Computational design of one–dimensional nanostructures with novel electronic properties

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Collaborators

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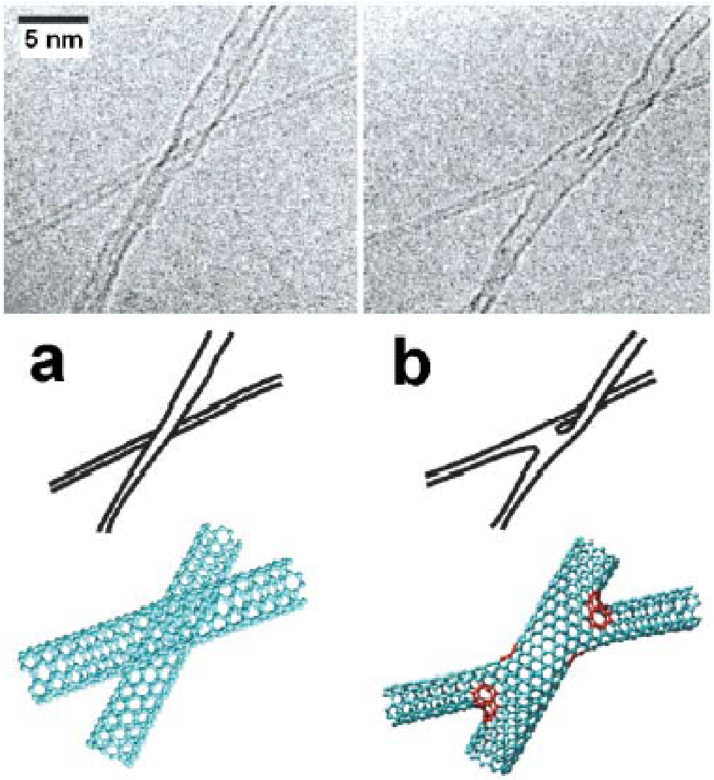
I. Orbital-Selective Quantum Conductance

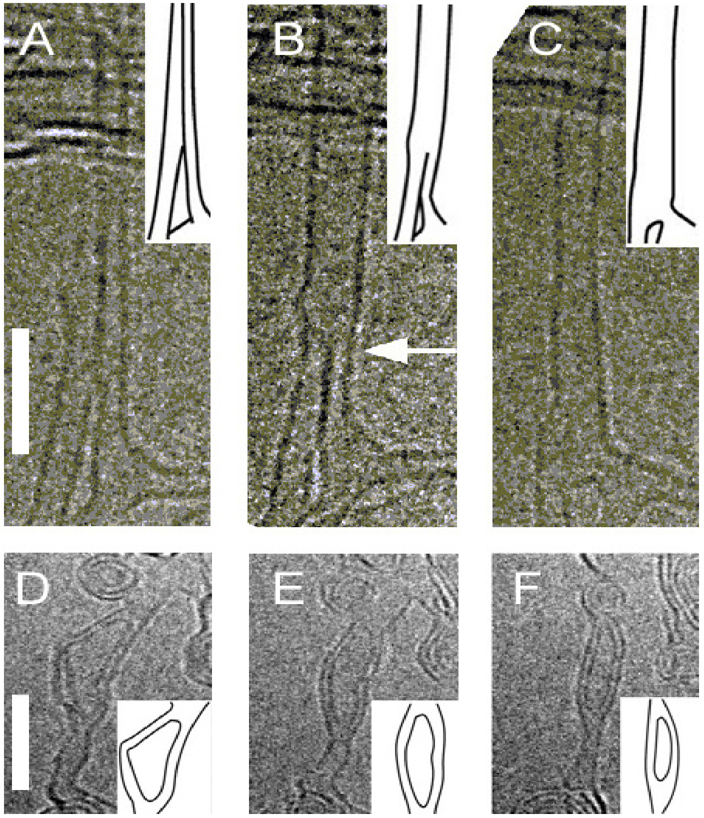
: electron filtering in carbon nanotubes

New Structures by Fusion of Carbon Nanotubes

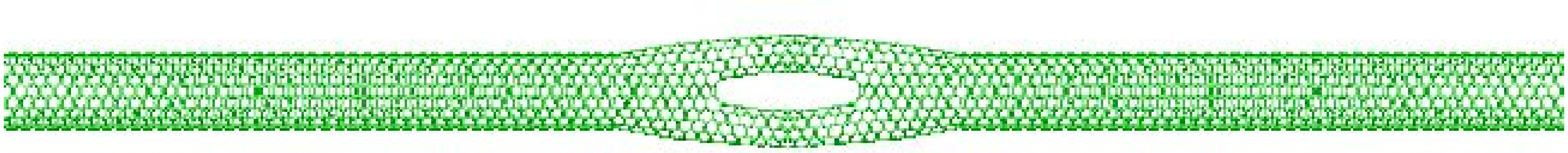
M. Terrones et. al., PRL 89, 75505 (2002); PRL 92, 75504 (2004).

- Molecular junction by welding single-walled carbon nanotubes with e-beam





Motivation



- PHASE-COHERENT TRANSPORT

Double-slit-like Aharonov-Bohm interference

(with or without B fields)

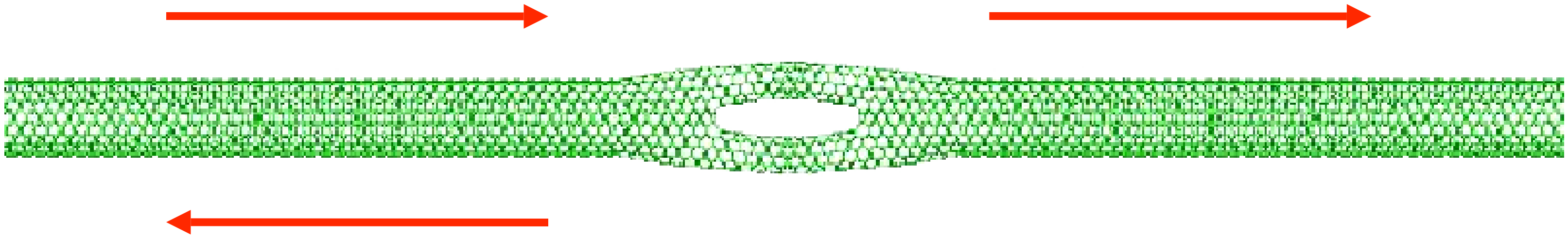
Interference between energy levels in the arm region

- POSSIBLE APPLICATION

Electron filtering of particular wave functions (Orbital STM)

(G. Kim et al. PRB 71, 205415 (2005) and J. Phys.: Cond. Mat. 19, 206217 (2007))

Model and Computational Method



(10,10) tube

metallic lead

(5,5) tubes

scattering region

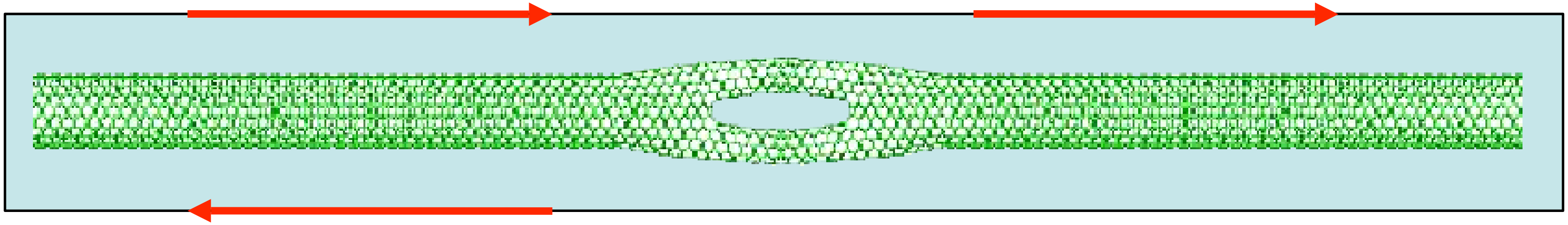
(10,10) tube

metallic lead

- π electron tight-binding approximation

$$H = V_{pp\pi} \sum_{<i,j>} a_i^\dagger a_j + h.c. \quad (V_{pp\pi} = -2.66 \text{ eV})$$

Model and Computational Method



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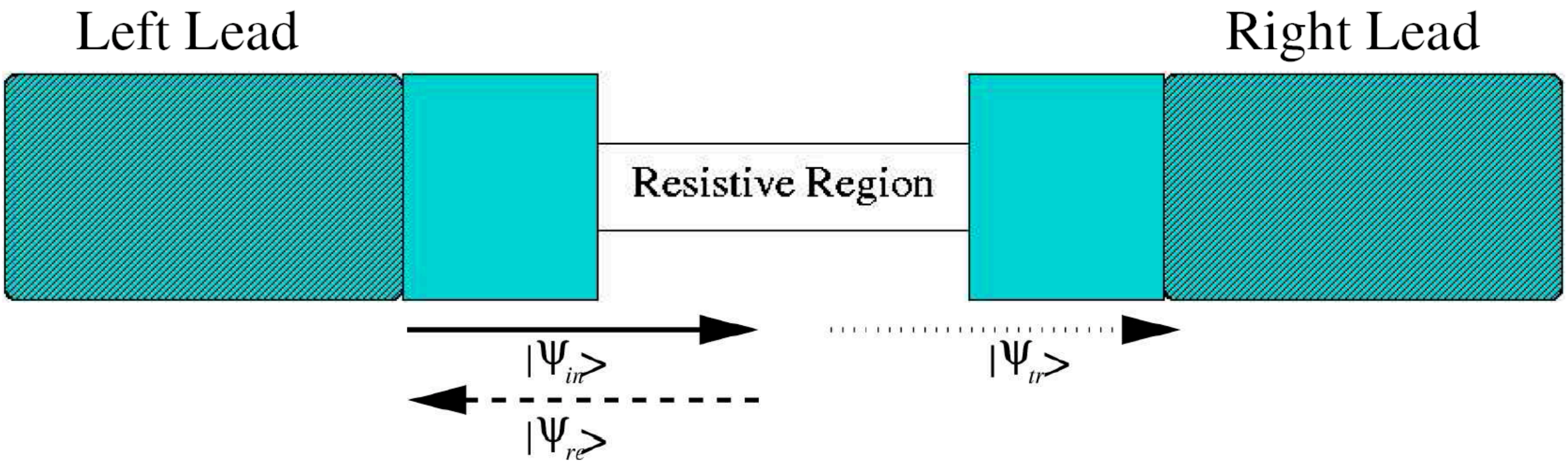


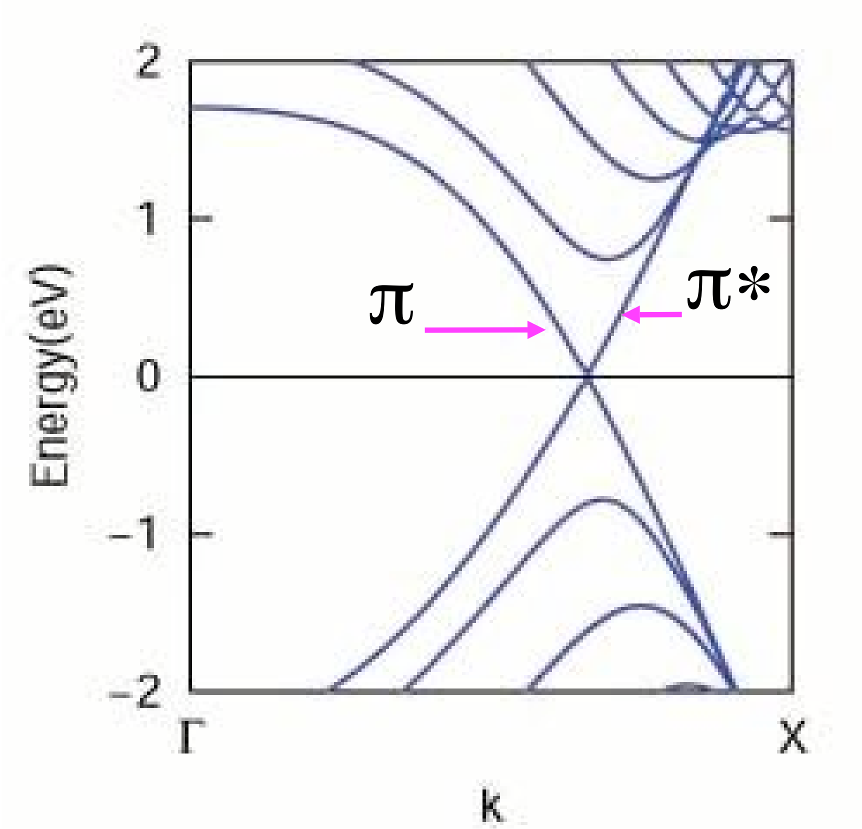
$$|\Psi\rangle = |\psi_{in}\rangle + \sum_p r_p |\psi_{re}^p\rangle + \sum_q t_q |\psi_{tr}^q\rangle + |\psi_{bd}\rangle$$

$$G = \frac{2e^2}{h}\mathrm{Tr}(\mathbf{t}^\dagger\mathbf{t}) \equiv G_0\mathrm{Tr}(\mathbf{t}^\dagger\mathbf{t})$$: Landauer formalism

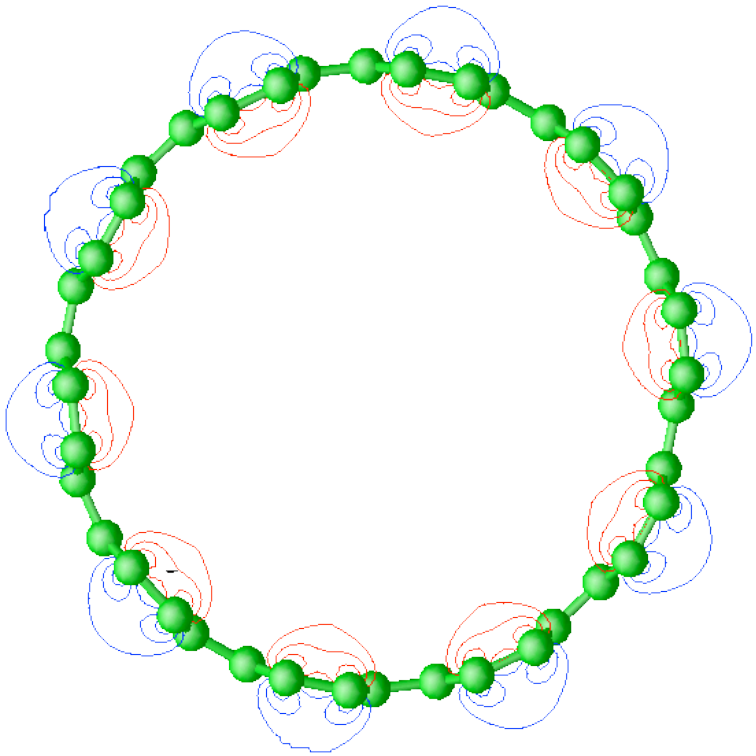
SCattering-state appRoach for eLEctron Transport (SCARLET)

H. J. Choi et al, PRB 59, 2267(1999), and in preparation

Band Structure of Armchair Carbon Nanotubes

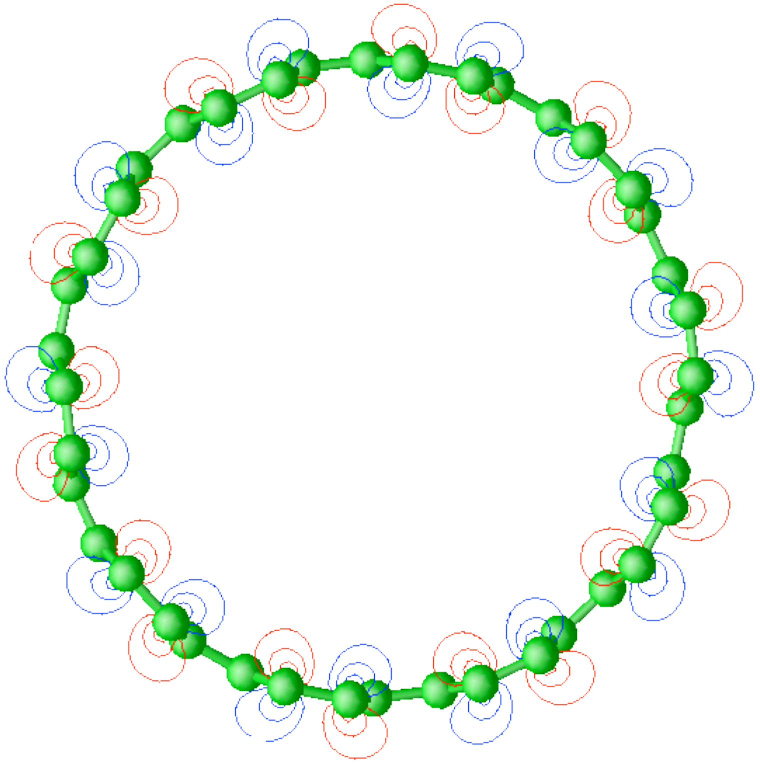


Near the Fermi level,
there are only π and π* energy bands.



π–state

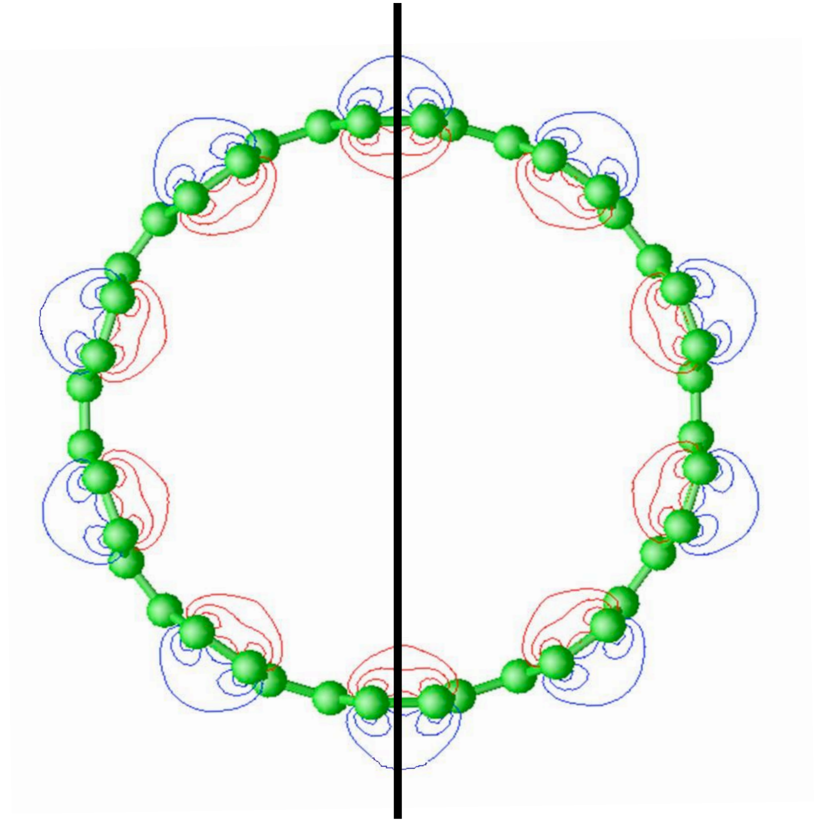
the same phase along the circumference of the tube



