Theoretical and experimental studies of the properties of nanostructured graphene

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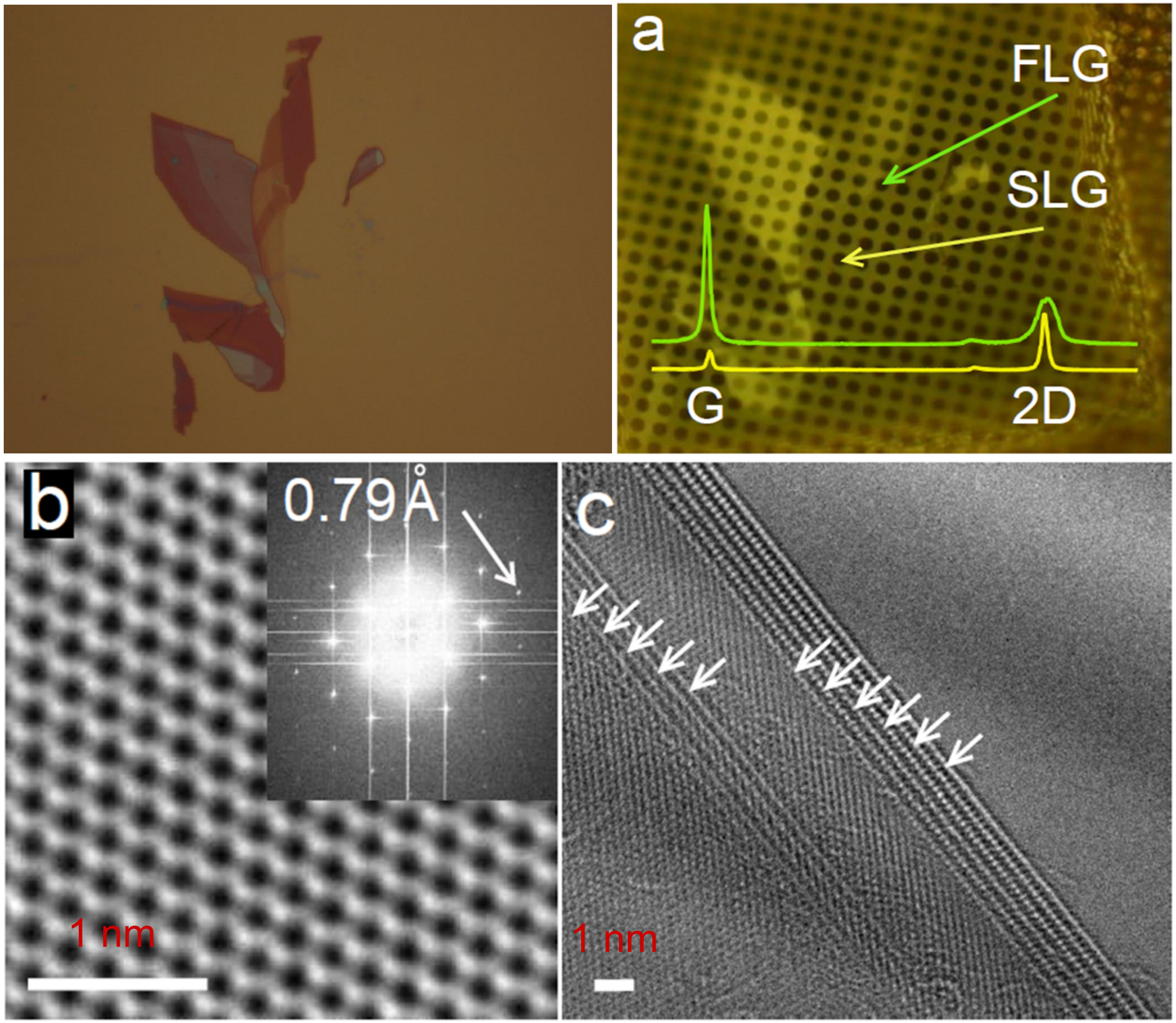
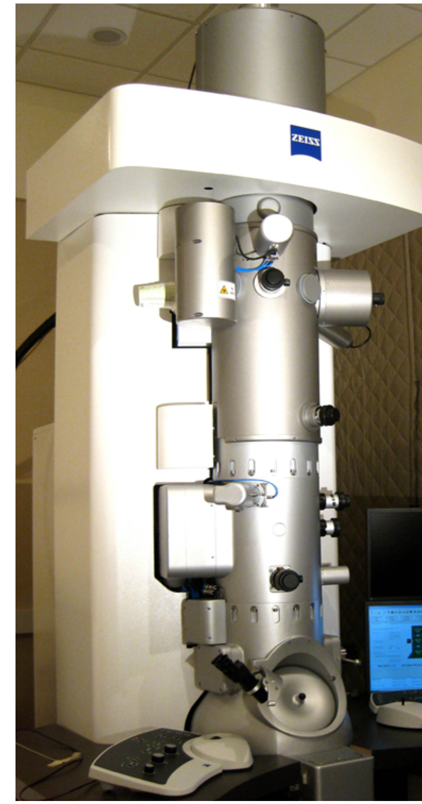
BACON Day 2013 – June 19, 2013
@ Boston University

- Graphene Nano Flakes (GFN’s) – magnetic properties (theory – WW, OY)
- Ripples in graphene (exp.+th. – WW)
- Functionalized graphene: mechanical, optical, magnetic, dielectric properties (theory – WW, ES)
- Single-atom chisel to sculpt graphene (exp.+th. – WW, ES)
- Graphene as substrate: organic PV’s (exp.+th. – WW, ES)
- Graphene in 2D layered devices (BN, MoS_2, …) (theory – ES)

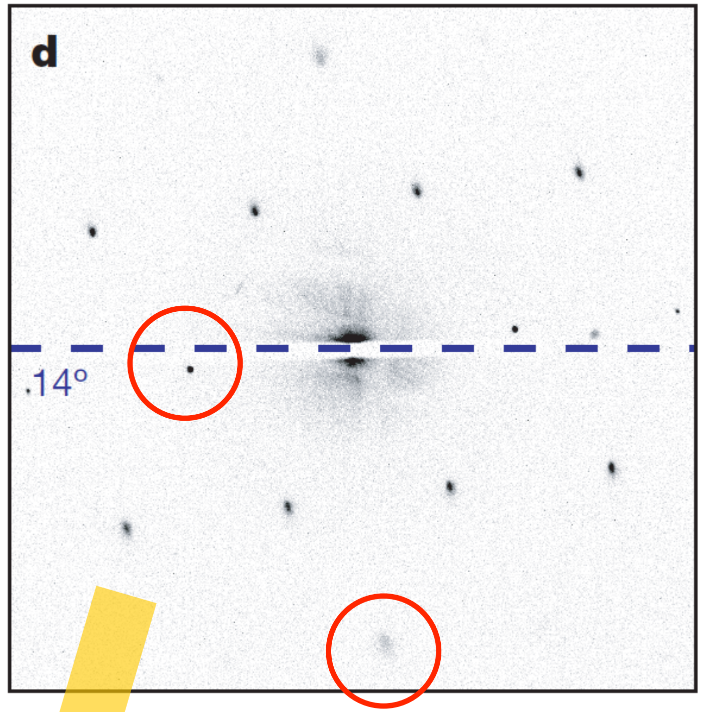
Real-space imaging of graphene (Wei Li Wang)

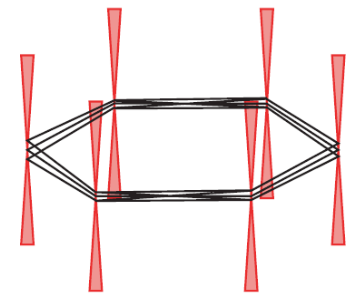


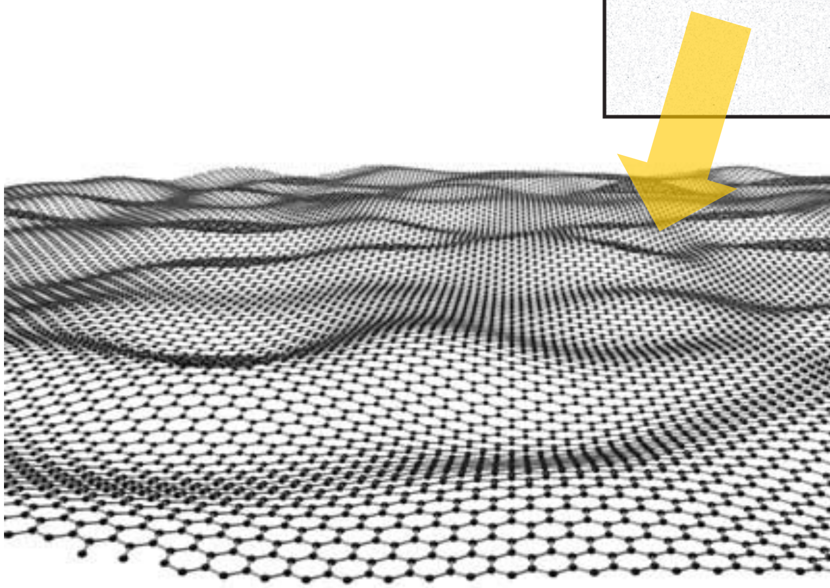


Libra MC 200-80
- Monochromated
- Aberration Corrected
- Operated at 80 kV

Intrinsic ripples in graphene

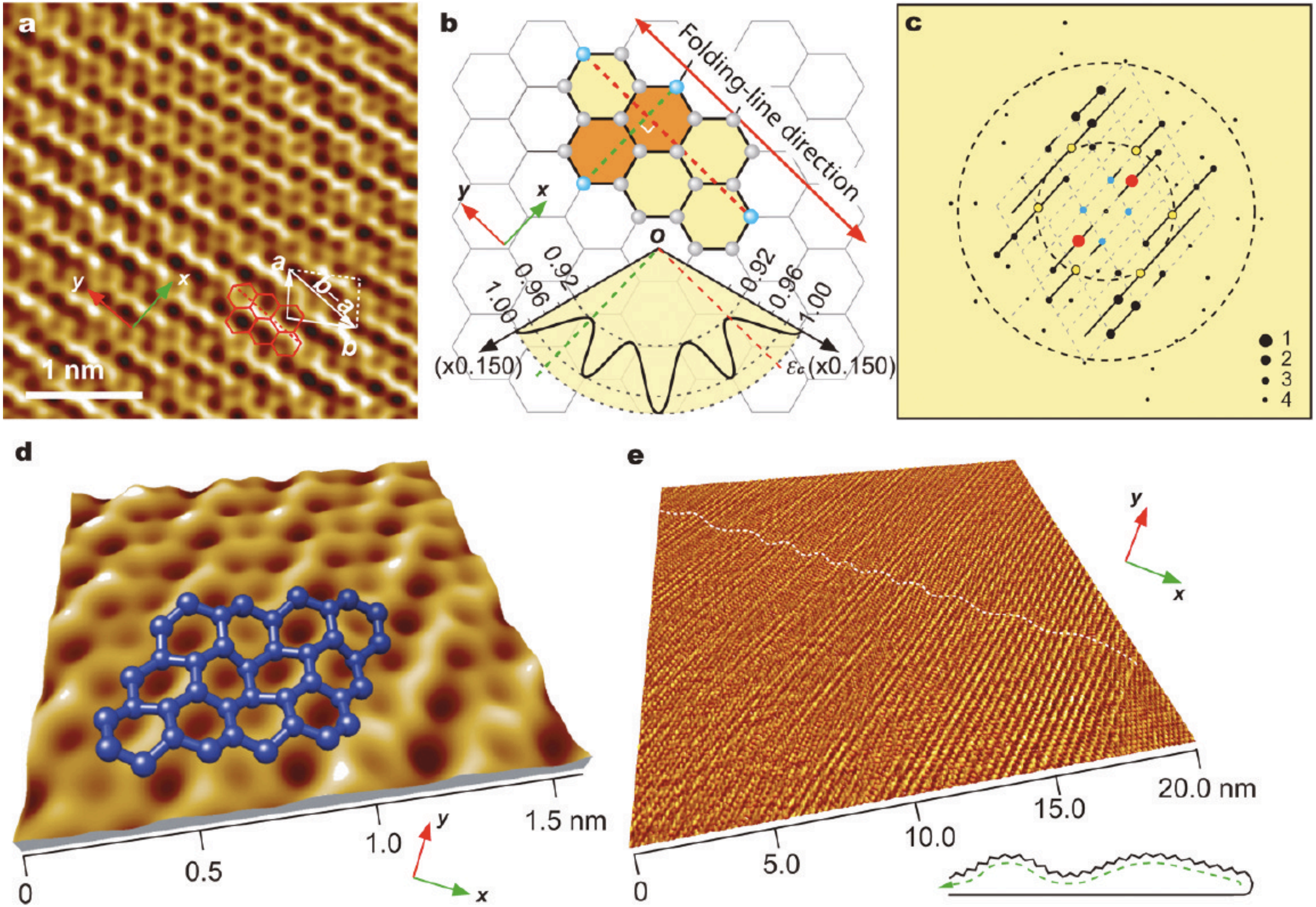






Experiment:
Meyer, J. C. et al. Nature **446**, 60-63, 2007.

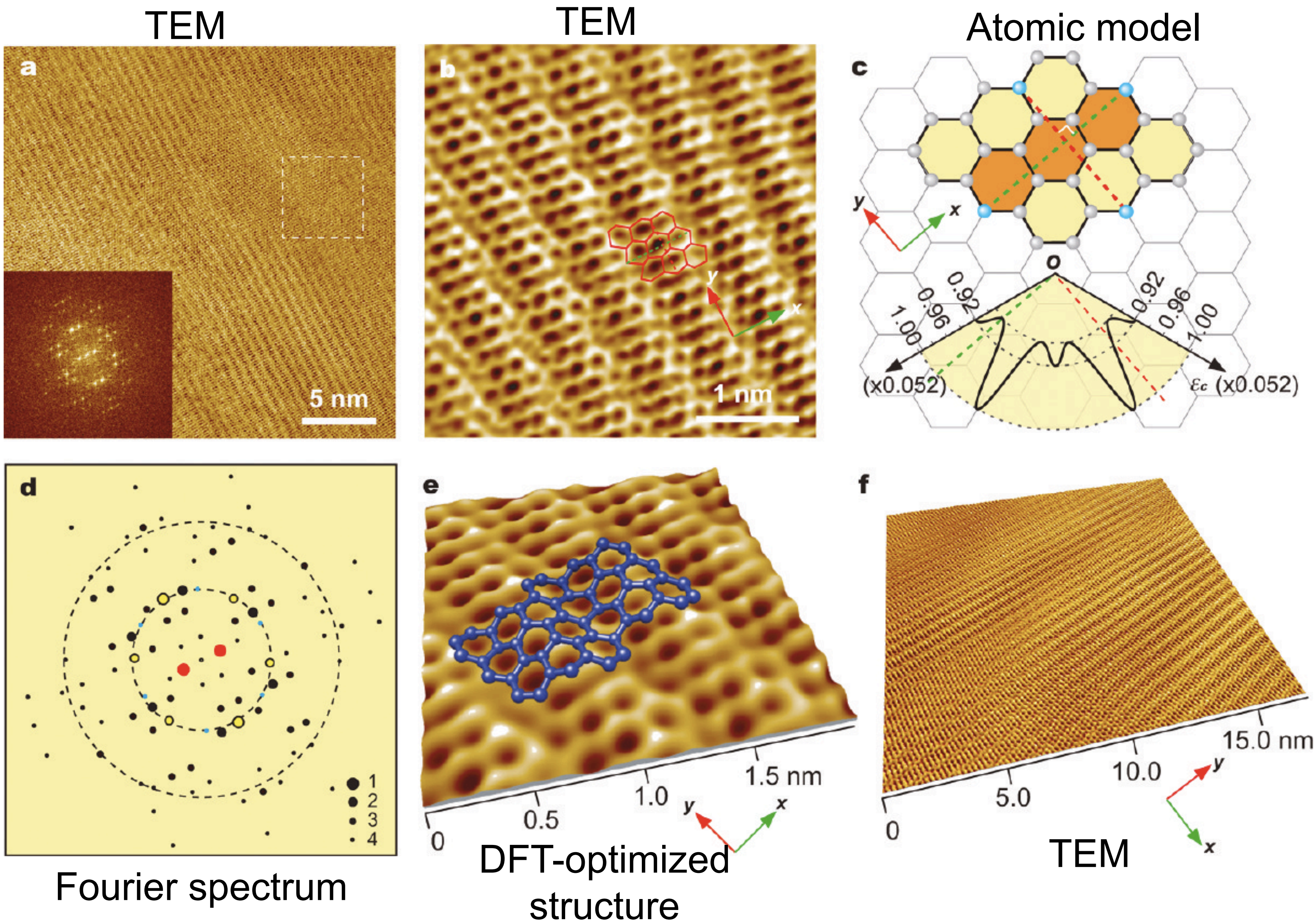
Theory:
Mermin, N. D. Phys. Rev. **176**, 250–254, 1968.
Nelson, D. R., Piran, T. & Weinberg, *World Scientific*, Singapore, 2004.



