 Structural, vibrational and quasiparticle properties of the Peierls semiconductor BaBiO$_3$: a hybrid functional and self-consistent GW+vertex-corrections study

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BaBiO$_3$ is characterized by a charge disproportionation with half of the Bi atoms possessing a valence 3+ and half a valence 5+. Because of selfinteraction errors, local and semi-local density functionals fail to describe the charge disproportionation quantitatively, yielding a too small structural distortion and no band gap. Using hybrid functionals we obtain a satisfactory description of the structural, electronic, optical, and vibrational properties of BaBiO$_3$. The results obtained using GW (Green’s function G and screened Coulomb potential W) based schemes on top of hybrid functionals, including fully selfconsistent GW calculations with vertex corrections in the dielectric screening, qualitatively confirm the HSE picture but a systematic overestimation of the bandgap by about 0.4 eV is observed.

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I. INTRODUCTION

The Peierls semiconductor BaBiO$_3$, parent compound of the high-T$_c$ superconductor Ba$_{x}$K$_{1-x}$BiO$_3$, has long been of theoretical and experimental interest due to its distinct negative-U nature. This behavior can be understood through the concept of "forbidden valence" suggesting that in BaBiO$_3$ bismuth atoms appear in two different valences (5+ and 3+), but skip the forbidden formal valence in-between (4+). The “valence-skipper” bismuth atoms hence disproportionate, i.e. every second Bi atom donates all 5 valence electrons to oxygen, whereas the other Bi atom retains two 6s electrons and only donates the three 6p electrons to the oxygen atoms. Such a behavior is usually explained by the concept of a negative U which invalidates the usual positive Coulomb repulsion between two electrons. The charge disproportionation goes in hand with significant structural changes from the ideal cubic perovskite crystal towards a distorted monoclinic structure characterized by a short-ranged charge density wave (CDW) state formed by alternating breathing-in and breathing-out distortions of oxygen octahedra around inequivalent Bi$^{5+}$ (Bi1) and Bi$^{3+}$ (Bi2) ions (Fig. 1). As a consequence of this charge ordering, the formally expected metallic state for the cubic perovskite BaBi$^{3+}$O$_3$ is replaced by an insulating regime characterized by a large direct CDW optical response $E_d$ $\approx$ 2.0 eV$^2$ and an indirect optical transition $E_i$. Although BaBiO$_3$ has been the subject of numerous optical investigations, dissenting opinions were reported on the value of the indirect gap $E_i$, for which conflicting measurements are reported in literature, ranging from 0.2 eV$^2$ and 1.1 eV$^2$.

Despite the apparent absence of strong electron localization usually associated with d and f electrons, standard semilocal density functionals exhibit severe problems in describing the basic properties of this material, yielding much too small or even negative band gaps$^{12}$, thus preventing a detailed description of the electronic properties. In a recent paper, we have explained the polaron-mediated insulator-to-metal transition experimentally observed in K-doped BaBiO$_3$ by means of hybrid density functional theory. We have shown that semilocal functionals are incapable (i) to disclose the underlying physics of this type of electronic transition and, more generally, (ii) to account for "long range" Peierls-like distortions in doped BaBiO$_3$. The objective of the present study is to apply the screened exchange hybrid density functional theory (DFT) Heyd-Scuseria-Emzerhof (HSE) functional$^{12}$ to the ground state structural, electronic and vibrational properties of BaBiO$_3$, and to investigate to which extent many-body effects may alter the ground state and quasi-particle (QP) properties of BaBiO$_3$. We address the latter issue by adopting the GW approach. These calculations essentially confirm the
II. METHODOLOGY

