Ab Initio calculations of the temperature-dependent band gap of inorganic halide perovskites

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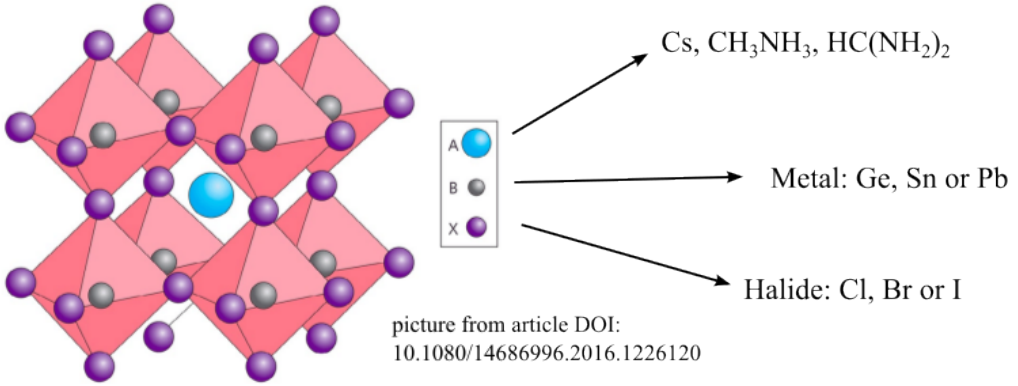
Practical applications of perovskites

Halide perovskites ABX_3:

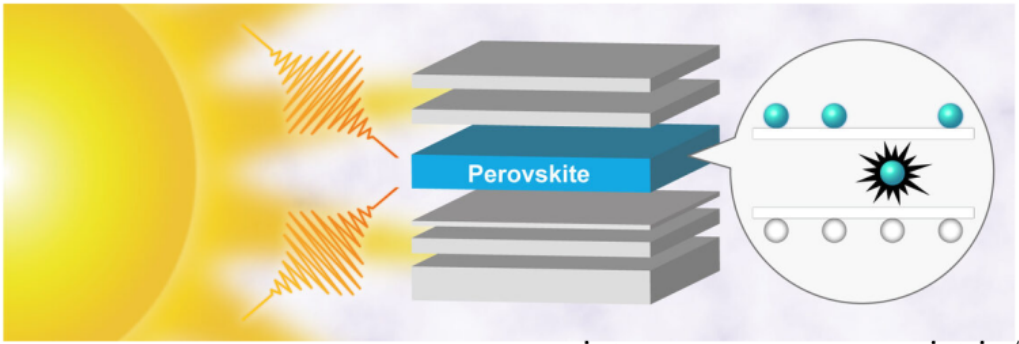
- Inorganic and organic halide perovskites.
- Low-cost and high-performance solar cells.
- Efficiency: 3.8% - 25% (2020).
- Cubic structure at high T.



picture from article DOI: 10.1080/14686996.2016.1226120

Research:

- Studied intensely experimentally.
- Difficult to obtain exp. gaps with ab initio methods.
- Accurate electronic structure for bulk from ab initio models is still lacking.



