Converged GW quasiparticle energies for transition metal oxide perovskites

Zeynep Ergönenc, Bongjae Kim, Peitao Liu, Georg Kresse, Cesare Franchini

1 Faculty of Physics, Computational Materials Physics, University of Vienna, Vienna A-1090, Austria

The ab initio calculation of quasiparticle (QP) energies is a technically and computationally challenging problem. In condensed matter physics the most widely used approach to determine QP energies is the GW approximation. Although the GW method has been widely applied to many typical semiconductors and insulators, its application to more complex compounds such as transition metal oxide perovskites has been comparatively rare, and its proper use is not well established from a technical point of view. In this work, we have applied the single-shot $G_0W_0$ method to a representative set of transition metal oxide perovskites including 3d ($SrTiO_3$, $LaScO_3$, $SrMnO_3$, $LaTiO_3$, $LaVO_3$, $LaCrO_3$, $LaMnO_3$, and $LaFeO_3$), 4d ($SrZrO_3$, $SrTcO_3$, and $Ca_2RuO_4$) and 5d ($SrHfO_3$, $KTaO_3$ and $NaOsO_3$) compounds with different electronic configurations, magnetic orderings, structural characteristics and bandgaps ranging from 0.1 to 6.1 eV. We discuss the proper procedure to obtain well converged QP energies and accurate bandgaps within single-shot $G_0W_0$, and highlight the difference between the adoption of norm-conserving and ultrasoft potentials in GW calculations. A minimal statistical analysis indicates that the correlation of the GW data with the DFT gap is more robust than the correlation with the experimental gaps; moreover we identify the static dielectric constant as alternative useful parameter for the approximation of GW gap in high-throughput automatic procedures. Finally, we compute the QP band structure and optical spectra within the random phase approximation and compare the results with available experimental data.

I. INTRODUCTION

Transition metal oxide (TMO) perovskites are a widely studied class of materials owing to the wide spectrum of interesting physical and chemical properties including colossal magnetoresistance,\textsuperscript{12} metal-insulator transition,\textsuperscript{3} superconductivity,\textsuperscript{4} two-dimensional electron gas,\textsuperscript{5} multiferroicity,\textsuperscript{6} spin and charge ordering\textsuperscript{7} and different types of anisotropic magnetic interactions.\textsuperscript{18–16} This impressive range of properties and functionalities is the result of two main factors: (i) chemical and structural flexibility and (ii) the occupation and spatial extension of the transition metal $d$ orbitals (see Fig. 1). Oxide perovskites can be formed with cations of different sizes and many different types of lattice and structural distortions can occur owing to the flexibility of the TM-O bond angles. The specific type of $d$ orbitals, instead, modulates the degree of electronic correlation (stronger for localized $3d$ states), electron and spin itinerancy (larger for $5d$) and spin-orbit coupling strength (larger for $5d$ orbitals). The strong interplay between lattice, spin and orbital degrees of freedom leads to a rich structural, electronic and magnetic phase diagram, characterized by highly tunable phase transitions.

One of the most important quantities of materials in general, and specifically for TMO perovskites, is the bandgap, which is essential for the characterization and understanding of the electronic structure and is crucial for virtually all possible practical functionalizations. Experimentally, the optical bandgap is measured using spectroscopy techniques such as photoemission, inverse photoemission, X-ray absorption, Electron Energy Loss Spectroscopy, to name a few. Spectroscopy experiments can be interpreted and simulated using the Green’s function formalism which allows the treatment of excited states beyond the single particle picture.

Density functional theory (DFT)\textsuperscript{17} has been a method of choice for decades to estimate the ground state properties of many materials. Despite its great success in interpreting existing results and predicting experimentally inaccessible properties, DFT is not capable to properly account for the band gap due to the approximation in treating many-body exchange-correlation effects which hinder the correct description and calculation of excitation processes.\textsuperscript{18–19} An elegant and increasingly popular method to overtake the limitations of DFT is the GW approximation, originally proposed by Hedin\textsuperscript{20} which uses single-particle Green’s functions and many-body perturbation theory to obtain the excitation spectrum by explicitly computing the self-energy $\Sigma$ of a many-body system of electrons. This is done by expressing $\Sigma$ in terms of the single particle Green’s function $G$ and the screened Coulomb interaction $W$, i.e. $\Sigma = iGW$. The resulting GW bandgaps are much improved with respect to the DFT ones and often very close to the measured values.\textsuperscript{15,21–23}

In GW calculations, it is common to start from DFT orbitals, with which the initial $G$ and $W$ are constructed. There exist different GW schemes depending on the way $W$ and $G$ are updated. The most common choice is the so-called single-shot $G_0W_0$ starting from DFT orbitals, which usually delivers band gaps in good agreement with experimental measurements.\textsuperscript{24–25} The practical disadvantage of the GW method is the huge computational cost and memory requirements due to the high number of unoccupied bands (and therefore a number of basis functions, $N$) required for the accurate calculation of the self-energy and the response function. The convergence of the QP energies with respect to the number of
basis functions $N$ is, therefore, a particularly crucial issue: even for small systems, such as ZnO, over thousand bands are necessary to achieve well-converged results.\textsuperscript{[22,23]} To address this issue, Klimeš \textit{et al.} have recently proposed a finite-basis-set correction scheme\textsuperscript{[27]} based on the formal proof that QP energies converge like $1/N$.\textsuperscript{[23,25]} Within this scheme, well-converged QP energies extrapolated to the infinite-basis-set limit were obtained for a representative material dataset including 24 elemental and binary semiconductors and insulators.\textsuperscript{[22]} Moreover, the authors pointed out the advantage of using norm-conserving (NC) pseudopotentials (PP), instead of the commonly employed ultrasoft (US) ones, since US-PP were found to severely violate the norm-conservation in the plane-wave representation for high-energy unoccupied orbitals.\textsuperscript{[22]}

These computational limitations have inhibited the application of GW for larger systems like perovskites, despite some efforts devoted to speeding up the GW calculations.\textsuperscript{[11,12]} While there are relatively many GW studies on (non-TMOs) hybrid halide perovskites\textsuperscript{[13,15]} the assessment of GW for TMOs perovskites is scarce, in particular for 4d and 5d perovskites.\textsuperscript{[13,15]} The scope of the present paper is the calculation of accurate QP energies at G$_0$W$_0$ level for a representative dataset of 3d, 4d, and 5d TMOs perovskite with different types and fillings of the TM $d$-orbitals, different crystal structure and lattice distortions and different magnetic orderings (see Tab. I). Specifically, we will consider: 1) Non-magnetic (NM) $d^0$ cubic perovskites: SrMO$_3$ ($M$= Ti, Hf, Zr) and KTaO$_3$; 2) Non-magnetic and structurally distorted 3d$^0$ LaScO$_3$; 3) Magnetic $d^3$ cubic perovskites SrMnO$_3$. Note that to model the G-AFM ordering it is necessary to adapt a supercell containing 4 formula units; 4) Magnetic and structurally distorted systems: (a) 3d LaMO$_3$ ($M$= Ti, V, Cr, Mn, Fe), (b) 4d SrTcO$_3$ and Ca$_2$RuO$_4$, and (c) 5d NaOsO$_3$ (in this case we have included spin-orbit coupling, SOC).

We will inspect and compare two different procedures to compute QP energies and bandgaps: (i) In the first scheme the QP energies are obtained by progressively increasing the size of the plane wave basis set $N$, the number of k-points and the cutoff energy for the plane wave expansion, without any extrapolation, and (ii) the basis set corrected method with QP energies extrapolated to $N \rightarrow \infty$.

Also, we will hand over a minimal technical set-up to achieve sufficiently well-converged calculations in standard GW calculations without basis-set extrapolation, which we will adopt to compute band structures, obtained by employing Wannier-function fitting of the QP energies (not feasible within the basis-set correction scheme), and optical spectra calculated from the frequency dependent dielectric tensor. In addition, we will test and discuss the choice of the PP by comparing US- and NC-based results.