π^*–state

alternating phase along the circumference of the tube

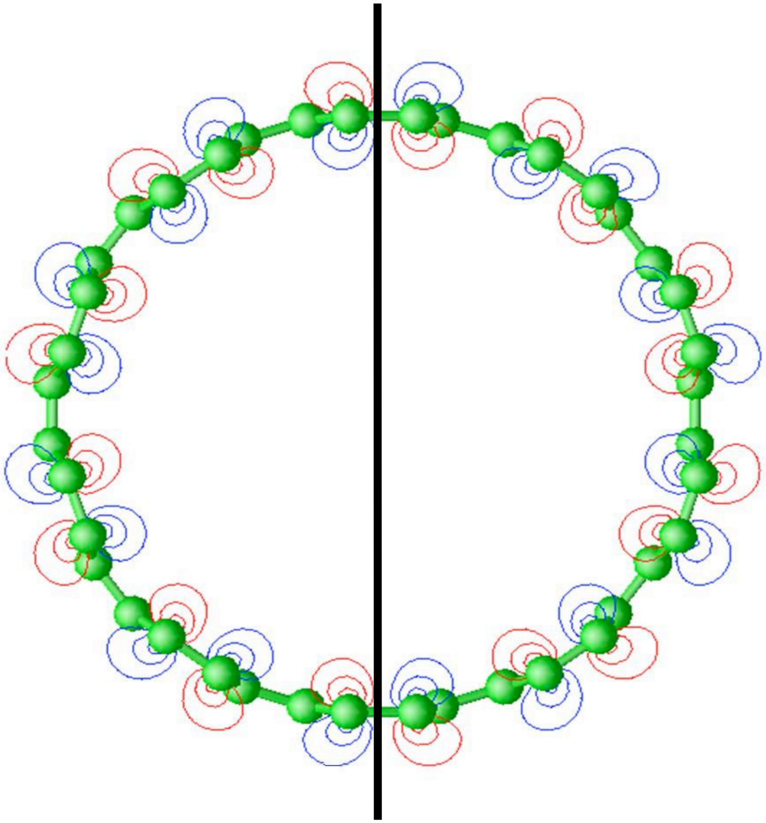
π–state



even–parity

the same phase along the circumference of the tube

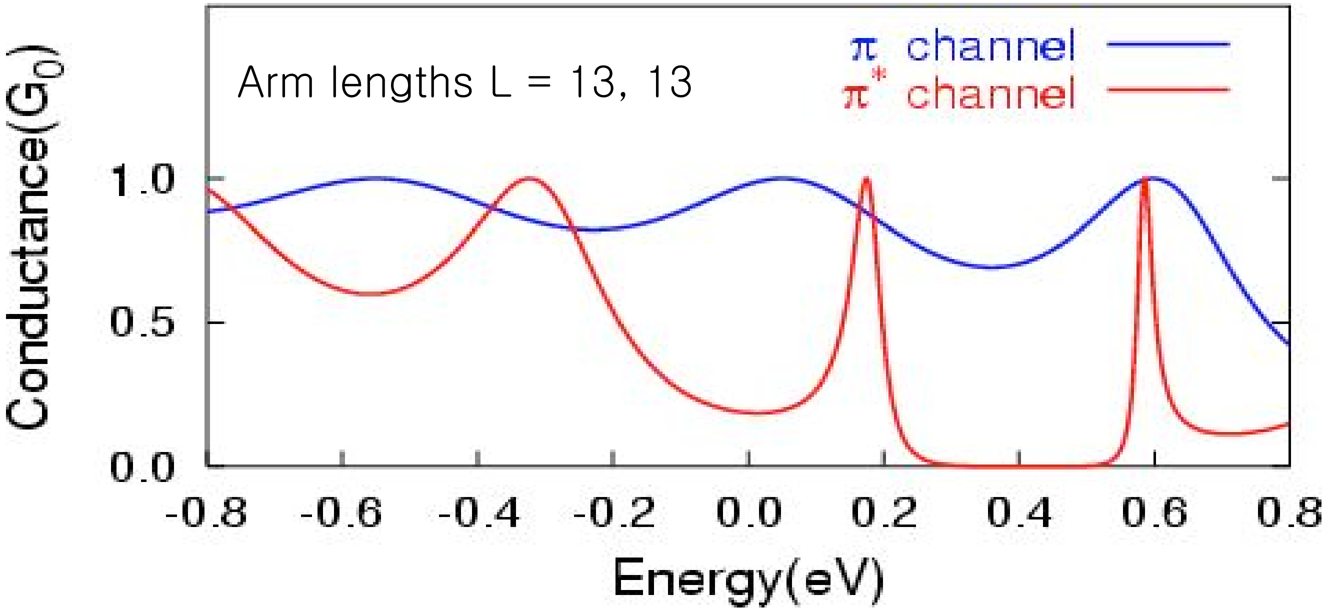
π^*–state



odd–parity

alternating phase along the circumference of the tube

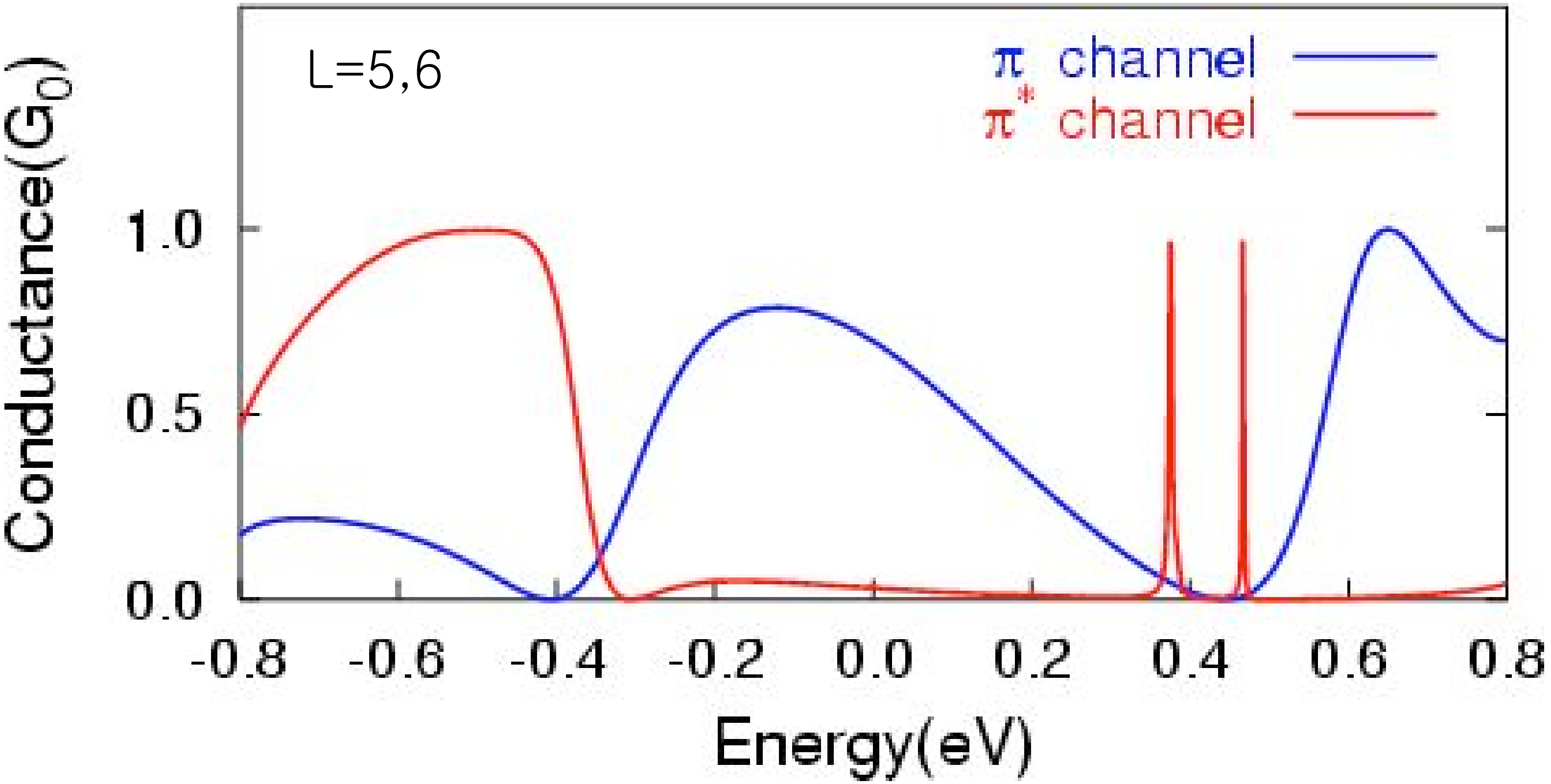
Different Conductance Pattern in Transport Channels



π channel : weak variation in conductance

π* channel : broad or narrow peaks

Conductance of MCCN with Different Arm Lengths

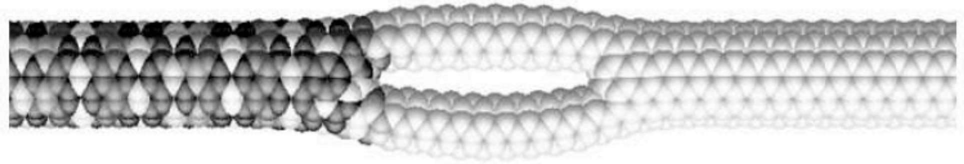


π* channel is suppressed around the Fermi level.

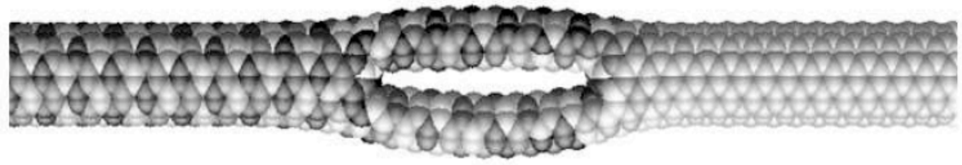
Charge density of reflected π* states

(a) L=12,12 E=0.77 eV (boundary mismatch)

(b) L=11,12 E=0.77 eV (boundary mismatch)

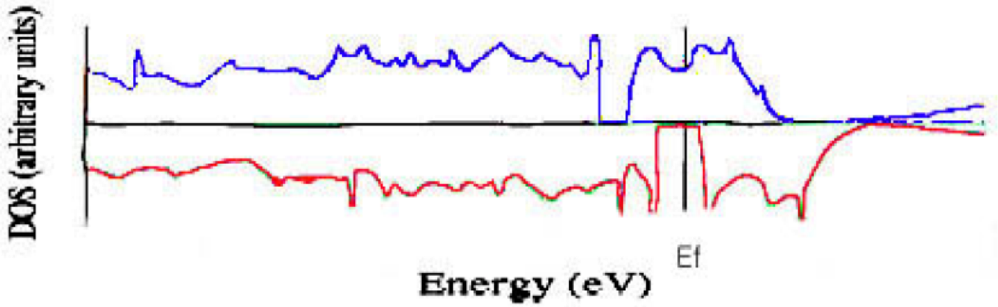


(c) L=11,12 E=0.0 eV (path length difference)

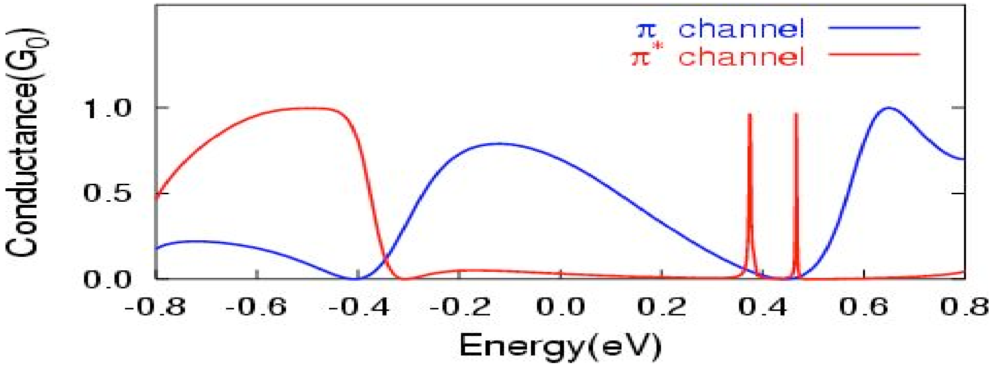


Similarity to Half-Metal in Spintronics

Spin filtering (spin valve) in half-metal (e.g. $La_{1-x}Sr_xMnO_3$)



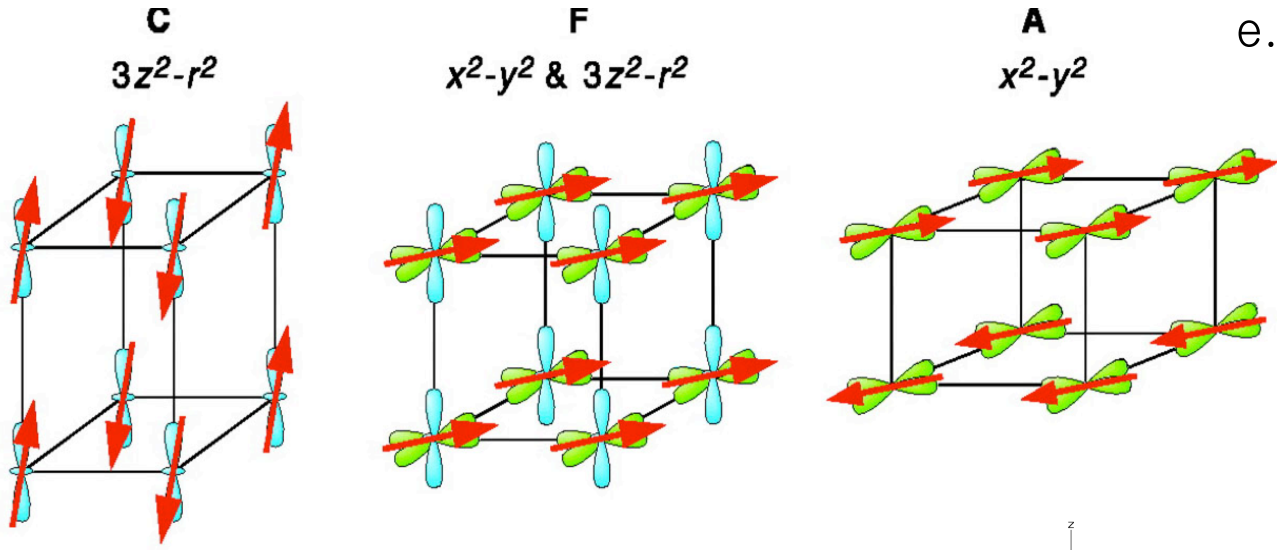
Orbital filtering in the present system (π-pass filter)



Applications : Orbital switch (valve)

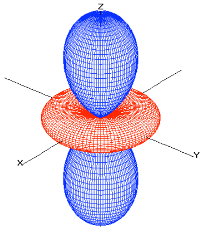
Sensor of particular orbitals

Orbital Ordering in Transition Metal Oxides

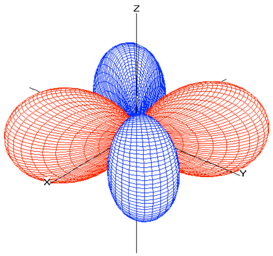


e.g. $La_{1-x}Sr_xMnO_3$

Tokura & Nagaosa, Science 288, 462 (2000)

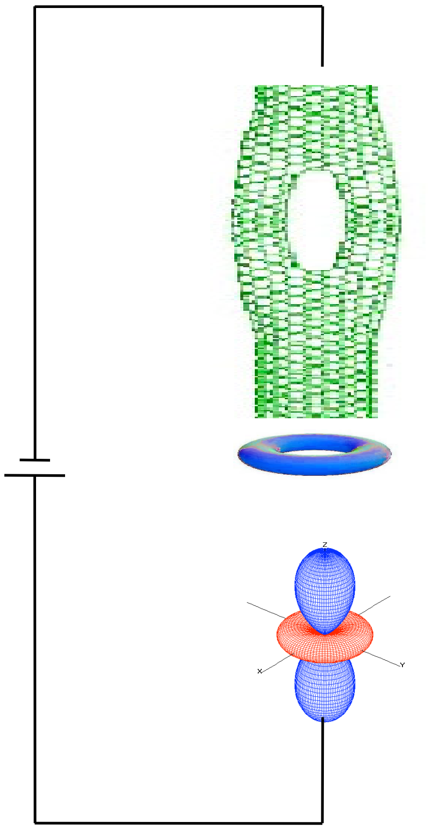


$d_{3z^2-r^2}$

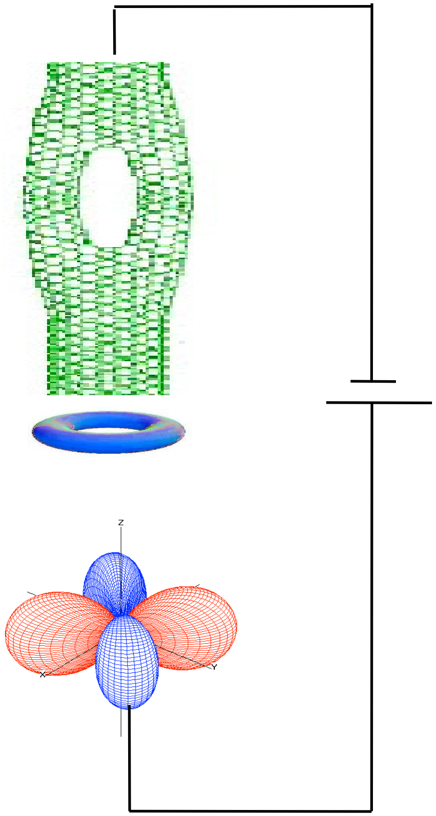


$d_{x^2-y^2}$

Probing Orbital Ordering Using MCCN as STM



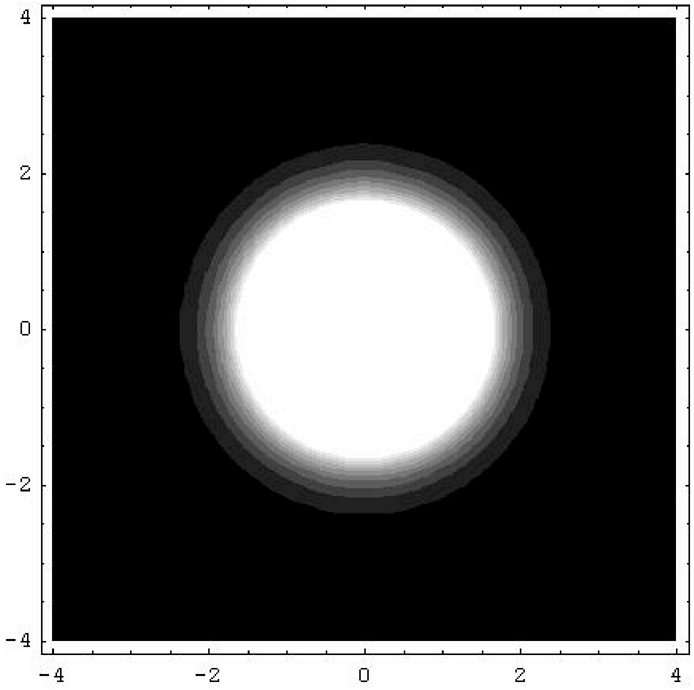
$d_{3z^2-r^2}$



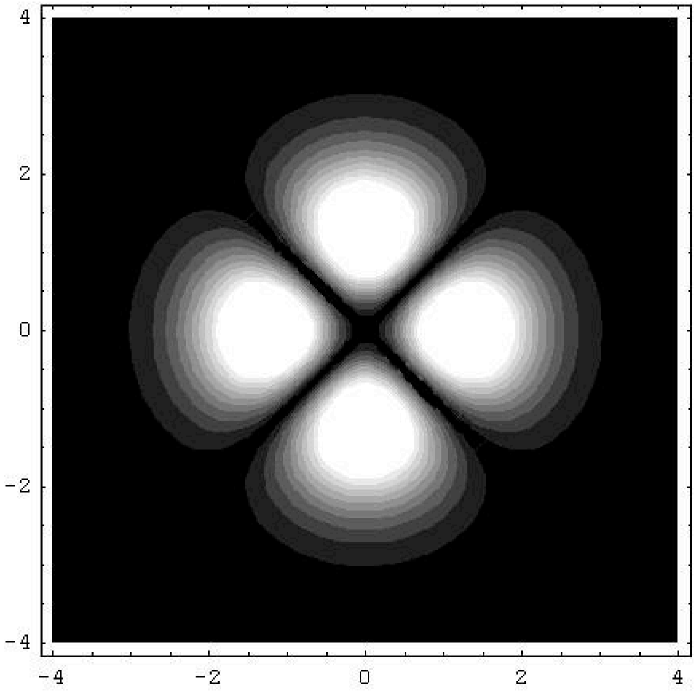
$d_{x^2-y^2}$

It is possible to probe the orbital shape of a molecule or orbital ordering in solids.

Overlap Integral for STM Simulation



$d_{3z^2-r^2}$

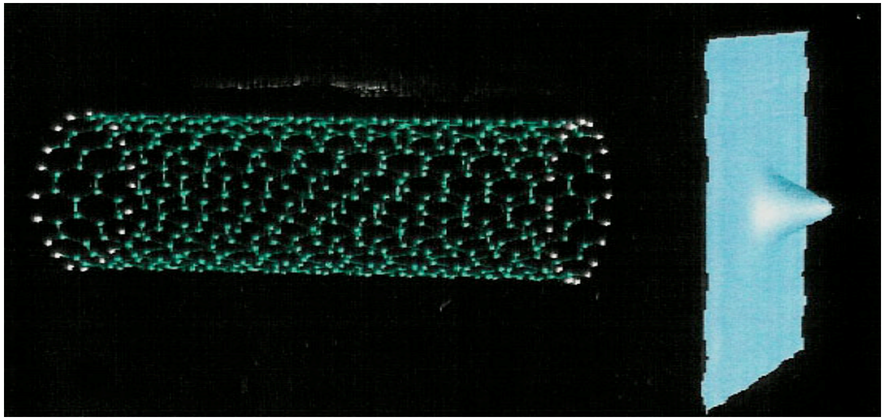


$d_{x^2-y^2}$

Summary

- In MCCN, the π^* channel exhibits asymmetric resonance lineshape and transmission zeros.
- MCCN can transmit predominately π over π^* electrons in a finite energy range (filtering of particular orbitals).

II. Orbital-Dependent Field Emission



Field emission from hydrogen passivated open tip (10,10) carbon nanotube

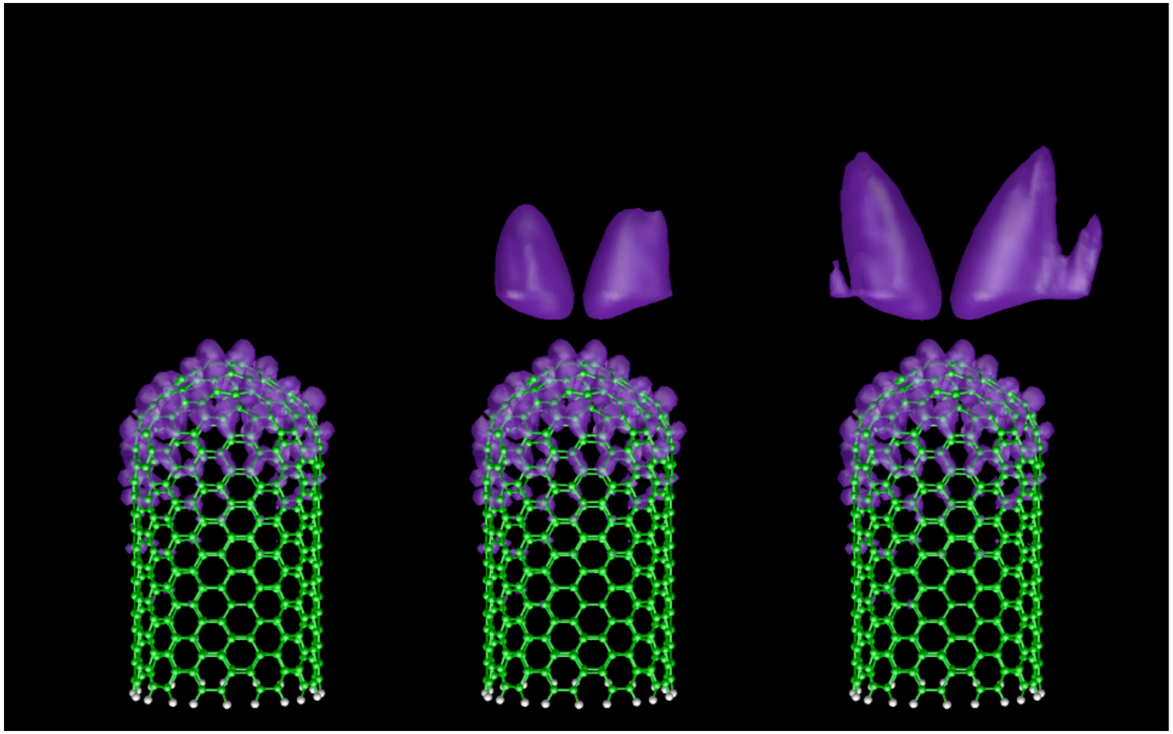
S. Han and J. Ihm, PRB **66**, 241402 (2002)

