

# 計算科学とナノサイエンス

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計算科学研究センター・シンポジウム 平成16年6月11日

# なぜ大規模計算が必要？

\* ナノ構造系の計算では必然的に  
大規模

特徴的なサイズ、外部系との相互作用  
実験のみでは攻め難い

\* 原子や電子の過程と、応用したい  
性質現象機能が直に関連

階層横断的なマルチフィジックス現象

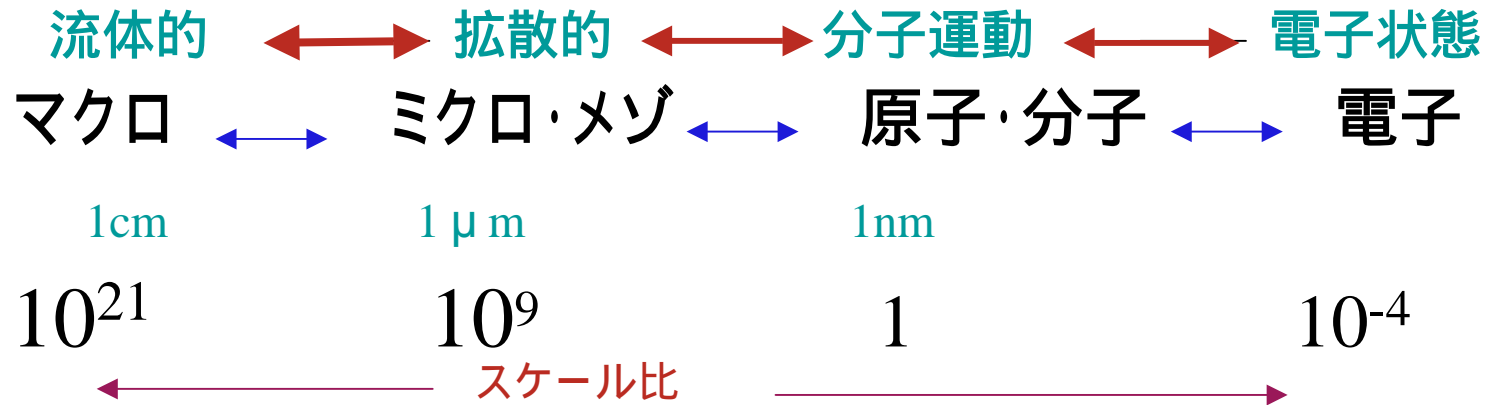
実験研究と相補的役割  
産業応用でも極めて重要

例：

光合成系・太陽電池の  
理論設計  
電界放射、界面反応設計  
光電気化学系、触媒設計  
分子エレクトロニクス系  
ナノバイオ系  
量子コンピュータ系  
ナノ材料機能開発  
ナノ計測・制御

その他、多数、

# 物質・材料設計における階層構造



半導体微細加工  
トップダウン

分子組立素子  
ボトムアップ

# ナノ構造設計

分子量子デバイス / 分子発光・分子磁石 / NEMS / 分子機械 / 量子コンピュータ / ナノ構造デバイス設計 / ドラッグデリバリー系 / クラスタ  
ー・CNT・フラーレン関連物質材料 / ナノ医療技術・材料 /



諸現象、生成法、物性、機能予測、  
非平衡開放系、強相関現象、非線形現象、  
分子 + 固体、無機 + 有機、

原子スケール  メゾ・マクロ

# 計算理論・計算技術の新展開

## 1) 大規模計算へ向けての新しい手法

有限要素法、ハイブリッド法、  
時間発展法、オーダN法、その他

## 2) 系の階層性をどう処理するか

階層連結のアルゴリズム？

## 3) 第一原理法（密度汎関数法）の新しい展開

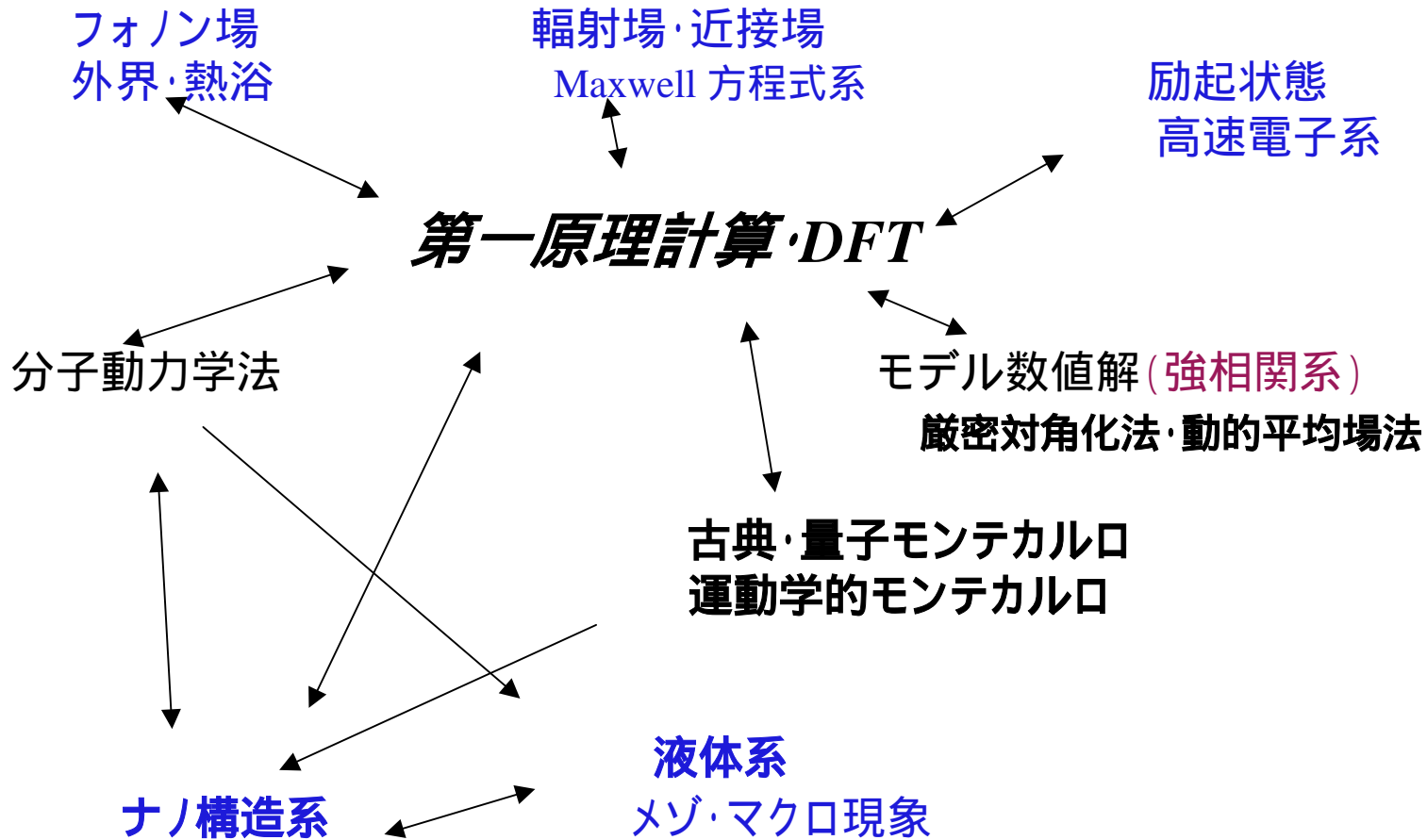
強相関をどう扱う？

原子振動と強く結合した系

非平衡系の散逸

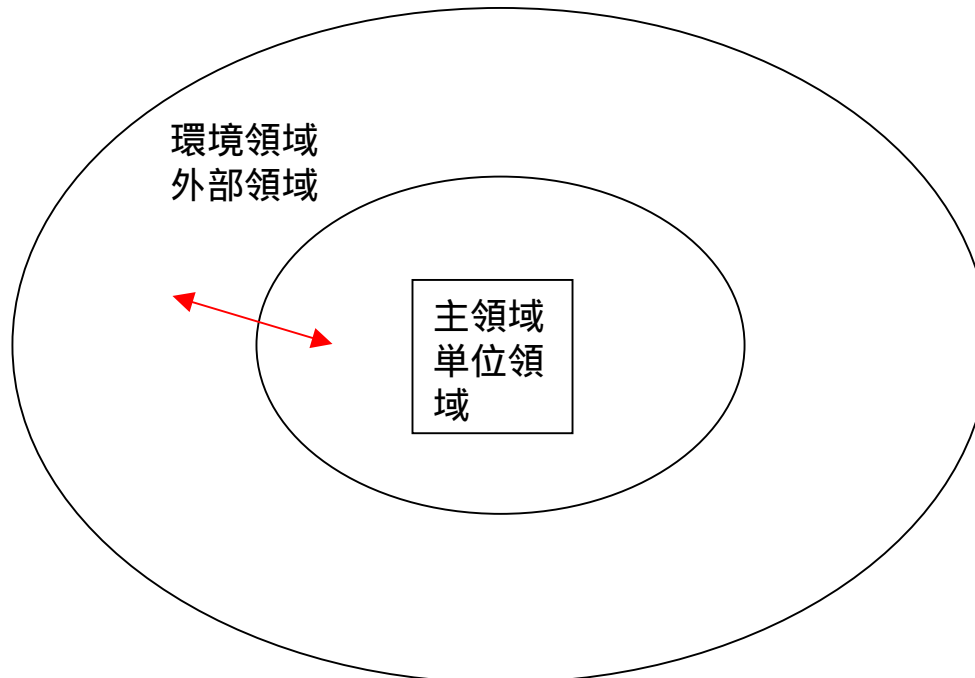
外場（輻射場、局所磁場）との連成系をどう解くか？

# 計算手法における階層構造



# 時空の階層性、 複雑さ・厳密さの階層性

遠方の扱い、熱浴・粒子浴、他自由度の扱い、繰り込み  
励起系の扱い、水分子（生体系）



# 実空間有限要素法

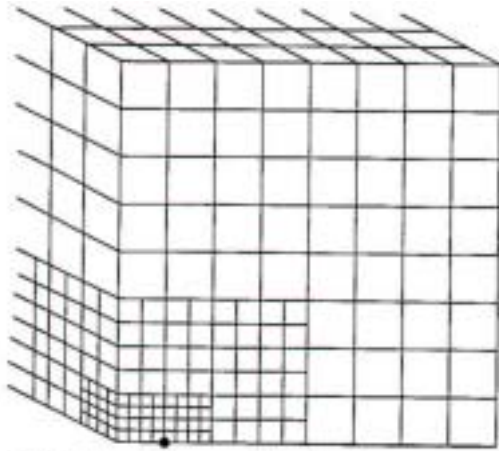


FIG. 4. In practice, we used the mesh twice as dense as this figure. The mesh is taken approximately logarithmic.

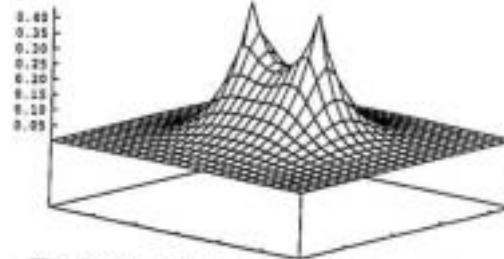


FIG. 5. The calculated electron density for the hydrogen molecule at the equilibrium bond length (in units  $e \times \text{bohr}^{-3}$ ). The two peaks indicate the position of the nuclei. The singularity at the nucleus is well reproduced.

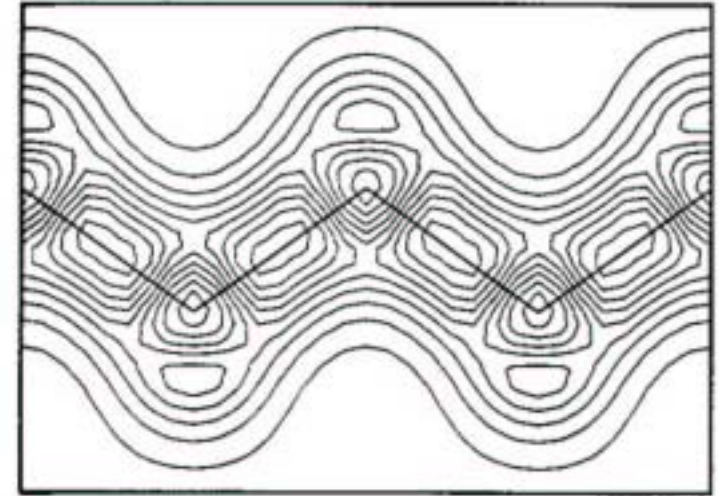


TABLE I. Properties of the hydrogen molecule. The other theory is from Ref. 20, in which LDA calculations are performed with Gaussian orbitals. The experimental data are from Ref. 21.

	Bond length (a.u.)	Vibrational frequency ( $\text{cm}^{-1}$ )
This work	1.46	4424
Other theory	1.45	4277
Experiment	1.40	4400

TABLE II. Properties of Si in the diamond structure. The experimental data are from Refs. 31, 32, and 33 of Ref. 14.

	Lattice constant (a.u.)	Cohesive energy (eV/atom)	Bulk modulus (Mbar)
This work	10.43	4.76	0.94
Other theory	10.45	4.70	0.97
Experiment	10.26	4.63	0.99

E.Tsuchida and M.Tsukada  
 Phys.Rev.B52(1995)5573-5578  
 Phys.Rev.B54(1996)7602-7605  
 J.Phys.Soc.Jpn.67(1998)3844-3858  
 Chem.Phys.Lett.311(1999)236-240



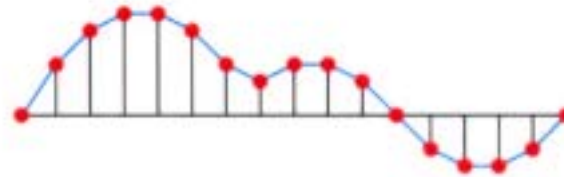
# 時間発展密度汎関数法

N.Watanabe and M.Tsukada  
PRE 62(2000)2914

Based on an Iterative method.

$$|\psi(t + \Delta t)\rangle = \exp \left[ -i \frac{\Delta t}{\hbar} \mathcal{H} \right] |\psi(t)\rangle$$

Based on a Real space method.



