# Density Functional Theory and Electronic Structure Calculations

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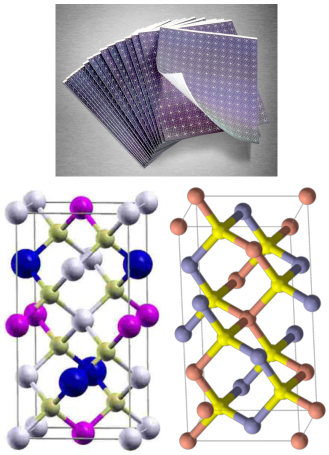
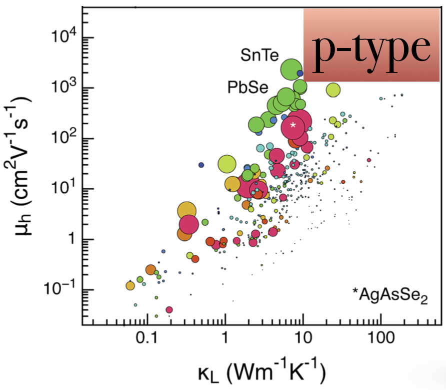
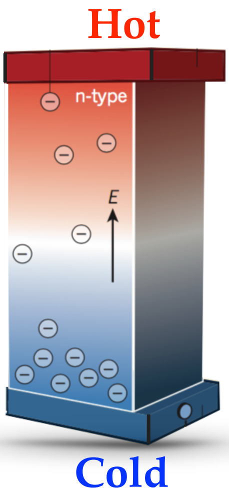
**Today's goal is to introduce how density functional theory can be used to predict the bulk and defect properties of chalcogenides.**







**photovoltaics**

**thermoelectrics**

what properties are we interested in?

what can be reliably calculated?
what needs more scrutiny?

ground vs. excited state?

equilibrium vs. non-equilibrium?

## We want to be able to predict the properties of chalcogenides (and all materials) accurately and effectively on a computer.

### Crystal structure

- Structure and total energies of compounds
- Lattice constants (at T = 0 K)
- Other properties derived from crystal structure

### Thermodynamic Stability

- Phase stabilities
- Composition space vs. chemical potential space

### Band Structure

- Dispersion spectrum for a compound
- Band gap, quasi-particle energies, optical properties
- Transport: electron and hole effective masses

### Defects & Doping

- Calculation of defect formation energies
- Translate to defect concentrations, carrier concentrations, dopability

# The Schrodinger equation describes all properties of all materials.

energy → wave function

$$H\psi(r_1,\dots,r_n) = E\psi(r_1,\dots,r_n)$$

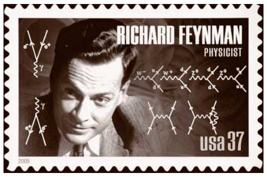
$$\hat{H} = \boxed{-\frac{1}{2}\nabla^2 - \sum\frac{Z_n}{r_{e-n}}} + \boxed{\sum\frac{1}{r_{e-e}}}$$

**Non-interacting part**

**Contains an Electron-Electron Distance!**

- The wave function encodes all information about a system of particles (here, electrons and nuclei)
- Many approximations already: non-relativistic, time-independent, Born-Oppenheimer.
- Eigenvalue/eigenfunction problem: wave functions are eigenfunctions and energies are the eigenvalues

> “Where did we get that (equation) from? Nowhere. It is not possible to derive it from anything you know. It came out of the mind of Schrödinger.” - Richard Feynman



# It is not possible to solve exactly the Schrodinger equation except in the simplest systems.

energy → wave function

$$H\psi(r_1,\dots,r_n) = E\psi(r_1,\dots,r_n)$$

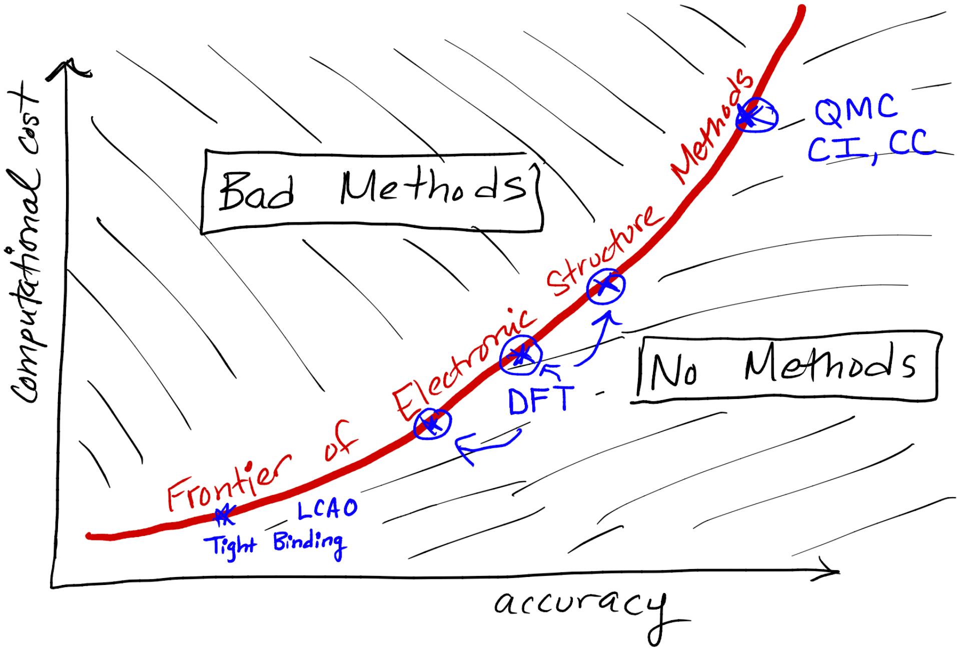
$$\hat{H} = \boxed{-\frac{1}{2}\nabla^2 - \sum\frac{Z_n}{r_{e-n}}} + \boxed{\sum\frac{1}{r_{e-e}}}$$

**Non-interacting part**

**Contains an Electron-Electron Distance!**

- Electron-electron term makes the solution non-separable
- For an n electron system, wave function is a function of 3n variables
- Quickly becomes unmanageable, e.g. storing a wave function on a 2x2x2 real space grid requires storing
  - 1 electron : 8 values
  - 10 electrons : $10^9$ values
  - 100 electrons : $10^{90}$ values
  - 1000 electrons : $10^{900}$ values

# Tradeoffs: Today DFT represents the best available compromise between accuracy and computational efficiency.



inspired by Lucas Wagner, UIUC

# DFT works by mapping the interacting Schrodinger equation onto an effective non-interacting equation.

$$\begin{tikzcd} \hat{V}_{ext} \arrow[r, "\hat{H}|\psi_{GS}\rangle = E_{GS}|\psi_{GS}\rangle"] \arrow[dr, leftrightarrow, "\text{one-to-one}"'] & |\psi_{GS}\rangle \arrow[d, "n_{GS}(\mathbf{r}) = |\psi_{GS}(\mathbf{r})|^2"'] \\ & n_{GS}(\mathbf{r}) \end{tikzcd}$$

