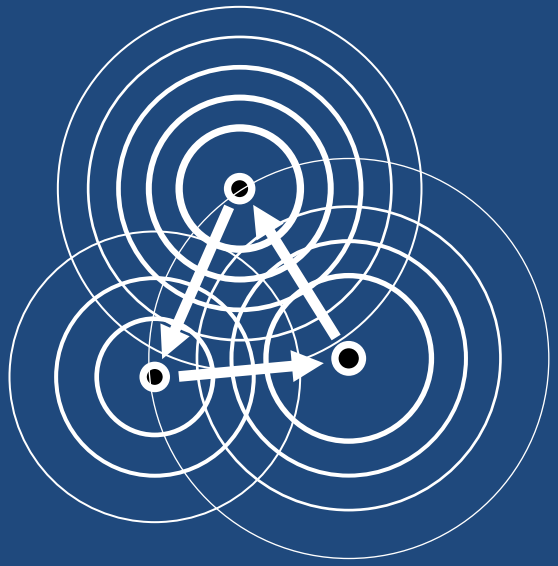
# X-ray Spectroscopy Theory Lectures

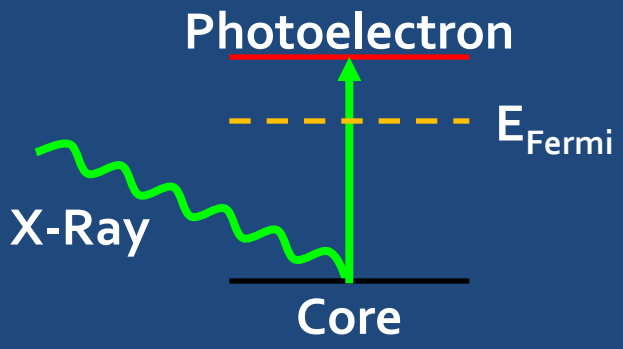
J. J. Rehr

I. Introduction to the Theory of X-ray spectra
II. Real-space Green's function Theory and FEFF
III. Inelastic losses and many-body effects
IV. Real-time approaches

# I. Introduction to the Theory of X-ray spectra

J. J. Rehr, J. J. Kas, and F. D. Vila





# Outline

Introduction - TIMES

Elementary theory & interpretation of x-ray spectra

Introduction to quantitative theories and methods

TIMES Software

Next generation x-ray spectrosopy theory

Examples

# Theory Institute for Materials and Energy Spectroscopies (TIMES)


**GOAL of TIMES**: World class program on materials dynamics, aimed at understanding, non-equilibrium behavior and dynamics of charge, spin, lattice, and orbital degrees of freedom using advanced theory and light sources spanning THz to x-rays, e.g. LCLS & SSRL at SLAC and the ALS at LBNL.

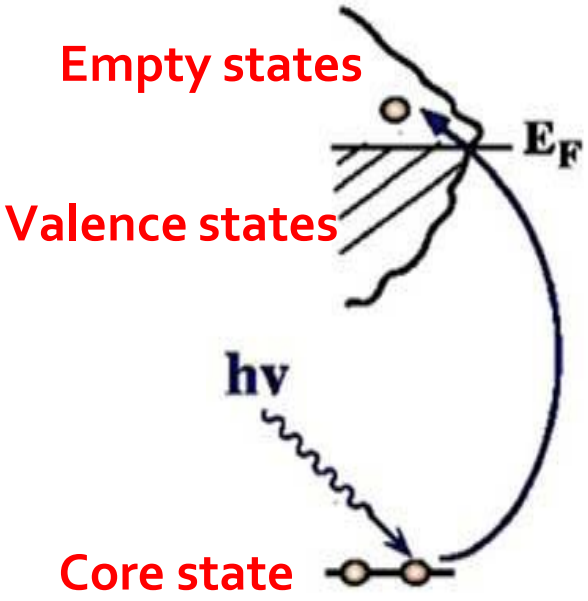
**TIMES Software**: Advanced theoretical codes and analysis tools for simulating and interpreting x-ray spectroscopies and workflow tools to facilitate calculations.

