Optoelectronic properties of Halide Perovskite: needs for extremely demanding high performance computing

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Chercheurs dans les domaines de la Chimie et Physique

(Workshop CINES)
Best research-cell efficiencies (NREL) chart (non-concentrator)
Introduction

\[ -\frac{\hbar^2}{2m_e} V_j^2 + V_{KS}[n](r) - \epsilon_j \right] \varphi_j(r) = 0 \]

\[ V_{KS}(r) = V_{ext}(r) + V_H(r) + V_{xc}(r) \]

\[ V_{xc}(r) = \frac{\partial E_{xc}[n](r)}{\partial n(r)} \]

- Spin-Orbit coupling
- Van der Waals bonding
- Band gap problem/Band structure accuracy

limits of current implementations of DFT

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Introduction

Spin-Orbit Coupling (SOC)

Electronic band structures of GaAs (left, SG: F-43m) and MAPbI$_3$ (right, SG: Pnma) materials without (blue) and with (red) SOC. The energy of the valence band maximum is set at zero and the SOC effect is marked in red as $\Delta_{\text{SOC}}$.

Phonon dispersion of 2H-PbI$_2$ material without (blue) and with (red) SOC

The disadvantage of the SOC is the computational cost about double and the memory is increasing around 5% compared to a LDA/GGA functional.

*J Even et al. J. Phys. Chem. Let. 4, 2999, 2013 (left)*

*HDR Pedesseau, 2019 (right)*
Van der Waals bonding

The disadvantage of the van der Waals corrections is the computational cost from 1.5 to 5 compared to a LDA/GGA functional.
i) Band gap problem/band structure accuracy

Band gaps for the DFT and HSE03\(^1\) functional with \(\mu=0.3\text{Å}^{-1}\). The latter yields consistently improved band gaps. Source (reference\(^2\))


Band gap energies calculated in PBE including SOC effect plus HSE corrections as a function of \(\mu\), in \(\text{Å}^{-1}\), the range separation parameter for CsPbI\(_3\) and MAPbI\(_3\) materials

\(\mu=0.2(0.3)\) is for HSE06(HSE03) respectively. @HDR Pedesseau, 2019

The disadvantage of the hybrid functional is the computational cost from 10 to 100 and the memory demanding compared to a LDA/GGA functional.
ii) Band gap problem/band structure accuracy

The disadvantage of the scGW corrections is the computational cost from 50 to 500 for each step and the memory demanding becomes huge compared to a LDA/GGA functional and even to hybrid functionals.

DFT and scGW band gaps with attractive electron-hole interaction (vertex corrections in W). Source (reference\(^1\)).

In reality, this method is so demanding that it is very challenging to use it for more than 250 occupied and unoccupied bands and a dozen of k points in the Brillouin zone.

The advantage of the scGW corrections is the computational cost from 50 to 500 for each step and the memory demanding becomes huge compared to a LDA/GGA functional and even to hybrid functionals.
Comparison of the basic parameter of the simulation such as the total number of cpu, the memory, the execution time, and the gap energy for each method applied to the 2H-PbI$_2$ material.

<table>
<thead>
<tr>
<th>Method</th>
<th>Total cpus</th>
<th>Memory used (Mb)</th>
<th>Time (s)</th>
<th>$E_{\text{gap}}^A$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>144</td>
<td>189.3</td>
<td>12.1</td>
<td>1.74</td>
</tr>
<tr>
<td>PBE+SOC</td>
<td>144</td>
<td>198.0</td>
<td>24.4</td>
<td>1.10</td>
</tr>
<tr>
<td>PBE+SOC+HSE06</td>
<td>144</td>
<td>373.8</td>
<td>6247.3</td>
<td>1.87</td>
</tr>
<tr>
<td>PBE+SOC+sc-GW</td>
<td>456</td>
<td>3418.5</td>
<td>119940.4</td>
<td>2.52</td>
</tr>
</tbody>
</table>

* Monkhorst-Pack grid (6x6x4), cut-off energy 500eV. From experimental measurement$^1$, the band gap energy $E_{\text{gap}}^A = 2.32$eV, at room temperature and 2.55 eV at 4 K.

**Introduction**

**Usual job: VASP on OCCIGEN, CINES**

- Total number of cores: $TNC$

**1\textsuperscript{st} \text{PARAMETER, NPAR}**

- $NPAR$ : number of bands which divided $NBANDS$ (adjusted $NBANDS$).

**2\textsuperscript{nd} \text{PARAMETER, KPAR}**

- $KPAR$ : number of k-points which divided the total number of k-points.

*The ratio has to be in between 6 to 10 to be very efficient!*  

In practice, the ratio has to be 2 or 4 to be very efficient!

