Density-Functional Approach to Nano- and Bio-Materials

- Carbon Nanotubes on Metal and Si Surfaces
  - Chemical bonding/Electron transfer at interfaces modulate their propertie

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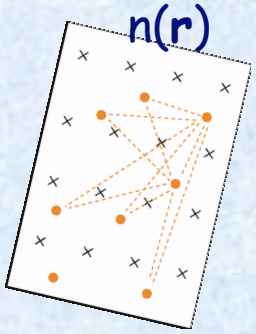
    [Kamiya, Boero, Tateno, Shiraishi & Oshiyama: J Am Chem Soc 129, 9663 (2007)]

Density Functional Theory (DFT)

The total energy of an interacting electron system under nuclear potentials $v_{\mathbf{nucl}}$ with its electron density n is exactly given by:

$$E[n] = <\Psi \mid T + V\mathrm{nucl} + V\mathrm{ee} \mid \Psi>$$

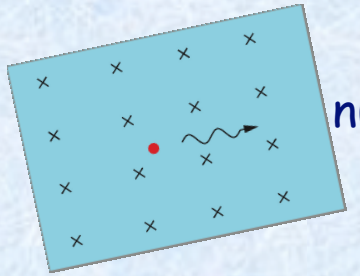
$$= T_s[n] + \int v_{\mathrm{nucl}}(\vec{r})\, n(\vec{r})\, d\vec{r} + \frac{1}{2}\int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}\, d\vec{r}' + E_{xc}[n]$$



By introducing a non-interacting quasi-particle system which has the density n identical to the above, we get Kohn-Sham equation:

$$[-\frac{1}{2}\nabla^2 + v_{\mathrm{nucl}}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}(\vec{r})\,]\varphi_j(\vec{r}) = \varepsilon_j(\vec{r})$$

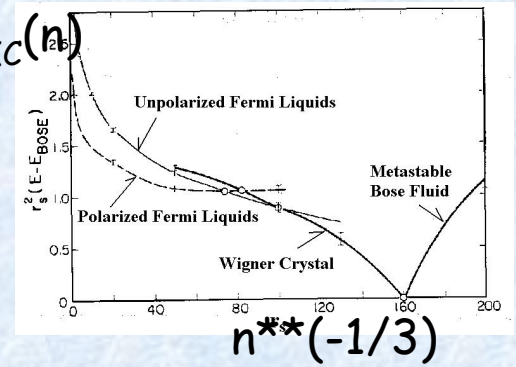
$$n(\vec{r}) = \sum_j |\varphi_j(\vec{r})|^2$$

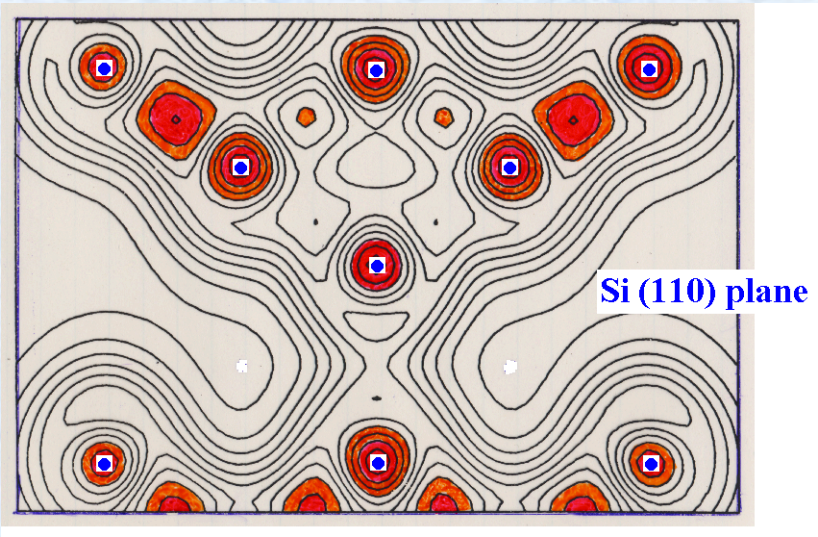


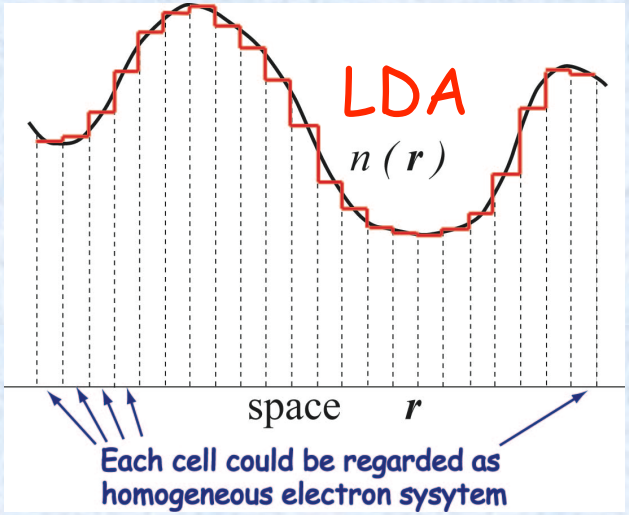
Density Functional Theory: approximation

Nobody knows the exact form of E_{XC} . Then,

- Local (Spin) Density Approximation
  (LDA, LSDA)
- Generalized Gradient Approximation
  (GGA)
- .....







$$E_{XC}[n(\mathbf{r})] = \int \varepsilon_{XC}(n(\mathbf{r}))\, n(\mathbf{r})\, d\mathbf{r}$$

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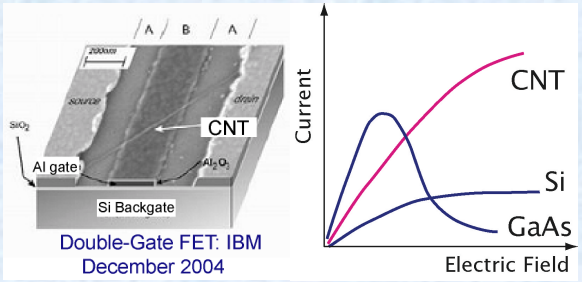
Hybrid Structures of Carbon Nanotubes and Others



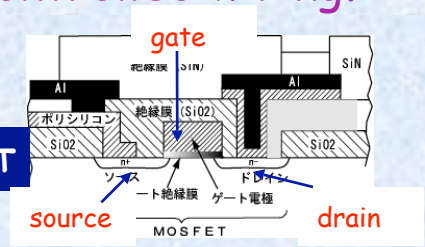
Characterization and control of interfaces are crucial in technology:

CNTs and conventional metals

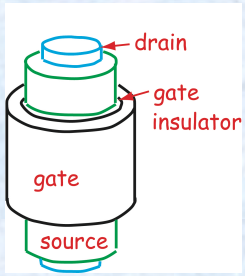
Si surfaces are wombs of everything that supports our electronic lives:

CNTs on Si surfaces

Possibility of controlled wiring?



Si MOSFET



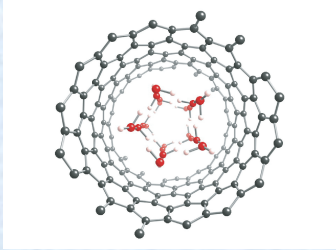
CNT as a Booster in Post-scaling (more-than-Moore) Si Technology:

Capacitance in Nanostructures

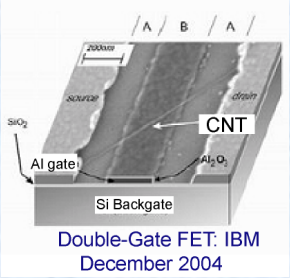
What about water?

Medical engineering application: e.g drug delivery

Behaviors of the material most familiar to us in confined space



(10,0) Semiconducting CNT on Ca and Al



Double-Gate FET: IBM December 2004

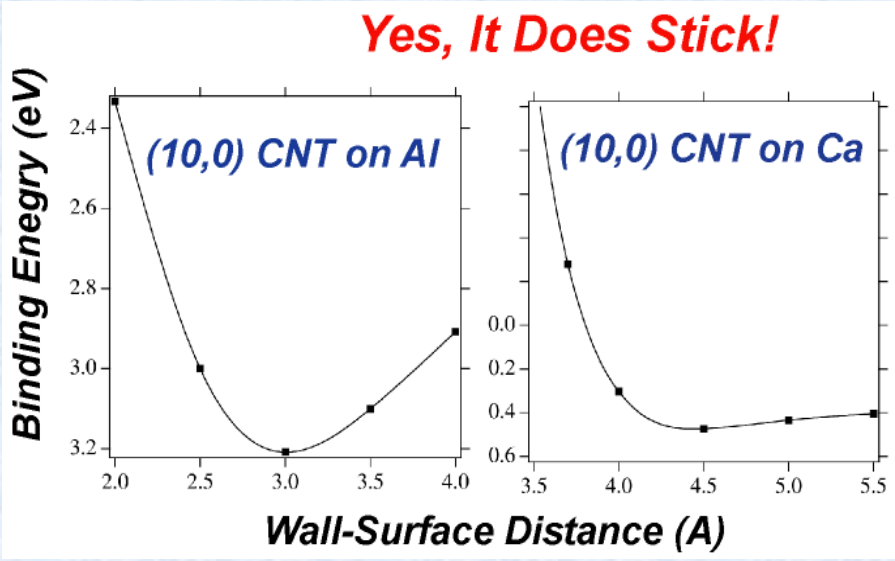
Various electrodes in current CNT-FET: Pt, Au, Ca, Al, Pd etc

