Lecture 4 – Density functional theory for solids II

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TYC Materials Modeling Course

Overview

1. Total energy
2. Planewave basis
3. Pseudopotentials
4. Supercells and point defects

Total energy

The total energy in Kohn-Sham DFT is given as,

$$E_{\text{tot}} = \int_{\Omega} \rho\left(\mathbf{r}\right) v\left(\mathbf{r}\right) d\mathbf{r} + T_{ks} + E_{\text{Har}} + E_{\text{xc}} \tag{1}$$

What does the exchange correlation energy E_{xc} include?

The total energy in Kohn-Sham DFT is given as,

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What does the exchange correlation energy E_{xc} include?

1. Correction from the non-interacting Kohn-Sham kinetic energy T_{ks} to the true many-body kinetic energy
2. Removes the self interaction included in the Hartree energy E_{Har}
3. Extra changes to the electron interaction due to changes to the wavefunction

To evaluate this energy we need the Kohn-Sham orbitals, and a definition for $v\left(\mathbf{r}\right)$.

Interactions with ions

The atomic nuclei are included as point charges,

$$E_{\mathrm{tot}} = \int_{\Omega} \rho\left(\mathbf{r}\right) v_{\mathrm{ions}}\left(\mathbf{r}\right) d\mathbf{r} + T_{\mathrm{ks}} + E_{\mathrm{xc}} + E_{\mathrm{Har}} + E_{\mathrm{ion-ion}}, \tag{2}$$

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The ions generate the external potential the atoms move in.

$$v_{\text{ions}}\left(\mathbf{r} + \mathbf{R}\right) = \sum_{i} \frac{1}{4\pi\varepsilon_{\infty}} \frac{q_i}{r_i}, \qquad (3)$$

The interactions between the nuclei is calculated using Ewald summation,

$$E_{\mathrm{ion-ion}} = \frac{1}{2}\sum_{I,J} Z_I Z_J e^2 \left\{ \sum_{i} \frac{\mathrm{erfc}\,(\eta|\mathbf{r}_I + \mathbf{R} - \mathbf{r}_J|)}{|\mathbf{r}_I + \mathbf{R} - \mathbf{R}_J|} - \frac{2\eta}{\sqrt{\rho}}\delta_{IJ} \right.$$
$$\left. + \frac{4\pi}{\Omega}\sum_{\mathbf{G}\neq 0}\frac{1}{|\mathbf{G}|^2}\exp\left(-\frac{|\mathbf{G}|^2}{4\eta^2}\right)\cos\left[(\mathbf{r}_I - \mathbf{r}_J)\cdot\mathbf{G}\right] - \frac{\pi}{\eta^2\Omega} \right\},$$

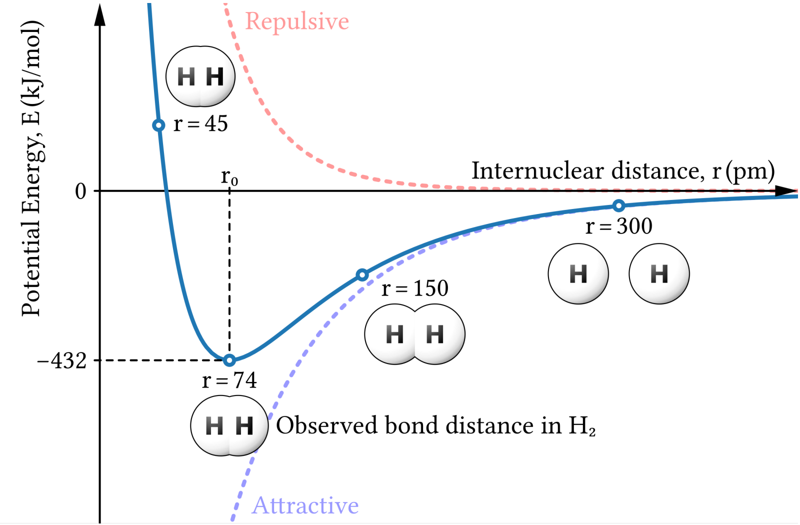
This is a combined realspace and reciprocal space expression.

A good derivation of this can be found at `http://micro.stanford.edu/mediawiki/images/4/46/Ewald_notes.pdf`

DFT can be used to calculate the energy of a particular arrangement of atoms, or to find the lowest energy arrangement of atoms:

1. The electron density $\rho(r)$ that minimises the total energy for an arrangement of atoms is found (SCF)
2. The force on each atomic nucleus is calculated for this electron density (Hellmann–Feynman theorem)
3. The atomic nuclei are moved in response to these forces to try and find a lower energy structure (Geometry optimisation)
4. Return to step 1 unless the required accuracy has been achieved

There are a few different algorithms available for steps 1 and 3.


