

The structural, electronic, and optical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$

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Abstract.

Organic-inorganic halide perovskites are promising candidates for low cost, high-efficiency solar cells. We examined the structural, electronic, and optical properties of the low temperature tetragonal phase of the halide perovskites $\text{CH}_3\text{NH}_3\text{PbI}_3$ using Density Functional Theory (DFT). Our numerically predicted structure is in agreement with existing experimental data. DFT electronic structure calculations show that relativistic effects are important for the heavy lead atom and spin-orbit coupling has to be included for accurate results. The experimental band gap of 1.63 to 1.66 eV is similar in magnitude to the DFT direct gap of 1.72 eV, which suggests that many-body and relativistic effects cancel in this compound. Our calculated fundamental gap, at the G_0W_0 level of approximation, is 2.48 eV. Optical anisotropy of tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ was investigated by including many-body effects at the time dependent Hartree Fock and the Bethe-Salpeter equation level of approximation, with input data from a range separated Heyd-Scuseria-Ernzerhof DFT functional calculation. The optical edge for radiation polarized parallel to the a - and b -axes differ by about 0.15 eV and for polarization parallel to the b - and c -axes the difference is about 0.05 eV.

1. Introduction

Since the high power conversion efficiency of 16% to 21% [1, 2, 3, 4] was reported for mixed perovskites based solar cell (PSCs) from 2012 to 2015, metal halide perovskites have attracted the interest of researchers in the materials science community due to their excellent photovoltaic properties [5]. A prototypical example is $\text{CH}_3\text{NH}_3\text{PbI}_3$, which is readily available and inexpensive, easy to manufacture, has a very high diffusion length and high absorption coefficient, making it a promising material for commercialization. At low temperatures $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystallises in an orthorhombic structure [6]. It undergoes a phase transition at 330.4 K to the room temperature tetragonal phase and above 330.4 K it has a cubic structure [7]. The objective of this work was to investigate the structural, electronic and optical properties of the room temperature tetragonal phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ using density functional theory (DFT) and post-DFT many-body perturbation theory.

2. Computational details

All simulations were performed with the Vienna *Ab-initio* simulation package (VASP) [8]. Structural properties were investigated using the Generalized Gradient Approximation (GGA) for the exchange-correlation energy as parametrized by Perdew-Burke-Ernzerhof (PBE) [9]. Atoms were relaxed till all forces were less than 10^{-3} eV/atom. These parameters were sufficient to produce converged results. The electronic structure was investigated at the DFT level using PBE and the Heyd-Scuseria-Ernzerhof (HSE) functional [10, 11] to describe electron exchange and correlation effects. In order to obtain the optical spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$, we used two different approaches. First, we solved the Bethe-Salpeter-equation (BSE) for electron-hole excitations [12, 13, 14, 15], using the PBE-GW results as input [16, 17]. Second, we used time-dependent hybrid functional calculations (TD-HSE) to include exciton effects, which depend on the exchange-tuned hybrid HSE functional. In this approach the exciton effects are approximately described by replacing the electron-hole ladder diagrams with the screened exchange [18].

3. Results and discussion

3.1. Structural parameters

The lattice parameters of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ tetragonal phase, space group P_1 , were fully optimized using the PBE exchange-correlation approximation. The calculated structural parameters are listed in Table 1, together with the results from representative previous calculations [19] and experimental values [20, 21, 22, 23]. From the results shown in Table 1, we can see that our PBE calculation gives a volume within 0.1% of the experimental volume. This is better than the volume reported in similar previous calculations [19, 24]. We do not have an explanation for the difference, apart from possible different convergence criteria used.

Table 1. Calculated equilibrium lattice constants and cohesive energy for $\text{CH}_3\text{NH}_3\text{PbI}_3$, together with the previously calculated and experimental values.

	a (Å)	c (Å)	V (Å ³)	E_{coh} (eV/atom)
This work (PBE)	8.800	12.685	982.33	-3.06
Previous [19]	8.887	13.020	1028.33	–
Previous [24]	8.940	12.980	1037.40	–
Exp. [20, 21].	8.855	12.659	992.60	–
Exp. [22, 23].	8.80	12.685	982.33	–

