Aalto University
School of Science

Atomistic modeling of point defects

Hannu-Pekka Komsa

(Tutorial at Conference on Physics of Defects in Solids, ICTP 9-13.7.2018)

9.7.2018

Outline

- Brief introduction to DFT
    - Underlying ideas
    - What it can/can't do

- Defect calculations
    - Supercell models
    - Formation energy
    - Chemical potentials
    - Defect levels

First-principles calculations and density functional theory

Schrödinger equation

$$\hat{H}|\Psi_m\rangle = E|\Psi\rangle$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$- \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},$$

$$\Psi(\{\mathbf{r}_i\};t) \equiv \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; t)$$

- Input: Nuclei positions, # of electrons
- Output: Energy, many-body wavefunction, everything

—— = First Principles ——

Aalto University
School of Science

9.7.2018

Empirical potential calculations

- Total energy "exactly" given as $E(\{\boldsymbol{R}_I\})$
- Expand as:

$$E = \sum_{I,J}' E_{pair}(R_I, R_J) + \sum_{I,J,K}' E_{3body}(R_I, R_J, R_K) + \cdots$$

- Atomic energy: $E = \sum_I E_{atom}(R_I, \{R_{J \neq I}\})$ Not possible in DFT!
- Not calculated from the Schrödinger eq., but parametrized.
- E.g.
- Lennard-Jones, repulsive core + van der Waals attraction:

$$E_{pair}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

- Or Coulomb interaction: $E_{Coulomb}(r) = 1/4\pi\epsilon \, q_I q_J /r$

Total energy methods, why is it enough?

- Optimized geometry, lattice parameters
- Forces: $F_i = -\partial E / \partial R_i$
  - Molecular dynamics
- Energy differences
  - Formation energies, reaction barriers
- Perturbations
  - Vibrations

Density functional theory

- Efficient method for calculating ground state total energy

- Hohenberg-Kohn: Mathematical basis

- Kohn-Sham: Practically working approach

- 50 years of fine-tuning the approximations

Hohenberg-Kohn 1

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Theorem I: For any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential $V_{\text{ext}}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.

Corollary I: Since the hamiltonian is thus fully determined, except for a constant shift of the energy, it follows that the many-body wavefunctions for all states (ground and excited) are determined. *Therefore all properties of the system are completely determined given only the ground state density $n_0(\mathbf{r})$.*

$$V_{\text{ext}}(\mathbf{r}) \quad \overset{\text{HK}}{\Longleftarrow} \quad n_0(\mathbf{r})$$
$$\Downarrow \qquad\qquad \Uparrow$$
$$\Psi_i(\{\mathbf{r}\}) \quad \Rightarrow \quad \Psi_0(\{\mathbf{r}\})$$

Hohenberg-Kohn 2

Theorem II: A *universal functional* for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$. For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.

Corollary II: The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density. In general, excited states of the electrons must be determined by other means.

- Tells us how to solve and fast: from 3N dimensions to 3
- All we need is E[n]. Maybe:

$$E{\downarrow}HK\,[n]{=}T[n]{+}E{\downarrow}int\,[n]{+}\int{\uparrow}\blacksquare d{\uparrow}3\,rV{\downarrow}ext\,(r)n(r$$

unknown

Kohn-Sham ansatz

- 1. The exact ground state density can be represented by the ground state density of an auxiliary system of non-interacting particles

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

→ $\{\varphi_i(r)\}, i = 1 \cdots N$ and

- 2. The auxiliary Hamiltonian is chosen to have the usual kinetic operator and an effective local potential $V_{eff}(r)$ acting on electron at point r.

Kohn-Sham energy

$$n = \sum_{i=1}^{N} |\varphi_i(r$$

$$\{\varphi_i(r)\}, i = 1 \cdots N \text{ and}$$

- Total energy:

$$E_{KS}[n] = T_s + E_{Hartree}[n] + E_{XC}[n] + \int d^3 r V_{ext}(r) \qquad _{II}$$

- Kinetic energy of non-interacting particles:

$$T_s = -1/2 \sum_{i=1}^{N} \varphi_i \nabla^2 \varphi_i$$

- Hartree energy: $E_{Hartree}[n] = 1/2 \int d^3 r d^3 r' n(r)n(r')/|r-r'|$

- All the rest (e-e interactions and $T[n] - T_s[n]$): $E_{XC} = ?$

Exchange-Correlation

- No exact form known

- Approximations approximations, hundreds of them

- Classified by the amount of input information:
  - LDA, GGA, meta-GGA, hybrid, double hybrid
  - $E_{XC}[n(r), \nabla n(r), \tau, \varphi_v, \varphi_c]$

- Benchmark: atomization energy, ionization potential, bond length/lattice constants, bulk modulus

- Attempts to improve on KS energies
  - Infamous band gap error
  - Does it make any sense?

