Perspectives on XAFS

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Outline of the Talk

- Introduction
  - Thanks for the invitation - SMH and JJR: two hard acts to follow!
  - so far: 46 years in XAFS, 7@UW, 7@Penn/UCSC, 33 @IIT as prof
    - 10 Founding Director BioCAT, 9 Sci+QXTSBIR+Book,14 @IIT Admin
- Some personal recollections of Stern Lab ca (1977-1984)
  - its ethos, denizens, and friends
- My own trajectory and various contributions to XAFS
- Comments on Decades of Growth of XAFS
- Extrapolations Future Possibilities

From Farrel Lytle's "The EXAFS family tree"

Many of the basic ideas re EXAFS were present since 1931; a world-wide enterprise, but specific key ideas for the adequate understanding it were missing for four decades.

It all came together in the synthesis ~1970 by Stern, Sayers, Lytle: appreciation of a key factor: the mean free path/many-electron excitations require a short range order theory. Fourier Transformation sealed the deal.

Subsequent progress in experiment, theory, and data analysis has been extensive. The XAFS field since has grown exponentially, together with synchrotron radiation.

Röntgen (1895)	Discovered X-rays
Maurice de Broglie (1913)	Measured first absorption edge
World War I (1914–1918)	
Fricke (1920)	Observed first fine structure
Kossel (1920)	First theory of XANES
Hanawalt (1931)	EXAFS in gases, temperature effect
Kronig (1931)	First theory of EXAFS
Cauchois (1932)	Curved crystal transmission spectrograph
Hayasi (1936, 1949)	Theory of EXAFS
World War II (1941–1945)	
Sawada (1955)	Amorphous/crystalline polymorphs
Shiraiwa (1958)	Improved theory
Kostarev (1939, 1946)	Theory and measured EXAFS in single crystals
Kozlenkov (1960)	Improved theory
Van Nordstrand (1960)	Instrumentation, fingerprint ID, used XAS to characterize catalysts
Lytle (14 July 1960)	Starts work at Boeing (BSRL)
Krogstad (1960)	Personal communication
Lytle (1962)	Particle-in-a-box model
Prins (1964)	Helped name EXAFS
Parratt (1965)	Personal communication; *Rev. Mod. Phys.* (1959). **31**, 616
Sayers, Stern, Lytle (1968–1971)	Modern theory, Fourier transform of EXAFS
Sayers, Stern, Lytle (1974)	First trip to synchrotron (SSRL)

Ed Stern, Dale Sayers, and Farrel Lytle receiving Warren Prize 1979

Ed was an intuitive physicist who always strived to get to the essence of things. He would invent or create whatever tools were necessary to do his research. He also was a kind, thoughtful, person with a good sense of humor. Ed passed away after a full life at age 85 on May 17, 2016.

Dale Sayers, a bright, creative, energetic, generous, broad-minded physicist, mentor, and friend, tragically passed away prematurely and unexpectedly at age 60 on Nov 25, 2004.

Farrel Lytle, who fortunately is still with us in 2023, has lived his life as a curious, creative, energetic, kind, and generous physicist, as were Ed and Dale.
Last I heard (which was a while ago) he was roaming the desert measuring the x-ray fluorescence of Mn-reducing biofilms near Pioche Nevada, and also just being human, near his ancestral home.

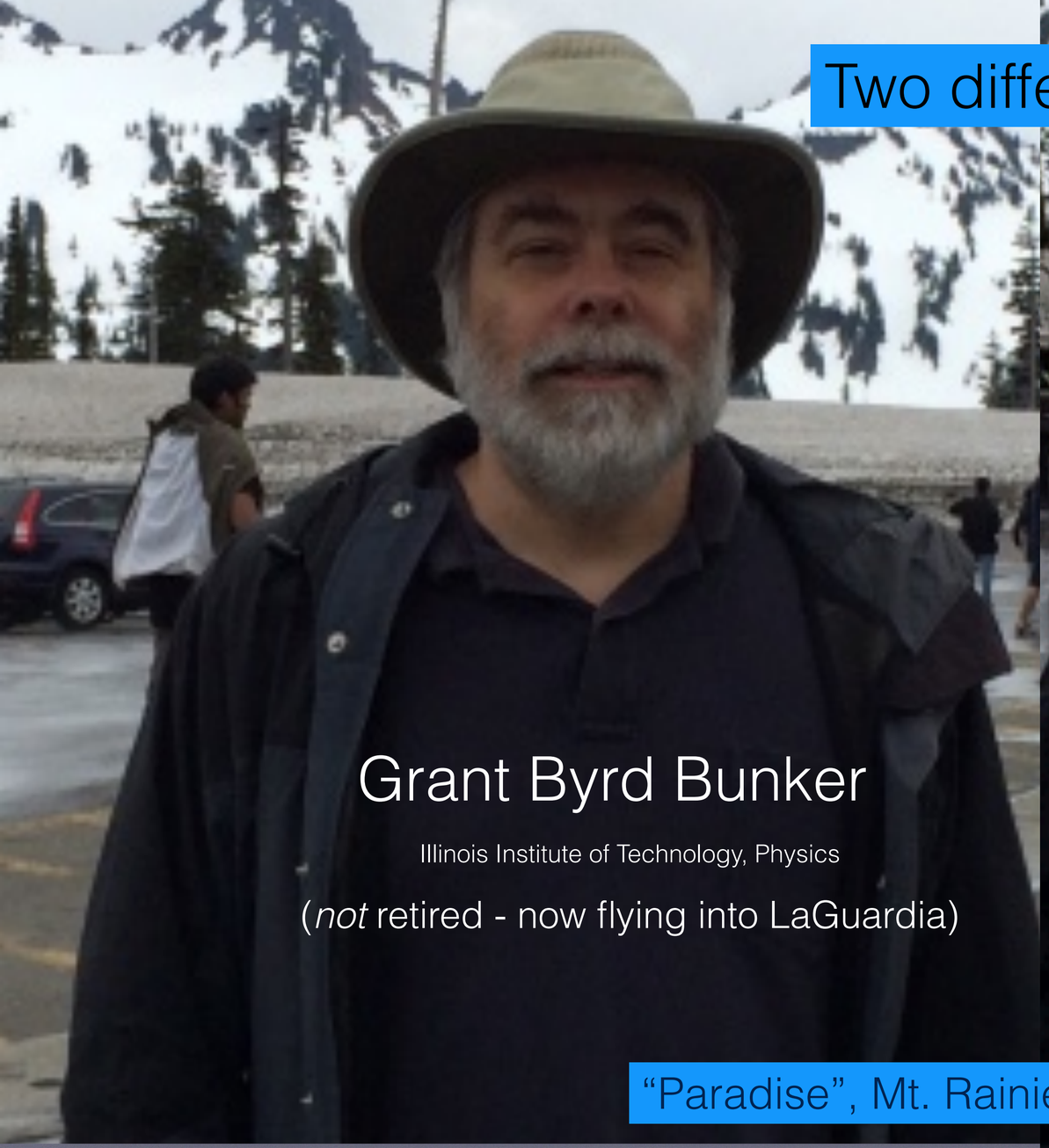
Farrel started the whole Seattle EXAFS phenomenon.

Some Stern Lab denizens ~ 1982?

from left:
Ernest Janzen
Kyungha Kim
Grant Bunker
Edward Stern
Yves Idzerda

About Stern Lab 1977-1984

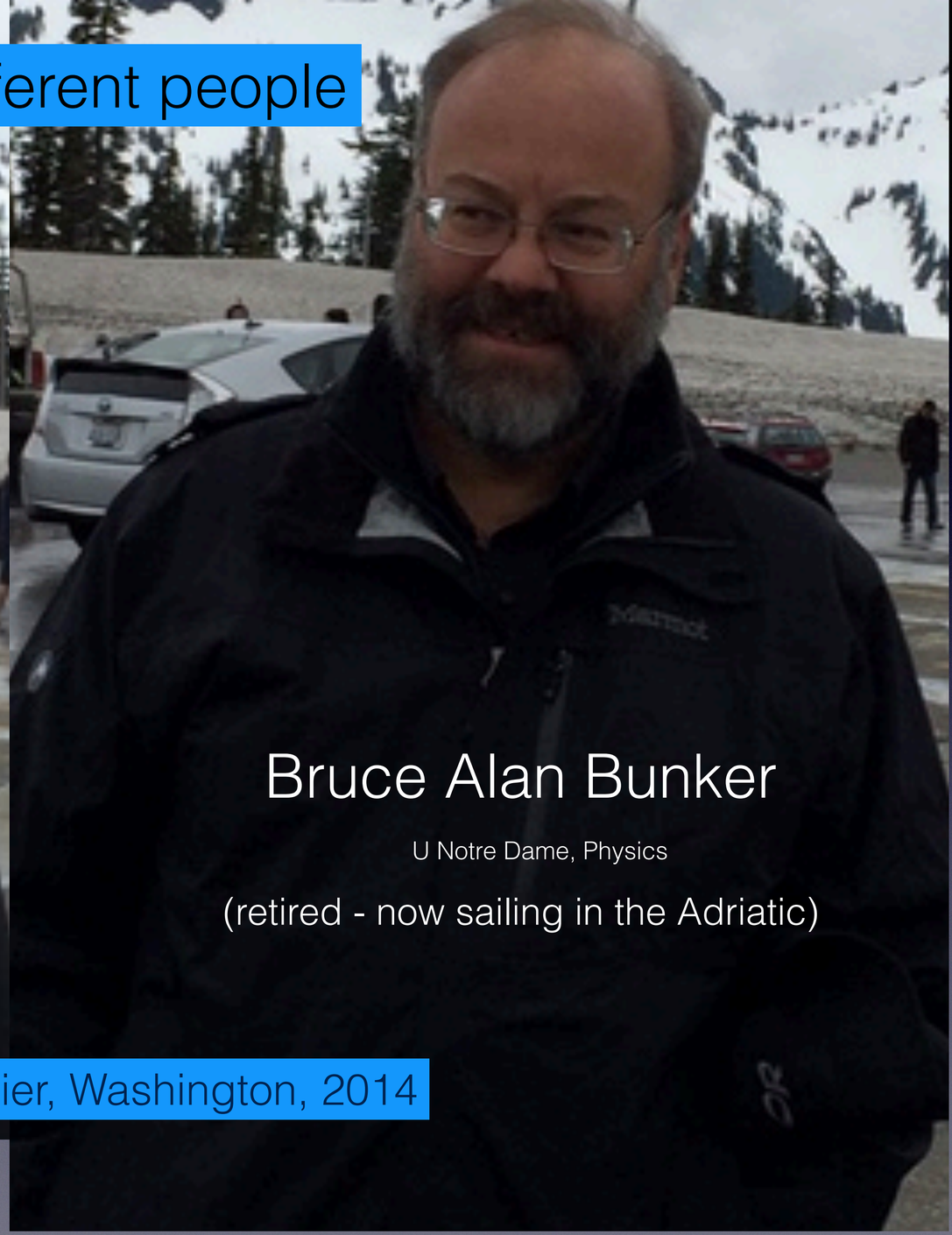
Two different people



Grant Byrd Bunker

Illinois Institute of Technology, Physics

(*not* retired - now flying into LaGuardia)



Bruce Alan Bunker

U Notre Dame, Physics

(retired - now sailing in the Adriatic)

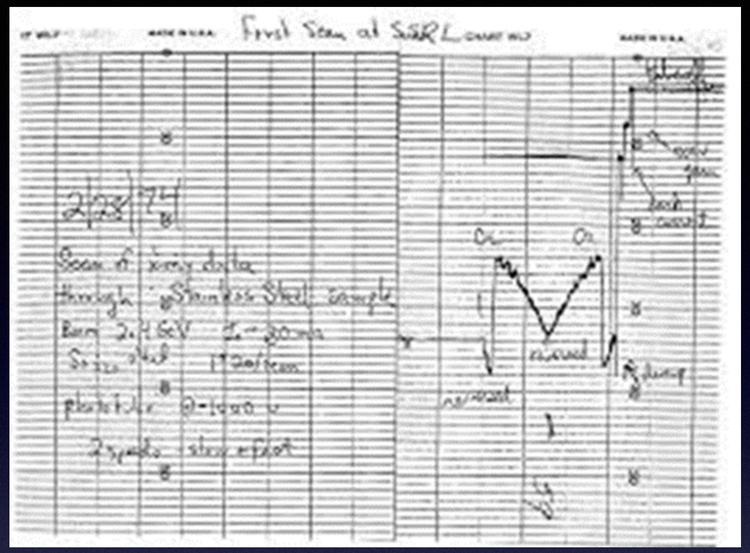
“Paradise”, Mt. Rainier, Washington, 2014

Stern lab culture

- Informal, open, and very collaborative - welcomed many international visitors
  - After Cultural Revolution, from China, early visiting scholar Lu Kunquan, student Zhang Ke
  - South American and European visitors, and students
  - Israeli collaborators (e.g. Y. Yacoby)
- Scientifically wide-ranging - think for yourself
- @ Intersection of theory and experiment.
- Build your own tools if you need to (instrumentation, computer programs)
- Highly interdisciplinary, but remained firmly rooted in physics and “practical theory”.
- Embraced Computation (B. Bunker’s early key role)
-  Experiment <==>Theory <==> Simulation

- Some People in lab (mid-1977- early 1984):
  - Postdocs: Steve Heald, (Fred Ellis), Tim Elam
  - Visiting scientists: Lu Kunquan, Yitzhak Jacoby, …
  - Students: *Chuck Bouldin (late, 2022)*, Bruce Bunker, Kyungha (“Hyde”) Kim, Zhang Ke, Ed Keller, (Yves Idzerda, Herman Meuth, Evelio Sevillano), Stefan Csillag, Olivier Petitpierre, Cesar Julian, Jacob Azoulay, …
  - Associated groups: Rehr, Ingalls, Dash, Fain students (e.g. Shih-Hung Chou, J. Tranquada, Mike Toney, Jackie Krim, Rene Diehl…)

All Stern Lab synchrotron radiation experiments at the time were done at Stanford/SLAC (SSRP funded as SSRL in 1977); we did build a lab EXAFS machine that worked in ~1979.



First XAFS scan at SSRP behind shield wall before any beamlines existed
Dale Sayers (2/28/74)

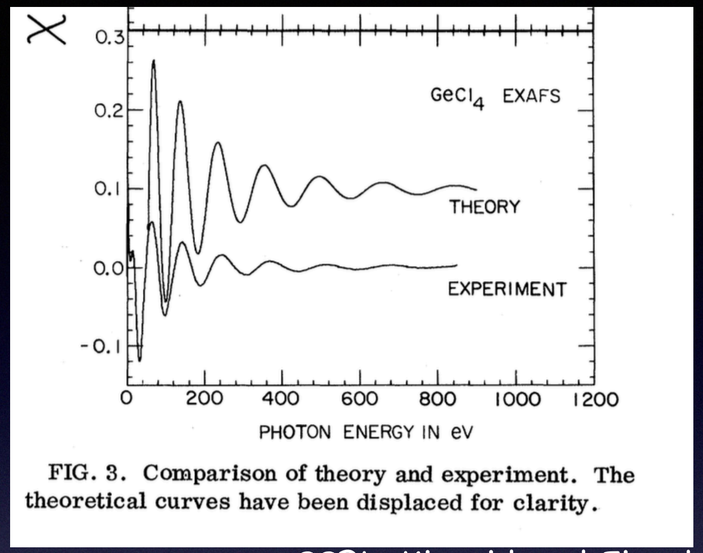


FIG. 3. Comparison of theory and experiment. The theoretical curves have been displaced for clarity.

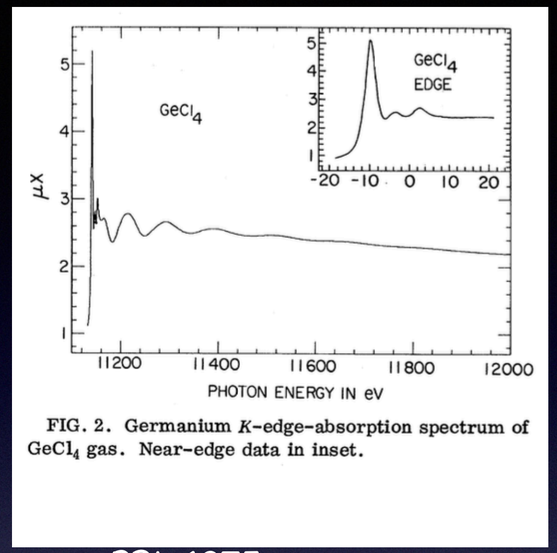
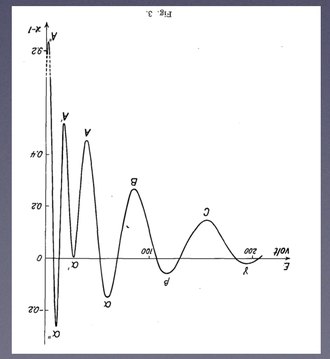
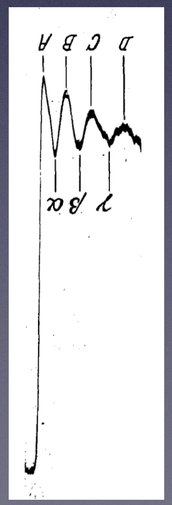


FIG. 2. Germanium K-edge-absorption spectrum of $GeCl_4$ gas. Near-edge data in inset.

