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Quantum Simulations on Nano-Structured Materials

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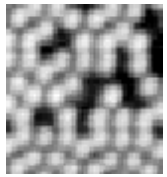
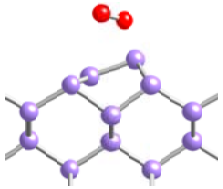
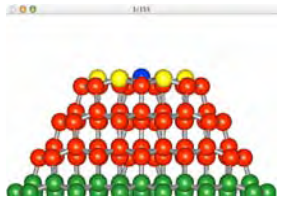
Nano-structured materials

To understand their formation processes & properties/functions at the atomistic level, FP simulation methods based on DFT are an ideal tool.

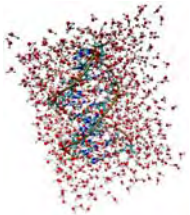
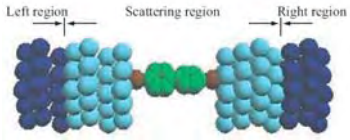
Surface dynamics (DFT/ Hybrid)

(i) Diffusion of F on Si(111) : *Si-F complex diffusion*
(ii) Adsorption of O2 on Si(001) : *Energy dissipation*
(iii) Atomic structure of AFM tip apex

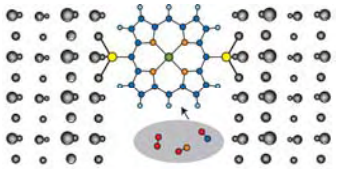
Large nano-structured systems

(i) PW electronic structure codes : shallow impurity in Si
(ii) Linear scaling algorithms:
  (a) Surface nano-structures; Ge cluster on Si(001)
  (b) Bio-molecules: DNA

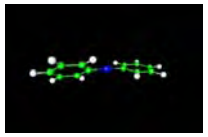
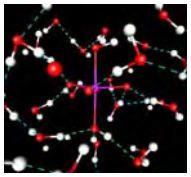
Transport through molecular junctions (NEGF)

(i) p-stacked systems: styrene wires on H/Si(001)
(ii) Molecular sensors: iron-porphyrin
(iii) Molecular switch: biphenyl dithiol

Photochemical reaction (RTP-TDDFT)

(i) Photoisomerization: azobenzene

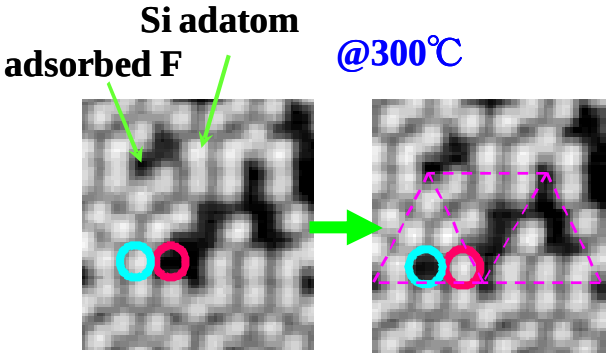
Redox reaction

(i) RuO4: $RuO_4^-(aq) + H_2O(l) + e^- \rightarrow [RuO_3(OH)_2]^{2-}(aq)$

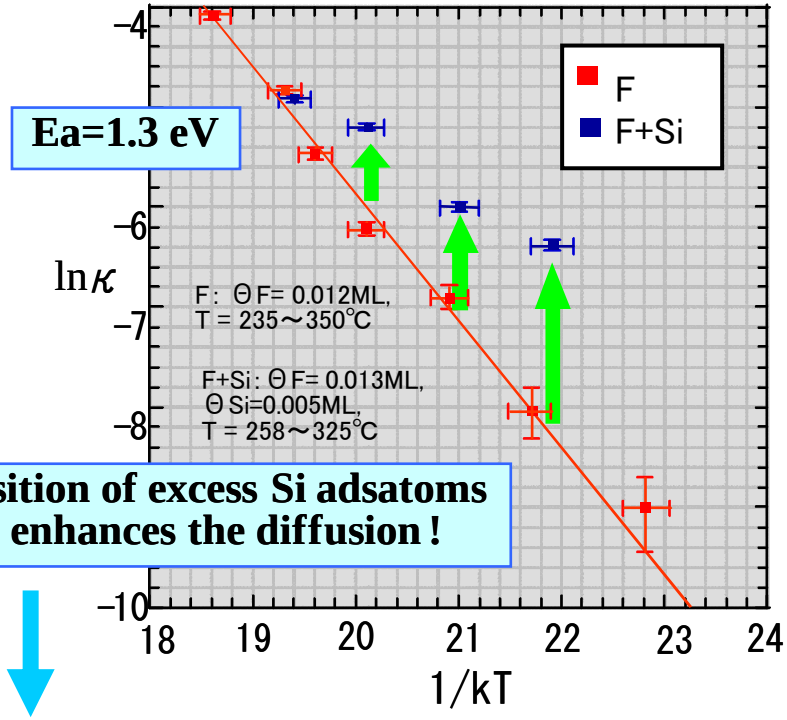
Diffusion of F on Si(111)

F diffusion on Si(111)-(7x7)

done by Prof. Sakurai's group



	Si(001)	Si(111)
n.n. Si-Si	3.8 A	4.5 A
Ediff	1.8 eV	1.3 eV



The deposition of excess Si adsatoms on Si(111) enhances the diffusion !

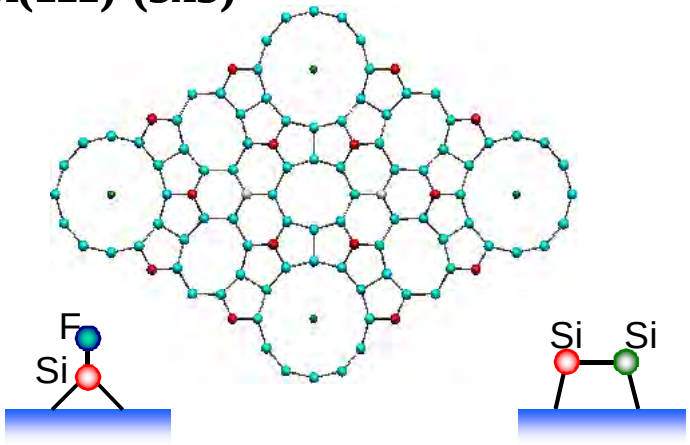
The F diffusion is assisted by excess Si atoms.

Surface diffusion which depends on diffusing Si density has not been observed so far. The diffusion mechanism in atomic scale is not clarified.

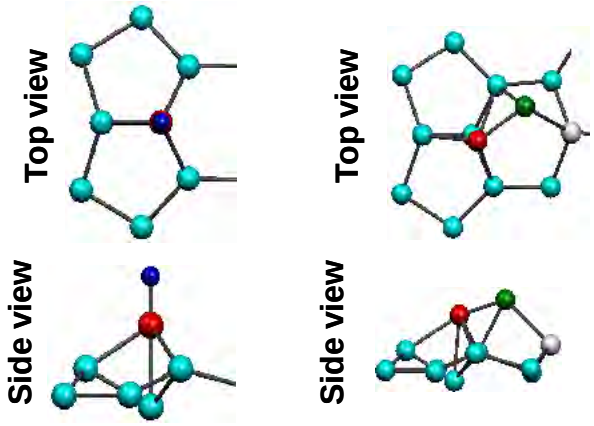
Diffusion of F on Si(111)

Y. Fujikawa, et. al. : J. Chem. Phys. 129, 234710 (2008)

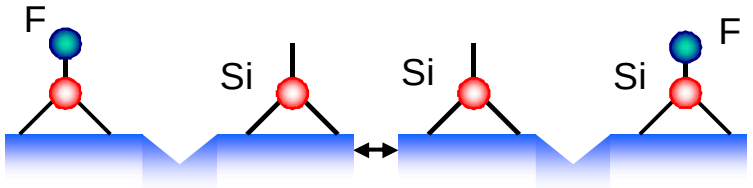
Si(111)-(5x5)



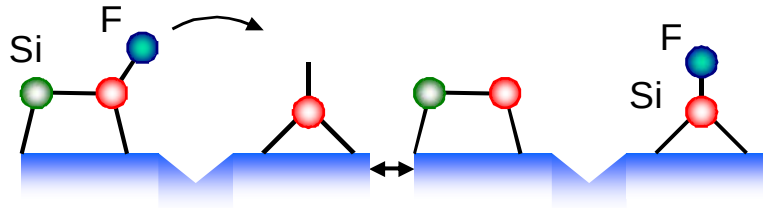
Adsorbed F **Adsorbed Si**



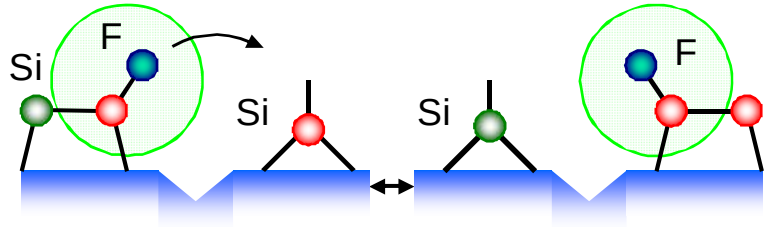
(1) Single F atom hopping **Ea=2.32 eV**



(2) Si assisted F diffusion **Ea > 2eV**

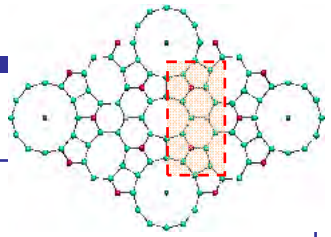


(3) Si-F complex diffusion **Ea=1.34 eV**

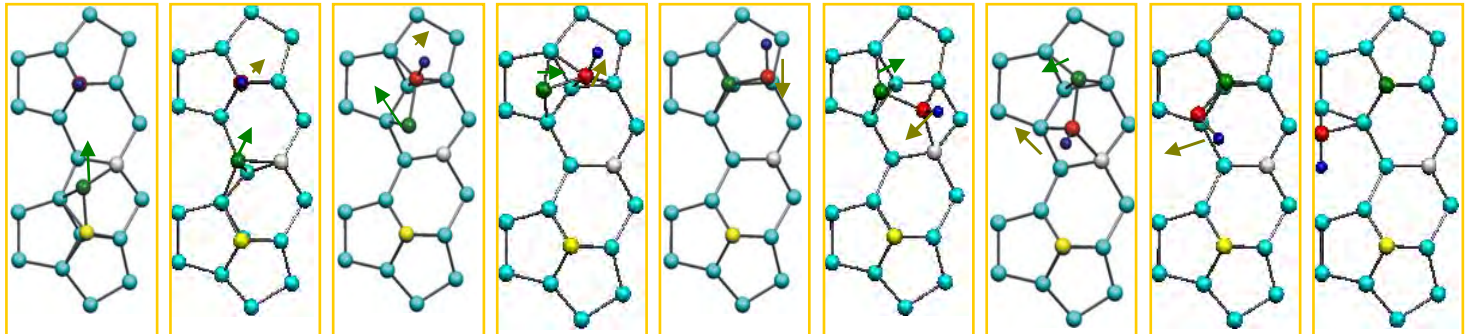


SiF complex diffusion model can explain experiments.

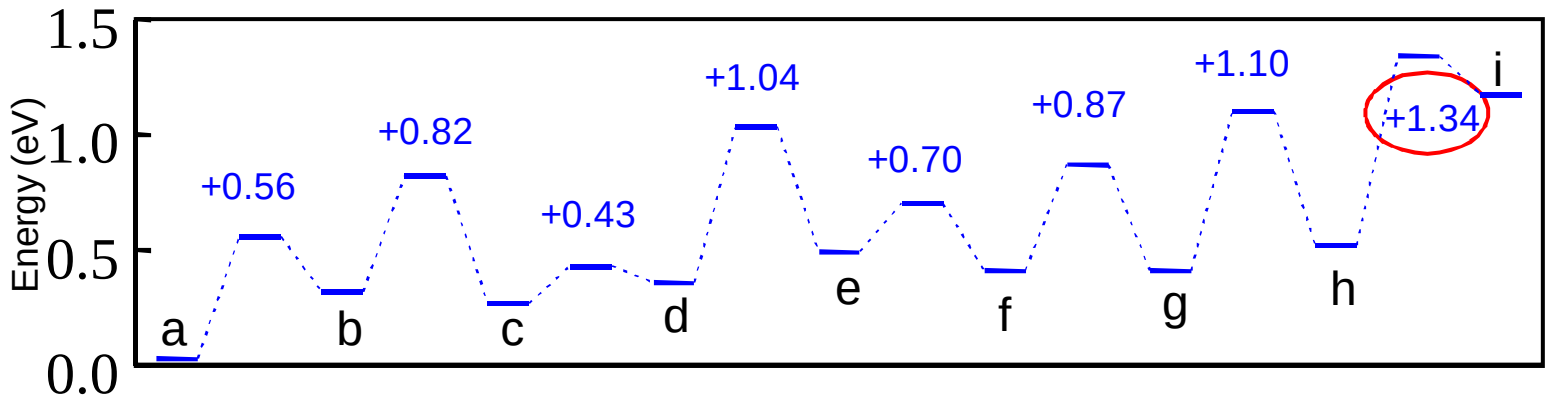
Diffusion of Si-F complex



●:F ●:excessSi ●: adatom (complex) ●: adatom ●:restatom



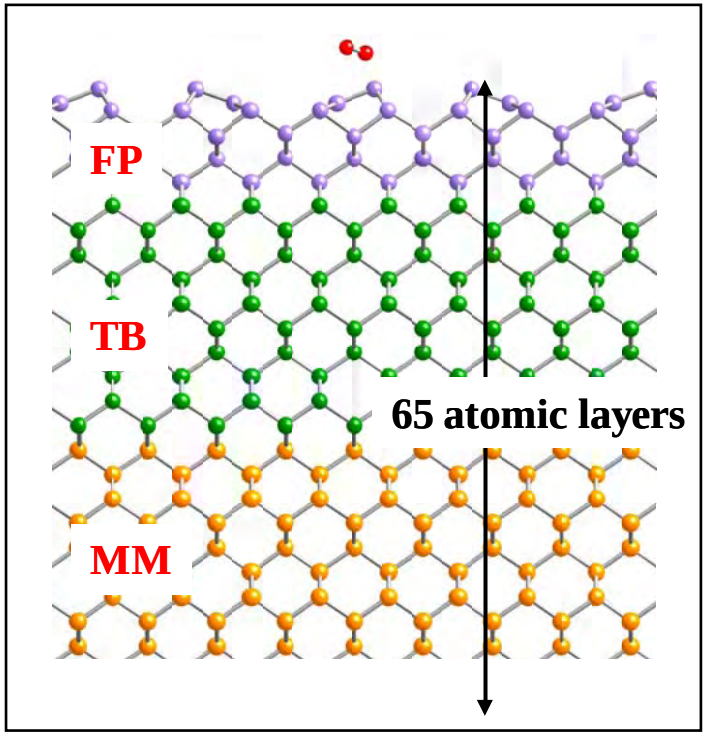
(単位: eV)



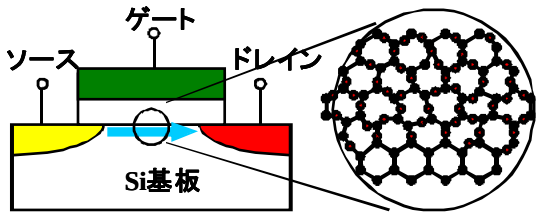
Adsorption of O2 on Si(111): hybrid method

How the adsorption/reaction energy is used for the formation of the final adsorption geometry.

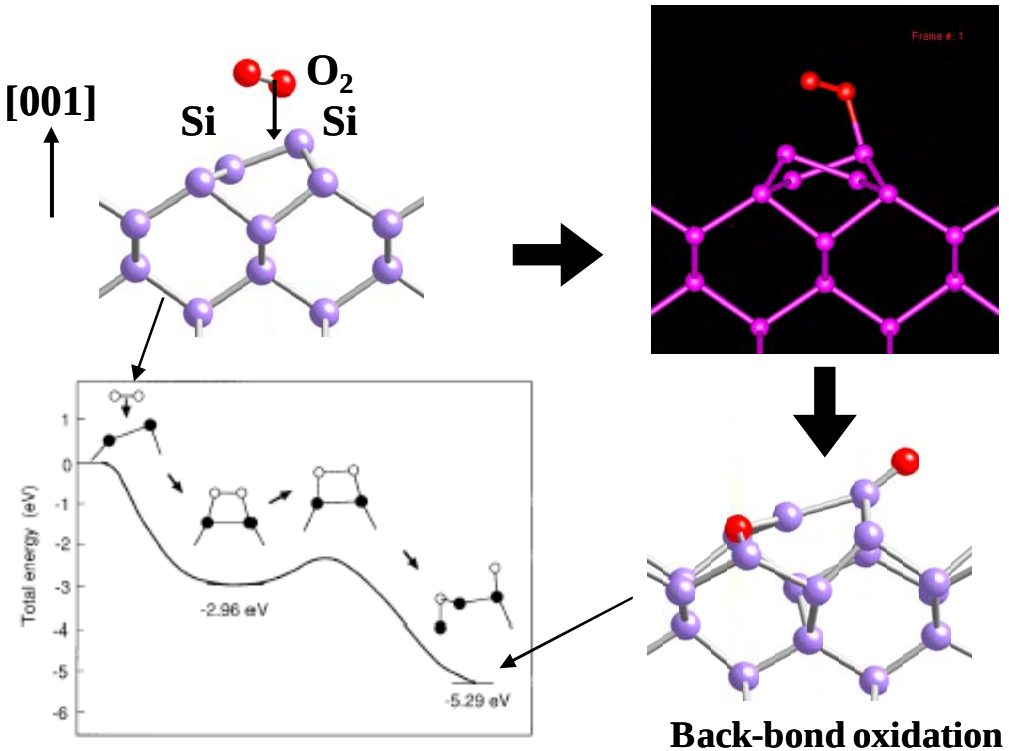
FP/TB/MM hybrid calculations



It is important to deal with the dissipation of the released energy properly.



