Electronic and optical properties of doped TiO$_2$ by many-body perturbation theory

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Doping is one of the most common strategies for improving the photocatalytic and solar energy conversion properties of TiO$_2$, hence an accurate theoretical description of the electronic and optical properties of doped TiO$_2$ is of both scientific and practical interest. In this work we use many-body perturbation theory techniques to investigate two typical n-type dopants, Niobium and Hydrogen, in TiO$_2$ rutile. Using the GW approximation to determine band edges and defect energy levels, and the Bethe Salpeter equation for the calculation of the absorption spectra, we show that many body corrections are crucial for accurately describing the energy position of the impurity states and the band gap narrowing of the doped material. The defect energy levels appear as non-dispersive bands associated with localized states lying at $\approx 0.7\,\text{eV}$ below the conduction bands. These states are also responsible for the appearance of low energy absorption peaks that enhance the solar spectrum absorption of rutile. The spatial distributions of the excitonic wavefunctions associated with these low energy excitations are very different for the two dopants, suggesting a larger mobility of photoexcited electrons in Nb-TiO$_2$.

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I. INTRODUCTION

Titanium dioxide (TiO$_2$) is one of the most abundant, chemically stable and functionally versatile oxide materials, with applications ranging from white pigment in paints to photocatalysis and solar energy conversion. Since TiO$_2$ has a large band gap (about 3.0 and 3.2 eV for rutile and anatase, respectively) that severely limits the photoabsorption in the visible, doping is often employed to improve the conductivity and photocatalytic properties. This has motivated an enormous interest in doped TiO$_2$ over the last decades, and a large variety of dopants, both metals and non-metals, have been explored. For example, the substitution of a lattice Oxygen with a non-metal atom like Nitrogen leads to acceptor states above the valence band maximum (VBM) whereas Oxygen substitution with Fluorine gives rise to donor states below the conduction band minimum (CBM). In this context, an accurate theoretical description of the band gap and impurity levels of doped TiO$_2$, combined with a study of the influence of doping on the optical absorption, can contribute insights that are scientifically interesting as well as practically useful.

Two of the most common dopants in TiO$_2$ are Niobium and atomic Hydrogen. They both act as donors, with Nb substituting a Ti atom, and Hydrogen forming an interstitial defect bound to an Oxygen of the lattice. Nb is usually described as a shallow donor that greatly improves the electrical conductivity of TiO$_2$. At the same time, however, valence-band photoemission spectra of Nb-doped rutile show a peak at about 0.8-1.0 eV below the Fermi energy, indicating an electron in a localized Ti$^{3+}$ state similar to that observed in Oxygen deficient rutile. This apparent contradiction between UPS and electrical measurements can be explained within a small polaron model, where the vertical excitation energy of the polaron, as observed in UPS, can be much larger than the energy of adiabatic excitations involved in electrical measurements. The small polaron model is actually believed to hold for most defects and impurities in rutile, including interstitial Hydrogen. Indeed, recent infrared absorption measurements in reduced and hydrogenated rutile have been interpreted on the basis of hybrid density functional calculations, where the self-trapping energy of a conduction band electron to form a localized Ti$^{3+}$ ion was predicted to be about 0.3 eV.

The electronic structure of doped TiO$_2$ has been the subject of many theoretical studies. It is now widely accepted that while standard local and semi-local Density Functional Theory (DFT) do not adequately describe the polaronic character of defect and impurity states in TiO$_2$, DFT+U and hybrid functionals are effective in determining the structure and energetics of the polaronic states. However, also these approaches are insufficient for precisely describing the electronic energy levels. For instance, hybrid functionals often overestimate the TiO$_2$ band gap thus leading to a substantial uncertainty in the position of the impurity levels. Recent many-body perturbation theory (MBPT) studies of the band structure and absorption spectrum of pristine TiO$_2$ have in fact provided evidence that approaches beyond DFT are required for a quantitative description of photoemission and light absorption experiments in this material.
The aim of this work is to investigate the electronic structure and optical properties of Nb- and H-doped TiO$_2$, going beyond mean-field theory. We adopt the MBPT approach, namely the GW approximation for the quasi-particle energies and the Bethe-Salpeter equation for the optical spectra. Following a description of the adopted methodology and computational details in Sec. III. Conclusions are presented Sec. IV. We find that in both systems optically allowed transitions are introduced well below the intrinsic optical gap of rutile, thus improving its solar energy absorption properties.