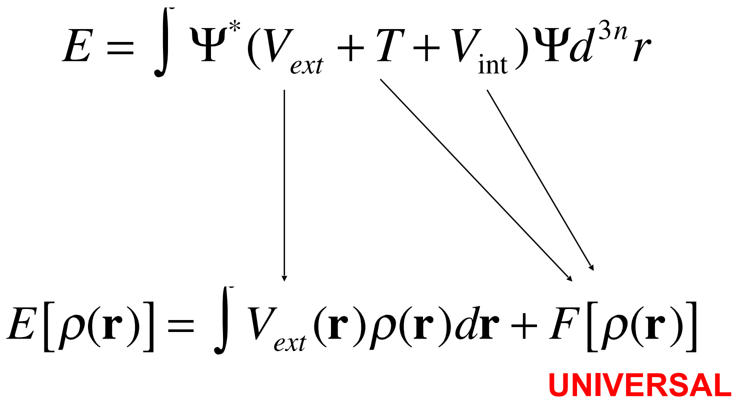
$$E[\rho(\mathbf{r})] = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \underbrace{F[\rho(\mathbf{r})]}_{\text{UNIVERSAL but unknown}}$$

Hohenberg and Kohn, 1964

- Founded on the two Hohenberg-Kohn theorems
- Hohenberg-Kohn I: one to one mapping between the external potential of the nuclei, ground state wave function, and ground state charge density
- Hohenberg-Kohn II: there exists a universal functional of the density F[ρ(r)] such that the ground state energy E is minimized at the true ground state density
- Typically formulated as an Euler-Lagrange system of equations

# The Kohn-Sham approach is most widely used in practice (I).

Comparison to Hartree-Fock:



$$E = \int \Psi^* (V_{ext} + T + V_{\text{int}}) \Psi d^{3n} r$$

$$E[\rho(\mathbf{r})] = \int V_{ext}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + F[\rho(\mathbf{r})]$$

**UNIVERSAL**

- Formulates a expression for the unknown universal functional
- The assumed form defines the exchange-correlation functional (which itself is still unknown)

By inspection:

$$F[\rho(\mathbf{r})] = E_{KE}[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]$$

# The Kohn-Sham approach is most widely used in practice (II).

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

$$\left\{ -\frac{\nabla_1^A}{2} - \left( \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} + V_{XC}[\mathbf{r}_1] \right\} \varphi_i(\mathbf{r}_1) = \varepsilon_i \varphi_i(\mathbf{r}_1)$$

- The total charge density is written as a sum of charge densities of a set of fictitious, orthonormal orbitals
- Giving rise to a set of non-linear equations that can be solved for the orbitals (again, eigenvalue/eigenfunction problem)
- Two common approaches: self-consistency loop and direct diagonalization

# DFT - the Kohn-Sham Equations

real Schrodinger Equation:

$$H\psi(r_1,\dots,r_n) = E\psi(r_1,\dots,r_n)$$

- electron-electron interactions explicitly present
- need to solve an interacting differential equation for a multi-dimensional function
- at least its a linear equation

instead, in Kohn-Sham DFT:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

$$\left\{-\frac{\nabla_1^A}{2} - \left(\sum_{A=1}^{M}\frac{Z_A}{r_{1A}}\right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} + V_{XC}[\mathbf{r}_1]\right\}\varphi_i(\mathbf{r}_1) = \varepsilon_i\varphi_i(\mathbf{r}_1)$$

electron kinetic energy

electron-ion Coulomb interaction

Hartree term. The electron-electron interaction expressed as the Coulomb interaction of a charge density interacting with itself

exchange and correlation. our best guess at fixing everything wrong with the prior terms.

## Since the exact form of the exchange correlation functional not known, it needs to be approximated.

The local density approximation (LDA) assumes that at each point in real space, the exchange -correlation energy at that point is equal to the exchange-correlation energy of a homogeneous electron gas of equivalent density.

The generalized gradient approximations (GGAs) describes the exchange-correlation energy at a point in terms of the total density at that point and its gradient.

Meta-GGAs use even higher order derivatives of the density at a point. e.g. SCAN

Hybrid functionals - incorporation of exact exchange, to eliminate some of the self-interaction in LDA, GGA.

van der Waals functionals - for weak interactions, layered materials, 2D material heterostructures.

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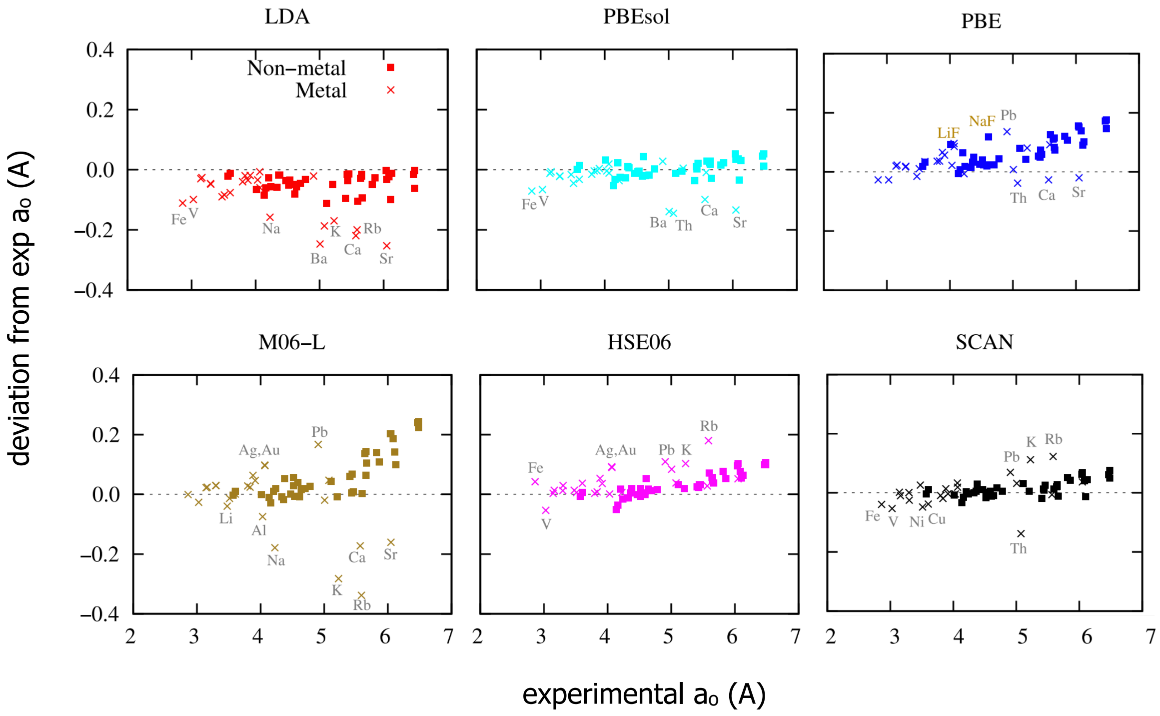
The uncertainty in the accuracy of DFT largely originates from the fact that we always need to select some form for this functional. Once the functional has been selected, we largely have to live with whatever physics comes out of it.