Si/SiO_2



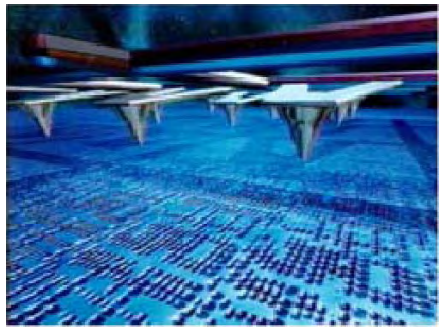
N. Takahashi, T. Ohno: Surf. Sci. 602, 768 (2008)

AFM tip apex: hybrid method

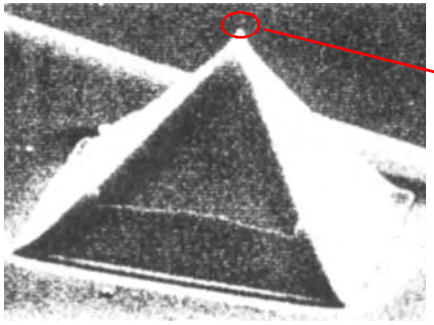
How does the atomic protrusion exists at the AFT tip apex?

■AFM

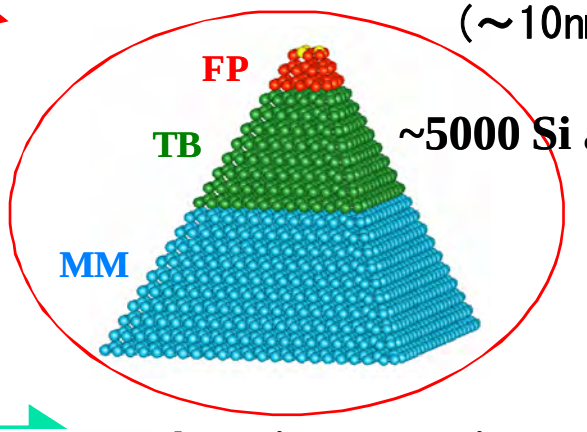
Nakamura, Takahashi, Uda, and Ohno: PRL 97, 086103 (2006)



SEM image（～μm）

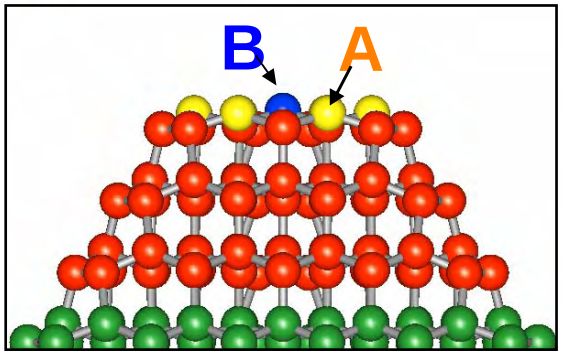


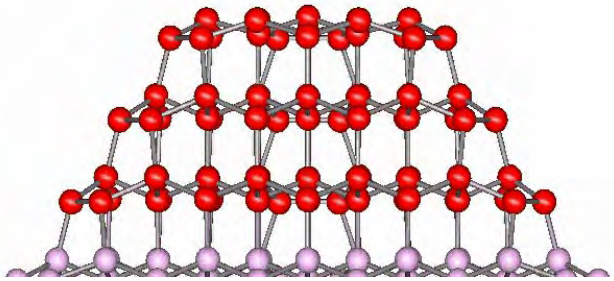
Hybrid calculations



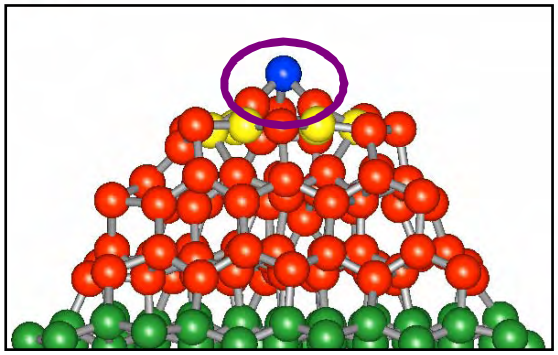
AFM performance depends on the atomic structure of the tip.
By the present techniques, the atomic geometry of the very end of the tip is practically impossible to control.
But, we can obtain AFM images with atomic resolution.

Atomic protrusion





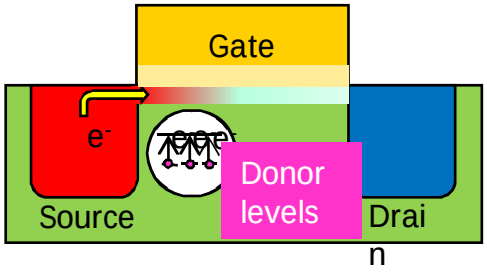
@300K

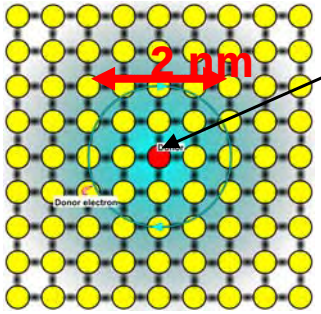


Shallow Impurity in Si

Conventional PW electronic structure code parallelized for Earth Simulator

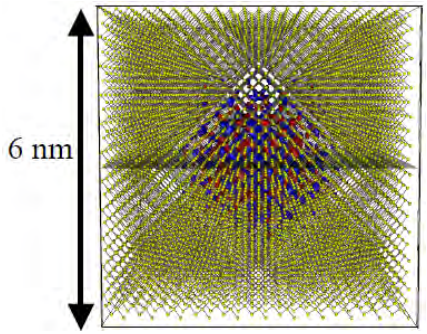
■ As shallow impurity in Si

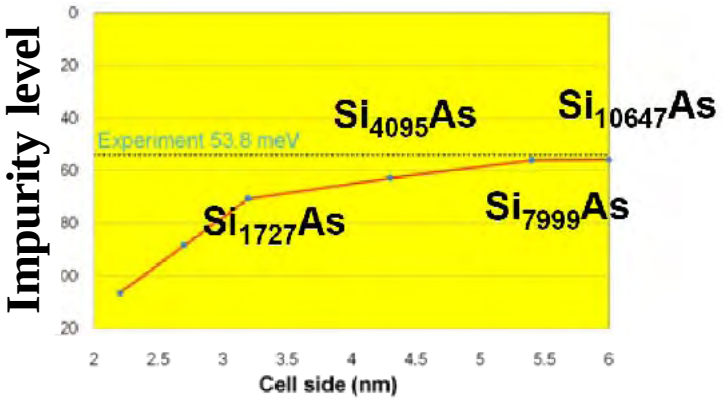




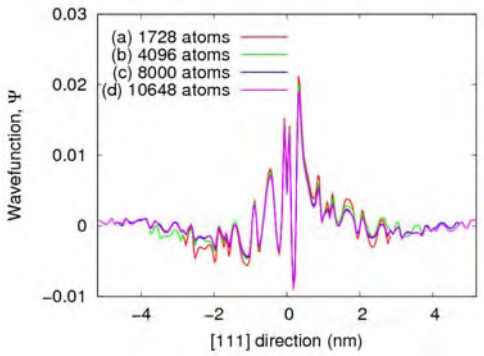
Concentration～10^{20}/cm^3

$Si_{10647}As$

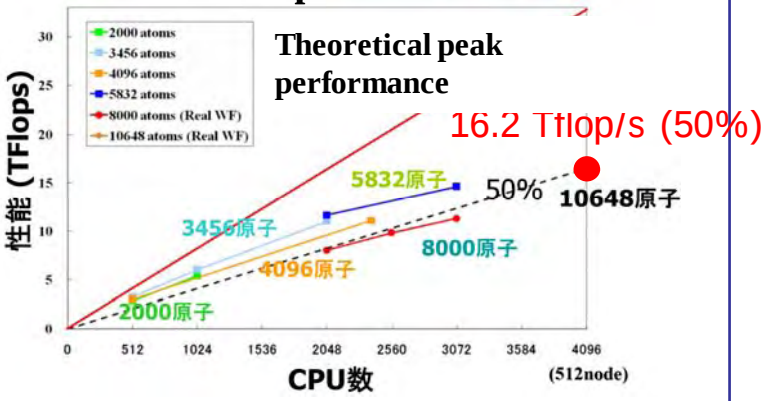




Wavefunction



PHASE performance on ES



***SC07: Gordon Bell prize finalist (2007/11/14)**

Linear-Scaling DFT Calculations
Order-N code: CONQUEST

First-Principles Order-N methods

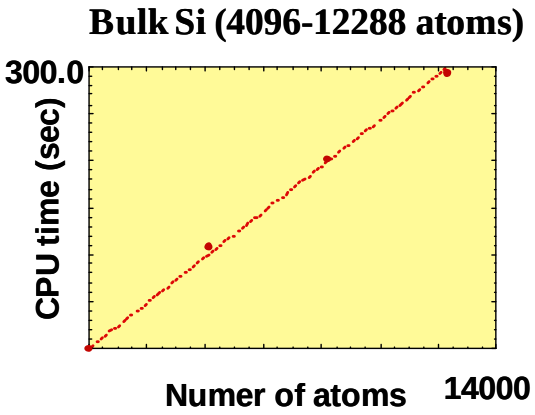
First-Principles Order-N methods

- CONQUEST: density matrix
  - In collaboration with Prof. Gillan (UCL)
  - limited β-version released on May 16th, 2007

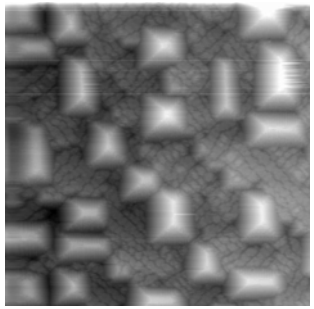
Application to nano-materials

- Quantum-dots
- Bio-materials

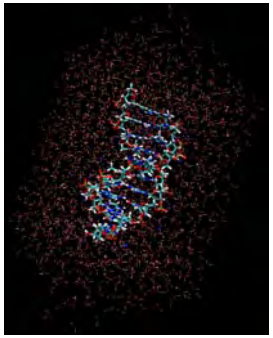
Scaling linearly with N



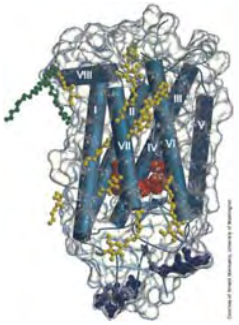
Ge clusters on Si(001)



DNA

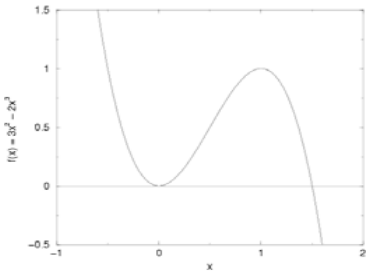


Bio-materials

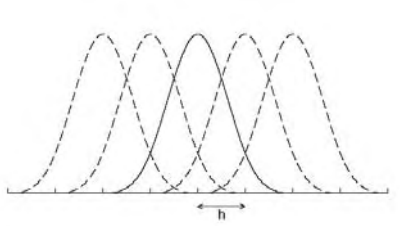


O(*N*) DFT code CONQUEST (I)

- **Density matrix minimization method**
  - Kohn-sham density matrix: $\rho(\mathbf{r},\mathbf{r}') = \Sigma_\nu f_\nu \psi_\nu^*(\mathbf{r})\,\psi_\nu(\mathbf{r}')$
    ($\psi_\nu(\mathbf{r})$: Kohn-Sham eigen-function, f_ν : occupation number)
  - Locality of density matrix: $\rho(\mathbf{r},\mathbf{r}')\rightarrow 0$ for $|\mathbf{r}-\mathbf{r}'|\rightarrow\infty$
  - Optimisation of ρ, using McWeeny purification
    + LNV (Lee, Nunes, Vanderbilt) method
    - Idempotency $\rho^2=\rho$
    - $\rho = 3\sigma^2-2\sigma^3$ (σ: auxiliary density matrix)



- **We express the density matrix using local orbitals $\phi_{i\alpha}(\mathbf{r})$**
  - $\rho(\mathbf{r},\mathbf{r}') = \Sigma_{i\alpha,j\beta}\phi_{i\alpha}^*(\mathbf{r})\,K_{i\alpha,j\beta}\,\phi_{j\beta}(\mathbf{r}')$
  - support functions $\phi_{i\alpha}(\mathbf{r})$: centered on atom j with the orbital α
- **Two types of basis sets are provided for $\phi_{i\alpha}(\mathbf{r})$.**
  - Blip functions: accurate
    - B-splines on 3D regular grids around each atom
  - PAOs (pseudo atomic orbital) : efficient
    - Common with Siesta or Plato



Blip functions

O(*N*) DFT code CONQUEST (II)

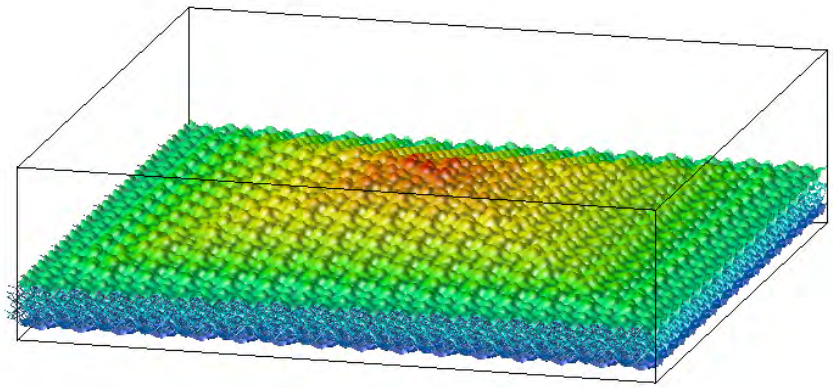
- **Efficient on parallel machines**
  - **Vector parallel, RISC-based, PC clusters**
  - **Diagonalisation with ScaLapack (not O(N))**

- **CONQUEST can employ various methods having different accuracies.**
  - **Full DFT:**
    - **optimization of support functions is performed.**
    - **SCF and density matrix minimization are also performed.**
  - **SC-AITB (self-consistent ab initio TB):**
    - **Fixed support functions (ex. single-ζ)**
  - **NSC-AITB (non-self-consistent ab-initio TB):**
    - **Harris-Foulkes energy functional + superposition of atomic charge**
  - **(Semi-empirical TB) by DensEl**

The Energetics of Hut-Cluster Self-Assembly in Ge/Si(001) using CONQUEST

T. Miyazaki, D. R. Bowler, M. J. Gillan, and T. Ohno

J. Phys. Soc. Jpn, 77, 123706 (2008)

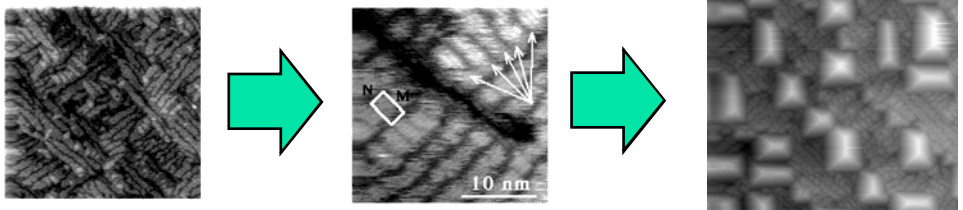


Ge 3D hut cluster on Si(001)

Ge/Si(001)

Self-assembled quantum dots

2 x N → M x N → “hut” cluster

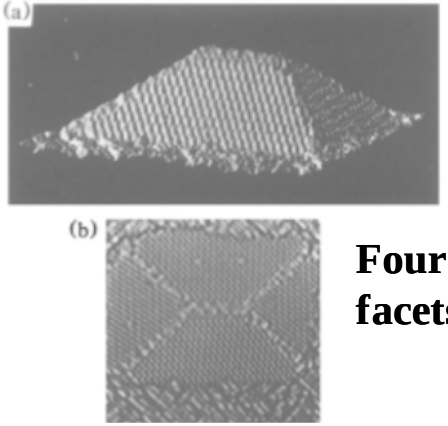


2D → 2D → 3D

Nano-strucure

~10nm x ~10nm

Pyramid-like shape



Four (105) facets

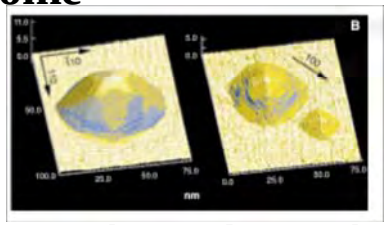
I. Goldfarb et al., PRL 78, 3959 (1997))

Hetero-epatixy system

Lattice mismatch（4%）

- Relaxation of strain
- SK-growth (Stranski-Krastanov growth)
  2D => 3D at ~3 ML coverage
- No dislocations

“dome”



G. Medeiros-Ribeiro et al., Science 279, 353 (1998)

Ge 3D hut cluster on Si(001)

O. E. Shklaev et al., PRL 94, 176102 (2005)

$E_{form} = E_{relax} + E_{surf} + E_{edge}$

- E_{relax} : relaxation by the 3D structure (calculated by Finite Element method.)
- E_{surf}: surface energy, usually unfavorable for 3D structure (calculated by DFT)
- E_{edge}: energy of the edges (difficult to calculate. A parameter in this work.)

