Modelling non-radiative carrier capture in photovoltaic materials

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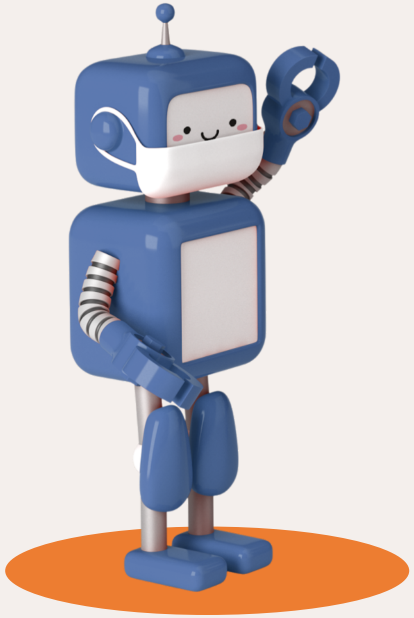
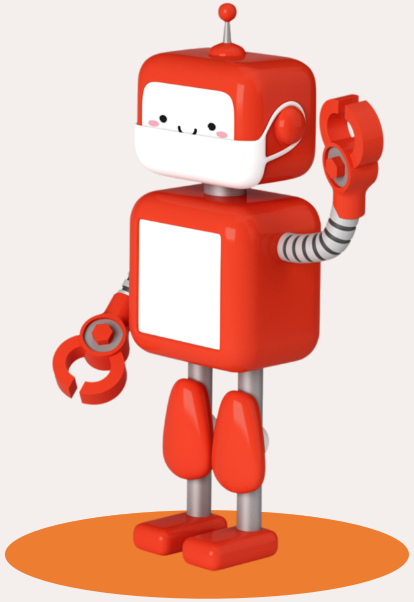
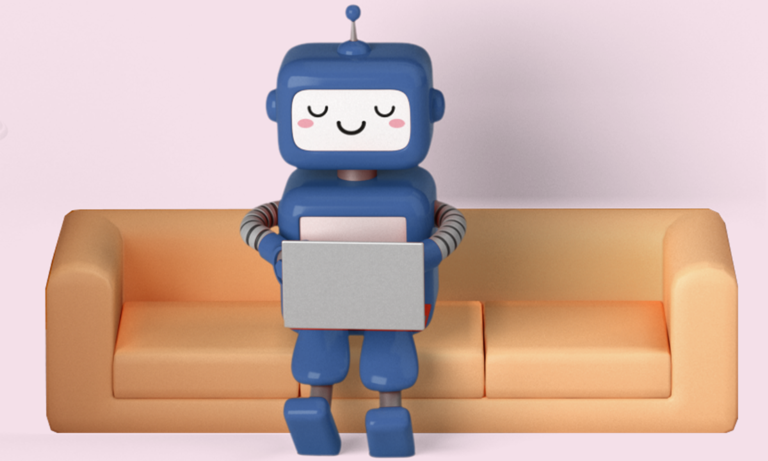
`lucydot.github.io`





< About Me >

- Trained in Physics (UG) and Materials Science (PhD)
- PGCE in post-compulsory education and training
- Vice Chancellor’s Research Fellow at Northumbria University
- Fellow at Software Sustainability Institute



< Academic Interests >

Energy materials

Photovoltaics
Battery cathodes

Atomistic modelling

Electronic structure
Solid state physics

Software engineering

Open source software development

Teaching

Software Carpentry
CodeRefinery

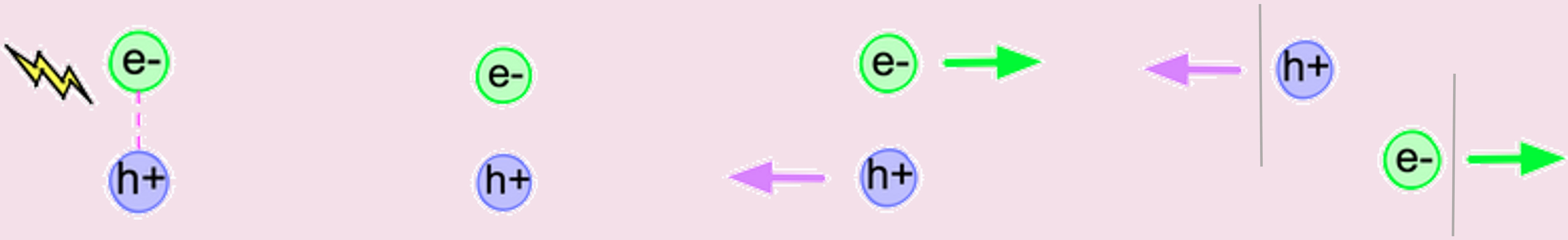
< Outline>

1. What makes a good photovoltaic absorber material?
2. Non-radiative carrier capture
   1. The electronic picture
   2. The importance of lattice relaxation
3. Large lattice relaxation in hybrid halide perovskites

*NRCC = Non-radiative carrier capture

< What makes a good photovoltaic absorber? >

Steps for efficient light-to-electricity conversion



1. Generation

2. Separation

3. Transport

4. Extraction

< Photovoltaic absorber shopping list>

1. Suitable band gap
2. Strong light absorption
3. Low exciton binding energy
4. High electron/hole mobility
5. Long electron/hole lifetime
6. Compatibility
7. Stability
8. Toughness
9. Elemental abundance
10. Elemental non-toxicity

