Electronic structure of TiSe$_2$ from a quasi-self-consistent $G_0W_0$ approach

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In a previous work it was shown that the inclusion of exact exchange is crucial for a first principles description of both the electronic- and the vibrational properties of TiSe$_2$ [Phys. Rev. Lett. 119 456325 (2017)]. The $GW$ approximation provides a parameter-free description of screened exchange but is usually employed perturbatively ($G_0W_0$) making results more or less dependent on the starting point. In this work we study the $GW$ band structure of TiSe$_2$ and show that it is a case extremely sensitive to the choice of $G_0$. We then develop a quasi-self-consistent scheme based on the random phase approximation (RPA) and the optimized effective potential of hybrid density functional theory. This approach generates an optimal $G_0W_0$ starting-point and a hybrid exchange parameter consistent with the RPA. The high-temperature phase of TiSe$_2$ is found to be semi-metallic, in agreement with most experimental results. Furthermore, the optimized hybrid functional accurately reproduces the low-temperature charge density wave phase.

I. INTRODUCTION

TiSe$_2$ is a layered quasi-two-dimensional material that undergoes an unconventional charge density wave (CDW) transition below 200 K. The apparent interplay between the CDW and superconductivity at finite pressure/doping$^{1,2}$ has lead to numerous studies over the past years aiming to understand the driving mechanism behind the CDW. Nevertheless, the relative role played by excitons and phonons is still debated. Experimentally, strong signatures are observed in both vibrational$^{3–6}$ and angle-resolved photoemission spectra (ARPES),$^{7–13}$ and some studies point to soft electronic modes.$^{14}$

First-principle calculations could explain the exact mechanism of the CDW transition. However, numerically tractable approximations such as the local density approximation (LDA) or generalized gradient approximations (GGAs) within density functional theory (DFT) fail to give a complete picture.$^{15–17}$ A dramatic improvement is found when including a fraction of Hartree-Fock (HF) exchange via the hybrid functionals.$^{18–20}$ With a result similar to the DFT+$U$ approach,$^{17,21}$ the Ti-$d$ levels are then well described. In addition, the hybrid functionals contain the long-range Coulomb interaction which was shown to be crucial to induce the CDW phase.$^{20}$ This fact suggests that strong electron-hole coupling is at play and that an excitonic transition could be of importance.$^{22,23}$ On the other hand, it was found that the standard medium-range hybrid functional already gives a quantitatively reasonable agreement between theory and experiment. However, the results also showed to be strongly dependent on the hybrid parameters, making it still uncertain whether a parametrization optimized on a test-set of standard semi-conductors is adequate.

The $GW$ method is computationally more expensive but provides a parameter-free and physical description of screened exchange. The bare Coulomb interaction is replaced by the screened Coulomb interaction, $W$, which is determined by the linear density response function approximated at the Hartree level, i.e., the random phase approximation (RPA).$^{24,25}$ The $GW$ approximation for the self-energy is known to produce accurate band-gaps on a wide range of systems.$^{26–28}$ It is, however, almost always employed perturbatively ($G_0W_0$), on top of a DFT Kohn-Sham (KS) band structure, assuming that the KS electronic structure is close enough to the final result. Other variants that bring results closer to self-consistency have also been developed.$^{29–32}$ An alternative to the fully self-consistent $GW$ scheme is to look for the optimal KS starting-point via the Sham-Schlüter equation.$^{33–35}$ The resulting KS potential produces a density similar to the $GW$ density and is known as the RPA potential.$^{36,37}$ The RPA band structure can be shown to provide a consistent starting-point for $G_0W_0$.$^{38,39}$

A high-level calculation of the electronic band structure of TiSe$_2$ in the high-$T$ phase would be valuable. While transport experiments all predict a semi-metallic behaviour some ARPES measurements have found a gapped system.$^{7,8}$ The latter scenario was supported by the first $G_0W_0$ calculation.$^{40}$ In this work, we will re-examine how $G_0W_0$ performs on TiSe$_2$ by first showing that it is a case extremely sensitive to exchange in the starting-point. As a fully self-consistent calculation is out of reach we then develop a quasi-self-consistent approach that exploits the local hybrid potential as an approximation to the local RPA potential. In this way, we produce a theoretically justified $G_0W_0$ solution that approximates the RPA solution. At the same time we generate an RPA-optimized hybrid functional that is used to study the CDW phase.
The paper is organized as follows. In Sec. II we start by reviewing the GW formalism and the RPA as a self-consistent way to do perturbative $G_0W_0$. We then introduce a hybrid functional approach based on the optimized effective potential. Using this potential we then develop a quasi-self-consistent $G_0W_0$ scheme and compare it to variants introduced by others. In Sec. III we present numerical results and compare different $G_0W_0$ schemes to hybrid functionals and experiment. We also use the RPA optimized hybrid functional to study the CDW phase. Finally, in Sec. IV we present our conclusions.

