Optical vs electronic gap of hafnia by ab initio Bethe-Salpeter equation

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We present first-principles many-body perturbation theory calculations of the quasiparticle electronic structure and of the optical response of HfO2 polymorphs. We use the GW approximation including core electrons by the projector augmented wave (PAW) method and performing a quasiparticle self-consistency also on wavefunctions (QSGW). In addition, we solve the Bethe-Salpeter equation on top of GW to calculate optical properties including excitonic effects. For monoclinic HfO2 we find a fundamental band gap of $E_g = 6.33$ eV (with the direct band gap at $E_g^d = 6.41$ eV), and an exciton binding energy of 0.57 eV, which situates the optical gap at $E_g^a = 5.85$ eV. The latter is in the range of spectroscopic ellipsometry (SE) experimental estimates (5.5–6 eV), whereas our electronic band gap is well beyond experimental photoemission (PE) estimates (< 6 eV) and previous GW works. Our calculated density of states and optical absorption spectra compare well to raw PE and SE spectra. This suggests that our predictions of both optical and electronic gaps are close to, or at least lower bounds of, the real values.

Introduction Hafnia (HfO2) is a transition metal oxide having attracted much attention due to its numerous technological applications, mainly related to its optical and electrical insulating properties. It is used for optical coatings1 in the near-ultraviolet (UV) to infrared (IR) wavelengths range, or as a high permittivity dielectric coating2 and electrical insulating properties. It is used for optoelectronic access memories (ReRAM)

Submicrometer silicon-based technologies. More recently, optical and dielectric properties. By using linearization and extrapolation techniques over measured spectra, these experiments extracted gap values ranging from 5.113 to 5.95 eV16. Surprisingly, the ranges for optical (5.1–5.95 eV) and electronic gaps (5.7–5.86 eV)10,11 overlap, making unclear the distinction between them.

The electronic structure of HfO2 polymorphs has also been studied theoretically. First works on m-HfO223–27, by using density functional theory (DFT) in the local density (LDA) or generalized gradient approximation (GGA)28, found band gaps (3.8–4.0 eV) underestimated by 30% with respect to experimental data. Most recent works, by using advanced semi-empirical functionals like TBmBJ29 or many-body perturbation theory (MBPT) in the GW approximation30–32, found band gaps in the range 5.7–5.9 eV and reconciled a good agreement with experimental data. These studies do not account for excitonic effects but agree well with optical gaps derived from SE and EELS.

In this work we revisit the situation. We calculate the electronic structure in the framework of MBPT within the GW approximation,33–35 also including core electrons by the projector-augmented wave (PAW) method36 and applying self-consistency on wavefunctions (QSGW).37 On top of QSGW, we perform Bethe-Salpeter equation (BSE) calculations38–40 of the optical gap and spectra including electron-hole interaction (excitonic effects). Furthermore, we perform a careful convergence study of our results (See supplementary material). Finally, instead of comparing our gaps with experimental values, we compare our DOS and optical absorption directly with the raw measured spectra. Our results indicate 5.85 eV (the energy of the first exciton) as a lower bound for the m-HfO2 optical gap. This is still in the range of the experimentally derived optical gaps. On the other hand, the comparison of our DOS with PES spectra clearly indicate 6.33 eV as a lower bound for the m-HfO2 electronic band gap. Our BSE calculation indicates the first peak of optical absorption as due to an exciton whose binding energy is 0.57 eV.

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FIG. 1. Left: Calculated band structure of monoclinic HfO$_2$ within the DFT-PBE (dotted line) and QSGW (plain red line) approximations. The QSGW band structure has been interpolated using MLWF. PBE and GW Fermi energies are aligned at zero. Top right: convergence of the QP gap at $\Gamma$ at the $G_0W_0$ level as a function of plane wave energy cutoff, with $N_b$ fixed to the maximum number of plane waves. Bottom right: convergence of the QP gap at $\Gamma$ at the $G_0W_0$ level as a function of the number of empty bands included ($N_b$) with a 500 eV plane wave energy cutoff.

