OSAKA UNIVERSITY

大阪大学
社会人教育プログラム

FLAPW法の応用

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HiLAPW

OUTLINE

- **Precision of the FLAPW Method**
  - **Wave Functions**
  - **Electron Density and Potential**
  - **Perturbative Consideration**
  - **Choice of MT Sphere Radius**
- **Typical Applications**
- **Summary**

WAVE FUNCTIONS

- **LAPW Basis**

$$\tilde{\phi}^{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$$

$$\phi^{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \sum_{\alpha lm} \left[A_{\alpha lm}^{\mathbf{k}+\mathbf{K}} R_l(r_\alpha) + B_{\alpha lm}^{\mathbf{k}+\mathbf{K}} \dot{R}_l(r_\alpha) \right] i^l Y_{lm}(\hat{\mathbf{r}}_\alpha)$$

- **Degrees of Variational Freedom**

$$K_{\max} \qquad l_{\max}$$

- **Choice of MT Sphere Radius**

ELECTRON DENSITY & POTENTIAL

$$\tilde{n}(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} n_{\mathbf{G}} \qquad n(\mathbf{r}) = \sum_{\alpha LM} n_{\alpha LM}(r_\alpha) i^L Y_{LM}(\hat{\mathbf{r}}_\alpha)$$

$$\tilde{v}(\mathbf{r}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} v_{\mathbf{G}} \qquad v(\mathbf{r}) = \sum_{\alpha LM} v_{\alpha LM}(r_\alpha) i^L Y_{LM}(\hat{\mathbf{r}}_\alpha)$$

- **Accuracy of Expansion**

$$G_{\max} \qquad L_{\max}$$

variational parameters?

- **Choice of MT Sphere Radius**

PERTURBATIVE CONSIDERATION

- **Second-Order Perturbation**

$$\Delta\varepsilon^{\mathbf{k}} = -\frac{|\langle \mathbf{k}+\mathbf{K}|\mathcal{H}|\mathbf{k}\rangle|^2}{|\mathbf{k}+\mathbf{K}|^2 - \varepsilon^{\mathbf{k}}}$$

- **Variational Parameters of the Wave Functions**

$$|\mathbf{k}+\mathbf{K}| \leq K_{\max}$$

$$l_{\max}$$

MT SPHERE RADIUS

When a sufficient l_{max} is assumed,

- **In case of large MT sphere radius, because of smaller volume in the interstitial region fewer PW expansion is needed.**
- **In case of small MT sphere radius, because of larger volume in the interstitial region more PW expansion is needed.**
- **A variational dimensionless parameter**

$$RK_{\max}$$

WAVE FUNCTIONS & ELECTRON DENSITY

$$n(\mathbf{r}) = \sum_{\mathbf{k},n} |\psi_n^{\mathbf{k}}(\mathbf{r})|^2$$

$$G_{\max} \geq 2K_{\max}$$

$$L_{\max} \geq 2l_{\max}$$

- **Convergency of the electron density and potential expansion should be checked, especially when GGA is used.**
- **For small MT spheres used, higher G_{max} may be required to represent pseudized charge density.**

MT SPHERE RADIUS

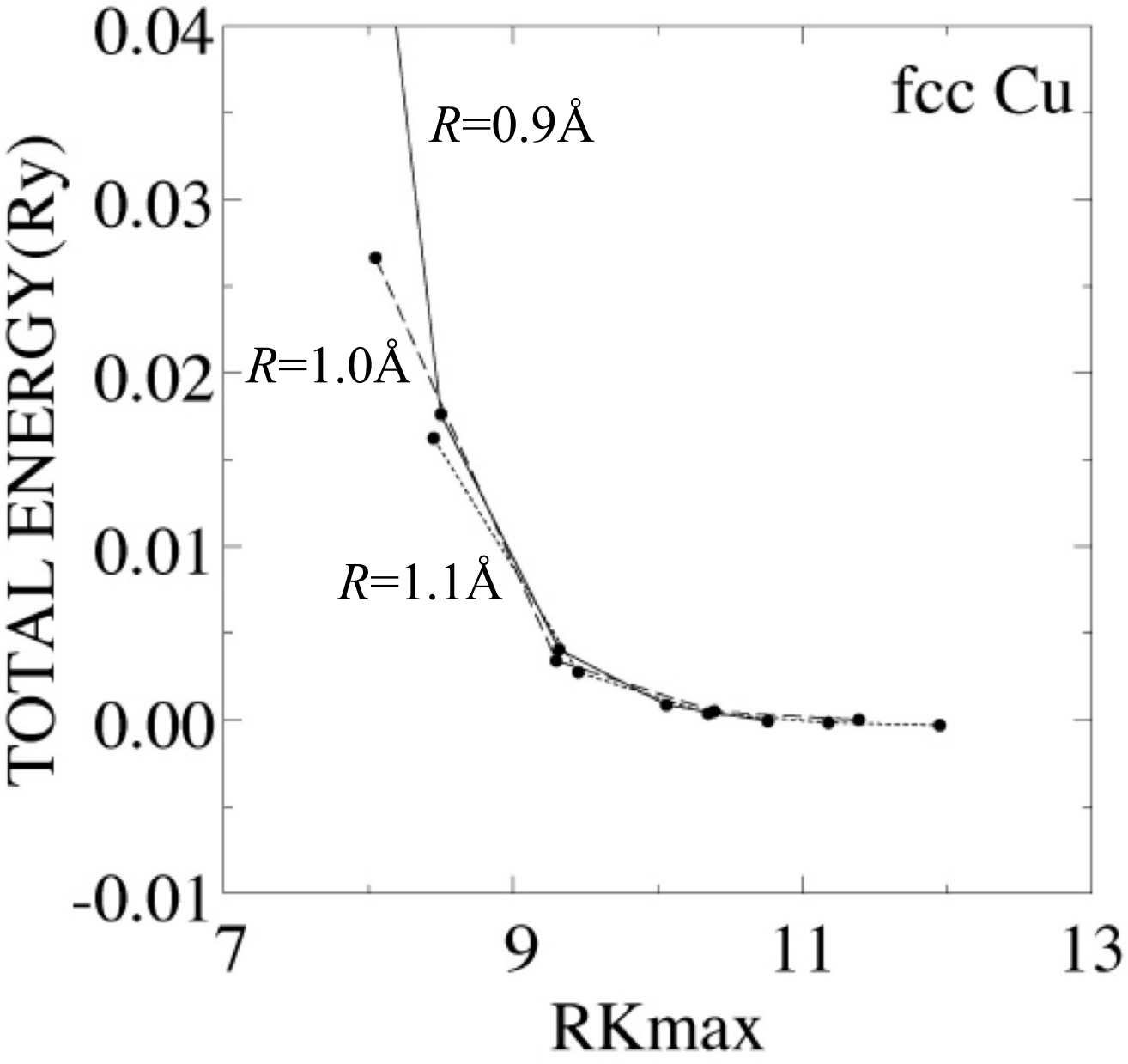
- **Non-overlapping spheres**

A margin should be considered if the atomic positions are changed, for example in a structural optimization calculation.

- **Negligible penetration of the core functions outside**

Within both assumptions with sufficient l_{max} and L_{max}, the accuracy does not depend on the choice of MT sphere radius but does on RK_{max}.

TOTAL ENERGY vs. MT RADIUS



PRECISION OF FLAPW METHOD

- **Wave Functions** $RK_{\max}$
- **Electron Density and Potential**

$$G_{\max} \geq 2K_{\max} \qquad L_{\max} \geq 2l_{\max}$$

- **Choice of MT Sphere Radius**

- **Over-completeness of APW Basis Functions**

Since the PW basis is a complete set in all the space, an APW basis with the excessive number of PW results in indefinite solutions.

