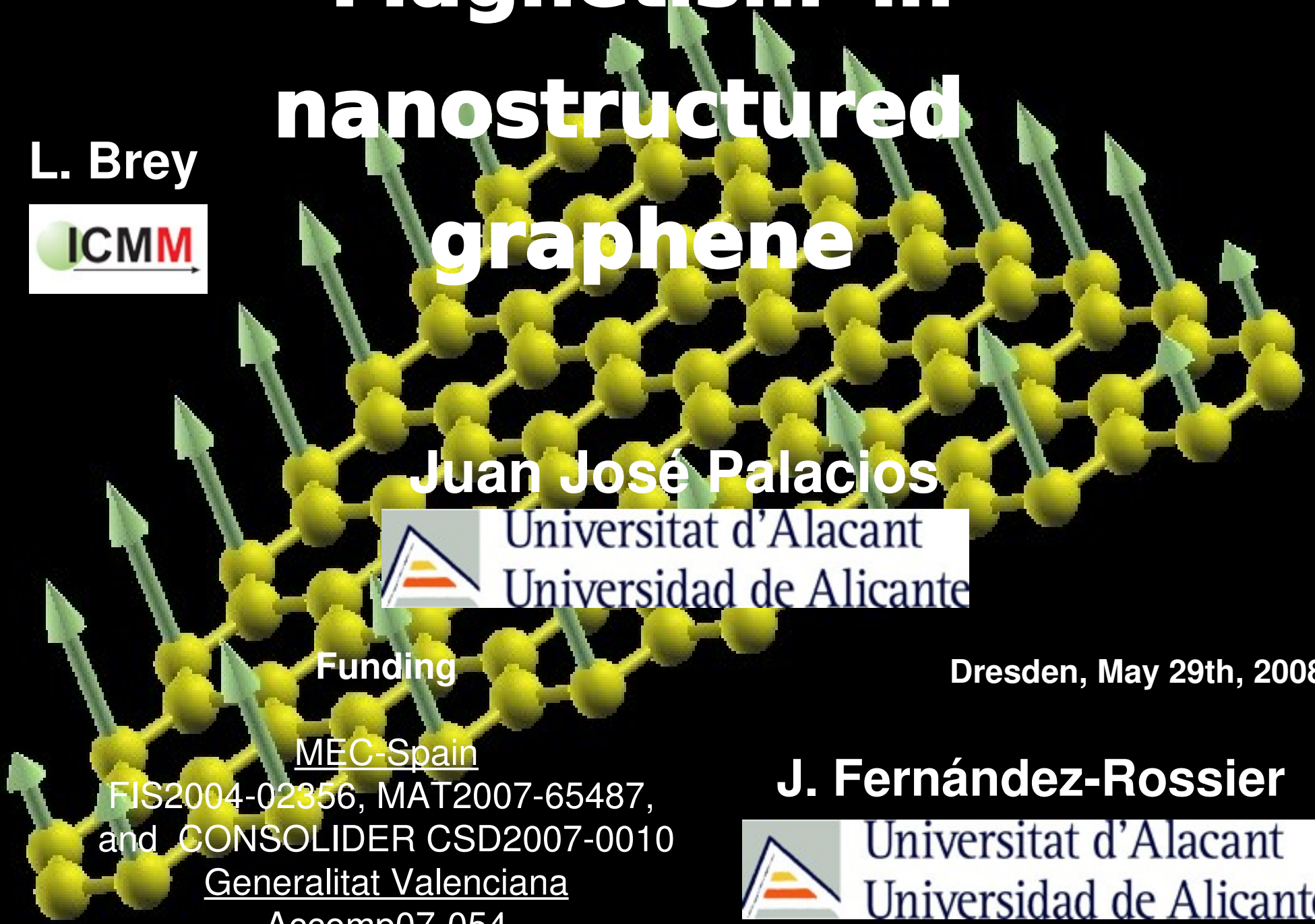
Magnetism in nanostructured graphene



L. Brey

ICMM

Juan José Palacios

Universitat d'Alacant
Universidad de Alicante

Dresden, May 29th, 2008

Funding

MEC-Spain
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Generalitat Valenciana
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J. Fernández-Rossier

Universitat d'Alacant
Universidad de Alicante


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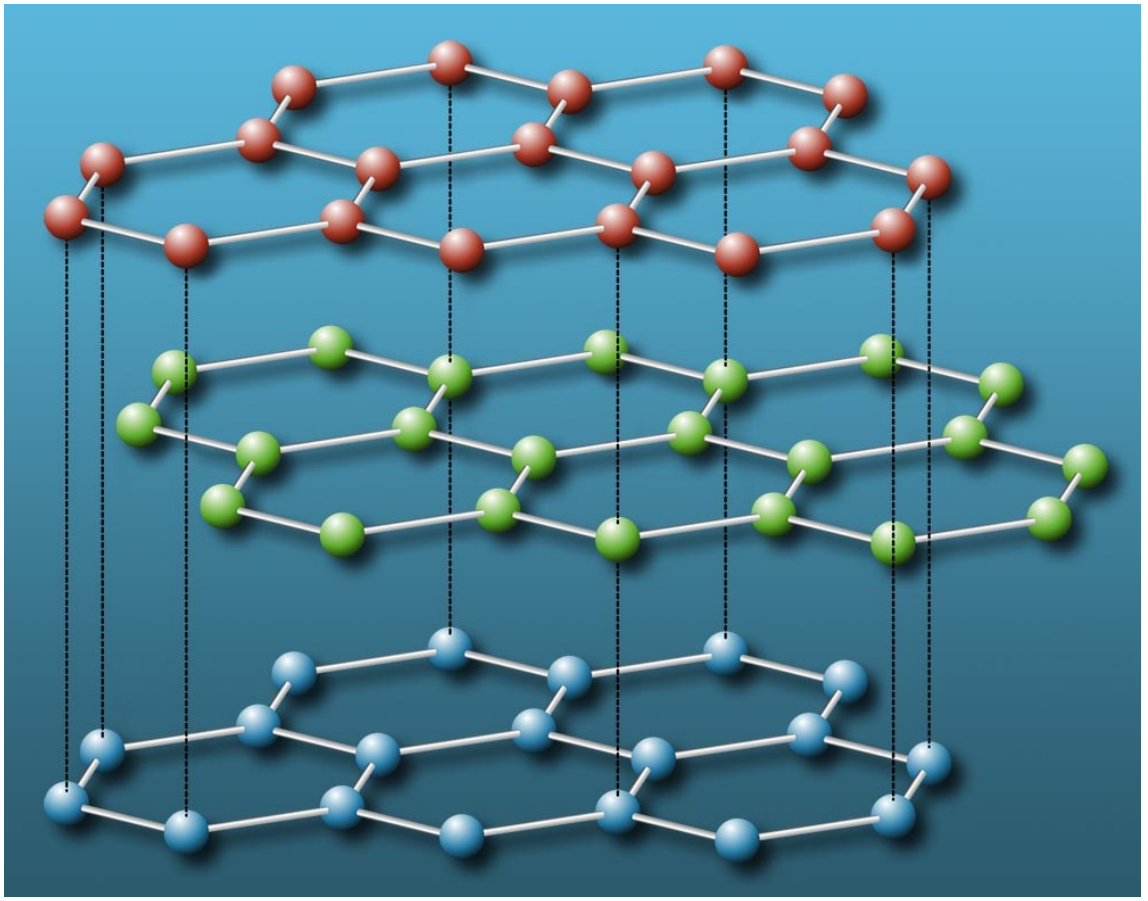
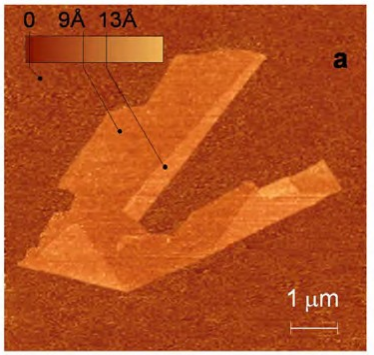
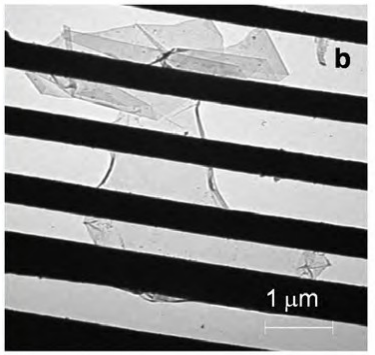
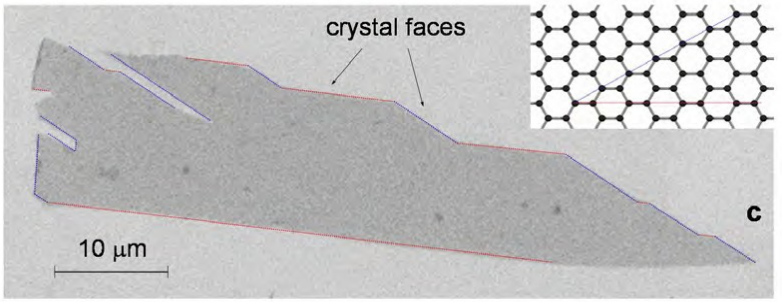
2 dimensional systems (top-down)

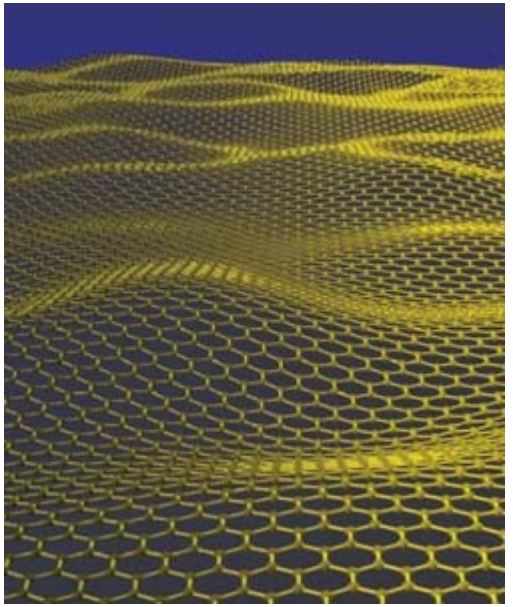
graphene







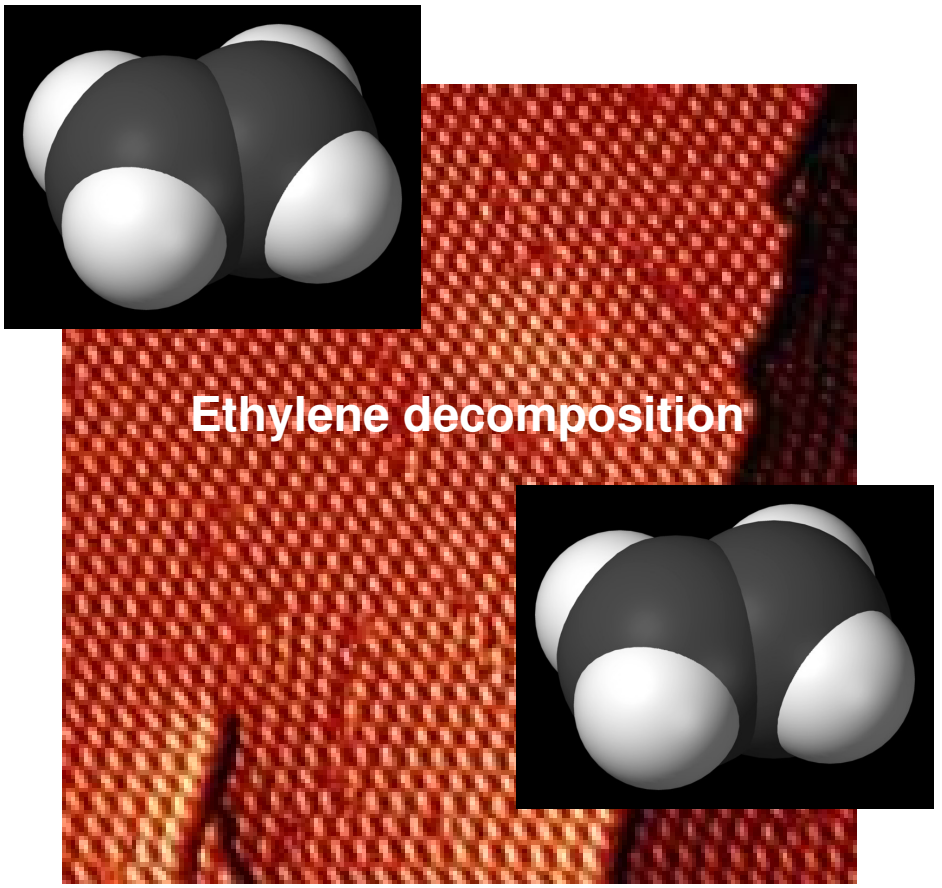


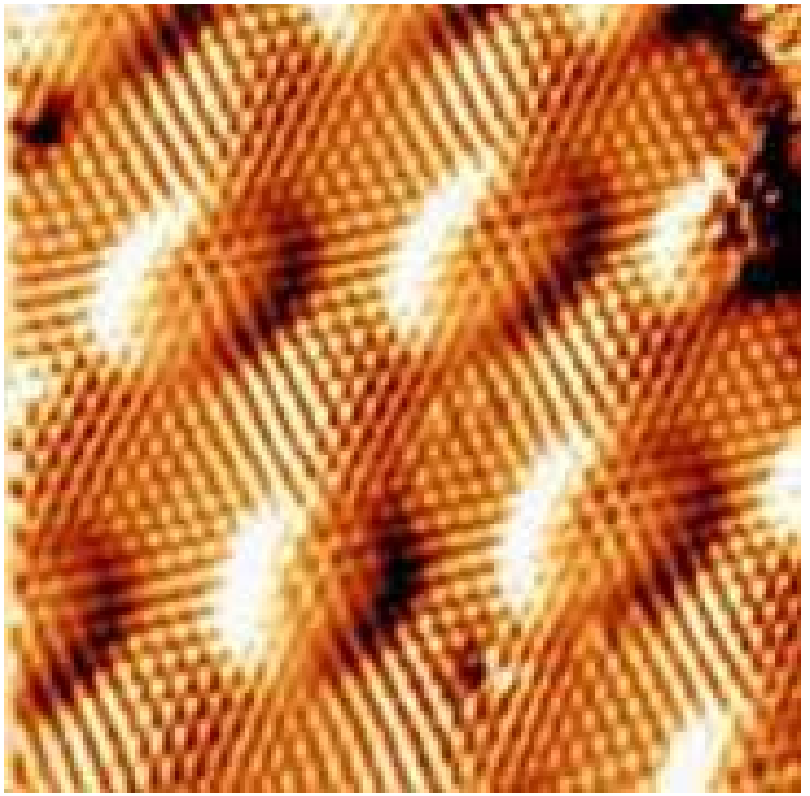


Novoselov, K.S. *et al*. "Electric Field Effect in Atomically Thin Carbon Films", *Science*, Vol 306 (5696), 666, 2004

2 dimensional systems (bottom-up)

graphene



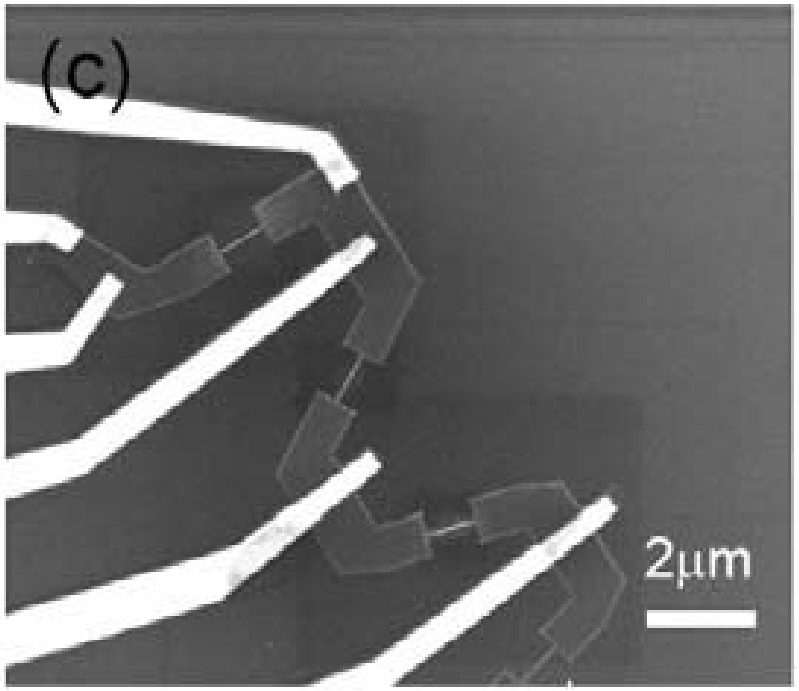


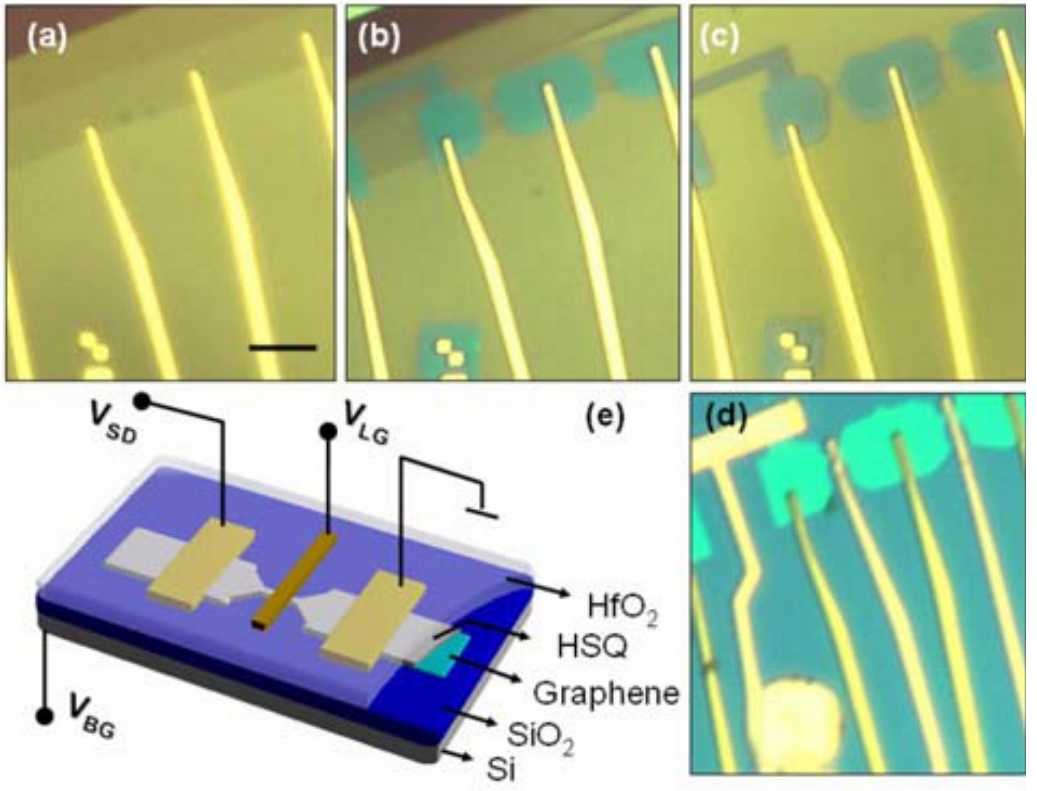
Vazquez de Parga et al., PRL (2008)

1 dimensional systems (top-down)

graphene

Melinda Y. Han , Barbaros Oezyilmaz, Yuanbo Zhang, Philip Kim,
Phys. Rev. Lett, 98, 206805 (2007)





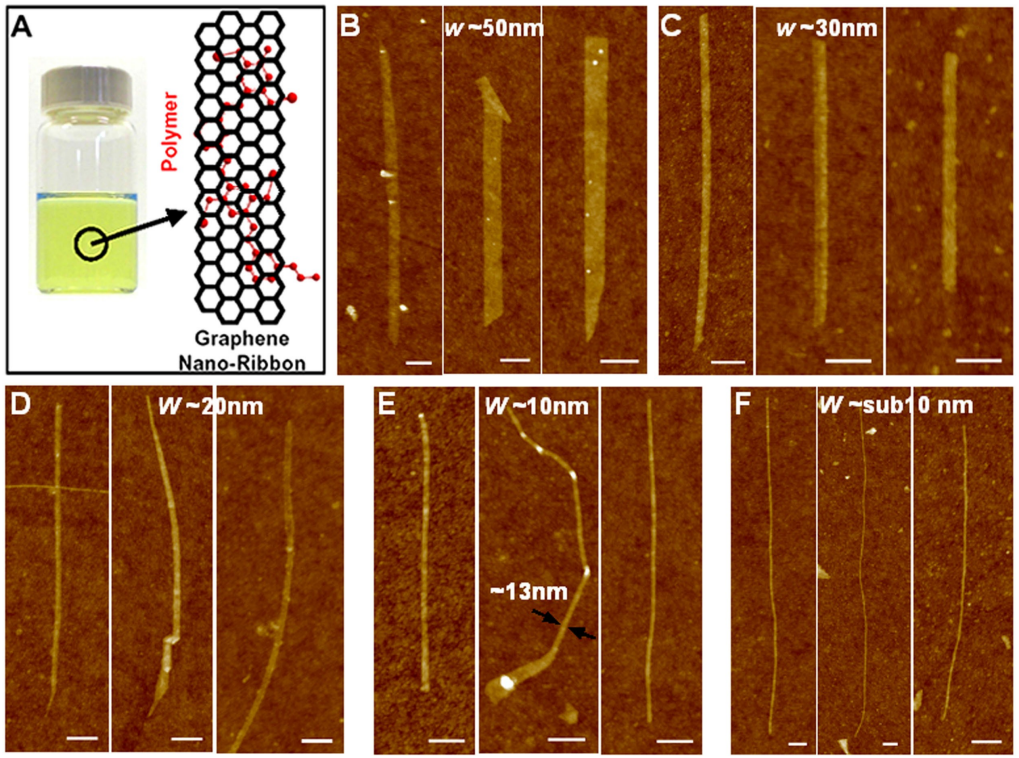
1 dimensional systems (bottom-up)

