A real-space hybrid approach for electronic structure of transition and post-transition metal oxides

Hengxin Tan,1 Haitao Liu,2 Yuanchang Li,3,∗ Wenhui Duan,1,4 and Shengbai Zhang5

1State Key Laboratory of Low-Dimensional Quantum Physics and Collaborative Innovation Center of Quantum Matter, Department of Physics, Tsinghua University, Beijing 100084, China
2Institute of Applied Physics and Computational Mathematics, PO Box 8009, Beijing 100088, China
3Advanced Research Institute of Multidisciplinary Science, Beijing Institute of Technology, Beijing 100081, China
4Institute for Advanced Study, Tsinghua University, Beijing 100084, China
5Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY, 12180, USA

(Dated: January 1, 2019)

Abstract

Improving electronic structure calculations for practical and technologically-important materials has been a never-ending pursue. This is especially true for transition and post-transition metal oxides for which the current first-principles approaches still suffer various drawbacks. Here we present a hierarchical-hybrid functional approach built on the use of pseudopotentials. The key is to introduce a discontinuity in the exchange functional between core and valence electrons. It allows for treating the localization errors of sp and d electrons differently, which have been known to be an important source of error for the band gap. Using ZnO as a prototype, we show the approach is successful in simultaneously reproducing the band gap and d-band position. Remarkably, the same approach, without having to change the hybrid mixing parameters from those of Zn, works reasonably well for other binary 3d transition and post-transition metal oxides across board. Our findings point to a new direction of systematically improving the exchange functional in first-principles calculations.
Transition and post-transition metal oxides are among the most popular class of inorganic solids as they show many interesting physical properties including, among others, metal-insulator transition, magnetism, ferroelectricity, colossal magnetoresistance, charge order, and high temperature superconductivity \[1\–3\]. They are also technologically important for numerous applications such as catalysis, gas sensors, and electro-/photo-/thermochromic devices \[4\–6\]. Understanding the vastly-diverse behaviors of these metal oxides requires an adequate description of their underlying electronic structure.

First-principles methods are routinely used to study electronic structure of solids from which to obtain mechanical, electrical, and optical properties. Density function theory (DFT) \[7, 8\] is one of the most employed such approaches. Although DFT has achieved great successes in the past, it runs into difficulties for transition and post-transition metal oxides due to the challenge in dealing with the localized \(d\) or \(f\) electrons \[9, 10\]. Self-interaction has been blamed for the errors as a result of an over-delocalization of the electrons. This leads to a too-small band gap \((E_g)\) and a too-high \(d\)-band energy \((E_d)\) relative to the valence band maximum (VBM). Hartree-Fock (HF) approach, on the other hand, overly localizes the electrons, giving rise to errors in the opposite direction of the DFT, namely, it overestimates \(E_g\) while produces a too low \(E_d\) with respect to the VBM \[11\]. As a logical choice, one may mix the DFT with HF, i.e., in a hybrid approach, to improve the numerical accuracy. Although working well for the \(sp\)-electron systems, the hybrid functional, e.g., the HSE \[12, 13\], can also run into difficulties for the transition and post-transition metal oxides \[14, 15\].

In the current implementation of hybrid functional approaches, a same amount, e.g., in HSE, 25% \[12, 13\] of HF has been used throughout. In the pseudopotential (PP) approach, the same logic prevails, as one may argue that it is the only approach which is consistent with the all-electron results. A priori, however, there is no fundamental reason why the amount of HF should be the same between the core region and valence region. As a matter of fact, the more localized the electrons, the larger percentage the HF contribution (as we will demonstrate below). This necessitates a larger HF portion for the spatially more localized \(d\) electrons than that of the more delocalized \(sp\) electrons. It can be made possible by using a PP approach, since the functional form used to generate the PP can be completely different from that for the DFT bulk calculations \[16, 17\].