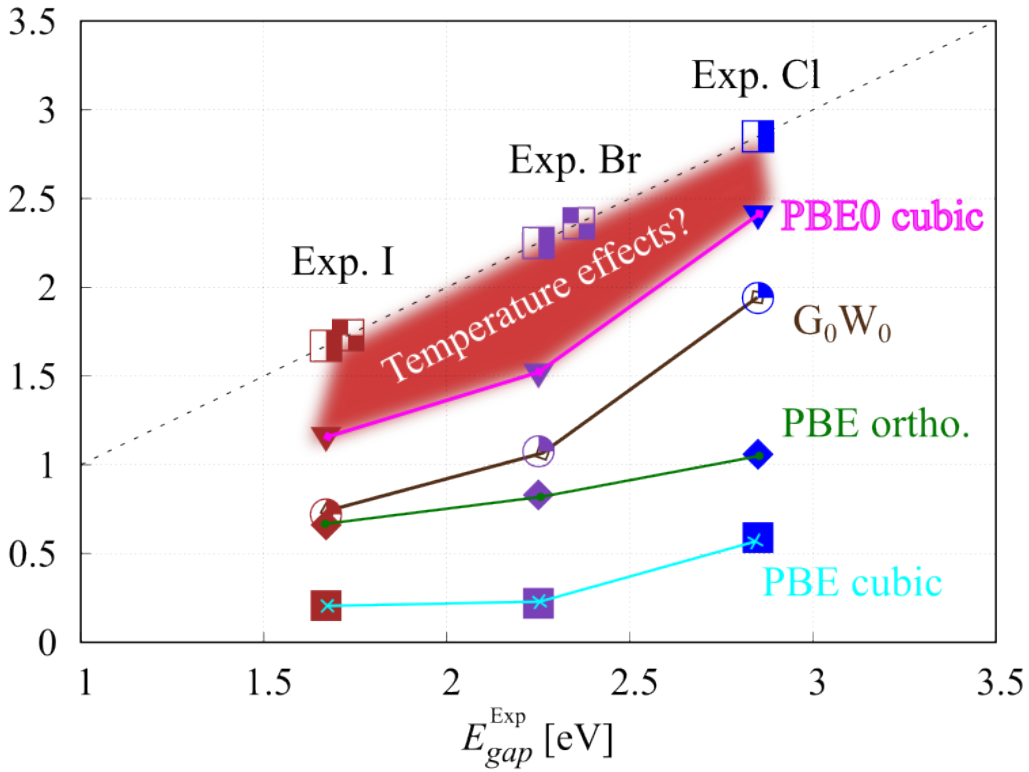
picture source: www.oist.jp/

Ab initio electronic structure - DFT gap problem

DFT improvements:

- GGA instead of LDA (e.g. PBE - cheap, manageable).
- Hybrid functionals (e.g. PBE0: expensive, not always possible).
- GW calculation (very expensive, manageable for small systems).
- Including T effects using electron-phonon interaction (EPI) from AHC theory?

Calculated (y-axis) and experimental (x-axis) gaps for perovskites in eV (SOC included)

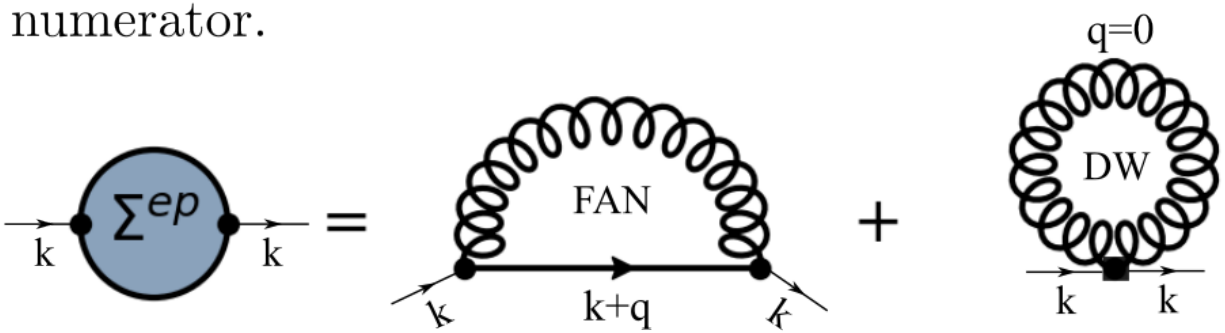


AHC equation and terms

Allen-Heine-Cardona (AHC) theory, in its adiabatic form gives us renormalization in the form of self-energy Σ:

$$\Sigma^{\mathrm{ep}}_{n\mathbf{k}}(T) = \frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}(n_{m\mathbf{q}}(T)+1/2)\sum_{n'}^{M}\left[\frac{\left|g^{\mathrm{FAN}}_{nn'm}(\mathbf{k},\mathbf{q})\right|^2}{\varepsilon_{n\mathbf{k}}-\varepsilon_{n'\mathbf{k}+\mathbf{q}}+i\delta}-\frac{\left|g^{\mathrm{DW}}_{nn'm}(\mathbf{k},\mathbf{q})\right|^2}{\varepsilon_{n\mathbf{k}}-\varepsilon_{n'\mathbf{k}}+i\delta}\right]$$

where $m, \mathbf{q}$ are phonon mode and vector indices and $n, \mathbf{k}$ are electron band and vector indices. In non-adiabatic form, we add/subtract $\hbar\omega_{m\mathbf{q}}$ phonon frequencies in the denomonator ans add/subtract fermion occupancy factors $f_{n,\mathbf{k}}$ in the numerator.



Giustino Phys. Rev. Lett. 105, 2465501 (2010)
Ponce Phys. Rev. B 90, 214304 (2014)
Ponce J. Chem. Phys. 143, 102813 (2015)

Challenges for perovskite electronic structure

DFT challenges:

- At T=0K orthorhombic structure is computationally expensive.
- At T=0K computationally feasible cubic struc. is not a true GS.
- From DFT/DFPT phonon dispersion produces $\omega^2_{m\mathbf{q}} < 0$ which results in imaginary frequencies (a.k.a. silent or negative modes).
- Wrong phonon dispersion will introduce a diveregence in AHC eq.

$$|g_{nn'm}(\mathbf{k},\mathbf{q})|^2 \propto \frac{1}{\omega_{m\mathbf{q}}}$$

high — Temperature — low

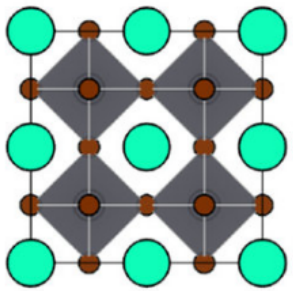
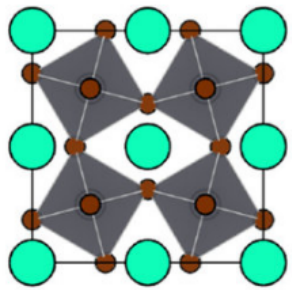
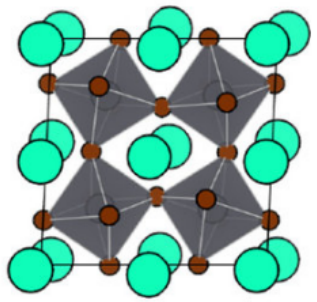
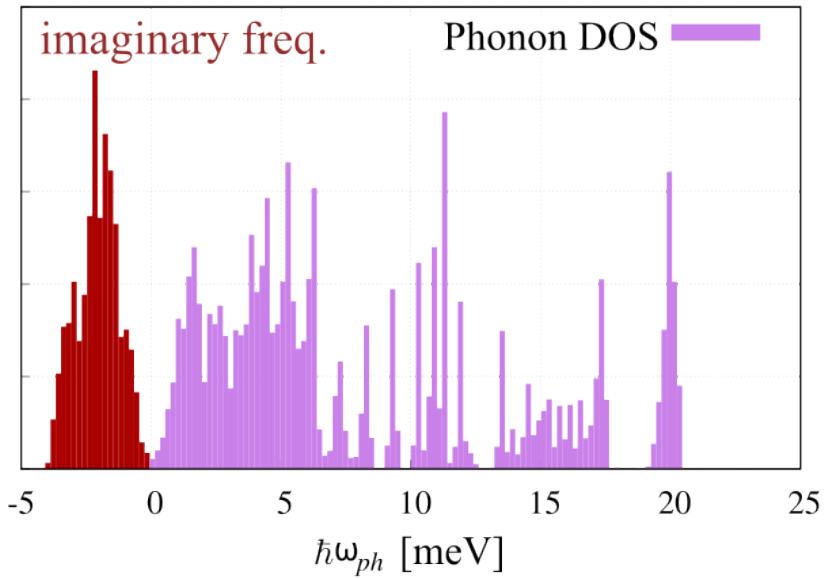
α	β	γ
cubic	tetragonal	orthorhombic
$Pm\bar{3}m$	$P4/mbm$	$Pnma$
		