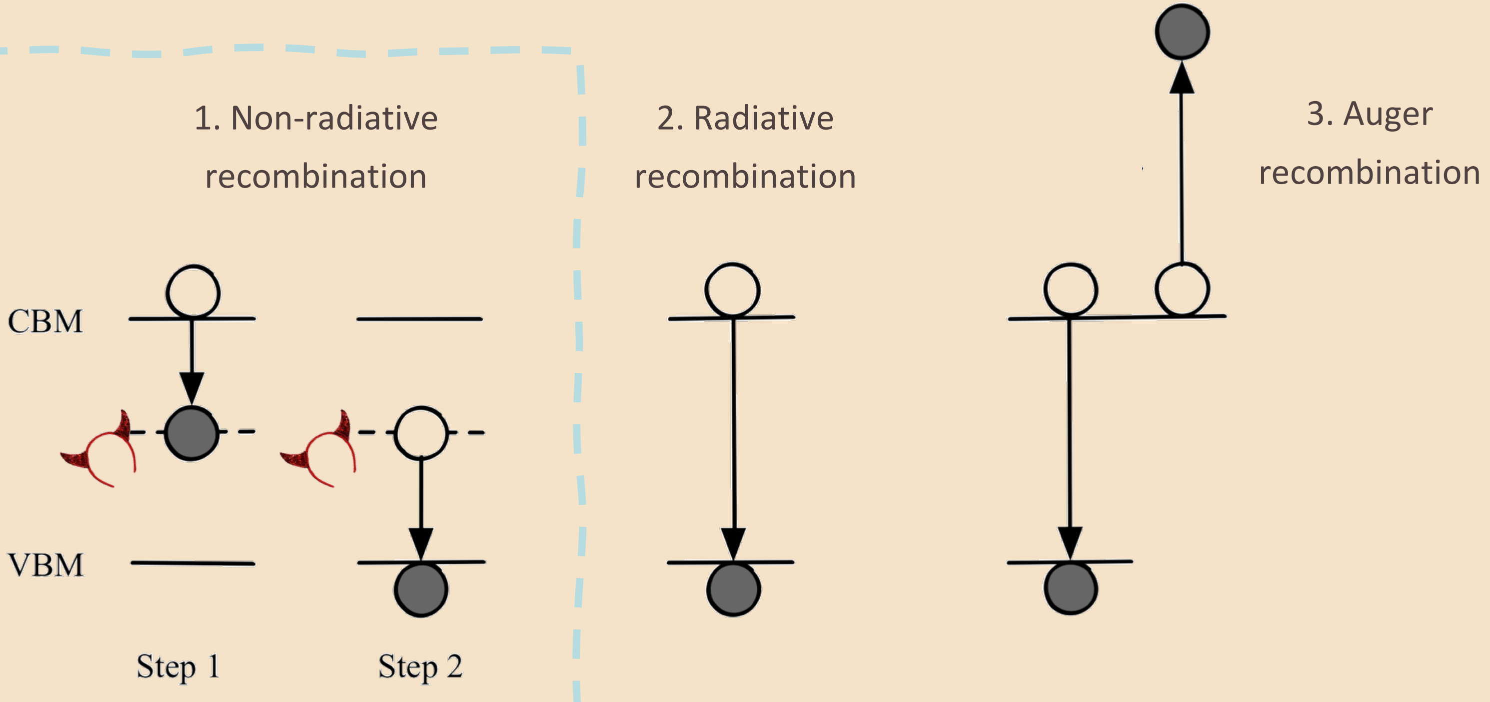
< Photovoltaic absorber shopping list>

1. Suitable band gap
2. Strong light absorption
3. Low exciton binding energy
4. High electron/hole mobility ← Limited by charge trapping
5. Long electron/hole lifetime ← Limited by recombination
6. Compatibility
7. Stability
8. Toughness
9. Elemental abundance
10. Elemental non-toxicity

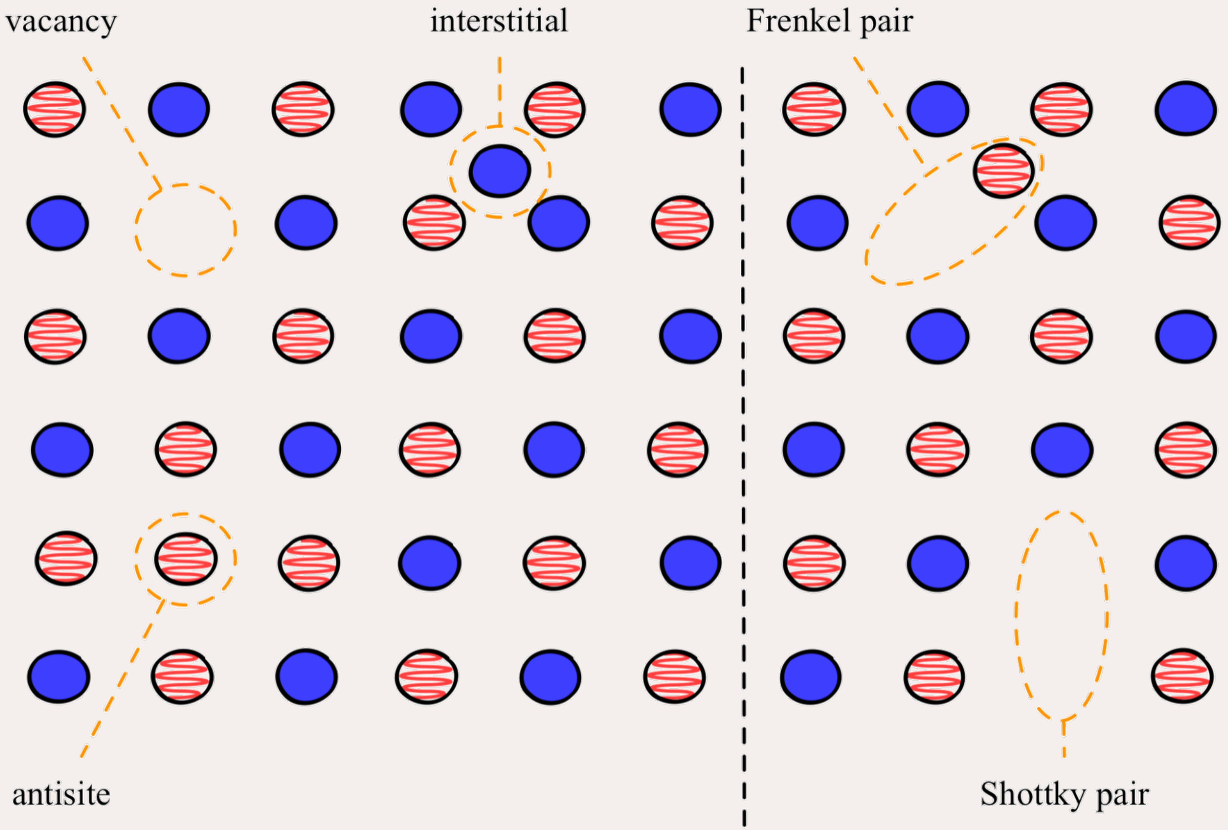
< Non-radiative capture and recombination >