S. B. Lee et al. PRB **75**, 075408 (2007)

Computational Method

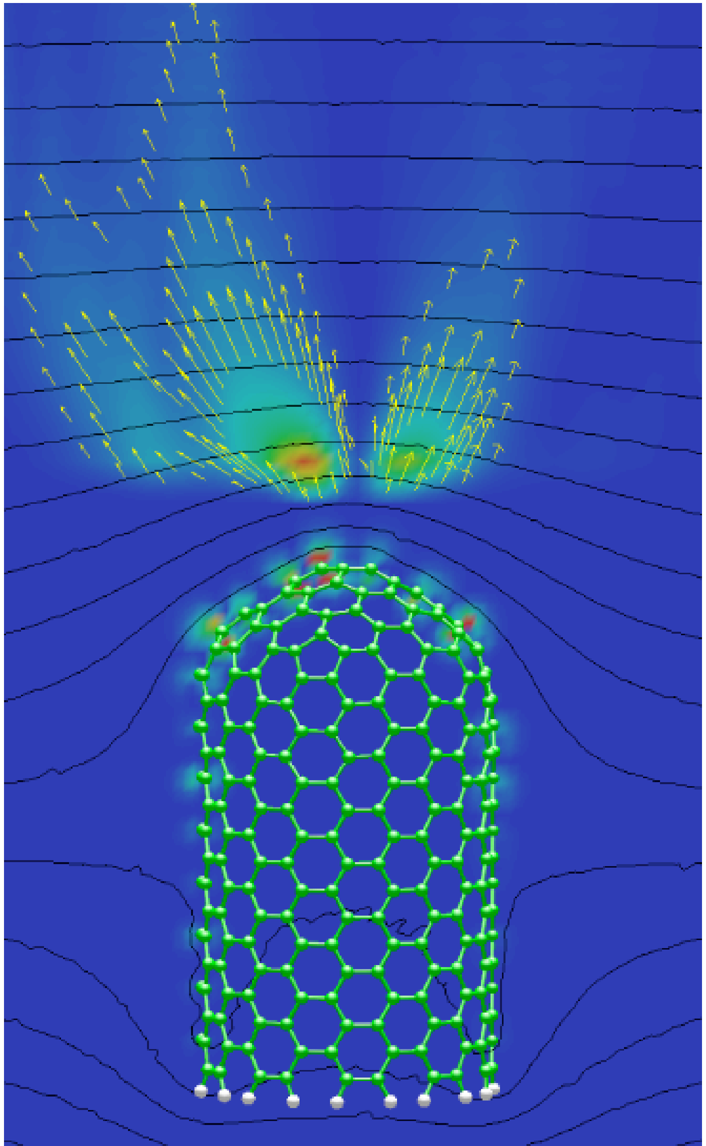
- First-principles density functional method with external fields
- Evolution of the wavefunction using time dependent Shrödinger equation (split operator method: Suzuki-Trotter, Sugino-Miyamoto)
  S. Han and J. Ihm, PRB 61, 9986(2000)

Time evolution of emitted electron from nanotube

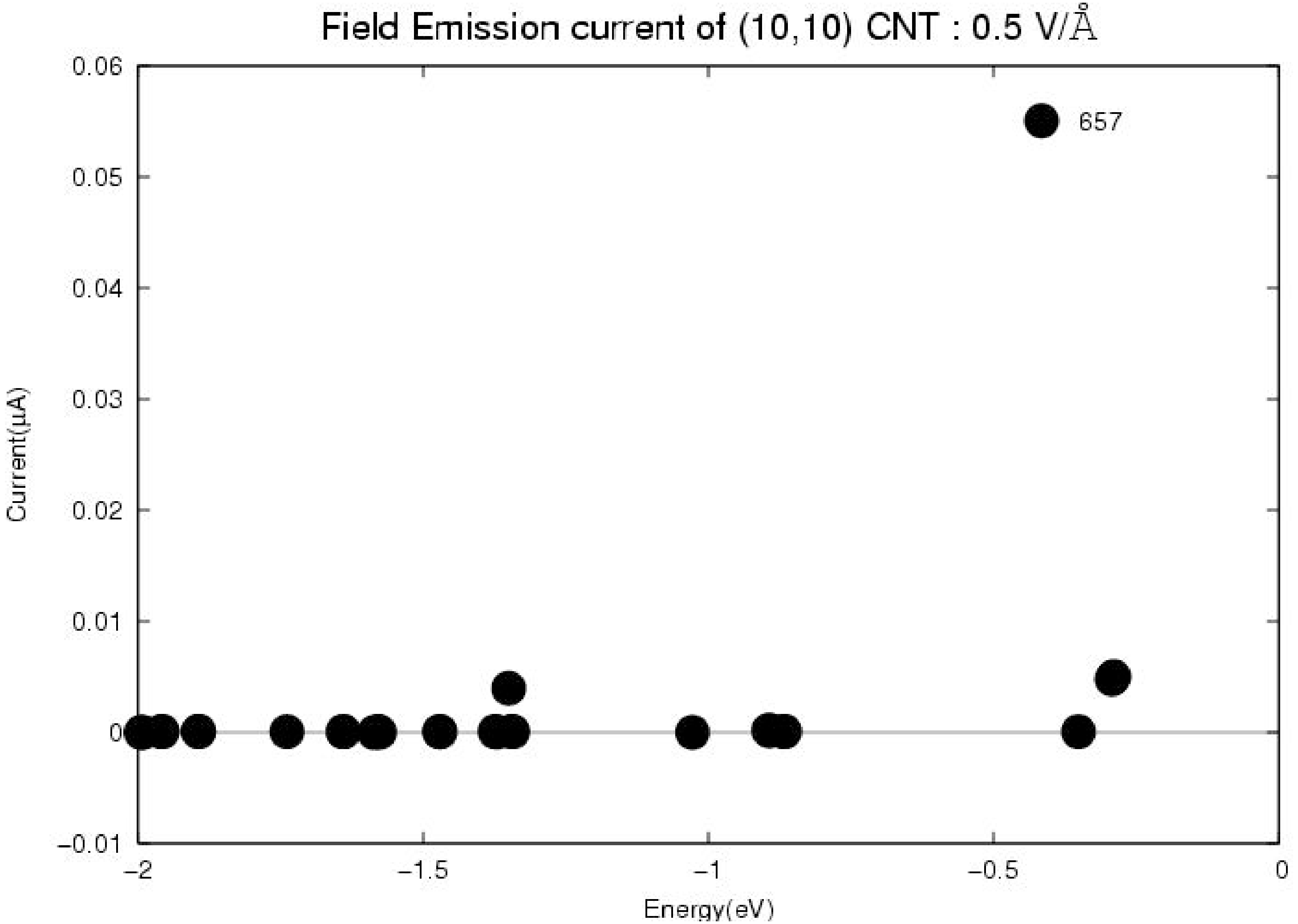


T = 0 T = 0.7 ×10^{-15} s T = 1.4 ×10^{-15} s

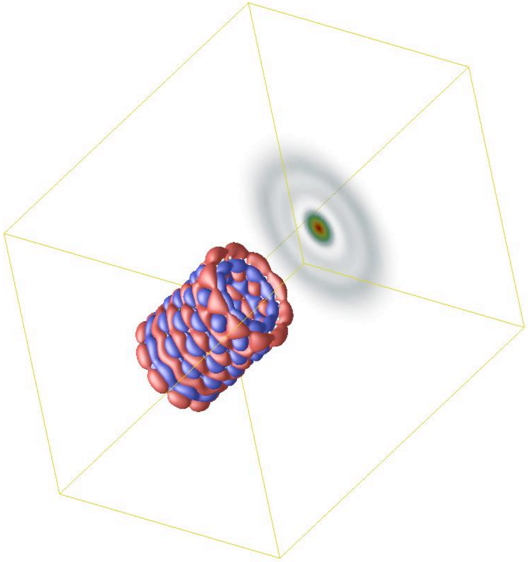
Current density distribution



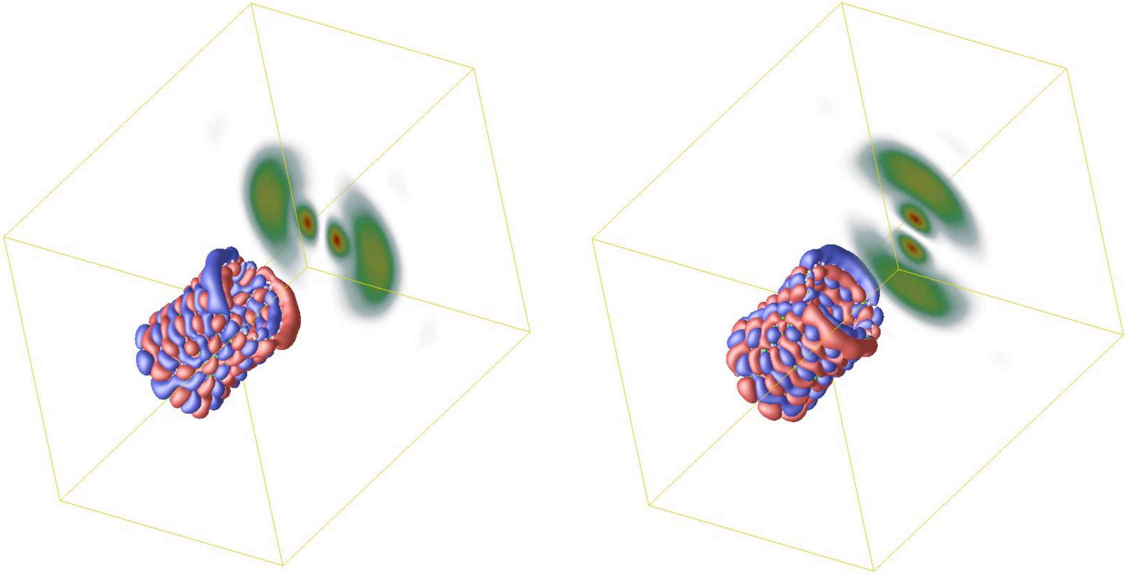
Emission current of each wavefunction : (10,10) CNT



Comparison of emission patterns : (10,10) CNT



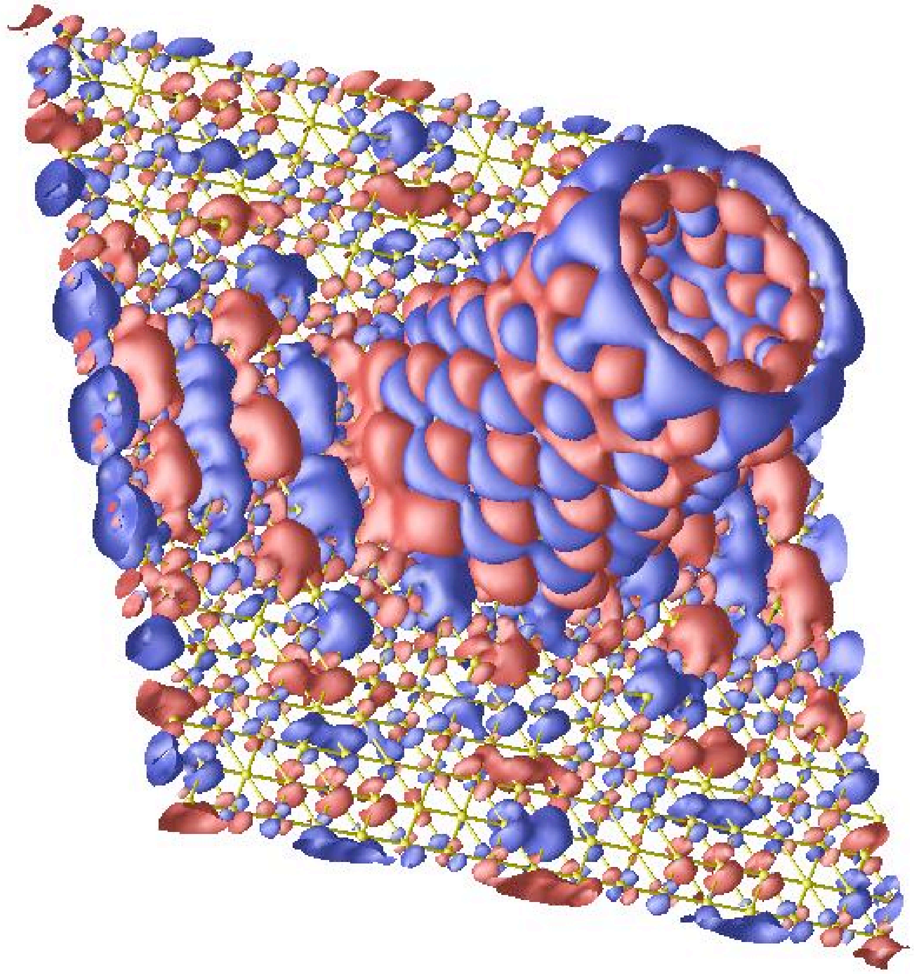
s-like state (*l* = 0)



a pair of p-like states (*l* = 1)

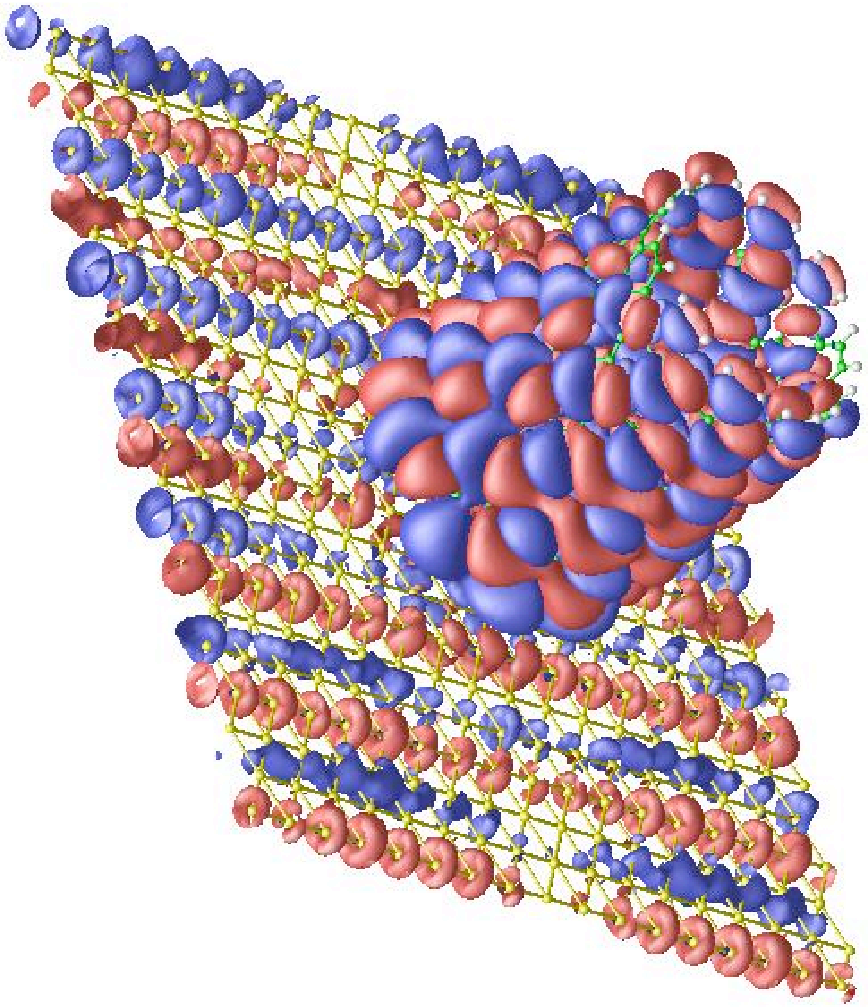
s-like states tunnel much more than p-like states.

Wavefunction : *l*=0 state (with gold substrate)



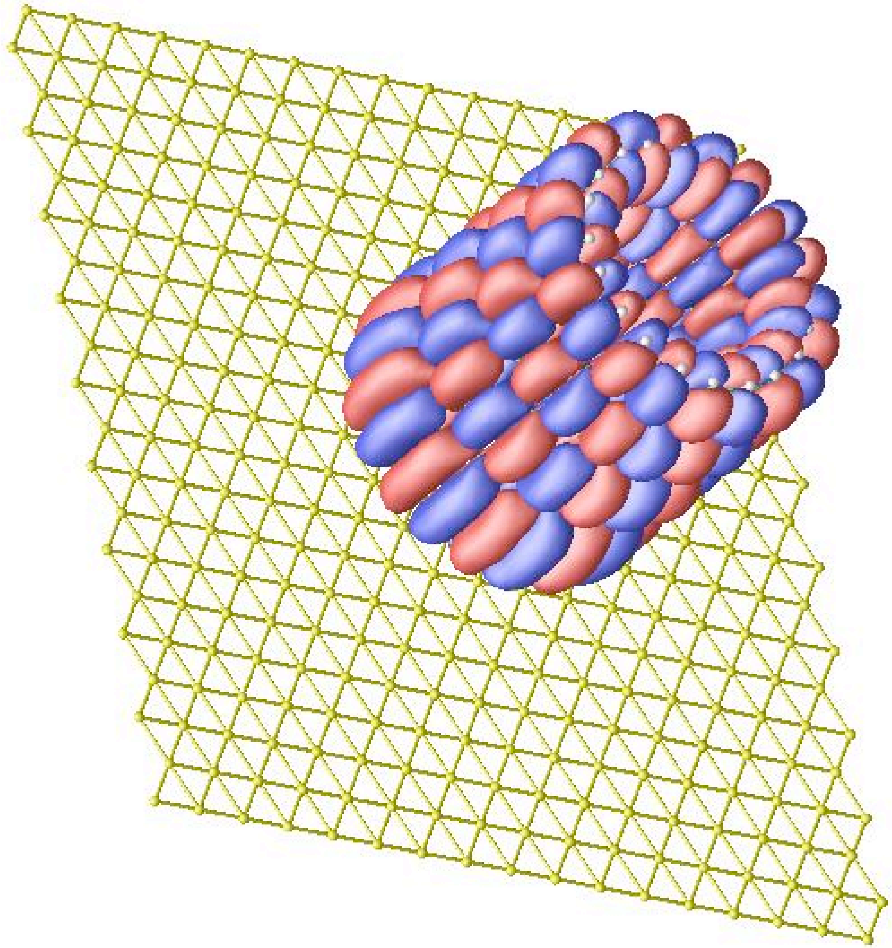
Energy = −0.036667 eV

Wavefunction : *l*=1 state



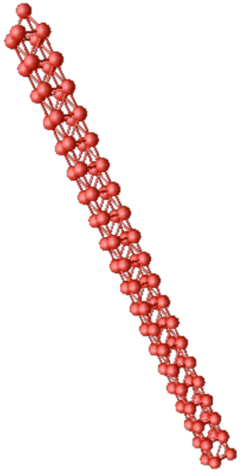
Energy = −0.929065 eV

Wavefunction : π*(effectively *l*=10) state

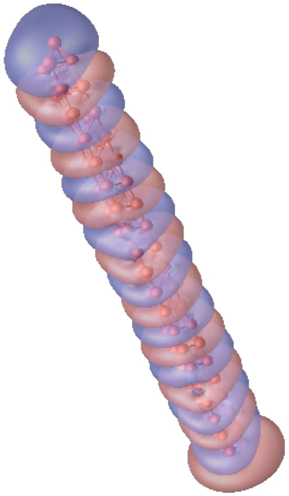


Energy = −1.488033 eV

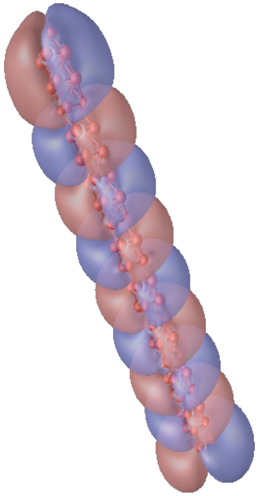
Other example : Silver Nanowire



atomic structure



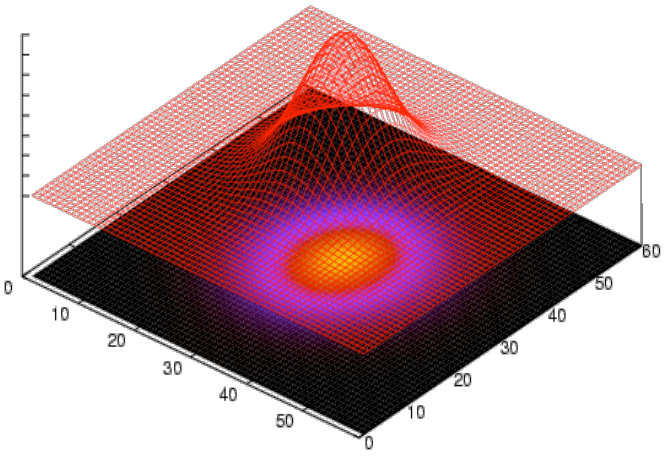
s-like state



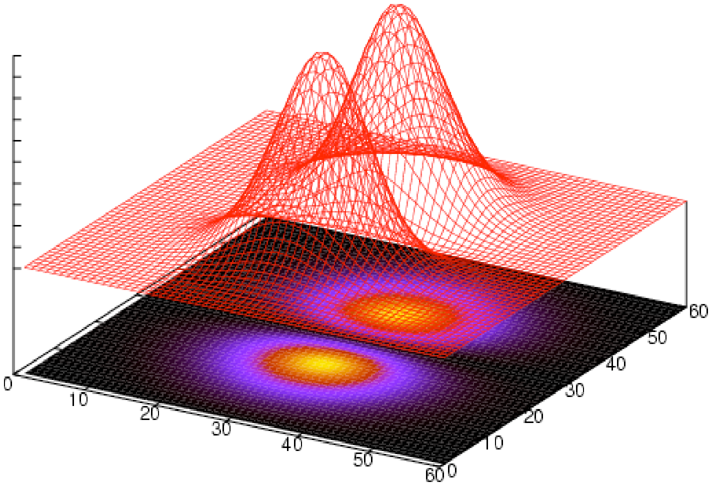
p-like state

C-K. Lee et al. Nanotech. 18, 475706 (2007)

Tunneling electron density profile



s-like state (*l* = 0)



p-like state (*l* = 1)

(Scale is 10 percent of s-like state.)

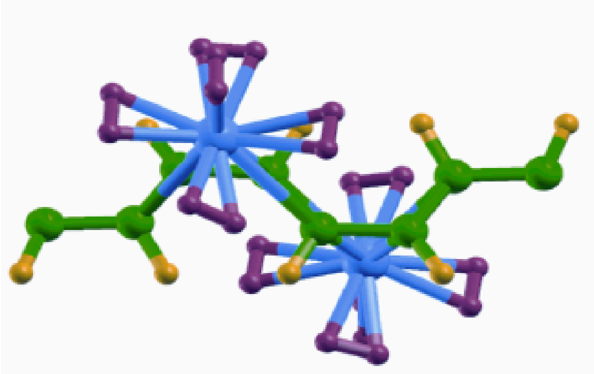
s-like states tunnel much more than p-like states.

