Division of Materials and Life Sciences: Computational Condensed Matter Science Group

- ✓ Clarify microscopic mechanisms of phenomena in materials,
- ✓ Predict new phenomena and explore new materials that are fascinating,

by computationally solving fundamental equations of quantum mechanics from first principles

- Multi-scale in space

  50,000 atoms in 10 nm^3 Si

  Elementary processes of electrons and ions (0.1 – 1 nm)

  ⇔ Structural change and appearance of new phenomena (10 – 100 nm)

- Multi-scale in time

  Electronic transition (10^{-15} sec) ⇔ Ionic motion (10^{-12} sec)

  ⇔ Structural change and appearance of properties (10^{-9} – 10^{-6} sec …)

Division of Materials and Life Sciences: Computational Condensed Matter Science Group

- Large-scale quantum theoretical calculations
  - Real-Space Density Functional Theory (RSDFT) Scheme
- Multi-scale dynamical calculations
  - Car-Parrinello Molecular Dynamics plus Meta-dynamics (CPMD-MeD)
- Exploration of new properties in condensed matters
  - Total-energy or Free-energy calculations based on DFT

People:
A. Oshiyama (Prof)
K. Shiraishi (Prof)
S. Okada (Associate Prof)
J.-I. Iwata (Researcher)
Y. Fujimoto (JST-Postdoc)
[K. Uchida (JST-Postdoc)]
[K. Kamiya (JST-Postdoc)]

HPC Division
D. Takahashi, T. Park
M. Sato, A. Ukawa

Life Science Group
M. Boero, M. Tateno

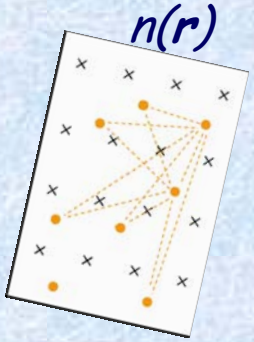
Quantum MB System Group
K. Yabana, T. Nakatsukasa

Density Functional Theory (DFT)

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

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

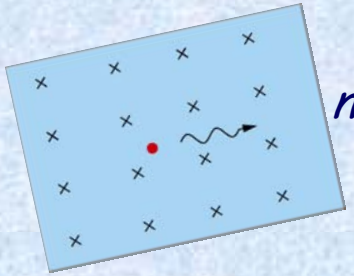
$$= T_s[n] + \int v_{\mathrm{nucl}}(\vec{r}) n(\vec{r}) d\vec{r} + \frac{1}{2}\int \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[n]$$



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

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

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

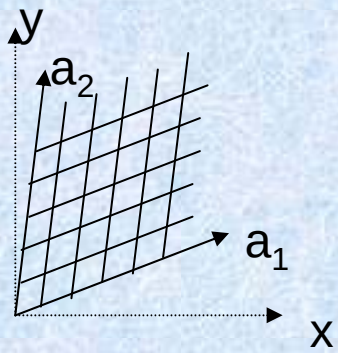


Real-space treatment is better for large-scale calculations (10,000 - 100,000 atoms)

Real-space Density Functional Theory (RS-DFT)

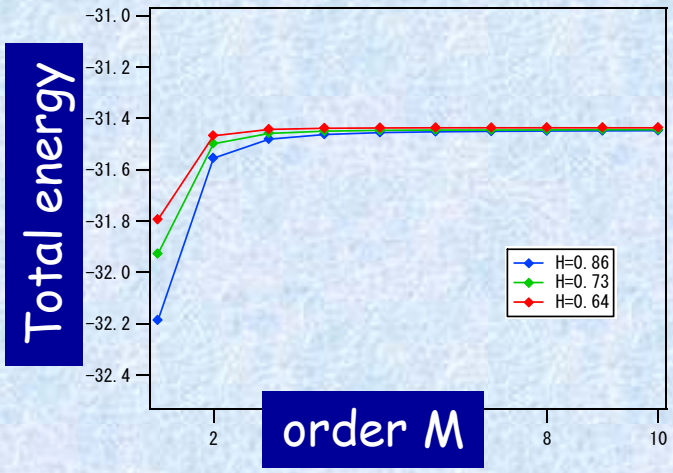
Introduce mesh points in a unit cell, compute all the quantities on the mesh. In the case Laplacian is expressed by finite difference:

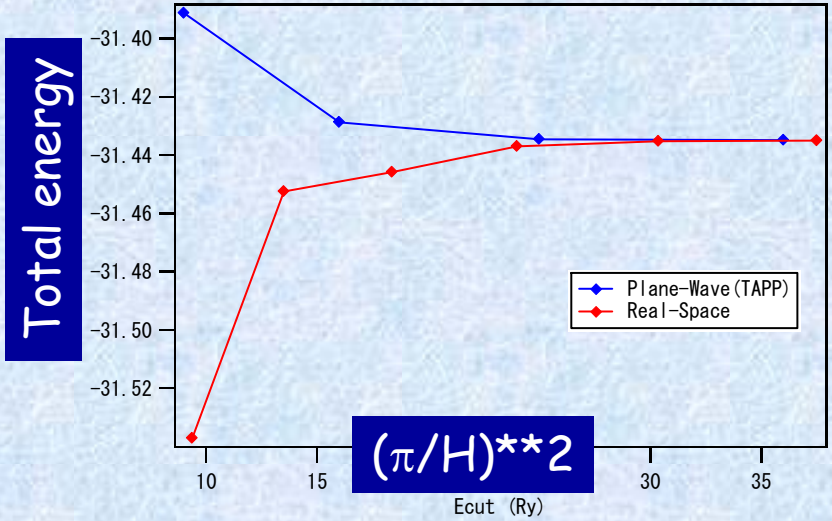
$$\frac{\partial^2}{\partial x^2}\phi(x,y,z) \approx \sum_{m=-M}^{M} C_m \phi(x+mH,y,z)$$