# STRUCTURE AND TOTAL ENERGIES

* can expect pretty good accuracy in the use of DFT for lattice constants, bulk moduli, etc. in comparison to experiment

**DFT is typically very useful for the prediction of ground state properties such as lattice constants, elastic moduli, and equation of state.**



Scheffler et al 2018 New J. Phys. 20 063020

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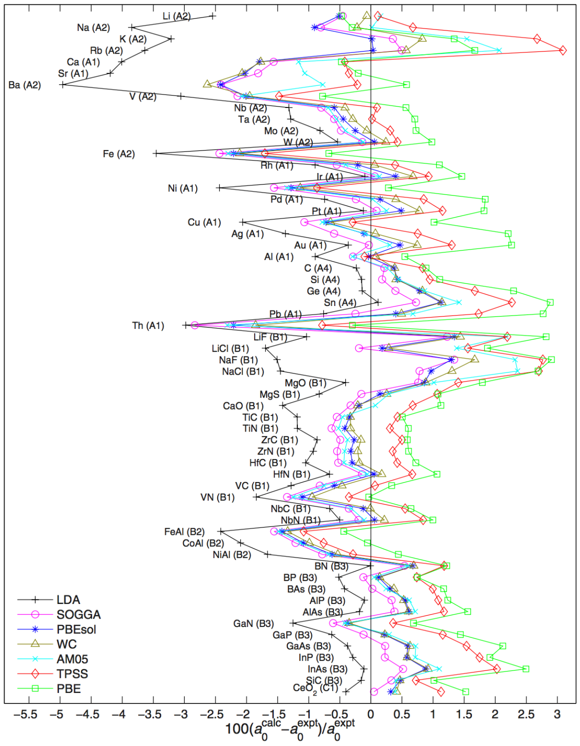

After HAAS, TRAN, AND BLAHA PHYSICAL REVIEW B 79, 085104 2009

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Can you find any systematic trends?

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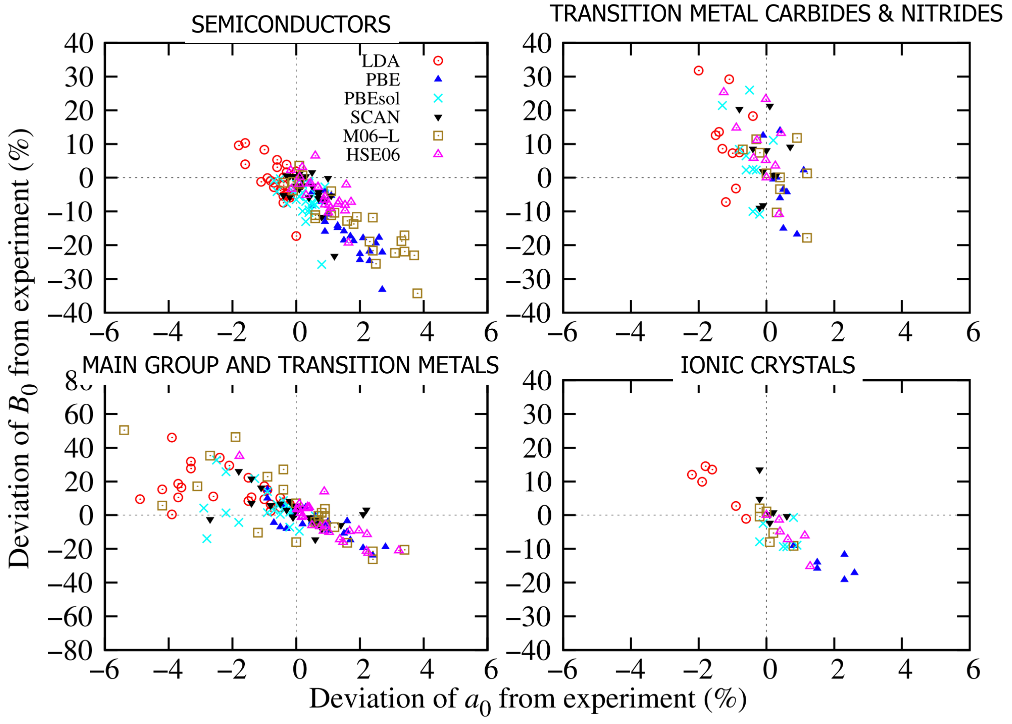
# DFT is typically very useful for the prediction of ground state properties such as lattice constants, elastic moduli, and equation of state.



Scheffler et al 2018 New J. Phys. 20 063020

# PHASE STABILITIES

* these can be trickier, because they rely on comparing total energies of different compounds to each other (rely on cancelation of errors)

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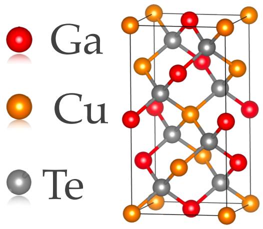
## phase stability, e.g. CuGaTe$_2$



- Thermodynamic equilibrium:

$$\mu_{Cu} + \mu_{Ga} + 2\mu_{Te} = E^{DFT}(\mathrm{CuGaTe_2})$$

- Elemental references for chemical potentials:

$$\mu_{Cu} = \mu^o_{Cu} + \Delta\mu_{Cu} \quad (1a)$$

$$\mu_{Ga} = \mu^o_{Ga} + \Delta\mu_{Ga} \quad (1b)$$

$$\mu_{Te} = \mu^o_{Te} + \Delta\mu_{Te} \quad (1c)$$

reference to solid elemental copper, $\mu^o_{Cu} = E^{DFT}(\mathrm{Cu(s)})$

shift from reference (variable)

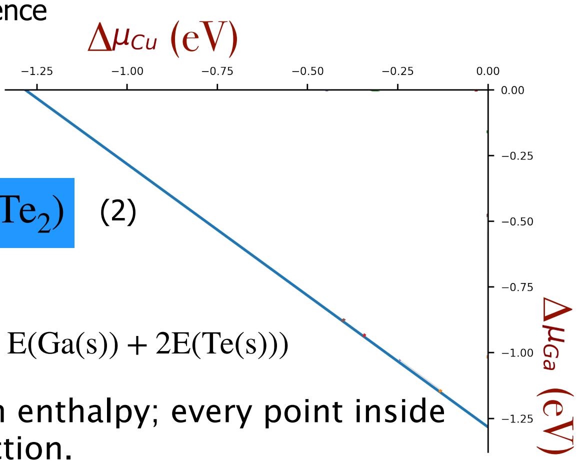
- Combine:

$$\Delta\mu_{Cu} + \Delta\mu_{Ga} + 2\Delta\mu_{Te} = \Delta H_f(\mathrm{CuGaTe_2}) \quad (2)$$

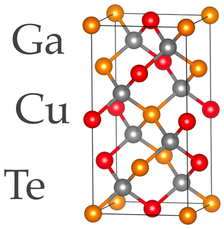
where:

$$\Delta H_f(\mathrm{CuGaTe_2}) = \mathrm{E(CuGaTe_2) - (E(Cu(s)) + E(Ga(s)) + 2E(Te(s)))}$$

- Size of the triangle set by the formation enthalpy; every point inside the triangle satisfies Eq. (2) by construction.