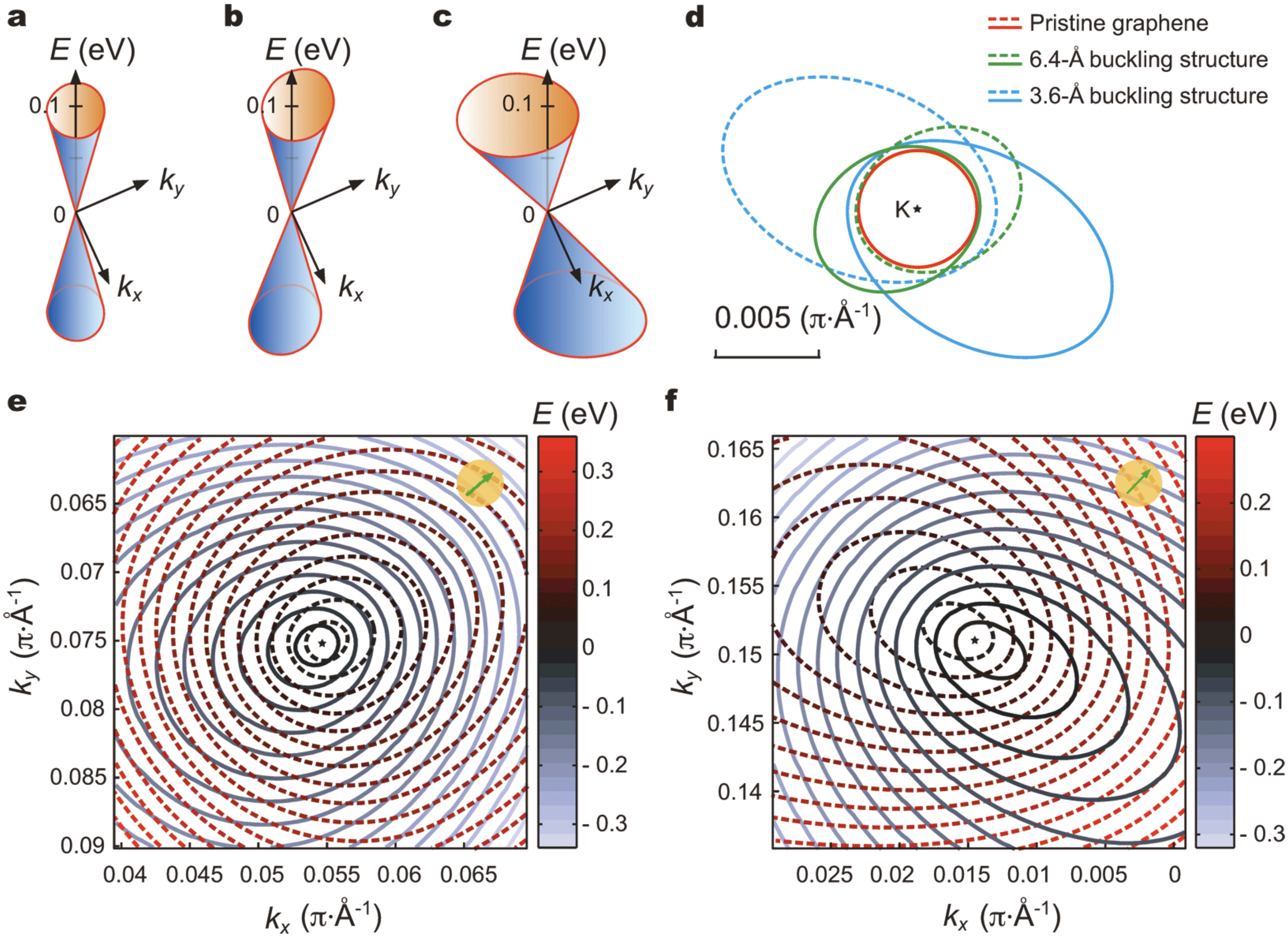
Graphene Structures at an Extreme Degree of Buckling

Youdong Mao, Wei L. Wang, Dongguang Wei, Efthimios Kaxiras, and Joseph G. Sodroski

ACS NANO, **5**, 1395–1400 (2011)

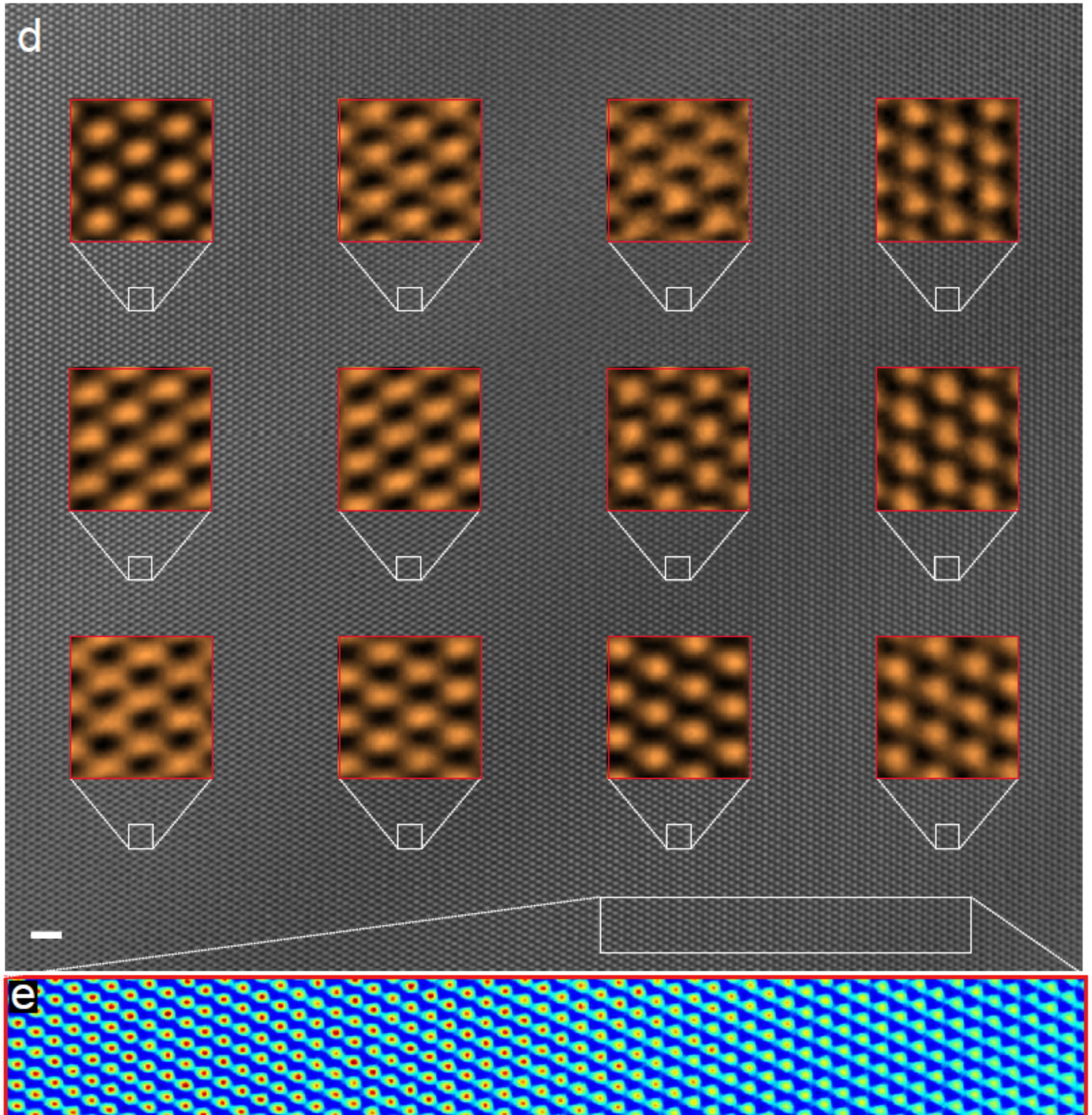


TEM
TEM
Atomic model
a
5 nm
b
1 nm
c
y
x
o
0.92
0.96
1.00
(x0.052)
εc (x0.052)
d
1
2
3
4
Fourier spectrum
e
0
0.5
1.0
1.5 nm
DFT-optimized structure
f
0
5.0
10.0
15.0 nm
TEM



a
b
c
d
E (eV)
0.1
0
k_y
k_x
Pristine graphene
6.4-Å buckling structure
3.6-Å buckling structure
K
0.005 (π·Å^{-1})
e
f
k_y (π·Å^{-1})
k_x (π·Å^{-1})
0.065
0.07
0.075
0.08
0.085
0.09
0.04
0.045
0.05
0.055
0.06
0.3
0.2
- 0.1
- 0.2
- 0.3
0.165
0.16
0.155
0.15
0.145
0.14
0.025
0.02
0.015
0.01
0.005

Imaging ripples in real space of CVD suspended graphene



Simulate scattering of incident electron beam by total electrostatic potential

Calculate total potential with a transferable core correction

DFT:

- Pseudopotential : wrong core
- All electron: too expensive
- Pseudopotential + core correction

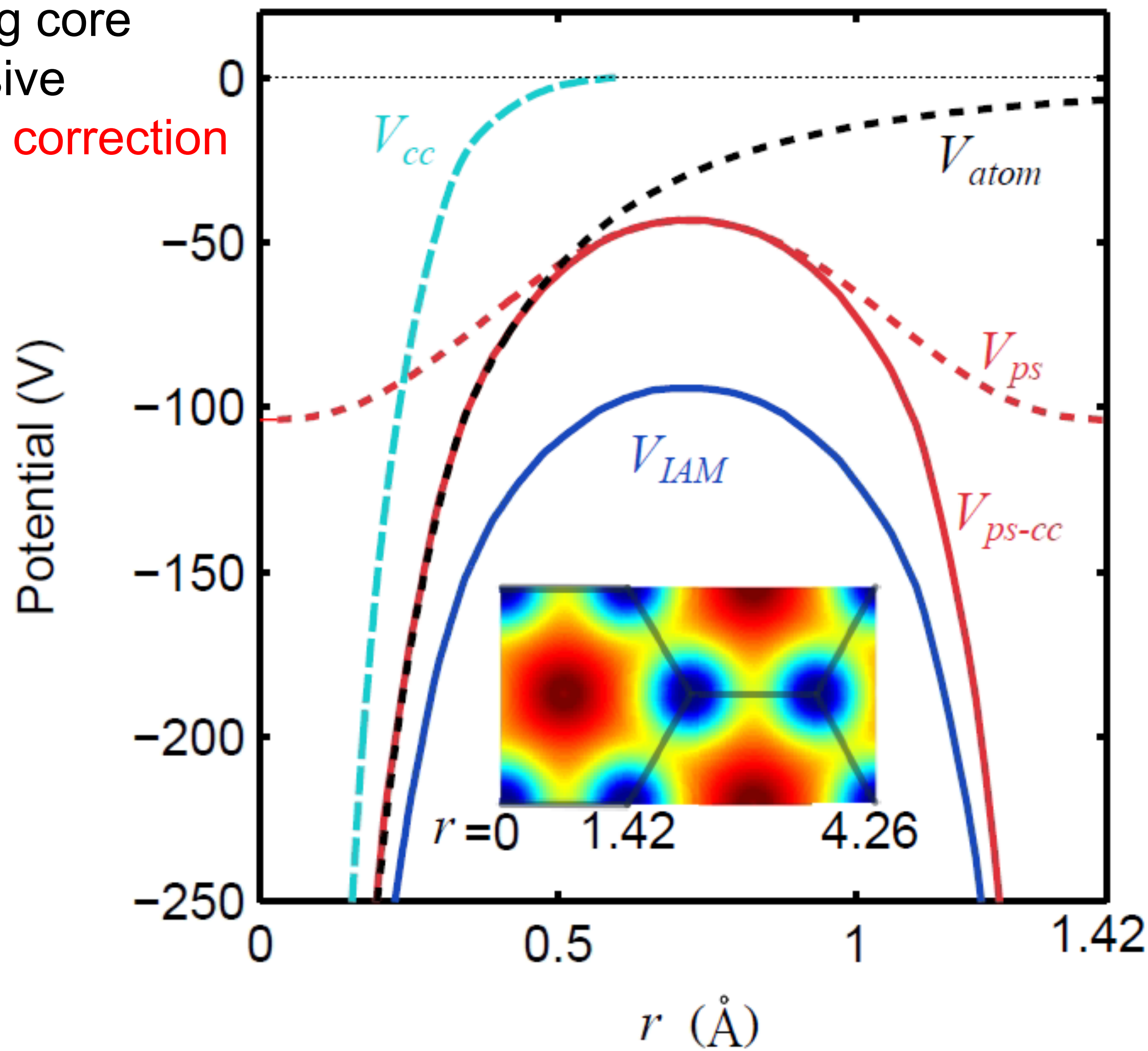
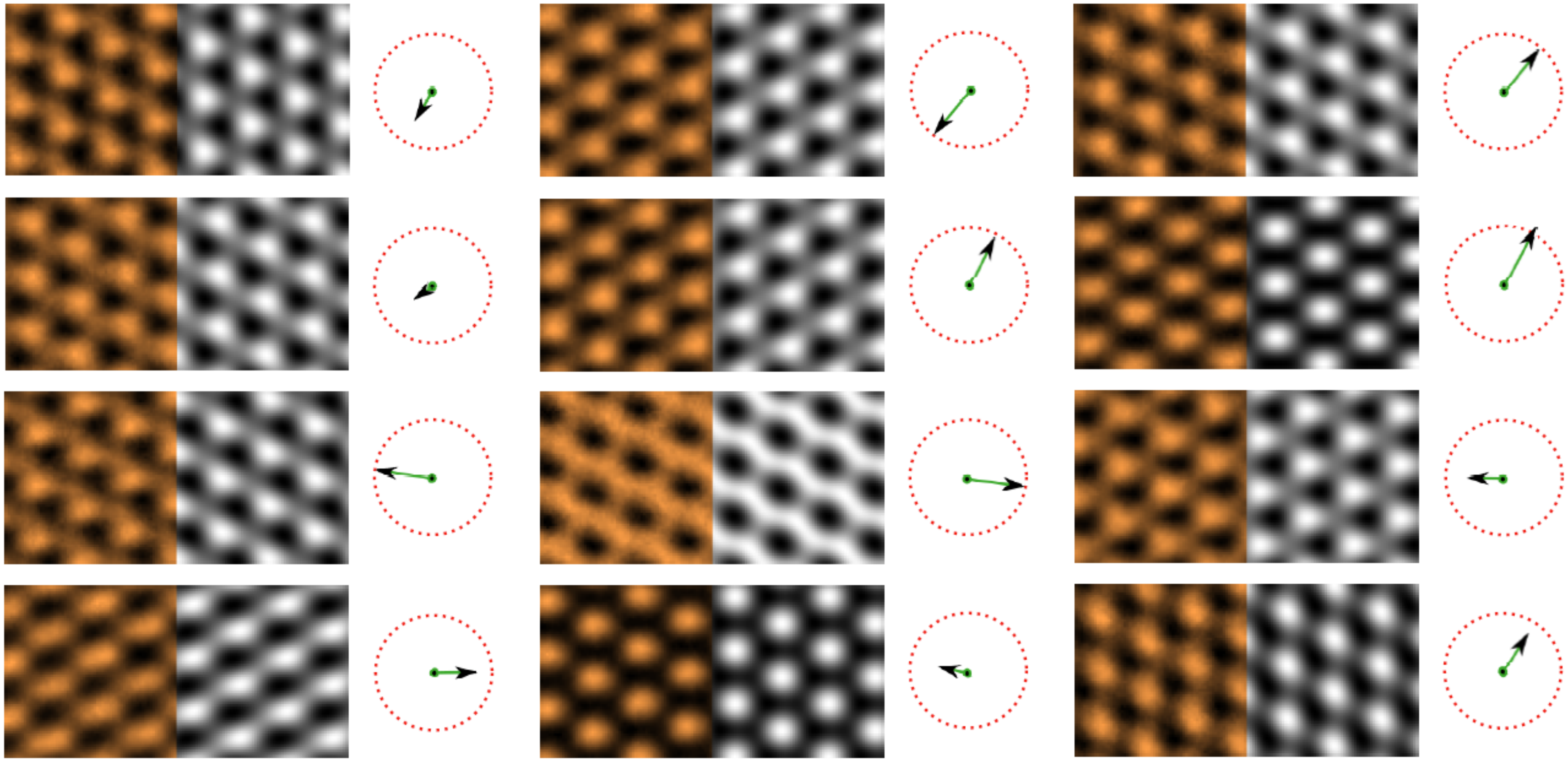
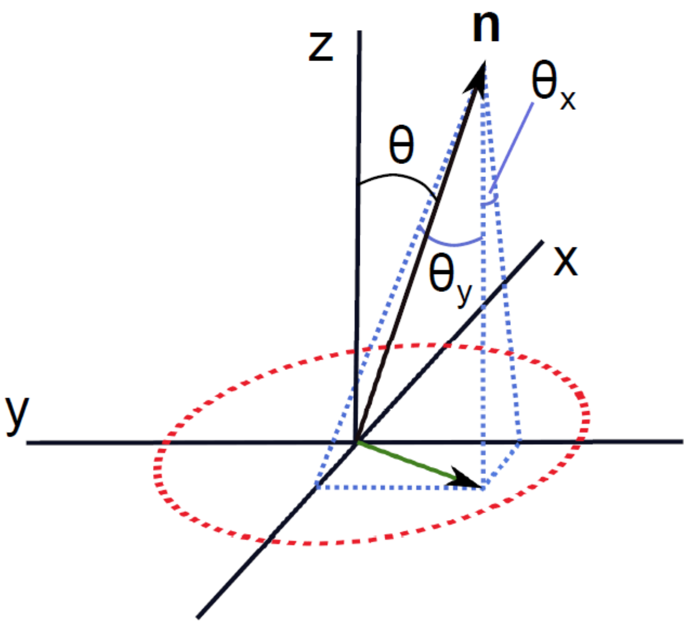
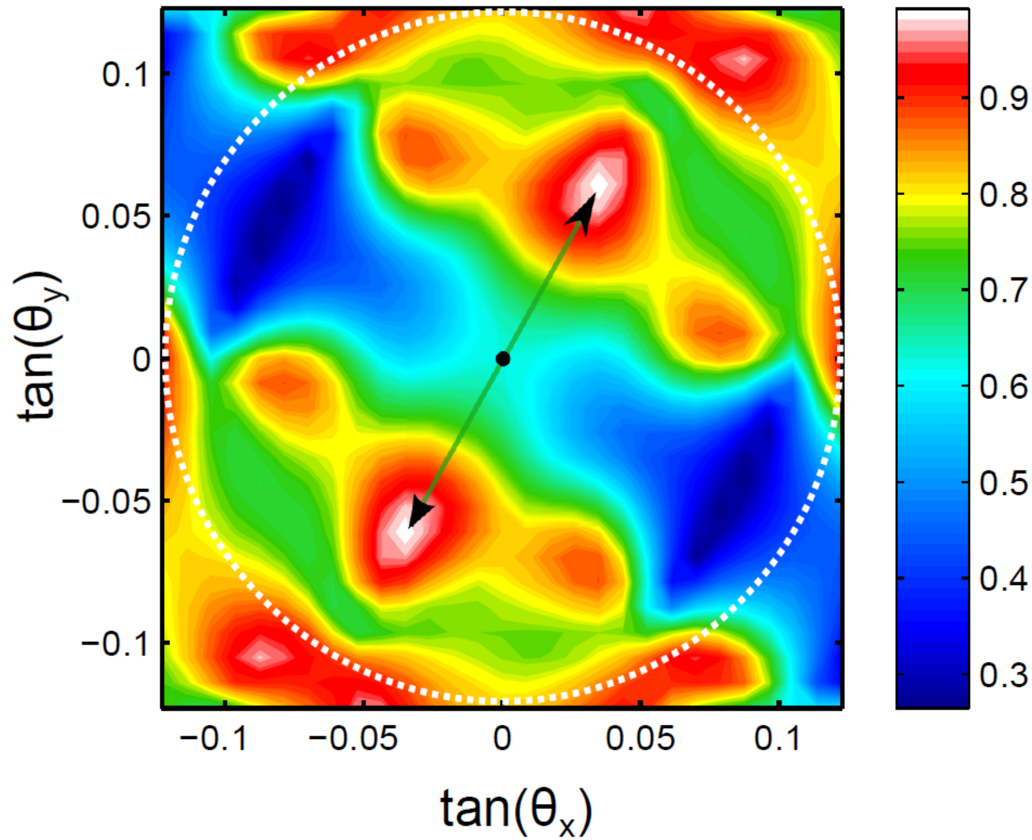