There are three possible electron-hole recombination pathways that limit charge carrier lifetime. Non-radiative capture and recombination reduces the light-to-electricity efficiency of photovoltaic materials.

Electron and hole KE is transformed to vibrational energy and cannot be used for useful work



< Beware! “killer defects” >



“Killer defects” are point defects in the material that are sufficiently abundant, and have a large coefficient for electron and hole capture

Non-radiative recombination rate

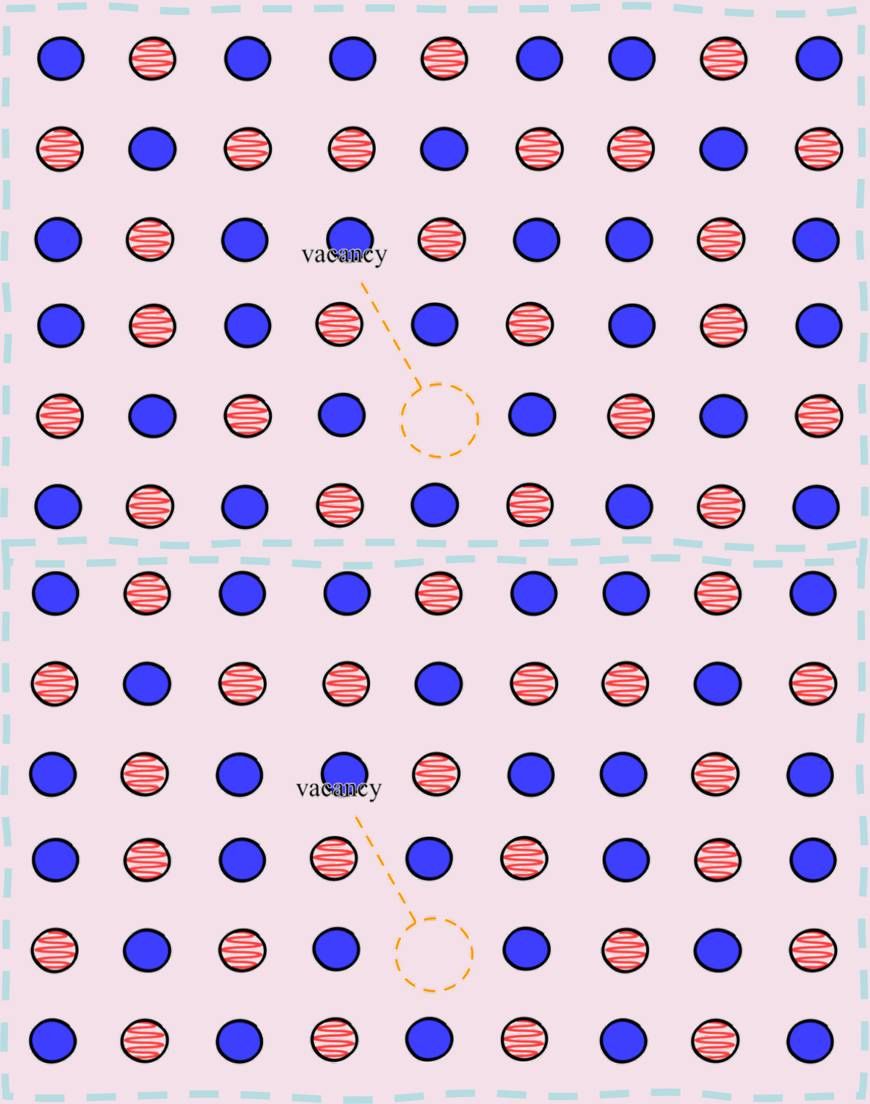
$$R = Nn\frac{C_nC_p}{C_n+C_p}$$

defect concentration

carrier concentration

Capture coefficients

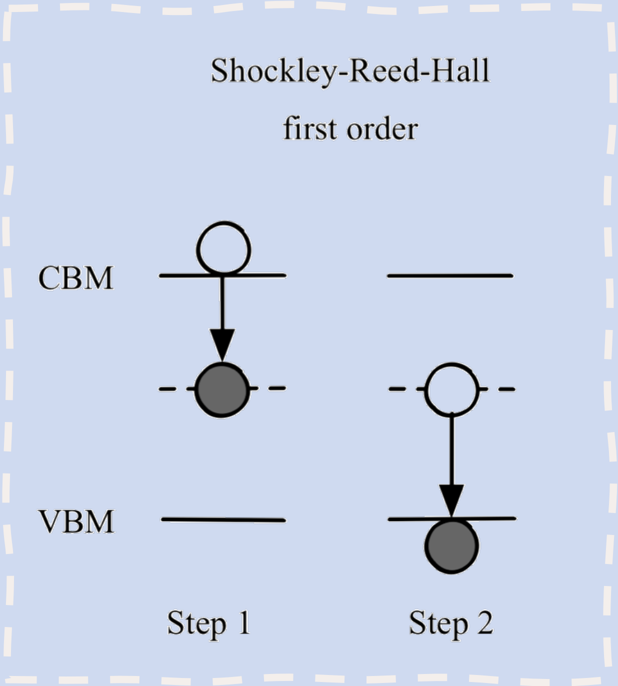
< Modelling “killer defects” >



One way to model point defects is using periodic plane-wave Density Functional Theory. Large supercells are needed to reduce defect-defect interactions, and post-processing can be tricky (square peg, round hole).