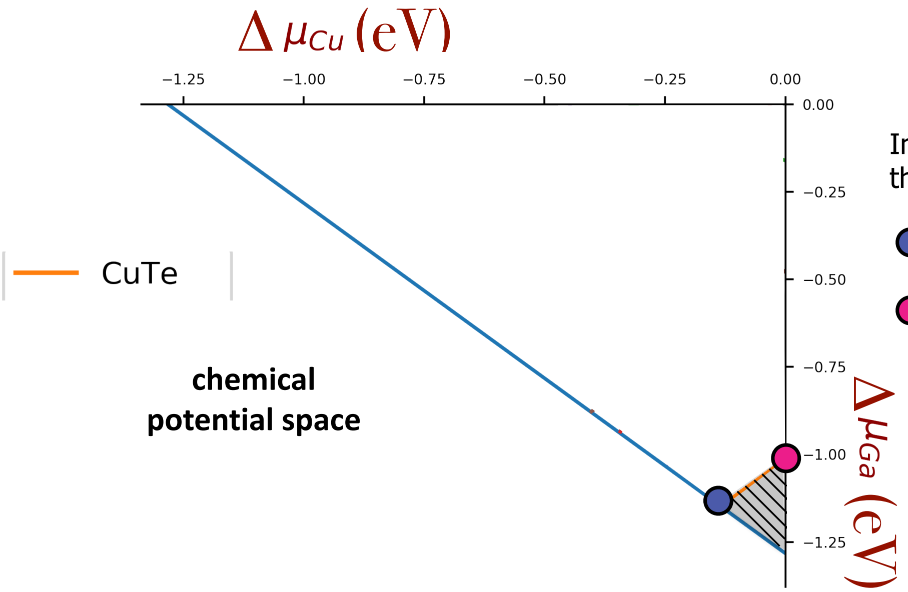


# phase stability, e.g. $CuGaTe_2$



- Need to avoid regions of phase space for which formation of competing compounds is favorable, e.g. for CuTe

e.g. for CuTe, require: $\Delta\mu_{Cu} + \Delta\mu_{Te} \le \Delta H_f(\mathrm{CuTe})$



Invariant points represent three-phase equilibria:

- ● Te, CuTe, $CuGaTe_2$
- ● Cu, CuTe, $CuGaTe_2$

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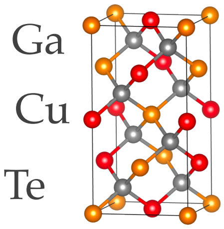
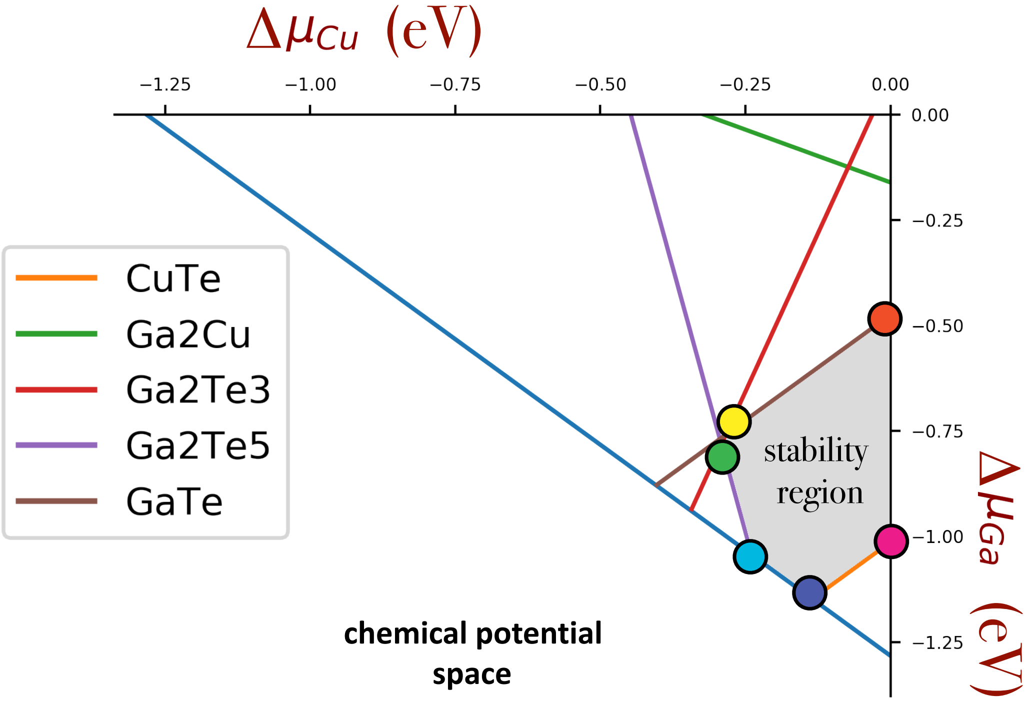
# phase stability, e.g. $CuGaTe_2$



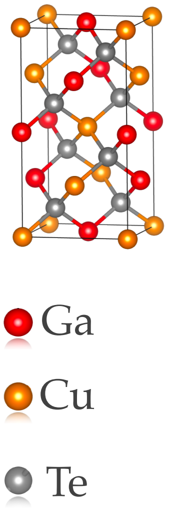
- Need to include all possible competing compounds

