計算科学：固いナノと柔らかいナノの橋渡し

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  - Space modifies electron states quantum mechanically
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  [J. Phys. Soc. Jpn, submitted]
  - Space inherent to proteins induces peculiar states

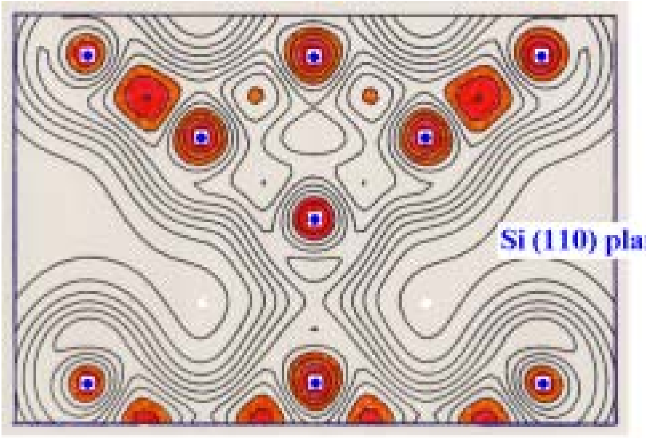
In collaboration with …

- Susumu Okada (計算科学研究センター,数理物質科学研究科)
- Kenji Shiraishi （数理物質科学研究科）
- Minoru Otani （物理学系．．．現東大物性研）
- Katsumasa Kamiya （数理物質科学研究科）

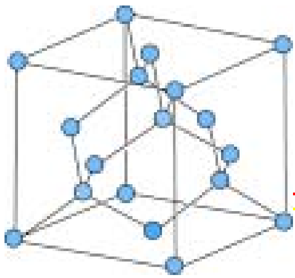
密度汎関数法

Total-Energy Electronic-Structure Calculations Based on DFT

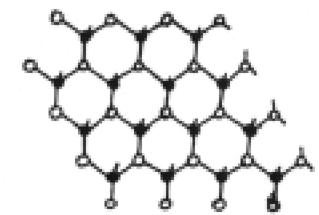
- ***Normconserving Pseudopotential***
- ***LDA or GGA for exchange-correlation***
- ***Plane-wave basis set***
- ***Iterative technique for both electronic and inonic degrees of freedom***
- ***Super-cell model***



$$E[n] = T[n] + \int v_{\text{nucl}}(\vec{r})n(\vec{r})d\vec{r} + \frac{1}{2}\int\int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}' + E_{XC}[n]$$

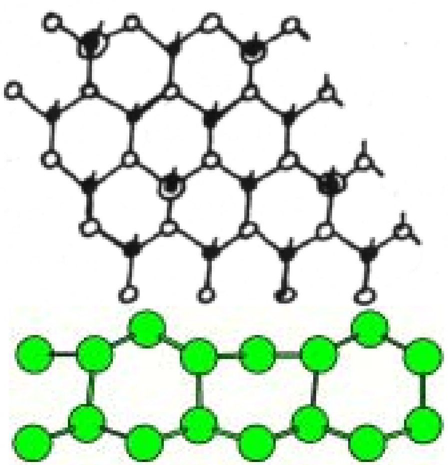


Surface Reconstruction of Si(111)



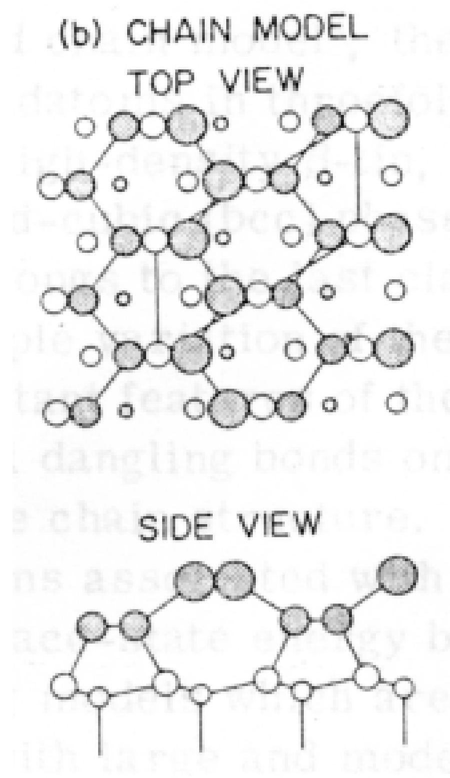
(d) "ideal" structure

2x1 structure



top view

side view



π-bonded Chain: *Pandey: PRL 47, 1913 (1981)*

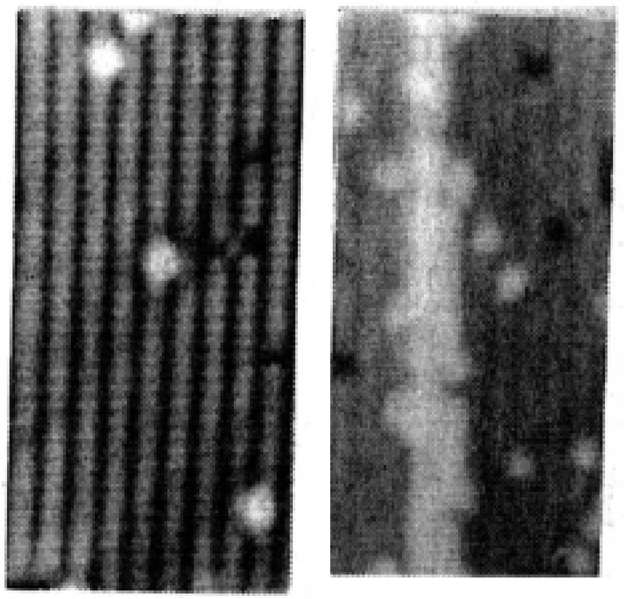
Buckling: *Haneman, PR 121, 1093 (1961)*

OR

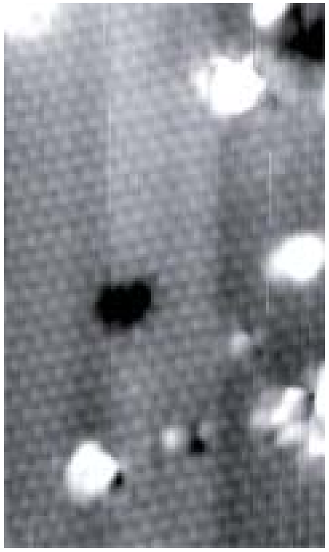
Antiferromagnetic up and down: *Northrup et al, PRL 47, 1910 (1981)*

