



Modelling solid-state systems: from electronic structure methods to reactive molecular dynamics

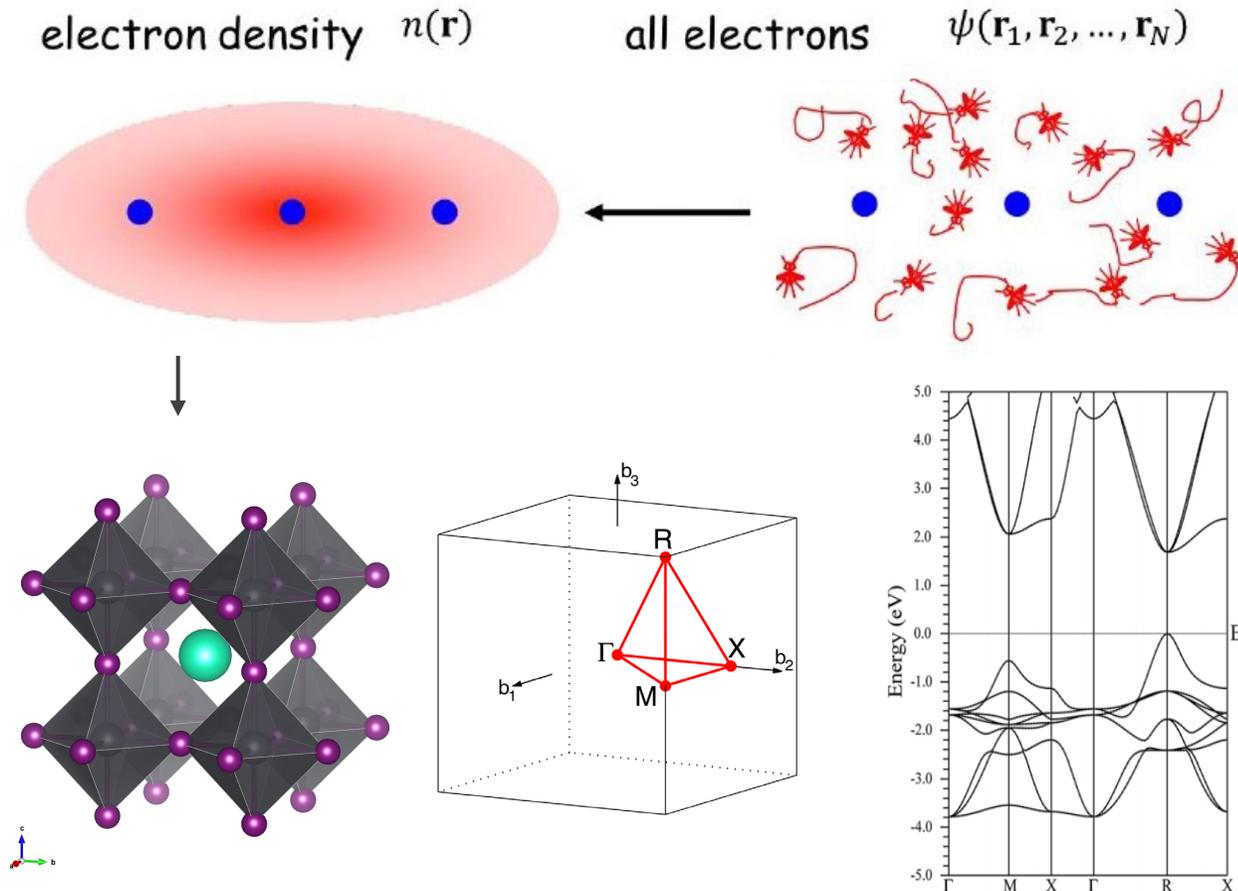
2-12-2021, HAN-SUR-LESSE

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Materials Simulation & Modelling (MSM), Applied Physics

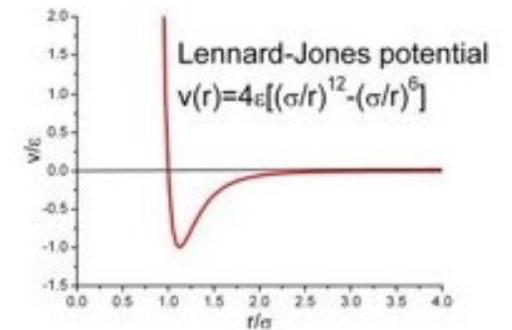
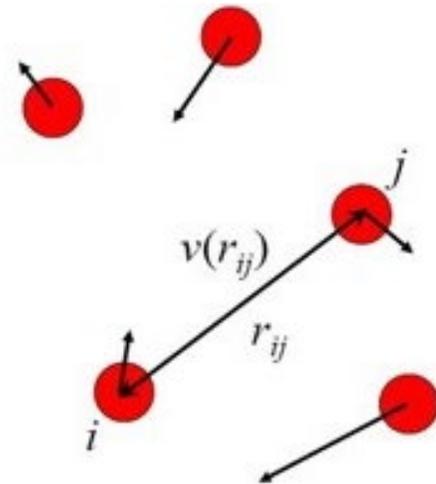
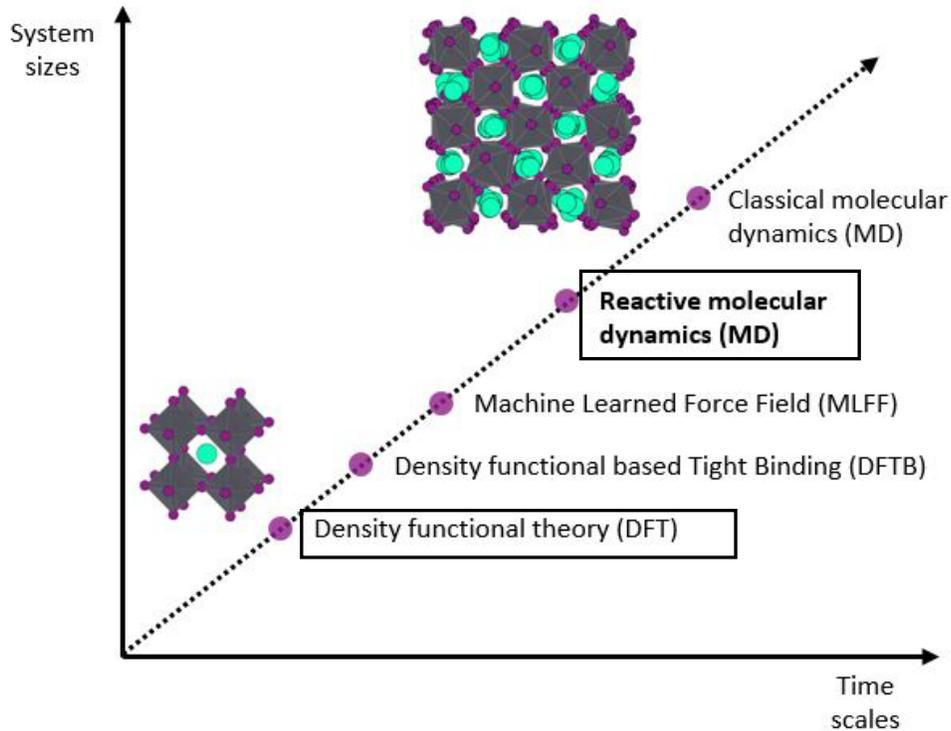
Our method: DFT based multiscale

Our research is mostly **application** focused: complex materials, interplay of physics and chemistry;
We use combinations of a wide range of computational methods and theory;
Our starting point is always **DFT**.



Scaling up DFT by combining with DFTB, MD/MC, ML, other theory (whenever relevant and available).

To study the impact of **dynamical processes** on the properties of materials, we needed efficient methods.

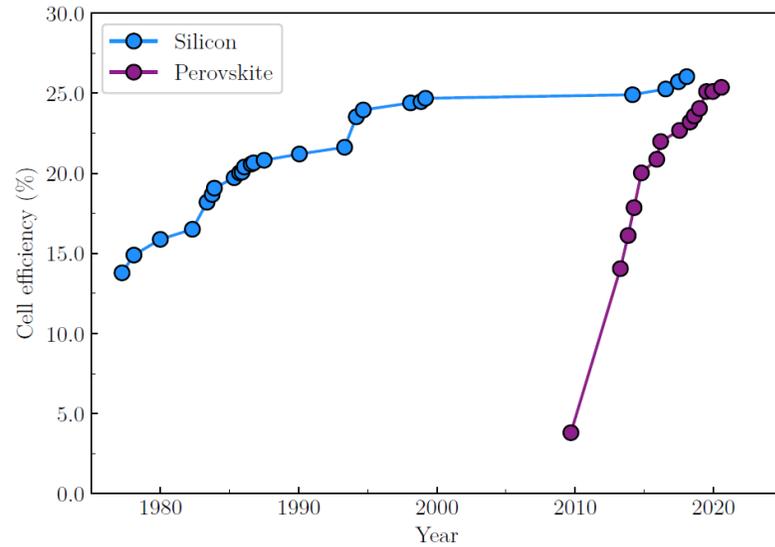


Molecular Dynamics solves Newton's equations of motion to produce **dynamical behavior** as a function of time. MD relies on the **availability of force fields** (interatomic potentials).

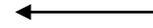
We are working on several FF/potentials. This lecture focuses on the combination of **DFT with ReaxFF reactive MD**.

Our applications: halide perovskites optoelectronics

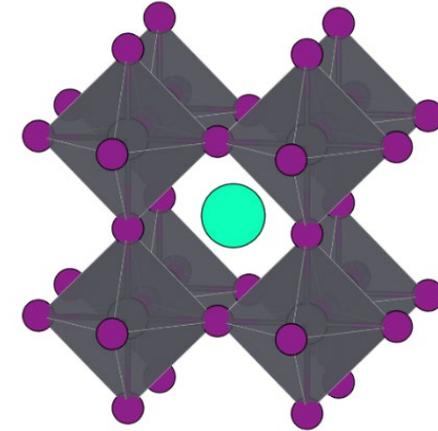
Research solar cell efficiencies:



Tunable band structures
 Room temperature processing
 Defect tolerance (electronically)
 Ideal electronic structures
Easy to make

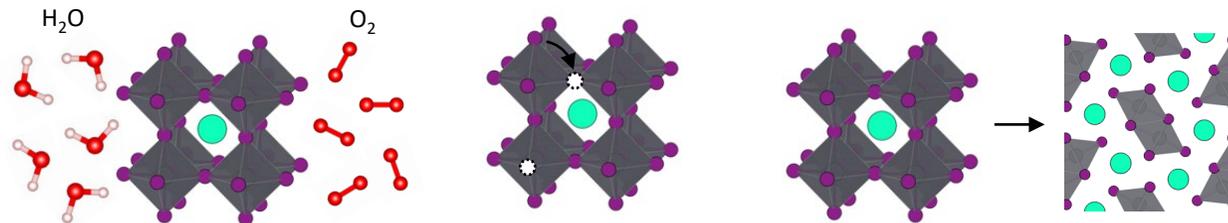
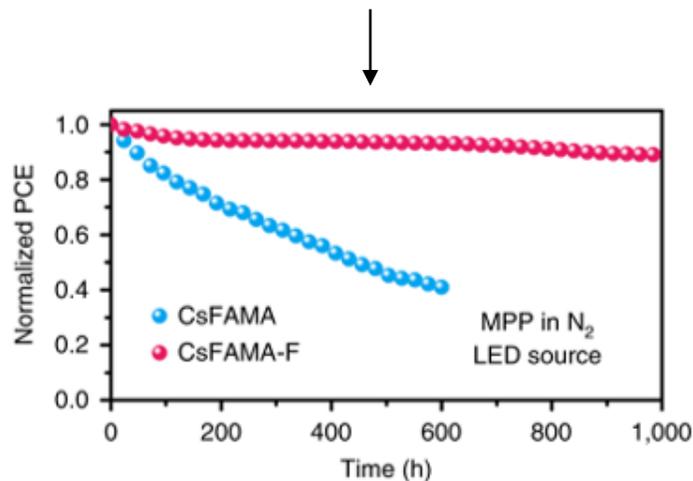


AMX₃ halide perovskite:



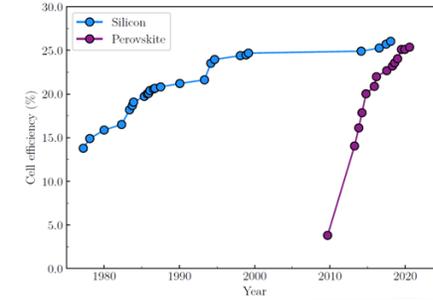
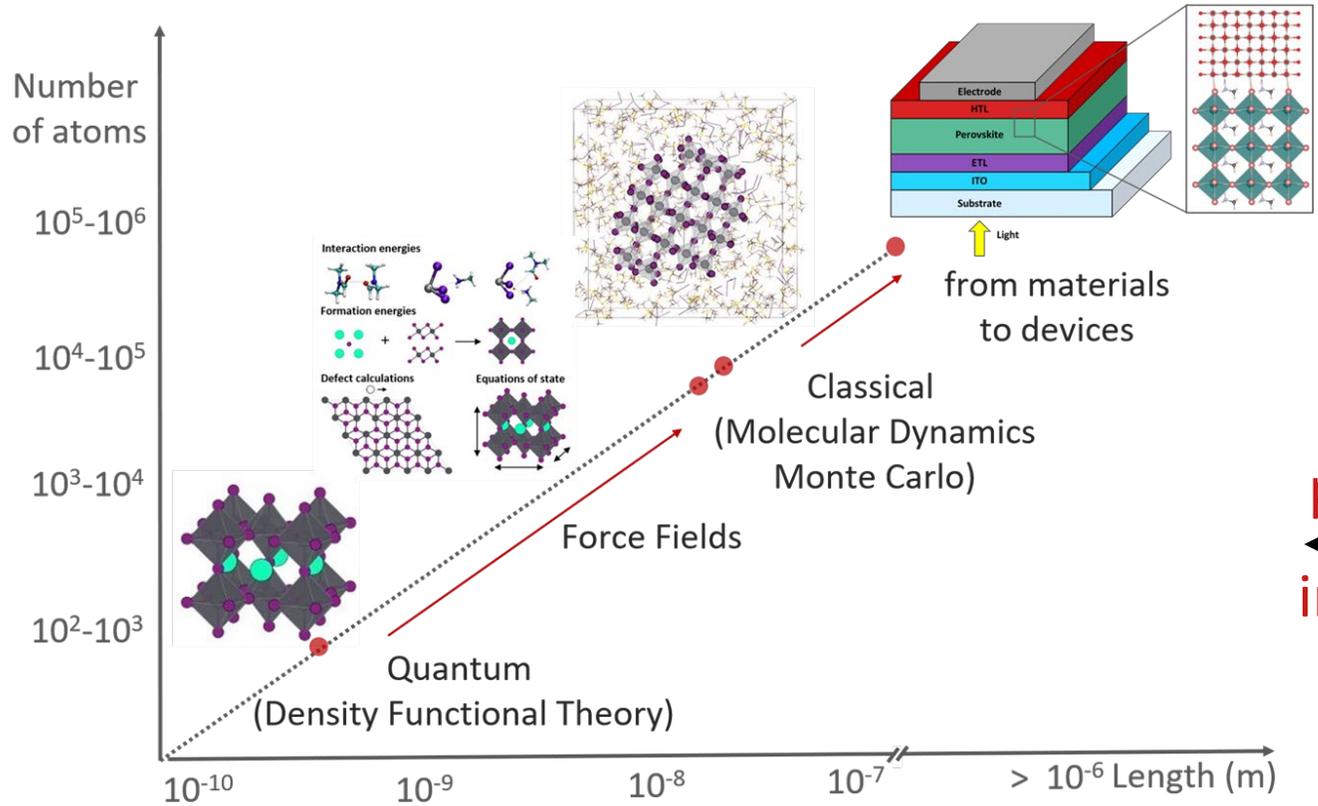
- = A⁺ (organic/inorganic cation)
- = M²⁺ (metal cation)
- = X⁻ (halide anion)

Instability: **easy to break**
 dynamical nature, defects and chemistry
 reactions (with the environments)

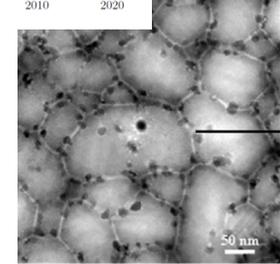


Nature Energy, 4, 408–415 (2019).

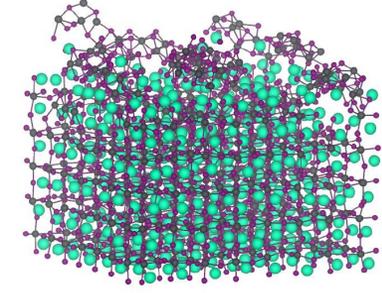
Multiscale method for halide perovskites



efficiency



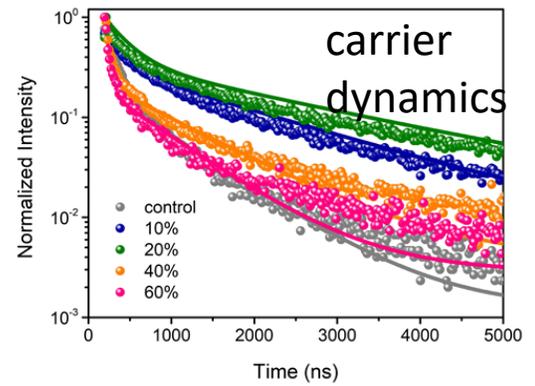
stability



predict

interpret

Experiments



Combining quantum with classical methods in a **multiscale framework**, we gain **predictive power** for large systems at longer time scales.

The framework is applicable for many materials systems.



emission colour

This lecture(s)

- **Theory of DFT (brief) with a focus on electronic structures of solid-state systems (1h)**
- DFT + chemical bonding analysis + tight binding + experiments for halide perovskites (1h) **Assignment 1**
- Theory of MD (brief) and various interactions in materials (basics of force fields) (1h) **Assignment 2**
- Theory of ReaxFF reactive force field (1h) **Assignment 3**
- Reactive MD for halide perovskites (1h)

Special acknowledgement to **Geert Brocks (DFT)** and **Adri van Duin (ReaxFF)** for providing materials, discussion and inspiration for this lecture!

Density Functional Theory calculations

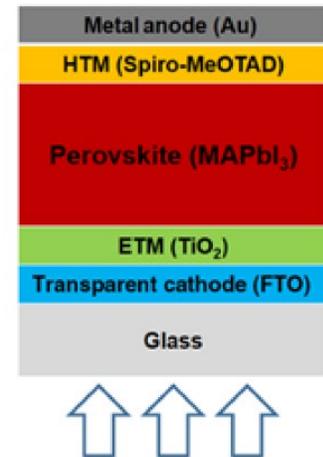
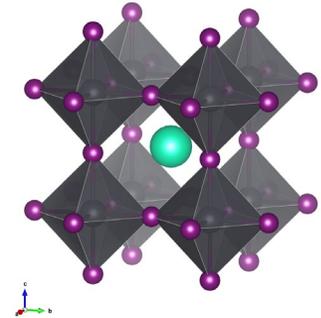
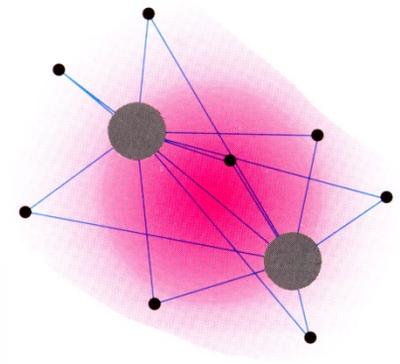
solve quantum mechanical equations for electrons and nuclei **with** approximations

by using standard and/or home-grown codes

calculate/predict structures, total energies, electronic structures, phonons, optical spectra...

of atomic and nano-structures

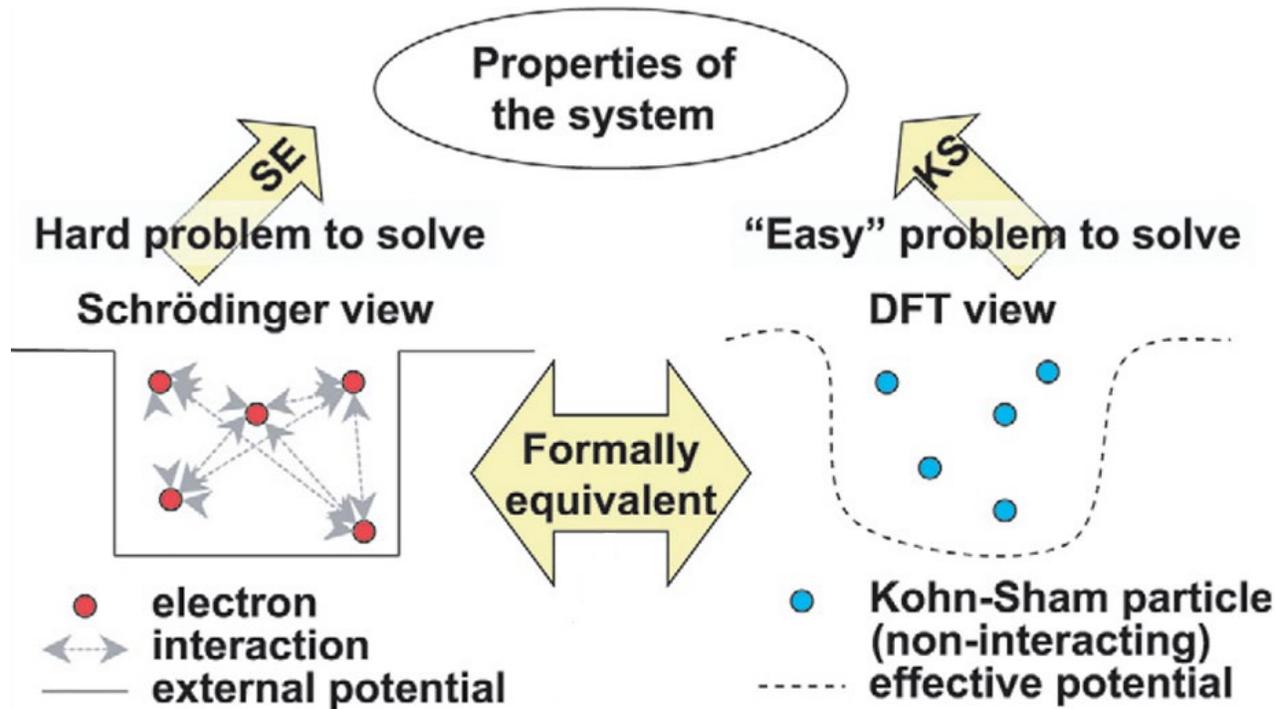
build physical/chemical models to describe physical phenomena **from** material properties **to** device performance



The basis of DFT: Hohenberg-Kohn theorems (1964)

1. The external potential and therefore the total energy is a unique functional of the electron density. Therefore, the Hamiltonian, and hence all ground state properties, are determined solely by the electron density.
2. The functional delivers the lowest/ground state energy of the system if and only if the input electron density is the exact ground state density.

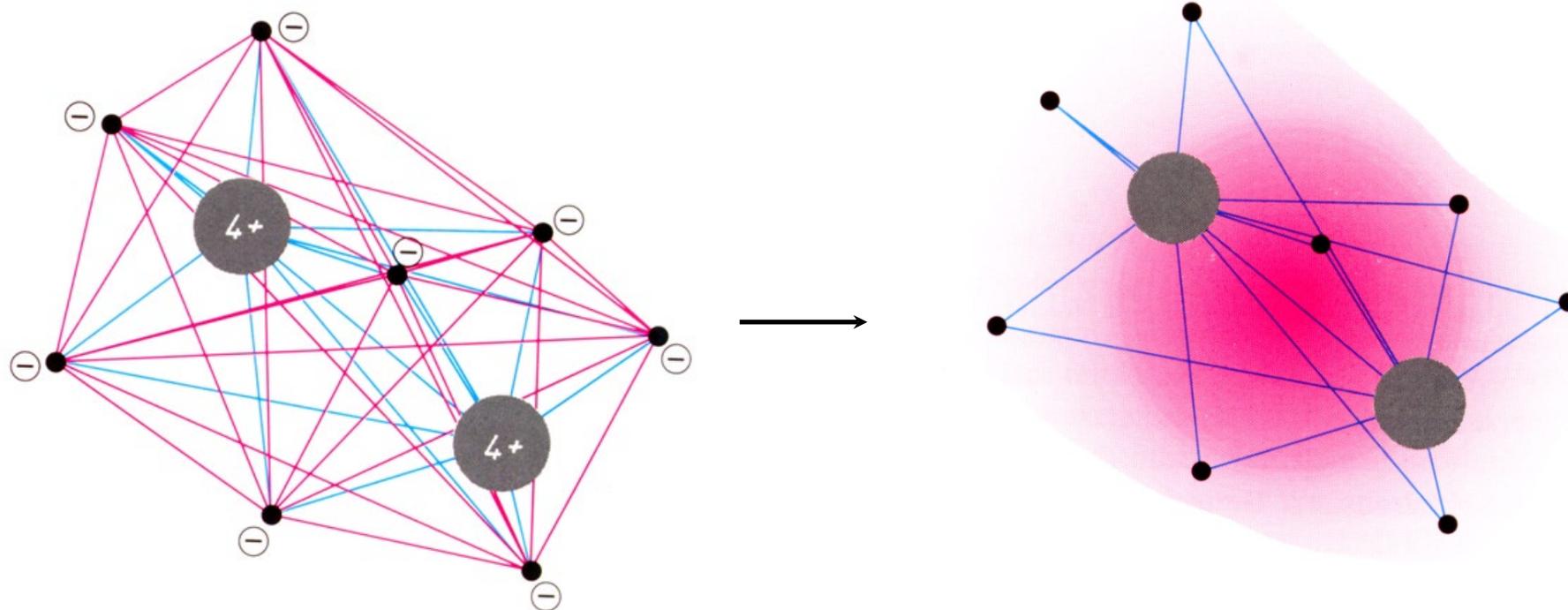
Kohn-Sham Density Functional Theory (1965)



Mattsson et al., Modeling. Simul. Mater. Sci. Eng. 13, R1, 2015.

1. Electrons are non-interacting but moving particles.
2. Each electron is coupled via effective potential instead of exact potential.

From QM to KS Density Functional Theory



From many (N) electrons to N one electron!

Kohn-Sham equations

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

Schrödinger equation
(N electrons)

$$\hat{h}_i[\rho]\psi_n(\mathbf{r}_i) = \epsilon_n\psi_n(\mathbf{r}_i); \quad i = 1, \dots, N$$

Kohn-Sham equations
(N x one electron)

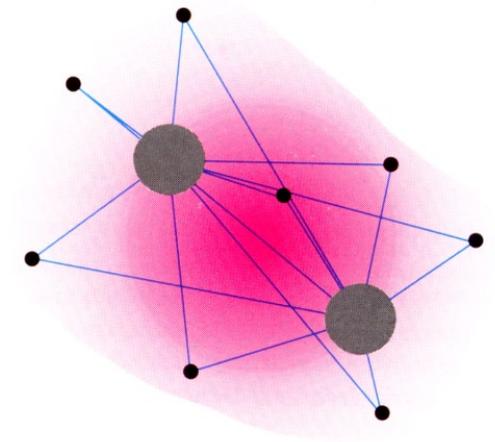
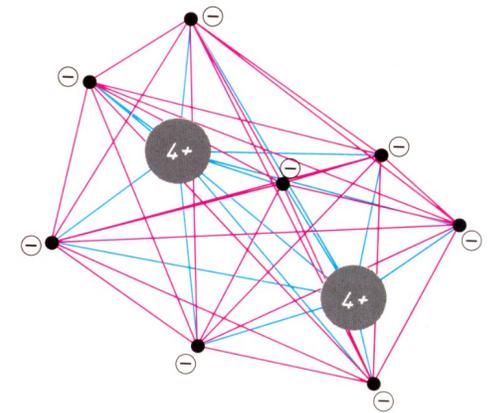
$$\hat{h}_i[\rho] = -\frac{1}{2}\nabla_i^2 + V_{nuc}(\mathbf{r}_i) + V_H[\rho](\mathbf{r}_i) + V_{xc}[\rho](\mathbf{r}_i)$$

where, $\rho(\mathbf{r}) = \sum_{n=1}^{E_F} |\psi_n(\mathbf{r})|^2$ is electron density

$$V_H[\rho](\mathbf{r}_i) = \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_i|} d^3r \quad \begin{array}{l} \text{Hartree Fock potential} \\ \text{(averaged e-e coulomb interactions)} \end{array}$$

$V_{xc}[\rho](\mathbf{r}_i)$ exchange-correlation potential is unknown!

Exchange is possible to solve; correlation is not.



Exchange-Correlation potential

$$\hat{h}_i[\rho]\psi_n(\mathbf{r}_i) = \epsilon_n\psi_n(\mathbf{r}_i); \quad i = 1, \dots, N$$

$$\hat{h}_i[\rho] = -\frac{1}{2}\nabla_i^2 + V_{nuc}(\mathbf{r}_i) + V_H[\rho](\mathbf{r}_i) + V_{xc}[\rho](\mathbf{r}_i)$$


LDA (Local Density Approximation)

Uses only the electron density, $\rho(\mathbf{r})$, at point \mathbf{r} to determine the exchange-correlation energy at that point. Over bind in (molecules), but not bad at all.

GGA (Generalized Gradient Approximation)

Includes the gradient of the density, $|\nabla \rho(\mathbf{r})|$, as an independent variable.

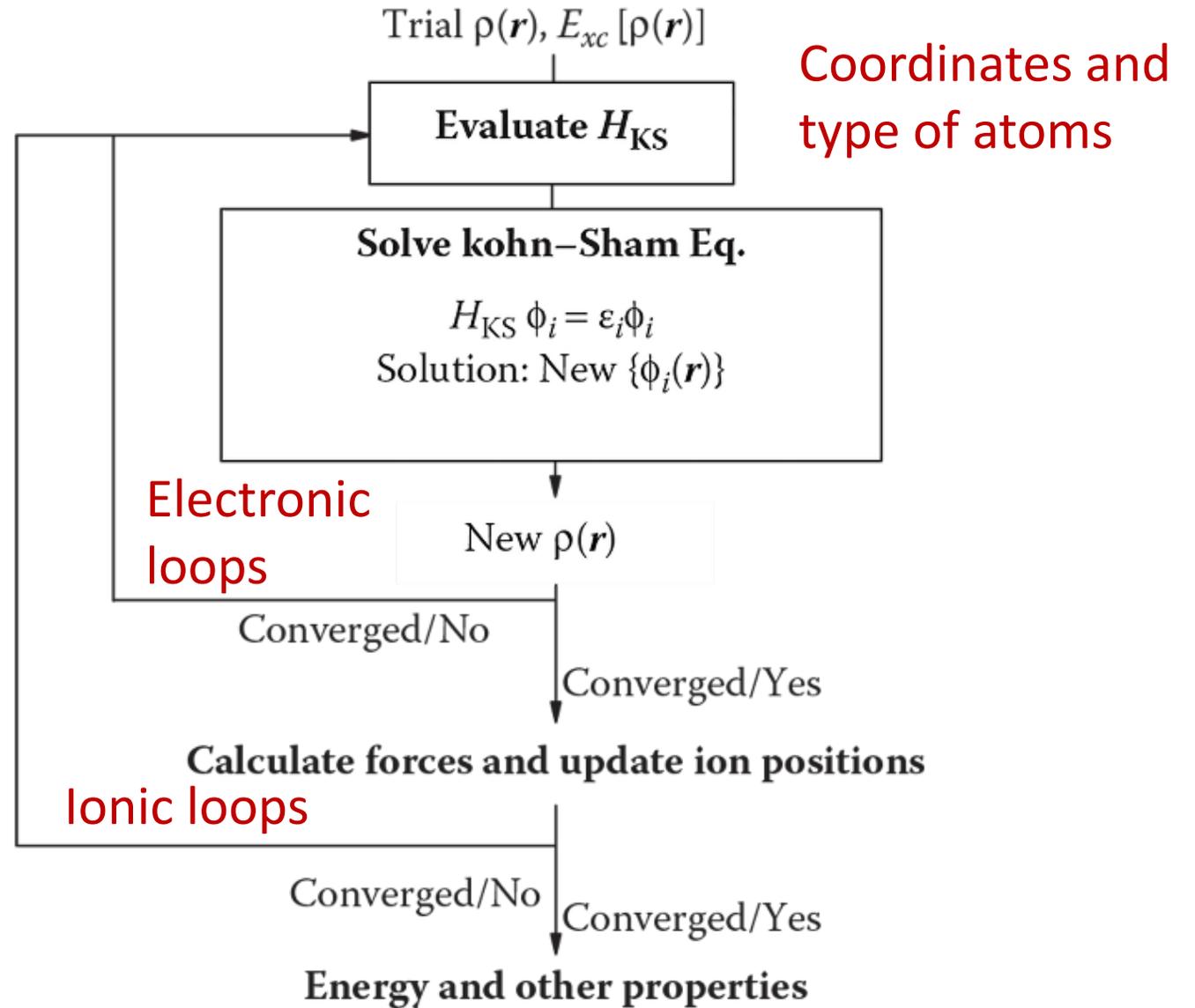
The gradient introduces **non-locality** into the description of exchange and correlation.

Hybrid-functionals (HSE, PBE0...)

Sometimes lead to better accuracy but computationally expensive.

Admix a certain amount of Hartree-Fock **exchange** to a local or semi-local density functional...

A typical DFT procedure is
iterative self-consistent loops



DFT

The **QM equation** is impossible to solve because of the N electrons problem.

KS equation simplifies the QM, converting **N electrons** problem to **N x one electron** using **electron density** as the key variable.

In KS equation, the **exchange-correlation potential** is however unknown.

Approximations are made possible, such as, **LDA, GGA, van der Waals** corrections...

Good news is reasonable scaling: N^n ($1 < n < 3$).

ab-initio nature allows **predictive** power: **only the types and the positions of the atoms are needed.**
Almost all materials properties can be predicted **at reasonable accuracy.**

DFT for solids

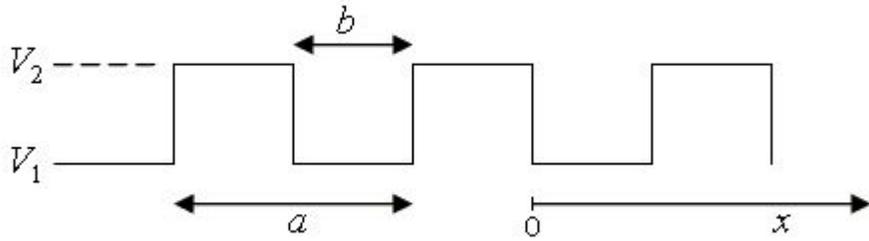
However, there is another challenge for **condensed matter systems: infinite number of e.**

Computation problem of infinite solids

The Bloch theorem changes the problem:

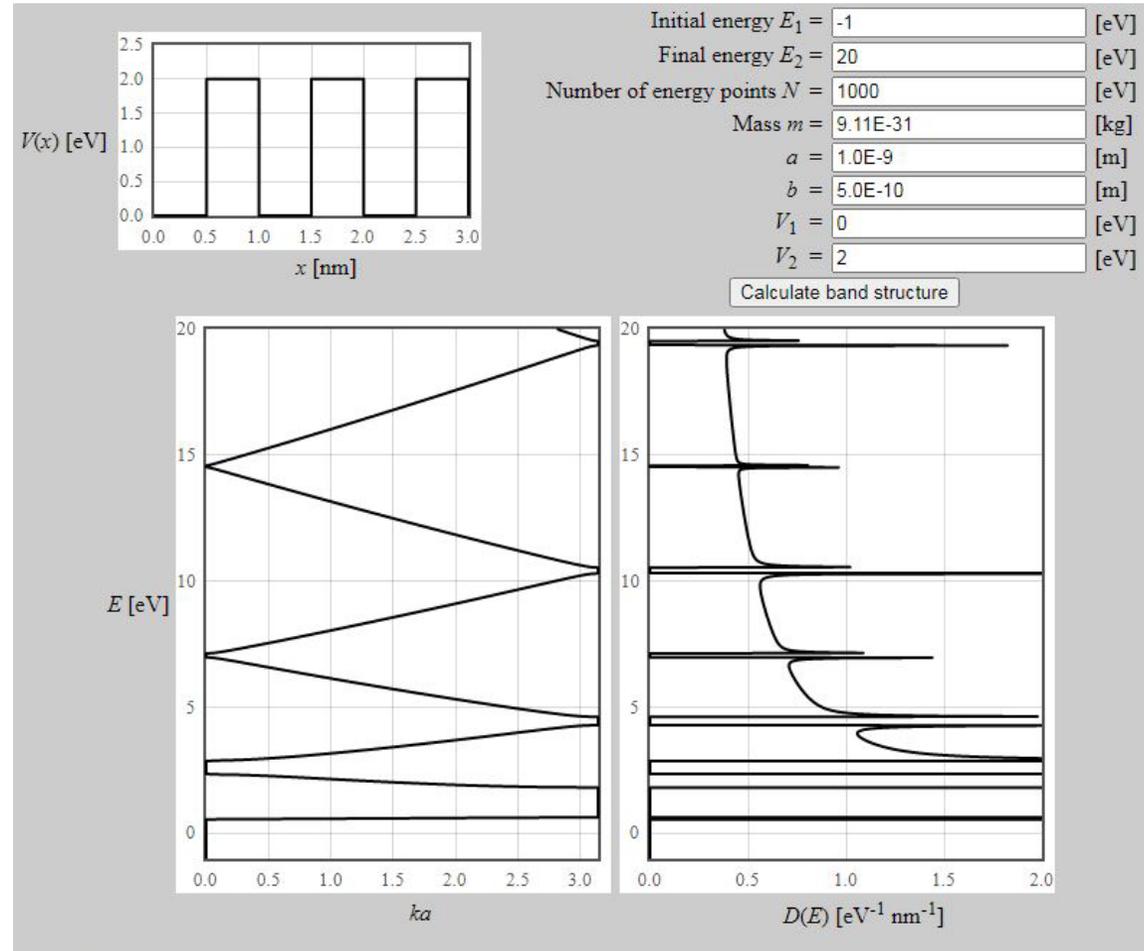
- Instead of computing an **infinite number** of electronic **wave functions** considering **finite number** of wave functions is sufficient (unit cell).
- By doing so, the **wave vector k** (**k points sampling/mapping the reciprocal lattice**) and the **band index n** (**first Brillouin Zone**) allow us to label each electron.

DFT for solids: Kronig-Penny Model



A simple, idealized 1D
quantum-mechanical system

<https://lampx.tugraz.at/~hadley/ss1/KronigPenney/KronigPenney.php>



Methods for efficient computations

- **Pseudopotentials (pp)** – specific exchange-correlation functional form representing frozen **core electrons** and **valence electrons** which takes part in bonding. For example: Si: $1s^2 2s^2 2p^6 3s^2 3p^2$; different choices are available. For example, Pb $[Xe] 4f^{14} (5d^{10}) 6s^2 6p^2$. **POTCAR**.
- **Energy cut-off value (Encut)** – only plane-waves with a kinetic energy smaller than Encut are included in the basis set. one of the tags in **INCAR**.
- **K-points (k) - discrete points** instead infinite points specified in **Brillouin Zone (BZ)** used to perform numerical integration properties of BZ. **KPOINTS**

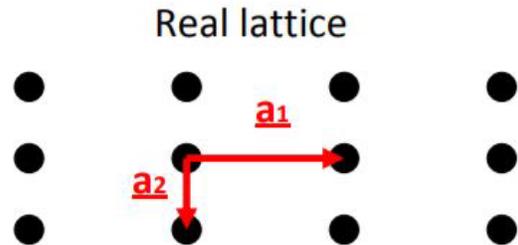
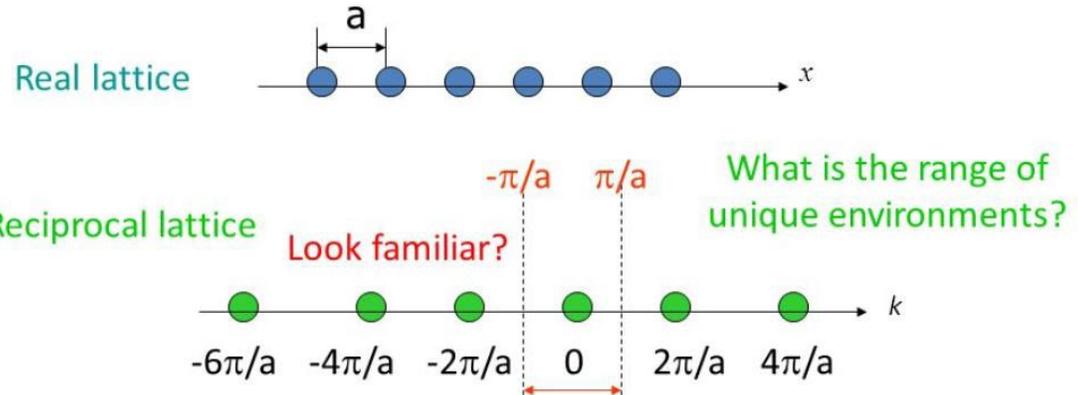
Note: Ensuring **k** and **Encut** Lead to a converged energy by **increasing** density of **k** grids and value of Encut until energy converges.