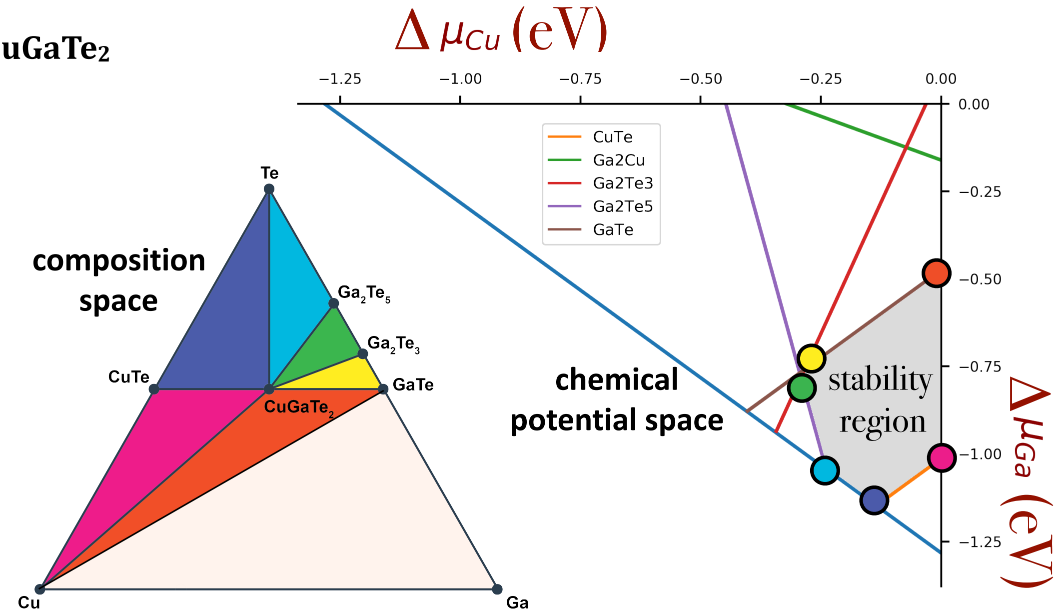


# phase diagrams: composition and chemical potential

- Can go back and forth between chemical potential and composition space.
- Invariant points (three phase equilibria) in chemical potential space become areas in composition space; areas in chemical potential space become single points in composition space (NB: they do have a finite span in practice)

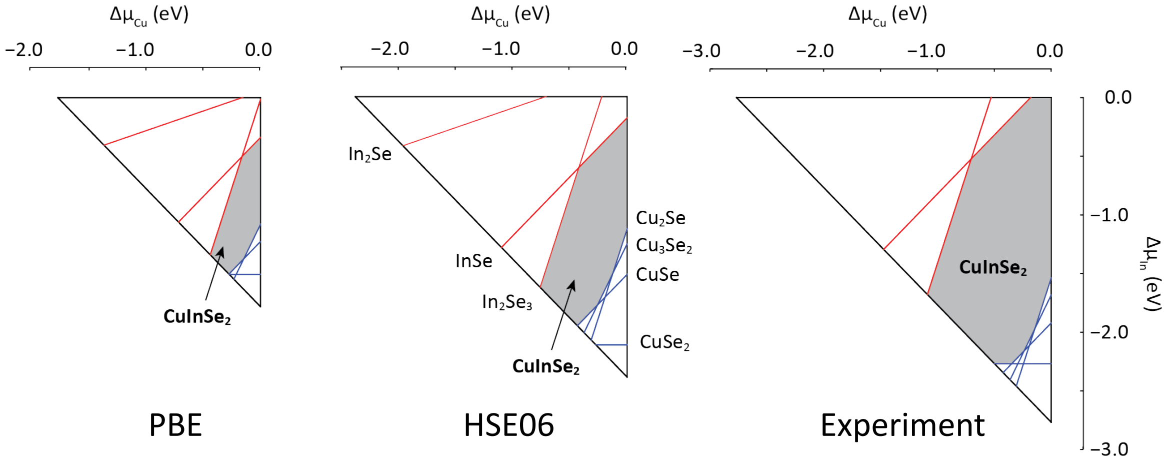
**example: $CuGaTe_2$**





# phase stability example

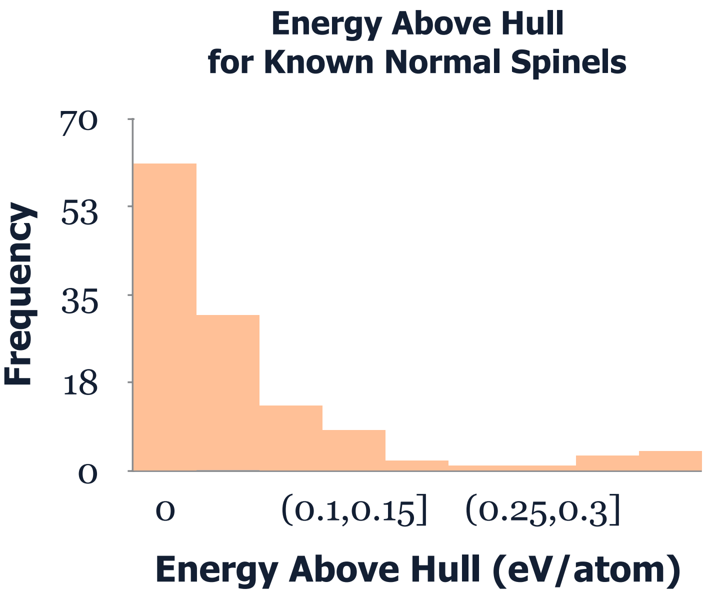
*Case study of chalcopyrite material $CuInSe_2$*

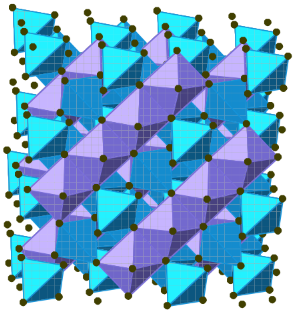


Kim, Pena-Martin, Rockett, Ertekin. Phys. Rev B 93 165202 (2016)

- The hybrid functional improves the agreement with experiment.
- Even so, DFT-computed PBE and HSE triangles are both too small: both methods underestimate the formation enthalpies of the chalcopyrite relative to experiment.
- This means that the compound is underbound relative to elemental phases in DFT. We see this often.
- Also note that both techniques do not get the correct phase boundaries

# example: spinels ($AB_2C_4$)


Energy Above Hull for Known Normal Spinels



- Distribution of formation energies about convex hull, pulled from Materials Project
- These are all stable spinels, but DFT-PBE predicts roughly half to be unstable
- Can be difficult to determine stability using only DFT-PBE

**insight: it is easier to predict instability than stability using conventional DFT**

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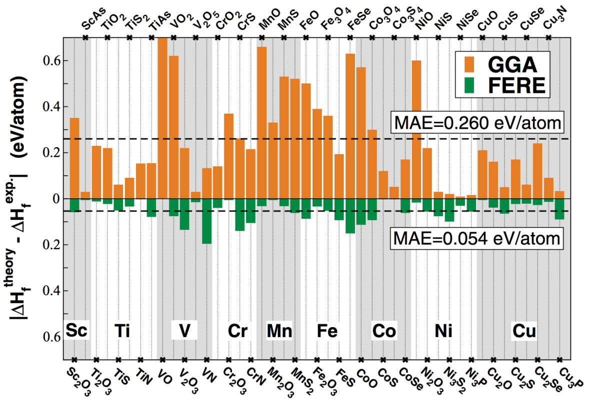
# FERE - Fitted Elemental Reference Energies

- Observation/Problem: Compound formation enthalpies are not very accurate in conventional DFT
- Origin of Problem: Incomplete error cancellation between compounds and elements
- Proposed solution: Fitted elemental reference energies (FERE)
  - introduce a shift for each elemental reference energy $\mu_a^{FERE} = \mu_a^{DFT} + \delta\mu_a$
  - solve for shifts $\delta\mu_a$ that minimize root means squared error in computed formation energies across a set of compounds:

$$\sum_{compounds} (\Delta H_f^{computed} - \Delta H_f^{exp})^2$$

$$\Delta H_f^{computed} = E^{DFT} - \sum_a n_a(\mu_a^o + \delta\mu_a)$$



- Improves thermodynamic boundary conditions for phase stabilities

Stevanovic, Lany, Zhang, and Zunger. Phys. Rev. B 85 115104 (2012).