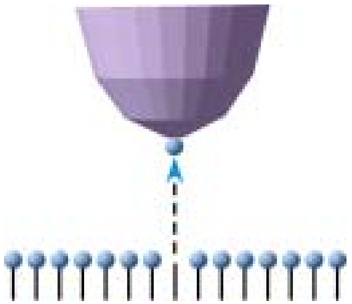
Hydrogen as an Atom-Scale Mask

Hashizume et al., 1996



Miki, 2003

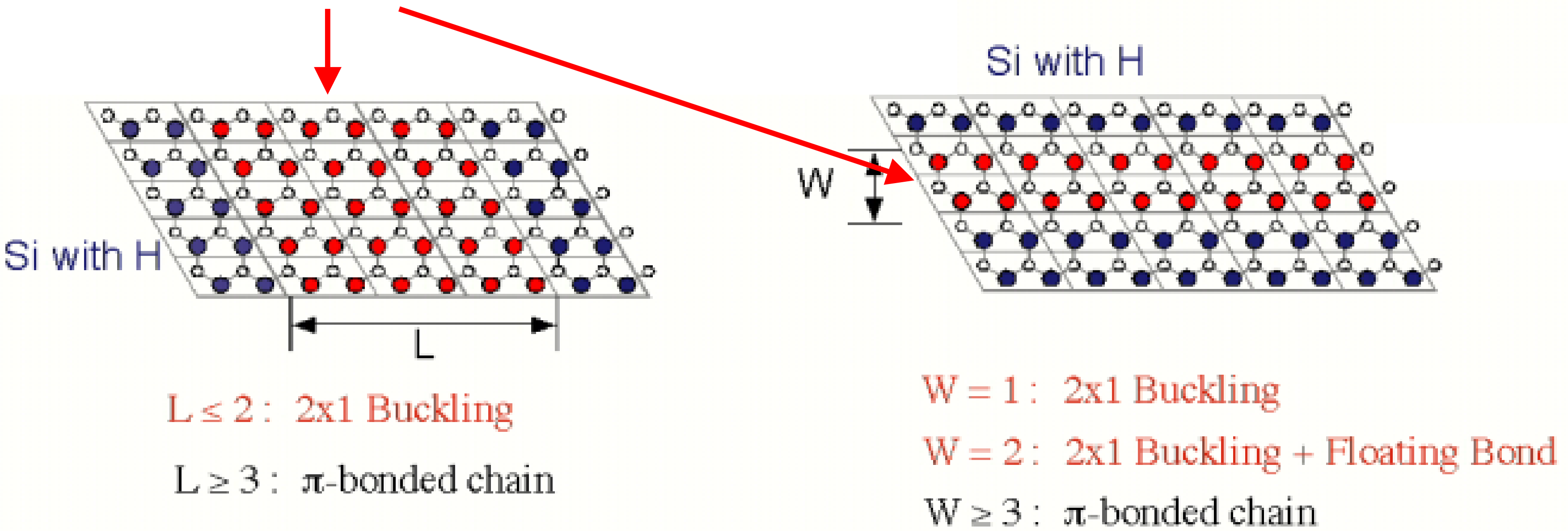




Nanometer-scale surfaces are realized

π-Bonded vs Buckling in Nanosurface

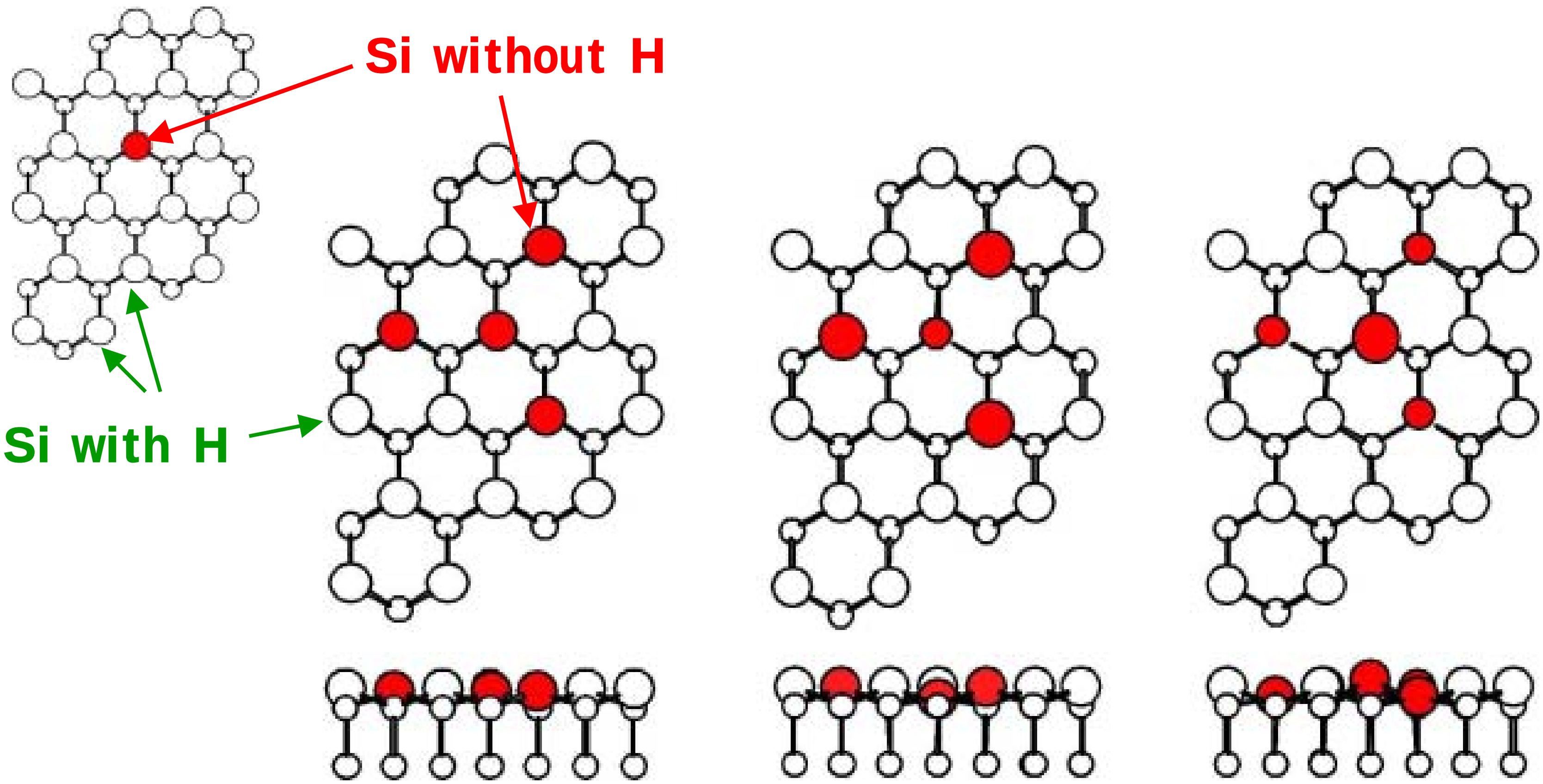
Nanostrip of Si atoms without Hydrogen



Important reconstruction on the nanometer-scale Si (111) is the buckling.

⇒ What about magnetic ordering ?

Ultimate Triangle Unit of Dangling Bonds



non-buckled (NB)

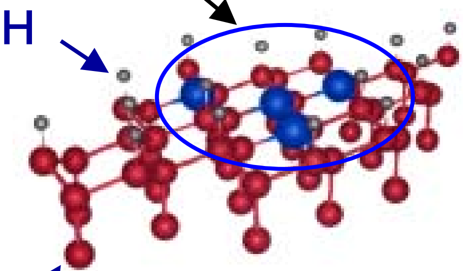
buckled: central Si down (B1D)

buckled: central Si up (B1U)

Ultimate Triangle Unit has High Spin

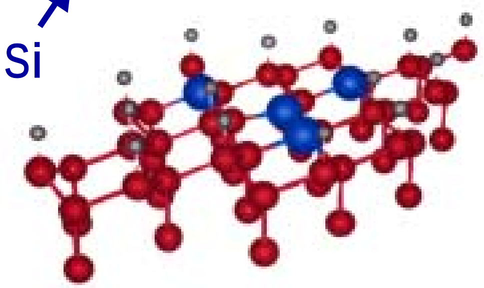
triangle unit

H

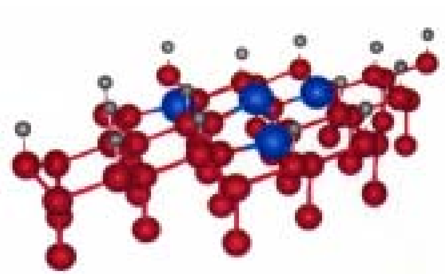


Si

non-buckled (NB)



Buckled 1down (B1D)



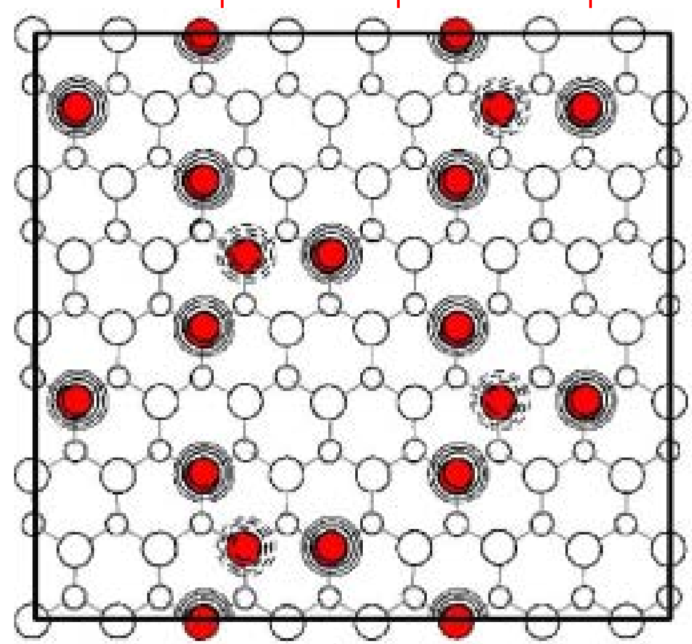
Buckled 1up (B1U)

Amount of Buckling (A):

0.4 – 0.5 A

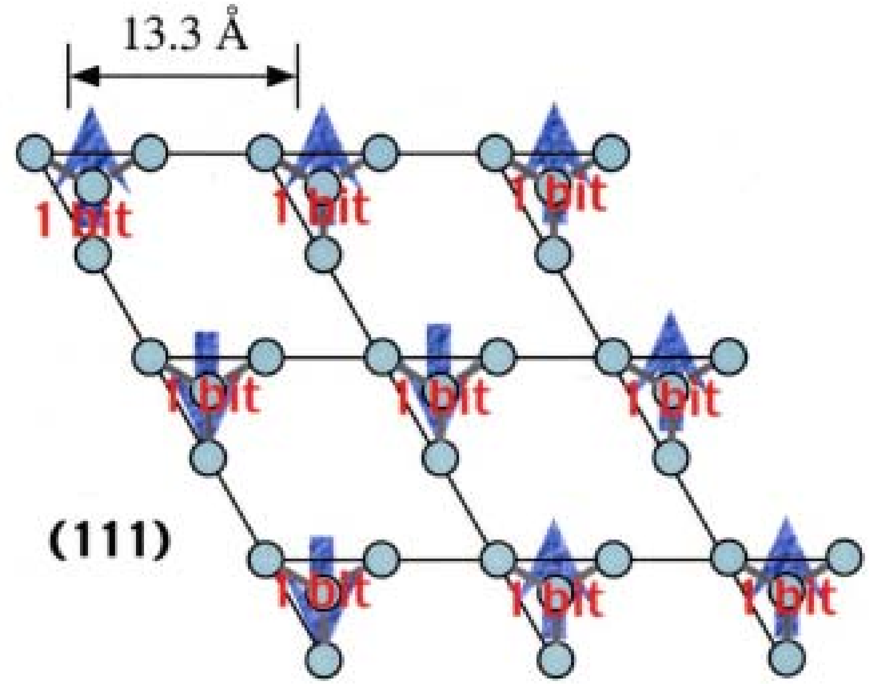
Energetics (eV / cell):

	NB	B1D	B1U
para	0	-0.67	-0.80
high-spin	-0.86	-0.84	-
spin S	*1*	*1*	*0*



spin density: $n_{up}(r) - n_{down}(r)$

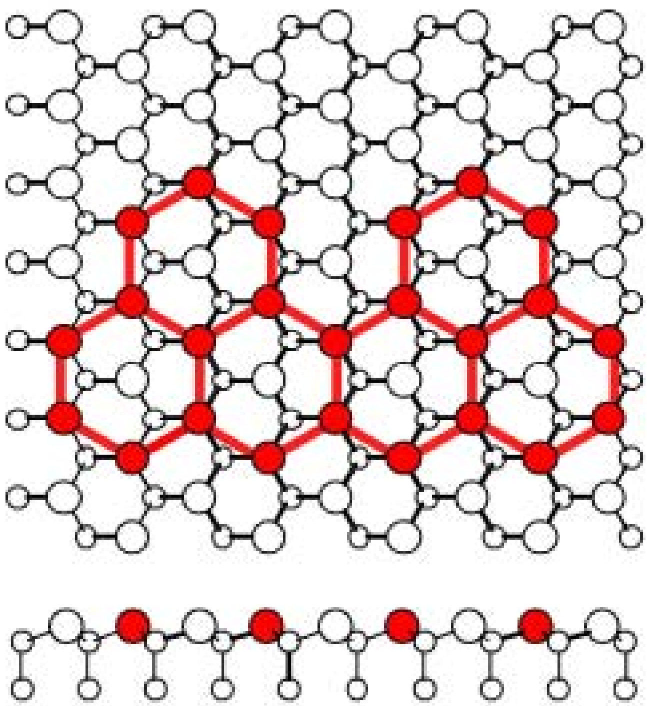
Ultimate Si-based Memory



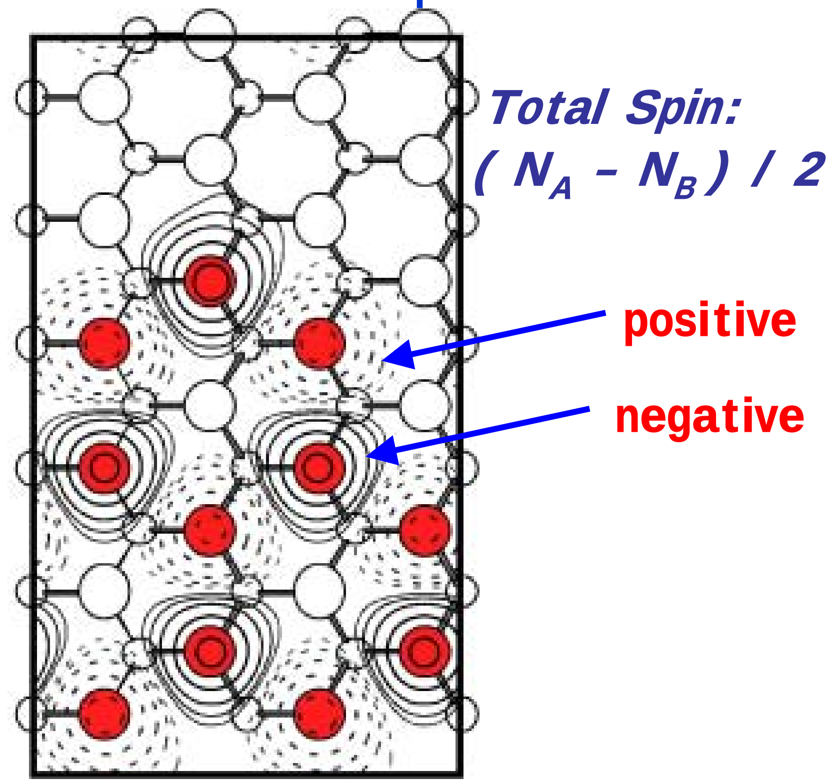
- **306.38 A^2 / bit**
- **Prepare 1 x 3 cm Silicon Fragment, and get 100 Terabit Capacity**

Ferrimagnetic Ordering on Si(111)

arrangement of top Si



spin density: $n_{up}(r) - n_{down}(r)$



- **Removal of H in a controlled way makes it a magnet**
- **Structural Bistability: Spin Polarized in both Buckled and Non-buckled Structures**