Based on exponential product technique.

$$|\psi(t + \Delta t)\rangle = \left[ \prod_n \exp [-i\Delta t \mathcal{H}_n] \right] |\psi(t)\rangle$$

Based on the Cayley method.

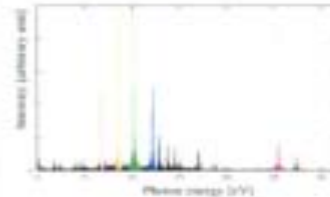
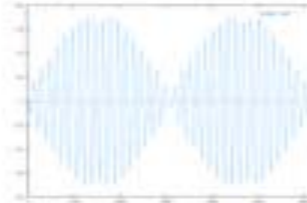
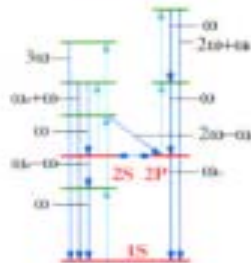
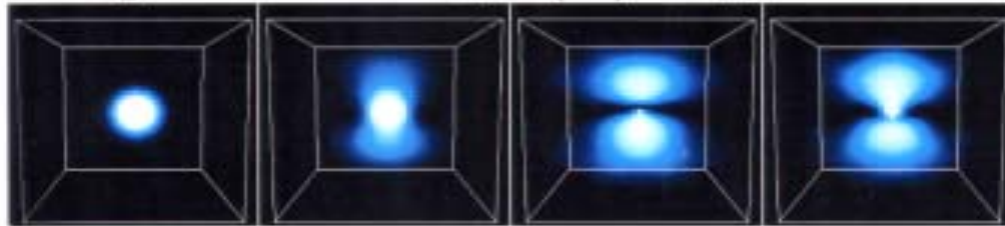
$$|\psi(t + \Delta t)\rangle = \frac{1 - i\Delta t \mathcal{H}/2}{1 + i\Delta t \mathcal{H}/2} |\psi(t)\rangle$$

Now we show our method in detail.

# 時間発展密度汎関数法の応用例

Excitation of Hydrogen atom:

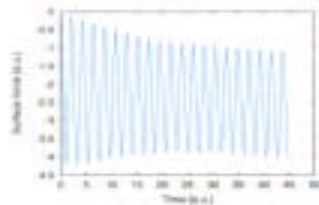
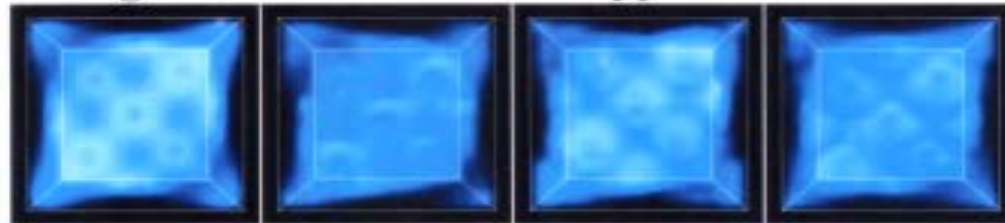
Strong electron field  $E_0 \sin(\omega t)$  is applied



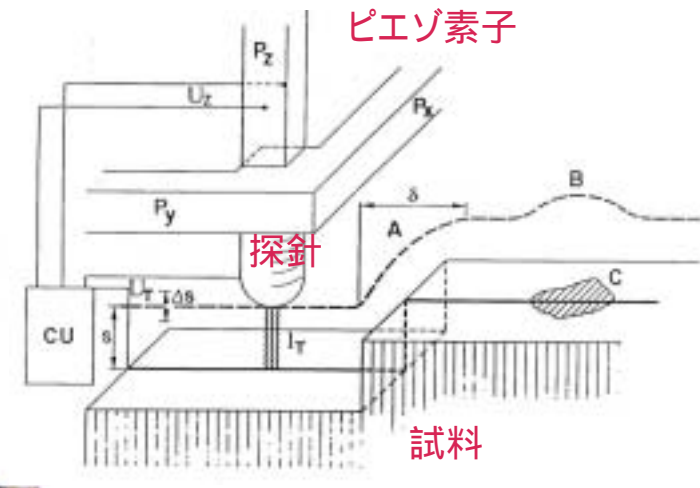
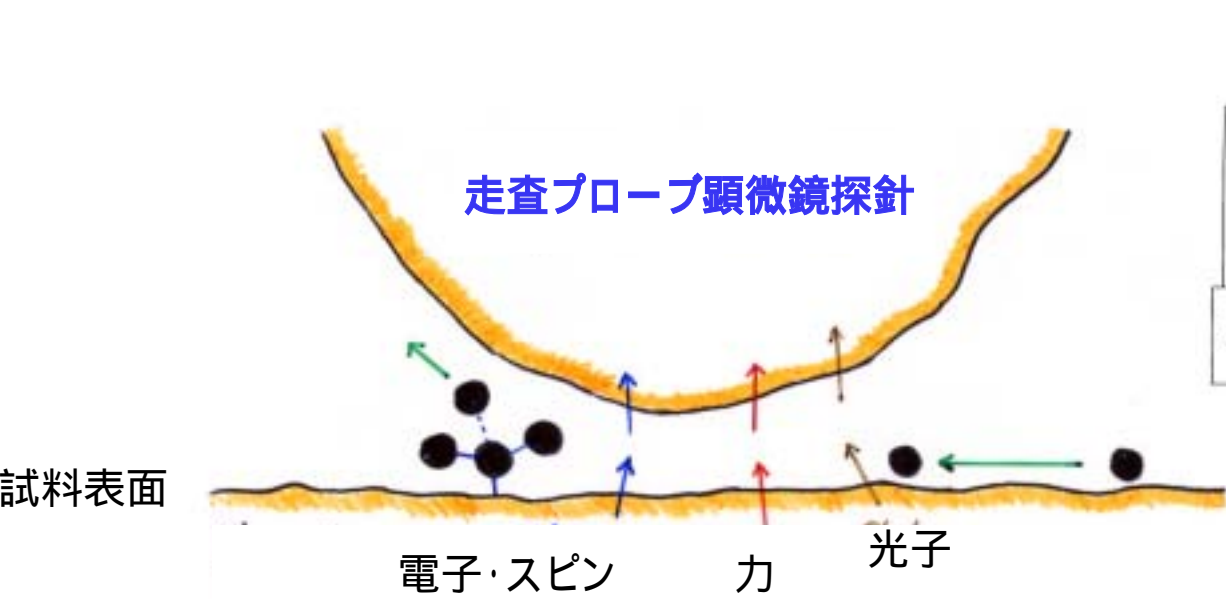
many optical processes cause non-linear scattering.

Solid plasma in diamond crystal:

Strong static electric field is applied



By taking account of the surface charge, the solid plasma occurs in the crystal.



走査プローブ顕微鏡(SPM) - STM, AFM, SNOM etc -  
 は、対象物の何をどのように観るのか？

情報伝達機構、 探針の原子構造・原子種の効果、 定量解析法

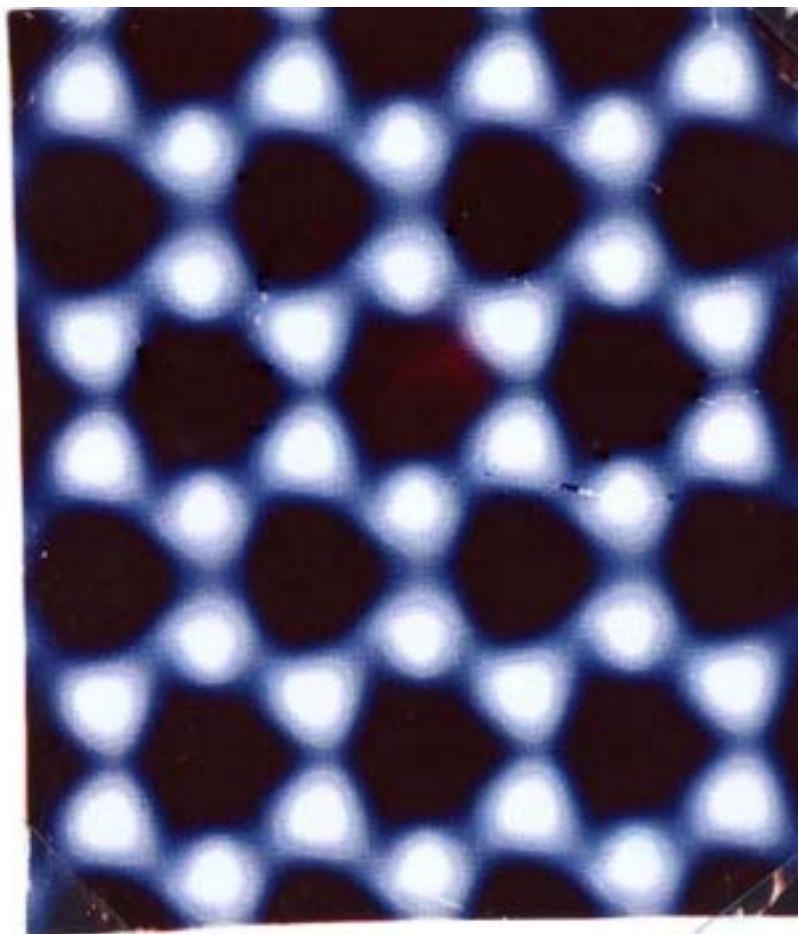
電子分光、 カスペクトル、 原子マニピュレーション

ナノ構造制御・機能開発

量子力学的第一原理計算(DFTなど)による理論シミュレーション

# Si(111) 3 × 3-Ag 表面のSTM像 実験と理論

Theory HCT model

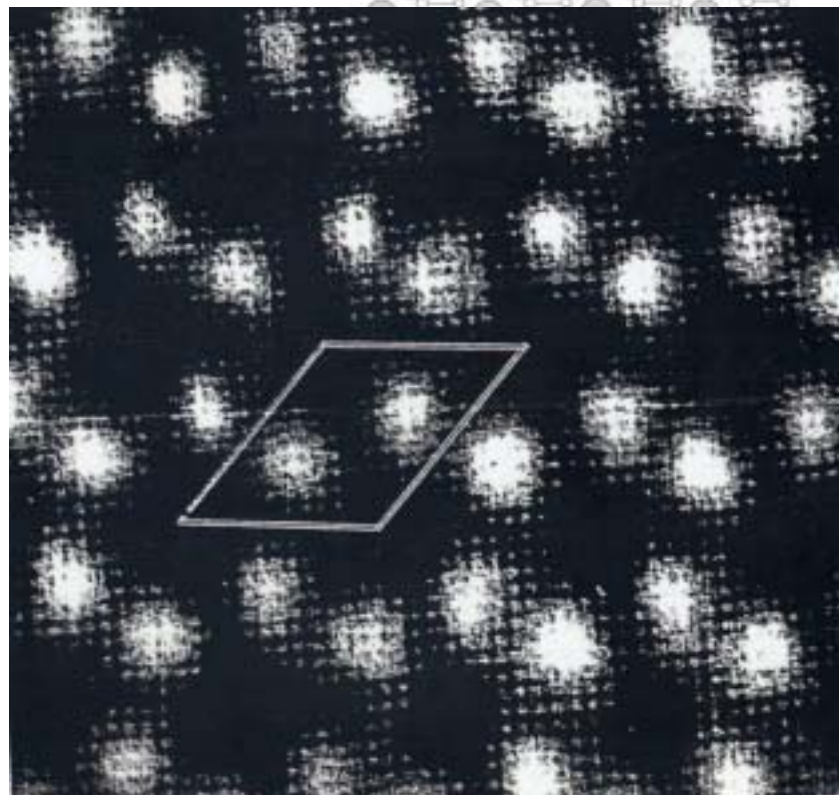
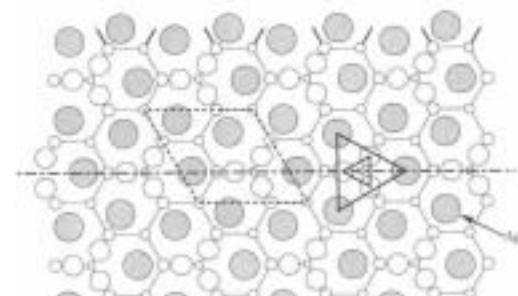