Image matching



Ambiguity: inversion symmetry



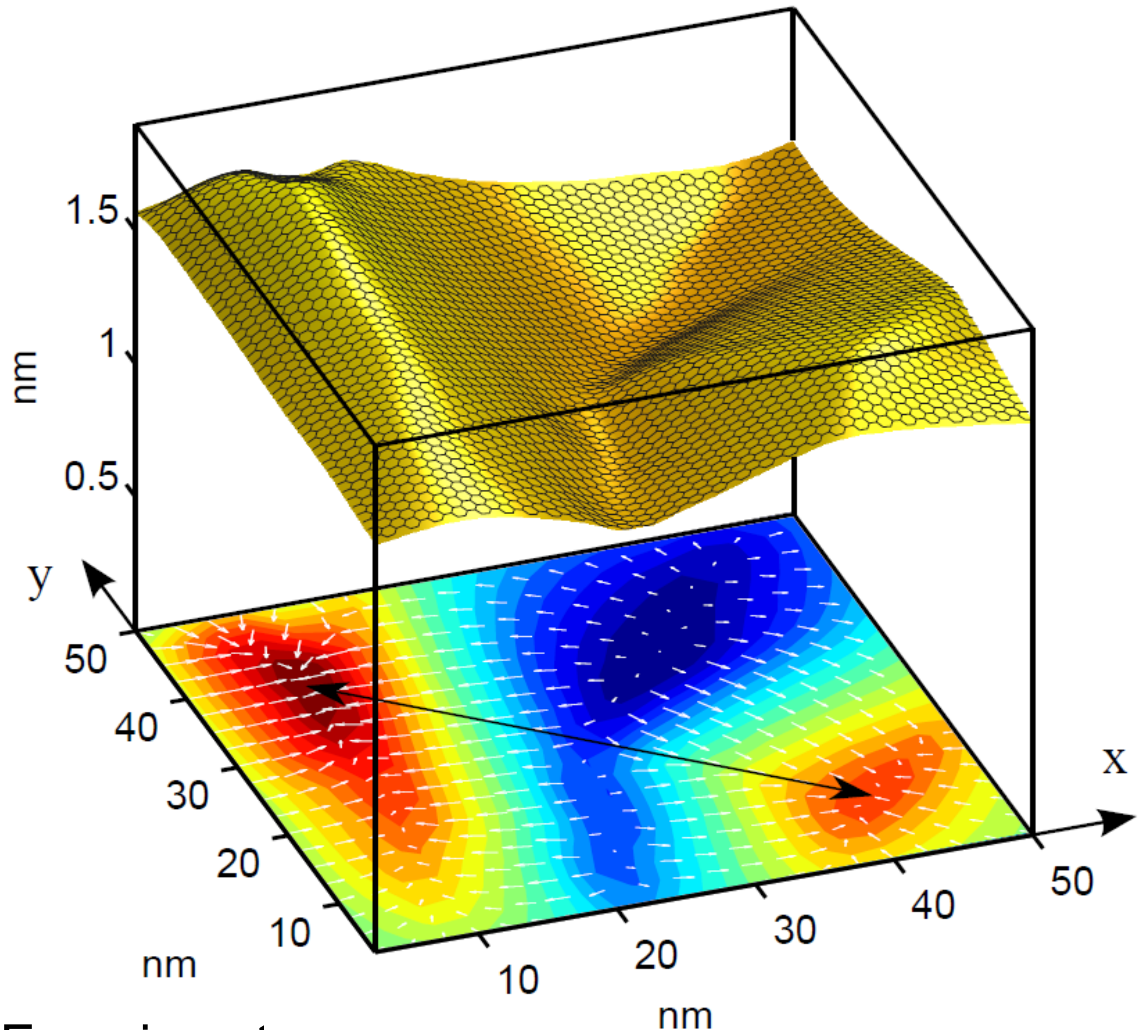


Matching based on a normalized cross-correlation functional:

$$C(f_{exp}, f_{sim}) = \frac{\sum_{xy}(f_{exp}(x,y) - \overline{f}_{exp})(f_{sim}(x,y) - \overline{f}_{sim})}{\sqrt{\sum_{xy}(f_{exp}(x,y) - \overline{f}_{exp})^2 \sum_{xy}(f_{sim}(x,y) - \overline{f}_{sim})^2}}$$

Kirkland, E. J. *Advanced computing in electron microscopy* (Springer, 2010).

Topography Reconstruction



Amplitude: 0.5 nm
Std. dev.: 0.13 nm
Typical width: 45 nm

NanoLetters (2012)

Experiment:

- Wei Li Wang, D. Bell, Wei Yi, S. Bhandari, R. Westervelt

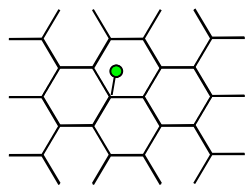
Theory:

- Wei Li Wang, E. G.J. Santos, E.Kaxiras

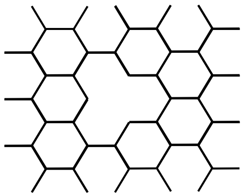
Origin of magnetism in graphene

- Defects

Chemisorptions of H
π orbitals

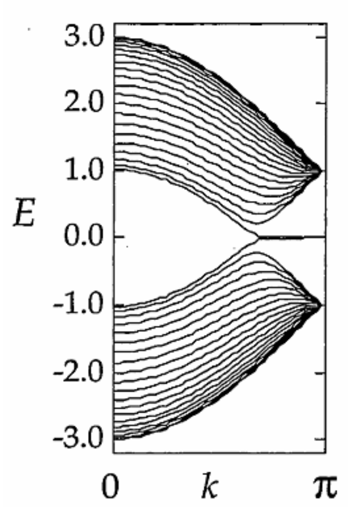


Vacancy
both π and sp^2 orbitals (reactive)

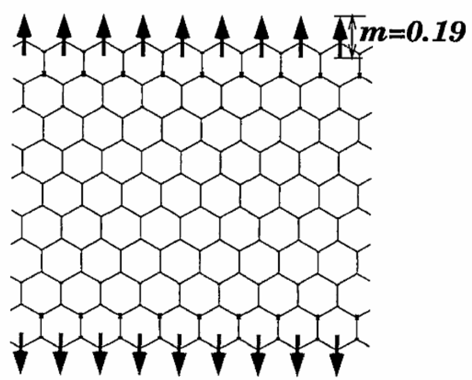


- Edge states – graphene nanoribbon

Flat band at the Fermi level

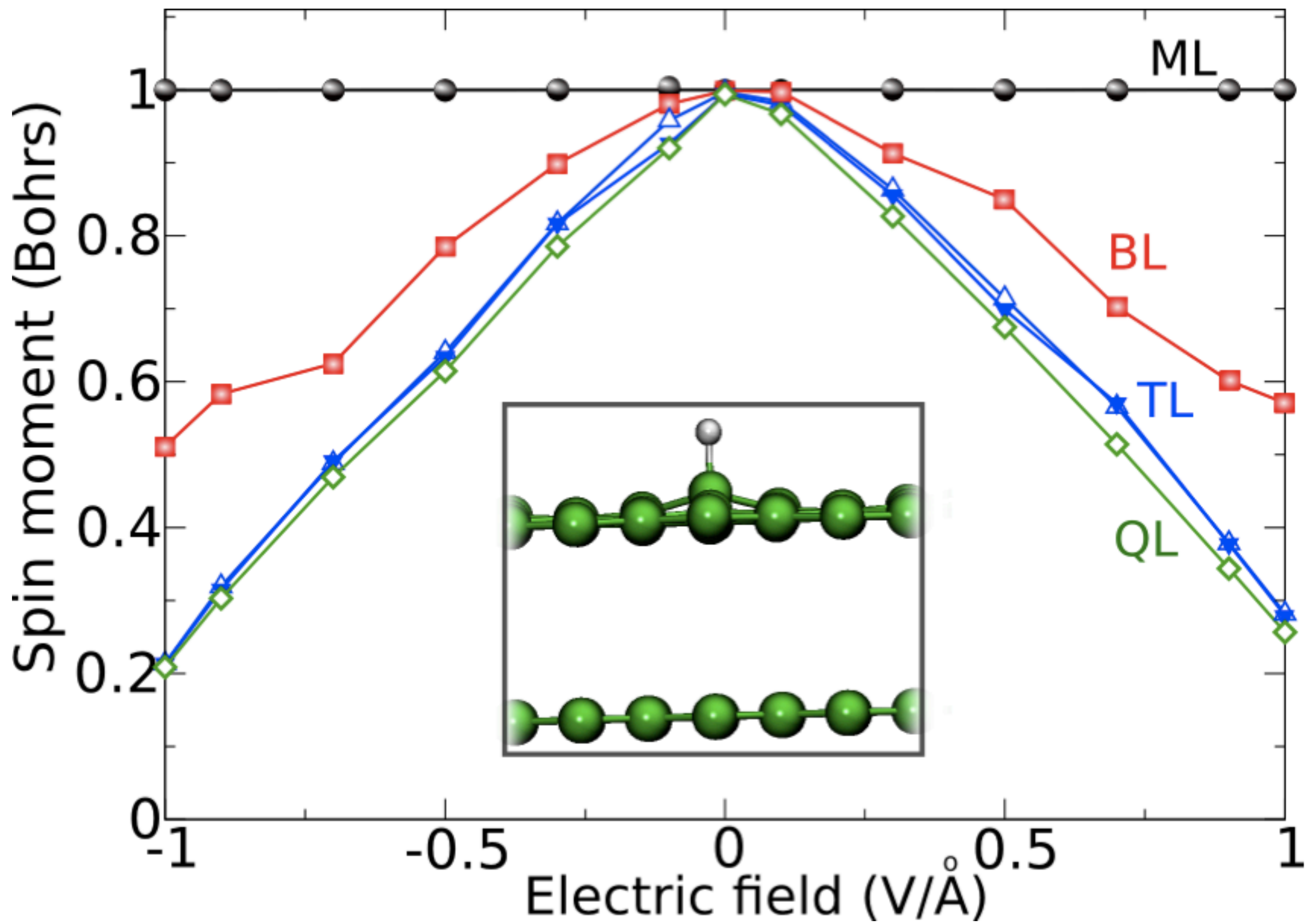


Antiferro-magnetic coupling at zigzag edges



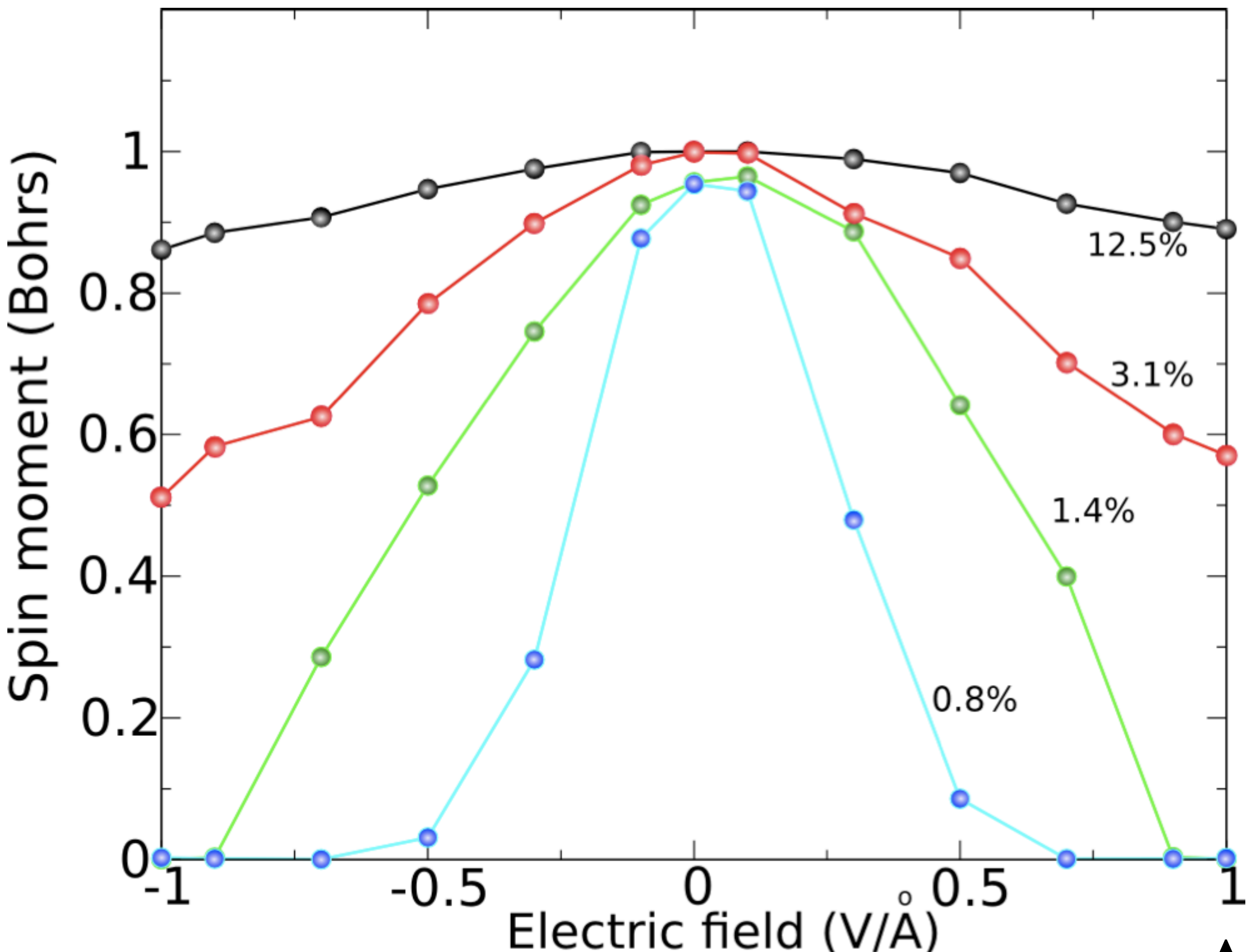
M. Fujita, et al., *J. Phys. Soc. Jpn*. (1996).

