Formation energies of charged defects

- In GaAs

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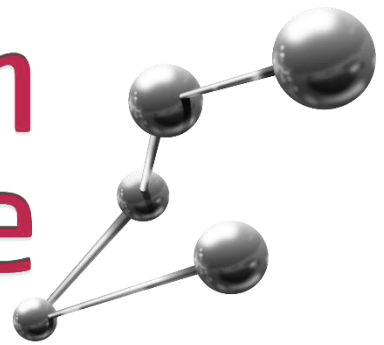
Quantum Wise



- Deals with bulk formation energy of compound
- Neutral bulk Ga vacancy in GaAs
- Surface O vacancy in MgO(100)

- How to calculate the formation energy of charged defects
- System and computational model
- How to calculate formation energy for neutral defect
  - How to set up this calculation
- How to include the charges correctly
  - Explain the correctional terms
  - How to set up the calculations
- Results
- Results for larger supercell

Calculating the formation energy for a defect X with a charge q, using the procedure of Freysoldt and Van de Walle et al.:

$$E^f[X^q] = E_{tot}[X^q] - E_{tot}[bulk] - \sum_i n_i \mu_i + \left(qE_{VBM} + \Delta\mu_e\right) + E_{corr}$$

The first two terms are total energies from DFT, the third is the chemical potential of elements involved in the defect, the parenthesis is the chemical potential of the electrons, assumed to be at the valence band maximum plus any contribution from doping etc. The last term is the correction for periodic interaction between charges.

C. Freysoldt et al., *Reviews of Modern Physics*, **86**, (2014)

- This tutorial will deal with GaAs, which contains defects which can sustain many different charge states, depending on the chemical potential of the electrons.

- We use PBESol for exchange-correlation, which is a GGA-level functional designed to work well with solids, giving good predictions for the bulk and surface properties.

PBESol reference: J. P. Perdew et al., *Physical Review Letters*, **100**, (2008)

For the neutral defect, the expression simplifies to:

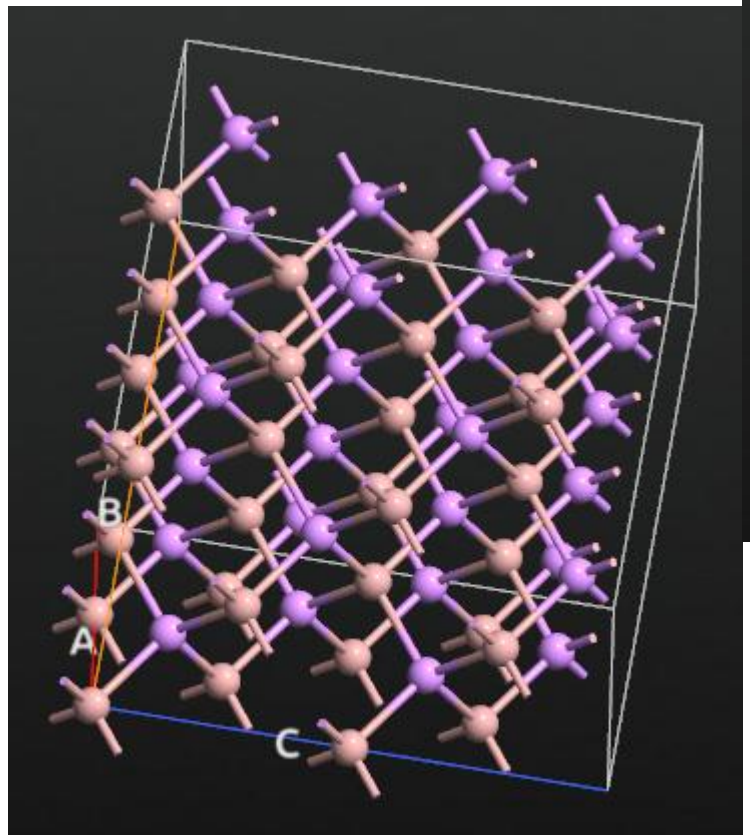
$$E^f[X^0] = E_{tot}[X^0] - E_{tot}[bulk] - \sum_i n_i \mu_i$$