But… Ca ⇒ spontaneous n-type doping

Pd ⇒ spontaneous p-type doping

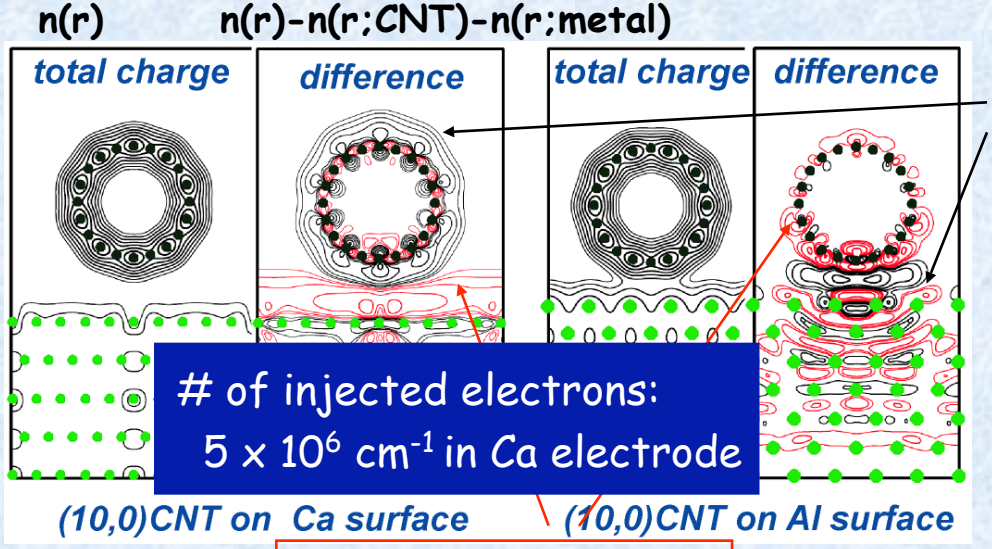
LDA Calculations for 12-layer repeating slabs with 20 A vacuum inbetween

- **Normconserving pseudopotentials + 45-Ry plane-wave basis set**
- **Ca and Al (100) surfaces**
- **CNT 3% elongated along tube axis**
- **diameter of (10,0) = 7.83 A**

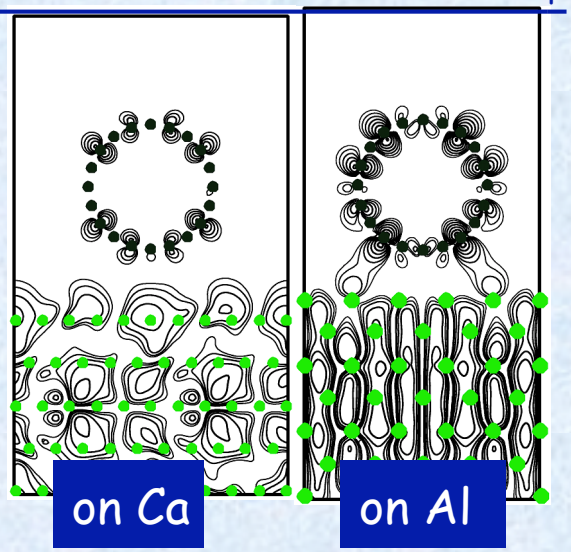


- ✓ CNTs stick on both metals
- ✓ Adsorption distance and energy are different
  - Al: 3.0 A & 3.21 eV
  - Ca: 4.5 A & 0.47 eV

Electron Density and Electron States near Fermi Energy



Kohn-Sham orbitals near E_F



p-character is essential to form covalent bonds

Properties sensitive to difference in chemical elements

- work function, orbital character

are decisive.

⇒ predictable in a sense

In contrast to conventional metal/semicon interfaces where E_F pinning takes place due to

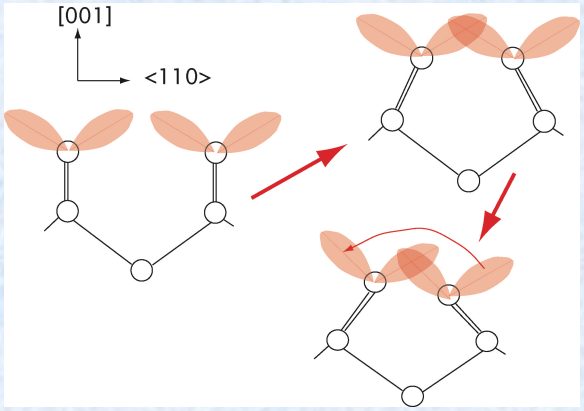
Si Surface that is a Stage of Fabrications

CNT-Si hybrids

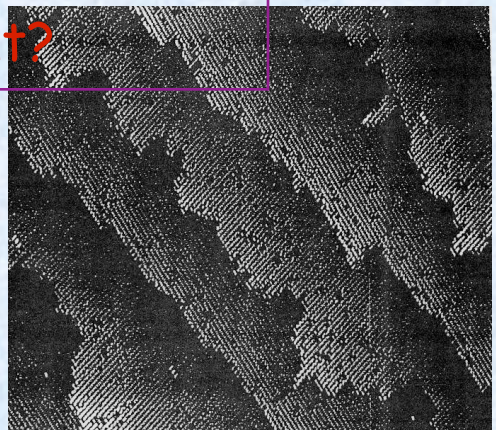
✓ Effects of local chemical environments

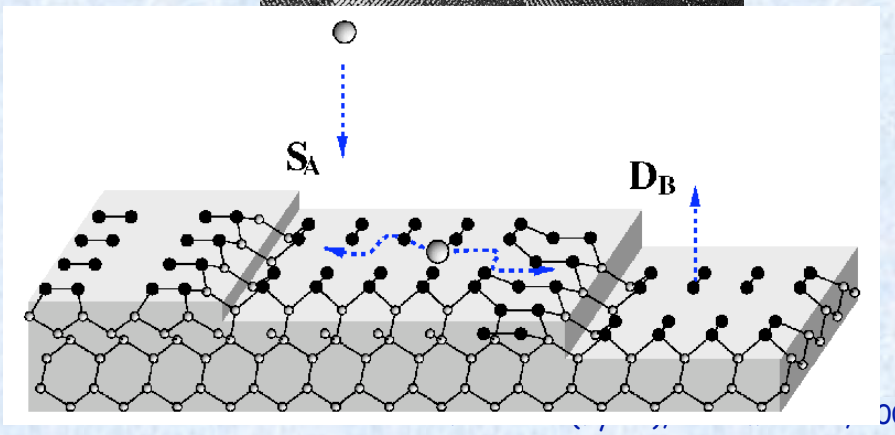
✓ Role of step morphology

Possibility of CNT alignment?

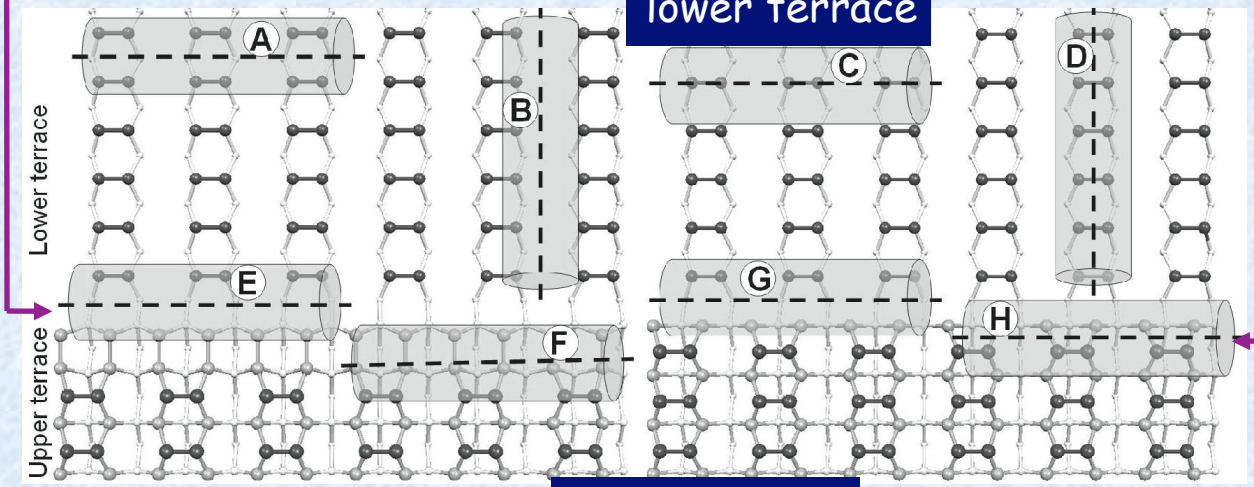


Si (001) surface

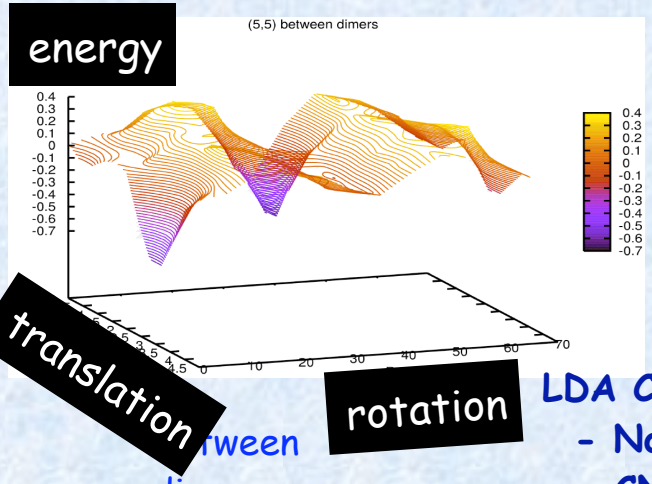




Exploration of Adsorption Geometries: (5,5) CNT on Si(001)



CNT Adsorption sites?
A, B, C, D on Terrace,
E, F, G, H near
double-layer Step

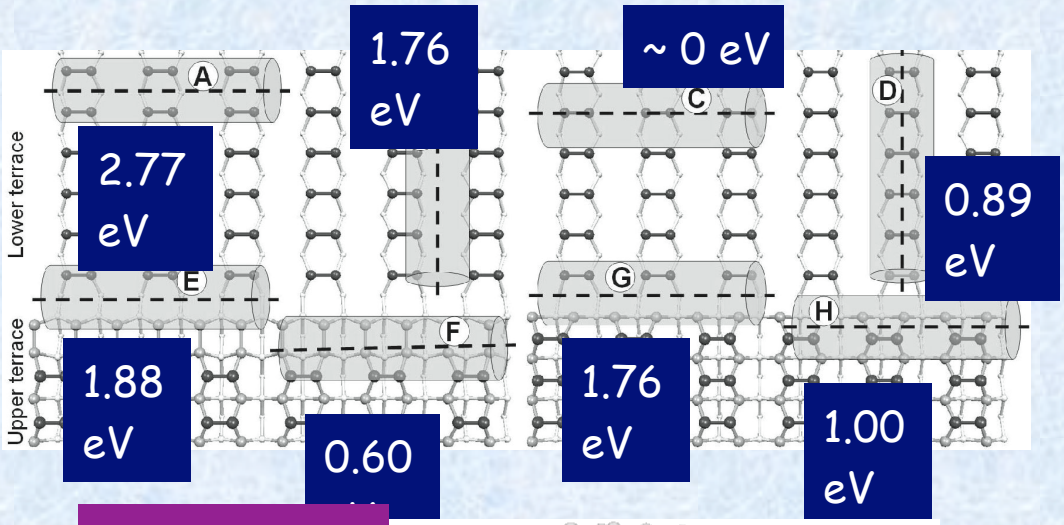


Exhaustive Search Without Relaxation
+
Full Relaxation at Candidate Sites

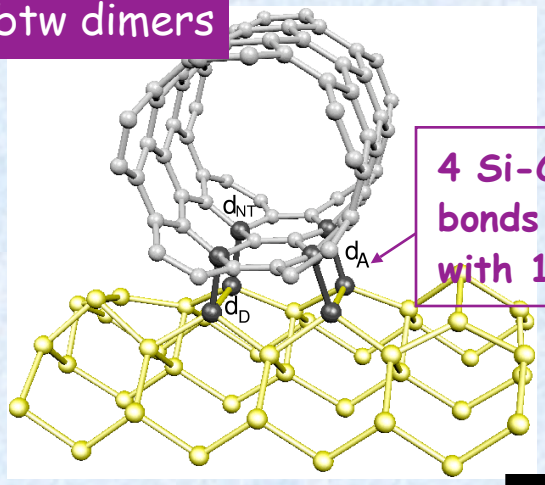
LDA Calculations for repeating slabs with 10 A vacuum inbetween
- **Normconserving pseudopotentials + 40-Ry plane-wave basis set**
- **CNT 3% elongated along tube axis**
- **diameter of (5,5) = 6.78 A**

