DEFECTS IN 2D MATERIALS:

HOW WE TAUGHT ELECTRONIC SCREENING TO MACHINES

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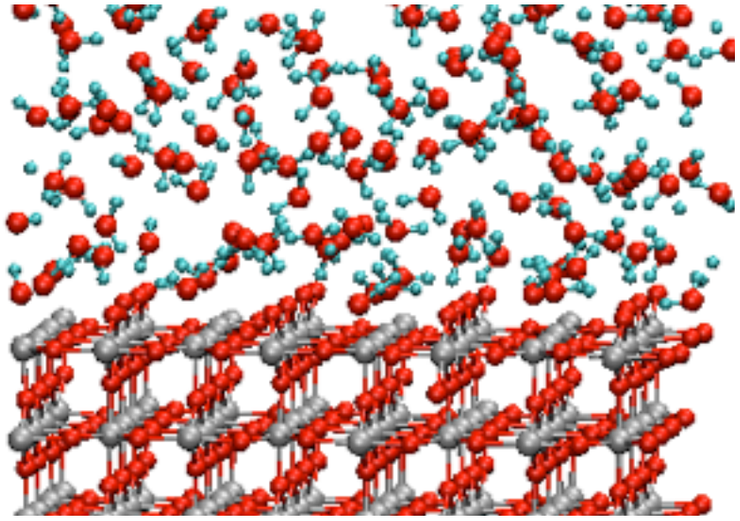
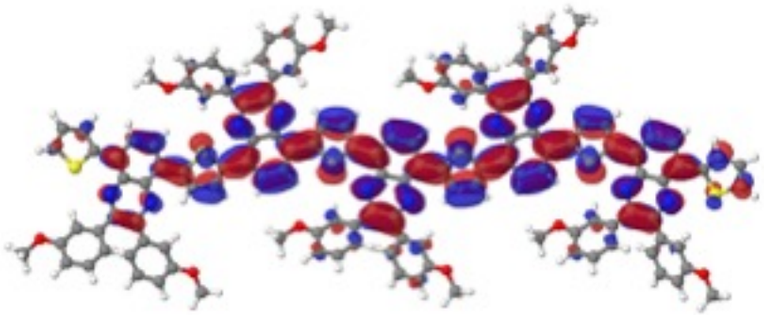
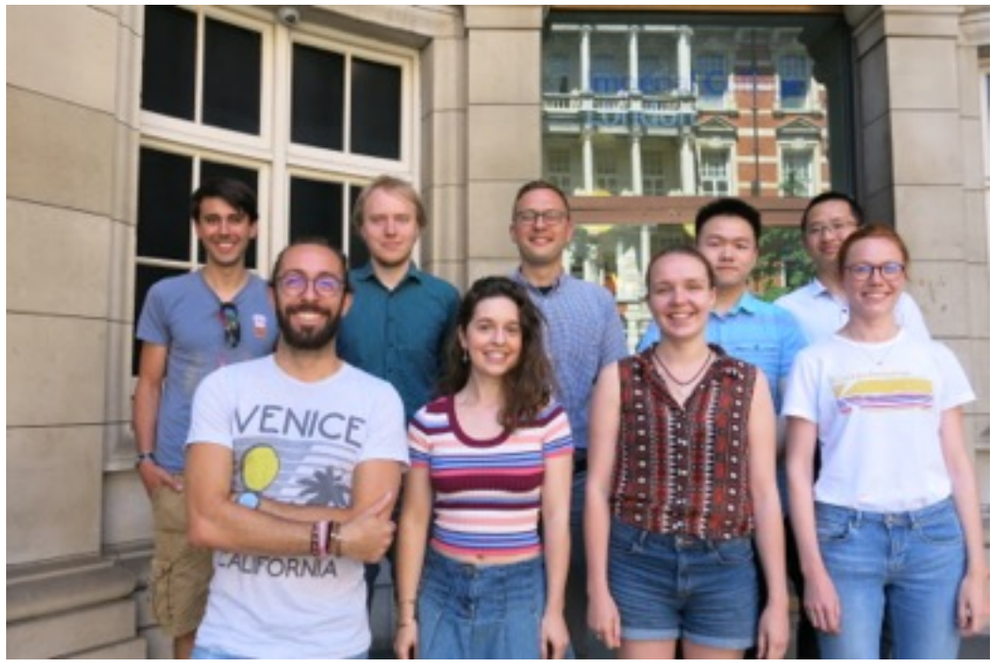
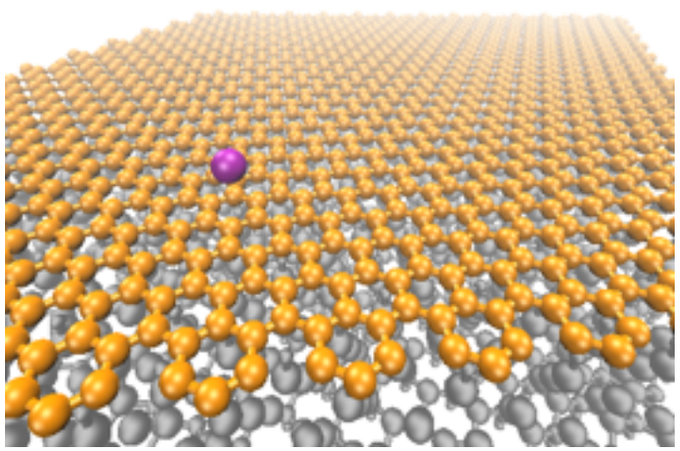
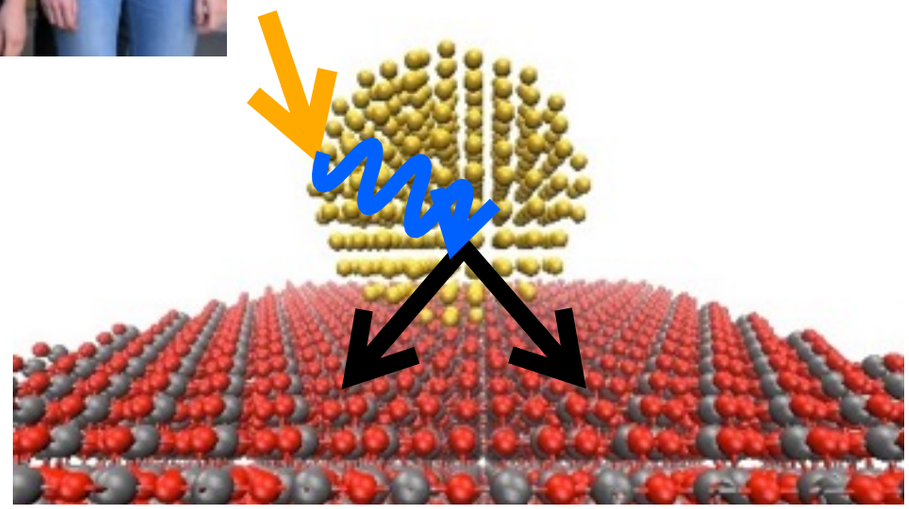
Theory and simulation of materials: focus on electronic excitations





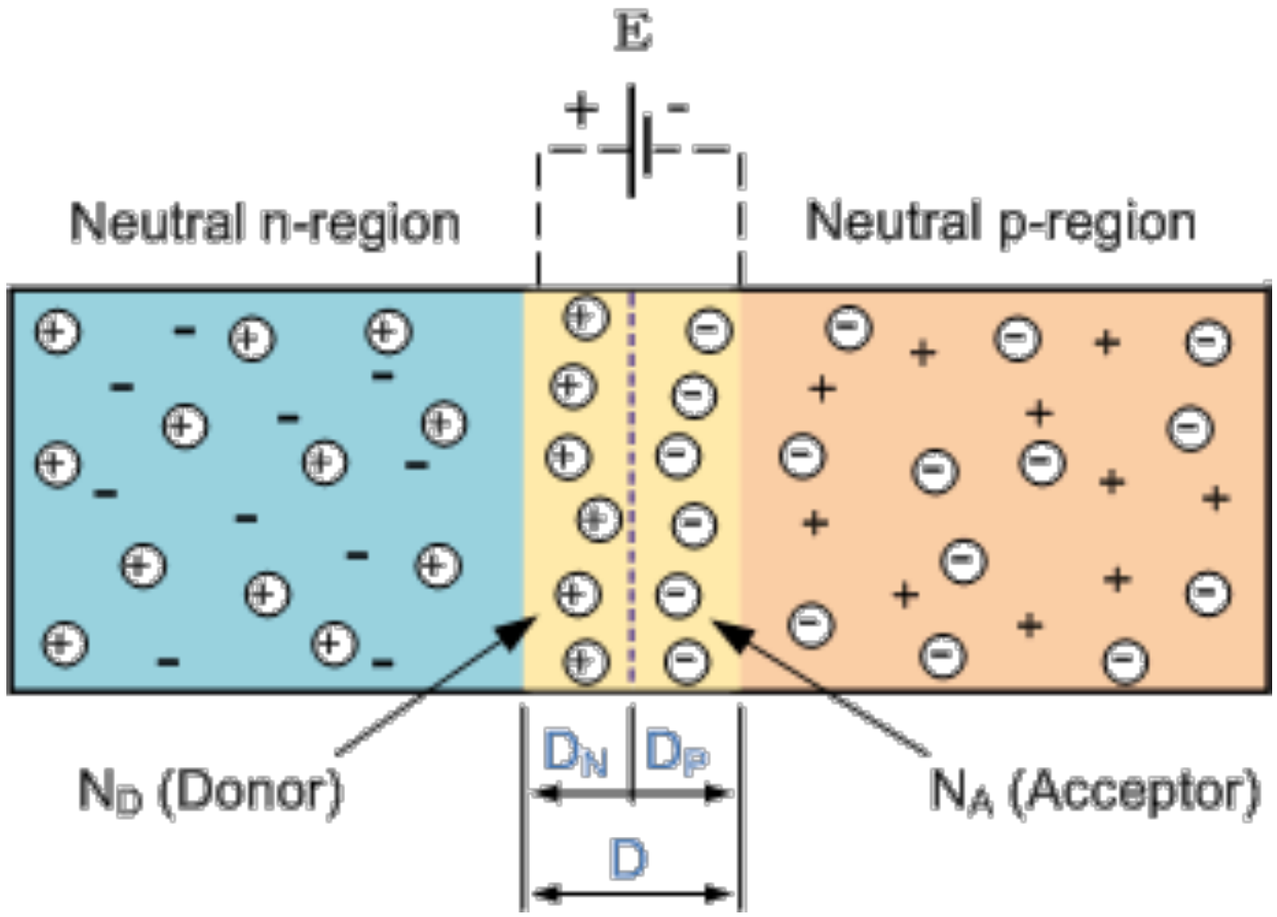






DEFECT ENGINEERING

PN-junction: building block of semiconductor technology

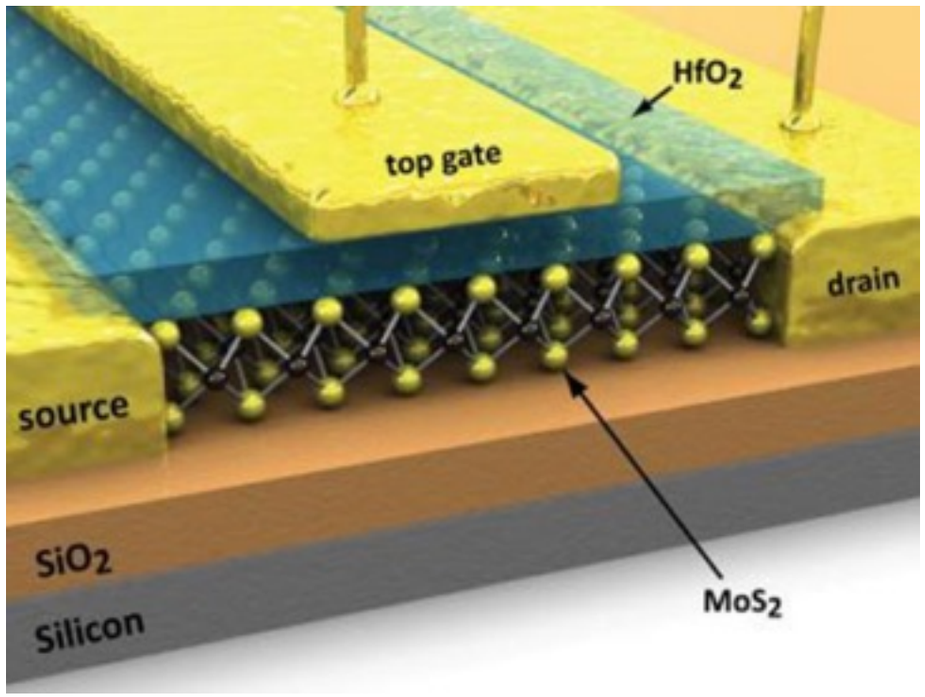


Defects play a key role:

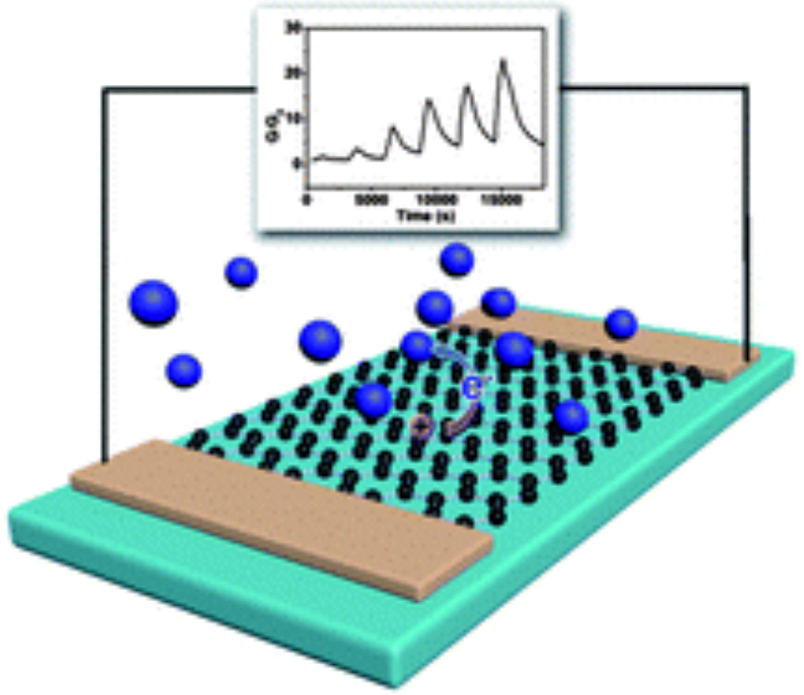
- donate electrons or holes to host material
- formation of charged ions
- charged defects scatter electrons

2D MATERIALS AND DEVICES

Promise of ultrathin devices with novel functionality



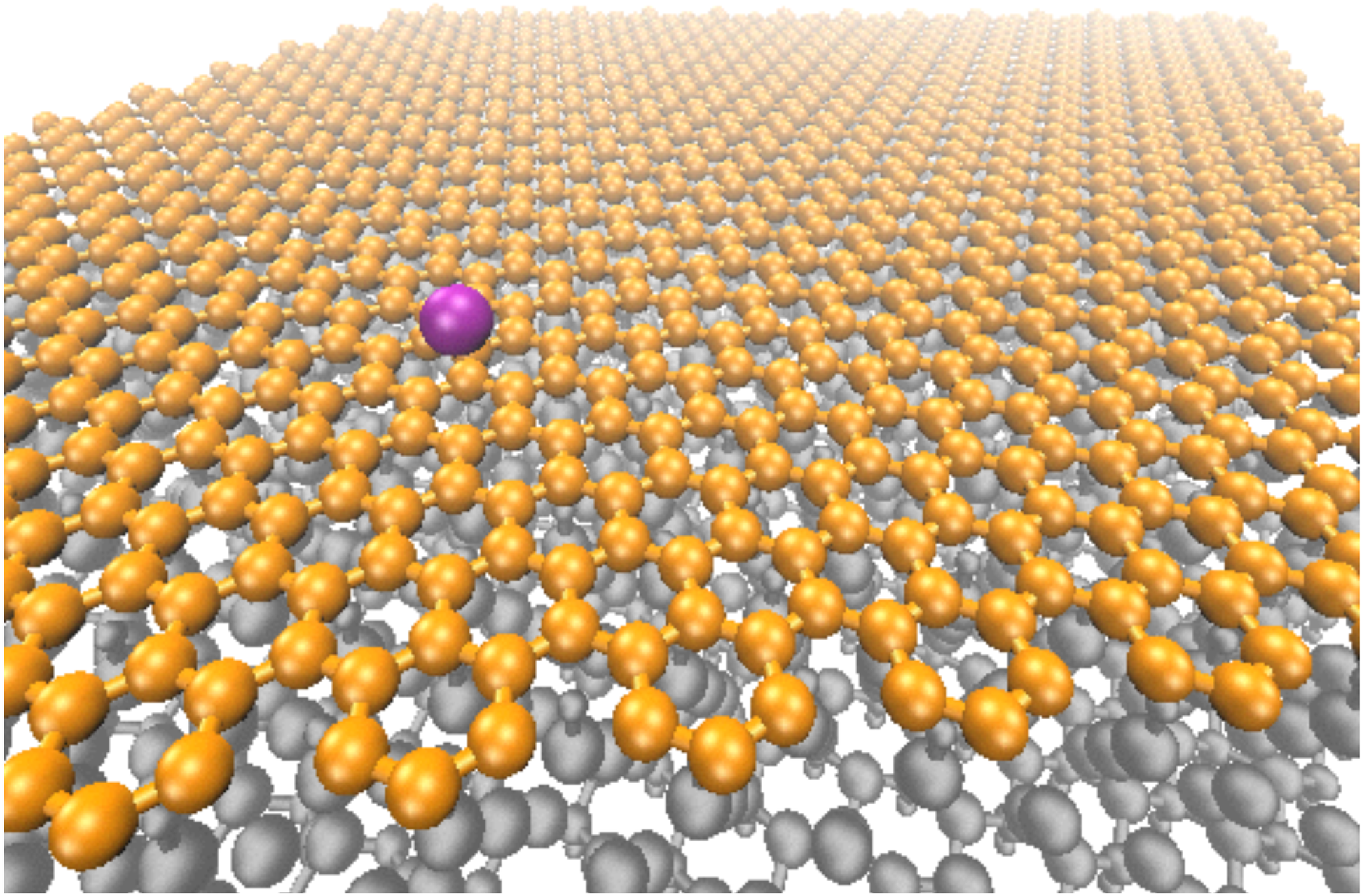
field effect transistor based on 2d semiconductor MoS_2