The paper is organized as follows: the first part is focused on the description of the two convergence procedures and on the computational setup. The main core of this article is the result section that is divided into three parts dedicated to the analysis of the convergence criteria, on the correlation analysis and on the discussion of the electronic structure and optical spectra.

![FIG. 1. Different types of lattice distortions (a-d) and TM $d$ orbitals (e) in the oxide perovskites studied in this paper. (a) $P_{m_3m}$ for SrMO$_3$ ($M$= Sr, Hf, Zr), SrMnO$_3$ and KTaO$_3$; (b) $P_{mmn}$ for LaScO$_3$, LaTiO$_3$, LaCrO$_3$, LaMnO$_3$, LaFeO$_3$, SrTcO$_3$, NaOsO$_3$; (c) $P_{21m}$ for LaVO$_4$; (d) $P_{mma}$ for Ca$_2$RuO$_4$. The blue and red balls represent the TM and O ions, respectively. (e) Different degree of spatial extension in 3d, 4d, and 5d orbitals (derived from atomic calculations).]

## II. TECHNICAL AND COMPUTATIONAL DETAILS

The calculations presented in this paper were conducted using the Vienna Ab Initio Simulation Package (VASP)\textsuperscript{[62,63]} in the framework of the projector augmented wave method (PAW).\textsuperscript{[62]} The many-body Schrödinger equation was solved within the single-shot G$_0$W$_0$ approximation starting from DFT orbitals using the generalized gradient parametrization introduced by Perdew, Burke, Ernzerhof (PBE).\textsuperscript{[63]} When the GGA was not able to open the gap a small on-site Hubbard $U$ was added following the scheme of Dudarev\textsuperscript{[62]} (LaTiO$_3$ and LaVO$_4$, $U$−$J$ = 2 eV). The one particle Green’s function constructed from PBE eigenfunction and the dynamically screened Coulomb interaction $W$ was computed from G$_0$ within the random phase approximation (RPA). For the calculation of the polarizability, we have used a discretized frequency grid with about 70 frequency points. We have used crystal lattices and atomic posi-
TABLE I. Fundamental characteristic of the TMO perovskites dataset used in this study. Crystal structures: C = cubic, T = tetragonal, O = orthorhombic, M = monoclinic; Electronic configuration of the transition metal d-shell decomposed over \( t_{2g} \) and \( e_{g} \) states; ground state magnetic ordering: NM = nonmagnetic, and different type of antiferromagnetic (AFM) spin configuration. The crystal structures and atomic positions are taken from the following experimental works: SrTiO$_3$ Ref. [47], SrZrO$_3$ Ref. [48], SrHfO$_3$ Ref. [49], KTaO$_3$ Ref. [50], SrMnO$_3$ Ref. [51], LaScO$_3$ Ref. [52], LaTiO$_3$ Ref. [53], LaVO$_3$ Ref. [54], LaCrO$_3$ Ref. [55], LaMnO$_3$ Ref. [56], LaFeO$_3$ Ref. [57], SrTiO$_3$ Ref. [58], Ca$_2$RuO$_4$ Ref. [59], NaOsO$_3$ Ref. [60]. For SrMnO$_3$ we have (erroneously) adopted the calculated lattice constant for the G-type AFM cubic phase, 3.824 Å, slightly larger than the corresponding experimental value, 3.80 Å.

| SrTMO$_3$ (TM= Ti, Zr, Hf) | KTaO$_3$ | LaScO$_3$ | SrMnO$_3$ | LaTiO$_3$ | LaVO$_3$ | LaCrO$_3$ | LaMnO$_3$ | LaFeO$_3$ | SrTiO$_3$ | Ca$_2$RuO$_4$ | NaOsO$_3$ |
|-----------------------------|----------|------------|------------|-----------|---------|---------|---------|---------|---------|------------|----------|
| C-P$_{3cm}$ | C-P$_{3cm}$ | O-P$_{m}$ | C-P$_{3cm}$ | O-P$_{m}$ | M-P$_{21}/b$ | O-P$_{nn}$ | O-P$_{nn}$ | O-P$_{nn}$ | O-P$_{nn}$ | O-P$_{nn}$ | O-P$_{nc} |
| \(d^0\) | \(d^0\) | \(d^0\) | \(t_{2g}\) | \(t_{2g}\) | \(t_{2g}\) | \(t_{2g}\) | \(t_{2g}\) | \(t_{2g}\) | \(t_{2g}\) | \(t_{2g}\) | \(t_{2g}\) |

The convergence criteria followed to calculate the response function and the correlation part of the self-energy, which requires a summation over many empty states, as well as the dependence of the results with respect to the size of the \( k \)-points sampling are discussed in the next subsections II A and II B. We have followed and compared two alternative strategies to reach converged results: (i) so-called non-extrapolated method because it does not involve any extrapolation to large \( N \); we refer to this method as conventional, since this is the scheme typically used in GW calculations. (ii) The basis set corrected method which does include an extrapolation of the QP energies to \( N \to \infty \).

A. The conventional non-extrapolated method

The conventional method consists on the convergence of the QP energies (and therefore of the QP energy gap \( E_g \)) with respect to a set of three parameters: number of bands \( N \), energy cutoff for the plane wave expansion (ENCUT) and the number of \( k \)-points. This procedure is schematically shown in Fig. 2. First, \( E_g \) is computed as a function of \( N \) for fixed values of ENCUJT and \( k \)-points [see Fig. 2(a)]. Then, by fixing \( N \) and ENCUJT to the optimum values which guarantee converged results within the required accuracy, \( E_g \) is converged with respect to the number of \( k \)-points [see Fig. 2(b)]. This scheme can lead to sufficiently well-converged results (as we will see later on), but it does not allow for a formally correct extrapolation to infinite \( N \). Within the conventional method some fitting procedures for extrapolating the QP energies for \( N \to \infty \) have been used in literature [27,41,42,43]; the exactness of this, however, is not supported by a mathematical proof.

Recently, inspired by similar convergence problems occurring in quantum chemistry calculations [58], Klimeš et al. have provided an explicit derivation which demonstrates that QP energies show a convergence proportional to the inverse of the number of basis functions and introduced the finite-basis-set correction method [27], which is briefly described in the next section. An important difference between these two approaches is that in order to perform a correct extrapolation it is necessary to work with the complete set of basis functions compatible with the given energy cutoff, implying that varying \( N \) for a fix energy cutoff as done in the conventional scheme is not a formally correct practice.

B. The basis-set extrapolation

The core aspect of the finite-basis-set correction method derived in Ref. [27] is that the (orbital-dependent) leading-order error of the QP energy \( \Delta E \) decays asymptotically with the inverse of the number of plane waves:

\[
\Delta E_m = \frac{2}{g\pi N_{pw}} \sum_{\mathbf{g}} \rho_m(\mathbf{g})\rho(-\mathbf{g}).
\]

Here, \( m \) is the orbital index, \( \mathbf{g} = \mathbf{G} - \mathbf{G}' \) (where the vectors \( \mathbf{G} \) are three-dimensional reciprocal lattice vectors of a cell with volume \( \Omega \), \( \rho \) and \( \rho_m \) are the total and orbital density in reciprocal space, respectively, and \( N_{pw}^m \) is the number of auxiliary basis-set functions used to represent density related quantities, that is controlled by a plane-wave cutoff \( E_{pw}^m \) (ENCUT in VASP). A similar expression can be derived for the dependence of the QP energies with respect to the number of unoccupied orbitals \( N_{pw} \) (restricted by the plane-wave cutoff \( E_{pw} \), ENCUJT in VASP). This brings to another important result: both

![Fig. 2](image-url)
the number of unoccupied bands $N_{pw}$, the corresponding orbital basis set $N$, and the size of the auxiliary basis set $N^A_{pw}$ need to be increased simultaneously at the same rate, meaning that fixing $E_{pw}^x$ and converge only with respect to $E_{pw}$ is not a good protocol.\(^ {27}\)