# BAND STRUCTURES

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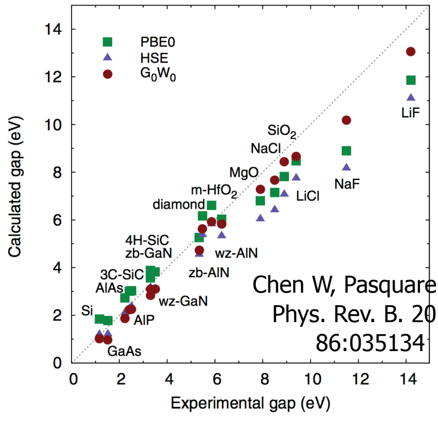
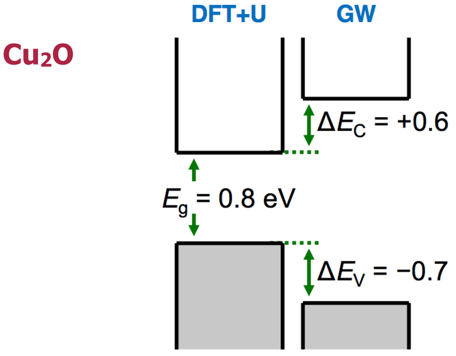
# Approaches to Band Structure

- Conventional DFT such as LDA and GGA tend to underestimate band gaps in generally non-systematic (unpredictable) ways
    - a result of the residual self-interaction error present in the exchange-correlation functional
- Hybrid functionals improve the description of band gaps by incorporating some amount of exact exchange in the Kohn-Sham Hamiltonian to cancel out the self-interaction error
    - standard hybrid functionals (PBE0, HSE06), e.g. 25% exchange mixing
    - it is also possible to modify the amount of exchange mixing (be careful)
    - some formulations or recipes, such as choosing the amount of exact exchange based on the dielectric constant [see Gerosa et al., J. Phys.: Condens. Matter 30 (2018) 044003]
    - more computationally expensive
- GW: many-body perturbation theory to obtain the self-interaction energy for quasi-particles
    - more computationally expensive, slow convergence, results sensitive to approach (i.e. single shot vs. self-consistent, vertex corrections, etc).



Chen W, Pasquarello A. Phys. Rev. B. 2012; 86:035134



S. Lany, J. Phys. Cond. Mat. 27 283203 (2015)

# DEFECTS AND DOPING

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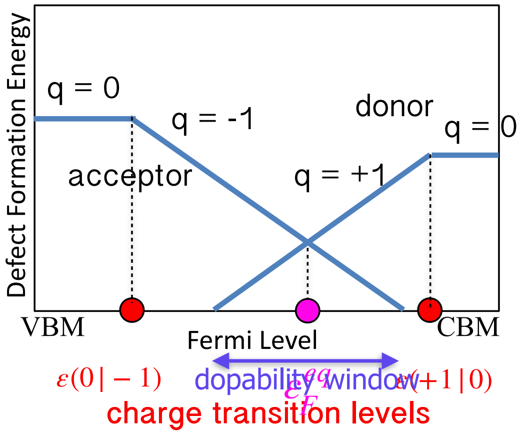
# general formalism

- Grand canonical thermodynamic formalism to obtain **formation energies** of neutral and ionized defects
- **Charge transition levels**: values of the Fermi level at which the stable charge state of the defect changes
- **Equilibrium Fermi level and carrier concentrations** are determined from charge neutrality,
- The range of achievable Fermi levels is indicated by the **dopability window**

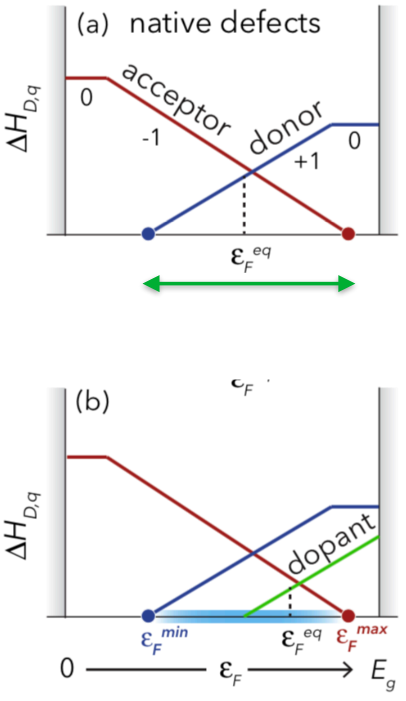
$$\Delta E_f = (E_{D,q} - E_{perf}) + \sum(n_i \mu_i) + qE_F$$



# early successes

- Negative-U model of DX centers in III-V semiconductors
  - Chadi, D. J. & Chang, K. J. Theory of the Atomic and Electronic Structure of DX Centers in GaAs and $Al_xGa_{1-x}As$ Alloys. *Phys. Rev. Lett.* 61, 873–876 (1988).
  - Jones, R. & Oberg, S. Structure and dynamics of the DX center in GaAs:Si. 44, 3407–3408 (1991).
- Description of hydrogen in silicon (amphoteric) and other semiconductors
  - Van de Walle, C. G., Denteneer, P. J. H., Bar-‐Yam, Y. & Pantelides, S. T. Theory of hydrogen diffusion and reactions in crystalline silicon. *Phys. Rev. B* 39, 10791–10808 (1989).
  - Chang, K. J. & Chadi, D. J. Hydrogen bonding and diffusion in crystalline silicon. *Phys. Rev. B* 40, 11644–11653 (1989).
- Identification of defects on surfaces
  - Ebert, P. *et al.* Symmetric Versus Nonsymmetric Structure of the Phosphorus Vacancy in InP(110). *Phys. Rev. Lett.* 5816–5819 (2000).
  - Zhang, S. B. & Zunger, A. Structure of the As Vacancies on GaAs(110) Surfaces. *Phys. Rev. Lett.* 77, 119–122 (1996).
  - Kim, H. & Chelikowsky, J. R. Theoretical Scanning Tunneling Microscopy Images of the As Vacancy on the GaAs(110) Surface. *Phys. Rev. Lett.* 77, 1063–1066 (1996).
- Identification of defects in new photovoltaic-active materials
  - Zhang, S. B., Wei, S.-‐H. & Zunger, A. Defect physics of the CuInSe2 chalcopyrite semiconductor. 1–15 (1998).
- Identification of defects in nitrides
  - Van de Walle, C. G. First-‐principles calculations for defects and impurities: Applications to III-‐nitrides. *J. Appl. Phys.* 95, 3851 (2004).