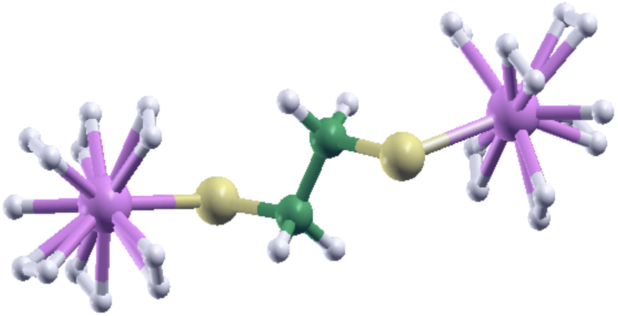
Sharper edge(3 Å) produces larger spot size (>10 Å)!

Summary

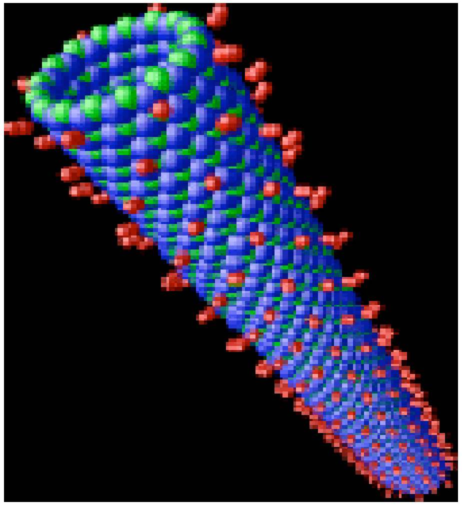
- Field emission of open-ended carbon nanotubes comes mainly from an s-like state.

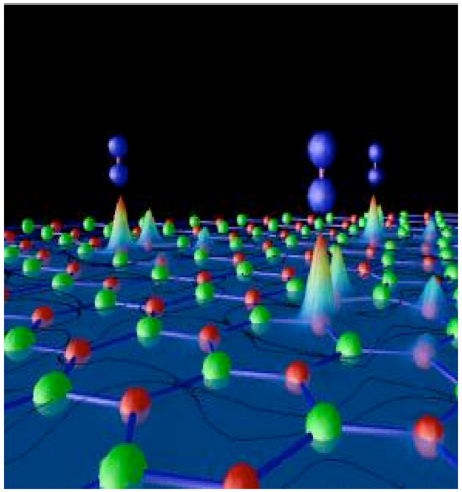
III. Computational design of hydrogen storage nanomaterials





Adsorption on nanostructured solids





- **Merits of Adsorption**

Safety (solid-state storage)

High storage capacity (large surface).

Low desorption temperature and

good reversibility (weaker bonding)

- **Drawback of CNT**

Too small binding energy ~0.08 eV

J. S.-H and K. Y.-K, Phys. Rev. B 69, 245120 (2004)

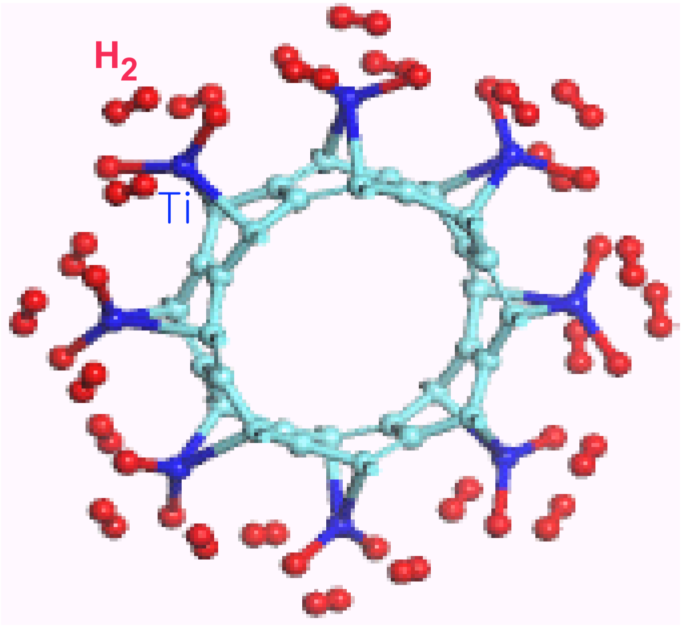
T. Yildirim and Hartman, Phys. Rev. Lett. 95, 215504 (2005)

Near room temperature and ambient pressure, required binding energy of H_2 is

0.2 - 0.6 eV (0.3 eV)

Metal decoration

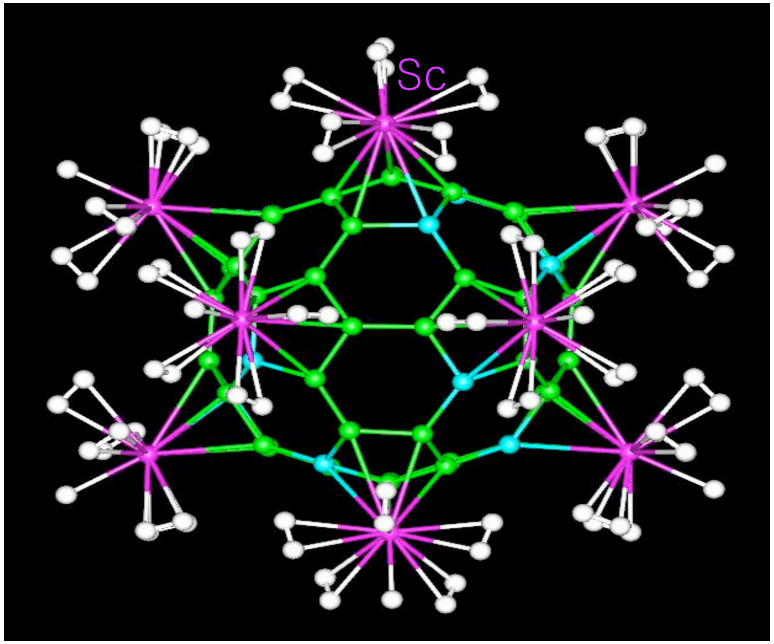
Ti-decorated CNT



7.7 wt%

T. Yildirim et al. PRL, 94, 175501 (2005)

Sc-decorated fullerene



8.8 wt%

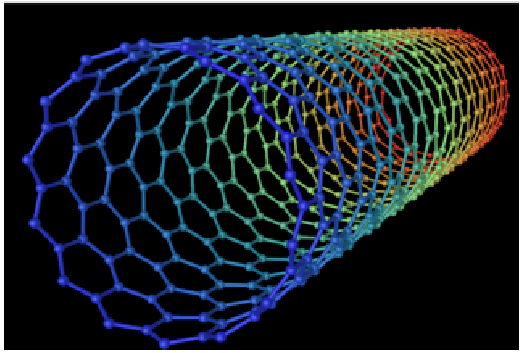
Y. Zhao et al. PRL, 94, 155504 (2005)

Meet 0.2-0.6 eV/H_2 (intermediate bonding strength) and

DOE goal for gravimetric capacity (6 wt%)

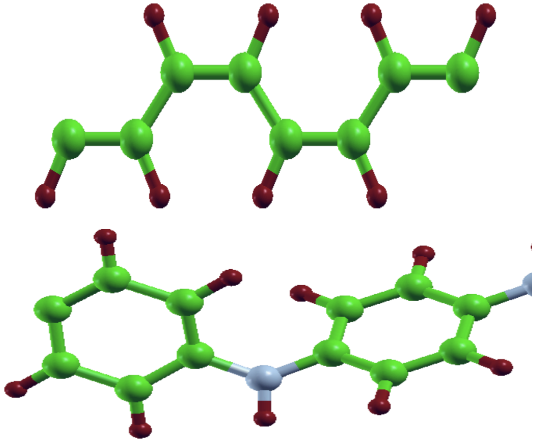
Metal decorated polymers

Disadvantages of CNTs and fullerenes



- Usable capacity is reduced (~4wt%).
- Non-solid form (fullerene).
- Unnecessary inside space.
- Ti clustering.

Advantages of polymers



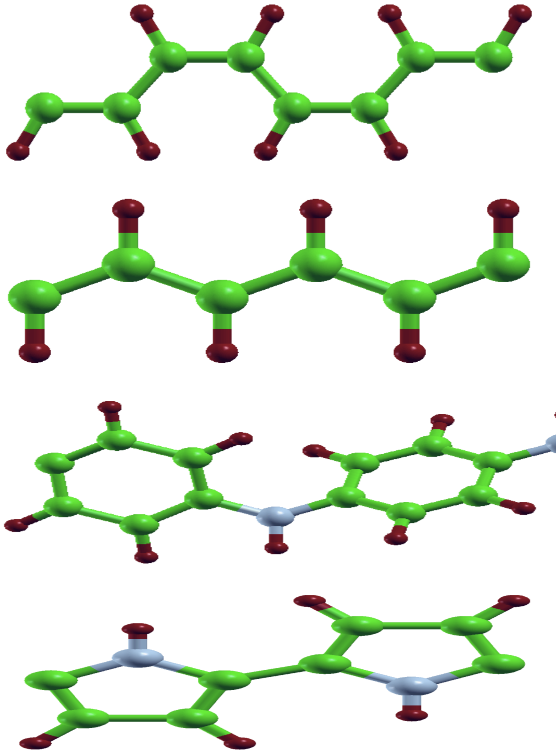
- Higher usable capacity (mass and volume).
- Diversity in geometry and composition.
- No unnecessary space.
- (Clustering problems remain.)

Computational Methods

1. Density Functional Theory (DFT)
2. GGA (LDA+U, QMC)
3. PWscf code (Plane wave basis)
4. Ultrasoft pseudopotential

Combinatorial metal decoration to polymers

Representatives for Polymers



Cis-PA

Trans-PA

Polyaniline

Polypyrrole

Combinatorial

Decoration

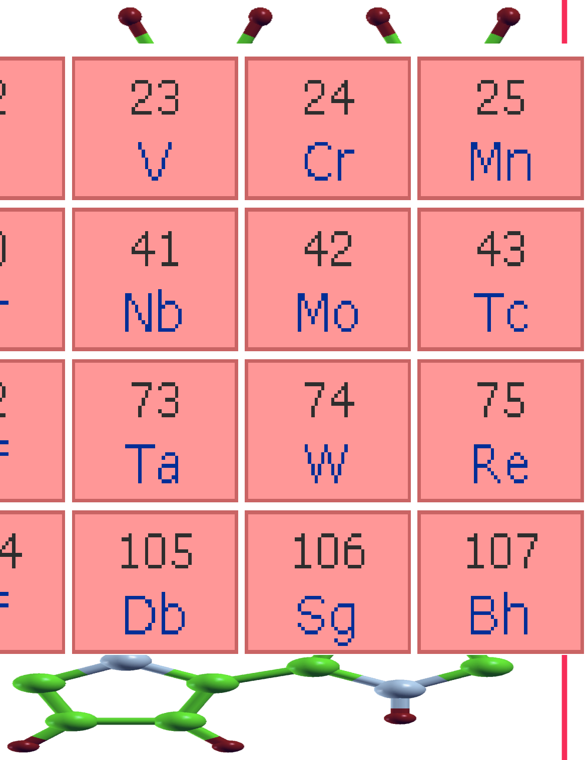
Selected decorating atoms

- ● Sc (Scandium)
- ● Ti (Titanium)
- ● V (Vanadium)

Combinatorial metal decoration to polymers

Representatives for Polymers

Selected decorating atoms



21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub

P

Polypyrrole

Combinatorial metal decoration to polymers

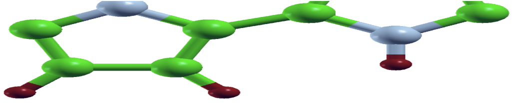
Representatives for Polymers

Selected decorating atoms

21 Sc	22 Ti	23 V

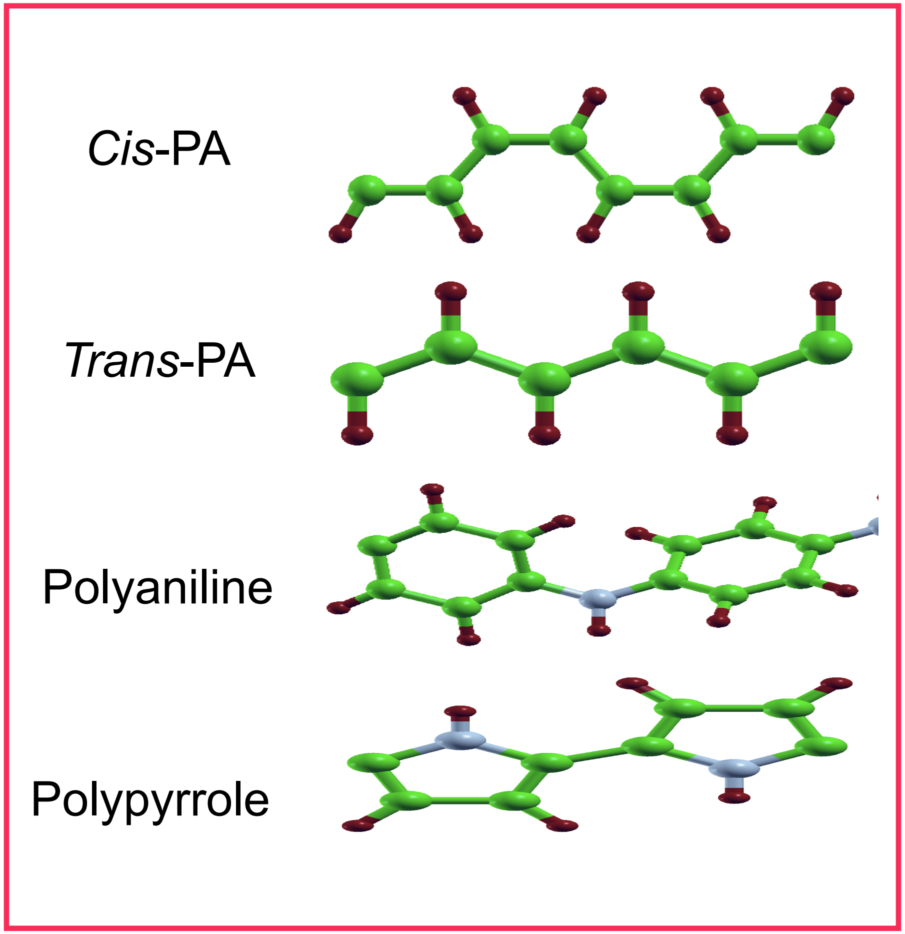
[redacted]

Polypyrrole



Combinatorial metal decoration to polymers

Representatives for Polymers

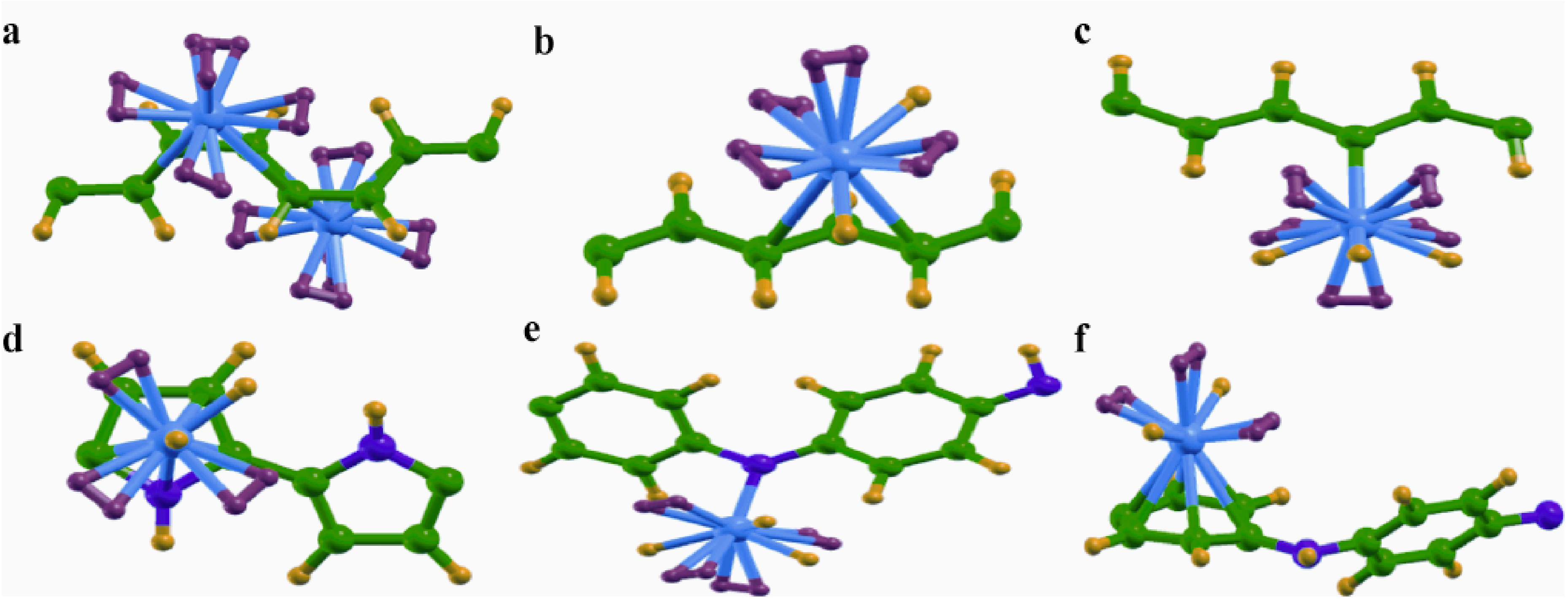


← Combinatorial Decoration

Selected decorating atoms

- ● Sc (Scandium)
- ● Ti (Titanium)
- ● V (Vanadium)

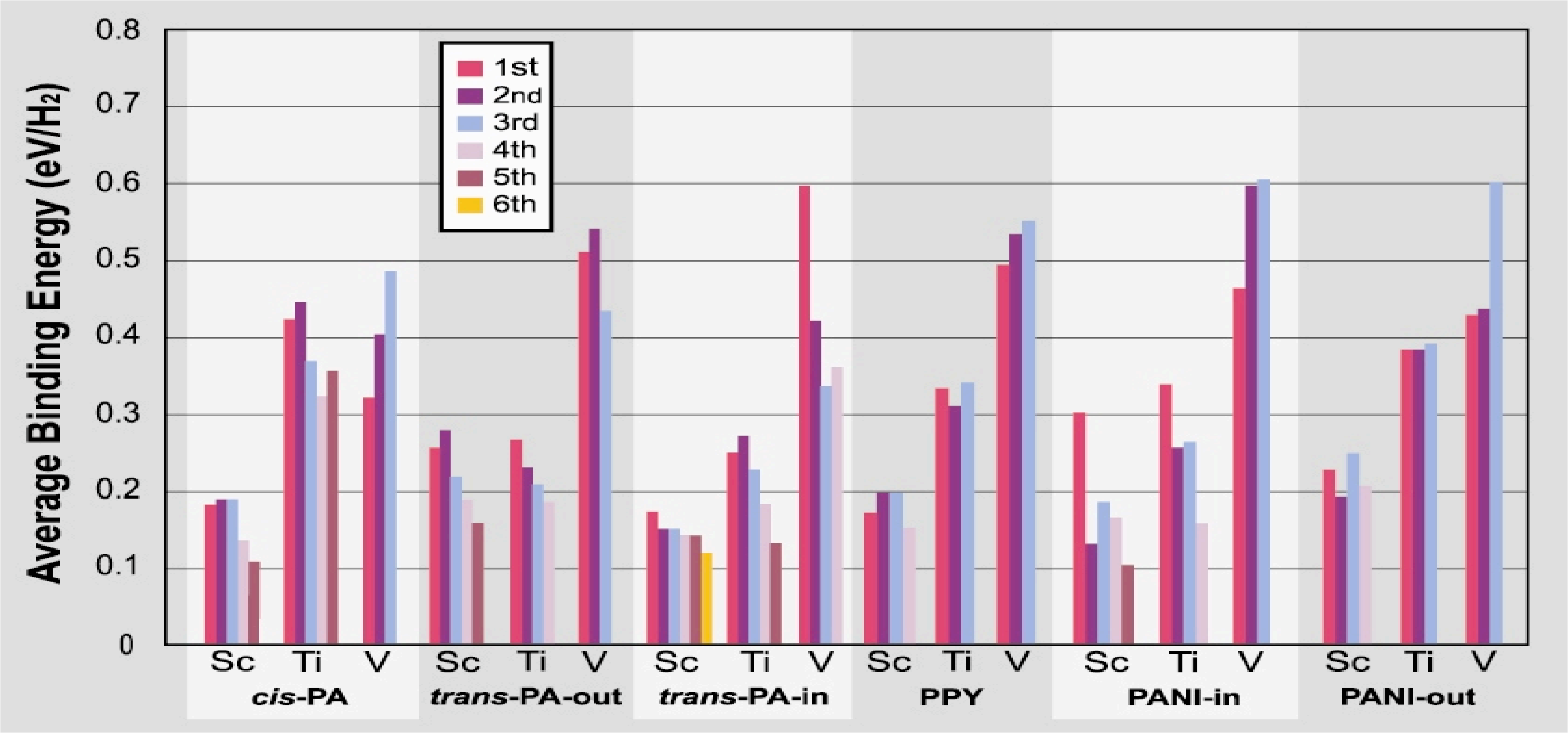
Six kinds of stable metal-decorated structures