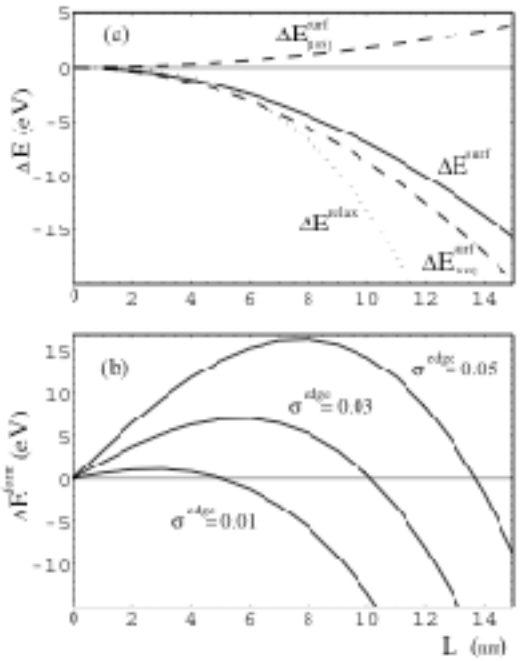


FIG. 3. Contributions to the formation energy of an isolated Ge {105} pyramidal island versus size (L). (a) ΔE^{relax} (dotted lines) and ΔE^{surf} (solid line) along with the {100} and {105} contributions to ΔE^{surf} (dashed lines); (b) ΔE^{form} for various edge energies, σ^{edge}, in eV/Å.

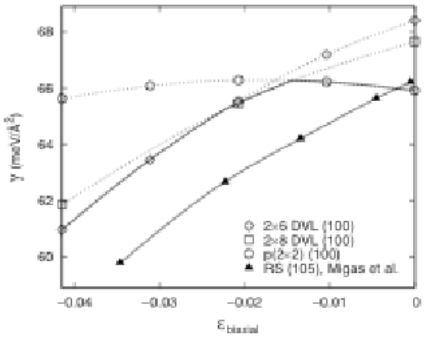
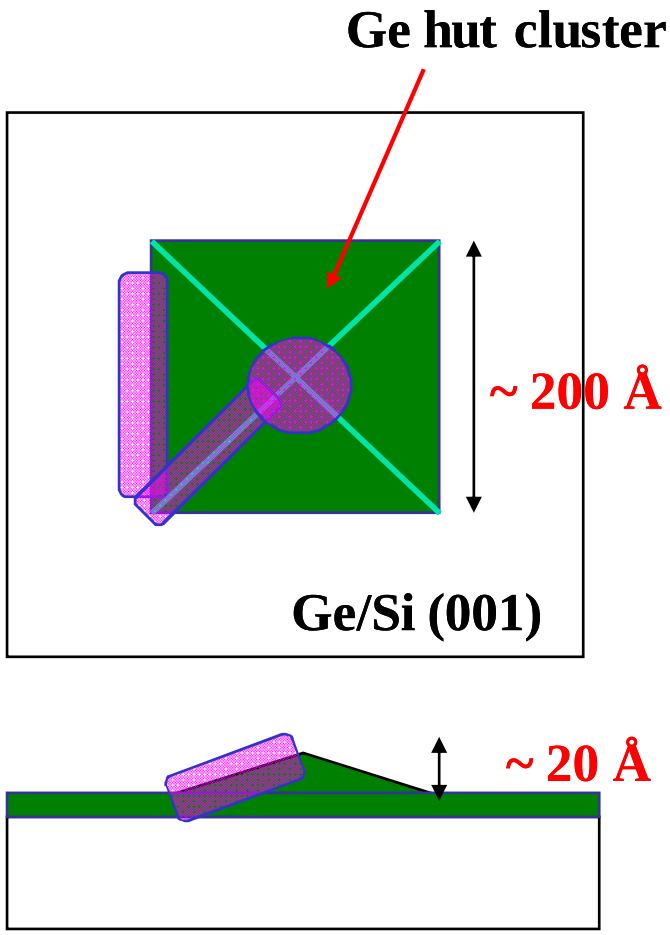


FIG. 2. Ge (100) and (105) surface energies (per unit area of deformed surface) versus biaxial strain. Triangles denote (105) results from Ref. [5]. Circles, squares, and diamonds are (100) results obtained in this work for $p(2 \times 2)$ and $p(2 \times 2)$ based 2×6 and 2×8 DVL reconstructions, respectively. Solid lines highlight the surface energy for the stable reconstruction of a given orientation.

FIG. 1 (color). Isolated {105} pyramidal hut island on Si(100), colored according to one-half the trace of the calculated *in-plane* surface strain fields (see text for discussion).

Si(001)表面上Geクラスター： 構造安定性



To determine the stability and size of the hut cluster,

- **effects of boundary, ridge, top**
- **effect of distortion from {105} planes**
- **effect of the finite surface area**

may be also important.

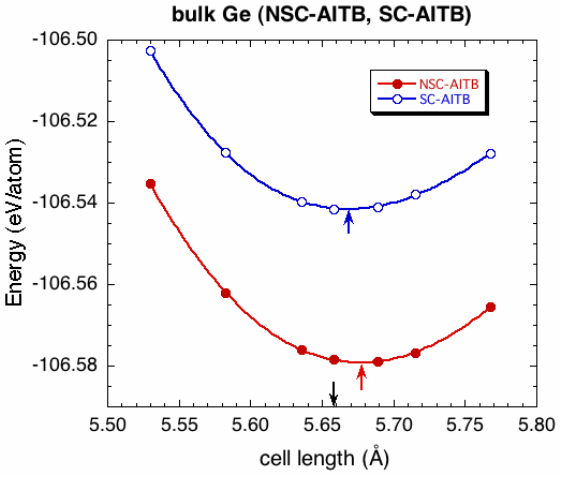
"DFT calculations on the entire hut cluster systems are desirable. "

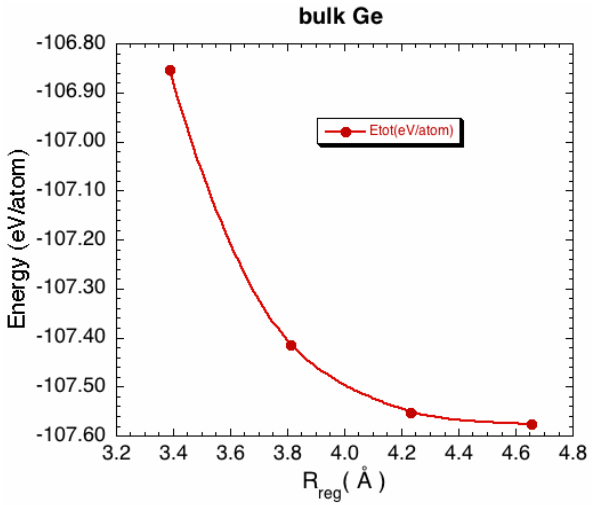
↓

order-N method

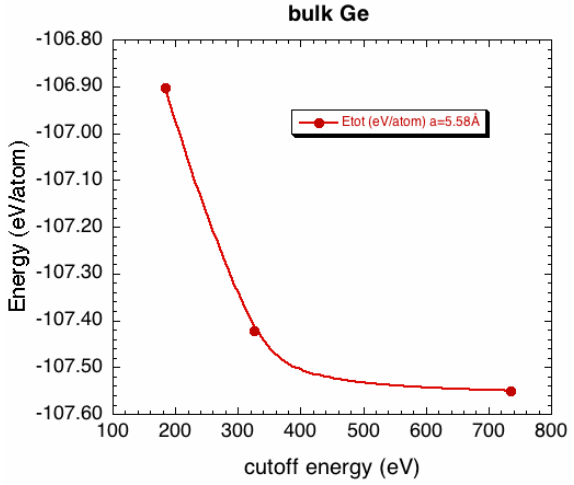
Results: bulk Ge - calculation condition -

Etot-a curve by
NSC-AITB or SC-AITB
(minimal basis set calculations)





Full DFT using
blip functions
1) Etot- Rreg
2) Etot- Ecutoff
(blip-grid spacing)



Method: strategy for Ge/Si(001)

Ge(2xN) <-> Ge hut cluster

- **Strained Ge(105)** ⟷
  - **Bulk Ge**
  - **Strained bulk Ge**
  - **Strained Ge(105)**

  "Accuracy and calculation conditions of various localized orbital methods"
  "modelling of Ge(105) surfaces"

semiempirical TB (DensEl)
NSC-AITB
SC-AITB (CONQUEST)
Full DFT
planewave (STATE or VASP)

- **Ge hut cluster on Si(001)** ⟷

  "Initial atomic positions are made by semiempirical TB calculations."

semiempirical TB
NSC-AITB
(SC-AITB)

strained Ge(105): accuracy of various methods

Surface energy of type-I strained Ge(105) surface

Method	Surface energy (meV/Å^2)	
semi-empirical	74.3	← DensEl
NSC-AITB	76.5	
SC-AITB	81.5	CONQUEST
full DFT(blip, R_{reg}=3.85 Å)	83.5	
full DFT(blip, R_{reg}=4.23 Å)	74.8	
planewave	70.0	← STATE

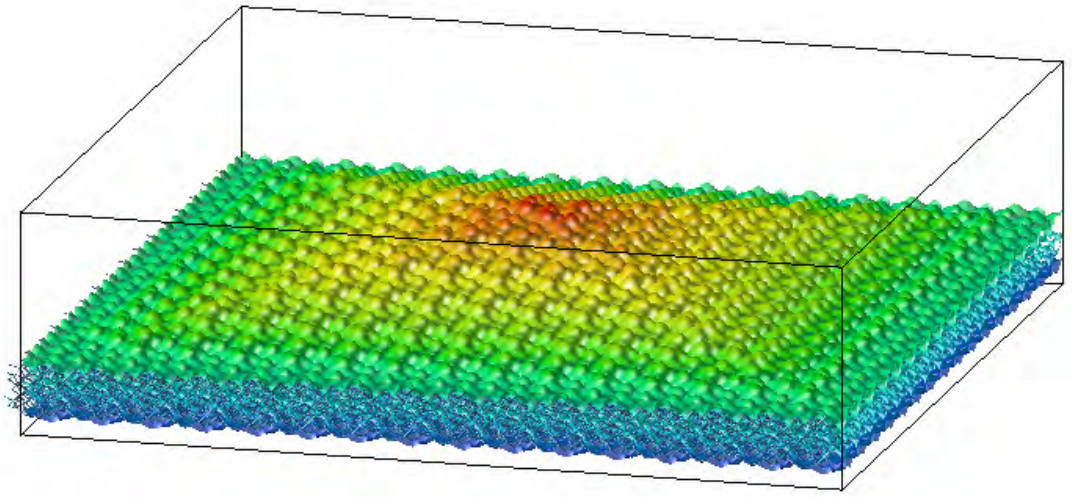
NSC-AITB is reasonably accurate.

Reliable calculation conditions have been determined.
(for surface energy, we need large R_{reg})

Ge ‘hut’ cluster on Si(001)　- system size -

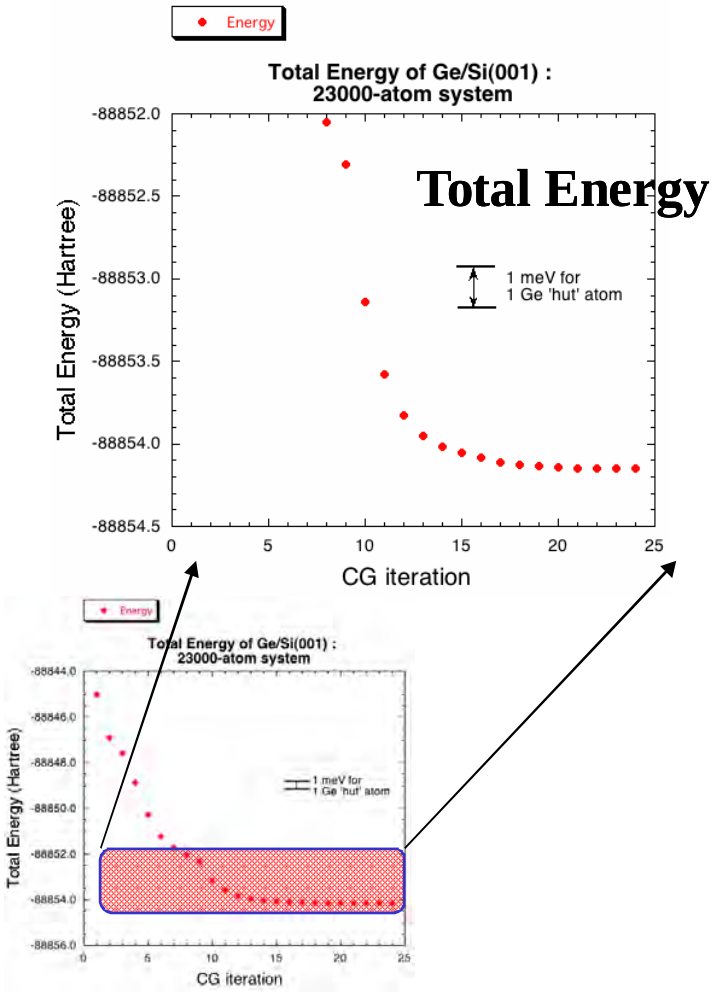
22746 atoms
174 x 174 x 47.5 Å^3

Earth Simulator 512 proc. (64 nodes)

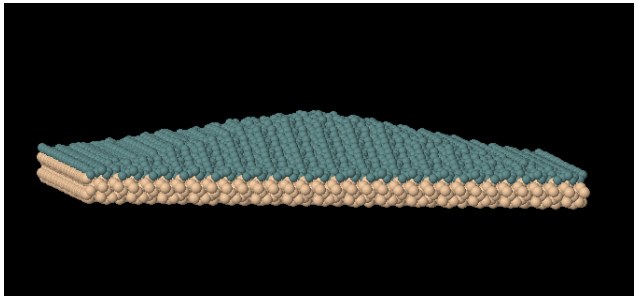


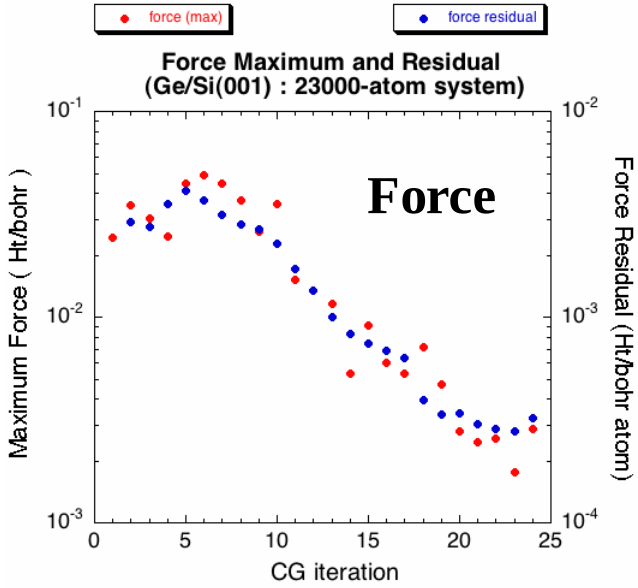
Ge ‘hut’ cluster on Si(001)： NSC-AITB

Structure optimization



28x28on32x32: 22747 atoms

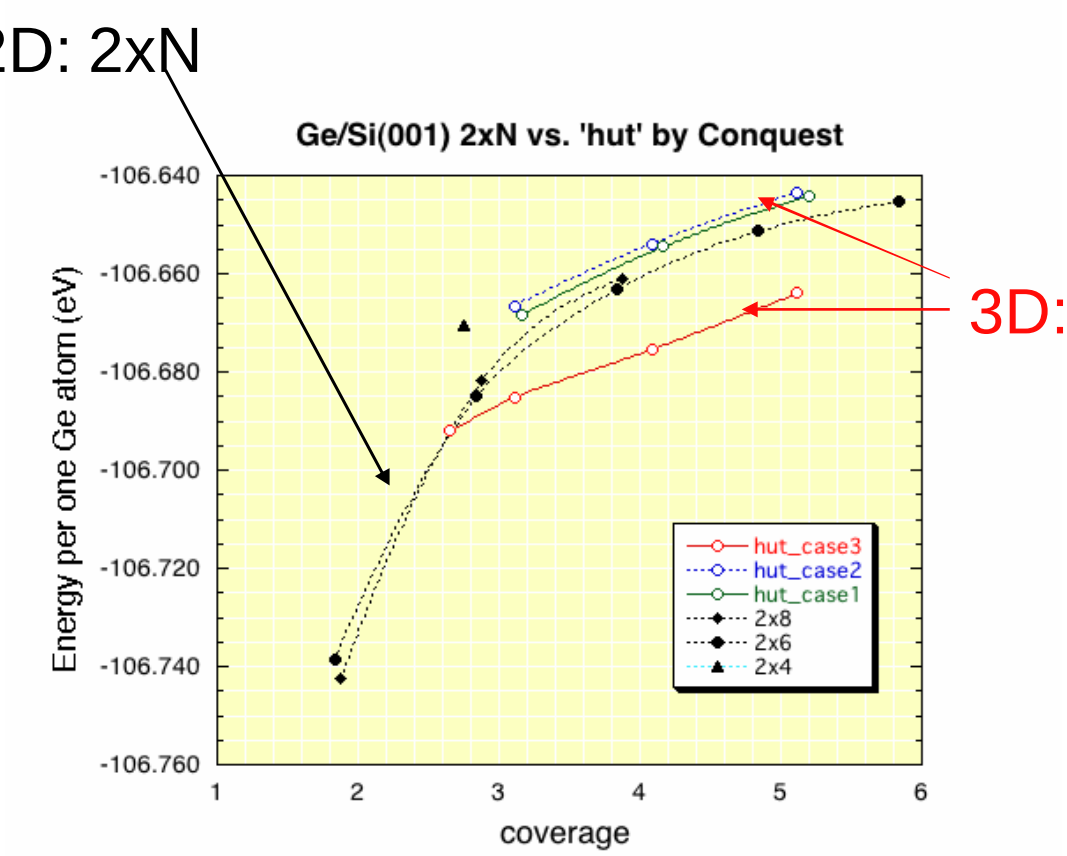




Stability: Ge/Si(001)-2xN vs 3D hut cluster

$\varepsilon_{Ge} = (E_{tot} - E_{sub})/(\#\ \text{of Ge hut atoms})$

2D: 2xN



3D: hut cluster

- **Accuracy and calculation condition for order-N calculations on Ge/Si(001) have been investigated by the study on the strained Ge(105) surfaces.**
- **Order-N DFT calculations with structure optimization are now possible for Ge/Si(001) 23,000-atom systems. (within NSC-AITB level)**
- **Ge hut 3D islands are more stable than Ge 2xN structure when the coverage of Ge is more than 3.**
- **Our results suggest that the initial emergence of 3D Ge hut clusters is determinde mainly by energetics, and that kinetic effects do not need to be considered.**

O(N) DFT calculations on DNA systems using CONQUEST

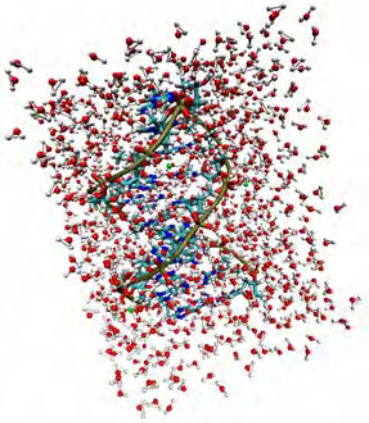
T. Otsuka, T. Miyazaki, T. Ohno, D. R. Bowler and M. J. Gillan, J. Phys.: Cond. Matter, 20, 294201 (2008)

1. **Pseudo Atomic Orbitals**
2. **Exchange-correlation functional**
3. **O(N) method by Density matrix minimisation**
   - **single DNA base**
   - **DNA base pairs**
   - **DNA + water molecules**

Bio-materials: DNA

Bio-materials: Proteins, DNA, et. al.
One of the important targets of O(N) calculations

DNA



Parameterized interaction model

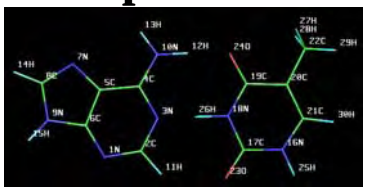
Transferability for different environments ?