$W_{10}[111]$ 探針模型

Watanabe, Aono, Tsukada(1991) Phys.Rev.B44 (1991)8330

$V_s = 1V$

Unoccupied  
states

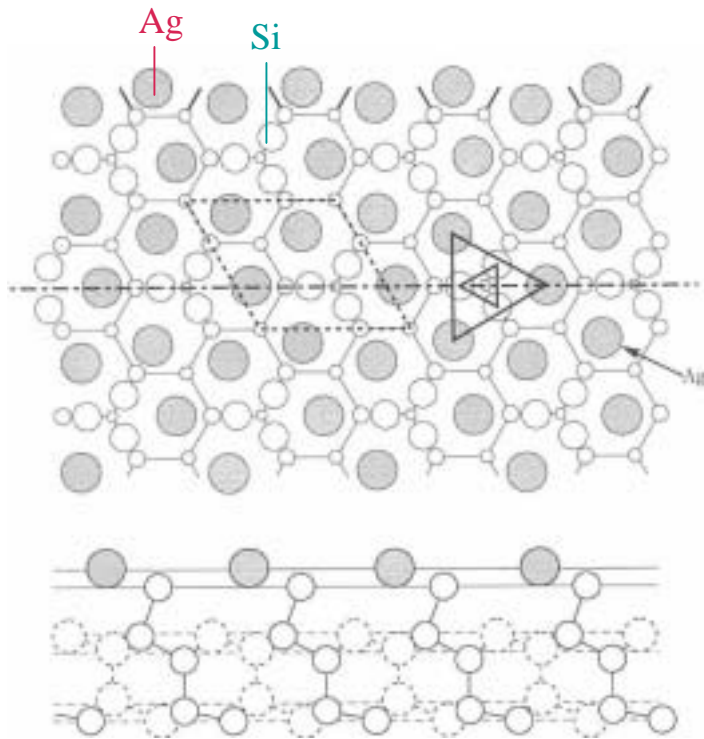


EJvan Loenen etal PRL 58('87)373

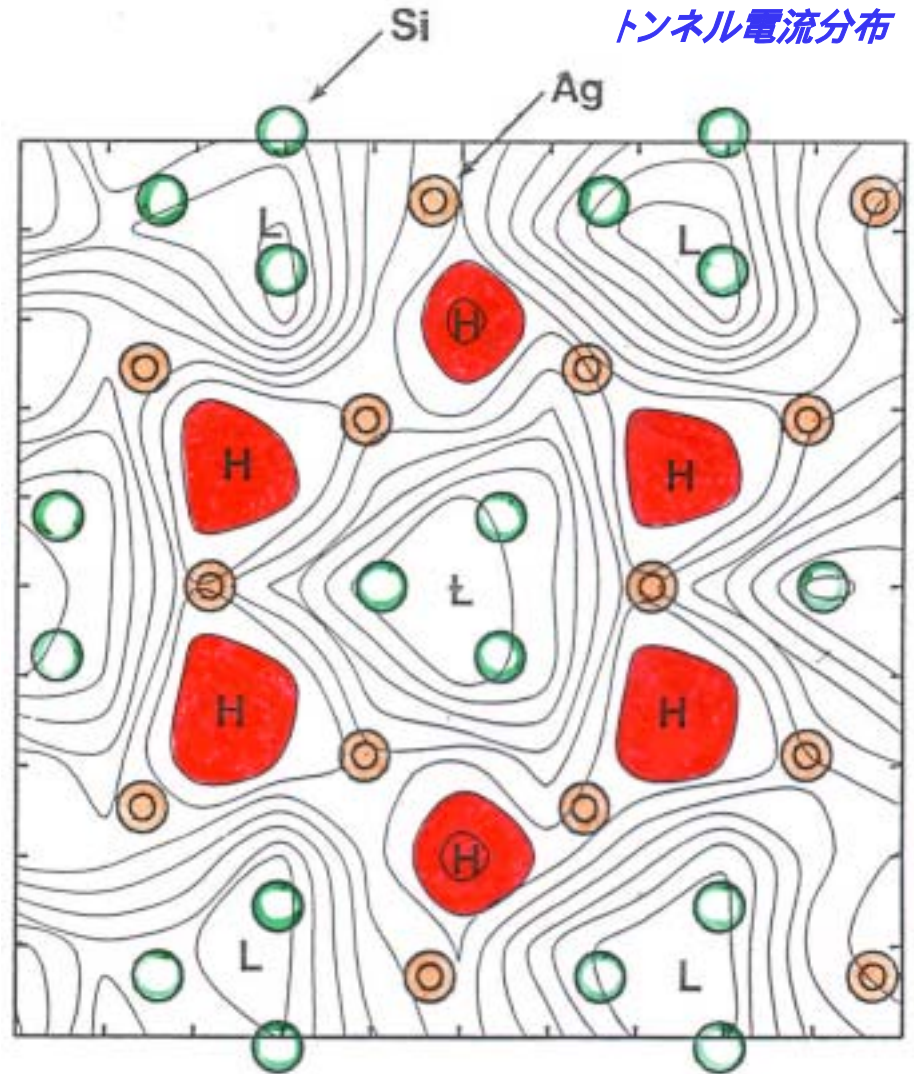


# Si(111) 3X 3-Ag 表面(HCT 模型)

Wartanabe, Aono, Tsukada(1991) Phys.Rev.B44 (1991)8330



X線回折、イオン散乱等の実験から  
決定されたHCT 模型



トンネル電流分布

# 探針の形状によるSTM像の変化(1)

(計算結果、 $V_{\pi} = -1.0\text{V}$ )

$W_{10}[111]$



$W_9[110]$



探針先端の頂点原子を除去するとSTM像が大きく変化する

$W_{14}[110]$

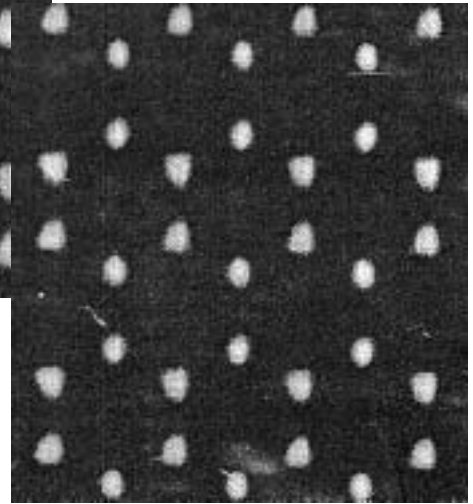
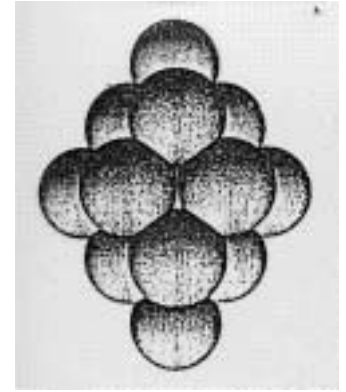
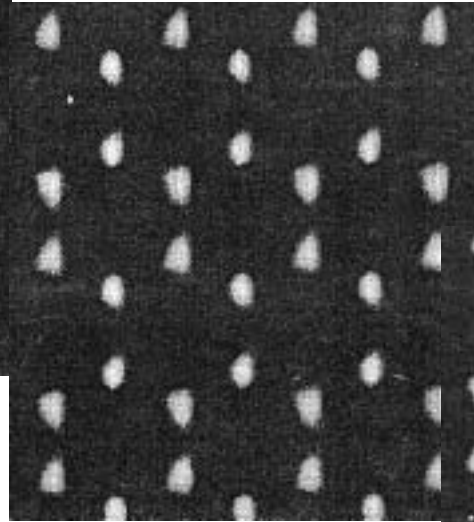
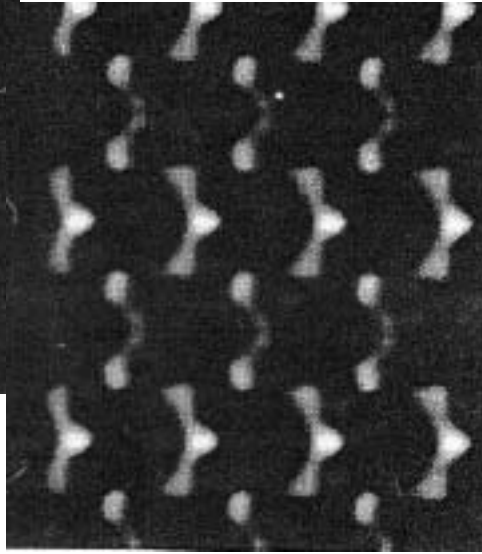
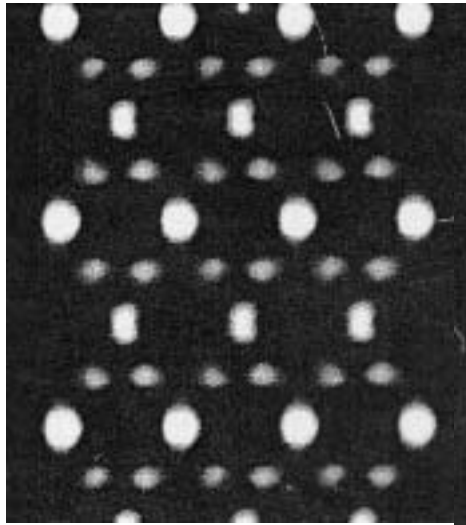


$W_{13}[110]$



Watanabe, Aono, Tsukada  
J. Vac. Sci. Technol.,  
B12(8)(1994)2167

# 探針の形状によるSTM像の変化(2)



傾き $0^\circ$



傾き $10^\circ$



傾き $20^\circ$

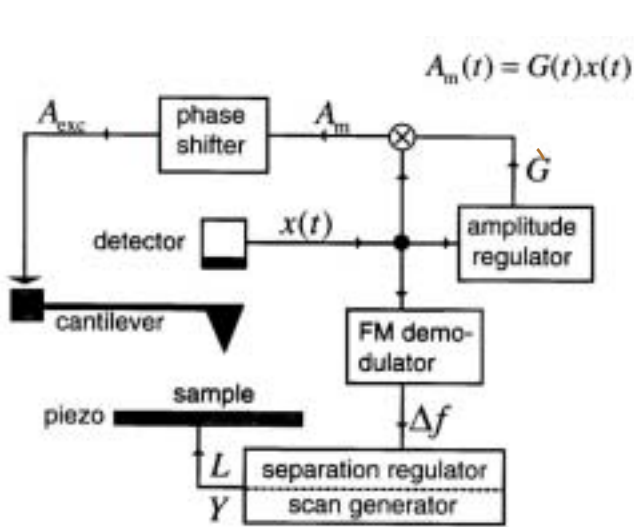


傾き $30^\circ$

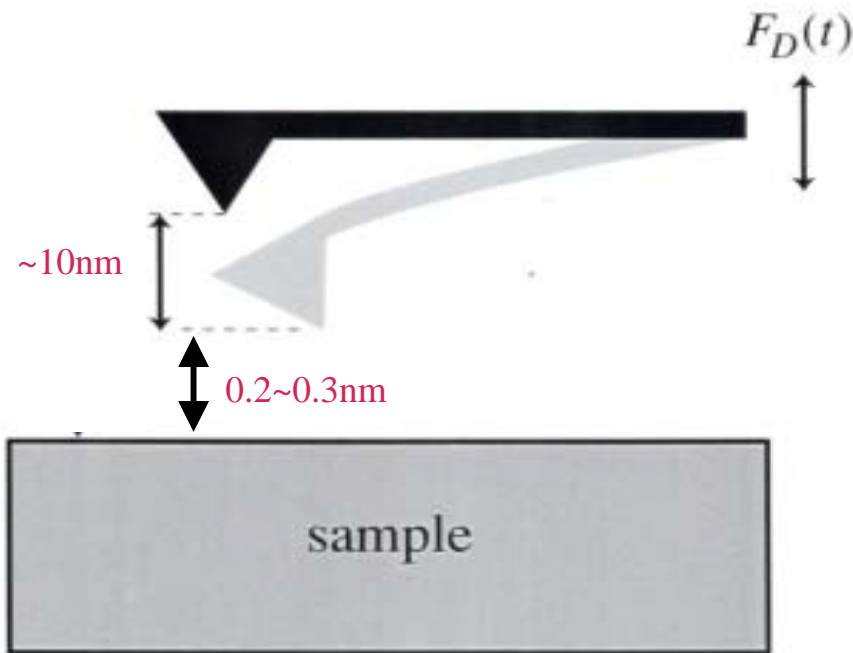
一個の原子のトンネル電流が  
STM像を構成する →  
原子尺度分解能の機構

# How the force by the individual atom can be observed ?

Theory of non contact Atomic Force Microscopy (ncAFM)



*Feedback circuit*



$$\ddot{x}(t) + \gamma \dot{x}(t) + \omega_c^2 (x(t) - L) = F_D(t) + F_I(t)$$

Friction const.

Cantilever  
resonant freq.

Driving force  
Of cantilever

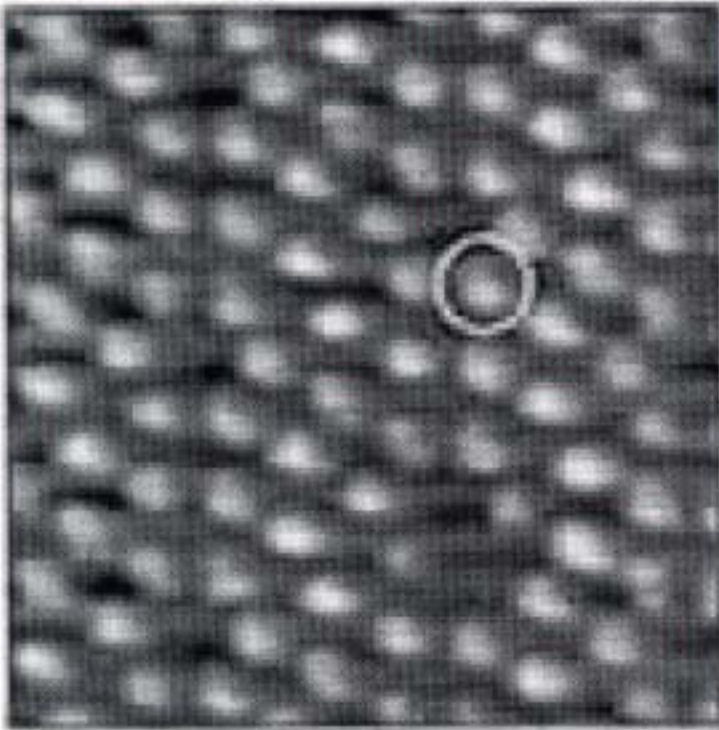
Tip-surface  
force



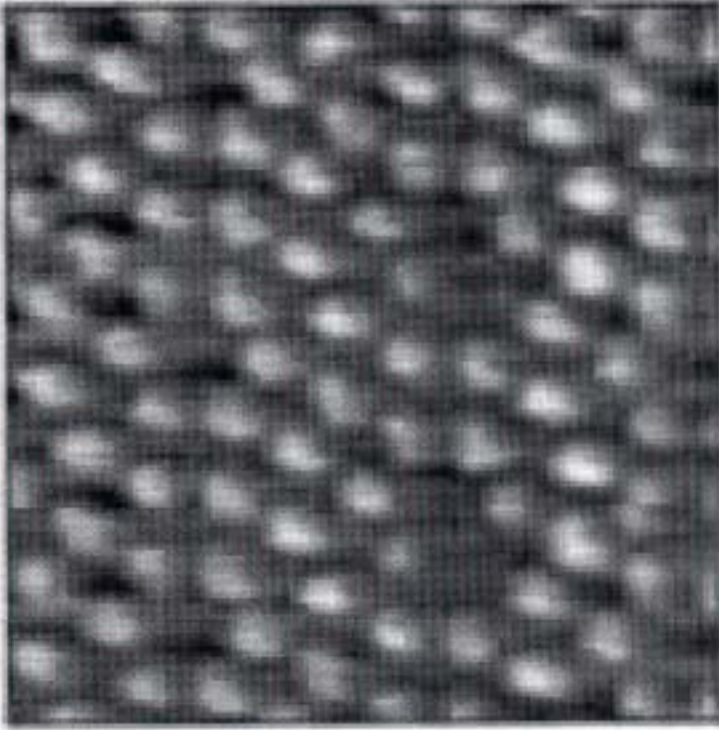
*Control of individual atoms by the tip of Nc-AFM*  
(S.Morita , Osaka Univ.)