SSRL, Kincaid and Eisenberger, PRL 1975
measured on beamline 1

GeCl4 theory 1934
Hartree, Kronig, Petersen





GeCl4 experiment 1934
Coster and Klamer

TABLE 4

	α	B	β	C	γ
E_{exp} volts	50	86	120	160	203
E_{theor} volts	59	85	117	155	196

comparison theory/experiment 1934

Back of the envelope distance estimate, using Coster-Klamer 1934 data - not bad!

```
In[•]:= Δk = Differences@Sqrt[.2625 * {50, 86, 120, 160, 203, 257}];
        Rs = π / (2 Δk) + .4;
        {Mean[Rs], germanium(IV) chloride CHEMICAL [ bond lengths ][[1]]}
Out[•]= {2.1324, 2.1 Å}
```

- Data Analysis and Simulation:
  - All our work from that era was pre-FEFF, which AFAIK had not yet been conceived
  - data analysis was almost entirely based on use of empirical standards:
    - Ratio Method, and nonlinear least squares fitting, used empirical amplitudes and phases extracted from compounds of known structure. Analysis programs were written by members of the group. Bruce Bunker wrote IDP (Interactive Data Plot), file database routines, some utility programs; Tim Elam: XFP plot subroutines; Chuck Bouldin: background subtraction; G. Bunker: Fourier Transform/filtering; Kyungha ("Hyde") Kim: nonlinear fitting program. They served very well.
  - GB's theoretical calculations were based on
    - SS theory Stern et al, Müller and Schaich, MS theory Lee and Pendry, XANES MS DLXANES (translated from F66 -> F77 by Bruce Bunker), Herman Skillman, potential MUFPOT, phase shift code (*IFORGET)*, SCATWV, and of programs that I wrote.
    - Computational facilities were primitive in 1977!

Stern Lab Computing in 1977 …

Wang Labs Calculator

Northstar Horizon S100 bus 8-bit Computer

Tektronix 4051

pointer controlled by joystick

image from https://t-lcarchive.org/tektronix-4051/

Used 300 baud acoustic coupler over phone line to send jobs to and get output from CDC Cyber mainframe

IDP (Interactive Data Plot): Bruce Bunker wrote his own memory manager on CDC to keep it under 100 kB RAM)

Later ~1980 Physics department got a VAX 11-780 and life was good!

D. Knuth starts TeX project in 1977

Apple Macintosh debuted in 1984

X-Window System debuted in 1984

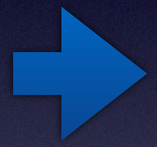
MS Windows1.0 debuted in 1985

All inspired by Xerox PARC

According to Merriam-Webster the terms “PC” and “Moore’s law” first appeared in print in 1977 as did “massively parallel” “cheesesteak”, and “Ebola”

About my trajectory

Seattle
U.W.
7 years



Philadelphia
UPenn
University City
Science Center
7 years

Chicago
Illinois Tech
33 years

Overview of GB contributions to XAFS to date

- **Methods and Facilities**
  - beamlines/facilities: NSLS X9, APS BioCAT sector 18
  - detectors/analyzers: MAAD, BCLA (Karanfil)
  - filter/slit optimization
  - sample prep (sedimentation)
  - **Data analysis and Simulation**
    - Ph.D. students Dimakis, Khelashvili, Tannazi
    - Symbolic and Parallel computing (1987…)
    - undulator spectrum calculation
    - model independent: (ratio method/cumulant, regularization => RDF)
    - model dependent" (FEFF+ DFT-MS-DWF/genetic algorithm 2004)
    - speciation/Monte Carlo x-ray propagation
    - GPU/CUDA accelerated FEFF (K Pedersen)
      - FEFF FMS >100x acceleration

- **Applications**
  - Metalloproteins and complexes, (reaction center, ribonucleotide reductase), time resolved MbCO, HT superconductors, nanoparticePs
  - environmental speciation Cd, Pb, …
  - toxicology = speciation in liver tissues Hg-Se microfocus XAFS

- XAFS Education
  - Tutorials/talks/papers
  - Graduate students
  - Book: *Introduction to XAFS (Cambridge U. Press)*
  - APS/IIT XAFS Summer Schools (~10 of them)

- **Current Projects**
  - "Phase Method": new mostly automatic computational QM method; monography nearing completion late 2023
  - XAFS: new experimental methods (stay tuned for more), instrumentation, and data analysis

- How I personally got involved in XAFS - (*the next 4 pages can be safely skipped for time*)
  - As an undergraduate at Evergreen and UW I studied physics (2@TESC+1@UW) and molecular biology (1@TESC) (P,P,P,B). I spent my junior year at UW in part so I could take classes (which I did) from Prof. John A. Wheeler, who was visiting that year. I took some graduate classes at that time. I returned to Evergreen my senior year to study molecular biology because I wanted to graduate from there. My undergraduate employment history (student firefighter, EMT, fire lookout) was interesting, but that's another story.
  - After working for a year to make some money, I looked around the country for various grad schools to combine physics and biology. Ed needed a student to work on metalloprotein EXAFS; he knew of me and my relevant background through Bruce, and offered me a job which I accepted starting summer 1977, right before the start of my graduate studies.
  - That was shortly after the first wave of Stern EXAFS students and postdocs. Dale Sayers had left for NCSU before I started. My brother Bruce was in the lab working on his Ph.D.; so was Steve Heald (as postdoc). John Rehr had started at UW two years before. After a few years Steve moved on to NSLS and Tim Elam moved in as postdoc.
  - In Ed's lab for several years I worked on various metalloproteins: hemerythrin, ATCase (Aspartate transcarmoylase - allosteric enzyme), PCD (protocatechuate 3,4 dioxygenase), and for years, **Fe site in photosynthetic reaction centers**. Fluorescence ion chambers were invented by Ed and Steve for this project. I didn't contribute to it, but I did use it, and we all used the EXAFS cryostats that Steve built. I remember showing Dale at SSRL how to use the fluorescence ionization chamber, and another time, Farrel showing us his version of it.
  - During my metalloprotein studies I got intrigued by similarities in the XANES between apparently very different materials ZnS and ATCase, so I temporarily put aside biology for better characterized systems. I didn't include my hard earned, peer-reviewed metalloprotein papers in my thesis, because I figured they were already published. I then just focussed on the understanding of K-edges of a series of transition metal compounds. I was supported by NSF mostly. I took nearly 7 years to do what normally might be considered two Ph.D.s, but I was in no rush: I just wanted to understand what was going on. Ed and NSF were supportive.
  - *This work was done pre-FEFF, so we rolled our own as best we could. JJR was quite helpful.*

- After Ph.D I did a postdoc with biophysicist Britton Chance @ U Penn Philadelphia (1 year) doing EXAFS on bio-things. Brit was a bright, creative, productive, competitive, colorful, patrician, yankee scientist who was good to me.

- Then I was offered a job (by Brit) as Assistant Director of "National Biostructures PRT" (our team built beamline X9 at NSLS and operating it as NIH Research Resource). Worked with Gerd Rosenbaum, essential beamline innovator in the dawn of synchrotron radiation research (at DESY). I planned on doing the job for a couple of years since I didn't know how to administer anything, and figured I might learn something.

- I ended up staying 7 years, with various promotions and title changes, obtained my own NIH research grants (one on Ribonucleotide Reductase), taught a bit at U Penn Department Biochemistry and Biophysics, was kindly welcomed there. Various biological-systems such as Ribonucleotide Reductase, various cytochromes, MBCO.

- I was then recruited to Illinois Institute of Technology in Chicago as Associate Professor of Physics, lured by a tenure-track job, and IIT's gritty, can-do ethos. CSRRI formed with Tim Morrison, Carlo Segre.

- Upon moving to IIT I immediately agreed to helm a new hypothetical project at the nascent Advanced Photon Source. For ~10 years I served as Founding Director of Biophysics Collaborative Access Team (BioCAT) at APS. This involved raising $8.6M, constructing and operating the facility. Our team comprised me, Tom Irving, Gerd Rosenbaum, Bob Fischetti, Ed Black, Ke Zhang, Shengke Wang, Sergey Stepanov, Rick Heurich, Clareen Krolik, …

- (More info on BioCAT later in the talk)

- *note: I want to acknowledge Zbigniew Richard (Rich) Korszun as having initiated the "SAXSXAS CAT", the first palendromic CAT that wasn't, but which eventually turned into BioCAT*

- Post-BioCAT: BioCAT is still operating in 2023, Tom Irving, Director, to whom I handed off the project more than two decades ago.
  - NIH SBIRs (phase 1 and 2) with Dean Chapman, Cahit Karanfil
    - BCLAs: Quercus X-ray Technologies, LLC
    - publications on BCLAs, and bent laue “Beam Cleaner”. FMB-Oxford sells the BCLAs.
  - I was approached by Cambridge University Press about writing a book for them and quickly accepted.
    - I wrote the book in 2009, in about six months, in my spare time.
    - *Introduction to XAFS* - Cambridge University Press. An expanded second edition seems warranted.
  - around 14 years ago I agreed to serve in various administrative roles at IIT
      - Assoc. Chair (2 years); Assoc. Dean (2 years); Physics Chair (last 10 years)
      - this has detracted noticeably from my research productivity
      - **This 14 year phase just ended Aug 15, 2023!**
  - Currently:
    - wrapping up a book on a new, effective, robust, automated, kind of weird, numerical QM method that I have developed I call the “Phase Method”
      - in addition: book includes justified deviations from conventional WKB(J) method for semiclassical calculations
        - exact scaling relation and explicit approximate formulae for eigenvalues of homogeneous potentials
    - Imaging: “Material Decomposition” in the absence of tell-tale absorption edges and fluorescence lines w/Clay Contee
    - Several external collaborations e.g. disorder in materials under extreme conditions
  - Near-future plans: a new modality for measuring polarized XAFS; improvements to analyzers and instrumentation; improved data analysis

- At IIT Ph.D. collaborators and students:
  - **Tim Morrison (ret), Carlo Segre, CSRRI - key players in XAFS at IIT**
  - Boyan Boyanov - fast undulator spectrum calculation YAUP by FFT (GB idea inspired by EXAFS analysis)
  - Habib Moltaji: DAFS (with help from John Quintana, at NSLS X18)
  - Nick Dimakis: combined DFT for MS DWFs + FEFF + genetic algorithm for automated XAFS analysis of metalloprotein active sites
  - Gocha Khelashvili: Inverse problem: Regularization for direct determination of RDFs from EXAFS
  - Firouzeh Tannazi: Speciation using XAFS - analytical and monte carlo modeling of particle size effects in materials and effect on speciation and LCF results
    - speciation experiments on soil sample cores
  - Cahit Karanfil: development of Bent Crystal Laue Analyzer (w. Dean Chapman, Zhong Zhong, B. Bunker, C. Segre, S. Heald …)
    later: Speciation of mercury in liver tissue (microfocus XRF and XAFS)
- Keith Pedersen: GPU computing summer project: accelerated FEFF FMS XANES with CUDA by >100
- Prof. Paul Anderson (environmental engineering), Lisa Axe, Shinwoo Lee
- Collaborator Prof. Ben Stark (student Aysel Golbahar): Vitreoscilla Hb: bacterial Hemoglobin
- Collaborator Prof. Chanoch Carmeli - FX iron sulfur protein; Vanadium complexes in other proteins
- Various adventures in high performance computing and symbolic computing

Introduction to

XAFS

X-ray absorption fine structure spectroscopy (XAFS) is a powerful and versatile technique for studying structures of materials in chemistry, physics, biology, and other fields. This textbook is a comprehensive, practical guide to carrying out and interpreting XAFS experiments.

Assuming only undergraduate-level physics and mathematics, the textbook is ideally suited for graduate students in physics and chemistry starting XAFS-based research. It contains concise executable example programs in Mathematica 7.

The textbook addresses experiment, theory, and data analysis, but is not tied to specific data analysis programs or philosophies. This makes it accessible to a broad audience in the sciences, and a useful guide for researchers entering the subject.

Supplementary material available at www.cambridge.org/9780521767750

- Mathematica code from the book
- Related Mathematica programs
- Worked data analysis examples

GRANT BUNKER is Professor of Physics at the Illinois Institute of Technology. He has over 30 years' experience in all aspects of XAFS spectroscopy, from technique development, instrumentation, and computation, to applications in biology, chemistry, and physics.

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BUNKER Introduction to XAFS

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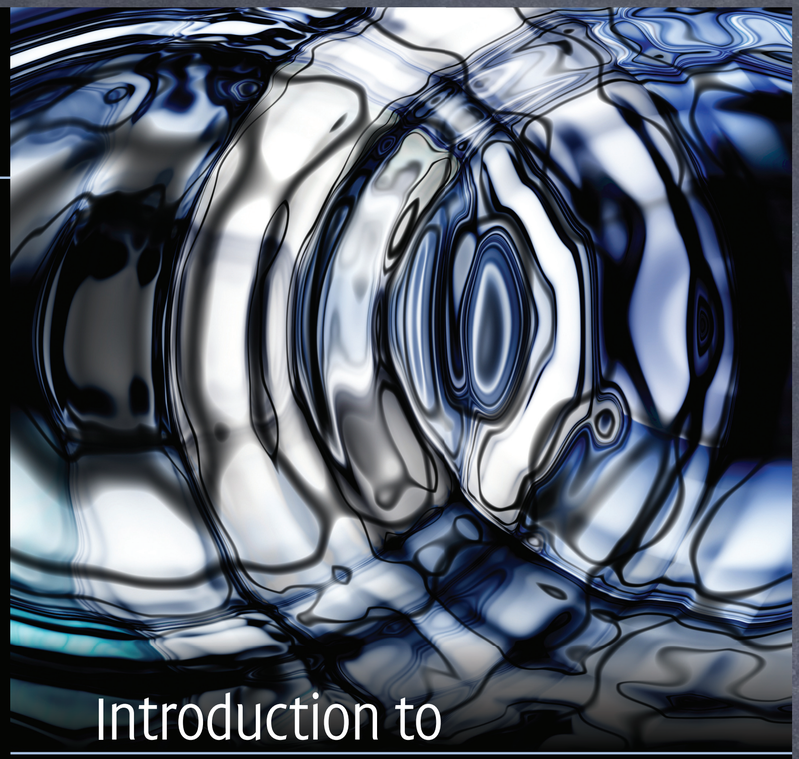


Introduction to

XAFS

A Practical Guide to
X-ray Absorption Fine Structure Spectroscopy

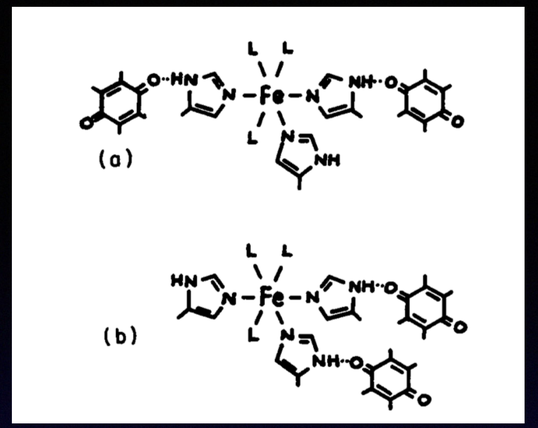
GRANT BUNKER

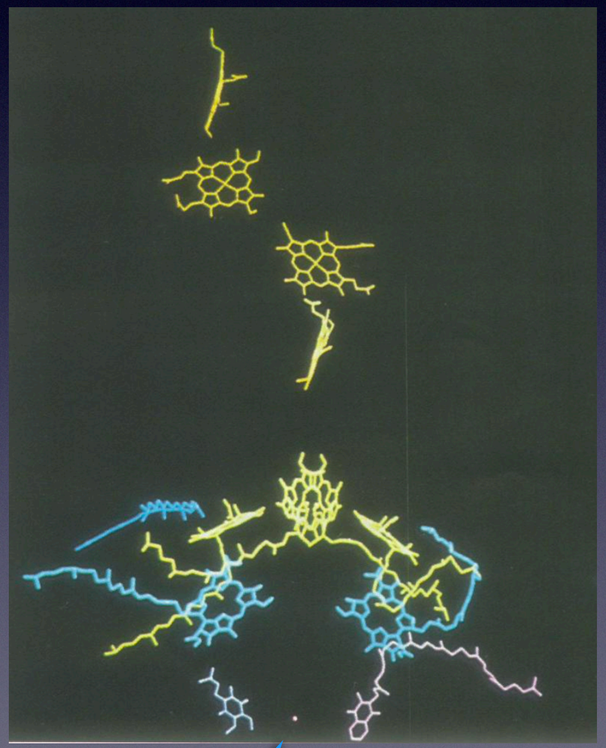
CAMBRIDGE

I wrote a book. It's useful, and it has material not available anywhere else.