Energetics and Structures of (5,5) CNT on Si(001)

Adsorption Energy of CNT per 3 primitive-cell length

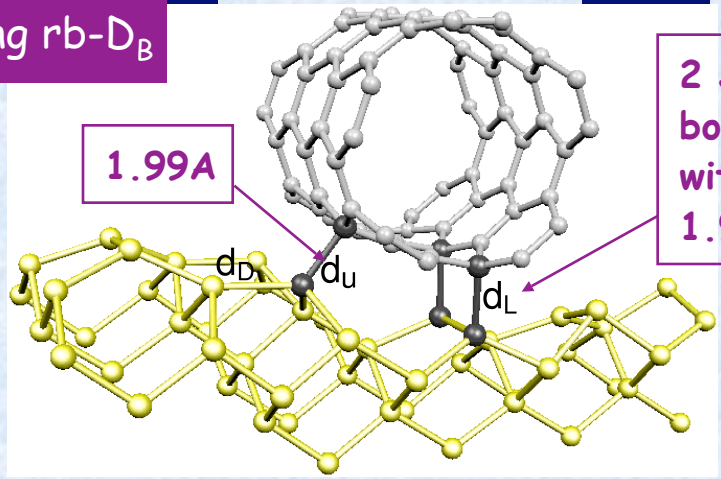


A: btw dimers



4 Si-C bonds with 1.97A

E: along rb-D_B



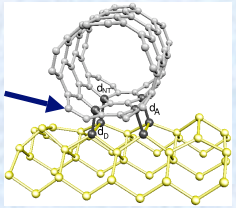
2 Si-C bonds with 1.96A

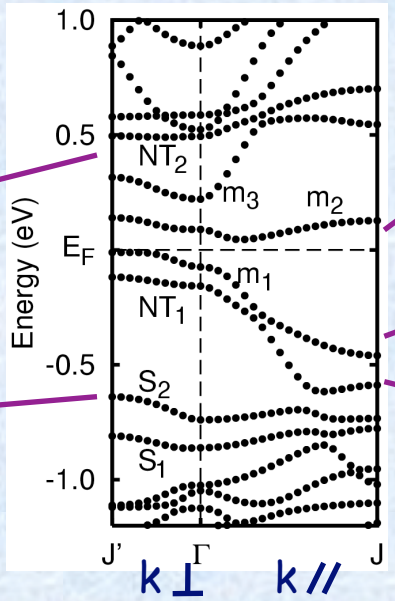
Cf) Si-C bonds in SiC = 1.89

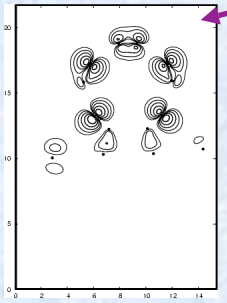
Thicker tubes may favor step edges
By forming bonds with upper and lower atoms

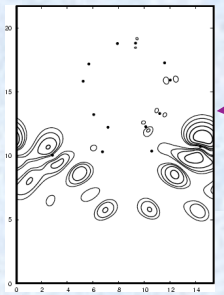
Modification of Electronic Structure

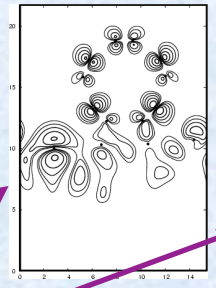
Site A:
Si-C bond Formation

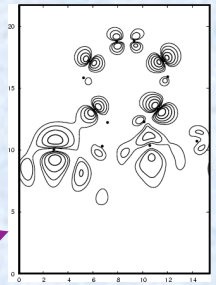


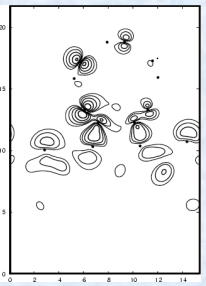






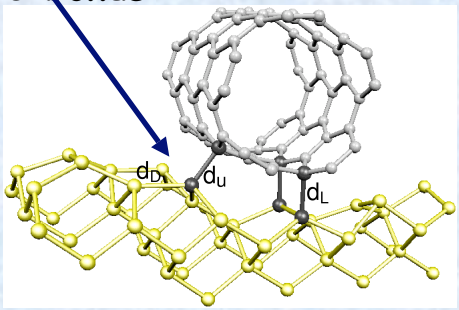


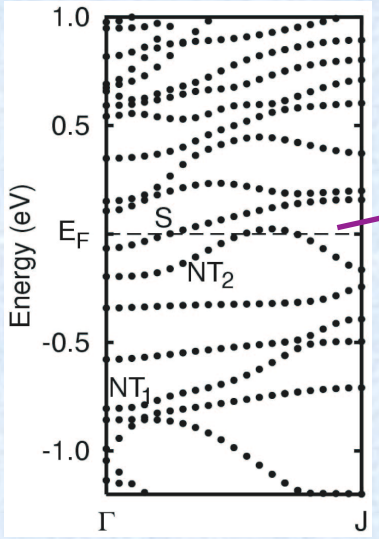


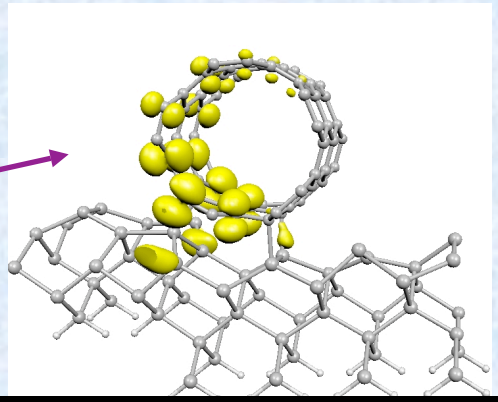


Si-C bond formation introduces sp3 configuration in πnetwork, hereby πopens the gap

Site E:
Along D_B step
Si-C bonds







Possible One Dimensional Conduction Free From Instability

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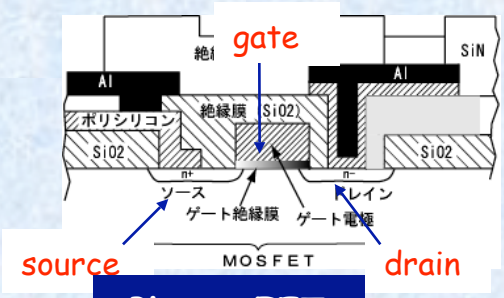
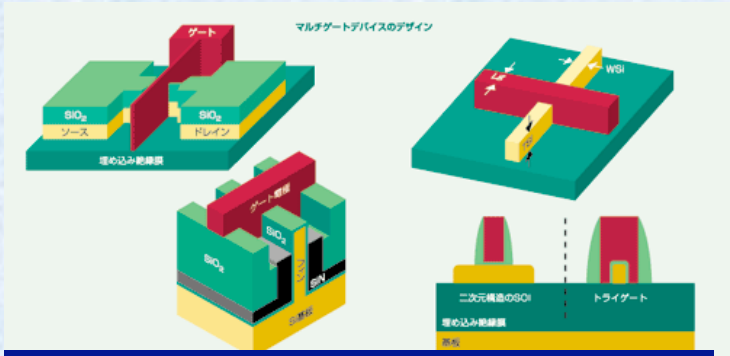
Capacitance that is Crucial in Circuit Design

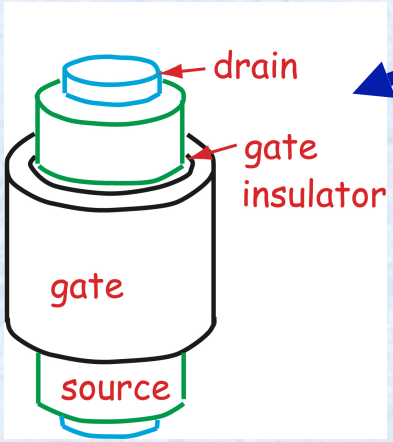


Planer FET

More Gates to increase channels!

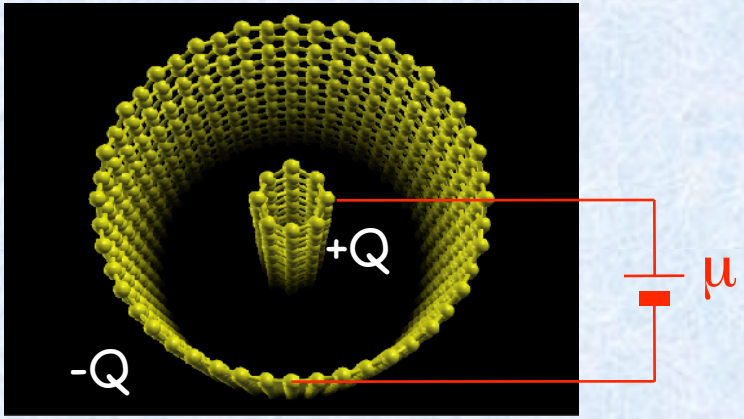


Double-gate Multi-gate FETs



Surrounding-gate FET

Doubel-walled CNT Capacitor as an first or ultimate example of cylindrical nano structure

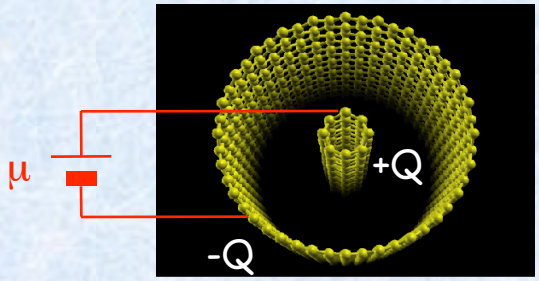


Bias Voltage μ

Technology booster?

