(semi-)quantitative modelling of point defects in semiconductors

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Central problem

Property, *p*, of a material is some function of defect concentration, [*X*] (e.g. conductivity)

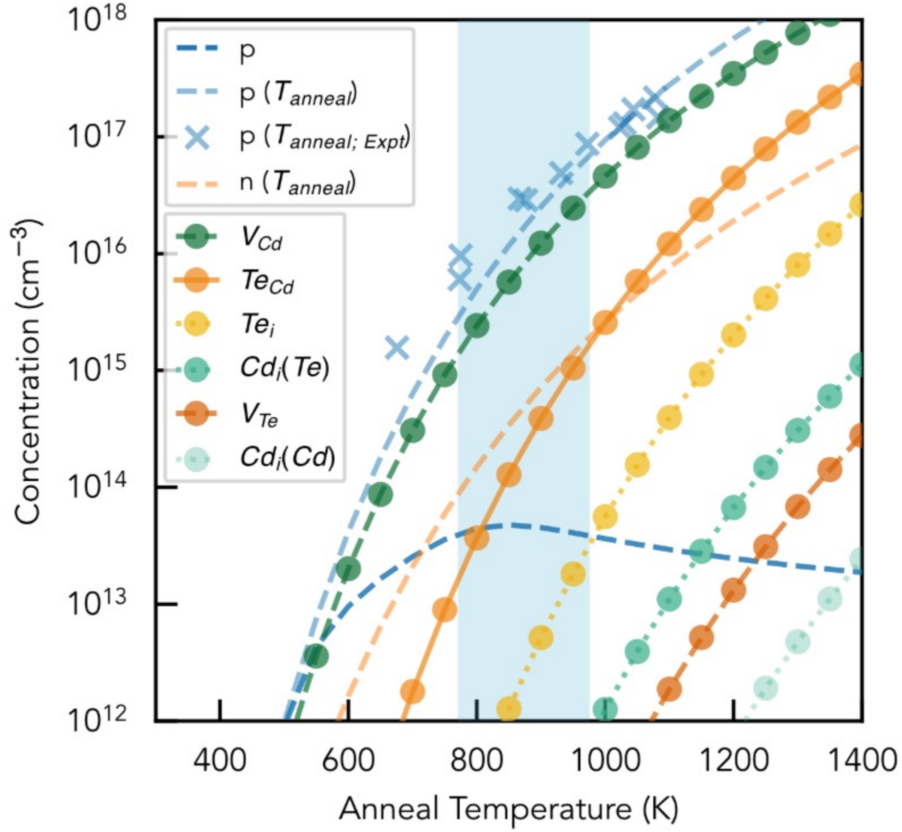
$$p = f([X])$$

Defect concentration is related to the formation energy, E_f, by a Boltzmann relationship

$$[X] = N_X g \exp\left(\frac{-E_\mathrm{f}^X}{\mathrm{k}T}\right)$$

The promise of solution

We can, in principle, get very accurate predictions of defect and carrier concentrations if we carry out careful point defect studies. These values can then be used to parameterise models.



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So how to calculate the formation energy?

I spent an embarrassingly long time getting my head around this equation as a new PhD student

$$\Delta E_{\mathrm{f}}^{X^q} = E^{X^q} - E^{\mathrm{bulk}} - \sum_i n_i \mu_i + qE_{\mathrm{F}}$$

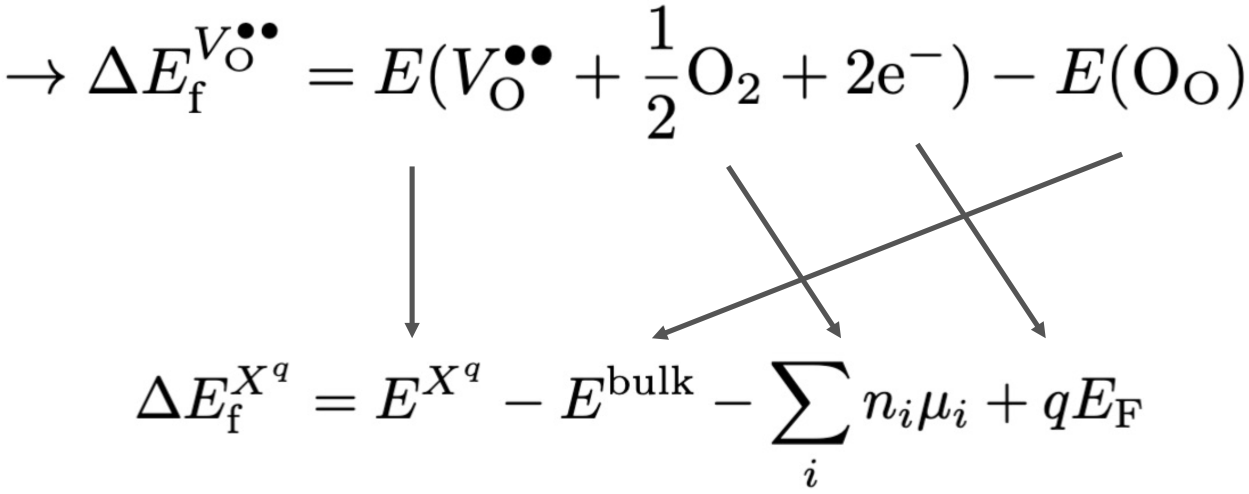
Before realising it was as simple as

$$\Delta E_{\mathrm{f}} = E(\mathrm{Products}) - E(\mathrm{Reactants})$$

So how to calculate the formation energy?

$$\mathrm{O_O} \rightleftharpoons V_{\mathrm{O}}^{\bullet\bullet} + \frac{1}{2}\mathrm{O_2} + 2\mathrm{e}^-$$

$$\Delta E_{\mathrm{f}} = E(\mathrm{Products}) - E(\mathrm{Reactants})$$



$$\rightarrow \Delta E_{\mathrm{f}}^{V_{\mathrm{O}}^{\bullet\bullet}} = E(V_{\mathrm{O}}^{\bullet\bullet} + \frac{1}{2}\mathrm{O_2} + 2\mathrm{e}^-) - E(\mathrm{O_O})$$

$$\Delta E_{\mathrm{f}}^{X^q} = E^{X^q} - E^{\mathrm{bulk}} - \sum_i n_i\mu_i + qE_{\mathrm{F}}$$

