

Electronic structure and optical properties of antiferromagnetic 3d-oxides from a Wannier-localized optimally tuned screened range-separated hybrid functional

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We apply the recently developed nonempirical Wannier-localized, optimally tuned, screened range-separated hybrid (WOT-SRSH) functional to prototypical bulk antiferromagnetic insulators—MnO, NiO, hematite (Fe₂O₃), and chromia (Cr₂O₃). Comparison to calculations based on well-established functionals, namely PBE0 and HSE06, as well as to self-consistent quasiparticle GW, dynamic mean-field theory calculations, and experiment, shows that the WOT-SRSH functional provides a good quantitative description of fundamental band gaps, spin magnetic moments, and photoemission and optical absorption spectra. Our calculations establish WOT-SRSH as an effective framework for predictive calculations of electronic, magnetic, and optical properties of magnetic insulators, as well as establishing it as an attractive starting point for subsequent many-body calculations.

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I. INTRODUCTION

Transition-metal oxides (TMOs) have attracted significant interest as they often present unusual physical properties with diverse potential applications, including superconductivity, colossal magnetoresistance, ferroelectricity, and metal-insulator transitions [1–6]. However, their fundamental understanding is challenging because they simultaneously exhibit both localized and itinerant electronic behavior.

Density-functional theory (DFT) [7] is a workhorse method for describing the electronic structure of both molecules and solids. Standard DFT encounters well-known difficulties in TMOs, arising mainly from the self-interaction error associated with localized orbitals [8], the lack of the derivative discontinuity in standard approximate exchange-correlation expressions [9], and possible strong correlation effects [10]. To address these issues, extensions of DFT are commonly employed, ranging from the DFT + *U* method [11] to the more advanced and computationally demanding DFT + dynamical mean-field theory (DMFT) approach [12]. These approaches provide improved agreement with experimental photoemission spectra (PES) of antiferromagnetic (AFM) binary metal oxides, but achieve only semiquantitative agreement with experimental band-gap values and inverse photoemission spectroscopy (IPES) data [12].

Recently, a screened range-separated hybrid (SRSH) functional based on a Wannier-localization-based optimal-tuning (WOT) approach was proposed as a systematic method for obtaining quantitatively accurate band gaps entirely within DFT, for a wide range of semiconductors and insulators [13–16]. Within time-dependent DFT (TDDFT), the same approach has also been shown to predict optical spectra with high accuracy in a variety of closed-shell TMOs [15]. However, these methods have not been applied previously to open-shell solids.

In this work, we explore the application of the WOT-SRSH functional to TMOs in the antiferromagnetically ordered phase. Prototypical examples of such materials include the monoxides MnO and NiO, the structure of which consists of planes of alternating spin orthogonal to the [111] crystallographic direction (type-II AFM) [17]. These have long served as testbeds for theories of strongly correlated electron systems (see, e.g., Refs. [12,18–20]) and have also attracted interest due to their potential applications in antiferromagnetic spintronics [21,22]. A different prototypical system is hematite, Fe₂O₃, extensively studied and widely applied in diverse areas of physics and chemistry [23]. In particular, it is an established photoanode material [24]. Chromia, Cr₂O₃, has attracted considerable attention because of its unique combination of electronic, optical, and magnetic properties [25]. Specifically, the presence of a linear magnetoelectric effect has established Cr₂O₃ as a model material for antiferromagnetic spintronics, including exchange-bias devices and voltage-controlled magnetic switching [26,27].

Here, we compute band gaps, photoemission spectra, and optical absorption spectra for the aforementioned materials, and compare our results with those obtained from many-body perturbation theory, from DMFT, and from experiment.

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The article is organized as follows. In Sec. II, we briefly describe the WOT-SRSH method. In Sec. III, we present its application to key electronic and optical properties of the aforementioned AFM TMOs and compare results with those obtained from other computational methods and from experimental measurements. Finally, conclusions are given in Sec. IV.

II. METHODS

Our approach is based on the screened range-separated hybrid (SRSH) class of functionals [28], rigorously defined within the generalized KS (GKS) framework [29–32]. The SRSH approach mixes exact exchange and semilocal exchange, making use of different fractions in the short range (SR) and long range (LR). Specifically, it expresses the exchange-correlation (xc) energy as

$$E_{xc}^{SRSH}(\alpha, \gamma, \epsilon_{\infty}) = \alpha E_{xx}^{SR} + (1 - \alpha) E_{KSx}^{SR} + \frac{1}{\epsilon_{\infty}} E_{xx}^{LR} + \left(1 - \frac{1}{\epsilon_{\infty}}\right) E_{KSx}^{LR} + E_{KSc}, \quad (1)$$

where xx denotes exact (Fock) exchange, and SR and LR denote short-range and long-range exact exchange contributions, given by

$$E_{xx}^{SR} = -\frac{1}{2} \sum_{ij} \int d\mathbf{r} d\mathbf{r}' \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \frac{\text{erfc}(\gamma|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \times \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}'), \quad (2)$$

$$E_{xx}^{LR} = -\frac{1}{2} \sum_{ij} \int d\mathbf{r} d\mathbf{r}' \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \frac{\text{erf}(\gamma|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \times \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}'), \quad (3)$$

with KSx and KSc denoting semilocal KS exchange and correlation, respectively.

In the above, α , γ , and ϵ_{∞} are parameters to be determined. The latter is the scalar high-frequency dielectric constant and its inverse ϵ_{∞}^{-1} determines the fraction of LR exact exchange, which is a common ingredient in the construction of advanced dielectrically screened hybrid functionals, see, e.g., Refs. [28,33–39]. The parameter α determines the fraction of SR exact exchange, and γ is the range-separation parameter, the inverse of which determines an effective crossover distance between SR and LR contributions. We note that commonly used hybrid functionals can be easily obtained as special cases of Eq. (1). Assuming the Perdew-Burke-Ernzerhof (PBE) [40] functional is used for the KS contributions, When $\alpha = \epsilon_{\infty}^{-1} = 0.25$, the PBE0 functional [41] is recovered, and when $\epsilon_{\infty}^{-1} = 0$, $\alpha = 0.25$, and $\gamma = 0.20 \text{ \AA}^{-1}$, the Heyd-Scuseria-Ernzerhof (HSE06) [42] short-range hybrid functional is obtained.

In the optimally tuned (OT) SRSH approach, γ is chosen to satisfy the ionization potential (IP) theorem

$$E(N-1) - E(N) + \epsilon_{HO} = 0, \quad (4)$$

where ϵ_{HO} is the highest occupied KS eigenvalue, $E(N)$ is the ground-state energy of the N -electron system, and $E(N-1)$ is the energy of the system with one electron removed.

I. Calculate the ion-clamped orientationally-averaged dielectric constant, ϵ_{∞} . Repeat steps until $|\Delta\epsilon_{\infty}^{-1}| < 0.01$ convergence.

II. Using a supercell, generate maximally localized Wannier functions and select the one with the highest expectation energy.

III. For a given choice of α , tune γ in the same supercell to satisfy the ionization potential ansatz until $|\Delta I_{\gamma}| < 0.02 \text{ eV}$.

IV. Calculate properties of interest in the primitive unit-cell using the optimal parameters.

FIG. 1. Flow chart of the WOT-SRSH procedure [13]. Steps I to III of this scheme are repeated iteratively: ϵ_{∞} in step I is initially calculated using HSE06, and after performing steps II and III, ϵ_{∞} is calculated again using the optimally tuned parameters found in step III. These steps are repeated until convergence of ϵ_{∞} and γ . After parameter convergence, step IV is performed once with the optimized parameters.

The OT-(S)RSH method has been proven to be successful for determining fundamental gaps in molecules [30,43–50] and molecular solids [28,33,51–56]. However, in covalent/ionic solids, it cannot be applied as is, because in the bulk limit, the IP theorem of Eq. (4) is trivially satisfied for any SRSH parameters [57–60]. This is because in this limit the IP theorem reduces to Janak's theorem [61], which is obeyed by any functional, exact or approximate. Instead, an IP ansatz [62,63], which relies on the constrained removal of an electron in a state that corresponds to a maximally localized Wannier function, is used to select the range-separation parameter γ , a procedure known as Wannier-localization-based optimal tuning of an SRSH functional (WOT-SRSH). This ansatz is expressed as [13]

$$\Delta I^{\gamma} = E_{\text{constr}}^{\gamma}[\phi](N-1) - E^{\gamma}(N) + \langle \phi | \hat{H}_{\text{SRSH}}^{\gamma} | \phi \rangle = 0. \quad (5)$$

Here, $E_{\text{constr}}^{\gamma}[\phi](N-1)$ is the total energy of the $(N-1)$ -electron system (including an image charge correction [64]), under the constraint that the state corresponding to the Wannier function is not occupied. ϕ is the Wannier function for which the expectation energy with respect to the SRSH Hamiltonian of the N -electron system, $\langle \phi | \hat{H}_{\text{SRSH}}^{\gamma} | \phi \rangle$, is the largest, although the results are generally insensitive to the precise Wannier-function choice [15].

The main steps involved in a practical WOT-SRSH calculation are summarized as a flow chart in Fig. 1, which emphasizes the self-consistent nature of the procedure for parameter determination. Further methodological details, including convergence tests, can be found in Refs. [13,15]. We note, however, three issues that are directly relevant to this work.

First, typically it is sufficient to calculate the Wannier functions from the eigenstates obtained from a PBE calculation, as done in some of our prior work [13–16], because the (G)KS

bands obtained from PBE and from a hybrid functional are qualitatively similar as far as the orbital character is concerned. Here, we find that for, e.g., hematite, a significant band reordering is obtained with a hybrid functional compared to PBE, as previously observed, e.g., in copper phthalocyanine [65,66]. We therefore employ the HSE06 functional for constructing the Wannier functions throughout.

Second, to date, the WOT-SRSH approach has only been applied to closed-shell systems. For the open-shell systems studied here, we construct the Wannier function from the generalized KS orbitals of a given spin channel and remove the localized electron from this spin channel. Here we study AFM systems, where the two spin channels are degenerate in energy, and the localized electron can be removed from either one. For ferro- or ferrimagnetic systems, the electron is typically removed from the majority spin channel—see Refs. [66–68] for analogous examples in OT-SRSH of molecules.