Real lattice vs Reciprocal lattice

Reciprocal:

$2 \times 1/2 = 1$ (mathematical)

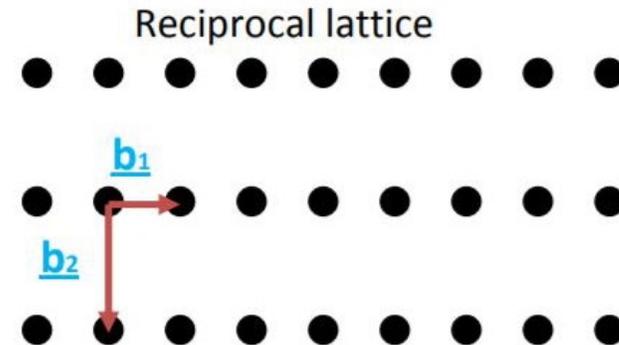
$a \times b = 2\pi$ (quantum mechanical)



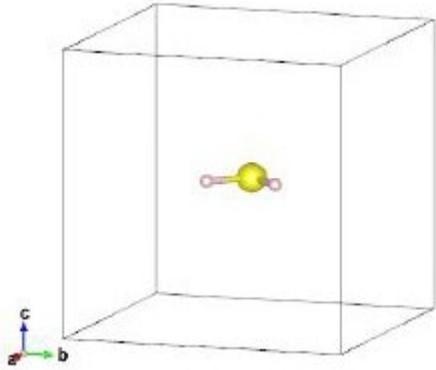
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}$$

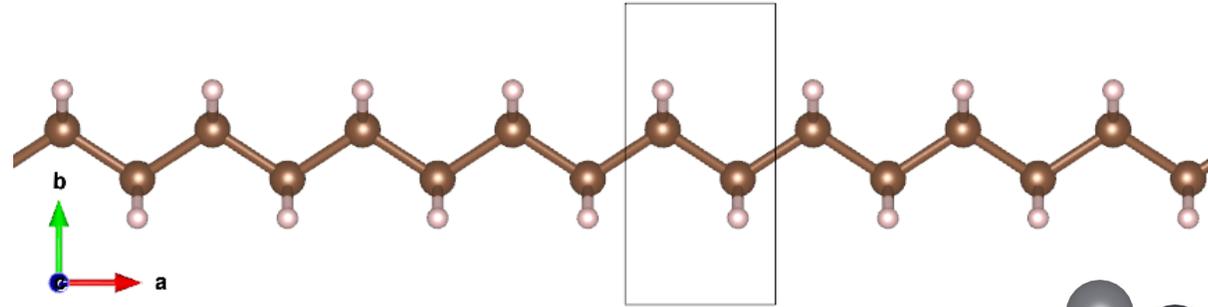
$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}$$



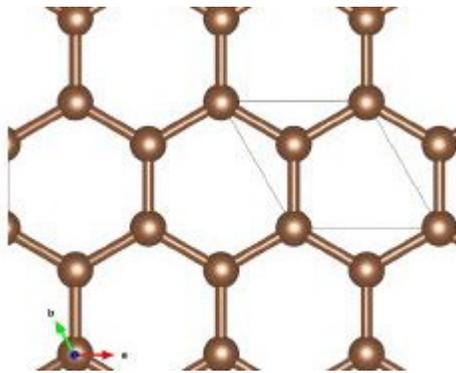
K-points for typical systems (general trend)



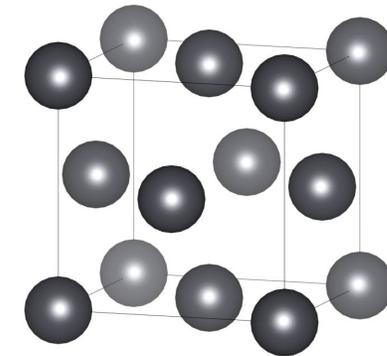
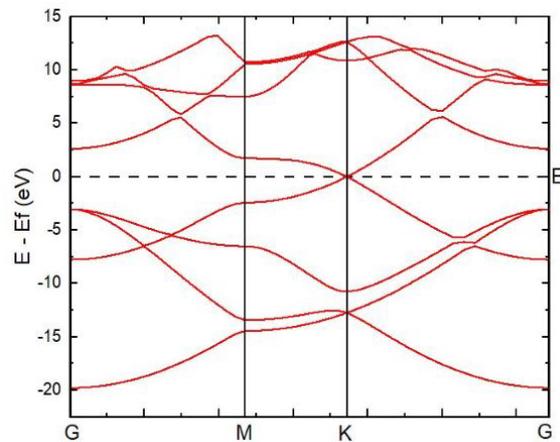
One k-point



1D Polymer 4 1 1



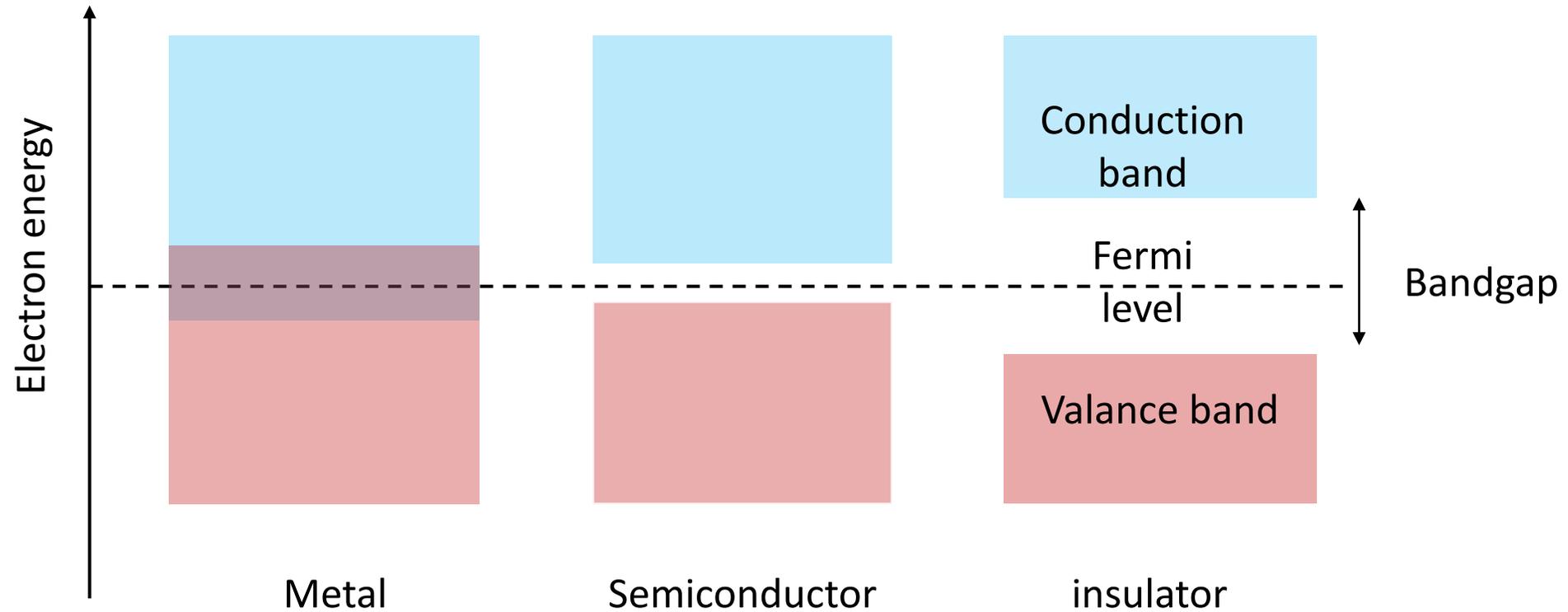
2D Graphene: 40 40 1



Metal: 9x9x9

Semiconductor: 4x4x4

Electronic structures of solids

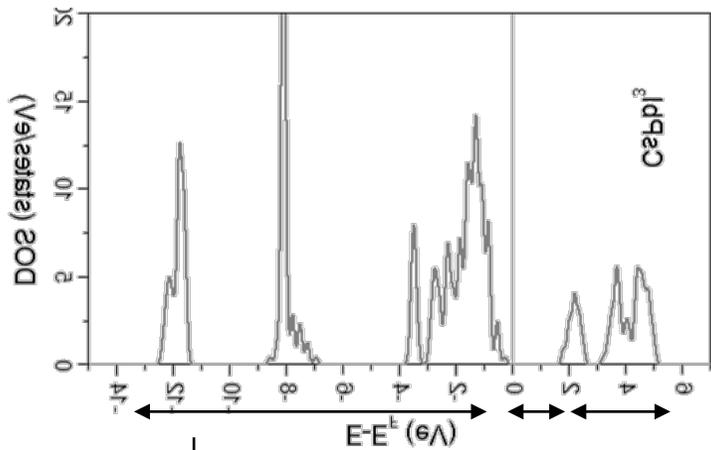
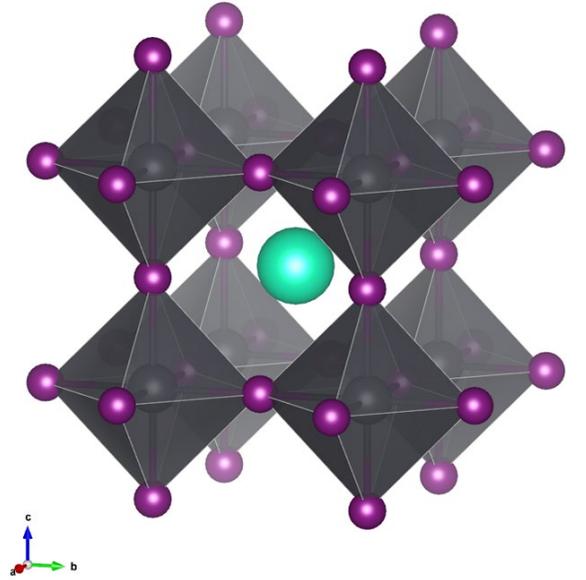


Density of states (halide perovskite, my favorite semiconductor)

Number of electronic states at each energy interval

$$D(\varepsilon) = \frac{\text{Number of states between } \varepsilon \text{ and } \varepsilon + \Delta\varepsilon}{\Delta\varepsilon}$$

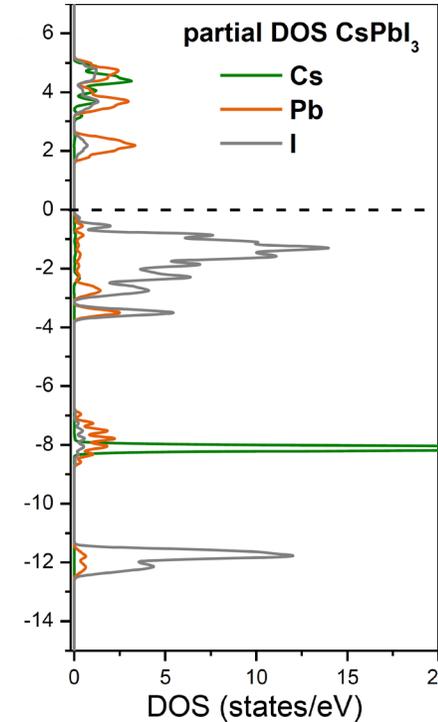
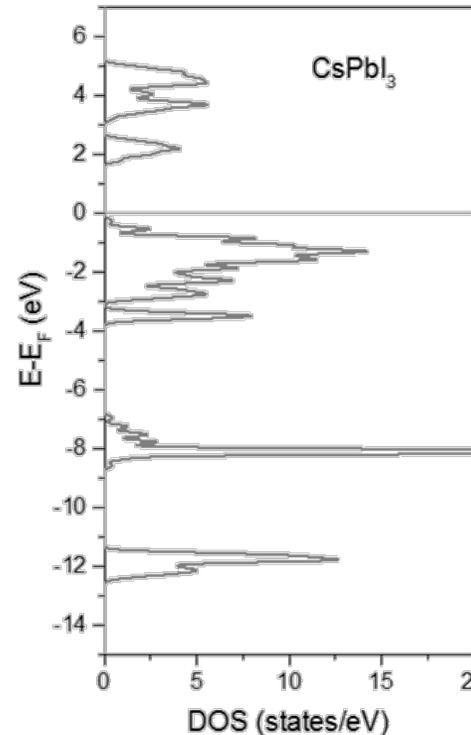
$$= 2 \sum_k \delta[\varepsilon - \varepsilon_n(k)]$$



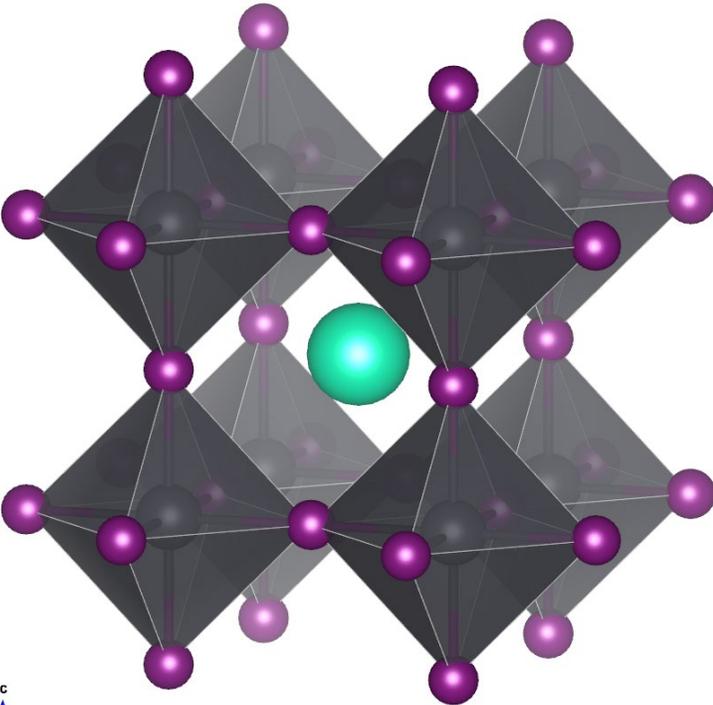
Valence
bands

Band
gap

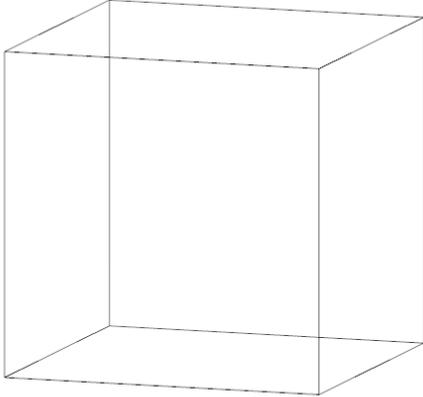
Conduction
bands



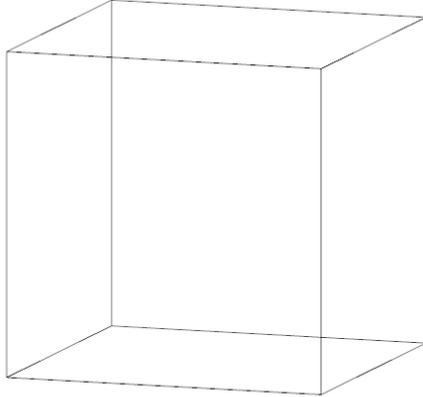
Band structure: from real to reciprocal space



Chemical structure

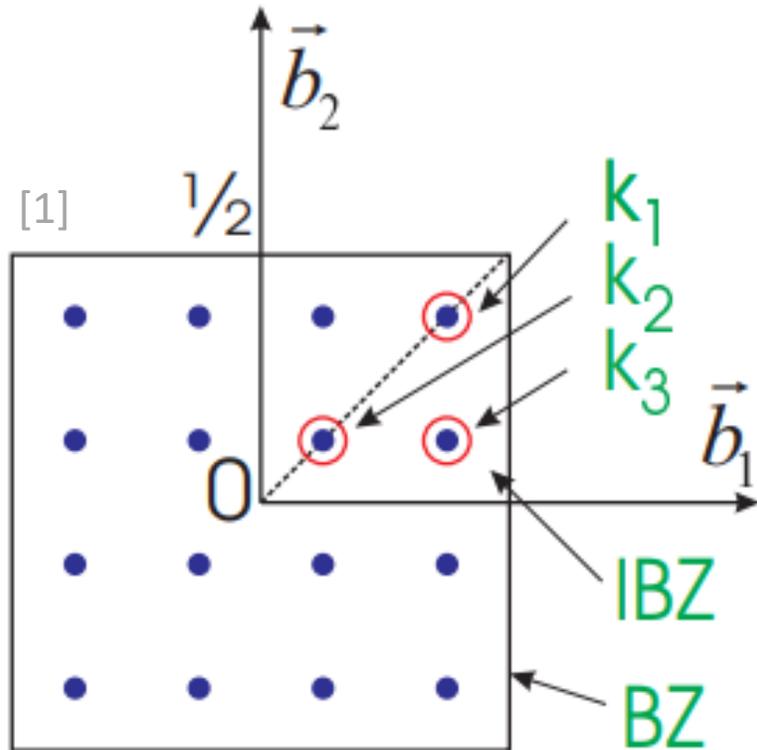


Unit cell
(Real space)

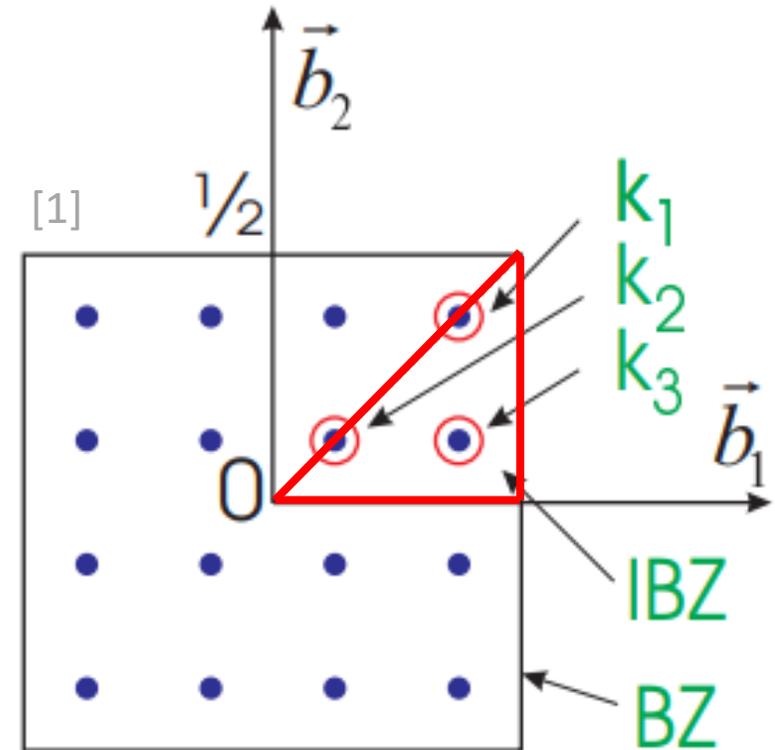


Unit cell
(Reciprocal space)

Sampling of reciprocal space

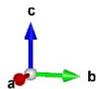
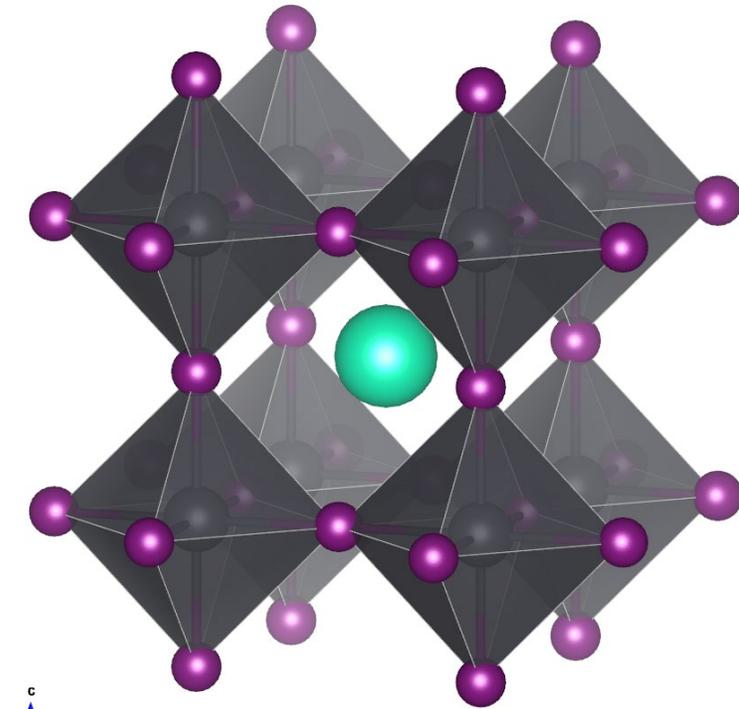


Density of states: representative sampling of reciprocal space

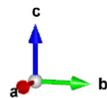
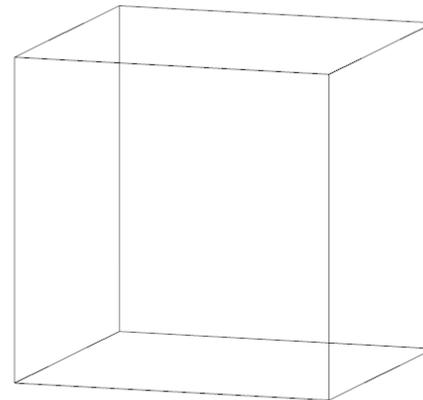


Band structure: sampling along high symmetry points / lines (points of interest)

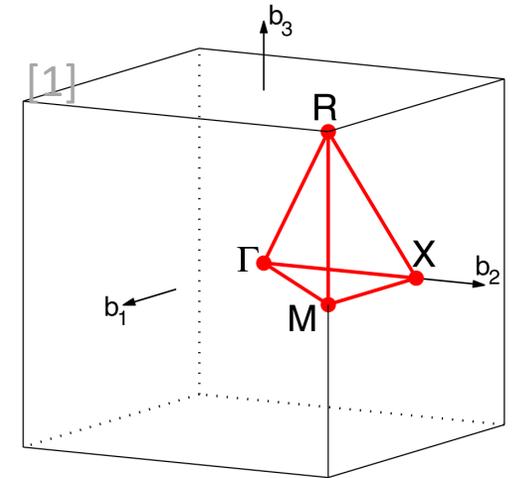
Band structure: application of sampling



Crystal structure



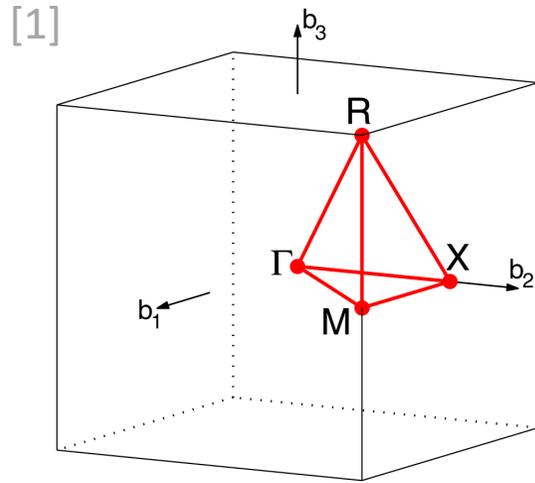
Unit cell, **simple cubic**
(Reciprocal space)



Path through k-space:
 Γ -X-M- Γ -R-X | M-R

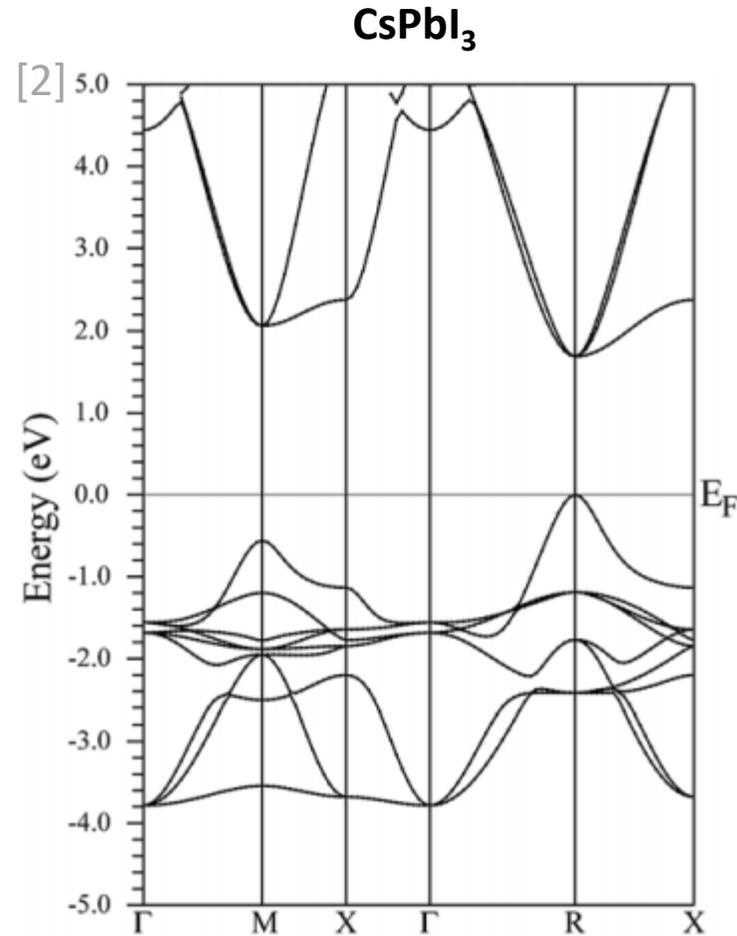
<https://www.materialscloud.org/work/tools/seekpath>

Band structure: final result



Path through k-space:

Γ -X-M- Γ -R-X | M-R



Band edges: Curvature \uparrow Effective mass \downarrow Carrier mobility \uparrow

Parabolic approximation:

$$E(\mathbf{k}) = E_0 + \frac{\hbar^2 \mathbf{k}^2}{2 m^*}$$

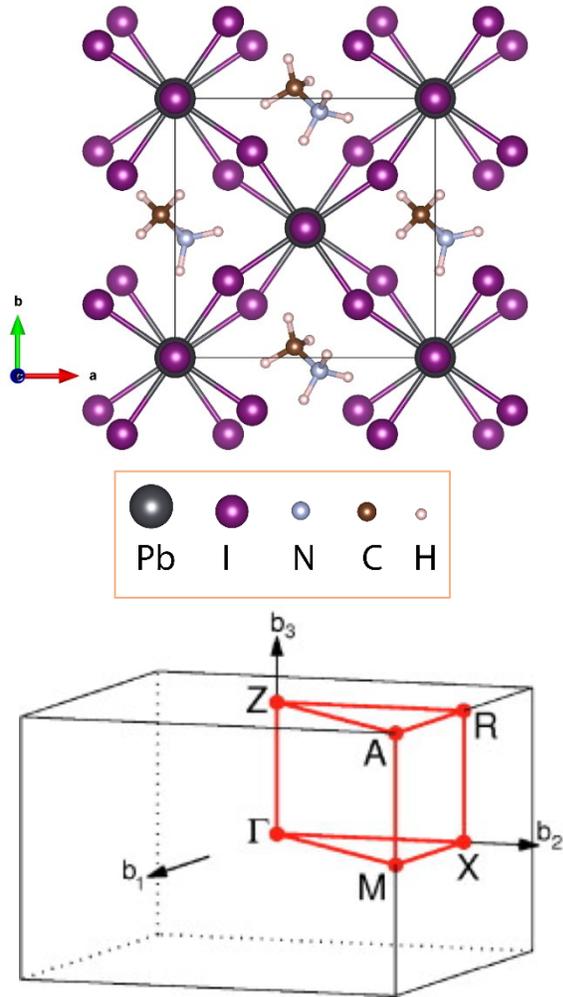


$$\frac{1}{m_{ij}^*} = \frac{1}{\hbar^2} \cdot \frac{\partial^2 E}{\partial k_i \partial k_j}$$

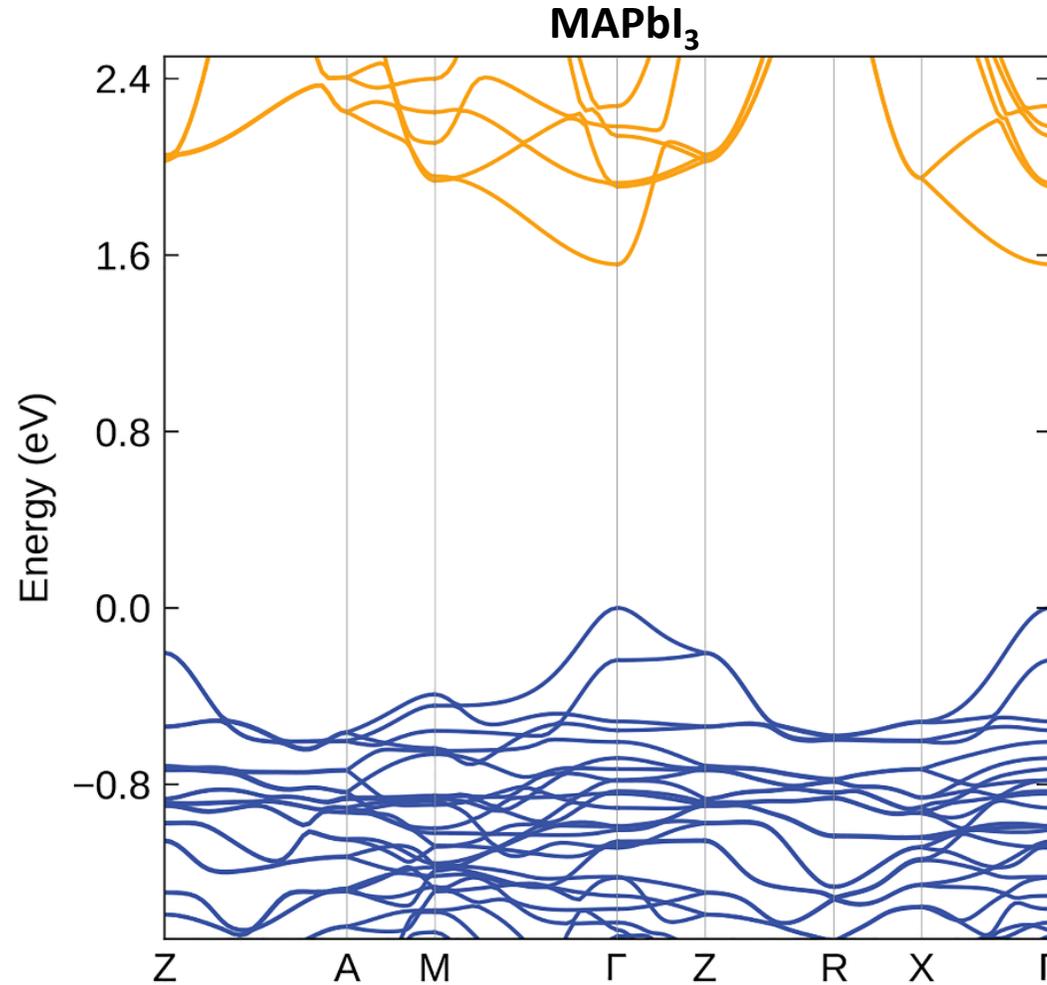
[1] - Setyawan, Wahyu, and Stefano Curtarolo. Computational materials science 49.2 (2010): 299-312.

[2] - Guo, San-Dong, and Jian-Li Wang. RSC advances 6.103 (2016): 101552-101559.

Electronic band structure (MAPbI₃ perovskite)



Brillouin Zone
of a **tetragonal** cell



Band edges: Curvature ↑ Effective mass ↓ Carrier mobility ↑

Limitations of DFT: the band gap problem

LDA/GGA is not designed to describe **the non-local nature of electron** correctly. It underestimates band gaps by up to 40%.

$$E_G = \varepsilon_{N+1}(N + 1) - \varepsilon_N(N) \quad \text{the true gap}$$

$$E_{KS} = \varepsilon_{N+1}(N) - \varepsilon_N(N) \quad \text{the KS gap}$$

DFT also introduces **false/spurious self-interaction (self-energy error)** in occupied states: delocalising them and pushing VBM up, therefore decreasing band gap. DFT fails to describe the **derivative discontinuity¹** of the actual XC potential.

1. J. P. Perdew, M. Levy: Physical Content of the Exact Kohn-Sham Orbital Energies: Band Gaps and Derivative Discontinuities, Phys. Rev. Lett. 51, 1884 (1983).

Limitations of DFT: possible remedies

Hybrid functional: LDA/GGA with **HF**

DFT+U (Hubbard parameter) for *d* and *f* block elements

Other self-interaction corrections (**SIC**) methods: DFT-1/2¹...

Green function techniques and **GW approximation** based on MBPT theory

Nevertheless, DFT is useful to predict **qualitative trends** for the same family of materials and for composition engineering.

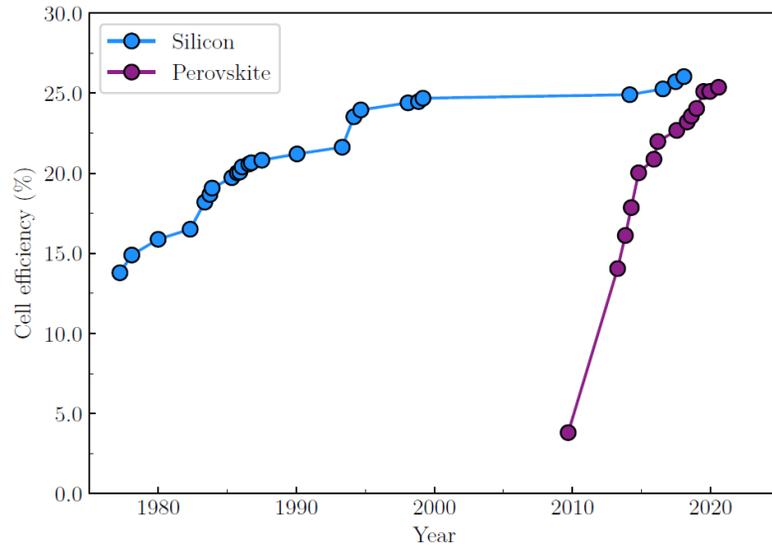
Apply DFT with adequate theoretical knowledge and analyse the results objectively:
always justify the approximations!

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- Theory of ReaxFF reactive force field (1h)
- Reactive MD for halide perovskites (1h)

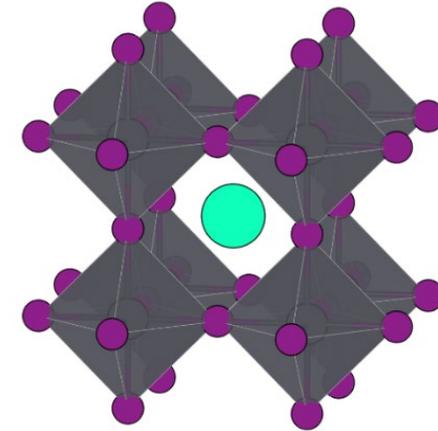
Halide perovskites optoelectronics

Research solar cell efficiencies:



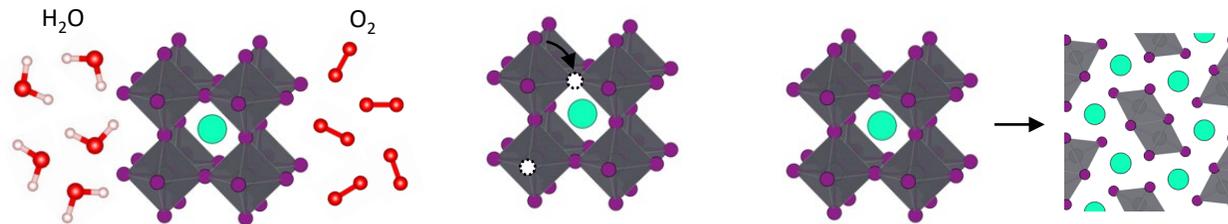
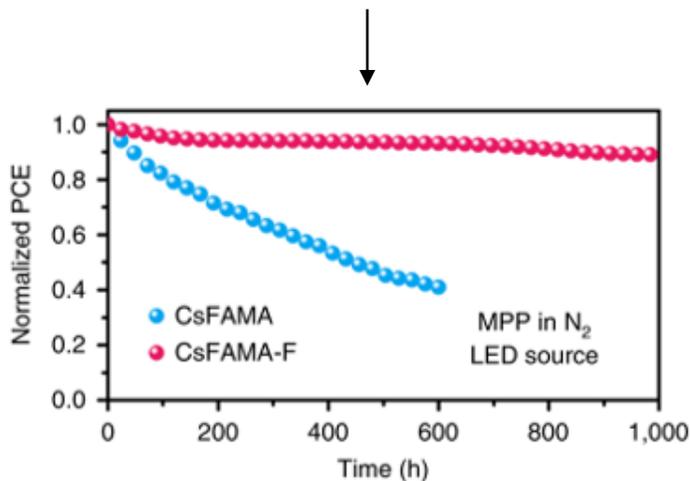
Tunable band structures
 Room temperature processing
 Defect tolerance (electronically)
 Ideal electronic structures
Easy to make

AMX₃ halide perovskite:

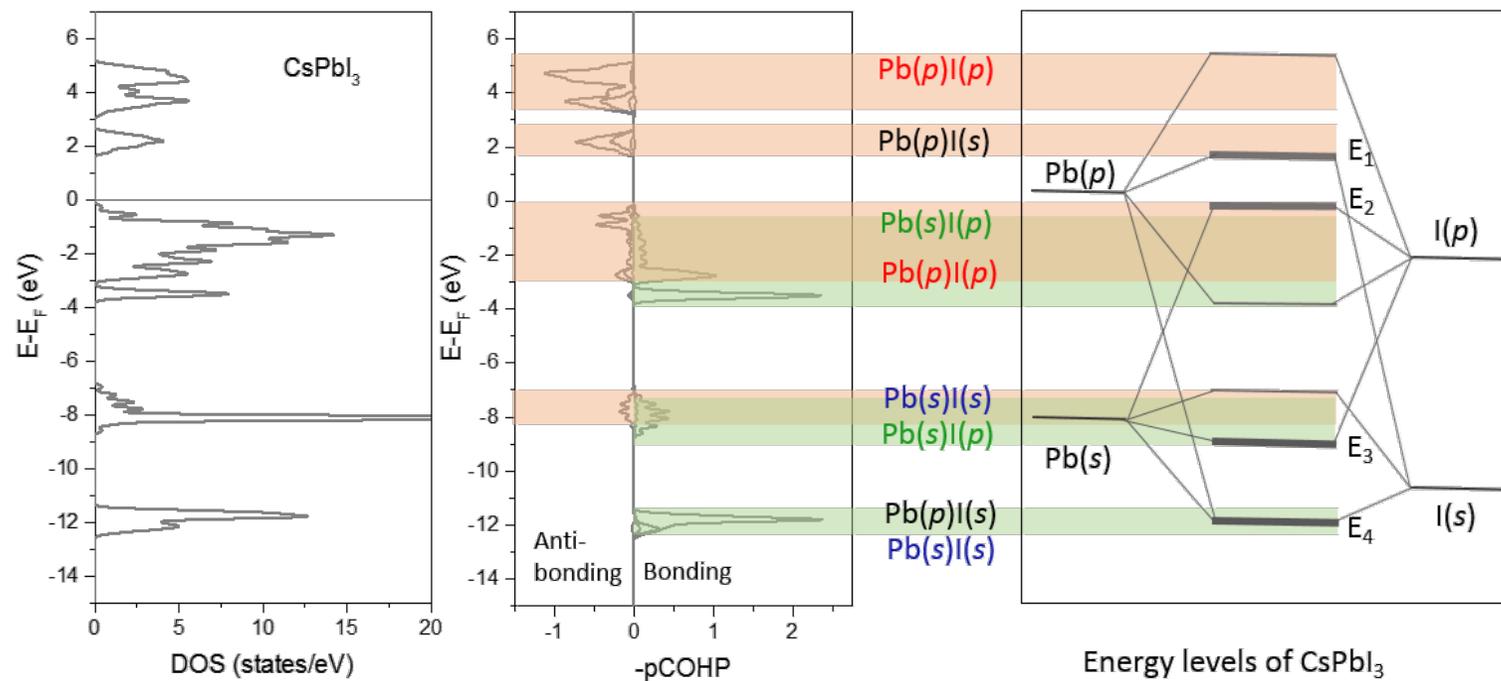


- = A⁺ (organic/inorganic cation)
- = M²⁺ (metal cation)
- = X⁻ (halide anion)

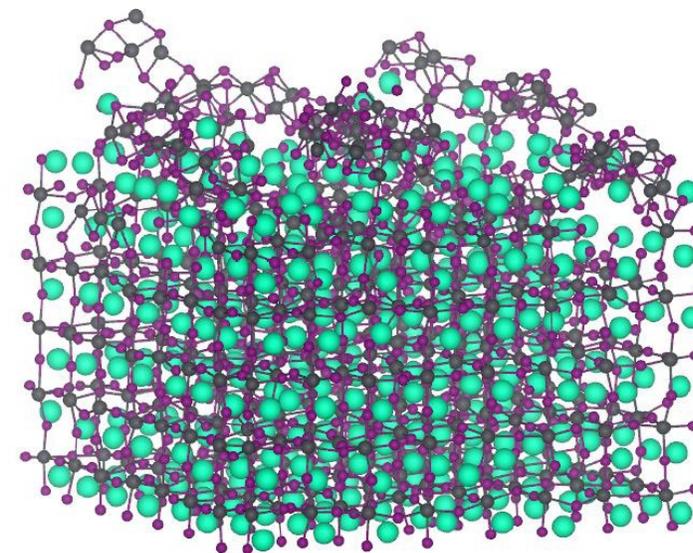
Instability: **easy to break**
 dynamical nature, defects and chemistry
 reactions (with the environments)



Our focus:

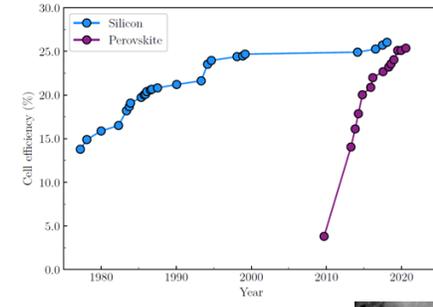
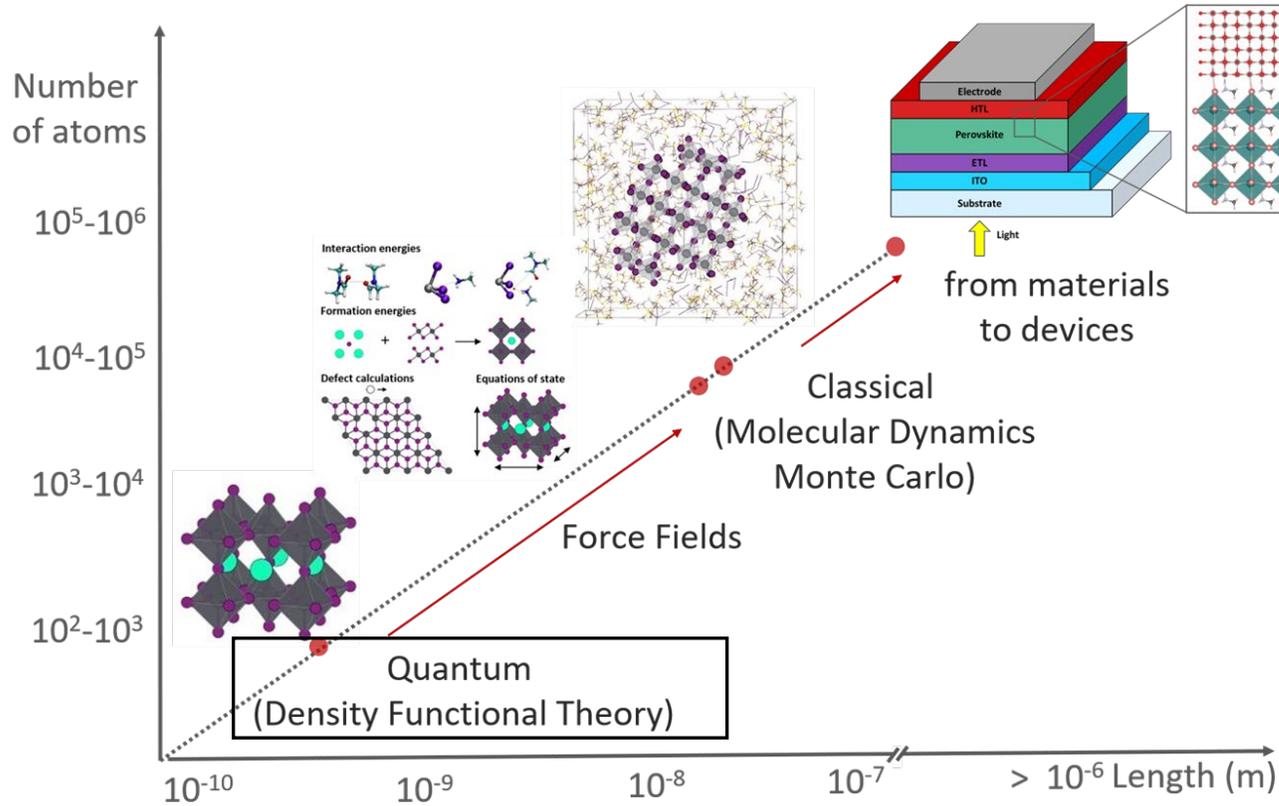


understanding the electronic properties

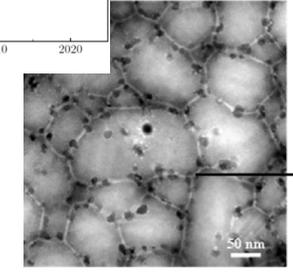


improving the stability

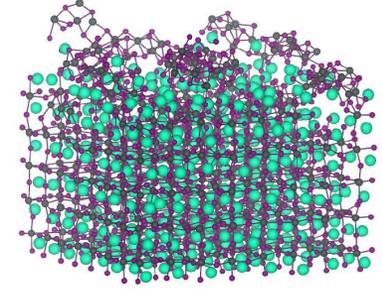
My group



efficiency

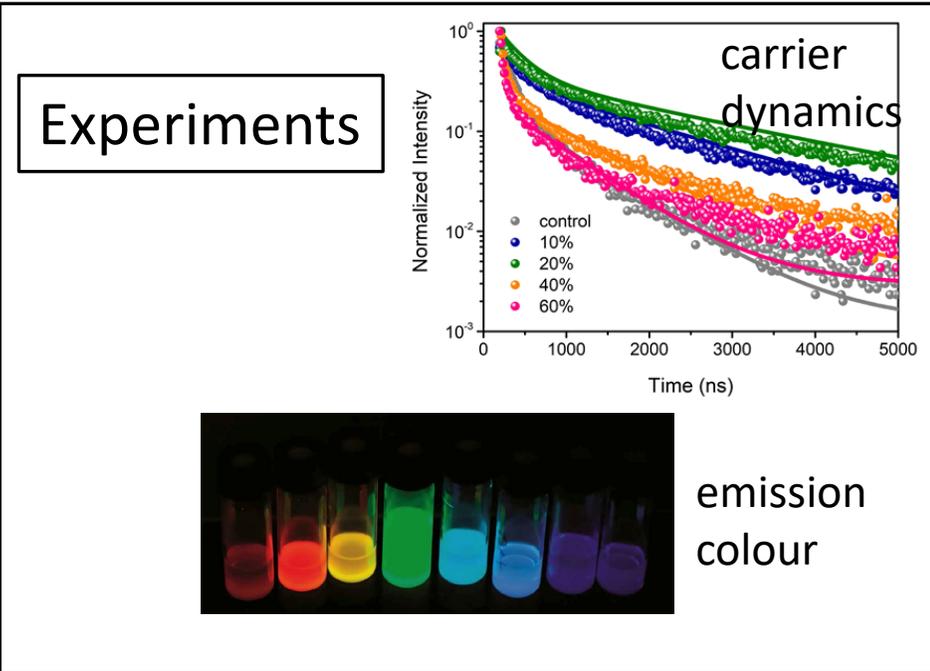


stability



predict

interpret



Tunable band gaps

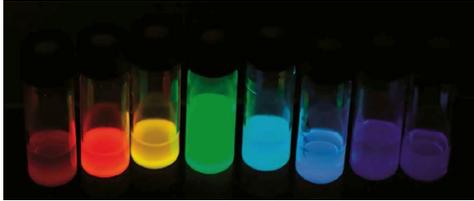
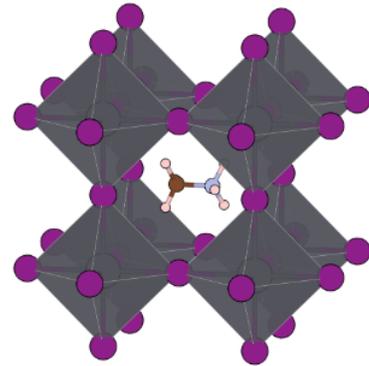
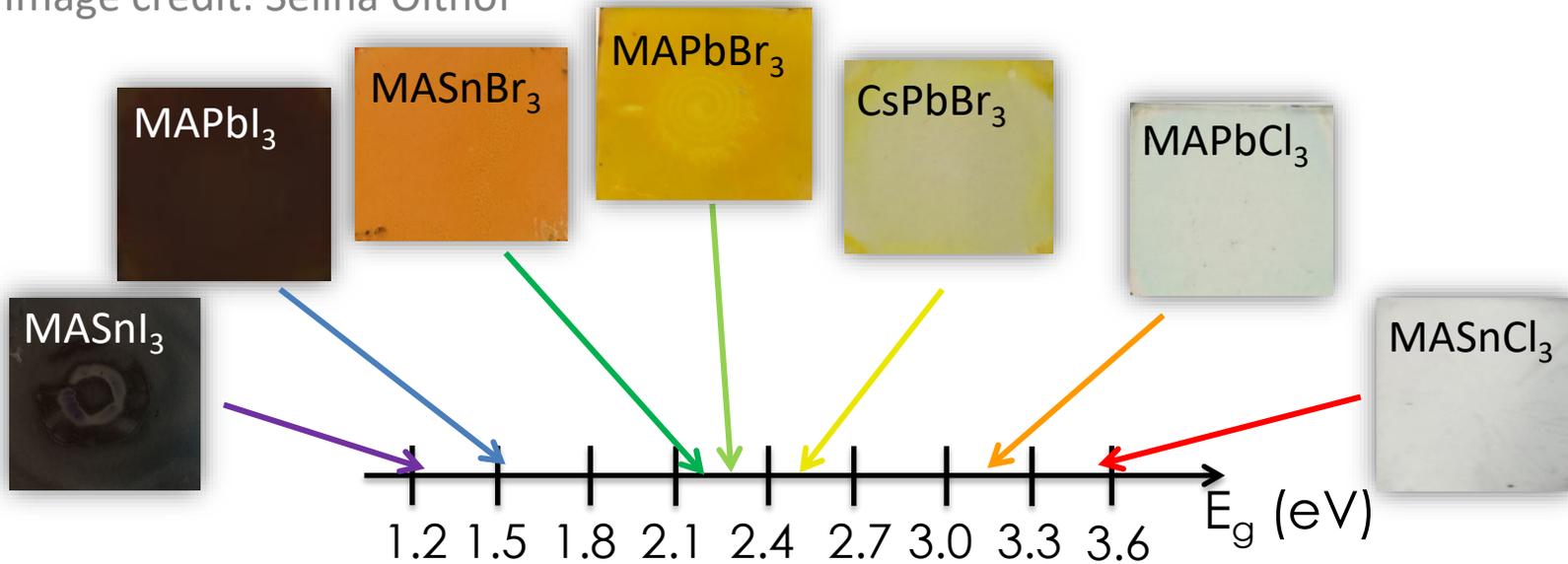
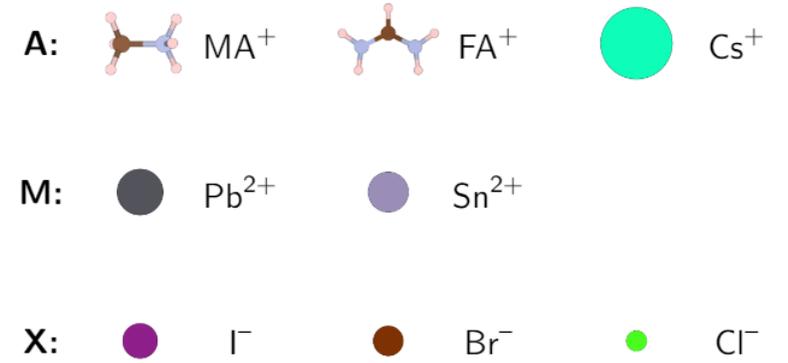


Image credit: Selina Olthof



MAPbI₃



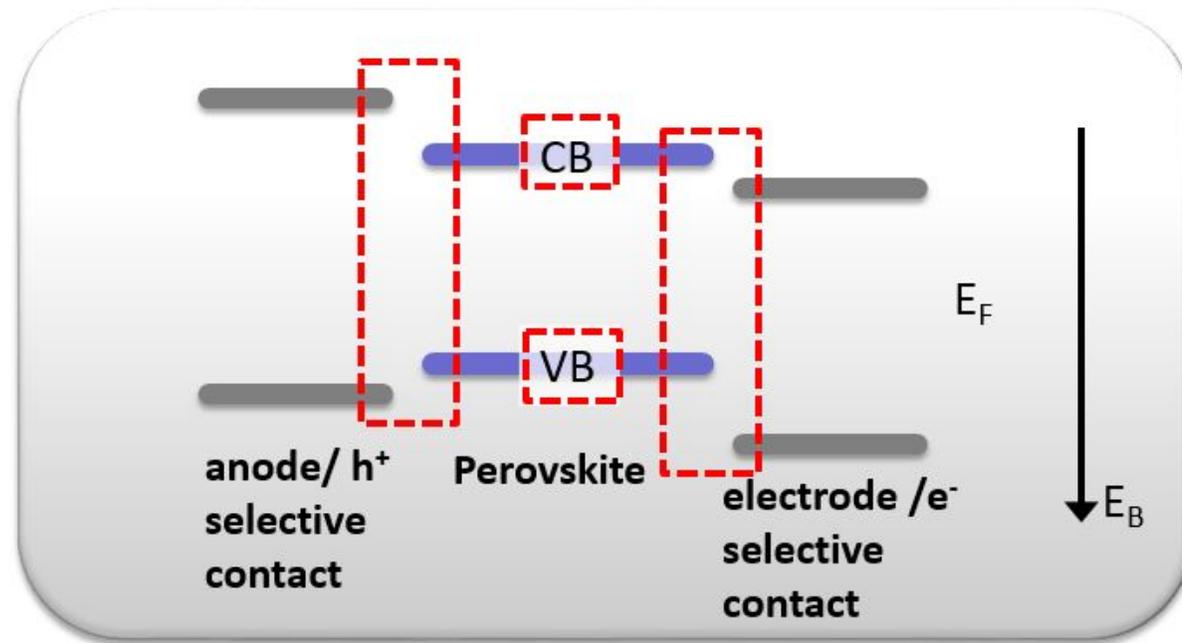
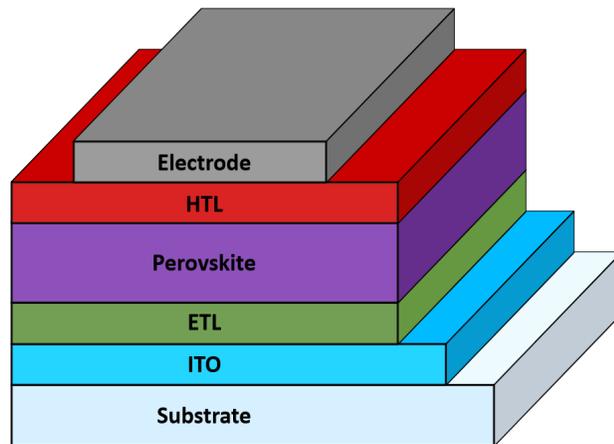
Bandgap can be tuned by the change of the composition of AMX₃.