(000)	$(00a^+)$	$(b^-b^-a^+)$

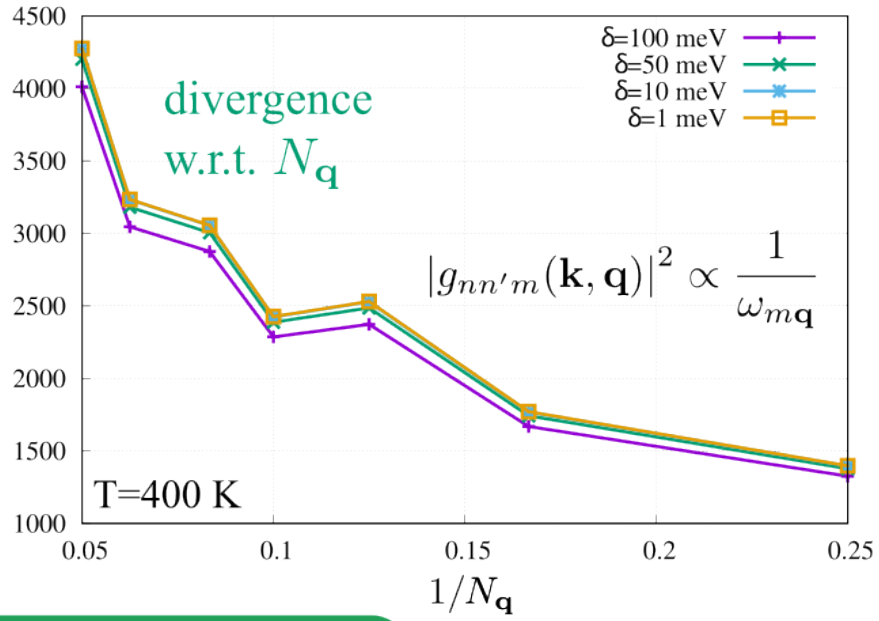
Image from: Phys. Rev. B. 100, 134101.

Challenges for perovskite electronic structure

Phonon density of states



Gap renormalization [meV]



- When performing DFT/DFPT on cubic perovskites, previously mentioned imaginary phonon frequencies appear.
- Even if we remove them completely, AHC equation will diverge w.r.t. the increasing number of sampled q-points.

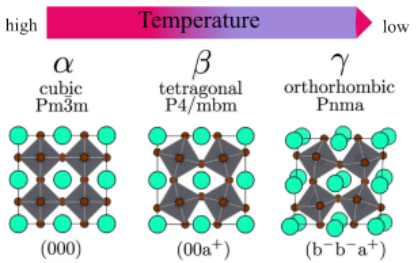
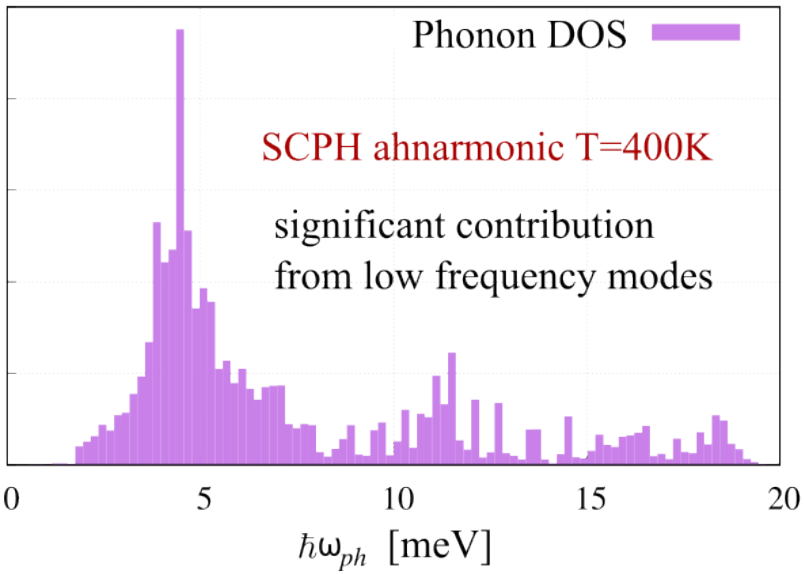