Quantifying defects

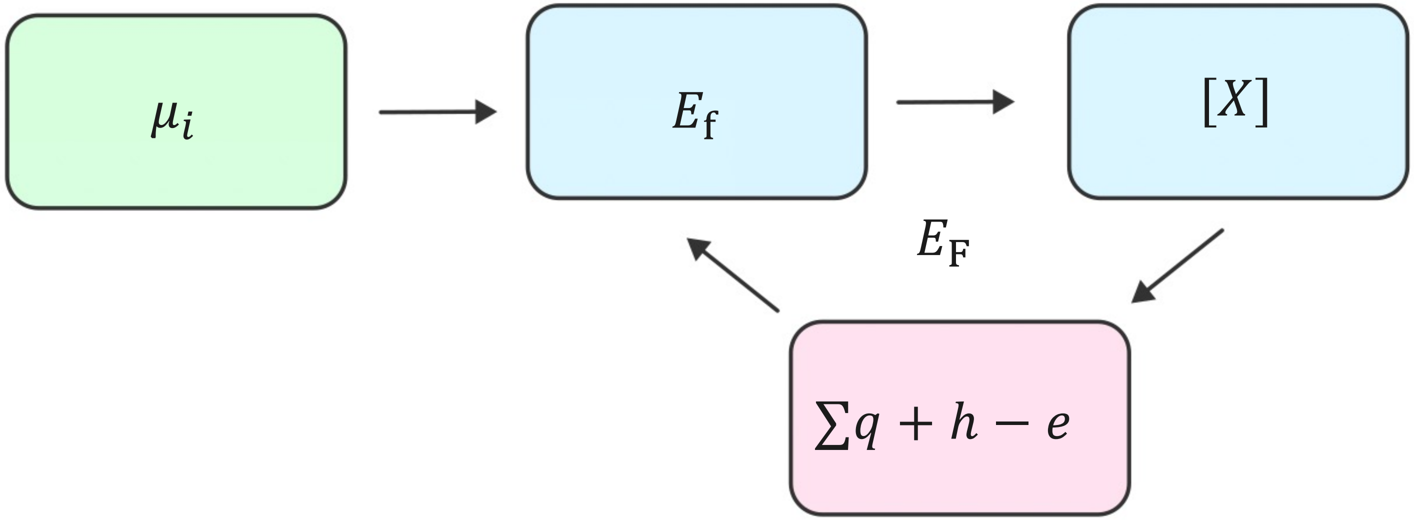
Direct from DFT

$$\Delta E_{\mathrm{f}}^{X^q} = E^{X^q} - E^{\mathrm{bulk}} - \sum_i n_i \mu_i + qE_{\mathrm{F}}$$???

Bounded by stability

Quantifying defects

Solving for the defect formation energies, and therefore concentrations is a coupled problem



μ_i

E_f

$[X]$

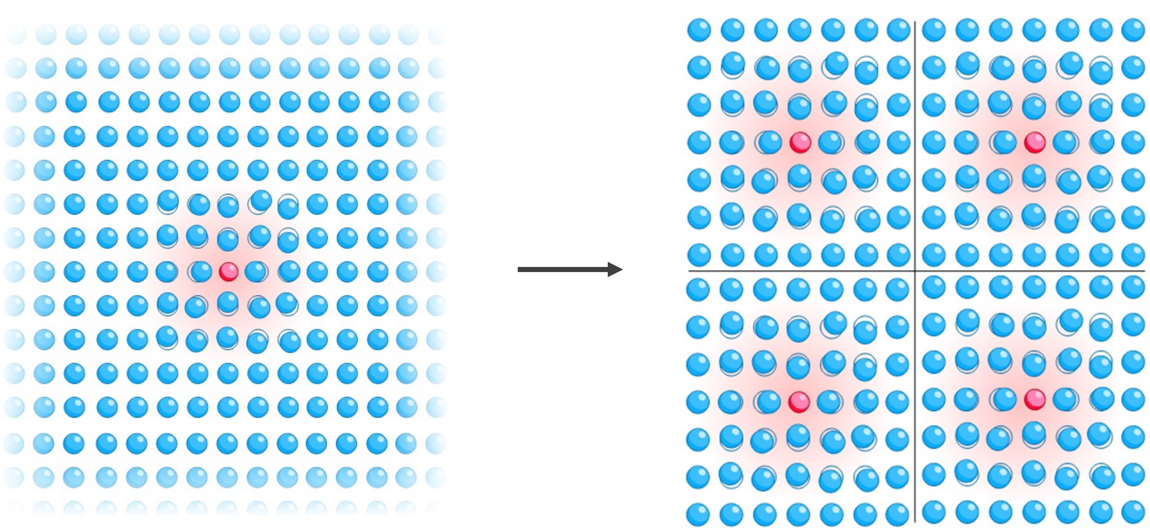
E_F

$\sum q + h - e$

"Getting one defect wrong" can mean getting the full thermodynamics wrong!

How is this done in practice?

The supercell method: representing the infinite bulk is too hard. What is easier is “tricking” your software into thinking you have an infinite bulk.



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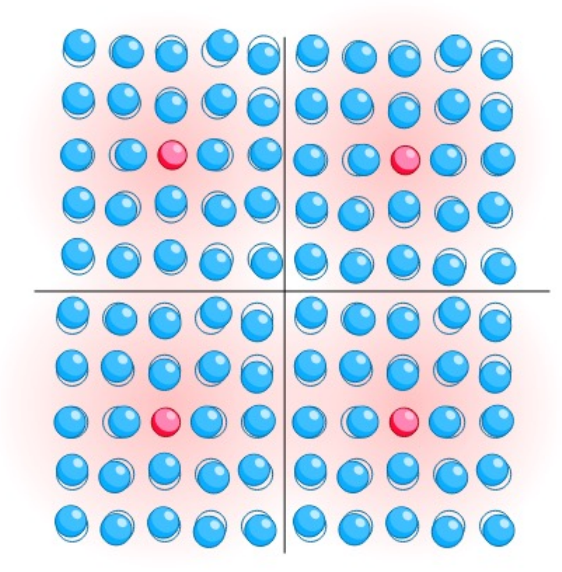
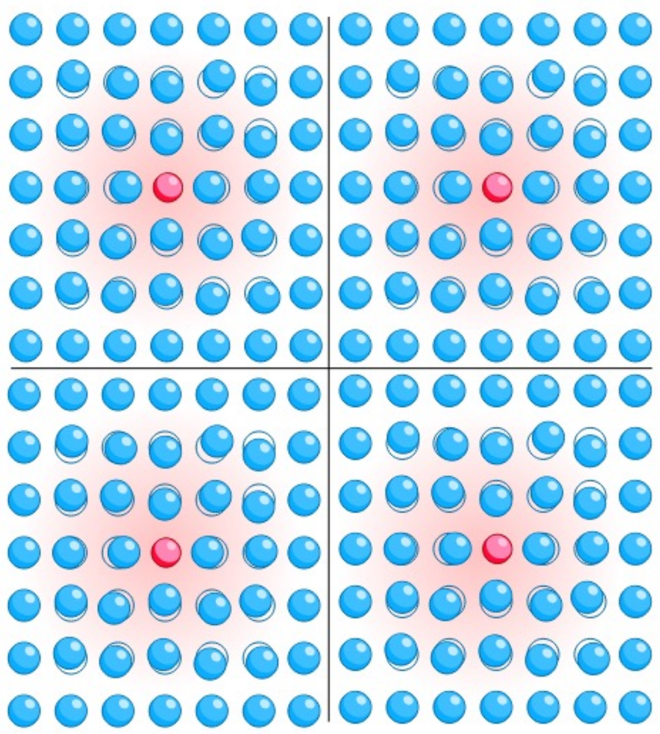
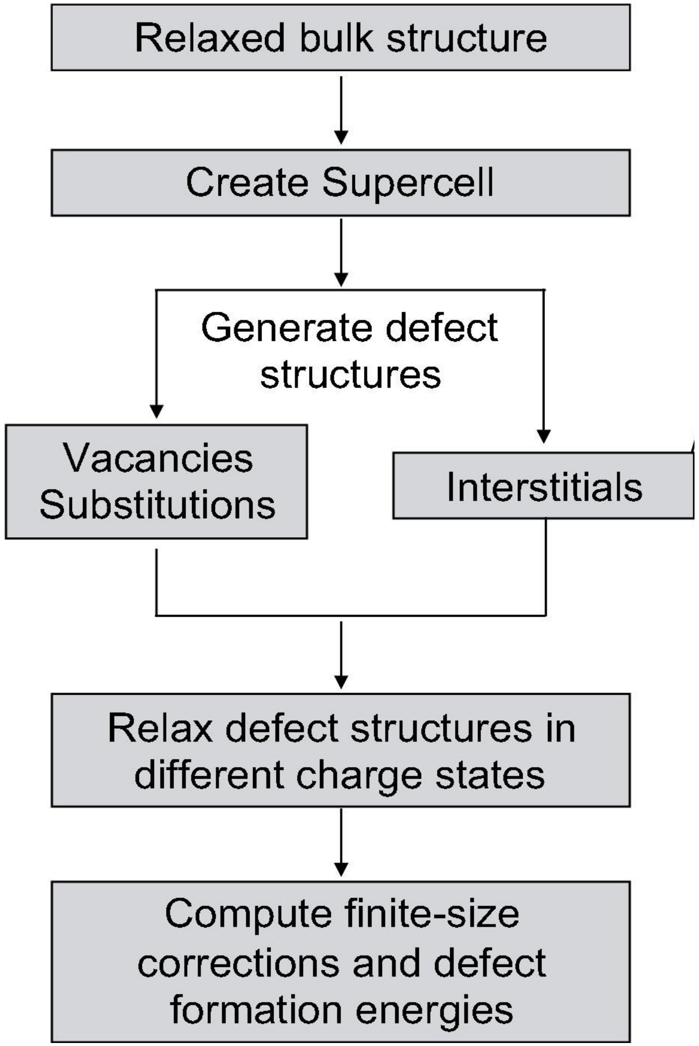
How is this done in practice?