II. METHODS

A. Ground state calculations

Ground state calculations were performed using Kohn-Sham (KS) DFT\textsuperscript{19} within the plane-wave-pseudopotential scheme, as implemented in the Quantum ESPRESSO package.\textsuperscript{20,21} We used the gradient-corrected GGA-PBE\textsuperscript{18} exchange-correlation functional and norm-conserving ONCV pseudopotentials,\textsuperscript{19} including the semi-core states for Titanium (3s and 3p). We obtained converged KS eigenstates and eigenvalues using a wavefunction kinetic energy cut-off of 80 Ry.

Doped rutile was modelled using a 2×2×3 supercell (SC) containing 72 atoms (73 atoms in the case of H doping), including one Nb replacing a Ti atom (one interstitial H impurity), which corresponds to a dopant concentration of ≈ 4\% (referred to the number of Ti ions). With this SC, reciprocal space was sampled using a Monkhorst-Pack grid of 2×2×2. For the sake of comparison, pristine rutile was modelled using both the same SC and the primitive cell with an equivalent k-point sampling. We verified that the two descriptions provide equivalent results, and therefore in the following only the results obtained using the 2×2×3 supercell are reported.

Relaxed geometries for both pristine and defective TiO$_2$ were computed including a Hubbard-U term\textsuperscript{21,22} in the Ti 3d orbitals. This correction has been shown to be essential for the description of polaronic effects.\textsuperscript{21,22} We set U = 3.5 eV, a typical value for TiO$_2$.\textsuperscript{22,23} With this choice, the computed cell parameters of pristine TiO$_2$ rutile are $a = 4.64$ Å and $c = 2.96$ Å, in good agreement with the experimental values, $a = 4.59$ Å and $c = 2.95$ Å.\textsuperscript{22}

B. MBPT calculations

The electronic and optical properties of pristine and doped rutile TiO$_2$ were investigated using the GW method for the self energy operator $\Sigma$ and the Bethe-Salpeter equation (BSE) for the absorption spectra.\textsuperscript{30,31} Specifically, we used the single-shot G$_0$W$_0$ approximation by treating the frequency dependence of the dielectric matrix via the Godby-Needs (GN) plasmon-pole model (PPM).\textsuperscript{35}

All the MBPT calculations were carried out using the plane-wave code Yambo.\textsuperscript{35,37} In the G$_0$W$_0$ calculations, converged results were obtained by considering 1200 bands (corresponding to 59.53 eV above the energy of the top of the valence band), and a kinetic energy cutoff of 8 Ry for the screening dielectric matrix. GW corrections were introduced on top of DFT-PBE calculations, without the inclusion of Hubbard U. The Bethe-Salpeter equation was built considering vertical transitions involving 20 occupied and 40 empty bands.

