STATE-Senri

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First-principles Electronic Structure Theory

- Based on basic principles of physics such as quantum mechanics, electromagnetism, and statistical mechanics.
- It does not depend on experimentally fitted parameters.
- Electronic structures of materials can be accurately reproduced by computer simulations.

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First-principles Electronic Structure Theory

- Understand important factors determining properties of materials.
- Predict properties of new materials.
- Design new desired materials.

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(Simulation Tool for Atom TEchnology)

- Density Functional Theory
    LDA、GGA、LDA+U
- Ultrasoft pseudopotential
- Plane wave basis set
- Iterative diagonalization
    Davidson method, RMM-DIIS method
- Broyden charge density mixing
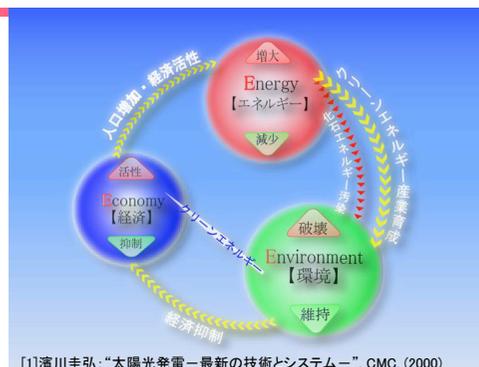
--> Applicable to wide range of materials.

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(Simulation Tool for Atom TEchnology)

- Structure Optimization
- Finite Temperature Molecular Dynamics
- Reaction Path Search
- Vibrational Spectra (IR, HREELS)、Electronic States (XPS, UPS)、STM Image calculations

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(Simulation Tool for Atom TEchnology)

- Tutorial course in "Computational Materials Design (CMD) Workshop".

  http://www.dyn.ap.eng.osaka-u.ac.jp/CMD14/
- Twice a year in CMD-WS(Mar. and Sep.).
- Open to both theoretical and experimental researchers.
- Open to Asian researchers and students.

3E-trilemma

- **Economy**
- **Energy**
- **Environment**

[1]濱川圭弘：“太陽光発電－最新の技術とシステムー", CMC, (2000)

Solve the trilemma by Quantum Simulations.

Pseudopotential Method

- Core Electrons：Tightly bound to nuclei --> Localized close to nuclei.
- Valence Electrons：Weakly bound to nuclei --> Delocalized around neighboring atoms.
- Physical and chemical properties of materials should be mainly governed by the valence electron states.

  --> Necessary to reproduce valence enectron states accurately.

Concept of Pseudopotential

- Atom：Scattering potential of electrons.
- Core electrons are localized within spheres of radius r_c
- If the scattering properties of pseudopotentials outside of radius r_c are the same as those of true atomic potentials, then the valence electron states should be reproduced by pseudopotentials exactly.

Electrons

True atomic potentials

Electrons

Pseudopotentials which have exactly the same scattering properties for valence electrons

Advantages of the pseudopotential method

- It is as accurate as an all-electron full-potential linearized augumented plane wave (FLAPW) method for valence states.
- It is computationally fast because it does not calculate core states explicitly.
- Required number of effective digits can be smaller compared with all-electron methods because it does not treat core states of which energies have large absolute values.
- Pseudopotentials and pseudowave functions are smooth and can be expanded by plane wave basis sets efficiently.

Norm-conserving pseudopotentials

To construct norm-conserving pseudopotentials, we first perform all-electron calculation for an isolated atom and obtain energy eigenvalues ε_l, wave functions $\psi_l(r)$, and, self-consistent effective potential $V^{AE}(r)$. l is an angular momentum quantum number of a valence state. satisfies the following Kohn-Sham equation.

$$\left(T + V^{AE}(r)\right)\psi_l(r) = \varepsilon_l\psi_l(r),$$

$$T = -\frac{1}{2r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{l(l+1)}{2r^2},$$

$$\langle\psi_l|\psi_l\rangle = \int_0^\infty |\psi_l(r)|^2 r^2 dr = 1.$$

Costruction of pseudo wave function

Next, we construct pseudowave function $\varphi_l(r)$ by smoothing true wave function $\psi_l(r)$ inside the cutoff radius of r_{cl}. Usually, we expand $\varphi_l(r)$ by polynomial functions inside the r_{cl}.

$$\varphi_l(r) = \begin{cases} \psi_l(r) & \text{for } r \geq r_{cl} \\ \sum_{t=0}^{M} c_{l,2t} r^{2t+l} & \text{for } r \leq r_{cl} \end{cases}$$

Two more constraints are imposed on $\varphi_l(r)$
- They are nodeless inside r_{cl}.
- The norm-conserving condition:
$$\int_0^{r_{cl}} |\psi_l(r)|^2 r^2 dr = \int_0^{r_{cl}} |\varphi_l(r)|^2 r^2 dr.$$

The norm-conserving condition is very important to ensure the accuracy of pseudopotentials.

Construction of pseudopotentials

By solving the Kohn-Sham equation inversely, pseudo-potential $V_l(r)$ which acts pseudowave function $\varphi_l(r)$.

$$V_l(r) = \frac{(\varepsilon_l - T)\varphi_l(r)}{\varphi_l(r)}.$$

Pseudopotentials become angular momentum dependent and therefore, they are non-local. Usually, angular momentum dependence are taken into account only up to $l=2$ and pseudo-potentials for $l>2$ are replaced by a common potential $V_{\text{loc}}(r)$.

$$V^{\text{ps}} = \sum_{l,m=0}^{l=l_{\max}, m=l} |Y_{lm}\rangle (V_l(r) - V_{\text{loc}}(r)) \langle Y_{lm}| + V_{\text{loc}}(r)$$

where, $|Y_{lm}\rangle$ are projectors onto states with angular quantum numbers of l and m momentum.

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Norm-conserving Pseudopotential

- The norm-conserving pseudopotentials are constructed by imposing the following three conditions.

1. They reproduce correct eigenenergies ε_l for valence electrons.

2. Pseudo-wave functions coincide with all-electron wave functions outside the cutoff radii r_{cl}.

3. Pseudo-wave functions have correct norm inside the cutoff radii r_{cl}.

$$4\pi \int_0^{r_c} \left|\psi_l^{\text{AE}}(r)\right|^2 r^2 dr = 4\pi \int_0^{r_c} \left|\psi_l^{\text{ps}}(r)\right|^2 r^2 dr$$

$$= -2\pi \left(r\psi_l^{\text{AE}}\right)^2 \frac{d}{d\varepsilon}\frac{d}{dr} \ln\psi_l^{\text{AE}}\bigg|_{r_c}$$
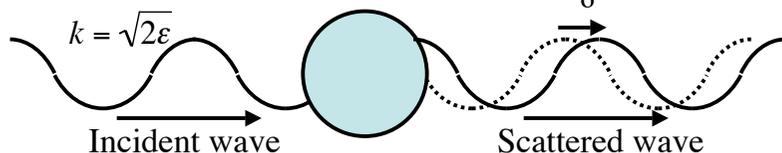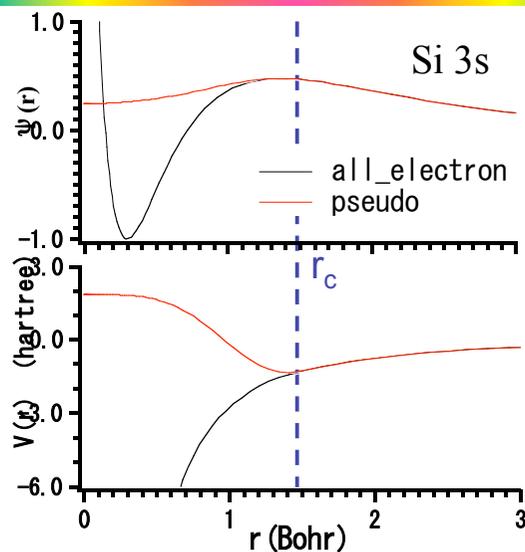
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The norm-conserving condition

