PACS-CS における物質・生命科学 I:
ナノ形状の量子論

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- Curvature-induced metallization of semiconducting double-wall carbon-nanotubes

  [Okada & Oshiyama: PRL 91, 216801 (2003), and unpublished results.]

  - *Balance of 2 nano-curvatures makes it. The similar happens at metal contacts.*
- C_{60} badminton shuttlecock: possible magnetism

  [Okada et al: CPL 399, 157 (2004).]

  - *Attachment of molecules becomes nano-scissors.*
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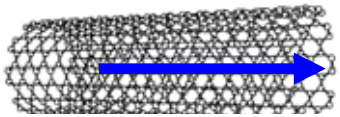
  [Boero, Silvestrelli & Oshiyama: 2005.]

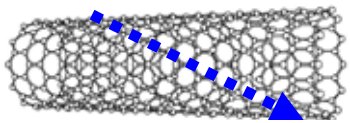
  - *Higher electron temperature that simulates electron-excitation-induced materials formation*
- What we are planning to do on PACS-CS

Thin Nanotube in Multiwalled Nanotubes

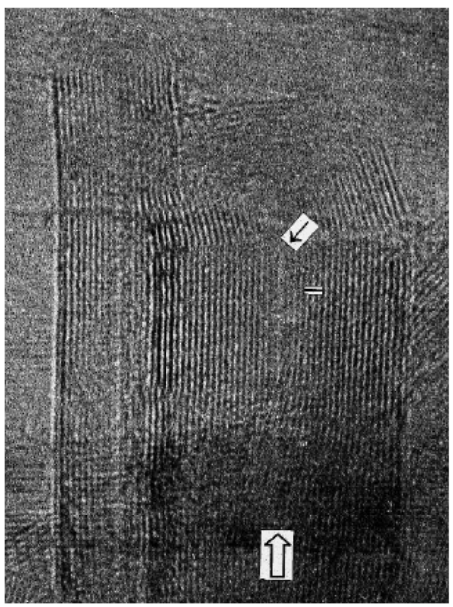
Hamada, Sawada & Oshiyama: PRL 68, 1579 (1992)



metallic armchair nt (n,n)



semiconducting zigzag nt (n,0)

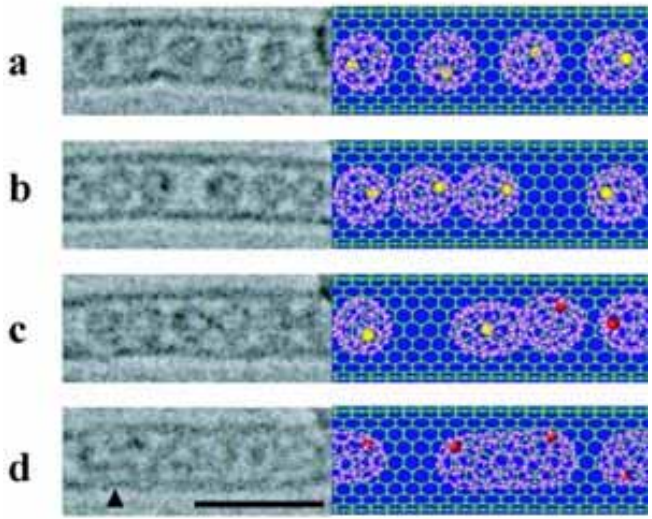


(7,0)@MWNT

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

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

4Å-nanotube@MWNT
(3,3), (4,2), (5,0)

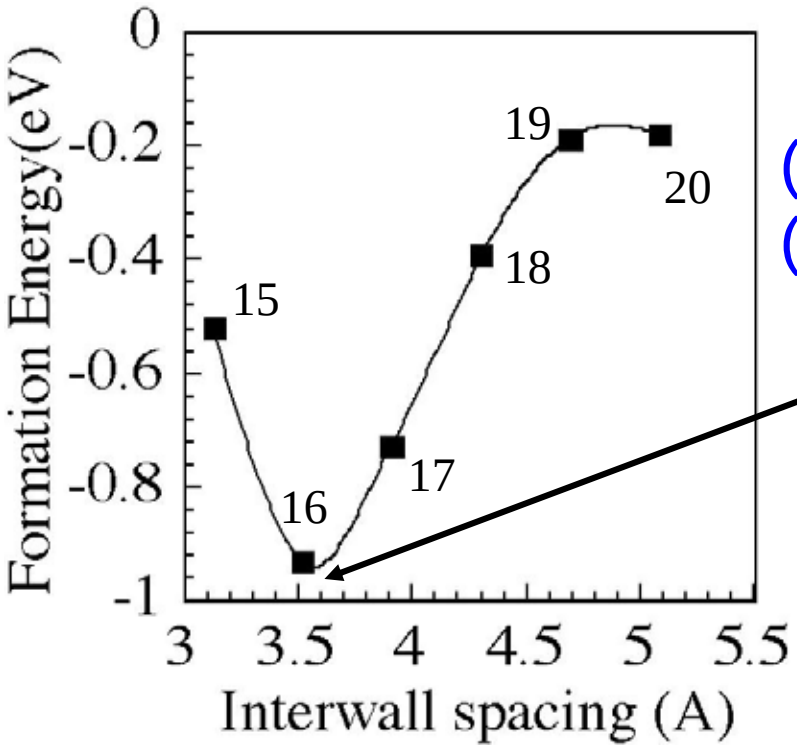


[Toshiya Okazaki (AIST, Japan):
Sm@C82@CNT]

Electron beam makes peapods DWNTs

What do we expect for DWNTs?

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



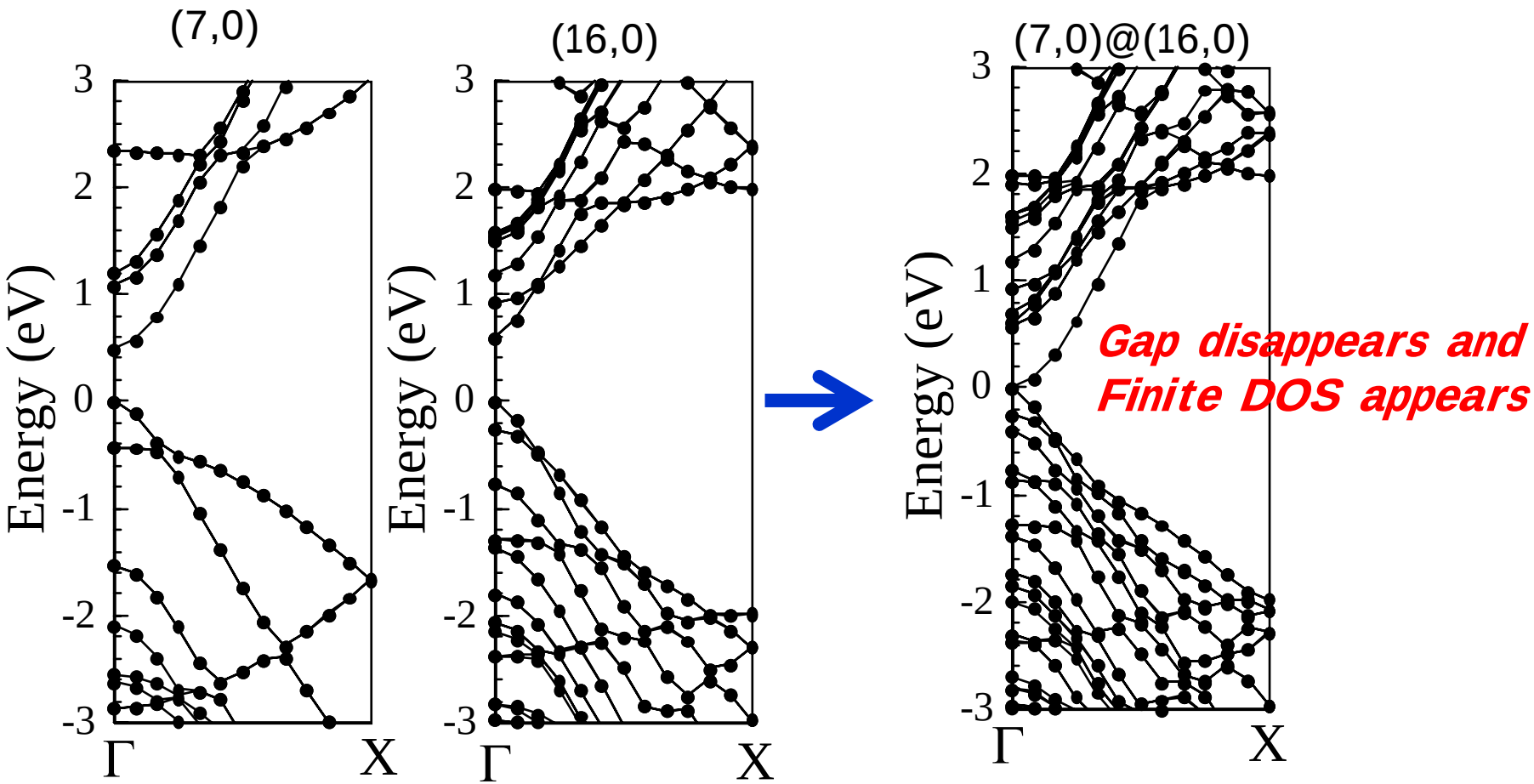
n in (7,0)@(n,0)

(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 & Iijima

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



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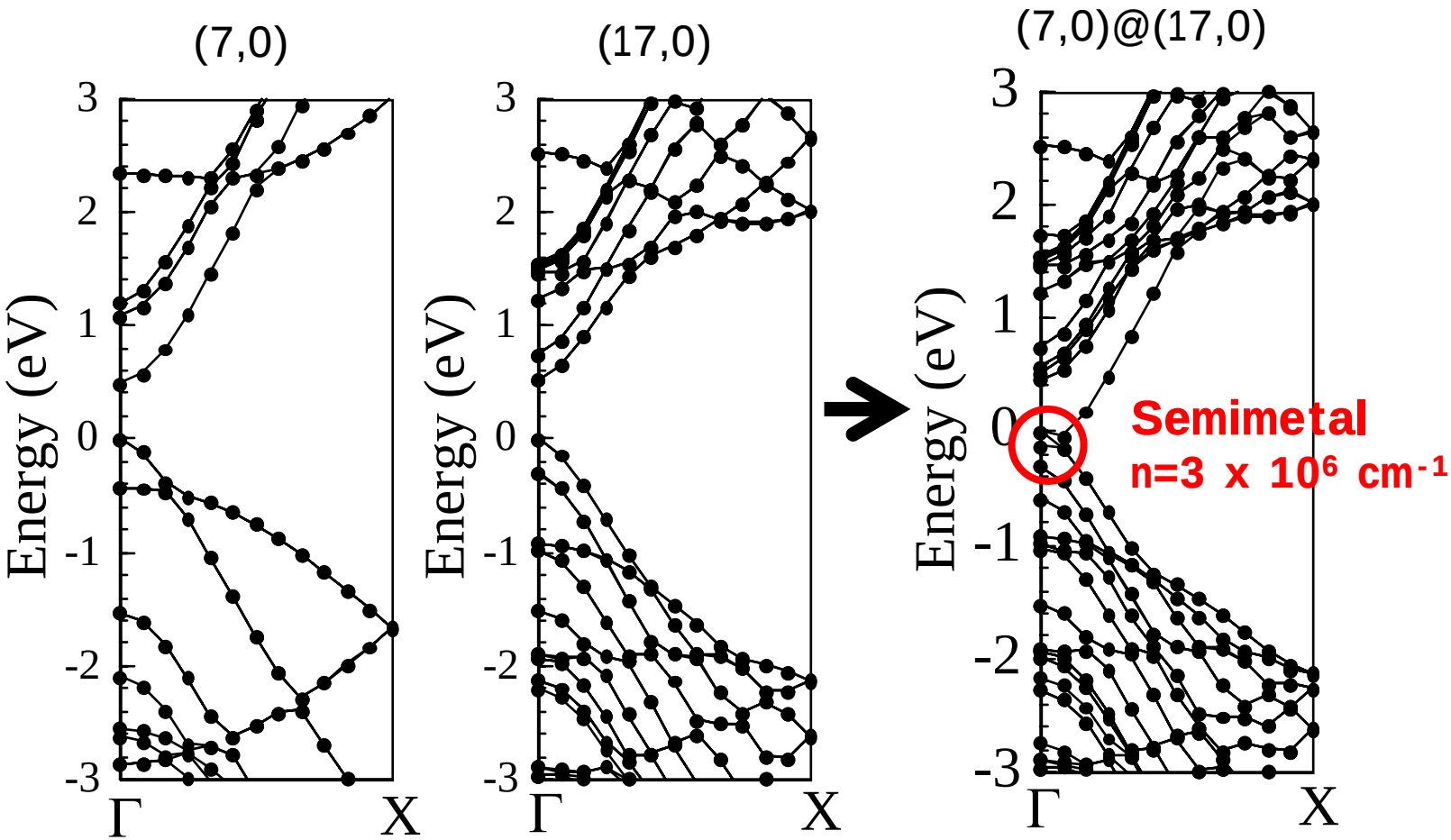
Electronic Structure of (7,0)@(17,0)