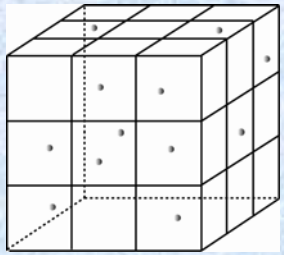
$$E_c = \left(\frac{\pi}{H}\right)^2$$

Accuracy is controlled by spacing H of the mesh:





Advantage of RS-DFT



[Iwata, Shiraishi & Oshiyama: PRB 2007, and unpublished results]

- Controlling accuracy systematically
- Benefits of RS-DFT in Next-Generation (maybe substantially Parallel) Super Computer
  - Utilize inherent locality of the system
  - Almost free from FFT, reducing communication burden
  - Flexible boundary condition to wave-functions

In addition, in our code,

- Residual minimization method instead of conjugate-gradient minimization to solve Kohn-Sham equation
- Change of algorithm for Gram-Schmidt orthgonalization to utilize BLAS-level3 matrix-matrix operations
  ⇒ almost peak performance
- Divide-and-Conquer algorithm to solve secular equation in subspace

Some Benchmark Data on PACS-CS

PACS-CS at Tsukuba:
Xeon 5.6 GFLOPS x 2560 nodes through 3D hyper-network
Peak performance (theoretical) 14.3 TFLOPS

Net Performance in each computation on 256 nodes (MFLOPS/node)

Gram-Schmidt

	Si1000	Si1728	Si2744	Si4096
Operation	2689	3335	3957	3603
Op + Communication	2072	2802	3557	3227

Diagonalization in subspace

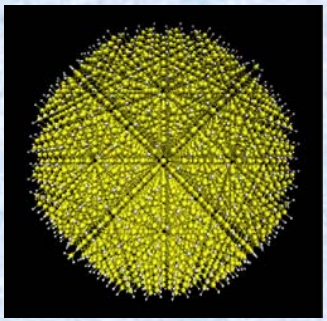
	Si1000	Si1728	Si2744
Operation	4117	4125	4329
Op + Communication	3434	2944	3999

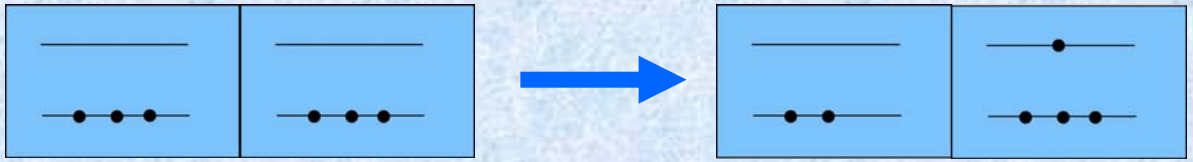
Hamiltonian operation (H Psi)

	Si1000	Si1728	Si2744	Si4096
Operation	93	132	112	202
Op + Communication	50	76	59	126

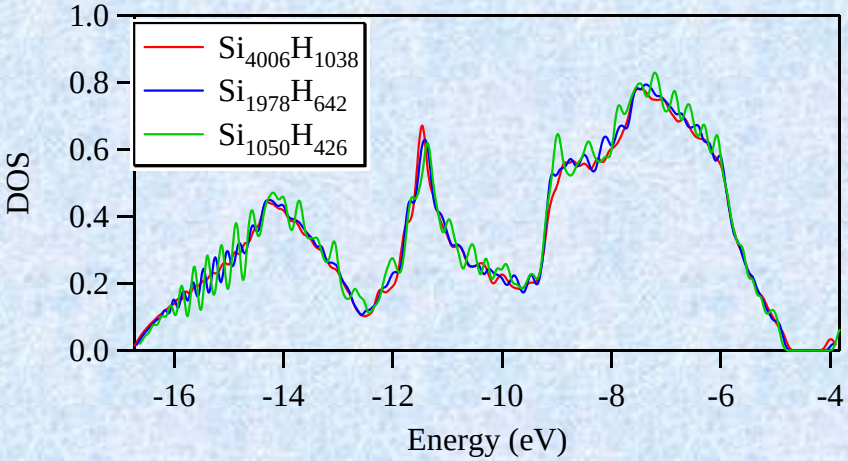
Excitation Energies of Si Cluster Containing Thousands of Atoms

Legitimate Definition of Electron Excitation Energy:
Total-Energy Difference between Charged and Neutral Systems:
i.e., E(N+1) + E(N-1) - 2 E(N)

