Modelling of charged point defects with density-functional theory

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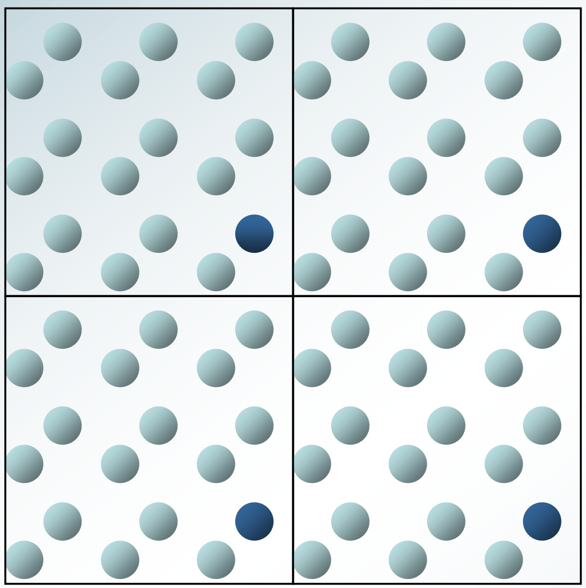
Models and Data on Plasma-Material Interactions 2019
June 18, 2019

Point defects

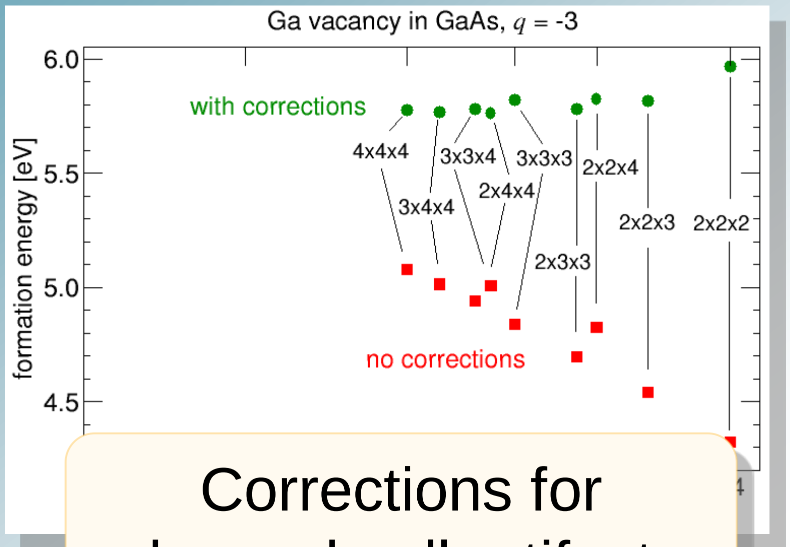
- Point defects (dopants, impurities, vacancies, interstitials, …) critical for semiconductor & insulator properties
- Low concentrations (10^{16}-10^{20} cm^{-3} ≈10^{-6} – 10^{-2} relative)
- Important insights from theory & calculations



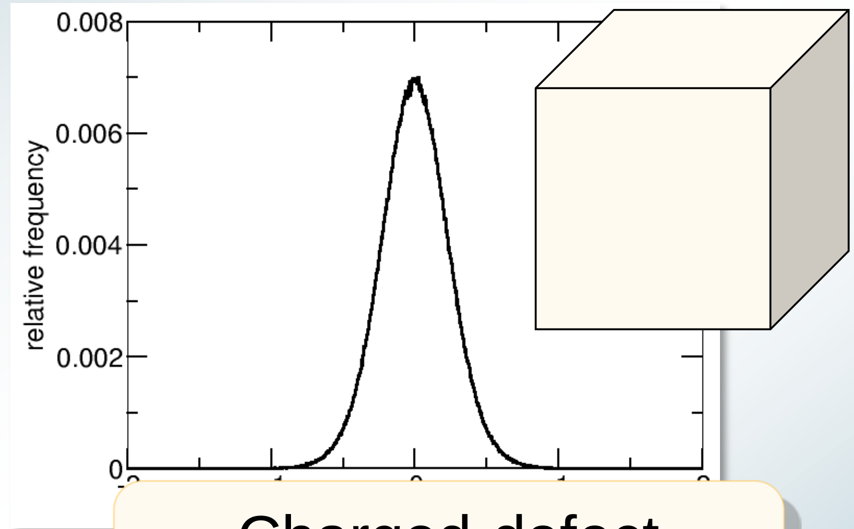
Theoretical modelling is challenging

- Supercell approach
- Defect-defect interactions
- Advanced electronic structure methods (beyond standard DFT, i.e. hybrid functionals, GW, QMC)

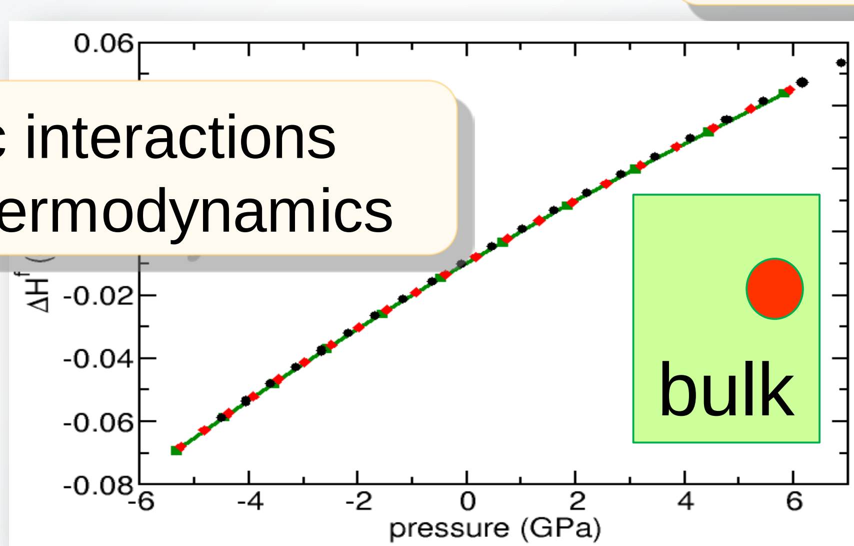
How should we deal with defect-defect interactions?



Corrections for charged-cell artifacts

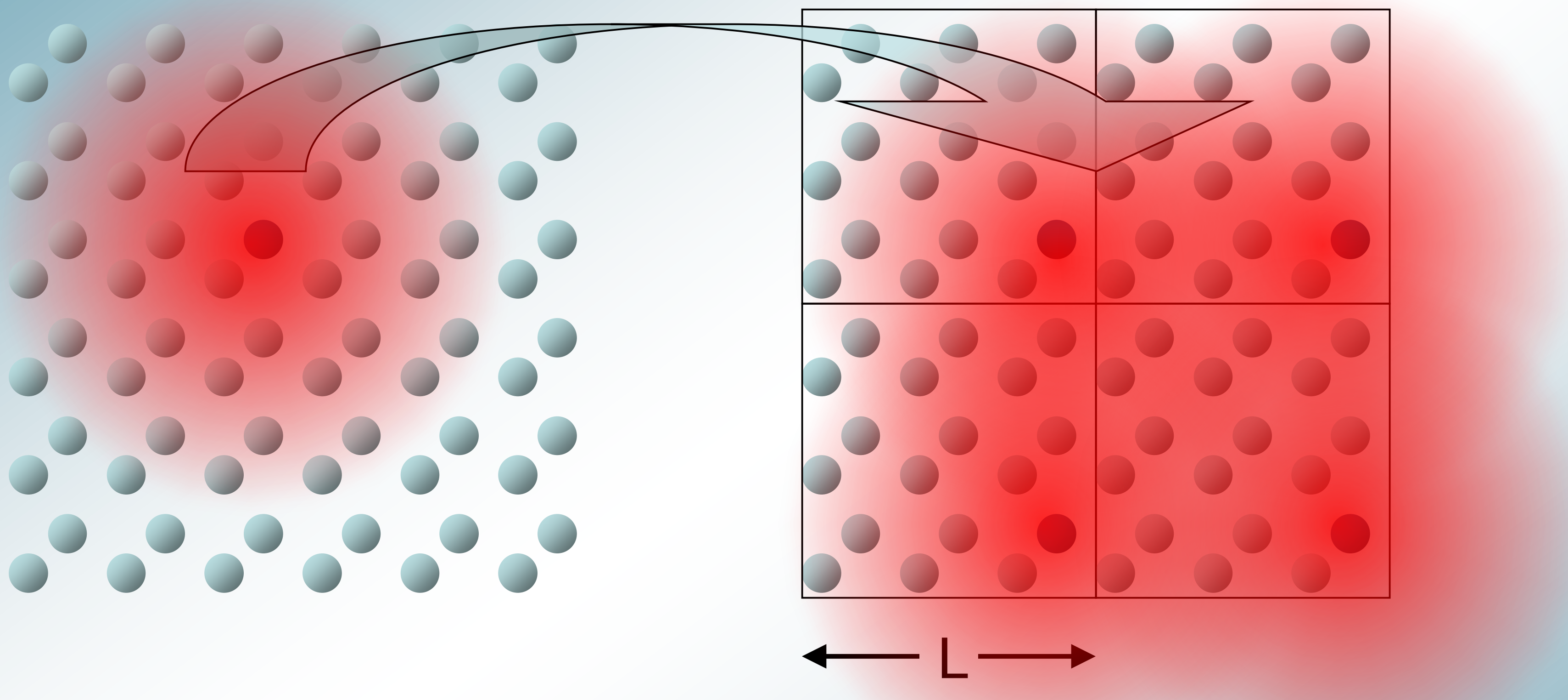


Charged-defect interactions at scale



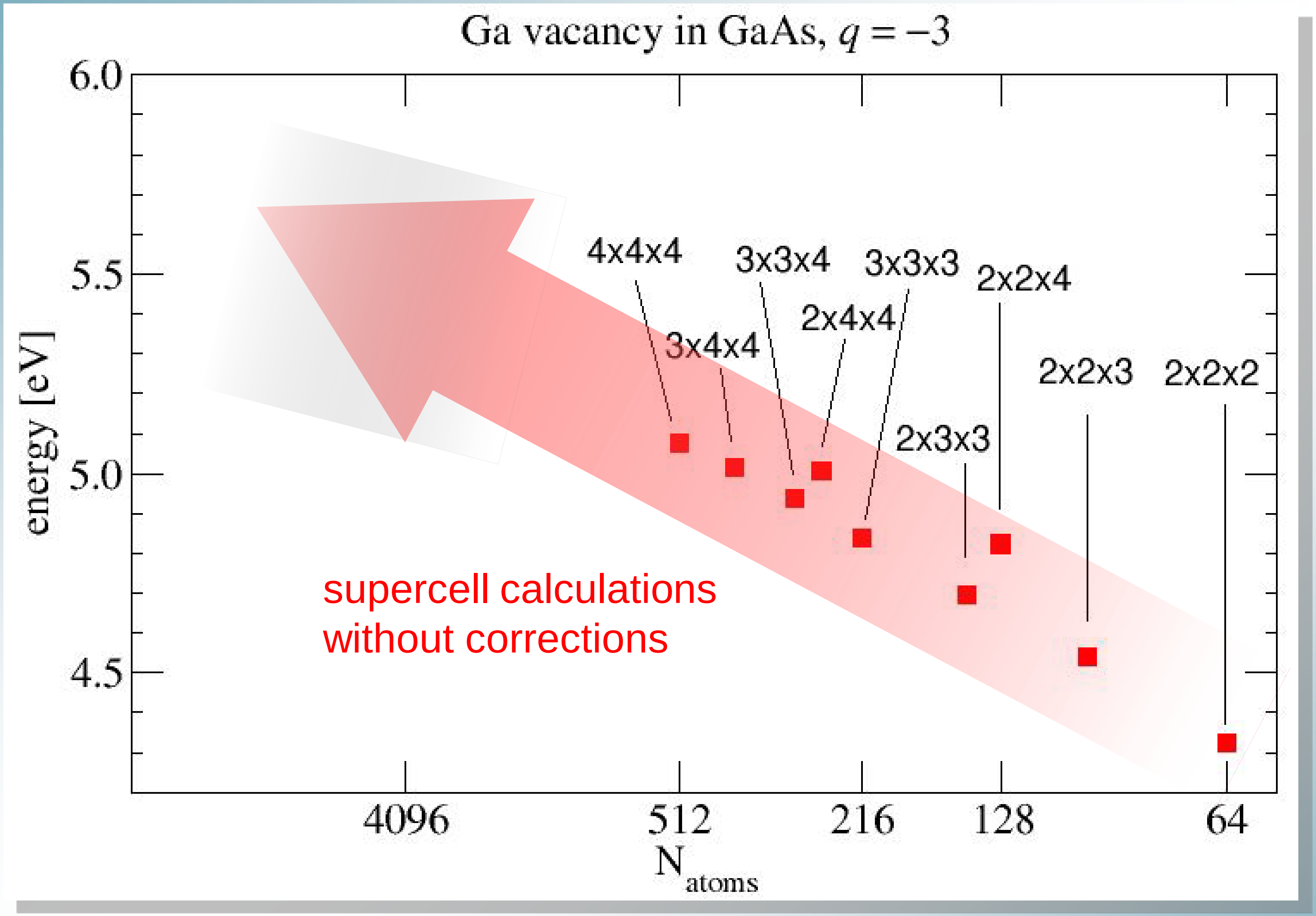
Elastic interactions within thermodynamics