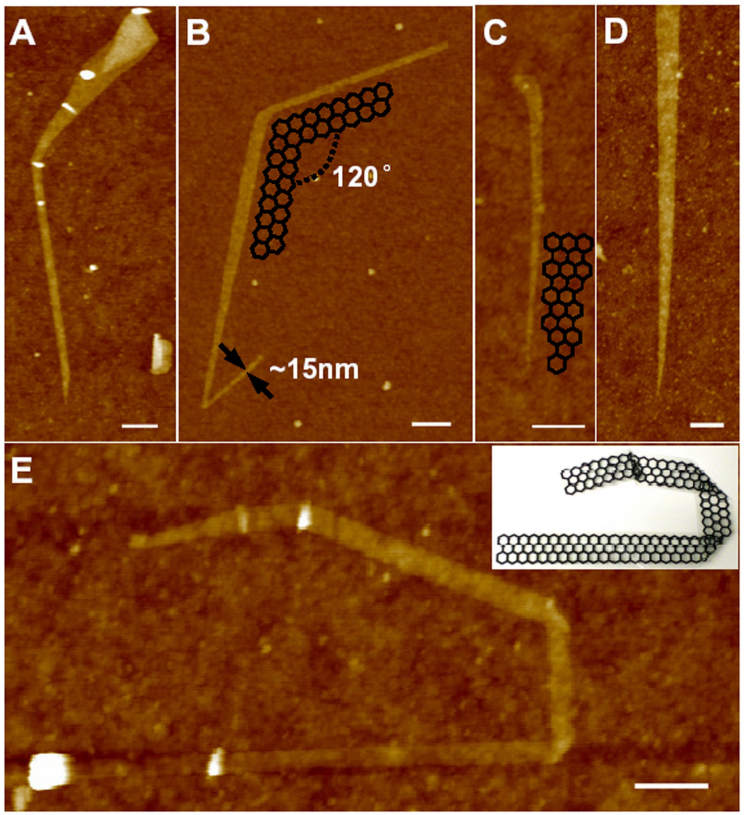
graphene

Chemically Derived, Ultrasmooth Graphene Nanoribbon Semiconductors

Xiaolin Li,† Xinran Wang,† Li Zhang, Sangwon Lee, and Hongjie Dai*

Science Express (2008)

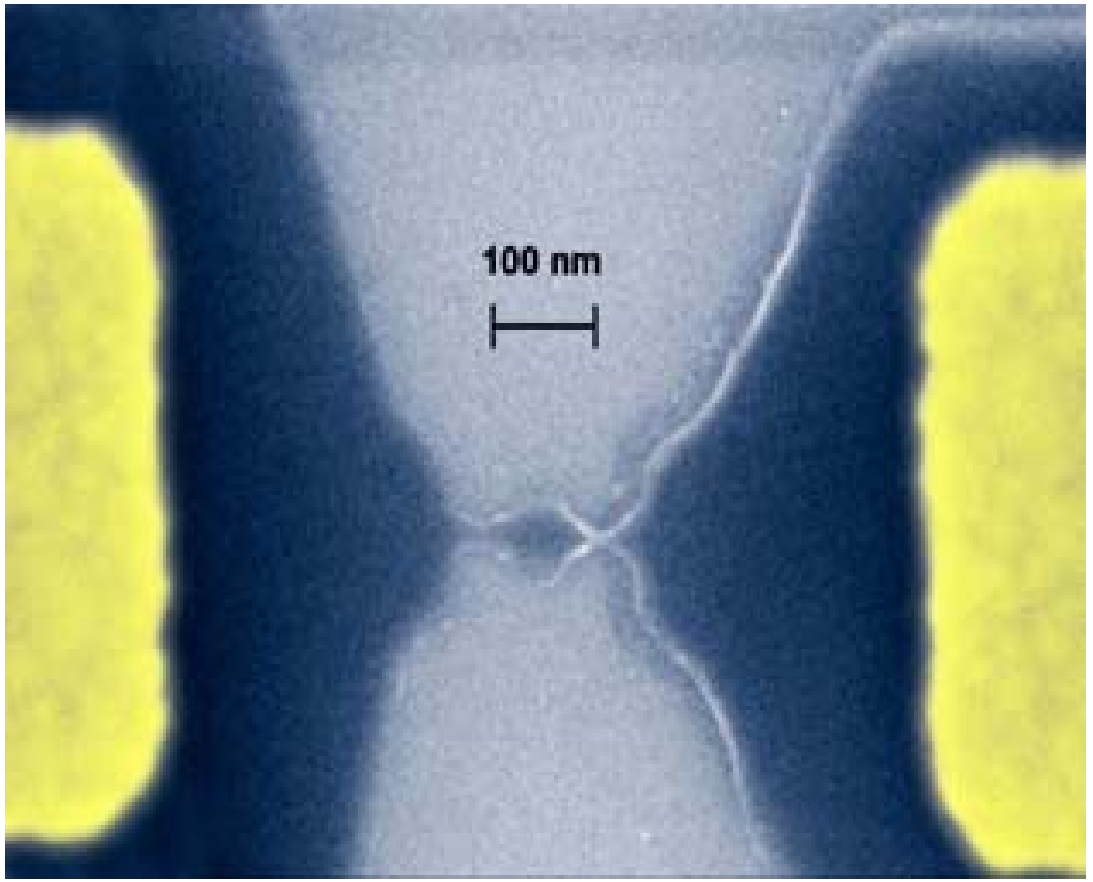


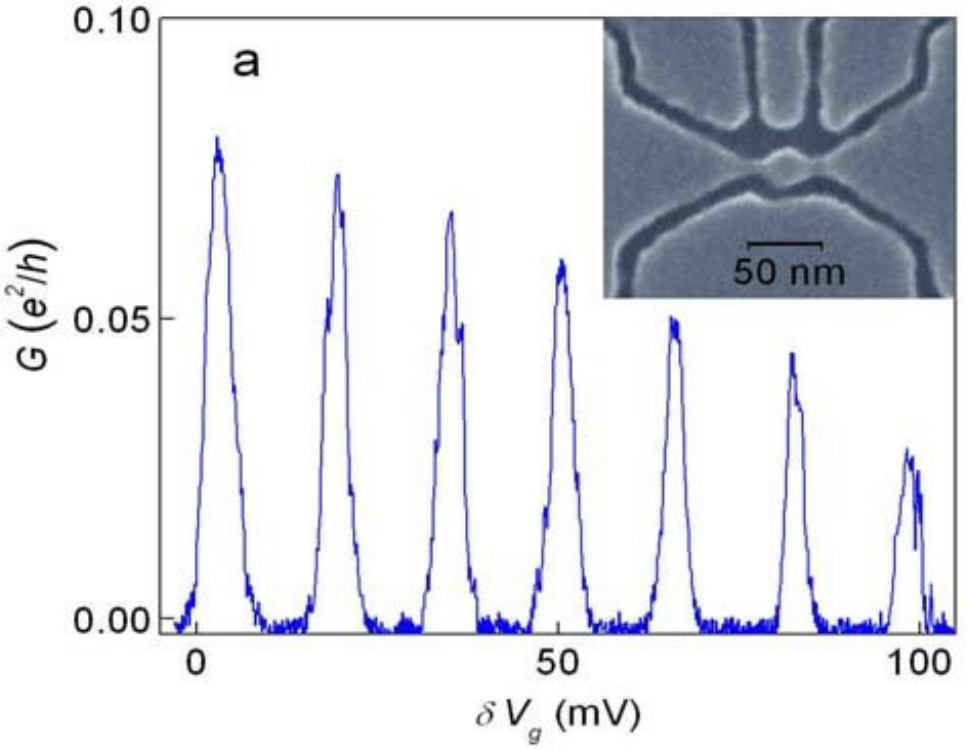


0 dimensional systems (top-down)

graphene

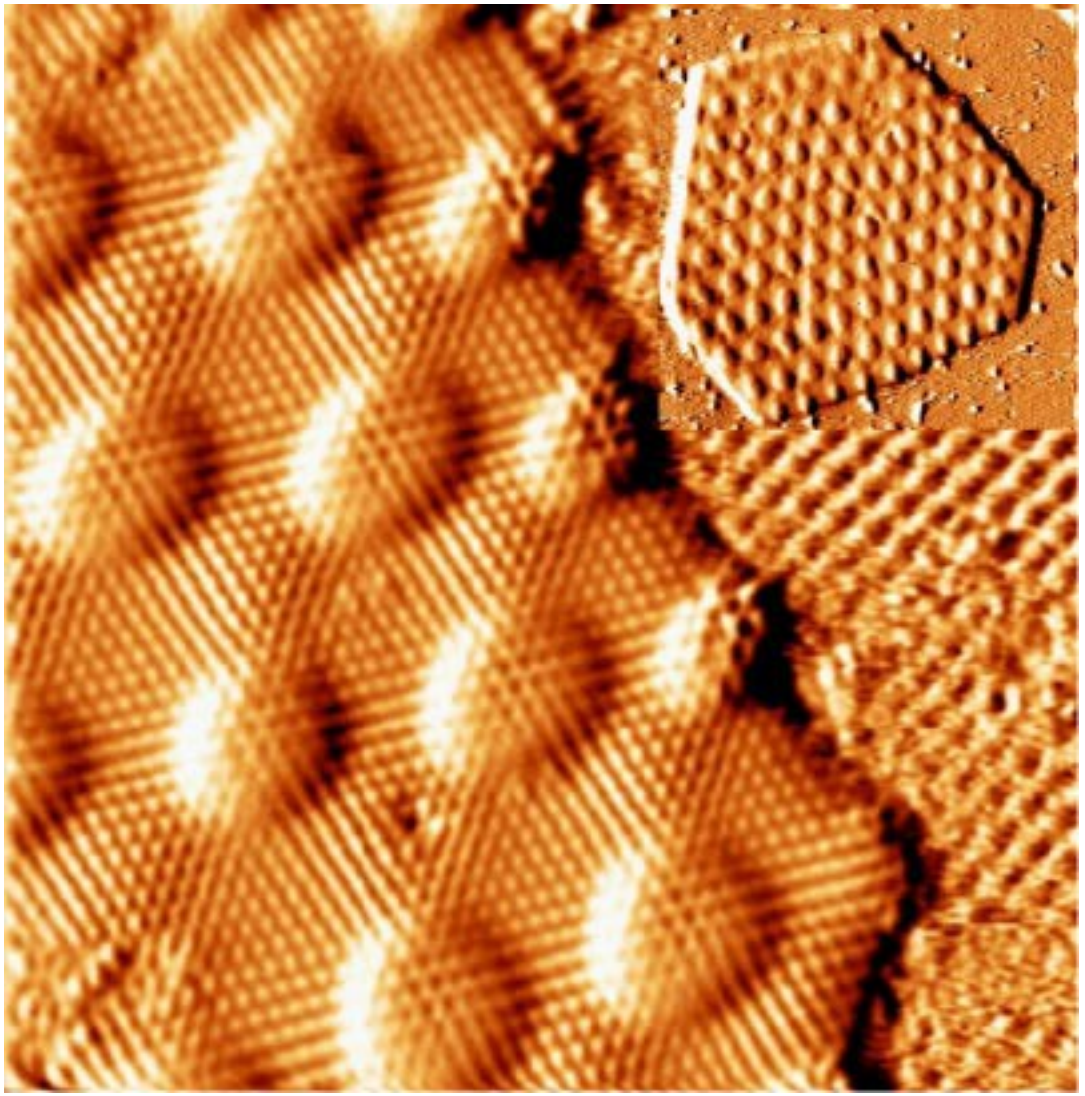
L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. H. Hill, K. S. Novoselov, A. K.Geim, Science (2008)





0 dimensional systems (bottom-up)

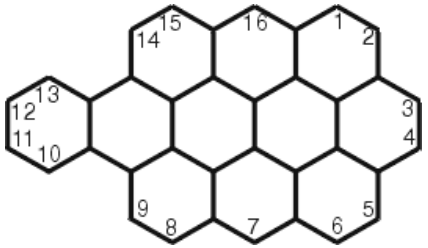
graphene



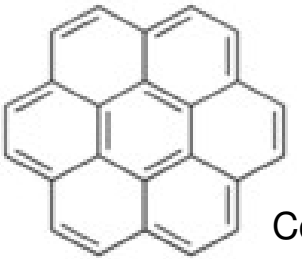
Vazquez de Parga et al., PRL (2008)

0 dimensional systems (bottom-up)

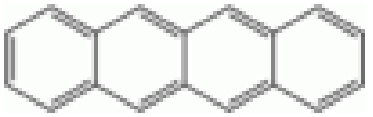
polycyclic aromatic hydrocarbons (PAH's)



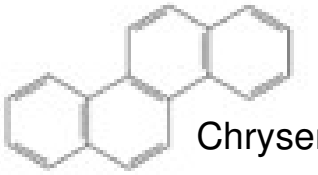
Benz[d]ovalene



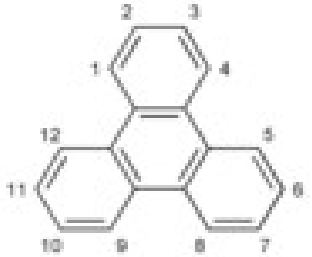
Coronene



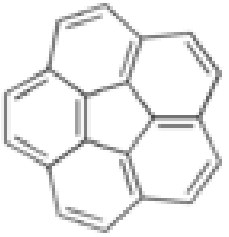
Naphthacene



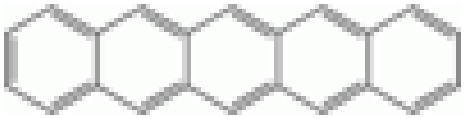
Chrysene



Triphenylene

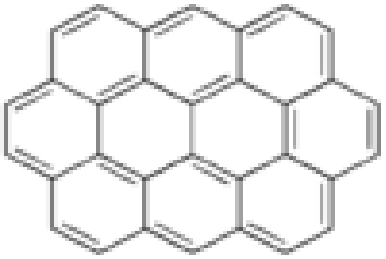


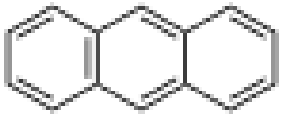
Corannulene



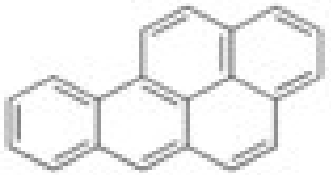
Pentacene

Ovalene



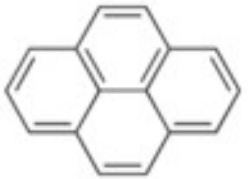


Anthracene

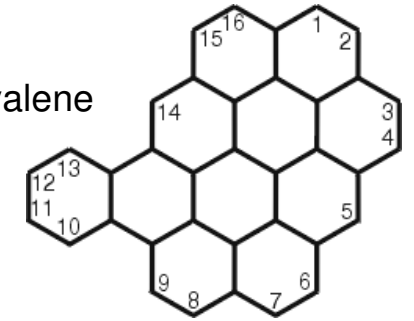


Benzo[a]pyrene

Pyrene

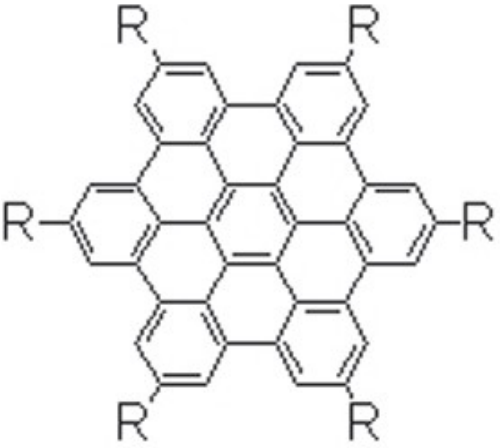


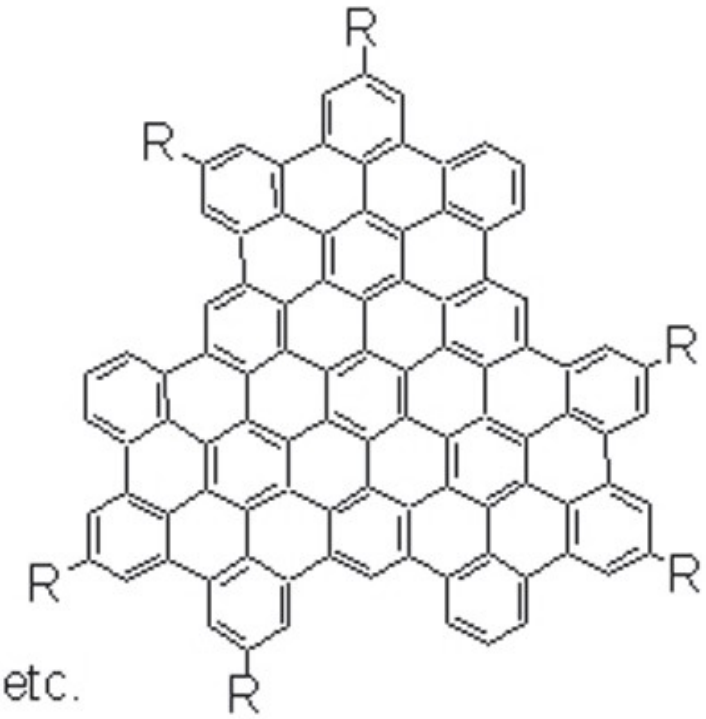
Benz[a]ovalene

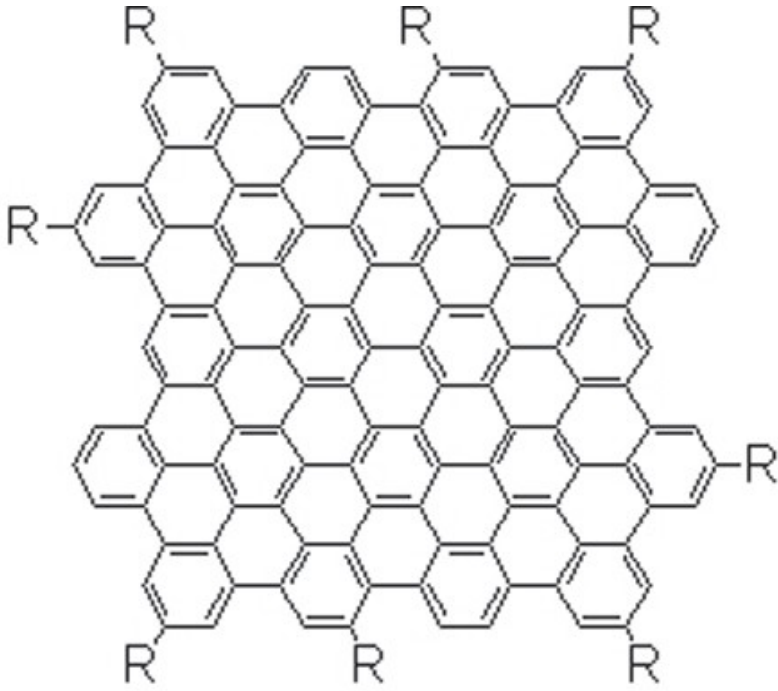


0 dimensional systems (bottom-up)

disk-like polycyclic aromatic hydrocarbons (PAH's)







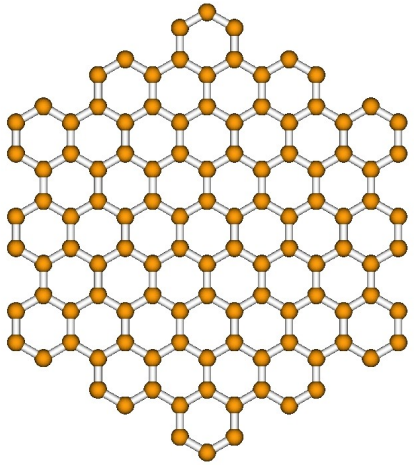
R = Alkyl, alkylphenyl etc.

