

# Introduction to XAFS

EXAFS Analysis Workshop  
SSRL Users Meeting 2008

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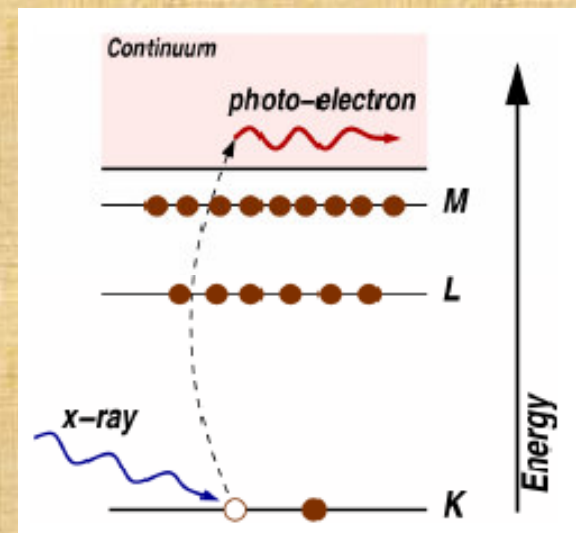
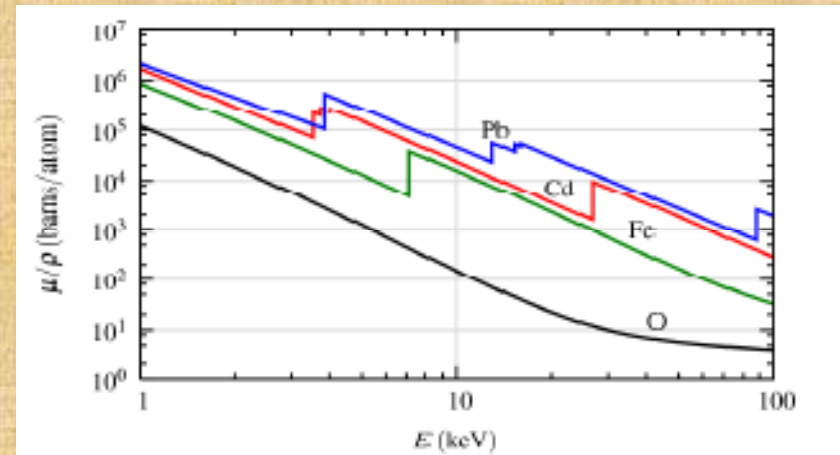
## In this talk ...

- Reminder about x-ray absorption spectroscopy
- A bit of history
- A bit of physics
- Related techniques
- The challenge of analysis
- What's ahead in this workshop

