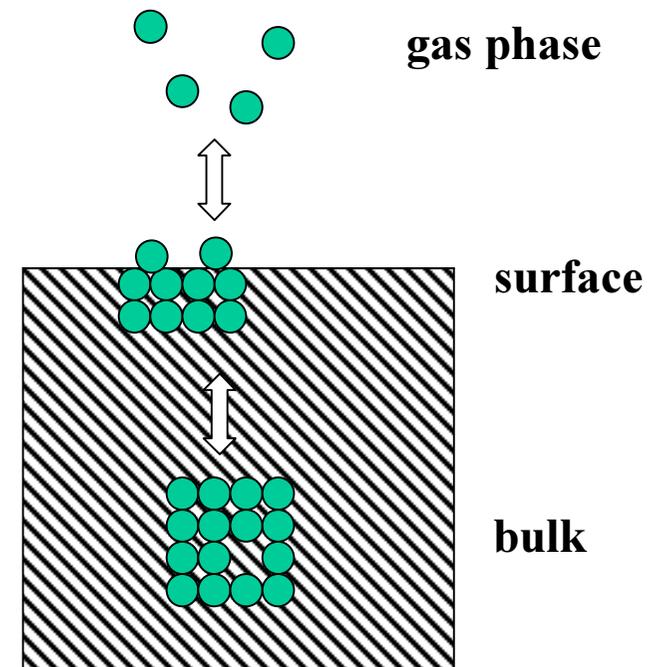
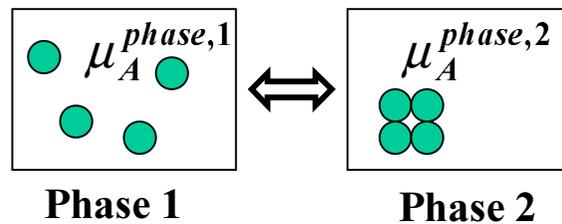


Thermodynamics, charge states and chemical potentials

Jörg Neugebauer
Fritz-Haber-Institut, Berlin

Goals:

- Extend the length scale
- Consider finite temperature effects



Outline

Thermodynamics

- **Basic concepts**
- **Connection to first principles calculations**
- **Chemical potentials**

Applications

- **Defects/Impurities**
- **Alloys**

Convergence aspects

- **Defect-defect interaction**
- **Charged defects**

Thermodynamic potentials

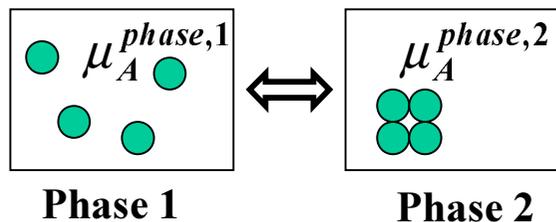
Key quantity:

Partition function: $Z(V, T) = \sum_i e^{-E_i / k_B T}$

Free energy: $F(V, T) = -k_B T \ln\{Z(V, T)\}$

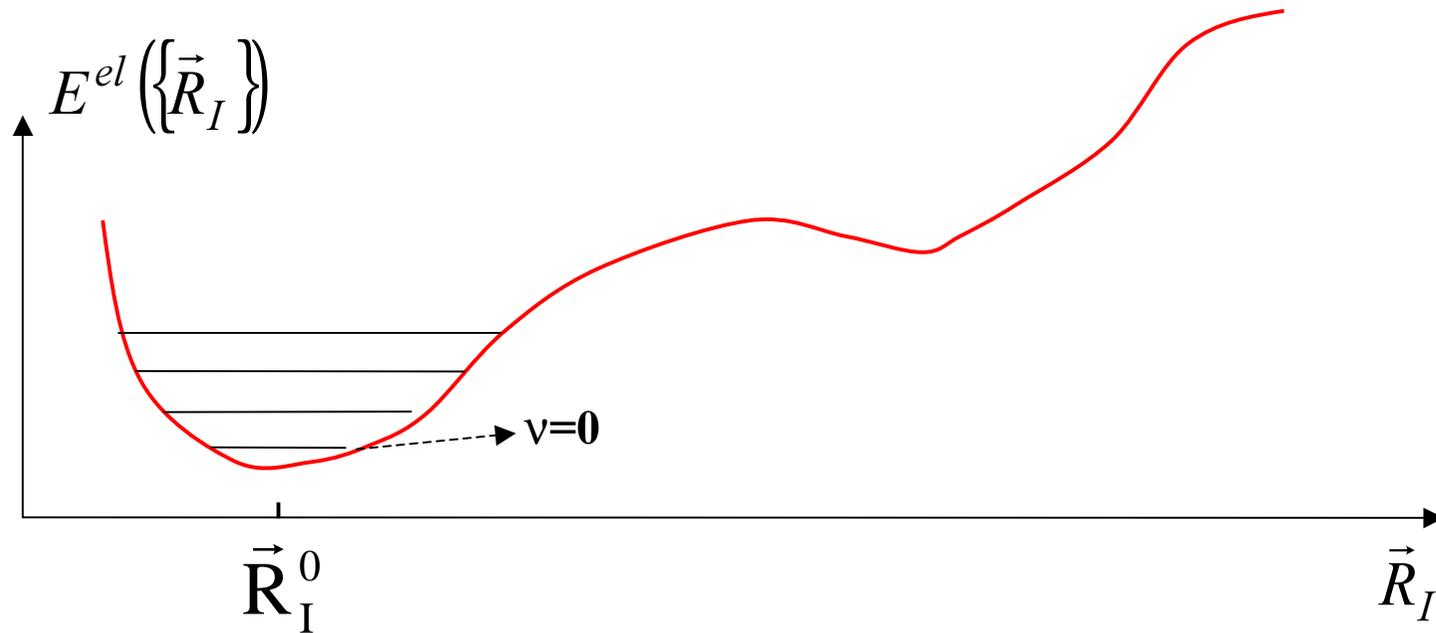
Gibbs Free energy: $G(p, T) = F(V, T) + pV$

Chemical potential: $\mu_A = \left(\frac{\partial G(A^n)}{\partial n} \right)_{T, p}$



Connection to first-principles calculations (I)

Total energy surface:



Total energy:
$$E_{0v}(\{\vec{R}_I^0\}) = E_0^{el} + E_{0v}^{ion}$$

electronic ground state index of the vibronic eigenstate

Connection to first-principles calculations (II)

Total energy: $E_{0\nu}(\{\vec{R}_I^0\}) = E_0^{\text{el}} + E_{0\nu}^{\text{ion}}$

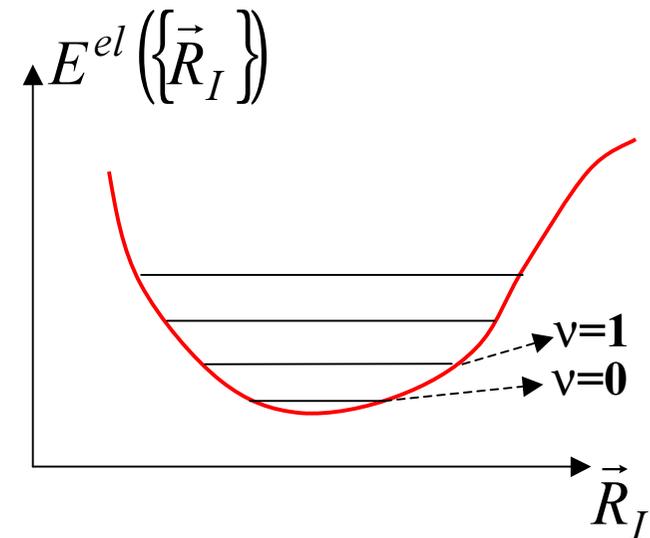
↑
↑
electronic ground state
index of the vibronic eigenstate



Partition function: $Z(V, T) = \underbrace{e^{-E_0^{\text{el}}/k_B T}}_{\text{electronic}} \sum_{\nu} \underbrace{e^{-E_{0\nu}^{\text{vib}}/k_B T}}_{\text{vibronic}}$

$$E_{0\nu}^{\text{vib}} = \sum_{l=1}^{3M-3} \hbar\omega_l \left(n_l + \frac{1}{2} \right)$$

↑
↑
Phonon mode
occupation number (Bose distribution)



How to obtain the phonon frequencies?

Calculate dynamical matrix:

$$D = \frac{1}{\sqrt{M_I M_J}} \left(\frac{\partial^2 E_0^{el}(\{\vec{R}_I\})}{\partial \vec{R}_I \partial \vec{R}_J} \right)_{\{\vec{R}_I^0\}}$$

dynamical matrix
can be calculated
by **M** selfconsistent
calculations!