1. Changes in bandgap well studied, but why?

Absolute energetic positions of perovskites

2. The knowledge of the energy levels and interface alignment will help to understand and **optimize device efficiency**.

Perovskite solar cell

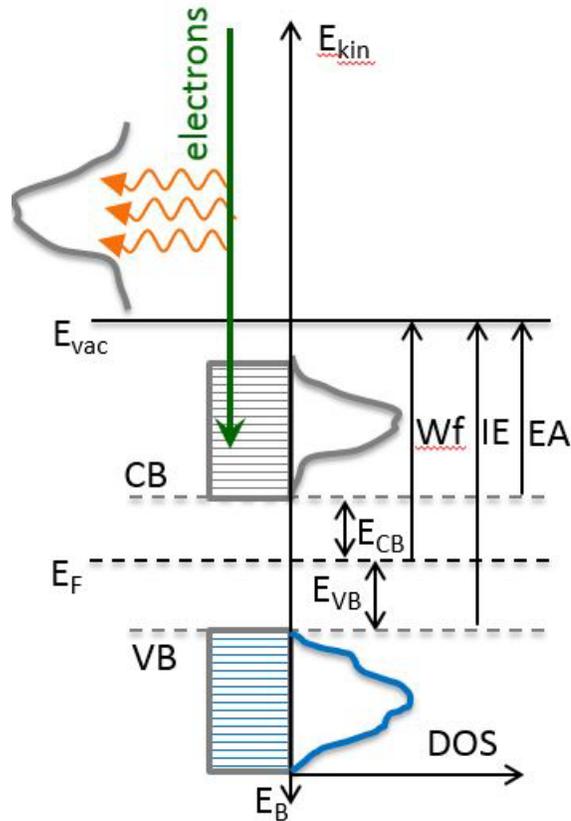


Experimental measurement of energy levels

Occupied density of states:

UV photoelectron spectroscopy

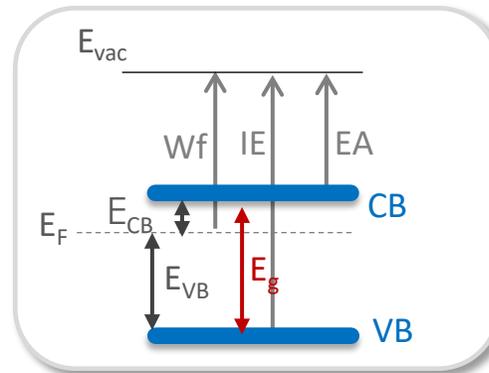
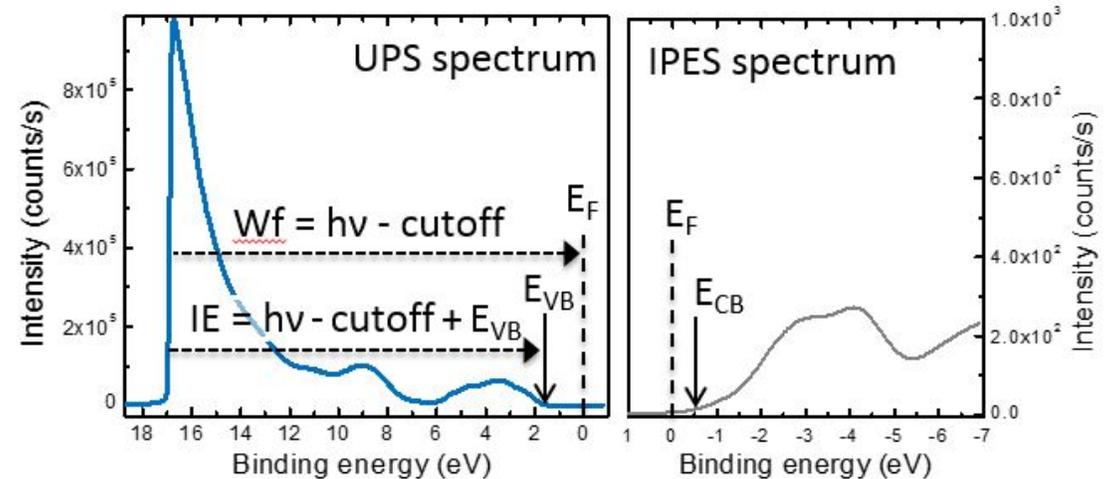
Excitation by UV light ($h\nu = 21.22\text{eV}$)



Unoccupied density of states:

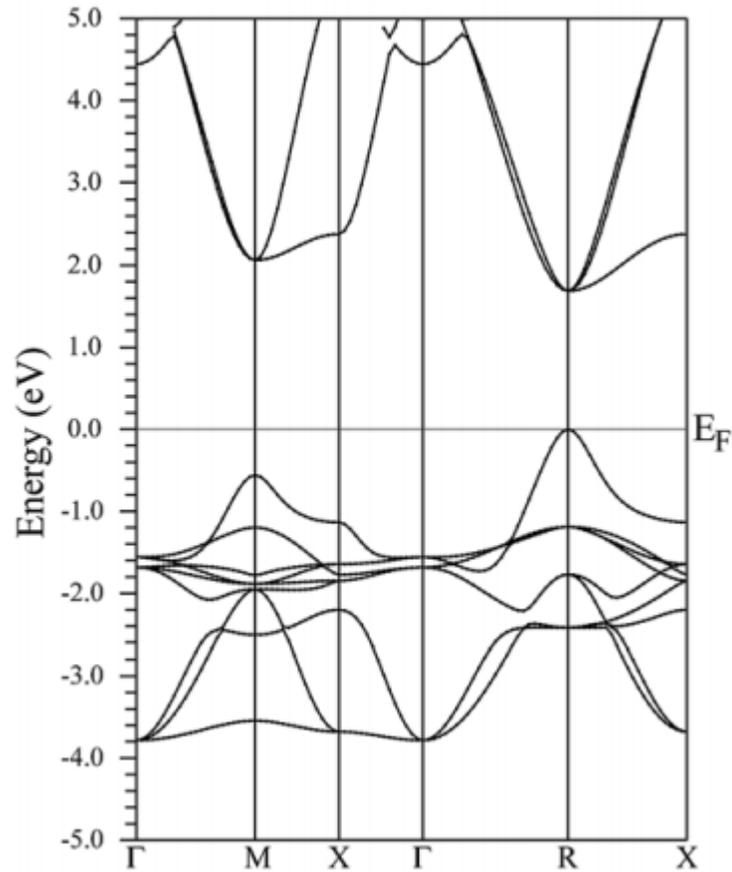
Inverse photoelectron spectroscopy

Electrons with energy 5-15eV shot onto sample

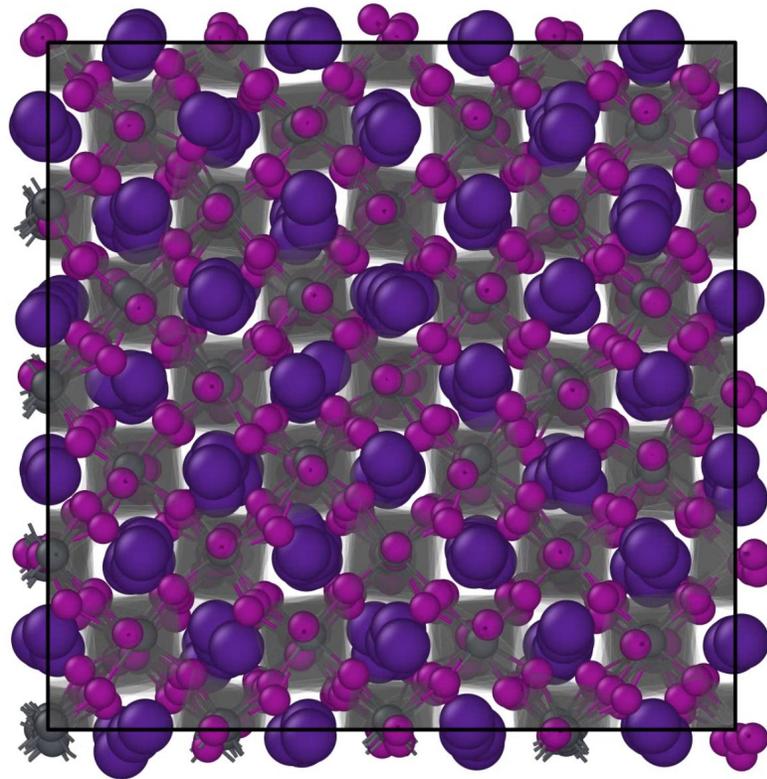


Combining UPS and IPES,
full energetic alignment
is accessible.

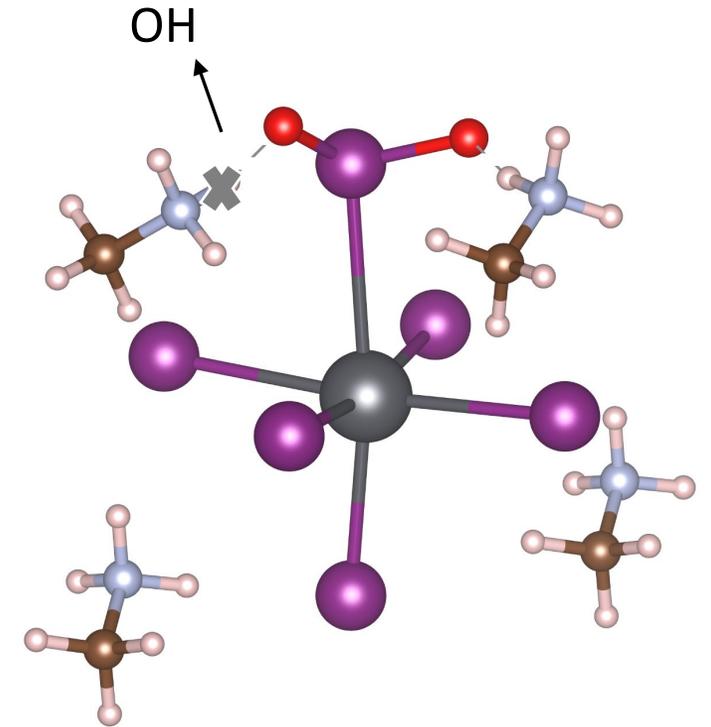
Challenges in measuring the DOSs



Low DOSs on band edges

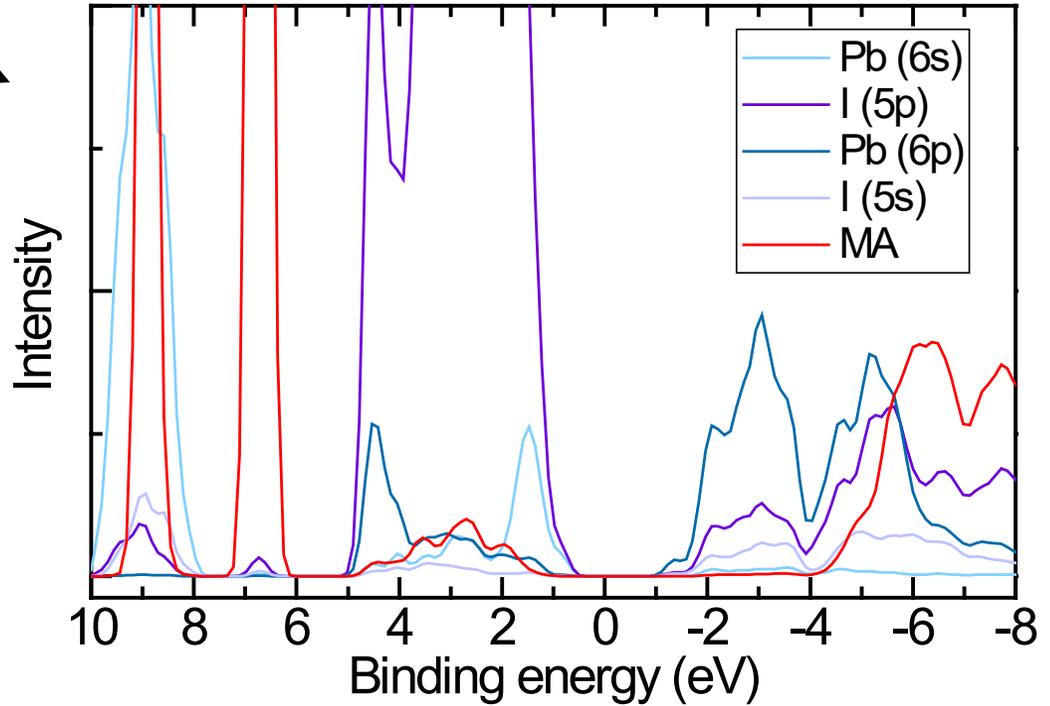
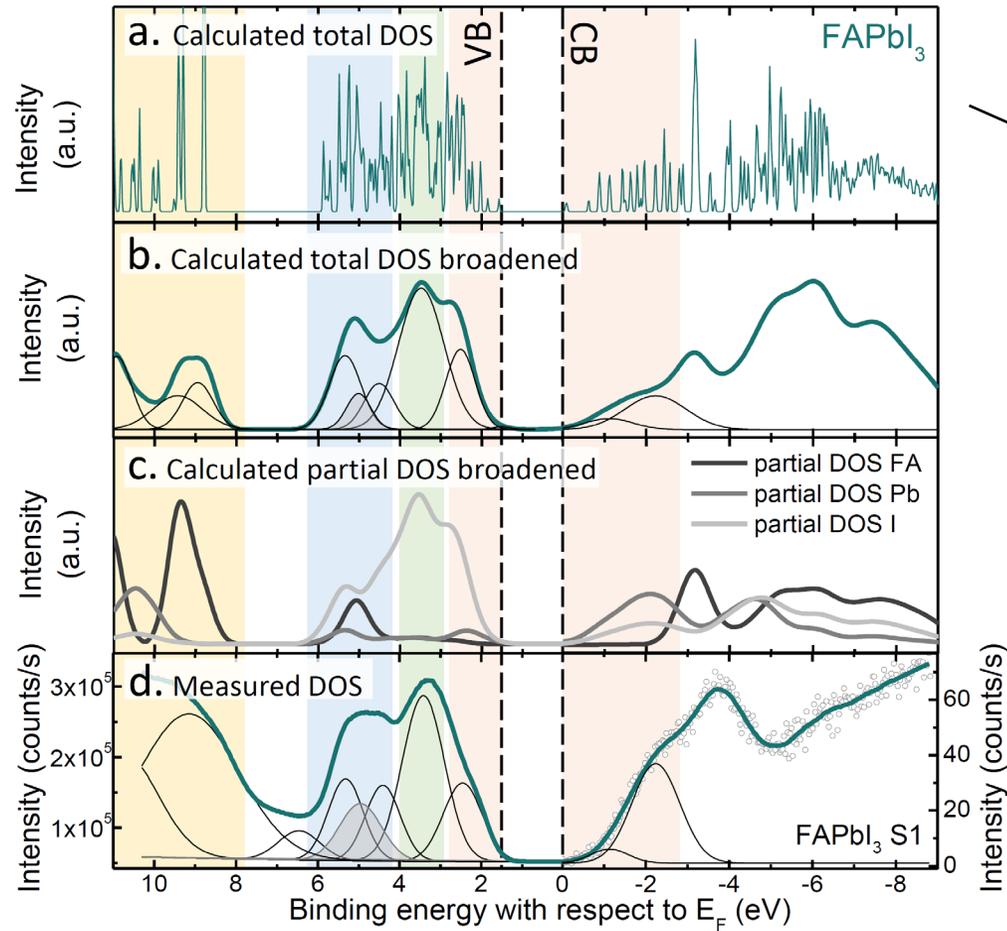


Dynamic/extra electronic feature

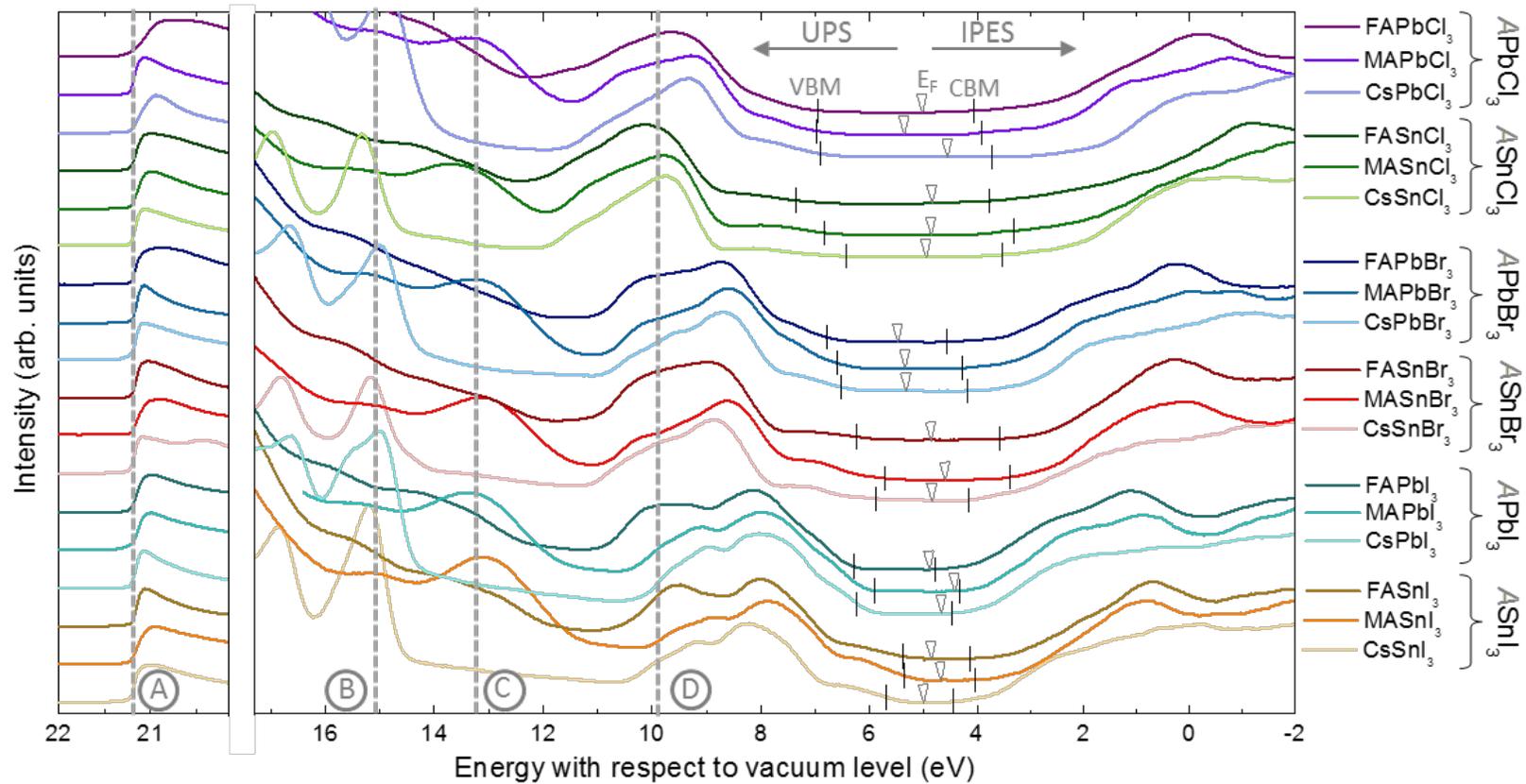


Defects and degradation

Combination of DFT and experimental DOSs

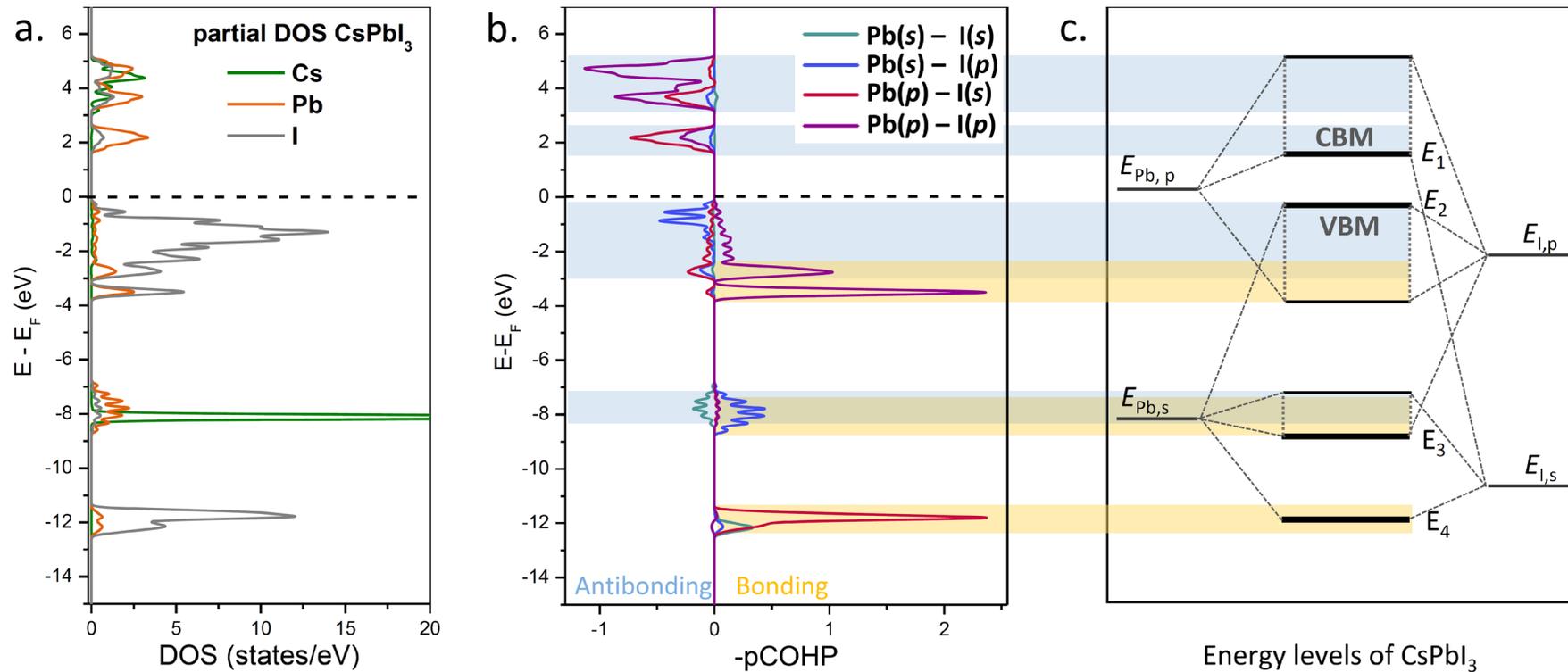


VBM and CMB position of all 18 perovskites



Tao, S., Schmidt, I., Brocks, G. *et al. Nat Commun* **10**, 2560 (2019).

The Chemical Bonding in CsPbI₃

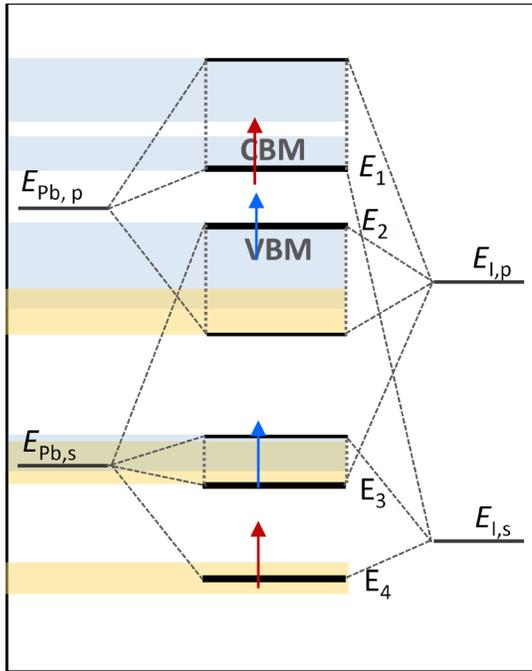


a. PDOS b. Orbital resolved COHP c. schematic energy level

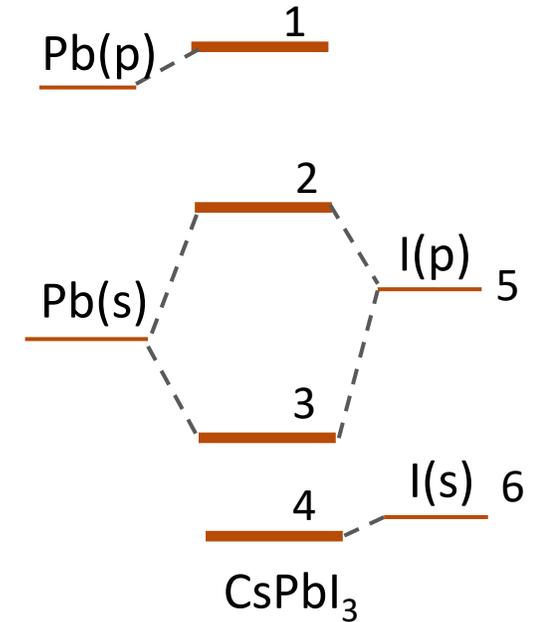
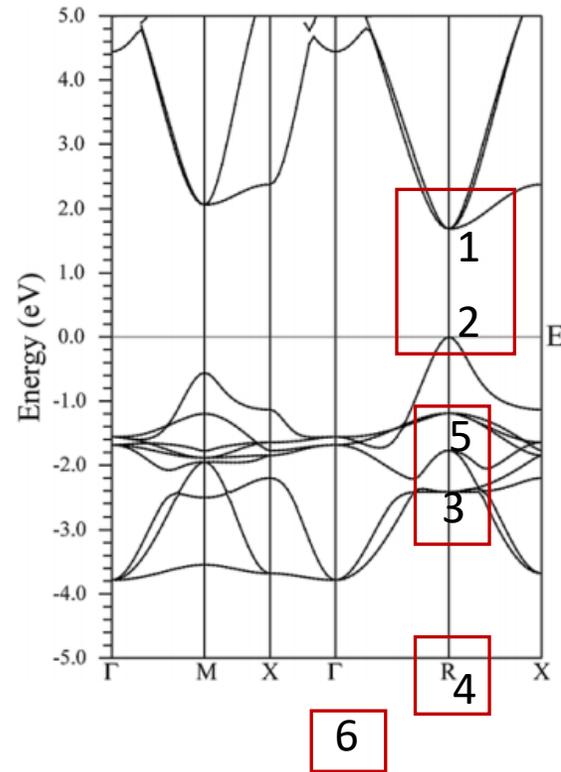
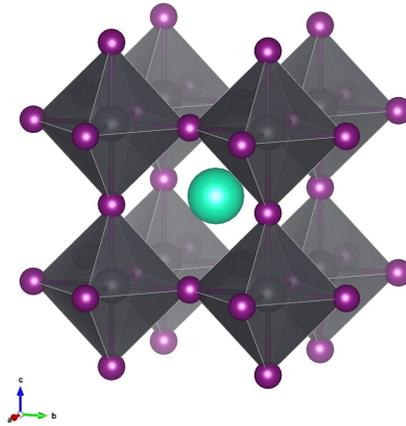
COHP (crystal orbital Hamilton population) <http://www.cohp.de/>

Tao, S., Schmidt, I., Brocks, G. *et al. Nat Commun* **10**, 2560 (2019).

The tight binding model of CsPbI₃



Energy levels of CsPbI₃



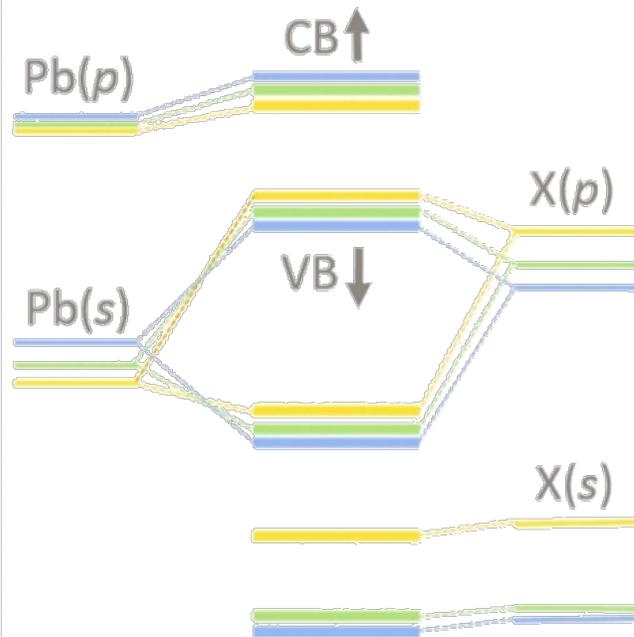
- Tight binding model focuses on the cubic symmetry, has 6 parameters: **4 atomic levels**: *p* and *s* of Pb and I; **2 hybridization strength** of Pb(*p*)I(*s*), Pb(*s*)I(*p*); the rest are symmetry forbidden.
- Energy levels of **I(*s*) I(*p*)** can be found in DFT calculations at Γ and R point (by identifying nonbonding states). **E1 to E4** can also be identified in DFT at R point because of certain symmetry.
- $E_{M,s}$, $E_{M,p}$, $V_{M,p-X,s}$, $V_{M,s-X,p}$ can be calculated from Equations.

$$E_{1,4} = \frac{E_{X,s} + E_{M,p}}{2} \pm \frac{[(E_{M,p} - E_{X,s})^2 + 16V_{M,p-X,s}^2]^{\frac{1}{2}}}{2}$$

$$E_{2,3} = \frac{E_{M,s} + E_{X,p}}{2} \pm \frac{[(E_{M,s} - E_{X,p})^2 + 48V_{M,p-X,s}^2]^{\frac{1}{2}}}{2}$$

Schematic energy levels in AMX₃ perovskites

CsPbI₃ vs CsPbBr₃ vs CsPbCl₃

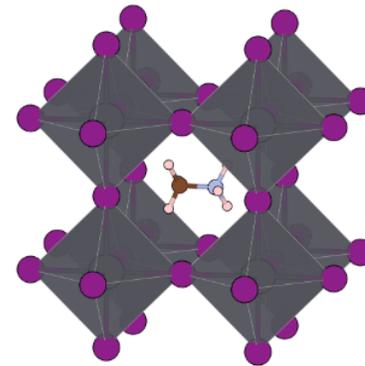
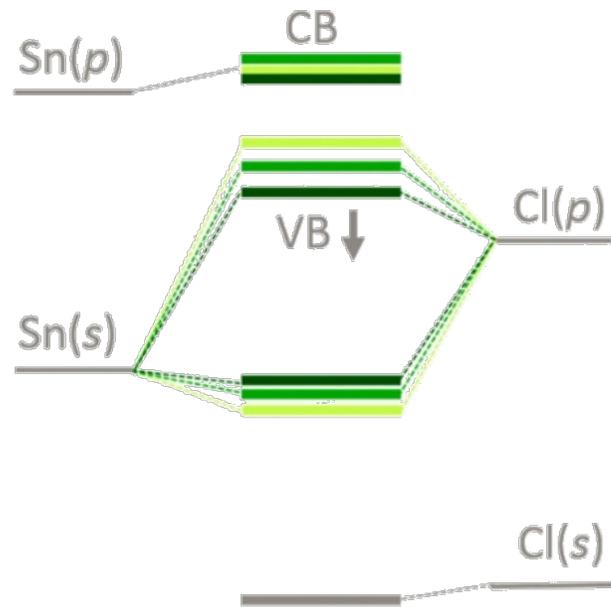


AMX₃

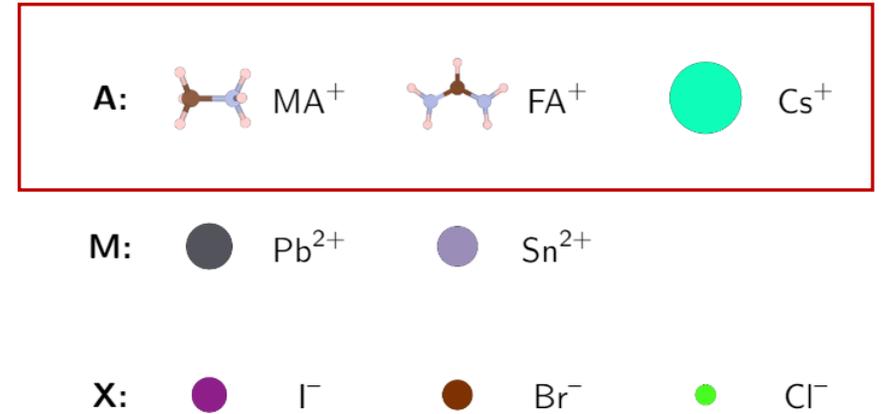
				helium 2 He 4.0026
carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
ununquadium 114 Uuq [289]				

Schematic energy levels in AMX_3 perovskites

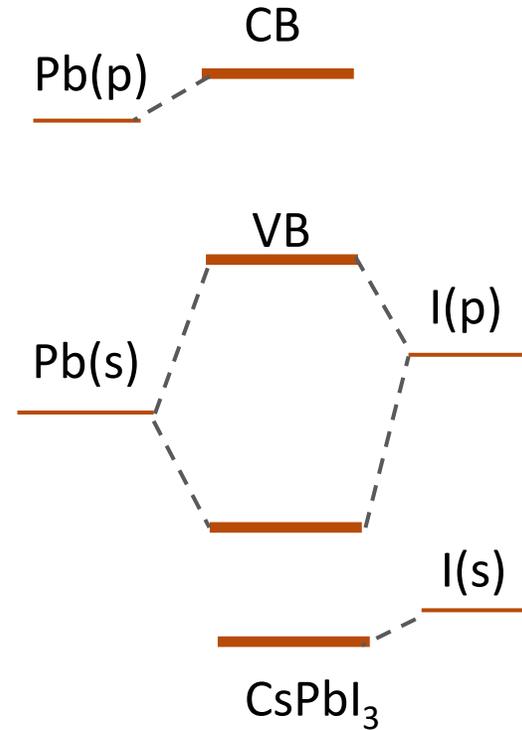
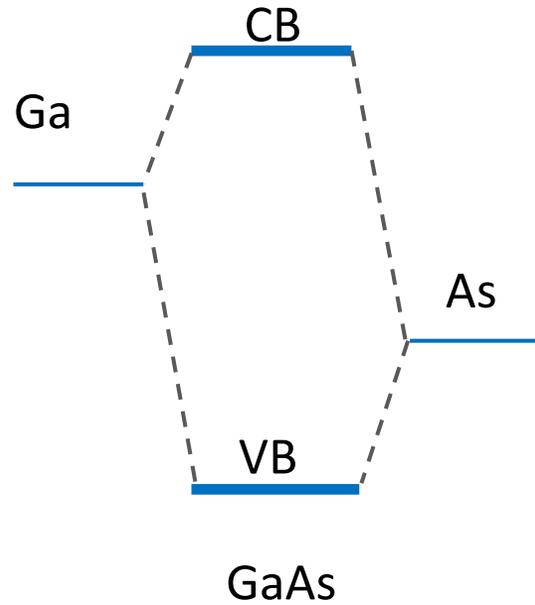
$CsSnCl_3$ vs $MASnCl_3$ vs $FASnCl_3$



MAPbI₃



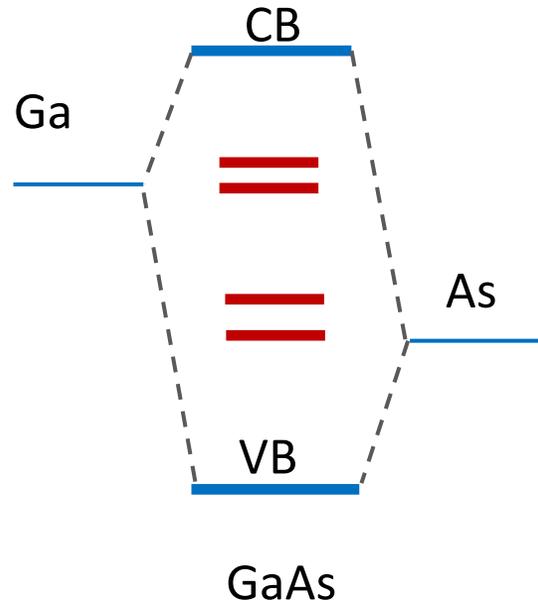
Assignment 1:



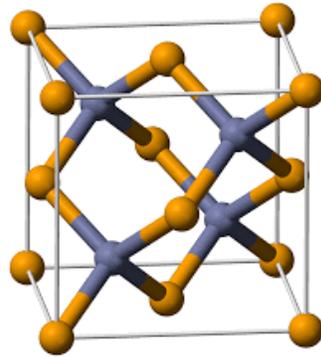
1. Expand the lattice parameters by 10% and how the bandgap change for the two compounds?
2. Change Pb to Sn: how does the bandgap of CsSnI₃ compared to CsPbI₃?
3. Mixed Sn and Pb, how does the bandgap change again compared to pure Sn or Pb perovskites?

