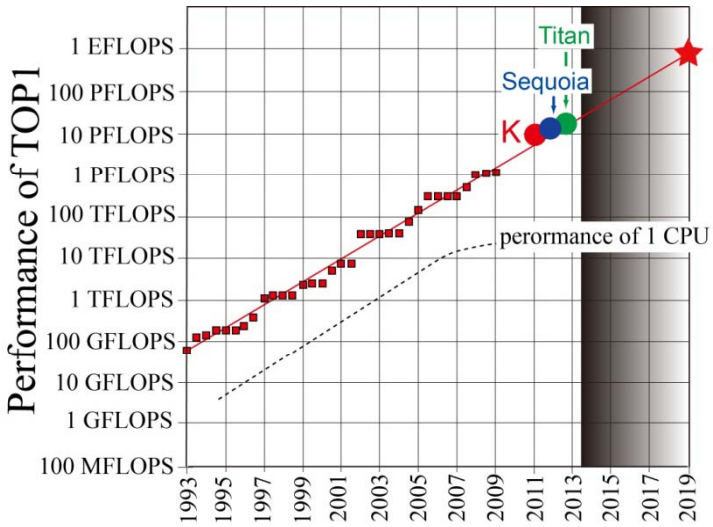
Materials Design through COMPUTICS: Large-Scale Density-Functional Calculations for Nanomaterials

- **Computational Nanoscience**
  - What is Nano? What is Interesting?
    - ✓ *Quantum Theory Required. Science and Technology are close to each other*
    - ✓ *Carbon nanotube, Graphene, Si nanowire,,,*

      Nanoshapes are decisive
- **Computics: Collaboration among Materials Science, Computer Science and Mathematics**
  - Density-Functional Theory (DFT)
    - ✓ *Material is an Interacting Many-Electron System*
  - HPC in DFT Calculations: RSDFT code
    - ✓ *Mathematical Methodology, Algorithm*
    - ✓ *How to Collaborate*

Computics: Fusion of Materials Science and Computer Science

Computers that are changing rapidly



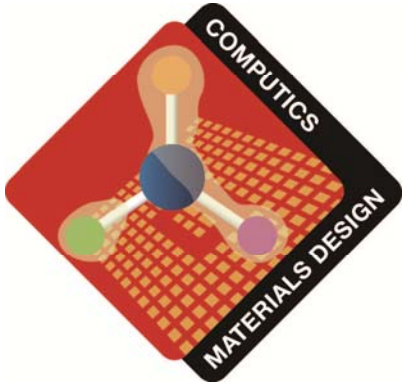
- ✓ Saturation of performance of a single computation processor
  Breakdown of Moore's Scaling Law
- ✓ Multi-core massively parallel architecture now
  Kobe-K : 80,000CPU x 8 cores
- ✓ Accelerator introduced in the current and next generation
  Supercomputer that is a monster

Collaboration between Computational Materials Science and Computer Science is Imperative

- ➢ Developments of Mathematical Methodology and Algorithms Suitable to Current and Future Hard wares
- ➢ Tuning of High Performance Computation codes based on deep knowledge of hard wares

Computics: Fusion of Materials Science and Computer Science

Computics,
A New Approach to
Materials Science in 21st Century,
in addition to *Mathematics*
that plays an important role from
Newton's Principia



http://computics-material.jp/

In collaboration with,

Jun-ichi Iwata (Univ Tokyo)
Shinnosuke Furuya (Univ Tokyo)
Shinya Kyogoku (Univ Tokyo)
Yuichiro Matsushita (Univ Tokyo)
Kenichi Koizumi (Unv Tokyo)
Mauro Boero (Strasbourg Univ)
Yasuteru Shigeta (Osaka Univ)

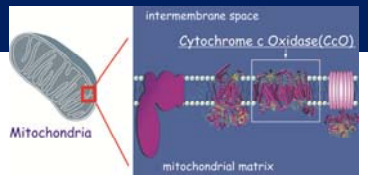
Yukihiro Hasegawa (Riken)
Kazuo Minami (Riken)
Mitsuo Yokokawa '(Riken)

Miwako Tsuji (Univ Tsukuba)
Daisuke Takahashi (Univ Tsukuba)
Taisuke Boku (Univ Tsukuba)

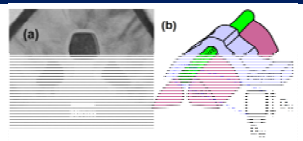
,,,

who are in the field of either
materials science
or computer science.

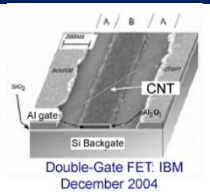
Challenges in Nanoscience



Cytochrome c Oxidase
X-ray determined structure
more than 10,000 atoms involved



Si-Nanowire FET
TokyoIT, IBM,,,



FET with CNT
IBM 2004

0.1 nm | 1 nm | 10 nm | sub μm

Theory

100 atoms | 10,000 atoms | 100,000 atoms

Experiment

Challenges along
3 Directions in Science

Space

Large scale:
Nano world =
100,000-atom
world

From sub-Femto sec
with electrons to
Nano sec with ions

Strongly Correlated System,
Excitation Spectrum

Accuracy

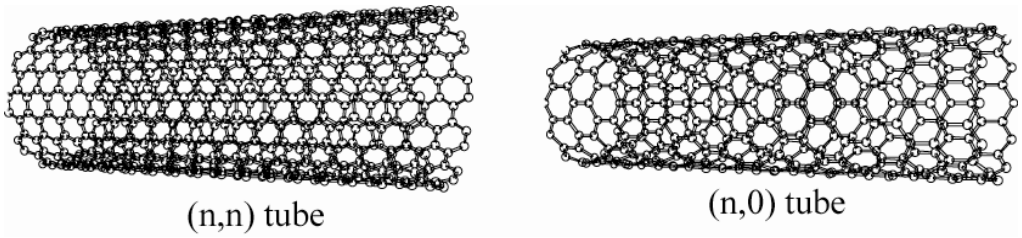
Time

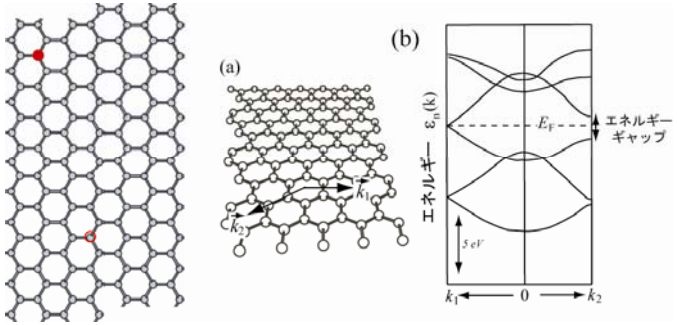
What is interesting in Nano?

Carbon Nanotube

Metal

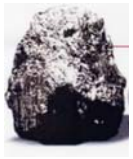
Semiconductor

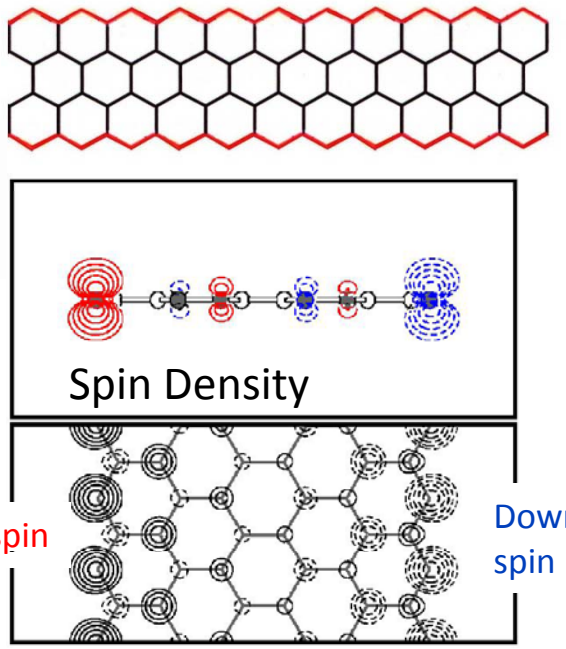




Hamada, Sawada & Oshiyama: Physical Review Letters 68, 1579 (1992)
Woldoer eta l., Nature 391, 59 (1998); Odom et al., Nature 391, 62 (1998)

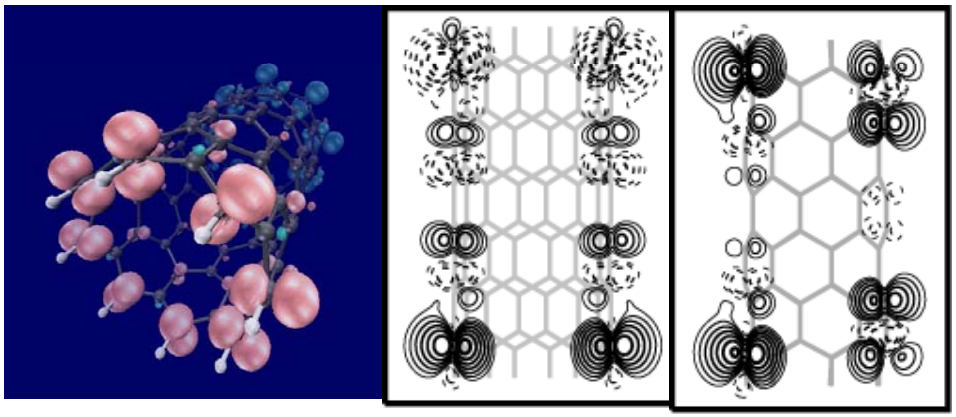
Edge states in zigzag graphene nanoribbon → Nanomagnet?