In the single shot G$_0$W$_0$ approximation, G$_0$ is built from single particle KS orbitals, and the quasi-particle energies are obtained as a first order perturbation correction. In practice, quasi-particle (QP) energies are obtained as:

$$E_{nk}^{QP} = \epsilon_{nk} + Z_{nk} \left[ \Sigma_{nk} (\epsilon_{nk}) - v_{xc}^{\epsilon_{nk}} \right],$$

(1)

where $\epsilon_{nk}$ are the KS eigenvalues, $\Sigma_{nk}(\omega)$ and $v_{xc}^{\epsilon_{nk}}$ are the expectation values of the self-energy and the exchange correlation potential, respectively, over the $nk$ KS-eigenvector, and $Z_{nk}$ the QP renormalization factor defined as:

$$Z_{nk} = \left[ 1 - \frac{\partial \Sigma_{nk}(\omega)}{\partial \omega} \right]_{\omega = \epsilon_{nk}}^{-1}. $$

(2)

Optical properties were calculated by solving the BSE whose kernel includes local field effects as well as the screened electron-hole interaction (with static screening). We also applied the Tamm-Dancoff approximation, which neglects the coupling terms between resonant and anti-resonant blocks, after having numerically verified its validity.

As an analysis tool, we computed atomically-projected DOS (pDOS) with the inclusion of GW QP corrections obtained by Yambo, according to:

$$\rho(\omega) = \frac{1}{N_k} \sum_{\alpha} \sum_{nk} |\langle \phi_\alpha | \psi_{nk} \rangle|^2 \delta(\omega - E_{nk}^{QP}),$$

(3)

where $|\phi_\alpha\rangle$ are atomic orbitals.

Quasi particle unfolded band structures for the doped systems\textsuperscript{35,36} were calculated considering the spectral function $A(\kappa, \omega)$, resolved with respect to the $\kappa$-vectors of the host pristine primitive cell (PC),

$$A(\kappa, \omega) = \sum_{mn} |\langle \psi_{mnk}^{PC} | \psi_{nk}^{SC} \rangle|^2 \delta(\omega - E_{nk}^{QP}),$$

(4)

where $\mathbf{k} = \mathbf{k}(\kappa)$ according to the folding induced by the supercell, and $|\psi_{mnk}^{PC}\rangle$’s form a complete set with $\kappa$ symmetry. Such band structures were obtained using the implementation of the unfolding procedure described in Refs. 39,40.
TABLE I: Bond lengths (in Å) for pristine and doped rutile TiO$_2$. For the doped systems, maximum and minimum values of type I and type II Ti-O bond lengths are given. Distances between the dopant and Ti (D-Ti) and O (D-O) are also reported.

| bond      | TiO$_2$ | TiO$_2$:H$_i$ | TiO$_2$:Nb$_{Ti}$ |
|-----------|---------|---------------|-------------------|
| Ti-O      | type I 1.96 | 1.91 - 2.07  | 1.90 - 2.07       |
|           | type II 1.99 | 1.94 - 2.03  | 1.94 - 2.01       |
| D-Ti      | 2.21    | 2.94 - 3.04   |                   |
| D-O       | 1.23    | 1.93 - 2.01   |                   |

III. RESULTS

A. Structural properties

The calculated structural parameters for pristine and doped rutile are summarized in Tab. I. In pristine rutile two slightly different Ti-O bond lengths are present, each TiO$_4$ unit having two longer apical (type II, 1.99 Å) and four shorter equatorial (type I, 1.96 Å) Ti-O bonds. In H-doped rutile (TiO$_2$:H$_i$), a large distortion of the TiO$_2$ crystal structure near the interstitial impurity takes place, with type I bond lengths ranging from 1.90 up to 2.07 Å, and similar but less pronounced distortions of type II bonds. The H atom is bound to an oxygen with a bond length of 1.23 Å and is at distance 2.21 Å from the closest Ti atom (Fig. 1). Significant distortions of the Ti-O bond lengths are found also for TiO$_2$:Nb$_{Ti}$, notably an elongation of the type I Ti-O bond for the first Ti atom adjacent to the defect (2.07 Å) and a shortening for the subsequent bond (1.90 Å). Distortions of type II bonds are less significant in the case of substitutional Nb. As for Nb-O bonds, those of type I are slightly shorter (1.94 Å) than type I Ti-O bonds, while those of type II are slightly longer (2.02 Å) than type II Ti-O bonds. The distances between Nb and the closest Ti atoms are 2.94 and 3.04 Å, to be compared to the Ti-Ti distance of 2.97 Å in pristine rutile.

