Reproducibility in $G_0W_0$ Calculations for Solids

Tonatiuh Rangel, 1, 2, * Mauro Del Ben, 3 Daniele Varsano, 4, 5 Gabriel Antonius, 2, 6, 7 Fabien Bruneau, 8, 1, 6 Felipe H. da Jornada, 2, 6 Michiel J. van Setten, 9, 5, 10 Okan K. Orhan, 11 David D. O’Regan, 11 Andrew Canning, 3 Andrea Ferretti, 4, 5 Andrea Marini, 12, 5 Gian-Mario Rignanese, 9, 5 Jack Deslippe, 13 Steven G. Louie, 2, 6 and Jeffrey B. Neaton 1, 2, 14, †

1 Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
2 Department of Physics, University of California at Berkeley, California 94720, United States
3 Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
4 Centro S3, CNR- Istituto Nanoscienze, I-41125 Modena, Italy
5 European Theoretical Spectroscopy Facility (ETSF)
6 Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
7 Département de Chimie, Biochimie et Physique, Institut de recherche sur l’hydrogène, Université du Québec à Trois-Rivières, QC, Canada
8 DEN, Service de Recherches de Métallurgie Physique, Université Paris-Saclay, CEA, F-91191 Gif-sur-Yvette, France
9 Institute of Condensed Matter and Nanoscience (IMCN), Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium
10 IMEC, Kapeldreef 75, 3001 Leuven, Belgium
11 School of Physics, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland
12 Istituto di Struttura della Materia of the National Research Council, Via Salita Km 29.3, I-00016 Montelibretti, Italy
13 NERSC, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
14 Kavli Energy Nanosciences Institute at Berkeley, Berkeley, California 94720, United States

* Correspondence: rangeltonatiuh@gmail.com
† Present address: Istituto di Struttura della Materia of the National Research Council, Via Salita Km 29.3, I-00016 Montelibretti, Italy

Abstract

Quantitative prediction of charged single-particle excitations in otherwise interacting many-particle systems such as solids is a key component of the design and discovery of materials and the fundamental understanding of matter at the atomic level. A rigorous formalism for computing such particle-like excitations is naturally applicable to solids and transition metal oxides (TMOs), with localized d-electrons, present a bigger numerical challenge for self-energy corrections. In the so-called GW method, 1 the self-energy $\Sigma$ is approximated, to lowest order in the screened Coulomb interaction $W$, as $iG^*W$, where $G$ is the one-electron Green’s function. In a standard approach, $G$ and $W$ are constructed from a (either regular or generalized) Kohn-Sham (KS) eigensystem, computed via density functional theory (DFT), and the KS eigenvalues are corrected perturbatively with a one-shot $G_0W_0$ self-energy, where the subscript indicates that $G$ and $W$ are not updated self-consistently. By accounting for the screening of the crystal environment, GW is naturally applicable to solids and has proven quite effective in predicting quasiparticle energies of a wide range of crystals. 3–8 However, because of the complexity, computational cost, and the number of convergence parameters involved, numerical approximations are required in GW calculations, and varying algorithms in different codes can sometimes yield distinct results.

Crystalline silicon is probably the most-studied testbed solid for GW. Having high crystal symmetry and containing only sp-bonded orbitals, silicon is a relatively-simple system, for which GW within standard approximations yields accurate quasiparticle energies and sizable self-energy corrections. 3, 4 Transition metals (TMs) and transition metal oxides (TMOs), with localized d or f electrons, present a bigger numerical challenge for GW. When dealing with TMs, care should be taken in the technical details and approximations used within GW. For instance, the convergence criteria, 9 and the choice of frequency-integration scheme 10–14 and pseu-

I. INTRODUCTION

Quantitative prediction of charged single-particle excitations in otherwise interacting many-particle systems such as solids is a key component of the design and discovery of materials and the fundamental understanding of matter at the atomic level. A rigorous formalism for computing such particle-like excitations is naturally applicable to solids and transition metal oxides (TMOs), with localized d-electrons, present a bigger numerical challenge for self-energy corrections. In the so-called GW method, 1 the self-energy $\Sigma$ is approximated, to lowest order in the screened Coulomb interaction $W$, as $iG^*W$, where $G$ is the one-electron Green’s function. In a standard approach, $G$ and $W$ are constructed from a (either regular or generalized) Kohn-Sham (KS) eigensystem, computed via density functional theory (DFT), and the KS eigenvalues are corrected perturbatively with a one-shot $G_0W_0$ self-energy, where the subscript indicates that $G$ and $W$ are not updated self-consistently. By accounting for the screening of the crystal environment, GW is naturally applicable to solids and has proven quite effective in predicting quasiparticle energies of a wide range of crystals. 3–8 However, because of the complexity, computational cost, and the number of convergence parameters involved, numerical approximations are required in GW calculations, and varying algorithms in different codes can sometimes yield distinct results.

Crystalline silicon is probably the most-studied testbed solid for GW. Having high crystal symmetry and containing only sp-bonded orbitals, silicon is a relatively-simple system, for which GW within standard approximations yields accurate quasiparticle energies and sizable self-energy corrections. 3, 4 Transition metals (TMs) and transition metal oxides (TMOs), with localized d or f electrons, present a bigger numerical challenge for GW. When dealing with TMs, care should be taken in the technical details and approximations used within GW. For instance, the convergence criteria, 9 and the choice of frequency-integration scheme 10–14 and pseu-

arXiv:1903.06865v1 [cond-mat.mtrl-sci] 16 Mar 2019
dopotentials\textsuperscript{15} can yield substantially different results. Several GW works for rutile TiO\textsubscript{2} have reported gaps ranging from 3.1 to 4.8 eV\textsuperscript{11,16-20} while for ZnO gaps published so far range from 2.6 to 4.5 eV\textsuperscript{9,12,15,21-24} Thanks to advances in computational resources and algorithms, recent works have explored convergence beyond past limits,\textsuperscript{9,12,15,21,22,24} and accurate pseudopotentials specific for GW have been proposed,\textsuperscript{15,25} a general agreement on the GW quasiparticle energies with different codes has yet to be perceived as being achieved for the difficult cases. The growing popularity of GW, the multiple dedicated codes used for GW, and the existing challenges and discrepancies encountered when performing GW on increasingly chemically complex systems, such as TMs and TMOs, make it imperative to have reproducibility of predictions from different GW codes.

In this work, we report the results of a detailed comparison of three different plane-wave-based GW codes, and we find that predictions from these codes can agree very well, under given similarly physically sound approximations. For purposes of assessment, we study the representative solids Si, Au, TiO\textsubscript{2}, and ZnO with the open-source GW codes ABINIT (ABI)\textsuperscript{20}, BERKELEYGW (BGW),\textsuperscript{27} and YAMBO (YMB).\textsuperscript{28} Our benchmark calculations provide a framework for users and developers to document the precision of new applications and methodological improvements, and provides standards for the reproducibility of GW calculations.