*Any target atoms can be removed by the ncAFM tip*

before



after



# *Theoretical Problems of ncAFM*

How the *atomic scale force* influences on the *cantilever oscillation* and how is it measured by *ncAFM images*?

*Frequency shift , Energy dissipation*

How the ncAFM images can be simulated by the calculated *tip-surface force, deformation, or atomistic irreversible processes* ?

*Effect of tip atomic structure and atom kinds?*

*Effect of reversible/irreversible structure change?*

*How the dynamic surfaces are observed?*

# Macroscopic *observable* quantities and *atomic scale interaction*

*Amplitude*

$$A = \frac{l}{2\sqrt{\left(\frac{f}{f_0} - 1 + r\right)^2 + h^2}}$$

**Resonant Curve**

*Frequency*

*Frequency shift*

$$\Delta f = rf_0 = -\frac{f_0}{2kA\pi} \int_0^{2\pi} F(A \cos \theta + L) \cos \theta d\theta$$

*Tip-surface interaction force*

*Peak width*

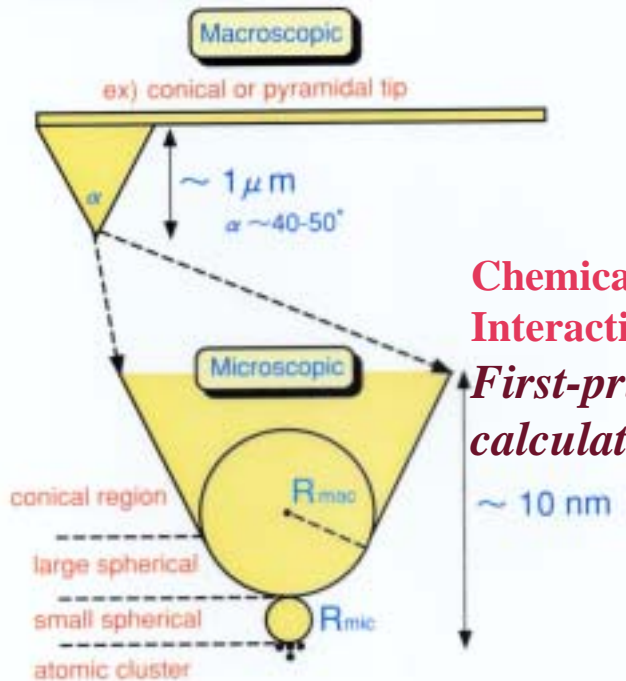
$$h = \frac{1}{\pi\omega_0} \int_0^{2\pi} \gamma(A \cos \theta + L) \sin^2 \theta d\theta$$

$$+ \frac{1}{2kA\pi} \int_0^{2\pi} F(A \cos \theta + L) \sin \theta d\theta$$

*Friction const.*

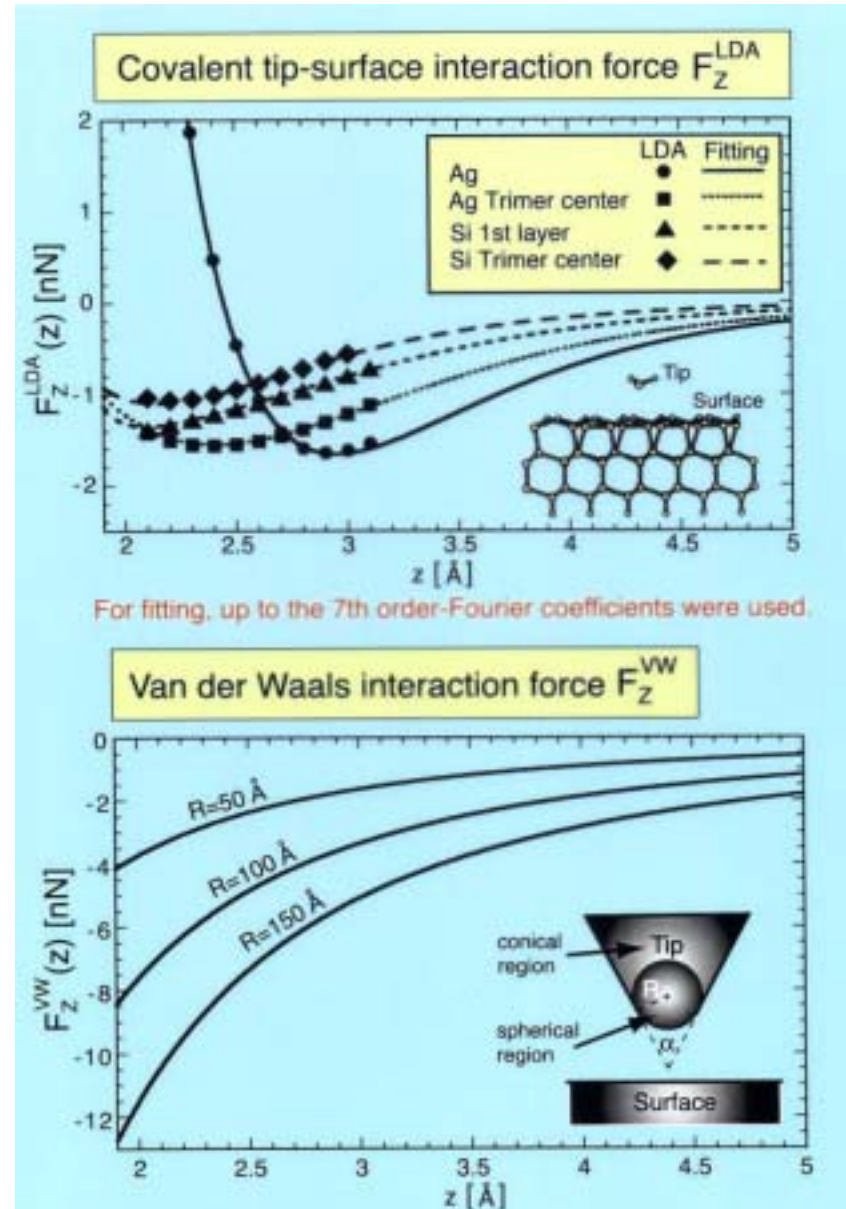
*Hysteresis force*

# Simulation by the first-principles method



**Chemical Interacting Force**  
*First-principles calculation*

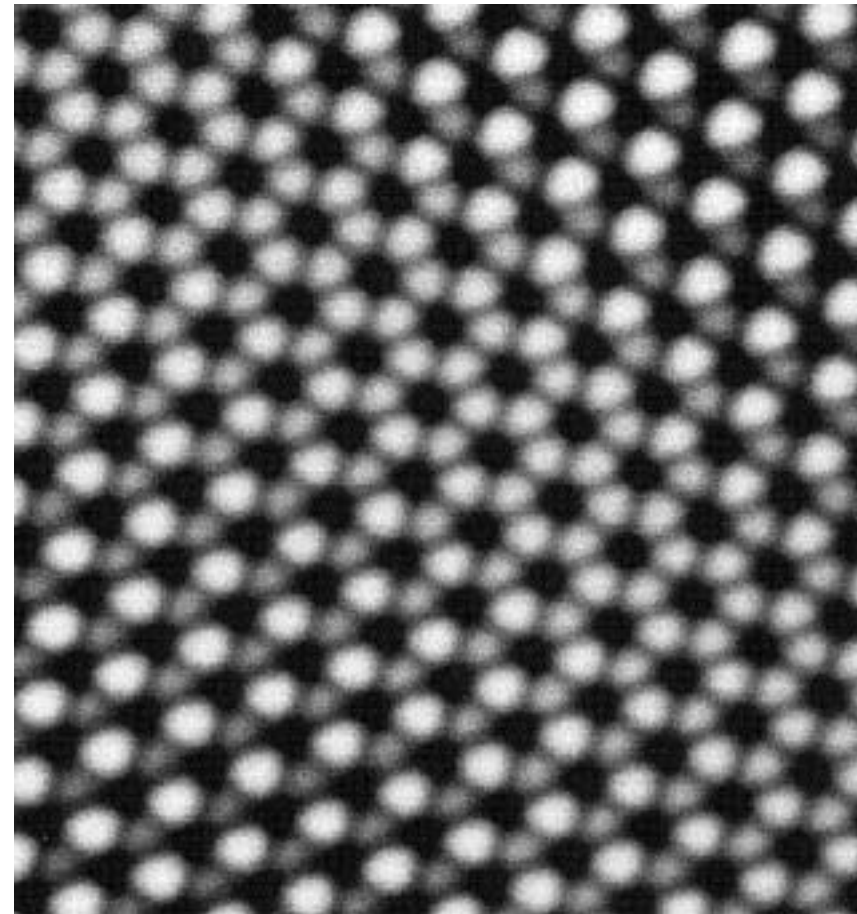
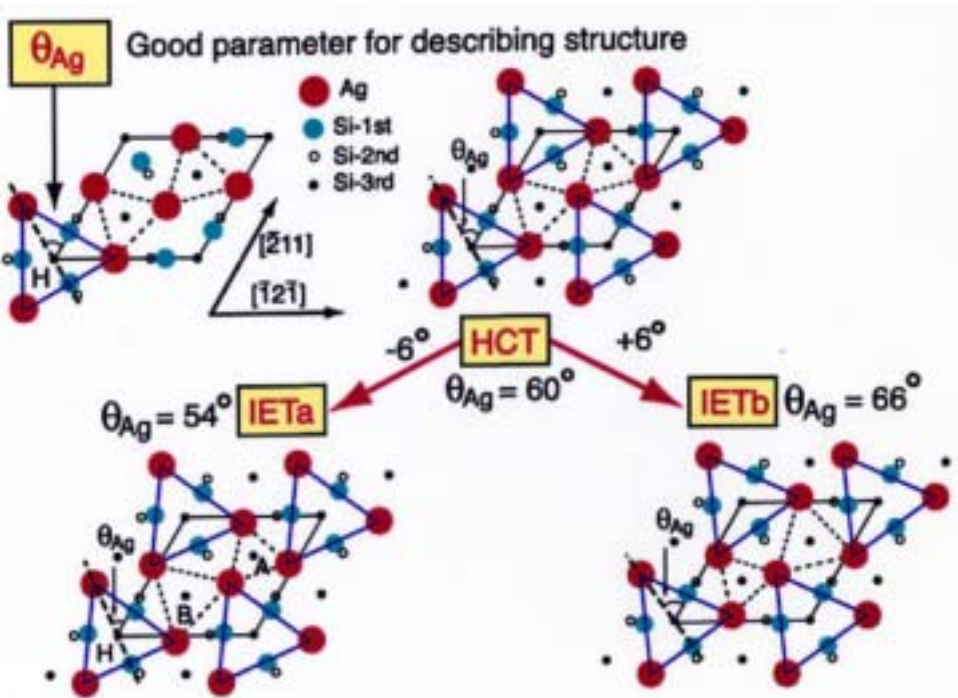
**Van der Waals Force**  
*Calculation with a continuum model*



# *IET structure of Si(111) 3 × 3 –Ag surface*

*STM image of at 62K by Hasegawa*

IET structure and HCT structure

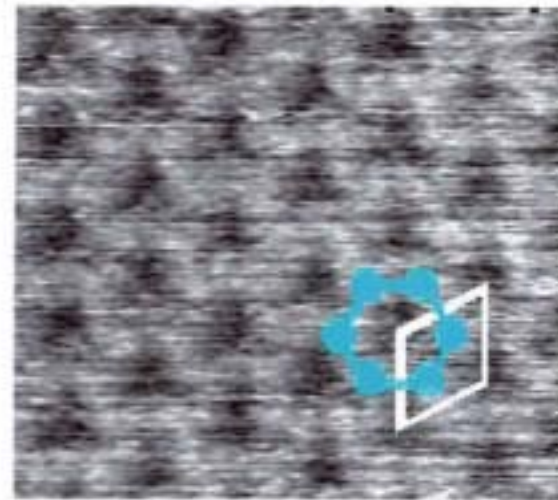
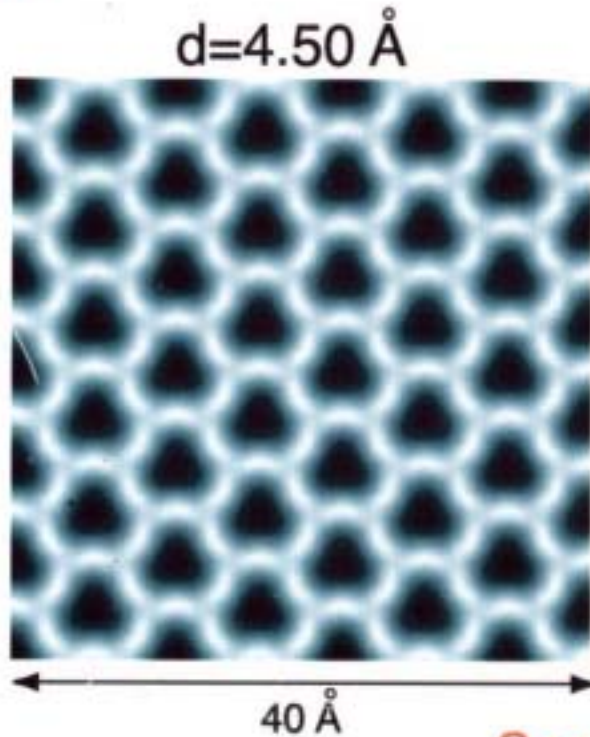