B. Band gap of pristine rutile

For pristine rutile, our calculations give a fundamental gap of 1.89 eV and 3.1 eV at PBE and G$_0$W$_0$ levels, respectively. The latter value is in excellent agreement with calculations by Malashevich et al. [31] (3.13 eV), who used a G$_0$W$_0$[PBE] implementation within the complex generalized plasmon-pole approximation described in Ref. [42].

Similar values were obtained also by other G$_0$W$_0$ studies. In particular, Kang and Hybertsen [13] obtained a band gap of 3.37 eV using a full-frequency contour-deformation (FF-CD) G$_0$W$_0$[PBE] approach; similarly, Zhang et al. [33] found 3.30 eV by full-frequency G$_0$W$_0$[LDA]; Patrick and Giustino [34] obtained 3.40 eV at the G$_0$W$_0$[PBE] level with the GN-PPM; Baldini et al. [35] obtained 3.30 eV using G$_0$W$_0$[PBE] with the PPM of Hybertsen and Louie [40]; Chiodo et al. [36] reported a gap of 3.59 eV using G$_0$W$_0$[PBE] with GN-PPM.

Overall, the differences between our results and previous studies can be attributed to the different approach to evaluate the frequency dependence of the self energy (PPA vs full-frequency methods and different flavours of PP model). In the case of Ref. [17], however, we explicitly verified that differences from our results are mainly due to the pseudopotential dataset used in that work. In this regard, we notice that a recent study [18] on the verification and validation of GW data across three widely used GW codes (Yambo, Abinit, and BerkeleyGW) found excellent agreement among the results obtained with these codes when the same pseudopotential dataset was used. GN-PPM and FF-CD GW methods were also compared and found to lead to a difference of the order of 0.1 eV for the fundamental gap of TiO$_2$ (changing from 3.2 eV with GN-PPM to 3.3 eV for FF-CD) when using FHI pseudopotentials with 12 valence electrons.

C. Quasi-particle levels

Figure 1 shows the unit cells of the relaxed structures of H- and Nb-doped TiO$_2$ together with the spin density associated with the donor states (in orange). We can see that for both H- and Nb-doped rutile the donated electron localizes on the neighbouring Ti atoms, even though with different distributions. The structural distortion close to the defect coupled to this density localization indicate the formation of localized polaronic states. Our results for H-doped rutile agree with the recent FTIR experiments of Ref. [51], which have provided evidence of small electron polarons, each bound to a Ti atom adjacent to the OH group of the hydrogen defect.

To evaluate the energy levels of the defect states in the TiO$_2$ band gap, we first examine the Density of States (DOS), and align the different DOS at the VBM, which is little affected by the dopants. Projections of the DOS (pDOS) on TiO$_2$ and defect atoms are shown in Fig. 2. At the KS-PBE level (left panels), defect states are found at the bottom of the TiO$_2$ conduction band. In the right
and 2.71 eV in TiO$_2$:H$_i$ and TiO$_2$:Nb$_{Ti}$, respectively, while a smaller narrowing of $\sim$ 0.2 eV is present in the spin-down channel, see Fig. S6 in the Supporting Information. The band gap narrowing can be attributed to combined single particle and many-body effects associated with the large concentration of donor ions in our calculations, as described, e.g., for Silicon in the presence of heavy n-type doping. From the comparison of the pDOS for pristine and doped rutile in Fig. 2, it is also evident that the band gap narrowing predicted by DFT-KS is less than 0.2 eV, thus much smaller than that given by $G_0W_0$. The large difference between the DFT-KS and $G_0W_0$ results clearly shows the importance of using MBPT for a reliable quantitative description of doping effects in TiO$_2$.