Repulsive
Potential Energy, E (kJ/mol)
r = 45
Internuclear distance, r (pm)
r_0
0
r = 300
r = 150
−432
r = 74
Observed bond distance in H_2
Attractive
H H
H H
H H
H H

Planewaves as a basis

The Kohn-Sham orbitals and their occupation define the density:

$$\rho\left(\mathbf{r}\right) = \sum_{\text{occupied states}} \left|\psi_n\left(\mathbf{r}\right)\right|^2 \tag{4}$$

We know that in the absence of interaction, electrons obey Bloch's theorem,

Bloch's theorem

$$\psi_k\left(\mathbf{r}\right) = U_k\left(\mathbf{r}\right)\exp\left(i\mathbf{k}\cdot\mathbf{r}\right) \tag{5}$$

The periodic part of the wavefunction

We can choose plane waves as our basis for $U_k\left(\mathbf{r}\right)$,

$$U_k\left(\mathbf{r}\right) = \sum_{\mathbf{G}}^{\infty} C_G \exp\left(i\mathbf{G}\cdot\mathbf{r}\right) \tag{6}$$

Our reciprocal lattice **G** has appeared again...

This time it is not related to k-point sampling

The periodic part of the wavefunction

A complex exponent is periodic with period 2π

$$\pm \exp\left(i\theta\right) = \cos\left(\theta\right) + i \sin\left(\theta\right) \tag{7}$$

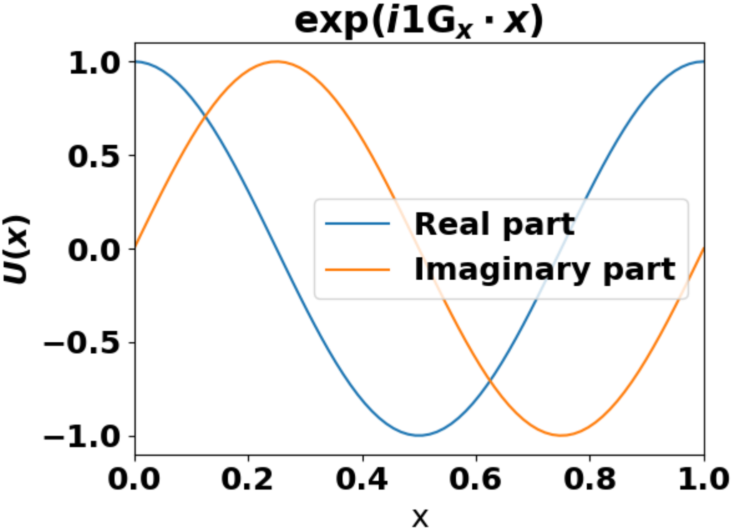
Only reciprocal lattice points will fit into the unit cell,

