Quasiparticle band structure based on a generalized Kohn-Sham scheme

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We present a comparative full-potential study of generalized Kohn-Sham schemes (gKS) with explicit focus on their suitability as starting point for the solution of the quasiparticle equation. We compare $G_0W_0$ quasiparticle band structures calculated upon LDA, sX, HSE03, PBE0, and HF functionals for exchange and correlation (XC) for Si, InN and ZnO. Furthermore, the HSE03 functional is studied and compared to the GGA for 15 non-metallic materials for its use as a starting point in the calculation of quasiparticle excitation energies. For this case, also the effects of selfconsistency in the $GW$ self-energy are analysed. It is shown that the use of a gKS scheme as a starting point for a perturbative QP correction can improve upon the deficiencies found for LDA or GGA starting points for compounds with shallow $d$ bands. For these solids, the order of the valence and conduction bands is often inverted using local or semi-local approximations for XC, which makes perturbative $G_0W_0$ calculations unreliable. The use of a gKS starting point allows for the calculation of fairly accurate band gaps even in these difficult cases, and generally single-shot $G_0W_0$ calculations following calculations using the HSE03 functional are very close to experiment.

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I. INTRODUCTION

Density functional theory (DFT) has become the most successful method for condensed matter calculations. This success is largely rooted in the simplicity of the exchange and correlation (XC) energy in the local density (LDA) or generalized gradient (GGA) approximation. However, the underlying Kohn-Sham (KS) formalism fails in the prediction of electronic excitation energies of semiconductors and insulators. A significant step forward to correct excitation energies was achieved when the ab initio calculations of quasiparticle (QP) states were performed. Their description is based on the quasiparticle equation with the XC self-energy $\Sigma$ for one excited electron or hole. In general, its solution is based on Hedin’s $GW$ approximation (GWA) for the self-energy and a perturbative treatment of the difference to the XC potential used in the KS equation. The central quantity is the dynamically screened Coulomb potential $W$, which characterizes the reaction of the electronic system after excitation. For many non-metals, such as the semiconductor silicon (Si), the method works well with an accuracy of 0.1–0.3 eV for their QP gaps if the Green’s function $G$ is described by one pole at the KS (i.e., $G_0$), or better, at the QP (i.e., $G$) energy. However, for systems with a wrong energetic ordering of the KS bands first-order perturbation theory is not applicable. Examples are semiconductors with a negative fundamental gap in DFT-LDA or -GGA, e.g. InN (and references therein), or with shallow $d$ bands, e.g. ZnO.

Besides the KS approach itself, the origin of the band gap problem is related to the semi-local approximation (LDA/GGA) for XC, which introduces an unphysical self-interaction and lacks a derivative discontinuity. These deficiencies can be partially overcome using self-interaction-free exact exchange (EXX) potentials, which are special realizations of an optimized effective potential (OEP) method, A, by conception, different way to address the band gap problem is the use of a generalized Kohn-Sham (gKS) scheme, which means starting from a scheme with a spatially non-local XC potential. In this framework, the screened-exchange (sX) approximation uses a statically screened Coulomb kernel instead of the bare kernel in the Hartree-Fock (HF) exchange and, with it, resembles the screened-exchange (SEX) contribution to the XC self-energy in the GWA. Other hybrid functionals such as those following the suggestions of Adamo and Barone (PBE0) or Heyd, Scuseria, and Ernzerhof (HSE03) combine parts of bare or screened exchange with an explicit density functional. The gKS eigenvalues are usually in much better agreement with the experiment than the LDA/GGA ones. Therefore, the gKS solutions are supposed to be superior starting points for a QP correction, since first-order perturbation theory should be justified. Hence the replacement of $G$ by $G_0$ calculated from solutions of a gKS scheme may be interpreted as a first step towards a self-consistent determination of the self-energy operator.