If I can't calculate it,

I don't understand it

R.P. Feynman

# X-ray absorption & core excitation



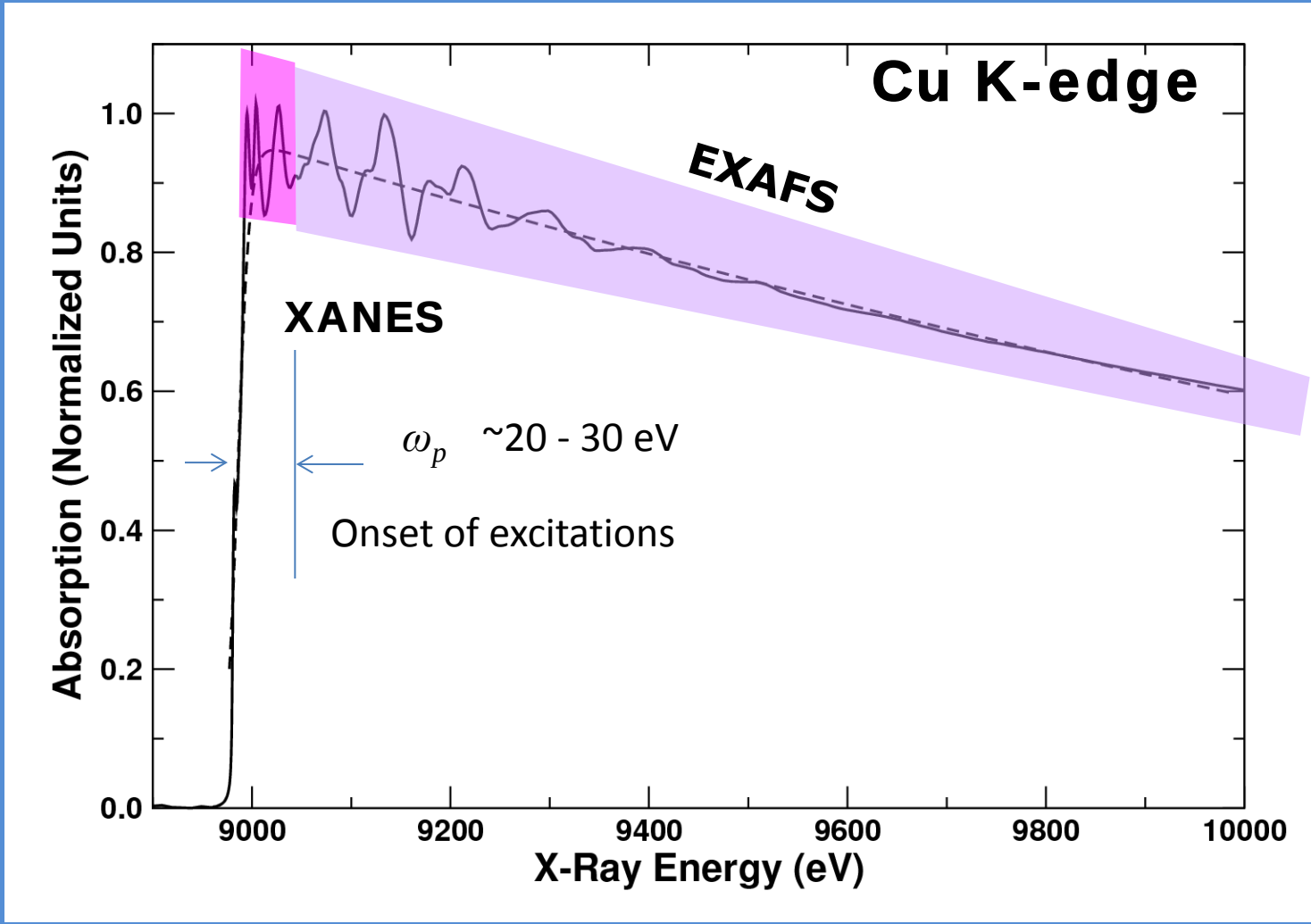

**X-ray absorption:**
**Process in which a photon is absorbed and a core electron is excited to an unoccupied state**

**Fermi level**

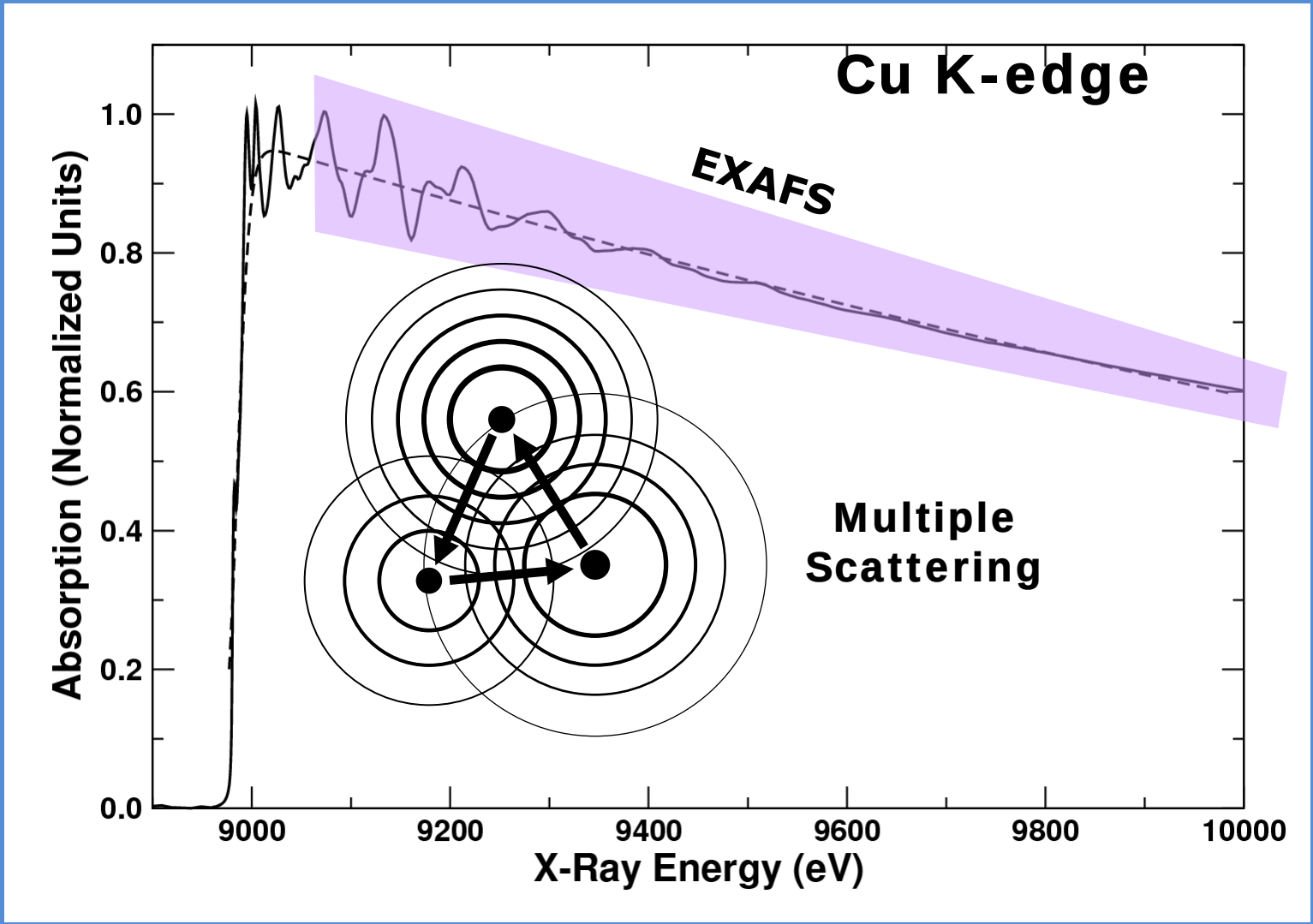
**Core energy $E_o$:**

**Different for every element:**
**XAS is element-specific**

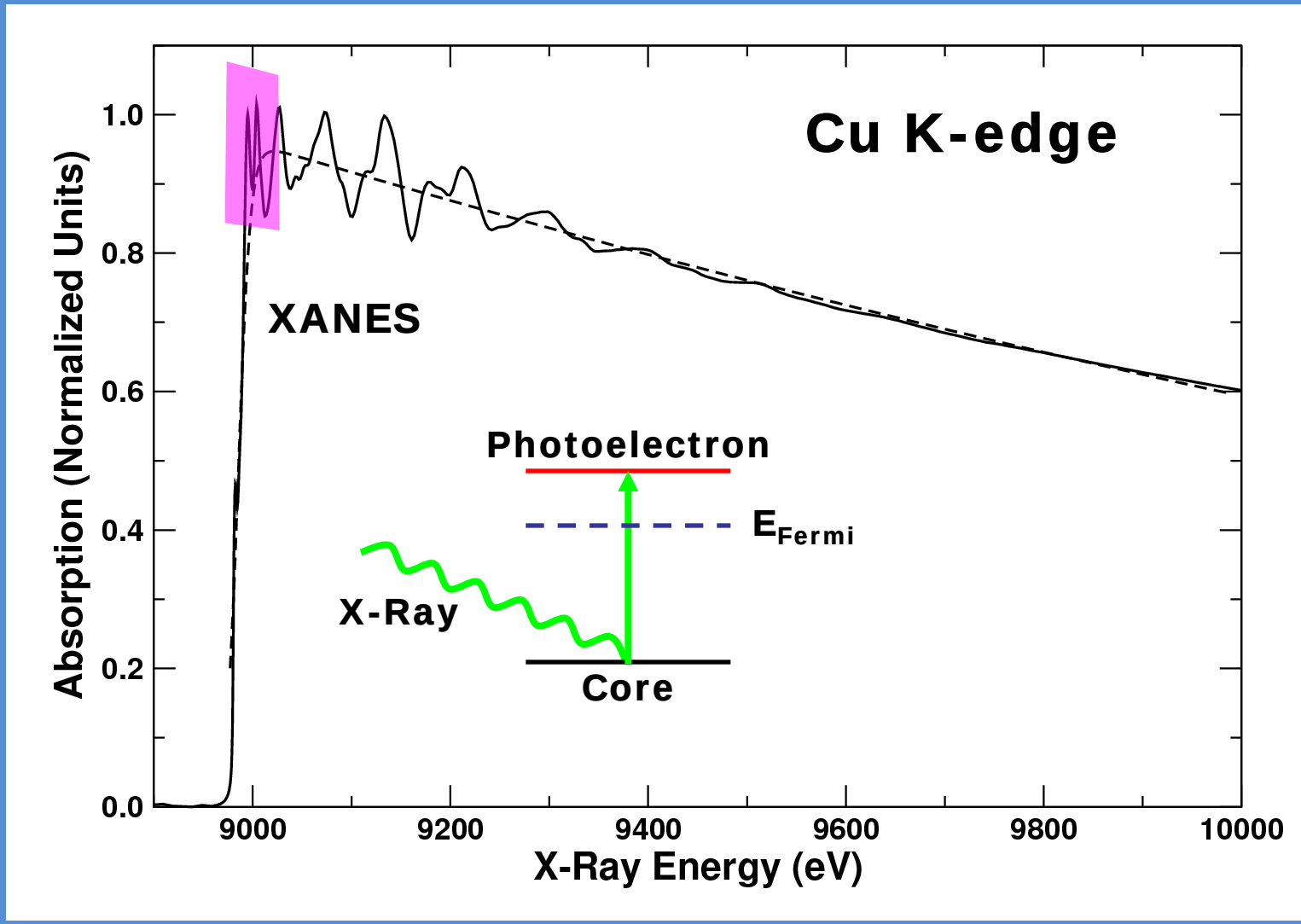
# XAS: XANES and EXAFS regions



# EXAFS: weak-scattering – calculate with low order multiple scattering theory



# XANES strong-scattering – need high order multiple scattering theory



# XANES *vs* EXAFS

EXAFS - high energy photoelectrons, weak scattering

- \+ Quantitative structural information
- \+ Well developed theory
- \+ Quantitative analysis
- – Low signal/noise

XANES - low energy photoelectrons, strong scattering

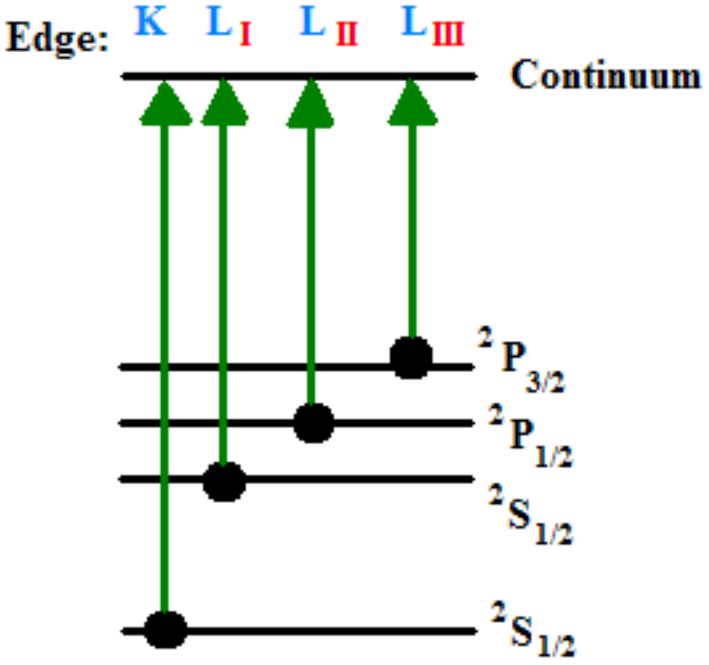
- \+ Chemical/Electronic Structure information
- \+ Large signal/noise
- – Short data range
- – LARGE errors in potentials & many-body effects