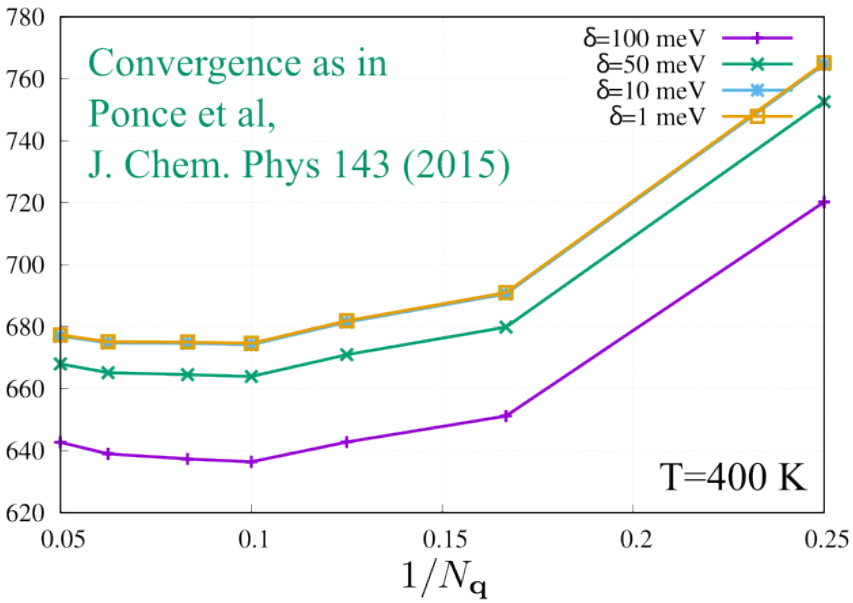
Image from: Phys. Rev. B. 100, 134101.

Going beyond harmonic approximation

Phonon density of states from SCPH



Gap renormalization [meV]



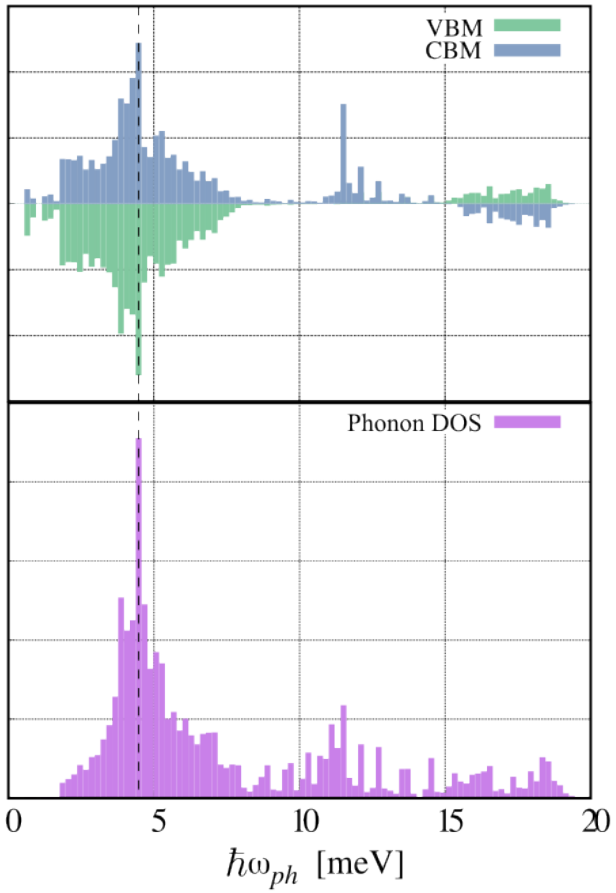
- Self-consistent phonon (SCPH) calculation results in stable structure with anharmonic freq. $\omega^{\text{anh}}_{m\mathbf{q}}$.
- When $\omega^{\text{anh}}_{m\mathbf{q}}$ are used, AHC equation will converge w.r.t. the increasing number of q-points.