Here we report a systematic study of QP energies calculated from GW corrections to the results of gKS schemes. First, in section III A we evaluate the performance of $G_0W_0$ corrections to different gKS starting points for Si, InN, and ZnO using the functionals sX, HSE03, PBE0, and HF. The results are compared to those of the standard KS approach based on an LDA functional. In section III B QP gaps are calculated for a benchmark set of fifteen non-metals utilizing the HSE03 starting point. The effects of selfconsistency in $G$ and $W$ are discussed in comparison to the results based on a GGA starting point used in Ref. [16].
II. METHOD

All calculations are performed at the experimental lattice constants. We use the projector augmented-wave (PAW) method as implemented in the Vienna Ab initio Simulation Package. For the details of the GW implementation we refer to Refs. [15] and [16]. The GW calculations are carried out using a total number of 150 bands for all materials. For the Brillouin-zone integrations, \(8 \times 8 \times 8\) k-point meshes including the \(\Gamma\) point were used, except in the case of ZnO (LDA) and InN (sX, HSE03) where the \(k\)-point convergence of \(W\) was found to be critical for meshes containing \(\Gamma\). In these cases, \(8 \times 8 \times 8\) Monkhorst-Pack k-point grids avoiding \(\Gamma\) were used for the evaluation of \(W\).

One problem of the presence of shallow \(d\) levels is the strong core-valence \(XC\) interaction. It can be estimated within the LDA or HF approximation, where the latter one is expected to be more reliable since the \(GW\) self-energy approaches the bare Fock exchange operator in the short wavelength regime (i.e., at large electron binding energies). Therefore, we apply the HF approximation to the core-valence \(XC\) self-energy for all \(GW\) calculations reported here (see Ref. [16] for a validation of this approach).

Here we do not update the QP wave functions corresponding to the neglect of non-diagonal matrix elements of the self-energy represented in terms of the gKS wave functions \(\psi_{\lambda}^{gKS}\). The QP excitation energy \(\epsilon_{\lambda}^{N+1}\) of a state \(\lambda\) in the \((N+1)\)-th iteration is related the \(N\)-th iteration through the linearized equation:

\[
\epsilon_{\lambda}^{N+1} = \epsilon_{\lambda}^{N} + Z_{\lambda}^{N} \times \text{Re} \left[ \langle \psi_{\lambda}^{gKS} | [T + V_{n-e} + V_{H} + \Sigma(\epsilon_{\lambda}^{N})] \psi_{\lambda}^{gKS} \rangle - \epsilon_{\lambda}^{N} \right],
\]

where \(T\) is the kinetic energy operator, \(V_{n-e}\) the nuclei-potential, \(V_{H}\) the Hartree potential, and \(Z_{\lambda}^{N}\) the renormalization factor given by

\[
Z_{\lambda}^{N} = \left( 1 - \text{Re}\langle \psi_{\lambda}^{gKS} | \frac{\delta}{\delta \epsilon} \Sigma(\epsilon) \rangle \langle \epsilon_{\lambda}^{N} | \psi_{\lambda}^{gKS} \rangle \right)^{-1}.
\]

The first iteration, usually denoted by \(G_{0}W_{0}\), is based on the gKS eigenvalues \(\epsilon_{\lambda}^{0} = \epsilon_{\lambda}^{gKS}\) as initial input to the \(GW\) calculation. Within this approximation the perturbation operator in (1) becomes \(\Sigma(\epsilon_{\lambda}^{gKS}) - V_{XC}^{gKS}\) corresponding to the difference between the \(GW\) self-energy and the non-local \(XC\) potential used in the gKS equation, and the \(G_{0}W_{0}\)-QP shift for a certain gKS state is given by:

\[
\Delta_{\lambda,\lambda} = Z_{\lambda}^{0} \text{Re} \langle \psi_{\lambda}^{gKS} | \Sigma(\epsilon_{\lambda}^{0} = \epsilon_{\lambda}^{gKS}) - V_{XC}^{gKS} | \psi_{\lambda}^{gKS} \rangle.
\]