$$\mathbf{G} = N_x \mathbf{G}_x + N_y \mathbf{G}_y + N_y \mathbf{G}_y \tag{8}$$

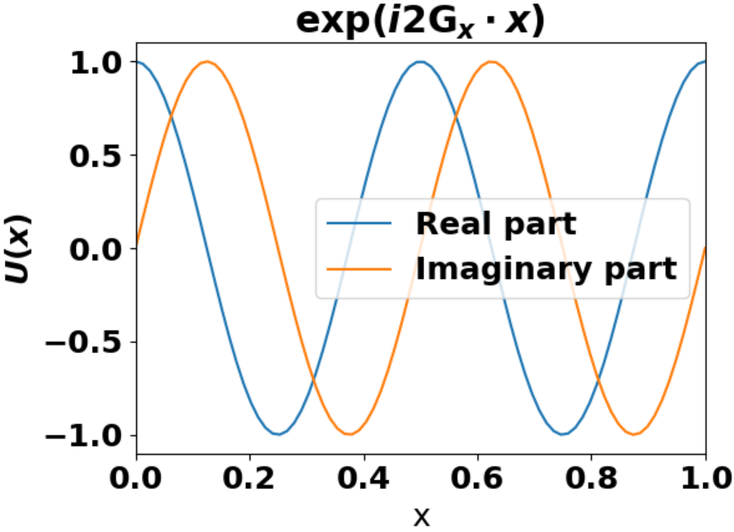
Due to the relationship,

$$\mathbf{G} \cdot \mathbf{R} = 2\pi \tag{9}$$

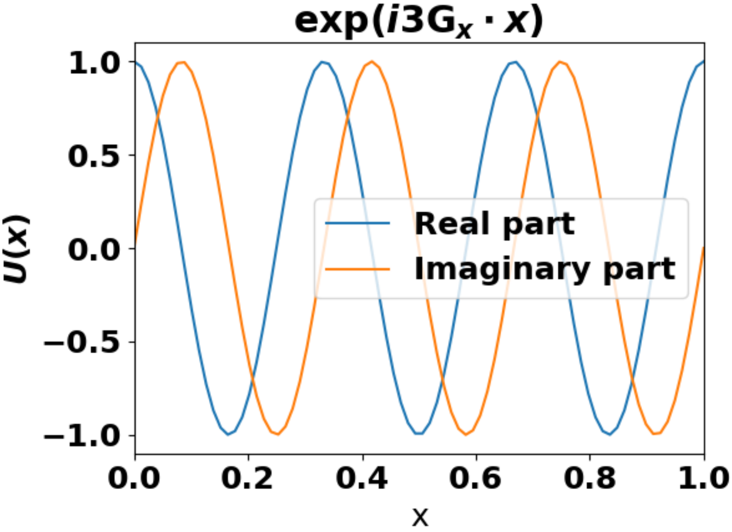
Example planewaves



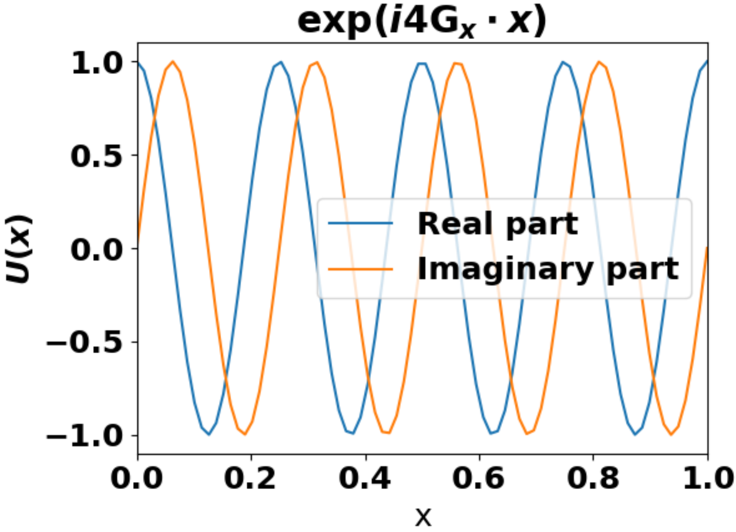
Example planewaves



Example planewaves



Example planewaves



We can't consider an infinite amount of planewaves, so we have to truncate the expansion

$$U_k\left(\mathbf{r}\right) = \sum_{\mathbf{G}}^{|\mathbf{G}|<G_{\text{max}}} C_G \exp\left(i\mathbf{G}\cdot\mathbf{r}\right) \tag{10}$$

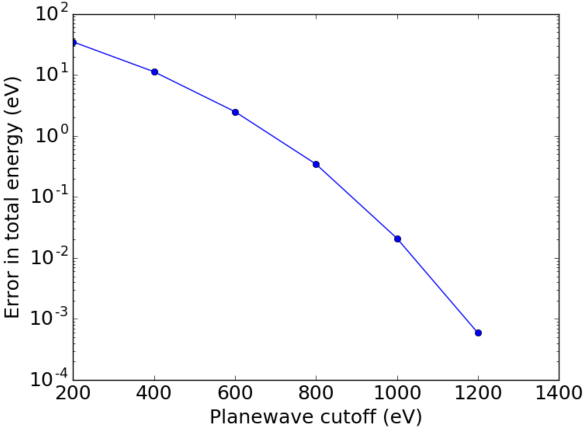
This is typically given as a cutoff energy,

$$E_{\text{cut}} = \frac{\hbar^2}{2m}\left|G_{\text{max}}\right|^2 \tag{11}$$

This would be the kinetic energy of a basis function if it described an electron in a non-interacting homogeneous electron gas.

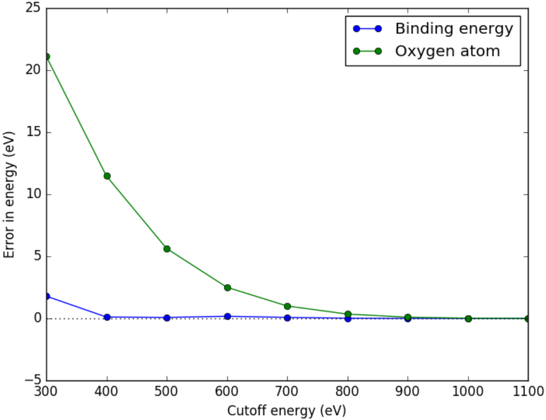
Energy cuttoff convergence

It is important to check that a high enough value of E_{cut} was used to achieve the required accuracy.



Total energy vs energy difference

Normally we are only interested in energy differences and these converge faster



Planewave DFT

These are some of the most popular DFT codes that use a planewave basis

CASTEP

Abinit

VASP
b-initio
ackage
imulation
ienna

CPMD

QUANTUMESPRESSO

Pros and cons of planewaves

Pros

- Treat whole system uniformly (non-biased)
- Very computationally efficient (FFT algorithm).
- Mathematically well behaved (Complete and orthonormal)
- Easy to evaluate forces (Hellmann–Feynman theorem)
- Systematically improvable

Cons

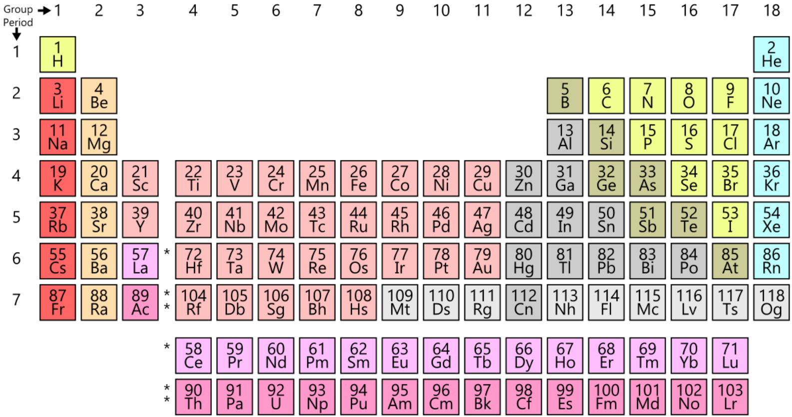
- Treat whole system uniformly (wasteful)
- Poor representation of atomic core regions (requiring pseudopotentials)
- Does not scale well to extremely large numbers of atoms.