ELECTRIC FIELD GRADIENT

- **Definition of EFG**

$$V_{ij} = \frac{\partial V(\mathbf{r})}{\partial i \partial j} \quad (i, j = x, y, z)$$

- **Maximum Term**

$$q = V_{ZZ}$$

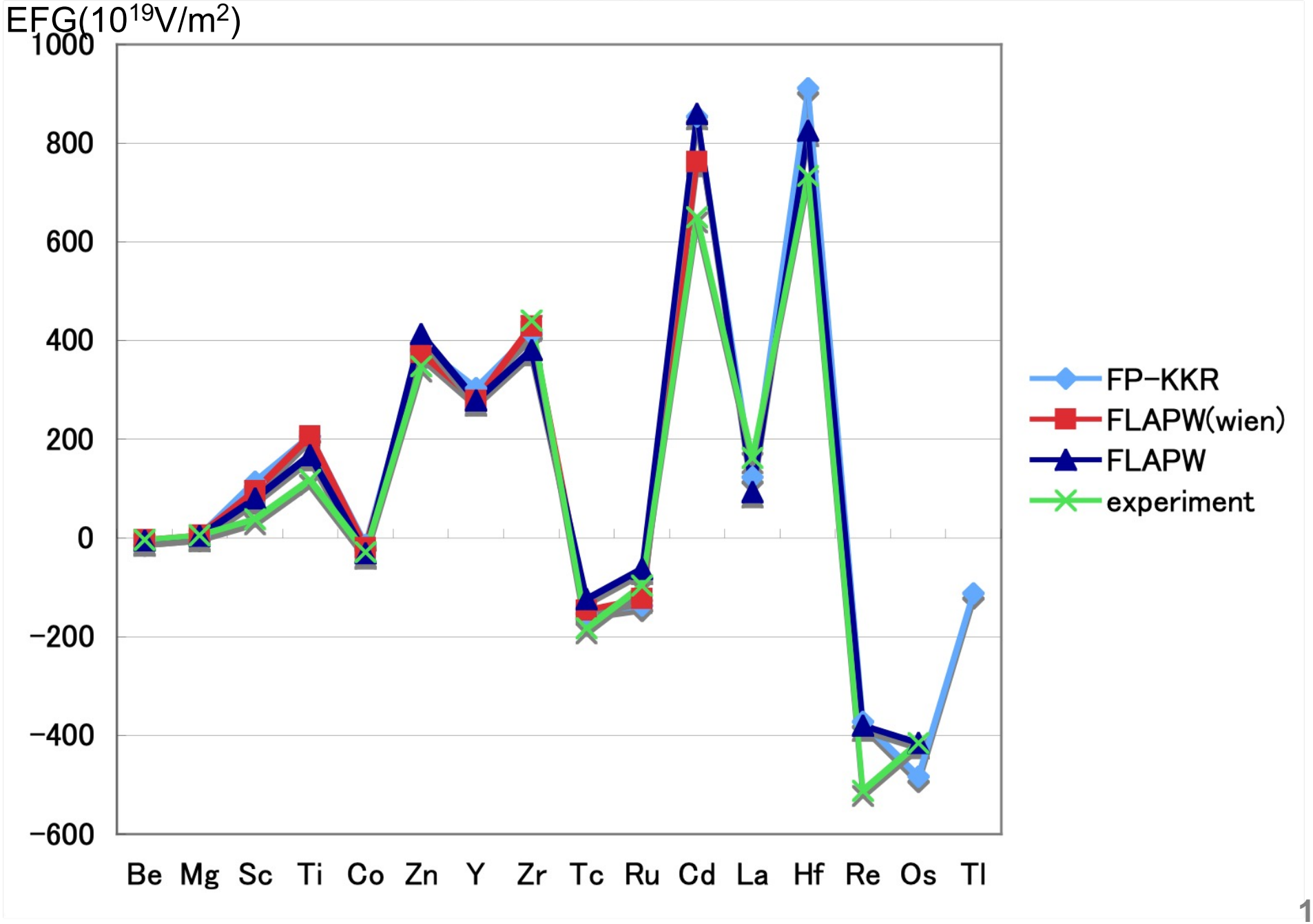
- **Asymmetric Parameter**

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

- **Nuclear Magnetic Resonance Measurements**

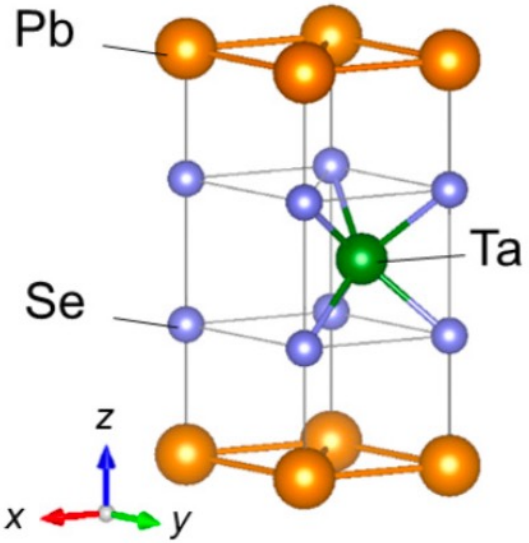
$$\nu_Q = \frac{3eqQ}{2I(2I-1)h}$$ **Quadruple coupling frequency**

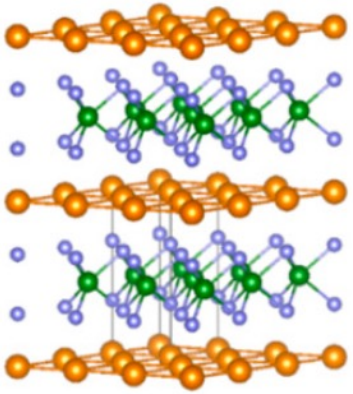
EFG IN HCP METALS



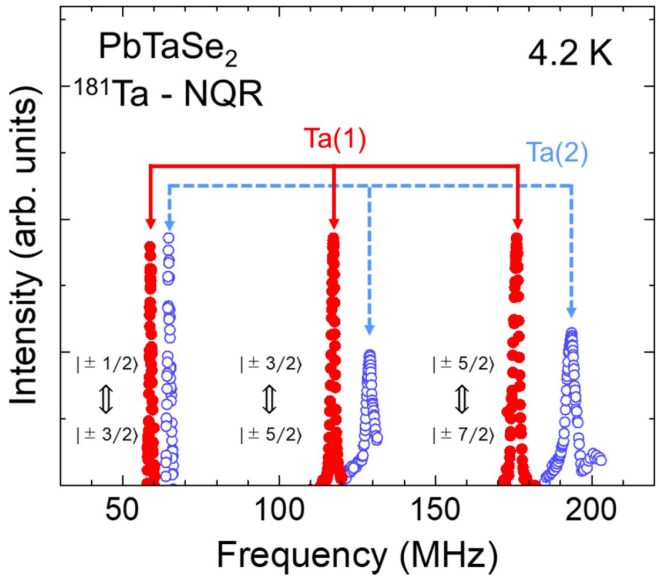
EFG at Ta in $PbTaSe_2$

PRB **102**, 214504 (2020)





P-6m2 structure



^{181}Ta NQR spectra

	ν_Q (MHz)	η
Experiment		
Ta(1) site	58.7 ± 0.5	0.00–0.02
Ta(2) site	64.5 ± 0.5	0.03–0.04
DFT calculation		
$P\bar{6}m2$	57.78	0.00
$P6_3/mmc$	46.39	0.00