The norm-conserving condition can be related to logarithmic derivatives of wave functions by the following equation.

$$\int_0^{r_c} \left|\psi_l(r)\right|^2 r^2 dr = \int_0^{r_c} \left|\phi_l(r)\right|^2 r^2 dr = -\frac{1}{2}\left(r\phi_l(r)\right)^2 \frac{d}{d\varepsilon}\frac{d}{dr} \ln\phi_l(r)\bigg|_{r_c}$$

The logarithmic derivatives of wave functions can be related to phase shifts of scattered wave functions by spherical potentials.

$$\frac{d}{dr}\ln\phi_l(r)\bigg|_{r_c} = \frac{k\left[j_l{'}(kr_c)\cos\delta_l - n_l{'}(kr_c)\sin\delta_l\right]}{j_l(kr_c)\cos\delta_l - n_l(kr_c)\sin\delta_l},$$

$$k = \sqrt{2\varepsilon}$$

Incident wave Scattered wave

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The norm-conserving condition

A pseudo-wave function $\varphi_l(r)$ is constructed in such a way that it has the correct scattering property at the eigen energy ε_l outside the cutoff radius r_{cl}. By imposing the norm-conserving condition, the scattering property becomes correct not only at the eigen energy ε_l but also at other energies ε up to the first order of ε-ε_l. Therefore, the norm-conserving condition is very important to ensure the accuracy of pseudopotentials.

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Norm-conserving pseudopotential

Si 3s

all_electron
pseudo

r_c

$\psi(r)$

$V(r)$ (hartree)

r (Bohr)

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Norm-conserving pseudopotential

- The logarithmic derivative of pseudo-wave function agrees with that of true wave function in wide range of energy.

$d\ln\psi/dr$

ε_l

Energy (hartree)

1 hartree = 27.211eV

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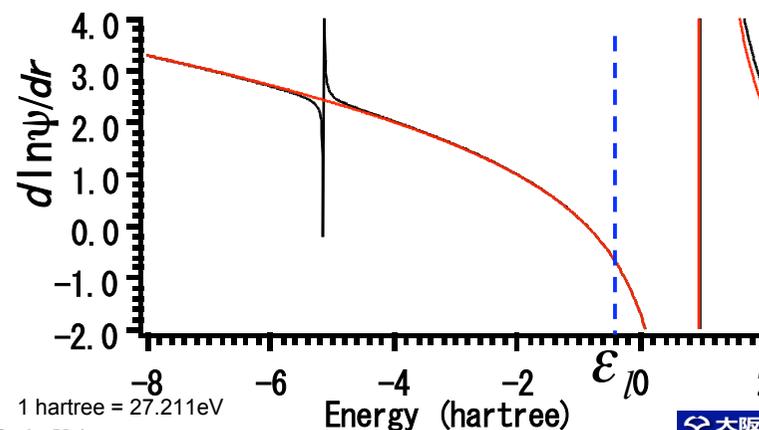
Plane Wave Basis Set

- Pseudopotentials and pseudo-wave functions can be expanded by plane waves efficiently because they are quite smooth.

$$\left|\psi_{i,\mathbf{k}}\right\rangle = \sum_{\mathbf{G}}^{|\mathbf{k}+\mathbf{G}|\le G_{max}} c_{i,\mathbf{k}+\mathbf{G}}\left|\mathbf{k}+\mathbf{G}\right\rangle,$$

$$\left\langle\mathbf{r}\middle|\mathbf{k}+\mathbf{G}\right\rangle = \frac{1}{\sqrt{\Omega_a}}\exp\left(i(\mathbf{k}+\mathbf{G})\bullet\mathbf{r}\right),$$

Ω_a : Unit cell volume

$$\left\langle\mathbf{k}+\mathbf{G}\middle|\mathbf{k'}+\mathbf{G'}\right\rangle = \delta_{\mathbf{kk'}}\delta_{\mathbf{GG'}}$$

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Cutoff Wavenumber (Cutoff Energy)

The number of reciprocal points G used in plane wave expansion is, in principle, infinite. However, in practice, it should be finite and the summation with respect to G should be cutoff. Usually, we cutoff G in such a way that the norm of $k+G$ is smaller than a cutoff wave number G_{max}.
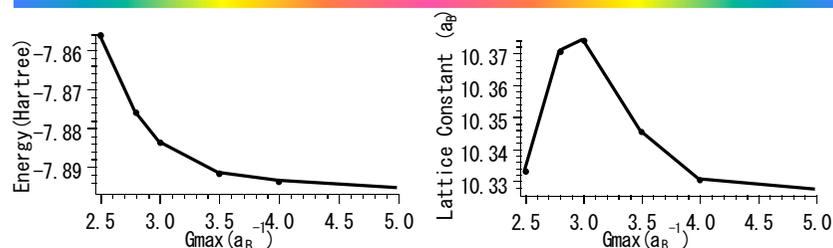
$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}}^{|\mathbf{k}+\mathbf{G}|\le G_{max}} c_{i\mathbf{k}+\mathbf{G}}\frac{1}{\sqrt{\Omega}}\exp\left(i(\mathbf{k}+\mathbf{G})\bullet\mathbf{r}\right),$$

c_{ik} is a Fourier transofrm of $\psi_{ik}(r)$.

$$c_{i\mathbf{k}+\mathbf{G}} = \frac{1}{\sqrt{\Omega}}\int_{\Omega}\exp\left(-i(\mathbf{k}+\mathbf{G})\bullet\mathbf{r}\right)\psi_{i\mathbf{k}}(\mathbf{r})d\mathbf{r}.$$

$2\pi/G_{max}$ corresponds to the spacial resolution of the basis set. Therefore, the required G_{max} depends on the steepness of pseudo-wave functions. G_{max}^2 is called "Cutoff Energy".