Electron Spin is polarized

All carbon Magnet?



Okada & Oshiyama: Physical Review Letters 87, 146803 (2001);
J. Phys. Soc. Jpn 72, 1510 (2003)

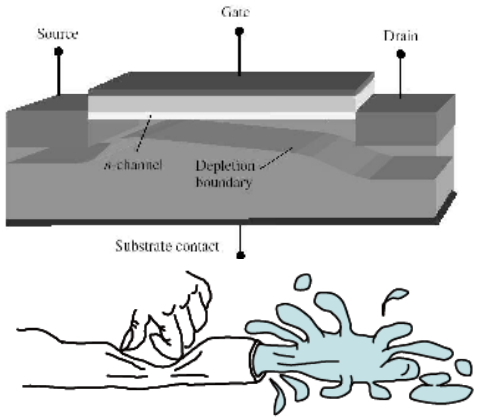
Prediction of Electron States of Si Nanowires

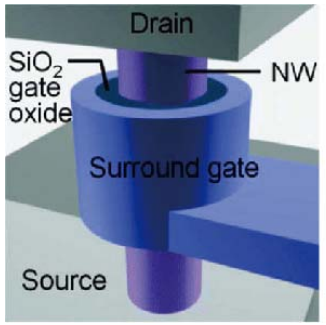
Si Nanowire, a Booster in the next-generation semiconductor technology

More Moore → More than Moore

International tech roadmap for semiconductors, http://www.itrs.net/

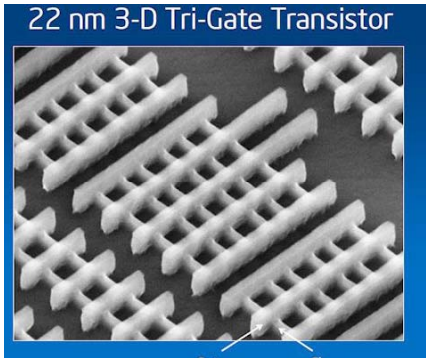
planar transistor





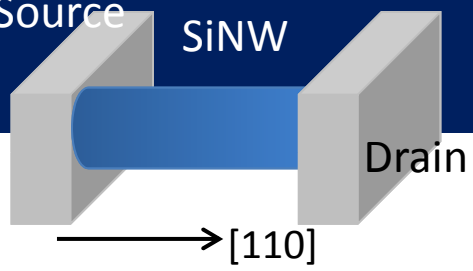
Surrounding gate transistor

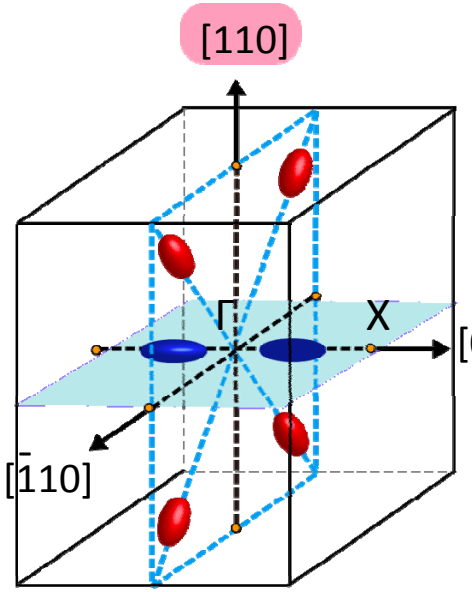
- Gate Controllability
  → Suppress short-channel effects
  Suppress leaks at off state
  → save energy
- Ballistic Conduction



