Combined hybrid functional and DFT+$U$ calculations for metal chalcogenides

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In the density-functional studies of materials with localized electronic states, the local/semilocal exchange-correlation functionals are often either combined with a Hubbard parameter $U$ as in the LDA+$U$ method or mixed with a fraction of exactly computed (Fock) exchange energy yielding a hybrid functional. Although some inaccuracies of the semilocal density approximations are thus fixed to a certain extent, the improvements are not sufficient to make the predictions agree with the experimental data. Here we put forward the perspective that the hybrid functional scheme and the LDA+$U$ method should be treated as complementary, and propose to combine the range-separated (HSE) hybrid functional with the Hubbard $U$. We thus present a variety of HSE+$U$ calculations for a set of II-VI semiconductors, consisting of zinc and cadmium monochalcogenides, along with comparison to the experimental data. Our findings imply that an optimal value $U^*$ of the Hubbard parameter could be determined, which ensures that the HSE+$U^*$ calculation reproduces the experimental band gap. It is shown that an improved description not only of the electronic structure but also of the crystal structure and energetics is obtained by adding the $U^*$ term to the HSE functional, proving the utility of HSE+$U^*$ approach in modeling semiconductors with localized electronic states.

I. INTRODUCTION

Static correlation arising from the tendency of electrons to distribute themselves over the various centers, is pronounced in materials containing localized $d$ or $f$ electrons such as some transition-metal or rare-earth compounds. The local density approximation (LDA) or the generalized gradient approximation (GGA) commonly employed in Kohn-Sham density functional theory (DFT) inherently assume a localized exchange-correlation hole, implying that static correlation is treated in an unrestricted manner in these approximations. Thus local or semilocal exchange-correlation energy $E_{\text{xc}}$ functionals are often either combined with a Hubbard parameter $U$ as in the LDA+$U$ method or mixed with a fraction $\alpha$ of exactly computed (Fock) exchange energy $E_{\text{xc}}^{\text{exact}}$, yielding a hybrid functional

$$E_{\text{xc}}^{\text{hybrid}} = E_{\text{xc}}^{\text{exact}} + (1-\alpha)(E_{\text{xc}}^{\text{GGA}} - E_{\text{xc}}^{\text{exact}}) + \alpha E_{\text{xc}}^{\text{GGA}},$$

(1)

where the second term models the static correlation energy. For $\alpha > 0$, the static correlation energy is reduced in favor of the suppression of electron fluctuations, leading to a better description for the localized electron states (as evidenced by the improved prediction of the binding energy of localized $d$ states, band gaps, and magnetic moments). Thus the hybrid functional scheme and the LDA+$U$ approach could be regarded as alternative means for fixing inaccuracies of the semilocal density approximations, which result from insufficient localization of $d$ electrons. Indeed, it has recently been proposed to derive the value of $U$ from hybrid functional calculations. In contrast, we think it is appropriate to adopt a perspective where the hybrid-functional and DFT+$U$ methods are treated complementary (inasmuch as they both reduce the static correlation energy), which led us to combine hybrid functionals with the Hubbard $U$. From a different point of view, this means that one of the two methods (DFT+$U$) is utilized to reduce the residual self-interaction error of the other one (hybrid-functional), which is pragmatically justified.

Furthermore, Ivády et al. (Ref. 42) have recently shown that a hybrid exchange-correlation potential could be cast into a mathematical form that is reminiscent of the on-site Hubbard potential for a subsystem of localized orbitals, providing theoretical justification for our methodology: An additional on-site (DFT+$U$) potential is added to the hybrid exchange-correlation potential, which is applied only to strictly localized states. This improves the physical description because localized $d$-band states and delocalized crystal states are differentiated in the hybrid-functional+$U$ approach, which are indifferent to the hybrid functional itself. It is also interesting in this regard to point out that the DFT+$U$ and hybrid-functional methods could both be regarded as approximations to the GW method, which is articulated in Refs. 43 and 44 respectively. The incentive of using these two methods together is then to increase the level of approximation, provided that they are complementary.

It is usually necessary to perform a calibration for the value of $U$ that is optimal with respect to the material properties under consideration. Besides $U$ is not only
FIG. 1. (Color online) Calculated versus measured values of the band gap $E_g$ (a) and the $d$ band position $\varepsilon_d$ relative to the valence band maximum (b) for zinc and cadmium monochalcogenides. The experimental values of $E_g$ and $\varepsilon_d$ are taken from Refs. 60–62 and Refs. 63 and 64, respectively. The values obtained from the present GGA (HSE) calculations are connected by blue dashed (red dot-dashed) lines to guide the eye. The solid black lines pass through the experimental values.