How to Calculate Capacitance

$$E_{\mathrm{DFT}}[n(\mathbf{r})] \; - \; \mu \, \Delta N[n(\mathbf{r})]$$



Variational principle wrt Electron Density

$$H_{\mathrm{KS}} = -\frac{\nabla^2}{2} + V_{\mathrm{nuclei}}(\mathbf{r}) + \frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' + V_{\mathrm{ex-cor}}[n(\mathbf{r})] \; - \; \mu \; (\mathbf{r})$$

Chemical Potential Difference Provided by Power Source

Uchida et al, Phys Rev B 74, 035408 (2006)

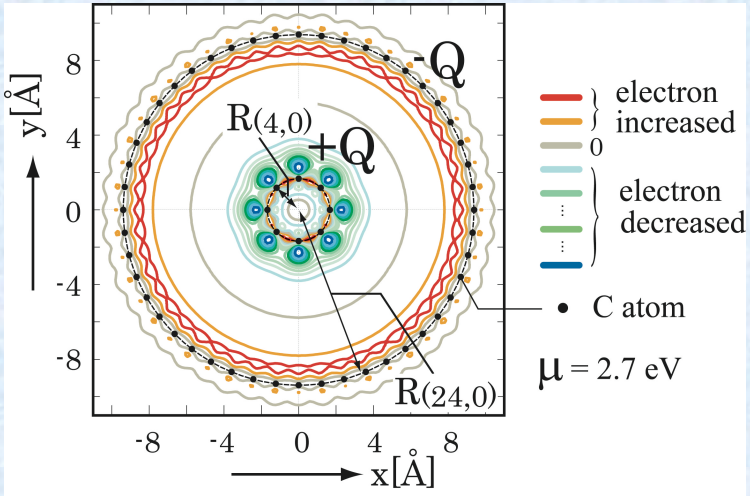
Classical Electrostatic Analog

$$E(Q) = \frac{Q^2}{2C} - QV \longrightarrow Q = CV$$

Minimization wrt Q

QV is work done by power source

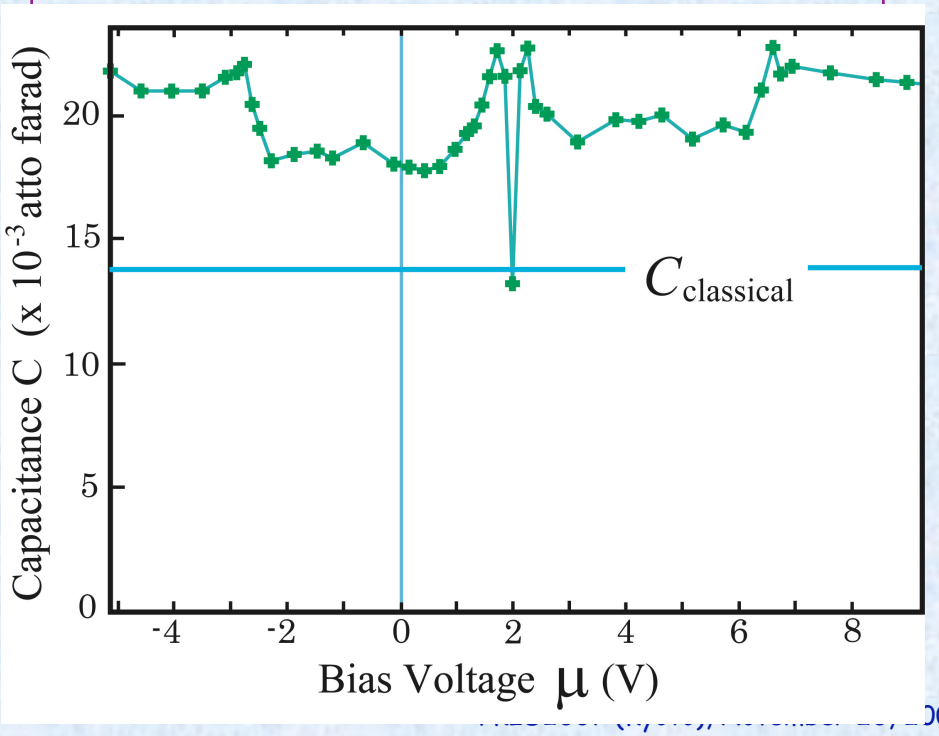
Capacitance of Double Walled CNT



Charge Redistribution in (4,0)@(24,0) DWCNT under Bias Voltage μ

[R(4,0) = 1.7 Å, R(24,0)=9.4 Å]

Capacitance $C = d(-e\,\Delta N)/d\mu$

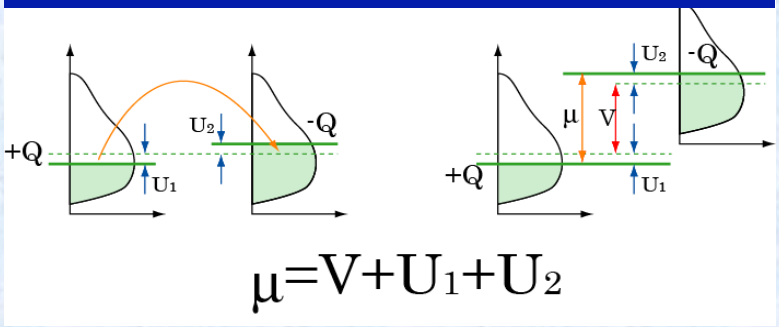


- ✓ C depends on bias voltage with spiky structures
- ✓ C is larger than the classical value

$$C_{cla} = \frac{2\pi\varepsilon_0 d_{unitcell}}{\ln[R(24,0)/R(4,0)]}$$

Quantum Effect I: Density of States

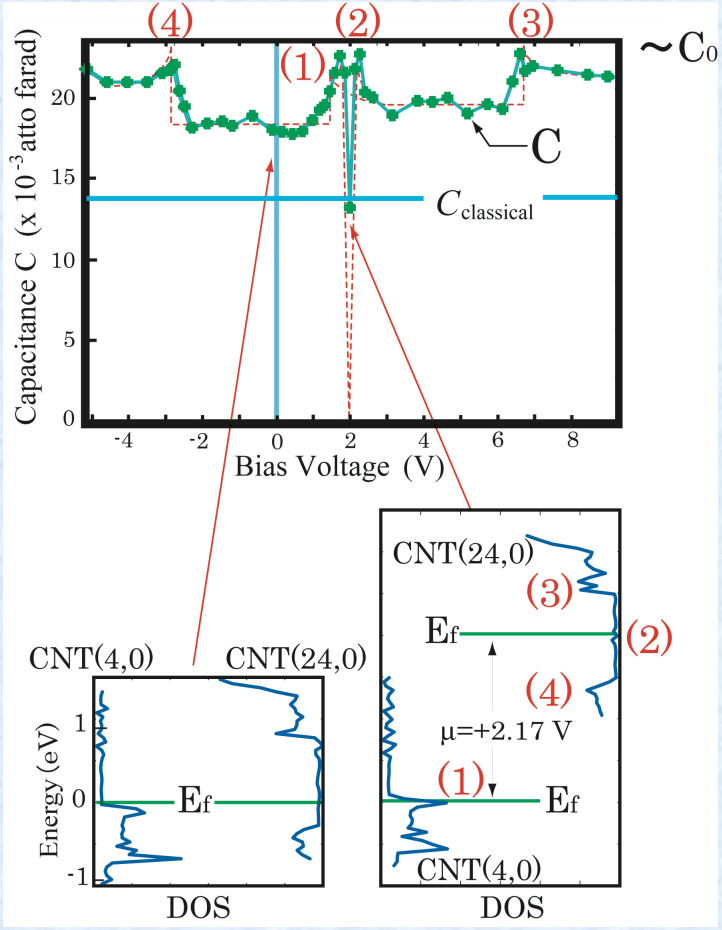
Density of States is NOT infinite…
Effect becomes prominent in small structures



$$\mu = V + U_1 + U_2$$

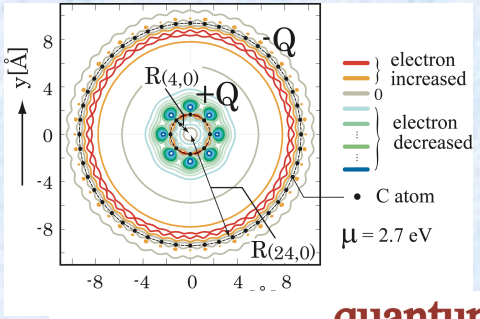
Correspondingly, electrostatic and DOS contributions