In the actual implementation of the gKS schemes, we split the gKS \(XC\) energy into the form:

\[
E_{XC}^{gKS} = E_{XC}^{DFT} + \alpha \left[ E_{CF}^{SR}(\mu) - E_{CF}^{DFT,SR}(\mu) \right],
\]

i.e., a short-range non-local exchange term is added and treated exactly resulting in a non-local (screened) exchange potential. The superscript \(DFT\) indicates that the respective quantity is evaluated in some (quasi)local approximation, while \(E_{CF}^{SR}\) corresponds to one of the (screened) Coulomb kernels given in Table I. The weight \(\alpha\) of the short range part and the inverse screening length \(\mu\) are also listed in this table. For simplicity, in the case of sX, the inverse screening length \(\mu\) corresponding to the Thomas-Fermi wave vector was chosen materials independent \(k_{TF} = 1.55 \text{ Å}^{-1}\). Gradient corrections were used for the HSE03 and PBE0 functionals.

III. RESULTS

A. \(G_{0}W_{0}\) quasiparticle band structure of Si, ZnO, and InN

1. Generalized Kohn-Sham bands

Results of the gKS calculations are summarized in Table I together with experimental results. We notice an increase of the computed gaps when going from the LDA to a truly non-local \(XC\) functional. This can be attributed to the reduction of the spurious self-interaction found in LDA, the inclusion of a potential discontinuity between filled and empty states in the \(XC\) functional [17,18] and the – in comparison to LDA – enhanced core-valence exchange. Furthermore, for direct gaps we observe the tendency to increase from LDA over HSE03, sX, and PBE0 to the HF values.

For ZnO and InN, the \(d\)-band binding energies increase with respect to the LDA, approaching the experimental values. This is an important fact to note, since the difficulties of the LDA+\(G_{0}W_{0}\) approach for these compounds partly result from too shallow \(d\) electrons in LDA, which is itself a result of the spuriously contained self-interaction in local and semi-local functionals. The too shallow \(d\) electrons hybridize too strongly with the \(p\) bands at the valence-band maximum (VBM), pushing them upwards, in turn decreasing the gap (\(pd\) repulsion) beyond the common LDA gap underestimation found for example in Si. Contrary to the LDA, the gKS starting points yield stronger bound \(d\) electrons (cf. Table I) with binding energies closer to the experimental values. Hence the gKS functionals can be expected to give a more reasonable estimate for the influence of the \(pd\) repulsion on the fundamental gap and to provide better starting wave functions for the \(GW\) calculations. For instance, in ZnO the Zn \(d\) character of the wave functions at the VBM is decreased from 0.3 for LDA to 0.25 for HSE03.

In comparison to experiment the gKS functionals, with ex-

| Functional | \(\alpha\) | \(sr\) Coulomb kernel | \(\mu\) [Å\(^{-1}\)] |
|------------|--------|----------------------|------------------|
| LDA        | 0.00   | 1/|x| | - |
| sX         | 1.00   | \(\exp(-\mu|x|)/|x|\) | 1.55 |
| HSE03      | 0.25   | \(\text{erfc}(\mu|x|)/|x|\) | 0.3 |
| PBE0       | 0.25   | 1/|x| | - |
| HF         | 1.00   | 1/|x| | - |
TABLE II: Direct and indirect generalized KS band gaps $E_{gKS}$ and average $d$-band binding energies $E_{gKS}^d$ calculated for cubic Si, InN, and ZnO. Experimental values are from data collections in Refs. 6, 16,20,21,22,23. In the case of InN and ZnO they refer to the wurtzite polytype. All values are given in eV.

| Energy | LDA | sX | HSE03 | PBE0 | HF | Exp. |
|--------|-----|----|-------|------|----|------|
| Si     | $E_{gKS}^d$ | 0.51 | 0.98 | 1.04 | 1.85 | 6.57 | 1.17 |
|        | $E_{gKS}$  | 2.53 | 3.23 | 3.15 | 3.98 | 9.08 | 3.40 |
| InN    | $E_{gKS}^d$ | -0.38 | 0.39 | 0.37 | 1.14 | 7.15 | 0.61 |
|        | $E_{gKS}$  | 13.1 | 17.2 | 14.6 | 14.7 | 18.6 | 16.0-16.9 |
| ZnO    | $E_{gKS}^d$ | 0.6  | 2.97 | 2.11 | 3.03 | 11.07 | 3.44 |
|        | $E_{gKS}$  | 4.6  | 8.2  | 5.7  | 5.8  | 9.3  | 7.5-8.8 |