It is appealing to employ a hybrid functional with an exchange mixing coefficient $\alpha$ that is in practice fixed to a single universal value, e.g., $\alpha = 1/4$ in both global and range-separated Heyd-Scuseria-Ernzerhof (HSE) hybrid functionals. It should, however, be noted that setting the optimal value for $\alpha$ as 1/4 in Ref. [49] was accomplished empirically (via error analysis of the atomization energies), which would not necessarily be optimal for other material properties. We found, in line with earlier reports, that the hybrid (HSE) functional calculations with $\alpha = 1/4$ improve the prediction of both the $d$ band position $\varepsilon_d$ relative to the valence band maximum and the band gap $E_g$ but these improvements are not sufficient to make the predictions agree with the experimental data. This is demonstrated in Fig. 1 for zinc and cadmium monochalcogenides, where the calculated and measured values of $E_g$ (left panel) and $\varepsilon_d$ (right panel) are plotted with respect to each other. Figure 1(a) shows that (i) the improvement for the band gap is impressive for systems with a somewhat small band gap, and (ii) the band gap is still significantly underestimated for wide band gap semiconductors such as ZnO. As explored in Appendix, both the GGA band gap error $\Delta E_g^{\text{GGA}}$ and the HSE correction $E_g^{\text{HSE}} - E_g^{\text{GGA}}$ are inversely proportional to the high-frequency dielectric constant $\varepsilon_\infty$ so that $\Delta E_g^{\text{GGA}} \approx A/\varepsilon_\infty$ and $E_g^{\text{HSE}} - E_g^{\text{GGA}} \approx A'/\varepsilon_\infty$, where the constants $A$ and $A'$ satisfy $A' < A$. Owing to the latter, the HSE improvement falls short for materials with relatively small dielectric constant (with the exception of CdO for which the HSE calculation yields the right direct and indirect band gaps, cf. Ref. [11]. Figure 1(b) shows that the HSE-calculated $\varepsilon_d$ is still too high although there is a significant correction of about 1.3 ± 0.4 eV. It should be noted that the prediction of $\varepsilon_d$ could further be improved by adding a Hubbard $U$ term to the hybrid functional, which would enable one to adapt just the $d$ band position. It is also interesting to note that the measured values of $\varepsilon_d$ could indeed be reproduced by using adjusted $U$ values, cf. Fig. 3 of Ref. [47] in the case of zinc monochalcogenides. These observations also motivate us to treat the hybrid functional scheme and the DFT+$U$ method as complementary rather than alternative approaches. Accordingly, we propose here to combine the screened hybrid functional of Heyd, Scuseria, and Ernzerhof with the Hubbard $U$. The main advantage of the latter is that strictly localized and delocalized states are screened differently since only the former are subject to an additional on-site (DFT+$U$) potential. In contrast, localized and delocalized states are indifferent to the original HSE functional as long as the same set of parameters, viz. the exchange mixing coefficient $\alpha$ and the screening parameter $\omega$, are used for all states. Additionally, we regard $U$ as a semiempirical parameter, in line with the perspective that the Hubbard term added to the density functionals is essentially a phenomenological many-body correction. Our findings show that the HSE+$U$ calculations performed by using an adjusted $U$ value reproduce the measured band gap and, at the same time, result in an improved physical description not only of the electronic structure but also of the crystal structure and energetics for the semiconductors with localized $d$ electrons. This is obviously very convenient for practical purposes such as setting the range of the electron chemical potential accurately in the point defect calculations, e.g., Ref. [59]. It is also very convenient because it enables one to employ the measured $E_g$, instead of $\varepsilon_d$, in setting the $U$ value. Note that there is usually some scatter in the measured data for $\varepsilon_d$, which partly reflects the fact that the width of the $d$ bands is nonzero no matter how localized the states are.