Third, once the optimal parameters are determined, the cost of an SRSH calculation is the same as the cost of other hybrid functionals. The WOT procedure requires some extra cost because of the need for a supercell calculation and because of the need to compute the dielectric constant. This is still significantly less expensive than a GW calculation, which requires computation of the full dielectric response function.

All calculations reported below have been performed using a modified version of the Vienna *ab initio* simulation package (VASP) [69,70]. All calculations employ experimental lattice constants [71,72] and an AFM-II magnetic order along the [111] direction for MnO and NiO. For hematite [73] and chromia [74], we use the crystallographic structure with the equilibrium AFM magnetic configurations, i.e., spins alternating along the [0001] direction. Note that the AFM ground states of Fe_2O_3 ($\uparrow, \downarrow, \downarrow, \uparrow$) and Cr_2O_3 ($\downarrow, \uparrow, \downarrow, \uparrow$) differ in to the ordering of Fe and Cr spins along the z axis of the rhombohedral unit cell. Complete computational details can be found in Sec. S.I of the Supplemental Material (SM) [75].

III. RESULTS

A. MnO and NiO

We start by employing Eq. (5) to optimally tune the exchange-correlation functional E_{xc}^{SRSH} in Eq. (1), i.e., to select the optimal parameters $(\alpha, \varepsilon_\infty, \gamma)$. As a starting point, we use the inverse of the orientationally averaged clamped-ion dielectric constant ε_∞^{-1} obtained from HSE06 calculations: $\varepsilon_\infty^{-1} = 0.294$ for MnO and $\varepsilon_\infty^{-1} = 0.286$ for NiO. We then evaluate the deviation from the IP ansatz of Eq. (5), as a function of the range separation parameter γ , for different values of the parameter α . Note that ε_∞ is recalculated with WOT-SRSH after the initial determination of γ , followed by retuning of γ and so on until convergence. Following these steps, as shown in Fig. 1, convergence of the dielectric constant ε_∞ is achieved after two self-consistent iterations. The resulting dependence of ΔI^γ of Eq. (5) on γ , for various α values in a range encompassing values for which the condition $\Delta I^\gamma = 0$ can be fulfilled, is shown in Fig. 2.

Several trends can be observed in Fig. 2. First, not every choice of α necessarily results in a value of γ that satisfies the

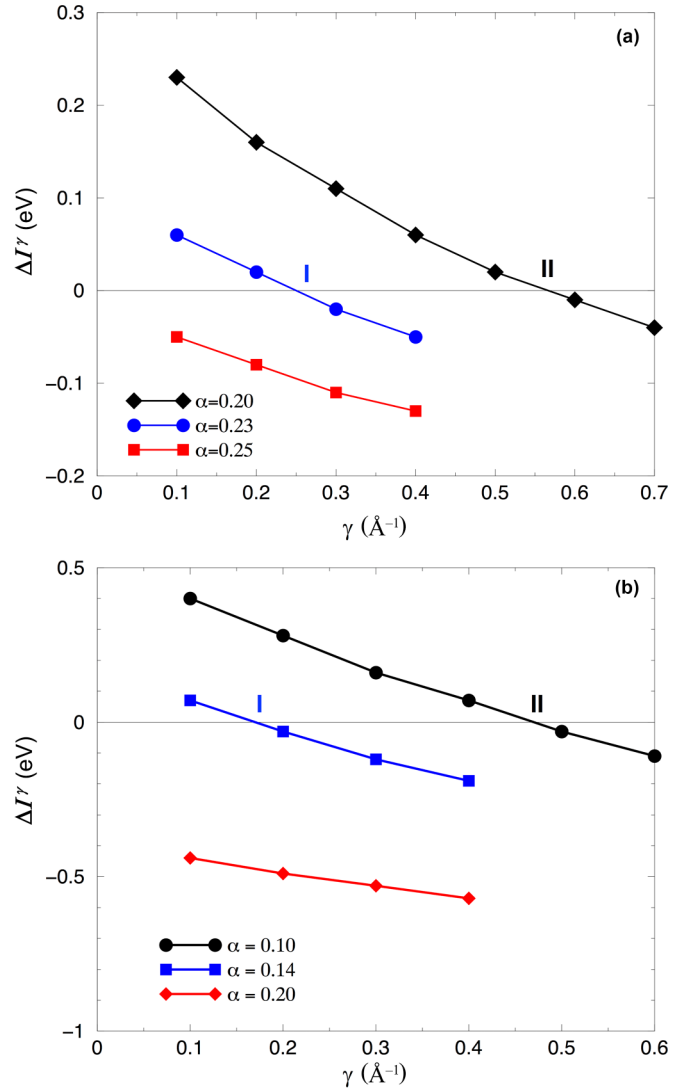


FIG. 2. Deviation from the IP ansatz ΔI^γ of Eq. (5), for different choices of α , as a function of the range-separation parameter γ for (a) MnO and (b) NiO, both in the AFM-II configuration. Curves denoted by I and II are those for which an optimal value for γ can be found.

IP ansatz (see, for example, the red curves in the figure). At the same time, and as discussed in Refs. [13,76], there exist multiple (α, γ) pairs that satisfy Eq. (5) (see, for example, the black and blue curves in the figure). We find, however (see below for details), that use of different optimal (α, γ) pairs changes the resulting band gaps by less than 0.1 eV and the resulting magnetic moments by less than $0.05 \mu_B$. Optical spectra and exchange interactions also remain almost unaffected (see Sec. S.II of the SM [75]). Given the weak sensitivity of the results to the choice of optimal parameters, in the following we use the WOT-SRSH solutions corresponding to the smaller value of γ in Fig. 2, namely, we use the blue curves denoted by 'I'. This finally leads to optimal parameters of $(\alpha = 0.23, \varepsilon_\infty^{-1} = 0.29, \gamma = 0.25 \text{ \AA}^{-1})$ for MnO and $(\alpha = 0.14, \varepsilon_\infty^{-1} = 0.26, \gamma = 0.17 \text{ \AA}^{-1})$ for NiO.

In Table I, we summarize WOT-SRSH results for the fundamental band gap and atomic magnetic moment, compared to those obtained using standard hybrid functionals (HSE06,

TABLE I. Fundamental band gap E_g of MnO and NiO, along with Mn or Ni magnetic moment M , calculated with PBE + U , HSE06, PBE0, WOT-SRSH, and QSGW, compared to experimental data.

	MnO		NiO	
	E_g (eV)	M (μ_B)	E_g (eV)	M (μ_B)
PBE + U^a	2.19	4.68	3.16	1.68
HSE06	2.93	4.53	4.56	1.68
PBE0 ^b	3.80	4.52	5.29	1.69
WOT-SRSH	3.63	4.53	3.58	1.58
QSGW ^c	4.02	4.58	3.89	1.67
Experiment ^d	4.1, 3.9 $\pm$ 0.4, 3.9	4.58	4.0, 4.3, 4.3	1.64, 1.90

^aCoulomb- U and exchange- J values were taken from Ref. [77] and are 6.9 (6.3) eV and 0.86 (1.0) eV, respectively, for MnO (NiO).

^bTaken from Ref. [78] for MnO and from Ref. [19] for NiO.

^cTaken from Ref. [20].

^dValues, from left to right, were taken from Refs. [79,80,81], and Ref. [82] for MnO and from Refs. [79,81,83,84], and Ref. [82] for NiO.

PBE0), as well as the computationally less expensive PBE + U approach [19,78,85], and the computationally more expensive quasiparticle self-consistent GW with vertex corrections (QSGW) approach [20], all at the experimental lattice constant, and to available experimental data. We omit PBE values as they are well known to be inaccurate for magnetic systems, but include them in Sec. S.III of the SM [75] for completeness. In the absence of further information, our discussion below is based on the as-reported experimental values. We note, however, that these were obtained from the combination of x-ray absorption and emission or from the combination of photoemission and inverse photoemission. The extraction of insulator band gaps from either approach is well known to be affected by several uncertainties, amounting to at least several tenths of an eV—see, e.g., Refs. [86,87]. Furthermore, zero-point renormalization effects lower the experimental band gap with respect to the purely electronic one, in this case likely by ~ 0.2 eV [15].

Several conclusions can be drawn immediately from Table I. First, we see that PBE + U substantially underestimates the experimental fundamental band gaps for both MnO and NiO. The PBE0 functional reproduces the MnO band gap quite well, but significantly overestimates the band gap of NiO, suggesting fortuitous agreement for MnO. The HSE06 band gaps are smaller than those obtained with PBE0, due to the absence of long-range Fock exchange in HSE06. This brings the NiO band gap closer to experiment but pushes the MnO band gap away from experiment, again indicating fortuitous agreement. Thus, neither PBE0 nor HSE06 can be relied on for a consistently accurate description of the band gaps of both compounds. In contrast, recent sophisticated QSGW calculations [20], also reported in Table I, yield band gaps in good agreement with experimental data for both systems.

WOT-SRSH band gaps are much improved with respect to the above-discussed conventional DFT values, and the agreement with experiment is similar for both materials. The WOT-SRSH gaps are smaller than those obtained from QSGW, by ~ 0.4 eV for MnO and ~ 0.3 eV for NiO, and are

less accurate than QSGW in both cases. It remains unknown at this point whether this reflects an actual advantage of QSGW calculations, or is simply a by product of the general tendency of self-consistent GW for slight overestimation of band gaps [88–91]. We do note, however, that the QSGW calculations are somewhat more accurate also with respect to the magnetic moments, especially for NiO where the WOT-SRSH result is smaller by $\sim 0.1 \mu_B$, not only with respect to GW , but also with respect to the other DFT methods [92]. Likewise, WOT-SRSH produces converged inverse dielectric constant ϵ_∞^{-1} values of 0.29 and 0.26 for MnO and NiO, respectively, which overestimate QSGW (0.24 and 0.16) and experimental values (0.20 [93] and 0.18 [94]). In summary, then, WOT-SRSH results appear to offer a consistent improvement of standard DFT and are quantitatively close to benchmark calculations and to experiment.

