CIC nanoGUNE
nanoscience cooperative research center

Density-functional-theory calculations on graphene and related materials

Emilio Artacho

Nanogune, Ikerbasque & DIPC, San Sebastian, Spain
Cavendish Laboratory, University of Cambridge

The SIESTA method

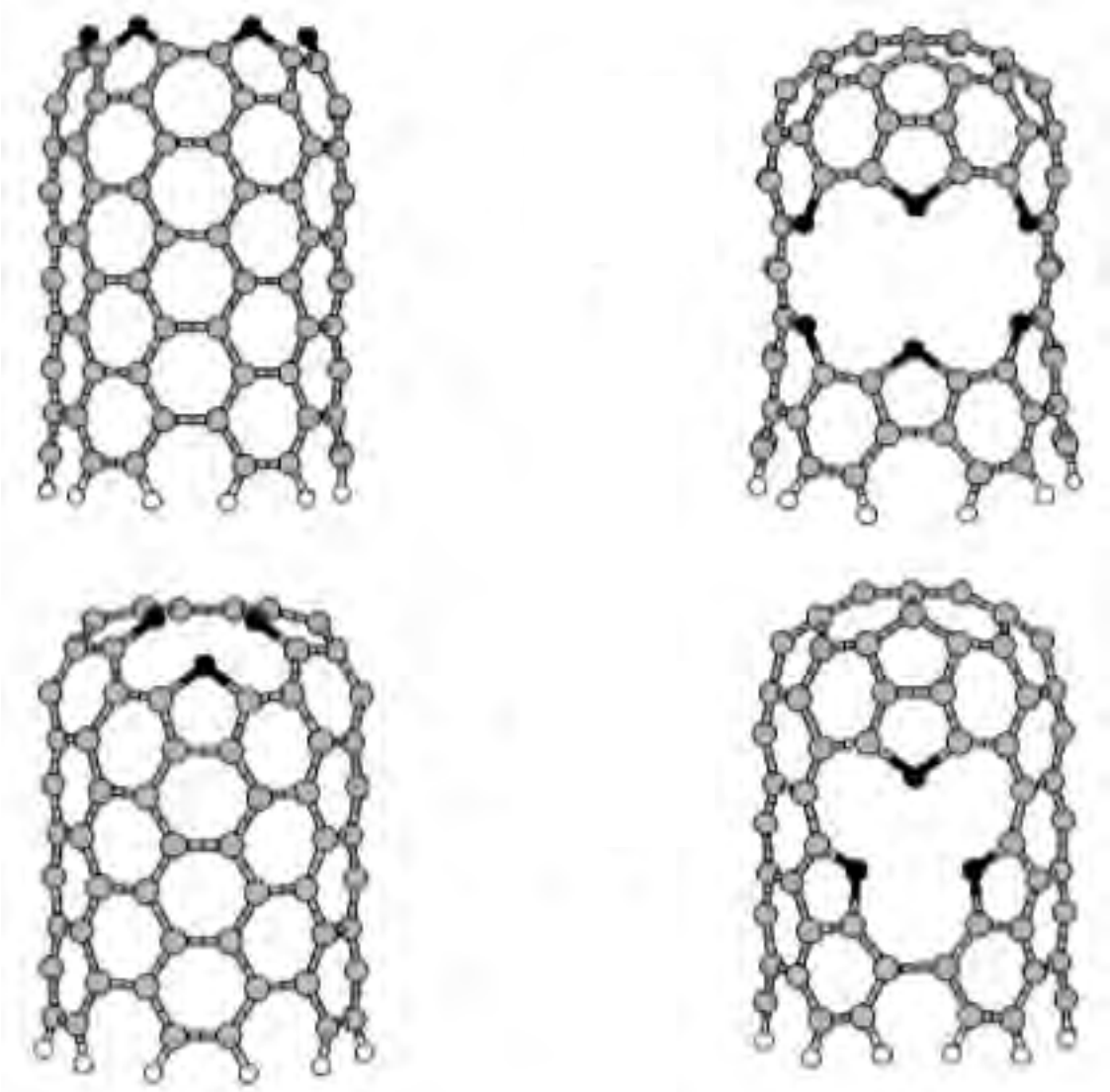
Linear-scaling DFT based on Numerical Atomic Orbitals

- *Born-Oppenheimer* *(relaxations, mol. dynamics)*
- *DFT* *(LDA, GGA)*
- *Pseudopotentials* *(norm conserving, factorised)*
- *Numerical atomic orbitals as basis* *(finite range)*
- *Numerical evaluation of matrix elements* *(3D grid)*

P Ordejón, E Artacho & JM Soler, *Phys. Rev. B* **53**, R10441-10444 (1996)

JM Soler, E Artacho, JD Gale, A Garcia, J Junquera, P Ordejon & D Sanchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002)

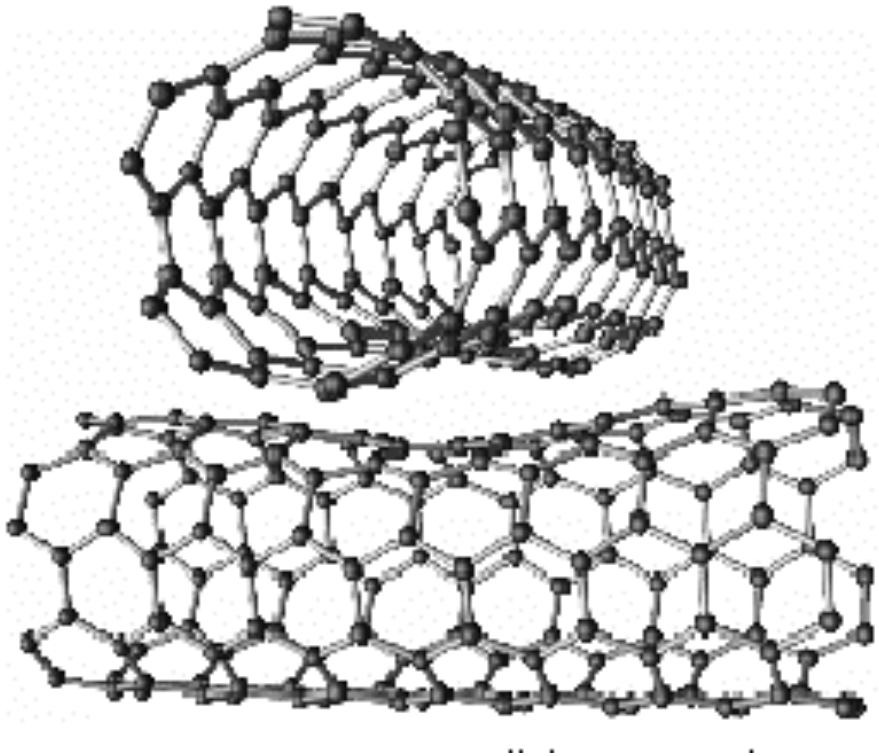
Oxidation of Carbon Nanotubes



M. S. C. Mazzoni, H. Chacham, P. Ordejón, D. Sánchez-Portal, J. M. Soler, and E. Artacho, Phys. Rev. B **60**, R2208 (1999)

Crossed nanotube junctions

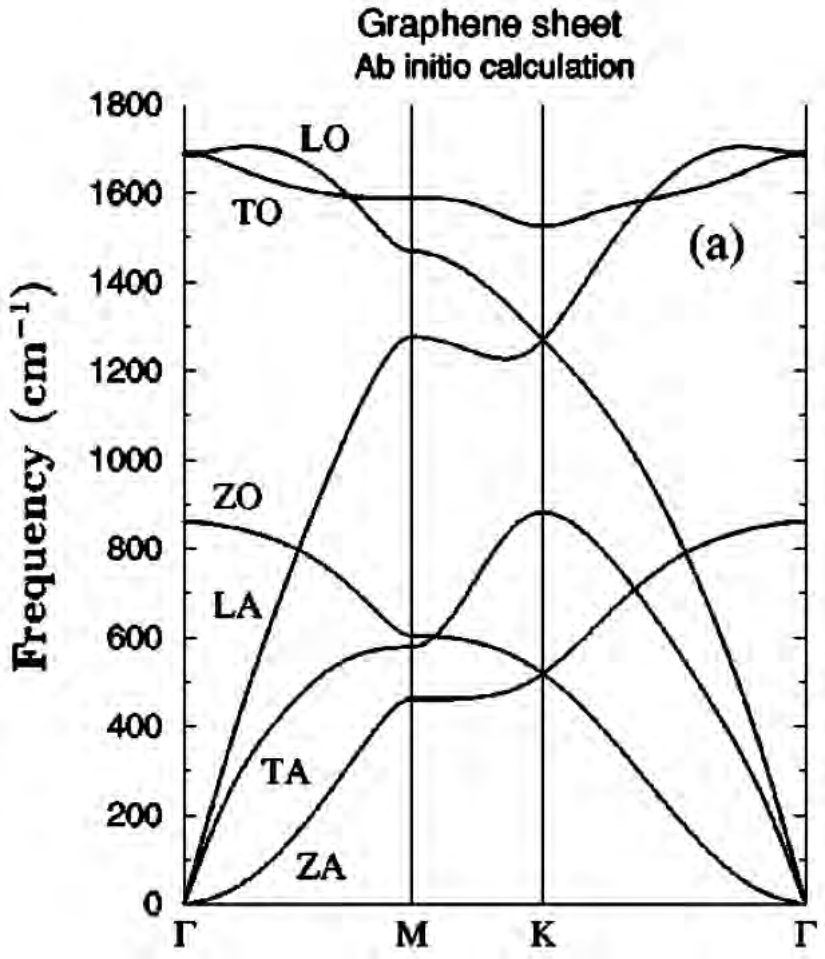
UC Berkeley, exp - th collaboration



M S Fuhrer *et al*, Science **288**, 494 (2000))

Phonons in graphene

From first principles



D Sanchez-Portal *et al*, Phys. Rev. B **59**, 12678 (1999))

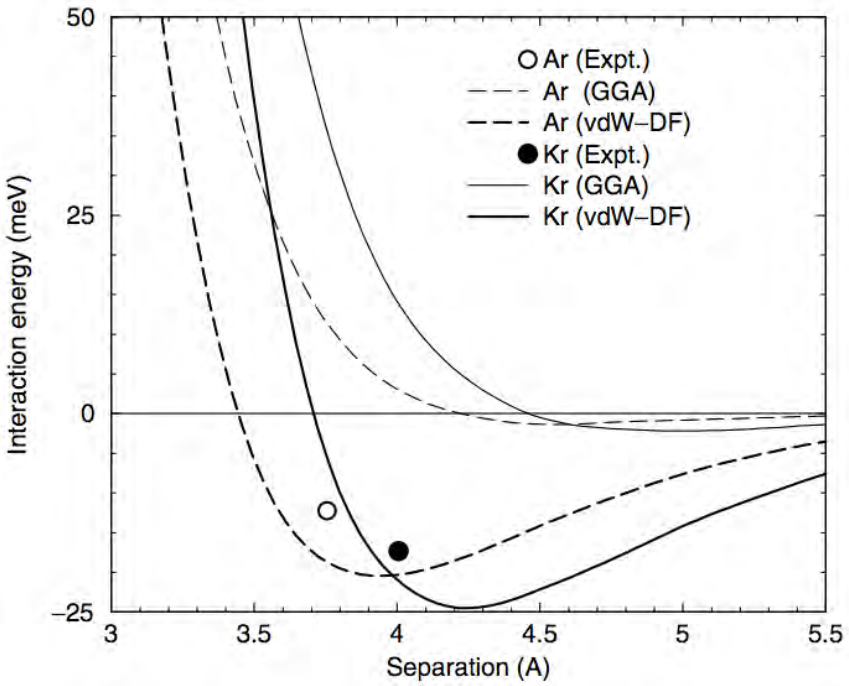
VOLUME 92, NUMBER 24 PHYSICAL REVIEW LETTERS week ending 18 JUNE 2004