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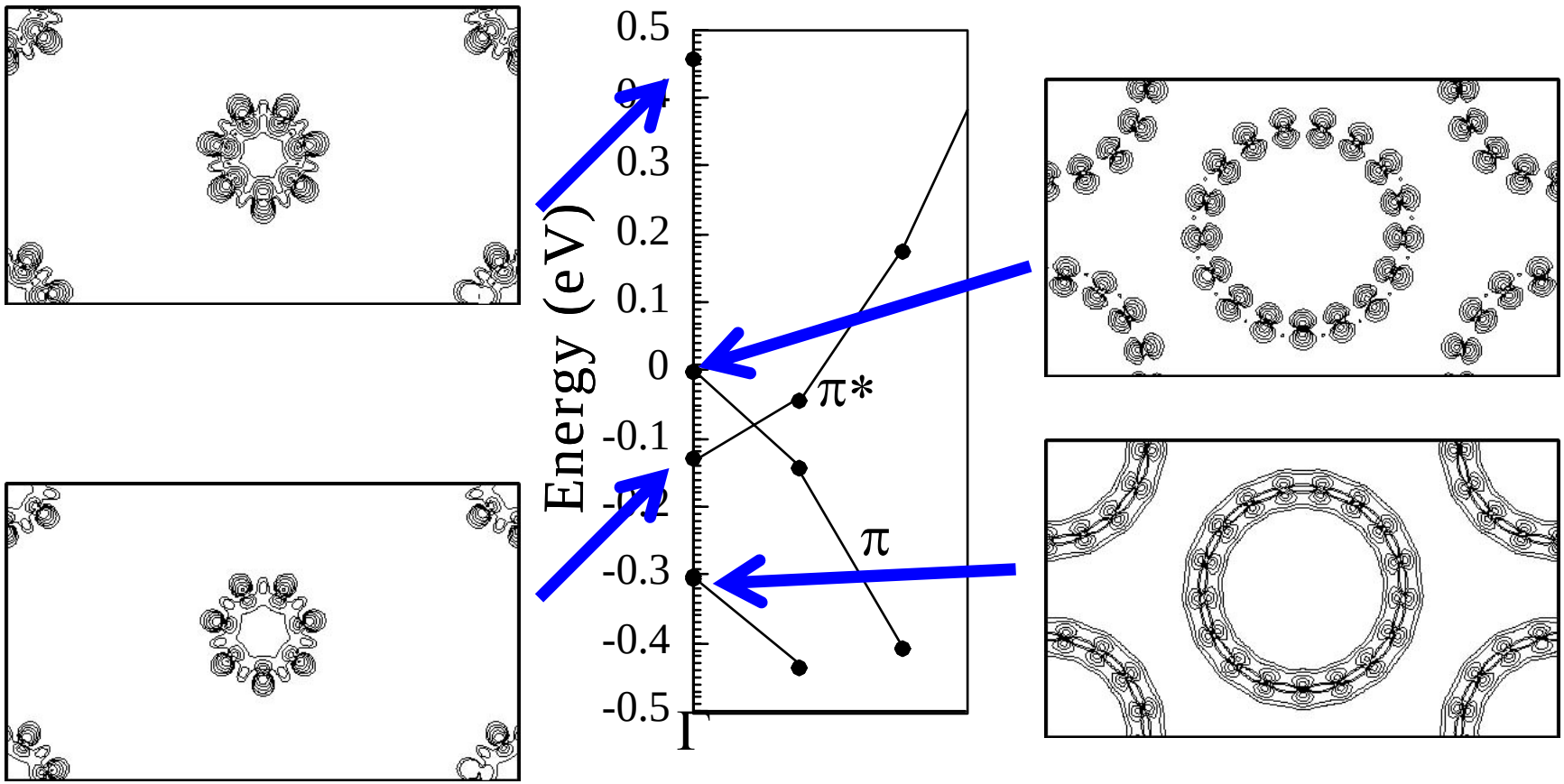
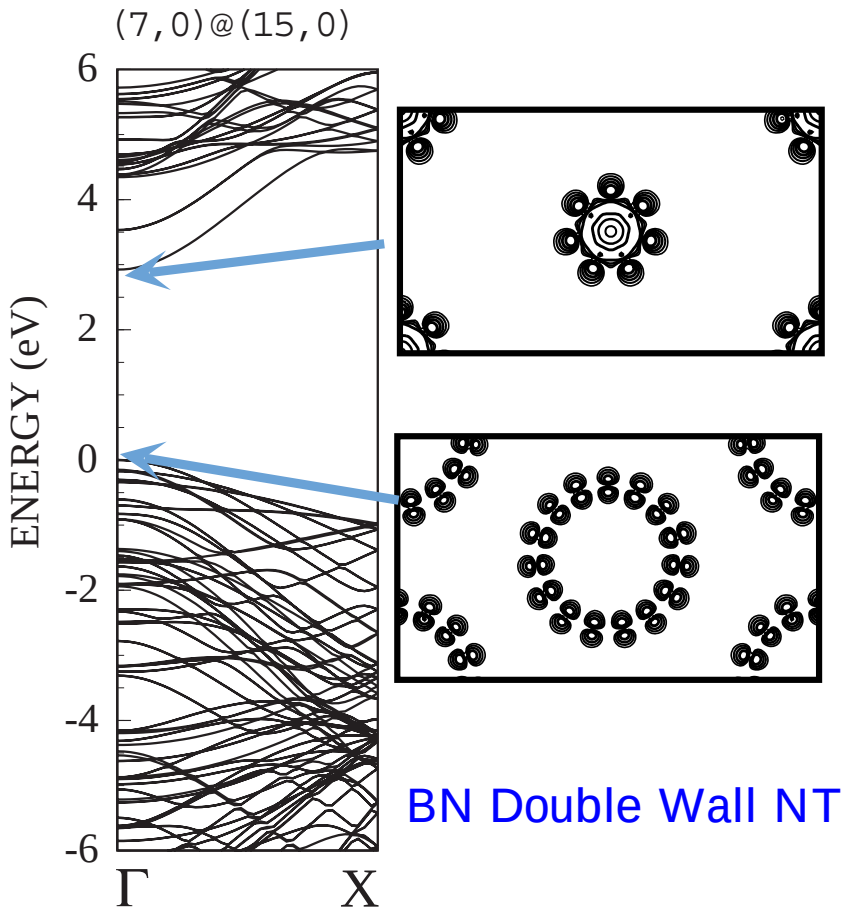
Curvature Induces s-p mixing and It depends on radii

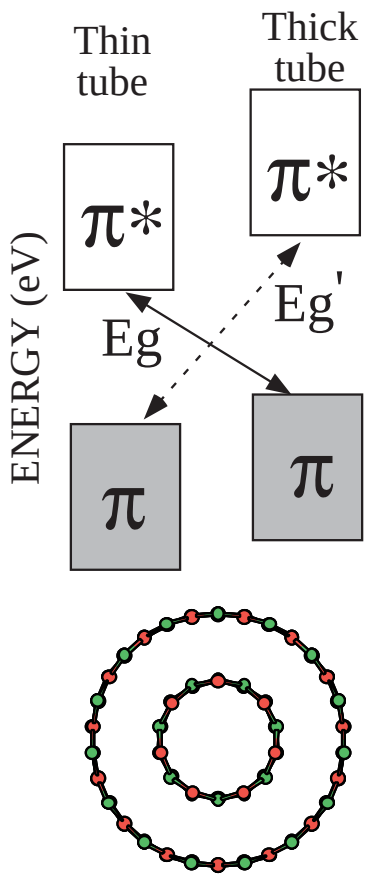
Extension of energy bands near E_F in (7,0)@(17,0)