gas sensor based on graphene

CHARGED DEFECTS IN 2D MATERIALS

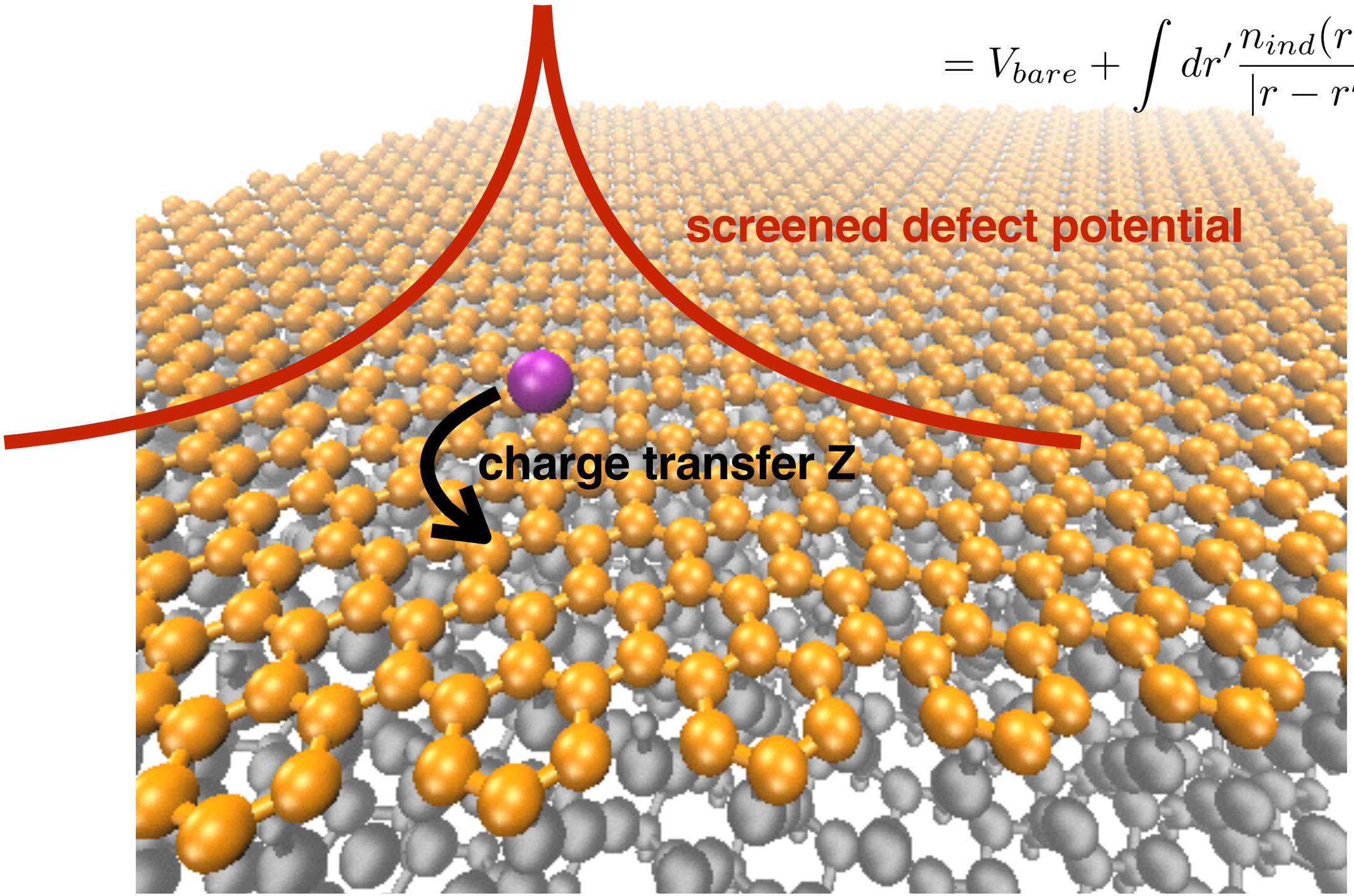
Example: adsorbed atom



CHARGED DEFECTS IN 2D MATERIALS

$$V_{scr}(r) = \int dr' \epsilon^{-1}(r, r') V_{bare}(r')$$

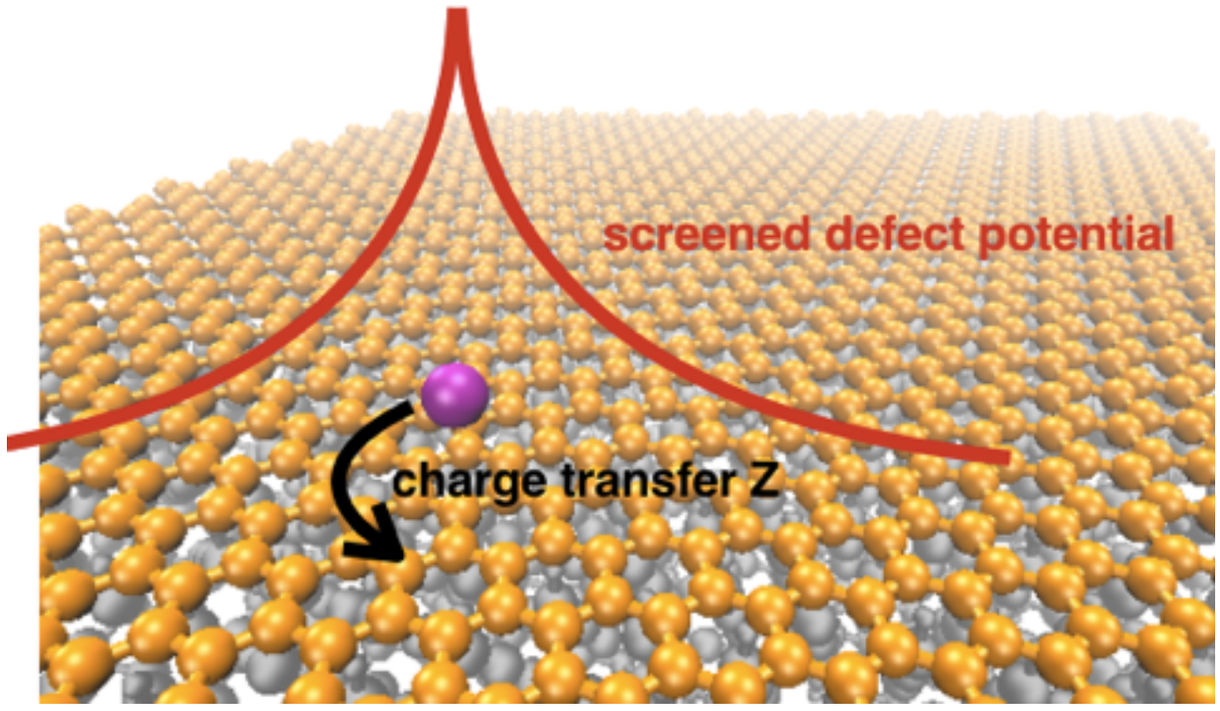
$$= V_{bare} + \int dr' \frac{n_{ind}(r')}{|r - r'|}$$



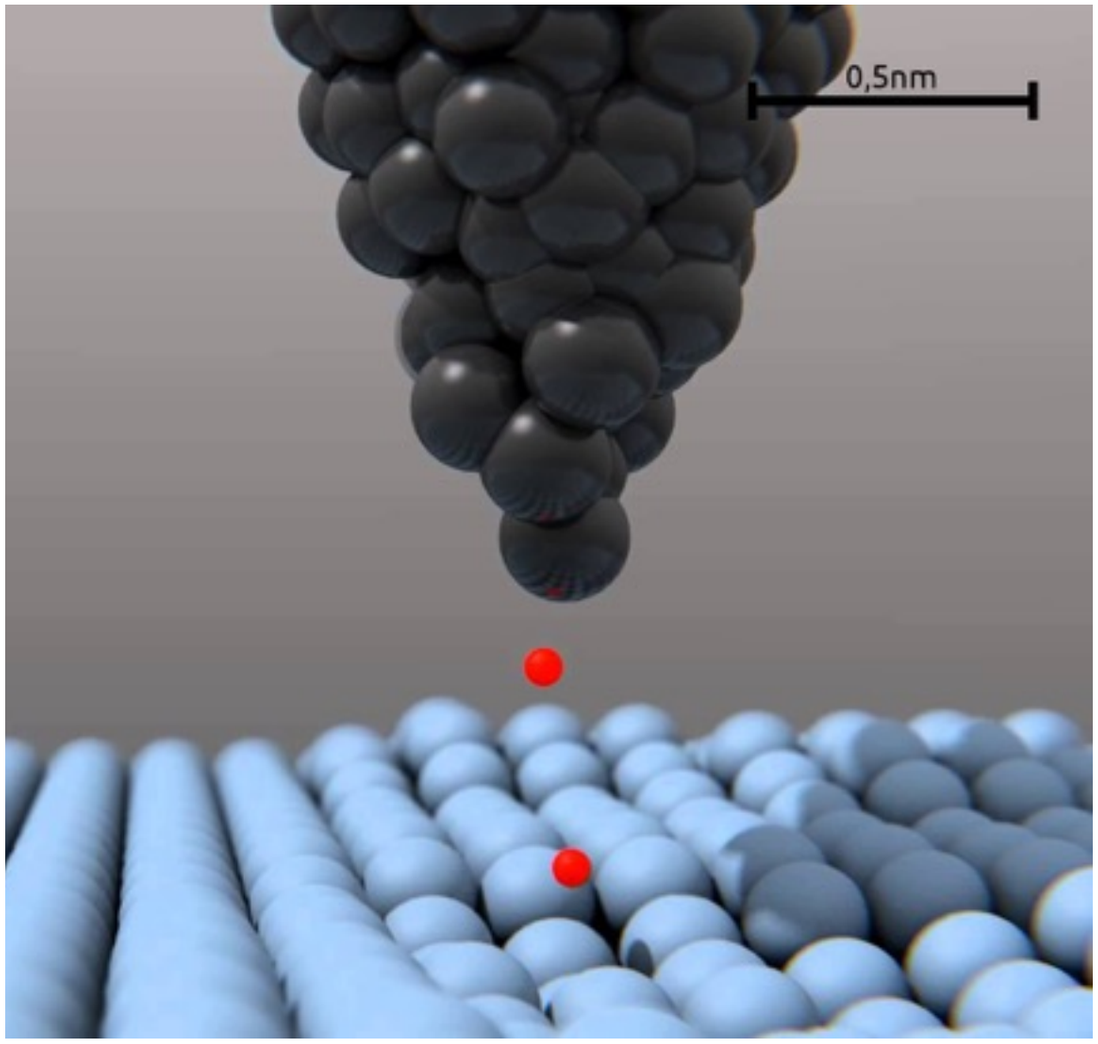
THEORETICAL DESCRIPTION

Challenges:

- screened potential has complicated spatial dependence
- screening in 2D is weaker than in 3D
  - ► large supercells
- charge transfer is difficult to compute



EXPERIMENTAL STUDY OF CHARGED DEFECTS

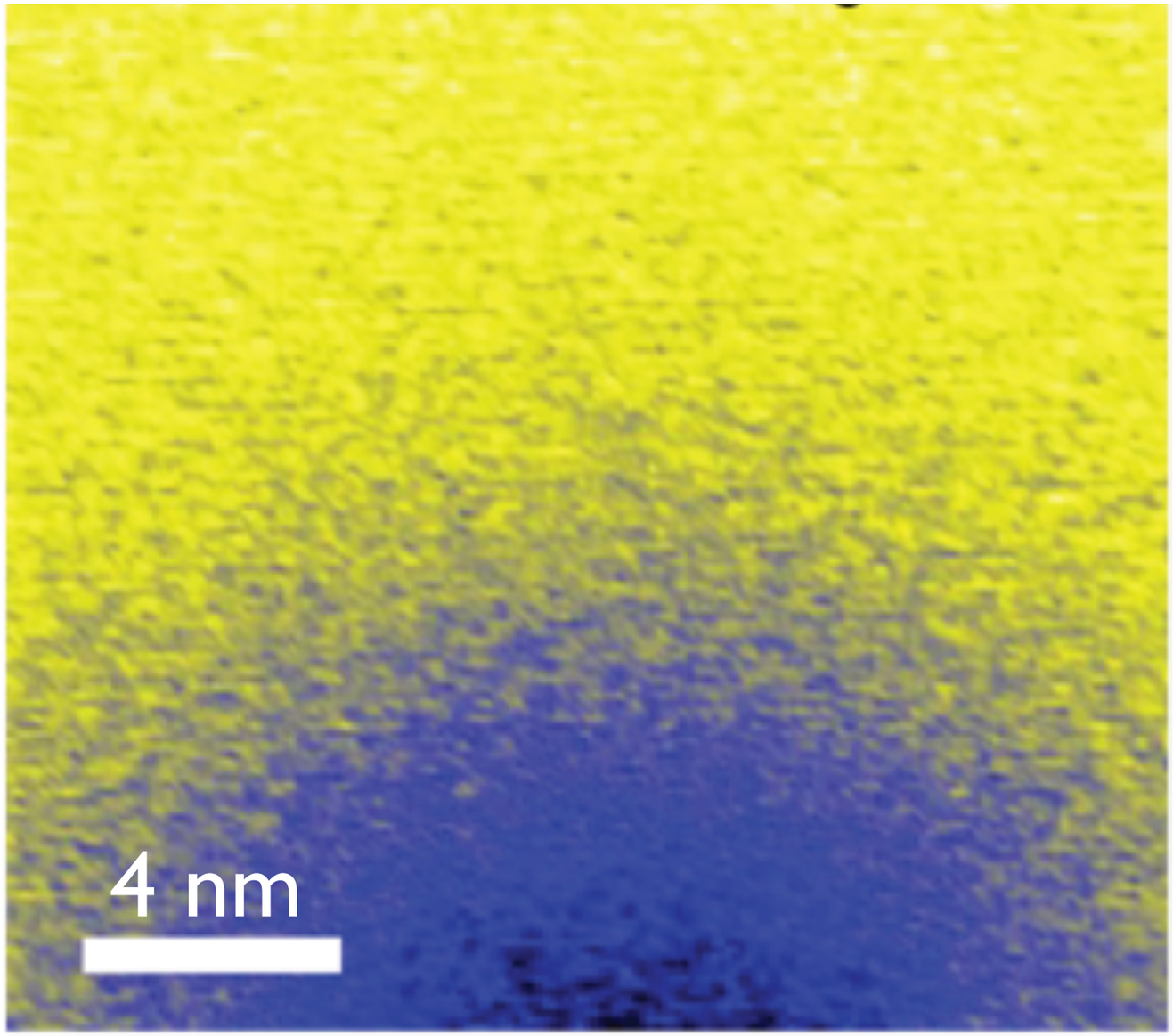


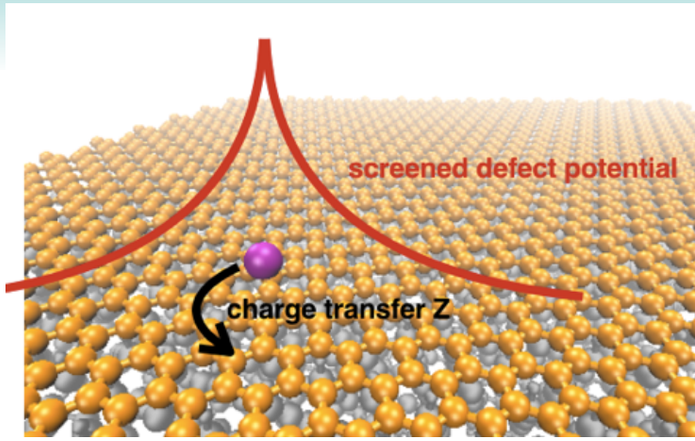
Scanning tunneling spectroscopy (STS):

- add or remove electrons from sample
- probe quasiparticle excitations
- experiments in Crommie group (Berkeley)