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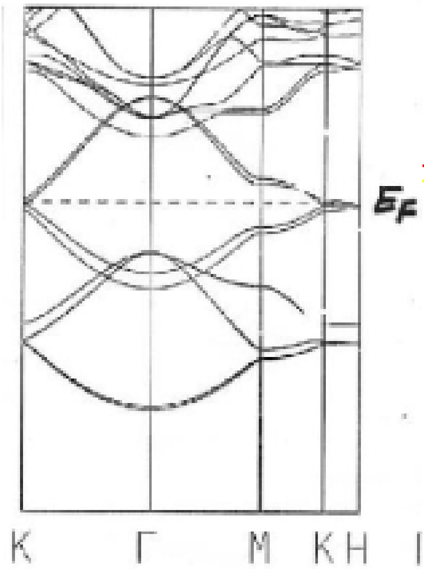
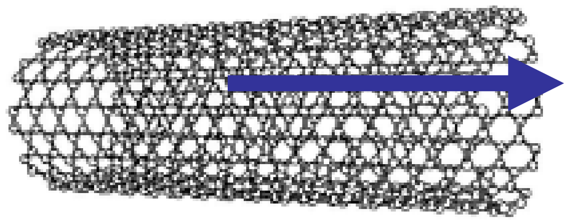
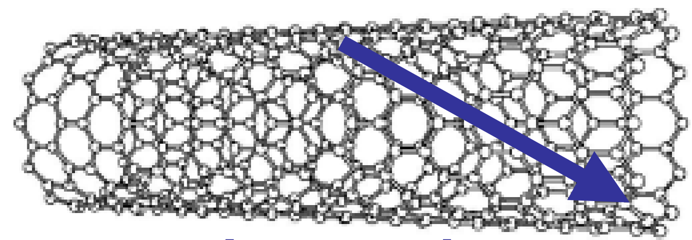
Carbon Nanotube: Energy Gap Control

N. Hamada, S. Sawada & A. Oshiyama: PRL 68, 1579 (1992)

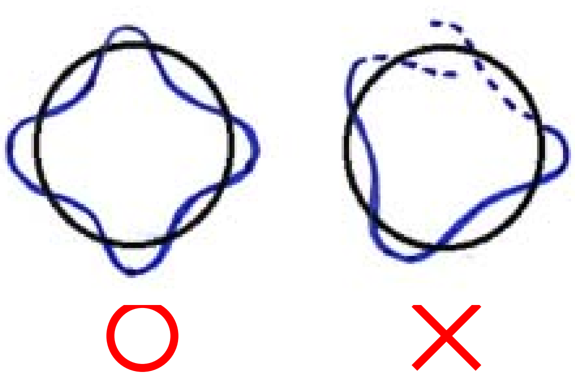


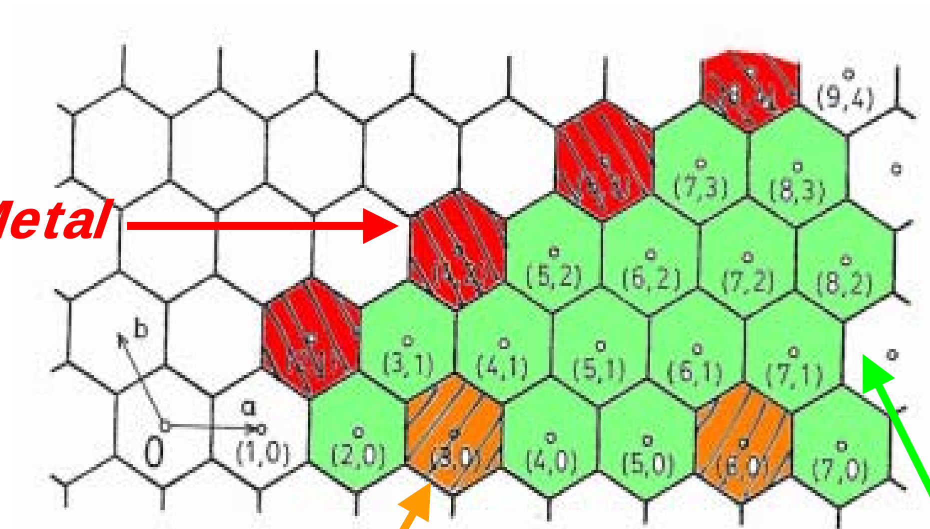


Armchair Tube



Zigzag Tube





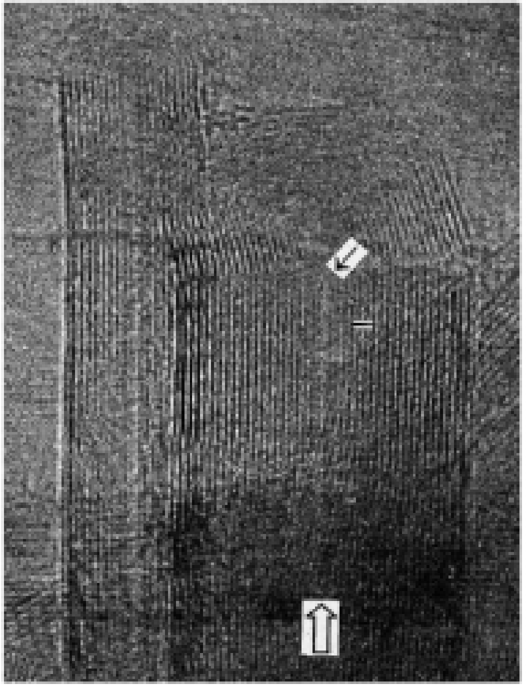
Metal

Semiconductor

Metal (or Very Narrow Gap Semiconductor)

Thin Nanotube in Multiwalled Nanotubes

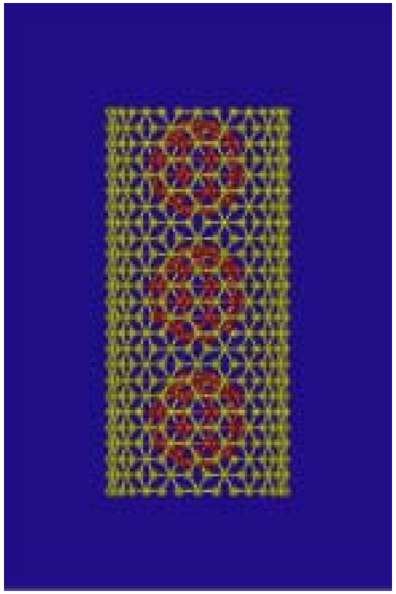
L. F. Sun et al.,
Nature **403** 384 (2000)



(7,0)@MWNT

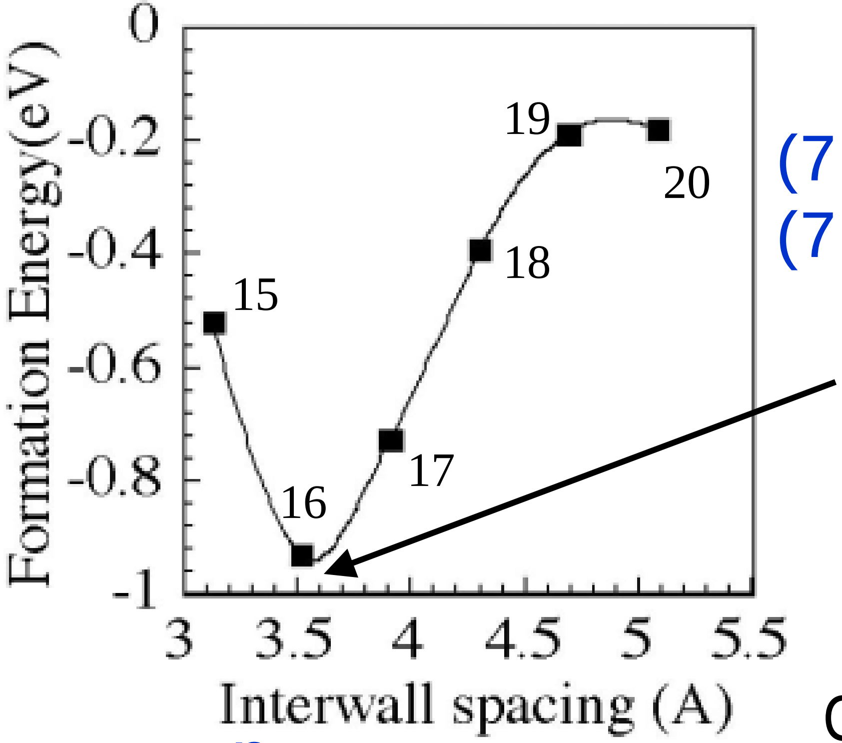
L.-C. Qin et al.,
Nature **408** 50 (2000)

4Å-nanotube@MWNT
(3,3), (4,2), (5,0)



Peapods become DWNTs

Energetics of (7,0)@(n,0)



n in (7,0)@(n,0)

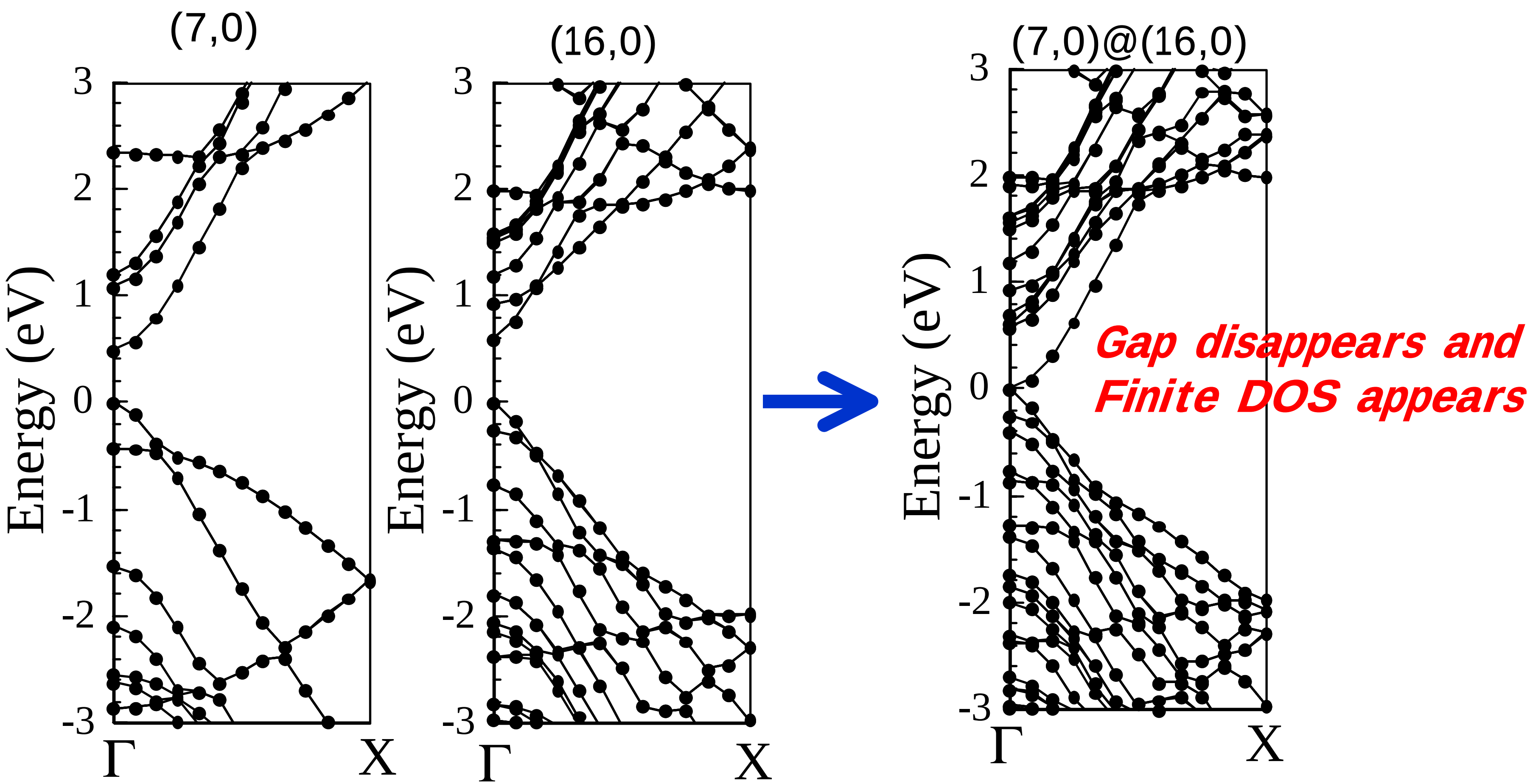
(7,0)@(16,0) is most stable
(7,0)@(17,0) is also preferable