Magneto-electric effect in covalently functionalized few-layer graphene



concentration: ~3%

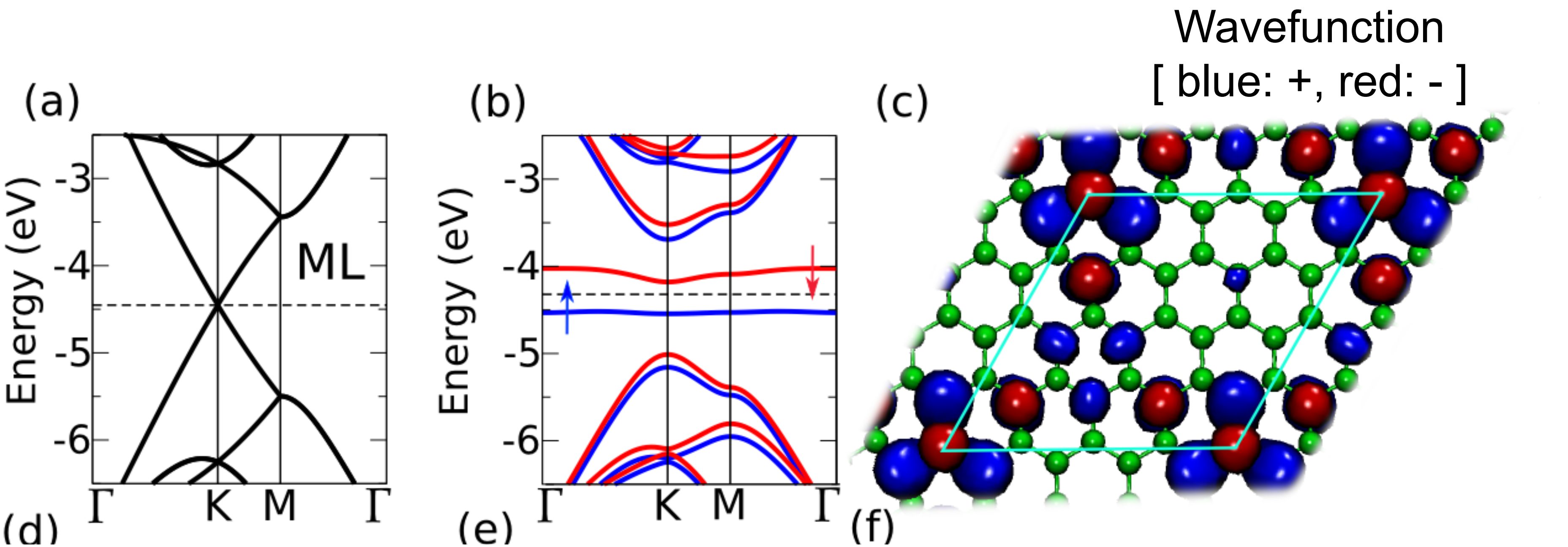
Impurity concentration plays a significant role



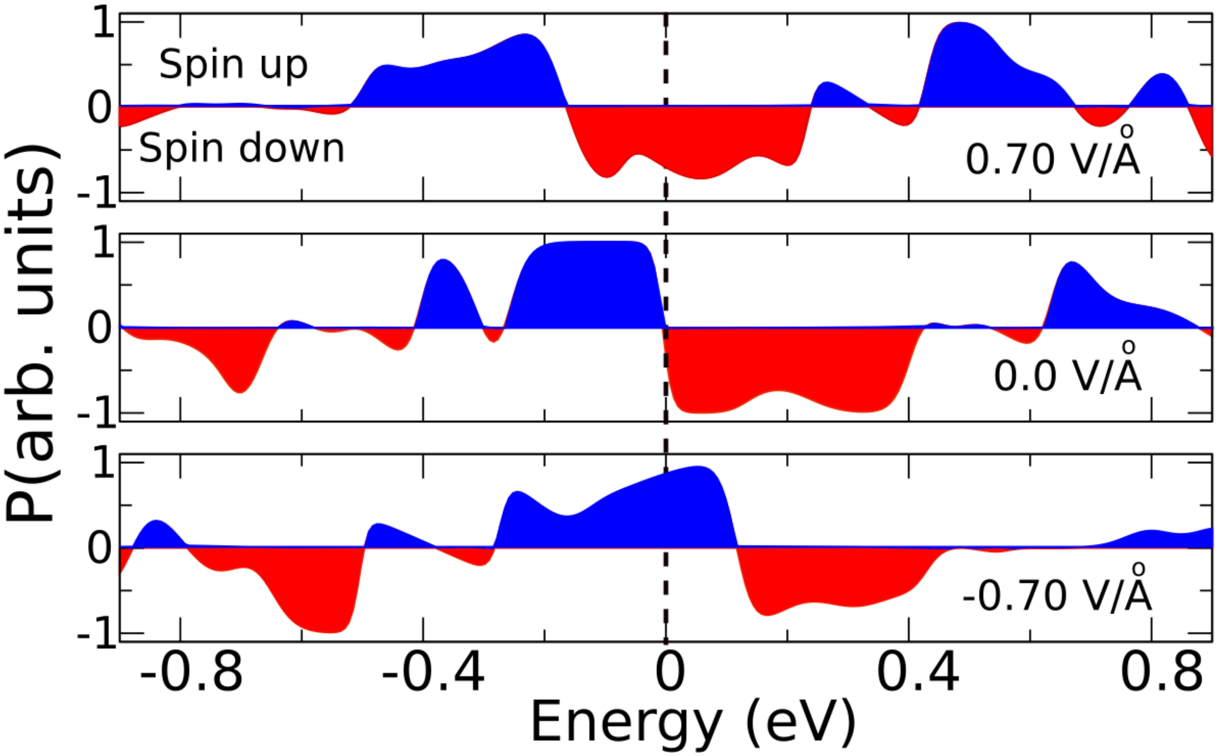
Magnetoelectric coefficient: $\alpha = \mu_0 \dfrac{\Delta S}{\Delta E}$

Same order of magnitude as in ferromagnetic films: Fe (001), Ni(001) and Co(001)

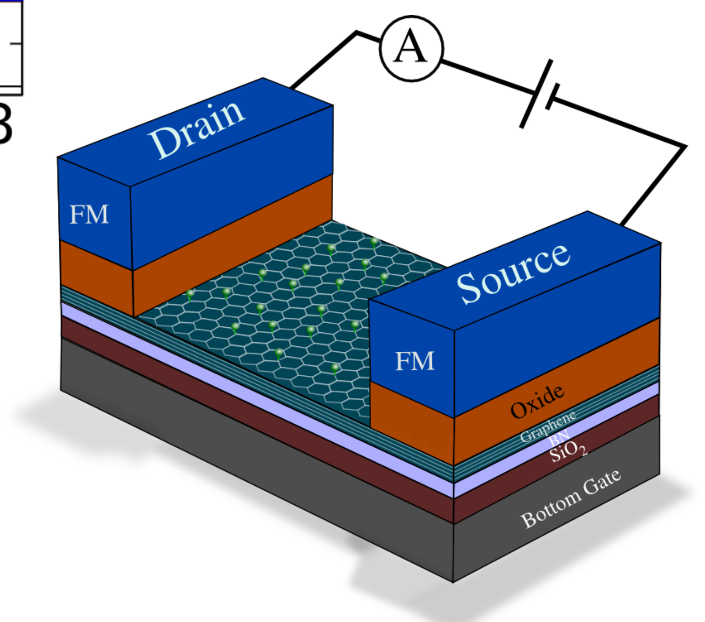
Interplay of defect-level and electric field on the electronic structure



Spin-polarized states in functionalized graphene bilayer



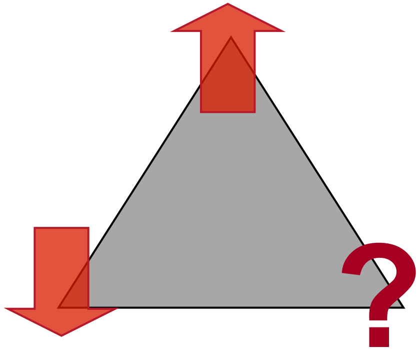
$$P = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}}$$

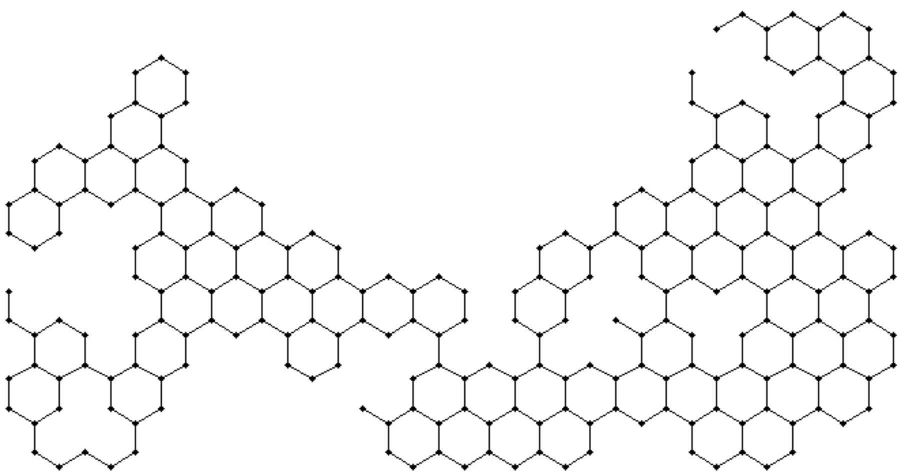


Selection of the spin-channel
with an electric bias

Magnetic behavior from topological frustration

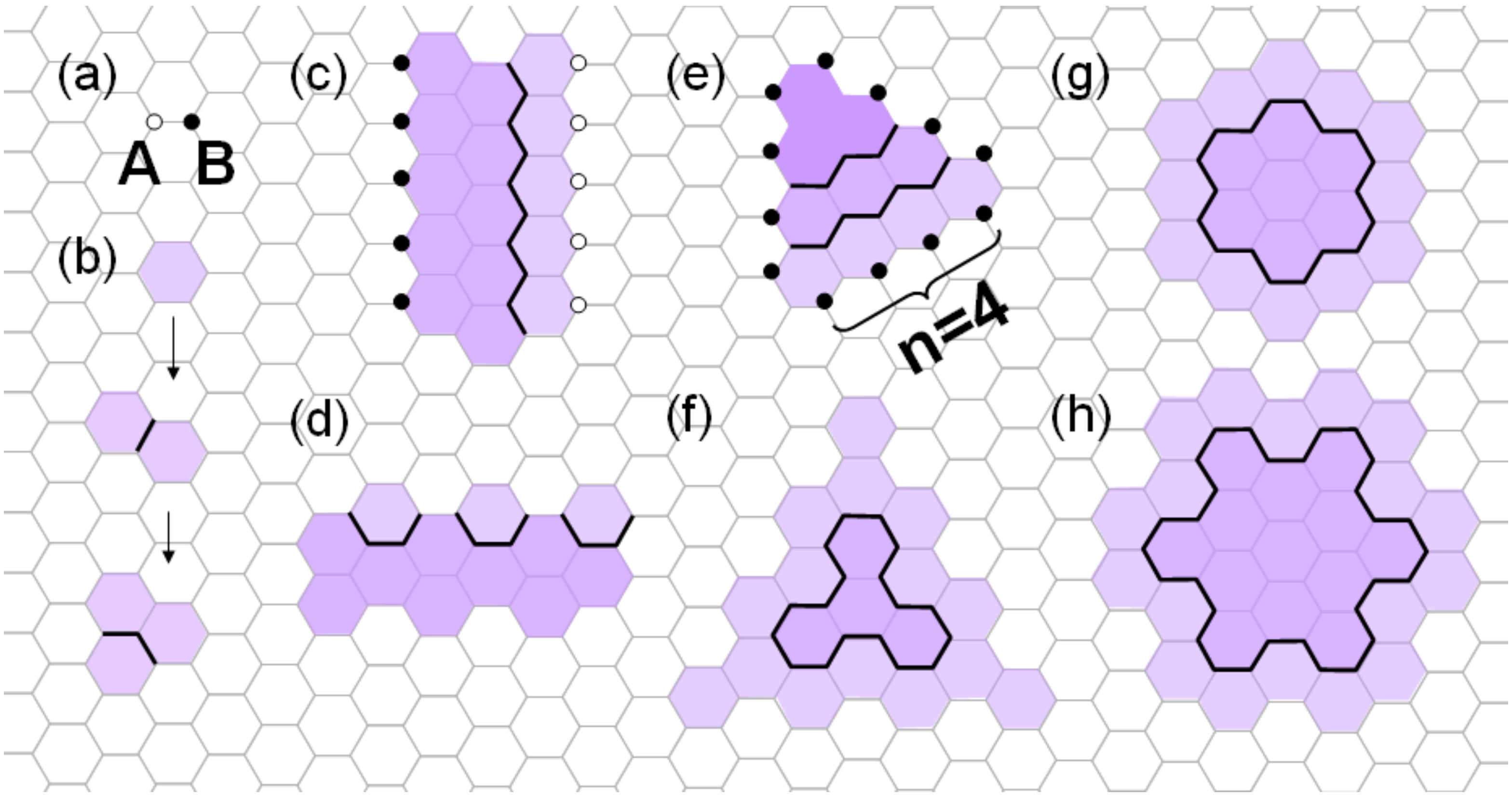
- Frustration: prevents simultaneous minimization of the interaction energies acting at a given site.
- Generalization of a simple counting rule.





Generalization in arbitrary
2-D network

Graphene Nano Flakes (GNFs) of high symmetry



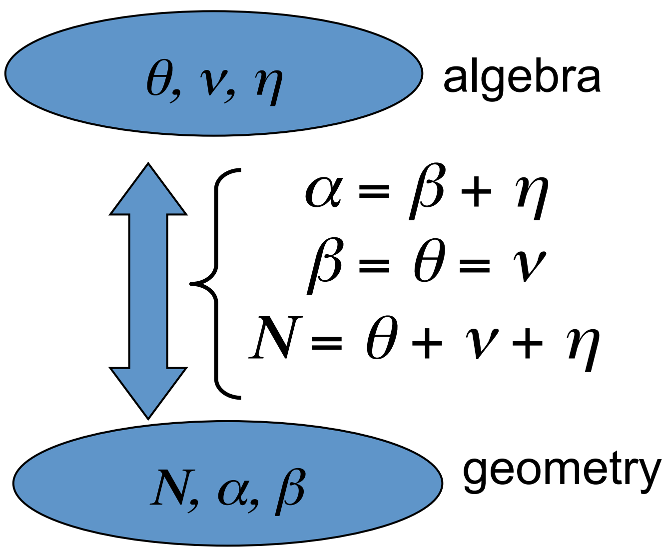
Hexagonal graph theory

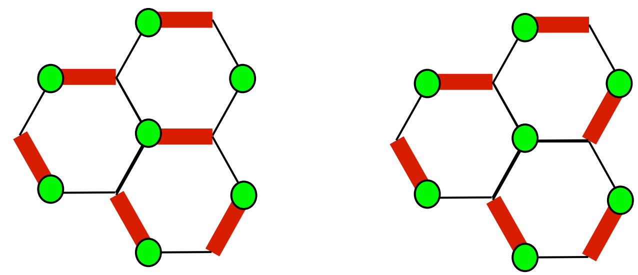
Tight binding Hamiltonian:
(π band)

$$\mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} c^{\dagger}_{i\sigma} c_{j\sigma}$$

α = pairwise non-adjacent vertices
β = non-adjacent edges
η = number of zero eigenvalues
θ = number of positive eigenvalues
ν = number of negative eigenvalues

Graph theory





Number of Nonbonding States:

$$\boxed{\eta = \alpha - \beta = N - 2\beta}$$

Fajtlowicz et al., *Croat. Chem. Acta* (2005).