The underestimation of the band gap in the HSE calculations, cf. Fig. 1(a), could partially be attributed to lacking the correlation part of the discontinuity of the exchange-correlation potential. Similarly, the discontinuity of the exchange-correlation potential is not fully restored in the LDA/GGA+$U$ calculations even though the $U$ term added to the density functionals yields a discontinuous contribution. It should also be commented that setting the right value of $U$ empirically is not straightforward because one needs to take accounts of hybridization and screening of $d$ electrons a priori. Furthermore, the measured value of $E_g$ could not be reproduced no matter how large a value of $U$ is used in the LDA+$U$ calculations performed for zinc monochalcogenides, cf. Fig. 3 of Ref. [47]. Our study provides a resolution to this difficulty with the aid of hybrid functional, and proves that an adequate $U$ value could be determined by simply matching the experimental band gap.

The rest of the paper is organized as follows: The next section is devoted to the method of calculation, which also summarizes the computational details. This is followed by a discussion of the calculation results before concluding remarks given in the last section.
II. METHOD

All calculated properties reported here were obtained via semilocal or hybrid DFT calculations using the Perdew-Burke-Ernzerhof (PBE) or Heyd-Scuseria-Ernzerhof (HSE) functionals, respectively. In the hybrid functional calculations, we employed the HSE06 functional by setting the screening parameter, \( \omega = 0.207 \text{ Å}^{-1} \) (and exchange mixing coefficient \( \alpha = 0.25 \)) as implied in Section I. In the HSE+U calculations we used the simplified (rotationally invariant) approach where the difference between the on-site Coulomb \( U \) and exchange \( J \) parameters is employed as the effective Hubbard parameter \( U = U - J \). We performed a variety of calculations for zinc and cadmium monochalcogenides by employing the projector augmented-wave (PAW) method as implemented in VASP code. The 2s and 2p, 3s and 3p, 4s and 4p, 5s and 5p, 3d and 4s, and 4d and 5s states are treated as valence states for oxygen, sulfur, selenium, tellurium, zinc, and cadmium, respectively. Plane wave basis sets were used to represent the electronic states, which were determined by imposing a kinetic energy cutoff of 520 eV for the systems that include oxygen atoms and 400 eV for the rest of the systems.

We first carried out optimization of the crystal structures where concurrent relaxations of the cell volume and shape as well as the ionic positions were performed until the total energy was converged within 1 meV and the maximum value of residual forces on atoms was reduced to be smaller than 0.01 eV/Å. In these optimizations, we used the primitive unit cells of the crystals, whose Brillouin zones were sampled by \( 8 \times 8 \times 6 \) (for the crystals with wurtzite structure) or \( 8 \times 8 \times 9 \) (for the crystals with rocksalt and zincblende structures) \( k \)-point meshes generated according to Monkhorst-Pack scheme enabling us to achieve convergence of the energy within 1 meV/atom. Using the optimized crystal structures, we then performed band-structure and density-of-states calculations in order to obtain the band gap \( E_g \) and the \( d \) band position \( \varepsilon_d \), respectively. Besides we performed geometry optimizations for the \( \text{O}_2 \) and \( \text{S}_8 \) molecules and the bulk solids of \( \text{Se}, \text{Te}, \text{Zn}, \) and \( \text{Cd} \), and employed the respective equilibrium total energies in the computation of the formation energy \( \Delta H_f \).

As indicated in Section I we set the value of \( U \) by reproducing the experimental value of the band gap in the HSE+U calculations, which is justified in Section III. Thus, we carried out the HSE+U calculations for a range of \( U \) values, and studied the calculated band gap as a function of \( U \). Since our results showed that the variation of the band gap with \( U \) is virtually linear, we performed a linear fit to obtain the value of \( U \) that corresponds to the measured band gap. The value of \( U \) obtained via this procedure, which is optimal in reproducing the experimental value of the band gap, is denoted by \( U^* \).

The HSE+U calculation that yields the experimental, i.e., targeted, value of the band gap is named here as the HSE+U* calculation.

It should be mentioned that the HSE band energy differences depend on the value of the screening parameter \( \omega \), which is not necessarily universal. It was, however, demonstrated that \( \omega = 0.207 \text{ Å}^{-1} \) as used in HSE06 is an average optimal value for which the band energy differences approximate rather accurately quasiparticle excitation energies, for a variety of semiconductors. Therefore, the HSE band energy differences are often directly compared to the experimental band gaps (e.g., in order to demonstrate the success of the HSE calculations in reproducing the experimental band gaps). In addition to this, as long as the HSE+U approach could be regarded as an approximation to the GW method, it would be preferential to use the quasiparticle energy differences (the GW-calculated band gaps) in our procedure for setting the value of \( U^* \). However, the GW-calculated band gaps are usually in good agreement with the experimental band gaps (e.g., Ref. [23]). It should, on the other hand, be also noted that the GW@HSE calcula-

