [22]. Through the screened Coulomb interaction W it captures the screening among itinerant electrons while at the same time treating exchange at the exact exchange level (given by the Hartree-Fock expression). The latter should account for a large part of the many-body interactions among localized d or f -electrons, as demonstrated recently for Cu_2O and VO_2 [23]. In this Letter we challenge the conventional view that regards many f -electron systems as *strongly correlated* electron systems for which band theory is inadequate [24]. In the hierarchy of many-body perturbation theory, strong correlation denotes correlation effects that go beyond exact exchange and the weak correlation regime of GW . The good agreement between our GW calculations and available experimental data demonstrates that the GW method can treat both itinerant *spd* bands and localized f -bands accurately for the materials we have considered. Since the screened exchange picture of the GW approach captures the essential physics we challenge the classification of these materials as *strongly correlated*.

The GW method is typically applied in a perturbative manner (henceforth denoted G_0W_0) in which the quasiparticle (QP) energies $\epsilon_{n\mathbf{k}}^{QP}$ are calculated as a first-order correction to the eigenenergies $\epsilon_{n\mathbf{k}}$ and eigenvectors $\psi_{n\mathbf{k}}$ of a reference single particle Hamiltonian \hat{H}_0

$$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}} + \Re \langle \psi_{n\mathbf{k}} | \Sigma^{xc}(\epsilon_{n\mathbf{k}}^{QP}) - V^{xc} | \psi_{n\mathbf{k}} \rangle \quad (1)$$

Here Σ^{xc} is the G_0W_0 self-energy calculated from the one-particle Green's function G_0 and screened Coulomb interaction W_0 , both evaluated using $\epsilon_{n\mathbf{k}}$ and $\psi_{n\mathbf{k}}$, and V^{xc} is the

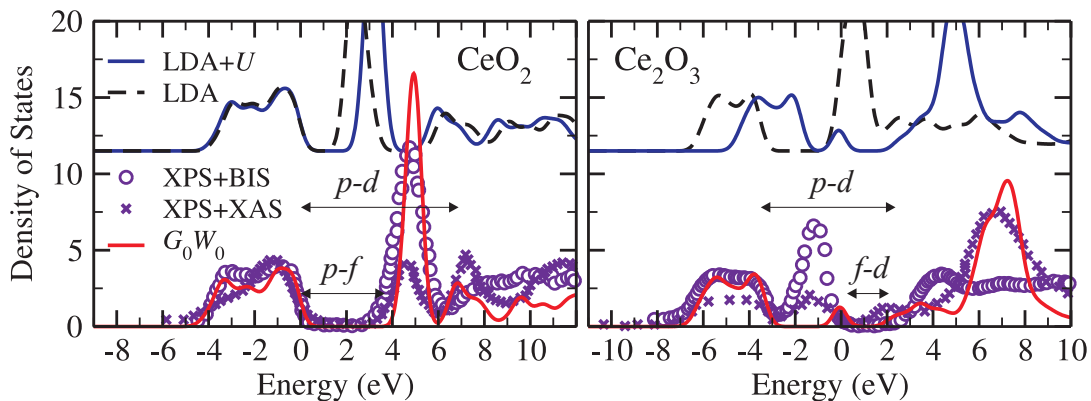


FIG. 1: (Color online) The DOS of CeO_2 (left) and Ce_2O_3 (right) from LDA, LDA+ U and G_0W_0 @LDA+ U with $U=5.4$ eV are compared to experimental data (XPS+BIS and XPS+XAS) [25]. The LDA and LDA+ U curves have been offset vertically for clarity.

exchange-correlation potential included in \hat{H}_0 . For most of the sesquioxides considered in this work LDA and GGA incorrectly predict a metallic ground state. In these cases first order perturbation theory based on LDA or GGA is not applicable and alternative reference \hat{H}_0 have to be employed [26, 27, 28, 29]. In this work we use the LDA+ U method [30] as the starting point for G_0W_0 . By adding a site- and orbital-dependent correction $\delta\hat{V}^U$ to the standard LDA single-particle Hamiltonian, LDA+ U significantly improves the description of highly localized states, and therefore overcomes the major failure of LDA for these systems. To describe highly localized states accurately, we have implemented an all-electron G_0W_0 approach [31] based on the full-potential linearized augmented plane wave method [32].