In our work we adopt the choice $E_{pw}^x = 2/3E_{pw}$ (ENCUT/GW = 2/3ENCUT in VASP) and we have used a complete basis set for the given $E_{pw}$, meaning that we have always included all plane waves with energies smaller than $E_{pw}$, quantified by the relation $N_{pw} \approx 2\frac{1}{\Delta \nu} E_{pw}^{3/2}$ (in VASP this is given by the maximum number of plane-waves per irreducible $k$-point). $E_{pw}$ was initially set to the maximum plane-wave energy cutoff used to build the element-specific PP in the considered material (the values, for US and NC PPs, are listed in Tab. III). In practice, we have systematically increased ENCUT until the corresponding total number of plane-waves become twice larger than the initial value (corresponding to the default ENCUT).

$$E_{\infty}(n_k, N) \approx E_{\infty}(N_k, N) - E(n_k, N) + E(N_k, N),$$

where $E(N_k, N)$ refer to the calculated QP energies with $N_k$ $k$-points and $N$ bands; the variables $n_k$ and $N_k$ indicate the number of $k$-points in the small and large $k$-points mesh, respectively. $\Delta_\nu(N) = E(N_k, N) - E(n_k, N)$ is the $k$-points correction and $\Delta_\nu(n_k) = E_{\infty}(n_k, N) - E(n_k, N)$ the basis-set correction. The graphical interpretation of the basis-set and $k$-points corrections is given in Fig. 3. Owing to the weak $k$-points dependence on the basis-set correction ($\Delta_\nu(n_k) \approx \Delta_\nu(N_k)$), in practice it is computationally more convenient to extrapolate $\Delta_\nu$ using a small $k$-points. Similarly, as $\Delta_\nu(N)$ is almost independent on $N$, the $k$-points correction computed for a small $N$ makes the computation less expensive. For the calculations presented in this paper we have used $n_k = 2 \times 2 \times 2$ and $N_k = 6 \times 6 \times 6$, with some exceptions specified in the text later on.

### C. Pseudopotentials

By extending the expression of the basis-set correction for the PAW method Klimeš et al. have recognized that using US-PP the correction converges to the wrong value, due to the incompleteness of the partial waves inside the atomic sphere.\(^ {23}\) The authors found that this error becomes smaller if the difference between the norm of the all-electron partial waves and the pseudized partial waves is small. This implies that the choice of the PP is critical and that the best results are obtained by using NC-PP, for which the norm is almost fully conserved. As shown in Tab. III the deviation between the all-electron and the pseudized norm, quantified by the difference $\delta_d = |\psi_{d_{AE}}^2| - |\psi_{d_{US}}^2|$ between the all-electron (AE) and US-pseudized norm of the $d$ orbitals, is larger for the more spatially localized $3d$ orbital and is substantially reduced for more extended and smoother $4d$ and $5d$ orbitals (see also Fig. 1(e)). Therefore we expect that the basis-set correction error should be larger for $3d$-based perovskites compared to $4d$ and $5d$ perovskites.

To inspect the influence of the choice of the PP on the basis-set correction results we have tested both types of PPs, US, and NC. For the TM ions, we have used GW-PP with the outermost $s, p$ and $d$ orbitals treated as valence states. The NC PAW potentials were constructed following the prescription described elsewhere.\(^ {24}\)

### III. RESULTS AND DISCUSSION

This section presents and discusses the results obtained for our TMOs perovskite dataset (see Tab. I). It is structured in three parts: the first one focuses on the application of the convergence schemes described above to a subset of representative compounds. In the second one, we provide a minimal statistical interpretation of the data obtain and finally the third section is dedicated to the calculation of the band structure and optical spectra for all compounds.
A. Convergence tests and extrapolations

In the following we show the results on the applications of the two convergence schemes, conventional non-extrapolated and basis-set extrapolation, for selected 3d, 4d, and 5d cases: (i) cubic NM SrTiO$_3$ (3d), SrZrO$_3$ (4d) and SrHfO$_3$ (5d) and (ii) structurally distorted and magnetically ordered SrMnO$_3$ (3d), SrTeO$_3$ (4d) and NaOsO$_3$ (5d). The complete set of results is given in the Supplemental Materials (SM).

1. Cubic non-magnetic systems

We start showing and examining the results for 3d SrTiO$_3$ and then we will extend the discussion by including the data for SrZrO$_3$ and SrHfO$_3$. In all these materials the gap is opened by the filled O-$p$ states at the valence band maximum (VBM) and empty TM-$d$ states at the conduction band minimum (CBM).

![Fig. 4](image)

**FIG. 4.** Conventional non-extrapolated method applied to SrTiO$_3$. Convergence of the indirect QP band gap $E_g$ of SrTiO$_3$ with respect to (a) number of bands $N$ and plane-wave cutoff energy ENCUT (k-point mesh fixed to 4×4×4), and (b) size of the k-point mesh for $N$ and ENCUT fixed to the optimum values for US and NC PP. The filled triangle indicate the experimental bandgap.

First, we show the convergence behavior of SrTiO$_3$ using the conventional non-extrapolated scheme by inspecting the variation of the QP indirect gap $E_g$ ($\Gamma$-$\Gamma$, highest occupied state at $\Gamma$ and the lower unoccupied state at $\Gamma$) as a function of $N$, ENCUT and number of k-points, using both US and NC PP. Similar results and conclusions are obtained for QP band energies, but since we are primarily interested in the behavior of the bandgap the discussion and analysis will be focused on the direct and indirect bandgap (i.e. differences of QP energies).

The results are displayed in Fig. 4. From panel Fig. 4(a) we note that using US-PP the results are largely sensitive on $N$, and to a lesser extent on ENCUT, and well-convolved values are achieved for $N \approx 1500$ and ENCUT $\approx 600$ eV. By employing NC-PP the convergence with respect to $N$ is much faster, $N \approx 1000$ is sufficient to obtain the same level of accuracy obtained at US level. However, owing to the generally larger default ENCUT for NC-PP (see Tab. II) it is computationally prohibitive to scan higher values of the cutoff energy. The dependence of $E_g$ on the number of k-points, displayed in Fig. 4(b) shows that a 4×4×4 is sufficient to achieve an accuracy of about 0.03 eV.

The final values of the US and NC indirect bandgaps $E_g$ are 4.06 eV (almost identical to the one reported in Ref. [41] using the same scheme) and 3.55 eV, respectively, differ by about 0.5 eV and are both larger than the measured value, 3.3 eV (see Tab. III). This is due to the relatively large norm-violation for the Ti US-PP, 0.2, which causes a very different QP shift of the empty d states at the bottom of the conduction band in US- and NC-based calculations (0.68 meV, see Tab. III). On the other side the difference in the QP shift between NC and US calculations is substantially reduced for the top of the valence band, mostly populated by O-$p$ state, 0.11 eV, see Tab. III. This issue will be further discussed in the context of the data obtained using the basis-set extrapolation, at the end of this subsection.

![Fig. 5](image)

**FIG. 5.** Basis-set correction data for SrTiO$_3$ using US (panels a, b, and c) and NC (panels d, e, and f) PP. For each type of PP three different graphs are shown: (a,d) convergence of the QP band gap $E_g$ with respect to the inverse of the number of bands (1000/N); (b,e) k-point correction $\Delta_{N}$ as a function of 1000/N; (c,f) basis-set correction $\Delta_{N}$ as a function of 1000/N.