Assignment 1:

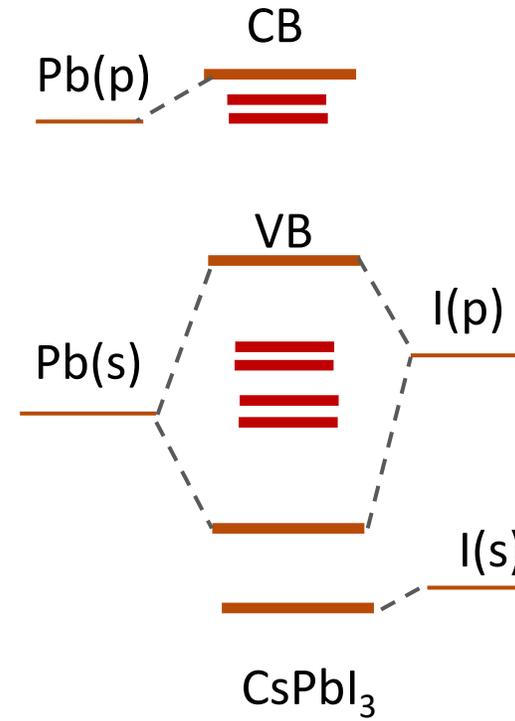
Defect-intolerant



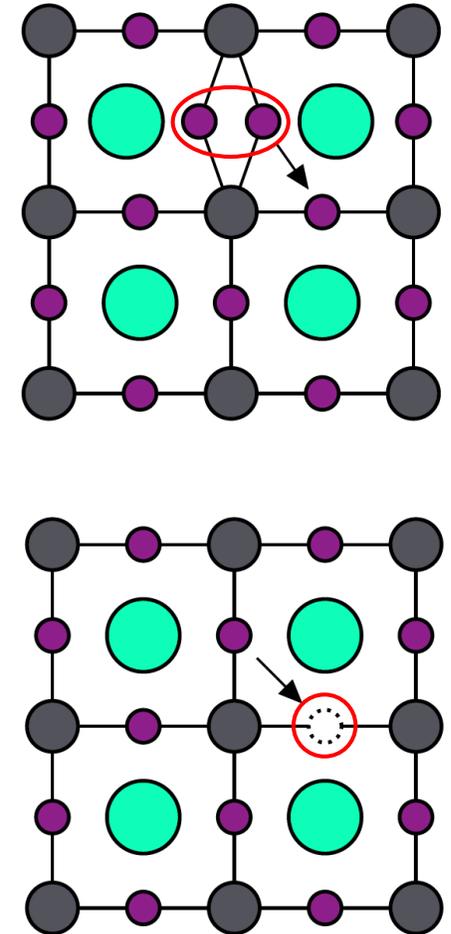
Mid-gap states



Defect tolerant

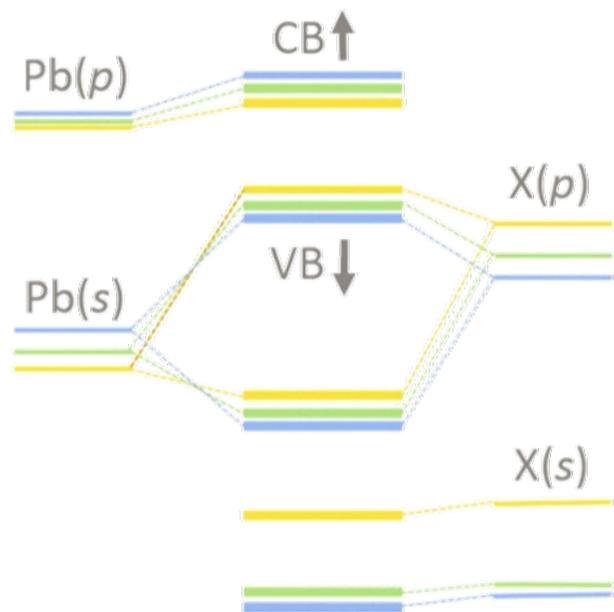


Shallow or intra-band states



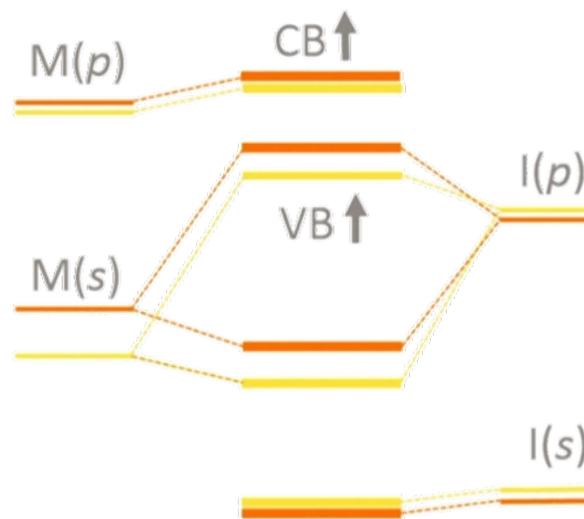
Schematic energy levels in AMX_3 perovskites

a $CsPbI_3$ vs $CsPbBr_3$ vs $CsPbCl_3$



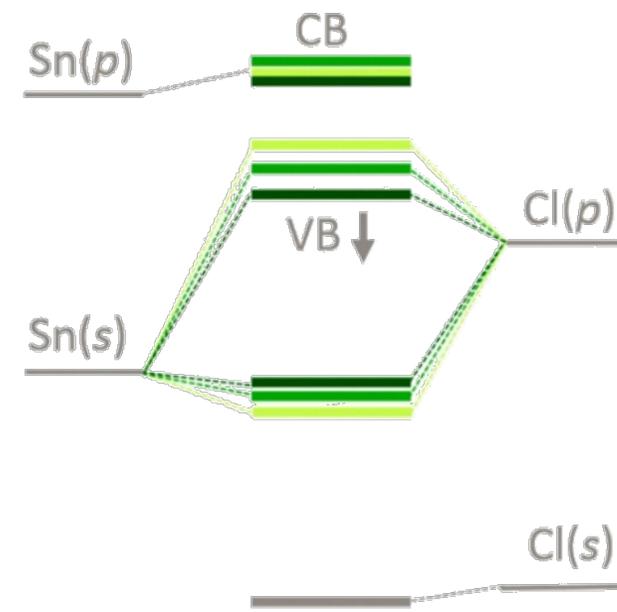
X

b $CsPbI_3$ vs $CsSnI_3$



M

c $CsSnCl_3$ vs $MASnCl_3$ vs $FASnCl_3$



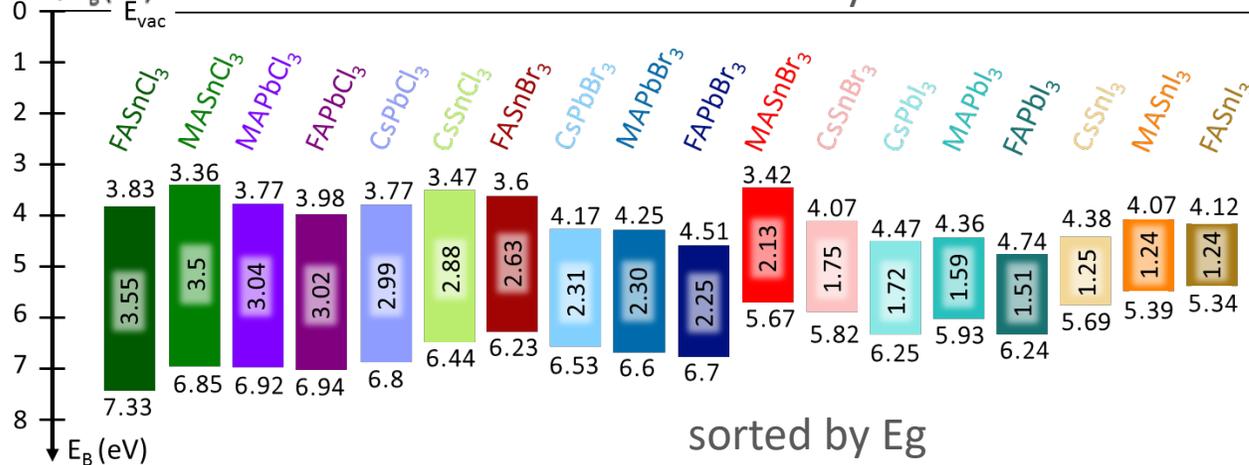
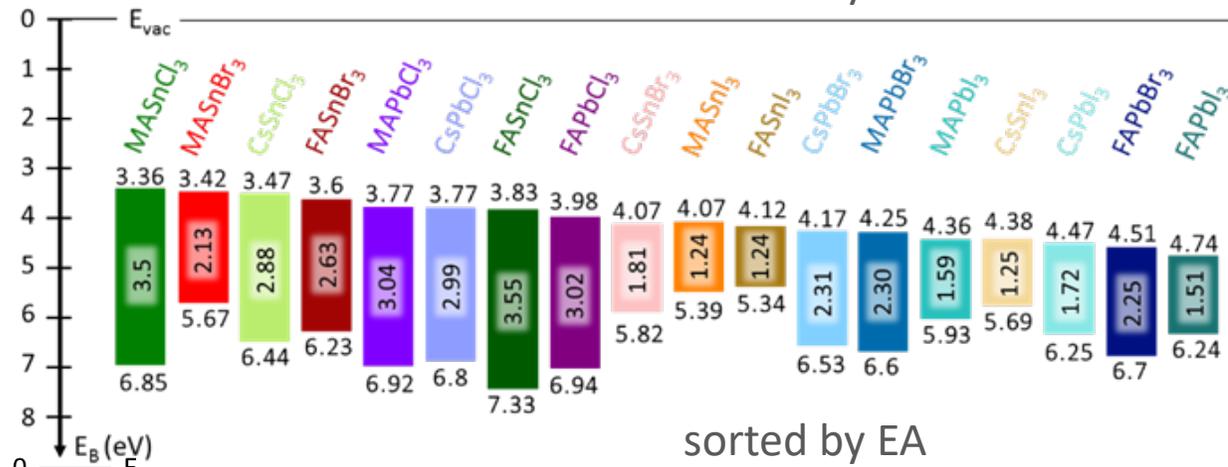
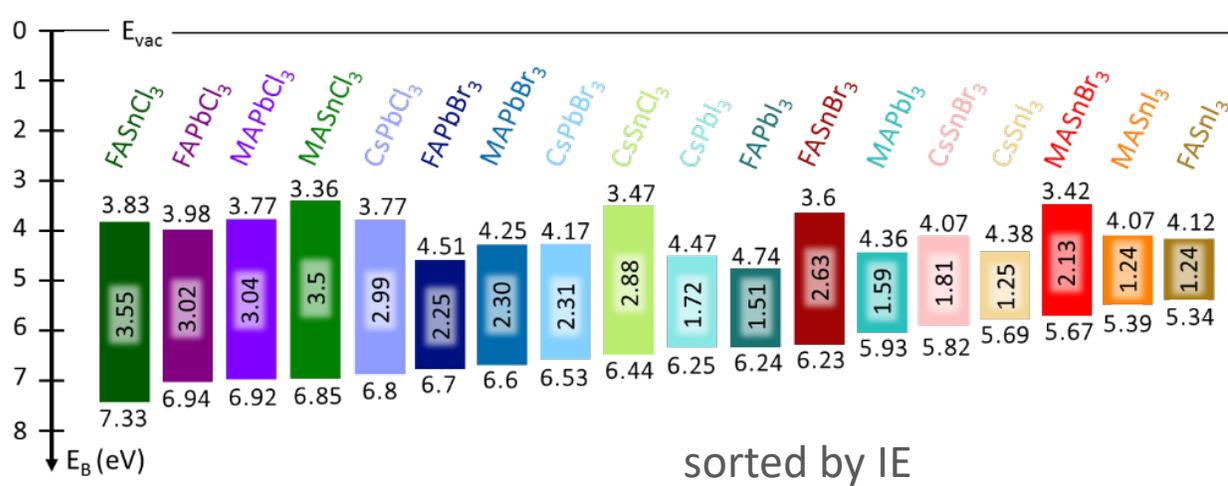
A

All trends in ABX₃ perovskites

Energy level variations are determined mainly by

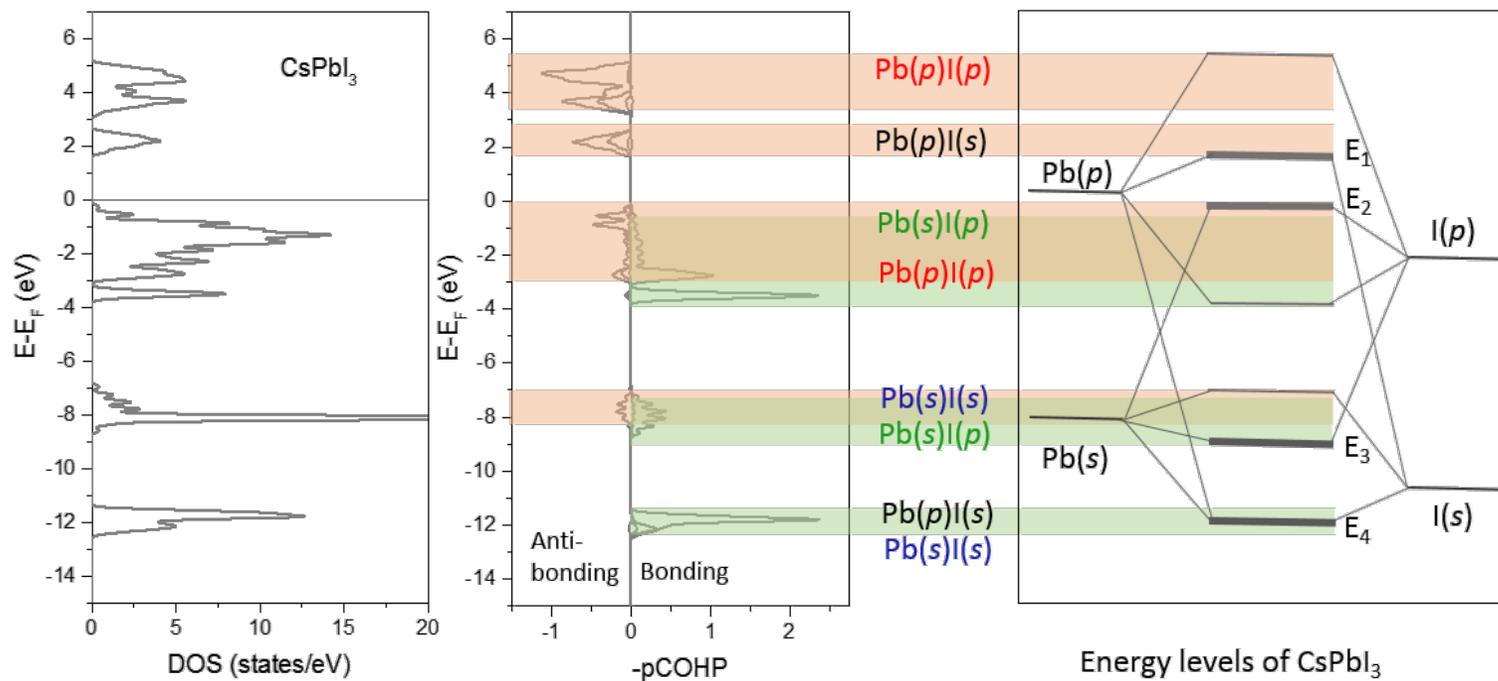
- (i) the relative positions of the atomic energy levels of B and X
- (ii) the A/B-X interaction strength.

Tao, S., Schmidt, I., Brocks, G. *et al. Nat Commun* 10, 2560 (2019).

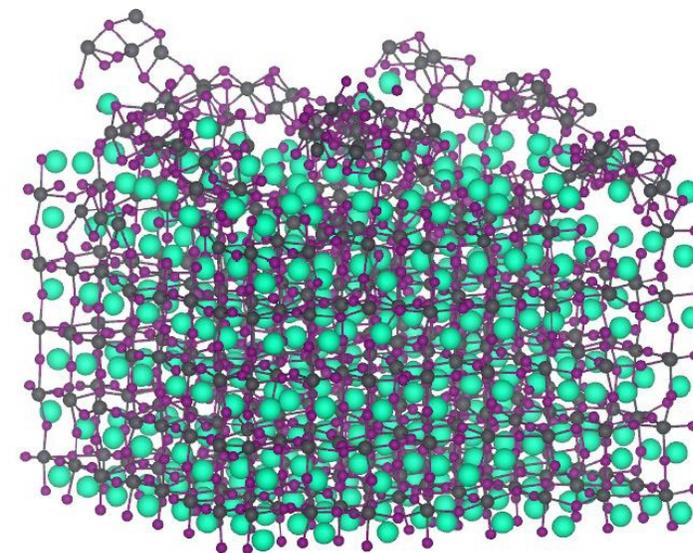


This lecture(s)

- Theory of DFT (brief) with a focus on electronic structures of solid-state systems (1h)
- DFT + chemical bonding analysis + tight binding + experiments for halide perovskites (1h)
- **Theory of MD (brief) and various interactions in materials (basics of force fields) (1h)**
- Theory of ReaxFF reactive force field (1h) **Assignment 3**
- Reactive MD for halide perovskites (1h)

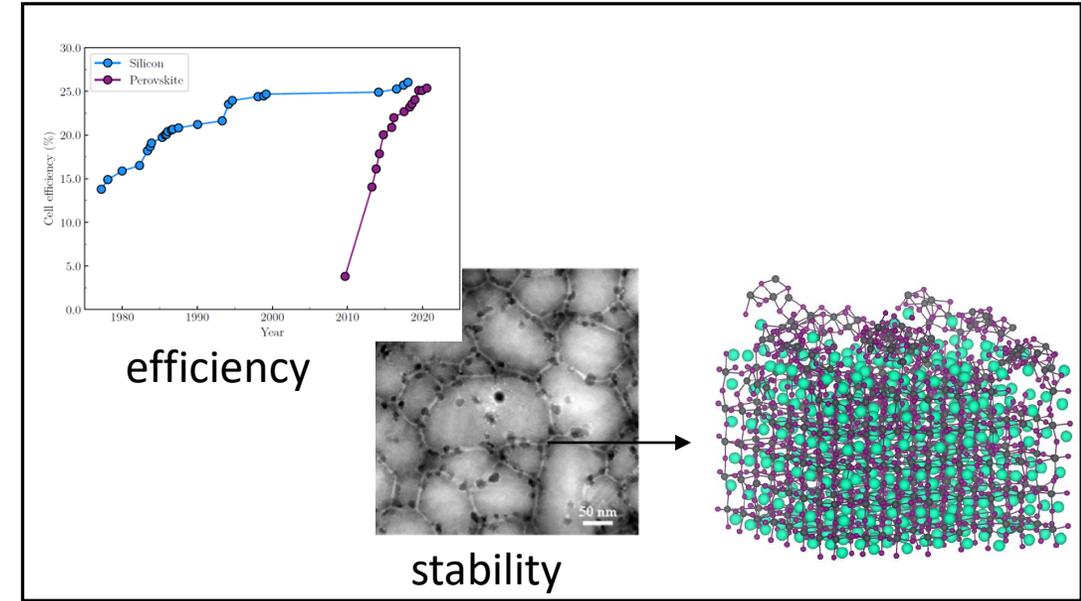
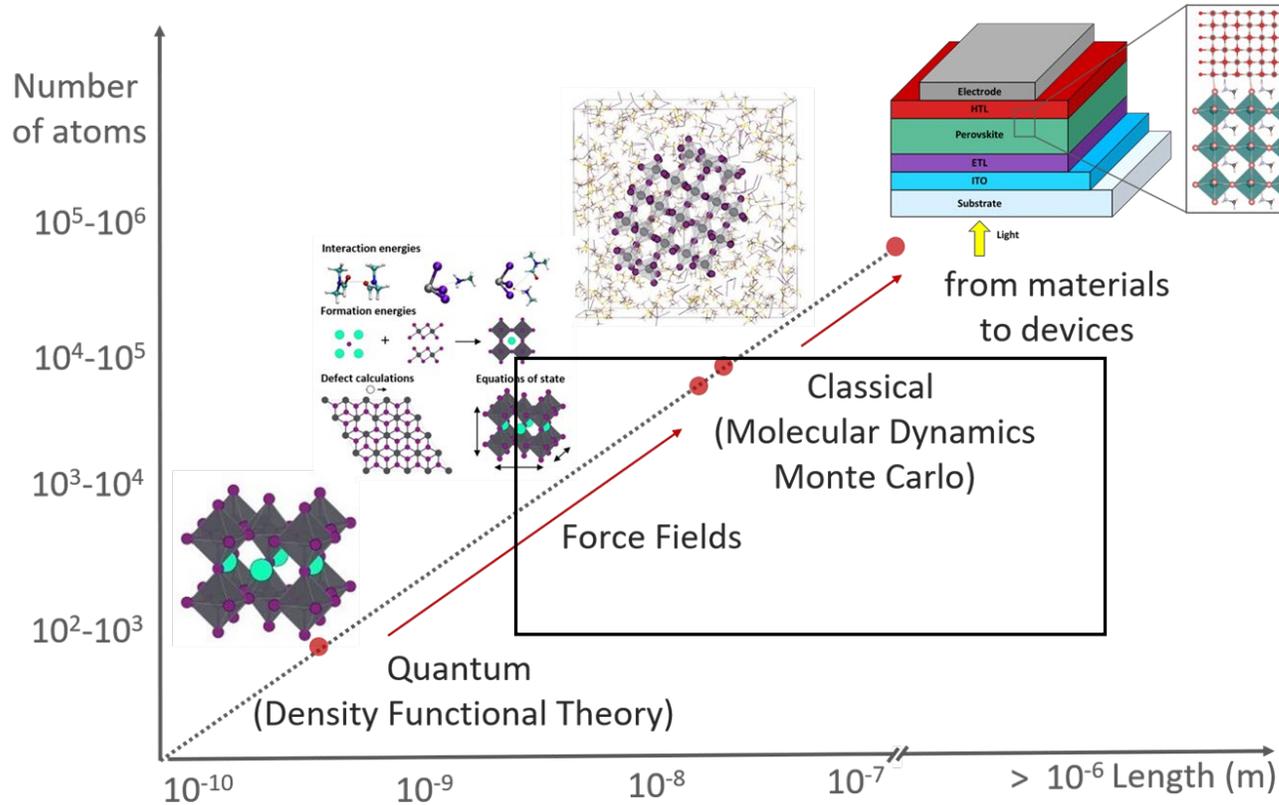


understanding the electronic properties
(DFT)



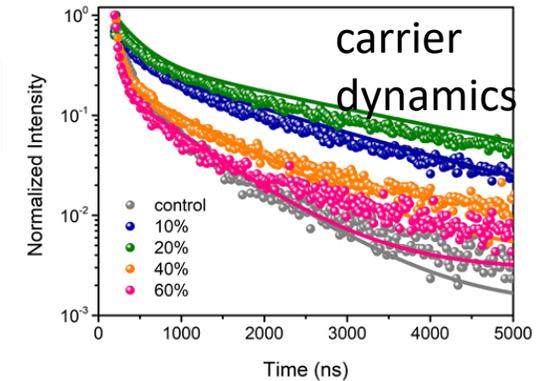
improving the stability
(MD)

From DFT to reactive MD



predict
interpret

Experiments

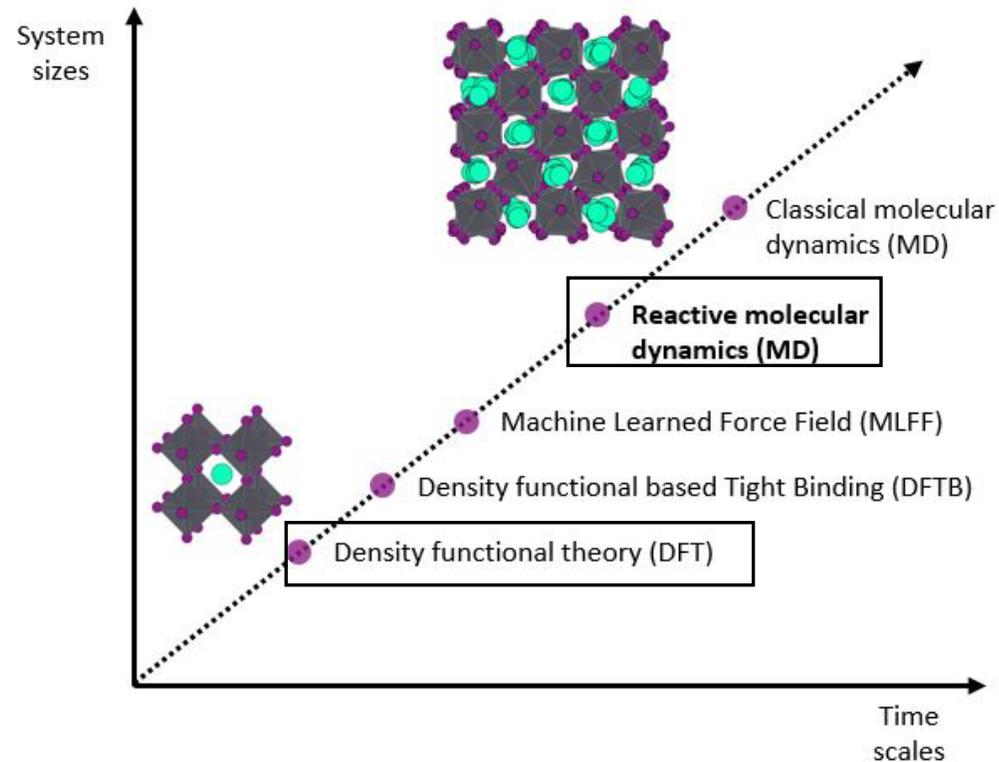


emission colour

Scaling up DFT

by combining, DFTB, MD, MC, ML, other theory (whenever relevant and available).

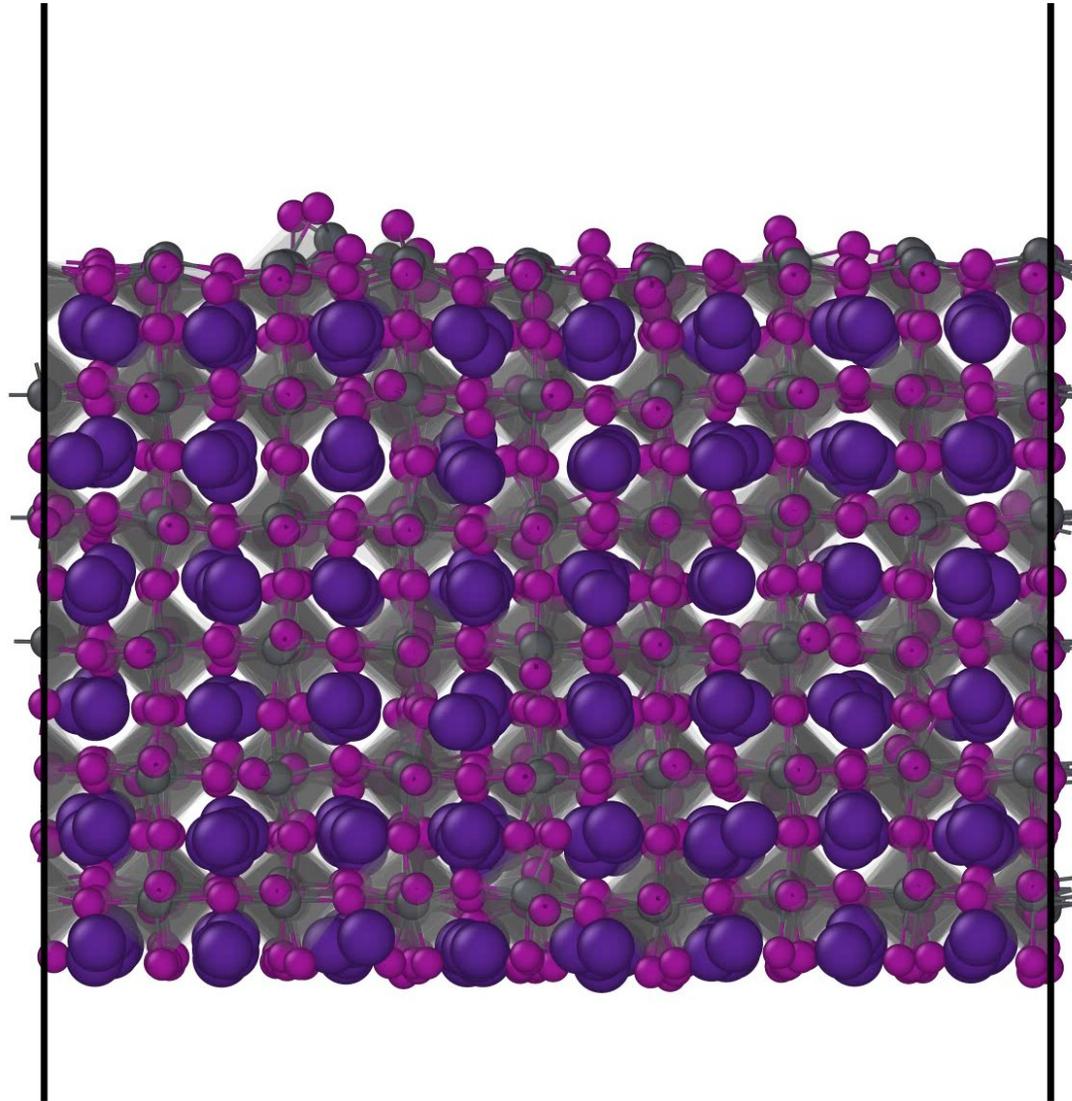
To study the impact of the **dynamical processes on the stability of halide perovskite**, we needed more efficient methods.



Molecular Dynamics solves newton's equations of motion to produce **dynamical behavior** as a function of time. MD relies on the **availability of force fields/interatomic potentials**.

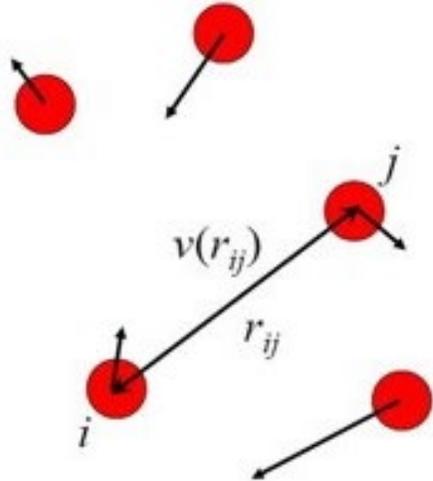
We use several level of potentials, today we focus on **ReaxFF**.

ReaxFF reactive Molecular Dynamics simulations



ReaxFF reactive MD simulations of surface degradation reactions of halide perovskite (CsPbI_3) at 700K.

Molecular Dynamics

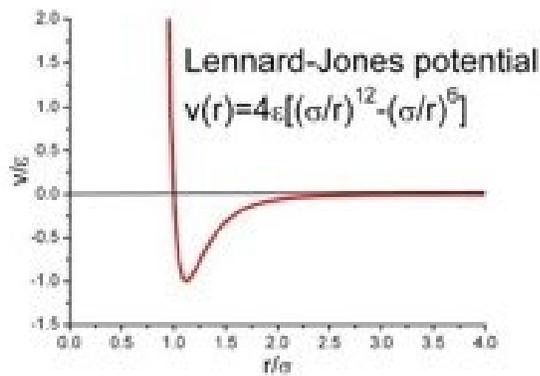


$$F_i = m_i a_i$$

$$F_i = -\nabla_i V$$

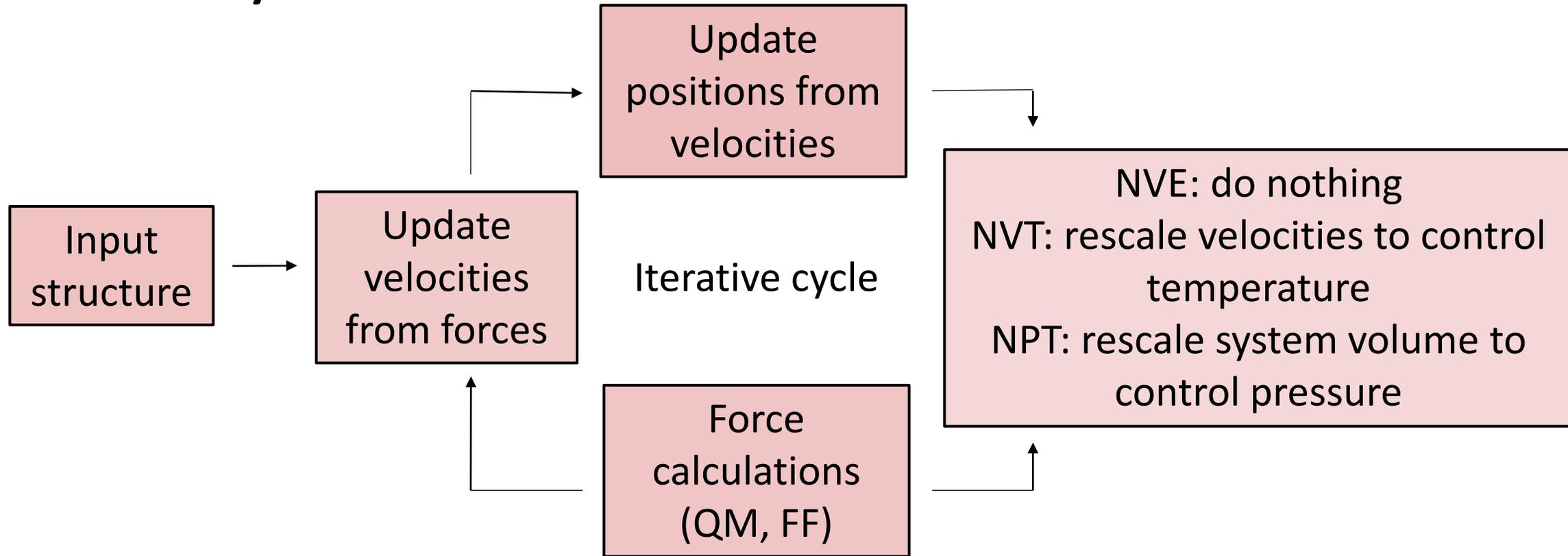
$$-\frac{dV}{dr_i} = m_i \frac{d^2 r_i}{dt^2}$$

F: force
m: mass
a: acceleration
V: potential energy
r: positions
t: time



- Molecular Dynamics solves **newton's equations** of motion to produce dynamical behavior/**positions of particles (r)** as a function of **time(t)**.
- Newton's equation of motion can relate the **derivative of the potential energy** to the changes in positions of particles as a function of time.
- MD relies on the availability of **potential energy (V)** of the system, which depends on the atomic coordinates (r) and the type of bond in accordance with the type of atom, its hybridization state, etc..
- Different mathematical functional forms to produce this potential energy led to the development of different **Force Fields (interatomic potentials)**.

Molecular Dynamics



Uniqueness: **T and P effects** as a function of **t**;

Properties: diffusion constants, reaction rates, probability distribution function, radius distribution function...

Applications: phase transitions, ion diffusion, chemical reactions, thermal conductivities...

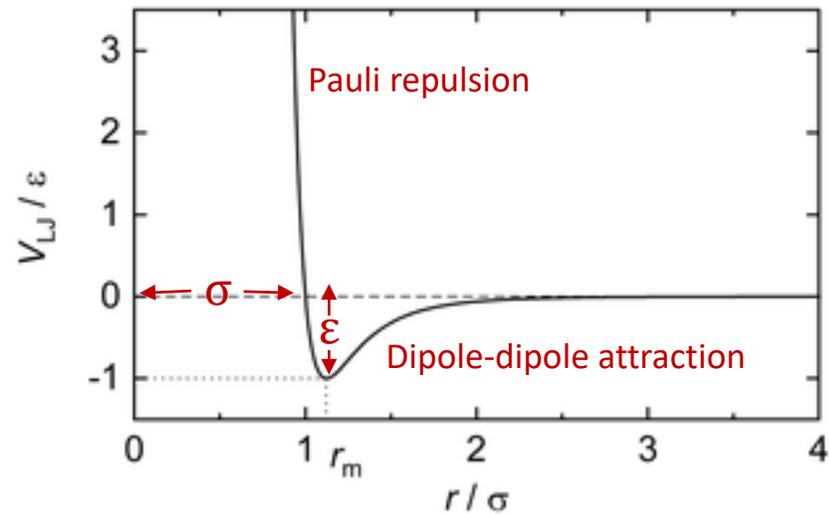
Relies on the availability of force fields.

Further information on Molecular Dynamics: **time-step, equilibration, thermostat, analysis...**
Allen and Tildesley: Computer Simulation of Liquids, Oxford University Press, New York 1987.
Frenkel and Smit: Understanding molecular simulation, Academic Press, San Diego 1996.

Force fields are set of empirical potentials to describe the **various interatomic interactions** in materials.

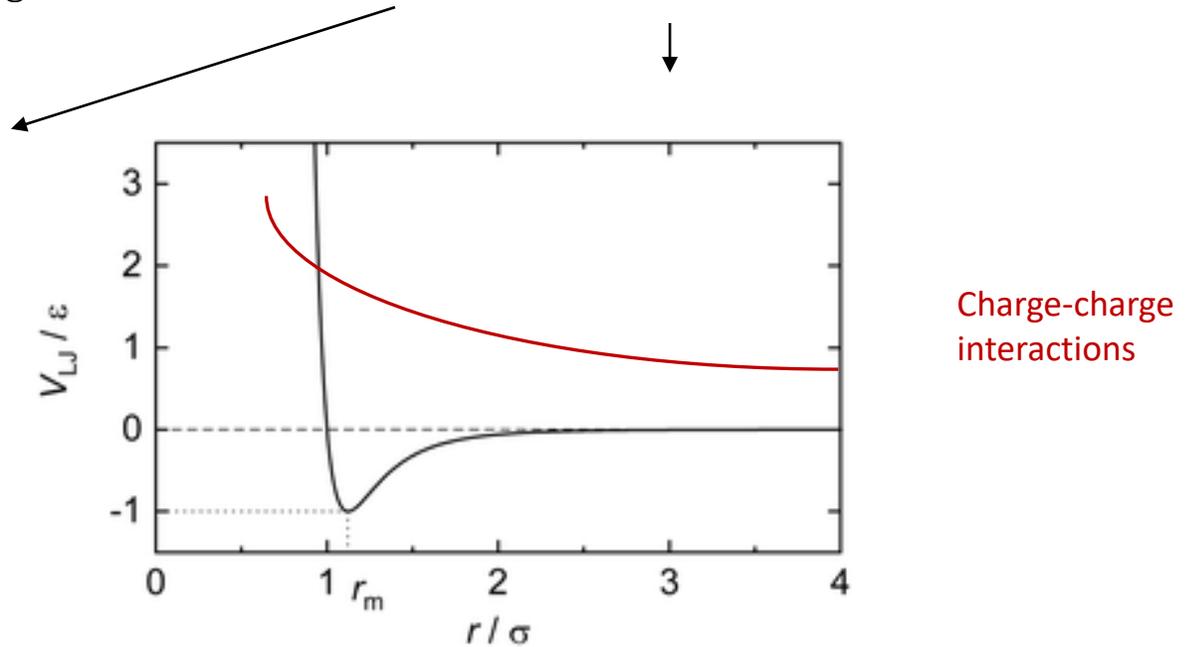
Force field system energy: **intermolecular** (nonbonded) interactions (the classical picture)

$$E_{\text{FF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$



$$V_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Lennard-Jones potential suited for simple atoms/molecules



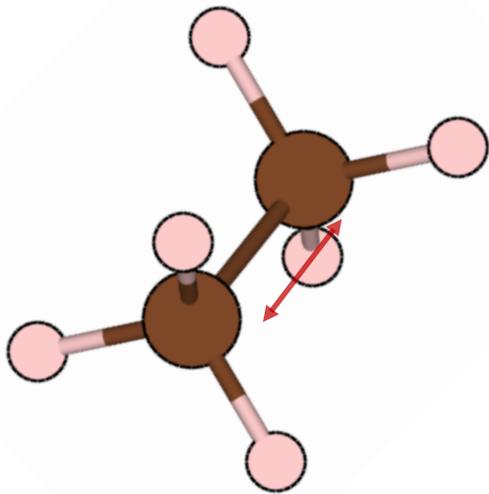
$$V_{\text{coul}}(r) = \frac{q_i q_j}{4\pi\epsilon_0 r}$$

Additional Coulomb term added for ionic systems

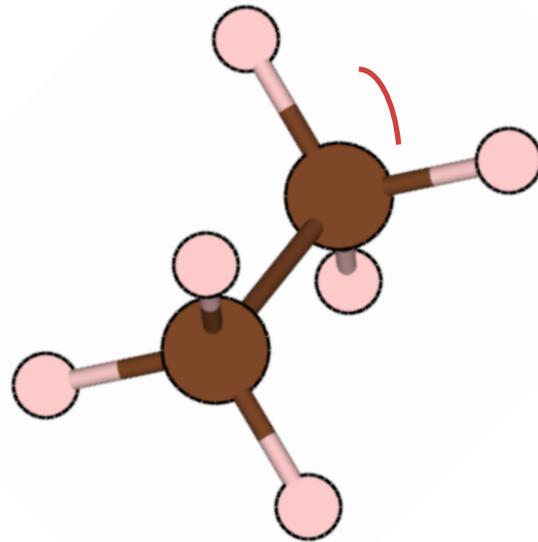
Force fields are set of empirical potentials to describe the **various interatomic interactions** in materials.

Force field system energy: **intramolecular (bond) interactions (the classical picture)**

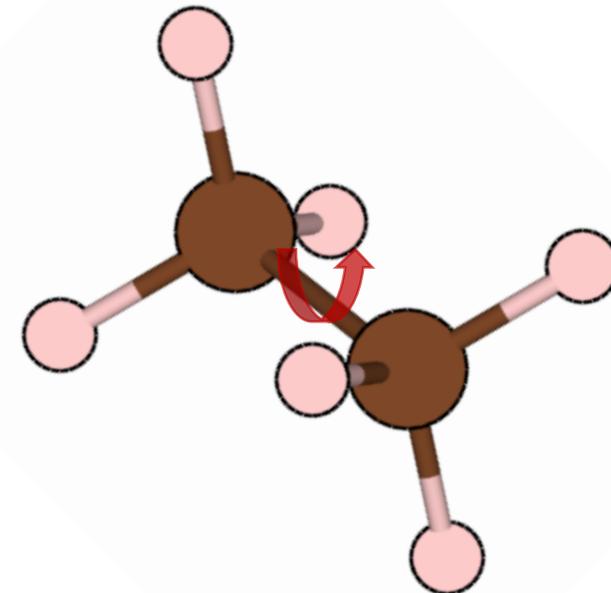
$$E_{\text{FF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$



$$E_{\text{bond-stretch}} = \sum K_b (b - b_0)^2$$



$$E_{\text{bond-bend}} = \sum K_\theta (\theta - \theta_0)^2$$

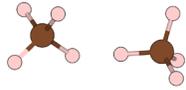


$$E_{\text{rotate-along-bond}} = \sum K_\phi (1 - \cos(n\phi))$$

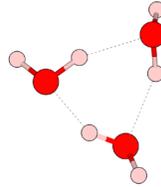
Quadratic polynomial and sometimes also higher order terms, K depends on the chemical type of atoms

Real-life materials systems: interplay/combination of many interactions

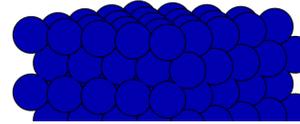
a) Methane (CH_4)



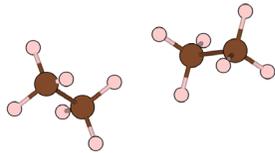
c) Water (H_2O)



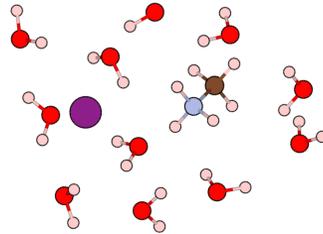
e) Cobalt (Co)



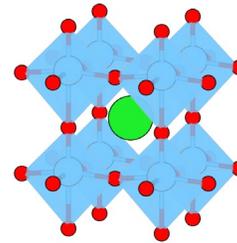
b) Ethane (C_2H_6)



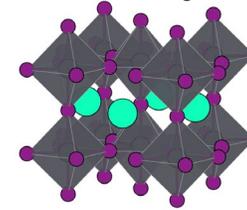
d) Methylammonium iodine (MAI) in water



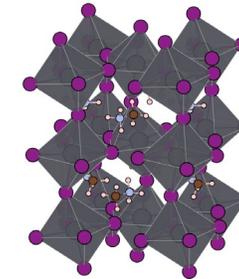
f) BaTiO_3



g) CsPbI_3



h) MAPbI_3



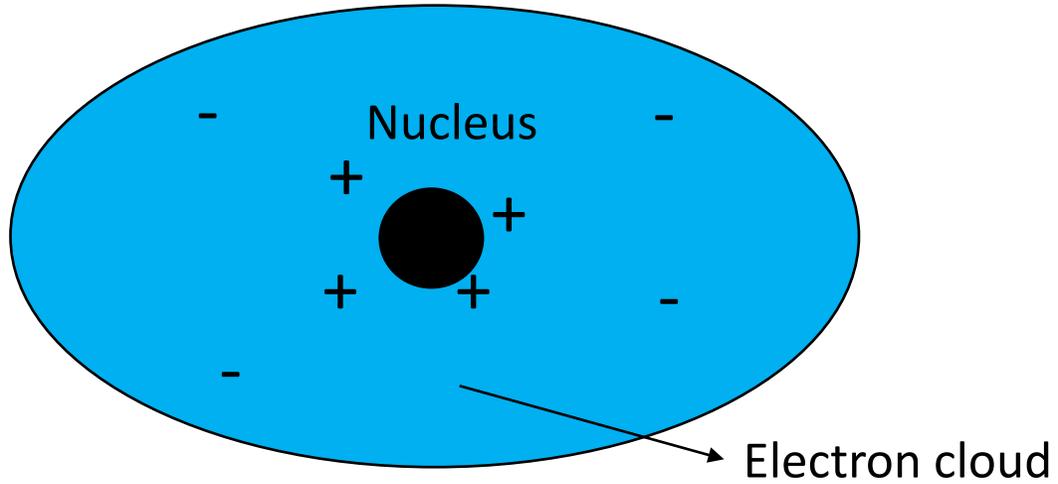
Interatomic interactions

- Covalent bonds
- Ionic bonds
- Metallic bonds
- Permanent dipole-dipole interactions including hydrogen bonds
- Induced dipole interactions (van der Waals)



Decreasing
strength

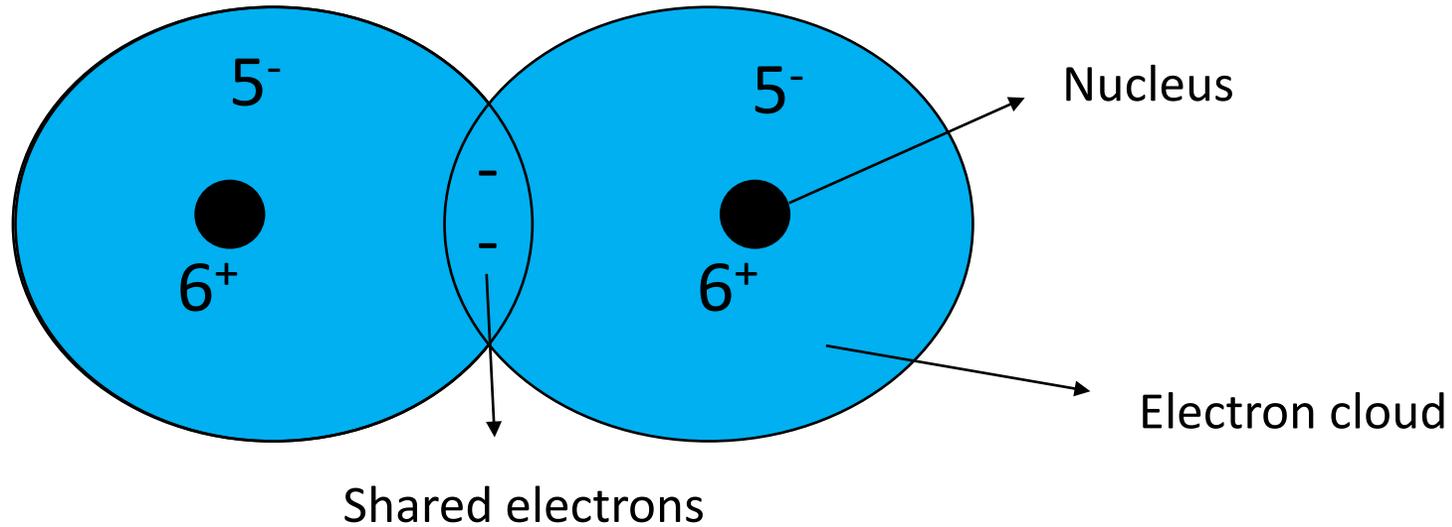
Simplistic atom model



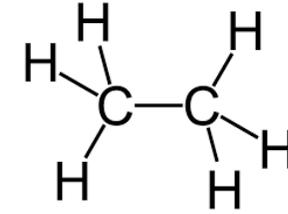
Atom model for **Beryllium** ($1s^2 2s^2$)

$$E_{Coulomb} = C \frac{q_i q_j}{R_{ij}}$$

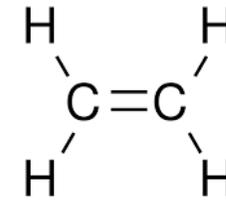
Covalent bond



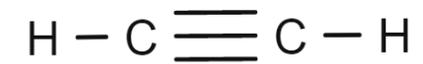
Carbon: $1s^2 2s^2 2p^2$



Ethane



Ethylene



Acetylene

- 2 atoms 'share' electrons and this creates a strong attractive interaction between the shared electrons and the effective charge of the nucleus and the remaining, unshared electrons
- Atoms can share 2 electrons (H_2), can also share 4 electrons (double bonds, O_2) or even 6 electrons (triple bond, N_2) making very strong bonds.
- Covalent compounds made of elements of nonmetals, and elements with similar electronegativity (differences < 2).