FIG. 1: (Color online) First-order quasiparticle shifts $\Delta_{\lambda \lambda}$ versus gKS eigenvalues for InN (a) and ZnO (b). The valence-band maximum (VBM) and the conduction-band minimum (CBM) are taken as energy zeros for occupied and empty states, respectively. Results for five different starting gKS band structures are shown.

3. Non-selfconsistent QP bands

Table III shows the results of the $G_0W_0$ calculations for the fundamental gaps and $d$-electron binding energies. In contrast to the LDA or gKS energies, these QP energies should have a physical meaning as measurable quantities and thus can be compared directly to the experimental gap values. However, it is necessary to note that the experimental values for InN and ZnO correspond to the wurtzite instead of the zincblende polytype used in the calculations. The zincblende gaps are expected to be about 0.2 eV smaller than the wurtzite ones. For silicon, the QP gaps calculated upon the LDA, sX, or HSE03 starting point are remarkably small with respect to the dispersion and amplitude, and they remain well below 1 eV. For ZnO (Fig. 1b) similar observations can be made, however, as discussed before, the smaller binding energy of the Zn 3d states causes a stronger hybridization of $p$ and $d$ states than in InN. This might explain the upward bending of the sX shifts close to the VBM and the stronger bending of the LDA conduction band shifts.
### Table III: Direct (d) and indirect (i) $G_0W_0$ QP band gaps, average $d$-band binding energies and static electronic macroscopic dielectric constants $\varepsilon_d$ calculated upon the respective gKS band structures for Si, ZnO, and InN. All energy values are given in eV. Experimental results are given for comparison.

| Material | LDA  | sX  | HSE03 | PBE0 | HF  | Exp. |
|----------|------|-----|-------|------|-----|------|
| Si       | 1.08 | 1.31 | 1.32  | 1.65 | 2.93| 1.17 |
| ZnO      | 2.14 | 3.36 | 2.87  | 3.24 | 5.71| 3.44 |
| InN      | 15.1 | 15.6 | 15.2  | 15.3 | 16.6| 16.0-16.9 |
|          | 12.2 | 6.6  | 6.8   | 4.9  | 2.4 | 7.96 |

### Table IV: Results for the fundamental gaps of the HSE03 and quasiparticle ($G_0W_0$, $GW_0$ and $GW$) calculations, and static electronic macroscopic dielectric constants as used in $W_0$ (RPA). The calculated values for the spin-orbit coupling (SO) induced gap-closing given in the last column have been included in the gaps. Also reported is the mean absolute relative error (MARE) and the mean relative error (MRE) for the gaps. Experimental data for the gaps and dielectric constants are given for comparison (for references see Ref. [16]). Underlined values indicate zero temperature values.