SINGLE ADATOM ON GRAPHENE

STM image of single calcium atom on graphene





electrons tunnel from graphene to tip

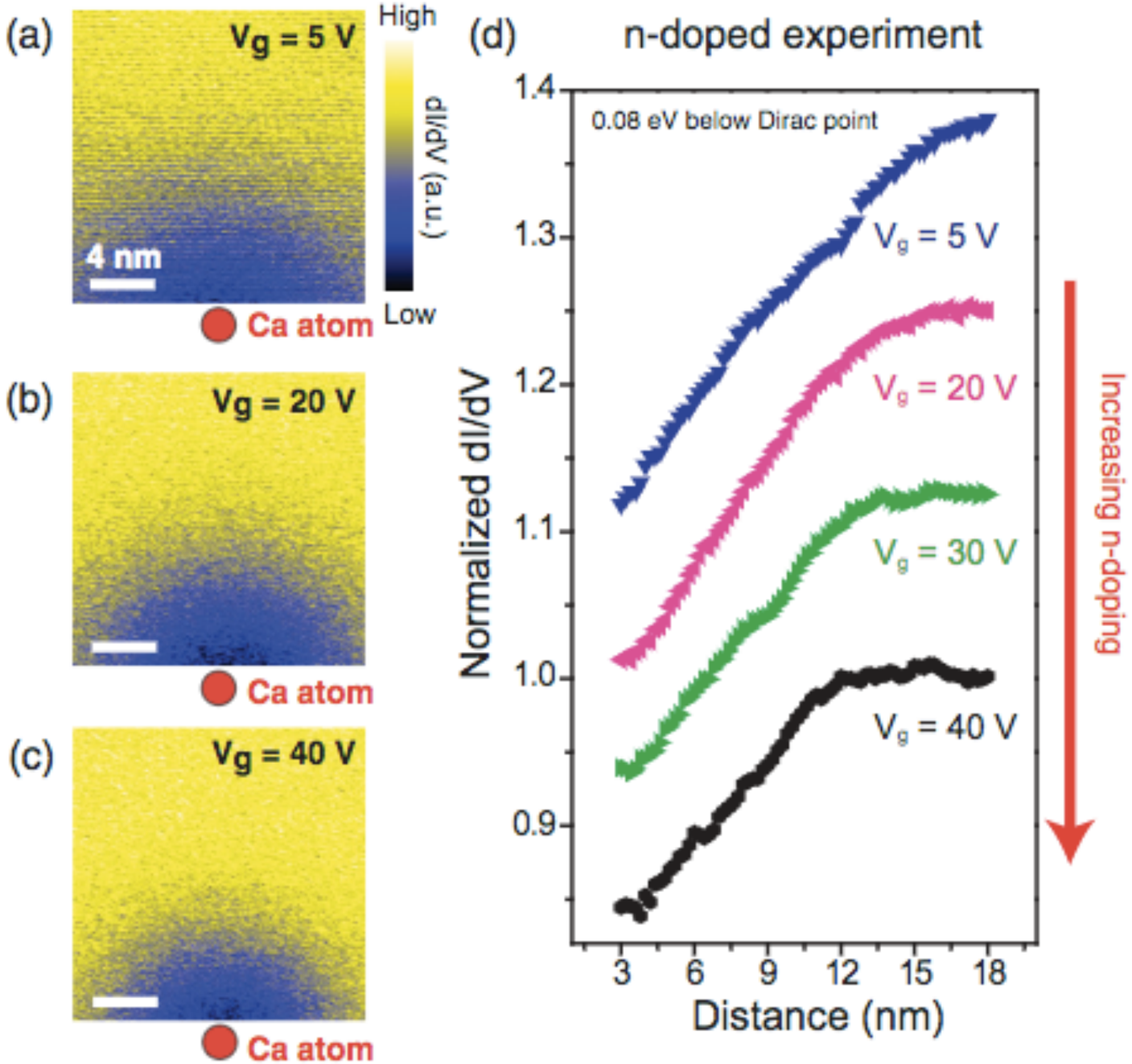
Ca

single adatom influences thousands of graphene atoms

Wong et al., Phys. Rev. B (2017)

DOPING DEPENDENCE

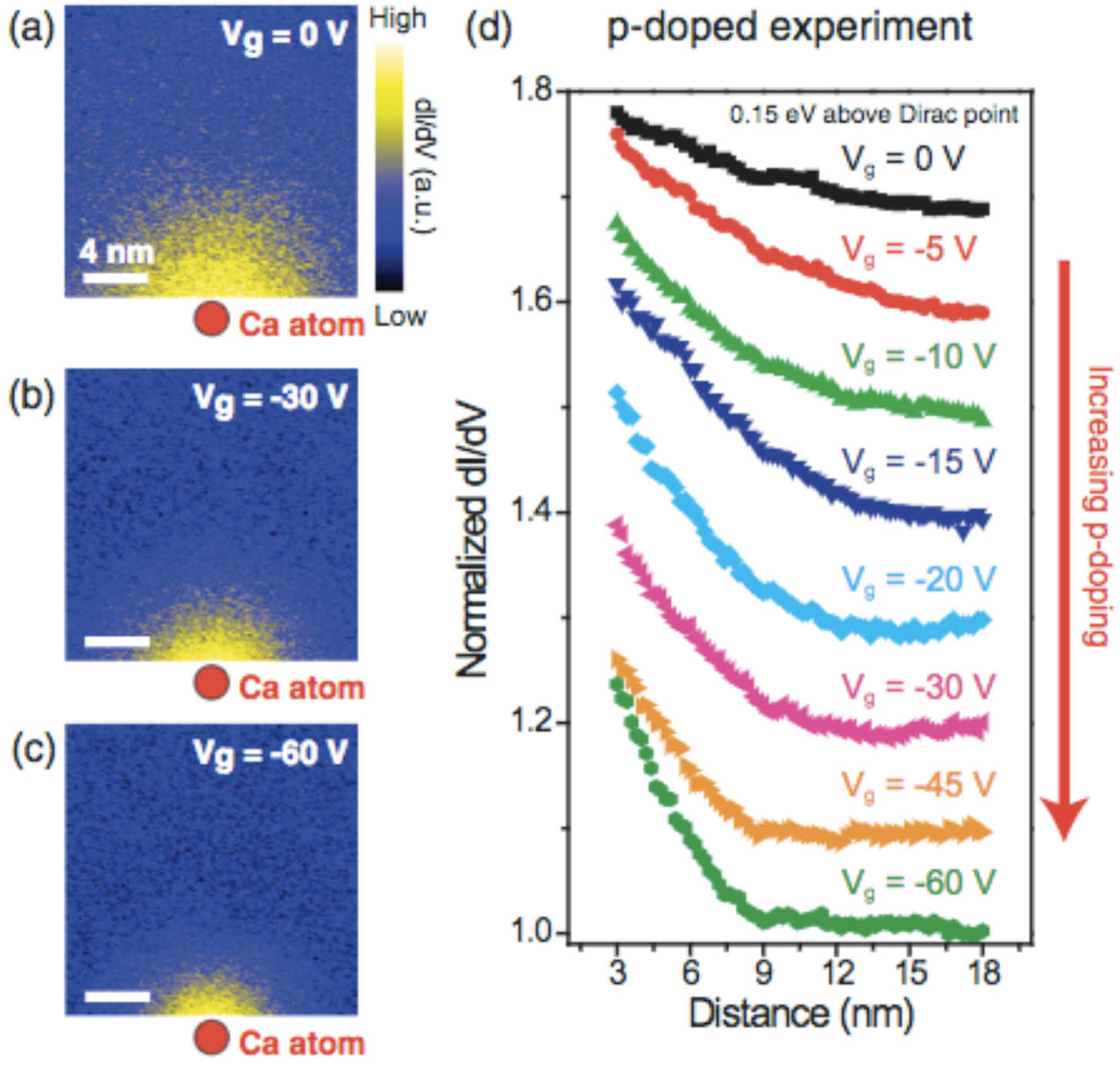
Effect of changing the graphene electron concentration via gate voltage V_g



Wong et al., Phys. Rev. B (2017)

DOPING DEPENDENCE

For tip voltage such that electron tunnel from tip to graphene:



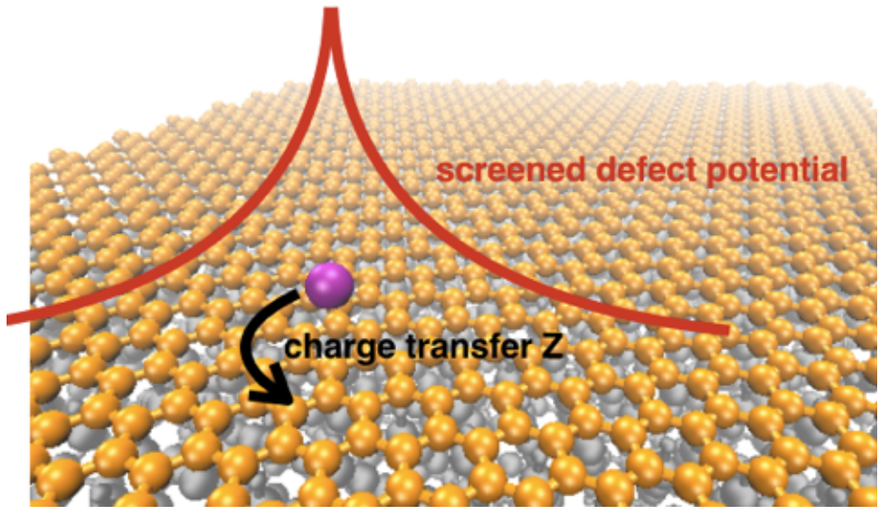
Wong et al., Phys. Rev. B (2017)

THEORETICAL DESCRIPTION

Modelling charged adsorbates on doped graphene:

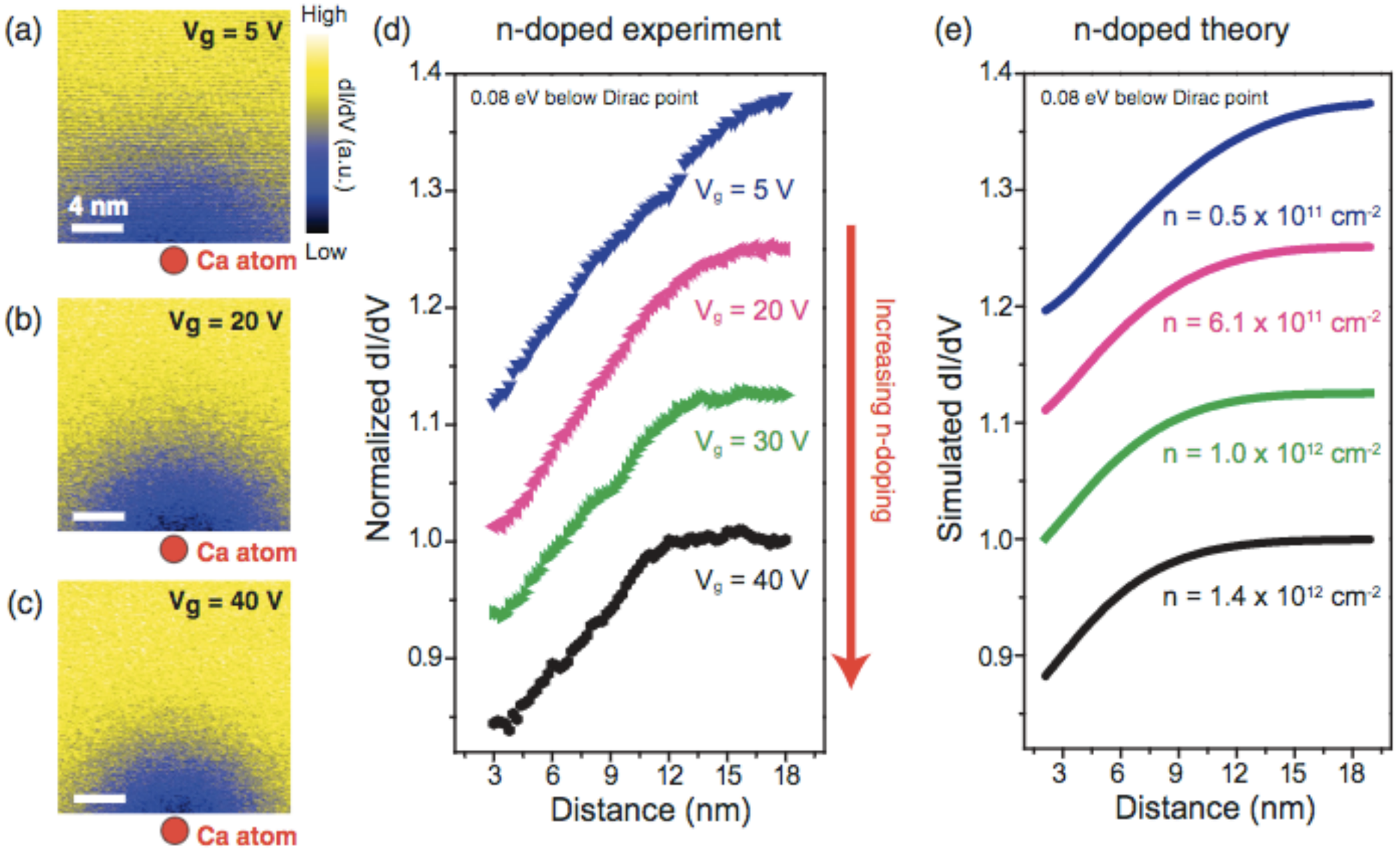
- use tight-binding to model supercells with 100,000 carbon atoms
- charge transfer Z = 0.7 lel
  - ► from experimental measurement of Fermi level shift
- screened potential: random phase approximation
- calculate local density of states (LDOS)

$$\epsilon(q) = \begin{cases} \epsilon_s + \frac{2\pi e^2 \mathrm{DOS}(E_F)}{q}, & q \leqslant 2k_F, \\ \epsilon_s + \frac{2\pi e^2 \mathrm{DOS}(E_F)}{q}\left[1 - \frac{1}{2}\sqrt{1 - \left(\frac{2k_F}{q}\right)^2} + \frac{q}{4k_F}\cos^{-1}\frac{2k_F}{q}\right], & q > 2k_F, \end{cases}$$



THEORY RESULTS

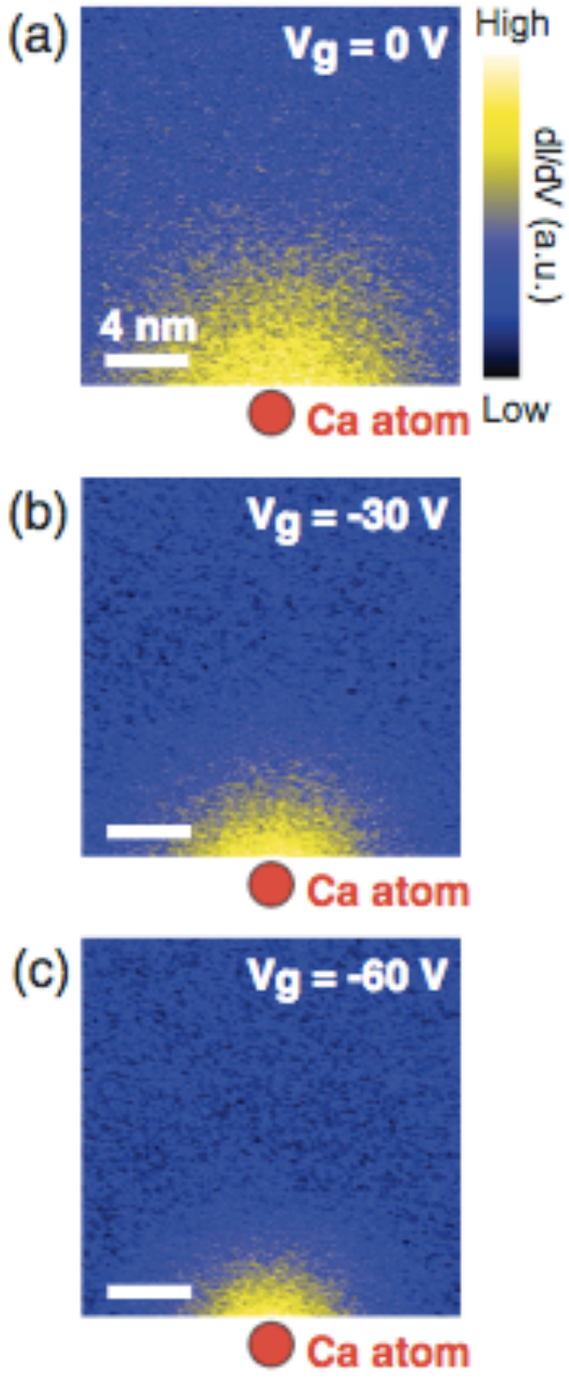
STS images for tunneling from graphene to tip:

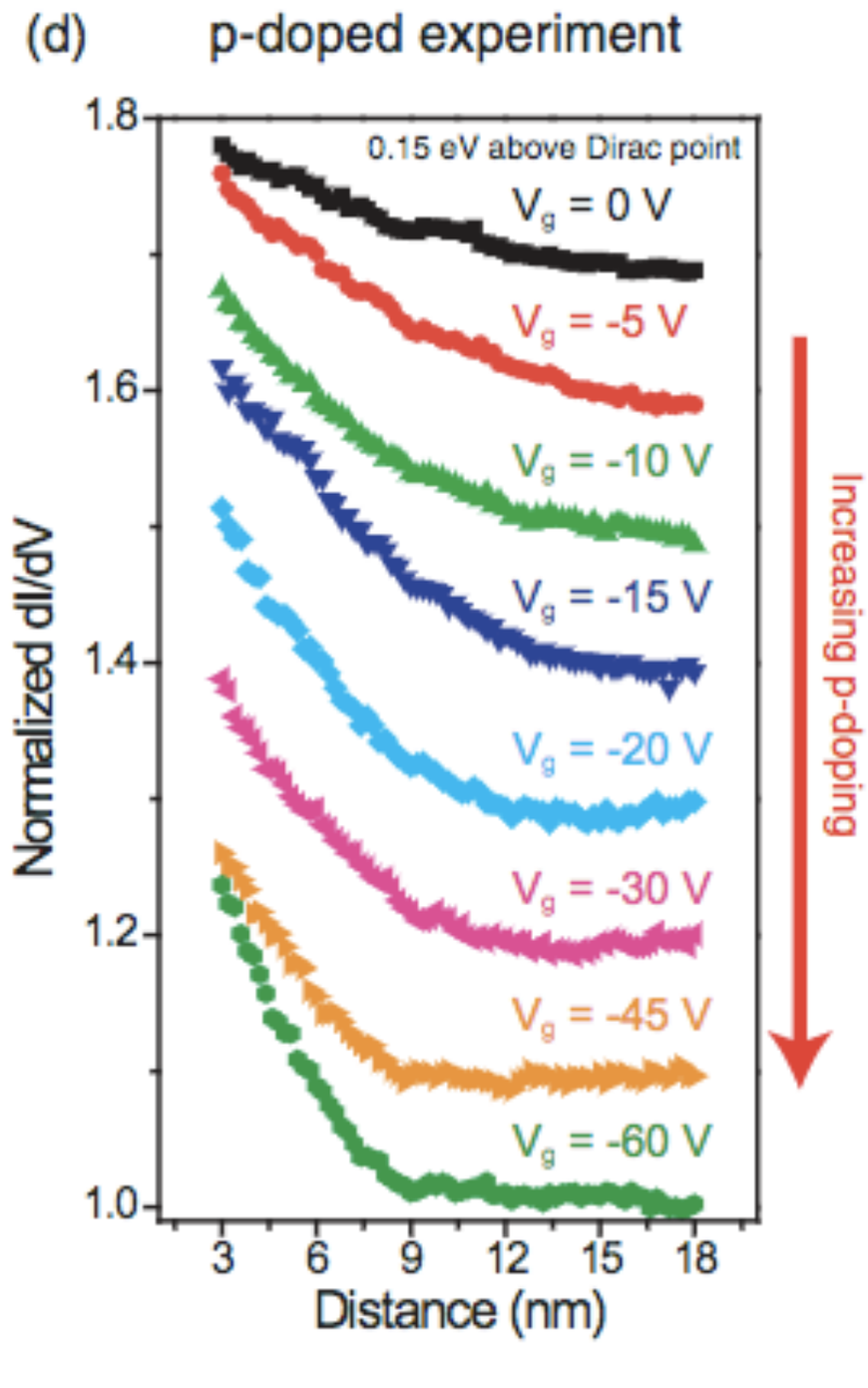


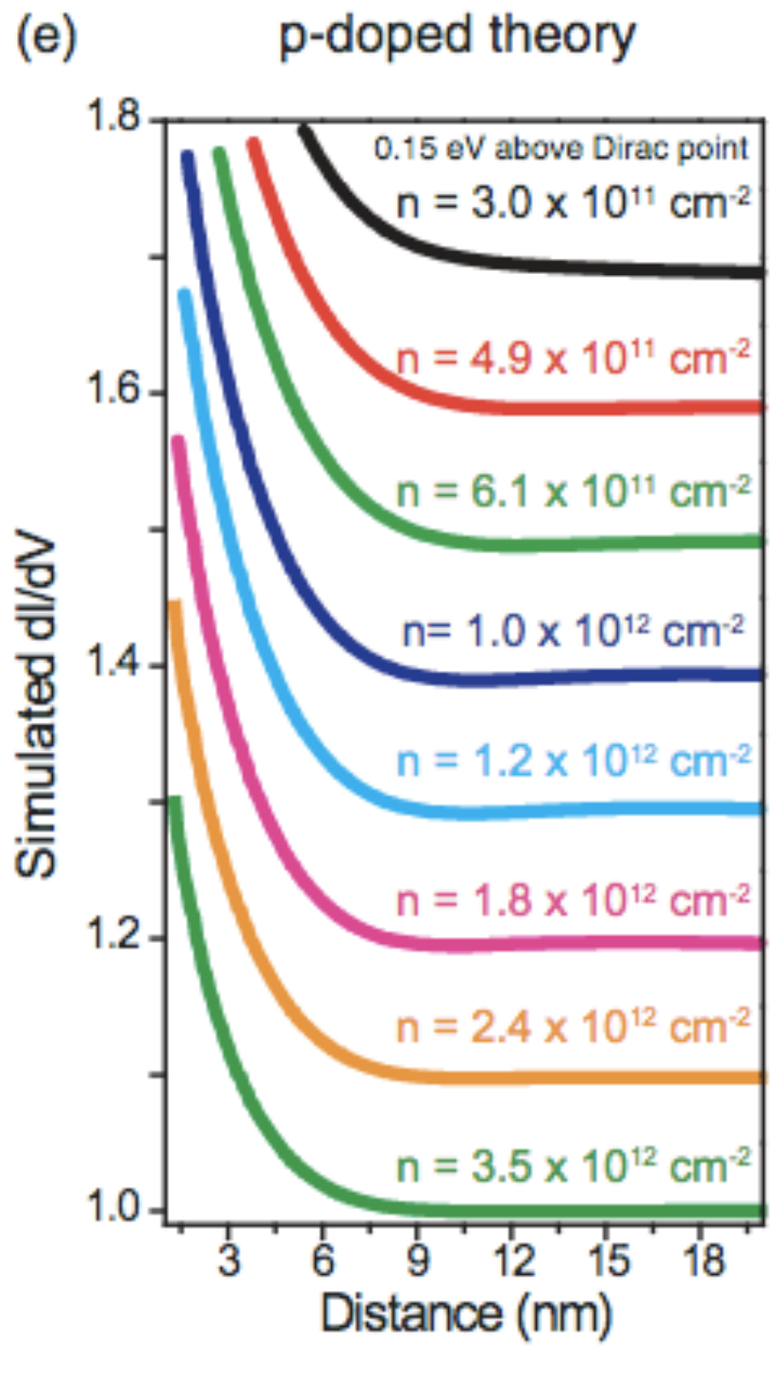
Wong et al., Phys. Rev. B (2017)

THEORY RESULTS

STS images for tunneling from tip to graphene:



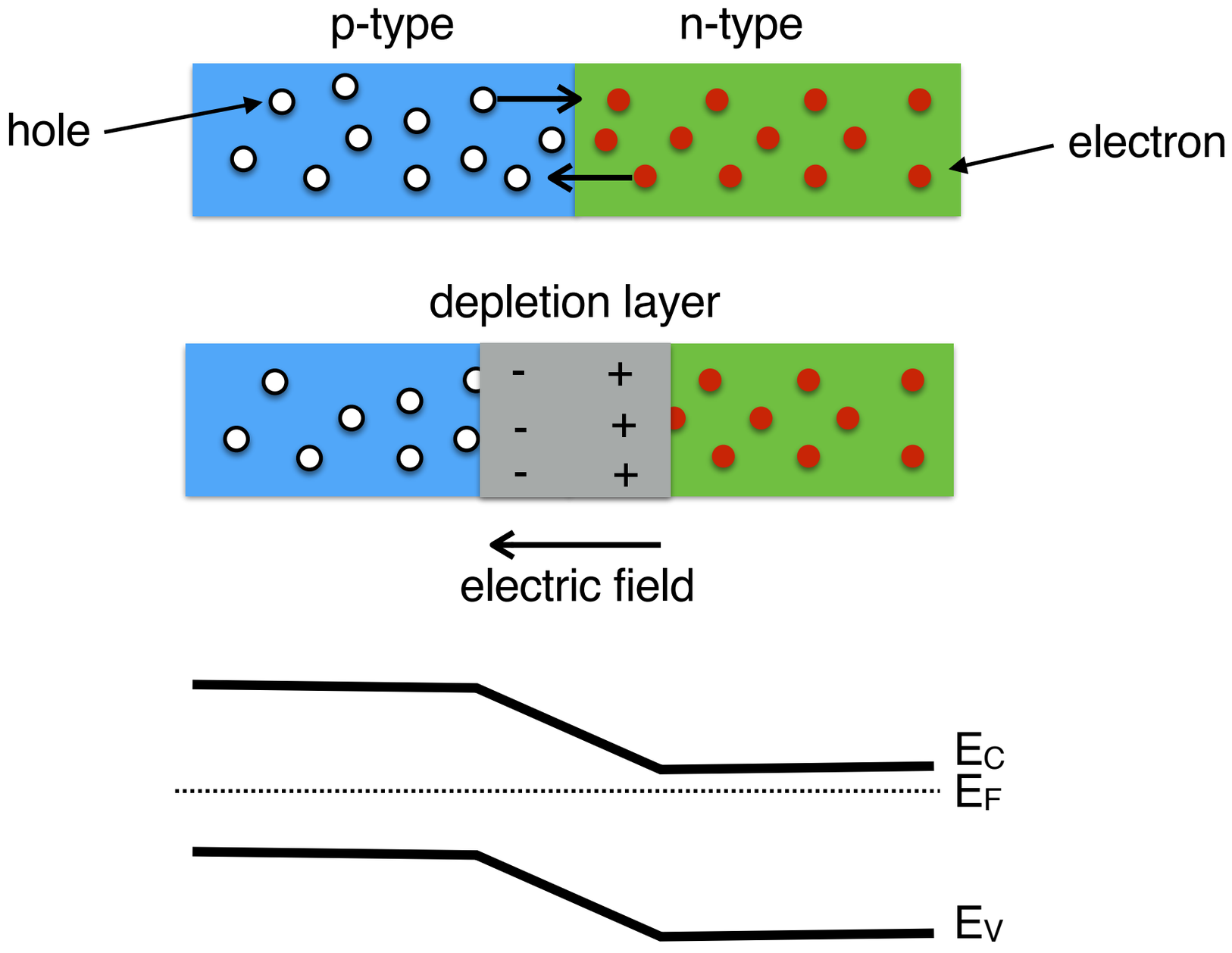




Wong et al., Phys. Rev. B (2017)

BAND BENDING

Electric potential shifts the energies of electronic states



Wong et al., Phys. Rev. B (2017)

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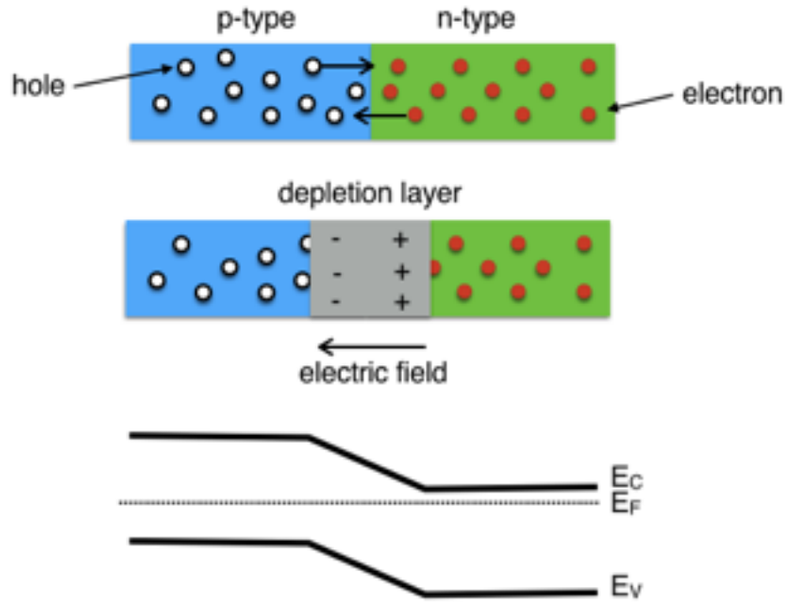

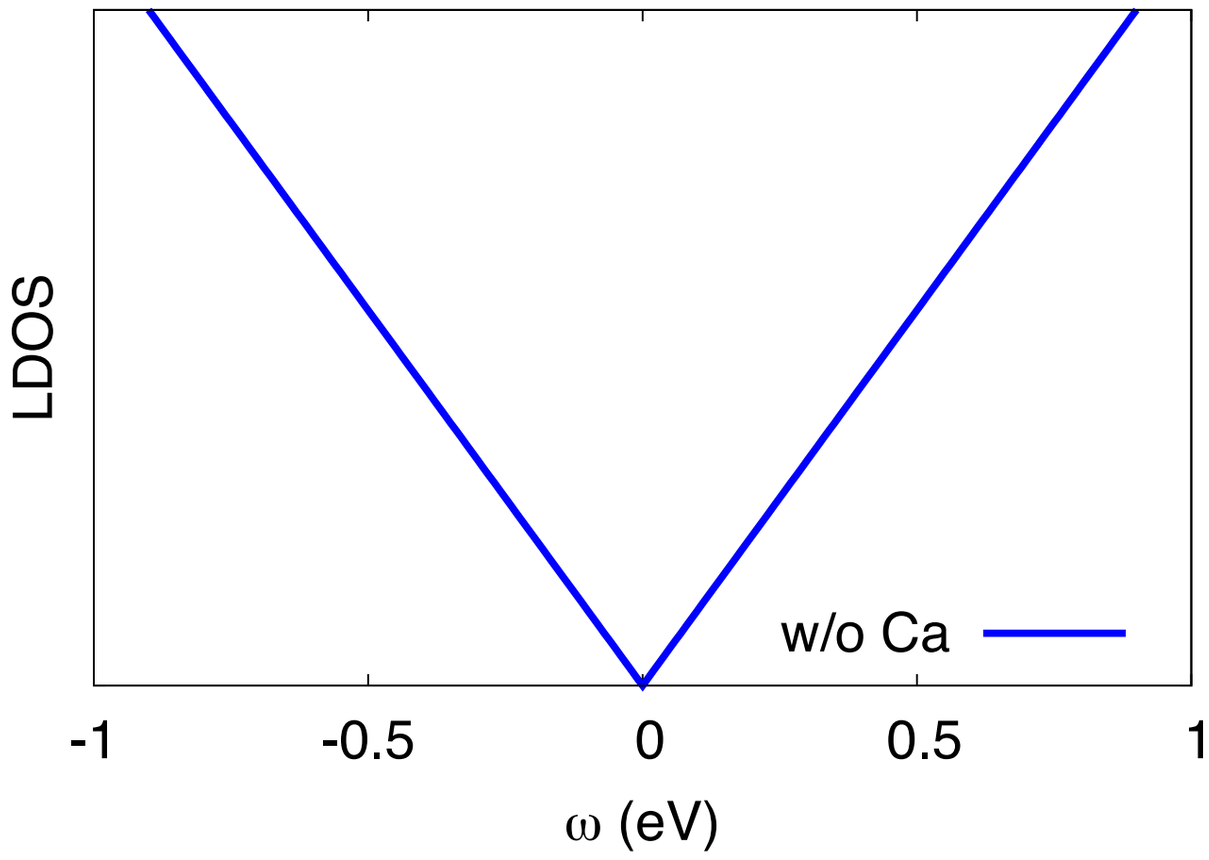

Wong et al., Phys. Rev. B (2017)

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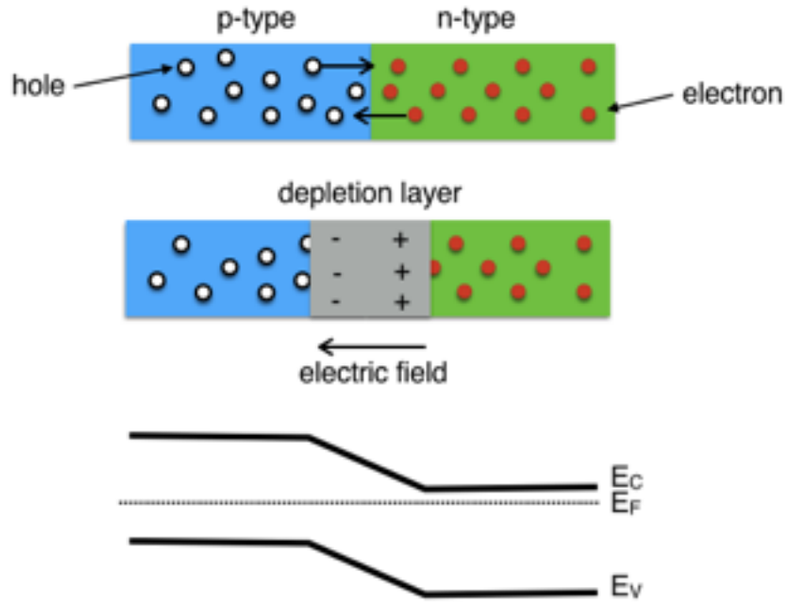

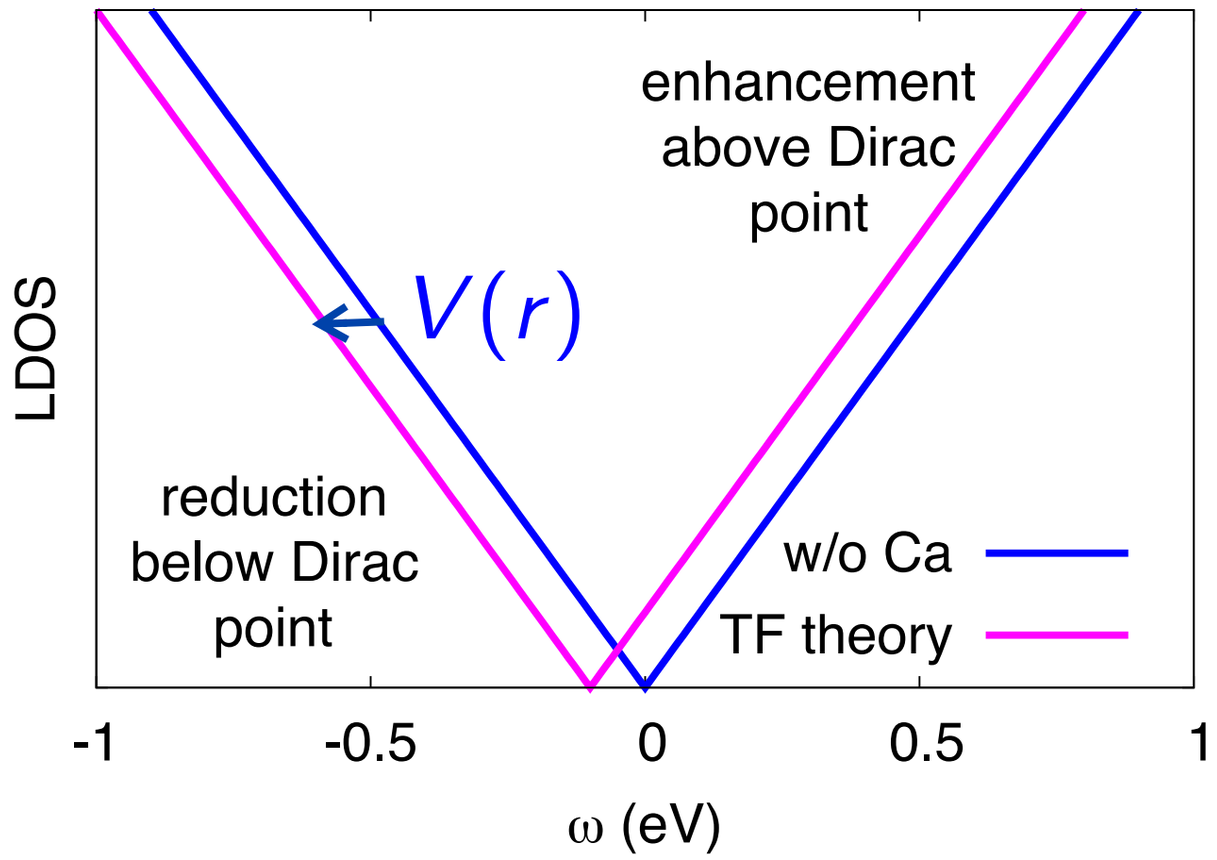

Wong et al., Phys. Rev. B (2017)