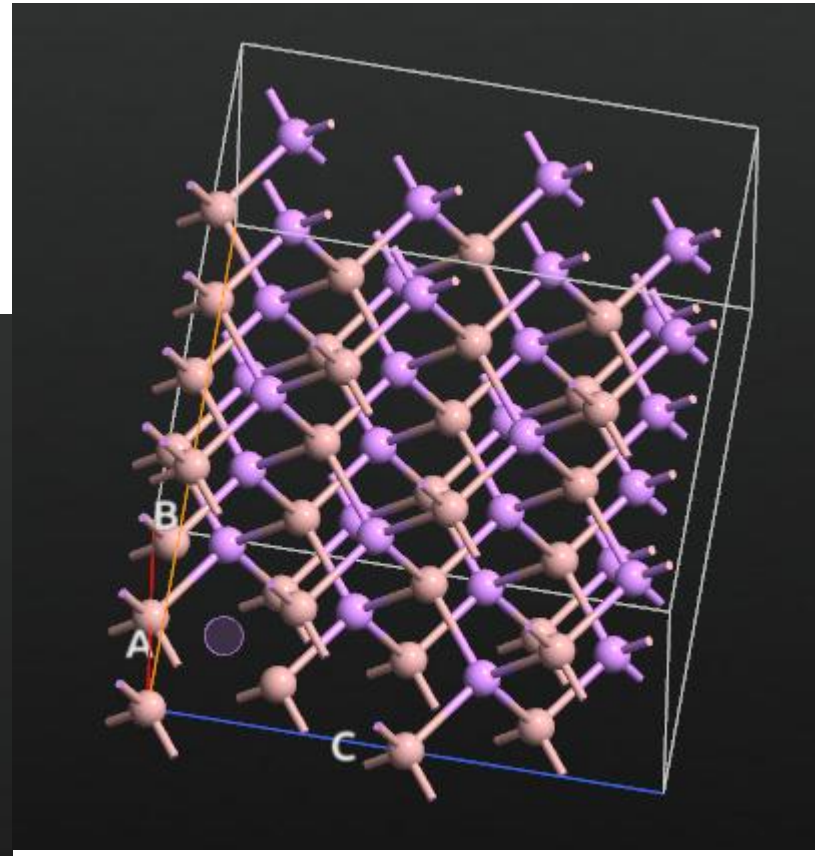
We now look at a neutral As vacancy, which gives us the expression:

$$E^f[V_{As}^0] = E_{tot}[V_{As}^0] - E_{tot}[bulk] - (-1)\mu_{As}$$

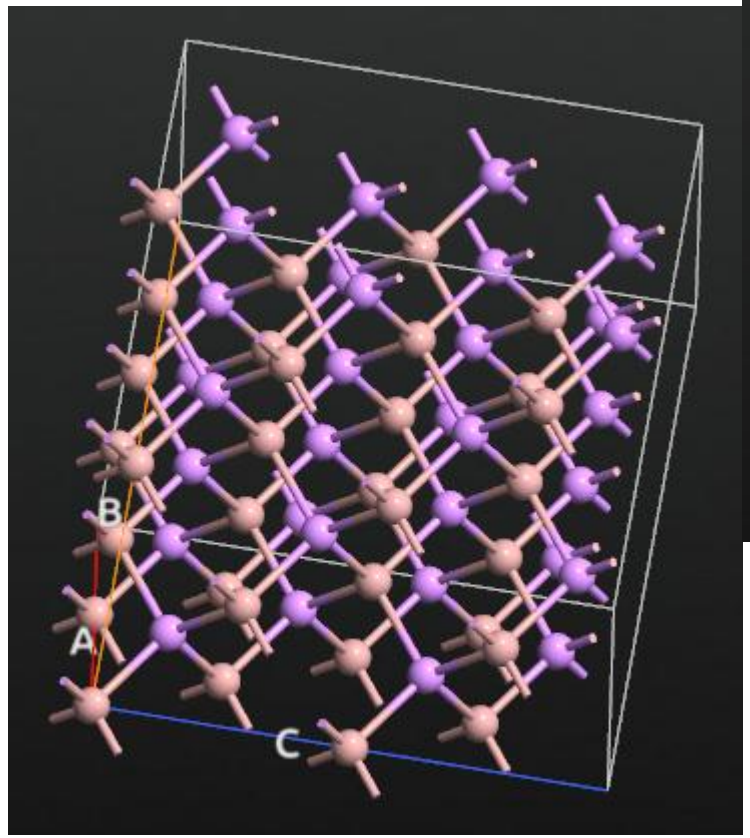
We use bulk As for the chemical potential, which can be calculated as described in many other tutorials, such as:
http://docs.quantumwise.com/tutorials/formation_energies.html