REFERENCE: EFG

- **EFG Calculations by FLAPW**
  - **PRL 54, 1192 (1985)** **Li_3N**
  - **PRB 37, 2792 (1988)** **hcp metals**
  - **PRB 102, 214504 (2020)** **$PbTaSe_2$**
- **EFG Calculations by FP-KKR**
  - **M. Ogura, PhD Thesis, Osaka University (2004)**
- **Review on EFG in NMR**
  - **Solid State Physics Vol. 5, pp. 321.**

PHONON CALCULATION

- **Equations of Motion** $M_\nu \ddot{u}_{n\nu\alpha} = -\sum_{n'\nu'\beta} \frac{\partial^2 E}{\partial u_{n\nu\alpha} \partial u_{n'\nu'\beta}} u_{n'\nu'\beta}$

- **Displacements** $u_{n\nu\alpha} = (M_\nu)^{-\frac{1}{2}} C_{\nu\alpha} e^{i(\mathbf{q}\cdot\mathbf{R}_n - \omega(\mathbf{q})t)}$

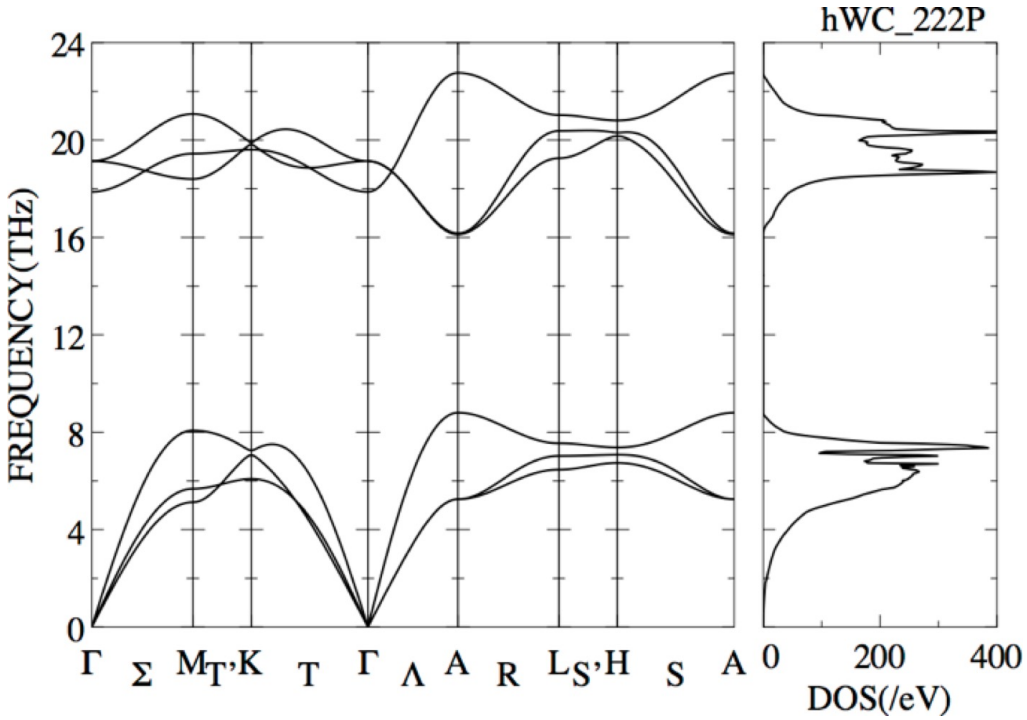
- **Dynamical Matrix**

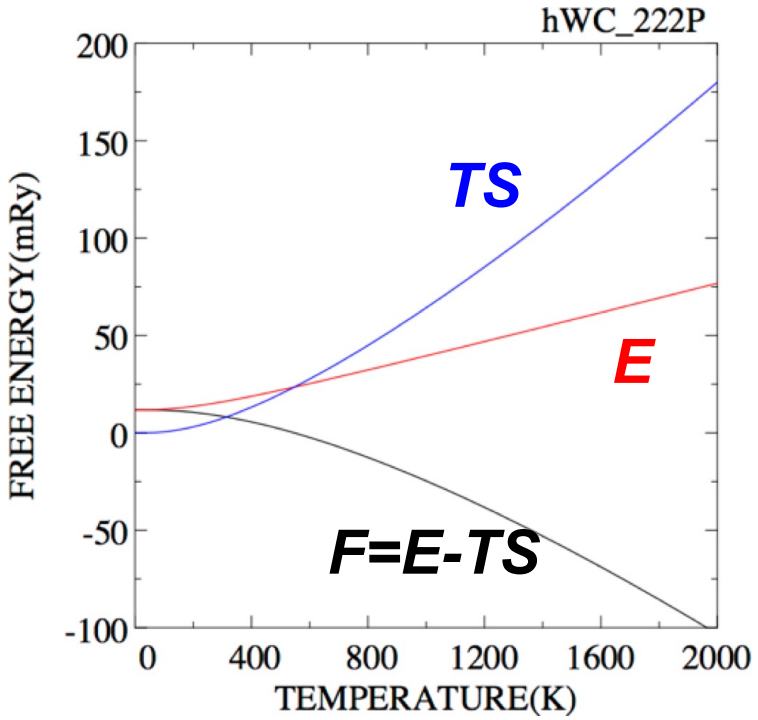
$$D_{\nu\alpha,\nu'\beta}(\mathbf{q}) = (M_\nu M_{\nu'})^{-\frac{1}{2}} \sum_{n'} \frac{\partial^2 E}{\partial u_{0\nu\alpha} \partial u_{n'\nu'\beta}} e^{i\mathbf{q}\cdot\mathbf{R}_{n'}}$$

$$\approx -(M_\nu M_{\nu'})^{-\frac{1}{2}} \frac{F_{0\nu\alpha}}{u_{0\nu'\beta}} \qquad \left(\begin{array}{l} u_{n\nu\alpha} = u_{0\nu\alpha} e^{i\mathbf{q}\cdot\mathbf{R}_n} \\ F_{n\nu\alpha} = -\dfrac{\partial E}{\partial u_{n\nu\alpha}} \end{array} \right.$$

$$\mathbf{D}(\mathbf{q})\mathbf{C} = \mathbf{C}\omega^2(\mathbf{q}) \quad \Rightarrow \quad \textbf{Phonon modes}$$

PHONON CALCULATION OF WC





$$E = \sum_{n,\boldsymbol{q}} \hbar\omega_n(\boldsymbol{q}) \left[\frac{1}{2} + (e^{\beta\hbar\omega_n(\boldsymbol{q})} - 1)^{-1}\right]$$

$$F = \sum_{n,\boldsymbol{q}} \left[\frac{\hbar\omega_n(\boldsymbol{q})}{2} + \beta^{-1} \ln\left(1 - e^{-\beta\hbar\omega_n(\boldsymbol{q})}\right)\right]$$