In Fig. 3 we show the unfolded quasi-particle band structures for the doped systems, from Eq. (4), compared to pristine rutile. We can recognize the formation of defect states below the CBM as indicated by the presence of non-dispersive bands along selected symmetry lines that can be attributed to the localized states. The color scale represents the value of the $\kappa$-resolved DOS, as defined in Eq. (4). In each panel, black corresponds to zero and yellow to the maximum value of the DOS. The sharper the DOS (i.e. the brighter the corresponding peak), the less hybridized the defect states. Within a mean field description, at fixed $\kappa$-vector a delta peak would indeed show at the energy of each band if no defects were present. In the presence of defects instead, each peak is broadened because of the broken translational symmetry and the hybridization: the more blurred the picture, the larger the hybridization induced by the defect. Comparing H- and Nb-doped TiO$_2$, a slightly higher degree of hybridization is apparent in TiO$_2$:H$_i$, which is consistent with the interstitial vs substitutional configuration of the defect.

D. Optical properties

Pristine rutile. Our computed BSE and independent particle (GW-RPA) spectra of pristine rutile are presented in Fig 4(a). The onset of the absorption in the BSE spectrum is at $\sim$ 3.0 eV, followed by an intense narrow peak at 3.7 eV and a shoulder at $\sim$ 4.4 eV. Fig. 5(a) further shows that the spectrum is anisotropic, with a characteristic double peaked structure for light polarized in the [001] direction, as already reported in previous calculations. Both the onset and the shape of the calculated spectrum are in agreement with recent measurements which show an onset at $\sim$ 3 eV, followed by a sharp peak at 3.93 eV, a shoulder at 4.51 eV and a broader peak at 5.42 eV. (We note that a larger number of bands in BSE and more k-points than used in the present calculations would be needed in order to reproduce also the high energy features of the experimental spectrum). Our results are also in line with recent GW-BSE calculations: our calculated red-shift of the first bright peak (0.55 eV) with respect to the independent quasi-
FIG. 3: Unfolded quasi-particle band-structure for pristine, TiO$_2$:H$_i$ and TiO$_2$:Nb$_{Ti}$. Results for spin-up channels are shown; results for spin down channels (which do not show any defect-related state) are reported in the Supplementary Material (Fig. S6). The color scale is such that black – yellow correspond to [0,1] (in arbitrary units).

particle picture is comparable to the results of Chiodo et al. 47 and to the redshift in the computed spectra of Baldini et al. 45 Differences observed for the excitation energies are due mainly to the different value of the computed fundamental gap (see discussion above).

Doped rutile. Upon doping, new features in the absorption spectra appear, as shown in panels (b) and (c) of Figs. 4 and 5. The most evident hallmark of the doped systems is the appearance of absorption peaks at low energy below 2 eV.

The low energy part of the spectrum of TiO$_2$:H$_i$ is characterized by a broad peak that has a maximum at 0.6 eV and extends up to 2 eV. This peak involves transitions from electrons in the gap states to the conduction bands. At higher energies, in the region of the spectrum where pristine rutile absorbs, we observe a small red-shift of the onset and the maximum of the absorption band with respect to the pristine crystal (from 3.68 to 3.62 eV for the maximum). We also note that the shift of the BSE with respect to the independent particle spectrum is smaller in TiO$_2$:H$_i$ in comparison to that found for pristine rutile, indicating an increased screening due to the excess electrons of the dopants.

In the case of Nb-doped rutile, Fig. 4(c), the spectrum in the low energy region shows a defect induced absorption characterized by a double peaked structure with maxima at 0.35 and 0.91 eV, sharper than those found for TiO$_2$:H$_i$. As in the case of hydrogen doping, in the higher energy region we observe again a small red-shift of the onset and the maximum of the absorption (3.64 eV) with respect to pristine rutile. More importantly, also for TiO$_2$:Nb$_{Ti}$ the shift of the BSE spectrum with respect to the independent particle calculation (0.3 eV) is reduced in comparison to the pristine case. Apart from the small rigid shift and an overall broadening, the shape of the absorption spectrum of rutile in the high energy region is not affected substantially by the dopants.