3.2. Electronic properties

We investigated the electronic structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ at the DFT level using PBE with spin-orbit coupling (PBE-SOC) and without spin-orbit coupling (PBE). The presence of the heavy Pb element introduces significant relativistic effects as can be seen in Figure 1. Our calculations confirm that tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ has a direct band gap at the Γ point. The PBE and PBE-SOC bands have similar structures, but the dispersion of the low lying PBE-SOC conduction bands show larger dispersion. Band gaps calculated using different approaches are shown in Table 2. Non-relativistic local and semi-local exchange-correlation Kohn-Sham (KS) approximations tend to under estimate band gaps while hybrid- and meta-GGA approximations in generalized Kohn-Sham calculations tend to improve band gap approximations [9]. Contrary to the general trend, both the KS PBE and generalized KS HSE gaps are larger than the experimental gap. Inclusion of spin-orbit coupling (SOC) reduces the KS-PBE gap from 1.72 eV

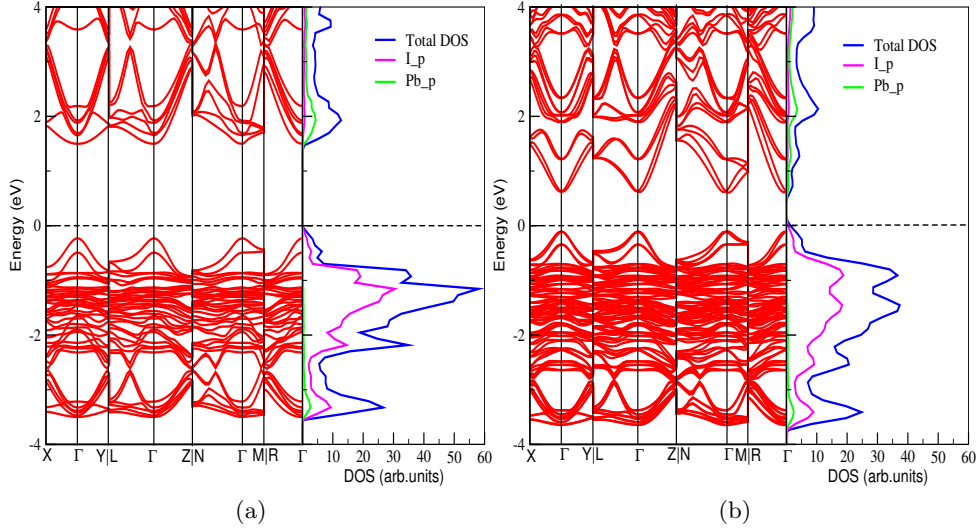


Figure 1. Band structure, total density of states, and partial density of states for $\text{CH}_3\text{NH}_3\text{PbI}_3$ using PBE (a) without SOC (b) with SOC.

to 0.71 eV, a change of 1.01 eV, which is of the same order of magnitude as the experimental gap. The generalized KS HSE gap is reduced by 1.34 eV when SOC is included and the resulting gap underestimates the experimental value. This clearly shows that relativistic effects are important for calculating electronic properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Table 2. Calculated band gap of $\text{CH}_3\text{NH}_3\text{PbI}_3$, together with the previously calculated and experimental values.

Method	Band gap (eV)
PBE	1.72
PBE-SOC	0.71
HSE	2.39
HSE-SOC	1.05
GW	2.48
Theory [19]	1.89
Theory [25]	1.33
Theory (PBE+SOC) [25]	0.09
Exp.[20, 21].	1.63
Exp.[22, 23].	1.66

3.3. Optical properties

We investigated optical properties for the room temperature tetragonal phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the TD-HSE and HSE-GW-BSE approximations without spin-orbit coupling by calculating the real part $\epsilon_{re}(\omega)$ and imaginary part $\epsilon_{im}(\omega)$ of the dielectric tensor, the absorption coefficient $\alpha(\omega)$ and the refractive index $n(\omega)$. In Table 3 we list the real part of the static dielectric constant $\epsilon(0)$ and static limit of the refractive indices. It is clear from the table that tetragonal