In this paper, we abandon the aforementioned “consistency” check, as it eliminates our
ability to improve the electronic properties of the oxides, and introduce instead a hybrid functional PP based hierarchical-hybrid functional (HHF) approach for electronic structure of transition and post-transition metal oxides. In this approach, we use different hybrid functionals, i.e., different HF mixing parameters $\alpha_c$ and $\alpha_v$, to treat the core and valence electrons of the metal elements, respectively, while leaving the treatment of the anion core, i.e., oxygen, unchanged. Note that in the widely-used PP-based HSE approach, the “consistency” check is also violated since such approach corresponds to having $(\alpha_c, \alpha_v) = (0, 0.25)$. To illustrate the usefulness of our approach, we first consider ZnO — a notoriously bad player among semiconductors with an awfully-large $E_g$ error in the range of an electron volt (eV). We show that, while the conventional HSE with whatever mixing parameter $\alpha$ cannot reproduce the experimental band gap and $d$-level positions, simultaneously, the hierarchical approach here works out exceptionally well for ZnO. The method works for other binary 3$d$ transition and post-transition metal oxides as well, especially for MnO and CuO, which are two other notoriously-bad examples for HSE. Note that these improvements are obtained without having to artificially adjusting $\alpha_v$ from the standard PBE0 value of 25%.

A hybrid functional is obtained by mixing PBE and HF as follows

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

where the mixing parameter $\alpha$ specifies the amount of HF exchange $E_{xc}^{HF}$ to replace the PBE functional. If $\alpha = 0$, Eq. (1) is reduced to the PBE functional; if $\alpha = 1$, on the other hand, it becomes 100% HF, while the correlation functional remains to be 100% PBE. When $\alpha = 0.25$, it is known as the PBE0 functional. The widely-used HSE functional is obtained by screening off the long-range tail of HF exchange in PBE0.

Our calculations were performed using the Quantum ESPRESSO code with a kinetic-energy cutoff of 60 Ry. All metal PPs were constructed by the OPIUM code (See Supplemental Material as well as Ref. 17 for details). As our focus here was on electronic structure, we used experimental lattice parameters for the oxides, except for ZnO for which we also performed structural relaxations. For comparison, we also performed all-electron calculations using the FHI-aims code. Magnetic structures used in calculations can be found in Supplemental Material.

Figure 1 shows the band structures of ZnO, which is used as the benchmark system in the exploration of various functional forms. Following Ref. 20, we consider $E_g$ and $E_d$ as the
FIG. 1: Band structures of ZnO. Panels (a) to (e) are the all-electron (AE) results with different exchange functional forms: (a) PBE, (b) HSE with α = 0.25, (c) HSE with α = 0.375, (d) HSE with α = 0.5, and (e) HF. Panels (f) and (g) are the HF PP results where (f) is PBE and (g) is 25% HSE for the valence electrons, respectively. In both panels (f) and (g), two different Zn HF PPs are considered with 12- and 18-valence electrons (12-val. and 18-val.), respectively. (h) Our HHF method with (αc, αv) = (0.75, 0.25). More details can be found in text. In the plots, black dashed lines denote the position of the VBM; the framed numbers denote the \( E_g \), while blue grids denote experimental \( E_d \). For clarity, the calculated \( E_d \) is the average \( d \)-band position below VBM.

two single-most important physical parameters for electronic structure. Experiment showed that \( E_g = 3.4 \text{ eV} \) \[27\], while \( E_d \) is located in the range of \( 7.5 \sim 8.8 \text{ eV} \) below the VBM \[28–34\]. More specifically, Figs. 1(a)–(e) show the all-electron results: (a) PBE, (b) HSE with α = 0.25, (c) HSE with α = 0.375, (d) HSE with α = 0.5, and (e) HF. One sees that, as α increases from 0 (i.e. PBE) to 0.5, \( E_g \) increases quickly while \( E_d \) decreases accordingly but to a much lesser degree. At the default α = 0.25 [Fig. 1(b)], \( E_g \) of 2.4 eV and \( E_d \) of −6.0 eV deviate from experiment by more than 1 eV. Increasing α to 0.375 can reproduce the experimental \( E_g \) but \( E_d \) is still considerably away from experiment [Fig. 1(c)]. At α = 0.5, the \( d \) bands approach the upper bound of the experimental value [Fig. 1(d)]. However, the corresponding \( E_g \) of 4.3 eV is too large when compared to experiment. At all-electron
HF in Fig. 1(e), the $d$ bands with an $E_d = -9.7$ eV are too deep and the $E_g$ of 11.3 eV is also too large. These all-electron results reveal the inability of the single $\alpha$ approach, as well as the inadequacy of imposing a “consistency” check to PP calculations. These all-electron PBE and HSE results also suggest that a larger amount of HF is required to correct $E_d$ than what is desired to correct $E_g$.