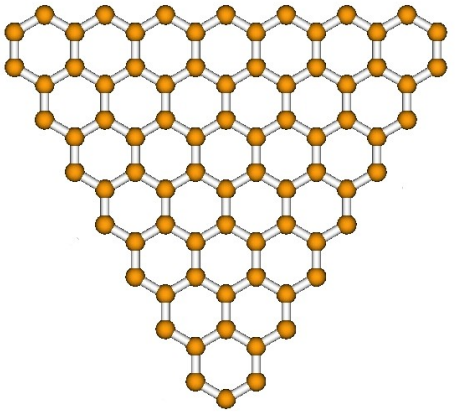
J. Wu, M. D. Watson, K. Müllen, Angew. Chem. Int. Ed. 42, 5329 (2003)

Outline

Nanographenes

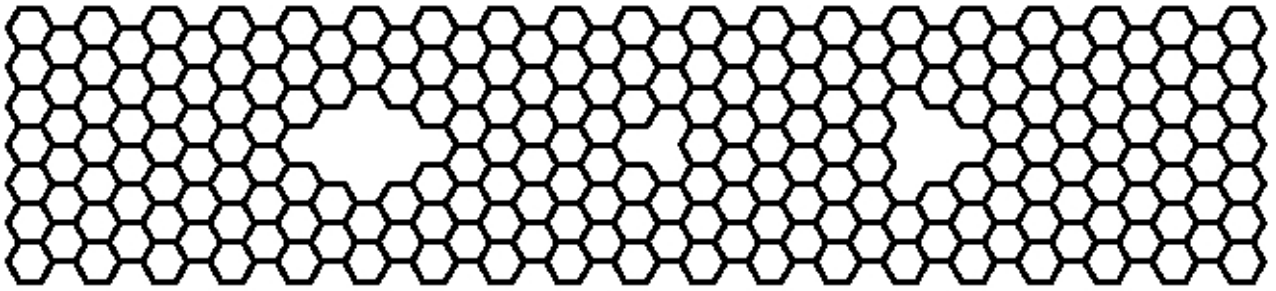
J. Fernández-Rossier and J. J. Palacios, Phys. Rev. Lett. **99**, 177204 (2007)





Vacancies and voids in graphene and graphene ribbons

J. J. Palacios, J. Fernández-Rossier, and L. Brey, Phys. Rev. B **77**, 195428 (2008)



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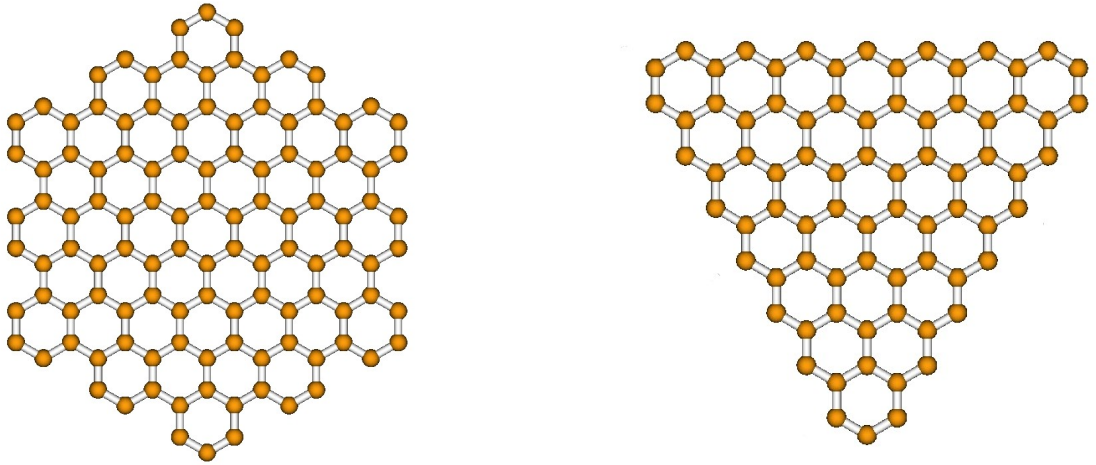

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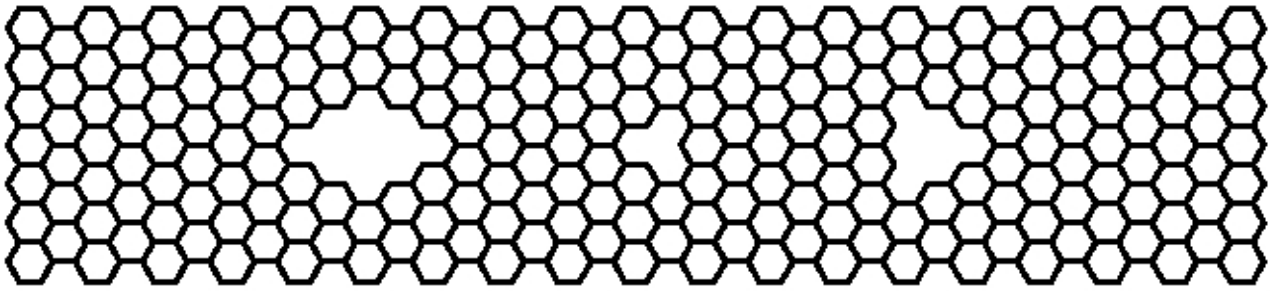
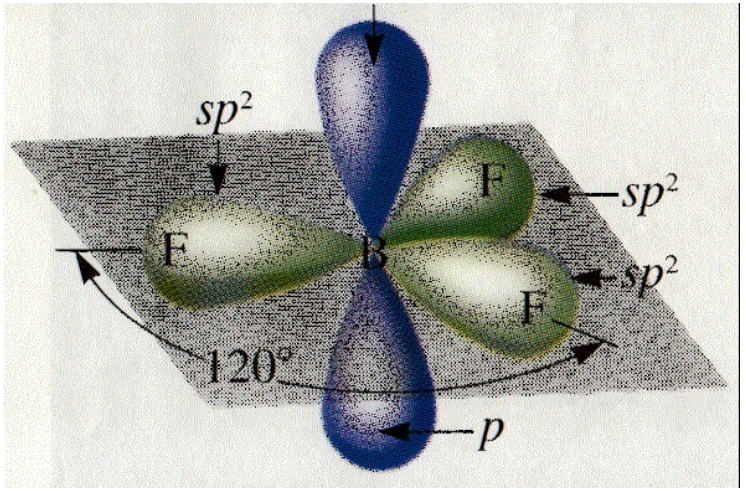


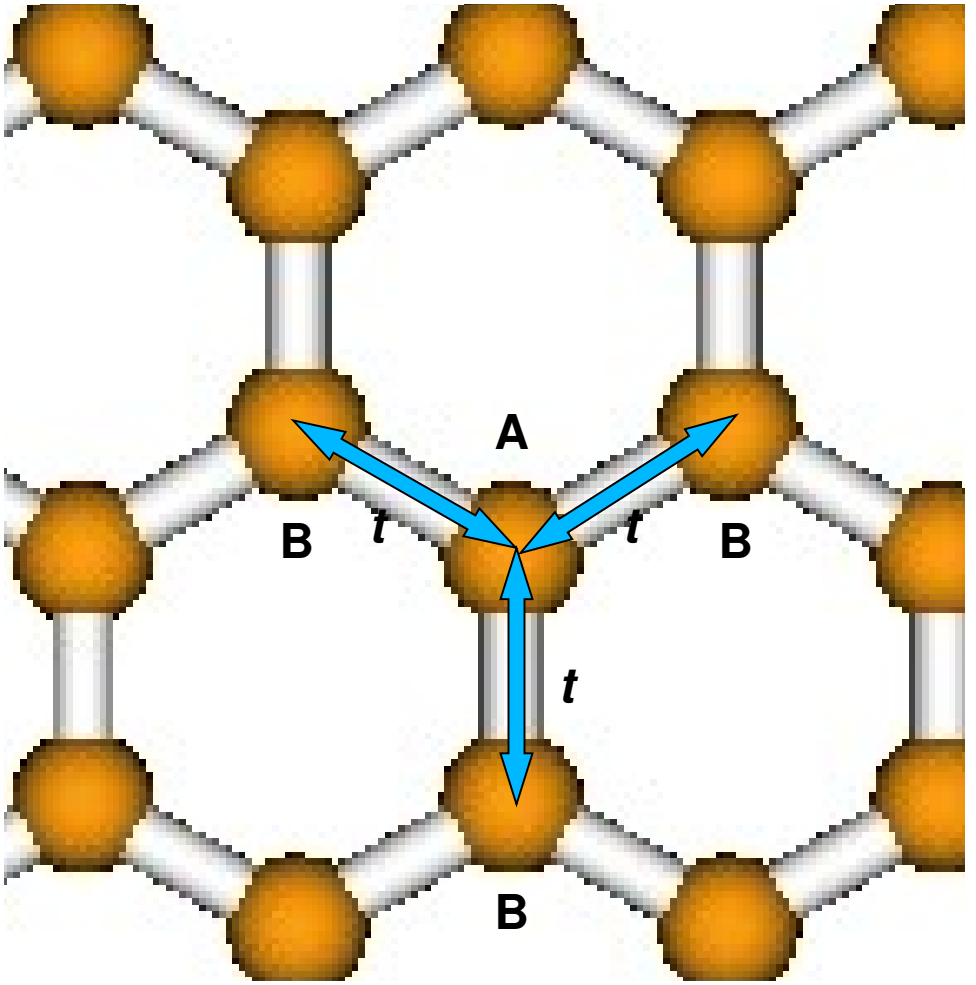
Theoretical description of graphene



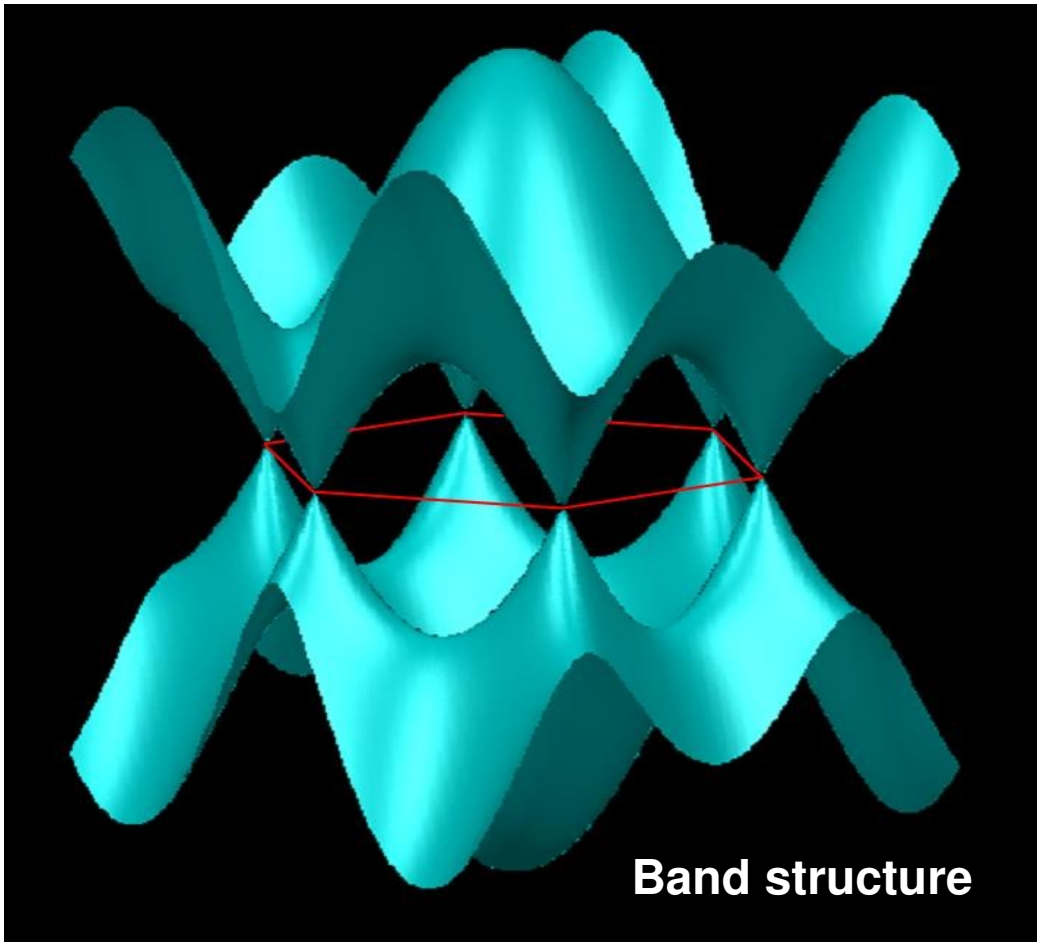
$$\hat{H} = \sum_i \varepsilon_i \hat{n}_i + \sum_{ij} t_{ij} \hat{c}_i^+ \hat{c}_j$$

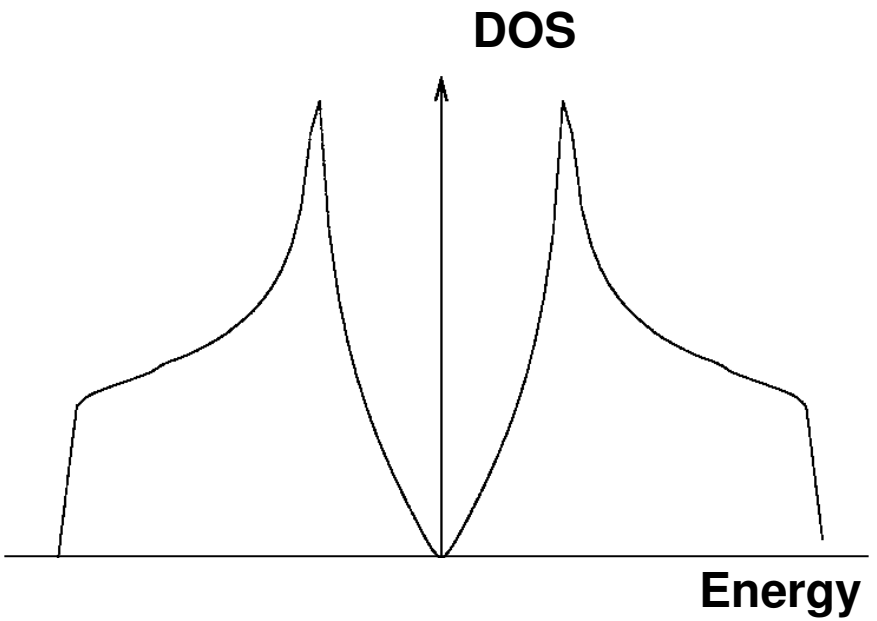
$t_{ij} = t = 2.5\,\text{eV}$ if first neighbors