More detail on scientific results

- GB contributions (during graduate work mid-1977- early 1984)
  - identified, using physics of multiple scattering and vibrational considerations, characteristic signature of histidines bound to metals, in this case, Fe in photosynthetic reaction centers. “Iron wire hypothesis”. At the time there was no evident path to producing crystals of such large complexes for XRD. Deduced that Fe is bound to histidines hydrogen-bonded to quinones to facilitate electron transfer. Later structure was confirmed by Deisenhofer and Michel using XRD (=> Nobel Prize Chemistry 1988).
  - Other work on metalloproteins (e.g. Hemerythrin - di-iron non-heme oxygen carrier, ATCase (Aspartate Transcarbamoylase - allosteric enzyme - intriguing XANES), Protocatechuate 3,4 Dioxgenase(non-heme oxygenase)





Fe • Deisenhofer and Michel

- Disordered systems:
  - Extended Ratio Method to handle moderate disorder via moments and cumulants
    - Derived novel recursion relation expressing cumulants in terms of moments
    - Derived the effect of *k-dependent* mean free path on cumulants
- Fourier filtering
  - Explained why ratio method largely cancels Fourier window distortions
    - Devised novel deconvolution algorithm to (nearly) eliminate them
    - Limits on uniqueness of amplitude and phase

$$C_0 = \ln P_0; \quad C_{n+1} = \frac{dC_n}{dq}; \quad P_{n+1} = \frac{dP_n}{dq},$$

where the q is a formal parameter of no consequence. For example

$$C_1 = \frac{dC_0}{dq} = \frac{d\ln P_0}{dq} = \frac{1}{P_0}\frac{dP_0}{dq} = \frac{P_1}{P_0} = p_1.$$

somewhat overlooked recursion relation from GB 1983 Ratio Method paper directly generates expressions relating cumulants to moments just by taking derivatives

C_1	p_1
C_2	$-p_1^2 + p_2$
C_3	$2\,p_1^3 - 3\,p_1\,p_2 + p_3$
C_4	$-6\,p_1^4 + 12\,p_1^2\,p_2 - 3\,p_2^2 - 4\,p_1\,p_3 + p_4$
C_5	$24\,p_1^5 - 60\,p_1^3\,p_2 + 30\,p_1\,p_2^2 + 20\,p_1^2\,p_3 - 10\,p_2\,p_3 - 5\,p_1\,p_4 + p_5$
C_6	$-120\,p_1^6 + 360\,p_1^4\,p_2 - 270\,p_1^2\,p_2^2 + 30\,p_2^3 - 120\,p_1^3\,p_3 + 120\,p_1\,p_2\,p_3 - 10\,p_3^2 + 30\,p_1^2\,p_4 - 15\,p_2\,p_4 - 6\,p_1\,p_5 + p_6$

```
C[n_] := ∂{γ,n} Log[P[0, γ]] //. {P^(0,j_)[m_, γ] → P[m + j, γ], P[0, γ] → 1, P[m_, γ] → p_m}
```

Mathematica Code does it

This is easily worked out by hand for low-ish orders.
Mathematica code generates all expressions up to n=30 in ~ 1 sec,
and *all* expressions up to n=50 in ~ 1 min, *1.3 million terms*, on laptop.
The number of terms grows a little slower than exponentially vs n.

- After Ph.D. => U Penn/University City Science Center/ISFS/Biostructures Institute (7 years)

  - Assistant Director of Biostructures PRT (NIH Research Resource - we built beamline X9 at NSLS (since moved). Worked with Gerd Rosenbaum, Larry Rock, Syed Khalid, Bob Fischetti, Ke Zhang, Dave McKeown, Guang Zhang, Mike Sullivan… GB later appointed Associate Director of Biostructures Institute.

  - ICSCXAFS: "International Committee on Standards and Criteria in XAFS" (late 80's - instigated by Sayers) I co-wrote various reports/recommendations (e.g. on Data Analysis with E.D. Crozier, and organized a round-robin test of experiment and analysis by different people and beamlines

  - Wrote tutorials on Basic Techniques in EXAFS (coined "HALO" - see http://gbxafs.iit.edu/) for users of beamline, ~1988, pre-WWW. Considering writing a book, but then Koningsberger and Prins came along.

  - Created/distributed enhanced version VAX/VMS distribution of UW EXAFS analysis package.

  - Various papers (and un-papers): MS in GeCl4 paper with C. Bouldin, D. McKeown et al; Ag nanoparticles, Cytochrome C' with Rich Korszun et al, Cytochrome C1 with Chong Kim et al, High Tc superconductor with Ke Zhang, optical pumping MBCO, rationalized change of LFIR for out of plane Fe motions in hemes due to MS, studied metalloproteins including Ribonucleotide Reductase (with B.M Sjöberg et al, Stockholm U), equipment development (LN2 cryostat with in-vacuum PIN diode detector, and fiber optical monitoring). Ag nanoparticles using best cryostat ever (styrofoam cooler with pipe through it and styrofoam end caps) at CHESS.

- GB Recruited to IIT -> Associate Professor of Physics
  Founding Director: Biophysics Collaborative Access Team (BioCAT) at APS

- ==> Rich (*Zbigniew Richard) Korszun must get credit for initiating the project, which was modeled on our previous work at the BioStructures PRT in Philadelphia/BNL.*

- CSRRI - initially Tim Morrison, Carlo Segre, Grant Bunker (and G. Rosenbaum for (SBC-CAT and BioCAT), and B. Dobson (Daresbury), Michael Hart (Manchester) for IMCA-CAT and MR-CAT.

- BioCAT - G. Bunker, T. Irving, R. Fischetti, (G. Rosenbaum, L. Rock), E. Black, K. Zhang, S. Wang ->S. Stepanov, R. Heurich, C. Krolik, … Advisory committee comprised J. Viccaro, D. Sayers, J Penner-Hahn, E. Westbrook, Ed Lattman, and other biological scattering folks

- I first sought funding for BioCAT as an “NIH Research Resource" in 1991, and was turned down flat by eminent (really) site visit committee: “too big for IIT, and too technically ambitious”. Followed up a year or so later, and eventually got funded for 5 years in 1995, $8.6M as an NIH Research Resource.

- First light attained in 1997 on time and on budget, performance much greater than proposed.
  Much credit to Ed Westbrook of SBC for agreeing co-develop beamline designs with BioCAT

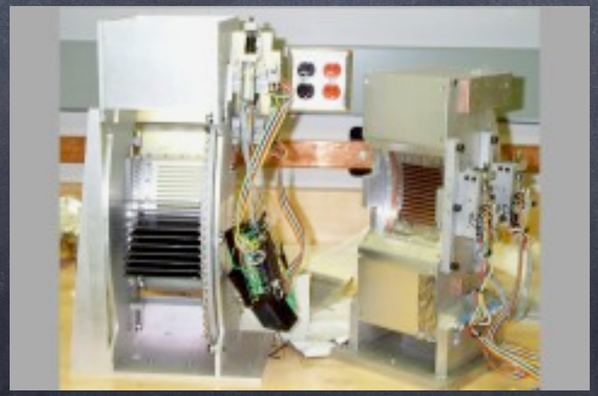
- Got funding in ~2000 for continued operations. I then handed off project to Associate Director Tom Irving.
  I pivoted away from management to being physics professor and making science gadgets (w. Dean Chapman)

- **About BioCAT - Biophysics Collaborative Access Team**
  - for study of *non-crystalline* biological structure and dynamics - NIH Research Resource
    - emphasis on versatility and close-to-theoretical performance, time resolved
      - fiber diffraction - (e.g. muscle, connective tissue)
      - membrane and solution scattering
      - “extreme” XAFS (small domains, time resolved, pump-probe etc)
  - Continuous full range EXAFS scans in ~10 seconds with 10^13 photons/sec into 20 micron x100 micron spot, fixed exit height
  - Automated system linearity testing, Multilayer Analyzer, Stopped Flow
  - Initiated (w/Dimakis)“APEX” open source cross-platform EXAFS analysis package - superseded by IFEFFIT
  - Early Inelastic X-ray Scattering experiments by Steve Cramer, Uwe Bergman, Pieter Glatzel were carried out at BioCAT ID line.
  - And lots of fiber diffraction and scattering but that’s another story

BioCAT beamline panorama (ca 2000)

Design by G. Rosenbaum, enhancements R. Fischetti

Flexible design
Si(111)& Si(311)
10-sec full XAFS scans
10^13/sec
H and V focus
100 u x 10 u
auto-testing
window less



Multilayer Array
Analyzer Detector

Flight tube (scattering)

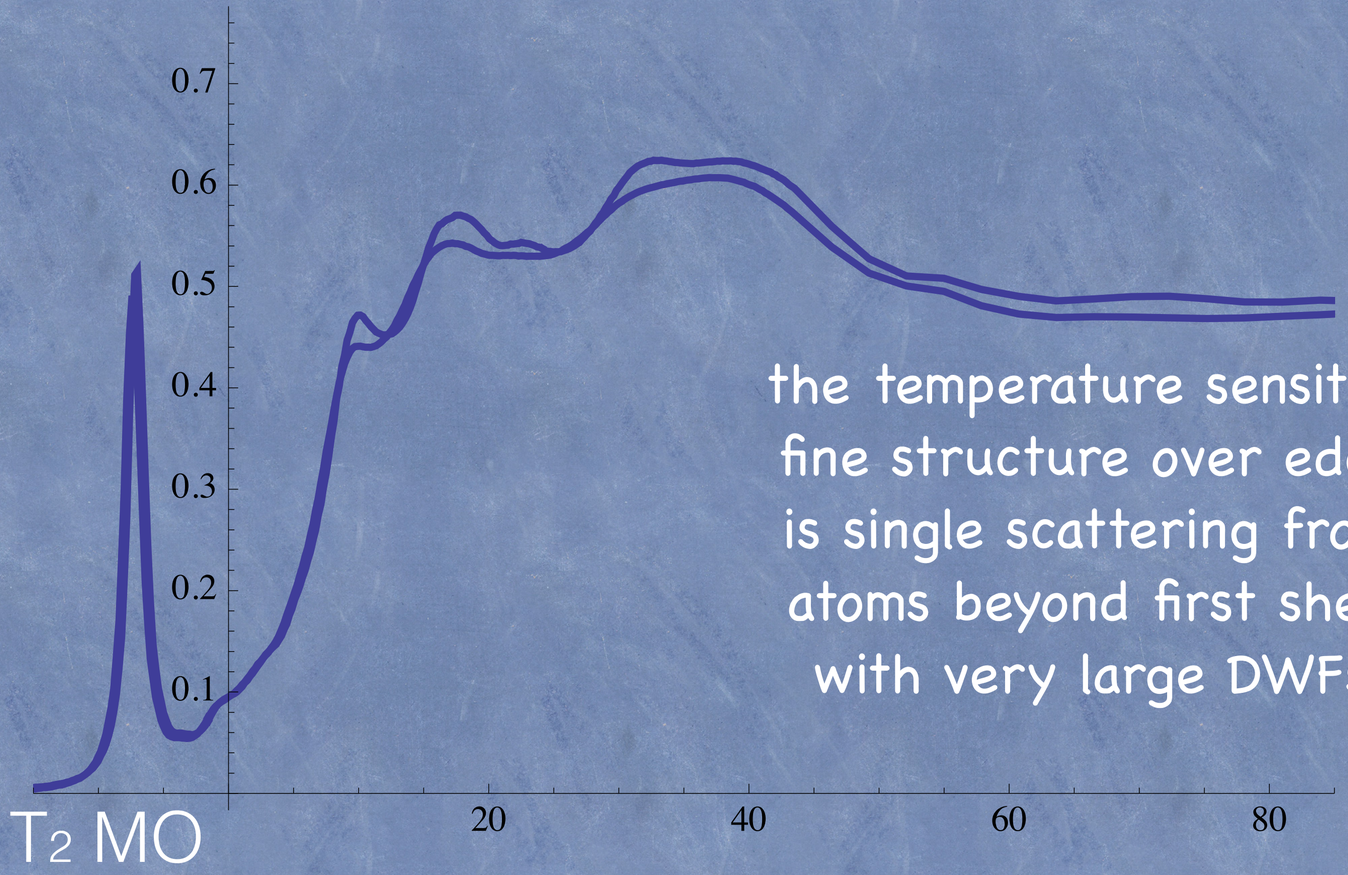
Some specific scientific results

thesis per se ~1980-83

- XANES: experimental and computational (pre-FEFF) single vs multiple scattering effects in transition metal oxides -> MS in MnO4
- temp dependent SS/MS results on KMnO4 (which was revealing) published in PRL
  - cleared up CrO4 edge mystery XANES (Kutzler)
  - showed utility of carrying EXAFS analysis right down to the edge in MnO4
- using theory and experiment, explained correlation between edge shifts and oxidation state in Mn-O coordination complexes
  - charge state <-> bond length <-> edge shift
- samples
  - showed thickness effects are described by cumulants of thickness distribution.
  - showed need for very small particles; developed sedimentation technique to get them.

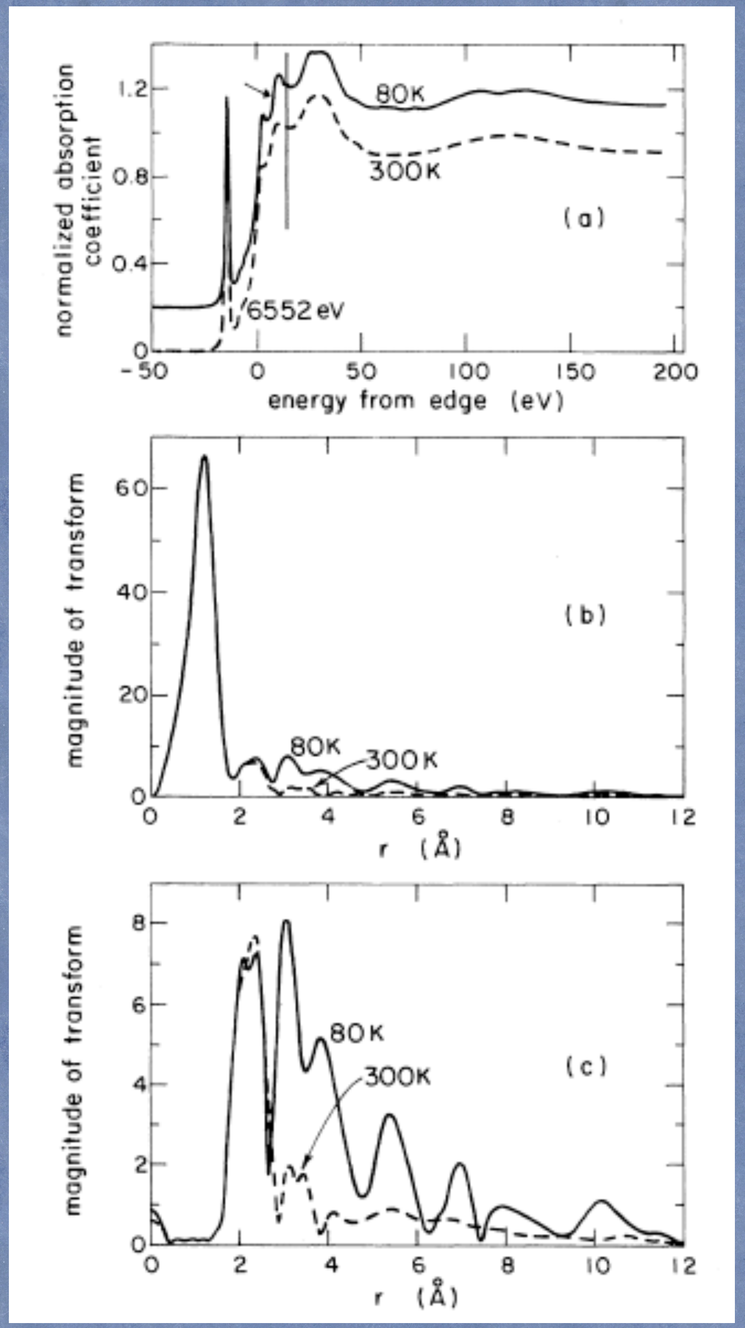
expt.