$$1/C \equiv d\mu/dQ = 1/C_0 + 1/D_{(4,0)} + 1/D_{(24,0)}$$

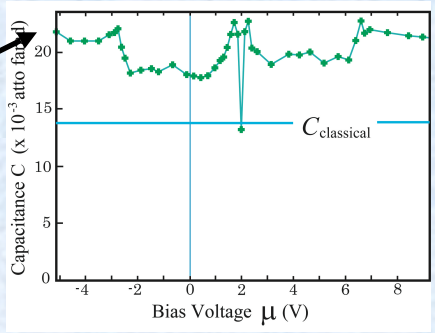


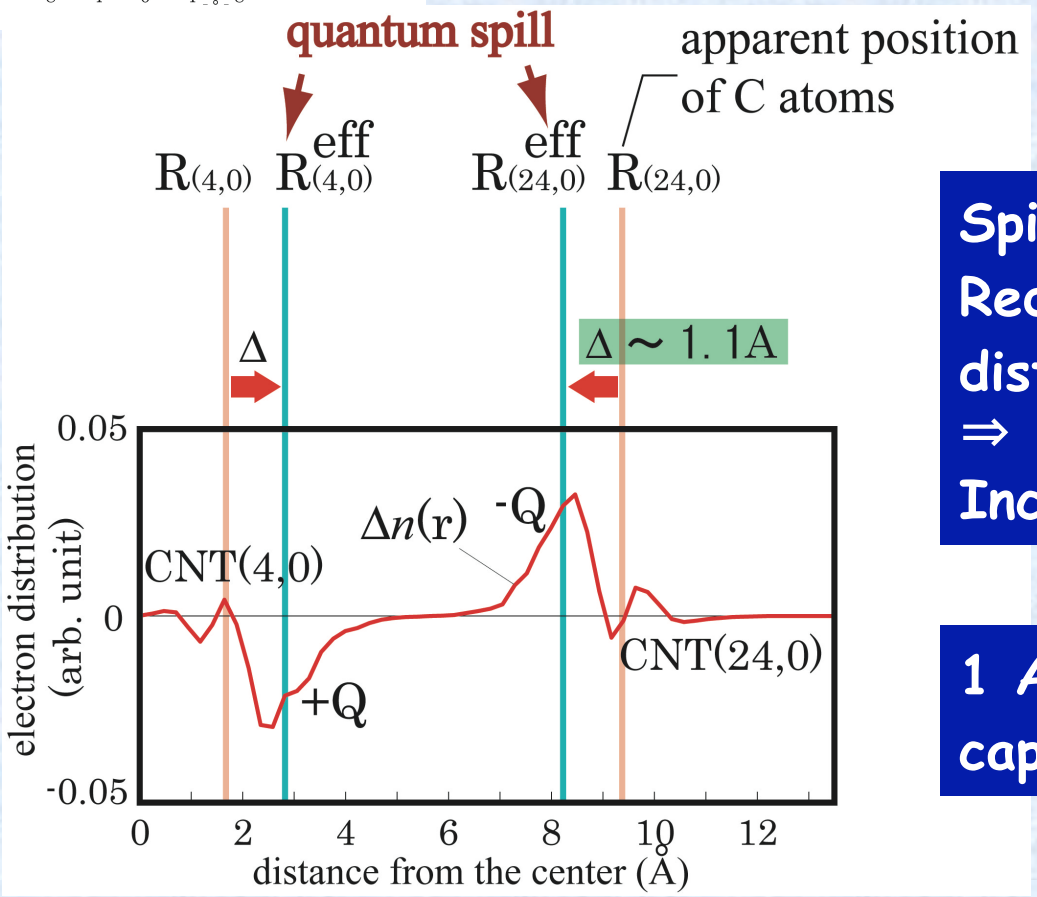
- ✓Van Hove singularity in 1D conductor
- ✓Chemical individuality

Quantum Effect II: Electron spill



$$C_{cla} = \frac{2\pi\varepsilon_0 \, d_{unitcell}}{\ln\left[R^{eff}(24,0)/R^{eff}(4,0)\right]}$$





Spill of Electron Density Reduces the Effective distance of two Electrodes
⇒
Increase of Capacitance

1 Angstrom Spill makes the capacitance larger by twice

Density-Functional Approach to Nano- and Bio-Materials

- Carbon Nanotubes on Metal and Si Surfaces
  - Chemical bonding/Electron transfer at interfaces modulate their propertie

    [Okada & Oshiyama: PRL 95, 206804 (2005), Berber & Oshiyama: PRL 96, 105505 (2006)]
- Double Walled CNT as a Nano-Capacitor
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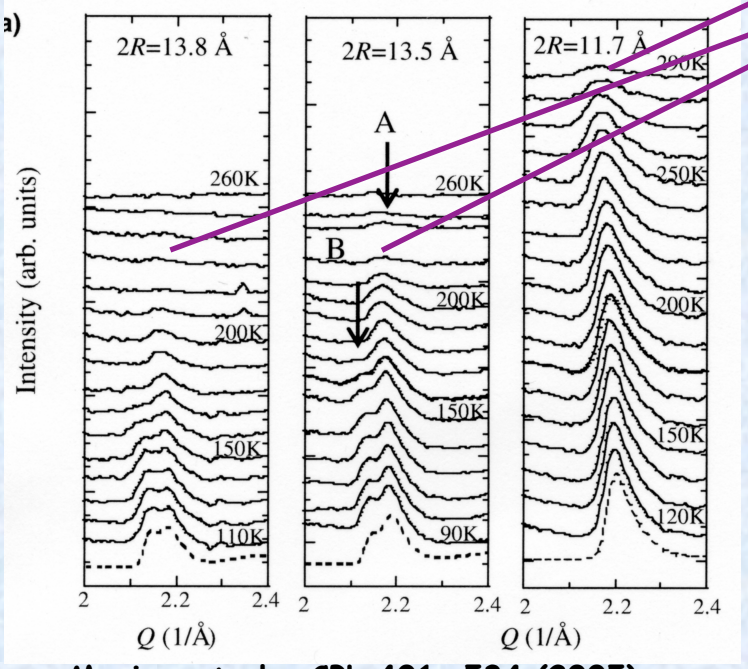
Ice Nanotube in Carbon Nanotube

X-ray Diffraction Measurement on Water in SWNT (d=11.7 – 14.4 A)



Maniwa et al.: CPL 401, 534 (2005)
JPSJ 78, 2863 (2002)

New Periodicity with 2.8 – 2.9 A comes up around RT!

New ordered H_2O in Nanospace?

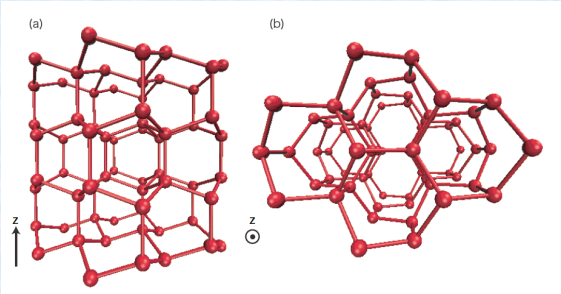
Previous classical MDs also predict ice nanotubes:

Koga et al: Nature 412, 802 (2001)
Naon et al: CPL 355, 445 (2002)

Is this real? What's the structure? Role of CNT?

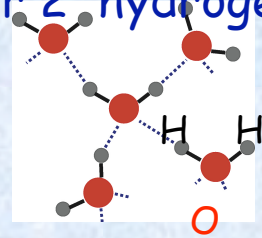
Ice Rules and Ice-CNT Interaction

Ice: more than 10 polymorphs depending on temperature and pressure

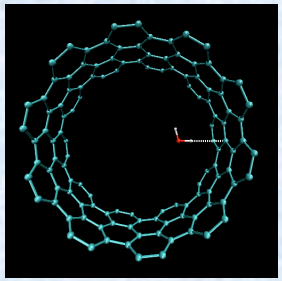


oxygen network in most stable ice I_h

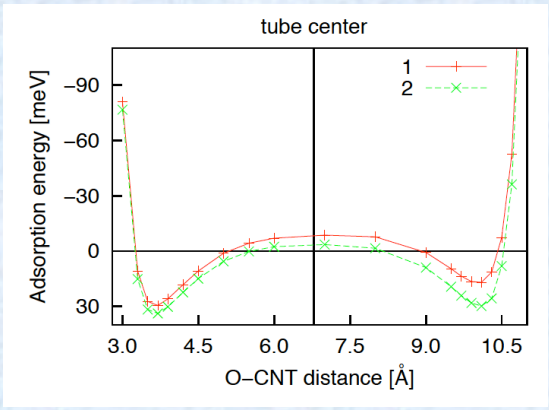
✓ **Ice rule:** each water molecule preserved; each H responsible for a single hydrogen bond; each O responsible for 2 hydrogen bonds



H_2O in Carbon Nanotube



Put a H_2O in CNT with the diameter of 6 A – 14 A. Calculate stable adsorption structures and energies with GGA(PBE96).



Common Characteristics

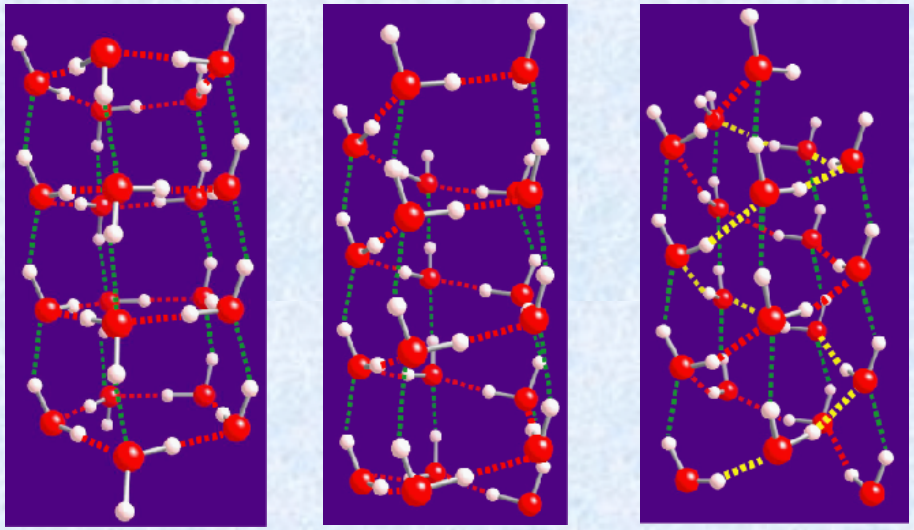
✓ **Adsorption Energy:** 20 -30 meV which is smaller than a typical value of H-bonding 200 meV

✓ **Distance between H_2O and CNT:** 3.7 – 3.9 A

Three Possible ice NTs & Suitable CNT

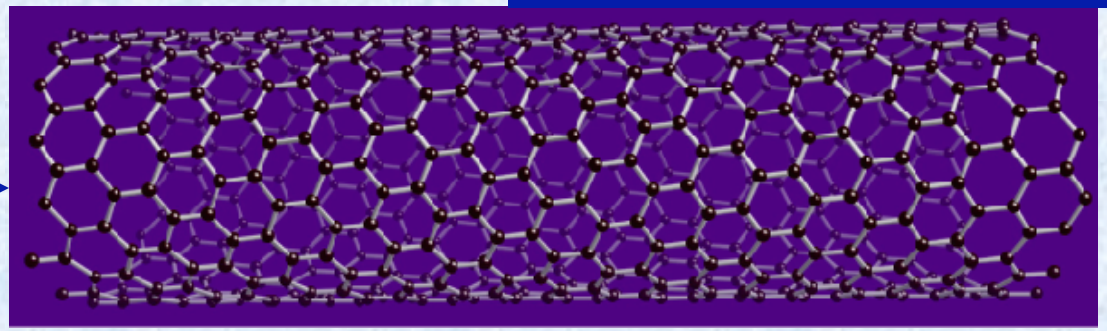
Ice nanotubes consisting of polygonal H_2O