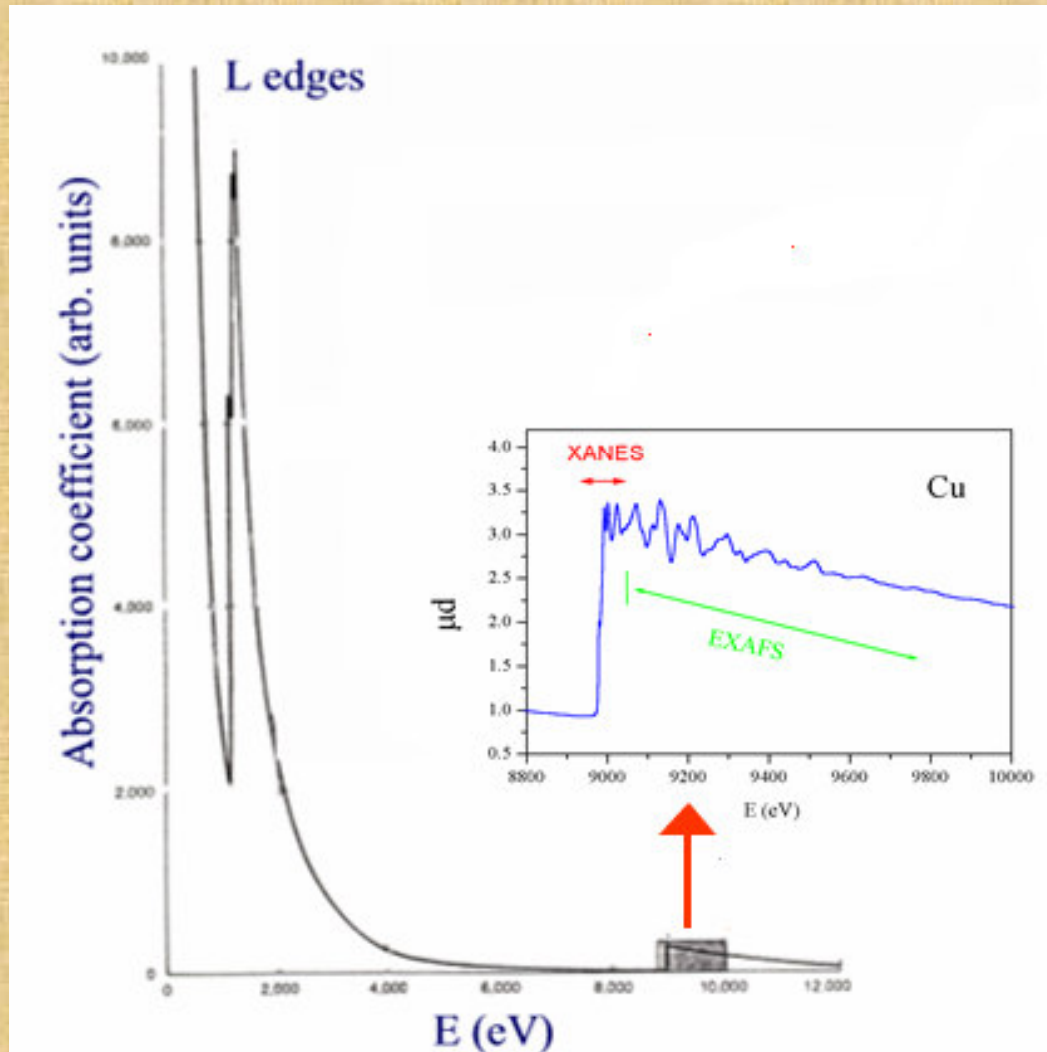
# X-ray Absorption

Many contributions to absorption, but largest in x-ray region is the **photoelectric effect: ionization of inner-shell atomic electrons**

Absorption Edge:  
High enough energy for excitation of **atomic core electrons** to **outgoing wave states**



If monatomic gas, generally smooth spectrum above edge.  
If molecules, liquid, or solid, see oscillatory structure.



# The x-ray spectroscopy acronym game

- X-ray Absorption Spectroscopy (**XAS**)
  - X-ray Absorption Fine-structure Spectroscopy (**XAFS**)
  - **Extended** X-ray Absorption Fine-structure Spectroscopy (**EXAFS**)
  - X-ray Absorption **Near-Edge** Spectroscopy (**XANES**) or
  - **Near-Edge** X-ray Absorption Fine Structure (**NEXAFS**)
  - And many more variations of techniques
- In all cases, variations in x-ray absorption coefficient as function of energy related to **structural or electronic properties** of sample

# Early Development of XAFS

- First noted in literature by students of Manne Siegbahn in Lund: Wilhelm **Stenström**, Hugo **Fricke** 1918-1920

- Lots of early experimental and theoretical work in first 60 years of the 20<sup>th</sup> century:

**Cauchois, Kossel, Yoshida, Kronig, Hayasi, Hanawalt, Petersen, Bogdanovich, Kostarev, Smoluchowski, Kurylenko, Izraileva, many more**

## **A History of X-ray absorption fine structure (\*)**

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**Abstract.** — This historical account of X-ray absorption fine structure (XAFS) spectroscopy from the origin to 1975 begins with the first observations of X-ray absorption edges and the experimental setups used at the turn of the century. Then, the discovery of XAFS and Kossel's early interpretation are discussed. A close look is taken at the three outstanding papers written by Kronig to explain XAFS in solids and molecules. Petersen's development of XAFS in molecules and Smoluchowski's investigation of XAFS in crystals during the thirties are reviewed. Then, the Japanese and Soviet contributions to X-ray absorption spectroscopy up to the sixties are described. We conclude with the advent of the present understanding of XAFS developed in the early seventies. Although many experiments are presented, we emphasize the conceptual evolution of the interpretation of XAFS, including false steps and overlooked works.