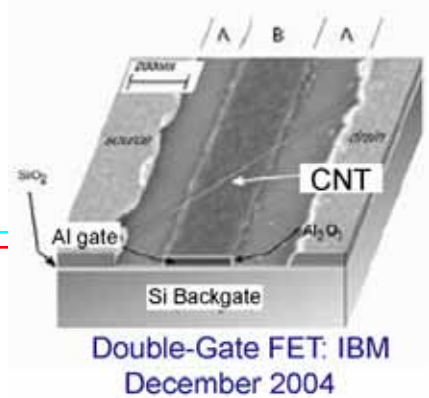
Common to Tubular Structure

S. Okada, S. Saito & A. Oshiyama: PRB 65, 165410 (2002)

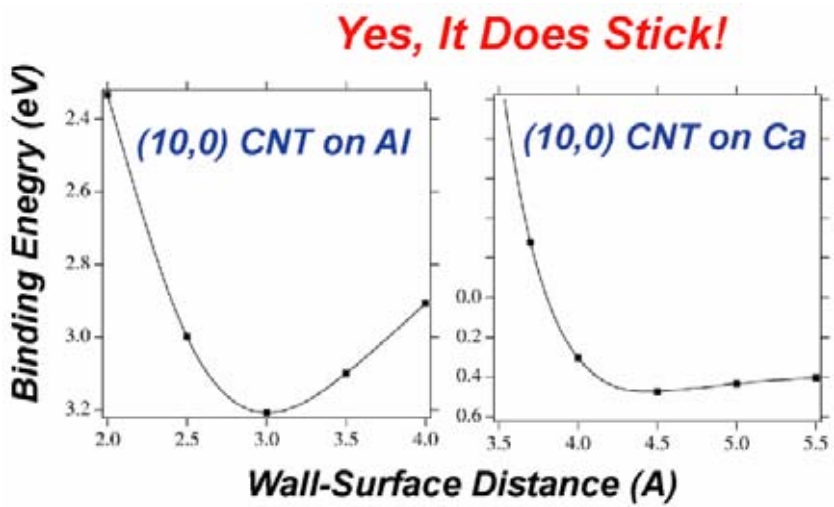


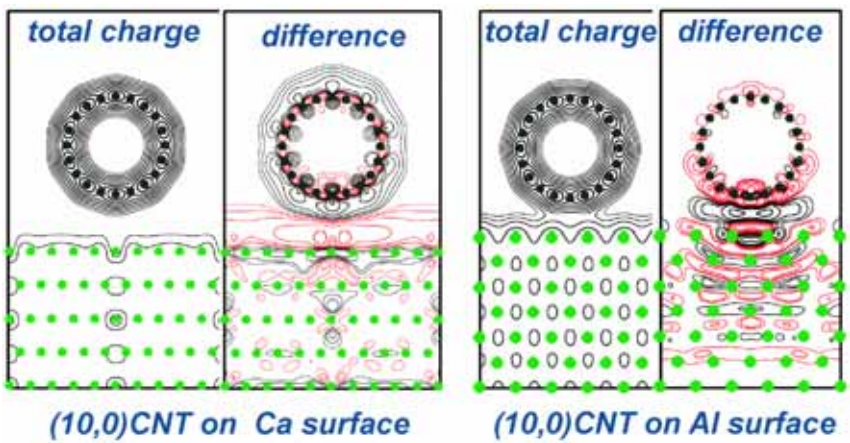


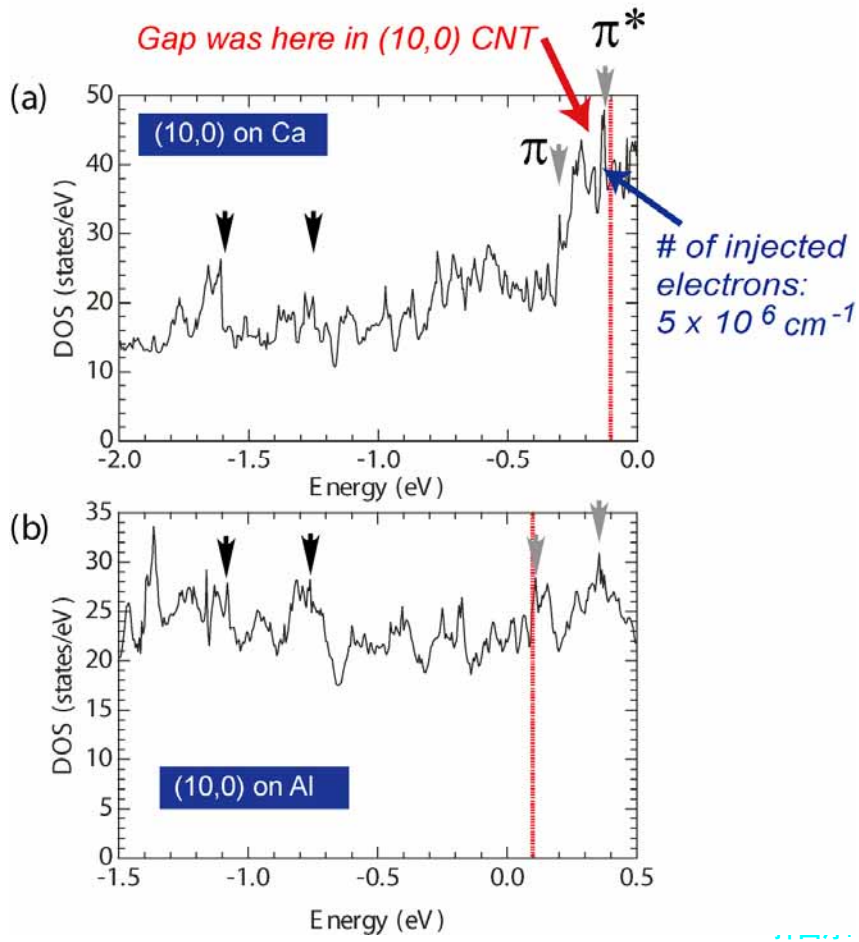
Nanotube/Metal Interfaces: a role of hybridization



Double-Gate FET: IBM
December 2004







Curvature could control number of injected electrons

Thinner (9,0) CNT on Al surface

Fermi Level is above original π^* due to small curvature, or in other words, to larger s mixing, and then

1.1×10^{6} cm^{-1} electrons are injected from Al to CNT

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Nano-scale badminton Shuttlecock

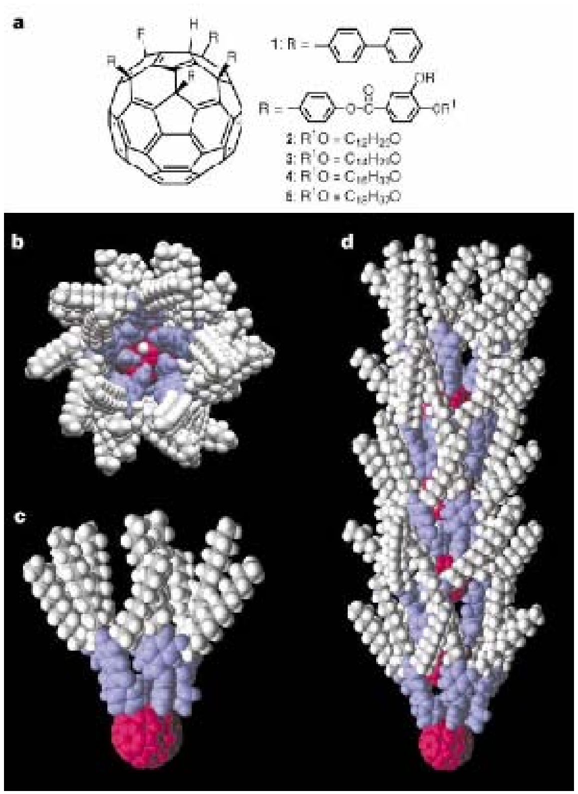
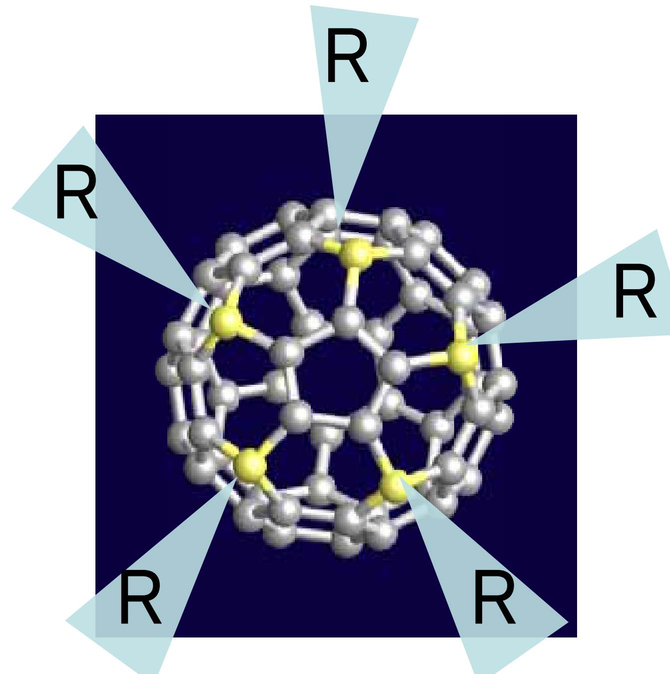


Figure 1 [illegible]

M. Sawamura et al., Nature, **419**, 702 (2002)



Chemical modifications

R= biphenyl ($C_{12}H_{10}$)
methyl (CH_3)
(C_6H_5)-Me
(C_6H_5)-polyacetylene, etc...

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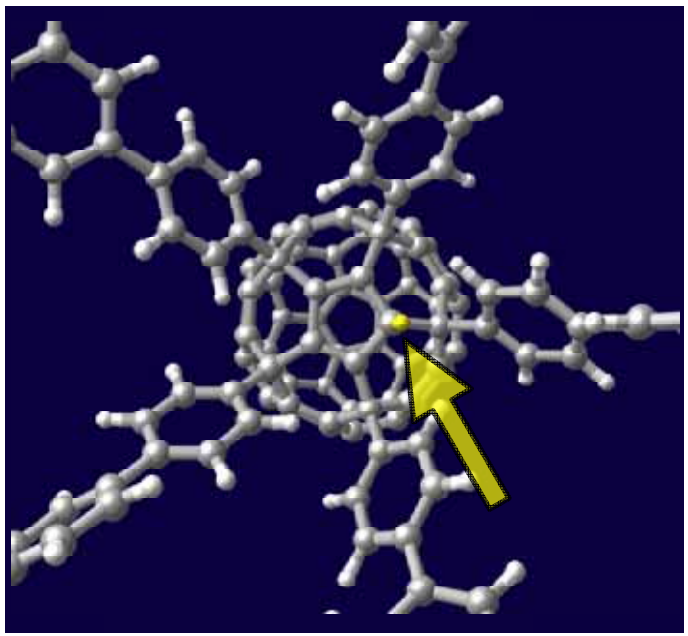
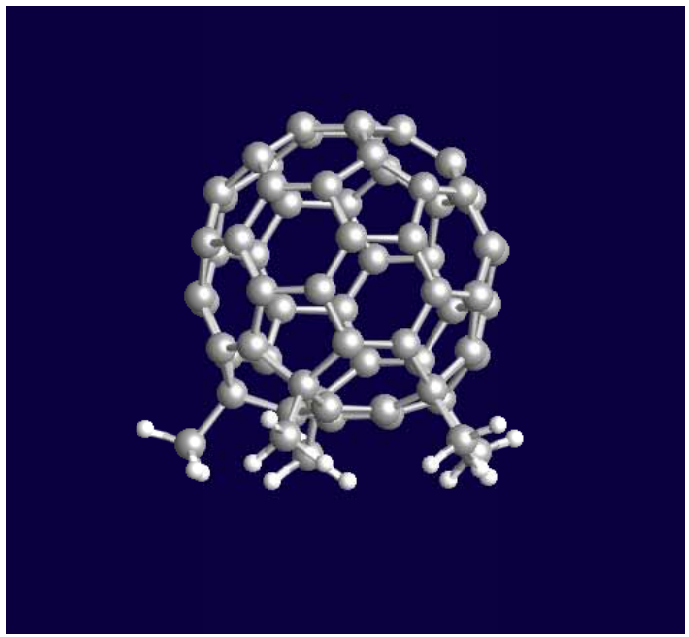
Let's calculate following Nano-scale Shuttlecock

$C_{60}H$-(biphenyl)$_5$

C_{60}(biphenyl)$_5$



C_{60}(Methyl)$_5$



They are all synthesized

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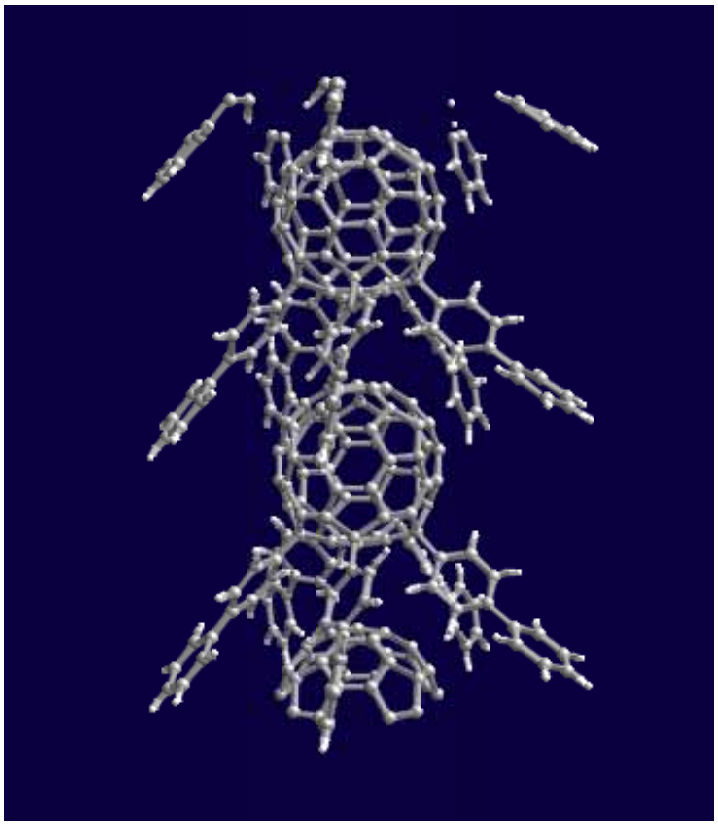
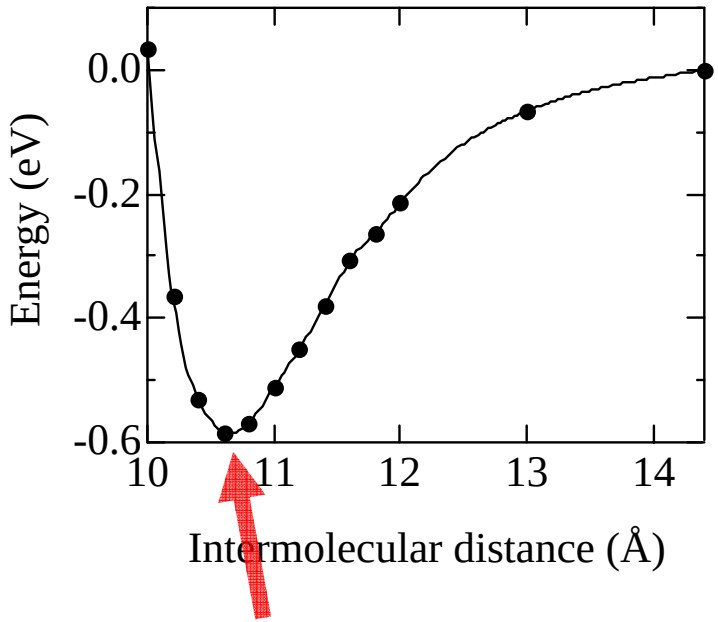
Geometric Structure of C60H-(biphenyl)5





C_{60}-C_{60} = 10.66 Å

cf. 10.0 Å for fcc C_{60}

Geometric hindrance (H atom & C_{60}) results in the large intermolecular spacing.