Lieb theorem

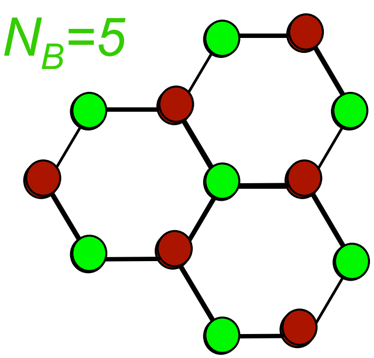
Hubbard model
(π band)

$$\mathcal{H} = -t \sum_{\langle ij \rangle,\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

$$S = |N_{\mathrm{A}} - N_{\mathrm{B}}|/2$$

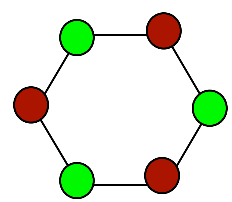
for U>0 in bipartite lattices

$N_A=6$, $N_B=5$



$S = |N_A - N_B|/2 = 1/2$

$N_A=3$, $N_B=3$



$S = |N_A - N_B|/2 = 0$

E. Lieb, *PRL* (1989).

Two classes of GNFs

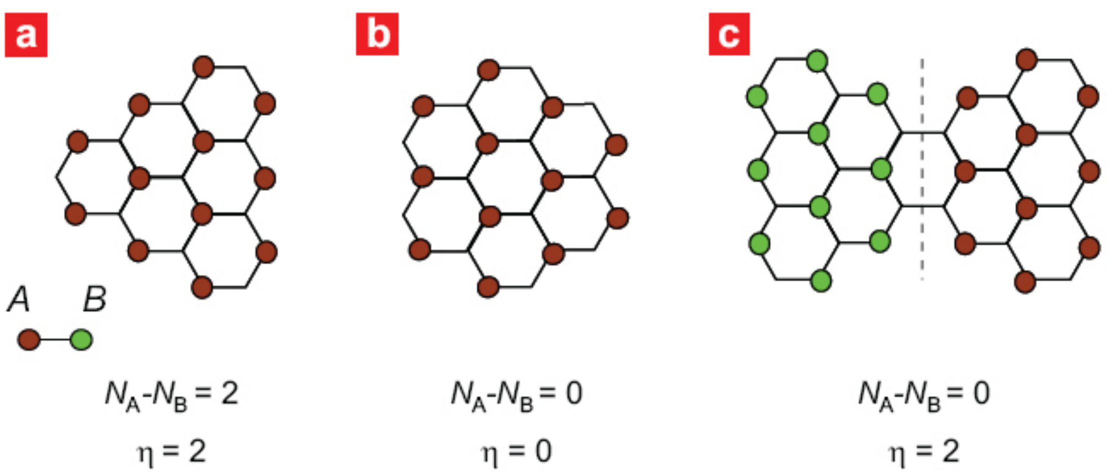
Class I. $\beta = \min\{N_A, N_B\}$ <u>Frustration on one or no sublattice</u>

therefore, $\eta = |N_\mathrm{A} - N_\mathrm{B}|$ and $S = \eta/2$ FM order

Class II. $\beta < \min\{N_A, N_B\}$ <u>Frustration on both sublattices</u>

therefore, $\eta > |N_\mathrm{A} - N_\mathrm{B}|$ and $S < \eta/2$ AFM order

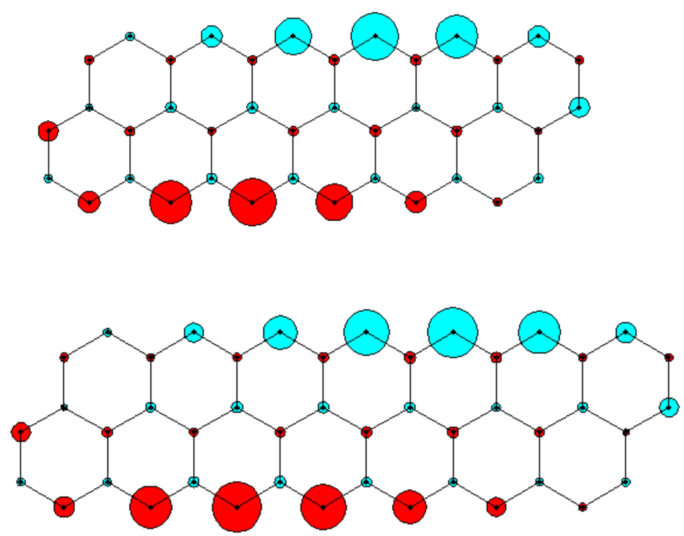
η -2S pairs of spin orbitals are AFM coupled



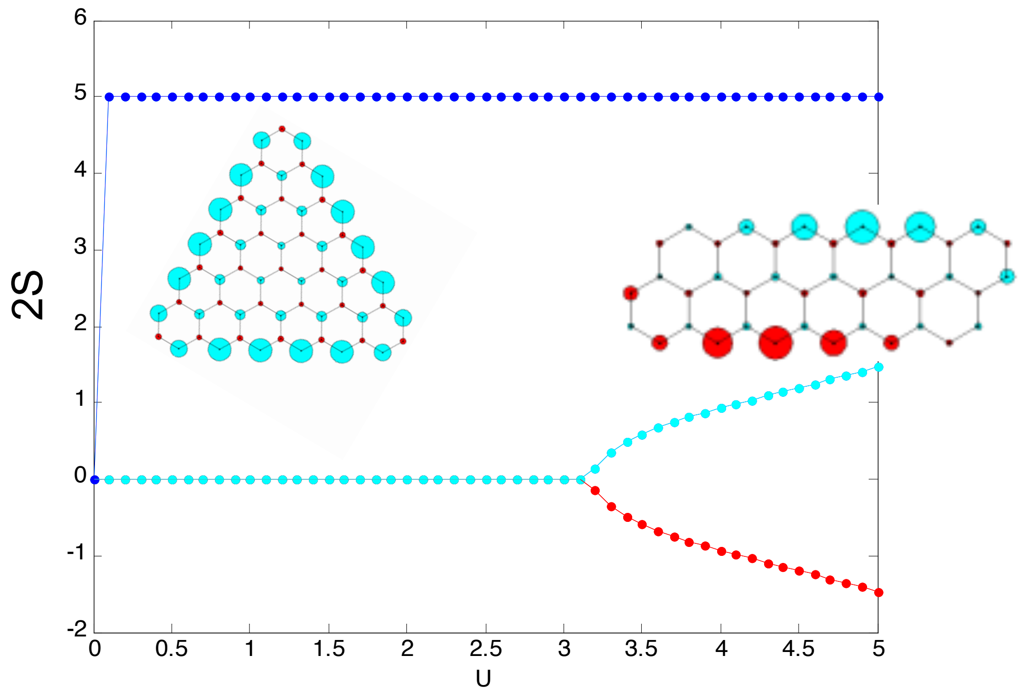
GNFs vs. Graphene Nano Ribbons

- No frustration in GNRs
- No strict zero energy eigenstates in GNRs
- No net spin in GNRs
- Different spin-size/U dependent

Size dependent



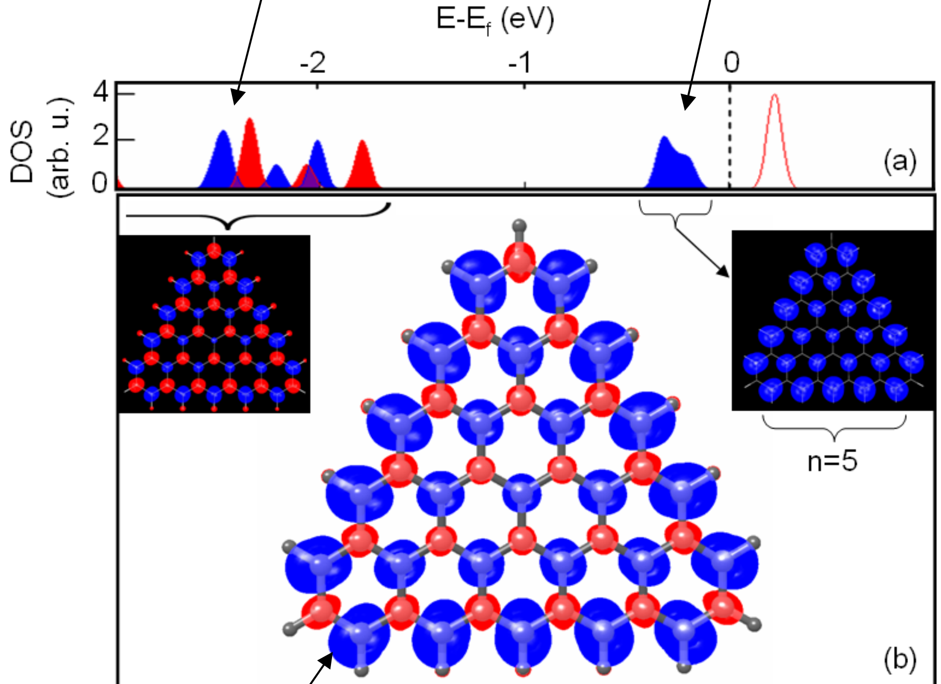
U dependent



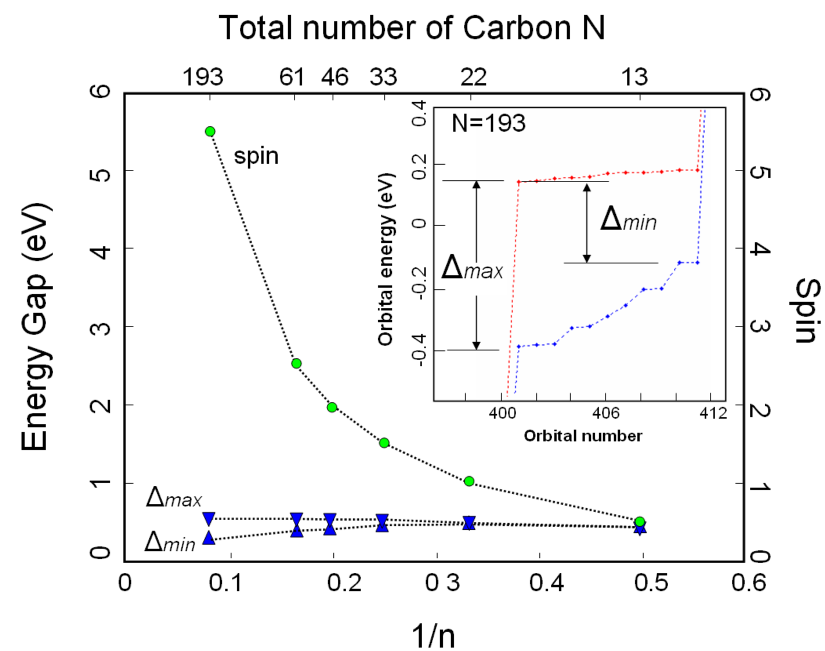
Ferrimagnetic order in triangular zigzag-edged GNF

splitting

SOMOs on majority lattice

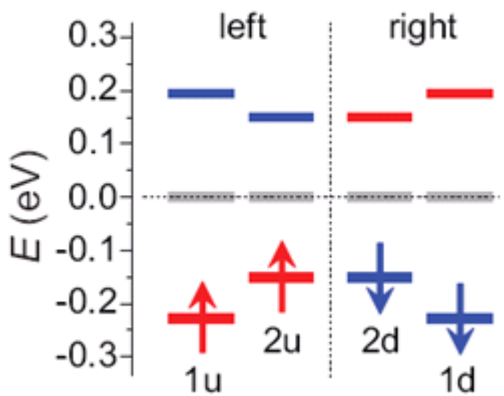


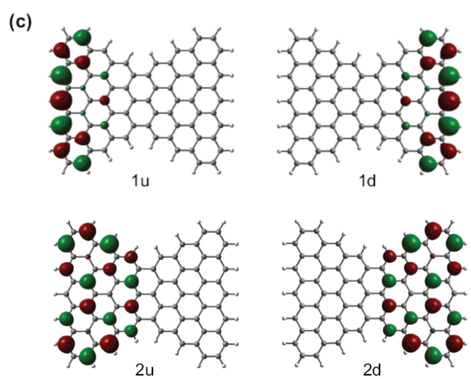
$[\rho_u(r) - \rho_d(r)]/2$ =0.0025/Å^3



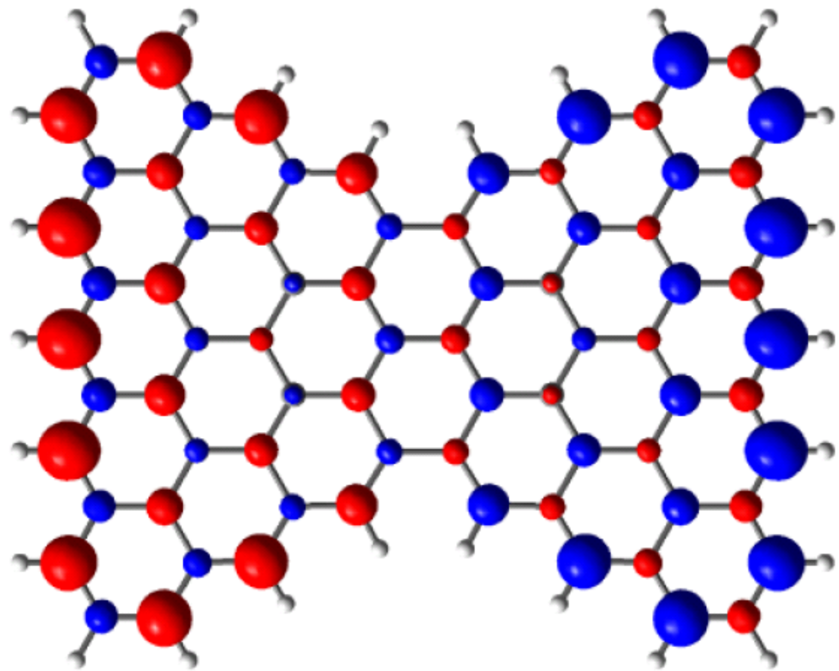
Wang, et al. Nano Lett. 8, 241(2008).

Spin orbitals in bowtie GNFs





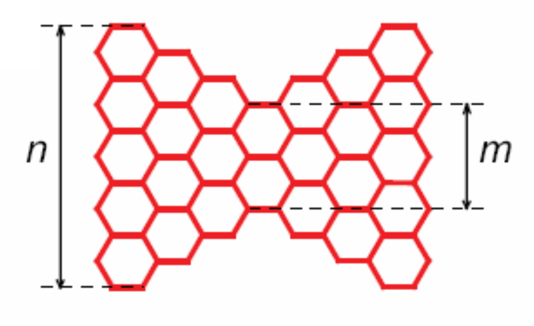
Frustration on both sub-lattices

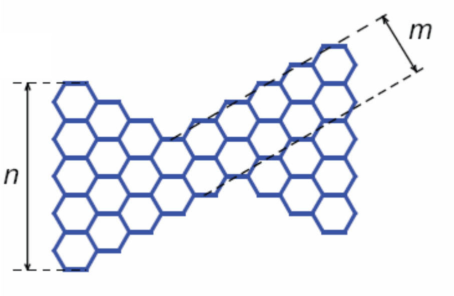


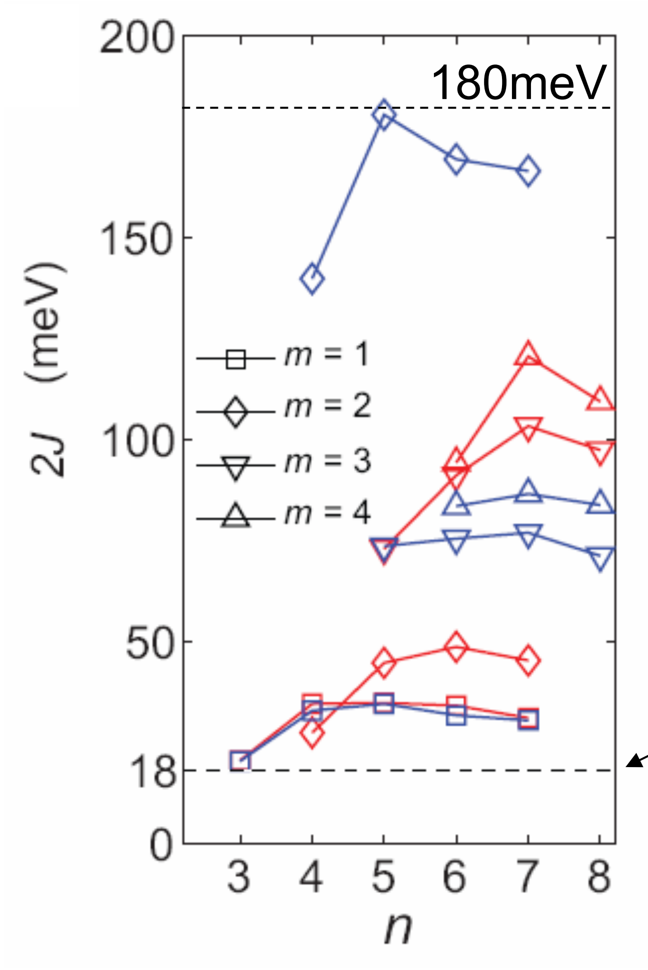
Symmetry broken: spin orbitals degenerate but spatially seperated.

Magnetic couplings in bowtie GNFs

Coupling strength:
$2J = E_{FM} - E_{AF}$

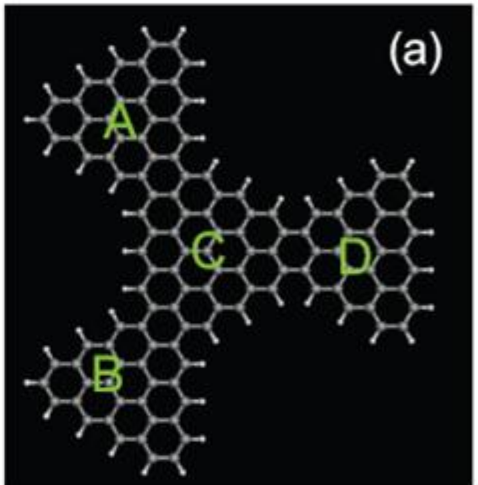




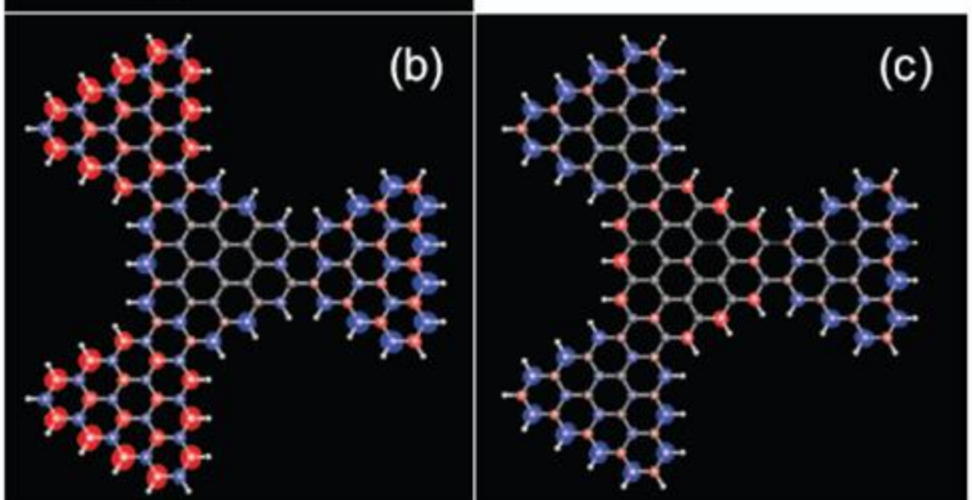


Minimum 2J for RT switching.