II. THE GW METHOD IN PRACTICE

The GW method is an interacting Green’s function formalism which accounts for the response of the system to addition or removal of a single electron in an interacting N-electrons system, via a non-Hermitian, non-local, and frequency-dependent self-energy operator

$$\Sigma(r,r';\omega) = i/2\pi \int d\omega' e^{i\omega'}G(r,r';\omega + \omega')W(r,r';\omega'),$$  

where $\eta$ is a positive infinitesimal and the bare Coulomb potential $v$ and the inverse of the dielectric matrix $\epsilon^{-1}$ are used to construct the screened Coulomb potential

$$W(r,r';\omega) = \int dr''\epsilon^{-1}(r,r'';\omega)v(r'',r').$$

In the so-called one-shot GW, also known as $G_0W_0$, the quasiparticle energies $E^{\text{QP}}$ are solved perturbatively from a mean-field Kohn-Sham (KS) starting point; that is, $G_0$ and $W_0$ are constructed from the KS mean-field. In this approach, which implicitly assumes the KS wavefunctions $\psi^{\text{KS}}$ are close to the QP wavefunctions $\psi^{\text{QP}}$, the QP energy of the $i$th state is given by\textsuperscript{1,4}

$$E^{\text{QP}}_i = E^{\text{KS}}_i + \langle\psi^{\text{KS}}_i|\Sigma(E^{\text{QP}}_i) - V_{xc}|\psi^{\text{KS}}_i\rangle$$

where $V_{xc}$ is the KS exchange-correlation potential, and $\Sigma$ is evaluated at the QP energy $E^{\text{QP}}_i$. A common approximation is to linearize $\Sigma$ in the QP energy with a first-order Taylor expansion around $E^{\text{KS}}_i$, such that

$$E^{\text{QP}}_i = E^{\text{KS}}_i + Z_i \langle\psi^{\text{KS}}_i|\Sigma(E^{\text{KS}}_i) - V_{xc}|\psi^{\text{KS}}_i\rangle - V_{xc}|\psi^{\text{KS}}_i\rangle,$$

with the renormalization factor

$$Z_i = \left[1 - \langle\psi^{\text{KS}}_i|\frac{\partial\Sigma(\omega)}{\partial\omega}\omega=E^{\text{KS}}_i|\psi^{\text{KS}}_i\rangle\right].$$

As discussed later, the standard linearization scheme should be used with care as it can lead to relatively large deviations (up to 0.2 eV in ZnO) in predicted QP energies.

A source of deviation among GW results with different codes is the numerical integration scheme used to evaluate the frequency dependence of $\Sigma$ in Eq. (1)\textsuperscript{10-13} A common practice to reduce computational cost is to approximate the dielectric function with a single-pole via a generalized plasmon-pole model (PPM). For each set of momentum components $(q, G, G')$, the inverse dielectric function $\epsilon^{-1}$ in this approximation takes the form

$$\text{Im} \epsilon^{-1}_{G,G'}(q,\omega) = A_{G,G'}(q) \times \left[\delta(\omega - \omega_{G,G'}(q)) - \delta(\omega + \omega_{G,G'}(q))\right]$$

$$\text{Re} \epsilon^{-1}_{G,G'}(q,\omega) = 1 - \frac{A_{G,G'}(q)\omega_{G,G'}^2(q)}{\omega^2 - \omega_{G,G'}^2(q)},$$

where the matrices $A_{G,G'}(q)$ and $\omega_{G,G'}(q)$ are to be determined.\textsuperscript{8} In the Hybertsen-Louie (HL) approach, the PPM parameters are determined from sum rules and by evaluating the dielectric function at $\omega = 0$.\textsuperscript{4} In the Godby-Needs (GN) scheme, the parameters are set by evaluating the dielectric function at $\omega = 0$.\textsuperscript{29} Both ABINIT and YAMBO use the PPM-GN scheme as default; BERKELEYGW uses a PPM-HL version modified to deal with non-centrosymmetric systems.\textsuperscript{27,30} When calculating $\epsilon^{-1}$ at two frequencies: $\omega = 0$ and an imaginary frequency close to the plasma frequency.\textsuperscript{29} Both ABINIT and YAMBO use the PPM-GN scheme as default; BERKELEYGW uses a PPM-HL version modified to deal with non-centrosymmetric systems.\textsuperscript{27,30} When calculating $\epsilon^{-1}$ at two frequencies: $\omega = 0$ and an imaginary frequency close to the plasma frequency.\textsuperscript{29} Both ABINIT and YAMBO use the PPM-GN scheme as default; BERKELEYGW uses a PPM-HL version modified to deal with non-centrosymmetric systems.\textsuperscript{27,30} When calculating $\epsilon^{-1}$ at two frequencies: $\omega = 0$ and an imaginary frequency close to the plasma frequency.\textsuperscript{29}
into the complex plane, into a region where the integrand is smooth; the alternative integration path must be supplemented with the residues from the poles of \( G \), as explained in detail in Refs. 5, 31, and 32. The FF-CD method is available in Abinit and has been recently implemented into BerkeleyGW. For other FF methods we refer the reader to Refs. 20, 35, and 36.

The self-energy is usually split into a frequency-independent exchange part \( \Sigma_x \) and a correlation part \( \Sigma_c \), so that \( \Sigma(x, r', \omega) = \Sigma_x(x, r') + \Sigma_c(x, r', \omega) \), where the matrix element of \( \Sigma_c \) between two Bloch states reads:

\[
\langle i | \Sigma_c | j \rangle = - \sum_{q,G} v(q + G) F_{ij}(q + G) \tag{8}
\]

and

\[
F_{ij}(q + G) = \sum_{v \in \text{occ.}} M_{iv}(q + G) M^*_{jv}(q + G) \tag{9}
\]

Here, \( M_{iv} = \langle i | v(q + G - r) | j \rangle \) are matrix elements for states \( i \) and \( v \) at point \( k \). The expression for \( \Sigma_c \) is given in Ref. 12.

The exchange term, also present in the evaluation of Fock exchange for hybrid functionals in DFT, features a divergence in the Coulomb potential \( v(q + G) = 4\pi e^2 / |q + G|^2 \) as \( q \rightarrow 0 \) for \( G = 0 \). Several schemes have been proposed to treat the divergence of the Coulomb term. For instance, in the spherical-cutoff technique, the Coulomb interaction is attenuated beyond \( R_c \) and \( v(0) \) is replaced with \( 2\pi e^2 R_c^2 / 3 \), where the sphere of radius \( R_c \) has volume equal to that of the unit cell times the number of k-points. In Abinit by default the Coulomb singularity is approached by an auxiliary-function integration method detailed in Ref. 43. Other codes avoid the Coulomb singularity by replacing the value of \( q \rightarrow 0 \) in Eq. (8) by an integral around \( q \geq 0 \). This method is applicable to any \( q \) point in the BZ by assuming,

\[
\langle i | \Sigma_c | j \rangle = - \sum_{q,G} \int_{R_{q+G}} dq' \frac{d}{dq'} v(q + q' + G) \times F_{ij}(q + G), \tag{10}
\]

where the integral is performed over the BZ region \( R_{q+G} \), which is associated with a volume \( \Omega(R_{q+G}) \), centered around each \( q + G \) point. This method gives the effect of a larger sampling of points around \( q \) assuming that \( F(q + G) \) is constant over that region.