More electropositive

More electronegative

s^1 s^2 d^1 d^{10} p^1 p^2 p^3 p^4 p^5 p^6

H 2.1

F 4.0

Na 0.9

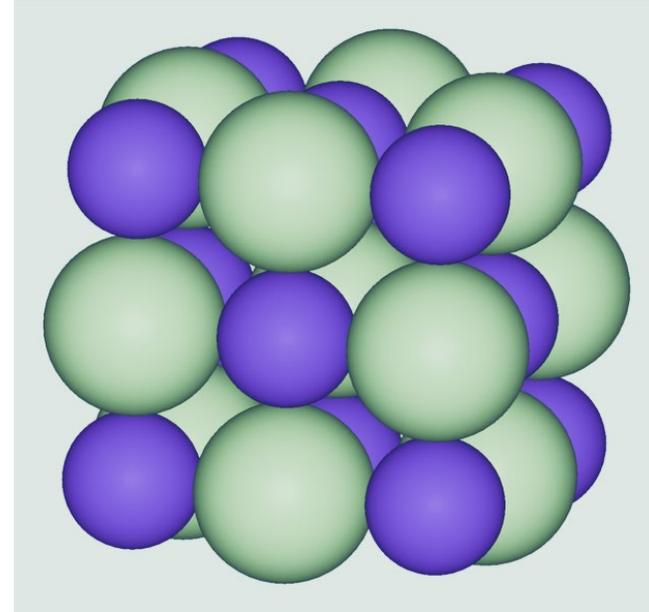
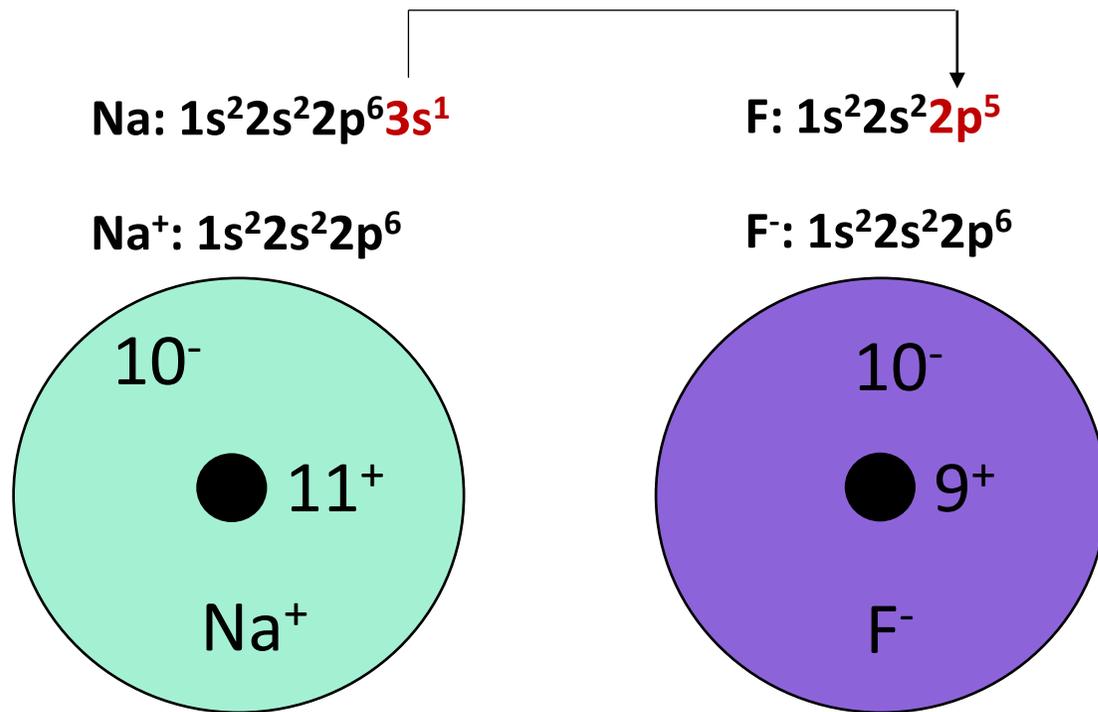
Cl 3.0

Cs 0.7

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnillium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]						ununquadium 114 Uuq [289]					

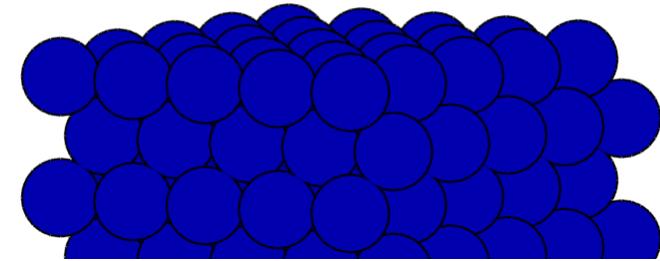
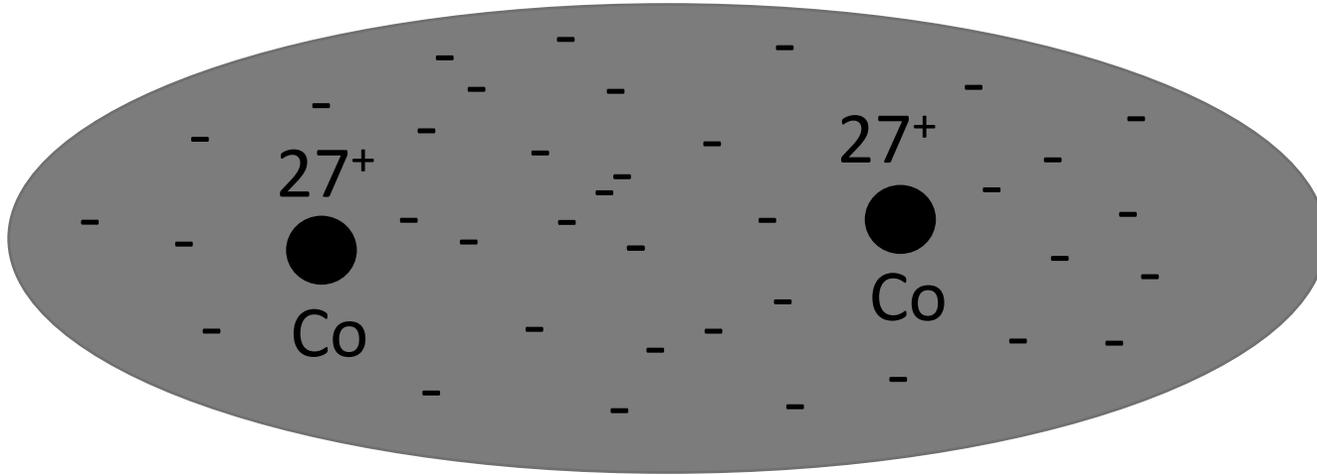
- Noble gas atoms have the most stable electron configurations: full s, p shells
- Non-noble metals strive to obtain a noble-gas configuration
- Elements on the left-side of the periodic system do this by trying to lose electron (s) (electropositive), while atoms on the right side try to gain electron (s) (electronegative).
- This forms ionic bonds in ionic compounds: **NaCl**, **NaF**, **MgO**, **Mg(OH)₂**...

Ionic bond



- 1 atom donates an electron to another atom; this electron transfer costs energy;
- The energy loss is compensated by the **Coulomb attraction** between the cations (positively charged atoms) and anions (negatively charged atoms);
- By organizing themselves into regular patterns (crystals) the cation/anion pairs maximize Coulomb stabilization.

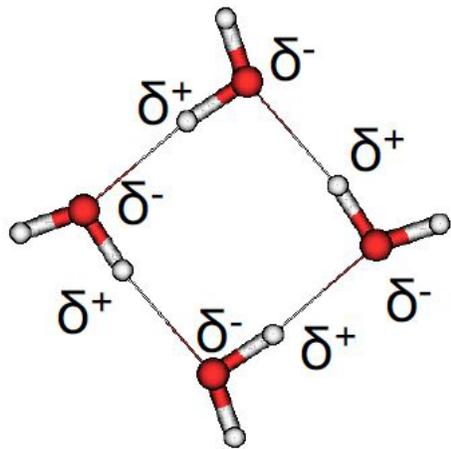
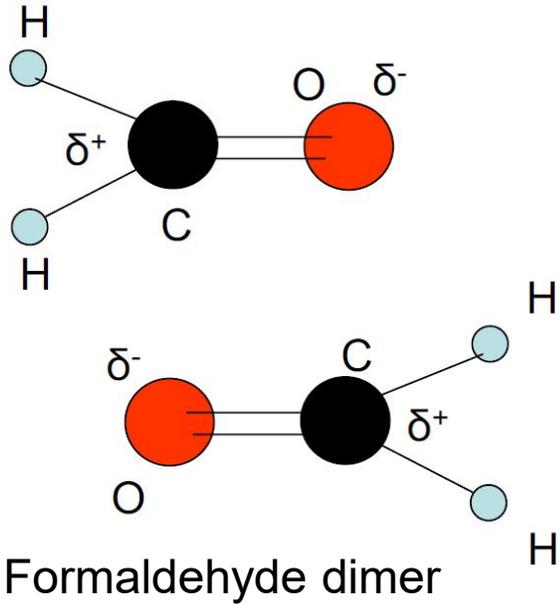
Metallic bond



hexagonal close-packed (hcp) Cobalt

- Atoms are sharing a lot of electrons;
- Electrons are highly delocalized, leading to high electrical and thermal conductivity;
- Metals make lots of weak bonds, while covalent materials make few very strong bonds; this partially explains the ductile nature of metals and the brittle behavior of covalent materials.

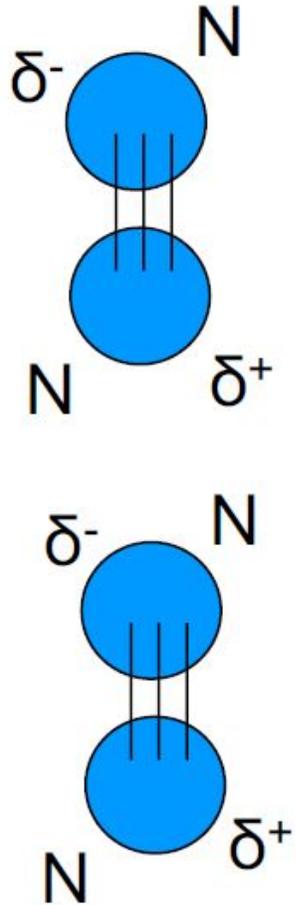
Permanent dipole-dipole interactions



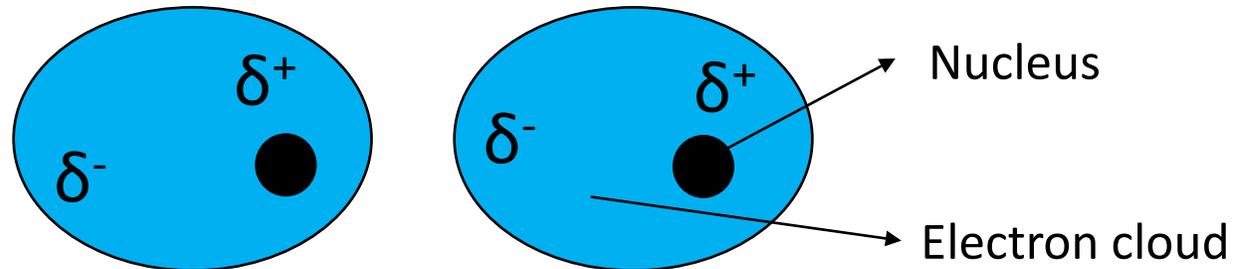
- Atoms connected by covalent bonds can transfer a partial charge, thus creating a **permanent dipole** that is stabilized within the molecule by **Coulomb interactions**
- Two molecules with a permanent dipoles will orient themselves to maximize dipole-dipole interactions by minimizing the distance between opposite-charged atoms
- Much **weaker than ionic bonds**, since the charge transfer is generally small
- Stronger distance dependency than ionic bond ($1/r^3$ instead of $1/r$) since at longer distance the influence of the local charge distribution in the molecule disappears
- **Hydrogen bonds** are a subclass of strong permanent dipole interactions usually associated with $-\text{OH}$, $-\text{NH}_2$, $-\text{FH}$ groups. They are very important for biological systems.

Hydrogen bond network in a water quadrimer

Induced permanent dipole-dipole interactions (van der Waals)



- Atoms with and without permanent dipoles can polarize each other, creating an **induced dipole**.
- The creation of the induced dipole raises the energy of the molecule, but the Coulomb-interaction resulting from the interaction between these induced dipole compensates for this.
- Much weaker than permanent dipoles, but very general.
- Very strong distance dependency than ionic bond ($1/r^6$) since molecules need to be very close to each other for this polarization to occur.
- Also known as attractive van der Waals interactions.



Re-arrangement of electron clouds due to polarization

Interatomic interactions (very general trend)

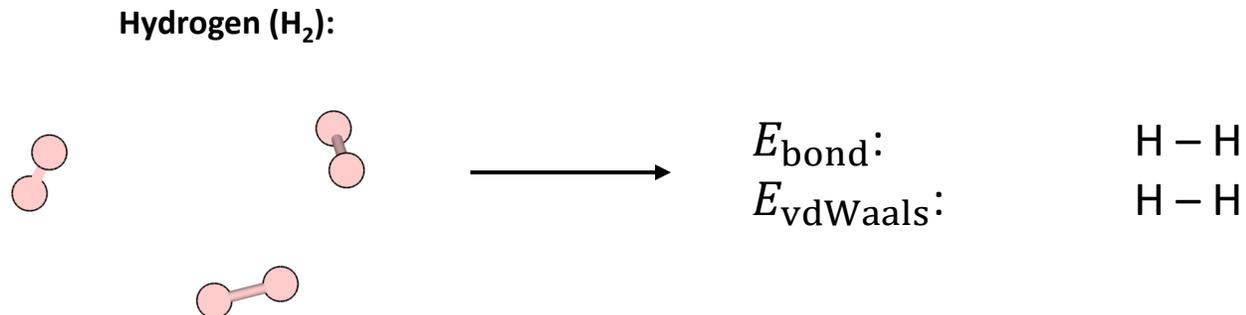
- Covalent bonds: 200-900 kJ/mol
- Ionic bonds: 100-500 kJ/mol (but many in crystals)
- Metallic bonds: 10-80 kJ/mol (but a lot of them)
- Permanent dipole-dipole interactions including hydrogen bonds: 5-25 kJ/mol
- Induced dipole interactions (van der Waals): 1-5 kJ/mol

*Most materials have the combination of several of these interactions/bonds.

Assignment 2: system exploration for force fields (1)

Exercise: With this exercise we hope to give you some insights into the process of developing a force field. From a range of given material systems we want you to elaborate on the **types of interactions** that you think are particularly important for an accurate and representative description of the material systems, highlighting the **elements involved** in these interactions.

Example exercise:
Hydrogen gas (H_2)



Assignment 2: system exploration for force fields (2)

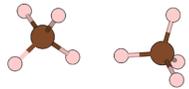
Force field system energy:

$$E_{\text{FF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

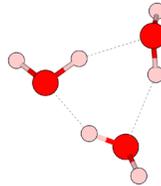
$$E_{\text{ReaxFF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{H-bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{spec}}$$

Material systems:

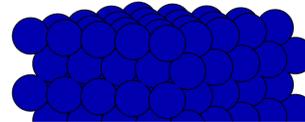
a) Methane (CH₄)



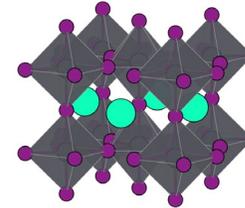
c) Water (H₂O)



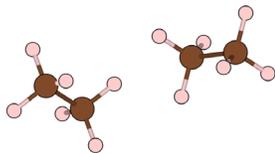
e) Cobalt (Co)



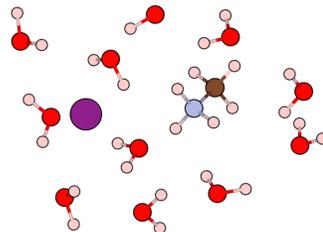
g) CsPbI₃



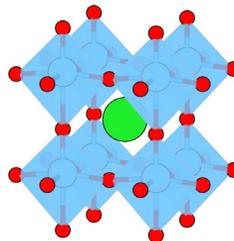
b) Ethane (C₂H₆)



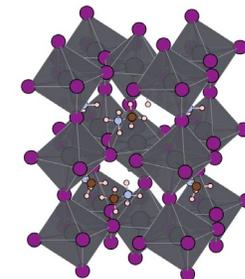
d) Methylammonium iodine (MAI) in water



f) BaTiO₃



h) MAPbI₃



This lecture(s)

- Theory of DFT (brief) with a focus on electronic structures of solid-state systems (1h)
- DFT + chemical bonding analysis + tight binding + experiments for halide perovskites (1h) **Assignment 1**
- Theory of MD (brief) and various interactions in materials (basics of force fields) (1h) **Assignment 2**
- **Theory of ReaxFF reactive force field (1h) Assignment 3**
- Reactive MD for halide perovskites (1h)

Interatomic interactions (very general trend)

- Covalent bonds: 200-900 kJ/mol
- Ionic bonds: 100-500 kJ/mol (but many in crystals)
- Metallic bonds: 10-80 kJ/mol (but a lot of them)
- Permanent dipole-dipole interactions including hydrogen bonds: 5-25 kJ/mol
- Induced dipole interactions (van der Waals): 1-5 kJ/mol

*Most materials have **the combination of several interactions/bonds**.

Force field energy: Classical FF vs ReaxFF

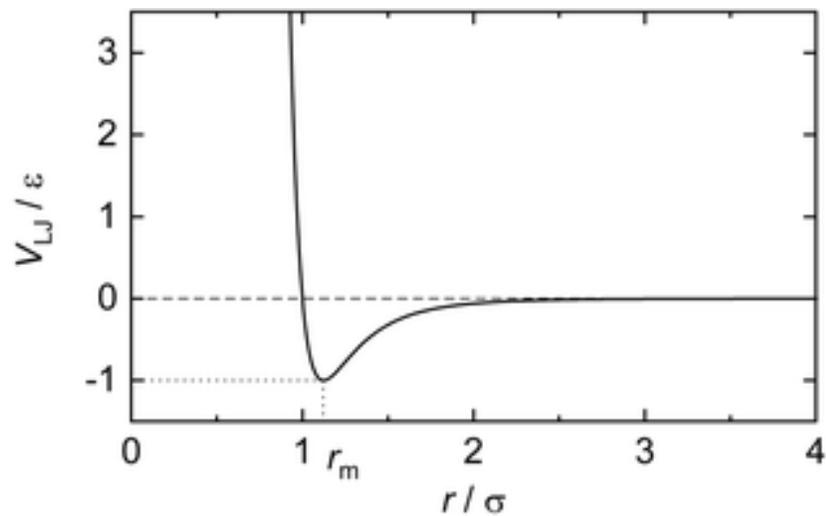
$$E_{\text{FF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

$$E_{\text{ReaxFF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{H-bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{spec}}$$

Force fields are set of empirical potentials to describe the **various interatomic interactions** in materials.

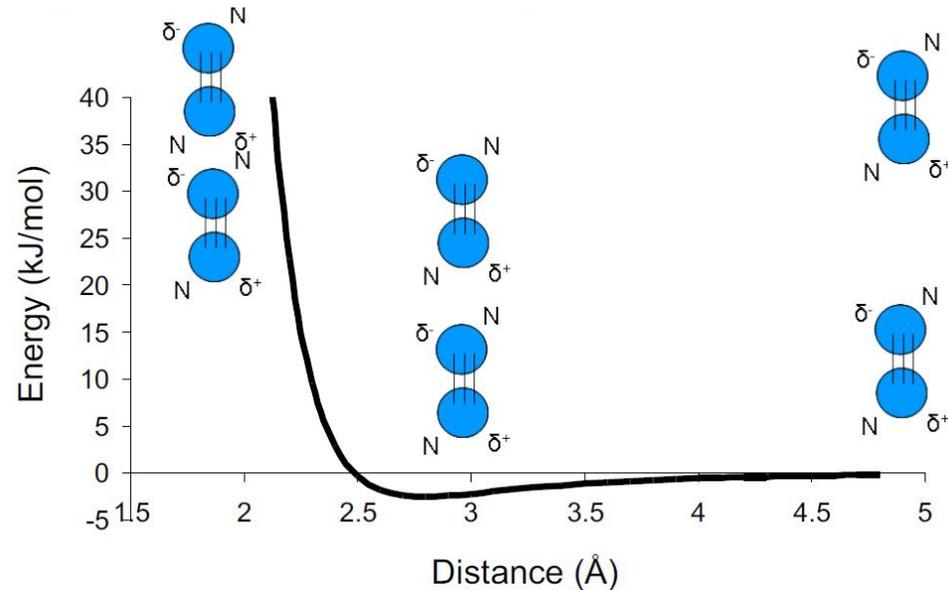
Force field system energy: **intermolecular** (nonbonded) interactions

$$E_{\text{FF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{vdWaal}} + E_{\text{Coulomb}}$$



$$V_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Lennard-Jones potential suited for simple atoms/molecules



N_2 gas

Concepts of covalent non-reactive force fields

System energy description for a simple **harmonic non-reactive** force field

$$E_{system} = E_{bond} + E_{angle} + E_{torsion} + E_{vdWaals} + E_{Coulomb}$$

$$E_{bond} = k_b (r - r_o)^2$$

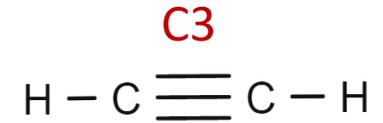
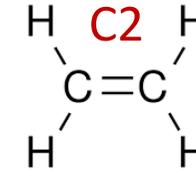
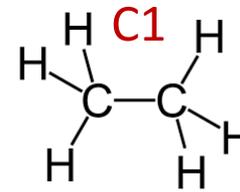
$$E_{angle} = k_v (\varphi - \varphi_o)^2$$

$$E_{torsion} = V_2 \cdot (1 - \cos 2\omega) + V_3 \cdot (1 + \cos 3\omega)$$

$$E_{vdWaals} = D_{ij} \left\{ \exp \left[\alpha_{ij} \cdot \left(1 - \frac{r_{ij}}{r_{vdW}} \right) \right] - 2 \cdot \exp \left[\frac{1}{2} \alpha_{ij} \cdot \left(1 - \frac{r_{ij}}{r_{vdW}} \right) \right] \right\}$$

$$E_{Coulomb} = C \cdot \frac{q_i \cdot q_j}{r_{ij}}$$

(multiple atom types to distinguish single, double and triple bonds)



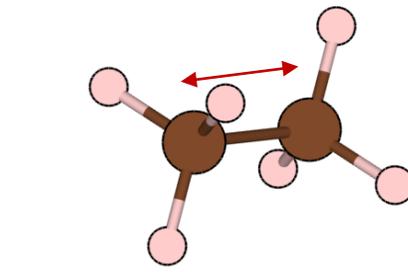
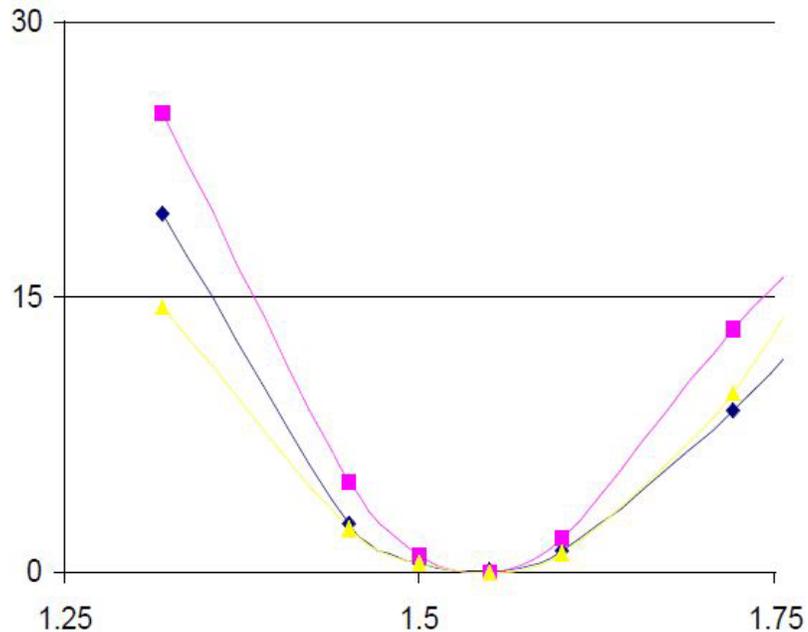
(L-J, Buckingham, **Morse potential...**)

(Fixed point charges)

- Can describe structures and energies close to equilibrium
- Expansion with anharmonic terms improves reliability and application range
- **Does not dissociate bonds properly, often transferability is limited**

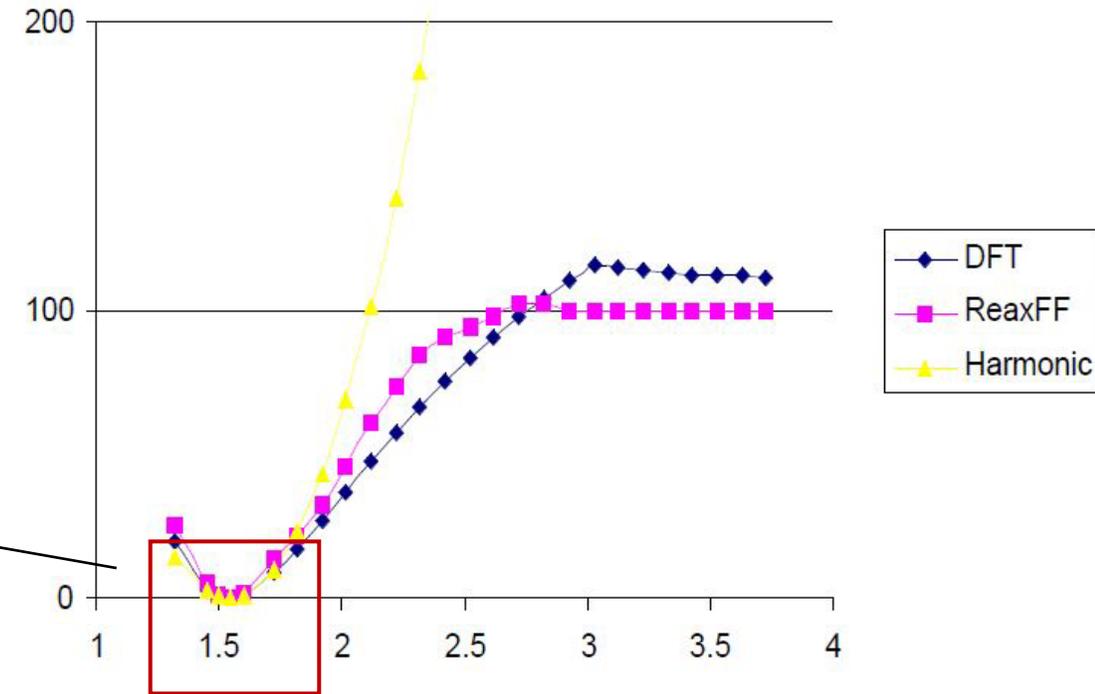
C-C bond stretching in Ethane

Around the equilibrium bond length



Legend for the first graph:
- DFT (blue diamonds)
- ReaxFF (magenta squares)
- Harmonic (yellow triangles)

Full dissociation curve



Legend for the second graph:
- DFT (blue diamonds)
- ReaxFF (magenta squares)
- Harmonic (yellow triangles)

- Although the harmonic approximation can describe the bond stretching around the equilibrium it cannot describe the **bond dissociation**.
- Harmonic force field needs to use **multiple atom types** to distinguish single, double and triple bonded carbons.

From non-reactive to reactive force fields: key features of ReaxFF

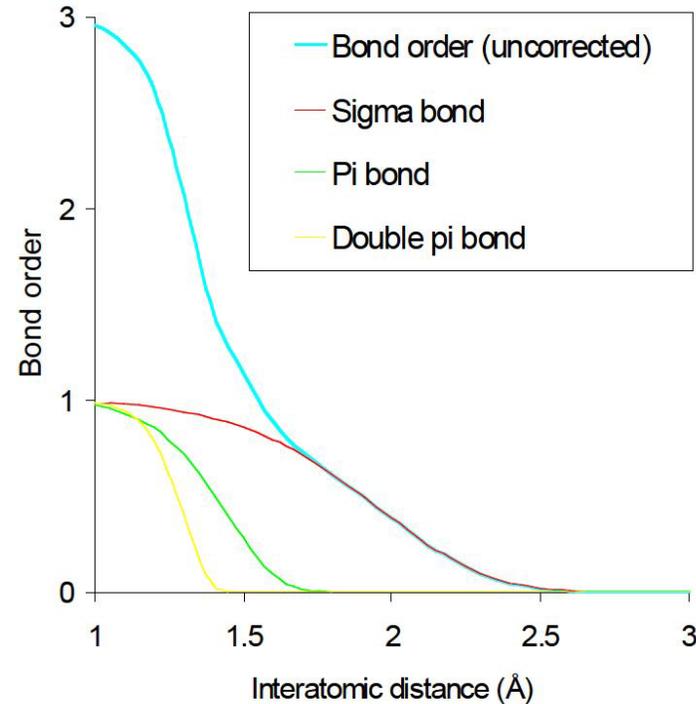
$$E_{\text{FF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

$$E_{\text{ReaxFF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{H-bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{spec}}$$

- To get a smooth transition from nonbonded to single, double and triple bonded systems ReaxFF employs a **bond length/bond order** relationship. Bond orders are updated every iteration.
- **All connectivity-dependent interactions** (i.e., valence and torsion angles) are made bond-order dependent, ensuring that their energy contributions disappear upon bond dissociation.
- Nonbonded interactions (van der Waals, Coulomb (ionic systems)) are calculated between **every atom pair**, irrespective of connectivity.
- Metal can be described by replacing the bond concept with a **density term**.
- ReaxFF uses a **geometry-dependent charge calculation scheme** that accounts for polarization effects.

Calculations of bond orders from interatomic distance

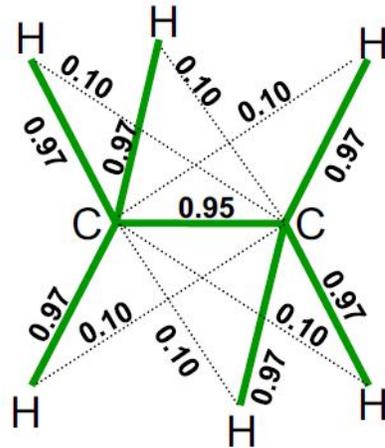
$$\begin{aligned}
 BO_{ij} &= BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} \\
 &= \exp \left[p_{bo,1} \cdot \left(\frac{r_{ij}}{r_0^{\sigma}} \right)^{p_{bo,2}} \right] + \\
 &\quad \exp \left[p_{bo,3} \cdot \left(\frac{r_{ij}}{r_0^{\pi}} \right)^{p_{bo,4}} \right] + \\
 &\quad \exp \left[p_{bo,5} \cdot \left(\frac{r_{ij}}{r_0^{\pi\pi}} \right)^{p_{bo,6}} \right]
 \end{aligned}$$



$$E_{\text{bond}} = -D_e^{\sigma} \cdot BO_{ij}^{\sigma} \cdot \exp \left[p_{be1} \left(1 - (BO_{ij}^{\sigma})^{p_{be2}} \right) \right] - D_e^{\pi} \cdot BO_{ij}^{\pi} - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}$$

Bond order corrections

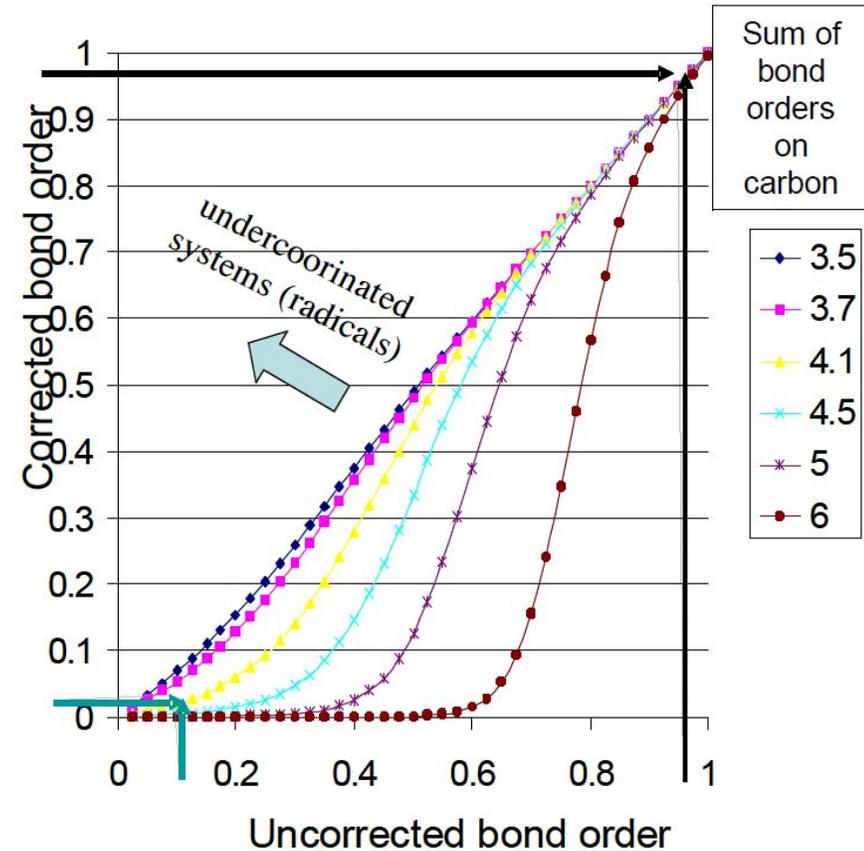
Uncorrected bond orders in ethane



$$\sum BO_C = 4.16$$

$$\sum BO_H = 1.17$$

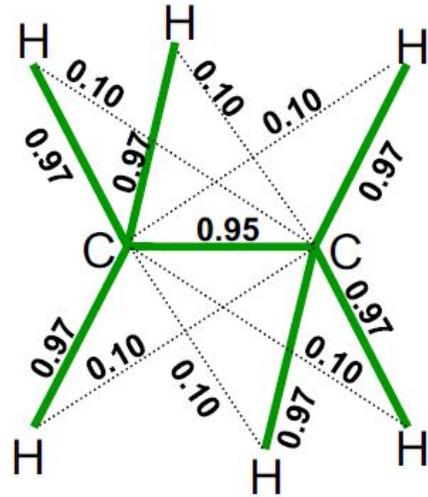
- Unphysical; normally coordinated atoms should not have binding interactions with next-neighbours



- Normally coordinated carbon will not make weak bonds (apply correction)
- Under-coordinated carbon (radical) can make weak bonds (no correction)

Bond order corrections

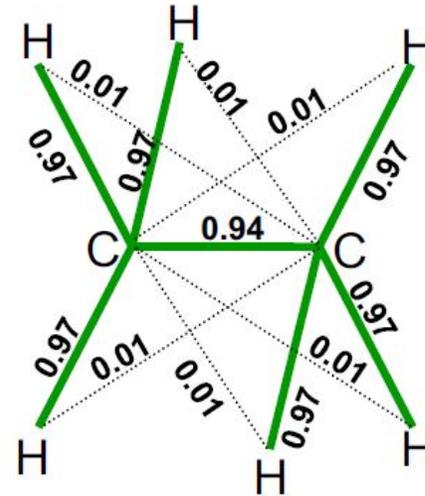
Uncorrected bond orders



$$\sum \text{BO}_C = 4.16$$

$$\sum \text{BO}_H = 1.17$$

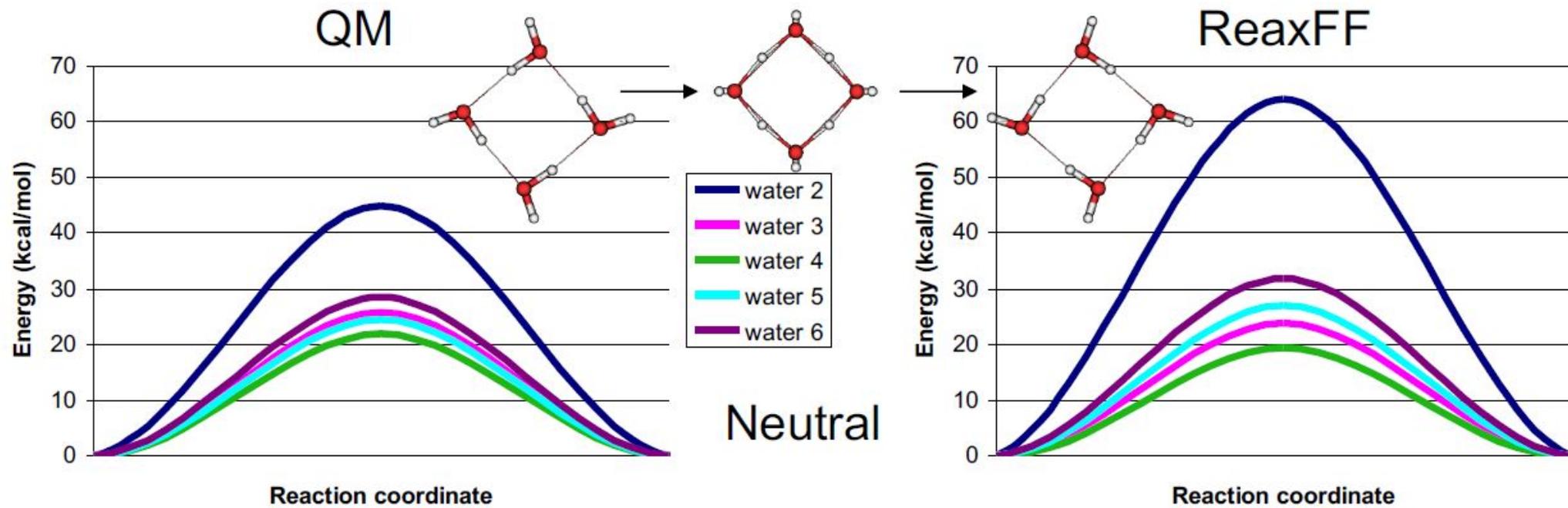
Corrected bond orders



$$\sum \text{BO}_C = 3.88$$

$$\sum \text{BO}_H = 0.98$$

- Correction removes unrealistic weak bonds but leaves strong bonds intact
- Increases computational expense as bond orders become multibody interactions
- Correction only applied for covalent-systems, not for metals



Reaction barriers for concerted reactions (good description of both fully coordinated atoms and under coordinated radicals)

Charge polarization

$$E_C = \sum_{j=1}^N \chi_j q_j + \sum_{j=1}^N \eta_j q_j^2 + C \cdot \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{\left(r_{i,j}^3 + \left(\frac{1}{\gamma_{i,j}} \right)^3 \right)^{\frac{1}{3}}}$$

$$\frac{\partial E_C}{\partial q_n} = \chi_n + 2\eta_n q_n + C \cdot \sum_{j=1}^N \frac{q_j}{\left(r_{n,j}^3 + \left(\frac{1}{\gamma_{n,j}} \right)^3 \right)^{\frac{1}{3}}}$$

$$\sum_{j=1}^N q_j = 0$$

EEM parameters:

- χ : electronegativity
- η : hardness
- γ : shielding

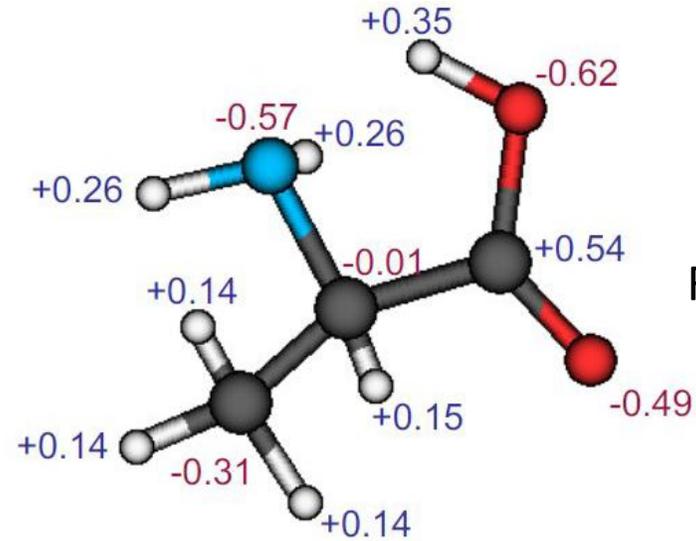
EEM-method (Mortier et al., JACS 1986);

Shielding: Janssens et al. Phys.Chem. 1995.

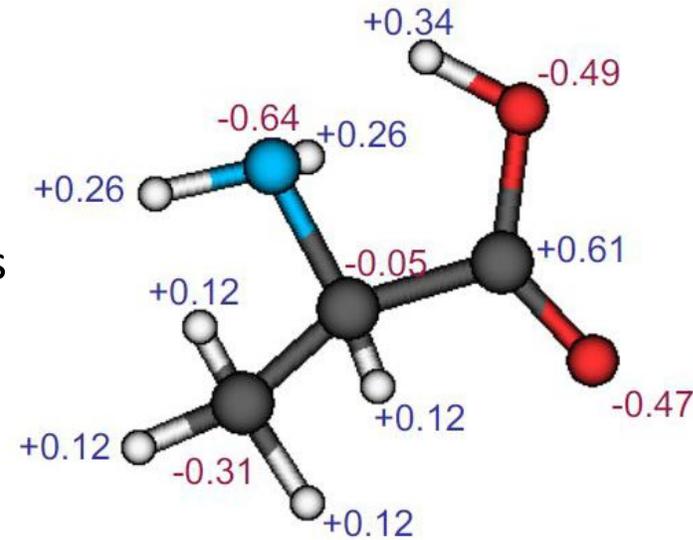
Similar to Qeq-method (Rappe and Goddard, J. Phys. Chem. 1991) with empirical shielding correction.

- Assign one **electronegativity** and **hardness** to each element
- Optimize these parameters against **QM**-charge distributions with a charge neutrality constraint
- Use system geometry in solving **Electronegativity Equilibration Methods (equations)** in every iteration

Charge polarization



ReaxFF charges



Mulliken charges from QM/DFT

Good reproduction of Mulliken charges

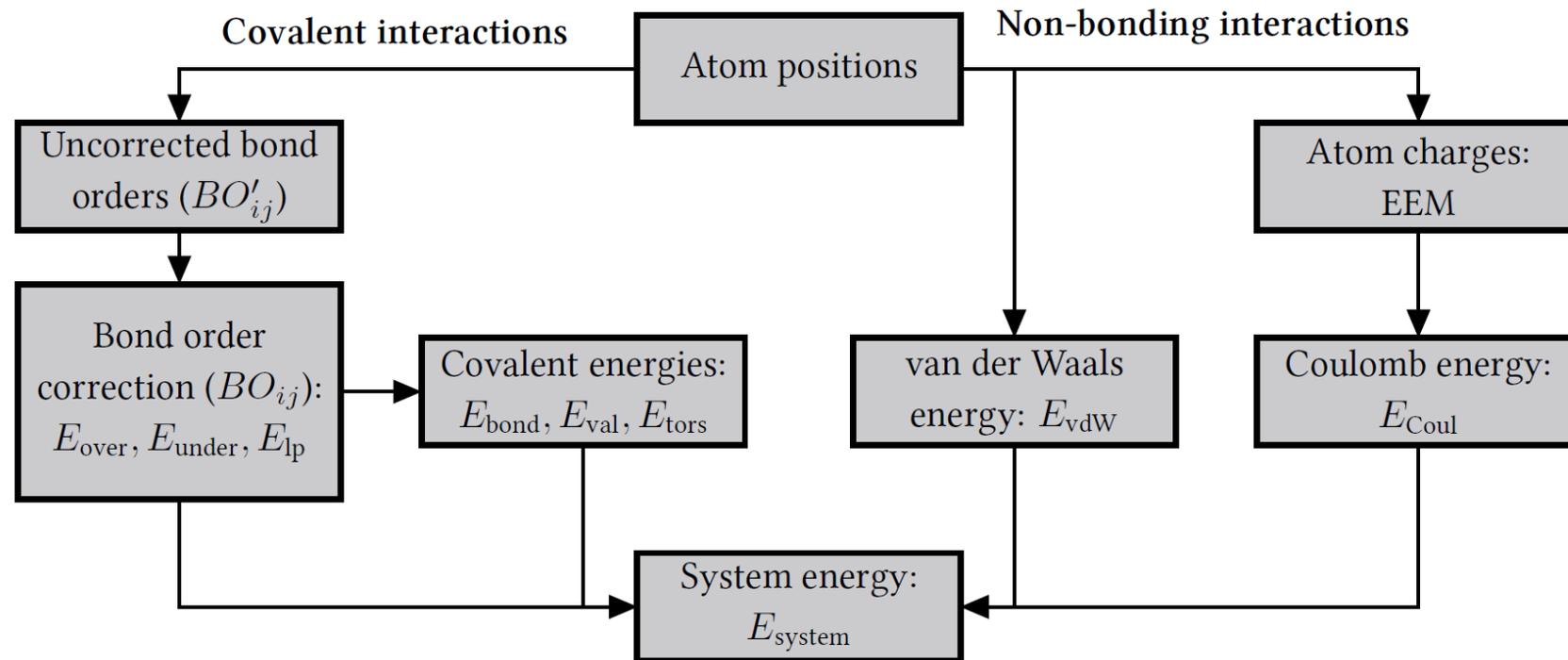
- Combined with Coulomb-interactions, this enables ReaxFF to simulate polarization effects on local chemistry
- EEM/Qeq methods work well around equilibrium; incorrect description of charge flow at high compression and dissociation (Chen and Martinez, Chem. Phys. Lett. 2006)
- Most expensive part of the reactive force field; needs to be updated every MD-step

General rules of ReaxFF

- MD-force field; no discontinuities in energy or forces even during reactions (in theory).
- User should not have to pre-define reactive sites or reaction pathways; potential functions should be able to automatically handle coordination changes associated with reactions.
- Each element is represented by only 1 atom type in the force field; force field should be able to determine equilibrium bond lengths, valence angles etc. from chemical environment.

Essence of ReaxFF

$$E_{\text{ReaxFF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{H-bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{spec}}$$



Current ReaxFF parameter sets

		Available																		
H																				He
Li	Be											B	C	N	O	F				Ne
Na	Mg											Al	Si	P	S	Cl				Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br				Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I				Xe
Cs	Ba	*Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At				Rn
Fr	Ra	**Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg										

* La, Ce, Pr-Yb
** Ac-No

our contribution?

Benefits:

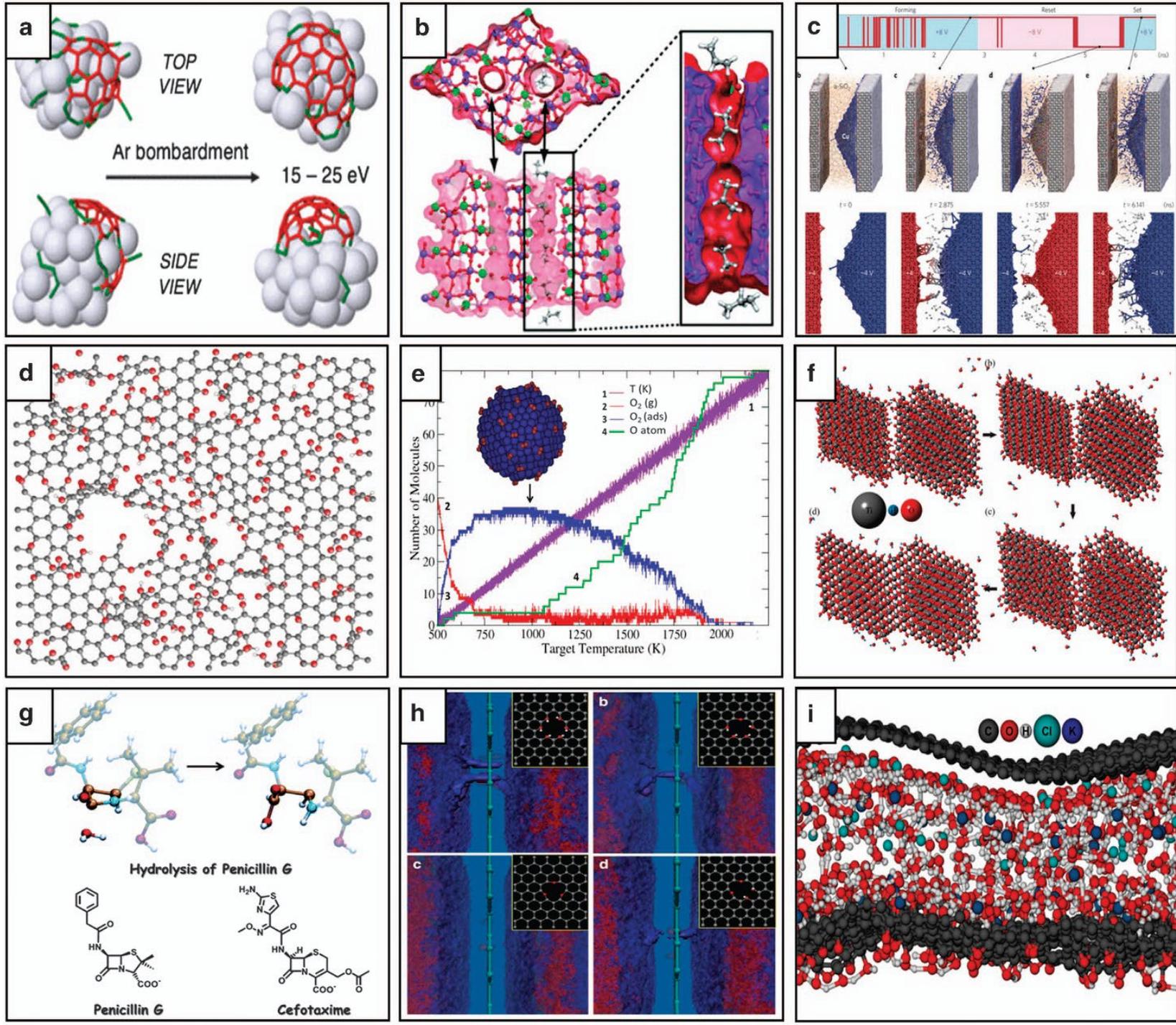
ReaxFF has proven to be transferable to a wide range of materials and can handle both complex chemistry and chemical diversity. Specifically, ReaxFF can describe covalent, metallic and ionic materials and interactions between these material types.