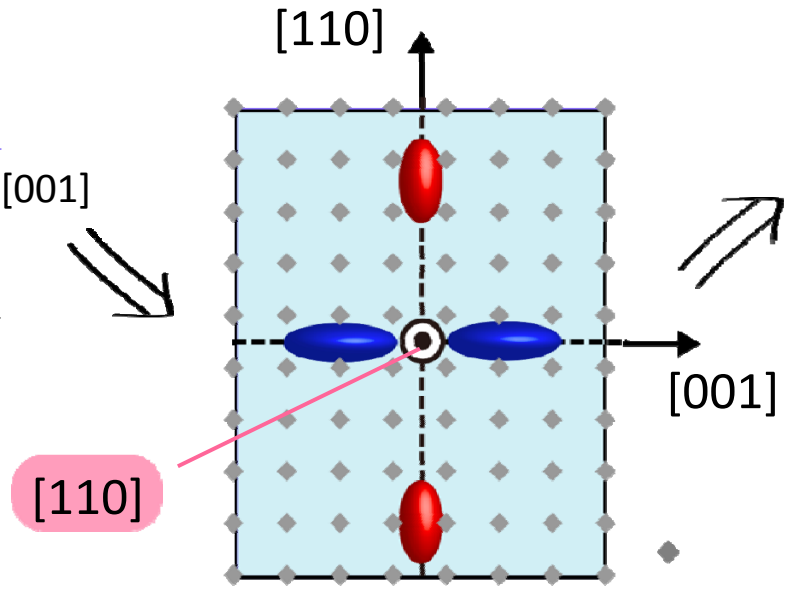
Actually tri-gate by Intel in 2011

Quantum Confinement in Si (110) Nanowires

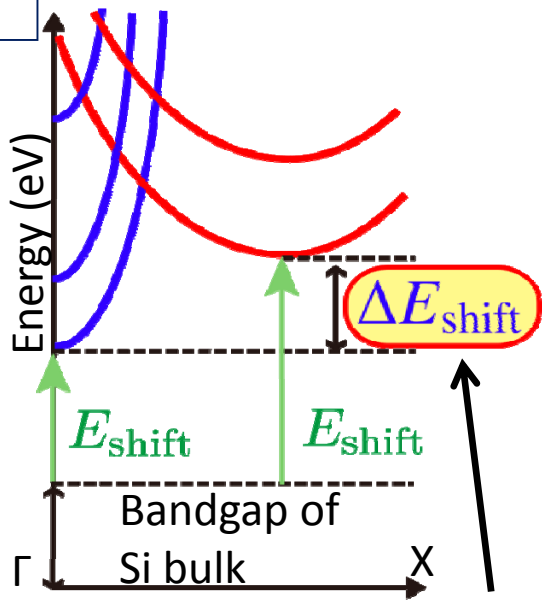




Six conduction-band valleys in Brillouin Zone



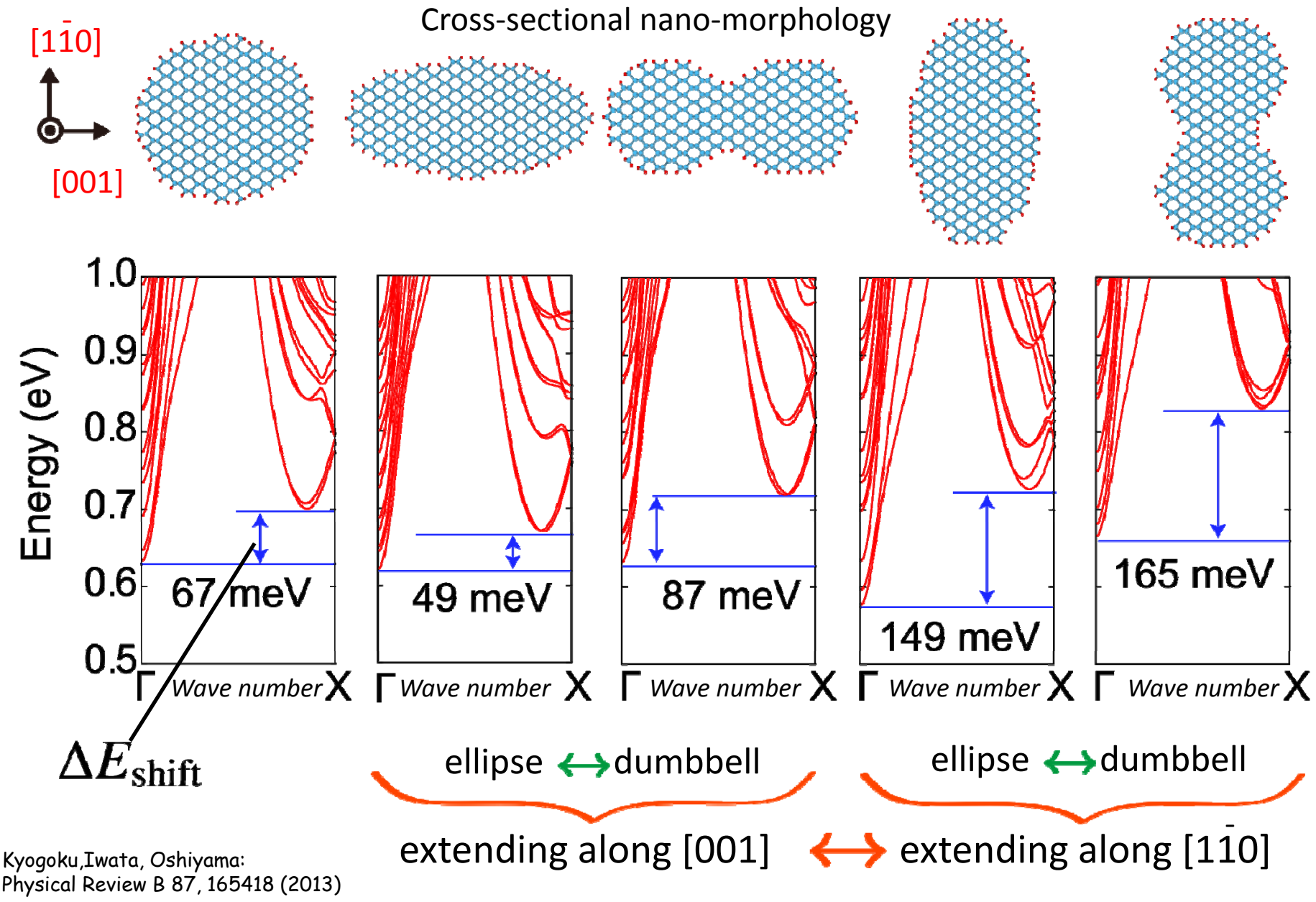
Conduction band structure of [110]-SiNW



This quantity is decisive in the number of the conduction channels.

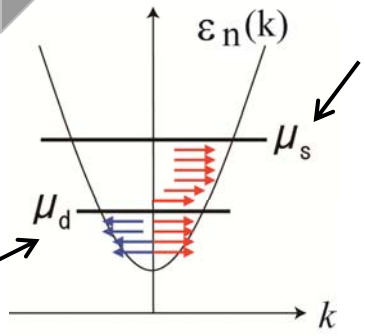
Properties of SiNWs are determined by the cross-sectional nano-morphology

Conduction Band Structures of Various Si(110) NWs



Kyogoku,Iwata, Oshiyama:
Physical Review B 87, 165418 (2013)

Ballistic Transport in Si Nanowires



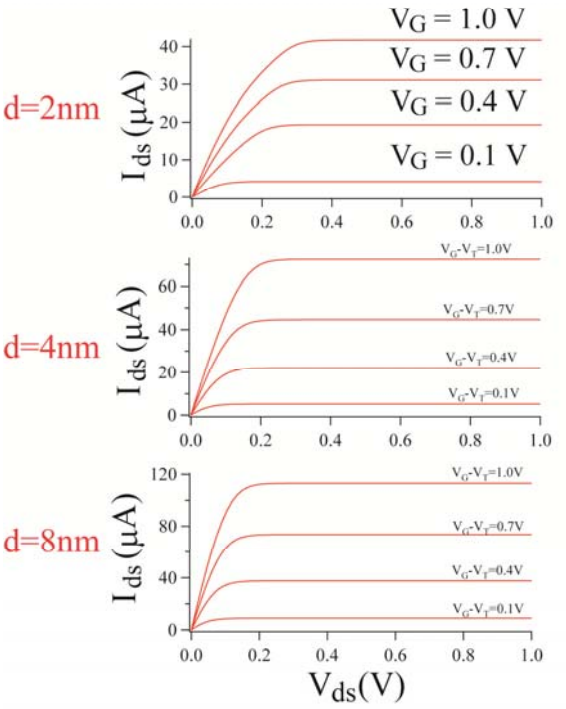
Source Chemical Potential

Drain Chemical Potential

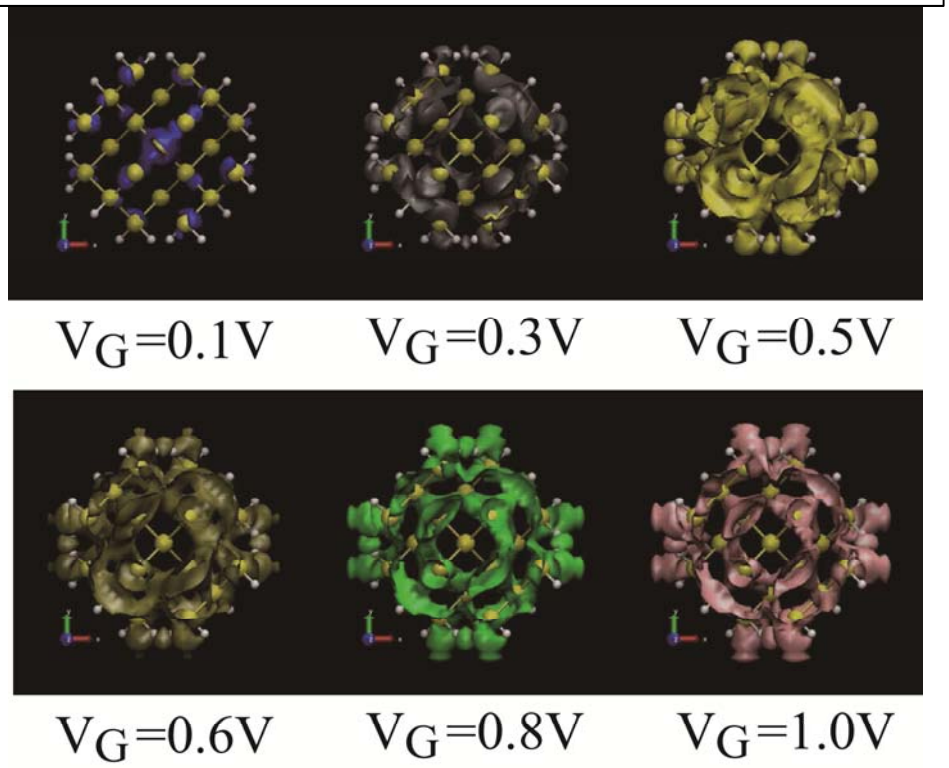
$$I = \frac{q}{\pi\hbar}\sum_n \int d\varepsilon_n \left[f(\varepsilon_n, \mu_S) - f(\varepsilon_n, \mu_d) \right]$$

$$j(r) = \frac{q}{im}\sum_n \left\{ \int_{v_k>0} dk \; f(\varepsilon_n(k), \mu_S)[\varphi^*_{nk}(r)\nabla\varphi_{nk}(r) - \varphi_{nk}(r)\nabla\varphi^*_{nk}(r)] \right.$$
$$\left. + \int_{v_k<0} dk \; f(\varepsilon_n(k), \mu_D)[\varphi^*_{nk}(r)\nabla\varphi_{nk}(r) - \varphi_{nk}(r)\nabla\varphi^*_{nk}(r)] \right\}$$

Current-Voltage Characteritics
Si(110) nanowires



Current Density depending on the gate voltage



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  - HPC in DFT Calculations: RSDFT code
    - ✓ ***Mathematical Methodology, Algorithm***
    - ✓ ***How to Collaborate***

Density Functional Theory (DFT)

Total energy of a material is a functional of the electron density:

$$E[n(\mathbf{r})] = \langle \Psi | H | \Psi \rangle = \langle \Psi | T + V_{nucl} + V_{ee} | \Psi \rangle$$

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

Quantum effects: exchange and correlation

When the electron density is written as $n(\mathbf{r}) = \sum_{i:\ \text{occupied}} |\varphi_i(\mathbf{r})|^2$

By minimizing E[n] with respect to n(r), we obtain Euler equation,

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}; n(\mathbf{r})) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$v_{eff}(\mathbf{r}) = v_{nucl}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})}$$

Kohn-Sham equation

KS equation should be solved self-consistently.
(Most time consuming process)

→ total energy, geometry optimization, physical properties,,,

Solving Kohn-Sham Equation

Introducing complete basis set $\chi_n(r)$ to expand Kohn-Sham wave function (orbitals):

$$\varphi_i(\vec{r}) = \sum_{\mu} c_{i\mu}\, \chi_\mu(\vec{r})$$

KS equation is converted to matrix equation:

$$\sum_{\mu'} H^{KS}_{\mu\mu'}(\{c_{i\mu}\})\, c_{i\mu'} = \varepsilon_i \sum_{\mu'} S_{\mu\mu'} c_{i\mu'}$$

that is solved usually by iterative techniques such as conjugate gradient or residual minimization.

The most standard basis set has been the plane wave basis set:

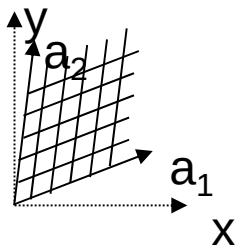
$$\chi_\mu(\vec{r}) = e^{\,i\,(\vec{k}+\vec{G}_\mu)\cdot\vec{r}}$$

However, in the plane-wave scheme, several quantities such as n(r), v(r) etc is Fourier-transformed and Inverse-Fourier-transformed frequently, which becomes a heavy burden on massively parallel-architecture computers.

$\Rightarrow$ Do it all in real space!