The basis-set extrapolated data for SrTiO$_3$ are collected in Fig. 5, where we show the evolution of $E_g$ and the k-points corrections upon $N$, as well as the basis-set correction $\Delta_{N}$.
TABLE III. Collection of data related to the convergence tests for selected 3d, 4d, and 5d perovskites (cubic-NM and distorted-AFM, see text). Energy differences between the US and NC QP energies at the conduction band minimum (CBM) and valence band maximum (VBM) at Γ

$$\Delta E_{Q-P} = |E_{Q-P}^{\text{CBM}} - E_{Q-P}^{\text{VBM}}|$$

and

$$\Delta E_{Q-P} = |E_{Q-P}^{\text{CBM}} - E_{Q-P}^{\text{VBM}}|$$

the norm-violation quantity $\delta$ (same as in Tab. III), the non-extrapolated (nE) and extrapolated (E) value of the indirect bandgap $E_g$, the basis-set correction $\Delta N$ and the k-point correction $\Delta k$ (evaluated with a reduced number of k-point $n_k = 2 \times 2 \times 2$ and $N=400 - 500$, respectively). $E_g$, $\Delta N$ and $\Delta k$ are provided for both type of PP (US and NC). Within the conventional method, we have used NC PP only for the representative case of SrTiO$_3$. For non-$$^d$$ compounds SrMnO$_3$, SrHfO$_3$, NaOsO$_3$ (without, wo, SOC), the amount of $\delta$ character in the conduction and valence band is also given (data listed in the additional row below the main list). Available experimental data for the gap are also listed. All energies are given in eV.

| Compound   | $\Delta E_{Q-P}^V$ | $\Delta E_{Q-P}^C$ | $\delta$ | $\Delta N$ | $\Delta k$ | $E_g$ (nE) | $E_g$ (E) | $E_g^{\text{Expt}}$ |
|------------|-------------------|-------------------|----------|------------|------------|-------------|-------------|------------------|
| SrTiO$_3$  | 0.11              | 0.68              | 0.20     | 0.20       | 0.01       | 0.56        | 0.59        | 4.08             |
| SrZrO$_3$  | 0.11              | 0.04              | 0.02     | 0.14       | 0.18       | 0.36        | 0.36        | 5.29             |
| SrHfO$_3$  | 0.10              | 0.09              | 0.03     | 0.19       | 0.12       | 0.34        | 0.36        | 5.69             |
| SrMnO$_3$  | 0.27              | 0.43              | 0.4      | 0.03       | -0.03      | 0.23        | 0.31        | 1.75             |
| SrTcO$_3$  | 0.46              | 0.9               |          |           |            |             |             |                  |
| NaOsO$_3$  | 0.30              | 0.33              | 0.1      | 0.01       | 0.02       | -0.13       | -0.14       | 1.14             |
|            | 0.68              | 0.66              |          |           |            |             |             | 1.18             |
|            | 0.62              | 0.66              |          |           |            |             |             | 0.28             |

![Graphs and diagrams](image-url)

FIG. 6. $E_g$, and QP corrections to Kohn-Sham eigenvalues for the CBM and VBM at Γ as a function of $N$ for SrTiO$_3$ (a,d), SrZrO$_3$ (b,e) and SrHfO$_3$ (c,f), computed within the basis set correction scheme using a 2×2×2 k-points mesh. The filled triangles indicate the position of the experimental gaps.

as a function of the size of the k-points mesh. We highlight once more that here $N$ refers to the maximum number of plane-waves compatible to a given plane-wave cutoff energy $E_{pw}$ (controlled by ENCUT). In this case (SrTiO$_3$) we have gradually increased $N$ from 1200 to about 2500 using US-PP ($E_{pw}$=434 eV), and from 3000 to 6000 using NC-PP ($E_{pw}$ is significantly larger for NC-PP, 785 eV, which leads to a much larger number of basis functions), and inspected the convergence for three different k-point meshes: 2×2×2, 4×4×4, and 6×6×6. The curves plotted in Fig.6a, d) clearly indicate that $E_g$ converges linearly with respect to $1/N$ for both type of PP. Notably, the values of $E_g$, in particular its $N \rightarrow \infty$ extrapolation, varies with the number of k-points but the k-points correction $\Delta k (\approx 600 \text{ meV})$ depends only marginally on $N$ [see Fig.6b,e] and Tab. III, which represents one of the great advantage of this extrapolation scheme: $\Delta k$ can be quantified using a small $N$ (the default value) thereby reducing the computational cost of the calculation. Moreover, $\Delta k$ does not depends on the type of PP used but it is sensitive to the specific k-point of the QP energy for which the correction is calculated: for $E_g$, $\Delta g$ is 600 meV, but the corresponding correction for the direct gap at $\Gamma$, $E_{\Gamma}^g (\Gamma - \Gamma)$ gap is reduced by about 100 meV. A further positive aspect of this convergence scheme is that the basis-set correction $\Delta N$ does not vary much with the size of the k-point mesh [Fig.6c,f]: $\Delta N$ can be evaluated using a small k-points mesh, typically 2×2×2, which also helps in decreasing the CPU time. However, unlike $\Delta k$ which is essentially insensitive to the choice of the potential, $\Delta N$ is one order of magnitude smaller for NC-PP (0.01 eV against 0.2 eV, see Tab. III), highlighting the robustness of the NC-based calculations. Also, the NC value of the fundamental gap, 3.55 eV (the same for both the conventional and the extrapolated method), is in better agreement with the measured value, 3.3 eV, as compared to the US gaps, which are substantially larger (3.94 eV and 4.08 eV, see Tab. III).

The convergence tests for the other two members of the
The most important result that one notices is that the difference between NC and US data is strongly attenuated for the large norm-violation $\delta$ (see Tab. III). This result can be readily explained by the much lower norm-violation $\delta_d$ in 4d Zr (0.02) and 5d Hf (0.03) as compared to 3d Ti (0.2), which originates from the smoothness of the 4d and 5d orbitals as compared to the more localized nature of 3d orbitals (see Fig. 1). This conclusion correlates well with the behavior of the QP corrections shown in Fig. 6, in particular by looking at the differences between the US and NC QP corrections at the CBM.

The most important result that one notices is that the difference between NC and US data is substantially reduced for SrZrO$_3$ and SrHfO$_3$, as compared to SrTiO$_3$. As already mentioned, the difference in $\Delta_N$ between NC and US energies in SrTiO$_3$ is more than one order of magnitude, whereas for SrZrO$_3$ and SrHfO$_3$ it is almost zero: US and NC PP calculations deliver roughly the same $\Delta_N$ for both materials, $\approx 0.15$ eV (see Tab. III). This result can be readily explained by the much lower norm-violation $\delta_d$ in 4d Zr (0.02) and 5d Hf (0.03) as compared to 3d Ti (0.2), which originates from the smoothness of the 4d and 5d orbitals as compared to the more localized nature of 3d orbitals (see Fig. 1). This conclusion correlates well with the behavior of the QP corrections shown in Fig. 6, in particular by looking at the differences between the US and NC QP corrections at the CBM.

and VBM at $\Gamma$, defined as $\Delta E^c_{QP} = |E^c_{QP,CBM} - E^c_{QP,VBM}|$ and $\Delta E^v_{QP} = |E^v_{QP,CBM} - E^v_{QP,VBM}|$: for the Ti-3d empty states $\Delta E^c_{QP}$ is 0.68 eV, whereas for Zr and Hf $d^5$ states as well as for the highest occupied O-$p$ states $\Delta E^c_{QP}$ and $\Delta E^v_{QP}$ are in the range 0.05-0.1 eV. The exact values are listed in Tab. III.

In terms of band gaps, US and NC lead to similar values, in particular for 5d SrHfO$_3$ (5.36 eV and 5.43 eV, respectively) in satisfactory agreement with the available experimental estimates (see Tab. III).

To conclude this part, we have shown that the type of convergence scheme, the type of potential employed in the calculations and the type of TM $d$-orbital affect the QP energies and therefore the final 'converged' value of the band gap. Overall, we have tested four different procedures to compute the gap: conventional scheme (no extrapolation, labeled 'nE' in Tab. III) and basis-set extrapolation (labeled 'E') using US or NC PP. As mentioned before, nE-NC calculations were only done for SrTiO$_3$. The main conclusion is that extrapolated-NC values agree better with the experimentally measured data, in particular for 3d SrTiO$_3$ for which the large norm-violation leads to an overestimation of the gap. For 4d SrZrO$_3$ and 5d SrHfO$_3$ the difference between NC and US is strongly attenuated and the final extrapolated values of the gap are almost identical. Also, our results suggest that there are not pronounced differences in gap between two schemes for a specific type of PP: two schemes yield identical the gap for SrTiO$_3$, 3.55 eV (see Tab. III). Qualitatively similar results are obtained for the larger and magnetically order 3d, 4d, and 5d systems, as discussed below.