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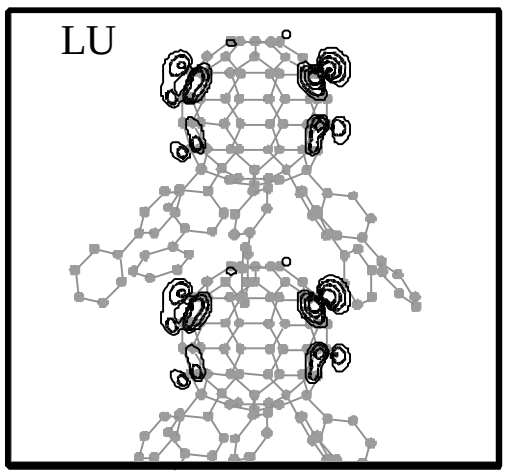
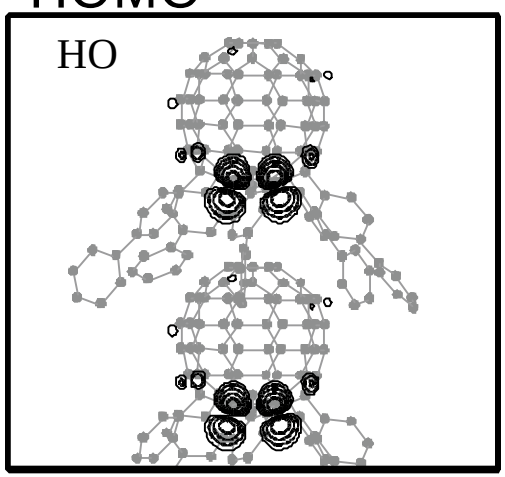
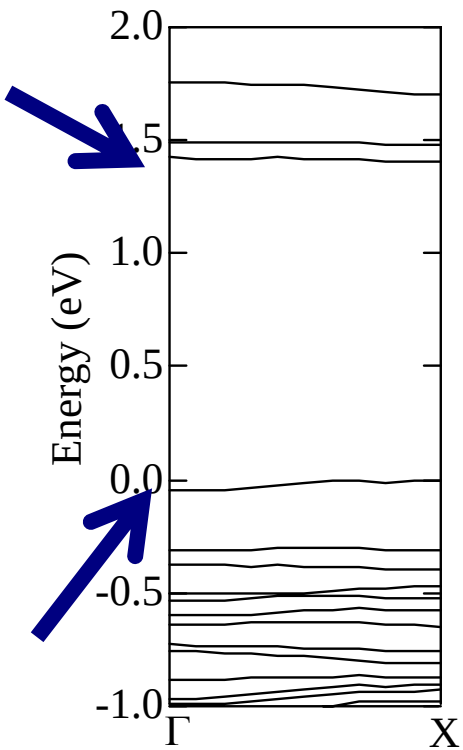
Electronic Structures: C60H-(biphenyl)5

LUMO

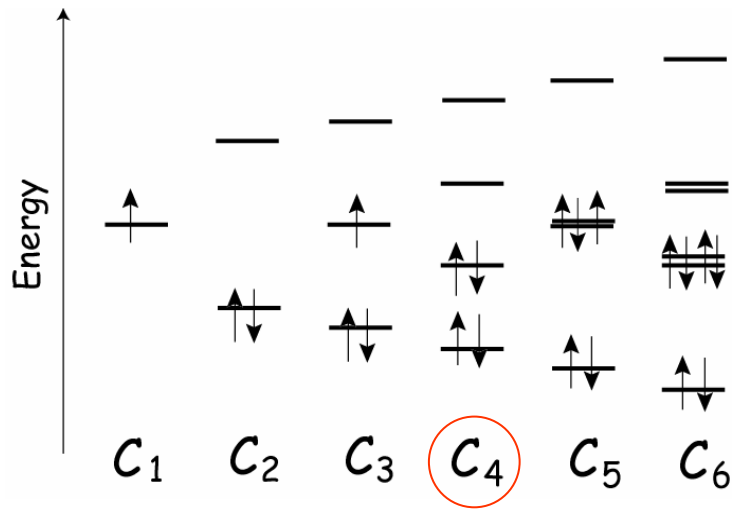


HOMO





- Energy gap: 1.4 eV
- LUMO Band width: 0.05 eV
- HOMO Band width: 0.02 eV



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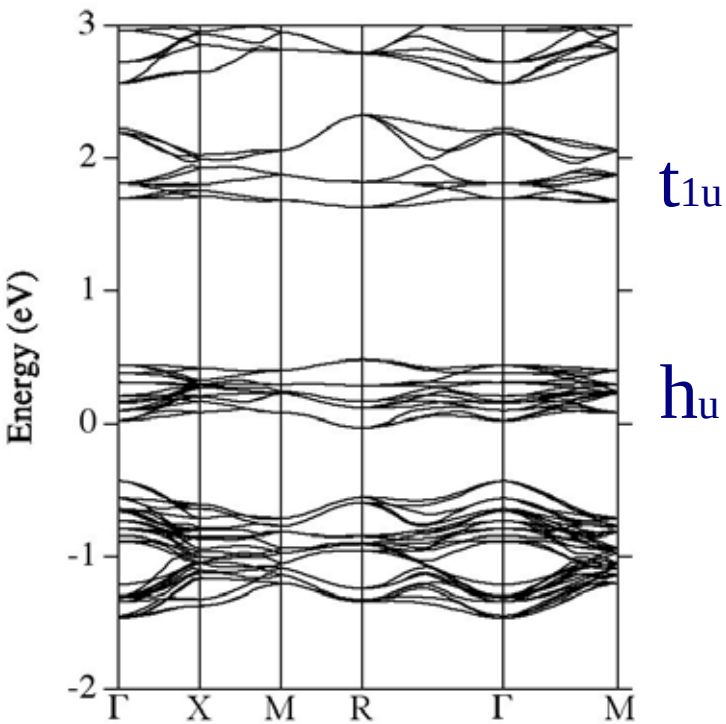
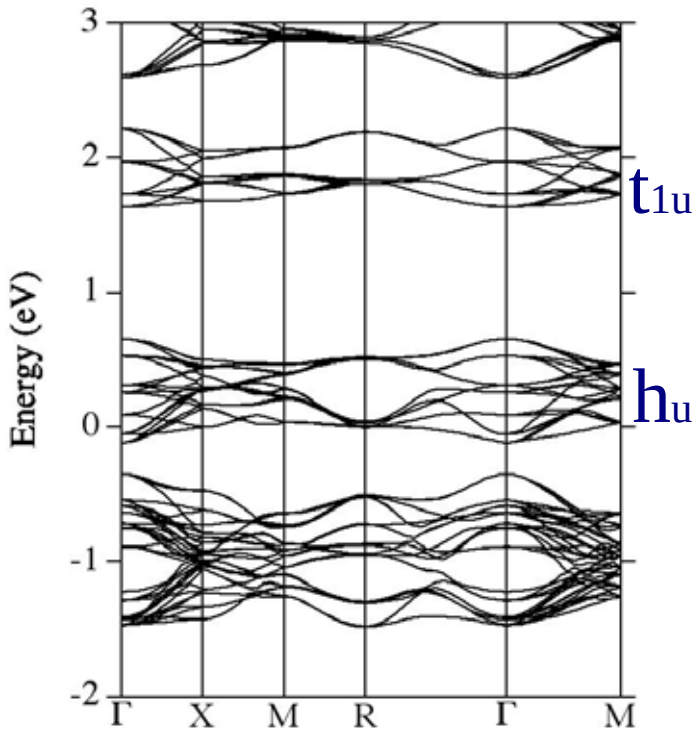
Compare: Electronic Energy Bands of Solid C_{60}

SC phase



FCC phase



Energy Gap is a half eV, much larger than 20-50 meV

C_{60}-C_{60} distance: 10.0(fcc) vs 10.6(shuttlecock)

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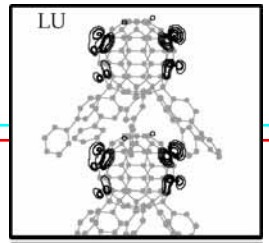
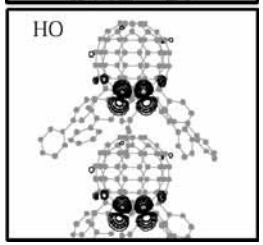
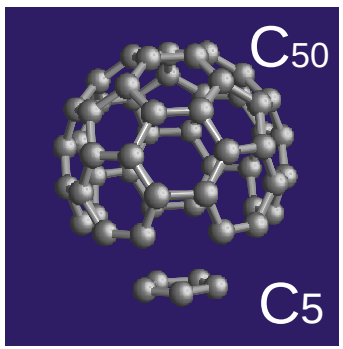
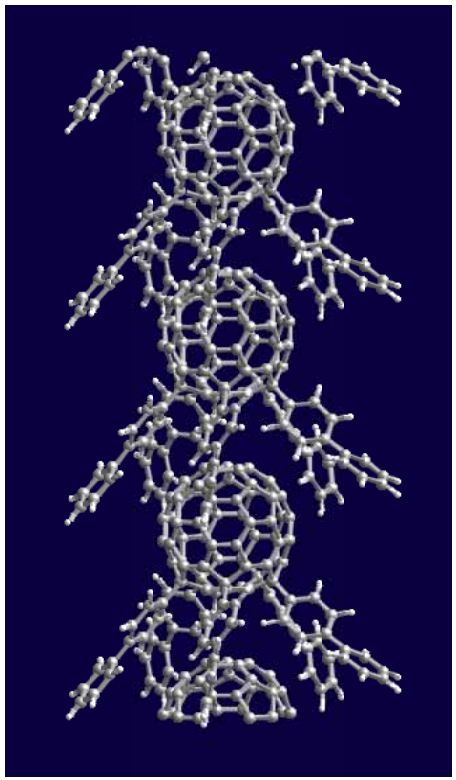
New π Electron Network



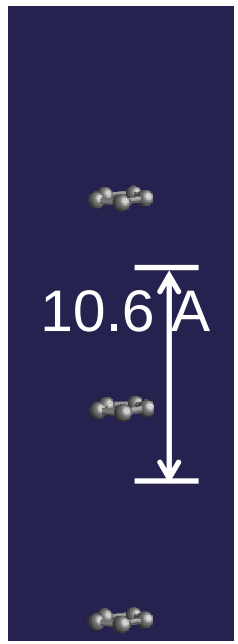


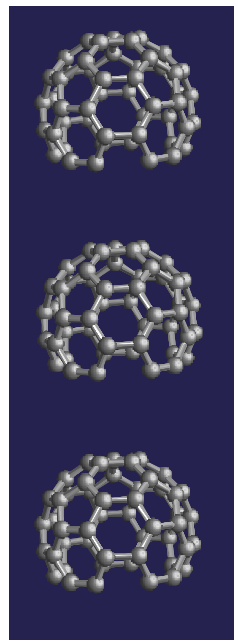




HOMO

LUMO





10.6 A

C5

C50

➢**Shuttlecock chain is a new π electron system in which attached molecules divide the C60 into C5 and C50 units.**