Spacing is larger than interlayer distance in graphite

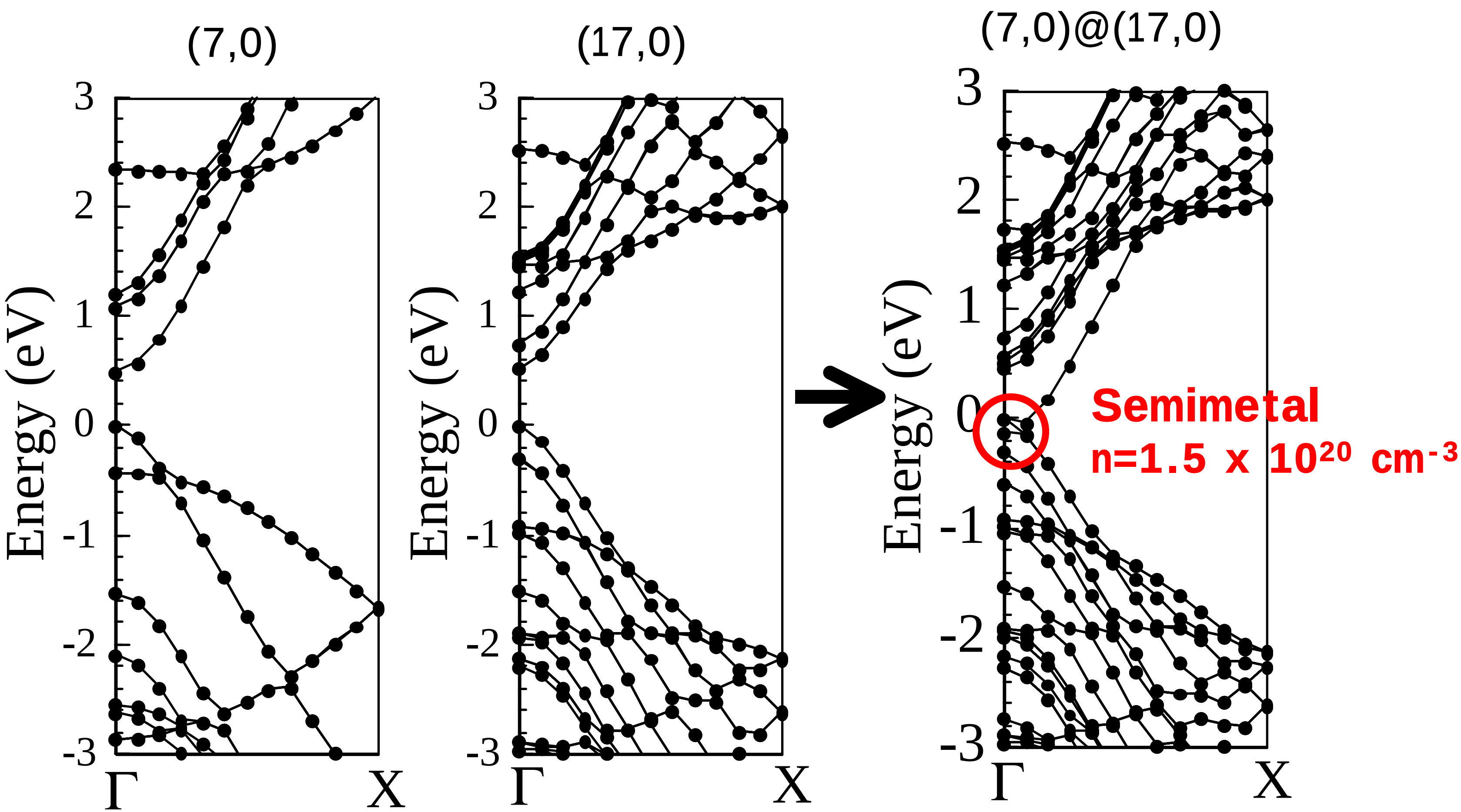
↕

Consistent with Electron Diffraction measurement by Hirahara

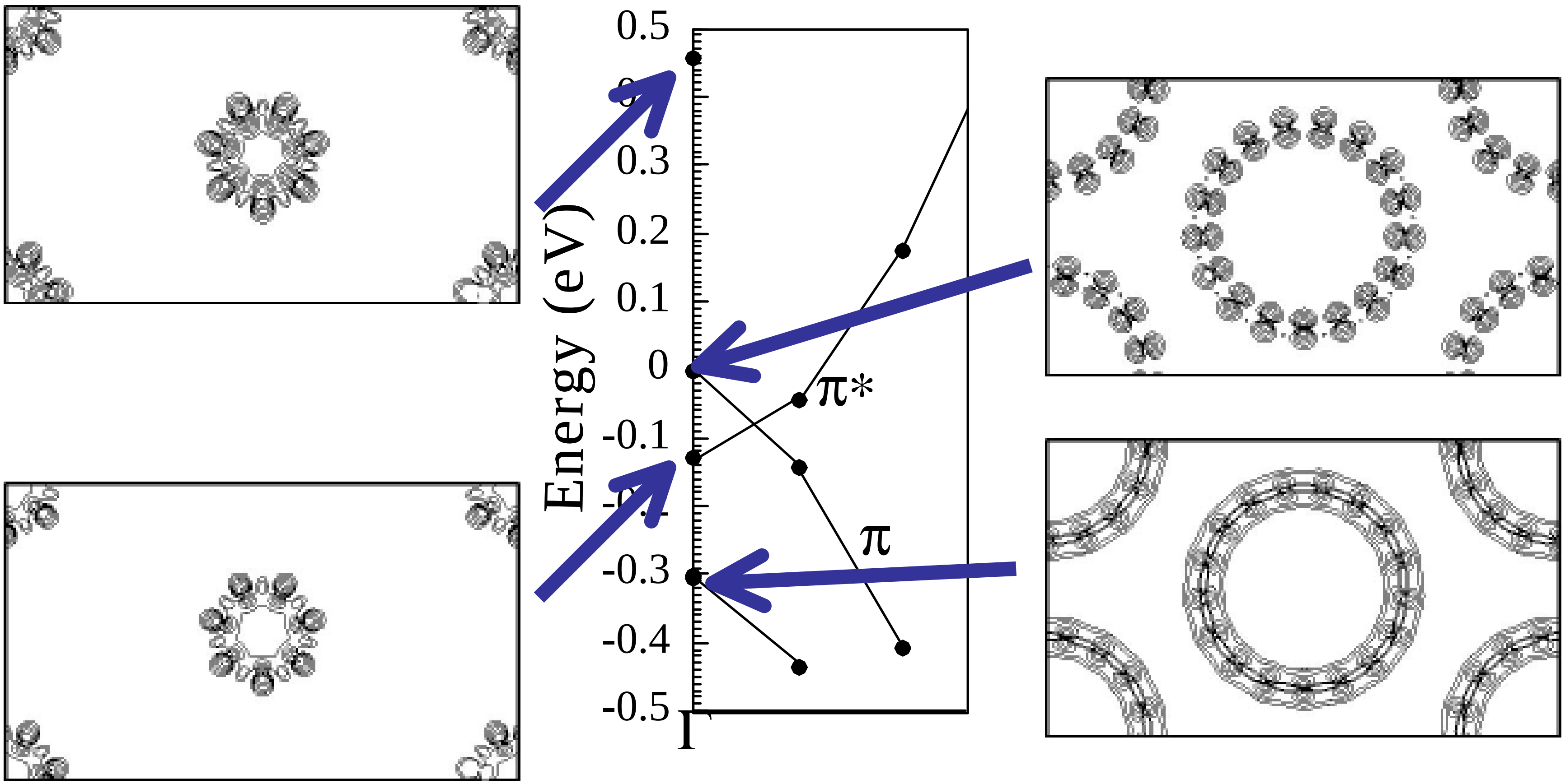
Electronic Structure of (7,0)@(16,0)



Electronic Structure of (7,0)@(17,0)



Curvature Induces s-p mixing and It depends on radii



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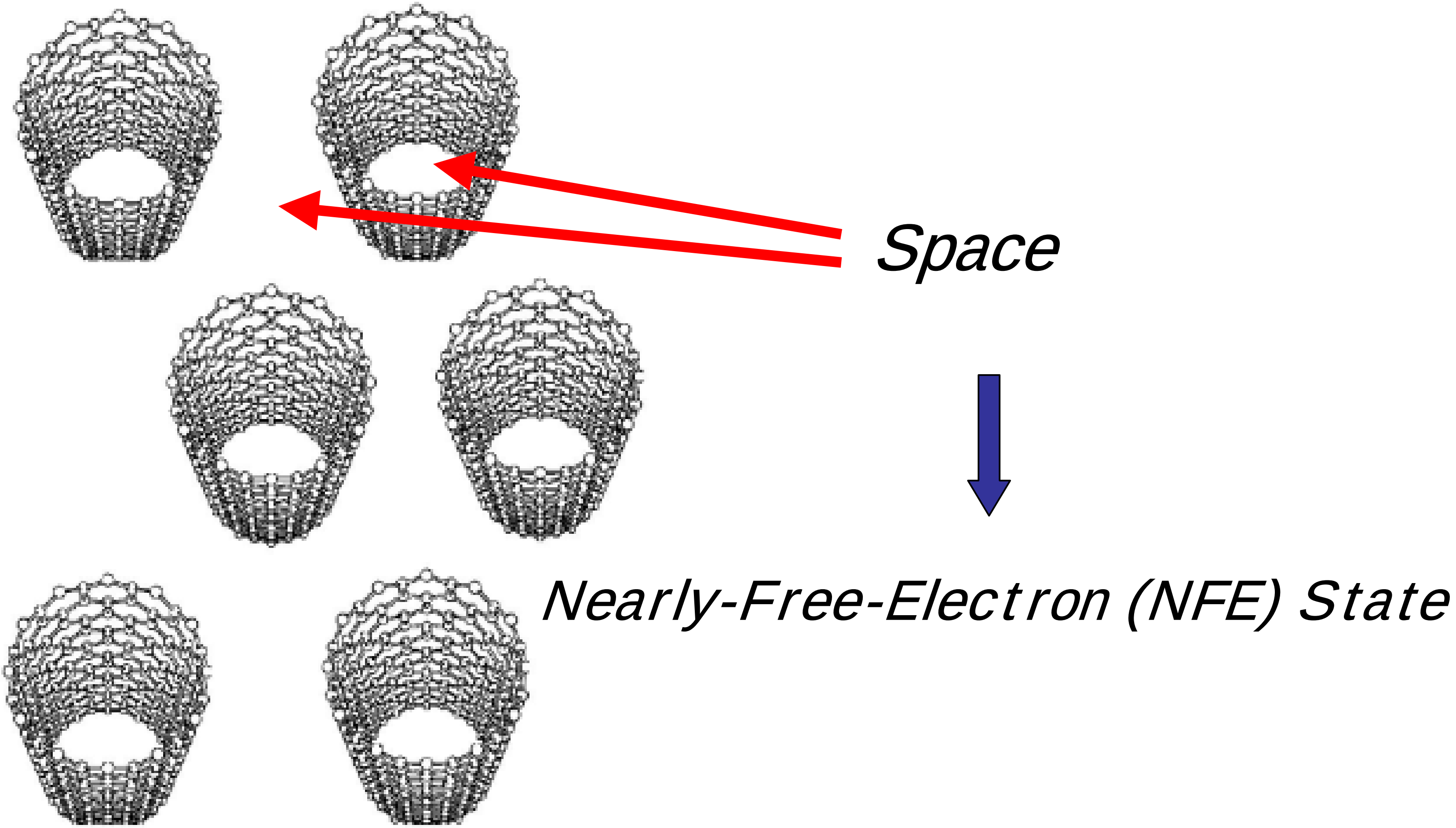
Spacious Solid