ELASTIC AND DYNAMICAL STABILITY OF QUATERNARY HEUSLER

CoCrScAl

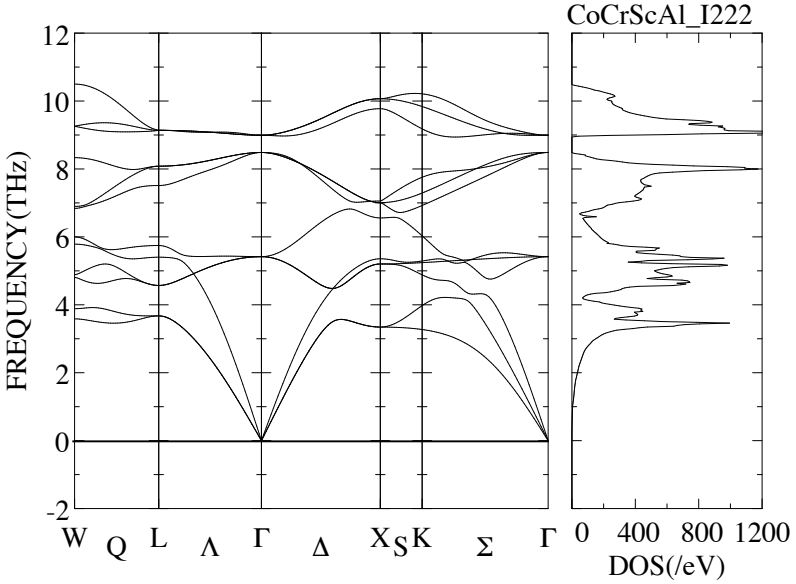
- **Elastic stability**

Born-Cauchy conditions

(GPa)

Bulk modulus :	$K=(C_{11}+2C_{12})/2$	116.1 > 0	Elastically stable
Shear modulus :	$Cs=(C_{11}-C_{12})/2$	61.9 > 0	
	C_{44}	103 > 0	

- **Dynamical stability**



No soft mode

Dynamically stable

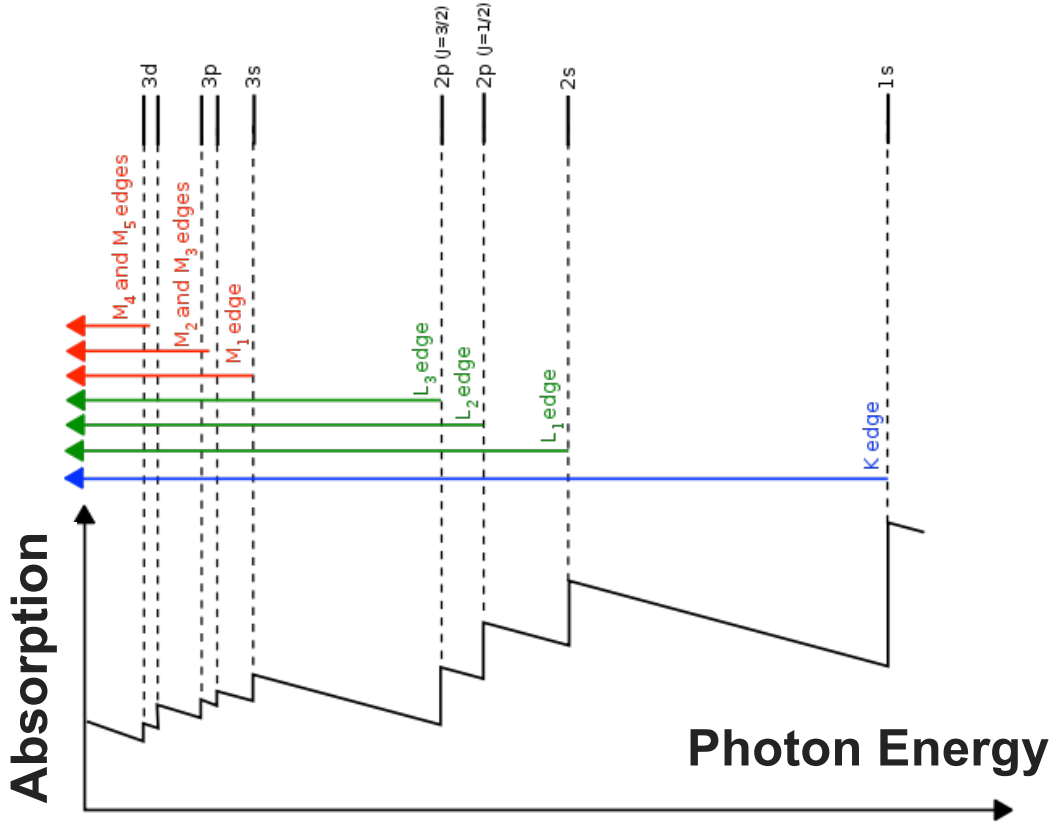
F. Kuroda, T. Fukushima, TO,
J. Appl. Phys. 127, 193904 (2020).

REFERENCE: ATOMIC FORCES BY FLAPW

- **Soler, Williams, PRB40, 1560 (1989); PRB42, 9728 (1990); PRB47, 6784 (1993).**
- **Yu, Singh, Krakauer, PRB43, 6411 (1991); PRB45, 8671 (1992).**
- **Goedecker, Maschke, PRB45, 1597 (1992).**
- **T. Oguchi, "Interatomic Potentials and Structural Stability", ed. by K. Terakura and H. Akai, (Springer-Verlag, 1993) p. 33.**
- **D. J. Singh, "Planewaves, pseudopotentials and the LAPW method" (Kluwer Academic, Boston, 1994).**

X-ray Absorption Spectroscopy (XAS)

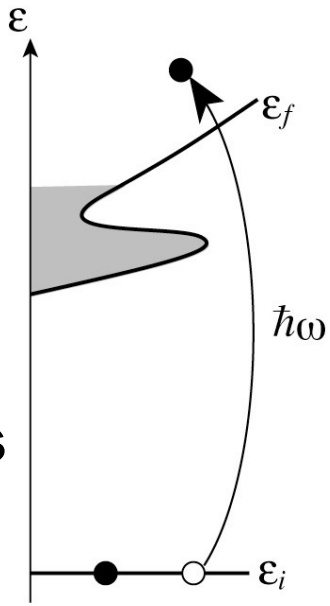
- **X-ray absorption: electronic transitions by photon from inner core states to empty states**
  - **suitable for studying valence states with specific element, orbital and symmetry by tuning the photon energy and polarization**



Fundamentals of XAS

- **Transition Probability by Fermi Golden Rule**

$$W(\omega) = \frac{2\pi}{\hbar} \sum_{f,i} |\langle f|\hat{F}|i\rangle|^2 \delta(\varepsilon_f - \varepsilon_i - \hbar\omega)$$



- **Rigorous Theory**

ε_i ε_f **Total energies of initial and final states**

$|i\rangle$ $|f\rangle$ **Many-body initial and final states**

$\hat{F}$ **Perturbation by photon in many-body hamiltonian**

- **Quasi-particle (One-electron) Approach**

ε_i ε_f **Orbital energies of initial and final states**

$|i\rangle$ $|f\rangle$ **One-electron initial and final states**

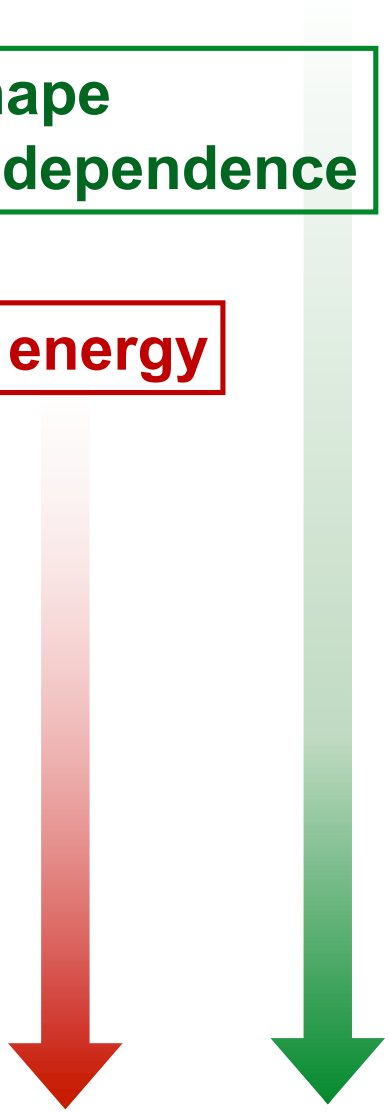
$\hat{F}$ **Perturbation by photon in one-electron hamiltonian**