# carrier concentrations etc.



- **equilibrium Fermi level**: defect concentrations and electron and hole concentrations simultaneously satisfy charge neutrality

concentration of defect $C_{D,q} = N\exp(\frac{-\Delta H_{D,q}}{k_B T})$

charge neutrality $\sum_{X,q} qc(X^q) + n_h - n_e = 0$

Intrinsic electron concentration:

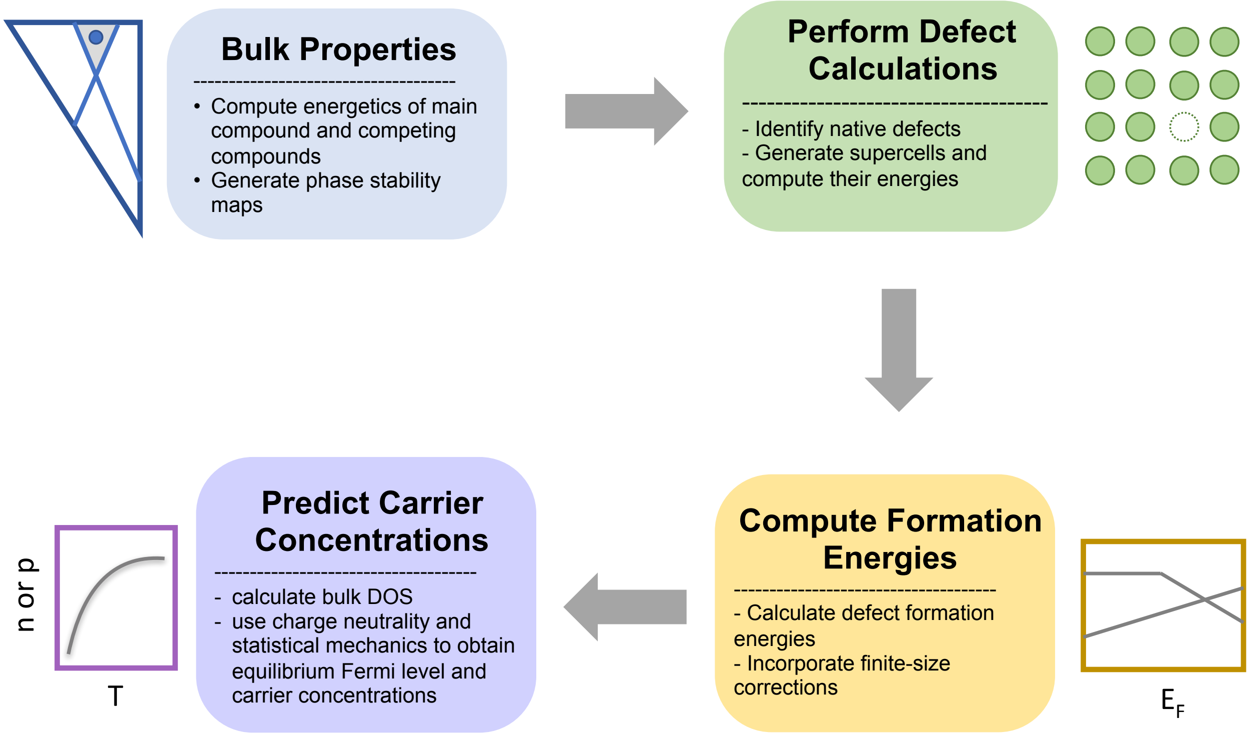
$$n = \frac{1}{V}\int_{Ec}^{\infty} g_c(E)\, f_e(E)\, dE \qquad f_e(E) = \frac{1}{1+\exp\left(\frac{E-E_f}{kT}\right)}$$

Intrinsic hole concentration:

$$p = \frac{1}{V}\int_{\infty}^{E_V} g_v(E)\, f_h(E)\, dE \qquad f_h(E) = \frac{1}{1+\exp\left(\frac{E_f-E}{kT}\right)}$$

- **dopability window**: range of Fermi energies that could be accessed by incorporation of extrinsic dopants
- **example**: shows a possible donor defect that pushes the Fermi energy high in the dopability window

# defect calculation framework



**Bulk Properties**

- Compute energetics of main compound and competing compounds
- Generate phase stability maps

**Perform Defect Calculations**

- Identify native defects
- Generate supercells and compute their energies

**Compute Formation Energies**

- Calculate defect formation energies
- Incorporate finite-size corrections

**Predict Carrier Concentrations**

- calculate bulk DOS
- use charge neutrality and statistical mechanics to obtain equilibrium Fermi level and carrier concentrations

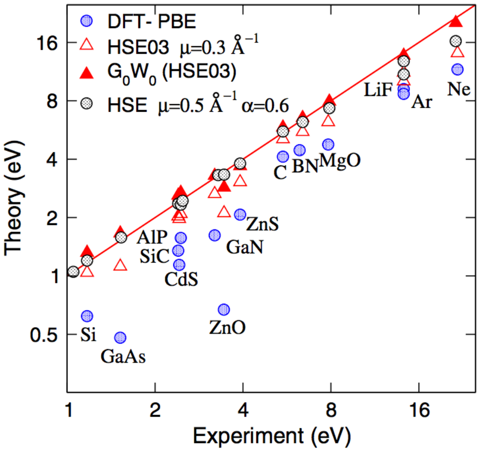
# How to Calculate & What Could Go Wrong?

Traditionally, we compute energies using DFT within the supercell approach with periodic boundary conditions.

Complications arise largely for **two reasons**: (i) **accuracy of computed quantities**, and (ii) **finite size of supercells** since we are generally interested in the dilute defect limit.

Typical computation engines:

- conventional DFT – most common; accurate band gaps, band edge positions, and reference energies are a prerequisite
- more recently:
  - conventional DFT with systematic correction schemes
  - hybrid density functional DFT
  - GW
  - quantum Monte Carlo