In the “random integration method” (RIM) implemented in Yambo and “Monte Carlo averaging” (MC average) technique used in BerkeleyGW the integral is evaluated using a stochastic scheme. In both codes a stochastic scheme is also used to evaluate every term of the form \( \int d^3q f(q) v(q) \) in \( \Sigma_c \), as the scheme can straightforwardly account for integration of arbitrary potentials in regions \( R_{q+G} \) with arbitrary boundaries. Moreover, with the MC averaging scheme, the analytical behavior of \( W(q \rightarrow 0) \) is also appropriately adjusted depending on whether the system behaves like a metal, semiconductor, or displays a graphene-like linearly vanishing density of states; it is also adjusted based on the dimensionality of the system, as discussed in Ref. 27.

These stochastic integration methods have shown success in accurately computing the Coulomb singularity and in improving the convergence of \( \Sigma \) with respect to k-point sampling. To facilitate a complete comparison, we also implemented the MC averaging method into Abinit for the present work, as will be discussed below.

Aside from the physical model employed for the dielectric matrix and the treatment of the Coulomb divergence, we emphasize that several parameters must be converged in order to achieve meaningful GW results. Both the calculation of \( \epsilon \) and \( \Sigma_c \) involve unrestricted sums over bands that are truncated up to \( N_{\text{eps.}} \) and \( N_{\text{sig.}} \), respectively. Additionally, the codes discussed here use plane-wave basis sets; the number of plane-wave basis functions, \( N_{\text{PW}} \), used to evaluate \( \epsilon \) and \( \Sigma \), is expanded up to an energy cutoff \( \epsilon_{\text{cut}} \). These three parameters \( N_{\text{eps.}}, N_{\text{sig.}}, N_{\text{PW}} \) are interdependent, and their convergence needs to be addressed simultaneously. Here, we extrapolate the GW QP gaps (energy eigenvalue differences) to the complete basis set (CBS) limit with a function of the form

\[
f(N_{\text{eps.}}, N_{\text{PW}}, N_{\text{sig.}}) = \left( \frac{a_1}{N_{\text{eps.}}} + b_1 \right) \left( \frac{a_2}{N_{\text{PW}}} + b_2 \right) \left( \frac{a_3}{N_{\text{sig.}}} + b_3 \right),
\]

where \( a_1, a_2, a_3, b_1, b_2, \) and \( b_3 \) are constants to be determined. Other important convergence parameters and considerations include the k-point sampling of the Brillouin zone, pseudopotential choice, basis used to describe the wavefunctions, and in the case of full-frequency calculations, the frequency sampling on the real and imaginary axis.

### III. TECHNICAL DETAILS

In what follows, we compare GW calculations for several materials using three codes implementing the same approaches. For all materials considered, we fix the lattice parameters to the experimental values. These are, for Si in the diamond structure, fcc Au, rutile TiO2, and wurtzite ZnO, respectively, 5.43 Å, 4.08 Å, \((a = 4.60, c = 2.9)\) Å, and \((a = 3.25, c = 5.20)\) Å. We use norm-conserving Fritz-Haber Institute pseudopotentials with 6, 4, 12 and 20 valence electrons for O, Si, Ti and Zn, respectively. For Au, we use Optimized Norm-Conserving Vanderbilt Pseudopotentials (ONCVP) with 19 valence electrons. We use a Perdew-Burke-Ernzerhof (PBE) starting point for GW, except for ZnO in which the Local Density Approximation (LDA) is used for the sake of comparison to previous works. Our DFT calculations use a k-point mesh and a plane-wave energy-cutoff which ensure that the total energies are converged within 50 meV per unit cell. The k-point mesh is consistent with
that for $GW$ calculations, see below; we use a plane-wave energy cutoff to represent wavefunctions of 40, 88, 300 and 300 Ry for silicon, gold, TiO$_2$ and ZnO, respectively. The $GW$ parameters are carefully set to converge quasiparticle energies to 0.1 eV: for silicon, we use a $Γ$-centered Monhorst-Pack grid of $12 \times 12 \times 12$ k-points, $ɛ_{cut} = 20$ Ry and 300 unoccupied states; for gold, we use a mesh of $16 \times 16 \times 16$ k-points, $ɛ_{cut} = 32$ Ry, and 400 unoccupied states; for rutile TiO$_2$, we use a shifted k-grid of $6 \times 6 \times 10$ k-points and the number of unoccupied states and $ɛ_{cut}$ value were extrapolated to the CBS, as detailed in the supplemental materials (SI); and for wurtzite ZnO, we use a shifted k-grid of $8 \times 8 \times 5$ k-points, and the unoccupied states and $ɛ_{cut}$ are also extrapolated to the CBS. We summarize in Table I of the Supplementary Information (SI) all convergence parameters used for tables and figures in this manuscript.

IV. RESULTS AND DISCUSSION

A. Silicon

We calculate the $GW$ quasiparticle corrections to the bandstructure of bulk silicon, a typical system for $GW$ calculations. We use a common pseudopotential for all $GW$ calculations, as defined in Section III. The effect of the pseudopotential approximation for silicon is discussed in Ref. 50.

We first study the accuracy of common approximations to treat the Coulomb divergence, which influences the rate of convergence with respect to k-points. In Fig. 1, we show the convergence of the matrix elements of $Σ_x$ for the valence band maximum (VBM) and conduction band minimum (CBM) at $Γ$. We consider different techniques to treat the Coulomb singularity, in particular the MC average in BERKELEYGW for only $q = G = 0$ (black lines, default up to version 1.1 of BERKELEYGW) and for all $G$ vectors and $q$-points in the BZ (blue lines, default starting from version 1.2); the RIM for $q = 0$ only (brown lines) and all BZ (orange line) in YAMBO and the auxiliary-function treatment in ABINIT (pink lines). As expected, both the convergence rate with respect to k-points and the converged number of k-points can differ with the choice of method to treat the Coulomb singularity. In this case the RIM and MC average approaches converge fastest, with a grid of $8 \times 8 \times 8$ k-points being sufficient to converge the $Σ_x$ matrix elements for the VBM and CBM within 0.05 eV.

In Table I, we show converged $G_0W_0$@PBE QP energies for bulk silicon using two different frequency integration schemes and different $GW$ codes. In fact, we find the same QP energies within 0.05 eV for all codes considered here. With respect to the frequency-integration schemes, we find that the PPM in the GN or HL fashions provide a gap for Si within 0.1 eV with respect to the full frequency (FF-CD) reference. Importantly, for a given frequency-integration scheme, the QP energies obtained with the different codes considered here agree within a tolerance better than 0.05 eV, demonstrating that the same $GW$ corrections can be found with different codes.