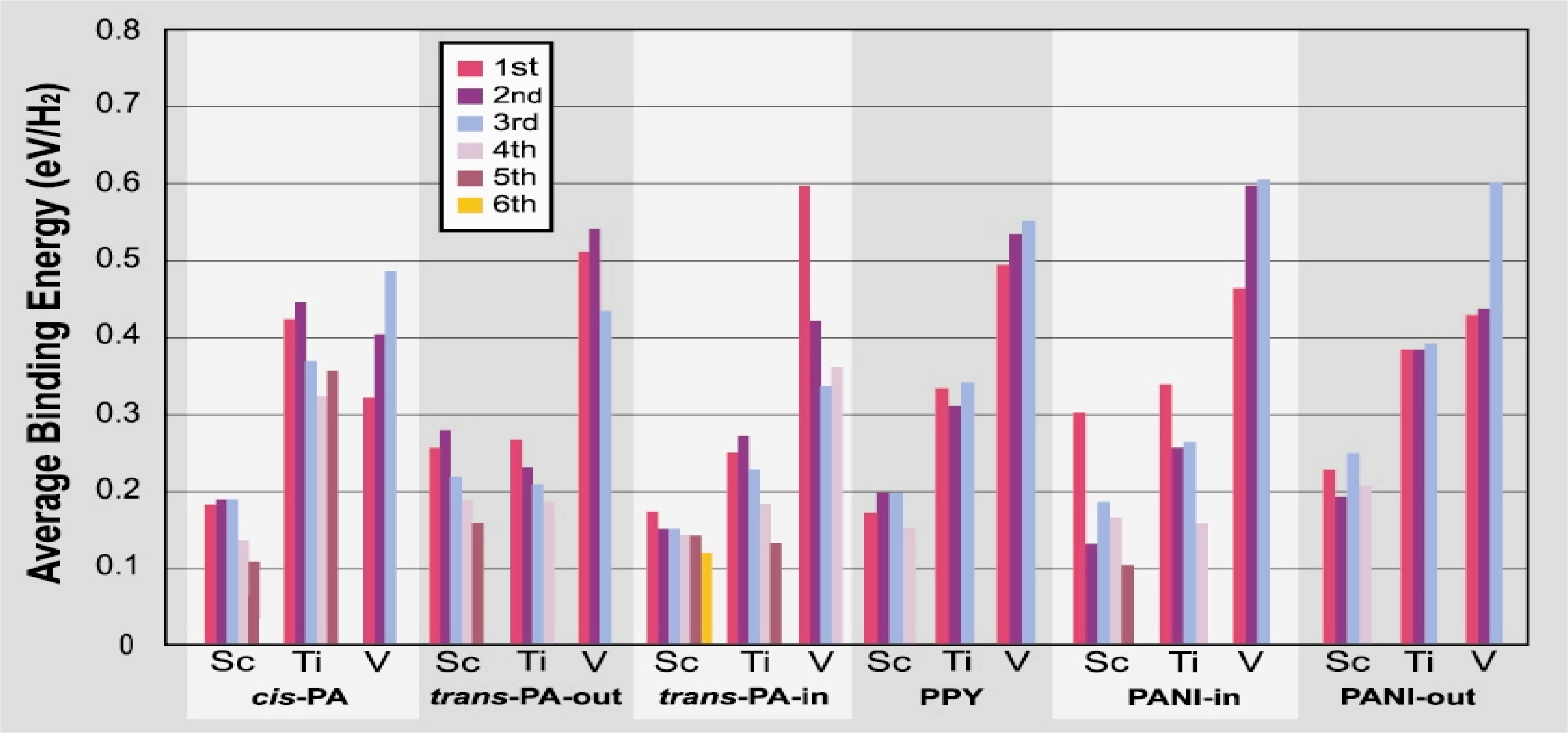
H. Lee, W. I. Choi, and J. Ihm, *Phys. Rev. Lett.* **97**, 056104 (2006)

H. Lee, W. I. Choi, M. C. Nguyen, and J. Ihm, *Phys. Rev. B* **76**, 195110 (2007)

Binding energy per H_2 & zero-point vibration energy correction

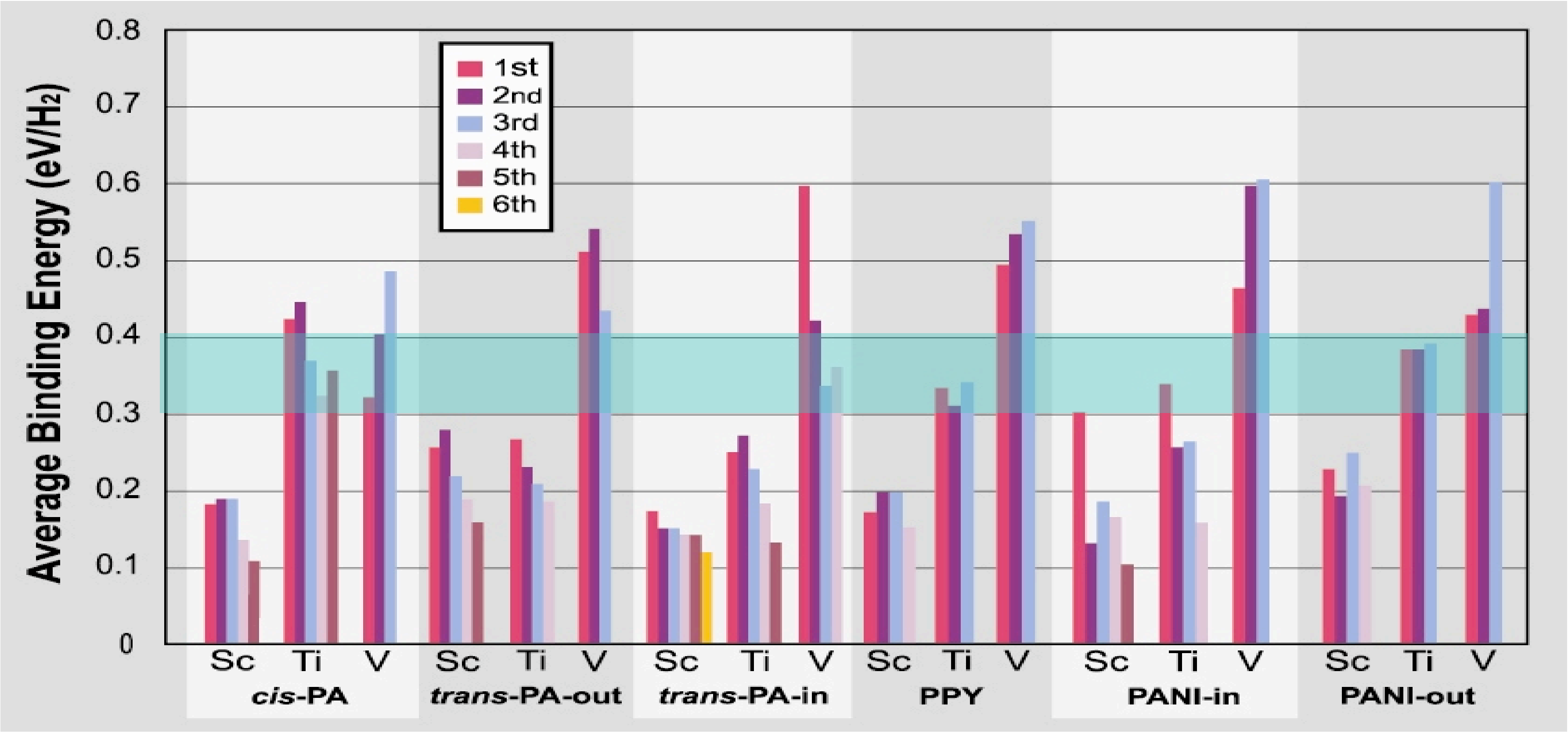


Binding energy per H_2 & zero-point vibration energy correction



Zero-point vibration energy is ~**25%** of the binding energy of H_2

Binding energy per H_2 & zero-point vibration energy correction



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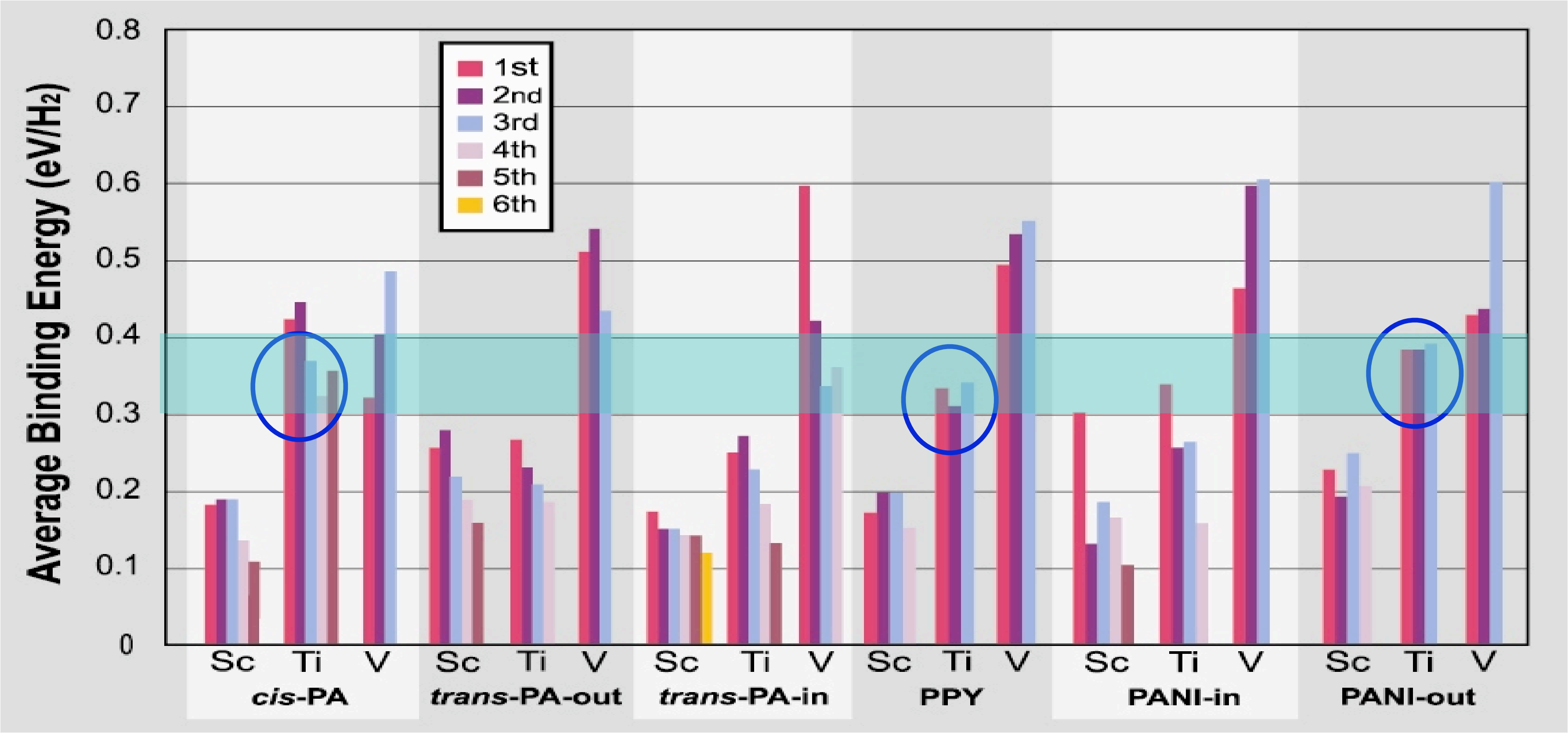
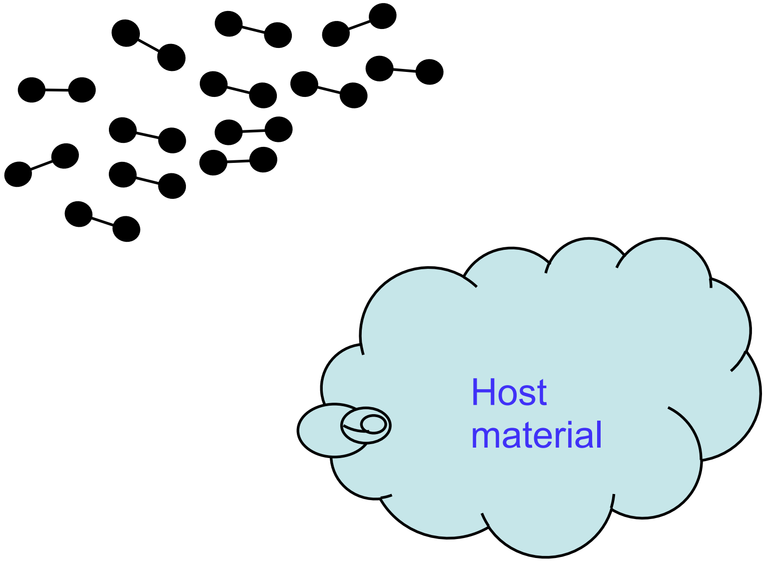


Zero-point vibration energy is ~**25%** of the binding energy of H_2

Hydrogen adsorption-desorption:



$$P_0, T_0 \longrightarrow P_1, T_1$$

$$f = kT\frac{\partial InZ}{\partial \mu}$$

$$\boxed{f = \sum_{n=0} n g_n e^{n\frac{\mu-\varepsilon_n}{kT}} \Big/ \sum_{n=0} g_n e^{n\frac{\mu-\varepsilon_n}{kT}}}$$

(average) Adsorption number (*f*) as P and T

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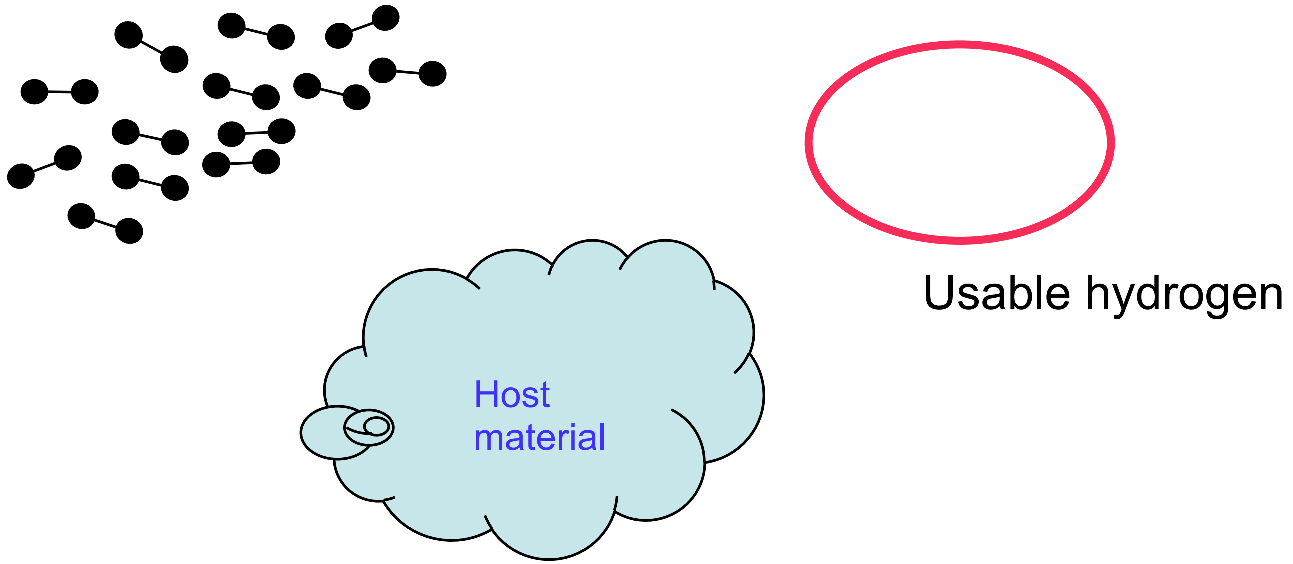

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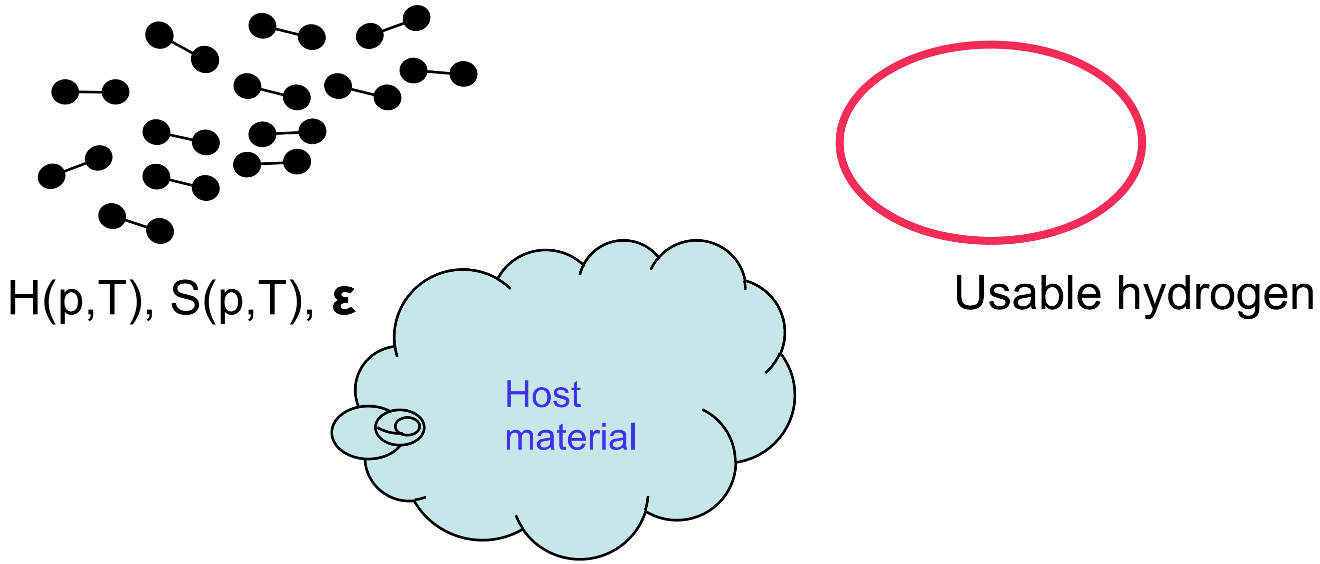

H(p,T), S(p,T), **ε**

Host material

Usable hydrogen

$P_0, T_0 \longrightarrow P_1, T_1$

$$f = kT\frac{\partial InZ}{\partial \mu}$$

$$\boxed{f = \sum_{n=0} n g_n e^{n\frac{\mu-\varepsilon_n}{kT}} \Big/ \sum_{n=0} g_n e^{n\frac{\mu-\varepsilon_n}{kT}}}$$

(average) Adsorption number (*f*) as P and T

f-P-T diagram : “Usable” hydrogen

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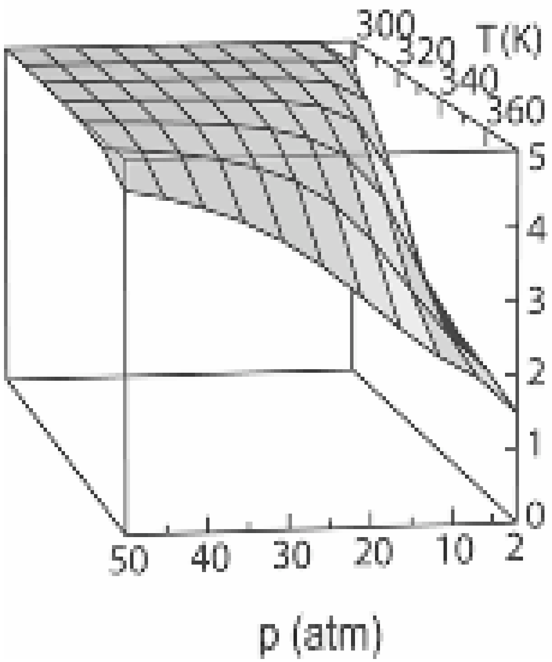
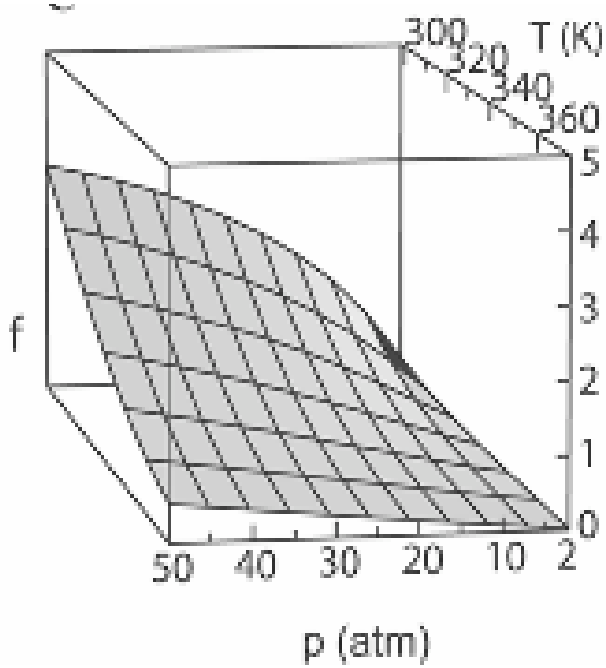
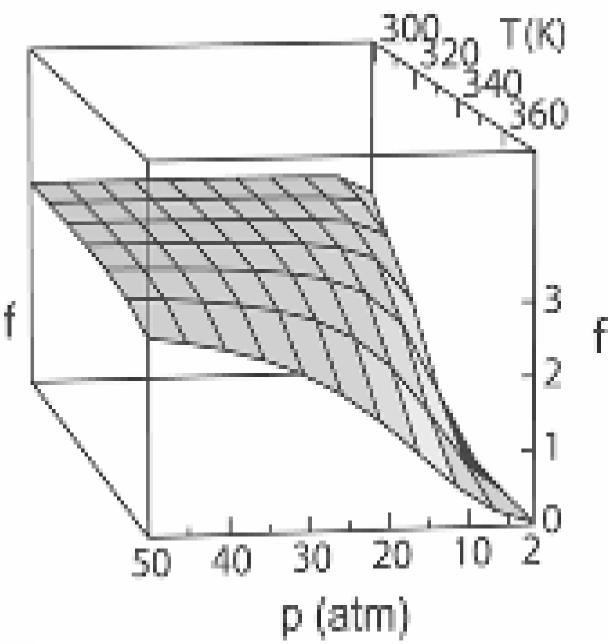


Ti-*cis*-polyacetylene



Sc-fullerene

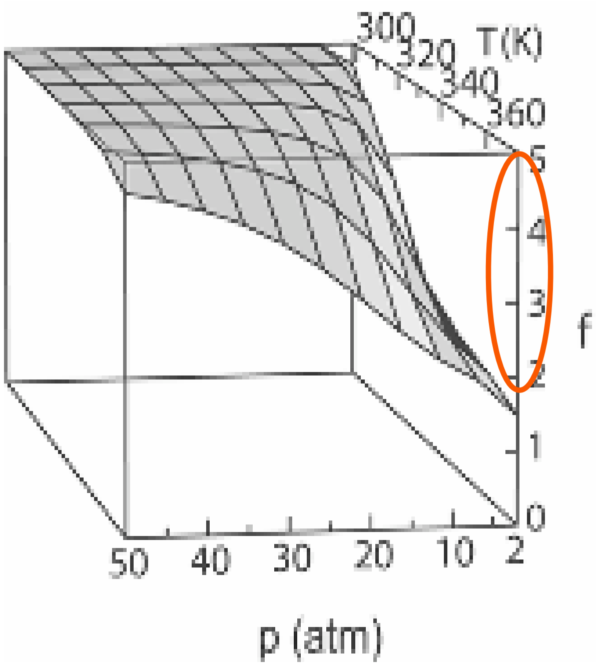


Ti-polypyrrole

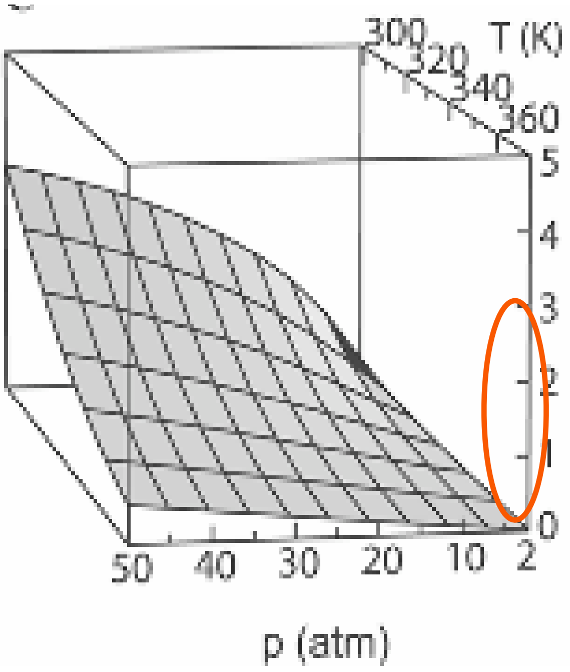
f-P-T diagram : “Usable” hydrogen

$$f = \sum_{n=0} n g_n e^{n\frac{\mu-\varepsilon_n}{kT}} \Big/ \sum_{n=0} g_n e^{n\frac{\mu-\varepsilon_n}{kT}}$$

