

## Band gaps of halide perovskites from a Wannier-localized optimally tuned screened range-separated hybrid functional

Guy Ohad<sup>1</sup>,<sup>2</sup> Dahvyd Wing,<sup>1</sup> Stephen E. Gant,<sup>2,3</sup> Ayala V. Cohen,<sup>1</sup> Jonah B. Haber,<sup>2,3</sup> Francisca Sagredo,<sup>2,3</sup> Marina R. Filip,<sup>4</sup> Jeffrey B. Neaton,<sup>2,3,5</sup> and Leeor Kronik<sup>1</sup>

<sup>1</sup>*Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovoth 76100, Israel*

<sup>2</sup>*Department of Physics, University of California, Berkeley, California 94720, USA*

<sup>3</sup>*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

<sup>4</sup>*Department of Physics, University of Oxford, Oxford OX1 3PJ, United Kingdom*

<sup>5</sup>*Kavli Energy NanoSciences Institute at Berkeley, University of California, Berkeley, California 94720, USA*



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The accurate prediction of the band gaps of halide perovskites within density functional theory is known to be challenging. The recently developed Wannier-localized optimally tuned screened range-separated hybrid functional was shown to be highly accurate for fundamental band gaps of standard semiconductors and insulators. This was achieved by selecting the parameters of the functional to satisfy an ansatz that generalizes the ionization potential theorem to the removal of charge from a state that corresponds to a Wannier function. Here, we present applications of the method to the band gaps of typical halide perovskites. We find a satisfyingly small formal mean absolute error of  $\sim 0.1$  eV with respect to experimental band gaps and very good agreement with previous many-body perturbation theory calculations.

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### I. INTRODUCTION

Halide perovskites (HaPs) have emerged as exceptionally promising materials for photovoltaics, owing to a rapidly increasing power conversion efficiency over the last decade [1–6]. Additional applications in optoelectronics, along with many intriguing physical and chemical properties, have also drawn great scientific attention towards HaPs in recent years [6–8]. The electronic band structure, especially the fundamental band gap, of HaPs is a critical material property when developing novel HaP compounds for solar cell and optoelectronic applications. The accurate prediction of these properties from first principles is hence highly desirable and an active area of research [9–24].

Many-body perturbation theory in the *GW* approximation is widely used to study band gaps of HaPs [15–24]. While in many cases this method was shown to yield quasi-particle band gaps in good agreement with experiment, the results are highly dependent on the self-consistency of the approach (or lack thereof) and the density functional theory (DFT) starting point, limiting predictive power. In addition, convergence is typically achieved upon including a large number of unoccupied states, leading to high computational cost and limited system size. Band-gap calculations based on DFT are less expensive, but are known to severely underestimate the band gap when using local and semilocal exchange-correlation functionals [14,19–21]. The use of more advanced functionals within DFT improves the accuracy substantially [9–12]. Still, finding a scheme that yields accuracy to within the experimental uncertainty in a nonempirical fashion, entirely within DFT, is an ongoing challenge [11,12].

Recently, we have developed a nonempirical method to select the parameters of a screened range-separated hybrid (SRS) functional for the prediction of semiconductor and insulator band gaps [25]. This approach, referred to as Wannier-localized optimally tuned SRS (WOT-SRS), enforces a generalized ionization potential ansatz to the removal of charge from a localized Wannier function. The method has been benchmarked against a set of prototypical semiconductors and insulators with band gaps ranging from 0.2 to 15.3 eV, yielding results in excellent agreement with experiment, with a mean absolute error (MAE) of  $\sim 0.1$  eV [25]. In this paper, we set out to assess the accuracy of WOT-SRS for more complex systems and choose to focus on HaPs, with the aim of providing an accurate and nonempirical method for HaP band-gap calculations. We calculate the fundamental band gaps of a set of seven typical HaPs and find a formal MAE of  $\sim 0.1$  eV with respect to experiment. We further compare our results with previous band gaps obtained from *GW* calculations and find a comparable level of accuracy at a significantly lower computational cost.