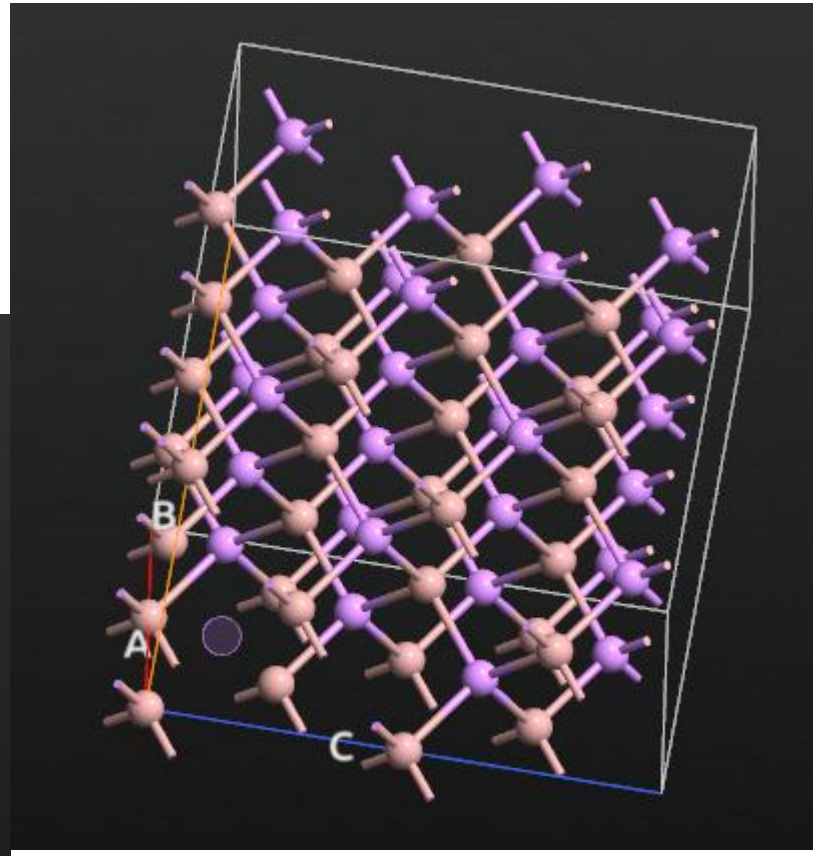
- 2x2x2 orthogonal unit cell
- 4x4x4 k-points
- PBESol
- Use optimized lattice constant
- Include Density of States for undefected cell