![Figure 2](http://dx.doi.org/10.1063/1.4890458) The band gap error \( \Delta E_g \) versus the difference \( \Delta E_{pd} = \varepsilon_{pd} - \varepsilon^{Me}_{pd} \) for zinc and cadmium monochalcogenides. The PBE- and HSE-calculated values are marked by the empty and filled symbols, respectively, in the top-most panel (a). In the lower panels (b)-(i), the results of the combined HSE+U* (\( U^* \)) calculations are presented together with those of the PBE (empty symbols) and HSE (filled symbols) calculations.
tions overestimate the band gap of a number of semiconductors including CdS and ZnS (Ref. 56). Hence, we preferred to utilize the experimental band gaps instead of the GW-calculated energy differences, which is also convenient from a practical point of view since it enables one to avoid performing quasiparticle calculations that might easily become computationally exhaustive, especially for large-scale (e.g., defect) calculations.

III. RESULTS AND DISCUSSION

We first quantify the relationship between the band gap error $\Delta E_g$ in the GGA and HSE calculations and the position of $d$ level in the case of zinc and cadmium chalcogenides since the latter is, in effect, adjusted by varying the value of $U$. Figure 2(a) shows a plot of $\Delta E_g$ versus the difference $\Delta \epsilon_{pd} = \epsilon_p - \epsilon_{d}$, where $\epsilon_p$ and $\epsilon_{d}$ denote the $p$- and $d$-state energies of the chalcogen and metal atoms, respectively. In zinc and cadmium chalcogenides, the $d$ band is located below and next to the topmost valence band. Thus, the valence-band maximum is therefore used here to quantify the relationship between the band gap error and the position of $d$ level. In Fig. 2(a), a linear trend is noticeable for each set of data, cf. the solid lines, with the exception of data points for CdO. It is seen that the band gap error is proportional (with a negative slope) to $\Delta \epsilon_{pd}$. We obtain, via fitting,

$$\Delta E_g = -0.48 \Delta \epsilon_{pd} + 3.33 \quad \text{(PBE)}$$

$$= -0.20 \Delta \epsilon_{pd} + 1.52 \quad \text{(HSE)}$$

for Zn chalcogenides, and

$$\Delta E_g = -0.50 \Delta \epsilon_{pd} + 3.84 \quad \text{(PBE)}$$

$$= -0.26 \Delta \epsilon_{pd} + 1.97 \quad \text{(HSE)}$$

for Cd chalcogenides (excluding CdO), where $\Delta E_g$ and $\Delta \epsilon_{pd}$ are both in eV. It is clear, comparing the data points represented by empty (PBE) and filled (HSE) symbols connected by dashed lines, that the band gap error is reduced when the difference between the chalcogen $p$- and metal $d$-state energies is increased. This applies to all II-VI semiconductors studied here, including CdO. As shown in Figs. 2(b) and 2(i), $\Delta \epsilon_{pd}$ is significantly increased in the HSE+$U^{*}$ calculations, making $\Delta E_g$ vanish. This is reassuring that the optimal Hubbard parameter $U^{*}$ could be determined by matching the experimental band gap.

We now determine the $U^{*}$ values that corresponds to vanishing $\Delta E_g$ for the II-VI semiconductors under consideration. Thus, the results of HSE+$U^{*}$ calculations for a range of $U$ values are given in Fig. 3 where the calculated band gap is plotted as a function of $U$. Note that the variation of the band gap with the effective Hubbard parameter is virtually linear (with a different slope for each system). For each compound, a linear fit is thus performed, which yields the solid lines in Fig. 3. The $U^{*}$ values are marked by vertical dot-dashed lines, which correspond to the measured band gap (marked by horizontal dot-dashed lines). Table I gives the optimal Hubbard parameters and corresponding band gaps for zinc and cadmium monochalcogenides. It should be remarked that one obtains $U^{*} = 0$ for CdO since the measured value of the band gap of CdO is reproduced already in the HSE calculation, as mentioned in Section 1.