Logic device



A	B	C	D
1	1	0	1
1	0	0	1
0	1	0	1
0	0	1	1
1	1	0	0
1	0	1	0
0	1	1	0
0	0	1	0



Set ↑= 1, ↓=0

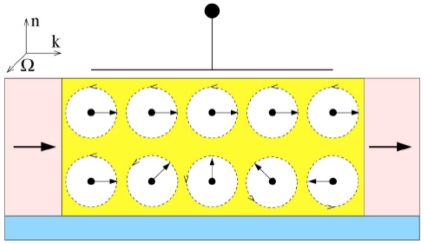
$$C = \overline{(A \cap B) \cup (B \cap D) \cup (A \cap D)}$$

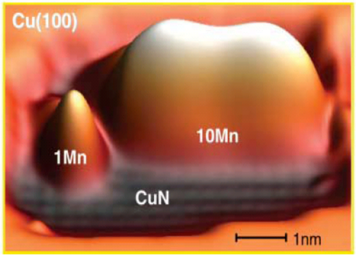
$$C = \overline{(A \cap B) \cup ((A \cup B) \cap D)}$$

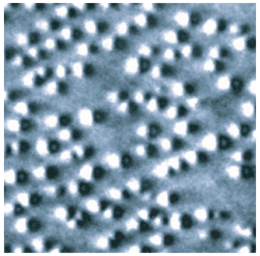
$$C = \begin{cases} \overline{(A \cup B)} & D = 1 \quad \text{NOR gate} \\ \overline{(A \cap B)} & D = 0 \quad \text{NAND gate} \end{cases}$$

Advantages of GNF spintronics

Compare other schemes:







Spin FET

transition metal atom on surface
$2J$ ~6 meV,

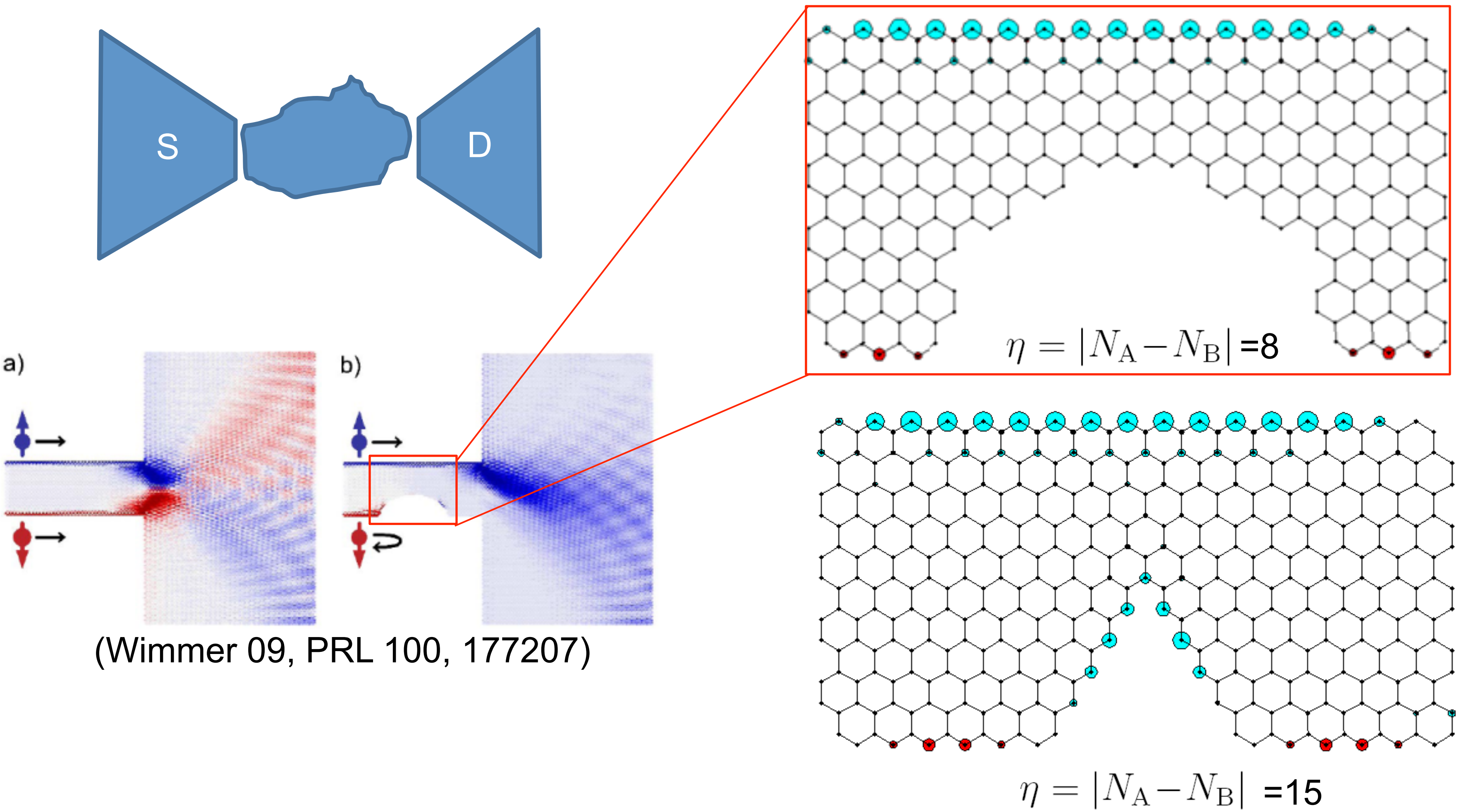
quantum dots
$2J$ ~1 meV,

- Customizable magnetic coupling mediated by π bond: 20 – 180 meV.
- Ultra fast switching: subpicosecond spin flipping $J = \pi\hbar/10^{-12}\ \mathrm{sec} \simeq 2\ \mathrm{meV}$
- Manageable error rate at room temperature, $p = e^{-2J/kT_{\mathrm{B}}} = 0.001$

Compare to GNR:

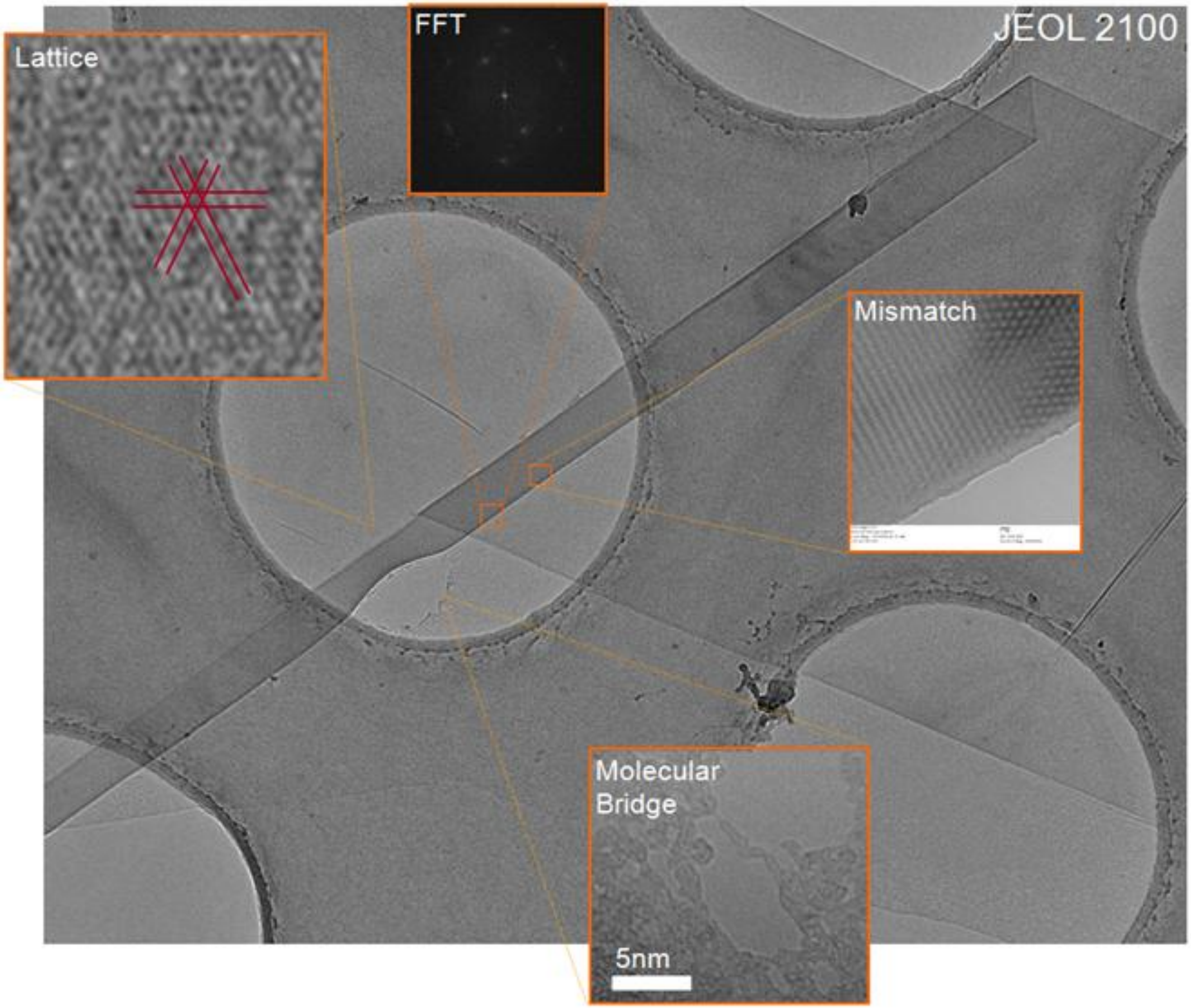
- More "nano" – do not rely on long range correlation
- More natural – for some formation processes, such as TEM
- Easy to create spin polarization – no need for strong external field

Spin transport

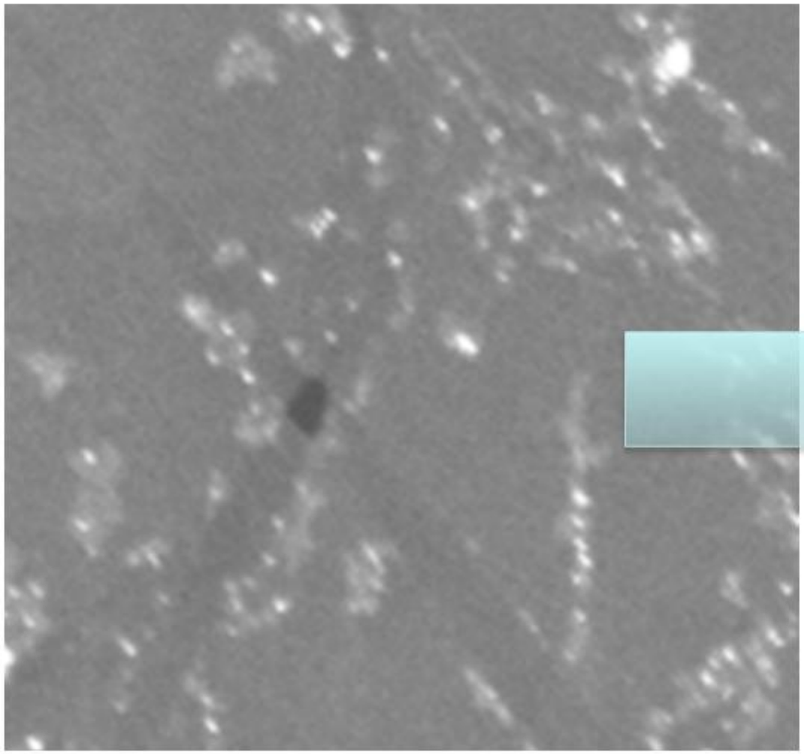


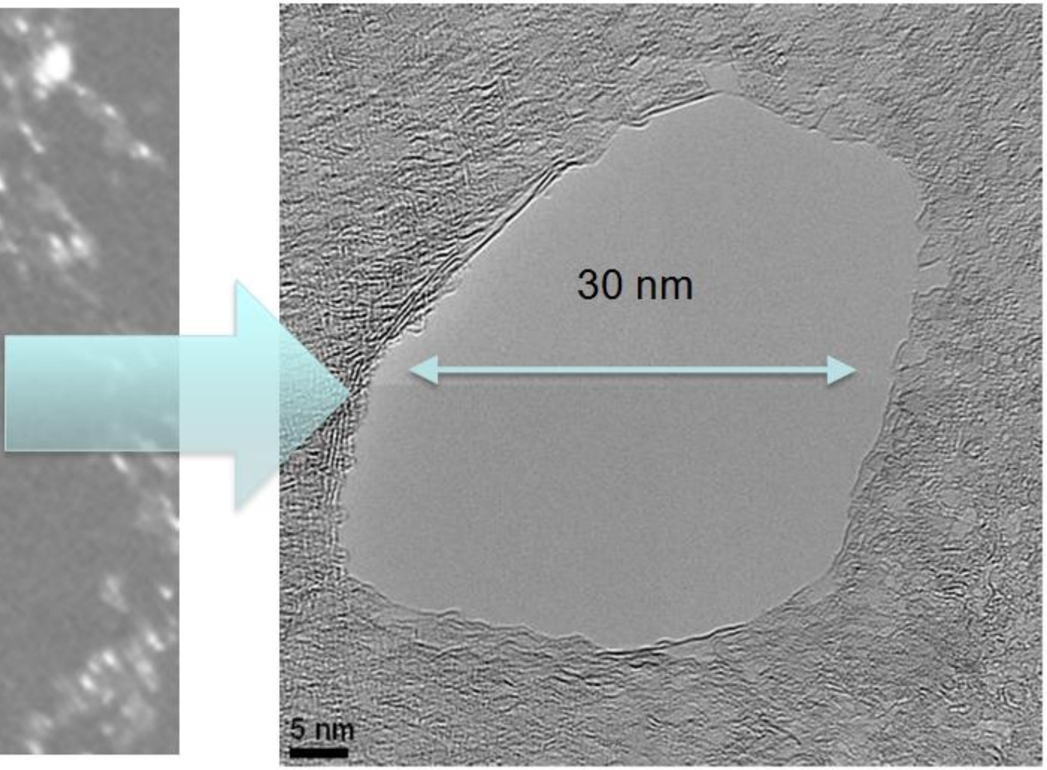
(Wimmer 09, PRL 100, 177207)