Of course, there is a cost-accuracy trade-off in terms of supercell size





The workflow



Relaxed bulk structure

Create Supercell

Generate defect structures

Vacancies Substitutions

Interstitials

Relax defect structures in different charge states

Compute finite-size corrections and defect formation energies

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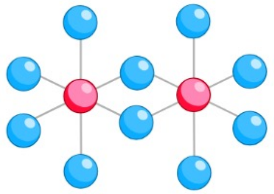
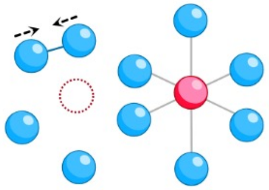
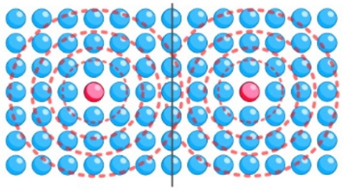
A very “bitty” procedure



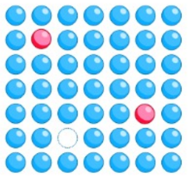
Host Compound
- Crystal structure
- Electronic structure
- Thermodynamic stability



Defect Charge and Structure
- Plausible charge states
- Structure searching
- Metastability



Formation Energies
- Periodic image interactions
- Eigenvalue perturbation
- Shallow vs deep states



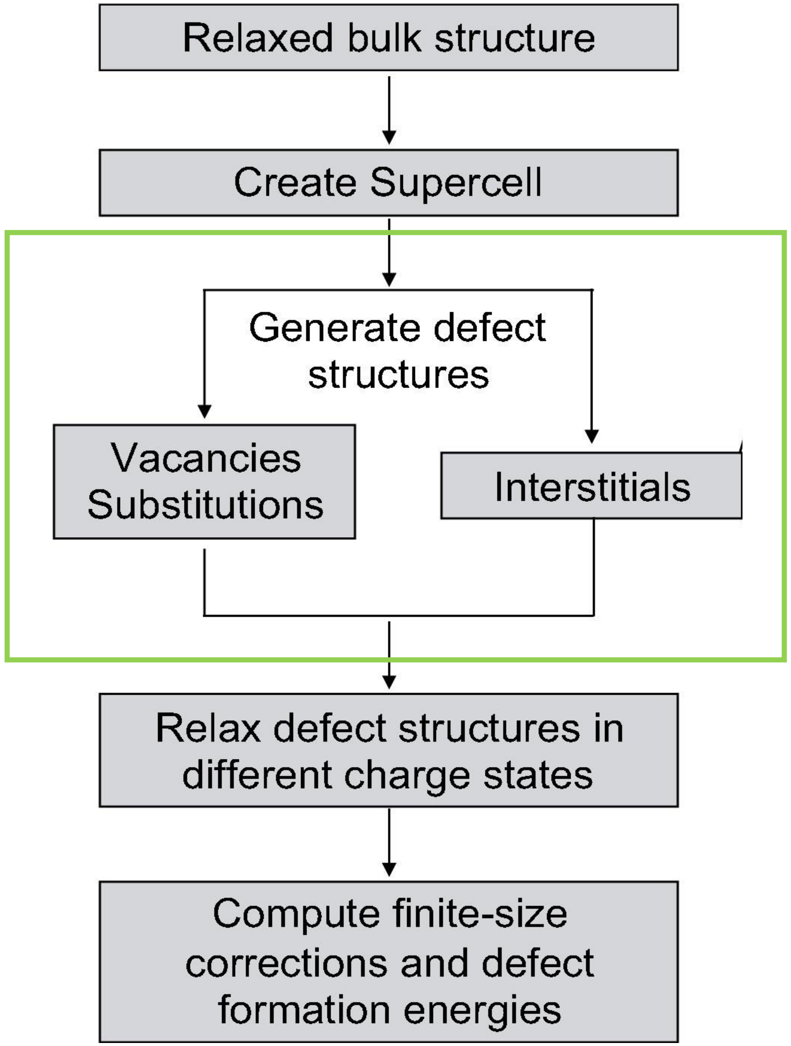
Defect Populations
- Degeneracy factors
- Temperature effects
- Complexes, annihilation...

A computational approach that can do all that is not easy to find

Abridged "Jacob's ladder"

- Post DFT
- Hybrid DFT – "not too expensive", well-implemented, Koopman's compliant(ish)
- MetaGGA
- GGA

The workflow



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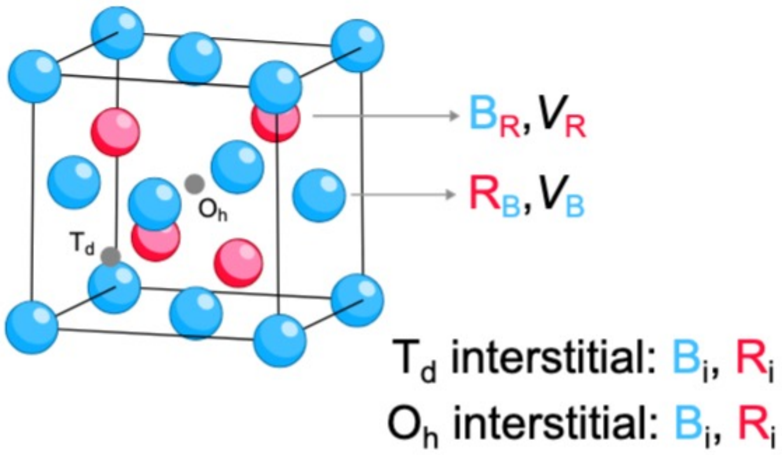
Enumerating defects

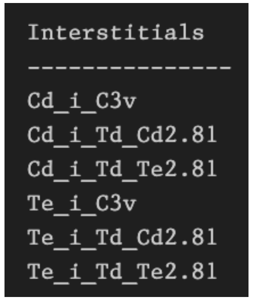
If we can’t miss a defect, why don’t we just calculate the formation energies of all the defects?