Supercell calculations

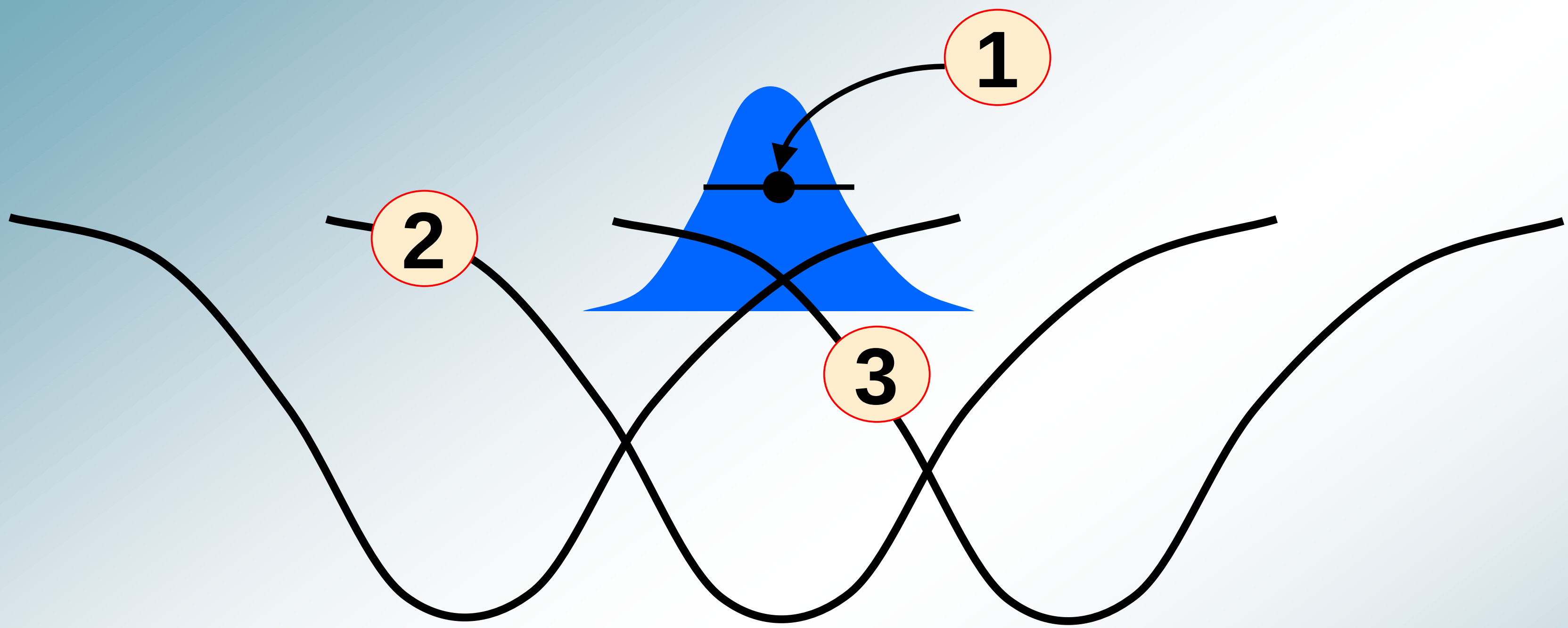


- Wave function overlap (decay $e^{-\alpha r}$) → **k**-integration
- Strain (decay $1/r^3$) → often small
- Coulomb interactions (decay $1/r$) → ?

Slow supercell convergence



DFT-LDA, norm-conserving PP, no ionic relaxation (=no strain)

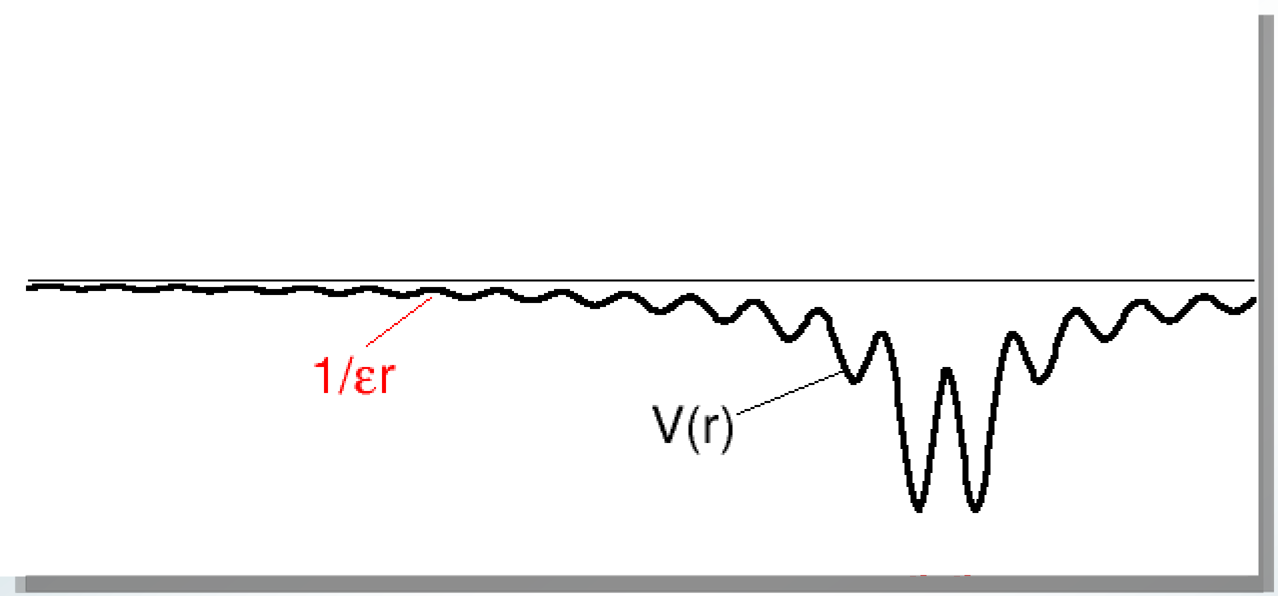


Three-step process

1. add N electrons to defect state — bare charge $q(\mathbf{r}) = -Ne|\psi(\mathbf{r})|^2$
2. relax other electrons — change in potential $\Delta V(\mathbf{r})$
3. Introduce periodicity +background — periodic potential $\Delta\tilde{V}(\mathbf{r})$

CF, J. Neugebauer, C.G. Van de Walle, PRL **102**, 016402 (2009).

Long-range treatment

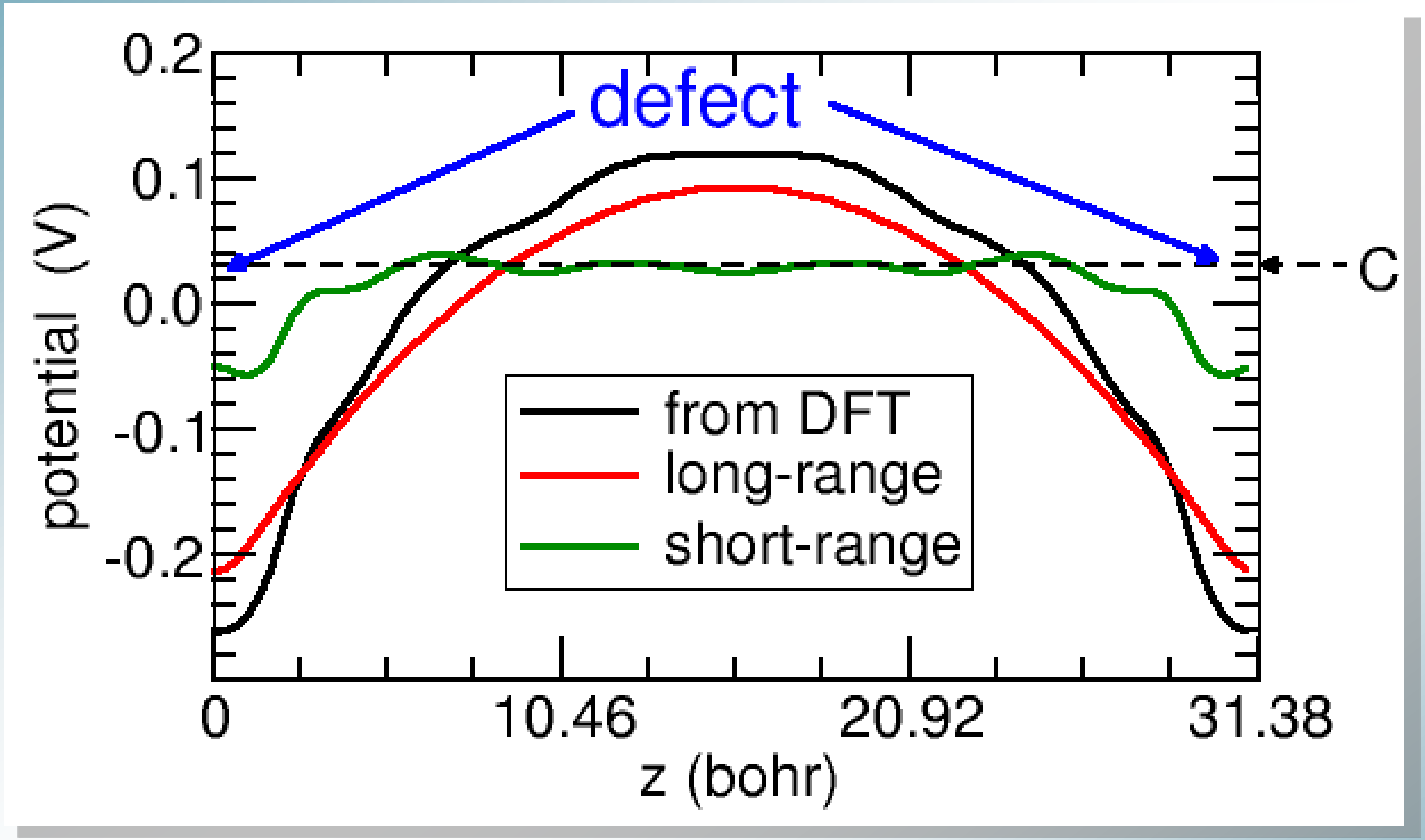


$$V(\mathbf{r}) = V^{\mathrm{lr}}(\mathbf{r}) + V^{\mathrm{sr}}(\mathbf{r})$$

$$V^{\mathrm{lr}}(\mathbf{r}) = \int d^3\mathbf{r}' \frac{q^{\mathrm{model}}(\mathbf{r}')}{\varepsilon|\mathbf{r}-\mathbf{r}'|}$$

$$V^{\mathrm{sr}}(\mathbf{r}) = \Delta\tilde{V}^{\mathrm{DFT}}(\mathbf{r}) - \tilde{V}^{\mathrm{lr}}(\mathbf{r}) - C$$