# Absorption edges

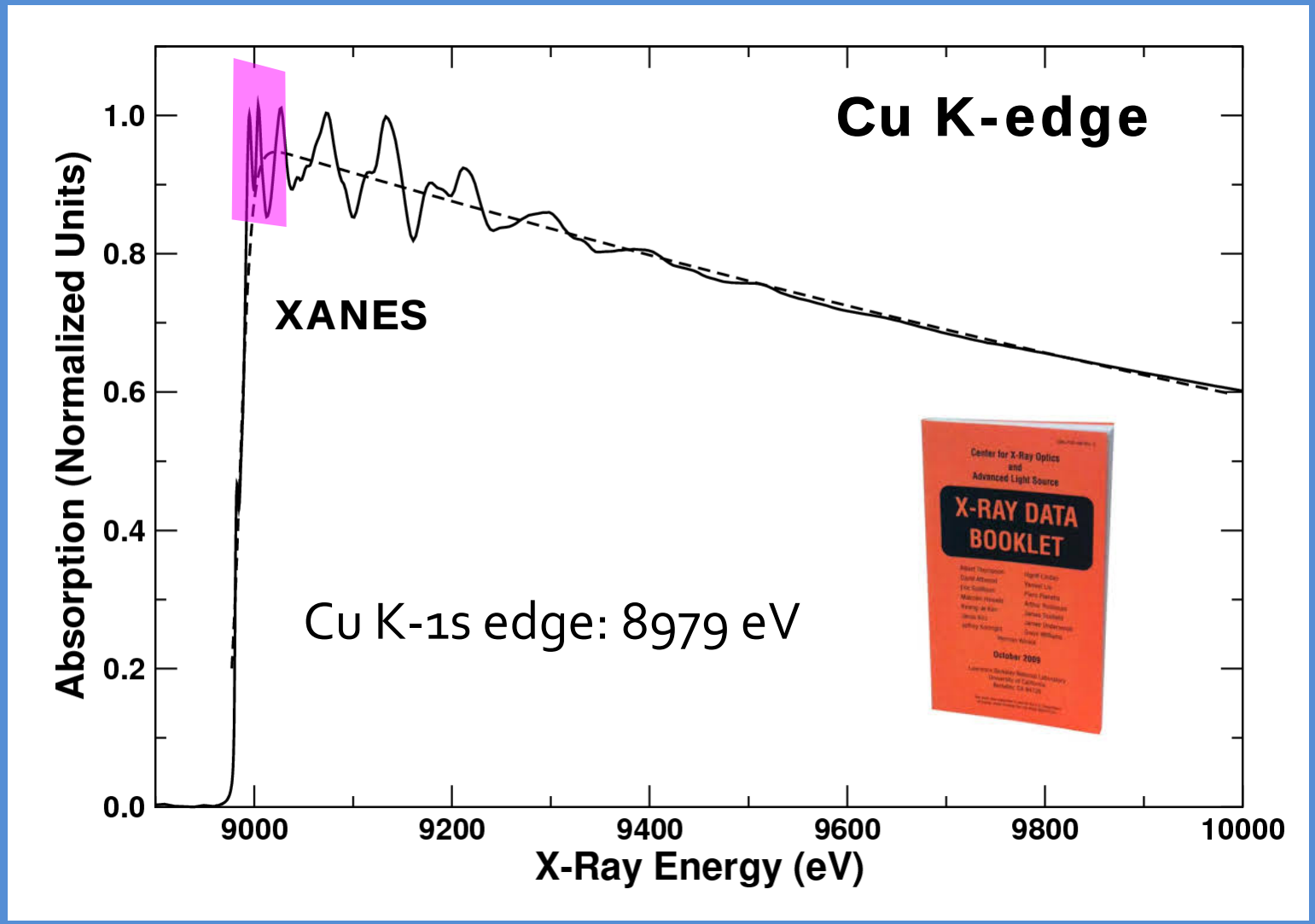
**Absorption edges: K, L1, …**

**An edge occurs when the x-ray energy reaches the binding energy of a given core electron**

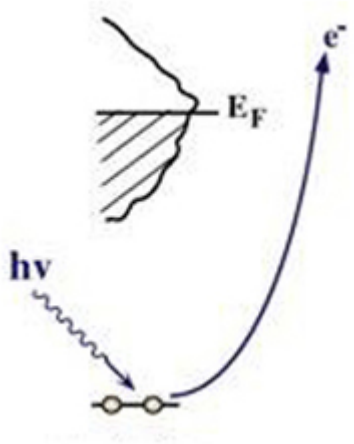
**Edges are labelled by the core electron shell K = 1S, L1 = 2S1/2 …**



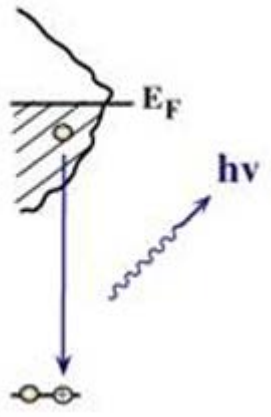
# XAS Data Booklet



# Other near-edge spectra: XPS, XES $|E\text{-}E_F| < 40\ eV$




X-ray Photoelectron Spectroscopy (XPS)




X-ray Emission Spectroscopy (XES)

# "Qualitative" theory of XAS and XES

Like all optical and x-ray transitions, the probability of a transition is given by Fermi's golden rule:

$$P_{i\to f} \propto \left|\langle f|H'|i\rangle\right|^2 \rho_f$$

where

- $\rho_f$ Density of final states
- $i, f$ Initial and final states
- $H'$ Light-matter interaction operator:

$$H' = \vec{p}\cdot\hat{\varepsilon}e^{i\vec{k}\cdot\vec{r}}$$

Goes to dipole approximation for low momentum transfer

# "Qualitative" understanding of XAS - Fingerprinting

Projected Density of States

Dipole matrix elements

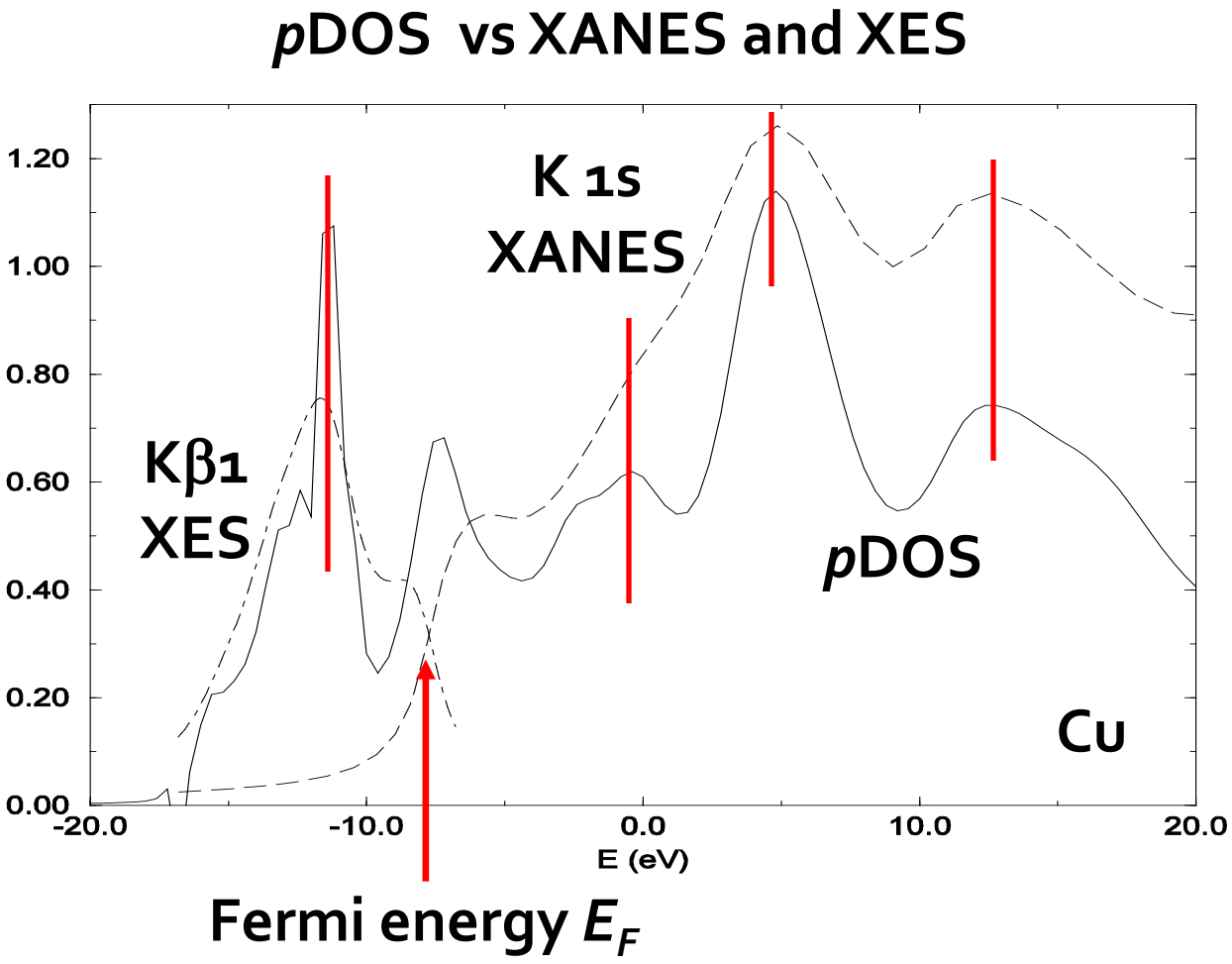
Core-hole (aka *excitonic*) effects

Coordination

Charge transfer

Oxidation state

# Local *p*DOS "mimics" absorption or emission peaks



# Selection rules: From atoms to complex systems



Atomic Spectroscopy

A Compendium of Basic Ideas, Notation, Data, and Formulas

**17. Spectral Lines: Selection Rules, Intensities, Transition Probabilities, Values, and Line Strengths**

**Selection rules for discrete transitions**

| | | Electric dipole (E1) ("allowed") | Magnetic dipole (M1) ("forbidden") | Electric quadrupole (E2) ("forbidden") |
|---|---|---|---|---|
| Rigorous rules | 1. | $\Delta J = 0, \pm 1$ (except $0 \not\leftrightarrow 0$) | $\Delta J = 0, \pm 1$ (except $0 \not\leftrightarrow 0$) | $\Delta J = 0, \pm 1, \pm 2$ (except $0 \not\leftrightarrow 0$, $1/2 \not\leftrightarrow 1/2$, $0 \not\leftrightarrow 1$) |
| | 2. | $\Delta M = 0, \pm 1$ (except $0 \not\leftrightarrow 0$ when $\Delta J = 0$) | $\Delta M = 0, \pm 1$ (except $0 \not\leftrightarrow 0$ when $\Delta J = 0$) | $\Delta M = 0, \pm 1, \pm 2$ |
| | 3. | Parity change | No parity change | No parity change |
| With negligible configuration interaction | 4. | One electron jumping, with $\Delta l = \pm 1$, $\Delta n$ arbitrary | No change in electron configuration; i.e., for all electrons, $\Delta l = 0$, $\Delta n = 0$ | *No* change in electron configuration; *or* one electron jumping with $\Delta l = 0, \pm 2$, $\Delta n$ arbitrary |
| For *LS* coupling only | 5. | $\Delta S = 0$ | $\Delta S = 0$ | $\Delta S = 0$ |
| | 6. | $\Delta L = 0, \pm 1$ (except $0 \not\leftrightarrow 0$) | $\Delta L = 0$ $\Delta J = \pm 1$ | $\Delta L = 0, \pm 1, \pm 2$ (except $0 \not\leftrightarrow 0$, $0 \not\leftrightarrow 1$) |