Total number of cores: $TNC = KPAR \times NPAR$,  
Total number of nodes: $TNN = TNC / 24$
UNUSUAL job: VASP on OCCIGEN, CINES

OCCIGEN, 1 node : 128 Go/24cores = 5.3Go per core

- vasp insufficient virtual memory:

  1\textsuperscript{st} : Try to increase NPAR and add KPAR=2 ou 4

  \[ \text{TNC} = \text{KPAR} \times \text{NPAR}, \]

  \[ \text{TNN} = \frac{\text{TNC}}{24 \times a}, \]

  Total number of nodes: TNN = TNC/(24*a)

  2\textsuperscript{nd} : Increase “virtually” the memory per core by using a ratio “a” of the available core

  \[ a = \frac{2}{3} \text{ of the available core : } 128 \text{ Go}/16\text{cores} = 8.0\text{Go per core} \]

  \[ a = \frac{1}{2} \text{ of the available core : } 128 \text{ Go}/12\text{cores} = 10.6\text{Go per core} \]
Introduction

Our approach: adapt solid state physics concepts to hybrid Perovskites

- Optical transitions due to Bloch states localized within the inorganic lattice
- Giant spin-orbit effect on the conduction band (CB)
- Strain effect and loss of inversion symmetry (Rashba effect)
- Excitonic effect treated by perturbation: Wannier exciton

J Even et al
PRB 86, 205301, 2012
J Even et al
Introduction

2D Ruddlesden-Popper perovskite solar cells


2D RP perovskite for solar cells
Stability is improved
Introduction

2D Ruddlesden-Popper perovskite solar cells

Flipped structure enhances carrier transport → better efficiency

Hybrid Perovskites: 2D / Quantum confinement

Type I confinement potential:
Schematic picture

Type I confinement potential:
quantitative analysis

D. Mitzi et al. IBM J. RES. & DEV. 2001


D. Mitzi et al. IBM J. RES. & DEV. 2001

B. Traore et al. ACS Nano 2018
Hybrid Dion–Jacobson 2D Lead Iodide Perovskites

L. Mao et al.
JACS, 2018
Hybrid Dion–Jacobson 2D Lead Iodide Perovskites

- Band gap energy decreases when N increases

Exp. data

L. Mao et al.
JACS, 2018
Hybrid Perovskites: 2D and 3D materials

Schematic representations of the in-plane projection of the M−M−X angle $\beta$ and the $\delta$ angle chosen to characterize the in-plane and out-of-plane octahedral tilting.

A distorted $(\text{Cs})_2\text{PbI}_4$ reference structure with axial $d_{\text{ax}}^{\text{Pb-I}}$ and equatorial $d_{\text{eq}}^{\text{Pb-I}}$ distances fixed to 3.18 Å.

Color map of the computed electronic band gap including SOC for a distorted $(\text{Cs})_2\text{PbI}_4$ reference structure as a function of $\beta$ and $\delta$ octahedral tilting angles.

L. Pedesseau et al. ACS Nano, 2016, 10 (11), pp 9776–9786
Dielectric confinement: from 3D to 2D HOPs

Schematic representation of the charge density response to $E$

$E=0$

$E \neq 0$

Electronic contribution

$\varepsilon_{\infty} \rightarrow$

Ionic contribution

$\varepsilon_{\infty} \rightarrow \varepsilon_s$

$\varepsilon(z) = \frac{\varepsilon_0 E_{ext}}{\varepsilon_0 E_{ext} - p_{ind}(z)}$

Even et al., *PCCP* 16, 2014

$\varepsilon_s \rightarrow$ Electronic + ionic contribution
Dielectric confinement: from 3D to 2D HOPs

\( \varepsilon_{\text{static}} \rightarrow \text{Electronic + ionic contribution} \)

D. Sapori et al. Nanoscale, 2016
2D Halide Perovskite: intercalation effect of I$_2$


Intercalation of I$_2$ decreases the Absorbance!
**2D HOP: intercalation effect of I₂**

Intercalation of I₂ increases the organic dielectric part

*M. Smith et al. Chemical science 8 (3), 1960-1968, 2017*
Intercalation of \( I_2 \) dramatically modifies the dielectric function orthogonal to the layers.
Hybrid Perovskites for spintronics?

First prediction in:

**Formulae:**
- $\text{CH}_3\text{NH}_3\text{PbI}_3$
- $\text{CH}_3\text{NH}_3\text{SnI}_3$

**Spin-splitting controlled by an external field**

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Beyond DFT → Tight-Binding modeling

A Marronnier et al. ACSnano 12, 3477, 2018

i) Cubic phase at high temperature (T > 360°C)
ii) Orthorhombic yellow phase at room temperature, very hard to avoid

(a–c) Computed electronic band structures using the TB model (solid lines) and at the scGW+SOC level of theory (symbols) for the experimentally determined crystal structures

Parameterized tight-binding with scGW
Beyond DFT → Tight-Binding modeling

Tight-binding calculations on DFT-relaxed structures

- Local maximum
- Symmetry-breaking
- Actual minimum

- Rashba effect that lifts the spin degeneracy
- Significant increase of the bandgap
- Shift of the energy minima from the high symmetry points of the Brillouin zone (R and Z)

Parameterized tight-binding with scGW
Conclusion

- Importance of dielectric confinement:
  - Layered HOP (contrast organic/inorganic layers)
  - 2D/3D HOP nanoplatelets
- Contributions of surface states in HOP
- Intercalation effect
- Band gap decreases with increasing number $N$ of inorganic layers
• Quantum confinement effects still present at N = 5
• Dielectric confinement almost disappears from N = 4
• Hence the larger exciton binding energies for these 2D systems even at room temperature is probably due to the quantum confinement effect
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