# Modern History

- 1960s and later: XAFS as a routine x-ray technique  
**Lytle, Stern, Sayers, Kincaid, Eisenberg, Vedrinskii, Mazalov, Schaich, Pendry, Lee, Rehr, many more**
- Web of Science Search: “EXAFS” or “XAFS”  
(but not “XAS” – too many false hits)
  - 1971-1975: **8 Publications**
  - Last year: **743 Publications**
  - Last 10 years: **7,199 Publications**
- Applications in **materials research, catalysis, molecular physics, biology/life sciences, environmental and geosciences, astronomy, others**

# Extended fine structure (EXAFS)

- With some approximations, oscillations can be represented as

$$\chi(k) = \sum_R S_0^2 N_R \frac{|f(k)|}{kR^2} \sin(2kR + 2\delta_C + \phi) e^{-2R/\lambda(k)} e^{-2\sigma^2 k^2}$$

$R$  : distance from central atom to surrounding atom

$N_R$  : number of backscattering atoms at distance  $R$

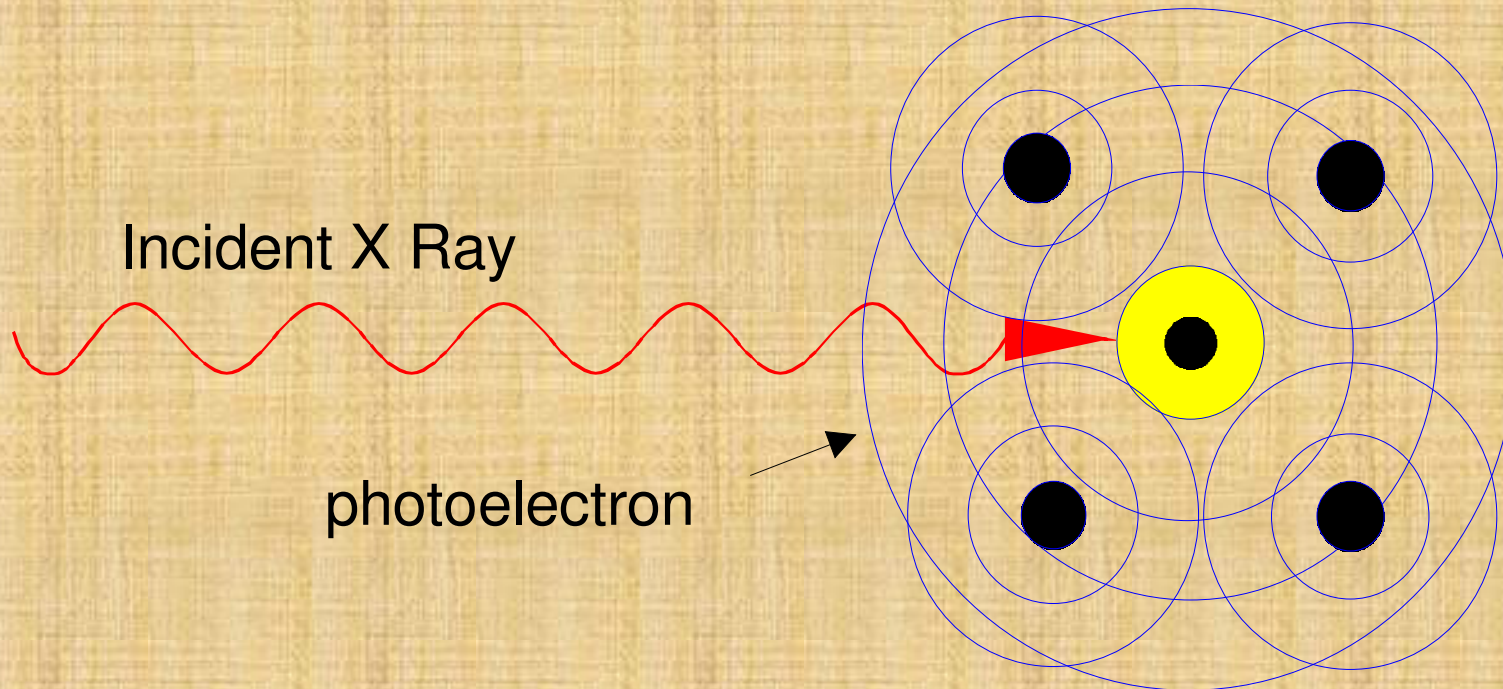
$\sigma^2$  : Debye - Waller factor from multiple (but close) distances

$f(k)$ ,  $\delta_C$ ,  $\phi$  : backscattering amplitude, phase shifts from central and backscattering atoms. (Only depend on atomic species)

$S_0^2$ ,  $\lambda$  : reduction factor, mean - free path due to inelastic processes, core - hole lifetime