Fan and DW terms are now proportional to:

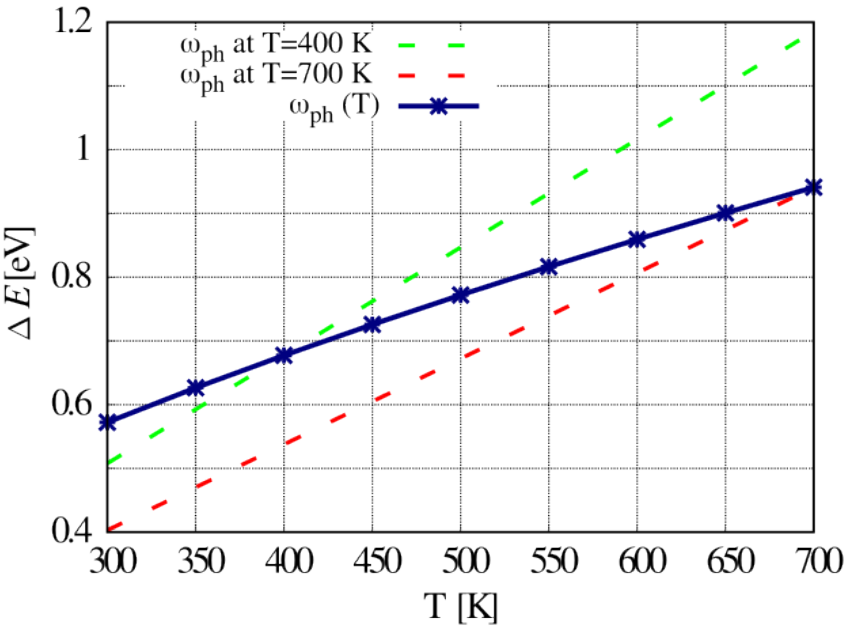
$$|g_{nn'm}(\mathbf{k},\mathbf{q})|^2 \propto \frac{|\mathbf{e}^{\text{DFPT}}_{m,\kappa\gamma}(\mathbf{q})|^2}{\omega^{\text{anh}}_{m\mathbf{q}}(T)} \left|\langle n\mathbf{k}|\, \partial_{\kappa\gamma,\mathbf{q}} v^{DFT}\, |n'\mathbf{k}+\mathbf{q}\rangle\right|^2$$

Going beyond harmonic approximation

Relative contributions of phonons to VBM and CBM renormalization:



Gap renormalization



Gap renormalization is now proportional to:

$$\Delta E(T) \propto \frac{n_{m\mathbf{q}}(\omega^{\mathrm{anh}}_{m\mathbf{q}}, T)}{\omega^{\mathrm{anh}}_{m\mathbf{q}}(T)}$$