We highlight that the VBM, CBM, and gap energies calculated with BERKELEYGW and ABINIT with FF-CD agree with the energies obtained with YAMBO and FF-RA. This result serves as a numerical verification of the equivalence between the implemented FF-CD and FF-RA integration schemes, which was demonstrated exactly only for the electron gas.$^{31}$

B. Gold

We now revisit the $G_0W_0$ corrections to the scalar-relativistic band structure of bulk gold, a relatively difficult case for $GW$ due to convergence issues, the non-negligible influence of semicore orbitals on the band structure, and relativistic effects.$^{51,52}$ In what follows, we neglect spin-orbit interactions. We first converge the number of bands and $ɛ_{cut}$, as detailed in the SI: 400 unoccupied states and $ɛ_{cut} = 32$ Ry ensures a convergence of 0.15 eV in the QP gaps between occupied and unoccupied bands across the Brillouin zone in a relatively large window of energies up to $\sim 15$ eV above the Fermi level. Secondly, we uniformly increase the k-point mesh up to $16 \times 16 \times 16$. We observe differences in k-point convergence rate that can be traced to the specific
QP energies of silicon (eV)

|          | PPM-GN | PPM-HL | FF-CD | FF-RA |
|----------|--------|--------|-------|-------|
| ABI BGW YMB | ABI BGW | ABI BGW | YMB   |
| VBM      | -0.64  | -0.64  | -0.64 | -0.95 |
| CBM      | 0.52   | 0.53   | 0.52  | 0.29  |
| Gap      | 1.16   | 1.17   | 1.16  | 1.24  |

TABLE I. VBM, CBM and fundamental energy-gap of silicon calculated within GW with several codes using different frequency-integration schemes. Band energies are shown with respect to the DFT VBM.

k-points, the codes considered here agree within 0.1 eV in the predicted self-energy of the VBM/CBM at Γ, demonstrating that for metals the codes predict the same QP energies when convergence is reached.

In Table II we show that the matrix elements of Σ for bands around the Fermi level calculated with the different codes. The scalar-relativistic DFT band structure and the Brillouin zone are shown in the SI. The GW corrections agree within 0.05 eV, corroborating that at convergence different codes give the same QP energies.

In Table II we show that the matrix elements of Σ for bands around the Fermi level calculated with the different codes. The scalar-relativistic DFT band structure and the Brillouin zone are shown in the SI. The GW corrections agree within 0.05 eV, corroborating that at convergence different codes give the same QP energies.

TABLE II. Absolute GW self-energy for gold at high-symmetry k points, obtained from a scalar-relativistic PBE DFT calculation. Calculations were performed with three different codes and with the PPM-GN.

C. Rutile TiO$_2$

Rutile has been the subject of several GW studies, and the reported $G_0W_0$ gaps range from 3.1 to 4.8 eV$^{11,16-20,24}$. Part of the reported disagreement comes from the treatment of the frequency dependence of Σ. As detailed in Ref. 11, the fundamental gap calculated with certain PPMs can deviate considerably (by up to 1.1 eV) from a full-frequency reference. The sensitivity of the TiO$_2$ gap to the manner in which the frequency dependence of Σ is treated makes rutile an interesting case to investigate the effect and accuracy of PPM and FF methods. As mentioned previously, we use FHI-type pseudopotentials including semicore states consistently in all calculations performed with different codes. Although the choice of pseudopotentials for GW is not studied in this work, we found that our results for rutile are somewhat modified (by less than 0.1 eV) relative to those obtained with other PPs, such as Gaussian$^{53}$ and pseudo-dojo-v0.2$^{25}$ PPs (see Appendix A for more details).

We first examine the $G_0W_0$@PBE QP energies of rutile TiO$_2$ obtained from different codes, frequency-integration schemes, and in the case of PPMs, choices
We now examine the PPM-HL and in particular the effect of the different choices for $\omega^{\text{unf}}$. Interestingly, when the terms with unfulfilled PPM modes are set to 1-Ha, the PPM-HL yields results within 0.1 eV of the PPM-GN and FF approaches, and when neglecting components with $\omega^{\text{unf}}$, the results tend to deviate by up to 0.8 eV from the FF reference. This clearly indicates that the performance of PPMs for rutile is highly sensitive to the treatment of unfulfilled PPM modes. For rutile, $\omega^{\text{unf}}$ make up an alarming proportion of the dielectric function (~54% of the matrix elements), which suggests the need for a full-frequency treatment of $\epsilon$, in agreement with Ref. 11. The fraction of unfulfilled PPM modes is therefore an important indicator of whether a full frequency approach is required.

We now compare the $G_0W_0$ self-energy calculated with different codes in Table III. When using the PPM-HL, the self-energy can deviate by up to 0.1 eV for the different codes used here, due to different variants of the PPM-HL being implemented; while ABINIT implements the original version of PPM-HL in Ref. 4, BERKELEYGW uses a modified version of the PPM to deal with non-centrosymmetric systems as detailed in Ref. 27. Assessing these small variations in the PPM is beyond the scope of this work. When using the PPM-GN or FF methods, the agreement is better than 20 meV, similar to the silicon case. Importantly, we find that the quasiparticle energies predicted by the different codes agree within 0.1 eV when using the same treatment of the frequency-dependence.

To converge the GW gap of rutile we extrapolate the interdependent GW parameters ($\epsilon_{\text{cut}}, N_{\text{sig}}, N_{\text{eps}}$) to the CBS limit, as described above and in the SI. The converged bandgap is 3.3 eV for the different codes used here; this result also agrees with previous full-frequency calculations of Refs. 11, 20, and 24, as reported in Table IV.

### D. Wurtzite Zinc Oxide

Historically, ZnO has been a challenging and controversial system for GW. For ZnO, the GW result is strongly affected by the slow convergence of the $\Sigma_c$ term\(^9\). Convergence issues are further aggravated when using PPMs\(^{12}\), although these PPM-related issues may be partially remedied as illustrated in Ref. 23. Here we only show results with FF methods and the PPM-GN (validated against FF references\(^{12}\)). For more on the PPM approximation for ZnO, we refer the reader to Refs. 12–14, and 23. Other discrepancies in the GW gap

---

**Table III.** QP energies for rutile within a spherical-cutoff technique. This comparison is performed with small convergence parameters: a $6 \times 6 \times 10$ k-point grid and $\epsilon_{\text{cut}} = 20$ Ry. The actual QP energies of rutile are shown in Table IV. We use different codes and frequency-integration schemes (see text) For PPM-HL, unfulfilled PPM modes ($\omega^{\text{unf}}$) are either * set to 1 hartree or † neglected.

**Table IV.** We show the fundamental energy-gap of rutile calculated with $G_0W_0$ using different set of approximations within different codes, such as the frequency-integration scheme, basis set and pseudopotentials/all-electron. * FF method in the complex plane\(^{20}\).