Next we compare the values of $\Delta E_g$ and $\Delta \epsilon_{pd}$ obtained in the HSE+$U^{*}$ calculations to those obtained in the PBE

TABLE I. The optimal Hubbard parameter $U^{*}$, the experimental band gap $E_g$, and the HSE band gap error $\Delta E_g$ (all in eV) for zinc and cadmium monochalcogenides.

| Semiconductor | Crystal structure | $U^{*}$ | $E_g$ (eV) | $\Delta E_g^{\text{HSE}}$ (eV) |
|---------------|------------------|--------|-----------|-------------------|
| CdO           | rocksalt         | 0.0    | 0.84      | 0.00              |
| CdTe          | zincblende       | 0.8    | 1.48      | 0.03              |
| c-CdSe        | zincblende       | 3.4    | 1.75      | 0.21              |
| w-CdSe        | wurtzite         | 5.0    | 2.35      | 0.38              |
| ZnTe          | zincblende       | 5.0    | 2.35      | 0.38              |
| c-CdS         | zincblende       | 4.2    | 2.40      | 0.27              |
| w-CdS         | wurtzite         | 4.5    | 2.50      | 0.31              |
| ZnSe          | zincblende       | 5.0    | 2.71      | 0.38              |
| c-ZnO         | zincblende       | 6.1    | 3.27      | 0.95              |
| w-ZnO         | wurtzite         | 6.0    | 3.37      | 0.92              |
| $\beta$-ZnS   | zincblende       | 5.0    | 3.72      | 0.45              |
| $\alpha$-ZnS  | wurtzite         | 6.0    | 3.91      | 0.58              |
and HSE calculations. Figures 4(b) and 4(i) show a plot of the band gap error $\Delta E_g$ versus the difference $\Delta \epsilon_{pd}$ for the II-VI semiconductors under consideration. As already noted, the HSE calculations yield an increased value for $\Delta \epsilon_{pd}$ in association with a reduced band gap error, in comparison to the PBE calculations. The difference $\Delta \epsilon_{pd}$ is further increased in the HSE+$U$ calculations, reducing the band gap error further. Having $U = U^*$ in this trend makes $\Delta E_g$ vanish, with adequate increase of $\Delta \epsilon_{pd}$.

It is seen in Table I that the larger $E_g$ the greater $U^*$ (with few exceptions). This implies that employing a large (small) $U^*$ would be necessary for a wide (narrow) band gap semiconductor for which the HSE band gap error $\Delta E_g^\text{HSE}$ is rather large (small), cf. Figure 4(a). Thus, having a large band gap error in the HSE calculation necessitates using a large $U^*$ for correction. Furthermore, there appears to be a roughly monotonous relationship between $U^*$ and $\Delta E_g^\text{HSE}$, cf. Table I. Our analysis presented in Fig. 4 shows that this relationship could be quantified by taking into account the screening effects through the high-frequency dielectric constant $\epsilon_\infty$. A plot of $\Delta E_g^\text{HSE}$ versus $U^*/2\epsilon_\infty$ is given in Fig. 4 where all data points satisfy

$$\Delta E_g^\text{HSE} = \frac{U^*}{2\epsilon_\infty} \pm 0.14 \text{ eV}. \quad (4)$$

Here both $U^*$ and $\Delta E_g^\text{HSE}$ are in eV. Note that the shift in the occupied (unoccupied) $d$ state energies due to the $U^*$ term would be $-U^*/2$ ($U^*/2$) if the hybridization and screening effects are ignored. Thus, the correction to the band gap would be proportional to $U^*/2$, ignoring the dielectric screening, for the II-VI semiconductors studied here since their lower conduction bands have virtually no contribution from the metal $d$ states. On the other hand, the band gap correction needs to be scaled by $\epsilon_\infty$ in order to reflect the dielectric screening of the Coulomb potential in a solid. Thus, the $U^*$ term added to the hybrid (HSE) functional results in a correction of $U^*/2\epsilon_\infty$ to the band gap. This explanation justifies our means of setting the value of $U^*$ by matching the experimental band gap. It also implies that an approximate value for the optimal Hubbard parameter could $a$ priori be obtained by inverting Eq. (4), i.e., $U^* \approx 2\epsilon_\infty(E_g - E_g^\text{HSE})$, provided that the experimental and HSE-calculated band gaps $E_g$ and $E_g^\text{HSE}$ as well as the high-frequency dielectric constant $\epsilon_\infty$ are available. Note that the hybrid-functional calculations could be utilized to obtain $\epsilon_\infty$ when the experimental data is not available, cf. Table I of Ref. 77.