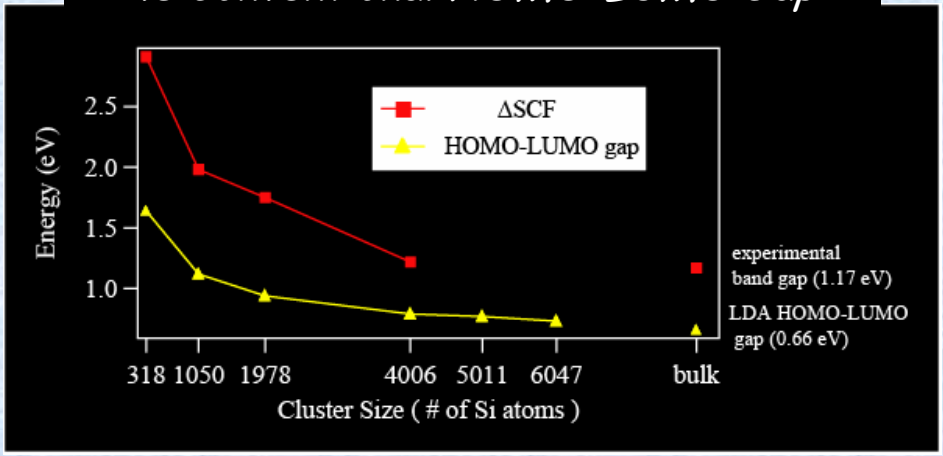




Cluster simulates Si Bulk? … Yes!



ΔSCF = E(N+1) + E(N-1) - 2 E(N)
vs Conventional HOMO-LUMO Gap



Car-Parrinello Molecular Dynamics (CPMD)

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

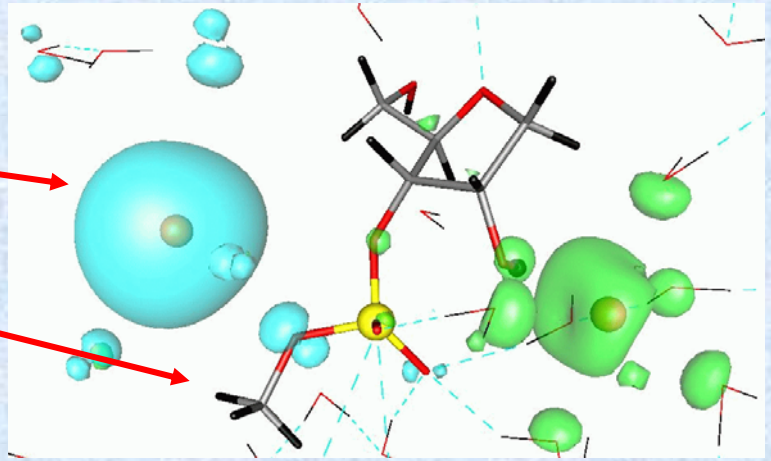
additional degrees of freedom (T, P etc)

Lagrangian equation of motion

$$\mu\ddot{\psi}_i = -\frac{\delta E^{DFT}}{\delta \psi_i^*} + \sum_j \Lambda_{ij}\psi_j$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I} E^{DFT}$$

$$\mu_q\ddot{\alpha}_q = -\frac{\partial E^{DFT}}{\partial \alpha_q}$$



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

Collective (reaction) coordinates: s_α

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

usual CP Lagrangean

fictitious kinetic energy

Restrain potential: coupling with other coordinates

Gaussian potentials added

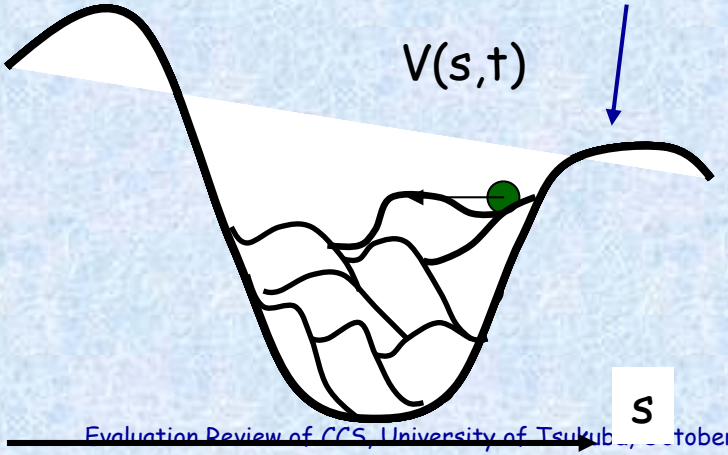
where the history dependent function V is