$$n = N_{\mathrm{sites}} \exp\left(-\frac{\Delta G}{k_{\mathrm{B}}T}\right)$$

< NRCC: The electronic picture >



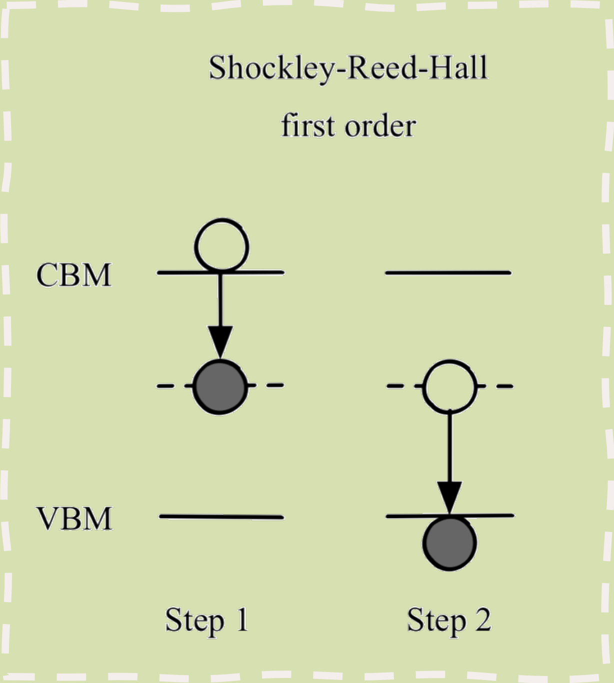
Shockley-Reed-Hall statistics (1952): The carrier capture rate depends exponentially on the energy from band edge. Killer defects have electronic states in the middle of ("deep in") the band gap.

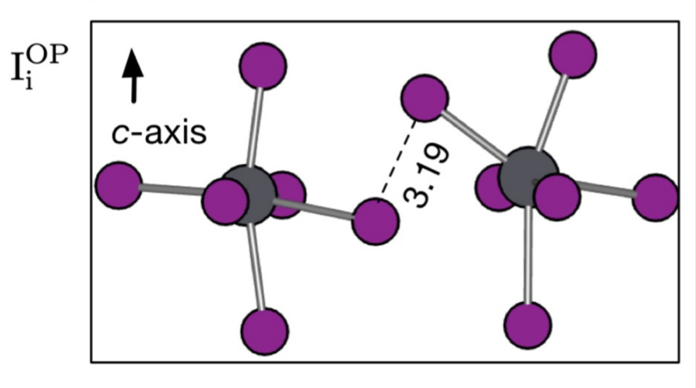
$$R_T = \frac{np - n_i^2}{\tau_p(n + n_1) + \tau_n(p + p_1)}$$

$$n_1 = N_c \exp\left(\frac{E_t - E_c}{kT}\right) \qquad p_1 = N_v \exp\left(\frac{E_v - E_t}{kT}\right)$$