| Material | HSE03 | $G_0W_0$ | $GW_0$ | $GW$ | exp. | $\varepsilon$ | $\varepsilon^{exp}$ | SO |
|----------|-------|----------|--------|------|------|--------------|-------------------|----|
| Ge       | 0.54  | 0.79     | 0.82   | 0.83 | 0.74 | 14.0         | 16.0             | 0.08 |
| Si       | 1.04  | 1.32     | 1.35   | 1.37 | 1.17 | 9.8          | 11.90            |    |
| GaAs     | 1.12  | 1.66     | 1.71   | 1.75 | 1.52 | 9.5          | 11.10            | 0.10 |
| SiC      | 2.03  | 2.60     | 2.68   | 2.76 | 2.40 | 5.6          | 6.52             |    |
| CdS      | 1.97  | 2.55     | 2.65   | 2.80 | 2.42 | 4.6          | 5.30             | 0.02 |
| AlP      | 2.09  | 2.69     | 2.77   | 2.86 | 2.45 | 6.3          | 7.54             |    |
| GaN      | 2.65  | 3.29     | 3.38   | 3.53 | 3.20 | 4.6          | 5.30             | 0.00 |
| ZnO      | 2.11  | 2.86     | 3.02   | 3.33 | 3.44 | 3.4          | 3.74             | 0.01 |
| ZnS      | 3.05  | 3.69     | 3.79   | 3.95 | 3.91 | 4.5          | 5.13             | 0.02 |
| C        | 5.08  | 5.84     | 5.92   | 6.03 | 5.48 | 4.9          | 5.70             |    |
| BN       | 5.54  | 6.54     | 6.66   | 6.85 | 6.14-6.4 | 3.9          | 4.50             |    |
| MgO      | 6.22  | 7.94     | 8.20   | 8.66 | 7.83 | 2.6          | 3.00             |    |
| LiF      | 11.2  | 14.1     | 14.5   | 15.2 | 14.20 | 1.8          | 1.90             |    |
| Ar       | 10.1  | 13.7     | 14.1   | 14.7 | 14.20 | 1.6          | -                |    |
| Ne       | 14.1  | 20.2     | 20.7   | 21.4 | 21.70 | 1.2          | -                |    |

### B. Selfconsistent QP calculations starting from the HSE03 functional

One important question concerns the influence of selfconsistency and the resulting QP corrections in the case of a gKS starting point, especially in comparison to local or semilocal DFT. For that reason, we have calculated the QP gaps for 15 materials, without and with partial (only in $G$) or full (in both $G$ and $W$) selfconsistency with respect to the eigenvalues, starting from the eigenvalues and wave functions of the HSE03 functional. In Section [II A 2] and [II A 3] this starting point was found to give the best results for the fundamental gaps and the smallest quasiparticle shifts. The materials addressed are non-metals, spanning the range from small-gap semiconductors to insulators. They are chosen as a subset of those considered in Ref. [16]. With the technical details kept largely identical, except for the different starting point, the data collected in Table [IV] allows for a direct and unbiased comparison of the GGA(PBE) starting point[16] and the HSE03 starting point used in this work. The only important differ-
ence to Ref. [16] is that we now restore the all-electron charge density exactly on the plane wave grid for the calculation of the correlation energy. This yields technically more accurate d-band binding energies. Details of the applied procedure will be published elsewhere.26

Our results show that the HSE03 gaps, even though they are generally closer to the experiment than the DFT-LDA/GGA ones, still underestimate the experimental gaps on average by 21%. This underestimation is cured and turned into a slight overestimation of about 2.3% upon the inclusion of $G_0W_0$ quasiparticle corrections. The mean absolute relative error (MARE) is reduced to 6.8%, which is a significant improvement compared to the 9.9% MARE obtained for the GGA+$G_0W_0$ gaps.16 Basically, this improvement results from the good performance of the HSE03 starting point for materials that comprise d electrons such as GaAs, CdS, GaN, ZnO, and ZnS, for which the HSE03+$G_0W_0$ gap-MARE is calculated to be 7.9%, while it is about 19.2% in the GGA+$G_0W_0$ approach. We attribute the better agreement to the improved description of the pd repulsion on the HSE03 level, which impacts the energy levels and wave functions (cf. Sec. IIIA1). For the rest of the materials, both approaches GGA/HSE03 perform on par with a MARE of 4.8/6.1%. While HSE03+$G_0W_0$ usually slightly overestimates the band gaps, the band gaps for ZnO, ZnS, LiF, Ar, and Ne remain underestimated compared to experiment. This may be related to the large errors of the HSE03 gap exceeding 30% for these materials. Thus, the inaccuracy of perturbation theory prevails for these systems, which share a relatively weakly screened core. Parallel to the findings for a GGA starting point the enhanced core-valence interaction in the HSE03 scheme is found pronounced underestimation of the binding energies. Analogue observations have been made for a GGA starting point, suggesting the common conjecture that wave functions have only a small effect on the band gaps. Similar changes were observed in the self-consistent quasiparticle GW (scQPGW) scheme,27,29,30