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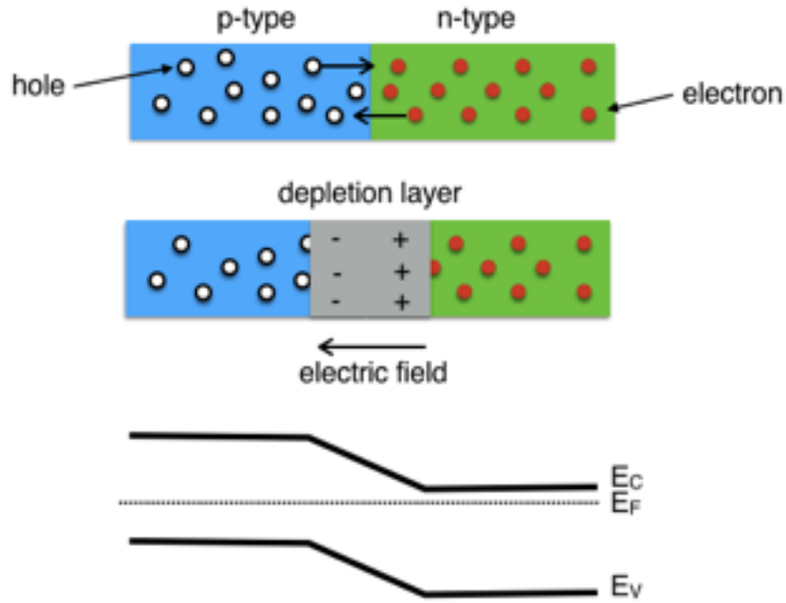
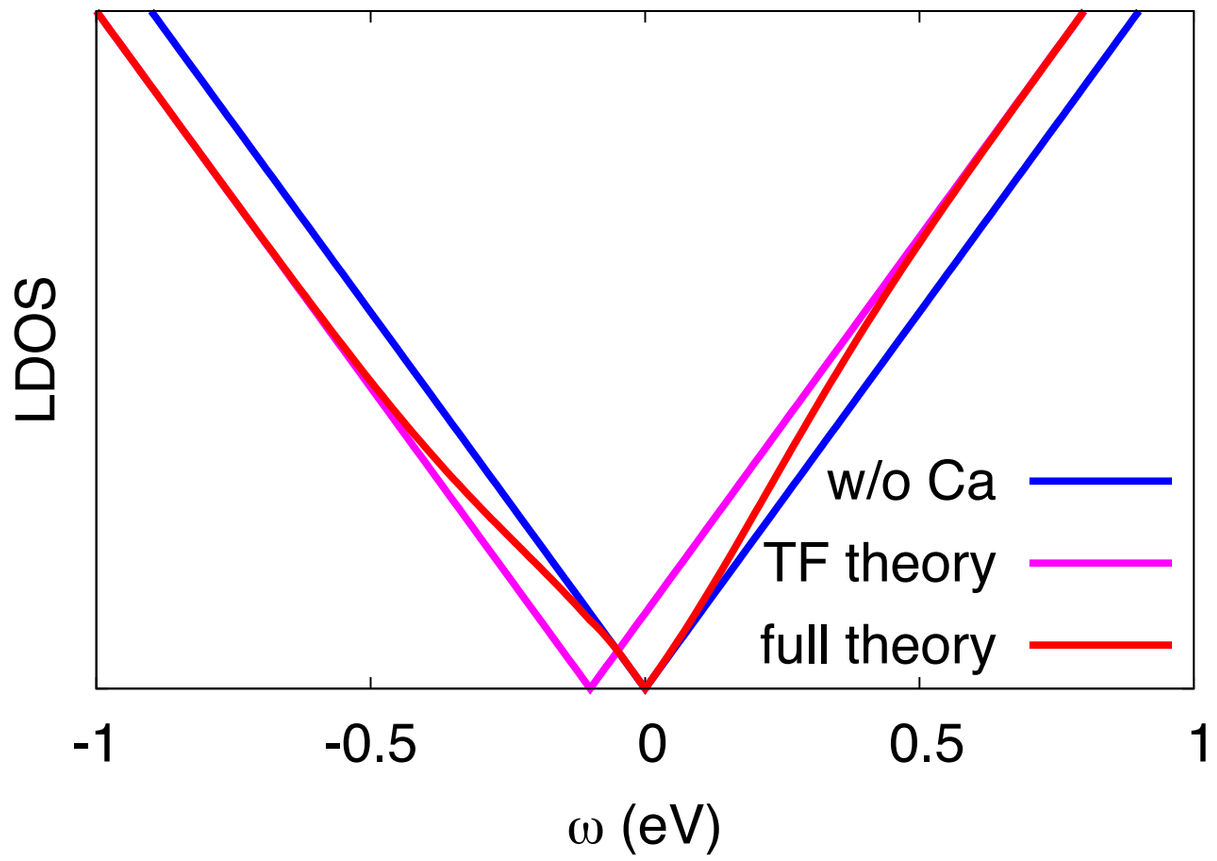




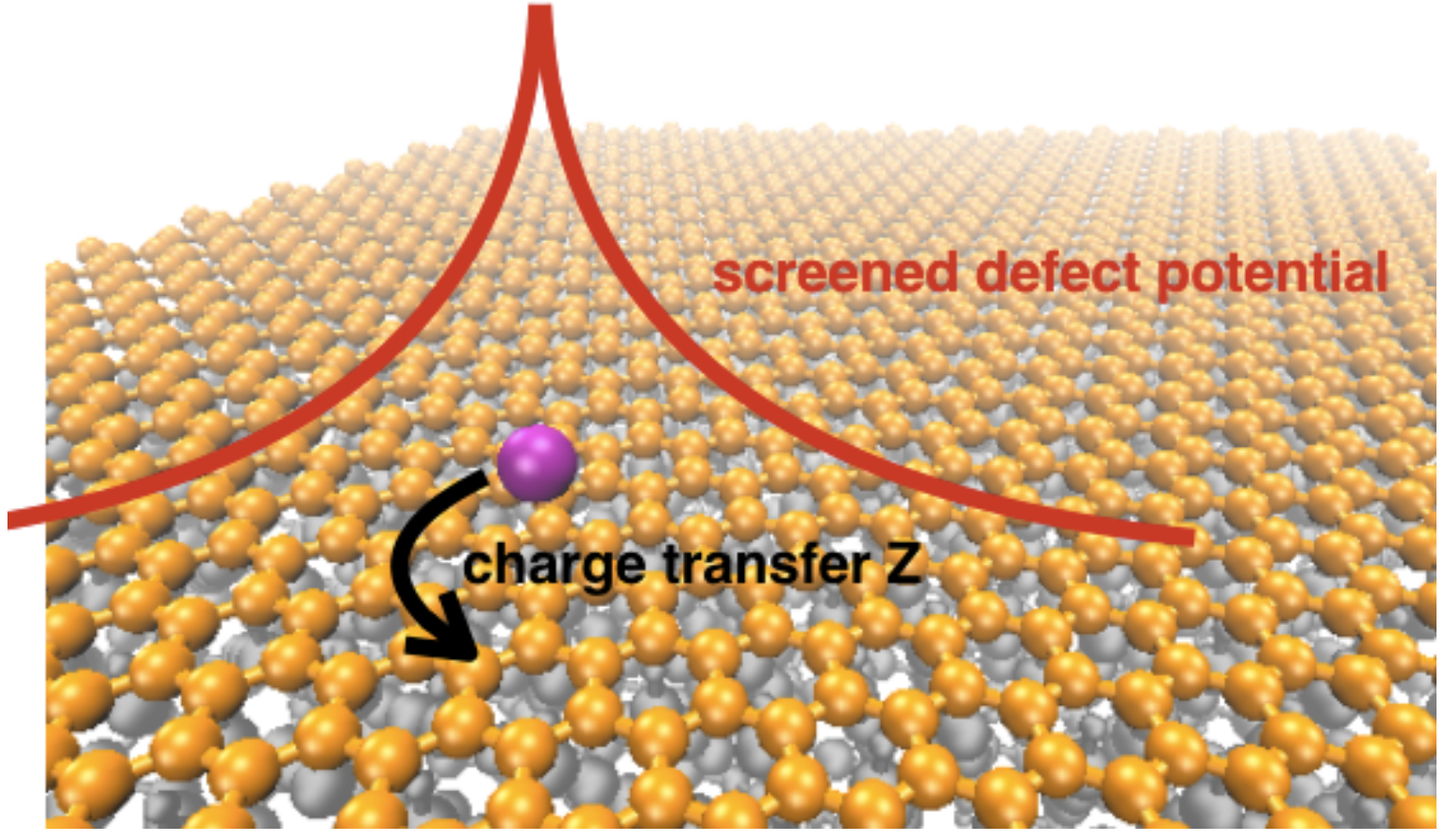
Wong et al., Phys. Rev. B (2017)

OPEN QUESTIONS

- How to calculate the charge transfer?
- Is screening model ok? Need nonlinear response?

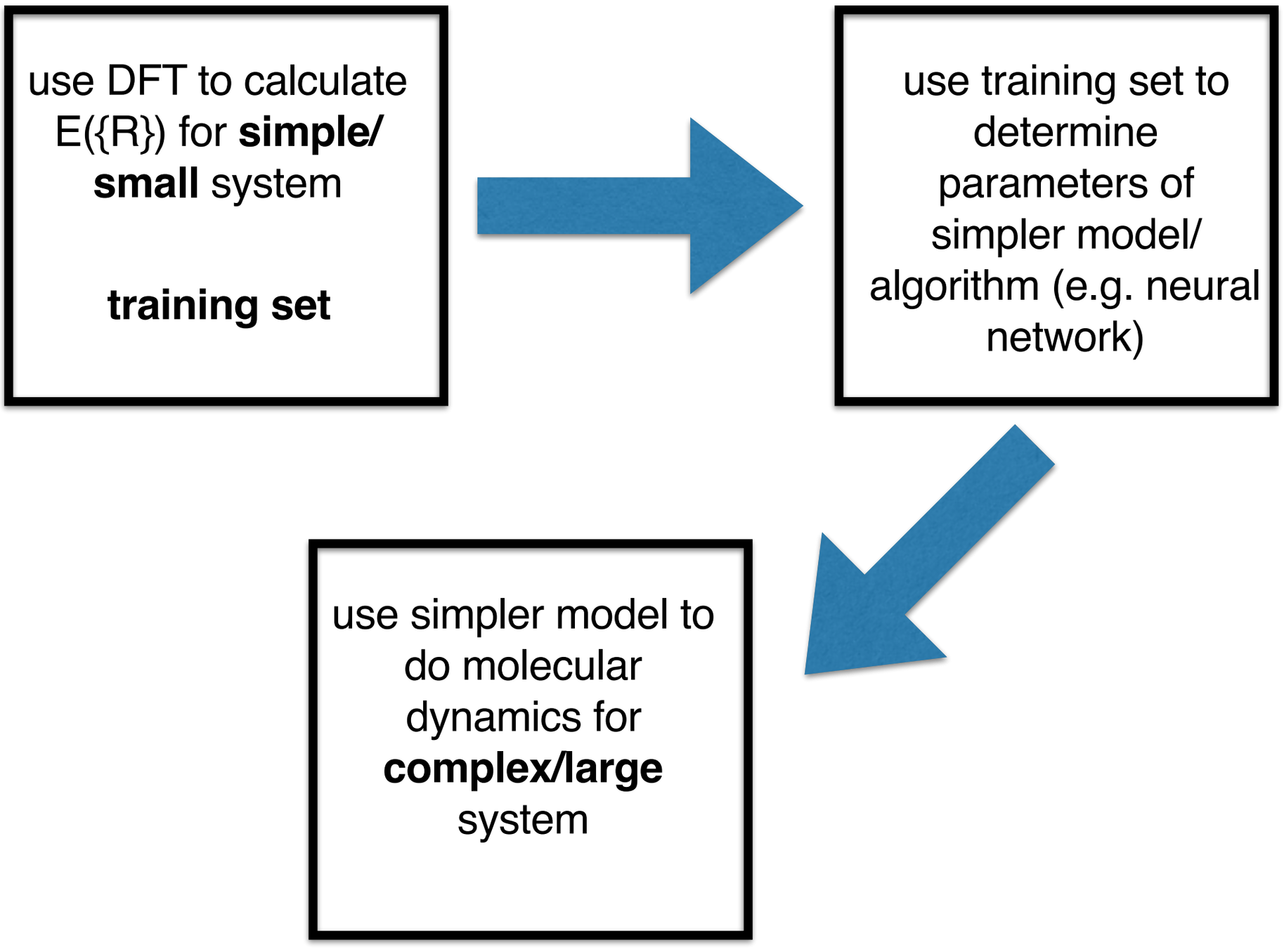
In principle: these questions can be answered by DFT calculations

But: DFT calculations for 100,000 atoms are … uncomfortable



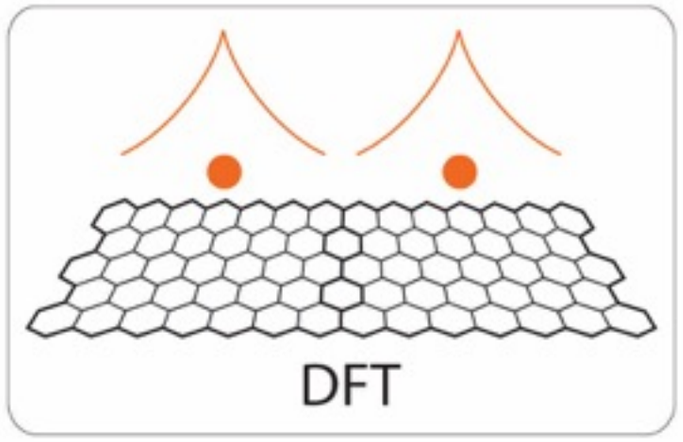
INSPIRATION FROM MACHINE LEARNING

Machine learning for classical molecular dynamics simulations



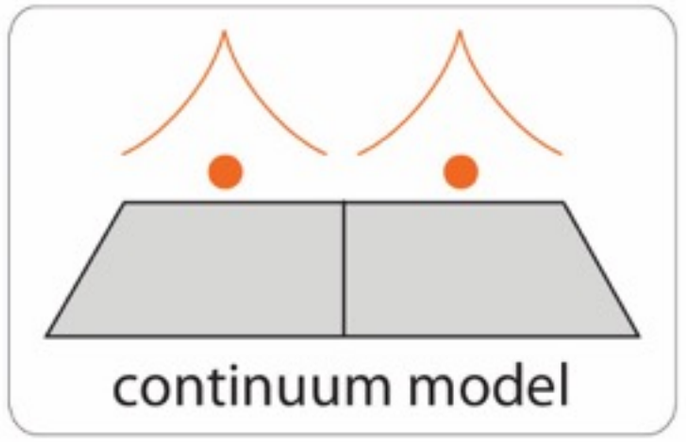
MULTISCALE APPROACH FOR CHARGED DEFECTS

DFT in small supercell



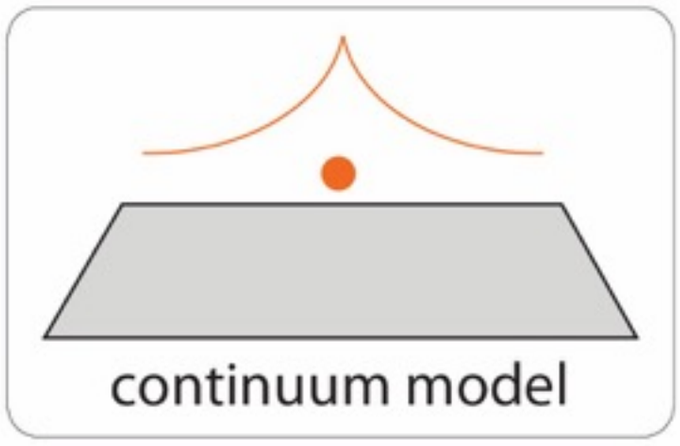
calculate screened potential (training set)

Parametrize model in small supercell

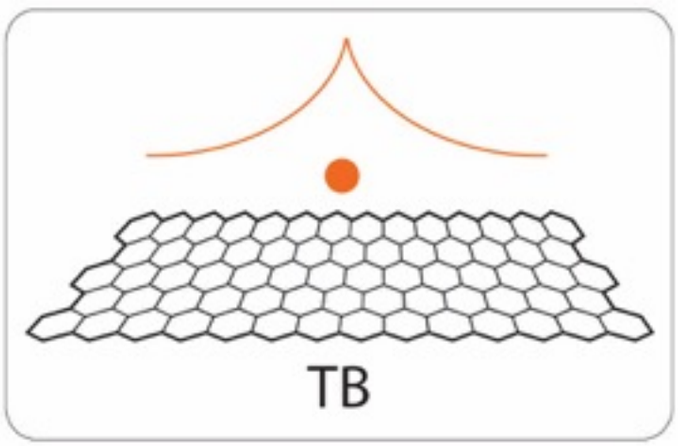


- use non-atomistic model for graphene
- point charge for defect
- Z and E_F are fitting parameters