Beyond the band gap, a comparison of the full density of states (DOS) to experimental PES data is of great interest. Although WOT-SRSH (and OT-RSH in general) is constructed to predict accurate band gaps, in practice such calculations have often been found to agree well with GW calculations for quasiparticle excitation energies away from the band edge [14,16,33,66,76,88], an issue that has been rationalized in terms of ensemble DFT [63]. A comparison between WOT-SRSH, HSE06, QSGW [20], and DMFT [12] calculated DOS curves, compared with PES and IPES data [80,83], is presented in Figs. 3(a) and 3(b) for MnO and NiO, respectively. To facilitate comparison between theory and experiment, the DFT-calculated DOS curves are broadened by a Gaussian with a 0.3 eV half-width.

For both MnO and NiO, the valence DOS obtained from WOT-SRSH is almost identical to the one obtained from HSE06. The WOT-SRSH conduction DOS, on the other hand, is slightly blueshifted (redshifted) compared to that of HSE06 for MnO (NiO), consistent with the band-gap difference. Additionally, for both materials, WOT-SRSH results agree reasonably well with those obtained from QSGW and DMFT. Finally, the WOT-SRSH DOS exhibits a similar level of agreement as QSGW and DMFT when compared with experimental (I)PES data. Agreement with experimental data is generally better in the valence band than in the conduction band.

As shown in Fig. 3(c), the WOT-SRSH band structure of NiO shows good overall agreement with QSGW, especially closer to the valence-band maximum. This result is in line with previous comparisons between SRSH- and GW -based band structures [14,88,96]. Both methods agree semiquantitatively with angle-resolved photoemission spectra (ARPES) measurements [95]. Additional comparison of MnO and NiO band structures obtained with the different computational approaches is given in Sec. S.IV of the the SM [75].

Next, we turn our attention to optical absorption spectra (i.e., the imaginary part of the dielectric function, ϵ_2), calculated using linear-response time-dependent DFT (TDDFT) by solving the Casida equation [97] within the Tamm-Dancoff approximation [98,99]. Comparing theory and experiment based on optical spectra is typically considered more reliable relative to comparison of electronic band gaps, because the latter are harder to measure and typically exhibit large

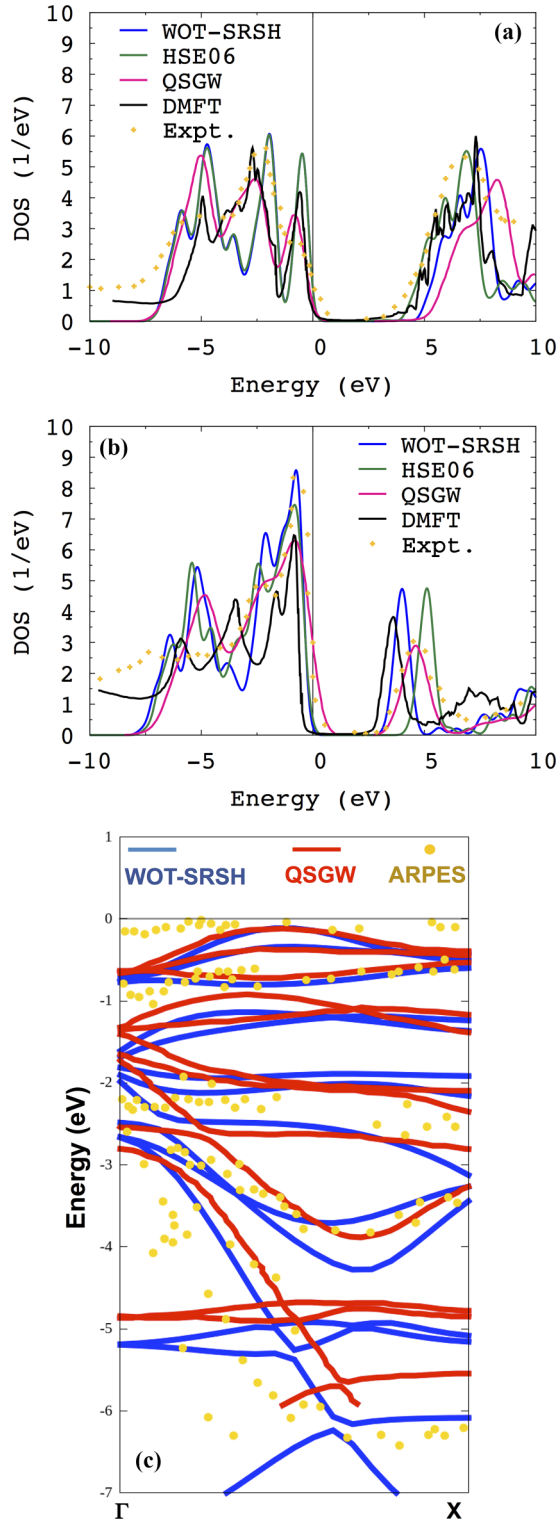


FIG. 3. Density of states (DOS) curves for (a) MnO and (b) NiO, calculated using WOT-SRSH and HSE06, compared to QSGW [20], DMFT [12], and experimental PES/IPES data (Ref. [80] for MnO, Ref. [83] for NiO). (c) Comparison of WOT-SRSH and QSGW computed band structures with experimental angle-resolved PES (ARPES, shown in dots) data [95], presented upon alignment of the valence-band maximum.

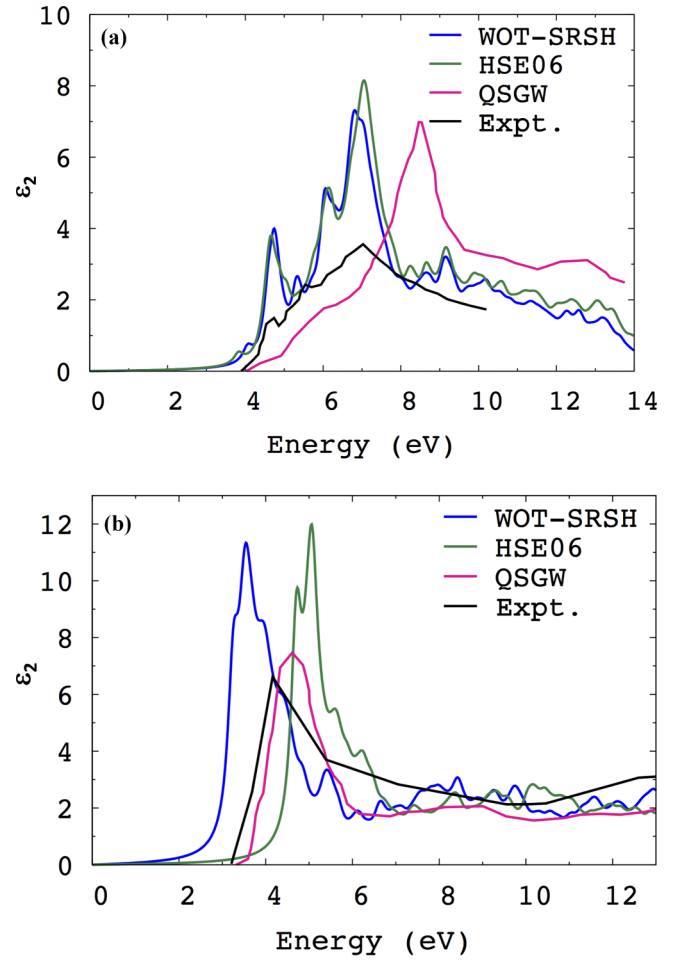


FIG. 4. Imaginary part of the dielectric function, as calculated using WOT-SRSH (this work) and BSE@QSGW (Ref. [20]), compared with experimental data (Ref. [101] for MnO and Ref. [102] for NiO) for (a) MnO, (b) NiO.

experimental uncertainties [81,100]. Furthermore, optical absorption spectra can be calculated directly by using the WOT-SRSH parameters in the hybrid TDDFT kernel, and have been shown to be highly accurate when compared with the single-shot *GW* plus Bethe-Salpeter equation (BSE) approach for closed-shell metal oxides [15].

In Fig. 4(a), we present TDDFT optical absorption spectra of MnO obtained with the WOT-SRSH and HSE06 functionals (this work), compared with the ones obtained from QSGW plus BSE (denoted BSE@QSGW, from Ref. [20]) and experimental measurements [101]. The absorption spectra predicted by WOT-SRSH and HSE06 are overall very similar and are in good agreement with experimental peak positions. Specifically, the principal experimental peak at ≈ 7 eV is well reproduced by WOT-SRSH, while HSE06 yields a slightly blueshifted value. In contrast, BSE@QSGW places the principal peak at ≈ 8 eV, noticeably blueshifted relative to both WOT-SRSH and experiment. An additional intermediate structure appears between 4 and 7 eV in the

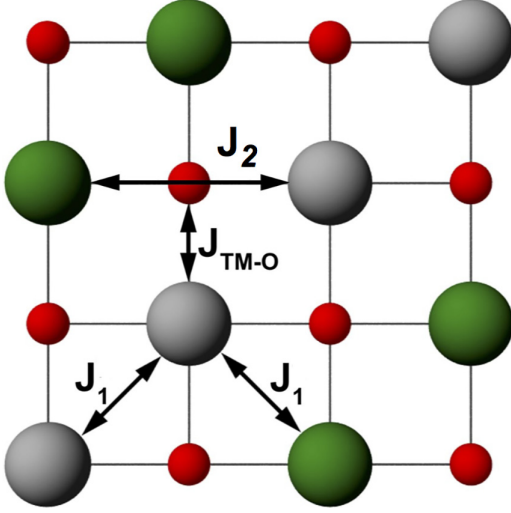


FIG. 5. Exchange interactions in the (100) plane of the rock-salt structure of a TMO. The green and grey sites indicate the up and down spins of the TM, and the red sites indicate oxygen atoms. Coupling to the oxygen atoms was neglected in the calculations and is shown for completeness.

calculated spectra, without a clear experimental counterpart, possibly due to spectral broadening in the measurements. Vibrational effects, present in experiment but absent from calculations, may also affect this.