Solving Kohn-Sham Equation Using Real-Space Finite-Difference Scheme

Introducing mesh points with spacing H in real space,

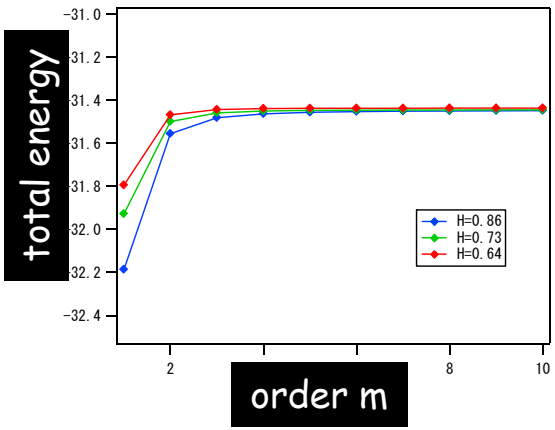


Kohn-Sham differential equation is converted to a M-th order finite-difference equation:

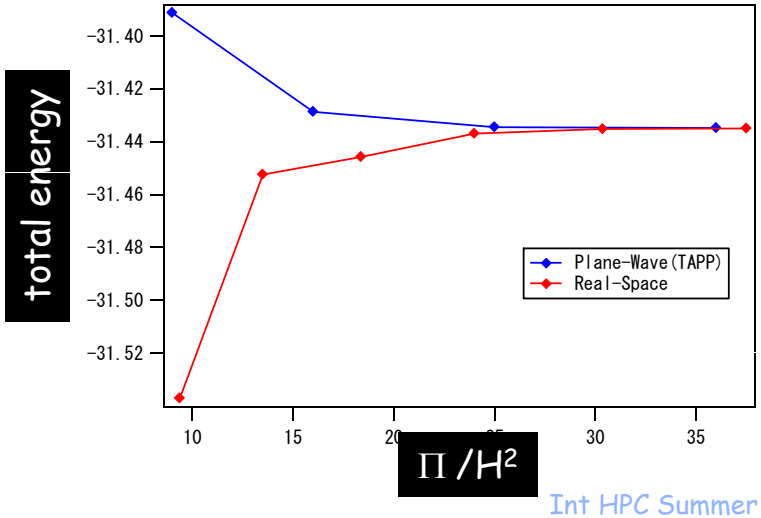
$$\frac{\partial^2}{\partial x^2}\varphi_j(x,y,z) = \sum_{m=-M}^{M} c_m \, \varphi_j(x+mH,y,z)$$

All the quantities computed at each mesh point, KS Hamiltonian expressed as a matrix.

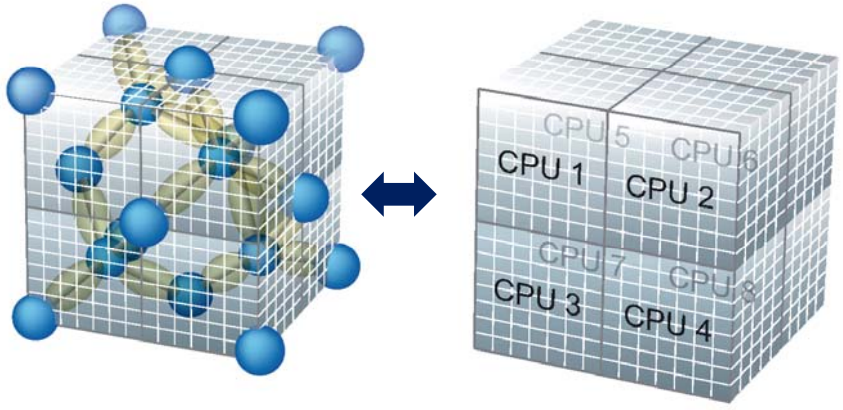
Check of finite difference



Check of mesh spacing
⇒ systematic accuracy improvement



Advantages of Real-Space DFT (RSDFT) in Parallel Computing



Real space CPU space

On multi-core parallel machines:
- Huge number of 3D mesh points divided into moderate-size cells
- Each cell treated by a single node or core
- Also, electron states (orbitals) are grouped and each group is treated by a single node or a core : Hybrid parallelization
- MPI for CPU and OpenMP for core

- Almost free from FFT, reducing communication burden
  ⇒ high efficiency
- Flexible boundary condition to wave-functions
  ⇒ targets expanded including charged objects
- Utilize inherent locality of the system
  ⇒ prospect to efficient O(N) scheme

Solving Kohn-Sham Equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}_k ;\, n(\mathbf{r}_k)) \right] \varphi_i(\mathbf{r}_k) = \varepsilon_i \varphi_i(\mathbf{r}_k)$$

Getting Self-Consistent Field (SCF) by Iterative Computationas

1. (CG) Conjugate gradient method — $O(N^2)$
2. (GS) Ortho-normalization by Gram-Schmidt method — $O(N^3)$
3. Density and potential update — $O(N)$
4. (SD) Subspace diagonalization — $O(N^3)$

GS and SD should be accelerated!

Memory is not the problem so far: $O(N^2)$

107,292-atom SiNW:

$$\varphi_i(r_k) = 576 \times 576 \times 576\ (\text{mesh } k) \times 229{,}824(\text{state } i) \times 8 = 351\ \text{TBite}$$

Gram-Schmidt Ortho-normalization: Active use of Level 3 BLAS in O(N³) Computation

$$\varphi_1 = \psi_1$$

$$\varphi_2 = \psi_2 - \varphi_1 \langle \varphi_1 | \psi_2 \rangle$$

$$\varphi_3 = \psi_3 - \varphi_1 \langle \varphi_1 | \psi_3 \rangle - \varphi_2 \langle \varphi_2 | \psi_3 \rangle$$

$$\varphi_4 = \psi_4 - \varphi_1 \langle \varphi_1 | \psi_4 \rangle - \varphi_2 \langle \varphi_2 | \psi_4 \rangle - \varphi_3 \langle \varphi_3 | \psi_4 \rangle$$

$$\varphi_5 = \psi_5 - \varphi_1 \langle \varphi_1 | \psi_5 \rangle - \varphi_2 \langle \varphi_2 | \psi_5 \rangle - \varphi_3 \langle \varphi_3 | \psi_5 \rangle - \varphi_4 \langle \varphi_4 | \psi_5 \rangle$$

$$\varphi_6 = \psi_6 - \varphi_1 \langle \varphi_1 | \psi_6 \rangle - \varphi_2 \langle \varphi_2 | \psi_6 \rangle - \varphi_3 \langle \varphi_3 | \psi_6 \rangle - \varphi_4 \langle \varphi_4 | \psi_6 \rangle - \varphi_5 \langle \varphi_5 | \psi_6 \rangle$$

.....

DGEMM on K:
96.6 % efficiency to the peak performance by making the necessary data kept on L1D and L2 cache

Most calculations can be performed as Matrix x Matrix operations!

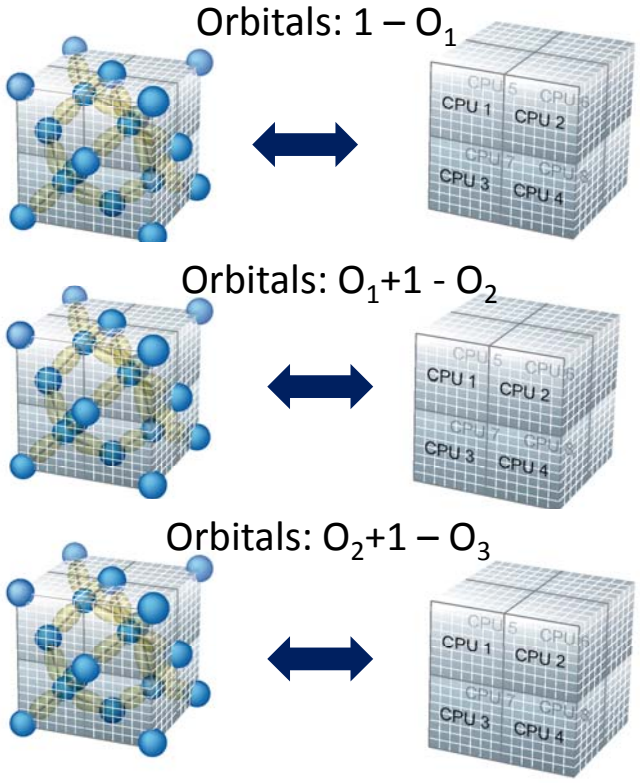
$$[\varphi_3, \varphi_4, \varphi_5, \varphi_6, \ldots] = [\psi_3, \psi_4, \psi_5, \psi_6, \ldots] - [\varphi_1, \varphi_2] \begin{bmatrix} {}^{\dagger}\varphi_1 \\ {}^{\dagger}\varphi_2 \end{bmatrix} [\psi_3, \psi_4, \psi_5, \psi_6, \ldots]$$