**Computational details** Ab initio calculations based on density functional theory\textsuperscript{41,42} in the LDA or PBE\textsuperscript{28} approximations are carried out using the \textsc{vasp} code.\textsuperscript{43,44} The core-valence interaction are described with PAW datasets including the semicore 5s and 5p states for Hf. Electron wave functions are expanded in a plane waves basis set with kinetic energy cutoff of 500 eV, and the Brillouin zone is sampled using 4 × 4 × 4, 6 × 6 × 4 and 6 × 6 × 6 Γ-centered Monkhorst-Pack meshes for monoclinic, tetragonal and cubic HfO$_2$ phases, respectively. Many-body effects are accounted for by computing the quasiparticle (QP) energies at the $G_0W_0$, GW (self-consistency only on the eigenvalues) and QSGW level on top of DFT but fixing $W$ at $W_0$. Indeed, fixing $W$ has been shown to improve the agreement with experimental band gaps than using self-consistent $W$.\textsuperscript{45} In contrast to $G_0W_0$ and $GW_0$, QSGW allows to reduce the influence of the DFT starting point (LDA vs. PBE) on the electronic structure. The cutoff for response function is taken to be 333 eV and about 500 empty bands per formula unit and 100 frequency grid points are needed to obtain converged band gaps within 0.1 eV (see supplementary material for details). QP band structures are interpolated using maximally localized Wannier functions (MLWF) with the \textsc{wannier90} code.\textsuperscript{46} To determine the optical properties, the Bethe-Salpeter equation (BSE) is solved on top of GW using the Tamm-Dancoff approximation.\textsuperscript{47}

**Band gap and electronic structure** In Fig. 1 we report the electronic band structure of m-HfO$_2$, as calculated within DFT in the PBE approximation and within QSGW. In the monoclinic crystal structure HfO$_2$ presents a direct band gap at $B$, whereas the fundamental minimum band gap is indirect at $\Gamma \rightarrow B$. Between DFT and the GW approximation there is some rearrangement of the bands, but the most important effect is a shift of both valence and conduction bands which increases band gaps. This is also what we found for the cubic and tetragonal phases.

In Table I we report the fundamental minimum gaps for all phases and approximations considered in this work, and we compare them to previous theoretical works and to experiments. Regarding DFT results, our PAW LDA and PBE gaps are more in agreement with the FP-LAPW (full potential linearized augmented plane wave) LDA and PBE gaps of, respectively, Ref. 31 and 29 (both are all-electron calculations), than with the norm-conserving pseudopotentials plane waves (NCPP PW) LDA gap of Ref. 30. On the other hand, both our $G_0W_0$ and $GW_0$ band gaps are systematically larger than the ones of Refs. 30 and 31. We remark however that

| method       | cubic | tetragonal | monoclinic |
|--------------|-------|------------|------------|
| DFT-LDA      | 3.68  | 4.41       | 3.93       |
| LDA+$G_0W_0$ | 5.63  | 6.40       | 5.95       |
| LDA+$GW_0$   | 6.01  | 6.79       | 6.36       |
| LDA+QSGW     | 6.14  | 6.89       | 6.37       |
| DFT-PBE      | 3.76  | 4.64       | 4.01       |
| PBE+$G_0W_0$ | 5.41  | 6.34       | 5.77       |
| PBE+$GW_0$   | 5.78  | 6.72       | 6.18       |
| PBE+QSGW     | 6.03  | 6.93       | 6.33       |

**TABLE I.** Fundamental minimum band gap for the cubic ($X \rightarrow X$), tetragonal ($Z \rightarrow \Gamma$), and monoclinic ($\Gamma \rightarrow B$) HfO$_2$ phases, as calculated in various approximations. Ref. 30 used a norm-conserving pseudopotentials plane waves approach, whereas Ref. 31 and Ref. 29 used FP-LAPW. The determination of the band gap from PES/IPS experiments relies on post-processing data analysis to remove tails due to impurities and fits: for the XPS+IPS experiment of Ref. 10 we quote two estimates removing or not the effect of tails.

| method       | cubic | tetragonal | monoclinic |
|--------------|-------|------------|------------|
| DFT-LDA      | 3.50  | 4.1        | 3.8        |
| LDA+$G_0W_0$ | 5.2   | 5.8        | 5.7        |
| LDA+$GW_0$   | 5.5   | 6.0        | 5.9        |
| DFT-LDA      | 3.55  | 4.36       | 3.95       |
| LDA+$G_0W_0$ | 4.91  | 5.78       | 5.45       |
| LDA+$GW_0$   | 5.20  | 6.11       | 5.78       |
| DFT-PBE      | 3.77  | 4.79       | 4.08       |
| TB-mBJ orig  | 5.88  | 6.54       | 5.76       |
| TB-mBJ imp   | 6.17  | 6.81       | 6.01       |
| TB-mBJ semi  | 6.74  | 7.35       | 6.54       |