The optical spectra of NiO calculated with the WOT-SRSH and HSE06 functionals are shown in Fig. 4(b), compared to BSE@QSGW results [20] and experimental data [102]. The principal peak in the WOT-SRSH spectrum appears at ≈ 3.5 eV, below the experimental peak at ≈ 4.1 eV. BSE@QSGW places this feature at ≈ 4.6 eV, while HSE06 shifts it further to ≈ 5.1 eV. Overall, WOT-SRSH yields an optical spectrum in closer agreement with experiment compared to HSE06 and a similar level of accuracy compared to BSE@QSGW, in absolute value.

Finally, we turn to the analysis of magnetic exchange parameters. These are typically described in terms of the Heisenberg model $H = -\sum_{i>j} J_{ij} s_i s_j$ [103], where the parameters J_{ij} represent the interatomic exchange interactions between spins s_i and s_j at sites i and j . These parameters can be obtained by evaluating the total energies of a set of distinct magnetic configurations (all with the same previously determined optimal parameters, to ensure consistency). Here, we considered three magnetic configurations: ferromagnetic (FM) order, antiferromagnetic order along [001] (AF-I), and antiferromagnetic order along [111] (AF-II). We then used these to extract nearest-neighbor J_1 , and next-nearest-neighbor J_2 exchange interactions per pair [77], using the relations

$$\begin{aligned} J_1 &= \frac{1}{16} (E_{\text{AFI}} - E_{\text{FM}}), \\ J_2 &= \frac{1}{48} (4E_{\text{AFII}} - E_{\text{FM}} - 3E_{\text{AFI}}), \end{aligned} \quad (6)$$

where E_{FM} , E_{AFI} , and E_{AFII} are the total energies of the corresponding magnetic configurations. These interactions are illustrated schematically in Fig. 5, where possible coupling to the oxygen atoms, not considered explicitly here, is shown

for completeness. Computed values for J_1 and J_2 are compared to experimentally deduced values in Table II. For MnO, PBE + U yields an incorrect ordering of J_1 and J_2 , whereas both HSE06 and WOT-SRSH recover the correct order but overestimate their magnitudes. In the case of NiO, the experimental sign and magnitude of J_1 remain uncertain. HSE06 produces values consistent with PBE + U , while WOT-SRSH slightly overestimates J_1 by about 0.4 meV. For J_2 , both PBE + U and HSE06 yield results close to experiment, whereas WOT-SRSH predicts a somewhat larger magnitude.

We note that in the conventional Heisenberg model for antiferromagnetic oxides, oxygen atoms are not considered explicitly, but rather are considered to mediate the magnetic interactions through superexchange or double exchange [6]. In the calculated FM state, however, magnetic moments of approximately $0.2\text{--}0.3 \mu_B$ are induced on the oxygen atoms due to O- p -TM- d hybridization, as shown in Table II. As a consequence, the exchange interaction $J_{\text{TM-O}}$, illustrated in Fig. 5, can contribute directly to the total energy of the FM configuration, E_{FM} . As demonstrated in Ref. [77], inclusion of $J_{\text{TM-O}}$ leads to a renormalization of the exchange interactions J_1 and J_2 , which can improve agreement with the experimental data. For simplicity and for facilitating the comparison to prior work, this was not considered explicitly here.

B. Fe₂O₃ and Cr₂O₃

We now consider the iron oxide α -Fe₂O₃, known as hematite. Hematite crystallizes in a centrosymmetric trigonal corundum structure [108] with a primitive unit cell containing two formula units. Below the Morin transition temperature ($T_M \approx 260$ K), the magnetic moments of the Fe ions align collinearly along the trigonal c axis, forming an antiferromagnetic (AFM) configuration [109]. Above T_M and up to the Néel temperature $T_N \approx 950$ K, the spins reorient into the basal plane and develop a small canting, giving rise to weak ferromagnetism [110]. This canting originates from spin-orbit coupling-induced Dzyaloshinskii-Moriya (DM) interactions [111]. We also note that hematite has recently been identified as an altermagnet [112], namely, a compensated collinear magnet in which time-reversal symmetry is broken in momentum space, resulting in spin-split electronic states and the absence of Kramers degeneracy. In the present work, spin-orbit coupling and noncollinearity are neglected, and the low-temperature collinear AFM phase is adopted for all calculations.

As in the previous section, we tuned the parameters of $E_{\text{xc}}^{\text{SRSH}}(\alpha, \gamma, \varepsilon_\infty)$ [Eq. (1)] for the antiferromagnetic α -Fe₂O₃ using Eq. (5). Starting from $\varepsilon_\infty^{-1} = 0.21$ obtained with HSE06, we evaluate ΔI^ν using a $2 \times 2 \times 1$ supercell, as a function of the range-separation parameter γ , for various values of α . In Fig. 6(a) we show the deviation from the IP condition, ΔI^ν , for different values of α . As for MnO and NiO, several (α, γ) pairs satisfy Eq. (5), but the resulting band gaps and magnetic moments vary by less than 0.1 eV and $0.05 \mu_B$, respectively, indicating the robustness of the approach. In the following, we adopt the WOT-SRSH solutions with the smaller γ values. Two self-consistent iterations (see Fig. 1) are sufficient to achieve a converged value of $\varepsilon_\infty^{-1} = 0.19$. This value is only slightly lower than the HSE06 value (0.21)

TABLE II. Exchange interactions J_1 and J_2 for MnO and NiO, calculated with HSE06 and WOT-SRSH hybrid functionals, compared with PBE + U and experimental data. The oxygen atom magnetic moment M_O , calculated in the FM configuration, is also provided.

	MnO			NiO		
	J_1 (meV)	J_2 (meV)	M_O (μ_B)	J_1 (meV)	J_2 (meV)	M_O (μ_B)
PBE + U^a	-2.80	-1.40	0.28	1.10	-11.90	0.30
HSE06	-3.33	-3.68	0.20	1.10	-10.75	0.20
WOT-SRSH	-3.47	-3.86	0.23	1.53	-15.71	0.28
Experiment ^b	-2.4, -2.7	-2.8, -2.95		0.7, -0.7	-9.5, -8.65	

^aFrom Ref. [77]

^bValues, from left to right, were taken from Refs. [104–107], and Ref. [107].

and marginally higher than experimental estimates (0.13–0.18 [113–115]). We then find that the final WOT-SRSH parameters for hematite are ($\alpha = 0.22$, $\varepsilon_\infty^{-1} = 0.19$, $\gamma = 0.30 \text{ \AA}^{-1}$).

WOT-SRSH results for the band gap and Fe magnetic moment in the AFM α -Fe₂O₃ are given in Table III, where they

are compared to results from other computational methods. Both WOT-SRSH and HSE06 predict Fe magnetic moments near experimental values [116,117], in good quantitative agreement with recent PBE + U calculations [118]. However, they predict a larger band gap compared to experiment. Recent PBE0 calculations [119] reported a strongly overestimated band gap of 4.30 eV, obtained with the effective $\alpha = \varepsilon_\infty^{-1} = 0.25$ of the default PBE0 parameters. Reducing α to 0.14

TABLE III. Fundamental band gap E_g and magnetic moment of Fe or Cr atoms M , calculated with PBE + U , PBE0, PBE0 with a modified α value of 0.14, HSE06, and WOT-SRSH, in comparison with experimental data. For Fe₂O₃, PBE + U calculations [118] employ Coulomb- U and exchange- J values of 5.5 eV and 0.5 eV, respectively. For Cr₂O₃, GGA + U calculations employ $U=5$ eV and $J=1$ eV [121] and LSDA + U calculations use $U=4$ eV and $J=0.58$ eV [122].

Method	Fe ₂ O ₃	
	E_g (eV)	M (μ_B)
PBE + U^a	2.19	4.01
PBE0 ^b	4.30	—
PBE0 ($\alpha = 0.14$) ^c	2.70	—
HSE06	3.35	4.16
WOT-SRSH	3.22	4.11
Experiment ^d	2.6, 2.2	4.2, 4.1
Method	Cr ₂ O ₃	
	E_g (eV)	M (μ_B)
GGA + U^e	2.6	3.01
LSDA + U^f	2.83	2.89
HSE06 ($\alpha = 0.17$) ^g	3.4	2.85
HSE06	4.21	2.87
WOT-SRSH	3.56	2.83
Experiment ^h	3.4	2.48, 2.76

^aValue is taken from Ref. [118].

^bValue is taken from Ref. [119].

^cValue is taken from Ref. [119].

^dValues, from left to right, were taken from Refs. [81,120,117], and Ref. [116].

^eValue is taken from Ref. [121].

^fValue is taken from Ref. [122].

^gValue is taken from Ref. [123].

^hValues, from left to right, were taken from Refs. [124,125], and Ref. [126].

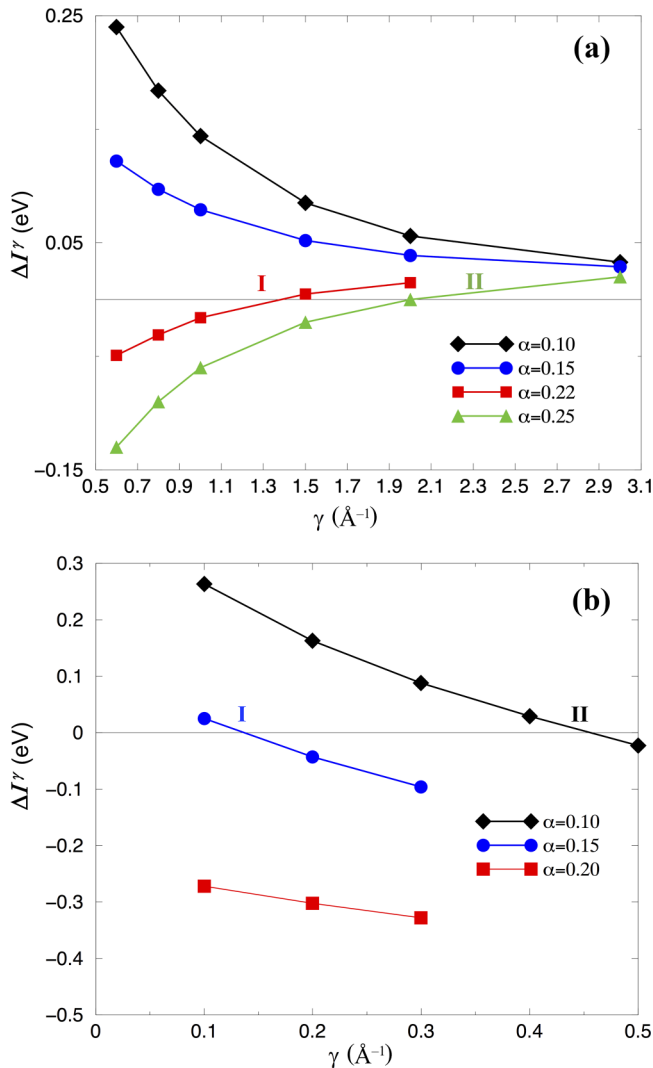


FIG. 6. Deviation from the IP condition $\Delta I'$ for the SRSH functional, as a function of the range separation parameter γ , shown for different values of α for AFM (a) Fe₂O₃, with $\varepsilon_\infty^{-1} = 0.19$, (b) Cr₂O₃, with $\varepsilon_\infty^{-1} = 0.24$.