Interaction between bio- and inorganic materials

Quantum mechanical modeling is required

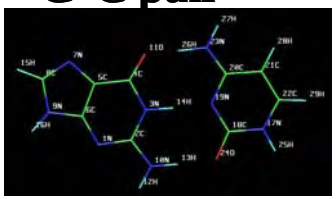
Base pairs

A-T pair



adenine **thymine**

G-C pair



guanine **cytosine**

Can describe base pairs properly?

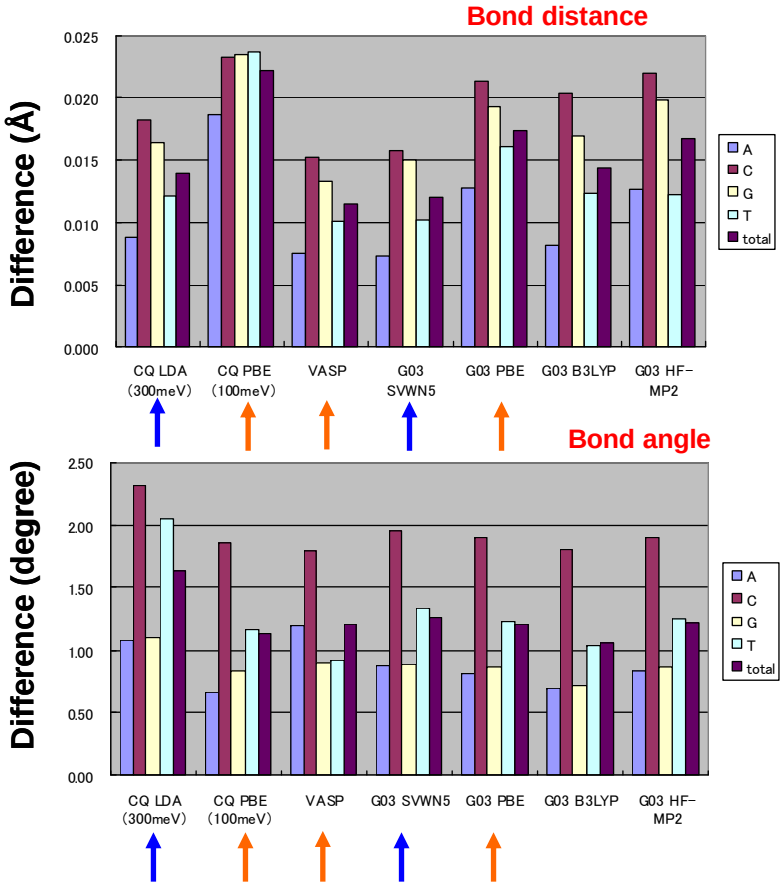
Pseudo Atomic Orbitals
- **SZ: single-ζ**
- **DZP: double-ζ with polarization function**

Exchange-correlation functional
- **LDA, GGA-PBE**

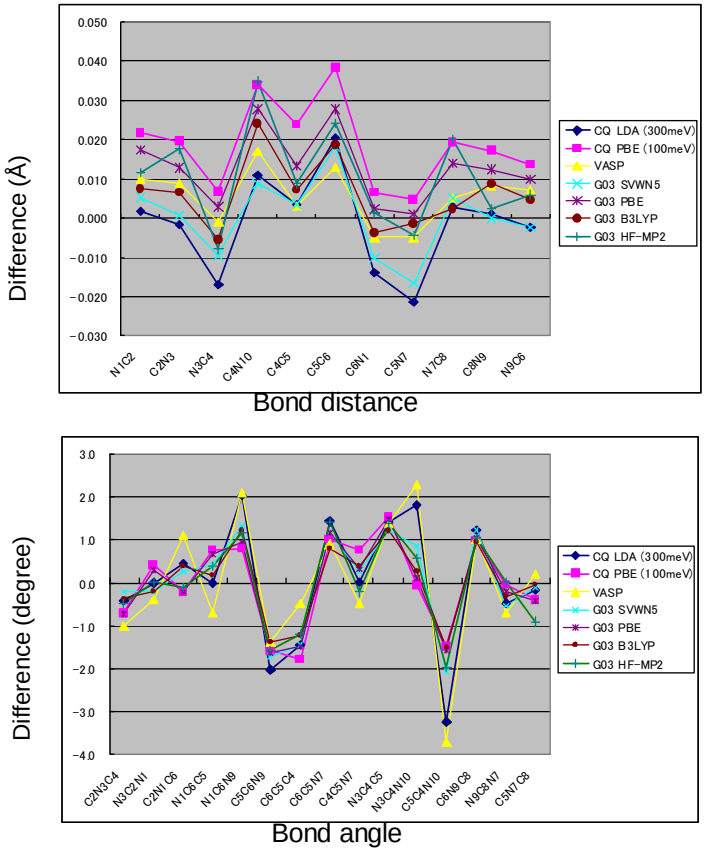
O(N) method by Density matrix minimization
- **single DNA base**
- **DNA base pairs**
- **DNA + water molecules**

Structure optimization: single DNA bases (A, C, G, T)

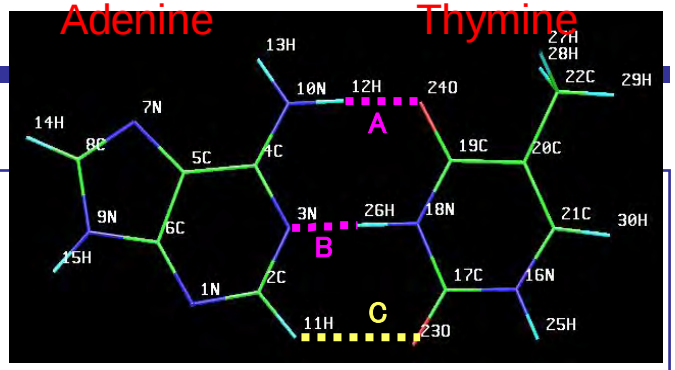
Difference of structure between theory and experiment.



Difference of structure for Adenine molecule between theory and experiment.



CQ on DNA systems: base pairs

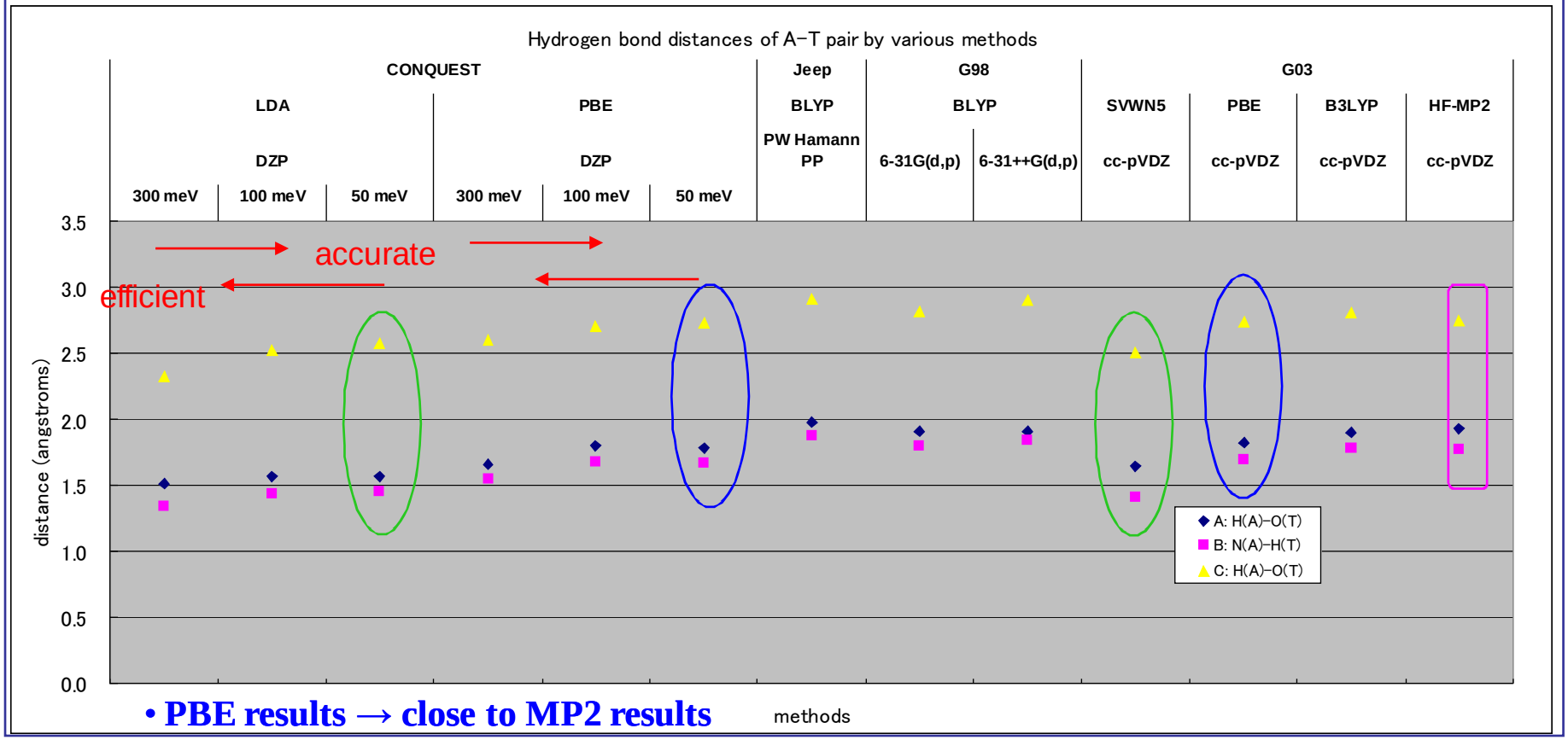


Hydrogen bond distances of A-T pair

Siesta PAOs : DZP

diagonalisation

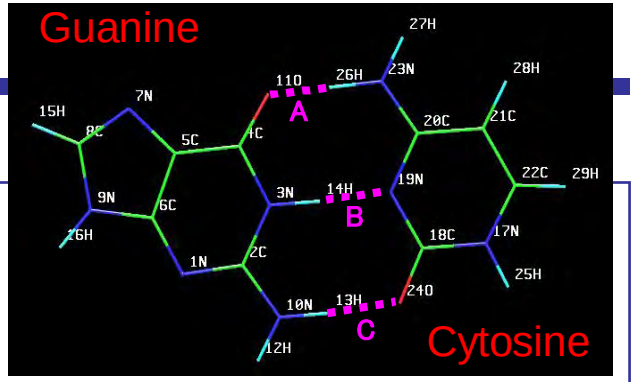
A-T pair



• **PBE results → close to MP2 results**

CQ on DNA systems: base pairs

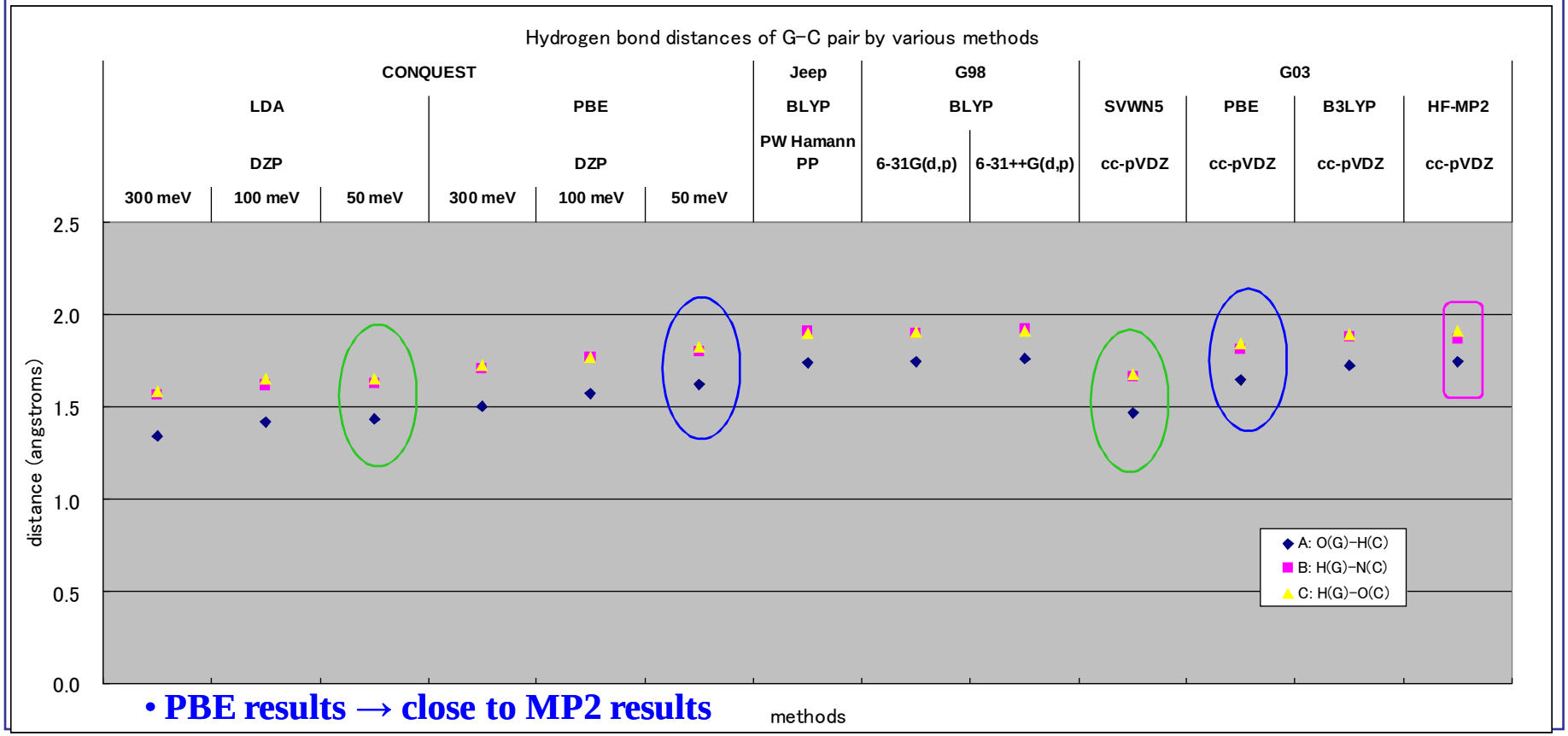
■ Hydrogen bond distances of G-C pair



Siesta PAOs : DZP

diagonalisation

G-C pair



• **PBE results → close to MP2 results**

Structure optimization: DNA base pairs (A-T, G-C)

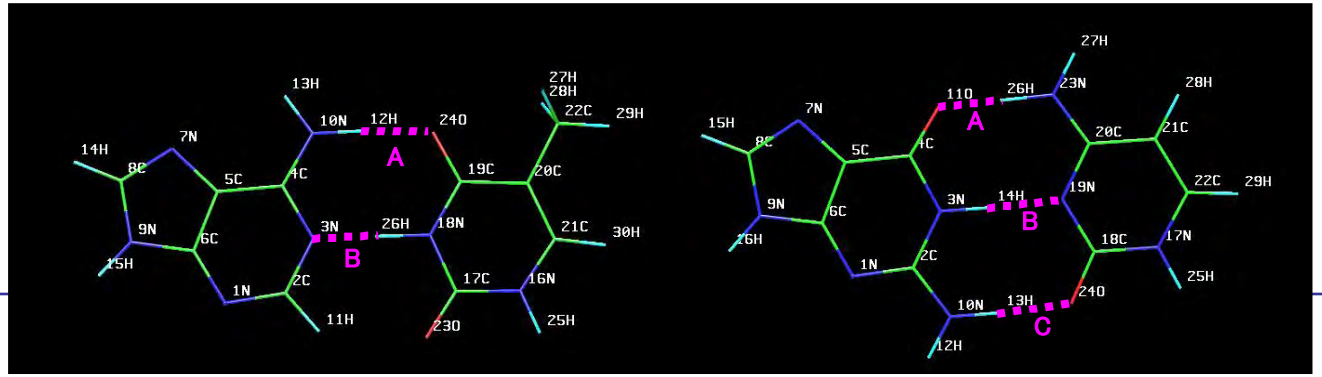
■ Binding energy (eV)

With Counterpoise correction for basis set superposition error (BSSE)

	CONQUEST		Gaussian03				Ref. (a)	
	LDA	PBE	SVWN5	PBE	B3LYP	MP2	RI-MP2	CCSD(T) corrected
basis	DZP		cc-pVDZ				CBS	
A-T	-1.11	-0.64	-1.05	-0.60	-0.50	-0.48	-0.67	-0.67
G-C	-1.84	-1.20	-1.77	-1.15	-1.05	-0.94	-1.22	-1.25

•PBE results are very close to RI-MP2 results
•PBE looks good for hydrogen bonds!