II. SCREENED EXCHANGE FROM GW

We will focus on studying the performance of the GW approximation in describing the band structure of the high-$T$ phase of TiSe$_2$. The results turn out to be strongly dependent on which approximate GW scheme is used. In this section we, therefore, start by reviewing the different ways to solve the GW equations and discuss the connections between GW, RPA, COHSEX (COoulomb Hole Screened EXchange) and hybrid functionals. This will allow us to finally motivate a quasi-self-consistent $G_0W_0$ approach based on the local hybrid potential.

A. The GW approximation

We define the self-energy as the nonlocal frequency dependent potential $\Sigma$ that contains all the many-body effect beyond the Hartree ($\Phi$) approximation. To first order, in an expansion in terms of the Green’s function, $G$, and the Coulomb interaction, $v$, $\Sigma$ is just the static but nonlocal Fock term of the HF approximation,

$$\Sigma^{\text{HF}} = iGv.$$

(1)

By replacing the bare Coulomb interaction in the Fock term with the dynamically screened Coulomb interaction, $W$, we obtain the self-energy within the GW approximation

$$\Sigma = iGW.$$

(2)

The screened interaction within the GW approximation is approximated at the time-dependent Hartree level for which the irreducible polarizability, $P$, is approximated with $P_0$, i.e., to zeroth order in the explicit dependence on the Coulomb interaction. We thus have

$$W = v + vP_0W, \quad P_0 = -iGG.$$

(3)

From Dyson’s equation,

$$G = G_H + G_H \Sigma[G]|G,$$

(4)

we then have access to the quasi-particle spectrum contained in $G$.

It can further be shown that the GW approximation is a $\Phi$-derivable approximation$^{41,42}$ that obeys physical conservation laws and has an underlying action functional. An example of such an action functional is the Klein functional$^{43}$

$$Y_K = -i\Phi[G] - U_H + i\text{Tr}[GG_H^{-1} - 1 + \ln(-G^{-1})],$$

(5)

where $U_H$ is the Hartree energy. With the choice

$$\Phi[G] = \frac{1}{2}\text{Tr}\{\ln[1 + ivGG]\}$$

(6)

it is easy to see that $Y_K$ is stationary when $G$ obeys Dyson’s equation (Eq. (4)), and the self-energy is equal to

$$\Sigma = \delta\Phi \delta G = iGW.$$

(7)

At the stationary point the Klein functional is equal to the GW total energy as obtained from the standard non-variational Galitskii-Migdal energy expression.$^{44}$ Instead of using the Hartree approximation as the zeroth order approximation for $G$ one can use the KS system of DFT. The Dyson’s equation can then be re-written in terms of the single-particle KS Green’s function, $G_s$, and the exchange-correlation (xc) part of the local KS potential

$$G = G_s + G_s[\Sigma[G] - v_{xc}]G.$$

(8)

The diagonal of $G$, i.e. the density, is, by the fundamental theorems of DFT, already exactly described by $G_s$. In this way, $G_s$ can be assumed to be ‘close’ to $G$, justifying a perturbative treatment of Eq. (8), and thus circumventing the full solution to the numerically challenging Dyson’s equation.$^{26}$ By writing Eq. (8) in the basis of KS orbitals and keeping only the diagonal terms we can write the quasi-particle energy corrections as

$$E_k^{(1)} = \varepsilon_k + (k)|\Sigma_s(\varepsilon_k) - v_{xc}|k$$

(9)

where $k$ refers to the Bloch orbital index and $\varepsilon_k$ is the KS eigenvalue. The subscript $s$ on the self-energy signifies that it is evaluated with $G_s$. The frequency dependence can either be treated to zeroth order, i.e. $\omega = \varepsilon_k$, or to first order in a Taylor expansion around $\varepsilon_k$. The latter implies that also a renormalization factor

$$Z_k = \left[1 - \frac{\partial\Phi\Sigma_s}{\partial\omega}\bigg|_{\omega=\varepsilon_k}\right]^{-1}$$

(10)

should be multiplied to the matrix element.

The $G_0W_0$ correction of Eq. (9), starting from PBE or LDA, is the most common GW approach to determine the band structure. The justification of this approach relies, however, on the assumption that PBE or LDA orbitals are similar to the true quasi-particle orbitals. The renormalization factors are usually incorporated but it
can be argued that these should be omitted. 38 The arguments are based on the connection between GW and the RPA for the total energy,36,45,46 as we will now discuss.