Numerical "approximations"

- Basis sets for describing potential, density, and wave functions:
  - Plane waves, localized atomic orbitals, real-space grid
- Brillouin zone sampling in solids:
  - k-point meshes
- Nuclei and core states:
  - All-electron approaches, pseudopotentials

- Level of theory: spin-polarization, non-collinear magnetism, DF perturbation theory, time-dependence

What is easy? What DFT gets right?

- Anything related to total energy and density (in ground state)
    - Geometry, formation energies
    - Reaction barriers, vibrations ($\rightarrow$ finite T)
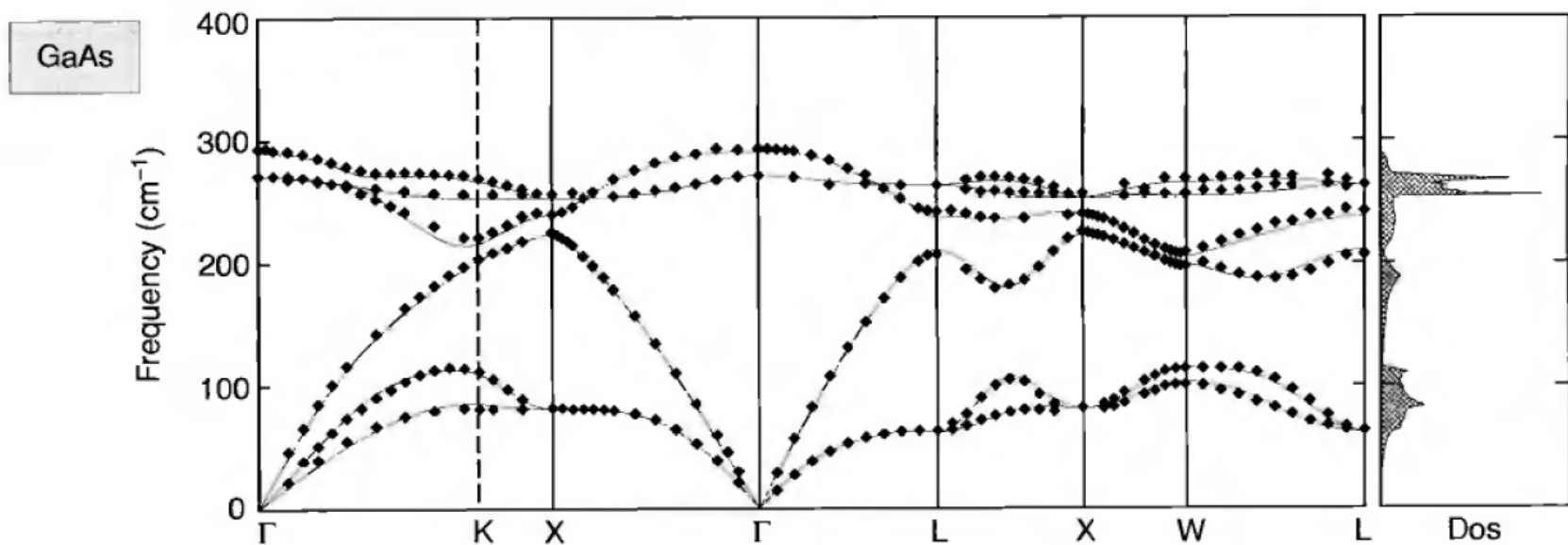
What is difficult? What DFT gets wrong?