Electron States Peculiar to Spacious Solids

- **Interlayer state**

  [Posternak et al., PRL 52, 863(1984)]

- **Intercluster state in C_{60}**

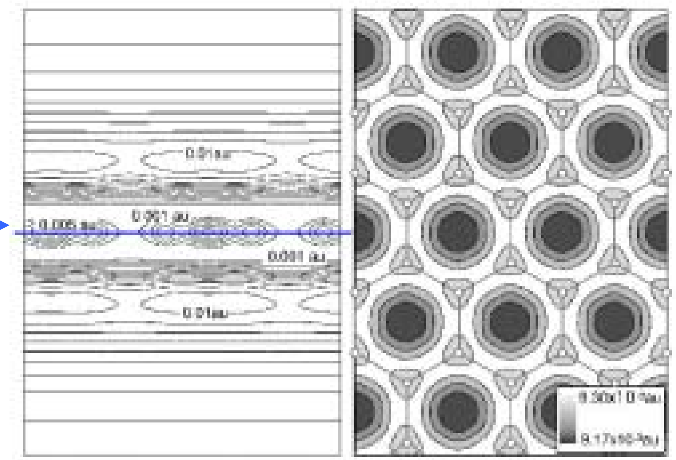
  [Saito and Oshiyama, PRL 71, 121 (1993)]

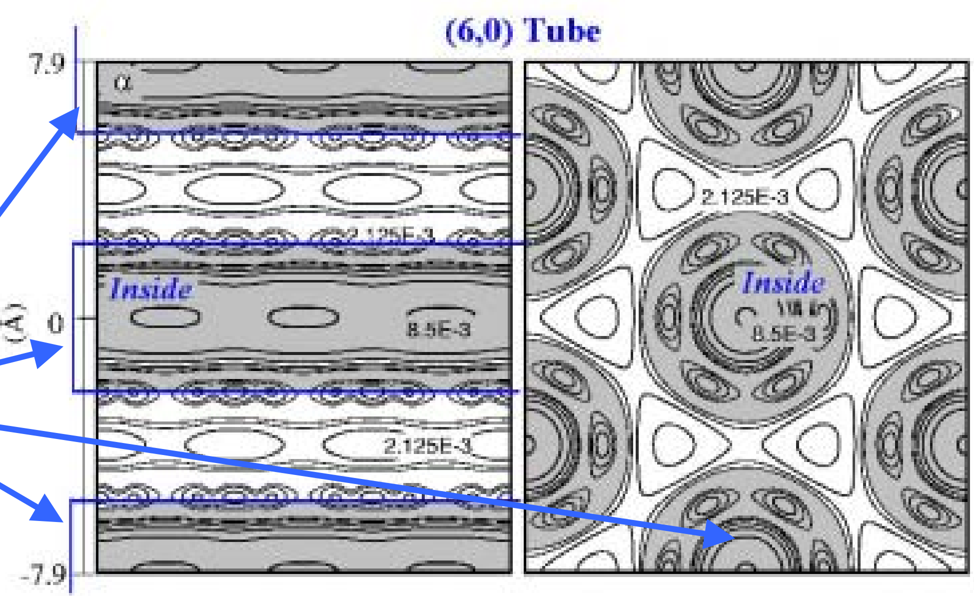
  Crucial role in determining Fermi-level density of states in Sr_6C_{60} and Ba_6C_{60}

- **Nearly-free-electron state in nanotubes**

  [Miyamoto et al, PRL 74, 2993 (1995)]

graphite plane

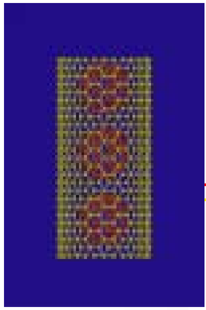




Large amplitude within tubes

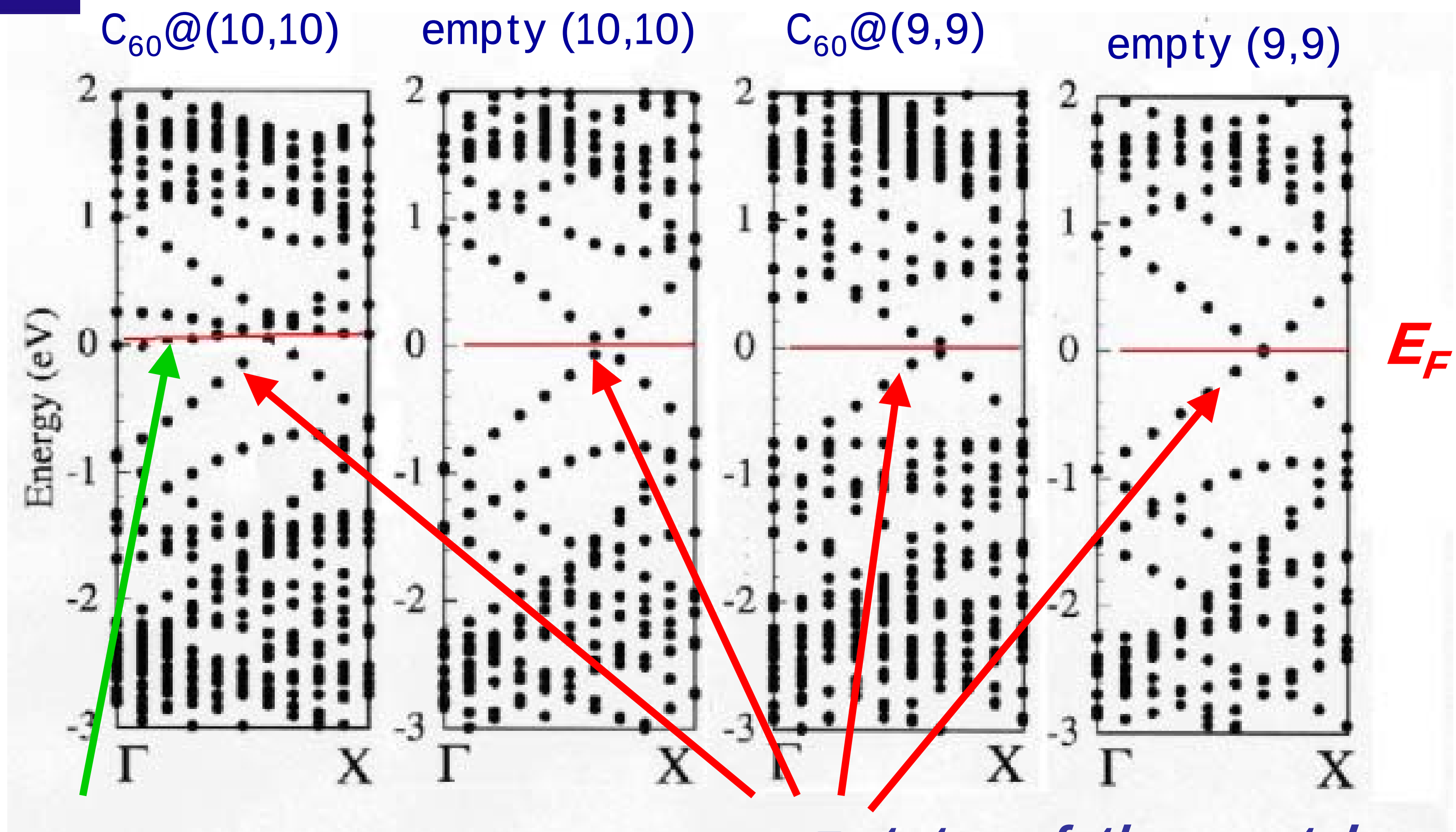
ε = 3 – 4 eV + Fermi energy

[Okada, Oshiyama & Saito, 62, 7634 (2000)]



Energy Bands in Peapods

Okada, Saito & Oshiyama, Phys. Rev. Lett. 86, 3835 (2001)