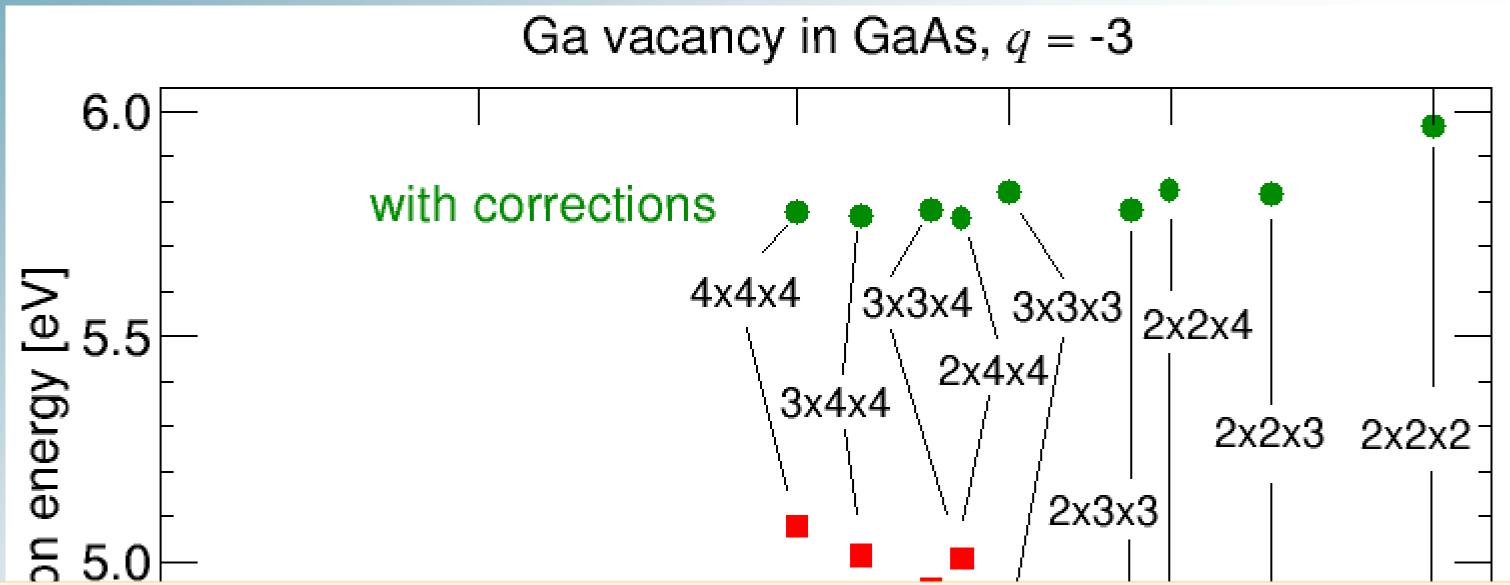
Short-range effects



$$V^{\mathrm{sr}}(\mathbf{r}) = \Delta\tilde{V}^{\mathrm{DFT}}(\mathbf{r}) - \tilde{V}^{\mathrm{lr}}(\mathbf{r}) - C$$

- plateau indicates a successful modelling of long-range effects

-3 Ga vacancy in GaAs (unrelaxed)



bulk: CF, J. Neugebauer, C.G. van de Walle, PRL **102**, 016402 (2009).

sxdefectalign available at https://sxrepo.mpie.de

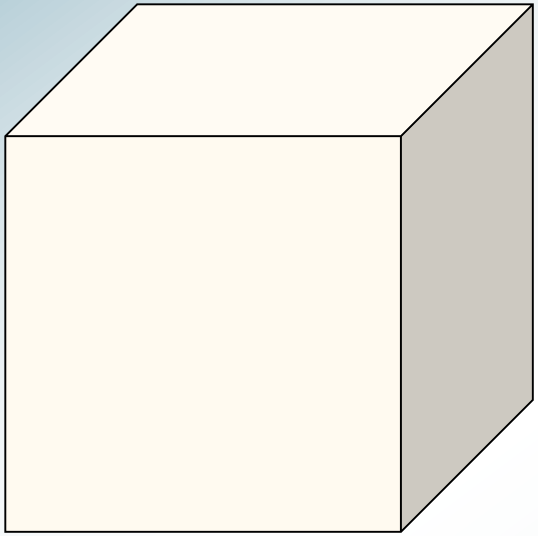
Surfaces, interfaces, 2D materials:
CF, J. Neugebauer, Phys. Rev. B **97**, 205425 (2018).

- Supercell-independent formation energies within 0.1 eV

Real interactions

- Real defects occur at finite concentrations ($10^{-6}..10^{-3}$ relative)
- Random distribution (at high T, low concentration)
- Formation energy will vary from site to site due to interactions

Simulation setup



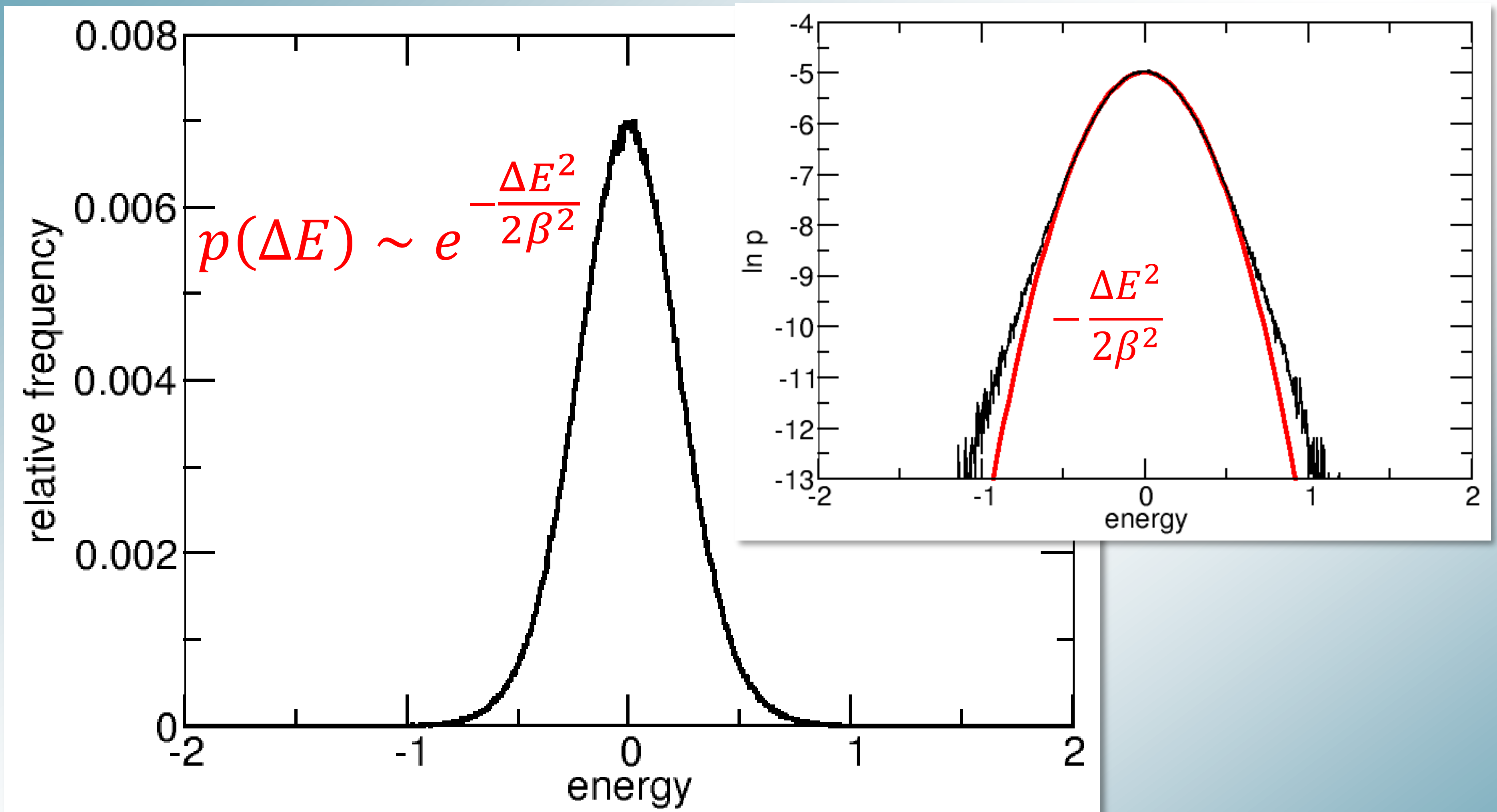
- Fully compensated $c^{+} = c^{-}$
- Randomly distributed charges
- Screening by mobile carriers

$$V(r) = \frac{1}{4\pi\epsilon}\frac{Q}{r}e^{-r/\lambda}$$

- Many realizations (10^{4} -10^{5} sites)
- Collect statistics

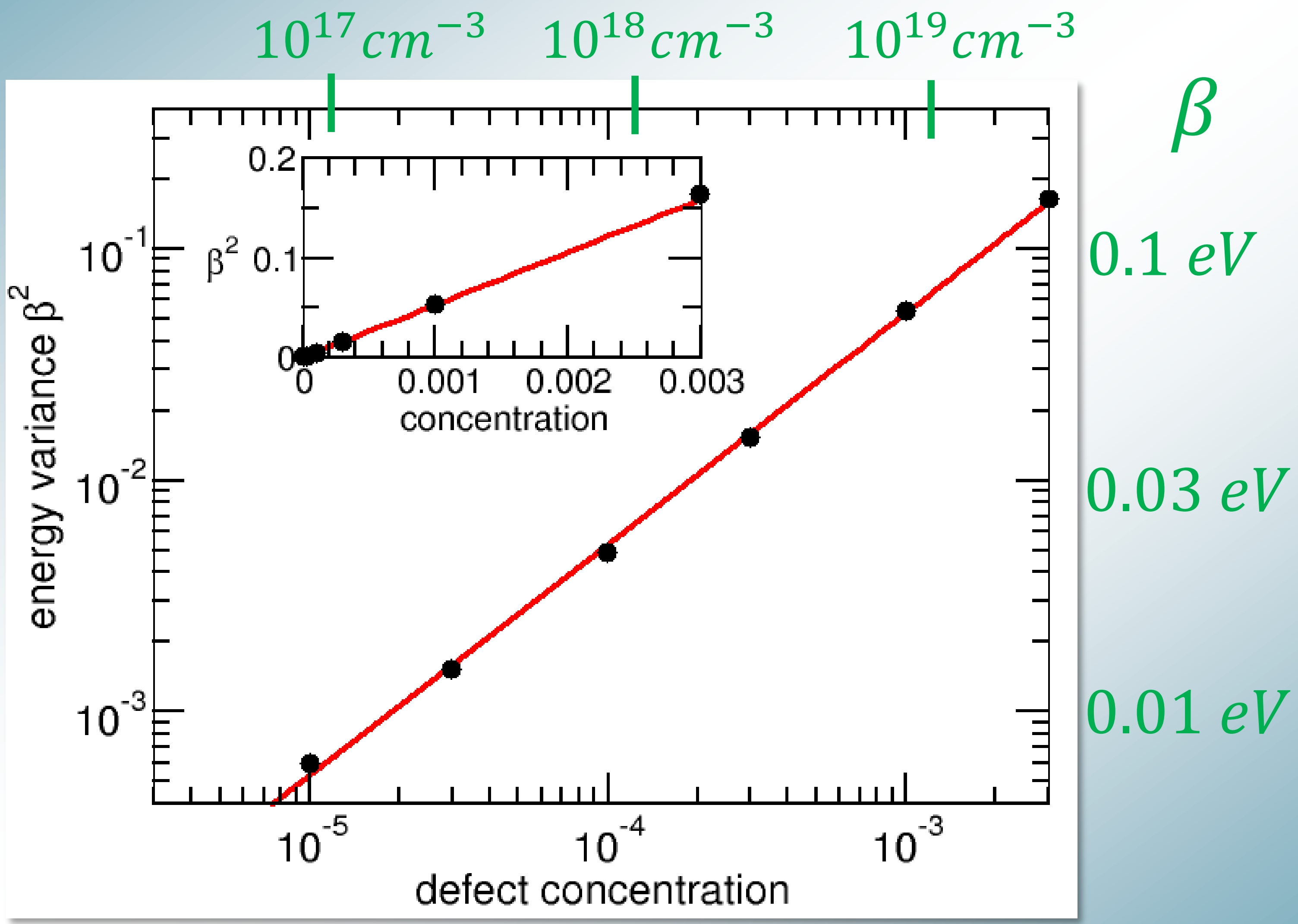
200x200x200 cells (8 million)
periodic boundary conditions

Interactions in random order



Coulomb interaction with randomly distributed defects yields Gaussian-like broadening of formation energy