- Vacancies generated at every site in the host, and should be able to reduce significantly by symmetry
- substitutions, similarly, generate all symmetrically distinct atoms swaps
- Interstitials… shove atoms in the gaps and hope for the best?

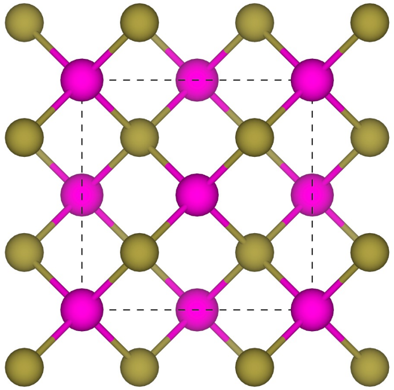


Interstitials

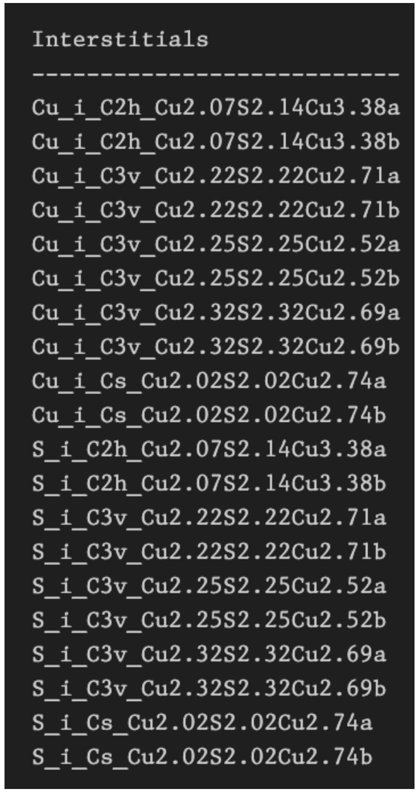
CdTe



```
Interstitials
---------------
Cd_i_C3v
Cd_i_Td_Cd2.81
Cd_i_Td_Te2.81
Te_i_C3v
Te_i_Td_Cd2.81
Te_i_Td_Te2.81
```