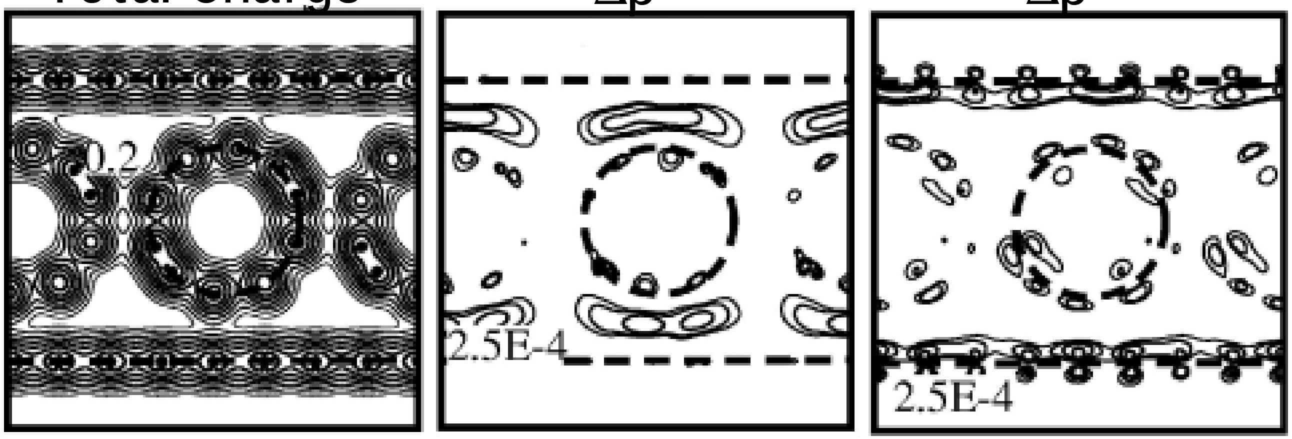
t_{1u} states of the C_{60} Chain

π states of the nanotube

Charge Density in Peapods

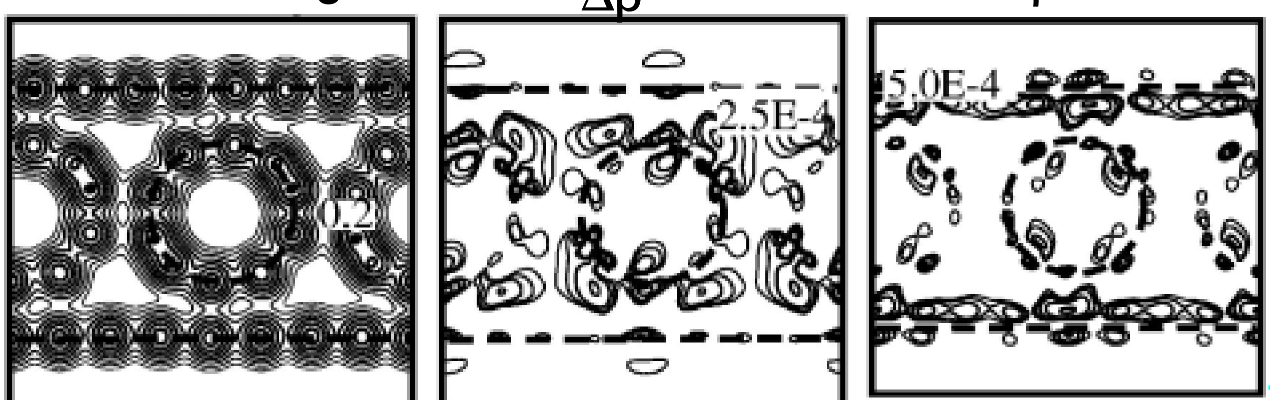
$\underline{C_{60}@(10,10)}$

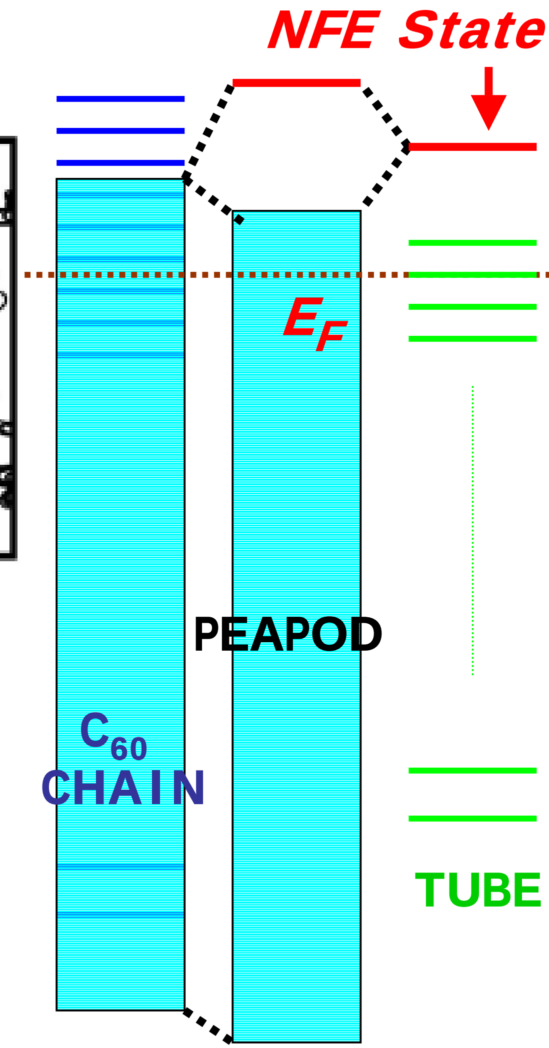
Total Charge | $\Delta\rho^-$ | $\Delta\rho^+$



$\underline{C_{60}@(9,9)}$

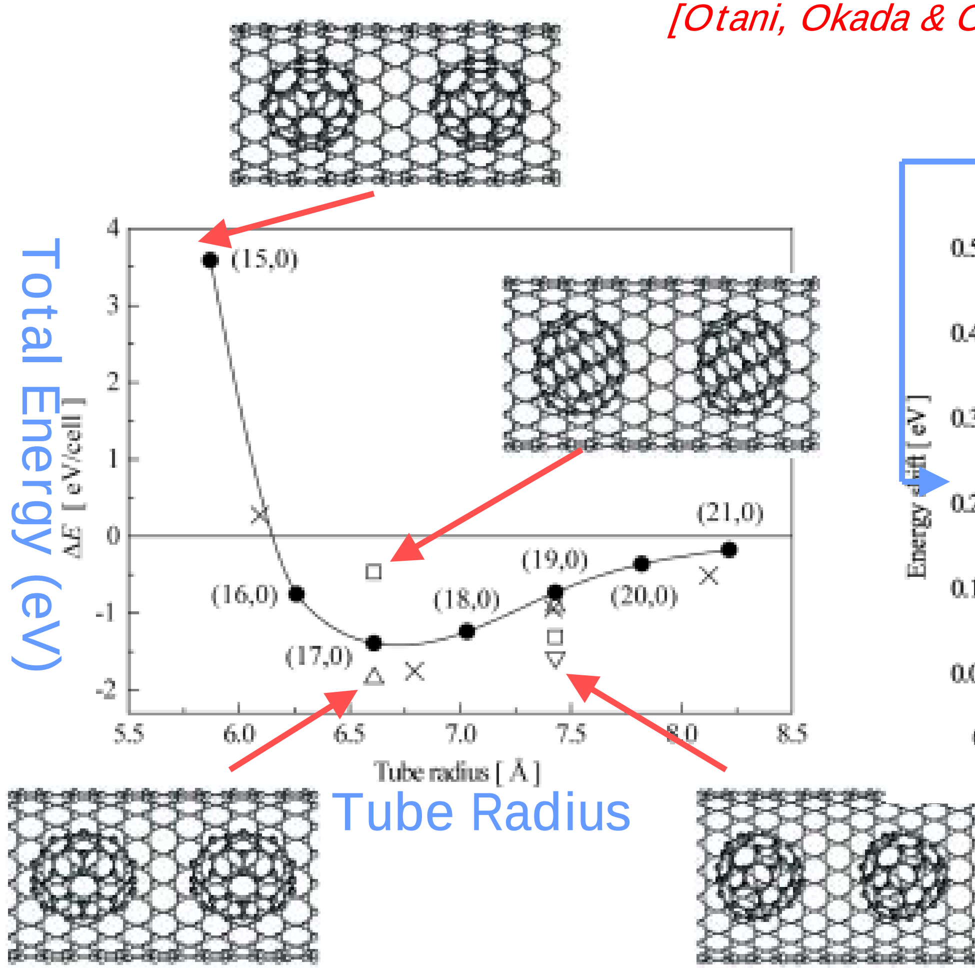
Total Charge | $\Delta\rho^-$ | $\Delta\rho^+$

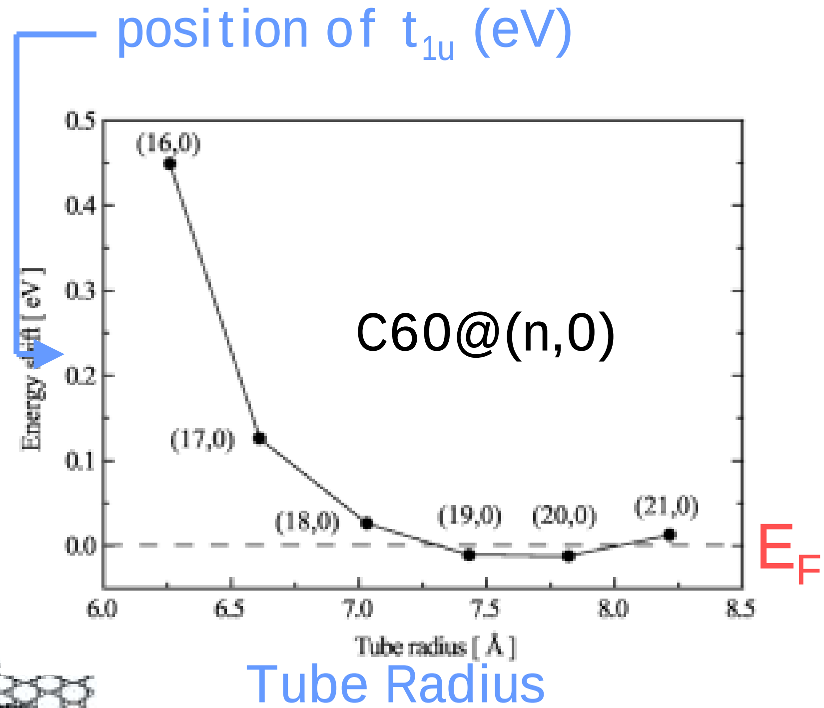




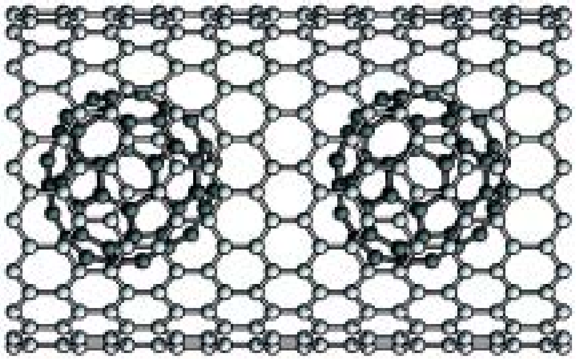
Energetics & t_{1u} state in zigzag peapod

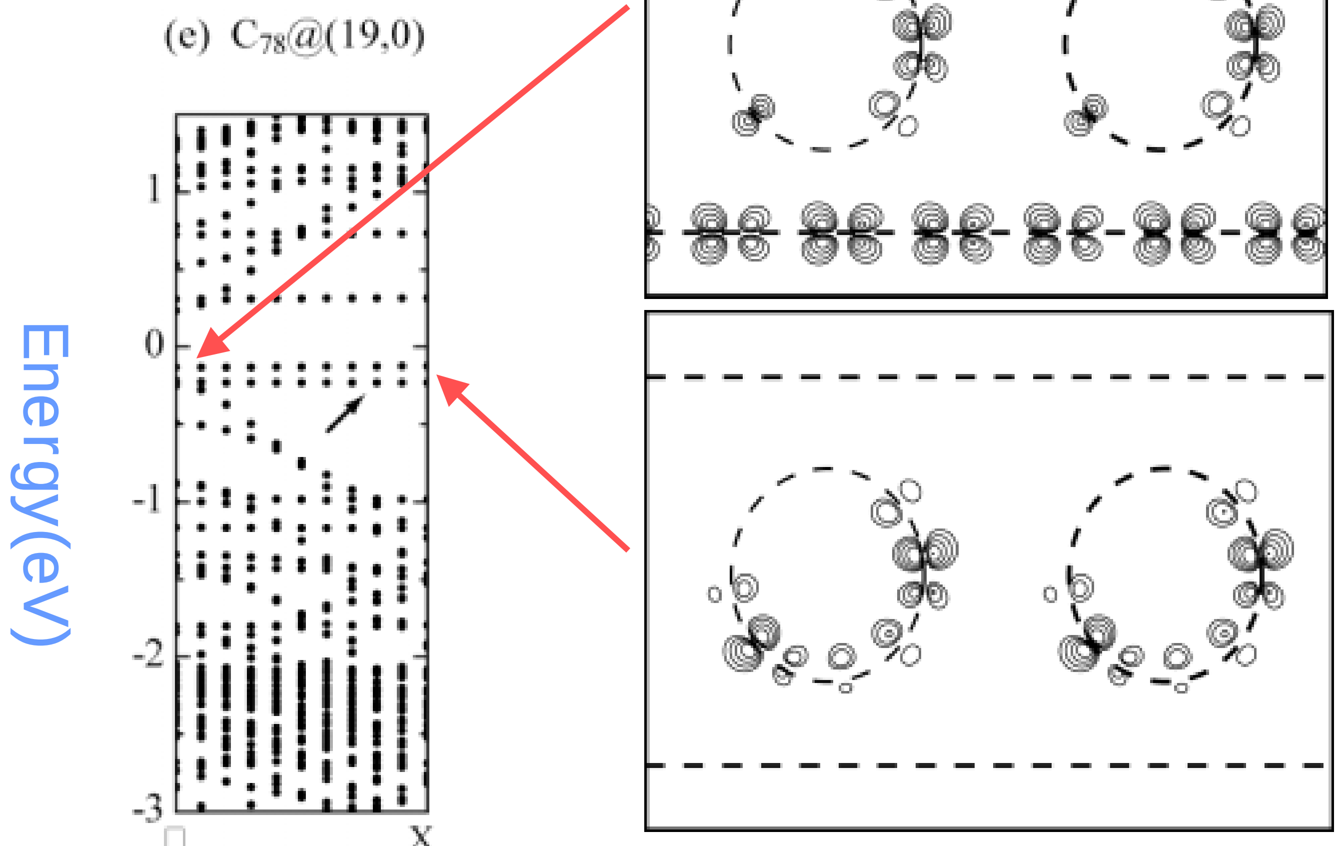
[Otani, Okada & Oshiyama, Phys. Rev. B68, 125424 (2003)]