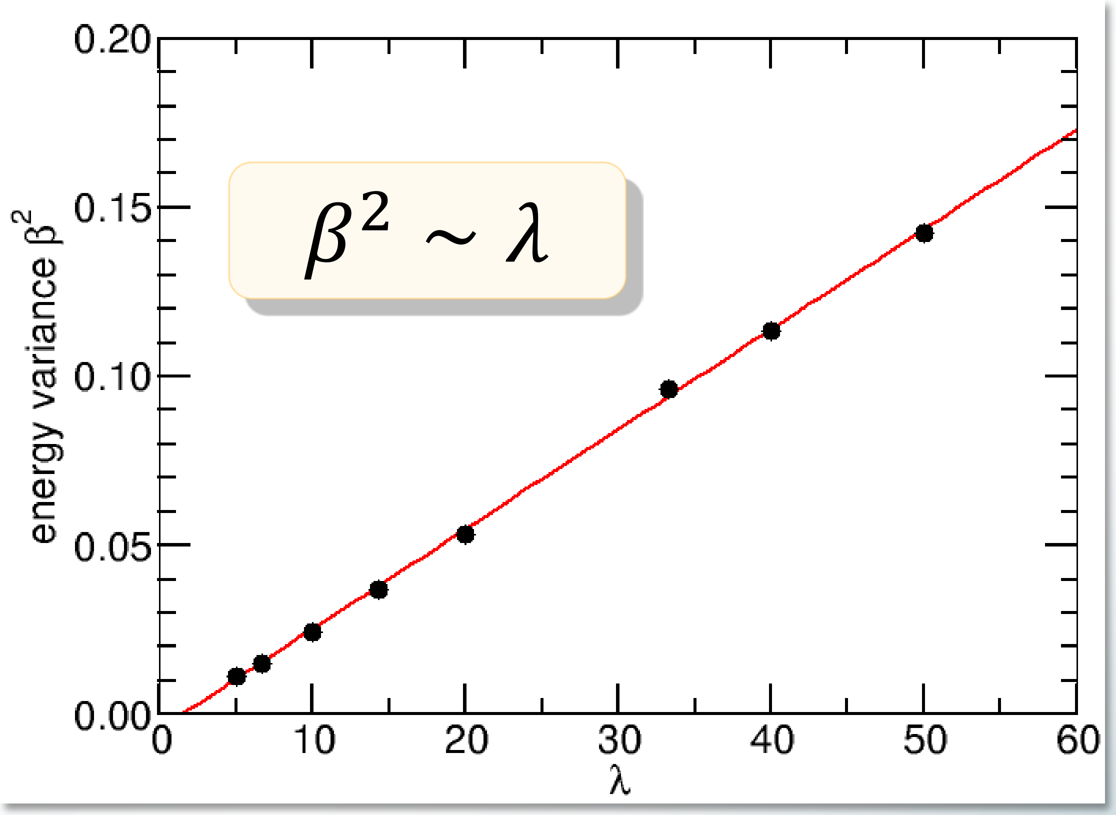
How does broadening change with c?



$$\beta^2 \sim c$$

$a_0 = 0.5\,nm,\ \epsilon = 10\epsilon_0$

How does broadening change with λ?

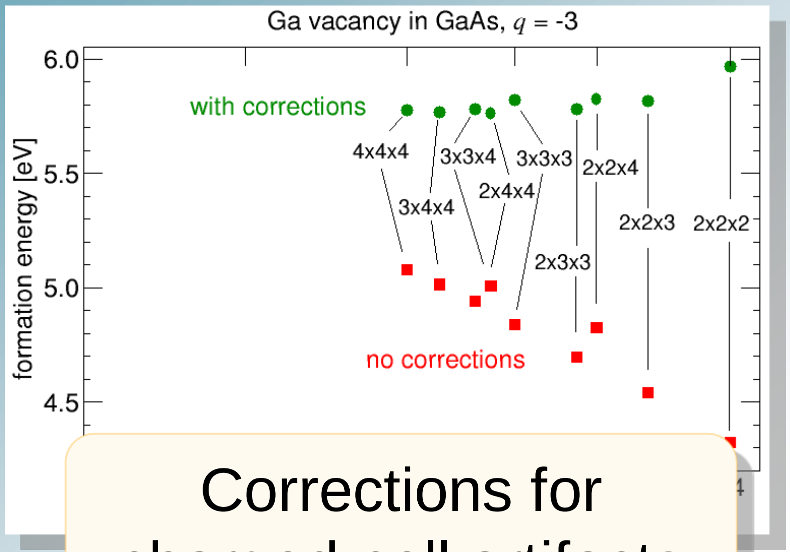


$$\beta^2 \sim \lambda$$

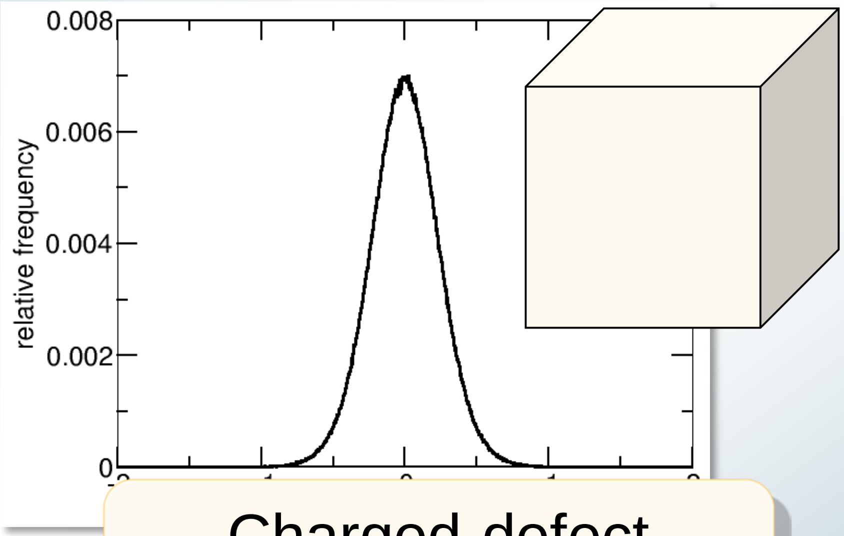
$a_0 = 0.5\,nm,\ \epsilon = 10\epsilon_0,\ \ Q = \pm 1e,\ \ \lambda = 10nm, c = 10^{18}cm^{-3}$

$$p(\Delta E) \sim e^{-\frac{\Delta E^2}{2\beta^2}} \qquad \beta \sim \frac{Q^2}{4\pi\epsilon a_0}\sqrt{c\lambda} \approx 0.03eV$$

Outlook

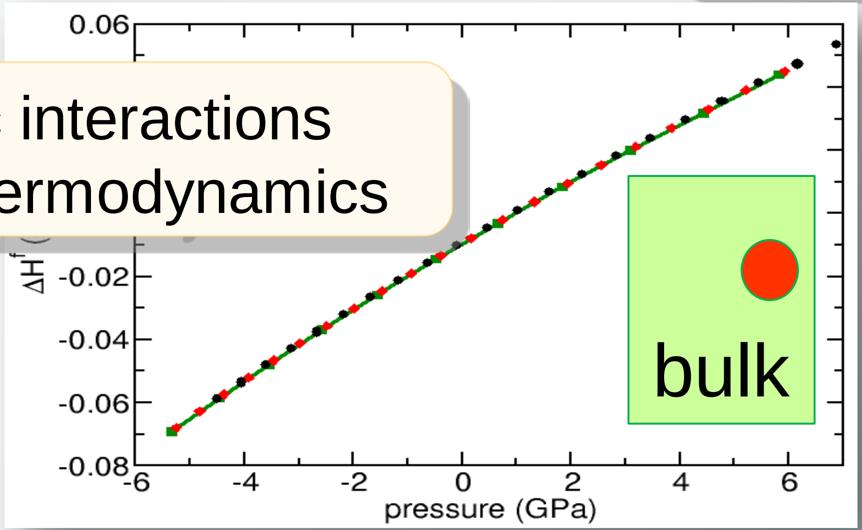


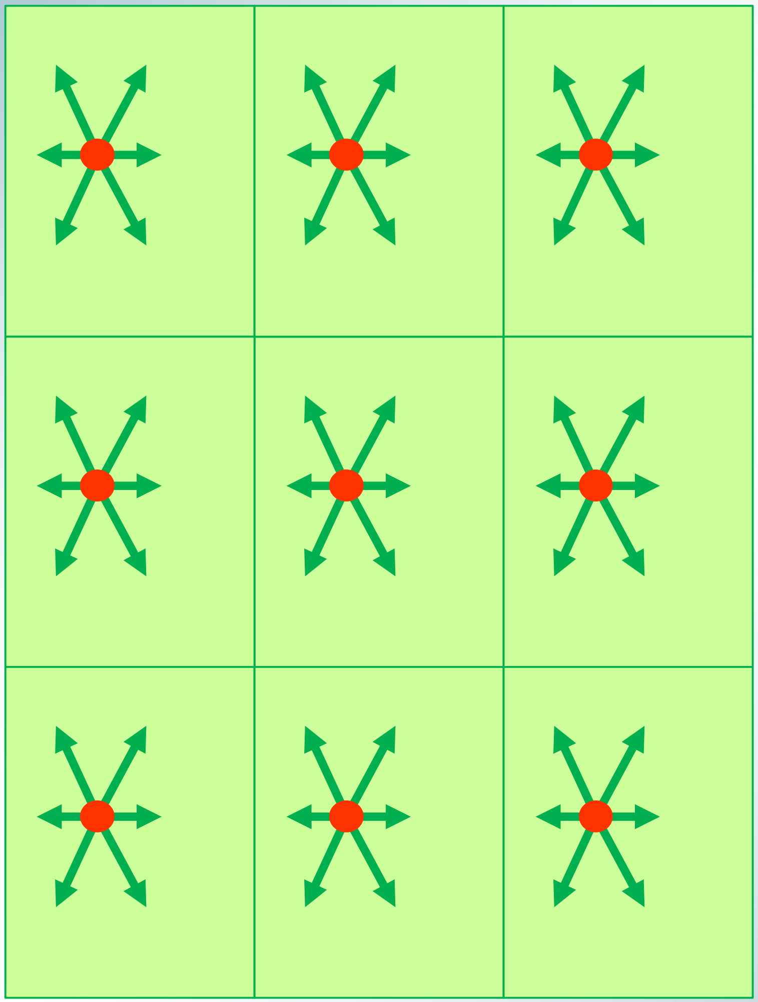
Corrections for charged-cell artifacts



Charged-defect interactions at scale

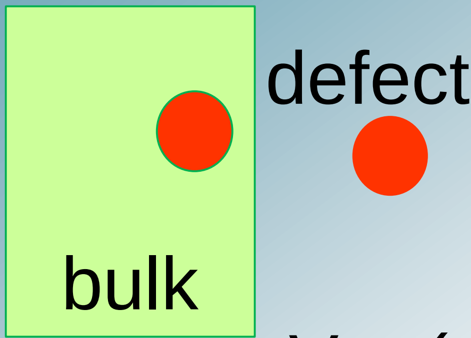
Elastic interactions within thermodynamics





One approach: Lattice Green's function [Tewary, Phys. Rev. B 094109 (2004)].