Evaluate model in large supercell

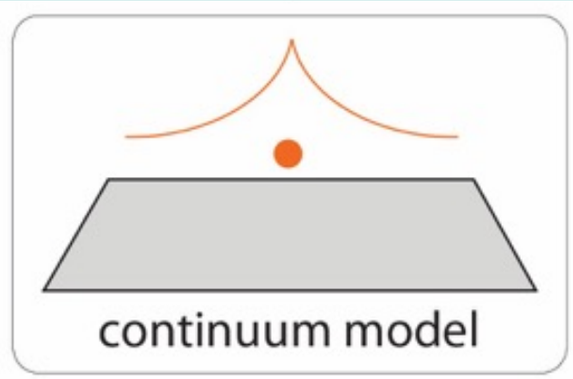


Use model potential in tight-binding



CONTINUUM MODELS

Non-linear Thomas-Fermi (NLTF) approach:



$$V_{\mathrm{scr}}^{\mathrm{cont}}(\mathbf{r};\mu) = Z\nu_{z_{\mathrm{imp}}}(\mathbf{r}) + \int \mathrm{d}^2\mathbf{r}'[n(\mathbf{r}') - n_0]\nu_0(\mathbf{r}-\mathbf{r}'), \tag{1}$$

$$\text{where } n_0(\mu) = \mu|\mu|/(\pi\nu_{\mathrm{F}}^2) \text{ and } n(\mathbf{r}) = n_0(\mu - V_{\mathrm{scr}}(\mathbf{r}))$$

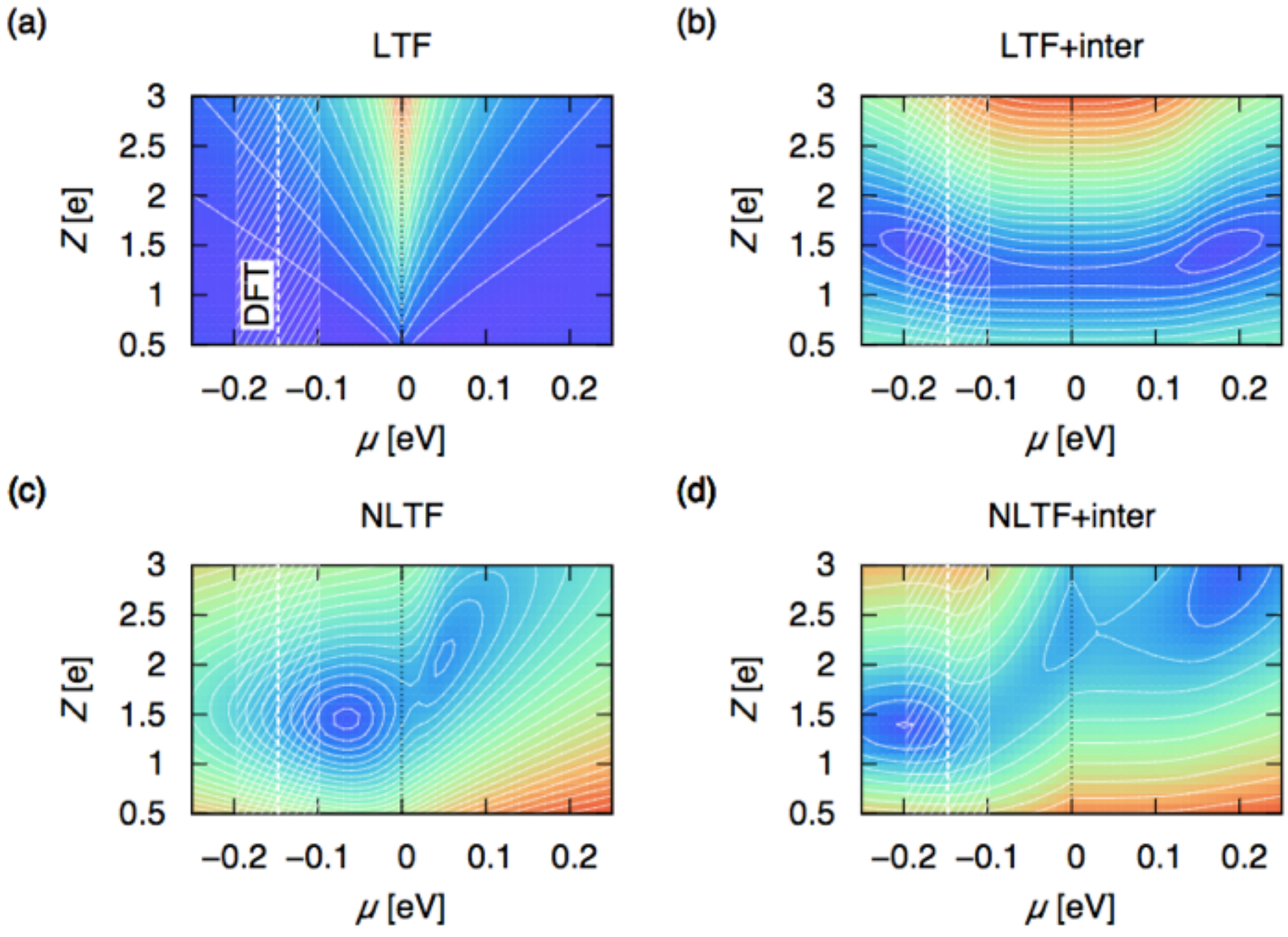
- Thomas-Fermi approach only captures intraband transitions
- include interband transition in linear response (via dielectric matrix)

*Corsetti, Mostofi, **JL**, 2D Materials (2017)*

RESULTS

Parametrization of continuum model using ab initio screened potential

Fitness metric F as function of model parameter E_F and Z



*Corsetti, Mostofi, **JL**, 2D Materials (2017)*

RESULTS

Parametrization of continuum model using ab initio screened potential

Optimal parameters for defect charge Z:

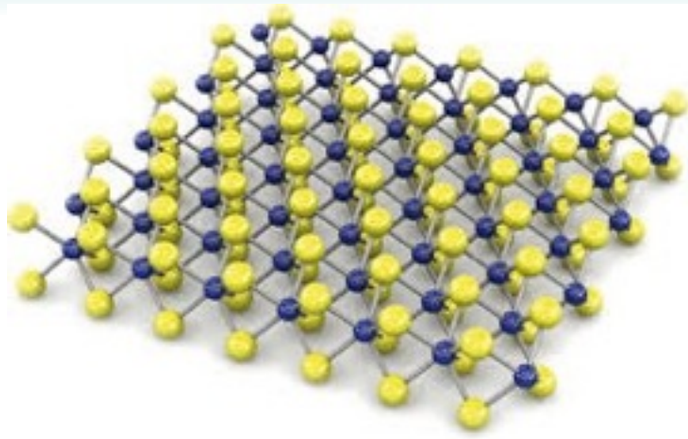
Model	Z (e)	$\mathcal{F}$ (eV)
LTF	0.3	8.9×10^{-3}
LTF + inter	1.3	8.4×10^{-3}
NLTF	1.6	9.3×10^{-3}
NLTF + inter	1.6	7.4×10^{-3}

- all theories have similar fitness, but different parameters
- nonlinearity and interband transitions are important
- But: **only manifest themselves as rescaling of screening potential**

*Corsetti, Mostofi, **JL**, 2D Materials (2017)*
Katsnelson, PRB (2006)

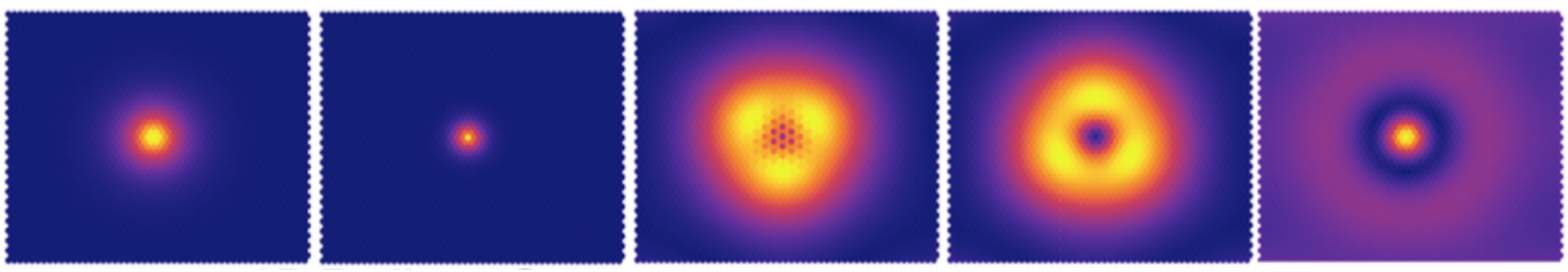
CHARGED DEFECTS IN 2D SEMICONDUCTORS

Impurity states of charged defects in MoS_2



- tight-binding calculations with 8,000 atoms
- screened potential from ab initio RPA calculation
- defect charge is parameter

Most strongly bound defect states for Z=-0.25 lel (=acceptor defect):

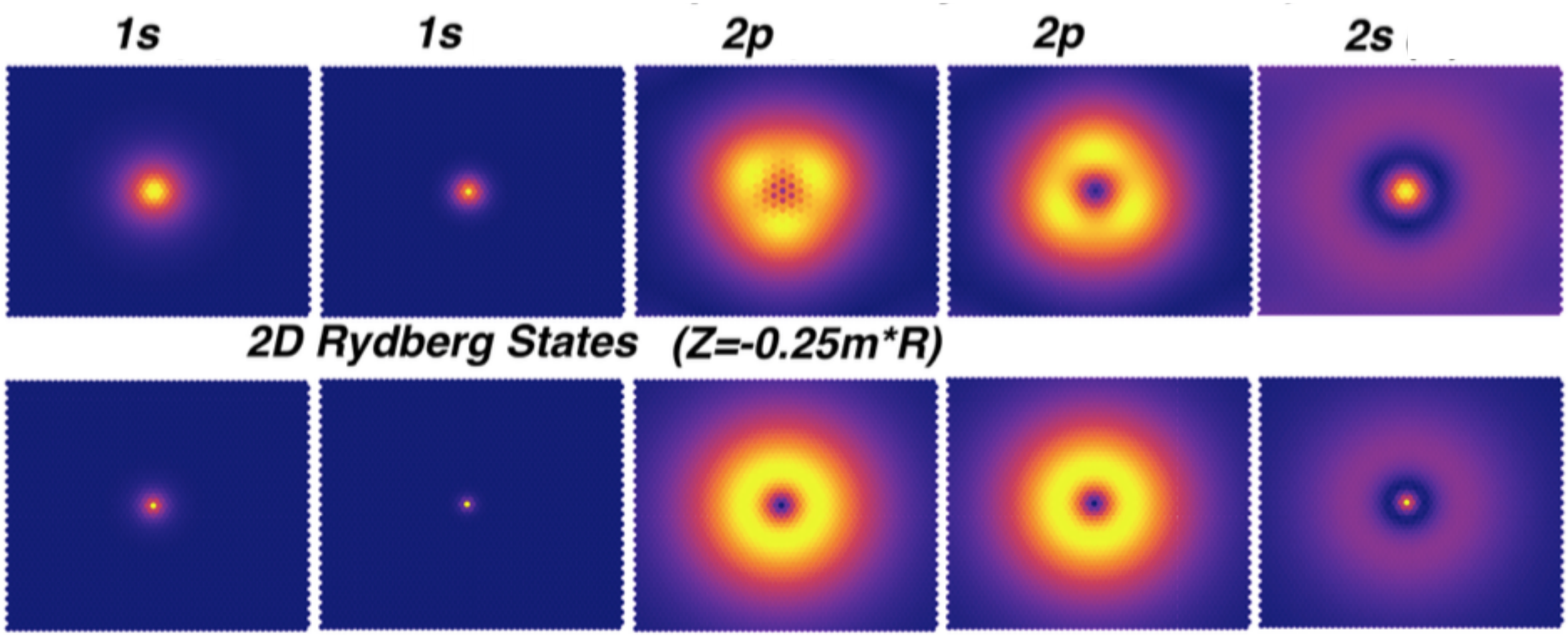


increasing binding energy

*Aghajanian, Mostofi, **JL**, Scientific Reports (2018)*

CHARGED DEFECTS IN 2D SEMICONDUCTORS

Comparison to 2d hydrogen model:

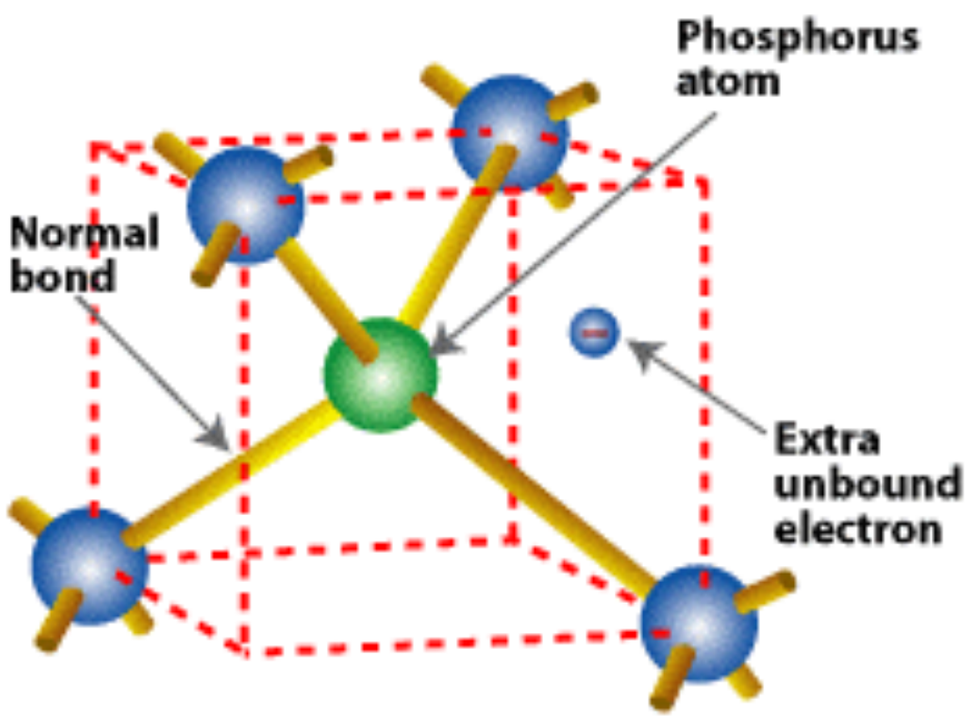


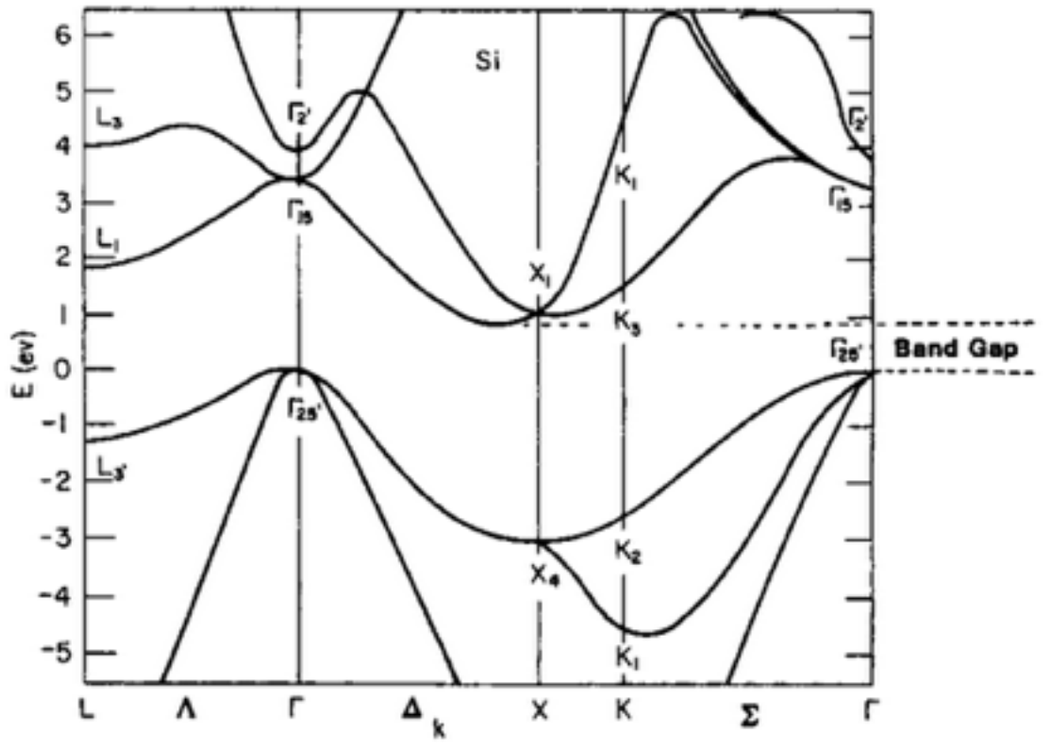
- impurity states similar to 2d hydrogen model
- But why multiple 1s states?