**Experimental works**

| method       |          |          |
|--------------|----------|----------|
| UPS+IPS (straight line extrapolation)\textsuperscript{11} | 5.7      |
| XPS+IPS (straight line extrapolation)\textsuperscript{10} | 5.86     |
| XPS+IPS (comparison with shifted DFT)\textsuperscript{10} | 6.7      |
our PAW $G_0W_0$ corrections, $\Delta E_g^{GW} = E_g^{GW} - E_g^{DFT}$, are closer to the NCPP PW ones$^{30}$ than to the FP-LAPW$^{31}$ ones, which are 0.3 to 0.6 eV lower. Differences between Refs. 30 and our $G_0W_0$ gaps could then be explained by the different starting DFT gap. Application of self-consistency only on eigenvalues, using the $GW_0$ approach, further increases the gap by $\sim 0.4$ eV in our study and by 0.2$\sim$0.3 eV in Refs. 30 and 31. Full self-consistency also on the wavefunctions,$^{49}$ using the QSGW approach,$^{37}$ removes any influence of the LDA or PBE starting point in our study, reducing the gap difference to less than 0.1 eV, a residual due to the use of different relaxed LDA and PBE atomic structures.

In the following we consider only PBE relaxed atomic structure, the closest to the experiment. Our $GW_0$ and QSGW calculations systematically yield larger band gaps than previous theoretical studies. For the monoclinic phase, our values are 0.4$\sim$0.5 eV larger than the highest $GW_0$ estimates of Refs. 30 and 31 and the TB-mBJ-orig of Ref. 29. The latter are in very good agreement with the 5.7 and 5.86 eV band gap values determined from photoemission experiments,$^{10,11}$ whereas our QSGW gap of 6.33 eV appears as a large overestimation. However, as discussed in Secs III.C and F of Ref. 10, there is some uncertainty in this determination of band gaps by the conventional method of linear extrapolation of photoemission band edges to the background intensity, due to the presence of band-tail and defects in the vicinity of the valence band maximum and conduction band minimum. For this reason we prefer to directly compare the experimental PES+IPS spectra to our calculated DOS (Fig. 2). This comparison was already suggested in the same Ref. 10 to provide a safer estimate of the real band gap. By using a DFT-LDA DOS and evaluating the scissors operator shift to make theoretical and experimental DOS coincide, they arrived to an estimate of 6.7 eV for the m-HfO$_2$ band gap$^{10}$. Our QSGW DOS favorably compares with photoemission spectra, especially on the shape, even though we have not taken into account extrinsic and finite state effects which are evident when comparing XPS with UPS shapes. As it can be estimated by the deviation of theory and experiment in the conduction edge (Fig. 2 inset), our QSGW band gap of 6.33 eV is still an underestimation of about 0.2 eV of the real band gap. Our more prudent conclusion is that the real band gap of monoclinic HfO$_2$ is $E_g > 6.33$ eV, and probably $E_g = 6.5$ eV. This is also what Ondračka et al.$^{29}$ found when modifying the TB-mBJ functional (“semi” version in Table I) to target the experimental DOS. The QSGW approximation has been reported to systematically overestimate band gaps in all studied materials.$^{50}$ In our case, for m-HfO$_2$, the close agreement between QSGW and experimental spectra may be due to fortuitous error cancellation with other effects not taken into account, such as electron-phonon,$^{51}$ and both single-particle (e.g. spin-orbit) or many-body (e.g. Breit interaction) relativistic corrections.

**Optical gap and spectra** In Table II we report all the DFT and GW direct band gaps, and we add the optical gaps calculated by solving the BSE on top of QSGW.

**TABLE II.** Direct electronic band gap (DFT or GW) and optical gap (BSE first exciton eigenvalue energy) for the cubic ($X \rightarrow X$), tetragonal ($\Gamma \rightarrow \Gamma$), and monoclinic ($B \rightarrow B$) HfO$_2$ phases. We report also the exciton binding energy equal to the difference between the QSGW direct band gap and the BSE optical gap, $E_b^{exc} = E_g - E_g^{exc}$. For m-HfO$_2$, BSE gap agrees well with SE (spectroscopic ellipsometry) optical onset. Energies are in eV.

