THEOS
THEORY AND SIMULATION OF MATERIALS

DFT and DFPT for 2D systems: 2D cutoff in PW and PH

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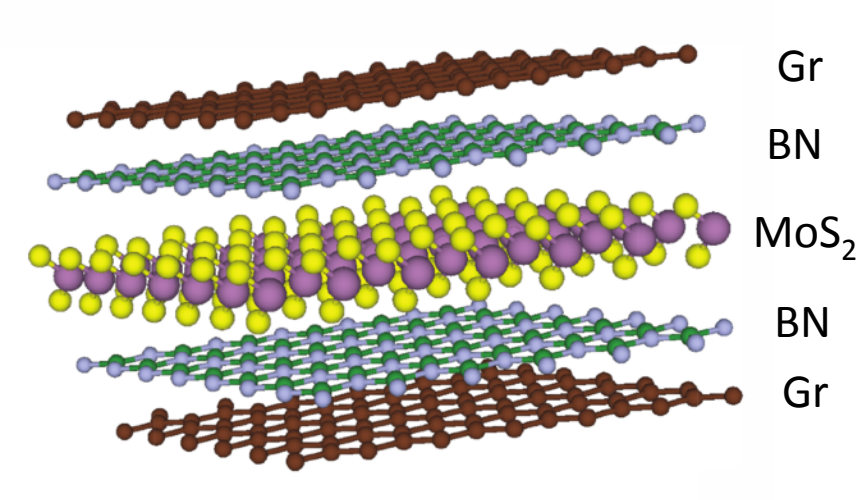
Objectives

The goal is to implement an easy and correct way to simulate 2D heterostructures:

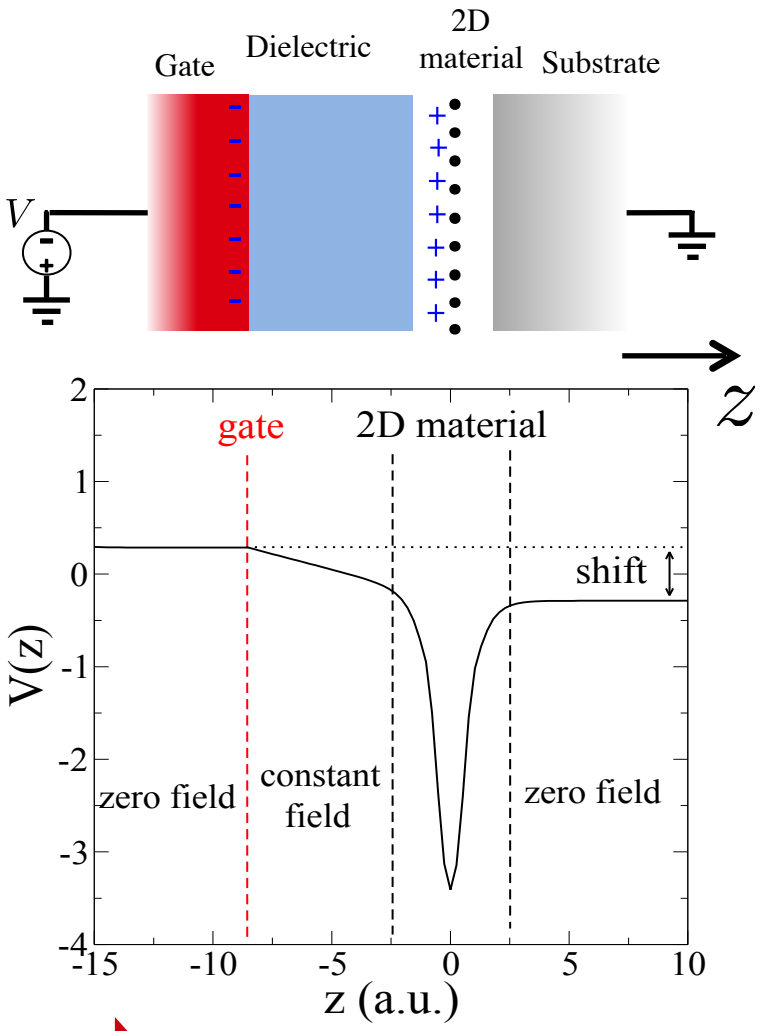


Currently, QE has difficulties with some key aspects of 2D materials:

- Doping in the field-effect transistor (FET) setup
- Linear response to long wavelength perturbations in a 2D framework
  - ➢ Screening
  - ➢ Phonons
  - ➢ Electron-Phonon Coupling (EPC)