Solid $KMnO_4$ at 80K and 300K experimental data*



the temperature sensitive fine structure over edge is single scattering from atoms beyond first shell with very large DWFs

* G Bunker thesis 1984



XANES landscape is from SS+MS among nearest neighbor tetrahedron
SS from distant atoms adds temp dependent fine structure

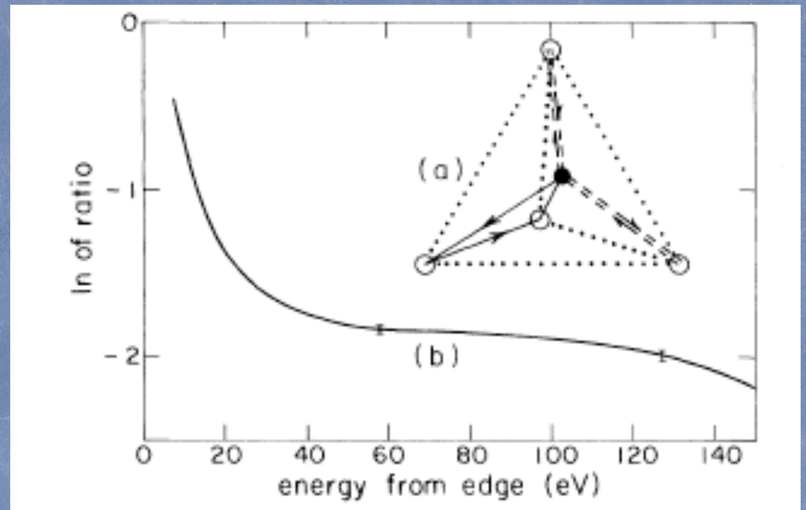


FIG. 2. (a) The two multiple-scattering paths that contribute to the second peak in the Fourier transform of $KMnO_4$, denoted by solid and dashed lines. The black dot is Mn, and the open dots are O atoms. (b) The logarithm of the ratio of the k dependence of the amplitudes of the first (SS) peak to the second (MS) peak of Fig. 1(b), plotted vs energy from the edge.

Bunker and Stern
PRL **52,** 22 (1984)

from GB thesis 1984

Calculated MnO4 spectra vs bond length using “extended continuum” atomic scattering phases held constant vs R (=> no charge rearrangement here!)

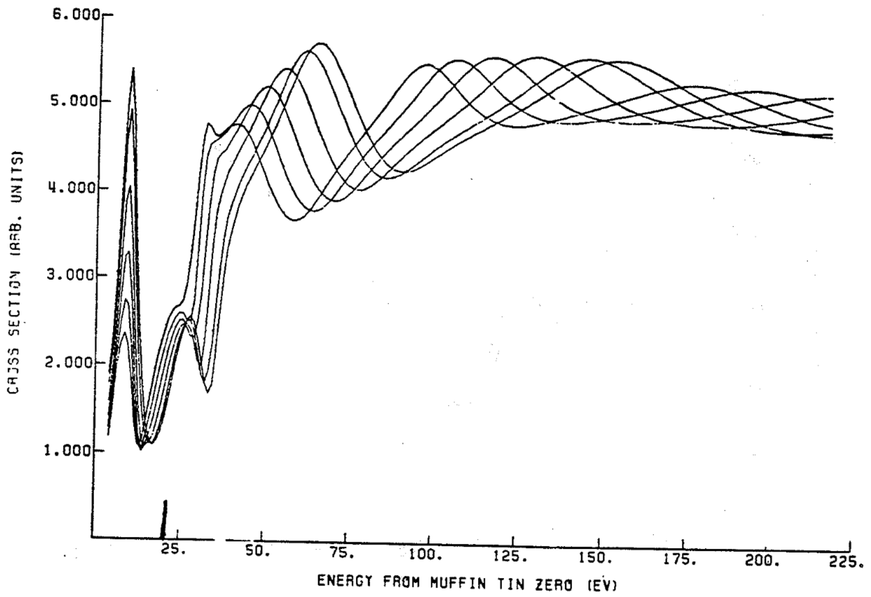


Figure 7.10

Tetrahedral cluster, bond lengths=3.08, 3.16, 3.32, 3.48, 3.64, 3.80 Bohr. Vertical line indicates approximate position of Fermi level.

Full MS vs SS

used
DLXANES
+ MUFPOT
+ other stuff
+ homebrew

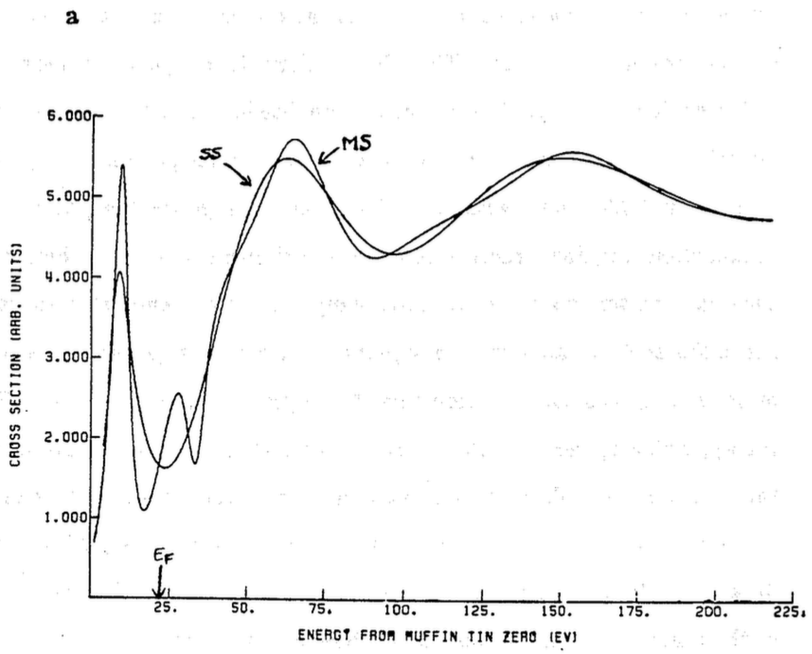


Figure 7.18 Multiple vs single scattering spectra

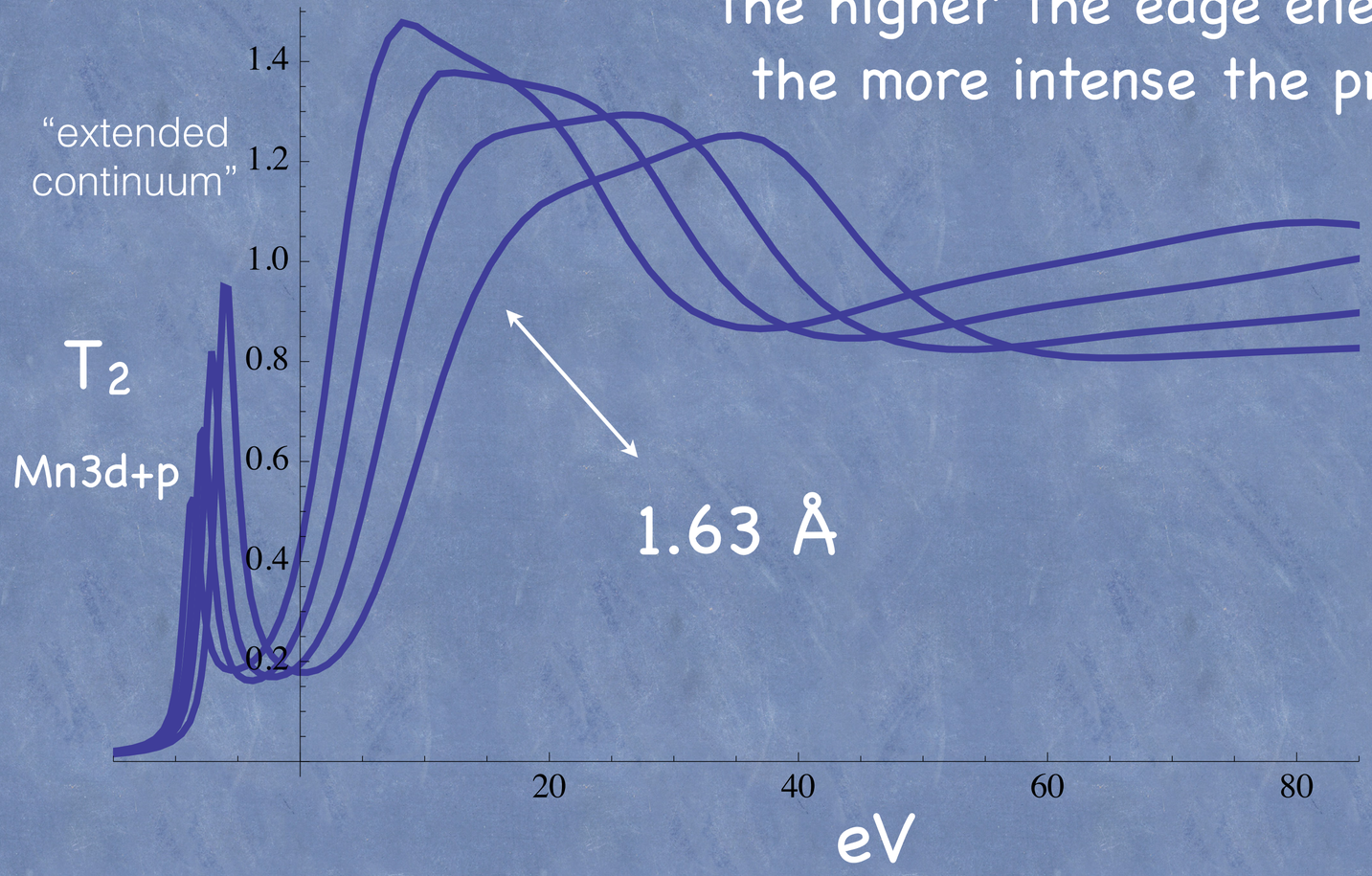
Single scattering vs multiple scattering MnO_4^- cluster; bond length=3.08 Bohr. Curves are cubic spline interpolates of calculated data points. The vertical line indicates the approximate position of the Fermi level.

theory FEFF

MnO_4 tetrahedral cluster

r=1.63,1.73,1.84,1.94Å feff8.2 SCF/FMS

the shorter the distance,
the higher the edge energy and
the more intense the pre-edge

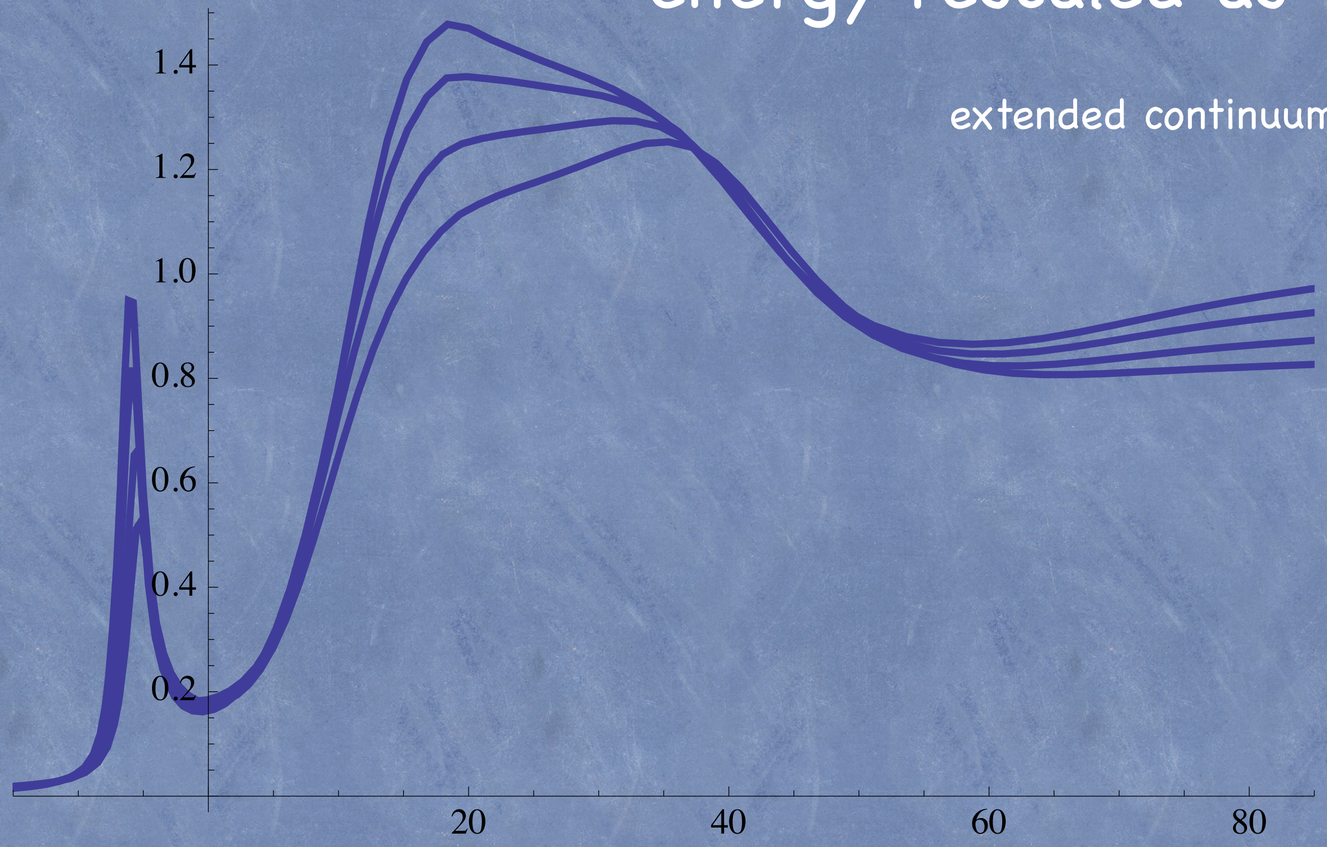


MnO_4 tetrahedral cluster

r=1.63,1.73,1.84,1.94Å feff8.2 SCF/FMS

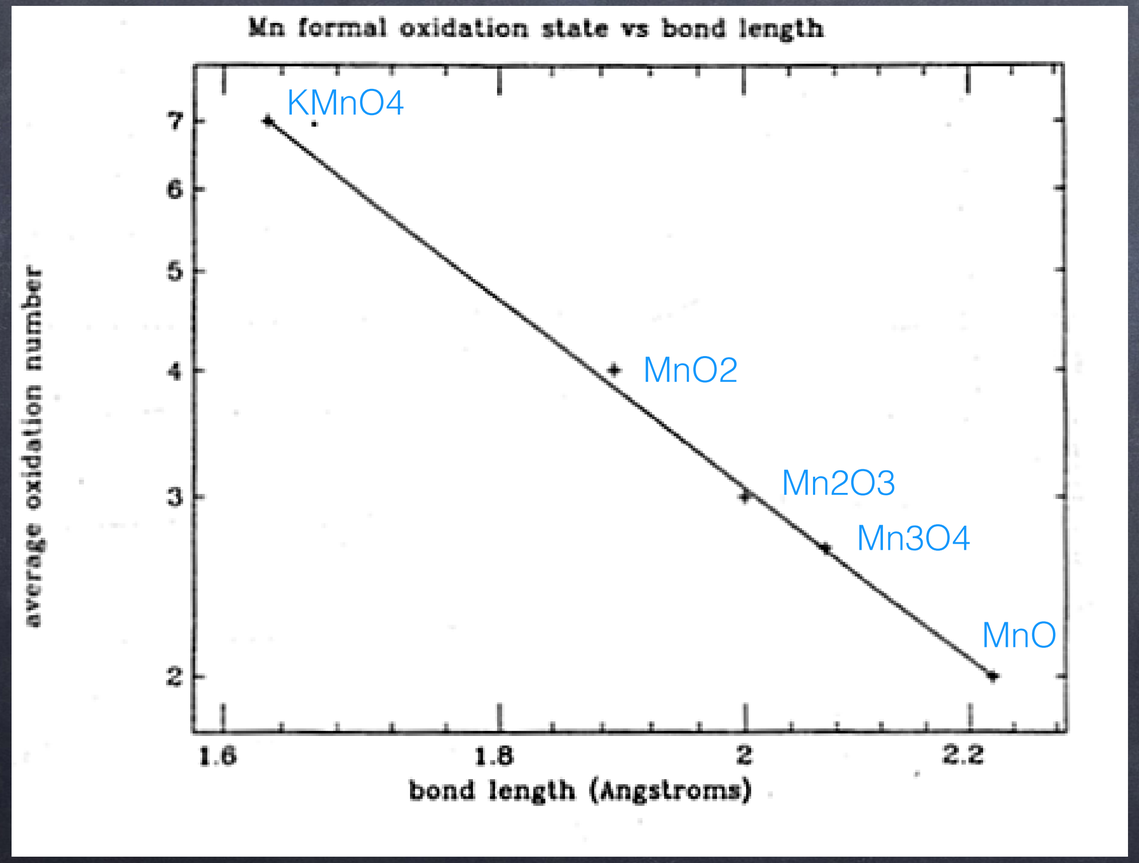
energy rescaled as 1/r^2

extended continuum -17eV



Edge shifts:
chemical *correlation* of bond length with formal charge
explains the large K-edge shifts associated with oxidation state
because edge shift primarily depends on average bond distance

from GB thesis 1984



*caveat: this is an *empirical* correlation for these materials*

The straight line on log-log plot implies a power law relation between formal charge and average bond length R:

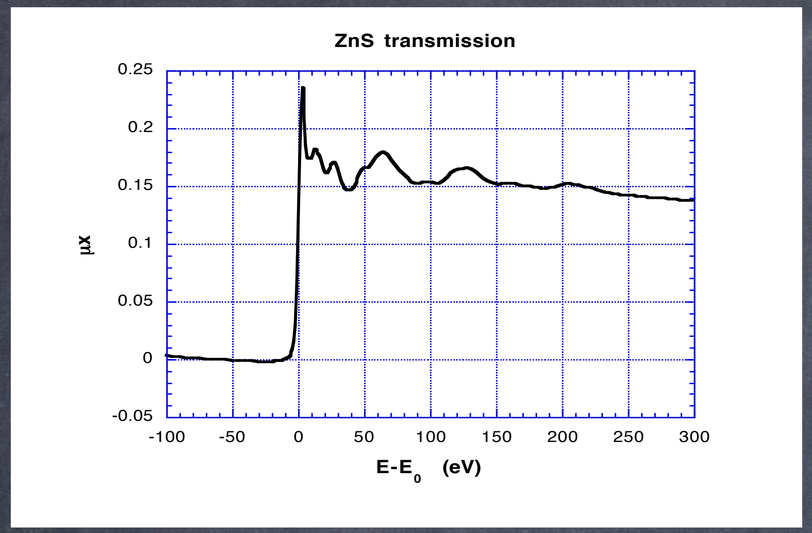
$$Q_f \propto \frac{1}{R^4}$$

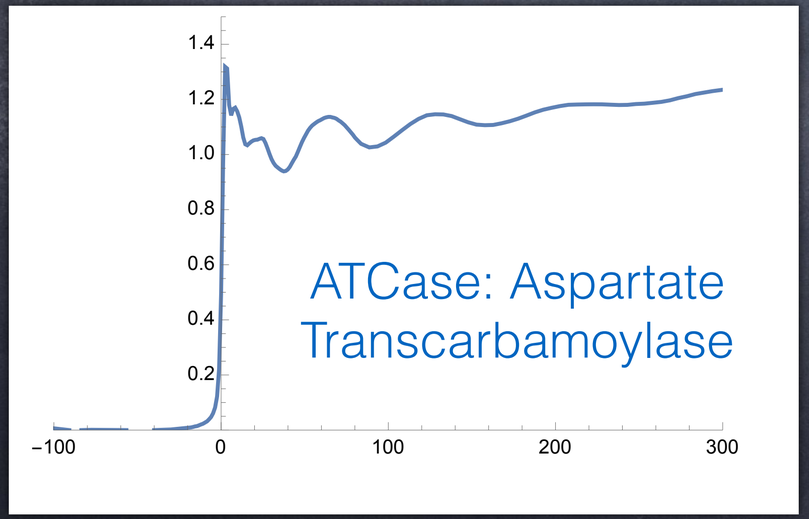
Roughly speaking: chemistry tells atoms where to go; physics of scattering shifts edge position

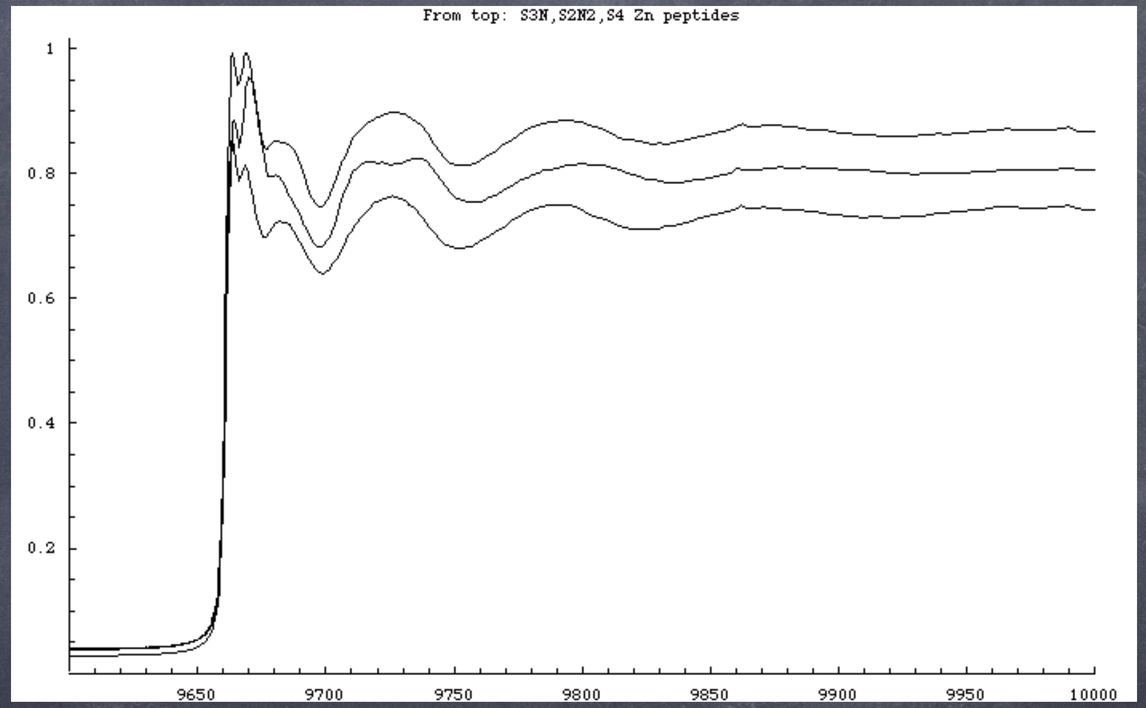
$$\Delta E \propto \frac{1}{R^2} \qquad \rightarrow \Delta E \propto \sqrt{Q_f}$$

old observation
by Hartree!

tetrahedral sites ZnS, ATCase, & peptide models







Koch models: spectra courtesy of J. Penner-Hahn

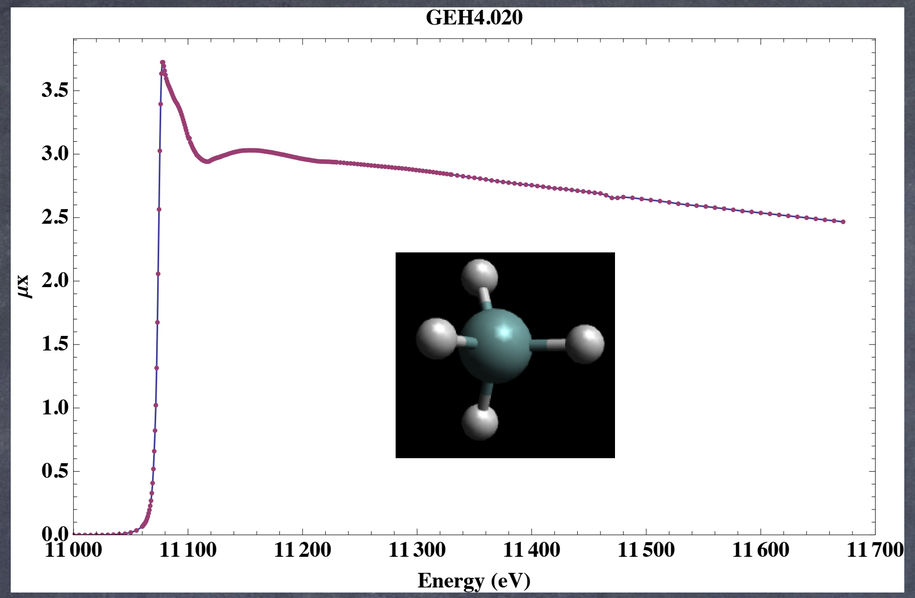
note the visible tetrahedral ZnS and histidine MS signatures

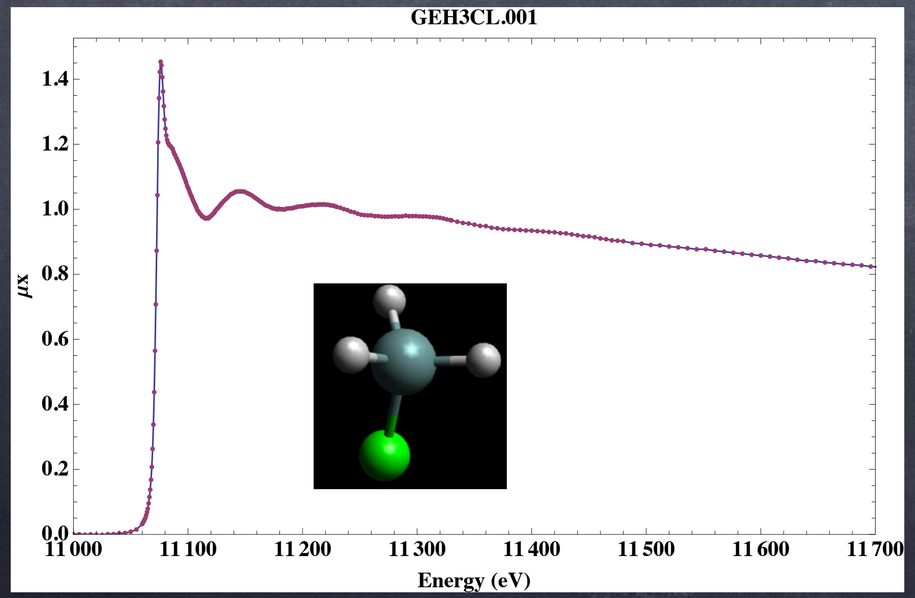
Post-Ph.D. project, for fun

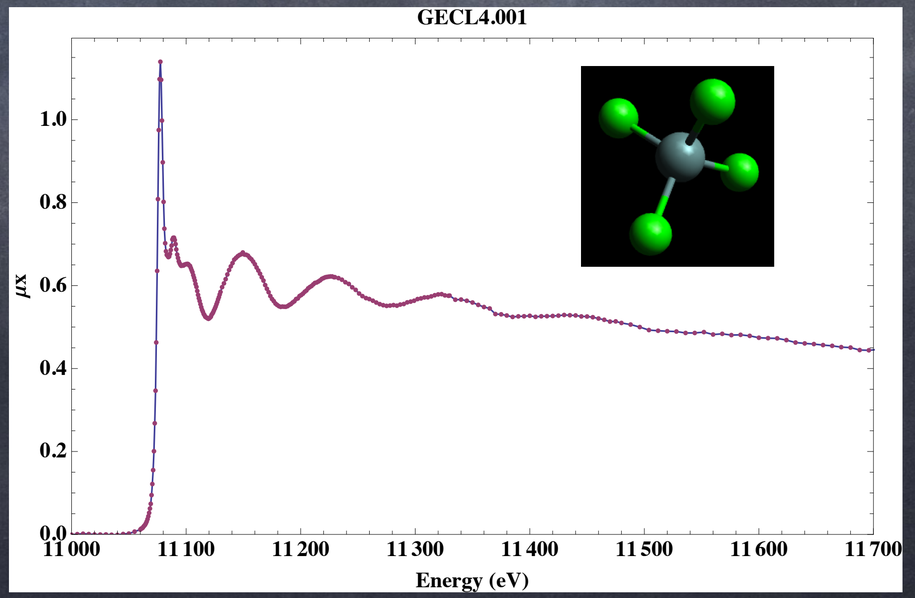
Molecular gases
GeH4, GeH3Cl, GeCl4
tetrahedral coordination

C. E. Bouldin, G. Bunker, D. A. McKeown, R. A. Forman, and J. J. Ritter, (1988) Phys. Rev. B 38, 10816

Note similar XANES structure in GeCl4 as in ZnS and ATCase - it's MS!







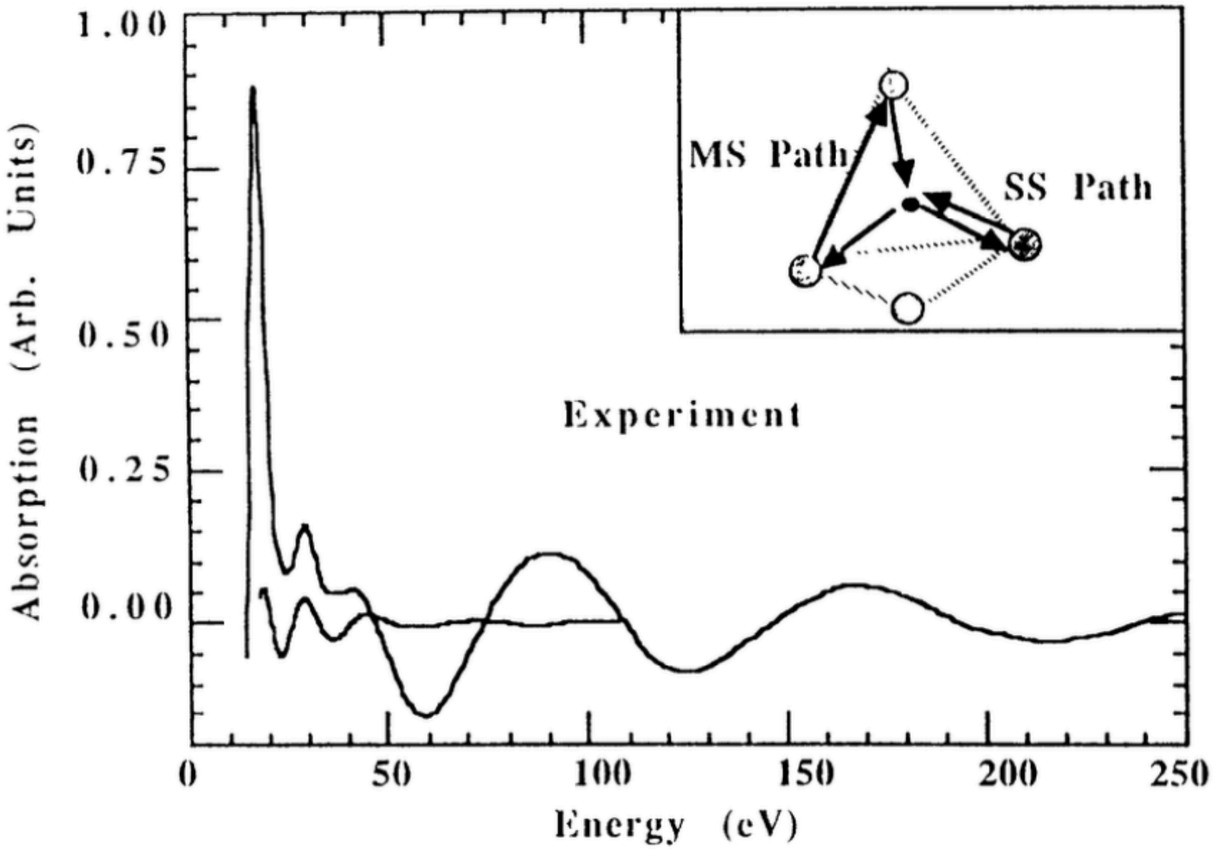


FIG. 2. The measured, normalized x-ray absorption of $GeCl_4$ and the multiple-scattering contribution to the x-ray absorption isolated by subtracting the single-scattering terms determined experimentally from GeH_3Cl and GeH_4. The MS contribution is given (per 4 Cl) by: $[GeCl_4] + 3[GeH_4] - 4[GeH_3Cl]$. Inset shows the single- and multiple-scattering paths in the $GeCl_4$ molecule.