Figure 5 shows the absorption spectra of pristine and doped rutile for light polarized along and orthogonal to the c directions. Pristine rutile exhibits a significant optical anisotropy, associated with its tetragonal symmetry, which has been extensively studied both theoretically and experimentally. 45 The anisotropy is present also for the doped systems, as expected, and is more pronounced in the low energy part of the spectra. In particular, the two low energy peaks in TiO$_2$:Nb$_{Ti}$ correspond to excitations that are optically active for light polarized along orthogonal directions. In order to verify that this anisotropy is not an artifact related to the small size of our supercell, we performed additional DFT-KS calculations using a (3 × 3 × 4) supercell with 216 atoms. The results confirmed the presence of a strong anisotropy in the low energy part of the independent particle spectrum (see Fig. S7 in the SI).

Figure 6 shows the real space excitonic wave functions corresponding to the lowest energy excitations of TiO$_2$:H$_i$ (top panel) and TiO$_2$:Nb$_{Ti}$ (bottom panel), which have very similar energies, 0.33 eV in TiO$_2$:H$_i$ and 0.35 eV in TiO$_2$:Nb$_{Ti}$. We see that these excitations have very different spatial distributions in the two systems: while in TiO$_2$:H$_i$ the electron is strongly localized on the Ti atom closest to the defect, it is almost completely delocalized in TiO$_2$:Nb$_{Ti}$. In TiO$_2$:H$_i$ the exciton is indeed composed of transitions from the gap state to conduction...
VI. CONCLUSIONS

The introduction of dopants into the rutile TiO$_2$ lattice leads to significant modification of the materials electronic and optical properties. Both interstitial Hydrogen and substitutional Niobium create a distortion of the crystal lattice around the defect and introduce electronic states localized mainly on adjacent Ti atoms. The corresponding quasi-particle defect states are non dispersive and their energies lie in the rutile gap, at ~ 0.7 eV below the CBM. The use of G$_0$W$_0$ is crucial in determining accurately the defect level positions, that are poorly described by DFT-KS, and similarly for the description of the band gap narrowing upon doping. While the high energy part of the optical spectrum (> 3 eV) is little affected by the presence of the dopant states, transition from the gap states to the conduction band give rise to new absorption peaks at low energy (< 2 eV) that enhance the absorption of rutile in the solar spectrum range. Interestingly, we found very different excitonic wavefunctions for the low energy excitations in H- and Nb doped rutile: while photoexcited electrons are largely delocalized in TiO$_2$:Nb$_{Ti}$, they remain localized close to the hole in TiO$_2$:H$_i$. These characteristics suggest a longer exciton lifetime and a larger mobility of photoexcited electrons in TiO$_2$:Nb$_{Ti}$, consistent with the use of Nb as an efficient dopant for improving the performance of TiO$_2$ in technological applications.