Extrapolated value of MP2 results with respect to the increase of basis sets



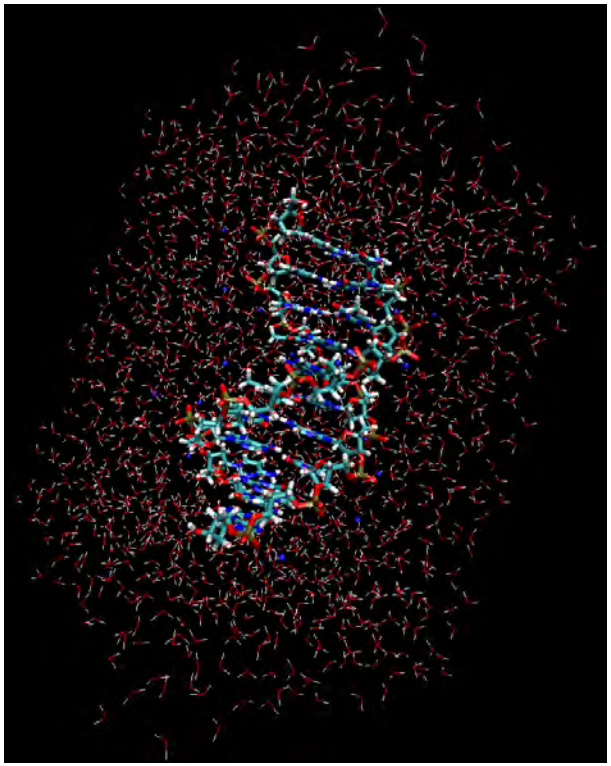
Application to DNA systems

DNA (1WQZ) :
by Neutron Diffraction Measurements

- **Hydrating water molecules were generated by AMBER.**
- **Snapshot of MD after the equilibrium by AMBER.**

- **DNA: 634 atoms**
- **Mg^{2+}: 9 atoms**
- **Total H_2O: 932 molecules**
  = 2796 atoms
- **Total # of atoms: 3439 atoms**

A MD snapshot from equilibrium

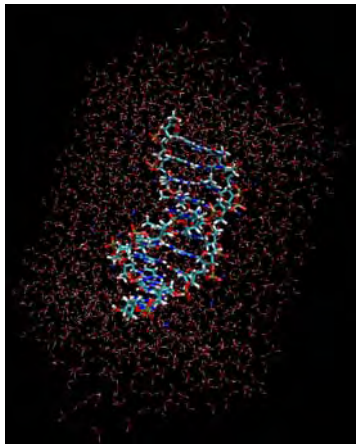


CQ on DNA systems

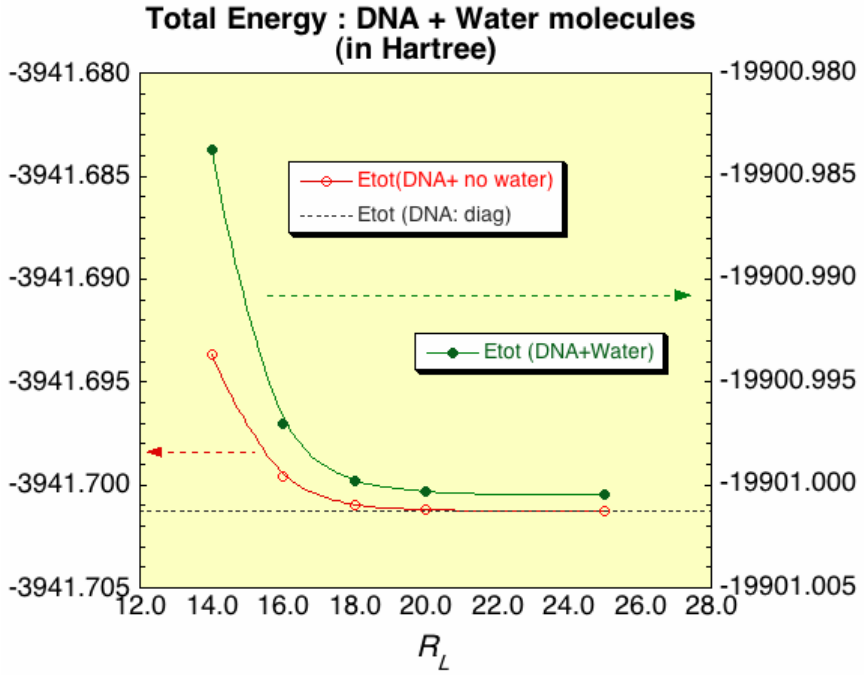
■ Hydrogen bond distances of G-C pair

SZ (single zeta) calculations on

- **DNA (+Mg) without water molecules : 643 atoms**
- **DNA (+Mg) with hydrating water molecules: 3439 atoms**



***L* matrix cutoff dependence of total energy**



- **without H_2O: diag. vs order-N**
  → convergence from R_L = 16.0
  the error is 1.7 mHartree/(643 atoms)

- **with H_2O → convergence is same behavior**
  at RL=16.0 bohr
  the error is 3.5 mHartree/ (3439 atoms)
  at RL=18.0 borh
  the error is 0.64 mHartree/ (3439 atoms)

CQ on DNA systems: Summary

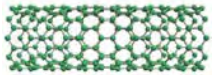
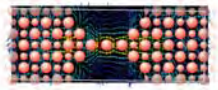
- CONQUEST calculations on single DNA bases agree with those by other codes (Gaussian, VASP).
- PBE is accurate to represent hydrogen bonds in A-T and G-C pairs.
- O(N) calculations using DMM technique is extremely accurate on DNA systems.
  - Error = 0.64 mHartree/3439 atoms at R_L = 18.0 bohr

Molecular Electronics

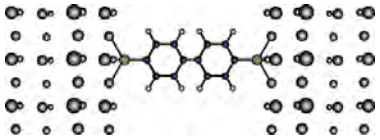
Novel Nano Devices

Bottom-up device（ ⟷ Top-down）

Elements of nano-structures
: CNT、atomic wires, molecular wires,

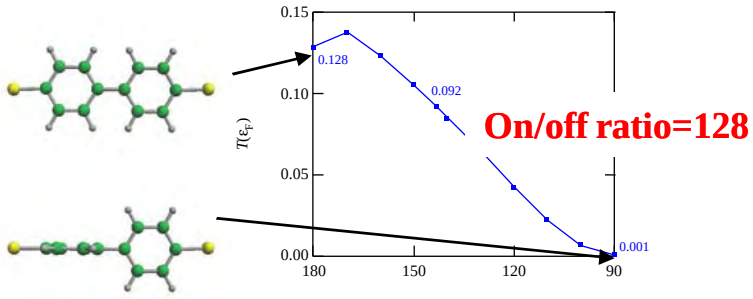



■ Molecular electronics




HP

● Structure change & conductance

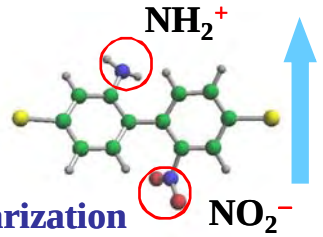


On/off ratio=128

Angle dependence of T

●Control of molecular structures (angles)

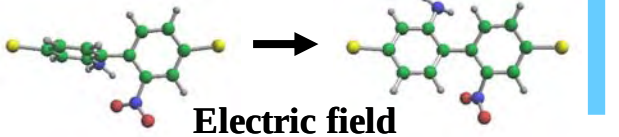
- **●Electric field**
- **●STM-manufacturing**
- **●Photo-isomerization**
- **●Gas adsorption**



polarization

E=0

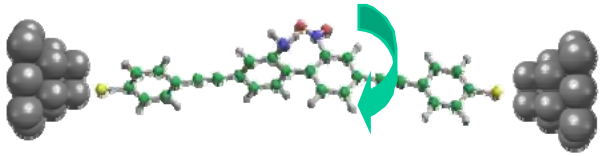
θ=89º（stable） **θ=180º**



Electric field

■ Design of molecular devices

Molecular switch, sensor, organic EL, ,



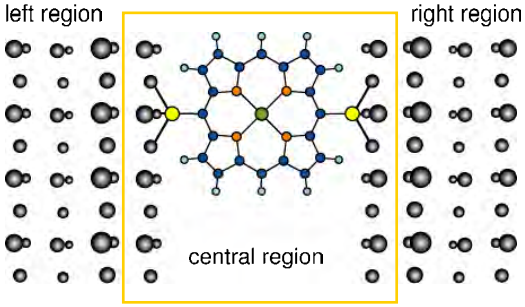
Non-Equilibrium Green's Function method (NEGF)

- Overlap matrix

$$\mathscr{S} = \begin{pmatrix} S_{\mathrm{L}} & S_{\mathrm{LC}} & 0 \\ S_{\mathrm{CL}} & S_{\mathrm{C}} & S_{\mathrm{CR}} \\ 0 & S_{\mathrm{RC}} & S_{\mathrm{R}} \end{pmatrix}$$

- Hamiltonian matrix

$$\mathscr{H} = \begin{pmatrix} H_{\mathrm{L}} & H_{\mathrm{LC}} & 0 \\ H_{\mathrm{CL}} & H_{\mathrm{C}} & H_{\mathrm{CR}} \\ 0 & H_{\mathrm{RC}} & H_{\mathrm{R}} \end{pmatrix}$$



OpenMX (T. Ozaki *et al.*)

Au: 6.0 a.u. s2p1d1
Fe: 6.0 a.u. s2p2d2
N: 4.0 a.u. s2p2d2
S: 5.5 a.u. s2p2d2
C: 4.5 a.u. s2p2
H: 4.0 a.u. s2p2

$\bullet\ V(r) \leftarrow \bullet\ V_{\mathrm{H}}(r) \leftarrow \bullet\ \rho(r)$

- Green function $\mathscr{G}(z)$

$$(z\mathscr{S} - \mathscr{H})\,\mathscr{G}(z) = \mathscr{I}$$

- Green function at central region

$$\begin{aligned} G_{\mathrm{C}}(z) &= [zS_{\mathrm{C}} - H_{\mathrm{C}} - \Sigma_{\mathrm{R}}(z) - \Sigma_{\mathrm{L}}(z)]^{-1} \\ \Sigma_{\mathrm{L}}(z) &= (zS_{\mathrm{CL}} - H_{\mathrm{CL}})(zS_{\mathrm{L}} - H_{\mathrm{L}})^{-1}(zS_{\mathrm{LC}} - H_{\mathrm{LC}}) \\ &= (zS_{\mathrm{CL}} - H_{\mathrm{CL}})\,G_{\mathrm{L}}(z)\,(zS_{\mathrm{LC}} - H_{\mathrm{LC}}) \\ \Sigma_{\mathrm{R}}(z) &= (zS_{\mathrm{CR}} - H_{\mathrm{CR}})(zS_{\mathrm{R}} - H_{\mathrm{R}})^{-1}(zS_{\mathrm{RC}} - H_{\mathrm{RC}}) \\ &= (zS_{\mathrm{CR}} - H_{\mathrm{CR}})\,G_{\mathrm{R}}(z)\,(zS_{\mathrm{RC}} - H_{\mathrm{RC}}) \end{aligned}$$

$\bullet\ \rho_{\mathrm{C}} = \dfrac{1}{2\pi \mathrm{i}} \displaystyle\int_{-\infty}^{\infty} \mathrm{d}\varepsilon\, G_{\mathrm{C}}^{<}(\varepsilon)$

- Transmission

$$\begin{aligned} T(\varepsilon) &= \mathrm{Tr}\left[\Gamma_{\mathrm{L}}(\varepsilon)\,G_{\mathrm{C}}^{r}(\varepsilon)\,\Gamma_{\mathrm{R}}(\varepsilon)\,G_{\mathrm{C}}^{a}(\varepsilon)\right] \\ \Gamma_{\mathrm{L}}(\varepsilon) &= \mathrm{i}\left(\Sigma_{\mathrm{L}}^{r}(\varepsilon) - \Sigma_{\mathrm{L}}^{a}(\varepsilon)\right) \\ \Gamma_{\mathrm{R}}(\varepsilon) &= \mathrm{i}\left(\Sigma_{\mathrm{R}}^{r}(\varepsilon) - \Sigma_{\mathrm{R}}^{a}(\varepsilon)\right) \end{aligned}$$

- Current flow

$$j_{ij}(\varepsilon) = \frac{e}{h}\mathrm{Re}\left[t_{ij}G_{\mathrm{C},ji}^{<}(\varepsilon)\right]$$

$$G_{\mathrm{C}}^{<}(\varepsilon) = G_{\mathrm{C}}^{r}(\varepsilon)\mathrm{i}\Gamma_{\mathrm{L}}(\varepsilon)G_{\mathrm{C}}^{a}(\varepsilon)$$

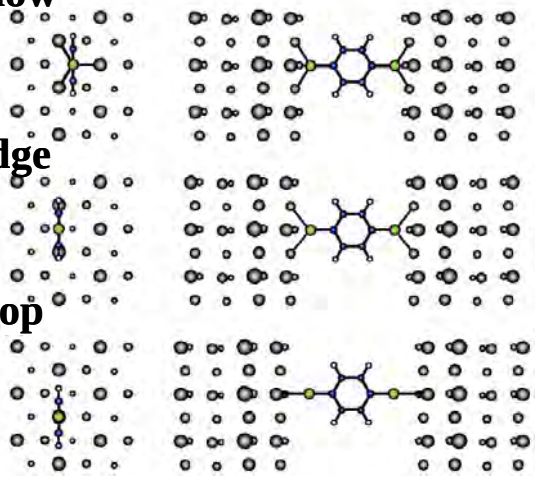
Transport: benzene dithiol molecule (BDT)

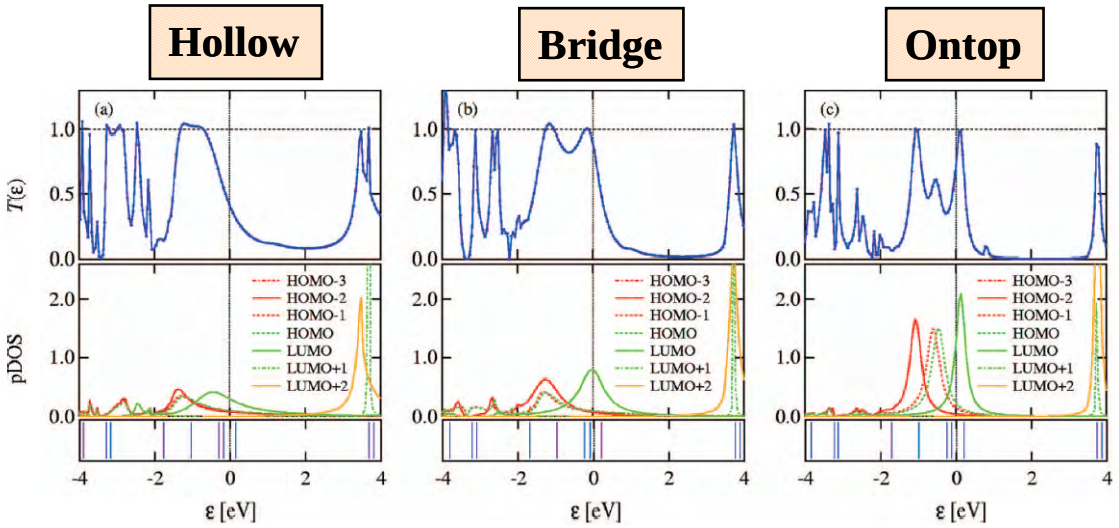
Contact geometries

Hollow

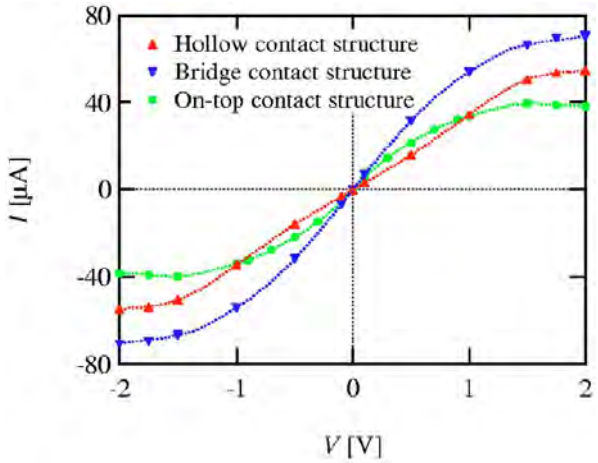
Bridge

Ontop





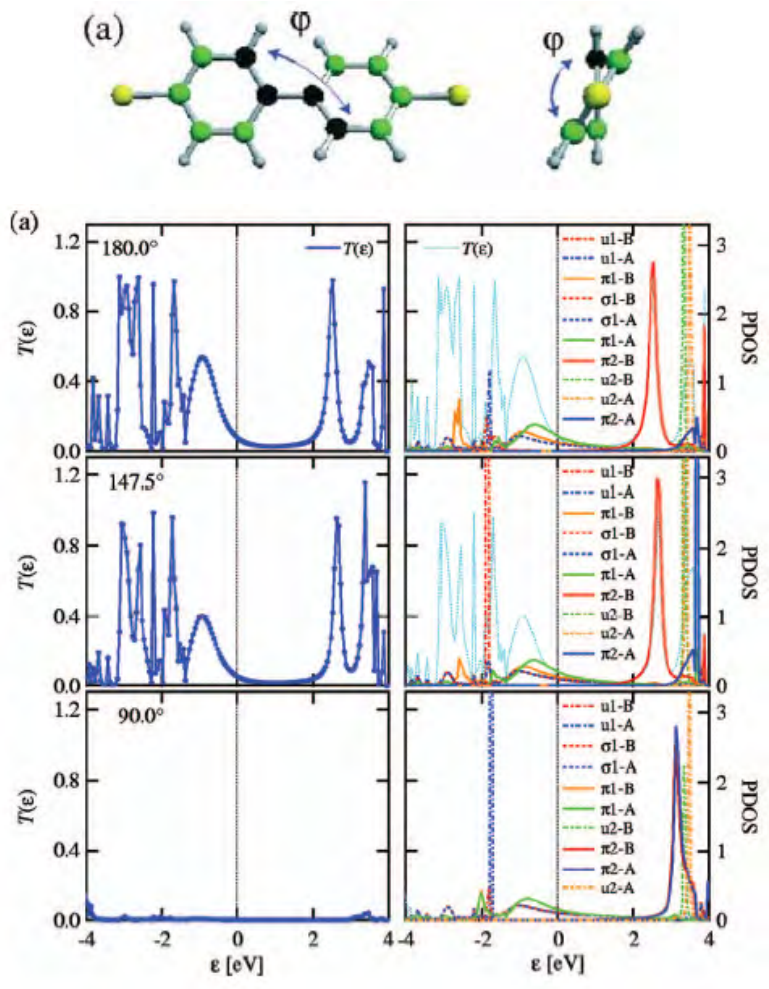
I-V curve



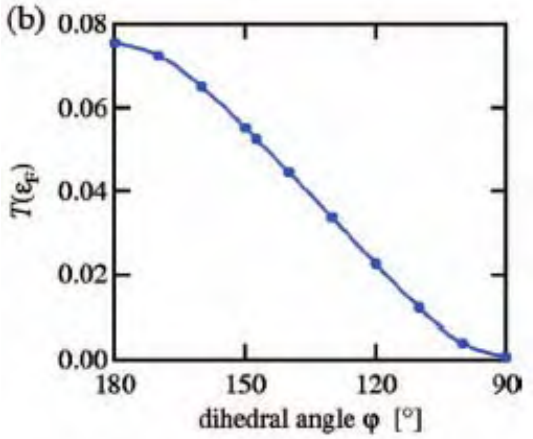
Dependence of the conduction of a BPD molecule on the dihedral angle between the phenyl rings and its application to a nano-rectifier