The ReaxFF reactive force-field: development, applications and future directions, Adri C T van Duin et al, npj Computational Materials, 2, 15011 (2016).

Applications of ReaxFF

- a) Ni-catalysed CNT growth
- b) Oxidative dehydrogenation over MMO catalysts
- c) Electrometallisation cells
- d) Reduction of graphene oxide
- e) Pd surface oxidation
- f) Oriented attachment mechanisms in TiO_2 nanocrystals
- g) Conformational dynamics of biomolecules
- h) Proton diffusion membranes
- i) Capacitive mixing by double layer expansion

Transferability among gas/liquid/solid phases and chemical diversity.



Assignment 3-1: exploring the energy contributions (1)

Valence bond energy contribution:

$$E_{\text{bond}} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot \exp \left[p_{be1} \left(1 - (BO_{ij}^\sigma)^{p_{be2}} \right) \right] - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}$$

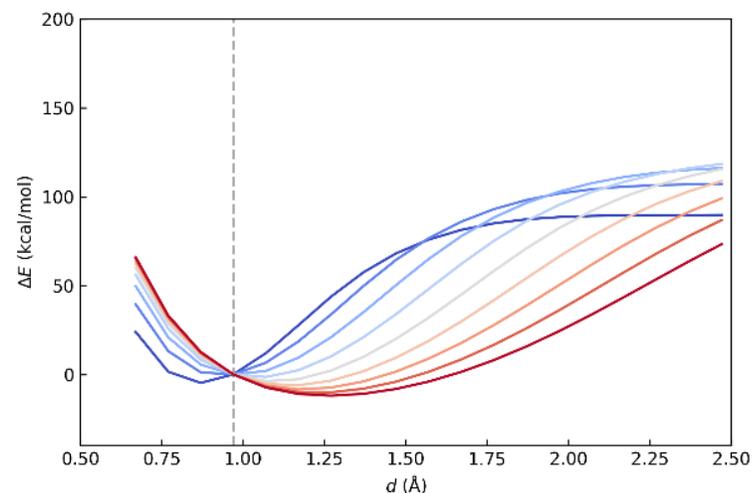
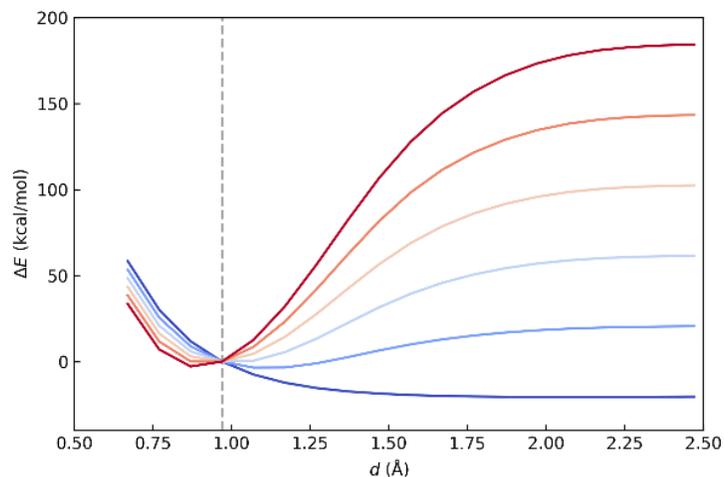
Motivate which terms are relevant in the valence bond energy contribution of a O – H bond in a water molecule (H₂O)?

Assignment 3-1: exploring the energy contributions (2)

Valence bond energy contribution:

$$E_{\text{bond,O-H}} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot \exp \left[p_{be1} \left(1 - (BO_{ij}^\sigma)^{p_{be2}} \right) \right]$$

Below we tweaked some parameters from the valence bond contribution, identify which parameter was changed (argue why you think so)!



Assignment 3-1: exploring the energy contributions (3)

Bond order expression:

$$BO_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} = \exp \left[p_{bo,1} \cdot \left(\frac{r_{ij}}{r_0^{\sigma}} \right)^{p_{bo,2}} \right] + \exp \left[p_{bo,3} \cdot \left(\frac{r_{ij}}{r_0^{\pi}} \right)^{p_{bo,4}} \right] + \exp \left[p_{bo,5} \cdot \left(\frac{r_{ij}}{r_0^{\pi\pi}} \right)^{p_{bo,6}} \right]$$

↓ Sigma bond / Single bond

$$BO_{ij} = BO_{ij}^{\sigma} = \exp \left[p_{bo,1} \cdot \left(\frac{r_{ij}}{r_0^{\sigma}} \right)^{p_{bo,2}} \right]$$

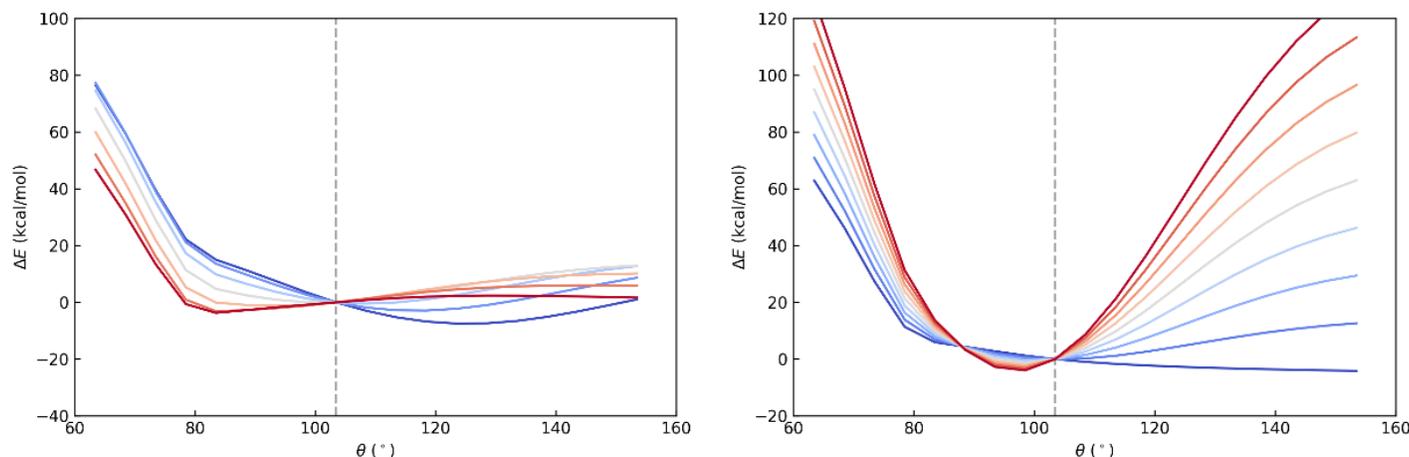
$$E_{\text{bond,O-H}} = -D_e^{\sigma} \cdot BO_{ij}^{\sigma} \cdot \exp \left[p_{be1} \left(1 - (BO_{ij}^{\sigma})^{p_{be2}} \right) \right]$$

Assignment 3-1: exploring the energy contributions (3)

Valence angle energy contribution:

$$E_{\text{angle}} = f_7(BO_{ij}) \cdot f_7(BO_{jk}) \cdot f_8(\Delta_j) \cdot \left\{ p_{val1} - p_{val1} \cdot \exp \left[-p_{val2} (\Theta_0(BO) - \Theta_{ijk})^2 \right] \right\}$$
$$\Theta_0(BO) = \pi - \Theta_{0,0} \cdot \{1 - \exp[-p_{val10} \cdot (2 - SBO2)]\}$$

Below we tweaked some parameters from the valence angle contribution, identify which parameters were changed (argue why you think so)!



Assignment 3-2: electronegativity equalization method (1)

Polarization scheme: electronegativity equalization method (EEM)

Coulomb energy

$$E_C = \sum_{j=1}^N \chi_j q_j + \sum_{j=1}^N \eta_j q_j^2 + C \cdot \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{\left(r_{i,j}^3 + \left(\frac{1}{\gamma_{i,j}} \right)^3 \right)^{\frac{1}{3}}}$$

$$\frac{\partial E_C}{\partial q_n} = \chi_n + 2\eta_n q_n + C \cdot \sum_{j=1}^N \frac{q_j}{\left(r_{n,j}^3 + \left(\frac{1}{\gamma_{n,j}} \right)^3 \right)^{\frac{1}{3}}}$$

Set of equations, with a charge neutrality constraint

$$\sum_{j=1}^N q_j = 0$$

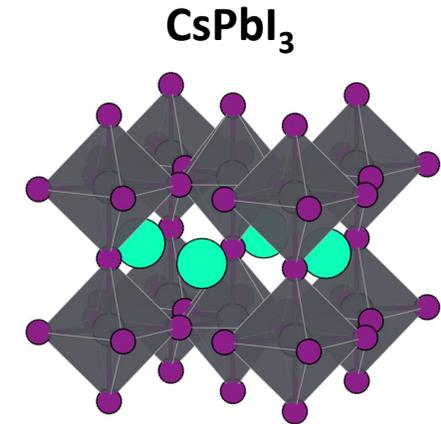
EEM parameters:

- χ : electronegativity
- η : hardness
- γ : shielding

Assignment 3-2: electronegativity equalization method (2)

Tuning the electronegativity of iodine:

- Can you rank the elements in CsPbI_3 according to their respective elemental electronegativities?
- Can you predict the effects of changing the electronegativity on the other elements (Pb/Cs)?
- Upon changing the electronegativity (χ) of the element I, the electrostatic behavior can be changed to that of different elements, which elements?



This lecture(s)

- Theory of DFT (brief) with a focus on electronic structures of solid-state systems (1h)
- DFT + chemical bonding analysis + tight binding + experiments for halide perovskites (1h)
- Theory of MD (brief) and various interactions in materials (basics of force fields) (1h)
- Theory of ReaxFF reactive force field (1h)
- **Reactive MD for halide perovskites (1h)**



A Reactive Force Field for Large Scale Simulations of Metal Halide Perovskites

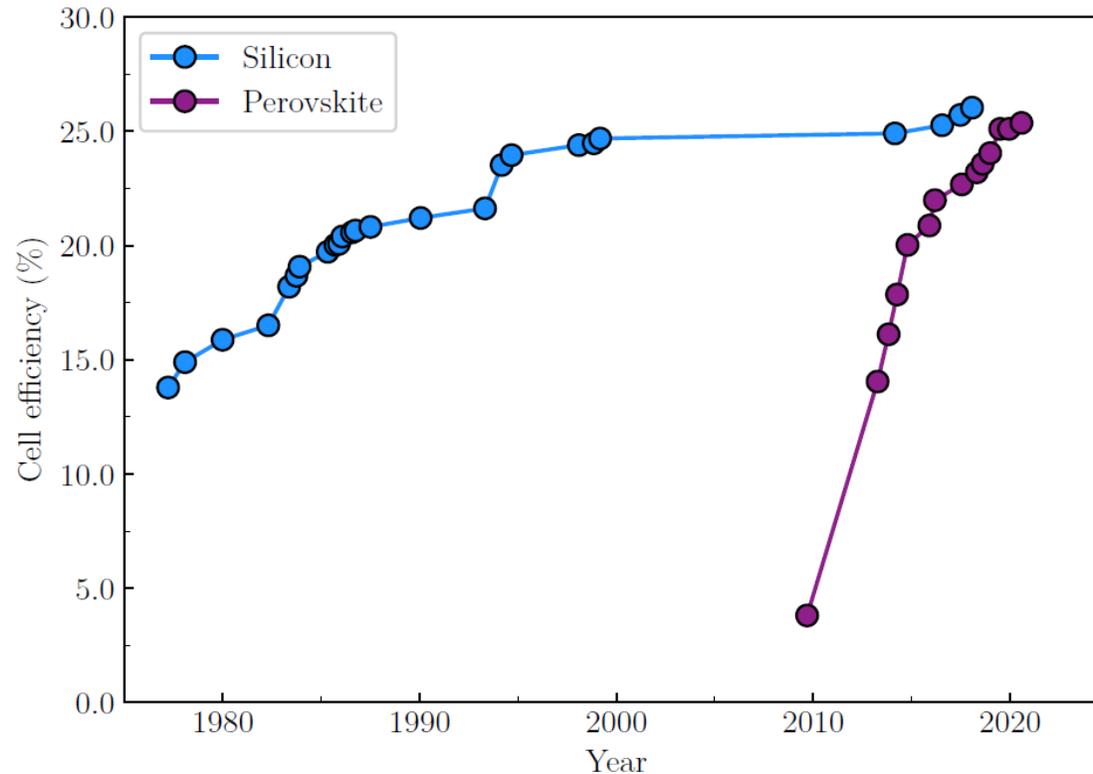
02-12-2021

Mike Pols

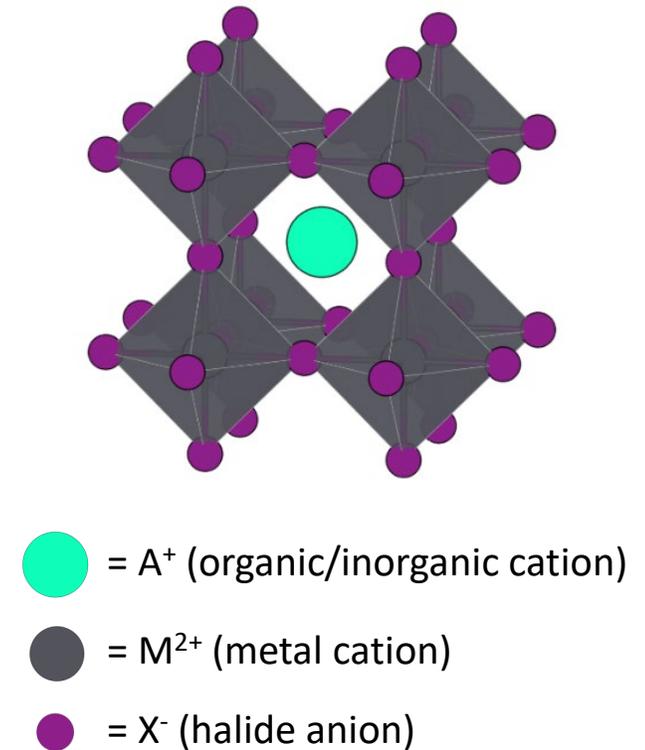
Materials Simulation & Modelling (MSM)

Metal halide perovskite solar cells

Research solar cell efficiencies^{1,2}:



AMX₃ metal halide perovskite:



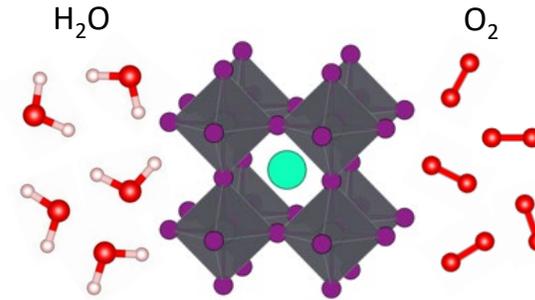
¹ National Renewable Energy Laboratory. Best Research-Cell Efficiency Chart, 2020. <https://www.nrel.gov/pv/cell-efficiency.html>.

² Kojima, Akihiro *et al.* *Journal of the American Chemical Society* 131, no. 17 (May 6, 2009): 6050–51.

Instability of the metal halide perovskites

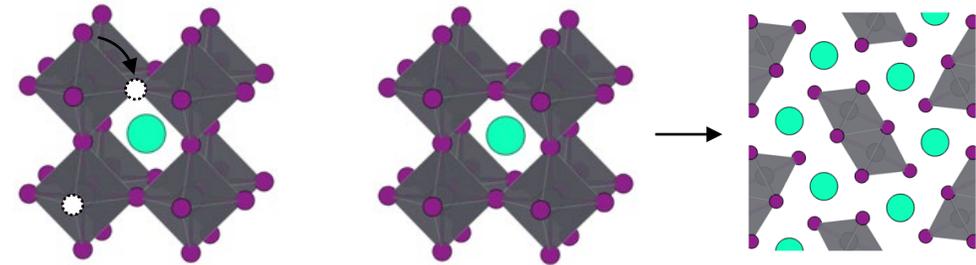
External factors:

- Moisture-induced decomposition¹
- Oxygen and ultraviolet light²



Intrinsic instabilities:

- Ion migration³
- Phase instability⁴



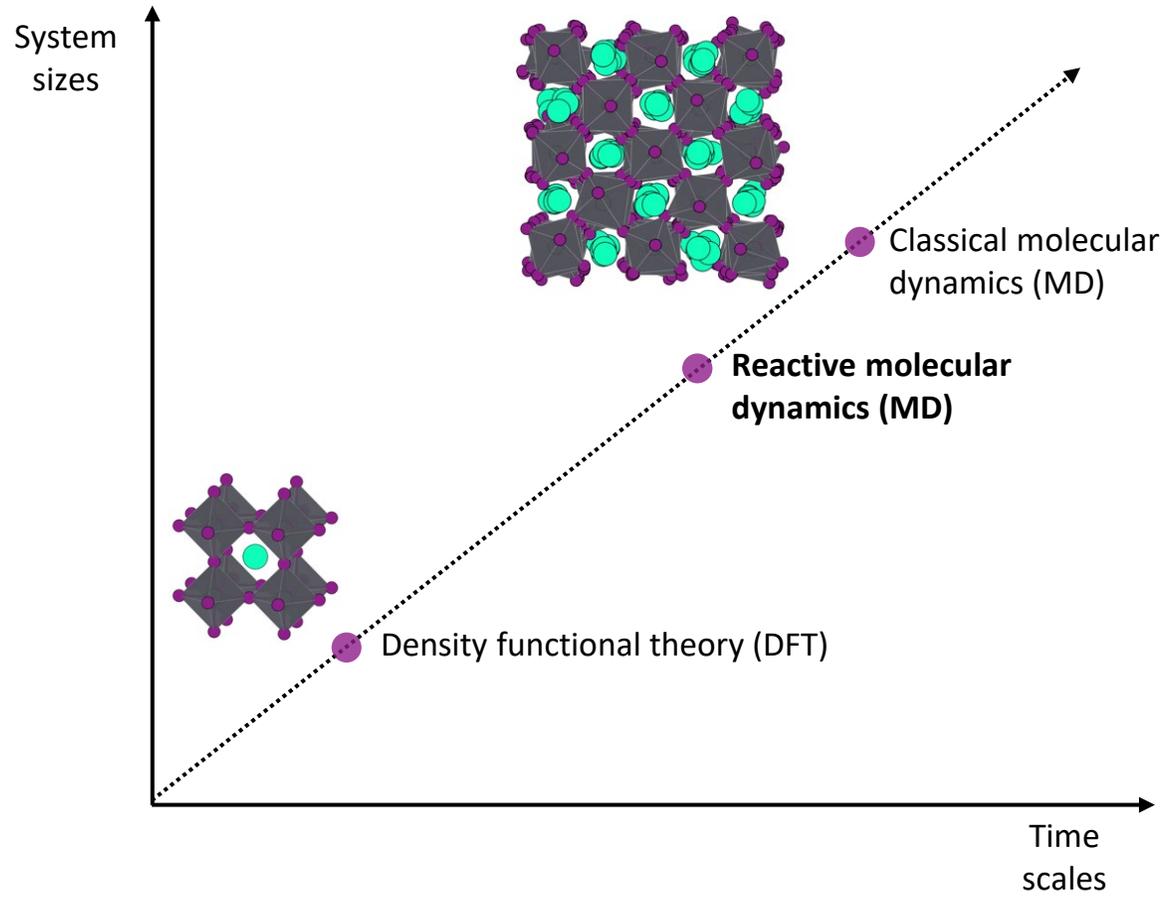
¹ Salado, Manuel *et al.* *Journal of Materials Chemistry A* 5, no. 22 (June 6, 2017): 10917–27.

² Abdelmageed, Ghada *et al.* *Applied Physics Letters* 109, no. 23 (December 5, 2016): 233905.

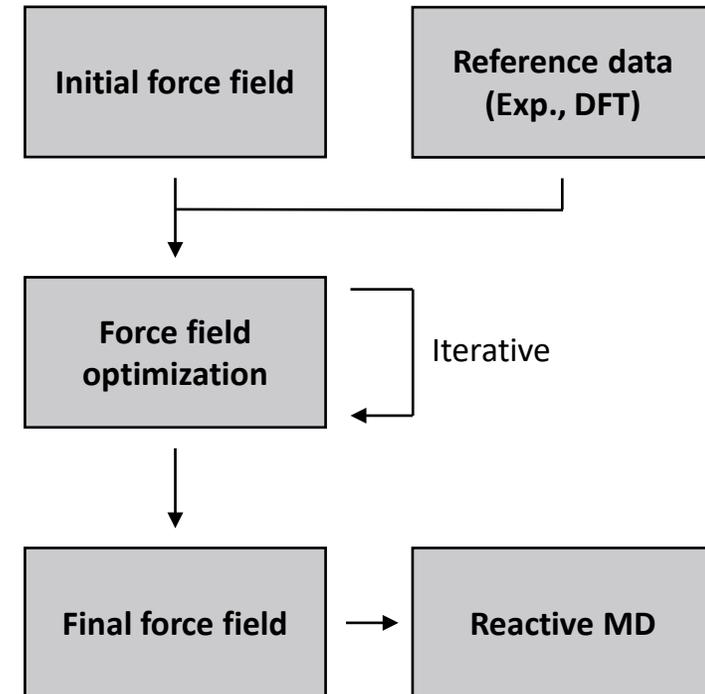
³ Girolamo, Diego *et al.* *Advanced Energy Materials* 10, no. 25 (2020): 2000310.

⁴ Qiu, Zhiwen *et al.* *Small Methods* 4, no. 5 (2020): 1900877.

Our computational approach



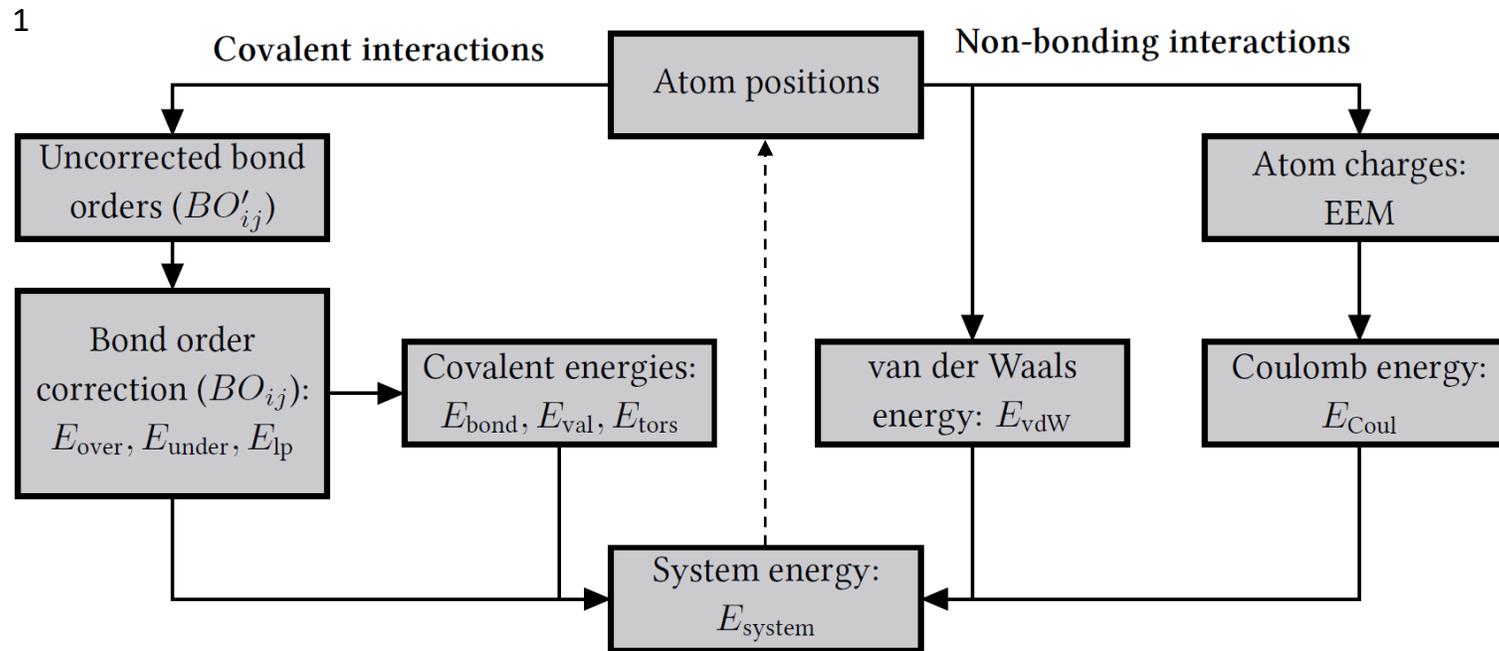
Workflow:



The principle of ReaxFF

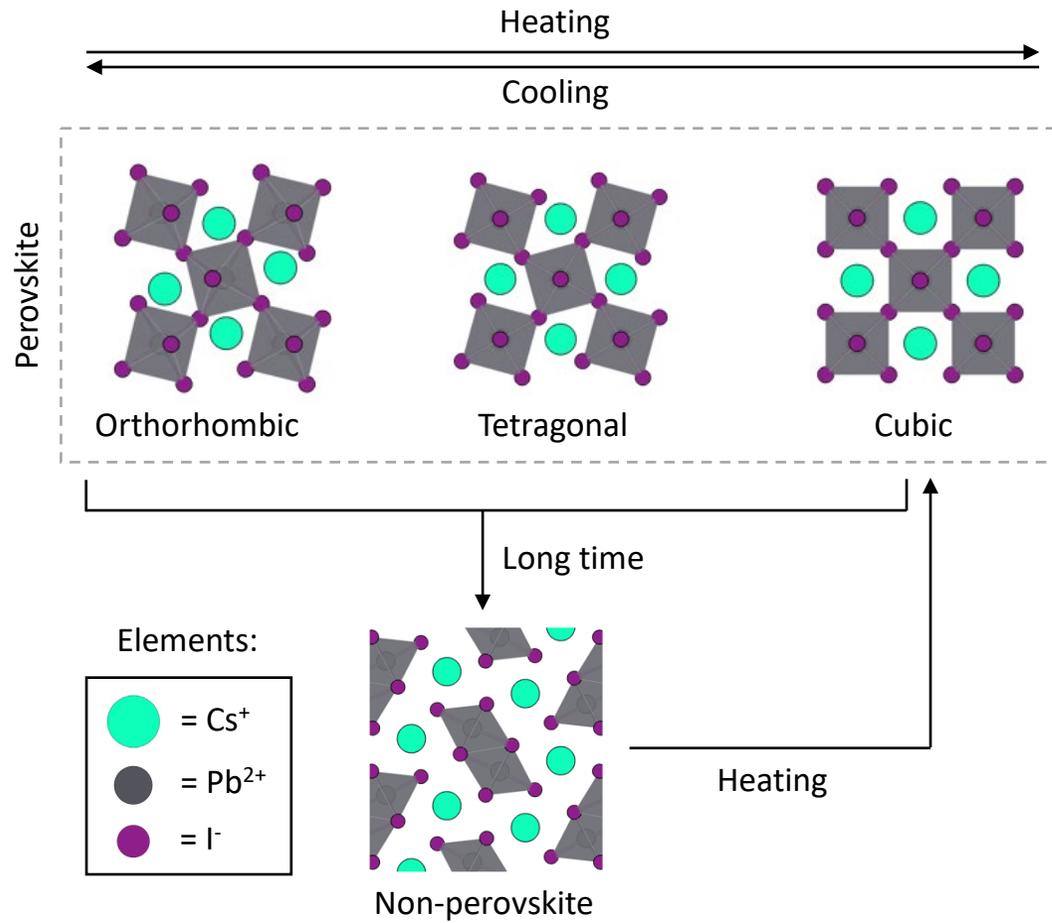
Potential energy expression:

$$E_{\text{system}} = \underbrace{E_{\text{bond}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}}}_{\text{Covalent}} + \underbrace{E_{\text{vdW}} + E_{\text{Coul}}}_{\text{Non-bonding}} + E_{\text{spec}}$$

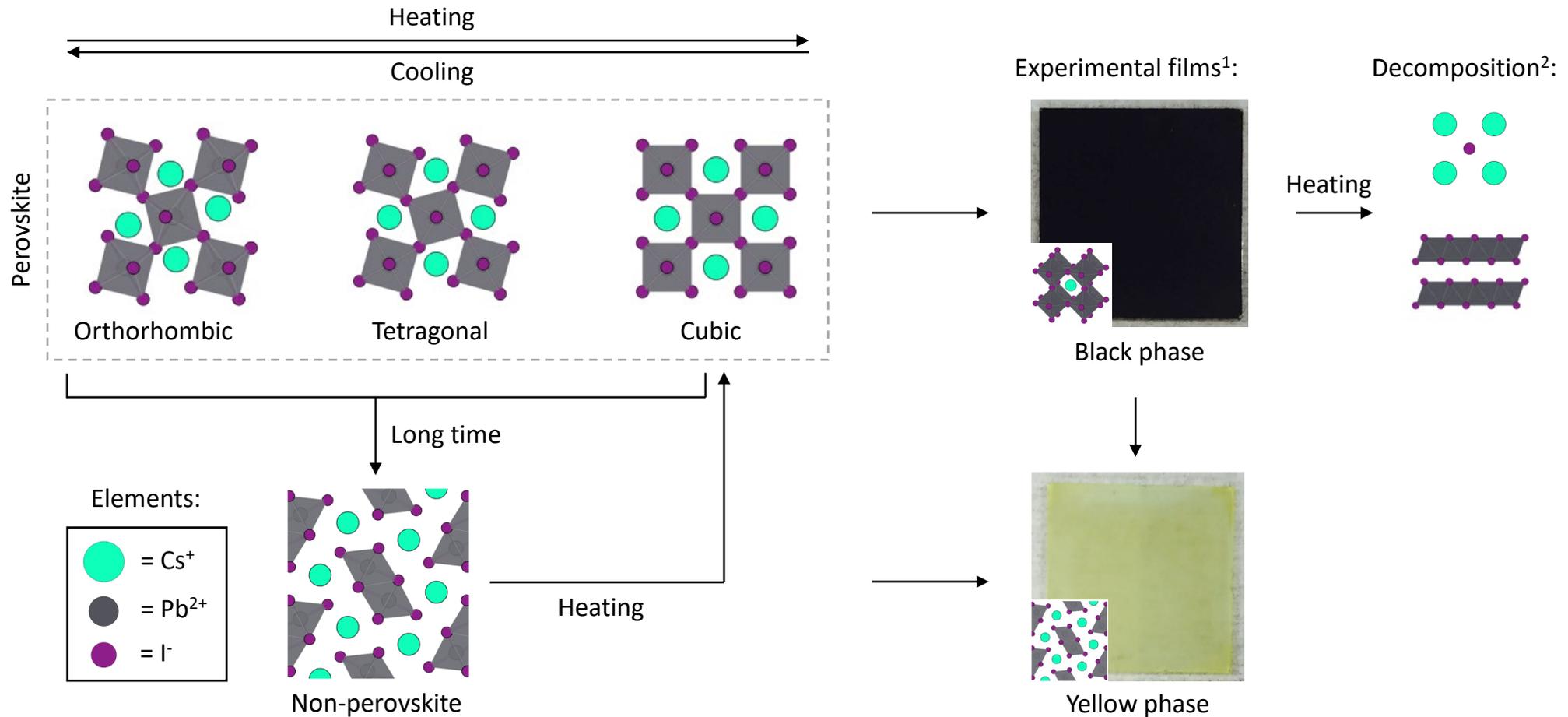


¹ Russo, Michael *et al.* Nuclear Instruments and Methods in Physics Research Section B 269, no. 14 (July 15, 2011): 1549–54.

A simple start: CsPbI₃



A simple start: CsPbI₃



¹ Wang, Qi *et al. Joule* 1, no. 2 (October 11, 2017): 371–82.

² Liao, Mengling *et al. The Journal of Physical Chemistry Letters* 10, no. 6 (March 21, 2019): 1217–25.

Training of a ReaxFF force field

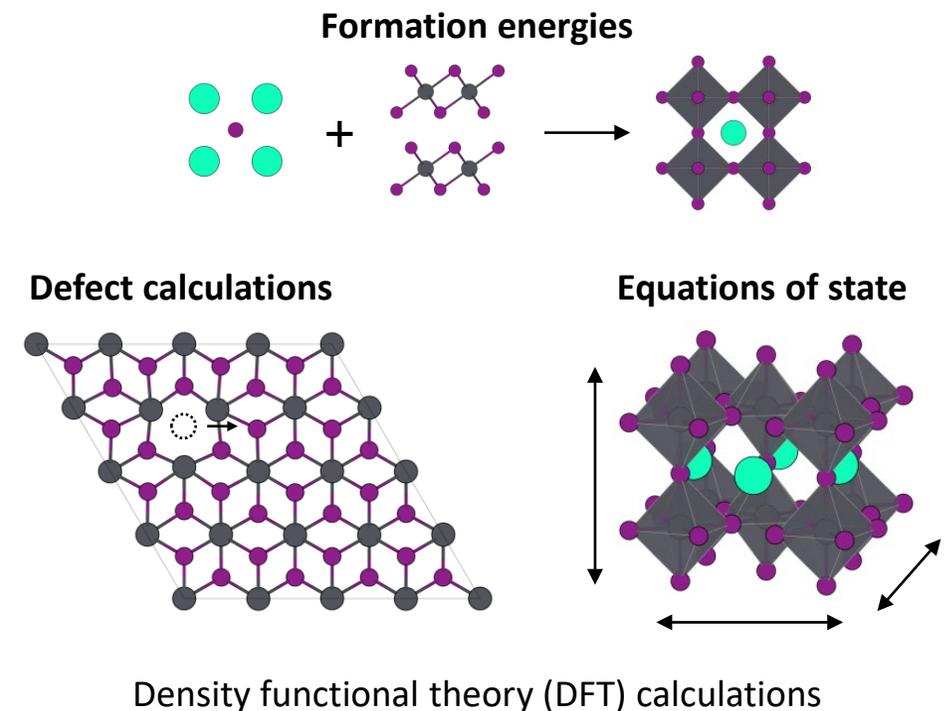
Creation of a set of ReaxFF parameters:

- Minimize the difference between reference data and ReaxFF predictions
- Simulated annealing optimization

Difference quantified by error function:

$$\text{Error}(\{p_j\}) = \sum_{i=1}^N \left[\frac{x_{i,\text{ref}} - x_{i,\text{calc}}(\{p_j\})}{\sigma_i} \right]^2$$

Training set for CsPbI₃:



Training of a ReaxFF force field

Creation of a set of ReaxFF parameters:

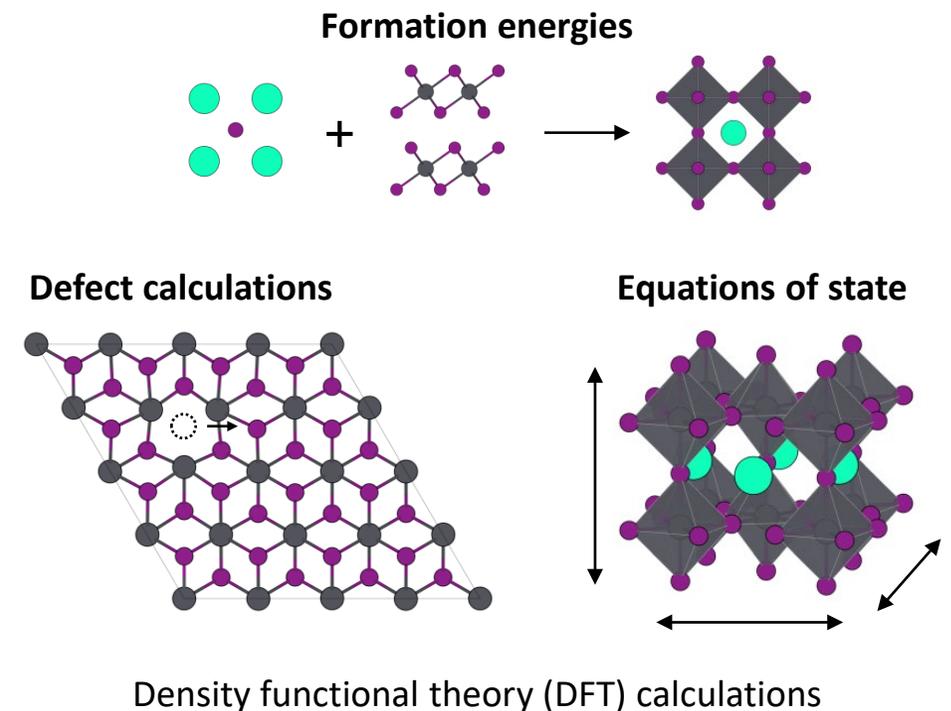
- Minimize the difference between reference data and ReaxFF predictions
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Difference quantified by error function:

$$\text{Error}(\{p_j\}) = \sum_{i=1}^N \left[\frac{x_{i,\text{ref}} - x_{i,\text{calc}}(\{p_j\})}{\sigma_i} \right]^2$$

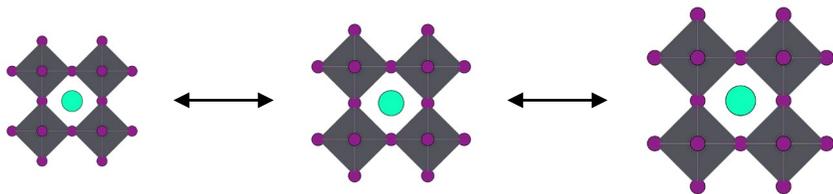
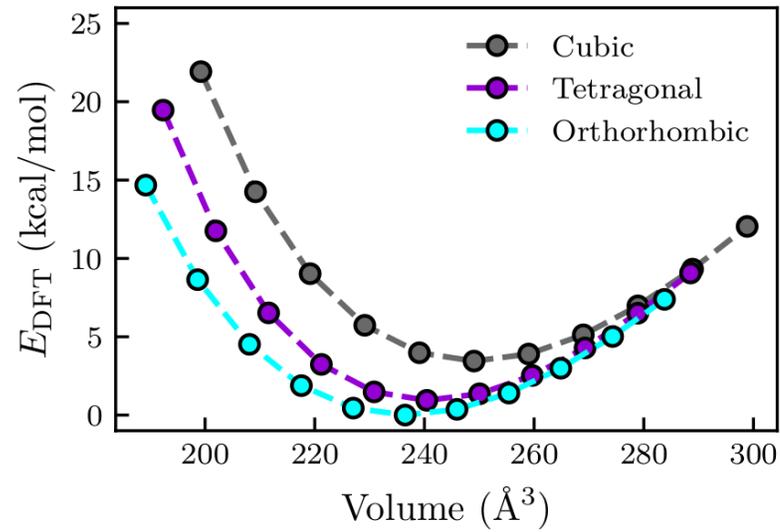
Energies, charges, bond lengths, valence angles

Training set for CsPbI₃:

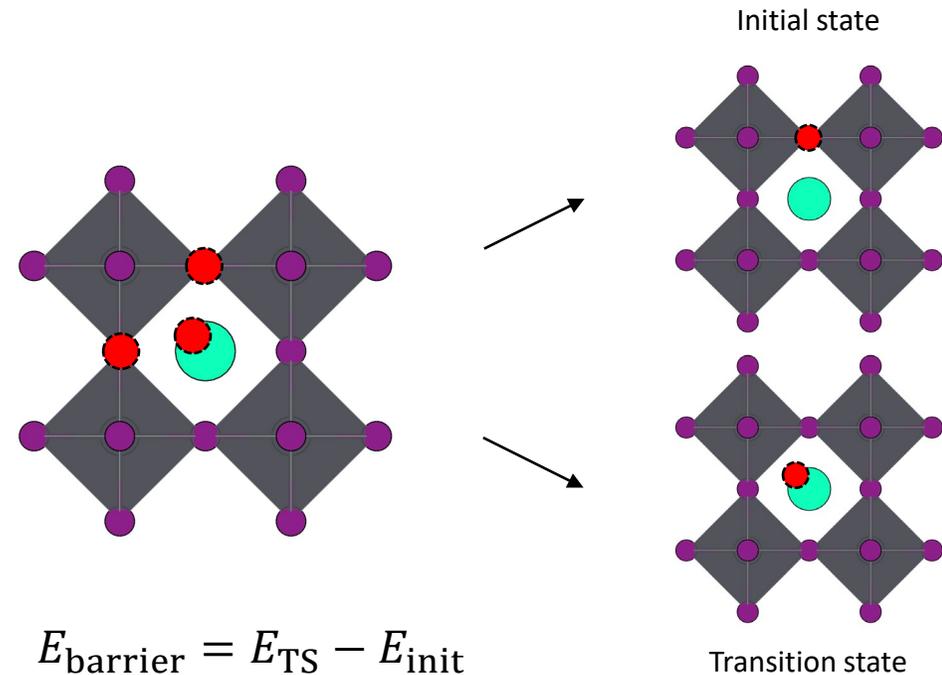


More details on the training data

Equation of state



Energy barriers

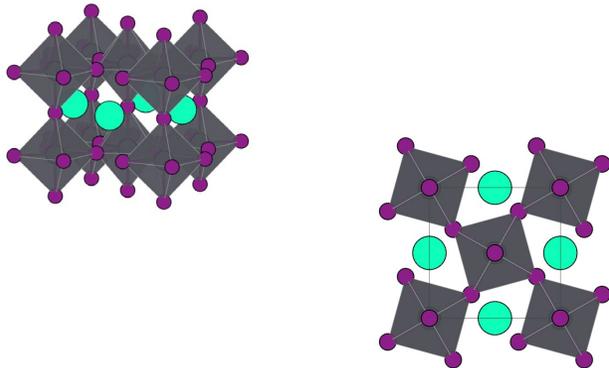


Recollection of relevant interactions (exercise 1)

Force field system energy:

$$E_{\text{ReaxFF}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{H-bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{spec}}$$

Relevant interactions:



Interactions	Elements
E_{bond}	Cs - I / Pb - I
E_{angle}	I - Pb - I / Pb - I - Pb / I - Cs - I / Cs - I - Cs / Cs - I - Pb / I - I - Pb / Pb - Pb - I
E_{Coulomb}	Cs, Pb, I
E_{vdW}	Cs, Pb, I
Atom parameters (Pb)	r_0^σ etc.

Monte Carlo-based optimizer

Monte Carlo-based optimizer¹:

- Simulated annealing optimization method² that employs the Metropolis Monte Carlo algorithm to sample the parameter space³

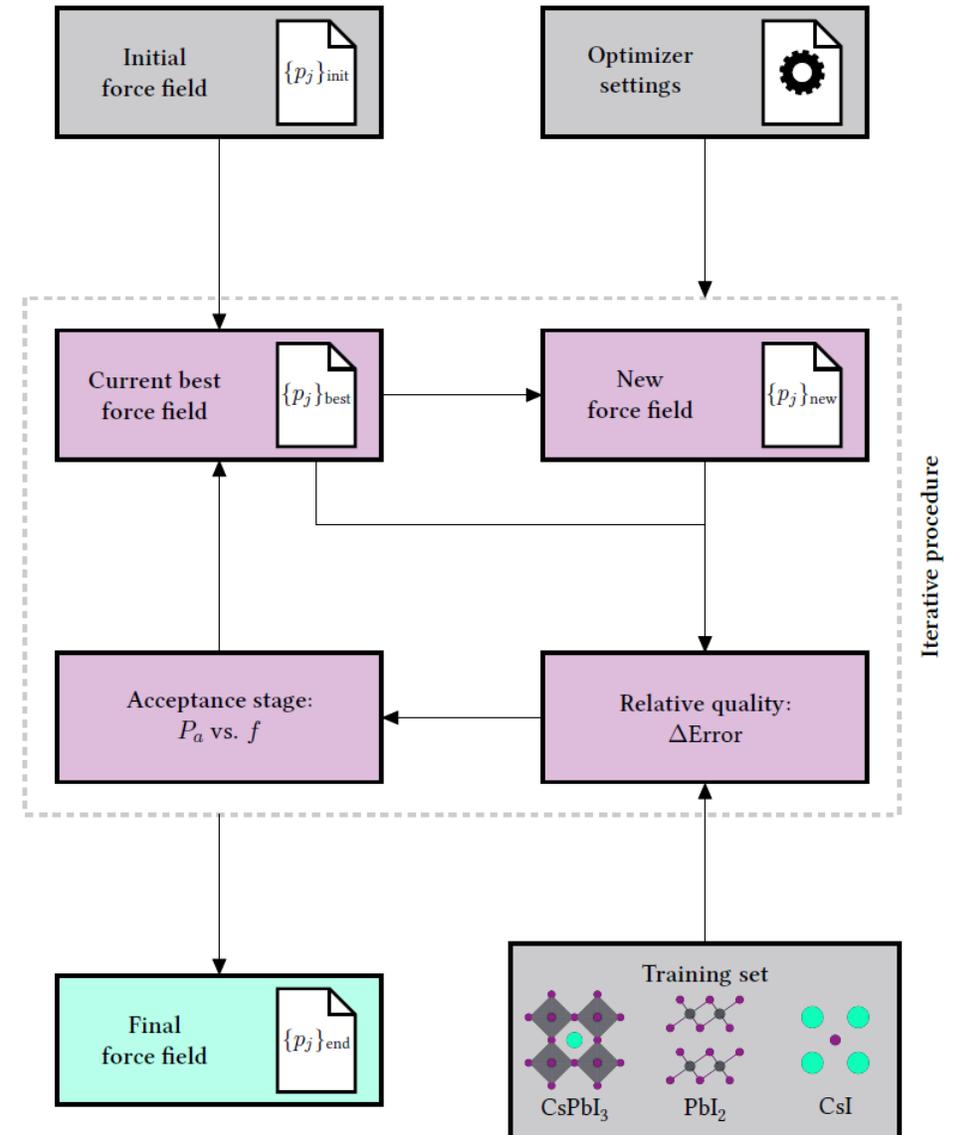
Difference in error functions:

$$\Delta\text{Error} = \text{Error}(\{p_j\}_{\text{new}}) - \text{Error}(\{p_j\}_{\text{best}})$$

Acceptance criterion:

$$P_a = \min[1, \exp(-\beta\Delta\text{Error})]$$

$$0 \leq f < 1$$



¹ Iype, E et al. *Journal of Computational Chemistry* 34, no. 13 (2013): 1143–54.