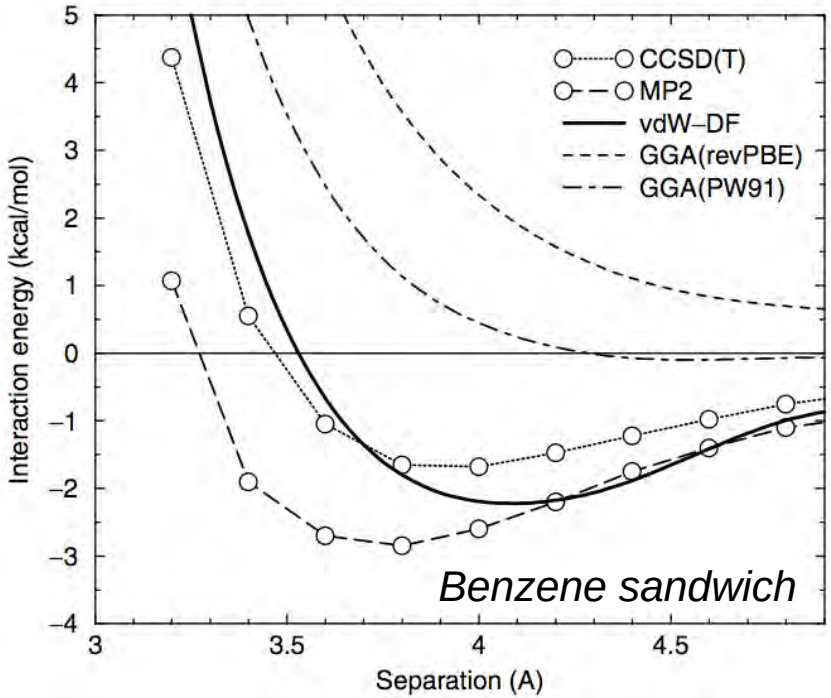
Van der Waals Density Functional for General Geometries

M. Dion,[1] H. Rydberg,[2] E. Schröder,[2] D. C. Langreth,[1] and B. I. Lundqvist[2]

[1]*Center for Materials Theory, Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA*
[2]*Department of Applied Physics, Chalmers University of Technology and Göteborg University, SE-412 96 Göteborg, Sweden*

(Received 30 January 2004; published 16 June 2004)





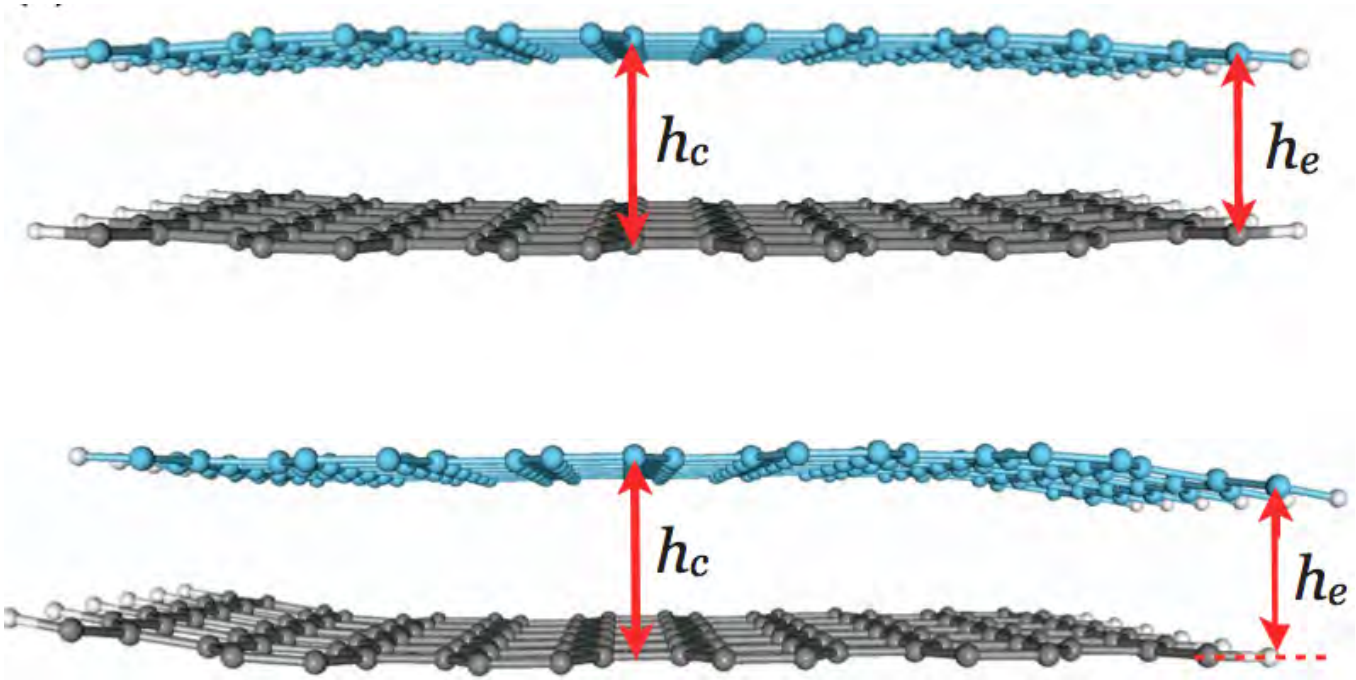
Fully from first-principles and within KS-DFT

Now efficiently calculated: overhead ~20% of GGA

G. Roman-Perez & JM Soler, PRL 2009

Bilayer graphene nanoribbons

Interplay between geometry, stacking and magnetism

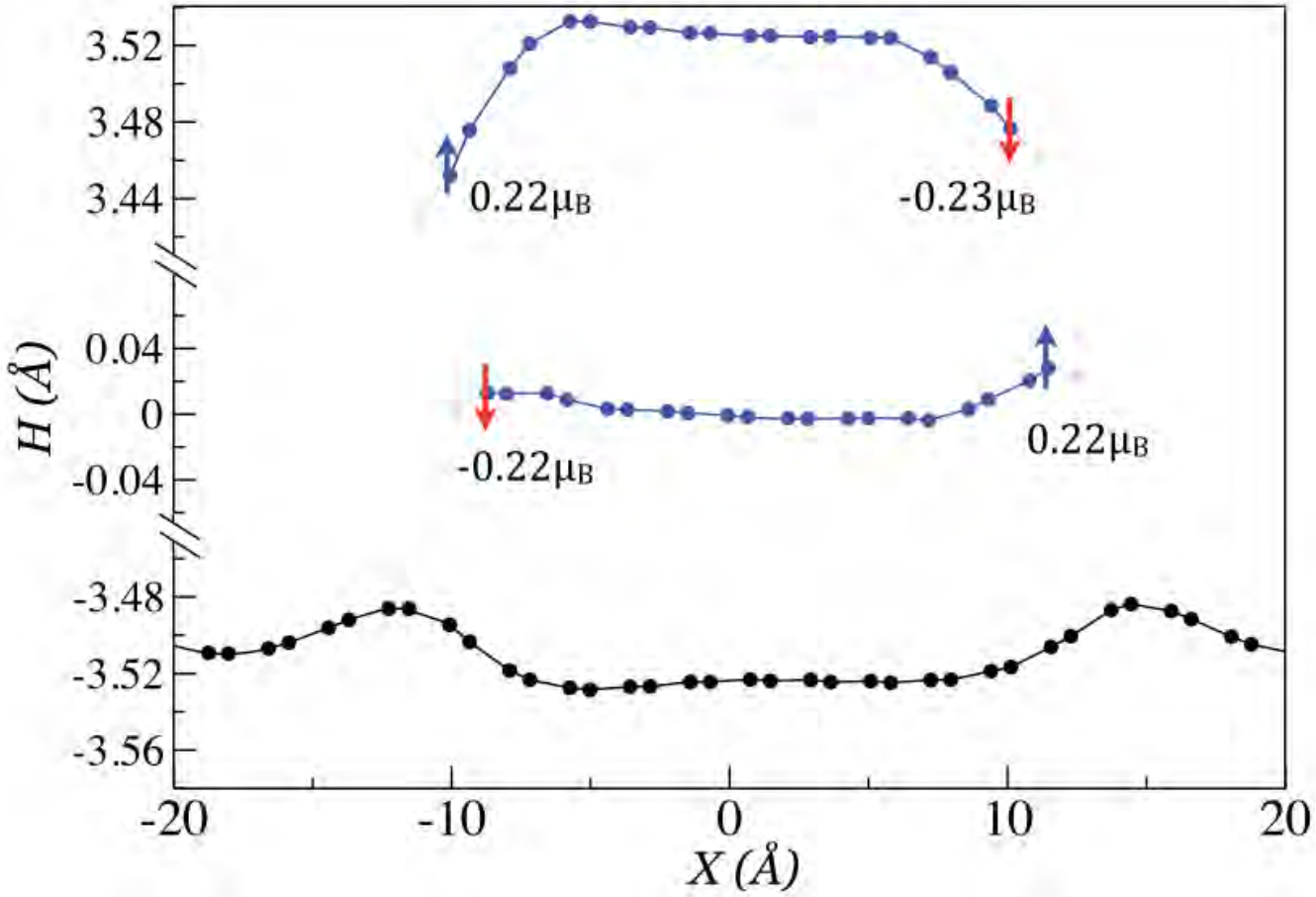


2 zigzag GNRs m=10, different stackings

H Santos, A Ayuela, L Chico & E Artacho, Phys. Rev. B **85**, 245430 (2012)

Bilayer graphene nanoribbons

Interplay between geometry, stacking and spin

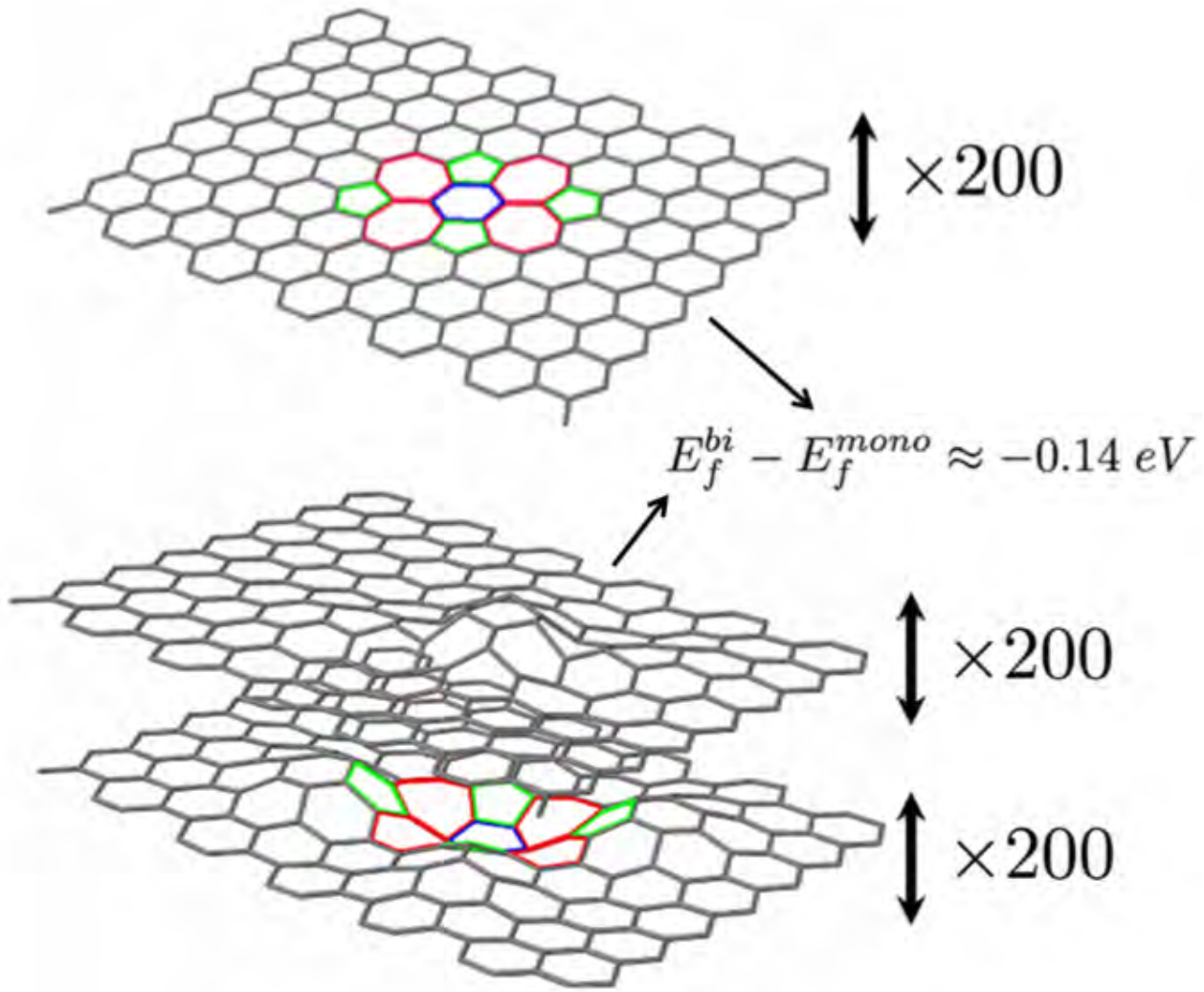


2 zigzag GNRs on graphene, m=10, AB stacking

H Santos, A Ayuela, L Chico & E Artacho, Phys. Rev. B **85**, 245430 (2012)