When PP is used, it is possible to adjust the mixing parameters in the core and valence regions independently. Let us consider first the simple case in Fig. 1(f) where HF PPs [17, 35, 36] are combined with PBE for valence electrons. Here, we consider two different Zn PPs with 12 and 18 valence electrons (denoted as 12- and 18-val.), respectively. The resulting band structures are noticeably different: increasing the number of valence electrons, $E_g$ decreases from 2.1 to 1.7 eV, while $E_d$ rises from 0.8 eV below the lower bound to 0.5 eV above the upper bound of the $d$-band set by experiment. If PBE for valence electrons is replaced by HSE as in Fig. 1(g), $E_g$ will increase to 3.5 (12-val.) and 3.1 eV (18-val.), respectively. For the $d$ bands, on the other hand, the effect of HSE in the 12-val. case is insignificant, while in the 18-val. case, they are pushed down into the experimental range.

From the above discussion, three trends emerge: (1) band structure depends on the choice of PP. In particular, $E_g$ and $E_d$ are both inversely proportional to the number of valence electrons. (2) Replacing PBE by a hybrid functional increases $E_g$, but decreases $E_d$ although the effect is noticeable only in the 18-val. case. (3) For HSE with $\alpha = 0.25$, the errors in $E_g$ and $E_d$ of all-electron [Fig. 1(b)] are opposite to those of 12-val. HF PP [Fig. 1(g)]. The last point is particularly important as it suggests that a simultaneous correction of $E_g$ and $E_d$ can be achieved if one develop a 12-val. hybrid functional PP [18, instead of the HF PP. This is indeed the case as illustrated in Fig. 1(h) where $(0.75, 0.25)$ for $(\alpha_c, \alpha_v)$ have been used, as explained below.

Figure 2 shows for ZnO the $E_g$ and $E_d$ dependences on $(\alpha_c, \alpha_v)$. It reveals that $E_g$ depends mainly on $\alpha_v$, while $E_d$ depends mainly on $\alpha_c$. To obtain the experimental $E_g$, $\alpha_v$ should be in the range of (0.23, 0.47) [See Fig. 2(a)]. To obtain the experimental $E_d$, $\alpha_c$ should be in the range of (0.43, 0.81). It is interesting to note that simultaneous corrections of $E_g$ and $E_d$ are obtained for $\alpha_v \sim 0.25$, which is the value deduced from a perturbation theory [20]. If one uses $\alpha_v = 0.25$, $\alpha_c$ should be approximately 0.75. These values are indicated in Fig. 2 by black stars. Figure 1(h) shows the corresponding band structure for the HHF approach.
FIG. 2: Maps of (a) $E_g$ and (b) $E_d$ as functions of $(\alpha_c, \alpha_v)$ for ZnO. Black dashed line in (a) represents the experimental $E_g$, whereas grid in (b) represents the experimental region for $E_d$. In (a) and (b), black diagonal lines are the allowed phase space if one is restricted to the “consistency” check [37], namely, $\alpha_c = \alpha_v$, while black stars denote $(\alpha_c, \alpha_v) = (0.75, 0.25)$, which fall within the experimental ranges of both $E_g$ and $E_d$. 
Table I: Theoretical lattice parameters, \(c/a\) ratios, and volumes (per formula unit), in comparison with experiment, for ZnO.

| Method      | \(a\) (Å) | \(c\) (Å) | \(c/a\) | \(V\) (Å\(^3\)) |
|-------------|------------|------------|---------|------------------|
| PBE\(^a\)   | 3.292      | 5.306      | 1.612   | 24.90            |
| HSE\(^a\)   | 3.253      | 5.254      | 1.615   | 24.07            |
| This work   | 3.293      | 5.278      | 1.603   | 24.78            |
| Experiment\(^b\) | 3.249    | 5.205      | 1.602   | 23.82            |

\(^a\)Ref. [38]. \(^b\)Ref. [27].

Using Fig. 2, one can understand the inadequacy of applying a “consistency” check in the hybrid approach, as shown by the black diagonal lines [37]. It shows that such lines intersect with experimental \(E_g\) at \(\alpha = 0.35\). To intersect with the experimentally-determined \(E_d\), however, \(\alpha\) would have to be equal to or larger than 0.51. One can qualitatively understand the underlying physics as follows: within a standard DFT such as the PBE, the \(d\) electrons have larger localization errors than the \(sp\) electrons do. Although these errors can be reduced by an inclusion of the HF exchange, there is no reason that the percentages should both be the same. As it turns out, when correction for the \(sp\) electrons is adequate, that for the \(d\) electrons is still not enough, leading to a higher \(E_d\). By contrast, the HHF approach with two parameters \(\alpha_c\) and \(\alpha_v\) retains the adequate degrees of freedom to minimize the localization errors throughout. As it turns out, although \(\alpha_c\) does not directly affect \(sp\) or \(d\) electrons in the outmost atomic shells, it affects the arrangement of energy levels inside the core, subsequently the effective core—valence interactions, and as such the energies of the valence electrons. In such a space-separated hybrid approach, \(\alpha_c\) affects more the states closer to the nucleus, while \(\alpha_v\) affects more the states that are spatially extended. They work together to produce adequate \(E_g\) and \(E_d\).