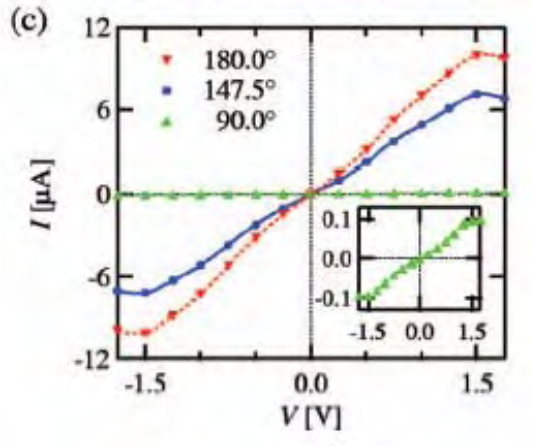
H. Kondo, J. Nara, H. Kino, and T. Ohno,
J. Chem. Phys. 128, 064701 (2008)

Transport: biphenyl dithiol molecule (BPD)



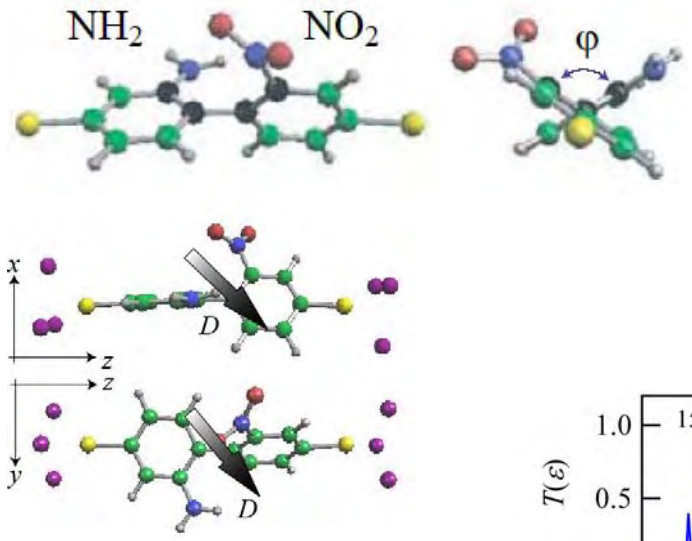
Dihedral-angle dependence





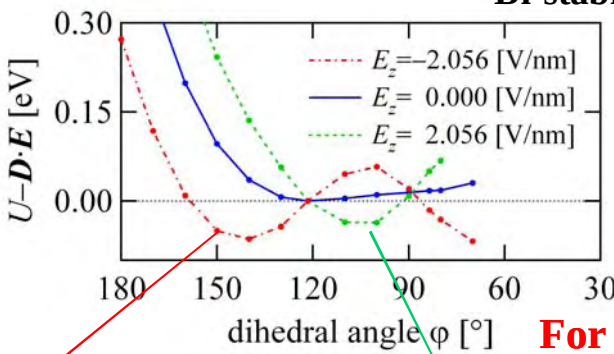
Molecular Rectifier

BPD Functionalized with NH2, NO2 groups



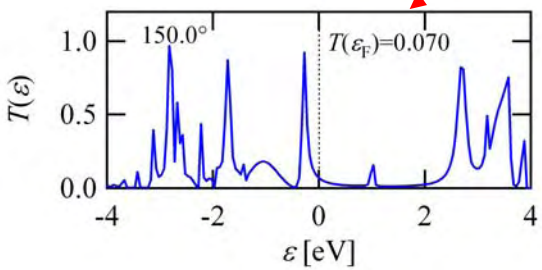
D: dipole moment
E: electric field

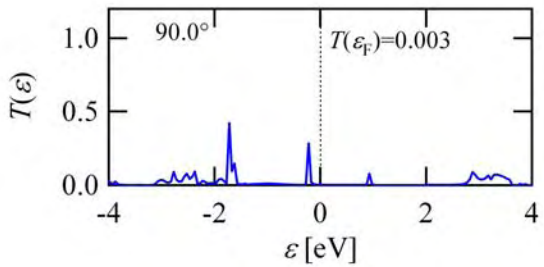
Total energy **Bi-stability**



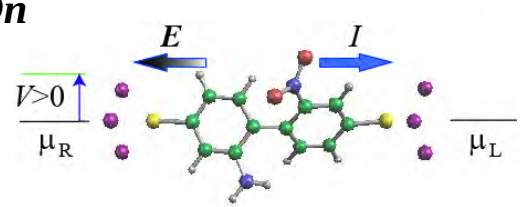
For E_z<0
φ ~ 150°

For E_z>0
φ ~ 90°



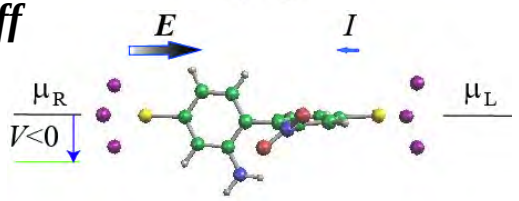


On



Current *I*: large

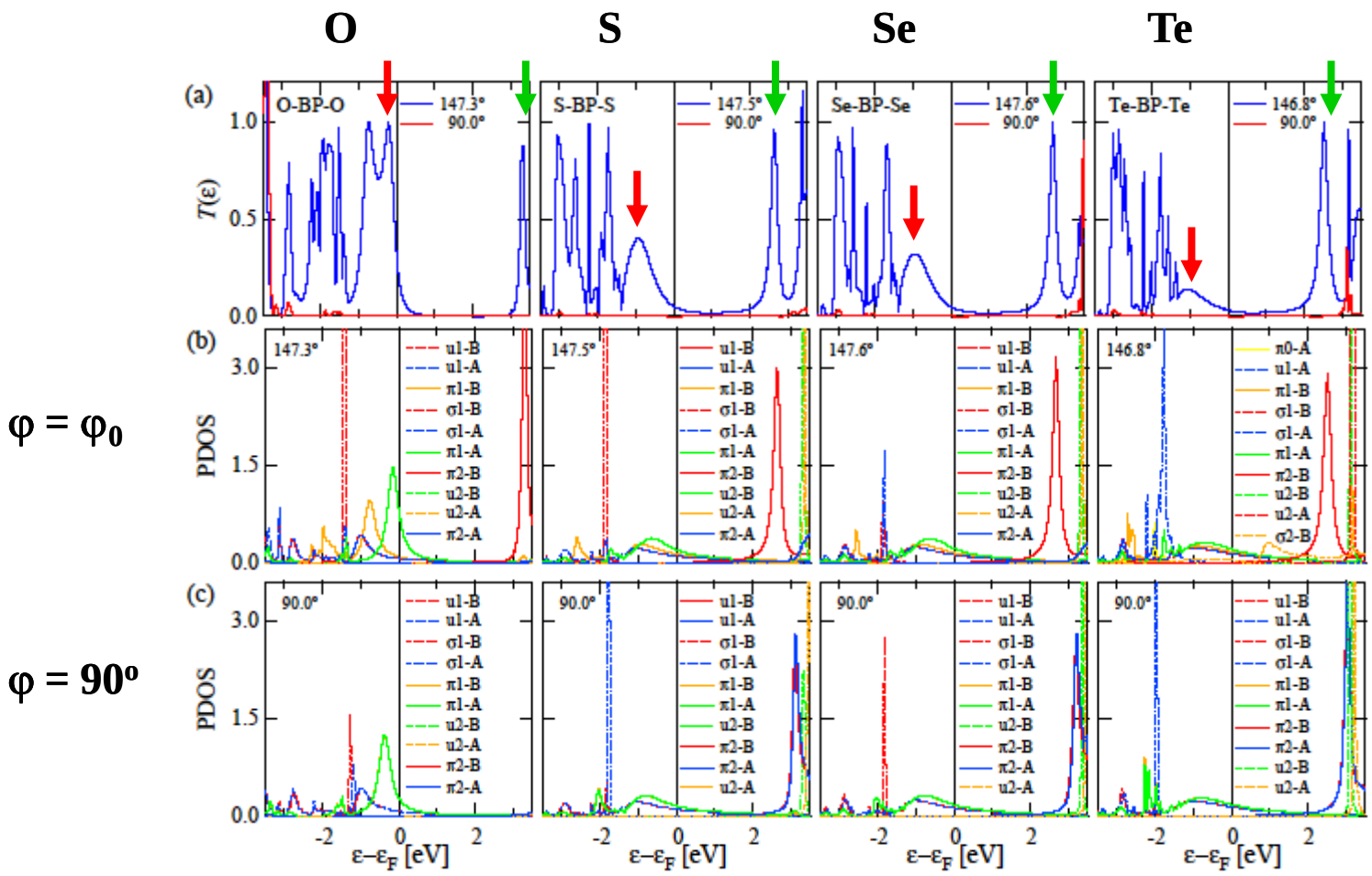
Off



Current *I*: small

**By applying an electric field,
the dihedral angle is controllable.
→ works as a nano-rectifier.**

Molecular Rectifier: End-group dependence

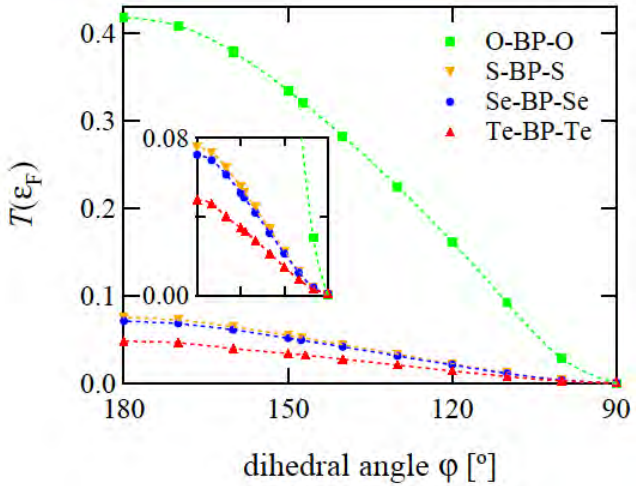


φ = φ0

φ = 90°

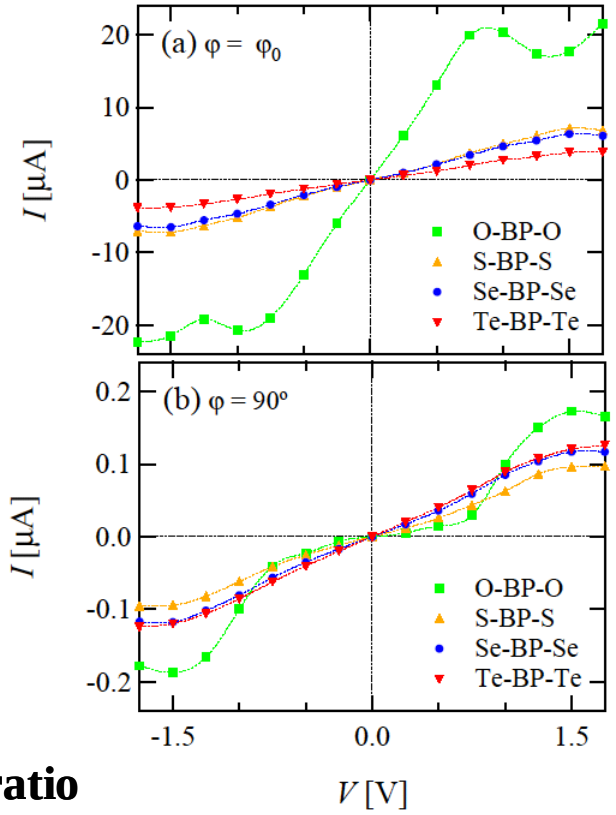
Molecular Rectifier: End-group dependence

Transmission



	$T_{\varphi_0}(\varepsilon_F)$	$T_{90°}(\varepsilon_F)$	$\frac{T_{\varphi_0}(\varepsilon_F)}{T_{90°}(\varepsilon_F)}$
O-BP-O	0.3210	0.0002	1598
S-BP-S	0.0525	0.0006	86
Se-BP-Se	0.0496	0.0009	57
Te-BP-Te	0.0323	0.0010	31

I-V curve

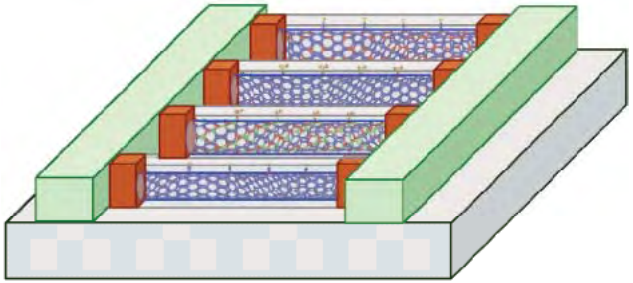


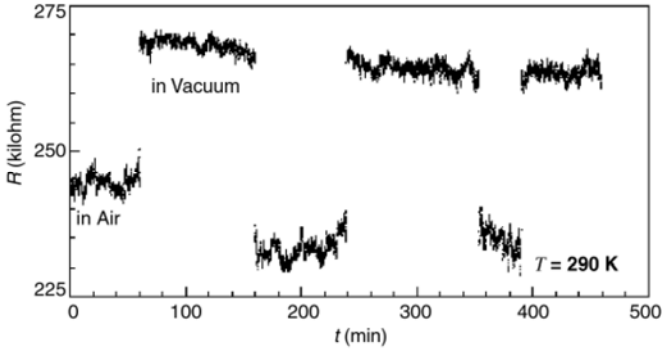
The O end-atom gives the largest ON/OFF ratio

Molecular Sensor

O2 sensitivity of SWNT

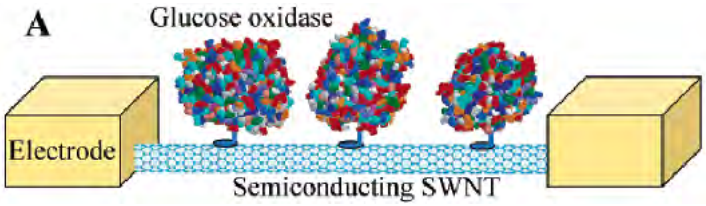
Science 207, 1801 (2000)

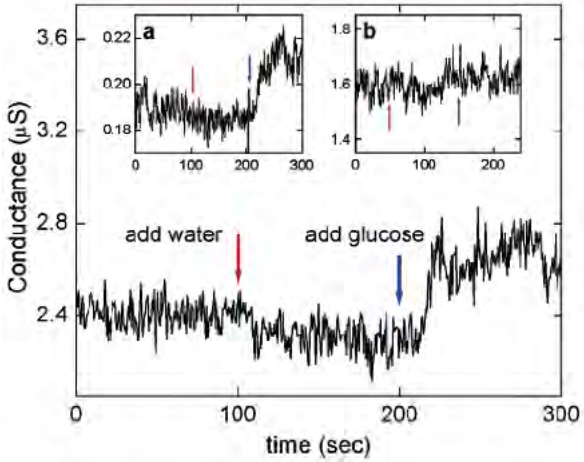




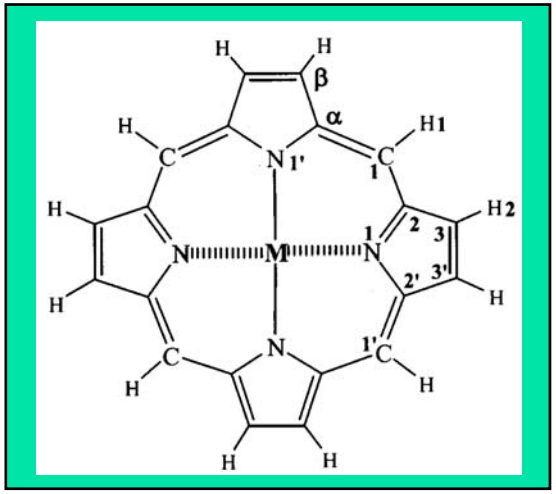
Enzyme-coated CNT as single molecule biosensors

Nano Letters 3, 727 (2003)

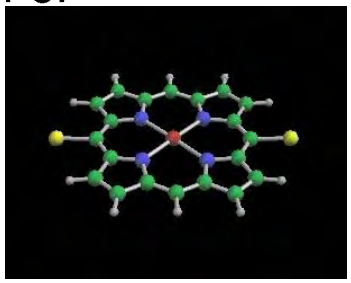




Iron-porphyrin (FeP)



FeP

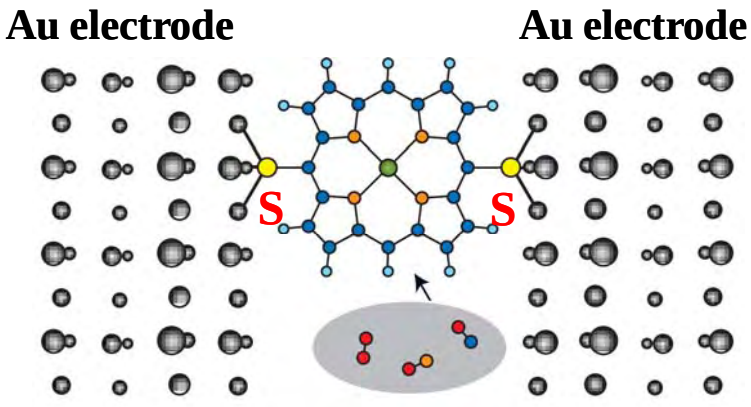


- Ion porphyrin (FeP) is an important molecule in biological systems.
- the basic unit of many proteins and enzymes
- a planar molecule with one Fe atom chelated at the center of a porphyrin cycle.
- its derivatives display a surprising variety of biological functions, acting as carriers of metabolic species (O2) and signal transmitters (NO), as well as redox centers.
- Fe plays a central role in molecular recognition and chemical selectivity of FeP.
- FeP will be used in the design of chemical sensors such as an electronic nose/tongue.