Divacancies in bilayer graphene

See poster 76



J Zubeltzu, F Corsetti, A Chuvilin & E Artacho (Graphene2013, poster 76)

2D honeycomb insulators

Nick Bristowe	(U Lieje)
Miguel Pruneda	(ICMAB Barcelona)
Peter Littlewood	(Argonne Ntl Lab)
Max Stengel	(ICMAB Barcelona)

EPSRC

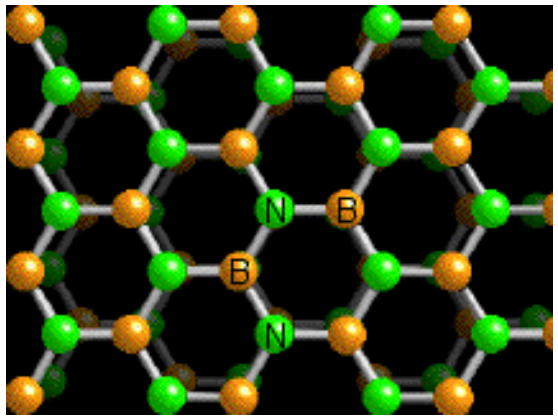
2D honeycomb (graphenic) insulators

Same honeycomb layers structure as graphene

2 atoms in the cell different

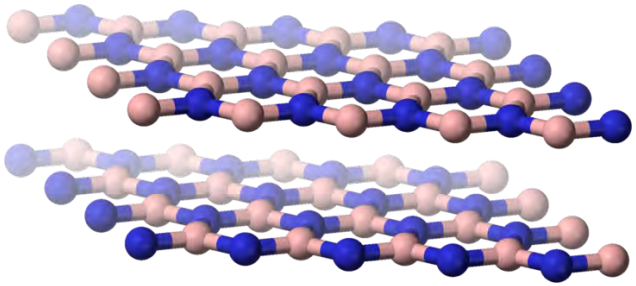
8 valence electrons per unit cell (f.u.)

Broken centre of symmetry mid-bond => gap



Prototypic: BN

Layers can be stacked as in graphite (h-BN)



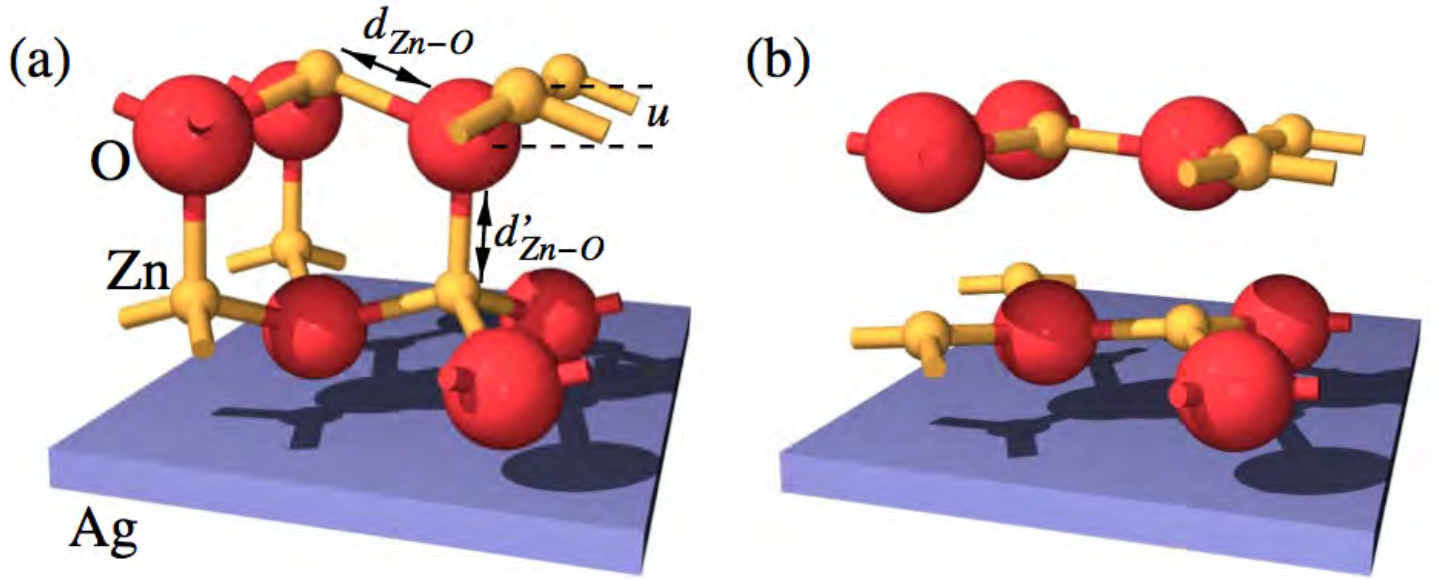
We will consider isolated layers, or heterostructures

ZnO graphenic sheets

PRL 99, 026102 (2007) PHYSICAL REVIEW LETTERS week ending 13 JULY 2007

Observation of Depolarized ZnO(0001) Monolayers: Formation of Unreconstructed Planar Sheets

C. Tusche,* H. L. Meyerheim, and J. Kirschner
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
(Received 21 February 2007; published 13 July 2007)



Wurtzite structure (in bulk)

Graphenic layers (on Ag(111))

Heterostructures: layered or in-plane

BN in Graphene sheets

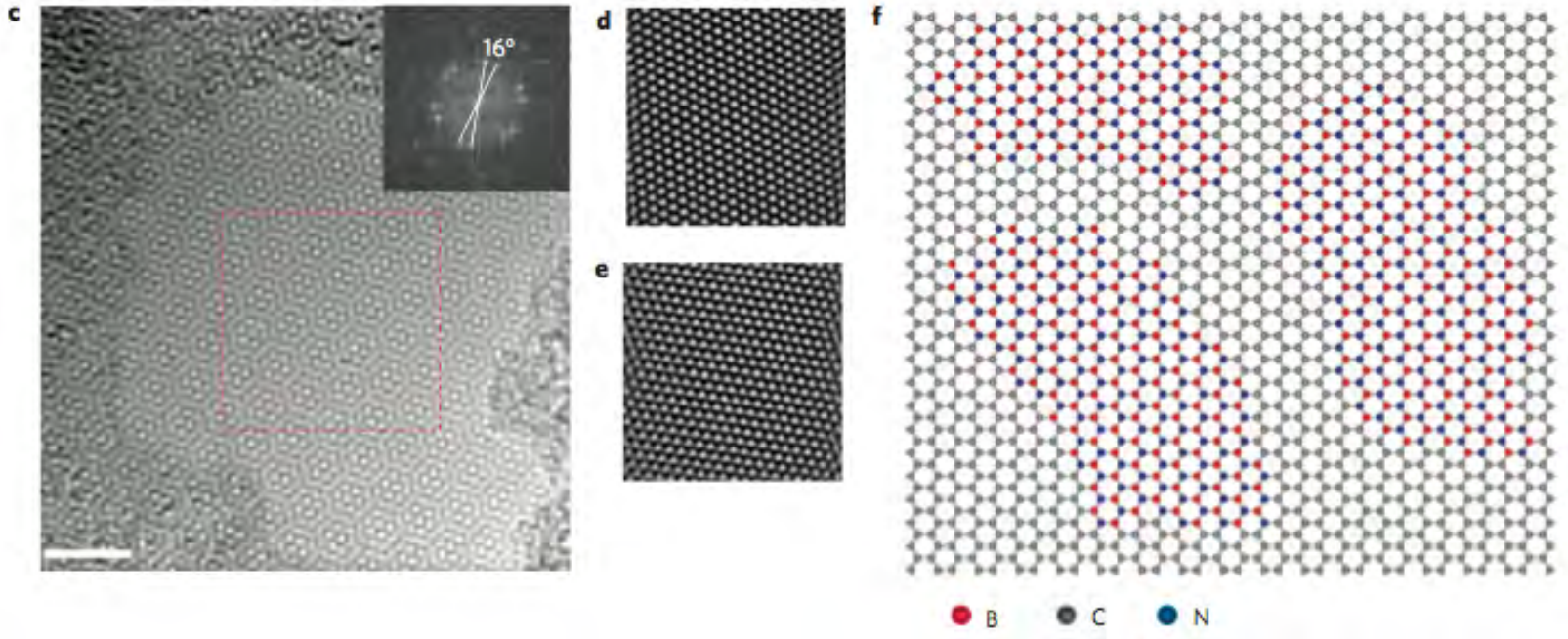
nature materials

ARTICLES

PUBLISHED ONLINE: 28 FEBRUARY 2010 | DOI: 10.1038/NMAT2711

Atomic layers of hybridized boron nitride and graphene domains

Lijie Ci[1]*, Li Song[1]*, Chuanhong Jin[2], Deep Jariwala[1†], Dangxin Wu[3], Yongjie Li[1†], Anchal Srivastava[1†], Z. F. Wang[3], Kevin Storr[4], Luis Balicas[5], Feng Liu[3] and Pulickel M. Ajayan[1‡]



See also: P. Sutter and co. 2012 (talk Tuesday); M Pruneda PRB 2010 (theo)

Polar interfaces

Calculations on repeated stripe heterostructures

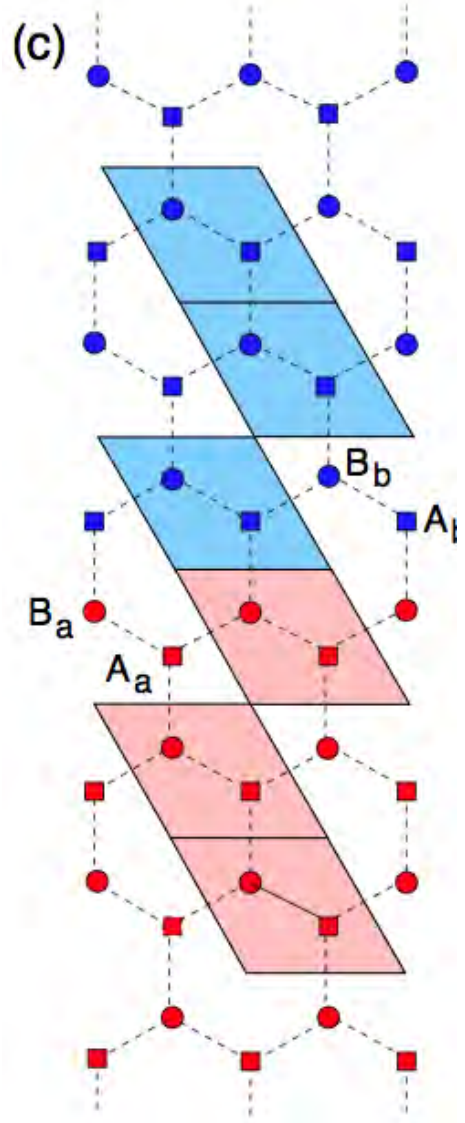
Explore the electrostatics across heterostructures and implications

Expected apparent charge at interface:

$\Delta P_{\perp}$ *(normal to interface)*

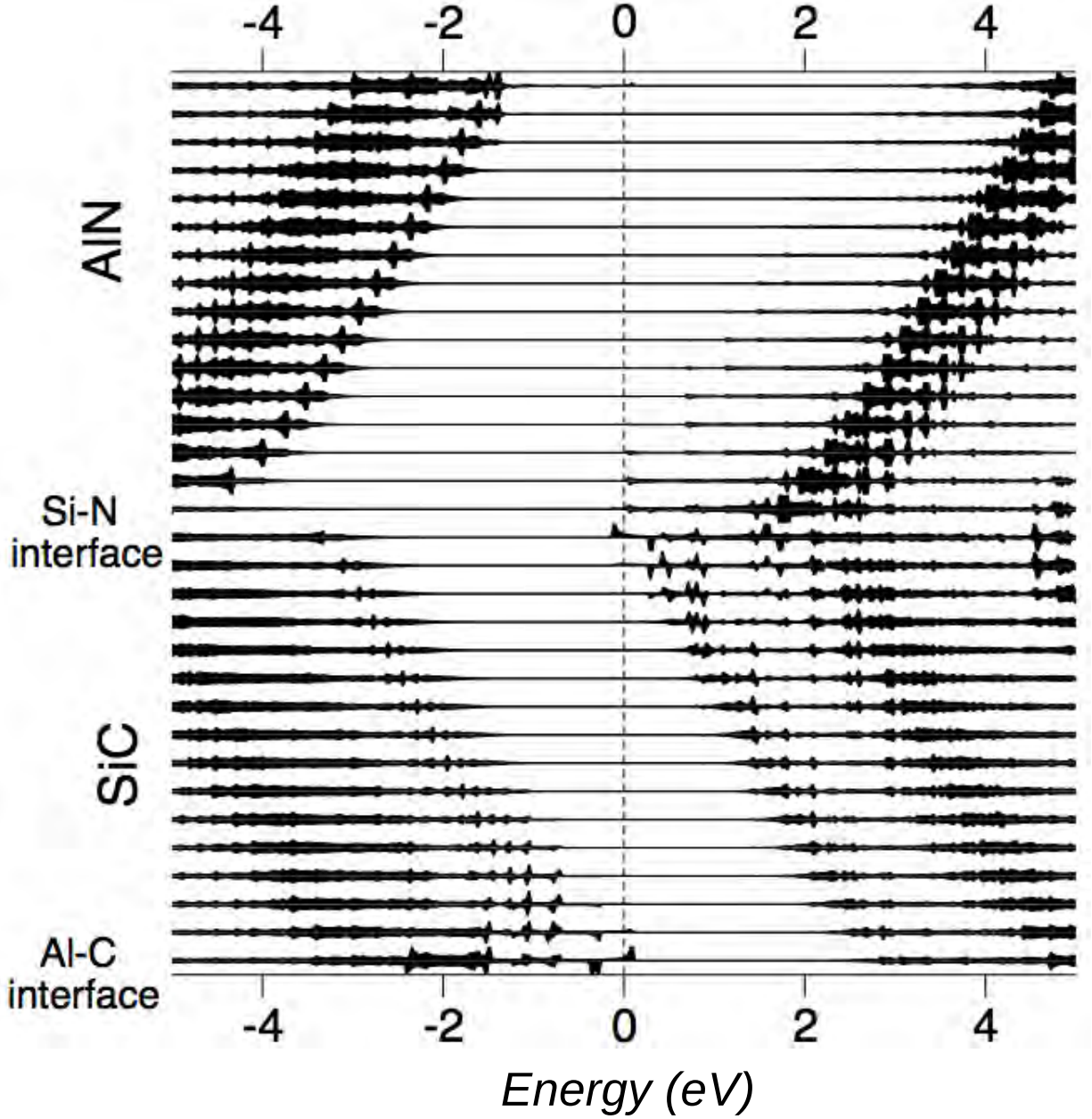
Instabilities (e.g. electrostatics may work against obtaining atomically sharp interfaces, see P. Sutter's talk on Tuesday)

Calculations: AlN-SiC & AlN-ZnO



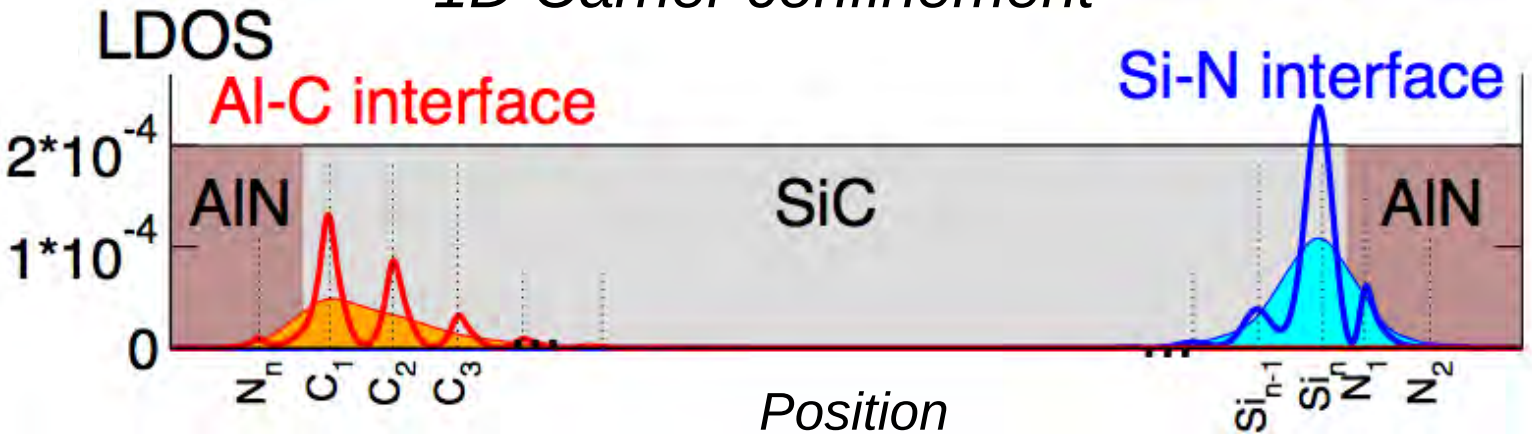
$(AlN)_m$ - $(SiC)_m$ superlattice (zigzag, m=16)

DOS projected on bilayers

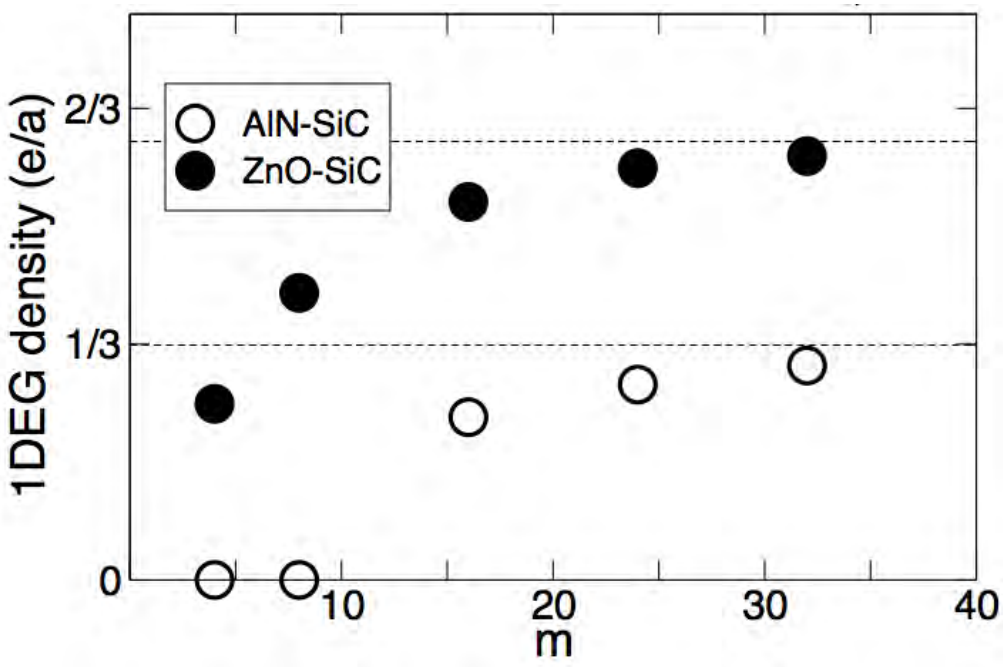


1DEG at interface

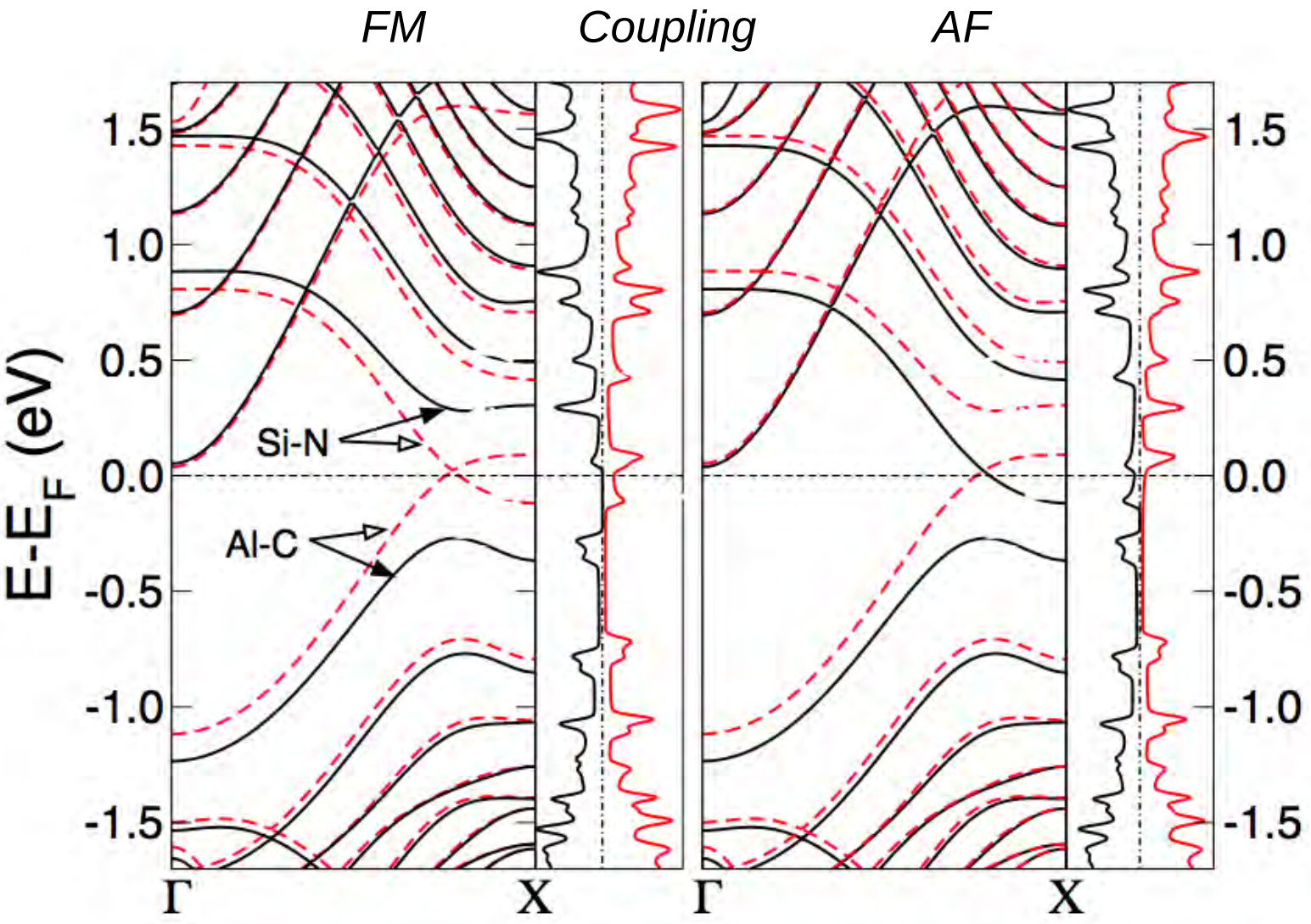
1D Carrier confinement



Carrier density vs ribbon width



1DEGs at interfaces: half metallic



AF & FM essentially degenerate (decoupled)

Electrostatics important for heterostructures

They are polar 2D insulators

Polar, meaning?

- *Chemically: bonds between atoms of different electronegativity*

  => Each bond is "polar"

  (Wannier displaced towards one; atomic "populations" different)

- *Physically:*

  Polarisation

  Polar surfaces, interfaces

Semiconductors (70s & 80s): III-V, II-VI vs IV

(GaAs, GaN, ZnSe, CdSe, CdS, even SiC, vs pure Si or Ge)

Lore: Polarisation

Polarisation: No absolute bulk value can be measured, only differences

$P = 0$ *reference whenever symmetry enforces it to be zero*

e.g. inversion symmetry.