| method                | cubic  | tetragonal | monoclinic |
|-----------------------|--------|------------|------------|
| DFT-LDA               | 3.68   | 4.58       | 4.03       |
| LDA+$G_0W_0$          | 5.63   | 6.57       | 6.05       |
| LDA+$GW_0$            | 6.01   | 6.96       | 6.46       |
| LDA+QSGW              | 6.14   | 7.04       | 6.47       |
| DFT-PBE               | 3.76   | 4.71       | 4.09       |
| PBE+$G_0W_0$          | 5.41   | 6.43       | 5.86       |
| PBE+$GW_0$            | 5.78   | 6.81       | 6.27       |
| PBE+QSGW              | 6.03   | 7.01       | 6.41       |
| PBE+QSGW+BSE          | 5.57   | 6.53       | 5.85       |
| $E_b^{exc}$           | 0.46   | 0.48       | 0.57       |
| Experimental works (optical gap) | SE$^7$ | 5.6–5.8 |     |
|                       | SE$^9$ | 5.5–6.0 |     |
We also report the first exciton binding energy, defined as the difference between the direct band gap energy and the energy of the first exciton, $E_{b}^{\text{exc}} = E_{g}^{d} - E_{g}^{\text{exc}}$, found to be 0.57 eV for m-HfO$_2$. Direct band gap and optical gap are significantly different in m-HfO$_2$. The simulated optical gap can now be compared with the measured one, e.g., in optical or X-ray absorption, spectroscopic ellipsometry (SE), or energy-loss (EELS). Refs. 7 and 9 reported values derived from SE spectra of 5.6–5.8 eV and 5.5–6.0 eV, respectively. The uncertainty is due, as for the band edges in the density of states, to the method (e.g. Tauc-Lorentz) used to linearly extrapolate to the background. We remark that now our QSGW+BSE optical gap is in the range of the experimental reports. Nevertheless, we again$^{52}$ prefer to compare the raw SE spectra to our calculated optical absorption, $\varepsilon_2(\omega)$ (see Fig. 3). The QSGW+BSE dielectric function significantly improves the lower level of approximation QSGW+RPA, and achieves a very good agreement with SE spectra. BSE introduces electron-hole interaction effects and gives rise to the exciton which is to be identified with the first peak of the BSE spectrum, absent in the RPA. Nevertheless we remark a 0.1–0.2 eV red shift of the exciton peak with respect to its position in SE spectra. Part of this red shift could be corrected by k-point sampling extrapolation to zero$^{53}$. Nevertheless, like the band gap, also our optical gap suffer an underestimation, so that they have both to be regarded as lower bounds of the real values.

The nature of this small peak at the optical onset observed in SE spectra$^{7–9}$ of crystalline samples has been attributed to different causes. By combining X-ray absorption (XAS), X-ray diffraction (XRD) and SE techniques, Hill et al.$^{9}$ found that this feature could be intrinsic to the monoclinic phase. According to our analysis, this is a real bound$^{54}$ exciton peak, as correctly interpreted in Refs. 15 and 29, and not a defect state, as interpreted by Nguyen et al.$^7$. The exciton is present only in the y polarization (see Fig. 4), confirming the unusual anisotropy in the dielectric properties of m-HfO$_2$. We find that an exciton also in c-HfO$_2$ and t-HfO$_2$, but their oscillator strength is zero or almost, so that they are dark excitons not detectable in SE spectra. Hence SE spectra can be used to characterize the HfO$_2$ monoclinic phase with respect to all other phases by simply detecting the presence or absence of the 5.85 eV exciton peak.

Conclusions In this work we combine QSGW calculations to compute the electronic structure of HfO$_2$ with BSE to compute optical spectra. We compare our calculated DOS and optical absorption with raw, as-acquired, experimental spectra measured for the monoclinic phase. Our calculated electronic band gap ($E_g = 6.33 \, \text{eV}$) is significantly larger than the values obtained in previous theoretical and experimental studies. However the direct comparison between QSGW DOS and experimental spectra shows a good agreement and even indicates that our band gap value slightly underestimates by $\sim 0.2 \, \text{eV}$ the real value. In contrast, we obtain an optical gap of 5.85 eV, in agreement with SE estimates. We find that the difference is due to the presence of a bound exciton with a large binding energy of 0.57 eV.

Supplementary Material See supplementary material for information about the relaxed structures and convergence studies of GW and BSE calculations.

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Appendix A: Supplementary material

Structural parameters All our calculations are based on density functional theory within local density approximation (LDA) or generalized gradient approximation (GGA) with the parametrization of Perdew-Burke-Ernzerhof (PBE) in the framework of plane wave projector-augmented wave (PAW) method as implemented in the VASP code.\textsuperscript{43,44} The DFT calculations are performed using the version 5.4 of LDA and PBE PAW potentials of VASP (Hf\textsubscript{SV}GW and O\textsubscript{GW} for Hf and O, respectively).