Let us go back to the Klein energy functional (Eq. (5)) and keep the \( \Phi \) functional in the GW approximation. From now on we will add superscripts \( (\Phi^{GW}, \Sigma^{GW}) \) as we focus only on this approximation. If we replace the interacting \( G \), in every term, with a non-interacting \( G_s \) we can, after a few manipulations, write Eq. (5) as

\[
Y_K^{GW}[G_s] = -i\Phi^{GW}[G_s] + T_s[n] + U_H + U_{ext} \tag{11}
\]

where \( T_s \) is the kinetic energy of non-interacting KS electrons and \( U_{ext} \) is the external potential energy. It is easy to see that \( \Phi^{GW}[G_s] \) is exactly the same functional as the xc energy of the RPA energy functional

\[
E^{RPA}_s \equiv -i\Phi^{GW}[G_s] = -\frac{i}{2} \text{Tr} \{ \ln [1 + ivG_sG_s] \}. \tag{12}
\]

Eq. (11) is thus nothing but the RPA total energy, i.e.,

\[
Y_K^{GW}[G_s] = E^{RPA} \tag{36,46,47}
\]

The RPA energy functional can be shown to have a minimum when varied with respect to the total KS potential \( V_s = v_{ext} + v_H + v_{xc} \). Such a variation can be carried out via the functional \( G_s[V_s] \). At the minimum \( v_{xc} = v^{\text{RPA}}_{xc} \) obeys the so-called linearized Sham-Schüller (LSS) equation

\[
\int d2 \chi_s(1, 2)\varepsilon^{\text{RPA}}_{xc}(2) = \int d2d3 \Lambda_s(3, 2; 1)\Sigma^{GW}(2, 3) \tag{13}
\]

where \( \Lambda_s(3, 2; 1) = -ig_s(3, 1)G_s(1, 2) \) and \( \chi_s(2, 1) = -ig_s(2, 1)G_s(1, 2) \).\textsuperscript{48} The LSS equation can also be derived from the condition that the GW density and the KS RPA density, i.e. the diagonals of \( G \) and \( G_s \), are the same to first order when expanding Dyson’s equation (Eq. (8)).

As the RPA potential is a local KS potential it does not reproduce the fundamental gap.\textsuperscript{33−35} One can, however, still calculate the gap, \( E_g \), corresponding to the RPA functional by taking the derivative of the energy functional with respect to particle number \( N \). One finds

\[
E_g = I - A = \left. \frac{\partial E^{RPA}_s}{\partial N} \right|_+ - \left. \frac{\partial E^{RPA}_s}{\partial N} \right|_- . \tag{14}
\]

Evaluating the derivative on the right hand side ‘+’, i.e., the negative of the ionization energy

\[
-I = \varepsilon_v + \langle v | \Sigma^{GW}_s(\varepsilon_v) - v^{\text{RPA}}_{xc}| v \rangle \tag{15}
\]

and the derivative on the left hand side ‘−’, i.e., the negative of the affinity

\[
-A = \varepsilon_c + \langle c | \Sigma^{GW}_s(\varepsilon_c) - v^{\text{RPA}}_{xc}| c \rangle \tag{16}
\]

we can write

\[
E_g = E^{KS}_g + \Delta_{xc} \tag{17}
\]

where \( E^{KS}_g \) is the KS gap and

\[
\Delta_{xc} = \langle c | \Sigma^{GW}_s(\varepsilon_c) - v^{\text{RPA}}_{xc}| c \rangle - \langle v | \Sigma^{GW}_s(\varepsilon_v) - v^{\text{RPA}}_{xc}| v \rangle . \tag{18}
\]

To derive these expressions Eq. (13) has to be used. The quantity \( \Delta_{xc} \) is the so-called derivative discontinuity.\textsuperscript{49−52}

It is now clear that the gap obtained from the RPA functional is nothing but the \( G_0W_0 \) correction of Eq. (9) evaluated with the RPA potential. The RPA potential can thus be seen as an optimal starting point for \( G_0W_0 \) producing a gap equal to the gap extracted from the RPA functional. As noted in previous works this correction is without the renormalization factor.\textsuperscript{38} It has been shown on a number of semiconductors\textsuperscript{39} that using the RPA potential for a \( G_0W_0 \) calculation brings gaps in closer agreement with self-consistent GW approaches.\textsuperscript{30}

By expanding the GW quasiparticle energy around the zeroth order RPA KS energy and using Eq. (13) the expressions in Eqs. (15)-(16) are easily extended to the whole band structure, making Eq. (9) rigorously a first order approximation\textsuperscript{48}

\[
E_{k}^{RPA} = \varepsilon_k + \langle k | \Sigma^{GW}_s(\varepsilon_k) - v^{\text{RPA}}_{xc}| k \rangle . \tag{19}
\]

To conclude we have reviewed how it is possible to calculate gaps and even the full band structure from the RPA and that this corresponds to the perturbative \( G_0W_0 \) result evaluated with the local RPA potential. These are well-known results that we will base the following discussions on.

### B. Hybrid functionals and the COHSEX approximation

We will now turn to the simpler COHSEX and hybrid functionals which are often used as cheaper but self-consistent alternatives to the GW approach.