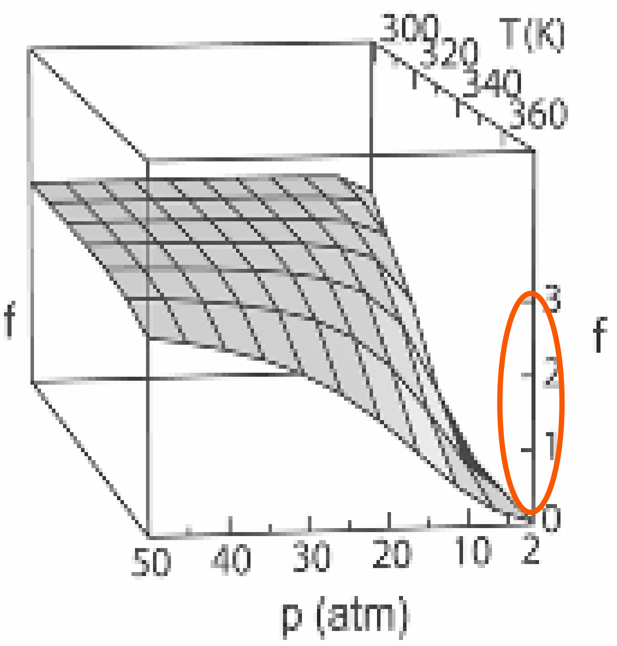
Usable ~3H_2



Ti-*cis*-polyacetylene



Sc-fullerene



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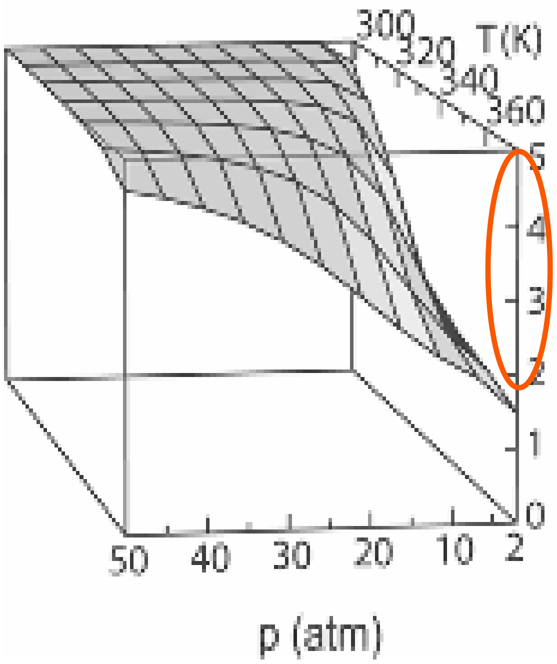
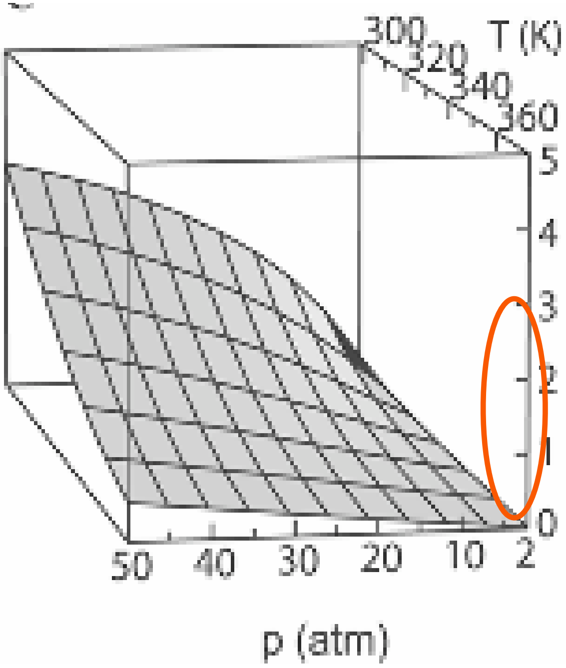


Ti-*cis*-polyacetylene



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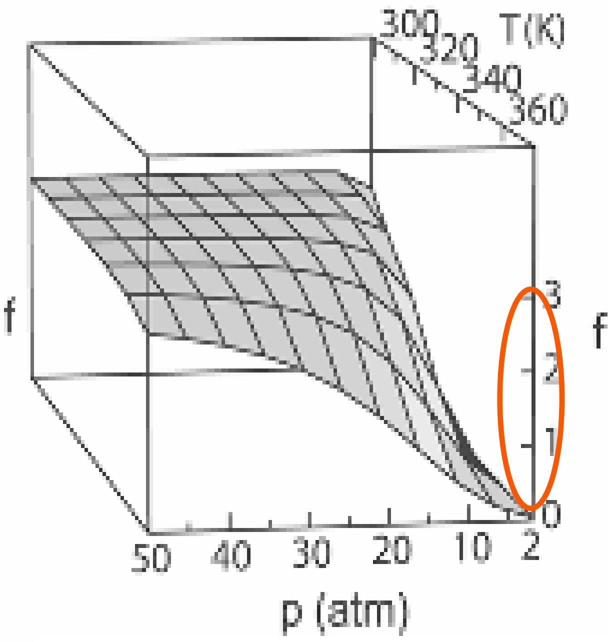


Ti-polypyrrole

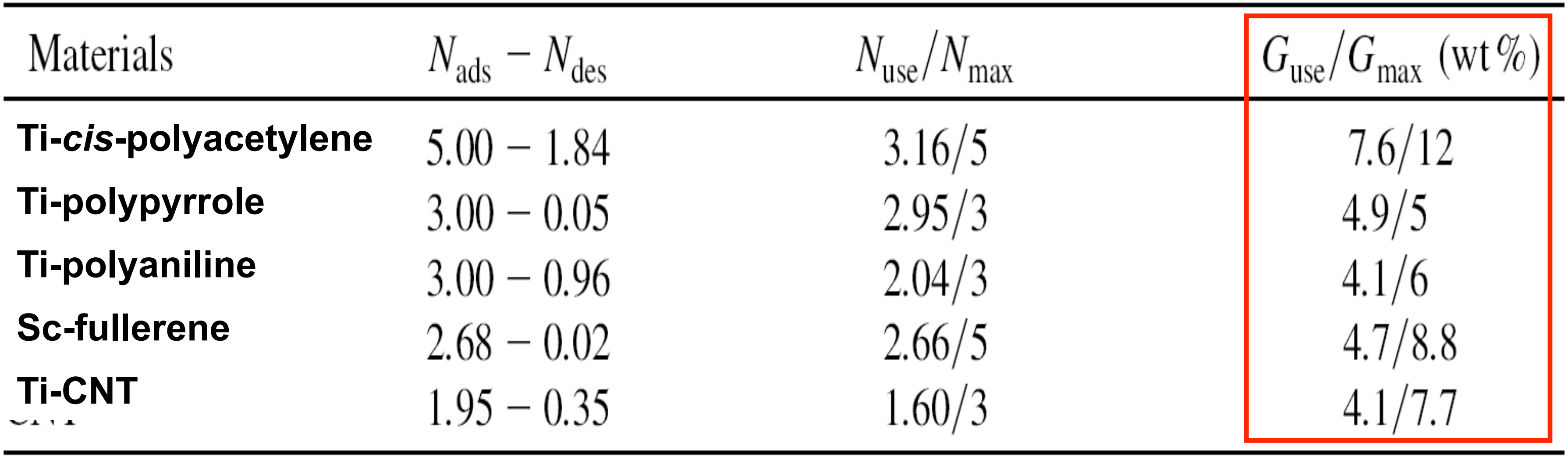
0.3-0.4 eV to fully use hydrogen: the most ideal

“Usable Capacity” : A criterion

Adsorption condition : 30 atm and 25 ^{o}C

Desorption condition : 3 atm and 100 ^{o}C

N_{use} = f(30,25) - f(3,100), N_{ads}=f(30,25), N_{des}=f(3,100)



Materials	$N_{ads} - N_{des}$	N_{use}/N_{max}	G_{use}/G_{max} (wt%)
Ti-*cis*-polyacetylene	5.00 − 1.84	3.16/5	7.6/12
Ti-polypyrrole	3.00 − 0.05	2.95/3	4.9/5
Ti-polyaniline	3.00 − 0.96	2.04/3	4.1/6
Sc-fullerene	2.68 − 0.02	2.66/5	4.7/8.8
Ti-CNT	1.95 − 0.35	1.60/3	4.1/7.7

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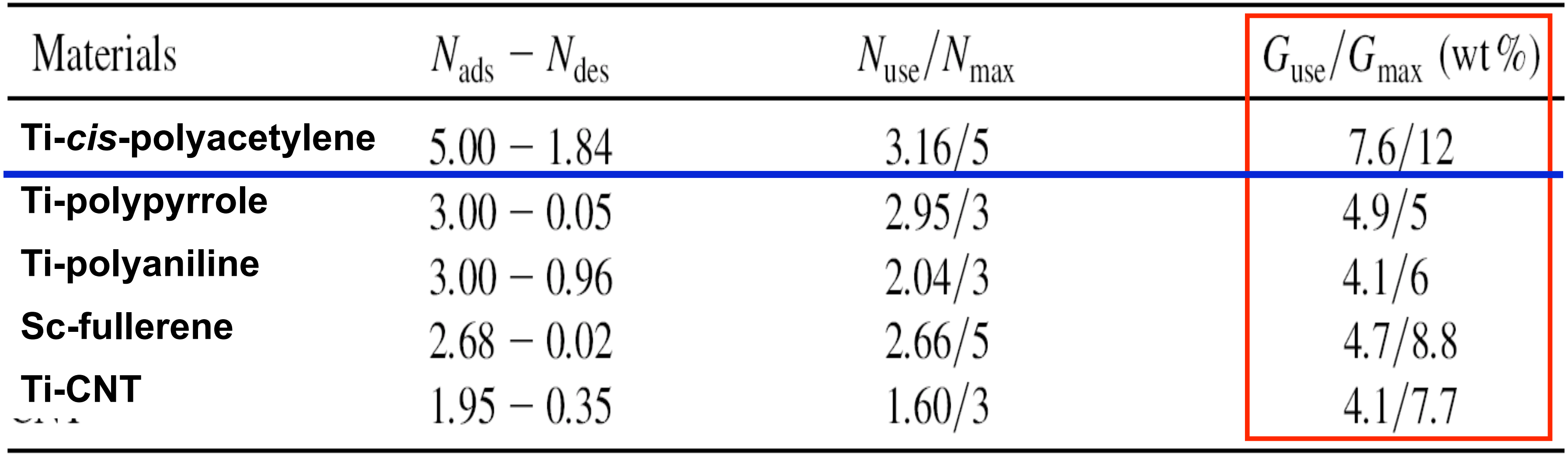

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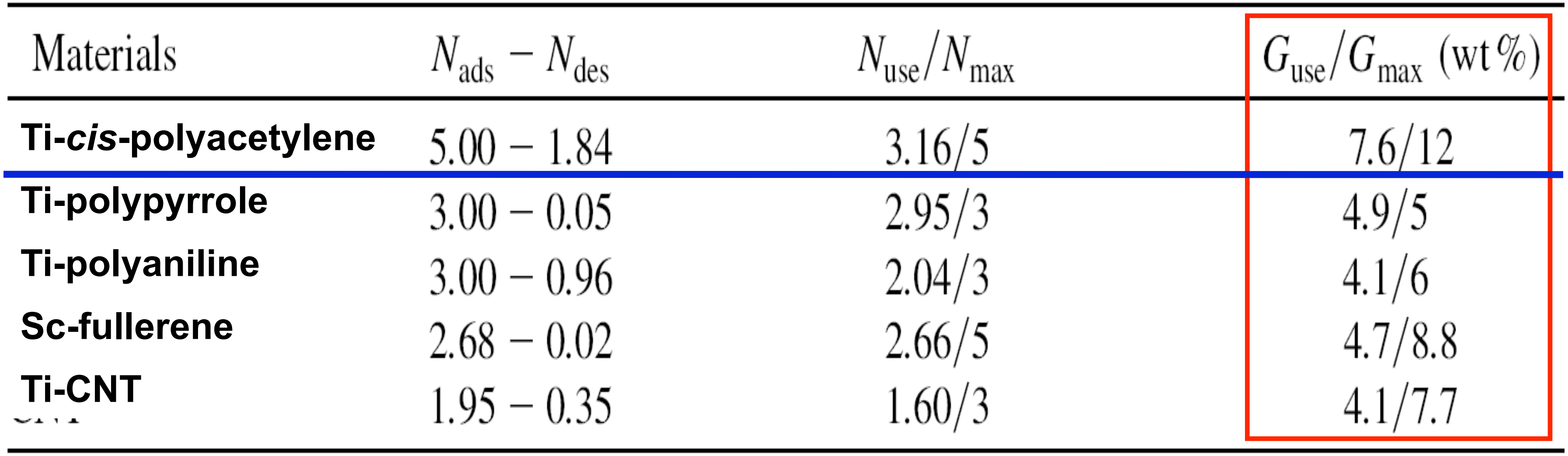

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Usable capacity should be a criterion.

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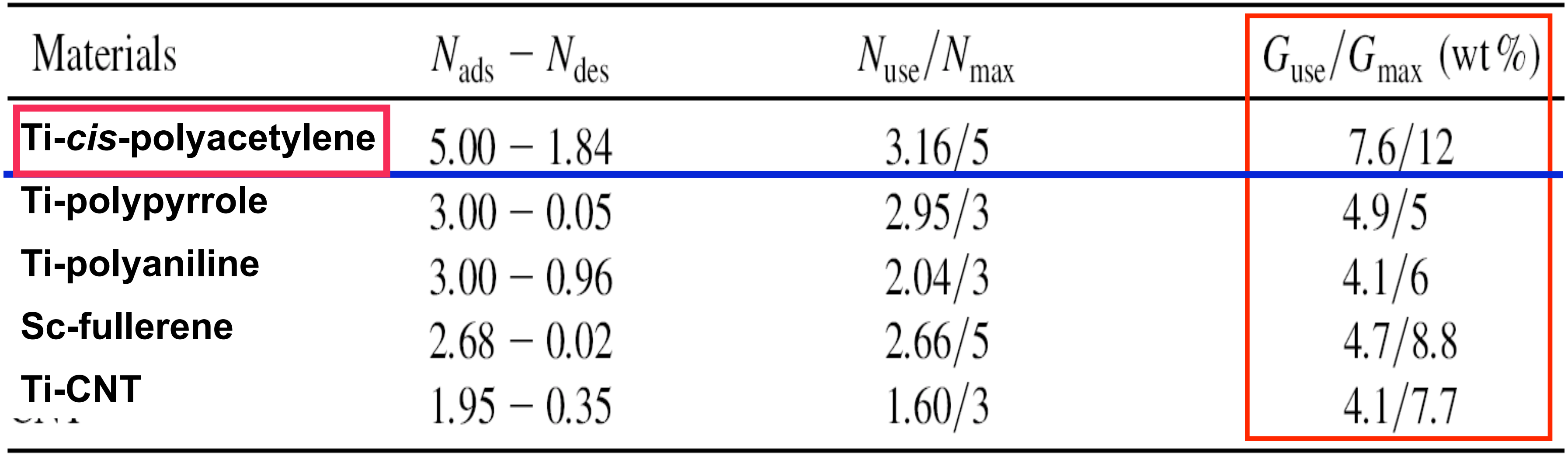

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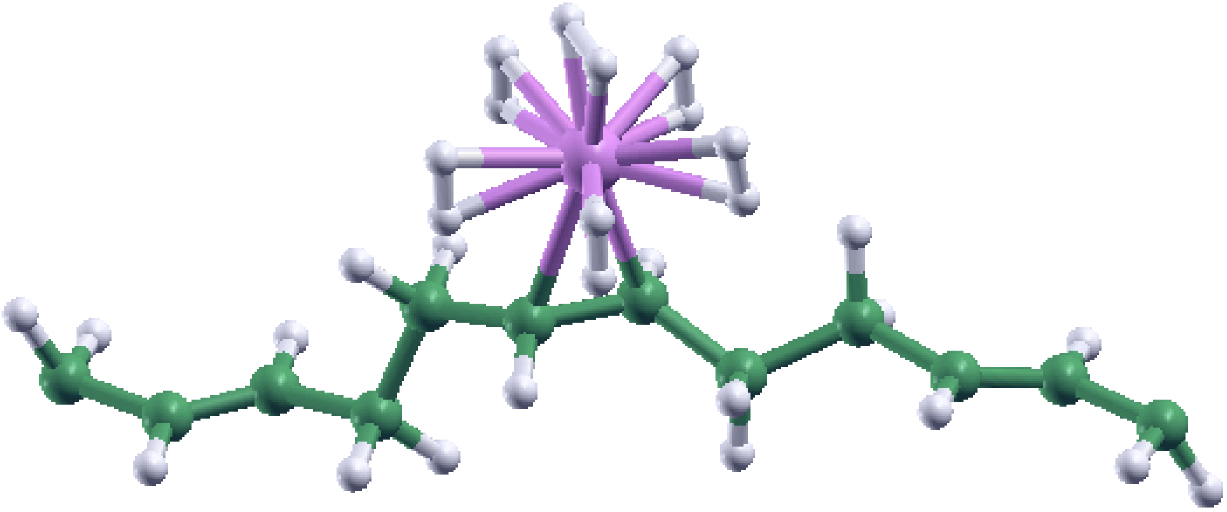
Usable capacity should be a criterion.

Experiment on Ti-polyaniline: degree of oxidation matters.

Research in Progress-I

Suppression of Ti-clustering in

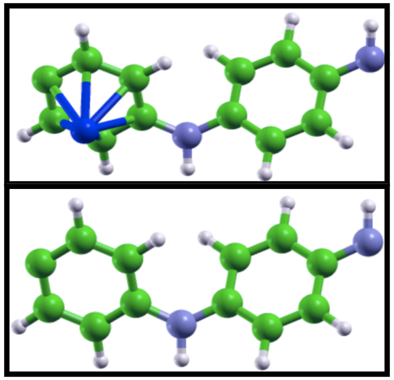
Polybutadiene $(C_4H_6)_n$



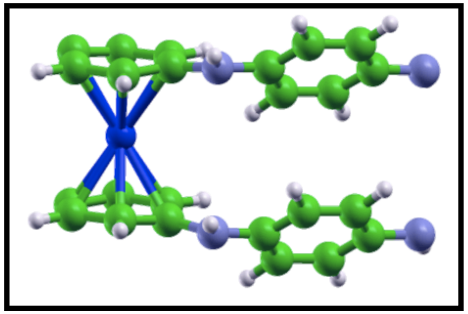
Research in Progress-II

Suppression of crosslinking of polymers

Ti insertion

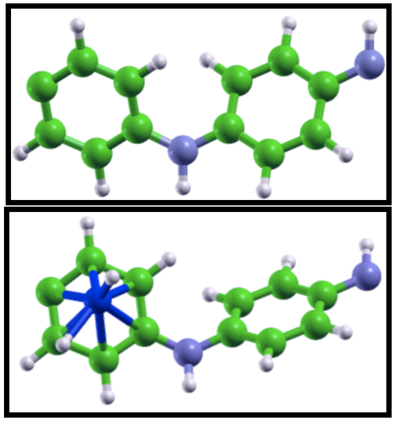


Each at infinite E = 0eV

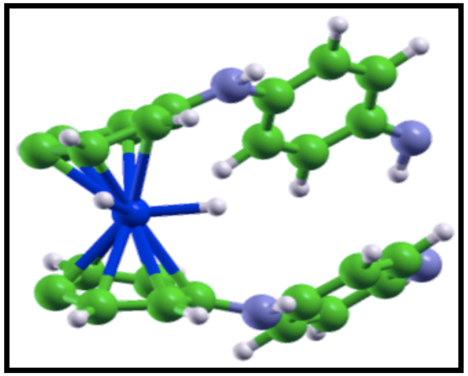


E=-2.51eV (Crosslinking occurs.)