Semiconductor tube becomes metal by putting C_{78}





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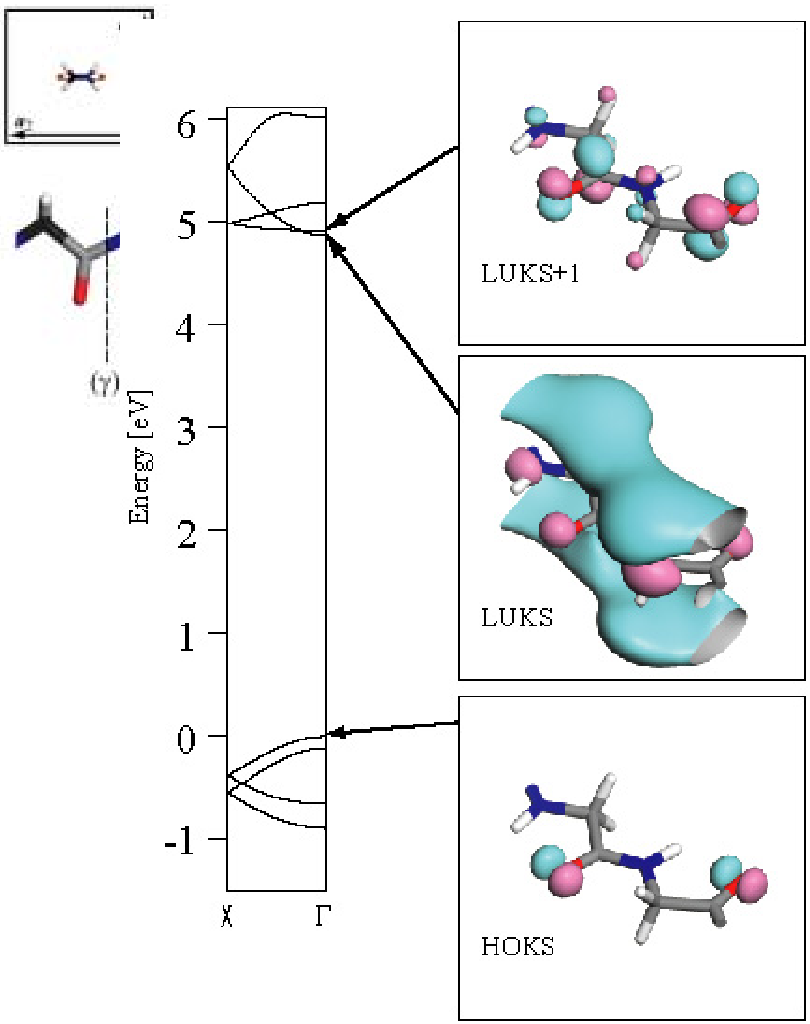
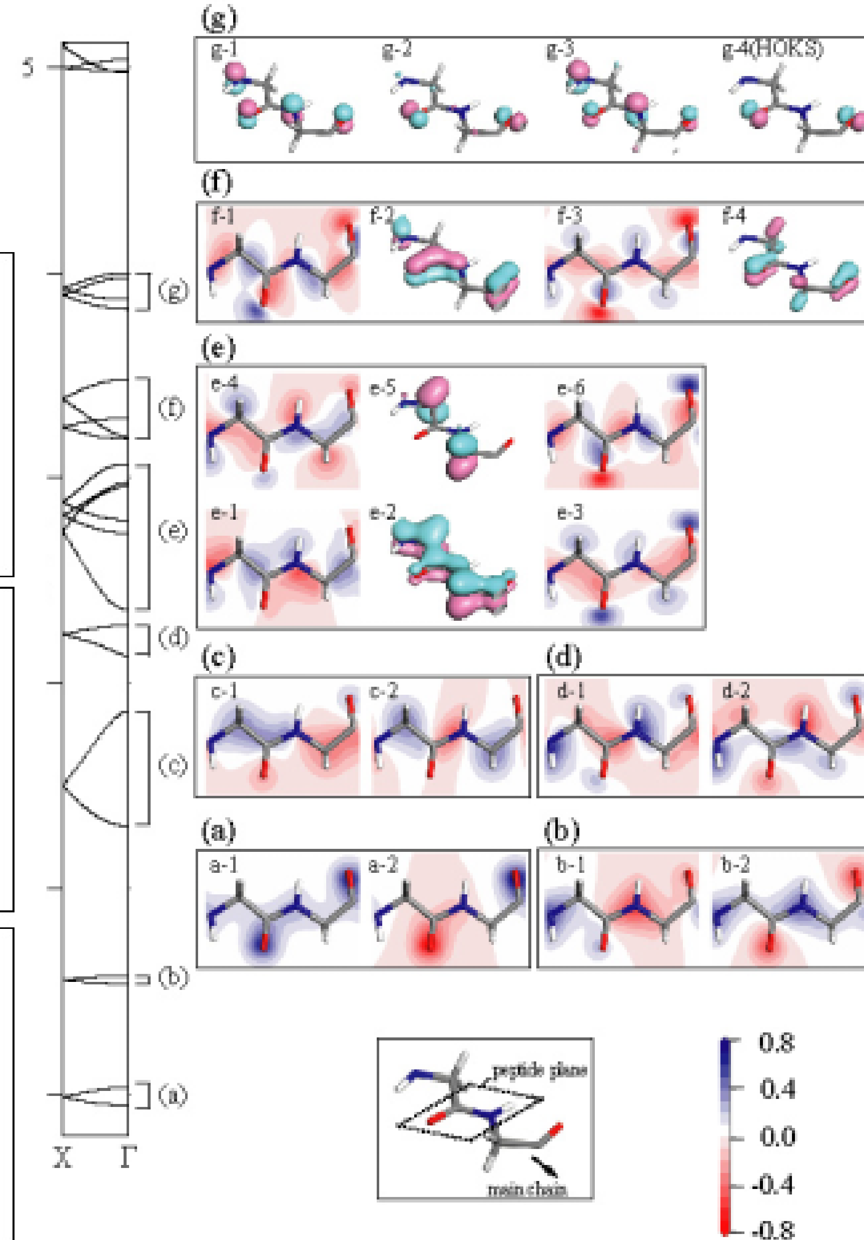
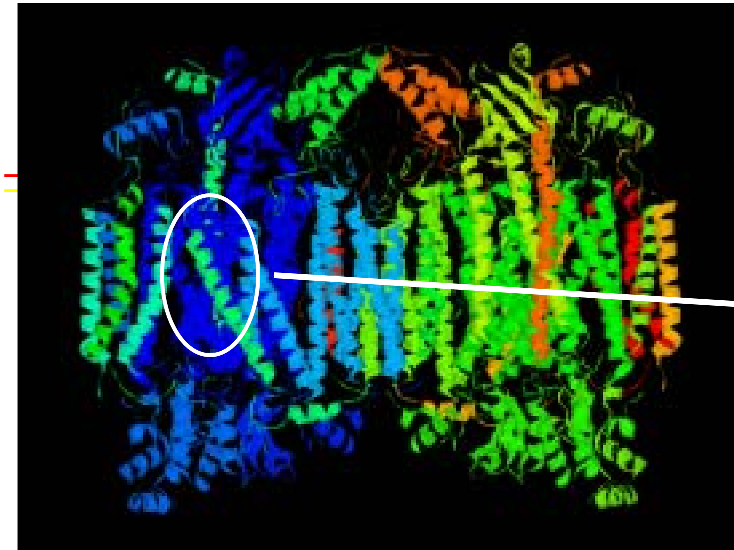
Polyglycine

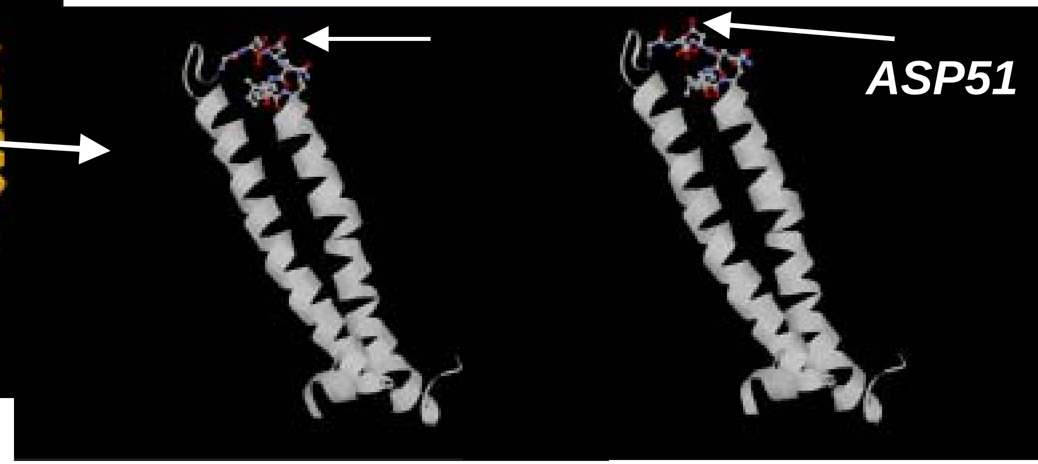




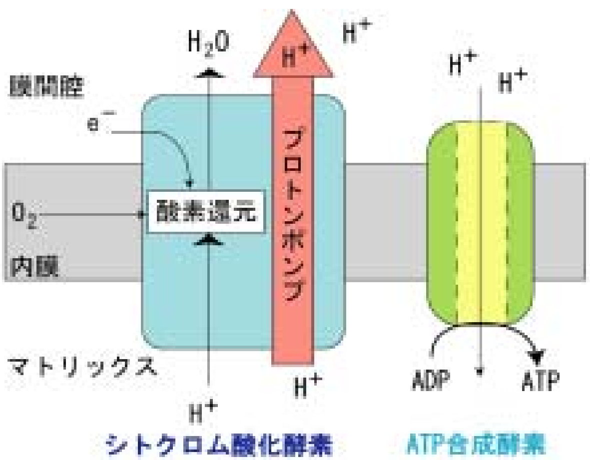
Cytochrome c Oxidase



シトクロム酸化酵素



電子移動前　　　電子移動後



精巧なナノマシン：電子移動 ⇒構造変化 ⇒プロトン移動 ⇒ATP合成

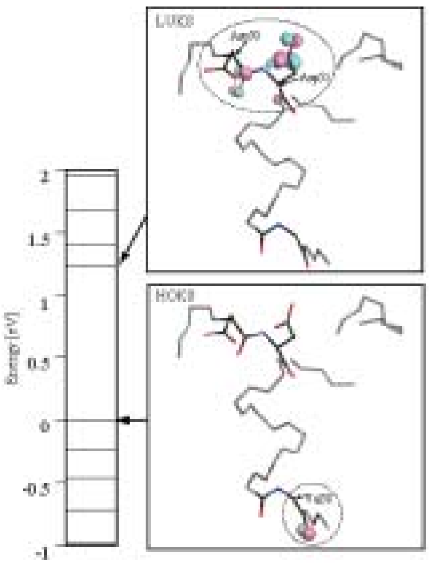
(吉川姫工大COE拠点、月原阪大蛋白研-COE拠点)