Thermodynamic view



$$U_{b+d} = U_b + U_d$$
$$V_{b+d} = V_b + V_d$$

$$p = -\frac{\partial U}{\partial V}$$

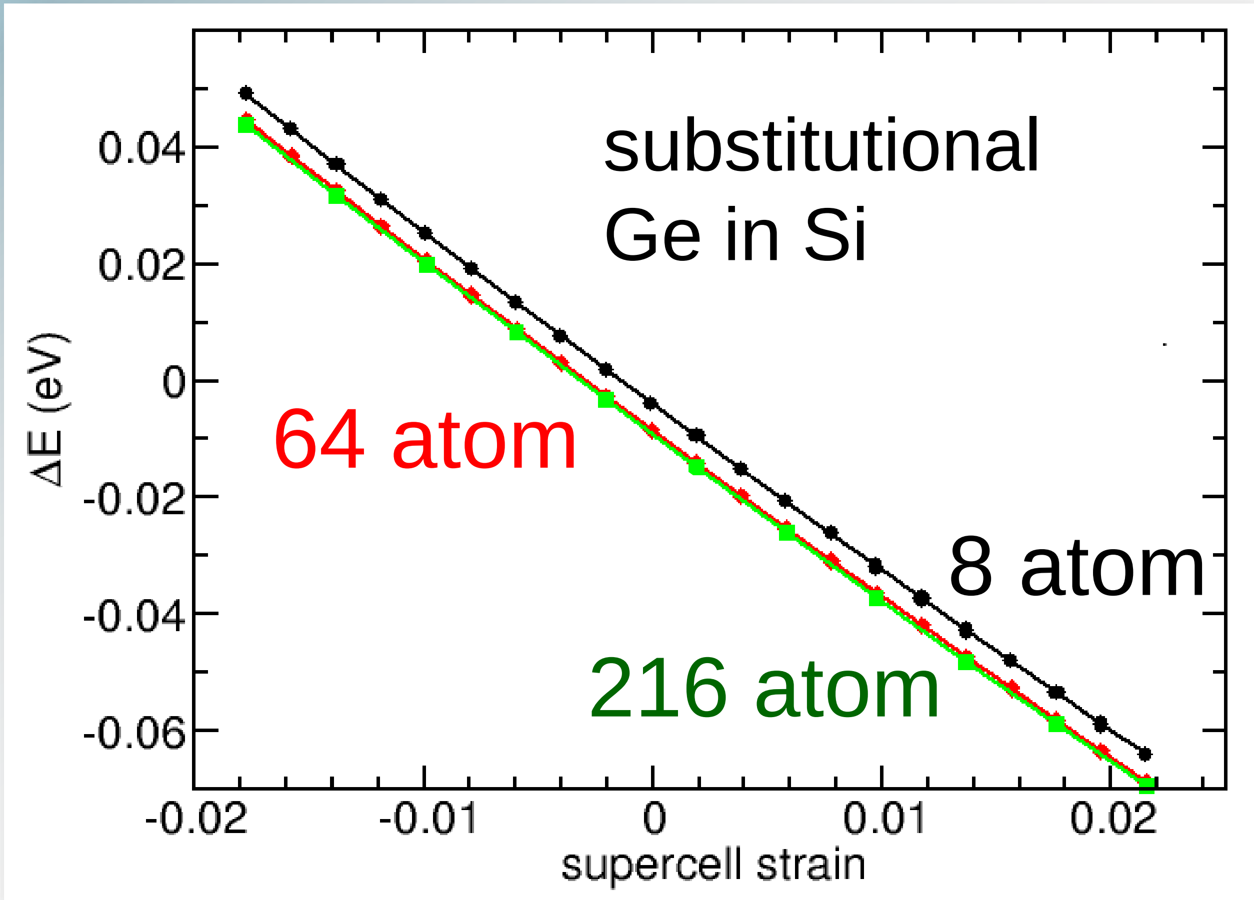
$$V_{b+d}(p) = V_b(p) + V_d(p)$$
$$U_{b+d}(V_{b+d}(p)) = U_b(V_b(p)) + U_d(V_d(p))$$

Enthalpy: $H(p) = U(V) + pV$

$$H_{b+d}(p) = H_b(p) + H_d(p)$$

$$\Delta E = U_{b+d}(V_{b+d}) - U_b(V_{b+d})$$

ΔE at constant volume



ΔE at constant volume converges to formation enthalpy ΔH^f

Get ΔU^f, ΔH^f, ΔV^{rel} from DFT

$$-\frac{\partial}{\partial V}$$

$$U_{b+d}(V_{b+d}) = U_b(V_{b+d}) + \Delta E$$

$$p = p_b + \Delta p$$

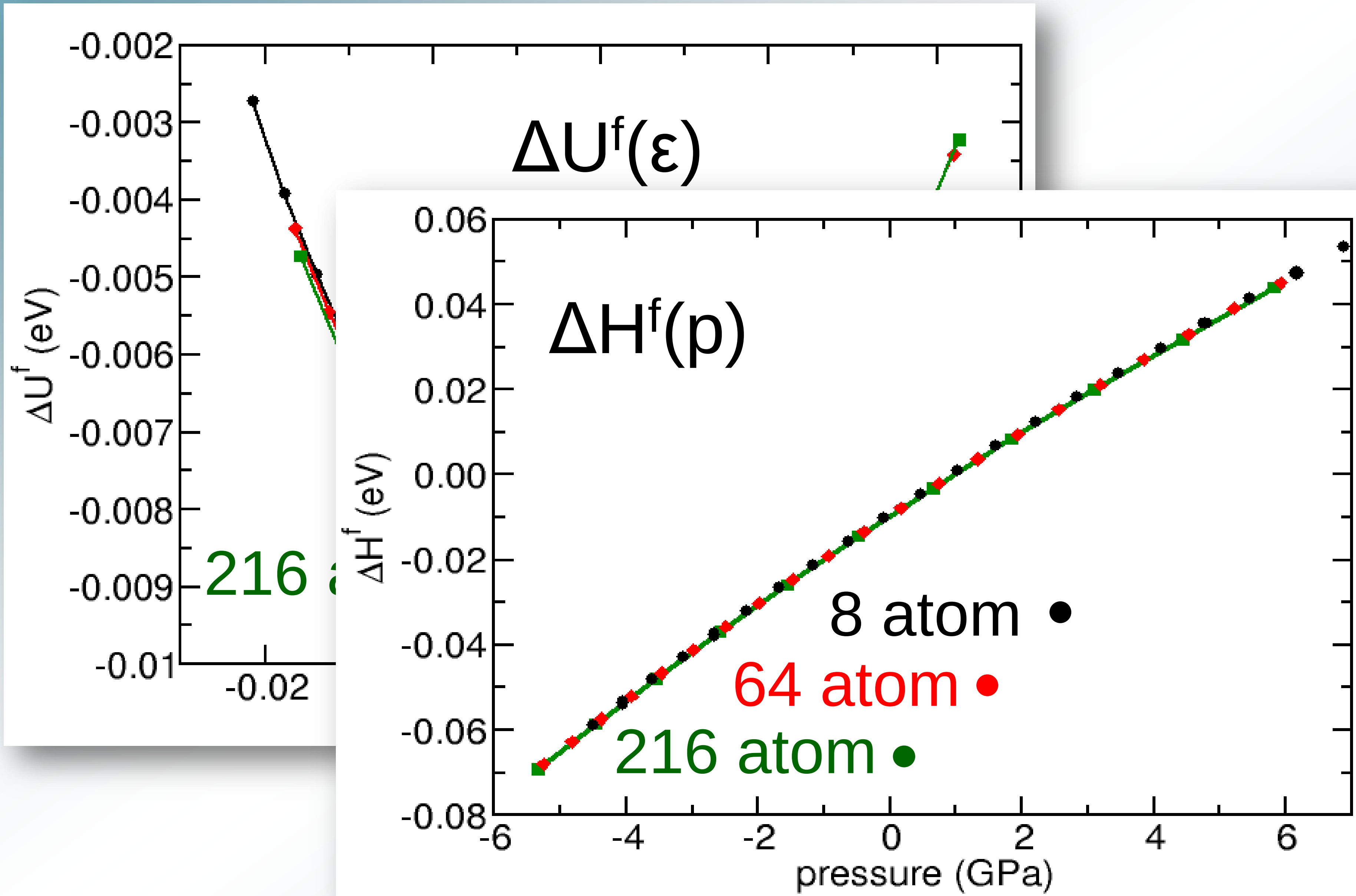
DFT error cancellation

Fitted analytic form, e.g. Murnaghan

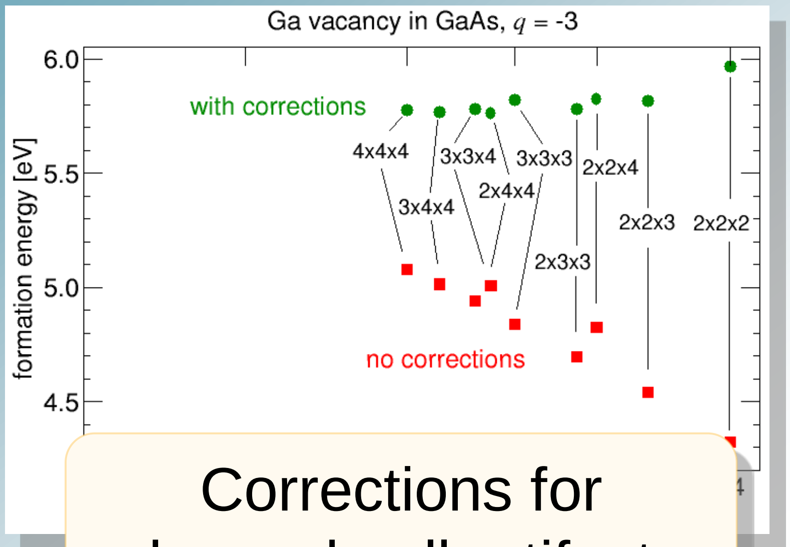
$$\Delta V^{rel}(p) = V_{b+d}(p) - V_b(p)$$

$$\Delta U^f = \Delta E + U_b(V_{b+d}) - U_b(V_b)$$

Ge in bulk Si: energy and enthalpy



Conclusions



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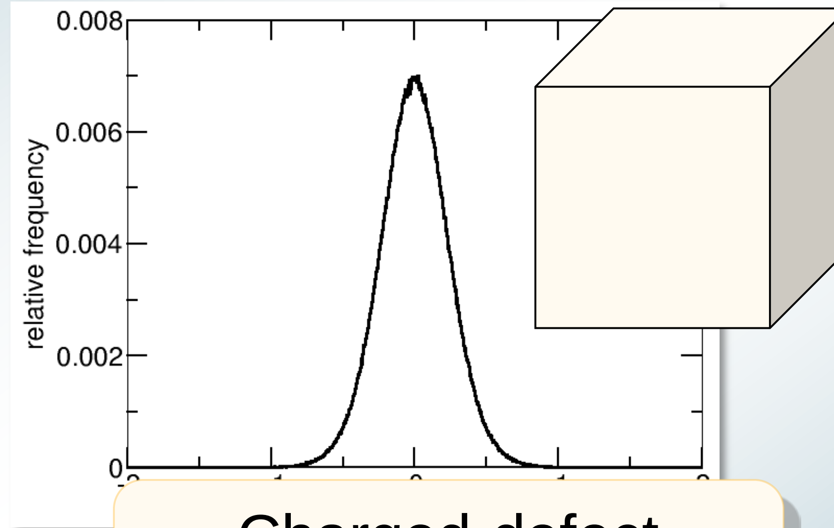

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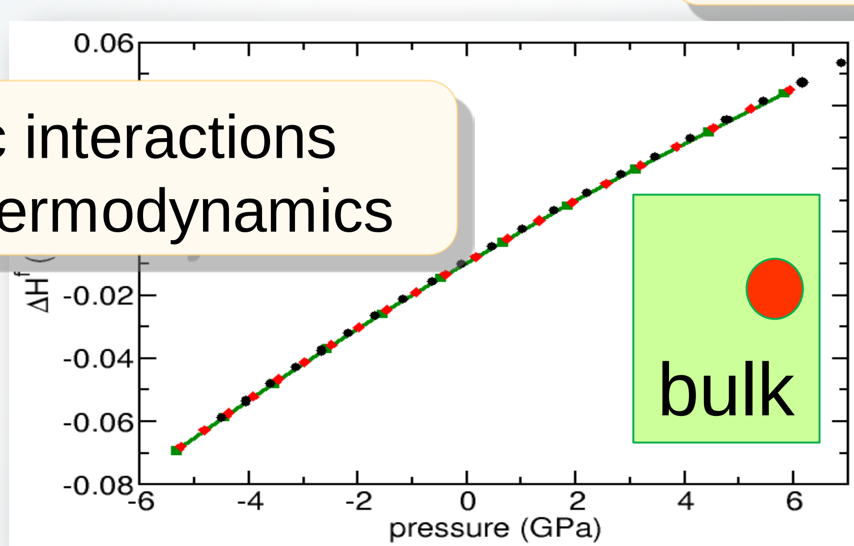


System containing defect "X" at concentration c_X (in total N_X)

$$G^{\text{system}} = G^{\text{bulk}} + N_X \boxed{\Delta G_X^f} - T\,S^{\text{conf}}[c_X] + \Delta G^{\text{interact}}[c_X]$$

