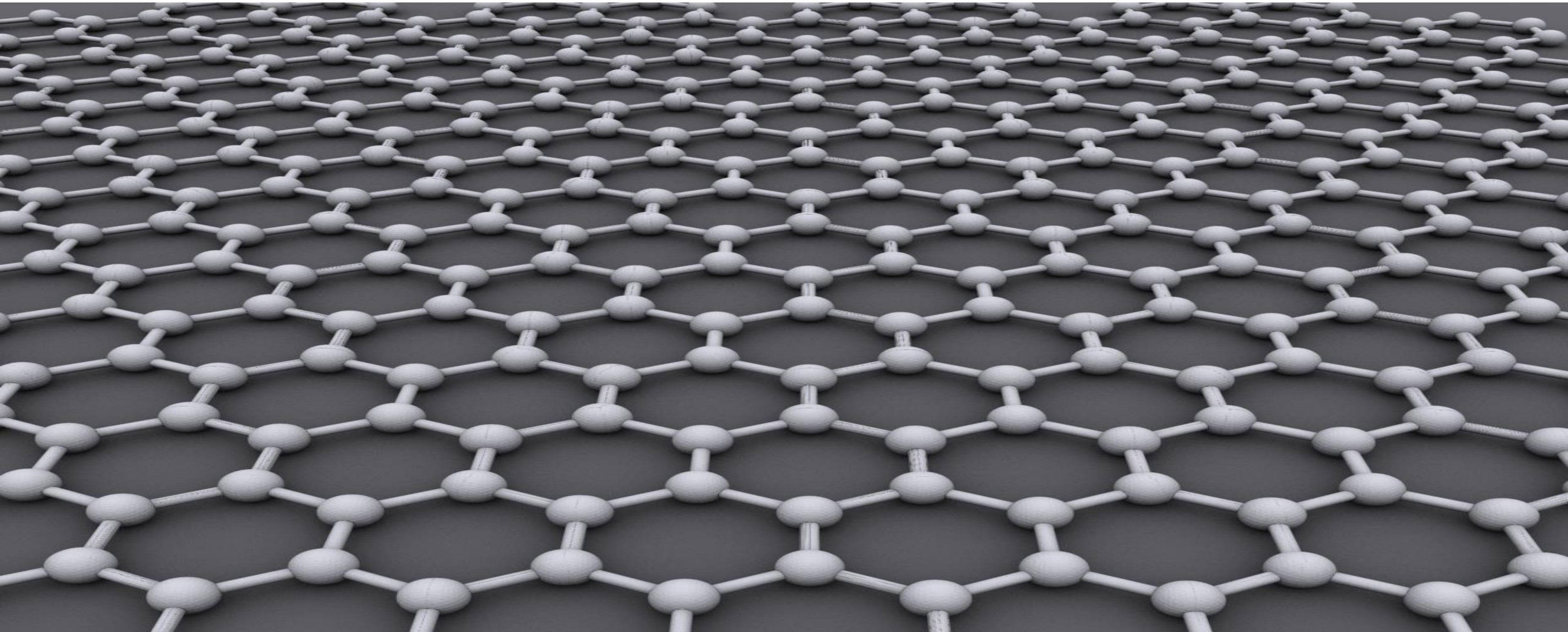
第一原理量子状態計算コード”Naniwa”の開発と研究事例

Quantum adsorbed states of hydrogen isotope atoms on graphene

H. Nakanishi, H. Kasai

Division of Precision Science & Technology and Applied Physics,
Graduate School of Engineering, Osaka University, JAPAN



Material Design through Computics:

Complex Correlation and Non-equilibrium Dynamics

A02-7: New physical properties and quantum dynamics proved by protons and muons (22104008)

A02-7 : プロトン・ミューオンで探る新物性と量子ダイナミクス

ビルデ　マーカス＠東京大学生産技術研究所
パラジウム(110)表面における水素吸収の機構
Hydrogen absorption mechanism at the palladium (110) surface

後藤英和＠大阪大学工学研究科
多体系量子状態計算手法の開発

下司雅章＠大阪大学ナノサイエンスデザイン教育センター
AlH_3の圧力誘起金属－半導体転移及び希土類水化物の高圧下での構造安定性

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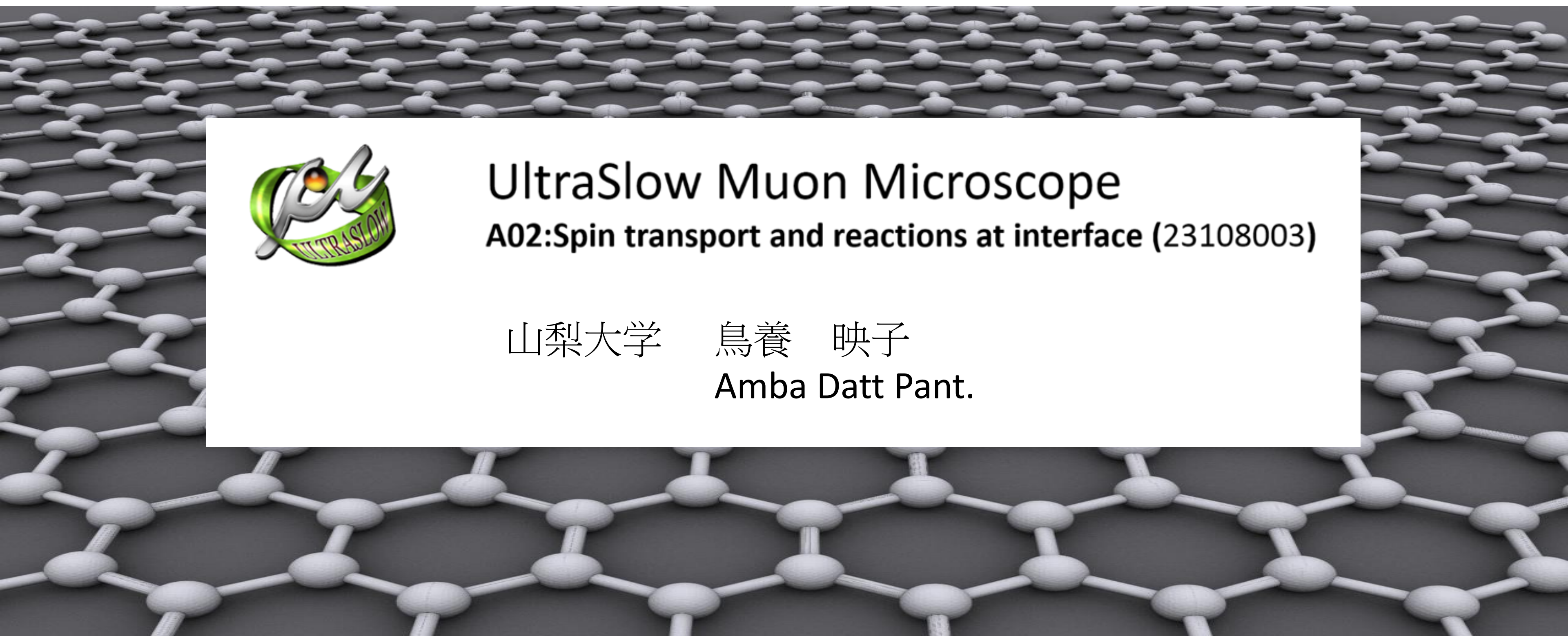


UltraSlow Muon Microscope

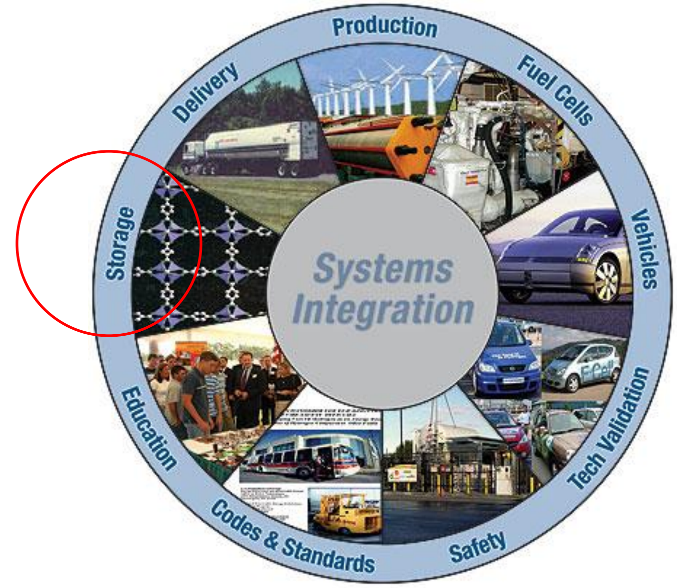
A02:Spin transport and reactions at interface (23108003)

山梨大学　鳥養　映子
Amba Datt Pant.

Hydrogen storage technology

It is required for the green hydrogen economy

- **Compressed hydrogen**
- **Liquid hydrogen**
- **Metal Hydride**
- ·
- · · · · ·



http://www.hydrogen.energy.gov

More efficient, safety, economy, moderate condition, environmentally friendly technology are strongly pursued.

Graphite or graphene based hydrogen storage

C:H = 1:1, Hydrogen storage weight ratio is 7.69 w%

Desired target values:

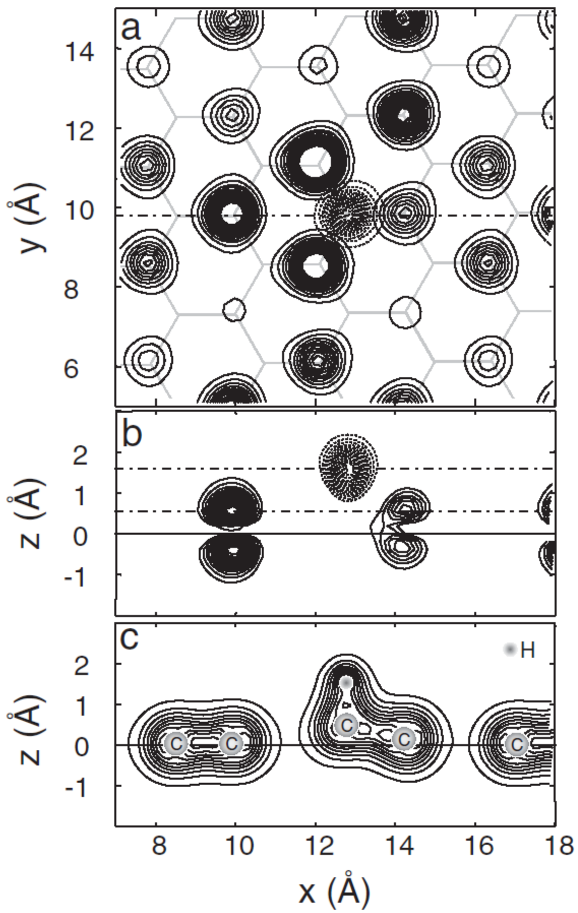
DOE (United States Department of Energy) : Over 6 w% @ under 100℃

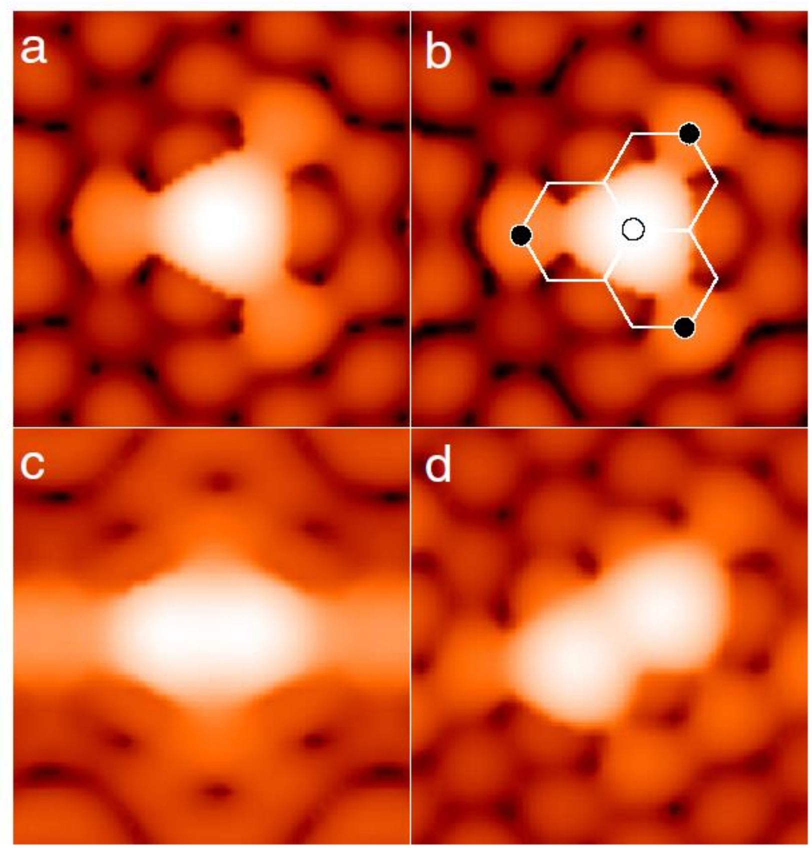
IEA (International Energy Agency) : 5.0 w%@ 80℃

“Identifying Hydrogen Atoms on Graphite”

T. ROMAN, W. A. DINO, H. NAKANISHI, H. KASAI, K. NOBUHARA, T. SUGIMOTO, and K. TANGE

Journal of the Physical Society of Japan
Vol. 76, No. 11, November, 2007, 114703





High-uptake graphene hydrogenation: a computational perspective

T Roman, W A Dino, H Nakanishi and H Kasai

J. Phys.: Condens. Matter 21 (2009) 474219

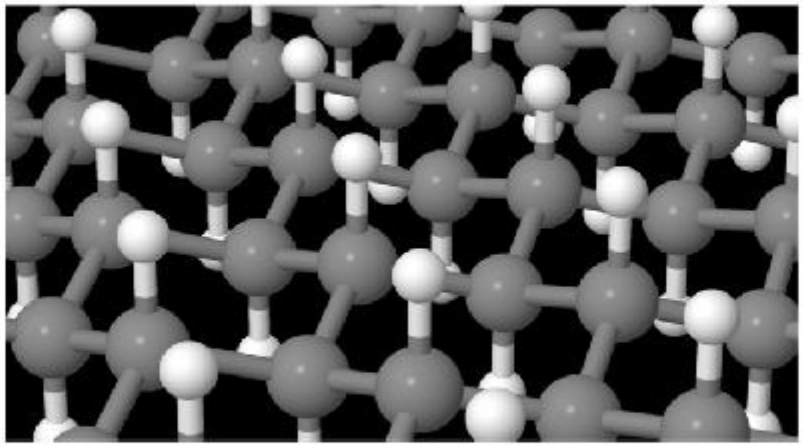
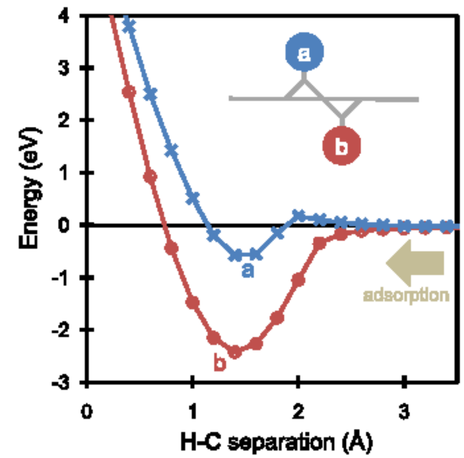
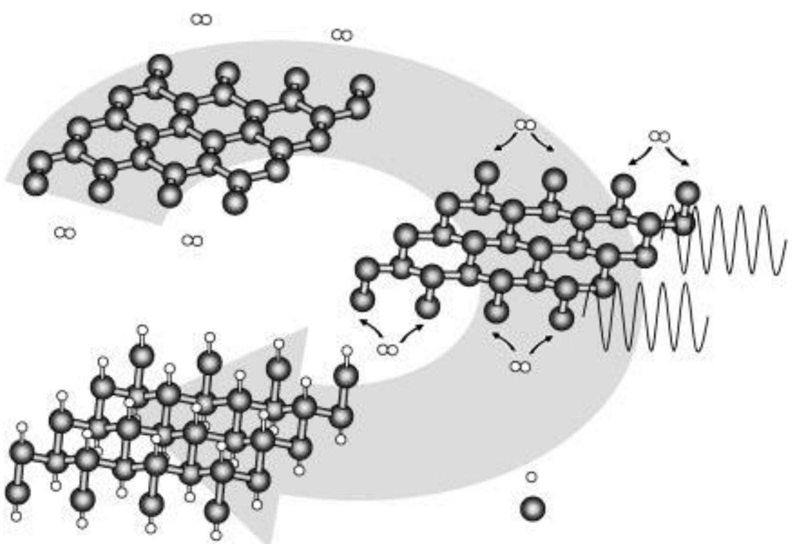


Figure 7. Stable form of fully hydrogenated graphene. Hydrogen atoms are shown in white.



Realizing a Carbon-Based Hydrogen Storage Material



T. Roman, et al., JJAP. 45,(2006) 1765.

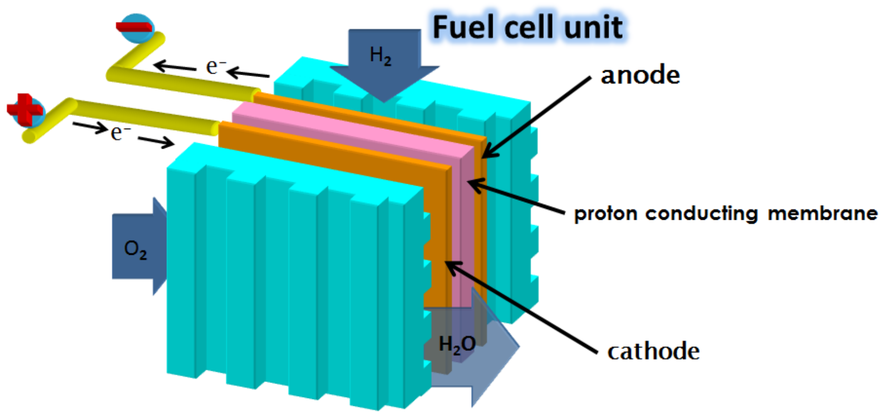
Fig. 1. Sections of fully relaxed structures of graphite (a) before, (b) during, and (c) after hydrogen adsorption. Graphite, as it is, has been shown not to readily react with molecular hydrogen, but dissociative adsorption proceeds when the graphene plane is slightly perturbed (b), initiated by the periodically changing field of infrared radiation. Maximum hydrogen uptake in the final assembly, a diamond-like carbon sheet covered with hydrogen, is shown in (c). The added contribution of the graphite edges in holding hydrogen is not included in these illustrations.

We want to treat the quantum behavior of the hydrogen in the material. Hydrogen is one of the key element for the future technology.

"energy technology", "biotechnology"

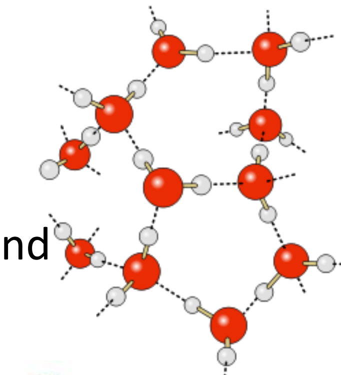
$M_{\mathrm{Proton}} >> m$

Hydrogen Reactions on Fuel cell anode



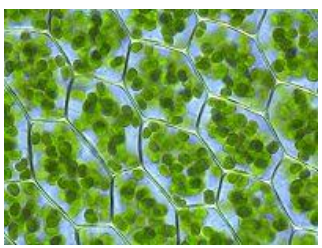
Polymer Electrolyte Fuel Cell (PEFC)

electrolyte



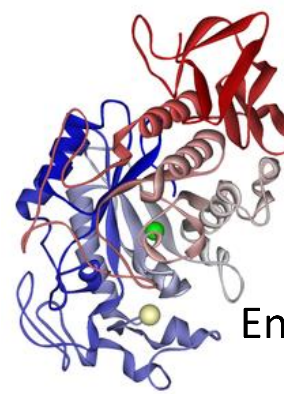
hydrogen bond

aqueous solution



Photosynthesis

biochemistry



Enzyme catalysis

Conventional ab initio simulations can treat electrons by quantum mechanics. We have been developing the quantum simulation code for both the nuclei and electrons, Naniawa: 浪速.

What is Naniwa ?

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

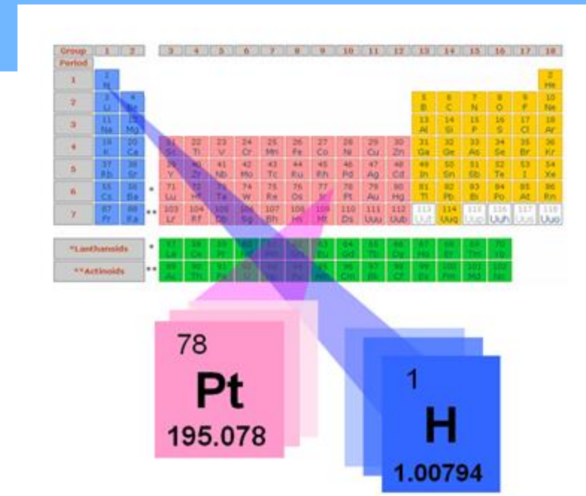
Naniwa for quantum reaction: It is a quantum mechanical version of the first principles molecular dynamics (MD) calculations, for reactions.

"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"

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

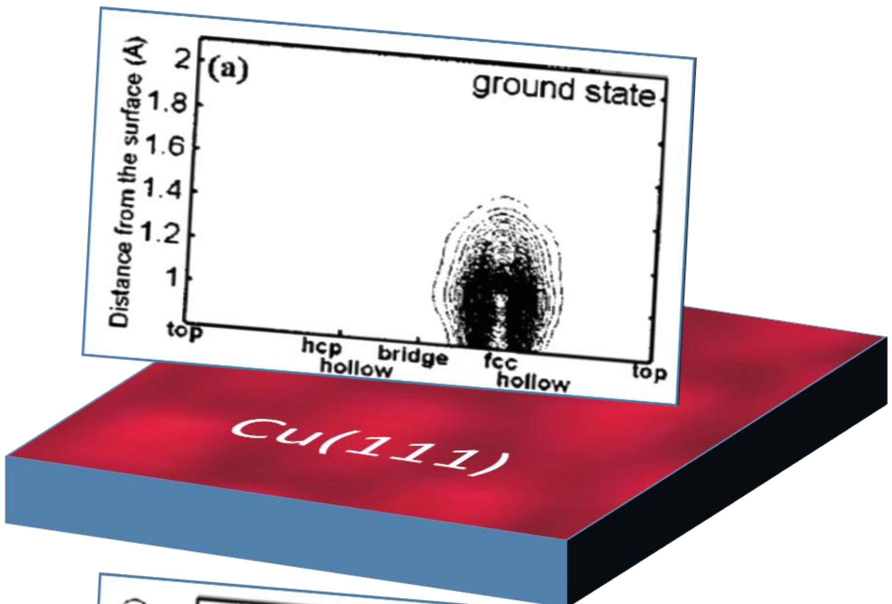
Derive the various physical quantities

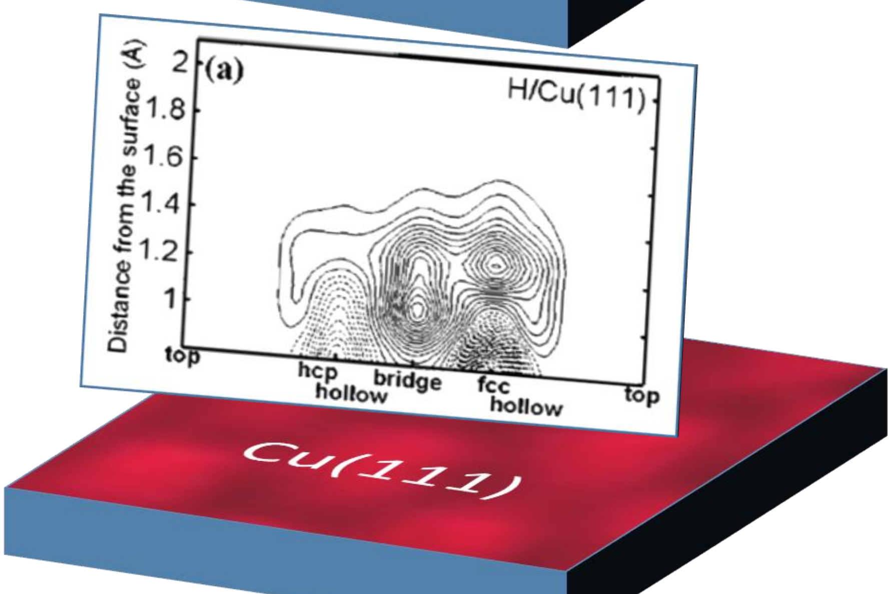
- -Parameters are only atomic number of elements
- -No fitting and no artificial procedure

Comparison between our simulation and experimental results Naniwa-Static

Calculate the Eigen states

for the atomic motions





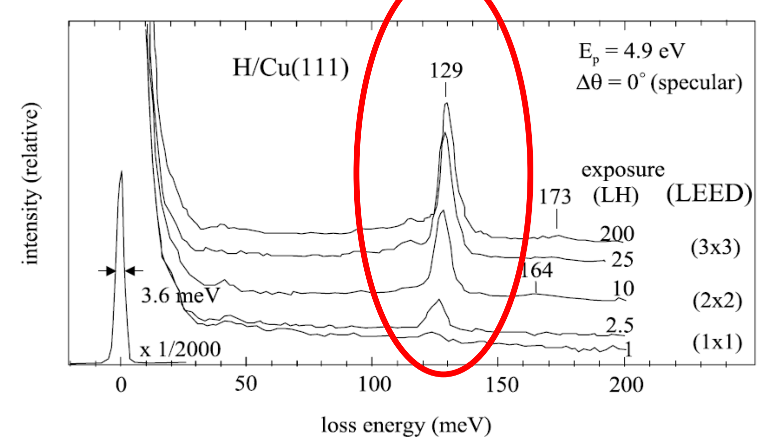
Surface-normal vibration energy of Hydrogen atom adsorbed on Cu(111) surface

Our simulation result *	135 meV
Experimental data **	129 meV

5% error

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

for Excited state



Electron energy loss spectroscopy (EELS)

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

No fitting parameters !

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 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%

Ratio in harmonic potential is $\sqrt{2} = 1.414$

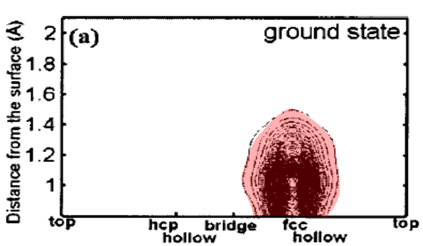
*G. Lee, *et al.*, Surf. Sci. **498** (2002) 229.

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

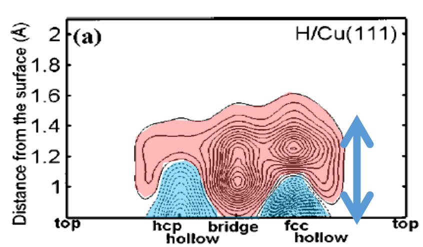
** H. Conrad, *et al*, J. Vac. Sci. Technol. A5, 452 (1987).

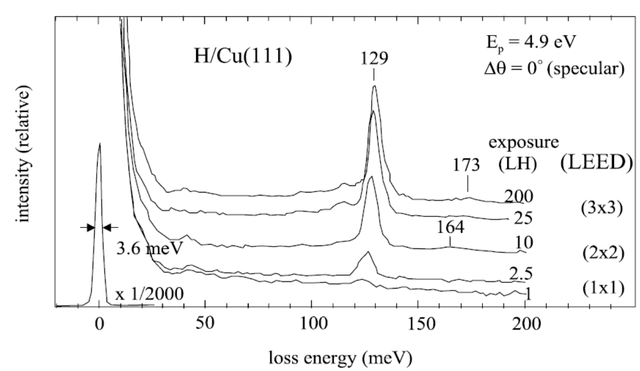
Less than 10% error

Ground state



Vivrational excited state



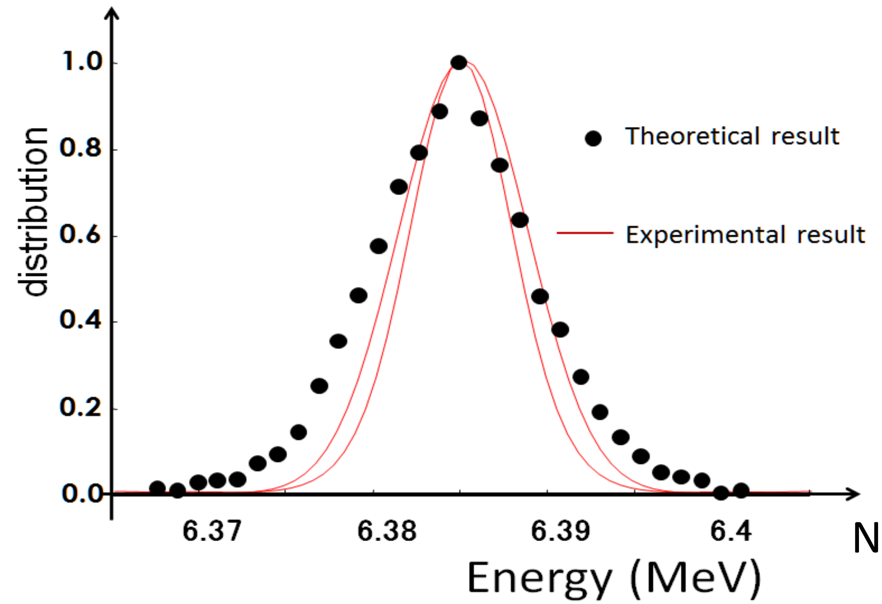


Electron energy loss spectroscopy (EELS)*

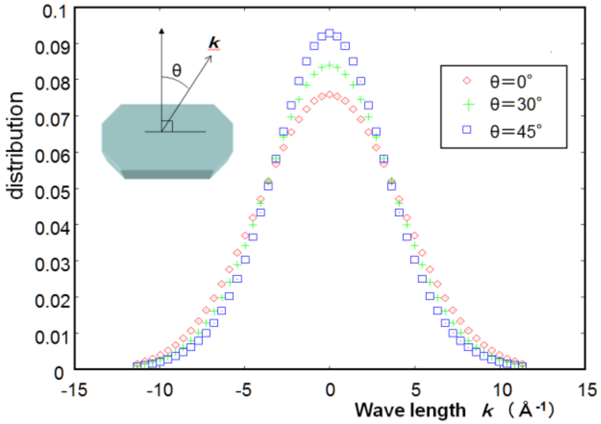
No fitting parameters !

Comparison between our simulation Naniwa and experimental results

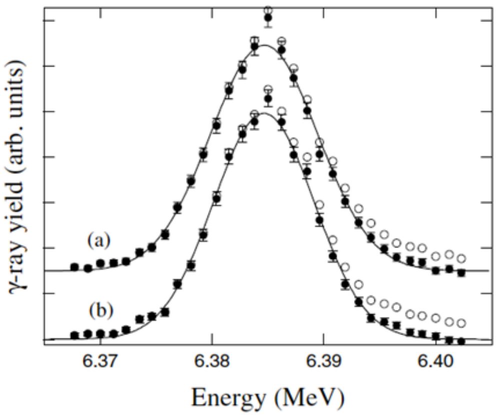
Momentum distribution of adsorbed hydrogen atom is observable in its ground state.



NRA : Nuclear Reaction Analysis



Naniwa



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

(Positive) muon μ^+

Particle statistics	Fermionic
Mass: m_μ	105.658369(9) MeV/c^2
Electric charge:	e
Spin:	½
Mean lifetime : τ	$2.19703(4)\times10^{-6}$ sec

Positive muon catches an electron, and forms the hydrogen like atom.

$\mu^+ + e^-$

Muonium
Its reduced mass and magnetic moment is different from a hydrogen atom.

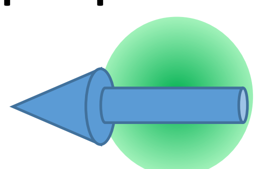
Isotope of hydrogen

$m_\mu \sim (1/9)\, m_p$
$\sim 207\, m_e$

μ^+ Antimuon -------> positron + Antimuon neutrino + electron neutrino

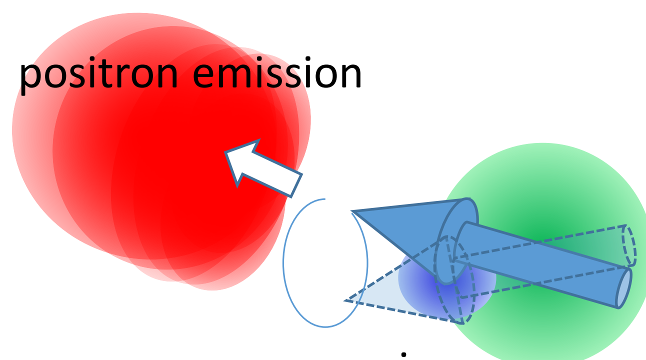
Life time : $\tau \sim 2.2\mu$sec

Muon spin spectroscopy : μSR



Spin: ½

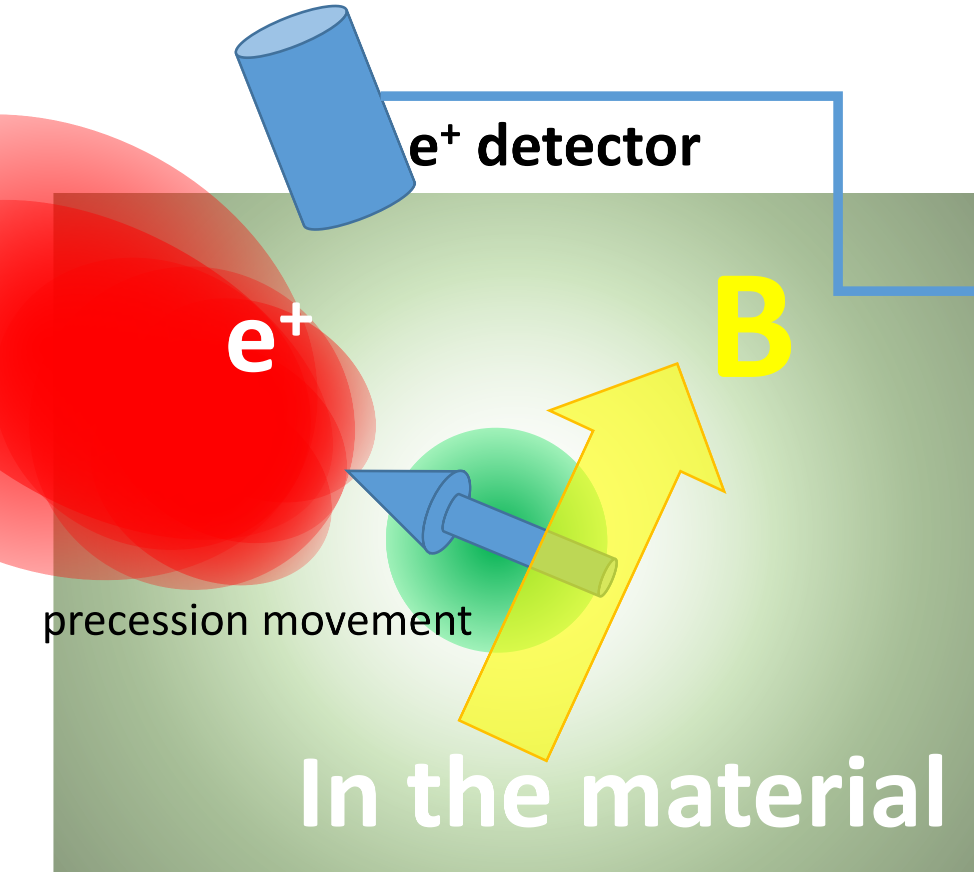
------->



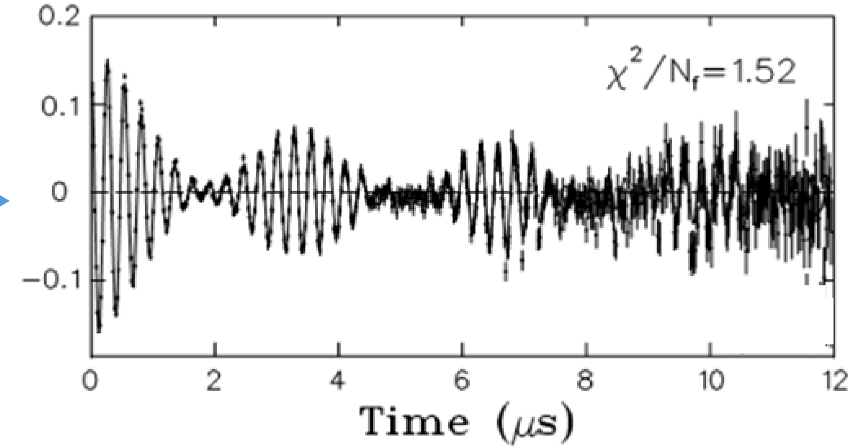
precession movement in the magnetic moment
sensitive magnetic measurement

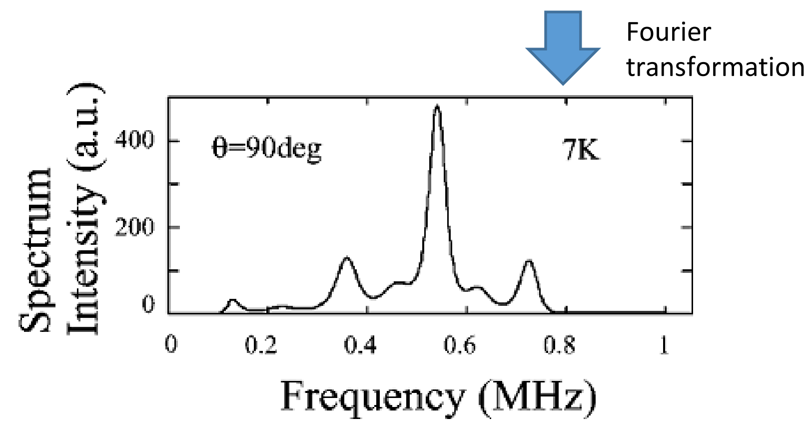
The primary decay mode of a pion is a purely leptonic decay into a muon and a muon neutrino. And the muon is 100% spin polarized

Gyromagnetic ratio : 135.53 MHz/T



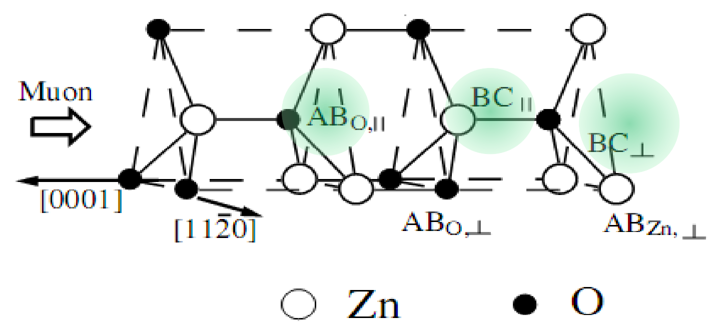
μSR　time spectrum.





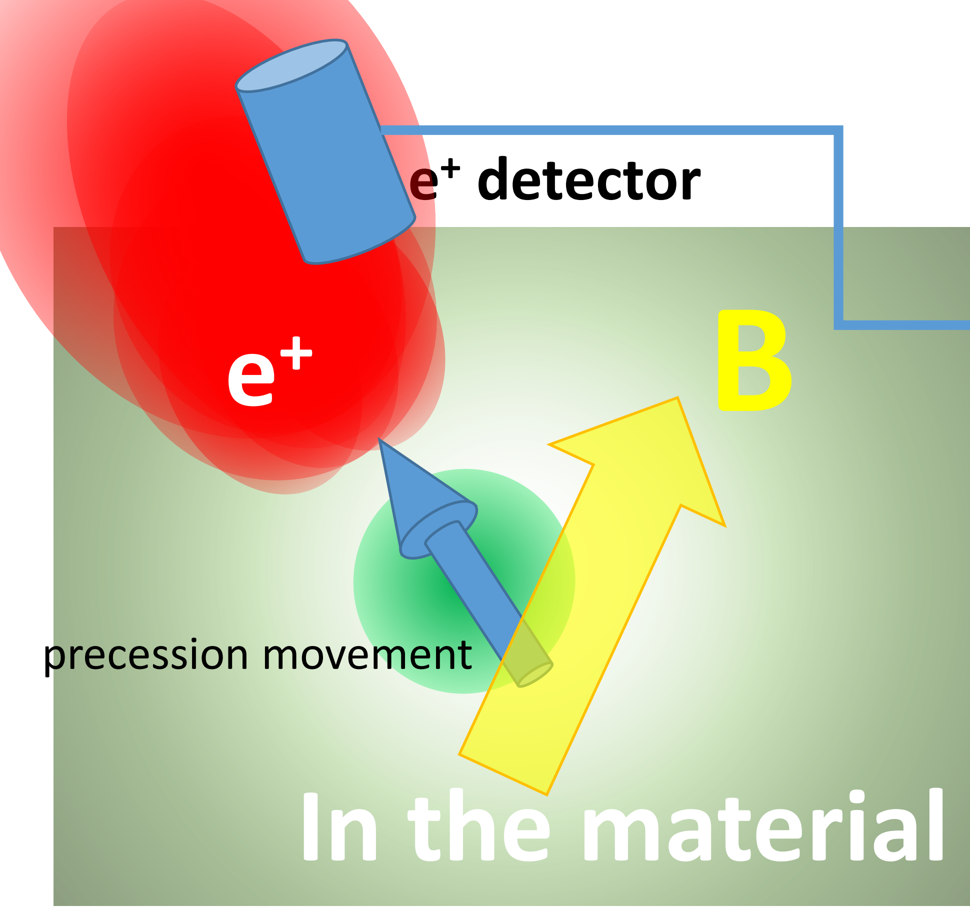
Muon plays as the small-mass proton with a communication function.

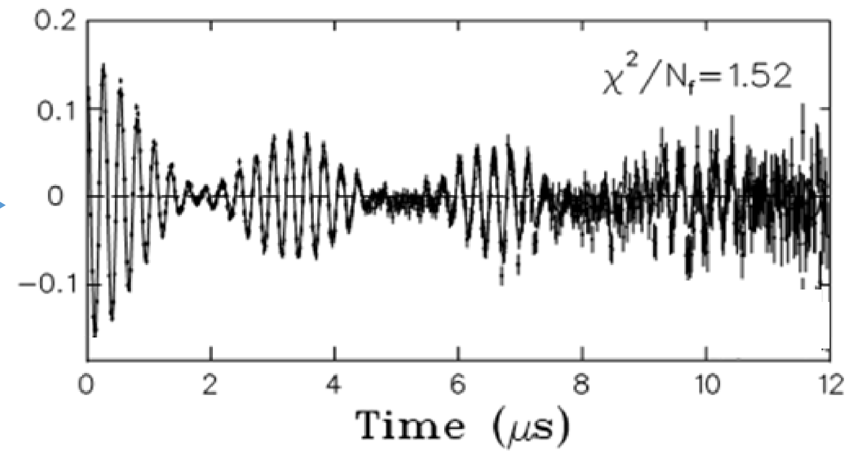
We can detect the quantum behaviors of Hydrogen-like particles in material.

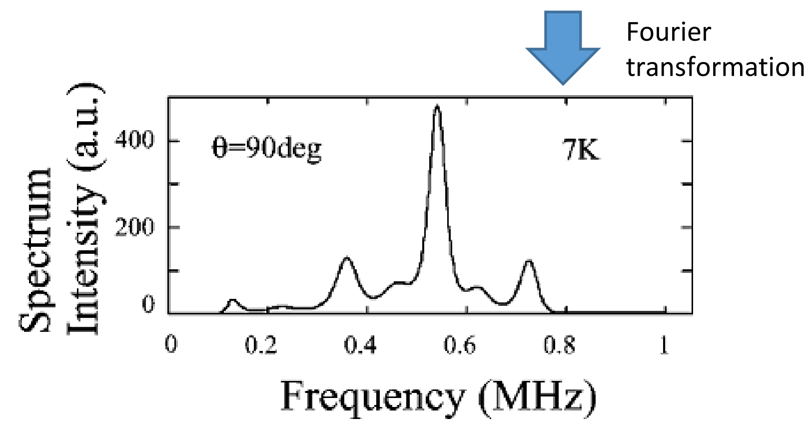


K. Shimomura et al., Phys. Rev. Lett. 89 (2002) 255051.

μSR time spectrum.







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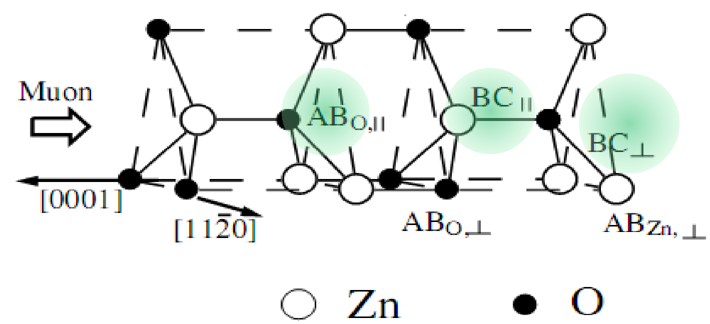
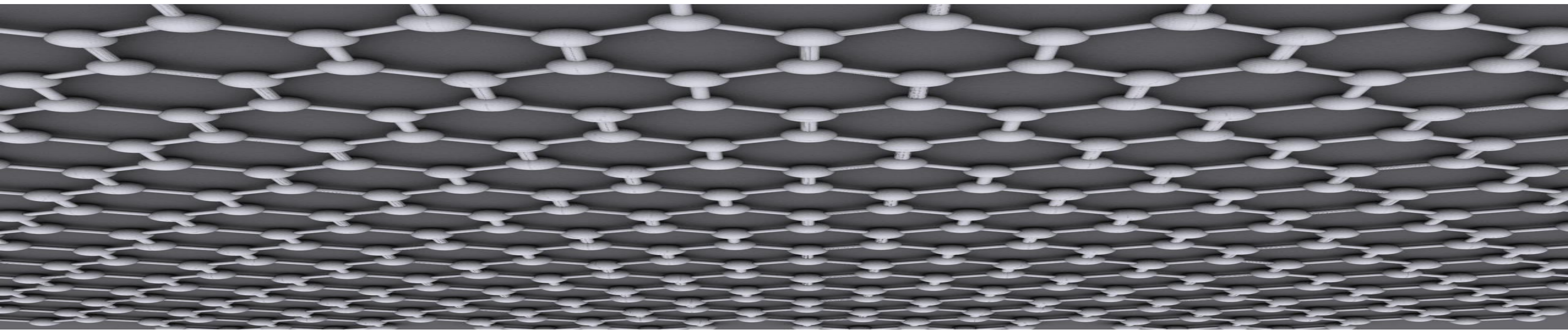


K. Shimomura et al., Phys. Rev. Lett. 89 (2002) 255051.



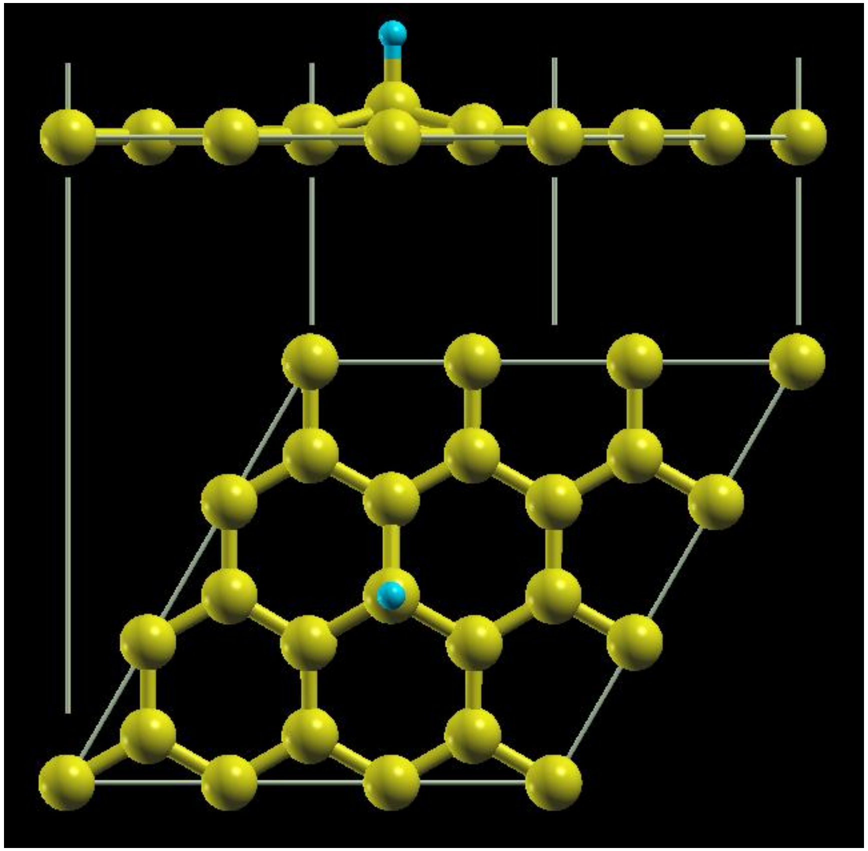
For electron

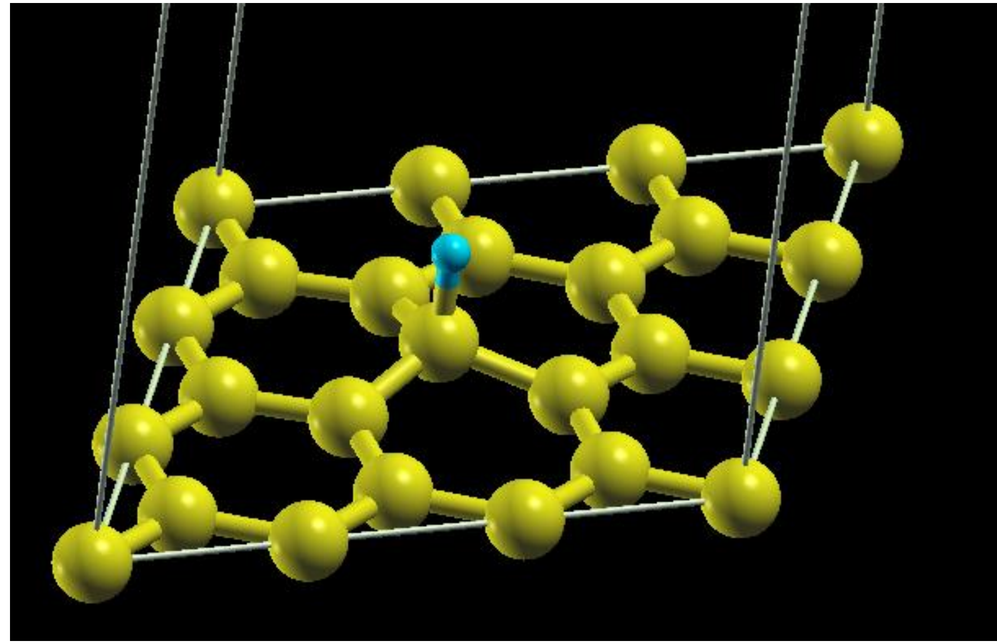
Hydrogen coverage: 1/18= 5.6%
Supercell: Slab model, 3x3 graphene units
with dipole correction parallel to c-axis
Spin: Polarized calculation
k-sampling points: 5x5x1
GGA: Perdew-Burke-Ernzerhof (PBE)
Vdw: DFT-D2 method of Grimme
Basis set: plane wave
Cut off energy: 400eV
Code Package: VASP 5.2.12

For nucleus

Supercell: Slab model, 1x1 graphene unit
Potential grid: 20 x 20 x 20
Basis set: 20 x 20 x 20 Gaussians
Symmetry Correction in graphene plane
Code Package: Naniwa (Ver. Syk20130524)

Classical hydrogen adsorbed structure on graphene





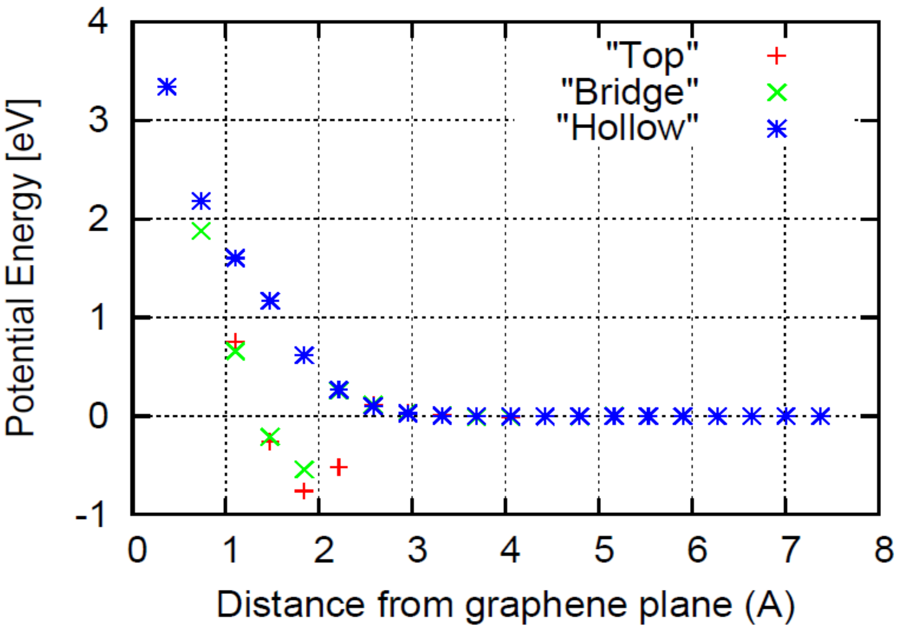
Hydrogen induces the corrugation in graphene structure. And the sp^3-like covalent bond is formed between hydrogen and carbon atoms.

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

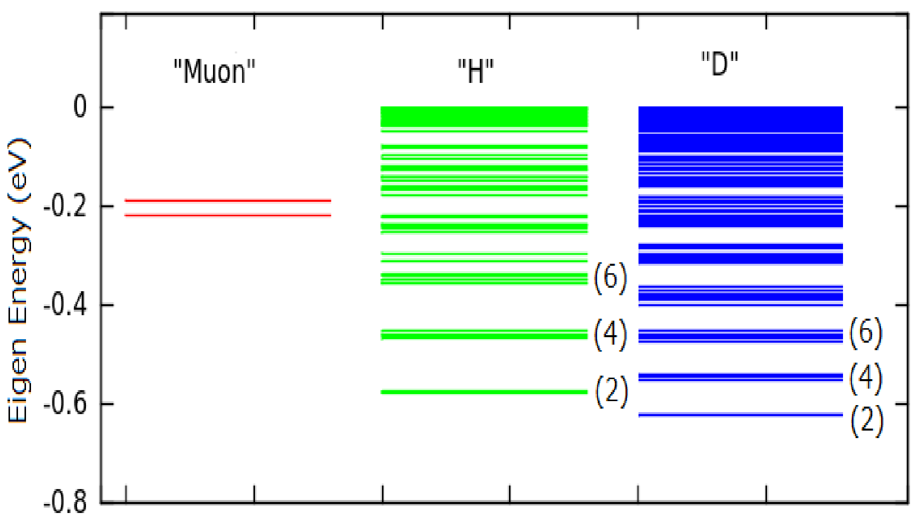
Relaxed graphene

Potential energy

Adiabatic potential energy for hydrogen on relaxed graphene



Naniwa results

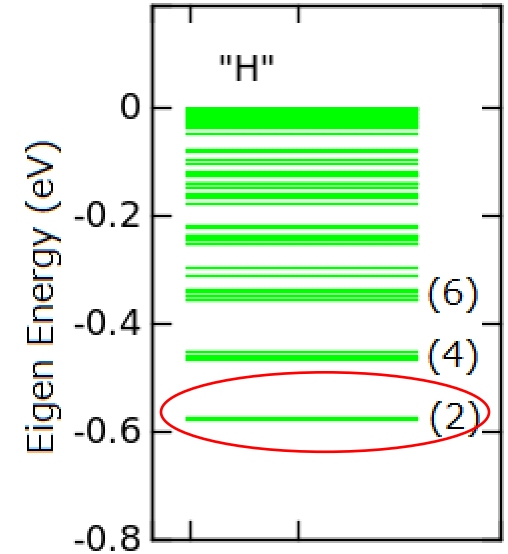


Eigen energies of positive muon, proton and deuteron on relaxed graphene

Quantum adsorbed energy of Muon: **-0.22 eV**

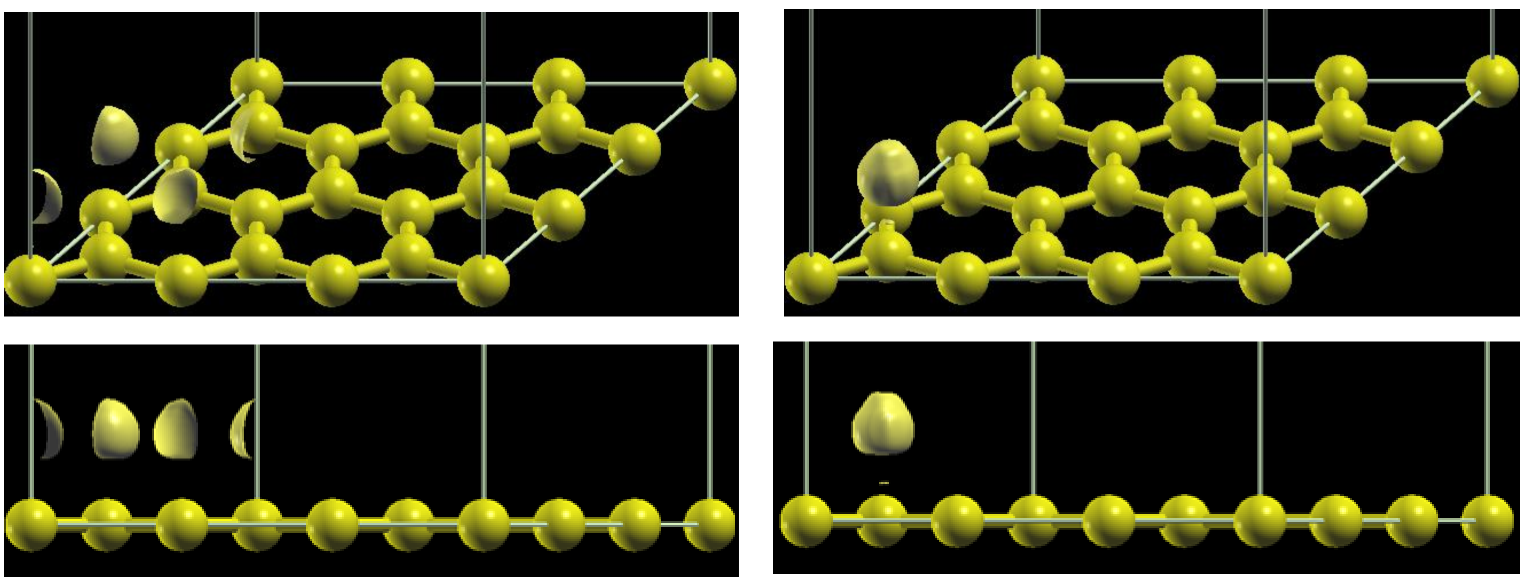
Quantum adsorbed energy of proton: **-0.58eV**

Wave function of proton in its ground states



Adsorbed energy: **-0.58 eV**

<2 degenerate energy states > in unit cell

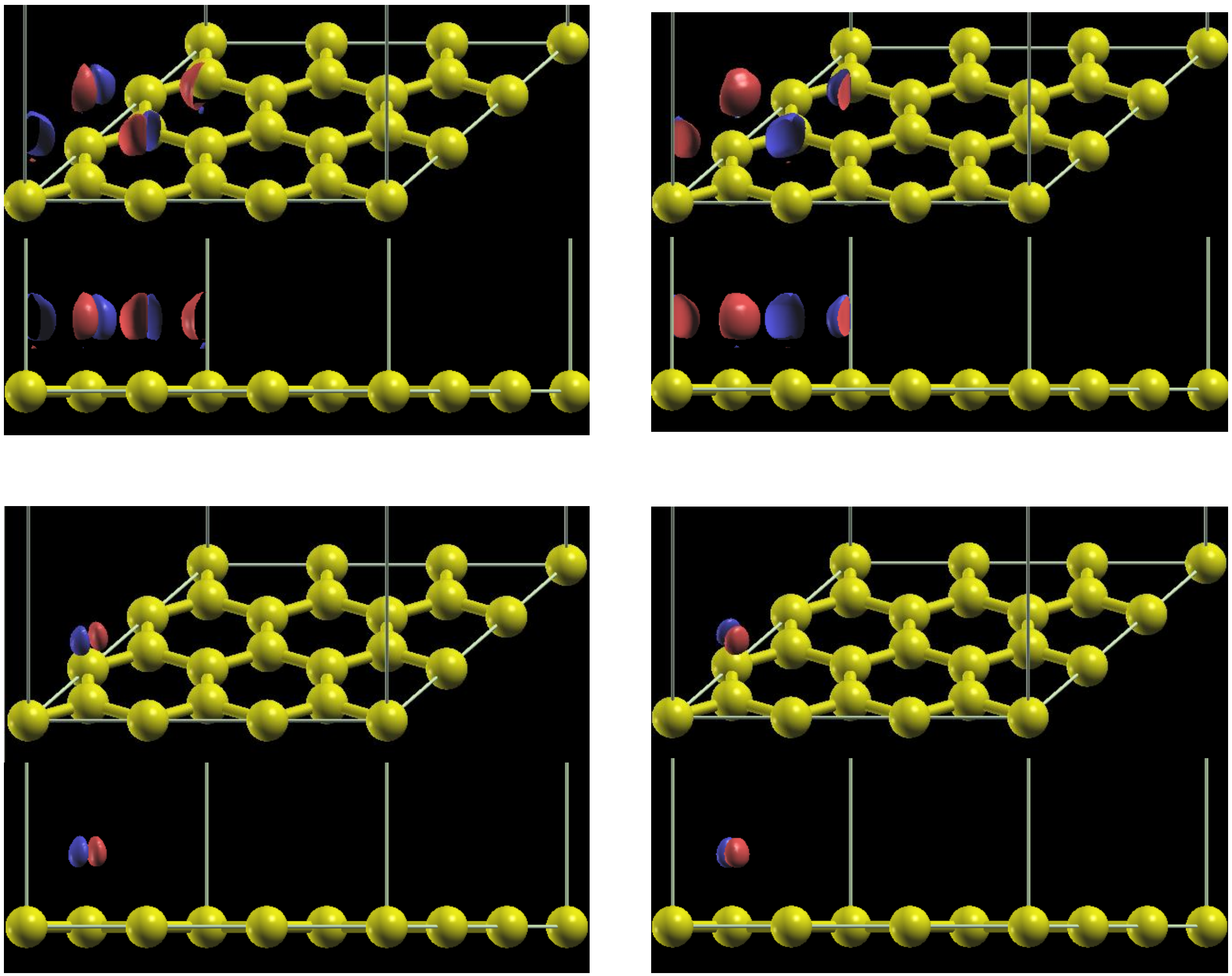


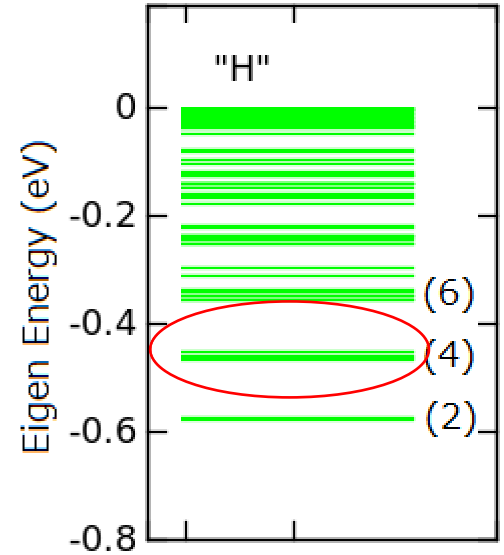
TDS experimental data : **-0.59 eV or -0.65eV**

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

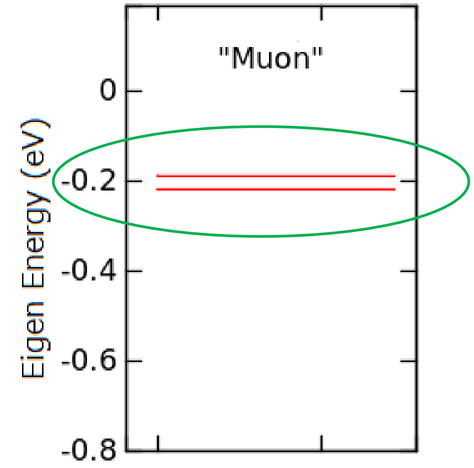
Wave function of proton in its 1st excited states

Vibrational excited parallel to the graphene plane
<4 degenerate energy states > in unit cell



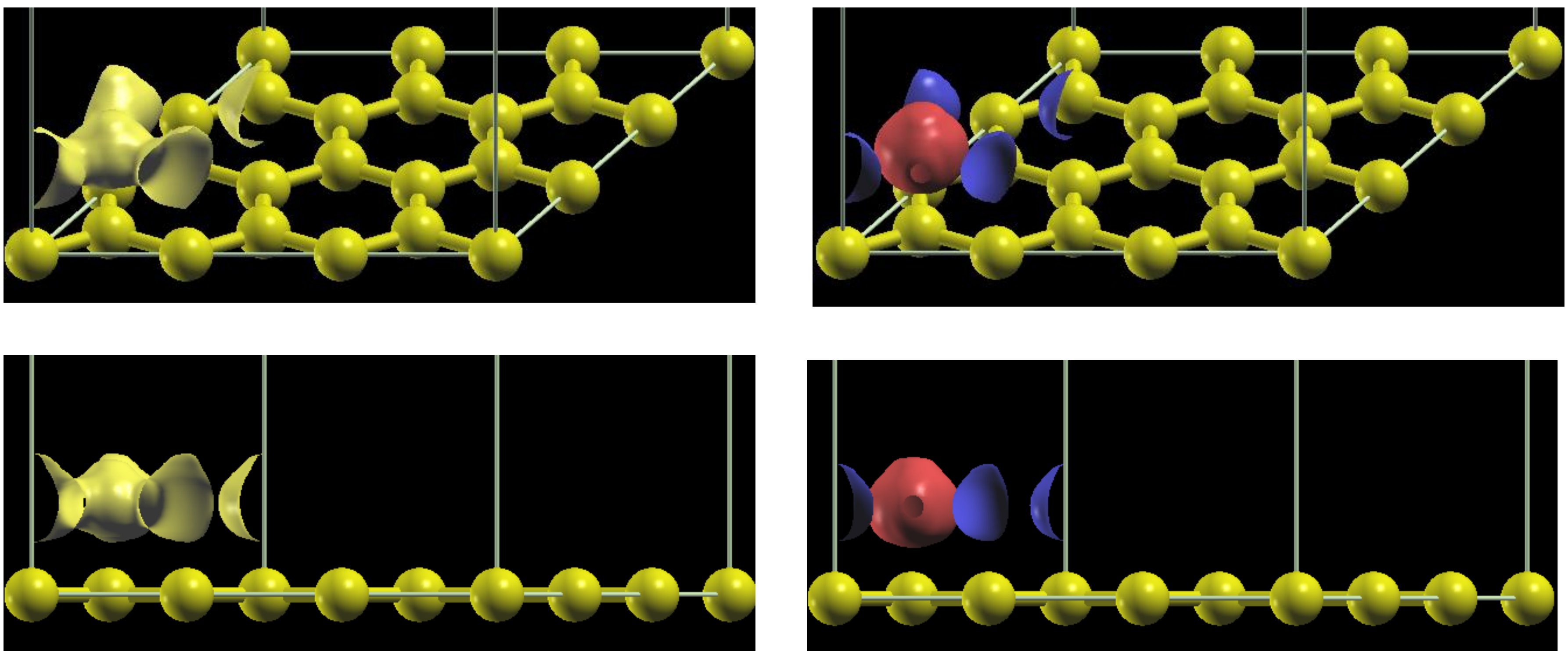


Wave function of muon in its ground state and 1st excited state

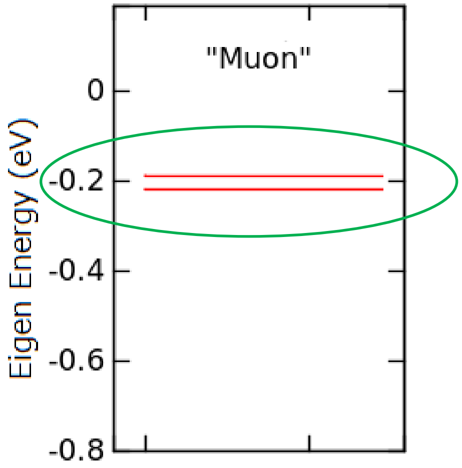


Adsorbed energy: **--0.22eV**

Split energy: δ = **0.03eV**

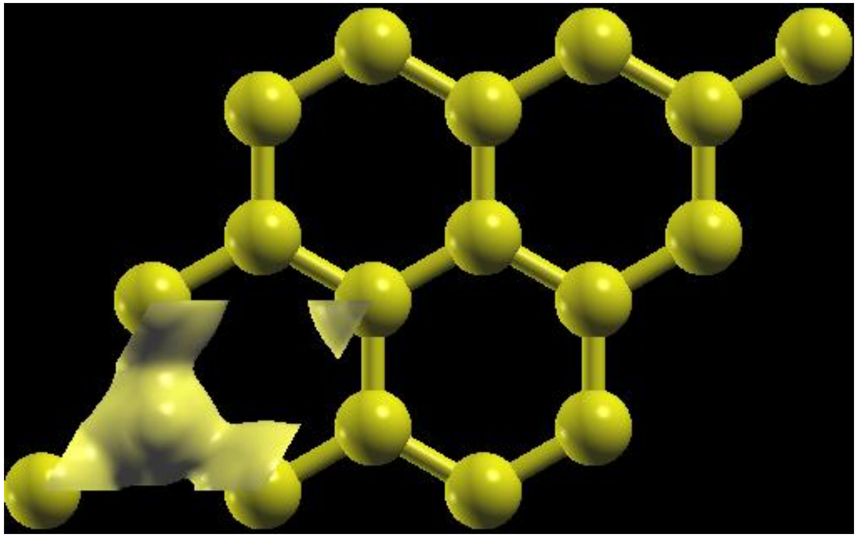


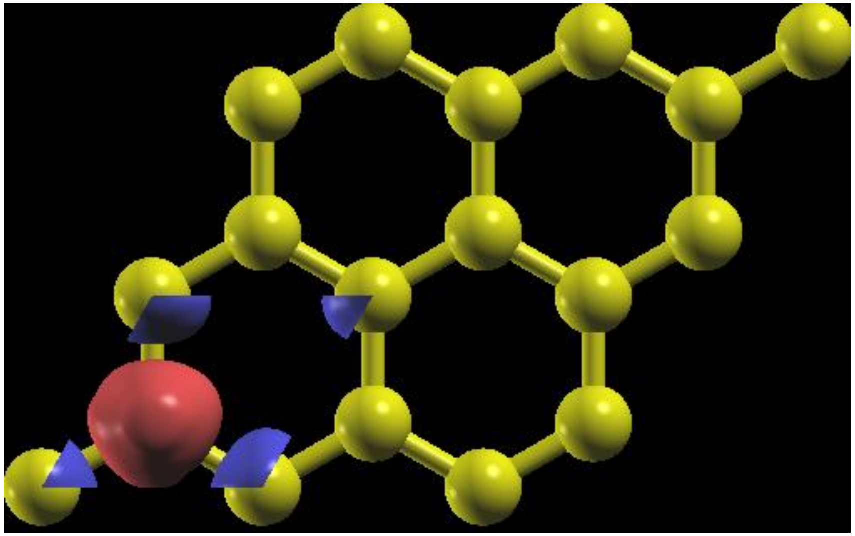
Wave function of muon in its ground state and 1st excited state



Adsorbed energy: **--0.22eV**

Split energy: δ = **0.03eV**

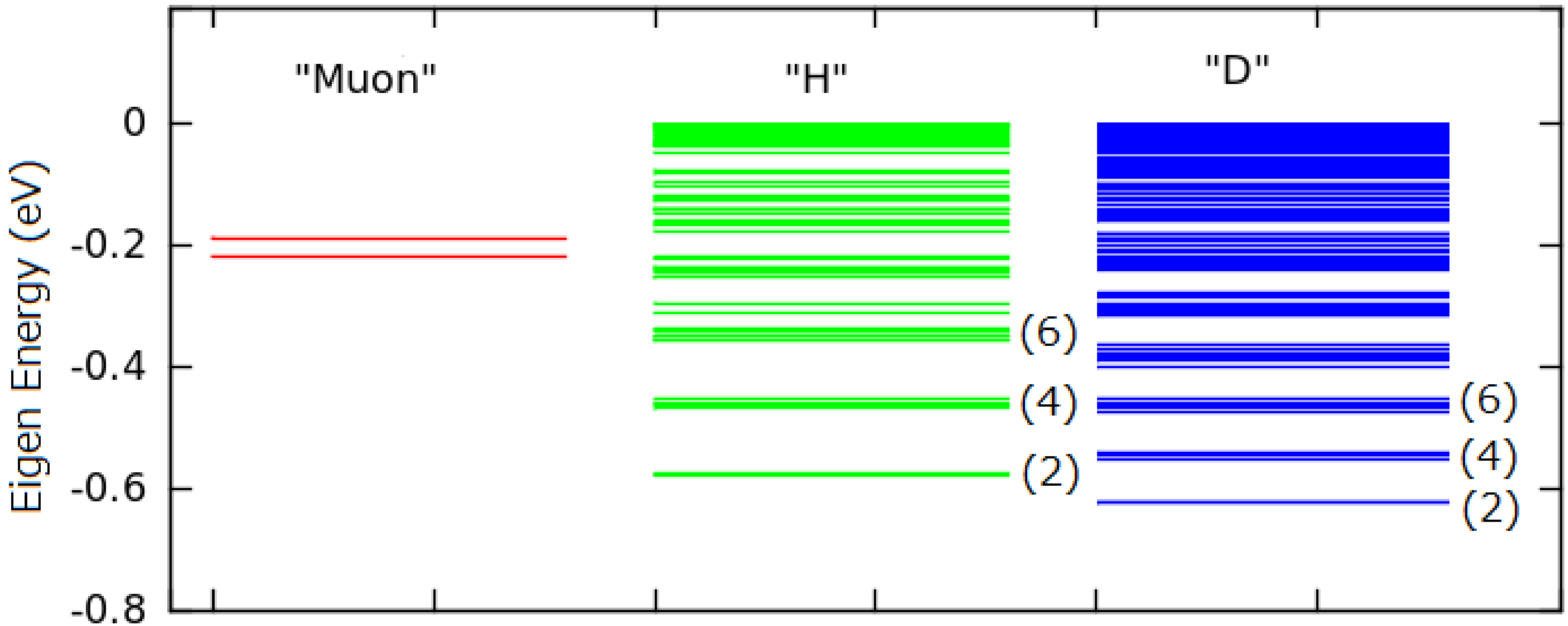




Relaxed graphene

Naniwa results

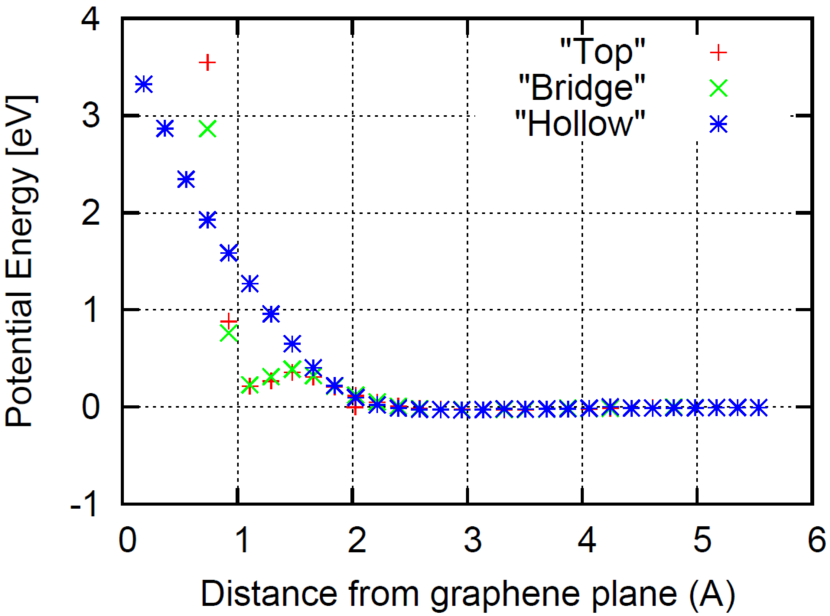
Eigen energies of positive muon, proton and deuteron on relaxed graphene



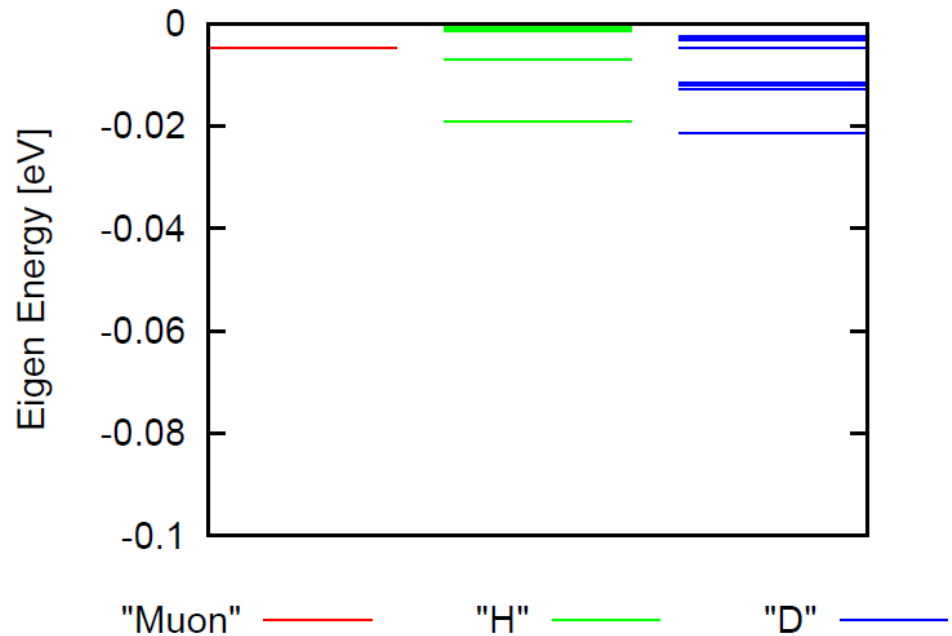
Flat graphene

Potential energy

Adiabatic potential energy calculation for hydrogen on fixed flat graphene



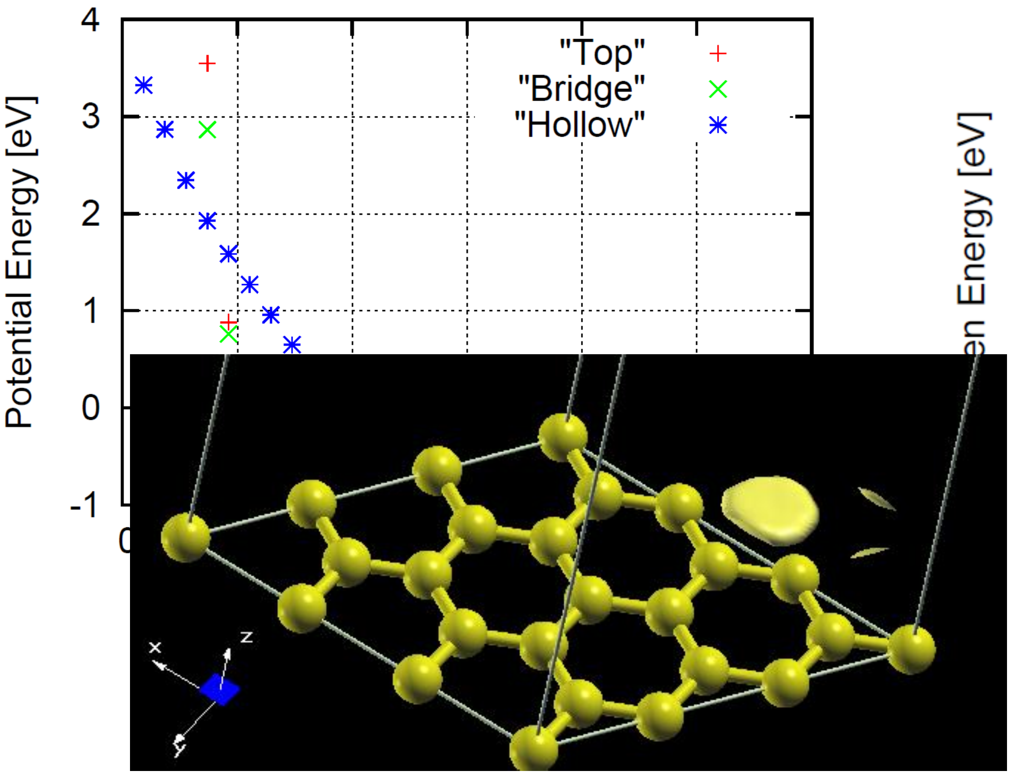
Naniwa results



Eigen energies of positive muon, proton and deuteron on fixed flat graphene

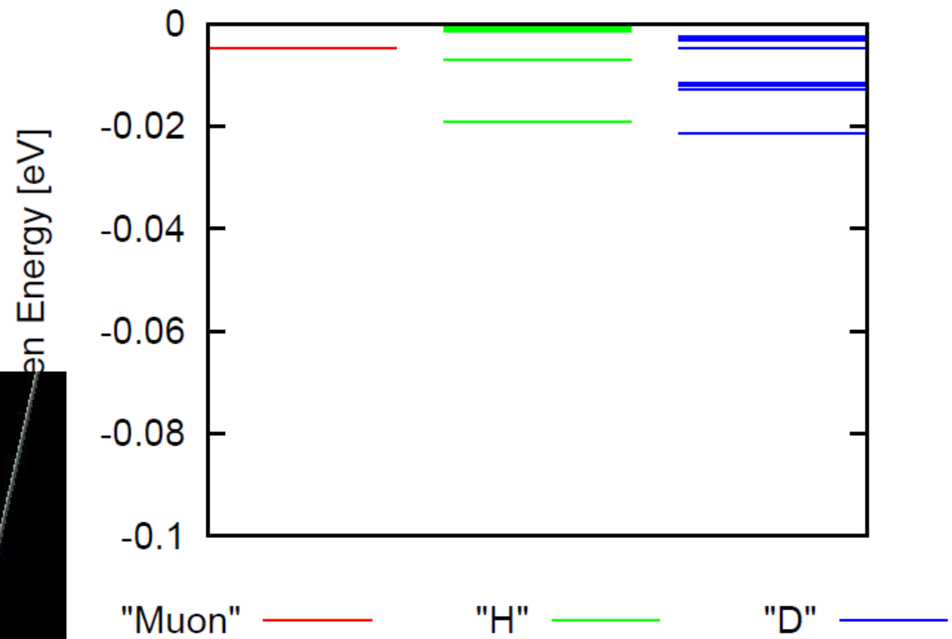
Flat graphene

Potential energy



Wave function for proton
in its ground state
with adsorbed energy: -0.019eV

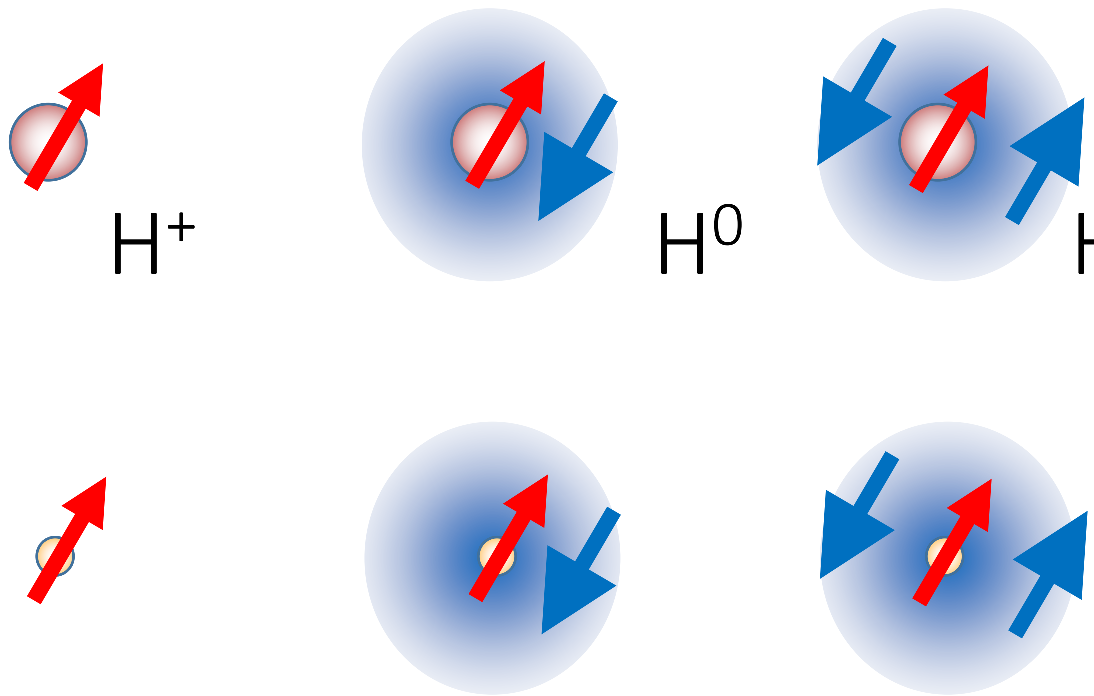
Naniwa results



Eigen energies of positive muon, proton and deuteron on freezed graphene

How about the charged states of particles

$\langle n_{a\uparrow} + n_{a\downarrow} \rangle =$ 0, 1 , 2



Muon: μ⁺ **Muonium: μ⁺ + e⁻** Negative ion **: μ⁺ + 2e⁻**

Charged states of target particle on Pd (001)

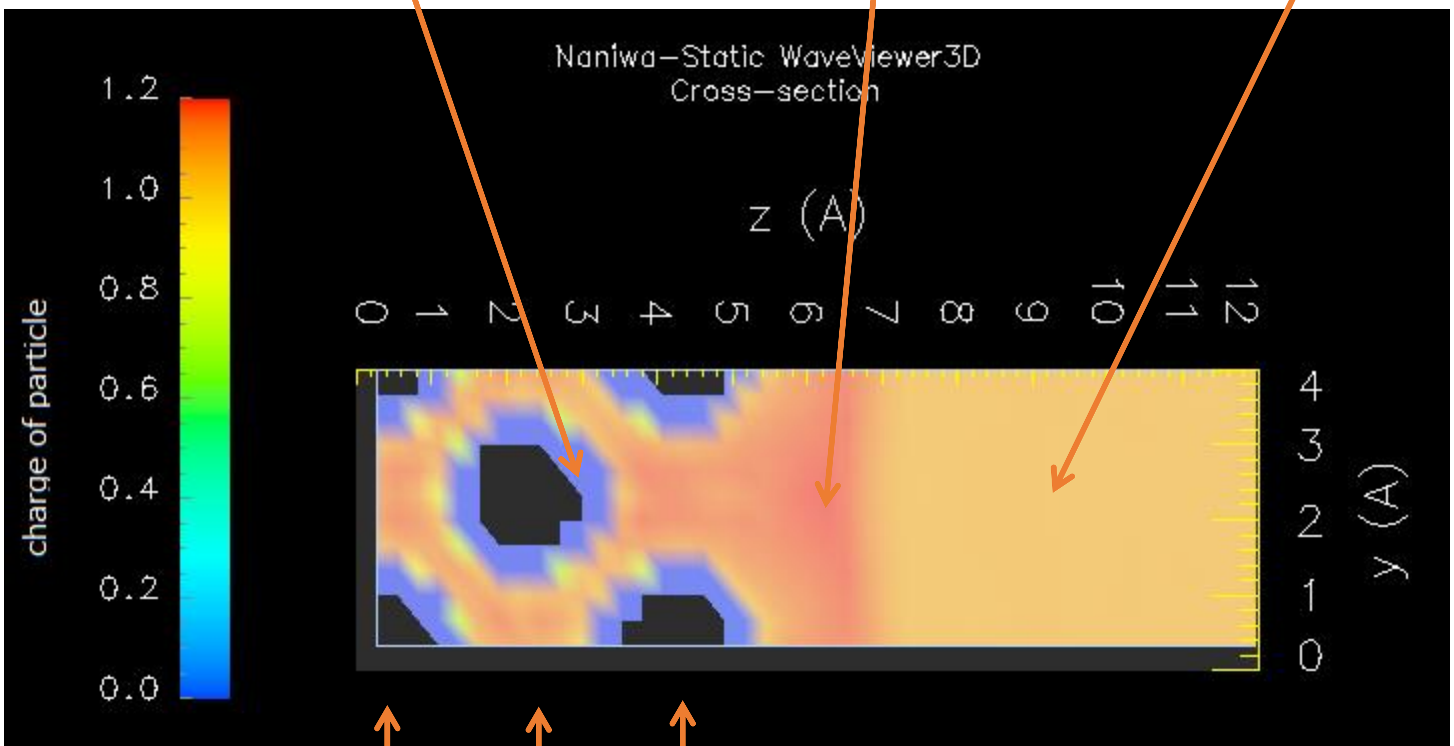
By use of Bader analysis

muonium

H^+ positive

$H^{-0.2}$ negative

H^0 neutral

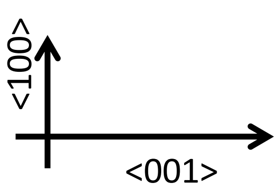


Vacuum area

1st layer atom

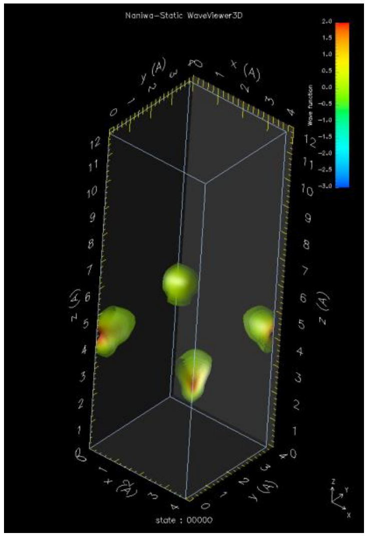
2nd layer atom

3rd layer atom

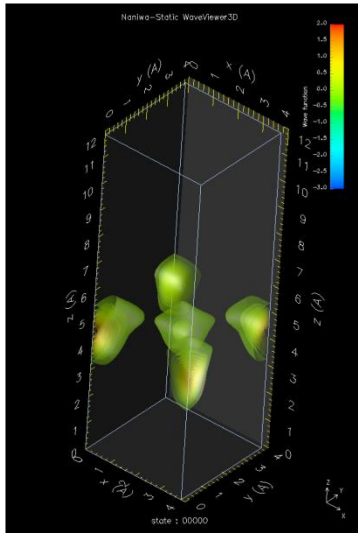


Electron charge of the proton and anti-muon on Pd (001) surfaces

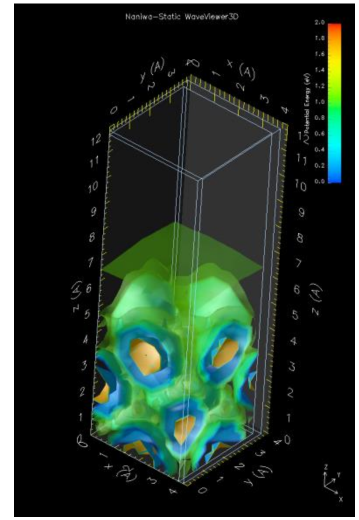
Ground state



$\Psi_0(\vec{R})$ for proton



$\Psi_0(\vec{R})$ for anti-muon



$$\iiint_{-\infty}^{+\infty} d\vec{r} \left\{ \left| \varphi_{a\uparrow}(\vec{r};\vec{R}) \right|^2 + \left| \varphi_{a\downarrow}(\vec{r};\vec{R}) \right|^2 \right\}$$

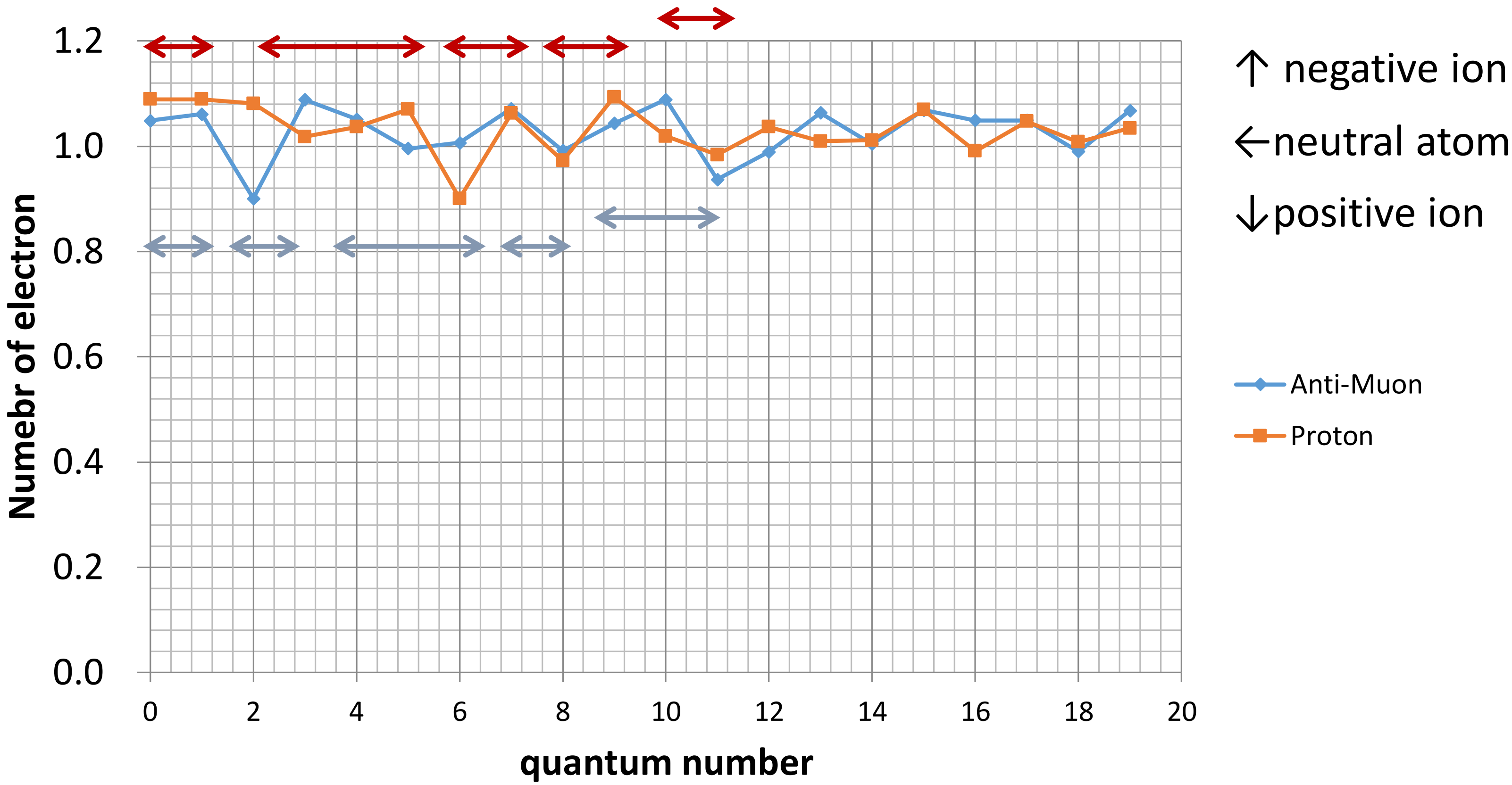
Expectation value of electron number on the particle'

$$\langle n_{a\uparrow} + n_{a\downarrow} \rangle_n = \iiint_{-\infty}^{+\infty} d\vec{R} \iiint_{-\infty}^{+\infty} d\vec{r} \left\{ \left| \varphi_{a\uparrow}(\vec{r};\vec{R}) \right|^2 + \left| \varphi_{a\downarrow}(\vec{r};\vec{R}) \right|^2 \right\} \cdot \left| \Psi_n(\vec{R}) \right|^2$$

Electron charge of target particle on Pd(001)

Ground state

Core	Number of electron
(Anti)Muon	1.05
Proton	1.09



for μSR experiment

potential energy (eV)

超微細相互作用

Summary

We have developing the parameter-free quantum simulation code “Naniwa: 浪速”

We investigate the quantum adsorbed states of positive muon (Mu^+) and hydrogen atom nuclei (H^+, D^+) on graphene by our quantum simulation codes, Naniwa .

For hydrogen atom nuclei (H^+, D^+)

The ground state wave function of hydrogen nucleus adsorbed on graphene is strongly localized at top site.

The adsorption energy is reduced from that expected by conventional DFT simulation. “It is more convenient for hydrogen storage usage.”

Vibrational excited states exist around this top site.

For positive muon (Mu^+)

There are only two adsorbed states, which are in their ground states.

No vibrational excited state.

Only the ground states can be measured by MuSR experiment.

*We can estimate the hyperfine interactions, which is useful to know the state of hydrogen isotope on graphene.

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MEXT Science Research on Innovative Areas:

Material Design through Computics:

Complex Correlation and Non-equilibrium Dynamics

A02-7: New physical properties and quantum dynamics proved by protons and muons (22104008**)**

UltraSlow Muon Microscope

A02:Spin transport and reactions at interface (23108003**)**