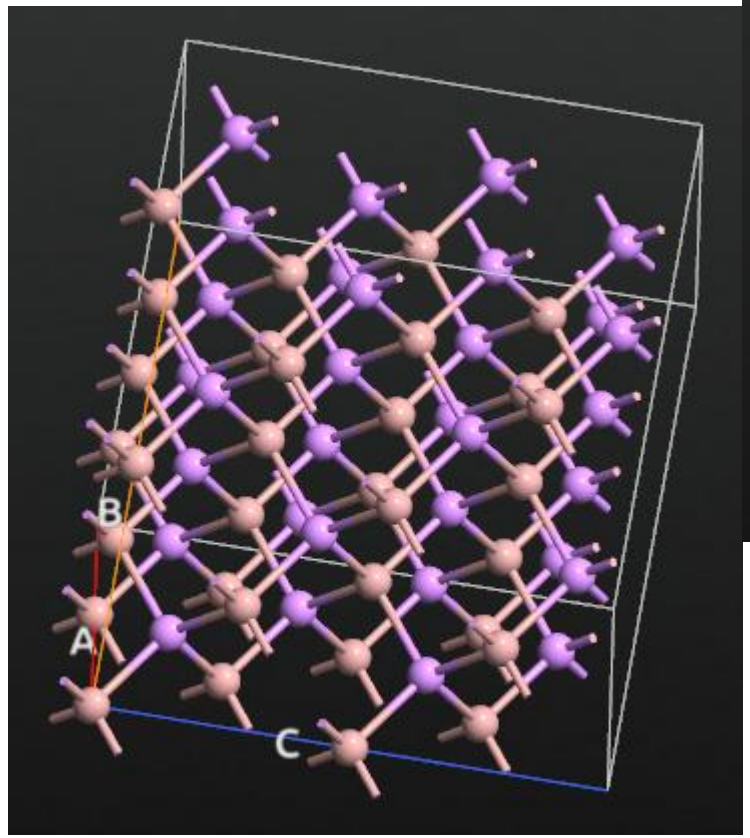


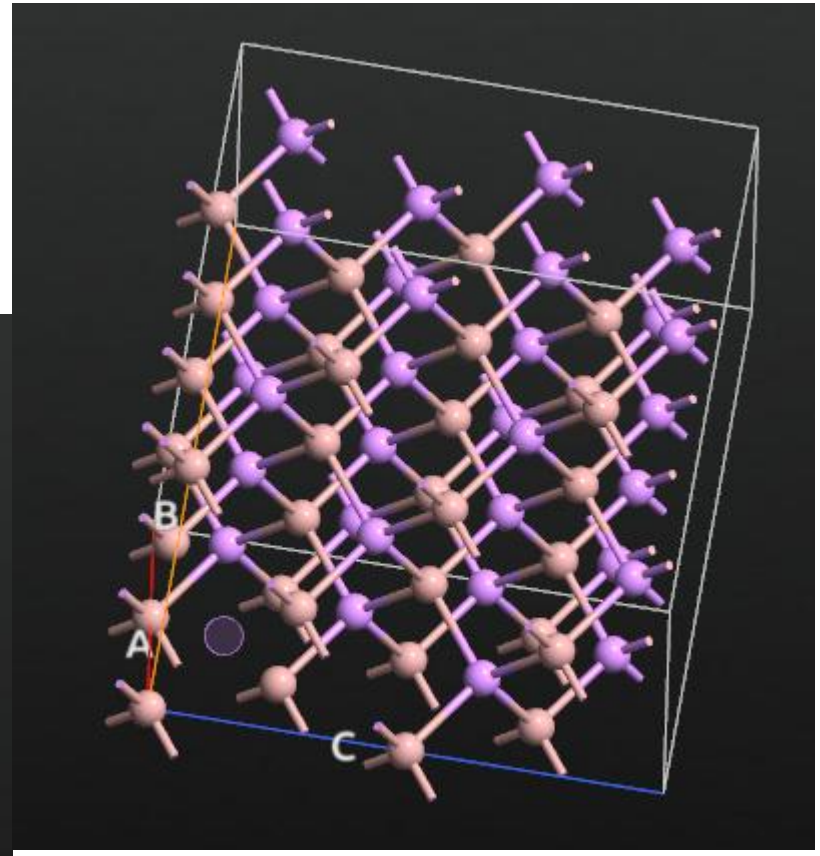
- 2x2x2 orthogonal unit cell
- 4x4x4 k-points
- PBESol
- Use optimized lattice constant
- Make the atom at the defect a Ghost Atom
  - instead of removing it
- Optimize geometry for vacancy – the Ghost Atom is fixed





- Result for neutral defect:
- 3.22 eV





We need:

- Total energy calculations of:
  - Bulk As
  - Bulk GaAs – in the same supercell as used for the vacancy calculations
  - Total energy calculations of all relevant vacancy states
- Density of States calculation for bulk GaAs – to get E_{VBM}
- Dielectric constant for GaAs – see tutorial on OpticalSpectrum: docs.quantumwise.com/tutorials/optical.html

We already have:

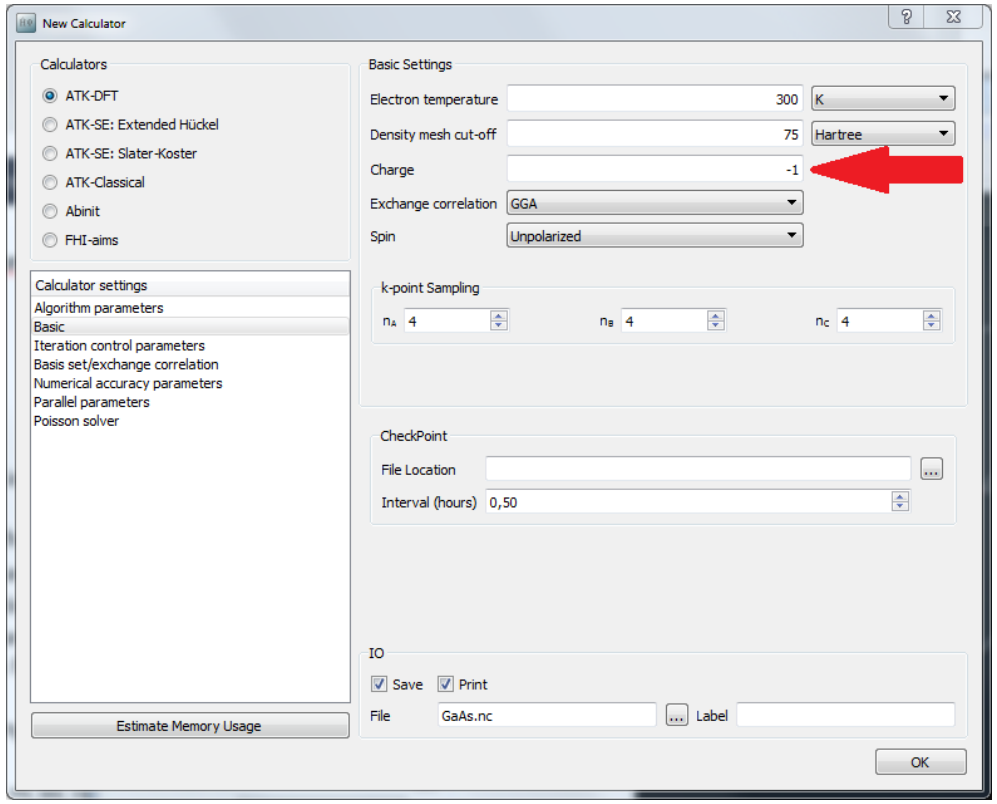
- Total energy calculations of:
  - Bulk As
  - Bulk GaAs – in the same supercell as used for the vacancy calculations
  - Total energy calculations of all relevant vacancy states