CuS



```
Interstitials
---------------------------
Cu_i_C2h_Cu2.07S2.14Cu3.38a
Cu_i_C2h_Cu2.07S2.14Cu3.38b
Cu_i_C3v_Cu2.22S2.22Cu2.71a
Cu_i_C3v_Cu2.22S2.22Cu2.71b
Cu_i_C3v_Cu2.25S2.25Cu2.52a
Cu_i_C3v_Cu2.25S2.25Cu2.52b
Cu_i_C3v_Cu2.32S2.32Cu2.69a
Cu_i_C3v_Cu2.32S2.32Cu2.69b
Cu_i_Cs_Cu2.02S2.02Cu2.74a
Cu_i_Cs_Cu2.02S2.02Cu2.74b
S_i_C2h_Cu2.07S2.14Cu3.38a
S_i_C2h_Cu2.07S2.14Cu3.38b
S_i_C3v_Cu2.22S2.22Cu2.71a
S_i_C3v_Cu2.22S2.22Cu2.71b
S_i_C3v_Cu2.25S2.25Cu2.52a
S_i_C3v_Cu2.25S2.25Cu2.52b
S_i_C3v_Cu2.32S2.32Cu2.69a
S_i_C3v_Cu2.32S2.32Cu2.69b
S_i_Cs_Cu2.02S2.02Cu2.74a
S_i_Cs_Cu2.02S2.02Cu2.74b
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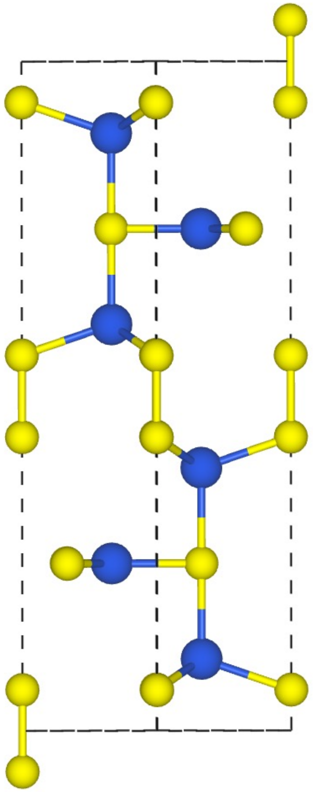
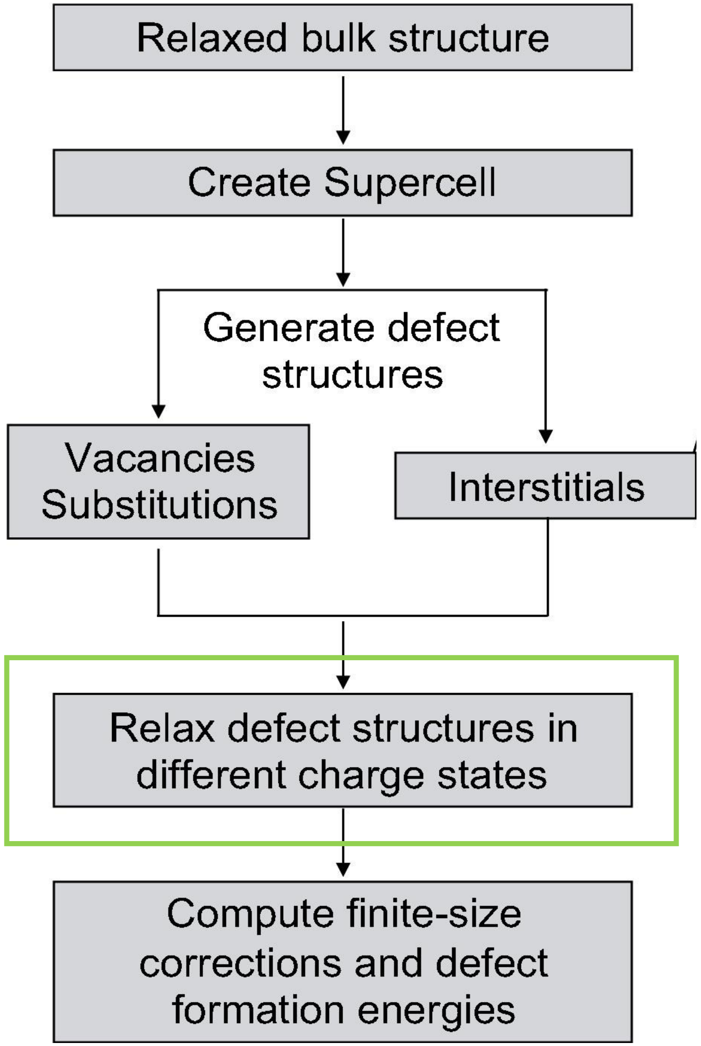


The workflow



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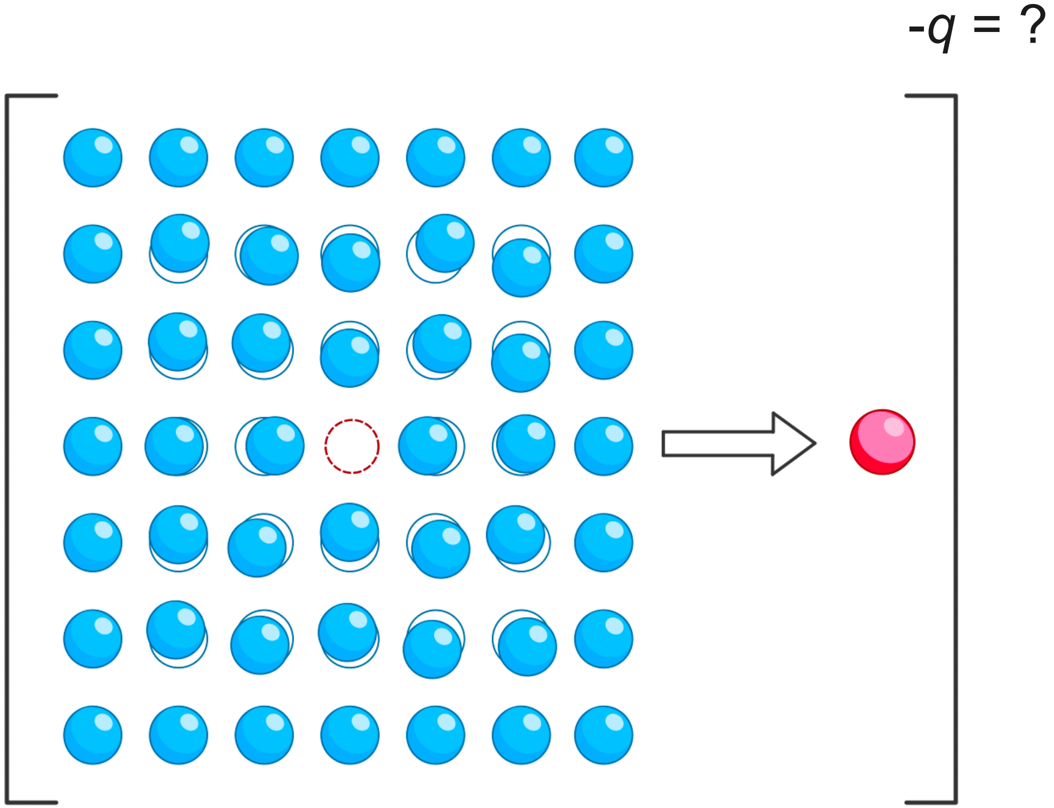
Enumerating charge states



Challenges in defect definition

- A false positive is a defect species with charge q that was found to be unstable/energetically irrelevant