It is interesting to point out that one could assign a single $U^*$ value of $\sim 5$ eV for ZnTe, ZnSe, and ZnS while $U^* \sim 6$ eV for w-ZnO, c-ZnO, ZnS, and $\beta$-ZnS, cf. Table 1. Thus, a mean value of $U_{Zn}^* \approx 5.5$ eV appears to be adequate for all Zn compounds studied here. It is clearly pleasing to obtain a single (universal) $U^*$ value for Zn, which is almost independent of the composition or crystal structure of the relevant zinc compounds, for its practical importance since it would allow one to set $U_{Zn}^* \approx 5.5$ eV in the studies on alloyed systems made of Zn, O, S, Se, Te atoms.

In order to assess the improvement of the HSE+$U$ approach in relation to the general physical description of the foregoing semiconductors, we computed the mean error in (i) the optimized crystal structures, (ii) the $d$ band positions, and (iii) the formation energies of the metal chalcogenides under consideration. Accordingly, a comparison of errors in the predictions of the HSE+$U^*$, HSE and PBE calculations is presented Fig. 5 where the comparison is performed for the unit cell volume $V$ [in Fig. 5(a)], for the ratio $c/a$ of (wurtzite) lattice parameters $a$ and $c$ [in Fig. 5(b)], for the internal parameter $u$ of wurtzite structure [in Fig. 5(c)], for the $d$ band position $\epsilon_d$ [in Fig. 5(d)], and for the formation energy $\Delta H_f$ [in Fig. 5(e)]]. Our analysis reveals the following:

First, we see in Figs. 5(a)-(c) that the optimization of the crystal structure via HSE or HSE+$U^*$ calculation results in a similarly more accurate description, in comparison to the PBE calculations. Thus, the HSE+$U^*$ calculations seem to preserve the accuracy of the HSE calculations in the crystal structure optimizations.

Secondly, Fig. 5(d) shows that there is a significant correction to the $d$ band position thanks to adding $U^*$ term to the HSE functional: The mean error in the $\epsilon_d$ prediction becomes $\sim 0.6$ eV in the HSE+$U^*$ calculations, compared to $\sim 2.3 \text{ (3.6)}$ eV in the HSE (PBE) calculations. It should also be noted that the variation of the difference $\Delta \epsilon_d^* = \epsilon_d^\text{HSE} - U^* - \epsilon_d^\text{HSE}$ with $U^*$ is almost linear, which is consistent with $\Delta \epsilon_d^* \approx -0.35 U^*$, where both $\Delta \epsilon_d^*$ and $U^*$ are in eV. Thus, using a larger $U^*$ yields a larger correction to $\epsilon_d$, shifting the $d$ band to
FIG. 5. (Color online) A comparison of errors in the predictions via HSE+U∗ (red bars), HSE (green bars) and PBE (blue bars) calculations for the unit cell volume $V$ (a), the ratio $c/a$ of lattice parameters $a$ and $c$ (b), the internal lattice parameter $u$ (c), the $d$ band position $\varepsilon_d$ (d), and the absolute value of formation energy $|\Delta H_f|$ (e).

a lower position that is closer to its experimental location. Recall that employing a larger $U^*$ is necessary for the systems with a larger HSE band gap error (cf. Table I). Hence, the improvement in predicting the $d$ band position via HSE+U∗ calculations is warranted since the value of $U^*$ is determined by matching the experimental band gap.

Finally, as for the improvement of the HSE+U approach in the prediction of formation energies, Fig. 5(e) shows that the mean absolute error in $|\Delta H_f|$ is on the order of $\sim 0.1$, $0.2$, and $0.4$ eV per formula unit in the HSE+U∗, HSE, and PBE calculations, respectively. Thus, the HSE+U∗ calculations result in a more accurate description of crystal energetics of zinc and cadmium monochalcogenides, compared to the HSE and PBE calculations. Note that the mean error in $|\Delta H_f|$ turns out to be positive in the HSE+U∗ calculations, which is negative in the HSE calculations. This indicates that the error in the formation energies could be further reduced, whenever necessary, by re-adjusting the value of $U^*$.