- Anything related to excitations
  - Band structure, absorption/PL spectra, finite T effects
  - Electron scattering, electron dynamics
  - Interpretation, KS energies vs. quasiparticle energies
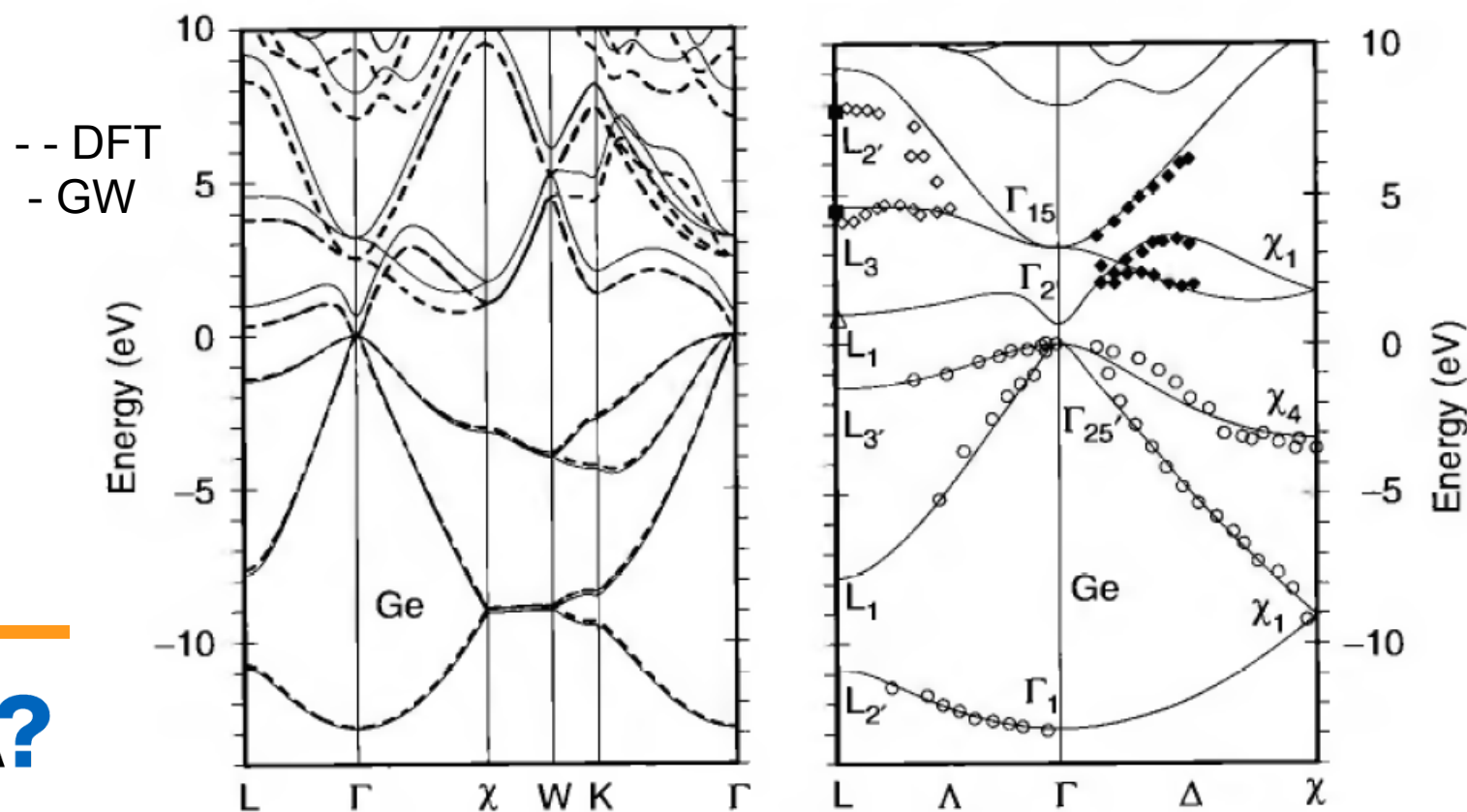
What is difficult? What DFT gets wrong?

- Fractional charges
  - E.g. dissociation of $H_2^+ \rightarrow H^{0.5+} + H^{0.5+}$

- Electron self-interaction due to mean-free description
 - Tendency to delocalize charge in many semilocal XC functionals