- A false negative is a defect species at site q that was not included in the calculations that is energetically relevant

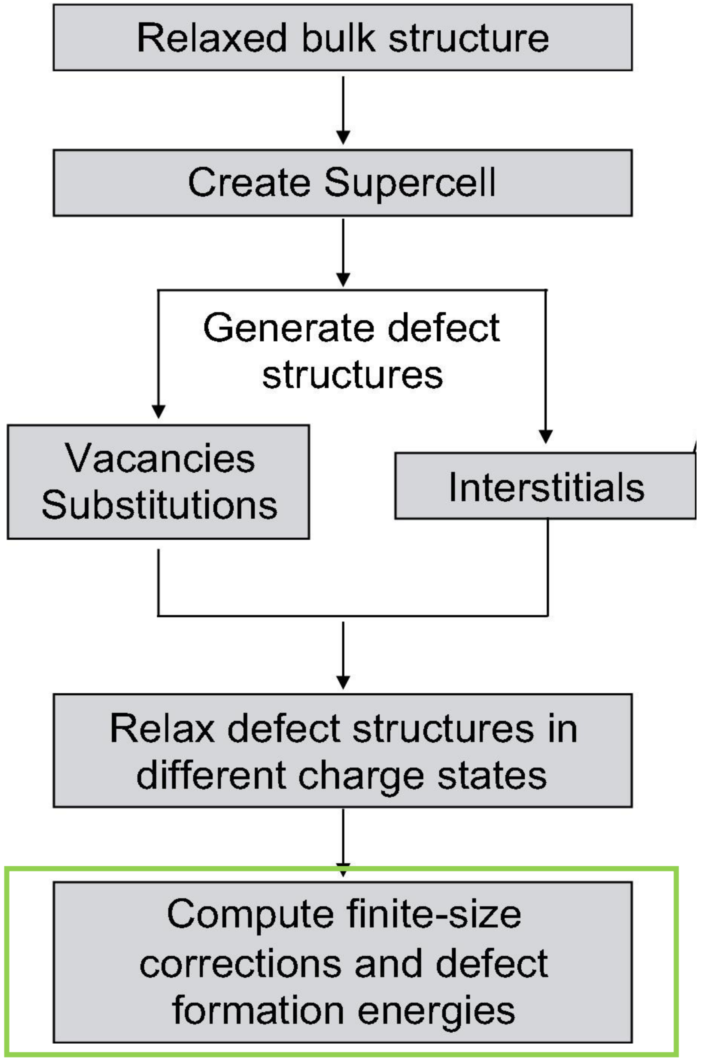
What is the cost of a false positive?

- “wasted” computed

What is the cost of a false negative?

- “missing piece” in the defect thermodynamics

The workflow



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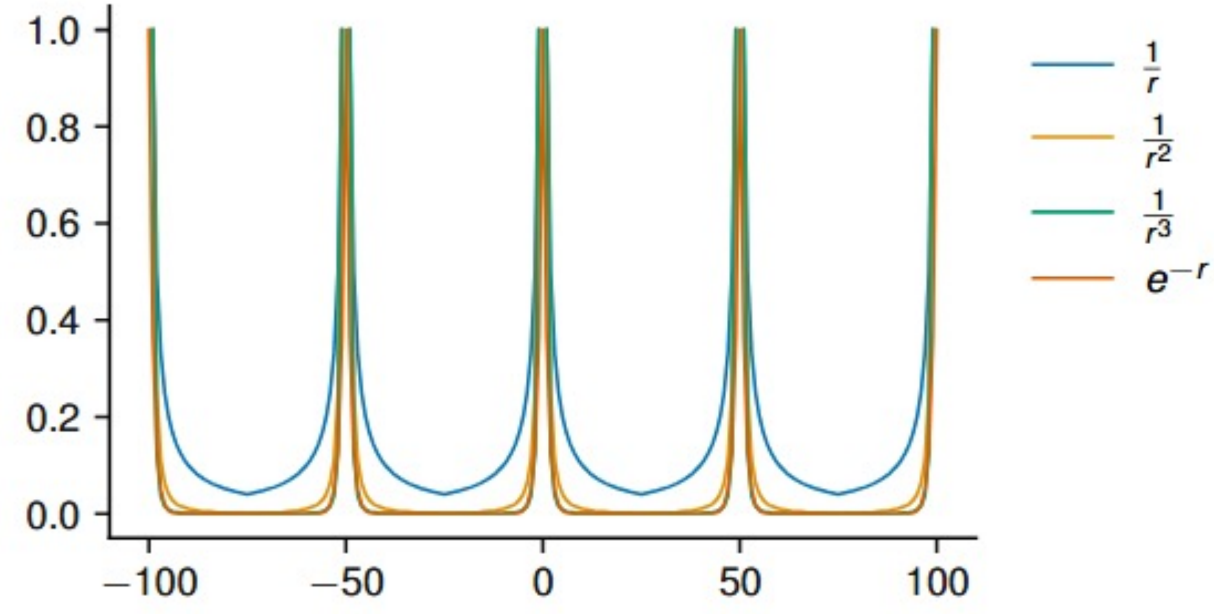
Correcting for the inherent issues with the supercell method

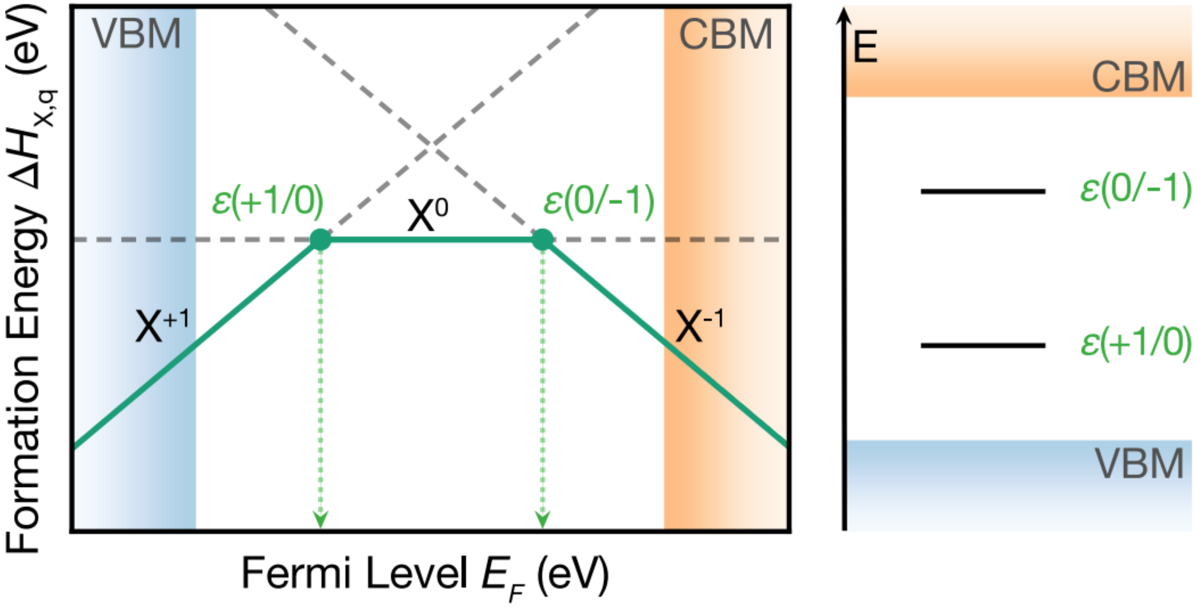
Most periodic image interactions decay quickly, except for the electrostatic interaction which needs correcting for



Putting it all together

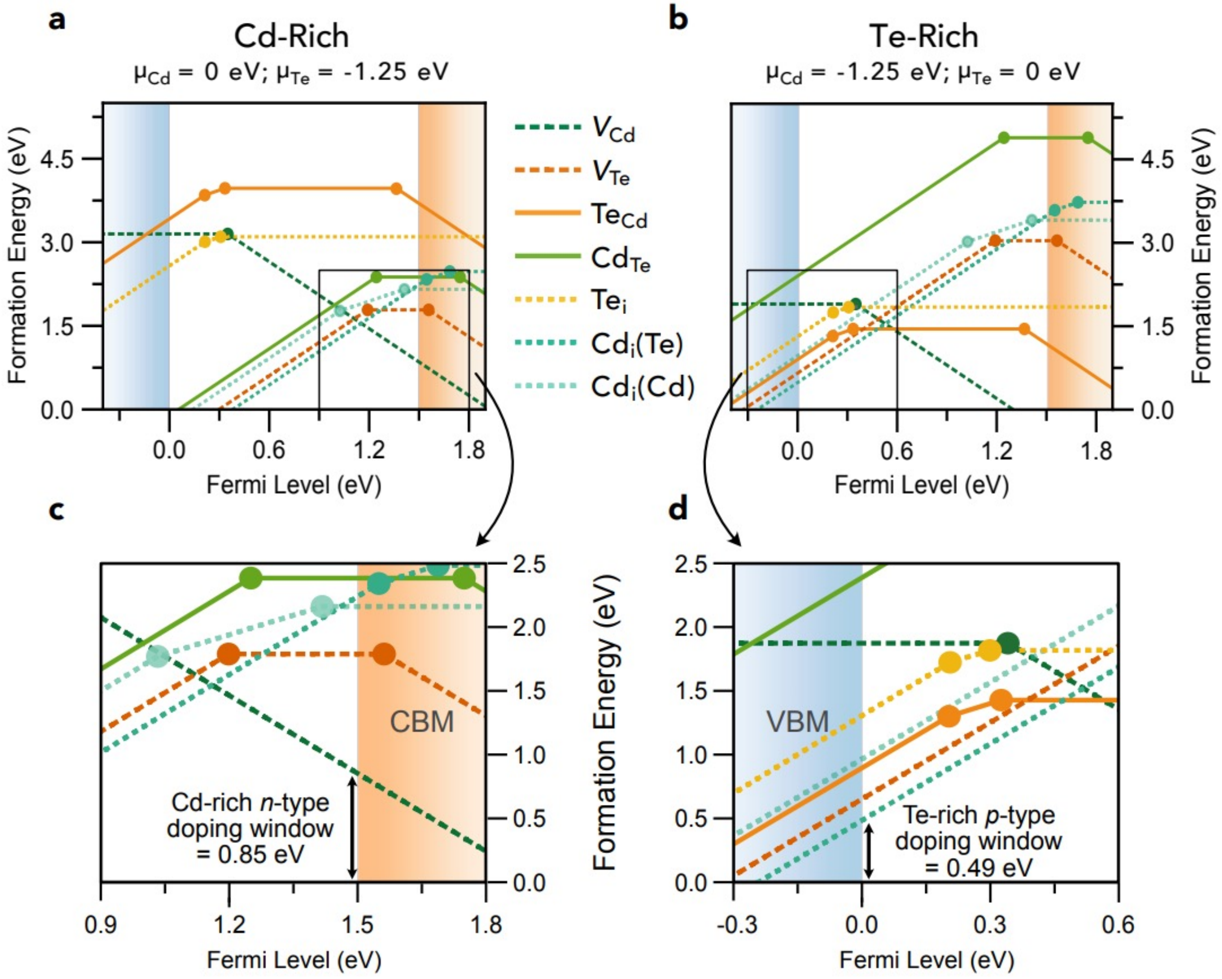
The transition level diagram is a popular way to summarise the defect formation energy set

$$\underline{\Delta E_{\mathrm{f}}^{X^q}} = \overline{E^{X^q} - E^{\mathrm{bulk}} - \sum n_i \mu_i} + \underline{qE_{\mathrm{F}}}$$



3d-materials-lab.gitbook.io/3dmaterialslab-tutorials/defects/interpreting-defect-and-energy-level-diagrams