We have used the projector augmented wave method based Vienna ab initio simulation package (VASP) employing the generalized gradient approximation scheme of Perdew et al. (PBE), the HSE hybrid functional and the GW formalism. The HSE functional is constructed by mixing 25% of the exact Hartee-Fock (HF) exchange with 75% of the Perdew-Burke-Ernzerhof (PBE) exchange functional. The resulting expression for the exchange (x) and correlation (c) energy is

\[ E^{\text{HSE03}}_{xc} = E^\text{PBE}_x - \frac{1}{4} E^{\text{PBE,ser}}_{x,\mu} + \frac{1}{4} E^{\text{HF,ser}}_{x,\mu} + E^\text{PBE}_c, \]

in which the parameter \( \mu \) controls the decomposition of the Coulomb kernel into short-range (sr) and long-range contributions to the exchange. \( E^{\text{HF,ser}}_{x,\mu} \) is the exact exchange screened at very long range, and \( E^{\text{PBE,ser}}_{x,\mu} \) is the corresponding short-range exchange functional constructed using the PBE exchange hole. According to the HSE06 recipe, we set \( \mu = 0.2 \) Å\(^{-1}\). This implies that non-local exchange is rather long ranged extending over several nearest neighbor shells. The HSE approach has been used to calculate the starting orbitals for different GW-based schemes of increasing complexity and precision in the evaluation of the self-energy \( \Sigma = iGW \). The screened Coulomb kernel \( W = \epsilon^{-1}v \) which enters in the previous expression requires the computation of the frequency dependent dielectric matrix \( \epsilon^{-1} = 1 + v \chi \), where the polarizability \( \chi \) is given by the Dyson equation

\[ \chi = [1 - \chi_0(v + f_{xc})]^{-1} \chi_0 \]

Here, \( \chi_0 \) indicates the independent particle polarizability, whereas \( f_{xc} \) represents the effective non-local exchange correlation kernel which describes the many-body interaction between electrons and holes (vertex corrections). We have adopted three different GW strategies:

(i) The widely used single shot (i.e. non-self-consistent) \( G_0W_0 \) approximation, where \( G_0 \) and \( W_0 \) are calculated using HSE eigenvalues and eigenfunctions within the so called random phase approximation (RPA) (i.e. excluding any vertex corrections, \( f_{xc} = 0 \)). The VASP implementation is detailed in Refs. 13 and 14. Using HSE orbitals, this approach usually slightly overestimates the band gap, but is very efficient.

(ii) A partially self-consistent procedure consisting of an update of the eigenvalues in the Green’s function \( G \) combined with HSE screening properties \( W_0 \) (GW\(_0\)). Within this scheme we have included electrostatic electron-hole interactions in the computation of \( W \) using time-dependent HSE (TD-HSE) through an effective non-local frequency-independent kernel \( f_{xc} \). This specific GW scheme, usually denoted as GW\(_T^{\text{CTC}} \) (test-charge/test-charge GW\(_0\)), is believed to remedy most of the problems of single shot \( G_0W_0 \) and is considered to be a convenient (less time-consuming) and trustable (experimental precision) alternative to fully self-consistent GW. The approach was found to yield excellent QP band gaps in simple \( sp \) bonded semiconductors, if and only if the electrostatic interactions between electrons and holes were taken into account. The electrostatic electron-hole interaction is included using an effective many-electron exchange correlation kernel constructed using the HSE functional (Nano-quanta kernel determined to mimic TD-HSE), for details we refer to Refs. 19, 20, 21, 22.

(iii) Finally, we employ the self-consistent quasiparticle GW (scQPGW\(_T^{\text{CTC}} \)) following the original ideas of Faulkner, Schilgaarde, and Kotani, with the inclusion of vertex corrections adopting the formalism of Reining et al. 19, 20, 21, 22. [Nano-quanta kernel constructed to mimic the Bethe-Salpeter equation (BSE)]. This approach is rather time-consuming but entirely free of any dependence on the starting orbitals. For \( sp \) bonded materials, it yields band gaps within a few percent of experiment, if the electrostatic electron-hole interaction is included using a many-electron exchange correlation kernel \( f_{xc} \).

The simulated unit cell containing 10 atoms, has been modeled using a \( 4 \times 4 \times 4 \) \( k \)-point grid and an energy cutoff of 400 eV, reduced to 300 eV within GW calculations. To calculate the frequency-dependent dielectric matrix the inclusion of 400 empty bands was sufficient to obtain well converged screening properties and QP eigenvalues.