Defect calculations

Calculation of point defects

- Modeling with supercells

- Formation energies

- Chemical potentials

- Charged defects

- Defect levels

Supercell approach

- Provides good description of host
- Defects interact with each other, concentration too high?
- What to do with total energy?
  - Minimize energy → defect geometry
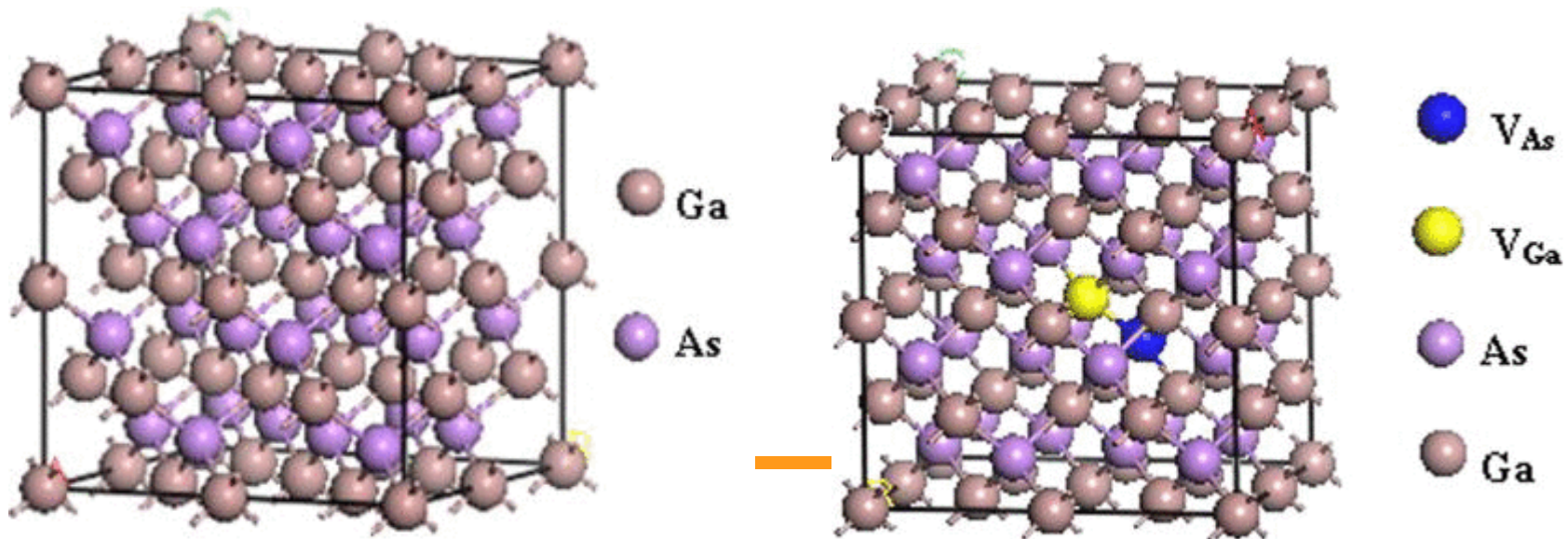
Formation energy

$$E_f = E_{\text{def}} \boxed{- E_{\text{host}} - \sum_i n_i \mu_i + q E_{\text{Fermi}}}$$

- $E{\downarrow}def$: Energy of supercell with defect
- $E{\downarrow}host$: Energy of pristine supercell

Or rather Gibbs free energy

- $n{\downarrow}i$: Number of missing/added elements
- $\mu{\downarrow}i$: Chemical potentials of these elements (parameter)
- q: Defect charge
- $E{\downarrow}Fermi$: Fermi-level (free parameter)

Free energy of formation

$$G_f = F(\text{def}) - F(\text{host}) + pV_f$$

$$- \sum_i n_i \mu_i + q(E_v + E_F) + E_{\text{corr}}$$

- F Helmholtz free energy of system

$$F = F^{\text{el}} + F^{\text{qh}} + F^{\text{ah}}$$

- Electronic (internal+el. Temperature), quasiharmonic, anharmonic effects (vibrations)
- Energy correction due to supercell (charged defects)

Concentration

- Formation energies always positive
- Can still form, overcome by configuration entropy

- Concentration of defects:

$$c = N_0 N_c \exp\left(-\frac{G_f}{k_B T}\right)$$

- N_0 number (or concentration) of defect sites
- N_c number of configurations

Chemical potential = tendency of a system to give particles

- Equilibrium → chemical potentials equal in host and reservoirs
- Limited by the elemental phases

$$\mu_{Ga} \leq \mu_{Ga}(Ga\ metal)$$

$$\mu_N \leq \mu_N(N_2, P, T)$$

- Energy of the host know

$$\mu_{Ga} + \mu_N = \mu_{GaN}$$

- Therefore:

$$\mu_{Ga} \geq \mu_{GaN} - \mu_N(N_2, P, T) \quad = \mu_{Ga}(Ga\ metal) + \Delta G_f$$

$$\mu_N \geq \mu_{GaN} - \mu_{Ga}(Ga\ metal) \quad = \mu_N(N_2, P, T) + \Delta G_f$$