Issues with periodic images

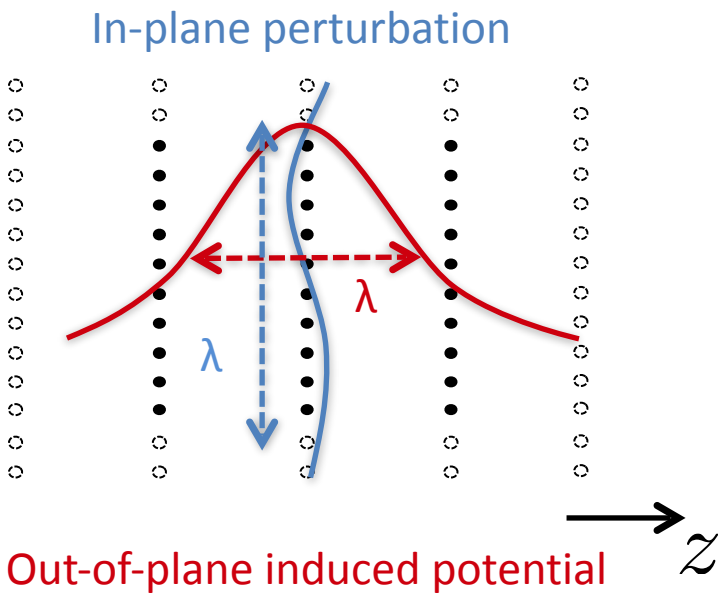
FET setup



Potential not 3D-periodic

Linear response…

… in 2D material + periodic images



Periodic images interact at long wavelengths.
Particularly relevant for:

- Electronic screening
- Electron-Phonon Coupling
- Polar-optical phonons (LO-TO splitting)

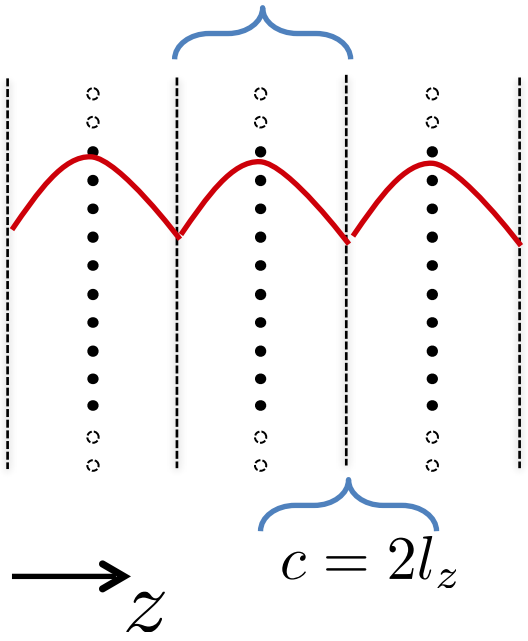
2D Coulomb cutoff

$$V(\mathbf{r}) = e \int \varrho(\mathbf{r}')v_c(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'$$

$$v_c(|\mathbf{r}|) = \frac{1}{|\mathbf{r}|}\theta(l_z - |z|)$$

$$l_z \equiv \text{cutoff distance}$$

Isolated slab



➢ Periodic images are still there, but don't see each other

[Rozzi, C. A., et al. PRB, 73, 205119 (2006)]

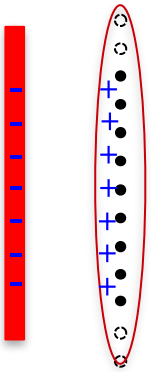
2D cutoff + field-effect setup implemented in QE 5.1 for:

DFT level	Total Energy Forces Stresses
DFPT level (linear response)	Phonons EPC

Works with NC, US, PAW pseudopotentials.

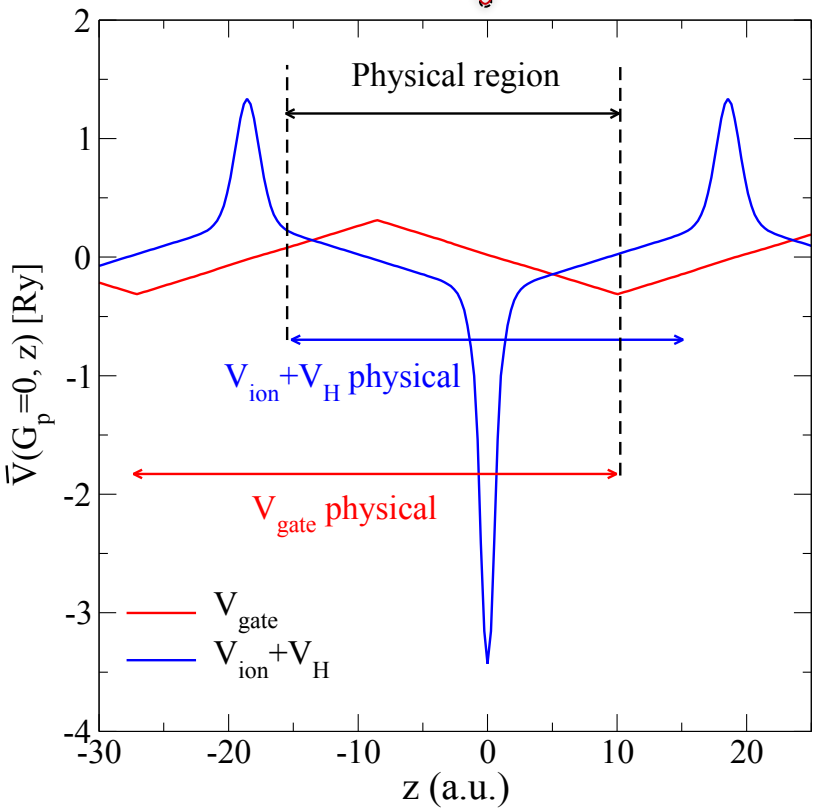
Details in: Sohier, T. , PhD thesis, UPMC (2015), supervised by Calandra, M., Mauri, F. (link)