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

Free-energy landscape that we want to get

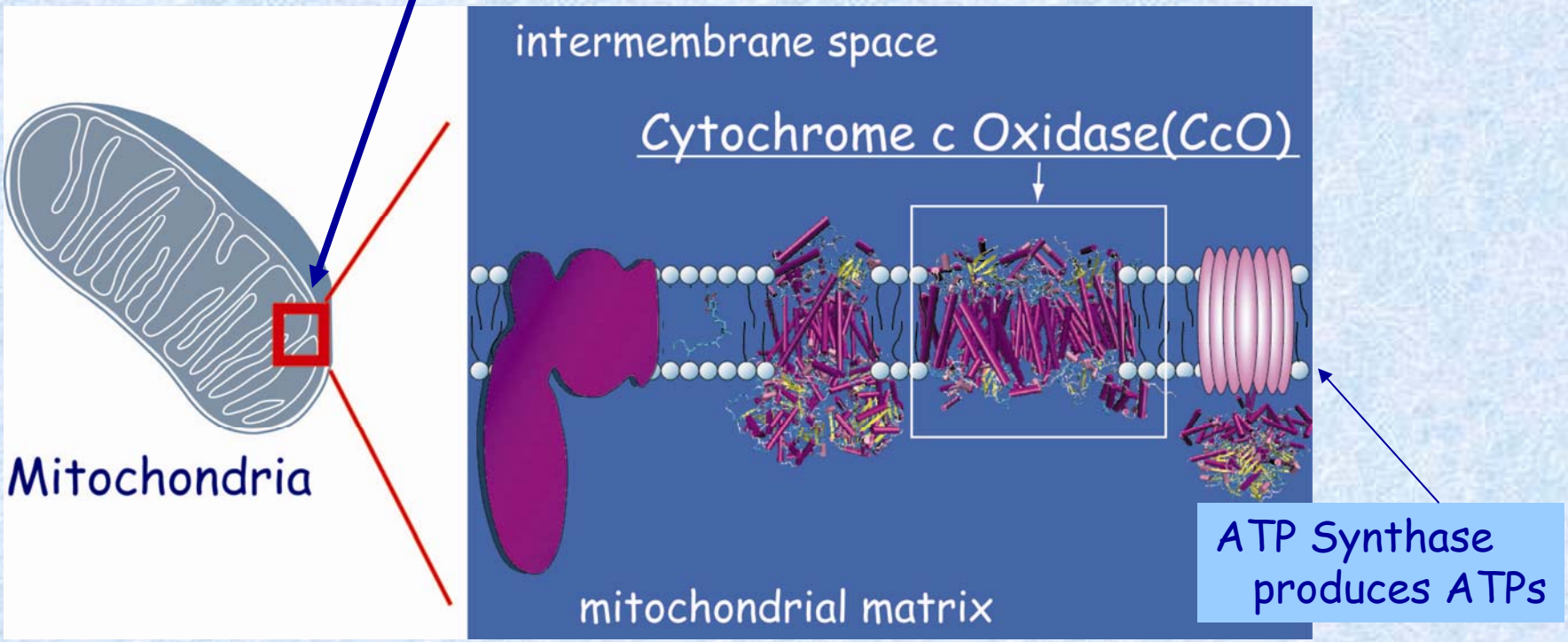
and sum of gaussians gives us Free-energy landscape

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



What is Cytochrome *c* Oxidase (CcO)?

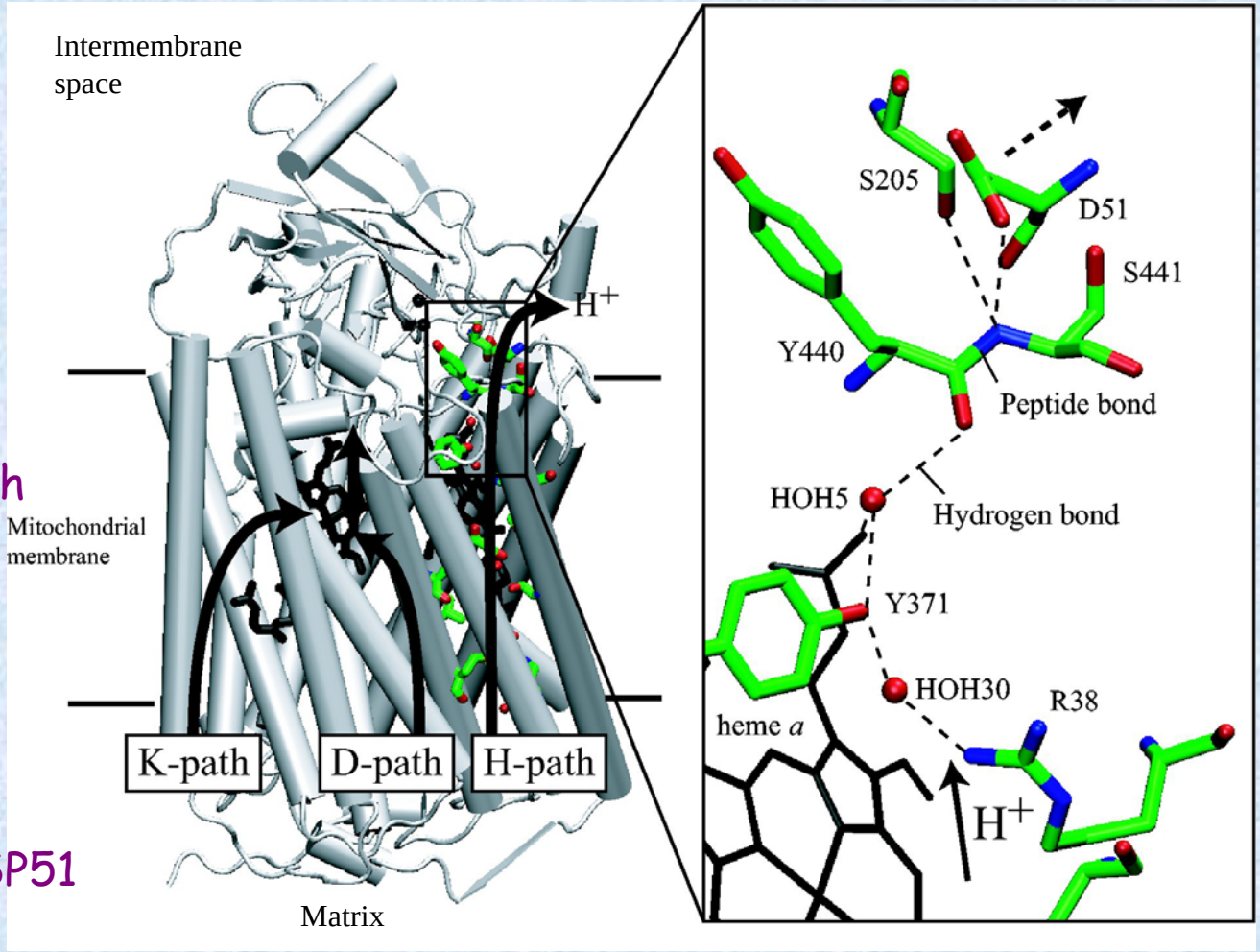
Foods ($C_6H_{12}O_6$ etc) , Oxygen ⇒ NADH, NAD^+ ⇒ Electrons & Protons