H.Aizawa et al, Surface Sci., 429(1999)509



# NC-AFM Images at Room Temperature

$T = 300 \text{ K}$



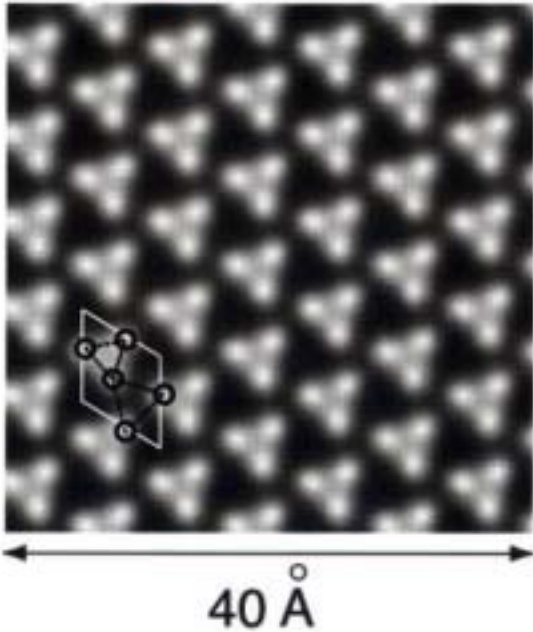
Experiment  
Good Agreement with

Sugawara et al.  
Surf. Interface Anal. 27, 45 (1999)

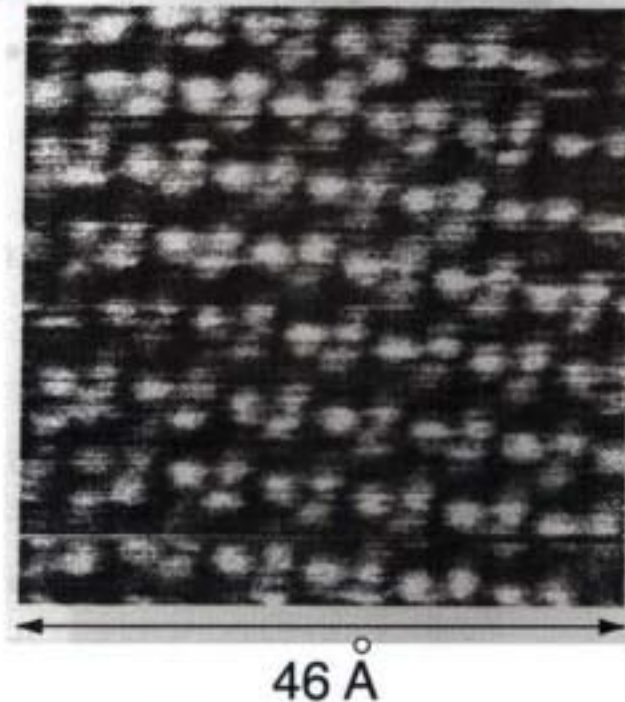
N.Sasaki, S.Watanabe and M. Tsukada

# NC-AFM Image at Low Temperature

Theory (IET Image)



Experiment (Morita, Sugawara Group)



IET structure appears in the low temperature NC-AFM experiment by Osaka Univ. group.

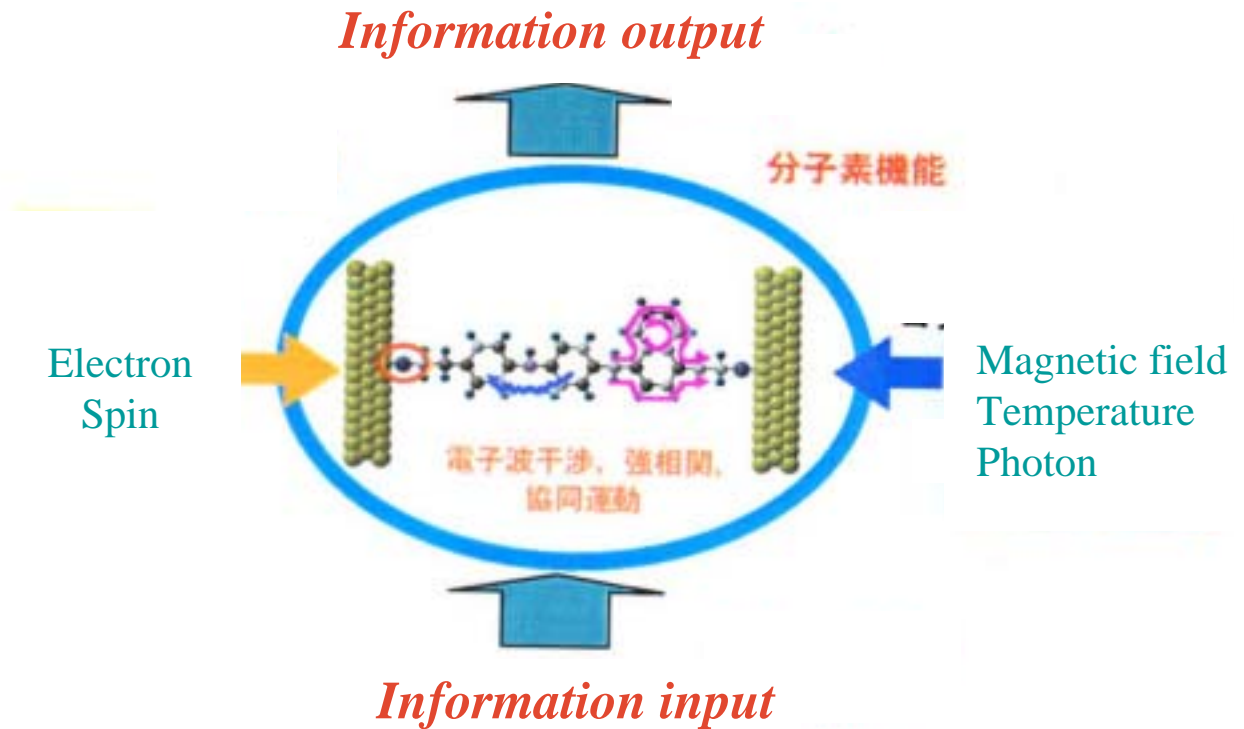
Low temperature experiment is reproduced !!

# Atom bridges and Molecular bridges

Quantum transport  
FET, Switches  
Memories, Sensors  
Molecular spintronics  
Light emission

*Novel quantum devices  
Using coherent states*

**non-locality,  
multiplicity,  
quantum entanglement,  
Instantaneous  
operation,**





# Methods of the calculation for open non-equilibrium systems

*First-Principles Recursion Transfer Matrix Method  
(FP-RTM)*

Lippman-Schwinger, non-local pseudopotential

*Density Functional Method/Tight-Binding Method  
+ Non-equilibrium Green's Function Method  
(DF-TB+NE-GF)*

parameters determined by DFT( TAPP, Gaussian etc)

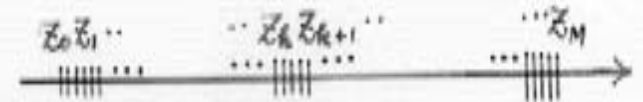
First-Principles

## Recursion Transfer Matrix Method

$$\Psi_n(\mathbf{r}_{//}, z_k) = \exp(i\mathbf{k}_{//} \mathbf{r}_{//}) \sum_m \underline{\Psi_n(\mathbf{G}_{//}^m, z_k)} \exp(i\mathbf{G}_{//}^m \mathbf{r}_{//})$$

Transfer matrix

$$U(z_k) = \begin{pmatrix} \Psi_0(\mathbf{G}_{//}^0, z_k) & \dots & \Psi_N(\mathbf{G}_{//}^0, z_k) \\ \vdots & \ddots & \vdots \\ \Psi_0(\mathbf{G}_{//}^N, z_k) & \dots & \Psi_N(\mathbf{G}_{//}^N, z_k) \end{pmatrix}$$



Matrix three terms difference equation

$$U(z_{k+1}) - K(z_k)U(z_k) + U(z_{k-1}) = 0$$

$$K(z_k) = 2 \begin{pmatrix} 1 + h^2(V_0(z_k) + \frac{|k_{//} + G_{//}^0|^2}{2} - E) & V_1(z_k) & \dots \\ \vdots & \vdots & \vdots \\ V_{-1}(z_k) & 1 + h^2(V_0(z_k) + \frac{|k_{//} + G_{//}^1|^2}{2} - E) & \dots \\ \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \end{pmatrix}$$

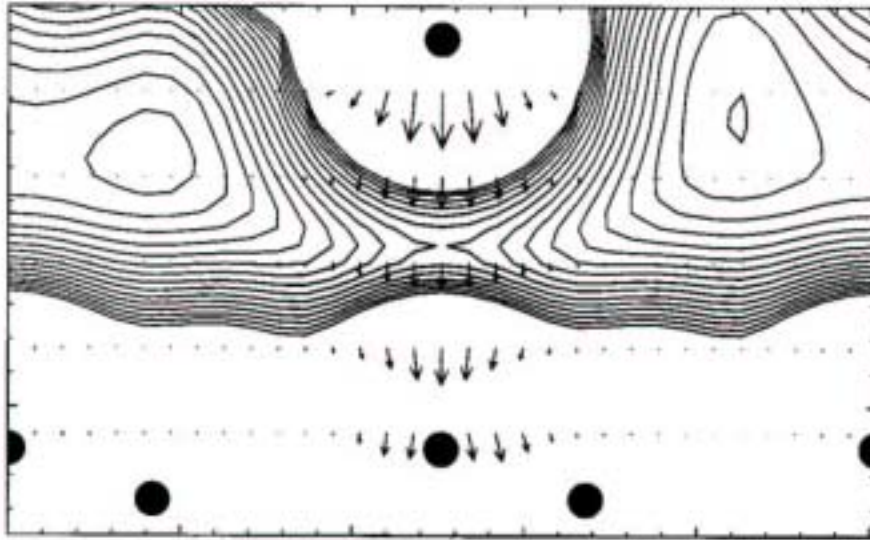
2D Fourier transform of  
DFT potential

Recursive relation

$$R_k = U(z_k)U(z_{k-1})^{-1} \rightarrow R_k = (K(z_k) - R_{k-1})^{-1}$$

*With an appropriate boundary condition, R and U are calculated  
From the right and left electrode wave-functions DFT potential determined.  
This is equivalent to Non-equilibrium Green's function approach.*