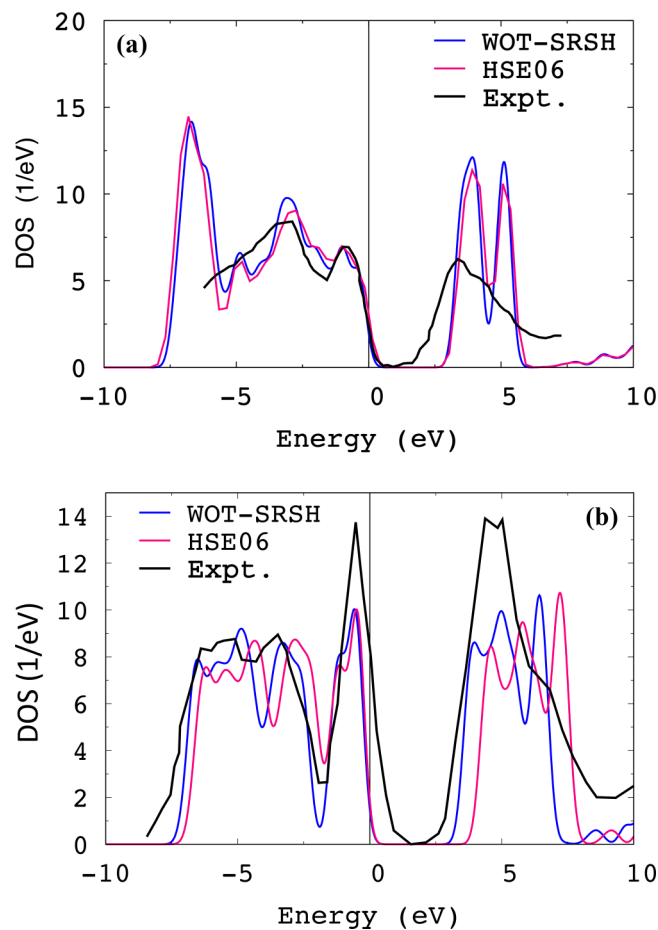


FIG. 7. Computed DOS, based on HSE06 and on WOT-SRSH, compared with experimental PES and IPES measurements [81,128] for (a) Fe_2O_3 and (b) Cr_2O_3 .

decreases the gap to 2.70 eV, which is more in line with experimental observations [81,120].

Figure 7(a) presents a comparison of the WOT-SRSH and HSE06 calculated densities of states with experimental PES and IPES spectra for Fe_2O_3 [81]. The topmost peaks in the valence band are well reproduced by both functionals, showing good agreement with the experimental PES. In the conduction region, the WOT-SRSH and HSE06 DOS exhibit a blueshift relative to the experimental IPES, consistent with the overestimation of the band gap discussed above.

Figure 8(a) shows the TDDFT-calculated optical spectra of Fe_2O_3 obtained with the WOT-SRSH and HSE06 functionals, compared with experimental data [127]. The onsets of the calculated spectra, appearing near 2 eV, are consistent with experiment. The principal experimental peak at approximately 3 eV is well reproduced by WOT-SRSH, while HSE06 places it at a slightly higher energy. Both functionals also capture additional structure between 4.5 and 6 eV, possibly corresponding to the experimental feature observed between 4 and 5 eV. Interestingly, the predicted position of the principal optical absorption peak agrees very well with experiment despite the overestimate of the band gap. This may reflect cancellation of errors, but may also reflect difficulties in the

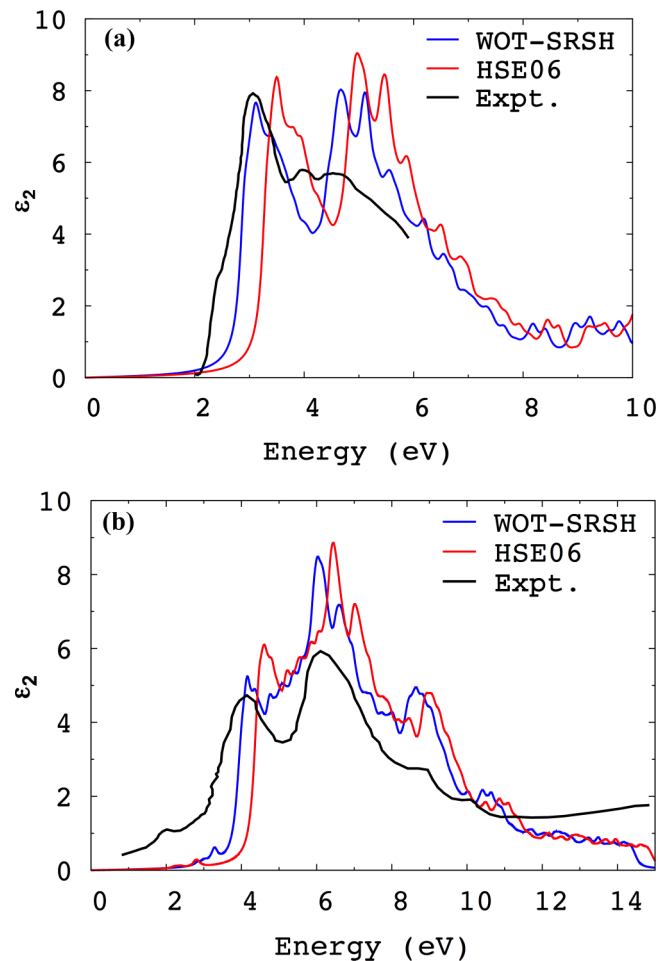


FIG. 8. HSE06 and WOT-SRSH computed imaginary part of the dielectric function, compared with corresponding experimental measurements [127,129] for (a) Fe_2O_3 and (b) Cr_2O_3 .

experimental determination of accurate fundamental gaps for large gap insulators [15].

Next, we consider the corundum-type $\alpha\text{-Cr}_2\text{O}_3$ (chromia). We tuned the parameters of $E_{xc}^{\text{SRSH}}(\alpha, \gamma, \epsilon_\infty)$ [Eq. (1)] for the antiferromagnetic $\alpha\text{-Cr}_2\text{O}_3$ phase using Eq. (5). Starting from $\epsilon_\infty^{-1} = 0.26$ obtained with HSE06, we evaluated ΔI^γ using a $2 \times 2 \times 1$ supercell, as a function of the range-separation parameter γ , for various values of α . In Fig. 6(b) we show the deviation from the IP condition ΔI^γ for different values of α . As above, various (α, γ) pairs satisfy Eq. (5) and we adopt the WOT-SRSH solutions with the smaller γ values. Two self-consistent iterations (see Fig. 1) are sufficient to achieve a converged value of $\epsilon_\infty^{-1} = 0.24$. We then find that the final WOT-SRSH parameters for chromia are $(\alpha = 0.15, \epsilon_\infty^{-1} = 0.24, \gamma = 0.14 \text{ \AA}^{-1})$.

WOT-SRSH results for the band gap and Cr magnetic moment for the AFM Cr_2O_3 are given in Table III, where they are compared to results from other computational methods. Both WOT-SRSH and HSE06 predict Cr magnetic moments near experimental values [125,126]. Recent DFT + U calculations [121,122] yield a Cr magnetic moments in reasonable agreement with hybrid functional results, but underestimate the band gap relative to experiment, whereas HSE06

overestimates it. Empirical tuning of the fraction of short-range exact exchange in HSE06 [123], which reduces α to 0.17, brings the calculated band gap in agreement with experiment, obviously in a nonpredictive manner. The WOT-SRSH calculations, using the optimized set of parameters, predict nonempirically a band gap that is in good quantitative agreement with experiment.

In Fig. 7(b) we show a comparison of the WOT-SRSH and HSE06 calculated DOS with experimental PES and IPES spectra for Cr_2O_3 [128]. The peaks in the valence band are reasonably well reproduced by both functionals, showing good agreement with the experimental PES, but still the agreement of WOT-SRSH with experiment is somewhat better. In the conduction region, the WOT-SRSH DOS agrees with experimental IPES, while the HSE06 DOS exhibits a blueshift relative to the experimental IPES, consistent with the overestimation of the band gap discussed above.

Figure 8(b) shows the TDDFT-calculated optical spectra of Cr_2O_3 , obtained with the WOT-SRSH and HSE06 functionals, compared with experimental data [129]. The onset of the calculated spectrum, as well as the principal experimental peak at approximately 4 eV, are well reproduced by WOT-SRSH, while HSE06 places the principal peak, as well as the subsequent peak around 6 eV, at somewhat higher energies.

IV. CONCLUSIONS

In summary, we have assessed the applicability of the WOT-SRSH method to selected antiferromagnetic insulators. For MnO and NiO, our results demonstrate that WOT-SRSH provides a consistent framework for describing the correlated electronic, magnetic, and optical properties of these materials. The material-specific WOT-SRSH functional yields more accurate band-gap predictions than both PBE + U and the global HSE06 hybrid functional. Moreover, WOT-SRSH results are in reasonable agreement with recent quasiparticle

GW calculations [20], at a substantially lower computational cost.