# Selection rules: From atoms to complex systems

$$M_{if} = \left\langle f \left| \vec{p} \cdot \hat{\varepsilon} + i (\vec{p} \cdot \hat{\varepsilon})(\vec{k} \cdot \vec{r}) \right| i \right\rangle$$

Dipole Quadrupole

For XANES:

Pretty good approximation (unless high symmetry)

Usually broken by distortions

Bottom line:

$$\Delta L = \pm 1 \qquad \Delta S = 0$$

Dipole allowed

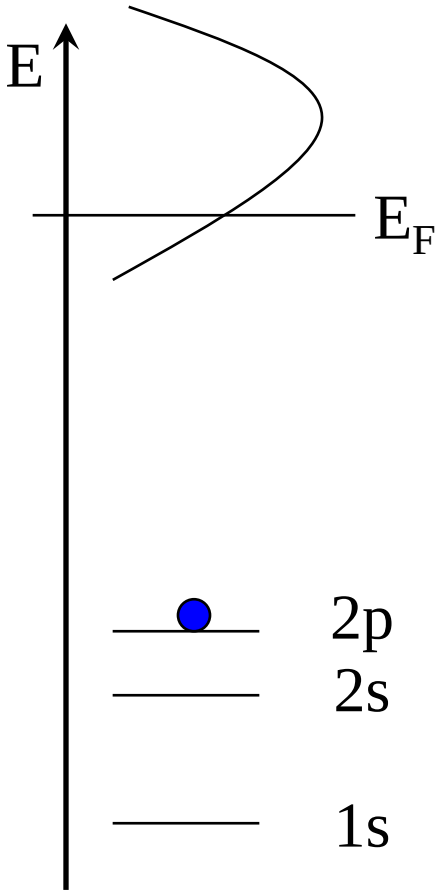
s ($K$, $L_1$) $\rightarrow$ p-like

p ($L_2$, $L_3$) $\rightarrow$ s-like and d-like

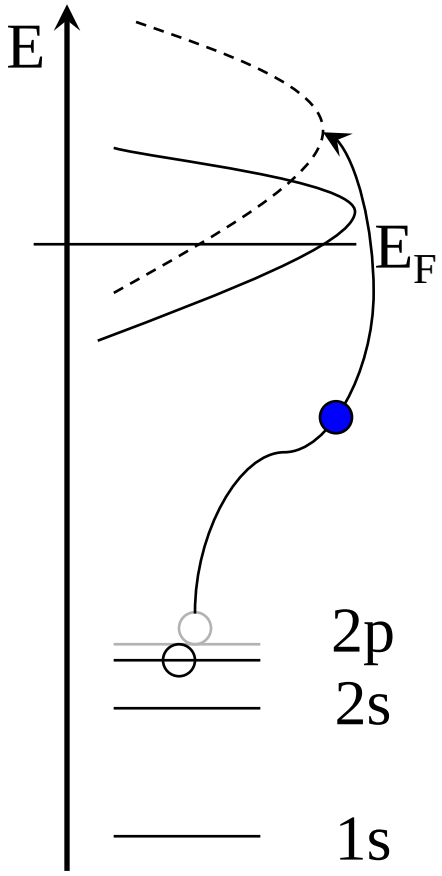
Quadrupole allowed

s ($K$, $L_1$) $\rightarrow$ s-like and d-like

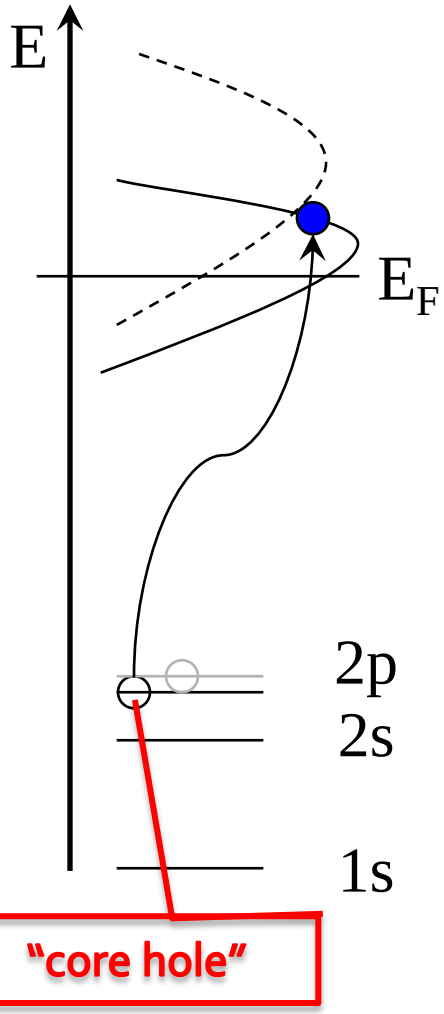
# Effect of core-hole on DOS – *excitonic red shifts*