# Barrier and Current Density

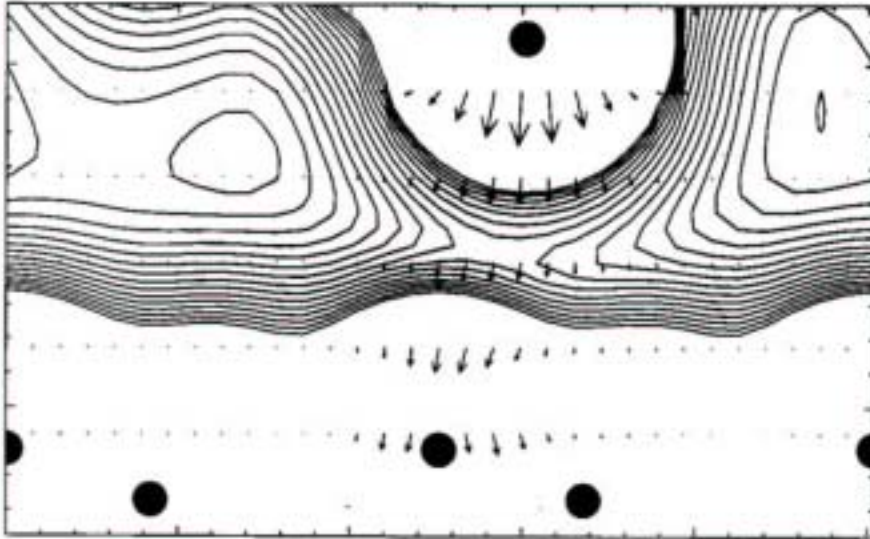


$d=12\text{au}$

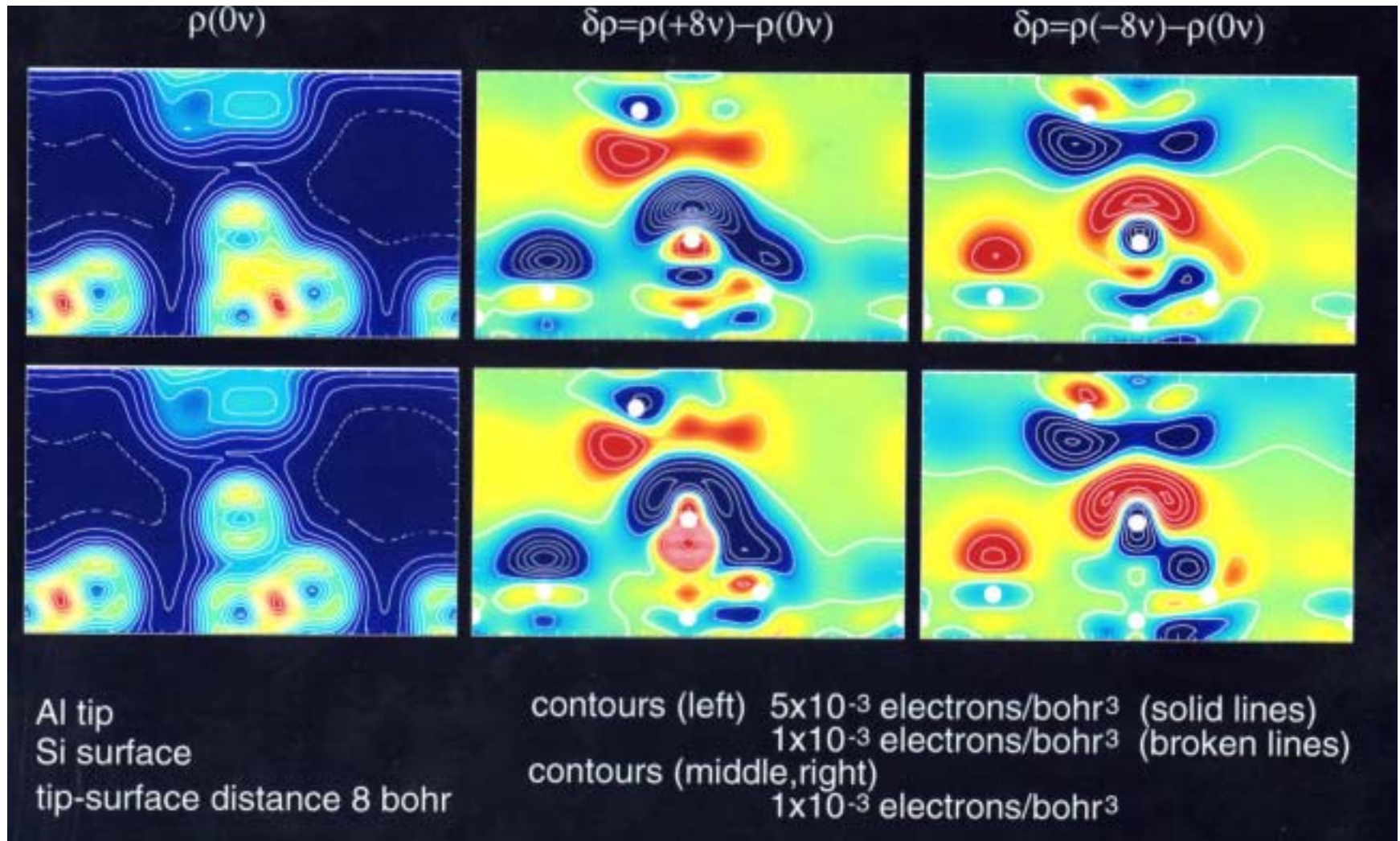
Al tip

$V_s=2\text{V}$

Si surface

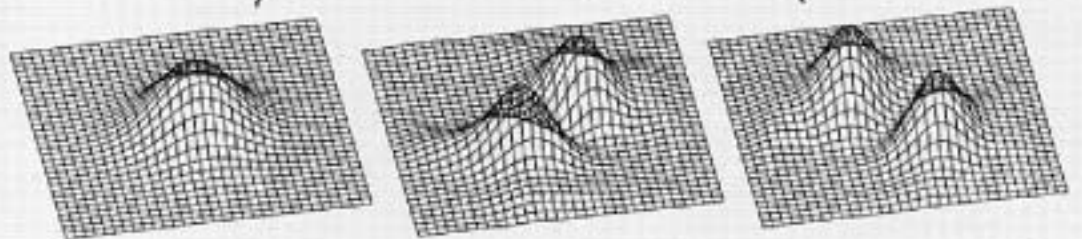
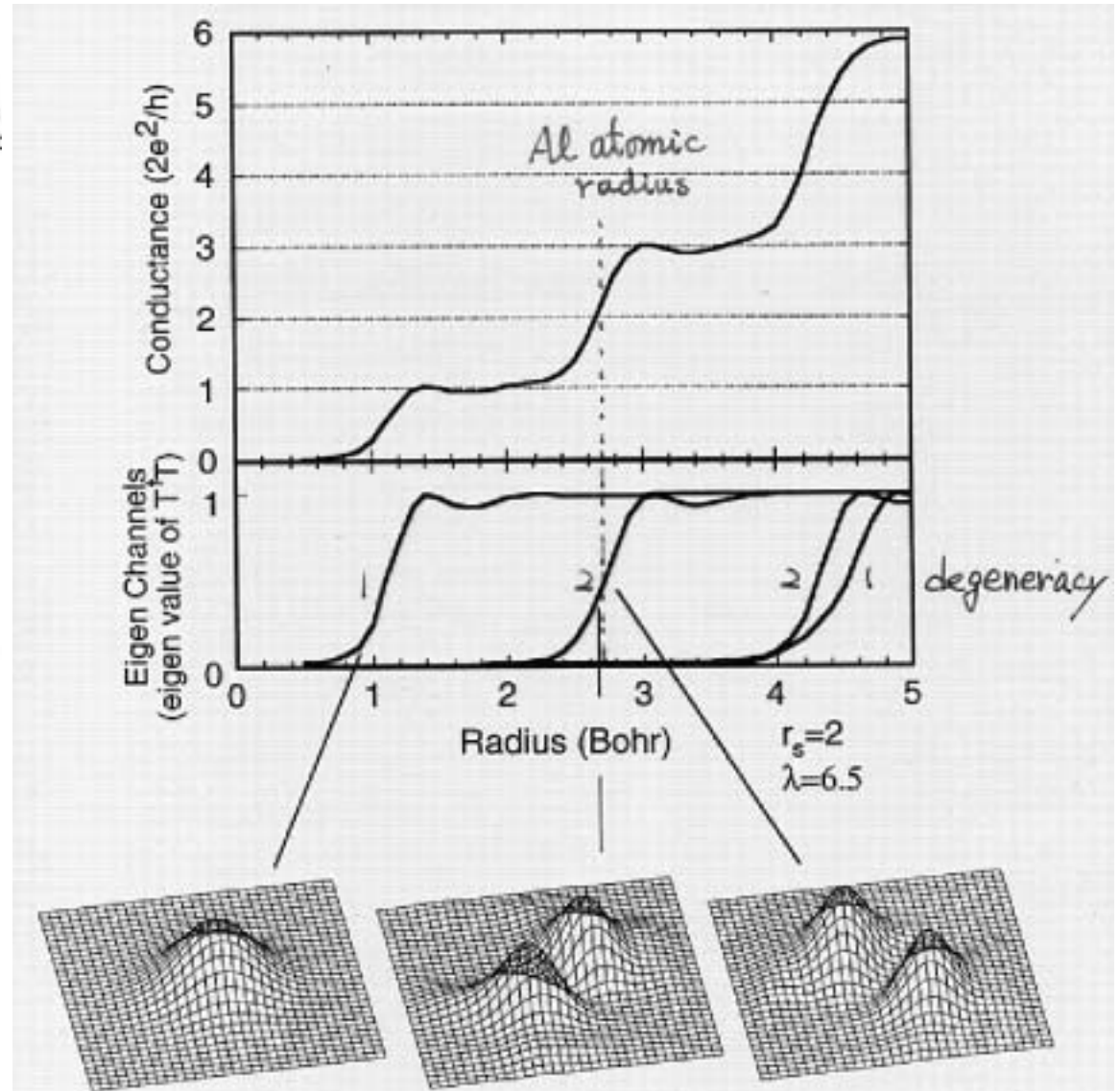
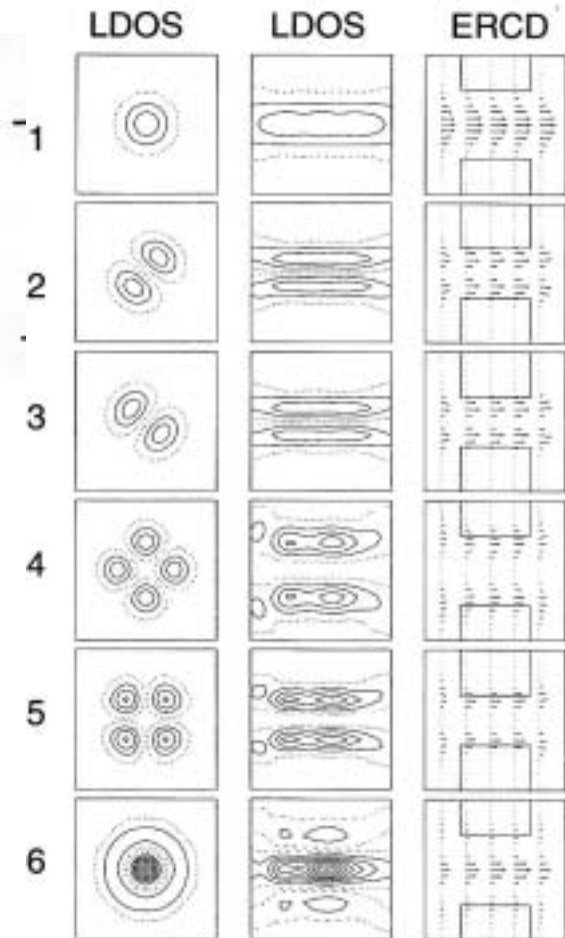
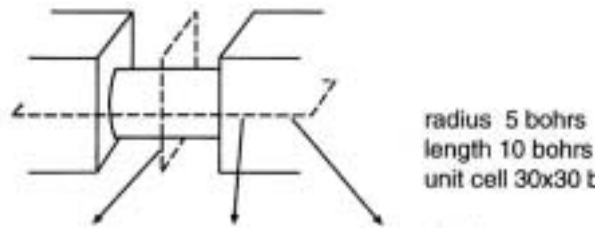


# Al探針によるSi表面からの原子引き抜き



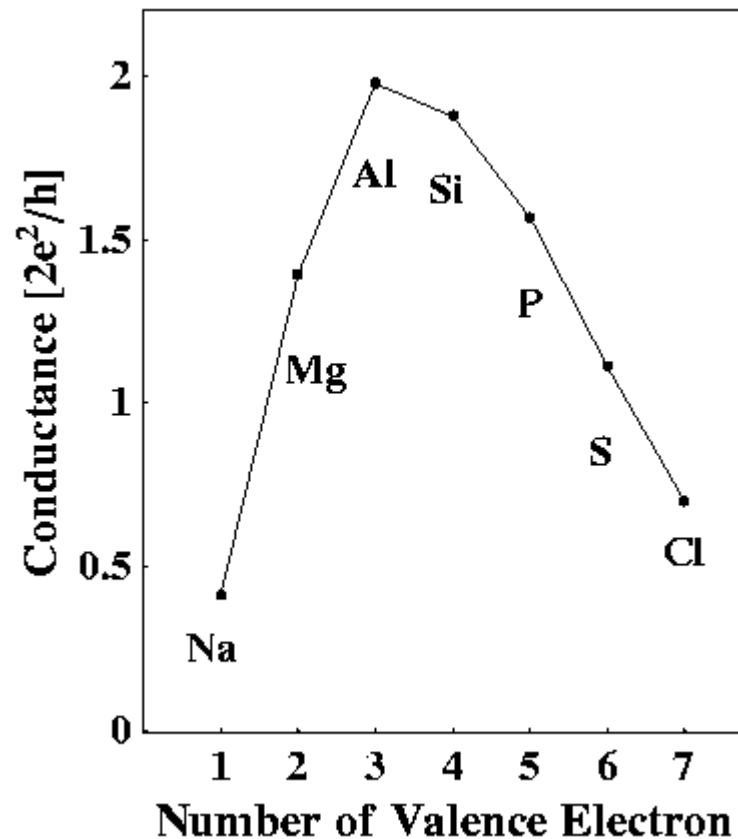
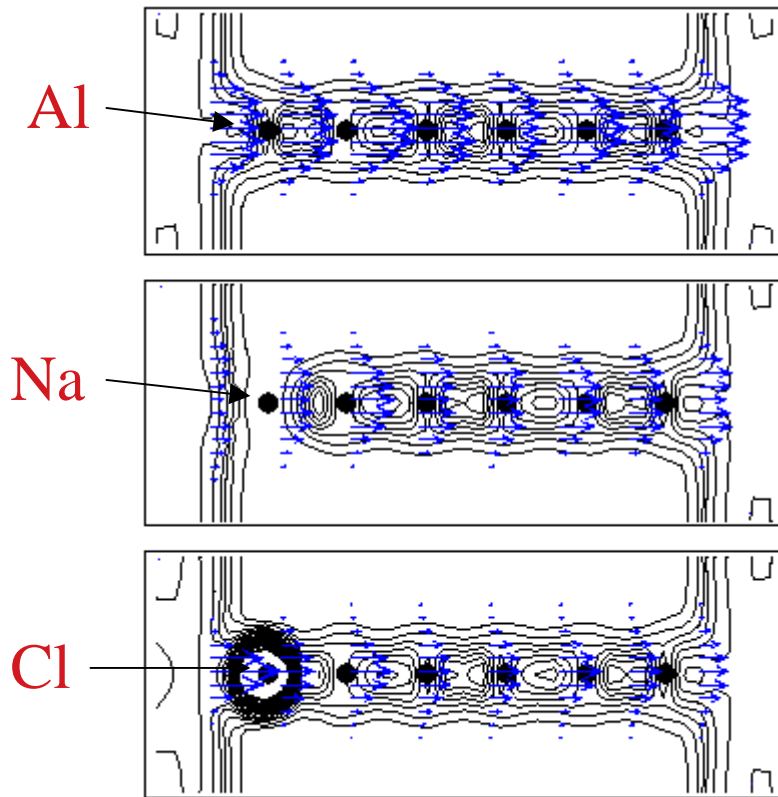


# Conductance of Jellium Cylinder



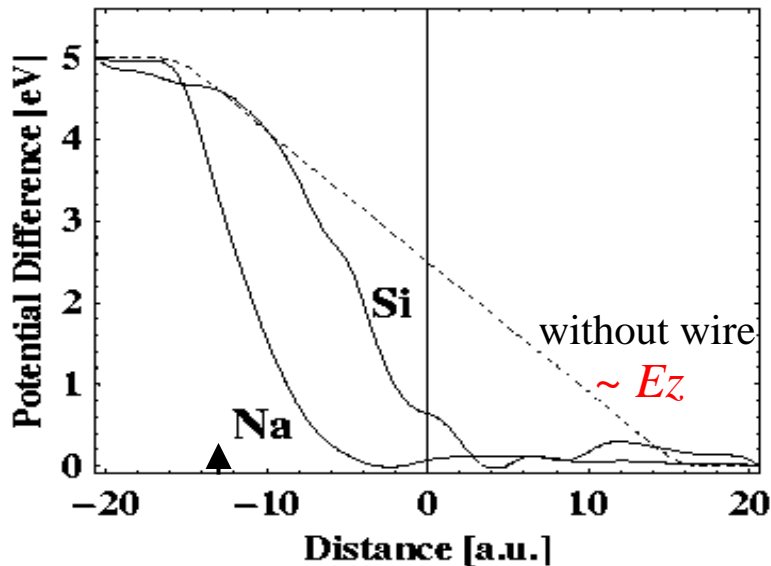
# Conductance through Al atomic-wires with various atoms mixed at contacts

K.Hirose, N.Kobayashi, M.Tsukada, to be appeared/ nonlocal p.p.