Effective polarisation,as measured w.r.t that reference

Polar surfaces and interfaces

e.g. III-V surfaces, Si/GaAs interfaces in 70s & 80s

e.g. Harrison's model: charges and covalency parameters

Recent surprises in an "old" field

The LAO/STO 2DEG

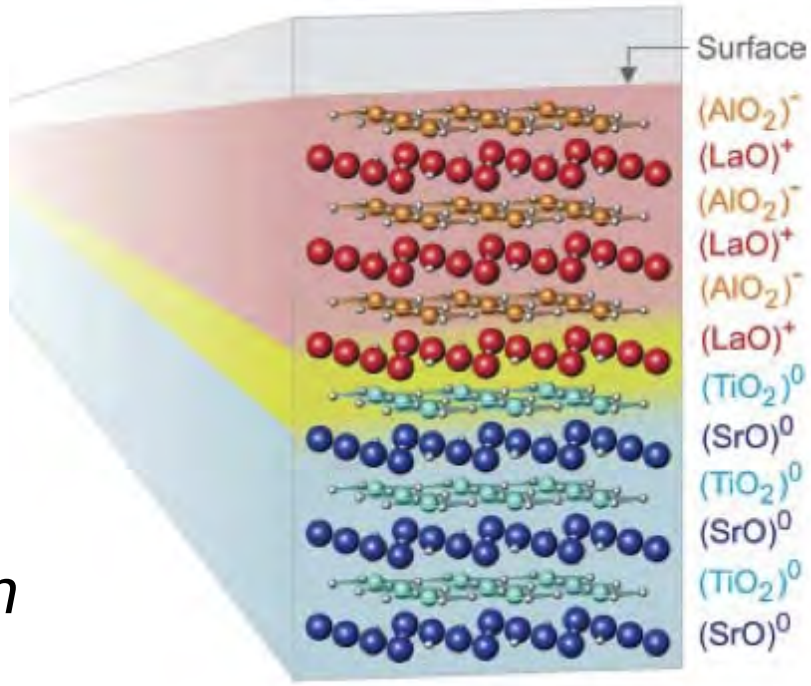
$LaAlO_3$ / $SrTiO_3$

Both band insulators (Ti, empty 3d band)

Heterostructures grown

to atomic precision; epitaxial growth (MBE, PLD)

Interface: conducting!



Formation of 2D electron gas

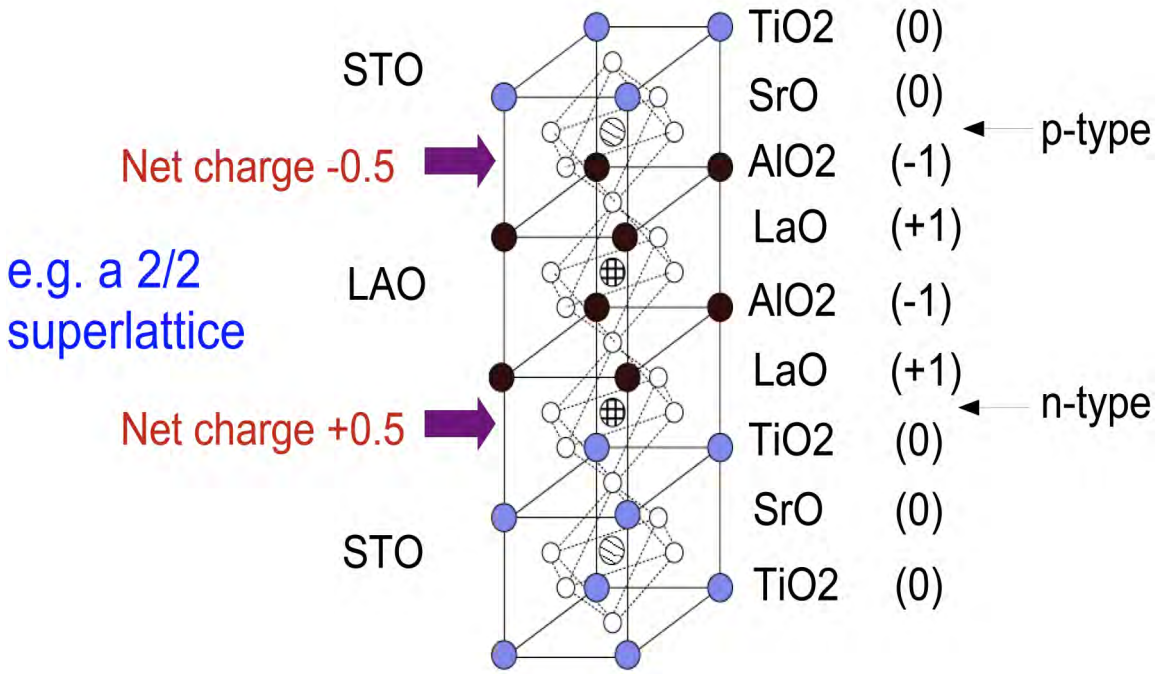
A Ohtomo & H Hwang,

Nature **427**, 423 (2004)

Superlattice of alternating n-p interfaces

Test net charge arguments on a model system

Superlattice of alternating n-p interfaces



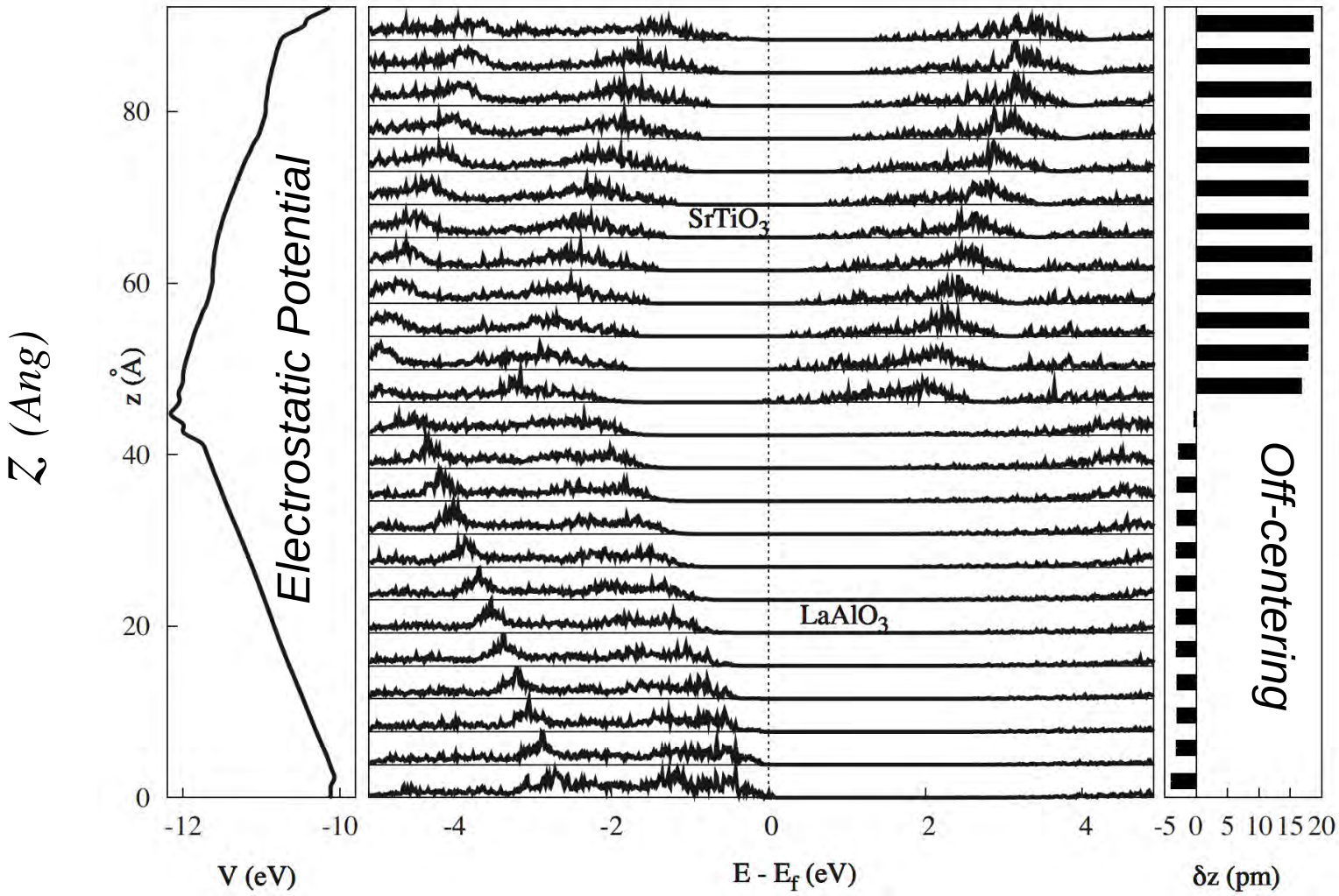
Compare electrostatic analysis with DFT calculations

(using SIESTA)

N C Bristowe, E Artacho & P B Littlewood, PRB 2009

Superlattice of alternating n-p interfaces

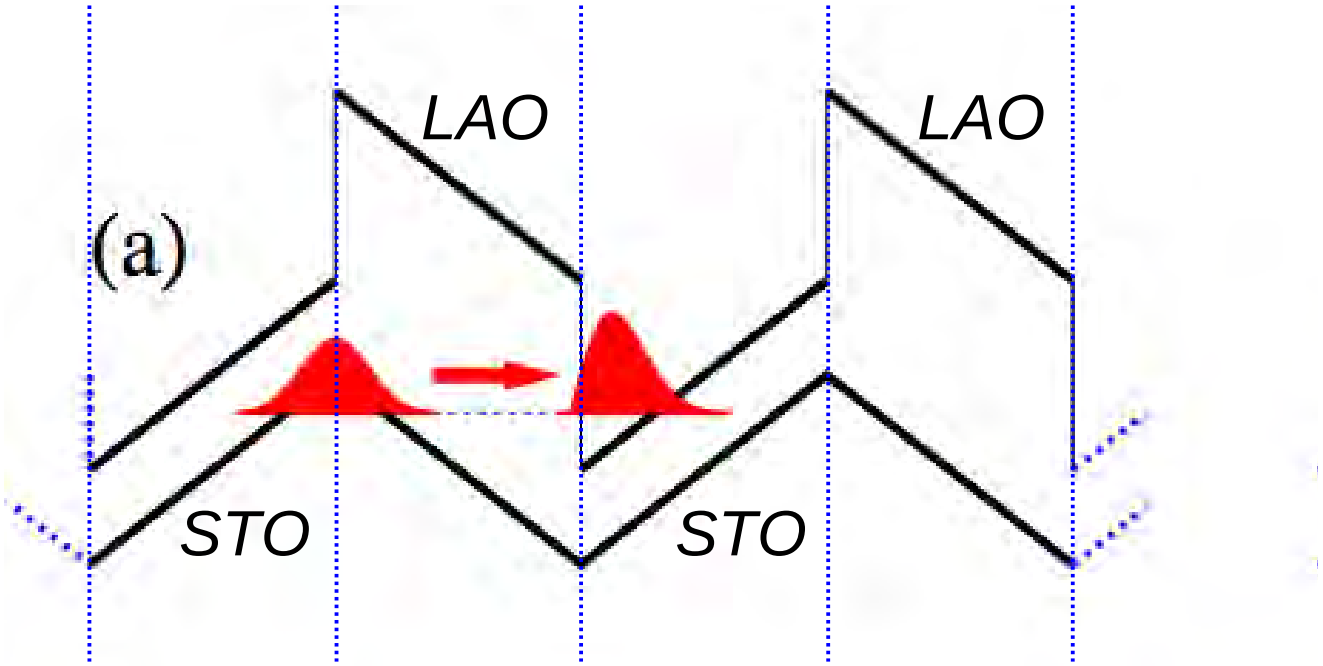
Electron density of states projected on each bilayer