usually $\varepsilon_i = 0$

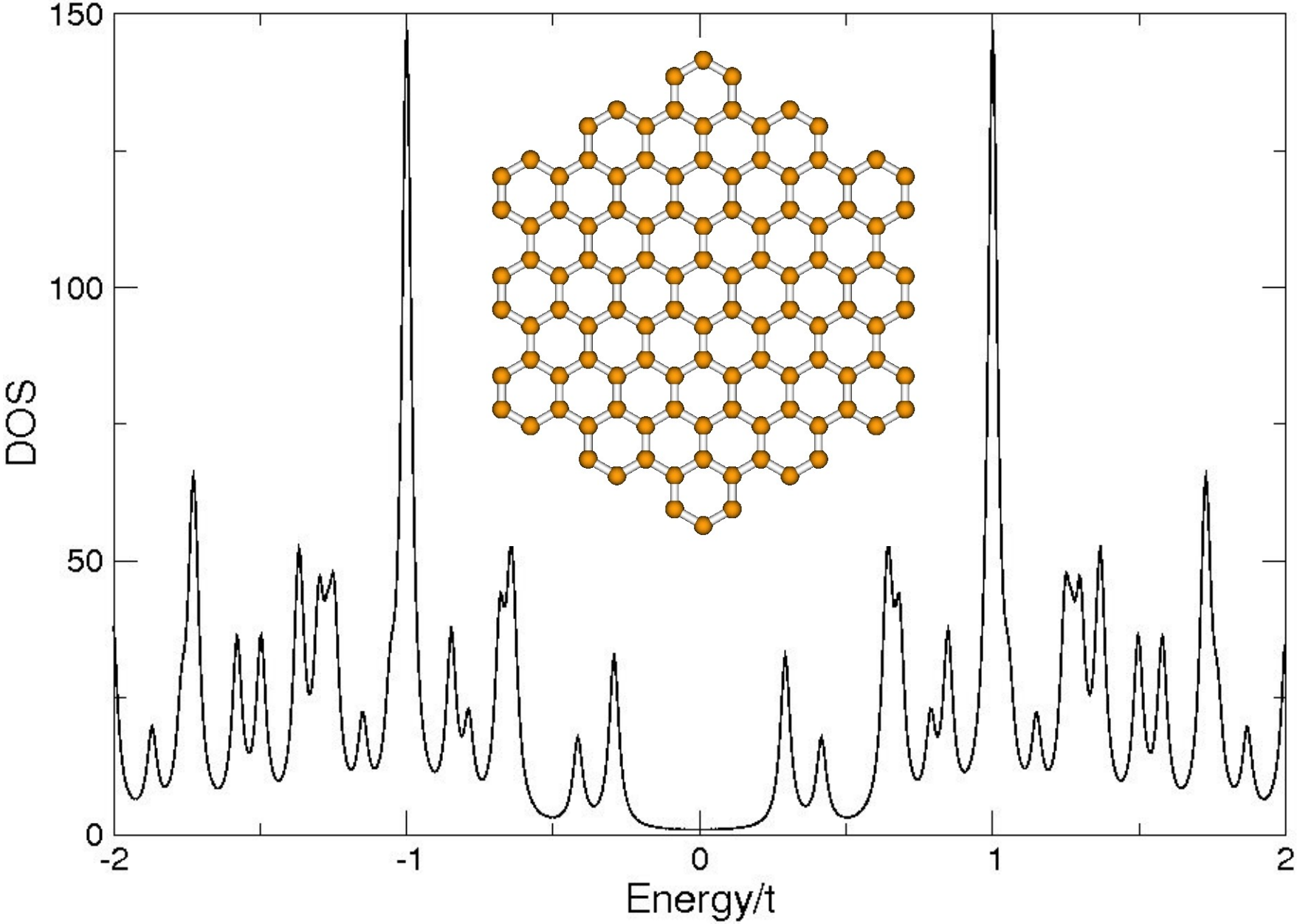


Electronic structure of graphene





Nanographenes



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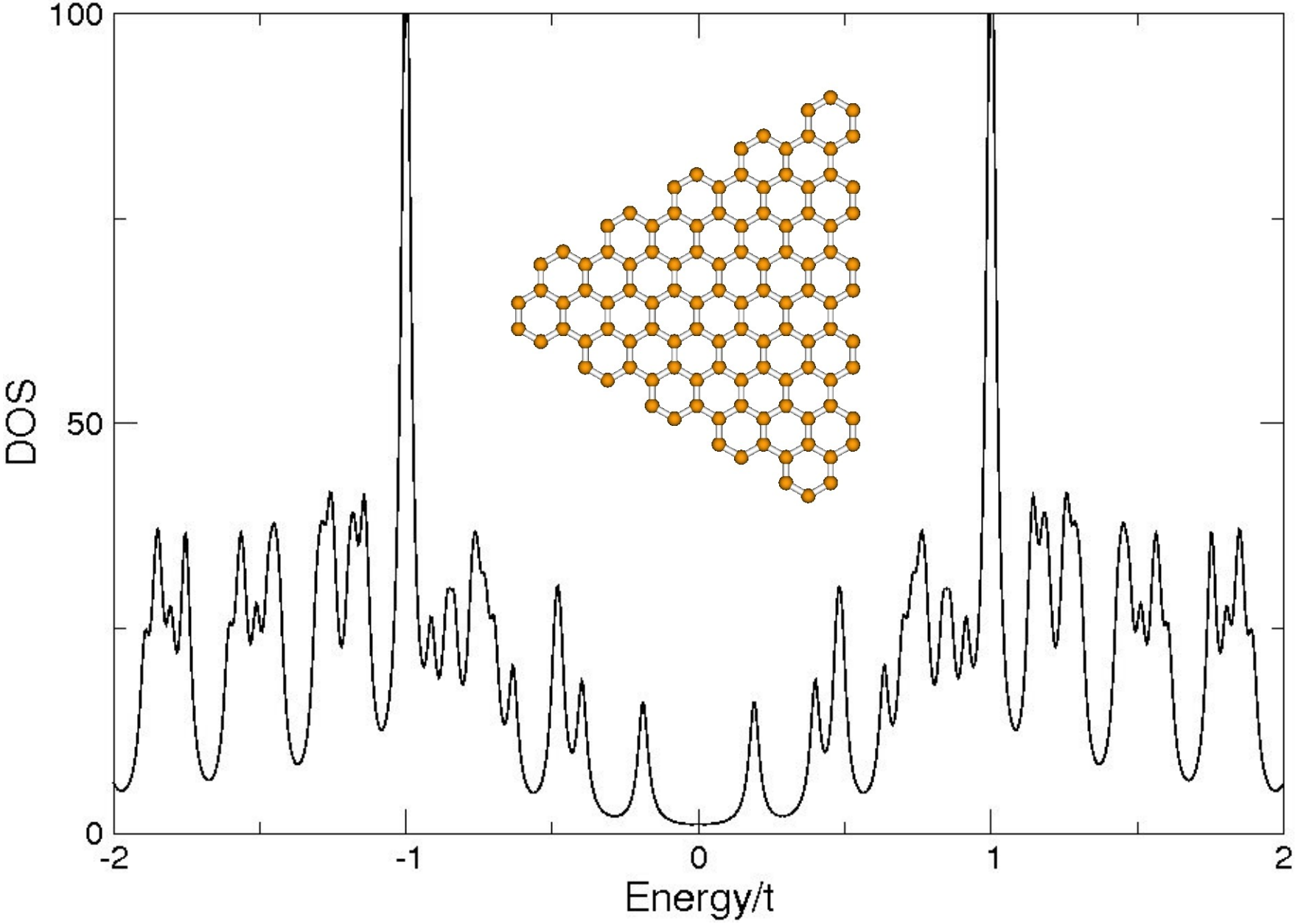
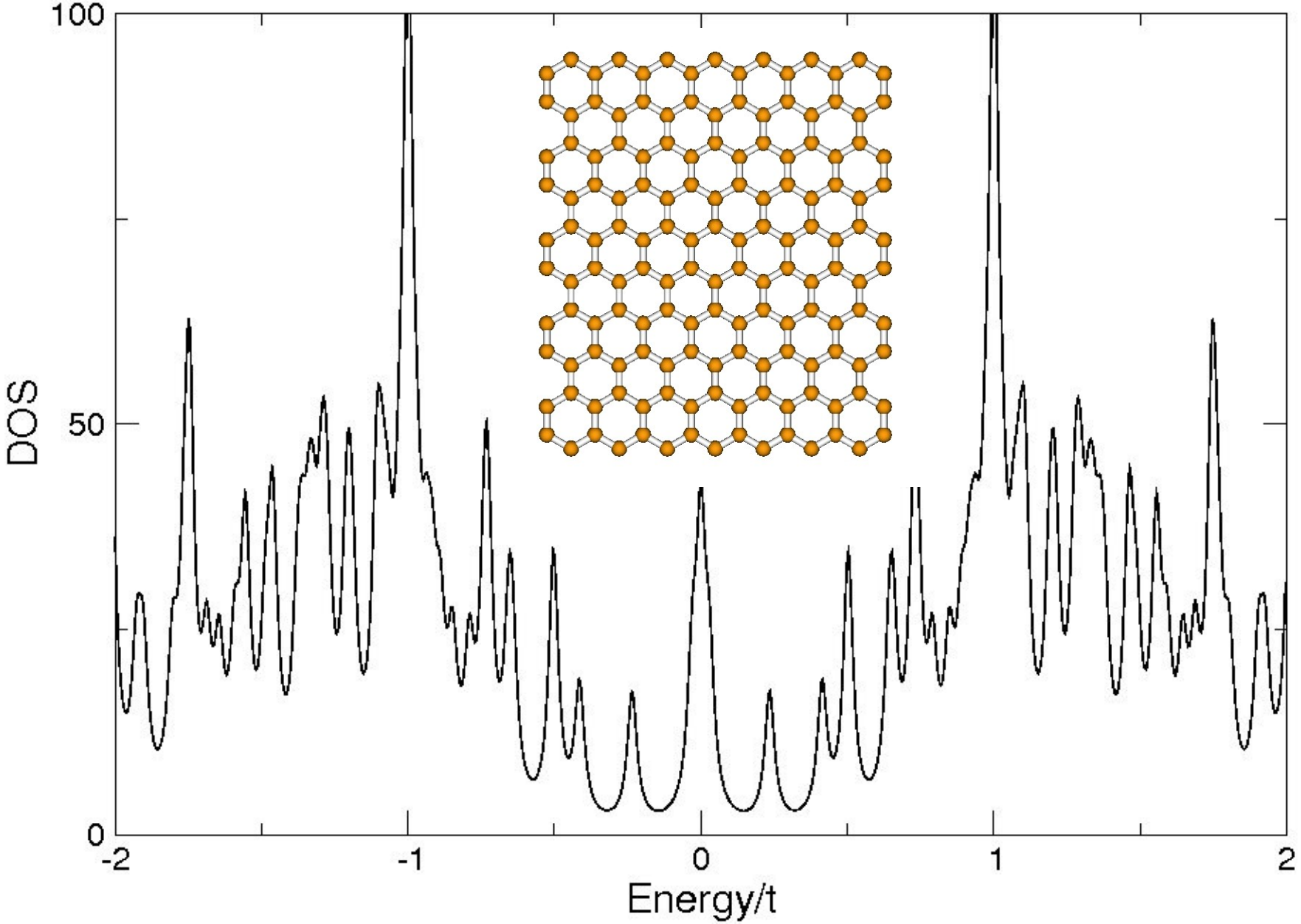
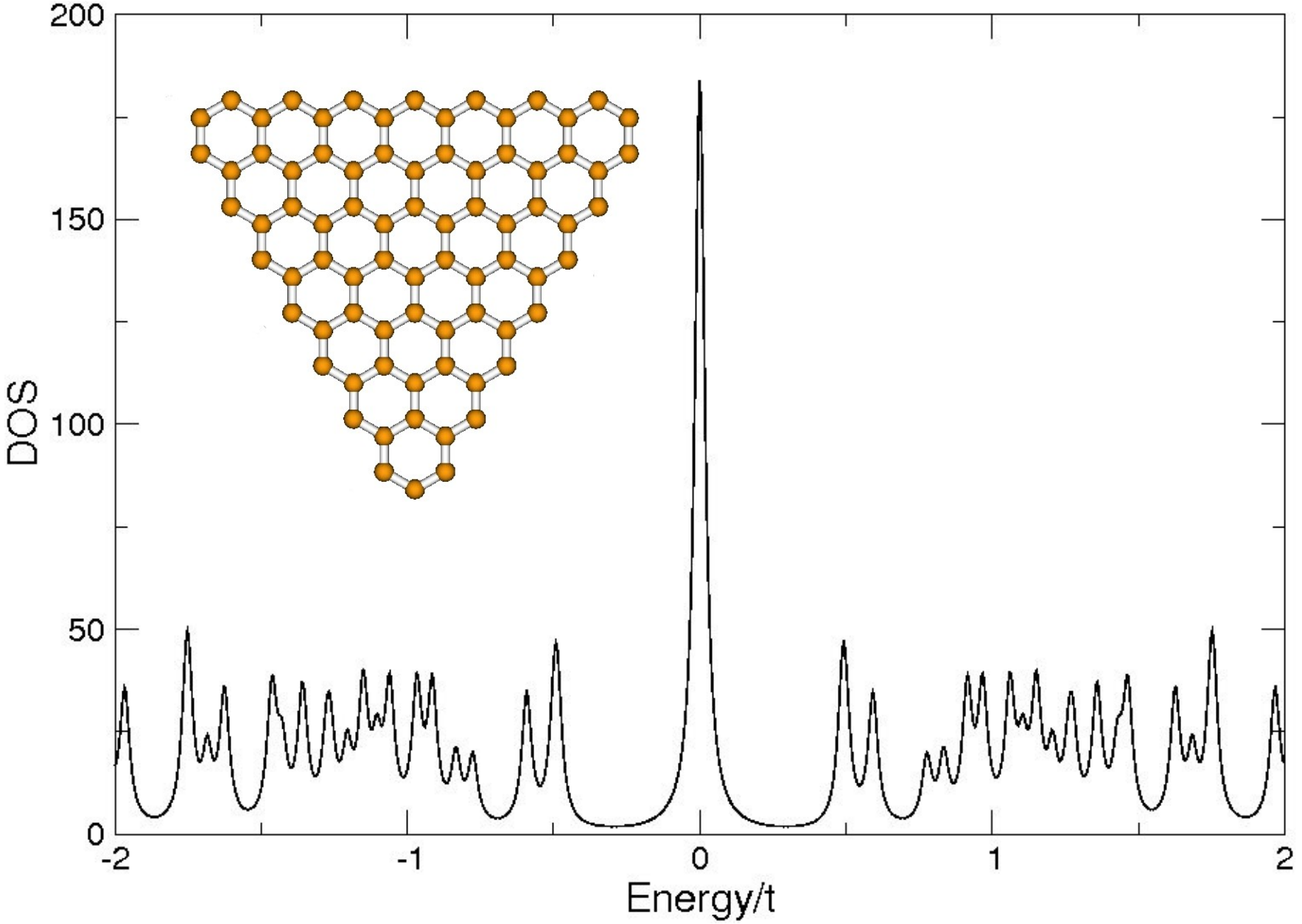


Nanographenes



Nanographenes



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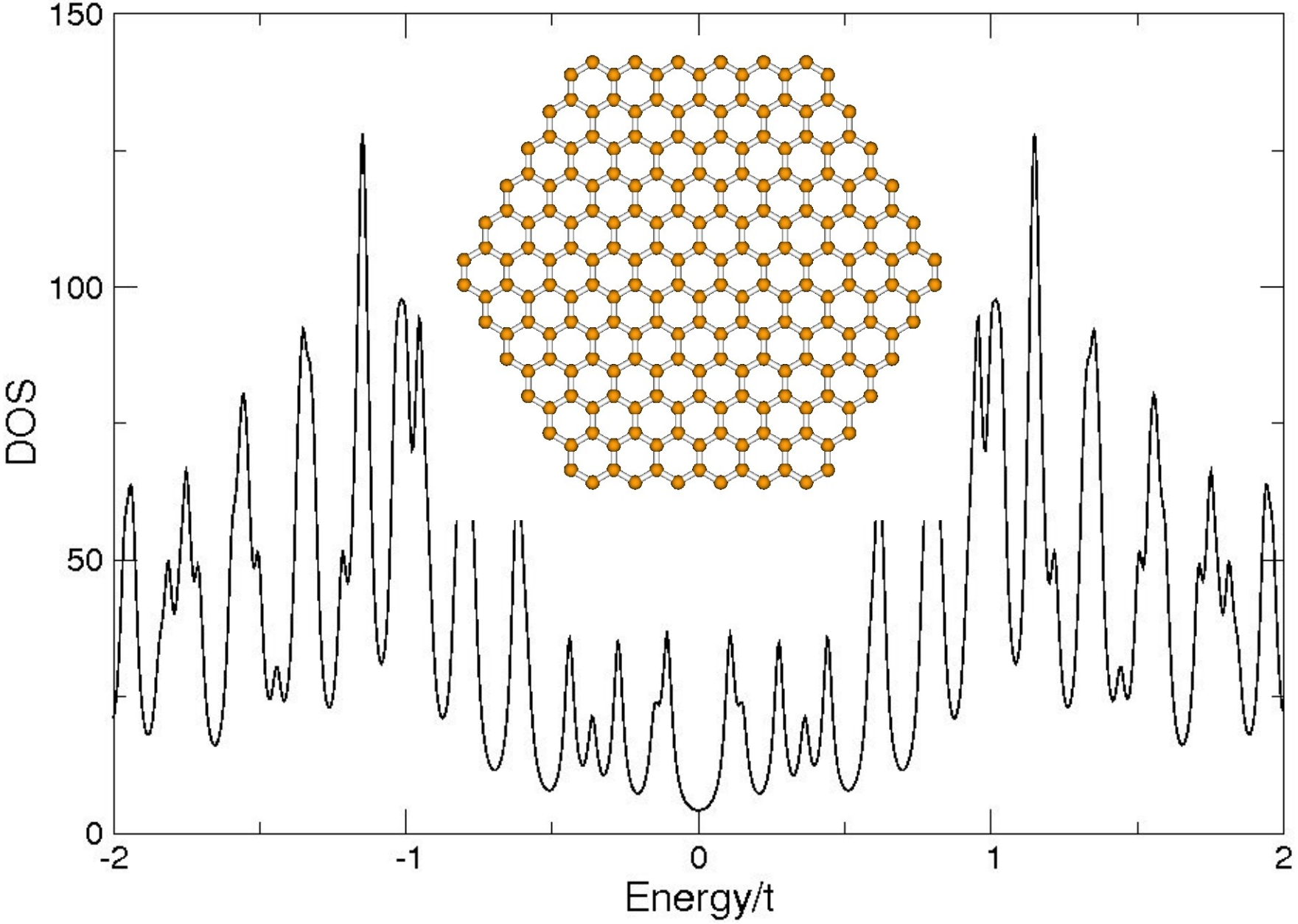


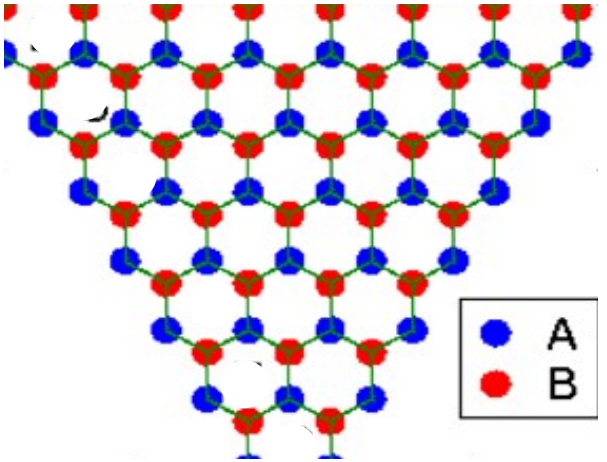
Understanding the spectra

$$\hat{P}_A = \sum_{i \in A} |i\rangle\langle i| \qquad \hat{P}_B = \sum_{j \in B} |j\rangle\langle j|$$

$$\hat{H}\left(\hat{P}_A + \hat{P}_B\right)|\phi\rangle = E\left(\hat{P}_A + \hat{P}_B\right)|\phi\rangle$$

$$\hat{H}\hat{P}_A|\phi\rangle = E\hat{P}_B|\phi\rangle \quad \text{and} \quad \hat{H}\hat{P}_B|\phi\rangle = E\hat{P}_A|\phi\rangle$$

$$H\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle = E\left(\hat{P}_B - \hat{P}_A\right)|\phi\rangle = -E\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle$$



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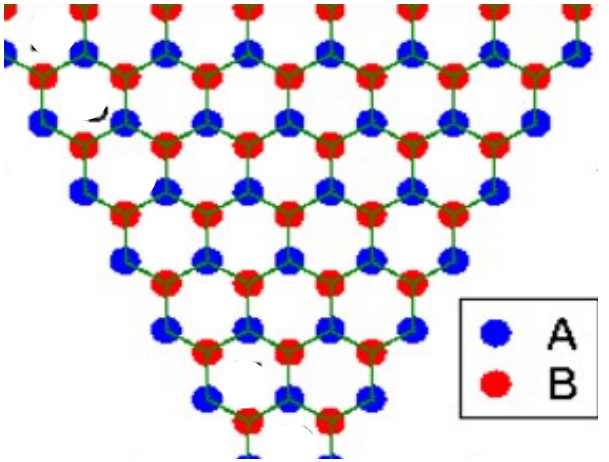
$$\hat{H}\hat{P}_A|\phi\rangle = E\hat{P}_B|\phi\rangle \quad \text{and} \quad \hat{H}\hat{P}_B|\phi\rangle = E\hat{P}_A|\phi\rangle$$

$$H\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle = E\left(\hat{P}_B - \hat{P}_A\right)|\phi\rangle = -E\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle$$



What if N odd, e.g., $N_A - N_B = 1$?

At least 1 state with $E = 0$

Let us consider a state with weight only on sites A :

$$\left.\begin{aligned} &\hat{H}|\phi\rangle_A = E|\phi\rangle_A \\ &\hat{H}\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle_A = -E\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle_A \Rightarrow \hat{H}|\phi\rangle_A = -E|\phi\rangle_A \end{aligned}\right\} \Rightarrow E = 0$$

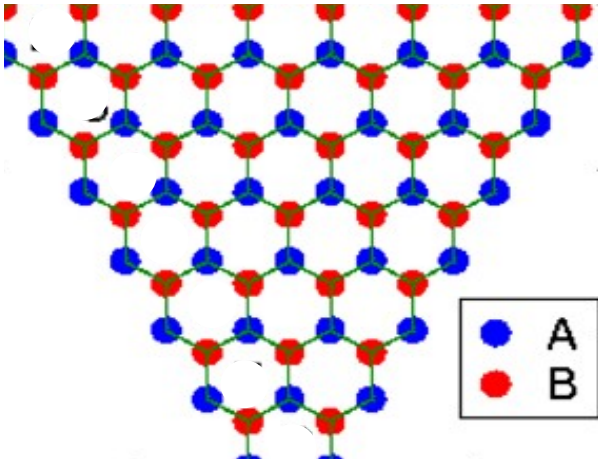
Understanding the spectra

$$\hat{P}_A = \sum_{i\in A} |i\rangle\langle i| \qquad \hat{P}_B = \sum_{j\in B} |j\rangle\langle j|$$

$$\hat{H}\left(\hat{P}_A + \hat{P}_B\right)|\phi\rangle = E\left(\hat{P}_A + \hat{P}_B\right)|\phi\rangle$$

$$\hat{H}\hat{P}_A|\phi\rangle = E\hat{P}_B|\phi\rangle \quad \text{and} \quad \hat{H}\hat{P}_B|\phi\rangle = E\hat{P}_A|\phi\rangle$$

$$H\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle = E\left(\hat{P}_B - \hat{P}_A\right)|\phi\rangle = -E\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle$$



M. Inui, S. A. Trugman, and E. Abrahams
Phys. Rev. B **49**, 3190 (1994)

What if N odd, e.g., $N_A - N_B = 1$?

At least 1 state with $E = 0$

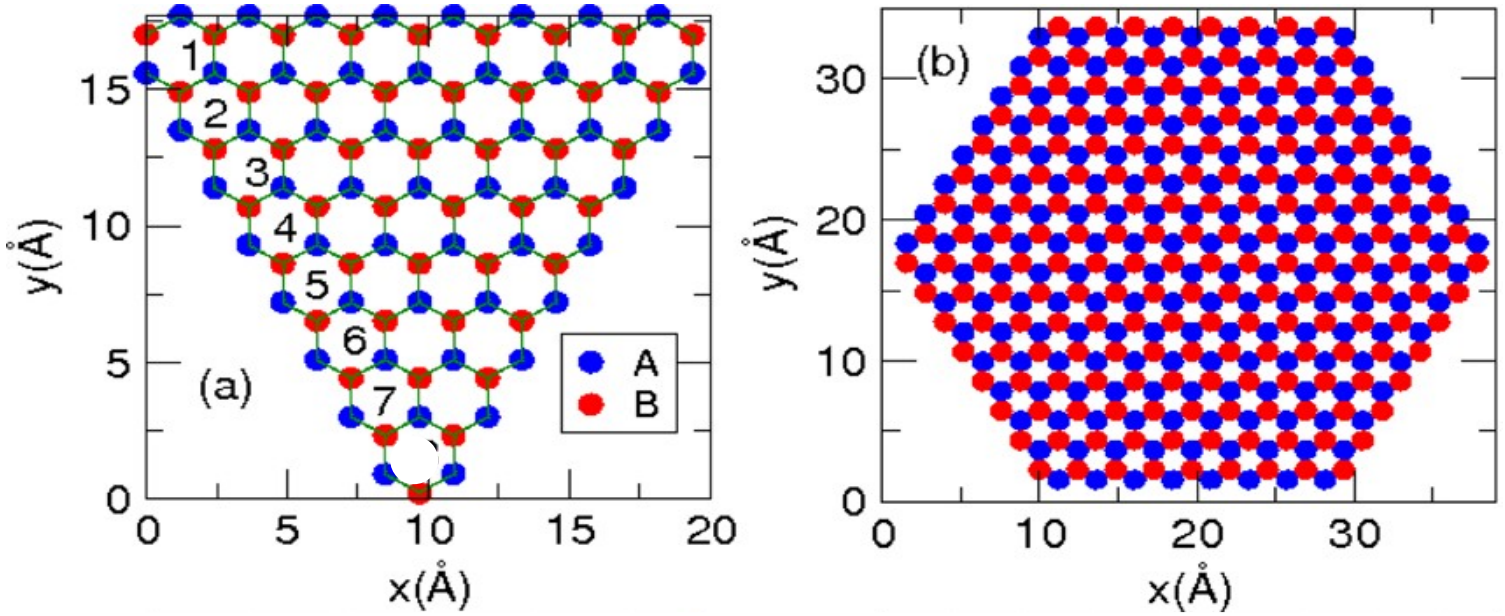
Let us consider a state with weight only on sites A :

$$\left.\begin{aligned} &\hat{H}|\phi\rangle_A = E|\phi\rangle_A \\ &\hat{H}\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle_A = -E\left(\hat{P}_A - \hat{P}_B\right)|\phi\rangle_A \Rightarrow \hat{H}|\phi\rangle_A = -E|\phi\rangle_A \end{aligned}\right\} \Rightarrow E = 0$$

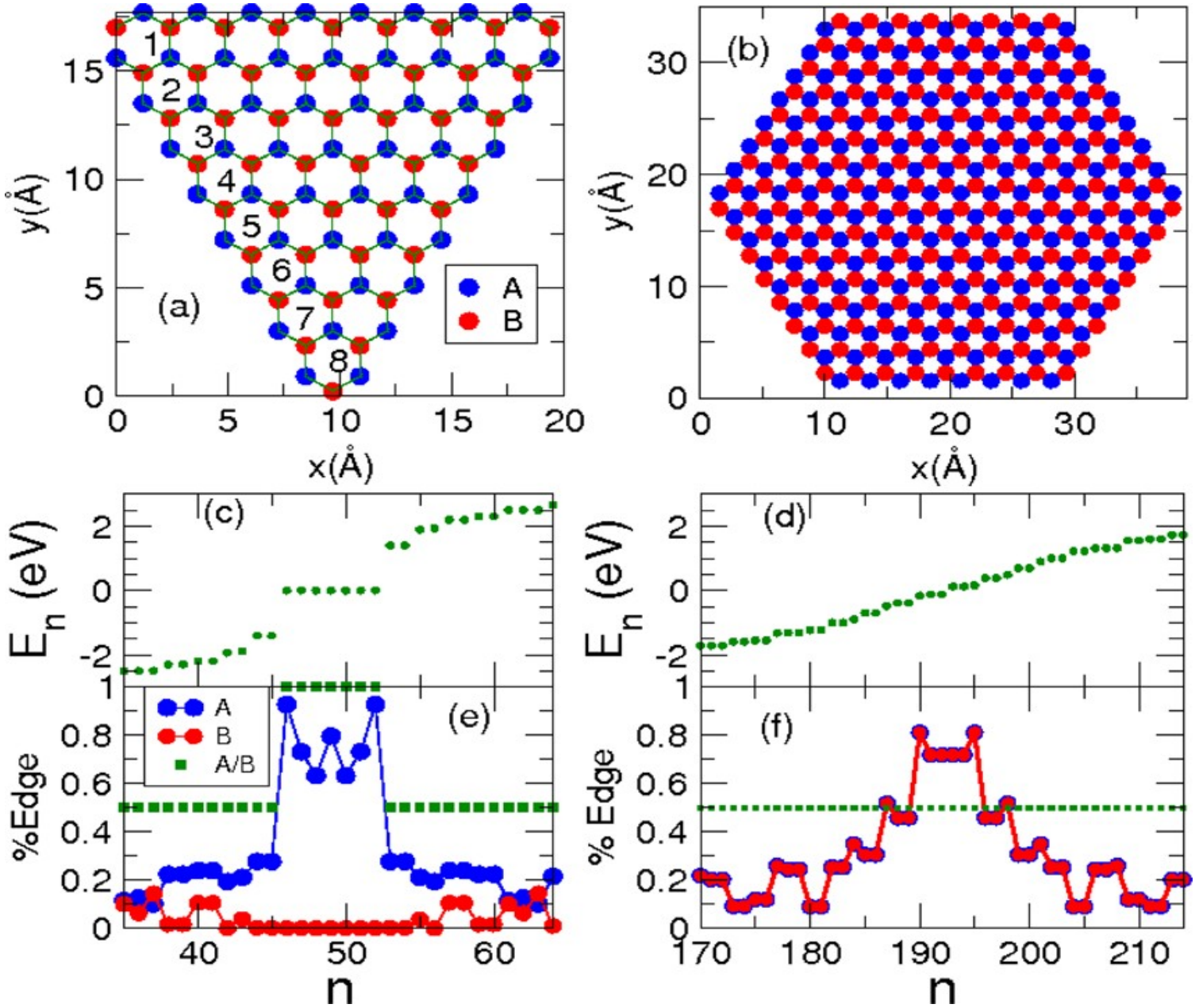
What if $N_A - N_B > 1$?