² Kirkpatrick, S et al. *Science* 220, no. 4598 (May 13, 1983): 671–80.

³ Metropolis, Nicholas et al. *The Journal of Chemical Physics* 21, no. 6 (June 1, 1953): 1087–92.

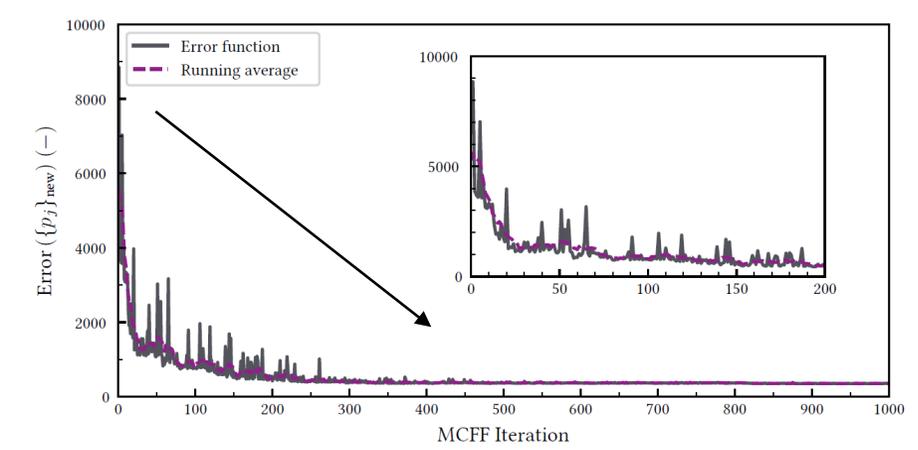
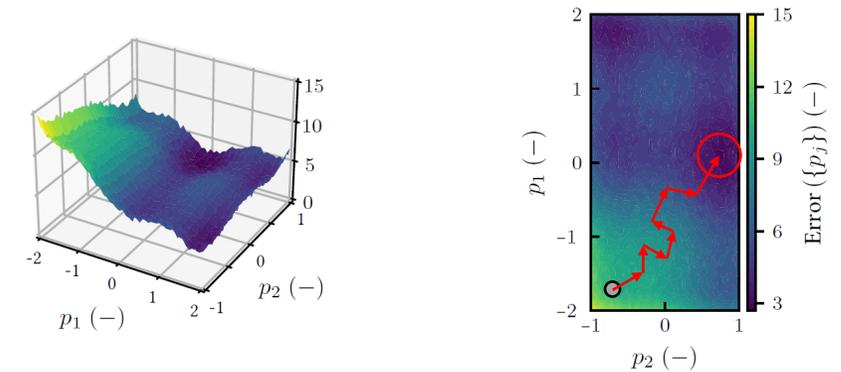
Parameter optimization

Simulated annealing optimization:

- Gradual progression through the error landscape to lower errors $\text{Error}(\{p_j\})$
- Occasional upward spikes, most of which are rejected (downward trend)

Additional optimization schemes:

- Evolutionary algorithms^{1,2}
- Deep Learning-based (INDEEDopt)³



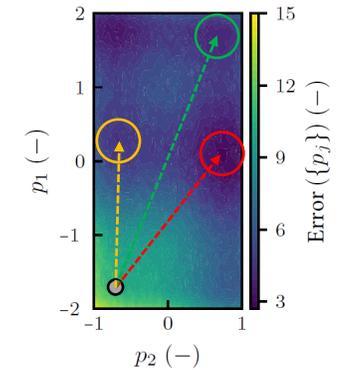
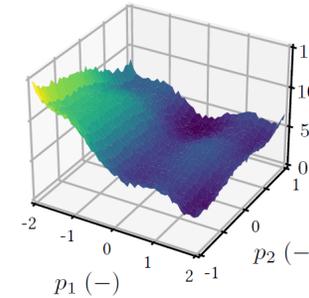
¹ Trnka, T et al. *Journal of Chemical Theory and Computation* 14, no. 1 (January 9, 2018): 291–302.

² Dittner, M. et al. *Journal of Computational Chemistry* 36, no. 20 (2015): 1550–61.

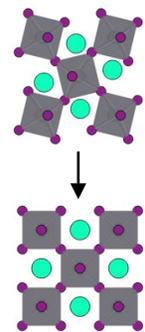
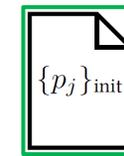
³ Sengul, M.Y. et al. *Npj Computational Materials* 7, no. 1 (May 19, 2021): 1–9.

Some practicalities of the parameterization

- ReaxFF force fields have up to 100 parameters per atom; easily over 50 parameters active in optimization
- Stochastic optimization procedure that is still somewhat sensitive to the many local minima¹
- Strategy: ensemble of optimizations from which the final force field is selected based on some validations



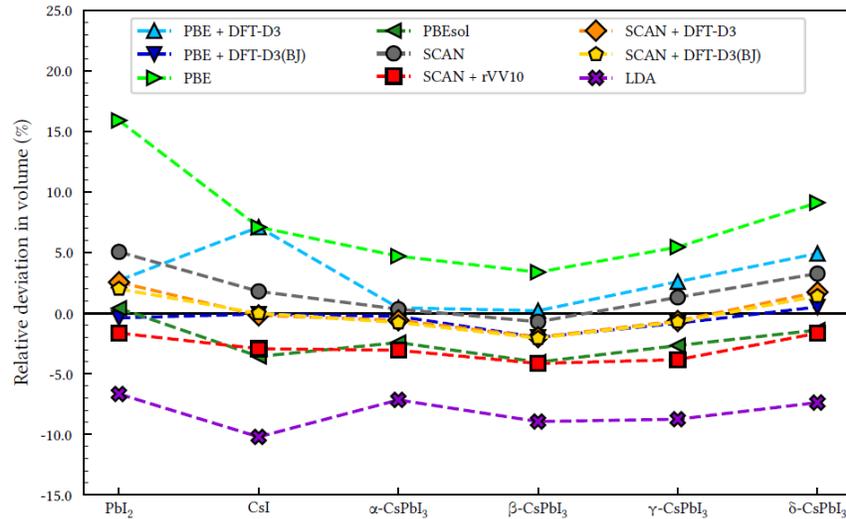
Ensemble of force fields:



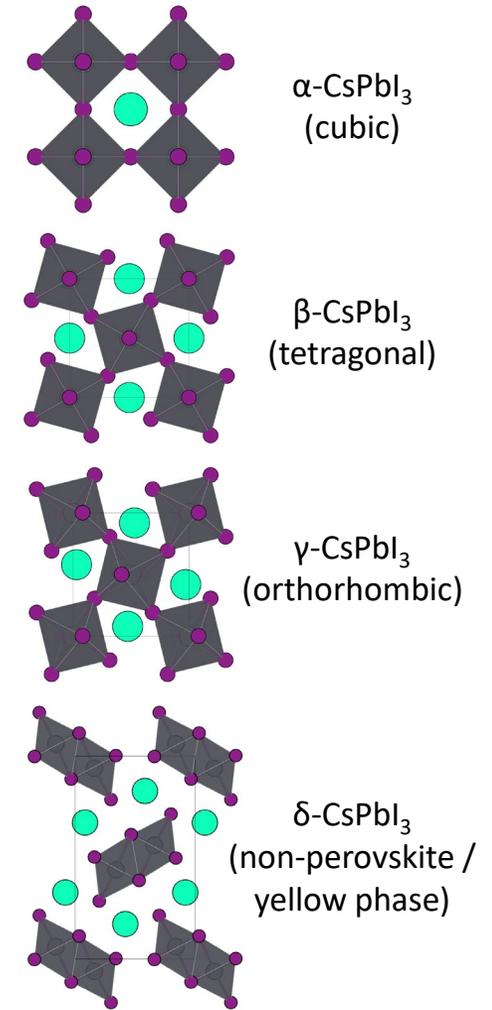
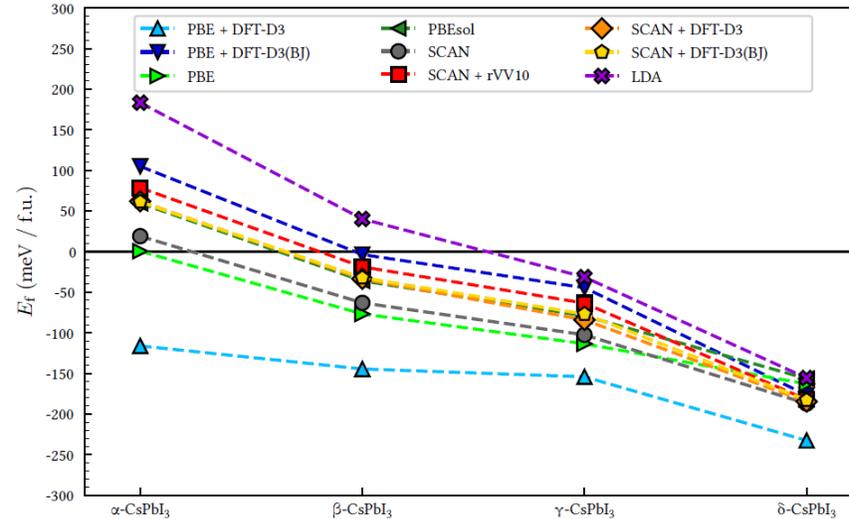
¹ Iype, E et al. *Journal of Computational Chemistry* 34, no. 13 (2013): 1143–54.

Accurate reference data for training

Geometry predictions:



Formation energies:



Tested XC-functionals

- GGA: PBE, PBE + DFT-D3, PBE + DFT-D3(BJ), PBEsol
- Meta-GGA: SCAN, SCAN + rVV10, SCAN + DFT-D3, SCAN + DFT-D3(BJ)
- LDA: LDA

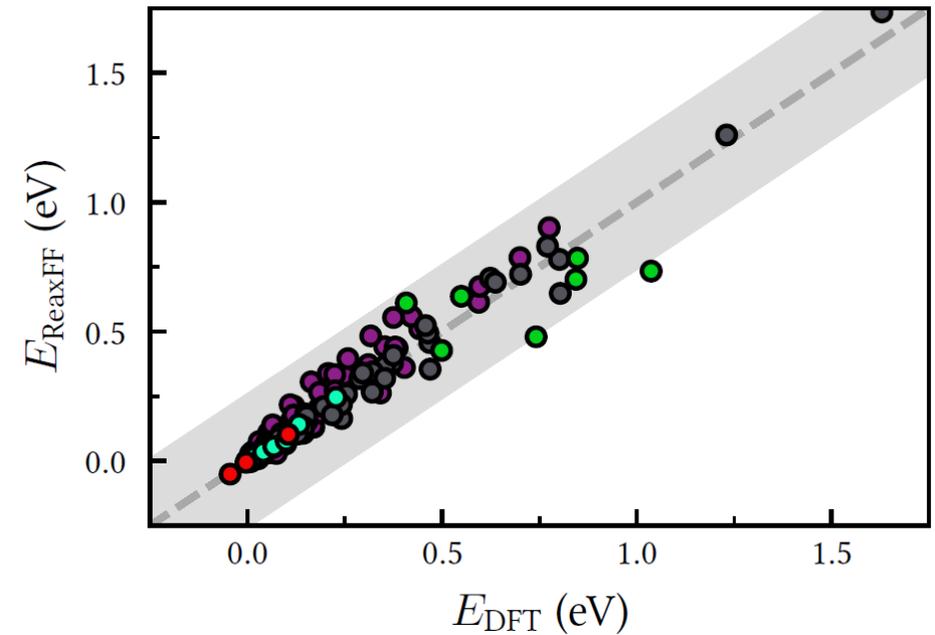
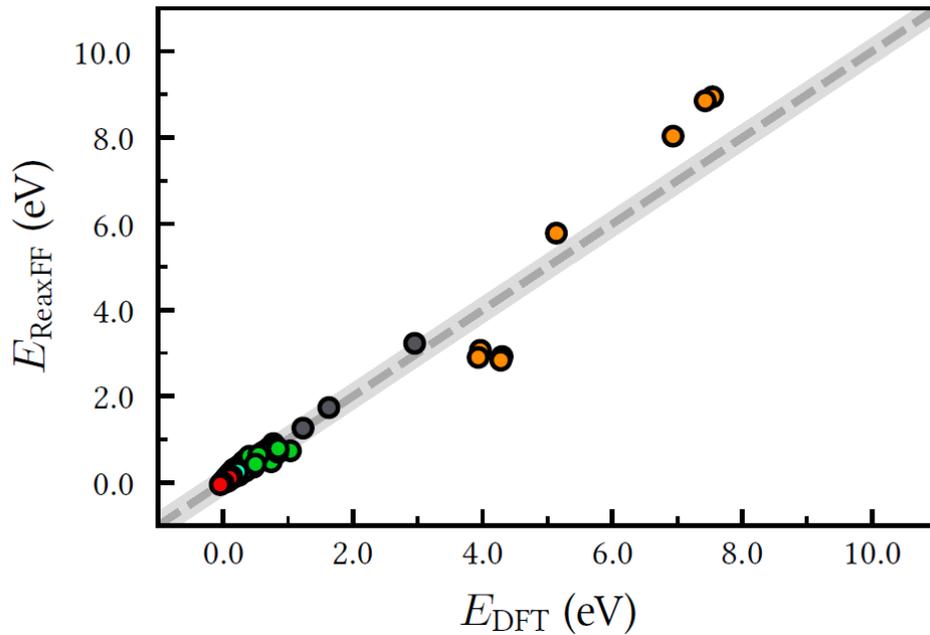
Perovskites: α = cubic; β = tetragonal; γ = orthorhombic; δ = non-perovskite

A representative parameter set

- PbI_2 equations of state
- CsPbI_3 formation energies

- CsI equations of state
- Defect formation energies

- CsPbI_3 equations of state
- Defect migration barriers

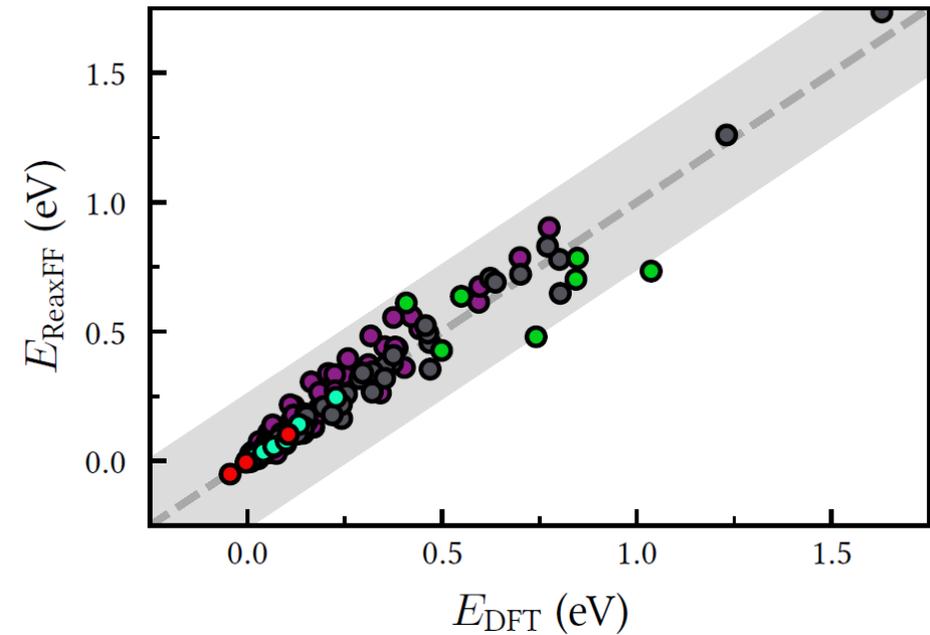
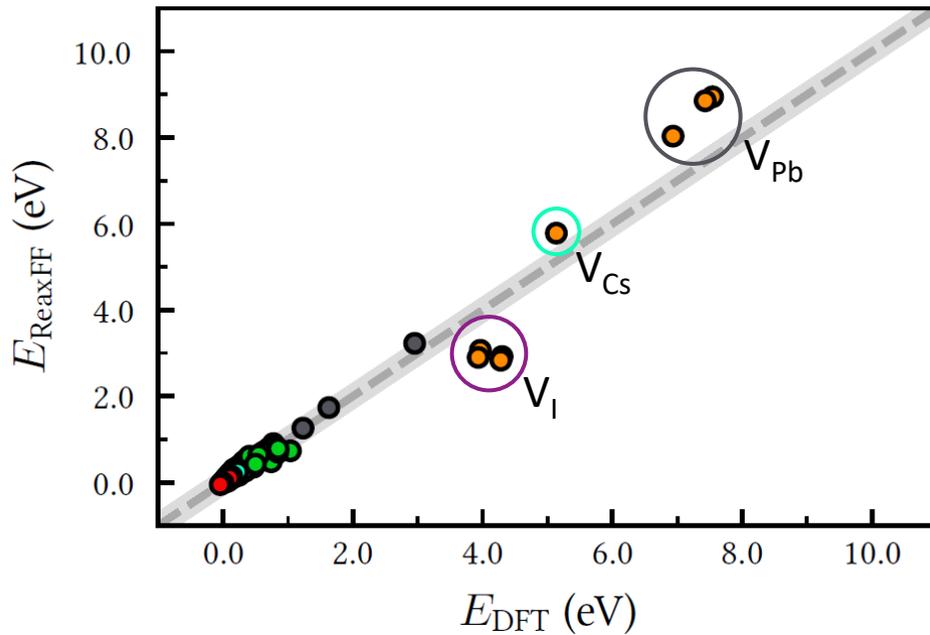


A representative parameter set

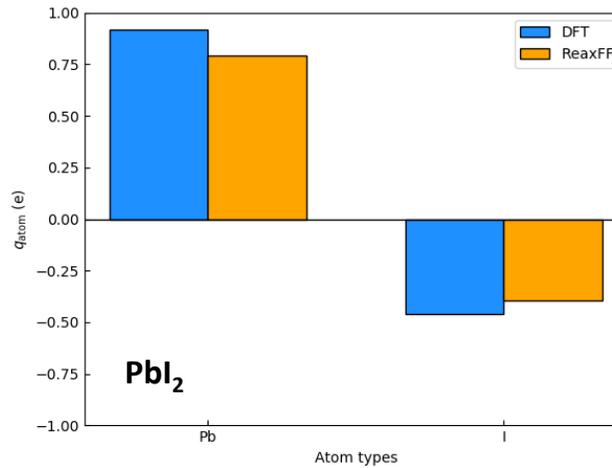
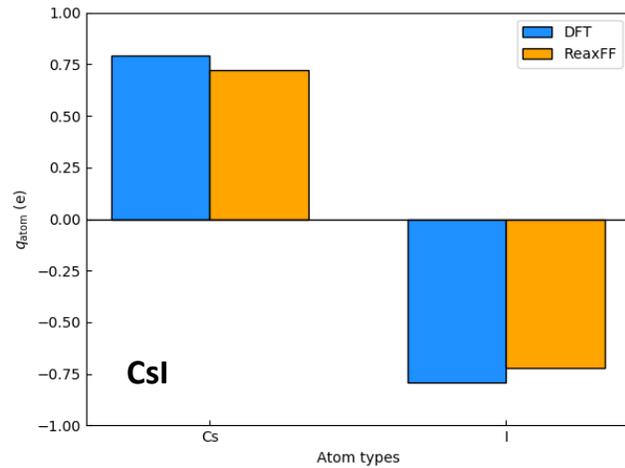
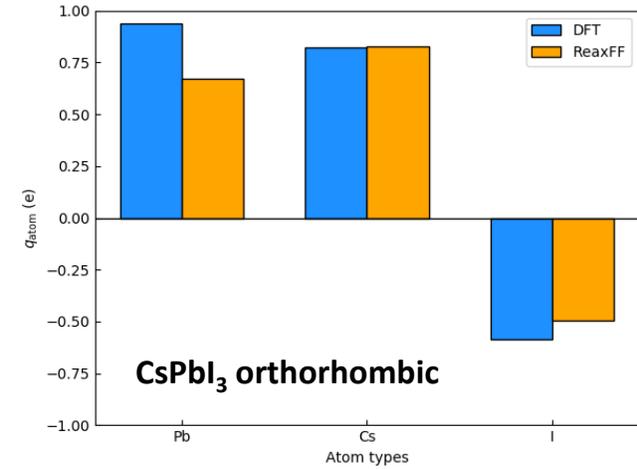
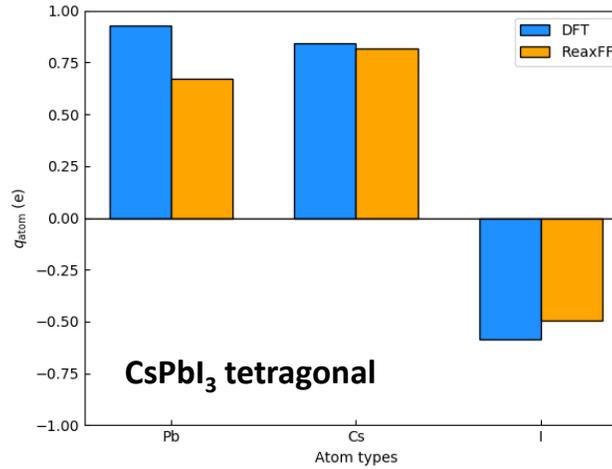
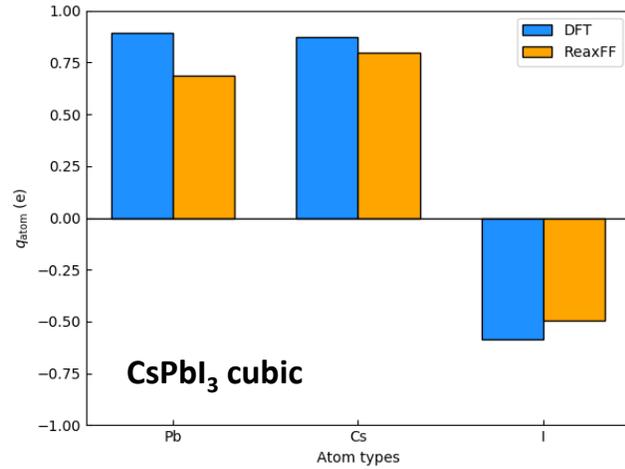
- PbI_2 equations of state
- CsPbI_3 formation energies

- CsI equations of state
- Defect formation energies

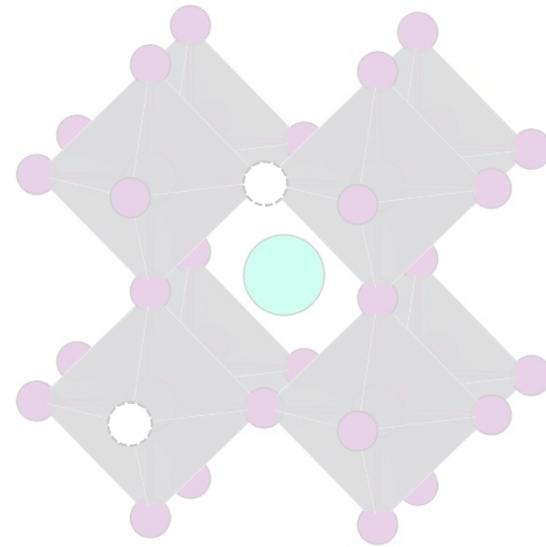
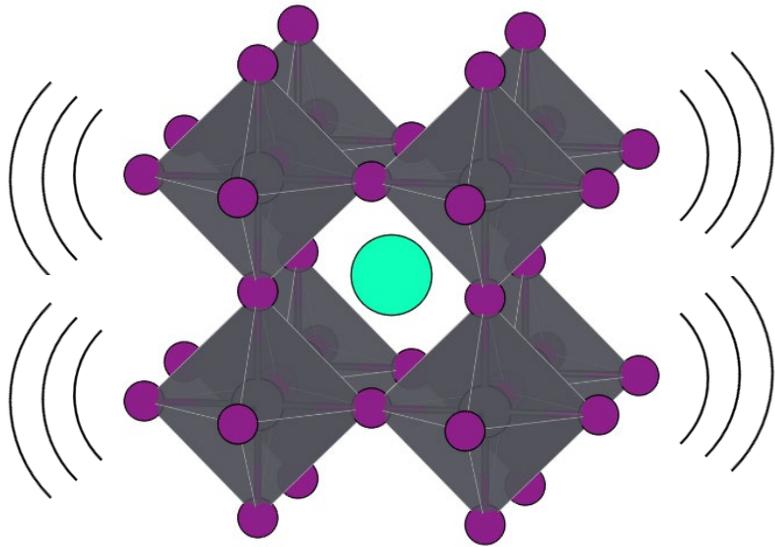
- CsPbI_3 equations of state
- Defect migration barriers



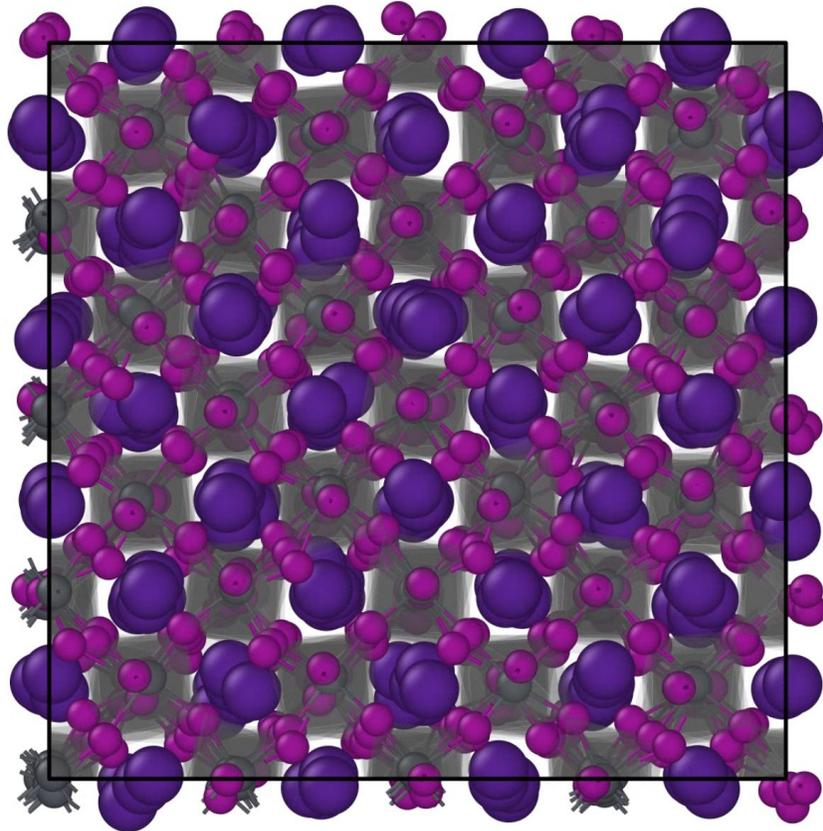
Benchmark of the EEM charges



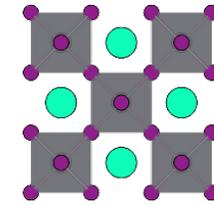
What roles do the **dynamical** and reactive processes play in the stability of metal halide perovskites?



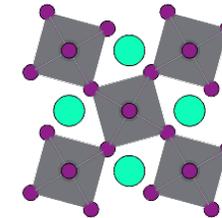
The dynamics of CsPbI₃



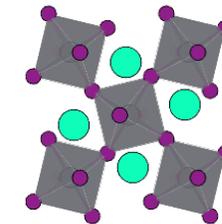
Cubic



Tetragonal

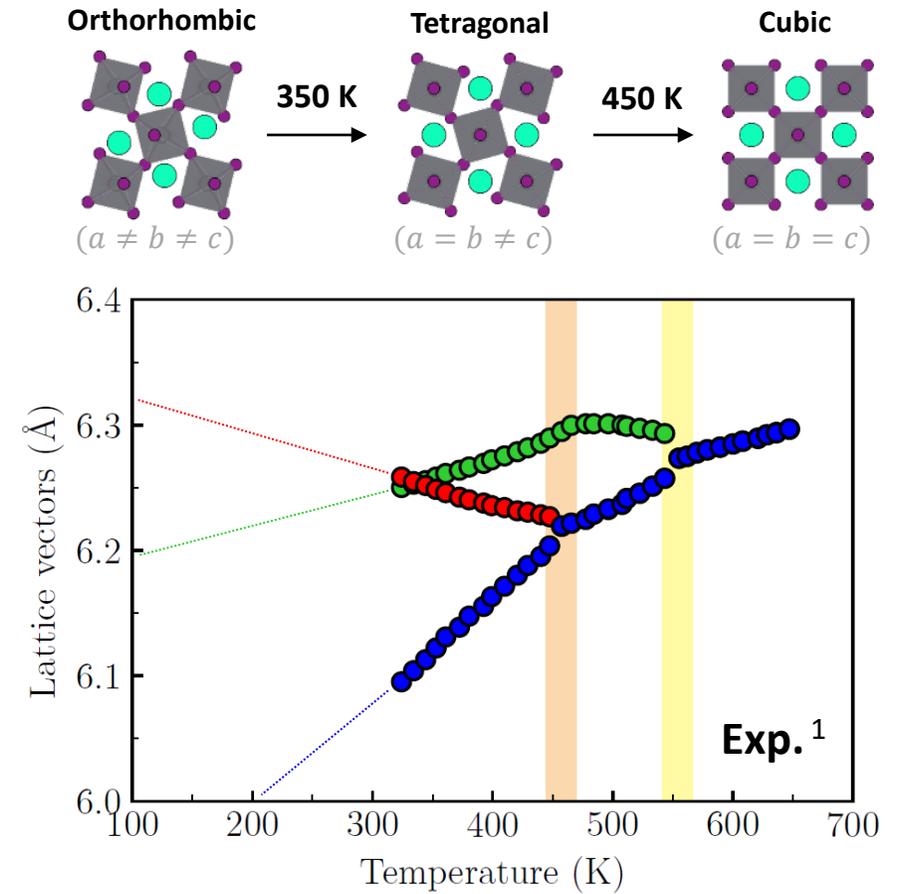
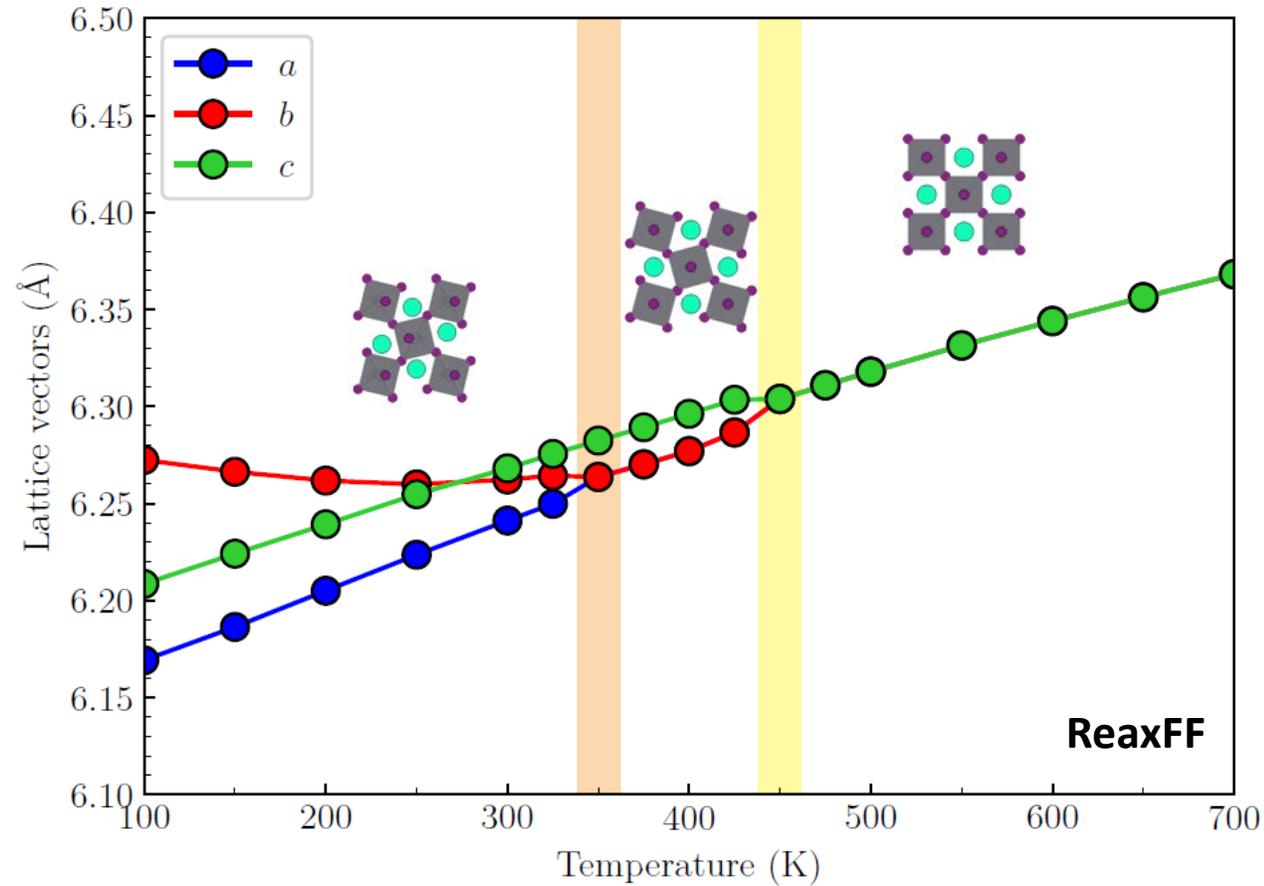


Orthorhombic



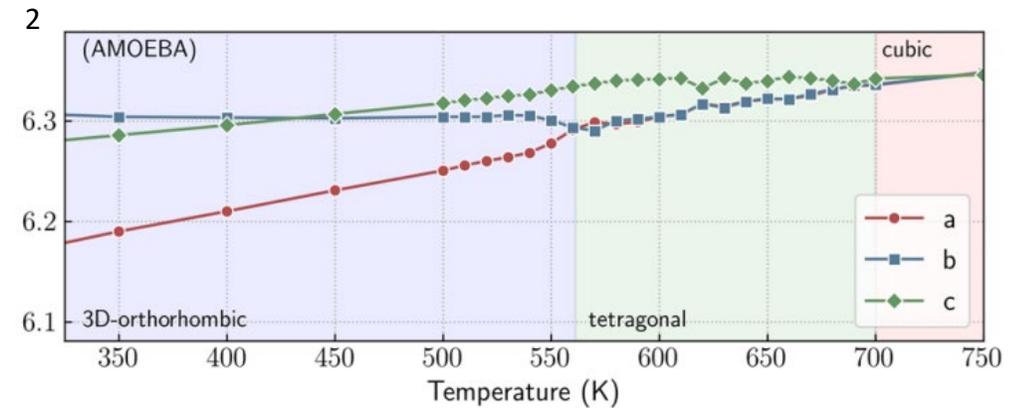
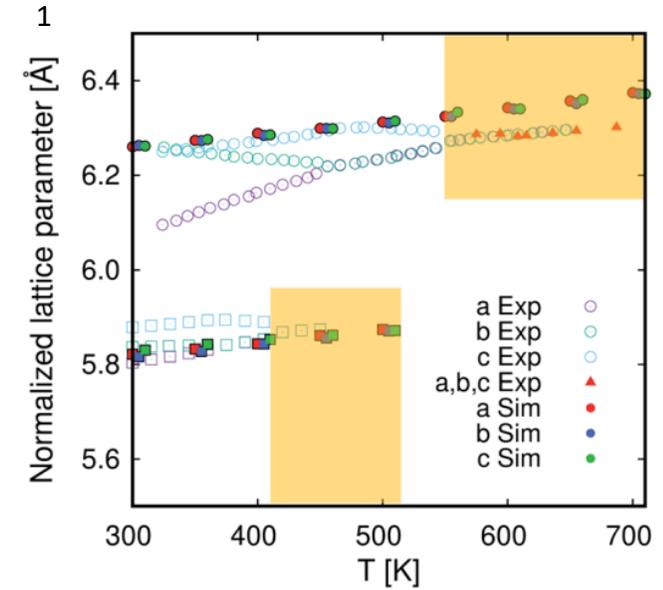
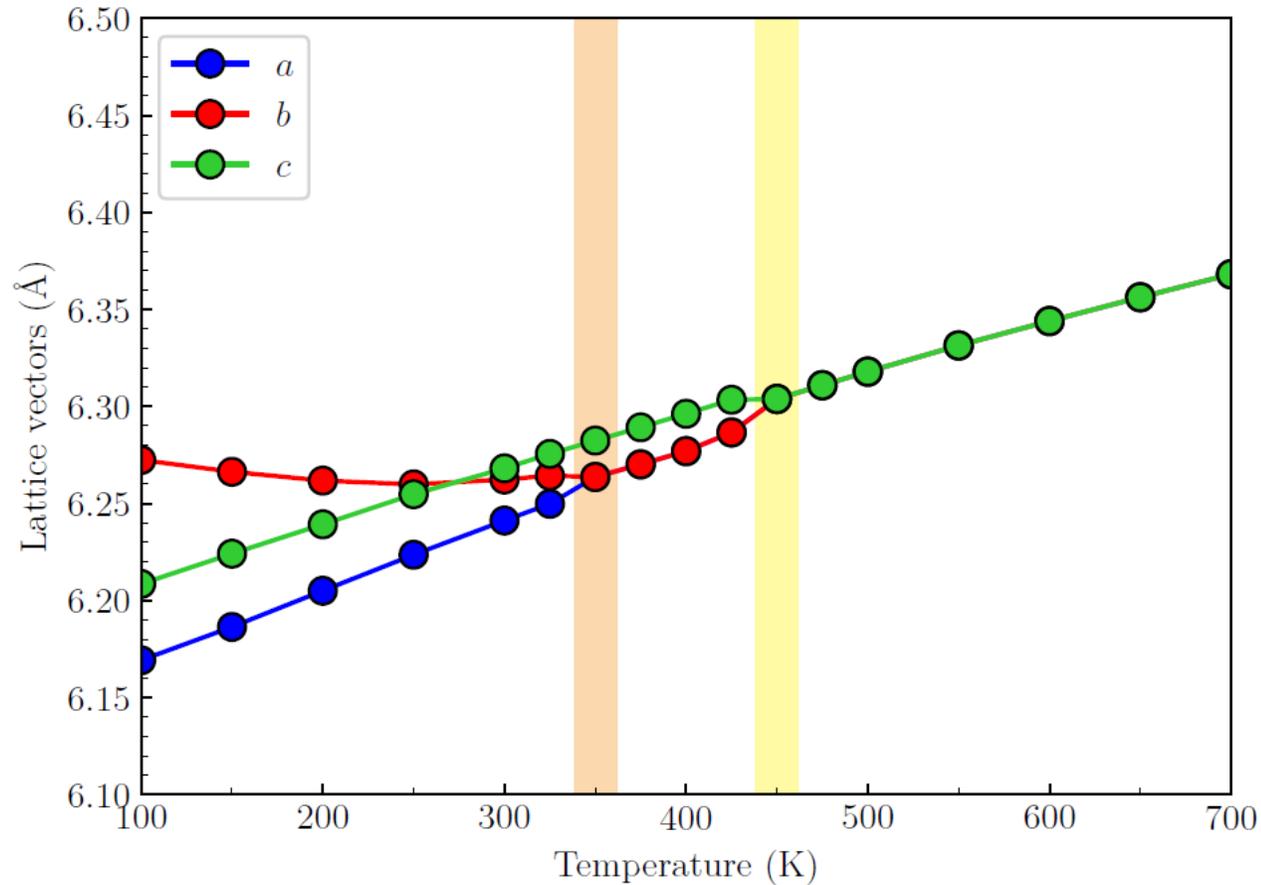
Increasing T

Phase evolution of CsPbI₃



¹ Marronnier, Arthur *et al.* *ACS Nano* 12, no. 4 (April 24, 2018): 3477–86.

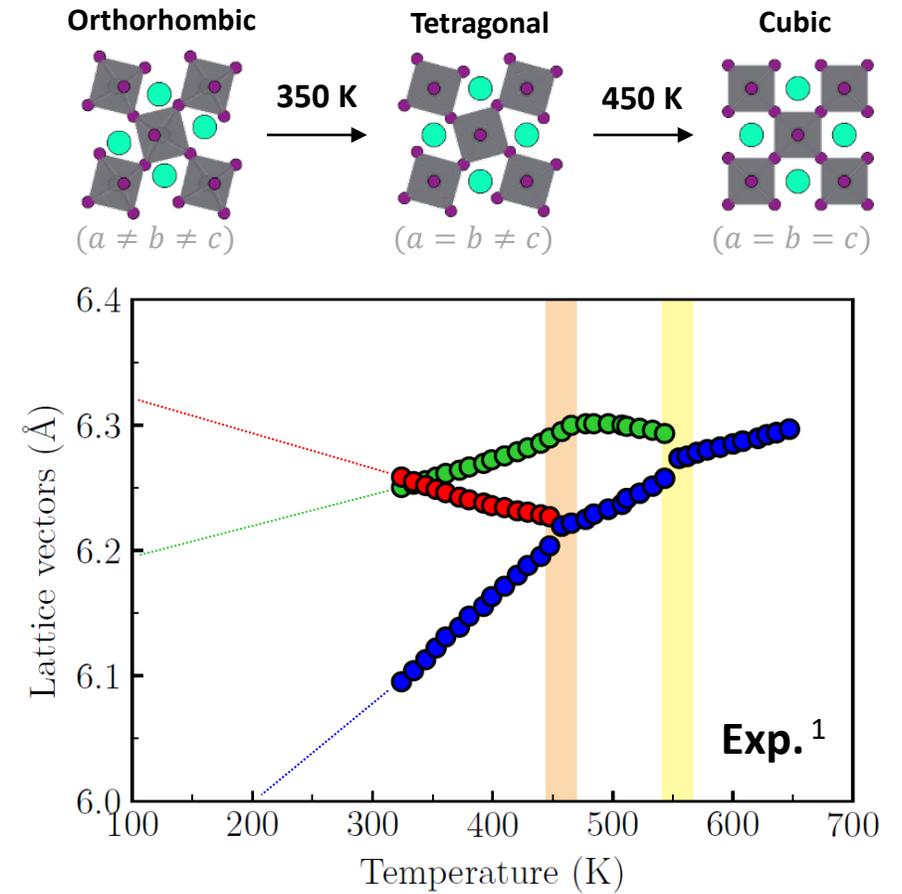
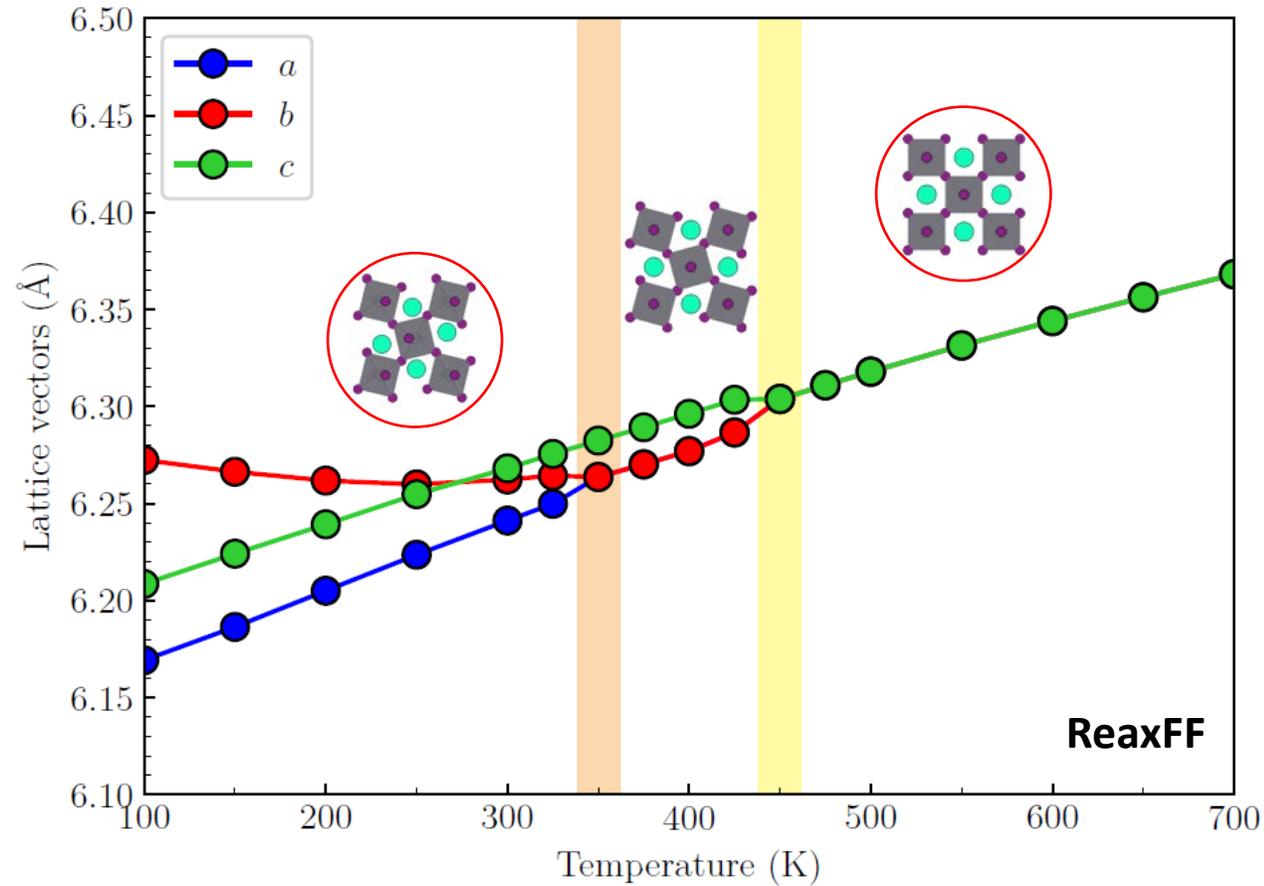
Comparison to classical force fields



¹ Balestra, S. *et al.* *Journal of Materials Chemistry A* 8, no. 23 (June 16, 2020): 11824–36.