III. RESULTS AND DISCUSSION

A. Structure

The low temperature phase of BaBiO\(_3\) is monoclinic and derives from the primitive cubic perovskite high temperature cell by simultaneous breathing (b) and tilting (\( \phi \)) distortions of the octahedra (Fig. 1). Unlike previous studies, we have performed a full structural relaxation by allowing for both \( b \) and \( \phi \) distortions as well as for volume (V) and shape (\( \beta \), the monoclinic angle) optimization. The resulting minimized geometries listed in Tab. 1 reveals that the structural properties are sensitive to the applied functional and are generally better reproduced within HSE. In particular, the PBE functional seriously overestimates the volume (\( \approx 4 \% \)), which is in fact well described using HSE. Also, the breathing displacement, which is responsible for the opening of the CDW gap, is better described using the hybrid functional. The minimum HSE Bi-O bond length splitting \( b = 0.09 \) Å matches exactly the experimental value. The volume and, to a lesser extent, the breathing displacement does not improve by using a revised version of the PBE functional designed to yield improved equilibrium volumes, the so called PBEsol functional (see Tab. 1).
TABLE I: Collection of calculated quantities along with the available experimental data. The abbreviations $V$ (volume), $b$ (breathing distortion), $\phi$ (tilting distortion), $\beta$ (monoclinic angle), $E_d$ (direct gap), $E_i$ (indirect gap) and $\epsilon_\infty$ (macroscopic dielectric constant) are described in the text and, partially, in Fig. 3(c). $^a$ Ref.20, $^b$ Ref.21, $^c$ Ref.22, $^d$ Ref.23, $^e$ Ref.24, $^f$ Ref.25, $^g$ Ref.

| PBE | PBEsol | HSE | G$_0$W$_0$ | GW$_0^{TCTC}$ | scQPGW$_0^{TCTC}$ | LMTO-LDA | PAW-LDA | Expt. |
|-----|--------|-----|------------|----------------|-----------------|---------|--------|-------|
| $V$ (Å$^3$) | 85.76 | 85.94 | 82.10 | - | - | - | 80.41 | 81.04 | 82.21 $^a$ |
| $b$ (Å) | 0.07 | 0.075 | 0.09 | - | - | - | 0.11 | 0.04 | 0.085 $^a$ |
| $\phi$ (°) | 12.1 | 12.2 | 11.9 | - | - | - | 9.6 | - | 11.2 $^a$ |
| $\beta$ (°) | 90.16 | 90.14 | 90.24 | - | - | - | - | - | 90.17 $^a$ |
| $E_d$ (eV) | 1.22 | 1.32 | 2.07 | 2.62 | 2.39 | 2.45 | 1.1 | - | 2.0 $^b$ |
| $E_i$ (eV) | 0.0 | 0.0 | 0.84 | 1.32 | 1.15 | 1.28 | 0.1 | 0.0 | 0.2 $^c$, 0.5 $^d$, 0.8 $^c$, 1.1 $^f$ |
| $\epsilon_\infty$ | 12.2 | 6.0 | 7.0 | 7.2 | - | - | - | - | 5 $^g$, 7 $^h$ |

B. Electronic properties

The approximations made in the exchange-correlation term, have an even more drastic impact on the predicted electronic and dielectric properties. In line with past findings, PBE predicts a zero-gap system ($E_i$ = 0.0 eV) with a much to small direct band gap $E_d$ ($E_i^{PBE} = 1.22$ eV). Although the origin of this failure has often been related to the deficient description of the structural instabilities at the PBE level, we found that the values $E_i^{PBE}$ and $E_i^{PBE}$ computed adopting the HSE and experimental geometries are only 0.05 meV larger than those calculated at the PBE structural minimum, and therefore still in conflict with the experimental measurements.

In order to capture the insulating character of BaBiO$_3$ we have adopted the HSE functional and the GW method at the three levels described in the methodological section. The computed band structure is shown in Fig. 3 where we plot the most relevant bands near the Fermi level ($E_F$=0) for PBE, HSE, G$_0$W$_0$, GW$_0^{TCTC}$ and scQPGW$_0^{TCTC}$. We observe that the pragmatic inclusion of 25% non-local Hartree-Fock exchange within the HSE approach shifts apart the bands near $E_F$ and increases both $E_i$ (0.84 eV) and $E_d$ (2.07 eV). These values are in good agreement with the available measurements.