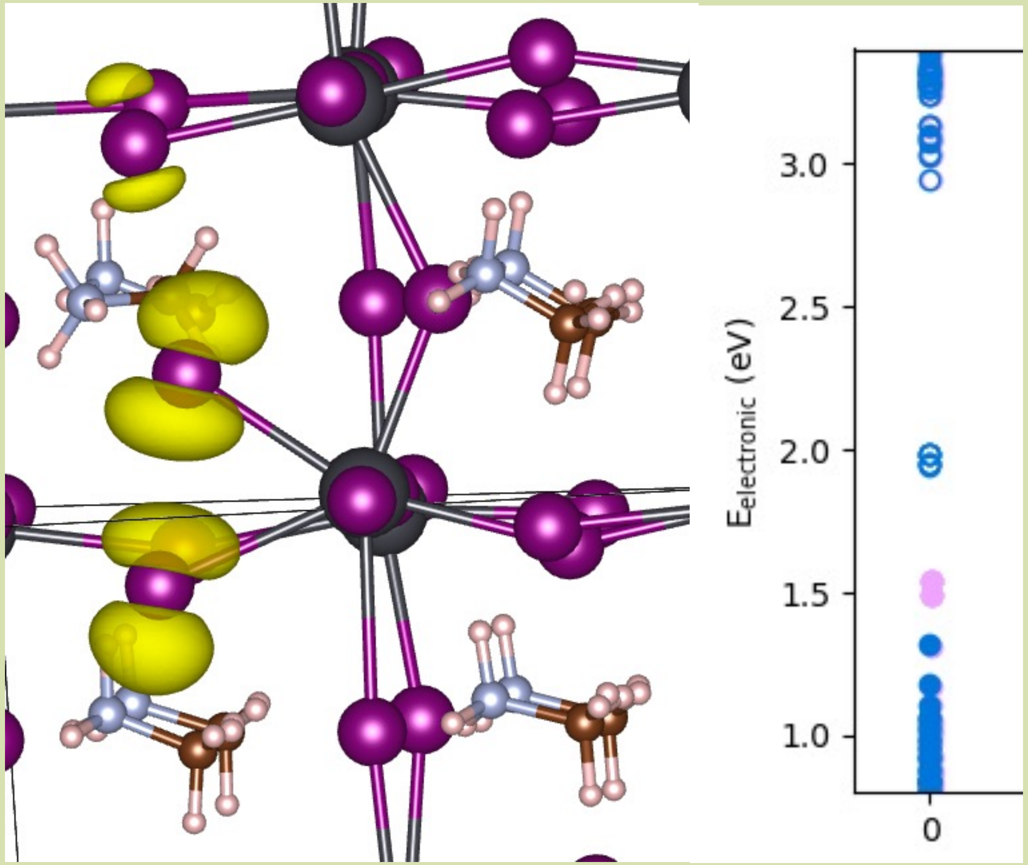
*NRCC = Non-radiative carrier capture

< NRCC: The electronic picture >





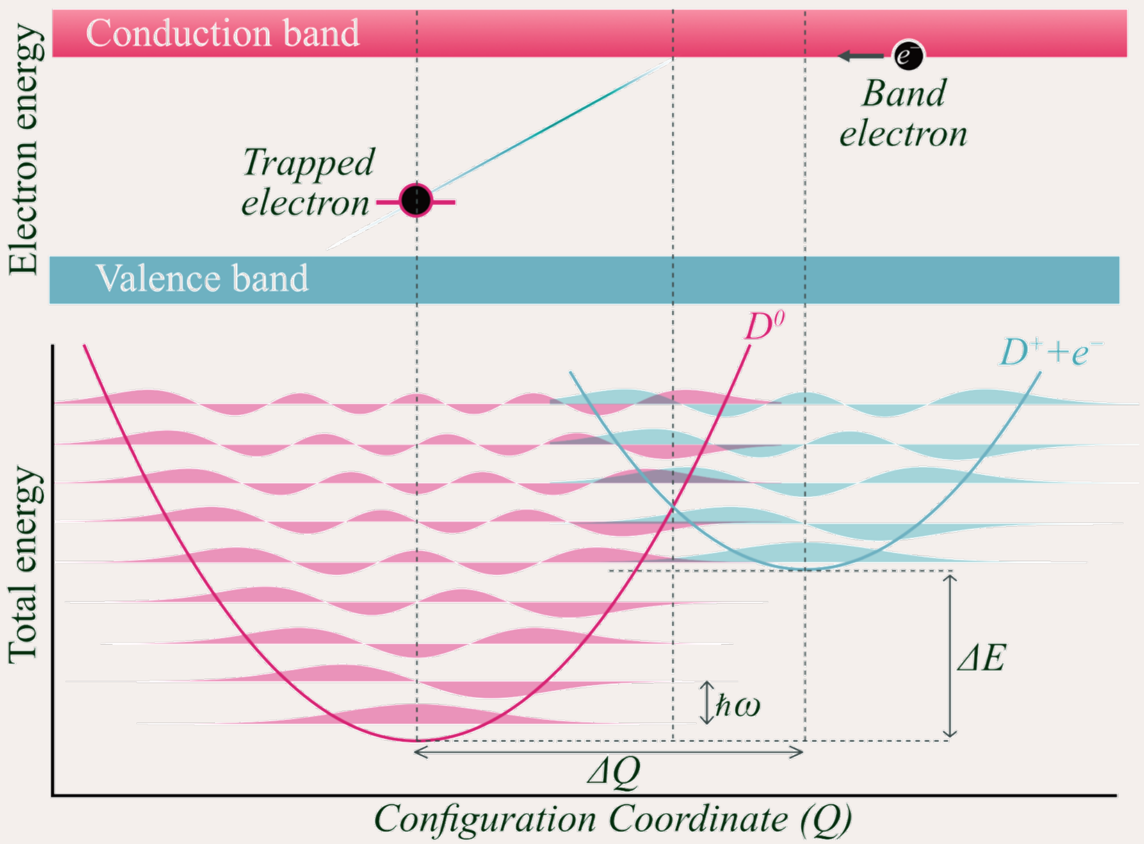
Localised mid-gap defect state formed by the iodine interstitial in hybrid halide perovskite



*NRCC = Non-radiative carrier capture

Whalley et al, “H-centre and V-centre defects..”, ACS Energy Letters (2017)

< NRCC: The importance of lattice relaxation >



*NRCC = Non-radiative carrier capture

Henry and Lang (1977): The thermal vibration of the defect, together with the electron-phonon coupling, results in charge transfer from a delocalised free carrier to a localised defect states.

Alkauskas, Yan and Van de Walle (2015): First-principles methodology for carrier capture by multiphonon emission.

Kim, Hood, van Gerwen, Whalley and Walsh (2020): Software code (`carriercapture.jl`) and extension to anharmonic surfaces.

< NRCC: The importance of lattice relaxation >

The carrier capture coefficient depends on the electron and phonon wave functions associated with the defect. Hybrid functionals are often required to describe the electron localisation.

$$C = V \frac{2\pi}{\hbar} W_{\text{if}}^2 \sum_m \Theta_m \sum_n |\langle \chi_{\text{im}}|\Delta Q|\chi_{\text{fn}}\rangle|^2 \times \delta(\Delta E + m\hbar\omega_i - n\hbar\omega_f)$$