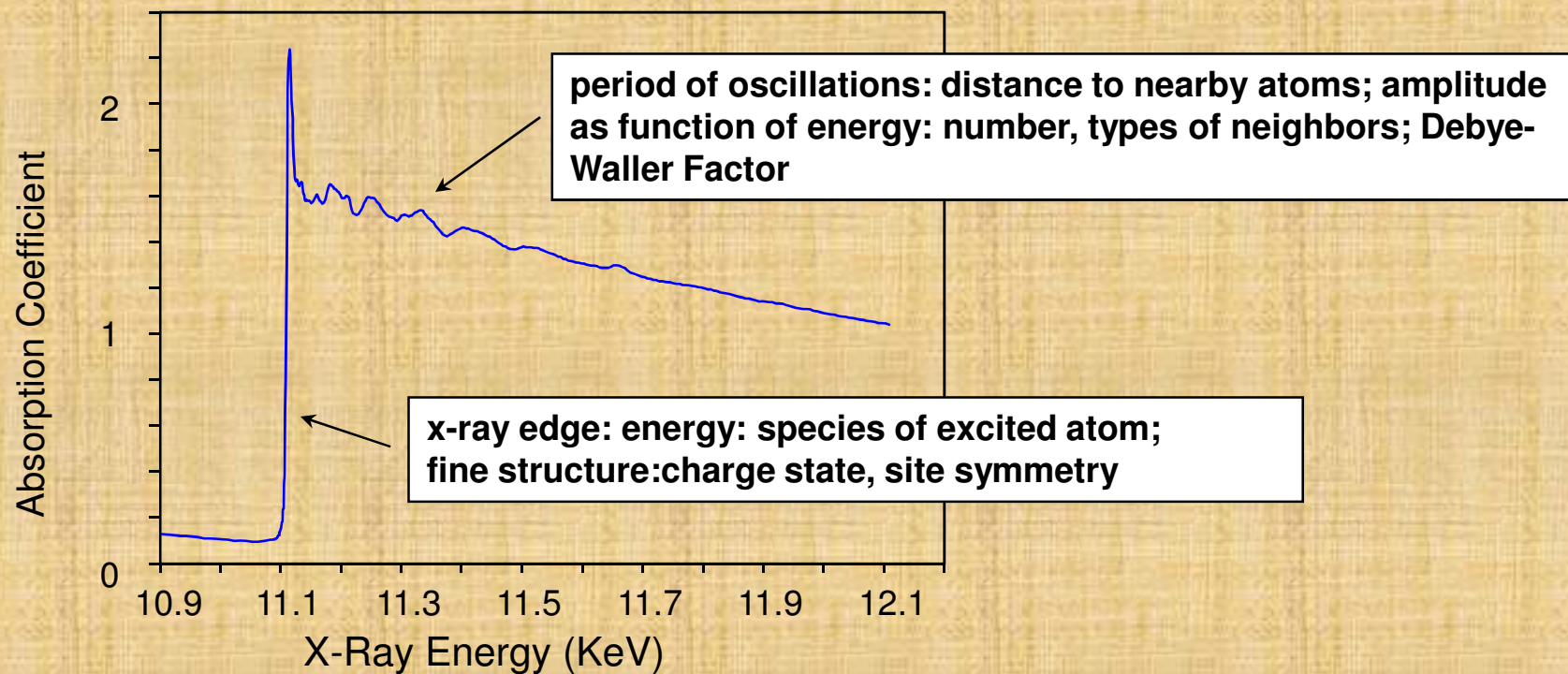
# Physics of XAFS

x-ray photon excites photoelectron from atom:



interference between **outgoing electron wave** and **backscattered wave** gives **oscillations** in x-ray absorption coefficient as function of **electron wavelength** and **x-ray energy**

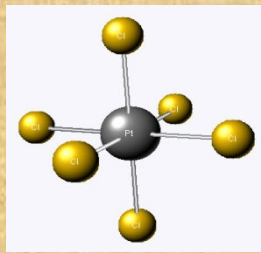
# Structural information from XAFS spectrum



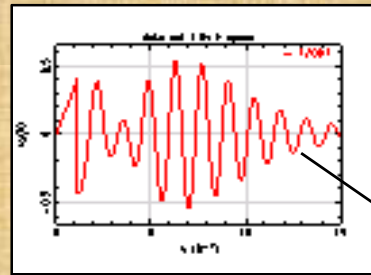
# Related techniques – same physics!