The G$_0$W$_0$ approximation evaluated using HSE orbitals further increases the band gap between the occupied and empty states resulting in significantly larger quasiparticle gaps than HSE (see Tab. I). The update of the eigenvalues in G and, in particular, the inclusion of $e$-$h$ (electron-hole) interactions (GW$_0^{TCTC}$) leads to a slight reduction of the quasiparticle band gaps ($\approx$ 4%). We note that the former approach (G$_0$W$_0$) is known to overestimate the band gaps for $s$-$p$ bonded semiconductors and insulators using HSE orbitals by typically 10 $^2$17,18 whereas the latter approach (GW$_0^{TCTC}$) yields very good values almost on par with fully self-consistent scQPGW$_0^{TCTC}$ calculations15,22. Indeed, in this specific material, the scQPGW$_0^{TCTC}$ band structure is very close to the GW$_0^{TCTC}$ band structure, although the indirect band gap increases slightly from 1.15 eV to 1.28 eV. Unfortunately, the experimental uncertainty in $E_i$ does not permit to ascertain which method yields the most accurate results, but the GW values are generally somewhat larger than the maximum values determined experimentally. Since the direct gap $E_d$ has been measured using optical techniques, it is possibly impaired by excitonic effects (see below), but overall it seems that GW does yield a slightly too large band gaps for BaBiO$_3$. However, compared to photoemission data23, the calculated total density of states (shown on the right side of Fig.2) show that GW$_0^{TCTC}$ and scQPGW$_0^{TCTC}$ yield a main valence band peak ($\approx$ -3.4 eV) in much better agreement with experiment (-3.2 eV) than PBE (-1.9 eV) and HSE (-2.8 eV). Once more, we underline the need of more detailed experimental data to unequivocally probe the predictive power of GW-type and HSE calculations. It should also be stressed that GW-like approaches, though employed for more than 20 years, have been applied so far mainly to prototypical semiconductors and insulators (GaS, ZnO, Cu$_2$O etc...) but, to our knowledge, their performance on more complex systems such as BaBiO$_3$, has not yet been assessed in literature. A comparison with accurate experimental measurements is therefore essential.

Let us proceed to shed light on the nature of the CDW gap $E_i$. It is accepted that $E_i$ is formed by the splitting of the conduction Bi($s$)-O($p$) anti-bonding orbitals into two subbands, but the electronic charge redistribution has not been discussed in details. Figure 3(a) reports the scQPGW$_0^{TCTC}$-projected density of states (DOS) on Bi and O sites which should be interpreted in conjunction with the band-projected charge (Tab. III). The formation of the CDW lowers the symmetry of the crys-
FIG. 2: (Color online) Calculated (left) band structure of monoclinic BaBiO$_3$ within PBE, HSE $G_0W_0$, GW$_0^{\text{TCTC}}$ and scQPGW$_{\text{TCTC}}$ and (right) corresponding total density of states. $E_i$ is opened between the A and R points of our modeled supercell, which correspond to the W and L points of the simple monoclinic cell. P refer to the measured main photoemission peak of the valence band.$^{32}$

FIG. 3: (Color online) Calculated scQPGW$_{\text{TCTC}}$ (a) partial DOS decomposed over Bi1, Bi2 and O (apical and planar Oxygen yield identical DOS) and (b) DOS difference between Bi1 and Bi2 decomposed into l quantum numbers.

TABLE II: scQPGW$_{\text{TCTC}}$, HSE and PBE band-projected charge (in partial number of electrons $e^{-}$) on Bi1 and Bi2. Charges have been determined inside the PAW spheres.

|       | s       | p       | d       |
|-------|---------|---------|---------|
| Bi1   | 1.280   | 1.199   | 10.254  |
| Bi2   | 1.642   | 0.871   | 10.065  |
| Bi1-Bi2 | -0.36   | +0.33   | +0.19   |

The calculated $\delta$ is indeed rather small ($\delta_{\text{PBE}} = 0.10e^{-}$, $\delta_{\text{HSE}} = 0.16e^{-}$, $\delta_{\text{scQPGW-TCTC}} \approx 0.16e^{-}$) but it is the result of a substantial transfer involving orbitals with different angular moments. HSE and GW provide essentially the same picture, whereas PBE underestimates significantly the $l$-decomposed charge transfer by about...
In more detail, the flow of charge induced by the charge disproportionation between Bi1 and Bi2 involves a \( s \)-like charge transfer from Bi1 to Bi2 (0.36e\(^{-}\)) which is compensated by a backtransfer of \( p \) (0.33e\(^{-}\)) and \( d \) (0.16e\(^{-}\)) charge mostly localized in the energy range from -8 and -4 eV. This backtransfer can be understood by realizing that the O atoms are much closer to Bi1. As a result, the tails of the O(\( p \)) orbitals overlap with the Bi1 spheres and are picked up as states with higher angular momentum specifically \( p \) and \( d \) like character.