C. E. Bouldin, G. Bunker, D. A. McKeown, R. A. Forman, and J. J. Ritter, (1988) Phys. Rev. B 38, 10816

MS signal was determined simply by taking raw linear combinations of the normalized XAFS spectra

[MS] = [GeCl4] - 4*[GeH3Cl] + 3*[GeH4]

(Ge-Cl and Ge-H distances approximated as constant)

Degeneracy of triangle MS paths =4*3/2 = 6

$\mu GeCl4 \rightarrow \mu 0\ (1 + \chi ClMS + 4\,\chi ClSS)$

$\mu GeH4 \rightarrow \mu 0\ (1 + 4\,\chi H)$

$\mu GeH3Cl \rightarrow \mu 0\ (1 + \chi ClSS + 3\,\chi H)$

$\mu GeCl4 - 4\,\mu GeH3Cl + 3\,\mu GeH4 \rightarrow \mu\,\chi ClMS$

cumulant recursion relation (GB 1983)

$$C_0 = \ln P_0; \quad C_{n+1} = \frac{dC_n}{dq}; \quad P_{n+1} = \frac{dP_n}{dq},$$

arbitrary origin

C_1 p_1

C_2 $-p_1^2 + p_2$

C_3 $2\,p_1^3 - 3\,p_1\,p_2 + p_3$

C_4 $-6\,p_1^4 + 12\,p_1^2\,p_2 - 3\,p_2^2 - 4\,p_1\,p_3 + p_4$

C_5 $24\,p_1^5 - 60\,p_1^3\,p_2 + 30\,p_1\,p_2^2 + 20\,p_1^2\,p_3 - 10\,p_2\,p_3 - 5\,p_1\,p_4 + p_5$

C_6 $-120\,p_1^6 + 360\,p_1^4\,p_2 - 270\,p_1^2\,p_2^2 + 30\,p_2^3 - 120\,p_1^3\,p_3 + 120\,p_1\,p_2\,p_3 - 10\,p_3^2 + 30\,p_1^2\,p_4 - 15\,p_2\,p_4 - 6\,p_1\,p_5 + p_6$

The recursion relation is general, but to derive it, I used an *unnormalized* (effective) distribution, and formal parameter q. Probably this is why it had not previously been discovered.

origin at centroid (p1=0)

C_2 p_2

C_3 p_3

C_4 $-3\,p_2^2 + p_4$

C_5 $-10\,p_2\,p_3 + p_5$

C_6 $30\,p_2^3 - 10\,p_3^2 - 15\,p_2\,p_4 + p_6$

C_7 $210\,p_2^2\,p_3 - 35\,p_3\,p_4 - 21\,p_2\,p_5 + p_7$

C_8 $-630\,p_2^4 + 560\,p_2\,p_3^2 + 420\,p_2^2\,p_4 - 35\,p_4^2 - 56\,p_3\,p_5 - 28\,p_2\,p_6 + p_8$

C_9 $-7560\,p_2^3\,p_3 + 560\,p_3^3 + 2520\,p_2\,p_3\,p_4 + 756\,p_2^2\,p_5 - 126\,p_4\,p_5 - 84\,p_3\,p_6 - 36\,p_2\,p_7 + p_9$

C_{10} $22\,680\,p_2^5 - 37\,800\,p_2^2\,p_3^2 - 18\,900\,p_2^3\,p_4 + 4200\,p_3^2\,p_4 + 3150\,p_2\,p_4^2 + 5040\,p_2\,p_3\,p_5 - 126\,p_5^2 + 1260\,p_2^2\,p_6 - 210\,p_4\,p_6 - 120\,p_3\,p_7 - 45\,p_2\,p_8 + p_{10}$

Mathematica code to calculate

```
C[n_] := ∂{γ,n} Log[P[0, γ]] //. {P^(0,j_)[m_, γ] → P[m + j, γ], P[0, γ] → 1, P[m_, γ] → pm}
```

calculates *all* such expressions up to n=30 in ~1 sec; up to n=50 in ~ 1min; 204226 terms in C[50]; total terms C[1]…C[50] >1.3M

Transmission: nonuniform sample

What's the problem with nonuniform samples?

nonlinearity! distortions!

Characterized by thickness distribution $P(x)$

$$\mu x_{\text{eff}}(E) = -\ln \int_0^\infty P(x) \exp\left(-\mu(E)x\right) dx$$

$$= -\sum_{n=1}^{\infty} \frac{C_n(-\mu)^n}{n!},$$

where C_n are the cumulants of the thickness distribution ($C_1 = \bar{x}$, $C_2 =$ mean square width, etc.)

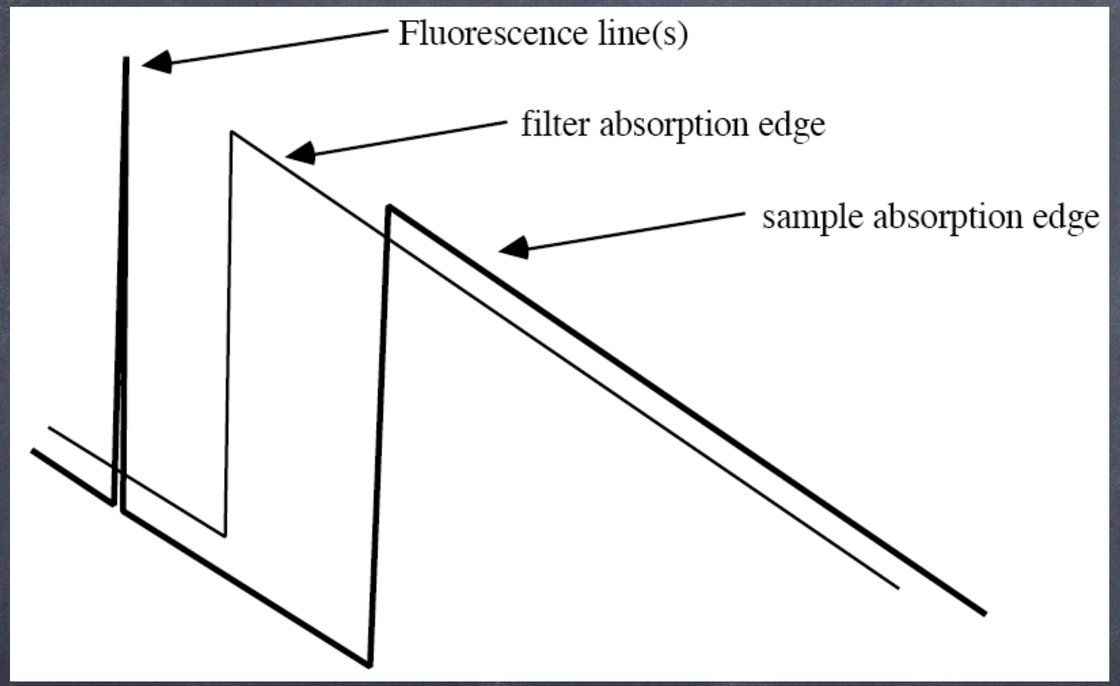
A Gaussian distribution of width σ has

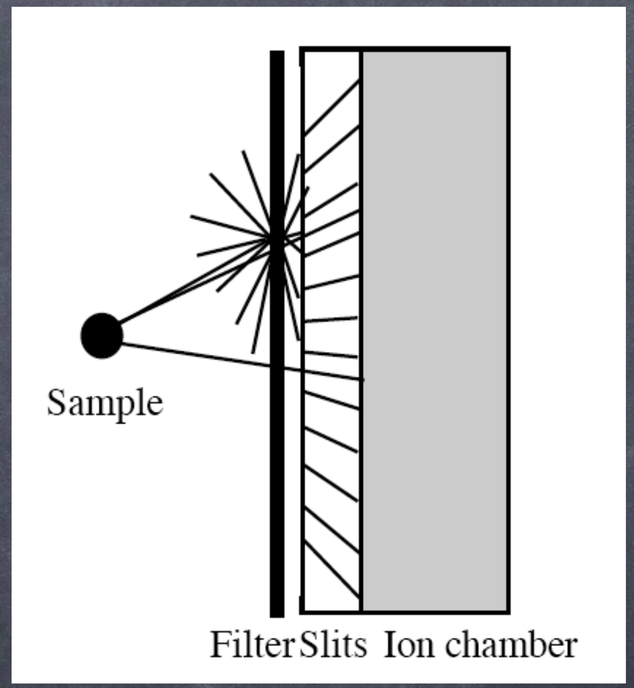
$$\mu x_{\text{eff}}(E) = \mu\bar{x} - \mu^2\sigma^2/2$$

ref gb dissertation 1984

Fluorescence ion chamber

Stern/Heald/Elam + Lytle

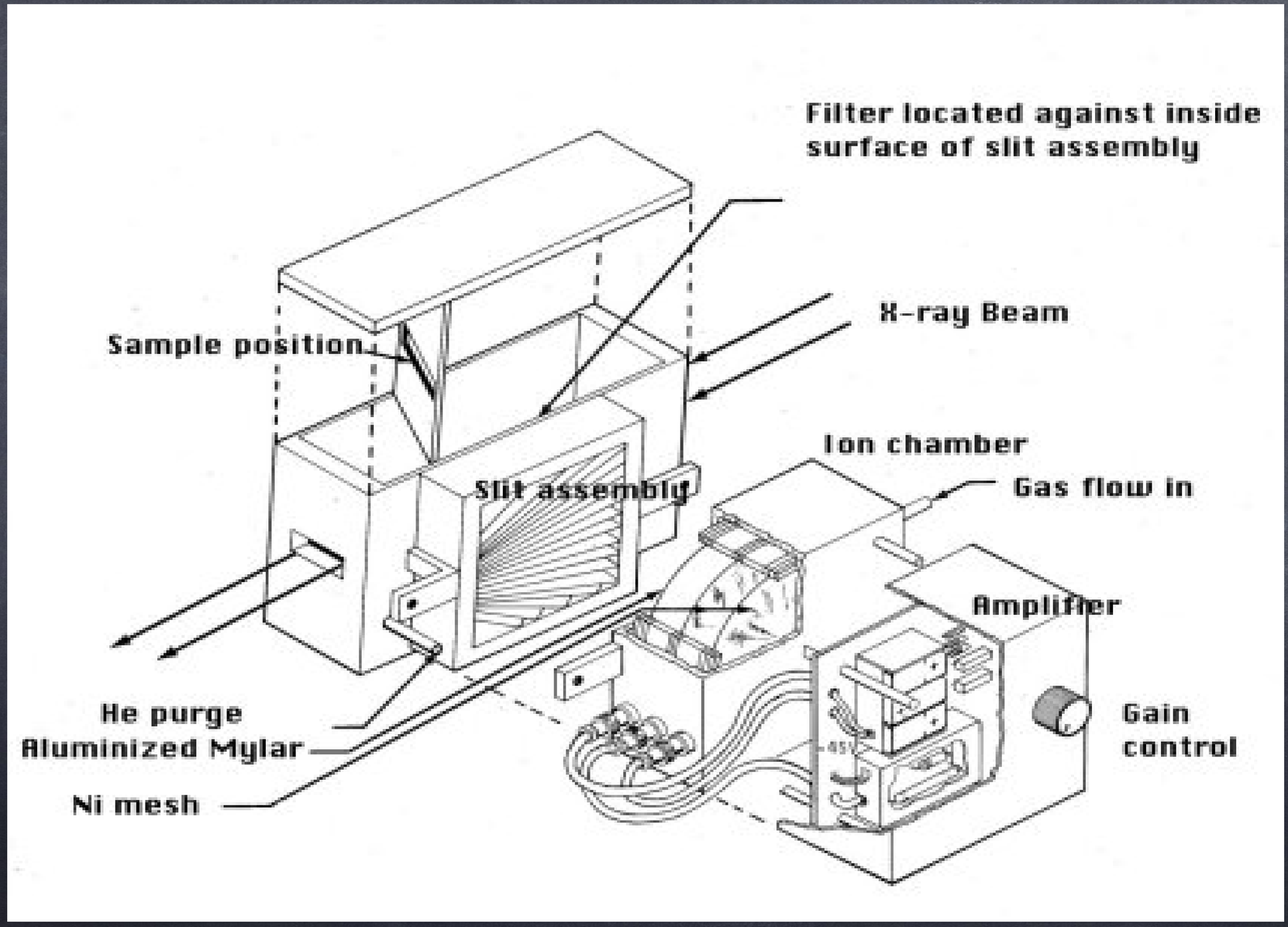




Often used with filter and soller slits to keep scattered background out of detector

"Lytle Detector"

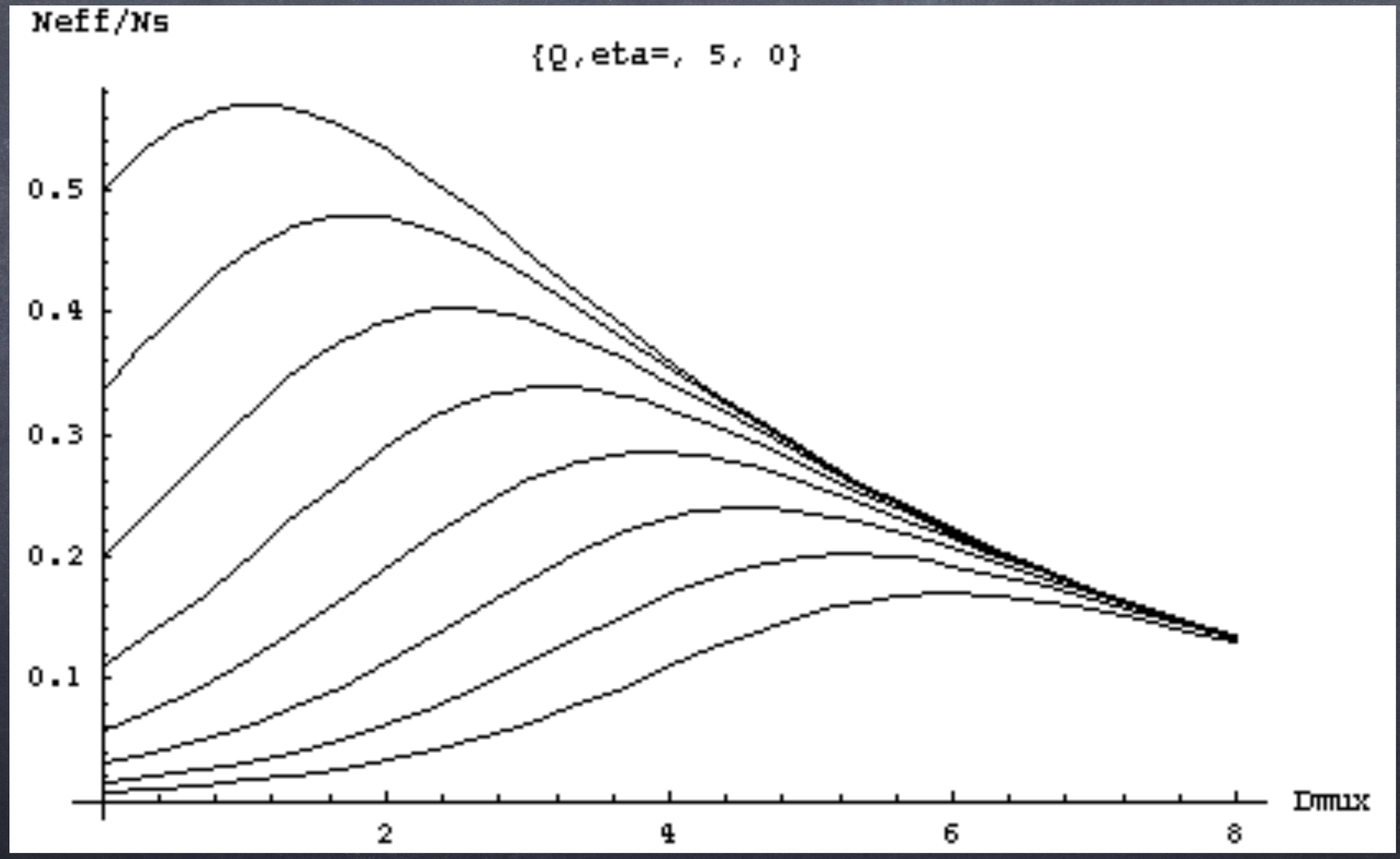
www.exafsco.com



Optimizing Filters and Slits for Stern/Heald/Lytle Detectors

Performance for dilute systems depends critically on filter and slit quality, and correct choice of filter thickness. This approach cannot eliminate fluorescence at lower energies.