At least $N_A - N_B$ states with $E = 0$ and weight only on sites A

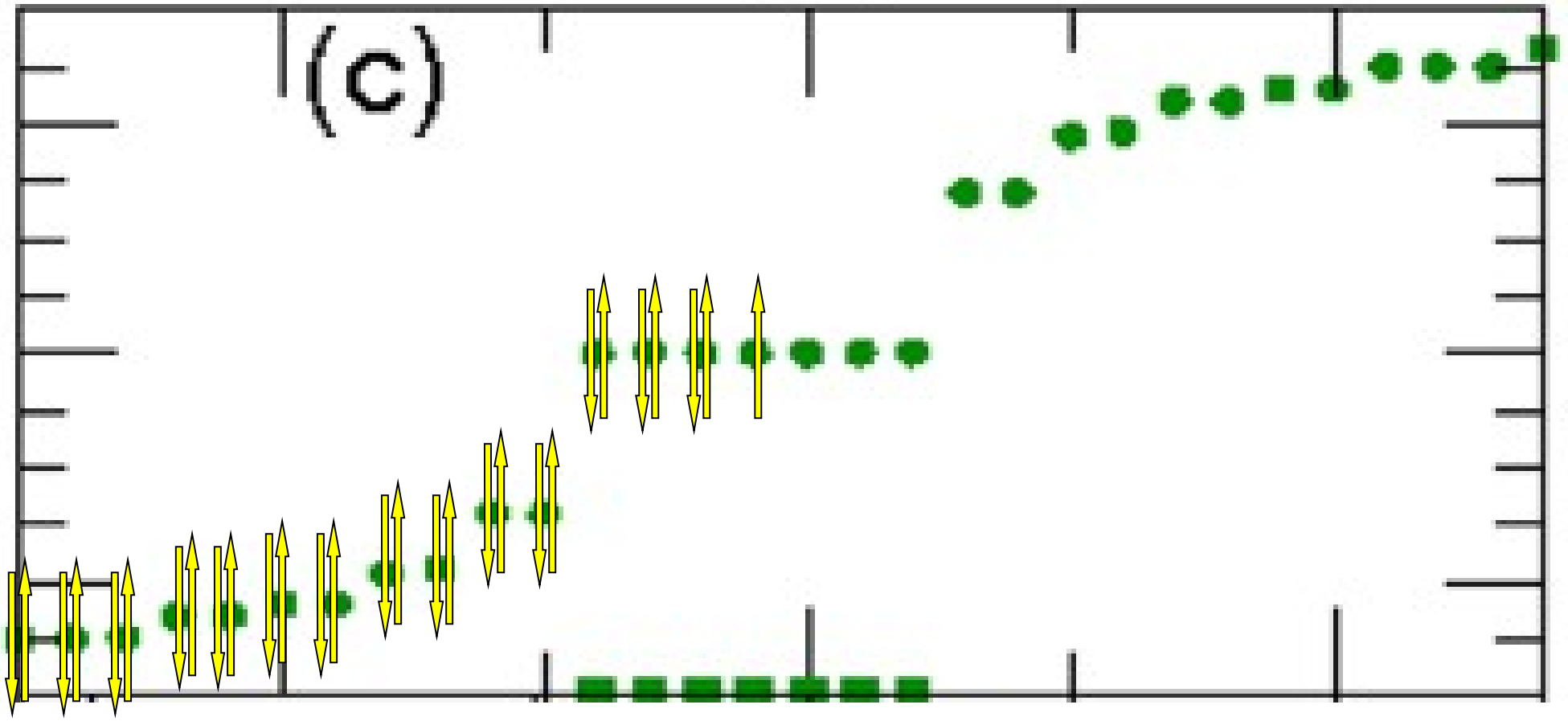
Triangles vs. hexagons



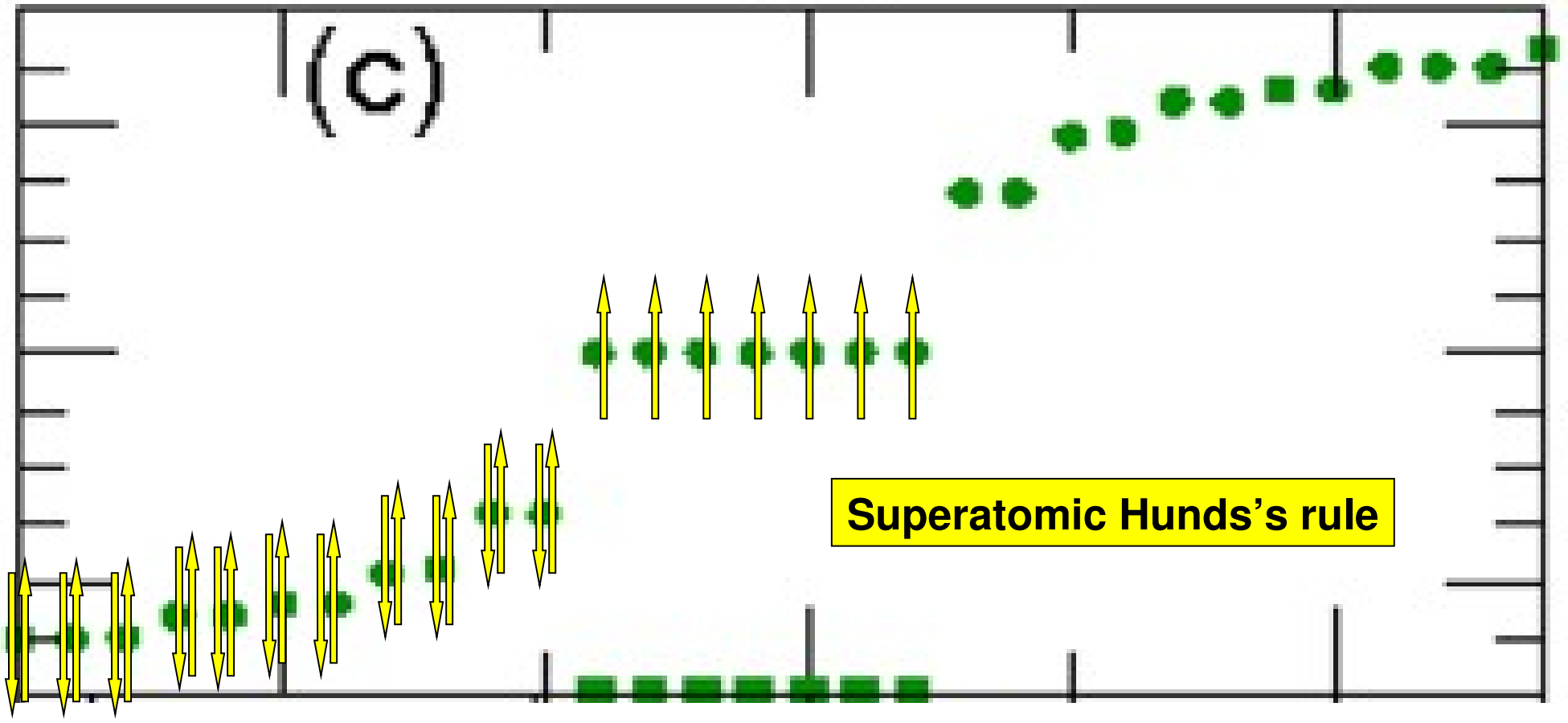
Triangles vs. hexagons



Electron-electron interactions



Electron-electron interactions



Electron-electron interactions

Hubbard model

$$H = \sum_{i\sigma} \varepsilon_{i\sigma} \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} \hat{c}^{+}_{i\sigma} \hat{c}_{j\sigma} + \mathrm{U} \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

Mean field self - consistent approximation :

$$H = \sum_{i\sigma} \varepsilon_{i\sigma} \hat{n}_{i\sigma} + \sum_{ij\sigma} t_{ij} \hat{c}^{+}_{i\sigma} \hat{c}_{j\sigma} + \mathrm{U} \sum_{i} \left(\left\langle \hat{n}_{i\uparrow} \right\rangle \hat{n}_{i\downarrow} + \left\langle \hat{n}_{i\downarrow} \right\rangle \hat{n}_{i\uparrow} \right) + \mathrm{cte}$$

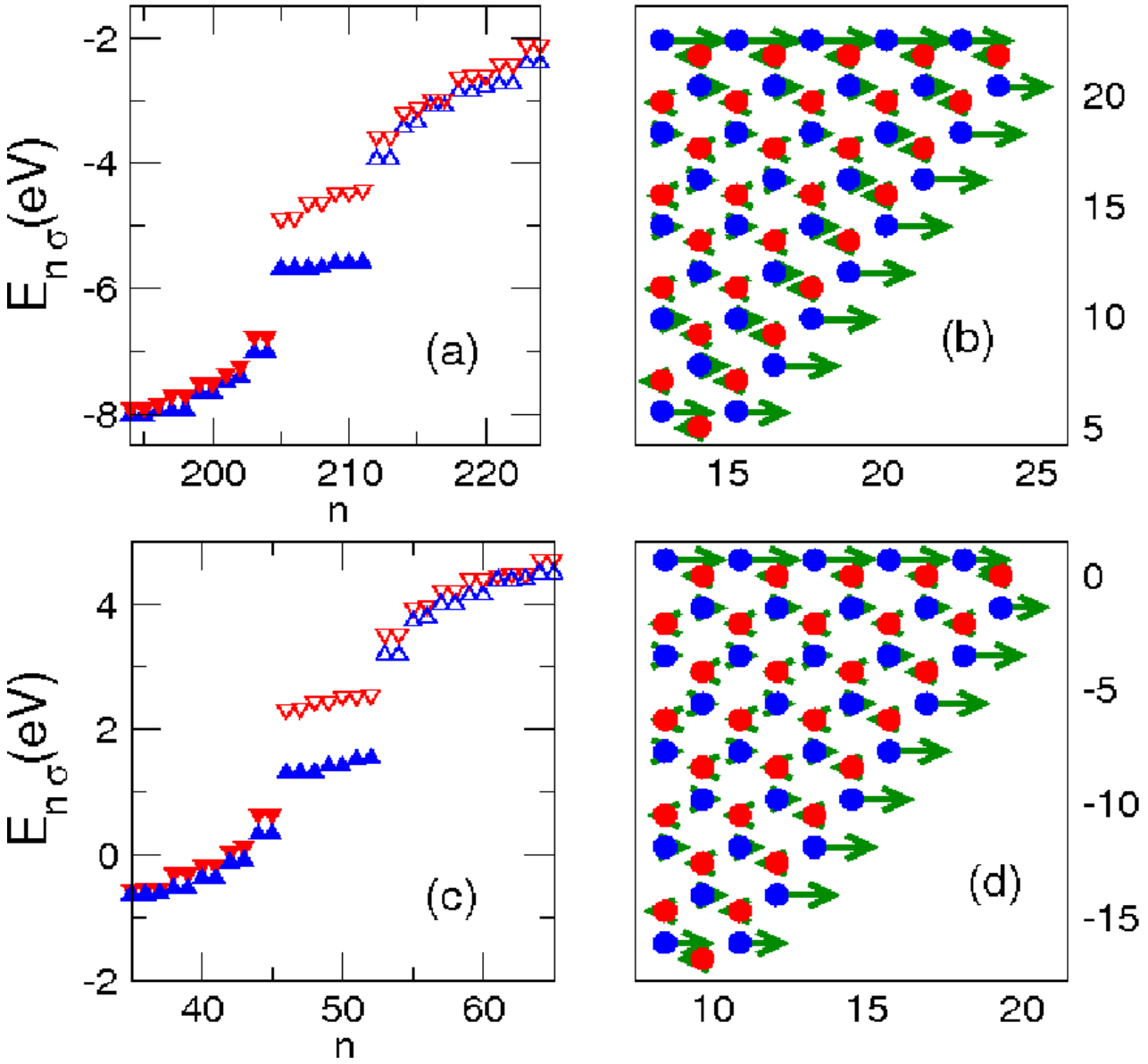
Density functional theory
(GAUSSIAN03)

- Kohn-Sham equations (unrestricted)
- GGA (BLYP) approximation to the functional (avoid hybrids, e.g., B3LYP)
- Saturation of dangling bonds with H

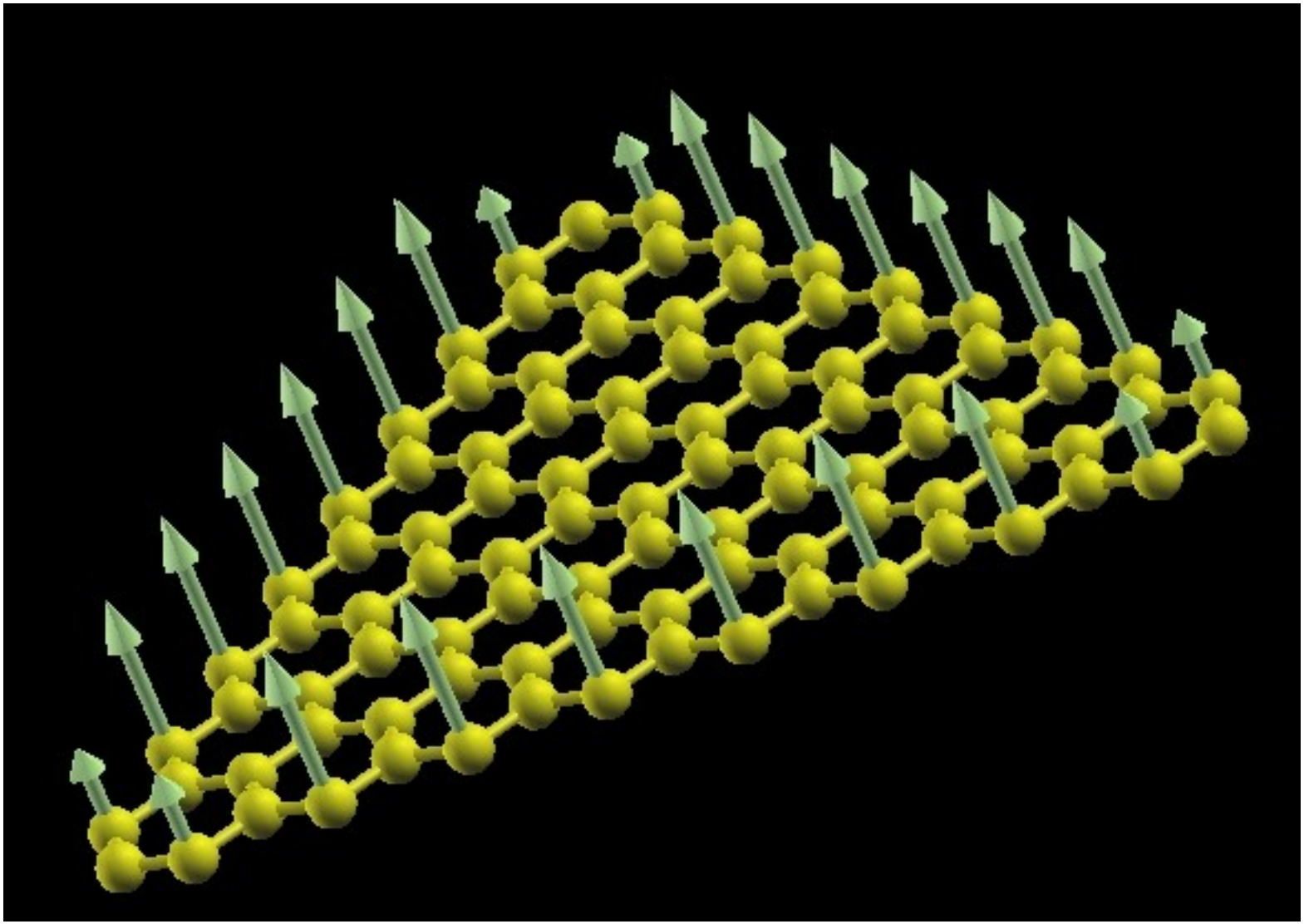
DFT vs mean-field Hubbard

Hubbard model
(*U*=3.85 eV, t=2.5 eV)

DFT



Ferromagnetic order



Lieb's theorem/ Longuet-Higgins conjecture

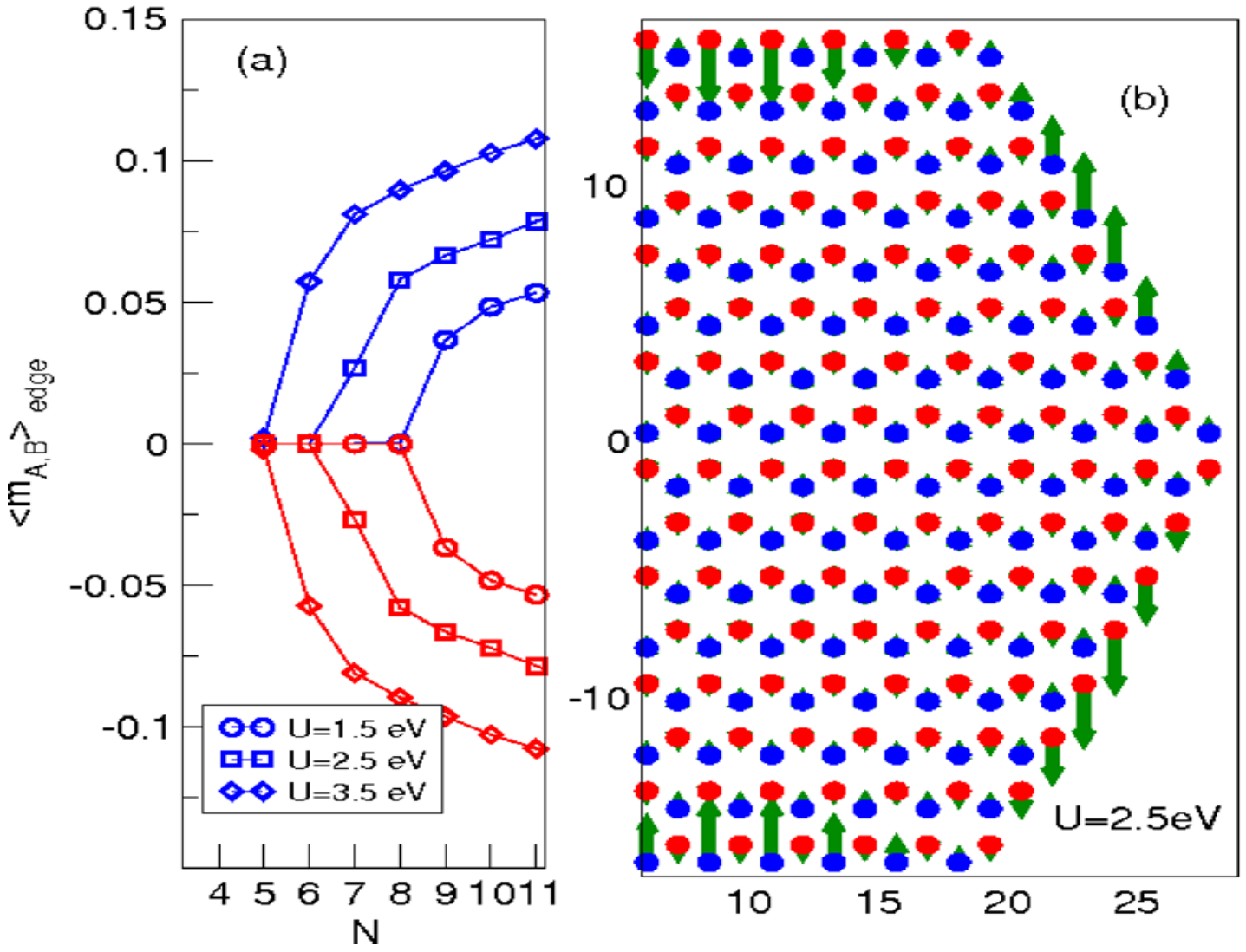
E. H. Lieb. Phvs. Rev. Lett. 62. 1201 (1989)

In the attractive Hubbard model (and some extended versions of it), the ground state is proved to have spin angular momentum $S=0$ for every (even) electron filling. In the repulsive case, and with a bipartite lattice and a half-filled band, the ground state has $S=\frac{1}{2}\,|\,|B|-|A|\,|$, where $|B|$ ($|A|$) is the number of sites in the B (A) sublattice. In both cases the ground state is unique. The second theorem confirms an old, unproved conjecture in the $|B|=|A|$ case and yields, with $|B|\neq|A|$, the first provable example of itinerant-electron ferromagnetism. The theorems hold in all dimensions without even the necessity of a periodic lattice structure.