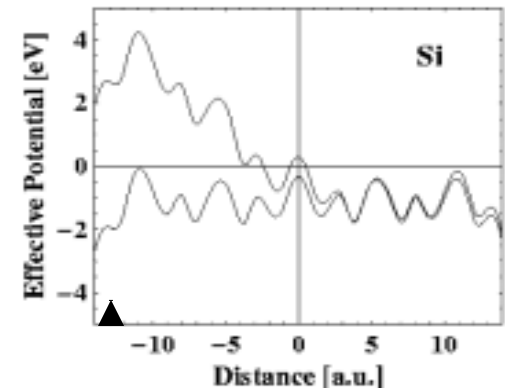
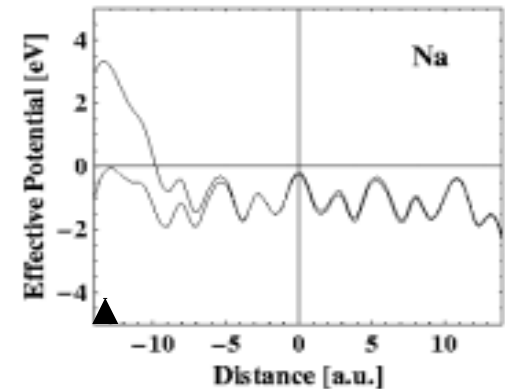


# Where does the bias drop in the wire ?

## Potential difference

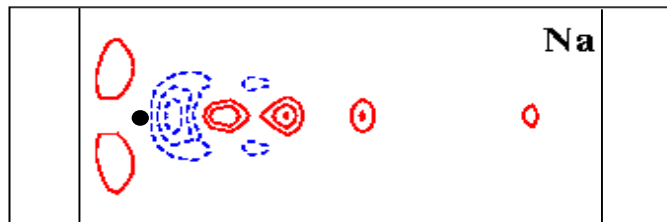


Bias = 5V

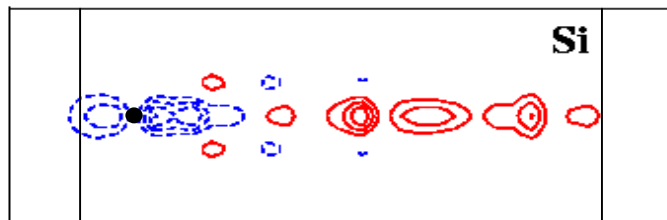


## Charge difference ( $\rho(r,5V) - \rho(r,0V)$ )

Local polarization (s-orbital)



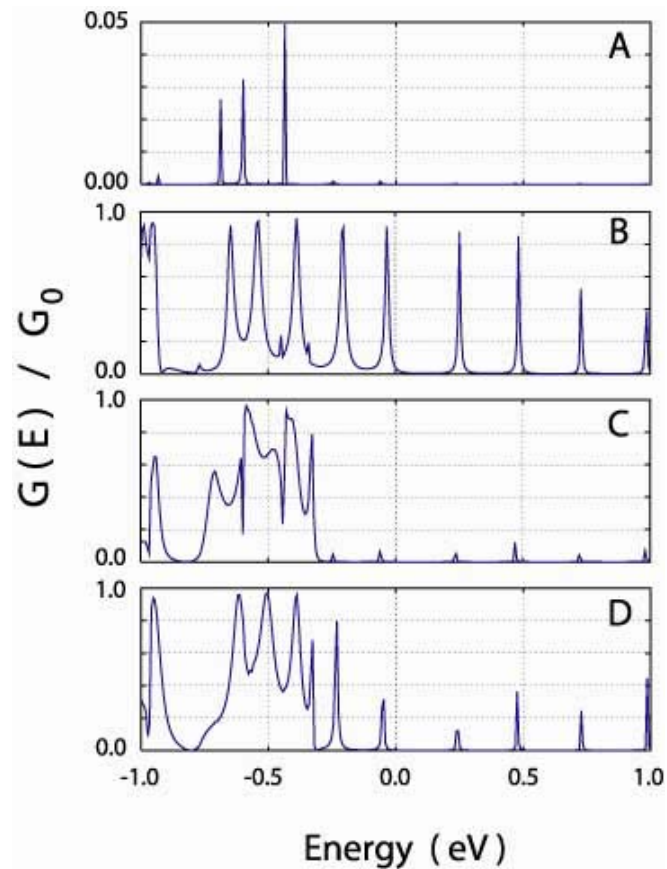
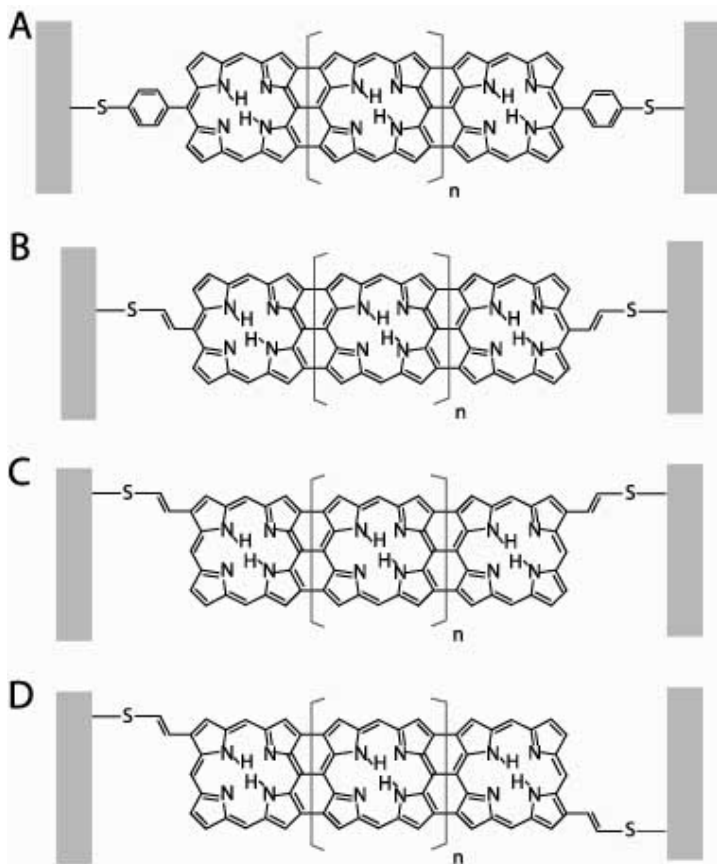
Spread-out (p-orbital)



Bias drop is determined by the local polarization.

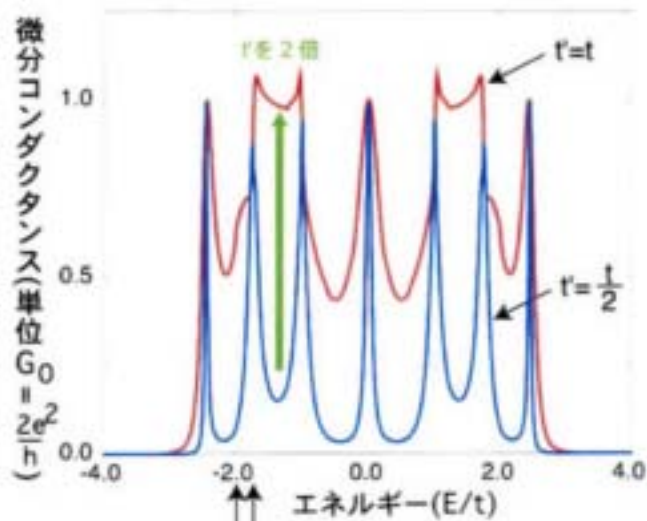
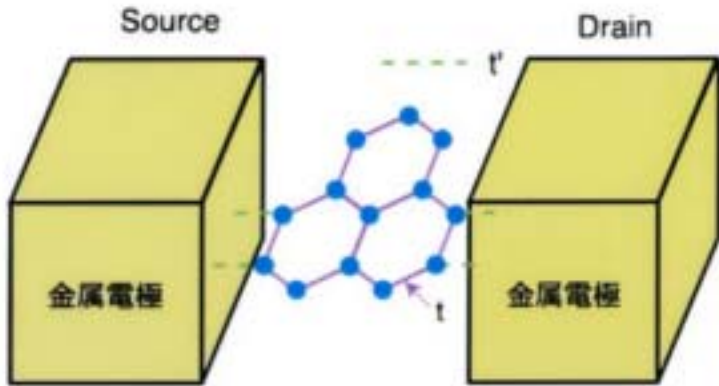
One impurity gives a significant influence!

# *Transmission Spectra of tape-porphyrin molecules*

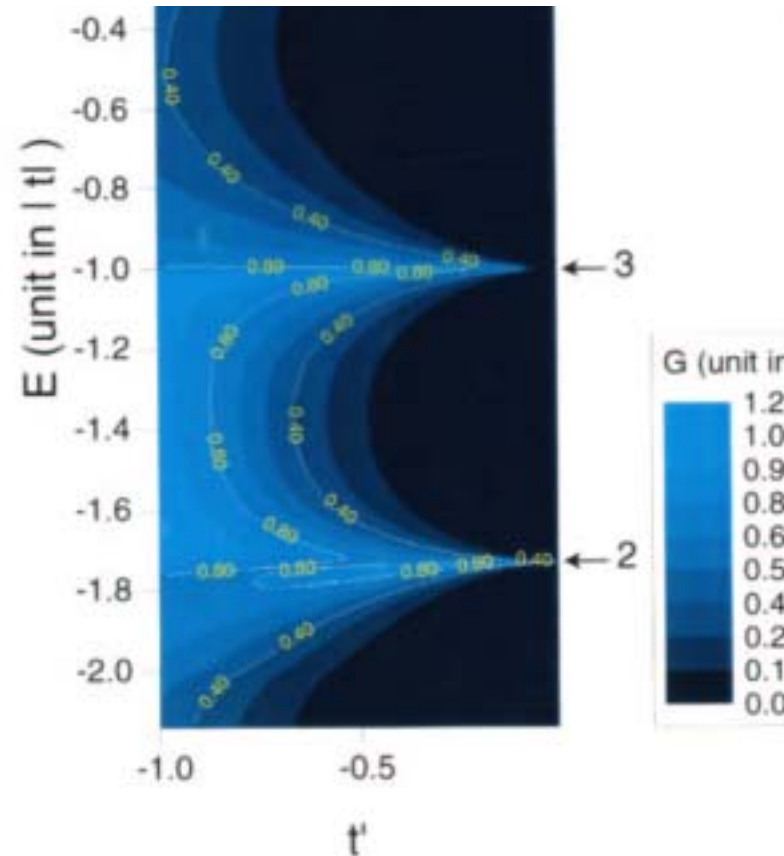




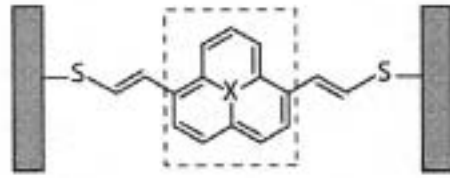
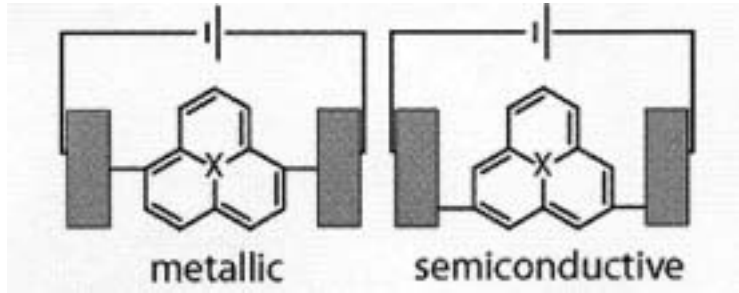
# Transmission spectrum of phenalenyl molecule



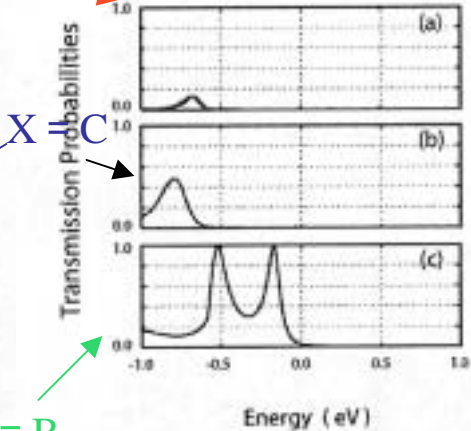
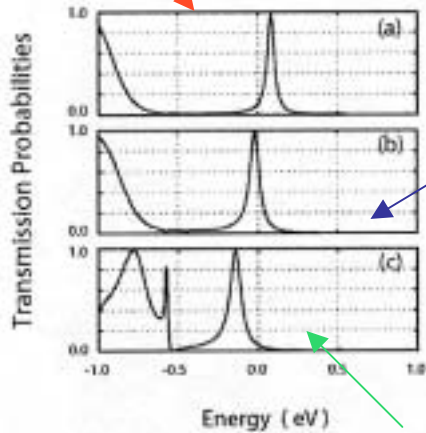
$t = \frac{1}{2}$  のときは、**共振トンネル機構**で電流が流れるが、  
 $t = t$  のときは**金属化した分子**の中を電流が流れる。



