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?
Outlook

Corrections for charged-cell artifacts

Charged-defect interactions at scale

Elastic interactions within thermodynamics
Supercell calculations

- Wave function overlap (decay $e^{-ar}$) $\rightarrow$ \textbf{k}-integration
- Strain (decay $1/r^3$) $\rightarrow$ often small
- Coulomb interactions (decay $1/r$) $\rightarrow$ ?
Slow supercell convergence

Ga vacancy in GaAs, $q = -3$

energy [eV]

4.5
5.0
5.5
6.0

N\text{atoms}

4096
512
216
128
64

Supercell calculations without corrections

DFT-LDA, norm-conserving PP, no ionic relaxation (=no strain)
Exact formulation of artifacts

Three-step process
1. add N electrons to defect state
2. relax other electrons
3. Introduce periodicity +background

bare charge $q(r) = -Ne|\psi(r)|^2$
change in potential $\Delta V(r)$
periodic potential $\Delta \tilde{V}(r)$

Long-range treatment

\[ V(\mathbf{r}) = V^{lr}(\mathbf{r}) + V^{sr}(\mathbf{r}) \]

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

\[ V^{sr}(\mathbf{r}) = \Delta \tilde{V}^{\text{DFT}}(\mathbf{r}) - \tilde{V}^{lr}(\mathbf{r}) - C \]
Short-range effects

\[ V_{sr}(r) = \Delta \tilde{V}^{\text{DFT}}(r) - \tilde{V}^{\text{lr}}(r) - C \]

- plateau indicates a successful modelling of long-range effects
-3 Ga vacancy in GaAs (unrelaxed)


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

Surfaces, interfaces, 2D materials:

• Supercell-independent formation energies within 0.1 eV
• 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
  \[ V(r) = \frac{Q}{4\pi\varepsilon r} e^{-r/\lambda} \]
• Many realizations (10^4 - 10^5 sites)
• Collect statistics

200x200x200 cells (8 million) periodic boundary conditions
Interactions in random order

\[ p(\Delta E) \sim e^{-\frac{\Delta E^2}{2\beta^2}} \]

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 $\lambda$?

\[ \beta^2 \sim \lambda \]

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

\[ p(\Delta E) \sim e^{-\frac{\Delta E^2}{2\beta^2}} \]

\[ \beta \sim \frac{Q^2}{4\pi\epsilon a_0} \sqrt{c\lambda} \approx 0.03 \text{eV} \]
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Bulk
One approach: Lattice Green’s function [Tewary, Phys. Rev. B 094109 (2004)].
Thermodynamic view

\[
\text{defect: } U_{b+d} = U_b + U_d \\
V_{b+d} = V_b + V_d
\]

\[
p = -\frac{\partial U}{\partial V}
\]

\[
V_{b+d}(p) = V_b(p) + V_d(p)
\]

\[
U_{b+d}(V_{b+d}(p)) = U_b(V_b(p)) + U_d(V_d(p))
\]

\textbf{Enthalpy: } H(p) = U(V) + pV

\[
H_{b+d}(p) = H_b(p) + H_d(p)
\]

\[
\Delta E = U_{b+d}(V_{b+d}) - U_b(V_{b+d})
\]
$\Delta E$ at constant volume converges to formation enthalpy $\Delta H_f$
Get $\Delta U^f$, $\Delta H^f$, $\Delta V^{\text{rel}}$ from DFT

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

\[ p = p_b + \Delta p \]

DFT error cancellation

Fitted analytic form, e.g. Murnaghan

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

\[ \Delta U^f = \Delta E + U_b(V_{b+d}) - U_b(V_b) \]
Ge in bulk Si: energy and enthalpy

\[ \Delta U^f(\epsilon) \]

\[ \Delta H^f(p) \]
Conclusions

Corrections for charged-cell artifacts

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Ga vacancy in GaAs, $q = -3$

with corrections

no corrections

Charged defects with DFT
Thermodynamics

System containing defect “X” at concentration $c_X$ (in total $N_X$)

$$G_{\text{system}} = G^\text{bulk} + N_X \left[ \Delta G^f_X - T S^{\text{conf}}[c_X] + \Delta G^{\text{interact}}[c_X] \right]$$

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

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

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

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

\[ \lambda^2 = \frac{\varepsilon kT}{n e^2} \]

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

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

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
• Corrections work perfectly for vacuum convergence
• and also improve NxN lateral convergence
Charged defects with DFT

Real materials may be strained

Goal: understand point defect formation energetics from DFT (here: LDA or PBE) with “reasonable” settings
Beyond isotropic pressure/volume

**Generalized enthalpy:**
\[ H(\sigma) = U(V_0 \varepsilon) + pV - V_0 \sigma^{\text{dev}} \varepsilon^{\text{dev}} \]

\[ \sigma_{ij} = \frac{1}{V_0} \frac{\partial U}{\partial \varepsilon_{ij}} \]

**General energy-strain curve:**
\[ U(\varepsilon) = P(\ln(1+ \varepsilon)_{ij}) \]

\[ n^{\text{th}} \text{–order polynomial} \]

**Example:** In in wurtzite GaN (32 atoms)
- free parameters: a and c lattice constant
- 4\text{th}-order P
In In GaN

\[ \Delta U_f \]

\[ \Delta H_f \]

\[ [\text{eV}] \]

\[ a \]

\[ [\text{bohr}] \]

\[ c \]

\[ 0.49 \]

\[ 0.46 \]

\[ [\text{eV}] \]

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\[ \text{Charged defects with DFT} \]
In In GaN

$\Delta V^a$

$\Delta V^c$

Relaxation volume varies with strain
Conclusions

• 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

electrostatic  elasticity

- charge  force
- potential  displacement

\( \vec{D} \)  stress \( \sigma \)
\( \vec{E} \)  strain \( \epsilon \)

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

nonlinear effects?
What is DFT’s ΔE in thermodynamics?

\[
\Delta E = \Delta U^f + pV_d - \frac{1}{2} \Delta pV_d = \Delta H^f - \frac{1}{2} \Delta pV_d
\]
Ge in bulk Si: relaxation volume

Relaxation volume varies with strain
Ge in bulk Si: improvement over $\Delta E$

$\Delta E$ (eV)

$\Delta E - \Delta H^f$ (meV)

strain

-0.02

0

0.01

0.02

Supercell strain

8-atom

64-atom

216-atom

I 5 meV

H 0.1%