Electron-phonon matrix element

Thermal occupation

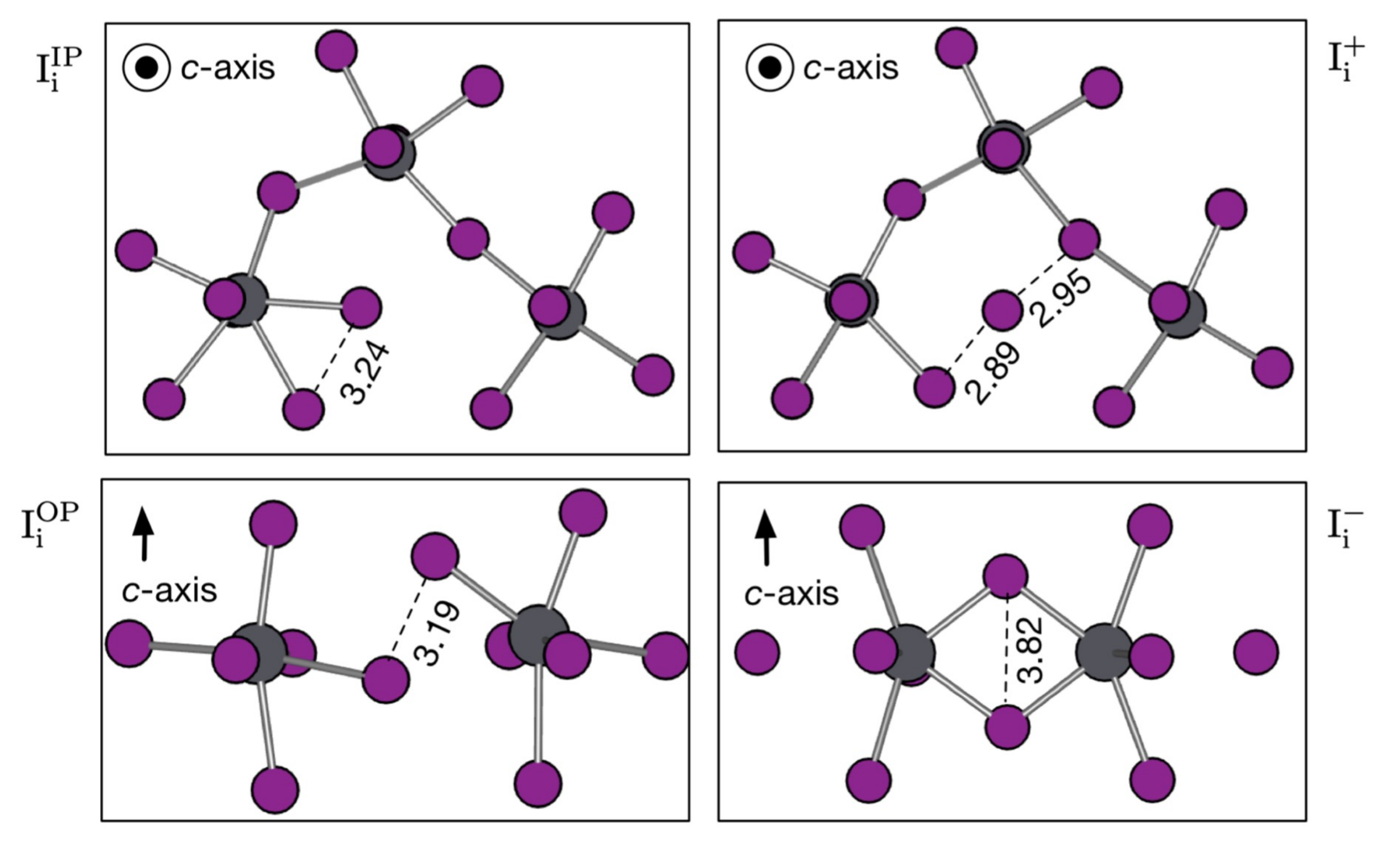
Vibrational wavefunction overlap

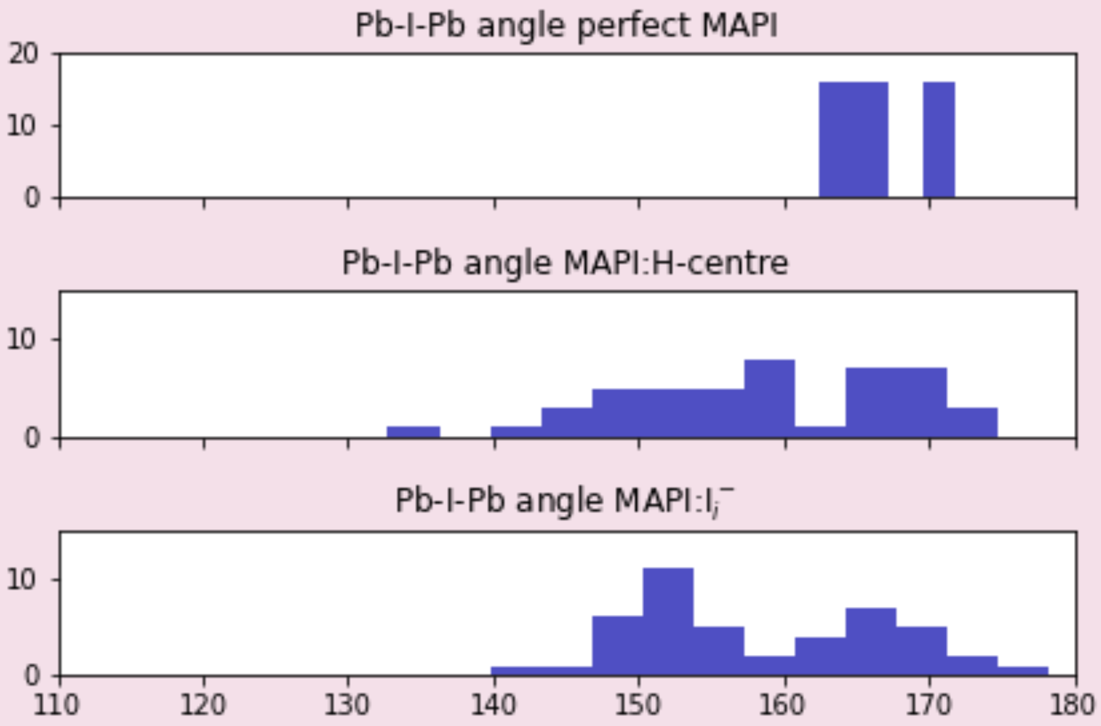
Ensures Conservation of energy

*NRCC = Non-radiative carrier capture

< Hybrid Halide Perovskites >

Hybrid halide perovskites are soft ($\varepsilon_0 \approx 24$) photovoltaic materials. The iodine interstitial has been implicated as an active site for non-radiative processes.