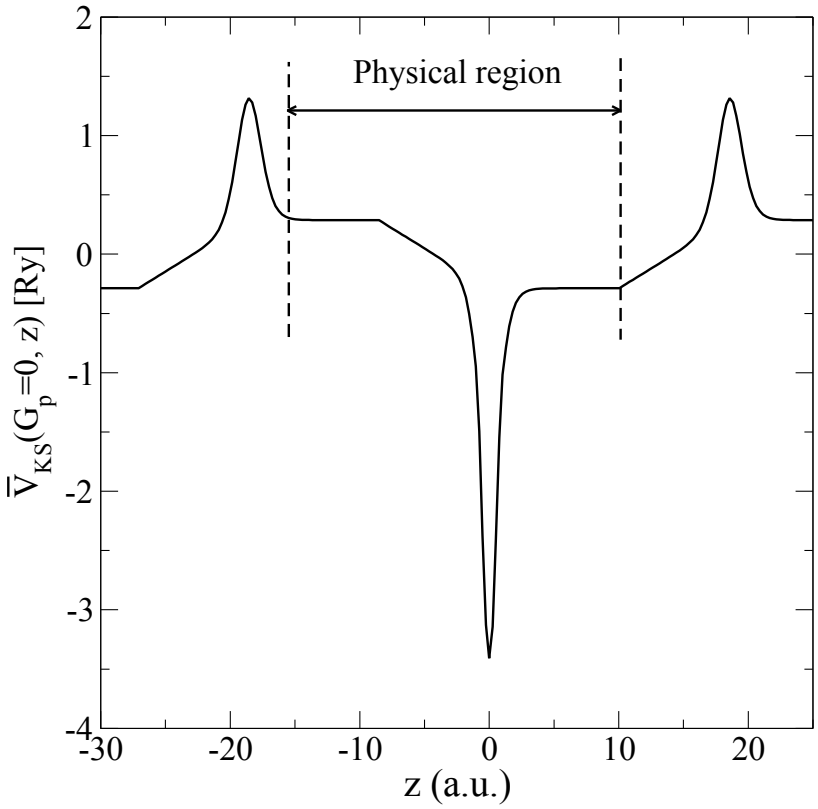
Potentials – FET setup



[Gate implementation inspired by
Brumme, Calandra, Mauri, PRB 89, 245406 (2014).]

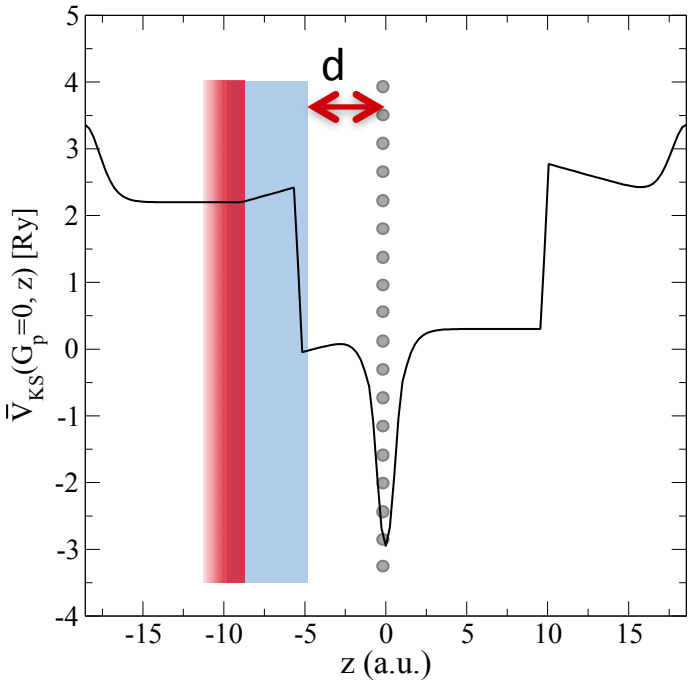
- Potential of each subsystem generated only in a certain slab
- physical region = overlap of the subsystems' slabs