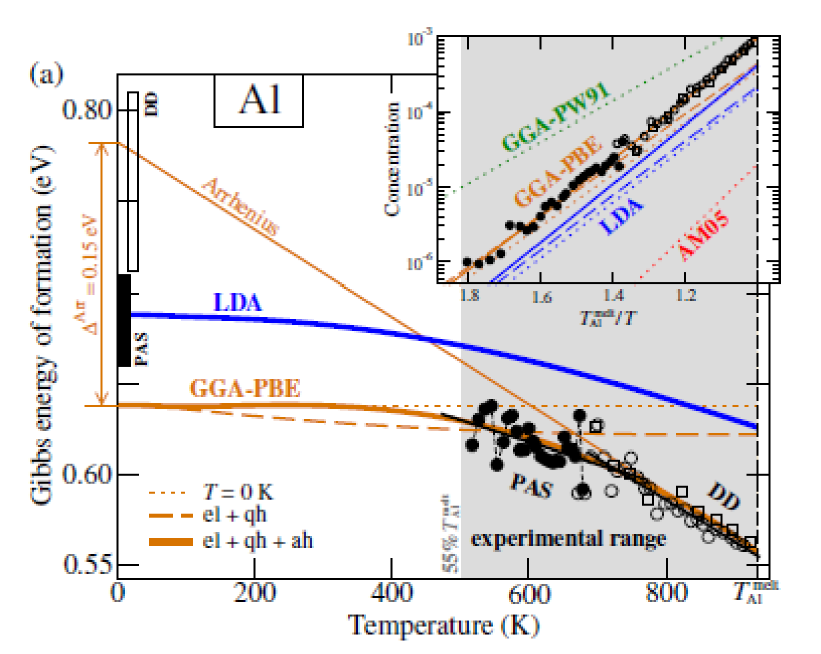
Gibb's free energy of formation of isolated(!) defect

interactions

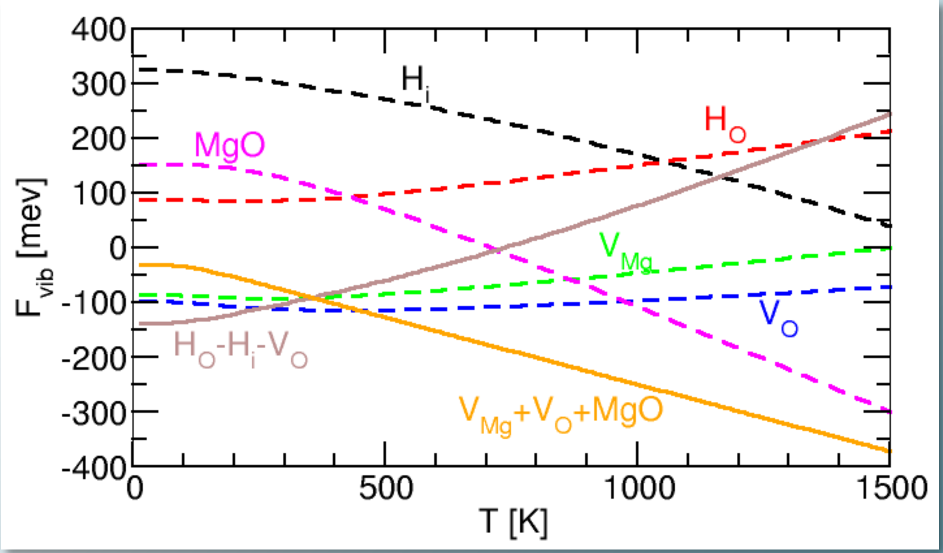
$$G(p,T,\mu_s) = U \qquad + pV \qquad - TS \qquad - \mu_s \Delta N_s$$

meV 0..±0.2 eV

0,



Glensk et al., PRX 4, 011018 (2014)



Coulomb interactions

$$\lambda^2 = \frac{\epsilon kT}{ne^2}$$

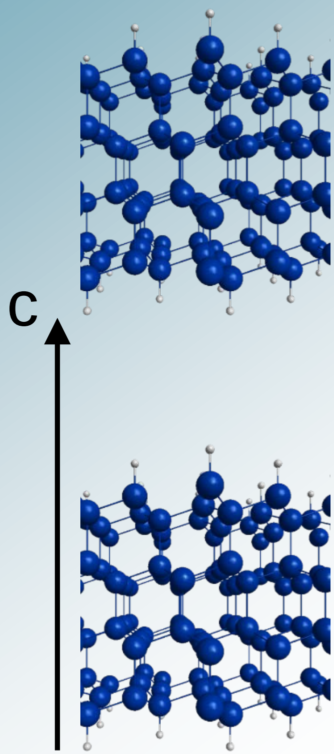
$$V(r) = \frac{1}{4\pi\epsilon}\frac{1}{r}e^{-r/\lambda}$$

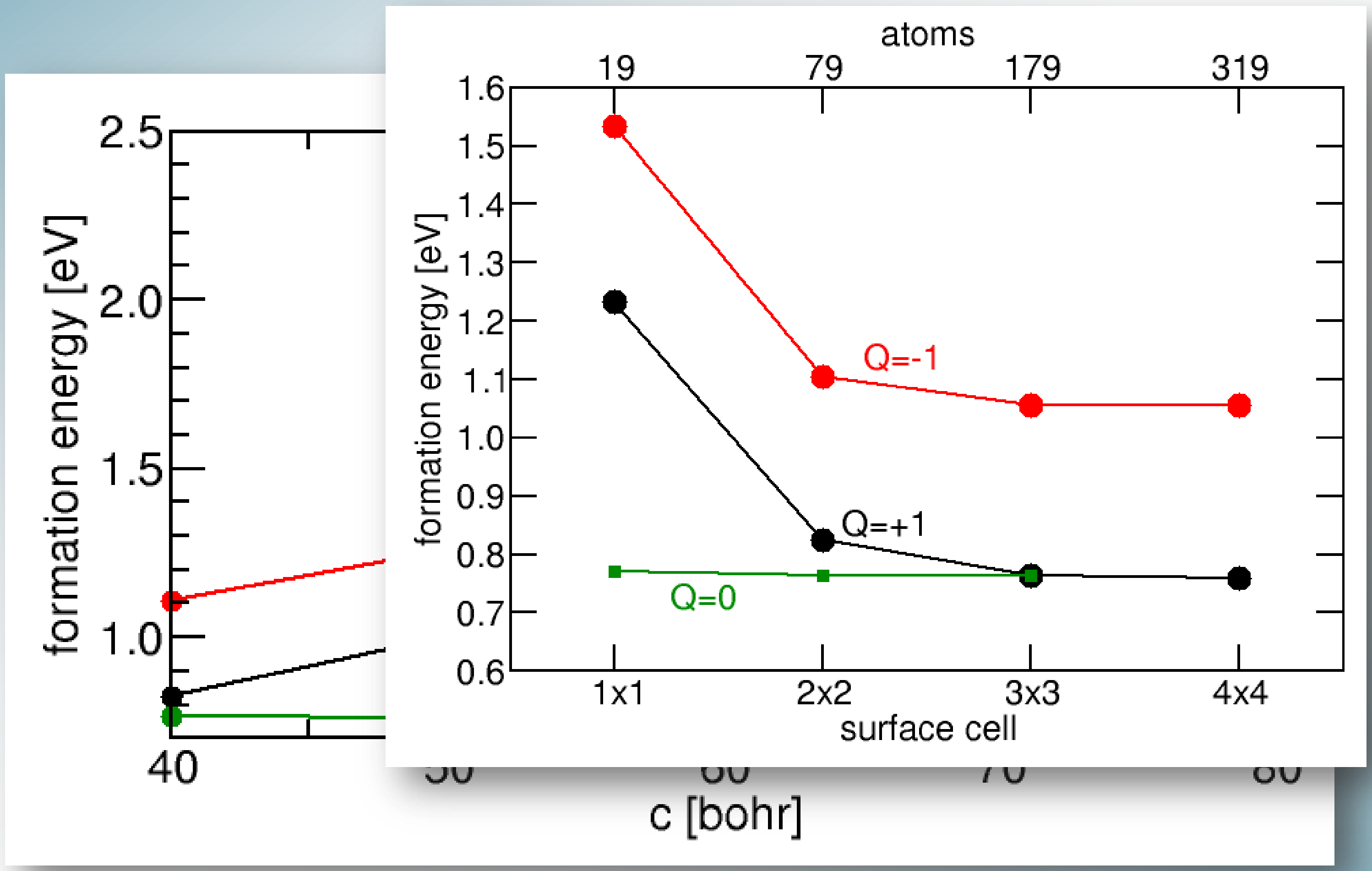
$$E \sim \frac{Q^2}{4\pi\epsilon a_0} \approx 0.3\ eV$$

$$a_0 = 0.5\,nm,\ \epsilon = 10\epsilon_0,$$
$$n = 10^{17}cm^{-3}, T = 300K \rightarrow \lambda = 12nm \approx 20a_0$$

Most calculations done on periodic 200x200x200 lattice (8 million sites)

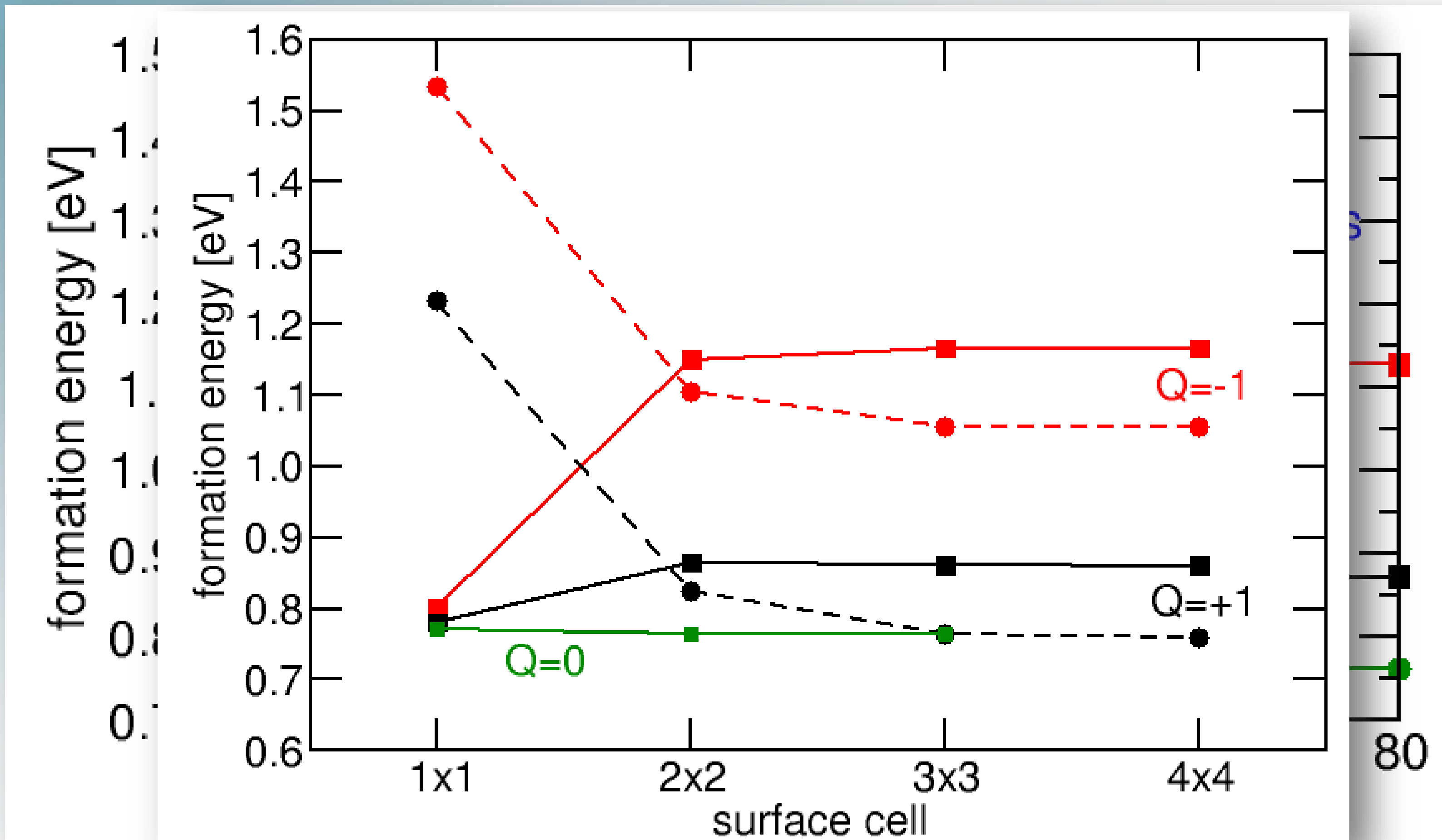
Si(111) surface: convergence





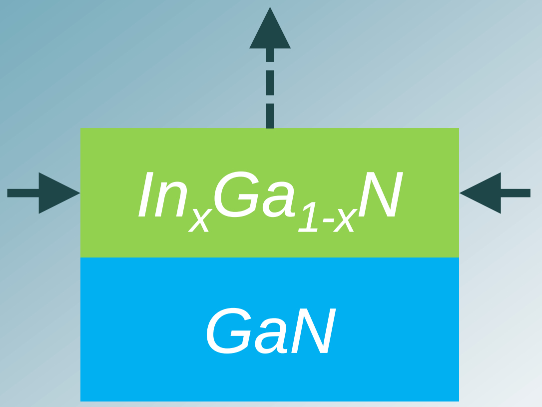
- Role of the vacuum (for lateral: 2x2)
- Need corrections for charge states
- Lateral convergence (size of surface unit cell) for c=40 bohr