Investigate whether the adsorption of molecules can be detected by the electronic transport?

Molecular sensor: iron-porphyrin (FeP)

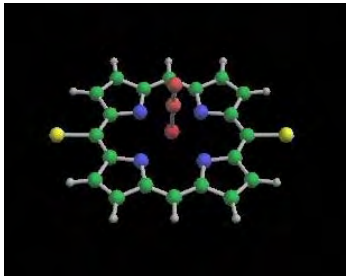
Geometry of molecular sensor



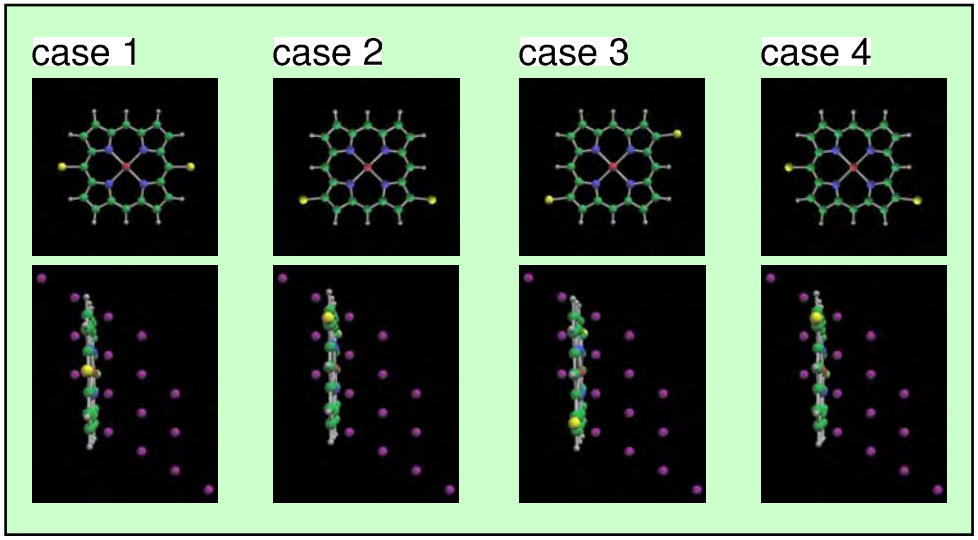
Adsorption of molecules

O2, CO, NO

O_2-FeP



Junction geometry

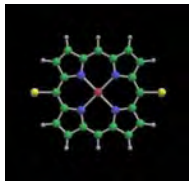


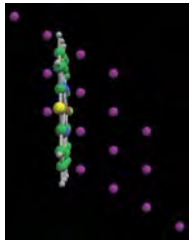
Dependence on junction geometry

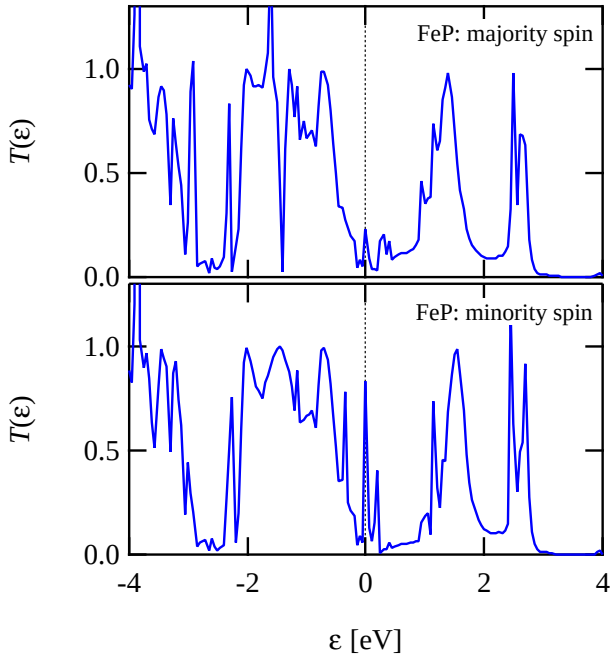
case 1

$T_{\uparrow}(\varepsilon_F) = 0.230$

$T_{\downarrow}(\varepsilon_F) = 0.446$



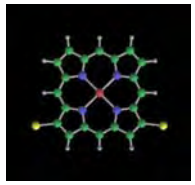


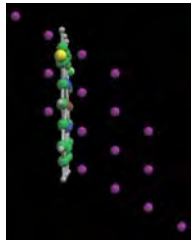


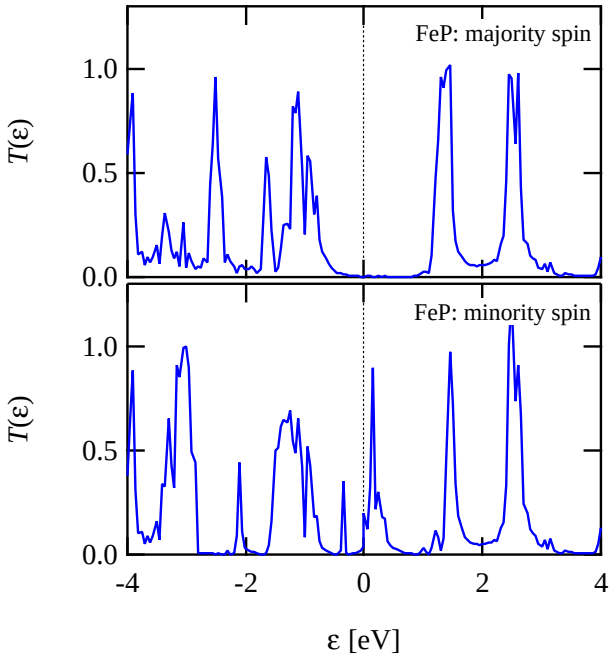
case 2

$T_{\uparrow}(\varepsilon_F) = 0.003$

$T_{\downarrow}(\varepsilon_F) = 0.199$







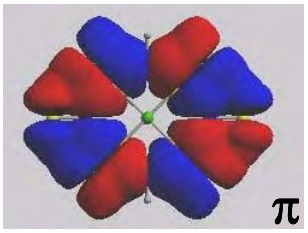
Molecular orbitals: FeP

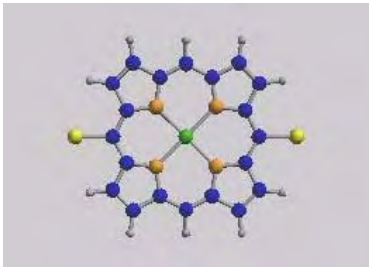
majority spin

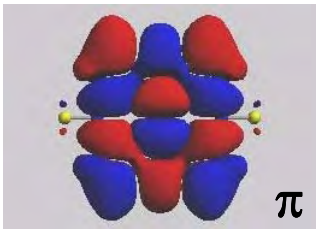
H-S-FeP-S-H

minority spin

HOMO

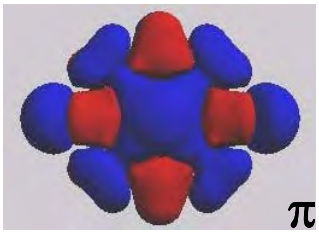


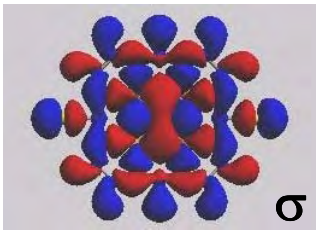




HOMO
d(yz)

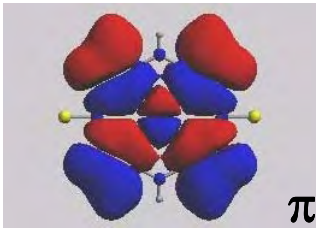
HOMO-1
$d(3z^2-r^2)$

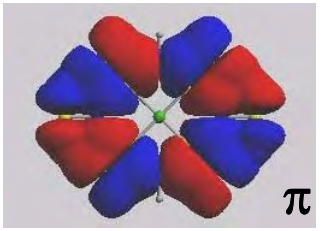




HOMO-1
$d(x^2-y^2)$

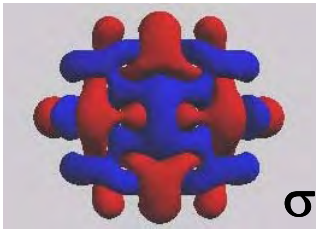
HOMO-2
d(yz)

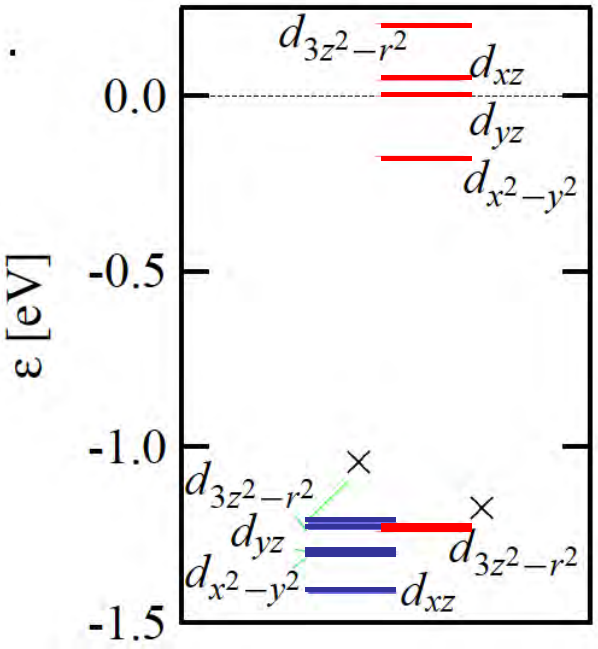


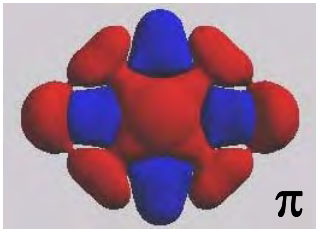


HOMO-2

HOMO-3
$d(x^2-y^2)$

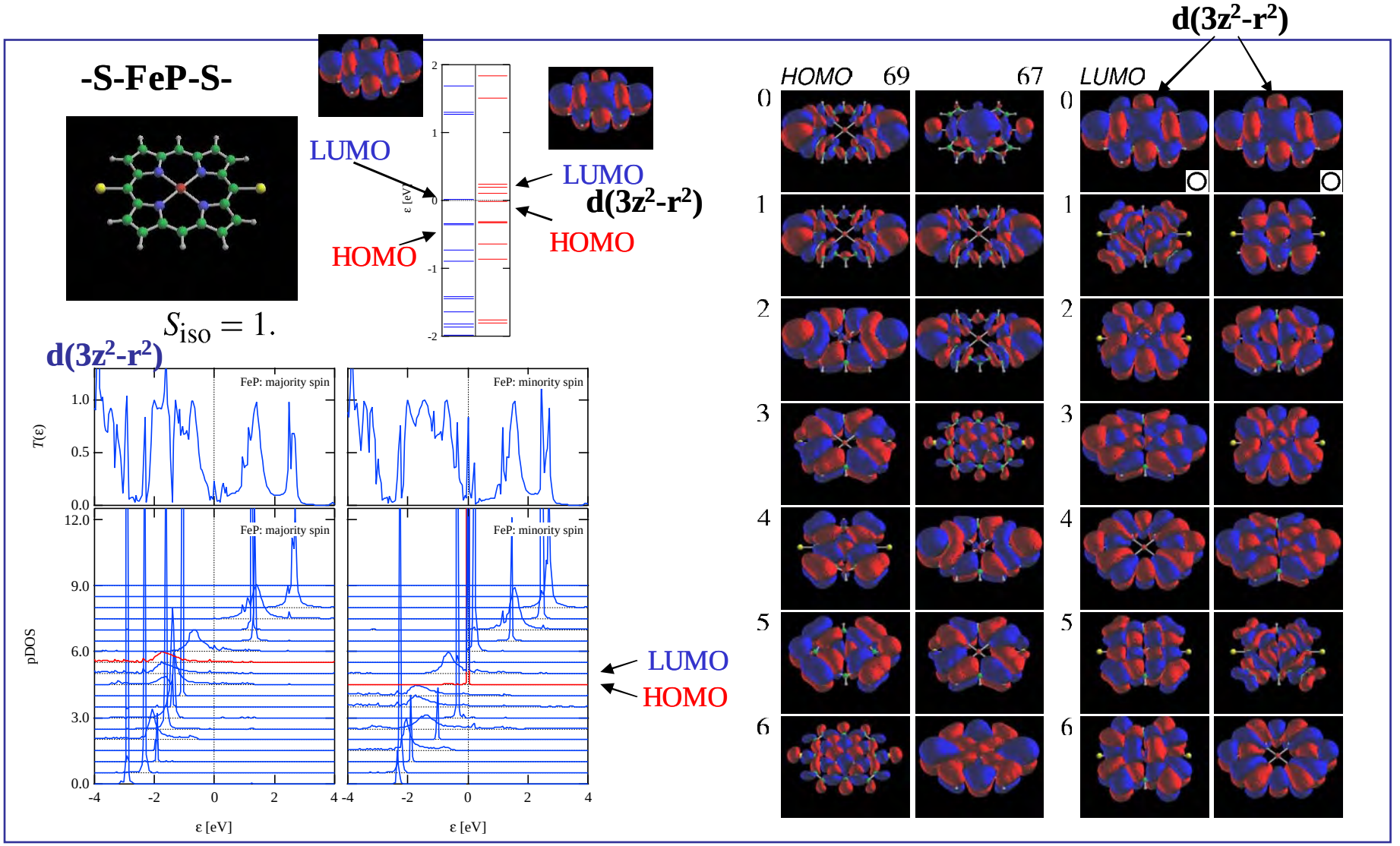






HOMO-3
$d(3z^2-r^2)$

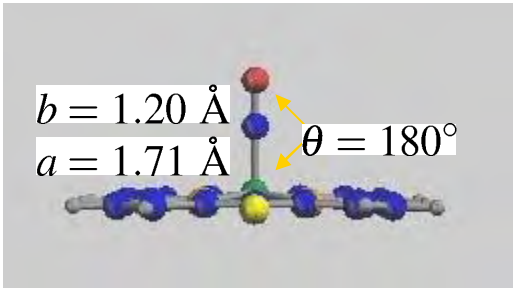
Transport property: **iron-porphyrin** (FeP)



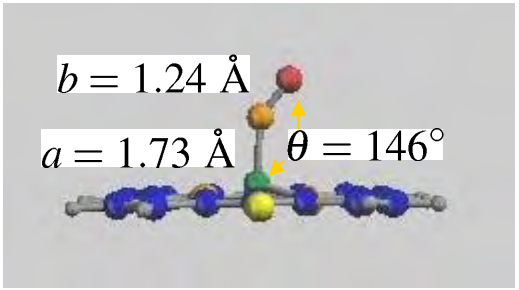
Adsorption geometries of XO on FeP

H-S-FeP-S-H

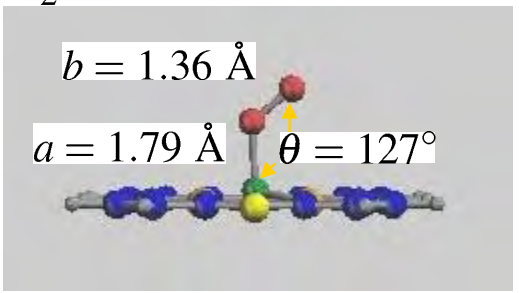
CO-FeP



NO-FeP



O_2-FeP



$a = r_{\text{Fe-}X}$ $b = r_{X\text{-O}}$

H-FeP-H

OpenMX

	θ	a	b
CO-FeP	180°	1.70 Å	1.19 Å
NO-FeP	148°	1.71 Å	1.23 Å
O_2-FeP	124°	1.73 Å	1.35 Å

cf.) plane wave basis

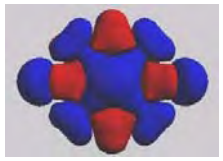
	θ	a	b
CO-FeP	180°	1.69 Å	1.17 Å
NO-FeP	150°	1.69 Å	1.19 Å
O_2-FeP	123°	1.74 Å	1.28 Å