Real Space Parallelization + Orbital Parallelization

Kohn-Sham equation

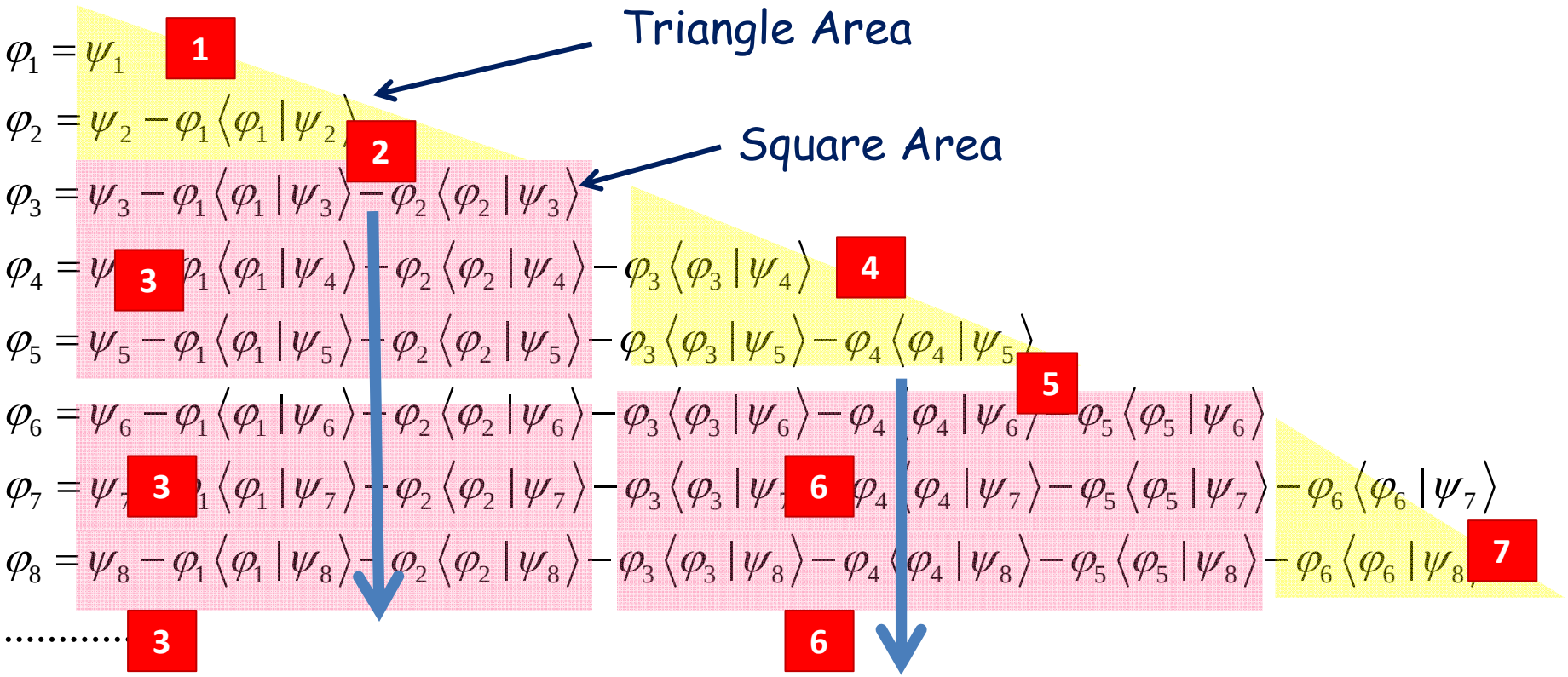
$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}_k ; n(\mathbf{r}_k)) \right] \varphi_i(\mathbf{r}_k) = \varepsilon_i \varphi_i(\mathbf{r}_k)$$

Real Space parallel $\{k\}$ + *Orbital Parallel* $\{i\}$



- Reduce communication cost
- Guarantee high performance in massively parallel computations

Gram-Schmidt Ortho-normalization: Orbital Parallel Coding of Matrix Operations



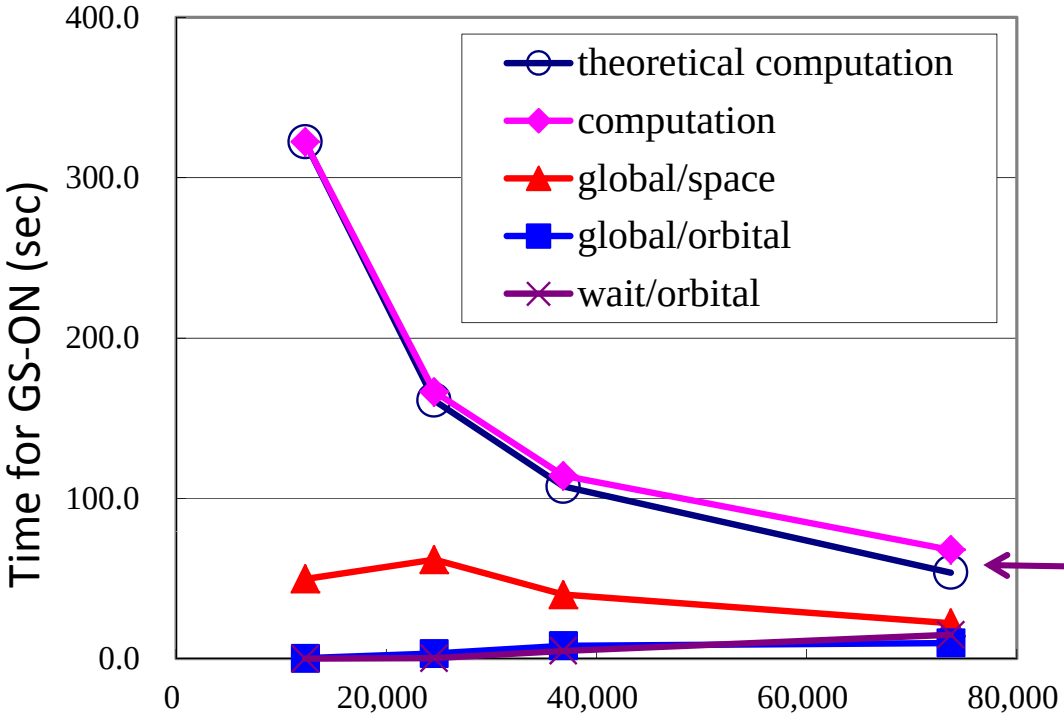
$$\varphi_1 = \psi_1$$
$$\varphi_2 = \psi_2 - \varphi_1\langle\varphi_1|\psi_2\rangle$$
$$\varphi_3 = \psi_3 - \varphi_1\langle\varphi_1|\psi_3\rangle - \varphi_2\langle\varphi_2|\psi_3\rangle$$
$$\varphi_4 = \psi_4 - \varphi_1\langle\varphi_1|\psi_4\rangle - \varphi_2\langle\varphi_2|\psi_4\rangle - \varphi_3\langle\varphi_3|\psi_4\rangle$$
$$\varphi_5 = \psi_5 - \varphi_1\langle\varphi_1|\psi_5\rangle - \varphi_2\langle\varphi_2|\psi_5\rangle - \varphi_3\langle\varphi_3|\psi_5\rangle - \varphi_4\langle\varphi_4|\psi_5\rangle$$
$$\varphi_6 = \psi_6 - \varphi_1\langle\varphi_1|\psi_6\rangle - \varphi_2\langle\varphi_2|\psi_6\rangle - \varphi_3\langle\varphi_3|\psi_6\rangle - \varphi_4\langle\varphi_4|\psi_6\rangle - \varphi_5\langle\varphi_5|\psi_6\rangle$$
$$\varphi_7 = \psi_7 - \varphi_1\langle\varphi_1|\psi_7\rangle - \varphi_2\langle\varphi_2|\psi_7\rangle - \varphi_3\langle\varphi_3|\psi_7\rangle - \varphi_4\langle\varphi_4|\psi_7\rangle - \varphi_5\langle\varphi_5|\psi_7\rangle - \varphi_6\langle\varphi_6|\psi_7\rangle$$
$$\varphi_8 = \psi_8 - \varphi_1\langle\varphi_1|\psi_8\rangle - \varphi_2\langle\varphi_2|\psi_8\rangle - \varphi_3\langle\varphi_3|\psi_8\rangle - \varphi_4\langle\varphi_4|\psi_8\rangle - \varphi_5\langle\varphi_5|\psi_8\rangle - \varphi_6\langle\varphi_6|\psi_8\rangle$$
$$\cdots\cdots\cdots$$

1. Calculate the triangle area
2. Transfer the calculated values to the square area
3. Calculate the square area in parallel

Efficiency of Gram-Schmidt Ortho-normalization

62 % (55,296 nodes of K) - 80% (1000 CPU of PACS-CS) efficiency to the peak performance