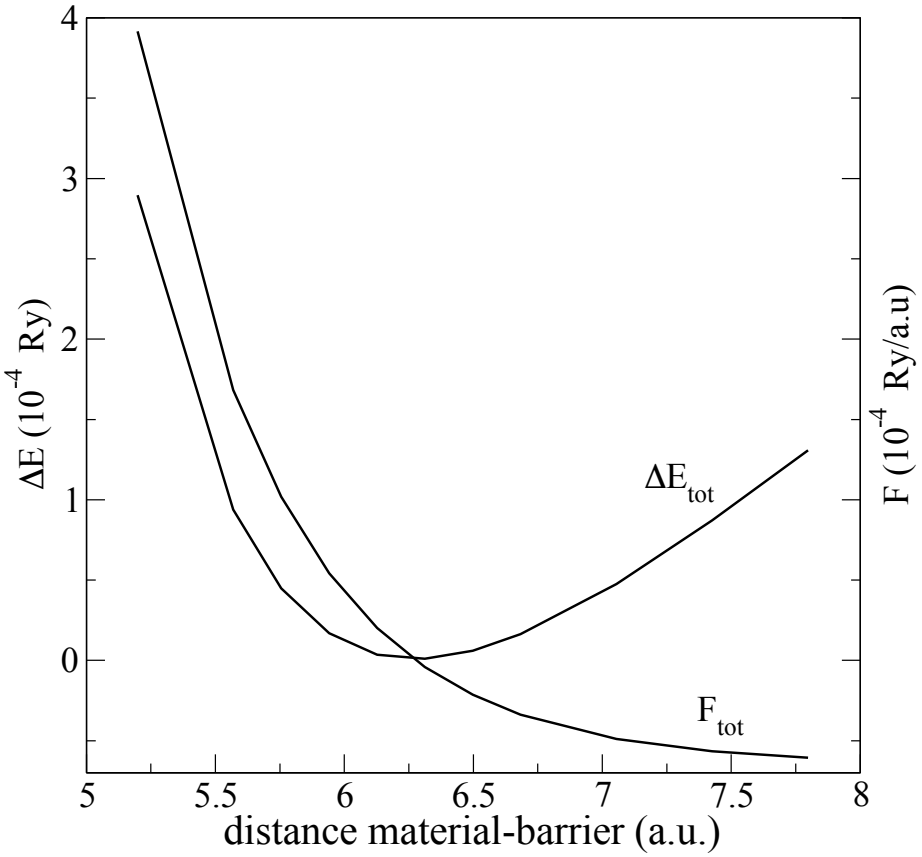




Total energy and forces – FET setup

Gate + barrier + doped graphene

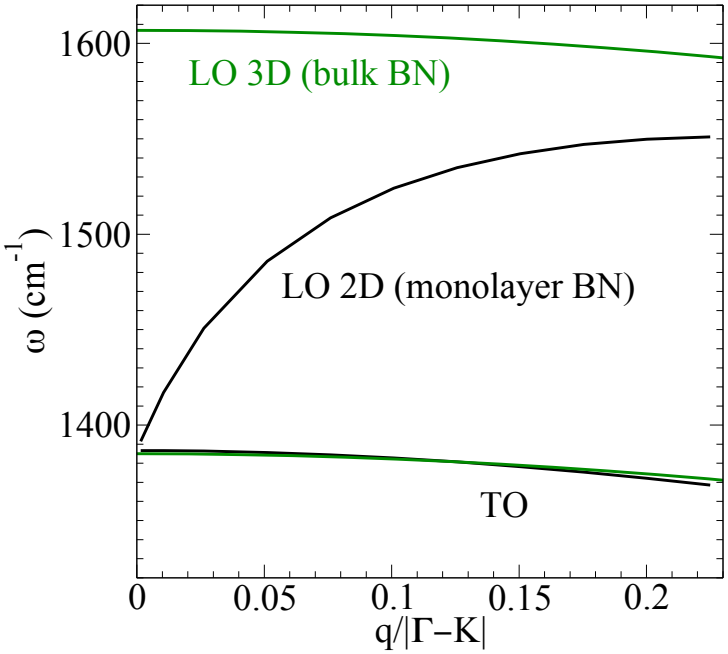




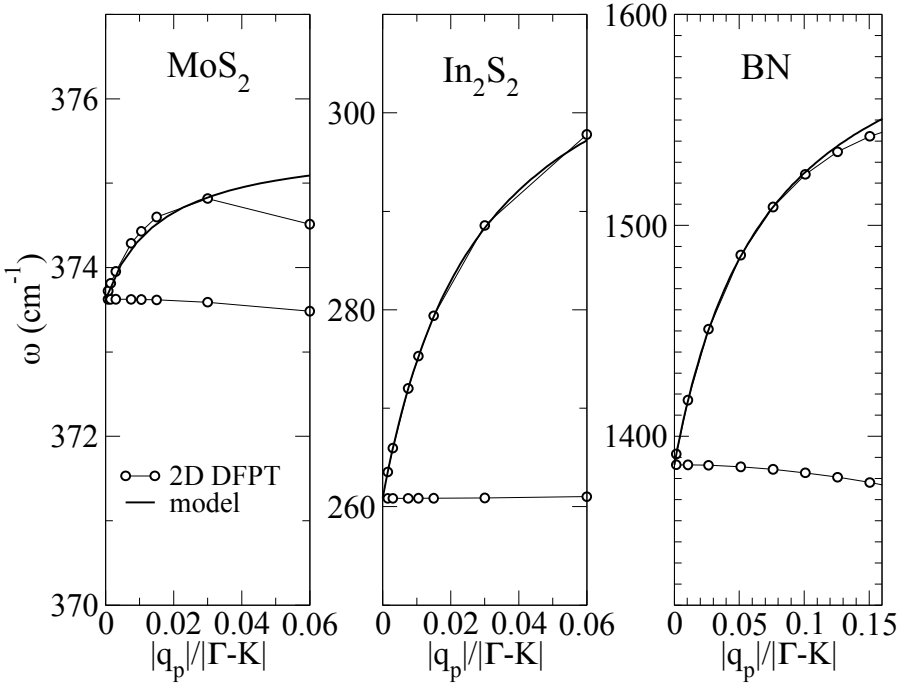
- Strong repulsion at small d
- Attraction from gate at large d
- Equilibrium around 6.25 a.u.