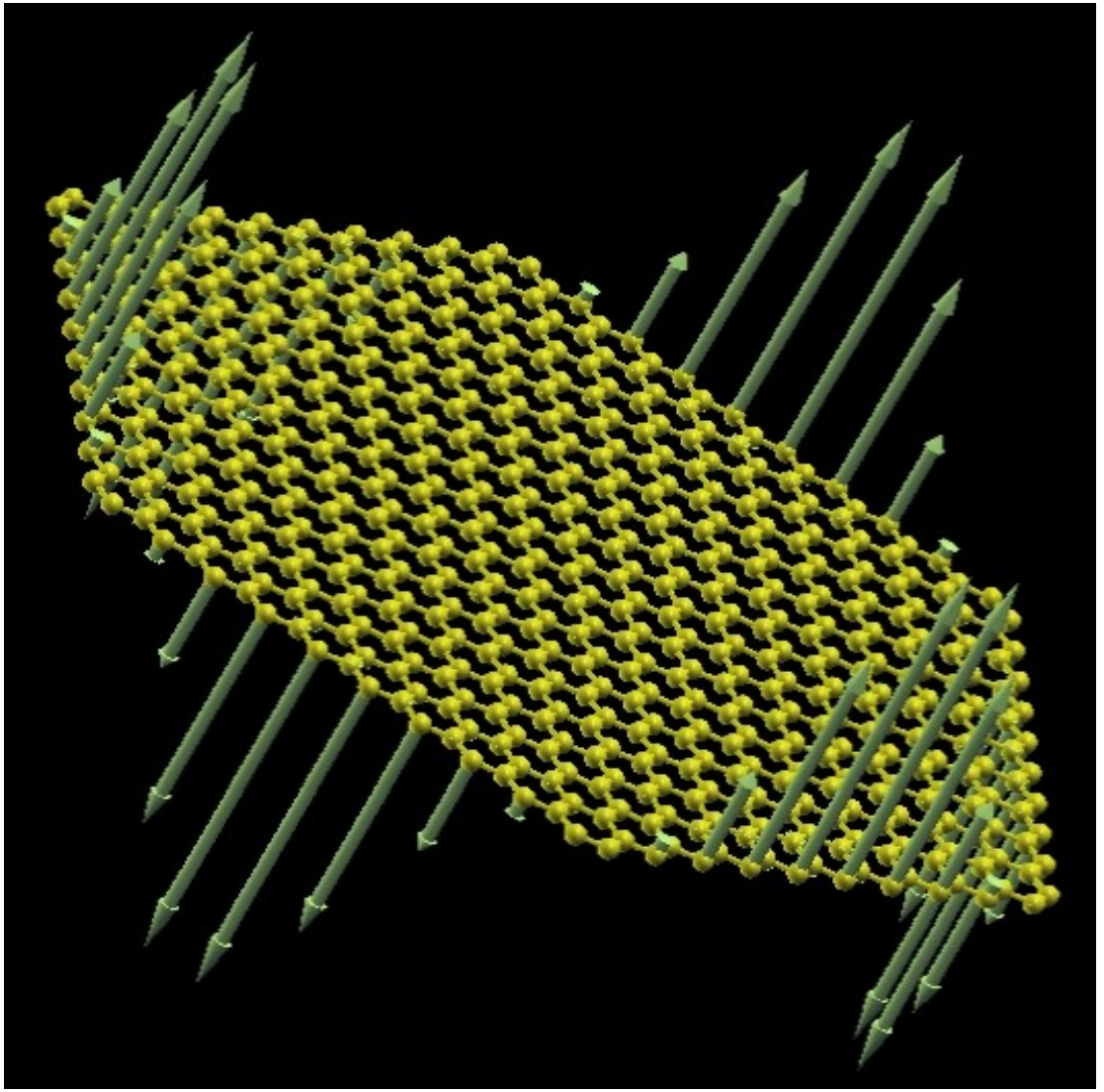
Longuet-Higgins, J. Chem. Phys. 18, 265 (1950)

(1) The number of unpaired electrons present in the ground state is at least as great as the number of carbon atoms having a deficiency of valence bonds in any principal resonance structure. (2) With a few special exceptions, these odd electrons are distributed over just those atoms which have a deficiency of valence bonds in one or more of the principal resonance structures. (3) In singly charged hydrocarbon anions or cations the ionic charge is located on just those atoms which bear charges in the various principal resonance structures.

Ferrimagnetic order



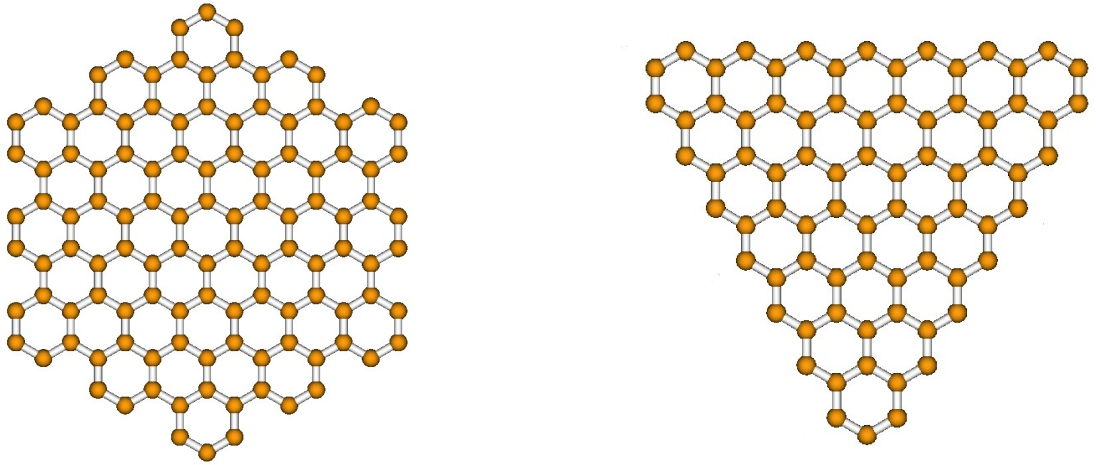
Ferrimagnetic order



Outline

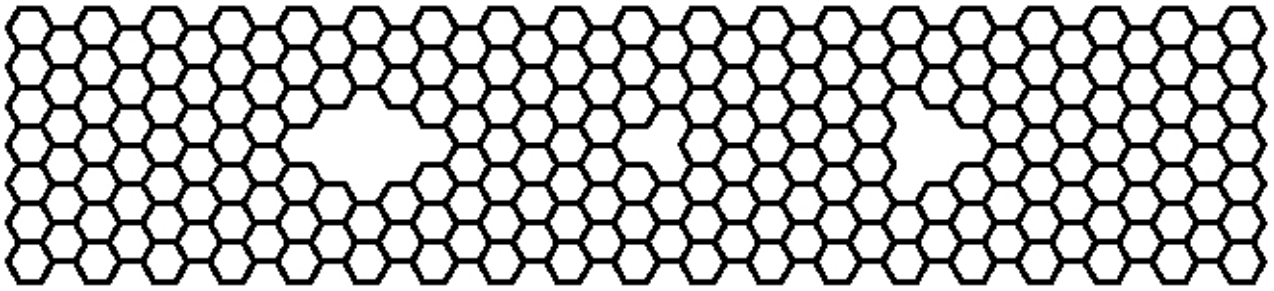
Nanographenes

J. Fernández-Rossier and J. J. Palacios, Phys. Rev. Lett. **99**, 177204 (2007)

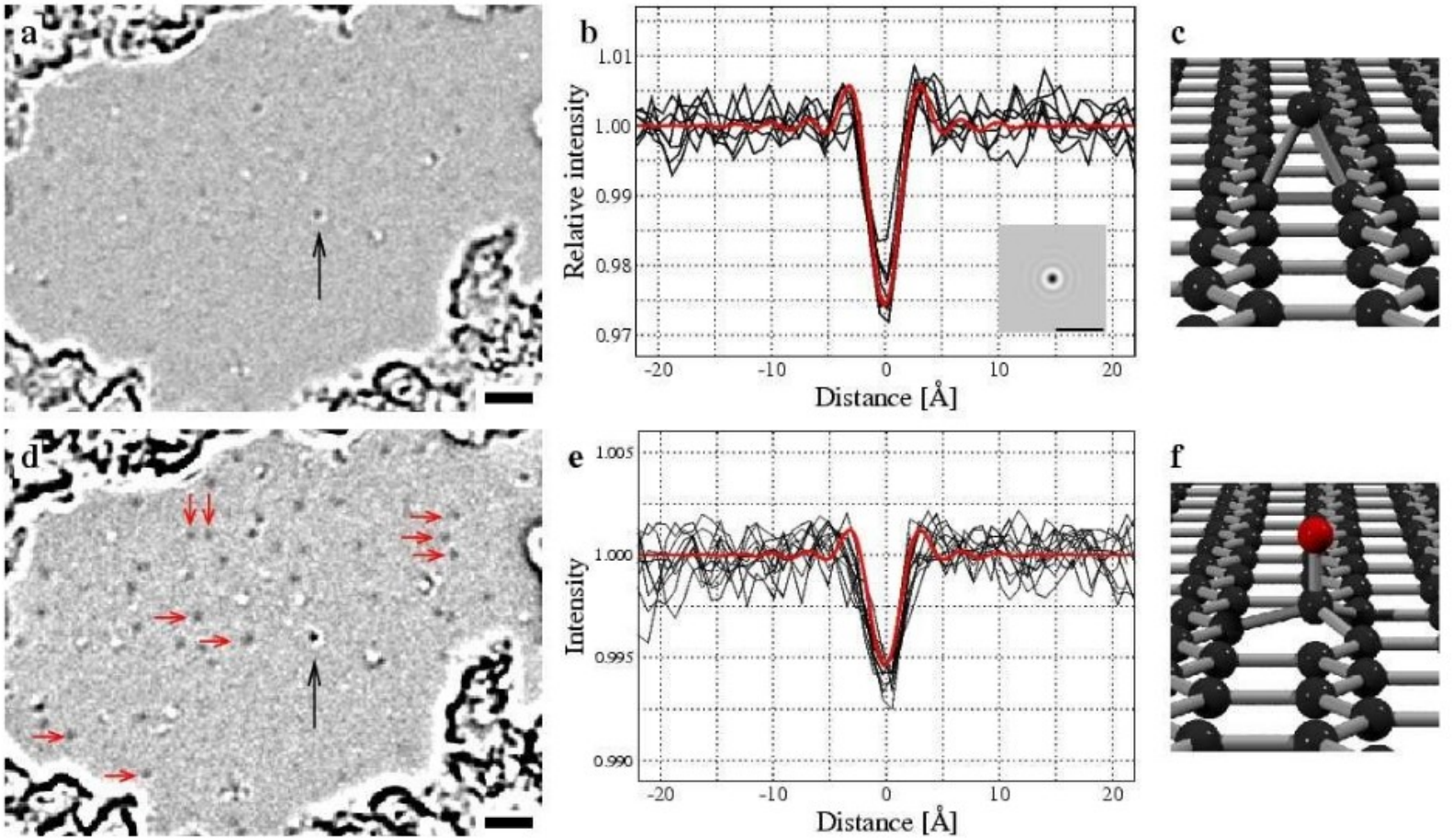


Vacancies and voids in graphene and graphene ribbons

J. J. Palacios, J. Fernández-Rossier, and L. Brey, Phys. Rev. B **77**, 195428 (2008)

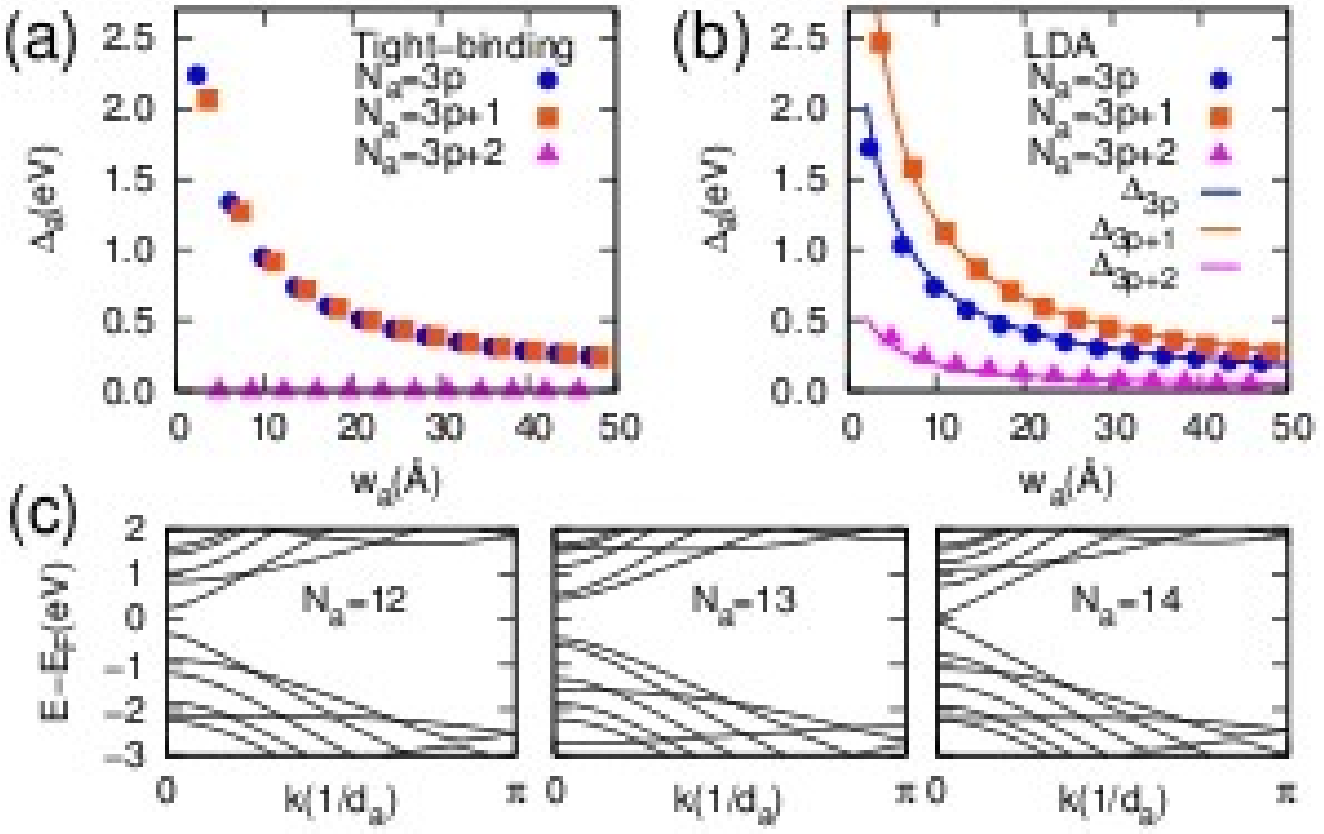


Vacancies = H adsorption



Jannik C. Meyer, C. O. Girit, M. F. Crommie, A. Zettl, arXiv:08053857

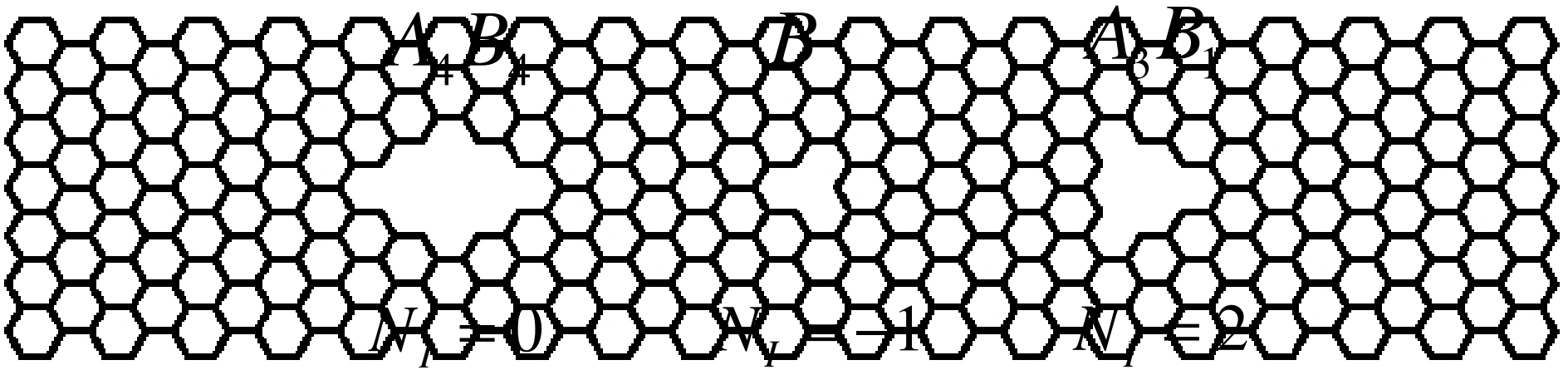
A few words about ribbons (armchair)



Son et al., Phys. Rev. Lett. 97, 216803 (2006)

Basic definitions

$$A_{N_A} B_{N_B}$$



$$\text{Local imbalance charge}: \quad N_A - N_B = N_I$$

$$N_Z^{\min} = \left| \sum_{\alpha} N_I^{+}(\alpha) + \sum_{\beta} N_I^{-}(\beta) \right|$$

$$N_Z^{\max} = \sum_{\alpha} \left| N_I^{+}(\alpha) \right| + \sum_{\beta} \left| N_I^{-}(\beta) \right|$$

Basic scenarios

1. $\boxed{N_Z^{\min} = N_Z = N_Z^{\max}}$: All the voids are of the same sign. The coupling between them is always ferromagnetic and the spin of the ground state is $2S = N_Z$. The splitting with smaller spin states will depend on the inter - void coupling.

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2. $\boxed{N_Z^{\min} = N_Z < N_Z^{\max}}$: All the voids of different sign are in proximity and interact, yielding a $2S = N_Z^{\min}$ state. Calculations will be necessary to ascertain the spin texture in these situations.

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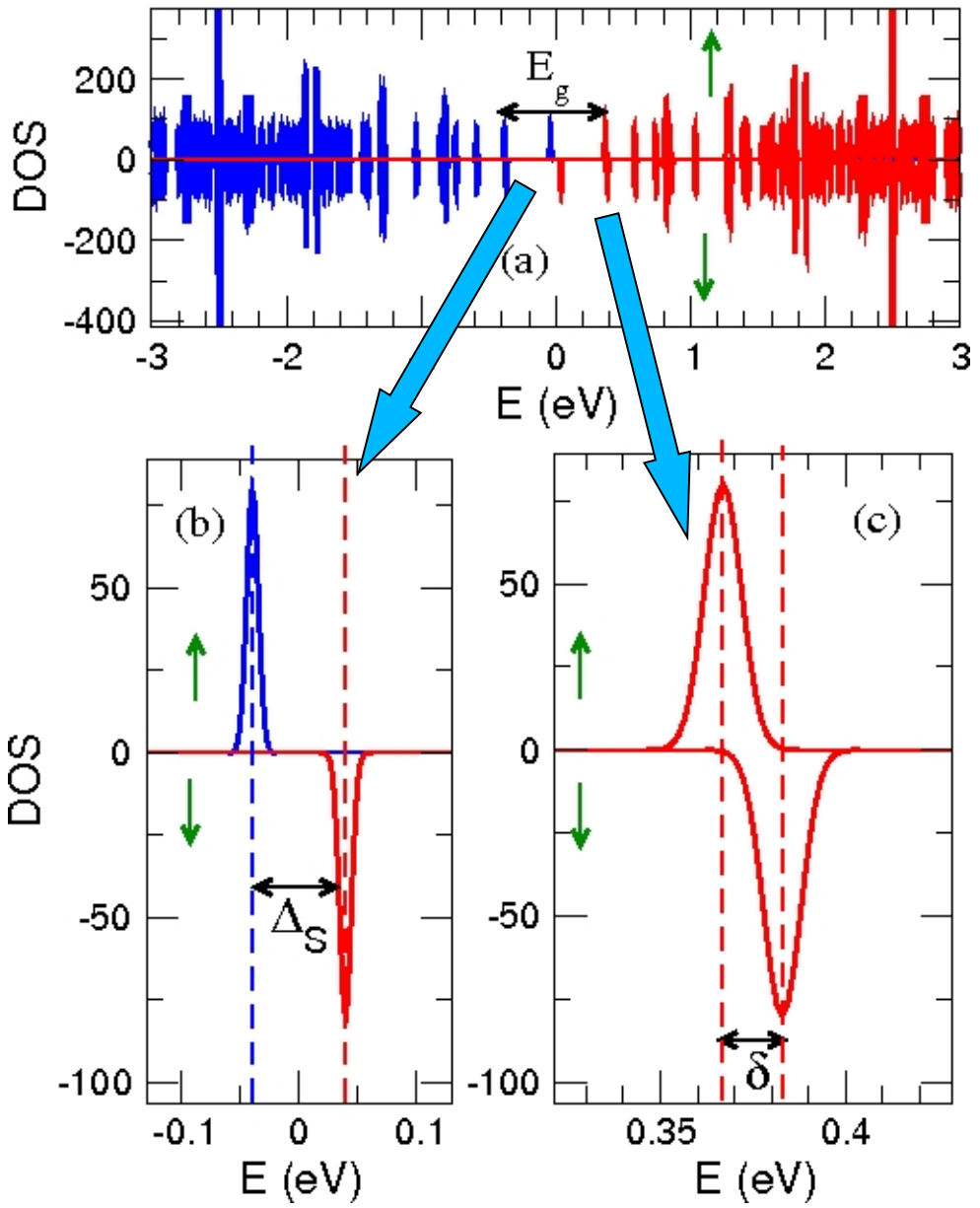
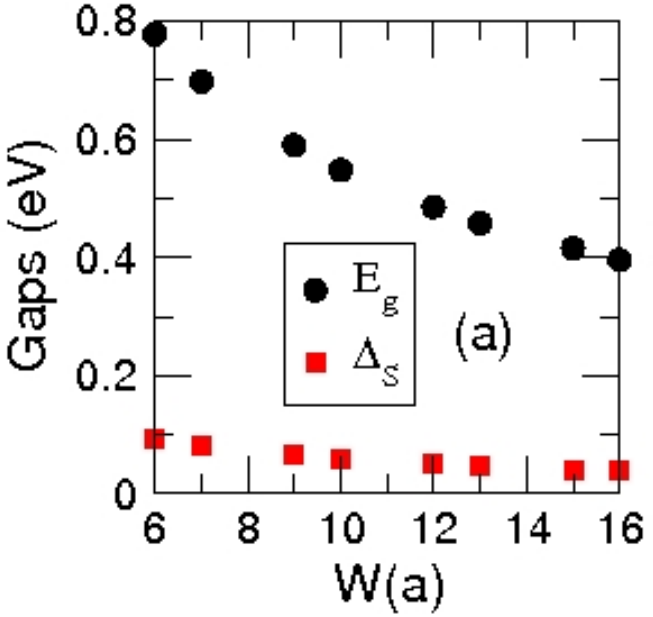
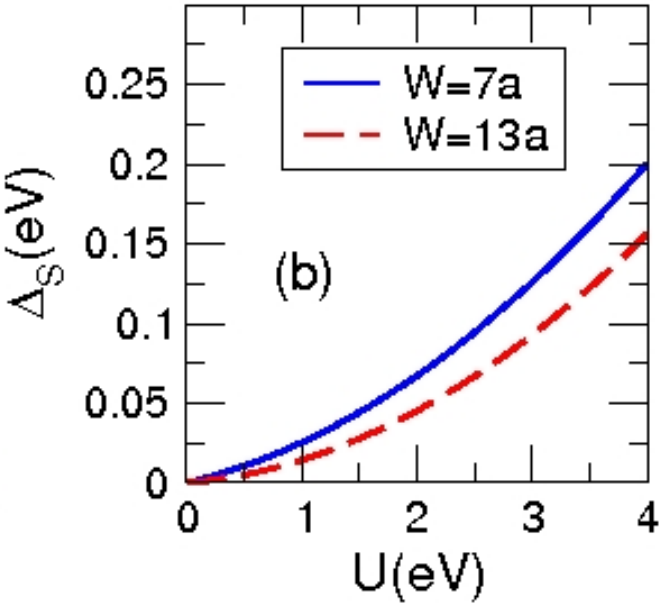
4. $\boxed{N_Z^{\min} < N_Z < N_Z^{\max}}$: There are voids of different sign, but some of them are uncoupled and some not. This is the most general case. The ground state has $2S = N_Z^{\min}$, but, as in the previous case, the spin - flip gap is negligible since there are uncoupled magnetic moments. Calculations will be necessary to ascertain the spin texture in these situations as well.