Theoretical Approaches

- Quasi-particle Approaches
  - Ground-state calculation
  - Core-hole calculation
  - Perturbation calculation (GW, ...)
  - .....
- ΔSCF Approach
  - (Excited State) – (Ground State)
- Many Body Approaches

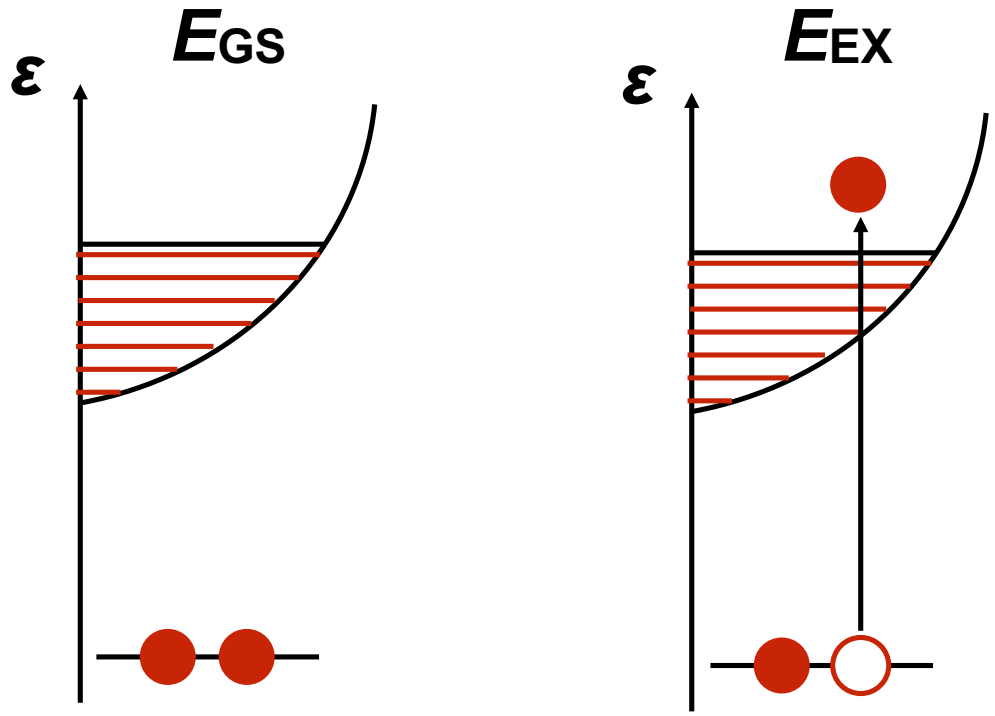
spectrum shape
polarization dependence

excitation energy

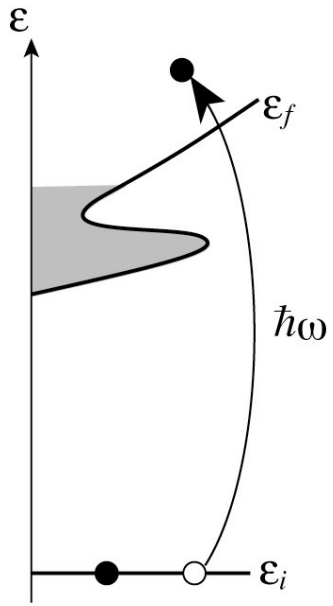


ΔSCF

- **Self-Consistent-Field (SCF) DFT Calculation**
  - **Grand state: E_{GS}**
  - **Excited state: E_{EX}**
- **Excitation Energy = E_{EX} - E_{GS}**

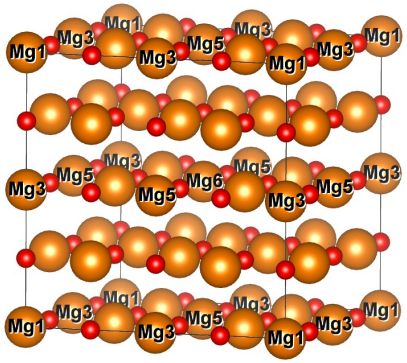
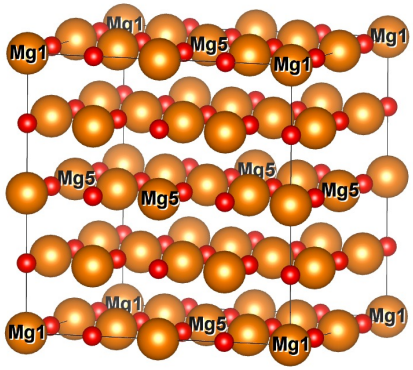
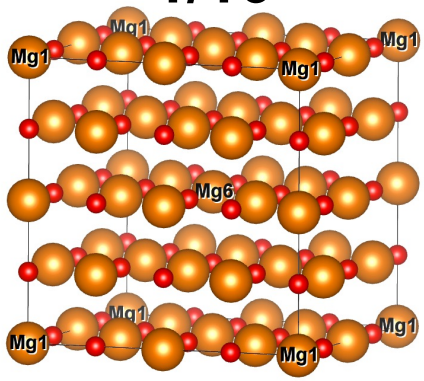
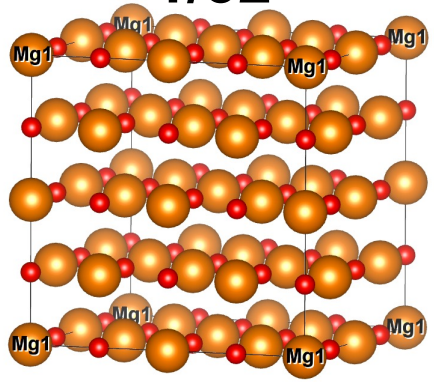


Supercell Model



- Core hole: well localized
- Excited electron: usually delocalized
  - Hybridization with neighbors
  - Electrostatic fields due to holes and excited electrons at neighboring sites