The frequency dependence of the GW self-energy allows for the description of many-body effects such as quasi-particle lifetimes and satellite spectra but severely complicates a fully self-consistent solution. Often one is, however, only interested in the quasiparticle excitation energy for which the nonlocality of the self-energy plays the most important role. It is then motivated to approximate \( \Sigma \) by ignoring dynamical effects in \( W \). This implies setting

\[
W_{\text{static}} = v + vP_0(\omega = 0)W_{\text{static}}, \tag{20}
\]

and results in the so-called COHSEX approximation

\[
\Sigma^{\text{COHSEX}} = iGW_{\text{static}} + \frac{1}{2}W^d_p, \tag{21}
\]

where \( W^d_p = \text{Diag} \{ vP_0(\omega = 0)W_{\text{static}} \} \) is a local Coulomb-potential and the first term is a nonlocal statically screened exchange operator. The COHSEX approximation can easily be solved self-consistently but can still
be numerically demanding since it requires the generation and summation over all conduction bands. A more drastic approach that avoids the inclusion of unoccupied bands is to keep the bare Coulomb interaction as in the HF approximation but scale it down with a constant \( \alpha \). If we then add a compensating fraction of the local PBE exchange and add a local PBE correlation term we get the so-called hybrid functionals

\[
\Sigma^{\text{HYB},\alpha} = \alpha \Sigma^{\text{HF}} + (1 - \alpha) v^{\text{PBE}}_x + v^{\text{PBE}}_c.
\]

(22)

These functionals are structurally similar to COHSEX but not more demanding than a HF calculation. One of the drawbacks is that a free parameter is introduced. A fraction 25\% (PBE0) has shown to be reasonable in many molecular systems. In HSE06 a second parameter, \( \mu = 0.2 \text{Å}^{-1} \), that controls the range of the Coulomb interaction is introduced.53 In this way, it is possible to get a good description of many semiconductors as well.

Although often used in a DFT context the hybrid functionals are almost always treated like the HF approximation, that is, by minimizing the energy with respect to orbitals that are generated by the nonlocal Fock potential. In this work we will instead use the optimized effective potential method and optimize the hybrid energy with respect to a local KS potential. The local KS potential corresponding to HF has been evaluated for solids before and is known as the exact-exchange (EXX) potential.55,56 The hybrid local potential is given by the sum of the local potentials derived from the PBE terms and a local exchange potential obtained from an equation similar to the LSS equation (Eq. (13)) but with \( \Sigma_{\text{GW}} \) replaced by the scaled HF self-energy. We have

\[
v^{\text{hyb}}_{\alpha} = v^{\alpha}_x + (1 - \alpha)v^{\text{PBE}}_x + v^{\text{PBE}}_c
\]

(23)

where

\[
\int d^2 \chi_s(1, 2)v^{\alpha}_x(2) = \alpha \int d^2 d^5 \Lambda_s(3, 2, 1) \Sigma^{\text{HF}}_{\alpha}(2, 3).
\]

(24)

The potential \( v^{\alpha}_x \) can again be seen as the local potential giving a density similar to the density of the fully nonlocal potential to first order. The gap will, however, differ from the gap of the nonlocal potential, but, when corrected with the discontinuity

\[
\Delta_{\text{xc}} = \langle c|\alpha \Sigma^{\text{HF}}_s - v^{\alpha}_x|c \rangle - \langle v|\alpha \Sigma^{\text{HF}}_s - v^{\alpha}_x|v \rangle
\]

(25)

the gap is expected to be close to that of the nonlocal hybrid functional.

C. Optimal \( G_0W_0 \) starting point based on a local hybrid potential

The common crucial ingredient in GW, COHSEX and hybrid functionals is the nonlocal exchange term. Due to this similarity the hybrids can be used as a way to do approximate self-consistent GW. Such an approach was developed in Refs. 32 and 57. By using a hybrid as a starting-point for \( G_0W_0 \) the \( \alpha \) parameter is varied until the GW correction vanishes. At this value, the GW and hybrid eigenvalues agree

\[
\langle k|\Sigma_{\alpha}^{\text{GW}}(\varepsilon_k) - \Sigma_{\alpha}^{\text{HYB},\alpha}|k \rangle = 0 \Rightarrow E^{\text{GW}}_k = \varepsilon_k.
\]

(26)

This method has shown to perform well for molecules, improving the ionization energies as compared to standard hybrid functionals and \( G_0W_0 \) based on the PBE starting-point.32 The GW correction in Eq. (26) can, however, not be derived from perturbation theory nor does it rely on a variational principle. In fact, the Klein GW energy functional has been shown to lack an extremum when varied in a restricted space of nonlocal but static potentials.58 It is, therefore, not possible to derive an expression similar to Eq. (17) under such assumptions. Care has therefore to be taken in interpreting the results as a step closer to full GW self-consistency.

