

Quantum simulation of atom motion in materials

中西 寛^{ABD}, Wilson Dino^C, 笠井秀明^D
Hiroshi Nakanishi^{ABD}, Wilson Dino^C, Hideaki Kasai^{AD}

^A明石工業高等専門学校

^B東京大学生産技術研究所

^C大阪大学大学院工学研究科

^D大阪大学

^A National Institute of Technology, Akashi College

^B Institute of Industrial Science (IIS), the University of Tokyo

^C Graduate School of Engineering, Osaka University

^D Osaka University

What is Naniwa ?

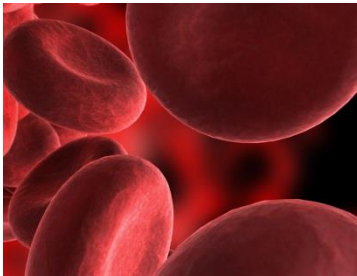
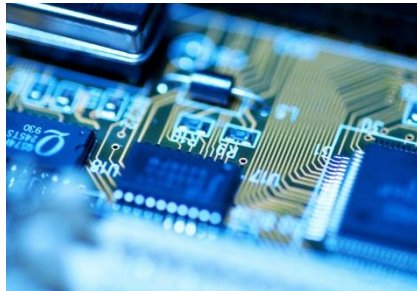
- “Naniwa” is the former name of Osaka, Japan



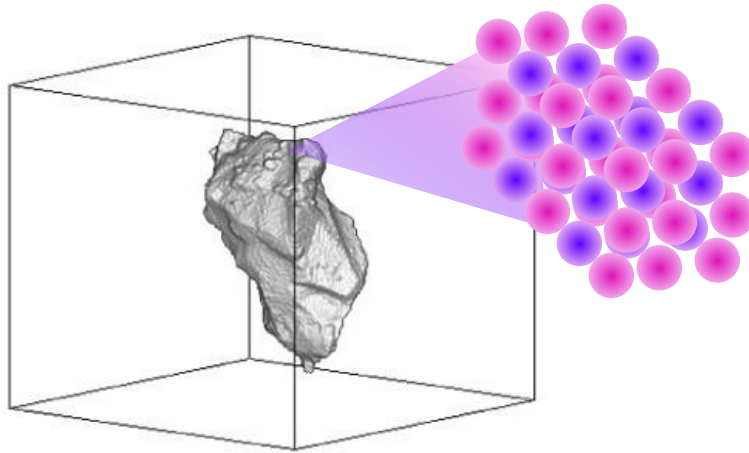
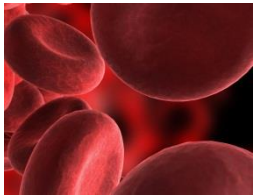
- **NANIWA** is the name of our simulation code.

- The fast wave

materials



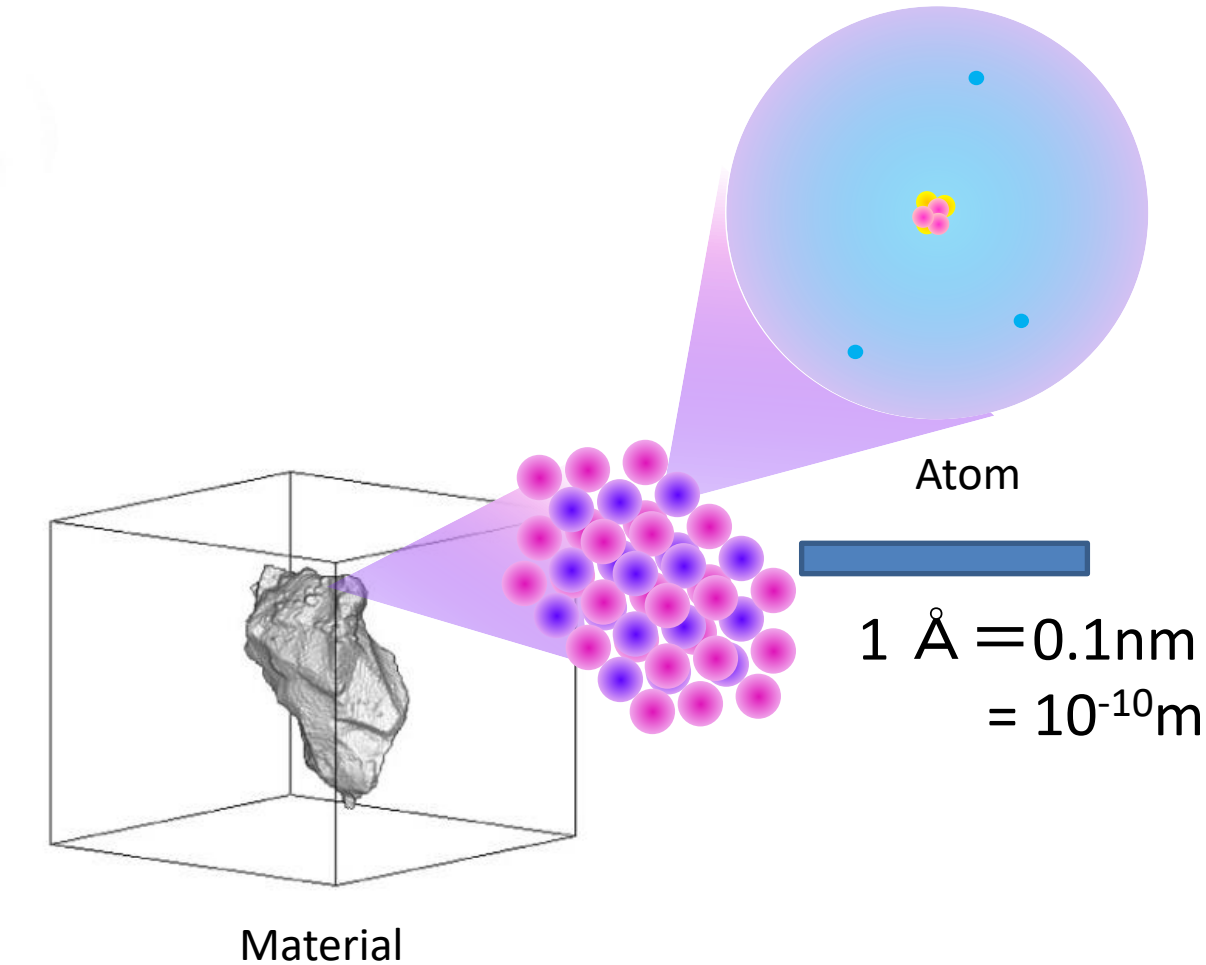
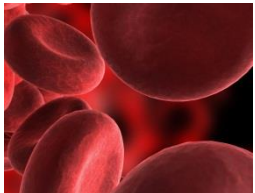
Particles which construct the materials



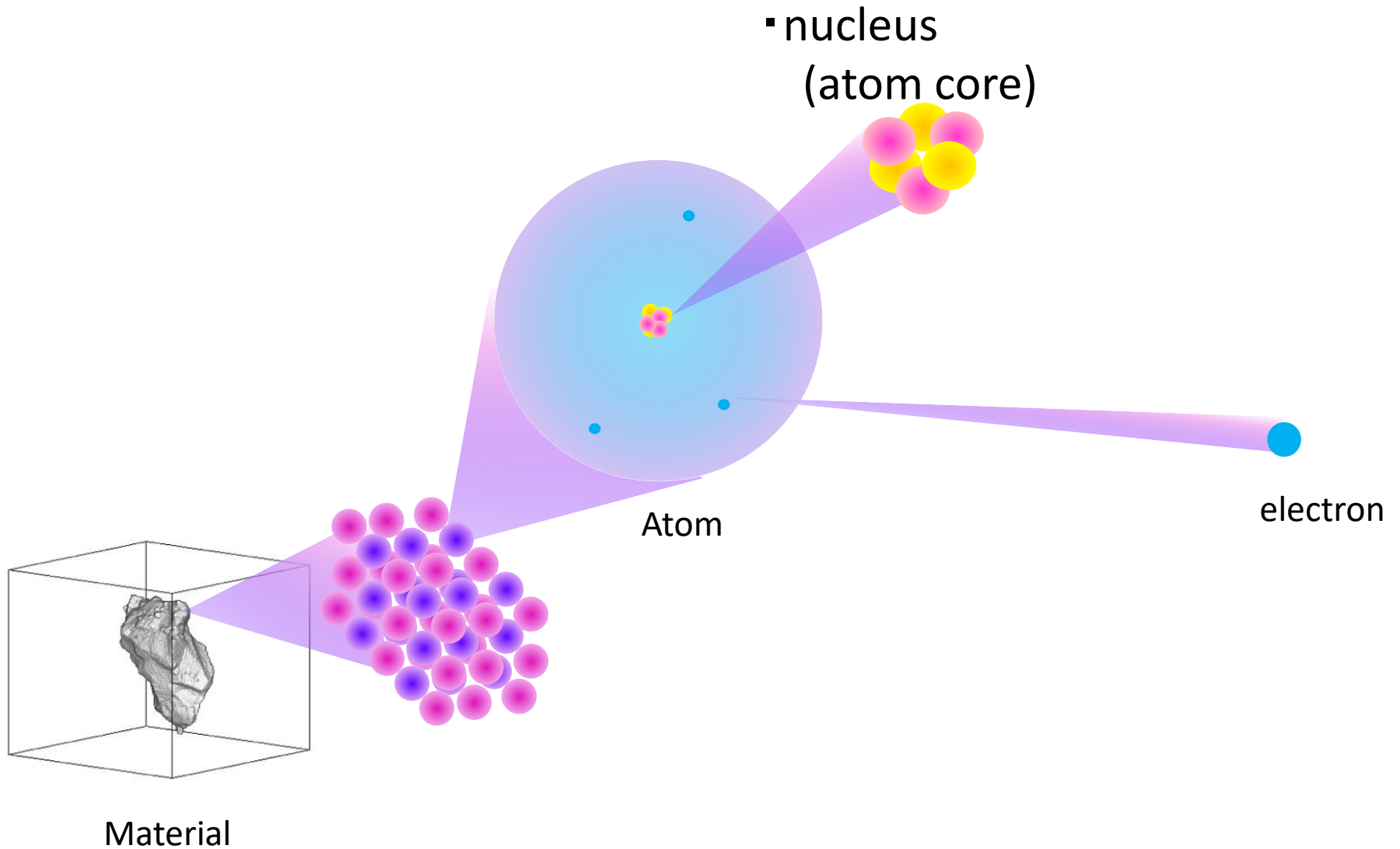
Material



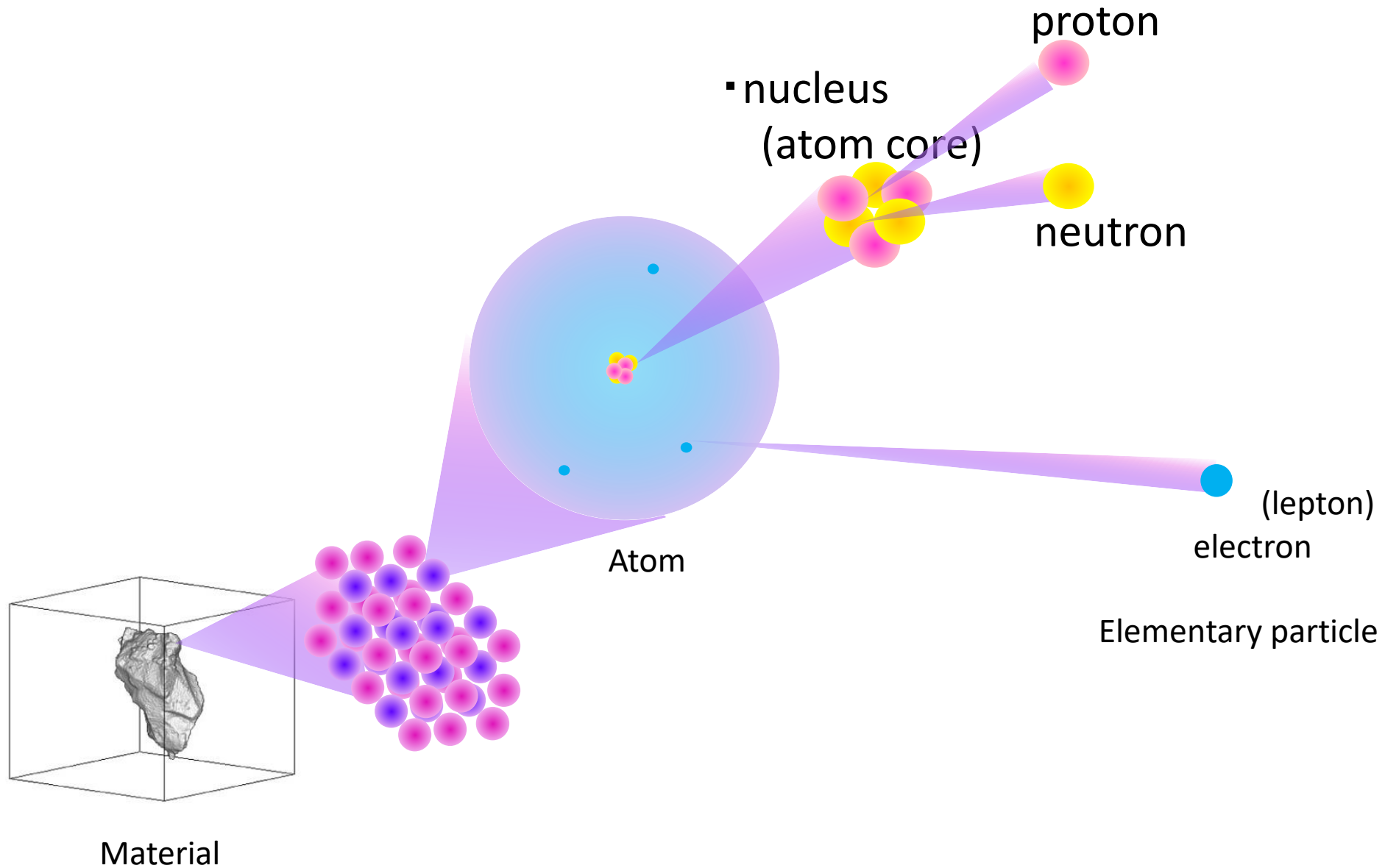
Particles which construct the materials



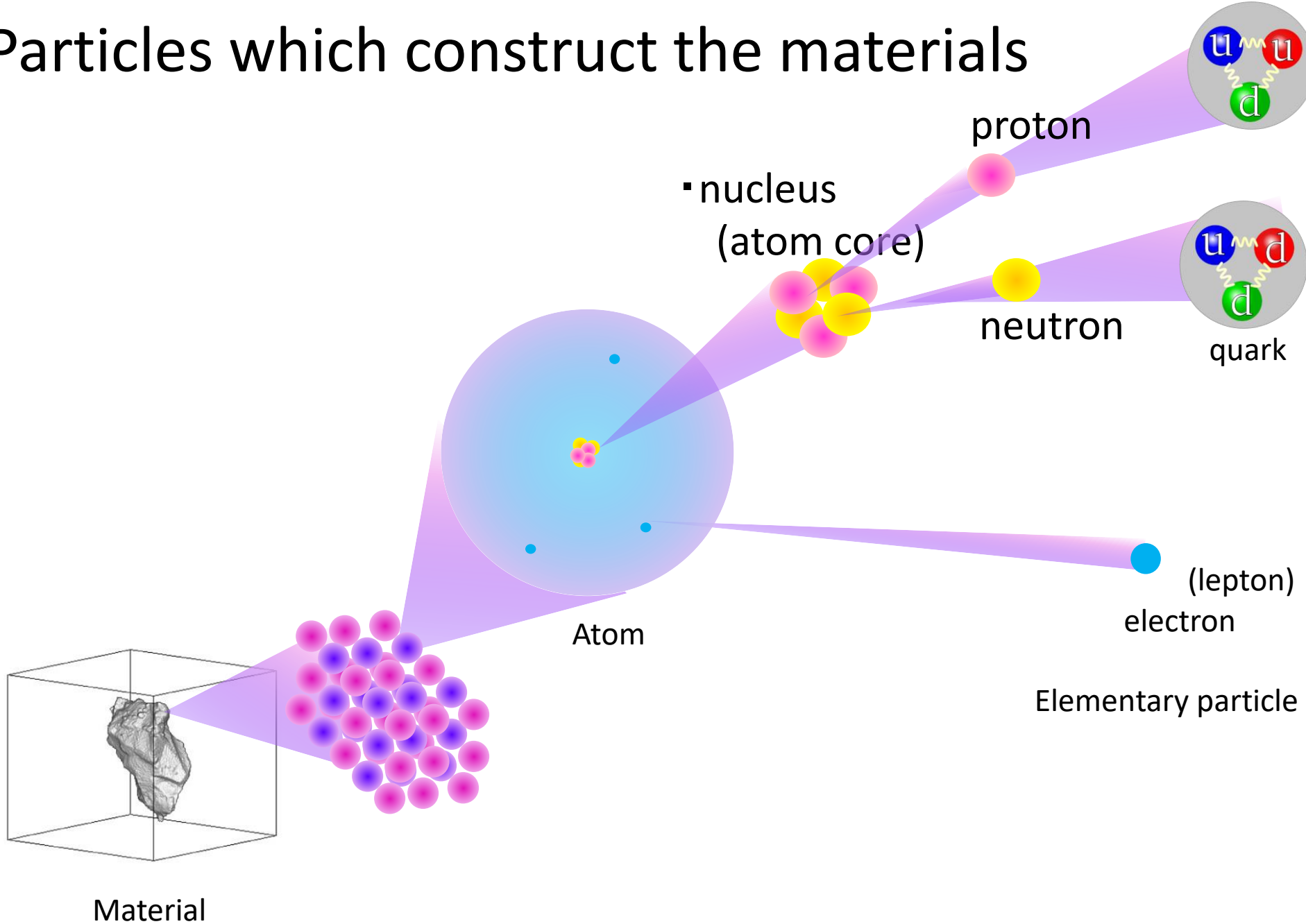
Particles which construct the materials



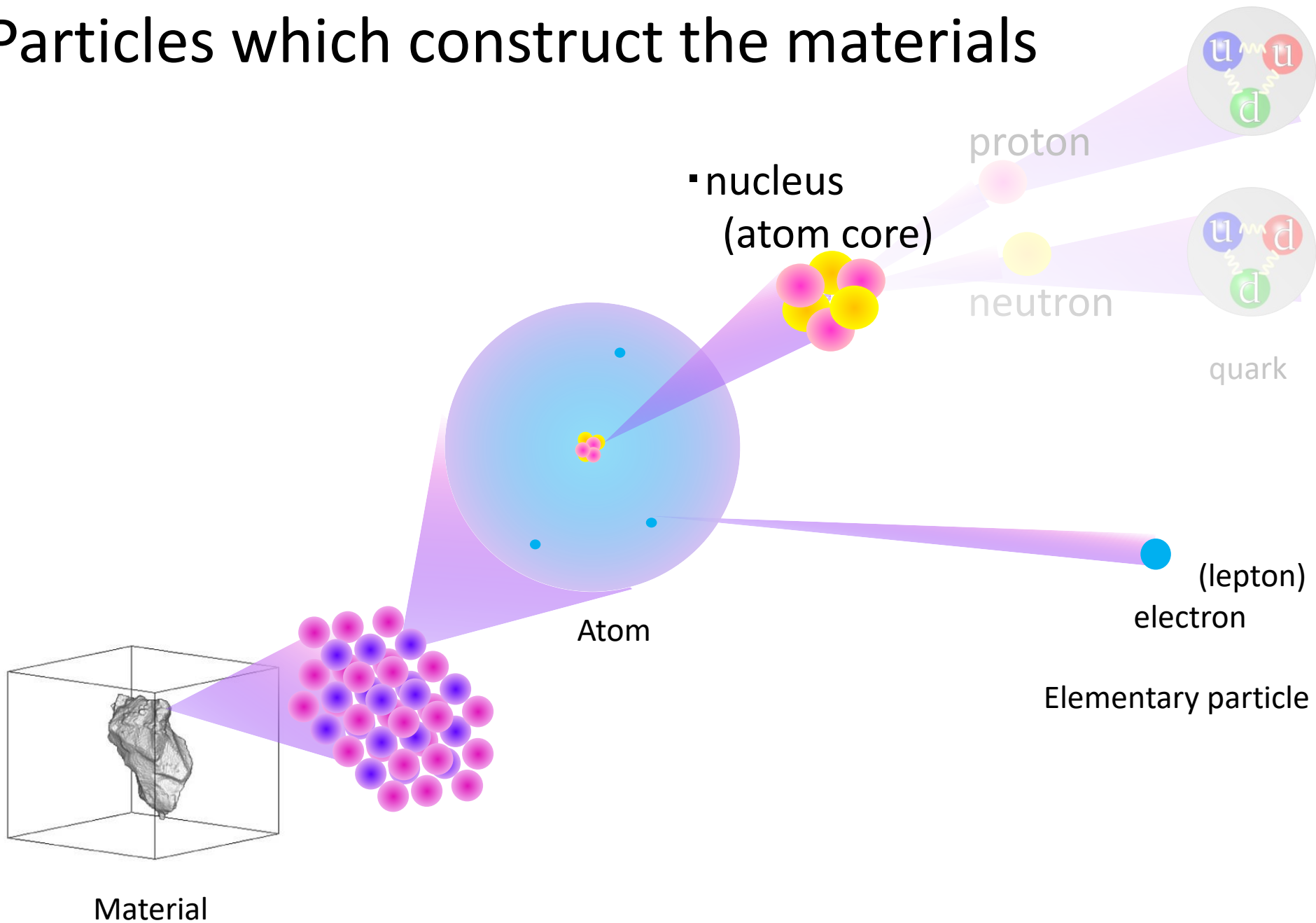
Particles which construct the materials



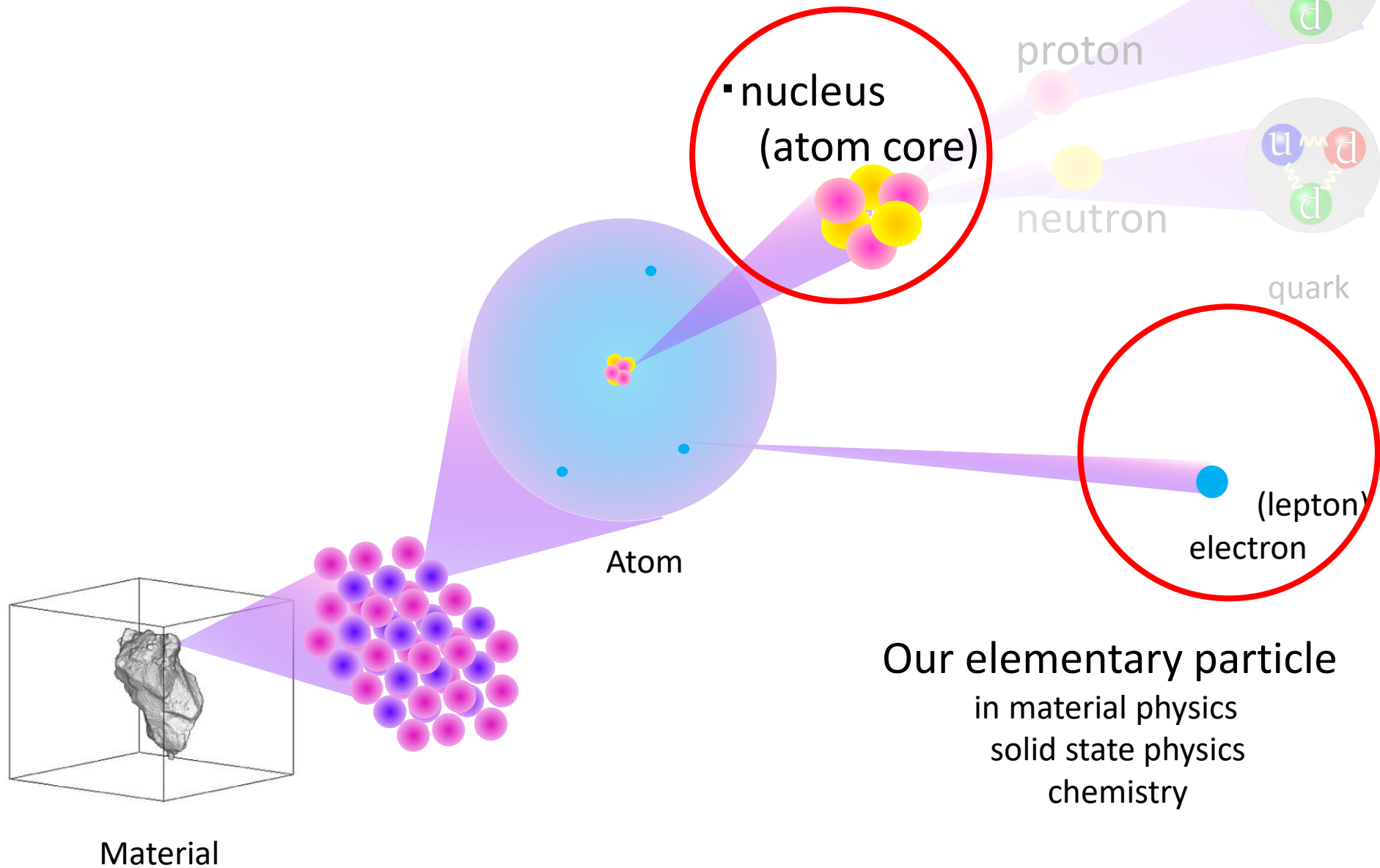
Particles which construct the materials



Particles which construct the materials



Particles which construct the materials



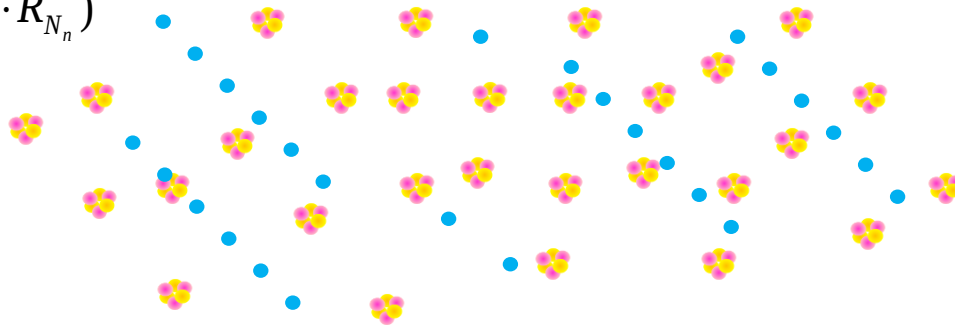
Many atomic nuclei and electrons are in the material

- Fundamental equation for describing behaviors of these particles:

Total Schrödinger equation: *partial differential equation*

$$\left[-\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla_i^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right] \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

$$= E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$



N_n ; Number of atoms

N_e ; Number of electrons $\sim 10^{23}$

Z_l : atomic number of the l th atom

● electron

M_l : Mass of the l th atom

● atomic nucleus

m : Electron mass

Many atomic nuclei and electrons are in the material

- Fundamental equation for describing behaviors of these particles: Total Schrödinger equation

Hamiltonian:

$$\left[-\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla_l^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right]$$

Wave function

$$\psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

As a function of all particle positions

$$= E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

Total energy

N_n ; Number of atoms N_e ; Number of electrons $\sim 10^{23}$

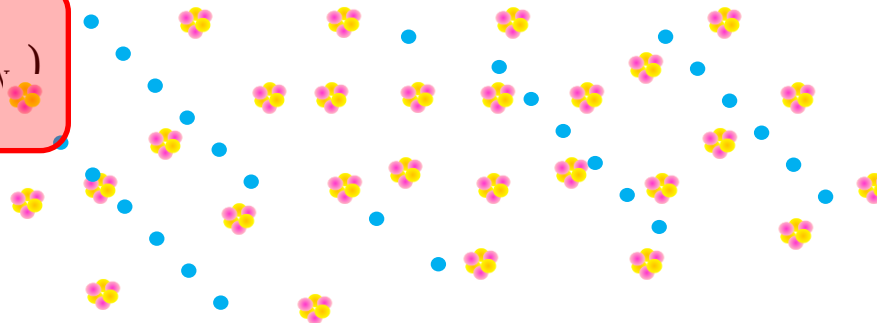
Z_l : atomic number of the l th atom

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● electron

● atomic nucleus

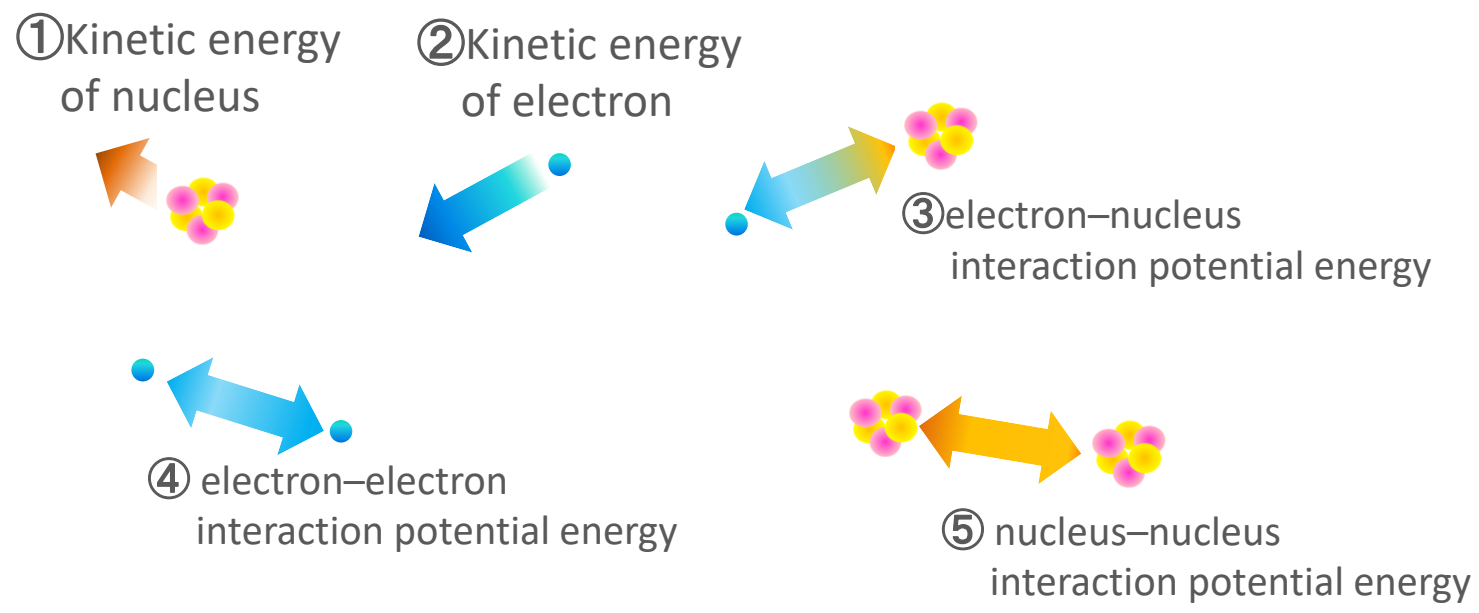


Hamiltonian = Energy operator for all particles

● electron

● atomic nucleus

$$\begin{aligned} & \textcircled{1} \quad \textcircled{2} \quad \textcircled{3} \quad \textcircled{4} \quad \textcircled{5} \\ & \left[-\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla_l^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right] \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) \\ & = E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) \end{aligned}$$



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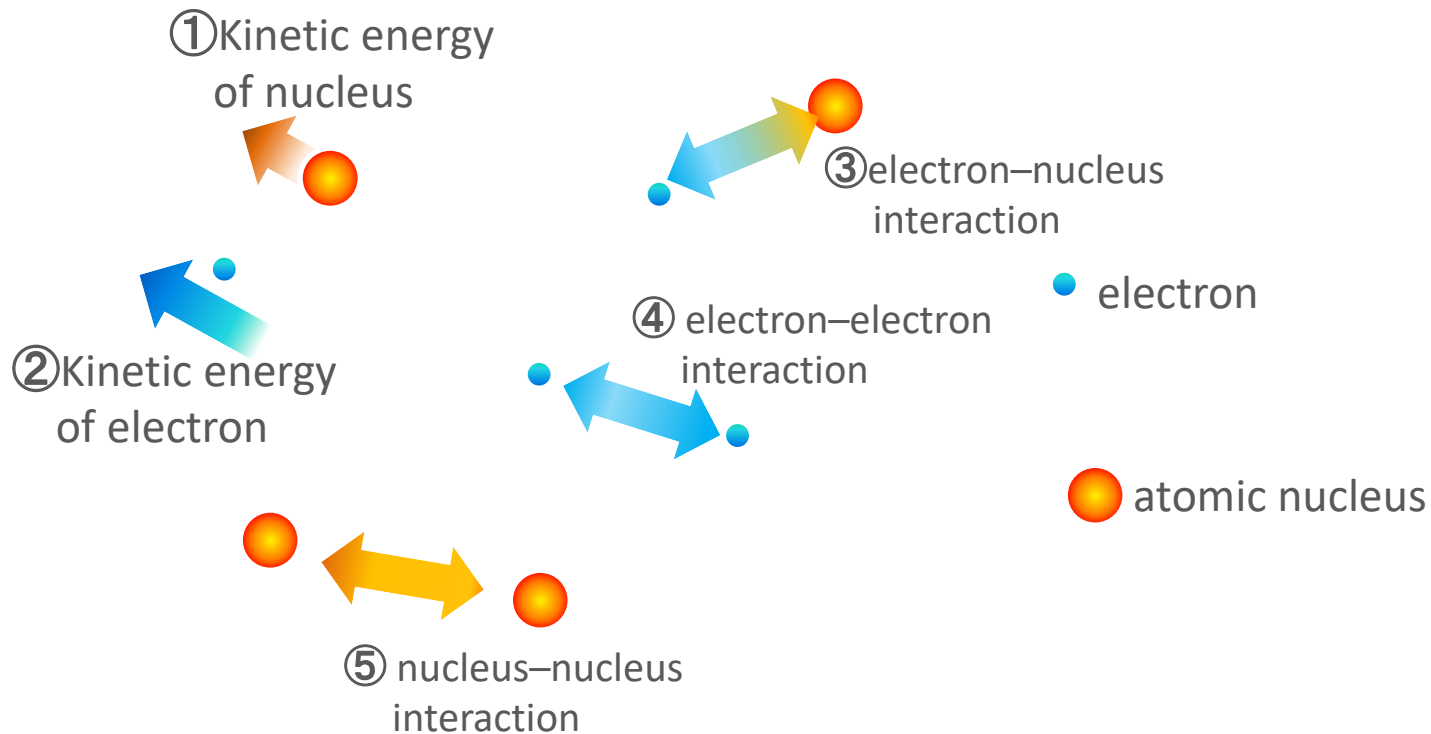
④

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$$\left[-\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla_l^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right] \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

$$= E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

If $M_l \gg m$ then ...



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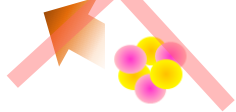
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$$\left[-\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla_l^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right] \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

$$= E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

If $M_l \gg m$ then ...

① Kinetic energy of nucleus



② Kinetic energy of electron



From the view point of electron motion, we can treat that nuclei does not move.

③ electron–nucleus interaction potential energy



④ electron–electron interaction potential energy



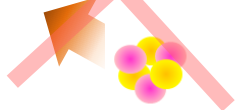
⑤ nucleus–nucleus interaction potential energy



$$\left[\cancel{\textcircled{1}} - \sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla_l^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right] \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) = E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

If $M_l \gg m$ then ...

~~① Kinetic energy of nucleus~~



② Kinetic energy of electron



From the view point of electron motion, we can treat that nuclei does not move.

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⑤ nucleus–nucleus interaction potential energy



- Fundamental equation for describing behaviors of electrons:
Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right] \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) = E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

- Information about the electron state in the material systems
→ Material properties

 Z_l : atomic number of the l th atom N_n ; Number of atoms
$$N_e ; \text{ Number of electrons } \sim 10^{24}$$

= 1000000000000000000000000000000 electrons

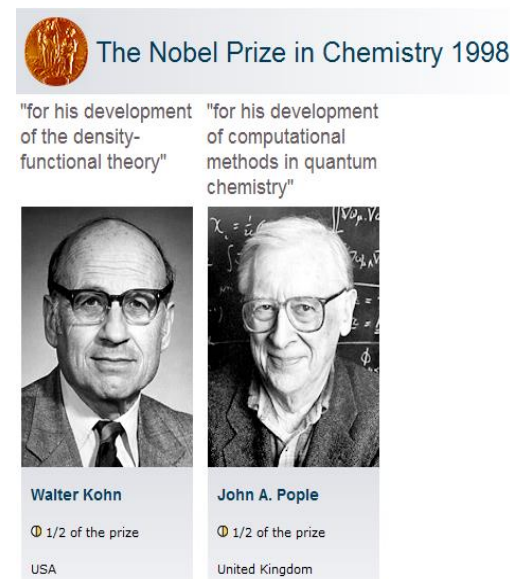
Density functional theory based ab initio calculation

Density functional Theory (DFT)

- Walter Kohn, Pierre Hohenberg (1964)
 - Hohenberg-Kohn theorems (H-K).
 - Kohn-Sham DFT
 - ▪ ▪
 - local-density approximation (LDA)
 - Generalized gradient approximations (GGA)

+

rapid progress of technological innovation
in Computer Science: Computics



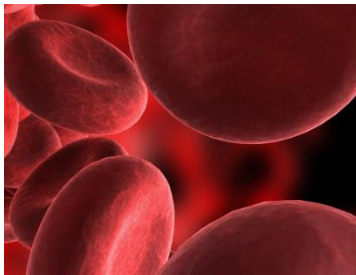
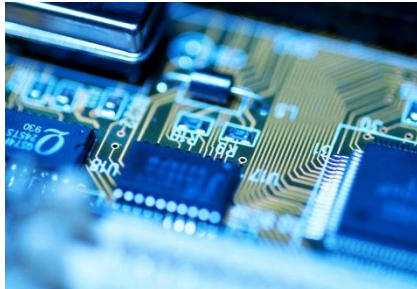
Walter Kohn & John A.Pople

<http://nobelprize.org/>

Unique equation

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right] \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) = E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

Various properties



$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right] \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n}) = E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

Aluminum Al ($Z=13$)

Silicon Si ($Z=14$)

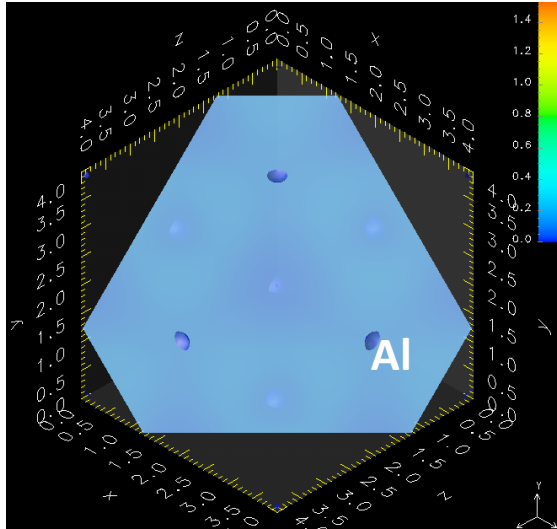
Sodium chloride Na ($Z=11$) Cl ($Z=17$)

Periodic table

1																		18
1 H	2												13	14	15	16	17	2 He
3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	ランタノイド	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	アクチノイド	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo	

Aluminum

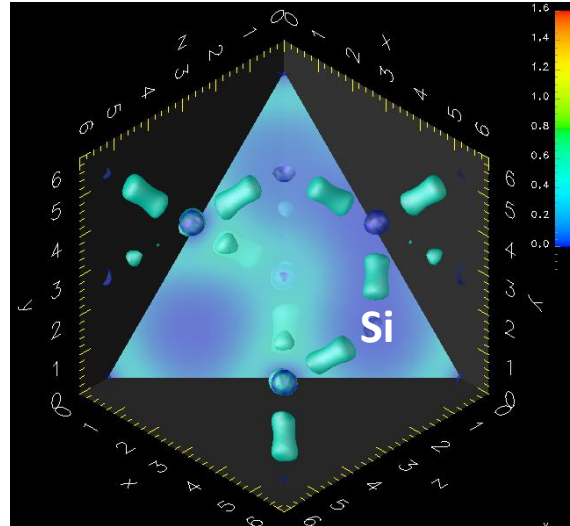
Al ($Z=13$)



electron density distribution

Silicon

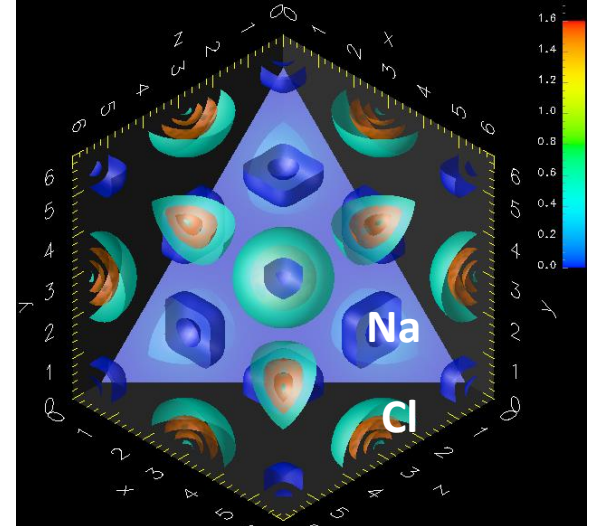
Si ($Z=14$)



electron density distribution

Sodium chloride

Na ($Z=11$) Cl ($Z=17$)



electron density distribution

Metallic bond

delocalized electrons
in the crystal

Covalent bond

Localized electrons
between atoms

Ionic bond

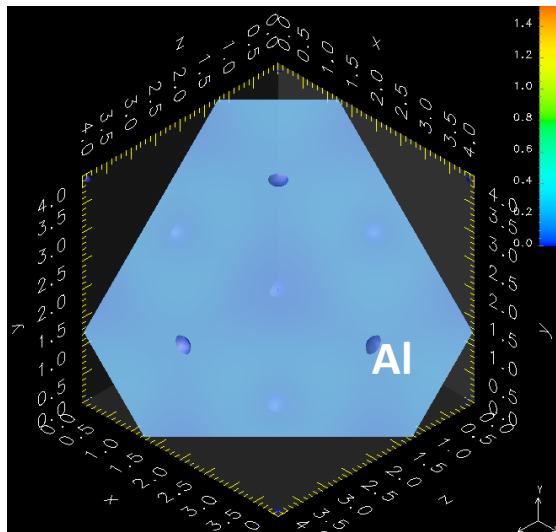
Localized electrons
at atoms

Na^+ ions, Cl^- ions

DFT-based ab initio calculation method is one of the most successful method.

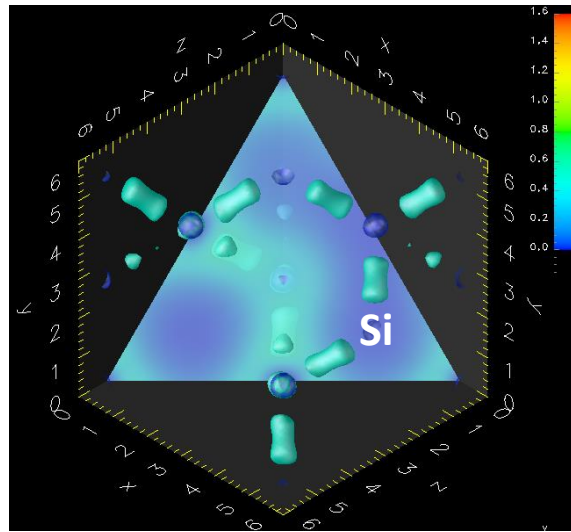
Parameter in the calculations is only atomic number, Z .

Aluminum
Al ($Z=13$)



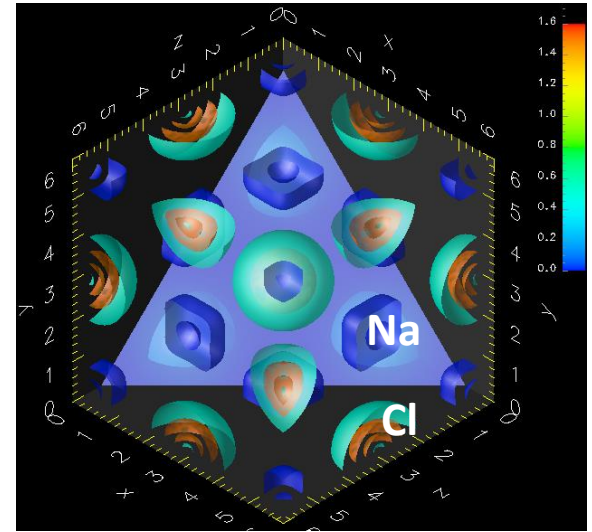
electron density distribution

Silicon
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electron density distribution

Sodium chloride
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electron density distribution

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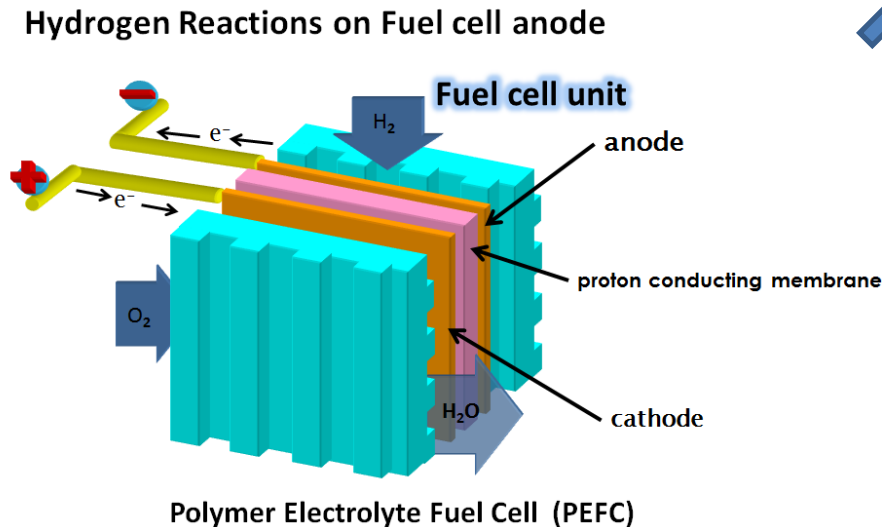
Ionic bond

Localized electrons
at atoms

Na^+ ions, Cl^- ions

We want to treat the behavior of the hydrogen in the material.
Hydrogen is one of the key element for the future technology.
“energy technology”, “biotechnology”

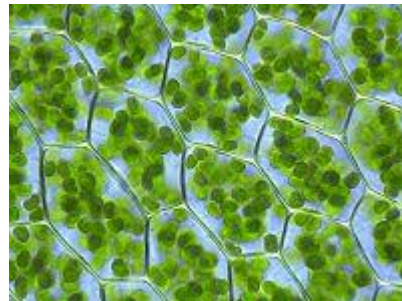
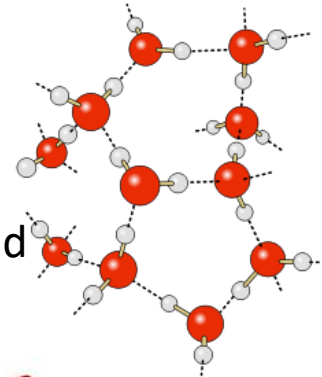
$$\times M_{\text{Proton}} \gg m$$



electrolyte

hydrogen bond

aqueous solution



Photosynthesis

biochemistry

Enzyme catalysis



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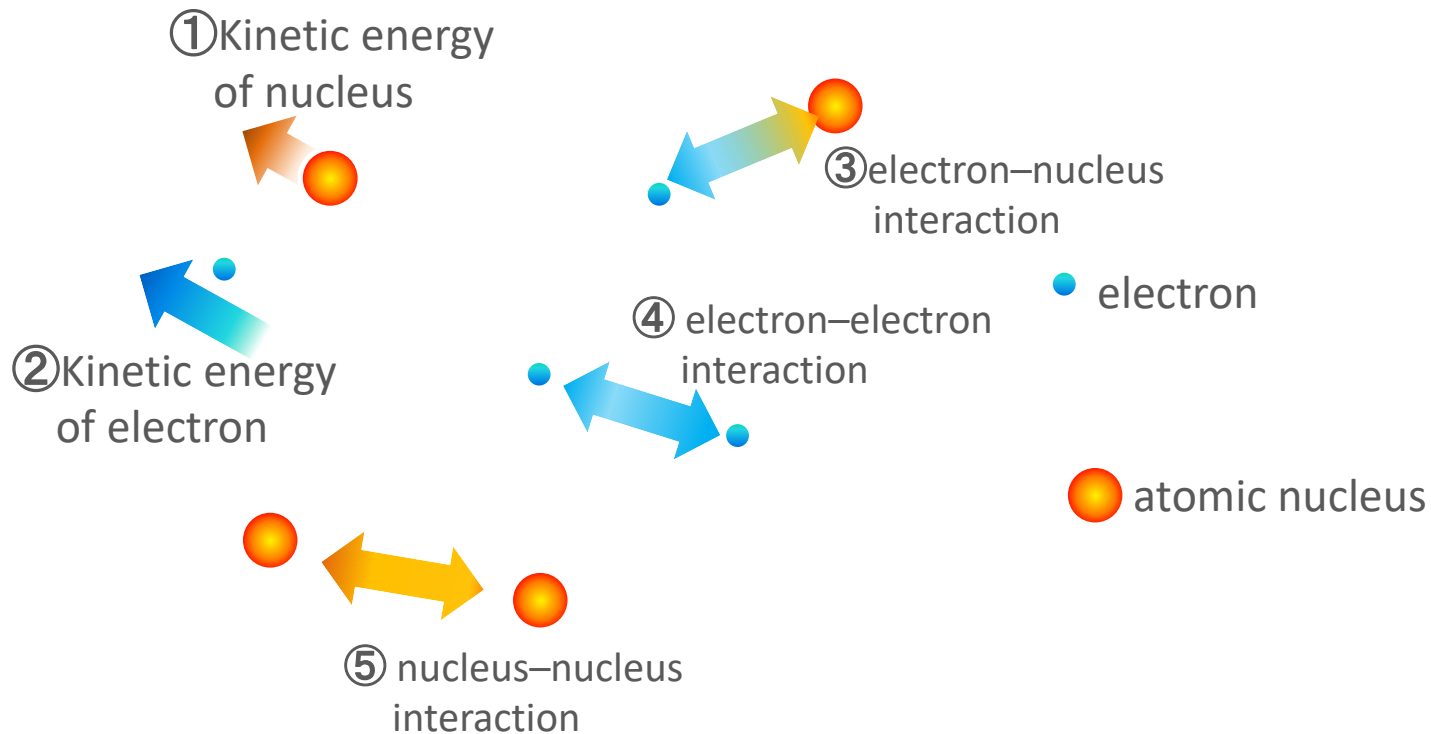
③

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$$\left[-\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla_l^2 - \frac{\hbar^2}{2m} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i=1}^{N_e} \sum_{l=1}^{N_n} \frac{Z_l e^2}{|\vec{r}_i - \vec{R}_l|} + \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1(i \neq j)}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{l=1}^{N_n} \sum_{k=1(l \neq k)}^{N_n} \frac{Z_l Z_k e^2}{|\vec{R}_l - \vec{R}_k|} \right] \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$

$$= E \psi(\vec{r}_1, \dots, \vec{r}_{N_e}; \vec{R}_1, \dots, \vec{R}_{N_n})$$



What is Naniwa ?

- **NANIWA** is a computational code for performing first principles quantum mechanical calculations.
- Two kinds of Naniwa codes.

Naniwa for quantum reaction: It is a quantum mechanical version of the first principles molecular dynamics (MD) calculations, for reactions.

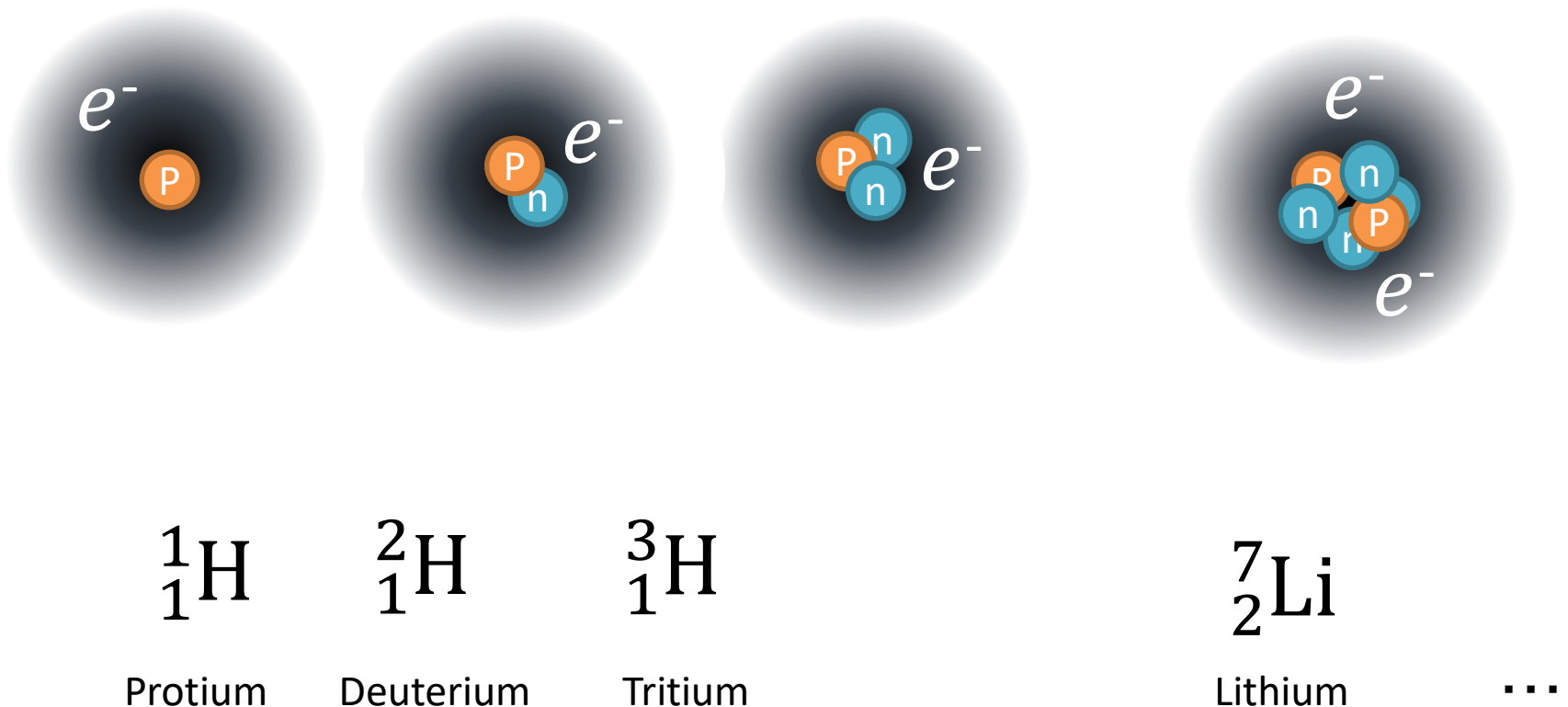
“we can solve the scattering problems, and obtain the probability of some events, adsorption, desorption, reflection, excitation, etc.”

Naniwa for quantum state: It is a nucleus version of the first principles quantum state calculations.

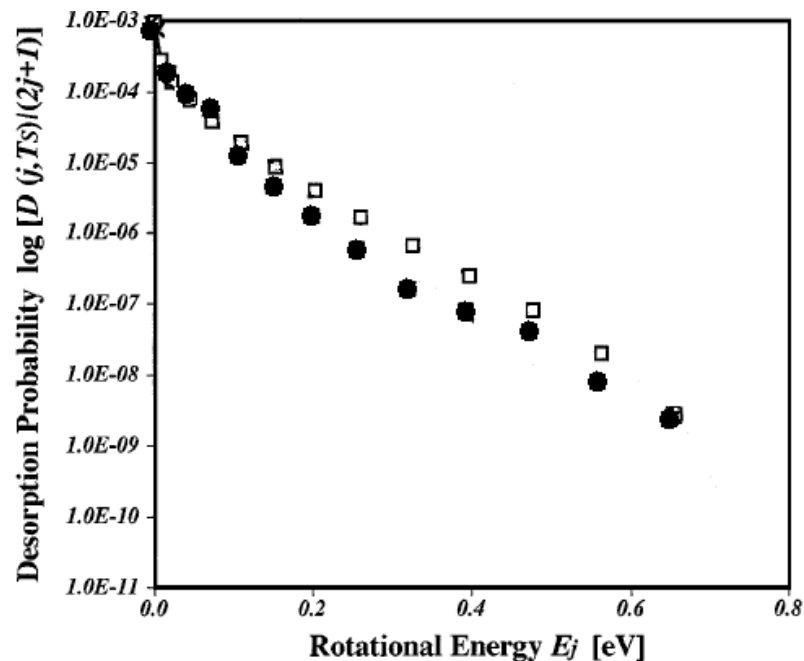
“We can solve the eigenvalue problem, and obtain the eigenstates and their eigenenergies for atom (nuclear) motion”

Naniwa codes

- We have been developing the quantum simulation code “Naniwa” for the small mass atoms, H, Li, ..., on the solid surface, in the subsurface as well as in the bulk.



Rotational energy distributions of hydrogen molecule desorbing from Cu(111) surface



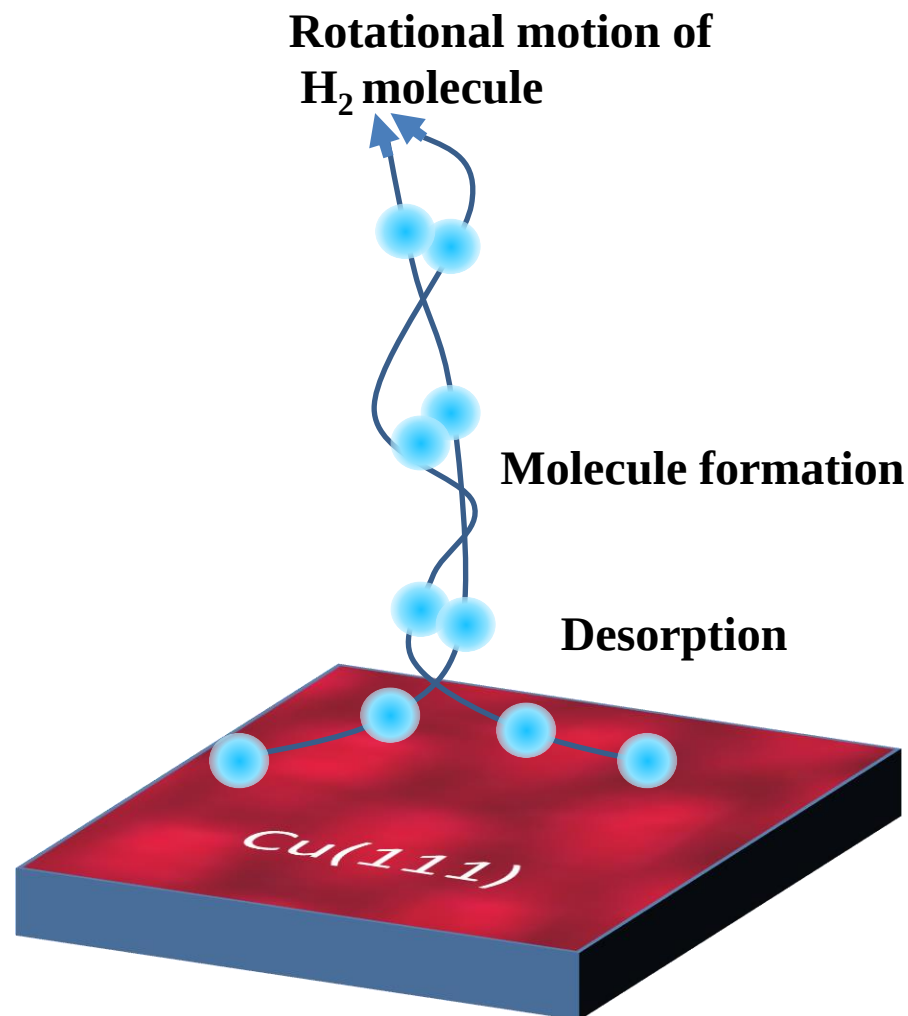
Our simulation results square

: W.A.Dino, *et al.*, PRL **78** (1997) 286.

Experimental data circle

: H.A.Michelsen *et al.*, J. Chem. Phys. **98**(1993) 8294 .

No fitting parameters !



Surface vibration energy of Hydrogen atom adsorbed on Pd(111) surface

Motion	Parallel	Perpendicular
Experiment*	96 meV	124 meV
Simulation	91 meV	114 meV
Error	5.2%	8.1%

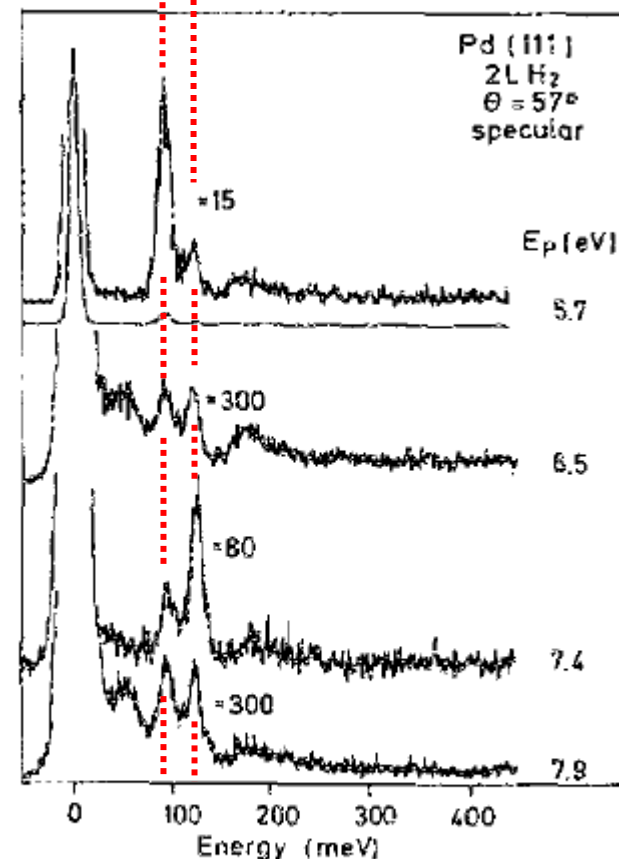
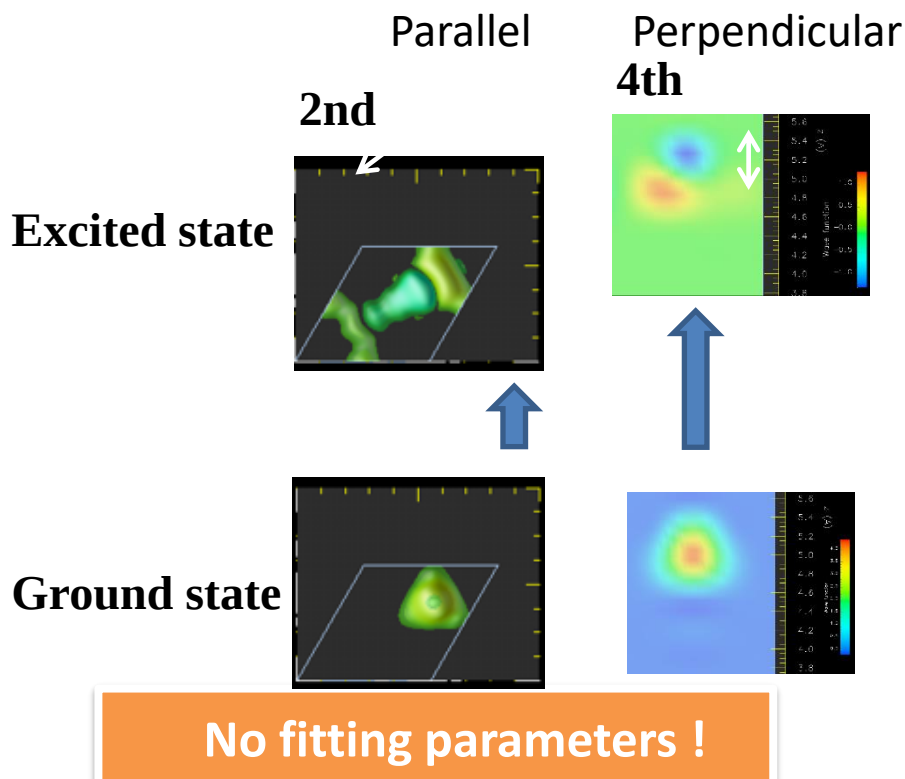


FIG. 1. HREELS of H on Pd(111)

Electron energy loss spectroscopy (EELS)*

H. Conrad, et al, J. Vac. Sci. Technol. A5, 452 (1987).

Comparison between our simulation Naniwa and experimental results

Surface-normal vibration excitation energy of hydrogen atom adsorbed on metal surface

	Naniwa	Experiment	Error
H on Pd(111)	114 meV	124 meV**	8.1%

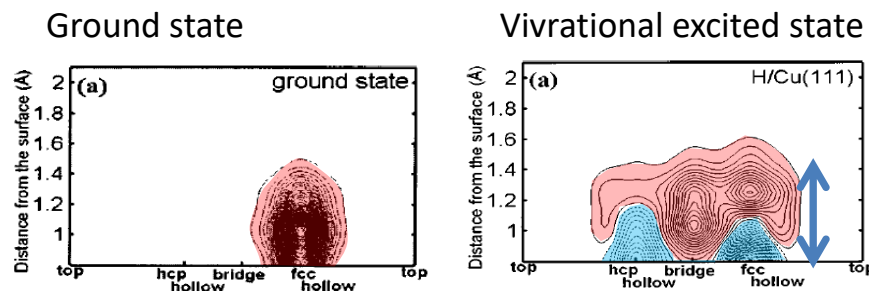
** H. Conrad, *et al*, J. Vac. Sci. Technol. A5, 452 (1987).

	Naniwa	Experiment	Error
H on Cu(111)	135 meV	129 meV*	4.7%
D on Cu(111)	104 meV	96 meV	8.3%
isotope effect	1.29	1.34	3.4%

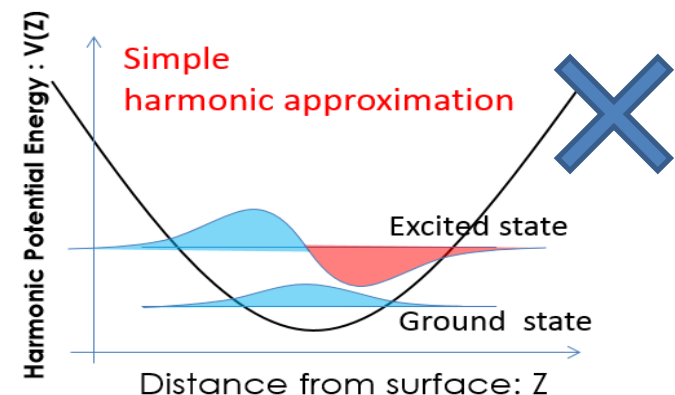
*G. Lee, *et al.*, Surf. Sci. **498** (2002) 229.

Less than 10% error

H on Cu(111)



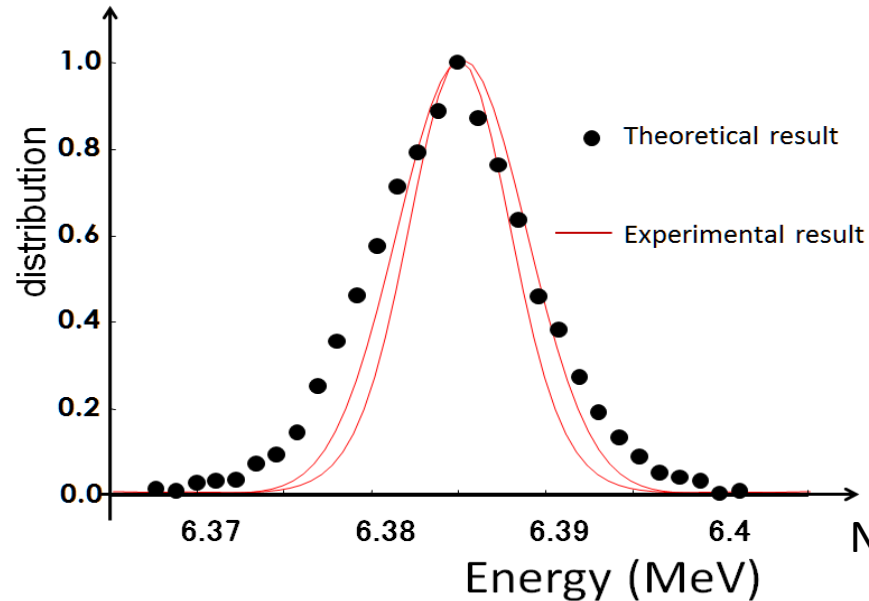
No fitting parameters !



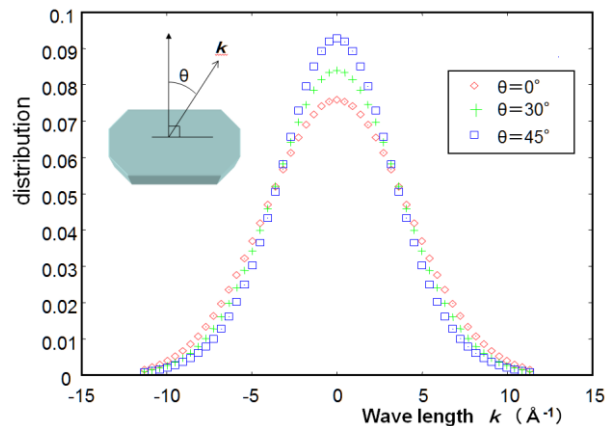
$$\text{isotope effect ratio} = \sqrt{2} \sim 1.414$$

Comparison between our simulation Naniwa and experimental results

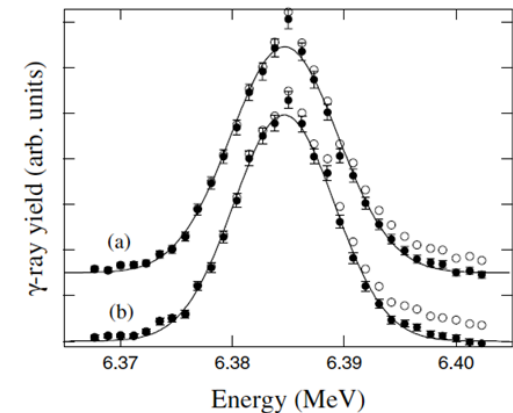
Momentum distribution of adsorbed hydrogen atom is observable in its ground state.



NRA : Nuclear Reaction Analysis



Naniwa

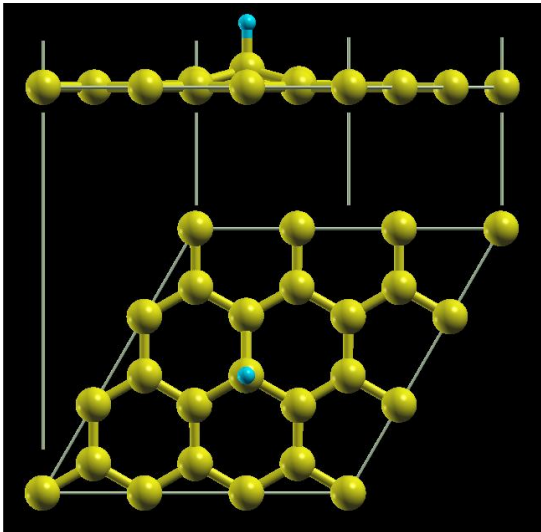


K. Fukutani et al., PRL 48(2002)116101.

Comparison between our simulation Naniwa and experimental results

Hydrogen adsorbed on graphene

Conventional ab initio cal.

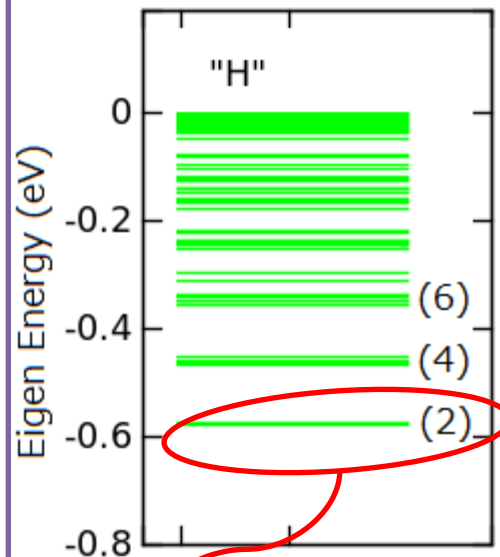


Adsorbed site: Top site

Adsorbed type: chemisorption

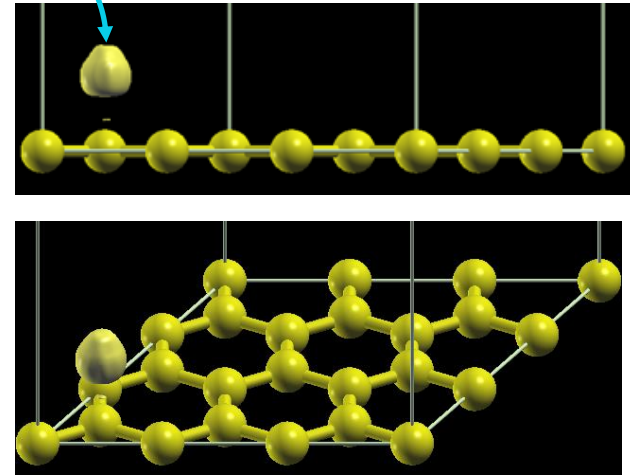
Adsorbed energy: **-0.816 eV**

Naniwa results



Quantum adsorbed energy of hydrogen: **-0.58eV**

Ground state Wave function

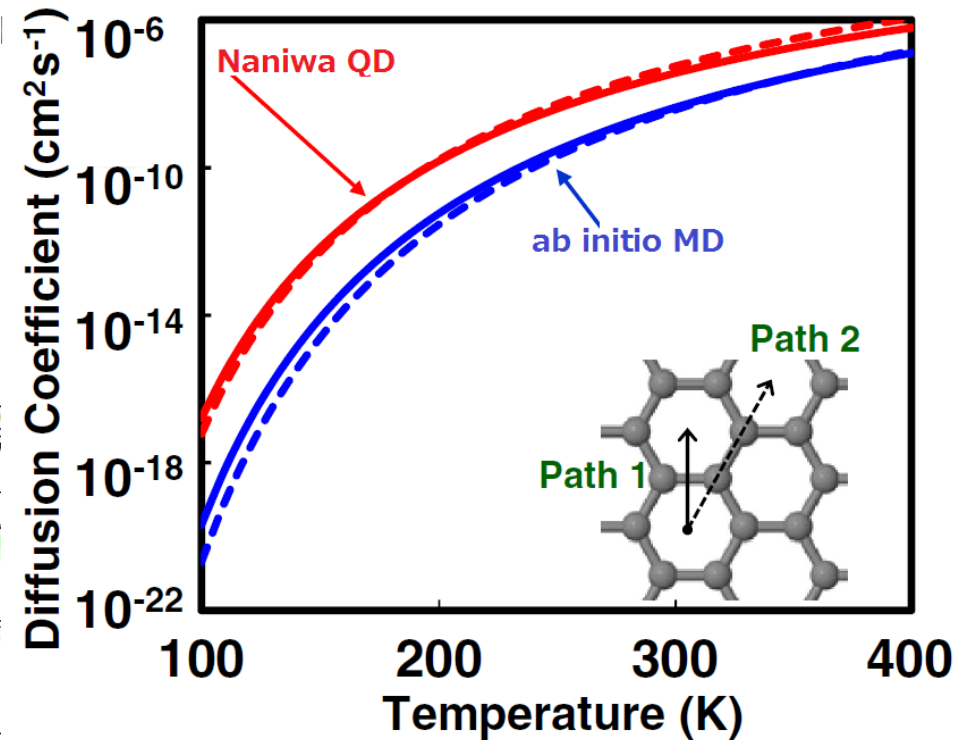
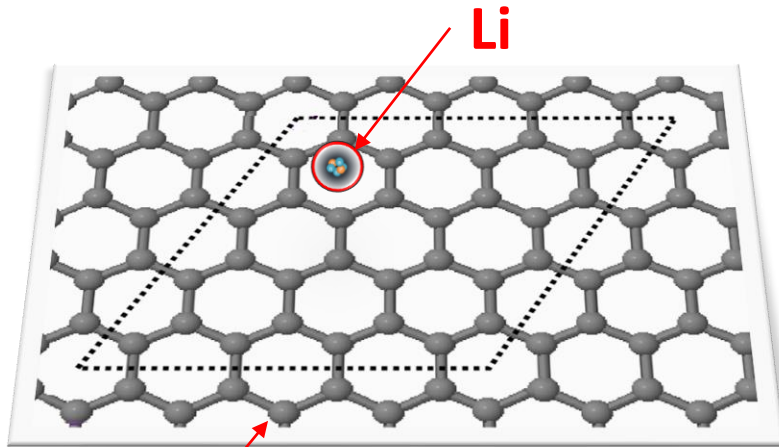


TDS experimental data : **-0.59 eV or -0.65eV**

X. Zhao, et al., J. Chem. Phys. 124(2006)194704

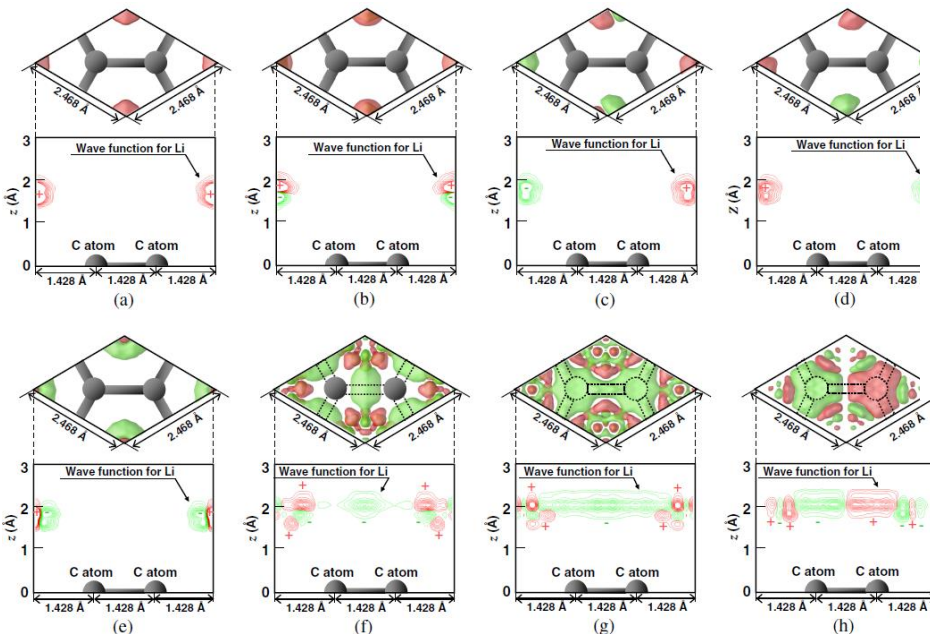
Li on graphene

Negative electrode of Lithium-ion battery



Activation barrier: $E_a(\text{path 1}) < E_a(\text{path 2})$

Y. Kubota, et al., JPSJ **79**(2010)014601.



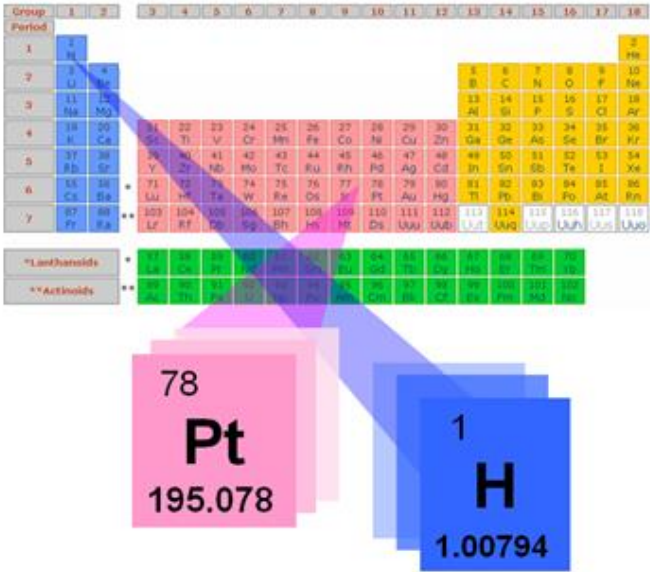
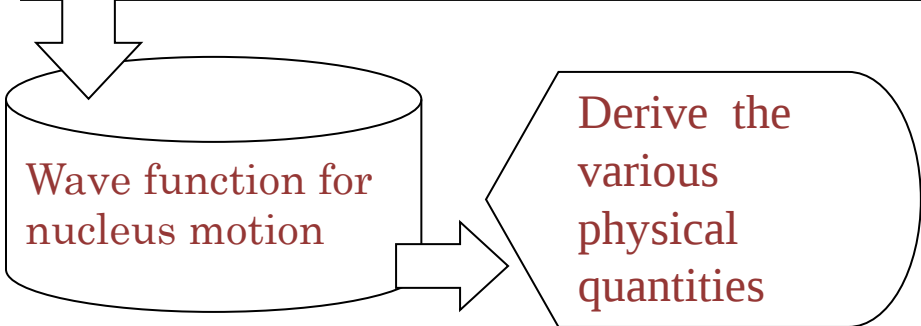
Our quantum simulation scheme: Naniwa

Interactions between nucleus is calculated by DFT based first principle calculations

... (*)

Potential energy for nucleus motions: $U_n(R)$

Solve the Schrödinger equation for nucleus motion ... (**)



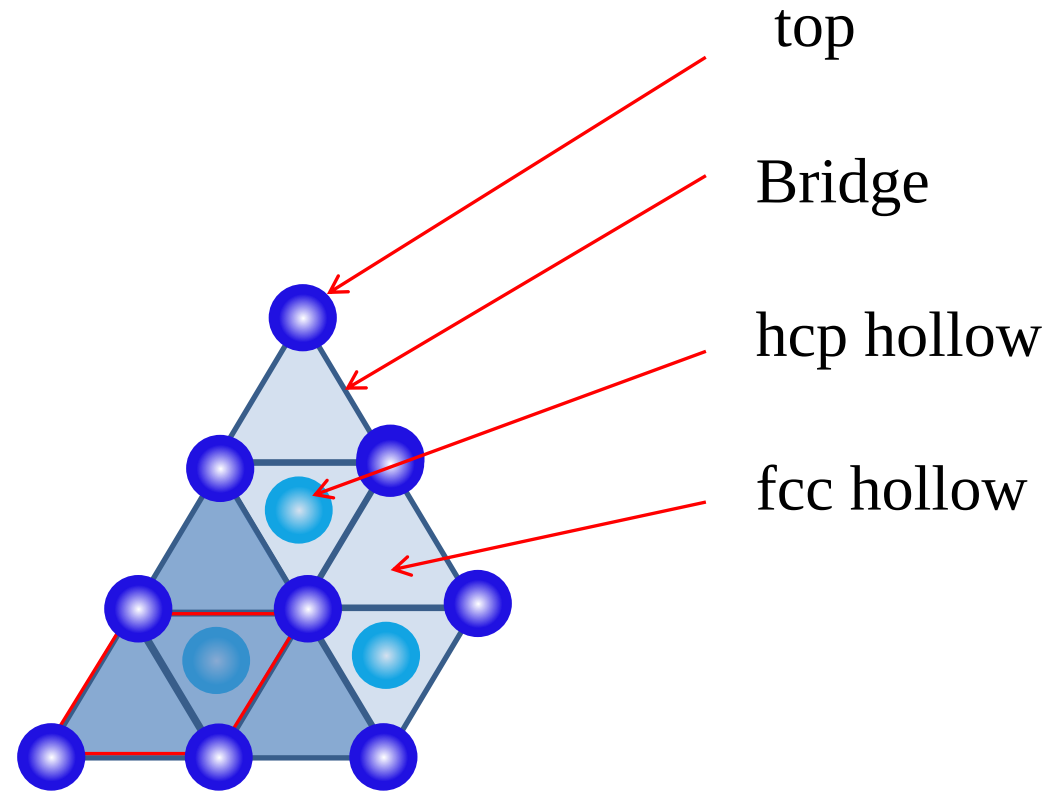
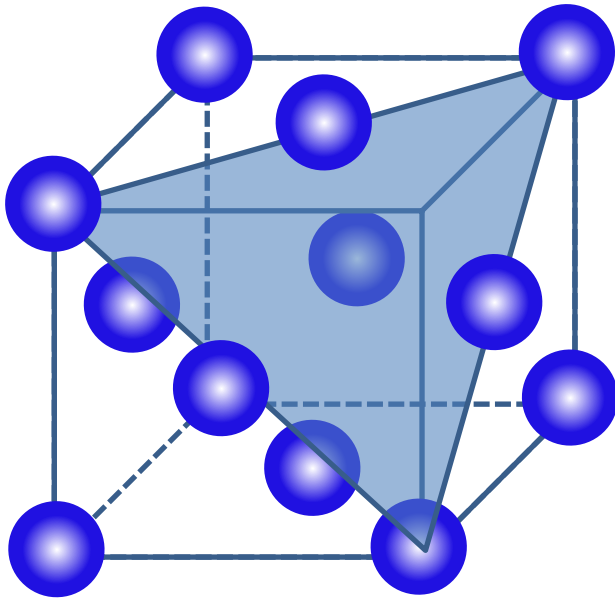
- Parameters are only atomic number of elements
- No fitting and no artificial procedure

- Some examples on (111) surface of fcc crystals

Quantum states of hydrogen atom motion
on the surface

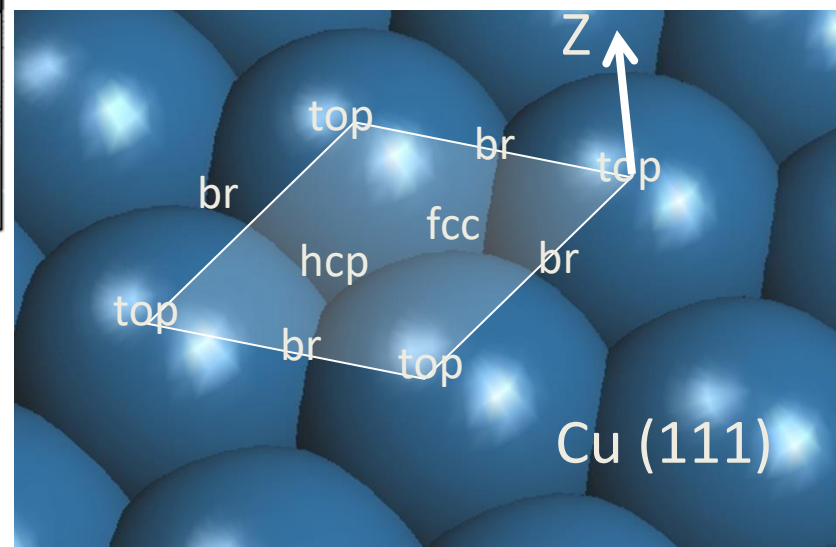
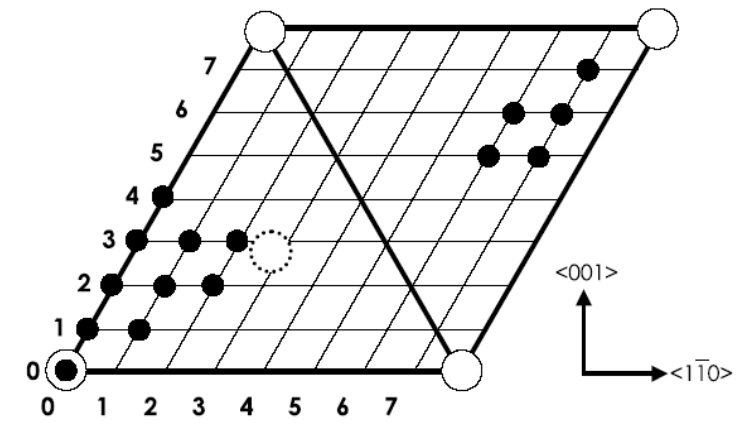
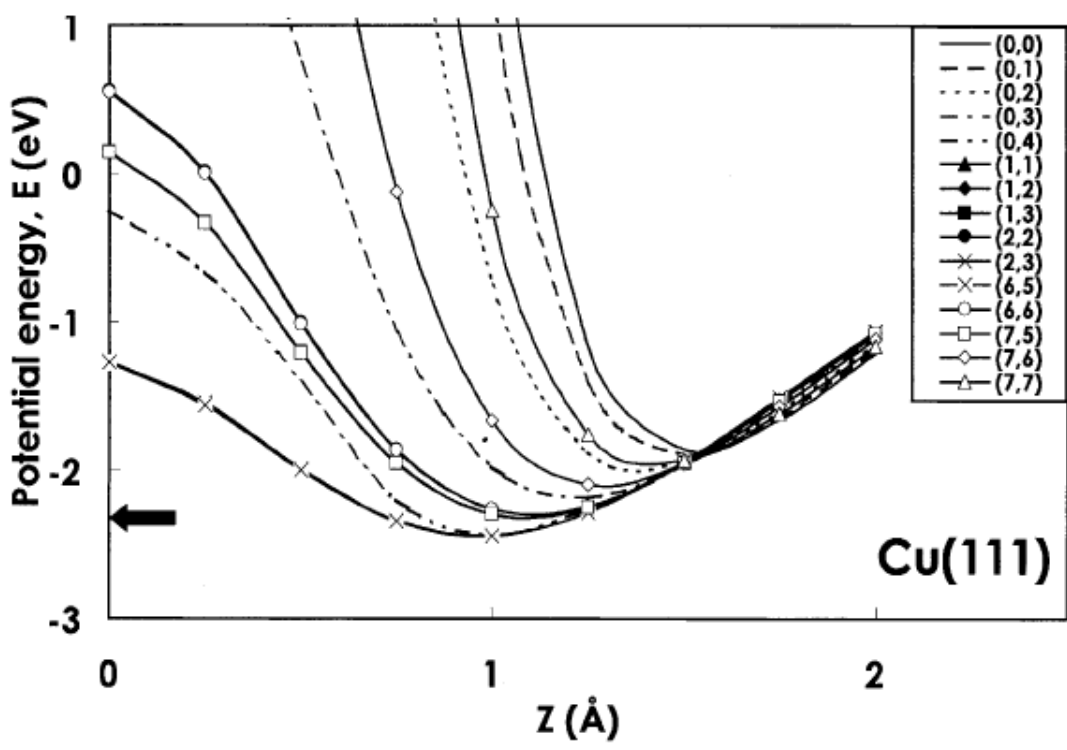
(111) surface of face center cubic crystals

(111) surface

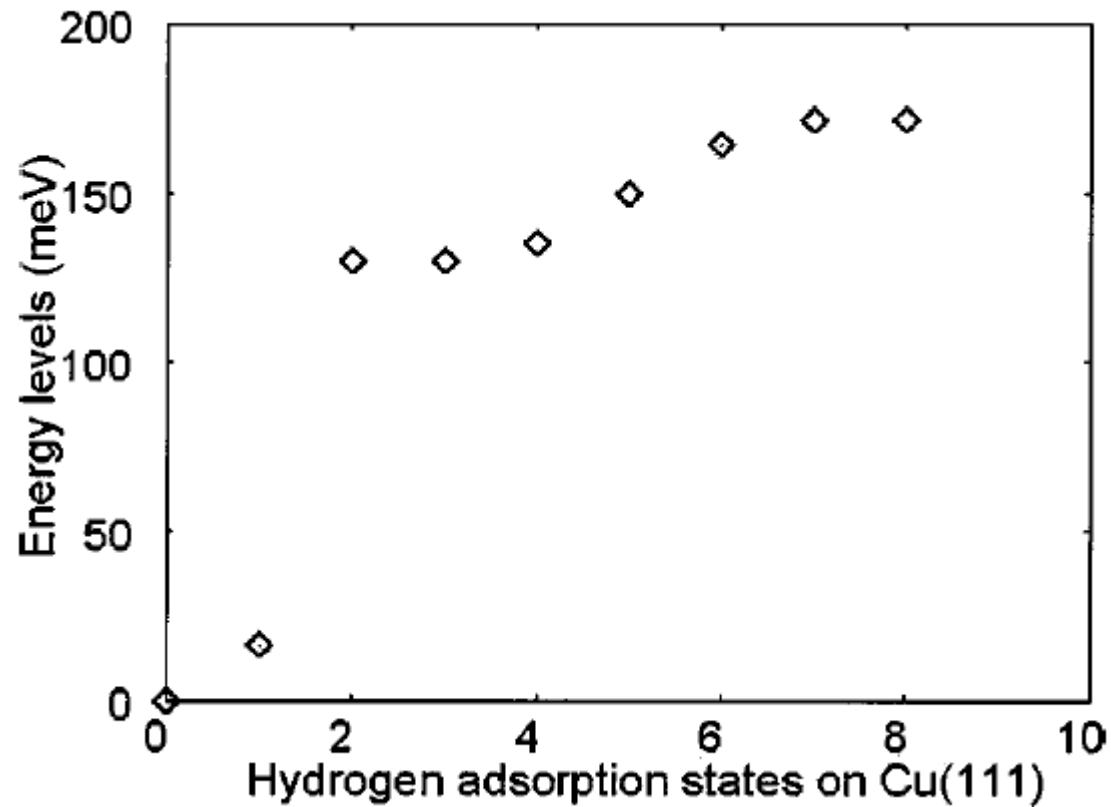


- First layer atom
- 2nd layer atom

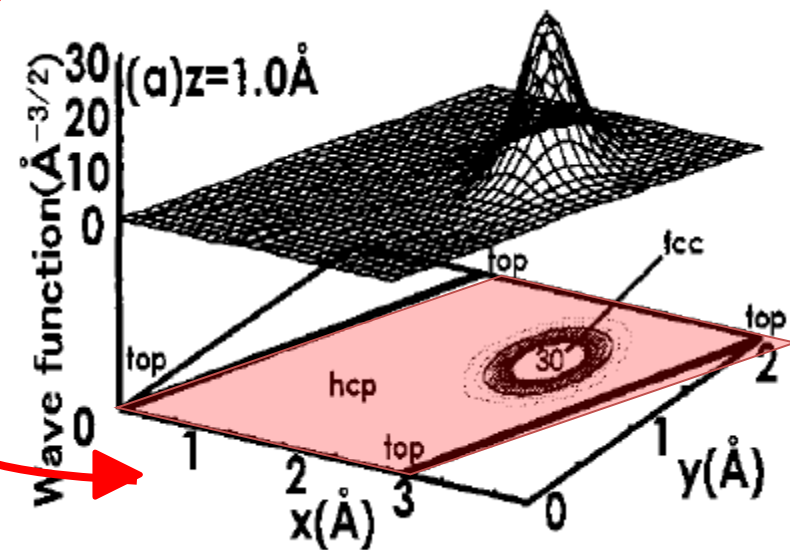
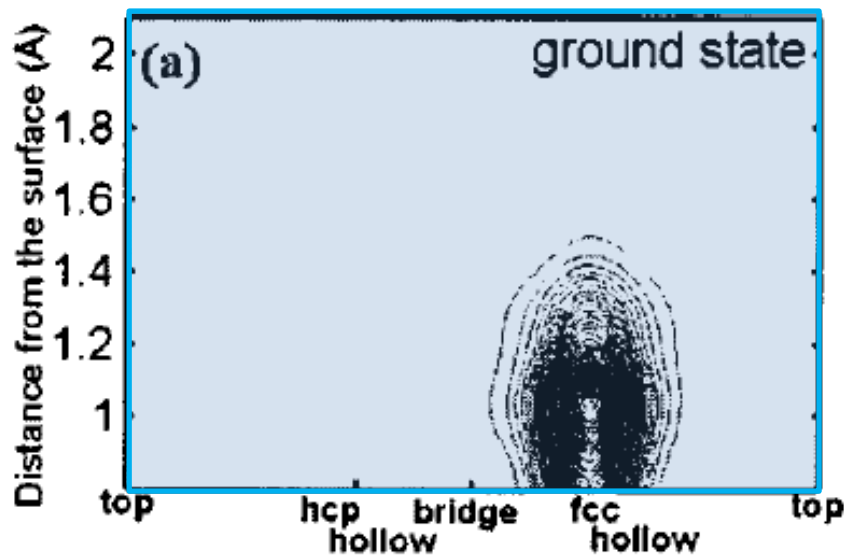
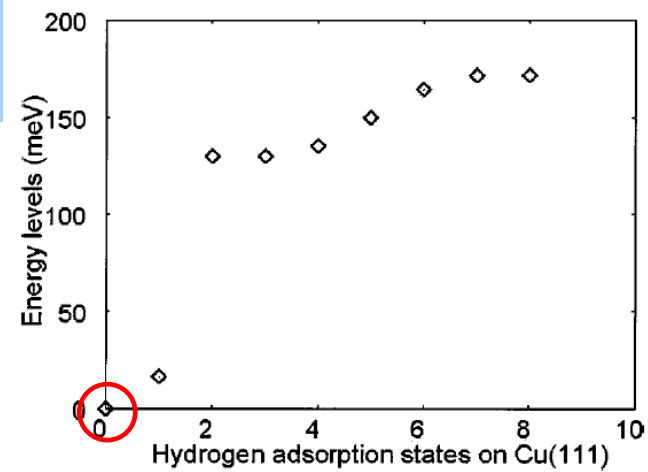
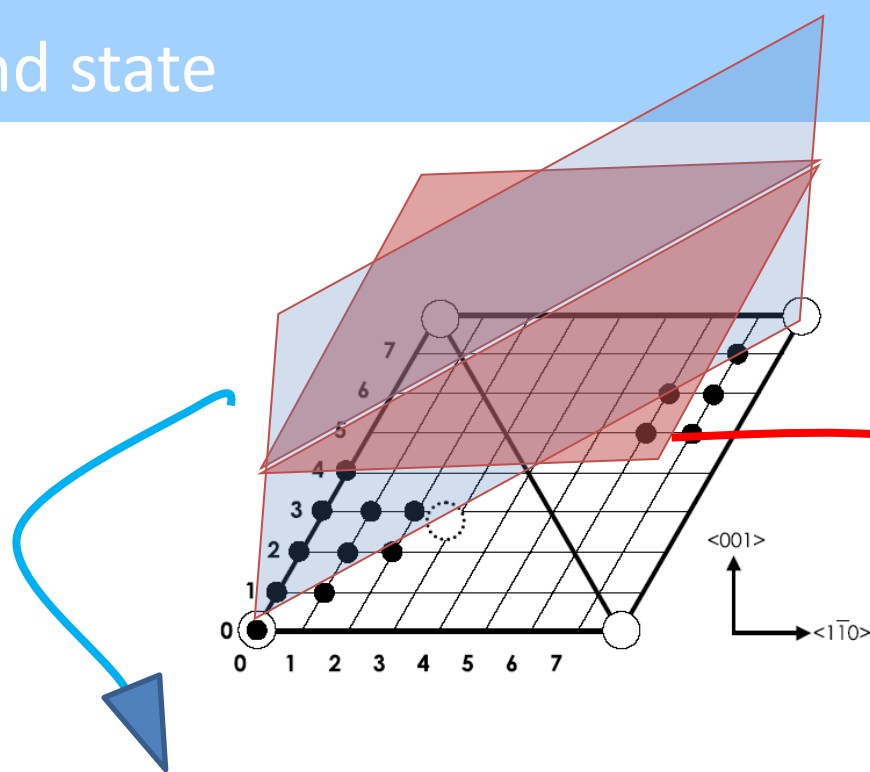
Potential energy surface of H motion on Cu(111)



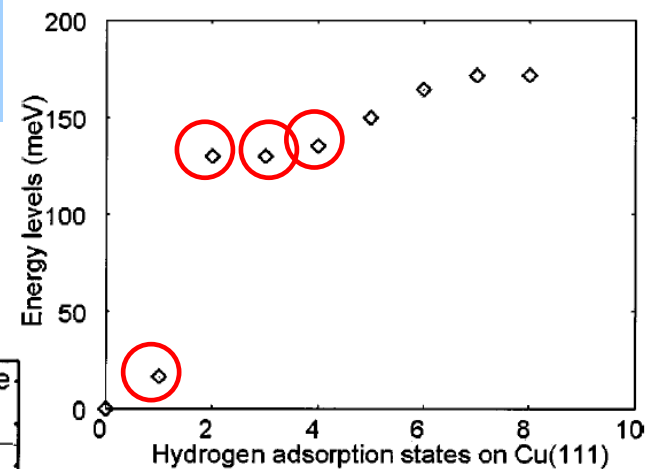
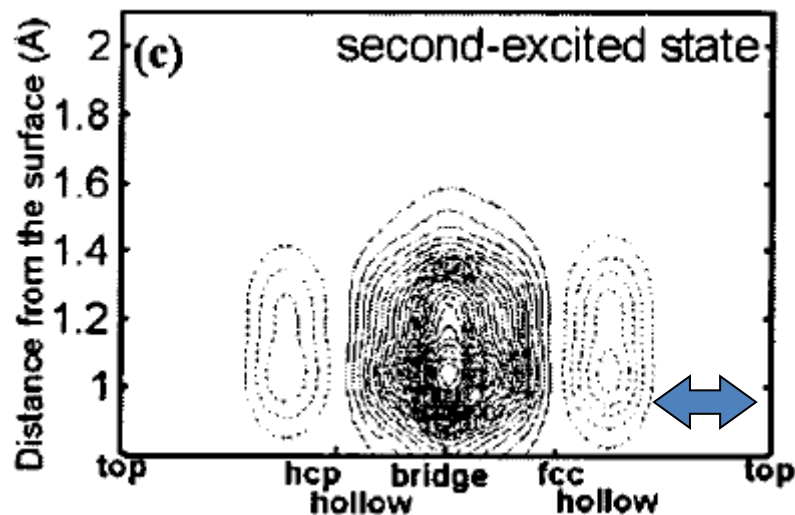
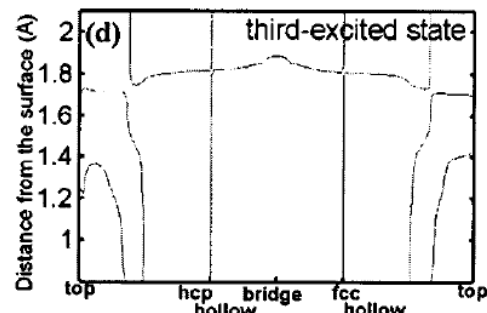
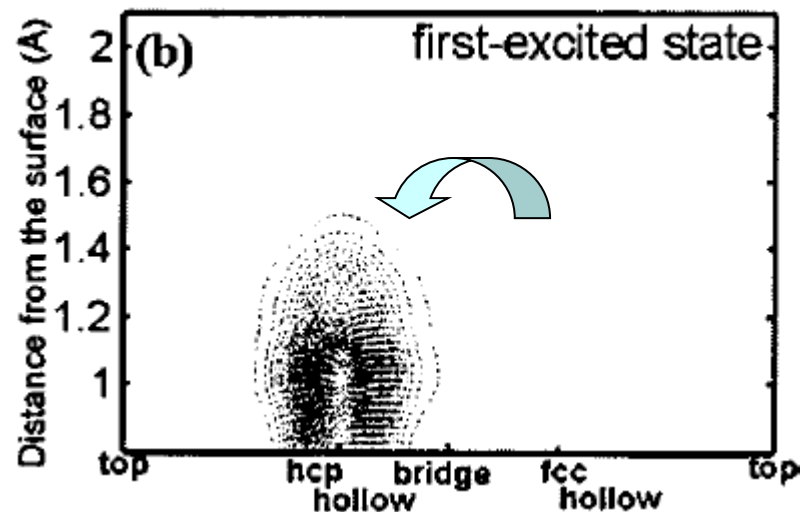
Eigenenergy for a H motion on Cu(111)



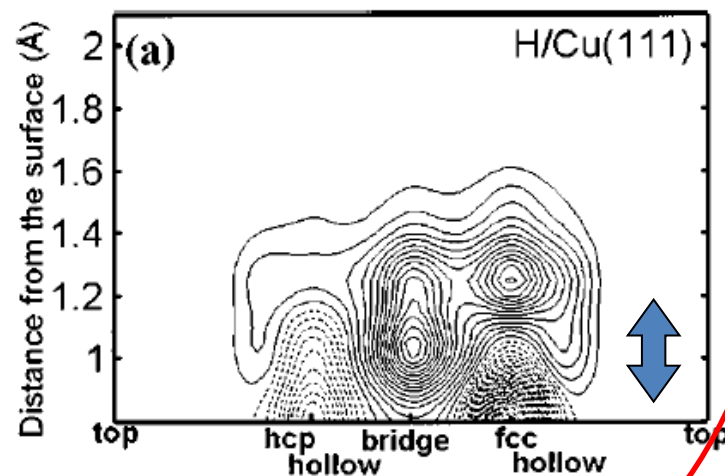
Ground state



The excited states



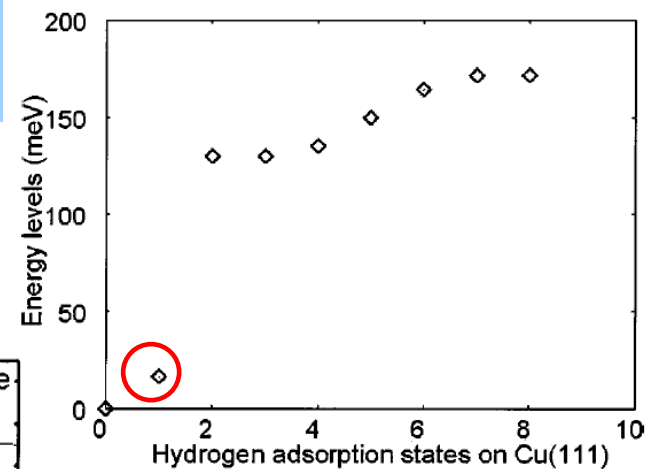
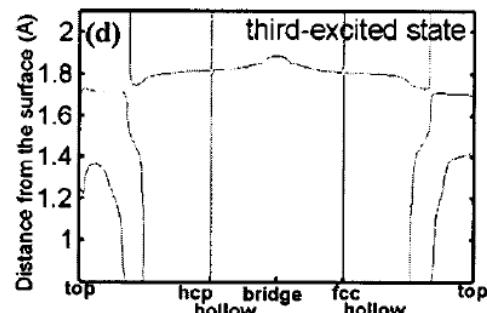
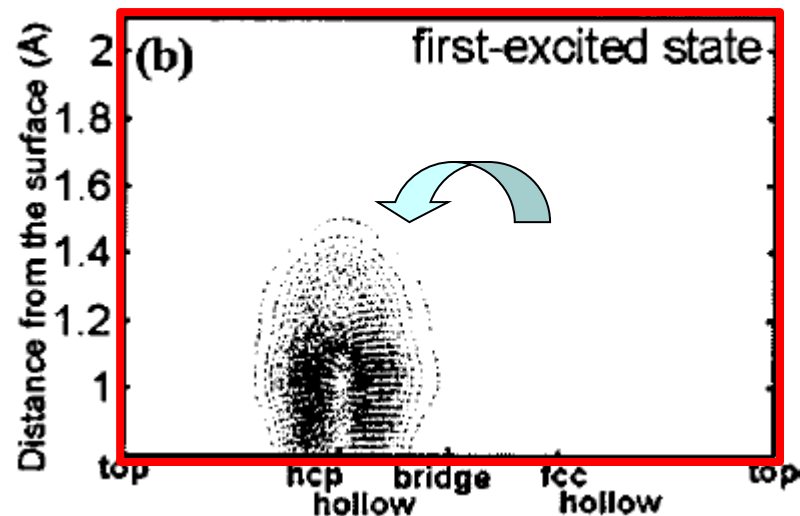
$$E_4 - E_0 = 135 \text{ meV}$$



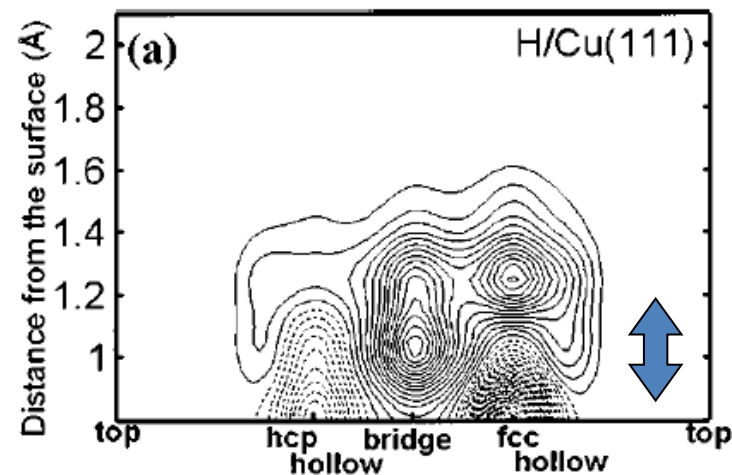
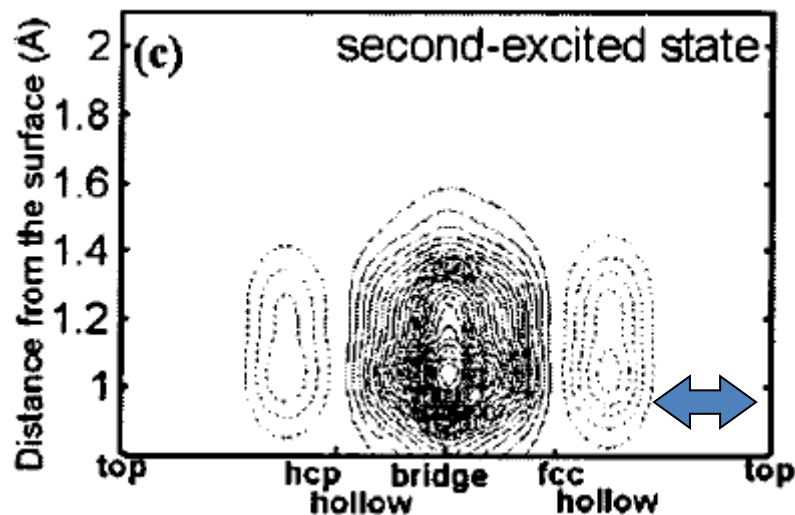
Exp. 129 meV by HREELS

G. Lee et al., Surf. Sci. 498 (2002) 229.

The excited states



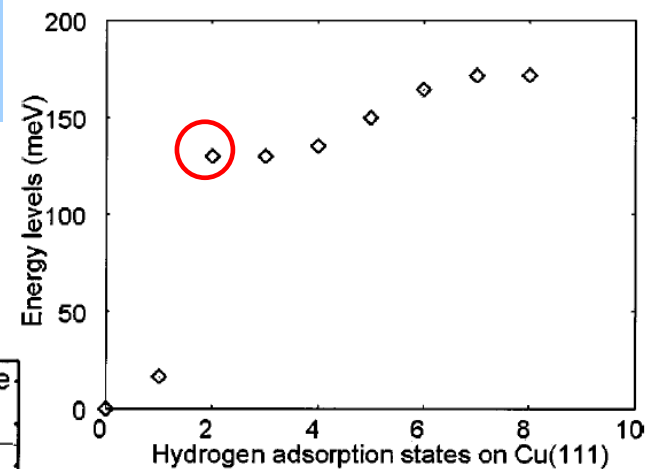
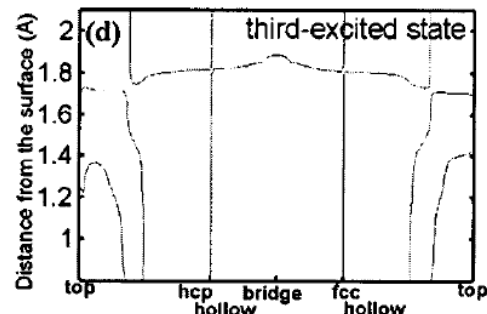
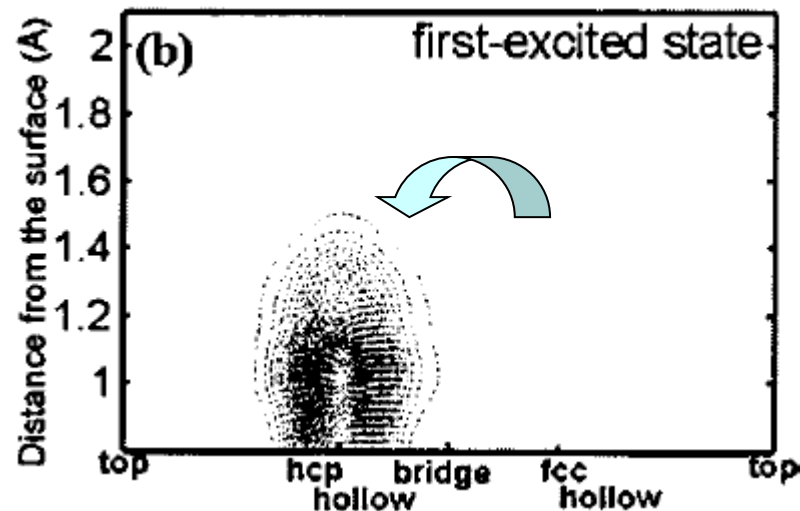
$$E_4 - E_0 = 135 \text{ meV}$$



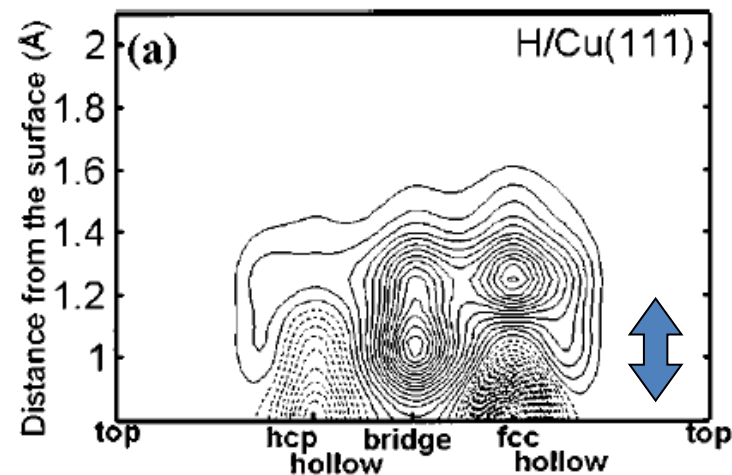
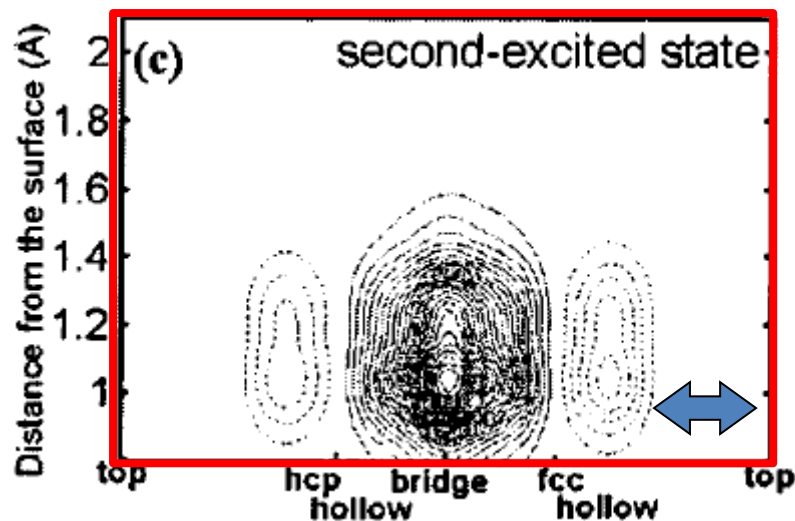
Exp. 129 meV by HREELS

G. Lee et al., Surf. Sci. 498 (2002) 229.

The excited states



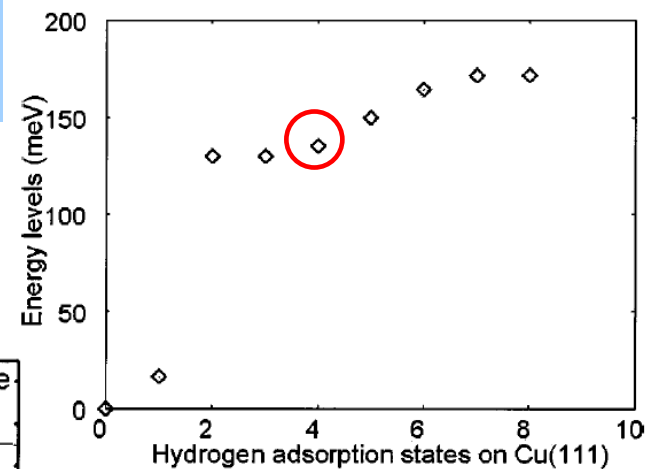
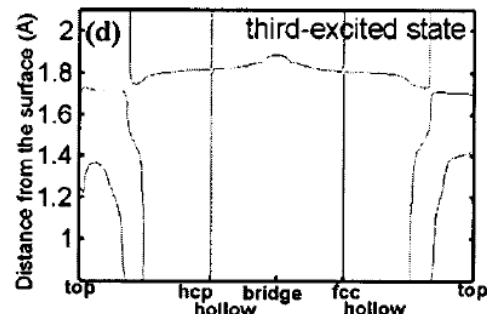
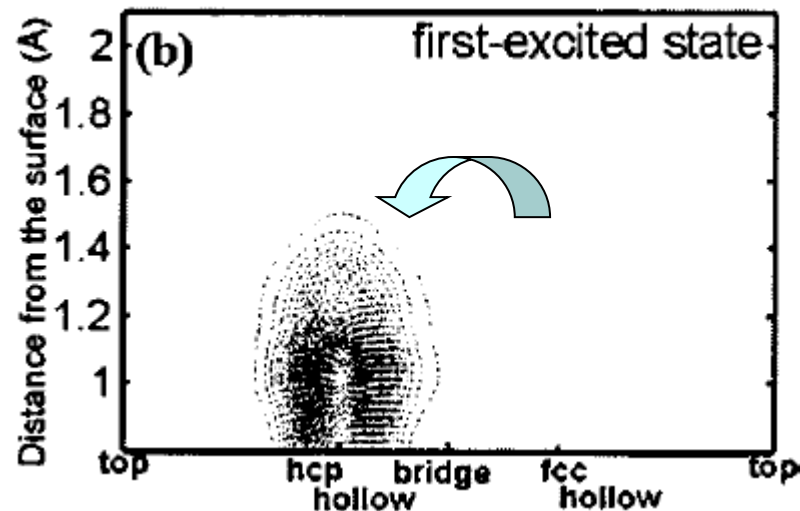
$$E_4 - E_0 = 135 \text{ meV}$$



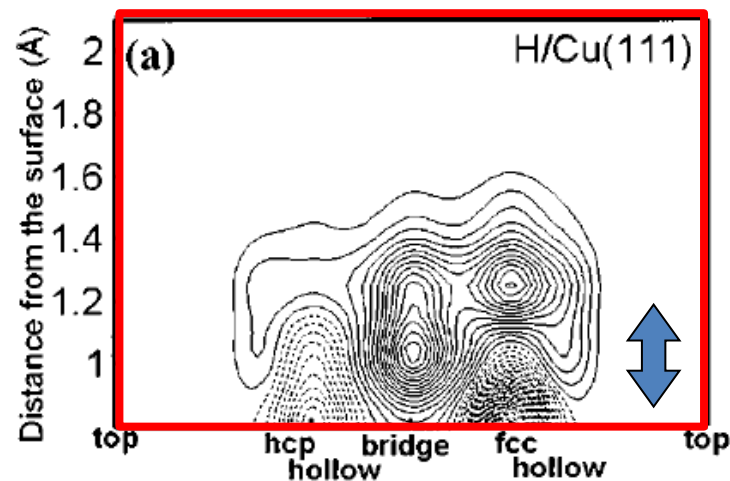
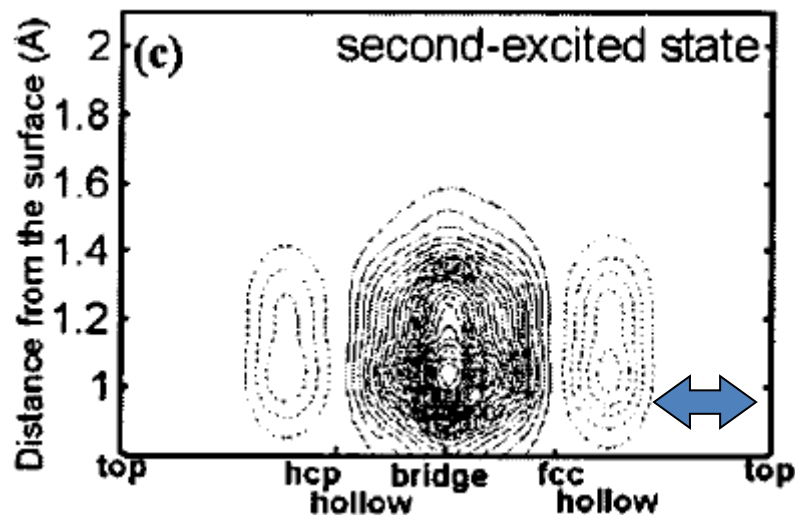
Exp. 129 meV by HREELS

G. Lee et al., Surf. Sci. 498 (2002) 229.

The excited states

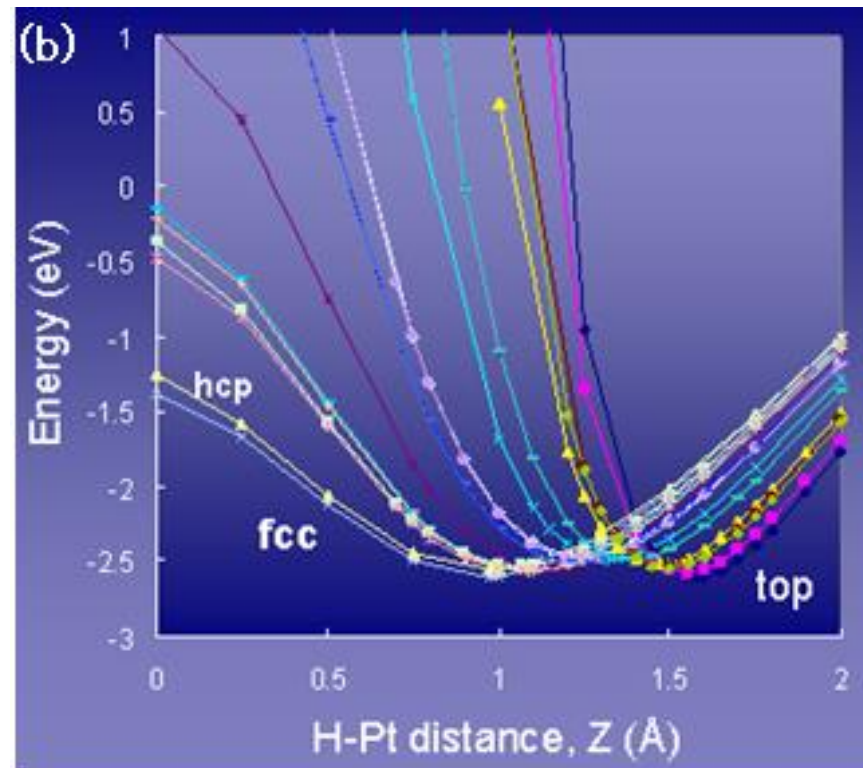
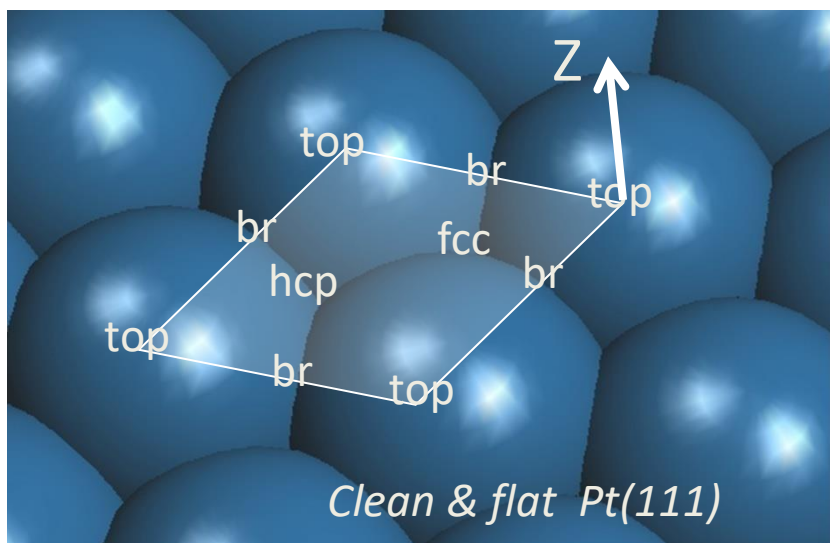


$$E_4 - E_0 = 135 \text{ meV}$$



Exp. 129 meV by HREELS

Potential energy surface of H motion on Pt(111)



H atom adsorption energy well depths:

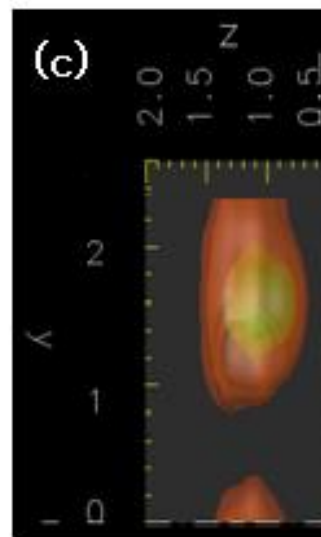
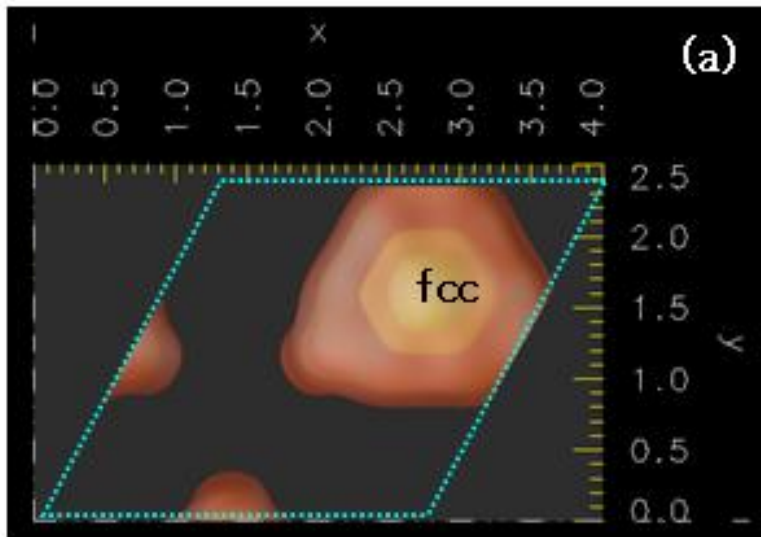
Top: 2.609 eV, fcc hollow: 2.607 eV, hcp hollow: 2.562 eV



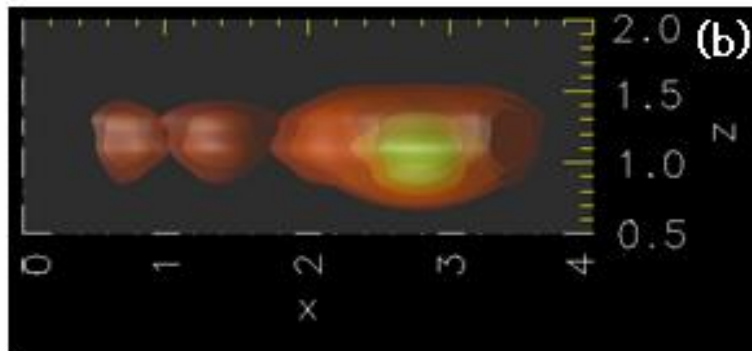
Most stable adsorbed site is On-top site !?

Quantum mechanical effects for hydrogen motions

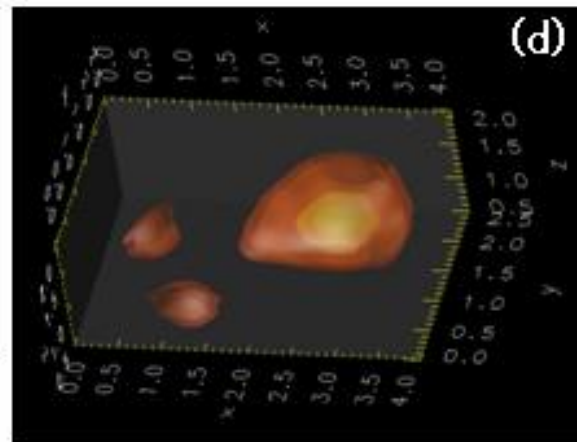
Ground state of hydrogen motion on Pt(111) surface



Ground state wave function: $\Psi_0(x,y,z)$.
Eigen energy: -2.461eV

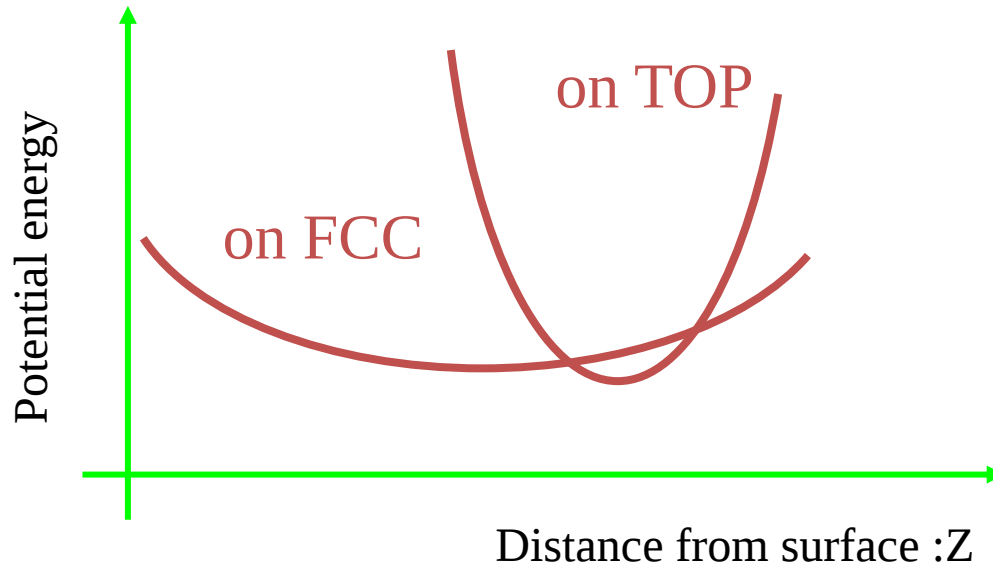


Å



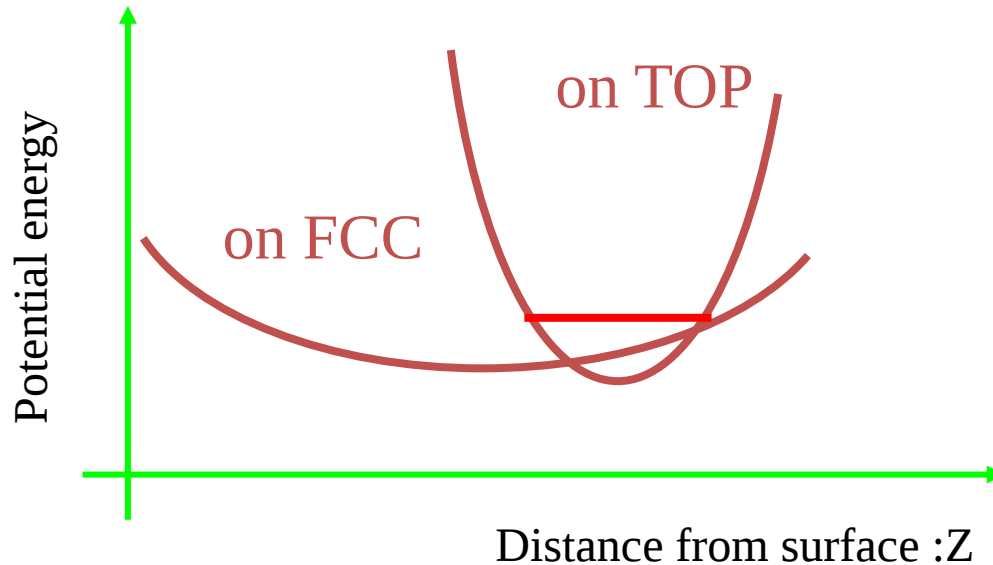
Why ground state is localized around fcc hollow site?

Potential energy : top site < fcc hollow site



Why ground state is localized around fcc hollow site?

Potential energy : top site < fcc hollow site



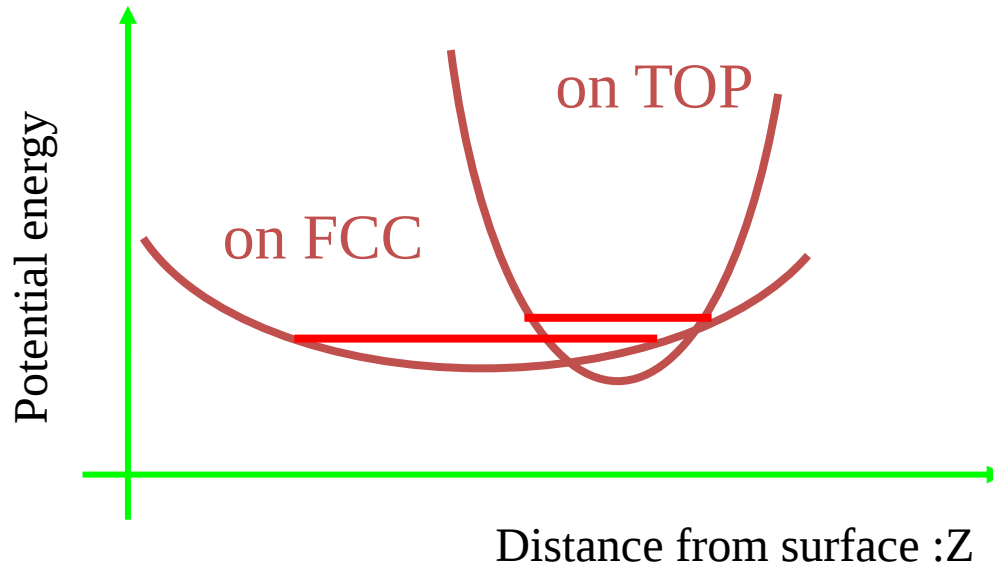
Heisenberg uncertainty principle

Narrower space confinement causes the higher kinetic energy.

Quantum mechanical effects

Why ground state is localized around fcc hollow site?

Potential energy : top site < fcc hollow site



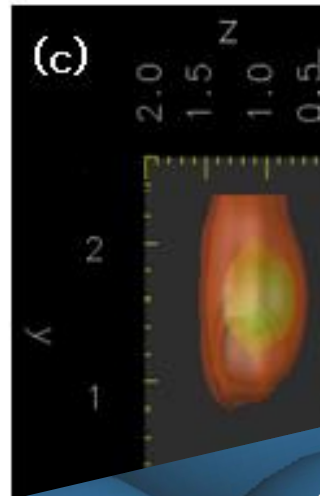
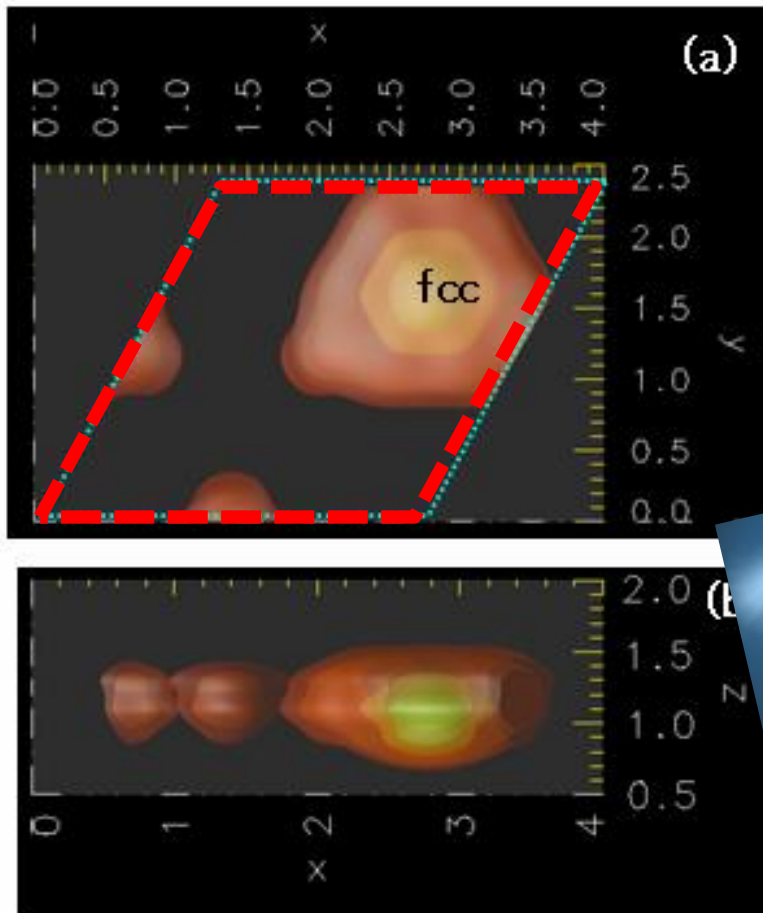
Heisenberg uncertainty principle

Narrower space confinement causes the higher kinetic energy.

Quantum mechanical effects

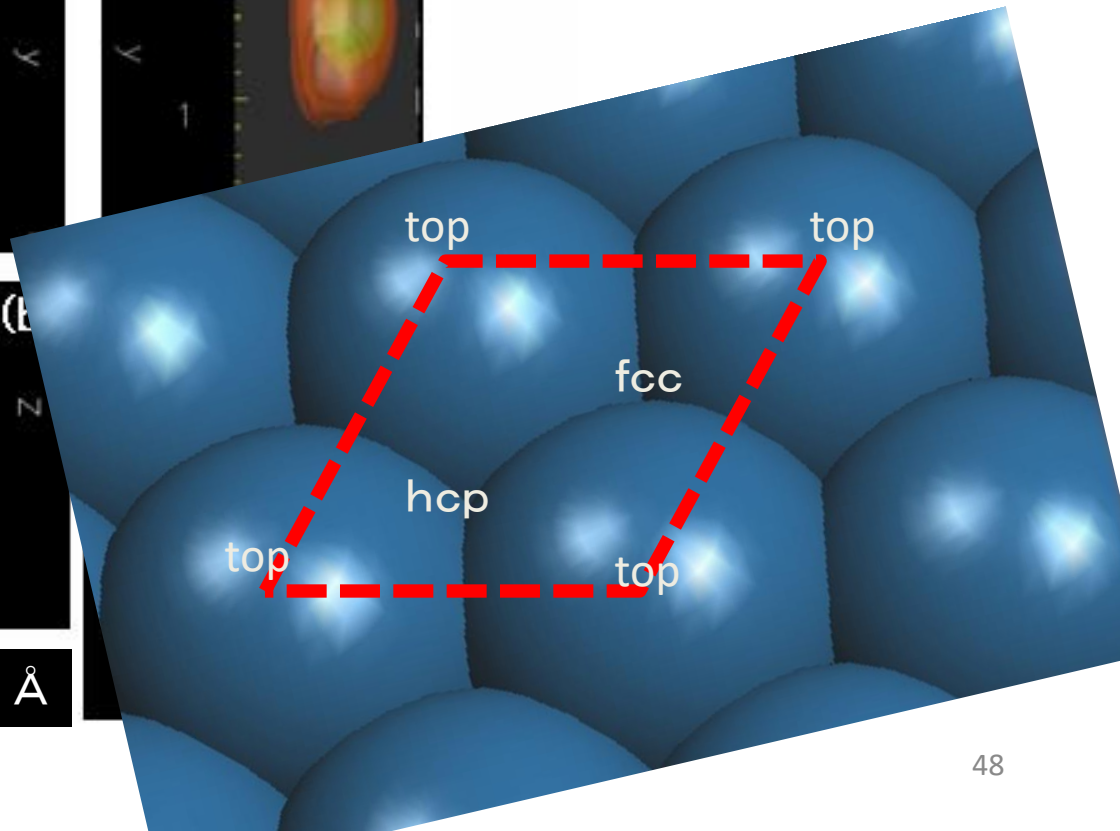
Quantum mechanical effects for hydrogen motions

Ground state of hydrogen motion on Pt(111) surface



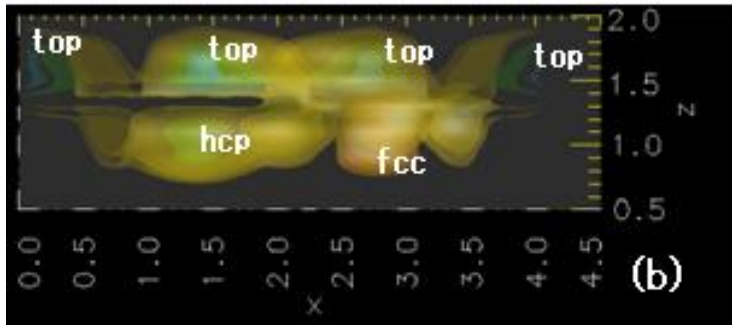
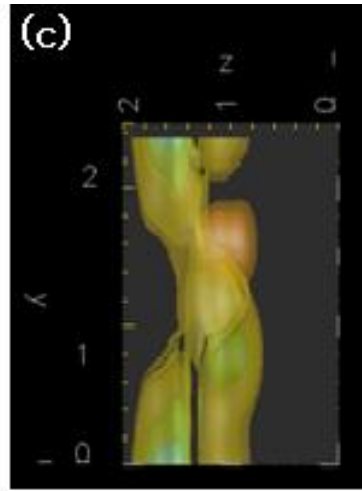
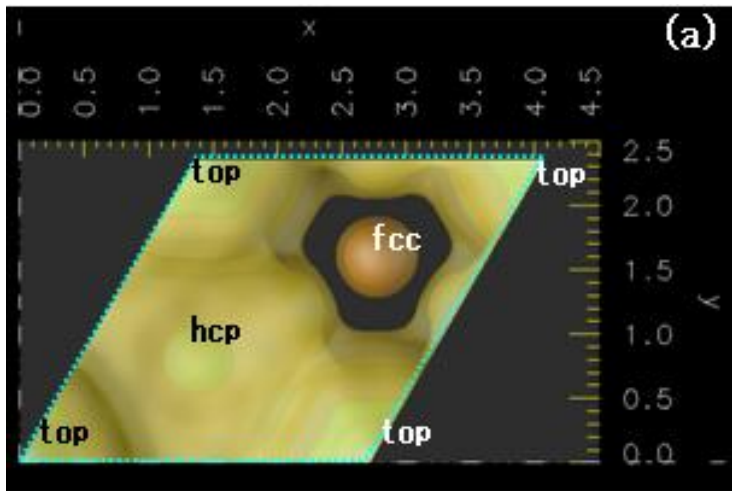
Ground state wave function: $\Psi_0(x,y,z)$.
Eigen energy: -2.461 eV

Å

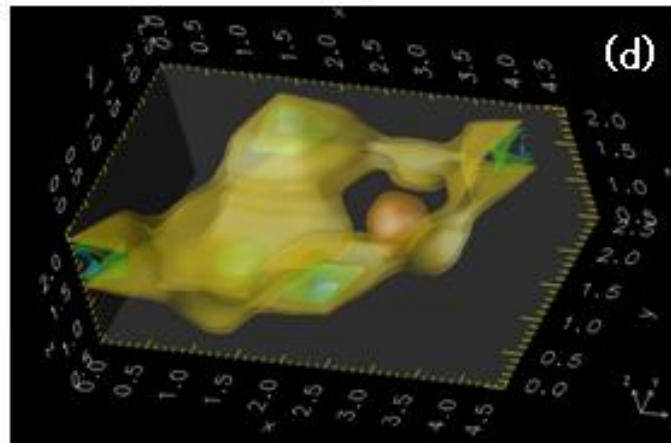


As for migration of H atom on the electrode surface

The 1st excited state wave function expands on the surface



Å

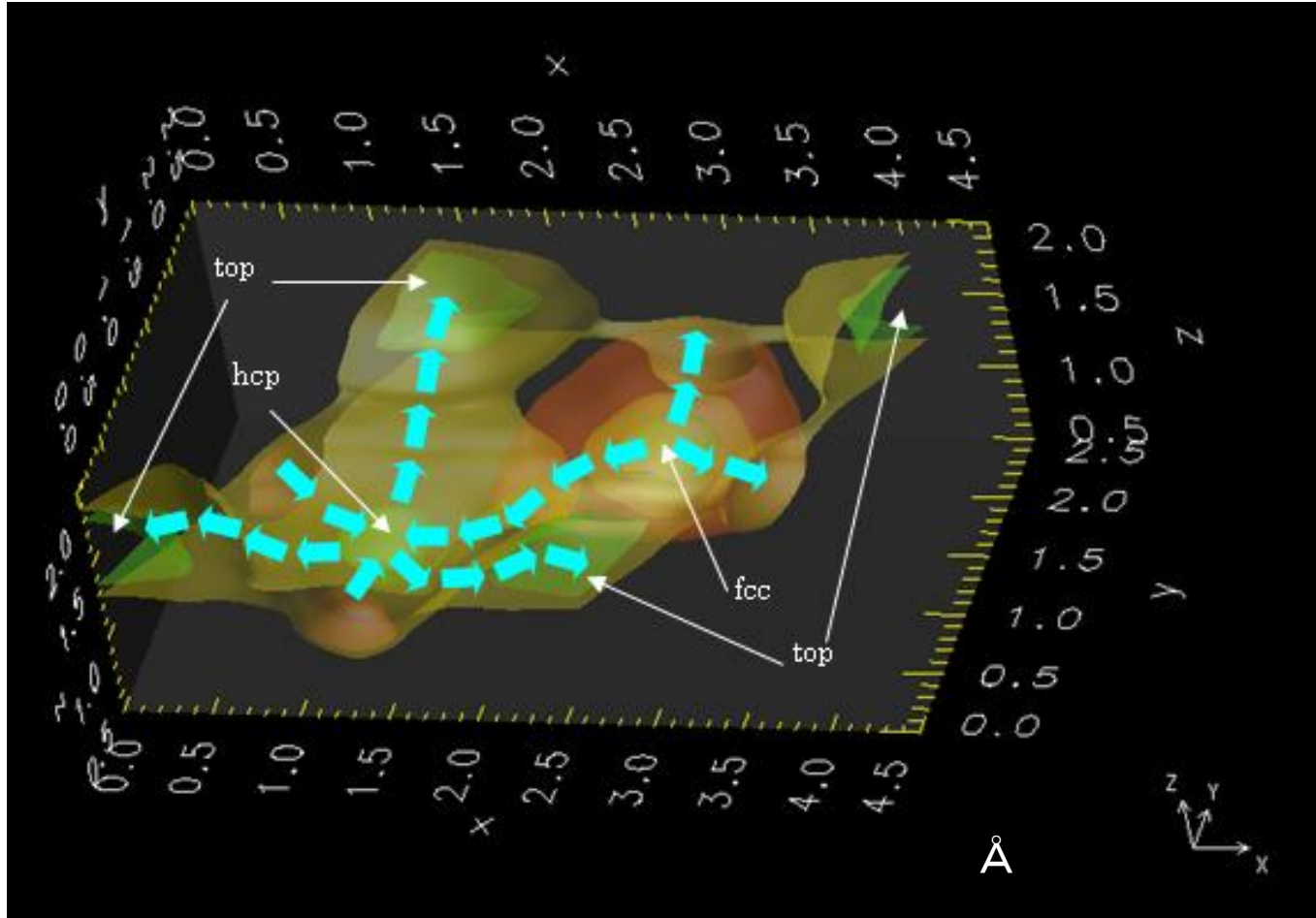


The first excited state wave function: $\Psi_1(x,y,z)$.

Eigenenergy: -2.431eV

Energy difference between first and ground state:

$$E_1 - E_0 = 30 \text{ meV}$$



Diffusion can occur at typical fuel cell operational temperature !

Naniwa codes

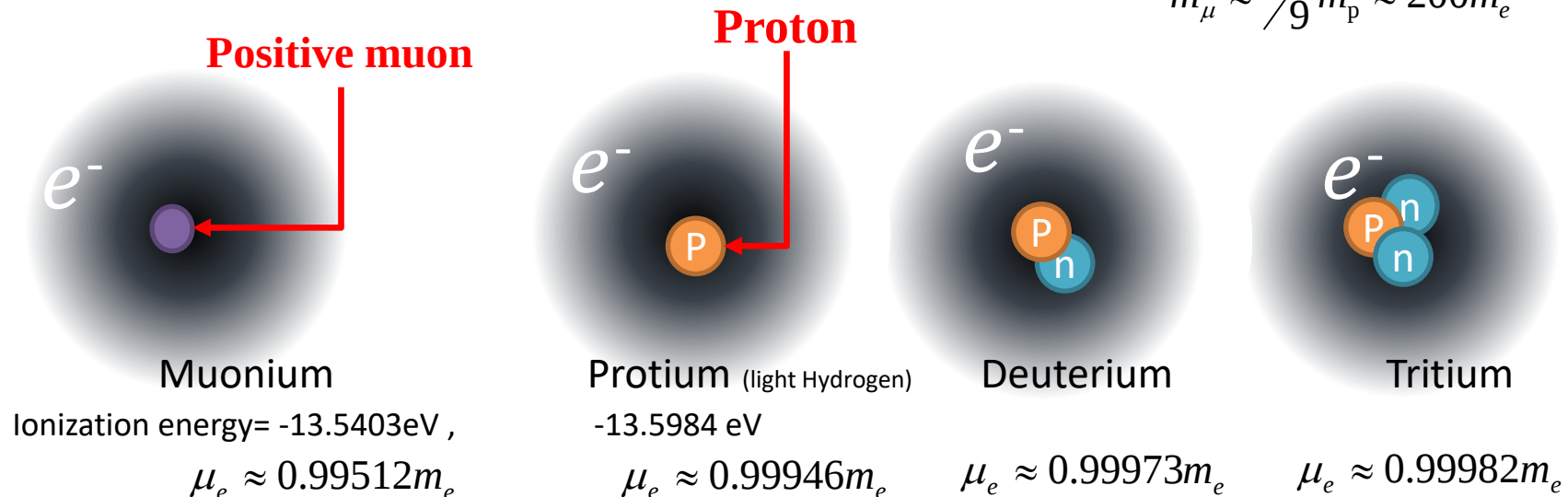
- Positive muon is also one of our target quantum particles as hydrogen isotope, which is useful as a magnetic probe in the materials, mu-SR.

Name	Anti muon (Positive muon)
Particle statistics	Fermionic
Mass	105.658369(9) MeV/c ²
Electric charge	+e $e_\mu = e_p$
Spin	$1/2$ $s_\mu = I_p$
Mean lifetime	$2.19703(4) \times 10^{-6}$ sec

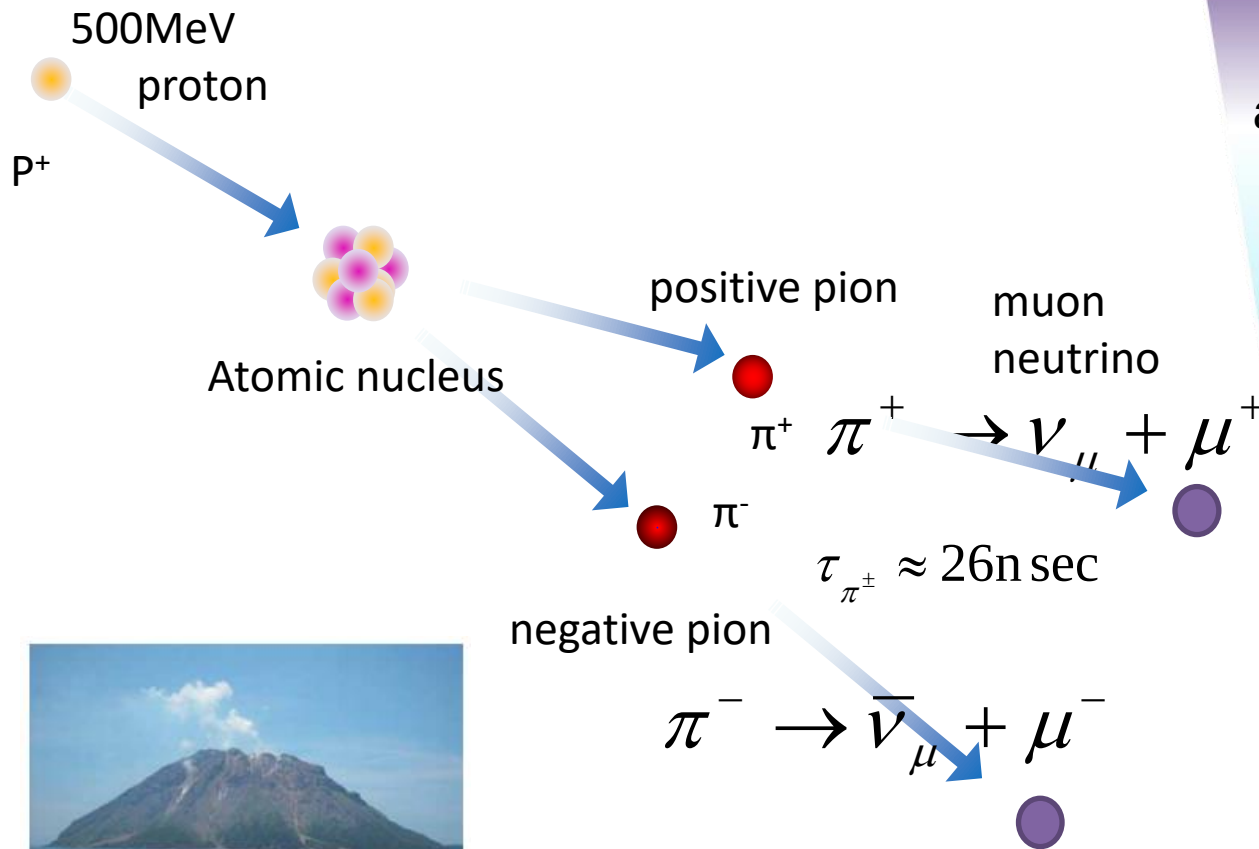
$$m_\mu \approx \frac{1}{9} m_p \approx 200 m_e$$

$$m_p > m_\mu \gg m_e$$

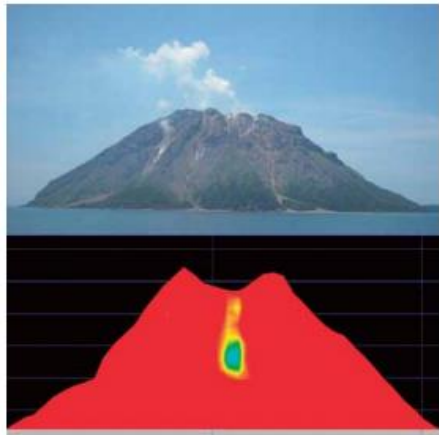
$$m_\mu \approx \frac{1}{9} m_p \approx 200 m_e$$



How to get the positive-muon ?

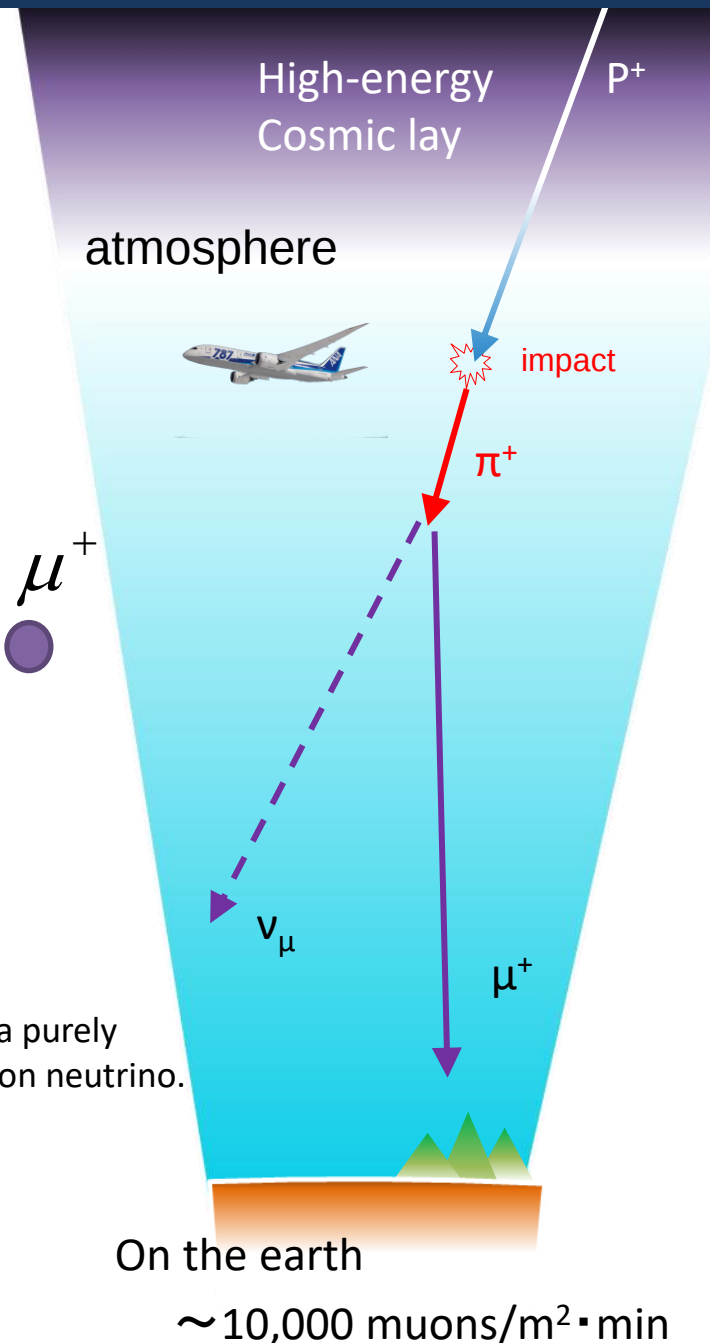


The primary decay mode of a pion is a purely leptonic decay into a muon and a muon neutrino.

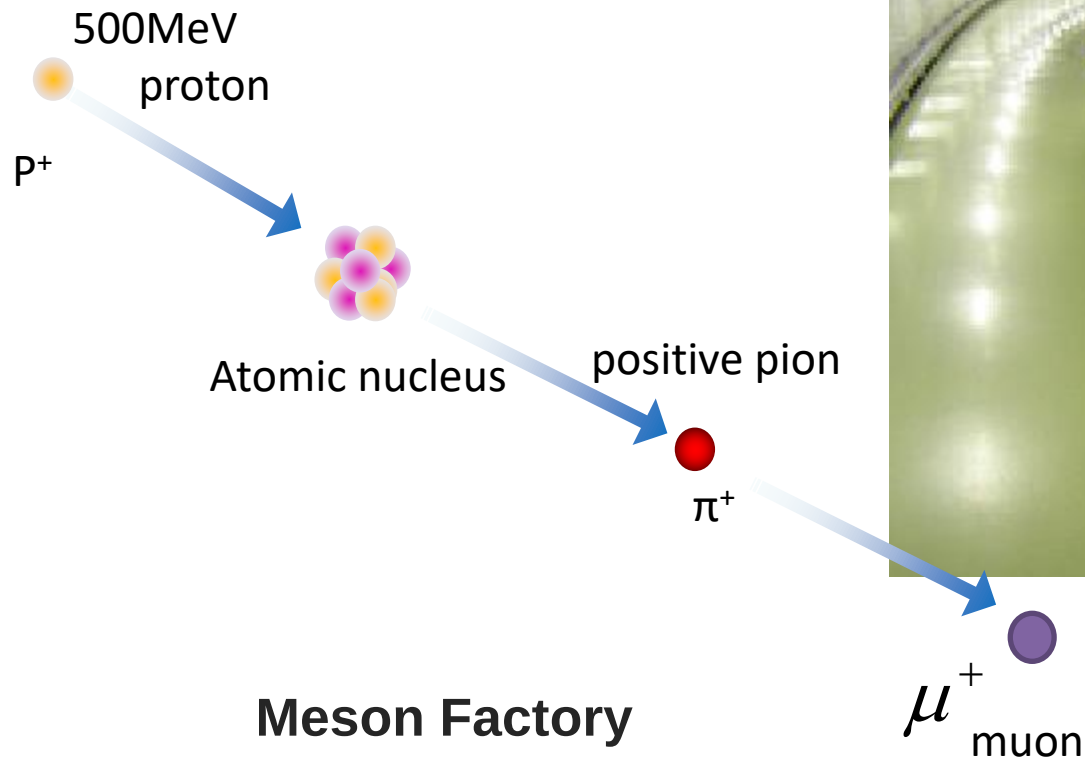


Magma image in volcano by muon

H.Tanaka, Butsuri (in Japanese) 65 (2010) pp. 70.



How to create the positive-muon ?

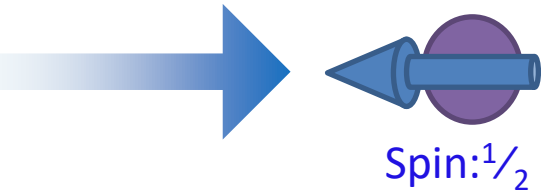


Japan Proton Accelerator Research Complex

20 muons/ ($\phi 3\text{mm spot}$) $\cdot \text{sec}$

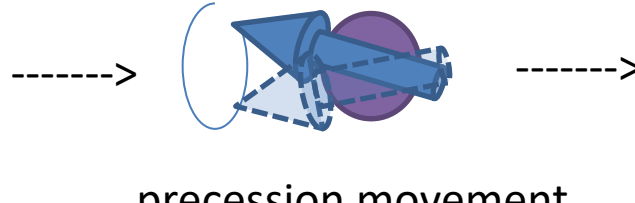
$\sim 2,000,000$ muons/ $\text{m}^2 \cdot \text{min}$

(Anti) muon μ^+



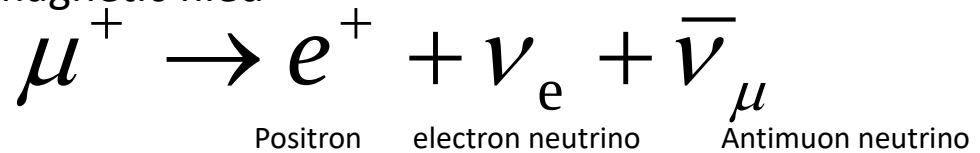
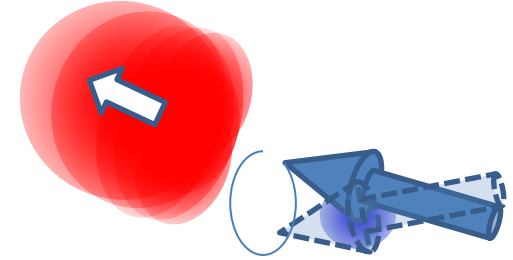
the created muon is 100% spin polarized

Muon spin spectroscopy : μ SR



precession movement
in the magnetic field

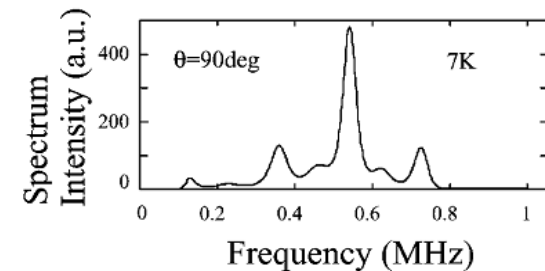
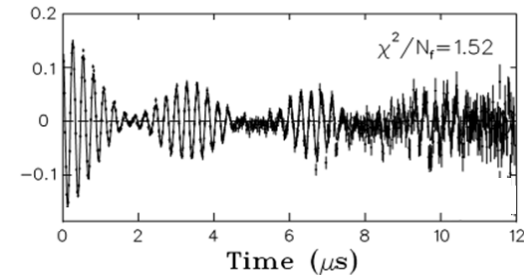
positron emission



Life time : $\tau \sim 2.2 \mu\text{sec}$

Larmor precession frequency: $f = \frac{\gamma}{2\pi} B$

gyromagnetic ratio of muon: $\frac{\gamma}{2\pi} = 135.53 \text{ MHz/T}$



μ SR muon spin rotation method

Gyromagnetic ratio : 135.53 MHz/T

We can measure the magnetic field around muon in materials

Effective Magnetic interaction =

Hyperfine interaction between muon spin and electron spin.

Muon



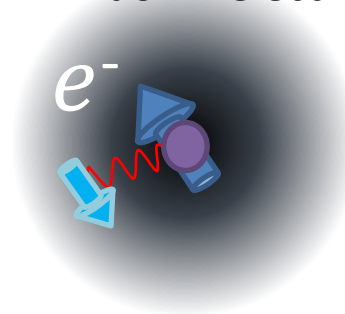
Hyperfine
interaction:

gyromagnetic
ratio:

135.53 MHz/T

Muonium

= muon + electron



4463 MHz

13940 MHz/T

We can also measure the occupation number of hydrogen isotope impurity in materials.

Muon or Muonium
Positive hydrogen ion(proton) or Hydrogen atom

Muon in the Si crystal

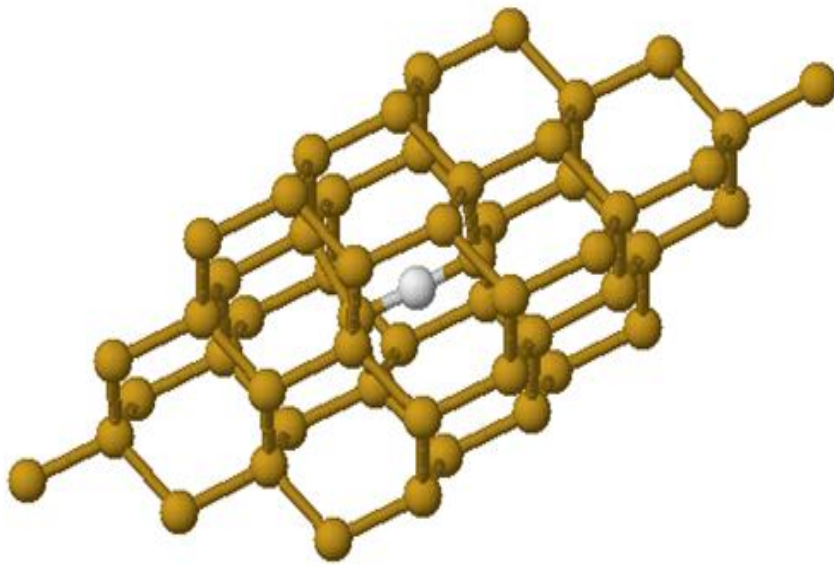
Experimental results of μ SR suggests two type of muon site.

hyperfine constant

BC-site (Bond center): **very low frequency** $\rightarrow$ shallow donors

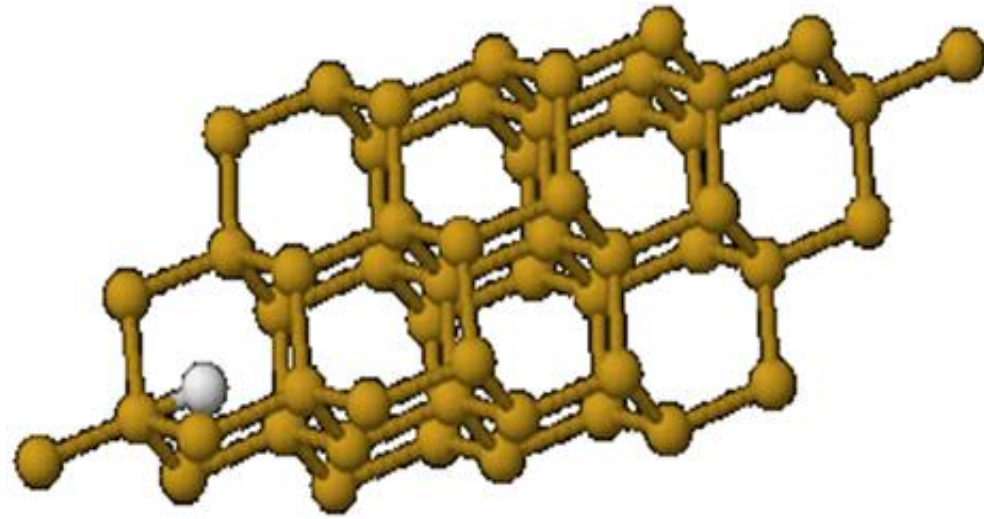
T-site (Cage center): **45 % of a free Muonium**, $A_0 = 4.46\text{GHz}$

S. F. J. Cox, Rep. Prog. Phys. 72 (2009) 116501.



BC-site

3x3x3
54 Si atoms



T-site

Muon in the Si crystal

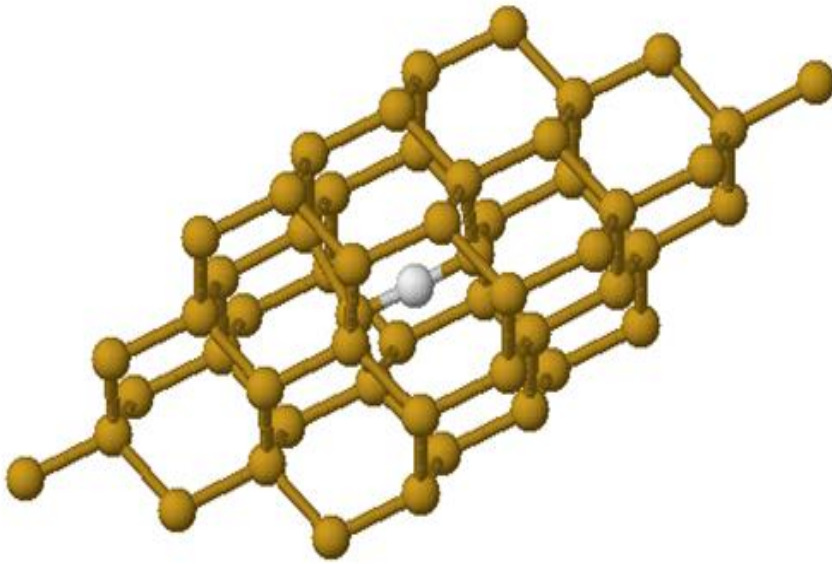
Experimental results of μ SR suggests two type of muon site.

hyperfine constant

BC-site (Bond center): very low frequency $\rightarrow$ shallow donors

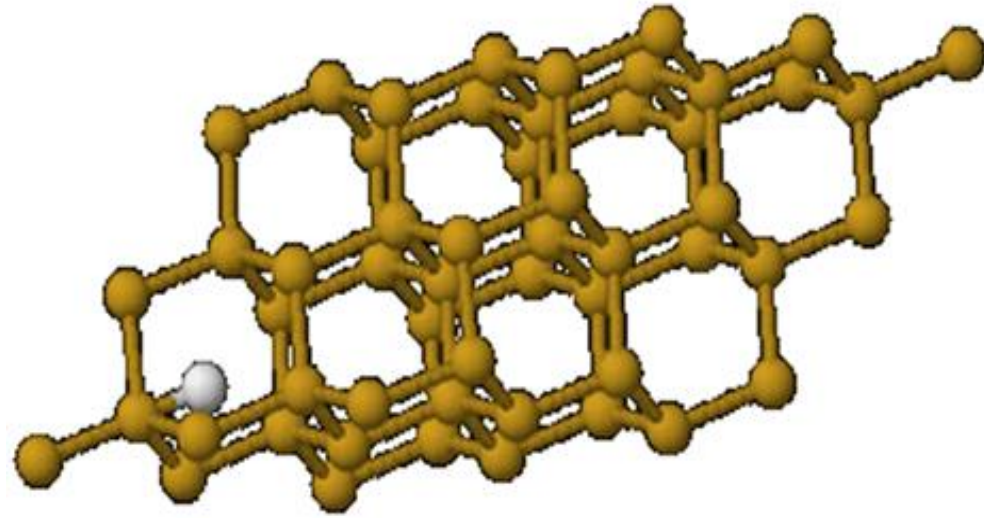
T-site (Cage center): 45 % of a free Muonium, $A_0 = 4.46\text{GHz}$

S. F. J. Cox, Rep. Prog. Phys. 72 (2009) 116501.



BC-site

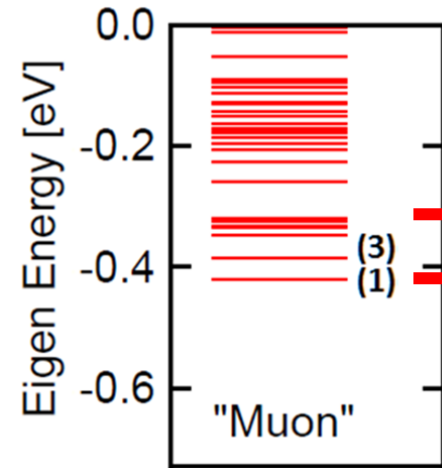
3x3x3
54 Si atoms



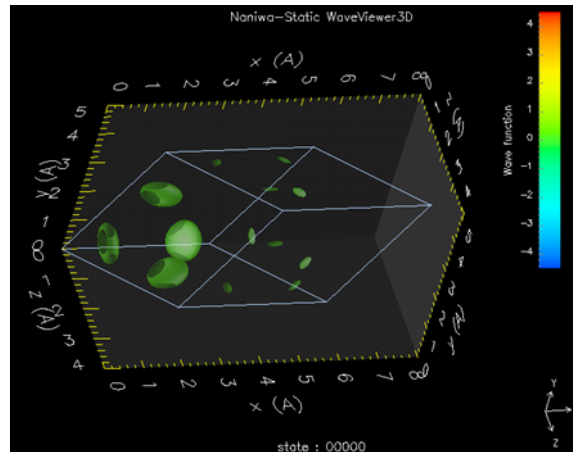
T-site

Naniwa results

diamond structure of Si



Ground state : BC-site

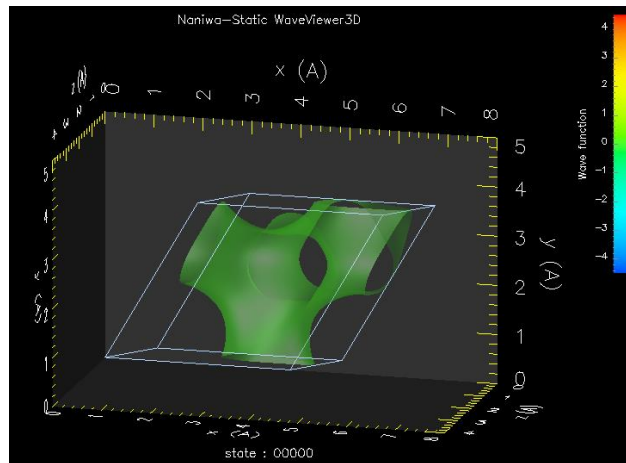


Calculated hyperfine constant

275 MHz

very low frequency

"shallow donor"

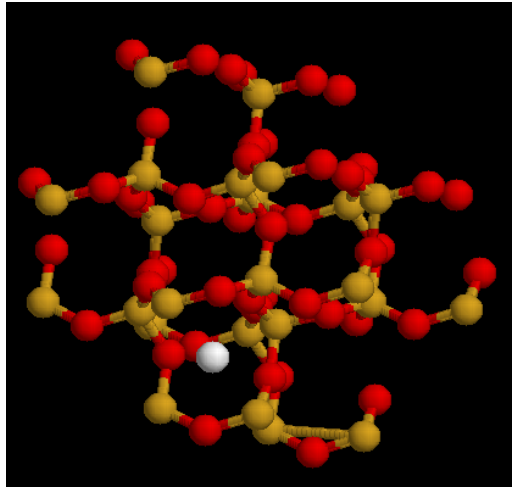


Excited state : T-site

1711 MHz

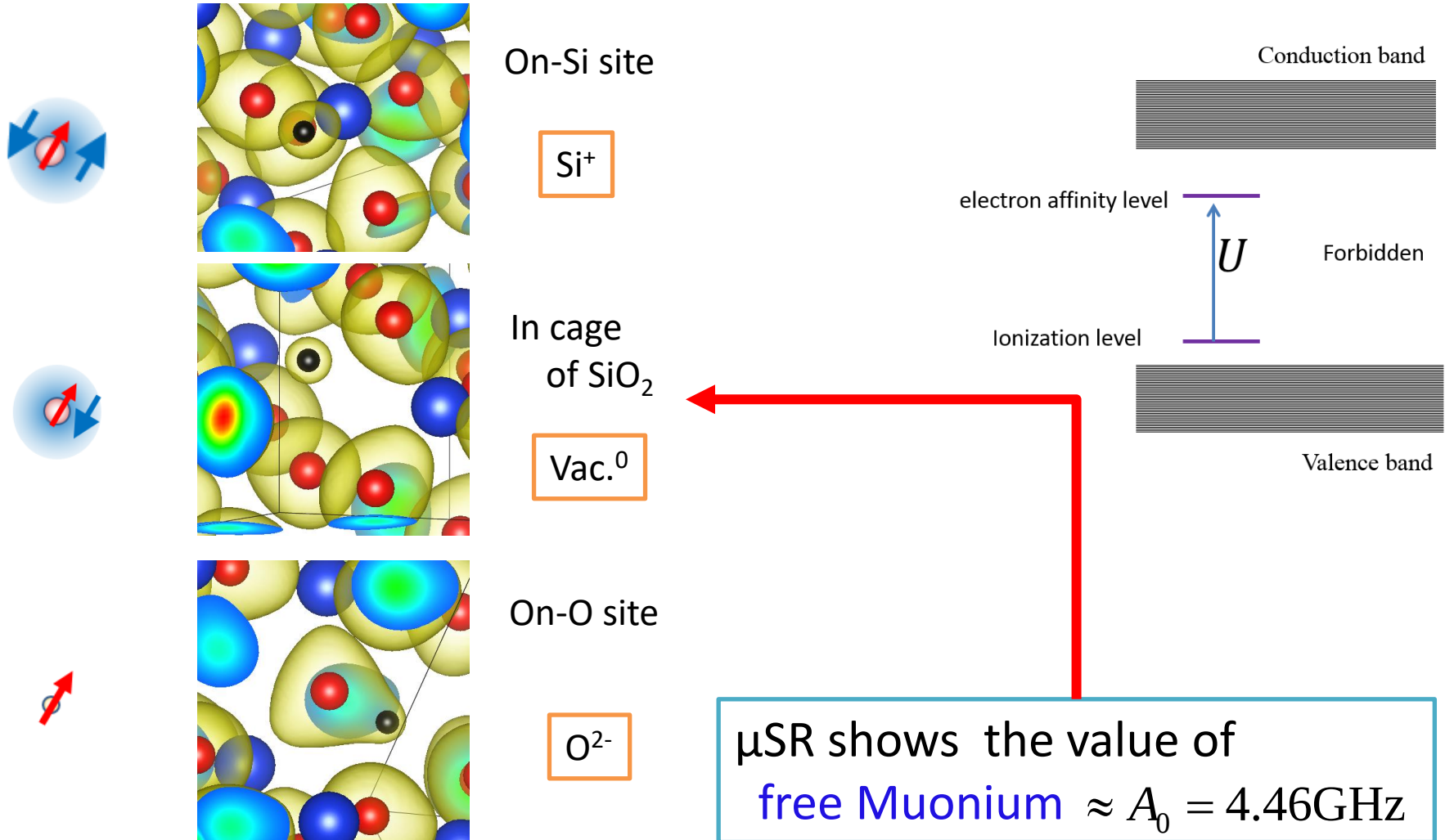
$\approx 45\%$ of A_0

Hydrogen isotope Muon in α -SiO₂ Quartz



In the case of insulator and semiconductor,
the charged state of impurity may be changed by its environment.

Hydrogen isotope in α -SiO₂ Quartz



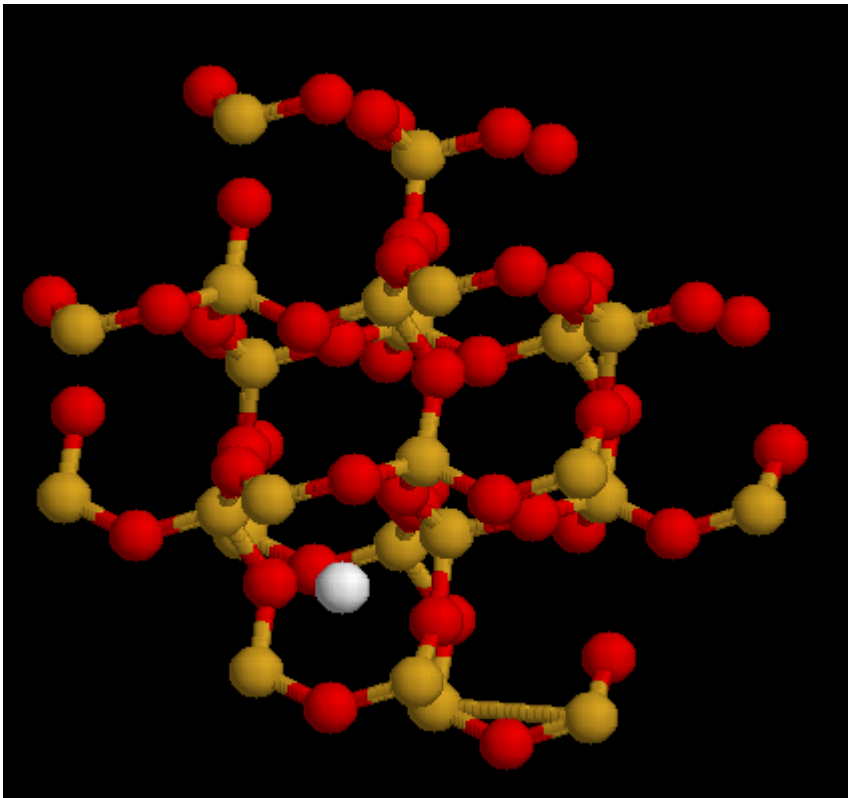
Hydrogen isotope in α -SiO₂ Quartz

2x2x2 cell

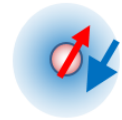
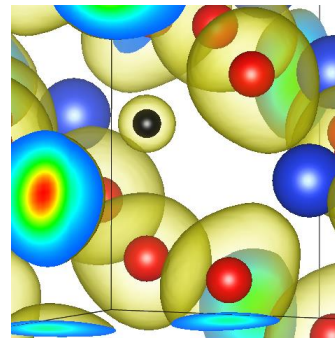
Si: 24 atoms

O: 48 atoms

H: 1 atom



4.2% impurity hydrogen



In-cage site

Previous study:

Binding Energy $\Delta E = +0.514\text{eV}$

$$\Delta E = E(\text{Mu}/\alpha\text{-SiO}_2) - (E(\text{Mu}) + E(\alpha\text{-SiO}_2))$$

Unstable ?

Significant lattice stress effects !?

Hydrogen isotope in α -SiO₂ Quartz

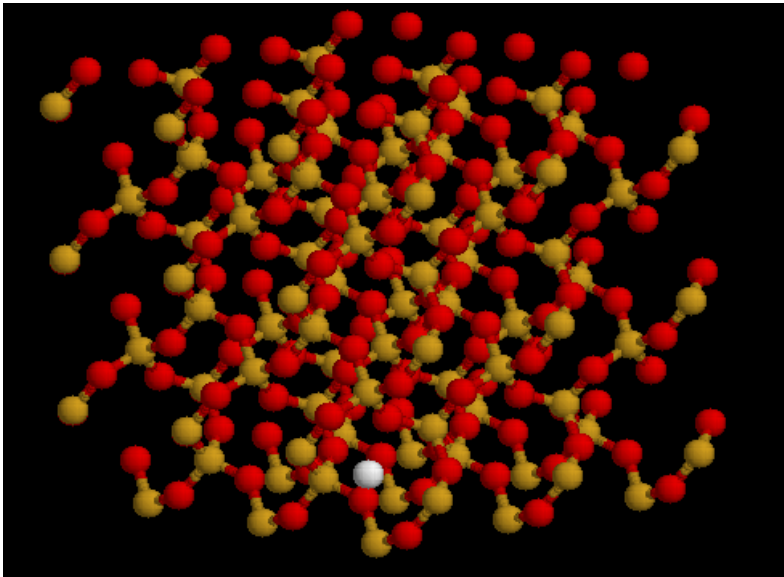
3x3x3 unit cells

Si: 81 atoms

O: 162 atoms

H: 1 atoms

1.2% hydrogen impurity

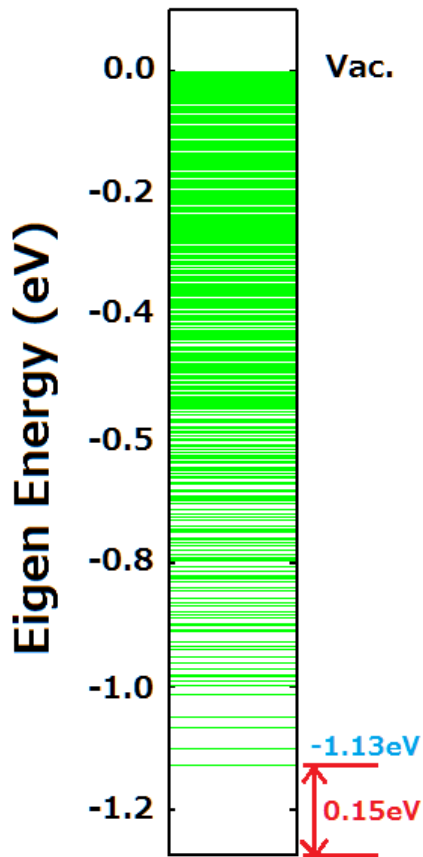


Energy: $\Delta E = -1.27\text{eV}$

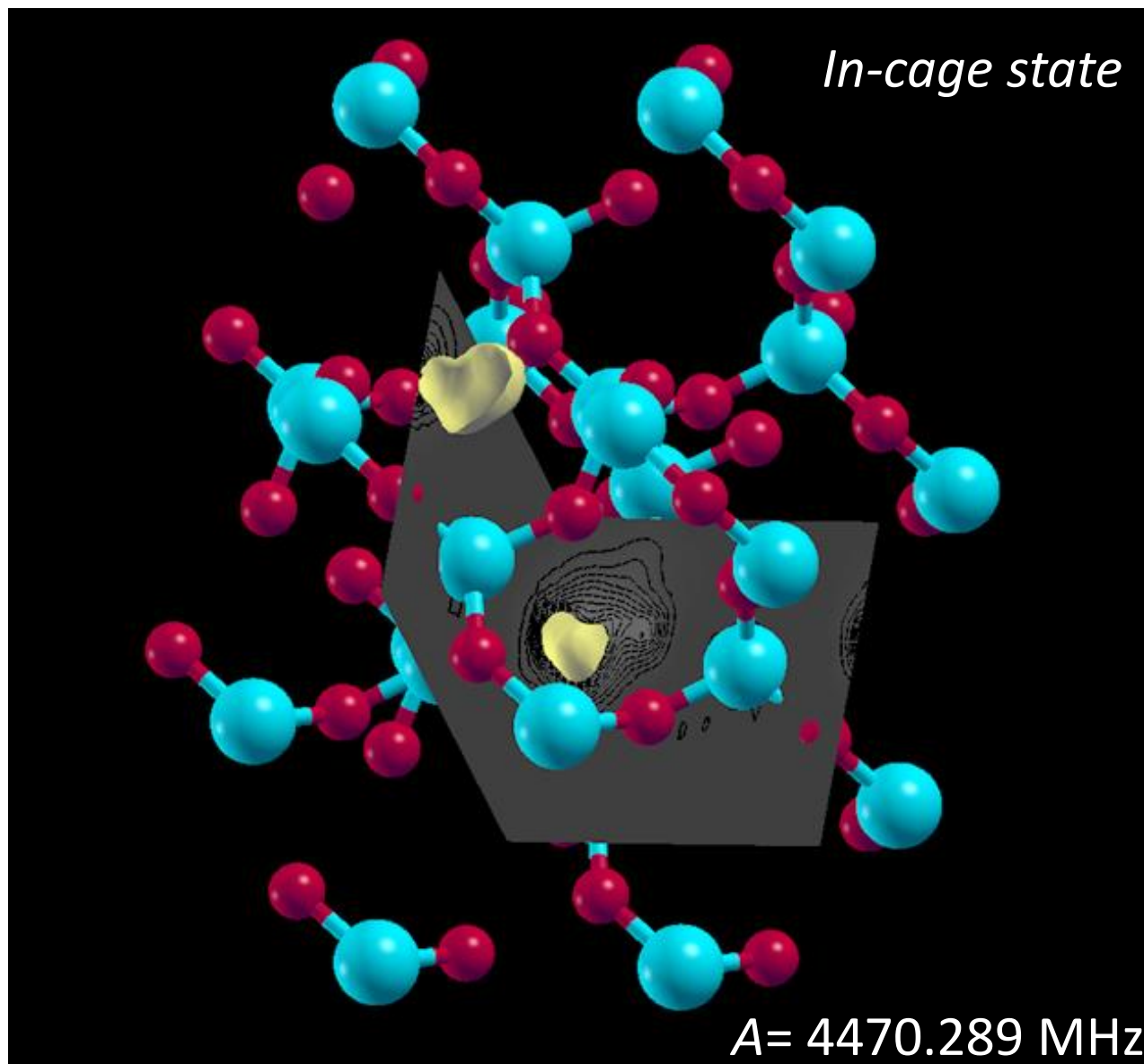
Stable !

Muonium in α -SiO₂ Quartz

Naniwa results

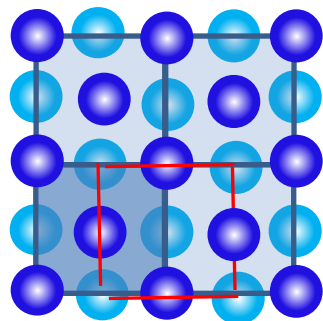
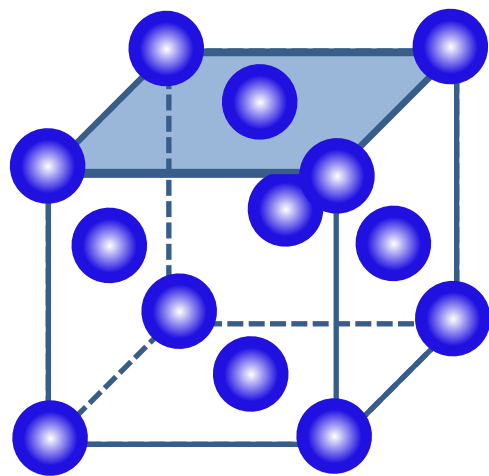


$$\Delta E = -1.13 \text{ eV}$$



Pd (001) surfaces

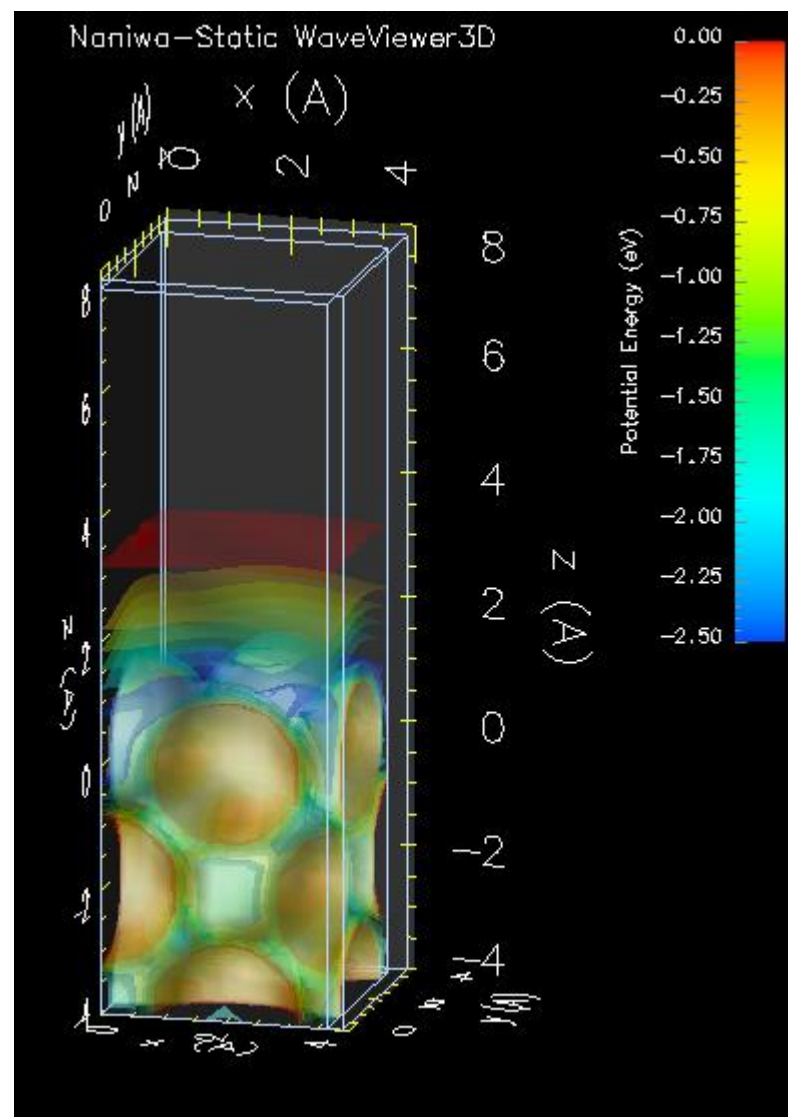
(001) surface



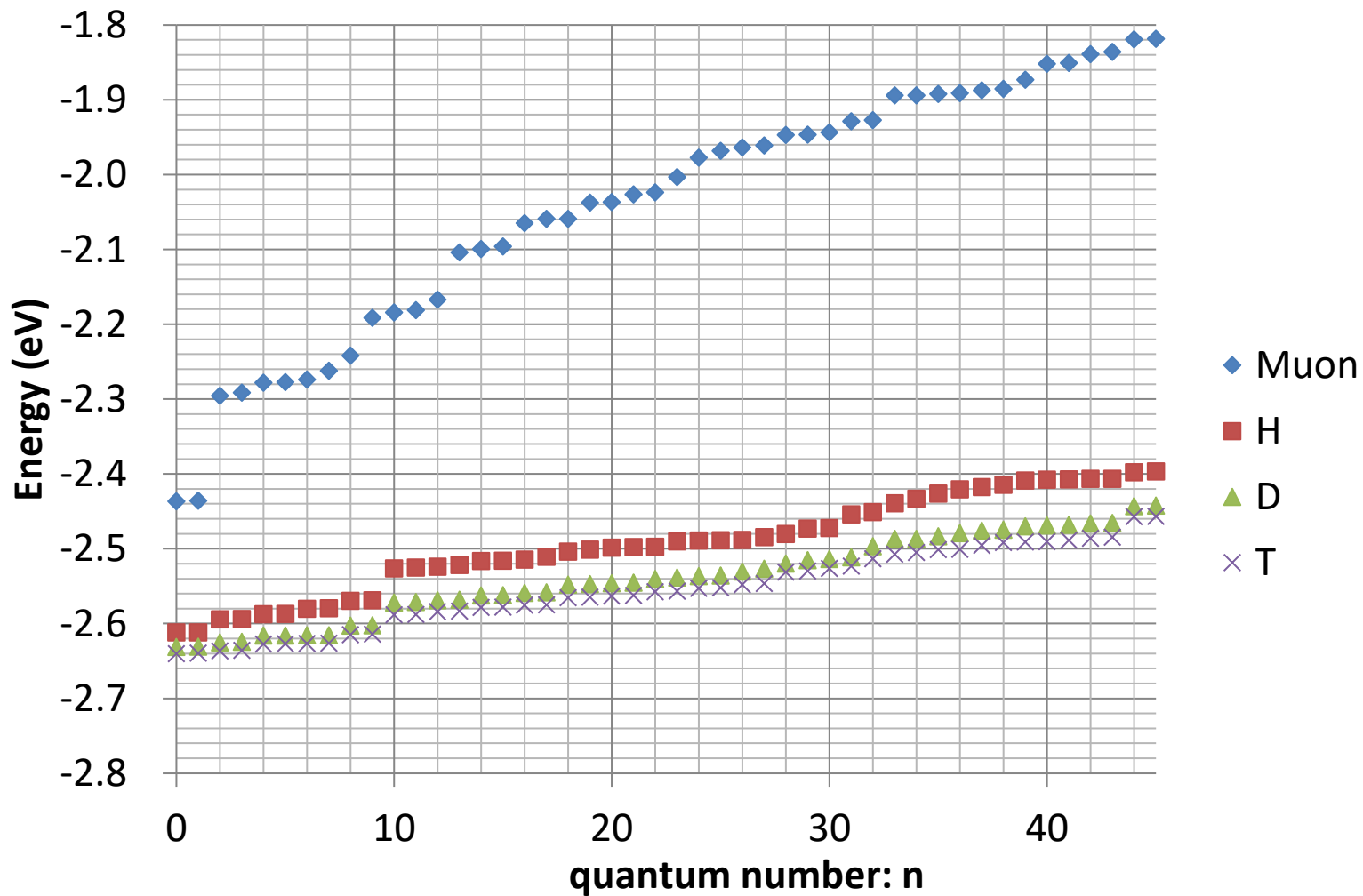
● First layer atom
● 2nd layer atom

face center cubic (FCC)

lattice constant: 3.99Å (calc.) ,
3.89Å (exp.)

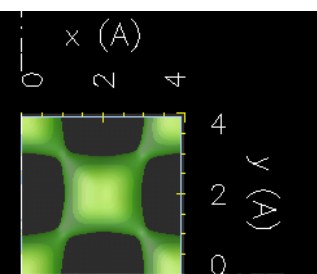


μ^+ , H, D, T on Pd (001) surfaces



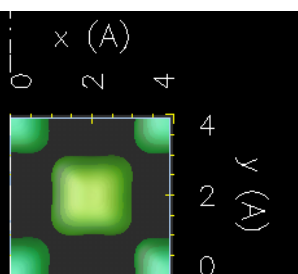
μ^+ on Pd (001) surfaces

Ground state



state : 00000

1st excited state



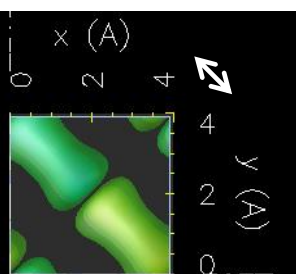
state : 00001

2nd excited state



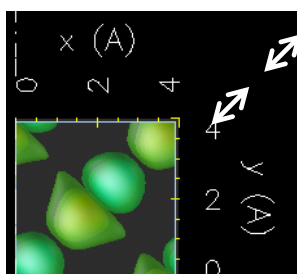
state : 00002

3rd excited state



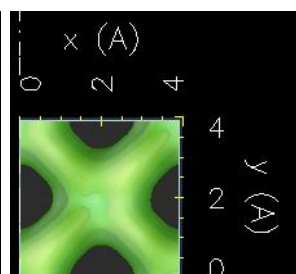
state : 00003

4th excited state

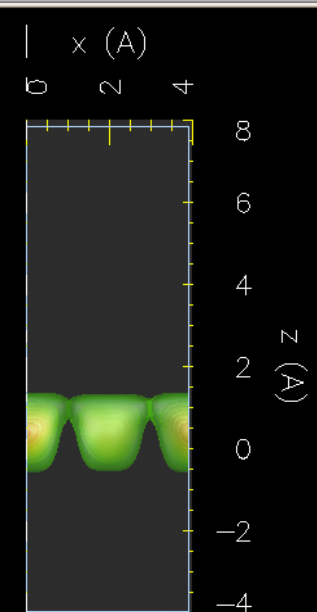


state : 00004

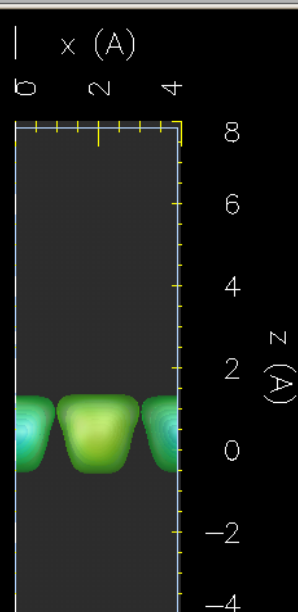
5th excited state



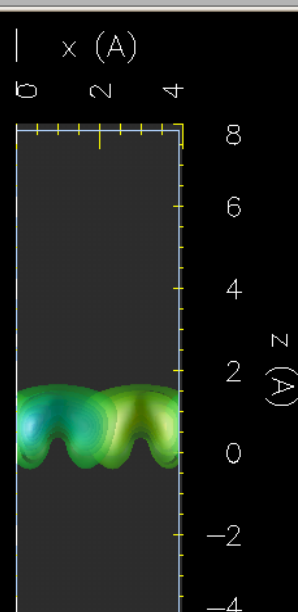
state : 00005



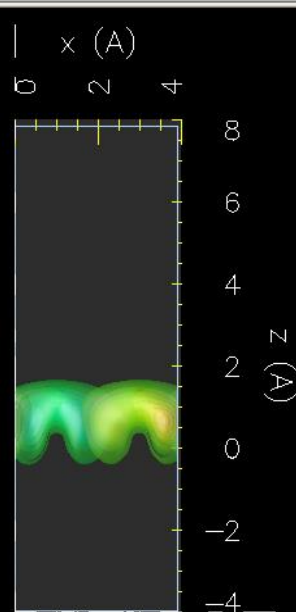
state : 00000



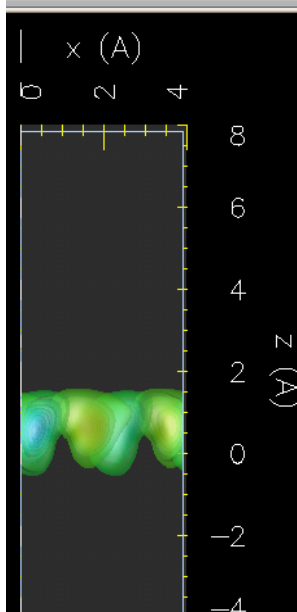
state : 00001



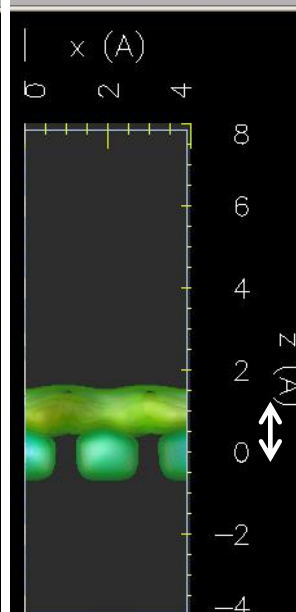
state : 00002



state : 00003



state : 00004



state : 00005

H on Pd (001) surfaces



Ground state

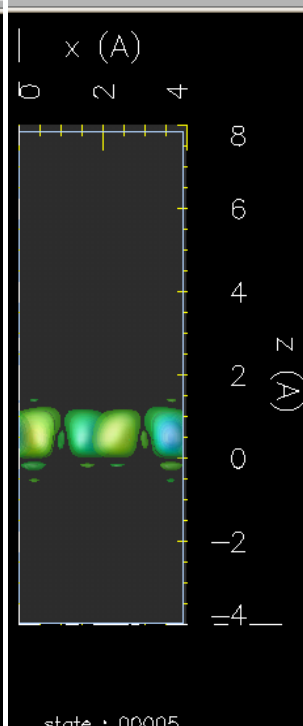
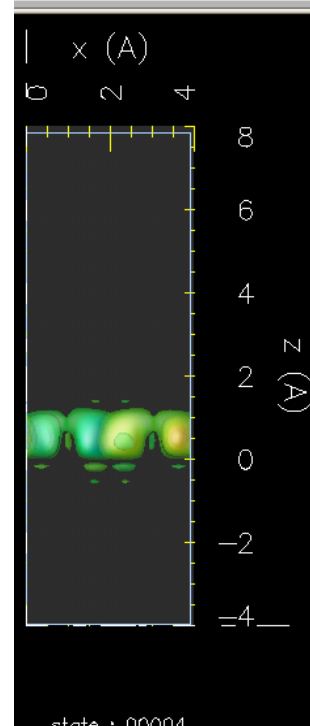
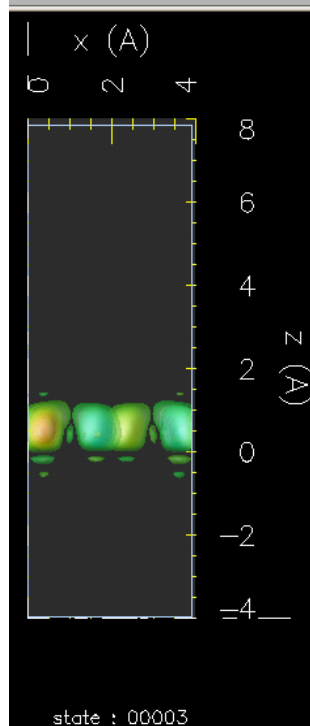
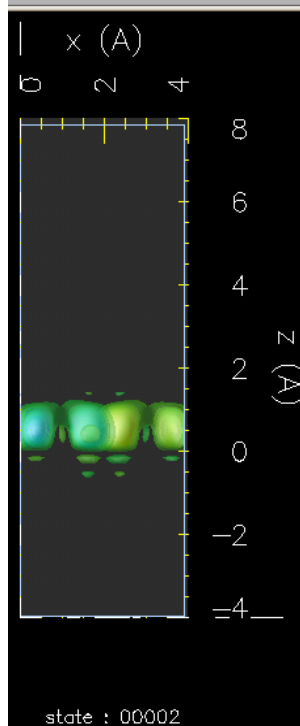
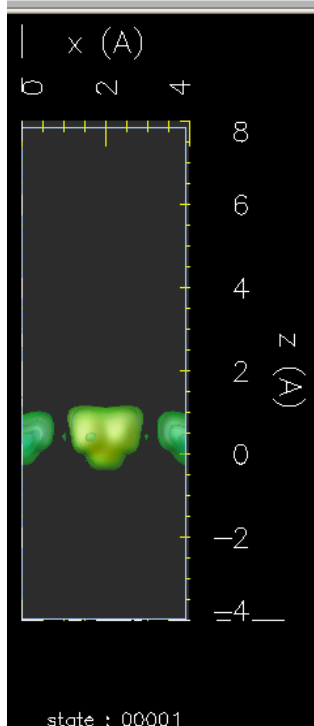
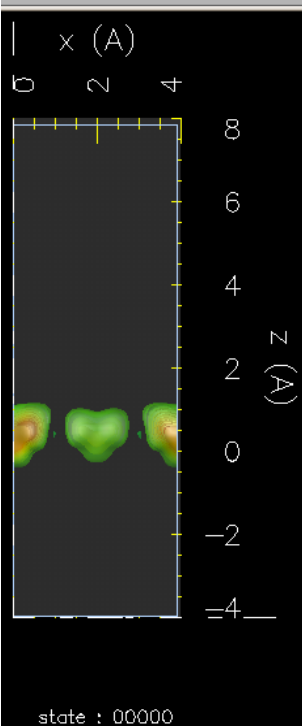
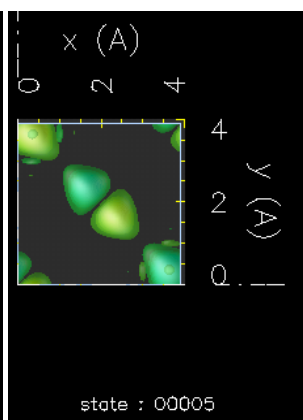
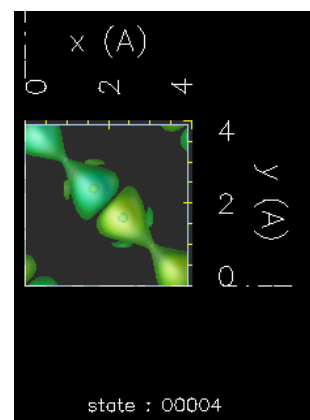
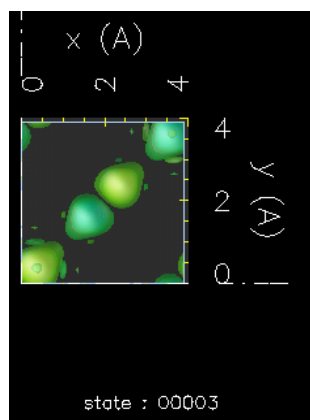
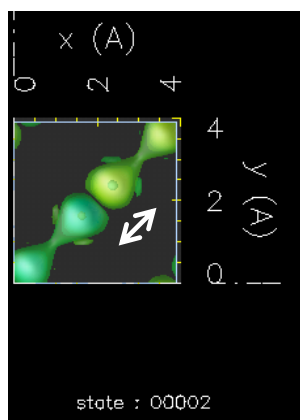
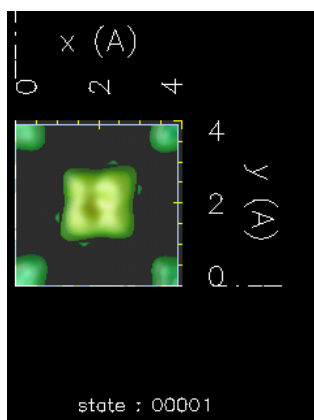
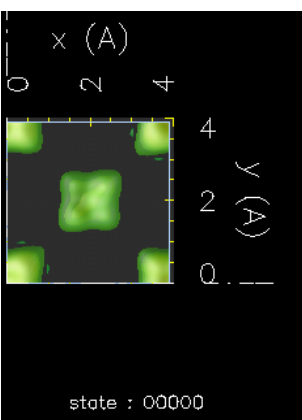
1st excited state

2nd excited state

3rd excited state

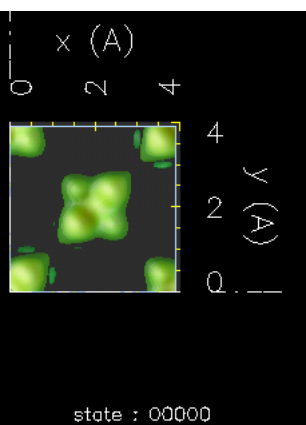
4th excited state

5th excited state

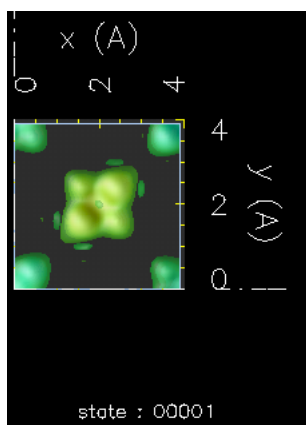


D on Pd (001) surfaces

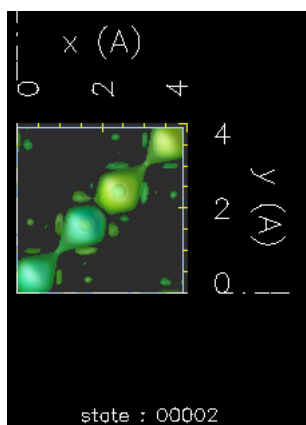
Ground state



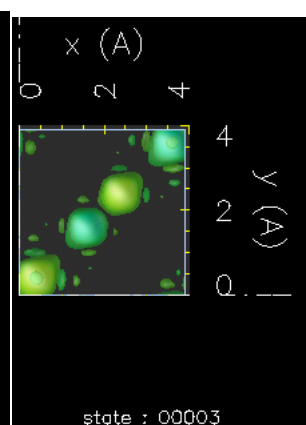
1st excited state



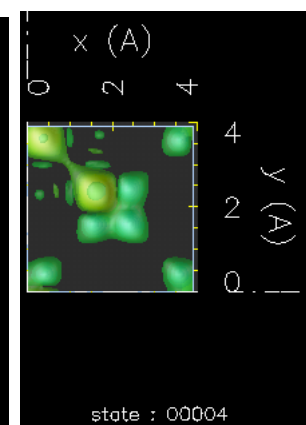
2nd excited state



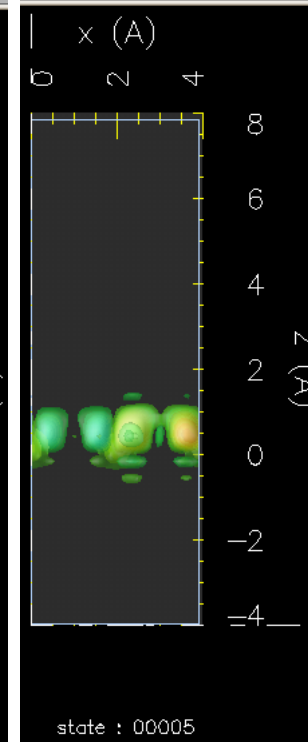
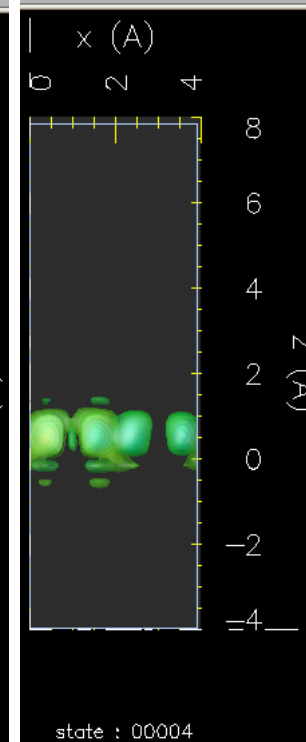
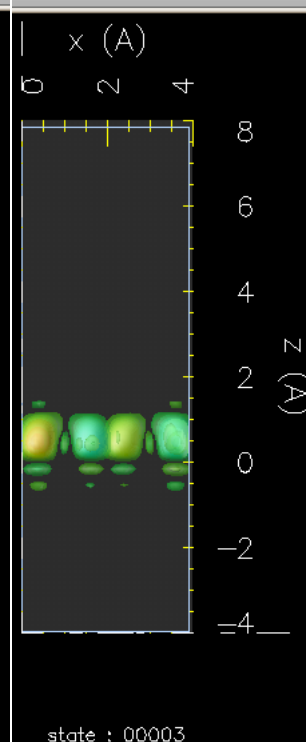
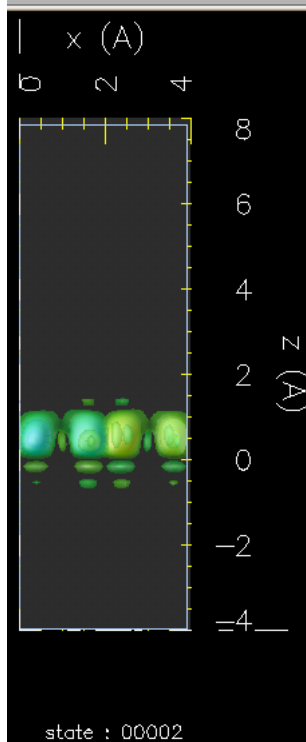
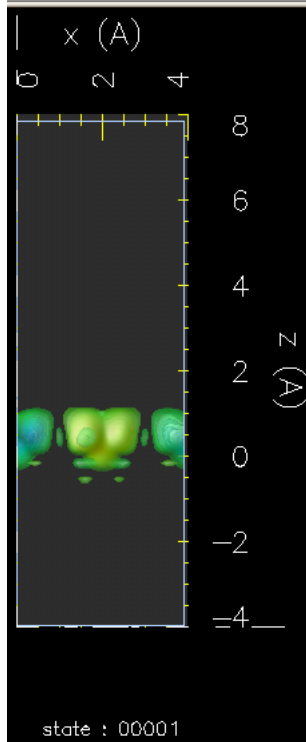
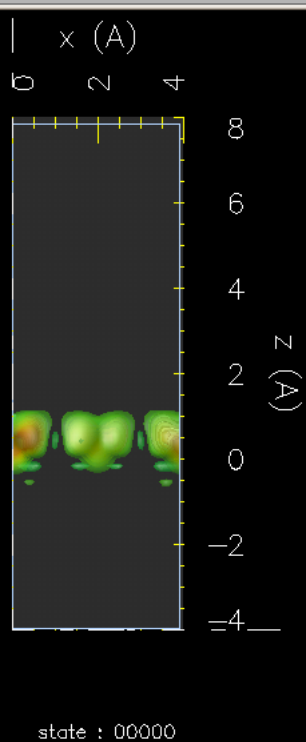
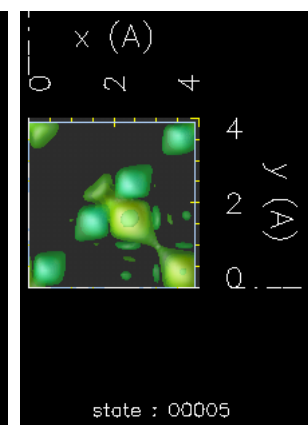
3rd excited state



4th excited state



5th excited state



T on Pd (001) surfaces

Ground state

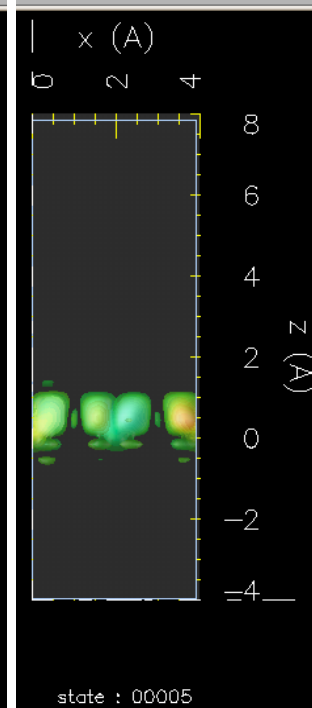
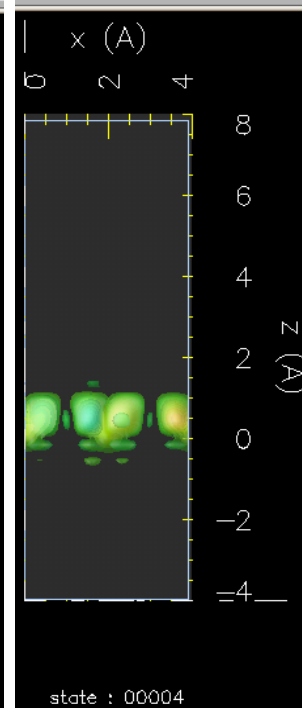
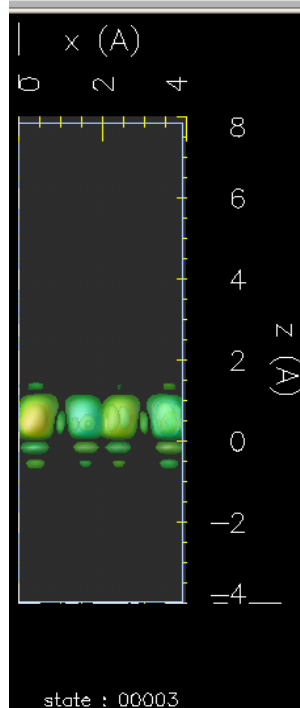
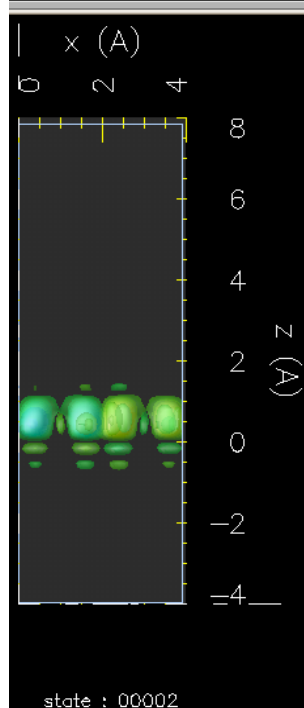
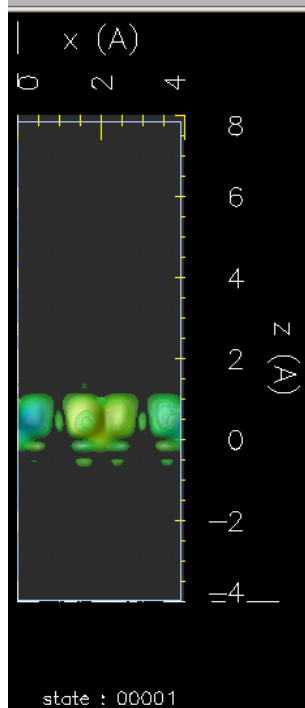
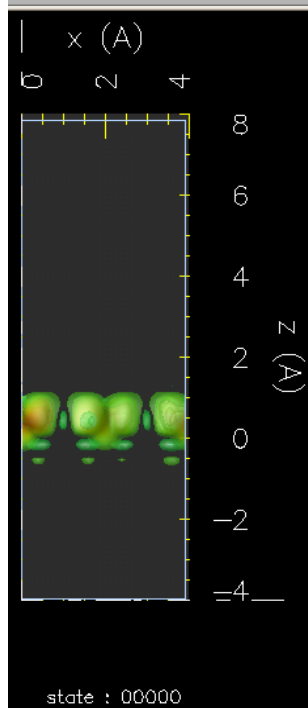
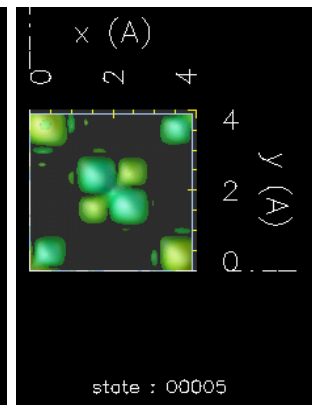
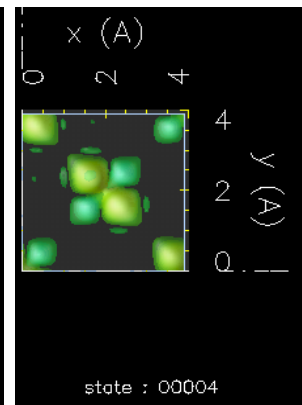
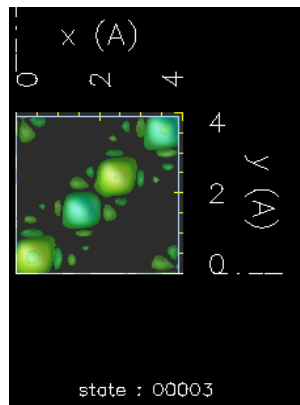
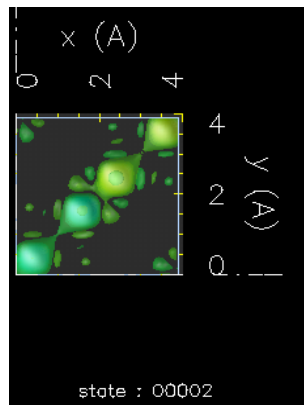
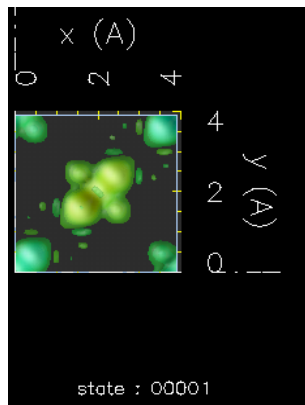
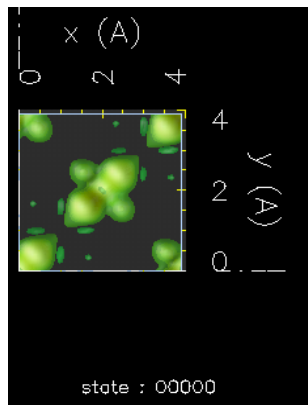
1st excited state

2nd excited state

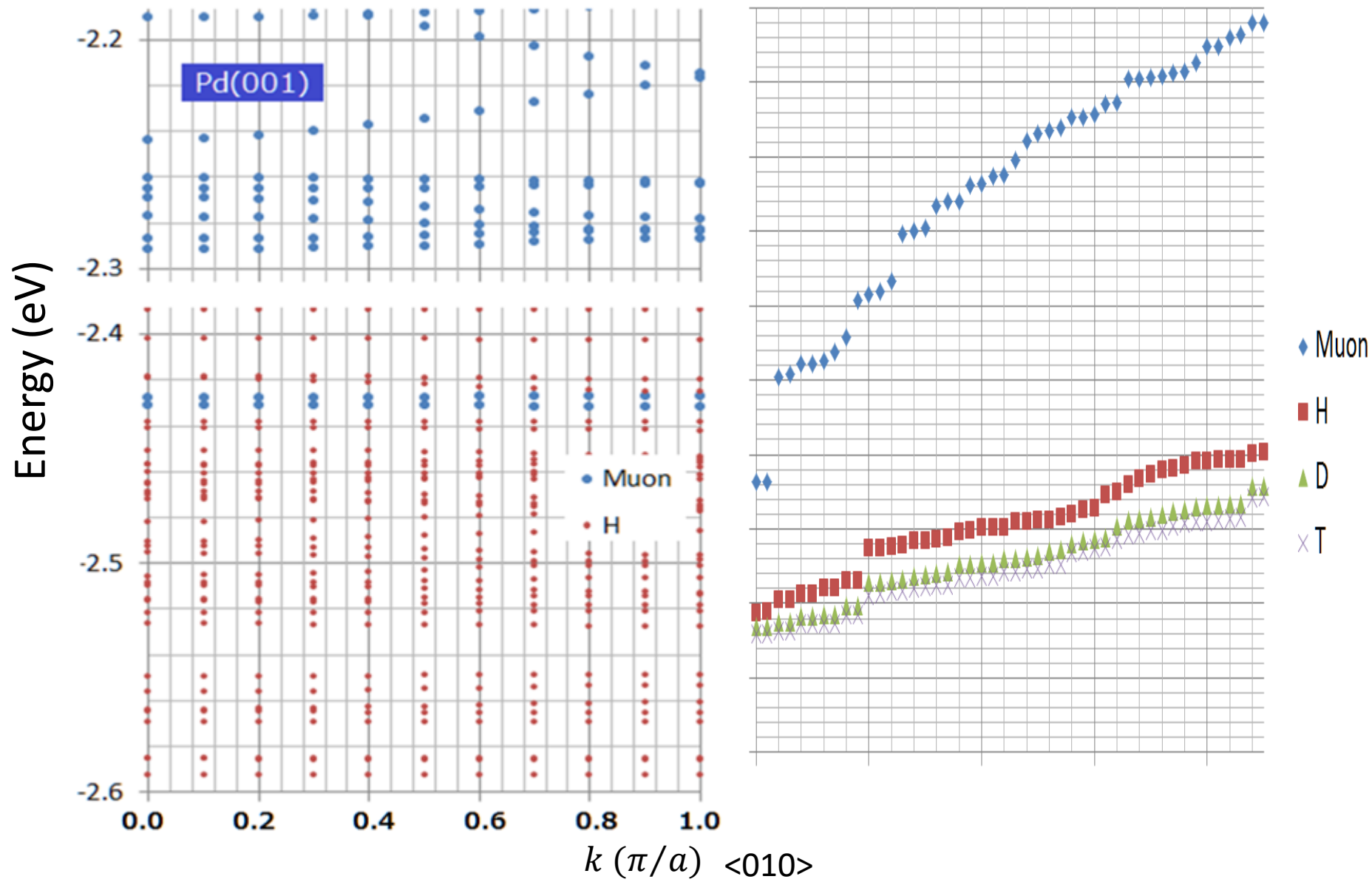
3rd excited state

4th excited state

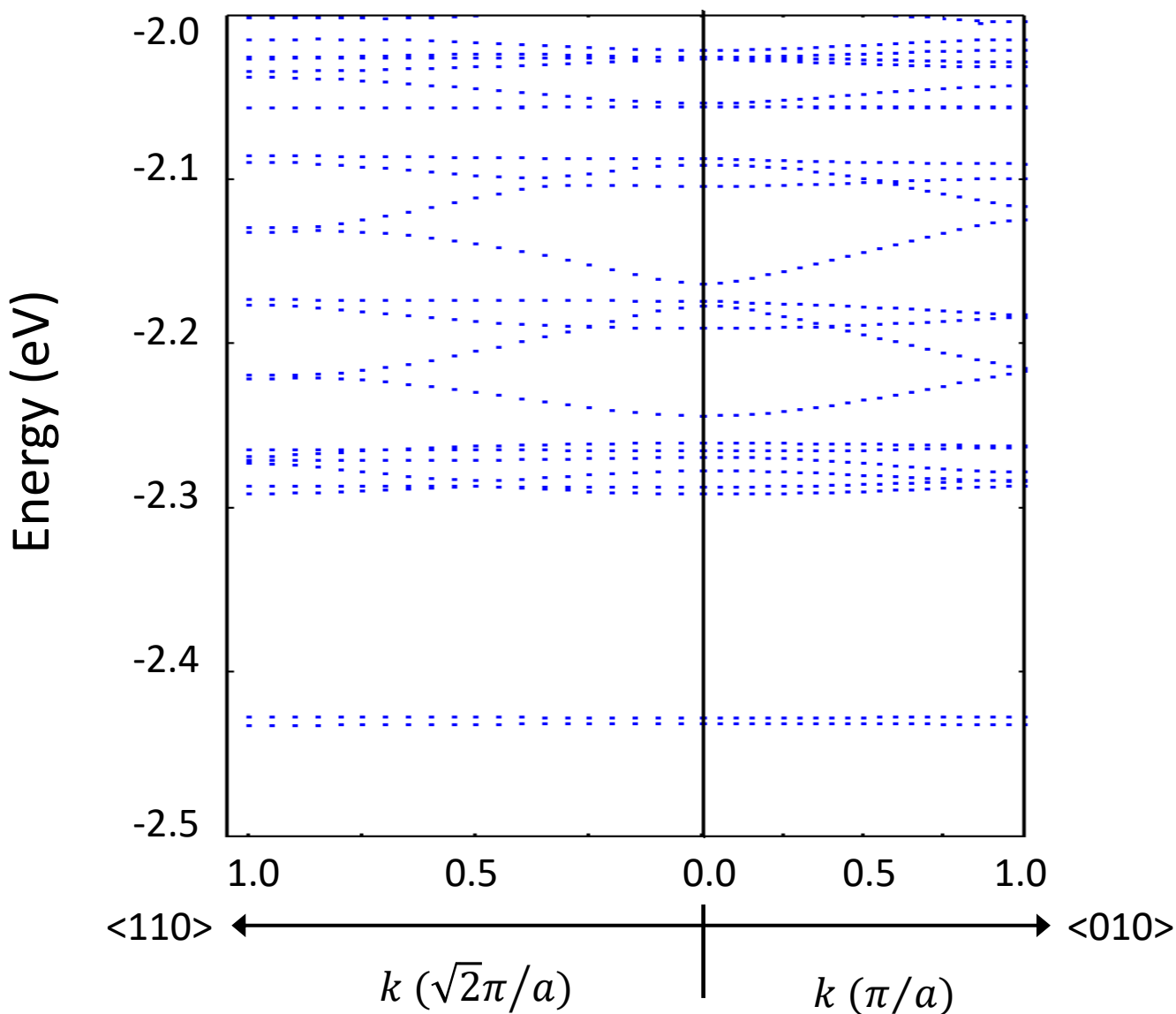
5th excited state



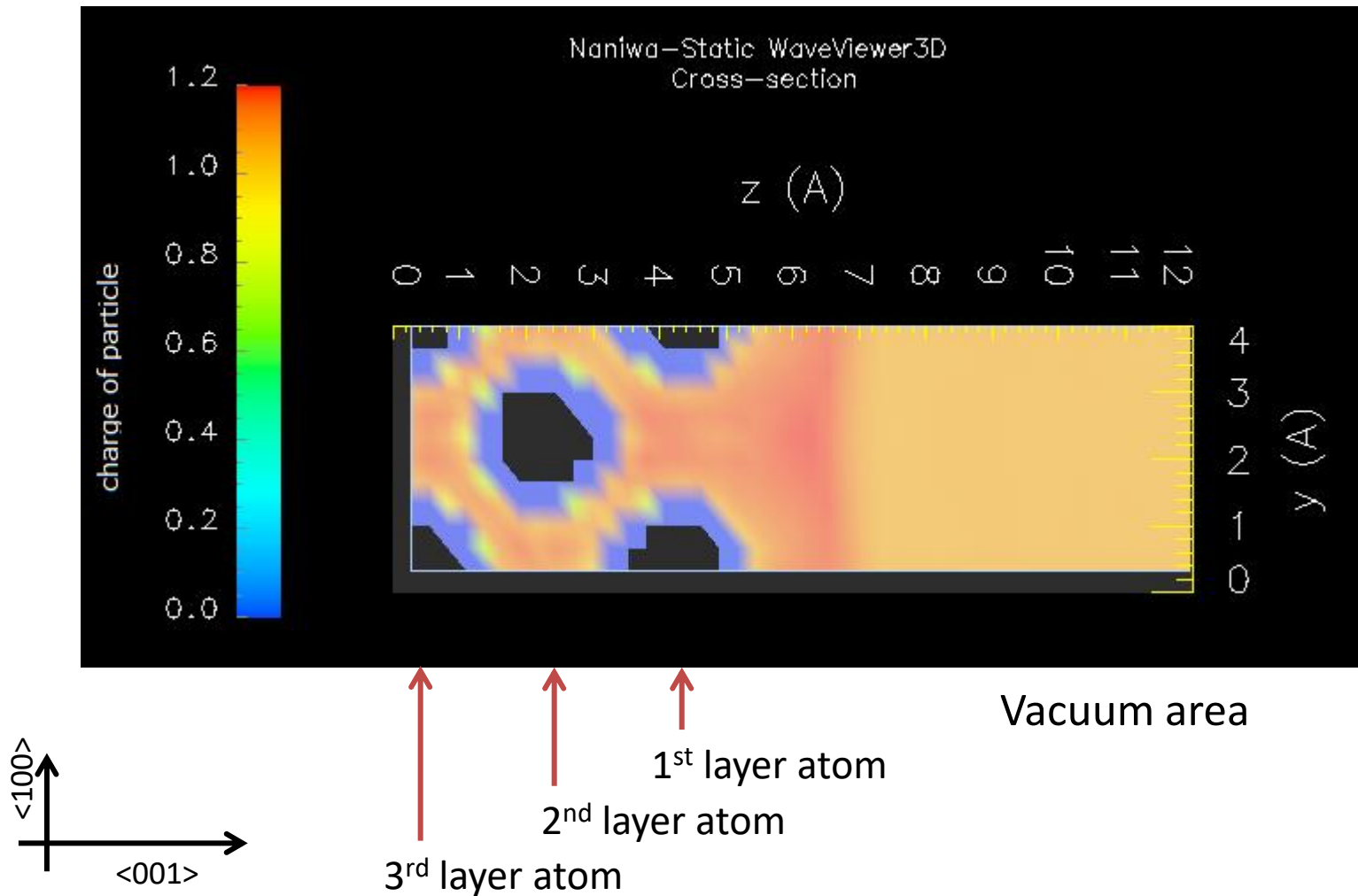
Energy Band (Wave vector dependence) of μ^+ & p^+ on Pd(001)



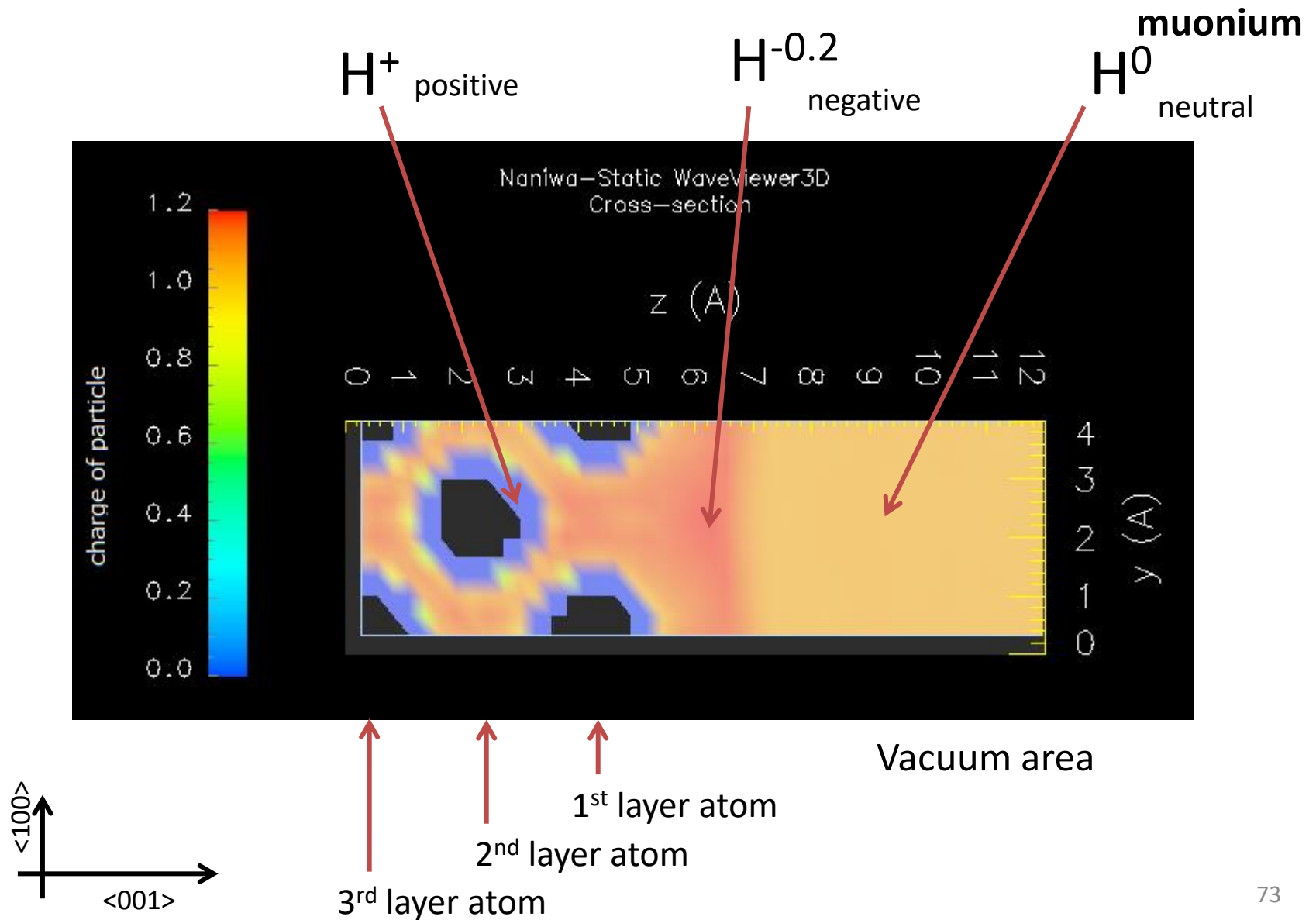
Energy Band (Wave vector dependence) of μ^+ on Pd(001)



Electron charge of target particle on Pd(001)



Charged states of target particle on Pd(001)



Naniwa codes

- We have been developing the **quantum** simulation code “Naniwa” for the **small mass atoms** on the solid surface, in the subsurface and bulk **without fitting parameters**.



Future Applications of Naniwa

Hydrogen related materials

- Hydrogen Fuel cell (FC) technology
- Hydrogen storage materials
- Hydrogen purification materials

Hydrogen bond ->

- Various chemical reactions in aqueous solution
--> biological material and its related reactions

Small mass atom related material

- Li : lithium-ion secondary battery
- Oxygen: cathode reaction of FC