### II. METHODS

Our starting point is the SRS functional [26], in which the Coulomb interaction operator is partitioned using the identity

$$\frac{1}{r} = \underbrace{\alpha \frac{\text{erfc}(\gamma r)}{r}}_{\text{xx, SR}} + \underbrace{(1 - \alpha) \frac{\text{erfc}(\gamma r)}{r}}_{\text{KSx, SR}} + \underbrace{\frac{1}{\epsilon_\infty} \frac{\text{erf}(\gamma r)}{r}}_{\text{xx, LR}} + \underbrace{\left(1 - \frac{1}{\epsilon_\infty}\right) \frac{\text{erf}(\gamma r)}{r}}_{\text{KSx, LR}}, \quad (1)$$

where exchange in the first and third terms is treated exactly (xx) and in the second and fourth terms exchange is approximated by a semilocal Kohn-Sham term (KSx). This leads to  $\alpha$  being the fraction of short-range (SR) exact exchange and  $\frac{1}{\epsilon_\infty}$  being the fraction of long-range (LR) exact exchange.  $\gamma$ , the range-separation parameter, determines the transition from short to long range with increasing interelectronic distance  $r$ . The next step is to determine the values of the three parameters in SRSR.  $\alpha$  is usually chosen to balance short-range exchange and correlation effects [27,28], an issue elaborated below.  $\epsilon_\infty$  is chosen to be the orientationally averaged high-frequency (ion-clamped) dielectric constant of the material, ensuring that the functional possesses the correct average long-range dielectric screening [26,28,29].

The only parameter left undetermined is the range-separation parameter  $\gamma$ . For finite systems,  $\gamma$  can be selected to satisfy the ionization potential (IP) theorem, an exact physical condition [30–33]. This method, known as optimal tuning, was shown to be very successful for determining fundamental band gaps in molecules [34–41]. For extended systems, however, this method fails in the sense that the IP theorem is trivially satisfied for every value of  $\gamma$  [42–45].

The origin of the above problem is the delocalized nature of the electronic orbitals in extended systems. Therefore, in the WOT-SRSR approach we exploit maximally localized Wannier functions [46] as a means of obtaining localized orbitals in solids. Because Wannier functions are not eigenfunctions of the DFT Hamiltonian, the IP theorem does not strictly hold upon the removal of charge from an orbital that corresponds to a Wannier function. The WOT-SRSR approach therefore adopts an ansatz generalization of the ionization potential theorem [47], according to which  $\gamma$  is selected to satisfy  $\Delta I^\gamma = 0$ , where

$$\Delta I^\gamma = E_{\text{constr}}^\gamma[\phi](N-1) - E^\gamma(N) + \langle \phi | \hat{H}_{\text{SRSR}}^\gamma | \phi \rangle. \quad (2)$$

Here,  $E^\gamma(N)$  is the total energy of the system with  $N$  electrons and  $E_{\text{constr}}^\gamma[\phi](N-1)$  is the total energy of a system with one electron removed, including an image charge correction (see Supplemental Material [48] for further details), under the constraint that the charge is removed from a state corresponding to a Wannier function,  $\phi$ .  $\hat{H}_{\text{SRSR}}^\gamma$  is the Hamiltonian of the SRSR functional with  $N$  electrons and  $\langle \phi | \hat{H}_{\text{SRSR}}^\gamma | \phi \rangle$  is the expectation value for the energy of the Wannier function.