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Cutoff Wavenumber: Example Si

By using G_{max}=3.5 a_B^{-1}, the total energy is converged within 0.1 eV and the lattice constant is within 0.001 nm. In general, energy differences among different structures converge better than the absolute values of total energies.
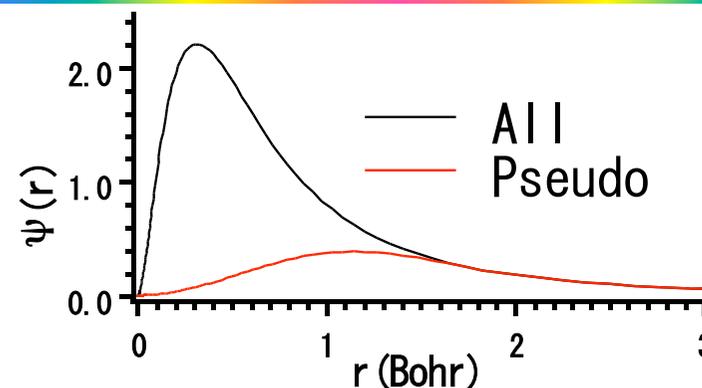
1 Hartree = 27.2116 eV

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Advantages of Plane Wave Basis Set

- The size of a plane wave basis set can be enlarged systematically by increasing the cutoff G_{max}.
  --> No Over Completeness Problem!
- The whole space can be covered with the same accuracy.
  --> No Basis Set Superposition Error!
- Atomic forces can be easily calculated because of the Hellmann-Feynman theorem for the derivative of the total energy with respect to atomic positions.

$$\mathbf{F}_I = -\frac{d}{d\mathbf{R}_I} E_T$$

$$= -\sum_{i\mathbf{k}} f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}} | \frac{\partial}{\partial \mathbf{R}_I} \left(V_{loc}^{ion} + V_{NL} \right) | \psi_{i\mathbf{k}} \rangle - \frac{d}{d\mathbf{R}_I} E_{EW}$$

- Very efficient FFT can be used.

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Problem in Norm Conserving Pseudopotentials

- Nodeless wave functions such as O2p and Cu 3d.
→ Wave functions have large amplitude cluse to nuclei.
→ To satisfy the norm-conserving condition, pseudo-wave functions should also have large amplitude near nuclei.
→ The required number of plane waves to expand steep pseudo-wave functions becomes large and calculations become very heavy.

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Ultrasoft Pseudopotential

- By removing the norm-conserving condition, pseudo-wave functions can be very smooth.

→ Ultrasoft Pseudopotential

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Generalized Norm-conserving Condtion

$$4\pi \int_0^{r_c} \left|\psi_l^{AE}(r)\right|^2 r^2 dr = \left\langle \psi_l^{AE} \middle| \psi_l^{AE} \right\rangle_{r_c} = \left\langle \psi_l^{PS} \middle| S \middle| \psi_l^{PS} \right\rangle_{r_c}$$

$$= -2\pi \left(r\psi_l^{PS}\right)^2 \frac{d}{d\varepsilon}\frac{d}{dr}\ln\psi_l^{PS}\bigg|_{r_c},$$

Generalized Norm-conserving Condition

$$S = 1 + \sum_{nm} q_{nm}\left|\beta_n\right\rangle\left\langle\beta_m\right|, \qquad \left\langle\psi_l^{PS}\middle|\beta_m\right\rangle = \delta_{lm}.$$

$$H\left|\psi_l^{PS}\right\rangle = \varepsilon_l S\left|\psi_l^{PS}\right\rangle.$$ **Generalized Eigen Value Problem**

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Ultrasoft Pseudopotential

Cu 3d

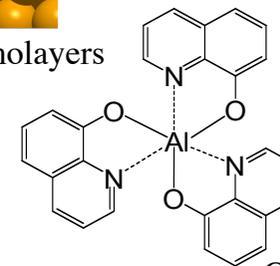**The accuracy of pseudopotentials can be improved further by employing multiple reference states.**

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Examples: Semiconductor Surfaces

Ge/Si(105) surface
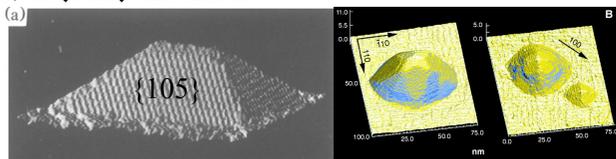
Ge/Si(105): Surface

Organic/Semiconductor

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Examples of calculations
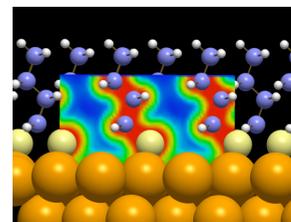
Self-assembled monolayers
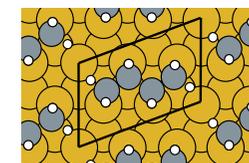
n-alkane/metal

Organic EL

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Examples of calculations

Heterogeneous Catalysis

Water

Fuel Cell

Adsorbates

Pt Layer

TiO_2

全エネルギー

$$E_T = E_K + E_H + E_{XC} + E_{loc} + E_{NL} + E_{EW},$$

$$E_K = \sum_{i\mathbf{k}} f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}} | -\frac{1}{2}\nabla^2 | \psi_{i\mathbf{k}} \rangle = \sum_{i\mathbf{k}} f_{i\mathbf{k}} \sum_{\mathbf{G}}^{|\mathbf{k}+\mathbf{G}| \le G_{max}} |c_{i\mathbf{k}}|^2 \frac{|\mathbf{k}+\mathbf{G}|^2}{2},$$

$$E_H = \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' = \frac{4\pi}{2}\Omega_a \sum_{\mathbf{G}}^{|\mathbf{G}| \le 2G_{max}} \frac{|\rho(\mathbf{G})|^2}{|\mathbf{G}|^2},$$

$$\rho(\mathbf{r}) = \sum_{i\mathbf{k}} f_{i\mathbf{k}} |\psi_{i\mathbf{k}}(\mathbf{r})|^2, \quad \rho(\mathbf{G}) = \frac{1}{\Omega_a}\int \rho(\mathbf{r})\exp(-i\mathbf{G}\bullet\mathbf{r})d\mathbf{r}.$$
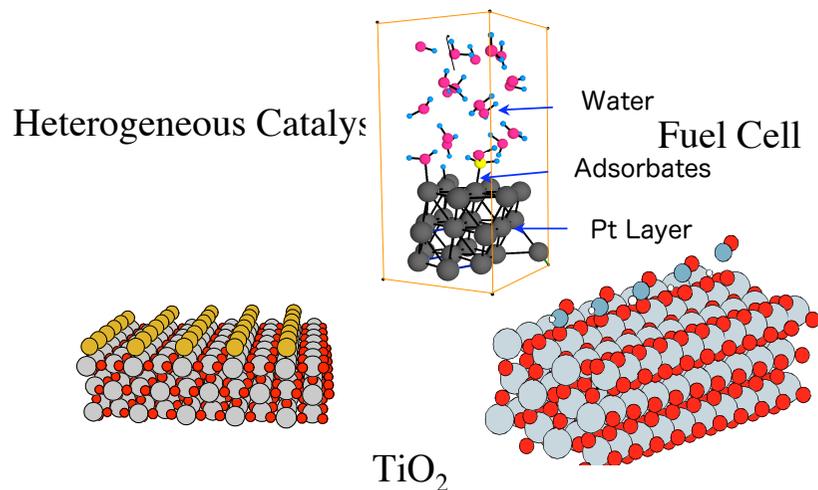
全エネルギー

$$E_{XC} = \int \varepsilon_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r},$$

$$E_{loc} = \int V_{loc}^{ion}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = \Omega_a \sum_{\mathbf{G}}^{|\mathbf{G}| \le 2G_{max}} V_{loc}^{ion}(\mathbf{G})\rho^*(\mathbf{G}),$$

$$E_{NL} = \sum_{i\mathbf{k}} f_{i\mathbf{k}} \sum_{Inm} D_{nm}^{ion} \langle \psi_{i\mathbf{k}} | \beta_n \rangle \langle \beta_m | \psi_{i\mathbf{k}} \rangle,$$

$$E_{EW} = \frac{1}{2}\sum_{I \ne J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}.$$