2. Large magnetic systems

We show here the convergence tests for the basis-set extrapolation scheme applied to the $t_{2g}$ series SrMnO$_3$, SrTcO$_3$, and NaOsO$_3$. For the other compounds included in our dataset as well as for the data obtained using the conventional scheme, we will only discuss the converged values of the gap and compare them to available experimental measurements. Further details and graphs can be found in the Supplemental Materials (SM) and in Ref. [75].

The unit cells used to model SrMnO$_3$, SrTcO$_3$, and NaOsO$_3$ contain four formula units (20 atoms), which are necessary to model the internal structural distortions and the antiferromagnetic ordering (see Tab. I). This leads to an increase of the number of basis functions and, therefore, to more substantial memory requirements and computing times. As a result, the calculations become technically heavier and almost prohibitive for NC-based calculations. Due to this computational limitation, in some cases, we have performed the NC-based extrapolation using only 2 or 3 points (see Fig. 7 and SM).

The trend of the QP energies and gaps for this series is plotted in Fig. 7. For US-PP calculations we have inspected the $N$ range from $\sim 5000$ up to $\sim 10000$ in about 10 steps (a denser mesh has been used for the largest $N$ in order to improve the extrapolation for $N \to \infty$); however, for NC calculations due to the computational restrictions mentioned above we could...
The violation of the norm is much larger for 3d Mn (0.4) compared to 4d Tc and 5d Os (0.1), which explains the bigger difference between NC and US results in SrMnO$_3$ as compared to SrTcO$_3$ and NaOsO$_3$, particularly evident for the QP gap shown in the top part of Fig. 7. Unlike $d^0$ cubic perovskites, for this $t_2^3$g series the difference between NC and US PP is not limited to the bottom of the conduction band, but is also manifested at the top of the valence band that has a strong $d$ character. This is shown in the bottom panels of Fig. 7 which displays the QP corrections at US and NC level for the VBM and CBM. The energy shifts $\Delta E^{\text{QP}}_{\text{V}}$ and $\Delta E^{\text{QP}}_{\text{C}}$ that measure the differences between the US and NC QP corrections at the CBM and VBM tabulated in Tab. III shows that in SrMnO$_3$ the difference is larger for the CBM (0.43 eV and 0.27 eV, for the CBM and VBM respectively), whereas in SrTcO$_3$ and NaOsO$_3$ the deviation is about the same for filled and empty states, $\approx 0.3$ eV. This behavior can be explained by the amount of $d$ states present in the CBM and VBM, which is also listed in Tab. III (see the additional row for SrMnO$_3$, SrTcO$_3$ and NaOsO$_3$): in SrTcO$_3$ and NaOsO$_3$ the CBM and VBM possess about the same amount of $d$ states, $\approx 0.6$, but in SrMnO$_3$ the CBM is almost completely formed by Mn-$d$ states, 90%, twice larger than the $d$-population at the valence band, 46%.

As expected from the above considerations, the final values of the extrapolated gap for this sub-series are about the same regardless of the type of potential employed in the calculations, and going from 3d (SrMnO$_3$) to 5d (NaOsO$_3$) the difference between conventional and basis-set correction scheme is much attenuated. This outcome is qualitatively similar to the situation discussed for the 3d, 4d, and 5d cubic non-magnetic perovskites (see Tab. III).

The complete collection of bandgaps for the entire series of perovskites considered in our study is compiled in Tab. IV. A graphical summary of the comparison between the computed (GW and DFT) and available photoemission and inverse photoemission spectroscopy measurements is provided in Fig. 8. The technical parameters (energy cutoff, number of k-points and number of bands $N$) that guarantee well converged QP energies (accuracy $\leq 5$ meV) within the conventional non-extrapolated scheme are listed in Tab. V.

Clearly, GW outperforms DFT, which underestimates the gaps by more than 50% and, in some cases (NaOsO$_3$, LaTiO$_3$, and LaVO$_3$) finds a metallic solution. This is a well-known behavior that has been widely discussed in literature.
Regardless of the specific convergence scheme and type of potential, the GW gaps are in overall good agreement with experiment. However, we should note that the experimental data must be treated with care because perovskite materials can often exhibit oxygen deficiencies that unavoidably alter the value of the gap. In addition to this, we should also mention that the GW gap refers to the fundamental gap, meaning that excitonic effects are not taken into account. The calculation and the experimental estimation of electron-hole interactions are not an easy task and remain a largely unexplored issue in TM perovskites.

**B. Statistical correlations**

Even though the material data set under scrutiny is limited to 14 compounds, a minimal statistical analysis of the results could be in any case useful, in particular considering the complexity of the systems, the degree of accuracy of the method adopted and the increasing interest in automatizing first-principles calculations within a high-throughput framework. To this aim, we have inspected possible correlations between different types of identifiers: QP gap, QP shift, DFT gap and the static dielectric constant \( \epsilon_\infty \). The results are summarized in Fig. 9 First, we note that there is a relatively strong correlation, \( \sim 0.97 \), between the calculated and experimental gaps, regardless of the specific GW flavor (NC-PP extrapolated data are slightly better than the others) and the correlation is essentially identical in between GW and DFT [see Fig. 9(a)]. This result is in line with the very recent results of van Setten and coworkers, who found a correlation of 0.962 (GW) and 0.957 (DFT) for a larger set of 77 materials including monoatomic and binary semiconductors. In the insets of Fig. 9(a) we provide the linear relations to reproduce the experimental gap starting from the calculated band gaps.

**TABLE V.** Set of parameters (energy cutoff ENCUt, \( k \)-points mesh and a number of bands \( N \)) used for the calculation of the band structures and optical spectra at \( G_0W_0 \) level within the non-extrapolated scheme. This setup guarantees well-converged QP energies within a accuracy less than 0.05 eV. All of the parameters are for US PP except \( \text{SrTiO}_3 \) where NC PP is used.

| Compound     | ENCUt (eV) | \( k \)-points mesh | \( N \) |
|--------------|------------|---------------------|--------|
| \( \text{SrTiO}_3 \) | 600        | 4x4x4               | 512    |
| \( \text{SrZrO}_3 \) | 650        | 4x4x4               | 1791   |
| \( \text{SrHIO}_3 \) | 650        | 4x4x4               | 2304   |
| \( \text{KTaO}_3 \) | 500        | 4x4x4               | 896    |
| \( \text{SrMnO}_3 \) | 500        | 4x4x4               | 400    |
| \( \text{SrCoO}_3 \) | 500        | 5x3x5               | 512    |
| \( \text{CaRuO}_3 \) | 500        | 4x4x4               | 512    |
| \( \text{NaOsO}_3 \) | 500        | 5x3x5               | 400    |
| \( \text{LaScO}_3 \) | 500        | 5x5x3               | 1280   |
| \( \text{LaTiO}_3 \) | 500        | 5x3x5               | 400    |
| \( \text{LaVO}_3 \) | 500        | 5x3x5               | 400    |
| \( \text{LaCrO}_3 \) | 500        | 5x3x5               | 400    |
| \( \text{LaMnO}_3 \) | 500        | 5x3x5               | 400    |
| \( \text{LaFeO}_3 \) | 500        | 5x3x5               | 400    |

US and NC data are generally very similar, apart from the 3d systems, in particular, titanates \( \text{SrTiO}_3 \) and \( \text{LaTiO}_3 \), for which the US gaps are larger by about 15% with respect to the NC values and, to a lesser extent, \( \text{LaCrO}_3 \), \( \text{LaFeO}_3 \), \( \text{LaMnO}_3 \) where the difference reduced to \( \approx 10\% \).: clearly, the discrepancy is correlated with the difference \( \delta_d \) between the all-electron and pseudized norm of the \( d \) orbitals, which is larger for \( d \) elements (as discussed previously, see Tab. II). Finally, the comparison between extrapolated and non-extrapolated schemes (here inspected for US PP only) confirms that these two convergence methods lead to similar results for the entire TM perovskite dataset, with differences of about 0.1 eV; the only exception is \( \text{LaScO}_3 \) for which the non-extrapolated value of the gap is 0.3 eV smaller than the extrapolated one. We reaffirm, however, that only the basis-set correction scheme is founded on a solid mathematical derivation and is, especially for US PP, computationally more efficient than the non-extrapolated scheme as it reduces the number of calculations to be performed with a large number of bands and \( k \)-points.