Strong Scaling in Orbital Parallelization for GS ON



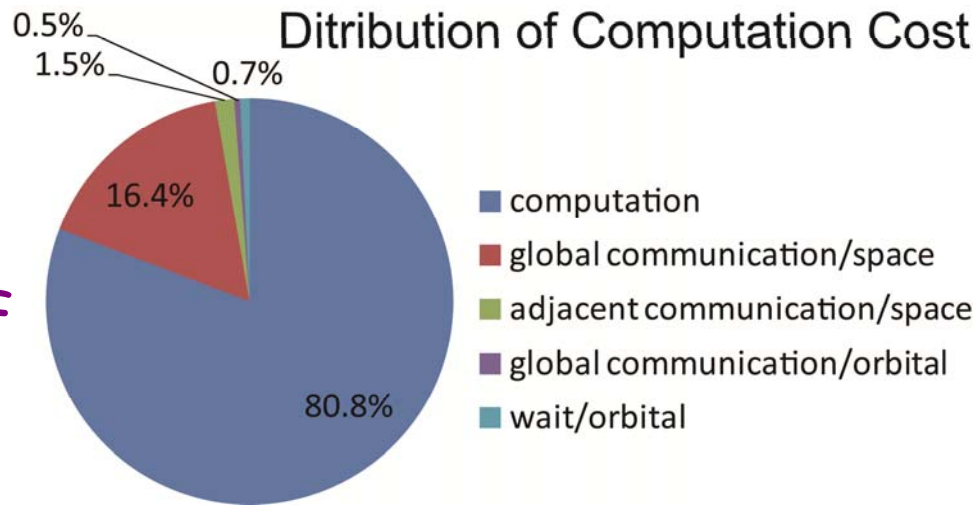
Si Nanowire 19,848 atoms
[Grids:320x320x120, Orbitals:40,992]

Number of parallel tasks
- 1,536 (fixed) in space
- 1, 2, 3, 6, in orbitals

Ideal efficiency

RSDFT on K 京 at Kobe

- ✓ 107,292-atom DFT calculations for Si Nanowires using 55, 296 nodes
  - 3.08PFLOPS =43.6% efficiency to peak performance
  - Single iteration in SCF = 5,500 sec



- ✓ 10,000-atom DFT calculations
  - Getting SCFields costs one day using several hundreds of nodes (less than 1 % of the total resource) with 34 % - 70 % efficiency
  - Good strong scaling (78 % - 88 %) for 4,608~15,552-atom systems using 768 ~ 12,288 nodes

Computation cost and Memory: Achieved values

- Memory: order N^2
  - 107,292-atom SiNW

$$\varphi_i(r_k) = 576 \times 576 \times 576\ (\text{mesh } k) \times 229,824(\text{state } i) \times 8 = 351\ \text{TBite}$$

  - SiNW with 10,000 atoms

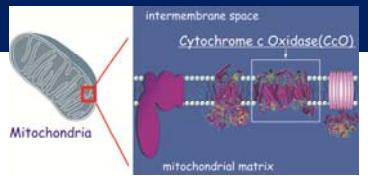
$$\varphi_i(r_k) \approx 3.5\ \text{TBite}$$

- Computation Cost: order N^3
  - 107,292-atom SiNW with 55,296 nodes (442,368 cores)
    - ✓ Solve KS equation with given n(r) = 5,500 sec
    - ✓ Get SCF potential = 5 days, geometry optimization = 50 days
    - ✓ *Several hundreds PFLOPS (of cource exa) machine makes it*
  - SiNW with 10,000 atoms with 2000 – 3000 nodes
    - ✓ Get SCF potential < 1 day, geometry optimization = 1 week

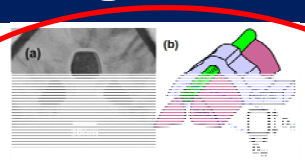
→

- HPC is the issue: perform $O(N^3)$ computations efficiently with some accelerators (GPU?).