The LDA+ U method is conceptually similar to GW . It is, however, *not* a substitute for GW even for localized states: 1) The link between the LDA+ U and the GW approximation relies on the assumption that the hybridization between localized and itinerant states can be neglected, which in many cases is not valid; 2) the $\delta\hat{V}^U$ correction in LDA+ U has *direct* effects only on the corresponding localized states; the description of itinerant states remains at the LDA level; and 3) screening in LDA+ U is *static*, while in reality screening is dynamic and, has a stronger energy-dependence for localized electrons than for itinerant ones. The LDA+ U approach by itself is therefore not expected to provide a satisfactory description to the electronic structure of f -electron systems.

An advantage of the G_0W_0 @LDA+ U approach lies in the fact that the Hubbard U corrections enter self-consistently in the ground state calculation. This becomes important when localized states hybridize with band states. A less appealing aspect of the LDA+ U approach concerns the parameter U , which, in many cases, is determined by fitting to experimental data. The onsite Coulomb interaction U , however, has a well-defined physical meaning, and can be calculated from first-principles (see, e.g. Refs. [33]). In addition we demonstrate below that G_0W_0 based on LDA+ U is much less sensitive to U than the LDA+ U itself. The G_0W_0 calculations also remove the problem of the double counting corrections that

are not well defined in the LDA+ U approach, by subtracting them out as part of V_{xc} in Eq. 1. Despite these advantages the G_0W_0 @LDA+ U approach will not be suitable in cases where strong correlation effects become important (e.g. the Kondo resonance), for which many-body interactions that go beyond the GW approach have to be included. This is currently the domain of DMFT, as alluded to in the introduction.

Figure 1 shows the density of states (DOS) of CeO_2 and Ce_2O_3 calculated from LDA, LDA+ U , and G_0W_0 @LDA+ U (with $U = 5.4$ eV [34]) together with the experimental spectra. The G_0W_0 density of states for CeO_2 agrees well with the experimental data from direct (XPS) and inverse (BIS) photoemission spectroscopy or X-ray absorption spectroscopy (XAS). In CeO_2 , the empty f -states introduce a sharp peak in the fundamental band gap formed between the O-2 p valence and Ce-5 d conduction band. The most important quantities here are therefore the p - f and p - d gaps. For the latter the G_0W_0 value of 6.1 eV is in good agreement with the experimental one of 6.0 eV. The p - f gap, however, cannot be unambiguously determined from XPS-BIS or other available measurements (See, e.g. Ref. [18] and references therein). As expected, LDA underestimates both gaps, but the p - d gap is only slightly smaller than in experiment (5.5 vs 6.0 eV), whereas LDA+ U decreases it to 5.1 eV. We also note that our G_0W_0 @LDA+ U DOS for CeO_2 is very close to that obtained from the recently proposed self-consistent GW method [35].

More intriguing features are observed for Ce_2O_3 . As expected, the on-site Hubbard correction in the LDA+ U splits the single f -peak in LDA to occupied and unoccupied f -bands (denoted as f^{occ} and f^{un} , respectively), the former falling within the p - d gap and the latter overlapping with the conduction bands. The p - d gap is nearly the same as in LDA, but the p - f^{occ} splitting is greatly reduced. Applying the G_0W_0 corrections to the LDA+ U ground state, we observe two remarkable features: 1) the O-2 p band is pushed to lower energy with respect to the f^{occ} band, and 2) the f^{un} -band shifts up in energy away from the conduction band edge increasing the splitting between the f^{occ} and f^{un} bands at the same time.

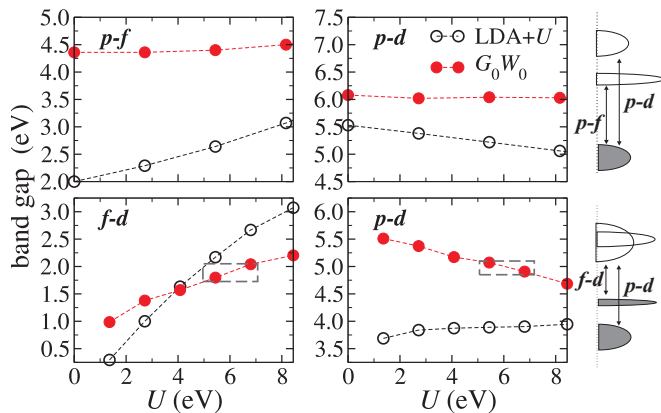


FIG. 2: (Color online) Band gaps of CeO_2 (p - f and p - d , upper row) and Ce_2O_3 (f - d and p - d , lower row) from LDA+ U and $G_0W_0@LDA+U$ as a function of U . The dashed rectangles in the lower panel indicate the range of physically meaningful values of U (see text).