TiH_2 insertion



Each at infinite E = 0eV

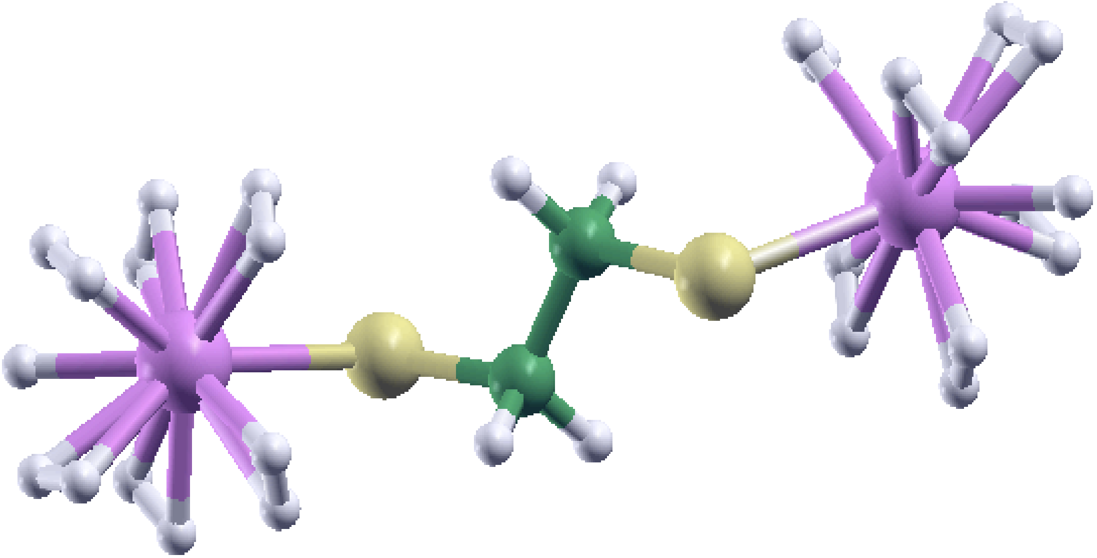


E = 3.93eV (No crosslinking)

Research in Progress-III

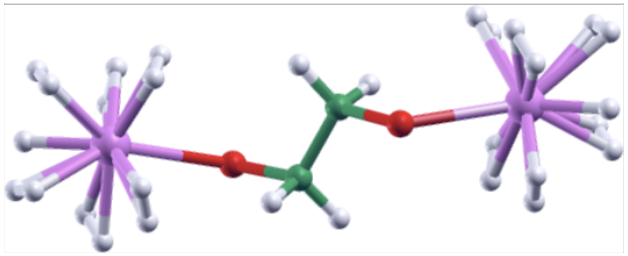
High gravimetric capacity using functional groups

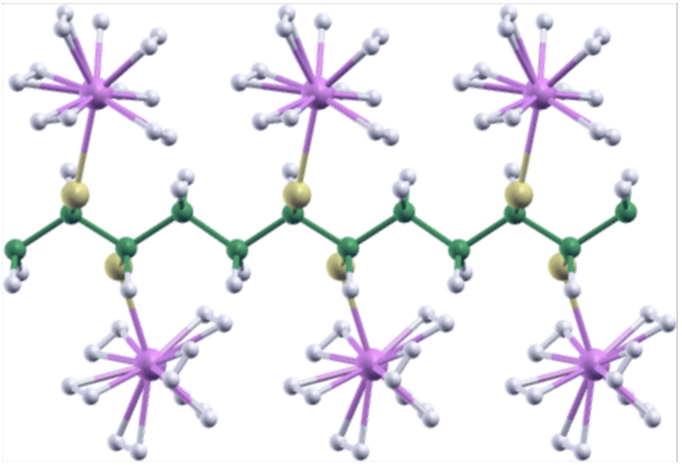
Metal-decorated ethane-1,2-diol ($C_2H_6O_2$)



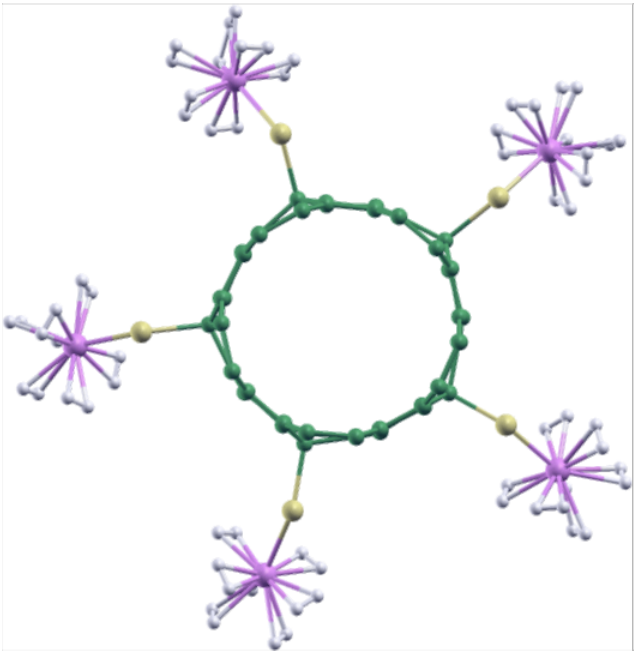
13 wt%

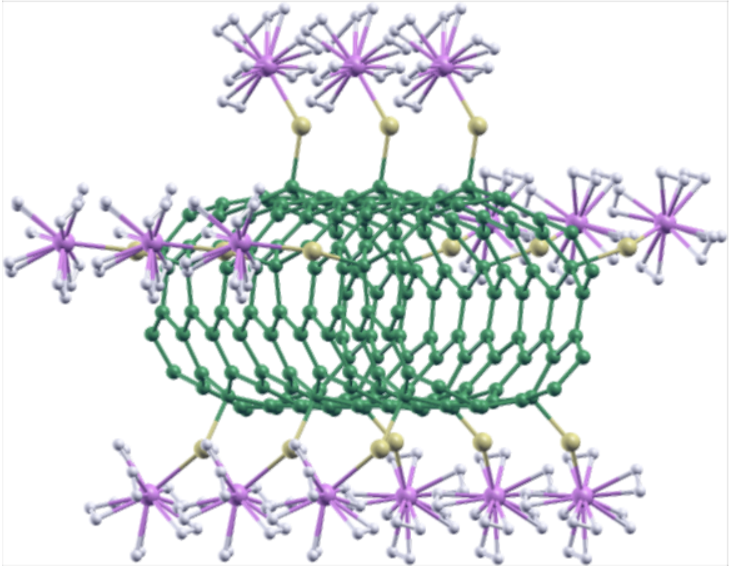
Various geometries of functional groups





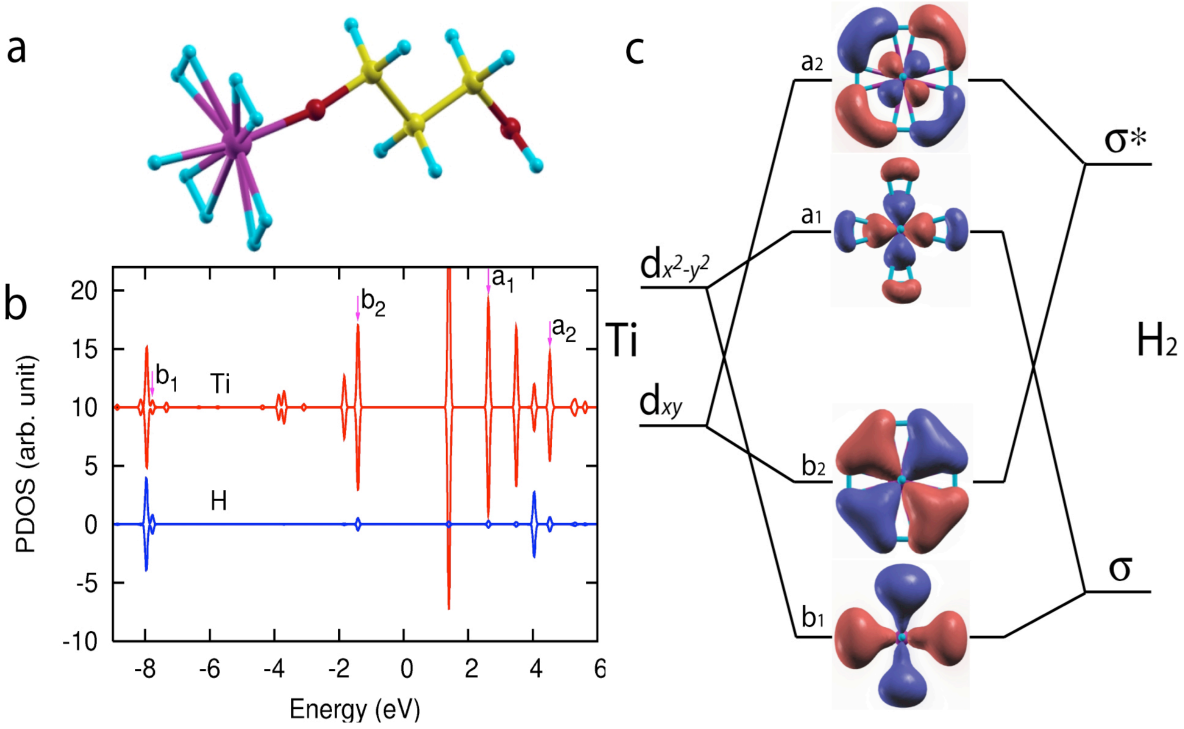
Ti clustering is suppressed as well.





Research in Progress-IV

Binding mechanism (Kubas interaction)

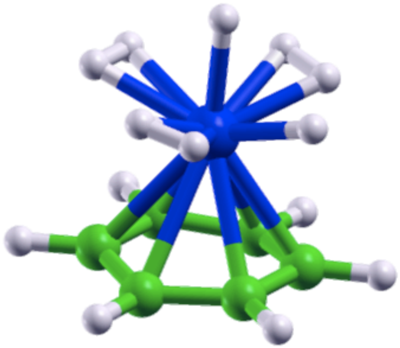


Splitting of Ti *d* orbitals into e_g and t_{2g}
(Octahedral ligand field)

Hybridization with H_2 σ and σ* orbitals

Research in Progress-V

I. H_2 Binding Energy with LDA+U



H_2 number dependence of U_{scf}

	$0H_2$	$1H_2$	$2H_2$	$3H_2$
U_{scf}(eV)	4.11	4.56	4.45	4.44

Kulik *et al.* PRL **97**, 103091 (2006)

H_2 Binding Energy (Benzene+TiH_2+nH_2)

method	$1H_2$	$2H_2$	$3H_2$
GGA	0.51eV/H_2	0.57eV/H_2	0.50eV/H_2
LDA	1.08eV/H_2	1.17eV/H_2	1.08eV/H_2
LDA+U_{scf} (U_{scf}=4.3eV)	0.55eV/H_2	0.60eV/H_2	0.54eV/H_2

II. Diffusion QMC: collaboration with UIUC (Dr. J. Kim)

Conclusions

Computational design for optimal H_2 storage medium

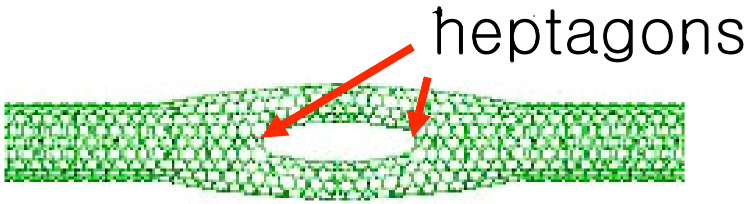
-High gravimetric and volumetric capacity in Ti-decorated polymers.

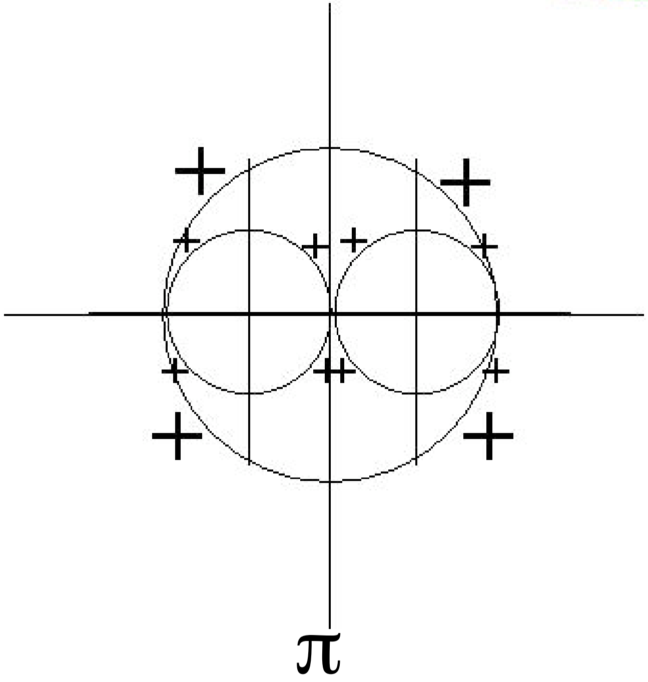
-Zero-point vibration energy : ~25 % of the binding energy of H_2.

-Ideal binding energy of H_2 : 0.3 eV to maximize usable capacity.

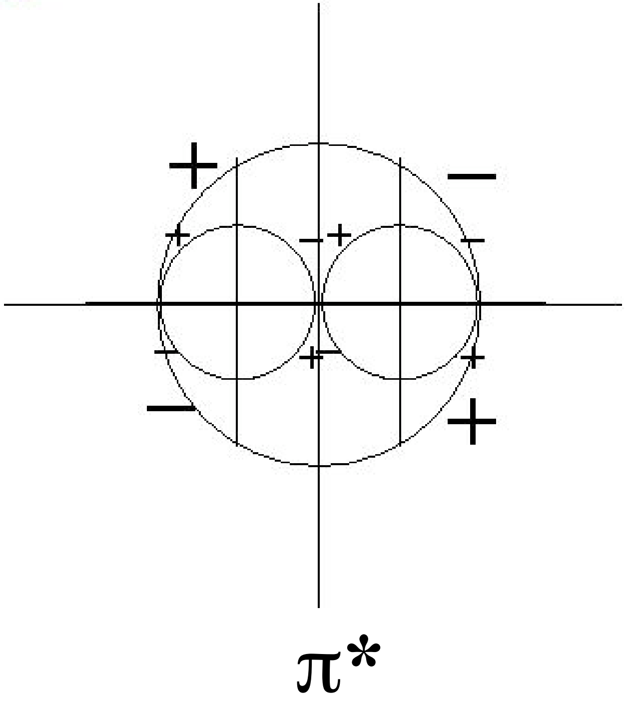
-Understanding of bonding character: LDA+U and QMC in progress.

Phase matching of π and π* bands at junction





Good matching



Bad matching
(Confinement effect is pronounced.)

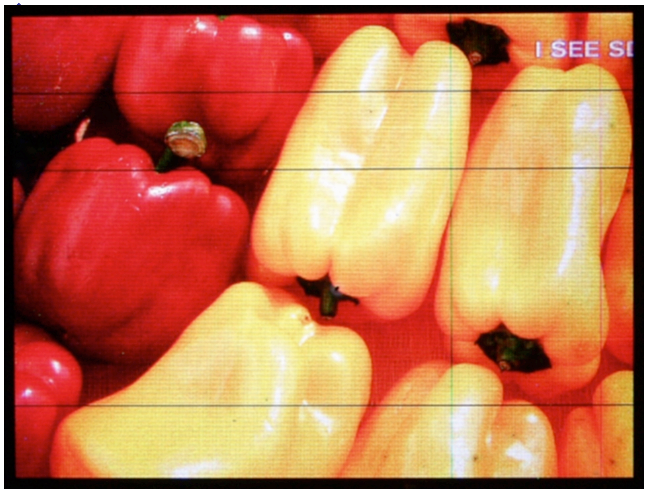
SAMSUNG SDI FED – 2005 –

Picture

#1

Picture

#2



Picture

#3

Picture

#4

Canon-Toshiba SED at CEATEC2004

Power consumption of SED, LCD, PDP (36in)