Solve eigenvalue problem:

$$\det(D - 1\omega_l^2) = 0$$

Calculate ionic contribution of the free energy/entropy:

$$F^{ion} = \sum_l \left[\frac{1}{2} \hbar \omega_l + k_B T \ln \left(1 - e^{-\hbar \omega_l / k_B T} \right) \right]$$
$$S^{ion} = -\frac{1}{T} F^{ion} + \frac{1}{T} \sum_l \left[\frac{1}{2} + \frac{1}{e^{\hbar \omega_l / k_B T} - 1} \right]$$

Note: Vibrational effects are often excluded

- contributions cancel to a large extent
- small energies ($\cong 1 \dots 10 k_B T$)

Gibbs free energy

Gibbs Free energy: $G(p,T) = F(V,T) + pV$

Free energy: $F(V,T) = F^{config} + F^{el} + F^{ion}$

$$F^{config} = -k_B T \ln W \quad \text{W...number of equivalent states}$$

$$F^{el} = E_0^{el} - k_B T \ln D_{deg}^{el}$$

Entropy: $S = -\left(\frac{\partial F}{\partial T}\right)_V$

$$S^{config} = k_B \ln W$$

$$S^{el} = k_B \ln D_{deg}^{el}$$

Note: The volume change is often small and can be neglected

$$G(p,T) \approx F^{config} + E_0^{el}$$

- Exceptions:**
- Equilibrium with a gas (pressure and entropy effects crucial)
 - Small energy differences
 - Temperature dependent properties (thermal expansion, ...)

Example: Point defects

Assumption: Thermodynamic equilibrium

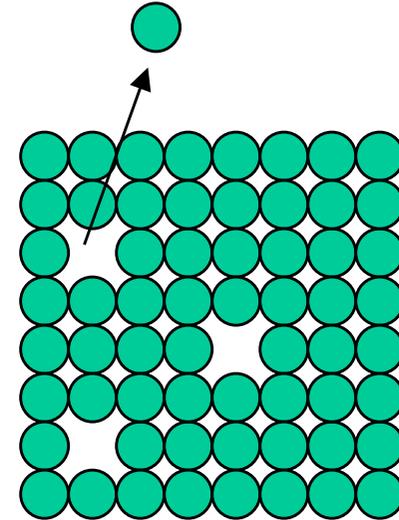
Free energy: $F = U - TS$

For isolated defects:

$$U = nE_D$$

number of defects

formation energy of
an isolated defect



Configurational entropy:

$$S^{config} = k_B \ln W \quad \text{with} \quad W = \frac{N(N-1)\dots(N-n-1)}{n!} = \frac{N!}{(N-n)!n!}$$

Minimize free energy:

$$\left(\frac{\partial F}{\partial n} \right)_T = E_D - k_B T \ln \frac{N-n}{n} = 0$$

➔ Defect concentration:

$$n = N \exp\left(-\frac{E_D}{kT}\right)$$

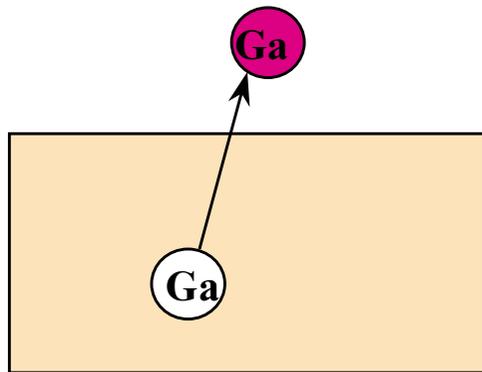
Defect Formation energy

Defect concentration: $n_{Defekt} = N_{sites} \exp\left(-\frac{E_D}{kT}\right)$

How can we calculate formation energy E_D ?

Note: To create a defect the number of atoms in the system may change!

Example: Creation of a vacancy in GaN (two steps)



a) DFT calculations

Ga atom gains energy μ_{Ga}



b) Thermodynamics

$$E_D(GaN : V_{Ga}^q) = E_{tot}(GaN : V_{Ga}^q) + \mu_{Ga} + qE_{Fermi}$$

Chemical Potentials

Specific value of the chemical potentials depends on the environment!

⇒ variables, which can be experimentally controlled

(via T, p, fluxes and flux ratio)

But: Boundary conditions are well defined and can be calculated

Example: Ga vacancy in GaN

Boundary conditions: $\mu_{\text{Ga}} < \mu_{\text{Ga(bulk)}}$

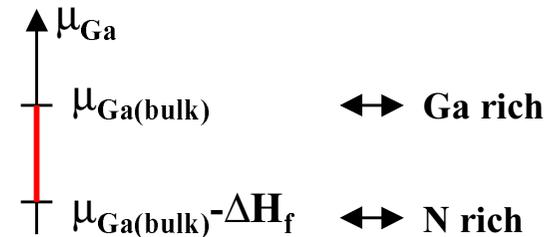
$\mu_{\text{N}} < \mu_{\text{N(molecule)}}$

$\mu_{\text{Ga}} + \mu_{\text{N}} = \mu_{\text{GaN(bulk)}}$

$\mu_{\text{Ga(bulk)}} + \mu_{\text{N(molecule)}} = \mu_{\text{GaN(bulk)}} + \Delta H_f$

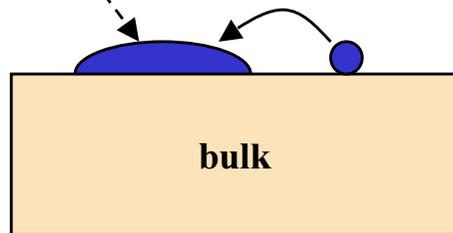


$$\mu_{\text{Ga(bulk)}} - \Delta H_f < \mu_{\text{Ga}} < \mu_{\text{Ga(bulk)}}$$



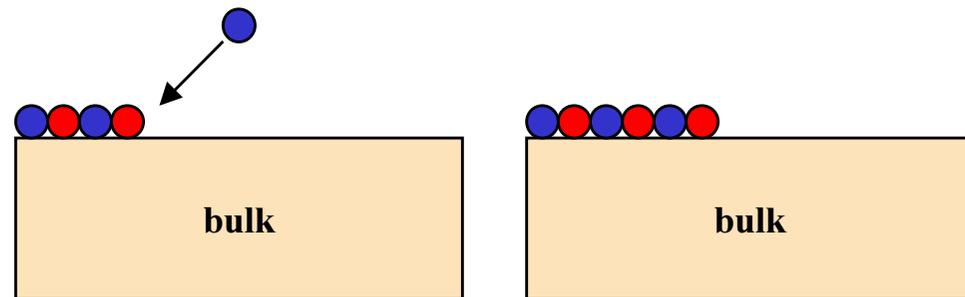
Interpretation:

Ga droplets ($\mu_{\text{Ga}} = \mu_{\text{Ga(bulk)}}$)



Ga rich

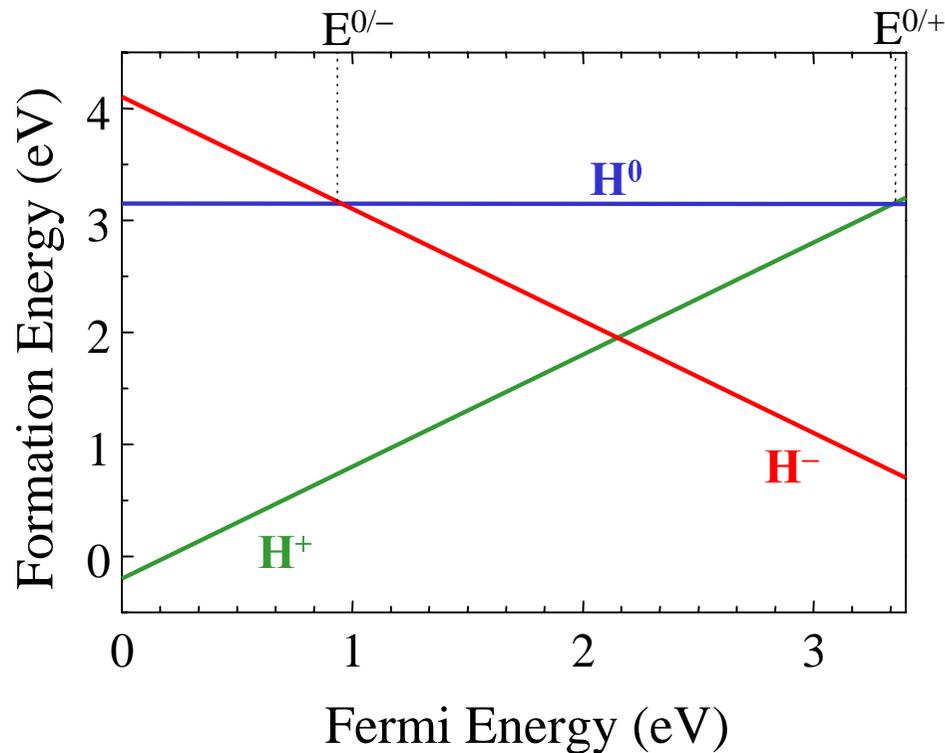
Incorporation at a Kink ($\mu_{\text{Ga}} = \mu_{\text{Ga(bulk)}} - \Delta H_f$)