Sculpting suspended graphene



Punching nanopore with STEM

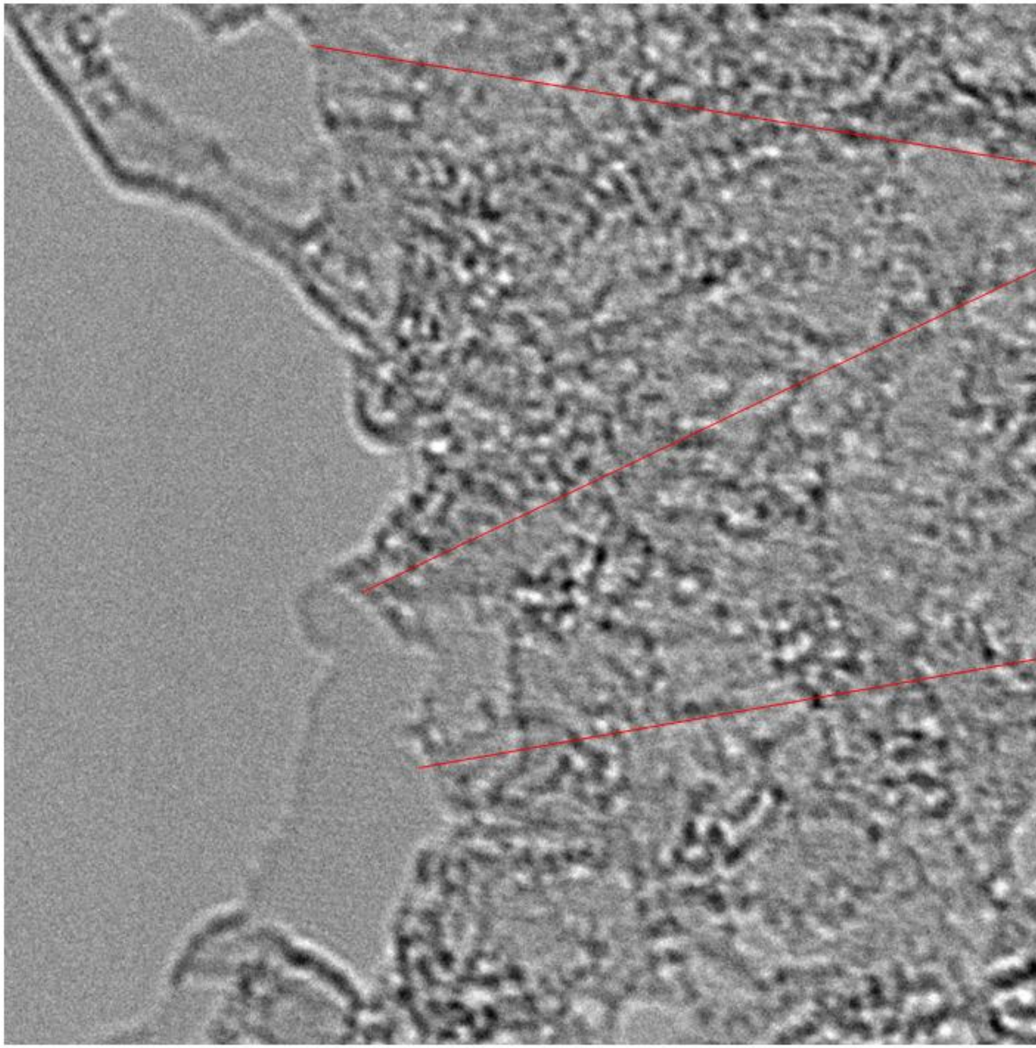




ADF Cs STEM Image at 200 KV

Imaging at 80 KV
Cs TEM Image

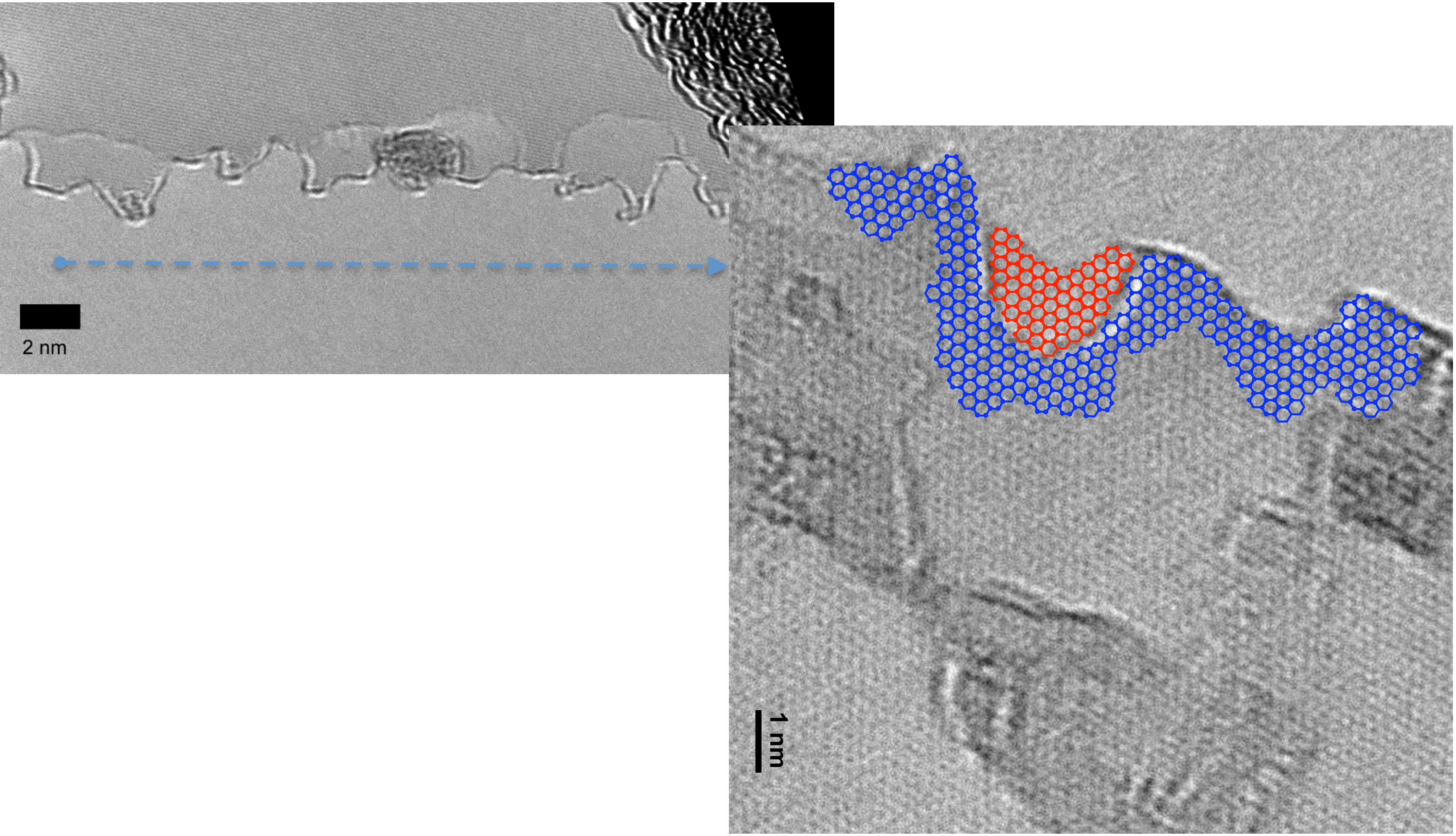
Magnetic coupling in GNFs



Graphene edge shows distinct restructure and reformation under the 80KV electron beam.

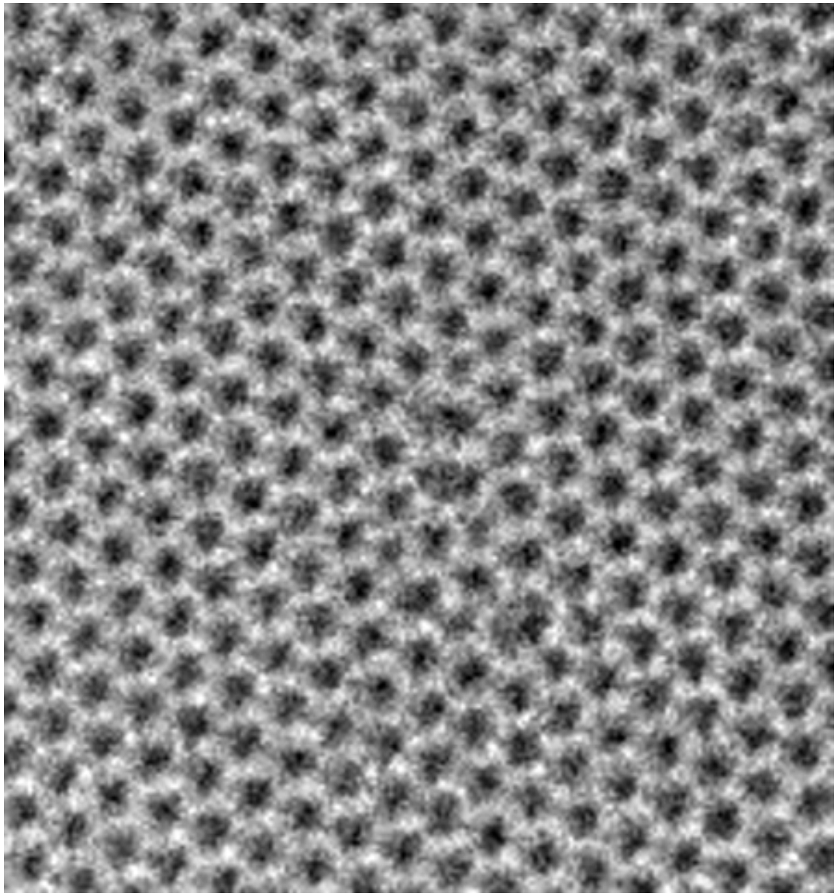
“Upper layer” carbon atoms relocate on the bottom layer under excitation, and fill defects to reduce the total energy.

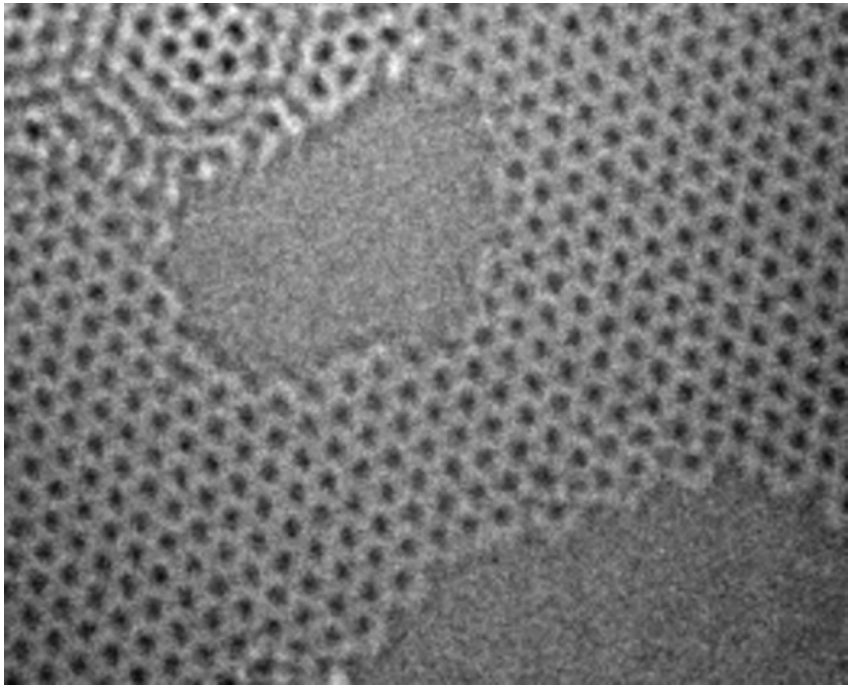
Cutting graphene edges

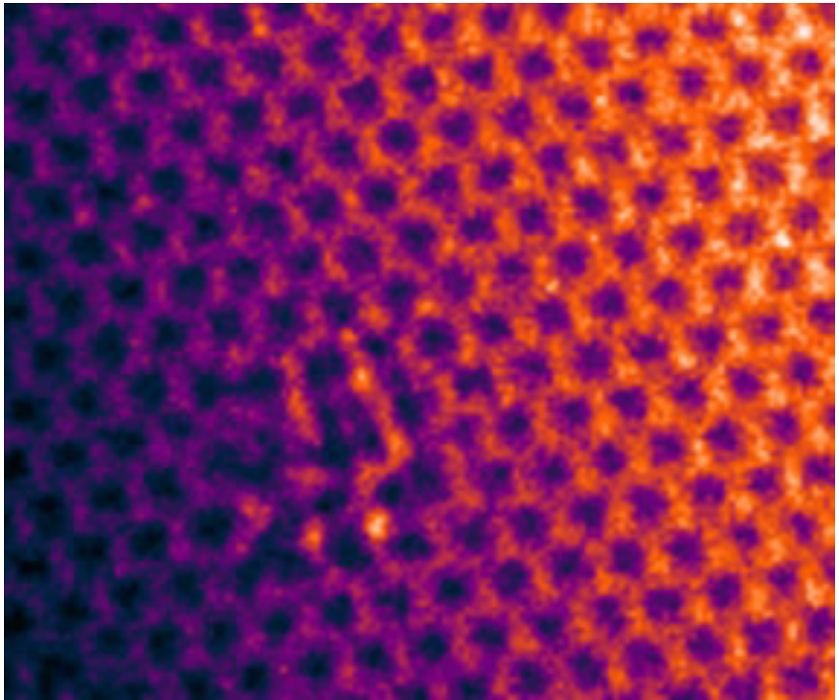


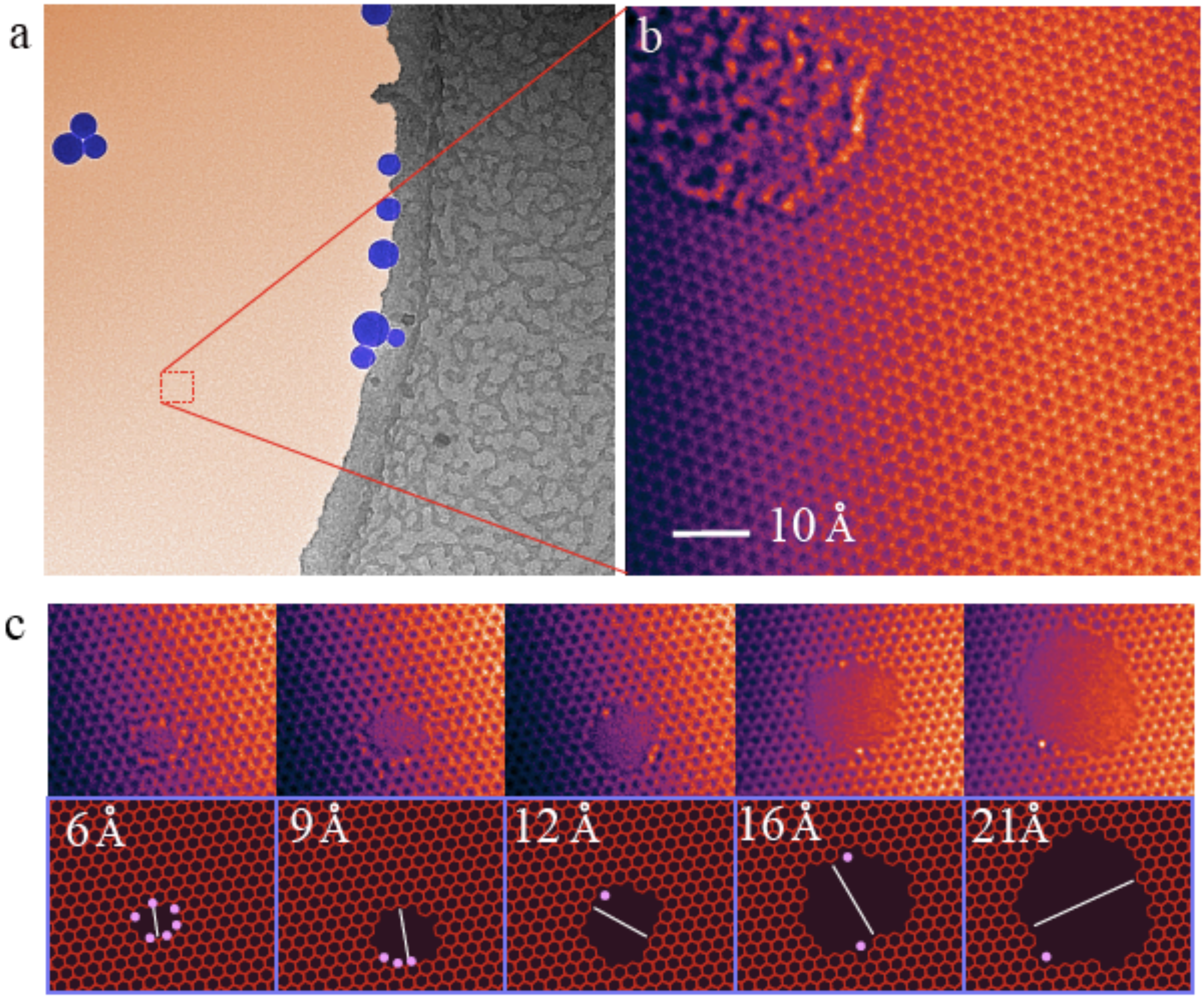
An atomic-scale chisel for sculpting graphene