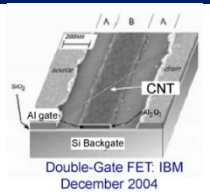
Challenges in Nanoscience



Cytochrome c Oxidase
X-ray determined structure
more than 10,000 atoms involved



Si-Nanowire FET
TokyoIT, IBM,,,



FET with CNT
IBM 2004

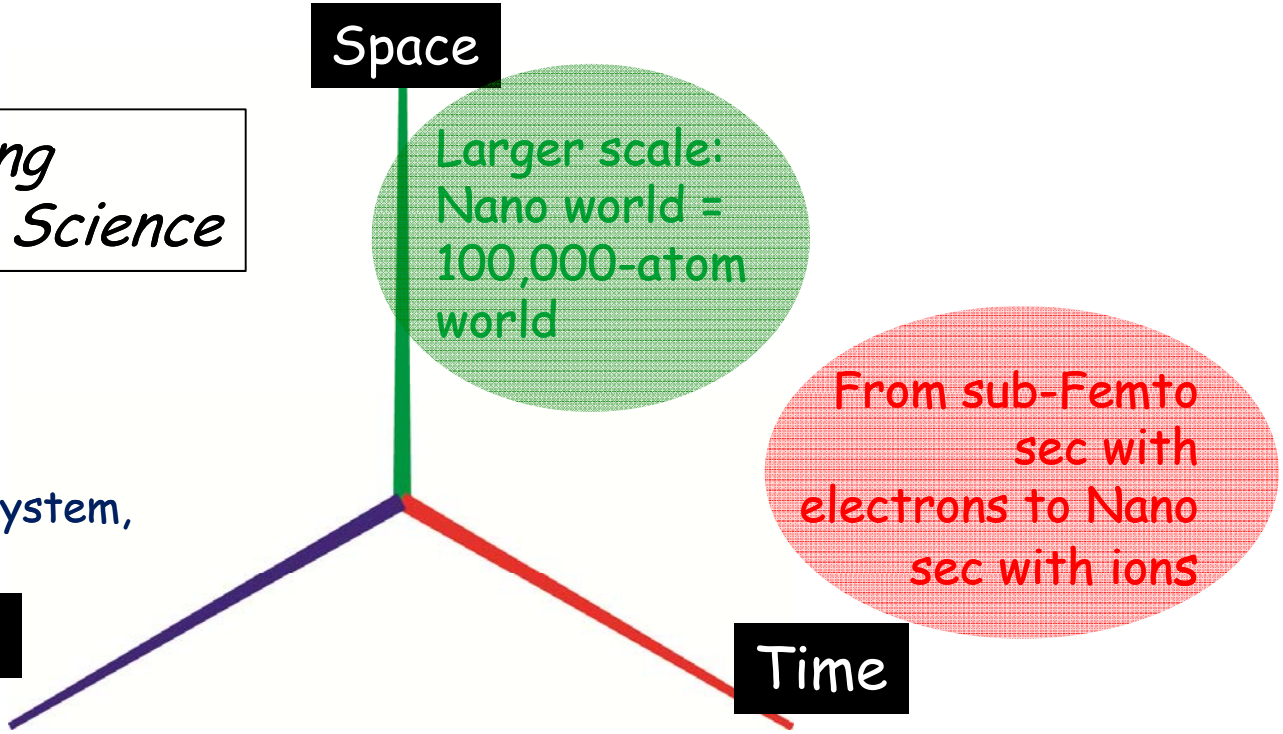
0.1 nm | 1 nm | 10 nm | sub μm

Theory

100 atoms | 10,000 atoms | 100,000 atoms

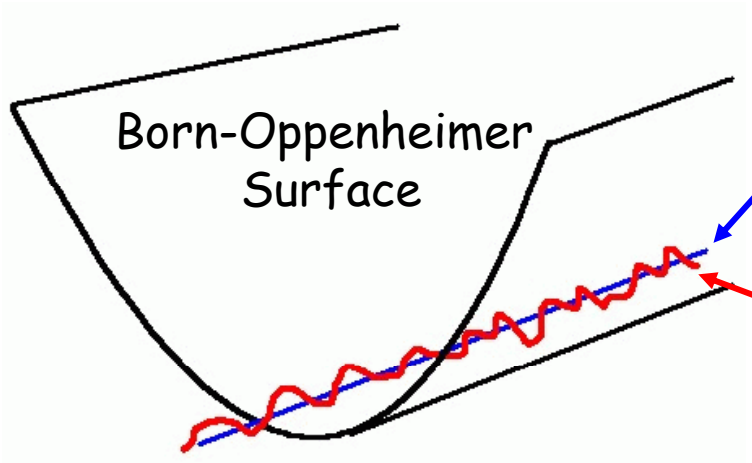
Experiment

Challenges along
3 Directions in Science



Strongly Correlated System,
Excitation Spectrum

Car-Parrinello Molecular Dynamics



$- H_{KS}\,\psi_i$

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

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

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

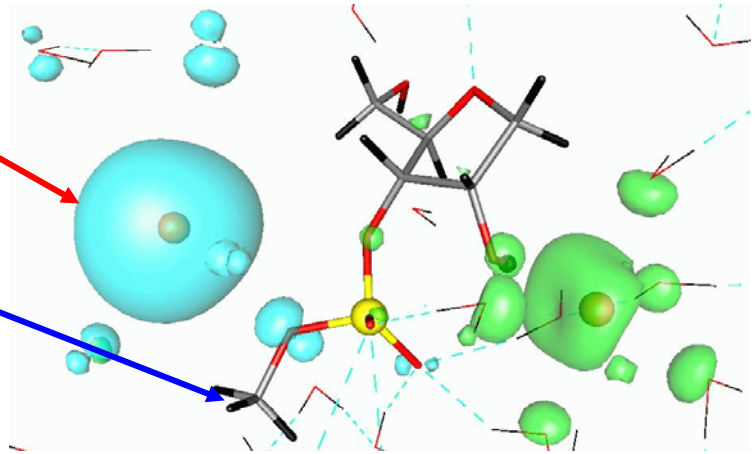
External Paremeters: T, P,,,

Computation Cost

Hamiltonian operation $\propto N^2$

Force Calculation $\propto N^2$

Lagrange Multiplier $\propto N^3$



Car-Parrinello MD + MetaDynamics

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

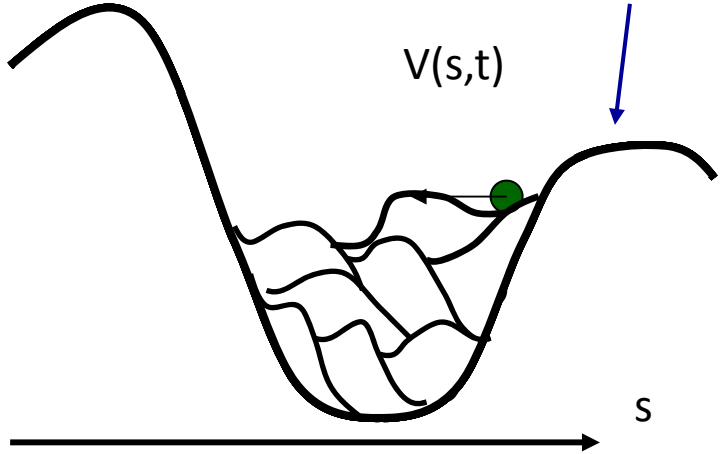
where the history dependent function V is

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

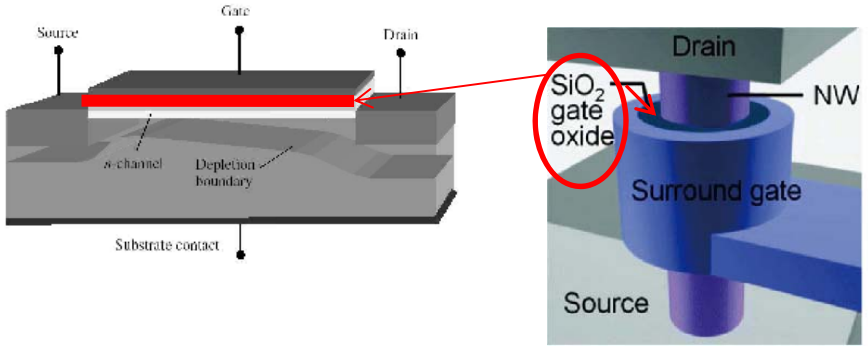
Free-energy landscape that we want to get

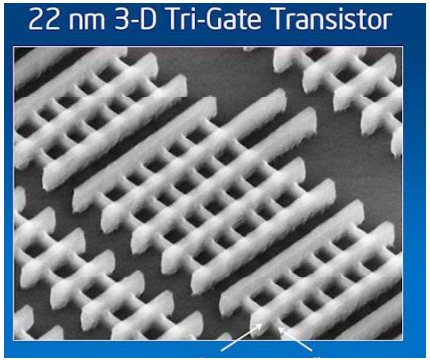
and sum of gaussians gives us Free-energy landscape

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



Silicon Oxidation: Essential Process in Device Fabrication





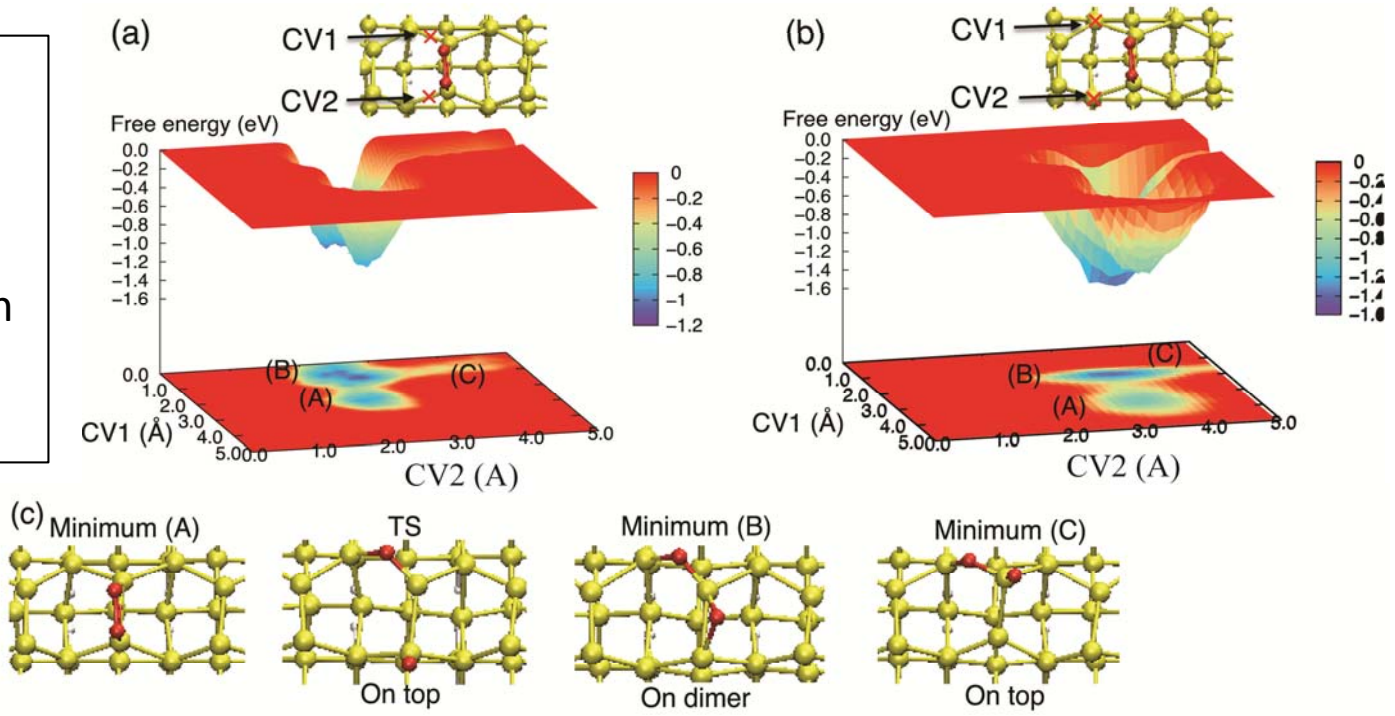
- ✓ Good Insulators for Gate Functions are Provided by Silicon Oxidation
- ✓ Film Thickness is about 1 nm or less
- ✓ New materials which have high dielectric constants are incorporated

→ Atom-scale Understanding of Oxidation Processes

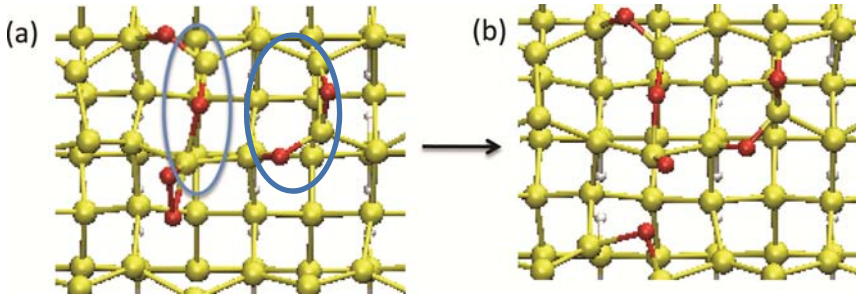
Si Oxidation: Free-energy Landscape

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

Stable Geometry Minimum(B) is reached from Geometry (A) with free-energy barrier of 0.8 eV



Minimum(B) is ubiquitous and further oxidation starts from there



Koizumi, Boero, Shigeta, AO: PRB 85, 205314 (2012)

Car-Parrinello Molecular Dynamics: Present an Future

- **Present**
  - 100 – 300 atoms are extracted from nano-structures and used as a model → Too small
  - Simulation continues only in 10 picoseconds at most → Meta-dynamics accelerate reactions,

But,,,

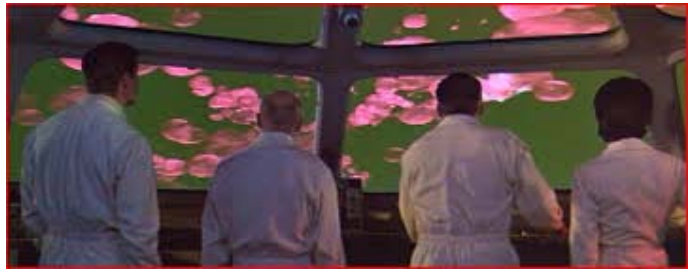
- **Future**
  - Real-Space CPMD required → now crossover at 1000-atom system
  - New scheme for Phase-space sampling???