N rich

Example: H in GaN

Formation energy: $E_D(\text{GaN} : \text{H}^q) = E_{tot}(\text{GaN} : \text{H}^q) - \mu_{\text{H}} + qE_{\text{Fermi}}$



⇒ p-type:

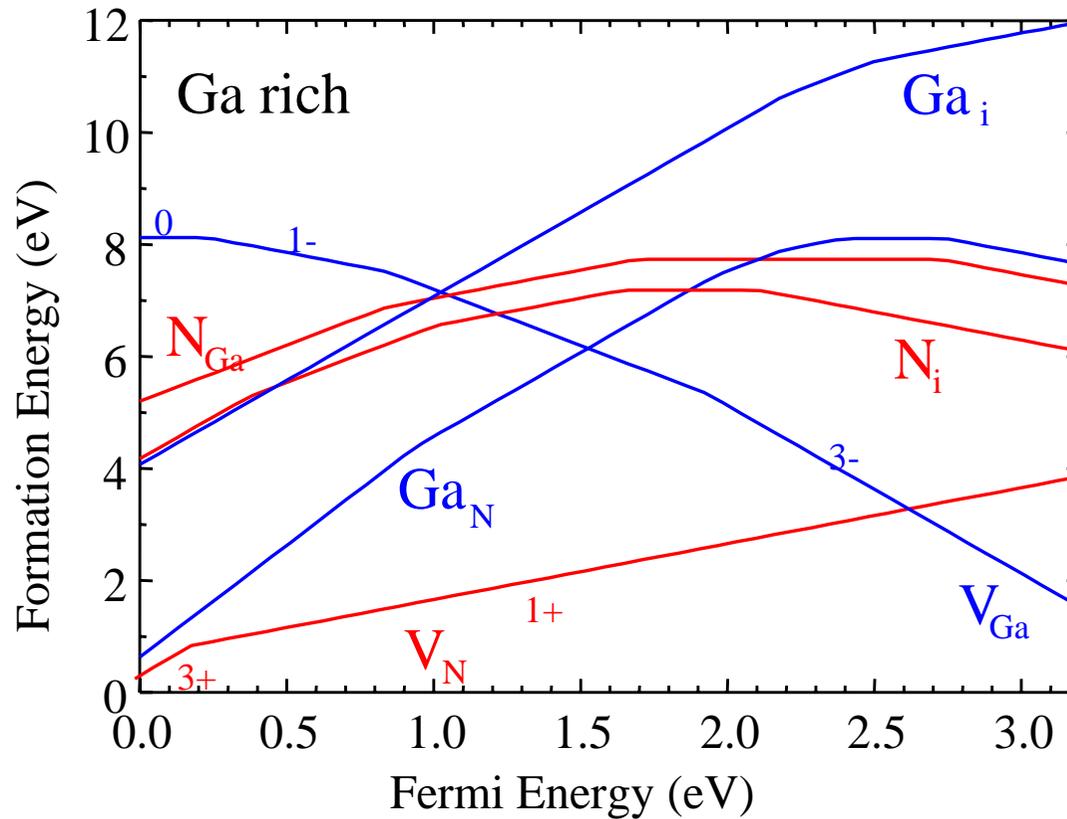
- H^+ is stable charge state
- low formation energy
→ high H solubility

⇒ n-type:

- H^- is stable charge state
- low formation energy
→ high H solubility

⇒ neutral charge state is unstable
→ acceptor state is above donor state
→ negative U center

Example: Point defects in GaN



- Identification of the dominant native defects
 - Identification of compensating centers
- ⇒ defect concentrations?

Defect concentrations: Charge neutrality

Is the Fermi level indeed a free variable?

→ No, it is controlled/fixed by charge neutrality condition!

$$D^+ + h = A^- + n$$

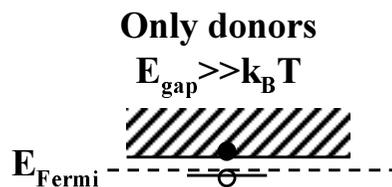
Number of ionized donors

number of ionized acceptors

$$n = N_c e^{-\frac{E_{CB} - E_{Fermi}}{kT}}$$

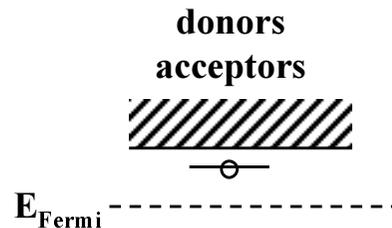
$$N_c = 2 \left(\frac{m_e kT}{2\pi\hbar^2} \right)^{3/2}$$

Special cases:



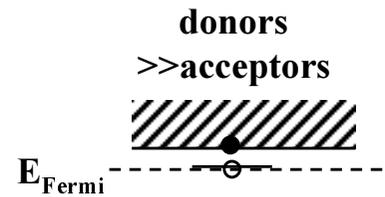
$$D^+ = n$$

n type



$$D^+ = A^-$$

compensation

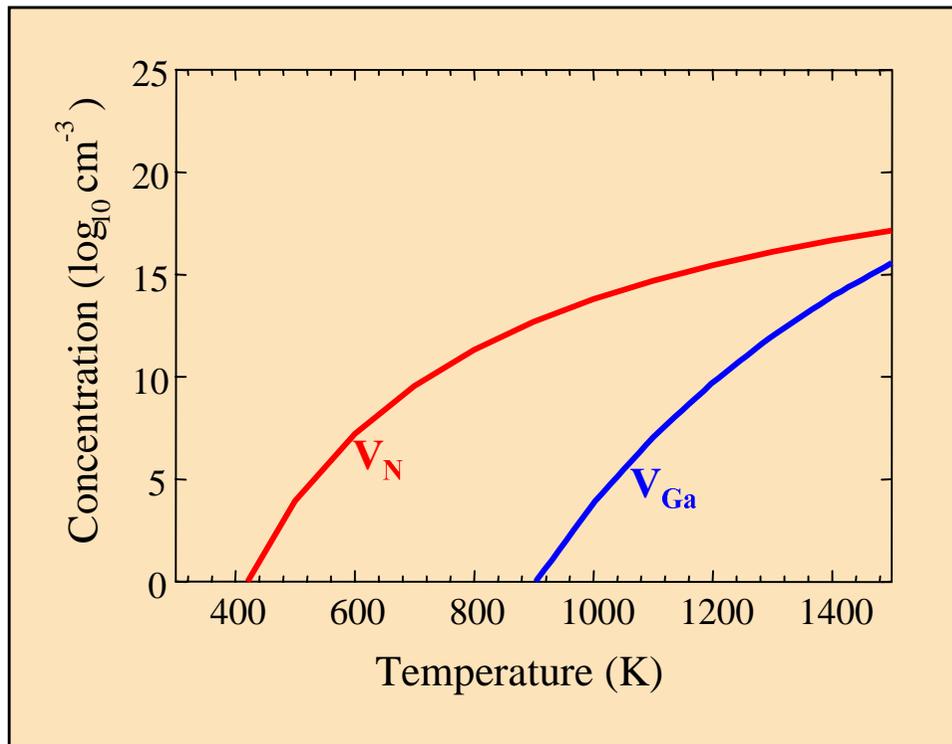


$$D^+ = A^- + n$$

partial compensation

Defect concentrations

Thermodynamic equilibrium: $n_{Defekt} = N_{sites} \exp\left(-\frac{E_D}{kT}\right)$

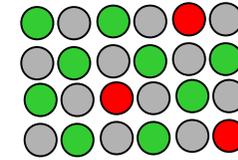


- Defect/impurity concentration directly accessible:
- All relevant effects included (compensation, doping efficiency, solubility)