**FIG. 9.** Statistical interpretation of the GW data by means of a regression obtained using an ordinary least square minimization. (a) Comparison between the calculated and experimental gaps. The calculated values include \( G_0W_0 \) results obtained following the different schemes discussed in the main text: conventional non-extrapolated scheme using US PP and the basis-set correction procedure using both NC and US PP. (b) Correlation between the \( G_0W_0 \) and the DFT gap. (c) Correlation between the \( G_0W_0 \) gap and the calculated static dielectric constant \( \epsilon_\infty \). (d) Comparison between the \( G_0W_0 \) gap at \( \Gamma \) and the corresponding QP shift. In each panel the linear relation and the \( R^2 \) factors are given in the insets.

In agreement with the conclusions of Ref. 83, we confirm that also for TMO perovskites the correlation between the GW and DFT gap, 0.99, [see Fig. 9(b)] is larger than the correlation between the calculated and experimental gap [see Fig. 9(a)], meaning that it is more accurate (smaller average error) to reproduce the GW gap starting from PBE gap than to approxi-
mate the experimental gap based on GW data.

Importantly, we found that the static dielectric constant $\varepsilon_\infty$ (the average of the diagonal part of the static dielectric tensor, see next section for more details) is another important identifier that can be used to improve the quality of high-throughput automatic GW calculations. In fact, the correlation between the $G_0W_0$ gap and $\varepsilon_\infty$ is rather large, 0.99, implying that the knowledge of the dielectric constant can be efficiently used to approximate GW gaps [see Fig. 9(c)]. Even though the linear relation between the GW gap and $\varepsilon_\infty$ is advantageous, the accurate calculation or measurement of $\varepsilon_\infty$ is not an easy task. A viable alternative could be to start from dielectric functions calculated by means of hybrid functionals, which have been shown to provide dielectric properties in generally good agreement with experiment.

Finally, we have also explored the possible relation between GW gaps and QP shifts, but the results indicate that in this case, the correlation is only 0.88 as shown in Fig. 9(d).

To conclude this part we collect in Fig. 10 the various identifiers used for the statistical analysis: band gap, QP shift and $\varepsilon_\infty$. The cubic $d^0$ compounds exhibit the largest gaps (4-6 eV) and the largest QP shifts ($\approx 1.5$ eV). In the 3$d$ series the gap $E_g$ decreases progressively depending on the filling of the $d$ orbitals (larger, 1.7-3 eV, for half-filled systems) and so does the QP shift (1.5-0.6 eV). Finally for 4$d$ and 5$d$ compounds with partially filled $d$ bands the direct gap at $\Gamma$ is $\approx 1$ eV, and the corresponding QP shift is about 0.5 eV. Summing up, for less correlated $d^0$ and 4-$5d$ materials the QP shift is roughly 25% of the direct gap, whereas in the more correlated 3$d$ perovskites the QP shift increases to 50-60% of the gap. As expected, the dielectric constant follows an opposite trend: increases with decreasing gap size and approaches a metallic-like limit for NaOsO$_3$ (which is on the verge of a Lifshitz insulator-to-metal transition) for which $\varepsilon_\infty \approx 27$.

### C. Band Structures and Optical Spectra

After having analyzed in details the convergence of the QP energies in the $G_0W_0$ method we turn now on the calculation of the electronic band structure and optical spectra for the considered TM perovskite dataset. To this aim we have used US PP and the non-extrapolated scheme according to the technical set-up given in Tab. [V]. In fact, for the calculation of the band structure the basis-set correction scheme is impractical because it would be necessary to apply the extrapolation procedure to each QP energy using a sufficiently large k-points mesh (required for the Wannier interpolation, see below). This would clearly result in a cumbersome procedure, and the need to use many k-points would wipe out the advantages of the k-points correction scheme.

Due to technical reasons related to the k-points sampling, it is presently not possible to calculate the QP energies for non-uniform k-points mesh in the GW method. A common alternative is the interpolation of the QP energies obtained for a uniform mesh using maximally localized Wannier functions (MLWF); in VASP this is done by using the VASP2WANNIER90 interface which connects VASP with the Wannier90 suit. We have followed this approach for the calculation of the band structures, and used as an orbital basis for the Wannier projections the full $d$ manifold of the TM ion ($e_g$ and $f_{2g}$) and the O-$p$ states. This choice is adequate to accurately describe the electronic bands in a few eV windows around the Fermi energy, as for all materials the top part of the valence band has mixed O-$p$/TM-$d$ character and the bottom portion of the conduction band is generally dominated by empty TM-$d$ states (see SM).

| Compound    | VBM O-$p$ | VBM TM-$d$ | CBM O-$p$ | CBM TM-$d$ |
|-------------|-----------|------------|------------|------------|
| SrTiO$_3$   | 0 %       | 100 %      | 0 %        | 100 %      |
| SiZrO$_3$   | 0 %       | 100 %      | 0 %        | 100 %      |
| SrHfO$_3$   | 0 %       | 100 %      | 0 %        | 100 %      |
| KTaO$_3$    | 0 %       | 100 %      | 0 %        | 100 %      |
| SrMnO$_3$   | 40 %      | 60 %       | 8 %        | 92 %       |
| LaSeO$_3$   | 98 %      | 2 %        | 20 %       | 80 %       |
| LaTiO$_3$   | 10 %      | 90 %       | 7 %        | 93 %       |
| LaVO$_3$    | 26 %      | 74 %       | 19 %       | 81 %       |
| LaCrO$_3$   | 22 %      | 78 %       | 8 %        | 92 %       |
| LaMnO$_3$   | 28 %      | 72 %       | 15 %       | 85 %       |
| LaFeO$_3$   | 40 %      | 60 %       | 12 %       | 88 %       |
| SrTeO$_3$   | 25 %      | 75 %       | 32 %       | 68 %       |
| Ca$_2$RuO$_4$ | 16 %   | 84 %       | 26 %       | 74 %       | (25 %)   | (75 %)   | (25 %)   | (75 %)   |
| NaOsO$_3$   | 42 %      | 58 %       | 22 %       | 78 %       |

The band structures are compiled in Fig. 11, where we show a comparison between PBE and GW-derived bands, along
FIG. 11. (Color online) Collection of the calculated band structures at DFT (gray lines) and GW (black) together with the GW density of TM-d (shadow, blue line) and O-p (full line, red) states. The filled circles indicate the calculated GW QP energies (used for the Wannier interpolation). As mentioned in the main text, the DFT calculations for LaTiO$_3$ and LaVO$_3$ were performed with the addition of a small effective $U$. 
with the computed GW density of states (DOS). First, we note that the quality of the Wannier interpolation is generally very good, as established by the excellent match between the interpolated bands and the actual GW QP energies used for the interpolation procedure (shown as filled circles) and by the smoothness of the electron dispersions; only for Ca$_2$RuO$_4$ the interpolation ends up with wiggly bands mostly due to the small k-point mesh used for the wannierization (unfortunately a denser mesh turned out to be computationally too much costly).