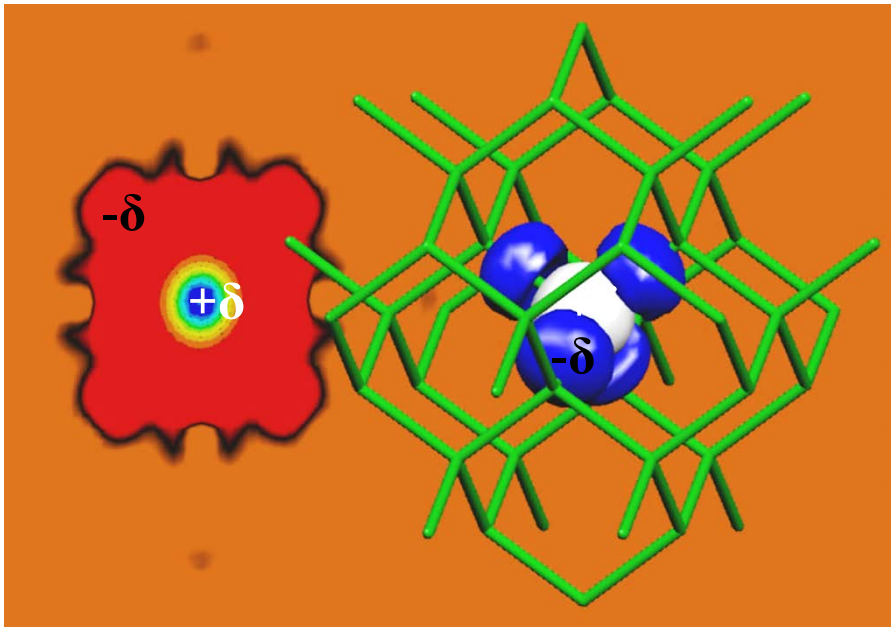

**Ground state**



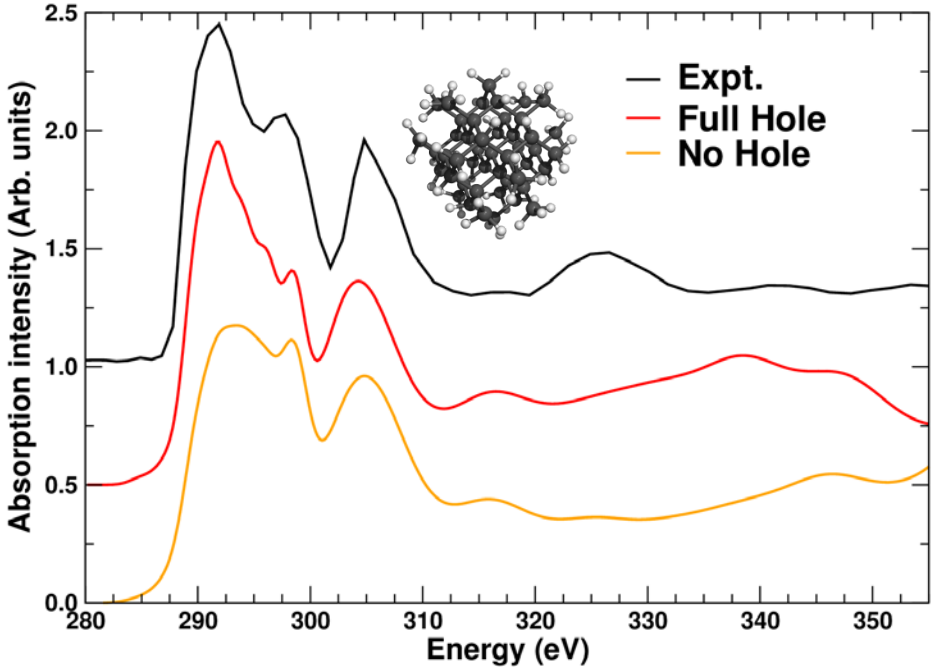

**Transition state**



# Core-hole effect on XAS – *Excitonic edge enhancement*

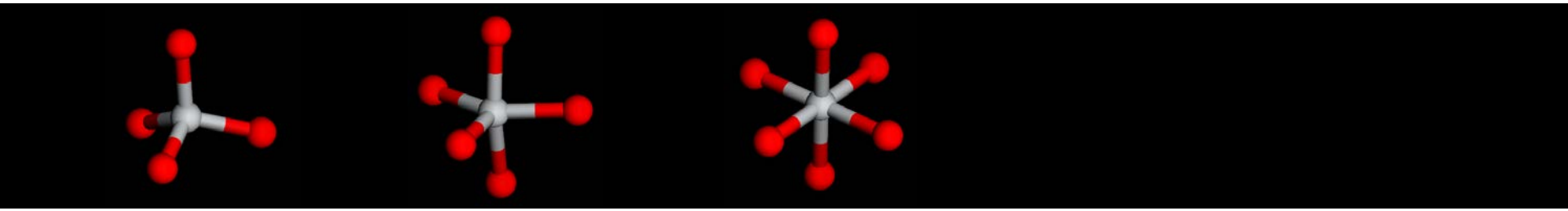


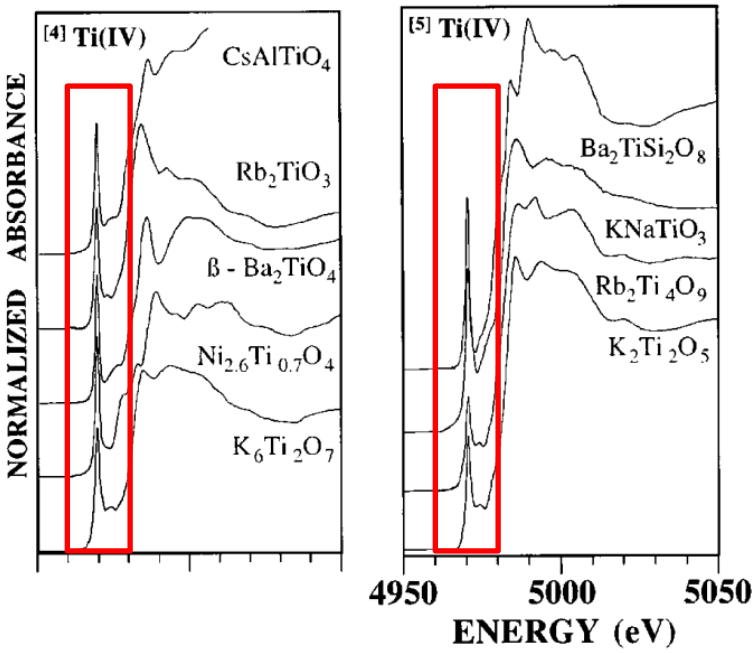

Density Relaxation
(Isosurface and Projection)

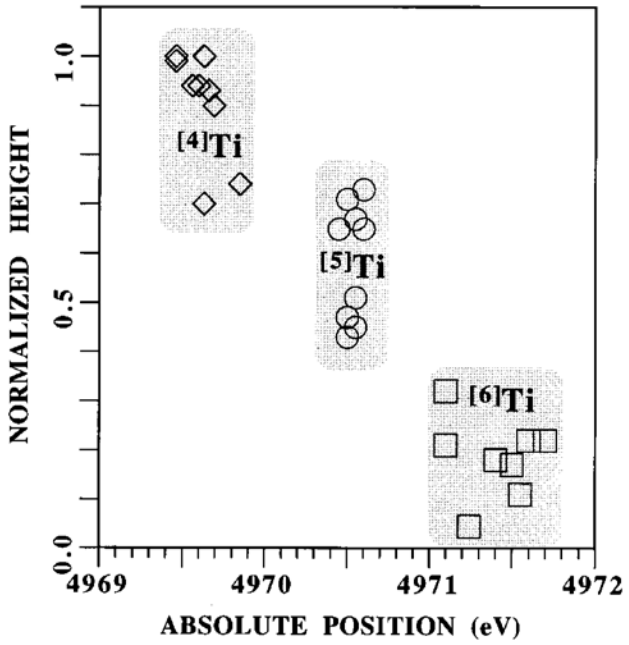



XAS

# Coordination vs pre-edge & near-edge features



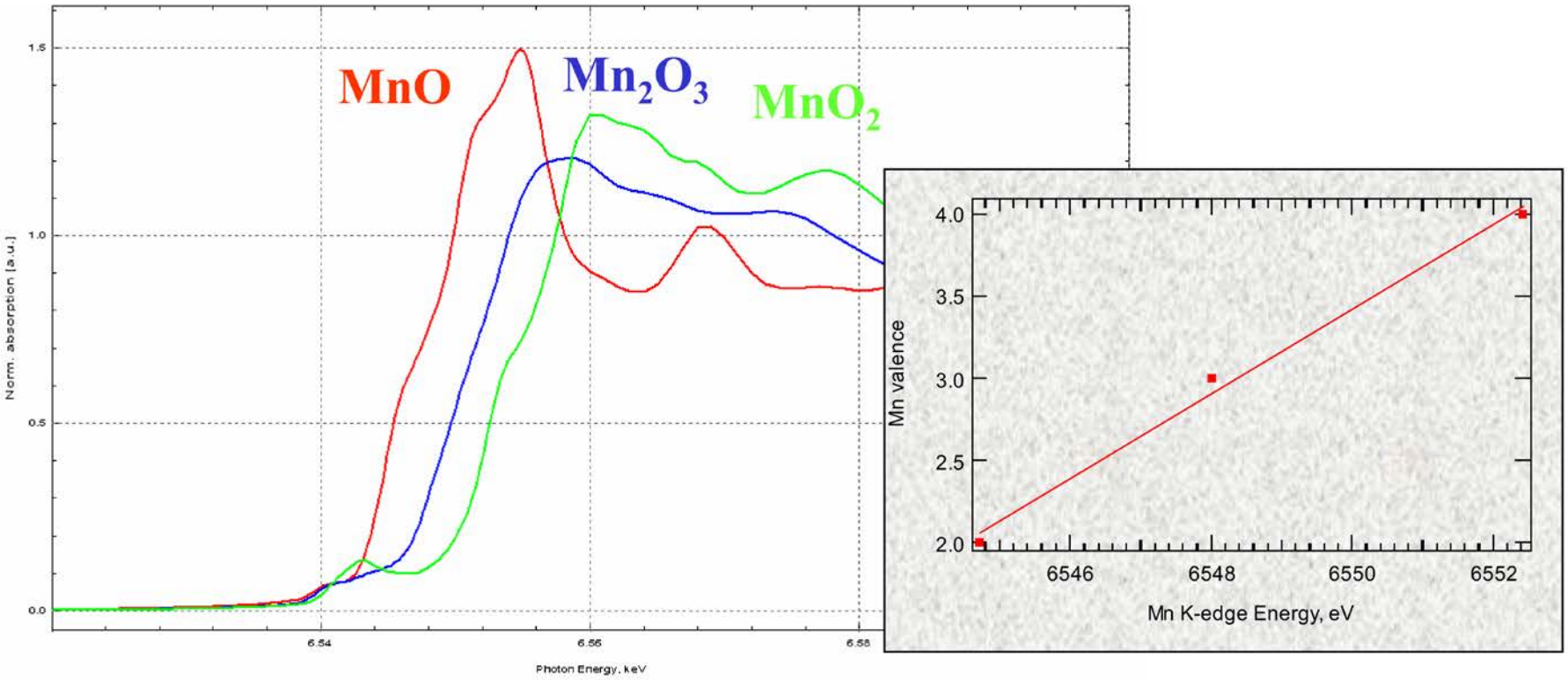



**Ti K pre-edge intensity and position depends on coordination**

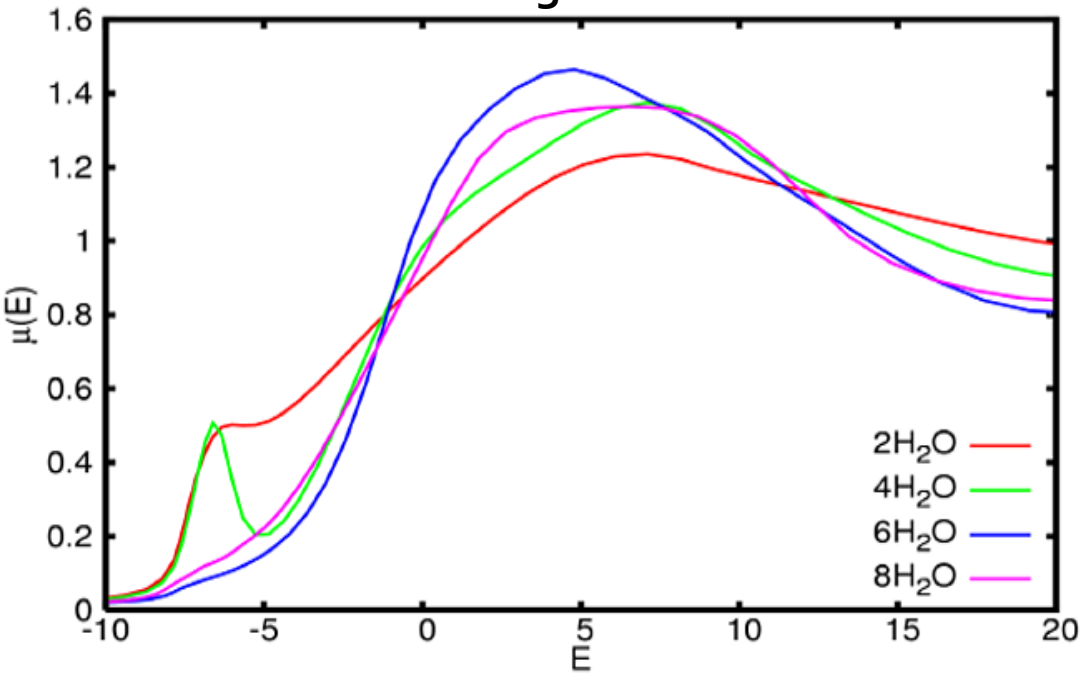
F. Farges et al., Phys. Rev. B 56, 1809 (1997)