We further tested the applicability of the WOT-SRSH functional to Fe_2O_3 and to Cr_2O_3 in the compensated collinear configurations. Our results demonstrate that WOT-SRSH accurately captures the electronic and magnetic properties of hematite and chromia. Furthermore, the TDDFT-calculated optical spectra obtained with WOT-SRSH closely match experiment, indicating that this approach can reliably predict optical properties in other magnetic materials.

Taken together, the above results expand the reach of the WOT-SRSH method from nonmagnetic materials to gapped magnetic insulators.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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- [1] J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963).
 - [2] J. Zaanen, G. Sawatzky, and J. Allen, Band gaps and electronic structure of transition-metal compounds, *Phys. Rev. Lett.* **55**, 418 (1985).
 - [3] M. Imada, A. Fujimori, and Y. Tokura, Metal-insulator transitions, *Rev. Mod. Phys.* **70**, 1039 (1998).
 - [4] V. A. Gubanov, A. I. Liechtenstein, and A. V. Postnikov, *Magnetism and the Electronic Structure of Crystals* (Springer Science & Business Media, Berlin, Heidelberg, 2012), Vol. 98.
 - [5] S. Maekawa, T. Tohyama, S. E. Barnes, S. Ishihara, W. Koshibae, and G. Khaliullin, *Physics of Transition Metal Oxides* (Springer, Berlin, Heidelberg, 2013), Vol. 144.
 - [6] D. I. Khomskii, *Transition Metal Compounds* (Cambridge University Press, Cambridge, 2014).
 - [7] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
 - [8] J. P. Perdew and A. Zunger, Self-interaction correction to density-functional approximations for many-electron systems, *Phys. Rev. B* **23**, 5048 (1981).
 - [9] L. Kronik and S. Kümmel, Piecewise linearity, freedom from self-interaction, and a Coulomb asymptotic potential: Three related yet inequivalent properties of the exact density functional, *Phys. Chem. Chem. Phys.* **22**, 16467 (2020).
 - [10] E. Dagotto, Complexity in strongly correlated electronic systems, *Science* **309**, 257 (2005).
 - [11] V. I. Anisimov, F. Aryasetiawan, and A. Lichtenstein, First-principles calculations of the electronic structure and spectra of strongly correlated systems: The LDA + U method, *J. Phys.: Condens. Matter* **9**, 767 (1997).
 - [12] S. Mandal, K. Haule, K. M. Rabe, and D. Vanderbilt, Influence of magnetic ordering on the spectral properties of binary transition metal oxides, *Phys. Rev. B* **100**, 245109 (2019).
 - [13] D. Wing, G. Ohad, J. B. Haber, M. R. Filip, S. E. Gant, J. B. Neaton, and L. Kronik, Band gaps of crystalline solids from Wannier-localization-based optimal tuning of a screened range-separated hybrid functional, *Proc. Natl. Acad. Sci. USA* **118**, e2104556118 (2021).
 - [14] G. Ohad, D. Wing, S. E. Gant, A. V. Cohen, J. B. Haber, F. Sagredo, M. R. Filip, J. B. Neaton, and L. Kronik, Band gaps of halide perovskites from a Wannier-localized optimally

- tuned screened range-separated hybrid functional, *Phys. Rev. Mater.* **6**, 104606 (2022).
- [15] G. Ohad, S. E. Gant, D. Wing, J. B. Haber, M. Camarasa-Gómez, F. Sagredo, M. R. Filip, J. B. Neaton, and L. Kronik, Optical absorption spectra of metal oxides from time-dependent density functional theory and many-body perturbation theory based on optimally-tuned hybrid functionals, *Phys. Rev. Mater.* **7**, 123803 (2023).
- [16] F. Sagredo, S. E. Gant, G. Ohad, J. B. Haber, M. R. Filip, L. Kronik, and J. B. Neaton, Electronic structure and optical properties of halide double perovskites from a Wannier-localized optimally-tuned screened range-separated hybrid functional, *Phys. Rev. Mater.* **8**, 105401 (2024).
- [17] W. Roth, Magnetic structures of MnO, FeO, CoO, and NiO, *Phys. Rev.* **110**, 1333 (1958).
- [18] D. Kasinathan, J. Kuneš, K. Koepernik, C. V. Diaconu, R. L. Martin, I. D. Prodan, G. E. Scuseria, N. Spaldin, L. Petit, T. C. Schulthess, and W. E. Pickett, Mott transition of MnO under pressure: A comparison of correlated band theories, *Phys. Rev. B* **74**, 195110 (2006).
- [19] P. Liu, C. Franchini, M. Marsman, and G. Kresse, Assessing model-dielectric-dependent hybrid functionals on the antiferromagnetic transition-metal monoxides MnO, FeO, CoO, and NiO, *J. Phys.: Condens. Matter* **32**, 015502 (2020).
- [20] M. S. Abdallah and A. Pasquarello, Quasiparticle self-consistent GW with effective vertex corrections in the polarizability and the self-energy applied to MnO, FeO, CoO, and NiO, *Phys. Rev. B* **110**, 155105 (2024).
- [21] T. Satoh, S.-J. Cho, R. Iida, T. Shimura, K. Kuroda, H. Ueda, Y. Ueda, B. Ivanov, F. Nori, and M. Fiebig, Spin oscillations in antiferromagnetic NiO triggered by circularly polarized light, *Phys. Rev. Lett.* **105**, 077402 (2010).
- [22] T. Kampfrath, A. Sell, G. Klatt, A. Pashkin, S. Mährlein, T. Dekorsy, M. Wolf, M. Fiebig, A. Leitenstorfer, and R. Huber, Coherent terahertz control of antiferromagnetic spin waves, *Nat. Photon.* **5**, 31 (2011).
- [23] H. Wan, L. Hu, X. Liu, Y. Zhang, G. Chen, N. Zhang, and R. Ma, Advanced hematite nanomaterials for newly emerging applications, *Chem. Sci.* **14**, 2776 (2023).
- [24] D. A. Grave, D. S. Ellis, Y. Piekner, M. Kölbach, H. Dotan, A. Kay, P. Schnell, R. van de Krol, F. F. Abdi, D. Friedrich, and A. Rothschild, Extraction of mobile charge carrier photogeneration yield spectrum of ultrathin-film metal oxide photoanodes for solar water splitting, *Nat. Mater.* **20**, 833 (2021).
- [25] N. A. Spaldin and R. Ramesh, Advances in magnetoelectric multiferroics, *Nat. Mater.* **18**, 203 (2019).
- [26] D. N. Astrov, The magnetoelectric effect in antiferromagnetics, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **38**, 984 (1960) [*Sov. Phys. JETP* **11**, 708 (1960)].
- [27] M. Fiebig, T. Lottermoser, D. Meier, and M. Trassin, The evolution of multiferroics, *Nat. Rev. Mater.* **1**, 16046 (2016).
- [28] S. Refaely-Abramson, S. Sharifzadeh, M. Jain, R. Baer, J. B. Neaton, and L. Kronik, Gap renormalization of molecular crystals from density-functional theory, *Phys. Rev. B* **88**, 081204(R) (2013).
- [29] A. Seidl, A. Görling, P. Vogl, J. A. Majewski, and M. Levy, Generalized Kohn-Sham schemes and the band-gap problem, *Phys. Rev. B* **53**, 3764 (1996).
- [30] L. Kronik, T. Stein, S. Refaely-Abramson, and R. Baer, Excitation gaps of finite-sized systems from optimally tuned range-separated hybrid functionals, *J. Chem. Theory Comput.* **8**, 1515 (2012).
- [31] R. Baer and L. Kronik, Time-dependent generalized Kohn-Sham theory, *Eur. Phys. J. B* **91**, 170 (2018).
- [32] R. Garrick, L. Kronik, and T. Gould, Adiabatic connection for range-separated hybrid functionals, *Adv. Theory Simul.* **5**, 2100550 (2022).
- [33] D. Lüftner, S. Refaely-Abramson, M. Pachler, R. Resel, M. G. Ramsey, L. Kronik, and P. Puschnig, Experimental and theoretical electronic structure of quinacridone, *Phys. Rev. B* **90**, 075204 (2014).
- [34] S. Refaely-Abramson, M. Jain, S. Sharifzadeh, J. B. Neaton, and L. Kronik, Solid-state optical absorption from optimally tuned time-dependent range-separated hybrid density functional theory, *Phys. Rev. B* **92**, 081204(R) (2015).
- [35] J. Zhan, M. Govoni, and G. Galli, Dielectric-dependent range-separated hybrid functional calculations for metal oxides, *Phys. Rev. Mater.* **9**, 053808 (2025).
- [36] H. Zheng, M. Govoni, and G. Galli, Dielectric-dependent hybrid functionals for heterogeneous materials, *Phys. Rev. Mater.* **3**, 073803 (2019).
- [37] J. Zhan, M. Govoni, and G. Galli, Nonempirical range-separated hybrid functional with spatially dependent screened exchange, *J. Chem. Theory Comput.* **19**, 5851 (2023).
- [38] W. Chen, G. Miceli, G.-M. Rignanese, and A. Pasquarello, Nonempirical dielectric-dependent hybrid functional with range separation for semiconductors and insulators, *Phys. Rev. Mater.* **2**, 073803 (2018).
- [39] S. Jana, A. Bhattacharjee, S. Mahakal, S. Śmiga, and P. Samal, Meta-GGA dielectric-dependent and range-separated screened hybrid functional for reliable prediction of material properties, *Phys. Rev. B* **111**, 115125 (2025).
- [40] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [41] J. P. Perdew, M. Ernzerhof, and K. Burke, Rationale for mixing exact exchange with density functional approximations, *J. Chem. Phys.* **105**, 9982 (1996).
- [42] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Erratum: Hybrid functionals based on a screened Coulomb potential [*J. Chem. Phys.* **118**, 8207 (2003)], *J. Chem. Phys.* **124**, 219906 (2006).
- [43] T. Stein, H. Eisenberg, L. Kronik, and R. Baer, Fundamental gaps in finite systems from eigenvalues of a generalized Kohn-Sham method, *Phys. Rev. Lett.* **105**, 266802 (2010).
- [44] S. Refaely-Abramson, R. Baer, and L. Kronik, Fundamental and excitation gaps in molecules of relevance for organic photovoltaics from an optimally tuned range-separated hybrid functional, *Phys. Rev. B* **84**, 075144 (2011).
- [45] J. Autschbach and M. Srebro, Delocalization error and functional tuning in Kohn-Sham calculations of molecular properties, *Acc. Chem. Res.* **47**, 2592 (2014).
- [46] H. Phillips, Z. Zheng, E. Geva, and B. D. Dunietz, Orbital gap predictions for rational design of organic photovoltaic materials, *Org. Electron.* **15**, 1509 (2014).
- [47] M. E. Foster, J. D. Azoulay, B. M. Wong, and M. D. Allendorf, Novel metal-organic framework linkers for light harvesting applications, *Chem. Sci.* **5**, 2081 (2014).
- [48] T. Körzdörfer and J.-L. Brédas, Organic electronic materials: Recent advances in the DFT description of the ground and