By combining the information included in the band structures and DOS with the quantitative analysis of the orbital character at the CBM and VBM at the Γ point (see Tab. VI) it is possible to draw some conclusions on the type of band gap. The $d^0$ cubic systems SrTiO$_3$, SrZrO$_3$, SrHfO$_3$, and KTaO$_3$ are band insulator characterized by a $p$-$d$ fundamental gap that is also well visible as first excitation peak in the calculated and experimental optical spectra shown in Fig. 12. Also LaScO$_3$ falls in the category of band insulator, even though the conduction band has a sizable amount of $O$-$p$ states, which causes a broadening of the first excitation peak (see Fig. 12). The other compounds have a predominant $d$-$d$ character, with some distinctions: LaTiO$_3$ exhibits a clear Mott gap with only marginal (about 10%) $O$-$p$ states at the valence band; LaV$_3$, LaCrO$_3$, LaMnO$_3$ and SrTiO$_3$ appear to have a predominant Mott character too, but it is known that the gap in LaMnO$_3$ originates also from the Jahn-Teller instability. SrTiO$_3$ was reported to possess a substantial itinerant character, which places it on the verge of a Mott transition. The data suggest that SrMnO$_3$ and LaFeO$_3$ can be assimilated to a charge-transfer nature, as they have a strong intermix of $O$-$p$ and TM-$d$ states at the valence bands, whilst the conduction bands are largely formed by empty $d$ orbitals. Also Ca$_2$RuO$_4$ shows a charge-transfer nature, with 25% of $O$-$p$ states at both VBM and CBM. NaOsO$_3$ is a peculiar case, characterized by electron and spin itinerancy, a relatively strong SOC and a weak electron-electron correlation, both the valence and conduction bands are formed by a strong mixture of $O$-$p$ and Os-$d$ states suggestive of a predominant charge-transfer like character.

Finally, based on the GW real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of dielectric functions $\varepsilon = \varepsilon_1 + i\varepsilon_2$ (shown in Fig. 12) we have computed the optical conductivity spectra as:

$$\sigma(\omega) = -i\omega\varepsilon_0 [\varepsilon(\omega) - 1],$$

where $\varepsilon_0$ is the vacuum dielectric constant. The results are displayed in Fig. 11 and include a comparison with the measured spectra from Ref. 86 (SrTiO$_3$, SrZrO$_3$, SrHfO$_3$), Ref. 87 and Ref. 72 (Lanthanum series). For SrMnO$_3$ and SrTiO$_3$ we could not find any experimental reports in the literature. The agreement between calculated and measured values are generally good. Unfortunately for the La-series, the experimental data are limited to a small frequency window, which only allows for a comparison with the onset of the optical excitations. The cubic systems exhibit two prominent structures. According to the electronic structure properties discussed above, the first peak corresponds to the interband transition from $O$-$2p$ to TM-$t_{2g}$, and the second one is associated with the transition from O-$2p$ to TM-$e_g$.

The energy separation between the two main peaks is a measure of the crystal field splitting energy 10Dq, which is underestimated in GW by about 15-20%: we obtained 1.5 eV (expt: 1.9 eV), 4.0 eV (expt: 5.1 eV) and 4.3 eV (expt: 4.9 eV) in SrTiO$_3$, SrZrO$_3$, SrHfO$_3$, respectively. The spectrum of KTaO$_3$ exhibits a less pronounced separation into two main peaks. This is due to the larger band-width of both the valence and conduction bands (see bandstructure in Fig. 11) which allows for more broaden optical transitions and the appearance of shoulders close at the main peaks.

For NaOsO$_3$ the calculated optical conductivity follows well the measurements of Lo Vecchio et al.: the main absorption edge is mainly associated to charge-transfer excitations among Os 5$d$ and O 2$p$ states (see bandstructure in Fig. 11).

The variation of the optical properties and of the band gaps in the La-series has been discussed in the seminal paper of Arima and coworkers. Also for this set of compounds, the agreement with the measured data is satisfactory, with the exception of LaVO$_3$ for which GW predicts a substantial blue-shift of the strongest excitation peak at about 2.5 eV. However, the onset of the optical spectrum at 1.2 eV is well reproduced by theory and corresponds to the characteristic $d$-$d$ transition, which is not much intense due to the low density of empty states at the bottom of the conduction band (see Fig. 11). LaScO$_3$ is a clear band insulator with the first (charge-transfer) optical excitation arising from the $O$-$p$ to Sc-$d$ transition; the experimental spectrum does not exhibit the tail at the bottom of the spectrum well visible in GW, which is the cause of the underestimation of the gap at GW level ($\approx$ 4.9 eV vs. 6.0 eV, see Tab. IV). This is clearly due to the large broadening of the bottom of conduction band along the direction Z-$\Gamma$=(0.4,0,4,0) which leads to an unusual increase of the band width going from DFT (0.6 eV) to GW (1.5 eV) (see Fig. 11). As the 3$d$ states start to become occupied (LaTiO$_3$, 3$d^1$) a Mott peak shows up in the low-energy region of the optical conductivity, but the overall spectra are still dominated by the intense charge-transfer peak located at about 9-10 eV (depending on the specific system). In LaFeO$_3$ a third relatively intense feature appears at 4.1 eV between the lowest Mott peak (2.3 eV) and the charge transfer peak (9.8 eV), which can be assigned to the transition from the VBM to the group of bands centered at 4 eV above the Fermi level which have a mixed O-$p$ and Fe-$d$ characters (see Fig. 11).

Finally, Ca$_2$RuO$_4$ displays 4 main peaks in the lowest part of the optical conductivity (i.e., in the energy window up to 5 eV for which experimental reports are available). On the basis of the electronic properties (bands and DOS) and following the labelling given in Fig. 11 we can tentatively assign the first peak at 1 eV to the $i \rightarrow a$ transition, the second two peaks at 2 and 2.5 eV can be interpreted as $j \rightarrow a$ and $i \rightarrow b$ excitations, and finally the broad and intense peak at about 4 eV should correspond to transition from the valence bands $i,j$ to the main $d$ bands $b$. While the more intense peak should have a clear charge-transfer character, the other transition might involve $d$-$d$ Mott-like transition. However, a more quantitative and certain analysis of the specific type of transition...
FIG. 12. Spatially average real ($\epsilon_1$) and imaginary ($\epsilon_2$) part of the dielectric function obtained by G$_0$W$_0$ for the entire materials dataset studied in this work. The values of the static ion-clamped dielectric function $\epsilon_\infty$ are listed in Tab. VII.

FIG. 13. Collection of calculated optical spectra along with available experimental curves; for SrTiO$_3$, SrZrO$_3$ and SrHfO$_3$ the experimental data are taken from Ref. 86 for KTaO$_3$ from Ref. 87 for NaOsO$_3$ from Ref. 74 for the La series from Ref. 77 (LaMnO$_3$ from Ref. 88) and for Ca$_2$RuO$_4$ from Ref. 89. For Ca$_2$RuO$_4$, the inset shows a zoom of the low-energy region. The calculated dielectric functions from which the optical conductivity spectra have been derived are shown in Fig. 12.

would require beyond GW approaches such as the solution of the Bethe-Salpeter equation, which will be the topic of a fu-
TABLE VII. Diagonal part of the static (\(\omega = 0\), ion-clamped) dielectric matrix \(\varepsilon_0^{\text{diag}}\) calculated by means of the \(G_0W_0\) approximation.

| Compound  | \(\varepsilon_0^{\text{X}}\) | \(\varepsilon_0^{\text{Y}}\) | \(\varepsilon_0^{\text{Z}}\) |
|-----------|-----------------|-----------------|-----------------|
| SrTiO\(_3\) | 3.40            | 3.40            | 3.40            |
| SrZrO\(_3\) | 2.77            | 2.77            | 2.77            |
| SrHfO\(_3\) | 2.67            | 2.67            | 2.67            |
| KTaO\(_3\) | 3.16            | 3.16            | 3.16            |
| SrMnO\(_3\) | 5.26            | 5.26            | 5.61            |
| LaScO\(_3\) | 3.46            | 3.67            | 3.66            |
| LaTiO\(_3\) | 5.31            | 5.05            | 4.89            |
| LaVO\(_3\) | 3.83            | 6.51            | 3.70            |
| LaCrO\(_3\) | 4.90            | 4.89            | 4.96            |
| LaMnO\(_3\) | 4.83            | 4.58            | 5.02            |
| LaFeO\(_3\) | 4.23            | 4.19            | 4.28            |
| SrTcO\(_3\) | 7.53            | 7.46            | 7.66            |
| Ca\(_2\)RuO\(_4\) | 5.80            | 5.90            | 3.90            |
| NaOsO\(_3\) | 26.02           | 28.63           | 27.05           |

This comment applies to the interpretation of all spectra.