Phonons – LO-TO splitting

BN (neutral): 3D vs 2D



Other polar monolayers



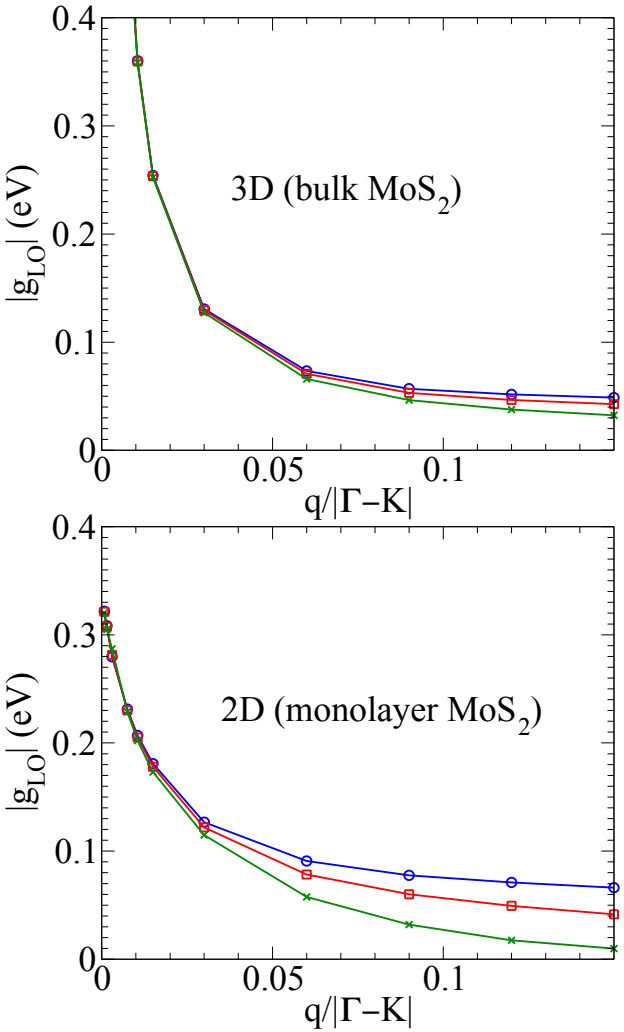
$$\omega_{\mathrm{LO}}^2 = \omega_{\mathrm{TO}}^2 + \frac{\mathcal{S}|\mathbf{q}_p|}{\epsilon_{\mathrm{ext}} + r_{\mathrm{eff}}|\mathbf{q}_p|}$$

← 2D screening

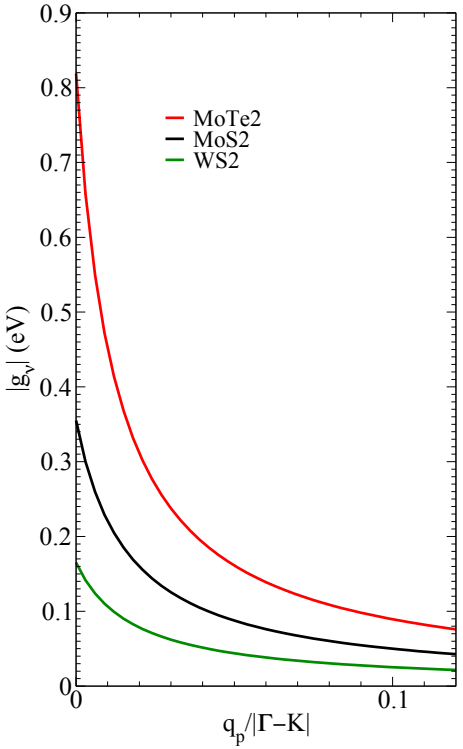
More details on poster at total energy

EPC – Fröhlich interaction

MoS_2 (neutral): 3D vs 2D



Other polar monolayers



$$|g_{\mathrm{Fr}}^{\mathrm{2D}}(\mathbf{q}_p)| = \frac{C_{\mathcal{Z}}}{\epsilon_{\mathrm{ext}} + r_{\mathrm{eff}}|\mathbf{q}_p|}$$

More details on poster at total energy…

Conclusion and perspectives

Done:

- ✓ Total energy, Kohn-Sham states, forces and stresses
- ✓ In-plane structural optimization
- ✓ Phonons: single-q and interpolation
- ✓ Electron-phonon interactions
- ✓ Norm conserving, Ultrasoft and PAW pseudopotentials
- ✓ Spin-orbit coupling, noncollinear magnetism
- ✓ AiiDA compatible (Pizzi et al., Comp. Mat. Sci., 111, 218–230. (2016))
- ✓ High-throughput friendly (see posters by N. Mounet, D. Campi, A. Marrazzo)

Perspectives

- ❑ Integration in official QE
- ❑ Compatibility with VdW functionals
- ❑ New exchange-correlation functionals?
- ❑ DFT+U?
- ❑ Molecular Dynamics?
- ❑ Third-order DFPT?
- ❑ Spectroscopy?

Thanks

Thank you for listening!