- Density of States calculation for bulk GaAs – to get E_{VBM}

- Dielectric constant for GaAs – see tutorial on OpticalSpectrum: docs.quantumwise.com/tutorials/optical.html
  - We can use the old bulk calculation as starting point

- Use the script provided
- Or: Put in charge = q in copies of the previous script
- Or: Use same procedure as before and add charge in GUI

- Relevant charge states:
  +1, -1, -2 and -3

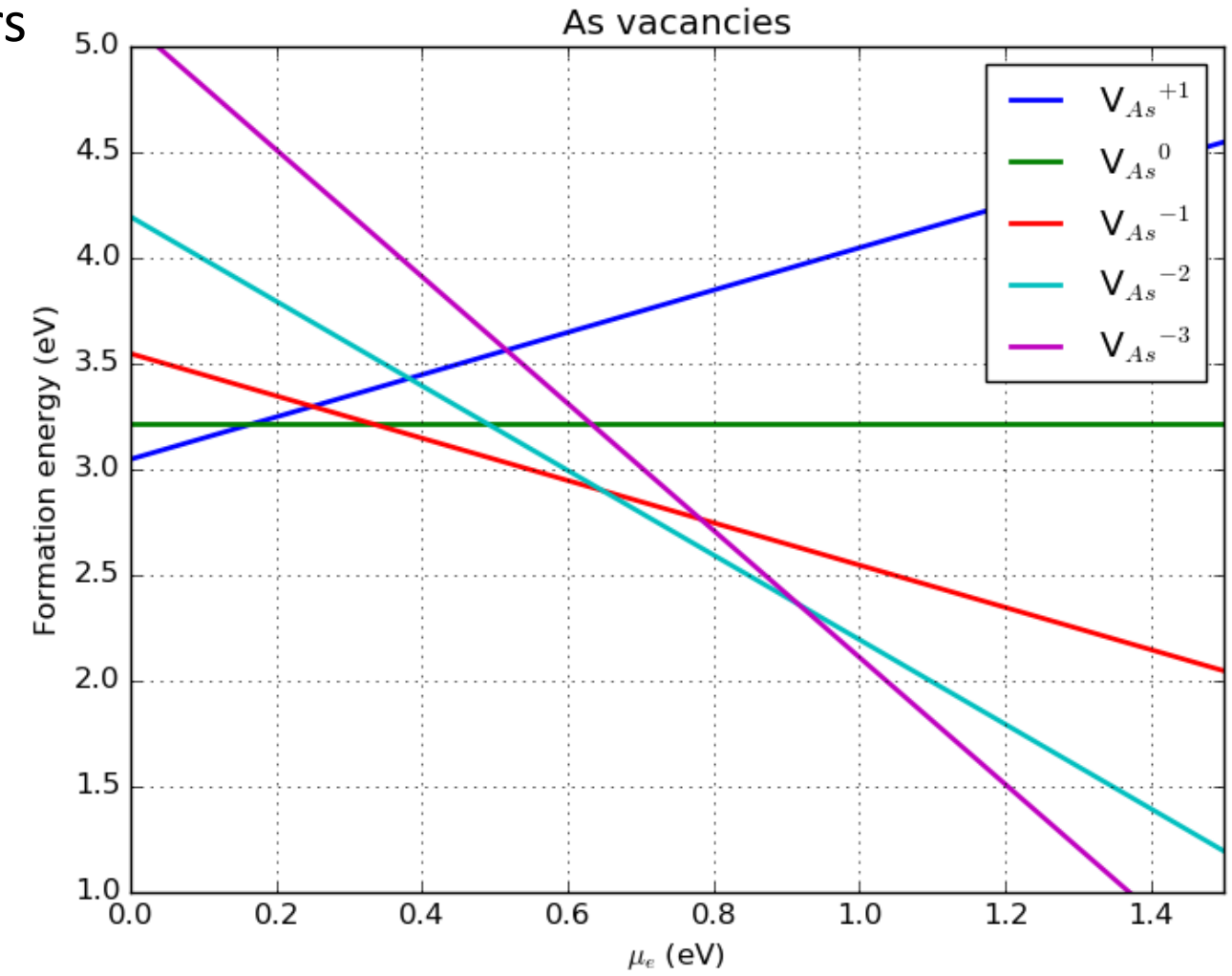