Putting it all together



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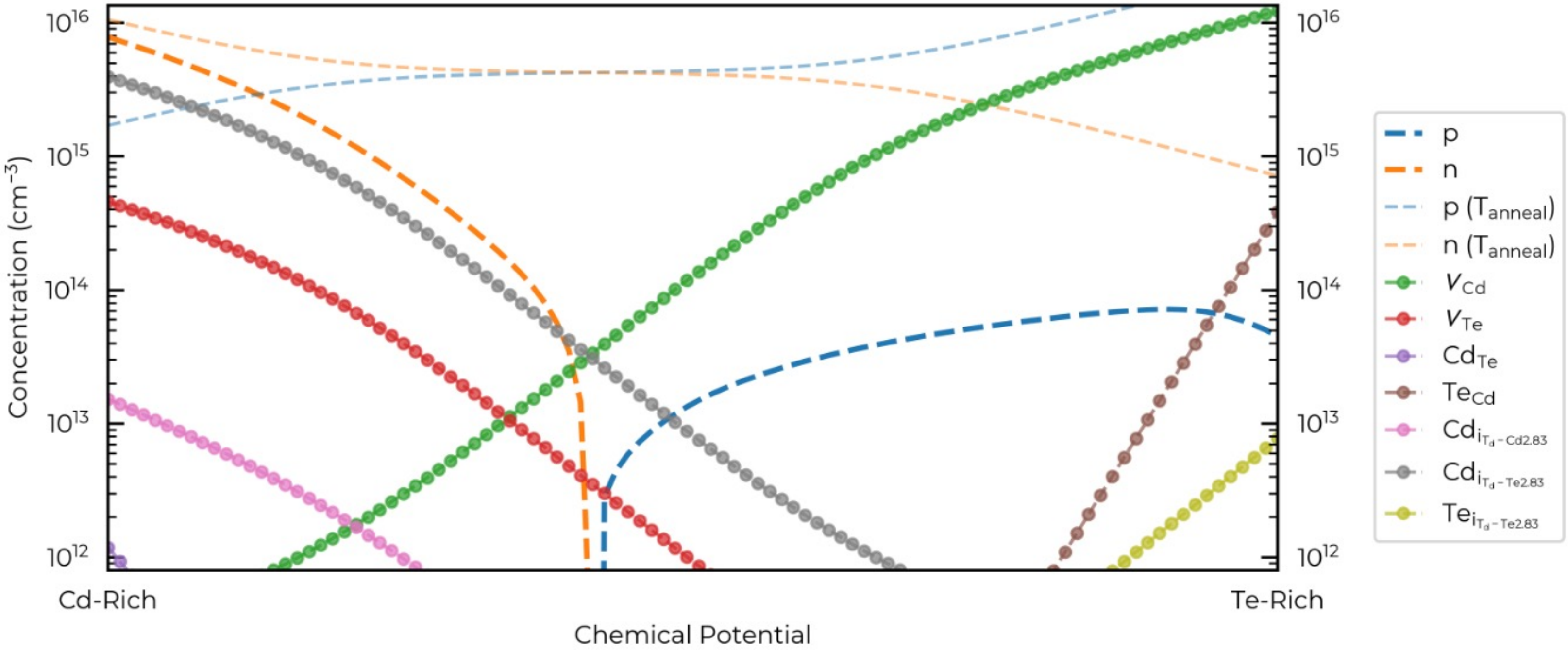
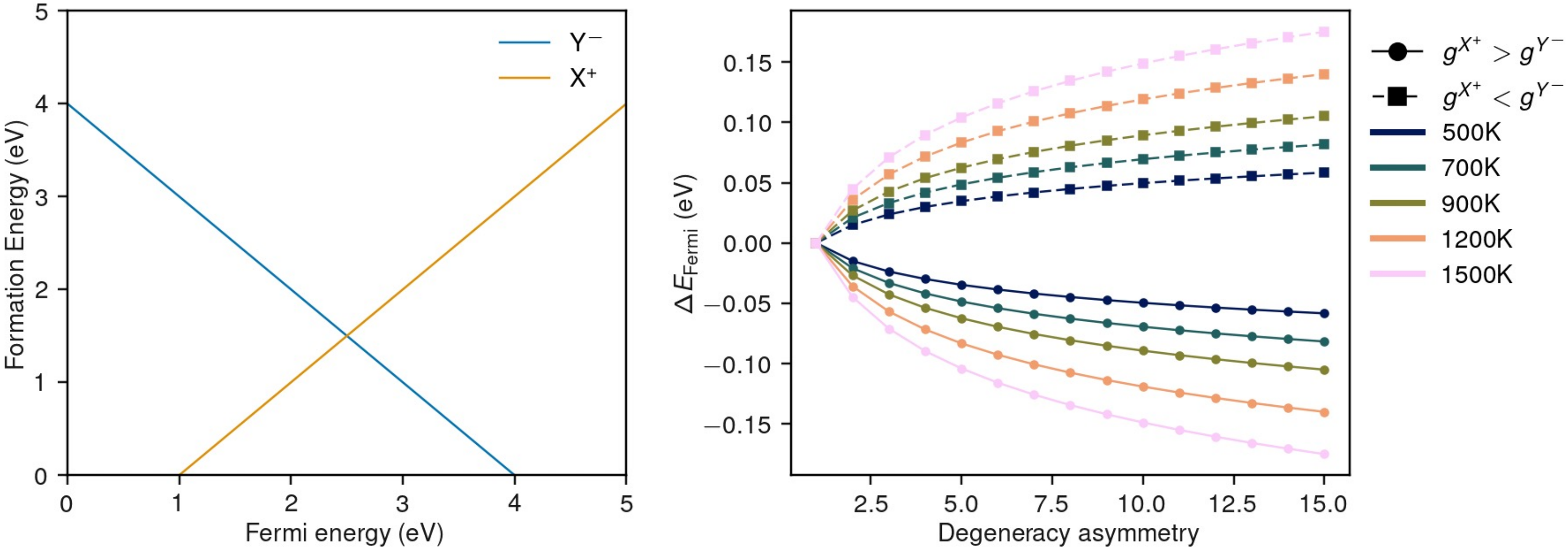
Putting it all together, defect concentrations

$$[X] = N_X g \exp\left(\frac{-E_\mathrm{f}^X}{\mathrm{k}T}\right)$$



Dangers of ignoring degeneracy

$$[X] = N_X g \exp\left(\frac{-E_{\mathrm{f}}^{X}}{\mathrm{k}T}\right)$$



Further reading

Imperfections are not 0 K: free energy of point defects in crystals

Chem. Soc. Rev., 2023, 52, 5812-5826

Quantitative Modeling of Point Defects in β-Ga_2O_3 Combining Hybrid Functional Energetics with Semiconductor and Processes Thermodynamics

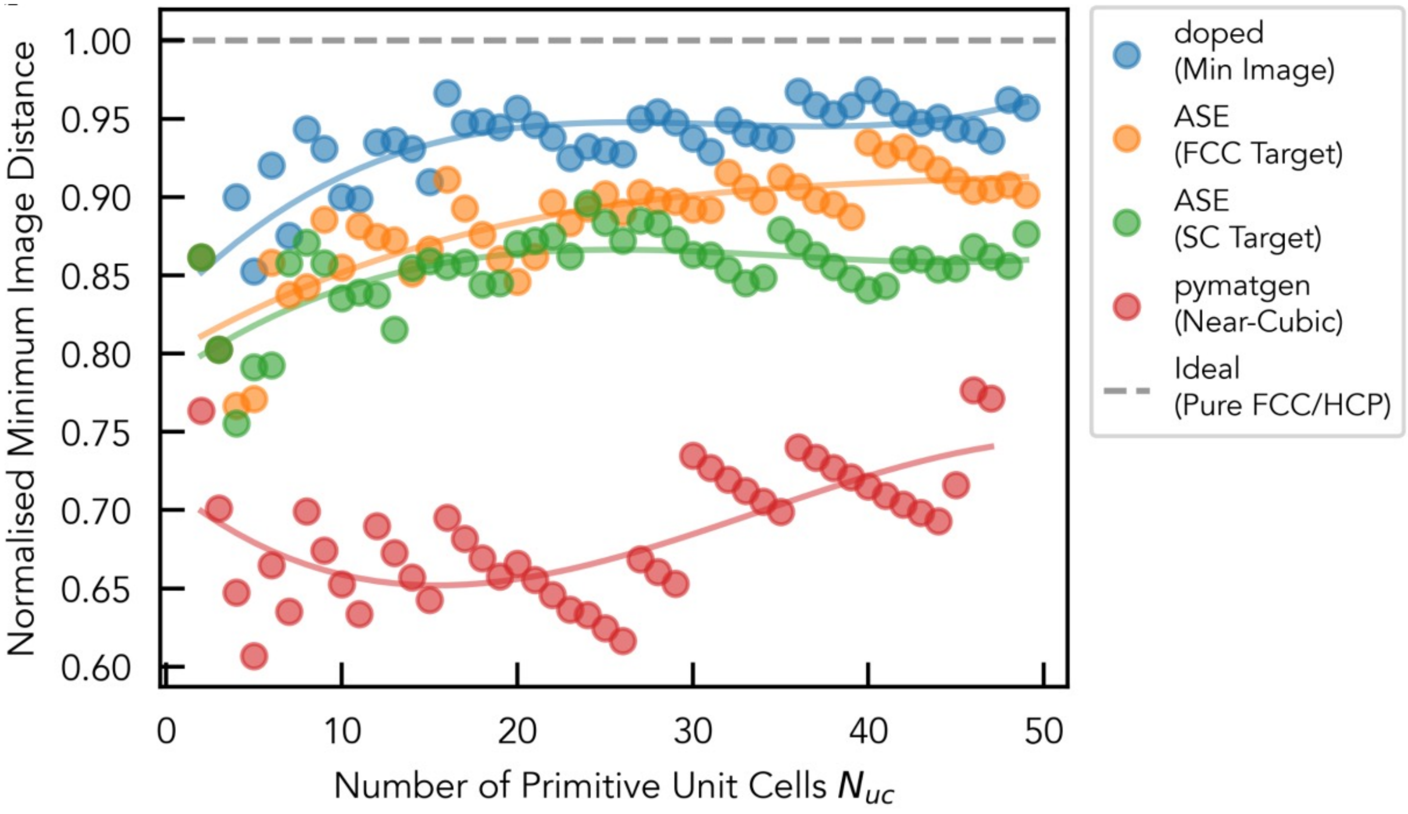
https://doi.org/10.48550/arXiv.2501.17373

Closing thoughts

- Extending this formalism helps us approach quantitative accuracy
- But the kinds orders of magnitude changes we get from adding a more complete description of the energetics are comparable to the kinds of shifts we are likely to get from errors