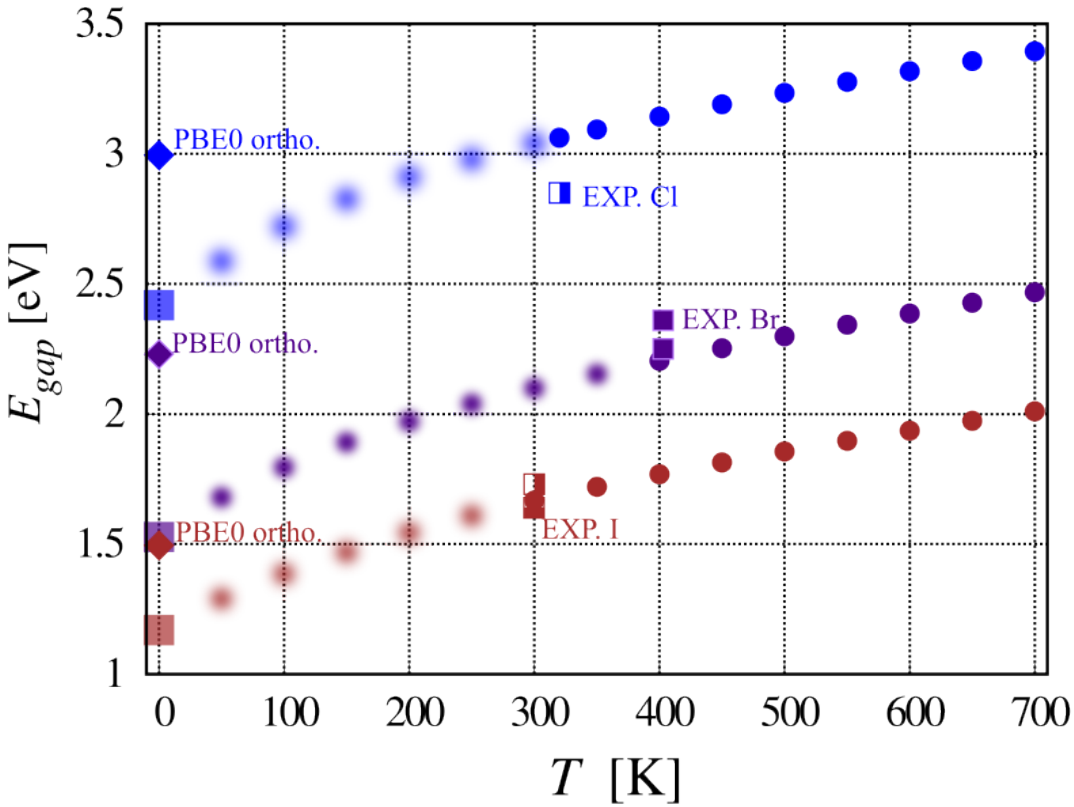
Renormalizing DFT gaps with EPI

Halide perovskite gap renormalization at finite temperature:

- $CsPbCl_3$, cubic phase at T=320 K
- $CsPbBr_3$, cubic phase at T=400 K
- $CsPbI_3$, cubic phase at T=300 K

Ab initio methods used:

- DFT-PBE0 for electronic structure.
- DFPT-PBE for EPI matrix elements.
- SCPH for anharmonic phonon frequencies.
- AHC (non-adiabatic) for temperature renormalization.



Electronic gap at T=0K is obtained from DFT-PBE0 as in:
T. Bischoff et al, Phys. Rev. Mater. 2019, 3, 123802

Conclusion

When performing ab initio calculations on bulk inorganic halide perovskites, we noticed that experimental gap cannot be obtained without the inclusion of temperature effects through EPI. This can be achieved with AHC equation.

Previously, AHC was successfuly used for diamond, Si, GaAs and other semiconductors. When that same type of calculation was performed on inorganic halide perovskites, results were diverging.

To remove this diverngence, we performed an anharmonic SCPH calculation to replace harmonic DFPT phonon frequencies in AHC equation. These phonon frequencies were calculated for a set of finite temperatures. AHC equation now gained temperature dependence in phonon frequencies also.

This renormalization was added to the DFT-PBE0 calculation.

We obtained temperature dependent band gaps for inorganic halide perovskites:

- CsPbCl3, relative error $< 7\%$
- CsPbBr3, relative error $< 6\%$
- CsPbI3, relative error $< 2\%$

Thank you for your attention.