We will now present a variant that utilizes the RPA energy and the optimization with respect to a local potential. As seen in the previous subsection a \( G_0W_0 \) correction based on the local RPA potential is justified via the GW LSS equation (Eqs. (13) and (19)). Analogously, a hybrid correction based on the local hybrid potential is justified via the hybrid LSS equation. We have

\[
E^{\text{HYB},\alpha}_k = \varepsilon_k + \langle k|\Sigma_{\alpha}^{\text{HYB},\alpha} - v^{\text{hyb},\alpha}_x|k \rangle.
\]

(27)

We will now approximate the RPA potential in Eq. (19) by the local hybrid potential

\[
E^{\text{RPA}}_k \approx \varepsilon_k + \langle k|\Sigma^{\text{GW}}_\alpha(\varepsilon_k) - v^{\text{hyb},\alpha}_x|k \rangle
\]

(28)

and optimize \( \alpha \) such that the correction in Eq. (27) and Eq. (28) are equal. This is equivalent to

\[
\langle k|\Sigma^{\text{GW}}_\alpha(\varepsilon_k) - \Sigma^{\text{HYB},\alpha}_\alpha|k \rangle = 0 \Rightarrow E^{\text{RPA}}_k = E^{\text{HYB},\alpha}_k.
\]

(29)
where the self-energy operators are evaluated with orbitals and eigenvalues from $\psi_{H^B,\alpha}$ (instead of $\Sigma_{s}^{HYB,\alpha}$ as in Eq. (26) above). In this way, we optimize $\alpha$ such that the DFT hybrid functional behaves like the RPA functional when varying the particle number. But note that the $G_0W_0$ correction never vanishes as in Eq. (26).

Due to lack of frequency dependence in $\Sigma_s^{HYB,\alpha}$ the condition in Eq. (29) is, in general, impossible to fulfill for all bands at every $k$, but can be made true for the difference between the highest occupied orbital and the lowest unoccupied orbital. One thus needs to optimize $\alpha$ using the following condition

$$\langle c | \Sigma_{s}^{GW} (\varepsilon_c) - \Sigma_{s}^{HYB,\alpha} | c \rangle - \langle v | \Sigma_{s}^{GW} (\varepsilon_v) - \Sigma_{s}^{HYB,\alpha} | v \rangle = 0. \quad (30)$$

### III. NUMERICAL RESULTS

In this section we start by discussing the system and the technical aspects of our calculations. We then present the different $G_0W_0$ results and investigate the performance of the RPA optimized hybrid functional.

#### A. System and computational details

The high-$T$ phase of TiSe$_2$ crystallizes in the space group $P3m1$. It belongs to the $1T$ family of the layered transition metal dichalcogenides with the Ti-atom octahedrally coordinated by six neighboring Se-atoms. A semi-metallic behaviour is found in most experiments. Below 200 K a CDW transition occurs, characterized by a $2 \times 2 \times 2$ superstructure (space group $P3\overline{1}c1$) and the opening of a small gap. The distortion pattern can be uniquely defined by the displacement $\delta\text{Ti}$ and the ratio $\delta\text{Ti}/\delta\text{Se} \approx 3$. Standard DFT functionals predict a phonon instability at the three equivalent $L$ points. A symmetric combination of these gives the correct CDW pattern, but with a severely underestimated distortion amplitude.$^{17}$ Hybrid functionals give a better description and have revealed the important role of HF exchange for the instability. This possibly hints to the presence of an excitonic instability. Although a weakly screened electron-hole interaction is clearly important, no spontaneous electronic CDW has so far been generated in bulk TiSe$_2$. Hybrid functionals induce the CDW via a strong electron-phonon coupling combined with the enhanced electronic susceptibility at the $L$ points. This mechanism is given support by the combined accuracy of the electronic bands, phonons and distortion amplitude.$^{20}$

In this work we aim for the more sophisticated GW method that allows for a physical description of the screened interaction. Due to the increase in computational cost we have been limited to the high-$T$ phase. The low-$T$ CDW phase will be studied with the RPA-based hybrid functional, optimized according to the procedure described in the previous section.

The hybrid calculations have been performed with VASP.$^{59-61}$ Quantum Espresso$^{62}$ (QE) and the CRYS-TAL program.$^{63}$ Whenever comparisons could be made these codes, despite using different pseudo potentials or in the latter case a Gaussian basis-set, agree rather well. For example, $p - d$ gaps agree within 0.05 eV. We have used a range-separation parameter of $\mu = 0.1$ Å$^{-1}$ in all hybrid calculations. A finite range separation parameter is not only physically more suitable for metals but also numerically advantageous by allowing for quicker and more stable convergence with respect to $k$-points. We chose a range twice as large as in HSE06 since our previous work indicated that HSE06 was somewhat too short ranged.$^{20}$ The local hybrid potential for solids was generated from an extension of a molecular code for solving the LSS equation.$^{64}$ The GW self-energy was subsequently evaluated using the YAMBO code.$^{65,66}$ For the optimization procedure of Eq. (26) we used the VASP code. We sampled the Brillouin zone with a $12 \times 12 \times 6$ $k$-point grid and used a plane-wave cutoff of 80 Ry (QE) and 380 eV (VASP). Around 360 unoccupied bands where included in the GW self-energy.