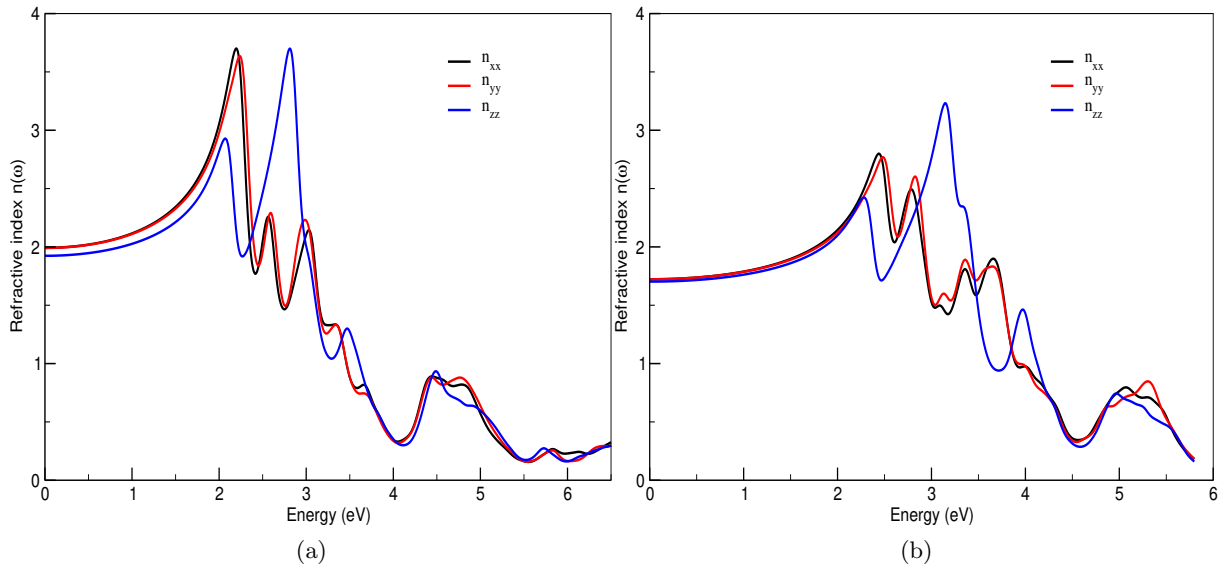


Figure 2. (a) The refractive indices obtained by (a) HSE-GW-BSE and (b) hybrid TD-HSE for $\text{CH}_3\text{NH}_3\text{PbI}_3$.

$\text{CH}_3\text{NH}_3\text{PbI}_3$ is optically anisotropic. Reflection for radiation polarized in the x - or (y -) plane differs from the reflection of radiation polarized in the z -plane where the x , y and z directions coincide with the a , b and c axes of the tetragonal system. Unfortunately the HSE-GW-BSE and TD-HSE approximations do not agree on the polarization for maximum static reflection. The energy dependent refractive index $n(\omega)$ is shown in Figure 2. The highest refractive index was found for polarization in the z -plane around 3.7 eV and 3.22 eV by using BSE and TD-HSE respectively, which is located in the ultraviolet range. The sharp peaks in the refractive index spectrum result from exciton transitions.

Table 3. The static dielectric constant $\epsilon(0)$ and static refractive indices $n(0)$ obtained with HSE-GW-BSE and TD-HSE.

METHOD	$\epsilon_1(0)$	$\epsilon_{1xx}(0)$	$\epsilon_{1yy}(0)$	$\epsilon_{1zz}(0)$	$n(0)$	$n_{xx}(0)$	$n_{yy}(0)$	$n_{zz}(0)$
GW(BSE)	3.75	3.91	3.91	3.60	1.95	1.99	1.99	1.91
TD-HSE	2.91	2.97	2.97	2.85	1.70	1.69	1.69	1.71

In Figure 4 we also see from the different energy dependence of the absorption coefficient components that the optical absorption is anisotropic. The optical band gap (E_g) was estimated using the Tauc approach [26] by plotting $(\alpha E) = A(E - E_g)^{1/2}$ as a function of energy. The gap is estimated by extrapolating the best linear fit to the x -axis ($\alpha E = 0$) as shown in Figure 3.

The absorption coefficient is an important optical constant $\alpha(\omega)$, and is a measure of the amount of light absorbed by given medium. In Figure 4 the main peaks in α_{zz} is higher than those for α_{xx} and α_{yy} which means that absorption polarization in the z -plane is greater than for polarization in x - or y -planes. The exciton binding energy E_b , defined as the difference between the GW band gap and the optical absorption edge at the BSE level of approximation. The lowest exciton binding energy for our calculations is $E_b = 0.38$ eV.