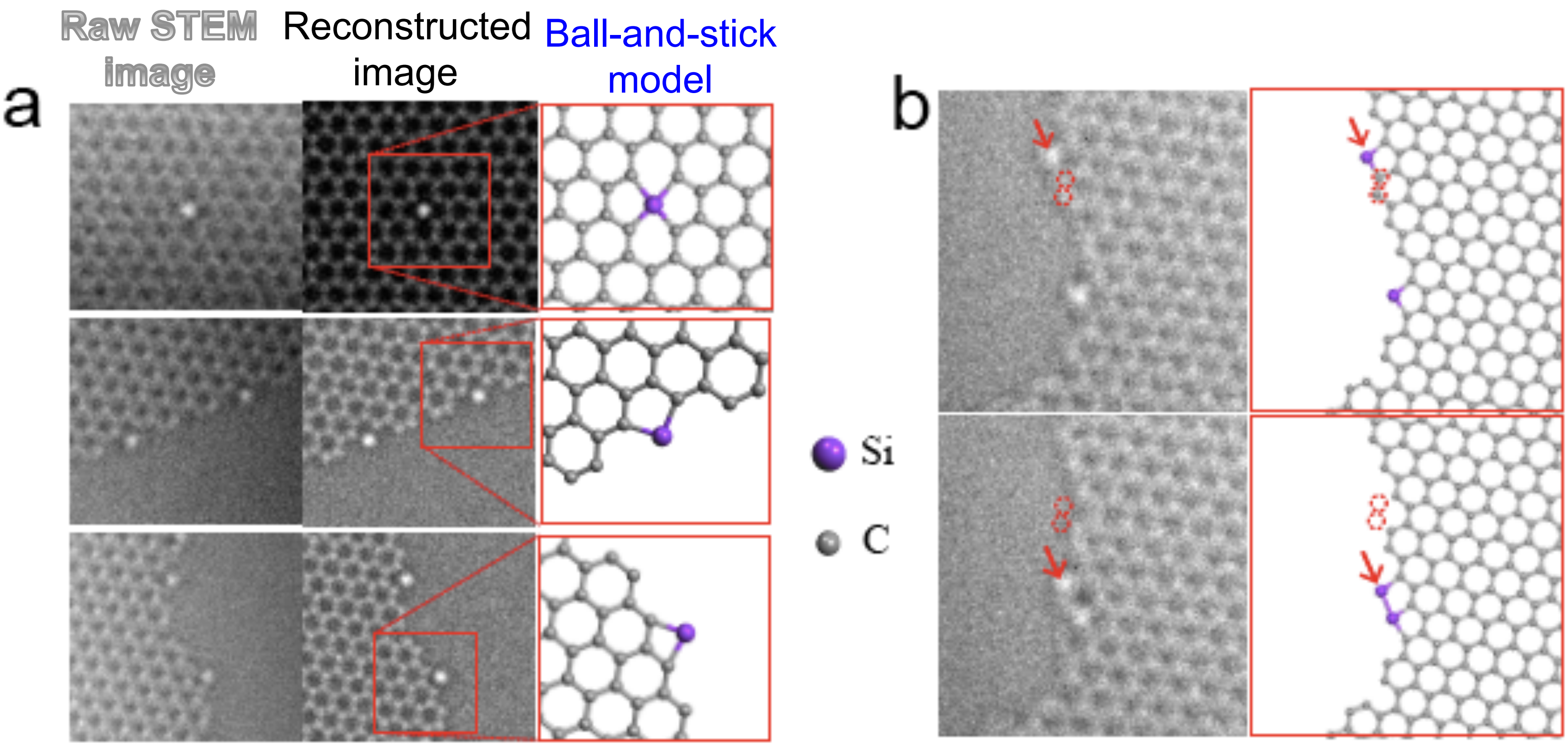
By Wei Li Wang
Expts. carried out at LBNL's NCEM



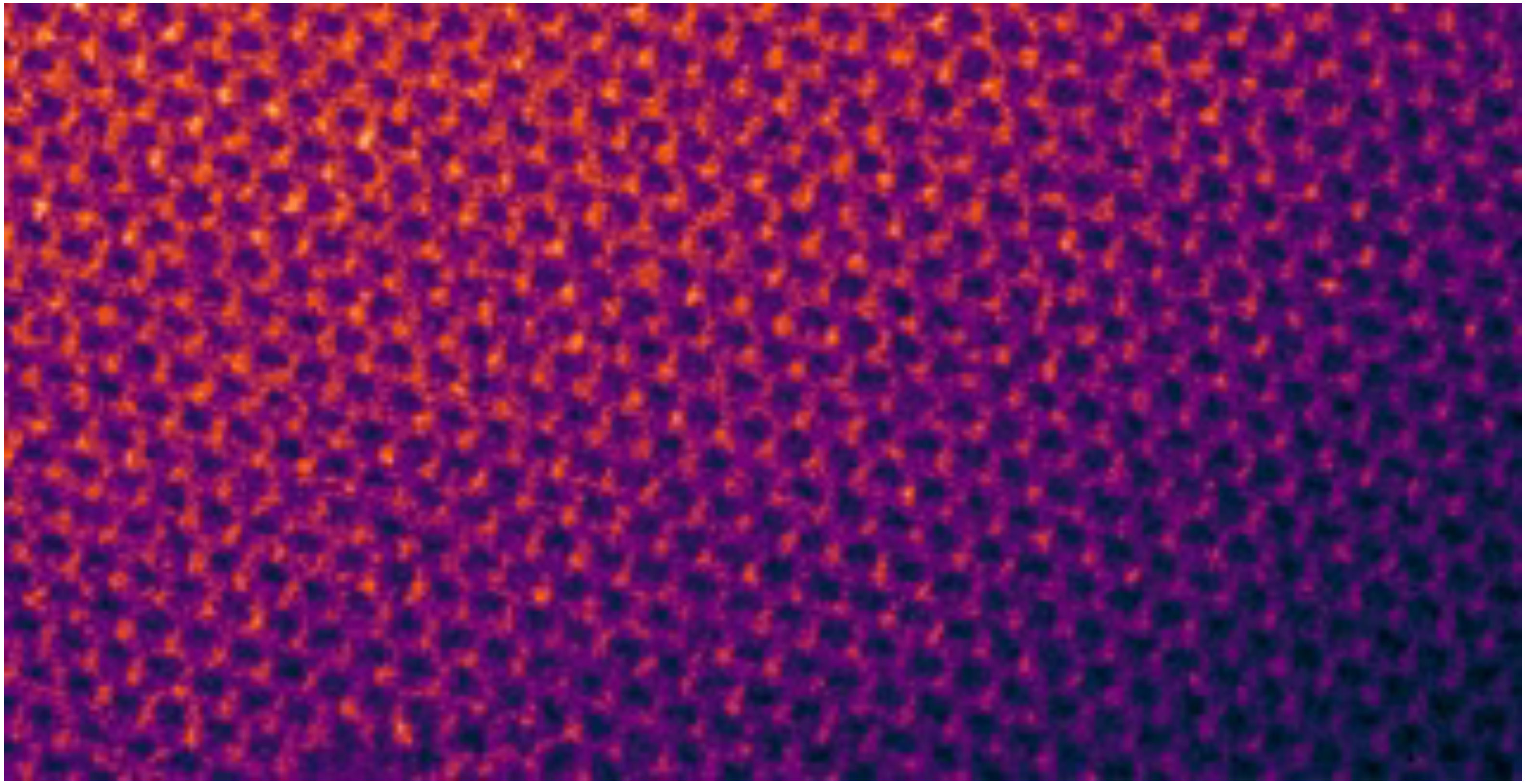


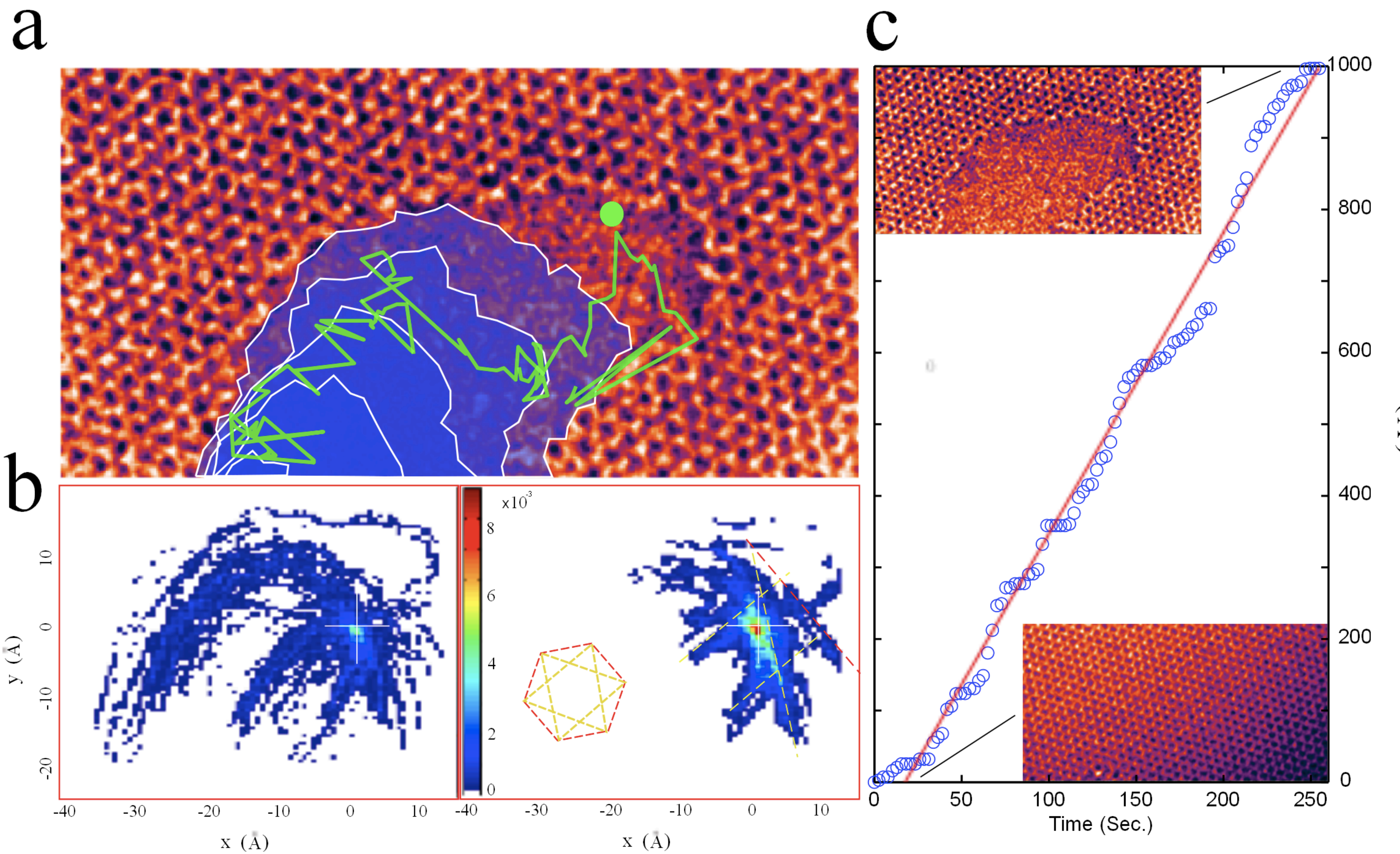



a
b
10 Å
c
6 Å
9 Å
12 Å
16 Å
21Å



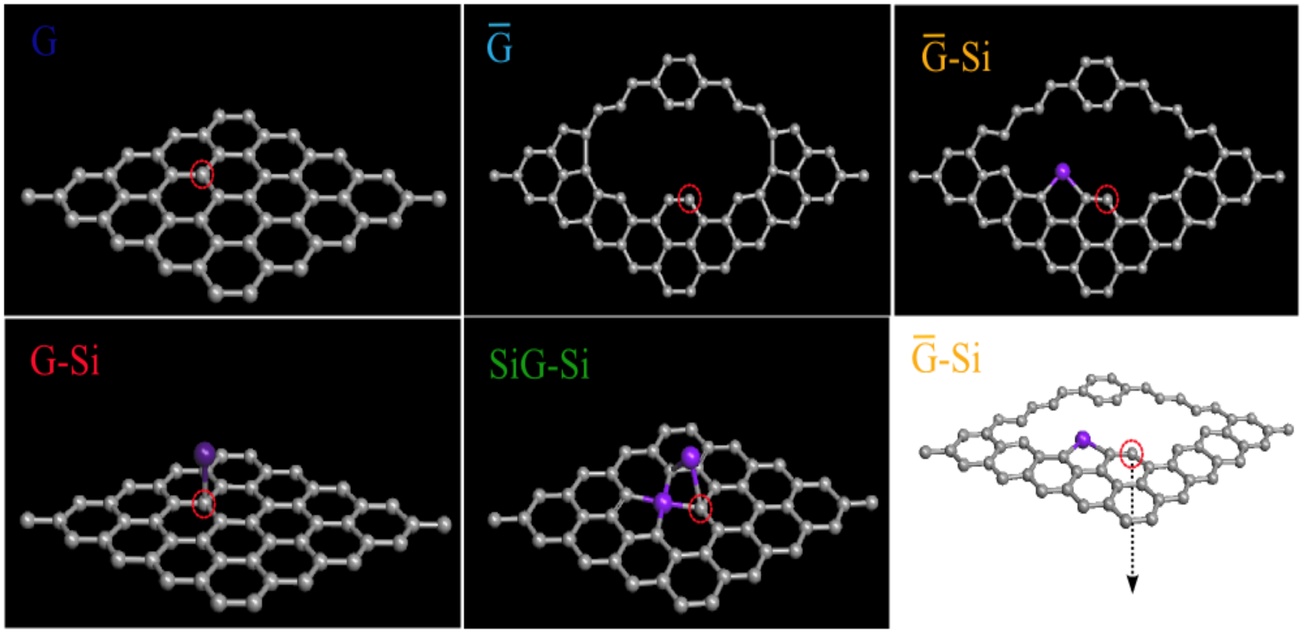
Raw STEM image
Reconstructed image
Ball-and-stick model
a
b
Si
C

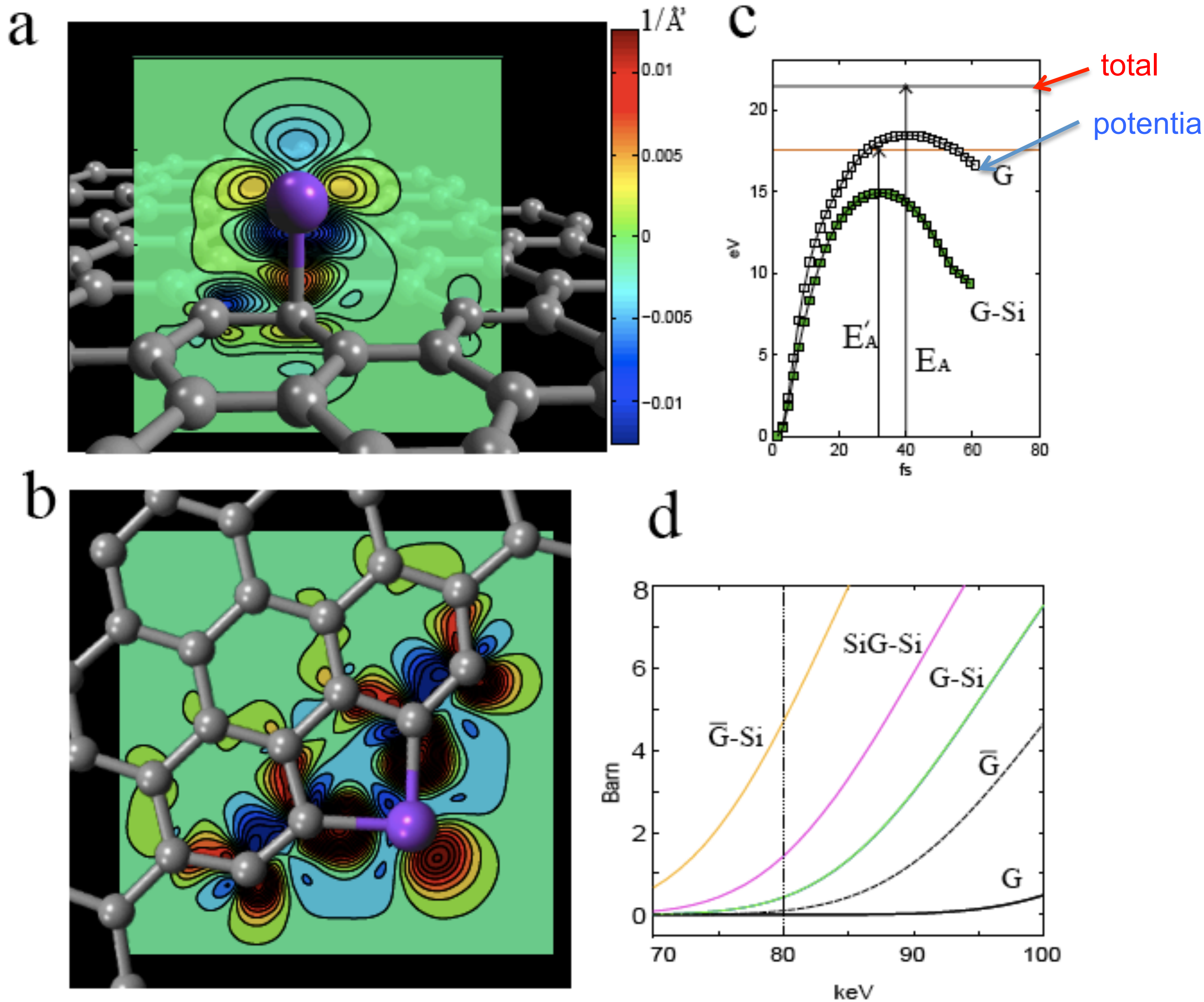




$$\mathbf{a} = \mathbf{r}_p - \mathbf{r}_{Si} \qquad \mathbf{b} = \mathbf{r}_m - \mathbf{r}_{Si}$$

Simulation of C atom removal from G with and without Si impurities





a
1/Å³
0.01
0.005
0
−0.005
−0.01
b
c
total
potential
eV
fs
G
G-Si
E′A
EA
d
Barn
keV
SiG-Si
G-Si
Ḡ-Si
Ḡ
G

Sculpting of graphene with atomic scale precision clearly feasible!

Many possibilities for new physics and devices

Theory:

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- Prof. Oleg Yazyev (EPFL)
- Dr. Elton Gomes Santos (Harvard)

Experiment:

- Dr. Wei Li Wang (Harvard-UCB)
- Prof. Robert Westervelt (Harvard)
- Dr. David Bell (Harvard, CNS)

Support: NSEC (NSF), MGHPCC