The removal of charge from a Wannier function is achieved by minimizing the total energy of the  $(N-1)$ -electron system with an additional constraint that fixes the ‘‘occupation’’ of the Wannier function [25]. This minimization yields the equation

$$\hat{H}_{\text{SRSR}} + \lambda |\phi\rangle \langle \phi| \psi_i\rangle = \epsilon_i |\psi_i\rangle, \quad (3)$$

which is solved self-consistently for the  $(N-1)$ -electron system. Here,  $\{\psi_i\}$  and  $\{\epsilon_i\}$  are the eigenfunctions and eigenvalues, respectively, of the constrained  $(N-1)$ -electron system and  $\lambda$  is a parameter that controls the occupation of the Wannier function. The value of  $\lambda$  is chosen such that the occupation of the Wannier function approaches zero.

We apply WOT-SRSR to a system of interest using a four-step procedure [25]. In step 1, we calculate  $\epsilon_\infty$  using a primitive unit cell. In step 2, we calculate Wannier functions composed of the topmost valence bands for a supercell of the

neutral system. In step 3, we calculate  $\Delta I$  of Eq. (2) of the supercell, using the SRSR functional with an initial guess for  $\gamma$ , where  $E_{\text{constr}}[\phi](N-1)$  is calculated using the Wannier function with the highest energy from step 2. We iterate step 3 until we find a  $\gamma$  for which  $|\Delta I| < 0.02$  eV. In step 4, we calculate the fundamental band gap of the material with this particular  $\gamma$ , using the primitive unit cell (see Supplemental Material [48] for complete computational details).

In this work we compute the fundamental band gaps of  $\text{CsPbX}_3$  ( $X = \text{I, Br, Cl}$ ),  $\text{CsSnX}_3$  ( $X = \text{I, Br}$ ), and  $\text{MAPbX}_3$  ( $X = \text{I, Br}$ ), where MA is methylammonium. We aim to compute band gaps that are comparable with experimental values. For this reason, we restrict our attention to a set of compounds for which the experimental low-temperature crystal structures, as well as associated band gaps, have been reported in past experimental literature. The high-temperature cubic phase of HaPs exhibits significant thermal fluctuations that cannot be captured by a theoretical frozen single cubic unit cell [12,15,49,50]. In principle, band gaps in the high-temperature phase from static calculations can be compared with experiment by including finite-temperature corrections [12,15] or low-symmetry motifs in large supercells [50]. For an assessment of our method, we circumvent this issue by using the low-temperature phase, which is in the orthorhombic structure (space group  $Pnma$ ) for the entire set.

To avoid discrepancies with experiment that arise from different geometries, we adopt the experimental lattice parameters throughout our calculations. Previous studies indicate that the effect of geometry optimization on the band gaps of HaPs is usually small (up to  $\sim 0.2$  eV) [9,13,16,51], but larger shifts have also been reported [21]. We compare the calculated band gaps with experimental results for the same orthorhombic phase, except for  $\text{CsSnBr}_3$  where the only available measurements to the best of our knowledge are for the cubic phase. In this context, it is important to emphasize that typically experimental band gaps of HaPs are not highly dependent on the crystal phase [52–54].

In our previous work, the default value used for  $\alpha$  in the SRSR functional was 0.25, as in the hybrid Perdew-Burke-Ernzerhof (PBE0) [55,56] and the Heyd-Scuseria-Ernzerhof (HSE) [57] functionals. For the systems studied in this work, we find this value inadequate for two reasons. First, the value of  $\frac{1}{\epsilon_\infty}$  for the studied systems is very close to 0.25, which makes  $\Delta I$  insensitive to variations in  $\gamma$ . Second, the value of 0.25 is often found to be too small to find a range-separation parameter for which  $\Delta I = 0$ . Therefore, we increase the value of  $\alpha$  to the smallest possible value for which an optimal  $\gamma$  that is at least  $0.1 \text{ bohr}^{-1}$  can be found. This ensures that the functional will exhibit the full asymptotic  $\frac{1}{\epsilon_\infty}$  behavior within the supercell. We find that choosing  $\alpha = 0.42$  is adequate for this purpose, and adopt this value for all studied systems. A similar value for  $\alpha$  in the HSE functional was proposed by Du [58] as a means of obtaining the experimental band gap of HaPs.