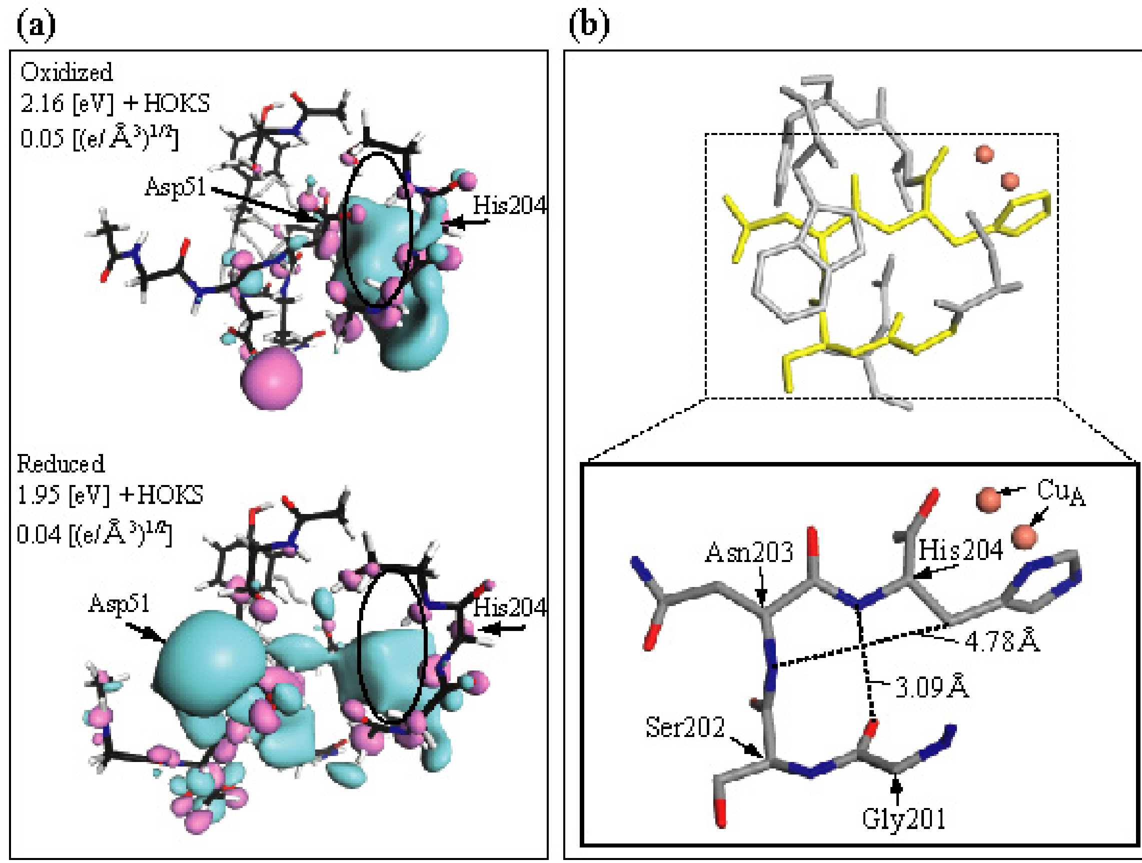
ナノマシンのからくりは？

構造・形・機能の量子論が必要

シトクロム酵素：呼吸作用の最終段階、ミトコンドリアでのプロトン移動とATP合成

Space Induces Nearly-Free-Electron States





Space!

- Proton Gate?
- NFE State: Role in Electron Transfer?

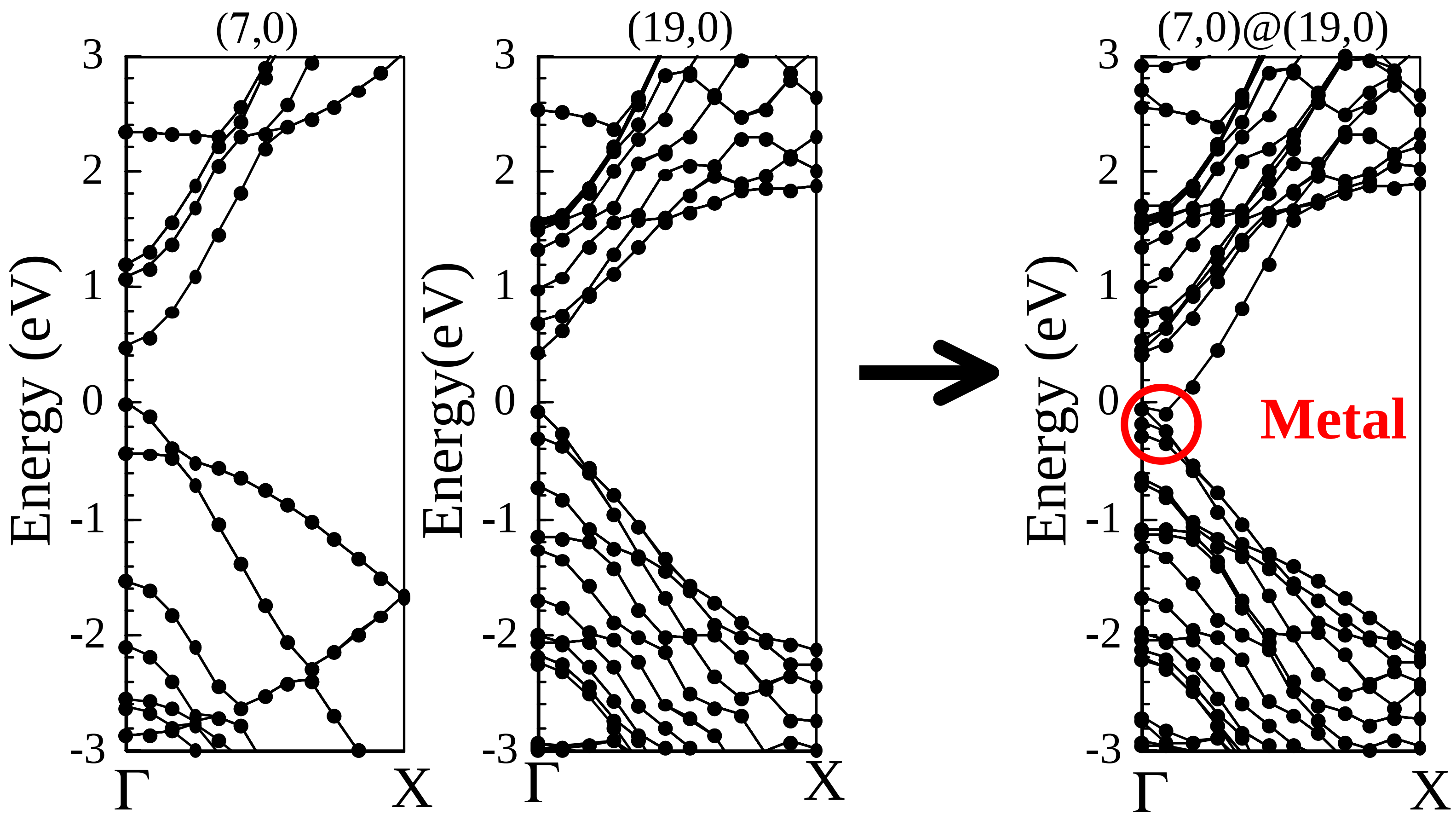
Summary

- **I have shown that**
  - *Hydrogenated Si(111) surfaces could have magnetic ordering when we control network shapes of dangling bonds*
  - *Double-walled nanotubes consisting of semiconducting nanotubes could be metallic when we control radii of the constituent tubes*
  - *Insertion of fullerenes into tubes induces drastic modification of electron states*

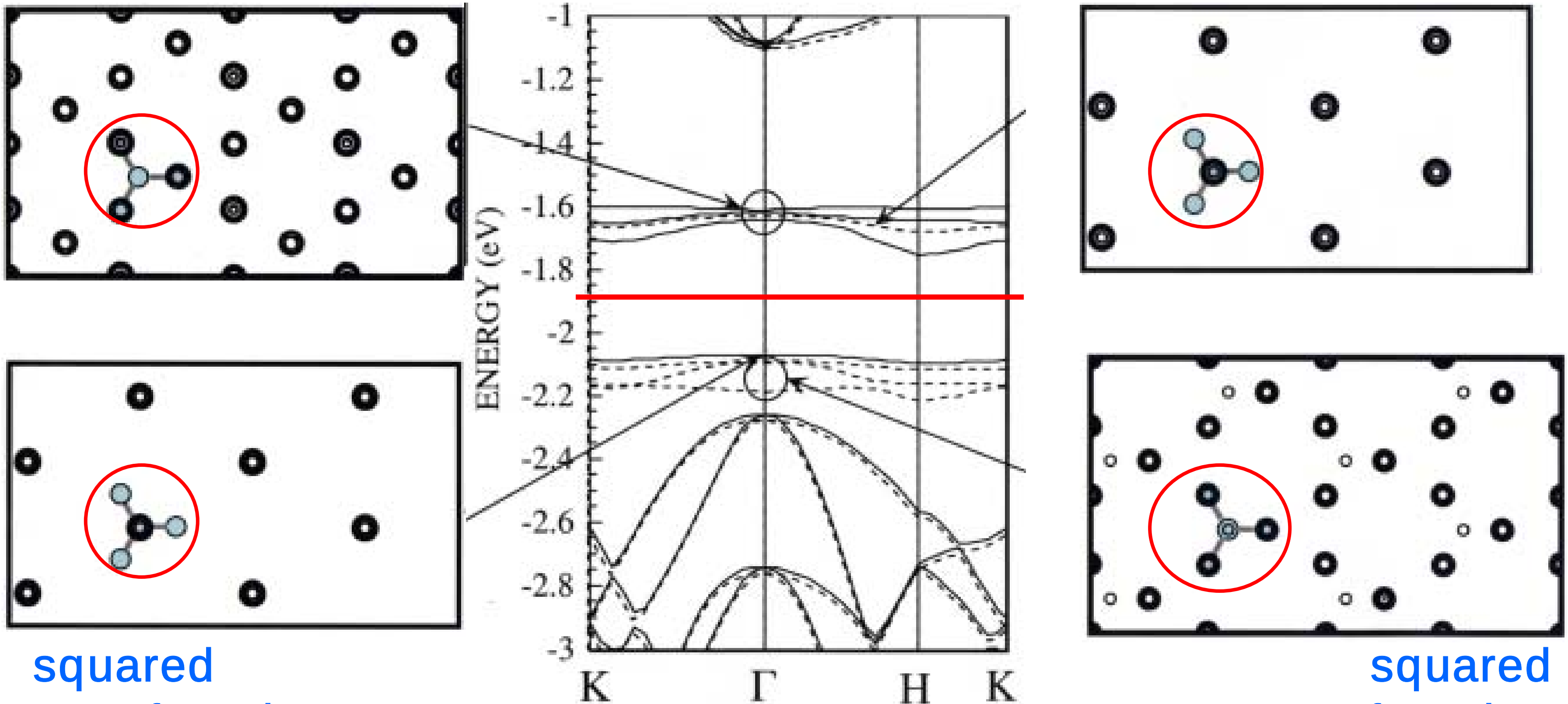
    - Shape in Nanoscale Alchemy –

    - Space seems to be a key player –
  - *Proteins also have space inside……*

Electronic Structure of (7,0)@(19,0)



Kohn-Sham levels of Triangle DB Units



squared wavefunction of minority spin state

squared wavefunction of majority spin state

Occupied below the red line:

Corresponding to Mott Insulator