Electronic structure follows "macroscopic" electrostatic potential

A Baldereschi, S Baroni & R Resta, PRL 1988

Band-bending picture



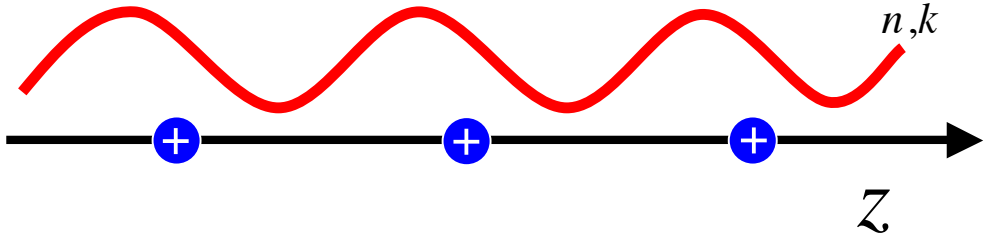
Slopes depend on fields in materials

Net gap depends on thickness

Polarisation

The problem defining polarisation
in a solid with delocalised electrons

$$\rho = \sum_{n,k}^{occ} \left|\psi_{n,k}\right|^2$$



P: *Dipole moment per unit volume*

ILL DEFINED

R M Martin PRB 1974

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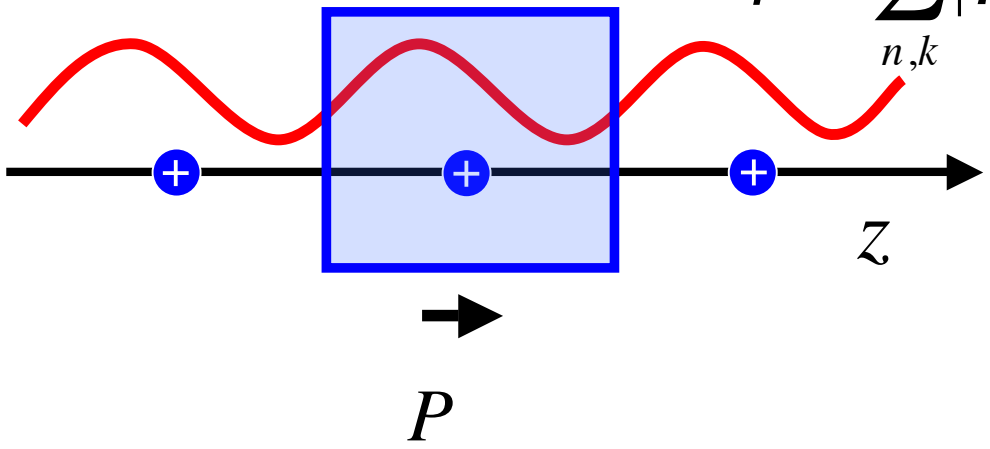

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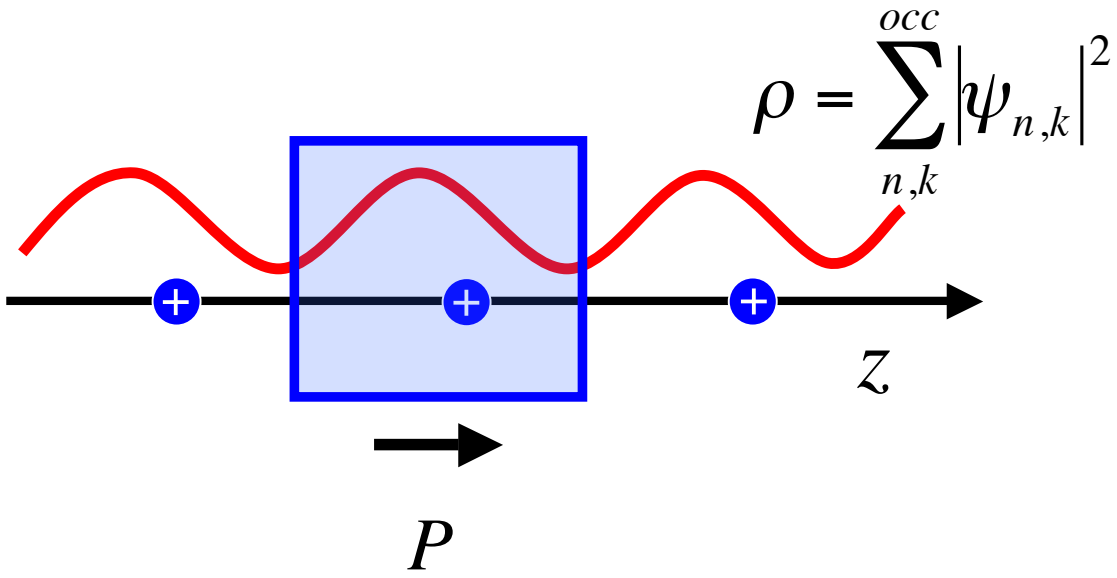

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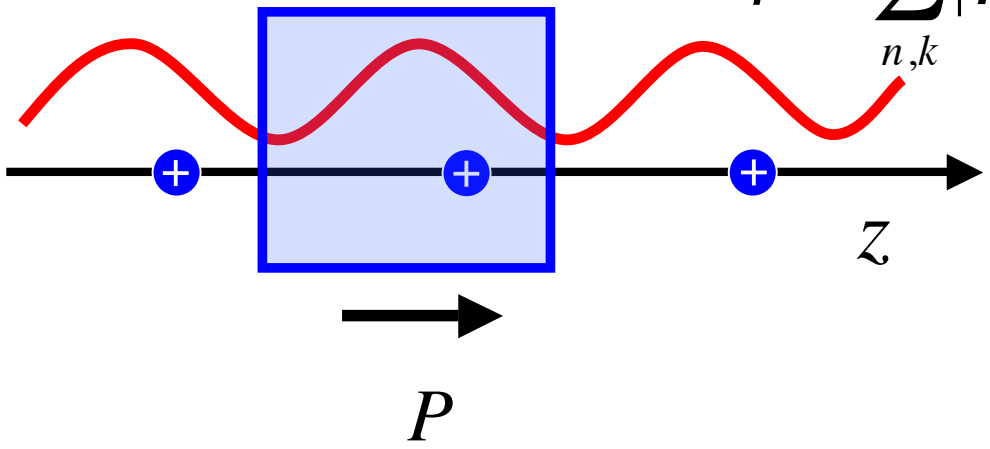


P: *Dipole moment per unit volume*

ILL DEFINED

R M Martin PRB 1974

Modern theory of polarisation

King-Smith, Vanderbilt and Resta, 90's

Not dipole per unit volume,

Define in terms of current flowing through circuit under the change of external parameter (structure, electric field)

Adiabatic change under external parameter

=> *Berry phase theory => Topological property*

R D King-Smith & D Vanderbilt, PRB 1993

Modern theory of polarisation

Defined in terms of Wannier centres

Define polarization as for a repeated set of point charges (Clausius Mossotti)

Take as point charges:

- *Atomic cores*
- *Centre of charge of valence-electron Wannier Functions*

Shown to be equivalent to Berry Phase polarization

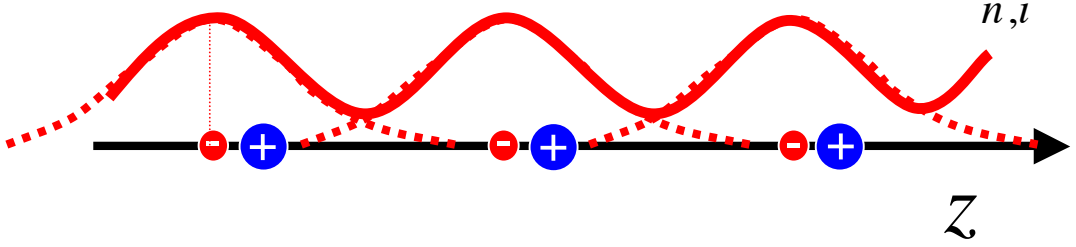
N Marzari & D Vanderbilt, PRB 1997

(We will use Wannier picture, but it relates back to Berry phase)

Modern theory of polarisation

Defined in terms of Wannier centres

$$\rho = \sum_{n,i}^{occ} \left| w_n(\vec{r} - \vec{R})_i \right|^2$$



P: *Dipole moment per unit volume of point charges*

DEFINED UP TO POLARISATION QUANTA

Modern theory of polarisation

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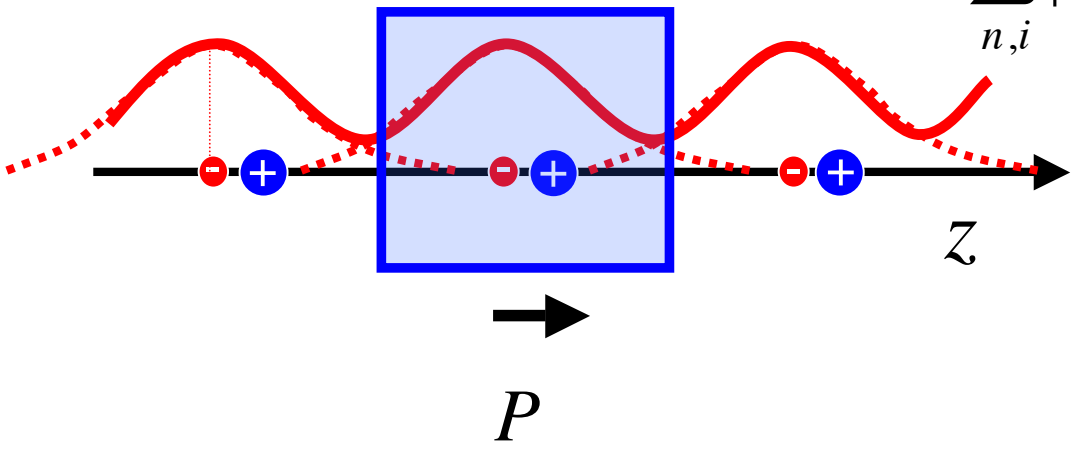

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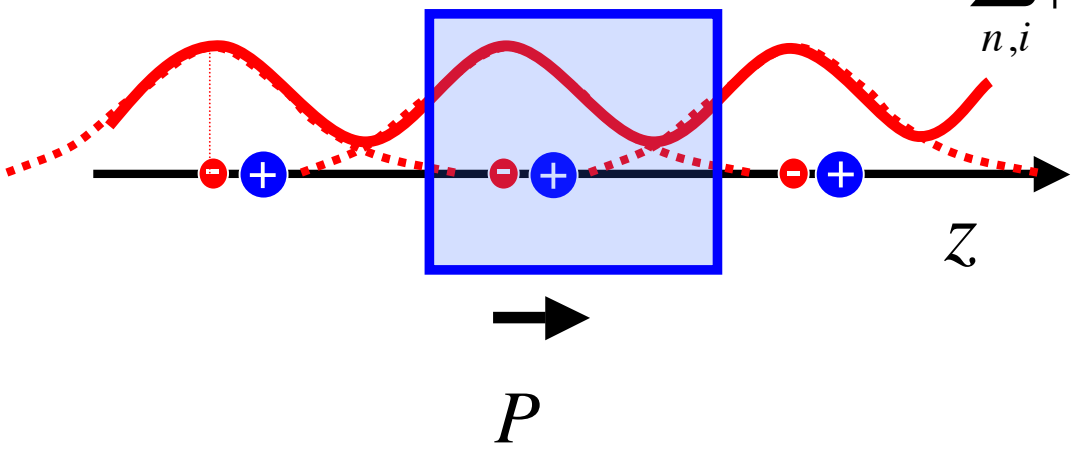

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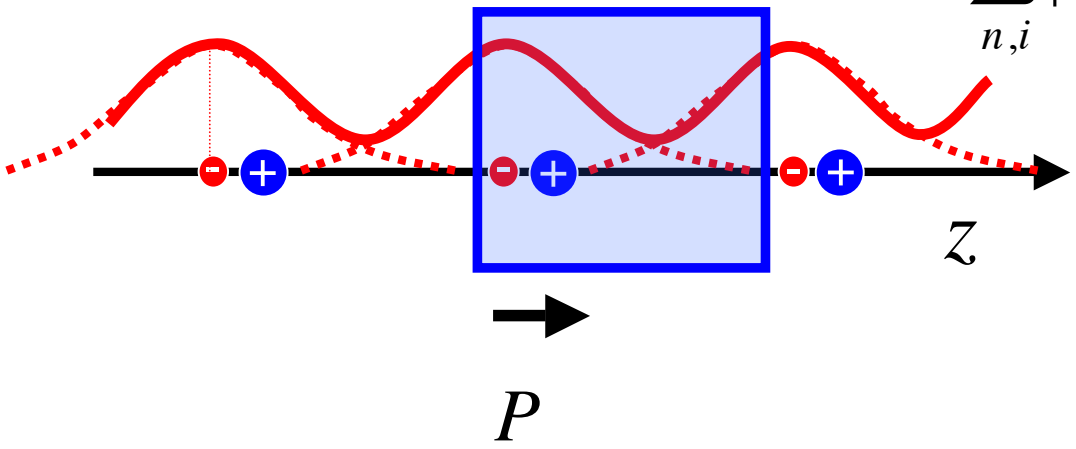

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DEFINED UP TO POLARISATION QUANTA