Pseudopotentials

The methods we've developed would work, but they are still too computationally demanding

The periodic table

The periodic table organises elements by their chemical properties



Group → / Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La *	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac **	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

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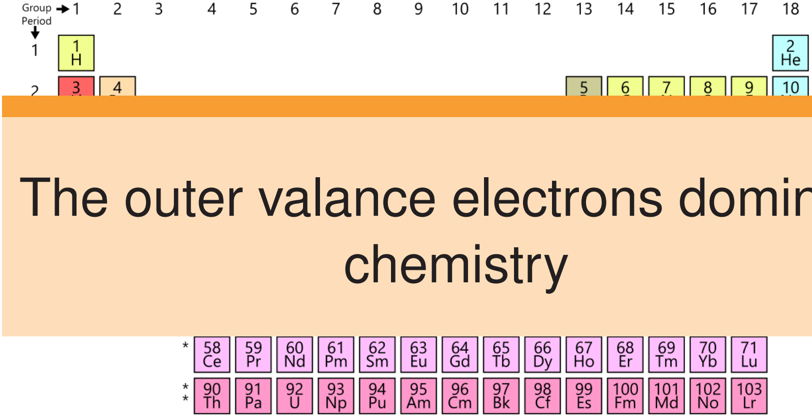
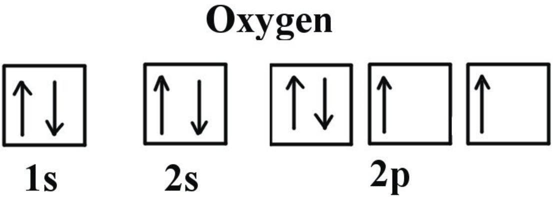
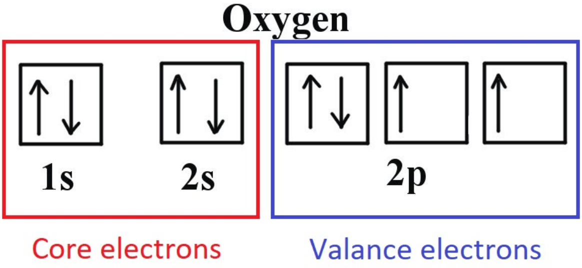


The outer valance electrons dominate chemistry

Frozen core approximation



Frozen core approximation



- Don’t allow the core electrons to move in our calculation
- Only explicitly include the valance electrons in the DFT calculation

Types of DFT

There are two main types of DFT calculation in the literature,

All electron

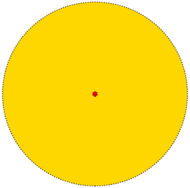
All electron calculations treat every electrons in the system explicitly. As a result the calculations are far more computationally demanding.

Pseudopotential

Some of the electrons are only included in the pseudopotential. We are approximating that these electrons are frozen in place.

By definition, good pseudopotentials lead to the same results as all electron calculations.

Pseudopotential construction



- Nucleus of the atom produces a potential V_{ext} in the DFT calculation.
- The electrons sit in orbitals around the atomic nucleus.

Pseudopotential construction

- Nucleus of the atom produces a potential V_{ext} in the DFT calculation.
- The electrons sit in orbitals around the atomic nucleus.

- We seek a pseudopotential V_{PP} that essentially contains the core elections too.
- We define a cutoff radius r_c such that there is no difference in electron density outside this.

Pseudopotential construction

Pseudopotentials are constructed by doing an atomic calculation, once with all electrons (AA) and once with the pseudopotential (PP). The PP has to satisfy certain conditions,

- The wavefunctions outside the cutoff should look identical

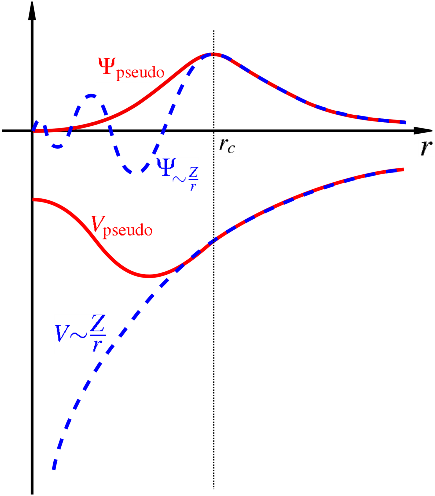
$$\psi^{PP}\left(\mathbf{r} > \mathbf{r}_c\right) = \psi^{AA}\left(\mathbf{r} > \mathbf{r}_c\right) \tag{12}$$

- The valance electron eigenvalues have to be the same

$$\varepsilon_i^{PP} = \varepsilon_i^{\mathrm{AA}} \tag{13}$$

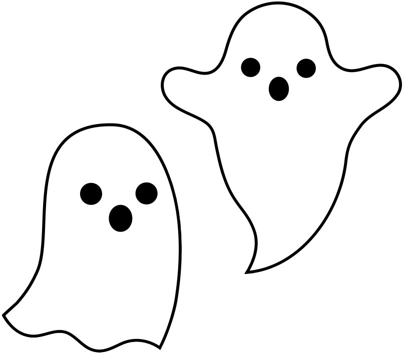
- The PP must also reproduce scattering properties of the atom.