- excited states using tuned range-separated hybrid functionals, *Acc. Chem. Res.* **47**, 3284 (2014).
- [49] C. Faber, P. Boulanger, C. Attaccalite, I. Duchemin, and X. Blase, Excited states properties of organic molecules: From density functional theory to the *GW* and Bethe–Salpeter Green’s function formalisms, *Philos. Trans. R. Soc. A* **372**, 20130271 (2014).
- [50] M. Alipour and S. Mohseni, Shedding light on the accuracy of optimally tuned range-separated approximations for evaluating oxidation potentials, *J. Phys. Chem. A* **121**, 4189 (2017).
- [51] L. Kronik and J. B. Neaton, Excited-state properties of molecular solids from first principles, *Annu. Rev. Phys. Chem.* **67**, 587 (2016).
- [52] S. Bhandari, M. S. Cheung, E. Geva, L. Kronik, and B. D. Dunietz, Fundamental gaps of condensed-phase organic semiconductors from single-molecule calculations using polarization-consistent optimally tuned screened range-separated hybrid functionals, *J. Chem. Theory Comput.* **14**, 6287 (2018).
- [53] L. Kronik and S. Kümmel, Dielectric screening meets optimally tuned density functionals, *Adv. Mater.* **30**, 1706560 (2018).
- [54] V. Coropceanu, X.-K. Chen, T. Wang, Z. Zheng, and J.-L. Brédas, Charge-transfer electronic states in organic solar cells, *Nat. Rev. Mater.* **4**, 689 (2019).
- [55] L. R. Franco, C. Marchiori, and C. M. Araujo, Unveiling the impact of exchange-correlation functionals on the description of key electronic properties of non-fullerene acceptors in organic photovoltaics, *J. Chem. Phys.* **159**, 204110 (2023).
- [56] M. Hartstein, G. Ohad, and L. Kronik, Predicting the color polymorphism of ROY from a time-dependent optimally tuned screened range-separated hybrid functional, *J. Chem. Theory Comput.* **20**, 5510 (2024).
- [57] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Localization and delocalization errors in density functional theory and implications for band-gap prediction, *Phys. Rev. Lett.* **100**, 146401 (2008).
- [58] E. Kraisler and L. Kronik, Fundamental gaps with approximate density functionals: The derivative discontinuity revealed from ensemble considerations, *J. Chem. Phys.* **140**, 18A540 (2014).
- [59] V. Vlček, H. R. Eisenberg, G. Steinle-Neumann, L. Kronik, and R. Baer, Deviations from piecewise linearity in the solid-state limit with approximate density functionals, *J. Chem. Phys.* **142**, 034107 (2015).
- [60] A. Görling, Exchange-correlation potentials with proper discontinuities for physically meaningful Kohn-Sham eigenvalues and band structures, *Phys. Rev. B* **91**, 245120 (2015).
- [61] J. F. Janak, Proof that $\partial E / \partial n_i = \epsilon_i$ in density-functional theory, *Phys. Rev. B* **18**, 7165 (1978).
- [62] J. Ma and L.-W. Wang, Using Wannier functions to improve solid band gap predictions in density functional theory, *Sci. Rep.* **6**, 24924 (2016).
- [63] G. Ohad, M. Camarasa-Gómez, J. B. Neaton, A. Ramasubramaniam, T. Gould, and L. Kronik, Foundations of the ionization potential condition for localized electron removal in density functional theory, *Phys. Rev. Lett.* **136**, 026401 (2026).
- [64] G. Makov and M. C. Payne, Periodic boundary conditions in *ab initio* calculations, *Phys. Rev. B* **51**, 4014 (1995).
- [65] N. Marom, O. Hod, G. E. Scuseria, and L. Kronik, Electronic structure of copper phthalocyanine: A comparative density functional theory study, *J. Chem. Phys.* **128**, 164107 (2008).
- [66] D. A. Egger, S. Weissman, S. Refaely-Abramson, S. Sharifzadeh, M. Dauth, R. Baer, S. Kümmel, J. B. Neaton, E. Zojer, and L. Kronik, Outer-valence electron spectra of prototypical aromatic heterocycles from an optimally tuned range-separated hybrid functional, *J. Chem. Theory Comput.* **10**, 1934 (2014).
- [67] I. E. Brumboiu, G. Prokopiou, L. Kronik, and B. Brena, Valence electronic structure of cobalt phthalocyanine from an optimally tuned range-separated hybrid functional, *J. Chem. Phys.* **147**, 044301 (2017).
- [68] S. Weissman, M. Antkowiak, B. Brzostowski, G. Kamieniarz, and L. Kronik, Accurate magnetic couplings in chromium-based molecular rings from broken-symmetry calculations within density functional theory, *J. Chem. Theory Comput.* **15**, 4885 (2019).
- [69] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
- [70] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* **59**, 1758 (1999).
- [71] K. H. Stone, M. R. Cosby, N. A. Strange, V. Thampy, R. C. Walroth, and C. Troxel, Jr., Remote and automated high-throughput powder diffraction measurements enabled by a robotic sample changer at SSRL beamline 2-1, *J. Appl. Crystallogr.* **56**, 1480 (2023).
- [72] S. Sasaki, K. Fujino, and Y. Takéuchi, X-ray determination of electron-density distributions in oxides, MgO, MnO, CoO, and NiO, and atomic scattering factors of their constituent atoms, *Proc. Jpn. Acad. Ser. B* **55**, 43 (1979).
- [73] R. L. Blake, R. E. Hessevick, T. Zoltai, and L. W. Finger, Refinement of the hematite structure, *Am. Mineral.: J. Earth Planet. Mater.* **51**, 123 (1966).
- [74] P. Fabrykiewicz, R. Przeniosło, I. Sosnowska, and F. Fauth, Positive and negative monoclinic deformation of corundum-type trigonal crystal structures of M_2O_3 metal oxides, *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.* **74**, 660 (2018).
- [75] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/126j-3fts> for computational details and further analysis, which includes Refs. [130,131].
- [76] M. Camarasa-Gómez, S. E. Gant, G. Ohad, J. B. Neaton, A. Ramasubramaniam, and L. Kronik, Excitations in layered materials from a non-empirical Wannier-localized optimally-tuned screened range-separated hybrid functional, *npj Comput. Mater.* **10**, 288 (2024).
- [77] R. Logemann, A. Rudenko, M. Katsnelson, and A. Kirilyuk, Exchange interactions in transition metal oxides: The role of oxygen spin polarization, *J. Phys.: Condens. Matter* **29**, 335801 (2017).
- [78] C. Franchini, R. Podloucky, J. Paier, M. Marsman, and G. Kresse, Ground-state properties of multivalent manganese oxides: Density functional and hybrid density functional calculations, *Phys. Rev. B* **75**, 195128 (2007).
- [79] E. Kurmaev, R. Wilks, A. Moewes, L. Finkelstein, S. Shamin, and J. Kuneš, Oxygen x-ray emission and absorption spectra as a probe of the electronic structure