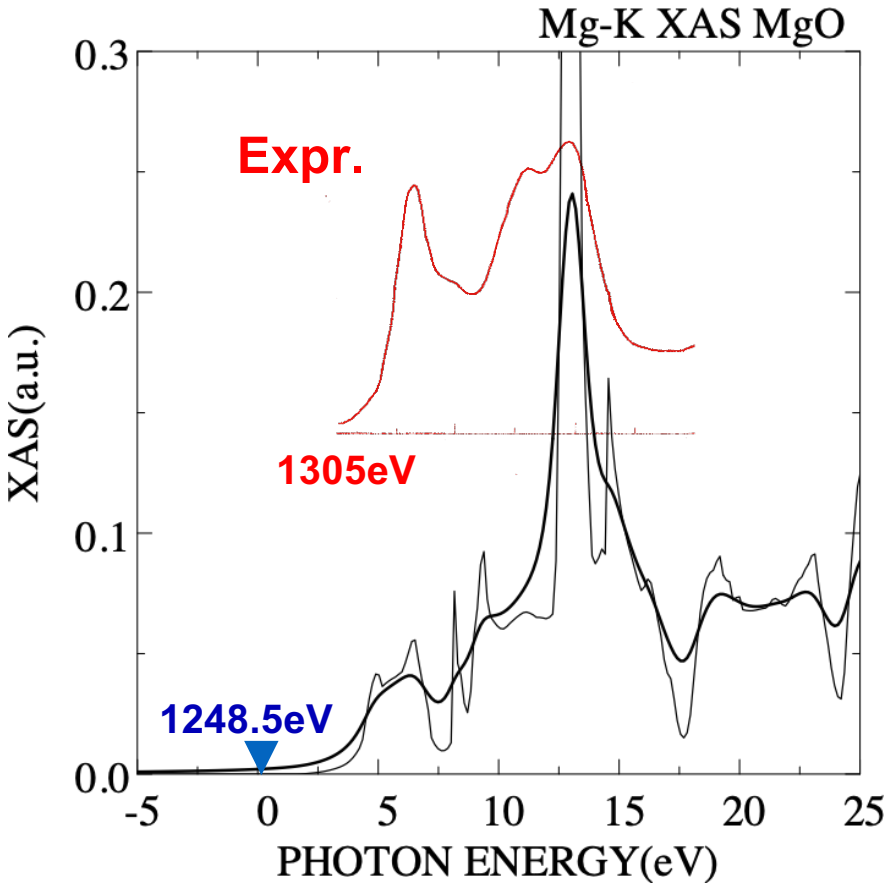
hole concentration

1/4	1/8	1/16	1/32
			
$(MgO)_4$	$(MgO)_8$	$(MgO)_{16}$	$(MgO)_{32}$
$4^3=64$	$8^3=512$	$16^3=4096$	$32^3=32768$

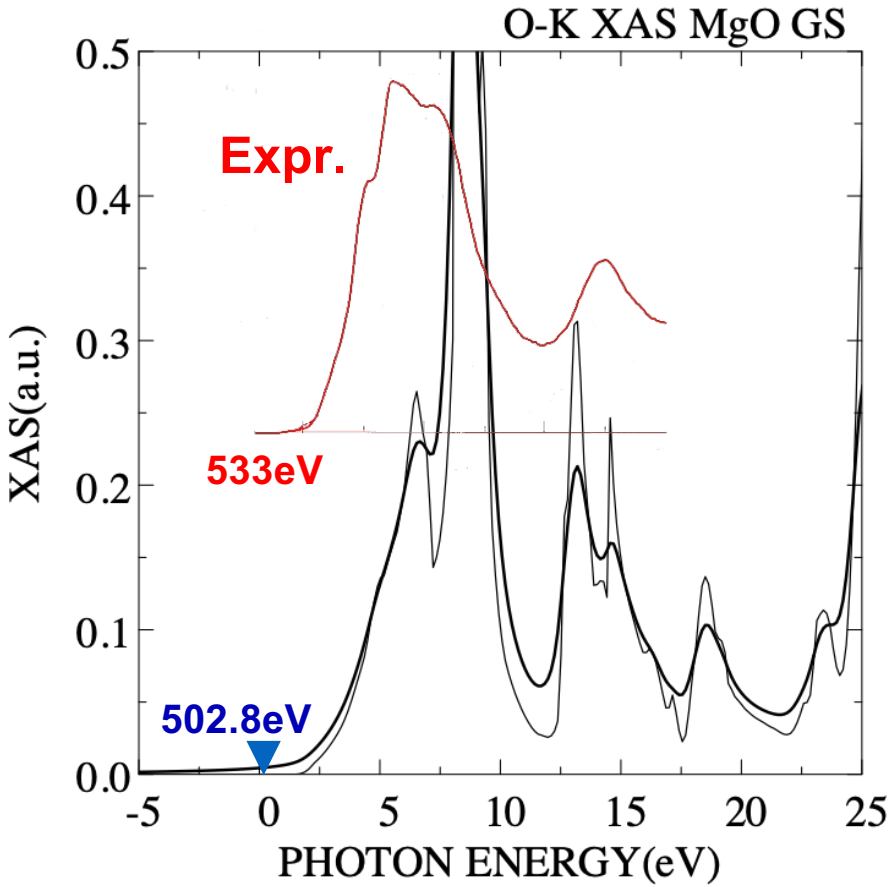
XAS of MgO

Grand-State Approximation

Mg K-edge (E1: 1s → 3p)

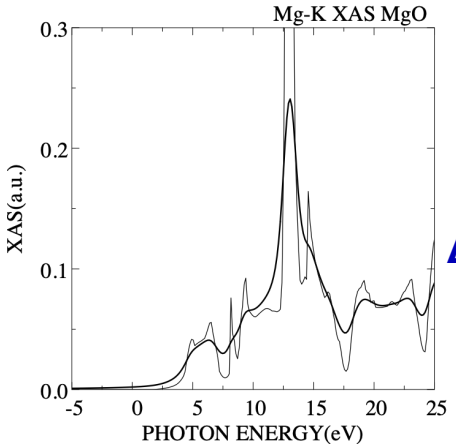


O K-edge (E1: 1s → 2p)



Thick lines: broadened by Lorentzian

Mg K-Edge of MgO with Core Hole in Mg-1s



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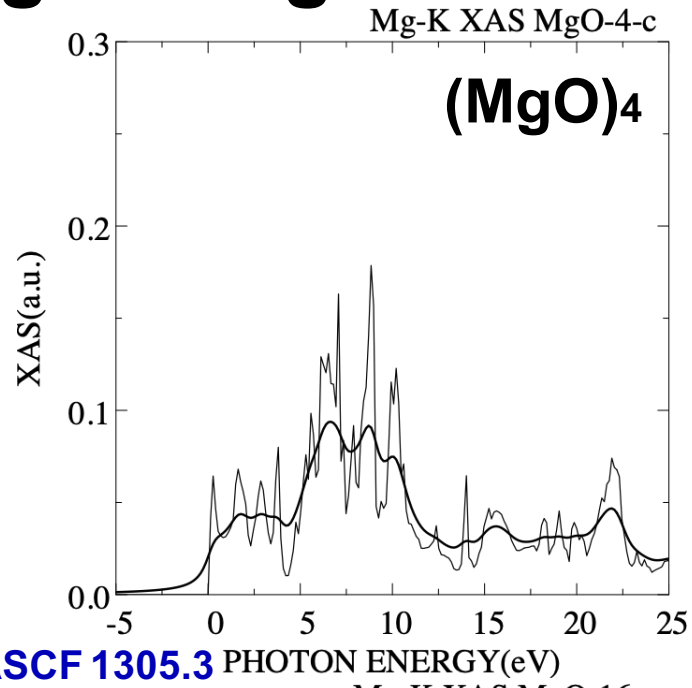
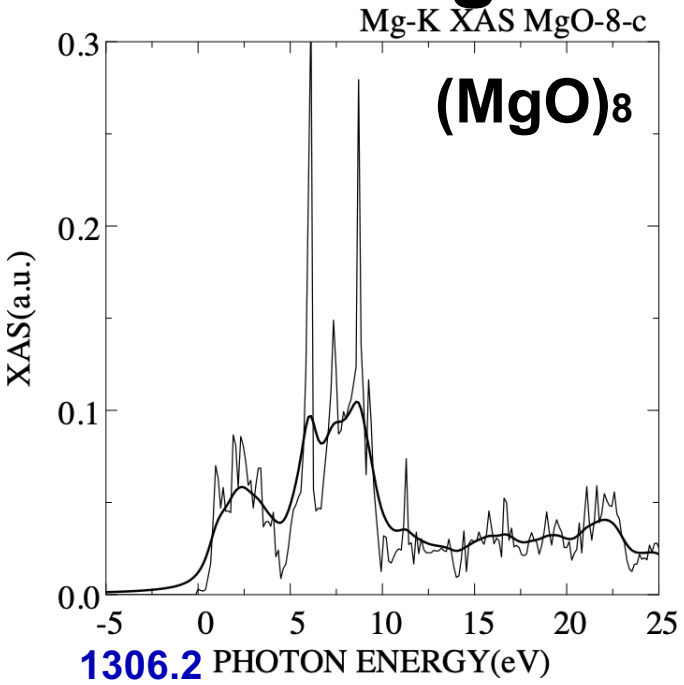
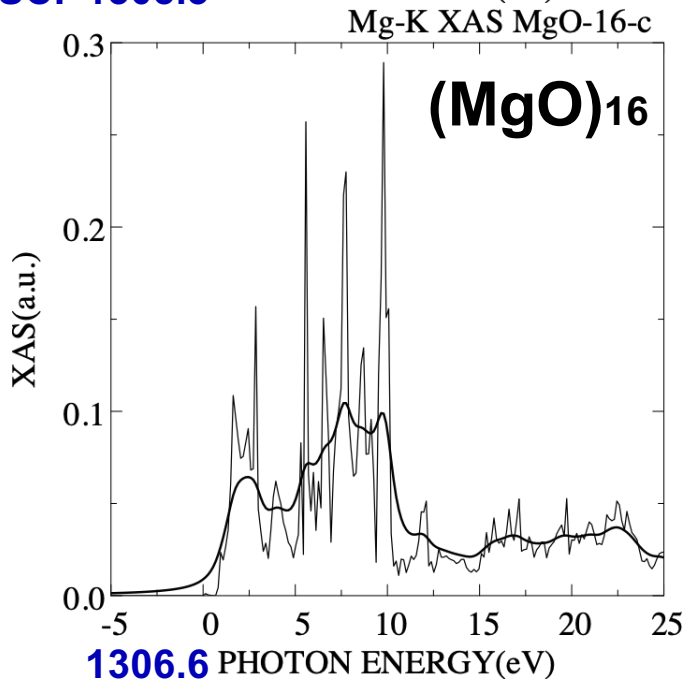