**Table V.** GW quasiparticle energies of ZnO within a spherical-cutoff technique. The three GW codes, ABINIT, YAMBO and BGW, agree for the calculated QP energies. This comparison is performed with under-converged parameters: a $5 \times 5 \times 4$ k-point grid and $\epsilon_{\text{cut}} = 30$ Ry.
of ZnO arise from the use of incomplete basis-sets and different pseudopotentials, such as projector-augmented waves. Due to these issues, the reported $G_0W_0$@LDA gaps with different approximations and codes range from 2.3 – 4.5 eV (see Table VI).

We start by showing that the different codes used here agree on the gap of ZnO, for a given pseudopotential. Again, although pseudopotential issues are not discussed here, we find that our results are insensitive (within 0.1 eV) to the choice of PPs tested in this work, as discussed in Appendix A. In Table V, we show underconverged QP energies for ZnO calculated using a spherical-cutoff scheme within $G_0W_0$@LDA. All ZnO results in Table V are computed at the same number of bands, dielectric matrix cutoffs, and k-point grid for the purposes of comparison. However, these parameters are underconverged.) We use the GN method, FF-CD method with ABINIT and BERKELEYGW, and the FF-RA method with YAMBO. We set $\epsilon_{cut} = 30$ Ry, a Coulomb cutoff radius of 19.7177 Bohr, a plasma frequency of 38.82 eV (for PPM-GN), a Γ-centered homogeneous grid of $5 \times 5 \times 4$.
k-points and 34 bands, and show that the unconverged GW gap of ZnO calculated with the different codes is consistent within 0.1 eV.

Linearizing the self-energy to the QP energy, especially when using coarse k-grids, can be inaccurate. An illustration of the difference between the linearized and graphically-solved QP energies is given in Fig. 3a. For the VBM, the linearized and graphical solutions can differ by \( \sim 0.2 \) eV; for an unconverged set of GW parameters \((5 \times 5 \times 4 \text{ k grid, } \epsilon_{\text{cut}} = 40 \text{ Ry and } N_{\text{eps}} = N_{\text{sig}} = 2000)\), we find \( E_{\text{QP}}^0 \{ \Sigma(E_{\text{QP}}^0) \} = 3.7 \) eV and \( E_{\text{QP}}^\text{KS} \{ \Sigma(E_{\text{QP}}^\text{KS}) \} = 3.9 \) eV, where \( E_{\text{KS}}^\text{KS} = 5.3 \) eV. In Fig. 3b we show the QP bandgap as a function of the number of bands used to evaluate \( \Sigma \). We use shifted grids of \( 5 \times 5 \times 4 \) and \( 8 \times 8 \times 5 \) k-point grids, \( N_{\text{eps}} = 2000 \) and \( \epsilon_{\text{cut}} = 40 \) Ry. Within the coarser grid the actual (blue dots) and linearized (cyan dots) solutions can disagree by more than 0.1 eV due to features in \( \Sigma(\omega) \), as shown in Fig. 3 (a). These features are smoothed out when using a finer grid, reducing the discrepancy associated with linearization.

Having demonstrated good agreement between different codes for ZnO QP energies, we then proceed to converge the gap of ZnO only with BERKELEYGW, excluding the other codes due to our limits on computational resources. To accelerate the convergence with respect to k-points, we use a shifted grid, a common practice well-documented in the past\(^{57}\). Using the finest grid of k-points (that is the \( 8 \times 8 \times 5 \) grid), we proceed to converge the \( N_{\text{eps}} \), \( N_{\text{sig}} \), and \( \epsilon_{\text{cut}} \) by extrapolating to the CBS limit (see SI). As shown in Fig. 4, the bandgap converges linearly with respect to \( N_{\text{PW}}^{-1} \) and a relatively high \( \epsilon_{\text{cut}} > 80 \) Ry is needed to assure convergence within 0.05 eV. At convergence, we find the \( G_0W_0 @\text{LDA} \) gap of ZnO is 2.8 eV, in agreement with recent calculations, as shown in Table VI.

Finally, we compare our \( G_0W_0 \) bandgaps with the corresponding electronic gaps measured in photoemission experiments. Here we use full-frequency \( G_0W_0 \) approaches (FF-CD or FF-RA). Note that when comparing to experiment the lattice-renormalization effect should also be included\(^{58,59}\), e.g., the measured/calculated zero-point renormalization (ZPR) of silicon is 62–64 meV, 150 meV for TiO\(_2\) and 150–164 meV for ZnO\(^{60,61}\). Our calculated indirect gap of 1.21–1.28 eV for silicon (without renormalization) is therefore in good agreement with the experimental gap of 1.17 eV\(^{62}\). Our result is also in agreement with the seminal work of Ref. 4. As mentioned above, since we neglect spin-orbit effects in this work, we do not compare the GW bandstructure of gold to experiment. Our calculated gap of 3.3 eV of rutile TiO\(_2\) is also in good agreement with the experimental gap of 3.3 ± 0.5 eV\(^{63,64}\). On the other hand, our GW gap of ZnO of 2.8 eV substantially underestimates the reported experimental gap of \( \sim 3.6 \) eV\(^{65,66}\). This well-known shortcoming of standard \( G_0W_0 \) for ZnO is due to a deficient LDA starting point\(^{55}\), and indicates the need for a more accurate starting point or self-consistent schemes.

This work reaches a consensus on the value of the \( G_0W_0 \) bandgaps of prototype systems, and hence facilitates future work studying beyond-standard GW schemes to improve the accuracy of GW when using a poor mean-field starting point.

V. CONCLUSIONS

In this work, we have revisited the GW approximation for prototype systems with three representative plane-wave-based codes: YAMBO, ABINIT and BERKELEYGW. Within certain choices of approximations and a given set pseudopotentials, the converged GW QP energies calculated with the different codes agree within 0.1 eV, addressing long-standing controversies on the GW results for difficult systems such as ZnO and rutile.

More specifically, we have studied the validity of approximations within one-shot \( G_0W_0 \) which can give rise to disagreement in GW results between different codes, in particular the treatment of the Coulomb divergence, convergence, plasmon-pole model approximations, and scheme for capturing the full frequency dependence of \( \Sigma \).

We have benchmarked different techniques to treat the Coulomb divergence, and identified several effective techniques, in particular an auxiliary-function method used in ABINIT, the RIM in YAMBO and the MC average in BERKELEYGW. The latter was implemented in ABINIT in this work. We have provided new insights into the details of PPMs and their effect on GW results, such as the treatment of unfulfilled PPM modes, which for some systems can lead to large deviations (> 0.5 eV) from FF references. We have shown that specific PPM techniques, when treated at the same level in the different codes, provide results in complete agreement independently of the code. Beyond the PPM approximation we have also shown that the FF-CD method implemented in BERKELEYGW provides results in agreement with FF implementations in ABINIT and YAMBO. We highlight that QP energies predicted with the FF-CD method (in the complex plane) agree quantitatively with real-axis FF references, a numerical proof of the validity of the FF-CD.

In summary, our work provides a framework for users and developers to validate and document the precision of new applications and methodological improvements relating to GW codes.

