

Calculations of X-ray photoemission spectra

- X-ray photoemission spectroscopy
- Multiple splitting of binding energies
- Energy expression of absolute energies
- Core hole calculations
- Benchmark calculations and Applications
- Usage of OpenMX for the XPS calc.
- Exercises

Taisuke Ozaki (ISSP, Univ. of Tokyo)

Institute for Materials Research (IMR), Tohoku University, Feb. 14, 2020.

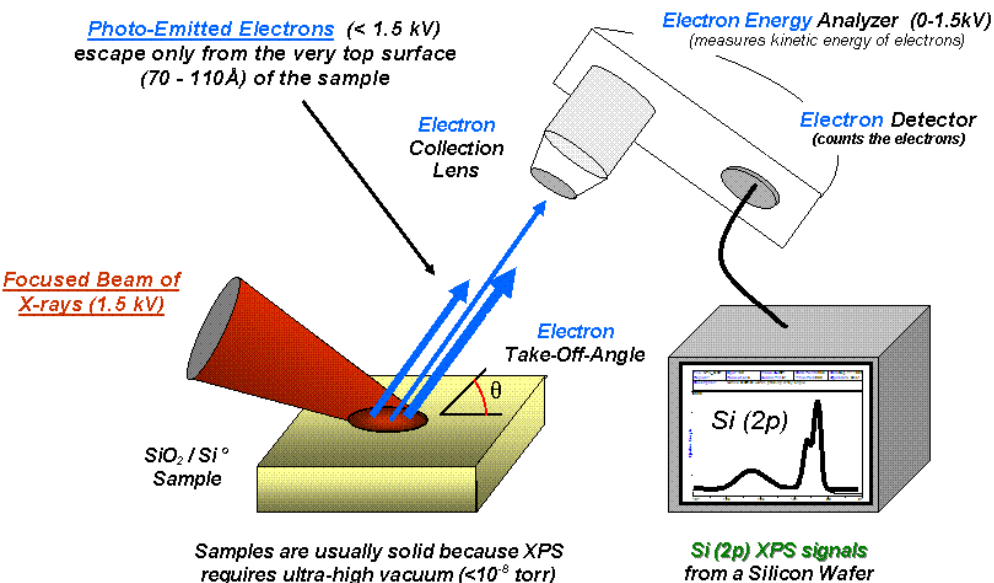
X-ray photoemission spectroscopy (XPS)

- Information of chemical composition, surface structure, surface adsorbate
- XPS with synchrotron radiation extends its usefulness, e.g., satellite analysis, core level vibrational fine structure, XPS circular dichroism, spin-resolved XPS, and XPS holography.
- How to calculate the **absolute binding energies** in solids?

We have developed a general method to calculate absolute binding energies of core levels in solids with the following features:

- applicable to **insulators** and metals
- accessible to **absolute** binding energies
- screening of core and valence electrons on the same footing
- SCF treatment of spin-orbit coupling
- exchange interaction between core and valence states
- geometry optimization with a core hole state

XPS experiments

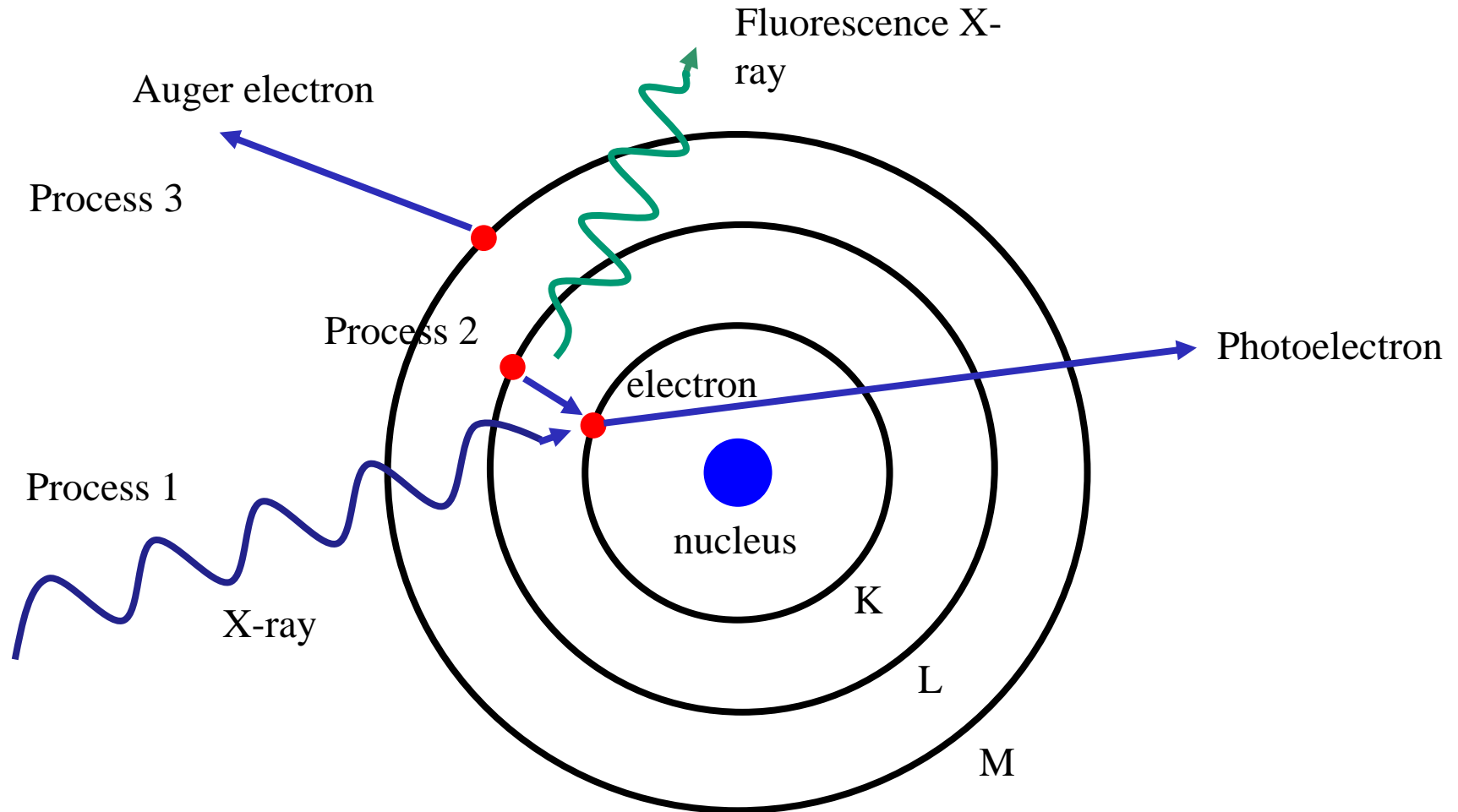


Appearance of XPS equipment



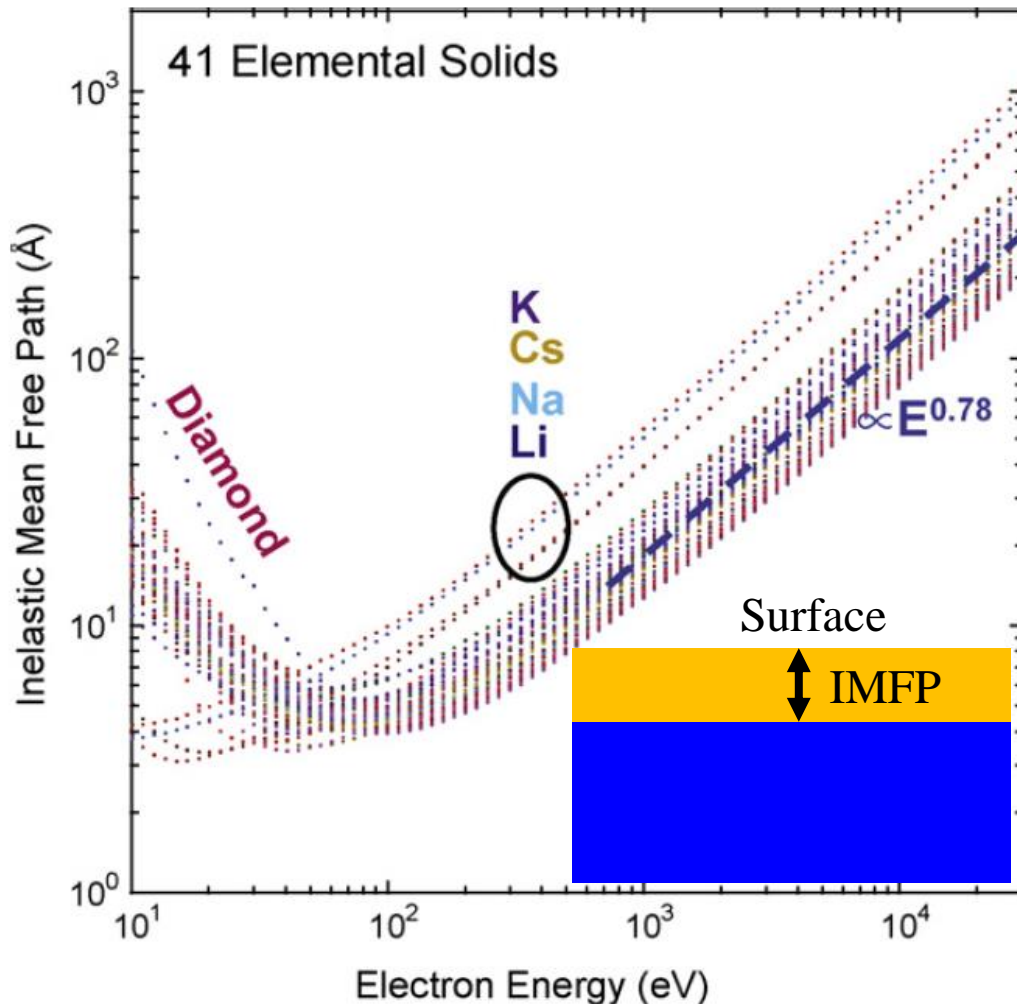
In general, XPS requires high vacuum ($P \sim 10^{-8}$ millibar) or ultra-high vacuum (UHV; $P < 10^{-9}$ millibar) conditions.

Basic physics in X-ray photoelectron spectroscopy (XPS)



Escape time of photoelectron seems to be considered around 10^{-16} sec., resulting in relaxation of atomic structure would be ignored.

Surface sensitivity



C.S. Fadley, Journal of Electron Spectroscopy and Related Phenomena 178-179, 2 (2010).

Fig. 2. Inelastic mean free paths (IMFPs) for 41 elements, calculated using the TPP-2M formula: Li, Be, three forms of carbon (graphite, diamond, glassy C), Na, Mg, Al, Si, K, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Cs, Gd, Tb, Dy, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Bi. Five “outlier” elements are indicated to provide some idea of what electronic structure characteristics can give rise to deviations from the majority behavior: diamond and the alkali metals. The dashed straight line for higher energies represents a variation as $\Lambda_e \propto E_{kin}^{0.78}$, and is a reasonable first approximation to the variation for all of the elements shown (from Ref. [23]).

- Inelastic Mean Free Path (IMFP) of photo excited electron for 41 elemental solids is shown the left figure.
- In case of the widely used aluminum K-alpha X-ray having 1486.7 eV, the IMFP is found to be 15 ~ 100 Å.
- On the other hand, when X-rays generated by synchrotron radiation is utilized, which have energy up to 15 keV, the IMFP can be more than 100 Å.

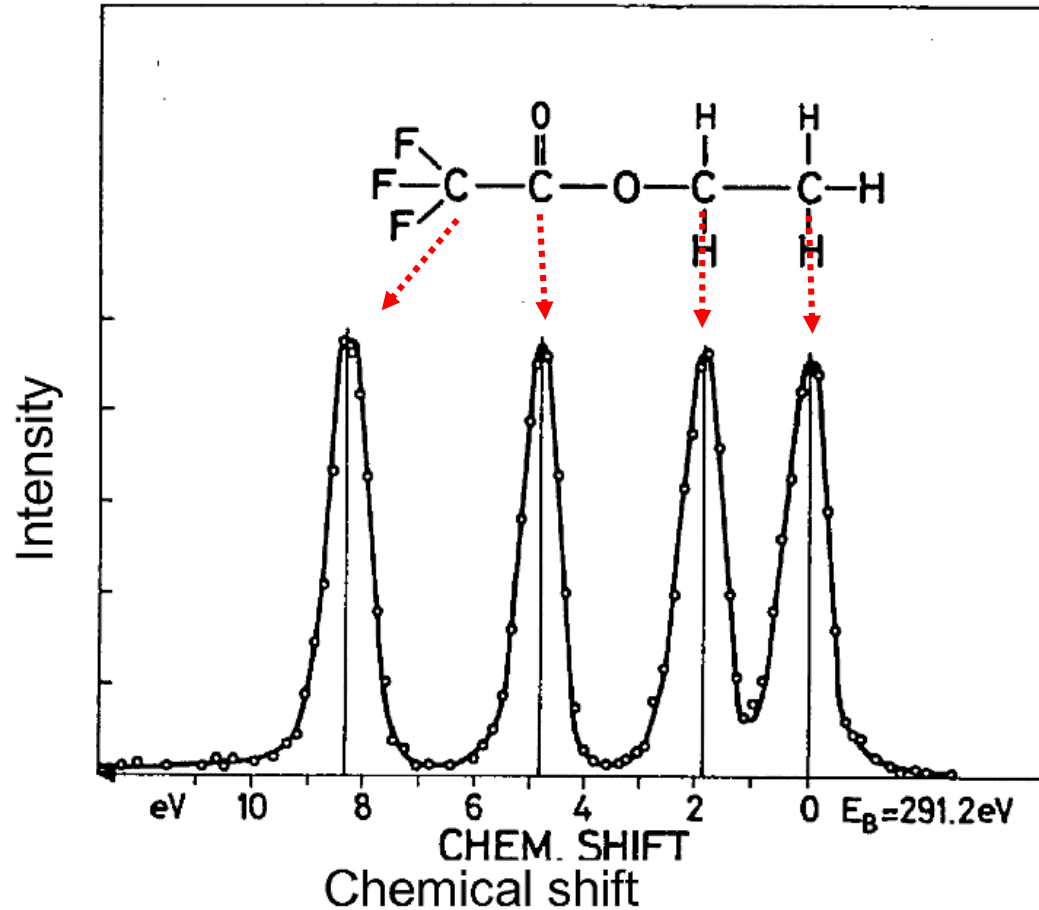
Multiple splitting of core level binding energies

There are four kinds of physical origins for multiple splitting of core level binding energies at least.

- Chemical shift
- Spin-orbit coupling
- Exchange interaction
- Chemical potential shift

Sensitivity to chemical environment

“PHOTOEMISSION
SPECTROSCOPY
Fundamental Aspects”
by Giovanni Stefani



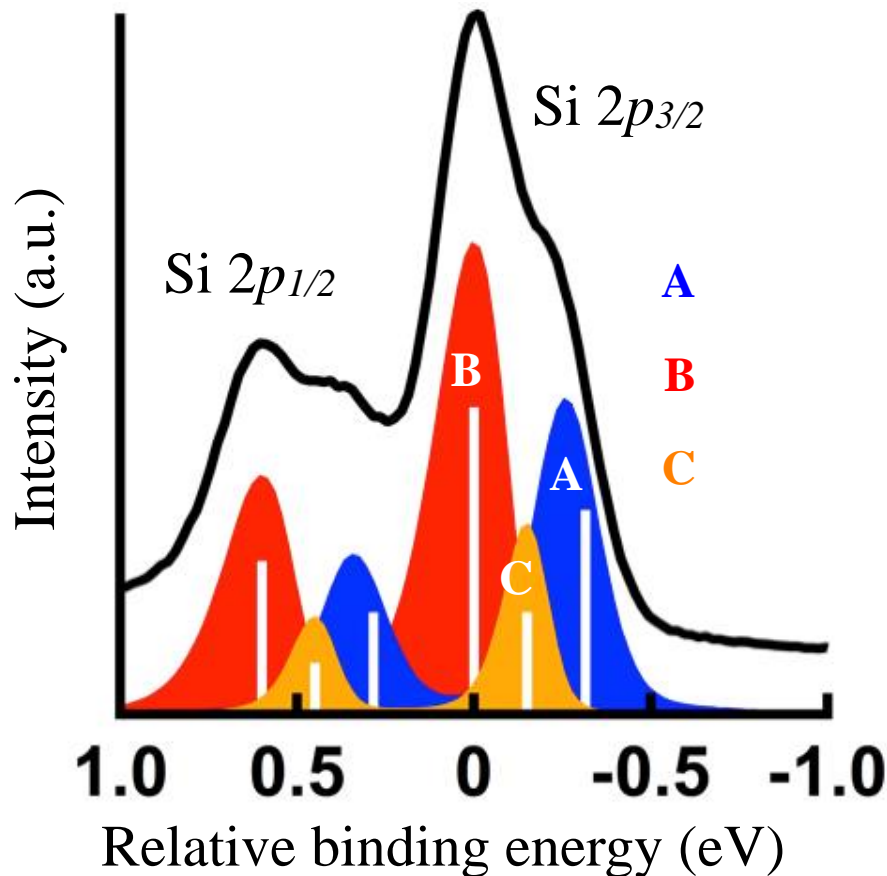
- The binding energy shifts depending on its chemical environment. The amount of shift is primarily determined by its charge state, known to be **initial state effect**.
- After creating the core hole, the screening of the core hole is also an important factor to determine chemical shift, known to be **final state effect**.

Core level multiplet splittings: Spin-orbit splitting

In addition to the chemical shift, there are other multiplet splittings.

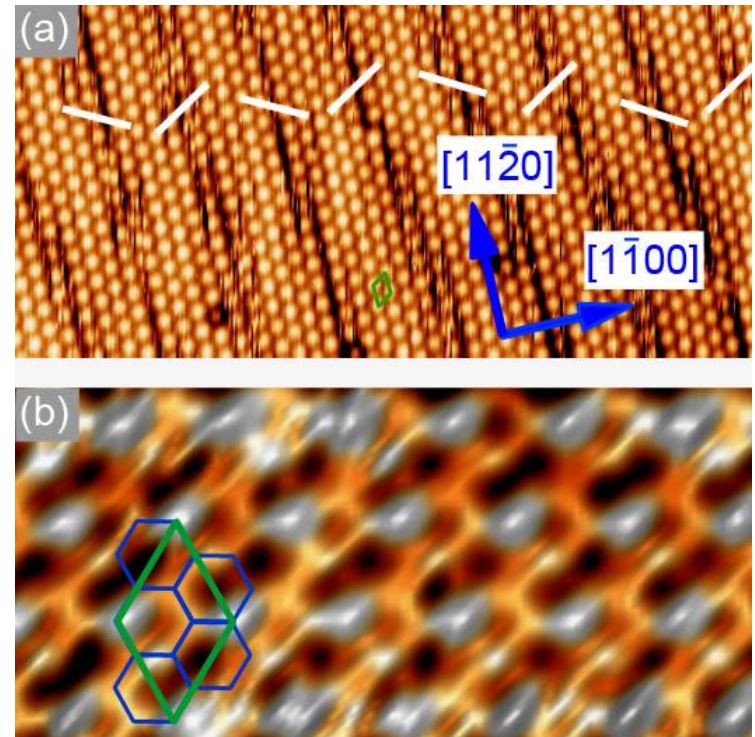
Spin-orbit coupling of core level

- Due to the strong SOC of core level states, the binding energy is split into two levels.
- The intensity ratio is $2l: 2(l+1)$ for $l-1/2$ and $l+1/2$, respectively.



A. Fleurence et al., PRL 108, 245501 (2012).

Silicene on ZrB₂ surface



Core level multiplet splittings: Exchange interaction

Exchange interaction between core and valence electrons

Molecules

Hedman et al.,
Phys. Lett. 29A,
178 (1969).

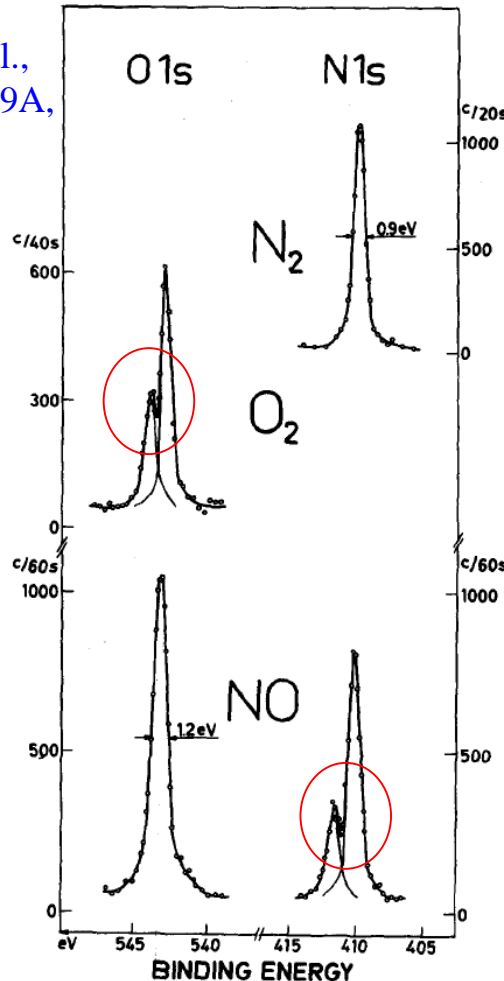


Fig. 1. ESCA spectra of core electron levels in N_2 , O_2 , and NO . Paramagnetic splitting is observed for the $1s$ levels in the O_2 and NO molecules.

Solids

Fadley and Shirley,
PRA 2, 1109 (1970).

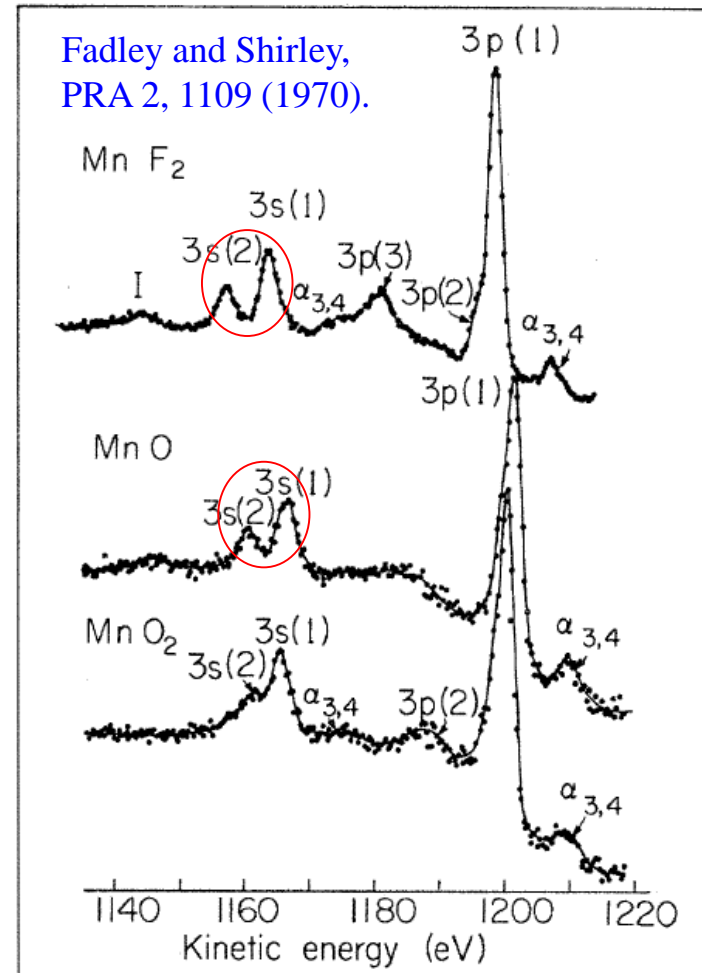
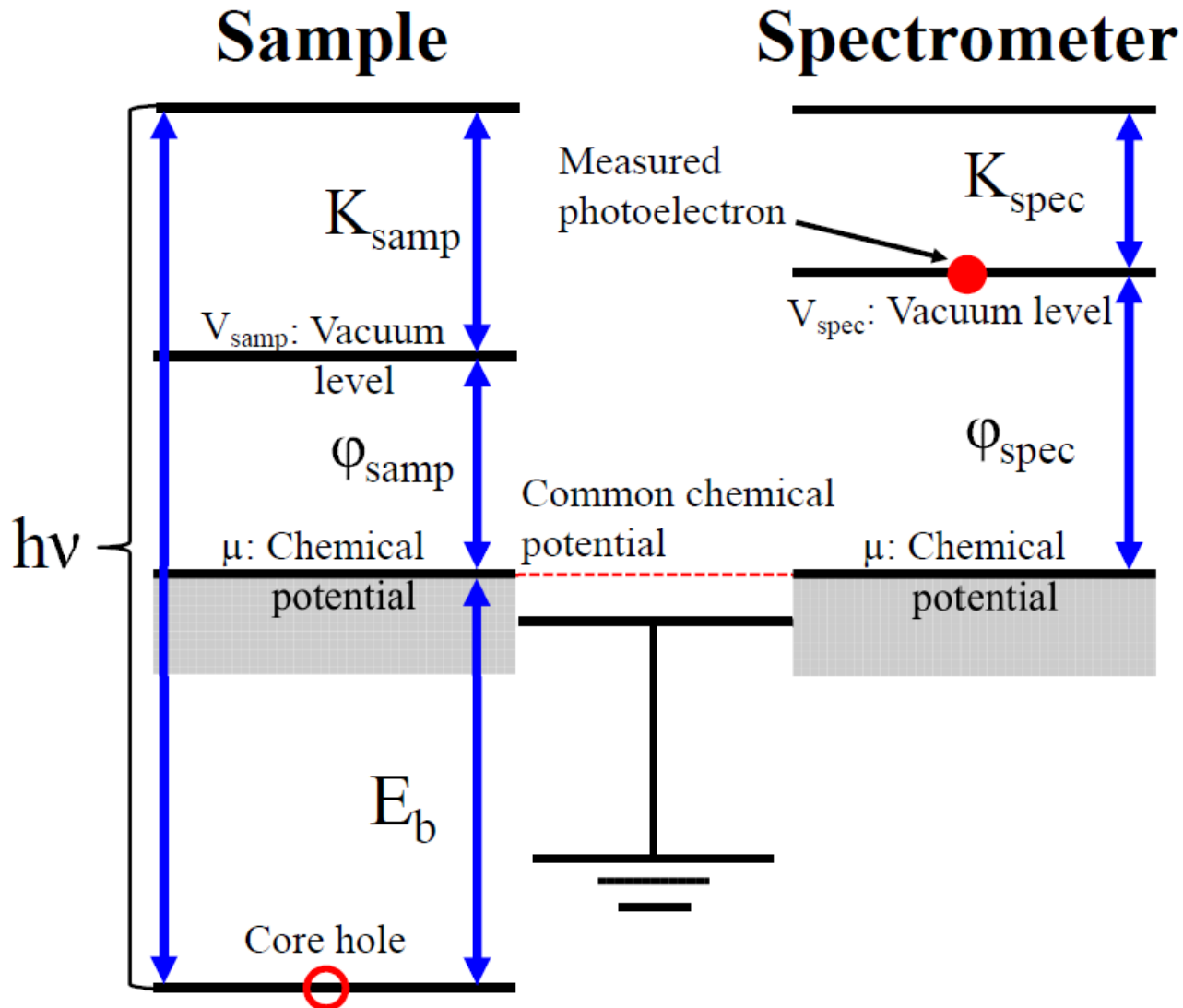


FIG. 1. Photoelectron spectra from MnF_2 , MnO , and MnO_2 in the kinetic-energy region corresponding to ejection of $Mn 3s$ and $3p$ electrons by $Mg K\alpha$ x rays.

Energy conservation in XPS

$$E_i(N) + h\nu = E_f(N-1) + V_{\text{spec}} + K_{\text{spec}}$$



Core level binding energies in XPS #1

$$E_i(N) + h\nu = E_f(N-1) + V_{\text{spec}} + K_{\text{spec}}$$

Using a relation: $V_{\text{spec}} = \mu + \phi_{\text{spec}}$ we have

$$E_b = h\nu - K_{\text{spec}} - \phi_{\text{spec}} = E_f(N-1) - E_i(N) + \mu$$

The experimental chemical potential can be transformed as

$$E_b = E_f^{(0)}(N-1) + (N-1)\Delta\mu - (E_i^{(0)}(N) + N\Delta\mu) + \mu_0 + \Delta\mu$$

A general formula of core level binding is given by

$$E_b = E_f^{(0)}(N-1) - E_i^{(0)}(N) + \mu_0$$

This is common for metals and insulators.

Core level binding energies in XPS #2

For metals, the Janak's theorem simplifies the formula:

$$E_{\text{f}}^{(0)}(N-1) - E_{\text{f}}^{(0)}(N) = \int dn \partial E_{\text{f}}^{(0)} / \partial n = -\mu_0$$

$$E_{\text{b}} = E_{\text{f}}^{(0)}(N) - E_{\text{i}}^{(0)}(N)$$

The formulae of core level binding energies are summarized as

Solids (gapped
systems, metals)

$$E_{\text{b}} = E_{\text{f}}^{(0)}(N-1) - E_{\text{i}}^{(0)}(N) + \mu_0$$

Metals

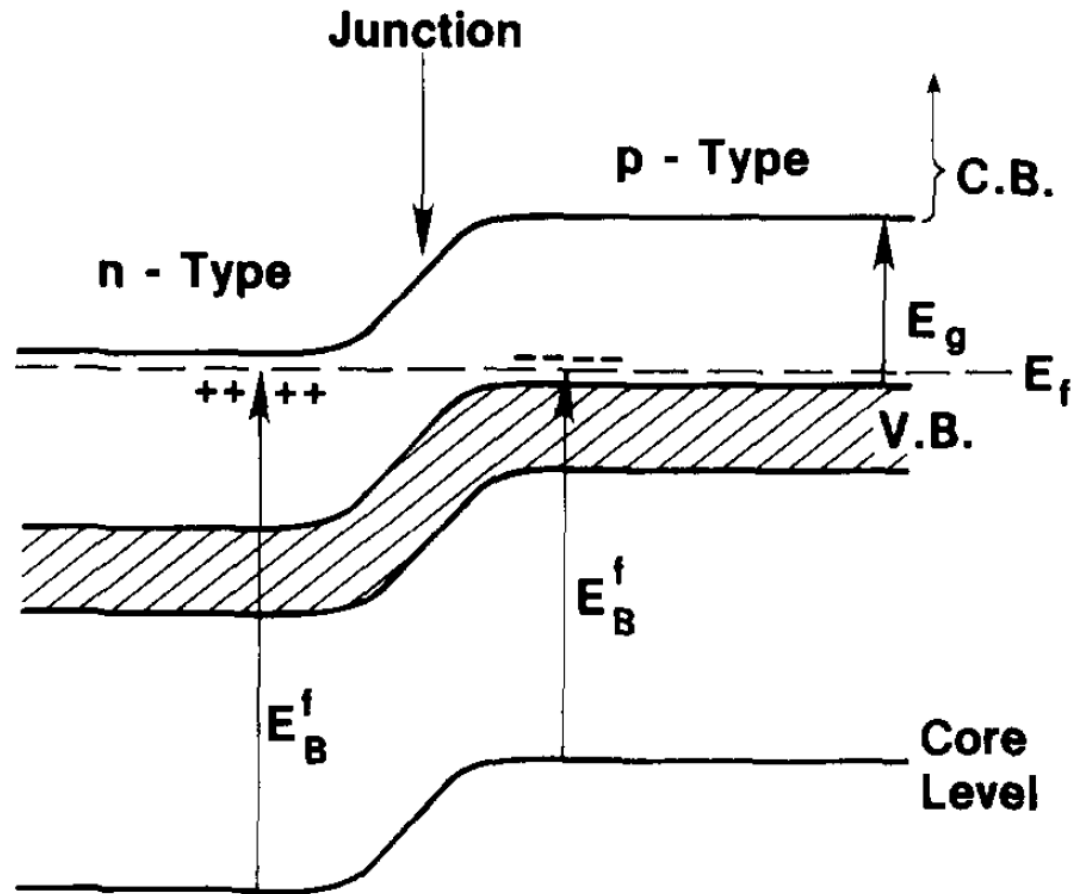
$$E_{\text{b}} = E_{\text{f}}^{(0)}(N) - E_{\text{i}}^{(0)}(N)$$

Gases

$$E_{\text{b}} = E_{\text{f}}^{(0)}(N-1) - E_{\text{i}}^{(0)}(N)$$

Chemical potential shift in gapped systems

In gapped systems, the chemical potential is highly sensitive to dopants, surface structure, and adsorbates.



This may explain the fact that reported binding energies are more dispersive for gapped systems than that for metals.

Calculations: core level binding energy

Within DFT, there are at least three ways to calculate the binding energies of core states as summarized below:

1. Initial state theory

Simply the density of states is taken into account

2. Core-hole pseudopotential method

Full initial and semi-final state effects are taken into account

E. Pehlke and M. Scheffler, PRL 71 2338 (1993).

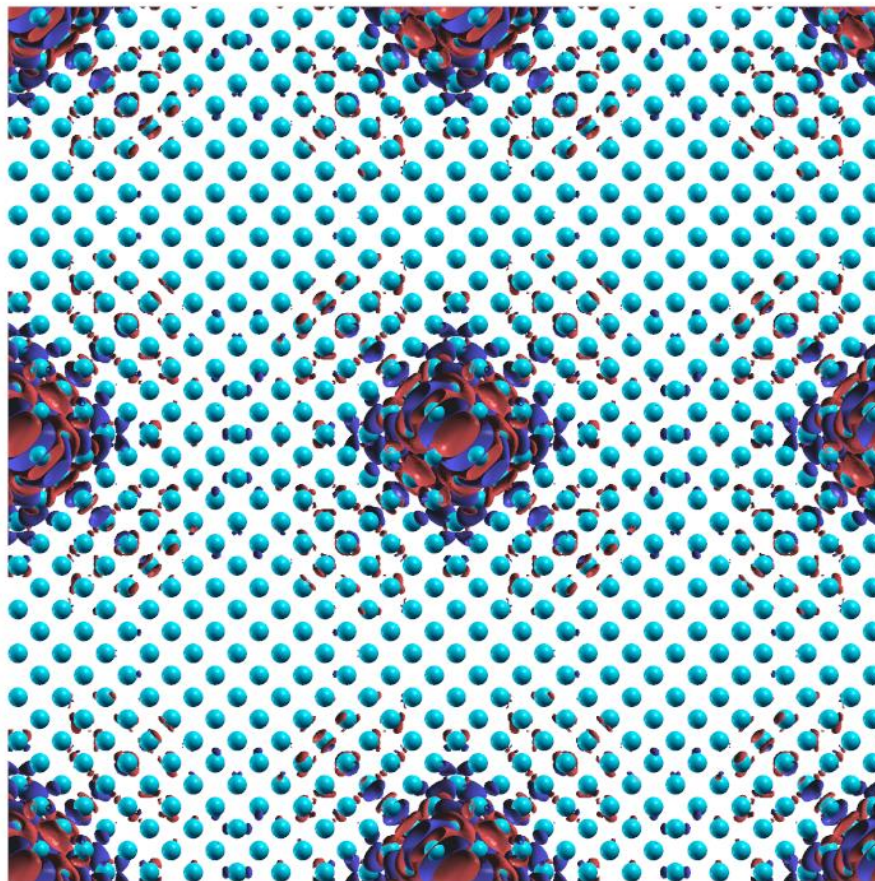
3. Core-hole SCF method

The initial and final state effects are fully taken into account on the same footing.

T. Ozaki and C.-C. Lee, Phys. Rev. Lett. 118, 026401 (2017) .

DFT calculation with a core hole

- ✓ How to create a core hole?
- ✓ How to eliminate the spurious interaction between supercells?



Constraint DFT with a penalty functional

$$E_f = E_{\text{DFT}} + E_p$$

E_{DFT} is a conventional functional of DFT, and E_p is a penalty functional defined by

$$E_p = \frac{1}{V_B} \int dk^3 \sum_{\mu} f_{\mu}^{(\mathbf{k})} \langle \psi_{\mu}^{(\mathbf{k})} | P | \psi_{\mu}^{(\mathbf{k})} \rangle$$

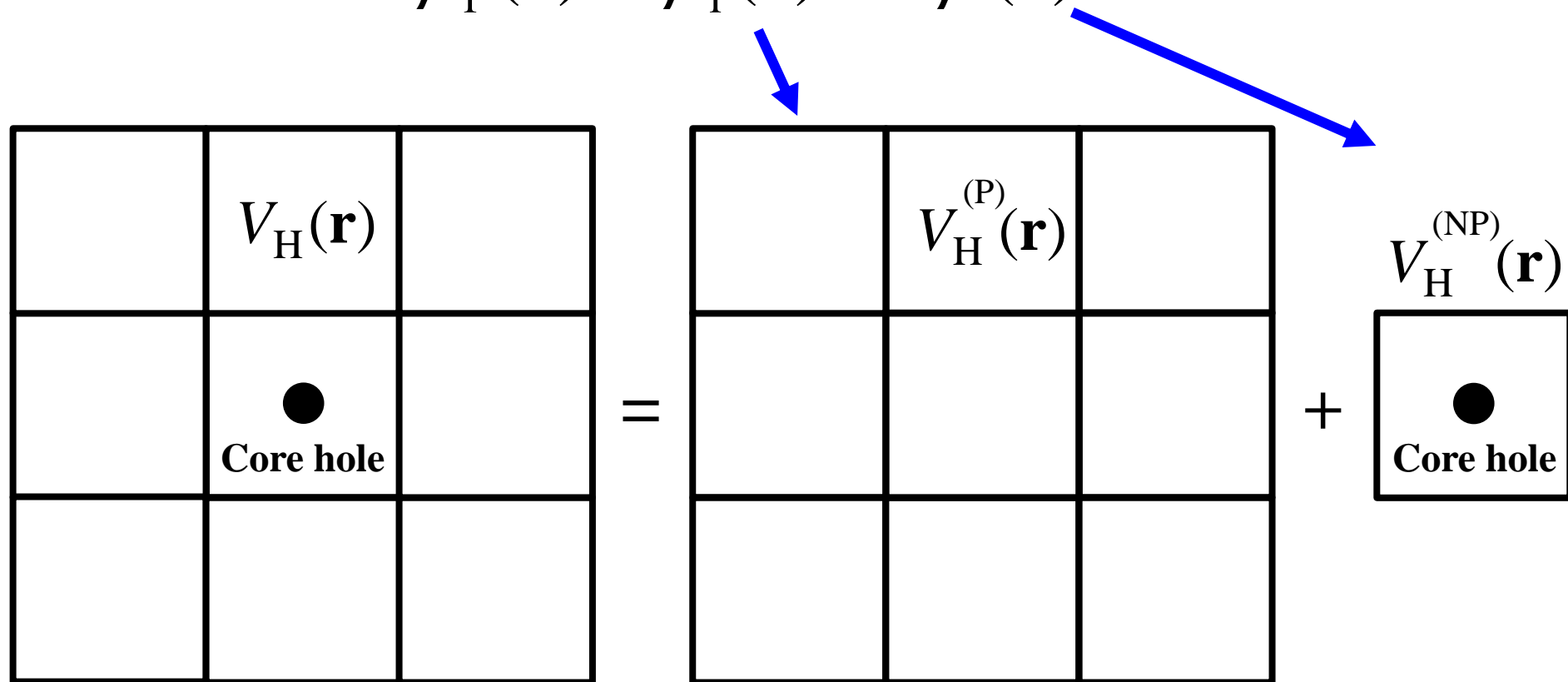
$$P = \left| R\Phi_J^M \right\rangle \Delta \left\langle R\Phi_J^M \right| \quad \text{R: radial function of the core level}$$

The projector is given by a solution of Dirac eq. for atoms.

$$\begin{aligned} J = l + \frac{1}{2}, M = m + \frac{1}{2} & \quad J = l - \frac{1}{2}, M = m - \frac{1}{2} \\ |\Phi_J^M\rangle = \left(\frac{l+m+1}{2l+1}\right)^{\frac{1}{2}} |Y_l^m\rangle + \left(\frac{l-m}{2l+1}\right)^{\frac{1}{2}} |Y_l^{m+1}\rangle & \quad |\Phi_J^M\rangle = \left(\frac{l-m+1}{2l+1}\right)^{\frac{1}{2}} |Y_l^{m-1}\rangle + \left(\frac{l+m}{2l+1}\right)^{\frac{1}{2}} |Y_l^m\rangle \end{aligned}$$

Elimination of inter-core hole interaction

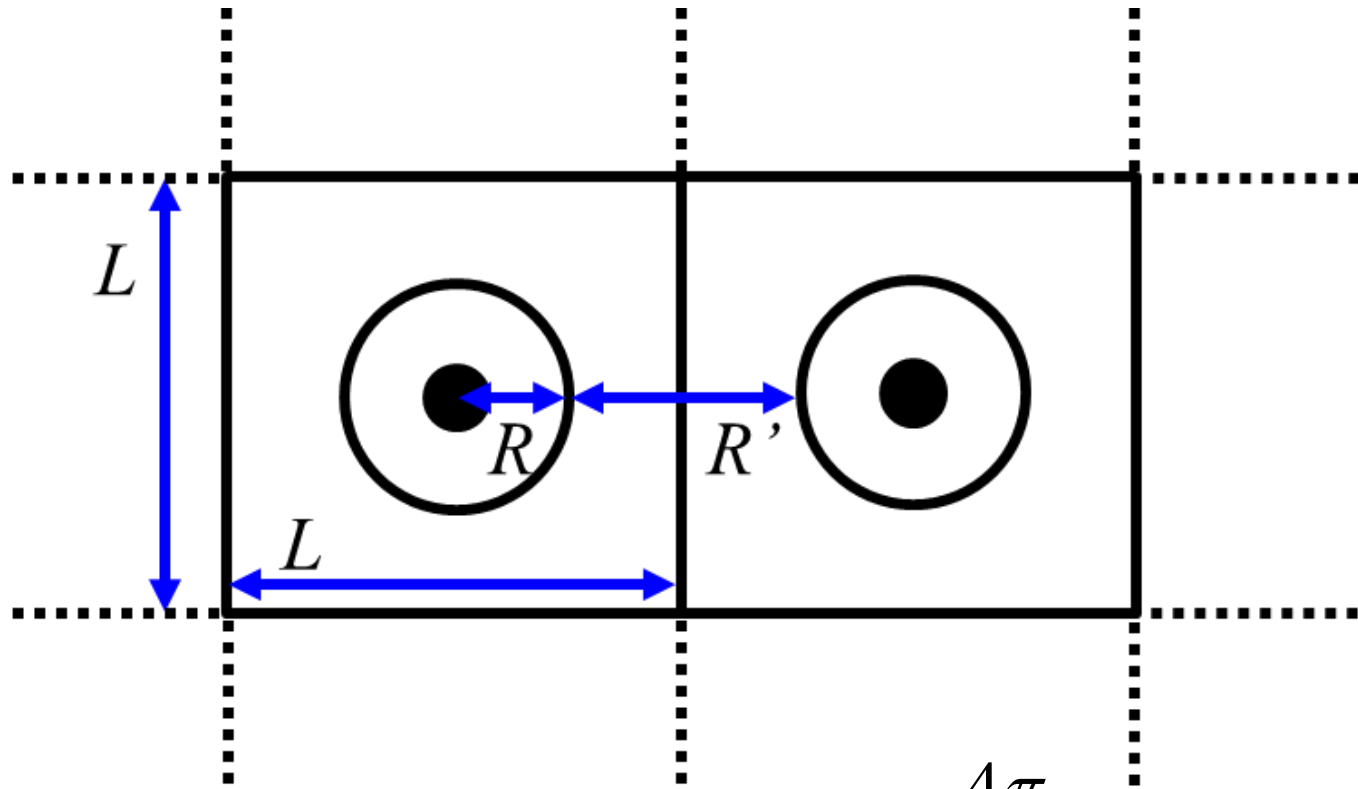
$$\rho_f(\mathbf{r}) = \rho_i(\mathbf{r}) + \Delta\rho(\mathbf{r}) \quad \Delta\rho(\mathbf{r}) = \rho_f(\mathbf{r}) - \rho_i(\mathbf{r})$$



- Periodic Hartree potential is calculated by charge density of the initial state.
- Potential by induced charge is calculated by an exact Coulomb cutoff method.

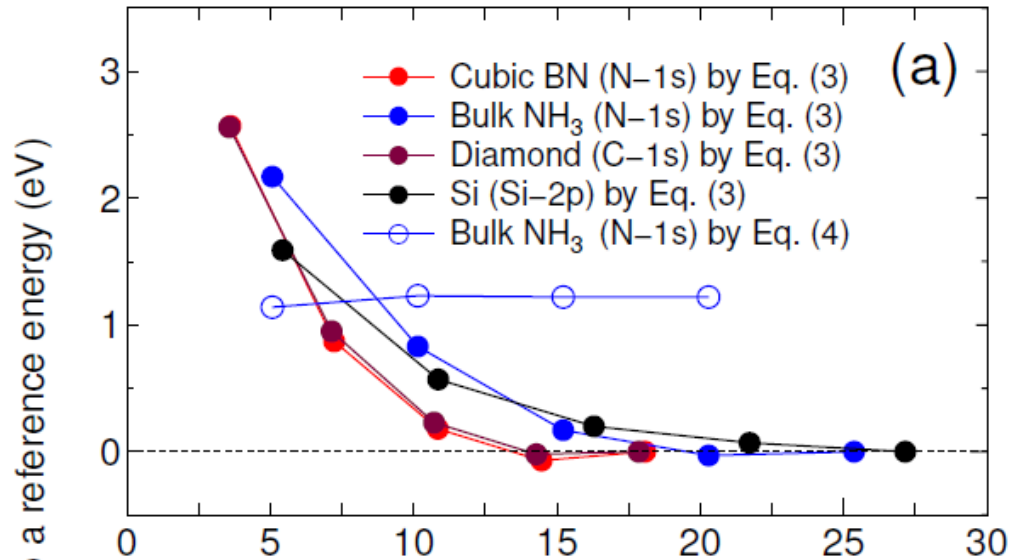
Exact Coulomb cutoff method #1

If the charge induced by a core hole localizes within a radius of R , we can set $R_c = 2R$, and the cutoff condition becomes $2R_c < L$ to eliminate the inter-core hole interaction.



$$v_H(r) = \sum_{\mathbf{G}} \tilde{n}(\mathbf{G}) \tilde{v}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} \quad \tilde{v}(\mathbf{G}) = \frac{4\pi}{G^2} (1 - \cos GR_c)$$

Convergence w. r. t cell size

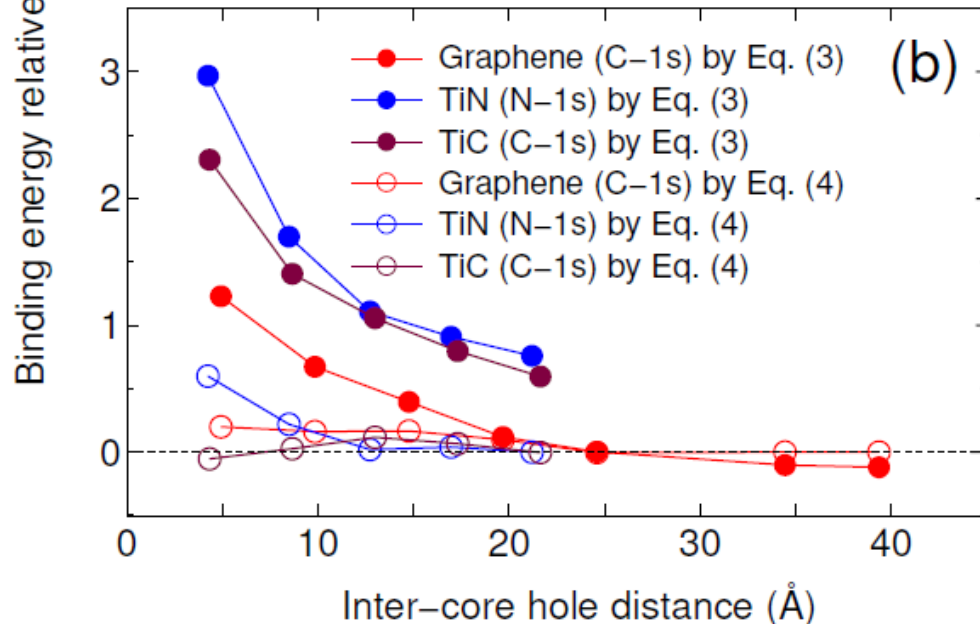


General formula

$$E_b = E_f^{(0)}(N-1) - E_i^{(0)}(N) + \mu_0 \quad \dots(3)$$

For metals

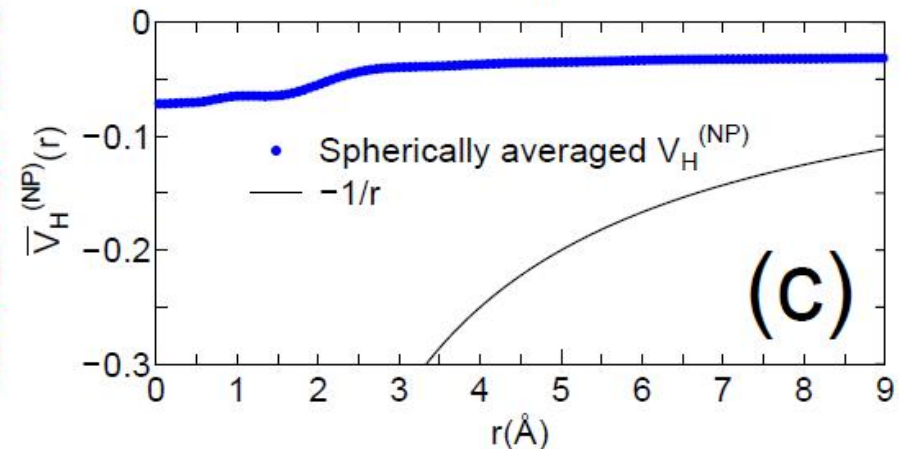
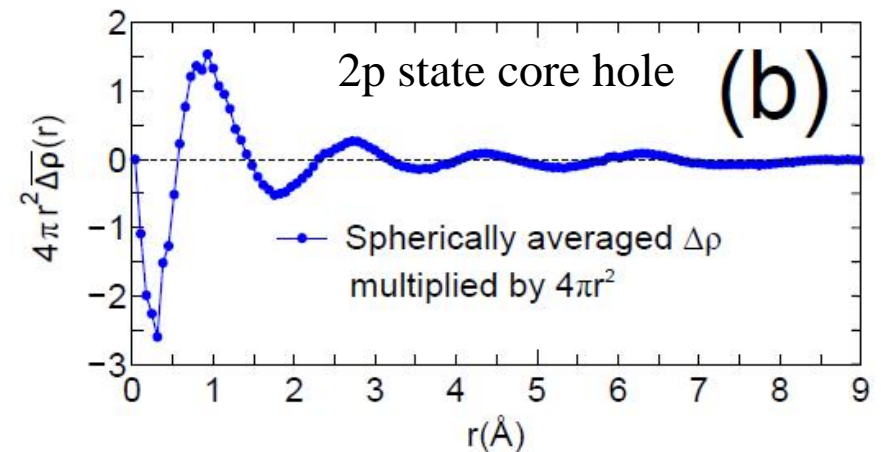
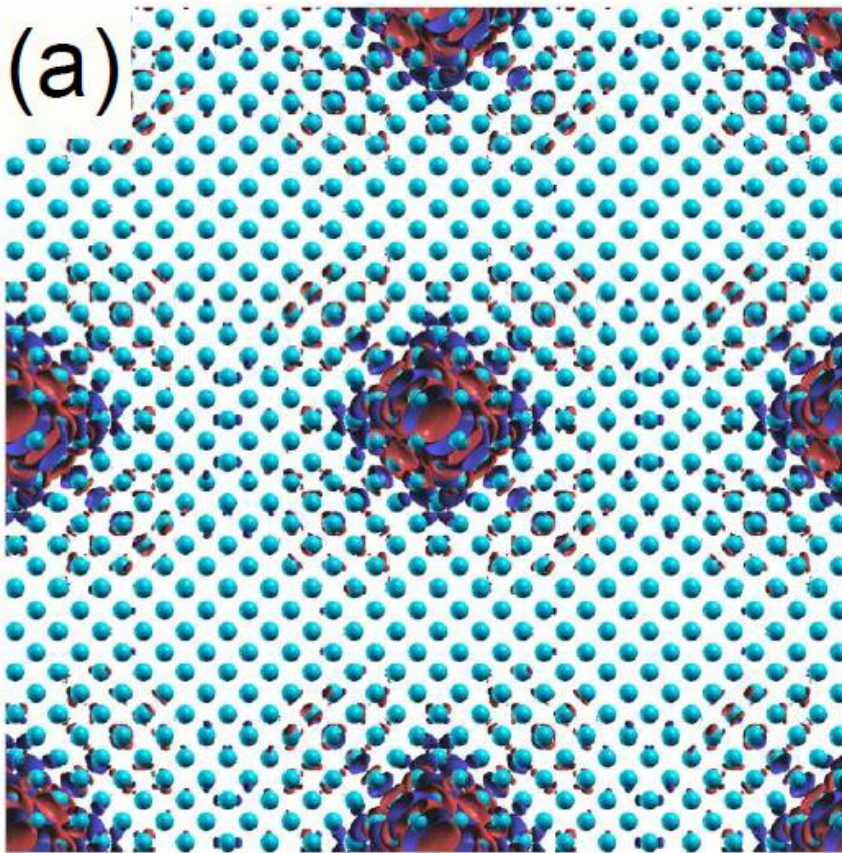
$$E_b = E_f^{(0)}(N) - E_i^{(0)}(N) \quad \dots(4)$$



- Convergence is attainable around 15~20Å.
- The formula for metals is not applicable for gapped systems.
- Very fast convergence by Eq. (4) for metals.

Difference charge induced by a core hole in Si

- The effective radius is about 7Å.
- The core hole is almost screened on the same Si atom.



Absolute values: Expt. vs. Calcs. for **solids**

Material	State	Calc. (eV)	Expt. (eV)
<i>Gapped system</i>			
c-BN	N-1s	398.87	398.1*
bulk NH ₃	N-1s	398.92	399.0 ⁺
Diamond	C-1s	286.50	285.6 [†]
Si	Si-2p _{1/2}	100.13	99.8*
Si	Si-2p _{3/2}	99.40	99.2*
<i>Semimetal or Metal</i>			
Graphene	C-1s	284.23	284.4 [†]
TiN	N-1s	396.43	397.1 [§]
TiC	C-1s	281.43	281.5*

Mean absolute error: 0.4 eV, Mean relative error: 0.16 %

Absolute values: Expt. vs. Calcs. for **gases**

Molecule	Calc. (eV)	Expt.* (eV)
<i>C-1s state</i>		
CO	295.87	296.19
C ₂ H ₂	291.24	291.17
CO ₂	296.89	297.66
HCN	293.35	293.50
C ₂ H ₄	290.50	290.79
H ₂ CO	294.00	294.47
<i>N-1s state</i>		
N ₂	409.89	409.83
NH ₃	404.70	405.60
N ₂ H ₄	404.82	406.1
HCN	406.16	406.36
<u>N</u> NO	408.24	408.66
<u>N</u> NO	411.98	412.57
NO(S=0)	410.62	411.6
NO(S=1)	410.10	410.2

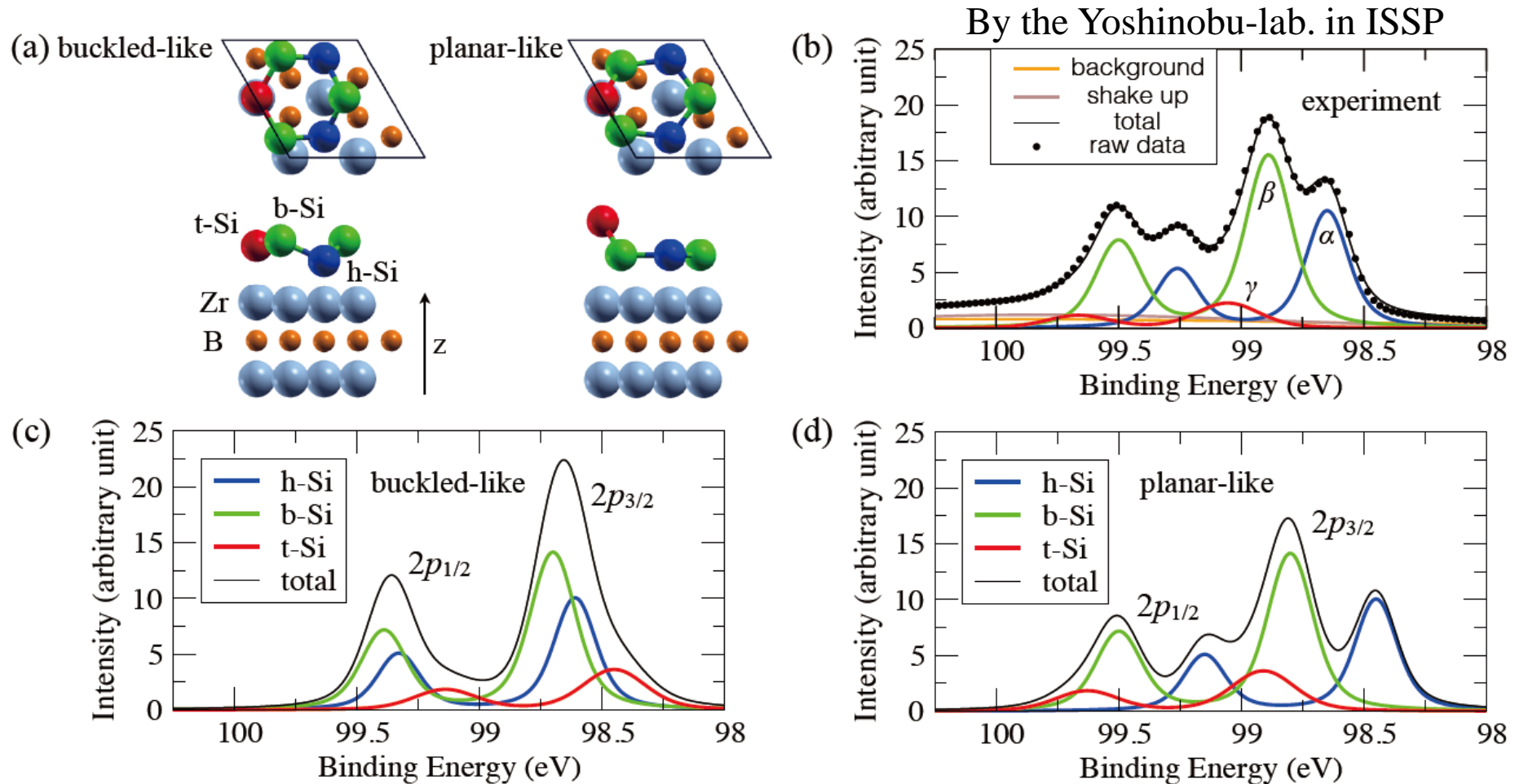
Molecule	Calc. (eV)	Expt.* (eV)
<i>O-1s state</i>		
CO	542.50	542.4
CO ₂	541.08	541.2
O ₂ (S= $\frac{1}{2}$)	543.15	544.2
O ₂ (S= $\frac{3}{2}$)	542.64	543.1
H ₂ O	539.18	539.9
<i>Si-2p state</i>		
SiH ₄	106.56	107.3
Si ₂ H ₆	106.21	106.86
SiF ₄	111.02	111.7
SiCl ₄	109.32	110.2

Mean absolute error: 0.5 eV

Mean relative error: 0.22 %

Silicene on ZrB_2

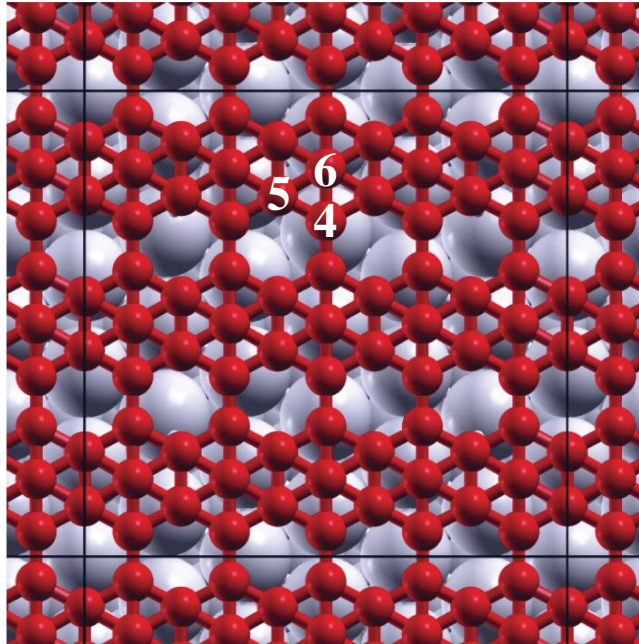
The XPS data is well compared with the calculated binding energy of planar-like structure.



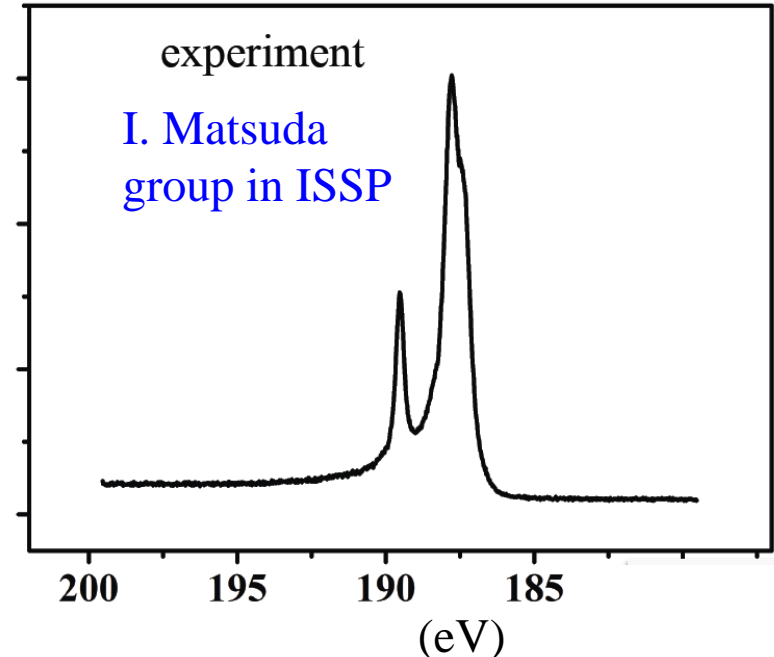
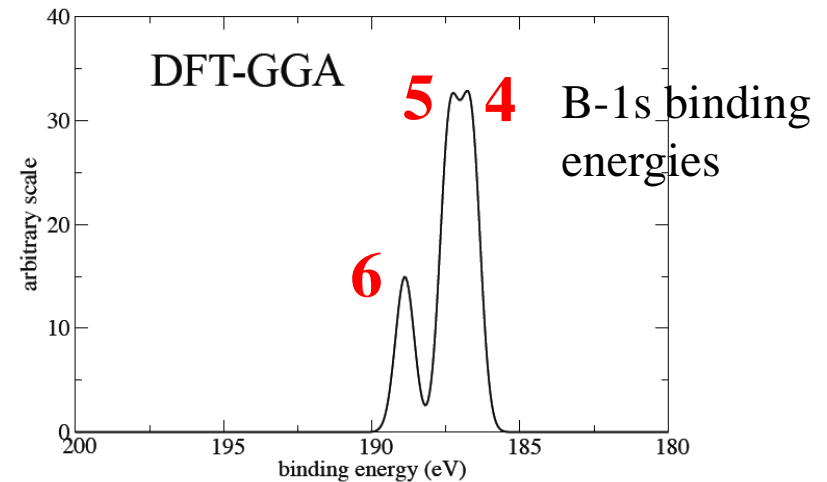
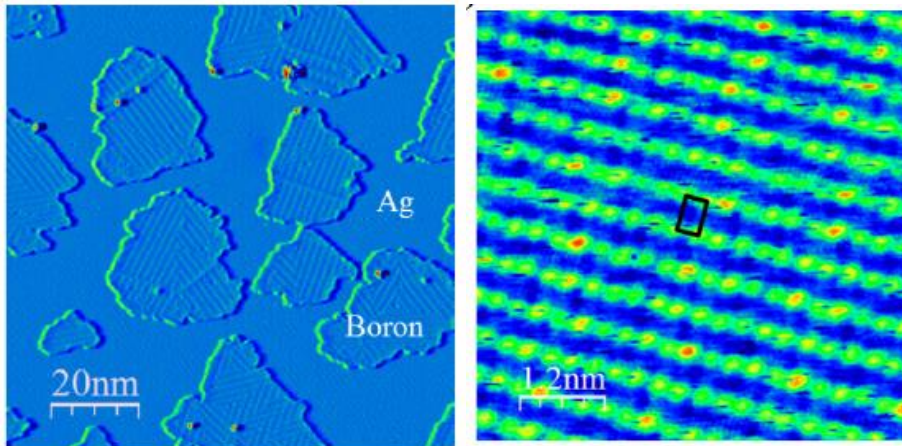
Borophene on Ag

In collaboration with the I. Matsuda group in ISSP

Computational model

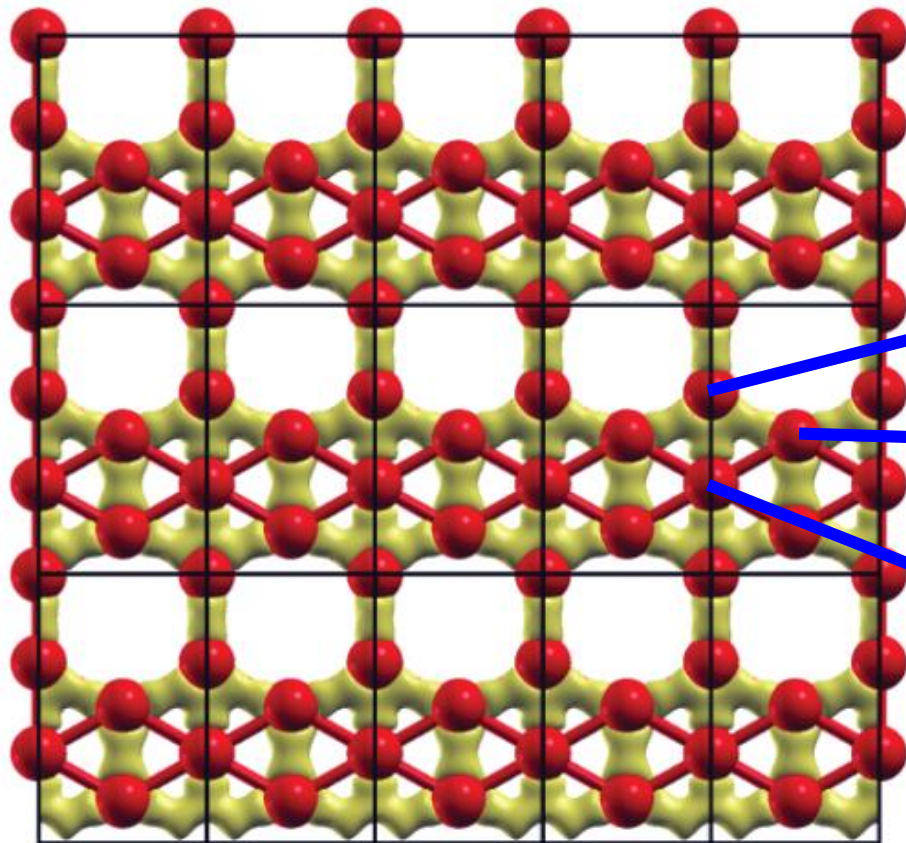


STM images from Feng et al, PRB 94, 041408 (3016).



C.-C. Lee et al., Phys. Rev. B **97**, 075430 (2018).

Bonding in borophene



0.125 e/bohr^3

Binding energy	Coordination	Bonds
186.228 eV	4	4
186.946 eV	5	3
188.646 eV	6	2

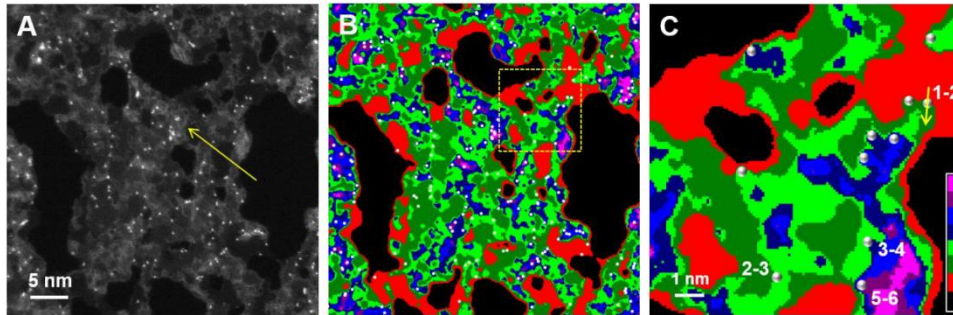
The higher coordination number, the lower number of bondings.

Single Pt Atoms Dispersed on Graphene

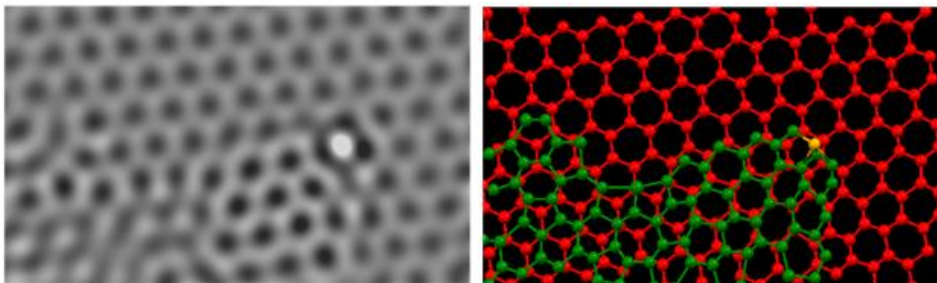
In collaboration with experiments and simulations, the local structure and the electronic states of Pt atoms monodispersed on graphene were clarified in details.

Yamazaki et al., J. Phys. Chem. C 122, 27292 (2018).

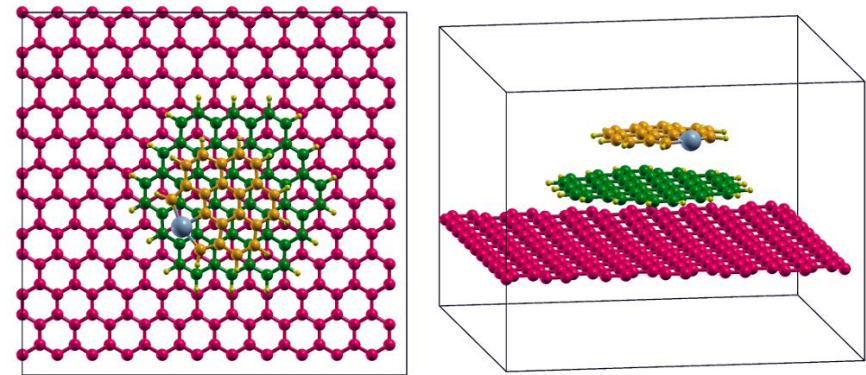
HAADF image by the Gohara group (Hokkaido Univ.)



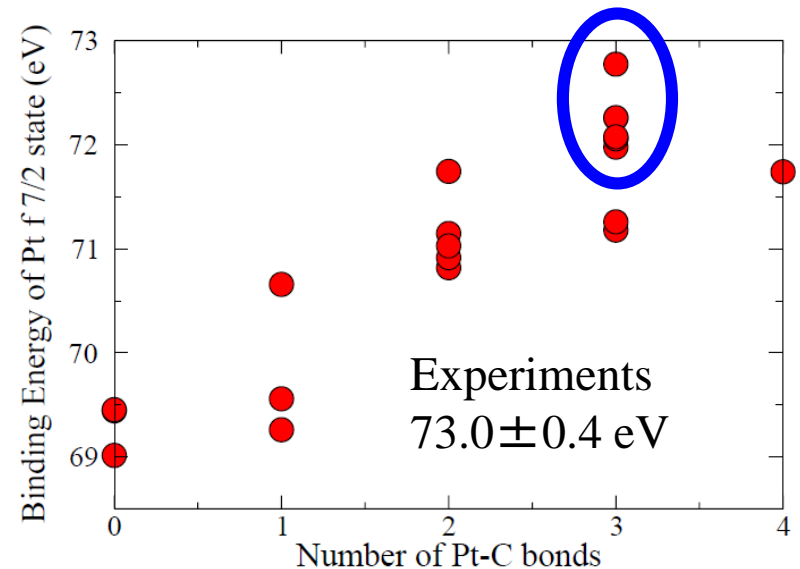
HRTEM image by the Gohara group (Hokkaido Univ.)



One of simulation models



Calculated XPS binding energies of Pt 4f_{7/2}



Usage #1

Let me explain the usage by taking an example, TiC, where the unit cell contains 8 atoms .
We define atomic species and unit vectors for both the ground and excited states as

Species.Number	3		Atoms.UnitVectors.Unit	Ang # Ang AU
<Definition.of.Atomic.Species			<Atoms.UnitVectors	
Ti	Ti7.0-s3p2d2	Ti_PBE19	4.327000000000	0.000000000000 0.000000000000
C	C6.0_1s-s3p2d1	C_PBE19_1s	0.000000000000	4.327000000000 0.000000000000
C1	C6.0_1s_CH-s3p2d1	C_PBE19_1s	0.000000000000	0.000000000000 4.327000000000
Definition.of.Atomic.Species>			Atoms.UnitVectors>	

The atomic coordinates are specified for both the cases as follows:

Ground state

```
<Atoms.SpeciesAndCoordinates
1 Ti 0.000000000000 0.000000000000 0.000000000000 6.0 6.0
2 Ti 2.163500000000 2.163500000000 0.000000000000 6.0 6.0
3 Ti 0.000000000000 2.163500000000 2.163500000000 6.0 6.0
4 Ti 2.163500000000 0.000000000000 2.163500000000 6.0 6.0
5 C 2.163500000000 0.000000000000 0.000000000000 3.0 3.0
6 C 0.000000000000 2.163500000000 0.000000000000 3.0 3.0
7 C 0.000000000000 0.000000000000 2.163500000000 3.0 3.0
8 C 2.163500000000 2.163500000000 2.163500000000 3.0 3.0
Atoms.SpeciesAndCoordinates>
```

Excited state

```
<Atoms.SpeciesAndCoordinates
1 Ti 0.000000000000 0.000000000000 0.000000000000 6.0 6.0
2 Ti 2.163500000000 2.163500000000 0.000000000000 6.0 6.0
3 Ti 0.000000000000 2.163500000000 2.163500000000 6.0 6.0
4 Ti 2.163500000000 0.000000000000 2.163500000000 6.0 6.0
5 C1 2.163500000000 0.000000000000 0.000000000000 3.0 3.0
6 C 0.000000000000 2.163500000000 0.000000000000 3.0 3.0
7 C 0.000000000000 0.000000000000 2.163500000000 3.0 3.0
8 C 2.163500000000 2.163500000000 2.163500000000 3.0 3.0
Atoms.SpeciesAndCoordinates>
```

It should be noted that a core hole is created in the atom 5 for the excited state by the following keyword:

```
<core.hole.state
5 s 1
core.hole.state>
```

The first: atomic index
The second: target l-channel (s, p, d, or f)
The third: orbital index (1 to 4l+2)

Note that the ground and excited state calculations have to be performed with “scf.SpinPolarization” = “on” or “nc”.

Usage #2

The orbital index corresponds to a state listed below:

Collinear case

s	1: $s\uparrow$	2: $s\downarrow$					
p	1: $p_x\uparrow$	2: $p_y\uparrow$	3: $p_z\uparrow$	4: $p_x\downarrow$	5: $p_y\downarrow$	6: $p_z\downarrow$	
d	1: $d_{3z^2-r^2}\uparrow$	2: $d_{x^2-y^2}\uparrow$	3: $d_{xy}\uparrow$	4: $d_{xz}\uparrow$	5: $d_{yz}\uparrow$		
	6: $d_{3z^2-r^2}\downarrow$	7: $d_{x^2-y^2}\downarrow$	8: $d_{xy}\downarrow$	9: $d_{xz}\downarrow$	10: $d_{yz}\downarrow$		
f	1: $f_{5z^2-3r^2}\uparrow$	2: $f_{5xz^2-xr^2}\uparrow$	3: $f_{5yz^2-yr^2}\uparrow$	4: $f_{zx^2-zy^2}\uparrow$	5: $f_{xyz}\uparrow$	6: $f_{x^3-3xy^2}\uparrow$	7: $f_{3yx^2-y^3}\uparrow$
	8: $f_{5z^2-3r^2}\downarrow$	9: $f_{5xz^2-xr^2}\downarrow$	10: $f_{5yz^2-yr^2}\downarrow$	11: $f_{5yz^2-yr^2}\downarrow$	12: $f_{xyz}\downarrow$	13: $f_{x^3-3xy^2}\downarrow$	14: $f_{3yx^2-y^3}\downarrow$

Non-collinear case

s	1: $J = 1/2$ $M = 1/2$	2: $J = 1/2$ $M = -1/2$						
p	1: $J = 3/2$ $M = 3/2$	2: $J = 3/2$ $M = 1/2$	3: $J = 3/2$ $M = -1/2$	4: $J = 3/2$ $M = -3/2$	5: $J = 1/2$ $M = 1/2$	6: $J = 1/2$ $M = -1/2$		
d	1: $J = 5/2$ $M = 5/2$	2: $J = 5/2$ $M = 3/2$	3: $J = 5/2$ $M = 1/2$	4: $J = 5/2$ $M = -1/2$	5: $J = 5/2$ $M = -3/2$	6: $J = 5/2$ $M = -5/2$		
		7: $J = 3/2$ $M = 3/2$	8: $J = 3/2$ $M = 1/2$	9: $J = 3/2$ $M = -1/2$	10: $J = 3/2$ $M = -3/2$			
f	1: $J = 7/2$ $M = 7/2$	2: $J = 7/2$ $M = 5/2$	3: $J = 7/2$ $M = 3/2$	4: $J = 7/2$ $M = 1/2$	5: $J = 7/2$ $M = -1/2$	6: $J = 7/2$ $M = -3/2$	7: $J = 7/2$ $M = -5/2$	8: $J = 7/2$ $M = -7/2$
		9: $J = 5/2$ $M = 5/2$	10: $J = 5/2$ $M = 3/2$	11: $J = 5/2$ $M = 1/2$	12: $J = 5/2$ $M = -1/2$	13: $J = 5/2$ $M = -3/2$	14: $J = 5/2$ $M = -5/2$	

Usage #3

The other keywords for the core hole calculation are given as

```
scf.restart                on
scf.restart.filename       TiC8
scf.coulomb.cutoff         on
scf.core.hole              on

<core.hole.state
  5 s 1
core.hole.state>

scf.system.charge          0.0
```

- In the final state, the restart files, generated by the initial state calculation, has to be read. The relevant keywords are **scf.restart** and **scf.restart.filename**.
 - Also, the non-periodic charge density is treated by the exact Coulomb cutoff method, specified by the keyword: **scf.coulomb.cutoff**.
-
- The core hole is introduced by the keywords: **scf.core.hole** and **core.hole.state**.
 - Also, due to the creation of core hole, the system is charged up by the keyword: **scf.system.charge**.

Examples

Database (2019) of optimized VPS and PAO for core level excitations

The database (2019) of fully relativistic pseudopotentials (VPS) and pseudo-atomic orbitals (PAO) which can be used for calculations of core level excitations in OpenMX. The VPS and PAO files were generated by ADPACK. The VPS and PAO files of elements with the underline are currently available. When you use these data, VPS and PAO, in the program package, OpenMX, then copy them to the directory, openmx*/DFT_DATA19/VPS/ and openmx*/DFT_DATA19/PAO/, respectively.

E	Examples of the calculations can be found at																	
H	https://t-ozaki.issp.u-tokyo.ac.jp/vps_pao_core2019/																	He
Li	Be											<u>B</u>	<u>C</u>	<u>N</u>	<u>O</u>	F	Ne	
Na	Mg											Al	<u>Si</u>	P	<u>S</u>	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	<u>Ge</u>	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	<u>Pt</u>	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	A																
	L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
	A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Exercises

- Calculate the core level binding energy of C-1s state in acetylene molecule. Please follow the guidance in the pages 278-281 of the manual.
- Calculate the core level binding energy of C-1s state in TiC bulk. Please copy the input files (TiC8.dat and TiC8-CH3.dat) in /home/hands-on/, and follow the guidance in the pages 281-283 of the manual.