Table I summarizes the lattice parameters, \(c/a\) ratios, and volumes of PBE, standard HSE with \(\alpha = 0.25\), the HHF approach with \((\alpha_c, \alpha_v) = (0.75, 0.25)\), and experiment. As one might expect, our approach works similar to PBE and HSE: i.e., the lattice constants \(a\) and \(c\) are both within 2% error of experiment, the \(c/a\) ratio is slightly better while the volume is slightly too large. Thus, it should be suitable for other electronic structure calculations as well.
FIG. 3: (Upper panel) $E_g$ error and (lower panel) relative $E_g$ error of the HHF approach with $(\alpha_c, \alpha_v) = (0.75, 0.25)$ and standard HSE with $\alpha = 0.25$ for 12 3$d$ transition and post-transition metal binary oxides. Zero here means perfect agreement with experiment. Shown at the topmost of the figure in parentheses are the experimental band gaps (in eV) from Refs. 39–49. The HSE results are from Refs. 43, 50–53. The experimental values for MnO and NiO display a large scattering. Here, the average values of 3.9 and 4.0 eV are used, respectively (See Table S2 of the Supplemental Material [24]).

Next, we apply the HHF approach to the electronic structures of 11 additional 3$d$ transition and post-transition metal binary oxides. Rather than adjusting $(\alpha_c, \alpha_v)$ for each case, these parameters are fixed at the values of ZnO, namely, $(0.75, 0.25)$. Also for simplicity, in the following we only consider $E_g$. Figure 3 compares errors between the current approach and standard HSE (For more details, see Table S2 of the Supplemental Material [24]). These errors are calculated using available experimental data as the reference. The mean absolute error and relative error of HHF are 0.30 eV and 14.0%, respectively, while those from HSE are 0.72 eV and 33.1%. Clearly, there is a noticeable systematic improvement over HSE.
FIG. 4: Band structures of (a) MnO and (b) CuO. The HHF results with \((\alpha_c, \alpha_v) = (0.75, 0.25)\) are given in red while those of standard HSE are given in dotted black. VBM is the energy zero. The labeling of the Brillouin zone follows the convention in Ref. 17 for MnO and Ref. 55 for CuO.

It is instructive to analyze the trends in Fig. 3. For example, a similar performance between HHF and HSE is obtained for Ti. Going to V and Cr, the errors of HHF decrease when compared to HSE. The same is true for Mn and Fe. For the late and post transition-metals, the performance of HHF is even more remarkable. For CuO and ZnO (the two notorious cases of binary metal oxides), the absolute HHF errors are less than 0.1 eV, versus +1.4 and −1.0 eV of HSE, respectively. This trend is expected to hold for other post-transition metal \(d^0\) systems such as GaAs as its \(d\) orbitals are also fully occupied. In general, HHF performs consistently better than HSE. The only exception is CoO [54], for which HHF yields an error of +0.6 eV, which is a slightly larger than the HSE error of −0.4 eV. Another important observation is that hybrid functional PPs [18] exhibit a remarkable transferability, as evidenced in the results of V, Fe and Cu. For HSE, however, it is not the case as very different errors due to valency change appear unavoidably, e.g., −0.2 versus +1.4 eV for Cu\(_2\)O and CuO respectively.

One can qualitatively understand the above results. In traditional DFT approaches, discontinuity in the functional derivative of the exchange-correlation energy holds the key to the underestimation of \(E_g\) [56, 57]. The standard HSE is a semi empirical fix to such
a discontinuity, presumably, for $sp$ electrons. The HHF approach here builds in it another discontinuity that is between the core and valence electrons, which in effect accounts for the difference between localized $d$ and delocalized $sp$ states. The HHF result should approach that of HSE when the $d$ states are empty, as in the case of TiO$_2$ in Fig. 3. The same is expected for alkali-metal and alkali-earth-metal oxides.