### III. RESULTS AND DISCUSSION

To demonstrate how WOT-SRSR is applied to HaPs, we use  $\text{MAPbI}_3$  as an example, which we find to be representative of all studied systems. In Fig. 1(a) we show

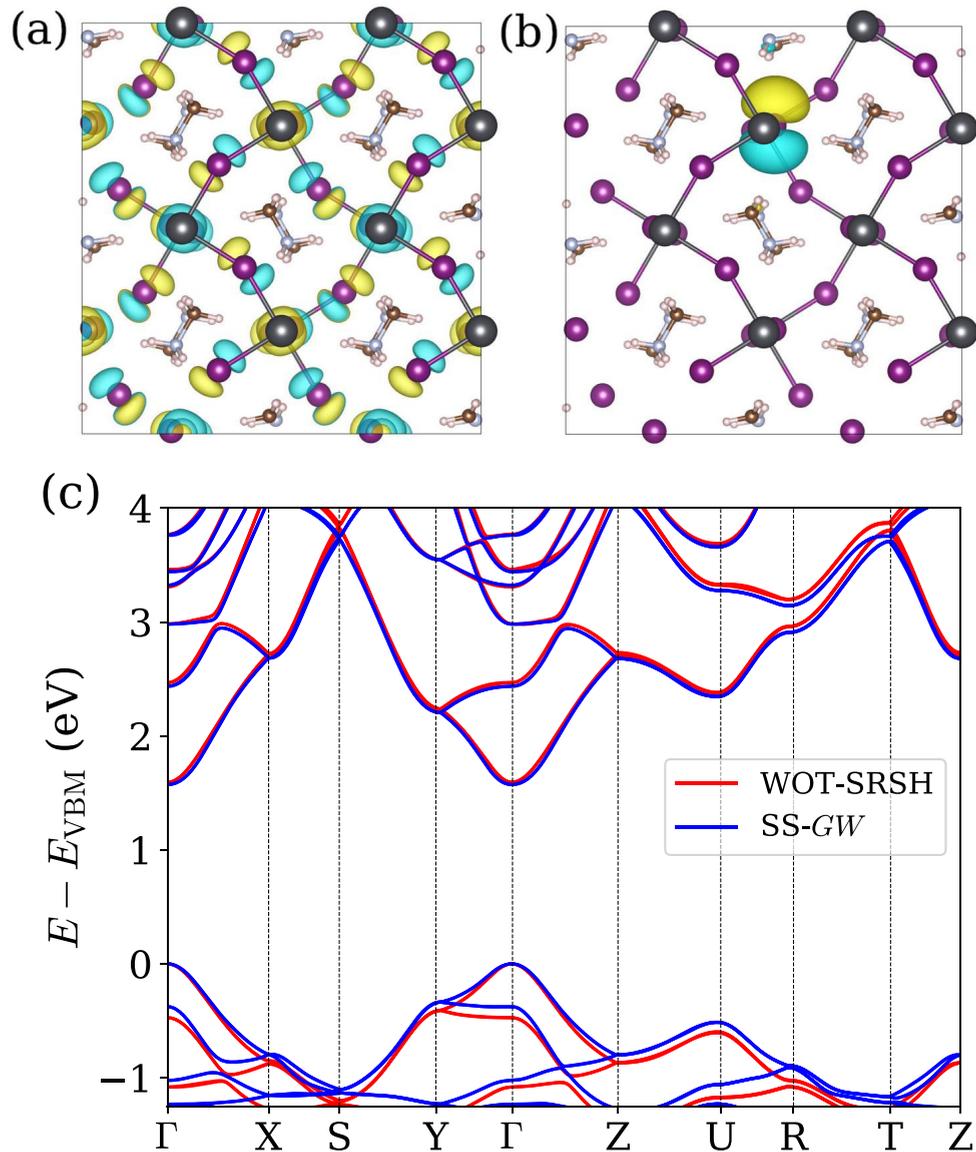


FIG. 1. Illustration of the WOT-SRSH approach for the case of  $\text{MAPbI}_3$ . (a) Orbital corresponding to the valence band maximum (VBM), obtained using the Perdew-Burke-Ernzerhof (PBE) functional [59], and (b) highest-energy maximally localized Wannier function used for calculating the constrained energy. Black: Pb atoms. Purple: I atoms. Gray: N atoms. Brown: C atoms. Pink: H atoms. The wave-function isosurface is shown in blue (positive values) and yellow (negative values) for values of  $\pm 2 \times 10^{-4} \text{ bohr}^{-3}$  for the VBM and  $\pm 1 \times 10^{-3} \text{ bohr}^{-3}$  for the Wannier function. (c) Band structure calculated using WOT-SRSH, compared with that obtained from self-consistent scissor  $\text{GW}$  (SS-GW) results of Ref. [23]. Both calculations include spin-orbit coupling.

the orbital corresponding to the valence band maximum, which as expected is delocalized over the supercell. In contrast, Fig. 1(b) demonstrates the localized nature of the highest-energy maximally localized Wannier function used for calculating  $E_{\text{constr}}^{\gamma}[\phi](N-1)$  in Eq. (2). This Wannier function has a dominant I  $p$ -orbital character (96%), in agreement with the expected valence band composition of the studied systems [60,61]. Because the valence band has a mixed character (mostly I  $p$ , Pb  $s$ , and Pb  $p$ ), there are multiple Wannier functions that are lower in energy and distinct in orbital character. As a typical example, if we choose a Wannier function that is 0.3 eV lower in energy, with 85% I  $p$  character