Visualization

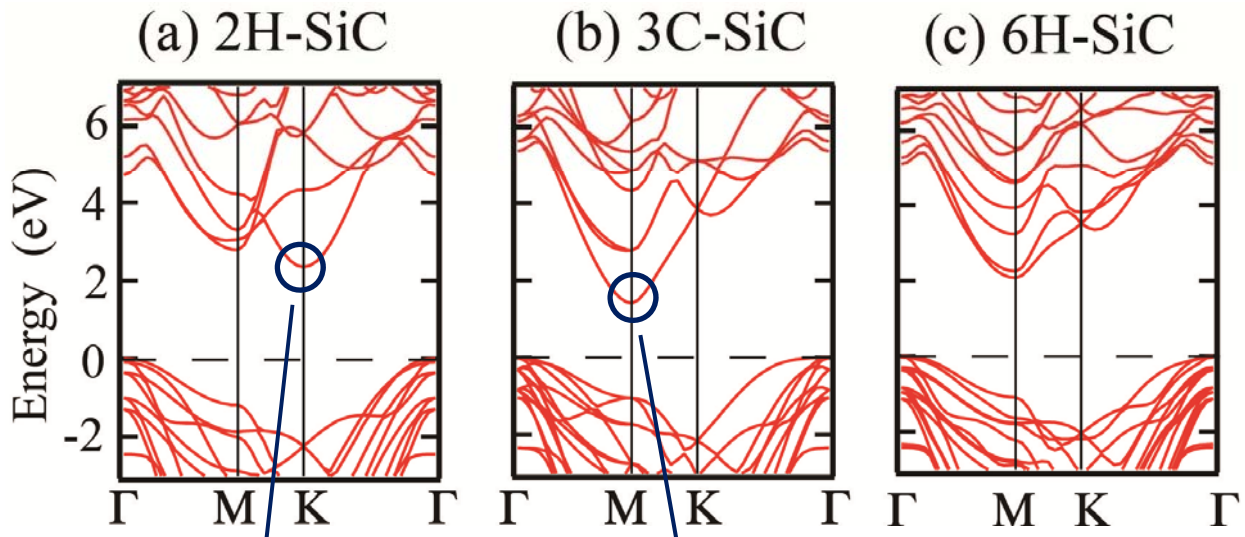
Visualization
- Not for demonstration, publicity, advertisement etc,
- But for the research tool.
- Not for explaining what we already know,
- But for exploring what we don't know.

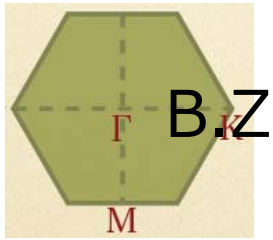
get into materials, see the position of nuclei,
see the electron clouds, think about possible reactions,
imagine new properties,,,,,, then do simulations.

Fantastic Voyage 1966



Calculated Energy bands and Kohn-Sham orbitals of SiC

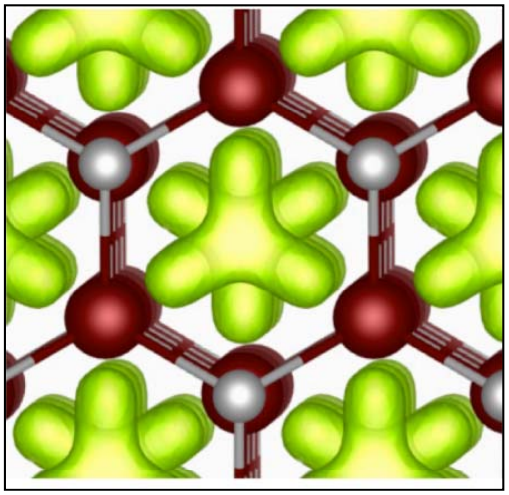




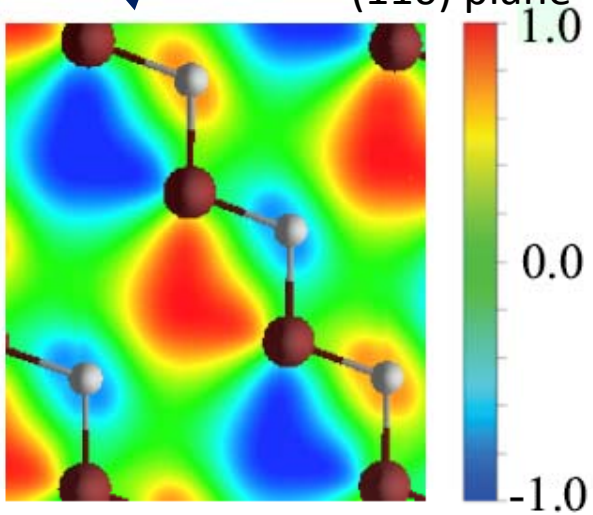
B.Z.

(0001) plane

(1$\bar{1}$0) plane



Isovalue surface

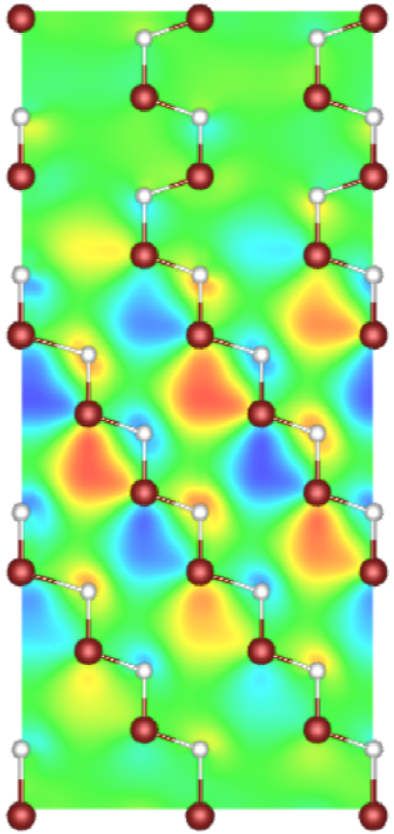


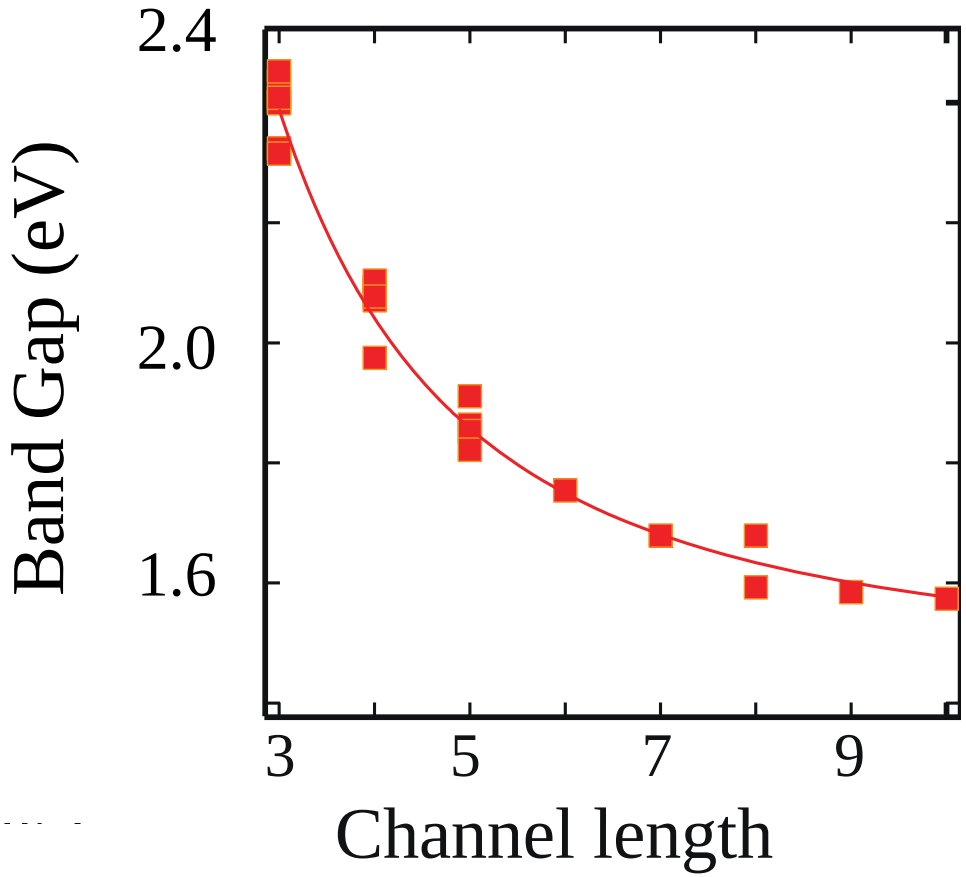
contour plot

Wave-function of the conduction band bottom floats in the internal space (channel)!

Y. Matsushita, S. Furuya and A. Oshiyama, Phys. Rev. Lett. 108, 246404 (2012).

Volume of the internal space makes it





Materials Design through COMPUTICS: Large-Scale Density-Functional Calculations for Nanomaterials

- **Computational Nanoscience**
  - What is Nano? What is Interesting?
    - ✓ *Quantum Theory Required. Science and Technology are close to each other*
    - ✓ *Carbon nanotube, Graphene, Si nanowire,,,*

      Nanoshapes are decisive
- **Computics: Collaboration among Materials Science, Computer Science and Mathematics**
  - Density-Functional Theory (DFT)
    - ✓ *Material is an Interacting Many-Electron System*
  - HPC in DFT Calculations: RSDFT code
    - ✓ *Mathematical Methodology, Algorithm*
    - ✓ *How to Collaborate*