VI. ACKNOWLEDGMENTS

This work was supported by the Center for Computational Study of Excited State Phenomena in Energy Materials at the Lawrence Berkeley National Laboratory, which is funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05CH11231, as part of the Computational Materials Sciences Program. This work is also supported by
the Molecular Foundry through the U.S. Department of Energy, Office of Basic Energy Sciences under the same contract number. We acknowledge the use of computational resources at the National Energy Research Scientific Computing Center (NERSC). We also acknowledge the use of HPC resources from GENCI-CCRT-TGCC (Grants No. 2014-096018). F.B. acknowledges the Enhanced Eurolateral program and the France Berkeley Fund for supporting his sabbatical leave in UC Berkeley. D.V., A.F. and A.M. acknowledge support from European Union H2020-INFRAEDI-2018-1 programme under grant agreement No. 824143 project “MaX - materials at the exascale”. AM acknowledges support from European Union H2020-INFRAIA-2015-1 programme under grant agreement No. 676598 project “Nanoscience Foundries and Fine Analysis - Europe”. O.K.O. and D.O.’R. acknowledge the support of Trinity College Dublin’s Studentship Award and School of Physics. Their work was supported by TCHPC (Research IT, Trinity College Dublin), where calculations were performed on the Lonsdale cluster funded through grants from Science Foundation Ireland, and on the Kelvin cluster funded through grants from the Irish Higher Education Authority through its PRTLI program. D.V. and A.F. acknowledge PRACE for awarding access to resource Marconi based in Italy at CINECA. M.J.v.S. and G.-M.R. are grateful to F.R.S.-FNRS for financial support through the CÉCI facilities funded by F.R.S.-FNRS (Grant No. 2.5020.1) and Tier-1 supercomputer of the Fédération Wallonie-Bruxelles funded by the Walloon Region (Grant No. 1117545).

Appendix A: The choice of pseudopotential for GW

In this appendix, we study the variation of the bandgap with respect to the choice of pseudopotential for TiO$_2$ and ZnO. We emphasize that the validation of pseudopotentials for GW requires all-electron references and is beyond the scope of the present manuscript. In Table VII we show the $G_0W_0$ direct gap of rutile calculated with different choices of pseudopotentials. We use a DFT-PBE starting point from ABINIT and consider norm-conserving PPs of the Fritz Haber Institute (FHI)\cite{48,68,69}, Optimized Norm-Conserving Vanderbilt (ONCV)\cite{48} and Hartwigsen-Goedecker-Hutter (HGH)\cite{33} kinds. The configuration of choice for Ti is [Ne]$3s^23p^63d^14s^2$ (including semicore states), and [He]$2s^22p^6$ for O. We only use PPs available in the literature (see Table VII). Note that the HGH and PD PPs contain non-local core corrections (NLCC), which are subtracted from $\Sigma$ when calculating the QP energies. In the table, we show the energy cutoff required to converge the DFT total energy per atom to 0.01 eV and the PP radii, which can be taken as a measure of the PP “hardness”. Here we use BERKELEYGW to compute the $G_0W_0$ direct gap of rutile using a set of under-converge parameters for GW: $N_{\text{eps.}} = N_{\text{sig.}} = 2000$, $\epsilon_{\text{cut}} = 20$ Ry, the MC avg. technique and a $\Gamma$-centered homogeneous grid of $6 \times 6 \times 10$ k-points. Importantly, the GW gaps corresponding to different PP types agree within 0.1 eV, indicating a small dependence of the gap of rutile with the choice of PPs used here.

We now study the sensitiveness of the GW results with respect to the choice of pseudopotential for ZnO. In Table VIII we show the QP gap of ZnO calculated with $G_0W_0@LDA$ using different PPs. The configuration of choice for Zn is [Ne]$3s^23p^63d^{10}4s^2$ (including semicore states), and [He]$2s^22p^6$ for O. As in the TiO$_2$ case, some of the HGH and PSP8 PPs considered here contain NLCCs. We also show the minimum kinetic energy cutoff for the plane-wave expansion to converge the DFT gap within 0.05 eV, and the corresponding DFT-LDA and GW gaps. Here we use BERKELEYGW, the FF-CD method with 20 imaginary frequencies, an uniform sampling of real frequencies spaced by 0.25 eV from 0 to 6 eV, the modified static-reminder method of Ref. 72 and unconverged GW parameters: $\epsilon_{\text{cut}} = 30$ Ry, $N_{\text{sig.}} = N_{\text{eps.}} = 500$. For ZnO the GW and DFT gaps change little, by up to 0.14 and 0.1 eV respectively, with the different choices of PPs. Therefore, the results for ZnO and TiO$_2$ presented in this manuscript are negligibly affected by the choice of PPs.

| PP type | PP radii (Bohr) | $E_{\text{cut}}$ (Ry) | DFT gap (eV) | GW gap (eV) |
|---------|----------------|----------------------|--------------|--------------|
| FHI\textsuperscript{a} | Ti: s 1.48, p 1.62, d 1.70 | 60 | 1.78 | 3.12 |
| HGH\textsuperscript{b} | Ti: s 0.34, p 0.24, d 0.24 | 280 | 1.88 | 3.23 |
| PD\textsuperscript{c} | Ti: s 1.35, p 1.30, d 1.65 | 60 | 1.88 | 3.23 |

\textsuperscript{a} FHI PPs: Ti is defined in the OPIUM-v3.8 user guide\cite{67} and O is from the FHI98 library\cite{68,69}.
\textsuperscript{b} HGH PPs from Refs. 53 and 69.
\textsuperscript{c} PD PPs from pseudo-dojo-v.2\cite{25,70}.

TABLE VII. Testing norm-conserving pseudopotentials for rutile. For each PP type we show the radii per angular momentum (s, p or d), the plane-wave energy-cutoff ($E_{\text{cut}}$) (see text), and the corresponding DFT and GW gap of rutile. We use $G_0W_0$ PPM-GN with a DFT-PBE starting point, at unconverged GW parameters (see text).
| PP type | PP radii (Bohr) | $E_{\text{cut}}$ (Ry) | DFT gap (eV) | GW gap (eV) |
|---------|----------------|----------------------|-------------|-------------|
| FHI$^a$ | Zn: s 0.80, p 0.80, d 0.80, O: s 1.20, p 1.20 | 300 | 0.67 | 2.76 |
| RRKJ$^b$ | Zn: s 1.00, p 1.00, d 0.85, O: s 1.10, p 1.10 | 300 | 0.73 | 2.87 |
| HGH$^c$ | Zn: s 0.40, p 0.53, d 0.25, O: s 0.22, p 0.21 | 300 | 0.73 | 2.90 |
| PD$^d$ | Zn: s 1.35, p 1.65, d 1.85, O: s 0.80, p 0.80 | 60 | 0.78 | 2.82 |
| PD$^e$ | Zn: s 0.80, p 0.80, d 0.60, O: s 0.80, p 0.80 | 500 | 0.74 | 2.84 |

$^a$ FHI PPs from Ref. 12.
$^b$ RRKJ PPs from Ref. 23.
$^c$ HGH PPs from Refs. 53 and 69.
$^d$ PD PPs from pseudo-dojo-v.2$^{25,70}$.
$^e$ PD PPs generated with the ONCVP code$^{48}$.