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

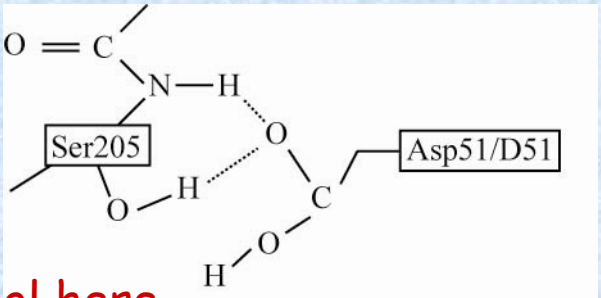
Candidate Proton Pathways deduced from X-Ray Measurements

- ✓ 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

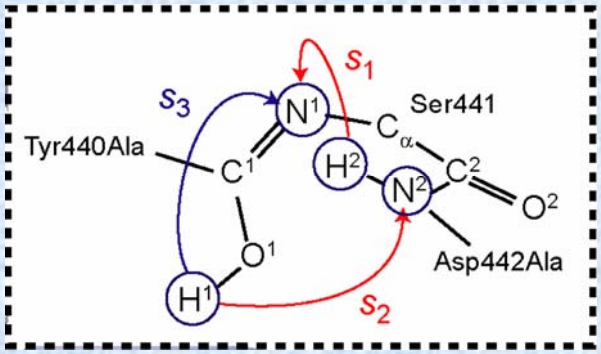


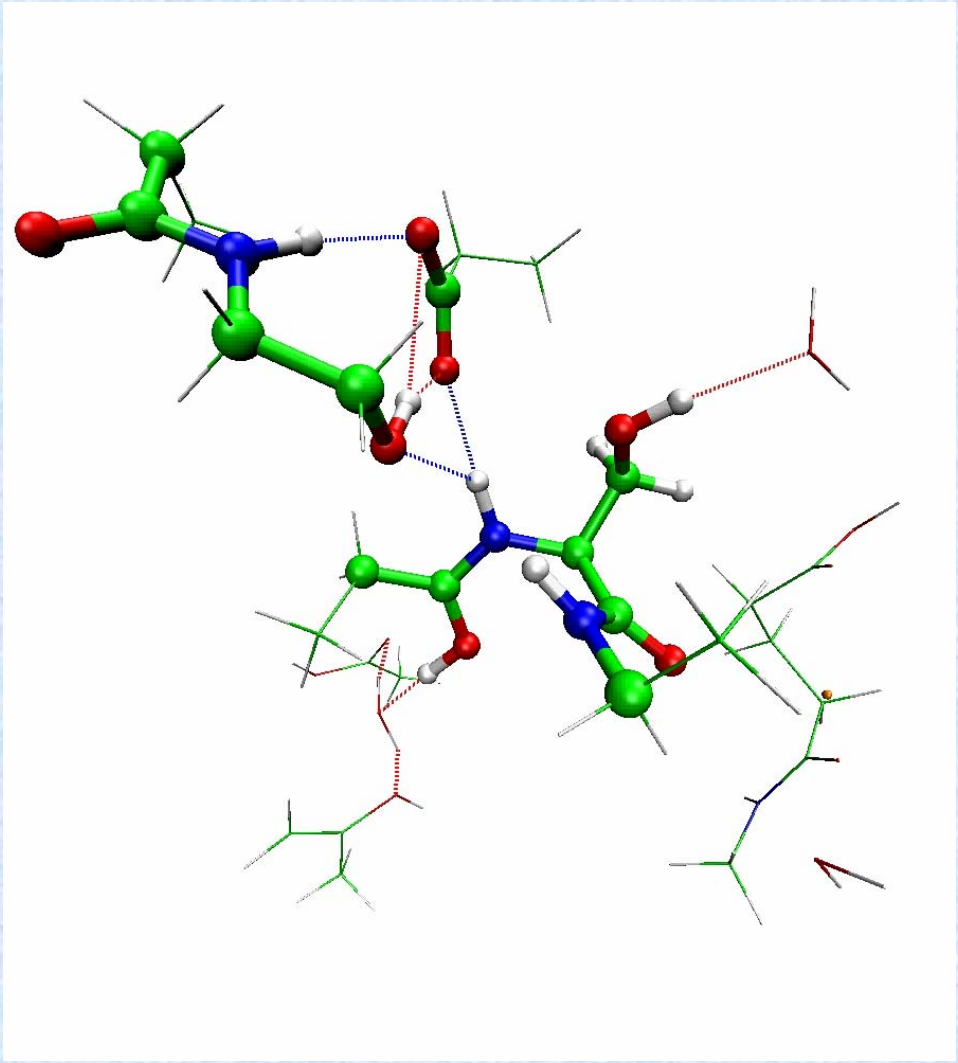
Tsukihara et al: Proc. Natl. Acad. Sci, 100, 15304 (2003)