Finally, we address the d-band binding energies calculated upon the HSE03 and PBE starting point for different levels of quasiparticle selfconsistency, as shown in Table VI. We have to note that the present calculations do not include the s and p orbitals with the same main quantum number as the semi-core d shell. However, since here the core-valence interaction is approximated by HF exchange rather than by LDA, as inherent to conventional pseudopotential calculations, the values given in Table VI already provide a reasonable estimate for the d-band binding energies (cf. Ref. [18] and [16]). Updated values for the PBE case are also supplied; the present values surpass those in Ref. [16] and are more accurate, since the all-electron charge density is now accurately restored on the plane wave grid.32 In general, the QP binding energies increase over the HSE03 one-electron values due to the quasiparticle corrections, which can be understood mainly from the effects of the enhanced core-valence interaction in the GW calculations. Only in the case of ZnS this trend does not hold for yet unknown reasons. However, compared to the experimental values all three quasiparticle schemes studied here underestimate the d-band binding energies. With increasing selfconsistency along the row ($G_0W_0$, $G_0W_0$, and $GW$) the d bands shift to larger binding energies. Thereby, for the Ga 3d levels, the calculated values approach the experimental ones. In the case of the Zn 3d levels, which are just below the $p$-like upper valence band complex, the situation is different with a more pronounced underestimation of the binding energies. Analogue observations have been made for a GGA starting point, which gives a smaller d-band binding energy than the HSE03

| Material | HSE03 | G0W0 | GW0 | GW | Exp. |
|----------|-------|------|-----|----|------|
| GaAs     | 17.2  | 17.5 | 17.6| 17.6| 18.9 |
| GaN      | 15.4  | 16.1 | 16.3| 16.5| 17.0 |
| ZnO      | 5.7   | 6.1  | 6.3 | 6.4 | 7.5-8.8|
| ZnS      | 7.5   | 7.2  | 7.2 | 7.3 | 9.0  |
| PBE      |       |      |     |     |      |
| GaAs     | 14.8  | 16.8 | 17.2| 18.9|
| GaN      | 13.3  | 15.4 | 16.1| 17.0|
| ZnO      | 5.2   | 6.1  | 6.4 | 7.5-8.8|
| ZnS      | 6.1   | 6.8  | 7.2 | 9.0 |
starting point for each level of selfconsistency. We note that Fleszar and Hanke observed that the inclusion of vertex corrections in the self-energy shifts the \( d \) states to stronger binding energies, suggesting that the neglect of such corrections is responsible for the erroneous behavior of the \( GW \) approximation for \( d \) states.

IV. SUMMARY AND CONCLUSIONS

We have presented \( G_0W_0 \) QP calculations starting from a variety of XC functionals: LDA, sX, HSE03, PBE0, and HF for Si, InN and ZnO. We have shown that the gKS schemes, which take into account a screened exchange potential or part of it (sX, HSE03), give rise to eigenvalues close to the QP excitation energies. The resulting \( G_0W_0 \) corrections were found to yield QP energies in good agreement with the experimental data, and the QP shifts are less dispersive than those calculated upon LDA. Overall the HSE03 and PBE0 functionals gave one-electron energies very close to the successive \( GW \) calculations, resulting in small \( QP \) gap corrections across the considered energy range. For the HSE03+\( G_0W_0 \) case, the final QP energies were in very good agreement with experimental, whereas the PBE0 functional was found to yield too large QP gaps. We traced this back to a significant underestimation of the screening for the PBE0 functional, when the random phase approximation is used (also applied to determine \( W \)).