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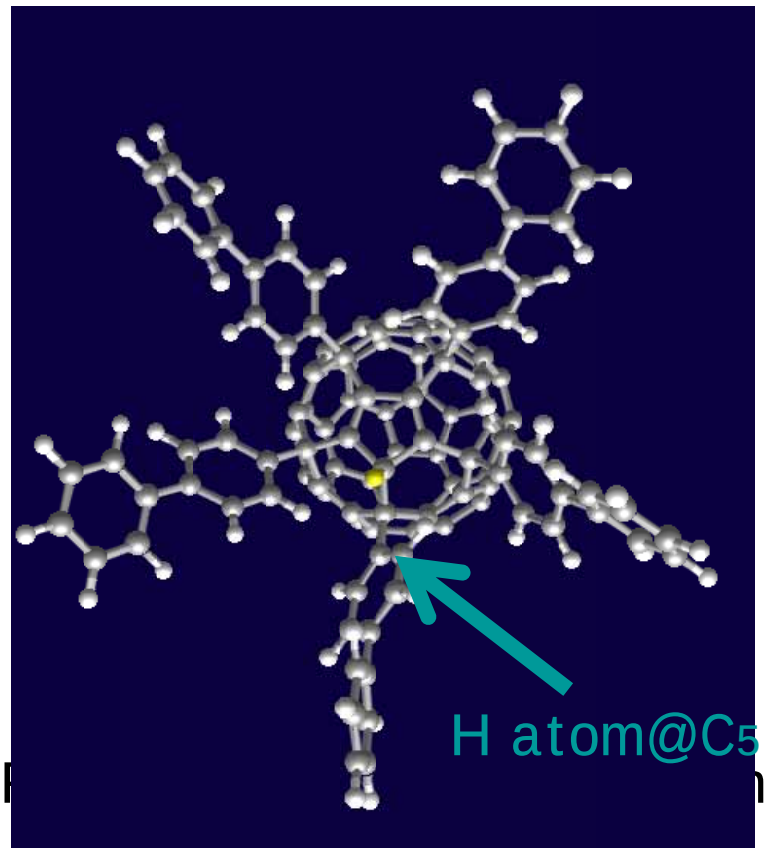
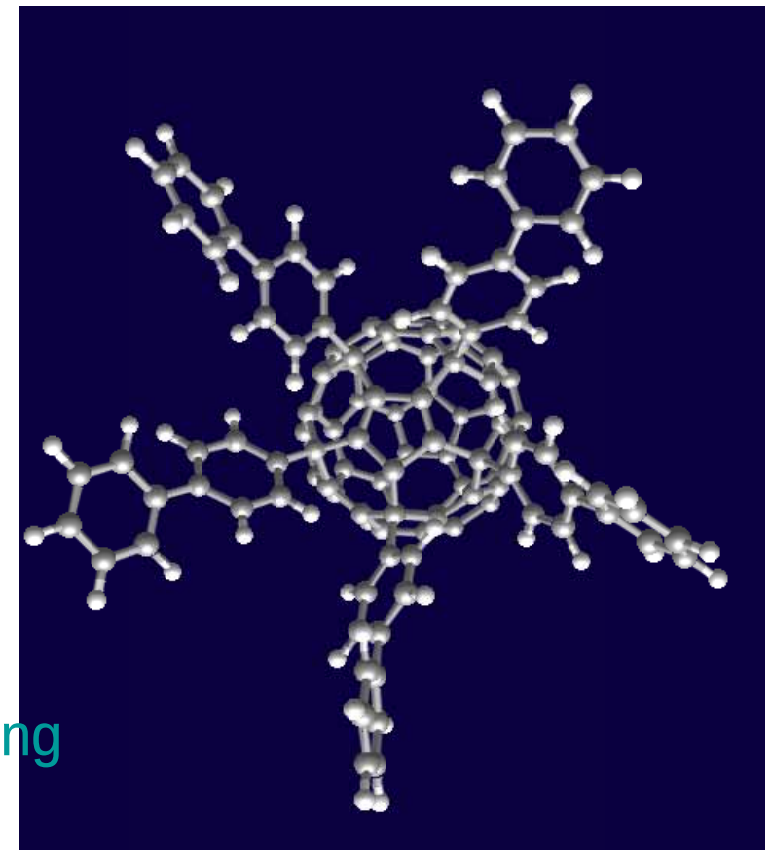
Hydrogen Removal could Modify Electron States of Shuttlecock

$C_{60}H$-(biphenyl)$_5$



C_{60}-(biphenyl)$_5$



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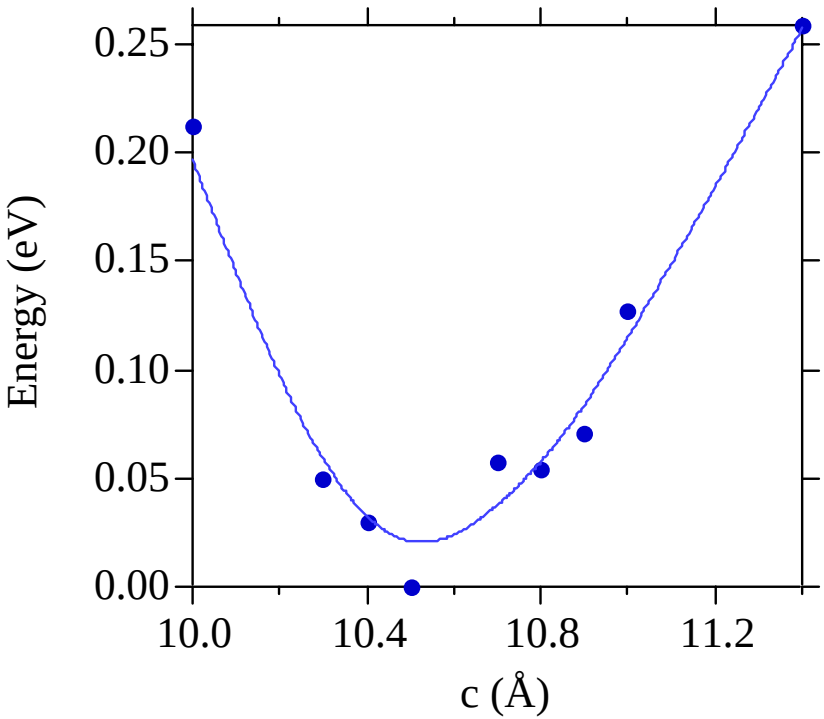
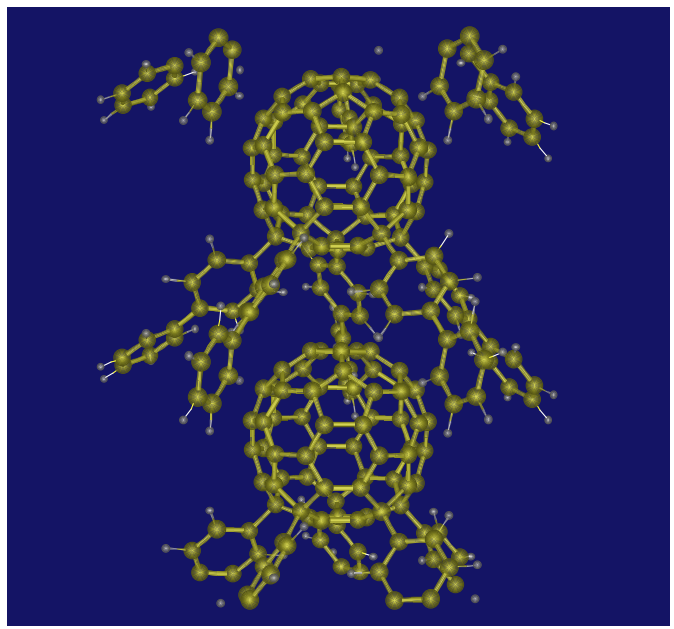
Geometric Structure of C_{60}-(biphenyl)$_5$





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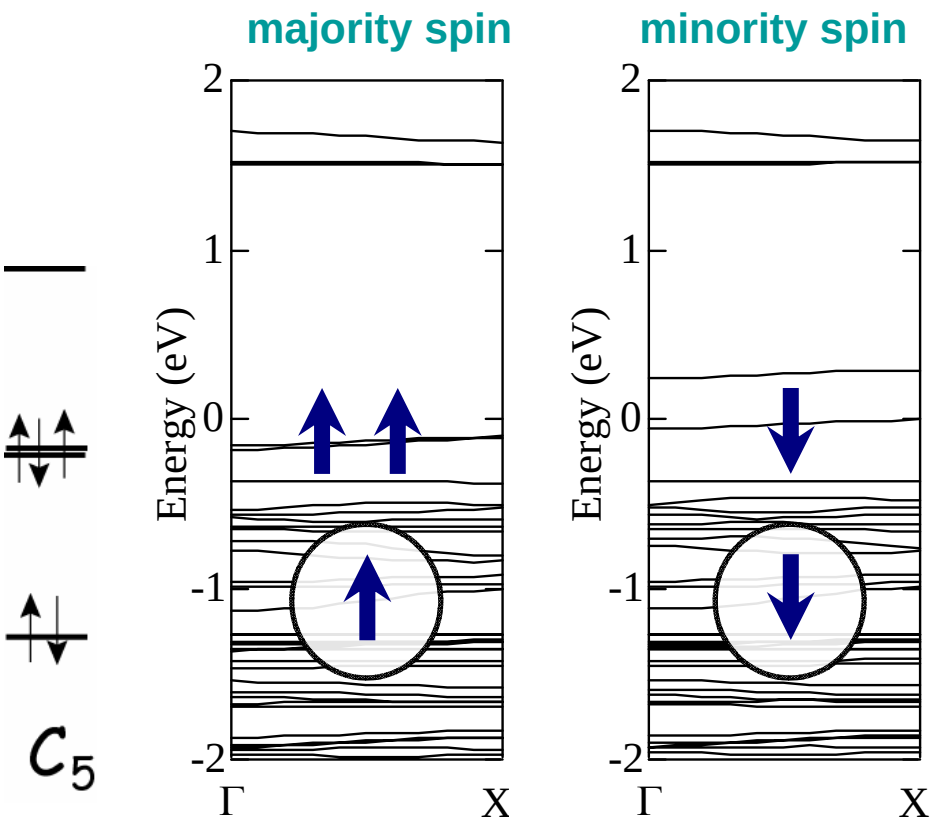
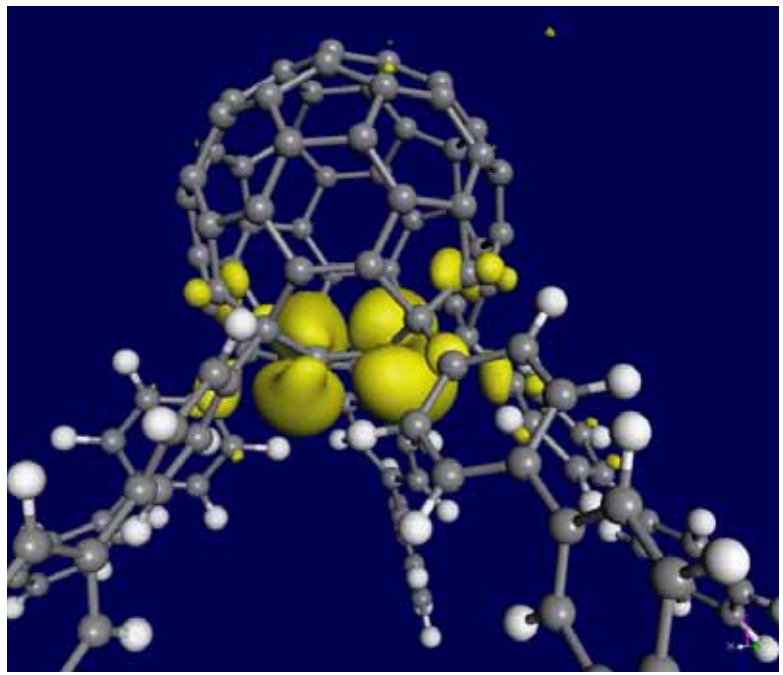
Electronic Structure: C60(biphenyl)5