IV. CONCLUSIONS

In summary, in this study, we have assessed the performance and accuracy of the single shot \(G_0W_0\) approximation for the calculation of converged QP energies for transition-metal perovskites using two different schemes (the basis-set correction procedure and the conventional non-extrapolated method) and inspected the dependence of the results on the type of pseudopotential used in the computation (ultrasoft vs. norm-conserving). In order to draw general conclusions valid for different physical environments, we have performed a series of calculations on a minimal TM perovskites dataset comprising 14 compounds representative of the variety of properties characteristic of this class of materials: magnetic and non-magnetic systems, with and without structural distortions, with different occupancy \((d^0 \rightarrow d^5)\) and spatial extension \([n\text{ (main quantum number) }= 3, 4 \text{ and } 5]\) of the outermost \(d\) shell, with band-gap ranging from 0.1 eV (NaOsO\(_3\)) up to 6.1 eV (SrHfO\(_3\)) and different types of main optical excitations (Mott-Hubbard, charge-transfer, relativistic and band insulators).

We reassert that the formally (mathematically) corrected procedure to obtain accurate QP energies requires a basis-set as well as a \(k\)-points correction. However, these corrections, in particular, the basis-set extrapolation, can become computationally prohibitive when combined with NC PPs because norm-conserving pseudopotentials are generally constructed with a much larger number of plane-waves compared to ultrasoft potentials (this is the case for Ca\(_2\)RuO\(_4\), for which we could not perform NC-based calculations). On the other side, the use of US PP makes the basis-set corrections scheme computationally much more advantageous than the non-extrapolated scheme because well-converged results can be achieved with few \(k\)-points and the \(k\)-point correction requires only a small number of bands (and energy cutoff). Even though the reliability of the conventional scheme, based on a progressive increase of the most important technical parameters influencing the convergence of the results (cutoff energy, number of bands, and number of \(k\)-points) is not supported by a mathematical demonstration, our numerical results indicate that in most cases this scheme leads to converged QP energies very similar to those achieved by means of the basis set correction scheme. This conclusion is of great practical importance as this allows to easily compute energy dispersion relations (band structures) and optical spectra, which cannot be computed using the basis-set correction method. The so obtained optical spectra, based on the calculation of the frequency dependent dielectric function (without the inclusion of excitonic effects), are in good agreement with experimentally available measurements and provide useful insights for the characterization of the most important optical transitions.

Concerning the difference between NC and US PPs, the main source of inaccuracy in US-based calculations is the degree of norm-violation for the \(d\) shell, which can be as large as 0.4-0.45 electrons for Mn and Fe. For most of the compounds considered in the present study, this inaccuracy is somehow compensated by using a robust technical setup in US-based calculations [typically ENCUT=500-600 eV, N=500 (in some cases up to 2000), and a \(4\times4\times4\) \(k\)-point mesh]. In this respect, the most problematic compounds turned out to be SrTiO\(_3\), for which US PPs deliver band gap 0.5 eV larger than the corresponding NC value.

Finally, a basic statistical analysis of our results indicates a strong correlation between the calculated and experimental band gap as well as a very robust correlation between the GW and DFT gaps. Also, we found a particularly strong correlation between the GW gap and the static dielectric function which could be particularly useful for automatic high-throughput calculations. A much weaker correlation was found between the GW gap and the QP shift. As expected, the QP shift decreases with decreasing band gap, and this trend is characterized by two distinct behaviors: for the less electronically correlated \(d^5\) \(p-d\) insulators and 4-5\(d\) compounds the QP shift is about 25% of the value of the gap, whereas for the more correlated 3\(d\) materials the QP shifts increase up to 50-60%.

We hope that the results and conclusions of our work will serve as useful references for future GW calculations on complex transition metal oxides.

ACKNOWLEDGMENTS

This work was supported by the joint FWF (Austrian Science Fund) and Indian Department of Science and Technology (DST) project INDOX (I1490-N19). Computing time at the Vienna Scientific Cluster is greatly acknowledged.
M. Takizawa, K. Maekawa, H. Wadati, T. Yoshida, A. Fujimori, H. Kumigashira, and M. Oshima, Phys. Rev. B 79, 113103 (2009).

Y. Tezuka, S. Shin, T. Ishii, T. Ejima, S. Suzuki, and S. Sato, J. Phys. Soc. Jpn 63, 347 (1994).

K. Van Benthem, C. Elsässer, and R. H. French, J. Appl. Phys. 90, 6156 (2001).

Y. S. Lee, J. S. Lee, T. W. Noh, D.-Y. Byun, K. S. Yoo, K. Yamaura, and E. Takayama-Muromachi, J. Phys. Soc. Jpn 67, 113101 (2003).

I. L. Vecchio, A. Perucchi, P. Di Pietro, O. Limaj, U. Schade, Y. Sun, M. Arai, K. Yamamura, and S. Lupi, Sci. Rep. 3, 2990 (2013).

Z. Ergönenc, GW quasiparticle energies for transition metal oxide perovskites (PhD Thesis, University of Vienna, 2017).

T. Saitoh, A. E. Bocquet, T. Mizokawa, H. Namatame, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B 51, 13942 (1995).

T. Arima, Y. Tokura, and J. B. Torrance, Phys. Rev. B 48, 17006 (1993).

G. E. Jellison, I. Paulauskas, L. A. Boatner, and D. J. Singh, Phys. Rev. B Condens. Matter Mater. Phys. 74, 1 (2006).

C. G. Fatuzzo, M. Dantz, S. Fatale, P. Olalde-Velasco, N. E. Shaik, B. Dalla Piazza, S. Toth, J. Pelliciari, R. Fittipaldi, A. Vecchione, N. Kikugawa, J. S. Brooks, H. M. Rønnow, M. Grioni, C. Rüegg, T. Schmitt, and J. Chang, Phys. Rev. B Condens. Matter Mater. Phys. 91, 1 (2015).

H. Wang, F. Wu, and H. Jiang, J. Phys. Chem. 3, 16180 (2011).

M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. 99, 246403 (2007).

S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, and O. Levy, Nat Mater 12, 191 (2013).

M. J. van Setten, M. Giantomassi, X. Gonze, G.-M. Rignanese, and G. Hautier, Phys. Rev. B 96, 155207 (2017).

J. He and C. Franchini, Journal of Physics: Condensed Matter 29, 454004 (2017).

A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comput. Phys. Commun 185, 2309 (2014).

D. Lee, Y. and Y. K. Seo, J. Korean Phys. Soc 56, 366 (2010).

L. G. A.M. Mamedov, Fiz. Tverd. Tela (Leningrad) 26, 583 (1984).

J. H. Jung, K. H. Kim, D. J. Eom, T. W. Noh, E. J. Choi, J. Yu, Y. S. Kwon, and Y. Chung, Phys. Rev. B 55, 15489 (1997).

J. H. Jung, Z. Fang, J. P. He, Y. Kaneko, Y. Okimoto, and Y. Tokura, Phys. Rev. Lett. 91, 056403 (2003).

E. Pavarini and E. Koch, Phys. Rev. Lett. 104, 086402 (2010).

J. He, M.-X. Chen, X.-Q. Chen, and C. Franchini, Phys. Rev. B 85, 195135 (2012).

C. Franchini, T. Archer, J. He, X.-Q. Chen, A. Filippetti, and S. Sanvito, Phys. Rev. B 83, 220402 (2011).

J. Mravlje, M. Aichhorn, and A. Georges, Phys. Rev. Lett. 108, 197202 (2012).

J. G. Vale, S. Calder, C. Donnerer, D. Pincini, Y. G. Shi, Y. Tsujimoto, K. Yamamura, M. M. Sala, J. van den Brink, A. D. Christianson, and D. F. McMorrow, arXiv:1707.05551 [cond-mat.str-el].