Quantum simulation of atom motion in materials

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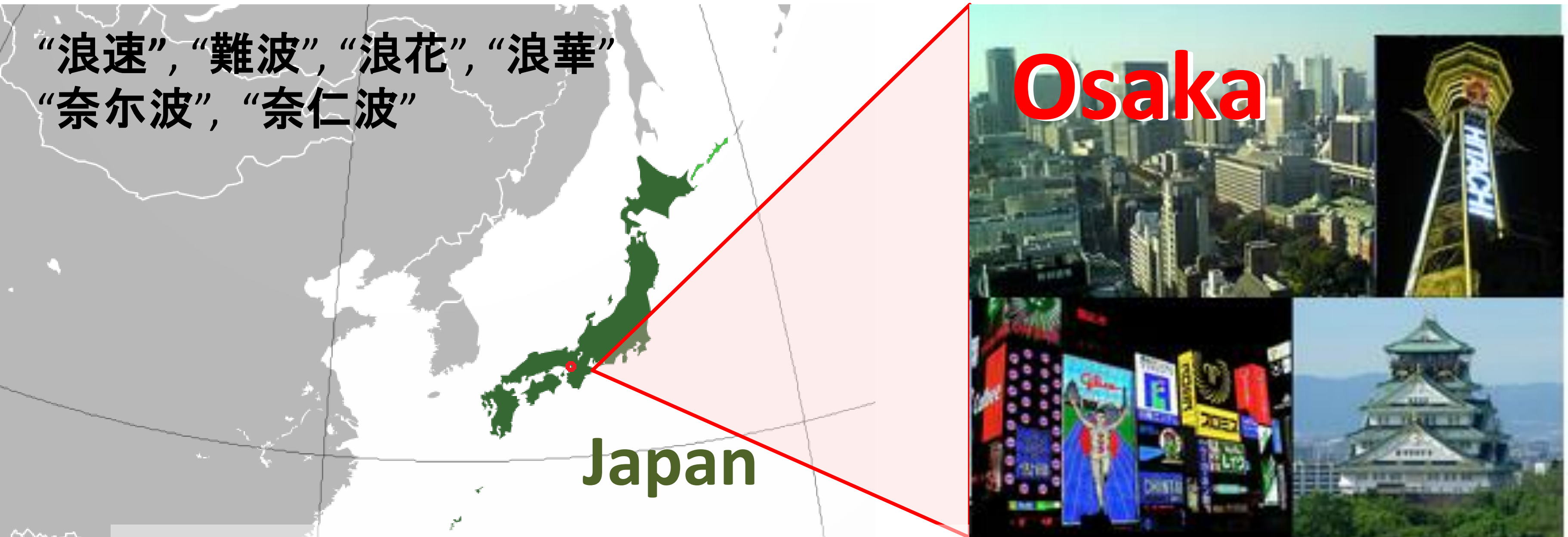
[B] Institute of Industrial Science (IIS), the University of Tokyo
[C] Graduate School of Engineering, Osaka University
[D] Osaka University

What is Naniwa ?

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

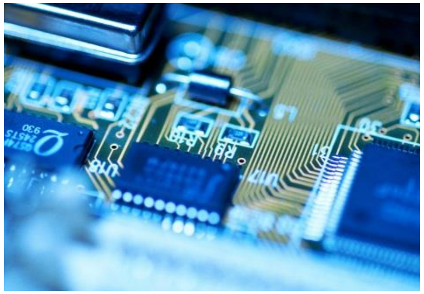


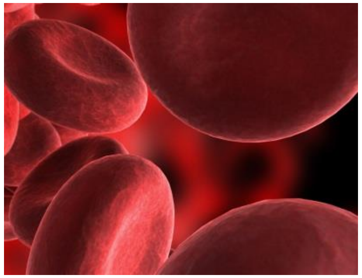
- **NANIWA** is the name of our simulation code.

浪速 Naniwa

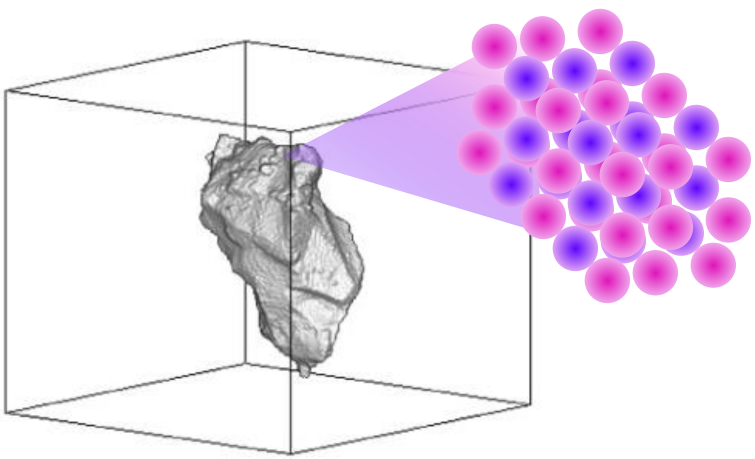
- The fast wave

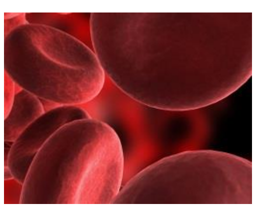
materials





Particles which construct the materials



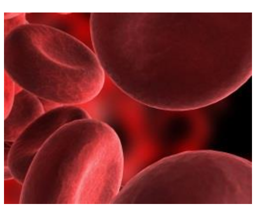


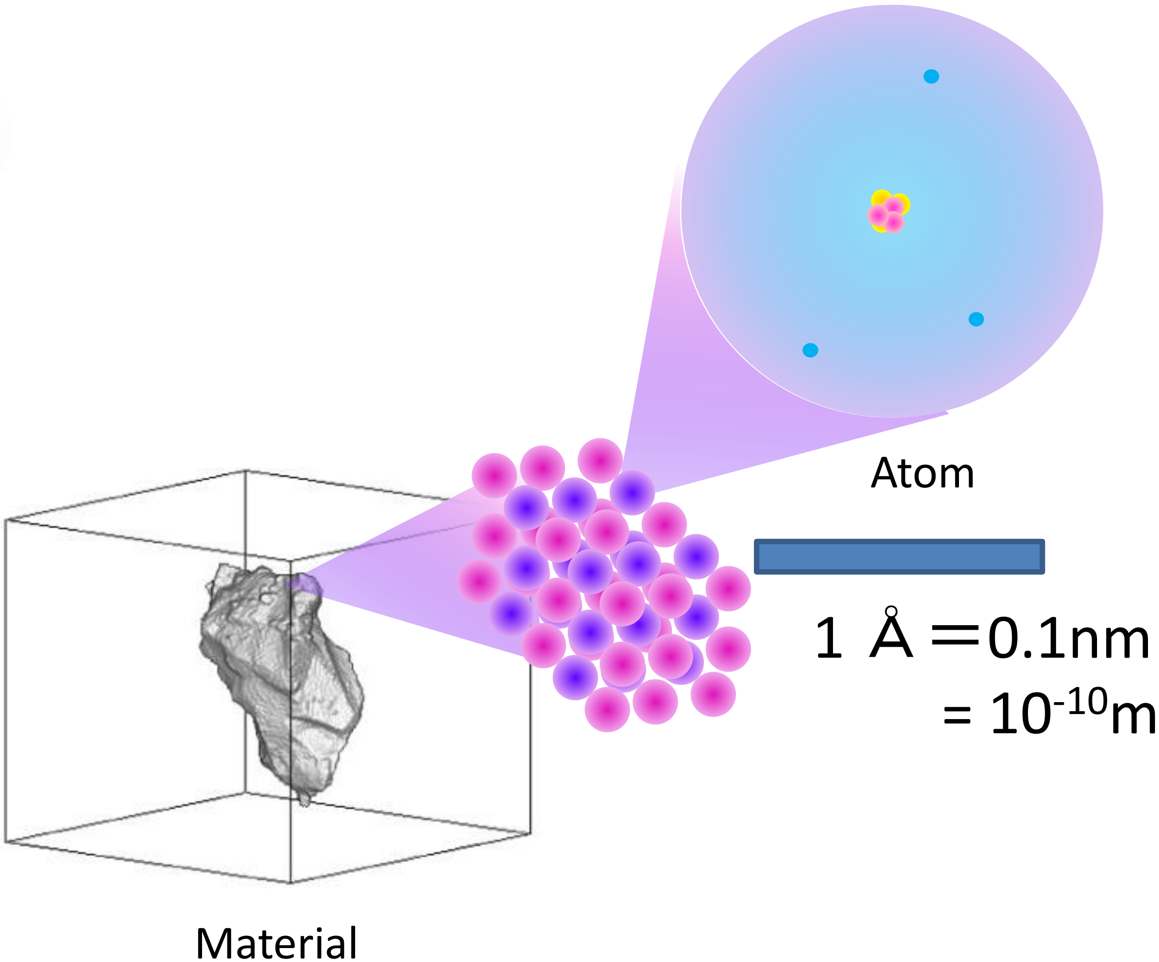
Material

Particles which construct the materials

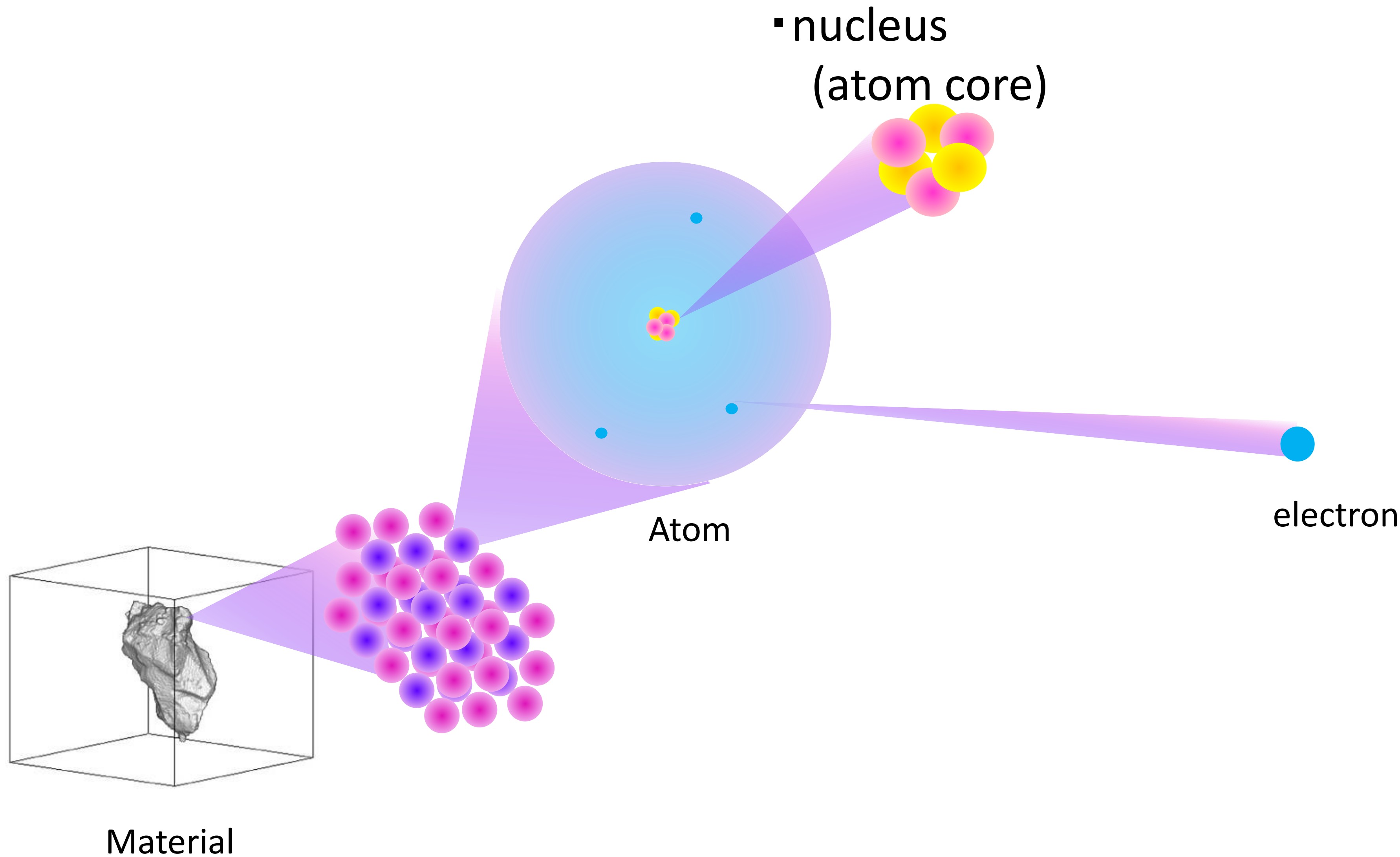




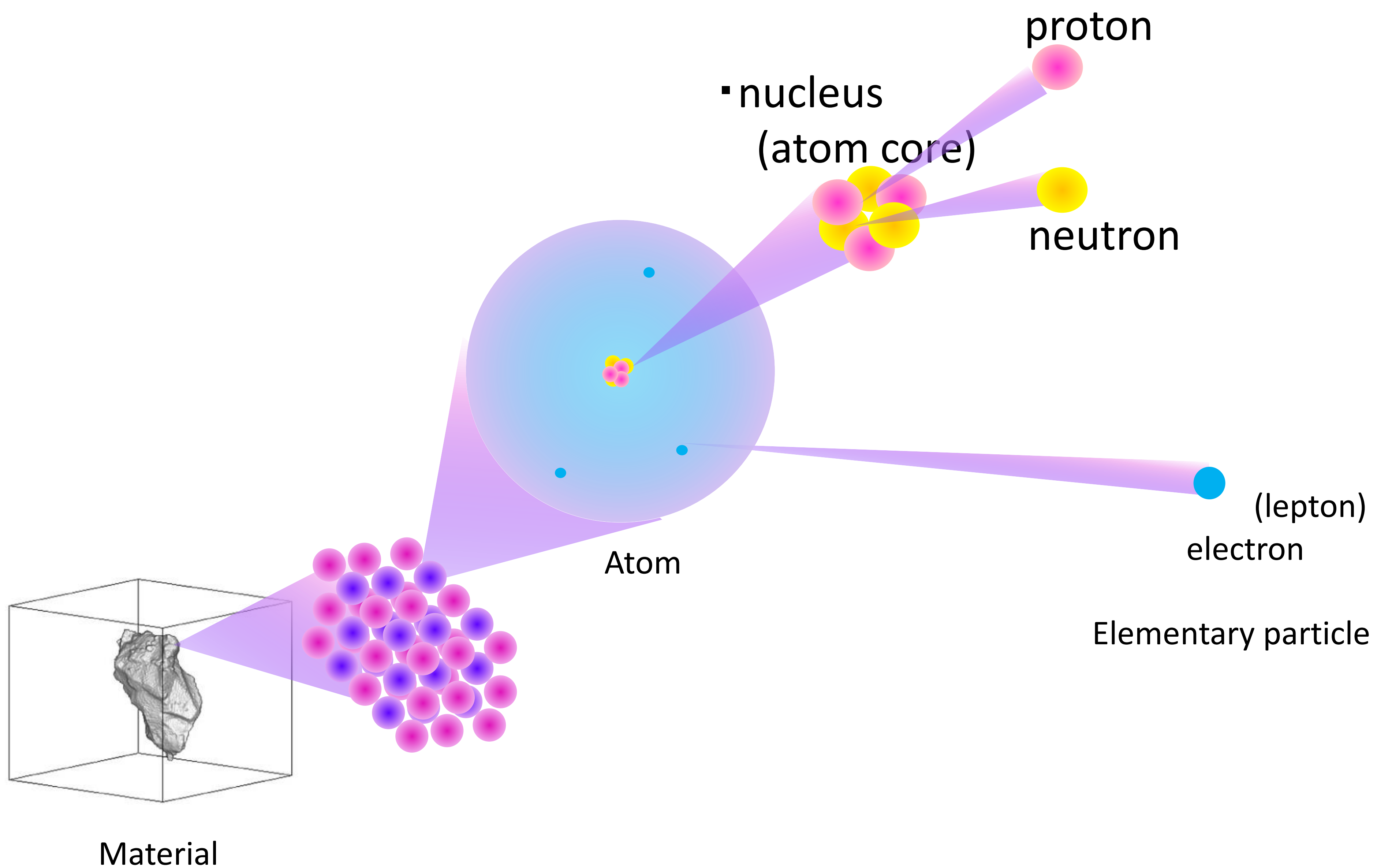




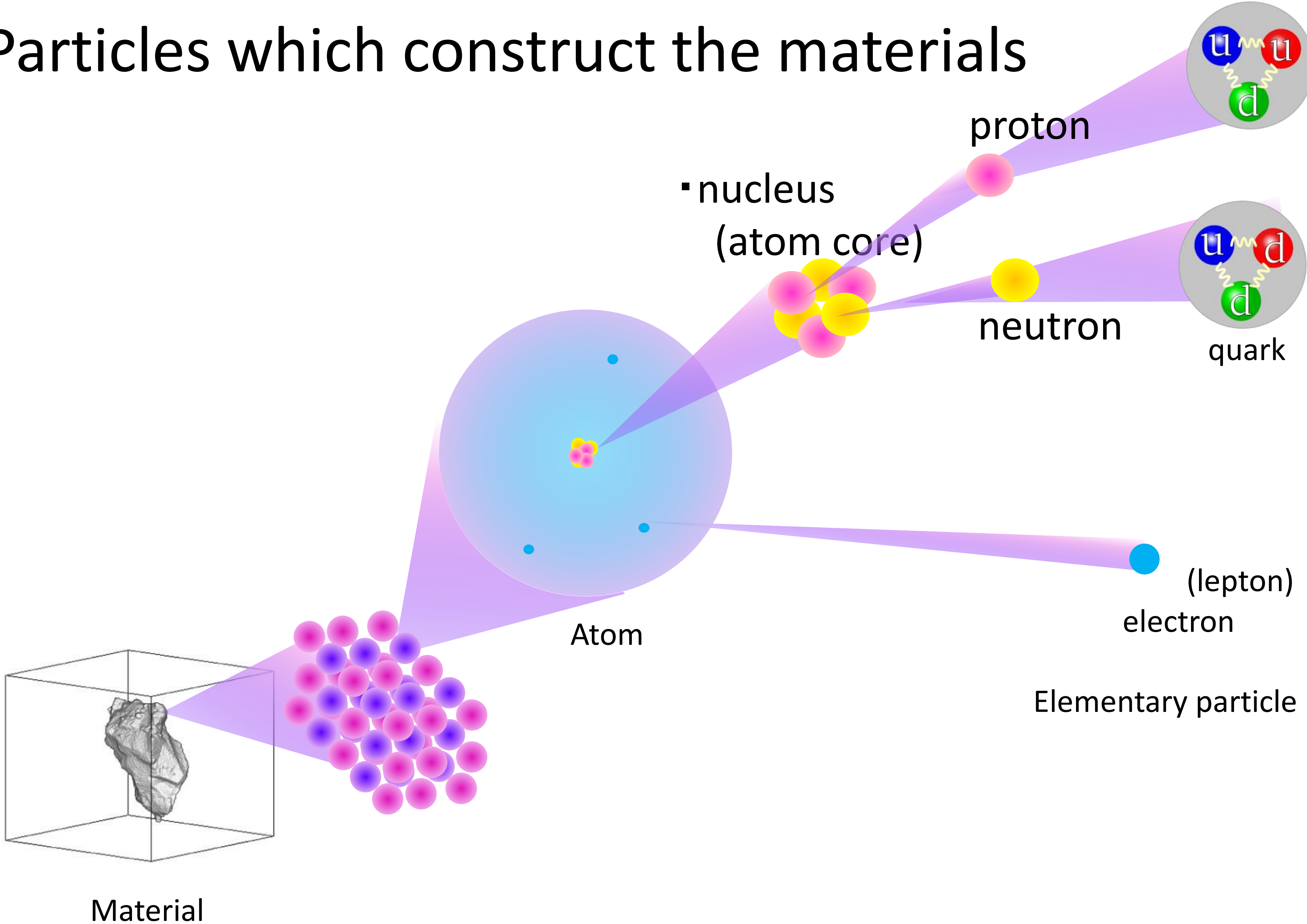
Particles which construct the materials



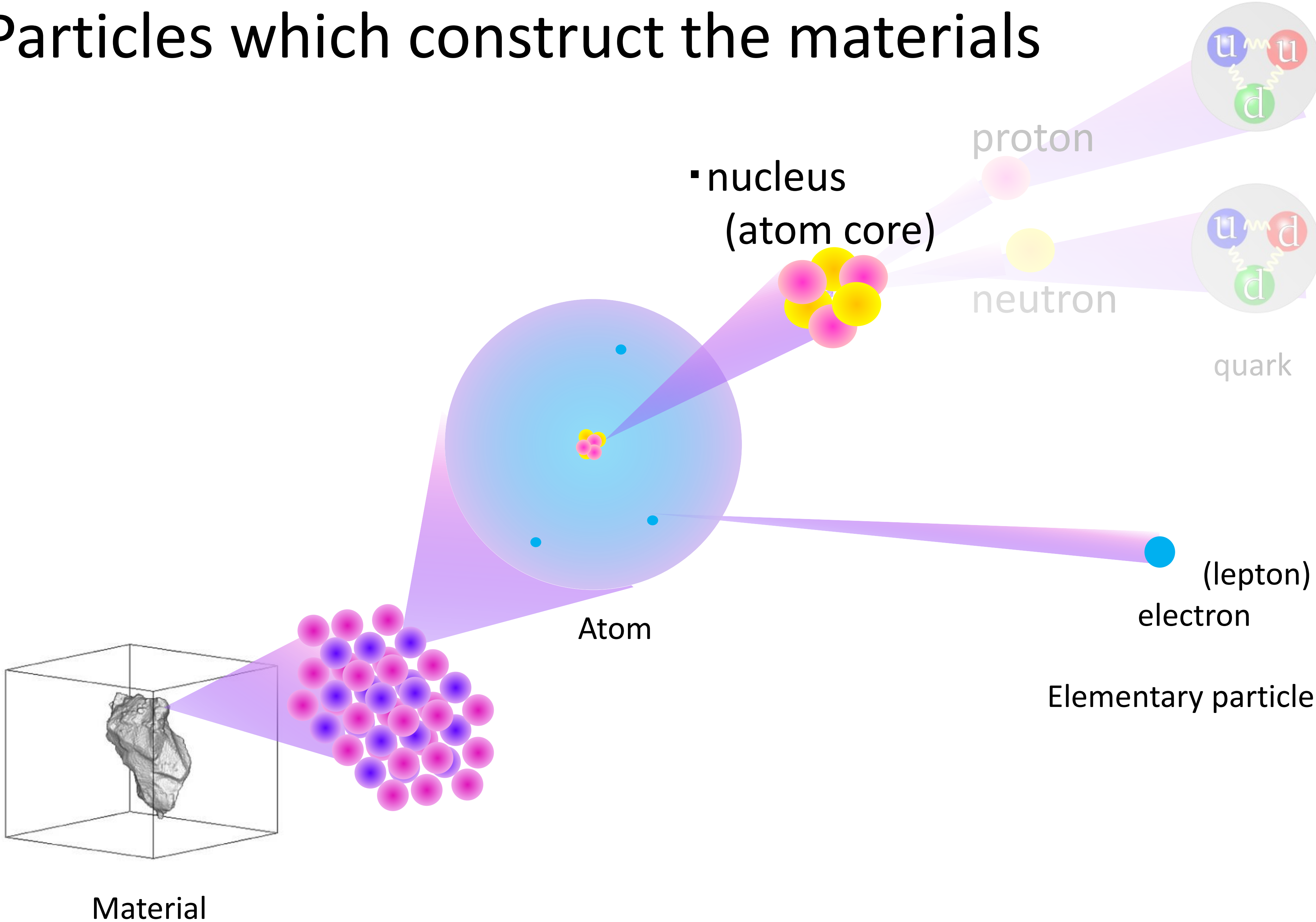
Particles which construct the materials



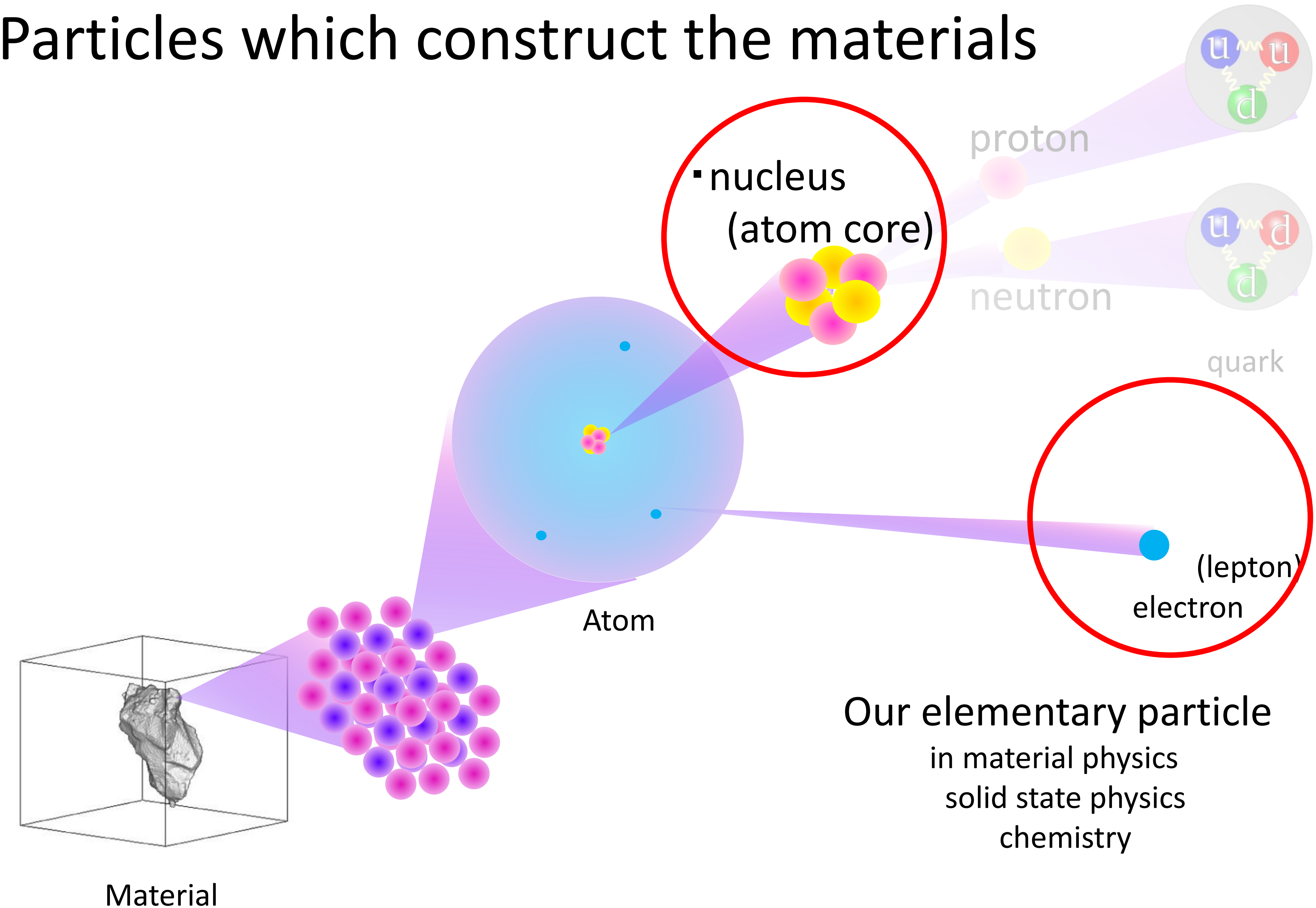
Particles which construct the materials



Particles which construct the materials



Particles which construct the materials



Our elementary particle

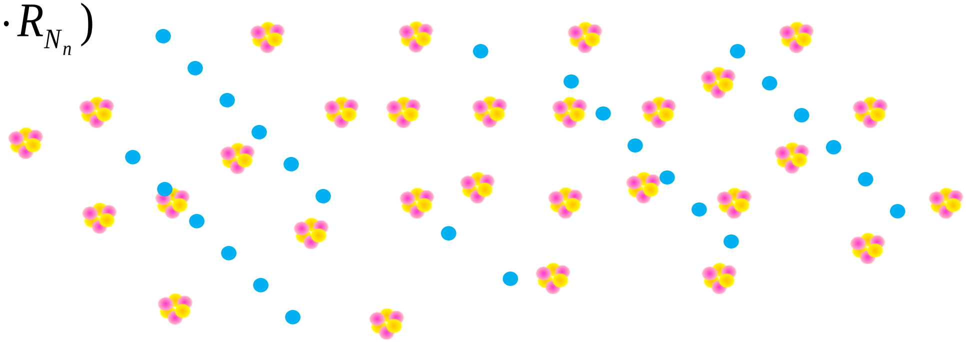
in material physics
solid state physics
chemistry