Stacked Polygon | Helix | Double Helix



Satisfying the ice rule and, when choosing the pentagon, (14.2) CNT is suitable with the distance of 3.7 A

Encapsulation

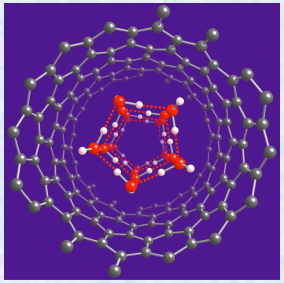


GGA(PBE96) calculations with
- Ultrasoft pseudopotentials + 36-Ry plane-wave basis set
- diameter of (14,2) = 11.8 A

Structure and Energetics of Ice NTs in Carbon Nanotubes

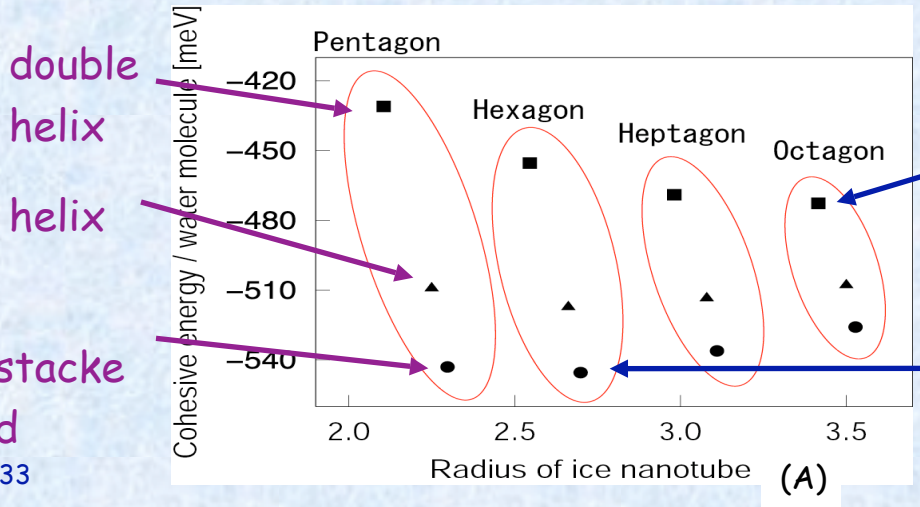
Energetics of Pentagonal Ice NT@CNT (meV/water molecule)

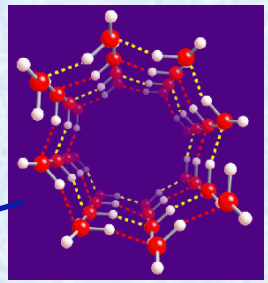
	cohesive energy	encapsulation gain
Stacked	543	9.2
Helix	509	10.2
Double-helix	431	8.3
Ice Ih	713	-

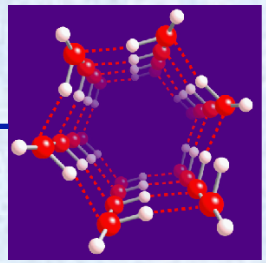


- ✓ ~~H-bonding cohesive energy >> encapsulation energy~~
- ✓ Tubular ice is certainly stable (60-76% of Ice I_h)

Energetics of Polygonal Ice NT







- Various polygonal ice NTs are possible.
- Stacked structures are relatively stable

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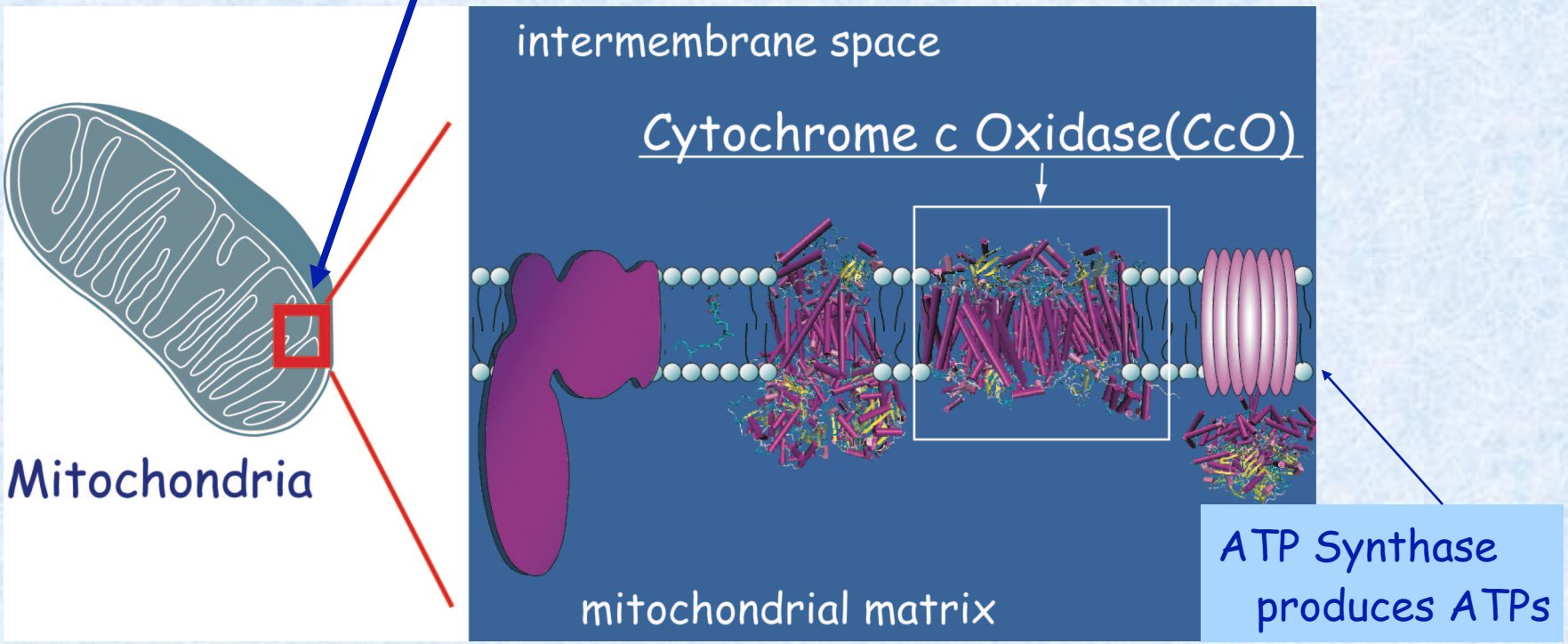
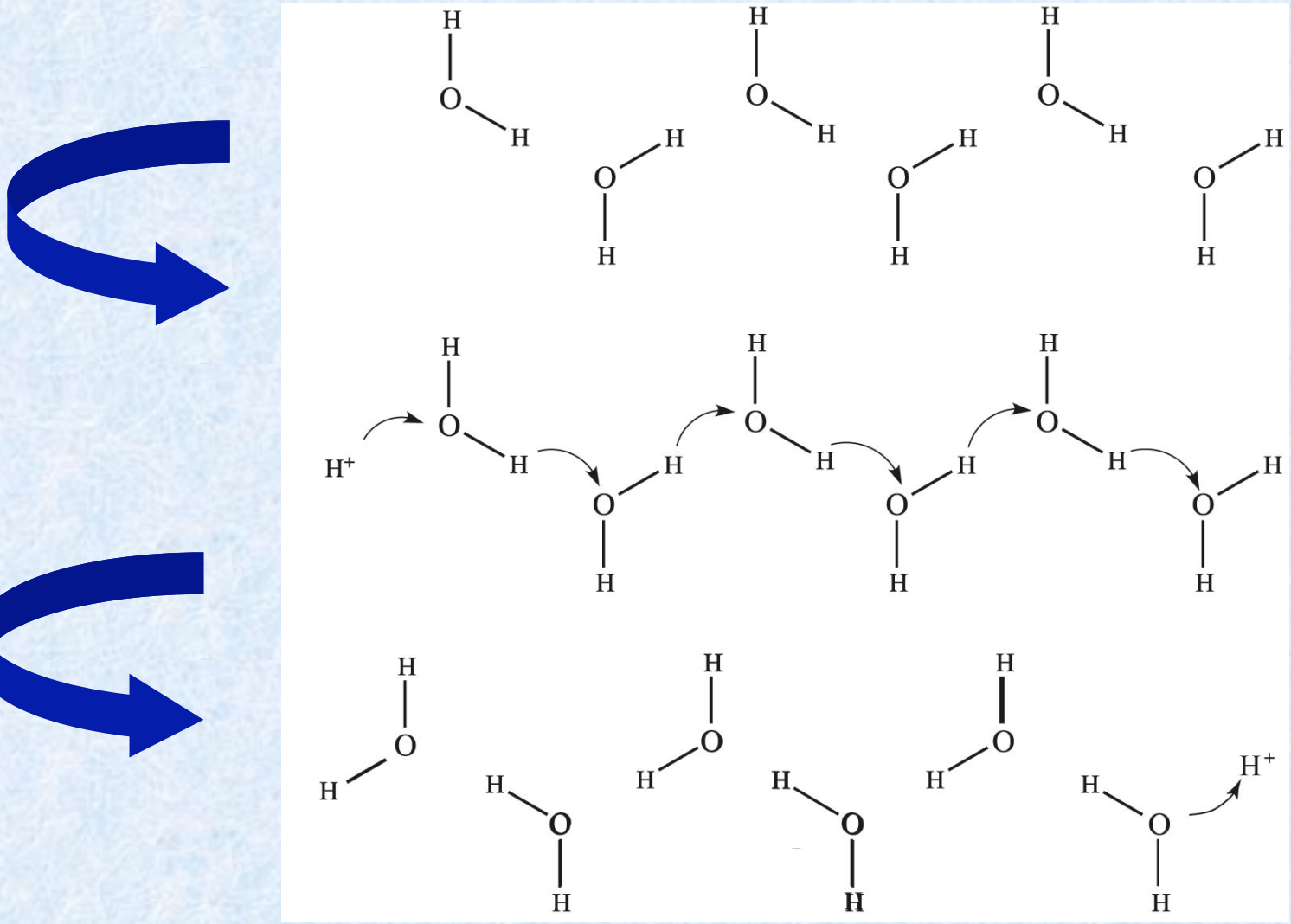
What is Cytochrome c Oxidase (CcO)?