#### B. $G_0W_0$ band structure

The high-$T$ phase PBE band structure of TiSe$_2$ has been published in several previous works.$^{17}$ To allow for comparisons with our new results it is repeated here in Fig. 1. The PBE results differ strongly from ARPES experiments. The Se-$p$ -Ti-$d$ band overlap is severely overestimated and even inverted at $\Gamma$, leading to strong $p - d$ hybridization$^{17}$ and excess $d$-electron occupation. These large errors in the occupations and the charge density questions the use of a standard PBE/LDA starting-point for $G_0W_0$. Similar problems have been found in many materials with localized $d$-states.$^{67-70}$

In the same figure we have plotted the results from the

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Table I. Direct $\Gamma - \Gamma$ and indirect $\Gamma - (M, L)$ gaps (or band-overlaps) (eV) in the high-$T$ phase of TiSe$_2$. $\text{HYB}^{\alpha=0.20}$ signifies a hybrid functional with $\alpha$ fraction of the nonlocal(local) Fock potential. The subscripts opt and lopt indicate that $\alpha$ was optimized using the procedure of Eq. (26) and Eq. (30), respectively.

|      | HSE06 | COHSEX | EXX$_c$ | HYB$_{opt}$ | HYB$_{opt}$ | HYB$_{opt}$ | HYB$_{opt}$ | HYB$_{opt}$ | HYB$_{opt}$ |
|------|-------|--------|---------|-------------|-------------|-------------|-------------|-------------|-------------|
| $\Gamma - \Gamma$ | 0.51  | 0.84   | 1.51    | 1.01        | 1.10        | 0.47        | 0.57        | 0.69        |
| $\Gamma - M$      | 0.10  | 0.36   | 0.93    | 0.62        | 0.63        | 0.11        | 0.21        | 0.22        |
| $\Gamma - L$      | -0.15 | 0.12   | 0.80    | 0.39        | 0.40        | -0.16       | -0.08       | -0.11       |

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where the self-energy operators are evaluated with orbitals and eigenvalues from $\psi_{2c}^{H^B,\alpha}$ (instead of $\Sigma_{s}^{HYB,\alpha}$ as in Eq. (26) above). In this way, we optimize $\alpha$ such that the DFT hybrid functional behaves like the RPA functional when varying the particle number. But note that the $G_0W_0$ correction never vanishes as in Eq. (26).

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The high-$T$ phase of TiSe$_2$ crystallizes in the space group $P3m1$. It belongs to the $1T$ family of the layered transition metal dichalcogenides with the Ti-atom octahedrally coordinated by six neighbouring Se-atoms. A semi-metallic behaviour is found in most experiments. Below 200 K a CDW transition occurs, characterized by a $2 \times 2 \times 2$ superstructure (space group $P3\overline{1}c1$) and the opening of a small gap. The distortion pattern can be uniquely defined by the displacement $\delta\text{Ti}$ and the ratio $\delta\text{Ti}/\delta\text{Se} \approx 3$. Standard DFT functionals predict a phonon instability at the three equivalent $L$ points. A symmetric combination of these gives the correct CDW pattern, but with a severely underestimated distortion amplitude.$^{17}$ Hybrid functionals give a better description and have revealed the important role of HF exchange for the instability. This possibly hints to the presence of an excitonic instability. Although a weakly screened electron-hole interaction is clearly important, no spontaneous electronic CDW has so far been generated in bulk TiSe$_2$. Hybrid functionals induce the CDW via a strong electron-phonon coupling combined with the enhanced electronic susceptibility at the $L$ points. This mechanism is given support by the combined accuracy of the electronic bands, phonons and distortion amplitude.$^{20}$

In this work we aim for the more sophisticated GW method that allows for a physical description of the screened interaction. Due to the increase in computational cost we have been limited to the high-$T$ phase. The low-$T$ CDW phase will be studied with the RPA-based hybrid functional, optimized according to the procedure described in the previous section.

The hybrid calculations have been performed with VASP.$^{59-61}$ Quantum Espresso$^{62}$ (QE) and the CRYS-TAL program.$^{63}$ Whenever comparisons could be made these codes, despite using different pseudo potentials or in the latter case a Gaussian basis-set, agree rather well. For example, $p - d$ gaps agree within 0.05 eV. We have used a range-separation parameter of $\mu = 0.1$ Å$^{-1}$ in all hybrid calculations. A finite range separation parameter is not only physically more suitable for metals but also numerically advantageous by allowing for quicker and more stable convergence with respect to $k$-points. We chose a range twice as large as in HSE06 since our previous work indicated that HSE06 was somewhat too short ranged.$^{20}$ The local hybrid potential for solids was generated from an extension of a molecular code for solving the LSS equation.$^{64}$ The GW self-energy was subsequently evaluated using the YAMBO code.$^{65,66}$ For the optimization procedure of Eq. (26) we used the VASP code. We sampled the Brillouin zone with a $12 \times 12 \times 6$ $k$-point grid and used a plane-wave cutoff of 80 Ry (QE) and 380 eV (VASP). Around 360 unoccupied bands where included in the GW self-energy.