ヘルマン-ファインマン力

・ 平面波基底を用いることにより、全エネルギー
の原子座標に関する微分に対してヘルマン-
ファインマンの定理が成り立ち、原子に働く力
の計算が容易となる。

$$\mathbf{F}_I = -\frac{d}{d\mathbf{R}_I}E_T$$

$$= -\sum_{i\mathbf{k}} f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}} | \frac{\partial}{\partial\mathbf{R}_I}\left(V_{loc}^{ion} + V_{NL}\right) \psi_{i\mathbf{k}} \rangle - \frac{d}{d\mathbf{R}_I}E_{EW}$$
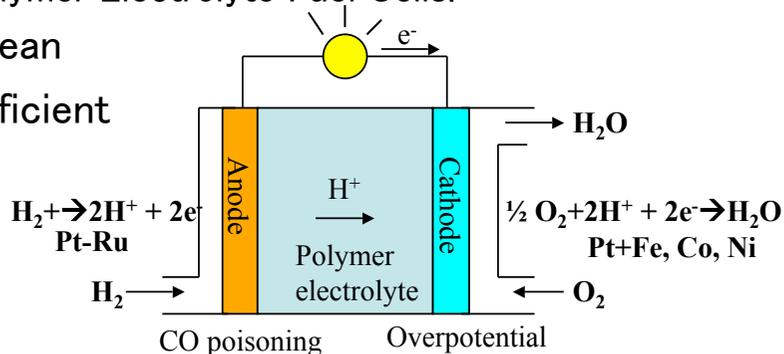
擬ポテンシャル法の利点

- 価電子の状態に関する限り、精度はフルポテンシャルの全電子計算にほぼ匹敵する。
- 内殻電子を取り扱わず、計算が比較的軽い。
- 絶対値の大きいエネルギーを持つ深い内殻電子を取り扱わないので、全エネルギーの有効桁数が少なくても良い。
- 擬ポテンシャルおよび擬波動関数は滑らかで、平面波基底で容易に展開可。
- 平面波基底によりヘルマン-ファインマンの定理が成り立ち、力の計算が容易。

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First-principles molecular dynamics simulations of chemical reactions at water/metal interfaces

Y. Morikawa, I. Hamada (*ISIR, Osaka Univ.*)

M. Otani, O. Sugino (*ISSP, Univ. Tokyo*)
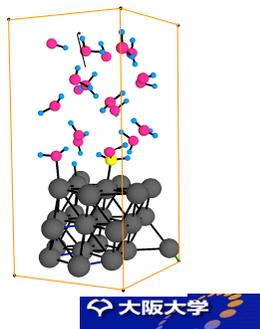
Y. Okamoto (*NEC*)

T. Ikeshoji (*RICS-AIST*)

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Fuel Cell

Polymer Electrolyte Fuel Cells.

Clean

Efficient

$H_2+\rightarrow 2H^+ + 2e^-$
Pt-Ru

H_2

Anode

H^+

Polymer electrolyte

Cathode

H_2O

$½ O_2+2H^+ + 2e^-\rightarrow H_2O$
Pt+Fe, Co, Ni

O_2

CO poisoning   Overpotential

e⁻

Electrode metals

- Pt: South Africa74%、Russia14%
- →New efficient catalysts are required.
- →Necessary to elucidate the reaction mechanisms.

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Chemical Reactions at Water/Metal Interface

Methanol Oxydation
Stability of Reaction
Necessary to include solvent effects

With Water

In Vacuum

Energy / eV

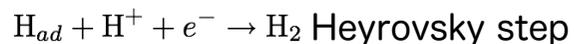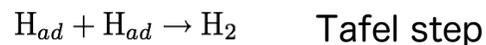Number of H atoms on the surface
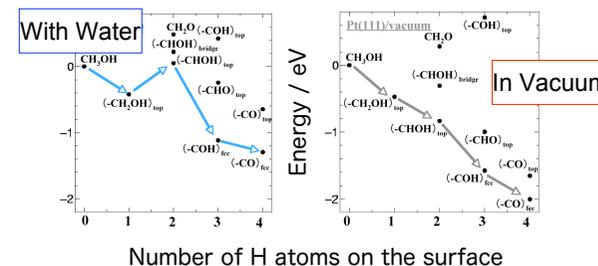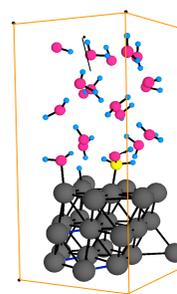
Y. Okamoto, O. Sugino, Y. Mochizuki, T. Ikeshoji, Y. Morikawa, "Comparative study of dehydrogenation of methanol at Pt(1 1 1)/water and Pt(1 1 1)/vacuum interfaces" *Chem. Phys. Lett.*, **3**

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Chemical Interactions at Metal/Water Interfaces

- Solvent effects.
- Statistically sample many meta-stable structures.
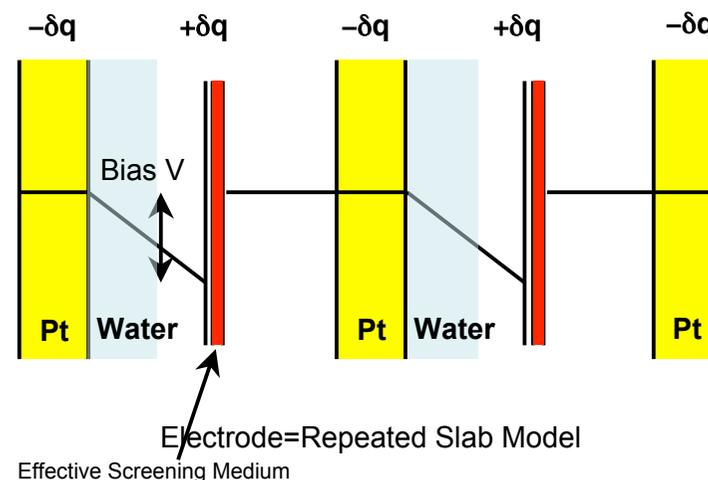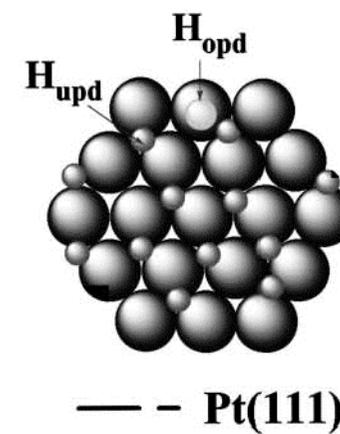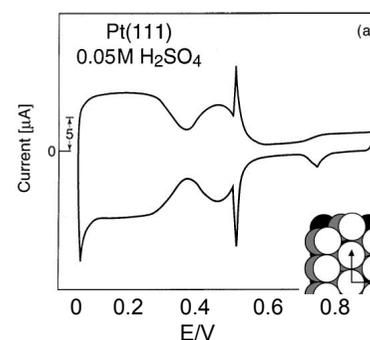- Effect of electric field at the interface

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Effective Screening Medium

M. Otani and O. Sugino, Phys. Rev. B **73** 115407 (2006)

$-\delta q$ $+\delta q$ $-\delta q$ $+\delta q$ $-\delta q$

Bias V

Pt   Water   Pt   Water   Pt

Electrode=Repeated Slab Model

Effective Screening Medium

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Hydrogen evolution reaction (HER)

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{Net reaction}$$

$$H^+ + e^- \rightarrow H_{ad} \quad \text{Volmer step}$$

$$H_{ad} + H_{ad} \rightarrow H_2 \quad \text{Tafel step}$$

$$H_{ad} + H^+ + e^- \rightarrow H_2 \quad \text{Heyrovsky step}$$

Clarify the Reaction Mechanism

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Hupd and Hopd

Pt(111)
0.05M H$_2$SO$_4$ (a)

Current [μA]

0   0.2   0.4   0.6   0.8
E/V

H$_{opd}$

H$_{upd}$

— — Pt(111)

N.M. Markovic and P.N. Ross Jr., Surf. Sci. Rep., 45 117 (2002).
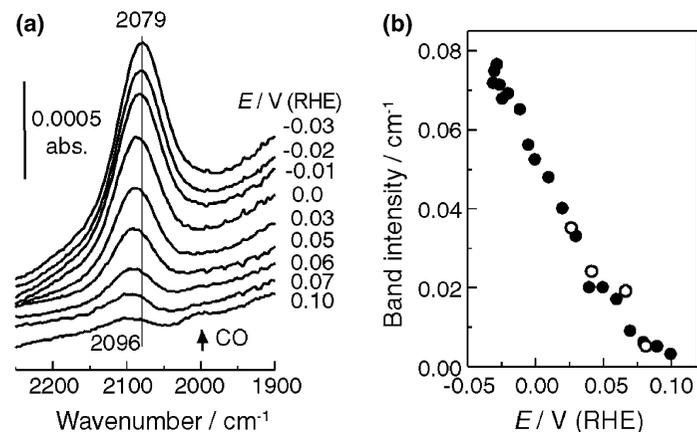
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Hydrogen Evolution Reaction on Pt

(a)

2079

0.0005 abs.

E / V (RHE)
-0.03
-0.02
-0.01
0.0
0.03
0.05
0.06
0.07
0.10

2096 ↑ CO

Wavenumber / cm^{-1}

(b)

Band intensity / cm^{-1}

E / V (RHE)

K. Kunimatsu, T. Senzaki, M. Tsushima, and M. Osawa, Chem. Phys. Lett., 401, 451 (2005).

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Hydrogen Evolution Reaction on Pt

(a)

log (Intensity / cm^{-1})

E / V (RHE)

slope = 60 mV / dec.

slope = 30 mV / dec.

log (*i* / A cm^{-2})

(b)

log (*i* / A cm^{-2})

slope = 2

log (Intensity / cm^{-1})

K. Kunimatsu, T. Senzaki, M. Tsushima, and M. Osawa, Chem. Phys. Lett., 401, 451 (2005).

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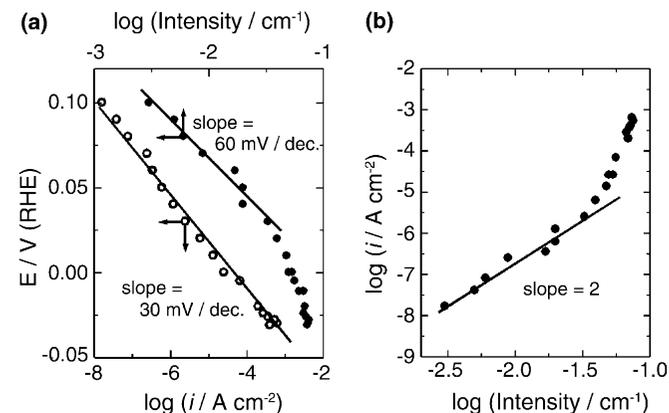
Technicalities

- STATE (Simulation Tool for Atom TEchnology)
- Plane wave basis set + ultrasoft pseudopotentials
- PBE-GGA for exchange-correlation
  - Cut-off energy
    - 25Ry (wave functions)
    - 225Ry (the augmentation charge)
- Born-Oppenhemer MD
  - Heavy water (D2O)
  - Time step: 1.2 fs
- ESM (Effective Screenig Medium) method (Otani and Sugino, PRB73, 115407 (2006)) to apply the bias voltage

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Water/Pt interface model

- **32 H$_2$O + H+(proton)**
- **Pt(111) (3x2√3) surface unit cell**
- **3-layer slab (32atoms)**
- **Temperature: 353K**
- **Negatively charged**
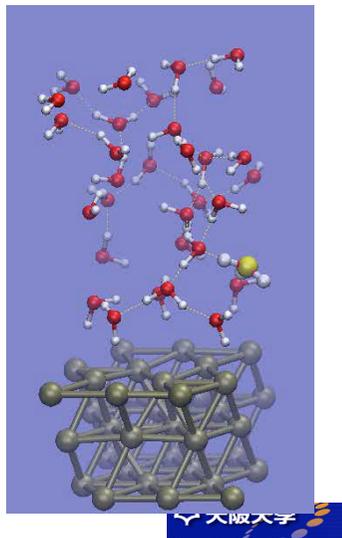- **+0.25 ~0.95 elec.**

Z
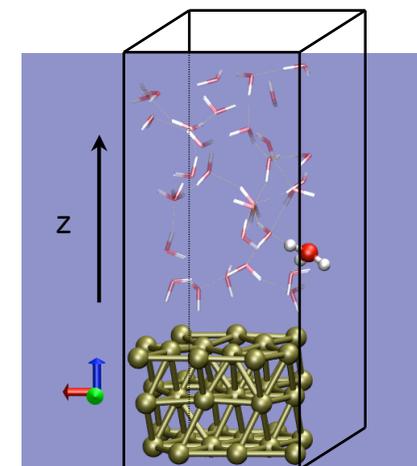
3D-Periodic Boundary Condition

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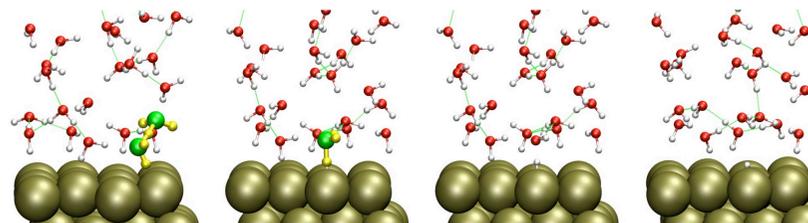# First-principles Molecular Dynamics Simulation of Electrode/Water Interface

- Total MD simulation time: 3.2 ps
- Added electrons: 0.25-0.40
- 353 K

Red: Oxygen
White: Hydrogen
Yellow: Oxygen in a hydronium ion
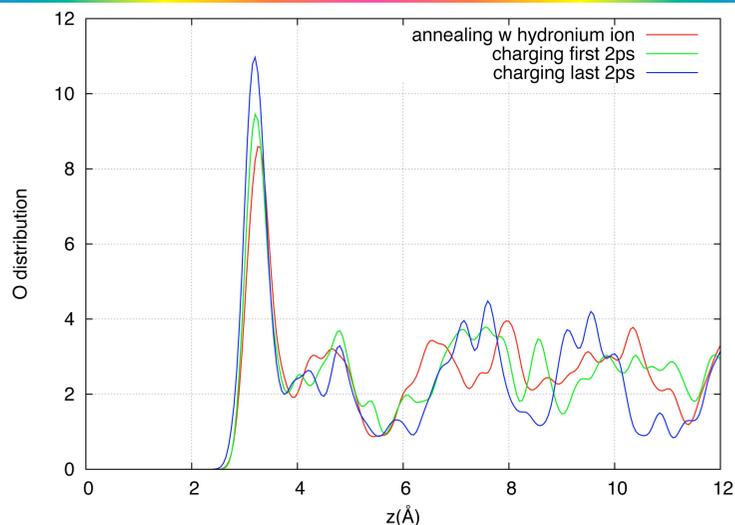Substrate: Platinum

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Snapshots

Protons form $H_9O_4^+$(Eigen cations), and, $H_5O_2^+$(Zundel cations) and diffuse around the interface through the Grotthuss mechanism.

Pt-H connectivity: 2 Å
(NB: Pt-H(atop) distance: ~1.5Å)

Pt-H radial distribution function

Water Density Near Electrode Surfaces

- Toney et al., Nature, 368, 444 (1994).

  water/Ag(111)

  1.4 g/cm^3 (−0.2 V vs pzc)

  2.3 g/cm^3 (+0.5 V vs pzc)

- Ito & Yamazaki, Phys. Chem. Chem. Phys., 8, 3623 (2006).

  water/Cu(111)

  1.7 g/cm^3 (−0.35V vs NHE)

- Present Simulation: water/Pt(111)

  1.3 g/cm^3 : Low Field (N_{ex}= 0.25)

  1.7 g/cm^3 : High Field (N_{ex}= 1.05)

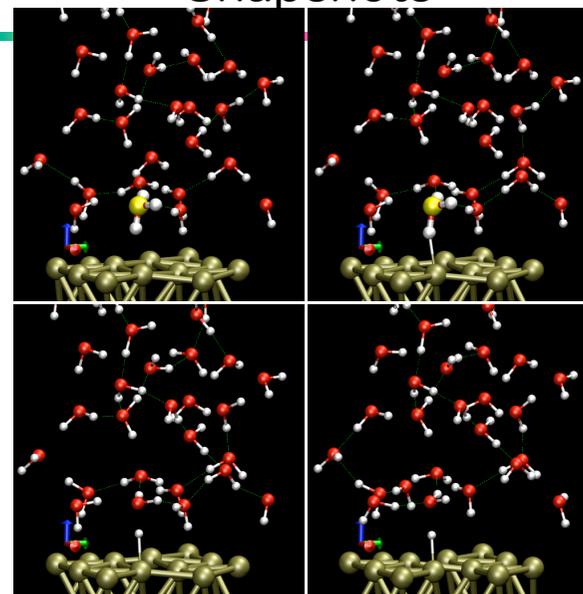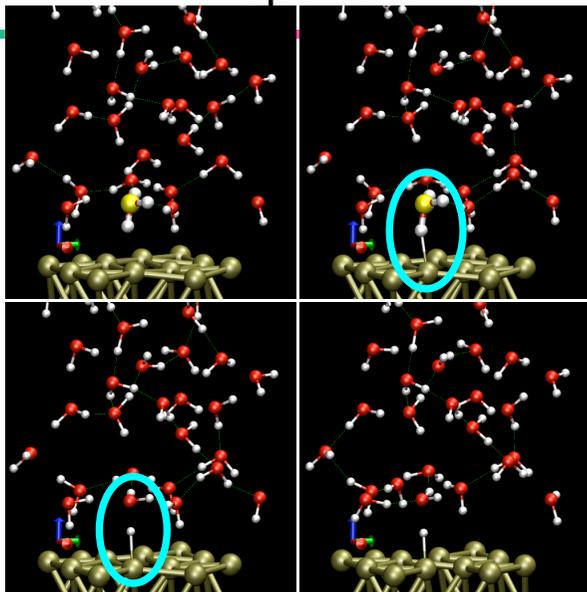# MD simulation of Volmer process

$$H^+ + e^- \rightarrow H_{ad}$$
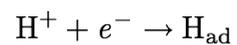
・Total MD simulation time: 2.6 ps
・Added electrons: 0.45-0.95
・353 K (velocity scaling)

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Snapshots

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Snapshots

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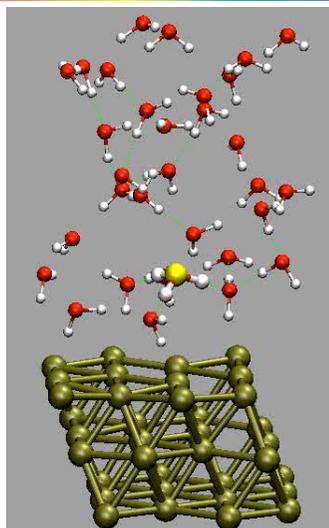
Charge State of Pt and H

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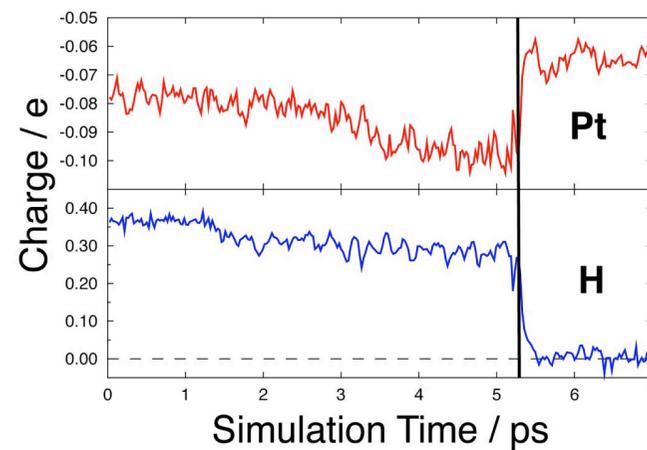
Charge Transfer

Red:　Negatively Charged.
Blue:　Positively Charged.

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Mulliken Population Analysis

LUMO of Hydronium Ion

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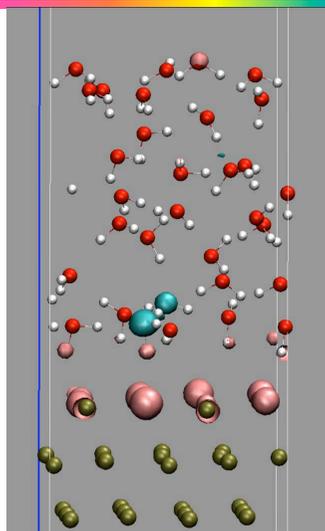
Summary

· Chemical reactions at water/metal interfaces can be successfully simulated by the first-principles molecular dynamics.

· Electric field at the water/metal interface increases the water density signficantly.

· Charge transfer process is clarified.

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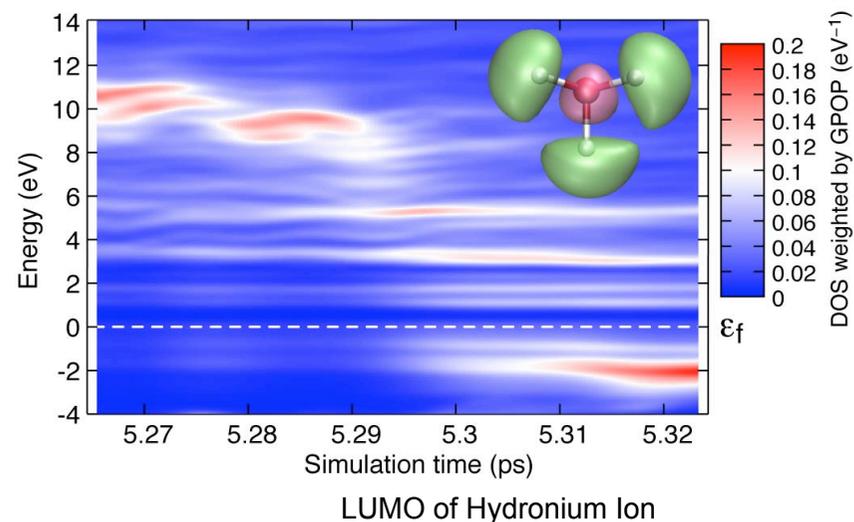
Input file: nfinp_1

• ENERGY_CUTOFF_FOR_WAVEFUNCTION
The cutoff energy of plane wave basis set for wave functions.
• ENERGY_CUTOFF_FOR_CHARGE
The cutoff energy of plane wave basis set for charge density.
These cutoff energies depend on pseudopotentials.
Example：
　pot.Cl_pbe1, pot.Br_pbe1, pot.Ge_pbe1, pot.Si_pbe1
　　wave function: 10〜16Ry, charge: 100Ry
　pot.H_lda3, pot.C_pbe3, pot.O_pbe3,
　　wave function: 25Ry, charge: 225Ry
　pot.H_lda1, pot.C_pbe1, pot.O_pbe1,
　　wave function: 30.25Ry, charge: 400Ry
It is necessary to check the dependence of total energies on cutoff.

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Input file: nfinp_1

- **INITIAL_CONDITION**

  How to prepare the initial wave functions.

  SCRATCH: Generate from scratch

  RESTART: Read from "restart.data" which has the latest date.

- **INITIAL_POSITIONS**

  How to prepare the initial atomic positions.

  INPUTS   : Read from nfinp_1.

  RESTART   : Read from "restart.data" which has the latet data.

  GEOMETRY_FILE : Read from "GEOMETRY" which can be modified by text editor.

- **TOTAL_STEP**

  Maximum number of molecular dynamics steps.

- **Max_CPU_TIME**

  Maximum CPU time in seconds.

Input file: nfinp_1

- **WAVEFUNCTION_OPTIMIZE**

  Choose optimization method.

  DAVIDSON   :Davidson method.

  RMM : Residual-vector Minimization Method.

  Davidson scheme is quite stable but computationally less efficient compared with RMM scheme. RMM is very fast but it is less stable compared with Davidson scheme. When you start calculations from scratch wave functions, you should use Davidson scheme for first 5-10 iterations and switch sot RMM scheme.

- **ENERGY_CRITERIA_CONVERGENCE_ELECTRON**

  Convergence criteria for wave function optimization.

  Recommended values: 0.10D-7～0.10D-8

- **NUMBER_OF_CHARGE_MIXING**

  Number of previous iterations included to estimate updated charge.

 Recommended value: 20 for easy systems, 50 for difficult systems.

Input file: nfinp_1

- **ALPHA_MIXTURE**

  Fraction of new charge density in charge density mixing. 0.3～0.8.

- **EXCHANGE_CORRELATION_TYPE**

  Selection of exchange-correlation function.

  GGAPBE :Generalized Gradient Approximation by Perdew, Burke and Ernzerhof, Phys. Rev. Lett. **77** 3865 (1996). (Recommended)

  LDAPW91 : Local Density Approximation.

- **SPACE_GROUP_NUMBER**

  Specify the symmetry of the system by the group space number.

- **BRAVAIS_LATTICE**

  Specify the type of Bravais lattice.

  **SIMPLE,   BODY_CENTER,   FACE_CENTER,
  A_CENTER,   B_CENTER,   C_CENTER,
  RHOMBOHEDRAL_CENTER**

Unit Cell

1）Specify the lengths of the lattice vectors and the angles among them.

&UNIT_CELL
    a b c
    α β γ
&END_UNIT_CELL
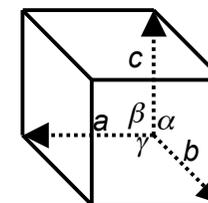
2）Specify the Cartesian coordinates of the lattice vectors.

&UNIT_VECTOR
    ax ay az
    bx by bz
    cx cy cz
&END_UNIT_VECTOR

K-points

&NUMBER_K-POINT_MESH_XYZ

   BROADENING   WIDTH

   kx   ky   kz

    1   1   1

&END_NUMBER_K-POINT_MESH_XYZ

Width>0 : Semiconductors or insulators.

Width<0 : Metallic systems.

The absolute value of width should be about 0.002 hartree.

Input file: nfinp_1

NUMBER_EIGENVALUES

   Number of eigen values per spin. Numbers of empty states (10-20) should be included.

&ATOMIC_TYPES

     Number of atomic types

     Atomic number   mass   spin polarization

     Atomic number   mass   spin polarization

...

&END_ATOMIC_TYPES

Input file: nfinp_1

&COORDINATES

   Number of atoms   Number of atoms

   CARTESIAN

INVERSION_SYMMETRY_COUNTED   NO

   x   y   z   IWEI   IMDTYP   ITYP

   x   y   z   IWEI   IMDTYP   ITYP

   x   y   z   IWEI   IMDTYP   ITYP

...

&END_COORDINATES

IWEI = 1

IMDTYP =   0   : Fix atomic position

            1   : Move atomic position

ITYPE   : Atom type number

Structure Optimization and Molecular Dynamics

&JOB_TYPE   *Job type*

&END_JOB_TYPE

QUENCHING: Quenching Molecular Dynamics

   This scheme works well when forces acting on atoms are larger than 0.02 hartree/a_B.

GDIIS: Generalized Direct Inversion of Iterative Subspace

   This scheme becomes efficient when the maximum force is smaller than about 0.02 hartree/a_B.

NORMAL_MODE: Vibration normal mode analysis.

NEB: Nudged Elastic Band Method

  Method for reaction path search proposed by Mills, Jonsson, Schenter, *Surf. Sci.* 324 305 (1994).

Structure Optimization and Molecular Dynamics

TIME_STEP

- Increment of time for each step of molecular dynamics simulation.
  (1 a.u. $= 2.4 \times 10^{-17}$ seconds)

- The time step should be carefully chosen to assure the accuracy of molecular dynamics. It depends on atomic types, maximum forces acting on atoms, and integration scheme of the Newton equation of motion.

- For QUENCHING and NEB schemes, the time step should be 50～300a.u.

- For GDIIS scheme, the time step should be 400～800a.u.

- For NORMAL_MODE, it is not used.

- For FINITE_TEMPERATURE_MD and if the system includes hydrogen, the time step should be about 20a.u. If hydrogen is not included, the time step should be 50～100a.u.
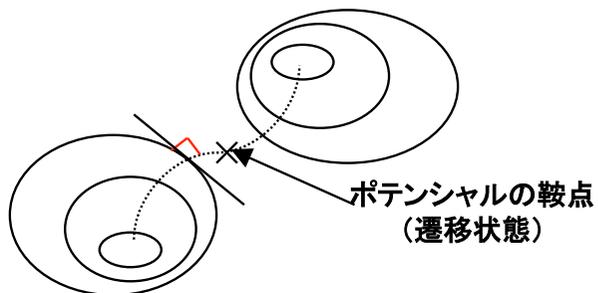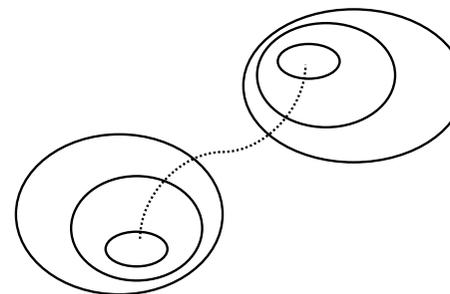

Reaction Path Search

&JOB_TYPE   NEB

&END_JOB_TYPE

NEB: Nudged Elastic Band Method

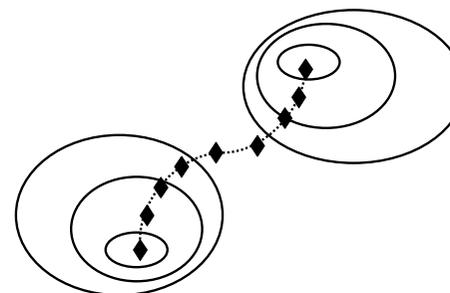**Mills, Jonsson, Schenter,** *Surf. Sci.* **324 305 (1994).**

反応経路探索

&JOB_TYPE   NEB

&END_JOB_TYPE

NEB: Nudged Elastic Band Method

Mills, Jonsson, Schenter, *Surf. Sci.* **324 305 (1994).**

**ポテンシャルの鞍点
（遷移状態）**

最小エネルギー経路はポテンシャルの等高線の接線に垂直

反応経路探索

&JOB_TYPE   NEB

&END_JOB_TYPE

NEB: Nudged Elastic Band Method

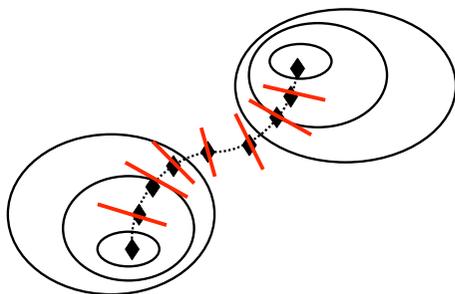**Mills, Jonsson, Schenter,** *Surf. Sci.* **324 305 (1994).**

反応経路探索

&JOB_TYPE   NEB

&END_JOB_TYPE

NEB: Nudged Elastic Band Method

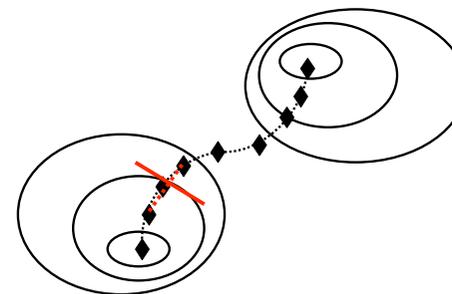**Mills, Jonsson, Schenter, *Surf. Sci.* <u>324</u> 305 (1994).**

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反応経路探索

&JOB_TYPE   NEB

&END_JOB_TYPE

NEB: Nudged Elastic Band Method

Mills, Jonsson, Schenter, *Surf. Sci.* <u>324</u> 305 (1994).
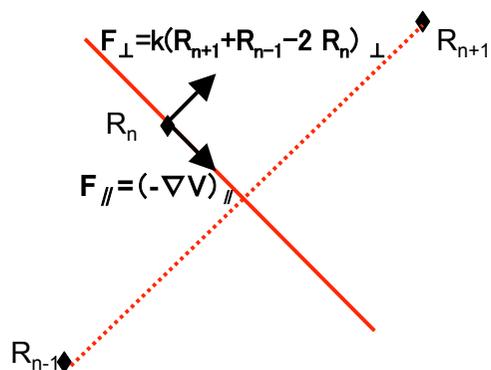

各レプリカを両隣のレプリカを結ぶ直線の垂直二等分面内で最適化

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反応経路探索

$$F_\perp = k(R_{n+1}+R_{n-1}-2\,R_n)_\perp$$

R_{n+1}

R_n

$$F_\parallel = (-\nabla V)_\parallel$$

R_{n-1}

各レプリカを両隣のレプリカを結ぶ直線の垂直二等分面内で最適化

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ジョブの投入

各自のパソコンをRedHatLinuxで起動。

各自のパソコンでログイン名 seminar でログイン。

ターミナルウィンドウを開く。

ssh –Xl adXX epcs00

でPCクラスターシステムにアクセスする。

unalias scout

scout –g pcc –f epcsYY –n 1

(YYの部分は各自のプロセッサー番号(01～36)を書く。

scrun ./STATE < nfinp_1 >& nfout_1 &

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