DFT results + sxdefectalign-2D corrections

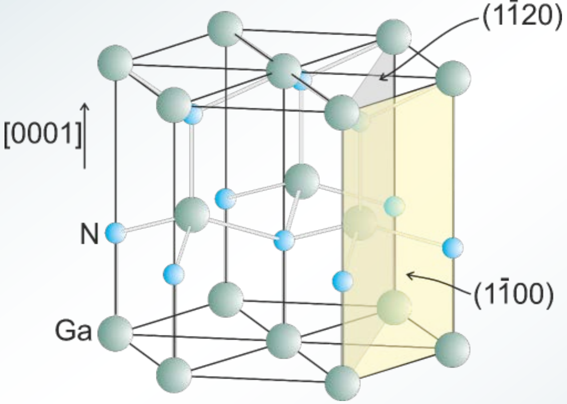


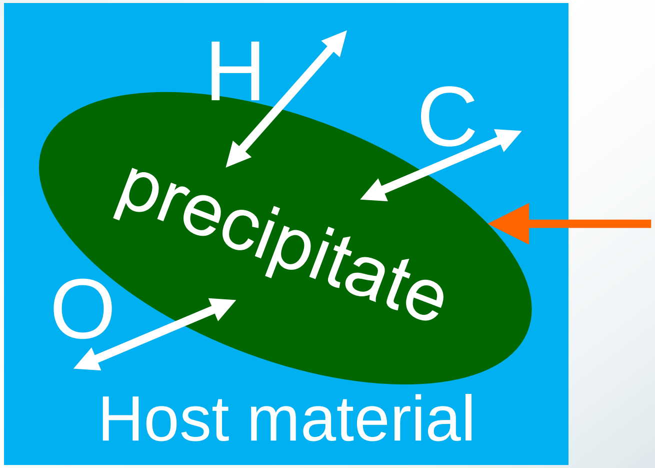
- Corrections work perfectly for vacuum convergence
- and also improve NxN lateral convergence

Real materials may be strained



compressive strain (x·11%)





coherently strained

Goal: understand point defect formation energetics from DFT (here: LDA or PBE) with "reasonable" settings

Generalized enthalpy:

$H(\sigma) = U(V_0\,\varepsilon) + pV - V_0\sigma^{dev}\boldsymbol{\varepsilon}^{dev}$

$$\sigma_{ij} = \frac{1}{V_0}\frac{\partial U}{\partial \epsilon_{ij}}$$

General energy-strain curve:

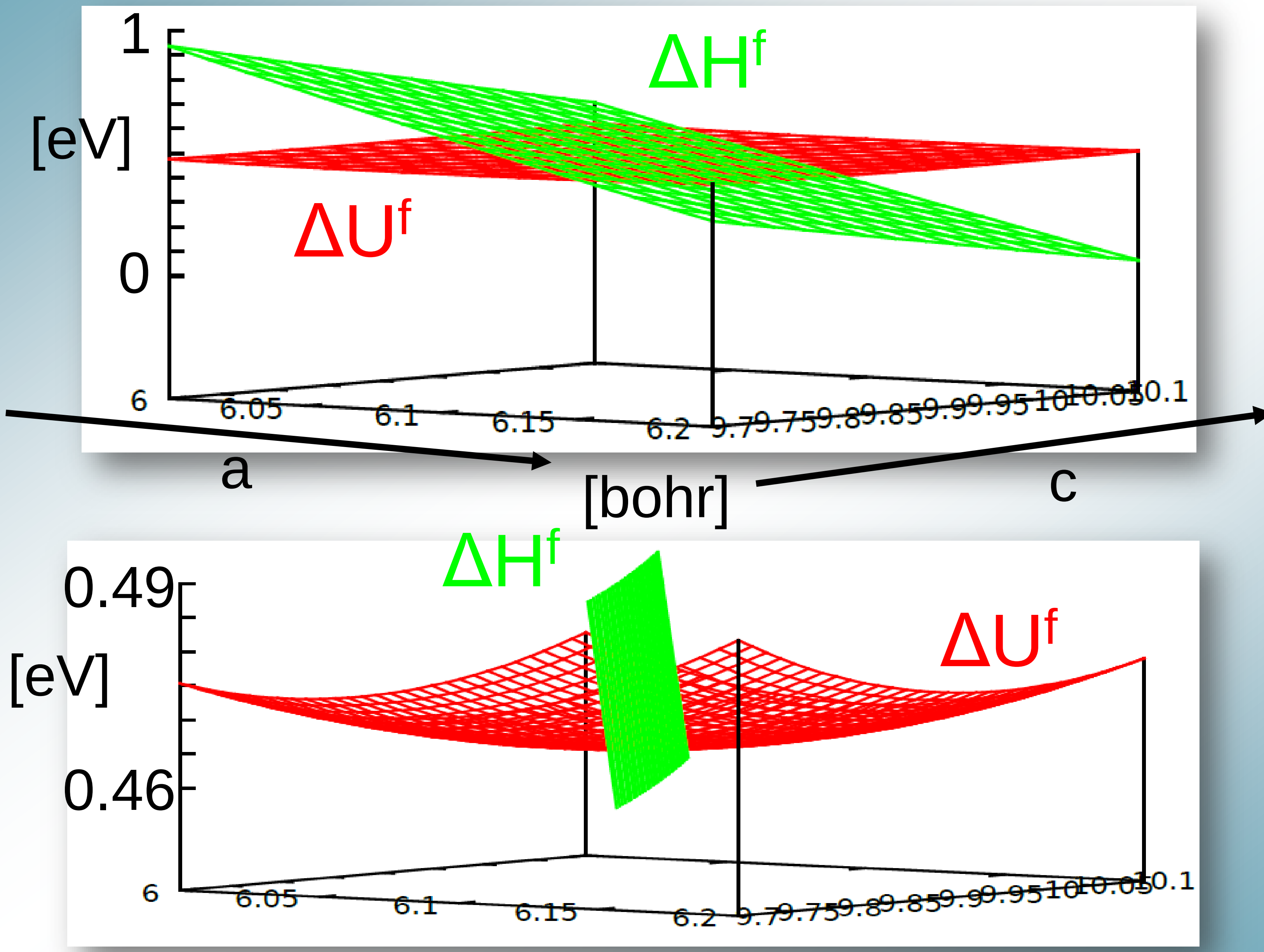
$U(\varepsilon) = P(\ln(1+\varepsilon)_{ij})$

n^{th} –order polynomial

Example: In in wurtzite GaN (32 atoms)

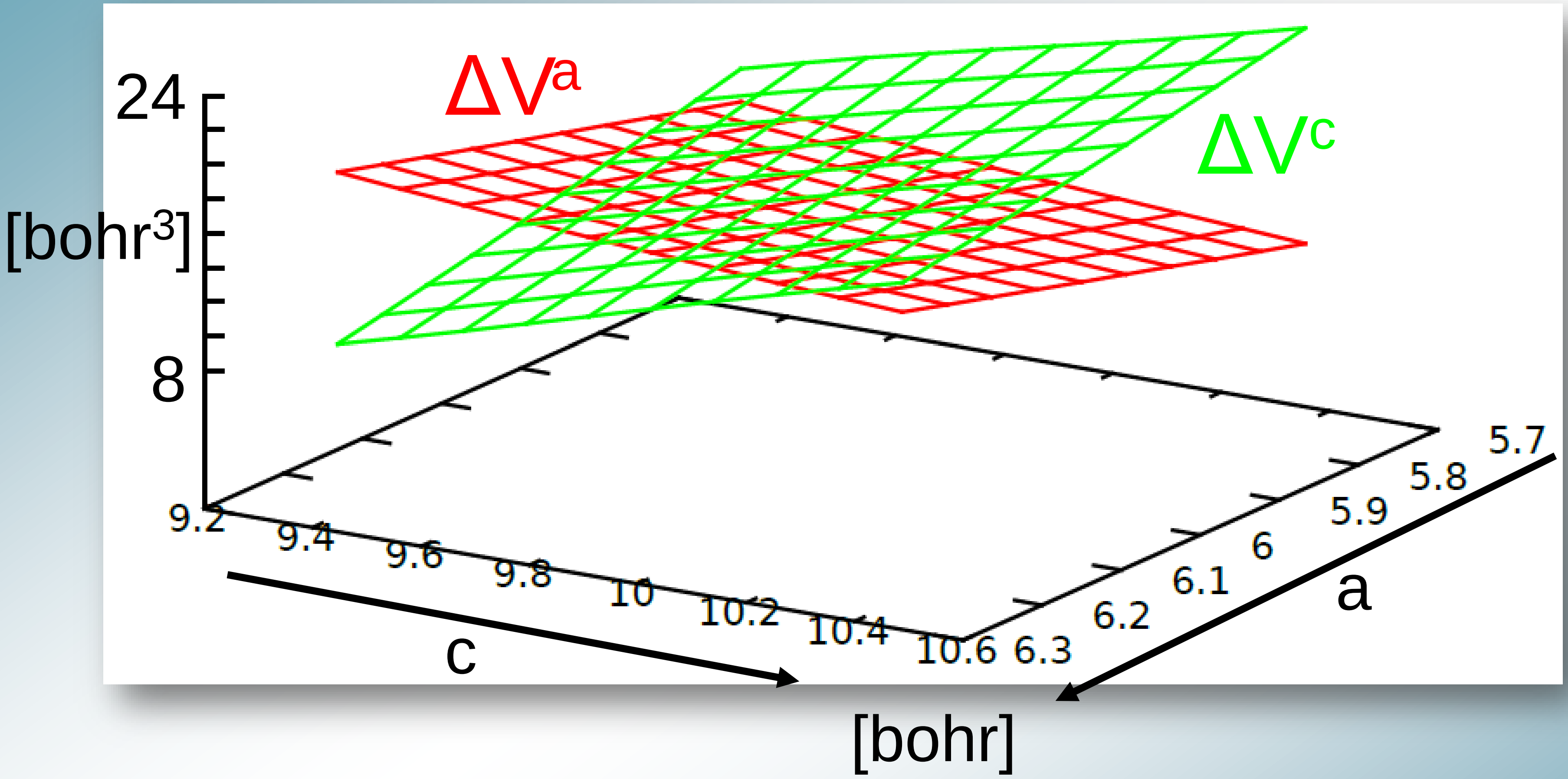
- free parameters: a and c lattice constant
- 4^{th}-order P

In in GaN



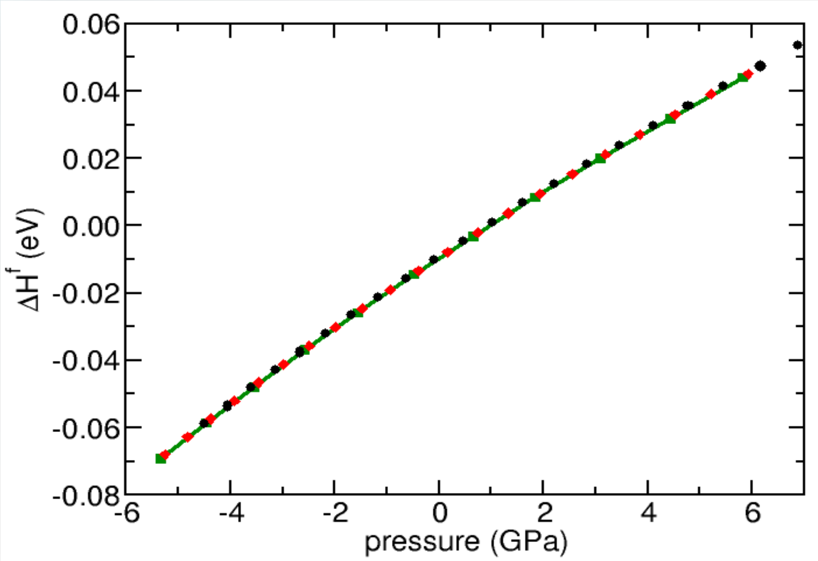
1
ΔH^f
[eV]
ΔU^f
0
6
6.05
6.1
6.15
6.2
a
[bohr]
c
ΔH^f
0.49
[eV]
ΔU^f
0.46
6
6.05
6.1
6.15
6.2