The situation for partially-occupied $d$ states can be more complex due to (a) a strong oxygen $p$-metal $d$ orbital hybridization and (b) a crystal-symmetry-related splitting of the $d$ bands. $E_d$ is therefore not as well-defined as in the case of $d^0$. Despite the complexity, the parameters $(\alpha_c, \alpha_v) = (0.75, 0.25)$ produce nearly perfect $E_g$ for MnO, Fe$_2$O$_3$ and CuO, without any additional adjusting parameters. In contrast, the standard HSE does a much poorer job, as can been seen in Fig. 3 or Table S2 of the Supplemental Material [24]. Figure 4 shows the band structures of MnO and CuO. It is interesting to note that HHF and HSE produce very similar band dispersions, except $E_g$. Noticeably, HHF increases $E_g$ for MnO but decreases $E_g$ for CuO. This is an indication that, despite its simplicity, HHF has captured the essential physics of transition-metal oxides.

In summary, we develop a PP-based HHF approach within the framework of DFT for transition and post-transition metal oxides. The discontinuity between core and valence in terms of the use of Hartree-Fock exchange provides a compensation to the different localization errors between $sp$ and $d$ electrons. This leads to improved $E_g$ and $E_d$ over the standard hybrid functional approaches. We construct the PP-based HHF approach based on ZnO to improve its band gap and $d$-band position (a problem that has plagued scientists for decades). This work might offer a new prospect in terms of understanding the electron correlation phenomena such as magnetism and superconductivity in complex transition-metal oxides, as well as in band engineering for applications in electronics, photovoltaics, and catalysis.

H.T. thanks Dr. Jing Yang for helpful discussions. Work in China was supported by the Basic Science Center Project of NSFC (Grant Nos. 51788104), the Ministry of Science and Technology of China (Grant No. 2016YFA0301001), the National Natural Science Foundation of China (Grant Nos. 11674071, 11874089 and 11674188), the Beijing Advanced Innovation Center for Future Chip (ICFC), and the Beijing Institute of Technology Research Fund Program for Young Scholars. Work in the US (S.Z.) was supported by US DOE under Grant No. de-sc0002623. S.Z. had been actively engaged in the design and development of
the theory, participated in all the discussions and draft of the manuscript.

* Electronic address: yuancli@bit.edu.cn

[1] C. N. R. Rao and G. V. S. Rao, *Transition Metal Oxides: Crystal Chemistry, Phase Transition and Related Aspects*, NSRDS-NBS; 49. (Washington: U.S., 1974).

[2] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).

[3] Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).

[4] D. B. Strukov, G. S. Snider, D. R. Stewart, and R. S. Williams, Nature **453**, 80 (2008).

[5] H. H. Kung, *Transition Metal Oxides: Surface Chemistry and Catalysis* (Elsevier Science Publ., Amsterdam, 1989).

[6] J. Meyer, S. Hamwi, M. Kröger, W. Kowalsky, T. Riedl, and A. Kahn, Adv. Mater. **24**, 5408 (2012).

[7] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).

[8] R. O. Jones, Rev. Mod. Phys. **87**, 897 (2015).

[9] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).

[10] A. J. Cohen, P. Mori-Sánchez, and W. T. Yang, Science **321**, 792 (2008).

[11] P. Mori-Sánchez, A. J. Cohen, and W. T. Yang, Phys. Rev. Lett. **100**, 146401 (2008).

[12] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).

[13] V. K. Aliaksandr, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. **125**, 224106 (2006).

[14] J. E. Coulter, E. Manousakis, and A. Gali, Phys. Rev. B **88**, 041107(R) (2013).

[15] F. Vines, O. Lamiel-García, K. C. Ko, J. Y. Lee, and F. illas, J. Comput. Chem. **38**, 781 (2017).

[16] M. Fuchs, M. Bockstedte, E. Pehlke, and M. Scheffler, Phys. Rev. B **57**, 2134 (1998).

[17] H. Tan, Y. Li, S. Zhang, and W. Duan, Phys. Chem. Chem. Phys. **20**, 18844 (2018).

[18] J. Yang, L. Z. Tan, and A. M. Rappe, Phys. Rev. B **97**, 085130 (2018).

[19] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[20] J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).

[21] C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).

[22] P. Giannozzi et al., J. Phys.: Condens. Matter **21**, 395502 (2009).
[23] [OPIUM] [http://opium.sourceforge.net/]

[24] See the Supplemental Material.

[25] V. Blum et al., Comput. Phys. Commun. 180, 2175 (2009).