Pseudopotentials in action



Beware of ghost states

Bad pseudopotentials can fail and introduce “ghost states” into calculations that are non-physical



A good reason not to use new pseudopotentials without testing, but well tested potentials won’t do this

Pseudopotential jargon

There are many different ways of generating pseudopotentials

Hardness

Hard pseudopotentials require large planewave basis sets, but soft pseudopotentials will still work with small basis sets.

Transferability

Transferable pseudopotentials work in many different chemical environments.

Constructing pseudopotentials is a compromise between these two properties.

DFT delta project

This has been systematically checked by the delta project, `https://molmod.ugent.be/deltacodesdft`

code	Basis	Electrons	Δ (meV/atom)
WIEN2K	LAPW/APW+lo	all-electron	0
FHI-AIMS	teir2 numerical	all-electron	0.2
EXCITING	LAPW+xlo	all-electron	0.2
ELK	APW+lo	all-electron	0.3
QUANTUM ESPRESSO	planewave	pseudopotential	0.3
VASP	planewave	pseudopotential	0.3
CASTEP	planewave	pseudopotential	0.4

With good pseudopotentials, these calculations can be essentially as good as all electron calculations.

Total energy

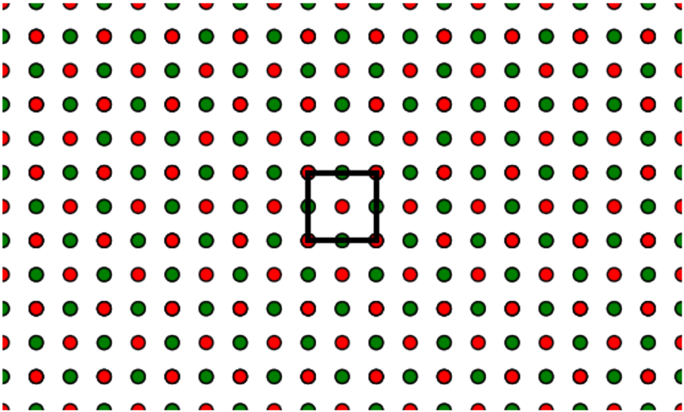
The expression for total energy is slightly modified by the use of pseudopotentials,

$$E_{\text{tot}} = \int \rho\left(\mathbf{r}\right) v_{\text{PP}}\left(\mathbf{r}\right) d\mathbf{r} + T_{\mathrm{ks}} + E_{\mathrm{xc}} + E_{\mathrm{Har}} + E_{\mathrm{ion-ion}} + E_{\mathrm{NC}}, \qquad (14)$$

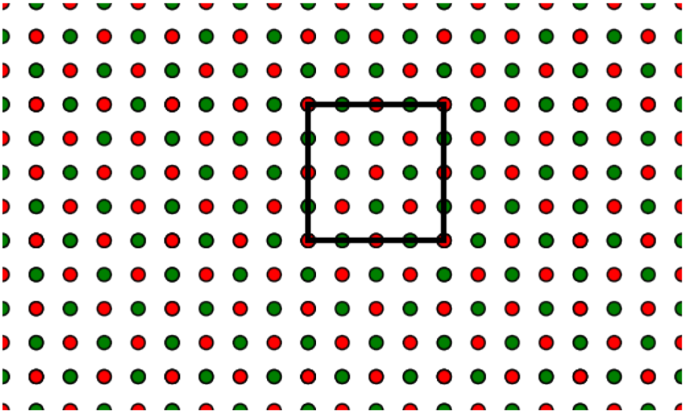
The new energy term E_{NC} is required, to allow for the fact that the pseudopotentials are no longer point charges.