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FIG. 6: Excitonic wavefunctions corresponding to the absorption peaks at 0.33 eV in TiO$_2$:H$_i$ (Top) and 0.35 eV in TiO$_2$:Nb$_i$ (Bottom). H and Niobium are shown in black; the gray ball indicates the position of the hole in the BSE calculations.
25. Y. Zhao, T. Hou, Y. Li, K. S. Chan, and S.-T. Lee, Appl. Phys. Lett. 102, 171902 (2013).
26. U. Aschauer and A. Selloni, Phys Chem Chem Phys 14, 16595 (2012).
27. C. Dette, M. A. Pérez-Osorio, C. S. Kley, P. Punke, C. E. Patrick, P. Jacobson, F. Giustino, S. J. Jung, and K. Kern, Nano Lett. 14, 6533 (2014).
28. U. Aschauer, J. Chen, and A. Selloni, Phys Chem Chem Phys 12, 12956 (2010).
29. D. T. Cromer and K. Herrington, J. Am. Chem. Soc. 77, 4708 (1955).
30. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002).
31. W. Hanke and L. J. Sham, Phys Rev Lett 33, 582 (1974).
32. W. Hanke and L. J. Sham, Phys Rev B 21, 4656 (1980).
33. G. Strinati, H. J. Mattausch, and W. Hanke, Phys Rev B(R) 25, 2867 (1982).
34. G. Strinati, Rivista Nuovo Cimento 11, 1 (1988).
35. R. W. Godby and R. J. Needs, Phys. Rev. Lett 62, 1169 (1989).
36. A. Marini, C. Hogan, M. Grünig, and D. Varsano, Comput. Phys. Commun. 180, 1392 (2009).
37. D. Sangalli, C. Hogan, A. Ferretti, D. Varsano, M. Grünig, M. Palummo, C. Attaccalite, E. Cannuccia, M. Marsili, F. Affinito, et al., preprint (2018).
38. V. Popescu and A. Zunger, Phys. Rev. B 85, 085201 (2012).
39. P. V. C. Medeiros, S. S. Tsirkin, S. Stafström, and J. Björk, Phys Rev B 91, 041116 (2015).
40. P. V. C. Medeiros, S. Stafström, and J. Björk, Phys Rev B 89, 041407 (2014).
41. A. Malashevich, M. Jain, and S. G. Louie, Phys Rev B 89, 075205 (2014).
42. S. B. Zhang, D. Tománek, M. L. Cohen, S. G. Louie, and M. S. Hybertsen, Phys. Rev. B 40, 3162 (1989).
43. M. Zhang, S. Ono, N. Nagatsuka, and K. Ohno, Phys. Rev. B 93, 155116 (2016).
44. C. E. Patrick and F. Giustino, J. Phys. Condens. Matter 24, 202201 (2012).
45. E. Baldini, A. Dominguez, L. Chiodo, E. Sheveleva, M. Yazdi-Rizi, C. Bernhard, A. Rubio, and M. Chergui, Phys Rev B 96, 041204 (2017).
46. M. S. Hybertsen and S. G. Louie, Phys. Rev. B 34, 5390 (1986).
47. L. Chiodo, J. M. García-Lastra, A. Iacomino, S. Ossicini, J. Zhao, H. Petek, and A. Rubio, Phys. Rev. B 82, 045207 (2010).
48. T. Rangel, M. Del Ben, D. Varsano, G. Antonius, F. Bruneval, F. da Jornada, M. van Setten, O. Orhan, D. D. O’Regan, A. Canning, et al., preprint (2018).
49. X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Côté, et al., Comput. Phys. Commun. 180, 2582 (2009).
50. J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, Comput. Phys. Commun. 183, 1269 (2012).
51. A. Hupfer, L. Vines, E. V. Monakhov, B. G. Svensson, and F. Herklots, Phys Rev B 96, 085203 (2017).
52. F. Filippone, G. Mattioli, P. Alippi, and A. Amore Bonapasta, Phys. Rev. B 80, 245203 (2009).
53. J. Stauschohl-Möller, H. H. Kristoffersen, B. Hinnemann, G. K. H. Madsen, and B. Hammer, J. Chem. Phys. 133, 144708 (2010).
54. P. Deák, B. Aradi, and T. Frauenheim, Phys. Rev. B 83, 155207 (2011).
55. K. F. Berggren and B. E. Sernelius, Phys Rev B 24, 1971 (1981).
56. M. Landmann, E. Rauls, and W. G. Schmidt, J. Phys. Condens. Matter 24, 195503 (2012).
57. G. Pizzi, A. Cepellotti, R. Sabatini, N. Marzari, and B. Kozinsky, Comput. Mater. Sci. 111, 218 (2016).