Tautomerization Reaction from Enol to Keto Forms



Enol here





K. Kamiya, M. Boero, M. Tateno, K. Shiraishi and A. Oshiyama, J. Am. Chem. Soc. (2007)

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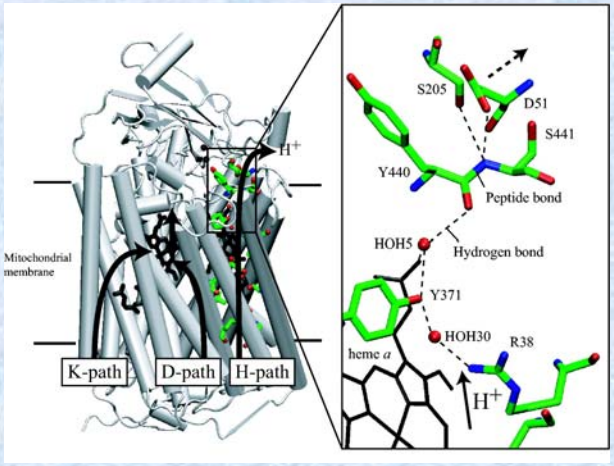
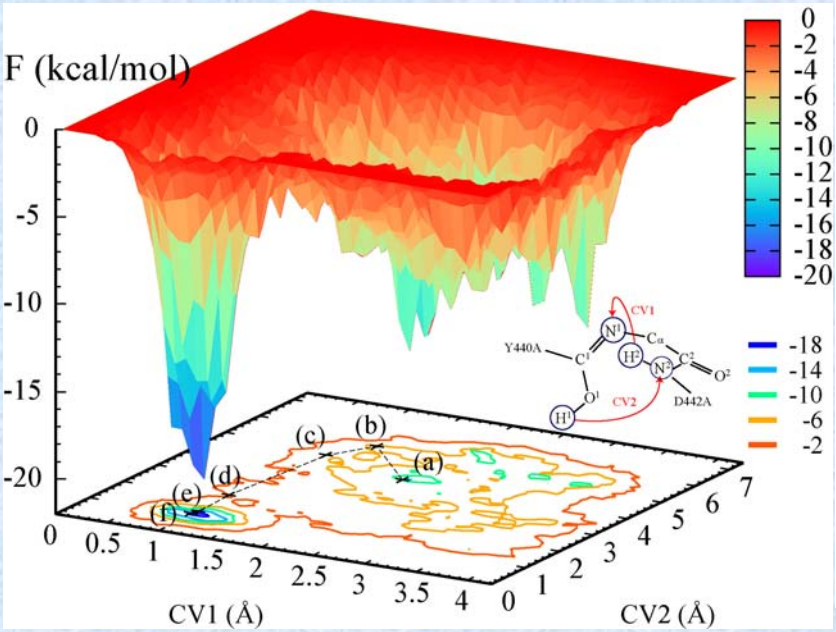
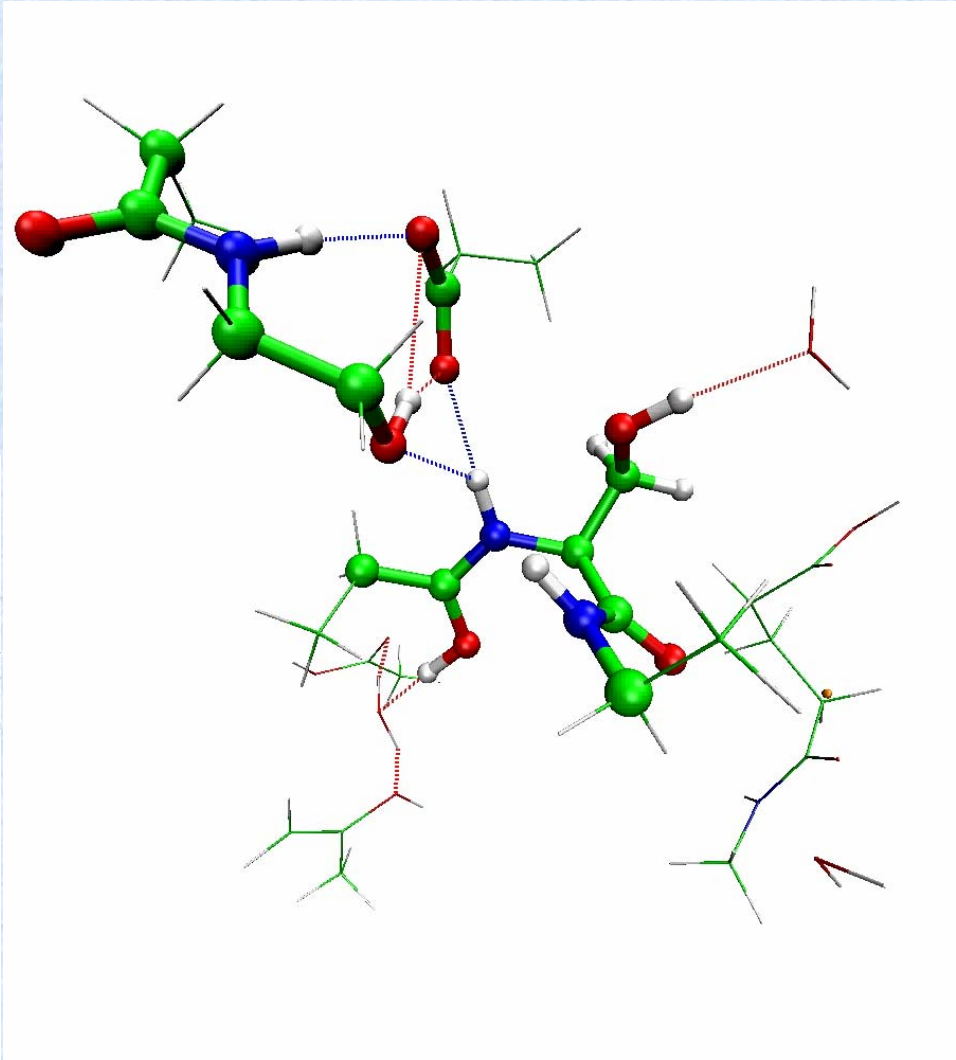