[26] S. H. Wei and A. Zunger, Phys. Rev. B 37, 8958 (1988).

[27] O. Madelung, *Semiconductors: data handbook* (Springer-Verlag, Berlin Heidelberg, 2004), 3rd ed.

[28] R. Powell, W. Spicer, and J. McMenamin, Phys. Rev. Lett. 27, 97 (1971).

[29] K. Ozawa, K. Sawada, Y. Shirotori, and K. Edamoto, J. Phys.: Condens. Matter 17, 1271 (2005).

[30] G. Zwicker and K. Jacobi, Solid State Commun. 54, 701 (1985).

[31] M. Ruckh, D. Schmid, and H. Schock, J. Appl. Phys. 76, 5945 (1994).

[32] C. Vesely, R. Hengehold, and D. Langer, Phys. Rev. B 5, 2296 (1972).

[33] C. Vesely and D. Langer, Phys. Rev. B 4, 451 (1971).

[34] L. Ley, R. Pollak, F. McFeely, S. P. Kowalczyk, and D. Shirley, Phys. Rev. B 9, 600 (1974).

[35] J. Trail and R. Needs, J. Chem. Phys. 122, 014112 (2005).

[36] W. Al-Saidi, E. Walter, and A. Rappe, Phys. Rev. B 77, 075112 (2008).

[37] Strictly speaking, this differs from the “consistent” hybrid functional calculations, mainly originated from the approximations used for generating the hybrid PPs. It includes the neglect of relativistic effect, the difference between screened and unscreened hybrid functionals. Nevertheless, our calculations show that such approximations just yield an energy difference of around 0.2 eV for either $E_g$ or $E_d$, hence not affecting the conclusion. Moreover, $\alpha = 0.375$ of Fig. 1(c) agrees well with $\alpha_c = \alpha_v = 0.35$ of Fig. 2(a) in the consideration of $E_g$. This is also true in the consideration of $E_d$, namely, $\alpha = 0.50$ of Fig. 1(d) versus $\alpha_c = \alpha_v = 0.51$ of Fig. 2(b). Such consistency again proves the validity.

[38] J. Wróbel, K. J. Kurzydłowski, K. Hummer, G. Kresse, and J. Piechota, Phys. Rev. B 80, 155124 (2009).

[39] D. Reyes-Coronado et al., Nanotechnology 19, 145605 (2008).

[40] S. Shin et al., Phys. Rev. B 41, 4993 (1990).

[41] N. Kenny, C. Kannewurf, and D. Whitmore, J. Phys. Chem. Solids 27, 1237 (1966).

[42] J. Zaanen, G. Sawatzky, and J. Allen, Phys. Rev. Lett. 55, 418 (1985).

[43] C. Rödl, F. Fuchs, J. Furthmüller, and F. Bechstedt, Phys. Rev. B 79, 235114 (2009).
[44] H. Jiang, Phys. Rev. B 97, 245132 (2018).
[45] H. Bowen, D. Adler, and B. Auker, J. Solid State Chem. 12, 355 (1975).
[46] B. Gilbert, C. Frandsen, E. Maxey, and D. Sherman, Phys. Rev. B 79, 035108 (2009).
[47] M. Gvishi and D. Tannhauser, J. Phys. Chem. Solids 33, 893 (1972).
[48] F. Koffyberg and F. Benko, J. Appl. Phys. 53, 1173 (1982).
[49] B. Meyer et al., Phys. Status Solidi B 249, 1487 (2012).
[50] M. Landmann, E. Rauls, and W. Schmidt, J. Phys.: Condens. Matter 24, 195503 (2012).
[51] F. Iori, M. Gatti, and A. Rubio, Phys. Rev. B 85, 115129 (2012).
[52] Z. D. Pozun and G. Henkelman, J. Chem. Phys. 134, 224706 (2011).
[53] M. Heinemann, B. Eifert, and C. Heiliger, Phys. Rev. B 87, 115111 (2013).
[54] It seems as if our method also performed worse than the HSE for the NiO. However, as can be
seen in Table S2 of the Supplemental Material [24], both two methods yield the $E_g$ within the
experimental range, and the appearance in Fig. 3 is the consequence of averaging experimental
results from different works.
[55] W. Setyawan and S. Curtarolo, Comput. Mater. Sci 49, 299 (2010).
[56] J. P. Perdew and M. Levy, Phys. Rev. Lett. 51, 1884 (1983).
[57] L. Sham and M. Schlüter, Phys. Rev. Lett. 51, 1888 (1983).