*Aghajanian, Mostofi, **JL**, Scientific Reports (2018)*

CHARGED DEFECTS IN 3D SEMICONDUCTORS

Phosphorus substitutional in silicon crystal:



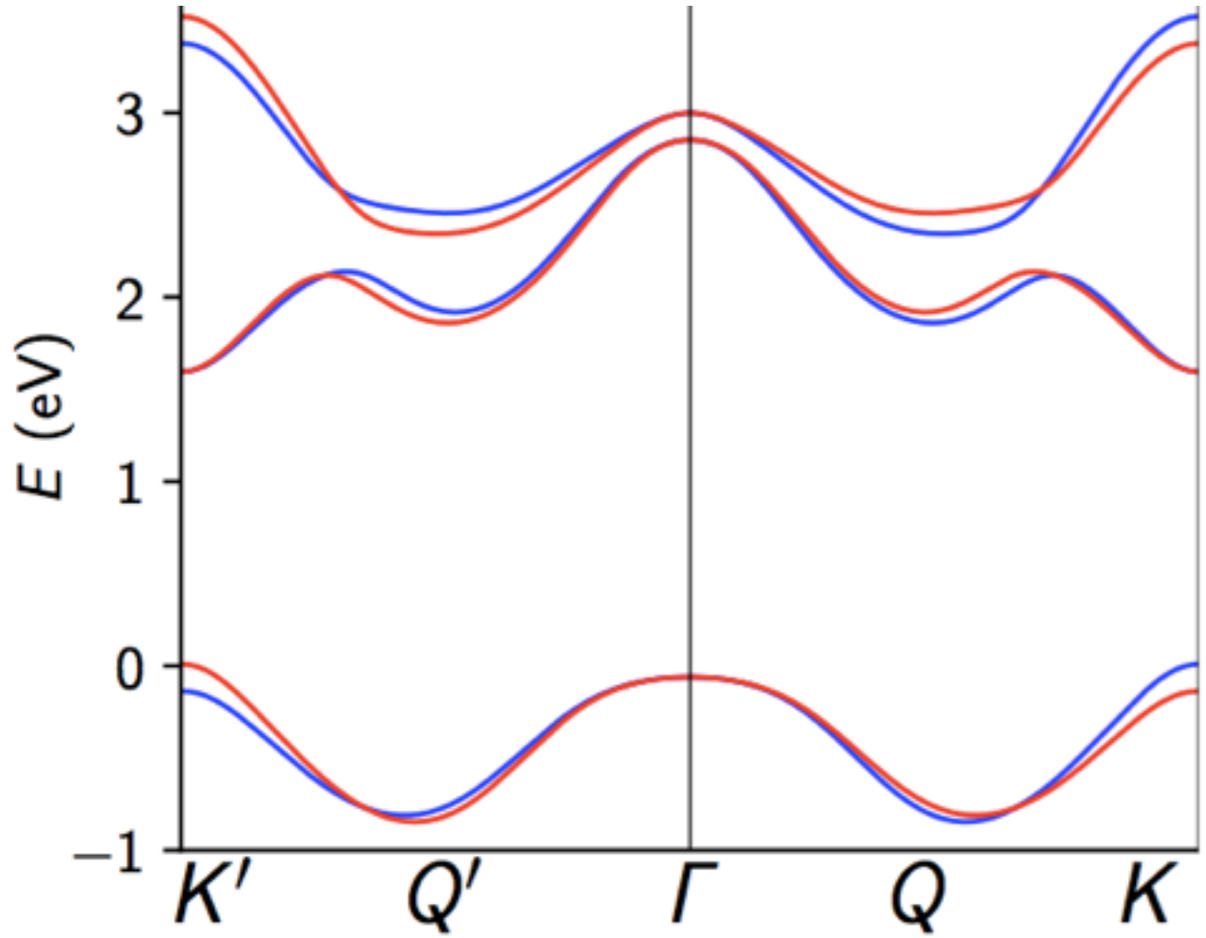


- phosphorus has one more valence electron than silicon
- extra electron forms 3D hydrogenic state with positive core
- But: replace electron mass by effective mass from band structure
- And: reduce attractive Coulomb interaction by dielectric constant

Binding energy: $$\varepsilon = \frac{m^*}{m}\frac{1}{\epsilon^2} \times 13.6\ \text{eV}.$$

CHARGED DEFECTS IN 2D SEMICONDUCTORS

Band structure of MoS_2:

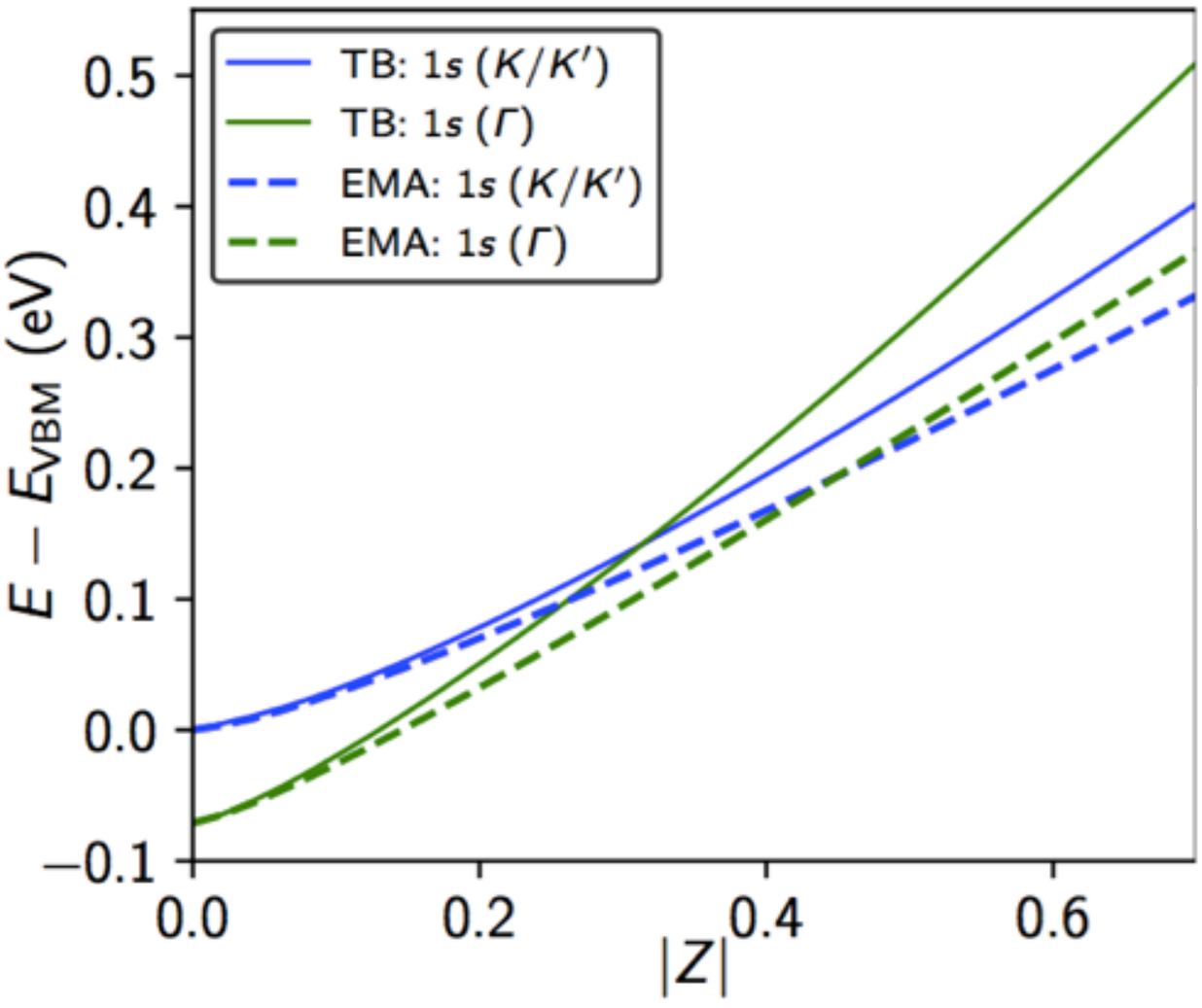


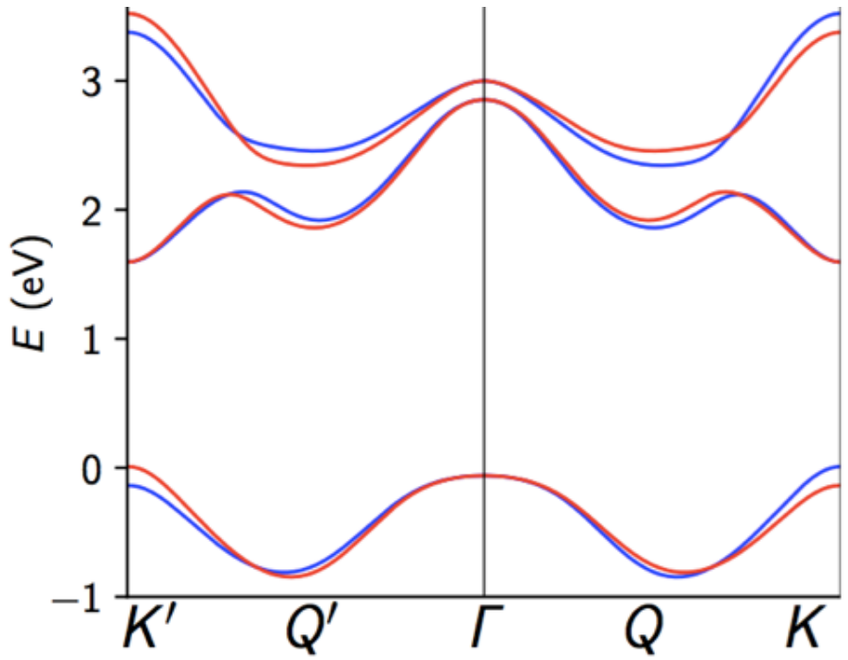
- valence band has multiple maxima: K, K', Gamma
- Each maximum acts as 2d hydrogen atom and contributes series of states

*Aghajanian, Mostofi, **JL**, Scientific Reports (2018)*

CHARGED DEFECTS IN 2D SEMICONDUCTORS

Binding energy as function of impurity charge Z:



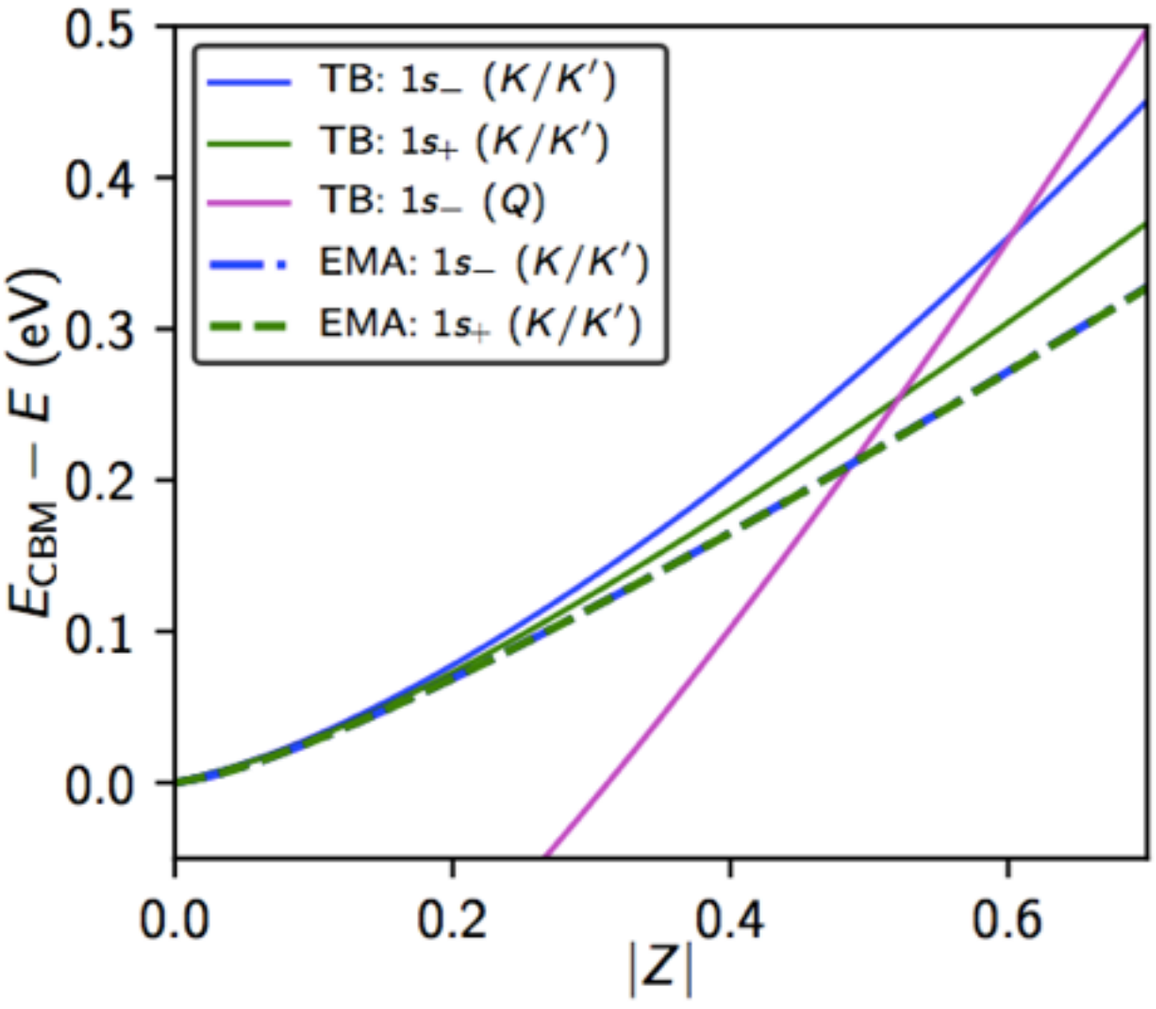


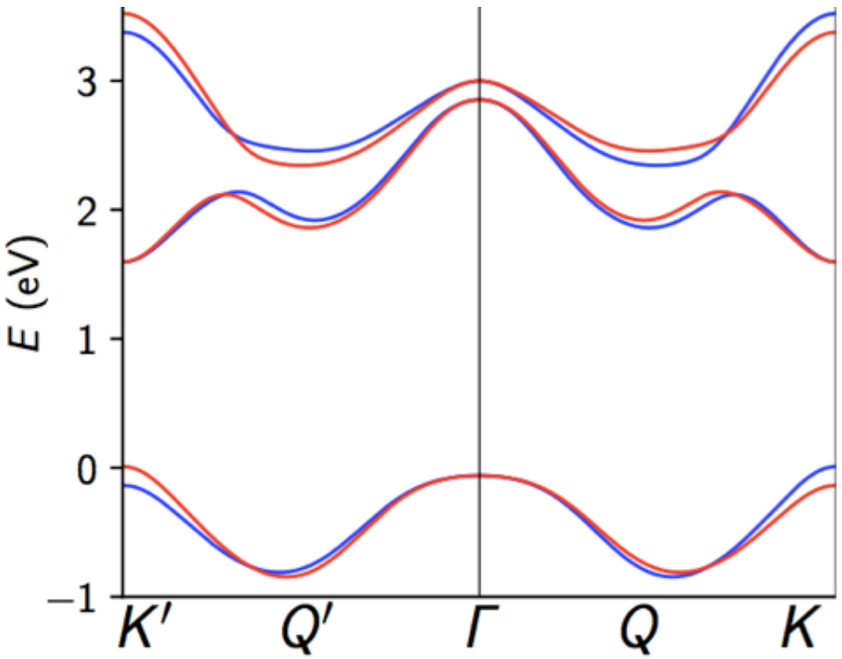
similar results with Keldysh model for screened potential (dashed lines)

- small |Z|: 1s state from K/K' (=VBM) more strongly bound
- larger |Z|: binding energy of 1s state at Gamma increases quickly due to large m*
- crossover at critical |Z| = 0.35

CHARGED DEFECTS IN 2D SEMICONDUCTORS

Donor atoms:

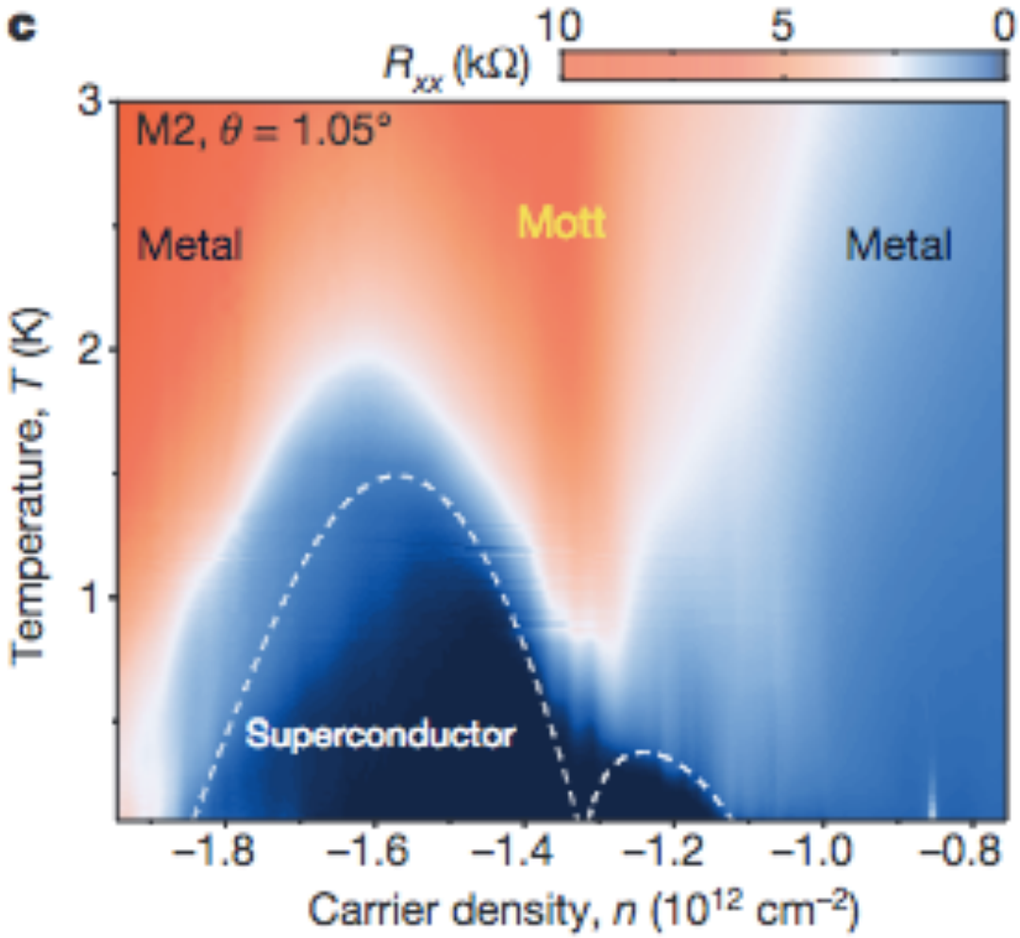


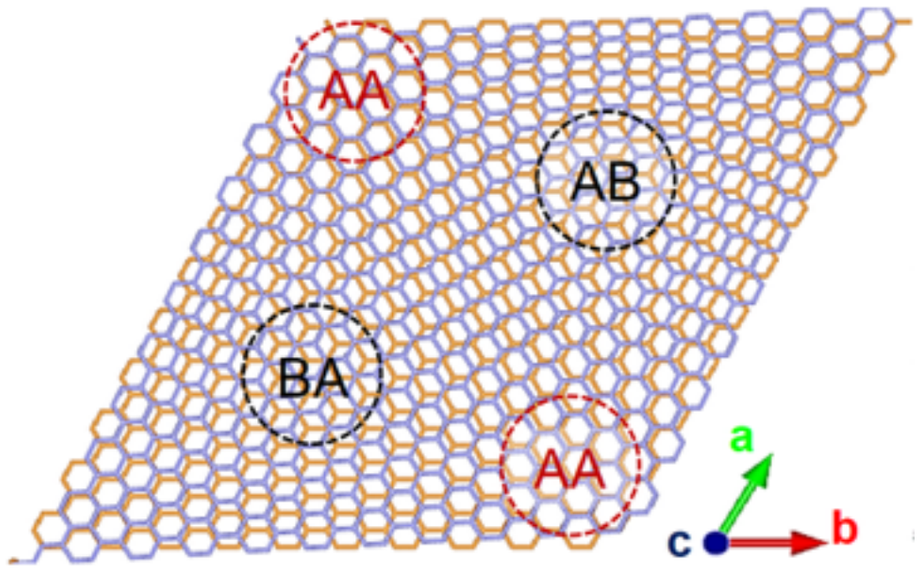


- weak spin-orbit coupling in conduction band
- 1s states from K and K' can hybridize: $\Psi_{\pm} = \frac{1}{\sqrt{2}}\left(\Psi_{1s,K} \pm \Psi_{1s,K'}\right)$
- splitting of hybridized states not captured by Keldysh model
- crossover from K/K' state to state from Q near |Z|=0.6

TWISTED BILAYER GRAPHENE

Strong electron correlations in two dimensions





Experimental observations (Cao et al.):

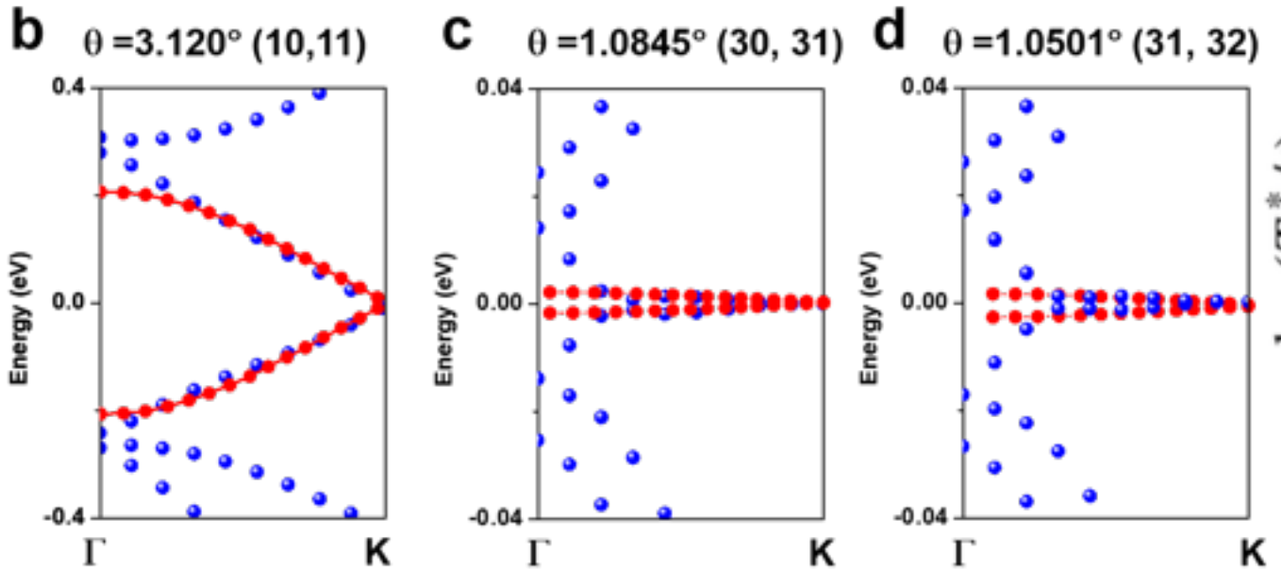
- at a magic twist angle of 1.1 degree, TBG becomes insulator at quarter filling
- at T=1.7 K, TBG becomes superconductor
- similar phase diagram to cuprates

TWISTED BILAYER GRAPHENE

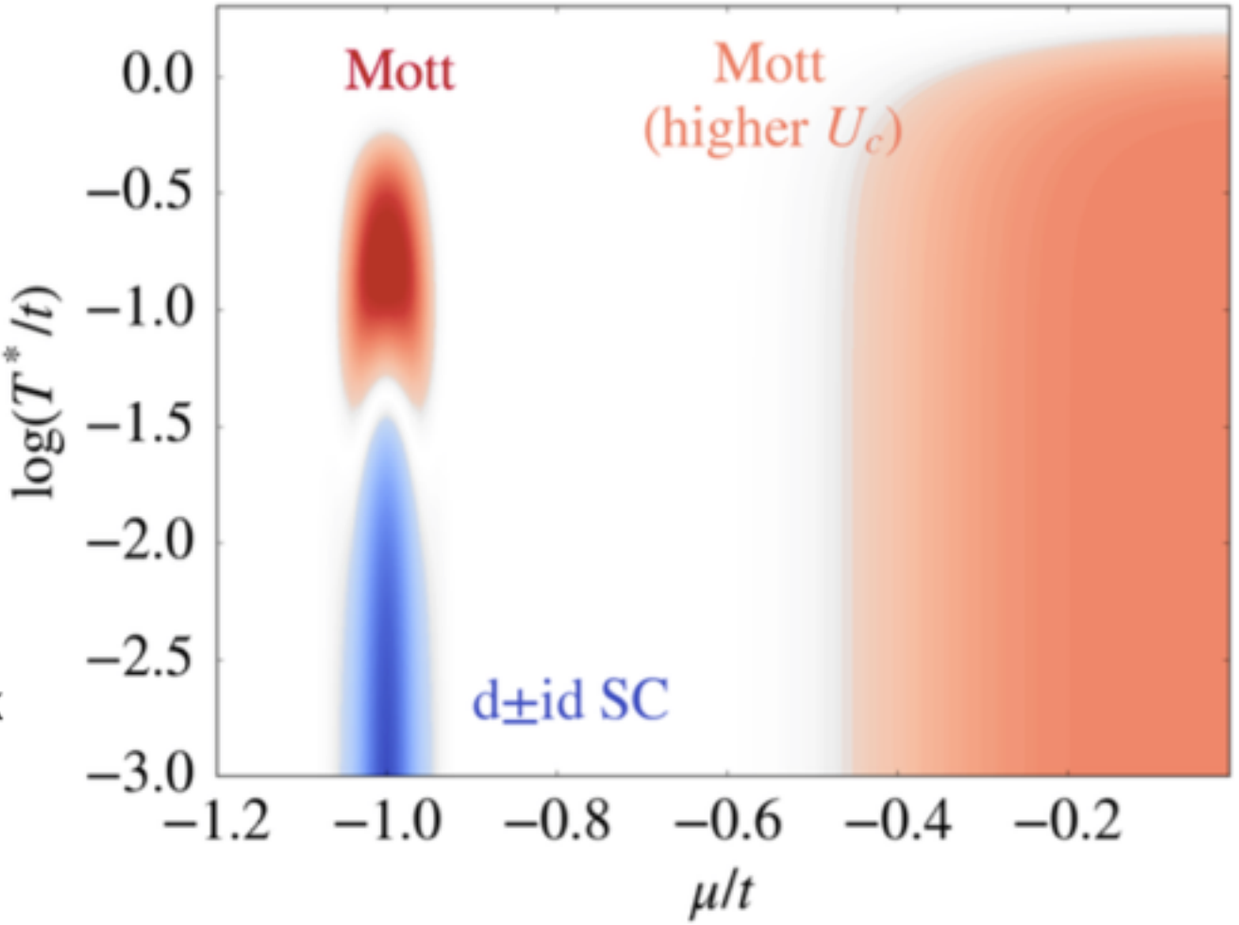
Theory: effective hopping model (Fu group, MIT) + renormalization group

$$H = -t \sum_{\langle i,j \rangle} \sum_{\substack{\sigma=\uparrow,\downarrow \\ p=x,y}} \left(c^{\dagger}_{i,\sigma,p} c_{j,\sigma,p} + \text{H.c.} \right) + U \sum_{i} n_i n_i,$$

flat bands near magic angle



phase diagram

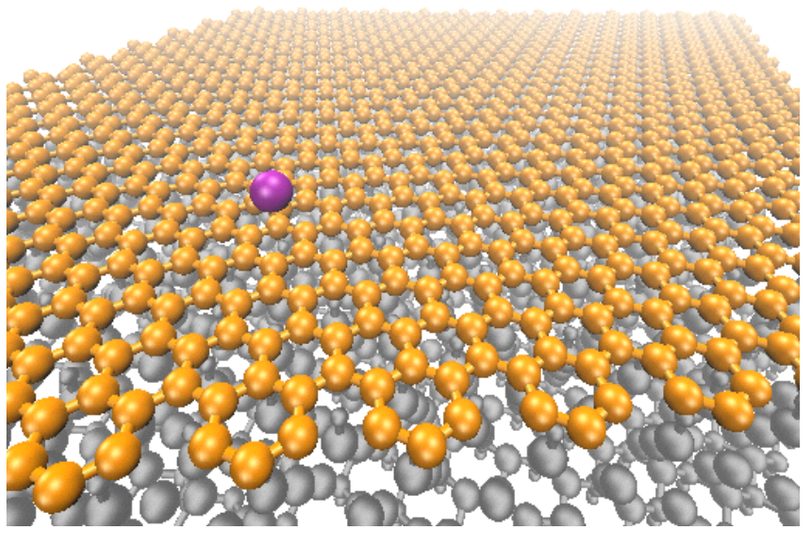


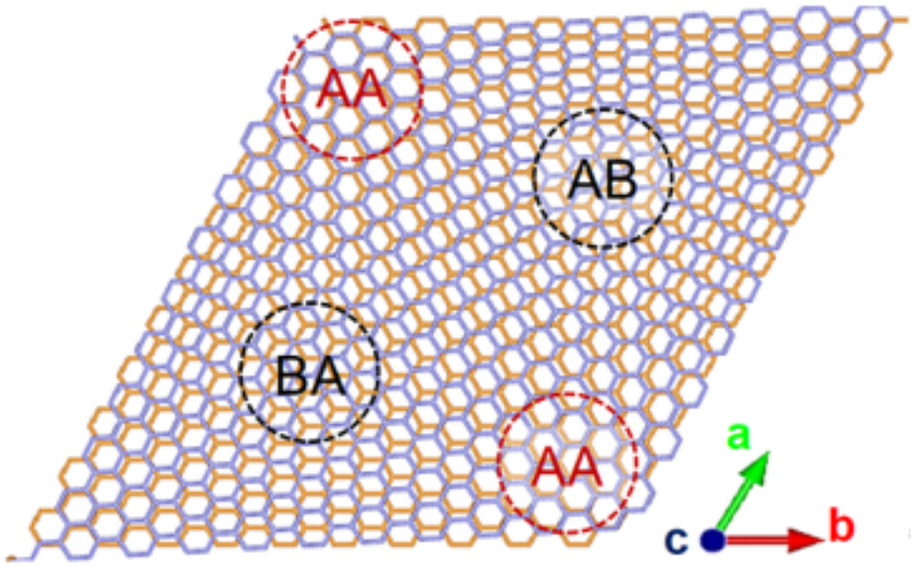
*Kennes, **JL**, Karrasch, arXiv: 1805.06310*

DEFECTS IN 2D MATERIALS

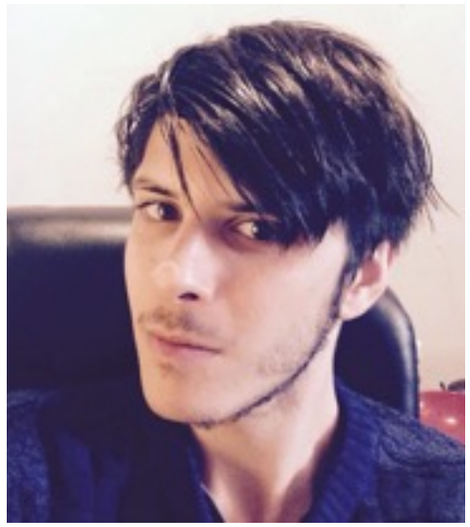
Summary:

- understanding of charged defects in 2d materials is required for new devices
- modelling defects is challenging due to multiscale behaviour
- combining ab initio DFT with simpler models allows accurate description





STUDENTS AND COLLABORATORS



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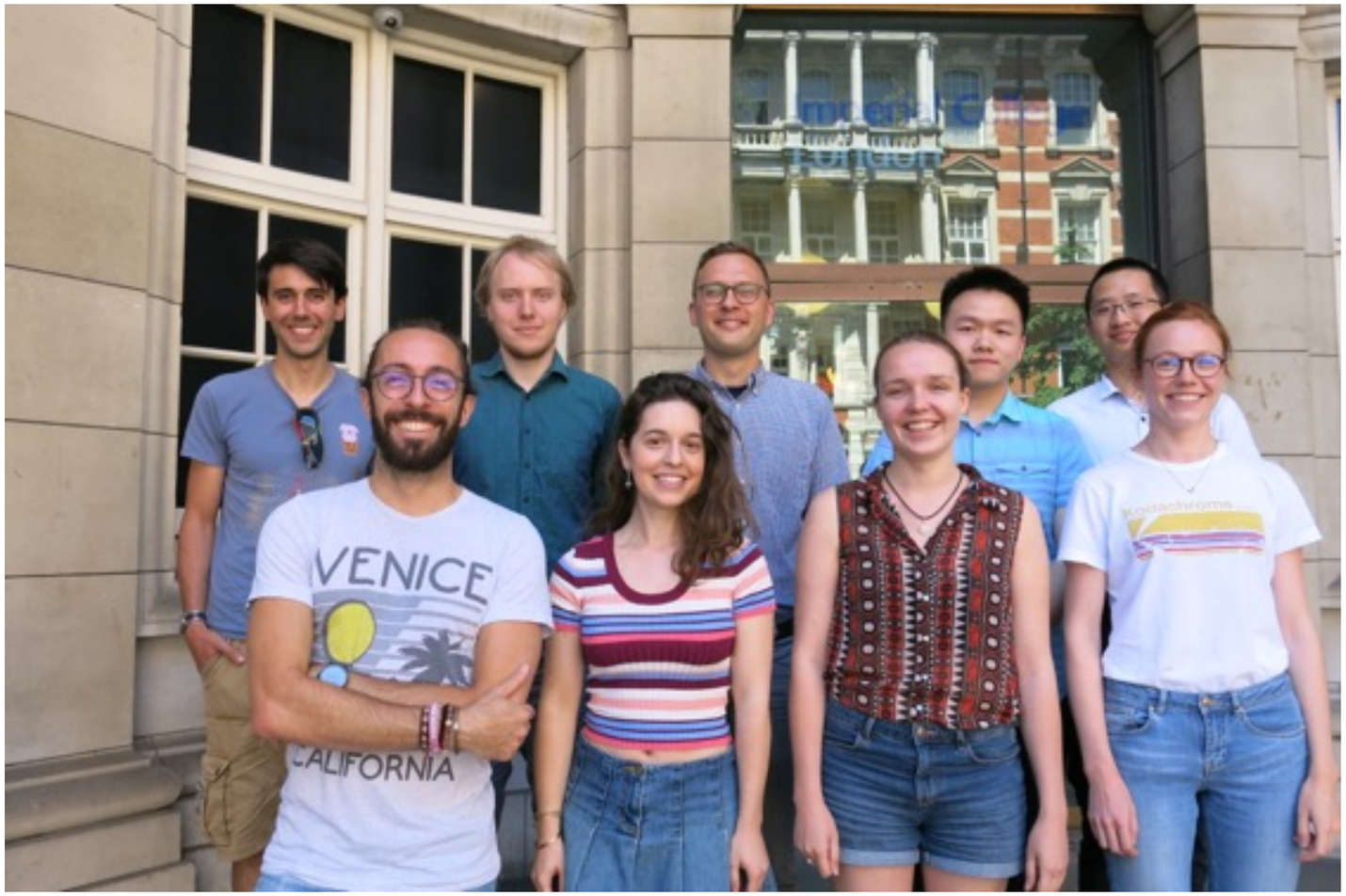
CHARGED DEFECTS IN 2D MATERIALS



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