spin: $S_{\uparrow} - S_{\downarrow} = 1 / 2$



Spin polarization: $E_{\text{high spin}} = E_{\text{no spin}} - 98$ meV

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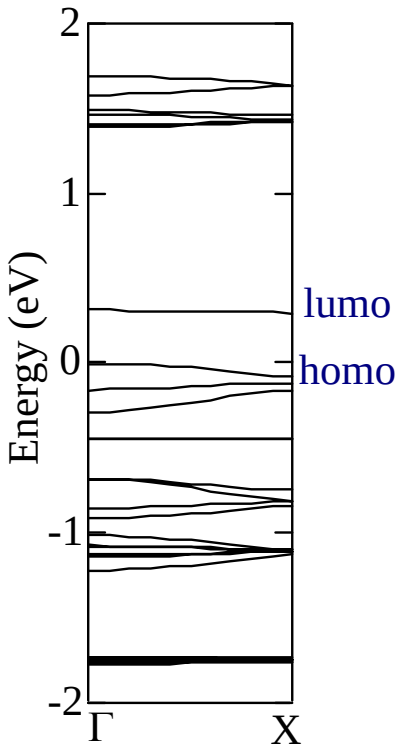
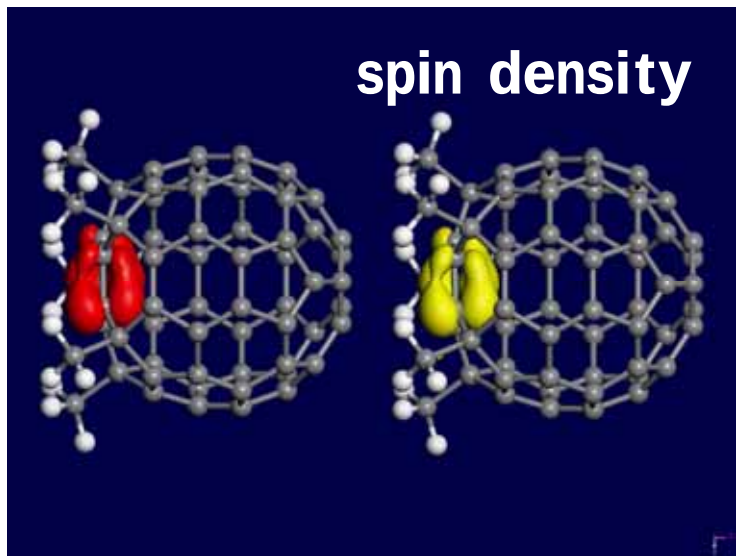
Decoration of Fullerene Makes it Magnetic Shuttlecock



	Total Energy (meV/C60-Me5)
Ferro	-48
AntiFerro	-58
No spin	0



Antiferromagnetic order!!

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  - *Higher electron temperature that simulates electron-excitation-induced materials formation*
- What we are planning to do on PACS-CS

Si Crystal from SiO_2 upon Electron Excitation

- Electron injection through wires causes local reduction of SiO_2, generating Si crystal

  [Nohira, Yasuda & Itoh: Nature Materials 2, 397, (2003)]

- Femto-second laser pulses seem to generate Si crystal

  [Sokolowski-Tinten et al: PRL 87, 225701 (2001); K. Hirao et al: Jpn APS Meeting; K. Murakami: unpublished]

⇒

New technique to grow materials?

If yes, then how is it made? → ***Free Energy MD Calculation with Excited electrons***

Electron Excitation
⇔ Electron Temperature Increase

- Laser pulses of different frequencies may be simulated via finite electronic temperature molecular dynamics within the Free Energy functional formalism
- This is supposed to reproduce what occurs when SiO_2 is perturbed as in femto-second laser experiments.
- 3 different electronic temperatures are considered, corresponding to 3 different laser frequencies:

T[e] = 20000 K $\longleftrightarrow$ $\hbar\omega = 1.72\,eV$

T[e] = 25000 K $\longleftrightarrow$ $\hbar\omega = 2.16\,eV$

T[e] = 30000 K $\longleftrightarrow$ $\hbar\omega = 2.59\,eV$

Free Energy Molecular Dynamics

Free Energy is written as

$$F[\rho(r),\{R_I\}] = -2k_B T_e \ln\det[1+\exp(-\frac{H-\mu}{k_B T_e})] + \mu N_e + E_{II}$$

$$- \int dr\, \rho(r)\left(\frac{V_H(r)}{2} + \frac{\delta E_{XC}}{\delta\rho(r)}\right) + E_{XC}$$

Then, equations of motion are introduced by the following forces:

$$\frac{\delta F}{\delta <\psi_i|} = \frac{\delta F}{\delta\rho(r)}|\psi_i> \quad \text{and} \quad \mathbf{f}_I = \nabla_I F$$

Here the electron charge density is given by

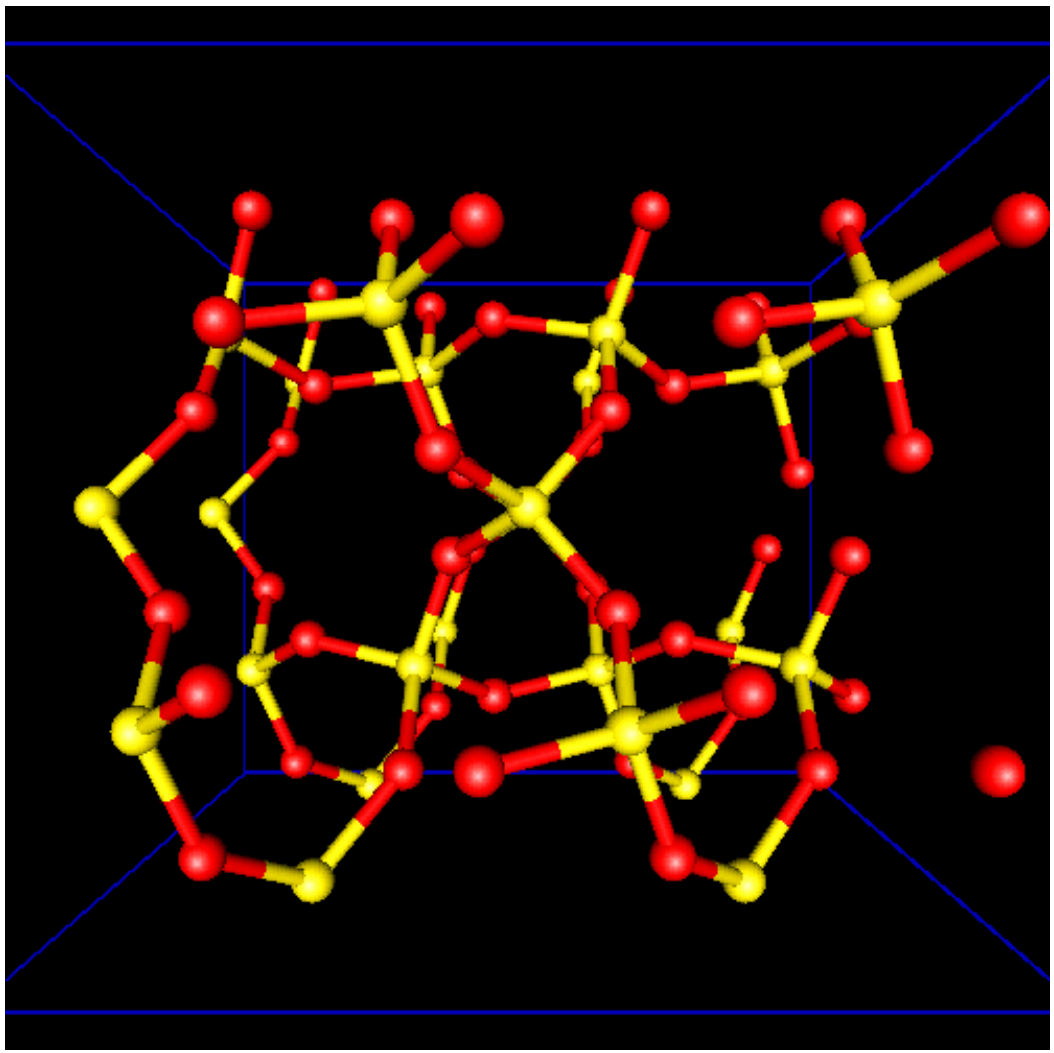
$$\rho(r) = \sum_i n_i |\psi_i(r)|^2$$

[Alavi et al: PRL 73, 2599 (1994)]

with

$$n_i = \frac{1}{1+\exp[(\varepsilon_i-\mu)/k_B T_e]}$$

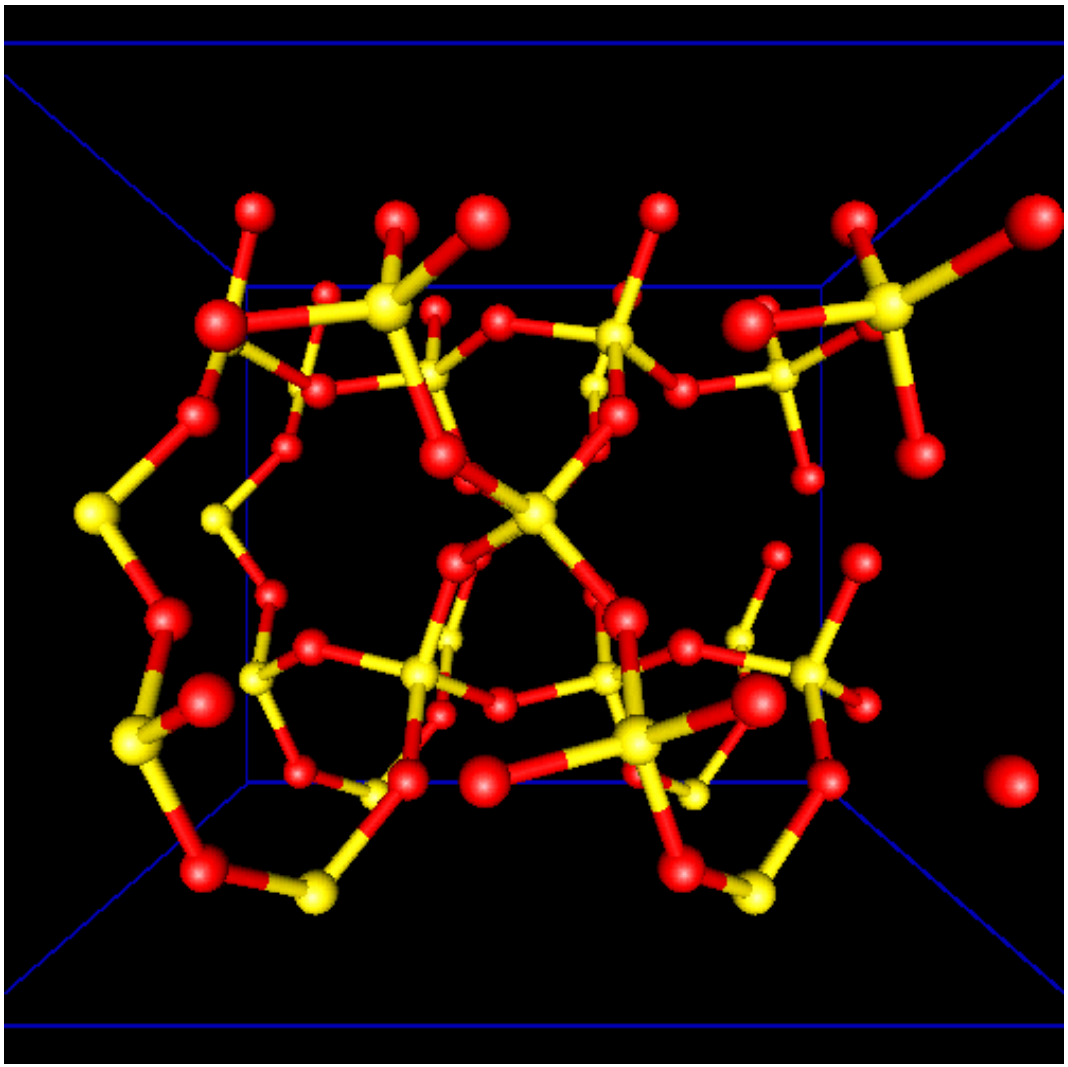
Simulation at T_e=20000 K (1.72 eV)



$\langle T_{ion} \rangle$ = 304 K

Just
a thermal motion

Simulation at T_e=25000 K (2.16 eV)