TABLE VIII. Sensitiveness of the GW gap of ZnO with respect to the choice of PPs. Same as TiO$_2$ in Table VII. We use $G_0W_0$ FF-CD with a DFT-LDA starting point at unconverged GW parameters (see text). Note that the GW gaps of ZnO shown in this table agree with the converged gap (= 2.8 eV) due to spurious cancellation of errors.
Supplemental Information for “Reproducibility in the $\text{G}_0\text{W}_0$ Calculations for Solids”

Tonatiuh Rangel,1, 2,* Mauro Del Ben,3 Daniele Varsano,4, 5 Gabriel Antonius,2, 6, 7
Fabien Bruneval,8, 1, 6 Felipe H. da Jornada,2, 6 Michiel J. van Setten,9, 5, 10 Okan K. Orhan,11 David D. O’Regan,11 Andrew Canning,3 Andrea Ferretti,4, 5 Andrea Marini,12, 5
Gian-Maro Rignanese,9, 5 Jack Deslippe,13 Steven G. Louie,2, 6 and Jeffrey B. Neaton1, 2, 14
1 Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
2 Department of Physics, University of California at Berkeley, California 94720, United States
3 Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, United States
4 Centro S3, CNR-Istituto Nanoscienze, I-41125 Modena, Italy
5 European Theoretical Spectroscopy Facility (ETSF)
6 Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
7 Département de Chimie, Biochimie et Physique, Institut de recherche sur l’hydrogène,
Université du Québec à Trois-Rivières, QC, Canada
8 DEN, Service de Recherche de Métallurgie Physique,
Université Paris-Saclay, CEA, F-91191 Gif-sur-Yvette, France
9 Institute of Condensed Matter and Nanoscience (IMCN),
Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium
10 IMEC, Kapeldreef 75, 3001 Leuven, Belgium
11 School of Physics, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland
12 Istituto di Struttura della Materia of the National Research Council,
Via Salaria Km 29.3, I-00016 Montelibretti, Italy
13 NERSC, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
14 Kavli Energy Nanosciences Institute at Berkeley, Berkeley, California 94720, United States

In this Supplemental Information we show convergence studies on the QP energies of silicon, gold, TiO$_2$, and zinc oxide. We show the technical parameters used in our GW calculations. We describe a simple strategy to compare the results from different GW codes. Finally, we study the sensitiveness of the GW gaps to the choice of pseudopotential.

I. TECHNICAL DETAILS

In Table I we summarize all parameters used in our GW calculations for Tables and Figures in the main manuscript.

II. STRATEGY TO VALIDATE CODES

Comparing the numerical accuracy of different GW codes is a complex task due to the various approximations used in the practice, such as the degree of convergence, the treatment of the Coulomb singularity and frequency dependence of $\Sigma(\omega)$ and the choice of pseudopotentials. Nevertheless, we can isolate the different sources of discrepancy following a simple strategy:

1. We start with exactly the same DFT input (wavefunctions and eigenvalues).
2. We avoid the Coulomb singularity by using the spherical-cutoff scheme; and we use the same frequency integration scheme, number of bands, and $k$-points in BZ integrations.
3. We explore $k$-point convergence, which is sensitive to the method used to treat the Coulomb singularity (see above).
4. We converge $\epsilon_{\text{cut}}$ simultaneously with the number of bands used to evaluate $\epsilon$ and $\Sigma$ ($N_{\text{eps.}}$ and $N_{\text{sig.}}$, respectively).

Below, we describe in more detail our application of this strategy to validate GW codes for bulk crystalline Si, Au, TiO$_2$, and ZnO.

In TABLE II, we show the GW corrections to the valence band maximum (VBM) and conduction band minimum (CBM) at the $\Gamma$ point for bulk silicon. We show the corrections calculated with/without the spherical-cutoff technique and using the three different codes used here ABINIT, BERKELEYGW and YAMBO. We set $\epsilon_{\text{cut}} = 20$ Ry, a grid of $4 \times 4 \times 4$ k-points and 10 empty states; with these settings, the GW corrections are underconverged but the level of accuracy is the same for the different codes, facilitating quantitative comparison. When using the spherical-cutoff technique (see last two columns in TABLE II), we obtain the same QP energies with different codes. This result shows that by disentangling the sources of discrepancy with our simple strategy, we can effectively compare output of different GW codes.

III. GOLD

Bulk gold is a more complex case for GW due to approximations to the metal dielectric and the partial band occupations at the Fermi energy. As mentioned in the manuscript, we study the GW corrections to the scalar
TABLE I. Parameters used in our GW calculations. We report our choice of k-point grid, energy cutoff for the screening ($\epsilon_{\text{cut}}$), number of bands used to calculate the dielectric function ($N_{\text{eps.}}$) and the GW self-energy ($N_{\text{sig.}}$), pseudopotential (PP), DFT starting point (St. point), whether a spherical cutoff was used (Sph. cut.). Additionally, a plasma frequency ($\Omega_p$) is shown when referring to PPM-GN calculations.

| Material | k-point grid | $\epsilon_{\text{cut}}$ | $N_{\text{eps.}}$ | $N_{\text{sig.}}$ | PP | St. point | Sph. cut. | $\Omega_p$ |
|----------|--------------|------------------|-----------------|----------------|-----|-----------|----------|-----------|
| Silicon  | Table I of main manuscript | 12 × 12 × 12, unshifted | 40 Ry | 300 | FHI$^a$ | PBE | No | 16.60 eV |
|          | Table I of main manuscript | 4 × 4 × 4, unshifted | 20 Ry | 4 | FHI$^a$ | PBE | Yes | 16.60 eV |
| Gold     | Table II of main manuscript | 16 × 16 × 16, unshifted | 32 Ry | 400 | PD$^b$ | PBE | No | 38.88 eV |
| Rutile   | Table III of main manuscript | 6 × 6 × 10, unshifted | 20 Ry | 100 | FHI$^c$ | PBE | Yes | 32.56 eV |
| Zinc Oxide | Table V of main manuscript | 5 × 5 × 4, unshifted | 30 Ry | 34 | FHI$^e$ | LDA | Yes | 38.82 eV |
|          | Table VI of main manuscript | 8 × 8 × 5, shifted$^g$ | extrapolated to CBS limit$^h$ | FHI$^e$ | LDA | No | 5.59 eV |

$^a$ FHI98 PP$^1$ from the ABINIT web site.
$^b$ PD PP from pseudo-dojo-v.2$^{2,3}$.
$^c$ FHI PPs: Ti is defined in the OPIUM-v3.8 user guide$^4$ and O is from the FHI98 library.$^{1,5}$.
$^d$ Number of bands and $\epsilon_{\text{cut}}$ extrapolated to the complete basis set (CBS) limit, see Section IV.
$^e$ FHI PPs from Ref. 6.
$^f$ Shifted and unshifted grids of 5 × 5 × 4 and 8 × 8 × 5 k-points.
$^g$ Extrapolation to the CBS limit, read Section D of main manuscript.