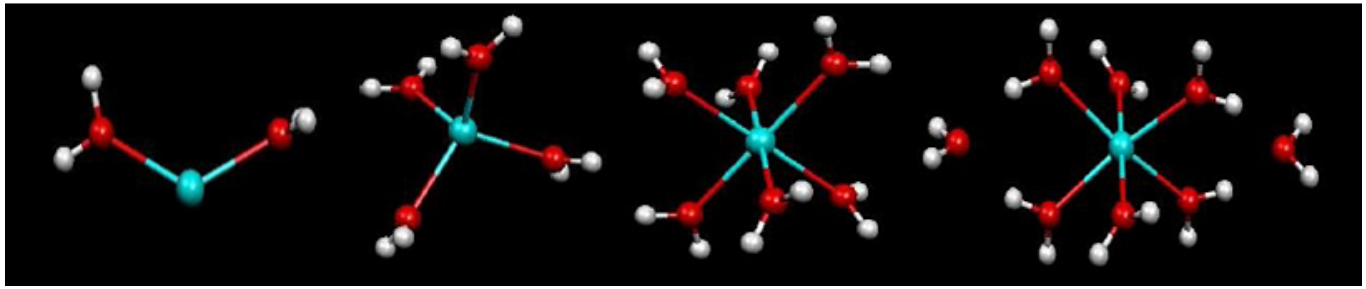
# Edge position and oxidation state




**Mn K-edge shifts with oxidation state**

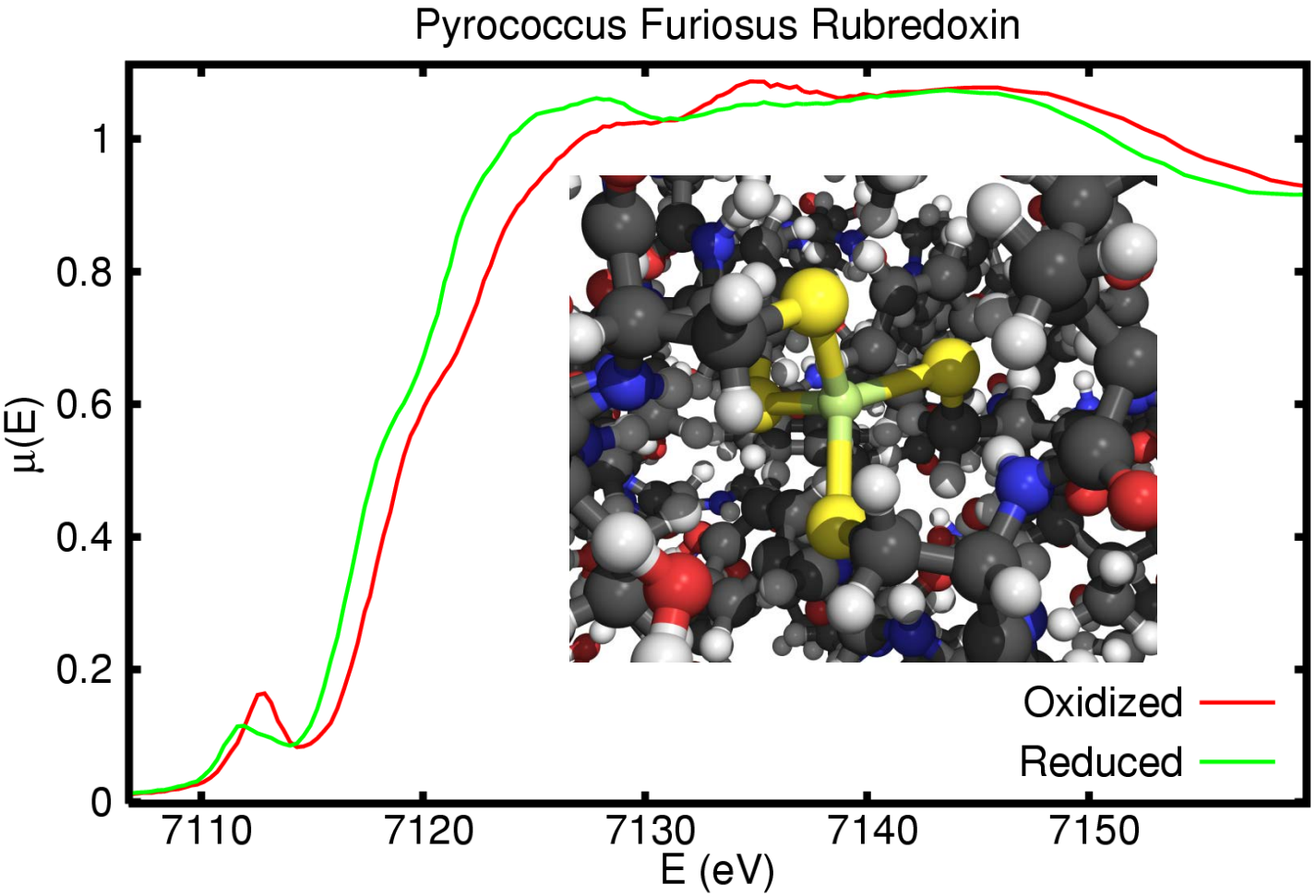
# Coordination vs pre-edge & near-edge features



2 $H_2O$ 4 $H_2O$ 6 $H_2O$ 8 $H_2O$

# Edge position and core-hole screening



# Quantitative theory of XAS

Starting point : Fermi golden rule

Key Approximations:

- Independent particle approximation:
  - many-body -> (effective) single particle theory
- Sudden approximation
- Single core-hole level
- Single channel (e.g. K-shell)

# Many-body $\rightarrow$ effective single particle theory

**XAS absorption coefficient**

**Many-body Fermi golden Rule**

$$\mu(\omega) \propto \sum_F |\langle I|\Delta|F\rangle|^2 \, \delta\left(E_F - E_I - \omega\right)$$

**Dipole operator (2nd quantized form)**

$$\Delta = \sum_{if} d_{if} a_f^\dagger a_i$$

# Many-body → effective single particle theory

| | XAS absorption coefficient |
|---|---|
| Many-body Fermi Golden Rule | $\mu(\omega) \propto \sum_F \left\|\langle I\|\Delta\|F\rangle\right\|^2 \delta\left(E_F - E_I - \omega\right)$ |
| Dipole operator (2nd quantized form) | $\Delta = \sum_{if} d_{if} a_f^\dagger a_i$ |
| Approx. Hamiltonian partition | $H_N = H'_{N-1} + h$ |
| Photoelectron Hamiltonian | $h = -\frac{\nabla^2}{2} + V_{coul}^{N-1} + \Sigma_{xc}\left(E, \rho(r)\right)$ |

# Many-body → effective single particle theory

**XAS absorption coefficient**

**Many-body Fermi golden Rule**

$$\mu(\omega) \propto \sum_F |\langle I|\Delta|F\rangle|^2 \, \delta\left(E_F - E_I - \omega\right)$$

**Photoelectron Hamiltonian**

$$h = -\frac{\nabla^2}{2} + V_{coul}^{N-1} + \Sigma_{xc}\left(E, \rho(r)\right)$$

**Photoelectron equation**

$$h\left|\phi_{ph}^{k}(E)\right\rangle = E\left|\phi_{ph}^{k}(E)\right\rangle$$

# Many-body → effective single particle theory

**XAS absorption coefficient**

**Many-body Fermi golden Rule**

$$\mu(\omega) \propto \sum_F |\langle I|\Delta|F\rangle|^2 \, \delta\left(E_F - E_I - \omega\right)$$

**Photoelectron Hamiltonian**

$$h = -\frac{\nabla^2}{2} + V_{coul}^{N-1} + \Sigma_{xc}\left(E, \rho(r)\right)$$

**Photoelectron equation**

$$h\left|\phi_{ph}^{k}(E)\right\rangle = E\left|\phi_{ph}^{k}(E)\right\rangle$$

**Thus we can approximate the initial and final states as**

$$|I\rangle = |\phi_c\rangle\left|\Psi_0^{N-1}\right\rangle$$

$$|F\rangle = \left|\phi_{ph}^{k}\right\rangle\left|\Psi_n^{N-1}\right\rangle$$

# Many-body → effective single particle theory

XAS absorption coefficient

Many-body Fermi golden Rule

$$\mu(\omega) \propto \sum_F |\langle I|\Delta|F\rangle|^2 \, \delta\left(E_F - E_I - \omega\right)$$

$$\mu(\omega) \propto \sum_{nk} \left|\left\langle \Psi_0^{N-1} \middle| \Psi_n^{N-1} \right\rangle\right|^2 \left|\left\langle \phi_c \middle| \hat{d}_c \middle| \phi_{ph}^k \right\rangle\right|^2 \delta(E_{ph} + E_n - E_0 - \omega)$$