We study cubic (spacegroup \textit{Fm}3\textit{m}), tetragonal (spacegroup \textit{P}4\textsubscript{2}2\textsubscript{1}/nmc) and monoclinic (spacegroup \textit{P}2\textsubscript{1}/c) phases of HfO\textsubscript{2}. Each structure is relaxed until the maximum residual forces are less than 10\textsuperscript{−3} eV/Å. For the relaxation we use a fine k mesh of 12\times12\times12, 12\times12\times8 and 8\times8\times8 for cubic, tetragonal and monoclinic phases, respectively. Calculated structural parameters are summarized in Table III.

One-shot \textit{G\textsubscript{0}W\textsubscript{0}} convergence We carefully examine the convergence of our \textit{GW} calculations in order to achieve \textit{QP} band gap values converged within 0.1 eV. Indeed, to calculate the response function and the correlation part of self-energy, a summation over empty states is required and quasi particle (QP) energies exhibit a very slow convergence with respect to the number of virtual orbitals. Furthermore, the number of empty bands \textit{N\textsubscript{b}}, the corresponding orbital basis set \textit{N\textsubscript{pw}} (controlled by the plane waves cutoff \textit{E\textsubscript{pw}}) and the size of the response function basis set \textit{N\textsubscript{\chi}} (controlled by the plane waves cutoff \textit{E\textsubscript{\chi}}) have to be increased simultaneously.\textsuperscript{56} Therefore, in our convergence study we fix \textit{E\textsubscript{\chi}} = \text{2/3} \times \textit{E\textsubscript{pw}} and use the complete plane waves basis set (i.e. \textit{N\textsubscript{b}} = \textit{N\textsubscript{pw}}) for each considered \textit{E\textsubscript{pw}}. We consider the monoclinic phase of HfO\textsubscript{2} with \textit{E\textsubscript{pw}} ranging from 350 eV to 700 eV. A frequency grid with 100 frequency points is used to represent the polarizability and a 4\times4\times4 \Gamma-centered k-mesh is used to sample the Brillouin zone.

Fig. 5 shows the QP corrections (\textit{\Delta}\textit{\epsilon}) of the Kohn-Sham eigenvalues as a function of 1/\textit{N\textsubscript{b}} (which equals 1/\textit{N\textsubscript{pw}}) for a \textit{G\textsubscript{0}W\textsubscript{0}} calculation on top of PBE (a similar behavior is observed for an LDA starting point). The dotted lines show the linear extrapolation of QP corrections (\textit{\Delta}\textit{\epsilon}(\textit{N\textsubscript{b}}) = \text{A/}N\textsubscript{b} + \text{\Delta}\textit{\epsilon}(\infty)) where only the values corresponding to \textit{E\textsubscript{pw}} ≥ 500 eV are included in the fit. The extrapolated QP corrections of the valence band maximum (VBM) at \Gamma and conduction band minimum (CBM) at \textit{B} are respectively -1.33 eV and 0.51 eV giving an extrapolated band gap of 5.85 eV. Our

![QP corrections](image1.png)

![Convergence of QP band gap](image2.png)

FIG. 5. QP corrections of the Kohn-Sham eigenvalues as a function of the inverse of the number of empty bands \textit{N\textsubscript{b}} (or number of plane waves \textit{N\textsubscript{pw}}). The dotted lines show the linear extrapolation of QP corrections (see text for details).

FIG. 6. Convergence of QP band gap as a function of self-consistent \textit{GW} iterations at \textit{GW\textsubscript{0}} (top panel) and QSGW (bottom panel) level.
This work

| xc functional | core elect. | k mesh | N_b | Dyn. Scr. | E_g (eV) | \(\Delta E^{GW}_{g}\) (eV) |
|---------------|-------------|--------|-----|-----------|---------|------------------|
| \(G_0W_0\)    | PBE         | 4 \times 4 \times 4 | 2000 | Full Freq.| 5.77    | 1.76             |
| LDA           | PAW         |        |      |           | 5.95    | 2.02             |
| \(GW_0\)      | PBE         | 4 \times 4 \times 4 | 2000 | Full Freq.| 6.18    | 2.17             |
| LDA           | PAW         |        |      |           | 6.36    | 2.43             |
| Ref. 30 and 48| \(G_0W_0\)   | 4 \times 4 \times 4 | 600  | GN-PPM   | 5.7     | 1.9              |
| LDA           | NCPP        |        |      |           | 5.9     | 2.1              |
| Ref. 31       | \(G_0W_0\)   | 2 \times 2 \times 2 | —    | Analytical cont.| 5.45    | 1.50             |
| LDA           | FP-LAPW     |        |      |           | 5.78    | 1.83             |