Many atomic nuclei and electrons are in the material

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

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

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

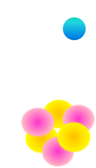


N_n ; Number of atoms N_e ; Number of electrons $\sim$ 10^{23}

Z_l : atomic number of the l th atom

M_l : Mass of the l th atom

m : Electron mass


electron

atomic nucleus

Many atomic nuclei and electrons are in the material

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

Hamiltoinan:

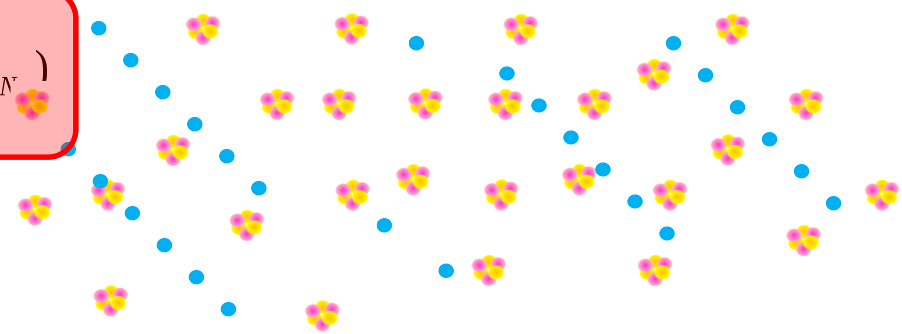
Wave function

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

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

As a function of all particle positions

Total energy



N_n ; Number of atoms N_e ; Number of electrons ~ 10^{23}

Z_l : atomic number of the l th atom

M_l : Mass of the l th atom

m : Electron mass

electron

atomic nucleus

Hamiltoinan = Energy operator for all particles

 electron

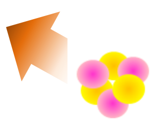
 atomic nucleus

① ② ③ ④ ⑤

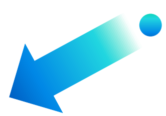
$$\left[-\sum_{l=1}^{N_n}\frac{\hbar^2}{2M_l}\nabla_i^2-\frac{\hbar^2}{2m}\sum_{i=1}^{N_e}\nabla_i^2-\sum_{i=1}^{N_e}\sum_{l=1}^{N_n}\frac{Z_l e^2}{\left|\vec{r}_i-\vec{R}_l\right|}+\frac{1}{2}\sum_{i=1}^{N_e}\sum_{j=1(i\neq j)}^{N_e}\frac{e^2}{\left|\vec{r}_i-\vec{r}_j\right|}+\frac{1}{2}\sum_{l=1}^{N_n}\sum_{k=1(l\neq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

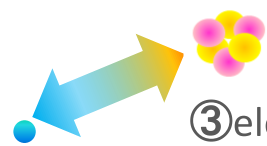
$$=E\psi(\vec{r}_1,\cdots\vec{r}_{N_e};\vec{R}_1,\cdots\vec{R}_{N_n})$$

①Kinetic energy of nucleus

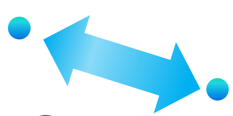


②Kinetic energy of electron

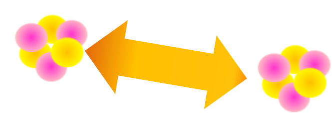




③electron–nucleus interaction potential energy



④ electron–electron interaction potential energy



⑤ nucleus–nucleus interaction potential energy

① ② ③ ④ ⑤

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

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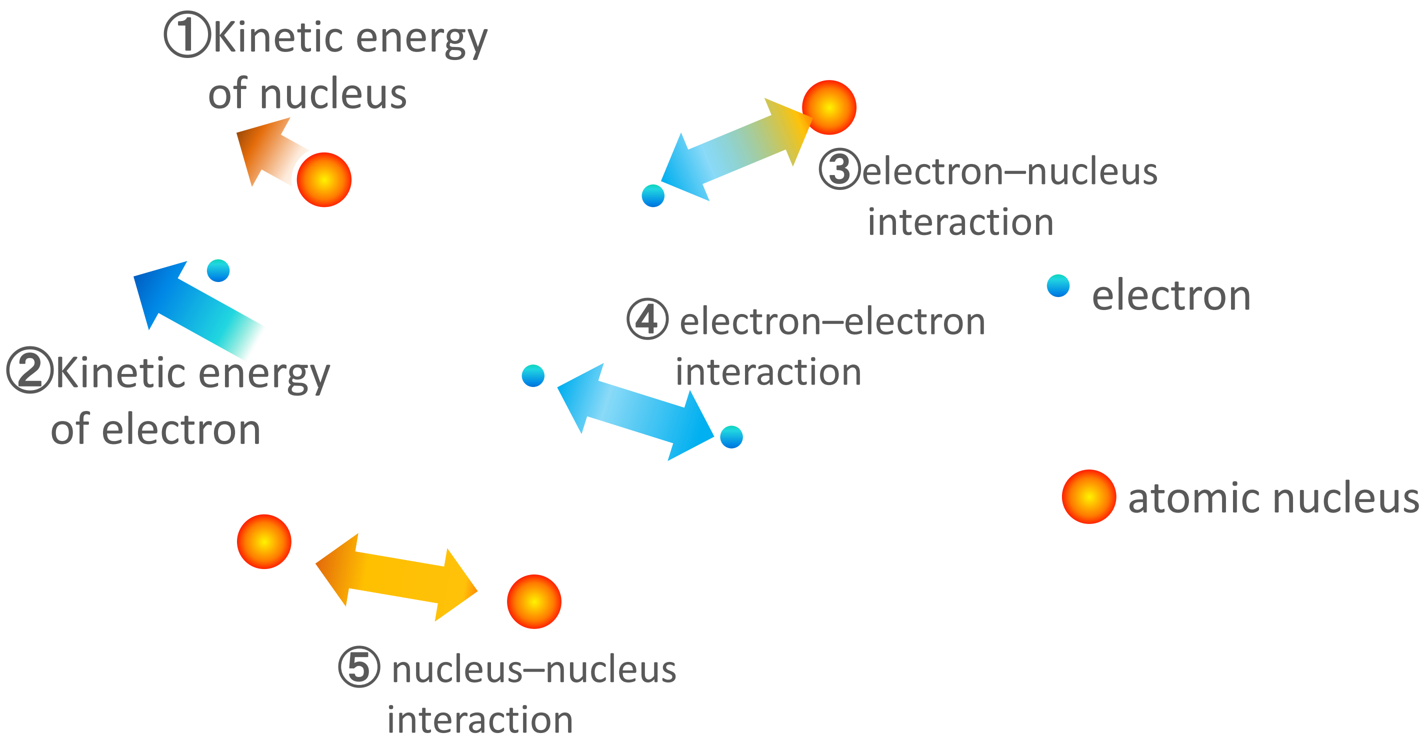
If $M_l \gg m$ then …



① ② ③ ④ ⑤

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

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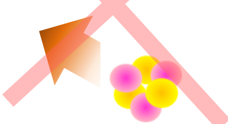
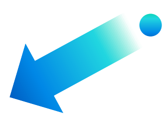
If $M_l >> m$ then …

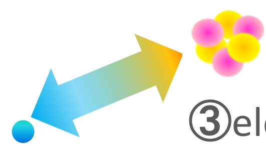
From the view point of electron motion, we can treat that nuclei does not move.

~~①Kinetic energy of nucleus~~

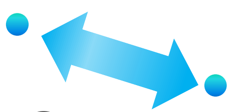


②Kinetic energy of electron

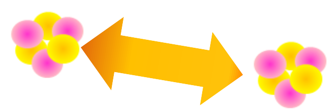




③electron–nucleus interaction potential energy



④ electron–electron interaction potential energy



⑤ nucleus–nucleus interaction potential energy

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

① ② ③ ④ ⑤

If $M_l >> m$ then …

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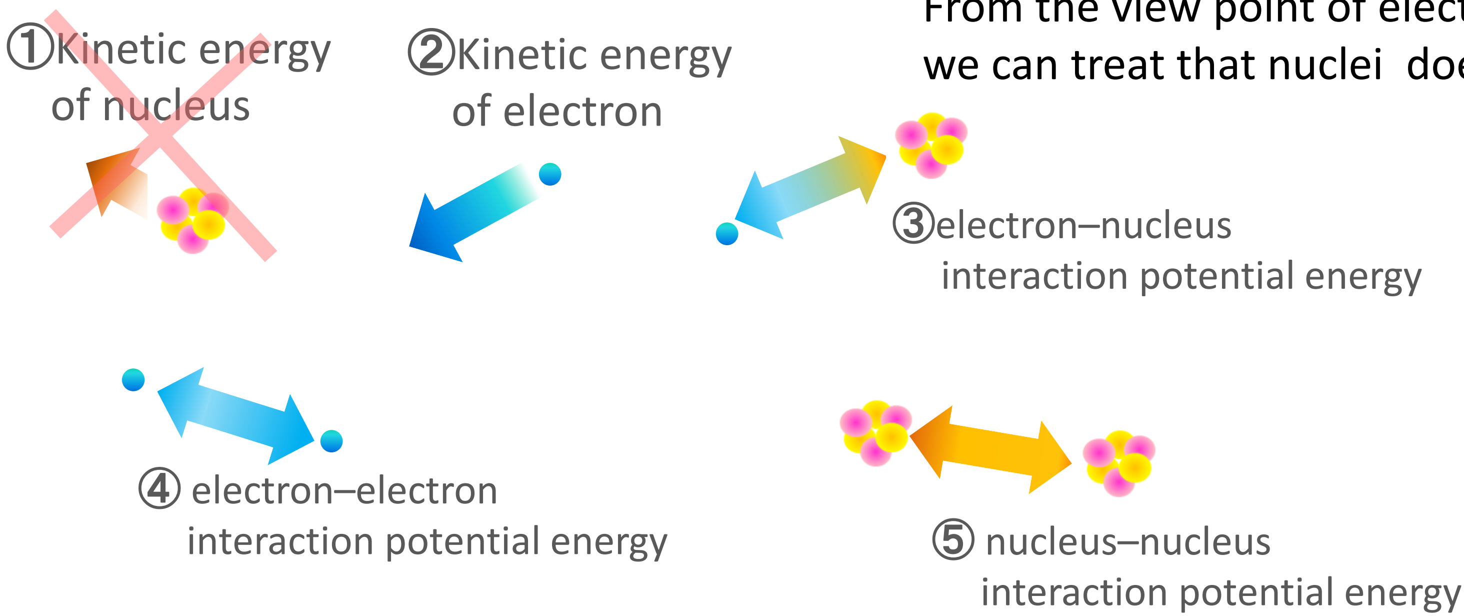

- Fundamental equation for describing behaviors of electrons:
  Schrödinger equation

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

・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 ; Number of electrons ～ 10^{24}

＝ 1000000000000000000000000 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)**

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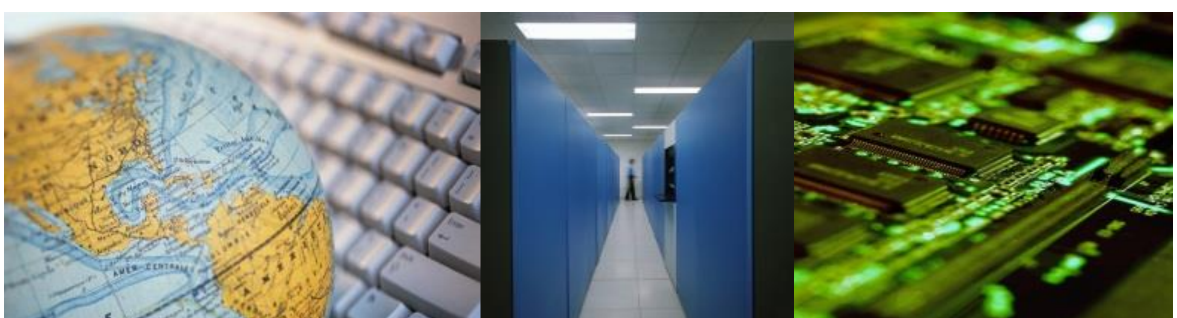
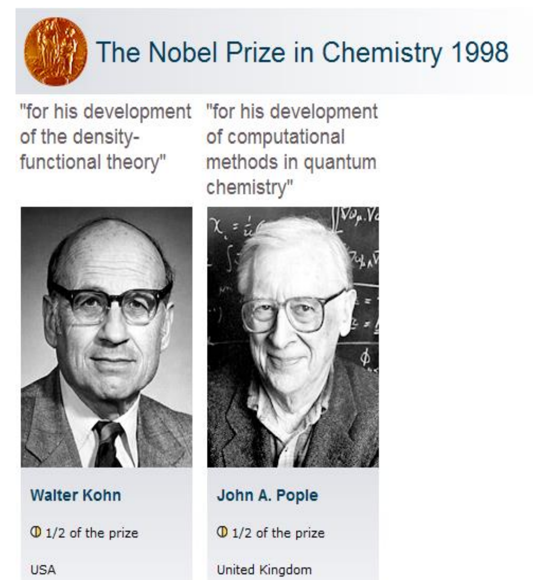
rapid progress of technological innovation
in Computer Science： Computics





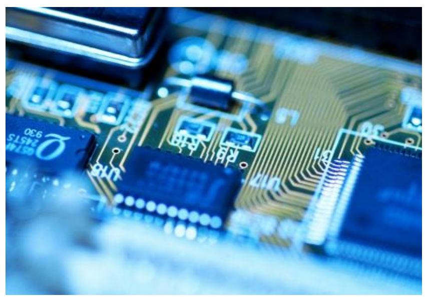
Walter Kohn & John A.Pople

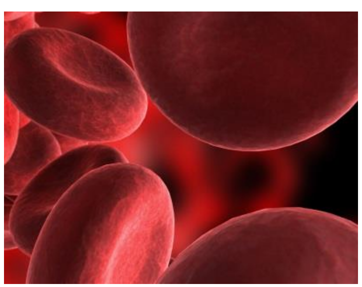
http://nobelprize.org/

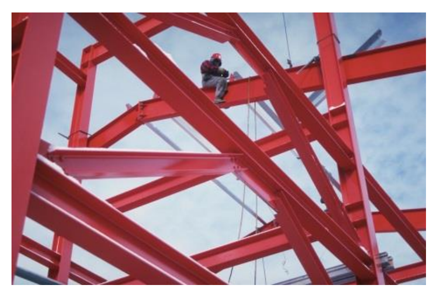
Unique equation

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

Various properties







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

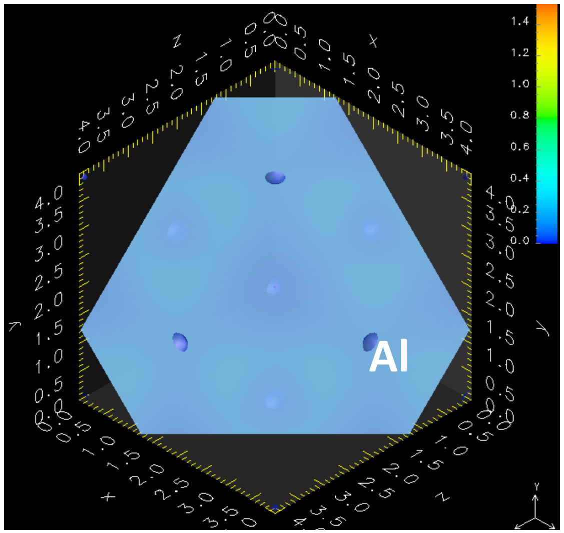
Aluminum Al ($\boxed{Z=13}$) Silicon Si ($\boxed{Z=14}$) Sodium chloride Na ($\boxed{Z=11}$) Cl ($\boxed{Z=17}$)

Periodic table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											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

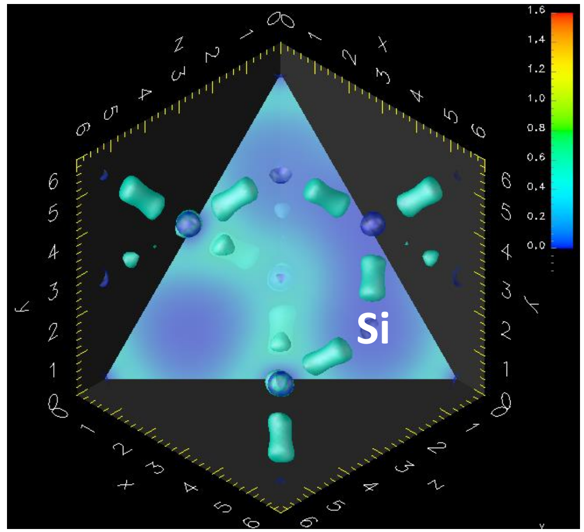
Al (Z=13)



electron density distribution

Silicon

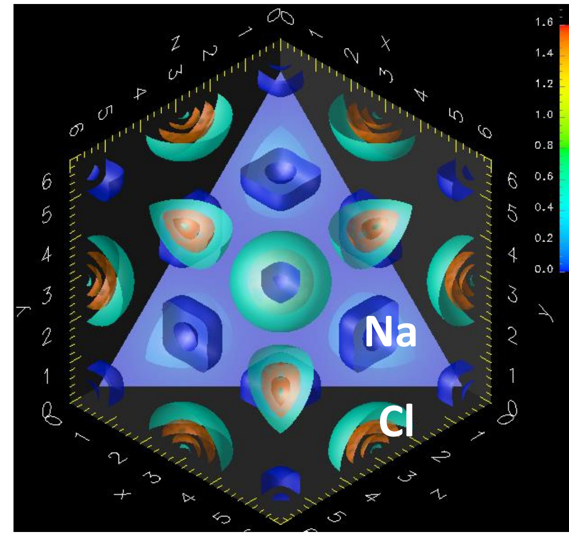
Si (Z=14)



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

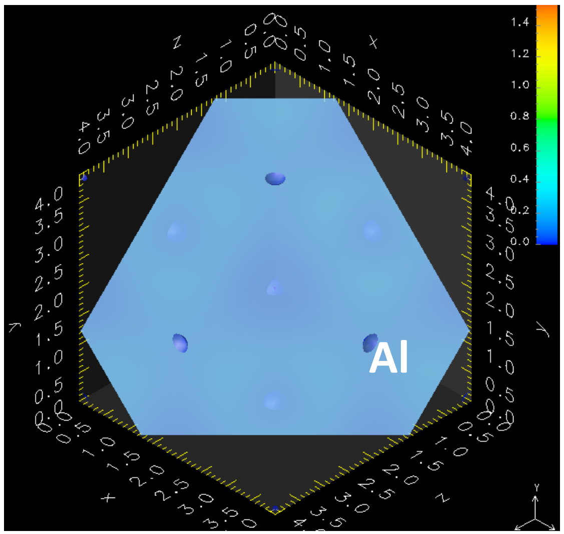
DFT-based ab initio calculation method is one of the most successful method.

Parameter in the calculations is only atomic number, Z.

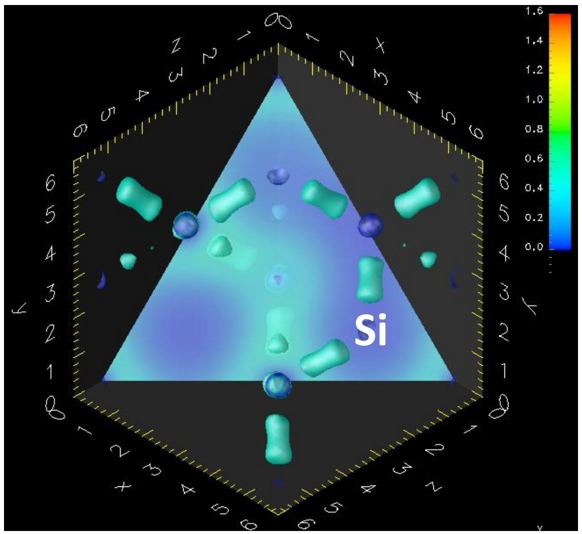
Aluminum
Al (Z=13)

Silicon
Si (Z=14)

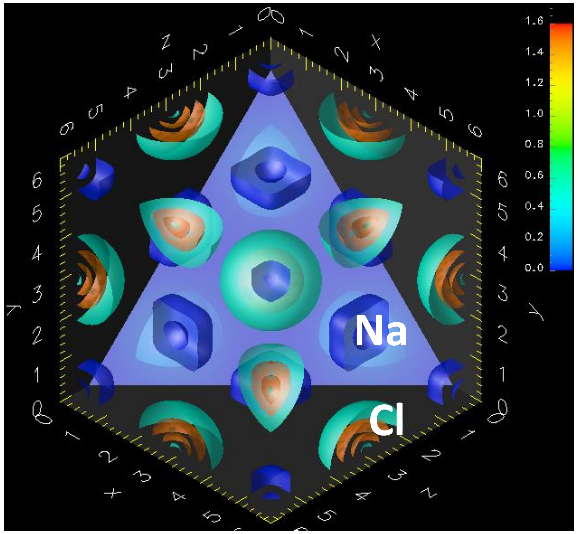
Sodium chloride
Na (Z=11) Cl (Z=17)



electron density distribution



electron density distribution



electron density distribution

Metallic bond

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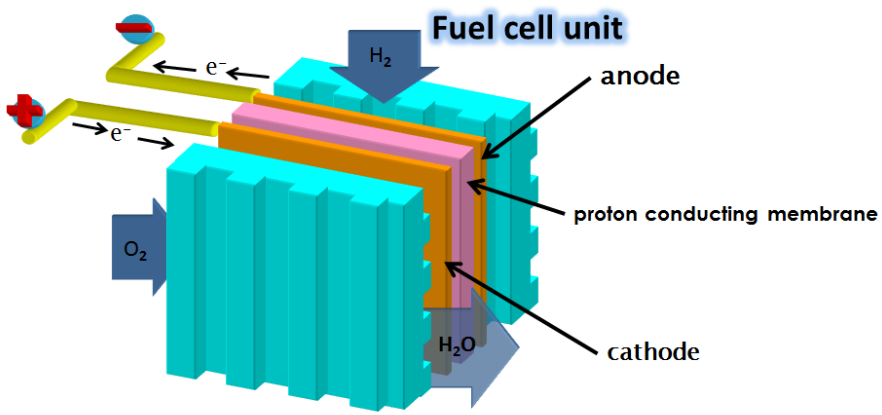
at atoms

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"

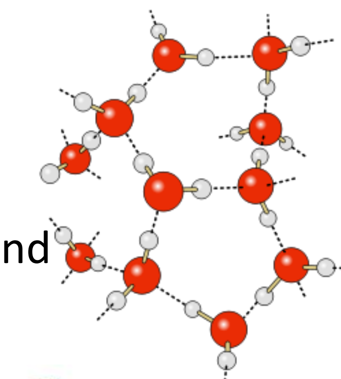
$M_{\mathrm{Proton}} >> m$

Hydrogen Reactions on Fuel cell anode



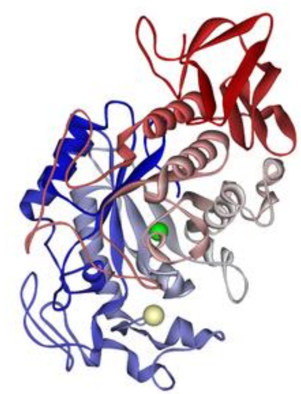
Polymer Electrolyte Fuel Cell (PEFC)

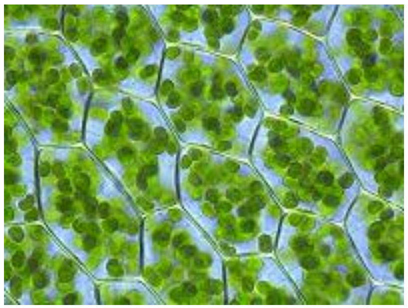
electrolyte



hydrogen bond

aqueous solution





biochemistry

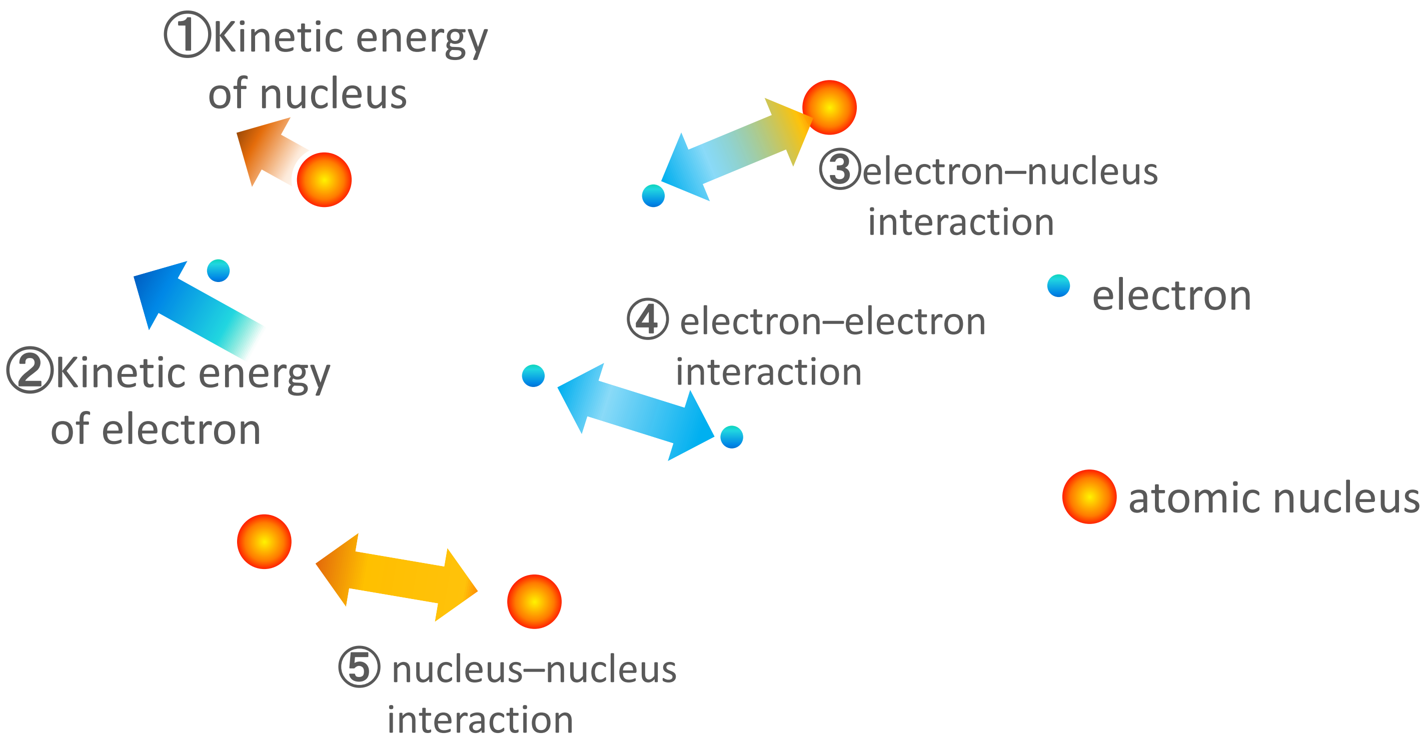
Enzyme catalysis

Photosynthesis

① ② ③ ④ ⑤

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

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



What is Naniwa ?