In in GaN

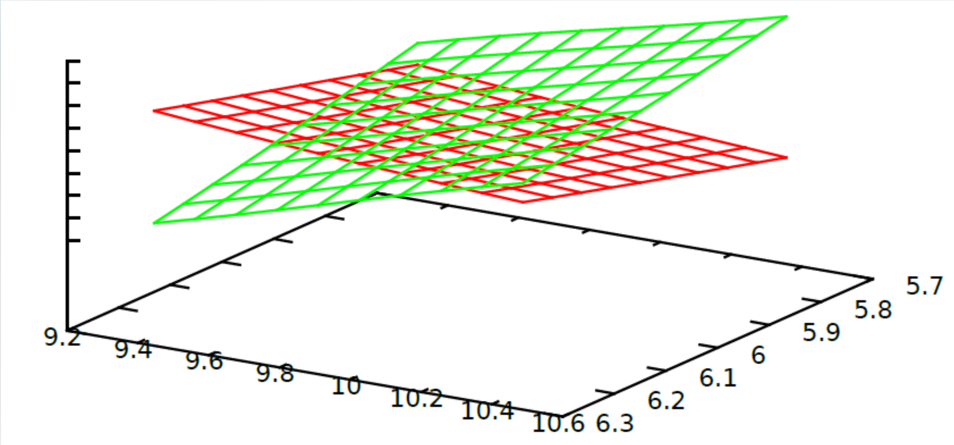


Relaxation volume varies with strain

- Robust, efficient scheme for thermodynamic properties of defects in strained material

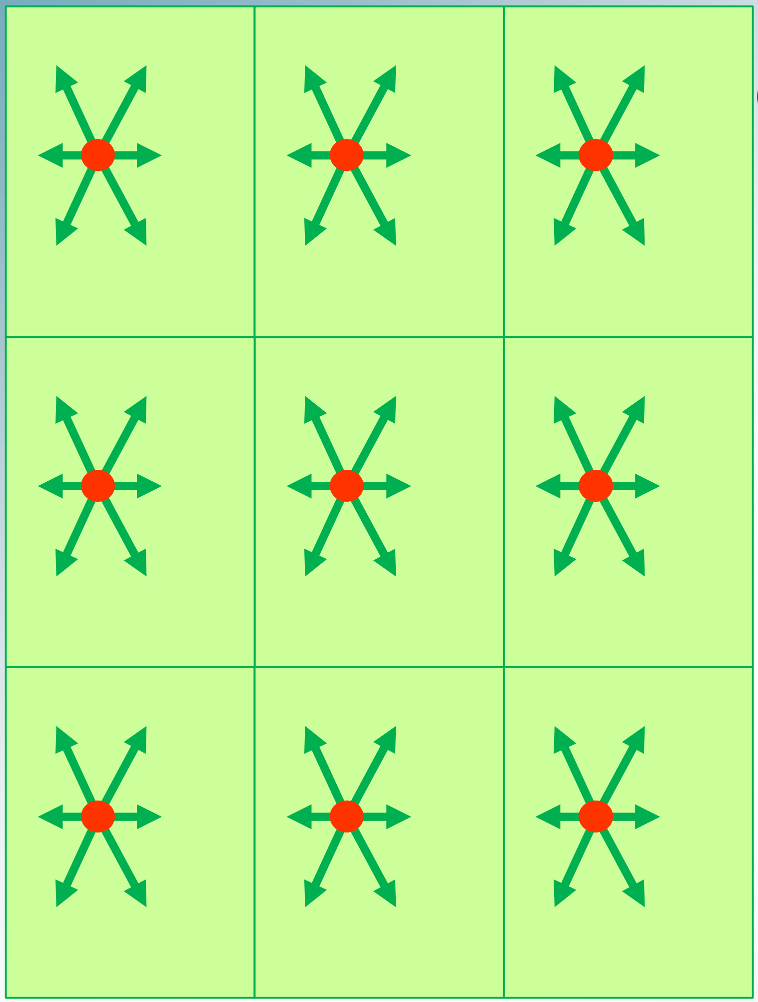


- General-purpose non-linear energy-strain model



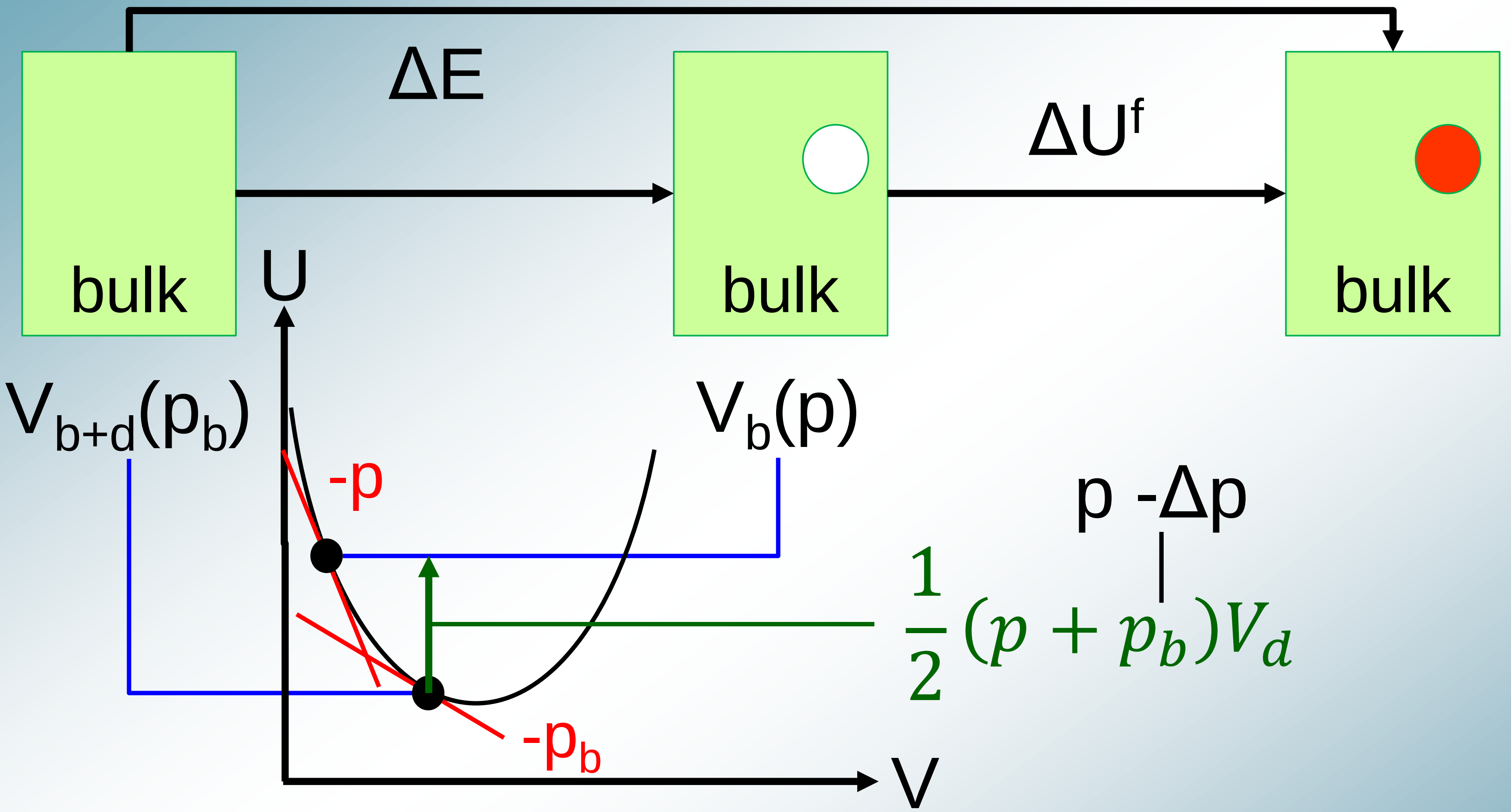
- Relaxation volume tensor depends on strain

Elastic interactions between defects



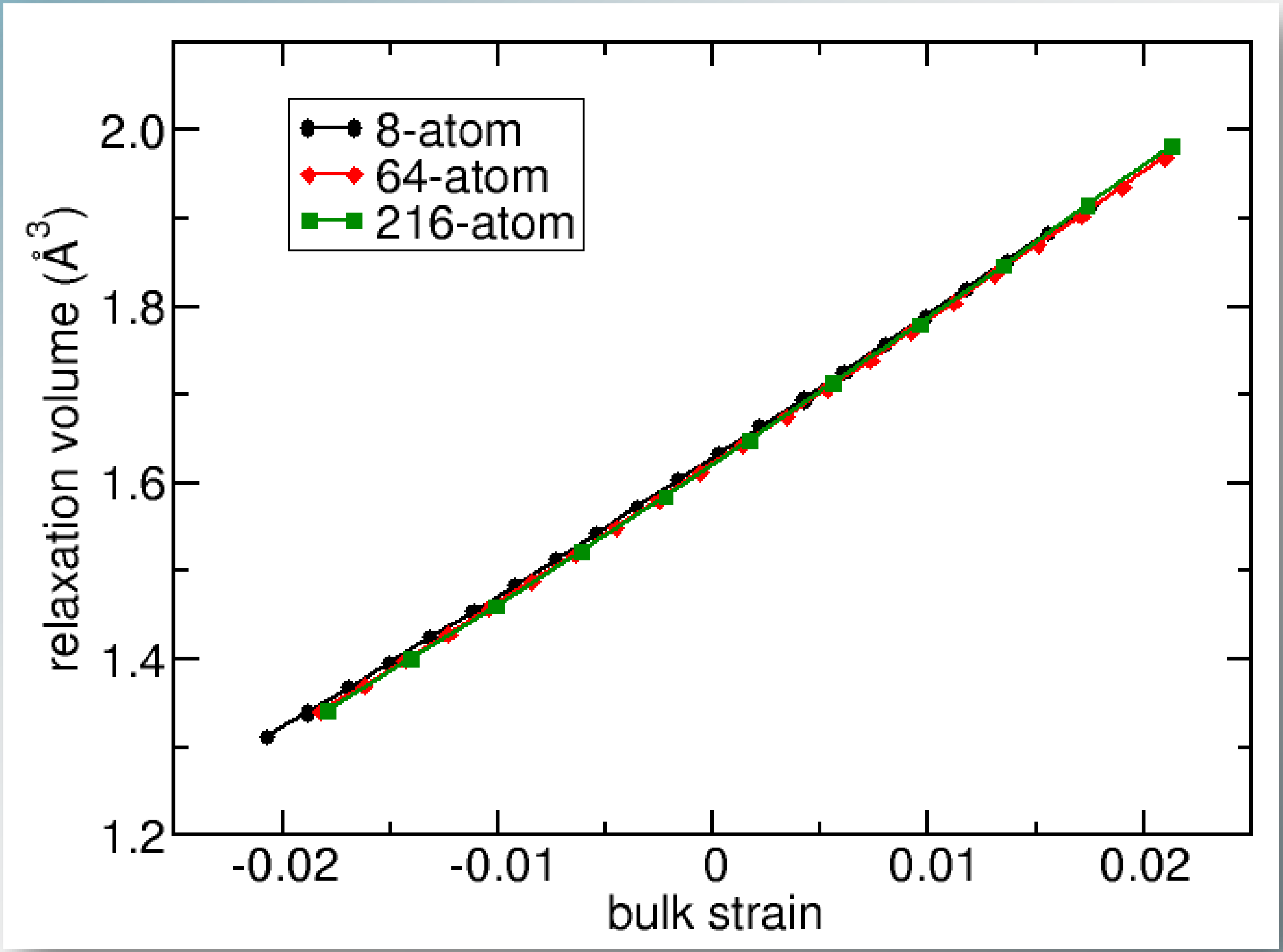
nonlinear effects?

electrostatic	**elasticity**
charge	force
potential	displacement
$\vec{D}$	stress σ
$\vec{E}$	strain ϵ
dipole	elastic dipole tensor
	relaxation volume tensor
scalar	vector
vector	rank 2 tensor
rank 2 tensor	rank 4 tensor
rank 3 tensor	rank 6 tensor



$$\Delta E = \Delta U^f + pV_d - \frac{1}{2}\Delta p V_d = \Delta H^f - \frac{1}{2}\Delta p V_d$$

Ge in bulk Si: relaxation volume



Relaxation volume varies with strain

Ge in bulk Si: improvement over ΔE