excellent filter Q=5 and ideal slits (eta=0)



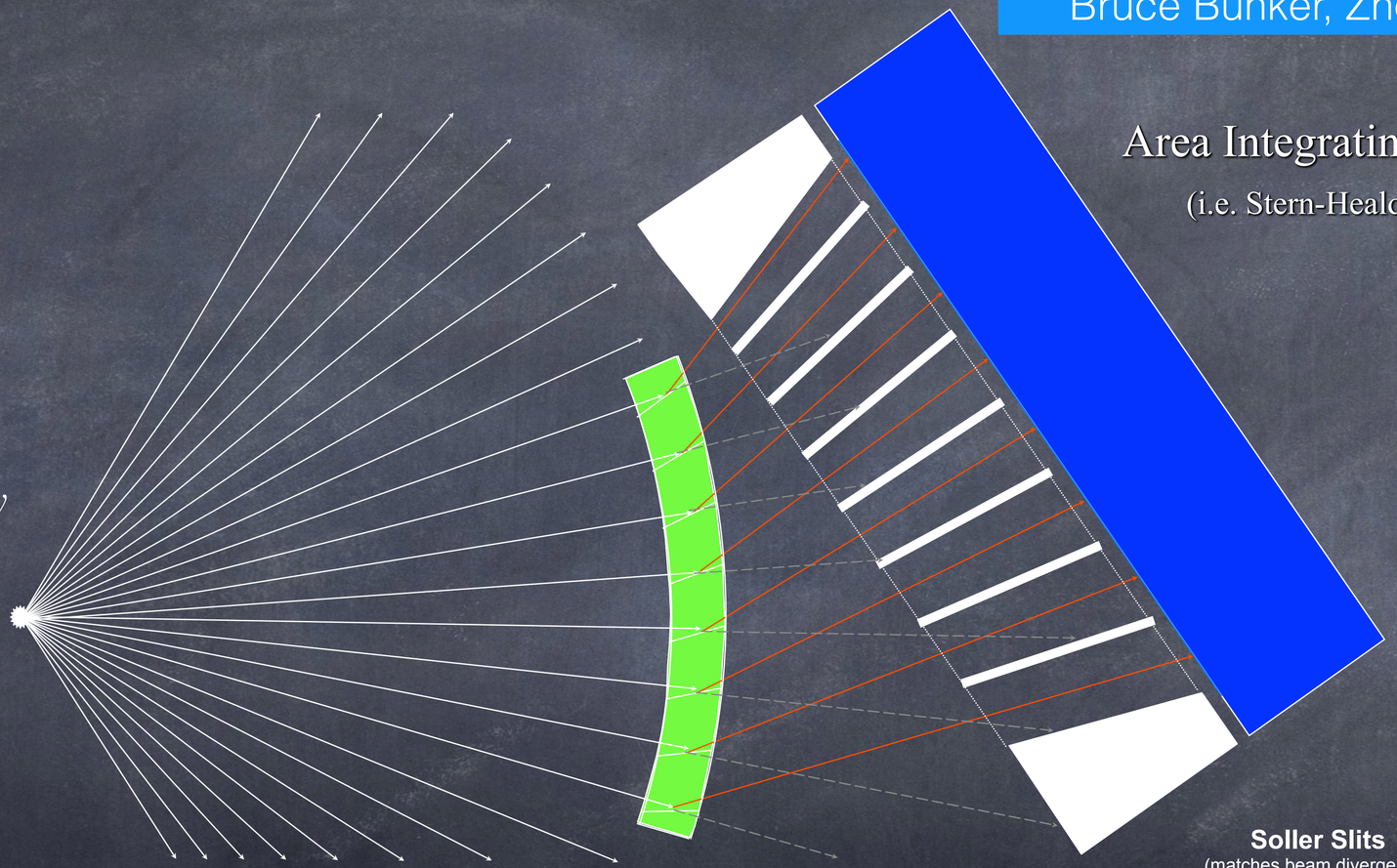
for more info see: http://gbxafs.iit.edu/training/tutorials.html

Multilayer Array Analyzer Detector

This device uses arrays of synthetic graded multilayers to diffract the signal and eliminate scattered background. It made possible some experiments that were otherwise intractable

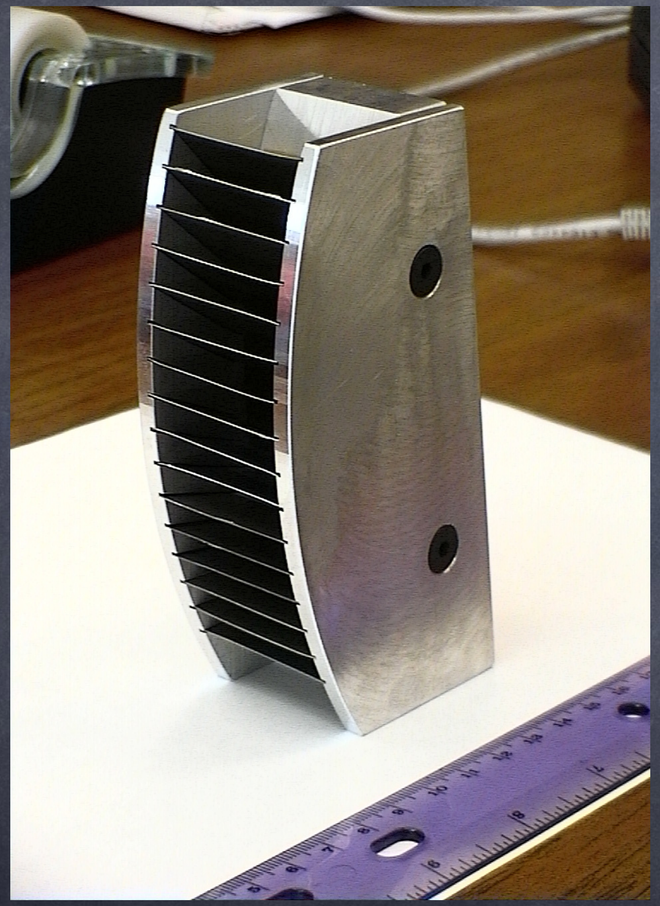
Bent Crystal Laue Analyzer

Grant Bunker, Dean Chapman, Cahit Karanfil,
Bruce Bunker, Zhong Zhong, Carlo Segre, ….



logarithmic spiral bent crystal
meets Bragg condition
along length of crystal

Bent Crystal Laue Analyzer

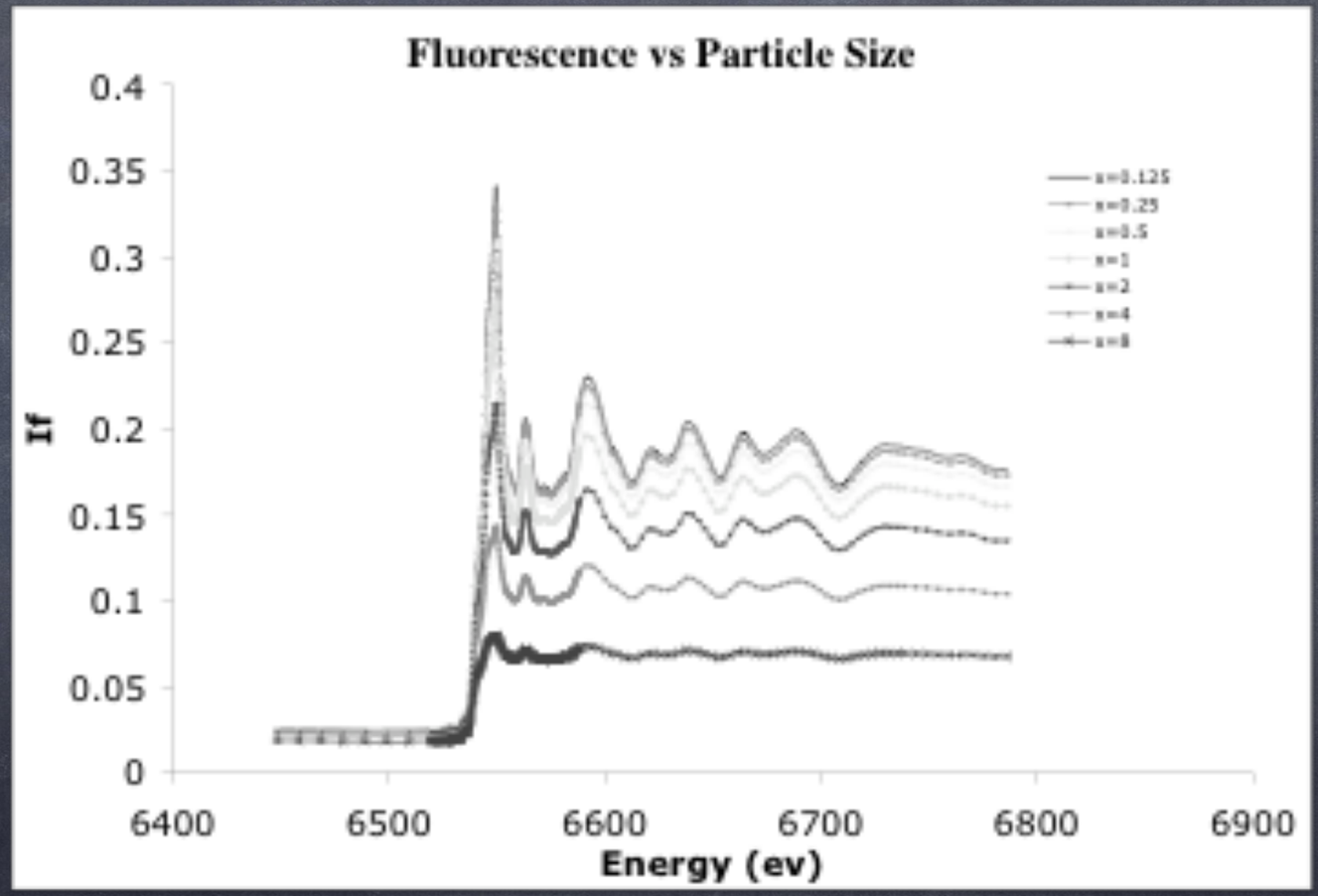


www.quercustech.com

www.fmb-oxford.com

Speciation problems

Nonlinear distortions of the spectra depend on particle size and distribution. This affects speciation results



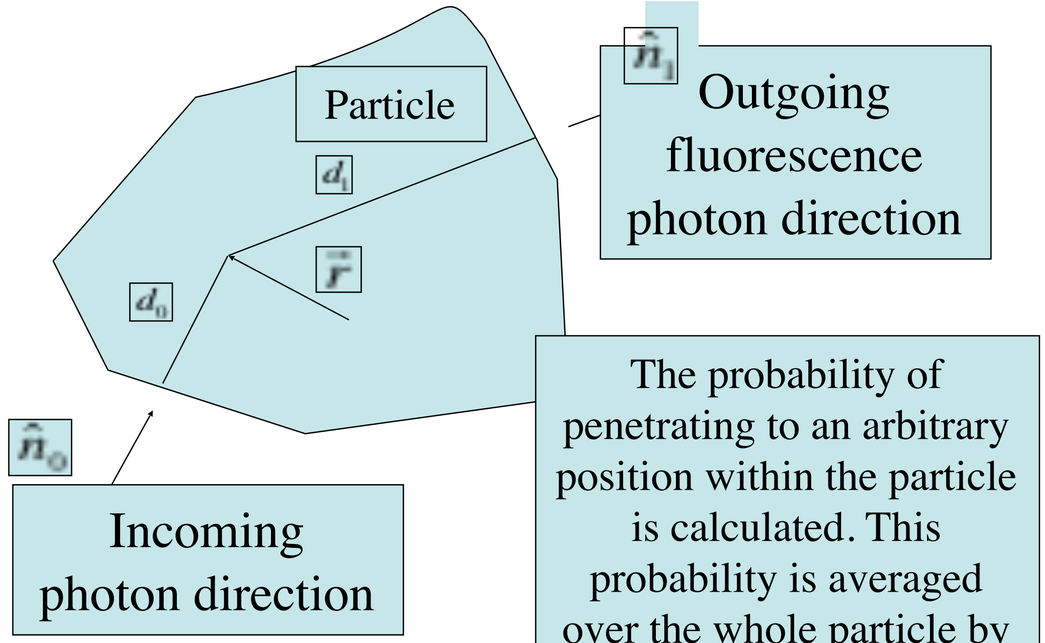
Firouzeh Tannazi 2004

Computation of fluorescence radiation from arbitrarily shaped convex particles by Monte Carlo methods

$$\hat{n}_0 = \sin\theta_0 \cos\phi_0 \, \hat{i} + \sin\theta_0 \sin\phi_0 \, \hat{j} + \cos\theta_0 \, \hat{k},$$

$$\hat{n}_1 = \sin\theta_1 \cos\phi_1 \, \hat{i} + \sin\theta_1 \sin\phi_1 \, \hat{j} + \cos\theta_1 \, \hat{k}$$

$$P_{\vec{r}} \propto e^{-\mu d_0} e^{-\mu_f d_1},$$

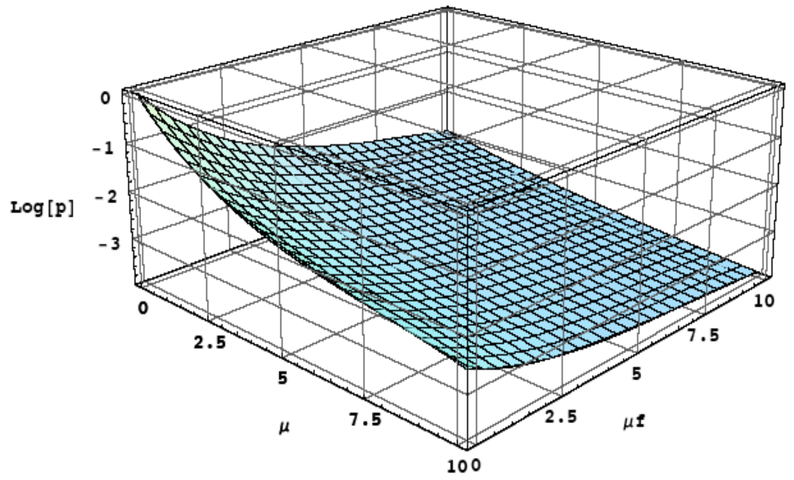


$$\bar{P} = \underbrace{\frac{P_{\vec{r}_1} + P_{\vec{r}_2} + \cdots + P_{\vec{r}_k}}{k}}_{Number\ of\ the\ points\ that\ satisfy\ the\ surface\ equation}$$

Cumulant Coefficients

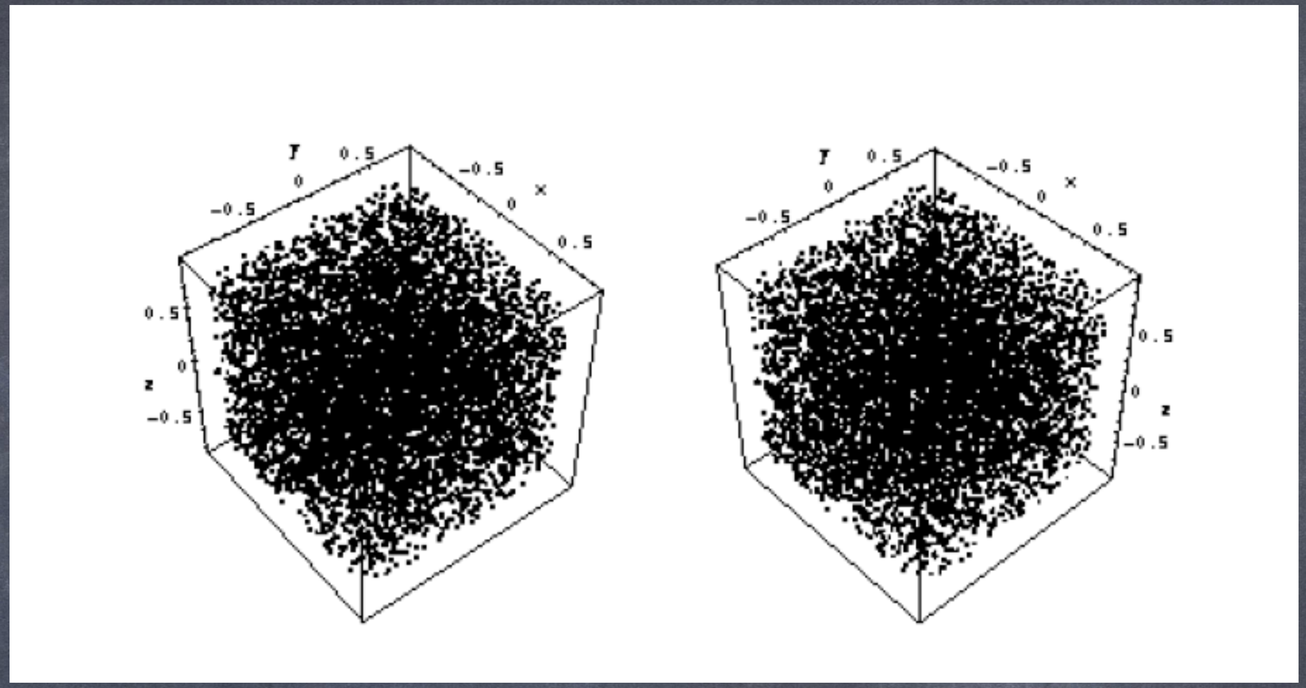
$$\bar{P} = \int F(d_0, d_1) e^{-(\mu d_0 + \mu_f d_1)} dd_0 dd_1.$$

$$\log \bar{P} = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{(\mu)^n}{n!} \frac{(\mu_f)^m}{m!} C_{nm}$$