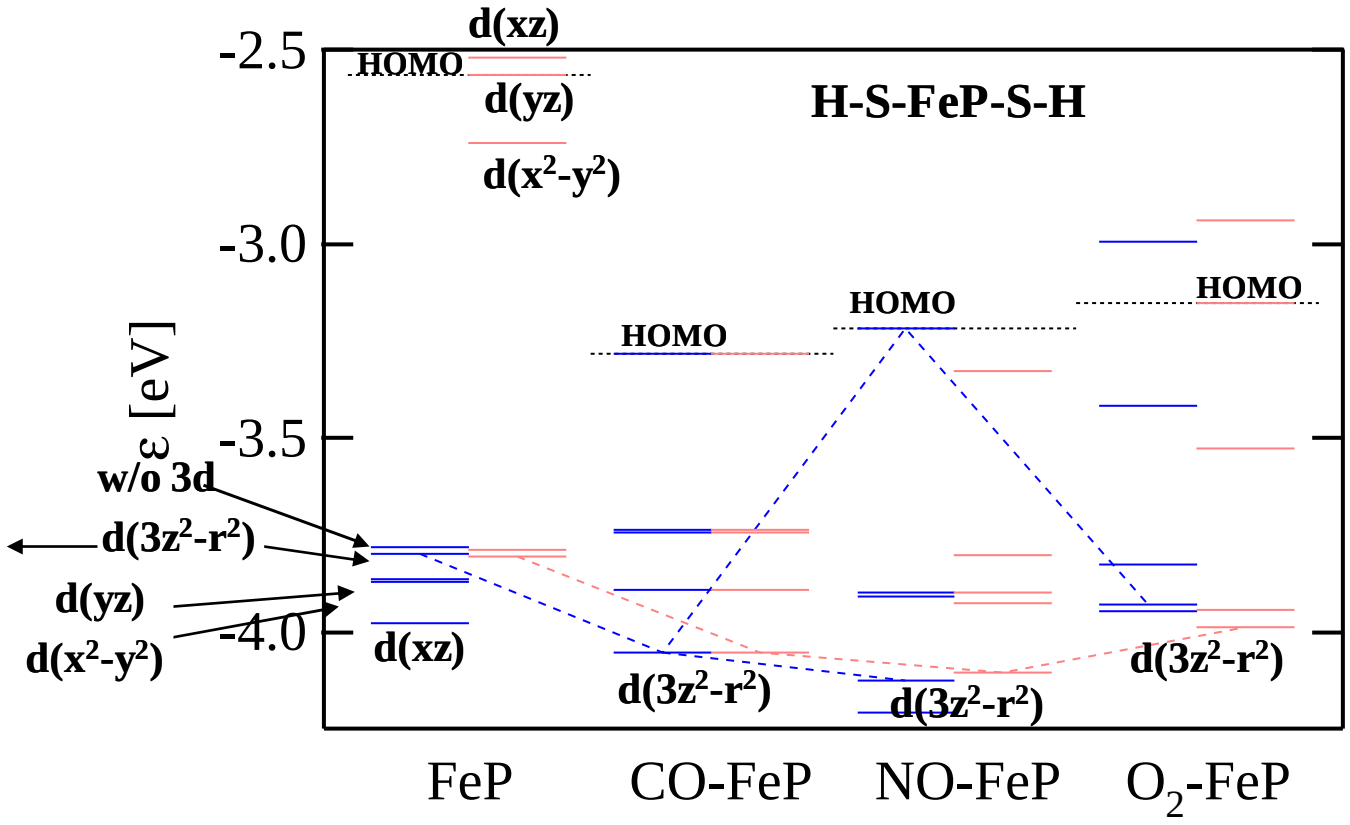
C. Rovira *et al.*: J. Phys. Chem. A **101**, 8914 (1997).

Molecular orbitals: XO adsorbed FeP

The influence of axial ligands on the MOs of FeP

The energy level of the Fe-dz^2 MO in FeP is sensitive to the presence of the ligands.





Transport: XO adsorbed FeP

FeP

$$T_{\uparrow}(\varepsilon_F) = 0.230$$
$$T_{\downarrow}(\varepsilon_F) = 0.446$$

CO-FeP

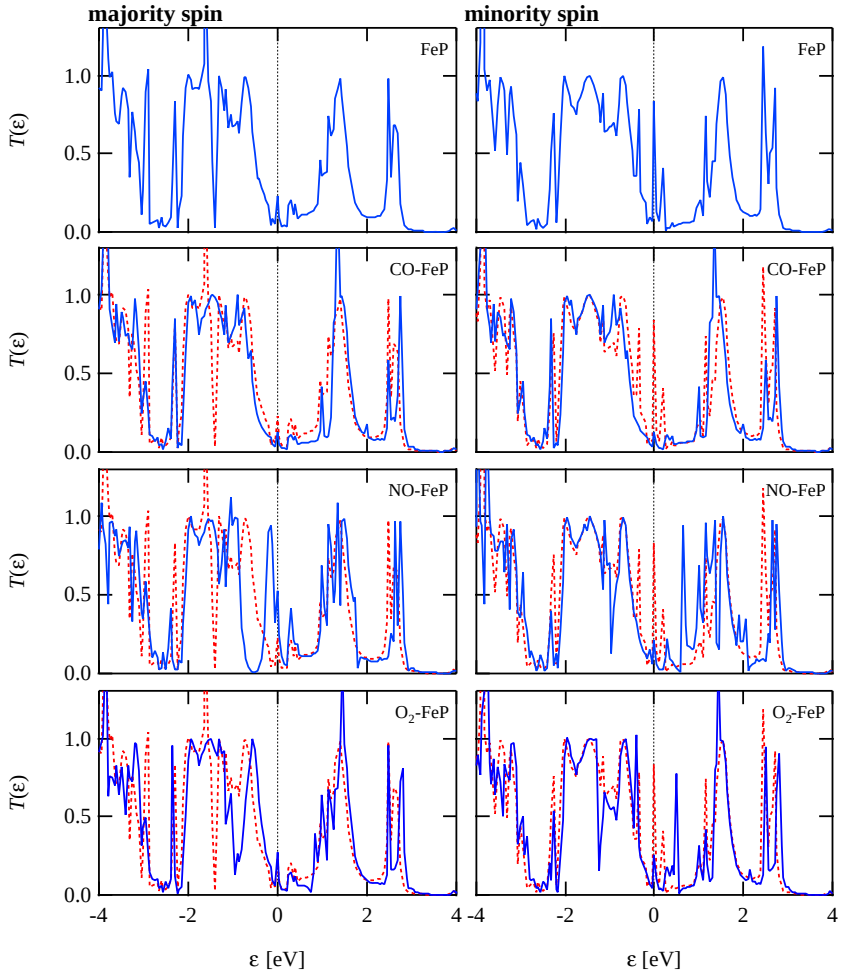
$$T_{\uparrow}(\varepsilon_F) = 0.124$$
$$T_{\downarrow}(\varepsilon_F) = 0.124$$

NO-FeP

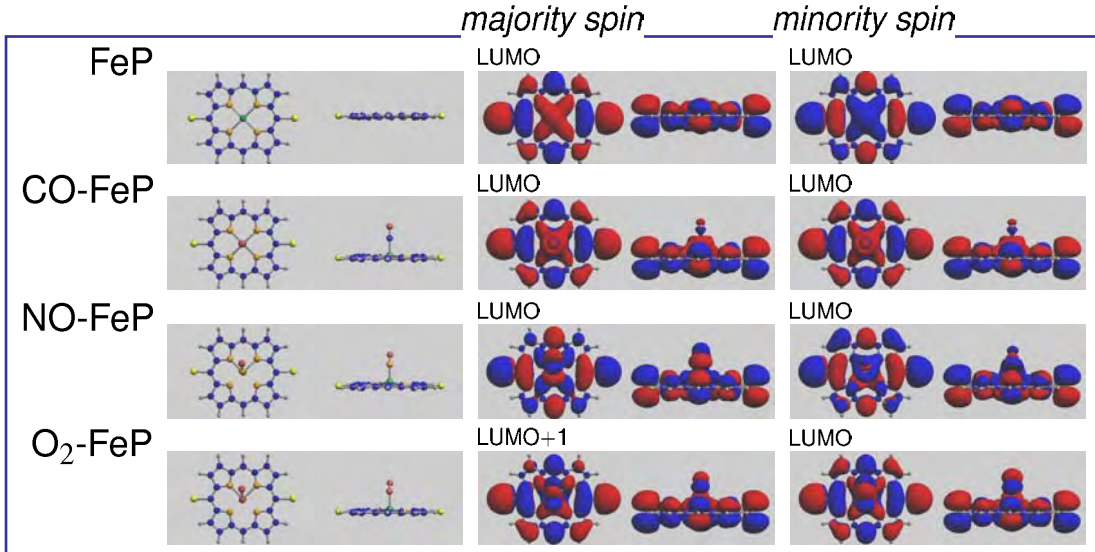
$$T_{\uparrow}(\varepsilon_F) = 0.561$$
$$T_{\downarrow}(\varepsilon_F) = 0.220$$

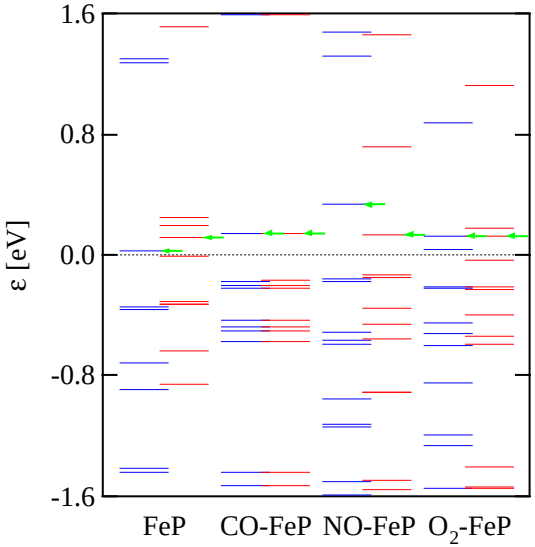
O_2-FeP

$$T_{\uparrow}(\varepsilon_F) = 0.425$$
$$T_{\downarrow}(\varepsilon_F) = 0.938$$



Transport: XO adsorbed FeP





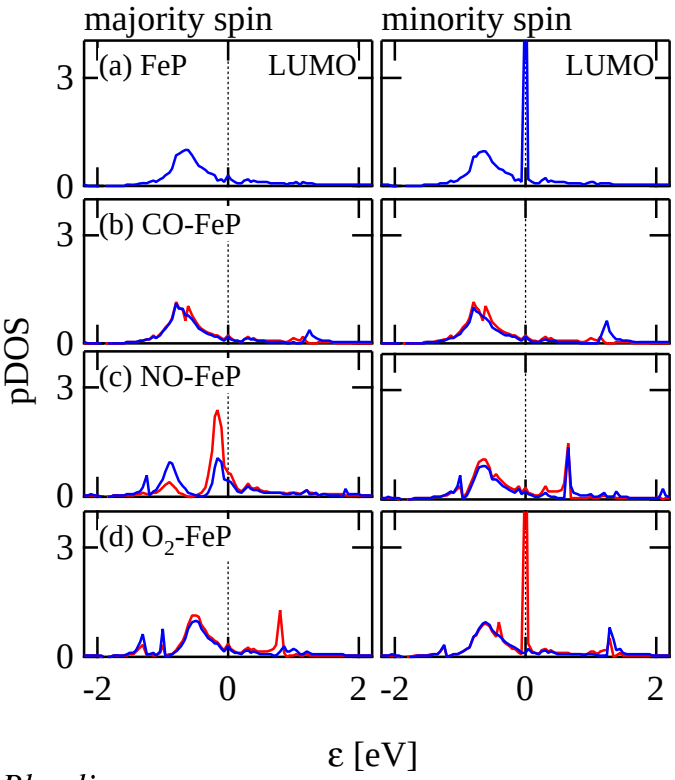
$$\overline{\mathscr{D}}(\varepsilon) = \mathscr{U}^{\dagger}\mathscr{D}(\varepsilon)\mathscr{U}$$

$$\mathscr{D}(\varepsilon) = -\frac{1}{\pi}\mathscr{G}(\varepsilon)$$

$$\mathscr{U} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & U_{\mathrm{mol}} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

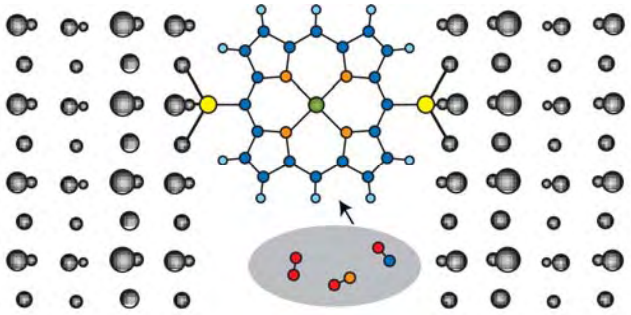
$$U_{\mathrm{mol}} = \begin{cases} U_{\mathrm{FeP}} & : \textit{Blue line} \\ U_{\mathrm{XO\text{-}FeP}} & : \textit{Red line} \end{cases}$$

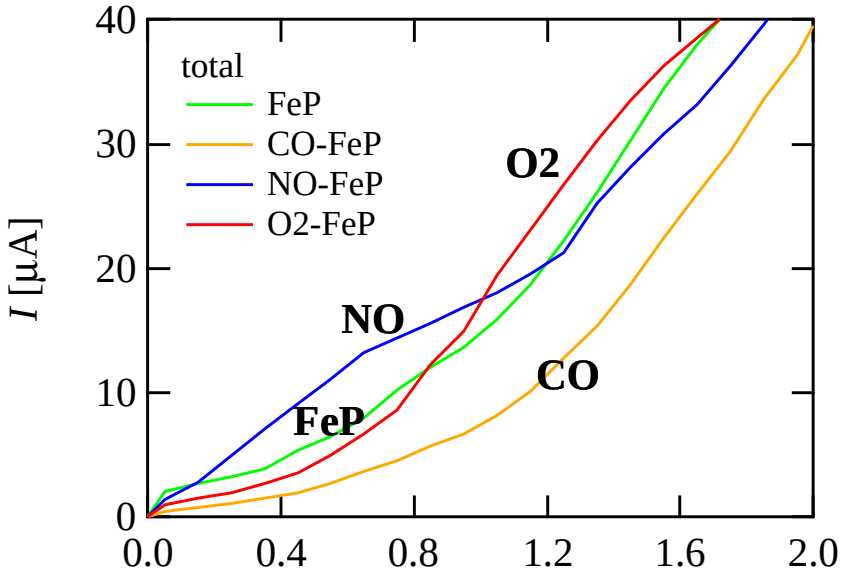
$$\left(H_{\mathrm{mol}}^{\mathrm{diag}} = U_{\mathrm{mol}}^{\dagger} H_{\mathrm{mol}} U_{\mathrm{mol}}\right)$$



-S-FeP-S-

Possibility of Molecular Sensing





$$I = \frac{2e}{h}\int d\varepsilon\, T(\varepsilon;0\ [\mathrm{V}])[f(\varepsilon-\mu+V/2)-f(\varepsilon-\mu-V/2)]$$

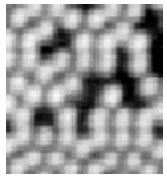
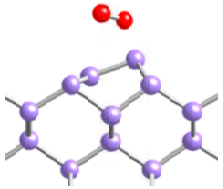
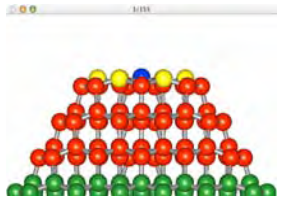
The adsorption of molecules (CO, NO, O2) can be detected by the electronic transport. The molecular species can be also distinguished from each other.

Nano-structured materials

To understand their formation processes & properties/functions at the atomistic level, FP simulation methods based on DFT are an ideal tool.

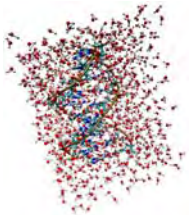
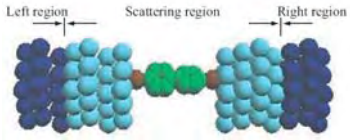
Surface dynamics (DFT/ Hybrid)

(i) Diffusion of F on Si(111) : *Si-F complex diffusion*
(ii) Adsorption of O2 on Si(001) : *Energy dissipation*
(iii) Atomic structure of AFM tip apex

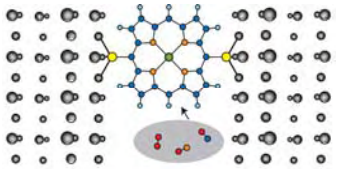
Large nano-structured systems

(i) PW electronic structure codes : shallow impurity in Si
(ii) Linear scaling algorithms:
  (a) Surface nano-structures; Ge cluster on Si(001)
  (b) Bio-molecules: DNA

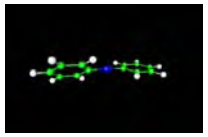
Transport through molecular junctions (NEGF)

(i) p-stacked systems: styrene wires on H/Si(001)
(ii) Molecular sensors: iron-porphyrin
(iii) Molecular switch: biphenyl dithiol

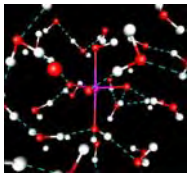
Photochemical reaction (RTP-TDDFT)

(i) Photoisomerization: azobenzene



Redox reaction

(i) RuO4: $RuO_4^-(aq) + H_2O(l) + e^- \rightarrow [RuO_3(OH)_2]^{2-}(aq)$



Advanced Simulation Technology for Innovation of Nano-Scale Materials

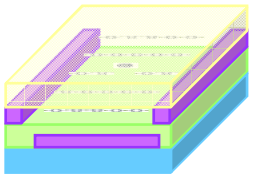
analysis of structures & properties	➡	design of properties & functions
mono-structures	➡	complex/ hierarchical structures
crystal, nano-structure, bio-polymers	➡	nano-devices, nano-complex, bio-systems

Simulations for nano-structured materials

Large-scale, multi-scale, multi-physics, high-accuracy

Nano-technology / Nano-science

Nano-electronics



Bio systems