Define Amplitude Reduction Factor

$$S_n^2 = \left|\left\langle \Psi_0^{N-1} \middle| \Psi_n^{N-1} \right\rangle\right|^2$$

Sum over channels

$$\mu(\omega) \propto \sum_n S_n^2 \sum_k \left|\left\langle \phi_c \middle| \hat{d}_c \middle| \phi_{ph}^k \right\rangle\right|^2 \delta(E_{ph} + E_n - E_0 - \omega)$$

# Many-body → effective single particle theory

XAS absorption coefficient

Many-body Fermi golden Rule

$$\mu(\omega) \propto \sum_F |\langle I|\Delta|F\rangle|^2 \, \delta\left(E_F - E_I - \omega\right)$$

Focus on principal channel

Effective Single particle Fermi's Golden Rule

$$\mu(\omega) \propto \sum_{i,f} |\langle i|d|f\rangle|^2 \, \delta\left(E_f - E_i - \omega\right) S_0{}^2$$

$$H = -(1/2)\nabla^2 + V$$

$$H' = H + V_{ch} + \Sigma(E)$$

# Sum-over-states to Green's function formalism

**Effective Single particle Fermi's Golden Rule**

$$\mu(\omega) \propto \sum_{ij} \left\langle i \left| d^{\dagger} \right| f \right\rangle \left\langle f \left| d \right| i \right\rangle \delta(E_f - E_i - \omega) \; S_0{}^2$$

# Sum-over-states to Green's function formalism

**Effective Single particle Fermi's Golden Rule**

$$\mu(\omega) \propto \sum_{ij} \langle i | d^{\dagger} | f \rangle \langle f | d | i \rangle \, \delta(E_f - E_i - \omega) \quad S_0^2$$

$$\rho(r, r', E) = \sum_f |f\rangle\langle f| \; \delta\left(E_f - E\right)$$

**Density Matrix**

# Sum-over-states to Green's function formalism

**Effective Single particle Fermi's Golden Rule**

$$\mu(\omega) \propto \sum_{ij} \left\langle i \left| d^{\dagger} \right| f \right\rangle \left\langle f \left| d \right| i \right\rangle \delta(E_f - E_i - \omega)\ S_0^2$$

$$\rho(r, r', E) = \sum_f |f\rangle\langle f|\ \delta\left(E_f - E\right)$$

$$\mathrm{Im}\left[G(r, r', E)\right] = -\frac{1}{\pi}\rho(r, r', E)$$

$$G = \left[E - H + i\Gamma\right]^{-1}$$

**Density matrix from Green's function**

# Sum-over-states to Green's function formalism

**Effective Single particle Fermi's Golden Rule**

$$\mu(\omega) \propto \sum_{ij} \langle i | d^{\dagger} | f \rangle \langle f | d | i \rangle \, \delta(E_f - E_i - \omega) \; S_0^2$$

$$\rho(r, r', E) = \sum_f |f\rangle\langle f| \; \delta\left(E_f - E\right)$$

$$\mathrm{Im}\left[G(r, r', E)\right] = -\frac{1}{\pi}\rho(r, r', E)$$

$$G = \left[E - H + i\Gamma\right]^{-1}$$

**Substitute sum over final states with Green's function**

$$\mu(\omega) \propto \mathrm{Im} \sum_i \langle i | d^{\dagger} G(\omega + E_i) d | i \rangle \, \theta_{\Gamma}(\omega + E_i - E_{Fermi}) S_0^2$$

# What's a Green's function?

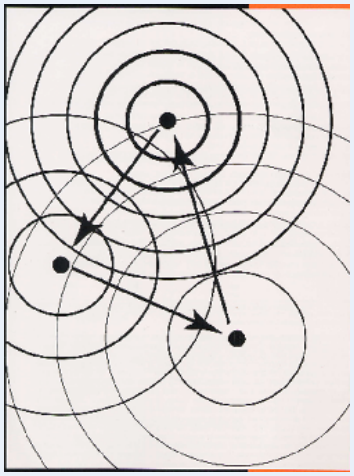
Wave function in QM $H \Psi = E \Psi$

$\Psi(r)$ = Amplitude to find particle at $r$

Green's function $(H - E)\, G = -\delta(r-r')$

$G(r,r',E)$ = *aka Propagator*

= Amplitude to go from $r$ to $r'$



# X-ray emission spectra

X-ray emission transition rate:

$$w = \frac{\alpha^3 \omega^3}{2\pi} \sum_i \left| \langle c \left| \hat{\varepsilon} \cdot \vec{r} \right| i \rangle \right|^2 \times \delta(\omega + E_c - E_i)$$

Dipole approx
c: Core state
i: Valence state

Similar to XAS, but with transitions to occupied states

"Initial state rule"

Initial state is in valence

Final state is core state

XES ~ ground state spectra

# Hierarchy of methods & codes TIMES Software

**Goal: Suite of available, optimized software for TIMES x-ray spectroscopy projects Now installed**

sophistication

Atomic + crystal field models:
DFATOM, atomic multiplet codes
DFT (Density Functional Theory): Ground state and near edge XAS
WIEN2k, ABINIT, VASP,NWCHEM, StoBe, Orca, CASTEP …
Quasi-particle Green's Function Theory:
FEFF9 Efficient for general x-ray spectra and excited states
BSE (Bethe-Salpeter Equation):
OCEAN, AI2NBSE , Exc!ting, Accurate but demanding.
First principles QC methods:
MRCI, MRCC, CASPT2, QMC, etc, accurate but intractable
Real-time methods: RT-XS, RT-Siesta

Workflow tools: CORVUS efficient tools for multiple codes

# Theoretical methods for near-edge XS: an overview

## Quick overview:

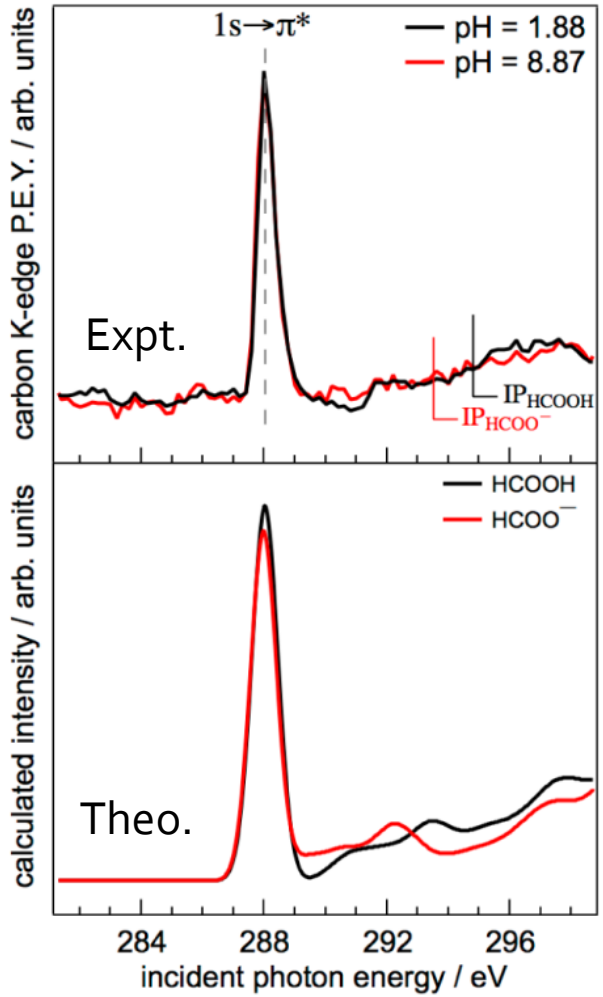
**Wavefunction** based methods
- Single determinant
- TDDFT

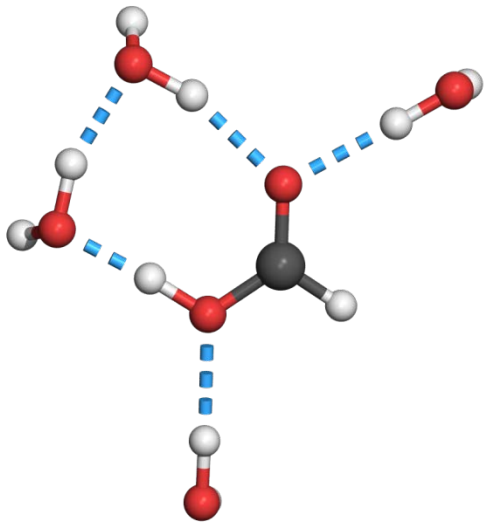
**Real-space multiple scattering** method
- See Lecture II. RSMS Theory and FEFF

**Bethe-Salpeter** equation (BSE) method, OCEAN
- See Lecture III. Many-body effects

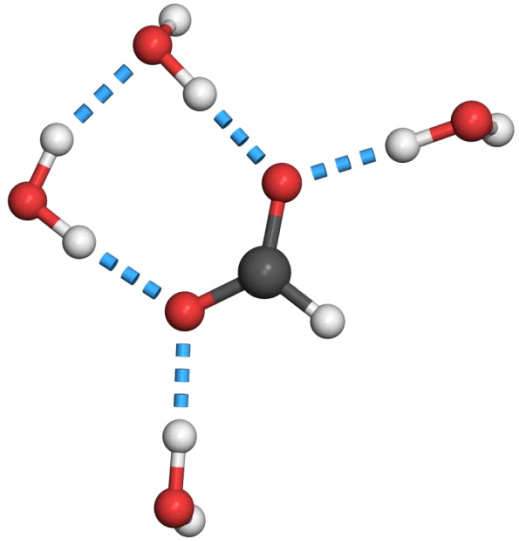
**Real-time** methods RTXS, RT-SIESTA
- See Lecture IV. Real-time approaches