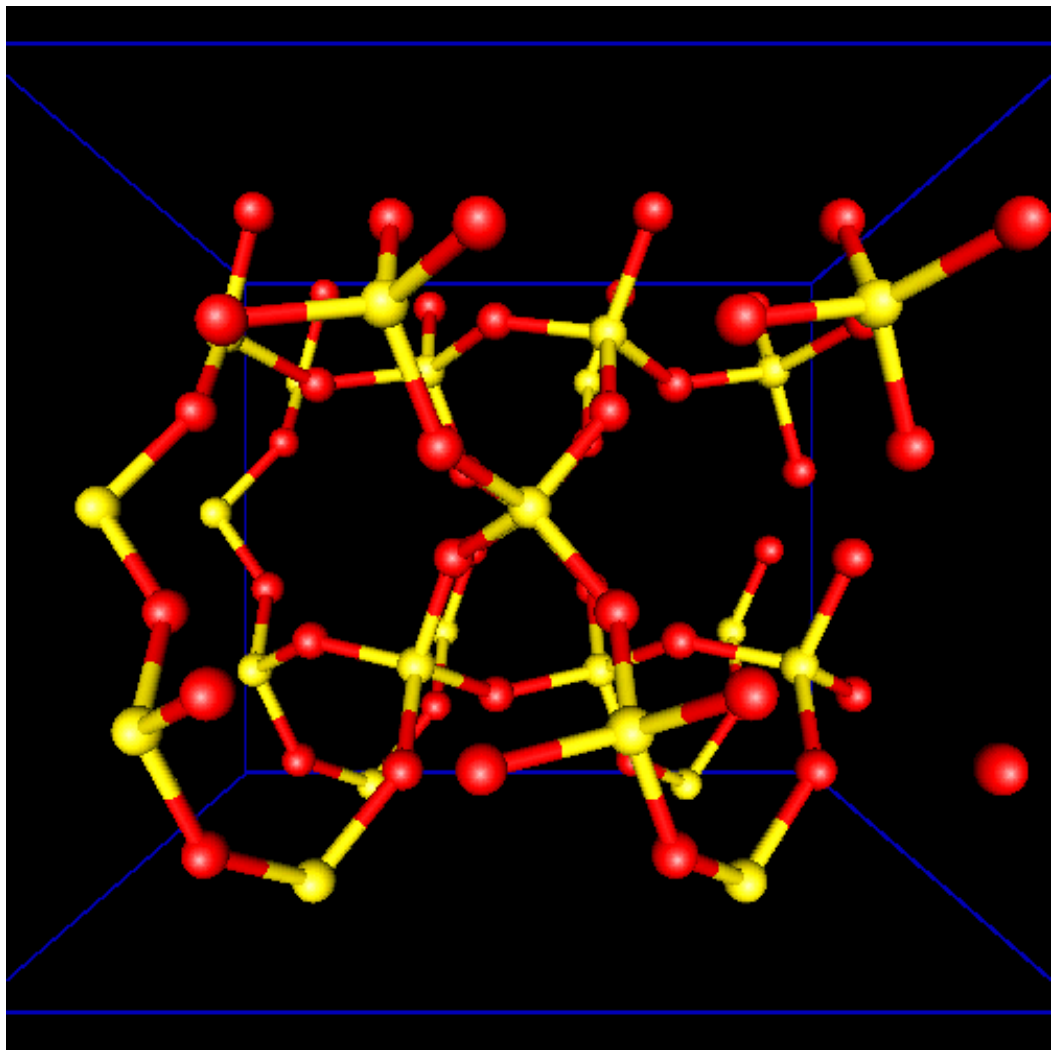


$\langle T_{ion} \rangle$ = 367 K

BUT!

Formation of Si-Si bonds

Simulation at T_e=30000 K (2.59 eV)



$\langle T_{ion} \rangle$ = 2870 K
(T_{melt}=1883 K)

Just melt

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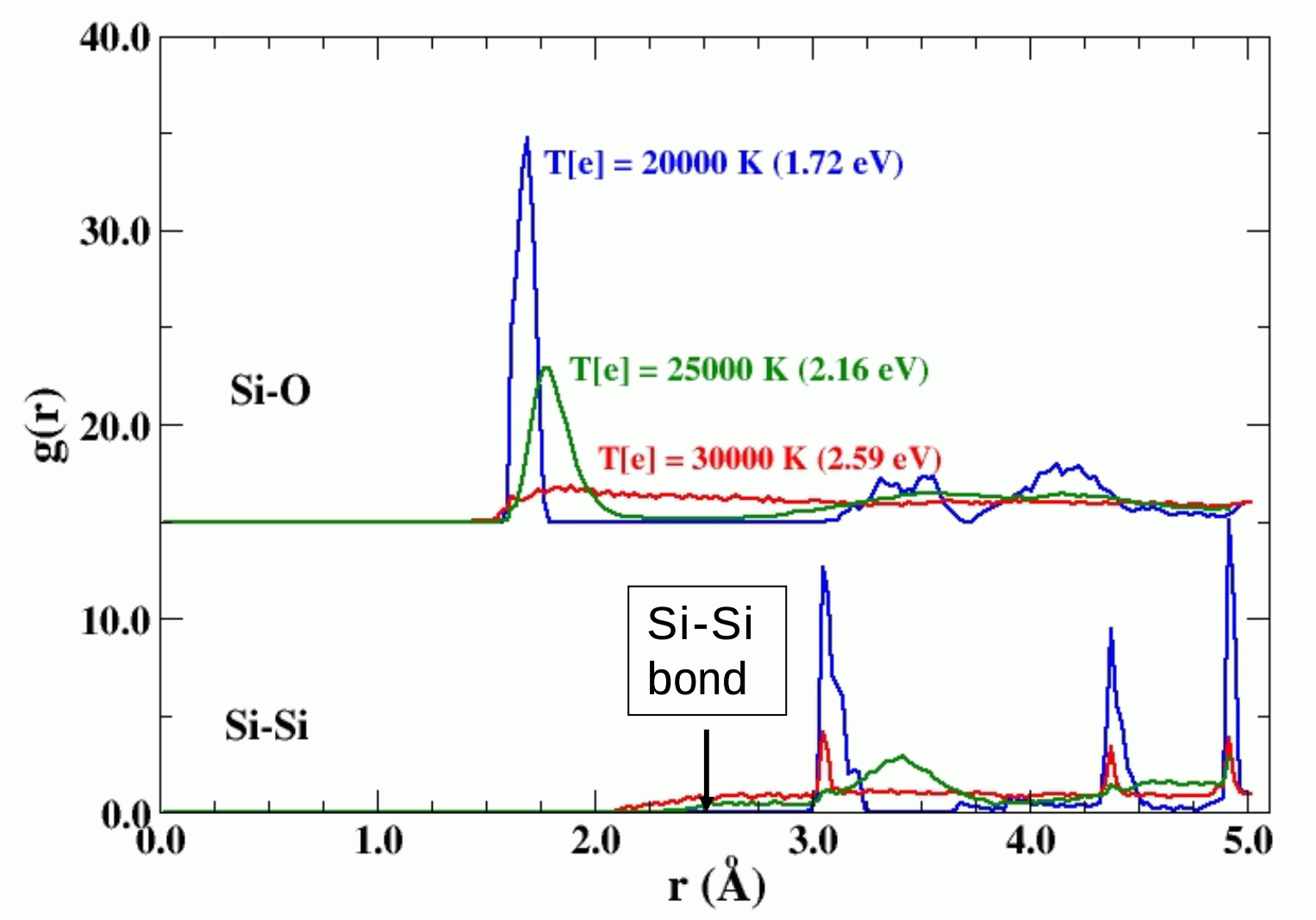
Radial distribution functions for the three electron temperatures



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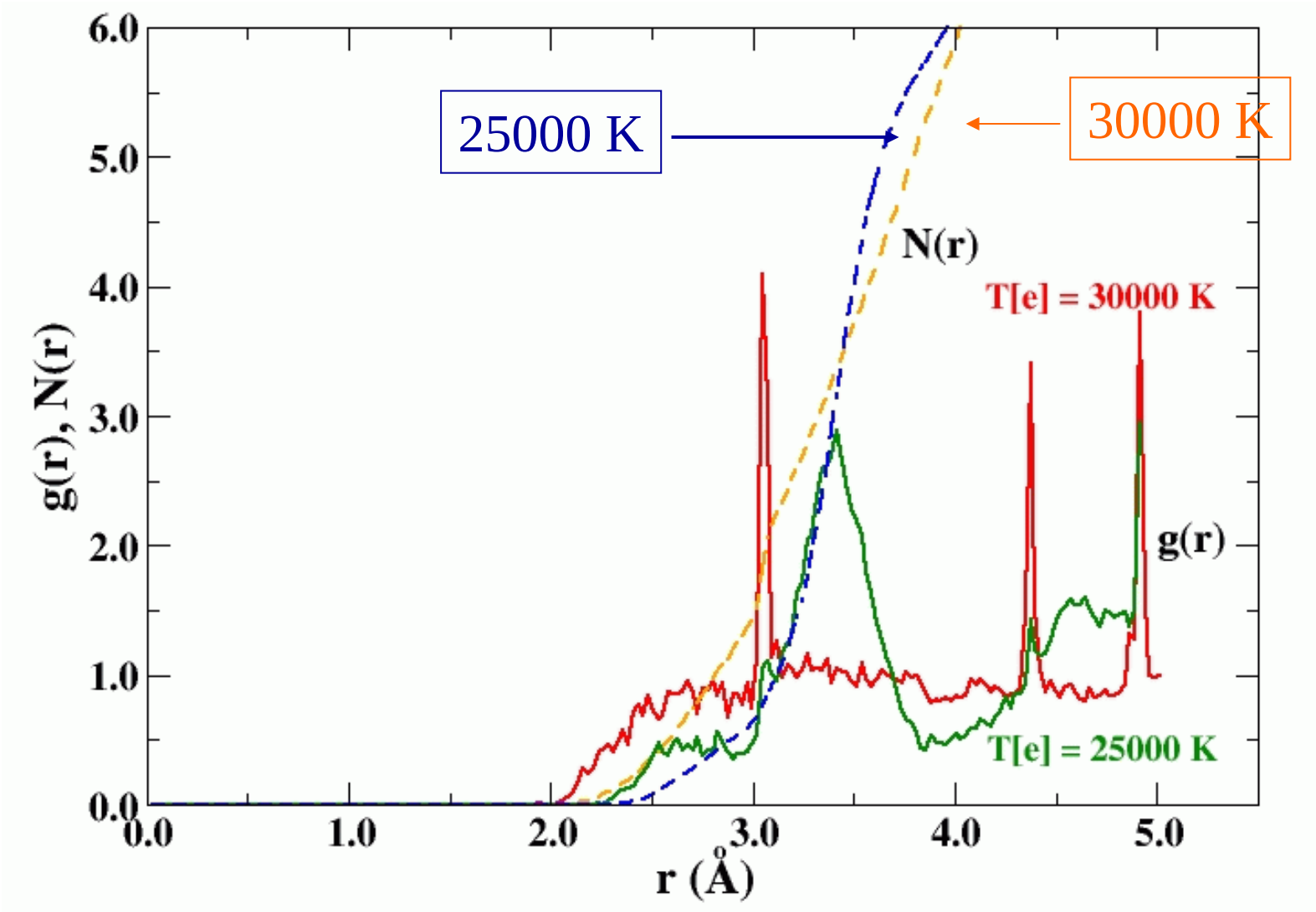
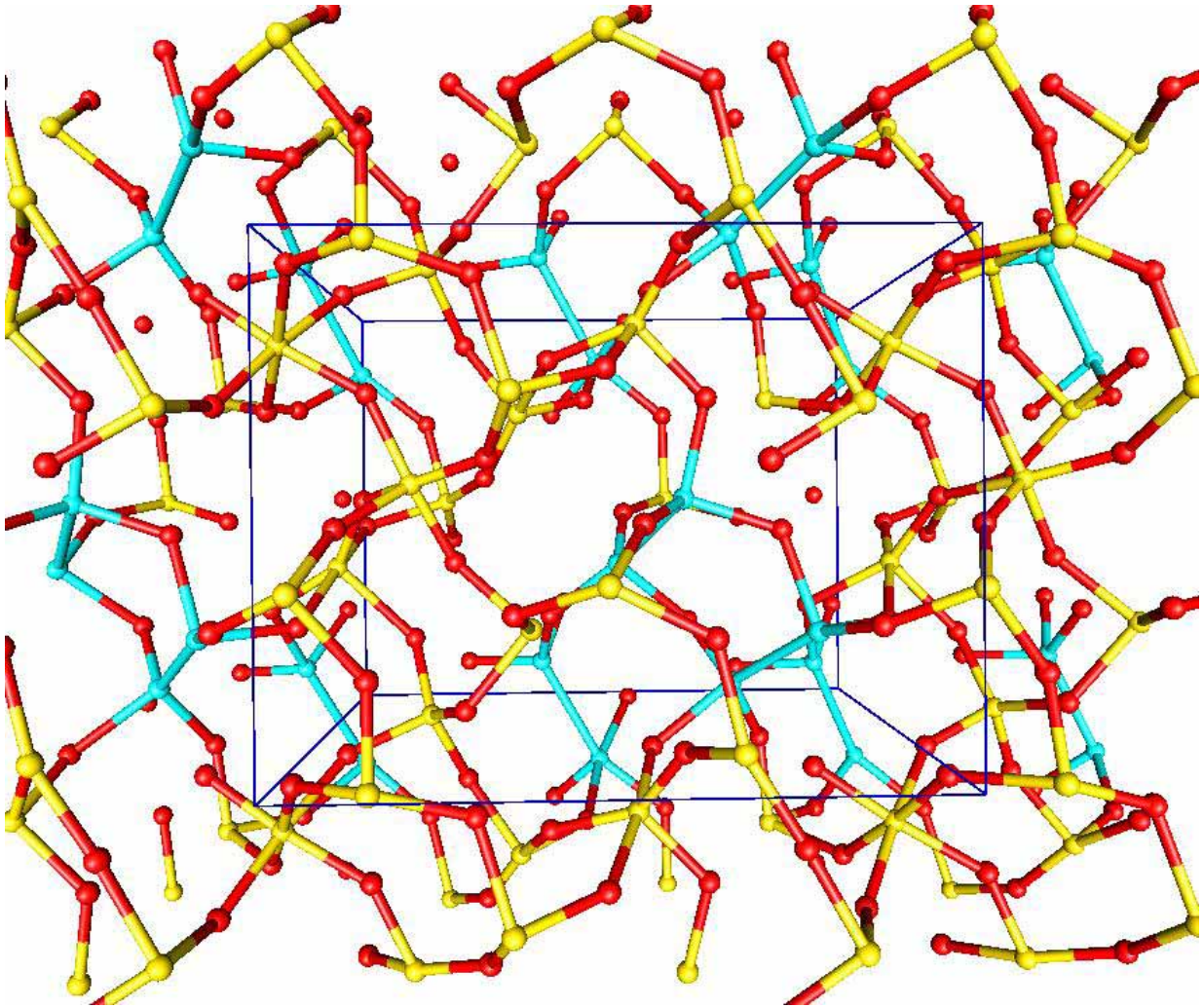
Si-Si RDF and integrated coordination number for the two electron temperatures