#### B. $G_0W_0$ band structure

The high-$T$ phase PBE band structure of TiSe$_2$ has been published in several previous works.$^{17}$ To allow for comparisons with our new results it is repeated here in Fig. 1. The PBE results differ strongly from ARPES experiments. The Se-$p$ -Ti-$d$ band overlap is severely overestimated and even inverted at $\Gamma$, leading to strong $p - d$ hybridization$^{17}$ and excess $d$-electron occupation. These large errors in the occupations and the charge density questions the use of a standard PBE/LDA starting-point for $G_0W_0$. Similar problems have been found in many materials with localized $d$-states.$^{67-70}$

In the same figure we have plotted the results from the
local hybrid using 100\% of exchange, here called EXX$_c$ with the subscript 'c' added since a local PBE correlation potential is included. The exchange part of the EXX$_c$ potential is thus calculated from Eq. (24) with the full HF self-energy. The corresponding projected density of states (PDOS) is shown in the side panel. We see that a large $p-d$ gap between the $\Gamma$ and $L$ points opens (0.8 eV) which corrects the occupations. The HF approximation is not expected to work well on TiSe$_2$ and, indeed, by adding the discontinuity (Eq. (25)) to the KS gap we find a gap of 3.75 eV, which is similar to the full HF calculation of 3.70 eV. This is a huge overestimation. The $d$-orbitals of the HF$_c$ and EXX$_c$ approaches are visualized in Fig. 2. Since the EXX$_c$ is defined to give a charge density similar to HF$_c$ by Eq. (24), it is not surprising to see that also the orbitals are very similar, even if the Ti-$d$ states are mostly unoccupied.

By reducing the fraction of exchange in the hybrid functional the gap reduces. With the standard parameterizations of PBE0 and HSE06 we find gaps of 0.43 eV and -0.15 eV respectively. The corresponding local hybrid approximations always produce smaller KS gaps than the nonlocal hybrid but, after the discontinuity is added, the results are very similar.

We will now apply the technique described in Sec. II for optimizing $\alpha$ via RPA. This will, at the same time, give us an optimal starting-point for $G_0W_0$. In order to identify the point where the condition in Eq. (30) is fulfilled (using the $p-d$ gap between $\Gamma$ and $L$ as reference) we evaluate the $G_0W_0$ self-energy on a set of hybrid potentials with $\alpha$ ranging between the two extrema: PBE ($\alpha = 0$) and EXX$_c$ ($\alpha = 1.0$). With PBE a $p-d$ gap of 0.2 eV opens. We also found 'mexican hat' features around the $\Gamma$ point similar to those reported in Ref. 40. We interpret these as an artifact of the incorrect orbital description within PBE. Similar features are found already in the HF term but disappears as soon as the orbitals are updated.

With EXX$_c$ we find the Ti-$d$-band to be pushed too low in energy with respect to the Se-$p$-band inverting the two bands. Thus, despite the fact that EXX$_c$ has a large gap it produces a highly metallic $G_0W_0$ solution. As $\alpha$ is reduced the position of the $d$-band improves, gradually reducing the $G_0W_0$ band overlap. At 20\% we find the condition in Eq. (30) to be fulfilled. At this value $G_0W_0$ produces a $p-d$ gap ($\Delta_{pd}$) of -0.11 eV and is denoted lh-$G_0W_0$ in Table I. This value should, according to Eqs. (25) and (30), agree with the KS gap of the local hybrid plus the hybrid discontinuity (denoted lh$_{hyb}^{\alpha=0.2} + \Delta_{xc}$ in Table I). Indeed, we see that the $\Gamma - L$ gap, which we optimized, agrees. But we also see that other gaps on the band structure are in good agreement. This suggests that the screened interaction within GW is only weakly anisotropic so that $\alpha$ remains the same over the entire Brillouin zone. Most experiments predict a negative gap of around 0.1 eV in the high-\textit{T} phase. Our value is thus a reasonable prediction. Previous calculations of RPA gaps on standard semiconductors have produced slightly overestimated gaps with respect to experiment.$^{39,73}$ This suggests that the actual band overlap could be somewhat larger than 0.1 eV.