C. Optical and dielectric properties

In addition to the formation of a band gap, the CDW also causes a strong optical resonance at \( \approx \) 2 eV. In Fig. 4 we compare the experimental imaginary part of the dielectric function \( \epsilon_234 \) with the theoretical spectrum computed within different approximations: (i) the random phase approximation (RPA) using HSE orbitals, (ii) TD-HSE (as described in Ref. 18) and (iii) TD-scQPGW\(^{TCTC} \). The first approach (i) neglects any electrostatic interactions between electrons and holes. The second approach (ii) is similar to TD Hartree-Fock but the electrostatic interaction between electrons and holes is only 1/4—more precisely it is described by the sr-exchange kernel in HSE —whereas in the final approach (iii) the interaction between electrons and holes is described fully ab-initio using the \( W \) determined in the scQPGW calculations. For (i) and (ii) HSE orbitals and one-electron energies are used, whereas (iii) is based on the scQPGW one electron energies and orbitals, and the results of (iii) are usually equivalent to Bethe-Salpeter calculations without the Tamm-Dankof approximation.\(^{18,20} \)

Finally, we calculated the ion-clamped (high frequency) macroscopic dielectric constant \( \epsilon_\infty \) (Tab. II). The HSE \( \epsilon_\infty \) was computed adopting the perturbation expansion after discretization (PEAD) method. Within the PEAD method we applied a finite field in the supercell and extracted the static dielectric constant from the resultant macroscopic field. This approach includes local field effects (electron-hole interactions). The so obtained macroscopic dielectric constant (\( \epsilon_\infty^{HSE}=6 \)) is in good agreement with the experimental estimations (5 and 7, see Tab. II) extracted through a fit of the reflectivity spectra. The \( G_0 \) and scQPGW values, 7.0 and 7.2 respectively, though still in good agreement with experiment are about 15% larger than the HSE values. As expected from the serious underestimation of the gap, TD-PBE fails dramatically in predicting \( \epsilon_\infty \) (\( \epsilon_\infty^{PBE}=12.2 \)).
D. Phonons and infrared reflectivity

We conclude our analysis by exploring the effect of non-local exchange on the zone-centered phonon frequencies and on the oscillator strengths of the infrared reflectivity (IR) active modes. Since within the GW method, the calculation of phonon frequencies is presently out of reach, we focus on PBE and HSE only. The evaluation of the Born effective charge (BEC) \(Z_{i,a\beta}^*\), required for the calculation of the IR spectra, were performed adopting the PEAD (HSE) and linear response (PBE) methods. Excluding the three acoustic modes (which are zero at \(\Gamma\)), the monoclinic phase (containing 10 atoms per unit cell) possesses 27 optical modes with the symmetry

\[7A_g + 5B_g + 6A_u + 9B_u\]

The gerade modes are Raman active and the ungerade modes are infrared active. In Fig. 3 we compare our calculated HSE IR spectra with the experimental reflectivity data. The results are remarkable: the inclusion of non-local exchange is essential to account for a correct prediction of the phonon modes with large oscillator strength. The three highest modes at 157, 256 and 463 cm\(^{-1}\) reproduce very well the corresponding experimental values, whereas the lowest mode at 119 cm\(^{-1}\) is shifted upward with respect to the measured one by \(\approx 20\) cm\(^{-1}\). In addition, we find that the highest frequency phonon (Raman active) corresponding to the Bi\(_6\) breathing mode responsible for the CDW instability, experiences a huge shift from PBE (453 cm\(^{-1}\)) to HSE (562 cm\(^{-1}\)). The HSE value coincides with the value provided by Raman scattering analysis, 570 cm\(^{-1}\). The problems of PBE can be attributed primarily to volume effects: Due to the large PBE volume the PBE phonon vibrations are located at lower frequencies. In addition to this, we note that the PBE inadequate description of the oxygen breathing distortions is also reflected in the phonon spectra: The frequency downshift is larger (45-60 cm\(^{-1}\)) for the oxygen-based modes lying at higher frequency than for the lower modes (20-30 cm\(^{-1}\)) emerging from the softer Bi and Ba vibrations which are actually very well describe at the PBE level. A similar behaviour has been observed in ZnO.\(^{35}\)