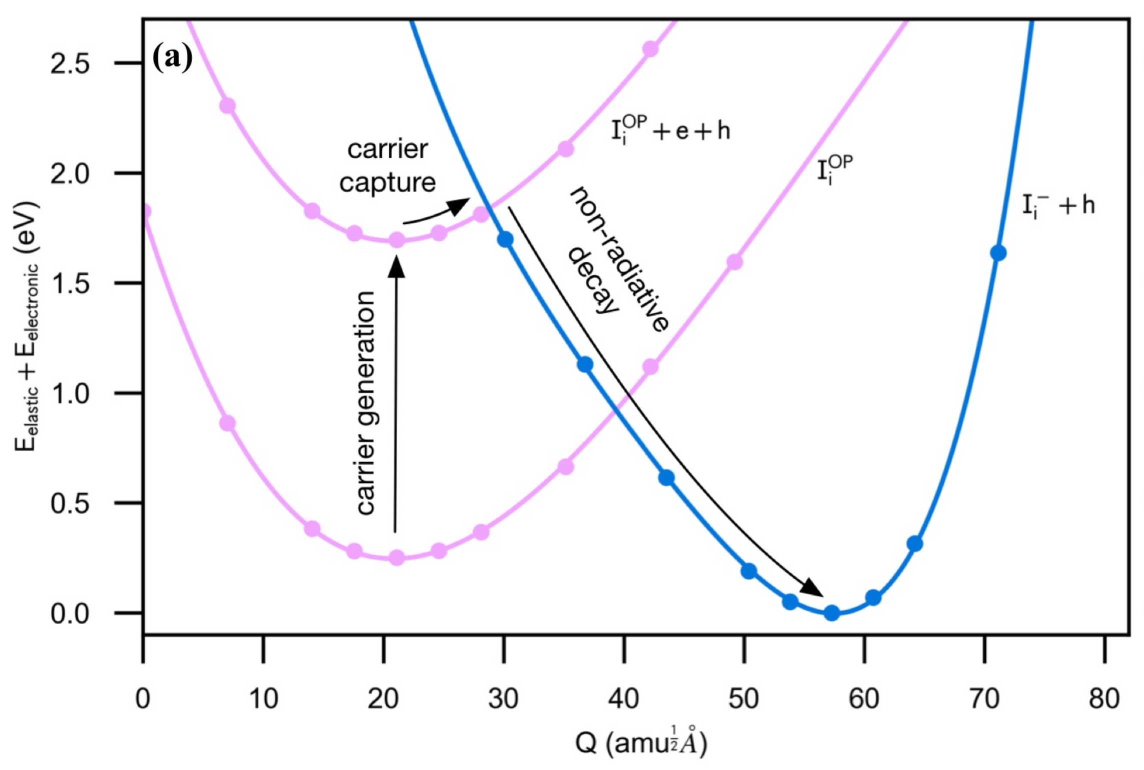

Pb-I-Pb angle perfect MAPI

Pb-I-Pb angle MAPI:H-centre

Pb-I-Pb angle MAPI:I_i^-

< Hybrid Halide Perovskites >

After electron capture at the iodine interstitial there is a large lattice relaxation associated with tilting of the PbI_3 octahedra. This leads to a giant Huang-Rhys factor, indicative of the strong electron-phonon coupling that is possible in soft semiconductors.



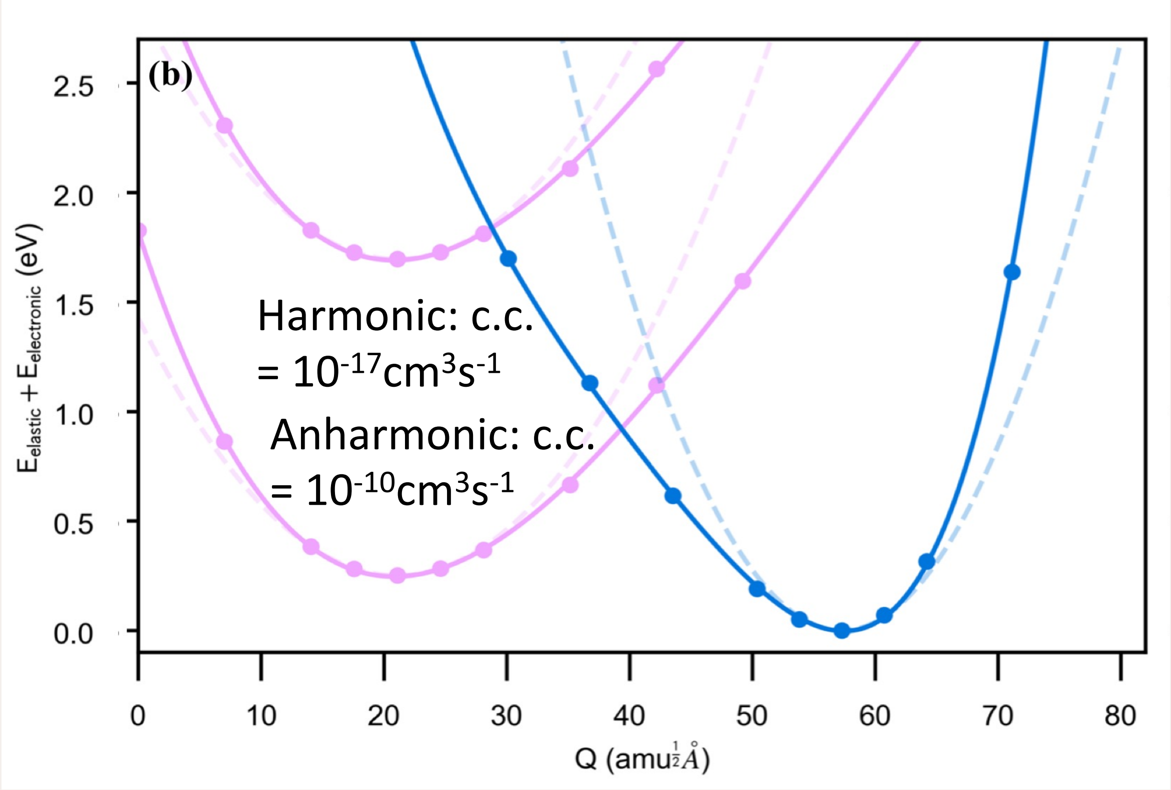
- The electron capture coefficient is $10^{-10}cm^3s^{-1}$ (compare to the radiative c.c. of $10^{-13}cm^3s^{-1}$)
- There is large charge-phonon coupling: S_{HR}=350 (compare to S_{HR}= 75 for the DX-center in GaAs)