SED

LCD

PDP

Hydrogen Fuels

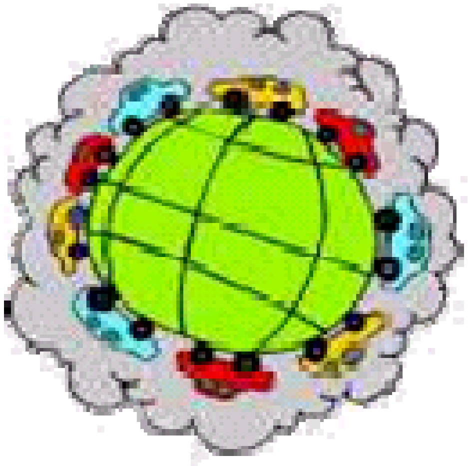
1. **Clean (CO_2-free).**

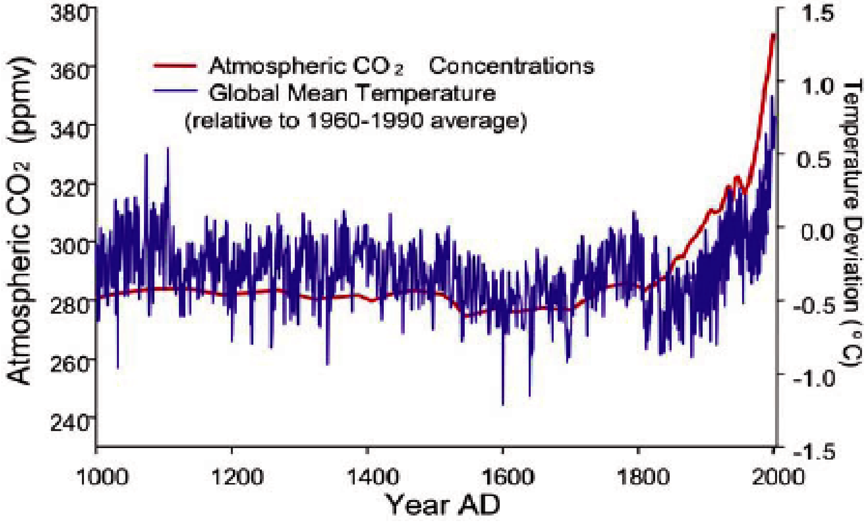
2. **Renewable.**

3. **Efficient.**

4. **Abundant (domestic resources).**

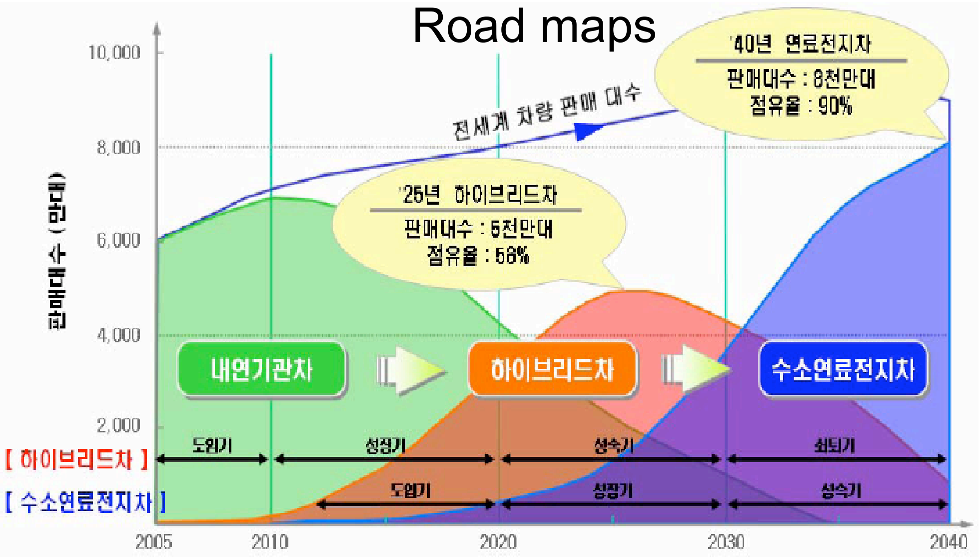
Global Warming by CO_2

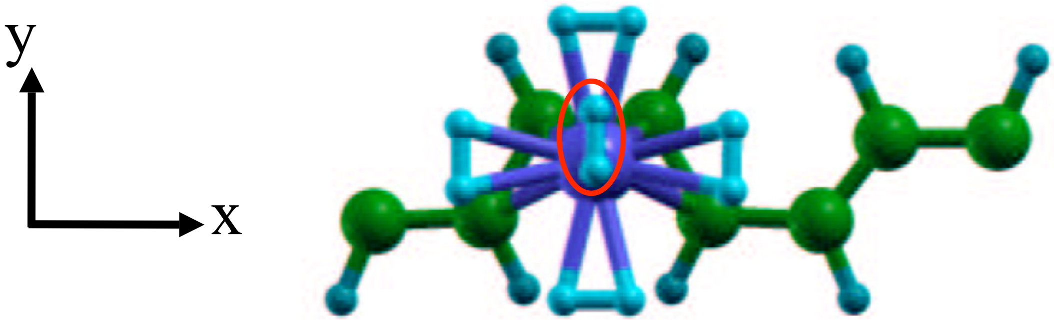




Fossil fuel shortage: International conflict

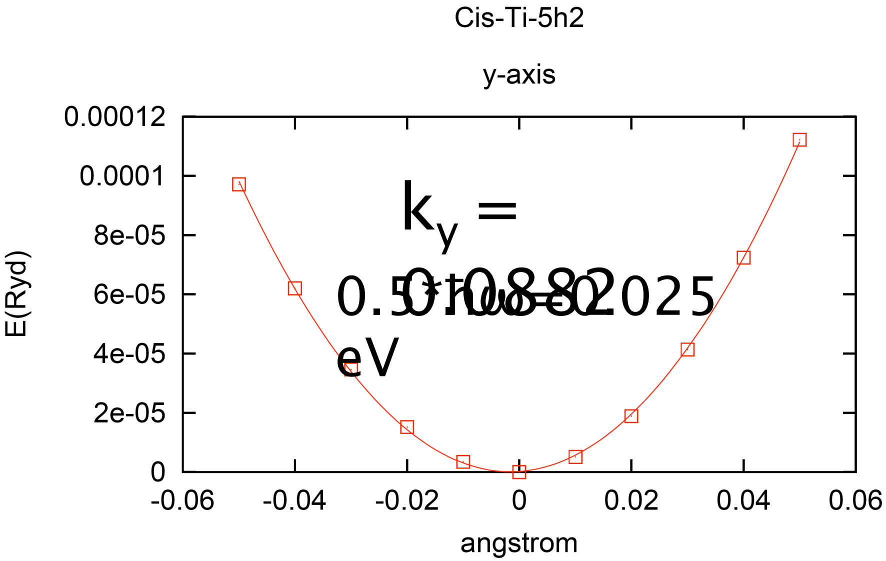
Road maps





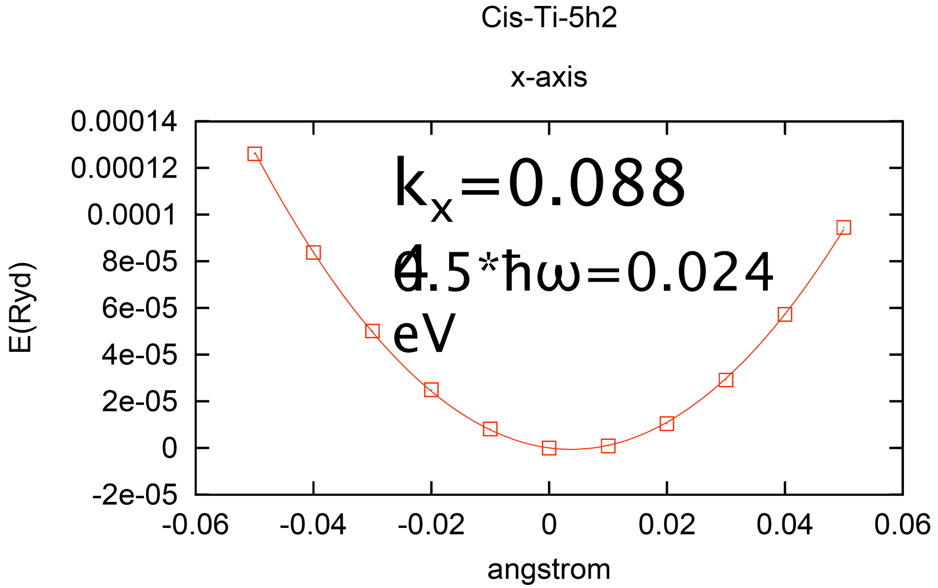
BE=0.48eV

ZP=0.085eV, 18%



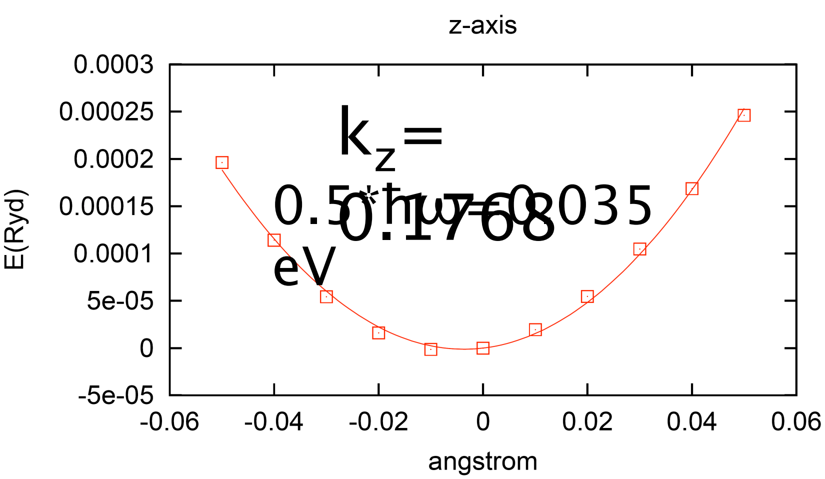
k_y = 0.0882

0.5*ħω=0.025 eV



k_x=0.0884

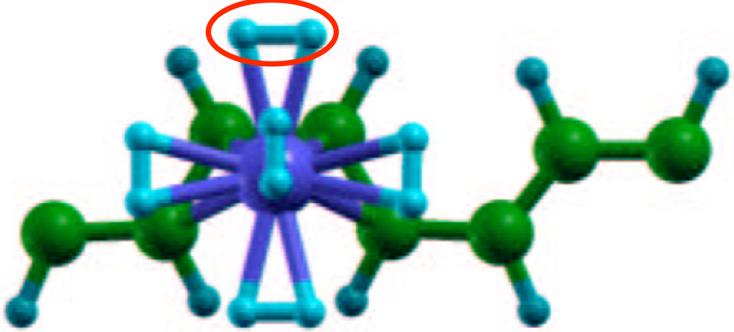
0.5*ħω=0.024 eV



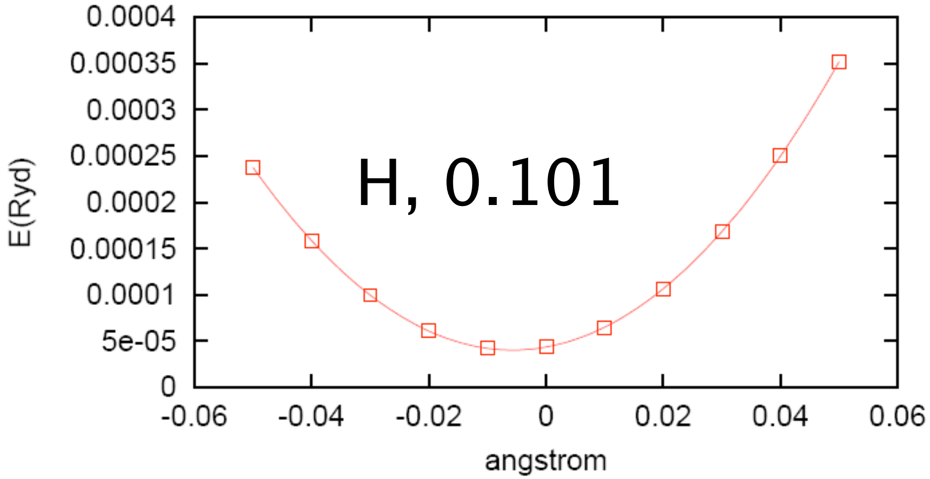
k_z= 0.1768

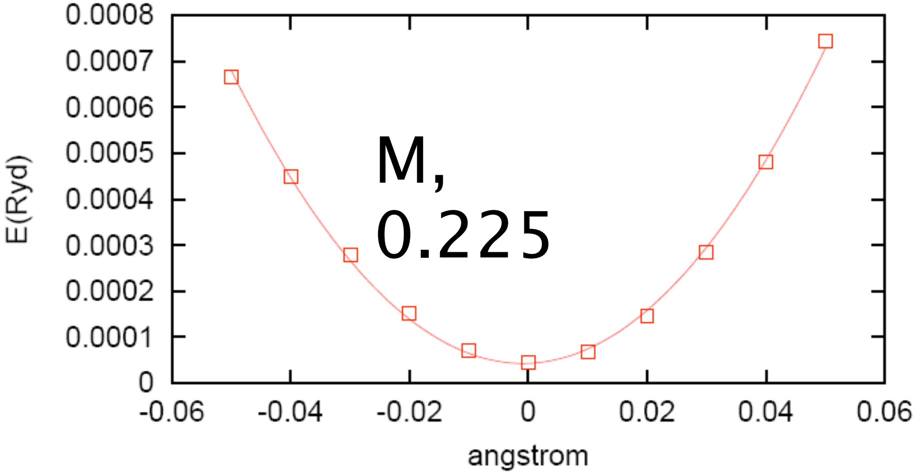
0.5*ħω=0.035 eV

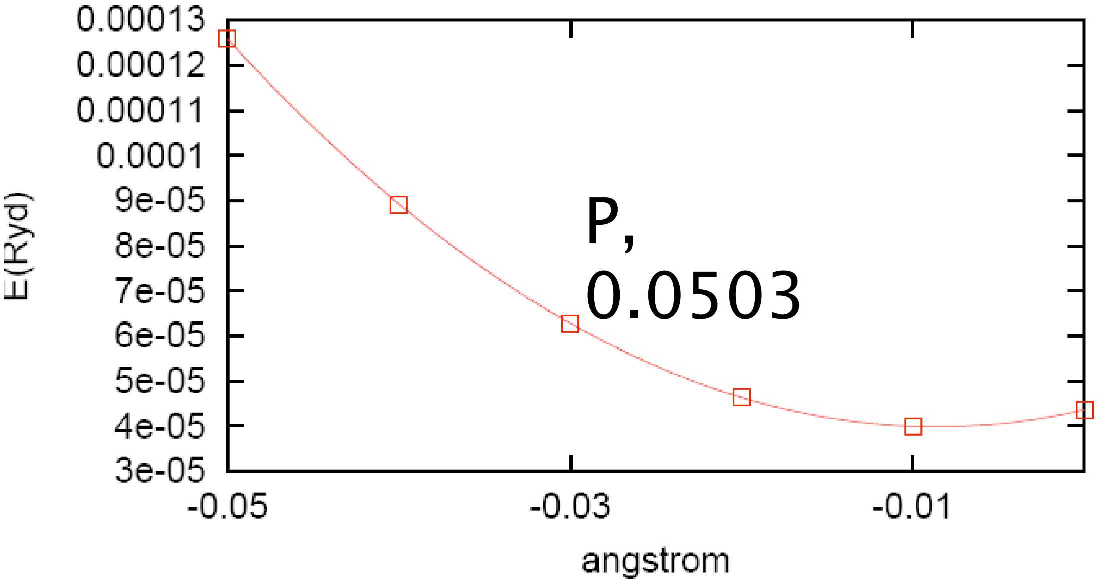
BE=0.48eV



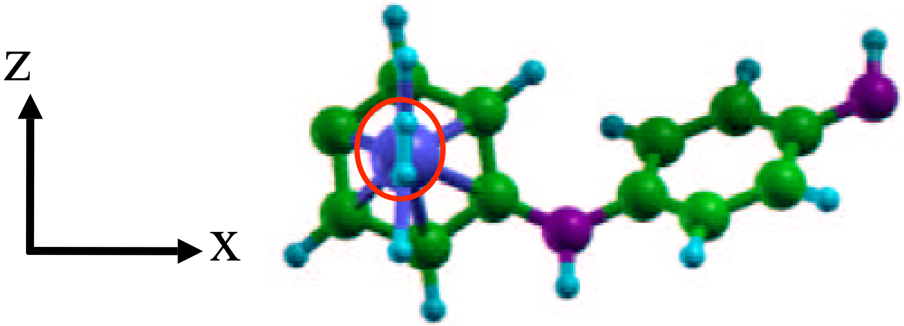
ZP=0.122eV, 25%



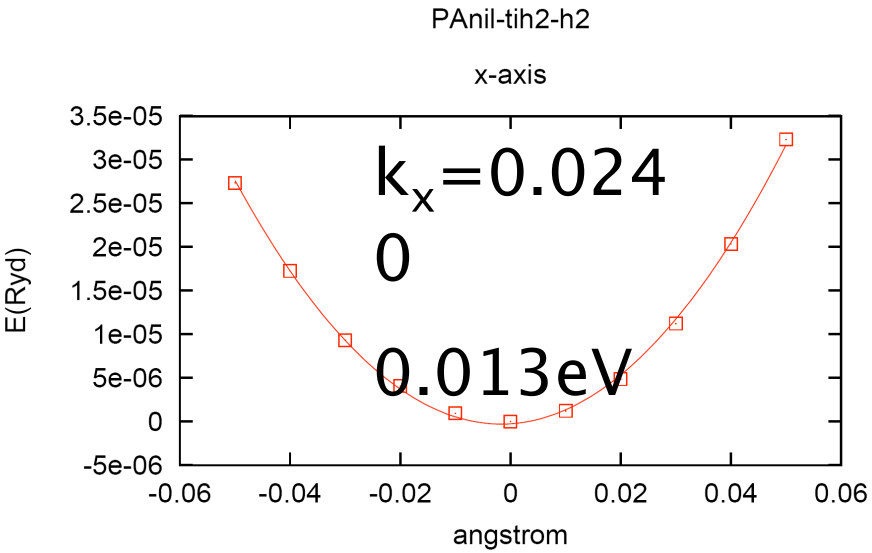




BE=0.42eV

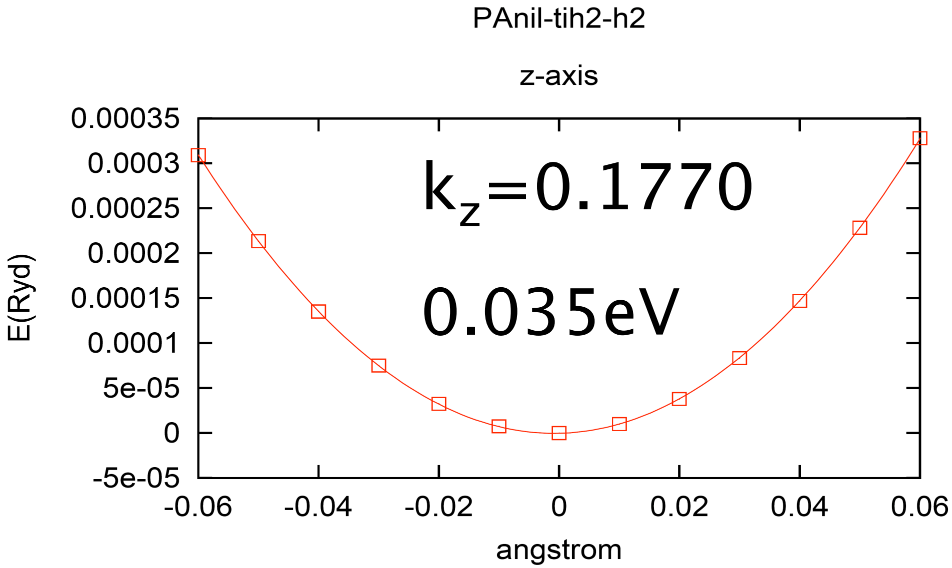


ZP=0.11eV,
26%



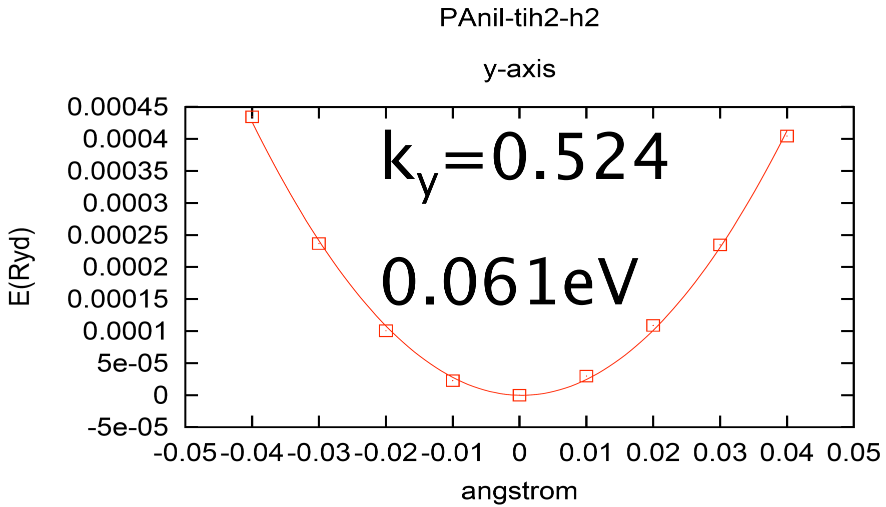
k_x=0.024
0

0.013eV



k_z=0.1770

0.035eV



k_y=0.524

0.061eV

Clustering of metal atoms

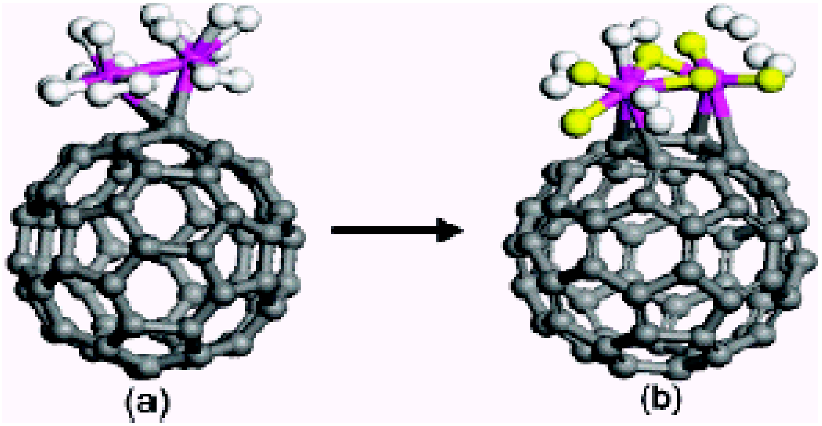
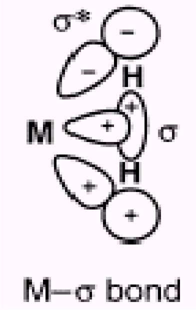


Figure 2. (a) Initial and (b) final configuration of eight H_2 molecules on Ti_2C_{60}. The atomic H atoms are shown in yellow.

Jena et al. JACS, 127, 14582 (2005)

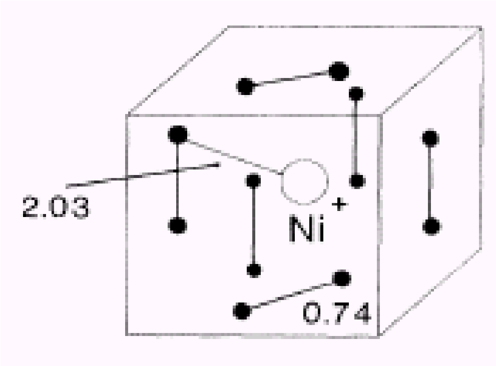
Kubas interaction

Metal-H_2 complex



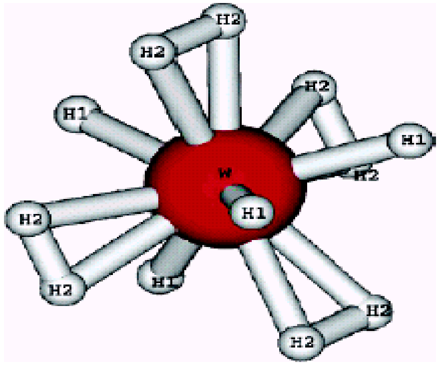
1982 ,

Kubas



PRL, 68,

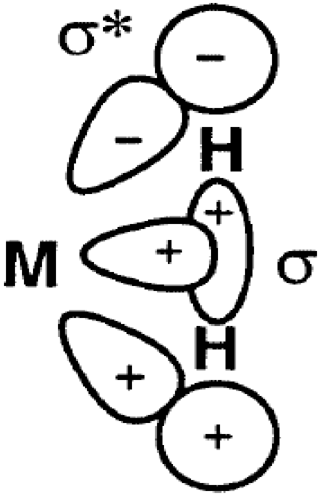
2277 (1992)



JACS, 126,

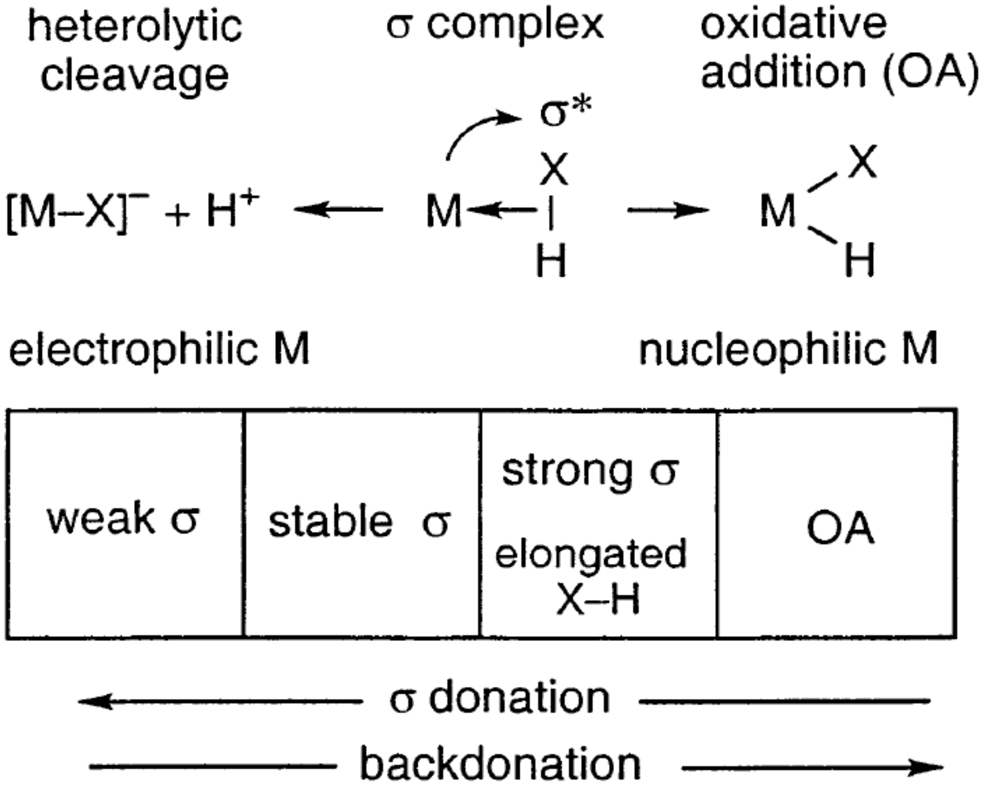
15014 (2004)

Origin of M-H_2 bonding:Kubas model



Empty ***d*** - σ : donation

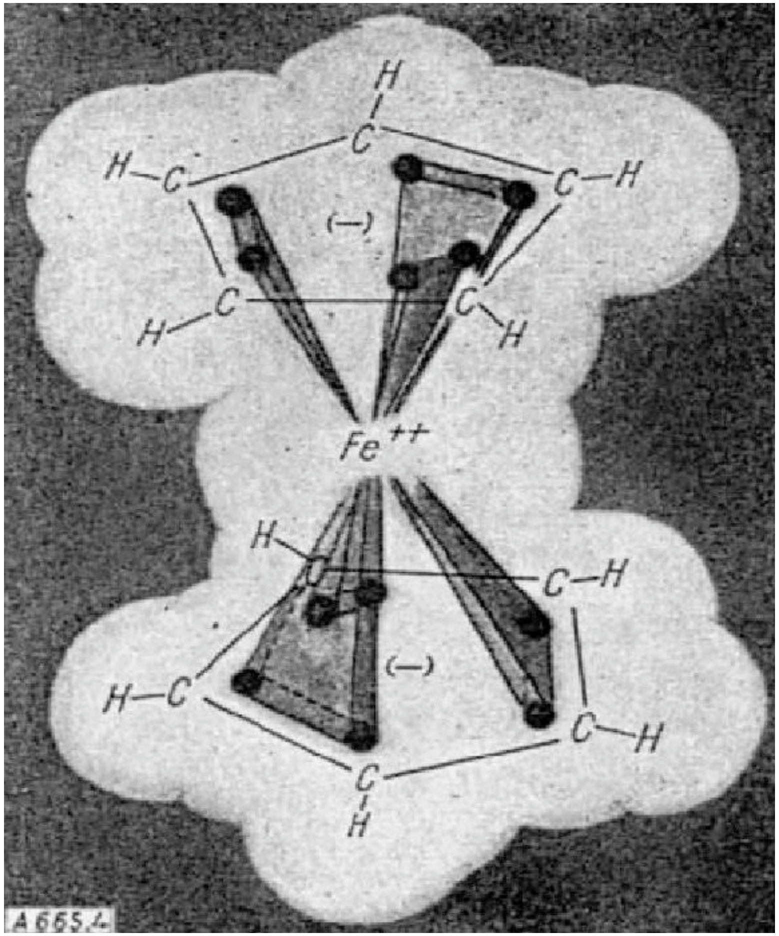
Filled ***d*** - σ* : backdonation

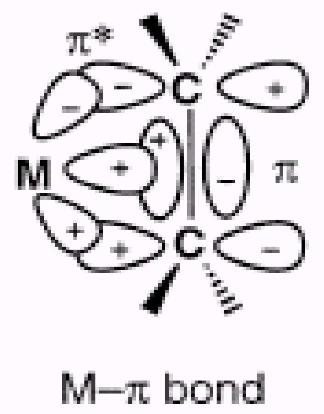


Kubas. J. Organomet..Chem. 635, **37**

(2001)

Dewar-Chatt-Duncanson model : Metal-Pi





M–π bond