Modern theory of polarisation

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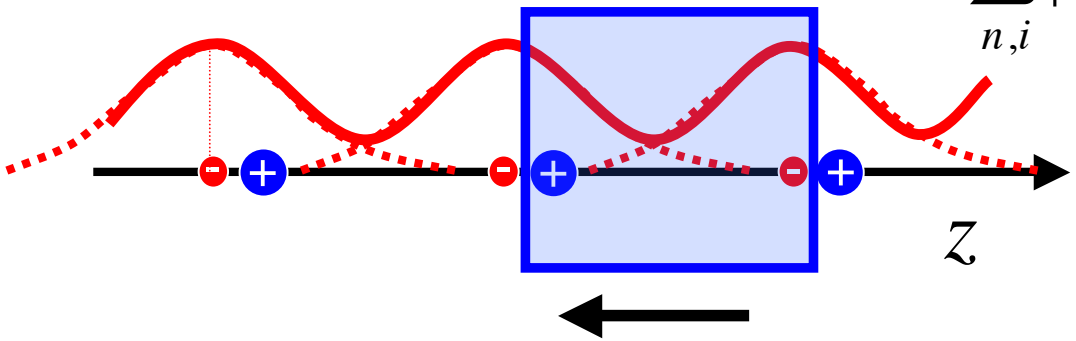


P *(jumped by a polarisation quantum)*

P*: Dipole moment per unit volume of point charges*

DEFINED UP TO POLARISATION QUANTA

Symmetry and quanta

The polarization is defined modulo P_0*, i.e. by the set*

$$\{P + n\,P_0\}$$

For centrosymmetric bulk systems (or more generally for this, any symmetry transforming z *into* $-z$*),* P_z *should be invariant:*

$$P_z = -P_z$$

should be invariant: which is the case for the two values

$$\{\ldots.. -2P_0, -P_0, 0, P_0, 2P_0 \ldots\ldots\}$$

$$\{\ldots.. -3P_0/2, -P_0/2, P_0/2, 3P_0/2 \ldots\ldots\}$$

which correspond to Berry phases 0 *and* π *(modulo* 2π*)*

Two kinds of centrosymmetric insulators

Two kinds of centrosymmetric insulators

LAO has $P = P_0/2$*; STO has* $P = 0$

Formal polarisation

D Vanderbilt & D King-Smith, PRB 1993

(as obtained from Wanniers or Berry phase)

=> Interface between bulk STO and bulk LAO => 2DEG

It implies:

The perfect (pristine) interface is intrinsically doped with a high and very well defined "dopant" density

Two kinds of centrosymmetric insulators

LAO has $P = P_0/2$*; STO has* $P = 0$

Berry phase for P (the one for Berry connection $< u_{\mathbf{k}} \mid \partial_{\mathbf{k}} \mid u_{\mathbf{k}} >$*)*

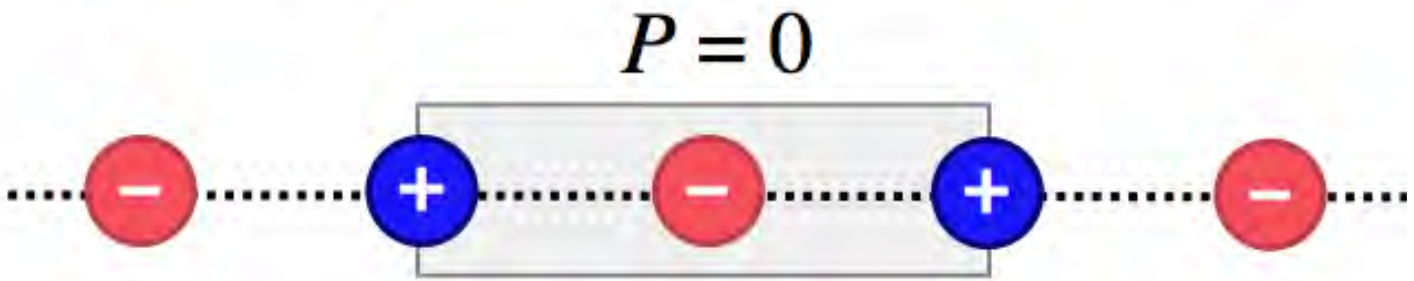
$\gamma = 0$ *or* π, mod 2π

Analogous to Z_2 *topological insulators*

Same condition (Chern number) on the relevant Berry phase for time-reversible insulators

Topological insulators generalised to inversion symmetry in
Ari M. Turner, Yi Zhang, Roger S. K. Mong, Ashvin Vishwanath, arXiv:1010.4335 (2010).

1D chain analog of (001) planes of LAO

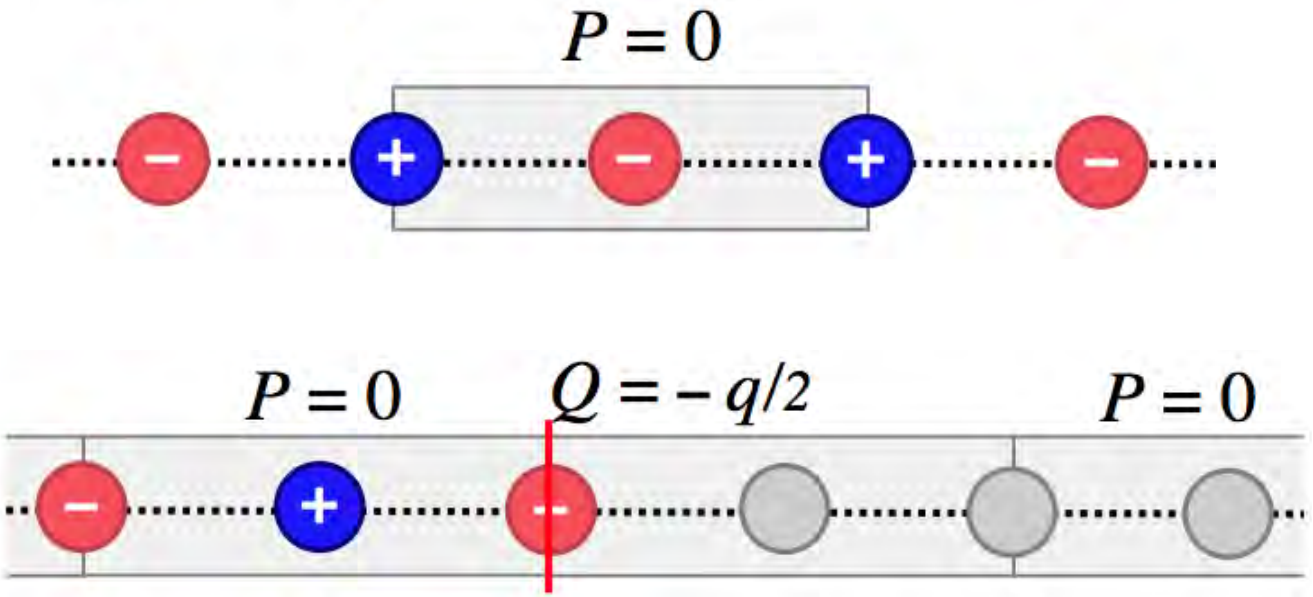


Usual choice: “polarization-free”

The polarization is defined as zero for a centrosymmetric system

(remember we defined polarization change)

1D chain analog of (001) LAO/STO interface



If bulk reference taken as $P_z = 0$ *for both materials*

σ_c = 0.5 e / *2D unit cell* *NO COVALENCY OR POPULATIONS*

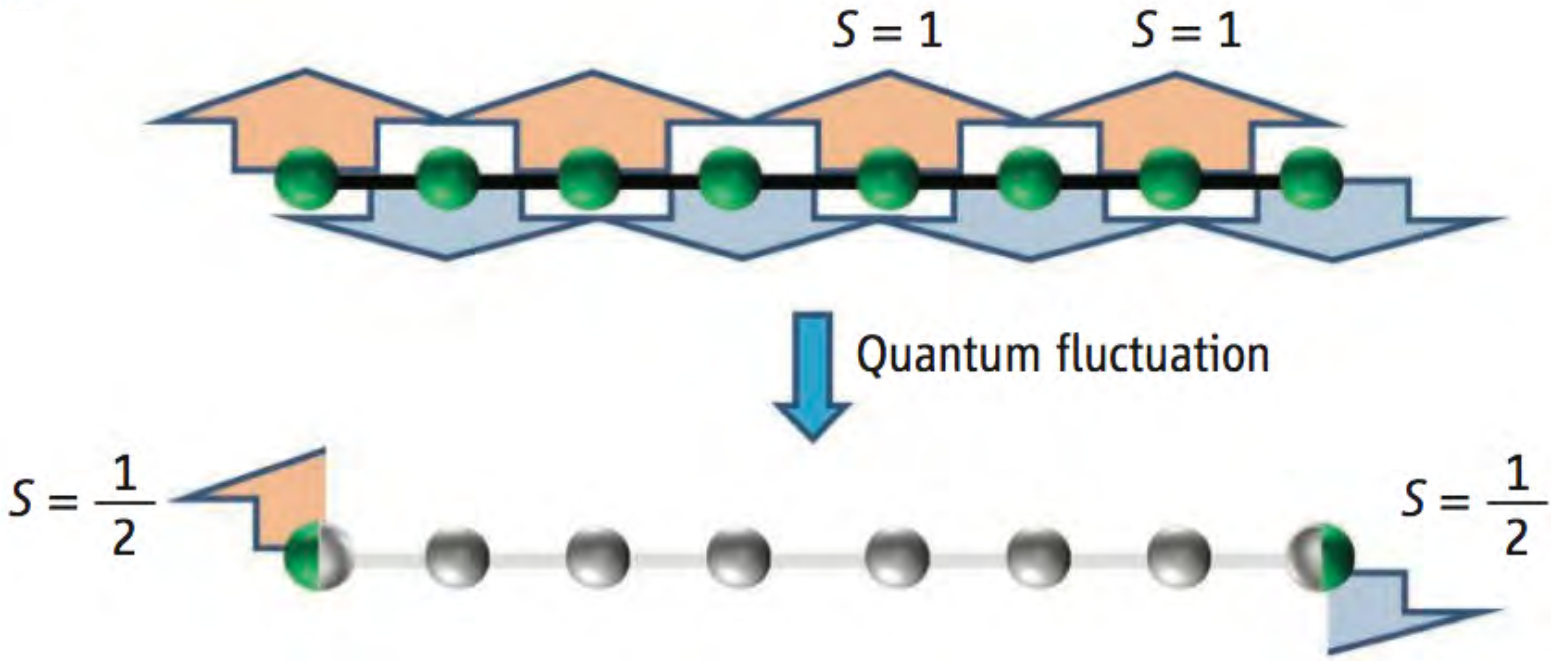
Symmetry protected topological states

PHYSICS

Symmetry Meets Topology

A unified theory may describe both the persistent spin of electrons and the design of novel materials.

Xiao-Liang Qi



Published by AAAS

Back to honeycomb insulators

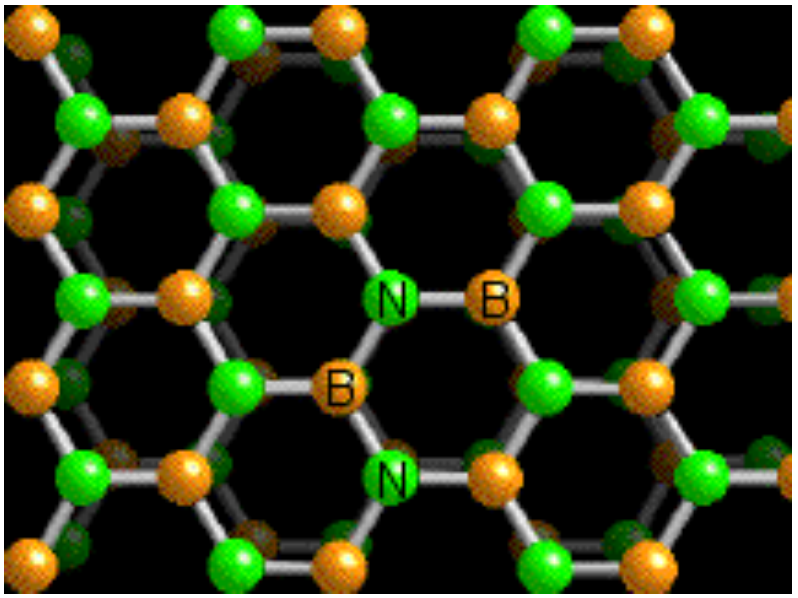
Polar (in plane)

Effective polarisation

$$\mathbf{P}_{eff} = 0$$

(three fold axis)

What about the formal polarisation?