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

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

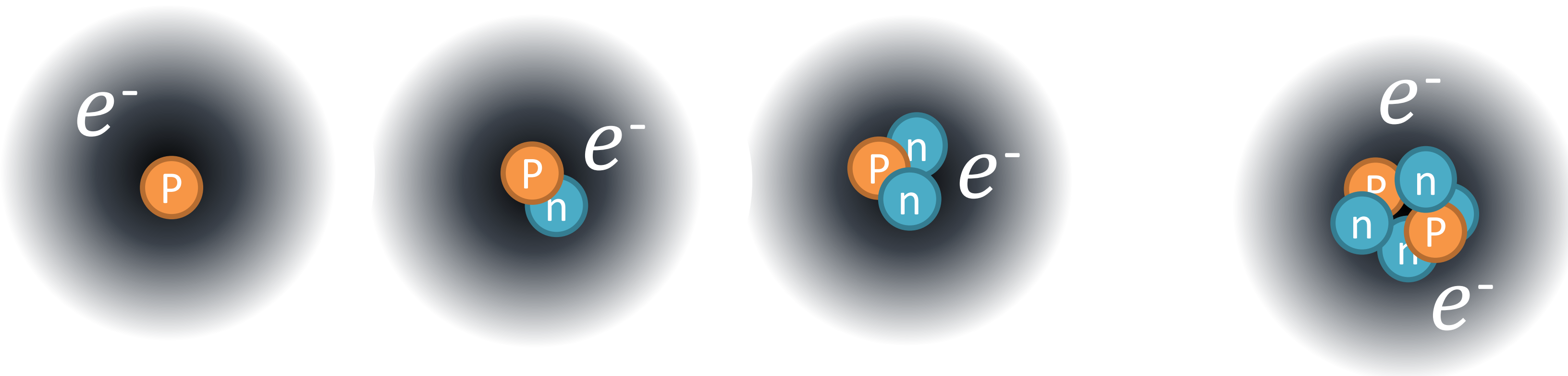
"we can solve the scattering problems, and obtain the probability of some events, adsorption, desorption, reflection, excitation, etc."

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.

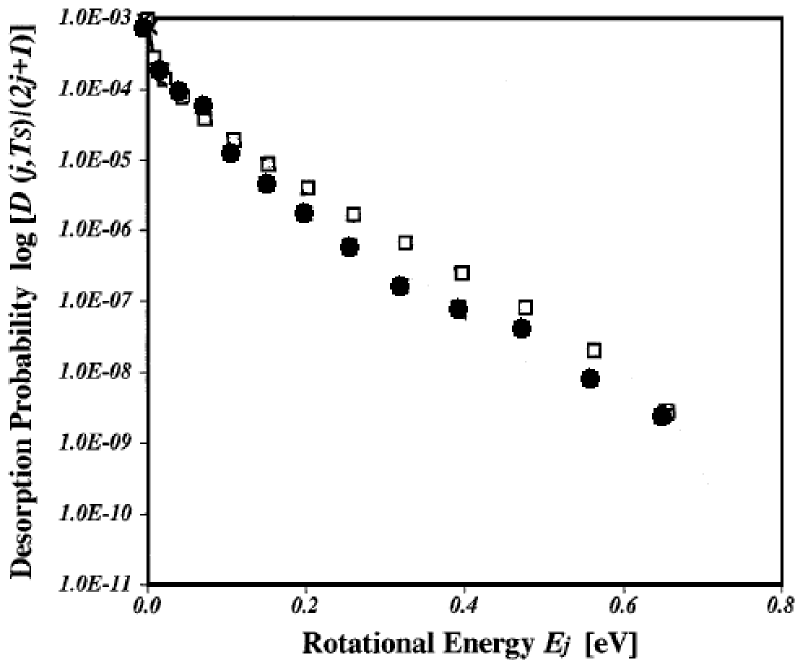


$^{1}_{1}\mathrm{H}$ $^{2}_{1}\mathrm{H}$ $^{3}_{1}\mathrm{H}$ $^{7}_{2}\mathrm{Li}$

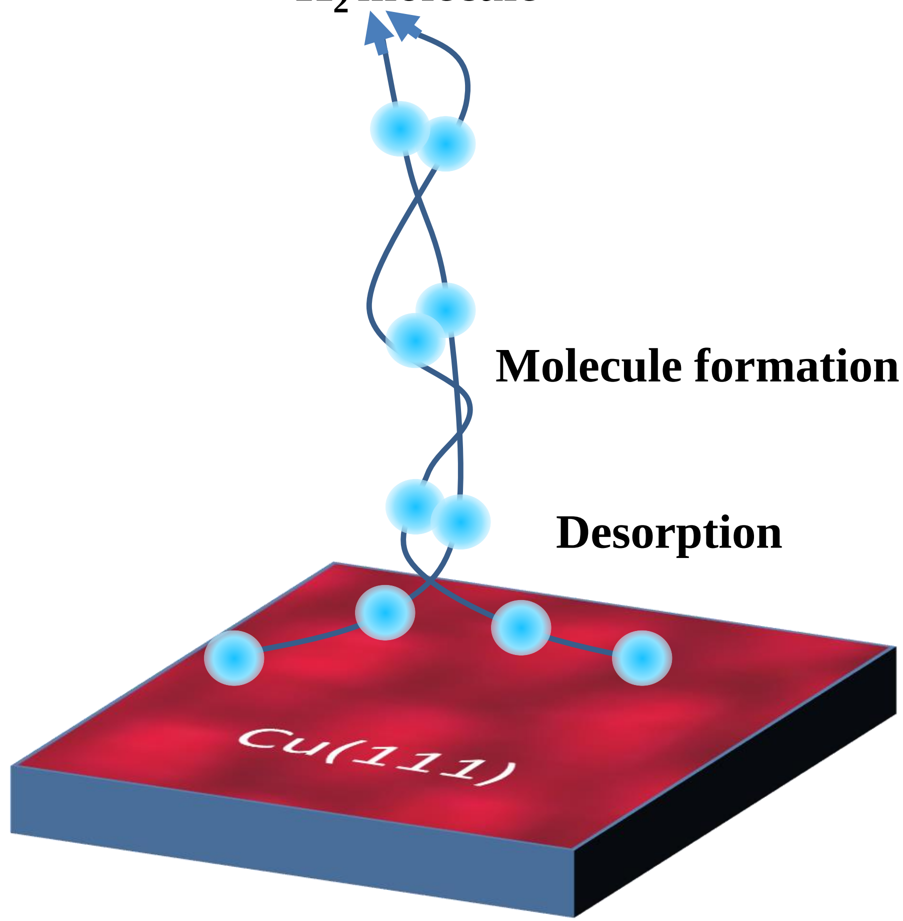
Protium Deuterium Tritium Lithium …

Comparison between our simulation and experimental results

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



Rotational motion of H_2 molecule



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 !

Comparison between our simulation and experimental results

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

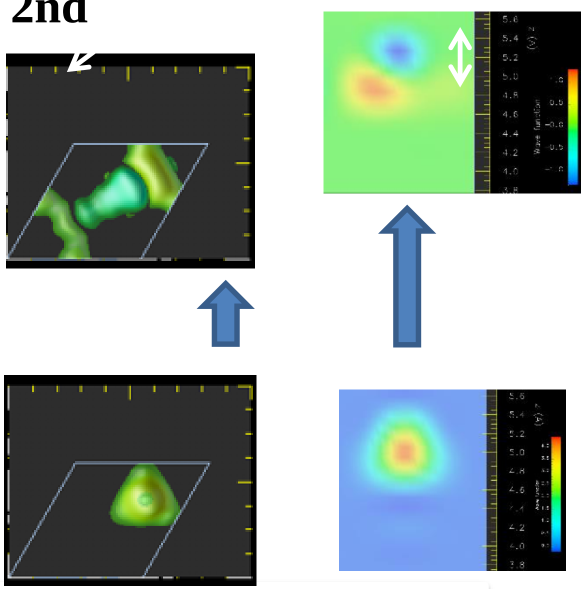
Motion	Parallel	Perpendicular
Experiment*	96 meV	124 meV
Simulation	91 meV	114 meV
Error	5.2%	8.1%

Parallel — Perpendicular

2nd — 4th

Excited state

Ground state



No fitting parameters !

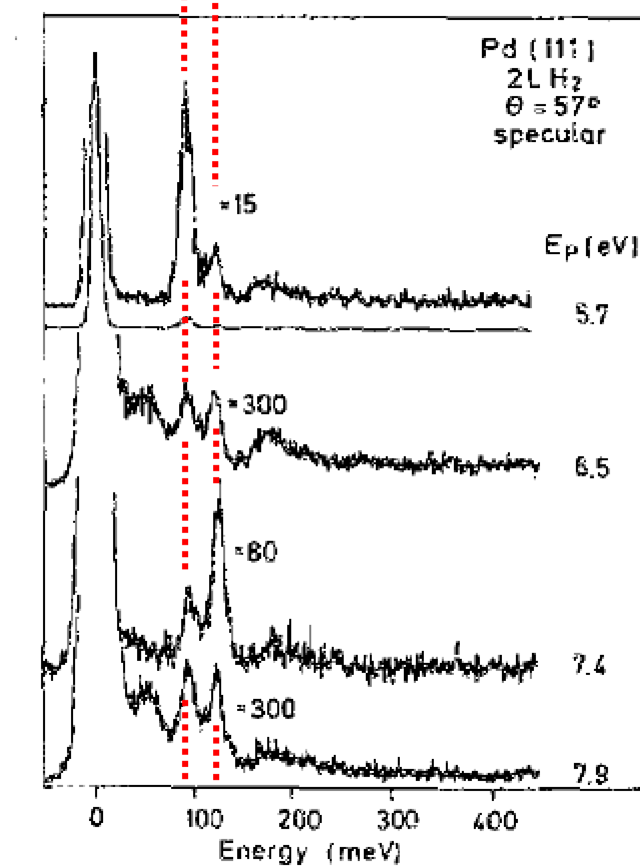


FIG. 1. HREELS of H on Pd(111)

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).

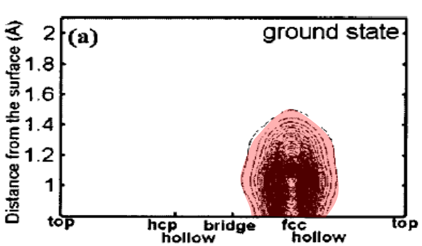
	Naniwa	Experiment	Error
H on Cu(111)	135 meV	129 meV*	4.7%
D on Cu(111)	104 meV	96 meV	8.3%
isotope effect	1.29	1.34	3.4%

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

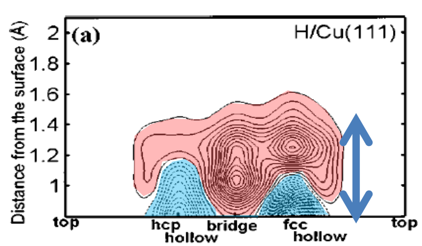
Less than 10% error

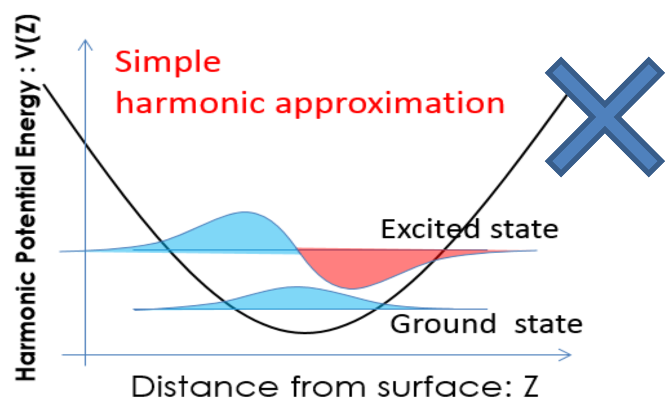
H on Cu(111)

Ground state



Vivrational excited state



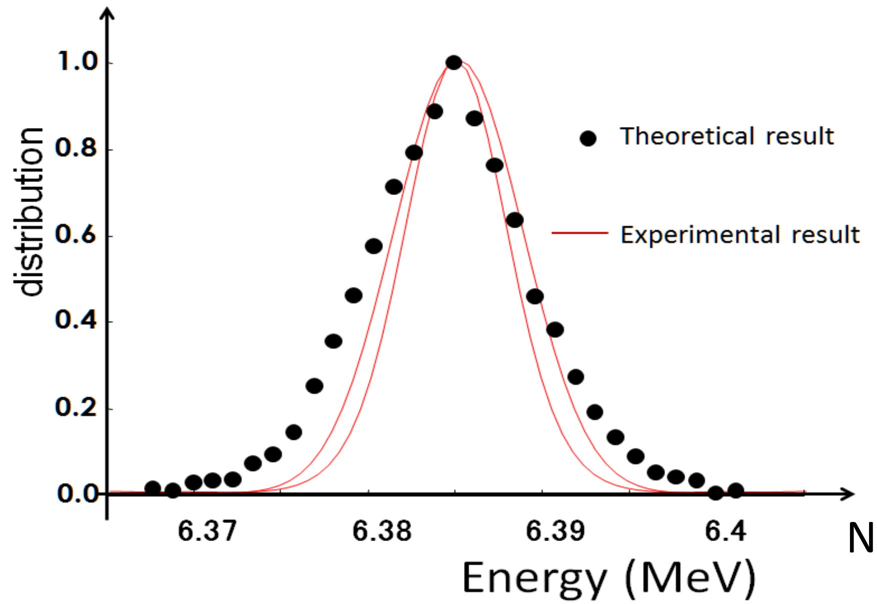


No fitting parameters !

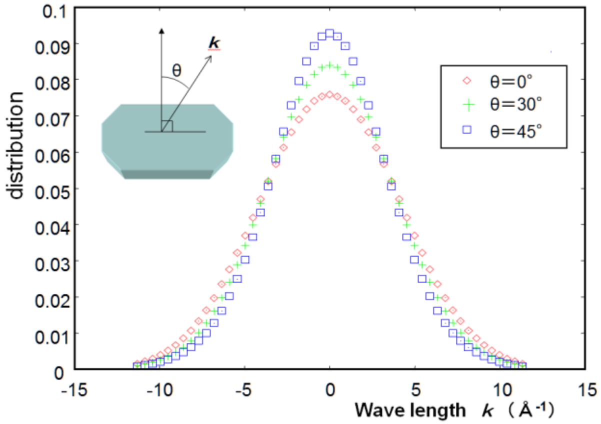
isotope effect ratio = $\sqrt{2} \sim 1.414$

Comparison between our simulation Naniwa and experimental results

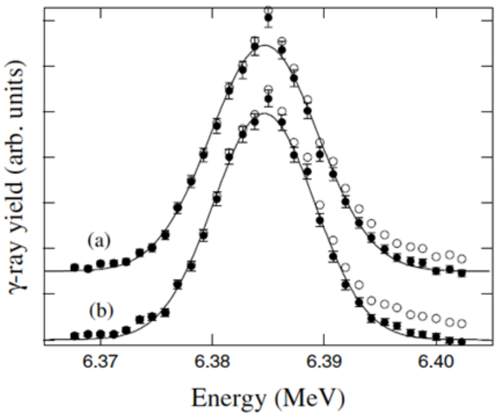
Momentum distribution of adsorbed hydrogen atom is observable in its ground state.



NRA : Nuclear Reaction Analysis



Naniwa

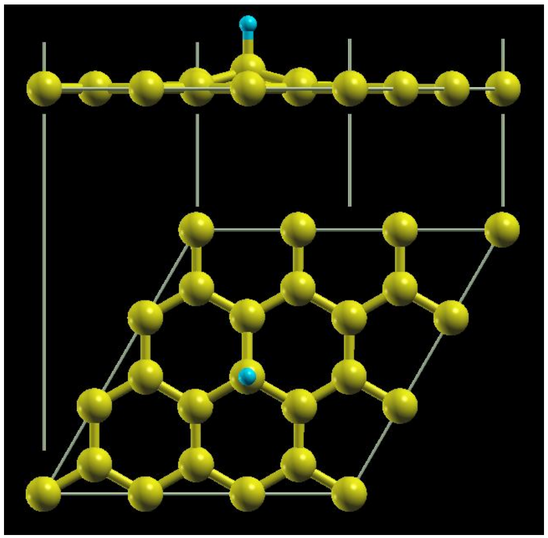


K. Fukutani et al., PRL 48(2002)116101.

Comparison between our simulation Naniwa and experimental results

Hydrogen adsorbed on graphene

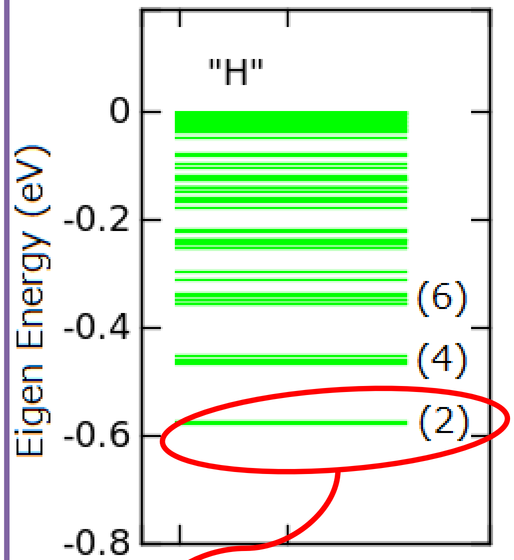
Conventional ab initio cal.

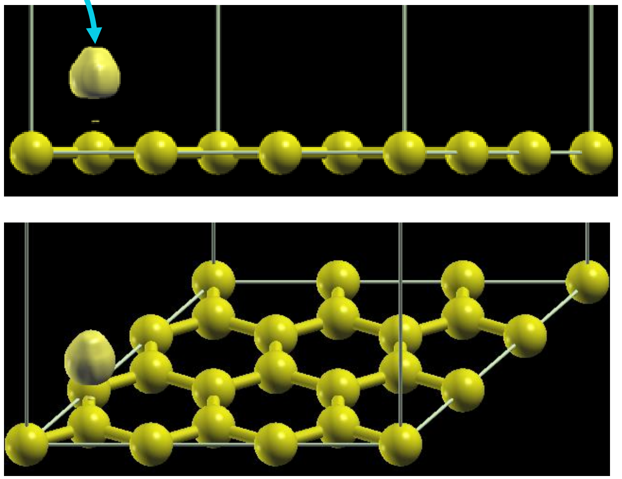


Adsorbed site: Top site
Adsorbed type: chemisorption
Adsorbed energy: -0.816 eV

Naniwa results

Ground state Wave function



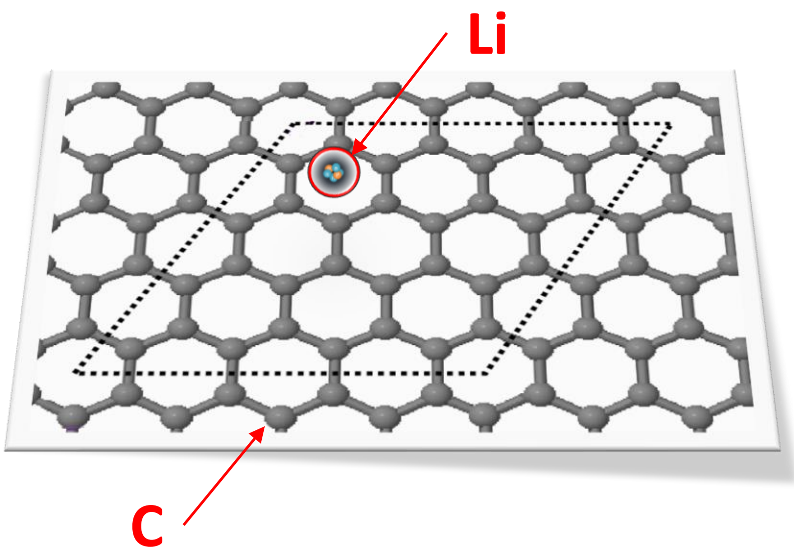


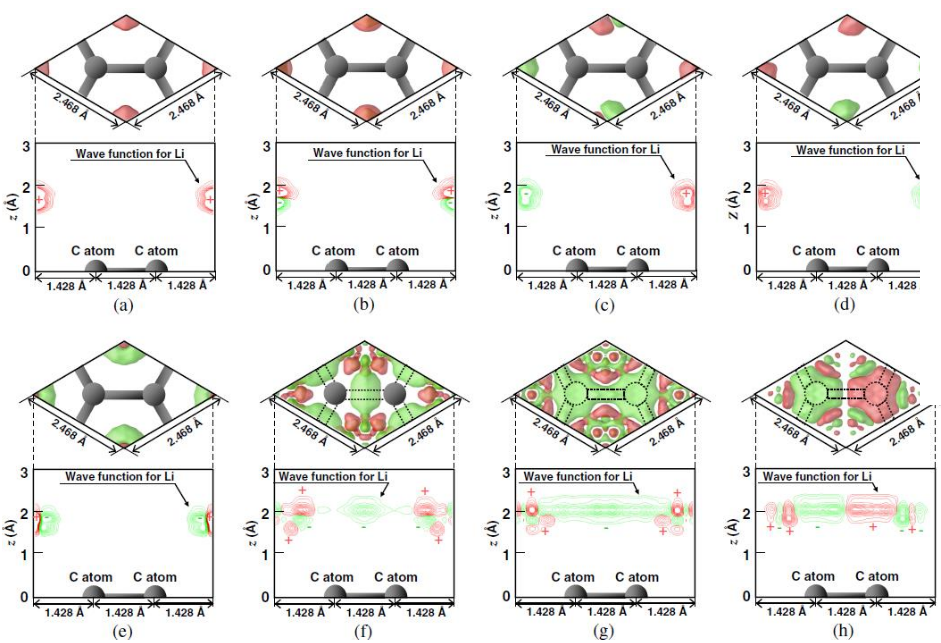
Quantum adsorbed energy of hydrogen: **-0.58eV**

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

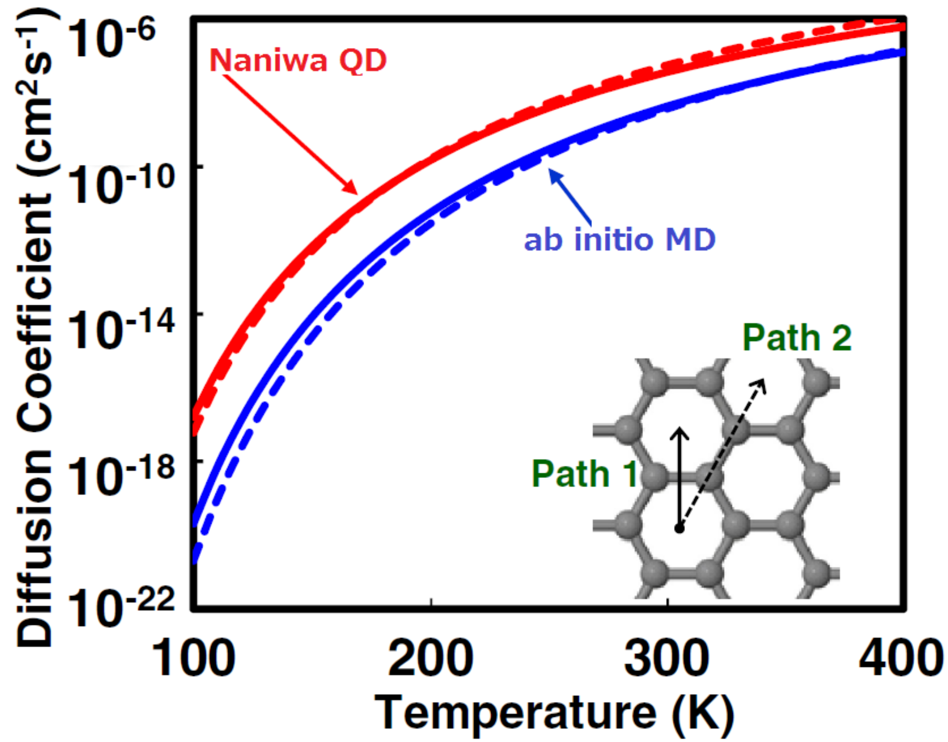
X. Zhao, et al., J. Chem. Phys. 124(2006)194704

Li on graphene





Negative electrode of Lithium-ion battery



Activation barrier: *E*a(path 1)<*E*a(path2)

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

Our quantum simulation scheme: Naniwa

Interactions between nucleus is calculated by DFT based first principle calculations

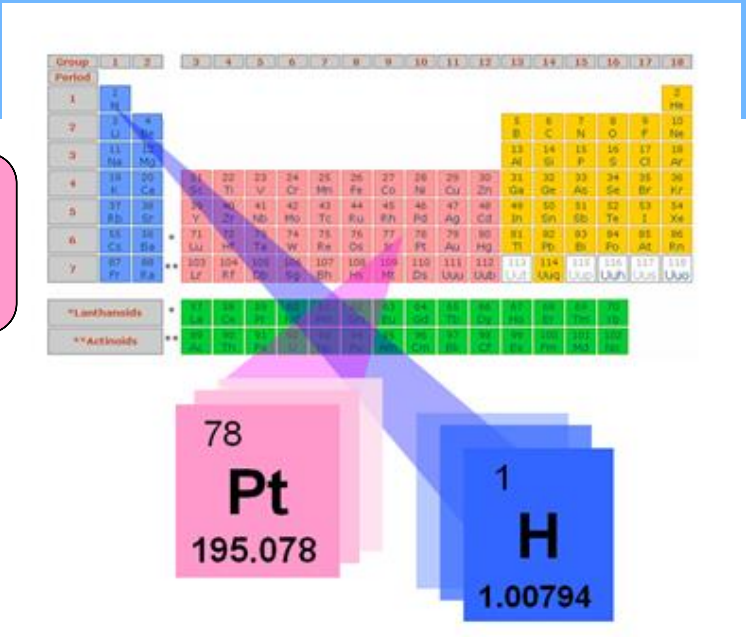
… (*)

Potential energy for nucleus motions: $U_n(\boldsymbol{R})$

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

Wave function for nucleus motion

Derive the various physical quantities

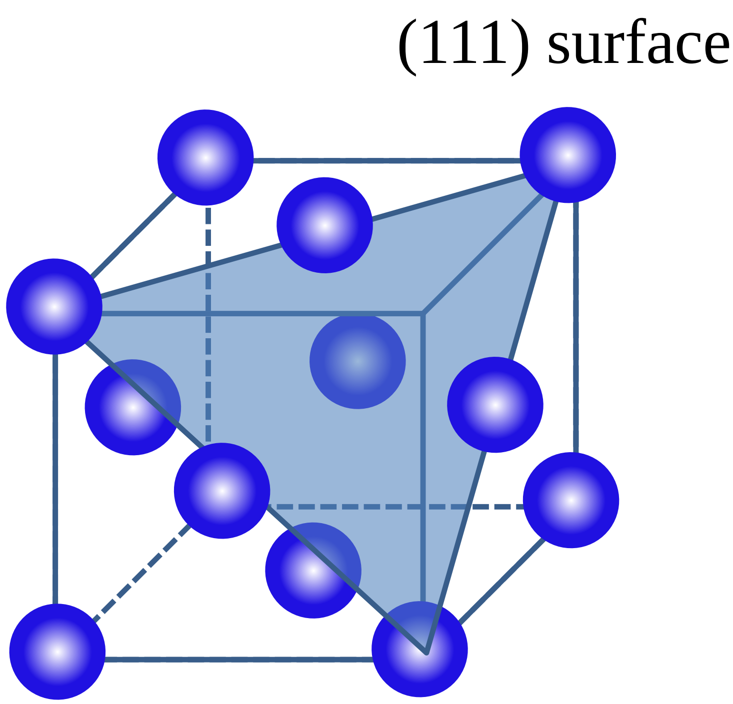


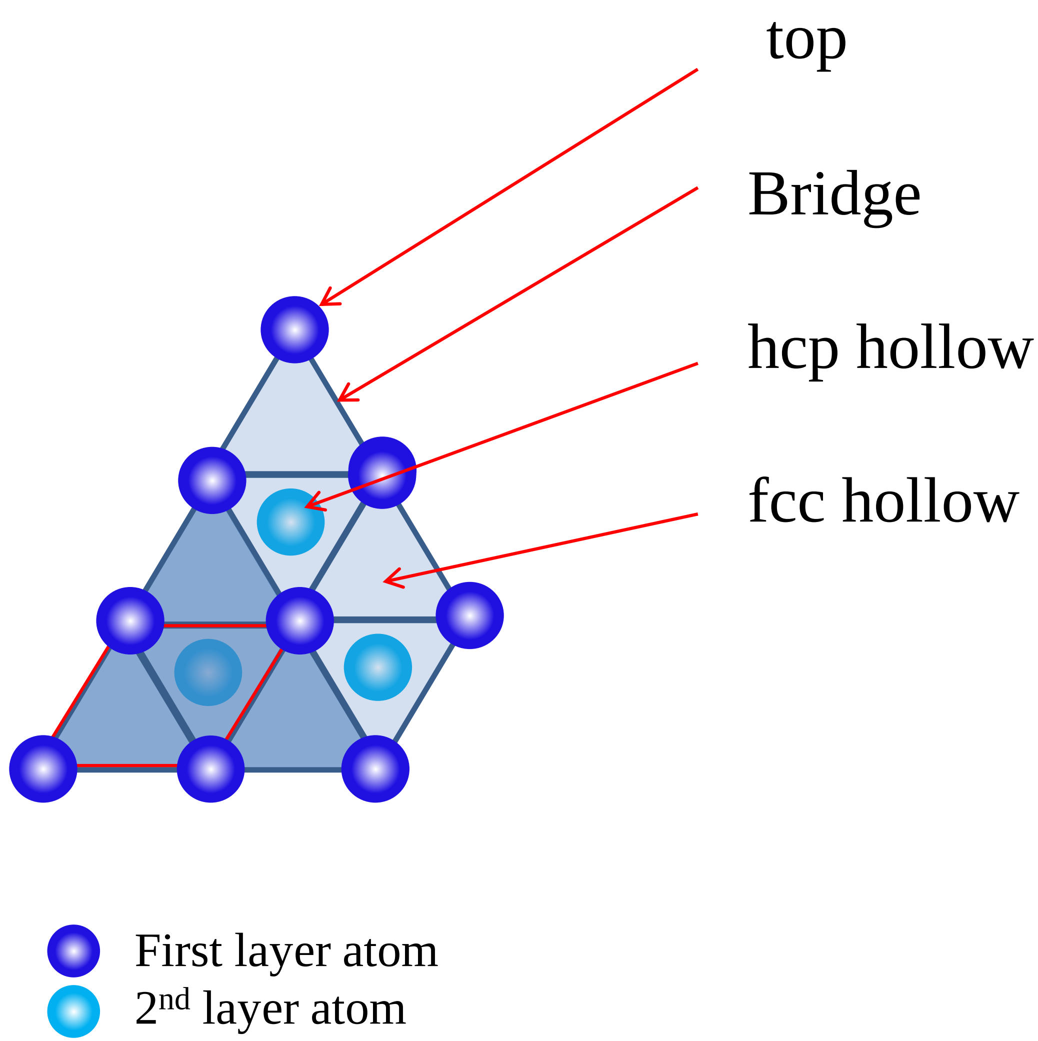
- Parameters are only atomic number of elements
- No fitting and no artificial procedure

- Some examples on (111) surface of fcc crystals

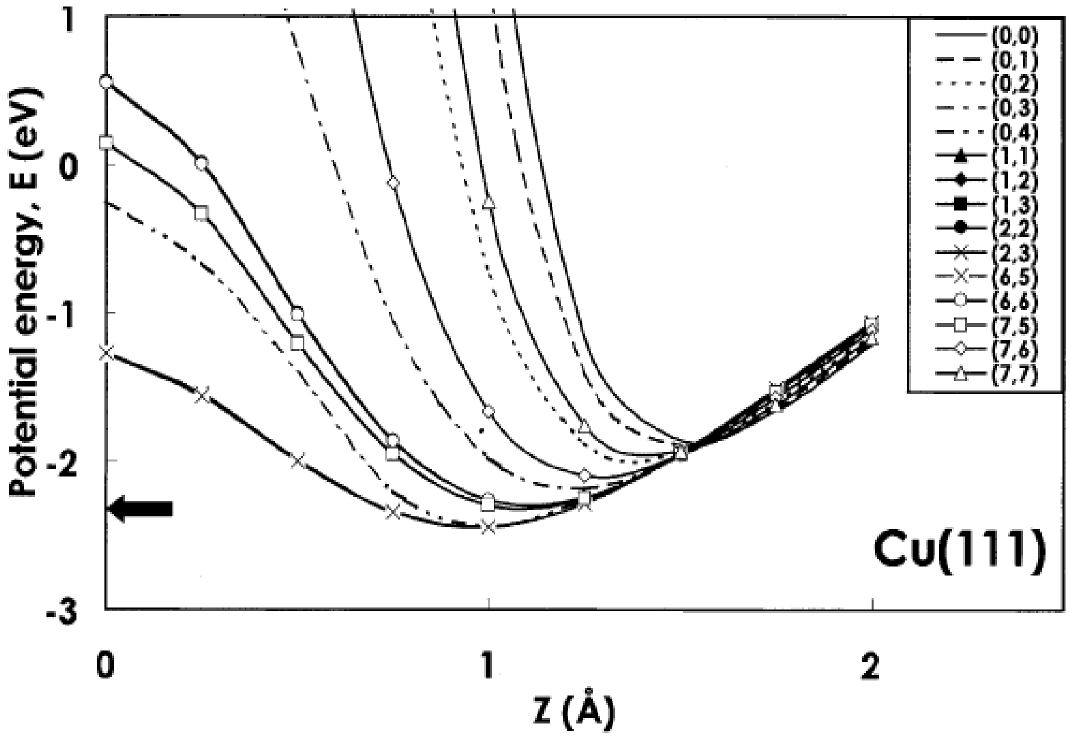
Quantum states of hydrogen atom motion
on the surface

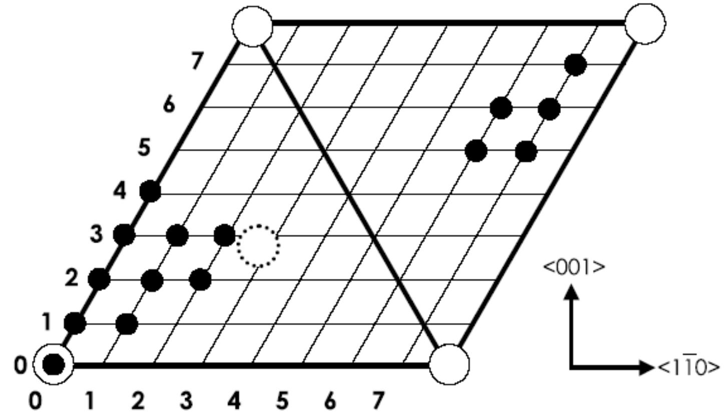
(111) surface of face center cubic crystals

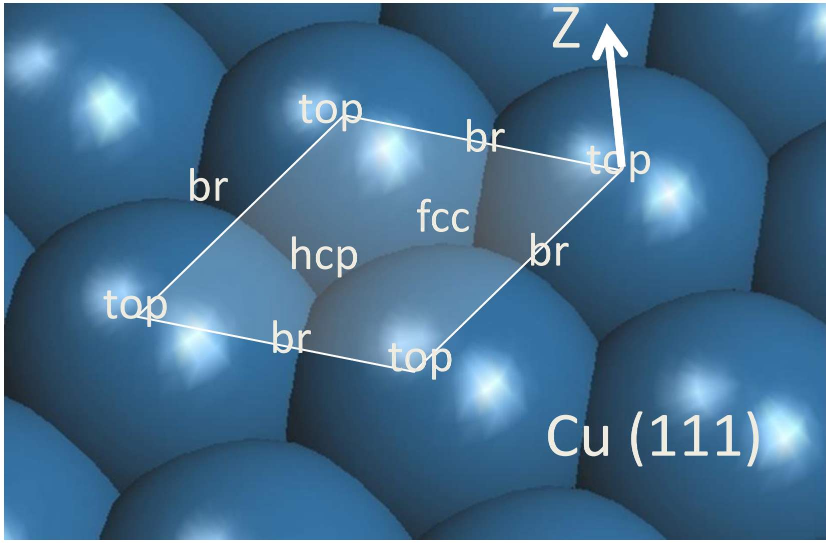




Potential energy surface of H motion on Cu(111)

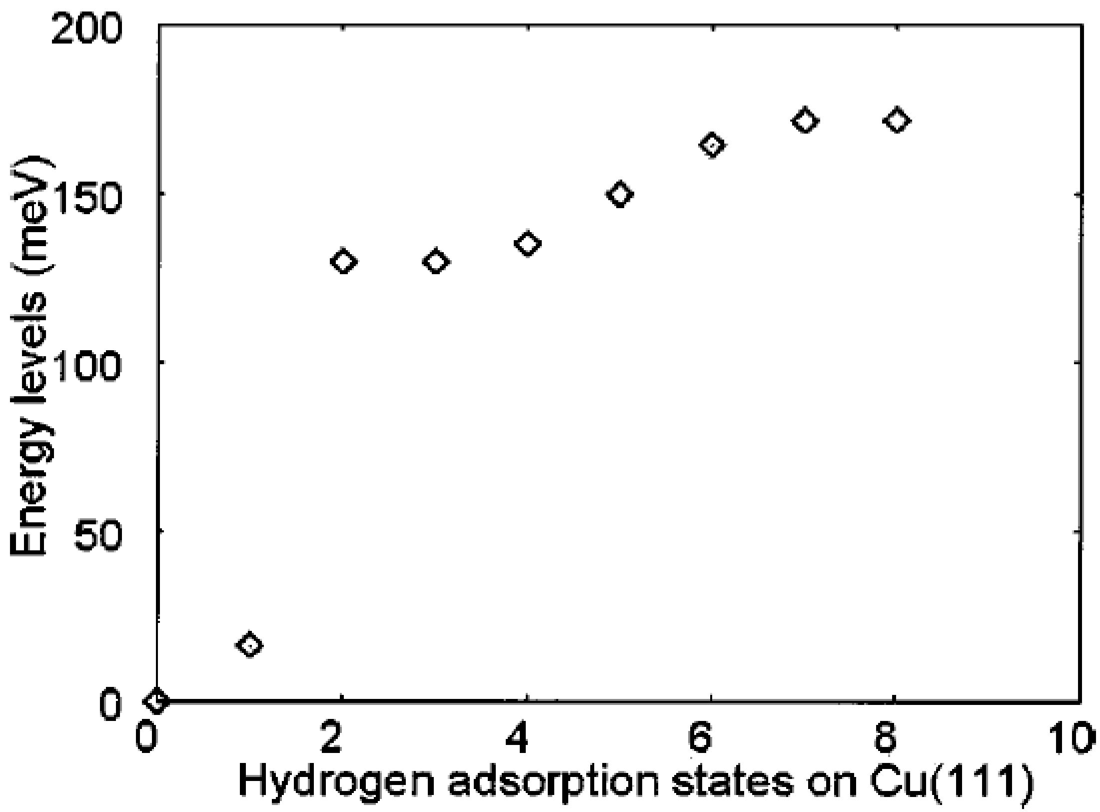






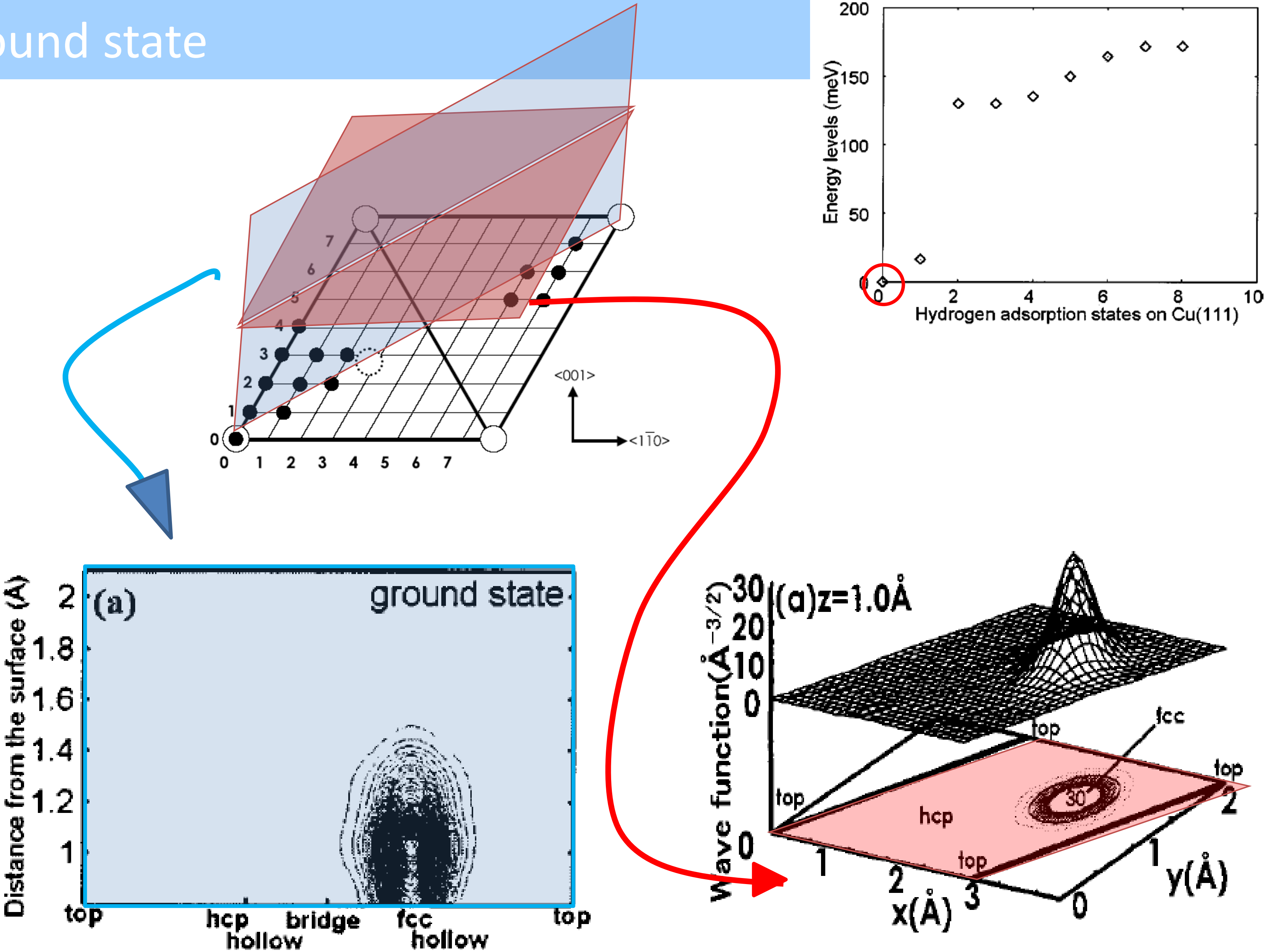
K. Nobuhara et al. / Surface Science 493 (2001) 271

Eigenenergy for a H motion on Cu(111)



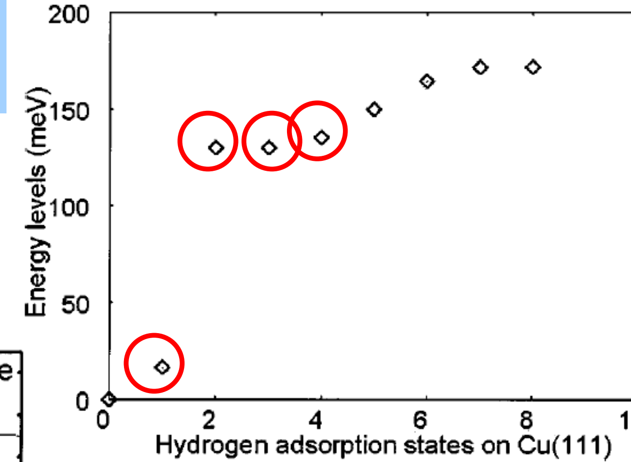
K. Nobuhara et al., J. Appl. Phys. 96 (2004) 5020.

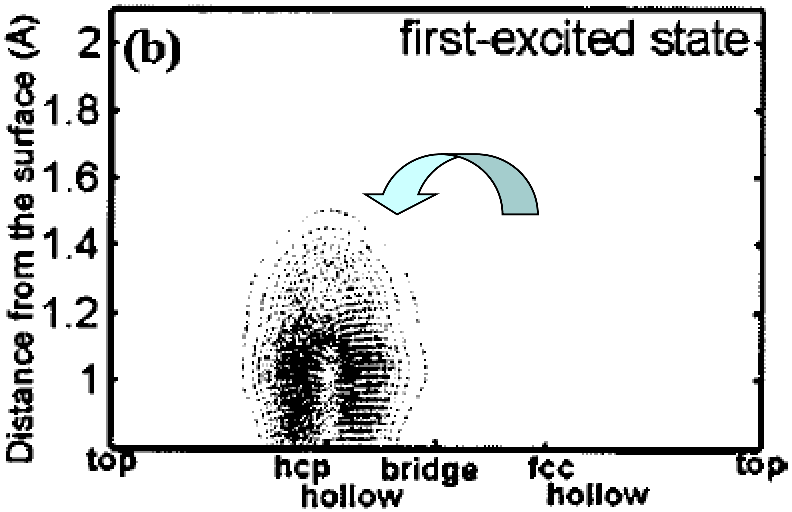
Ground state

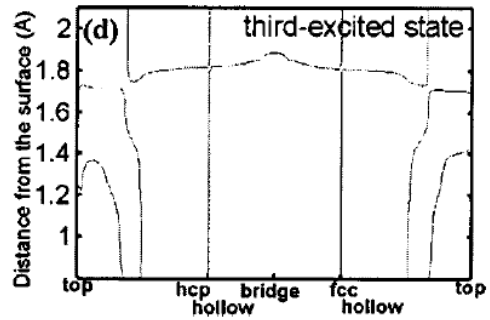


K. Nobuhara et al., J. Appl. Phys. 96 (2004) 5020.

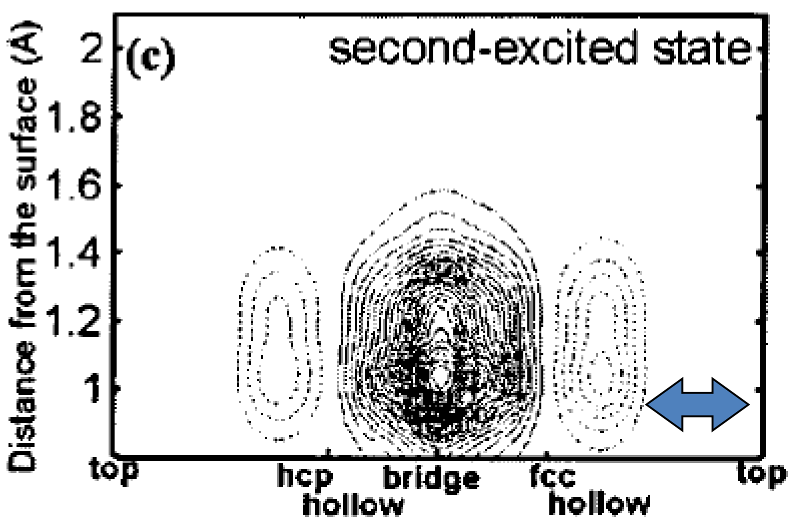
The excited states

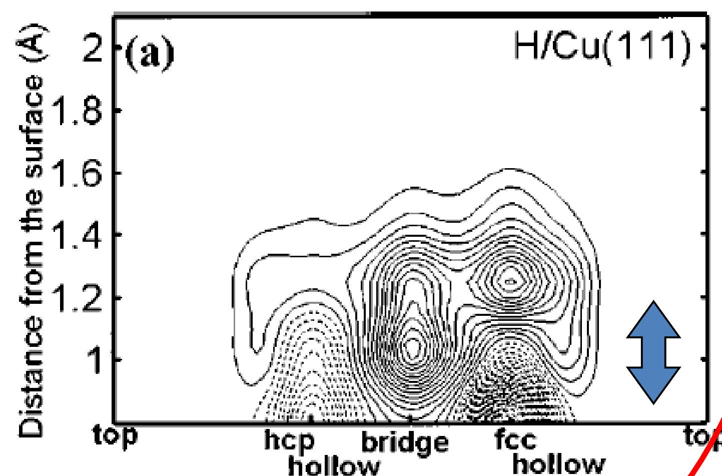






E_4-E_0=135meV



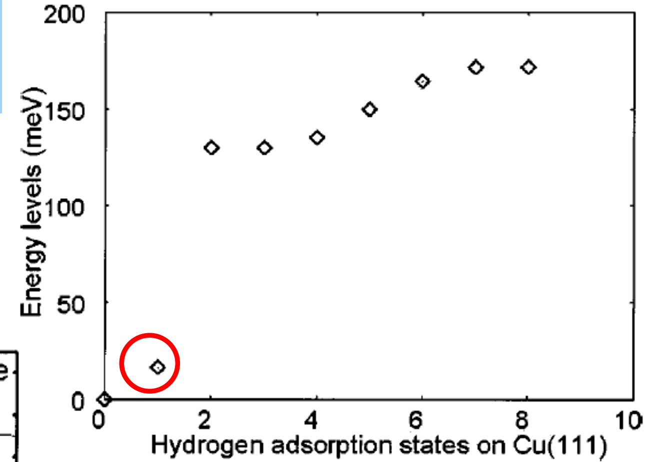


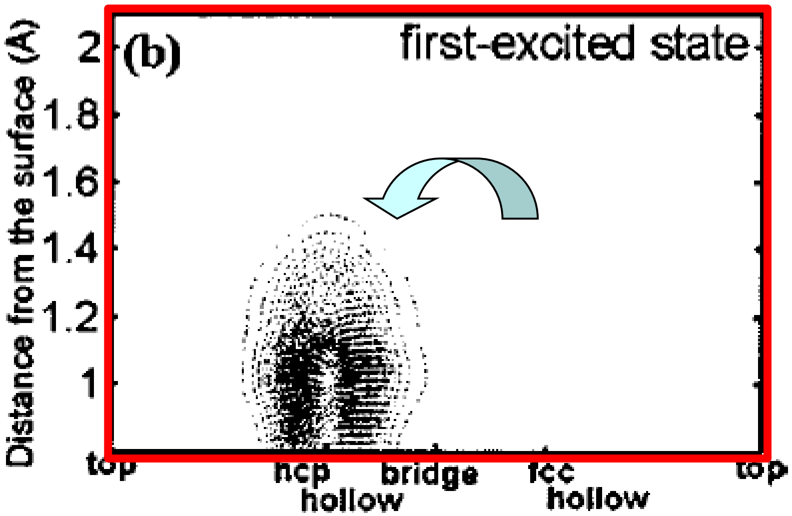
Exp. 129meV by HREELS

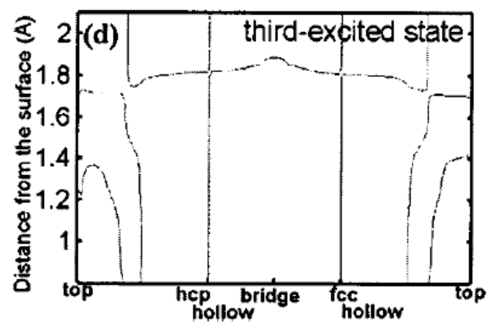
K. Nobuhara et al., J. Appl. Phys. 96 (2004) 5020.

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

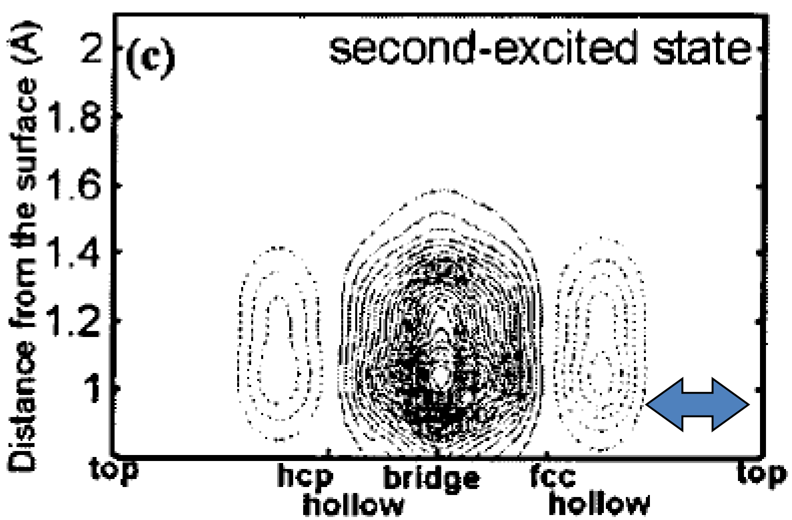
The excited states

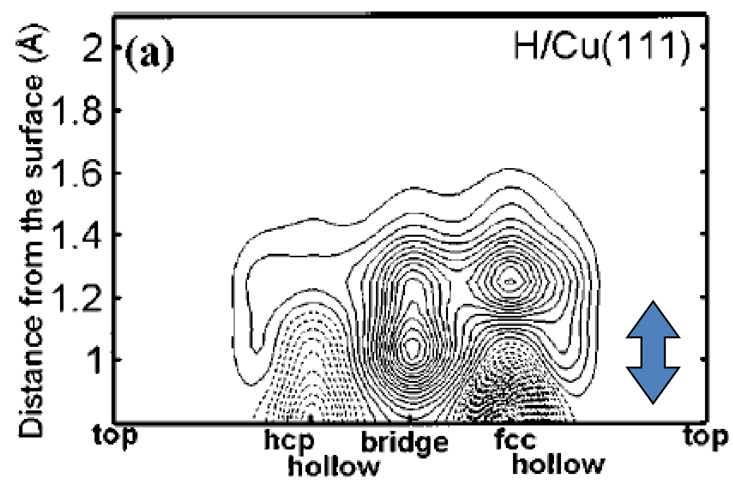






E_4-E_0=135meV





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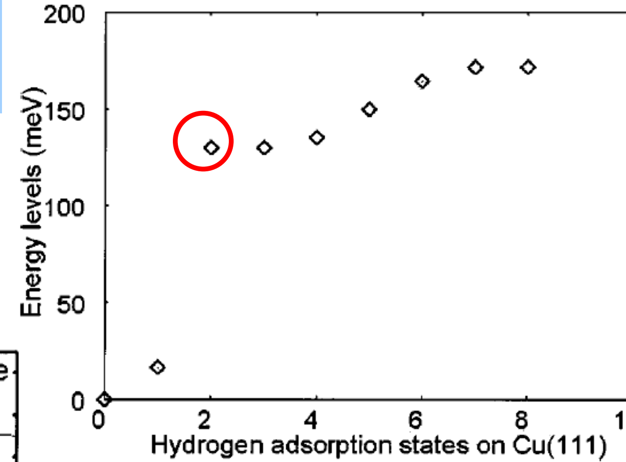
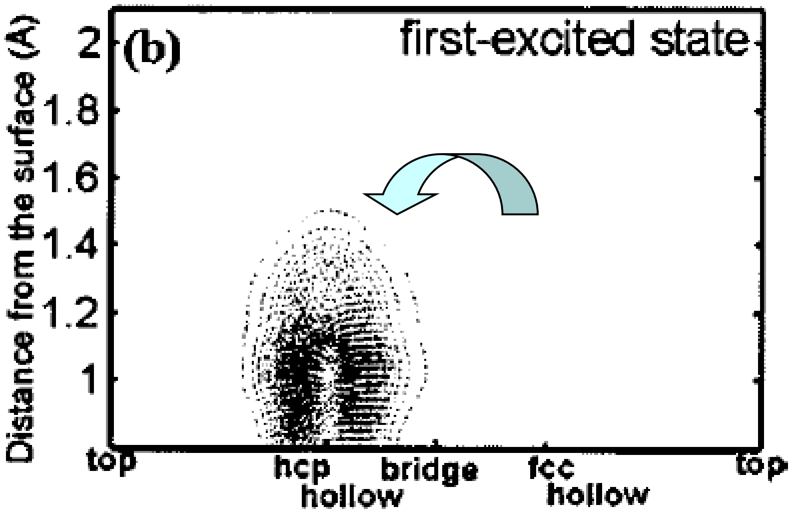
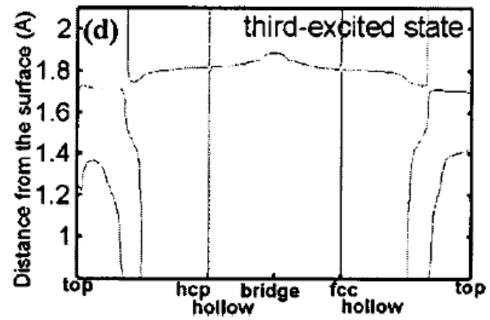
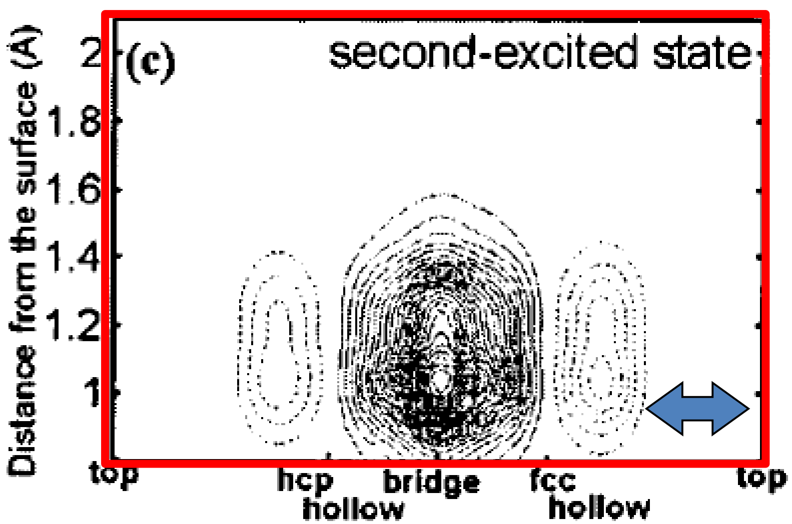
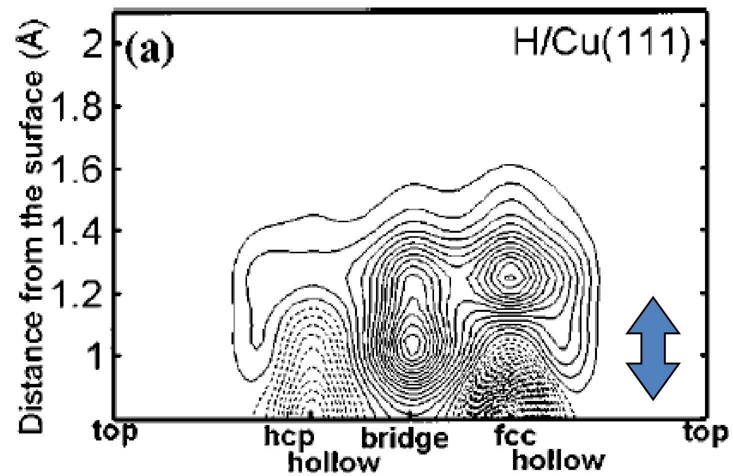






$E_4-E_0=135\text{meV}$





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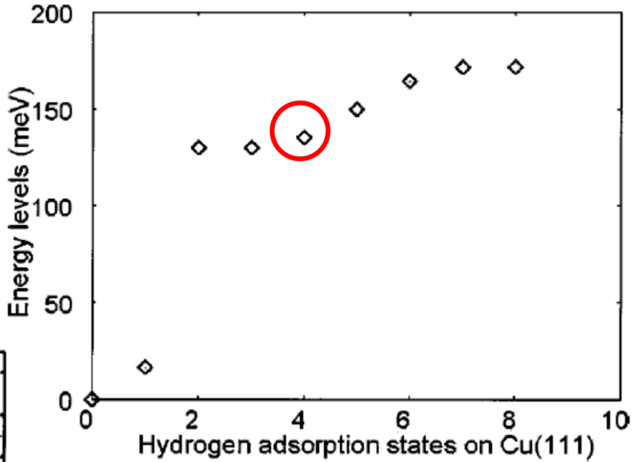
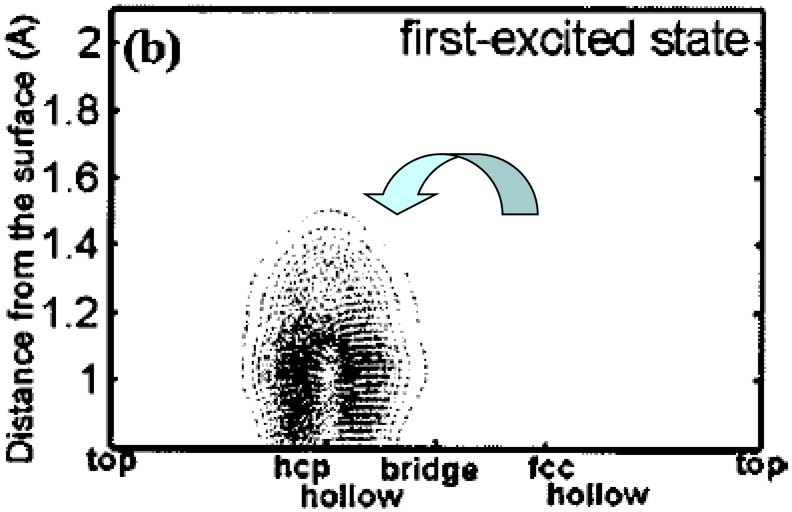
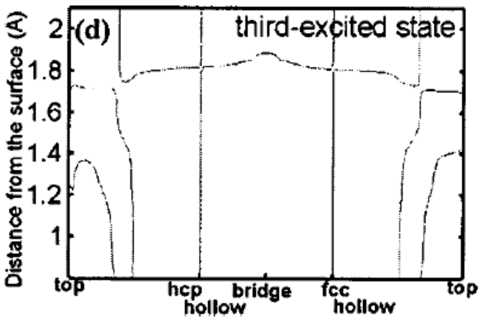
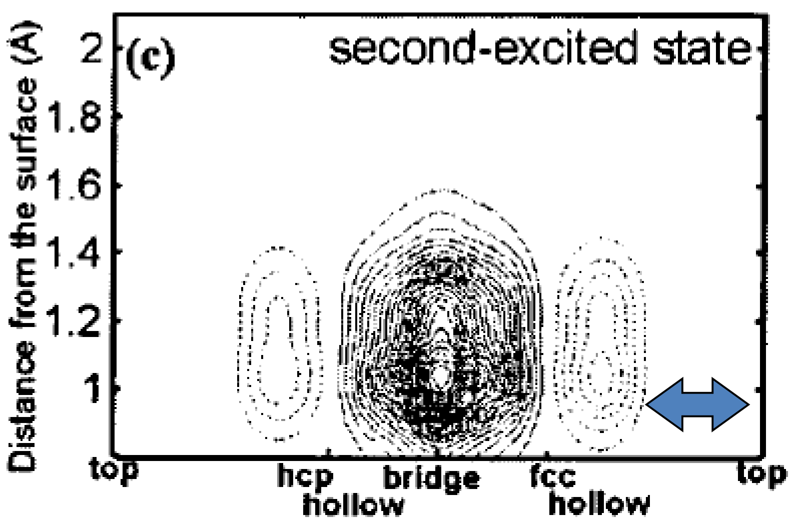
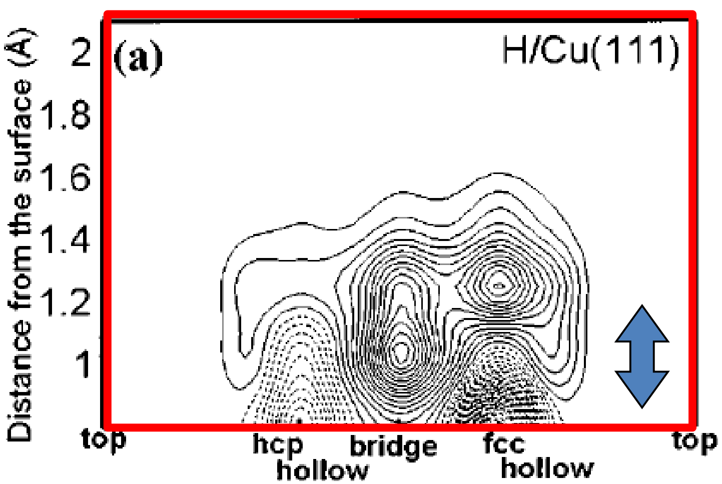






E_4-E_0=135meV



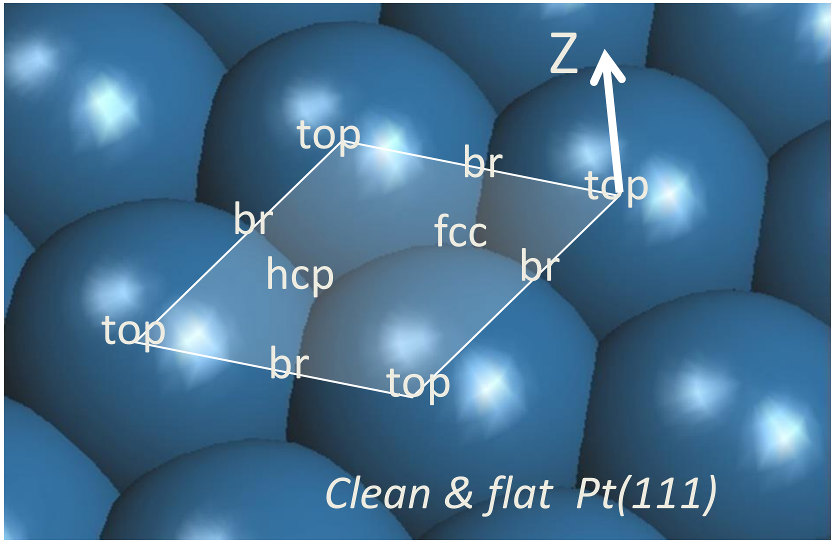


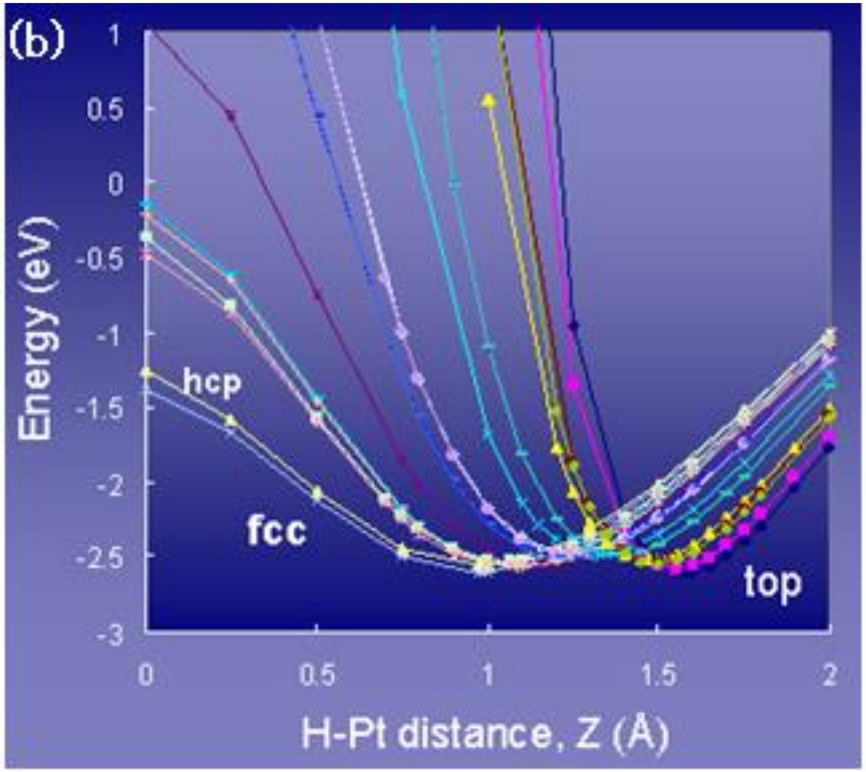
Exp. 129meV by HREELS

K. Nobuhara et al., J. Appl. Phys. 96 (2004) 5020.

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

Potential energy surface of H motion on Pt(111)



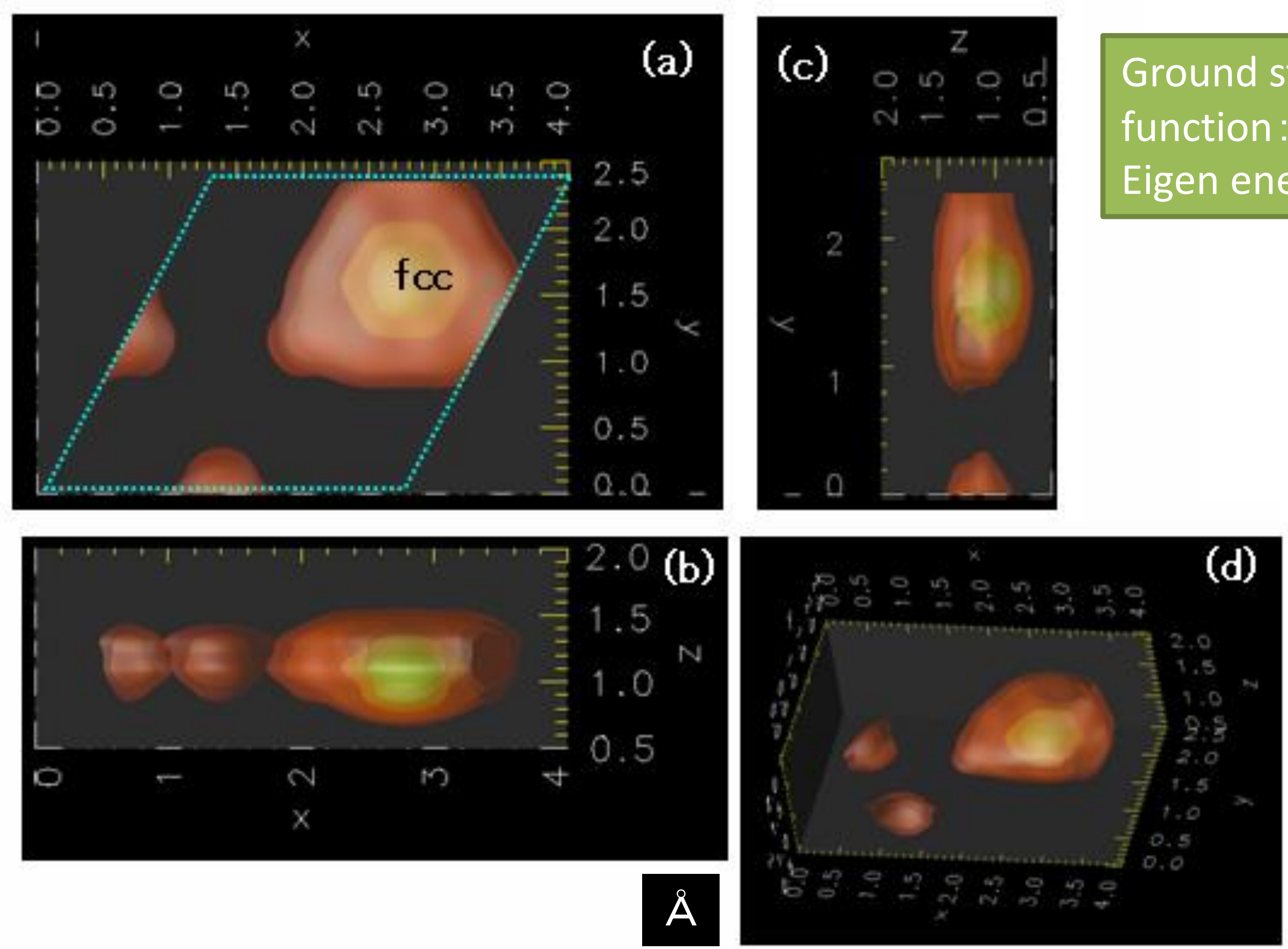


H atom adsorption energy well depths：
Top：2.609 eV、 fcc hollow： 2.607 eV、 hcp hollow： 2.562 eV

Most stable adsorbed site is On-top site !?

Quantum mechanical effects for hydrogen motions

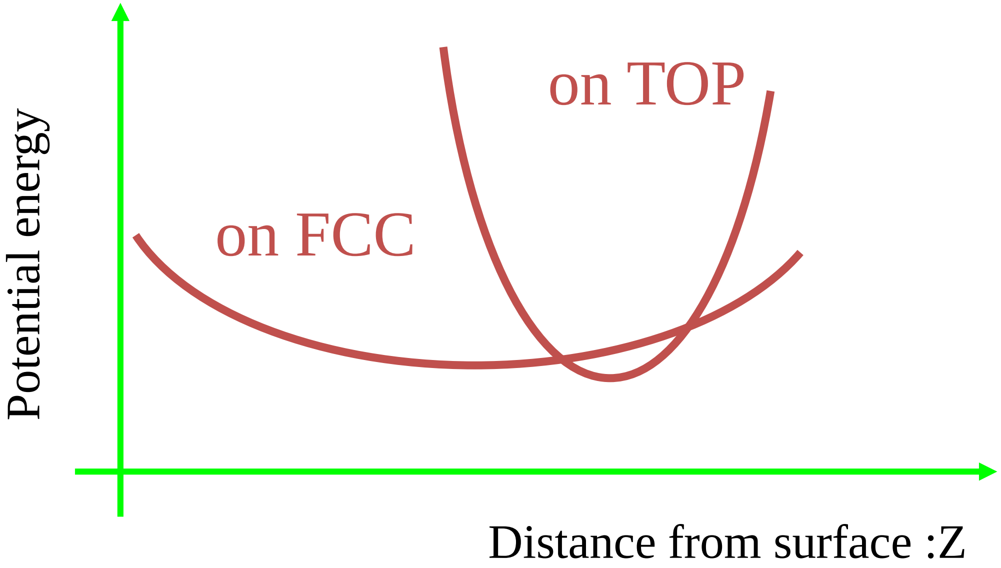
Ground state of hydrogen motion on Pt(111) surface



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

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?

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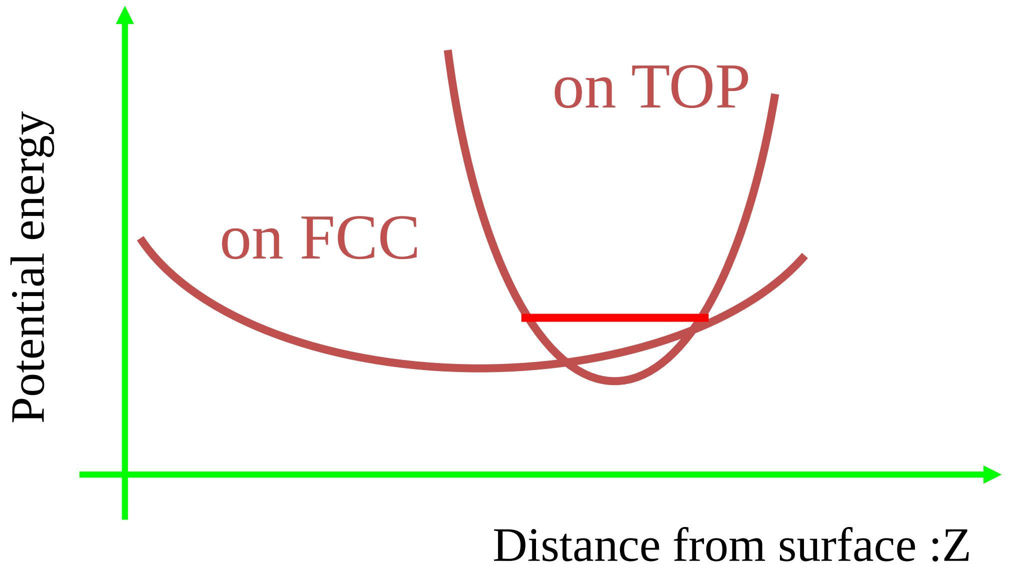


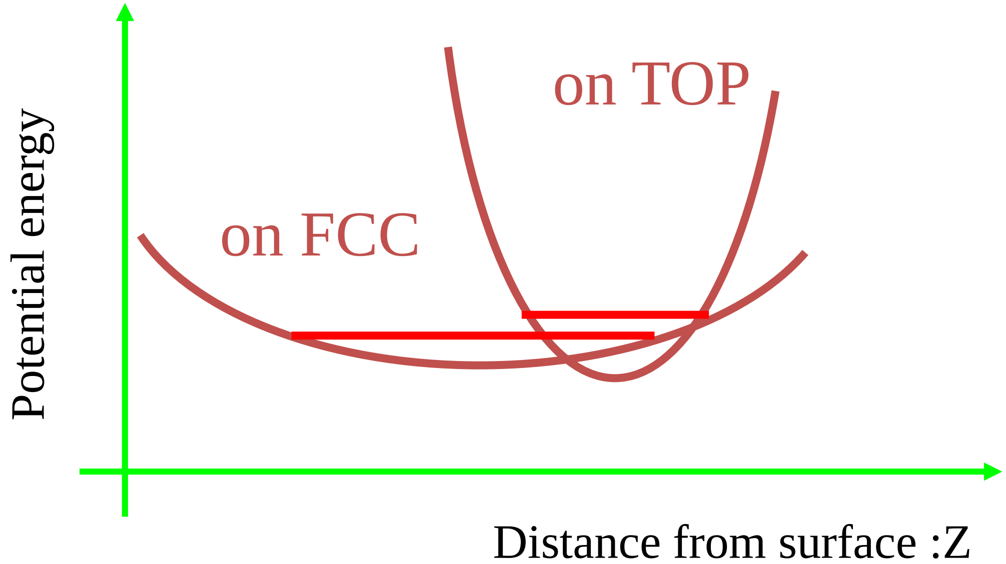
Heisenberg uncertainty principle

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

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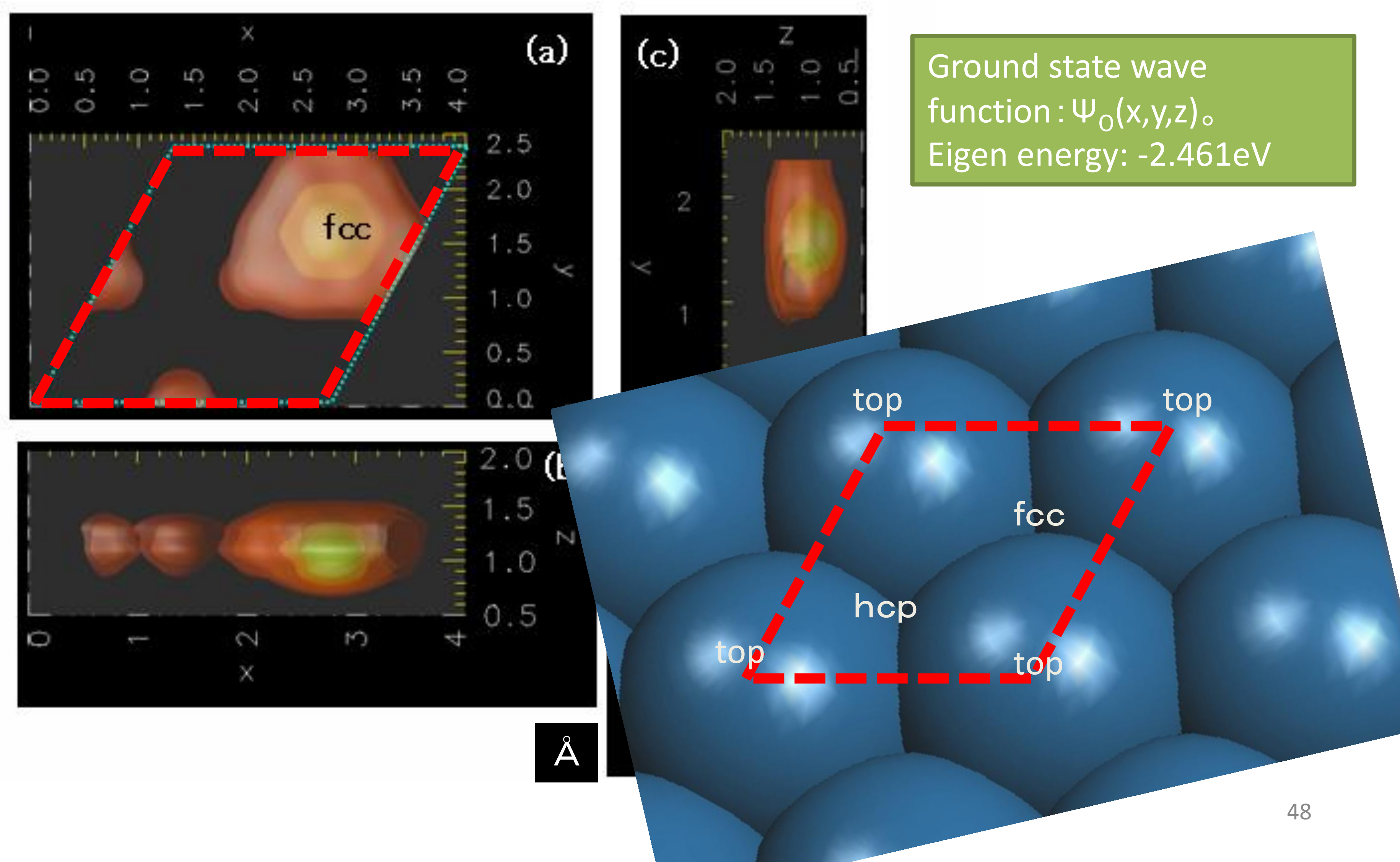
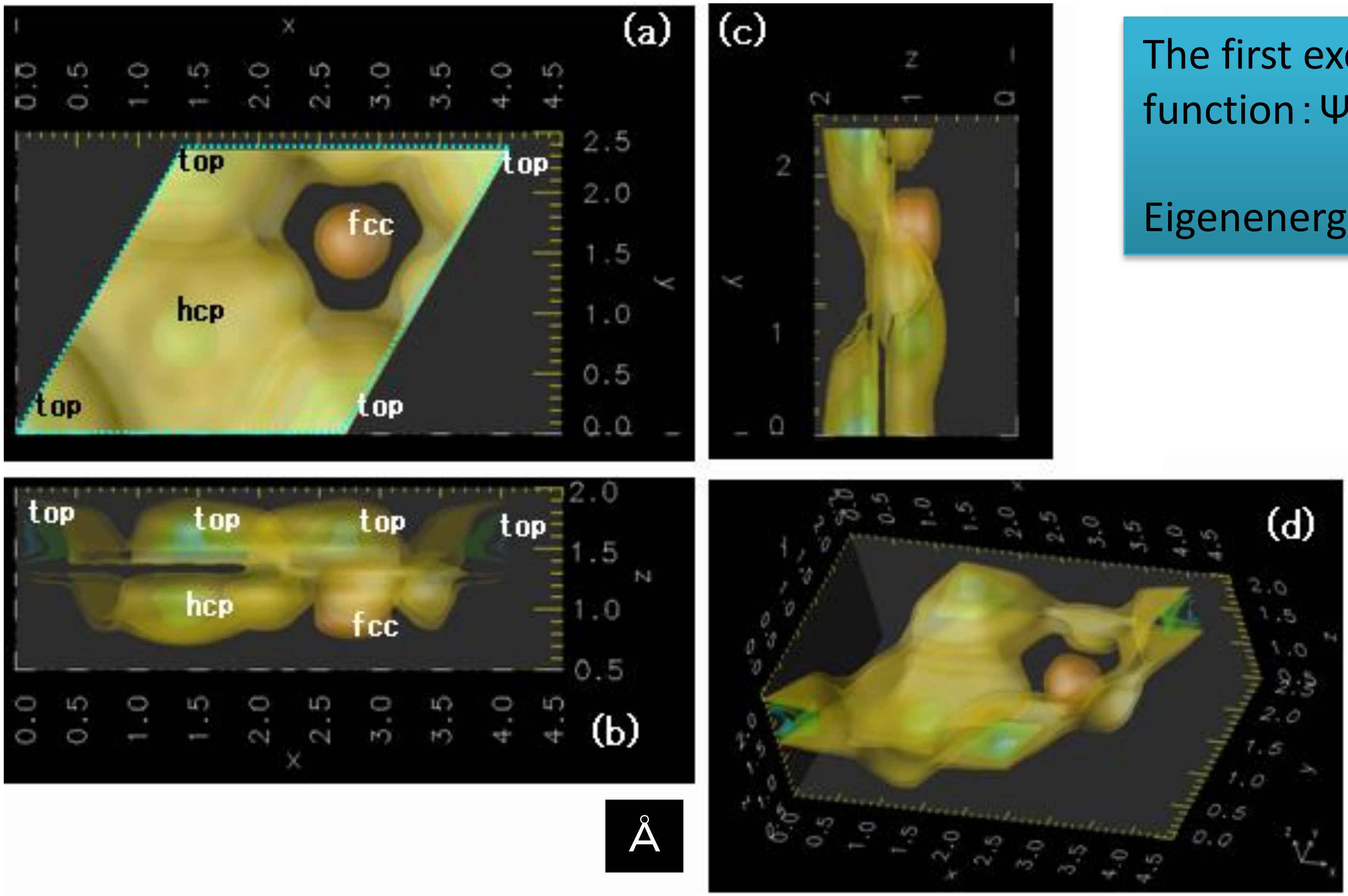
Ground state wave function : $\Psi_0(x,y,z)$。
Eigen energy: -2.461eV



As for migration of H atom on the electrode surface

The 1st excited state wave function expands on the surface

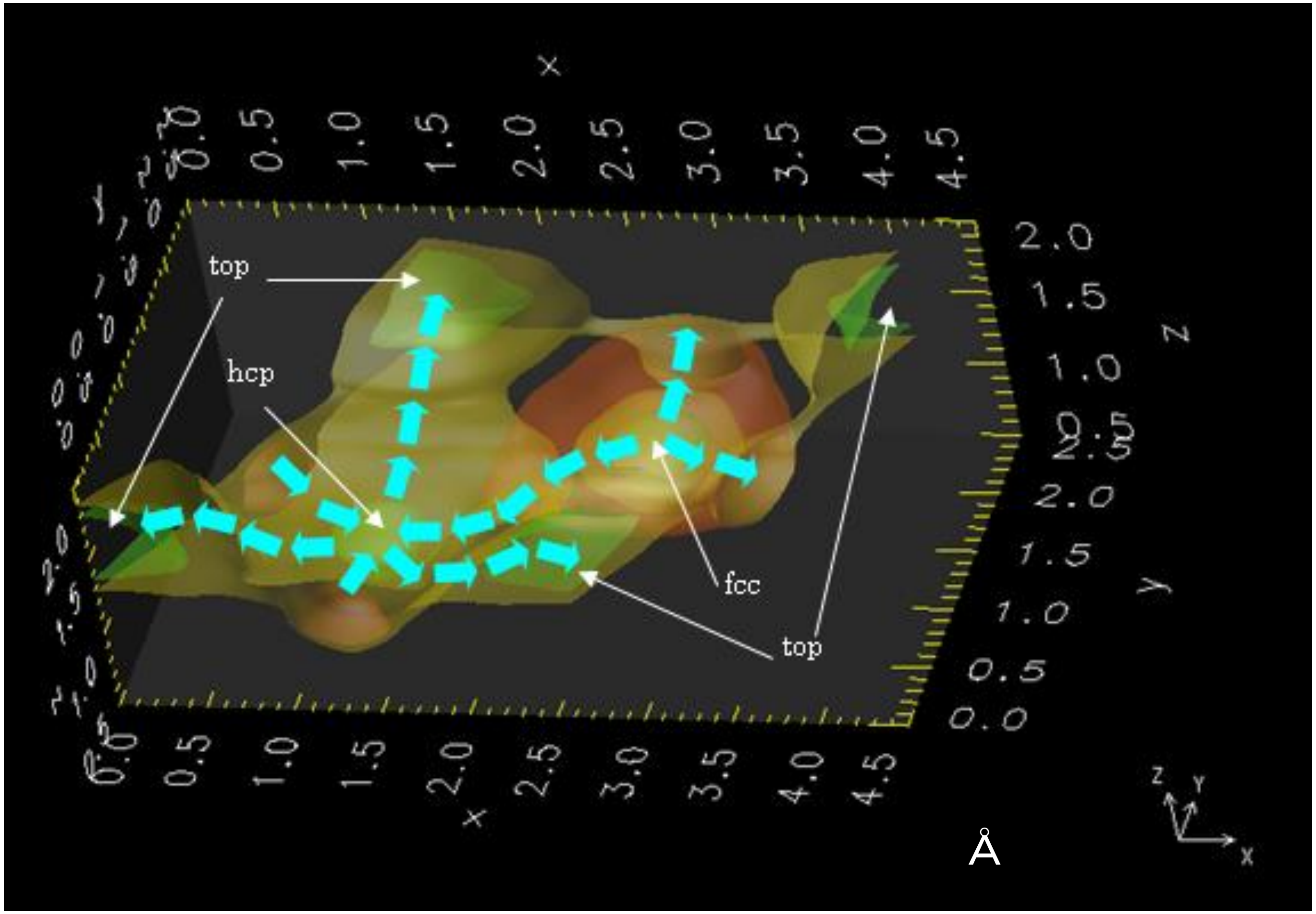


The first excited state wave function : $\Psi_1(x,y,z)$。

Eigenenergy: -2.431eV

Energy difference between first and ground state:

E_1-E_0 = 30 meV



Diffusion can occur at typical fuel cell operational temperature !

Naniwa codes

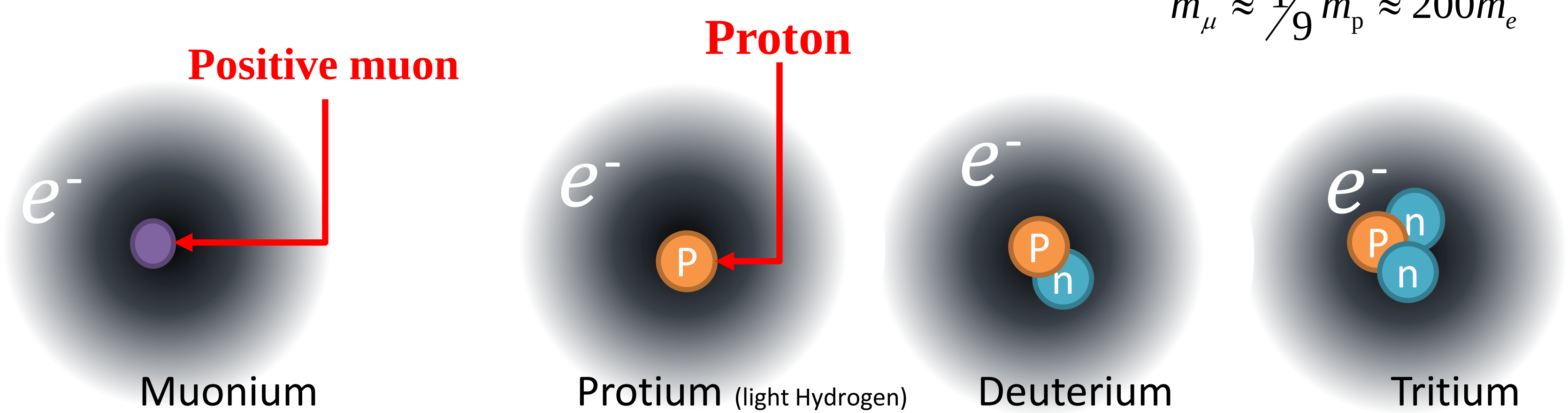
- Positive muon is also one of our target quantum particles as hydrogen isotope, which is useful as a magnetic probe in the materials, mu-SR.

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

$$m_\mu \approx \tfrac{1}{9} m_\mathrm{p} \approx 200 m_e$$

$$m_\mathrm{p} > m_\mu >> m_e$$

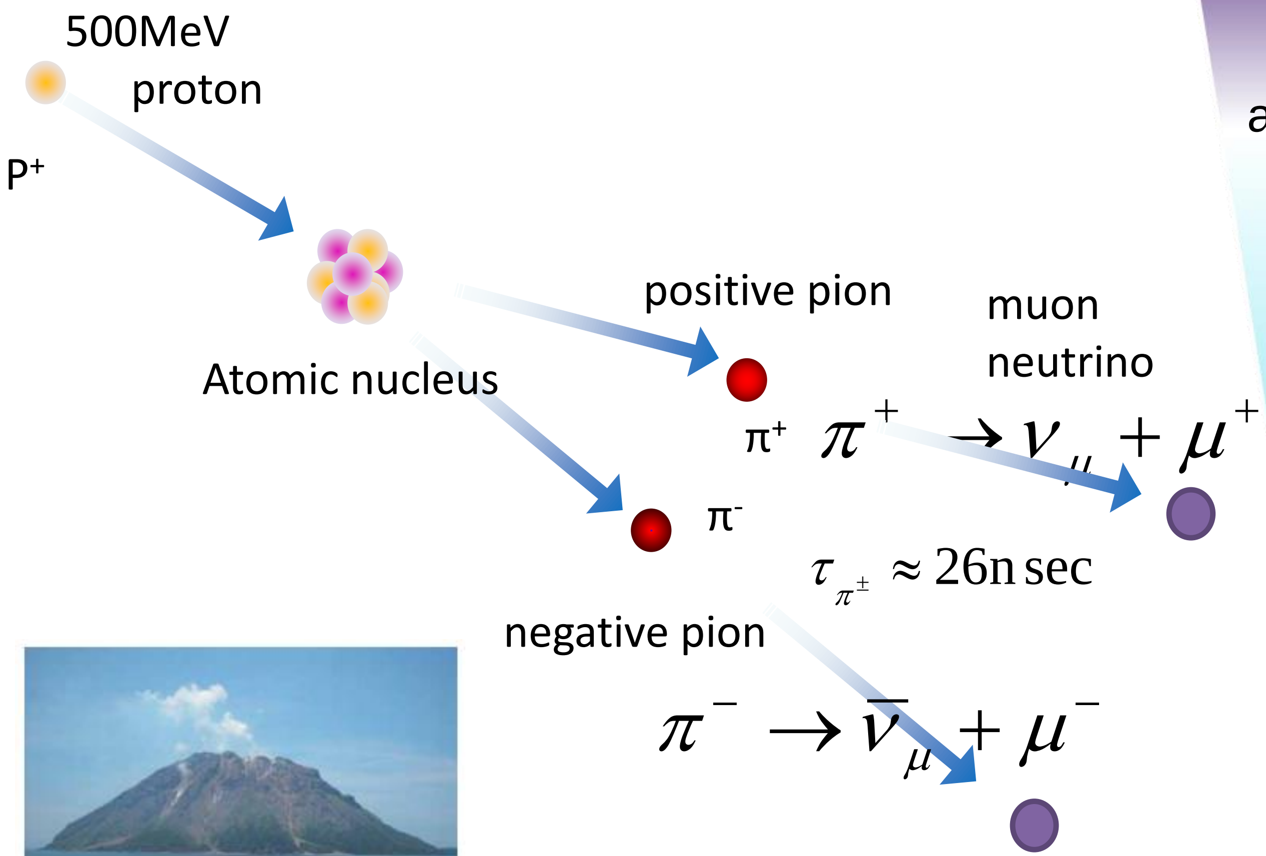
$$m_\mu \approx \tfrac{1}{9} m_\mathrm{p} \approx 200 m_e$$



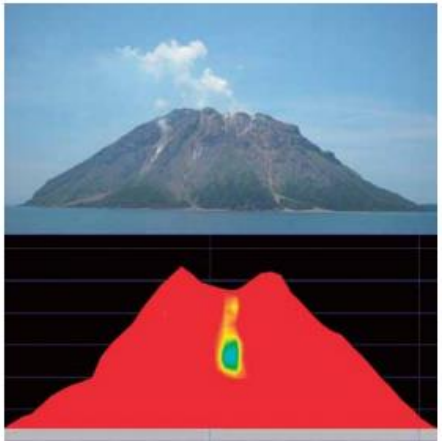
Ionization energy= -13.5403eV , -13.5984 eV

$\mu_e \approx 0.99512 m_e$ $\mu_e \approx 0.99946 m_e$ $\mu_e \approx 0.99973 m_e$ $\mu_e \approx 0.99982 m_e$

How to get the positive-muon ?

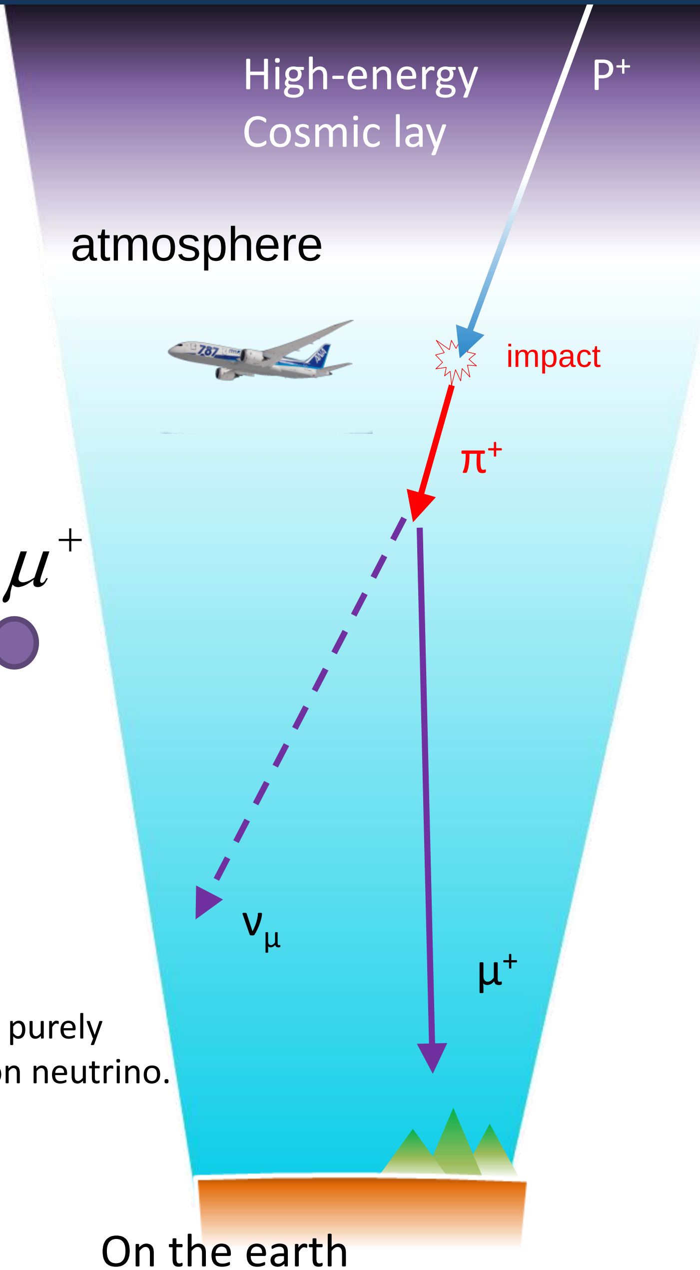


The primary decay mode of a pion is a purely leptonic decay into a muon and a muon neutrino.

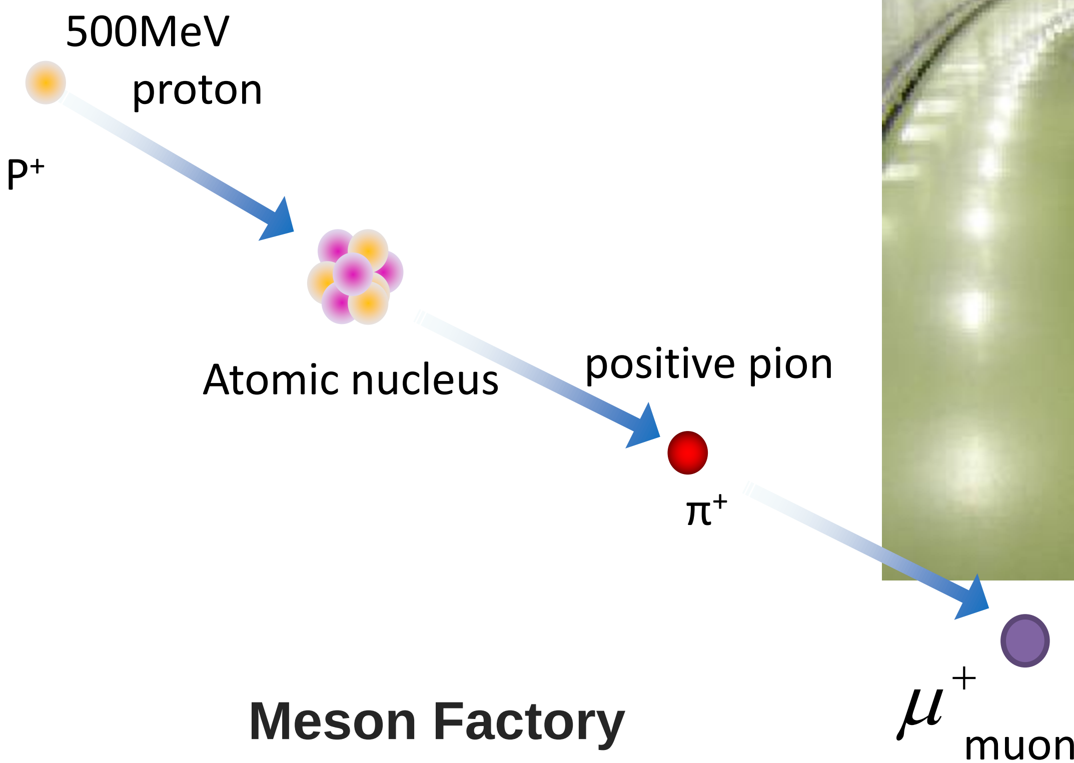


Magma image in volcano by muon

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



How to create the positive-muon ?



Meson Factory

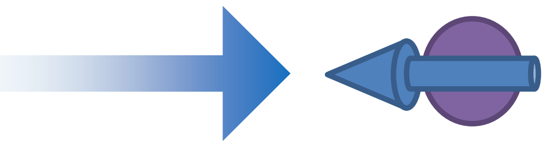
Japan Proton Accelerator Research Complex

20 muons/ (ϕ3mm spot)・sec

～2,000,000 muons/m^2・min

(Anti) muon μ^{+}

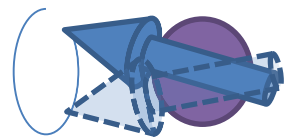
positron emission



Spin: $^{1}/_{2}$

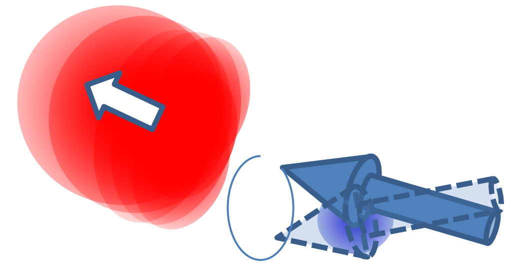
the created muon is 100% spin polarized

------->



precession movement
in the magnetic filed

------->

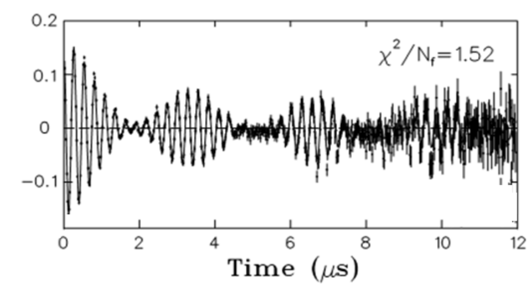


Muon spin spectroscopy : μSR

$$\mu^{+} \rightarrow e^{+} + \nu_{\mathrm{e}} + \overline{\nu}_{\mu}$$

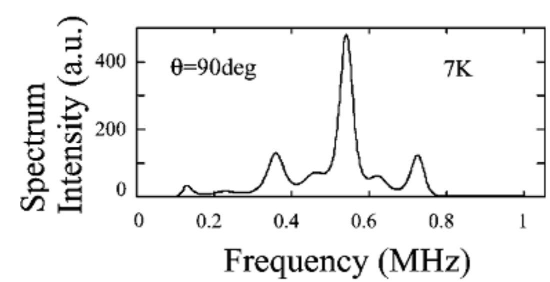
Positron | electron neutrino | Antimuon neutrino

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



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

gyromagnetic ratio of muon: $\dfrac{\gamma}{2\pi} = 135.53\,\mathrm{MHz/T}$



K. Shimomura et al., Phys. Rev. Lett. 89 (2002) 255051.

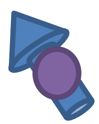
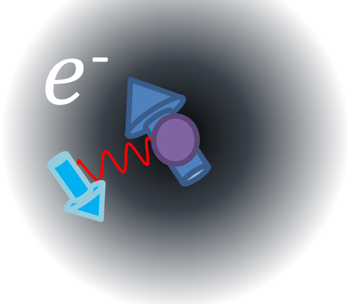
μSR muon spin rotation method

Gyromagnetic ratio ：135.53 MHz/T

We can measure the magnetic filed around muon in materials

Effective Magnetic interaction =

Hyperfine interaction between muon spin and electron spin.

	Muon	Muonium = muon + electron
		
Hyperfine interaction:		4463 MHz
gyromagnetic ratio:	135.53 MHz/T	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

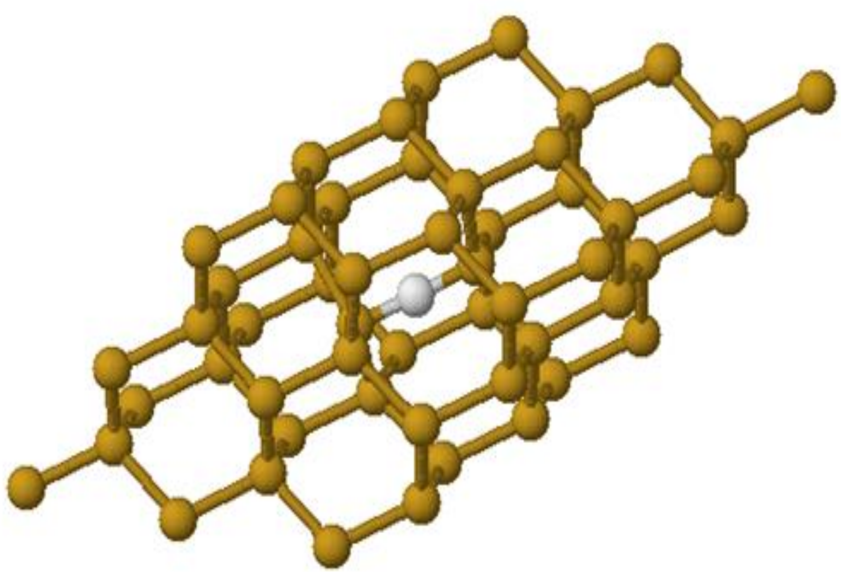
Experimental results of μSR suggests two type of muon site.

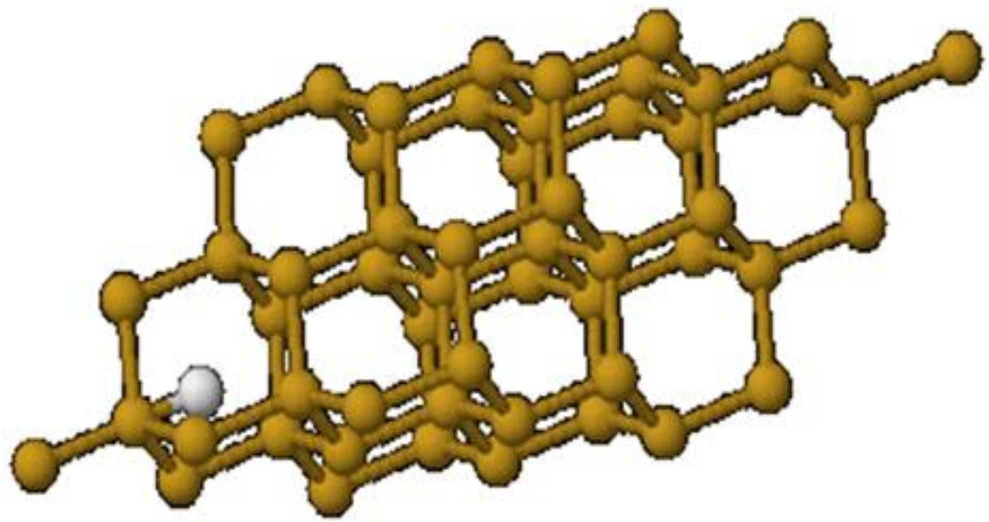
hyperfine constant

BC-site (Bond center): very low frequency → shallow donors

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

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





BC-site

3x3x3
54 Si atoms

T-site

Muon in the Si crystal

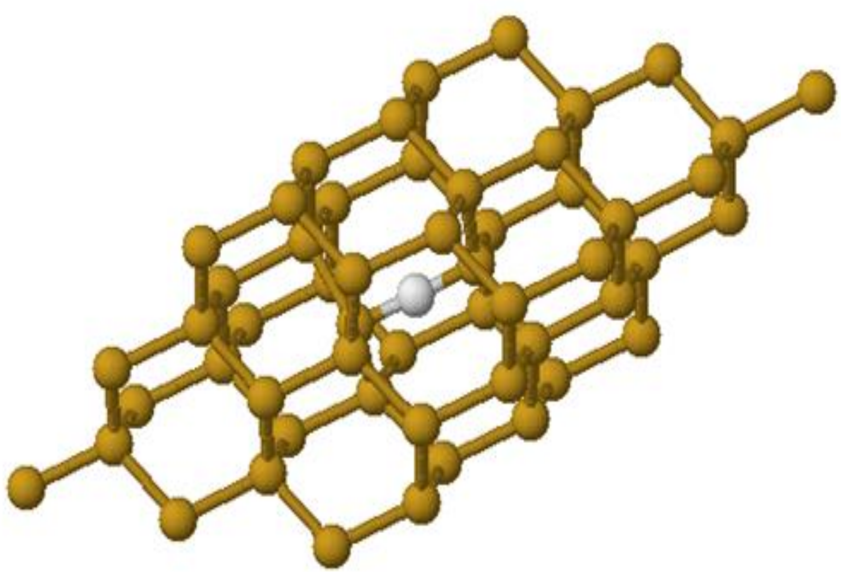
Experimental results of μSR suggests two type of muon site.

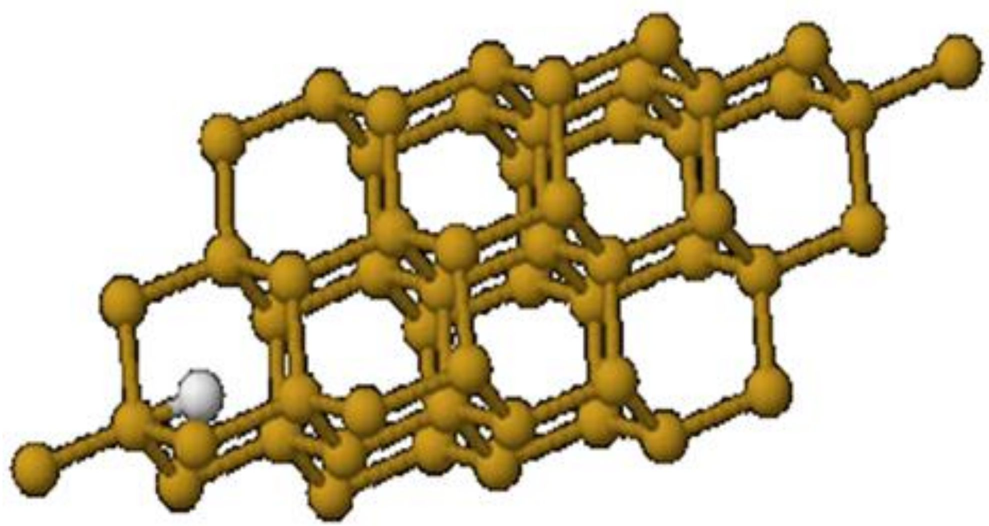
hyperfine constant

BC-site (Bond center): very low frequency → shallow donors

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

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





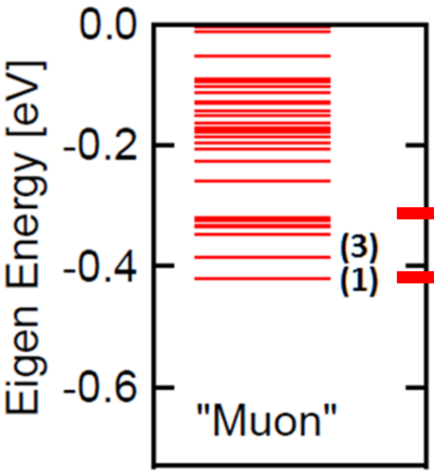
BC-site

3x3x3
54 Si atoms

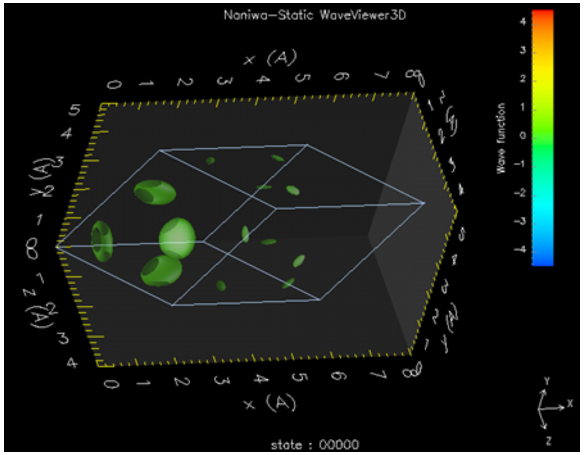
T-site

Naniwa results

diamond structure of Si



Ground state : BC-site

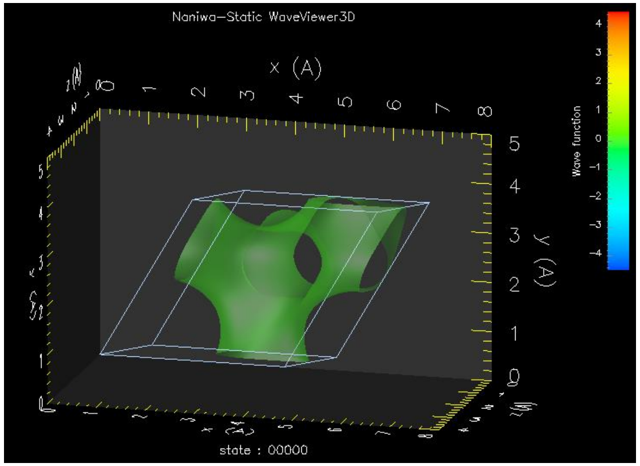


Calculated hyperfine constant

275 MHz

very low frequency

“shallow donor”

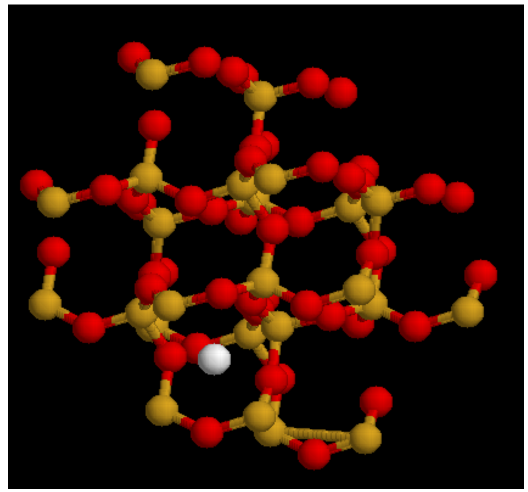


1711 MHz

$\approx 45\%$ of A_0

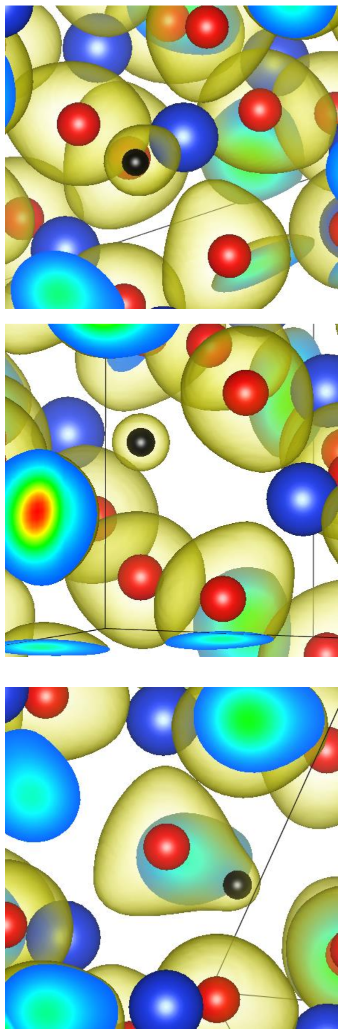
Excited state : T-site

Hydrogen isotope Muon in α-SiO_2 Quartz



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

Hydrogen isotope in α-SiO_2 Quartz



On-Si site

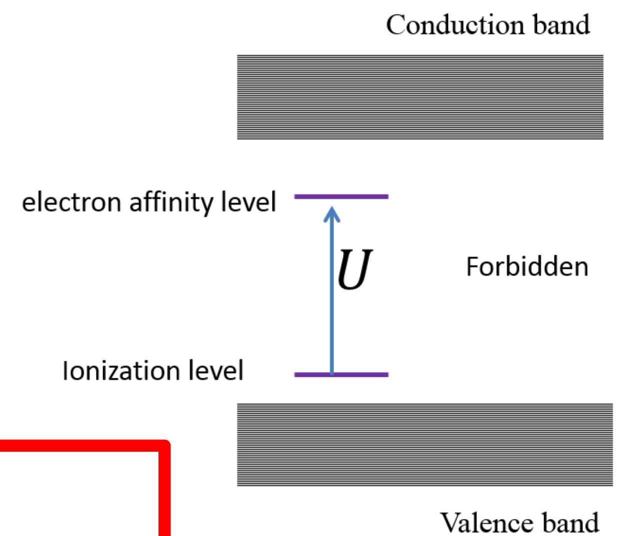
Si^{+}

In cage of SiO_2

$Vac.^{0}$

On-O site

O^{2-}

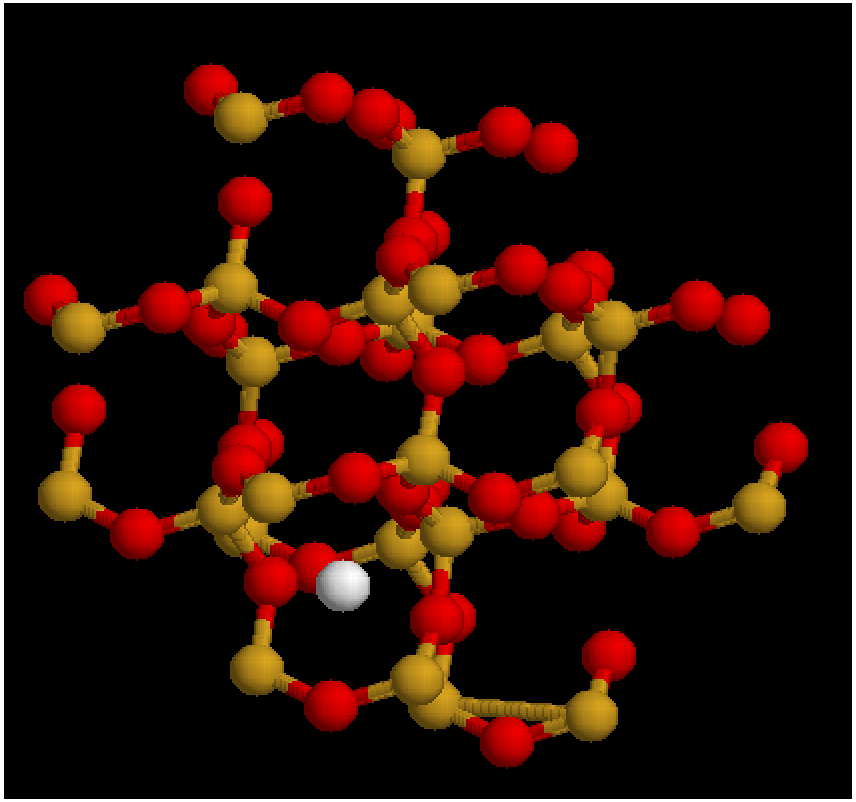


μSR shows the value of
free Muonium $\approx A_0 = 4.46\mathrm{GHz}$

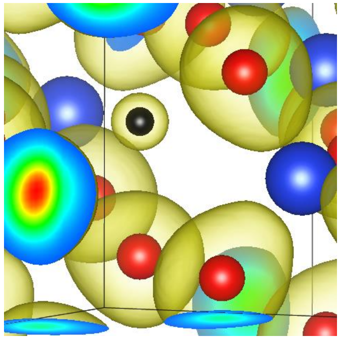
S. F. J. Cox, Rep. Prog. Phys. 72 (2009) 116501.

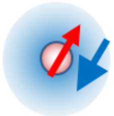
Hydrogen isotope in α-SiO_2 Quartz

2x2x2 cell
- Si: 24 atoms
- O : 48 atoms
- H: 1 atom



4.2% impurity hydrogen





In-cage site

Previous study:

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

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

Unstable ?

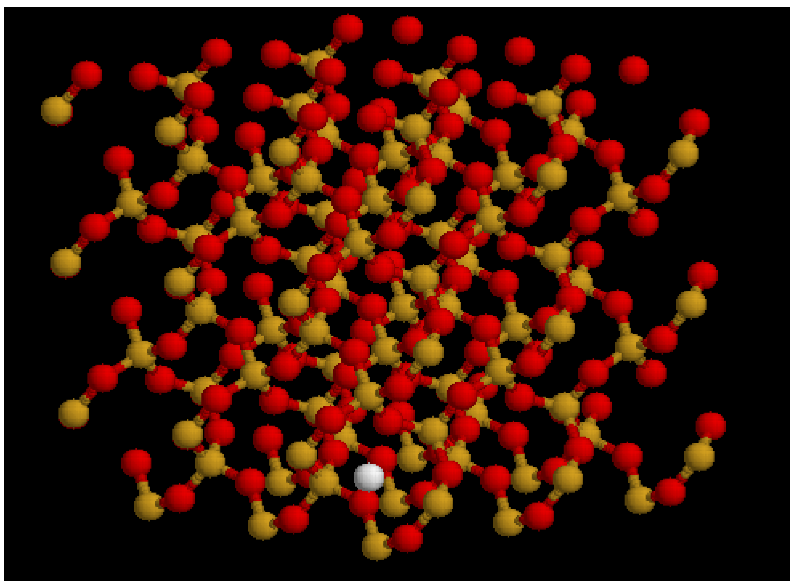
Significant lattice stress effects !?

Hydrogen isotope in α-SiO_2 Quartz

3x3x3 unit cells

Si: 81atoms
O: 162atoms
H: 1atoms

1.2% hydrogen impurity

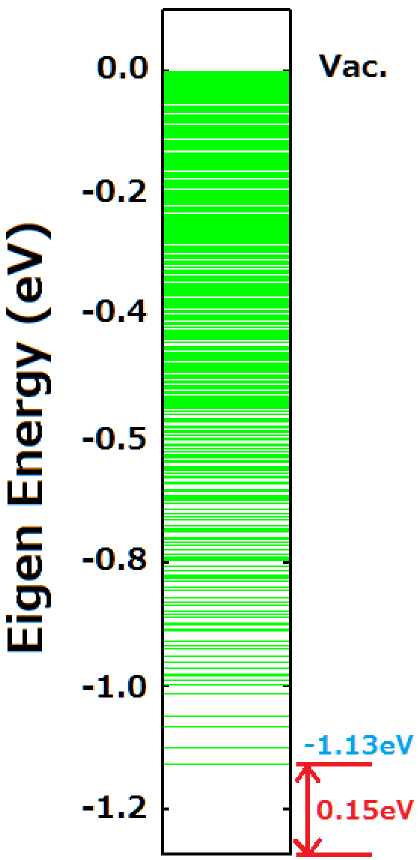


Energy: ΔE= -1.27eV

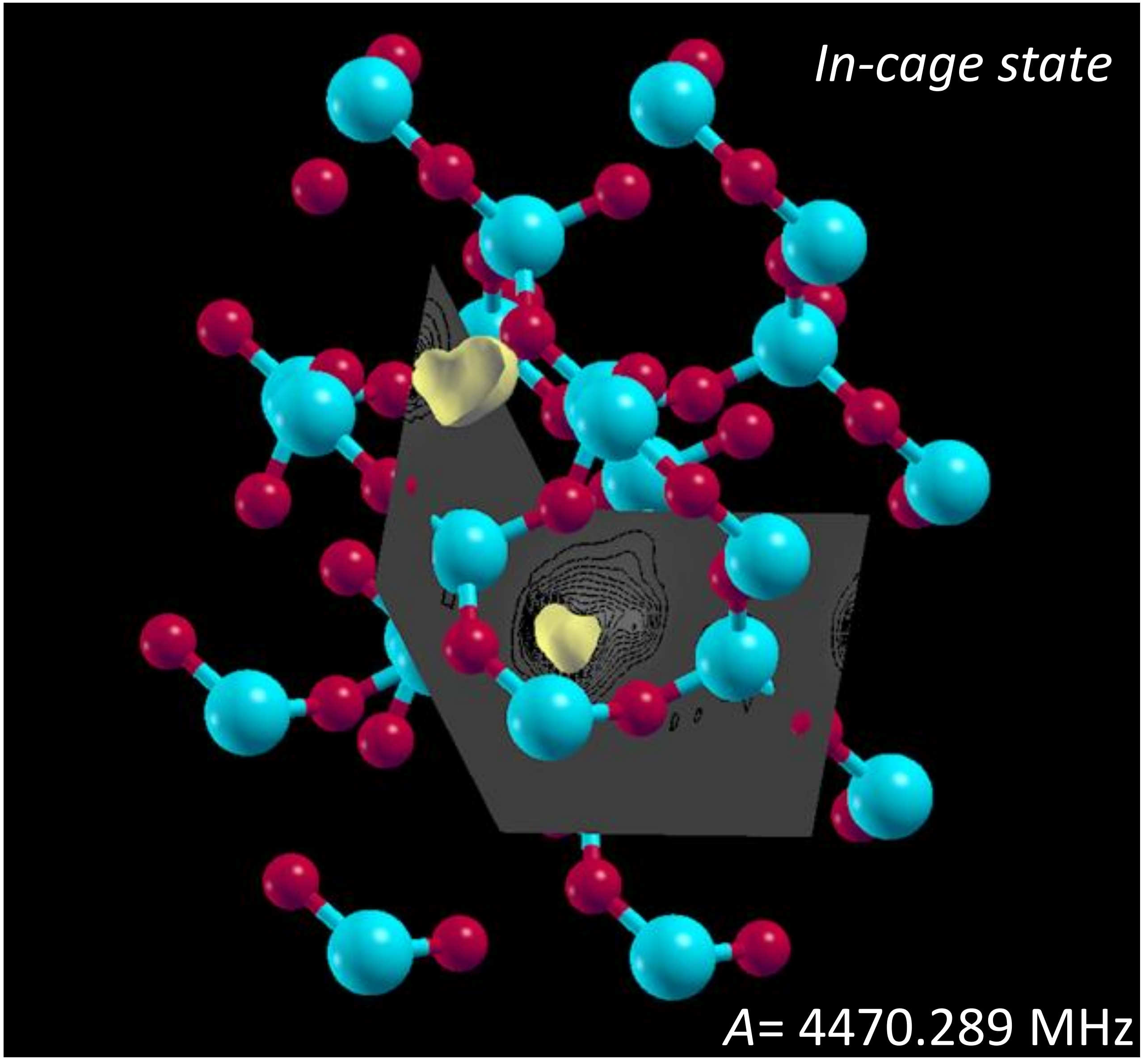
Stable !

Muonium in α-SiO_2 Quartz

Naniwa results

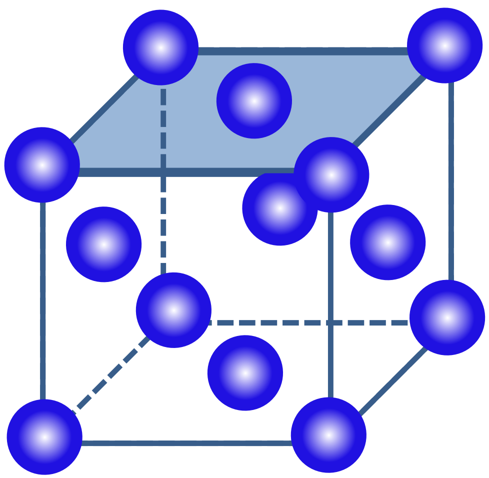


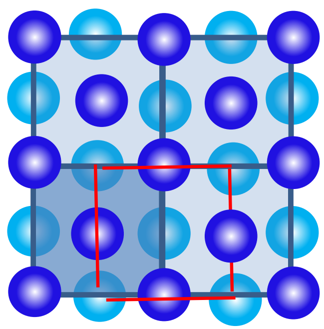
ΔE= -1.13eV



Pd (001) surfaces

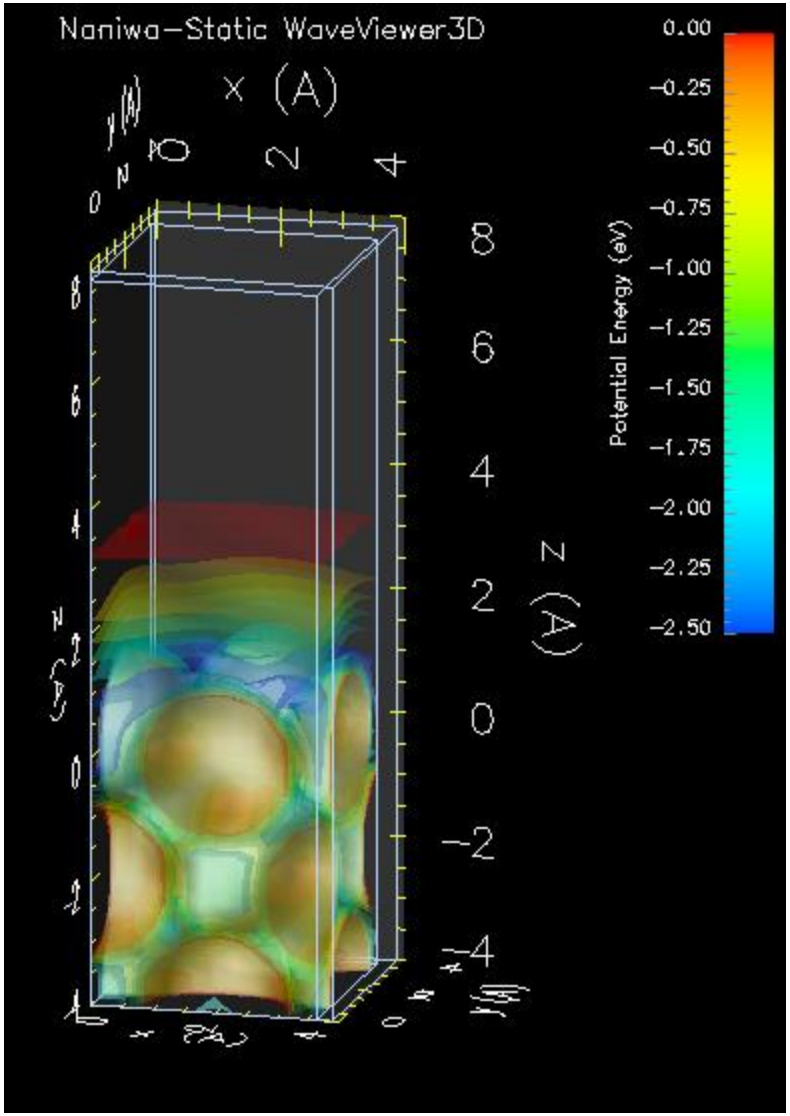
(001) surface





First layer atom

2nd layer atom

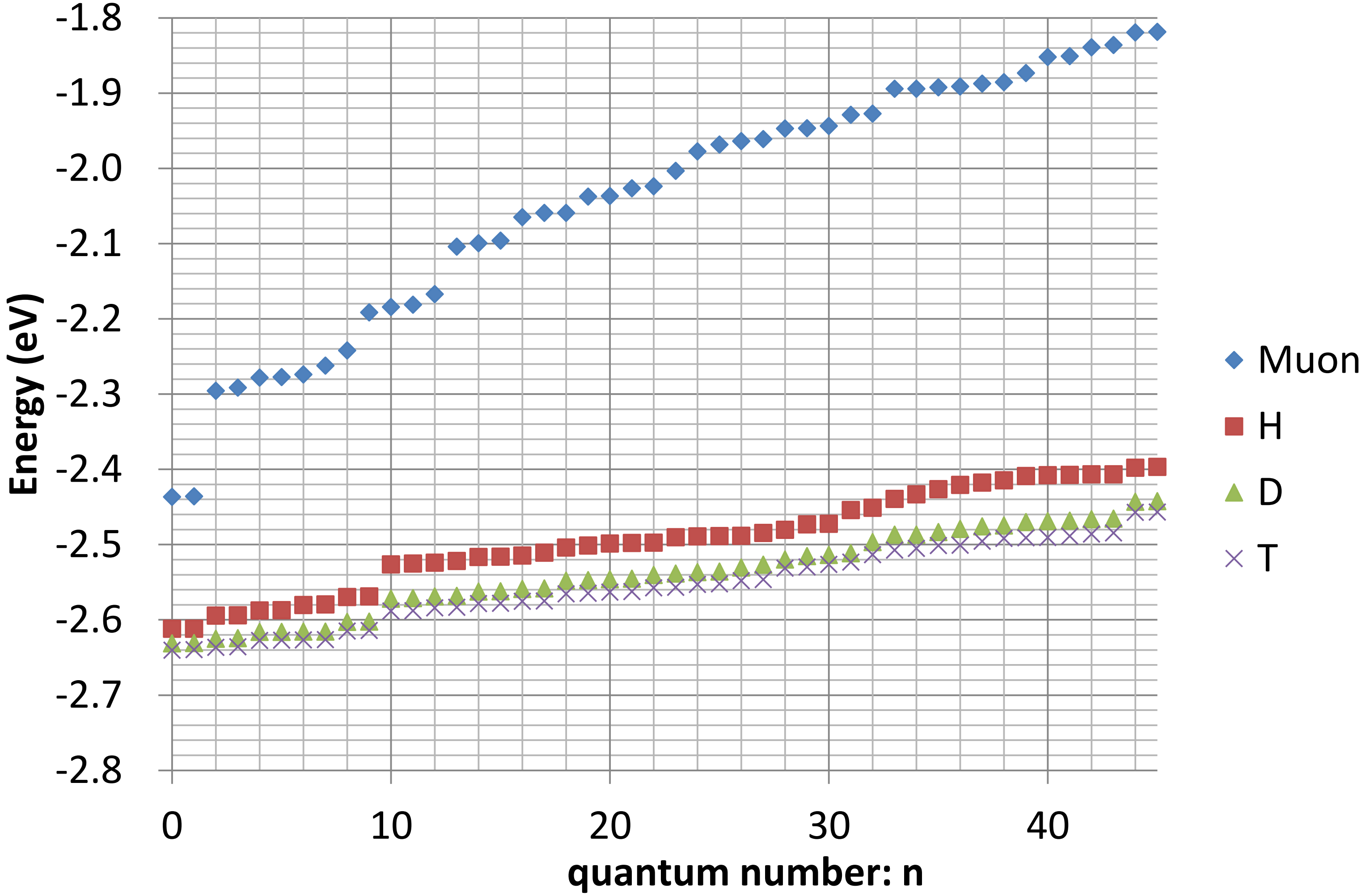


face center cubic (FCC)

lattice constant: 3.99Å (calc.) ,

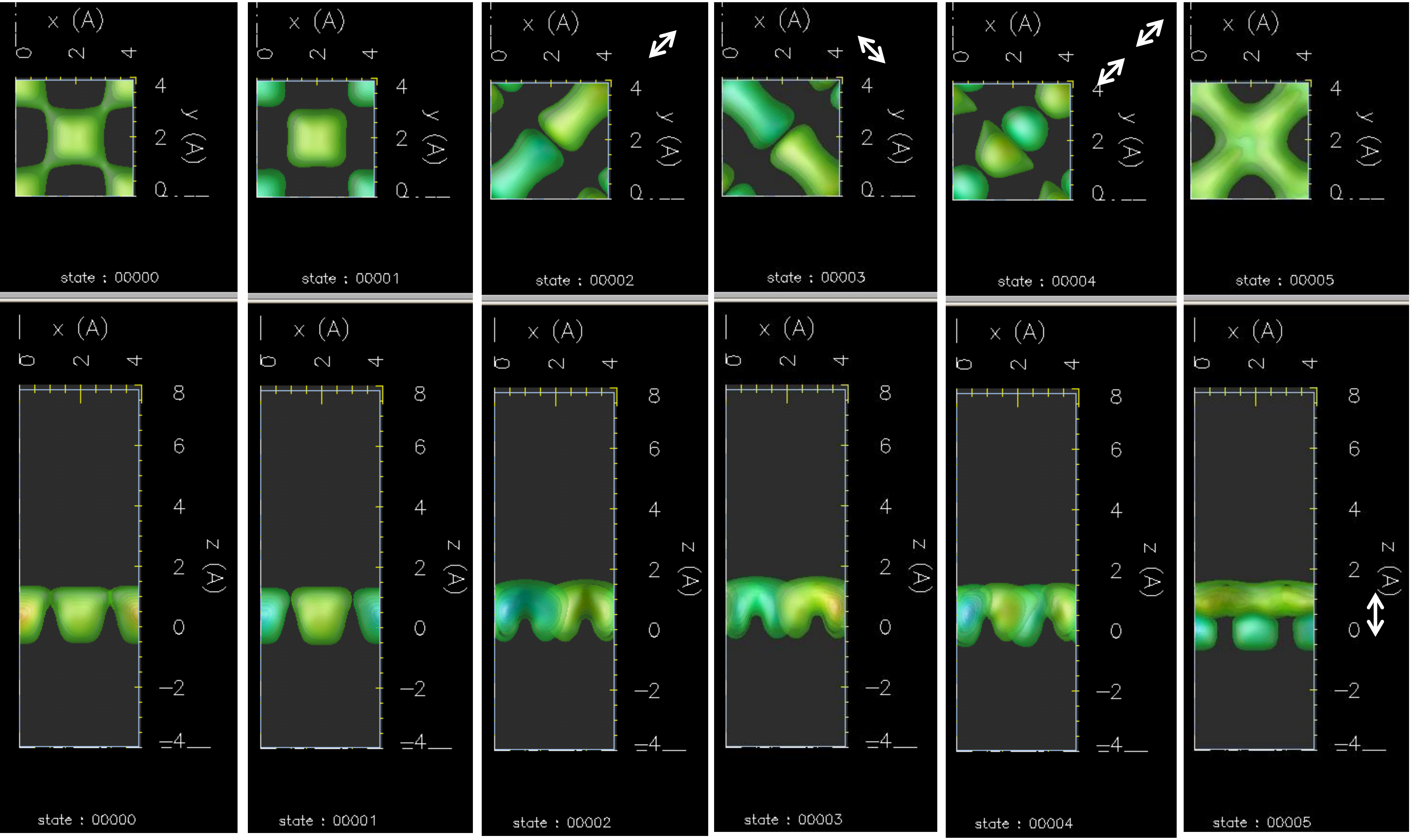
3.89Å (exp.)

μ^+, H, D, T on Pd (001) surfaces



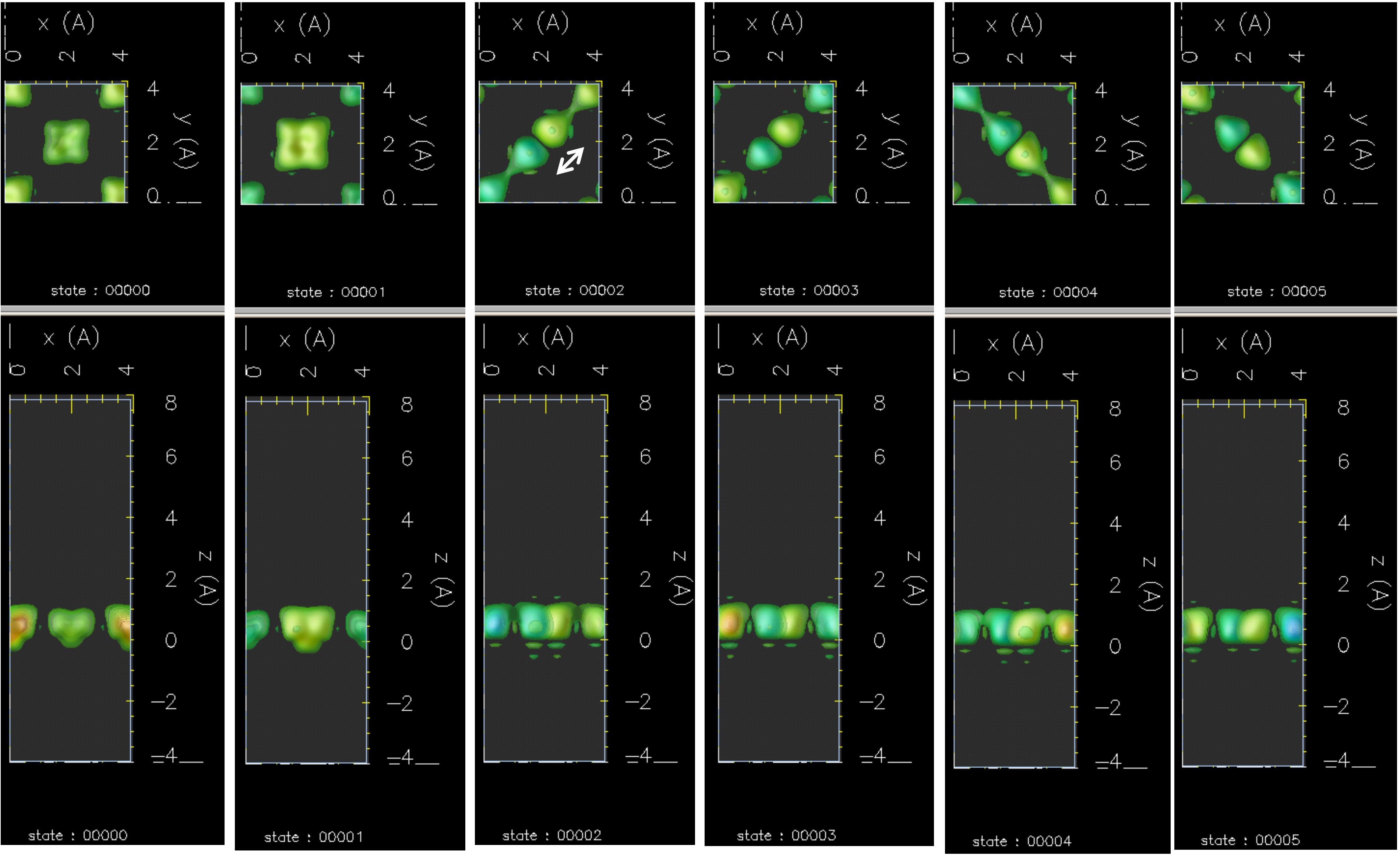
μ^+ on Pd (001) surfaces

Ground state | 1st excited state | 2nd excited state | 3rd excited state | 4th excited state | 5th excited state



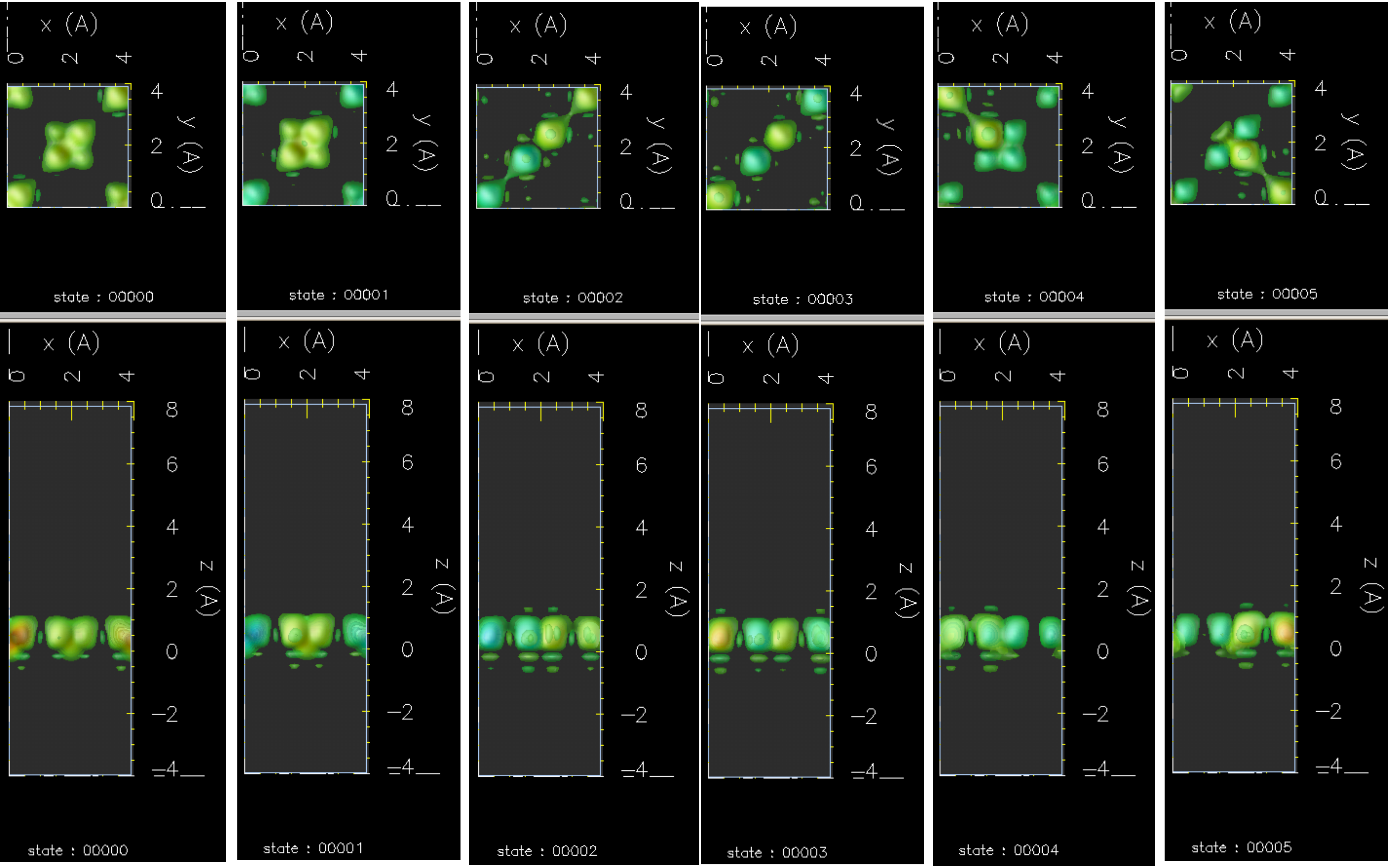
H on Pd (001) surfaces

Ground state | 1st excited state | 2nd excited state | 3rd excited state | 4th excited state | 5th excited state



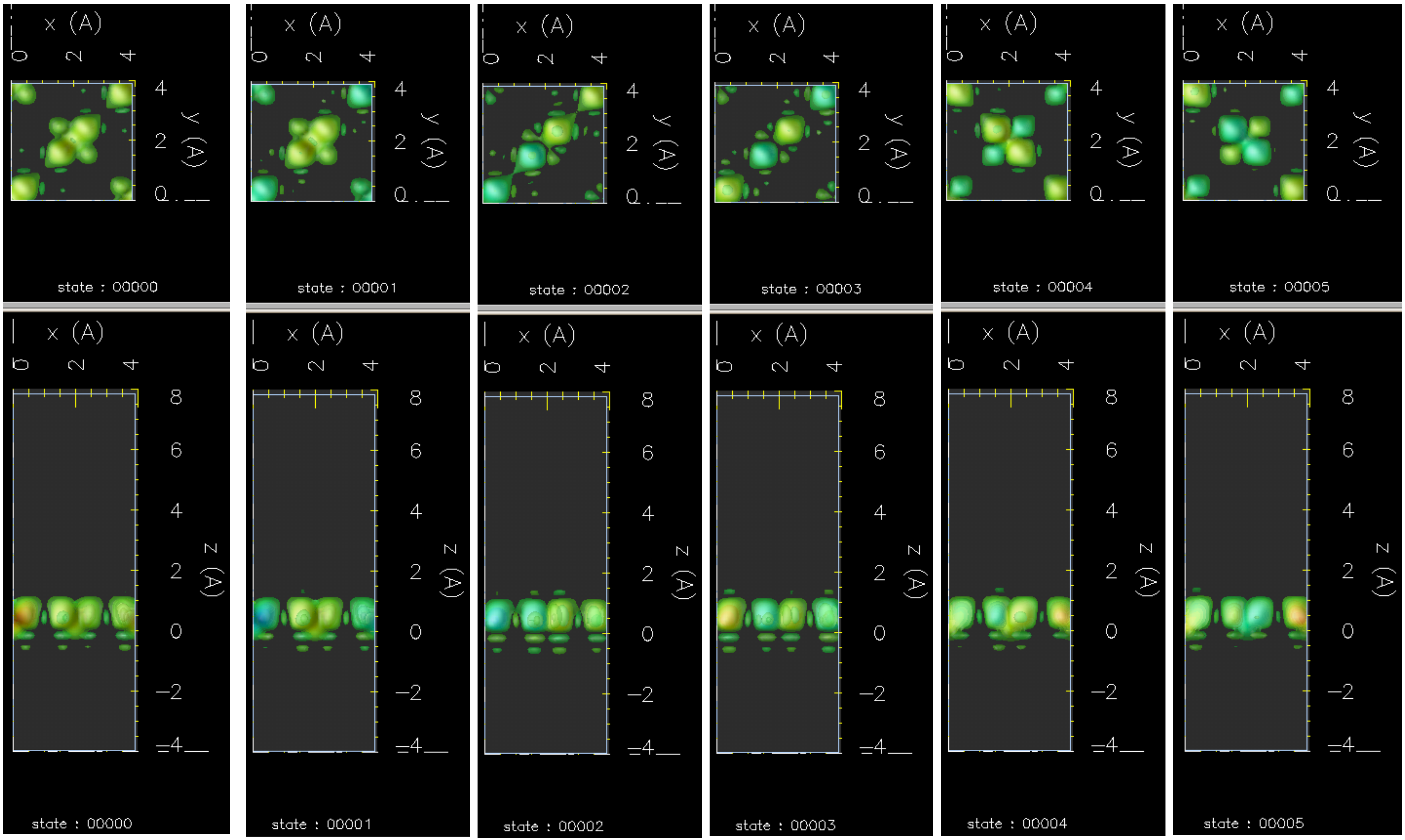
D on Pd (001) surfaces

Ground state | 1st excited state | 2nd excited state | 3rd excited state | 4th excited state | 5th excited state

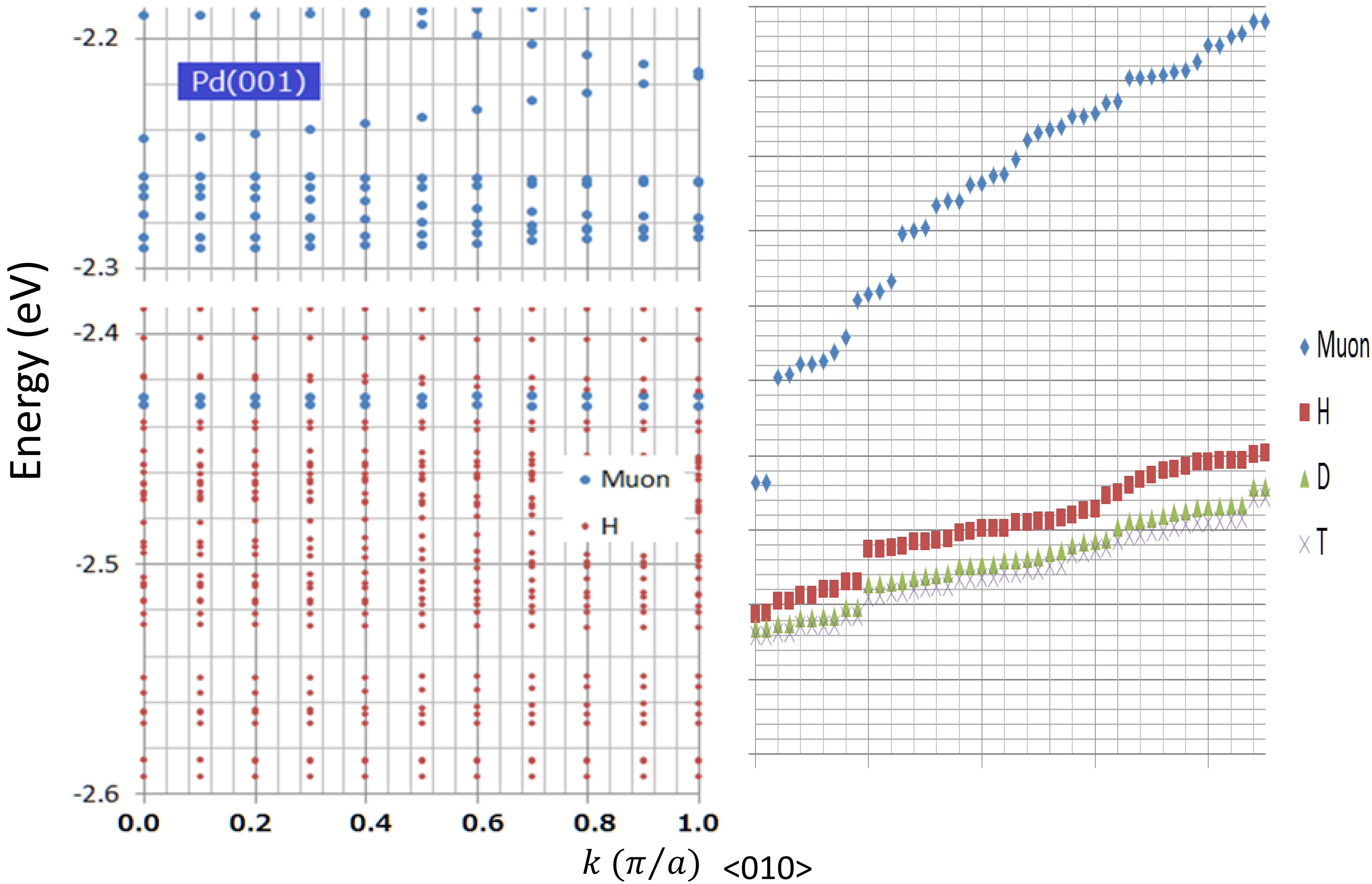


T on Pd (001) surfaces

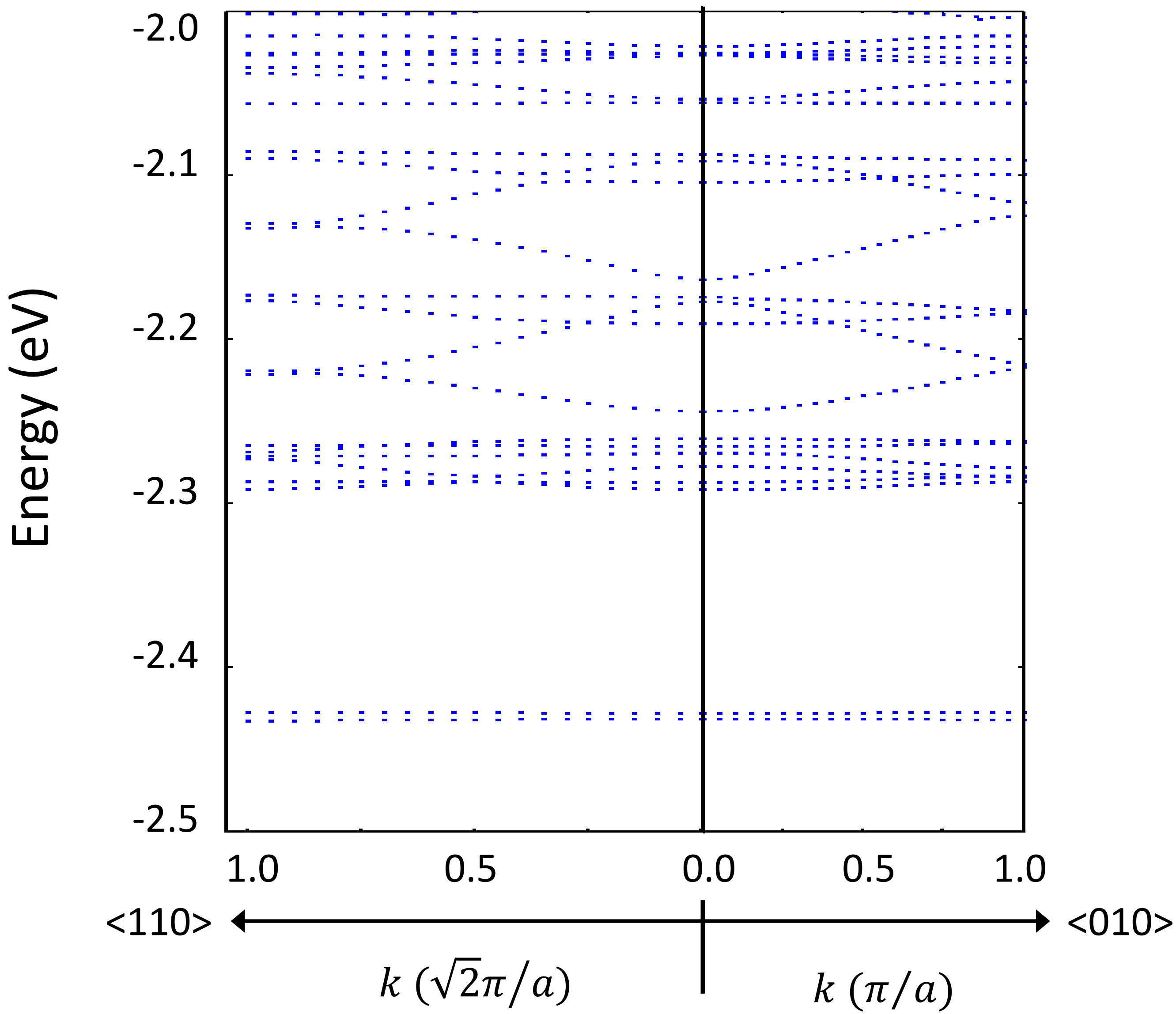
Ground state	1st excited state	2nd excited state	3rd excited state	4th excited state	5th excited state



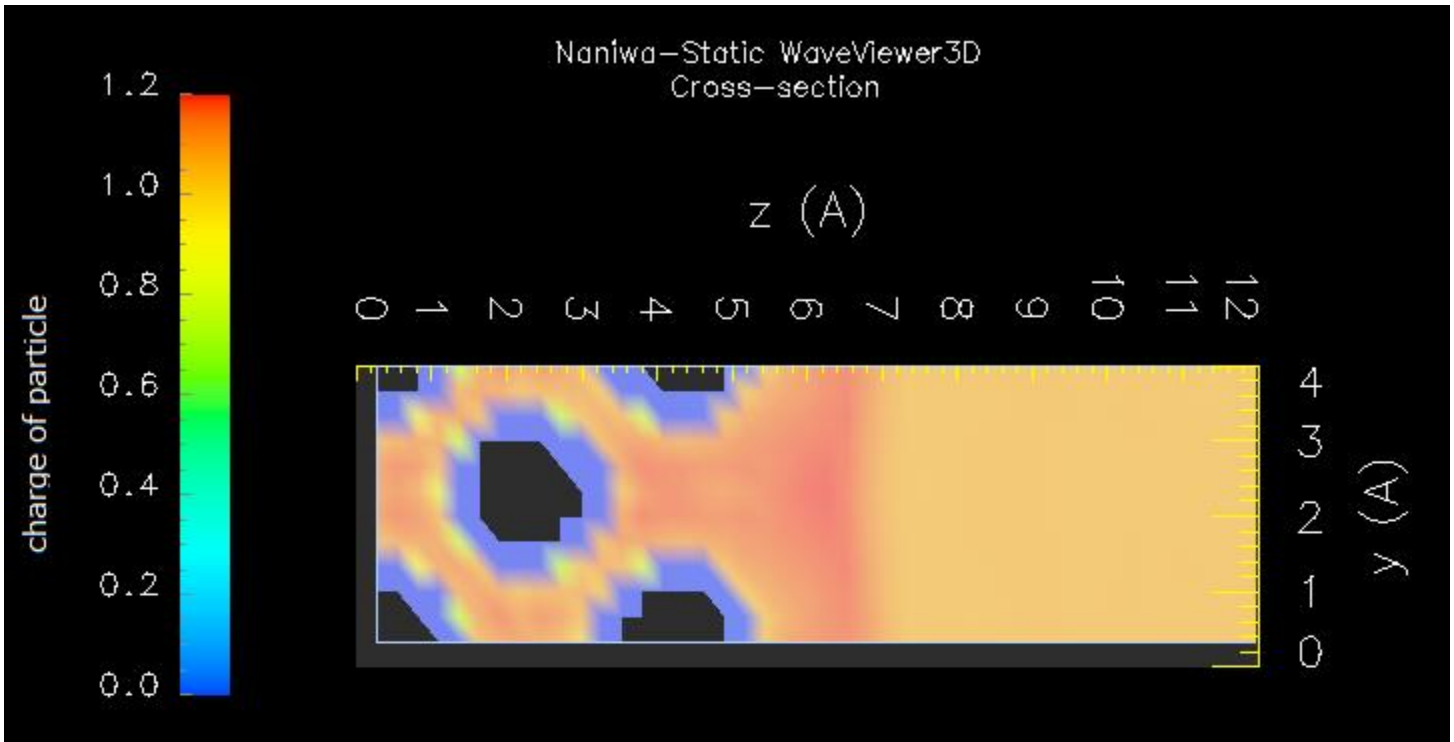
Energy Band (Wave vector dependence) of μ^+ & p^+ on Pd(001)



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



Electron charge of target particle on Pd(001)

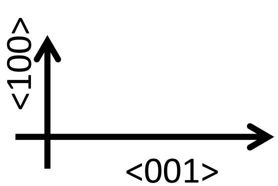


Vacuum area

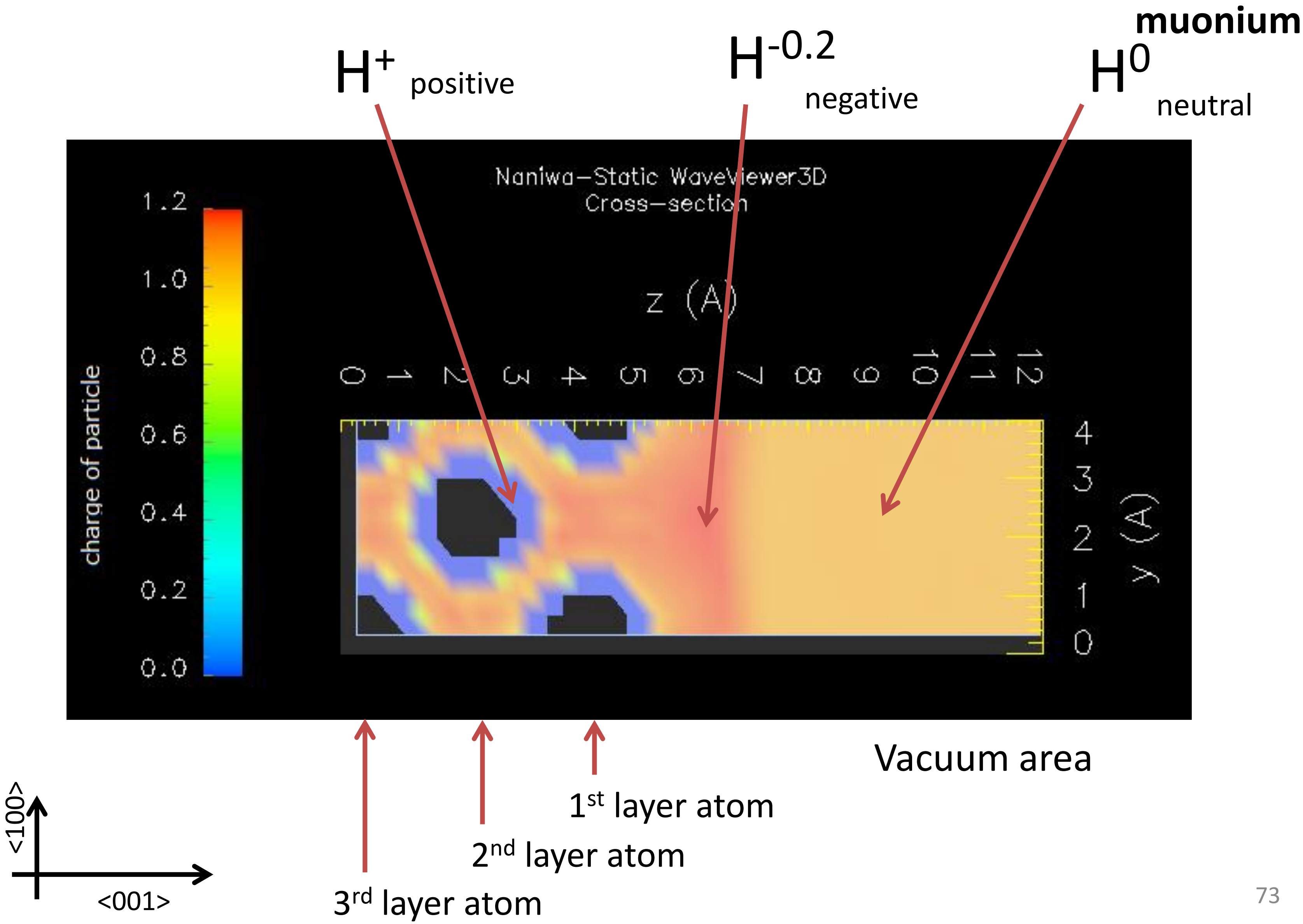
1st layer atom

2nd layer atom

3rd layer atom

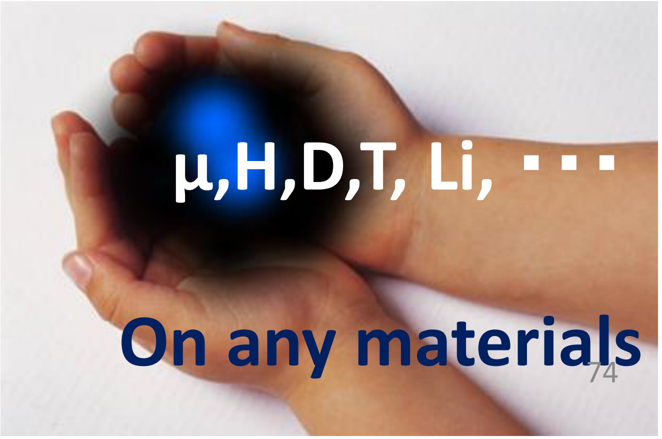


Charged states of target particle on Pd(001)



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