TABLE IV. Comparison of QP band gaps (\(E_g\)) and \(GW\) corrections (\(\Delta E^{GW}_{g} = E^{GW}_{g} - E^{DFT}_{g}\)) from different \(GW\) calculations on monoclinic HfO\(_2\). The calculations differ by the level of self-consistency, starting mean-field theory and \(GW\) convergence parameters. The convergence parameters include: the k mesh, the number of empty bands (\(N_b\)) and the method to describe dynamical screening (Dyn. Scr.).

Our convergence study shows that the numerical convergence of our calculated QP band gaps is below 80 meV. In table IV, we summarize the convergence parameters used in our work with those from previous theoretical studies.

We also check the influence of the number of frequency points and k mesh. We find that increasing the frequency grid from 100 to 200 points only changes the QP band gap by 15 meV but tend to compensate the error done due to incompleteness of the plane waves basis set. When using a finer k-point sampling of 6 \times 6 \times 6, change in the QP band gap is below 1 meV.

Our convergence study shows that the numerical convergence of our calculated QP band gaps is below 80 meV. In table IV, we summarize the convergence parameters used in our work with those from previous theoretical studies.

Self-consistent \(GW\) convergenceSELF-CONSISTENT \(GW\) convergence

Self-consistent \(GW\) calculations are carried out with the same parameters as for \(G_0W_0\). For \(GW_0\) and QSGW calculations, we include respectively 256 and 512 QP energies in the self-consistent procedure for monoclinic HfO\(_2\). In the case of \(GW_0\), 4 self-consistent iterations are enough to get converged band gap. For QSGW, 8 self-consistent \(GW\) iterations allowed to get converged QP energies and band gaps within 5 meV as shown in Fig. 6.

Bethe-Salpeter equation (BSE) convergence

The excitonic properties are determined by solving the Bethe-Salpeter equation (BSE) within the Tamm-Dancoff approximation on top of the \(GW\) quasiparticle band struc-

FIG. 7. Imaginary part of the dielectric function \(\varepsilon_2\) for the monoclinic phase of HfO\(_2\) calculated on top of PBE+\(G_0W_0\) for 4 \times 4 \times 4 and 6 \times 6 \times 6 k\ mesh. A Gaussian broadening of 0.1 eV is used.

FIG. 8. Density of states (DOS) of monoclinic HfO\(_2\) in the \(G_0W_0\), \(GW_0\), and QSGW approximations compared to UPS+IPS\(^{11}\) and XPS+IPS\(^{10}\) spectra. The theoretical DOS have been interpolated using MLWF on a 40 \times 40 \times 40 k-point grid and convoluted with a gaussian broadening of 0.7 eV. Experimental spectra have been aligned at the valence band-edge (the zero of the energy for all theoretical DOS), and the conduction IPS and valence PS independent measurements have been rescaled separately to match the height of the theoretical DOS.
ture. BSE calculations usually require fine k-point sampling to converge exciton spectra. However such calculations are computationally very expensive for both GW and BSE. In the case of monoclinic HfO$_2$, we test the k-point convergence of the BSE calculation on top of $G_0W_0$ using $4 \times 4 \times 4$ and $6 \times 6 \times 6$ grids. Fig. 7 shows the imaginary part of the dielectric function $\varepsilon_2$ (we ignore the polarization dependence and assume $\varepsilon = (\varepsilon_{xx} + \varepsilon_{yy} + 2\varepsilon_{zz})/3$). A simple visual inspection suggests that the two k-meshes give very similar spectra. More quantitatively, the exciton binding energies of $4 \times 4 \times 4$ and $6 \times 6 \times 6$ meshes are 0.56 eV and 0.52 eV, respectively.

A more complete convergence study with respect to k-mesh could be carried out using a model BSE (mBSE) scheme or interpolation techniques but have not been considered in this work.

**DOS** For monoclinic HfO$_2$, we present in Fig. 8 the density of states (DOS) calculated in the $G_0W_0$, GW$_0$, and QSGW approximations compared to the experimental UPS+IPS and XPS+IPS spectra. The figure shows that the theoretical underestimation of the band gap decreases from $G_0W_0$, passing by GW$_0$, to QSGW.