Foods ($C_6H_{12}O_6$ etc) , Oxygen ⇒ NADH, NAD^+ ⇒ Electrons & Protons



Mechanisms / Pathways / Free-energy Barriers for the Proton Transfer in CcO?

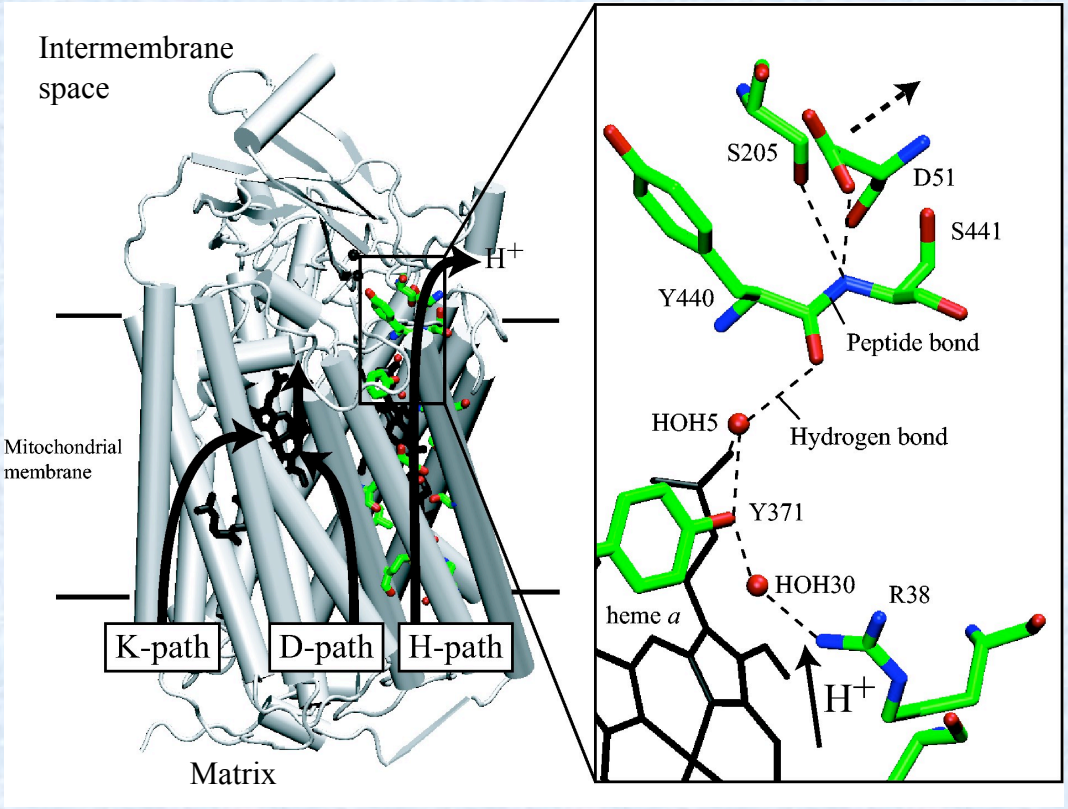
Proton-Relay Mechanism (Grotthuss-like mechanims)



Candidate Proton Pathways deduced from X-Ray Measurements

- ✓ CcO: 40 thousands of atoms
- ✓ Subunits I and II (7000 atoms) are responsible for proton transfer
- ✓ Structures are a set of helices connected with each other
- ✓ Reduction and Oxidation changes its structure
- ✓ Biggest and suggestive change takes place for ASP51 along H pathway

Tsukihara et al: Proc. Natl. Acad. Sci, 100, 15304 (2003)



- ➢ Can proton move with moderate free-energy barrier through peptide bonds?
- ➢ A new process different from what Grotthuss speculated in two centuries ago?
- ➢ What is the actual atomic mechanism?

Car-Parrinello Molecular Dynamics

electron degrees of freedom

nuclear degrees of freedom

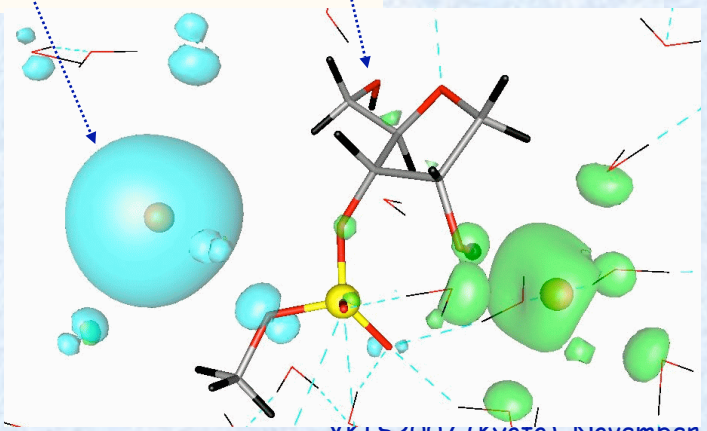
$$\mathcal{L}^{CP} = \tfrac{1}{2}\sum_i \mu \int d^3x\, |\dot{\psi}_i|^2 + \tfrac{1}{2}\sum_I M_I \dot{\mathbf{R}}_I^2$$

$$+\tfrac{1}{2}\sum_q \mu_q \dot{\alpha}_q^2 - E^{DFT}[\psi_i, \mathbf{R}_I, \alpha_q]$$

$$+\sum_{ij} \Lambda_{ij}\left(\int d^3x\, \psi_i^* \psi_j - \delta_{ij}\right)$$

coupling between electrons and nuclei described by DFT

additional degrees of freedom (temperature, stress etc)



Car-Parrinello + Meta Dynamics to Overcome Multiscale Problem in Time

Collective (reaction) coordinates: s_α

$$L = L_{CP} + \sum_\alpha \frac{1}{2} M_\alpha \dot{s}_\alpha^{\,2} - \sum_\alpha \frac{1}{2} k_\alpha \left(s_\alpha(R) - s_\alpha\right)^2 - V(s,t)$$

usual CP Lagrangean

fictitious kinetic energy

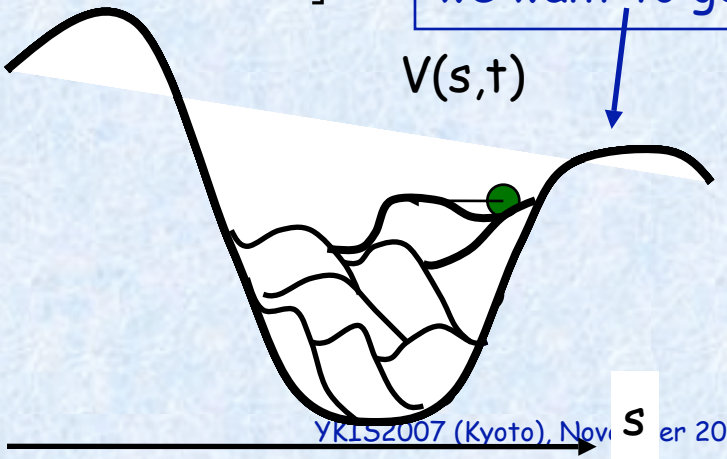
Restrain potential: coupling with other coordinates

Gaussian potentials added

where the history dependent function V is

$$V(\mathbf{s},t) = \sum_{t_i<t} W_i \exp\left(-\frac{1}{2} \frac{(\mathbf{s}-\mathbf{s}_i)^2}{(\Delta s^\perp)^2} \right) \exp\left[-\frac{1}{2} \frac{\left((\mathbf{s}_{i+1}-\mathbf{s}_i)(\mathbf{s}-\mathbf{s}_i)\right)^2}{(\Delta s_i^{\parallel})^4} \right]$$

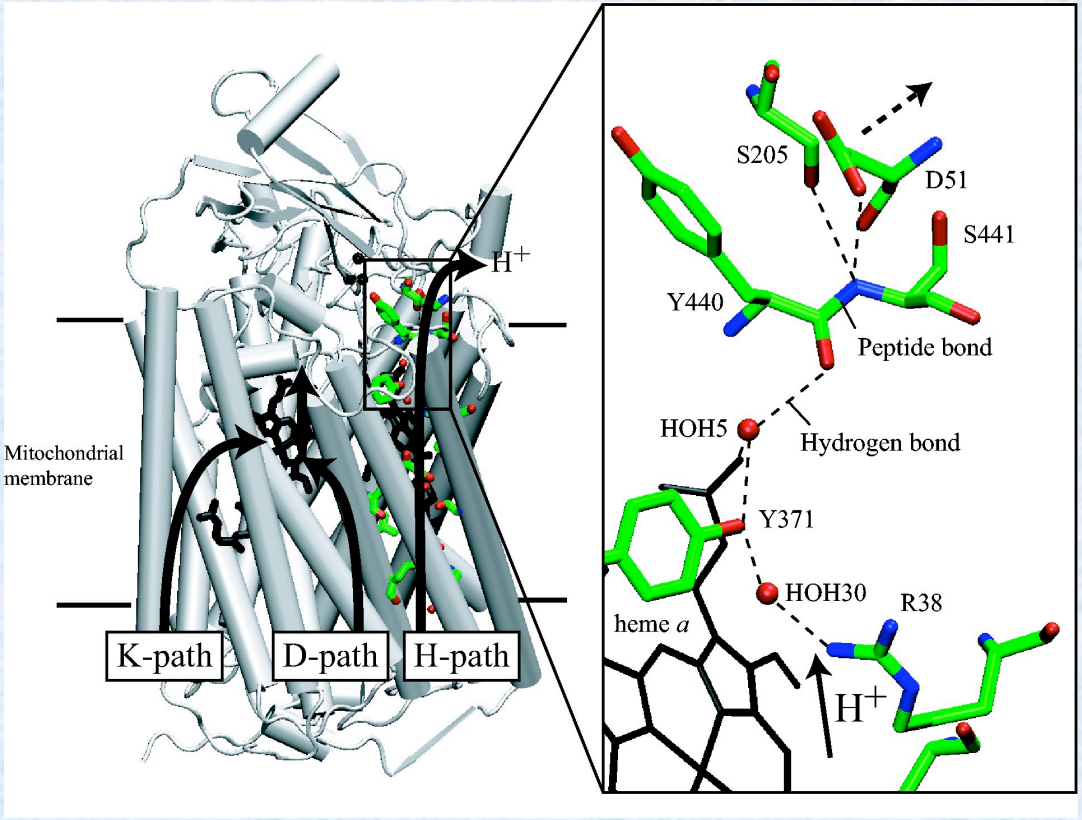
Free-energy landscape that we want to get