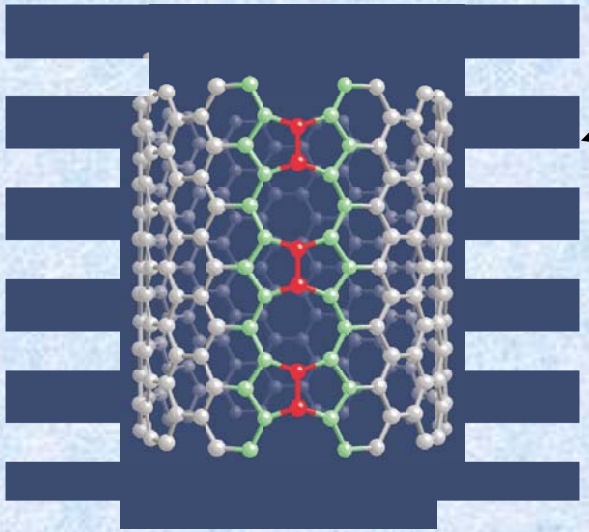
Free-energy Landscape



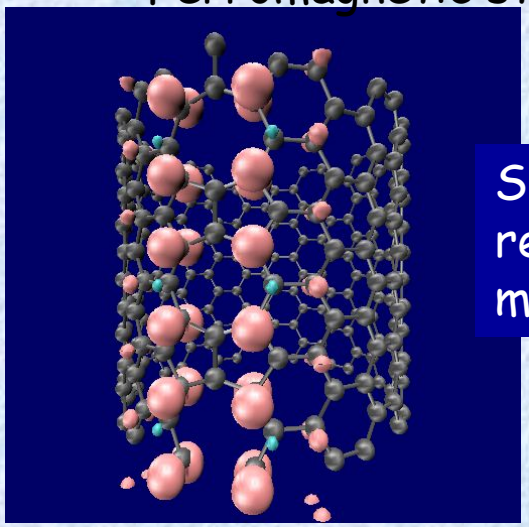
K. Kamiya, M. Boero, M. Tateno, K. Shiraishi and A. Oshiyama, J. Am. Chem. Soc. (2007)

Prediction of Magnetic Carbon Nanotubes

When topological defects in hexagonal network in carbon nanotubes,



Ferromagnetic states appear.



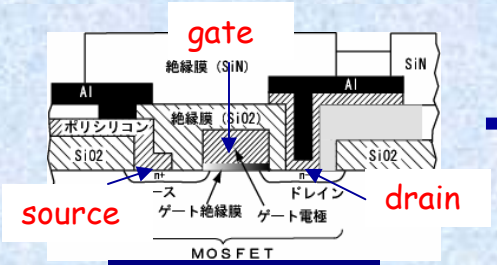
Spin density that is responsible for magnetism

Okada et al:
Physical Review B (2006);
Applied Physics Letters (2007)

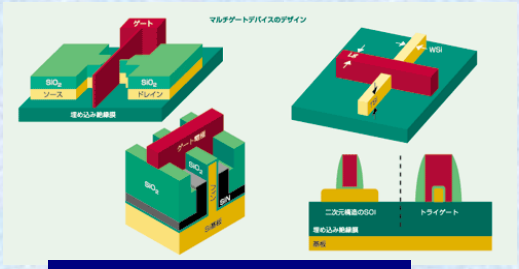
- Also, calculation predicts that linear line defects generated on carbon nanotubes by, e.g., electron radiation, selfheals to be the above topological defects (no energy barrier for healing).

Nano World Emerges in Post-scaling Technology

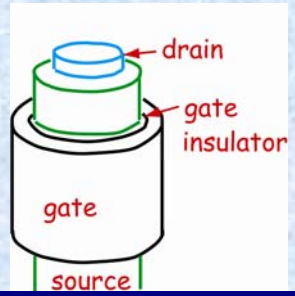
e.g., Field effect Transistor (More gates to increase channels)