Supervision:

Matteo Calandra
Francesco Mauri

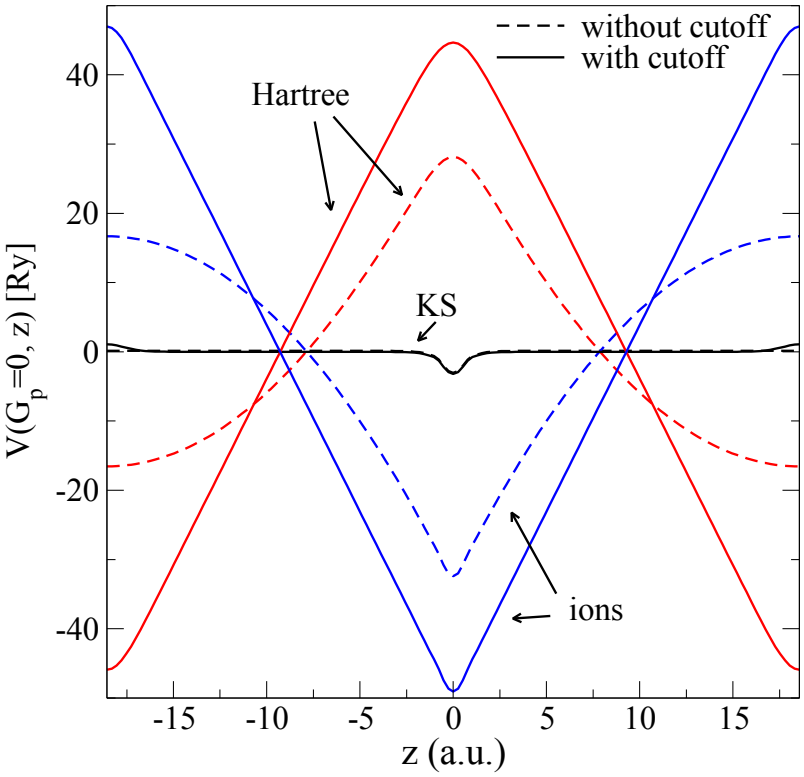
Helpful discussions:

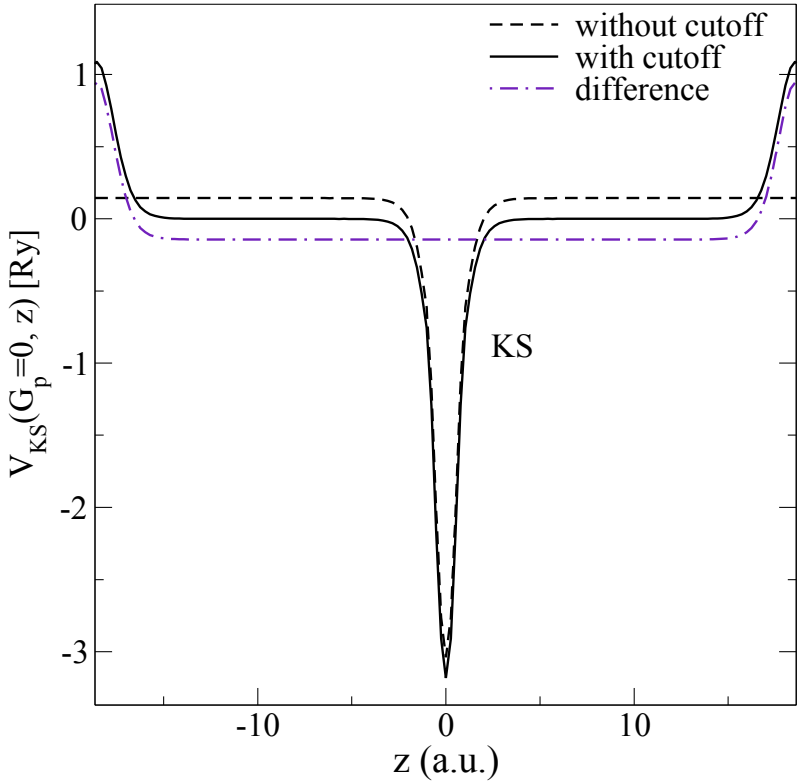
Lorenzo Paulatto
Thomas Brumme

And also, concerning more recent fine tuning:

Nicola Marzari
Marco Gibertini
Nicolas Mounet
Davide Campi
Antimo Marrazzo

Potentials – neutral system

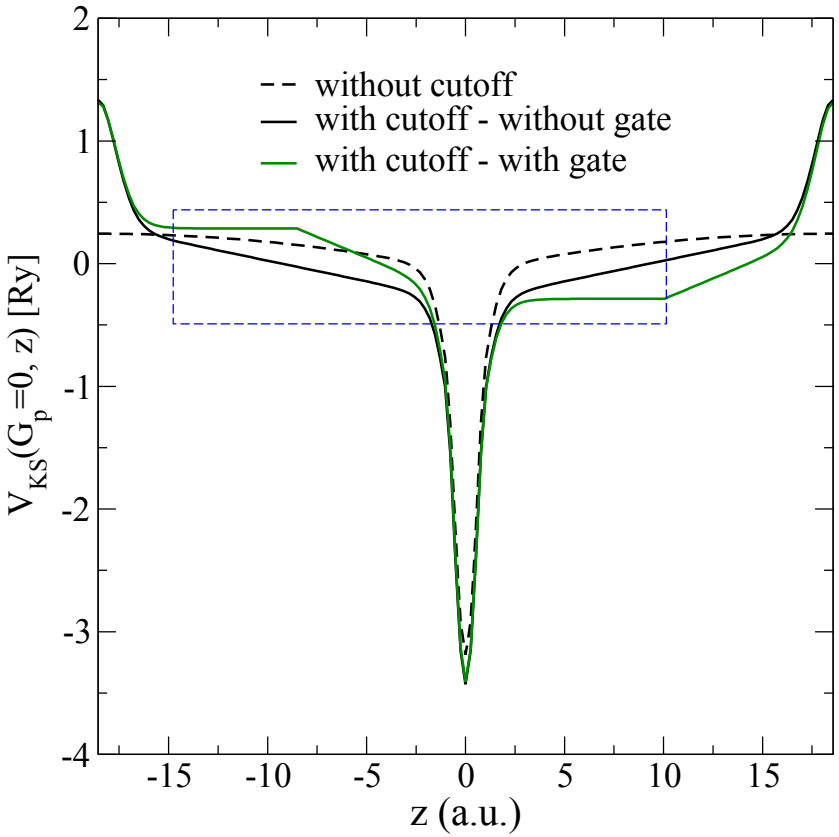


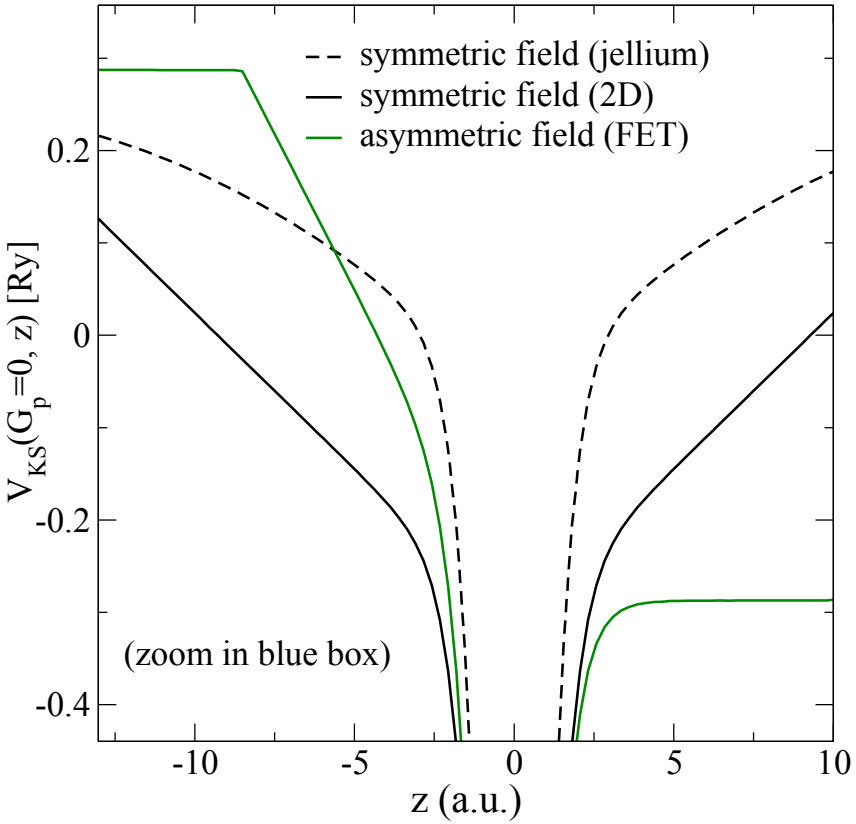


- Pseudopotentials are not isotropic. Radial Fourier Transform not possible.
- No more “jellium” – Different treatment of G=0 divergences.

Potentials – FET setup

Gate doping VS charged plane VS jellium doping

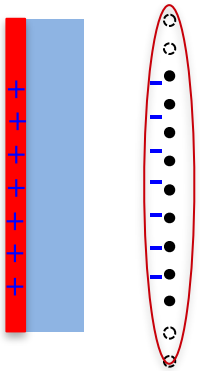


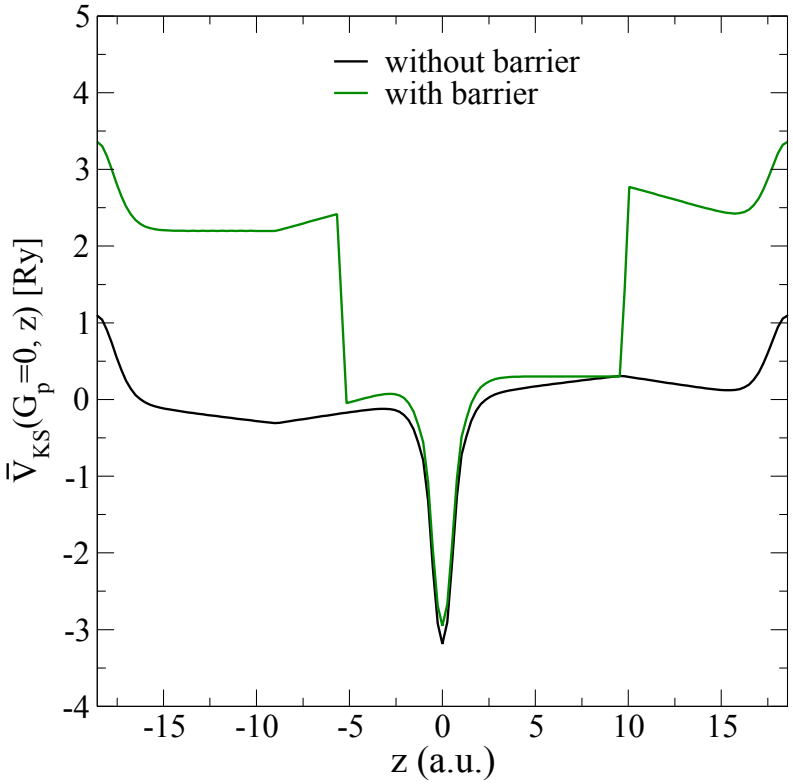


- Completely different electrostatic setup

Sohier, T. , PhD thesis, UPMC (2015), supervised by Calandra, M., Mauri, F. (link)