Whalley et al, “Giant Huang-Rhys factor for electron capture…”, under review with JACS

< Lattice Anharmonicity in PV materials>

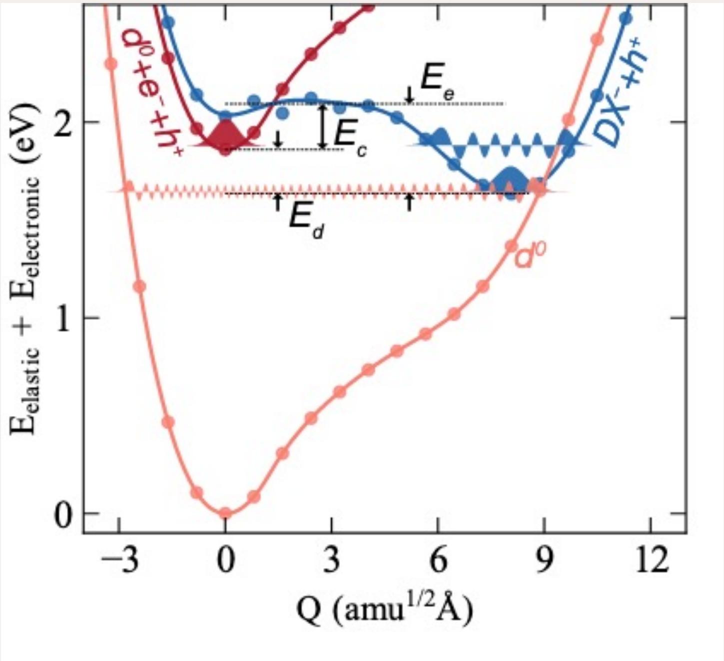
Assuming that the potential energy surface is harmonic can lead to carrier capture coefficients that are incorrect by many orders of magnitude. This has been demonstrated for $CH_3NH_3PbI_3$, CdTe and GaAs.

Iodine interstitial in $CH_3NH_3PbI_3$, under review with JACS



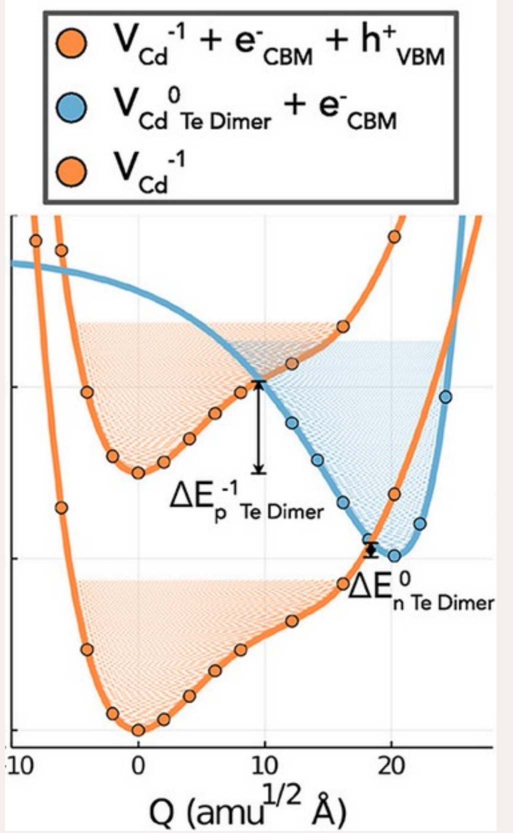
Harmonic: c.c. = $10^{-17} cm^3 s^{-1}$

Anharmonic: c.c. = $10^{-10} cm^3 s^{-1}$



DX centre in GaAs: *Anharmonic Lattice Relaxation during Non-radiative Carrier Capture*, PRB 2019

CdTe: Kavanagh, Walsh, Scanlon
Rapid Recombination by Cadmium Vacancies in CdTe
ACS Energy Letters 2021



< Summary >

- “Killer defects” act as sites for **non-radiative carrier capture** and recombination, often reducing optoelectronic performance
- To calculate the carrier capture or recombination rate *ab-initio* we need to consider **electronic processes *and* lattice relaxation**
- Large lattice relaxation leads to a **giant Huang-Rhys factor** for electron capture by the iodine interstitial in $CH_3NH_3PbI_3$
- **Lattice anharmonicity** is an important factor for carrier capture in a range of photovoltaic materials: $CH_3NH_3PbI_3$, CdTe and GaAs

< Follow-on questions >

1. **Could cation engineering reduce the rate of carrier capture in hybrid perovskites?** Lattice relaxation is associated with octahedral tilting, which is suppressed in mixed cation materials. What affect does this have on carrier capture processes?
2. **Is lattice relaxation linked to degradation in hybrid perovskites?** Hybrid perovskites degrade under laser. Could the combination of large lattice relaxation and ultra-low thermal conductivity lead to local lattice heating and thermal degradation?

Thank-you

Slides available at my website

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Puck van Gerwen (EPFL)
Sunghyun Kim (Samsung)
Rachel Crespo Otero (Queen Marys)

Plug: Do you need get an effective mass from your DFT bandstructure?
→ Try using effmass!
github.com/lucydot/effmass