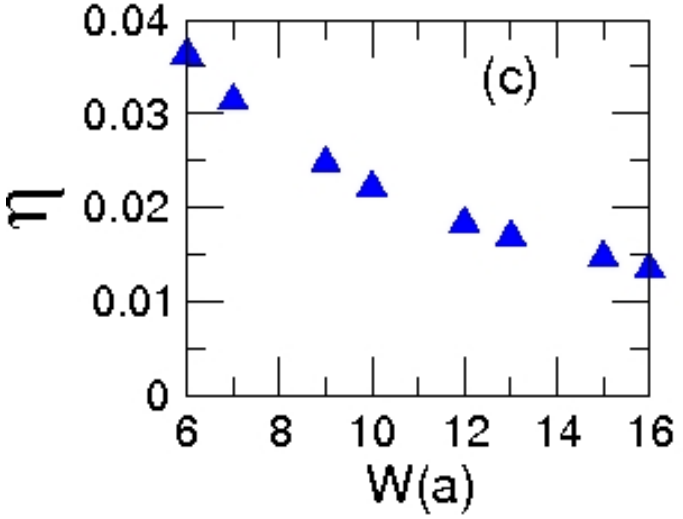
Single vacancy: A

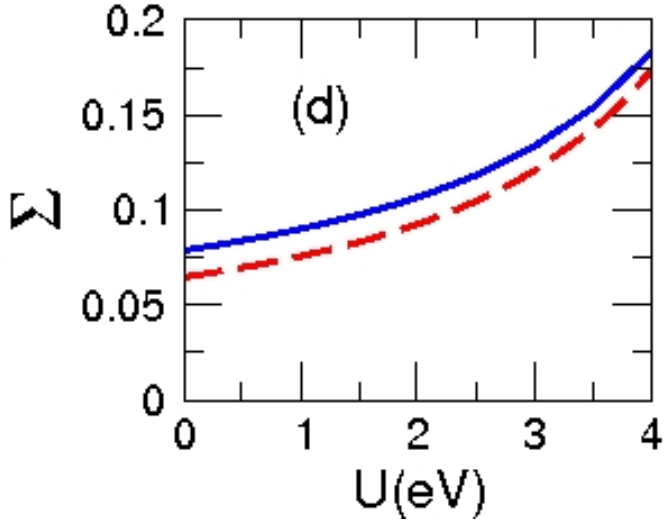


Single vacancy: A









$$\Sigma = \sqrt{\sum_i \langle m_i \rangle^2}$$

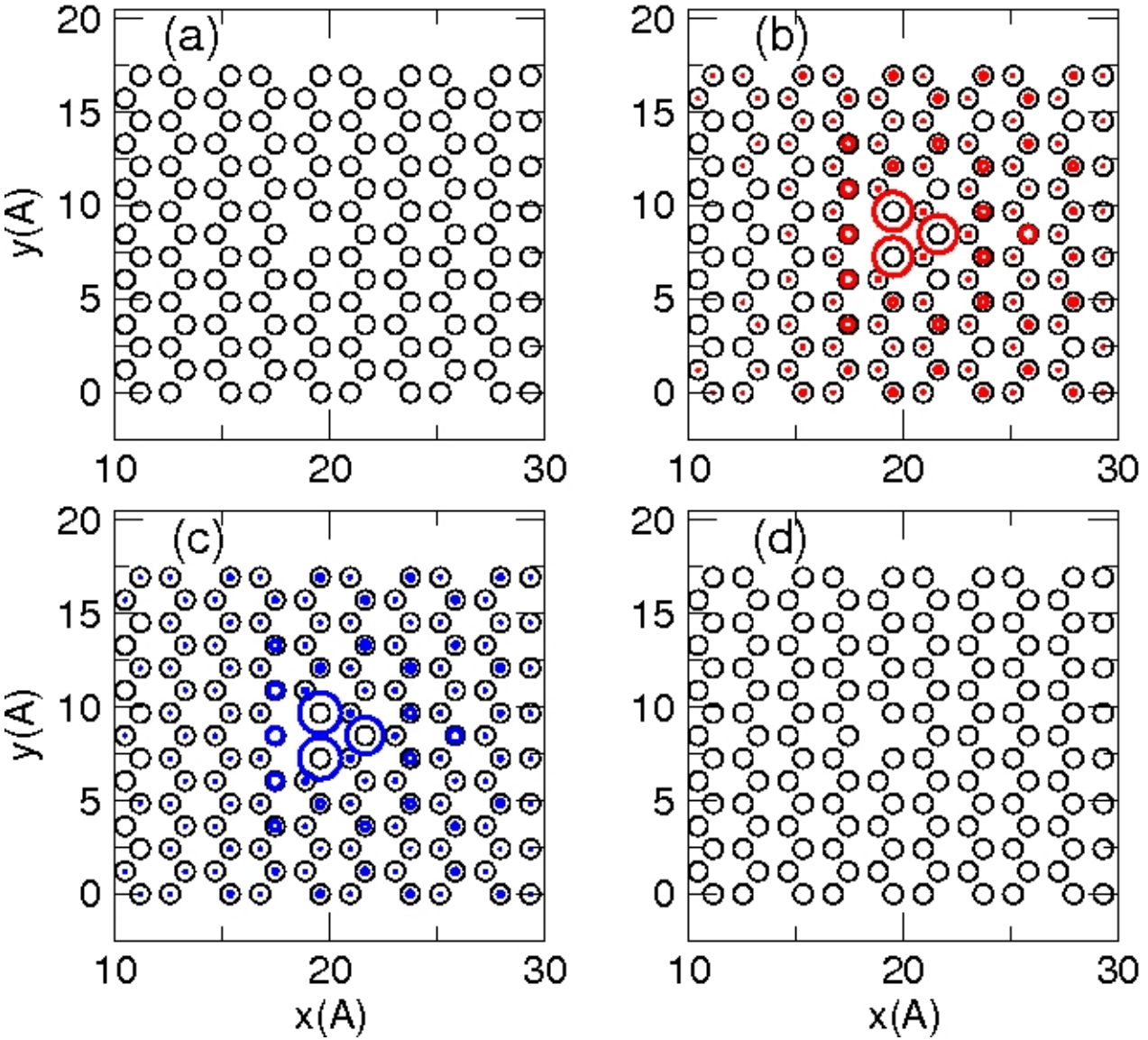
$$\eta = \sum_i |\phi_v(i)|^4$$

Spin-charge separation

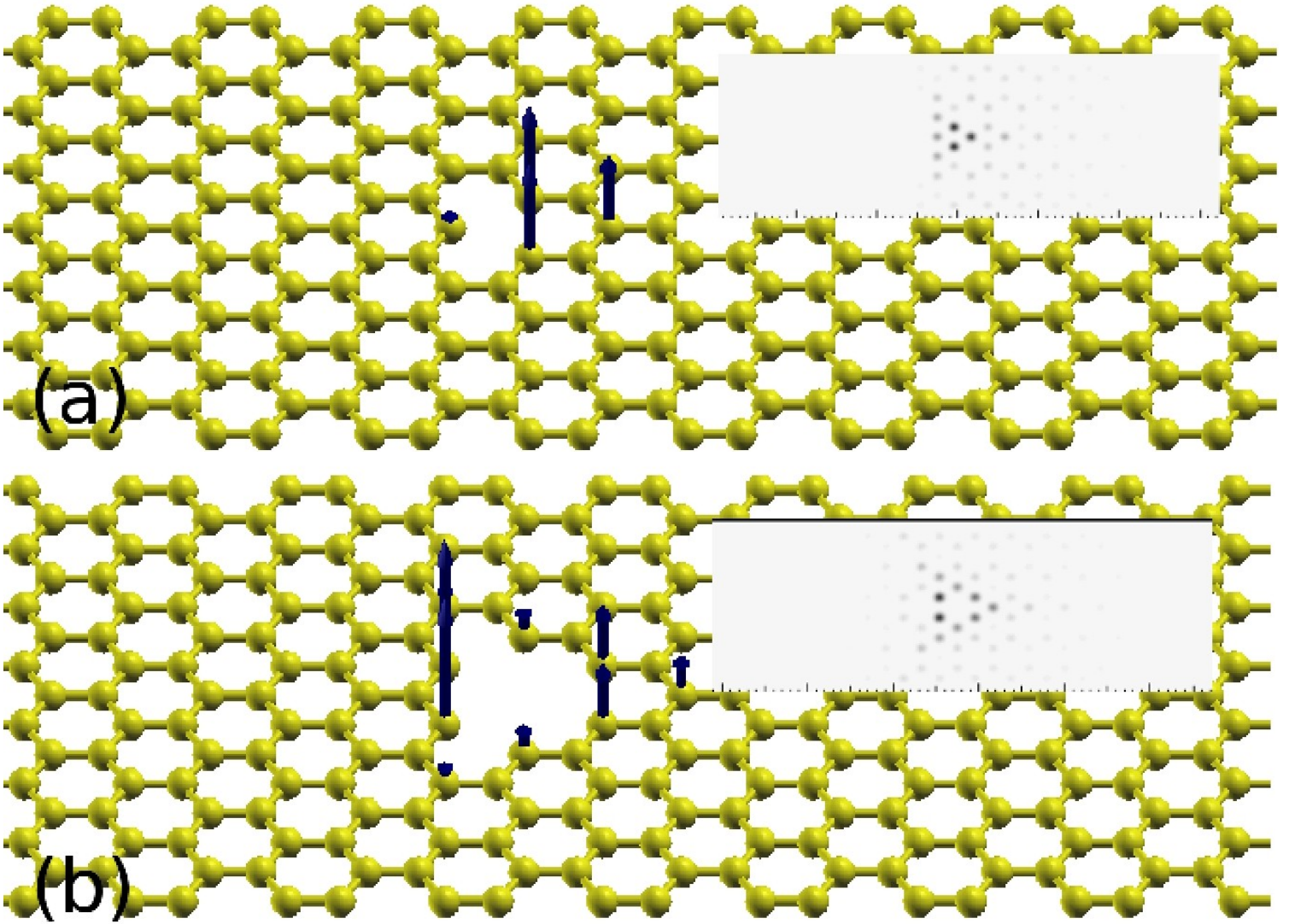
Charge **Spin**

$Q = 0$

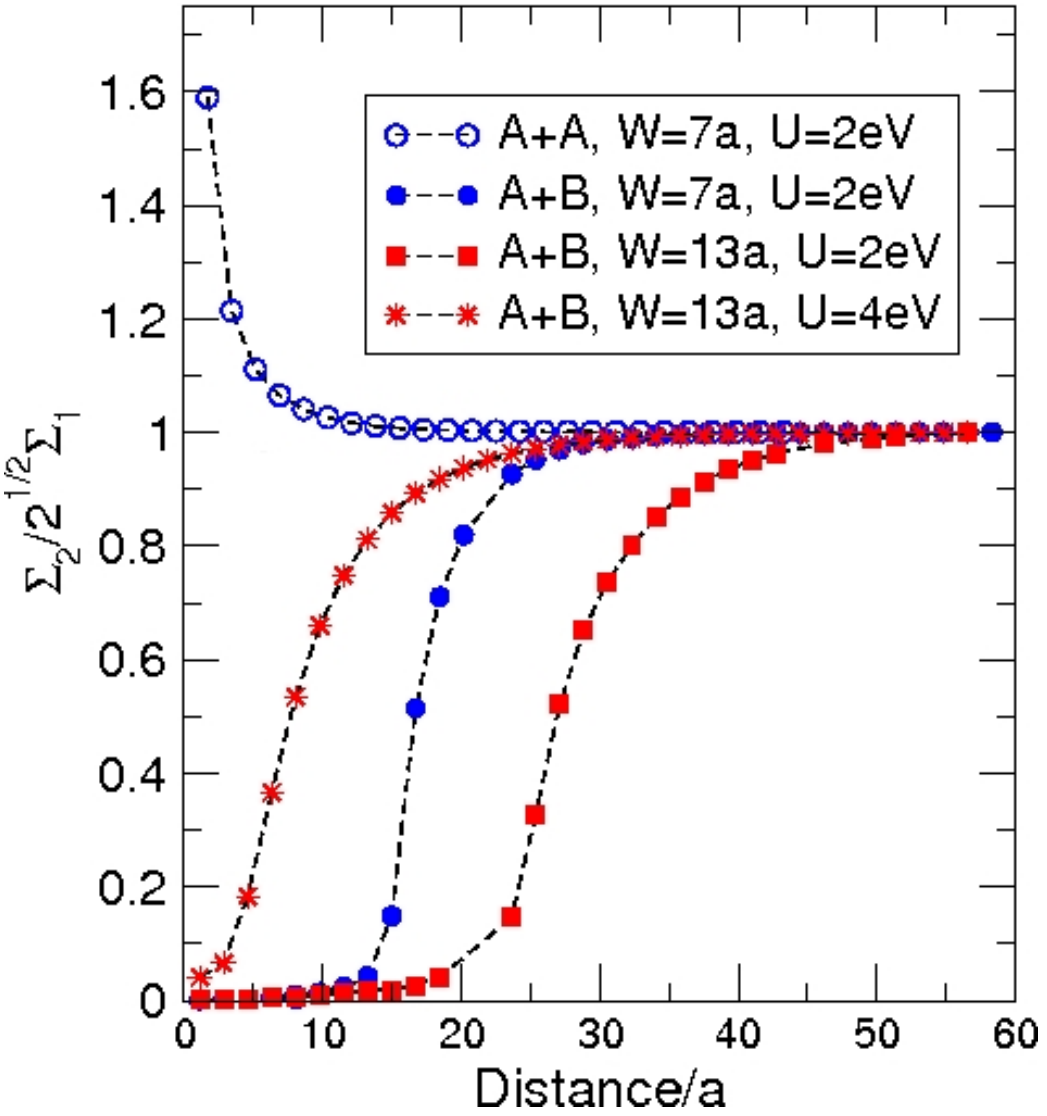
$Q = 1$



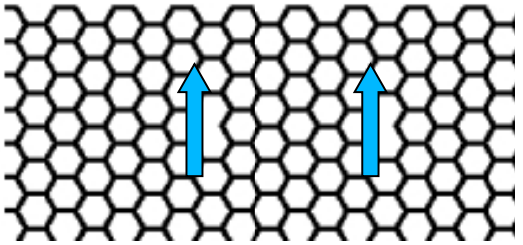
A and A_2



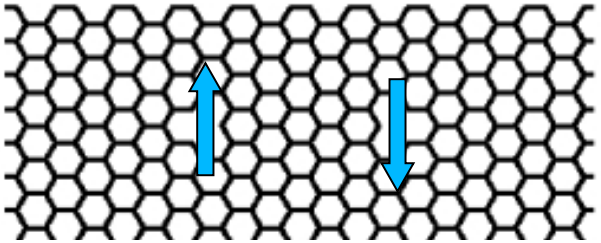
Two vacancies



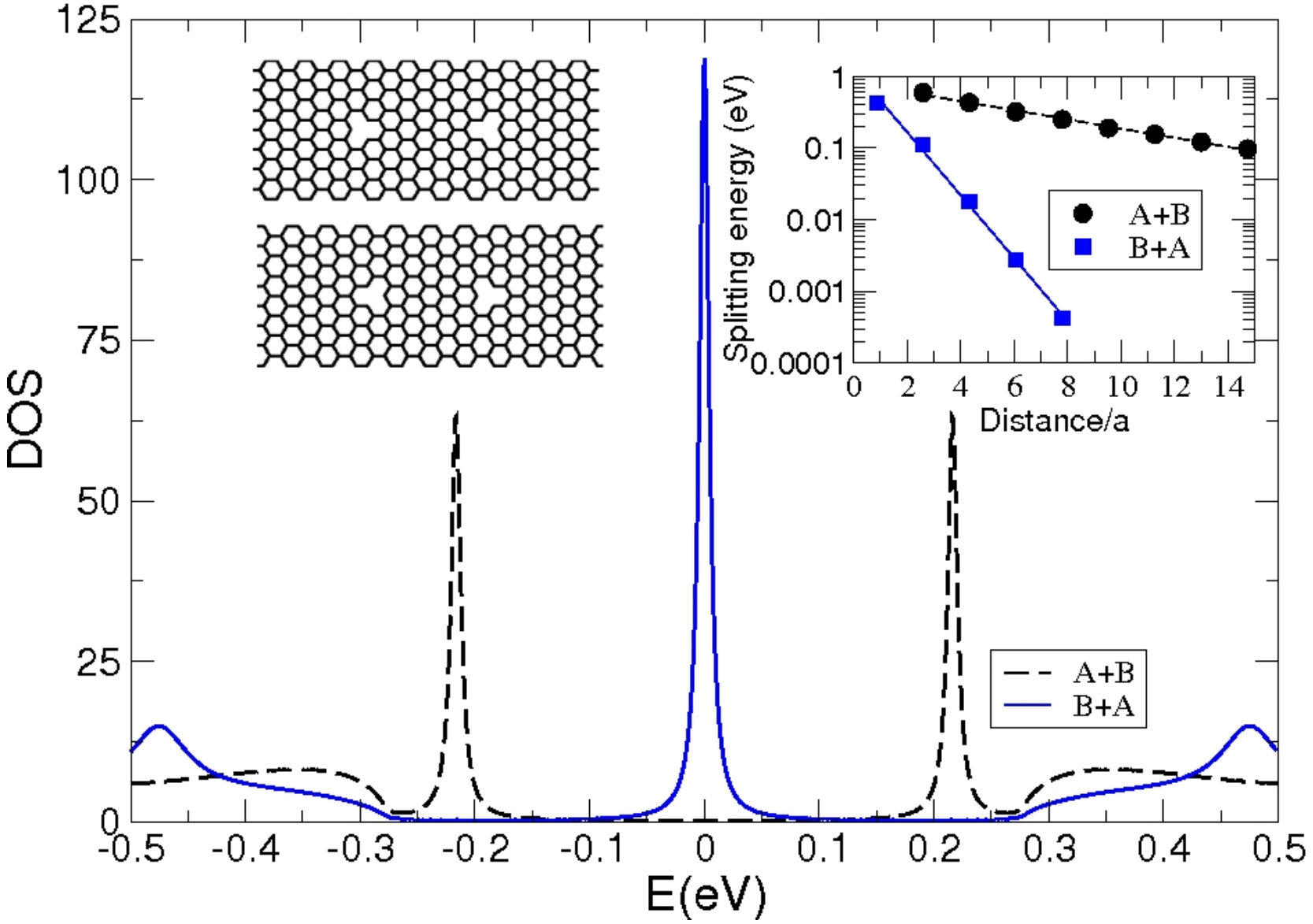
A+A



A+B

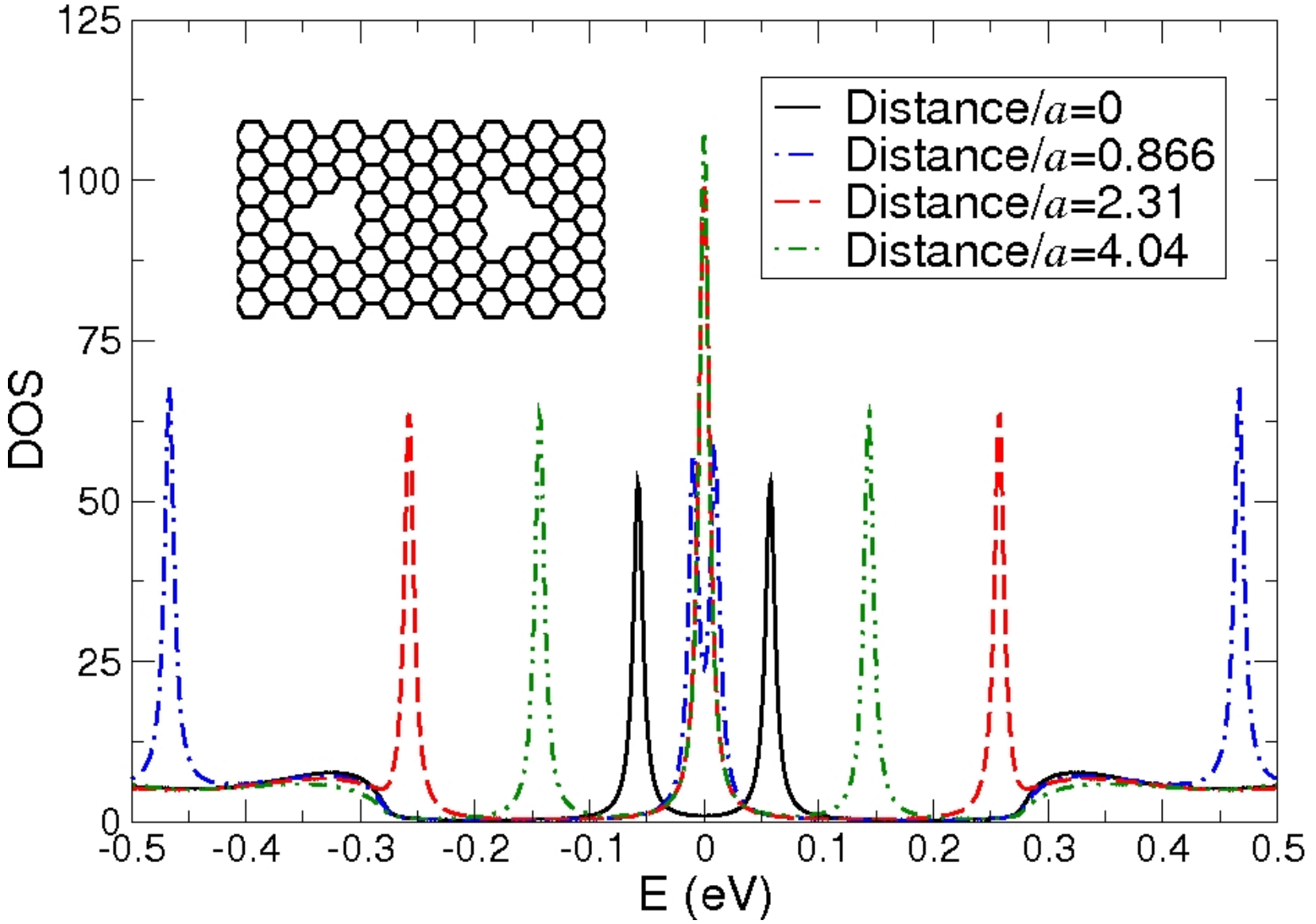


Two vacancies: A and B
(no interactions)