Results for 2x2x2 supercell :

Charge state	Formation energy [eV]	Per. Corr. [eV]	Band corr. [eV]
+1	3.04	0.13	-0.03
0	3.22	0.00	0.00
-1	3.56	0.13	0.00
-2	4.23	0.54	-0.03
-3	5.18	1.20	-0.10

Intercepts are the numbers in the table on the previous slide

2x2x2 supercell



Results for 3x3x3 supercell (2x2x2 k-points):

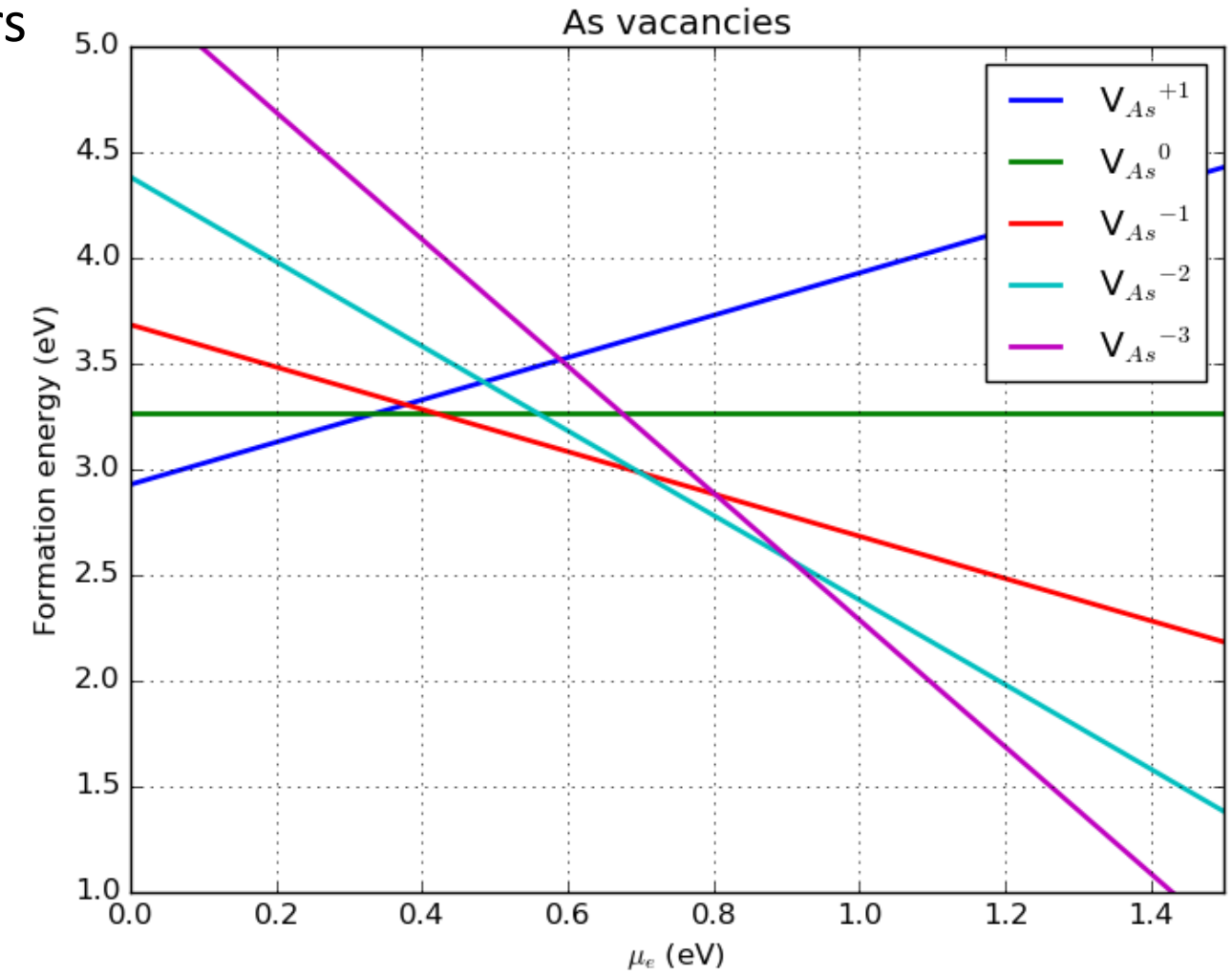
Note that the reference does not use a ghost atom in the vacancy