and 11% Pb  $p$  character, the resulting band gaps change by  $\sim 0.1$  eV.

To assess the accuracy of our method, in Fig. 1(c) we compare the band structure obtained from WOT-SRSH (see Supplemental Material [48] for computational details) to the one obtained from self-consistent scissor  $\text{GW}$  (SS-GW) in Ref. [23]. SS-GW is based on iteratively applying a rigid scissor shift of energies appearing in both the Green's function and the screened Coulomb interaction [16], and has achieved good accuracy in predicting the quasiparticle band gap and reduced effective mass of orthorhombic  $\text{MAPbI}_3$  [23]. We observe very good agreement between the two band structures. For the top four valence bands and bottom four conduction

TABLE I. Effective masses of MAPbI<sub>3</sub> from WOT-SRSH compared to SS-GW (from Ref. [23]) and experiment (from Ref. [64]).  $m_e^*$ ,  $m_h^*$ , and  $\mu$  are the electron, hole, and reduced effective masses, respectively, where  $\mu = [(m_e^*)^{-1} + (m_h^*)^{-1}]^{-1}$ , given in units of the electron rest mass.

	WOT-SRSH	SS-GW	Experiment
$m_e^*$	0.16	0.22	
$m_h^*$	0.15	0.23	
$\mu$	0.08	0.11	$0.104 \pm 0.003$

bands (each of which allows for spin-orbit splitting) the mean absolute deviation is 0.08 eV and the largest deviation is 0.18 eV. These deviations are small and in line with previous comparisons of SRSH and GW band structures [62,63]. In Table I we further compare between the effective masses extracted from the two band structures (see Supplemental Material [48] for computational details). Notably, the effective masses obtained from WOT-SRSH are smaller than the ones obtained from SS-GW. However, the reduced effective mass is in good agreement with experimental measurements. A smaller effective mass is an indication of wider bandwidth,

in line with previous comparisons of SRSH and GW bandwidths [62,63].

In Table II and Fig. 2 we compare the fundamental band gaps predicted using WOT-SRSH to experimental band gaps. We emphasize several important considerations for this comparison. First, when comparing the WOT-SRSH fundamental band gaps with experimental band gaps deduced from optical experiments, we neglect the effect of the exciton binding energy, which is of the order of 20–150 meV for the studied materials [53,64,76–78]. Second, the zero-point renormalization energy, shown to be important in our previous work [25], especially for wide band-gap insulators, is neglected here as it is expected to be very small for compounds containing heavy elements as Pb, Sn, I, and Br. Third, we note that thermal fluctuations are present in the orthorhombic phase, but are expected to be small (up to  $\sim 0.1$  eV) in the temperature range at which this phase is stable [12,15,77]. Furthermore, Das *et al.* [13] have recently reviewed the experimental band gaps of many HaPs in different phases, demonstrating a spread of 0.1–0.2 eV in the measured band gap for each material, depending on the experimental technique used.

We observe excellent agreement with respect to experiment, with a formal (i.e., excluding the effects discussed above) MAE of only  $\sim 0.1$  eV and a largest error of  $\sim 0.3$  eV,

TABLE II. Parameters of WOT-SRSH and the resulting predicted fundamental band gaps, compared to experimental optical band gaps (see text for a discussion of experimental and computational uncertainties) and prior GW results. All band-gap measurements are for the orthorhombic phase, except for CsSnBr<sub>3</sub>, where the measurement is for the cubic phase. All WOT-SRSH and GW band gaps include spin-orbit coupling effects. The reference GW values are for the same orthorhombic phase unless otherwise indicated. Also given are the formal mean absolute error (MAE) and mean sign error (MSE),  $E_g^{\text{WOT-SRSH}} - E_g^{\text{expt}}$ .

	Lattice parameters $a, b, c$ (Å)	$\alpha$	$\gamma$ (bohr <sup>-1</sup> )	$\epsilon_\infty$	$E_g^{\text{WOT-SRSH}}$ (eV)	$E_g^{\text{expt}}$ (eV)	$E_g^{\text{GW}}$ (eV)
CsPbI <sub>3</sub>	8.86, 8.58, 12.47 <sup>a</sup>	0.42	0.12	4.84	1.6	1.6 <sup>g</sup>	2.0, <sup>m</sup> 1.7, <sup>n</sup> 1.8 <sup>o</sup>
CsPbBr <sub>3</sub>	8.25, 8.20, 11.75 <sup>b</sup>	0.42	0.10	3.99	2.2	2.3 <sup>h</sup>	2.2 <sup>o</sup>
CsPbCl <sub>3</sub>	7.90, 7.90, 11.25 <sup>b</sup>	0.42	0.10	3.50	2.9	2.9 <sup>h</sup>	2.7 <sup>o</sup>
CsSnI <sub>3</sub>	8.69, 8.64, 12.38 <sup>c</sup>	0.42	0.14	5.71	1.0	1.3 <sup>i</sup>	1.5, <sup>o</sup> 1.3 <sup>p</sup>
CsSnBr <sub>3</sub>	8.20, 8.02, 11.58 <sup>d</sup>	0.42	0.14	4.34	1.7	1.7 <sup>j</sup>	1.7 <sup>o</sup>
MAPbI <sub>3</sub>	8.84, 8.55, 12.58 <sup>e</sup>	0.42	0.13	4.89	1.6	1.6 <sup>k</sup>	1.8, <sup>q</sup> 1.6 <sup>r</sup>
MAPbBr <sub>3</sub>	8.57, 8.00, 11.86 <sup>f</sup>	0.42	0.15	4.00	2.2	2.3 <sup>l</sup>	
MAE (eV)					0.1		
MSE (eV)					-0.1		

<sup>a</sup>Reference [49].

<sup>b</sup>Reference [65].

<sup>c</sup>Reference [66].

<sup>d</sup>Reference [67].

<sup>e</sup>Reference [68].

<sup>f</sup>Reference [69].

<sup>g</sup>Reference [70]. From optical absorption spectra at room temperature (RT).