IV. CONCLUSION

In this work, we treated the hybrid functional scheme and the DFT+U method as complementary rather than alternative approaches in studying a set of II-VI semiconductors with localized $d$ states. This led us to introduce the HSE+U approach where the range-separated HSE hybrid functional is combined with the Hubbard $U$. Furthermore, we regarded $U$ as a semiempirical parameter. This enabled us to determine an optimal value $U^*$ of the Hubbard parameter, for which the HSE+U calculation yields a targeted (e.g., experimental) value of the band gap. We find that the correction to the band gap due to the additional $U^*$ term is roughly given by $U^*/2\epsilon_\infty$, which is in line with theoretical reasoning. The results of a variety of HSE+U∗ calculations performed for zinc and cadmium monochalcogenides, viz., a subset of the semiconductors with localized $d$ states, indicate that an improved description of the electronic structure as well as crystal structure and energetics is obtained in these calculations, compared to the hybrid functional calculations employing the HSE functional without an additional Hubbard term. The present study thus shows that adding the $U^*$ term to the HSE functional leads to more accurate prediction of both the electronic and crystal structures of II-VI semiconductors with localized states.

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Appendix: Band gap error in DFT and hybrid-functional calculations

Figure 6(a) shows a plot of the band gap error $\Delta E^\text{PBE} = E_g - E^\text{PBE}$ in the GGA calculation versus the inverse high-frequency dielectric constant $1/\epsilon_\infty$, where a nearly linear trend is noticeable for each set of data. It is clear that the band gap error is larger for materials with smaller $\epsilon_\infty$. This is in line with the finding of $\epsilon_\infty$ that the self-energy correction to the DFT-calculated band gap is inversely proportional to the high-frequency dielectric constant. Employing the LDA-calculated band gaps, it was found that the product $\epsilon_\infty\Delta E^\text{LDA} \approx 9.1 \pm 0.2$ eV is a material-independent constant. We find that the product $\epsilon_\infty\Delta E^\text{PBE} = A$ is also roughly a constant, but with a different value for each class of systems: $A_{\text{Zn}} = 9.4 \pm 0.6$ eV and $A_{\text{Cd}} = 7.2 \pm 0.5$ eV for Zn and Cd chalcogenides, respectively. Note that the data points in red
the other hand, our results presented in Fig. 6(b) show that the difference $\Delta E_{\text{PBE}}$ given by $\Delta E_{\text{PBE}} = A_2n / \epsilon_\infty$ (where $A' = 6.4 \pm 0.5$ eV is a material-independent constant). Combining $\Delta E_{\text{PBE}} = A_2n / \epsilon_\infty$ for ZnO and $\Delta E_{\text{PBE}} = A_2n / \epsilon_\infty$ for TiO$_2$ [cf. Fig. 6(b)], we obtain $\Delta E_{\text{PBE}} \approx A' / \epsilon_\infty$. Note that both $A_2n$ and $A_\text{Cd}$ are greater than $A'$. Thus, the band gap is underestimated in the HSE calculations in proportionality with $1/\epsilon_\infty$ albeit there is a significant improvement in comparison with the respective GGA calculations.

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SUPPLEMENTAL MATERIAL

The total (DOS) and projected (PDOS) density of states of zinc and cadmium monochalcogenides, obtained via density-functional (PBE), hybrid-functional (HSE), and combined HSE+$U^*$ calculations, are given Figs. S1-S12. Figure S13 shows a plot of the difference $\Delta \varepsilon_d^* = \varepsilon_{HSE+U^*}^d - \varepsilon_{HSE}^d$ versus the optimal Hubbard parameter $U^*$. 
FIG. S7. The total and projected density of states of $w$-ZnO.

FIG. S8. The total and projected density of states of $c$-ZnO.
FIG. S9. The total and projected density of states of α-ZnS.

FIG. S10. The total and projected density of states of β-ZnS.
FIG. S11. The total and projected density of states of ZnSe.

FIG. S12. The total and projected density of states of ZnTe.
FIG. S13. The total and projected density of states of CdO.

FIG. S14. The total and projected density of states of \(w\)-CdS.
FIG. S15. The total and projected density of states of $c$-CdS.

FIG. S16. The total and projected density of states of $w$-CdSe.
FIG. S17. The total and projected density of states of c-CdSe.

FIG. S18. The total and projected density of states of CdTe.
FIG. S19. (Color online) The difference $\Delta \varepsilon_d^* = \varepsilon_d^{\text{HSE}+U^*} - \varepsilon_d^{\text{HSE}}$ as a function of the optimal Hubbard parameter $U^*$. 

$\Delta \varepsilon_d^* \approx -0.35 U^*$