Supercells

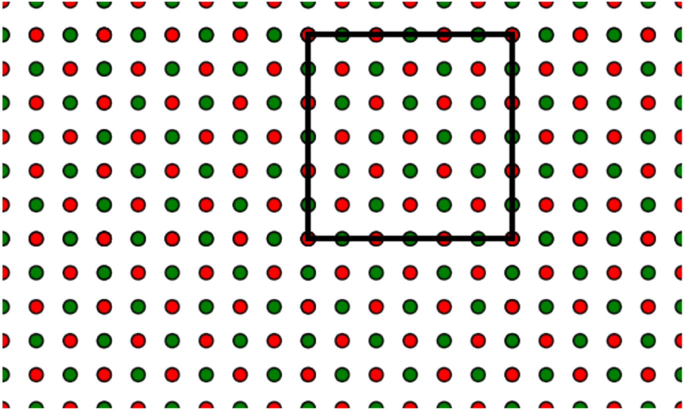
1x1x1 conventional unit cell



2x2x2 supercell

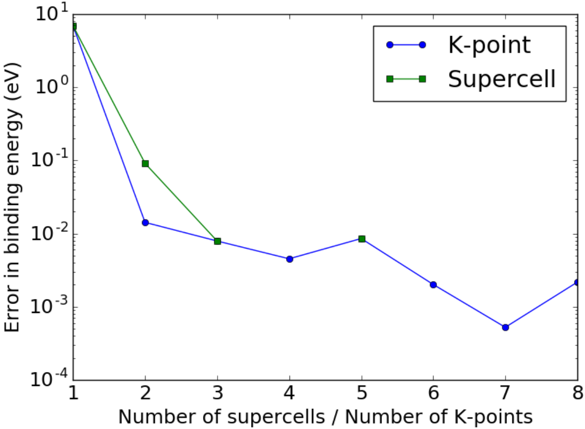


3x3x3 supercell



Supercell approach

When applied to fully periodic atomic structures (ideal crystals), supercells provides another strategy for dealing with the quasiperiodicity of Bloch waves.



Supercells

The developed approach requires full lattice symmetry. But this doesn’t stop us considering systems with less symmetry.

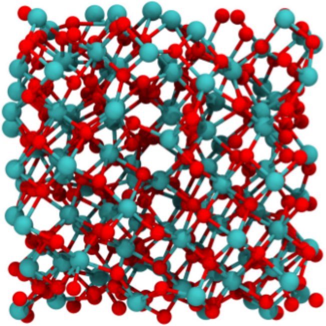
Supercells

The developed approach requires full lattice symmetry. But this doesn't stop us considering systems with less symmetry.

Then symmetry becomes an approximation that we force on the system. We need to ensure that the results we calculate don't depend on the supercell size.

Amorphous materials

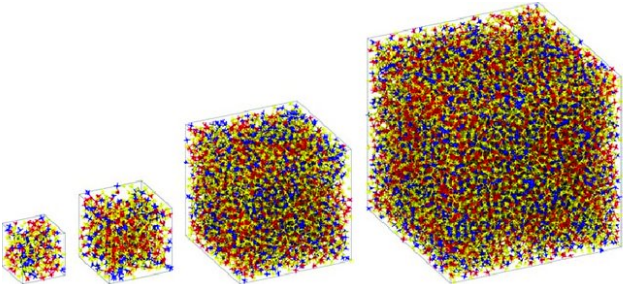
Amorphous materials are highly disordered



They can be approximated by infinitely repeated disordered blocks

Amorphous materials

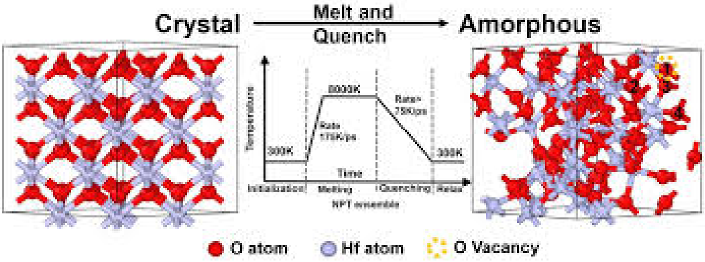
The larger the block, the better the model



Models beyond a certain size will match the properties of the real amorphous system

Amorphous materials

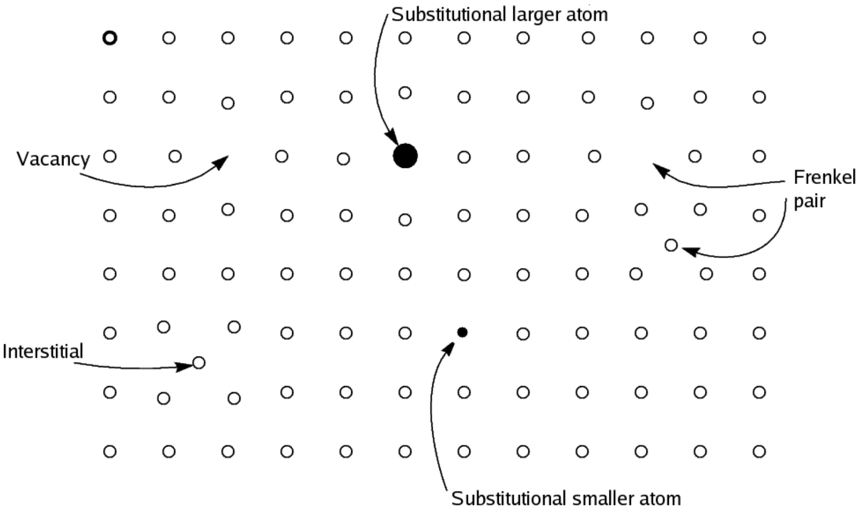
Such models are generated using the “melt and quench” method