Planer FET

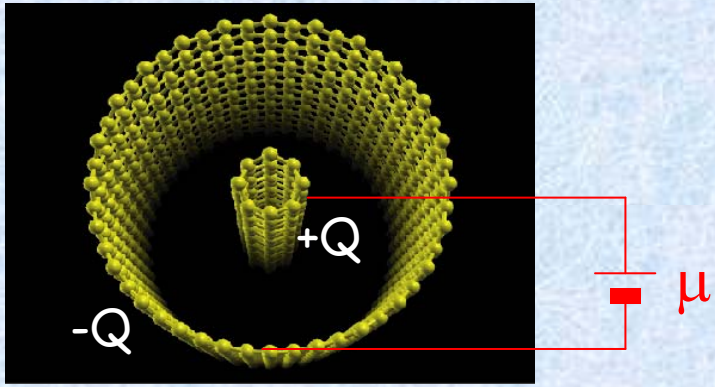


Multi-gate FETs



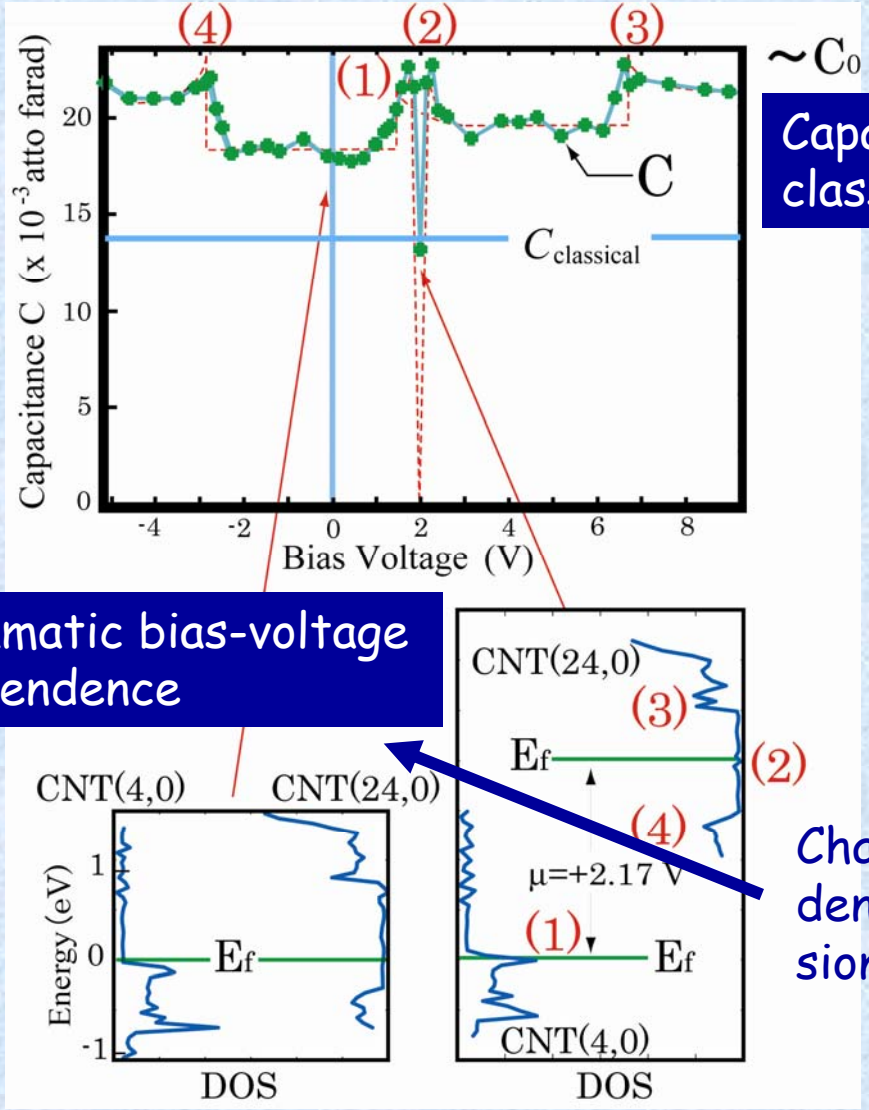
Surrounding-gate FET

An Untimate Cylindrical Structure: Double-walled Carbon Nanotube



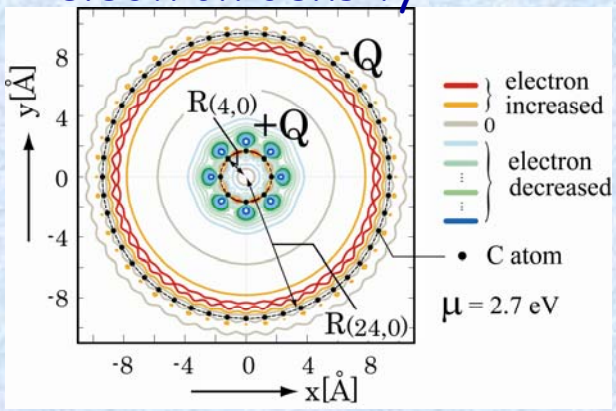
Quantum Theoretical Free-enerngy Calculation:
Uchida, Okada, Shiraishi & Oshiyama: Physical Review B (2007)

Two Quantum Effects in Carbon Nanotube Capacitor



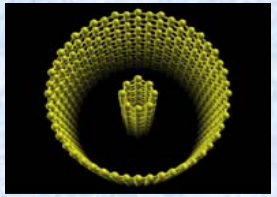
Capacitance much bigger than classical value ($C_{classical}$)

Quantum spill of electron density



Dramatic bias-voltage dependence

Characteristic feature in density of states of 1 dimensional conductors



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- Large-scale quantum theoretical calculations
  - Real-Space Density Functional Theory (RSDFT) Scheme

    Collaboration with HPC division was and will be imperative
- Multi-scale dynamical calculations
  - Car-Parrinello Molecular Dynamics plus Meta-dynamics (CPMD-MeD)

    Collaboration with Life science group has been essential
- Exploration of new properties in condensed matters
  - Total-energy or Free-energy calculations based on DFT

    Our quantum theoretical calculations predict interesting phenomena that await experimental confirmation