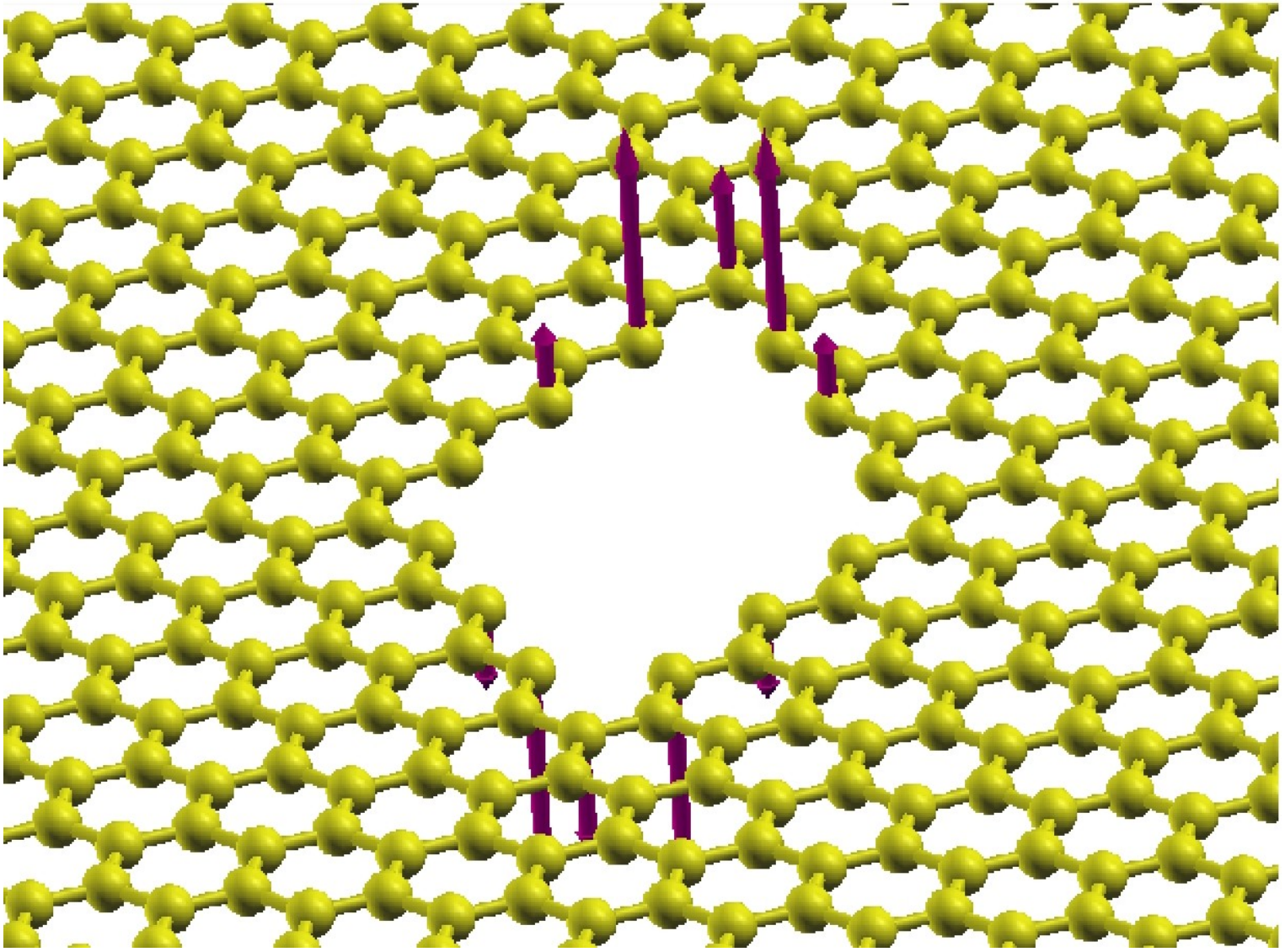


Two voids: A_2 and B_2

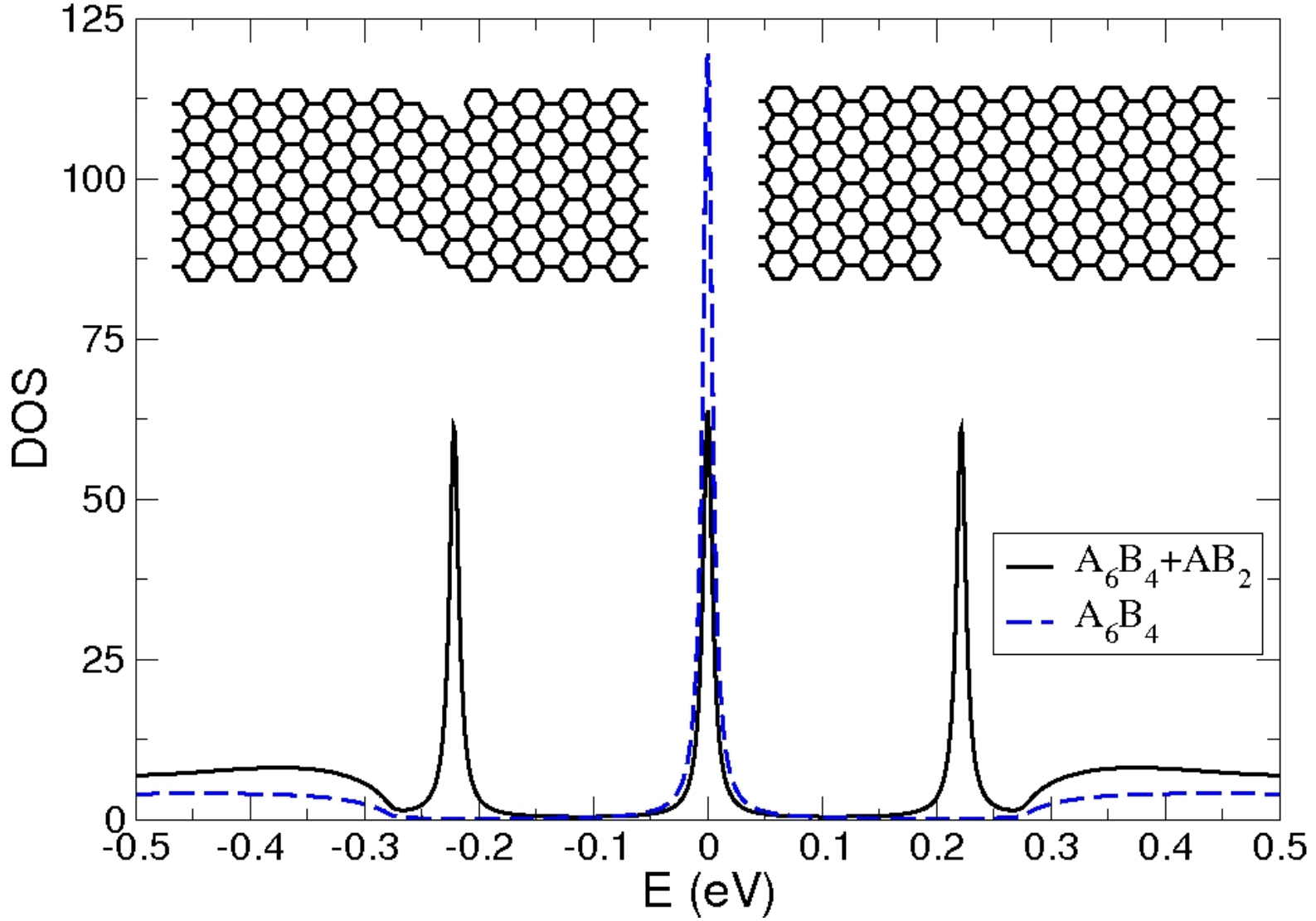
(no interactions)



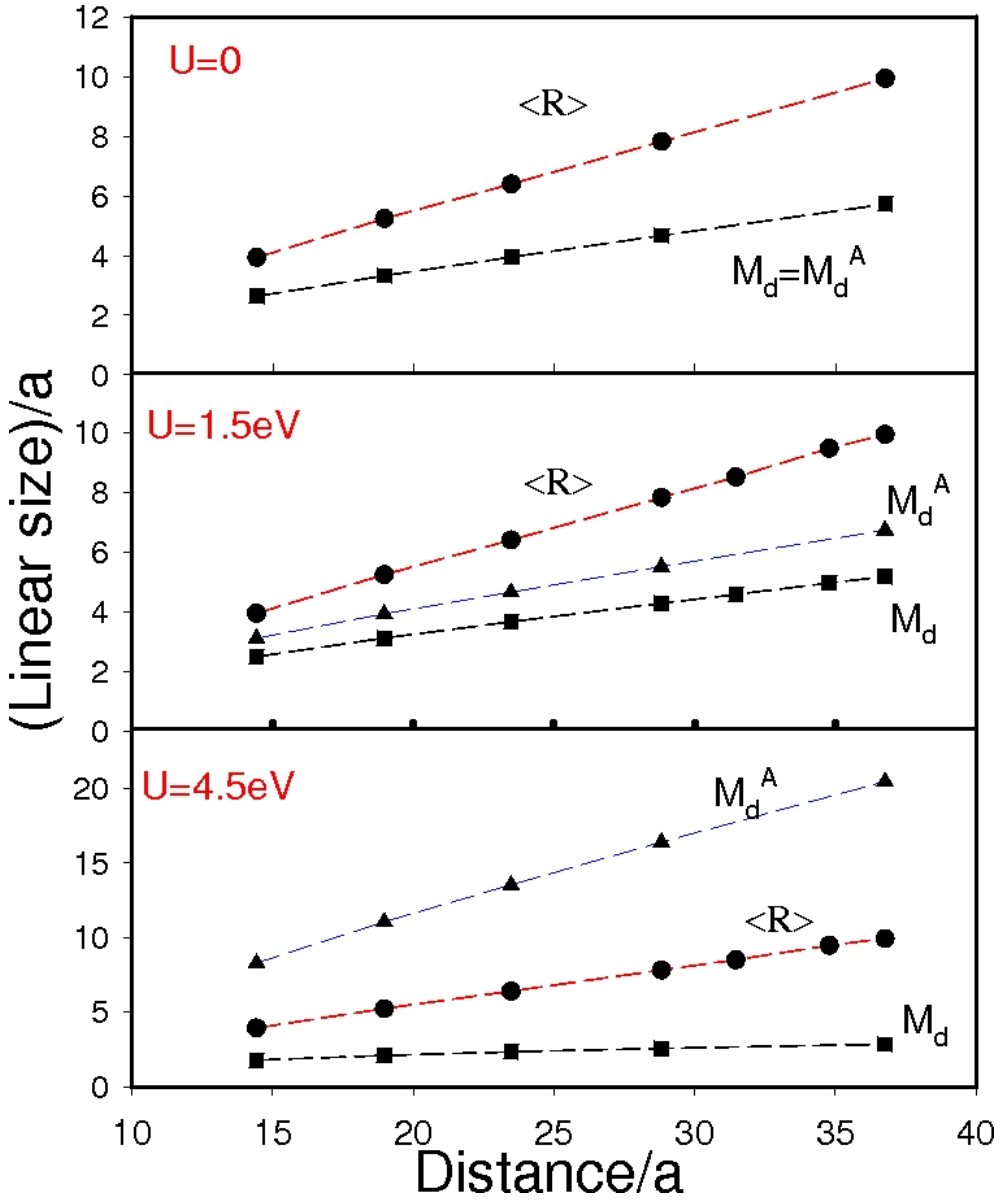
Large voids with $N_l=0$



Two notches


125
100
75
50
25
0
DOS
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
E (eV)
A6B4+AB2
A6B4

Single vacancy in bulk graphene

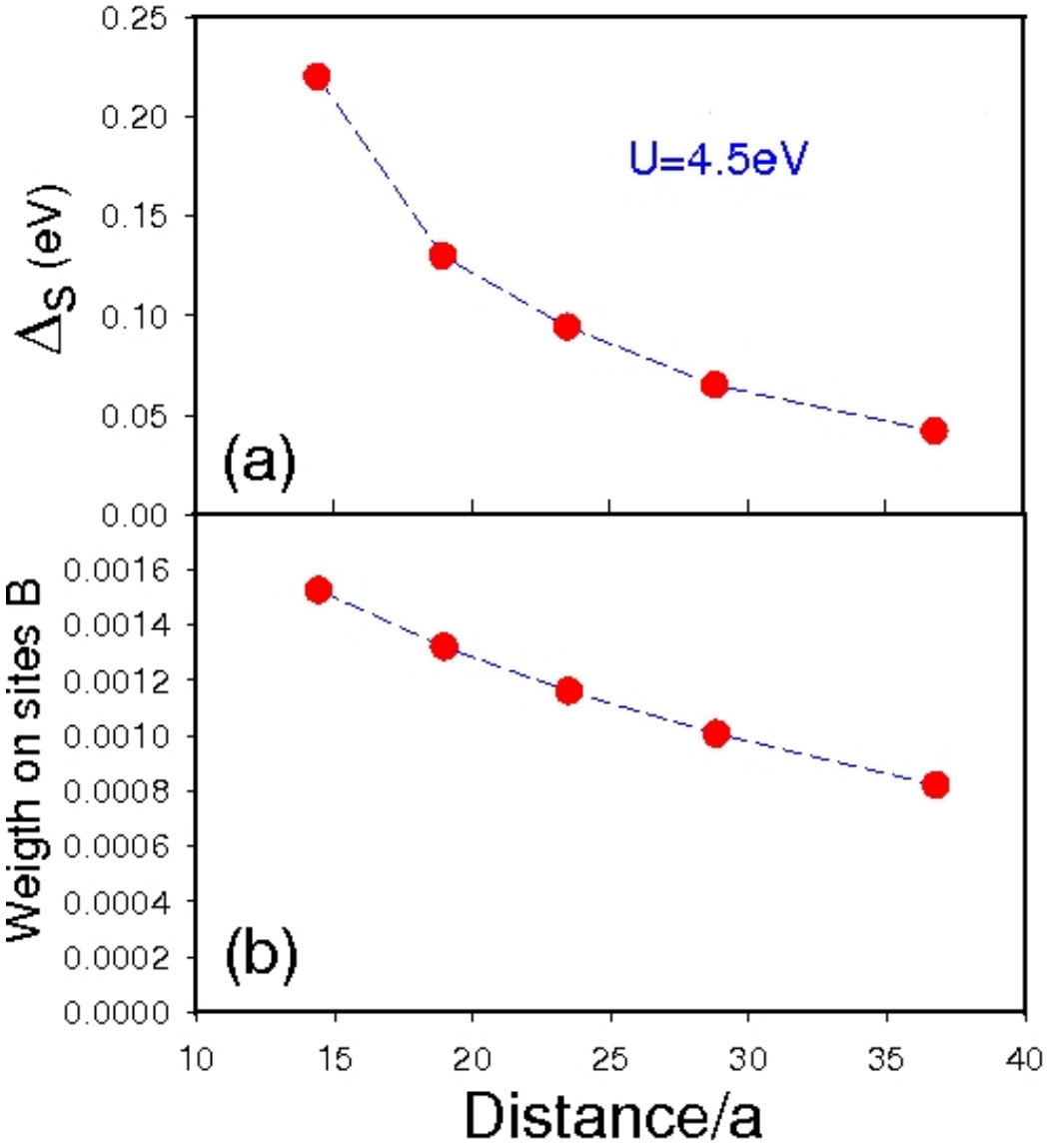


$$\langle R \rangle = \sum_i |r_i - r_0| |\phi_v(i)|^2$$

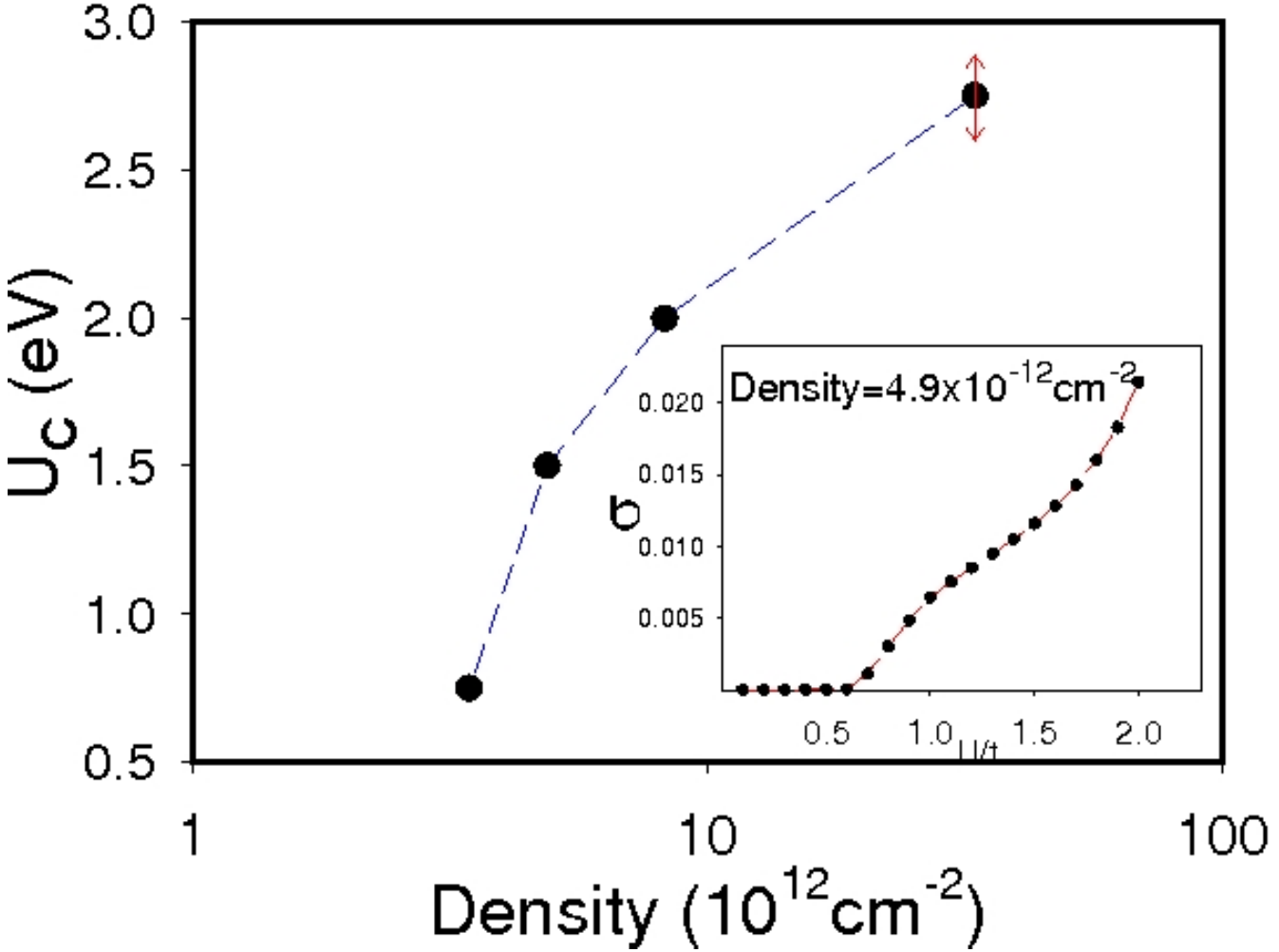
$$M_d^{A(B)} = \sum_{i \in A(B)} |r_i - r_0| \langle m_i \rangle$$

$$M_d = M_d^A + M_d^B$$

Single vacancy in bulk graphene



Finite density of vacancies: Compensated graphene ($N_I=0$)



Future work

- Magnetic structure of more generic PAH's or nanographenes
- Thermal fluctuations: Superparamagnetism
- Stability of open shell structures (radicals)
- Change of properties when deposited on surfaces
- Devices