# Example Restricted window TDDFT: Gaussian



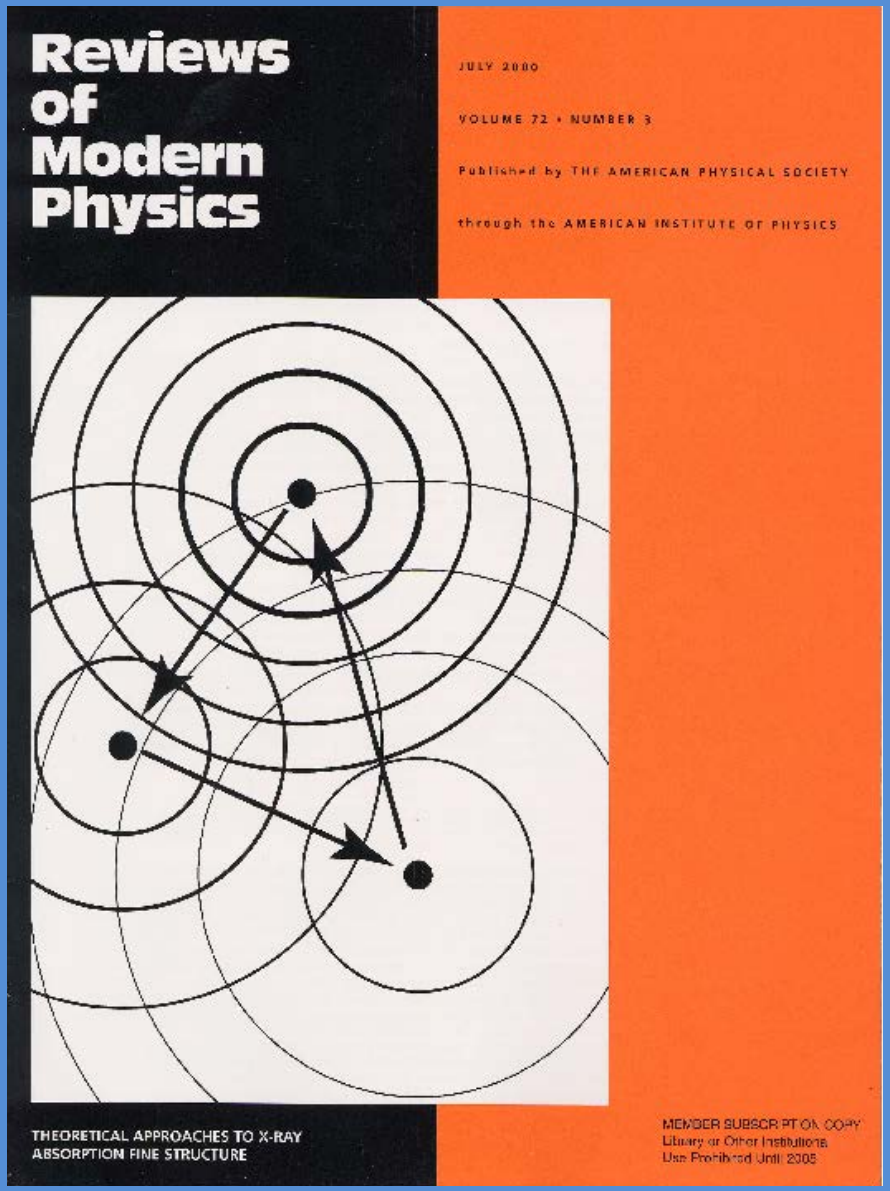
Solvated HCOOH



Solvated $HCOO^-$

Brown et al, JPC Lett. 3, 1754 (2012)

# Real-space Multiple-scattering theory FEFF




Quantitative theory of EXAFS:

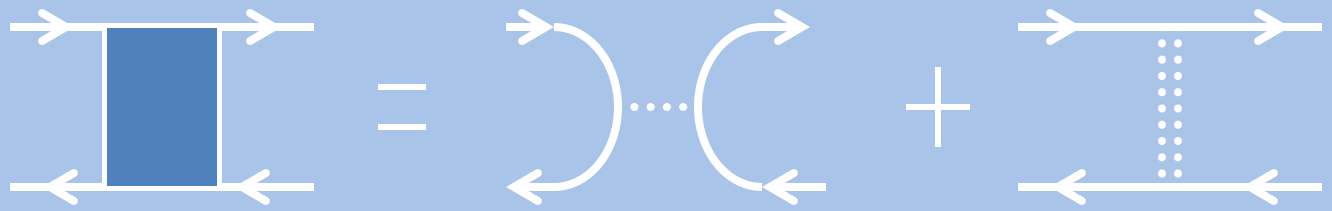
see Lecture II.

J. J. Rehr & R.C. Albers
Rev. Mod. Phys. 72, 621 (2000)

# GW/Bethe-Salpeter Equation*

- Particle-hole Green's function - see Lecture III.

$$-\mathrm{Im}\,\epsilon^{-1}(\mathbf{q},\omega) = \frac{4\pi}{q^2}\mathrm{Im}\,\langle\Psi_0|\hat{D}^\dagger \frac{1}{E_0+\omega-\hat{H}+i\gamma}\hat{D}|\Psi_0\rangle$$



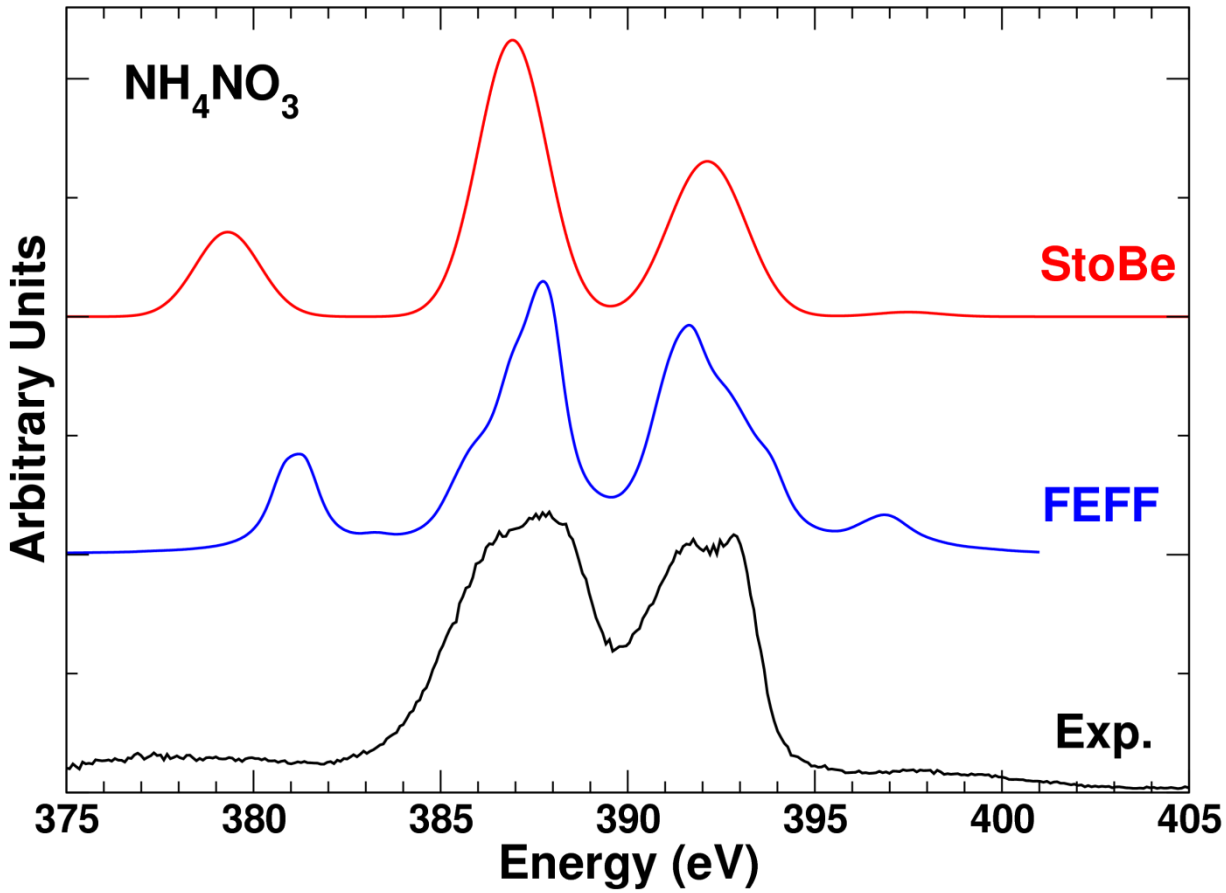
Ingredients: Particle-Hole Hamiltonian

$$H = h_e - h_h + V_{eh} \qquad h_{e/h} = \varepsilon_{nk} + \Sigma_{nk}$$

$\Sigma$ GW self-energy

$V_{eh} = V_x + W$ Particle-hole interaction

# Example: XES of molecular $NH_4NO_3$



# Summary

Take home messages from Lecture I.

Goals of the TIMES Project
Elements of the basic phenomena in XAS
Starting point to interpretation of the spectra
Elementary understanding of XAS theory
Overview of some current methods & codes
References for further work