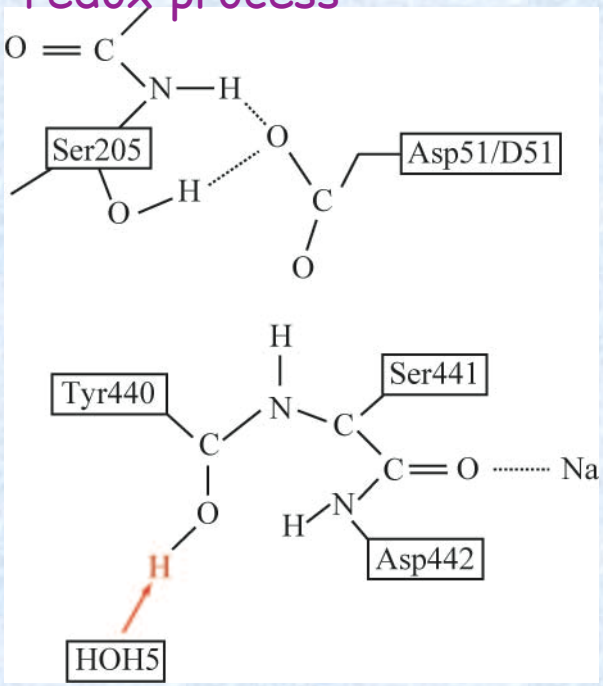
and sum of gaussians gives us Free-energy landscape

$$\lim_{t \to \infty} V(\mathbf{s},t) = -F(\mathbf{s}) + const.$$

H-pathway in Cytochrome c Oxidase (CcO)

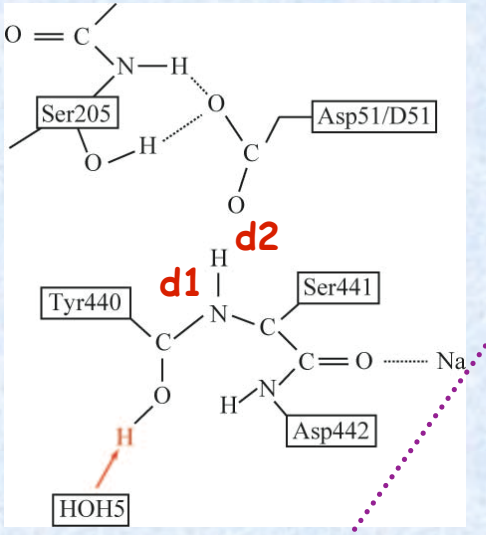


Asp51/D51 goes outside and comes inside during redox process



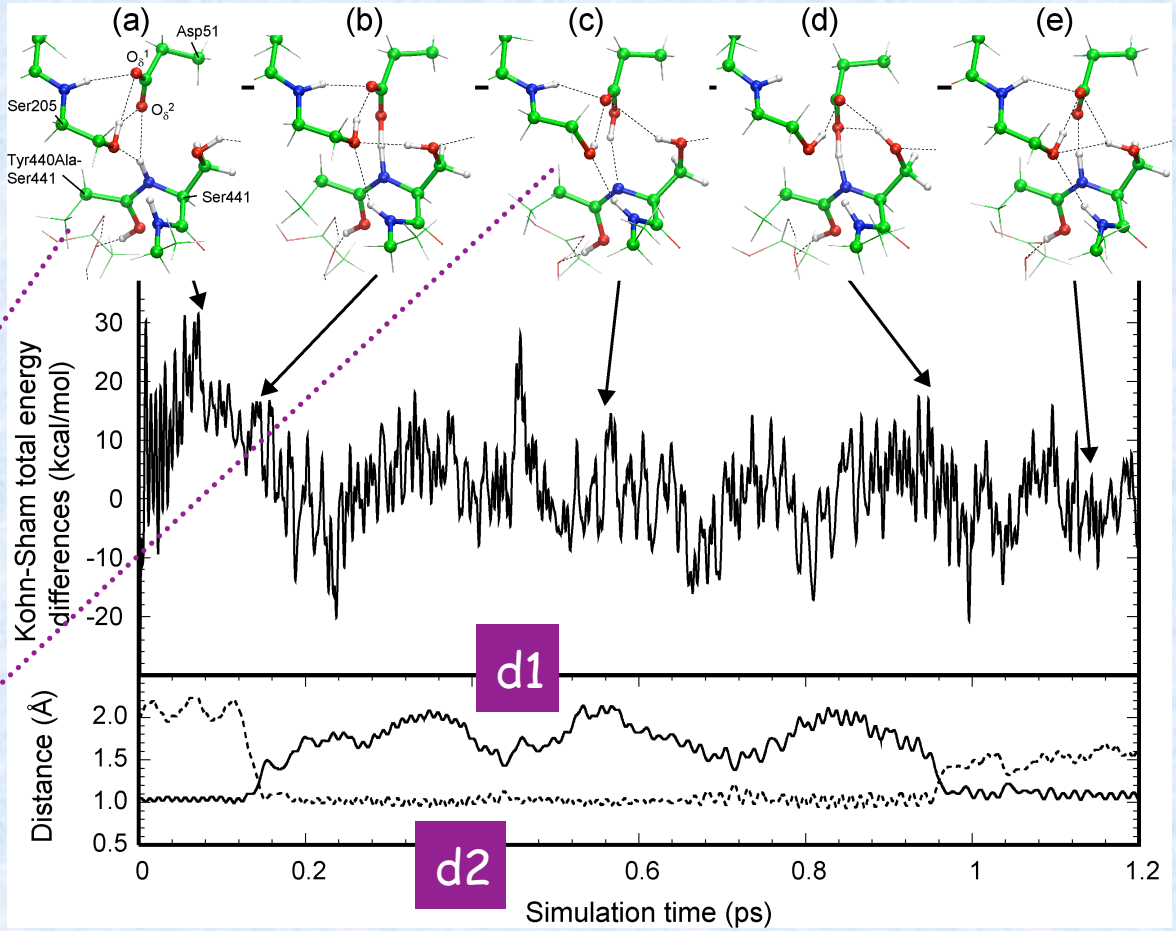
How is the proton above the peptide bonds drafted by D51/Asp51?
How does the next proton come to the position above the peptide bonds?

Enol Form is Produced in Usual CPMD Simulation



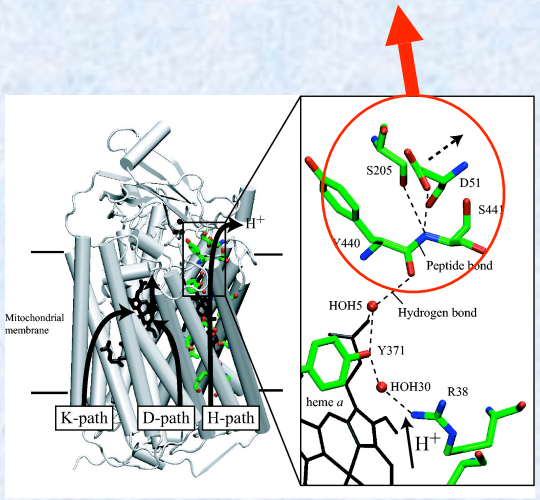
Imidic acid

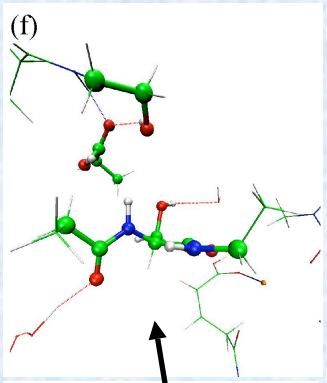
Enol form



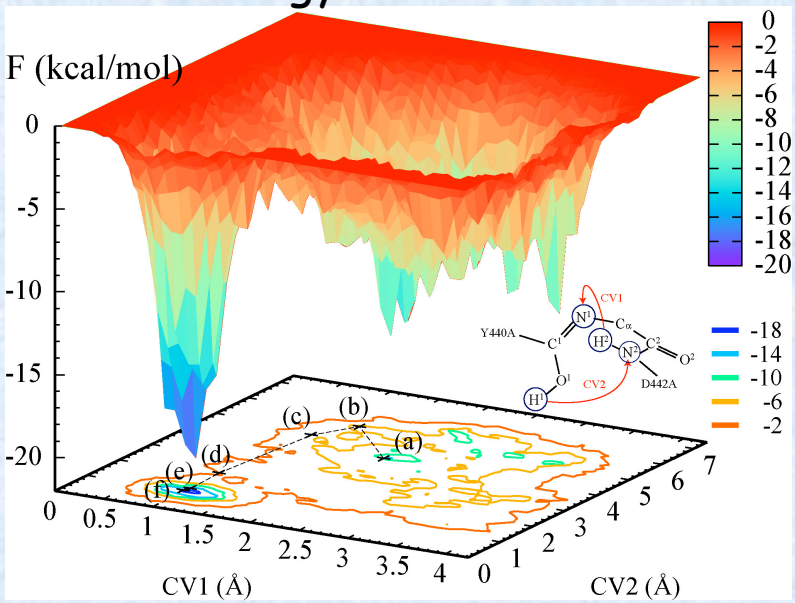
Reaction generating the enol form is plausible under thermal fluctuation at room temperature

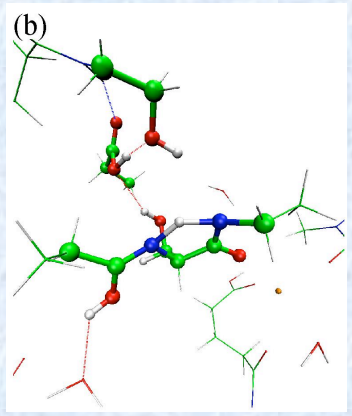
Proton gets through the peptide bond: Concerted reaction

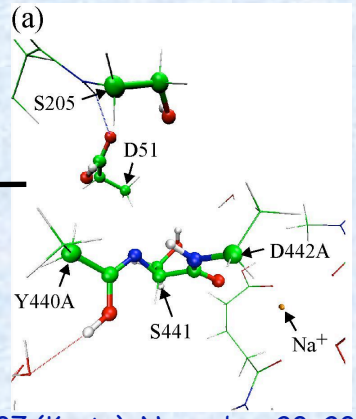




Free energy barrier: 13kcal/mol







Kamiya, Boero, Tateno, Shiraishi & Oshiyama: J. Am. Chem. Soc. (2007)

Dynamics/metadynamics in a nutshell