- In addition to transmission or fluorescence, detection by
    - Auger or secondary electron emission
    - Optical luminescence
    - Electrical conductivity
    - others ...
- 
- Diffraction Anomalous Fine Structure (DAFS)
  - Electron energy loss spectroscopy (e.g. in TEM)
  - X-ray Raman spectroscopy
    - Resonant
    - Non-resonant
  - X-ray magnetic circular dichroism (ok, maybe a little different physics)

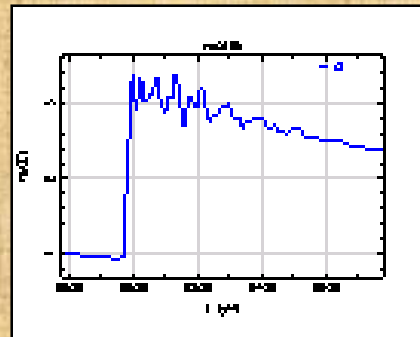
# Structural information from XAFS using model-dependent fitting



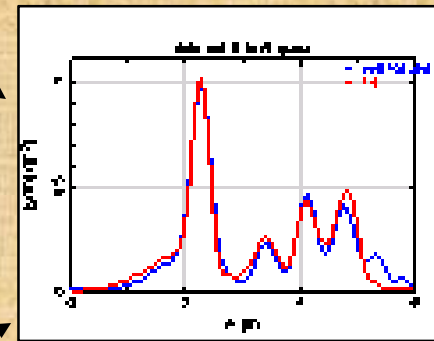
Theoretical Model



Numerical calculation



Data from standard compound with similar structure



Fit with data

Extract structural information from the fit based on the generalized EXAFS equation (curved wave)

$$\Delta\mu = \sum_j \frac{f(k)S^2(k)}{2k^2R_j^2} \sin(2kR_j + \delta_j(R, k)) \exp(-2k^2\sigma^2) \exp\left(\frac{2kR_j}{\lambda_j}\right)$$

# Things to worry about in analysis...

- For simple systems (e.g. single type of atom in a shell, small disorder) interpretation generally straightforward
- For more complicated systems:
  - multiple inequivalent sites
  - larger non-gaussian disorder, etc.
  - may need complex modeling
  - Have to remember that your interpretation depends completely on your how good your model (this is true for any data fitting)

# Challenges of analysis and interpretation

- Ideally, would like analysis to be **model-independent**, with straightforward (and foolproof) **determination of uncertainties**
  - Probably not going to happen!
  - Except for Monte Carlo simulations, most rely on some sort of model-dependent fitting
- Would also like to **systematically include other sources of information** (e.g. x-ray PDF, etc.)
- Will always have problems with multiple inequivalent sites, etc.

# Resources: XAFS Analysis Software

- ESRF EXAFS Software Catalog:
  - Many choices! Alphabetically:  
CDXAS, Cerius2 XAFS, CHOOCH, DARES BURY, EDA, EXAFS (for Mac), EXAFSPAK, Excurv98, **FEFFIT**, GNXAS, LASE, MURATA, NPI, SEDEM, TT-MULTIPLETS, **UWXAFS**, VIPER, WINXAS, XAFS, XAID, XANES dactyloscope, XDAP, XFIT
- International XAFS Society (now the International X-ray Absorption Society, [www.i-x-s.org](http://www.i-x-s.org))
- XAFS.ORG - open Wiki for XAFS users

# Talks This Morning: Cutting Edge of Analysis

- Fundamental Aspects of EXAFS Analysis: Fourier Concepts and Random Errors (Corwin Booth)
- Advances in EXAFS Analysis with IFEFFIT and FEFF (Matt Newville)
- Pair Distribution Function, Monte Carlo Modeling, and Factor Analysis (André Rossberg)
- Error Analysis in XAS: Which Method for Which Situation? (Emmanuel Curis)
- Bayesian Analysis Techniques: Obtaining and Using a Priori Information for XAS Analysis (Joshua Kas)

# This Afternoon: Applications

- Exploring Spin-Lattice Coupling in Multiferroic Oxides (Trevor Tyson)
- Studies of Zinc in Biological Systems (Jim Penner-Hahn)
- Complementary techniques for studies of nanoparticles (Glen Waychunas)
- Molecular- and Nano-scale Structure and Reactivity of Biogenic Uranium(IV) (Eleanor Schofield)
- Use of Dispersive EXAFS to Study Subnanosecond Materials Dynamics (Patrick Allen)

## **A Possible Goal for this Workshop**

- Presentation of new, interesting, powerful analysis techniques
- Presentation of novel applications, often involving multiple techniques and analysis challenges of their own
- How do we get these different groups together, so that these new approaches can be “mainstreamed” into the commonly used packages?