The choice of linear extrapolation is motivated by recent work$^7$, and here the fit is satisfactory with a standard deviation of $< 0.005$ eV. We find an extrapolated gap at $X$ ($X_5 \rightarrow X_1$) of 5.59 eV. Setting this gap as the reference, we find that the set of parameters $\epsilon_{\text{cut}} = 32$ Ry and $N = 400$ are sufficient to converge the gap within $< 0.1$ eV.

We first converge the number of bands and planewaves used for the dielectric function and $\Sigma$, using a fixed k-point sampling of 8 × 8 × 8 k-points, the PPM-GN, and the ABINIT code. The linear extrapolation to an infinite number of bands and planewaves is done in a two-step procedure. First, for a fixed $\epsilon_{\text{cut}}$, we extrapolate the number of bands $N$ for $\Sigma$ and $\epsilon$ to $N \rightarrow \infty$ (see FIG. 2). Second, the resulting gaps are linearly extrapolated to the complete basis set limit (CBS) (see the inset). The choice of linear extrapolation is motivated by recent work$^7$, and here the fit is satisfactory with a standard deviation of $< 0.005$ eV. We find an extrapolated gap at $X$ ($X_5 \rightarrow X_1$) of 5.59 eV. Setting this gap as the reference, we find that the set of parameters $\epsilon_{\text{cut}} = 32$ Ry and $N = 400$ are sufficient to converge the gap within $< 0.1$ eV.

FIG. 1. Scalar-relativistic bandstructure of gold calculated with DFT-PBE. The Brillouin zone is shown as an inset.
TABLE II. GW corrections to the VBM/CBM of silicon with low convergence parameters (read text). The unconverged GW corrections are identical for different codes when using the spherical-cutoff technique (last two columns), illustrating how to cheaply evaluate the numerical accuracy of GW codes.

|            | Valence band maximum | Conduction band minimum |
|------------|----------------------|-------------------------|
|            | No cutoff            | Spherical cutoff        |
| BERKELEYGW | \( \Sigma_x \)       | \( \Sigma_c \)         |
|            | \( \Sigma_x \)       | \( \Sigma_c \)         |
| ABINIT     | -12.746              | 2.030                   |
|            | -13.049              | 0.969                   |
| YAMBO      | -12.630              | 1.975                   |
|            | -13.050              | 0.969                   |

IV. TiO\(_2\)

For rutile TiO\(_2\), we first study the convergence of \( \Sigma \) with respect to the number of bands and cutoff used for the GW sums. In FIG. 4, we show \( \Sigma_{ik} \) matrix elements as a function of the \( k \)-point mesh. Consistent with the silicon case (see main manuscript), some methods, such as the YAMBO analytic method (brown lines) and the BERKELEYGW MC avg. on \( q \approx 0 \) (black lines) can exhibit a slow convergence rate. Importantly, with a mesh of \( 6 \times 6 \times 10 \) \( k \)-points or denser, when using the RIM (orange lines) or MC average (blue lines) over the entire BZ, or the auxiliary function of Carrier (pink lines), all codes converge \( \Sigma_{ik} \) for the VBM/CBM within \(< 0.1 \) eV. Moreover, in TABLE III and IV of the main manuscript, we show that the GW codes used in this work agree within 0.1 eV in the predicted gap of rutile.

We now converge the GW parameters with BERKELEYGW. In FIG. 5, we show the gap of rutile for given values of \( \epsilon_{\text{cut}} \) and \( N_{\text{sig.}} \), fixing \( N_{\text{eps.}} \) to 2000 (blue dots). For each value of \( \epsilon_{\text{cut}} \), we linearly extrapolate the gaps...
we obtain a converged $GW$ gap of rutile of 3.3 eV.

V. ZnO

We show that the $GW$ codes considered here can predict the same QP energies for ZnO within a given choice of PPs and frequency-integration method. In TABLE V of the main manuscript we show the VBM, CBM and fundamental gap of ZnO calculated with different codes and using a spherical-cutoff technique. As our aim is to compare output of different codes, we reduce computational cost and use under-converged $GW$ parameters: $\epsilon_{cut} = 80$ Ry, $5 \times 5 \times 4$ $k$-points and 34 bands to evaluate $\Sigma$. As expected, we find a negligible deviation for the PPM (GN) with respect to FF-integration, in agreement with Refs. 6, 8, and 9. Remarkably, the QP energies obtained with different codes agree within 0.03 eV.

Next, we converge the QP gap of ZnO with BERKELEYGW. Here we use an LDA starting point, a shifted grid of $8 \times 8 \times 5$ $k$-points for $\epsilon$ and $\Sigma$, and FF-CD with the same frequency grid as above. We then extrapolate the fundamental gap of ZnO, similar to previous cases. First, we calculate the gap for fixed values of $\epsilon_{cut}$ and extrapolating to $N_{sig.} \to \infty$ with $1/N_{PW}$; a linear extrapolation results in a gap of $3.26 \pm 50$ meV, and the accuracy is increased with a quadratic extrapolation resulting in $\Delta E_g = 3.27 \pm 10$ meV (see the inset). With this procedure, or alternatively by extrapolating simultaneously the parameters ($\epsilon_{cut}$, $N_{eps.}$, and $N_{sig.}$) via Eqn. 7 of the main text,

$$f(N_{eps.}, N_{PW}, N_{sig.}) = \left(\frac{a_1}{N_{eps.}} + b_1\right) \left(\frac{a_2}{N_{PW}} + b_2\right) \left(\frac{a_3}{N_{sig.}} + b_3\right),$$

we obtain a converged $GW$ gap of rutile of 3.3 eV.

---

* trangel@lbl.gov
1 M. Fuchs and M. Scheffler, Comput. Phys. Commun. 119, 67 (1999).
2 http://www.pseudo-dojo.org.
3 M. van Setten, M. Giantomassi, E. Bousquet, M. Verstraete, D. Hamann, X. Gonze, and G.-M. Rignanese, Comput. Phys. Commun. 226, 39 (2018).
4 http://opium.sourceforge.net.
5 http://www.abinit.org.
6 M. Stankovski, G. Antonius, D. Waroquiers, A. Miglio, H. Dixit, K. Sankaran, M. Giantomassi, X. Gonze, M. Côté, and G.-M. Rignanese, Phys. Rev. B 84, 241201 (2011).
7 J. Klimeš, M. Kaltak, and G. Kresse, Phys. Rev. B 90, 075125 (2014).
8 A. Miglio, D. Waroquiers, G. Antonius, M. Giantomassi, M. Stankovski, M. Côté, X. Gonze, and G.-M. Rignanese, Eur. Phys. J. B 85, 1 (2012).
9 P. Larson, M. Dvorak, and Z. Wu, Phys. Rev. B 88, 125205 (2013).