Back to graphenic insulators

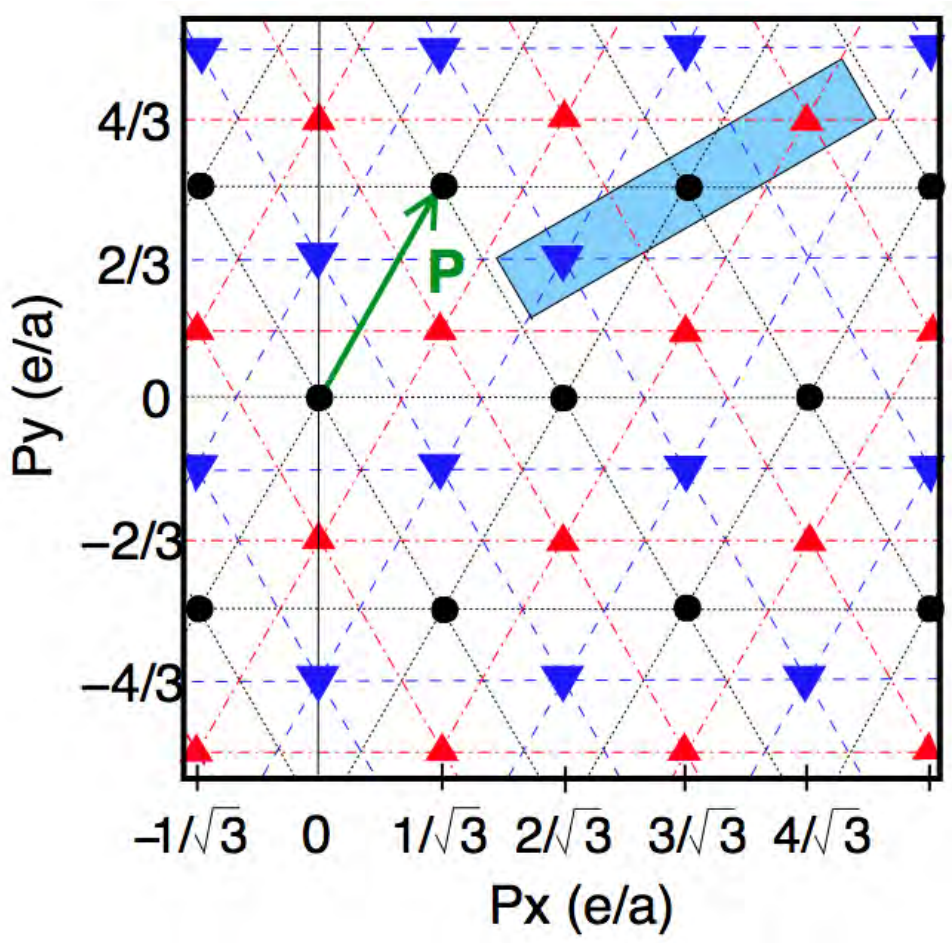
Polar (in plane)

Effective polarisation

$$\mathbf{P}_{eff} = 0$$

(three fold axis)

What about the formal polarisation?



A lattice of possible P vectors; three diff values compatible with symmetry

Three different (topological) kinds of graphenic insulators

Three values: way of seeing it

In terms of Wanniers

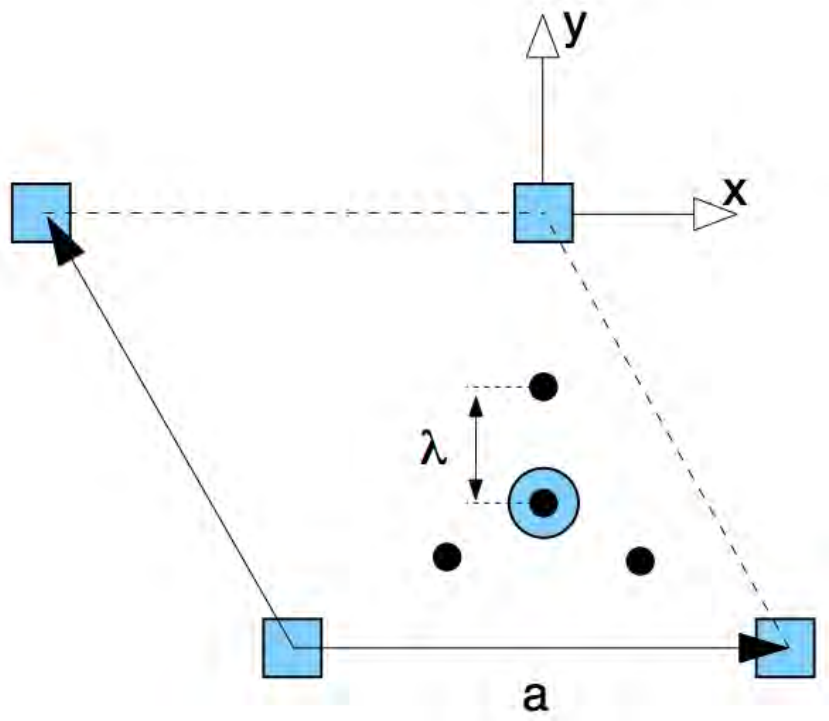
Wannier centres as depicted:

You can choose to put the π Wannier on A or B

Three σ Wanniers around it, in bond directions (at different distances but respecting 3-fold axis)

The 3 values correspond to core ions: +4,+4; +3,+5; +2,+6

(+1,+7 = +4,+4 + one quantum)



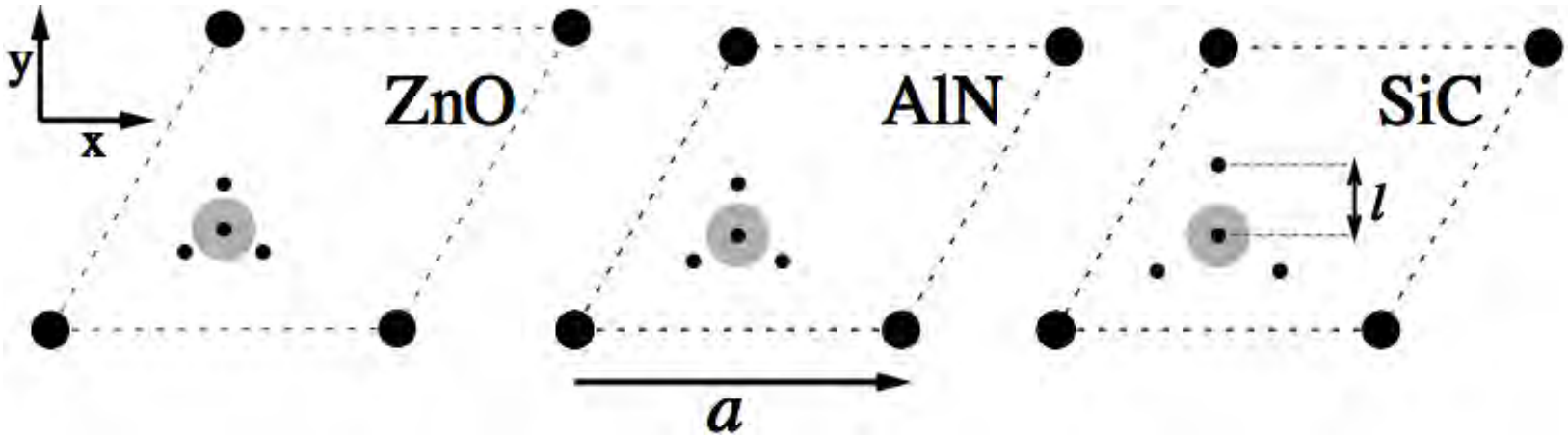
Checked with calculations

Both Berry phase and Wanniers

Chosen 3 insulators with smallest mismatch

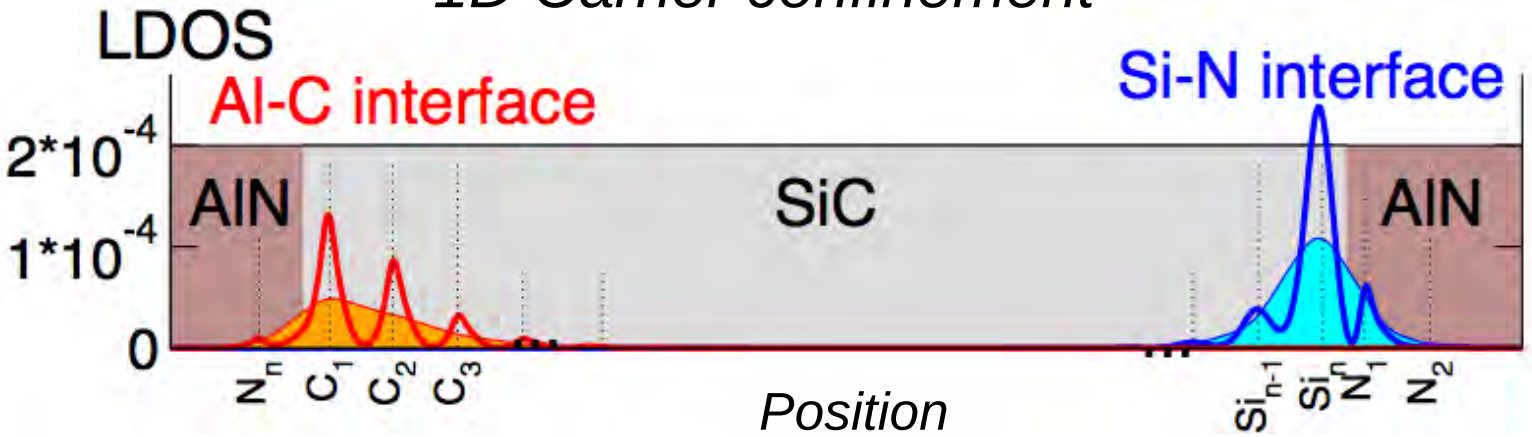
With SIESTA (Berry phase) $P = 2/3, 3/3, 4/3\ e/a \mod e/a$

and SIESTA + Wannier90

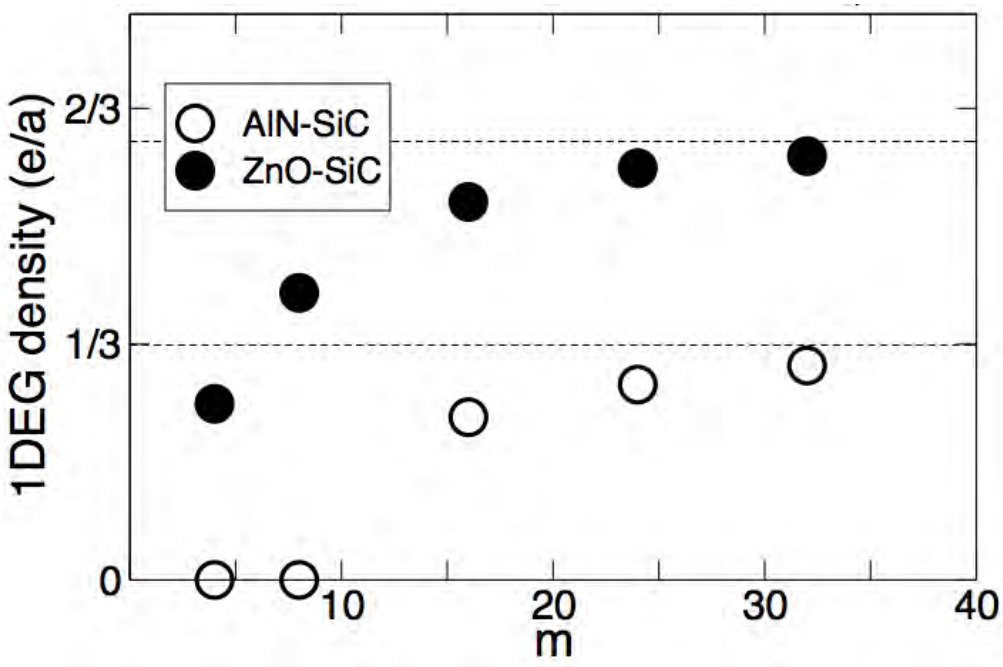


1DEG at interface

1D Carrier confinement



Carrier density vs ribbon width



Summary

- *Analogously to centrosymmetric solids, which can be classified according to*

$$P = 0,\ P_0/2 \pmod{P_0} \quad \textit{or} \quad \gamma = 0, \pi \pmod{2\pi}$$

graphenic insulators are classified, given the C_{3v} *symmetry, as*

$$P = 0,\ P_0/3,\ 2P_0/3 \pmod{P_0}$$

- *Interfaces give rise to 1DEGs*

- *1DEGs seem they could be half-metallic*