The G_0W_0 and the experimental spectrum in Fig. 1 are aligned at the upper valence band edge and not the Fermi level since this is not well defined at the 0 K at which the calculations are performed. We again find the f^{un} peak to be in good agreement with the BIS data. The position of the f^{occ} peak, however, differs by approximately 1 eV. With respect to the band gap the comparison with experiment is aggravated by the limited experimental resolution. Taking the difference between the conduction band edge and the upper edge of the XPS-XAS f^{occ} peak gives a band gap that is consistent with the optical band gap of ~ 2.4 eV [8, 36] and the G_0W_0 gap of 2.0 eV. If one instead references against the peak center of the f^{occ} states, the experimental band gap of Ce_2O_3 would be larger than 3 eV. Further experimental evidence is clearly needed to determine the actual value.

Figure 2 illustrates the influence of U on the LDA+ U and $G_0W_0@LDA+U$ calculations for the examples of CeO_2 and Ce_2O_3 . Since the f -states are essentially empty in CeO_2 , the effect of U is relatively weak: For $U=0$ to 8 eV, the p - f and p - d gaps from LDA+ U change only by approximately 1.0 and 0.5 eV, respectively, and become nearly constant in G_0W_0 . The situation is more complex in Ce_2O_3 . In LDA+ U , the f - d gap depends sensitively on U and varies by nearly 3 eV, but the p - d gap remains almost unaffected. In contrast, both the f - d and the p - d gap exhibit a slight U -dependence in G_0W_0 , changing by 1.2 and 0.6 eV over the full U range explored here. Most importantly, however, the U -dependence reduces to only approximately 0.3 eV in the range of “physically meaningful” values of U (~ 5 -7 eV [18, 19]), which is already in the range of experimental error bars. We note in passing that the relatively weak dependence on U has also recently been reported by Kioupakis *et al.*, who applied a similar approach to solid hydrogen [37]. In addition, Figure 2 shows that within LDA+ U one could obtain an apparently more accurate p - f (in CeO_2) and f - d (in Ce_2O_3) gap by using a significantly larger U , which, however, would not improve the

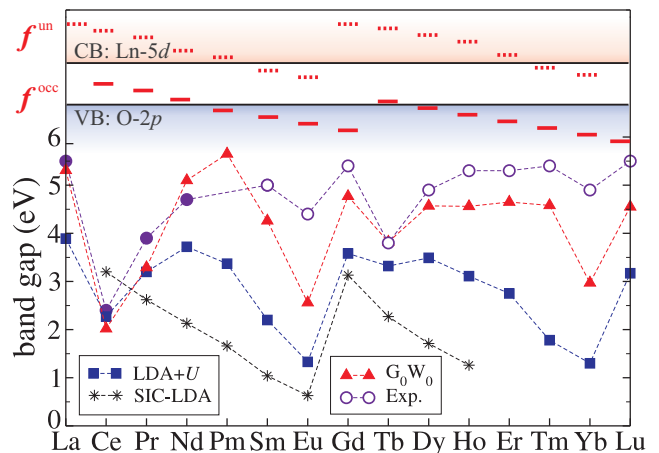


FIG. 3: (Color online) Band gaps of the Ln_2O_3 series from LDA+ U and G_0W_0 ($U=5.4$ eV) are compared to SIC-LDA results [10] and experimental optical gaps [8]. The schematic in the upper part of the figure illustrates the position of the f^{occ} and f^{un} states extracted from the $G_0W_0@LDA+U$ calculations in relation to the valence and conduction band edge (VB and CB).

description of itinerant states including, in particular, the p - d gap.