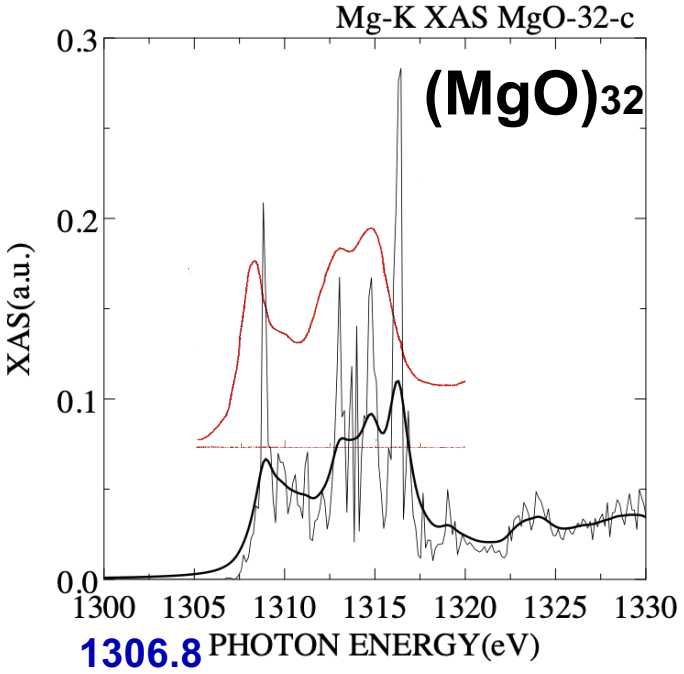
ΔSCF 1305.3



1306.2

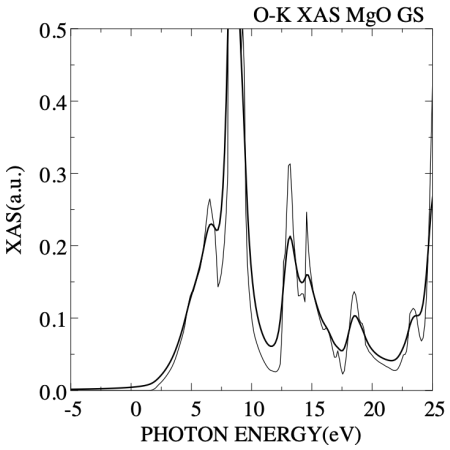


1306.6



1306.8

O K-Edge of MgO with Core Hole in O-1s



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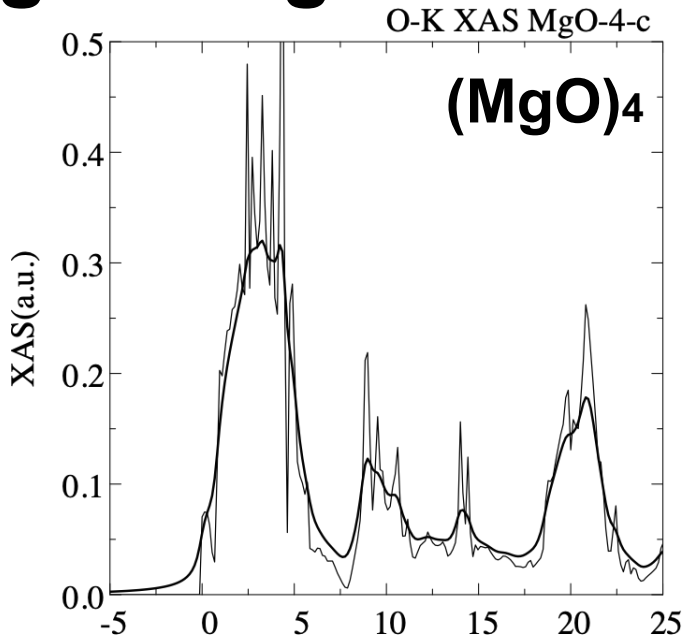
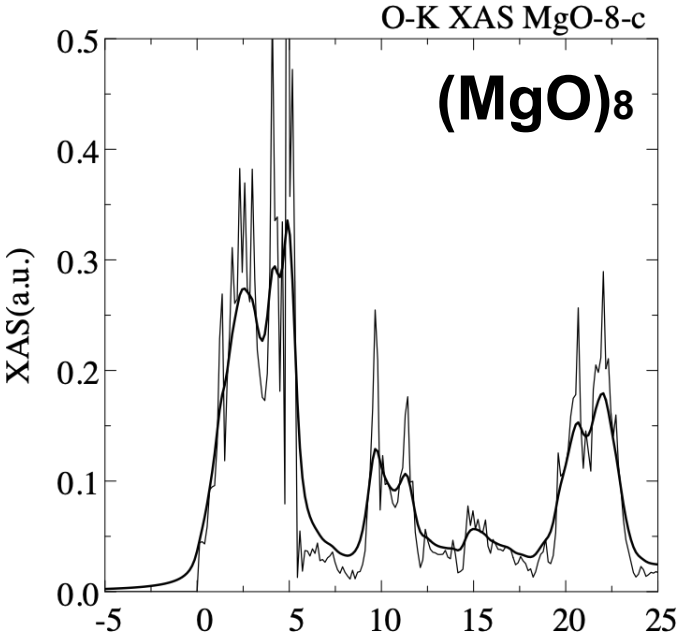
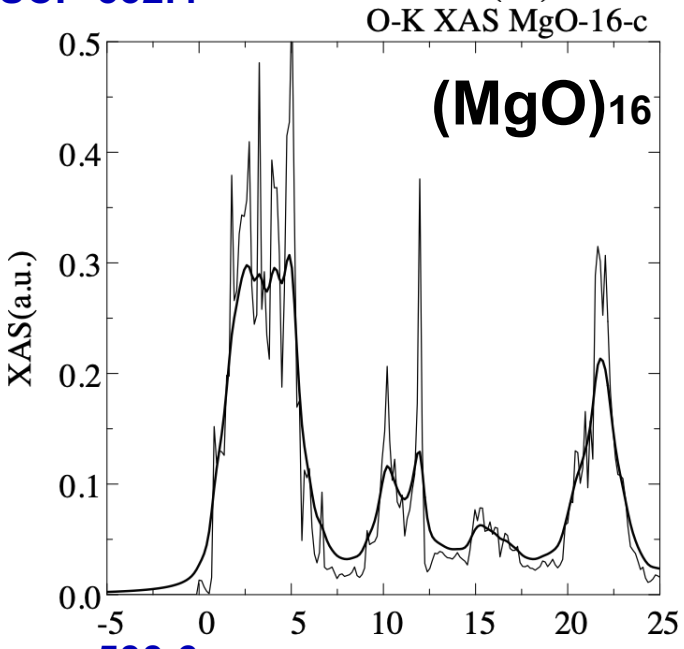