Potentials – FET setup barrier



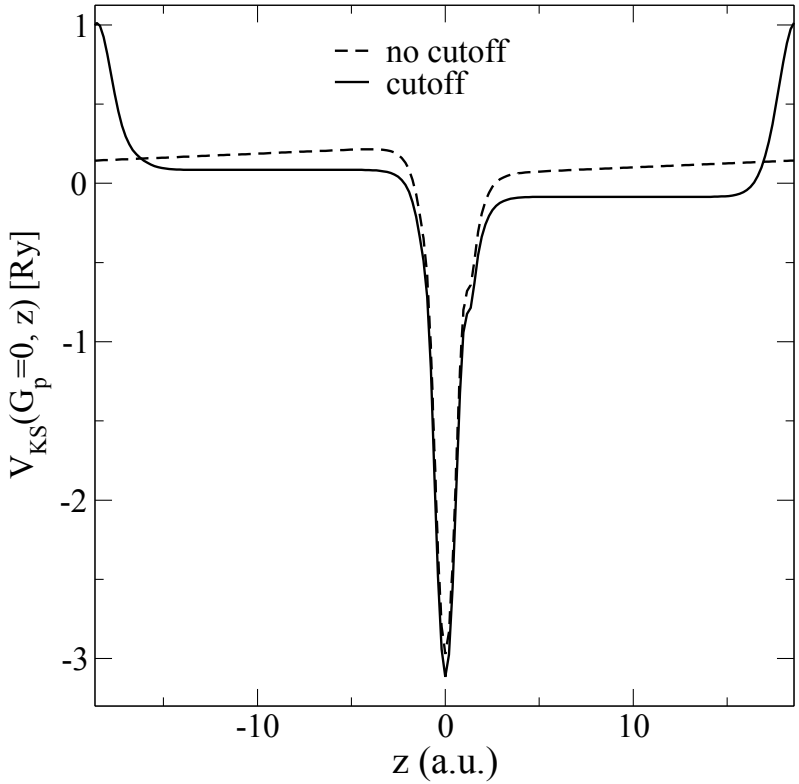


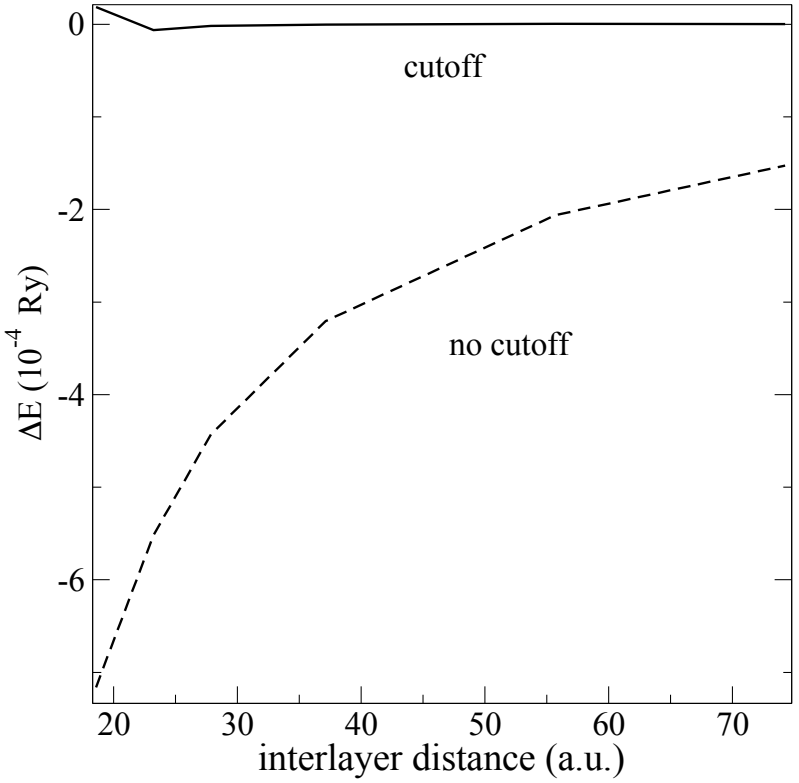
- Variations of the potential outside of the physical region may cause electron to leak out of the 2D material.
- The barrier prevents electrons from going outside the physical region.
- The barrier can also be simulated by an insulating 2D material, but at larger computational cost.
- The barrier also compensates the attractive force from the gate.

Sohier, T. , PhD thesis, UPMC (2015), supervised by Calandra, M., Mauri, F. (link)

Total Energy – dipolar system

Graphene with H on top of half the C atoms…





Consistency checks with varying d = distance between periodic images:

- Total energy is independent of d
- 3D code total energy approaches 2D code total energy for infinite d
- Lower limit to d: when unphysical region (bumps) get to close to system

Sohier, T. , PhD thesis, UPMC (2015), supervised by Calandra, M., Mauri, F. (link)