Finally, in Tab. III the computed BEC \(Z_{i,a\beta}^*\). We find that the BEC tensor is diagonal and reduces to a scalar matrix for Ba and Bi (i.e. \(Z_{Ba/Bi,11}^* = Z_{Ba/Bi,22}^* = Z_{Ba/Bi,33}^*\)) and to two components \(Z_{\parallel}^*\) and \(Z_{\perp}^*\) for O with respect to the Bi-O bond. In agreement with precedent estimations of Thonhauser and Rabe,\(^{22}\) we observe a significant BEC disproportionation between Bi1 and B2 (\(Z_{Bi2}^* - Z_{Bi1}^*\)), substantially larger than the corresponding static charge transfer \(\delta\) discussed above (see Tab. III). The incorporation of non-local exchange effects through HSE reduces the dynamical charge disproportionation from 1.66 \(|e^-|\) (PBE) to 0.97 \(|e^-|\) (HSE) and leaves the Ba and O BEC’s unchanged. The average BEC of oxygen -3.13 \(|e^-|\) equals the experimentally derived value of -3.2 \(|e^-|\)\(^{31}\).

|       | Bi1 | Bi2 | Ba | O |
|-------|-----|-----|----|---|
| HSE   | 5.01| 5.98| 2.71|   |
| PBE   | -4.39| -1.88|    |   |
| LDA   | -4.36| -1.89|    |   |
|       | 4.65| 6.31| 2.71|   |
|       | 4.78| 6.22| 2.75|   |
|       | -5.55| -1.85|    |   |

IV. SUMMARY

In summary, by means of beyond-DFT methods we have computed ground and excited state properties of BaBiO\(_3\). On the basis of hybrid functionals and fully \textit{ab initio} GW methods, we have shown that the inclusion of non-local exchange effects is essential to reproduce and understand the complex physical properties of BaBiO\(_3\). Our calculated structural distortions (oxygen instabilities and cubic-to-monoclinic transition), optical excitations (direct/indirect band gap and optical spectrum), dielectric (dielectric constant) and vibrational properties (phonon frequencies, infrared reflectivity and Born effective charges) reproduce well the available experimental findings. Overall, our study suggests that the GW approaches tend to overestimate the band gap, which seems to be better predicted within the screened hybrid HSE functional. Although the inclusion of an effective non-local exchange-correlation kernel \(f_{xc}\) at TD-HSE (GW\(_0\)\(^{TCTC}\)) and BSE-GW (seQPGW\(^{TCTC}\)) level improves the single-shot \(G_0W_0\) description, the resulting band gap is still \(\approx 15\%\) (\(E_d\)) and \(40\%\) (\(E_i\)) larger than the corresponding \textit{bare} HSE value. The source of this error as far as it can not be attributed to uncertainties in the experimental results likely resides in the neglect of many-body vertex corrections in the self-energy \(\Sigma\), which are entirely neglected in this work, or any other GW implementation. Though seQPGW\(^{TCTC}\) has proven to be excellent for the prediction of the band gaps of typical semiconductor, insulator and noble gas solids it was never applied to more complex oxides such as BaBiO\(_3\). Given the lack of accurate experimental information on
the electronic properties of BaBiO$_3$ (especially for the indirect gap E$_i$) the assessment of these GW techniques to less critical oxides for which well established experimental data exists is highly required.

Concluding, our research on BaBiO$_3$ clarifies the serious drawbacks of standard DFT and provide a key to understand and design similar charge-ordered materials.

We hope that our study can boost for new experiments as well as for thorough theoretical and computational efforts aiming to straighten the issues still under debate. Furthermore, we have shown that the hybrid functional HSE yields a description which is at least on par with sophisticated man-body techniques.

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