Charge state	This work [eV]	Ref. [eV]
+1	2.95	2.79
0	3.26	3.25
-1	3.67	3.33
-2	4.35	4.52
-3	5.25	5.86

Ref.: F. El-Mellouhi et al., *Physical Review B*, **71**, (2005)

Intercepts are the numbers in the table on the previous slide

3x3x3 supercell



Appendix

The FNV correction method contains two terms:

Script notation:

$$E_{corr} = E_{lat} - q\Delta \mathrm{V}_{\mathrm{q}/b}$$

$$E_{lat} = \int_{\Omega} \left[\frac{1}{2} q\left(\tilde{V}_q^{lr} - V_q^{lr}\right)\right] d^3\boldsymbol{r} \qquad \Delta \mathrm{V}_{\mathrm{q}/b} = \widetilde{\mathrm{V}}_{q/b} - \widetilde{\mathrm{V}}_q^{lr} \qquad \bar{V} = \left(V_{q/b} - V_q^{lr}\right)_z$$

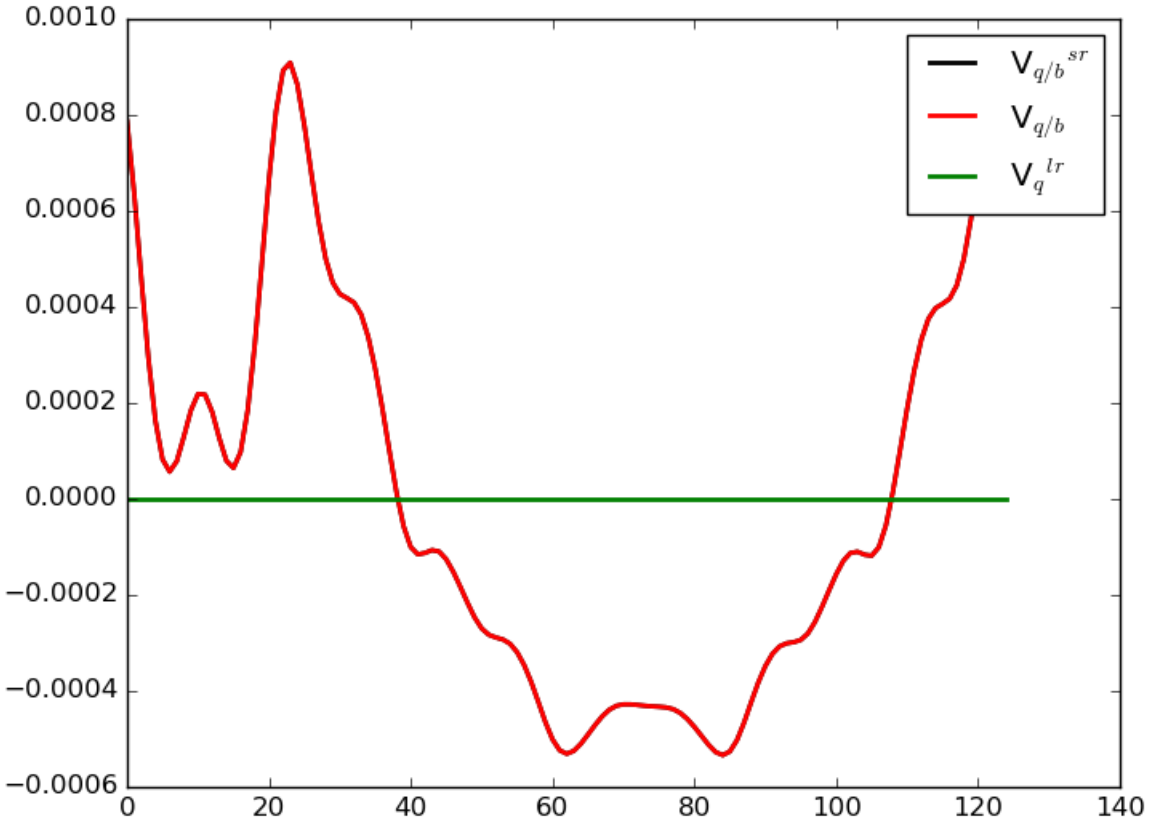
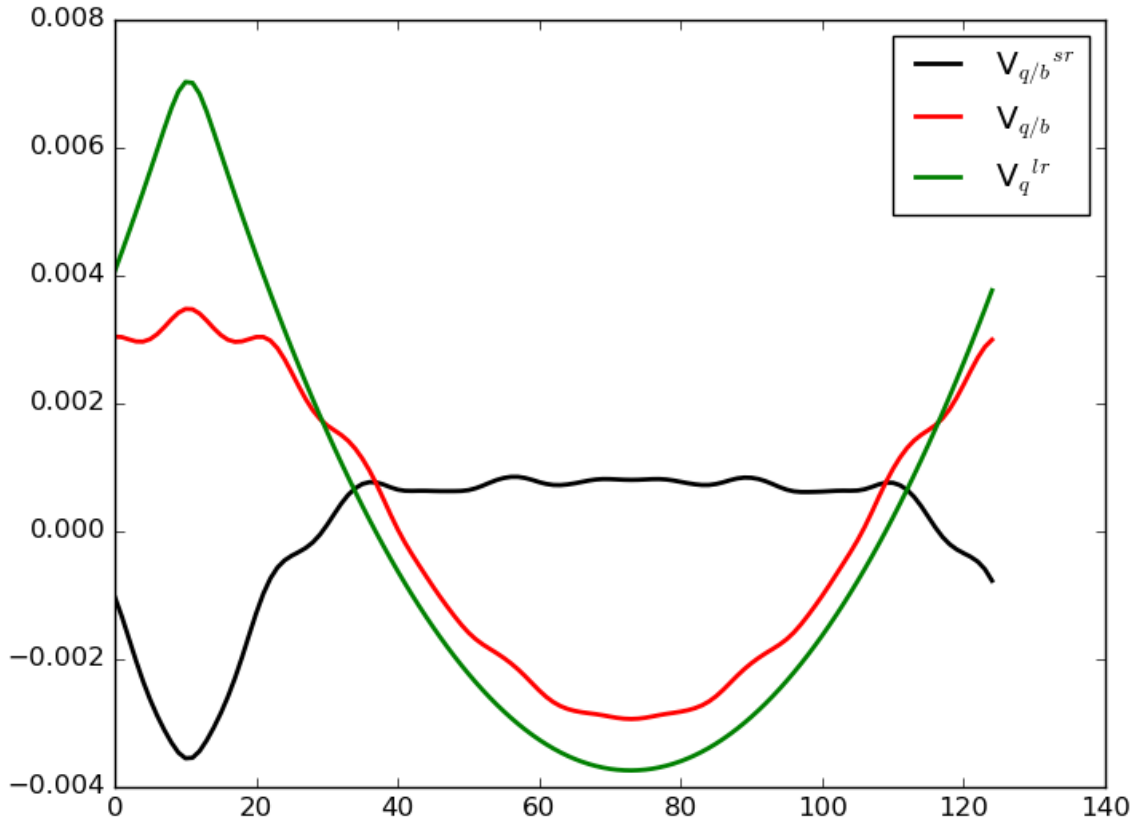
E_{lat} corrects for the electrostatic interaction due to image charges.

$q\Delta \mathrm{V}_{\mathrm{q}/b}$ corrects for the offset in the VBM due to the introduction of the defect. V_q^{lr} is the long-range potential of the model charge distribution defect and $\tilde{V}_q^{lr}$ is the corresponding quantity in the periodic cell. $\widetilde{\mathrm{V}}_{q/b}$ is the difference between the potential in the pristine bulk configuration and with the defect added. $\Delta \mathrm{V}_{\mathrm{q}/b}$ should then be evaluated far from the defect, where it is constant, in order to get the offset in the ZP reference energy. In our implementation, it is averaged over the five grid points furthest from the defect.

We obtain V_q^{lr} and $\tilde{V}_q^{lr}$ by modelling the charge distribution as a gaussian with a default width of approximately 3 bohr.

C. Freysoldt, J. Neugebauer and C. G. Van de Walle, PRL **102**, 016402, (2009)
C. Freysoldt, J. Neugebauer and C. G. Van de Walle, Phys. Status Solidi B **248**(5), 1067, (2011)

Neutral vacancy:



-3 vacancy: