# 多重散乱法を用いたプラズモンロス計算の使用例

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17.09.25

$$\langle\psi_{\vec{k}}^{-}|\Delta|\phi_i\rangle \approx \sum_{\alpha} e^{-i\vec{k}\cdot\vec{R}_\alpha} \sum_{L_1,L_2} \sum_{A,L_3} Y_{L_1}(\hat{\mathbf{k}})[(1-X)^{-1}]^{\alpha,A}_{L1,L2} M^{A}_{L_2,L_3}$$

**多重散乱理論** **Multiple Scattering theory**

Enable us to simulate the behavior of photoelectrons

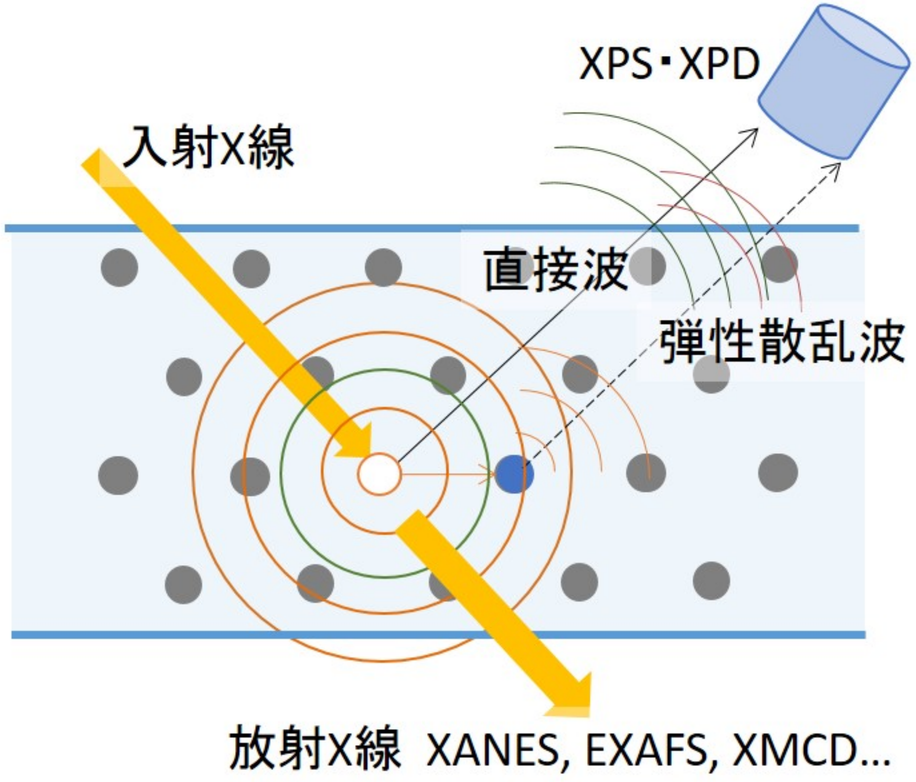
It appropriate for considering the

unoccupied states = continuum state

= the behavior of photoelectron

$$|\psi_{\vec{k}}^{-}\rangle = |\phi_{\vec{k}}\rangle + \frac{1}{E_k - H_0 - i0^+} V\,|\psi_{\vec{k}}^{-}\rangle$$

$$V(\vec{r}) = \sum_{\alpha} v_\alpha\left(|\vec{r}-\vec{R}_\alpha|\right)$$



## Multiple Scattering theory

Enable us to simulate the behavior of photoelectrons

Is appropriate for considering the unoccupied states=continuum state= the behavior of photoelectron

Partition the real space into atomic scattering regions

$$V(\vec{r}) = \sum_{\alpha} v_{\alpha}\left(|\vec{r} - \vec{R}_{\alpha}|\right)$$

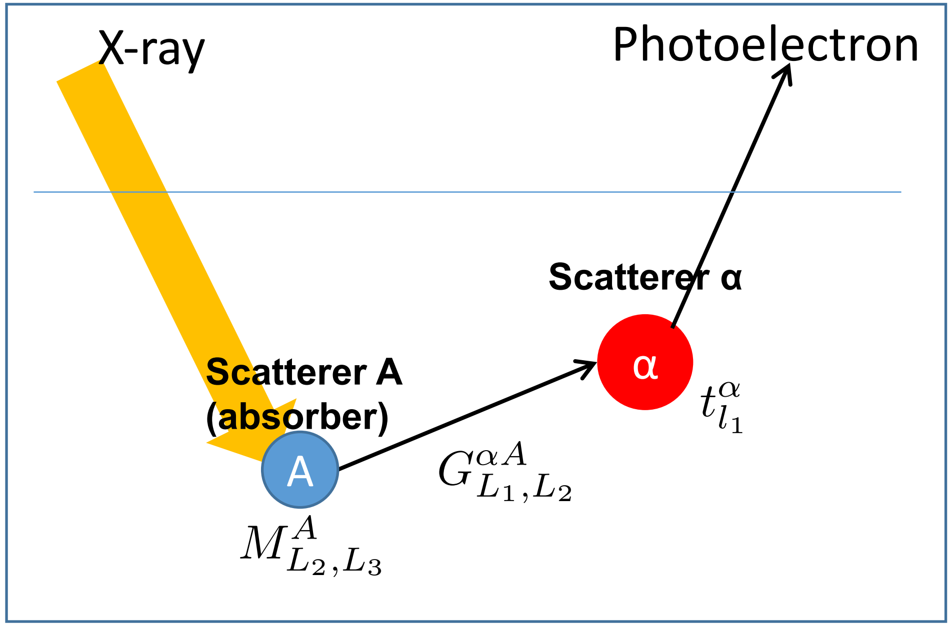
Apply Lipmann-Schwinger Eq. for final state

$$|\psi_{\vec{k}}^{-}\rangle = |\phi_{\vec{k}}\rangle + \frac{1}{E_k - H_0 - i0^{+}} V |\psi_{\vec{k}}^{-}\rangle$$

Scattering amplitude

$$\langle\psi_{\vec{k}}^{-}|\Delta|\phi_i\rangle \approx \sum_{\alpha} e^{-i\vec{k}\cdot\vec{R}_{\alpha}} \sum_{L_1,L_2} \sum_{A,L_3} Y_{L_1}(\hat{\mathbf{k}})[(1-X)^{-1}]^{\alpha,A}_{L1,L2} M^{A}_{L_2,L_3}$$

propagation / scattering — optical transition in atom A




**Initial state WF**
- Atomic WF
- Molecular Orbital ( Gaussian )

→ Potential →

**Atomic scattering**
- Radial integral
- Phase shift

→ MS theory →

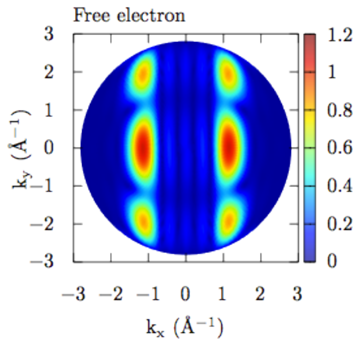
Photoemission amplitude

# Our lab…

**Electronic state**
**Adsorbing effects**

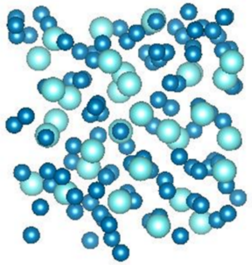
Full potential Pentacene

ARPES




**Surface structure**
**Magnetic anisotoropy**

$Fe_2O_3$ surface



Amorphous
magnetic thin film

## Multiple Scattering theory

To explore physical properties

科研費 若手B

**Plasmon loss**

EXAFS
XMCD

Heusler alloy systems
Electrode of Li-ion battery

XPS

Metal
Thin Film （Graphene...)
Nano particles,

Today’s Topic

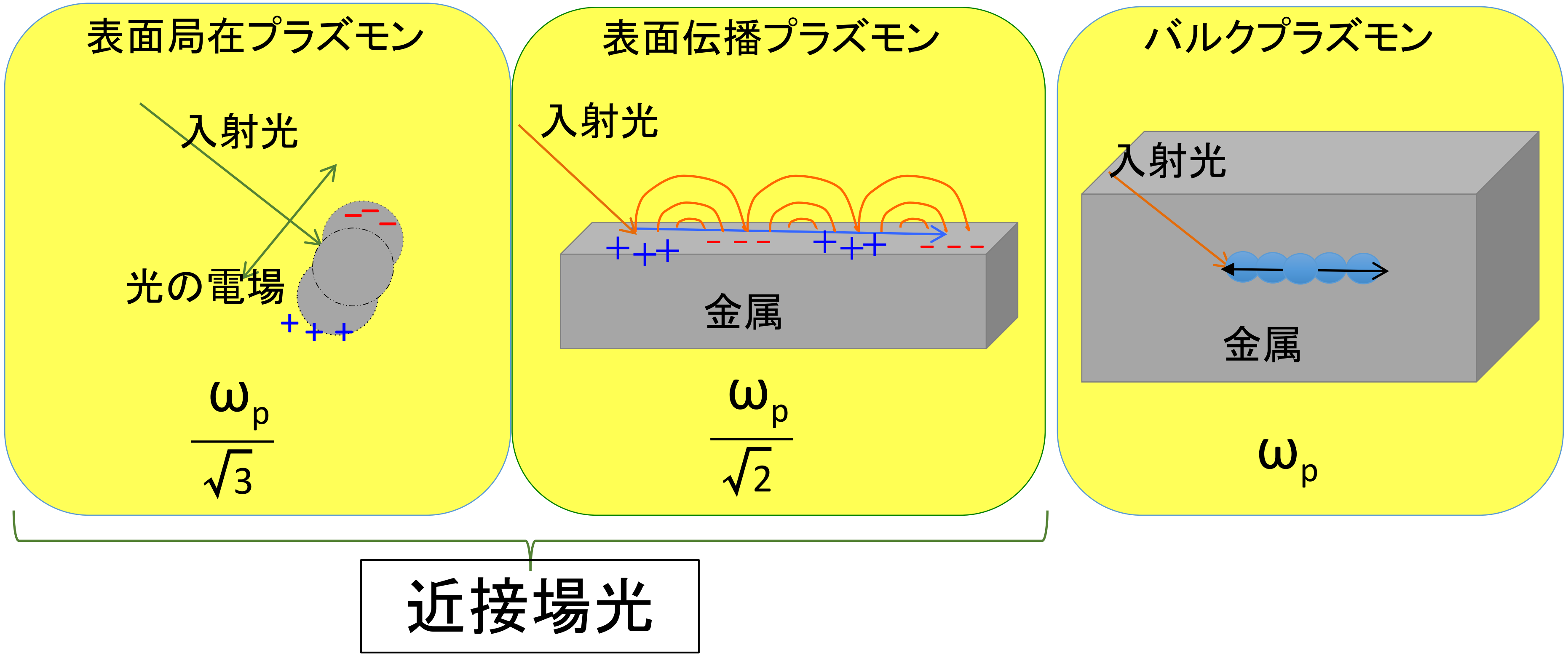
# Satellite peaks in XPS; plasmon loss peaks

1. Expressions for plasmon loss intensity
   which is called Quantum Landau formula.

2. Extension to other systems
   … graphene sheet and nano particles.

# プラズモン

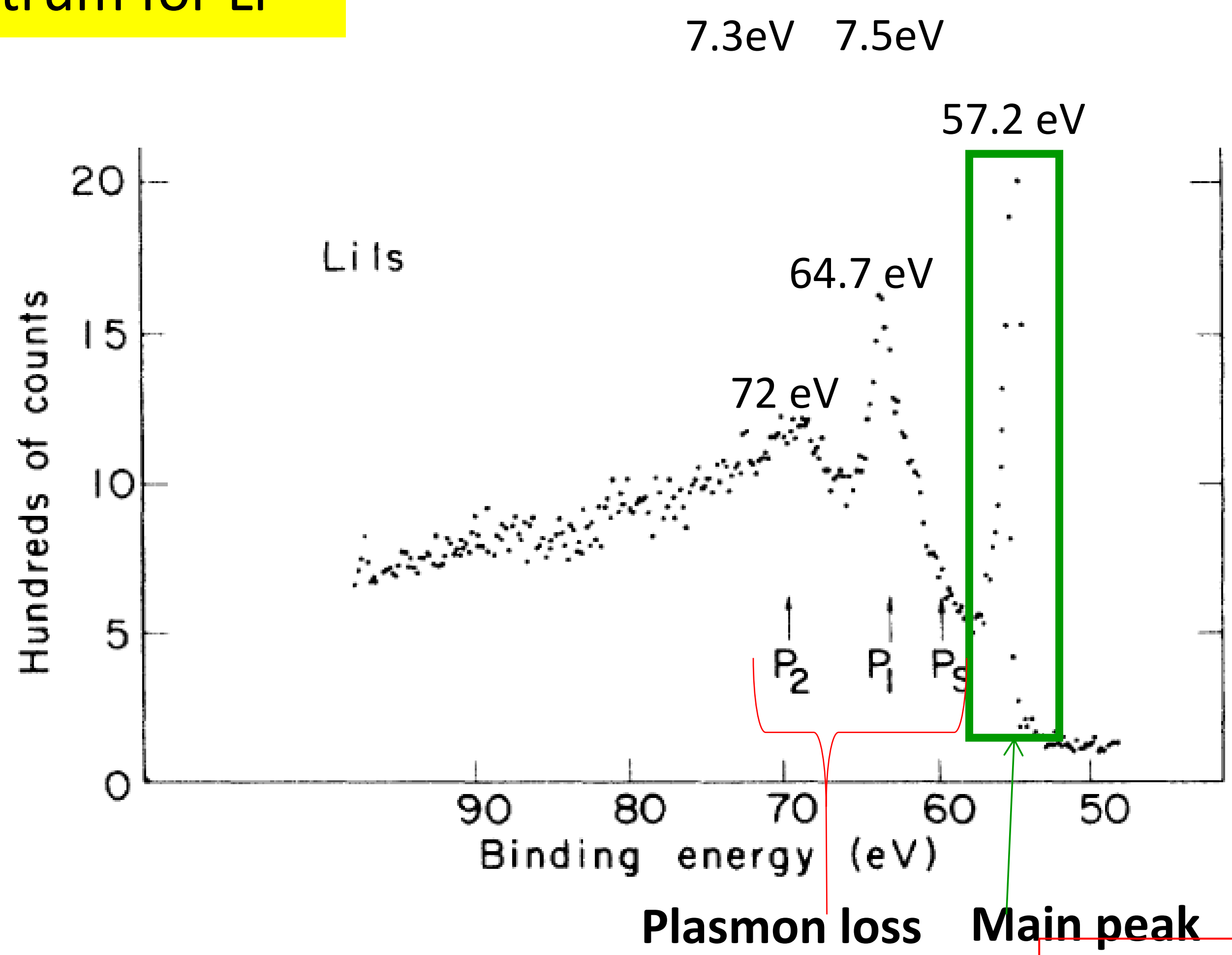
固体物質中での自由電子の集団振動
電荷分布のずれにより誘起される。
物質固有の共鳴振動数$\omega_p$をもつ。

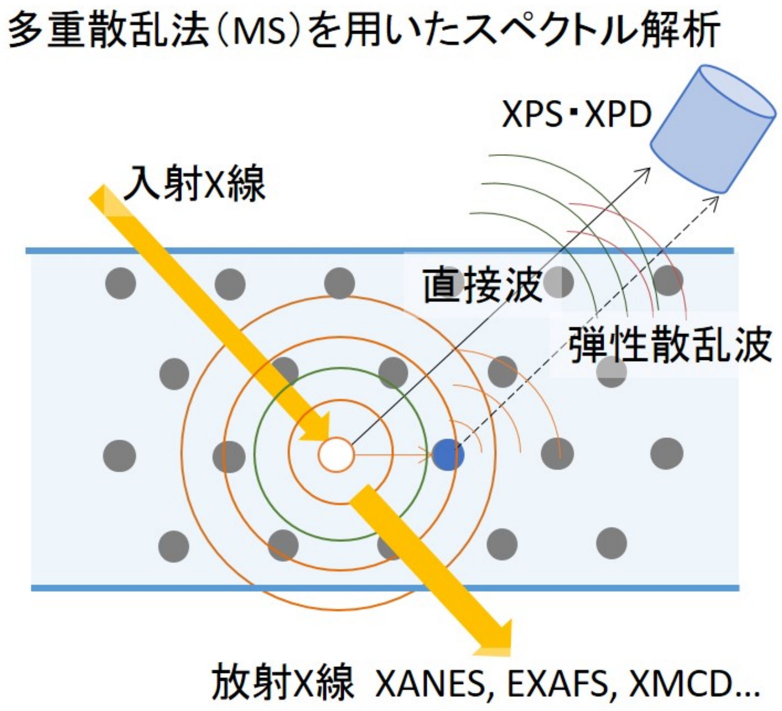



→ ナノフォトニクス・プラズモニクスへの応用

# XPS spectrum for Li

S. P. Kowalczyk *et al*., Phys. Rev. B 8, 3583 (1973).




$$I(\mathbf{p};w)_c^1 + \cdots ??$$

$$I(\mathbf{p};w)_c^0 = 2\pi \left| \left\langle f_{\mathbf{p}}^- \middle| \Delta \middle| \phi_c \right\rangle S_0 \right|^2 \delta\left(E_0 + \omega - E_0^* - \varepsilon_p\right)$$

Plasmon is collective electron oscillation excited by Δρ.
Plasmon loss peaks in XPS are observed due to excite the plasmon by photoelectron.

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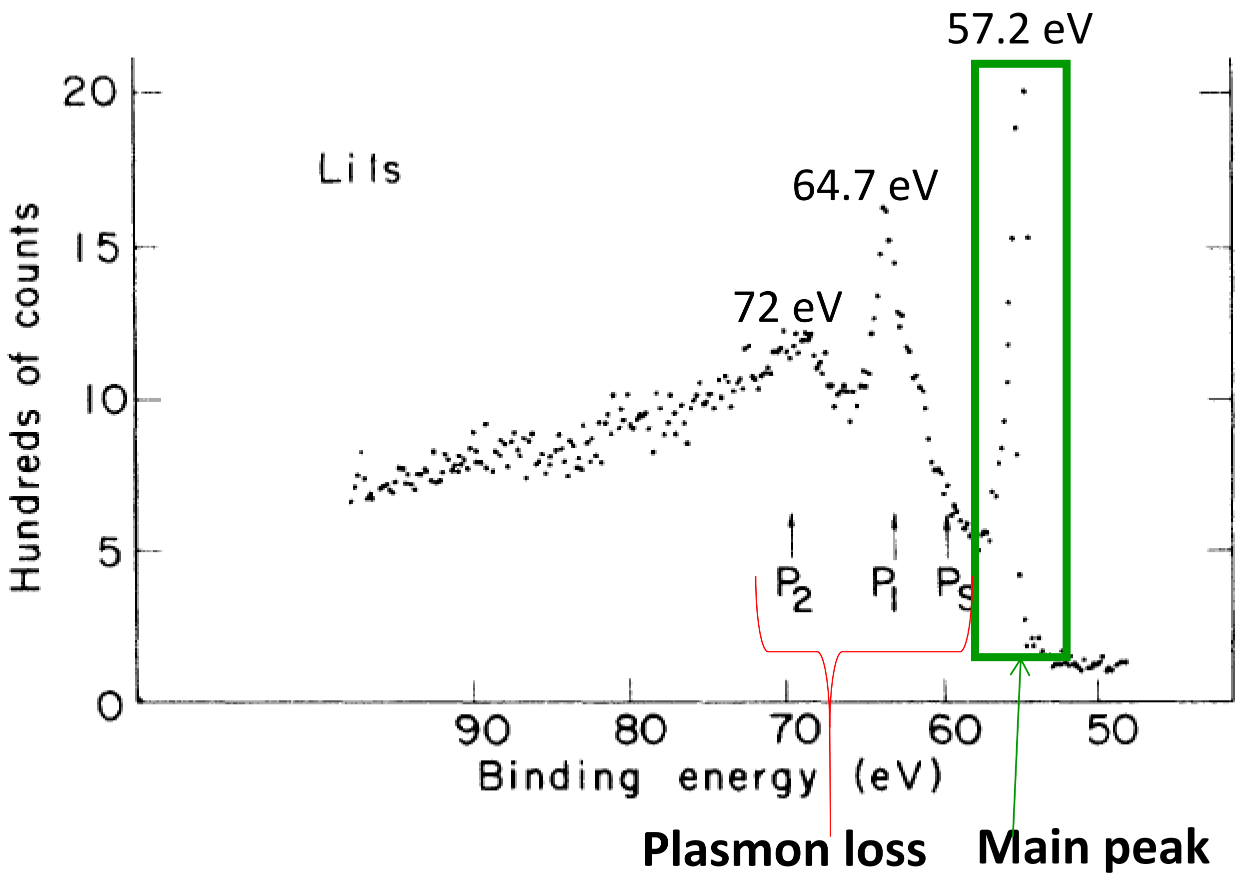


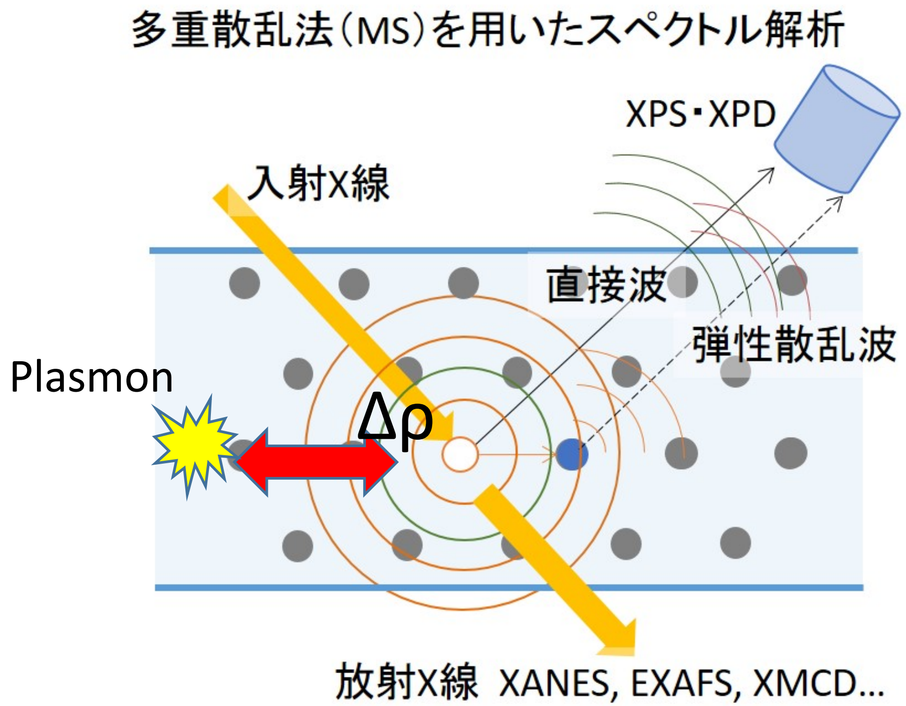


$$I(\mathbf{p};w)_c^1 + \cdots ??$$

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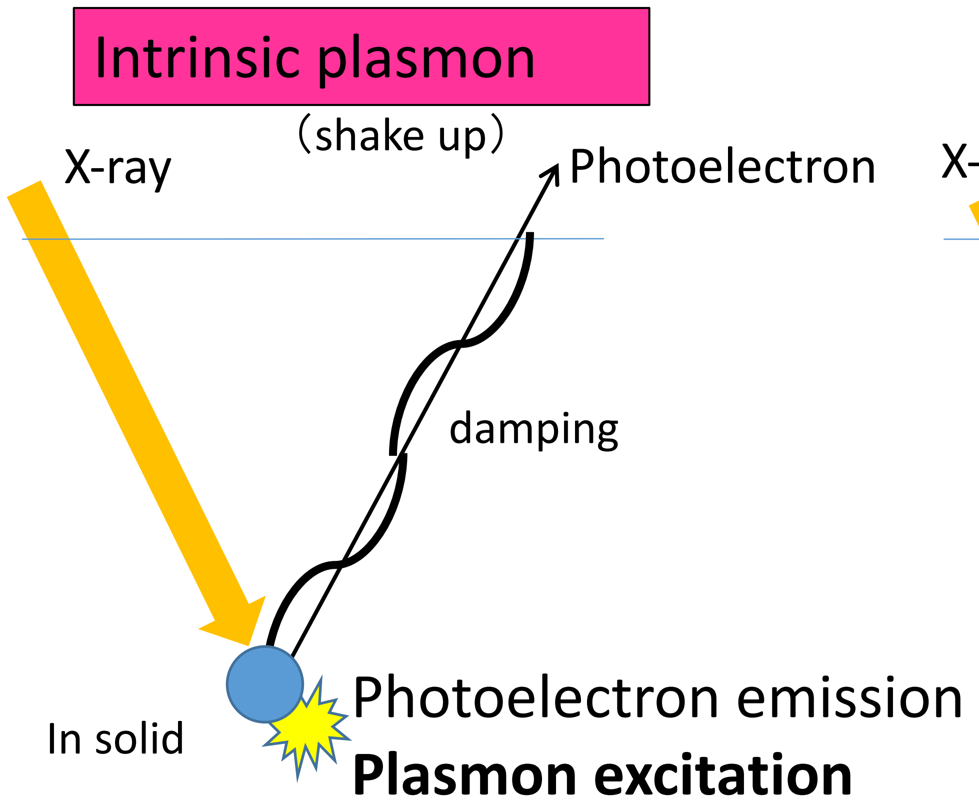
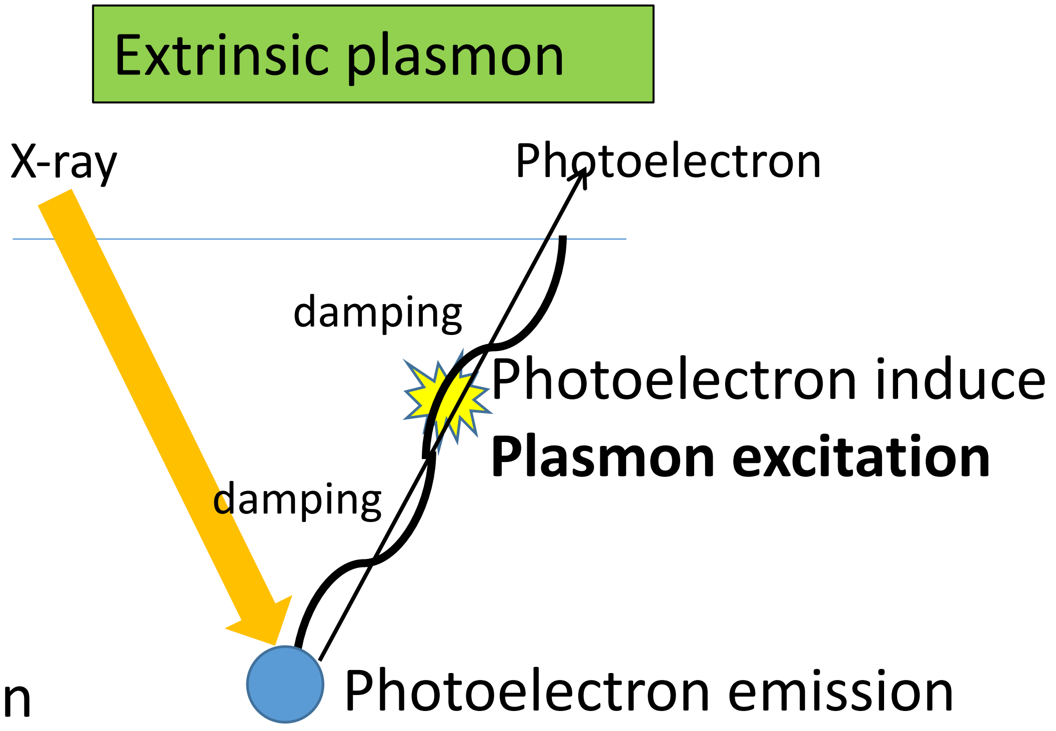
Plasmon is collective electron oscillation excited by Δρ.

Plasmon loss peaks in XPS are observed due to excite the plasmon by photoelectron.

# Plasmon Losses in XPS




$$I(\mathbf{p};w)^1 = 2\pi \sum_m \left| \underbrace{\langle f_\mathbf{p}^- | \Delta | \phi_c \rangle \langle m_v^* | 0_v^* \rangle}_{\text{Int}} + \underbrace{\langle f_\mathbf{p}^- | v_m g(\varepsilon_p + \omega_m) \Delta | \phi_c \rangle e^{-\frac{a}{2}}}_{\text{Ext}} \right|^2 \times \delta\left(E_0 + \omega - E_0^* - \omega_m - \varepsilon_p\right)$$

Int / Ext / loss / propagation

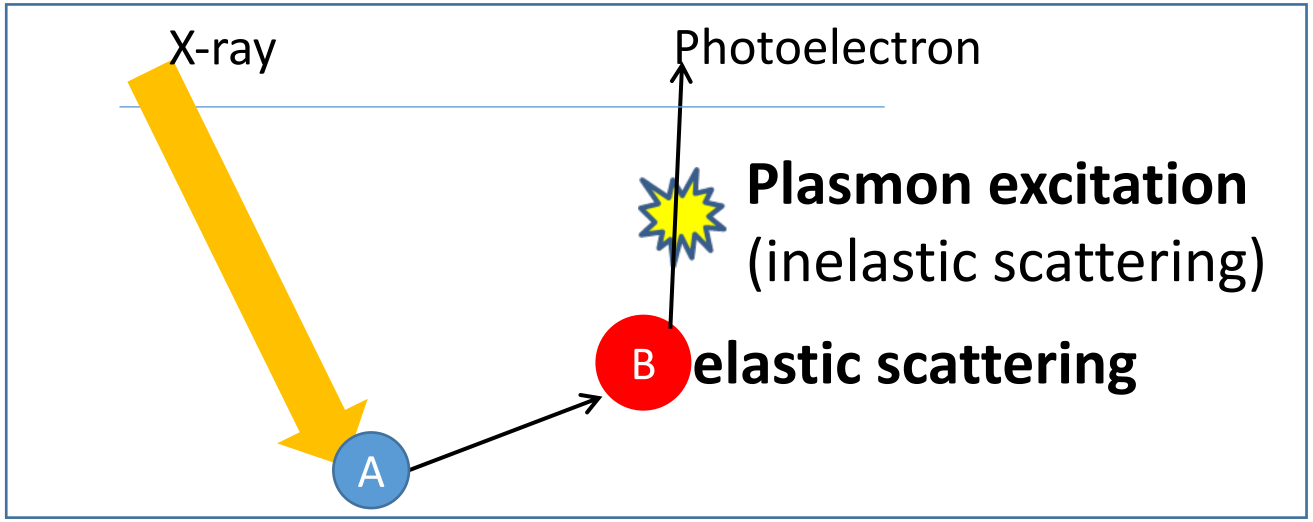
干渉！！

valence electrons
pote by no core

The fluctuation potential $v_n(\boldsymbol{r}) = \int d\boldsymbol{r}' v(\boldsymbol{r} - \boldsymbol{r}') \langle n_v | \psi^\dagger(\boldsymbol{r}') \psi(\boldsymbol{r}') | 0_v \rangle.$

# Extrinsic plasmon loss with the elastic scattering

T. Fujikawa, M. Kazama, H. Shinotsuka, e-J. Surf. Sci. Nanotech. 6 (2008) 263.




Take account into the elastic scattering during propagation for extrinsic term

$$\tau_{ext}(\mathbf{p}) = \langle f_{\mathbf{p}}^{-} | v_m g(\varepsilon_p + \omega_m)\Delta | \phi_c \rangle e^{-\frac{a}{2}}$$

$$\langle \phi'_p | (1 + t g_0)$$

rewrite the T-matrix using the site-T matrix

$$= \langle \phi'_{\mathbf{p}} | \left( 1 + t_A g_0 + \sum_{\substack{\alpha \neq A \\ \beta = A}} t_\alpha g_A + \sum_{\substack{\alpha \neq A \neq \beta \\ \gamma = A}} t_\beta g_0 t_\alpha g_A + \cdots \right) v_m (g_A + \sum_{\beta \neq A} g_0 t_\beta g_A + \cdots)\Delta | \phi_c \rangle e^{-\frac{a}{2}}$$

The effect of scattering

$$= e^{-\frac{a}{2}} \{ \langle \phi'_{\mathbf{p}} | (1 + t_A g_0) v_m g_A \Delta | \phi_c \rangle + \langle \phi'_{\mathbf{p}} | (1 + t_A g_0) v_m \sum_{B \neq A} g_0 t_B g_A \Delta | \phi_c \rangle + \cdots$$

Without elastic scatterings — Single scattering by atom B

$$= \tau_m^{ex}(\boldsymbol{p}) \langle f_{\boldsymbol{p}}^{-} | \Delta | \phi_c \rangle$$

$$\tau_m^{\mathrm{ex}}(\boldsymbol{p}) = (2\pi)^{3/2} \int d\boldsymbol{r}\, f_{\boldsymbol{p}}^{-*}(\boldsymbol{r}) v_m(\boldsymbol{r}) g_0(\boldsymbol{r} - \boldsymbol{R}_A; p'). \qquad g_A = g_0 + g_0 t_A g_0$$

## **Quantum Landau formula** For lower calculation cost

**Int** **Ext**

$$I(\mathbf{p};w)^1 = 2\pi \sum_m \left| \langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle \langle m_v^* | 0_v^* \rangle + \langle f_{\mathbf{p}}^- | v_m g(\varepsilon_p + \omega_m) \Delta | \phi_c \rangle e^{-\frac{a}{2}} \right|^2 \times \delta\left(E_0 + \omega - E_0^* - \omega_m - \varepsilon_p\right)$$

loss propagation

Sub stitute $\tau_m^{ex}(\mathbf{p}) \langle f_{\mathbf{p}}^- | \Delta | \phi_c \rangle S_0$

光電子が固体中の原子に散乱される影響

$$\tau_m(P) = \tau_m^{ex}(P) + \frac{S_m}{S_0} \qquad \frac{\alpha(\varepsilon)}{\varepsilon} = \sum_m |\tau_m(P)|^2 \delta(\varepsilon - \omega_m) \qquad \varepsilon = \omega + E_0 - E_0^* - \varepsilon_p$$

**Quantum Landau formula with full multiple scattering**

◆Single loss : spectrum of one plasmon excitation

$$I^1(\boldsymbol{p},\omega) = \left| \langle f_{\boldsymbol{p}}^- | \Delta | \phi_c \rangle \right|^2 \frac{\alpha(\varepsilon)}{\varepsilon} \exp\left[ \int_0^\infty d\varepsilon \frac{\alpha(\varepsilon)}{\varepsilon} \right]$$

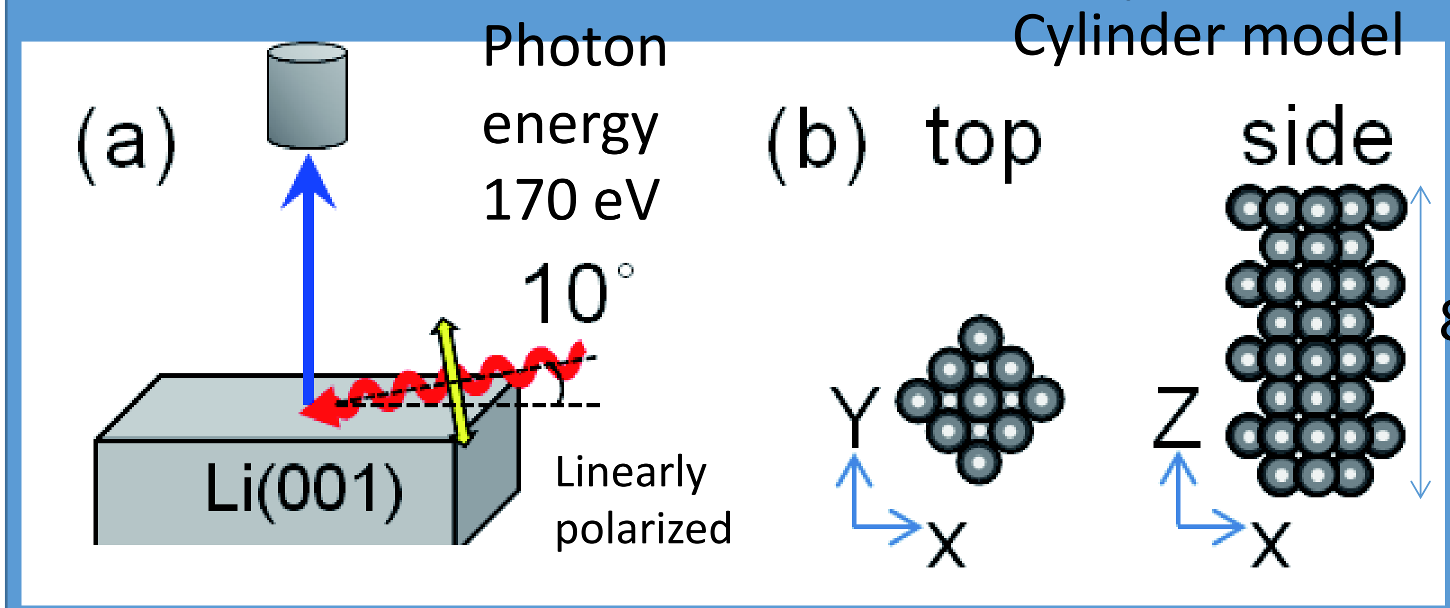
Photo emission | Plasmon Excitation | nolmarization

Peak hight | Shape of loss function

**Purpose**

We calculate single-plasmon loss features associated with Li 1s photoemission using the QLF that includes full multiple scatterings.

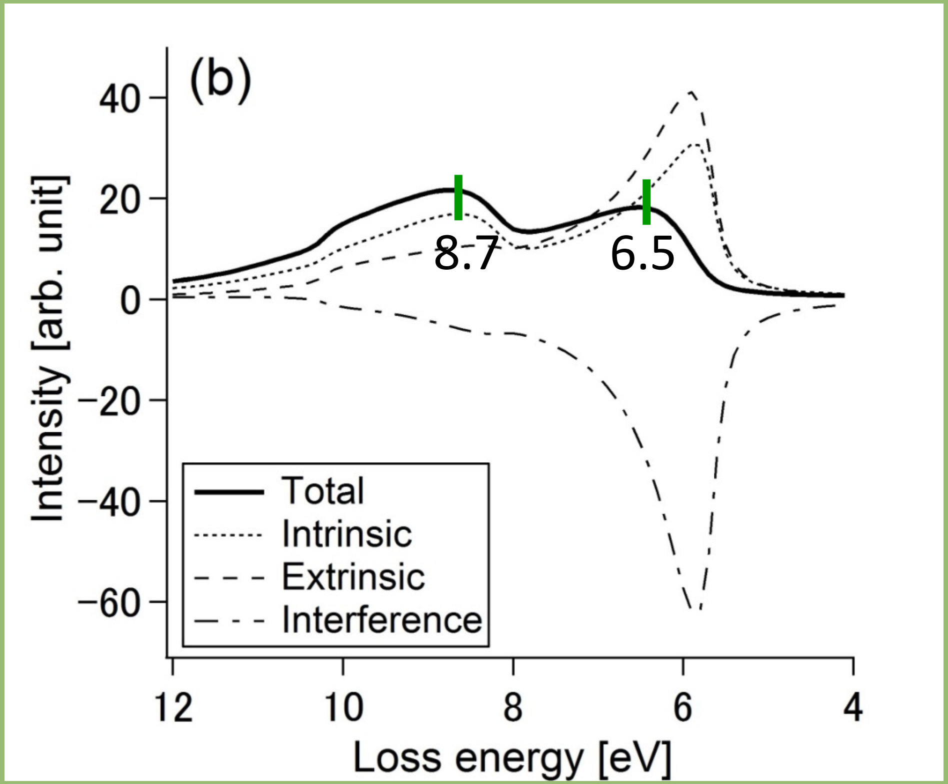
The schematic view of the calculation setup



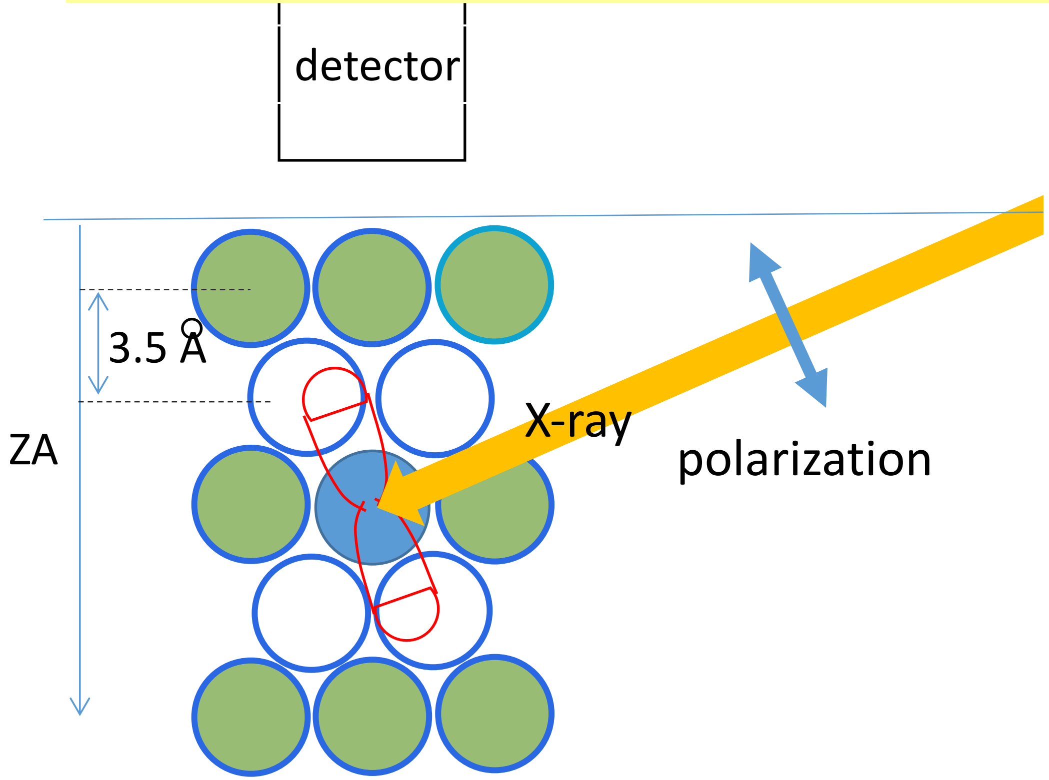

The energy of photoelectrons from Li 1s are about 100 eV.

Cylinder model contains 52 atoms.

Calculation result



# Calculated single-plasmon loss intensities excited from Li 1s




Bcc
atom diameter 1.52 Å

## Depth profile of plasmon loss

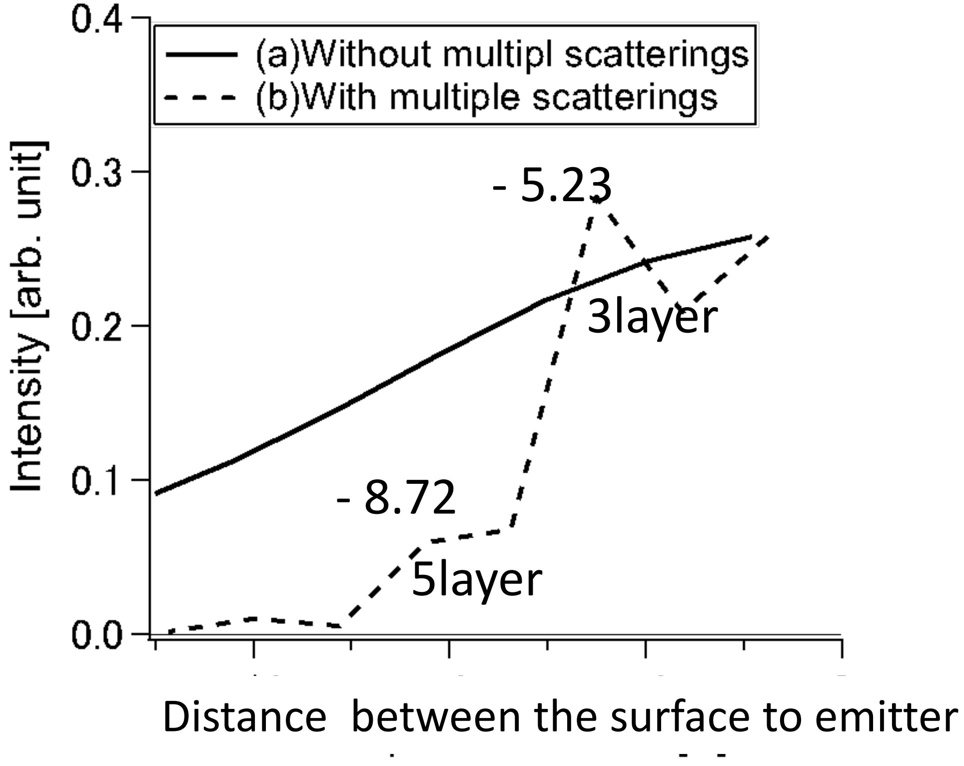



Photo electron emitted parallel to polarization from Li 1s is effected by defocusing effect.

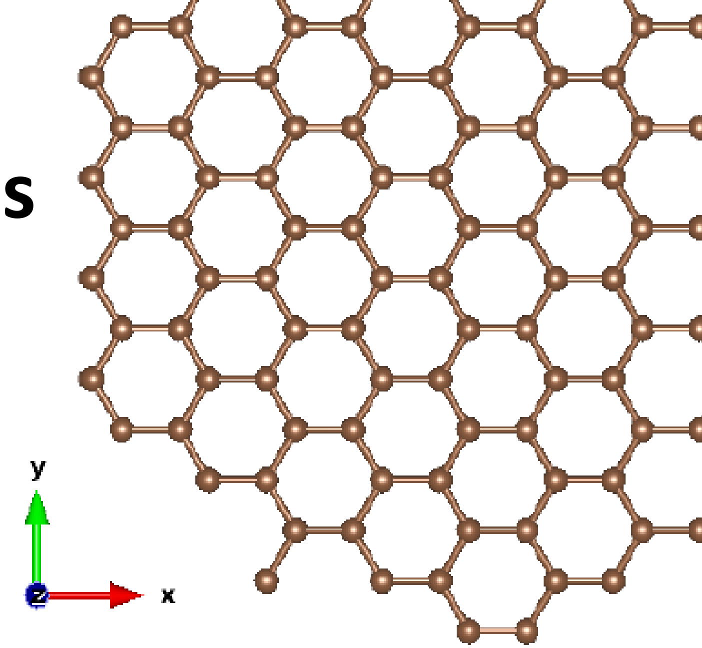
3rd and 5th layer are also emphasized due to the defocusing effect.

Info from only calculation!!

Li is light atom,
However we can't neglect the effect of elastic scattering.

# Expansion to other systems…低次元電子系

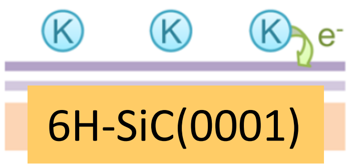
## For metamaterials and photoelectronics devices



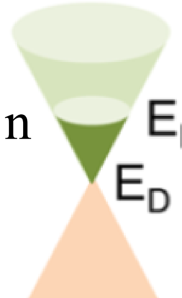
# Observation of the low energy Π plasmon in a single layer graphene by charge doping using EELS

Control of the Π plasmon in a single layer graphene by charge doping

S. Y. *Shin et al.*, APPLIED PHYSICS LETTERS 99, 082110 (2011).




n




On a single layer graphene (SLG)

- They report a Π plasmon excitation
  $n = 1.2 \times 10^{13}$ $cm^2$ (naturally doped from the substrate).

ng

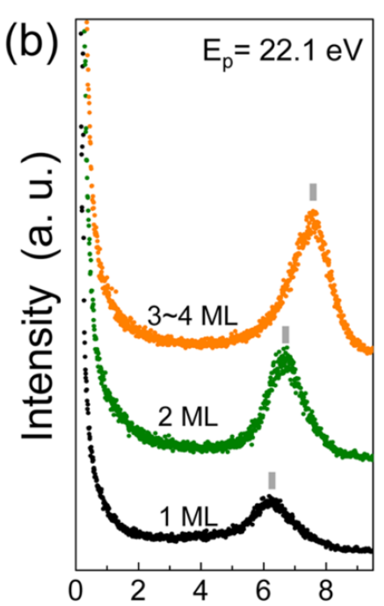
- They find a low-energy Π plasmon excitation arising from doped electron density $1.2 \times 10^{13}$ $cm^2$ corresponding to 0.44 eV above the Dirac point ED

  (additional charge transfer from K to an SLG epitaxially grown on SiC).

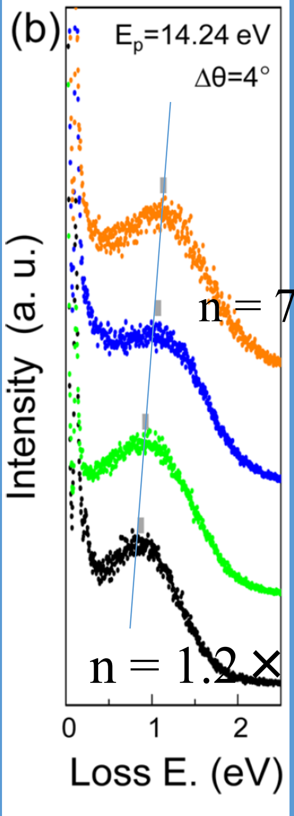
- This low-energy plasmon arises from the collective excitation of electrons within the partially occupied π* conduction band.

**EELS**

Π plasmon




a low-energy Π plasmon




$n = 7 \times 10^{13}$ cm

$n = 1.2 \times 10^{13}$ $cm^2$

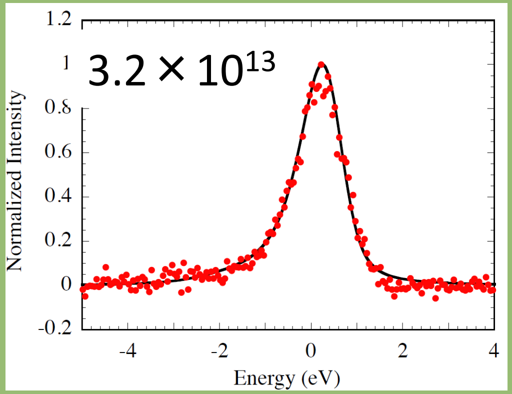
Ep is a primary electron beam energy,
ΔΘ is an incident (scattered) angle.

# Observation of the Π plasmon in a single layer graphene by charge doping using XPS

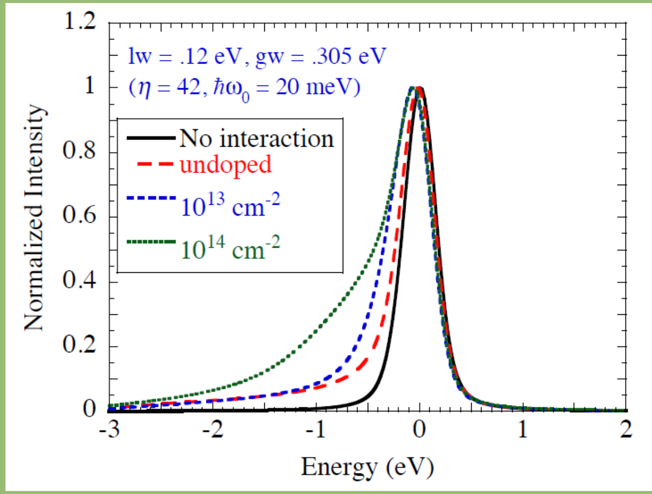
Core-level spectra from graphene
Bo E. Sernelius P R B (91), 4, 045402 (2015).

Experimental (μ-XPS) C 1s core-level spectrum of a suspended single graphene sheet on a gold sheet using the photon energy 480 eV.

For an doped




experiment
calculation



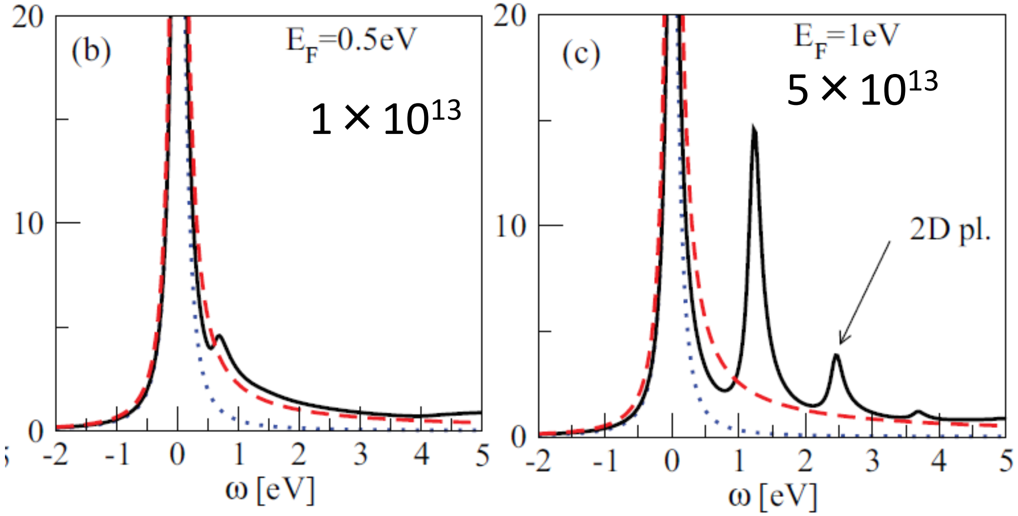

calculation

**Theory of core-level spectra in x-ray photoemission of pristine and doped graphene**

V. Despoja[1,2,3,*] and M Šunjić[1,2]

They calculate singularity indices in pristine and doped graphene using dynamically screened Coulomb interaction

in doped graphene.




calculation

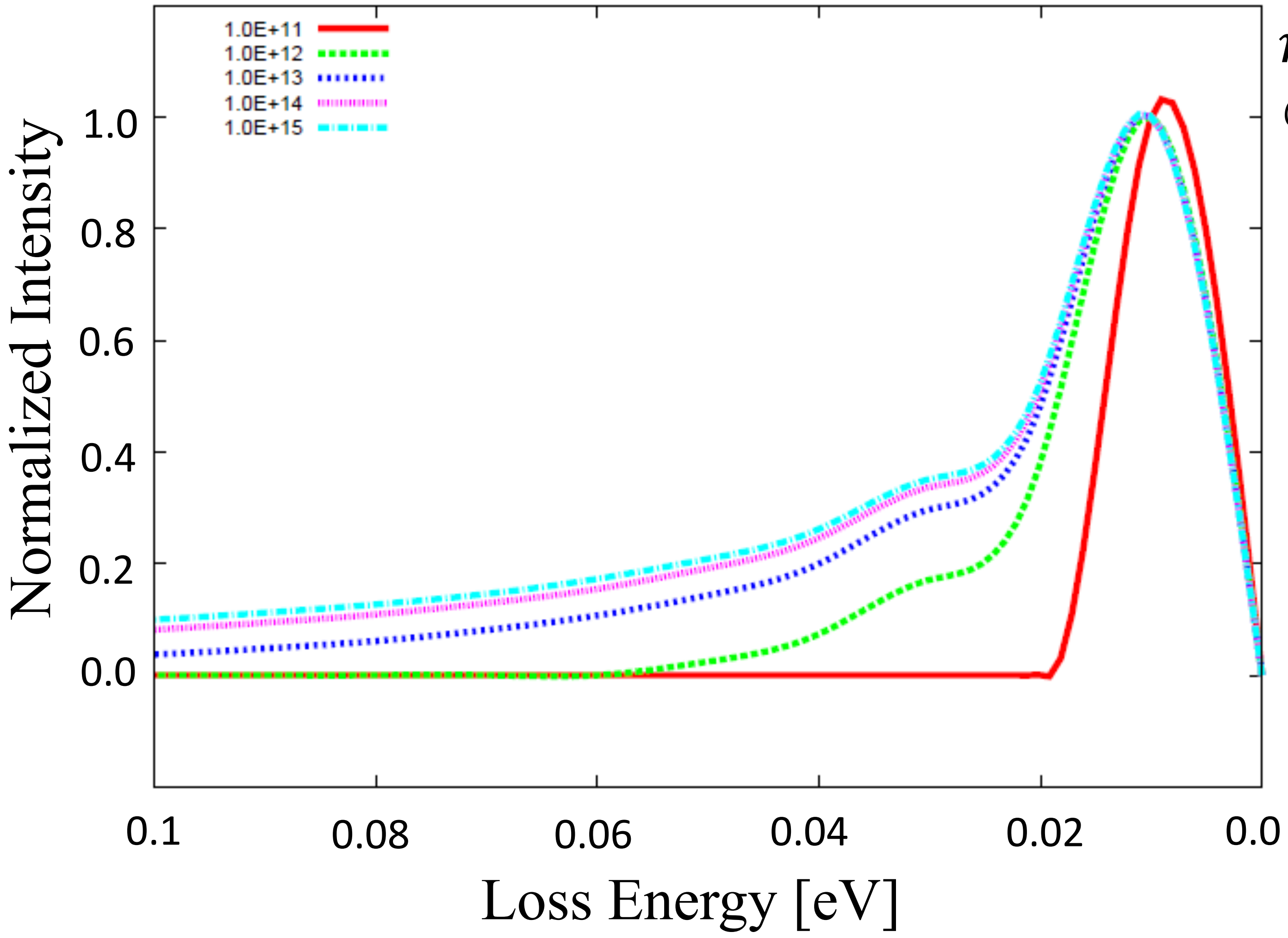
We can not see sharp a plasmon loss peak due to singularity even if increasing doping.

We can see sharp plasmon loss peaks with doping.

P R B , 88, 245416 (2013).

We want to extract a information about from singularity.
extent to electron-hole pair, excitation near fermi level….. Collaborate with Rennes uni. based on JASSO.

# ○キャリア密度依存性




・$h\nu = 450$ eV条件

$n = 1.0\times10^{11}, 10^{12}, 10^{13}, 10^{14}, 10^{15}\mathrm{cm}^{-2}$
の場合のそれぞれ計算

ピーク位置のシフトはほとんどない
→密度依存性は現れない

密度が高いほど高ロスエネルギー側に
裾の長いピークになる
→キャリア密度がプラズモン分散に関与

# まとめ

量子ランダウ方程式からメインピークのサテライトピークである
プラズモンロスピークが計算できる

単純金属、2次元電子系グラフェン、0次元電子系のナノ粒子などへの
拡張が見込まれる