- of strongly correlated oxides, *Phys. Rev. B* **77**, 165127 (2008).
- [80] J. van Elp, R. H. Potze, H. Eskes, R. Berger, and G. A. Sawatzky, Electronic structure of MnO, *Phys. Rev. B* **44**, 1530 (1991).
- [81] R. Zimmermann, P. Steiner, R. Claessen, F. Reinert, S. Hüfner, P. Blaha, and P. Dufek, Electronic structure of 3d-transition-metal oxides: On-site Coulomb repulsion versus covalency, *J. Phys.: Condens. Matter* **11**, 1657 (1999).
- [82] A. Cheetham and D. Hope, Magnetic ordering and exchange effects in the antiferromagnetic solid solutions $\text{Mn}_x\text{Ni}_{1-x}\text{O}$, *Phys. Rev. B* **27**, 6964 (1983).
- [83] G. Sawatzky and J. Allen, Magnitude and origin of the band gap in NiO, *Phys. Rev. Lett.* **53**, 2339 (1984).
- [84] H. A. Alperin, The magnetic form factor of nickel oxide, *J. Phys. Soc. Jpn. Suppl. B* **17**, 12 (1962).
- [85] All DFT + U results reported in this article are quoted values from the literature, provided for comparison. In all cases, numerical values used by the original authors are given. Further details as to their determination can be found in the original articles.
- [86] F. de Groot. and A. Kotani, *Core level Spectroscopy of Solids* (CRC Press, Boca Raton, FL, 2008).
- [87] S. Suga and A. Sekiyama, *Photoelectron Spectroscopy: Bulk and Surface Electronic Structures* (Springer, Berlin, Heidelberg, 2013).
- [88] S. E. Gant, J. B. Haber, M. R. Filip, F. Sagredo, D. Wing, G. Ohad, L. Kronik, and J. B. Neaton, Optimally tuned starting point for single-shot GW calculations of solids, *Phys. Rev. Mater.* **6**, 053802 (2022).
- [89] M. Shishkin and G. Kresse, Self-consistent GW calculations for semiconductors and insulators, *Phys. Rev. B* **75**, 235102 (2007).
- [90] M. Shishkin, M. Marsman, and G. Kresse, Accurate quasiparticle spectra from self-consistent GW calculations with vertex corrections, *Phys. Rev. Lett.* **99**, 246403 (2007).
- [91] M. Grumet, P. Liu, M. Kaltak, J. Klimeš, and G. Kresse, Beyond the quasiparticle approximation: Fully self-consistent GW calculations, *Phys. Rev. B* **98**, 155143 (2018).
- [92] It should be noted that an unquenched orbital moment of approximately $0.3 \mu_B$ has been experimentally observed in NiO [132]. This additional orbital contribution arises from spin-orbit coupling, which is not included in the present HSE06 and WOT-SRSH calculations.
- [93] J. Plendl, L. Mansur, S. Mitra, and I. Chang, Reststrahlen spectrum of MnO, *Solid State Commun.* **7**, 109 (1969).
- [94] P. J. Gielisse, J. Plendl, L. Mansur, R. Marshall, S. Mitra, R. Mykolajewycz, and A. Smakula, Infrared properties of NiO and CoO and their mixed crystals, *J. Appl. Phys.* **36**, 2446 (1965).
- [95] Z.-X. Shen, R. S. List, D. S. Dessau, B. O. Wells, O. Jepsen, A. J. Arko, R. Bartlett, C. K. Shih, F. Parmigiani, J. C. Huang, and P. A. P. Lindberg, Electronic structure of NiO: Correlation and band effects, *Phys. Rev. B* **44**, 3604 (1991).
- [96] D. Wing, J. B. Haber, R. Noff, B. Barker, D. A. Egger, A. Ramasubramanian, S. G. Louie, J. B. Neaton, and L. Kronik, Comparing time-dependent density functional theory with many-body perturbation theory for semiconductors: Screened range-separated hybrids and the GW plus Bethe-Salpeter approach, *Phys. Rev. Mater.* **3**, 064603 (2019).
- [97] M. E. Casida, in *Recent Advances in Density Functional Methods Part I*, edited by D. P. Chong (World Scientific, Singapore, 1995), Chap. 5, pp. 155–192.
- [98] S. Hirata and M. Head-Gordon, Time-dependent density functional theory within the Tamm–Dancoff approximation, *Chem. Phys. Lett.* **314**, 291 (1999).
- [99] C. Ullrich, *Time-Dependent Density-Functional Theory: Concepts and Applications* (Oxford University Press, Oxford, UK, 2011).
- [100] Y. Tezuka, S. Shin, T. Ishii, T. Ejima, S. Suzuki, and S. Sato, Photoemission and bremsstrahlung isochromat spectroscopy studies of TiO_2 (rutile) and SrTiO_3 , *J. Phys. Soc. Jpn.* **63**, 347 (1994).
- [101] L. Messick, W. Walker, and R. Glosser, Direct and temperature-modulated reflectance spectra of MnO, CoO, and NiO, *Phys. Rev. B* **6**, 3941 (1972).
- [102] R. Powell and W. Spicer, Optical properties of NiO and CoO, *Phys. Rev. B* **2**, 2182 (1970).
- [103] R. M. White, *Quantum Theory of Magnetism* (Springer, Berlin, Heidelberg, 2007).
- [104] M. Kohgi, Y. Ishikawa, and Y. Endoh, Inelastic neutron scattering study of spin waves in MnO, *Solid State Commun.* **11**, 391 (1972).
- [105] M. Lines and E. Jones, Antiferromagnetism in the face-centered cubic lattice. II. Magnetic properties of MnO, *Phys. Rev.* **139**, A1313 (1965).
- [106] M. T. Hutchings and E. Samuelsen, Measurement of spin-wave dispersion in NiO by inelastic neutron scattering and its relation to magnetic properties, *Phys. Rev. B* **6**, 3447 (1972).
- [107] R. Shanker and R. Singh, Analysis of the exchange parameters and magnetic properties of NiO, *Phys. Rev. B* **7**, 5000 (1973).
- [108] L. Pauling and S. B. Hendricks, The crystal structures of hematite and corundum, *J. Am. Chem. Soc.* **47**, 781 (1925).
- [109] F. Morin, Electrical properties of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ containing titanium, *Phys. Rev.* **83**, 1005 (1951).
- [110] P. Flanders and J. Remeika, Magnetic properties of hematite single crystals, *Philos. Mag.* **11**, 1271 (1965).
- [111] L. Sandratskii, M. Uhl, and J. Kübler, Band theory for electronic and magnetic properties of $\alpha\text{-Fe}_2\text{O}_3$, *J. Phys.: Condens. Matter* **8**, 983 (1996).
- [112] L. Šmejkal, J. Sinova, and T. Jungwirth, Beyond conventional ferromagnetism and antiferromagnetism: A phase with nonrelativistic spin and crystal rotation symmetry, *Phys. Rev. X* **12**, 031042 (2022).
- [113] K. Iwachi, S. Yamamoto, Y. Bando, T. Hanai, N. Koizumi, T. Takada, and S. Fukushima, Dielectric properties of the mixtures of $\alpha\text{-Fe}_2\text{O}_3$, TiO_2 and Fe_2TiO_5 , *Jpn. J. Appl. Phys.* **10**, 1513 (1971).
- [114] S. Onari, T. Arai, and K. Kudo, Infrared lattice vibrations and dielectric dispersion in $\alpha\text{-Fe}_2\text{O}_3$, *Phys. Rev. B* **16**, 1717 (1977).
- [115] C. Chen and B. Cahan, Visible and ultraviolet optical properties of single-crystal and polycrystalline hematite measured by spectroscopic ellipsometry, *J. Opt. Soc. Am.* **71**, 932 (1981).
- [116] V. Baron, J. Gutzmer, H. Rundlöf, and R. Tellgren, Neutron powder diffraction study of Mn-bearing hematite,

- α -Fe_{2-x}Mn_xO₃, in the range $0 < x < 0.176$, *Solid State Sci.* **7**, 753 (2005).
- [117] A. H. Hill, F. Jiao, P. G. Bruce, A. Harrison, W. Kockelmann, and C. Ritter, Neutron diffraction study of mesoporous and bulk hematite, α -Fe₂O₃, *Chem. Mater.* **20**, 4891 (2008).
- [118] X. Verbeek, D. Voderholzer, S. Schären, Y. Gachnang, N. Spaldin, and S. Bhowal, Nonrelativistic ferromagnetotriakontadipolar order and spin splitting in hematite, *Phys. Rev. Res.* **6**, 043157 (2024).
- [119] S. Piccinin, The band structure and optical absorption of hematite (α -Fe₂O₃): A first-principles GW-BSE study, *Phys. Chem. Chem. Phys.* **21**, 2957 (2019).
- [120] B. Gilbert, C. Frandsen, E. R. Maxey, and D. M. Sherman, Band-gap measurements of bulk and nanoscale hematite by soft x-ray spectroscopy, *Phys. Rev. B* **79**, 035108 (2009).
- [121] A. Rohrbach, J. Hafner, and G. Kresse, *Ab initio* study of the (0001) surfaces of hematite and chromia: Influence of strong electronic correlations, *Phys. Rev. B* **70**, 125426 (2004).
- [122] S. Shi, A. L. Wysocki, and K. D. Belashchenko, Magnetism of chromia from first-principles calculations, *Phys. Rev. B* **79**, 104404 (2009).
- [123] S. Dabaghmanesh, R. Saniz, E. Neyts, and B. Partoens, Sulfur-alloyed Cr₂O₃: A new p-type transparent conducting oxide host, *RSC Adv.* **7**, 4453 (2017).
- [124] R. Zimmermann, P. Steiner, and S. Hüfner, Electron spectroscopies and partial excitation spectra in Cr₂O₃, in *Proceedings of the 11th International Conference on Vacuum Ultraviolet Radiation Physics* (Elsevier, Amsterdam, 1996), pp. 49–52.
- [125] P. J. Brown, J. B. Forsyth, E. Lelièvre-Berna, and F. Tasset, Determination of the magnetization distribution in Cr₂O₃ using spherical neutron polarimetry, *J. Phys.: Condens. Matter* **14**, 1957 (2002).
- [126] L. Corliss, J. Hastings, R. Nathans, and G. Shirane, Magnetic structure of Cr₂O₃, *J. Appl. Phys.* **36**, 1099 (1965).
- [127] A. Galuza, V. Eremenko, and A. Kirichenko, Kramers-Kronig analysis of reflection spectra of hematite, *Sov. Phys. Sol. State* **21**, 654 (1979).
- [128] T. Uozumi, K. Okada, A. Kotani, R. Zimmermann, P. Steiner, S. Hüfner, Y. Tezuka, and S. Shin, Theoretical and experimental studies on the electronic structure of M₂O₃ (M = Ti, V, Cr, Mn, Fe) compounds by systematic analysis of high-energy spectroscopy, *J. Electron Spectrosc. Relat. Phenom.* **83**, 9 (1997).
- [129] T. Allos, R. Birss, M. Parker, E. Ellis, and D. Johnson, Ultraviolet absorption spectrum of Cr₂O₃ from reflectivity measurements, *Solid State Commun.* **24**, 129 (1977).
- [130] C. Rödl, F. Fuchs, J. Furthmüller, and F. Bechstedt, Quasiparticle band structures of the antiferromagnetic transition-metal oxides MnO, FeO, CoO, and NiO, *Phys. Rev. B* **79**, 235114 (2009).
- [131] G. Pizzi, V. Vitale, R. Arita, S. Blügel, F. Freimuth, G. Géranton, M. Gibertini, D. Gresch, C. Johnson, T. Koretsune, J. Ibañez-Azpiroz, H. Lee, J.-M. Lihm, D. Marchand, A. Marrazzo, Y. Mokrousov, J. I. Mustafa, Y. Nohara, Y. Nomura, L. Paulatto, *et al.*, Wannier90 as a community code: New features and applications, *J. Phys.: Condens. Matter* **32**, 165902 (2020).
- [132] W. Neubeck, C. Vettier, V. Fernandez, F. de Bergevin, and C. Giles, Observation of orbital moment in NiO using magnetic x-ray scattering, *J. Appl. Phys.* **85**, 4847 (1999).