If we perform a self-consistent hybrid calculation with 20\% of nonlocal exchange, HYB$_{\alpha=0.2}$, we see that self-consistency increases the band-overlap by around 0.1 eV. The full band structure is shown in Fig. (3) with the lh-$G_0W_0$ results along $\Gamma - M$ and $\Gamma - L$ superimposed. We see that not only the band overlap around the Fermi-level agrees but also the band dispersions. Dynamical effects in the self-energy seem important around -3 eV where the $p-d$ mixed flat band is shifted downwards in the hybrid functional with respect to lh-$G_0W_0$. Experiments place this band somewhere in between.$^{74}$ In Fig. (4) we have superimposed the HYB$_{\alpha=0.2}$ results on an ARPES experiment by Rohwer et al.$^{75}$ Since spin-orbit coupling (SOC) is not included care should be taken when comparing with experiment. Previous studies have shown that SOC splits the degenerate $p$-bands at $\Gamma$ which could have a small effect on the comparisons. Overall we see a very good agreement between theory and experiment noting that some of the deviations can be explained by looking at different values for $k_z$ (see discussion in Ref. 20).

To the right in Fig. 2 we have compared the $d$-orbital of the local hybrid with the same orbital of the nonlocal hybrid. Again, the orbitals are very similar despite very different underlying gaps. By comparing with EXX$_c$/HF$_c$ we also see that there is a strong effect of exchange on the $d$-orbitals which might explain the sensitivity of $G_0W_0$ to the fraction of exchange in the starting-point. The larger is $\alpha$ the more charge localize between the Ti-atoms. The charge on the Se atoms, i.e., the hybridization with Se-$p$-orbitals, is instead seen to reduce with $\alpha$.

We have tested the approach in Eq. (26) previously devised for molecules. With this approach the GW gap ranges from 0.2 eV (with PBE) to 1 eV (with HF$_c$). It thus exhibits the opposite trend for the gap as compared to the approach that uses a local hybrid. The optimal $\alpha$ is found at 32\% of exchange (H-$G_0W_0$ in Table 1), yielding a gap 0.4 eV. This value is much larger than any experiment measured and it is hard to believe that the inclusion of SOC and lattice vibrations would rectify it.
Finally, we have performed a self-consistent COHSEX calculation yielding a gap of 0.12 eV which is a more reasonable result, although again appears overestimated.

C. RPA optimized hybrid functional

The approach applied above shows that $G_0W_0$ predicts a value for the $p-d$ band-overlap which is in good agreement with most experiment. It also gives us a prediction of $\alpha$ based on the derivative of the RPA functional. This hybrid functional can now be used to study the CDW instability too expensive for an approach like $GW$ or RPA.

To the right in Fig. (3) we have used the RPA optimized $\alpha$ to calculate the energy gain in the supercell after distorting the atoms according to the CDW pattern. The set of parameters $\alpha = 0.2, \mu = 0.1 \text{Å}^{-1}$ lies close to the path used in Ref. 20 and is not so different from the set that agreed best with experiment. We therefore find very good results for both the energy gain and the $\delta\text{Ti}$-distortion. Note, however, that in contrast to Ref. 20, where the $\alpha$-parameter was fitted to the band gap and the phonon-frequencies, here it results from a self-consistent calculation.

If we look at the results for the H-$G_0W_0$ optimized hybrid functional with 32% of exchange the energy gain is quite small and the $\delta\text{Ti}$ distortion worsen as compared to PBE. In this case, we expect the phonon frequencies to largely deviate from experiment.

IV. CONCLUSIONS

In this work we have applied the high-level $GW$ method to TiSe$_2$ in order to give an accurate estimate of the much debated band-gap/band-overlap. First of all, it was found that the standard $G_0W_0$ prescription based on a PBE/LDA starting-point is unreliable due to qualitative errors in describing the band structure within PBE/LDA. To overcome this problem we have developed a quasi-self-consistent approach based on the local hybrid potential and the RPA functional. This approach allows for a systematic inclusion of exact-exchange in the starting-point, which, in the case of TiSe$_2$ has a large impact on the description of the Ti-$d$-orbitals. It is shown that $G_0W_0$ converges to a semi-metallic ground-state with a band-overlap of 0.1 eV. This is in line with the majority of experimental results but contradicts first $G_0W_0$ results based on the LDA starting-point.

The $G_0W_0$ approach generates a hybrid $\alpha$-parameter consistent with RPA. With a motivated choice for $\mu$ this hybrid functional produces an electron-phonon coupling strong enough to induce the CDW transition. Furthermore, the potential energy surface lies very close to our earlier published hybrid results which gave very accurate phonons. While in our previous work, the $\alpha$-parameter was chosen as a best fit to both the band gap and the phonon frequencies, here it has been calculated via a self-consistent procedure supporting the physical mechanism of the CDW distortion in TiSe$_2$.

The approach for calculating $G_0W_0$ gaps is general but particularly useful for systems where exchange is a crucial ingredient as, e.g., in the transition metal compounds. How well the approach works for predicting the gap/$\alpha$-parameter on a wider range of such systems will be investigated in future work.
Figure 4. Band structure of HYB\textsuperscript{$\alpha=0.2$} compared to ARPES at 300 K.\textsuperscript{75} Red lines corresponds to the $A-L$ path and black lines to the $\Gamma-L$ path.

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We note that these approximations have different $\mu$-parameters than otherwise used throughout this work.

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