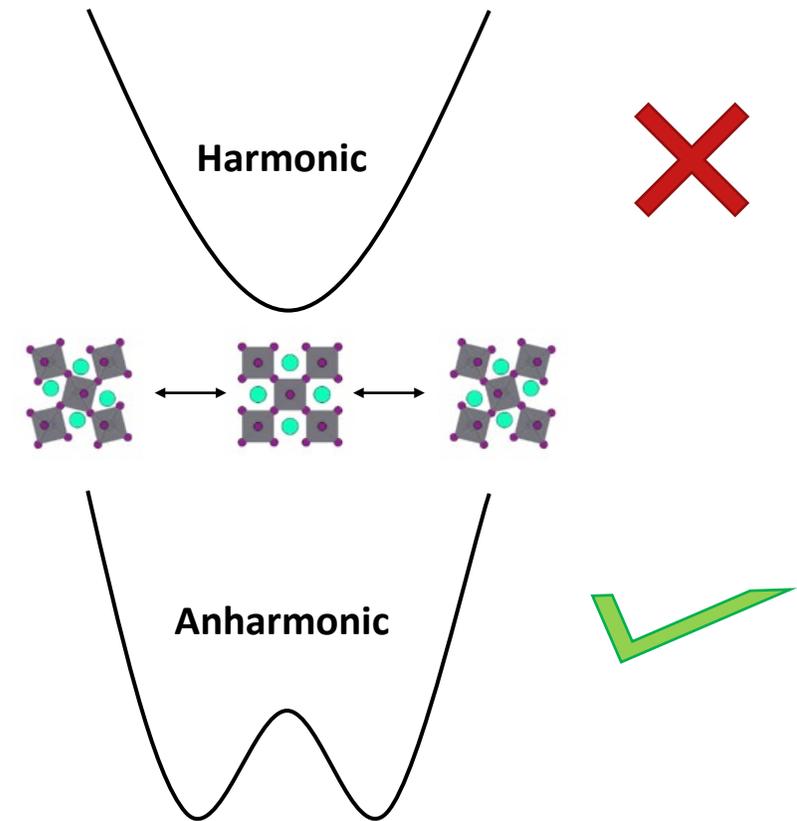
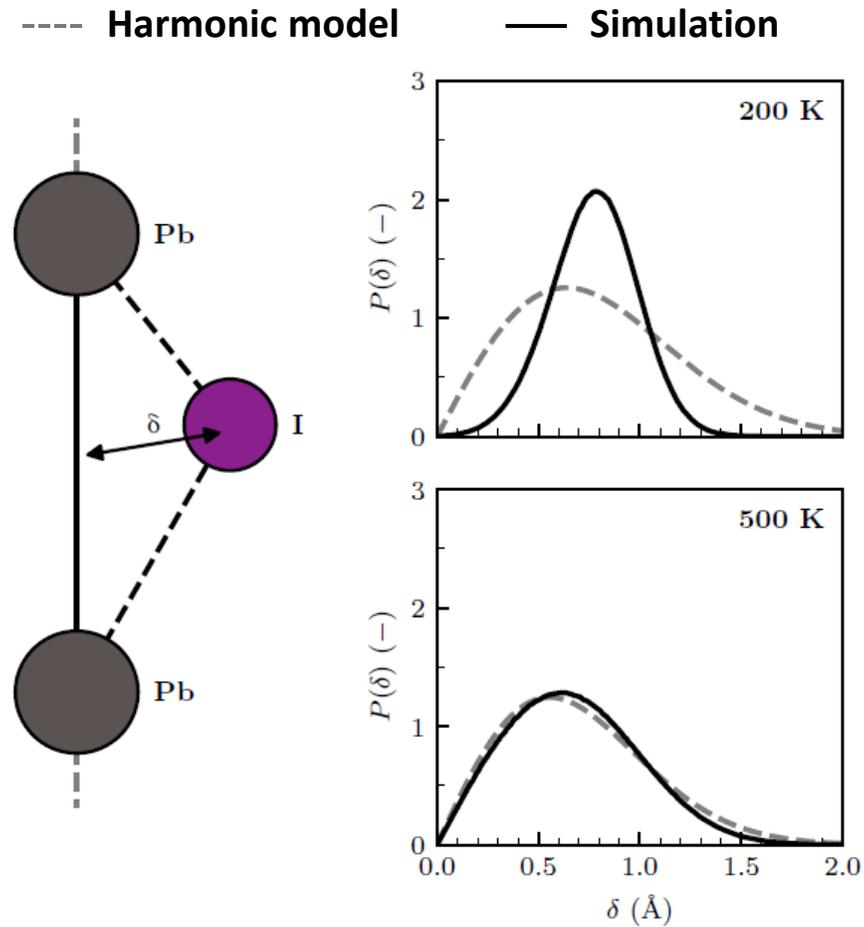
² Rathnayake, P. *et al.* *The Journal of Chemical Physics* 152, no. 2 (January 13, 2020): 024117.

Focus on two phases

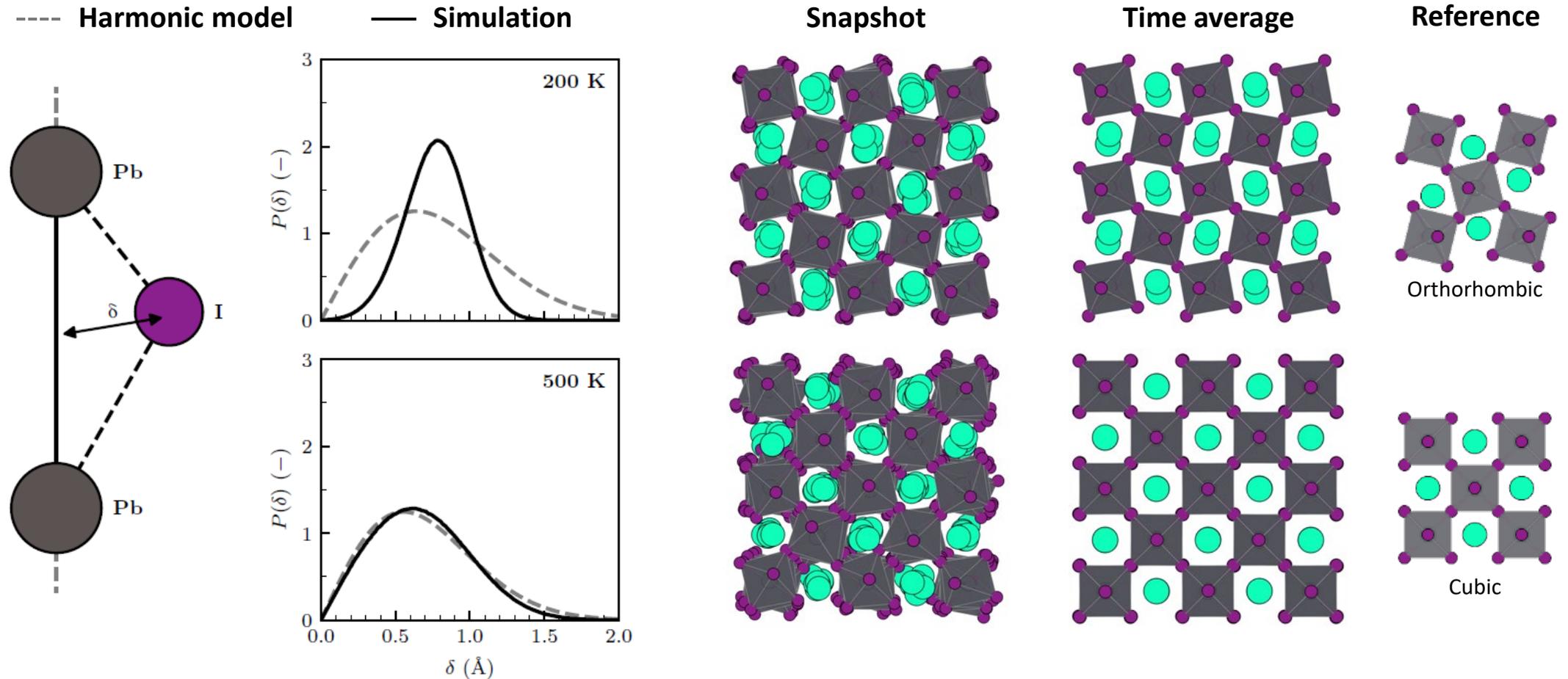


¹ Marronnier, Arthur *et al.* *ACS Nano* 12, no. 4 (April 24, 2018): 3477–86.

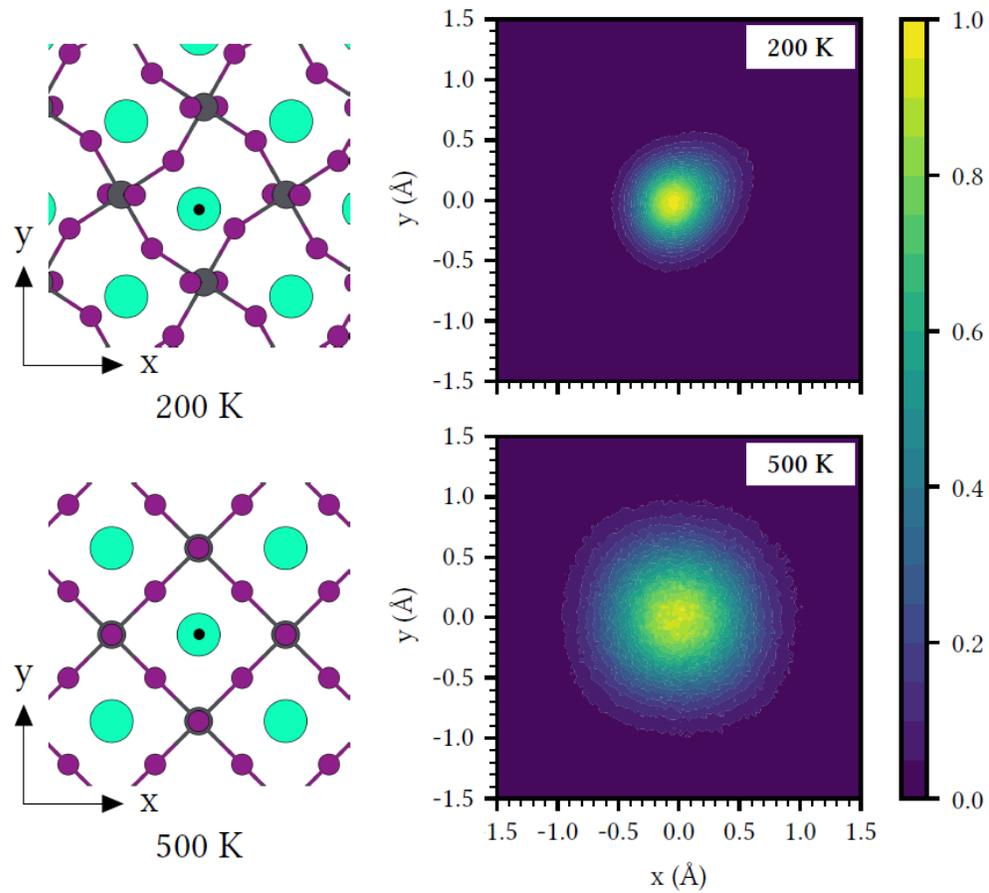
Character of the metal halide framework



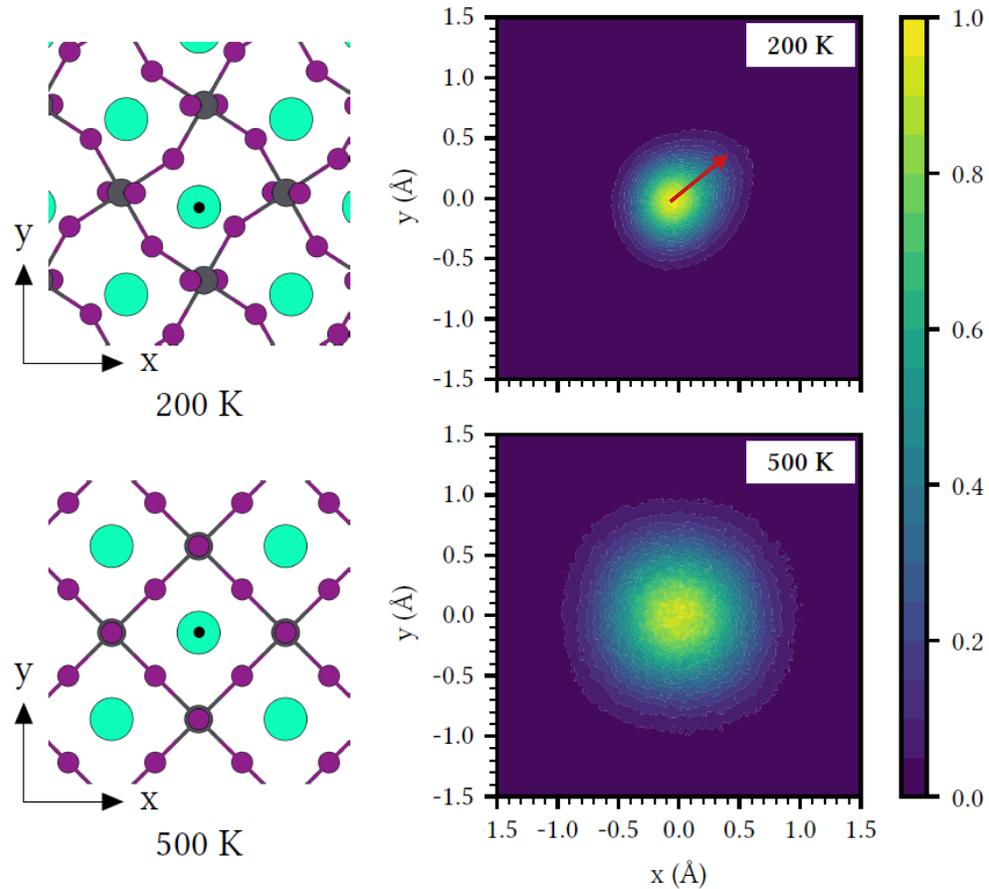
Character of the metal halide framework



The dynamical cation



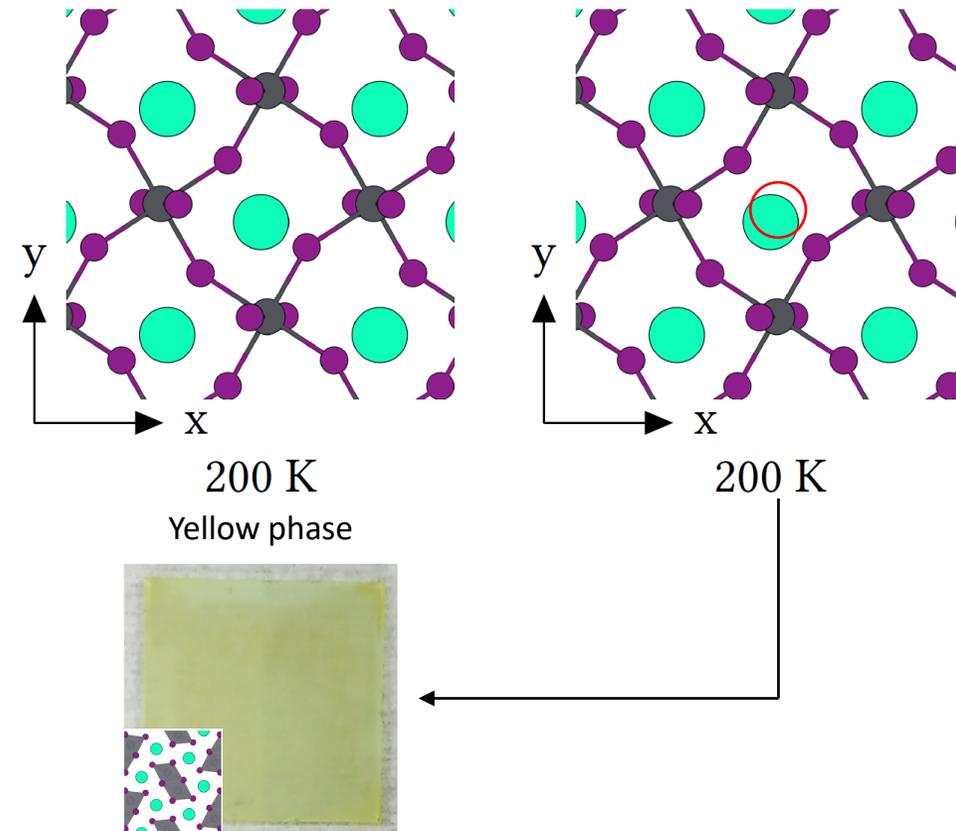
The dynamical cation



Low temperature CsPbI₃ perovskite:

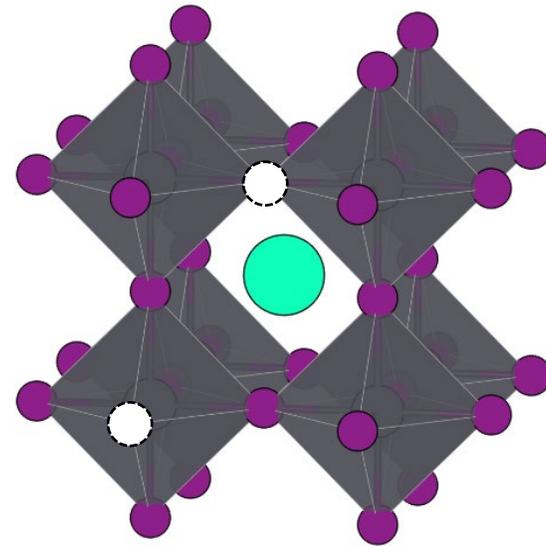
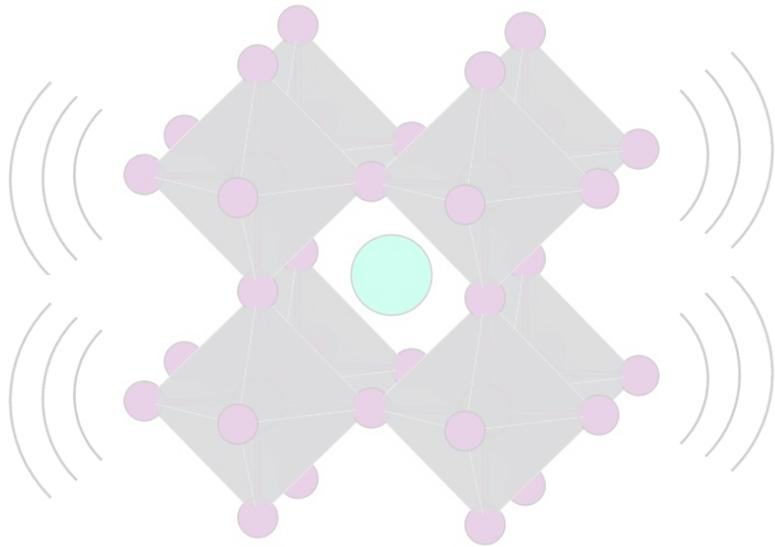
Stabilizing

Destabilizing¹



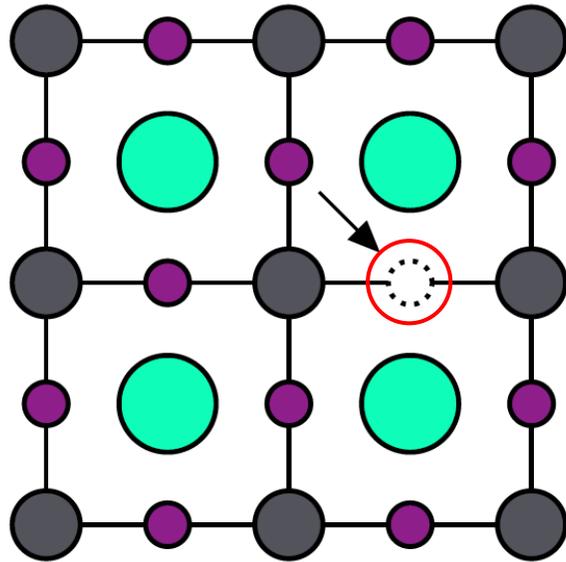
¹ Straus, D.B. *et al. Advanced Materials* 32, no. 32 (2020): 2001069.

What roles do the dynamical and **reactive** processes play in the stability of metal halide perovskites?

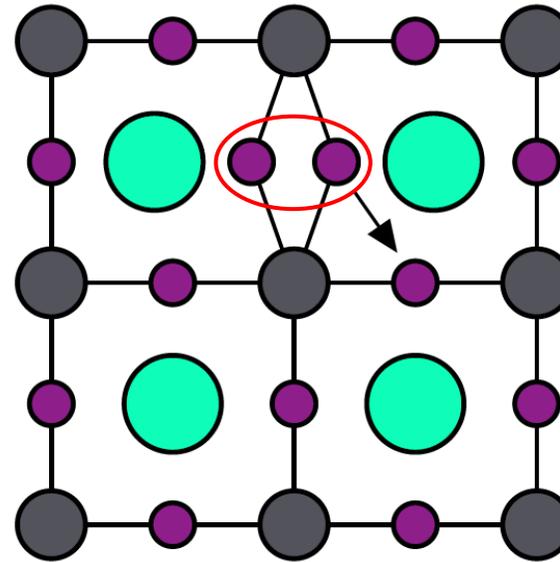


Imperfect metal halide perovskites

Iodine migration mechanisms:



Vacancy-assisted
iodine migration (V_I)



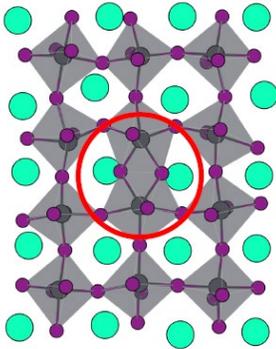
Interstitial-assisted
iodine migration (I_I)

Defect-assisted ion migration mechanisms

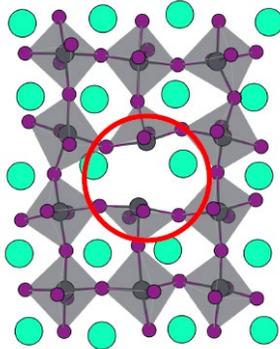
Arrhenius analysis:

$$D = D_0 \cdot \exp\left(-\frac{E_a}{k_B T}\right)$$

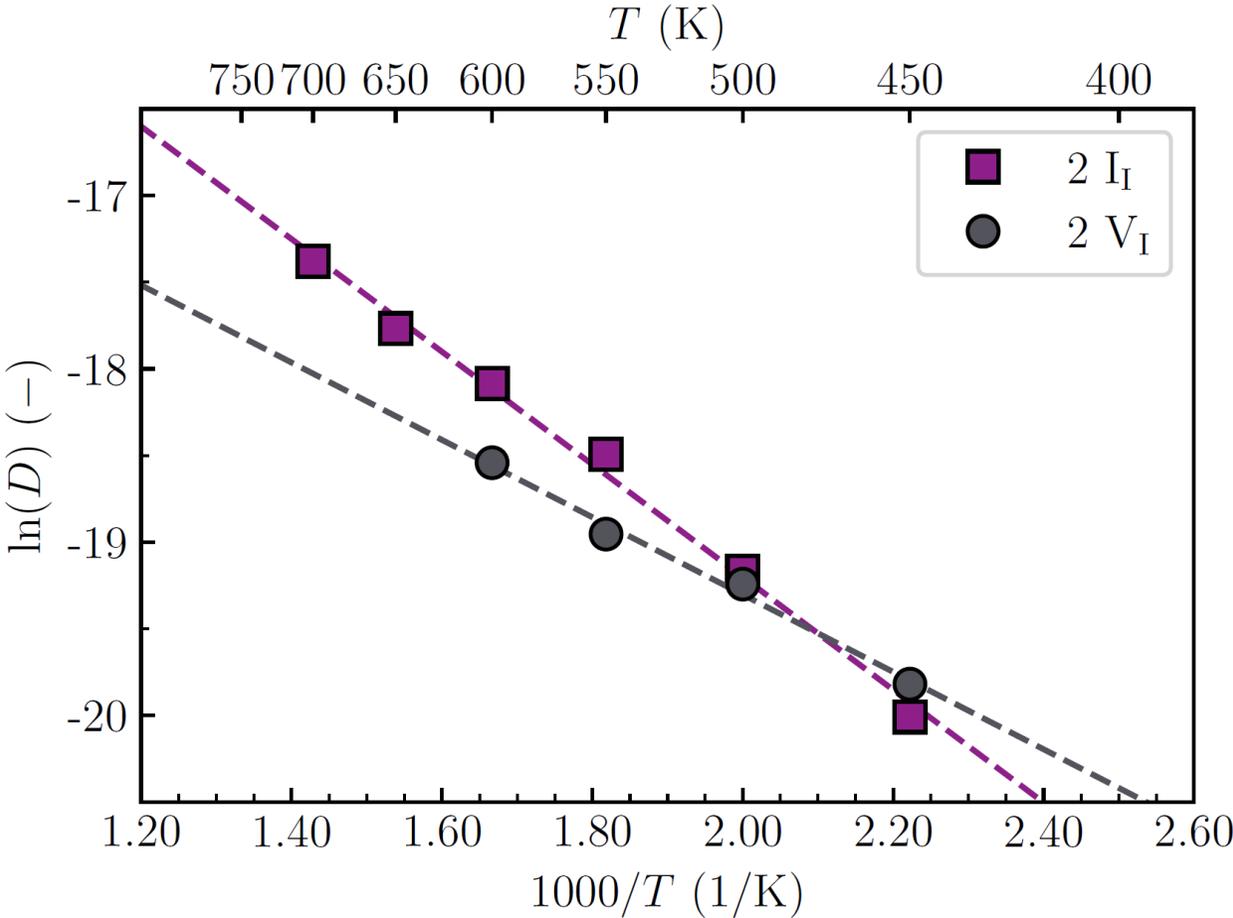
Activation energy



$I_I: E_a = 0.28 \text{ eV}$



$V_I: E_a = 0.19 \text{ eV}$

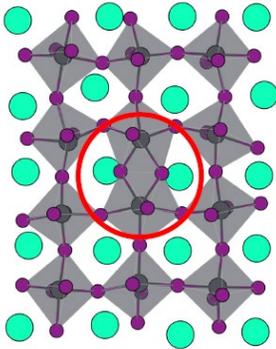


Defect-assisted ion migration mechanisms

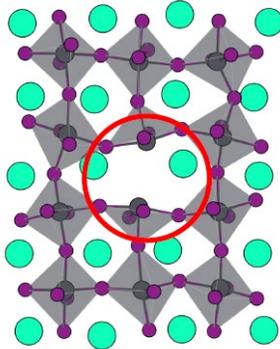
Arrhenius analysis:

$$D = D_0 \cdot \exp\left(-\frac{E_a}{k_B T}\right)$$

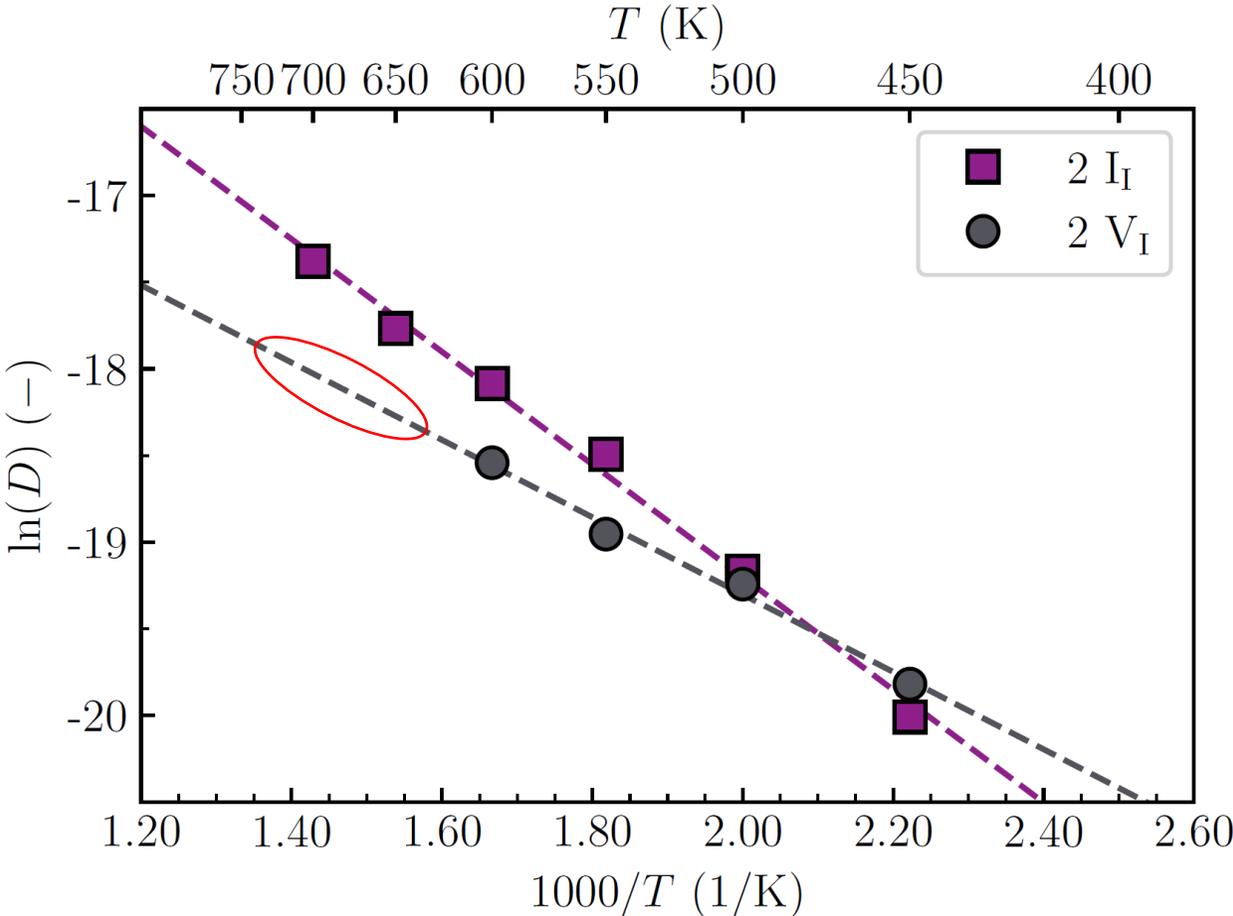
Activation energy



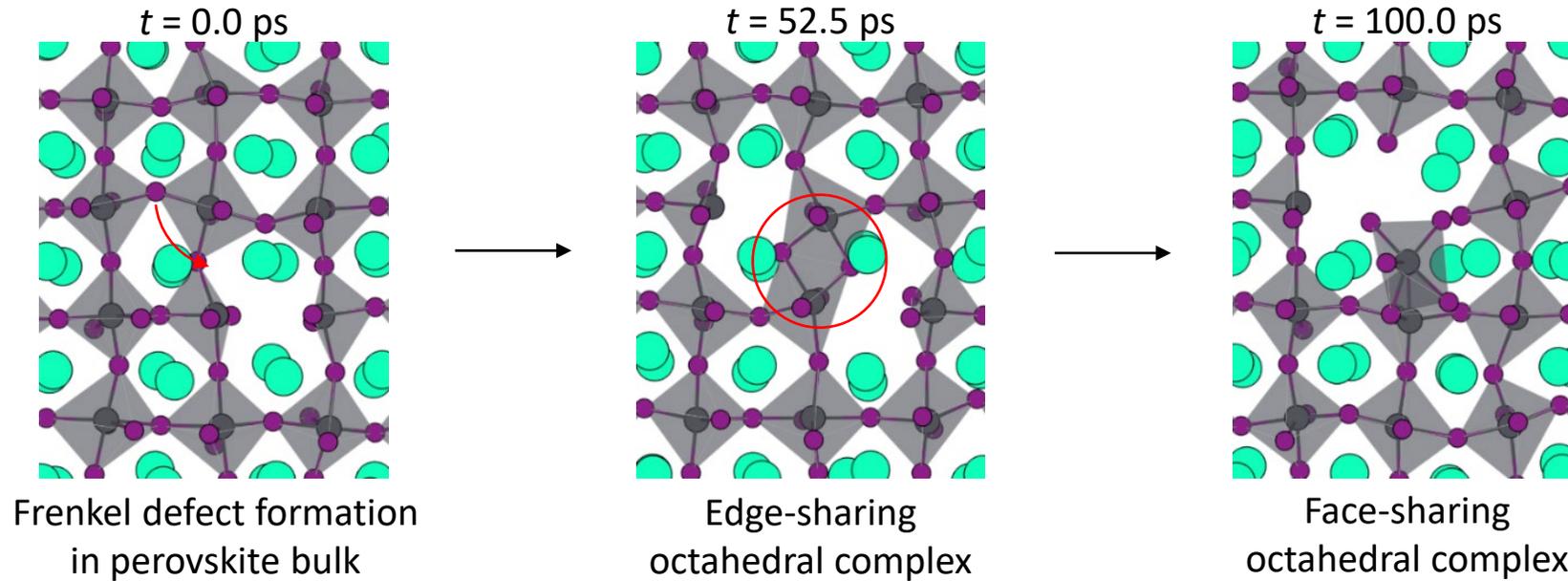
I_i: E_a = 0.28 eV



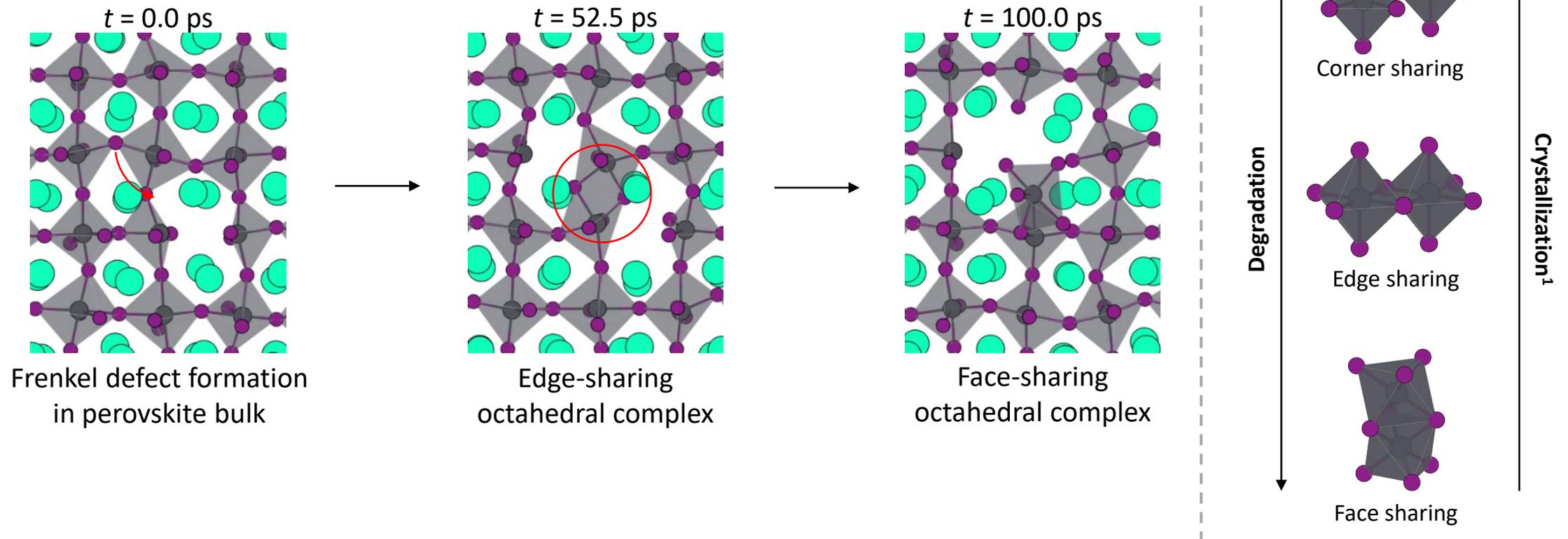
V_i: E_a = 0.19 eV



Defect-accelerated perovskite decomposition



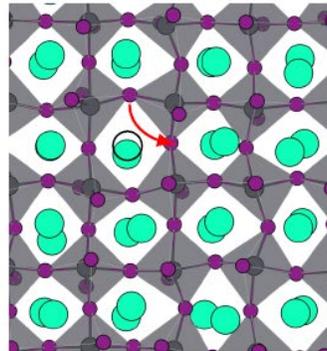
Defect-accelerated perovskite decomposition



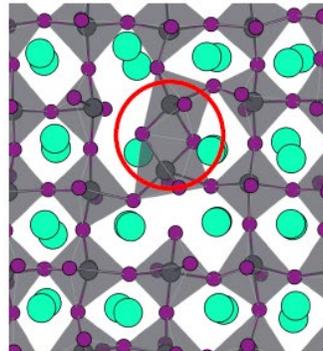
¹ Ahlawat, P *et al.* *Chemistry of Materials* 32, no. 1 (January 14, 2020): 529–36.

The effect of other vacancy defects

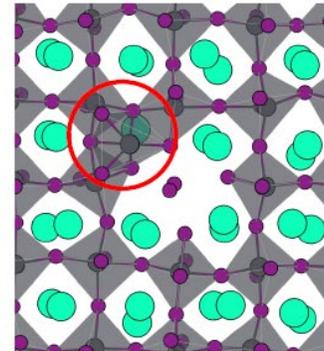
Cesium vacancy (V_{Cs})



0.0 ps

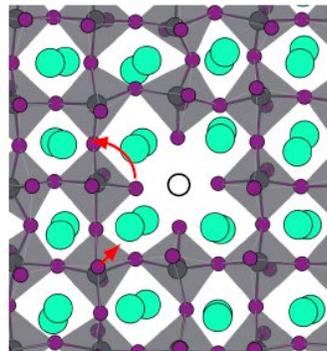


25.0 ps

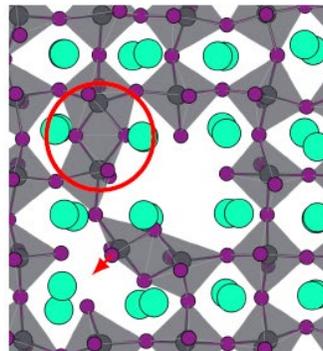


50.0 ps

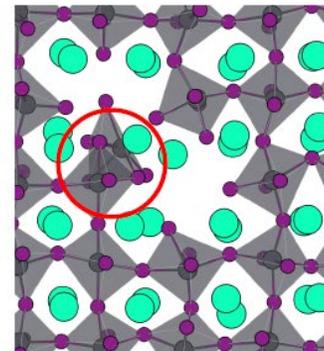
Lead vacancy (V_{Pb})



0.0 ps



25.0 ps



50.0 ps

Onset temperatures:

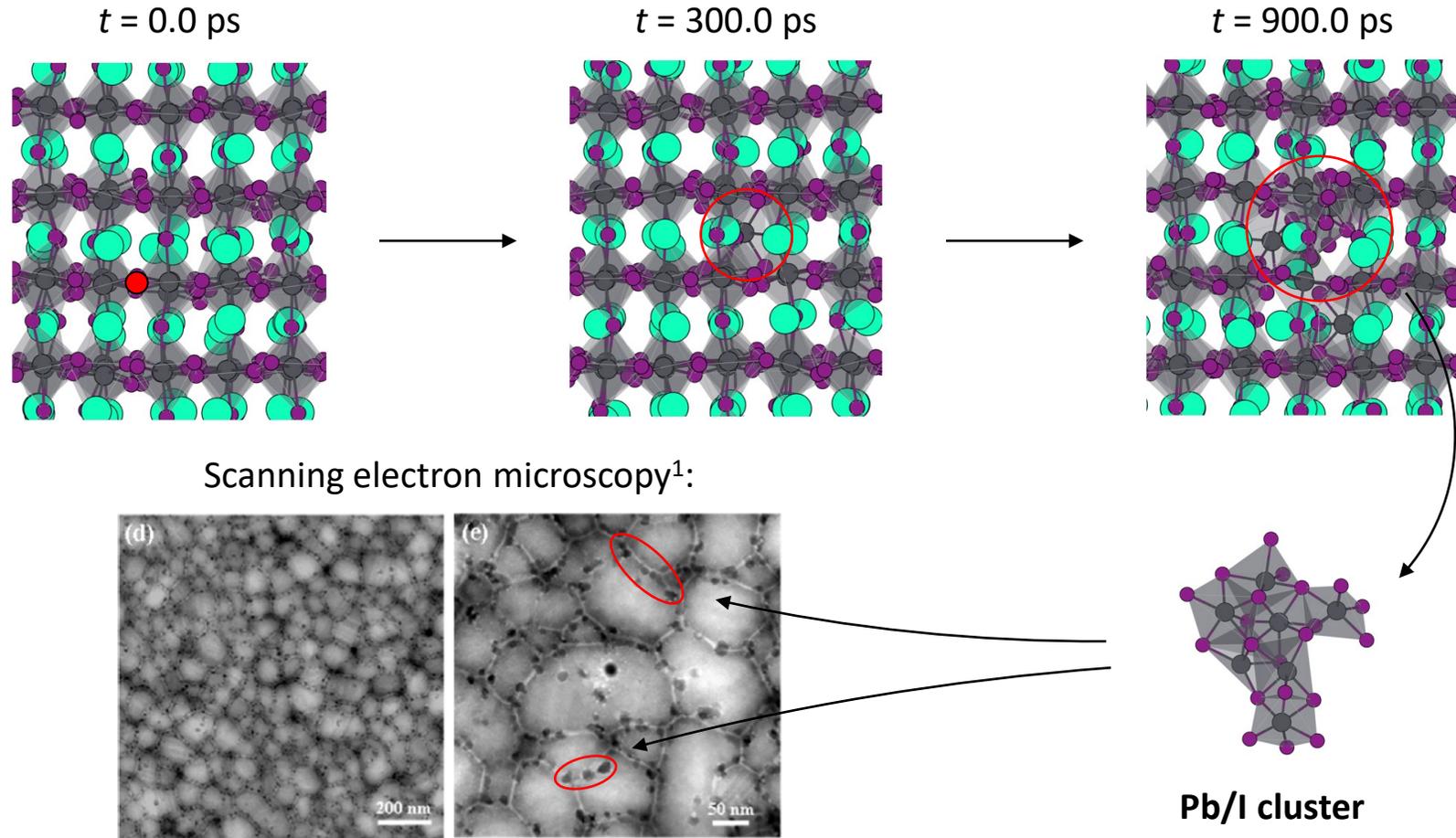
V_I : $T = 600$ K

V_{Cs} : $T = 700$ K

V_{Pb} : $T = 700$ K

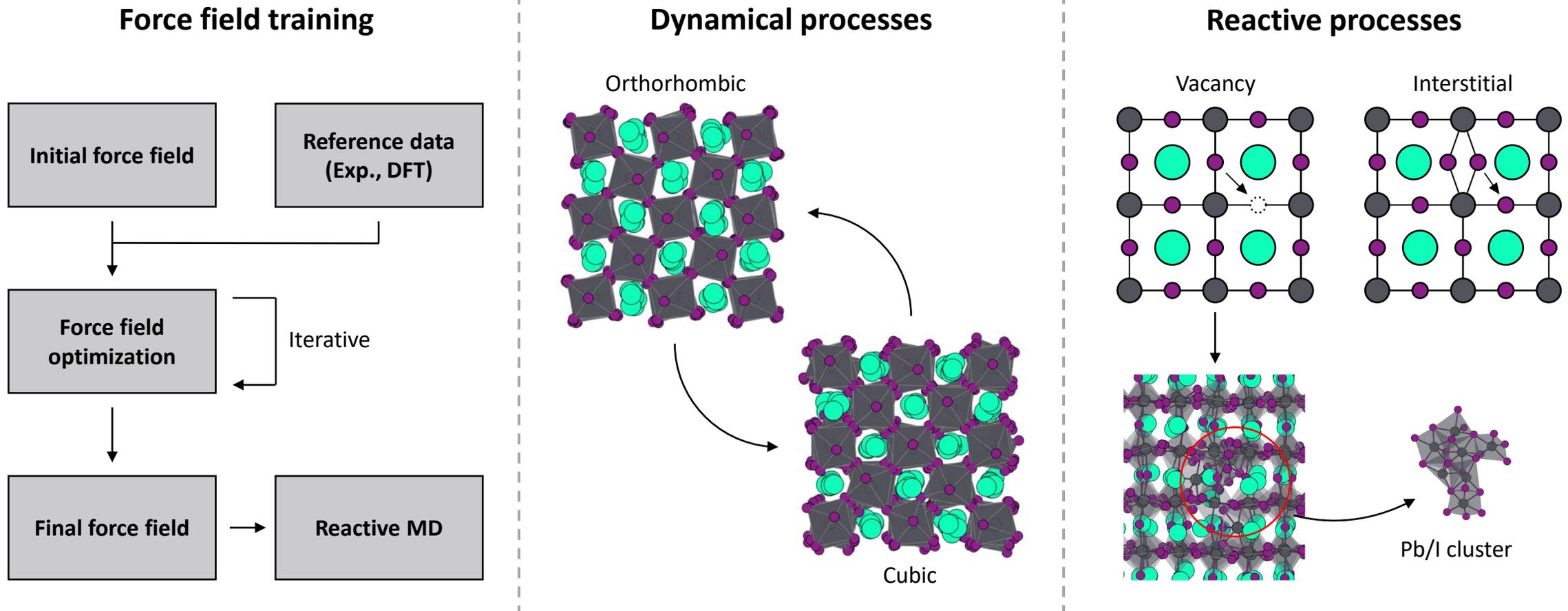
Larger temperature stability for V_{Cs} and V_{Pb} as compared to V_I defects

Defect-accelerated perovskite decomposition



¹ Manekkathodi, A *et al.* *ACS Applied Energy Materials* 3, no. 7 (July 27, 2020): 6302–9.

Overall performance of ReaxFF



¹ Pols, M et al. *The Journal of Physical Chemistry Letters* 12, no. 23 (June 17, 2021): 5519–25.