Furthermore, the QP gaps for 15 materials comprising small and large gap systems were calculated, in order to provide a benchmark of the HSE03 starting point against the GGA one. It was shown that the HSE03+\( G_0W_0 \) approach yields an almost halved overall error for the fundamental gaps compared to the GGA starting point. The largest improvement over the LDA/GGA starting points were found for materials with shallow \( d \) states such as ZnO, ZnS, InN, GaAs, and GaN, where the LDA/GGA starting point suffers from a significant underestimation of the \( d \)-band binding energies and a consequently overestimated repulsion between \( p \)- and \( d \)-like states. Since the \( d \)-band binding energies calculated using one of the gKS schemes (e.g. HSE03) are closer to the experiment, the influence of the \( pd \) repulsion on the gap is described more accurately.

Furthermore, the effects of different degrees of selfconsistency were investigated. It was found that both, selfconsistency in \( G \) (\( GW_0 \)) and selfconsistency in \( G \) and \( W \) (\( GW \)), impair the agreement with experimental data. For \( GW_0 \), this is in contrast to the findings for a GGA starting point. This could be traced back to the poorer description of the dielectric screening for the HSE03 starting point. Selfconsistency according to the \( GW \) scheme with an update of eigenvalues in both \( G \) and \( W \) further diminishes the agreement with measurements, due to a further reduction of the already underestimated screening. This is analoge to the findings for GGA based \( GW \) calculations. In general, concerning selfconsistent QP schemes, the present work confirms the observation already made in previous work: to obtain accurate QP gaps it is essential to use an electronic response function and a screened interaction \( W \) that agree closely with experiment, and to combine this screened interaction with an accurate Green’s function \( G \). For the \( GW_0 \) case based upon HSE03 wave functions, the overestimation of the gaps clearly relates to an underestimation of the static electronic screening employing HSE03 and the random phase approximation. In this light, the success of the perturbative single-shot HSE03+\( G_0W_0 \) approach is a little bit fortuitous, since the overestimation of the screening is partially canceled by too small gap corrections obtained using the single-shot perturbative \( G_0W_0 \) approach. Probably the same is true for some other single shot approaches, such as EXX-OEP+\( G_0W_0 \). Nevertheless, if computational efficiency is an important issue— and it more often is than not —then the HSE03+\( G_0W_0 \) approach is indeed an excellent balance between accuracy and speed. The calculations are as efficient as for the commonly used LDA+\( G_0W_0 \) method, and, with very few exceptions, the errors are smaller than 10 \%. If better accuracy is required, it can be achieved, but only by updating the wave functions and including excitonic effects in the calculation of the screening properties, i.e., vertex corrections in \( W \). For most mater, such calculations are currently not feasible due to the large computational requirements.

A similar accuracy as for the HSE+\( G_0W_0 \) approach can be achieved by starting from GGA wave functions and eigenvalues, and updating the eigenvalues in \( G \) until convergence is reached (see Ref. [16]). This approach yields comparable errors as HSE03+\( G_0W_0 \), but it is computationally more demanding, since several iterations are required to converge \( G \). The latter method is also problematic for materials with an inverted band order in LDA/GGA. Which approach to choose (HSE03+\( G_0W_0 \) or GGA+\( GW_0 \)) is to some extend a matter of taste, and the final results are usually very close and often bracket the experiment. If efficiency and robustness (band order) are issues, the HSE03+\( G_0W_0 \) approach seems to be preferable, and it is certainly much more accurate than the traditional LDA+\( G_0W_0 \) method.

Concerning the position of the \( d \) levels, the HSE03+\( G_0W_0 \) method shows an underestimation of the \( d \)-band binding energies by about 1 eV for almost all materials. Similar observations were made for the LDA/GGA case, and LDA+U based \( GW \) calculations, and self-consistent quasiparticle \( GW \) (SCQPGW) calculations. The underestimation of the \( d \)-band binding energy is thus universal to the \( GW \) approximation and not related to the starting wavefunctions. The origin for this underestimation is yet unknown, but it is most likely related to the fact that the \( GW \) approximation is not entirely free of self-interaction errors, and only inclusion of vertex corrections in the self-energy might remedy this deficiency.

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