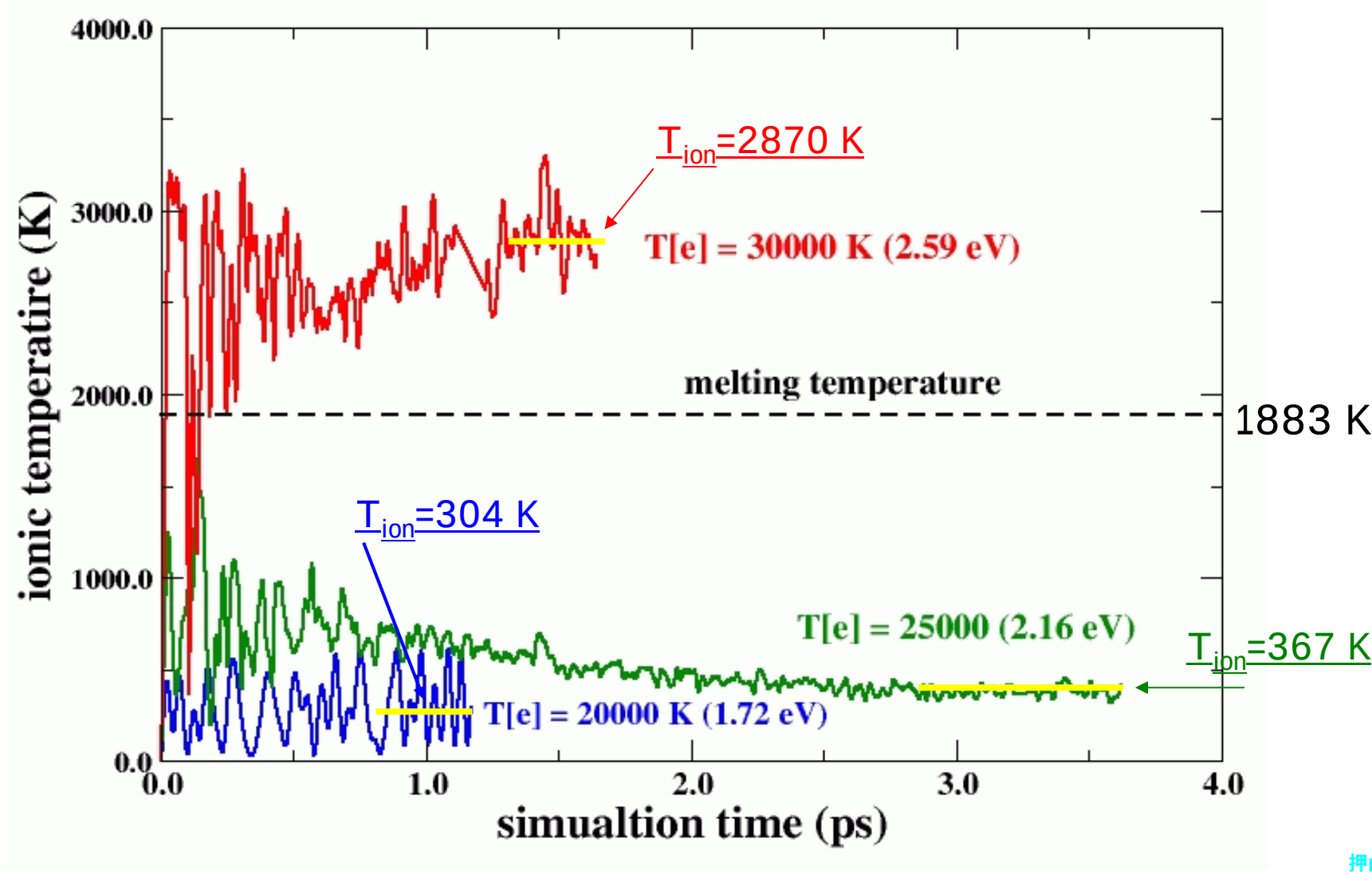


Final stable structure obtained at T_e= 25000 K (Si-Si bonds in light blue)



Si-Si bonds
(d=2.51A - 2.64A)
are 20% of the total Si related bonds

Ionic Temperature:
Si Formation below Melting Temperature



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Diffusion Coefficients for Si & O

T[e] (K)	T_{ion} (K)	D_{Si} (cm^2/s)	D_O (cm^2/s)	Si-Si bond
20000	304+/-151	1.004 x 10^{-9}	1.252 x 10^{-9}	No
25000	367+/-102	4.100 x 10^{-9}	8.489 x 10^{-9}	Yes
30000	2870+/-220	1.415 x 10^{-7}	3.401 x 10^{-7}	Yes **(but melt)**

$$D_j = \frac{1}{3}\int_0^{\Delta t} \left\langle \frac{1}{N_j} \sum_{I=1}^{N_j} \vec{v}_I(t)\vec{v}_I(0) \right\rangle$$

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PACS-CS における物質・生命科学 I: ナノ形状の量子論

- Curvature-induced metallization of semiconducting double-wall carbon-nanotubes

  [Okada & Oshiyama: PRL 91, 216801 (2003), and unpublished results.]

  - *Balance of 2 nano-curvatures makes it. The similar happens at metal contacts.*
- C_{60} badminton shuttlecock: possible magnetism

  [Okada et al: CPL 399, 157 (2004).]

  - *Attachment of molecules becomes nano-scissors.*
- Formation of Si seeds in SiO_2 upon laser irradiation

  [Boero, Silvestrelli & Oshiyama: 2005.]

  - *Higher electron temperature that simulates electron-excitation-induced materials formation*
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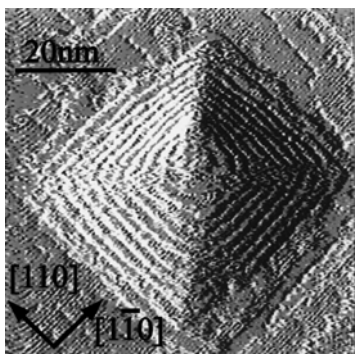
10,000 – 100,000 原子群の量子論的計算

- なぜ？
  - ナノ･バイオ物質は10^4原子群から成る
  - 局所的な量子論的化学反応が大局的な構造形成･変化を引き起こし，物としての機能が発現

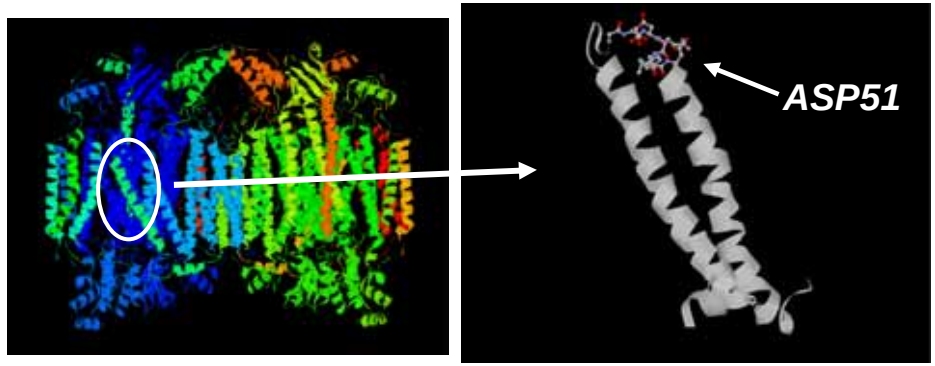
⇒ マルチスケールの量子論，形と機能の量子論

原子構造，電子状態，反応機構，．．．



10nmのSi立方体には5万個の原子

シリコン･ナノピラミッド



シトクローム酸化酵素

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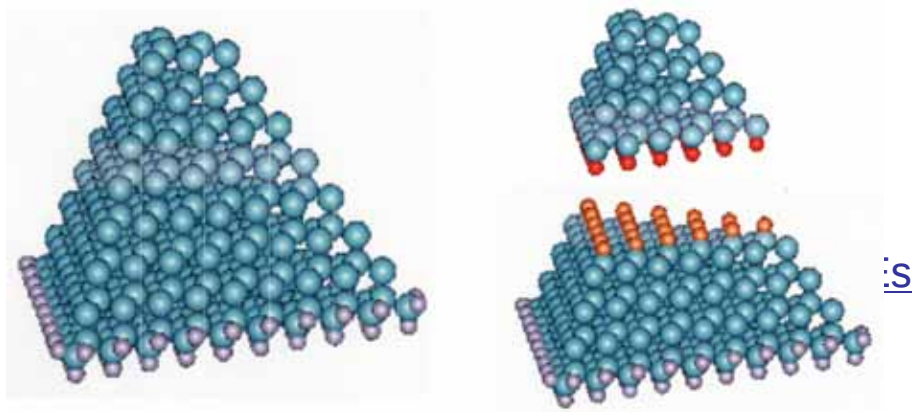
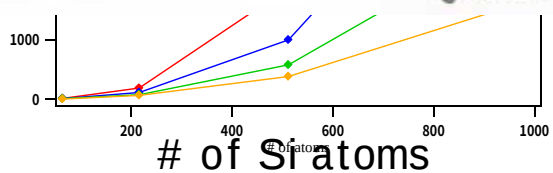
10,000 – 100,000 原子群の量子論的計算

- どうやって？
  - 10,000 原子群の密度汎関数法計算
    - *擬ポテンシャル・実空間差分法をPACS-CS上で*
  - 100,000原子群のハイブリッド計算
    - *DFT-Tight Binding-MM ハイブリッド*

✓ 擬ポテンシャルの局所性を活用
✓ Residual Minimization
✓ No FFT





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