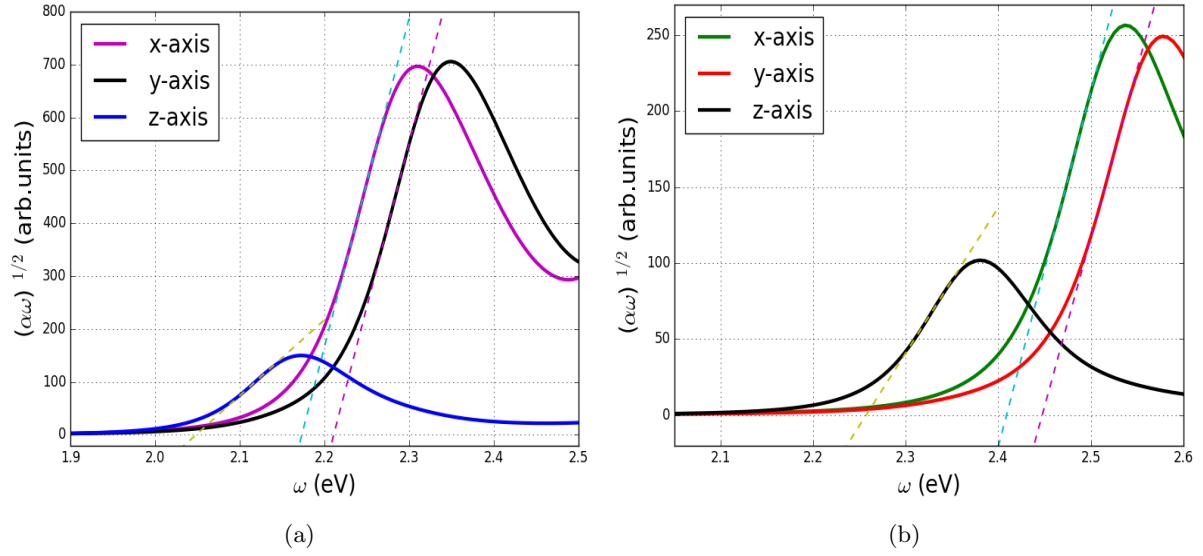


Figure 3. Optical band gaps obtained by Tauc plots for (a) HSE-GW-BSE and (b) hybrid TD-HSE calculations for $\text{CH}_3\text{NH}_3\text{PbI}_3$.

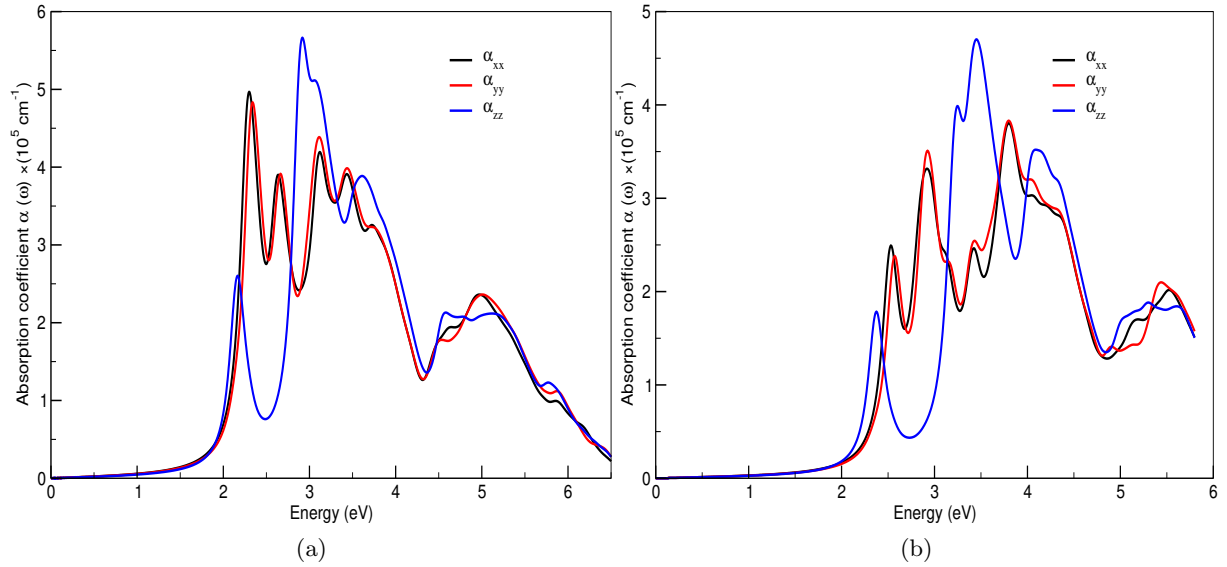


Figure 4. (a) The absorption coefficient obtained by HSE-GW-BSE and (b) hybrid TD-HSE.

3.4. Conclusion

In summary, structural, electronic and optical properties of the organic-inorganic halide perovskites were investigated using Density Functional Theory. The PBE predicted structural lattice parameters and volume are in good agreement with experimental values. Electronic properties were studied by calculating the band structure, with and without SOC. The results show that tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ is a direct band gap semiconductor with a gap at Γ . Relativistic effects are important due to the presence of heavy Pb atoms. Optical properties

show anisotropy with peak absorption strength for polarization parallel to the c -axis.

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