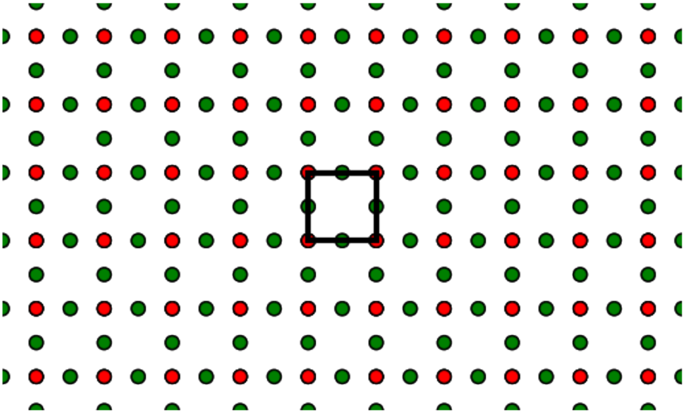
Models beyond a certian size will match the properties of the real amorphous system

Example application: Charged defects

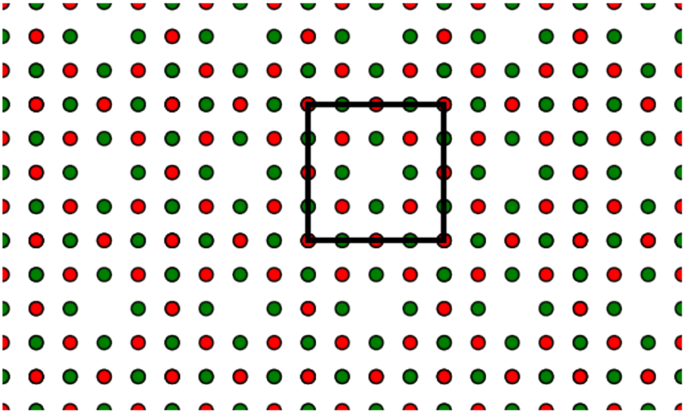
Types of point defect



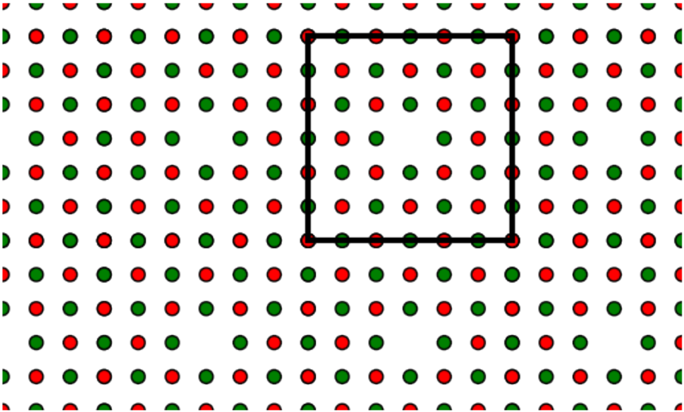
1x1x1 defective unit cell



2x2x2 defective supercell



3x3x3 defective supercell



Defect formation energy

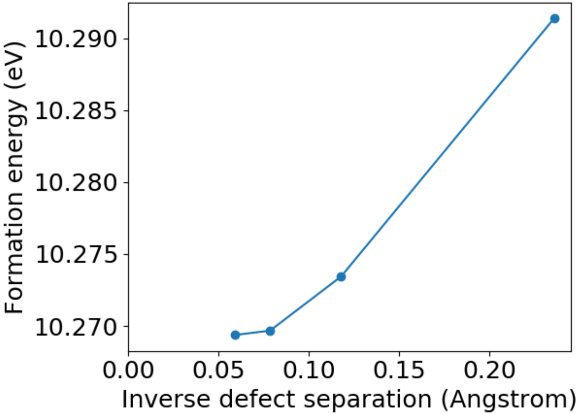
Supercell size defines defect density.

The energy cost to form a neutral defect is

$$E_f = E_{\text{defect}}^{\text{DFT}} - E_{\text{bulk}}^{\text{DFT}} - \sum_i n_i \mu_i \tag{15}$$

- $E_{\text{defect}}^{\text{DFT}}$: DFT energy of a supercell containing the defect
- $E_{\text{bulk}}^{\text{DFT}}$: DFT energy of a supercell of perfect crystal
- μ_i : Atomic chemical potential of the element *i*.
- n_i : Number of atoms of element *i* exchanged.

MgO F^0 formation energy



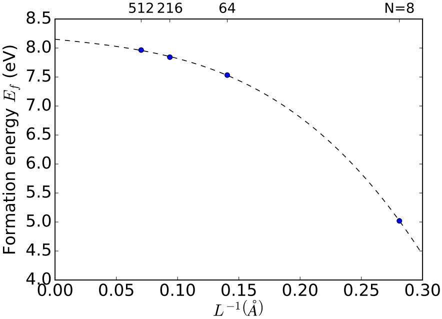
We don’t need very large supercells for a neutral defect.