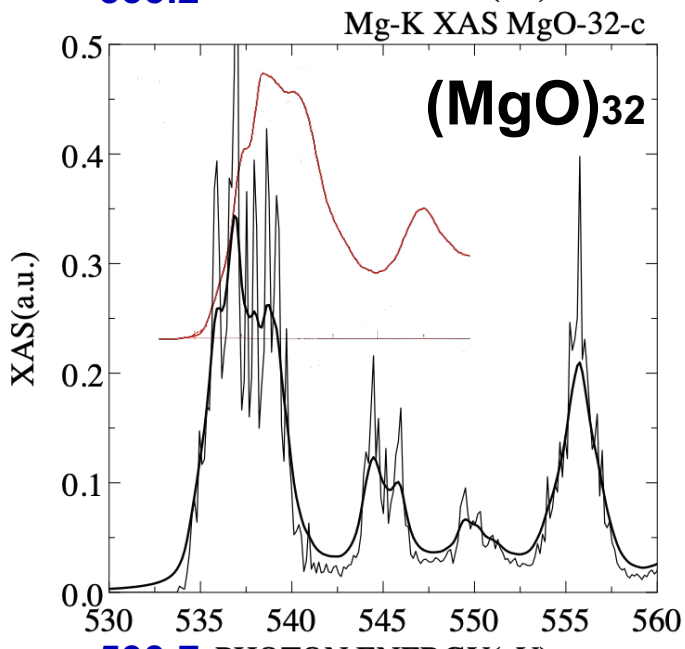
ΔSCF 532.4



533.2



533.6



533.7

Summary of XAS

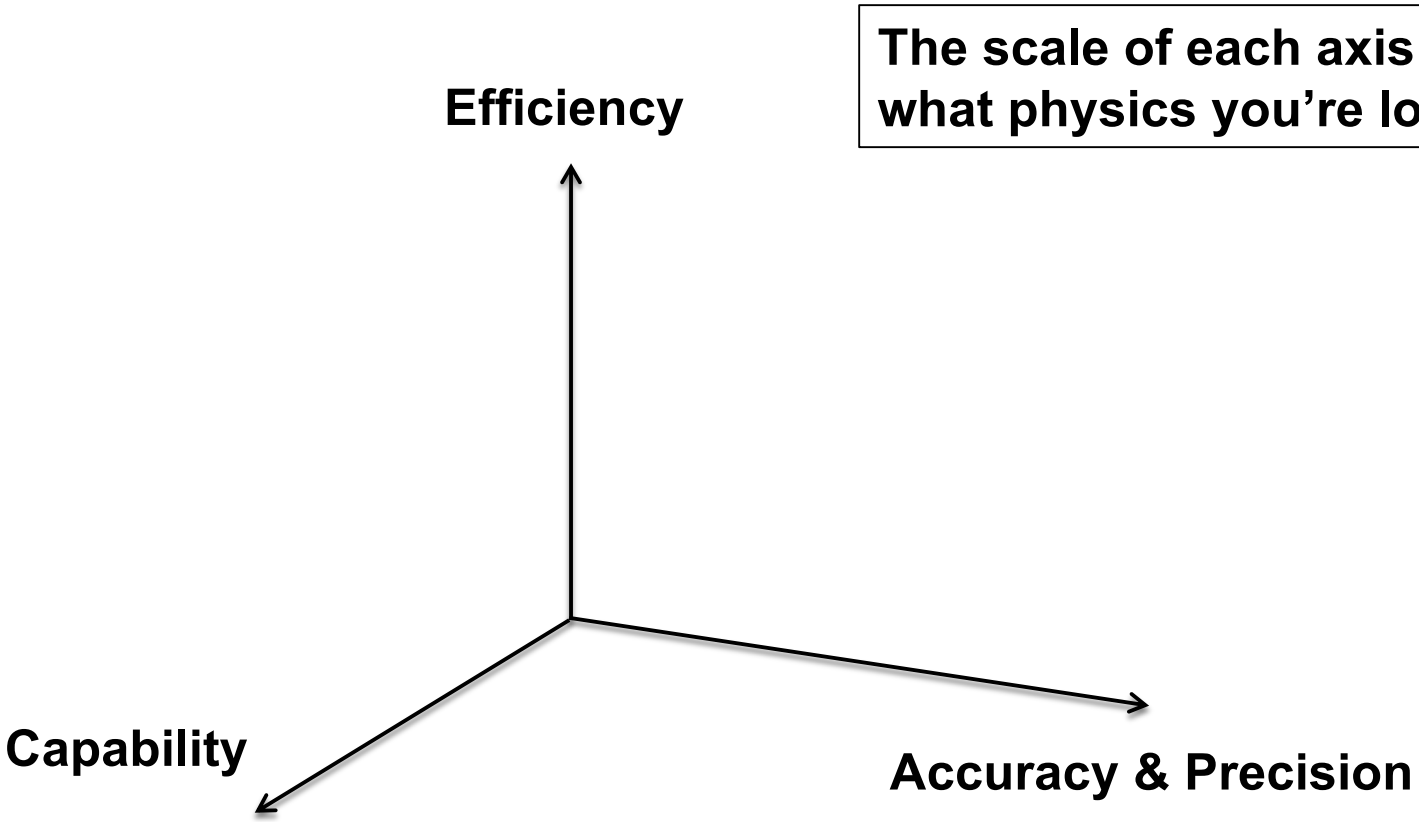
- **XAS calculations with core hole**
  - **Better shape of the spectra**
  - **Better excitation energy in the ΔSCF sense**
- **Test calculations at *K* edges of MgO**

- **Further test**
  - ➢ **Different edges (L, M, N, …)**
  - ➢ **Different materials (magnetic, …)**
  - ➢ **Effects on polarization (MCD, LD, …) …..**

SUMMARY

- **FLAPW Method**
  - **Precise and robust, but often heavy**
    - ➢ **CPU ~ N_{atom}^3**
  - **Complementary role with PP-PW**
  - **Care of the convergency in several parameters involved**
- **A wide variety of applications of FLAPW**

First-Principles Calculations



The scale of each axis depends on what physics you're looking at.