<sup>h</sup>Reference [65]. From UV-vis spectroscopy diffuse reflectance at RT.

<sup>i</sup>Reference [71]. From optical diffuse reflectance measurements at RT.

<sup>j</sup>Reference [72]. From UV-vis-NIR absorption spectra at RT. Cubic phase.

<sup>k</sup>Reference [52]. From UV-vis absorption spectra at 4 K.

<sup>l</sup>Reference [73]. From magneto-optical transmission spectroscopy at 2 K.

<sup>m</sup>Reference [24].  $G_0W_0$ @PBE0.

<sup>n</sup>Reference [24].  $G_0W_0$ @HSE.

<sup>o</sup>Reference [11]. Quasiparticle self-consistent GW, including vertex corrections in the screening and finite-temperature effects. Cubic phase.

<sup>p</sup>Reference [74]. Quasiparticle self-consistent GW.

<sup>q</sup>Reference [75]. Quasiparticle self-consistent GW.

<sup>r</sup>Reference [23]. Self-consistent scissor GW.

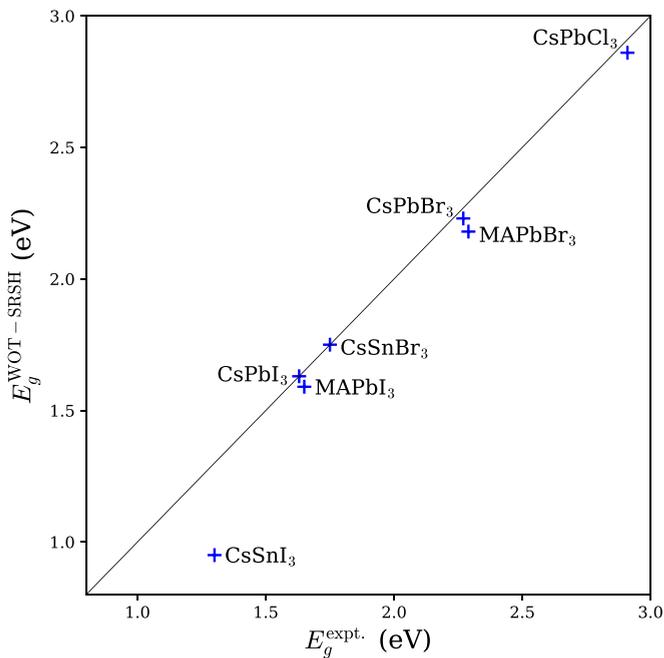


FIG. 2. Band gaps predicted by WOT-SRSH, including spin-orbit coupling effects, compared to experimental band gaps. The straight line indicates perfect agreement.

for CsSnI<sub>3</sub>. Taking into account all the considerations discussed above, a formal MAE of  $\sim 0.1$  eV indicates that the theoretical result is consistently within the experimental uncertainty window. Finally, we note that the small MAE is of the same order of errors in DFT calculations that can occur owing to various implementation issues [79], in particular the level at which spin-orbit coupling is treated.

We further compare to band gaps obtained from *GW* calculations of different flavors. The *GW* band gaps are either

for the same orthorhombic phase or for the cubic phase with appropriate finite-temperature corrections. The WOT-SRSH band gaps also compare well with the *GW* band gaps, with CsSnI<sub>3</sub> again being a slight outlier, indicating a comparable level of accuracy.

#### IV. CONCLUSIONS

In this paper, we have applied our recently developed WOT-SRSH method for the nonempirical prediction of band gaps of crystalline solids, to a set of seven well-studied HaPs. We found a formal MAE of  $\sim 0.1$  eV with respect to experimental values, indicating excellent agreement, and demonstrated a comparable level of accuracy with *GW* at a significantly lower cost. We showed that WOT-SRSH is predictive beyond the prototypical semiconductors studied in our previous work [25], thus demonstrating its accuracy for more complex systems.

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