- Range given by heat of formation:

$$\Delta G_f = \mu_{GaN} - \mu_{Ga}(Ga\ metal) - \mu_N(N_2, P, T)$$

Stability diagram

μ_{Ga} $G_f(GaN)$ 0 Elemental phases

0

Equilibrium with GaN$_2$

Accumulation of GaN

Equilibrium with GaN

$G_f(GaN)$

Depletion of GaN

μ_N
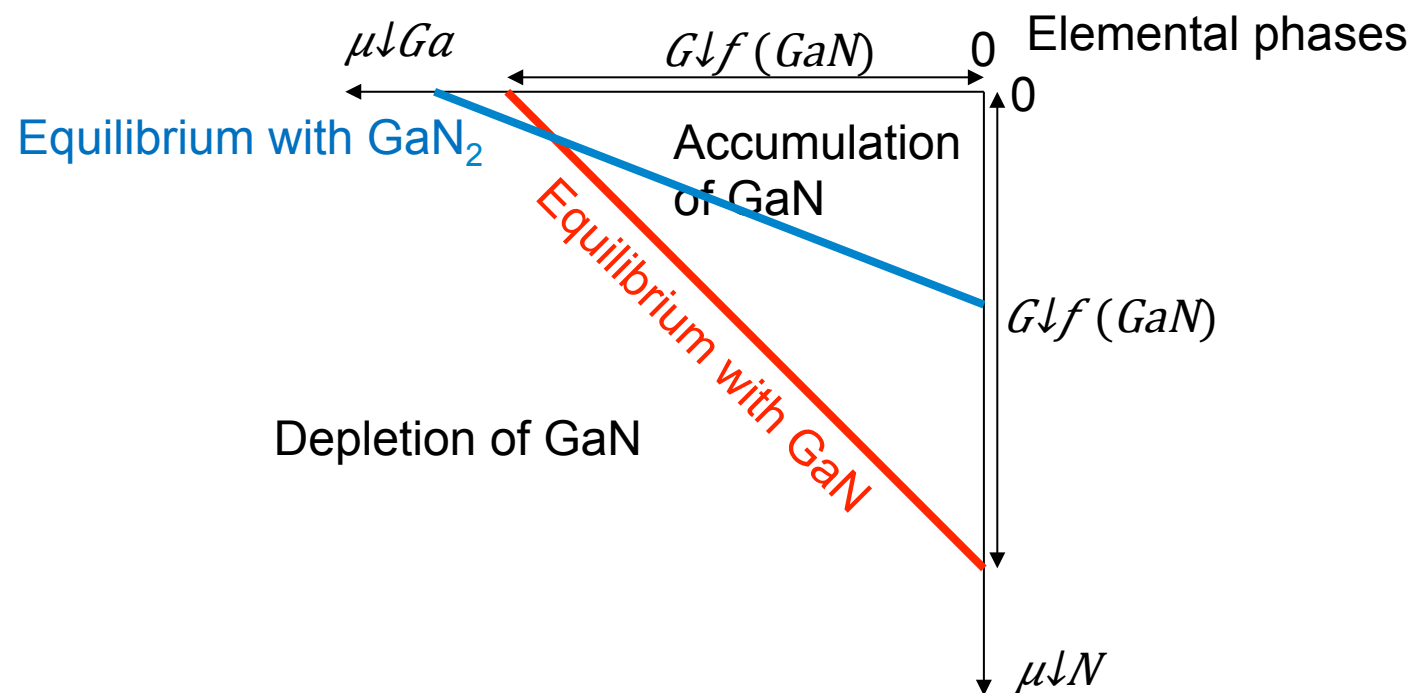
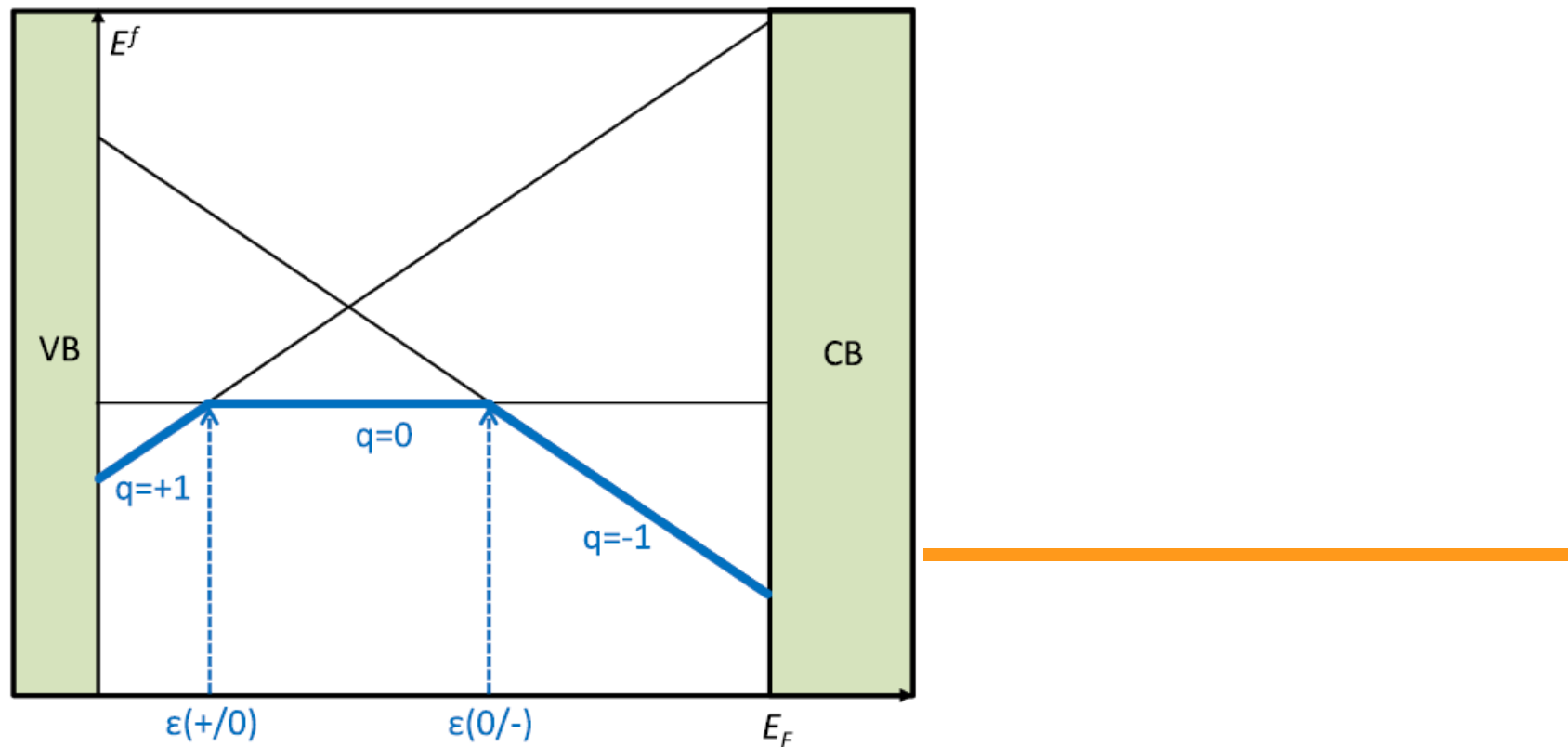# Charged defects

- Dependence on the free parameter E_{Fermi}

$$E_f = E_{\text{def}} - E_{\text{host}} - \sum_i n_i \mu_i + q(E_v + E_{\text{Fermi}})$$

Defect levels

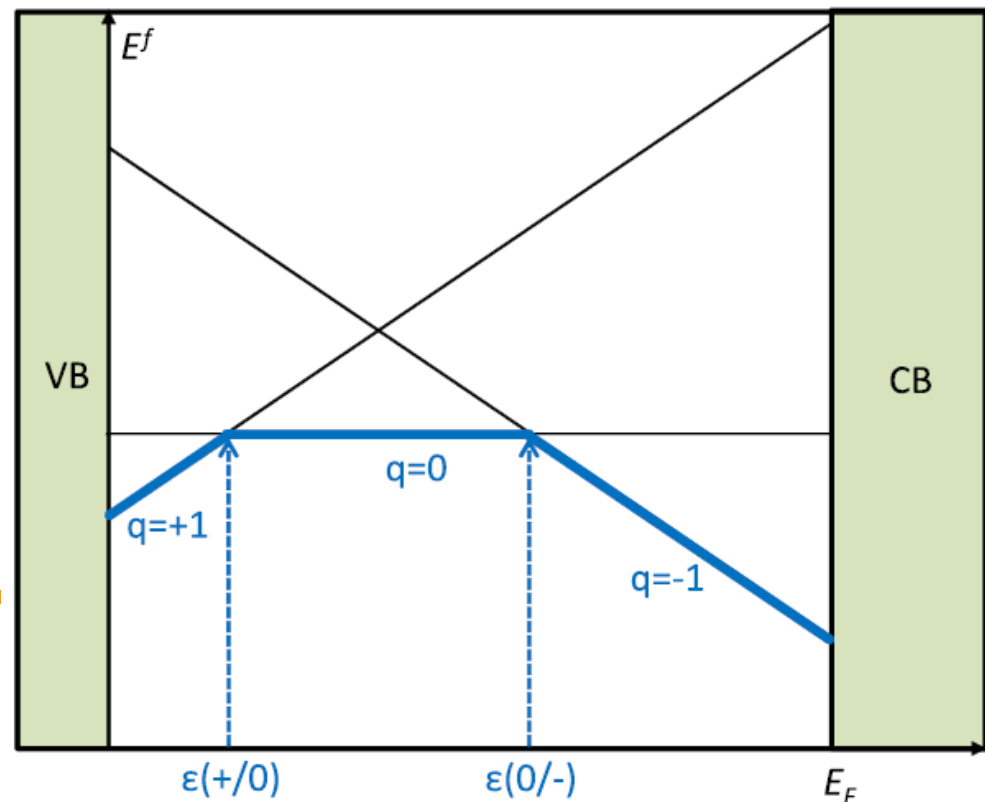$$E_f = E_{\mathrm{def}} - E_{\mathrm{host}} - \sum_i n_i \mu_i + q(E_v + E_{\mathrm{Fermi}})$$
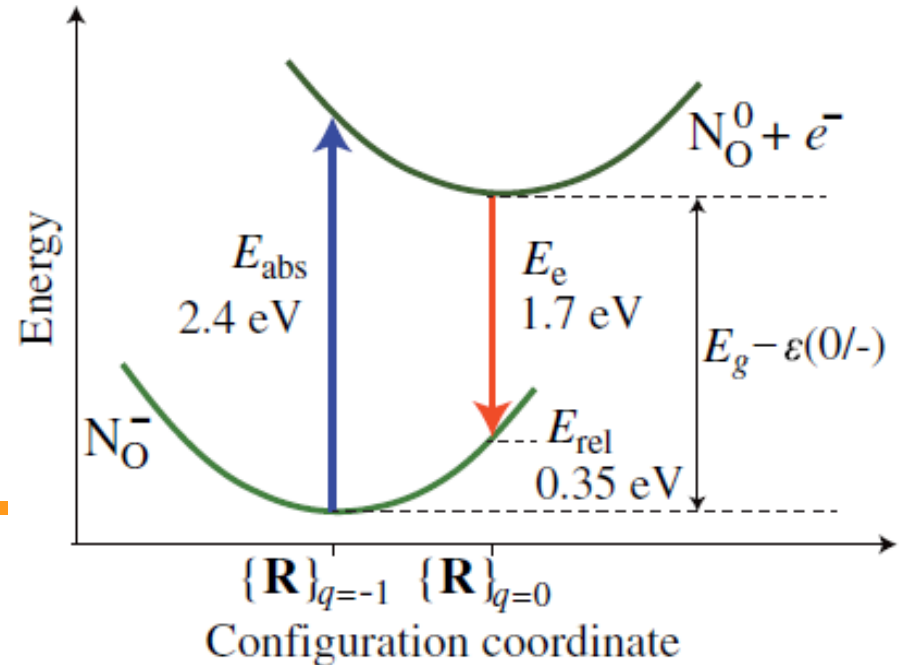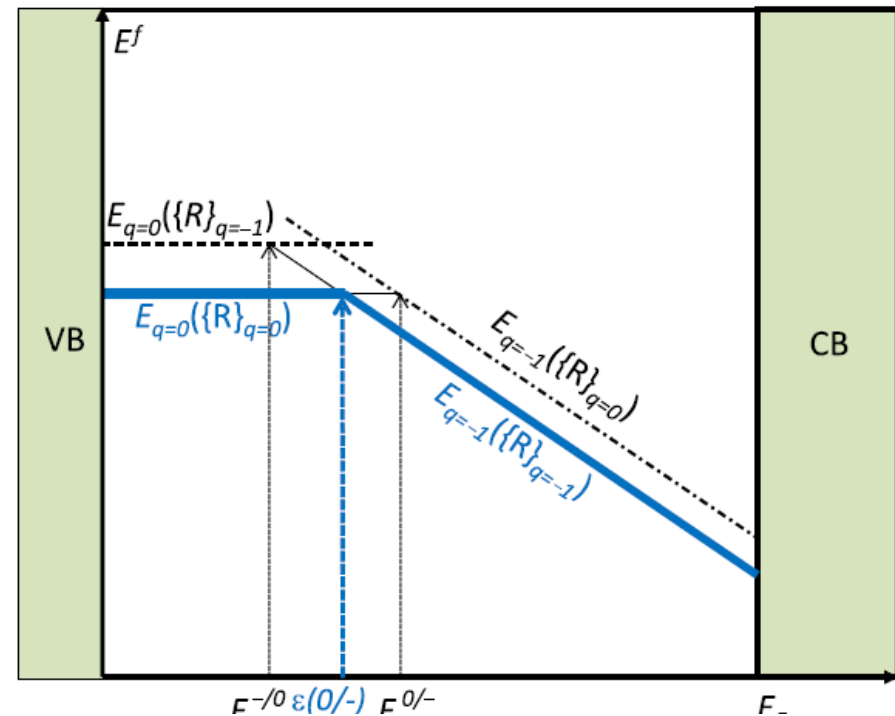
- Thermodynamic charge transition level

$$\varepsilon(q_1/q_2) = \frac{E^f(X^{q_1}; E_F = 0) - E^f(X^{q_2}; E_F = 0)}{q_2 - q_1}$$

- Ionization energy (DLTS)

- There must be a corresponding KS level in gap

Aalto University
School of Science

Defect levels

- Optical charge transition levels
  - Without ionic relaxation
  - Rate/cross section from matrix element

- Excitation or not?
  - Description of e/h in VBM/CBM

Charged defects in supercells

- The sum of interactions diverge for any periodicity
  - Harmonic series:
    $$\sum_{n=1}^{\infty} \frac{1}{n} = \infty$$

- Get rid of periodicity or go to neutral system
- The former not possible in first principles
  - And periodicity good for host states
- The latter leads to unwanted contributions and leaves the periodic images
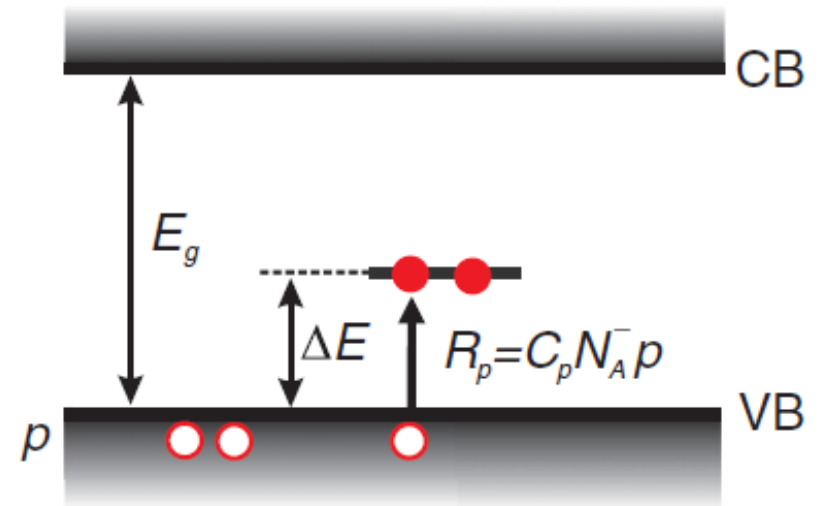 - We can try to correct them afterwards

Charged defects in bulk

- These errors can be treated in bulk
- Remove interactions with periodic images
  - Point-charges in homogeneous neutralizing background => analytic treatment (Madelung, MP)
  - Don't touch the self-interaction (handled better by DFT)
- E_{corr} to add to E_f
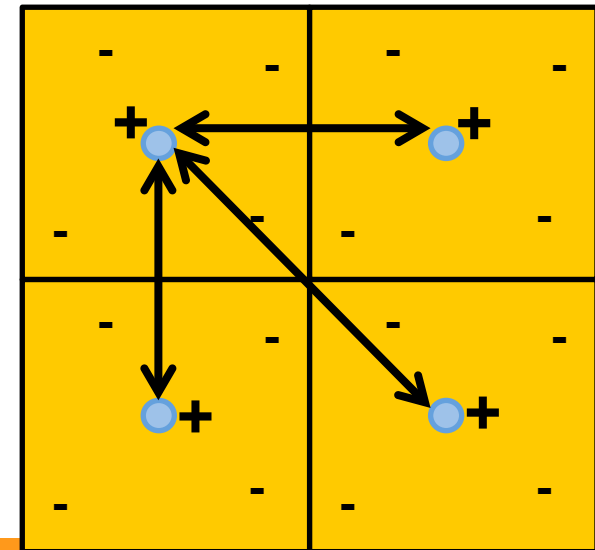
Other defect properties

- Magnetism (EPR)
- Vibrations (Raman, linewidths)
- Positron trapping (PAS)
- Excitation probability, capture cross section

$$r = \frac{2\pi}{\hbar} g \sum_m w_m \sum_n \left| \Delta H^{e-ph}_{im;fn} \right|^2 \delta(E_{im} - E_{fn})$$

$$\Delta H^{e-ph}_{im;fn} = \sum_k \underbrace{\langle \Psi_i | \partial \hat{H} / \partial Q_k | \Psi_f \rangle}_{W^k_{if}} \langle \chi_{im} | Q_k - Q_{0;k} | \chi_{fn} \rangle$$