Size convergence of defect formation energy

Studies of supercell size scaling have suggested the following form for cubic supercells[1],

$$E_f(L) = E_f(\infty) + \frac{a_1}{L^1} + \frac{a_2}{L^3}$$

Example size convergence of the V_C^{+2} defect in diamond:



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[1] Castleton *et al.* Phys. Rev. B 73 035215 (2006)

Charged defect formation energy

The energy cost to form a charged defect is

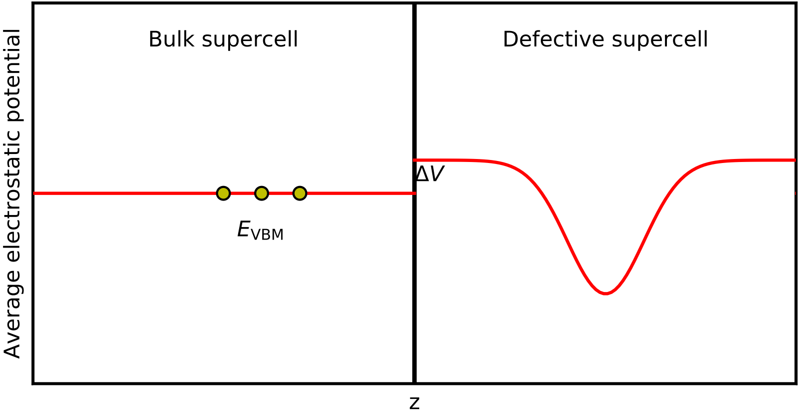
$$E_f = E_{\text{defect}}^{\text{DFT}} - E_{\text{bulk}}^{\text{DFT}} - \sum_i n_i \mu_i + E_{\text{corr}} + q\left(\mu_e + \Delta V\right) \tag{16}$$

- E_{corr} : Correction for finite-size dependant electrostatics
- μ_e : Chemical potential of electrons
- μ_i : Correction to chemical potential of electrons, needed due to neglect of the average potential

Potential alignment, $q\Delta V$

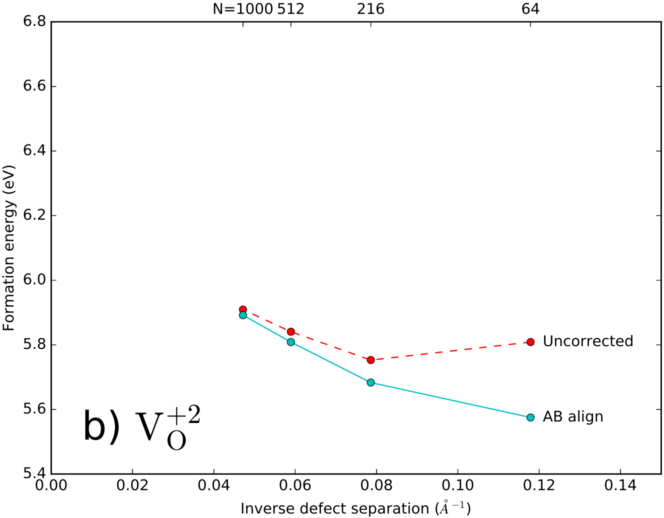
In periodic DFT, the average value of the electrostatic potential V can't be calculated and is conventionally set to zero,

$$\langle V(\mathbf{r}) \rangle = 0$$



MgO bulk

Supercell size convergence of the +2 Oxygen vacancy in MgO



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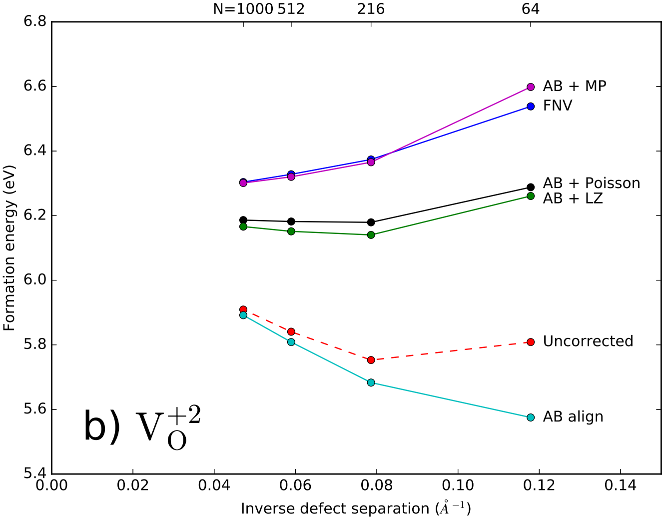
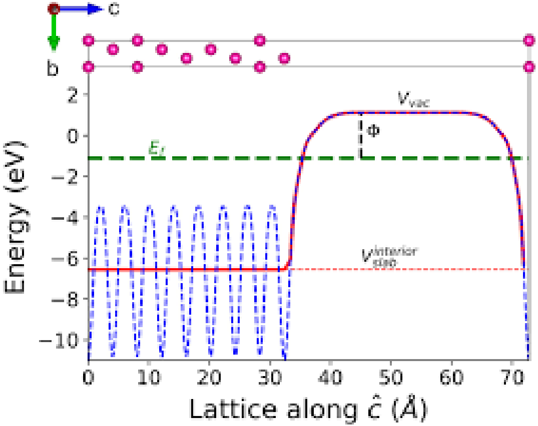


Work function

Another example of this average potential problem is in the calculation of work-functions



Conclusions

- We can use a planewave basis and pseudopotentials to simulate real materials
- It is important to converge these calculations with respect to the planewave cutoff energy and the **k**-space sampling.
- Pseudopotentials allow a significant reduction in computational cost, but should always be checked carefully.
- Periodic DFT formalism can be used to study non-periodic systems (such as surfaces and defects) but care must be used to ensure that the size of the supercell doesn't introduce errors.