Example: Alloys

Free energy of an alloy $A_{1-x}B_xC$:

$$F(x, T) = \Delta H_0(x) - TS(x)$$



Total energy difference (>0)

$$\Delta H_0(x) = H_{A_{1-x}B_xC} - (1-x)H_{AC} - xH_{BC}$$

drives segregation

mainly configurational entropy

$$S = -k[x \ln x + (1-x) \ln(1-x)]$$

drives alloying

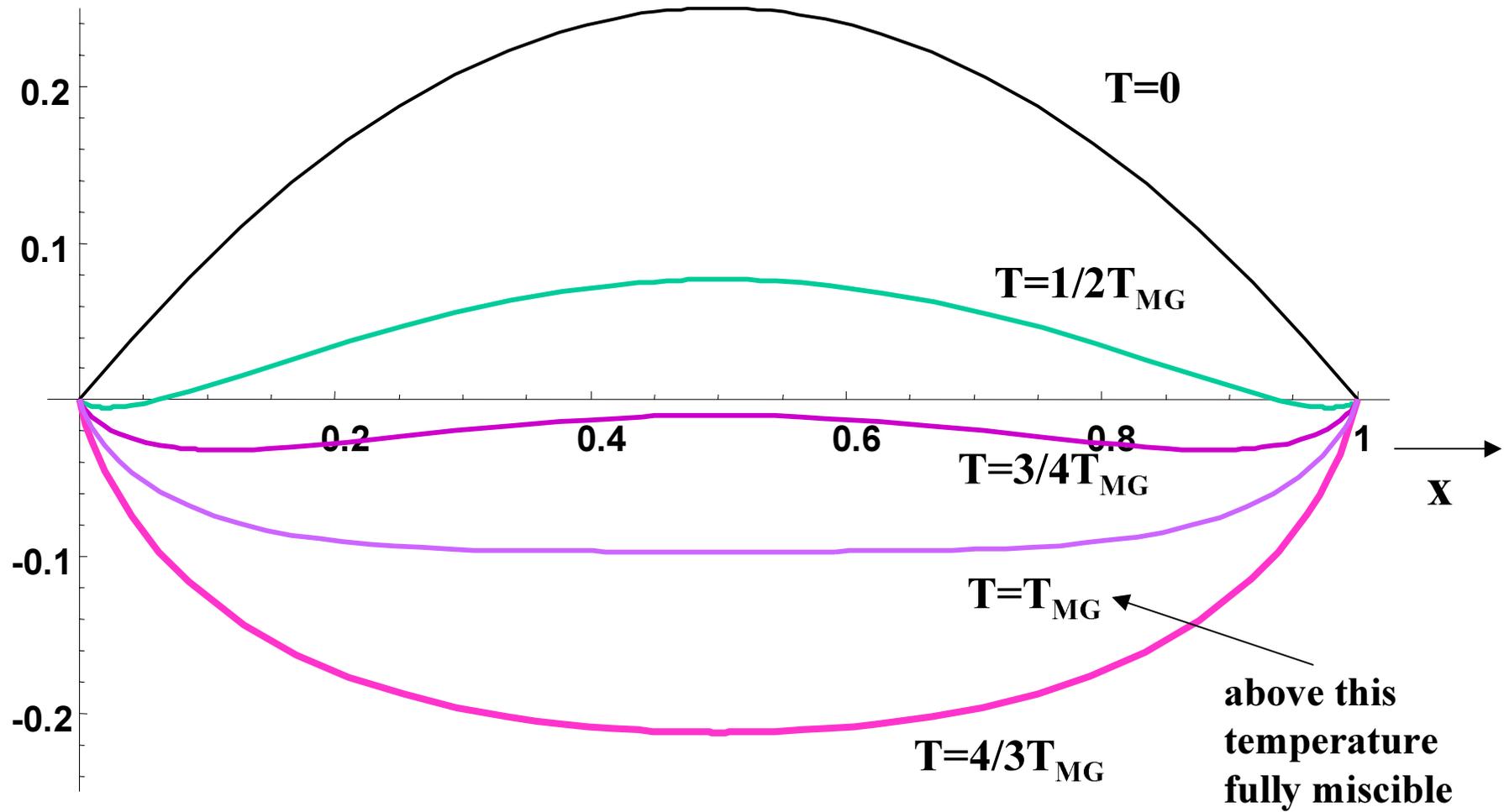
Alloys are thermodynamically unstable at $T=0K$ (phase segregation)!

Assumption: $\Delta H_0(x) = \Omega x(1-x)$

interaction parameter

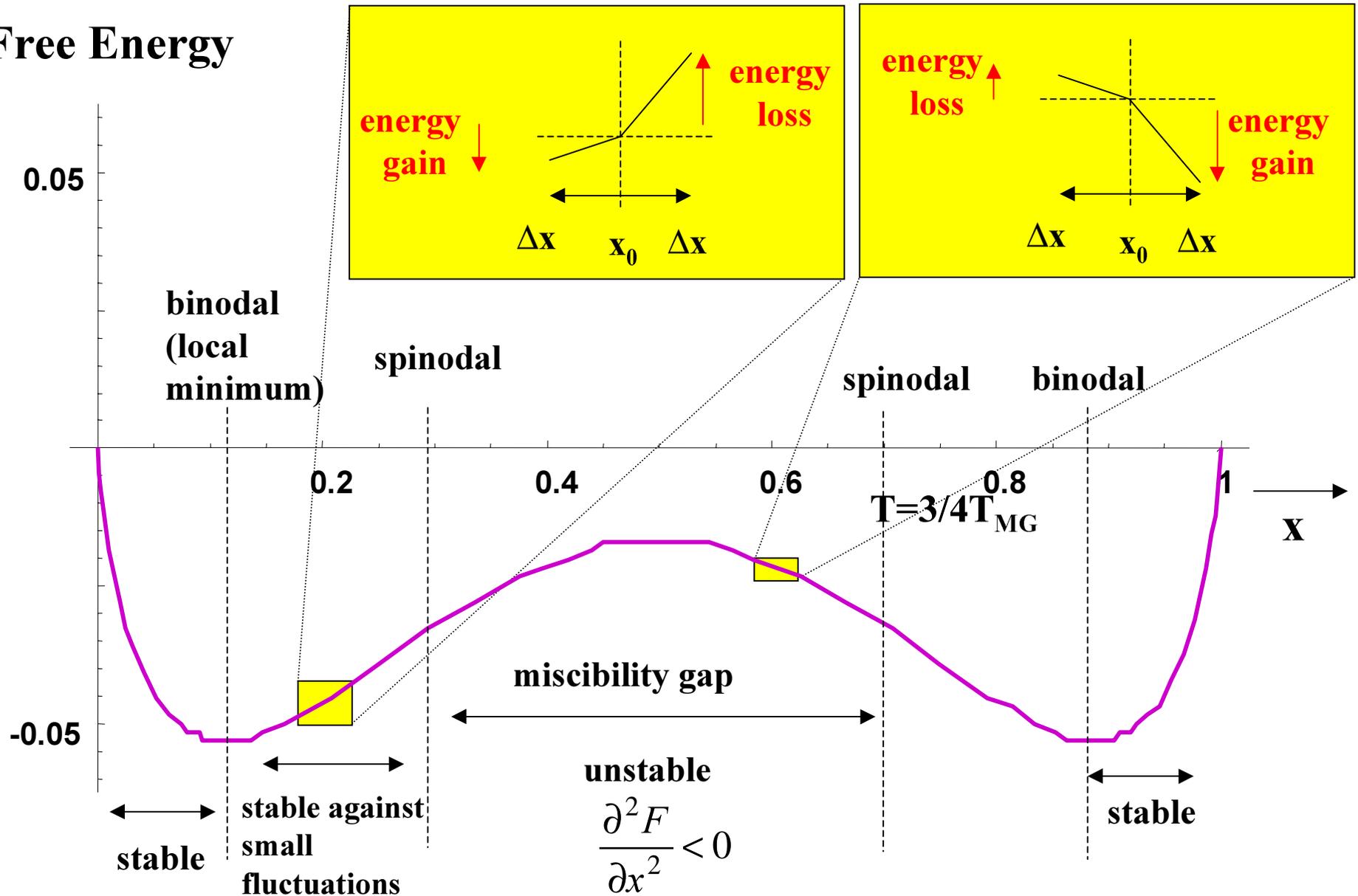
Solubility

Free Energy



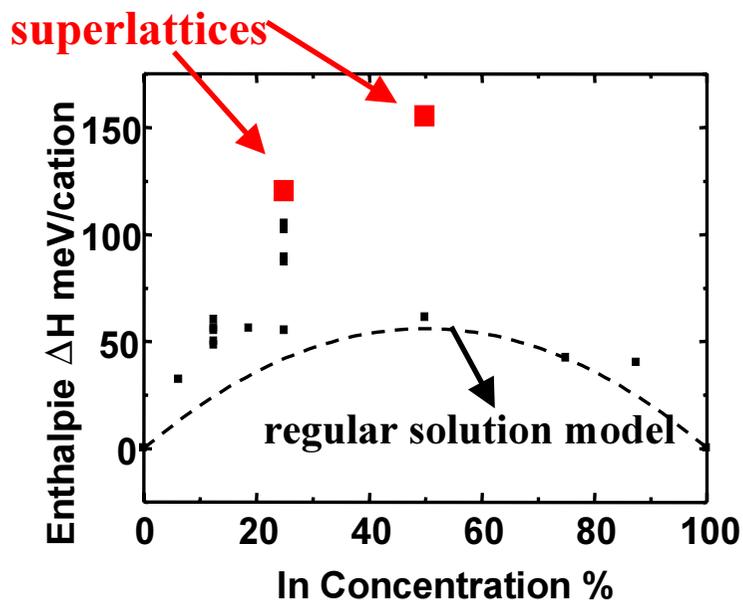
Discussion

Free Energy



InGaN alloys: Phase stability and solubility

Calculated formation enthalpy:



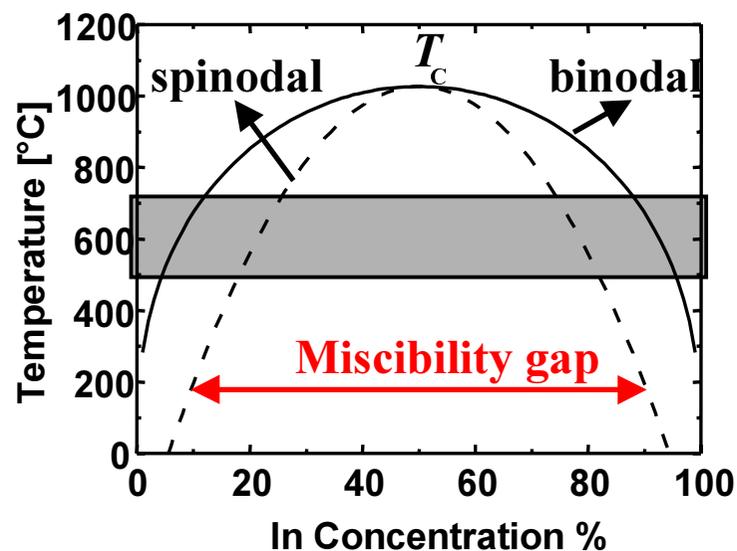
Fit to the **regular solution model**:

$$\Delta H = \Omega x(1-x)$$

⇒ **Interaction parameter $\Omega = 242$ meV**

Phase diagram:

(Assumption: regular solution model)



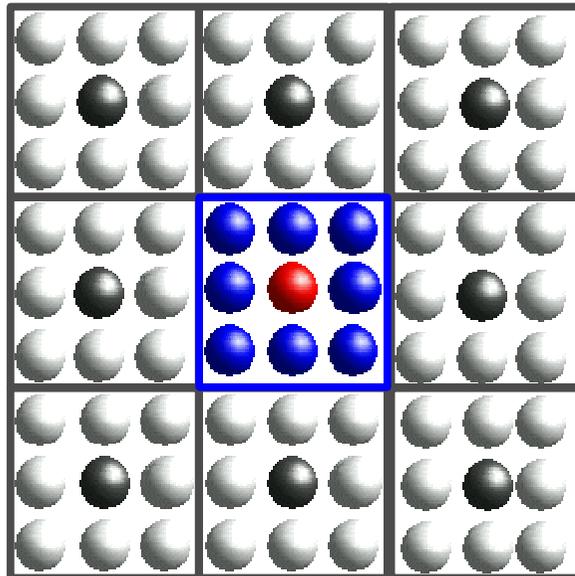
Critical temperature:

$$T_c = 1030 \text{ }^\circ\text{C}$$

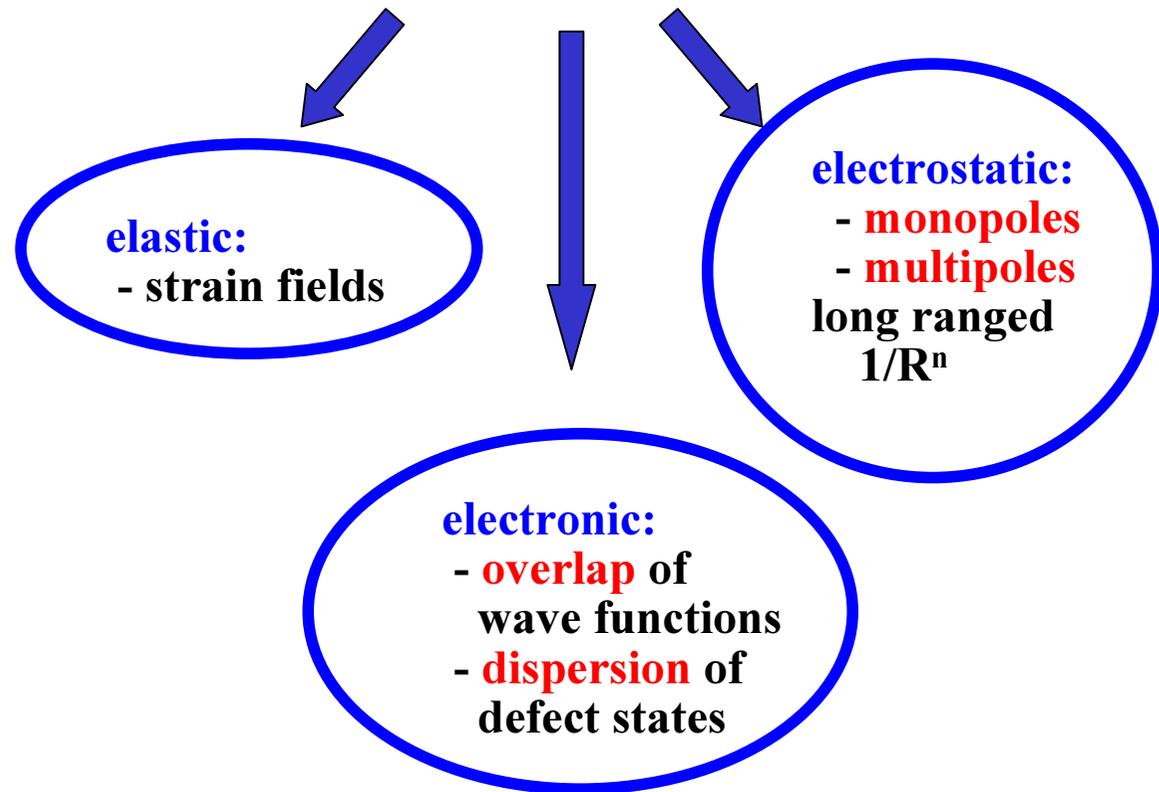
⇒ **Solubility at typical growth temperatures below 10 %!**

Convergence aspects for defect calculations

Periodic boundary conditions



⇒ interaction across cell boundaries:

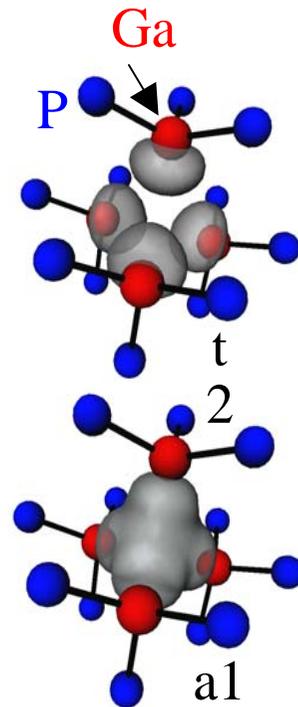
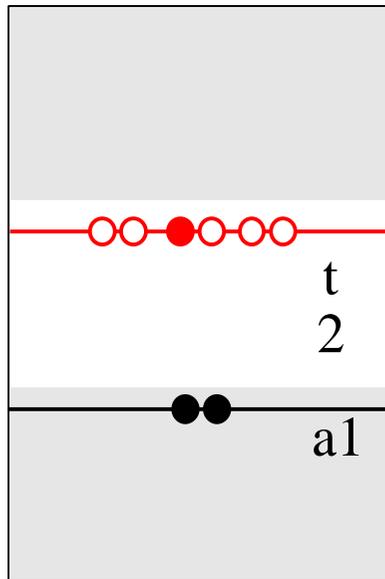


- all physical quantities converge with increasing cell size
- error estimation and reduction for 'small' cells is highly desirable

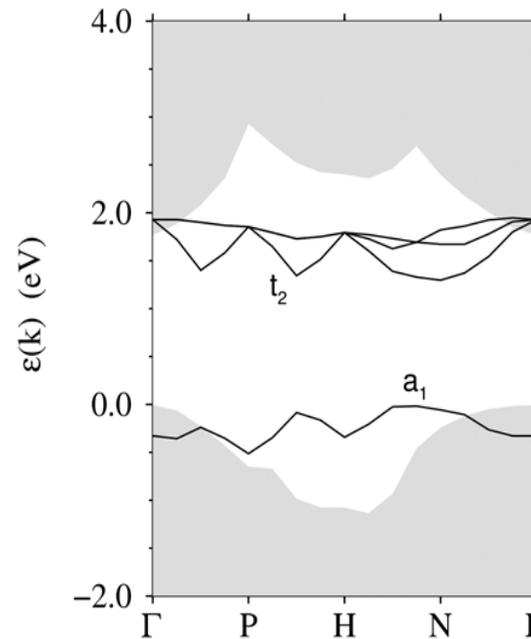
Electronic effects (I)

Example: Neutral GaP P-Vacancy:

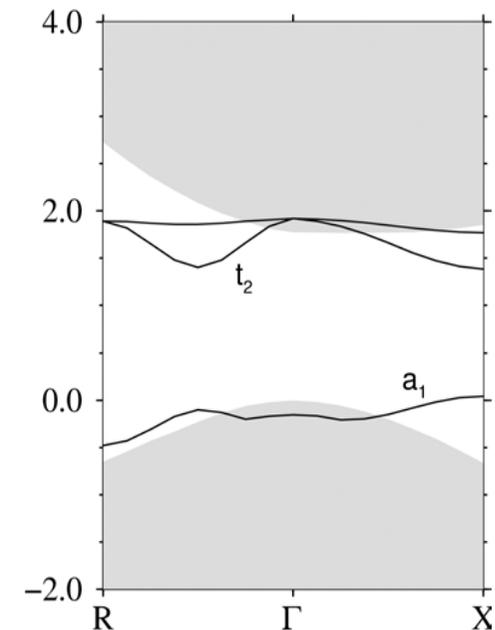
ideal P-vac. [1]



32-atom bcc cell



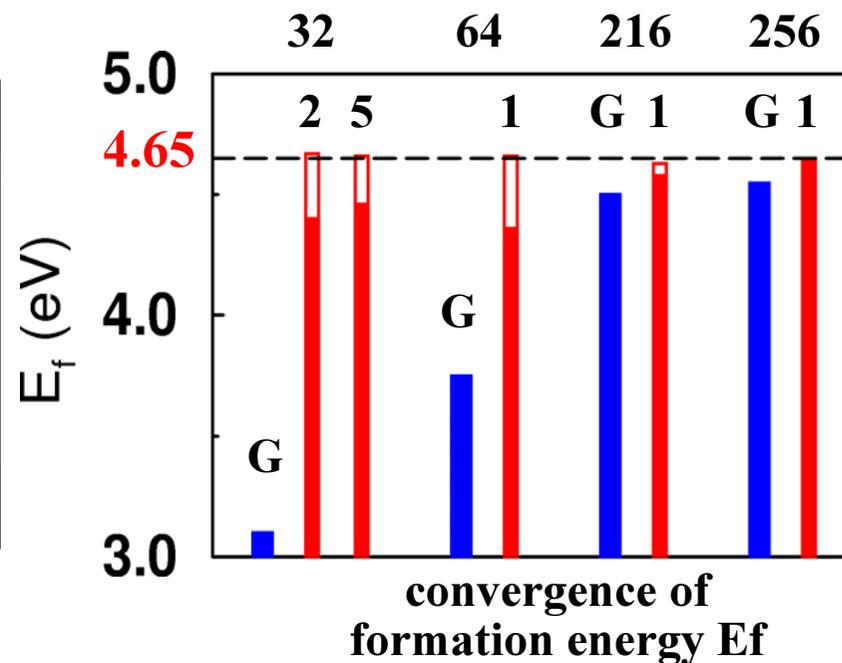
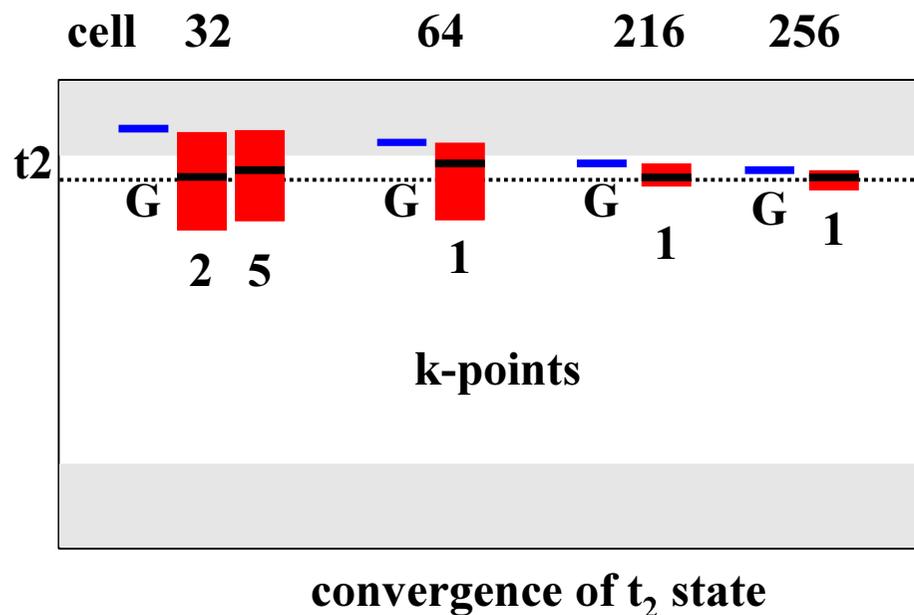
64-atom sc cell



- large dispersion due to defect-defect interaction
- unphysical splitting of degenerate t2 defect state

Electronic effects (II)

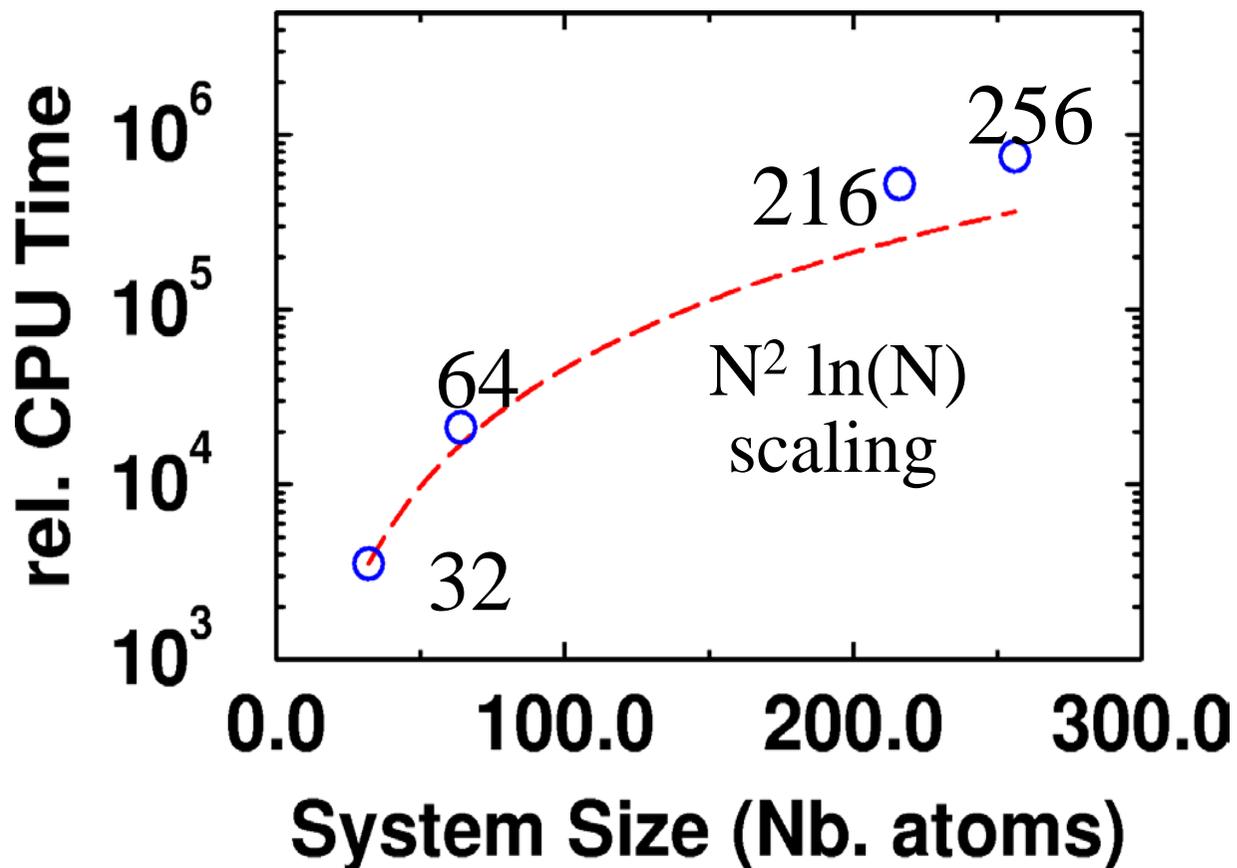
Convergence Tests: Cell Size and k-Points
Example: Neutral Ideal GaP P-Vacancy



- slow convergence of defect state and energy at the Γ point
- average over special k-points converges significantly faster (error < 0.02eV)

Relative CPU Time Consumption

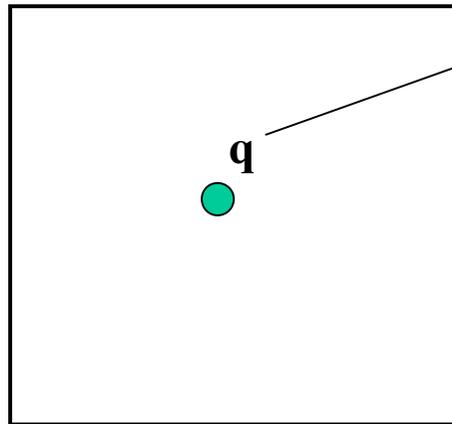
Example: Neutral GaP P-Vacancy



By a proper treatment of defects in supercells more than two orders of magnitude in CPU time can be saved!

Calculating charged defects

Charged defect in an infinite cell

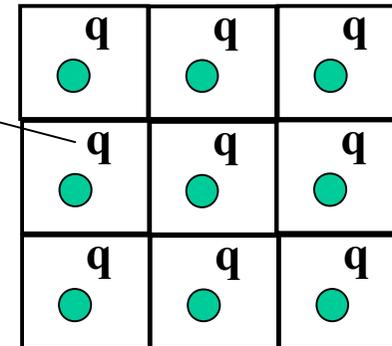


asymptotic behavior:

$$V \propto \frac{q}{\epsilon\epsilon_0 r}$$

screened Coulomb potential

Charged defect in a supercell



electrostatic potential

$$V^{Hartree} \propto \frac{\rho(G)}{|G|^2}$$

$$\rho(G=0) = \int_{\Omega} \rho(\vec{r}) d\vec{r}$$

For non-neutral systems the $G=0$ component of the potential diverges

($V^{Hartree}$ ill defined!)

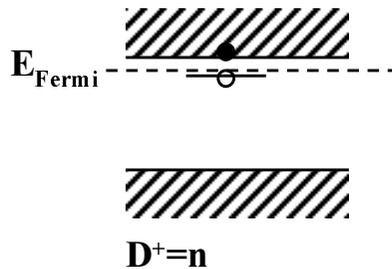
\Rightarrow supercell must be always charge neutral!

Charge compensation

How to realize a charge neutral supercell?

⇒ Look at nature!

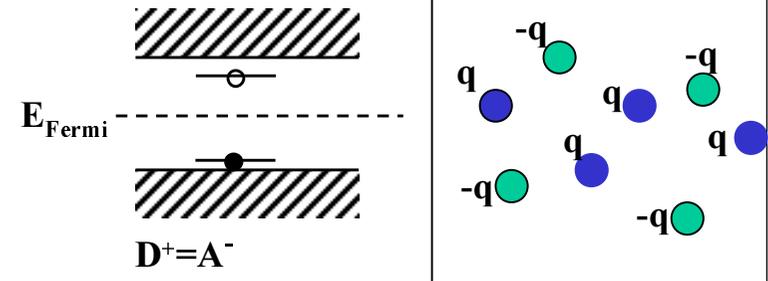
Example: Donor



Transfer electron from donor level to bottom of conduction band



delocalized state



Transfer electron from donor acceptor level

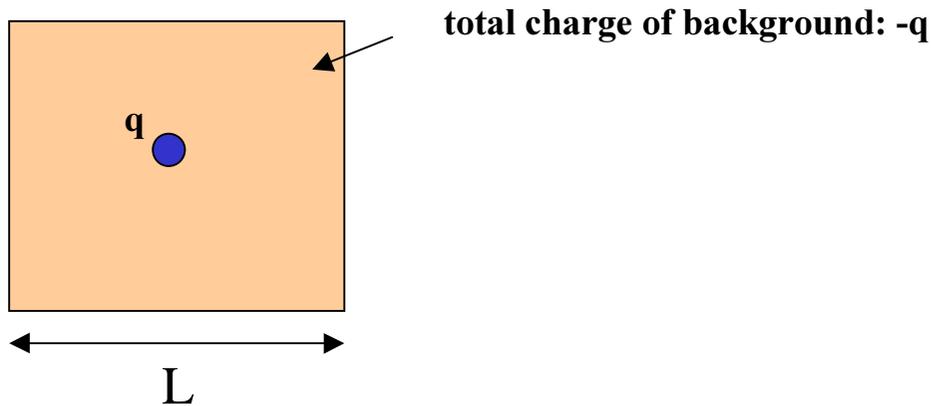


statistically homogeneous distribution

first approximation: constant background [set $V^{\text{Hartree}}(\mathbf{G}=0) = 0$]

Compensation by constant background

Problem: Slow convergence with supercell size



$$\Delta E = -\frac{q^2 \alpha}{2\epsilon L}$$
$$\alpha = 2.84$$

Electrostatic interaction between charged defects in neighboring supercells:

$$E \propto \frac{q^2}{\epsilon L}$$

ϵ bulk dielectric constant

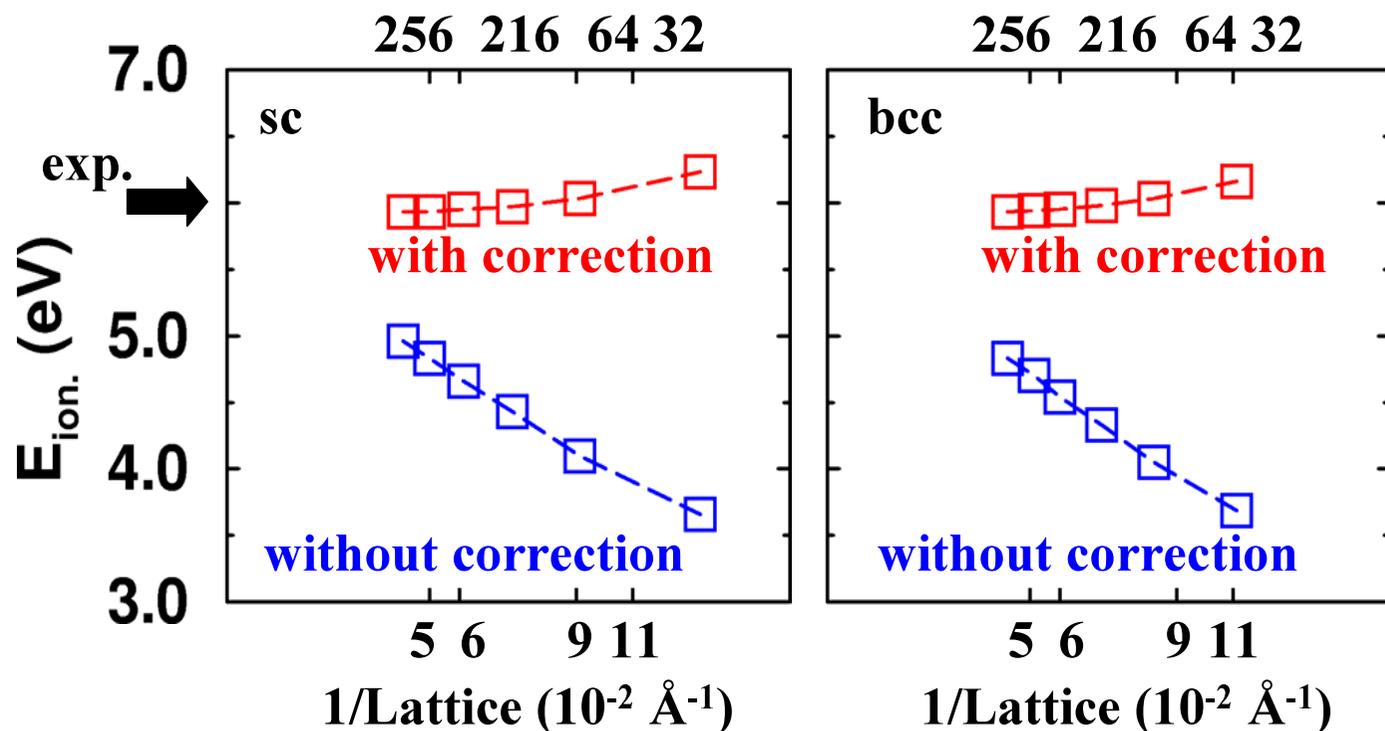
Defect-defect interaction vanishes asymptotically like $1/L$!

Suggestion (Ref. [1]): Correct explicitly for this error

\Rightarrow subtract it from total energy

Example: First ionization energy of an atom

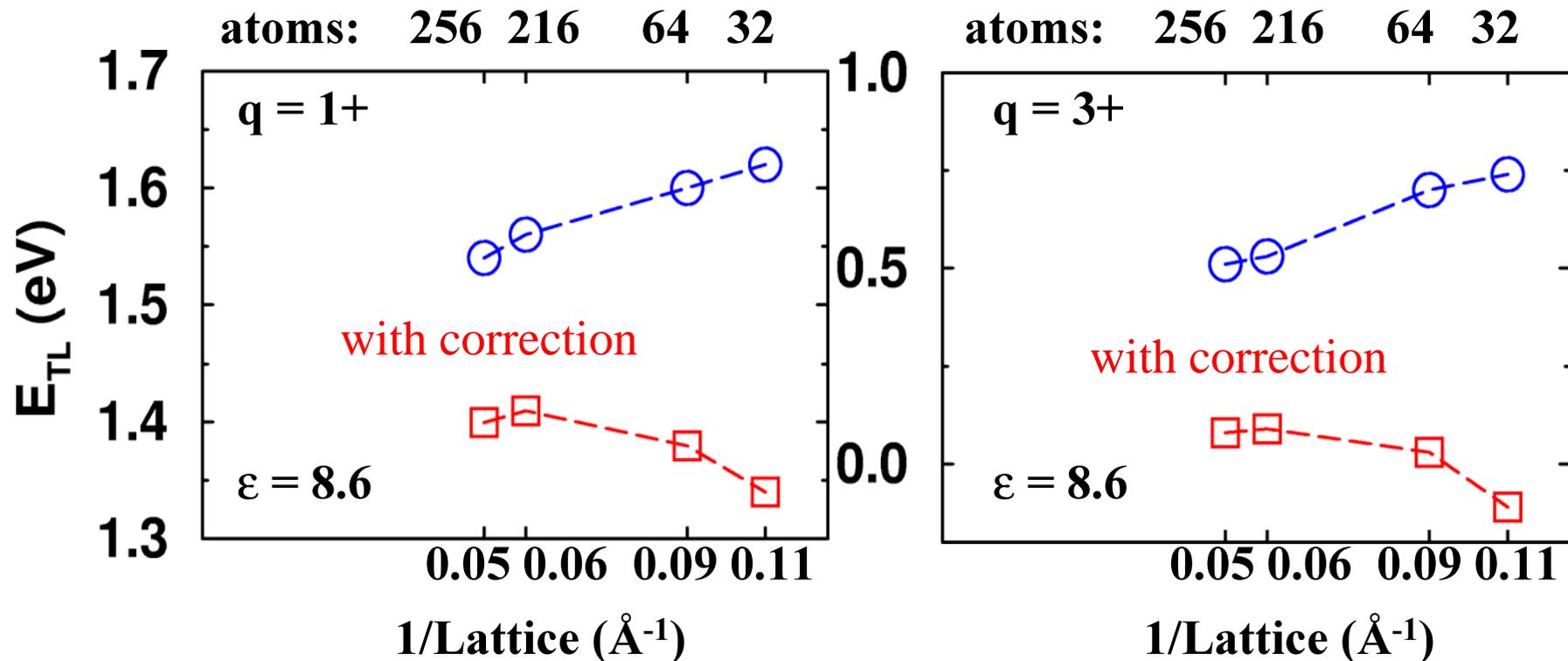
System: Ga Atom in Cubic Cells



Makov/Payne correction significantly improves convergence with respect to supercell size for this system!

Example: Positively Charged Vacancy

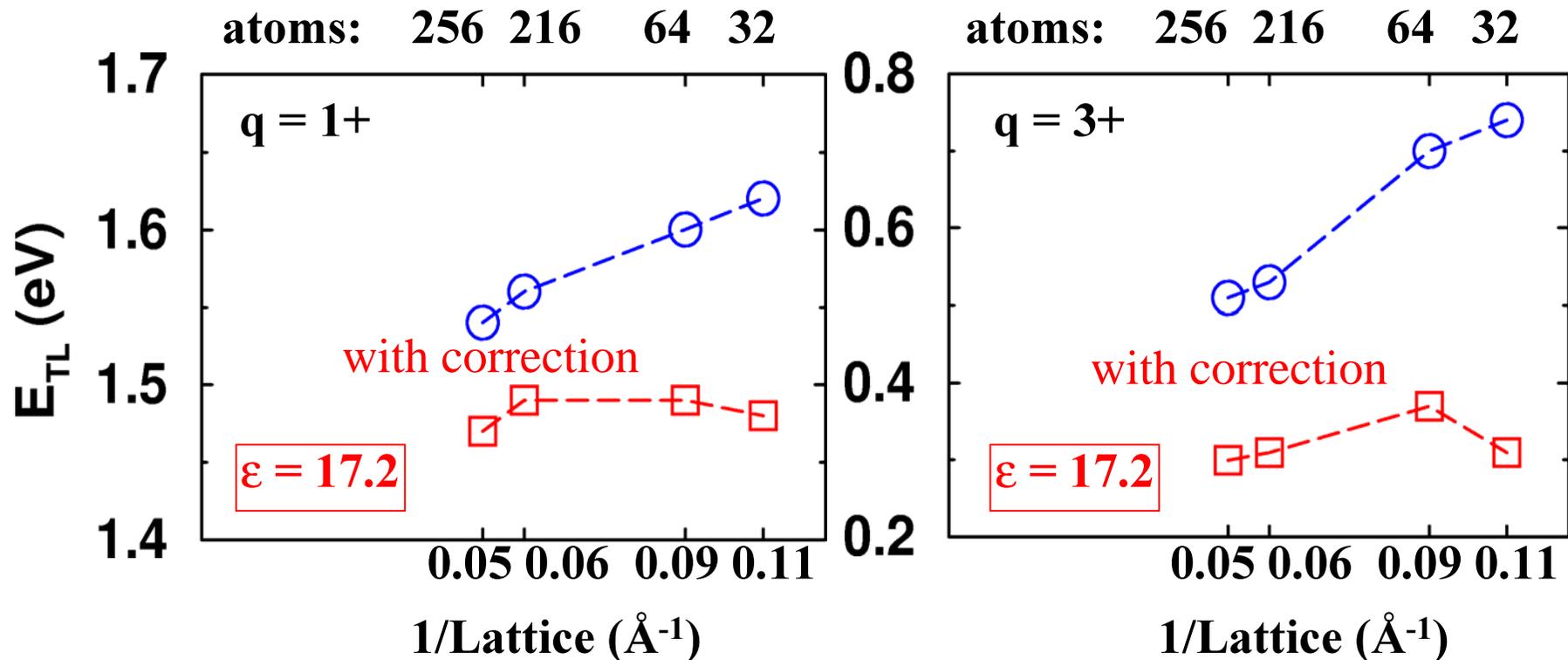
Charge Transfer Level ETL for 1+ and 3+



Makov/Payne correction overestimates the error!
Problem: bulk dielectric constant not appropriate
 \Rightarrow enhanced screening around defect

Example: Positively Charged Vacancy

Charge Transfer Level ETL for 1+ and 3+



Assumption of enhanced screening leads to faster convergence!

Problem: How to determine “effective” dielectric constant?

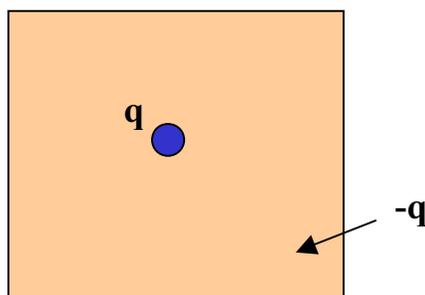
⇒ better approaches needed!

Alternative compensation schemes

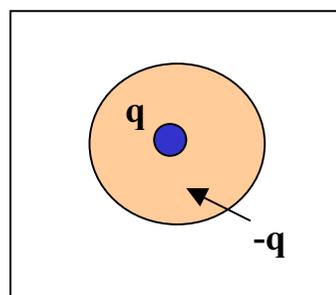
Idea: Use localized compensation charge

⇒ electrostatic interaction of neutral objects between supercells

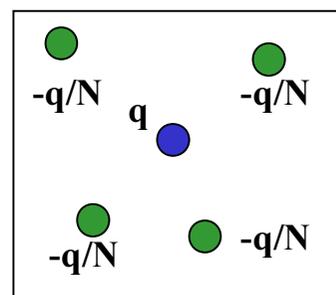
constant background



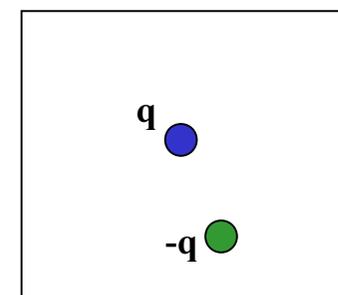
Gauss sphere



“virtual” donors



“real” donor/acceptor



**Create new pseudopotential
with $Z_{\text{virtual}} = Z + q/N$
replace N original atoms by
the new pseudopotential**

fastest convergence!

More localized compensation charges lead to a better convergence with supercell size!