It has long been recognized that, although many properties of rare-earth compounds exhibit a monotonous behavior across the lanthanide series, some show a striking variation. For example the optical band gaps of rare earth sesquioxides [8] shown in Fig. 3 exhibit clear dips for Ce, Eu, Tb, and Yb, which appear to be unaffected by structural variation across the series. In Fig. 3 the optical gaps of the Ln_2O_3 series [36] are compared to LDA+ U , $G_0W_0@LDA+U$ and previous self-interaction corrected LDA (SIC-LDA) results [10]. Since U is the effective e-e interaction among f -electrons screened by spd states, which are very similar in all Ln_2O_3 compounds, we expect U to be only weakly dependent on the number of localized f -electrons, and therefore use a constant $U=5.4$ eV for the whole series. Compounds denoted by filled circles in Fig. 3 crystallize preferentially in the hexagonal structure, for which all calculations have been performed. Starting from Sm_2O_3 (denoted by open circles), the most stable phase at room temperature is cubic bixbyite, but the middle members can also exist in the monoclinic phase [9].

As can be seen from Fig. 3 all the essential features in the experimental curve are reproduced by the G_0W_0 calculations including the four dips and the behavior in between. Even the quantitative agreement is good for most compounds. In addition our first principles calculations provide easy access to the character of each peak in the DOS and thus the character of the band gap, which is schematically shown in the upper part of Fig. 3. In La_2O_3 (empty f -shell) the band gap is formed between the O- $2p$ valence and the La- $5d$ conduction band. As the occupation of the f -states increases, both f^{occ} and f^{un} continuously move downward in energy and the band gap evolves from p - d via f - d to p - f . This process repeats itself in the second part of the series (starting from Gd_2O_3)

where the spin-up f -states have become fully occupied (and lie deep below the O- $2p$ states) and the spin-down f -states move downward in energy with increasing occupation.

The character of the band gap across the series agrees well with the experimental conjecture derived from phenomenological arguments [7, 8, 38]. This is not the case in SIC-LDA and LDA+ U . Not only does LDA+ U underestimate the band gaps of most Ln₂O₃ compounds, it also only shows a weak minimum at Tb₂O₃ and fails to reproduce the plateau between Ho₂O₃, Er₂O₃, and Tm₂O₃.

The remaining quantitative differences between the G_0W_0 and experimental curve (especially for the later members of the series) could be due to several factors: 1) the experimental error bar, sample quality and instrumental resolution are not known [8]; 2) to exclude the influence of excitonic effects the G_0W_0 results should be compared to photoemission (both direct and inverse) spectra, which are unfortunately not available for most members of the Ln₂O₃ series; 3) spin-orbit and multiplet effects are not taken into account in our calculations; and 4) our G_0W_0 calculations are performed for the hexagonal structure, but the later members of the Ln₂O₃ series (after Ln=Sm) crystallize in the monoclinic or cubic bixbyite structure [6]. Further investigations of these issues will be addressed in the future.

We close this Letter with some remarks about strong correlation. A system is often commonly (but by no means satisfactorily) classified as strongly correlated if DMFT provides an improved description over LDA and it is therefore interesting to compare $G_0W_0@LDA+U$ and LDA+DMFT [5]. Both methods add dynamic (i.e. energy dependent) effects to the LDA+ U Hamiltonian. LDA+DMFT is based on an underlying picture of *localized states*, in which higher order correlation effects among the localized states can be easily incorporated. However, delocalized states (e.g. *spd* states in f -electron systems) are still treated at the LDA level. In contrast, G_0W_0 based on LDA+ U improves upon LDA+ U in the band picture and both localized and itinerant states are treated at the same level (i.e. G_0W_0). For Ce₂O₃ this can be directly quantified by comparing the $G_0W_0@LDA+U$ density of states with that from recent LDA+DMFT calculations by Pourouvsikii *et al.* [20]. The f -states are described in a similar manner, but the p - d gap in LDA+DMFT amounts to only ~ 3.5 eV, which is significantly smaller than the experimental (~ 5.5 eV) and the $G_0W_0@LDA+U$ (~ 5.1 eV) value. For many open d - or f -shell compounds it can therefore be expected that the GW approach can provide a consistent and accurate treatment for both localized and itinerant states and it will be illuminating to see when many-body effects beyond the G_0W_0 approximation become significant.

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U , and its use in $G_0W_0@LDA+U$ will be reported elsewhere.

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