- The field needs consistency and better reporting to help improving the utility of the predictions made by such defect calculations.

Discussion slides

The supercell method



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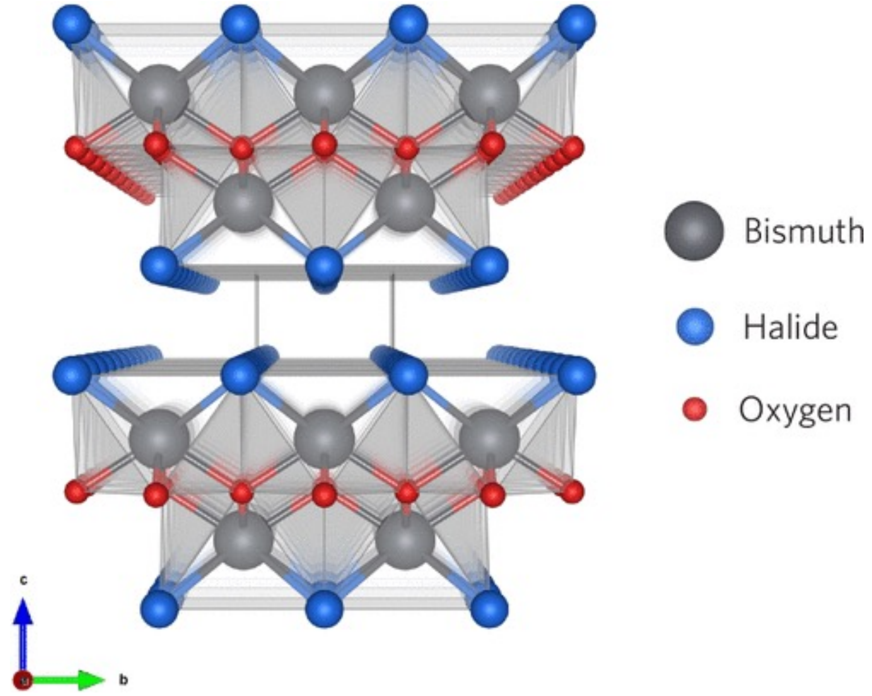
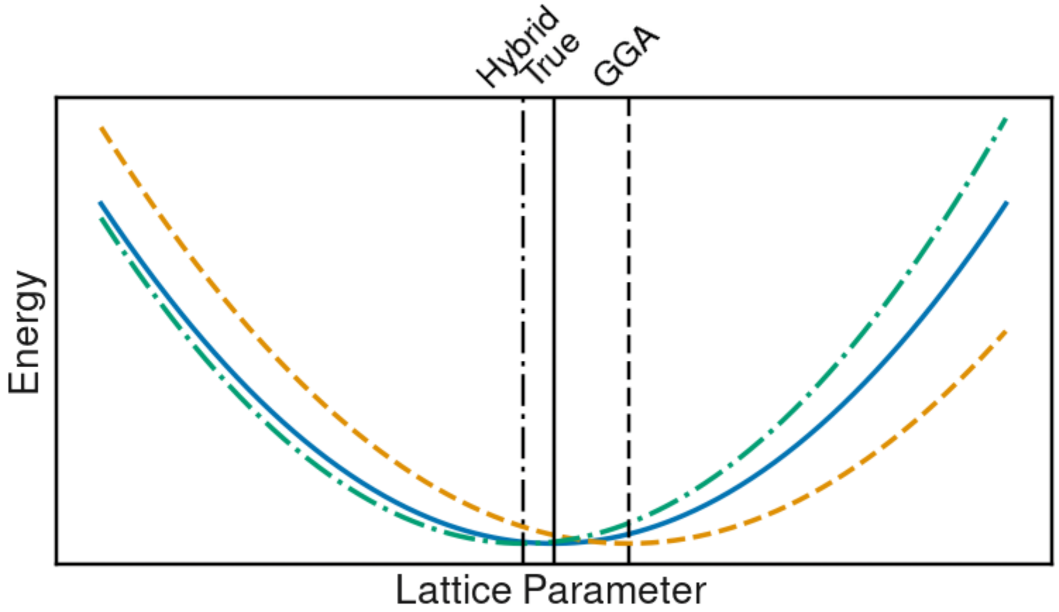


The dangers of the “functional shuffle”



The importance of Koopmans' compliance

The "tricky" defects all concern electron removal/addition

Koopman's compliance tells us when we are modelling that accurately

$$\Delta_{\mathrm{KC}}^{(\mathrm{gap})} = |(\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}) - (\mathrm{IP} - \mathrm{EA})| = \left| E_{\mathrm{gap}}^{\mathrm{KS}} - E_{\mathrm{gap}}^{\mathrm{fund}} \right|$$

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The importance of Koopmans' compliance

$$\Delta_{\mathrm{KC}}^{(\mathrm{gap})} = \left|(\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}) - (\mathrm{IP} - \mathrm{EA})\right| = \left|E_{\mathrm{gap}}^{\mathrm{KS}} - E_{\mathrm{gap}}^{\mathrm{fund}}\right|$$