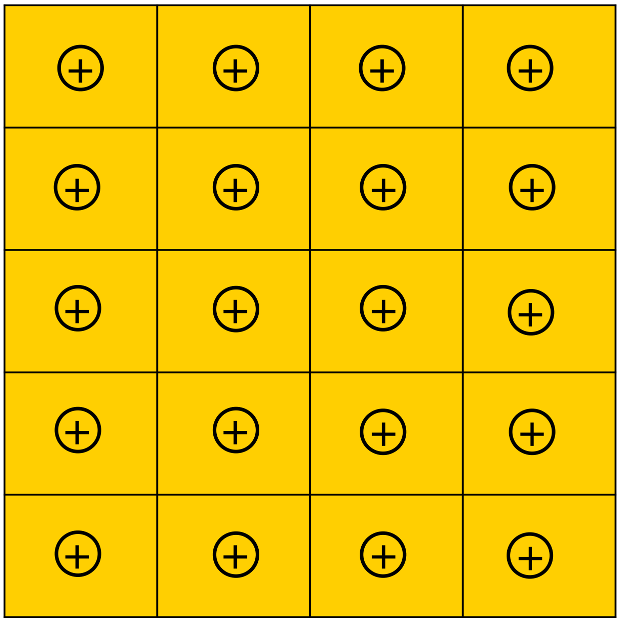


*Rev. Mod. Phys. 86, 253 (2014).*

# finite size effects

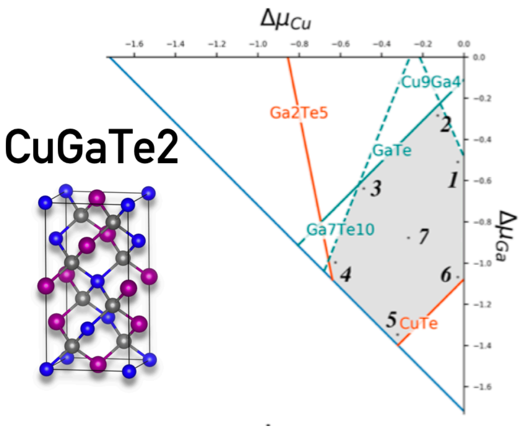
$$\Delta E_f = (E_{D,q} - E_{host}) - \sum_i n_i \mu_i + q(E_V + E_F)$$

**Finite Size Effects**

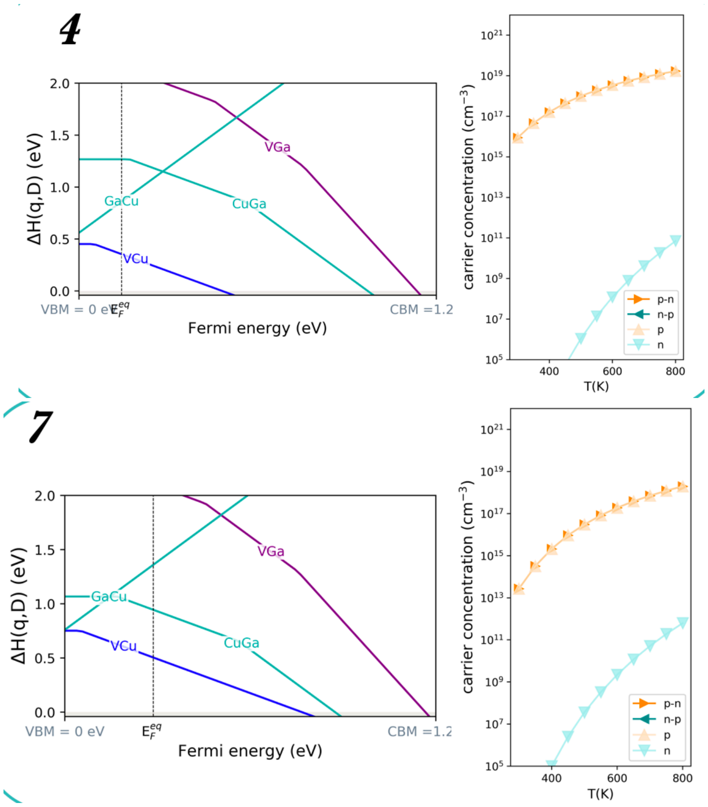


- elastic finite size effect for any defect
- electrostatic finite size effect for charged defects (spuriously stabilizes charged defects)
- many ways to estimate:
  - Leslie & Gillan (1985)
  - Makov-Payne (1995)
  - Freysoldt, Neugebauer, van de Walle (2009)
  - Lany & Zunger (2008)

# example: carrier concentrations in ternary diamond like semiconducting tellurides

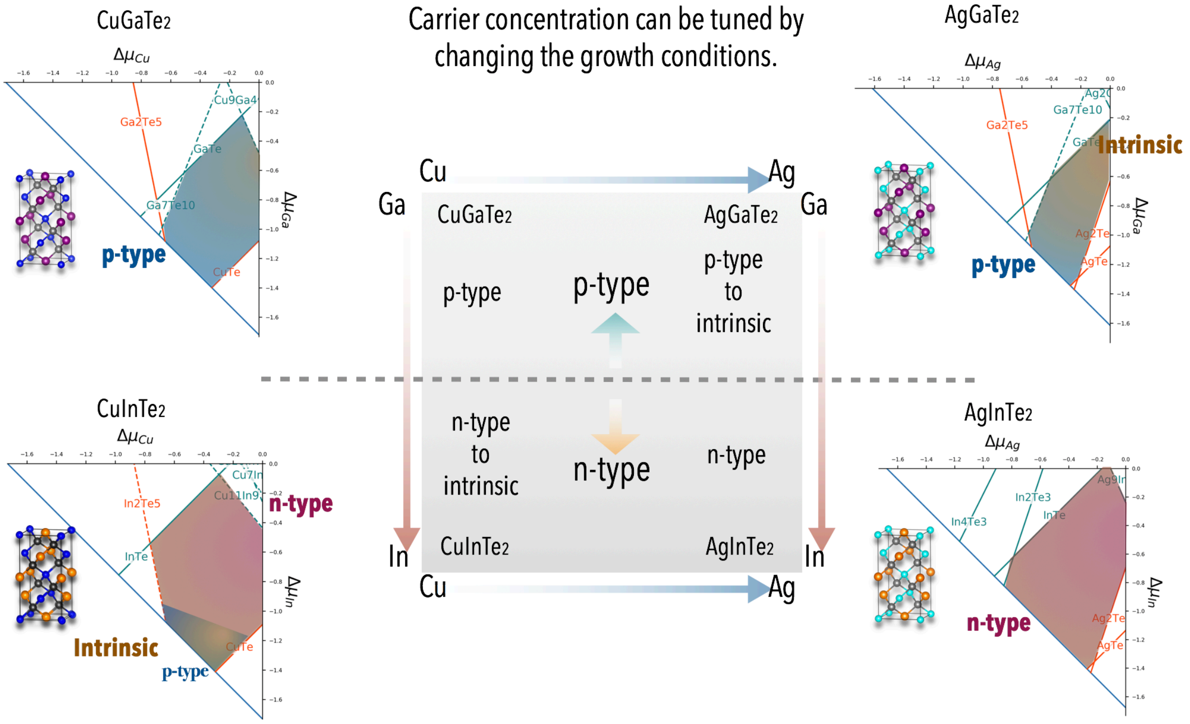


- strongly p-type material, across whole stability region
- $V_{Cu}^{-1}$ : killer defect that makes extrinsic n-type doping impossible



# example: carrier concentrations in ternary diamond like semiconducting tellurides

Carrier concentration can be tuned by changing the growth conditions.



# Summary

- Density functional theory as the best available compromise today between accuracy attainable and computational cost; most practically well-suited for calculation of semiconducting solids
- Useful for prediction of crystal structures, lattice constants, elastic constants
- With some tweaks, can be made reasonably predictive for phase stability analysis
- Band structure and band gaps: conventional DFT vs. hybrids vs. GW
- Defects and dopability: defect formation energies, thermodynamic modeling, and carrier concentrations