# Phenalenyl based molecules

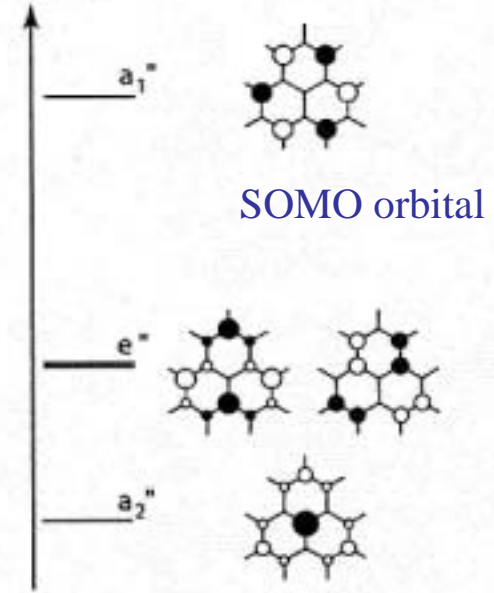


X = N

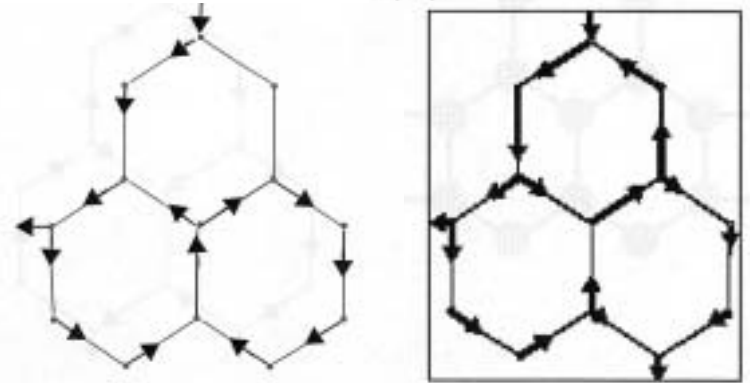


X = B

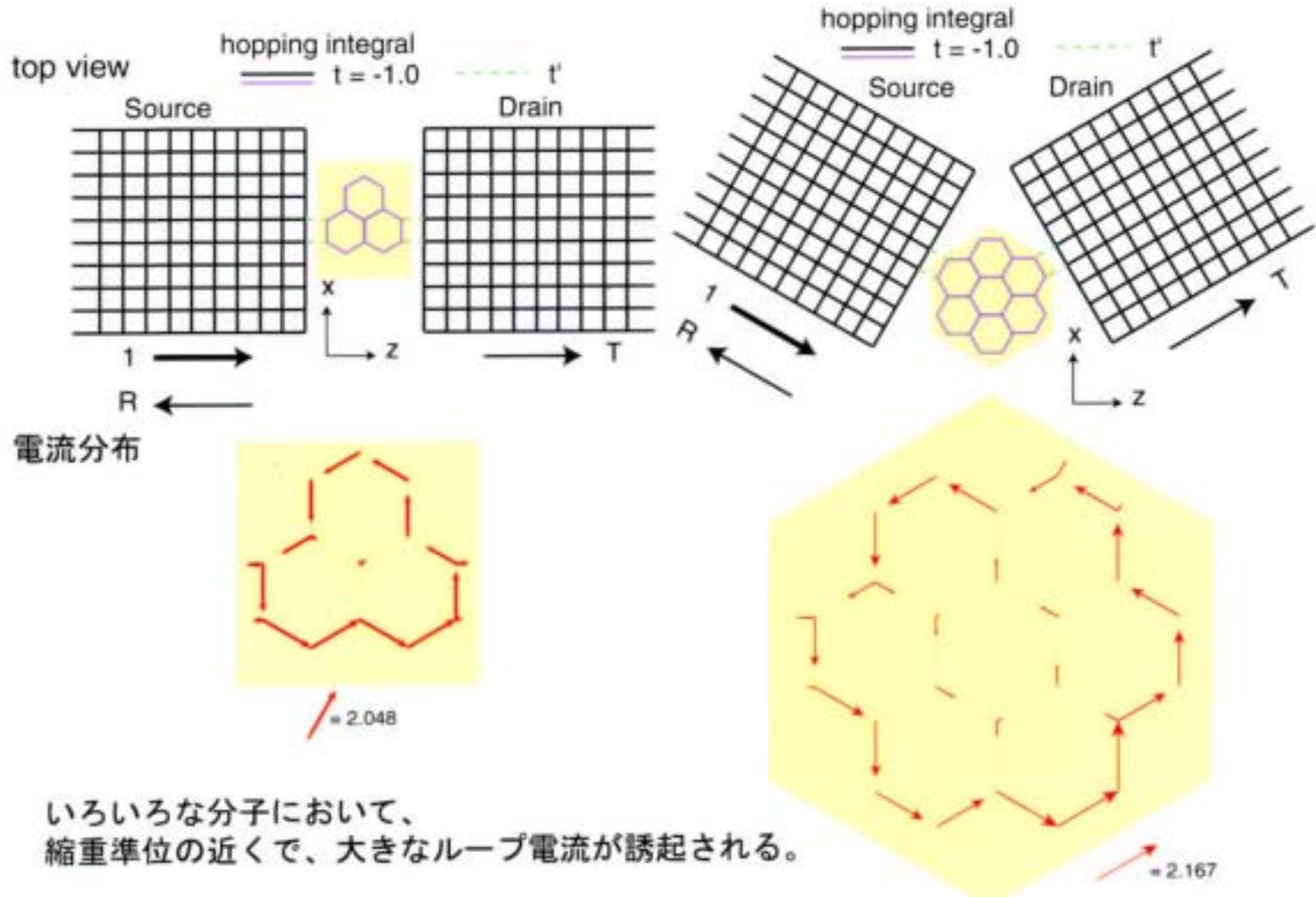
Energy



(b)

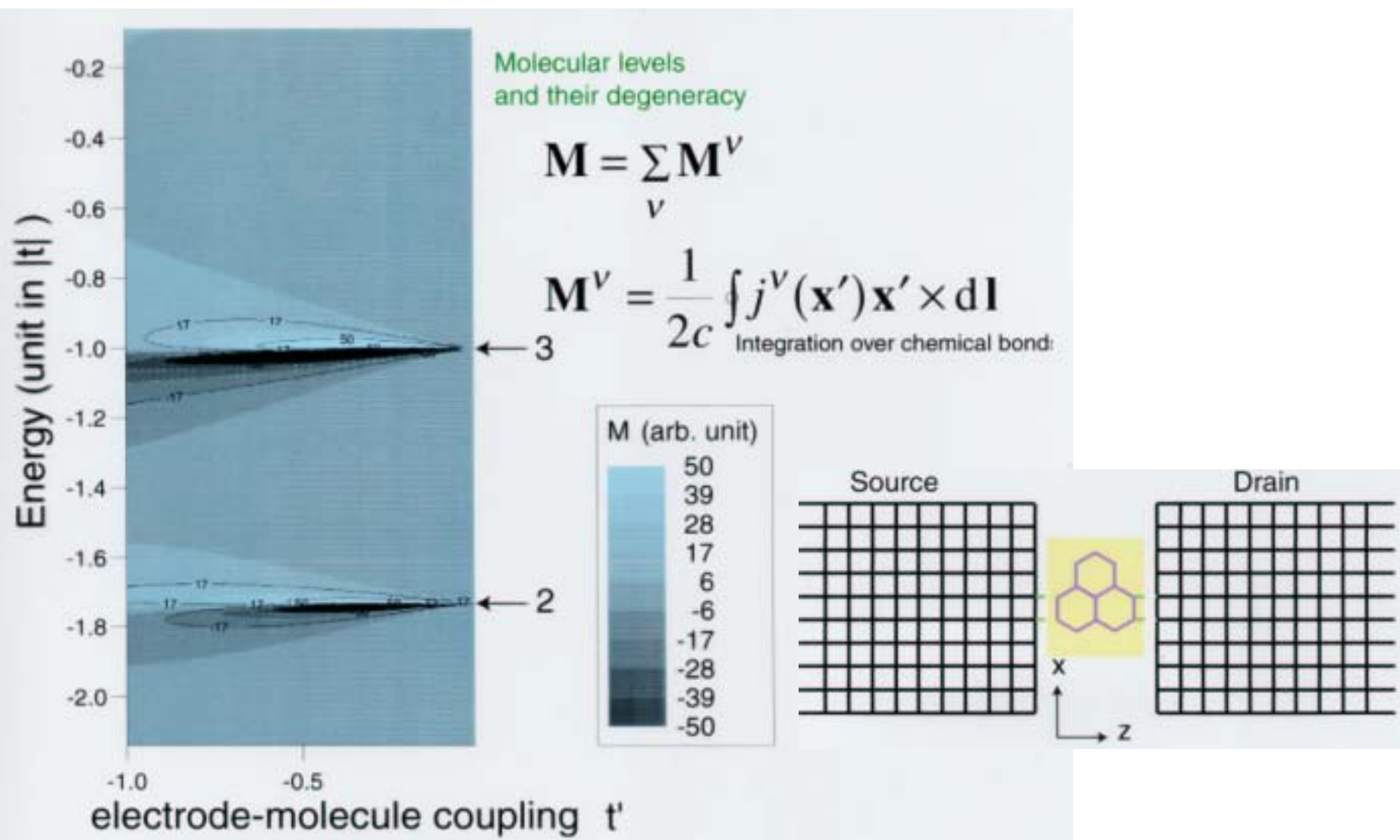


# Induced large loop current near degenerate levels

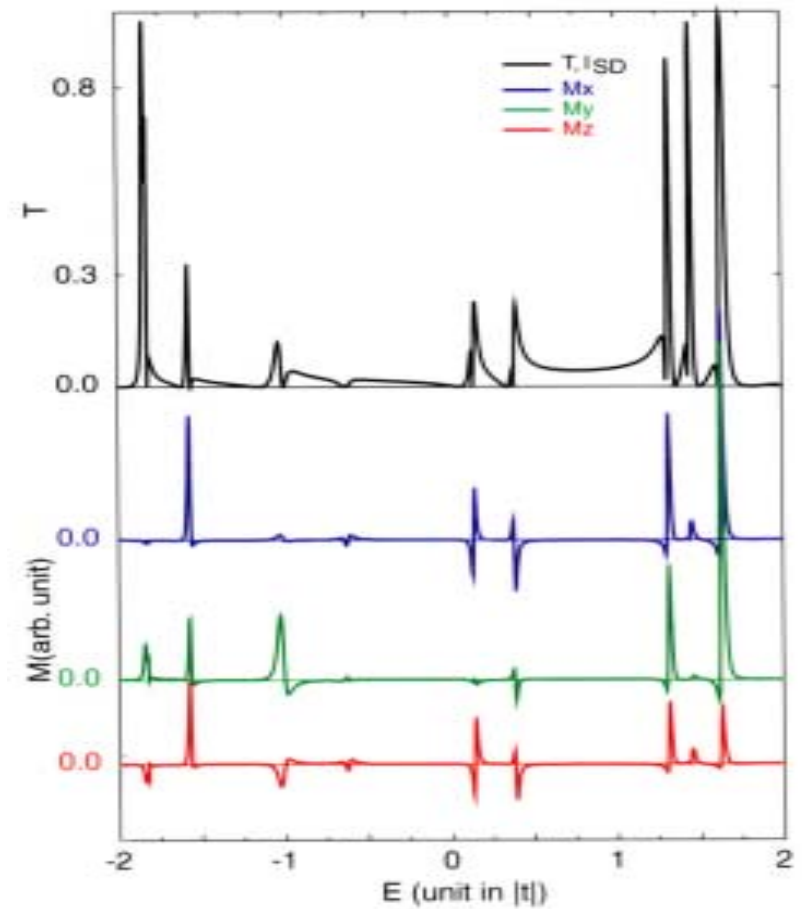
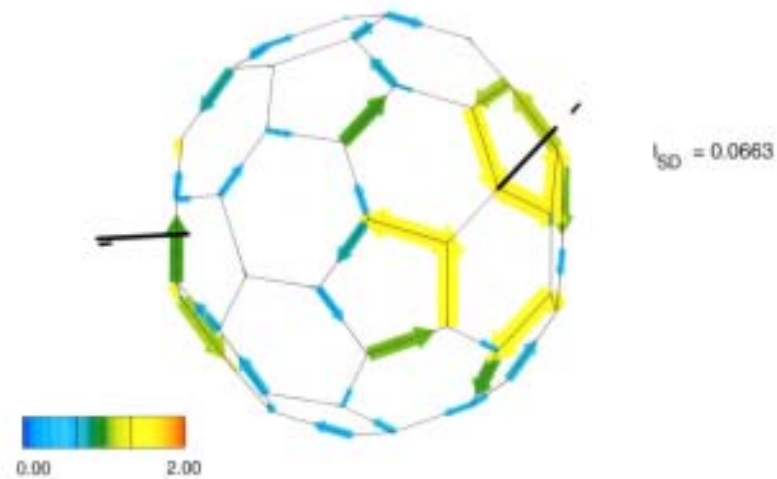
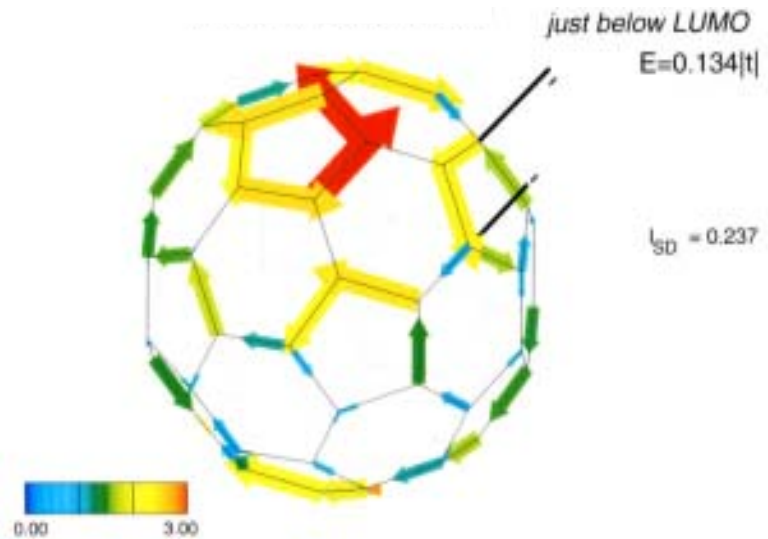


いろいろな分子において、縮重準位の近くで、大きなループ電流が誘起される。

# Condition for the large loop current



# Transmission of Fullerene $C_{60}$ and loop current



# 分子デバイスのシミュレーション課題

- \* 基板電極との接続

- \* 興味ある分子の探索

- \* 分子架橋3端子系

(量子ゲート/スイッチ、量子機能)

- \* スピン、永久電流、内部電流、動的過程

- \* 分子架橋近藤系

- \* デコヒーレンス、分子Qビット

- \* 単電子過程とコヒーレンス過程の協奏



将来展望