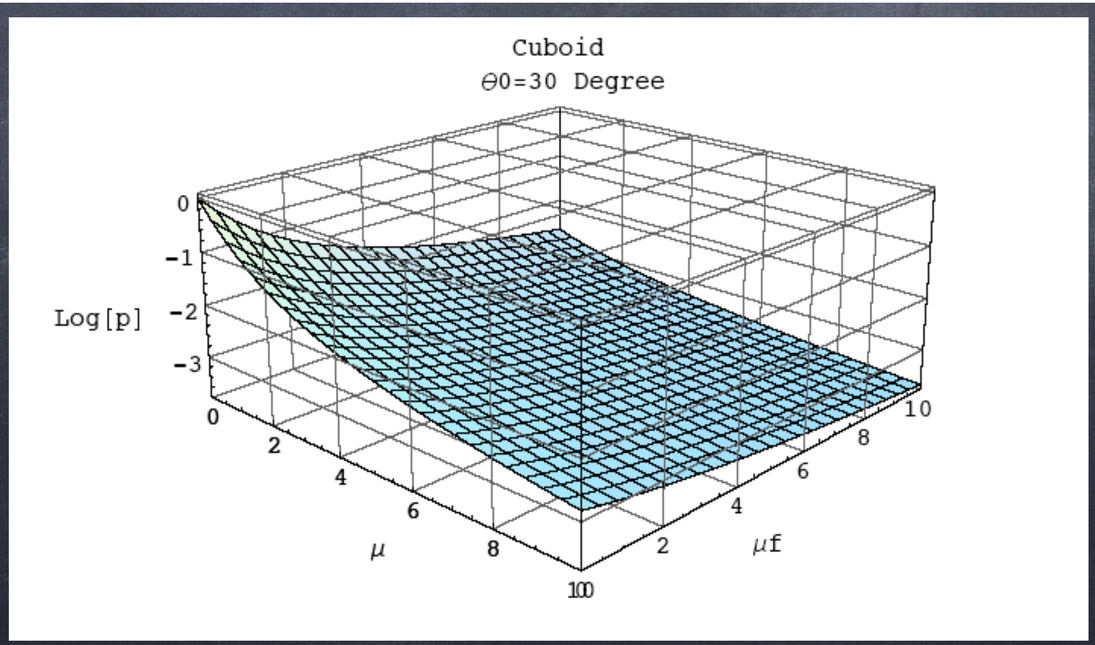


- The log of the mean probability can be expanded as a power series in both μ and $\mu_{f.}$ The coefficients are related to the cumulants of the (2D) distribution of distances d0,d1.The main point is that the probabilities for a given shape of particle (and theta, phi) can be parameterized by a handful of numbers, the coefficients.

Cuboidal Particles (stereo)



Calculate the probability as function of mu and mu_f



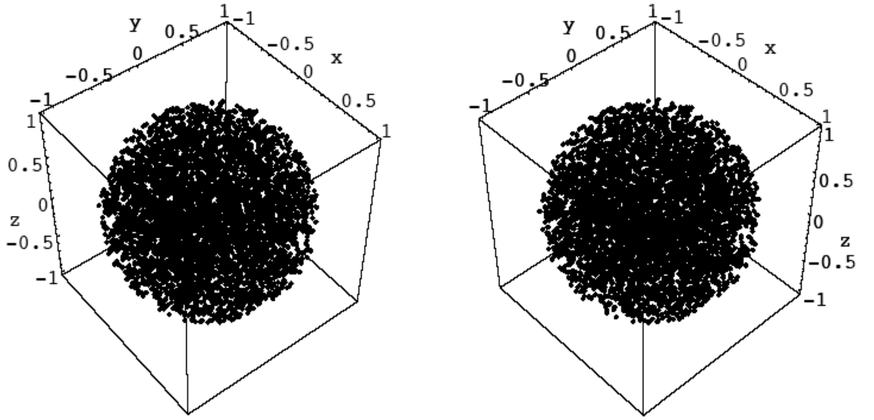


Figure 5.11. Sphere

Table 5.3. Cumulant Coefficients Table for Sphere

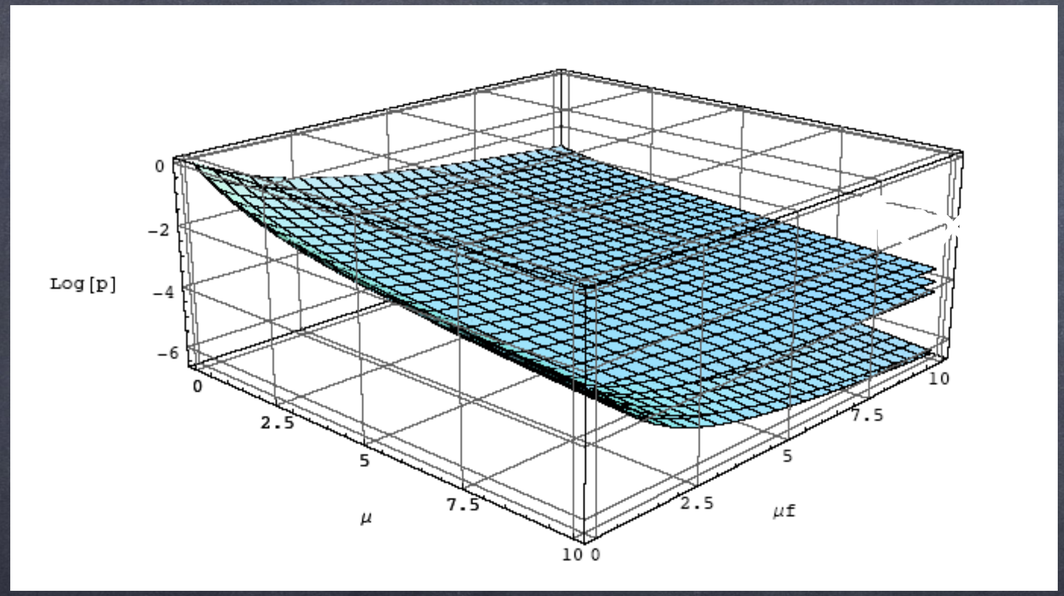
$Coef.$	$\theta_0 = 30°$	$\theta_0 = 60°$	$\theta_0 = 90°$	$\theta_0 = 120°$	$\theta_0 = 150°$	$\theta_0 = 180°$
1	-0.0509	-0.051	-0.051	-0.0499	-0.0492	-0.0501
μ	-0.6484	-0.651	-0.645	-0.6552	-0.6624	-0.6572
μ^2	0.068	0.0677	0.0673	0.06798	0.0687	0.0683
μ^3	-0.0029	-0.003	-0.0029	-0.0029	-0.0029	-0.0029
$\mu\mu_f$	0.13399	0.017	-0.1328	-0.1407	0.0033	0.12685
$\mu^2\mu_f$	-0.0158	0.0011	0.0173	0.0187	0.0034	-0.01459
$\mu^3\mu_f$	0.0007	-0.0001	-0.0008	-0.0008	-0.00023	0.00062
$\mu{\mu_f}^2$	-0.016	0.0018	0.0168	0.01783	0.0029	-0.01451
$\mu^2{\mu_f}^2$	0.0019	-0.0006	-0.0019	-0.00202	-0.00076	0.0017
$\mu^3{\mu_f}^2$	-0.00008	0.00004	0.00008	0.00008	0.00004	-0.000074
$\mu{\mu_f}^3$	0.00068	-0.00017	-0.00074	-0.00078	-0.00021	0.00062
$\mu^2{\mu_f}^3$	-0.00008	0.00004	0.00008	0.000081	0.00004	-0.00007
$\mu^3{\mu_f}^3$	3.5×10^{-6}	-2.1×10^{-6}	-3.01×10^{-6}	-3.08×10^{-6}	-2.2×10^{-6}	3.12×10^{-6}
μ_f	-0.6521	-0.672	-0.6562	-0.6548	-0.663	-0.6468
${\mu_f}^2$	0.0678	0.07063	0.0681	0.0683	0.0689	0.0663
${\mu_f}^3$	-0.0029	-0.00301	-0.0029	-0.0029	-0.0029	-0.0028

Other particle shapes tabulated in Firouzeh Tannazi dissertation 2004

these cumulants are easily calculated for any convex particle shape

Different Orientations

d0, d1 maps



Even the particle orientation matters if particles too large (!)

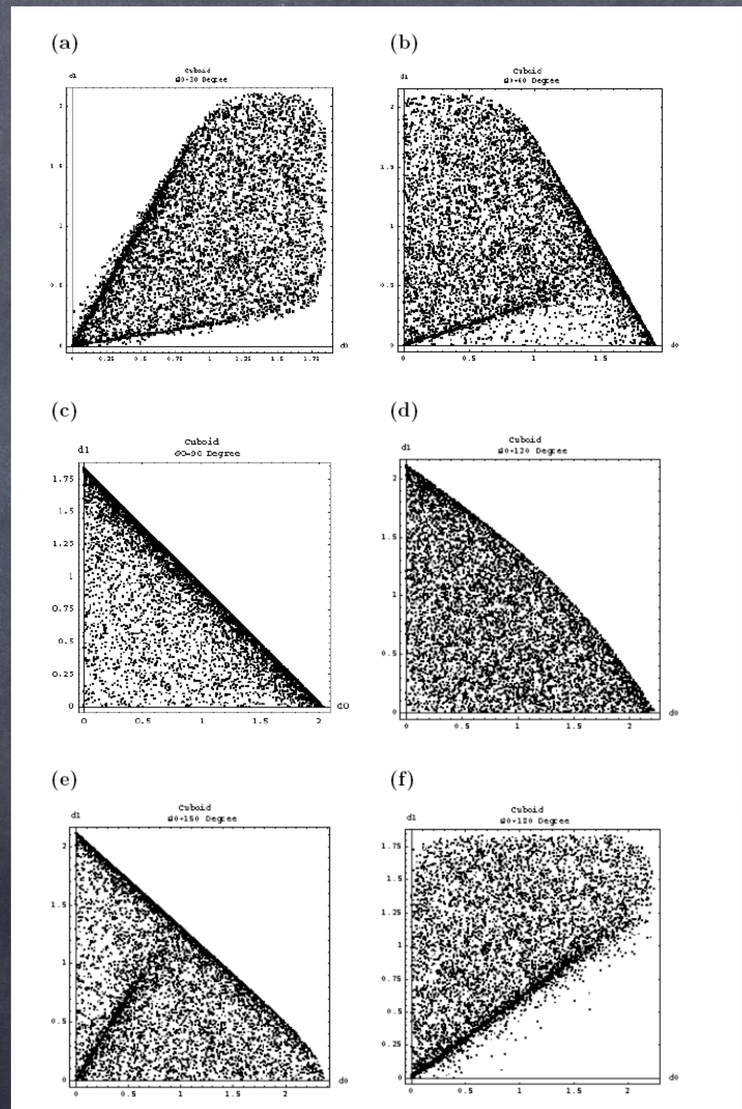


Figure 5.8. $\{d_0, d_1\}$ Maps for Cuboid at $\theta_0 =$: (a) 30, (b) 60, (c) 90, (d) 120, (e) 150, and (f) 180 degrees and $\theta_1 = \pi - \theta_0$ degrees.

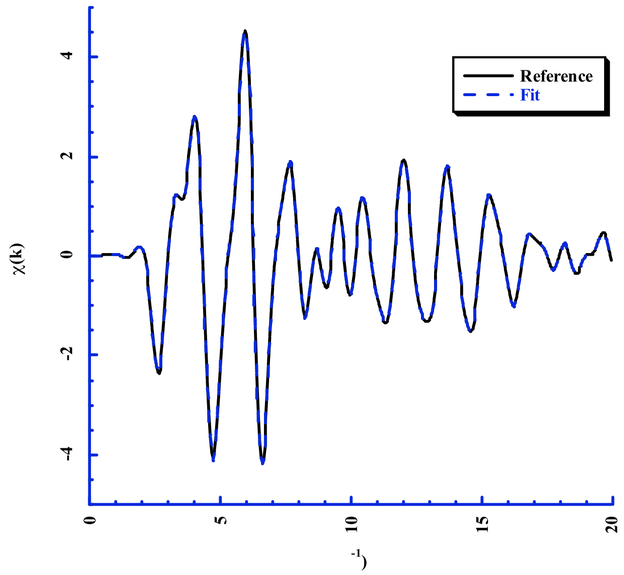
Automated metalloprotein analysis including DFT-calculated MS DWFs

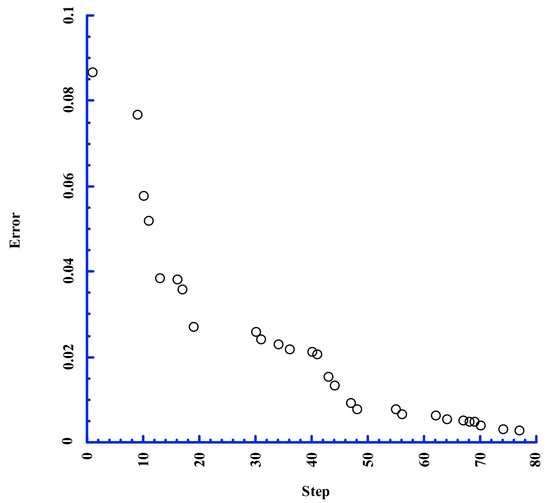
example: Zn metalloprotein

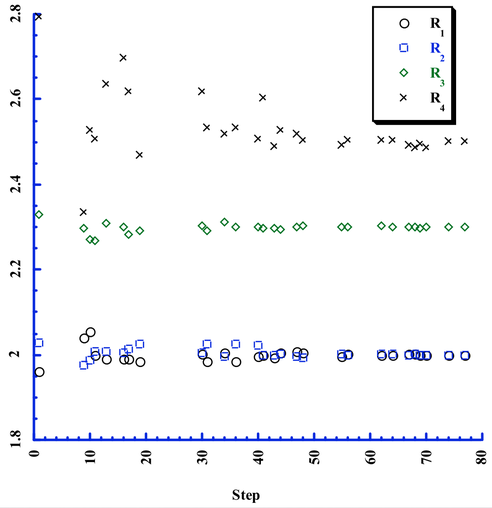
3-His, 1-Cys

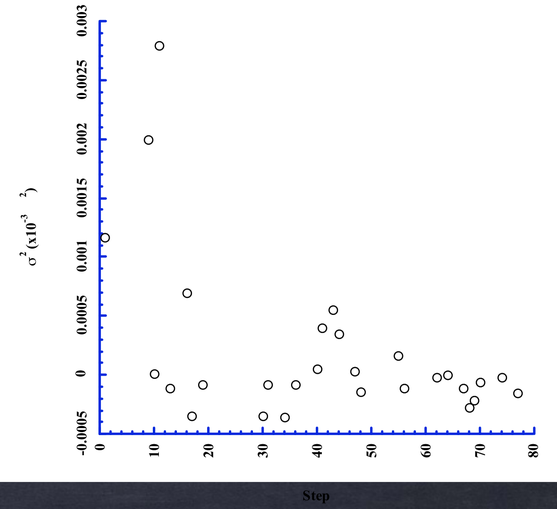
Automated group fitting using a differential evolution genetic algorithm + FEFF7 + structure-parameterized DFT-calculated MS DWFs

(Dimakis & Bunker, Biophys. Lett. 2006)



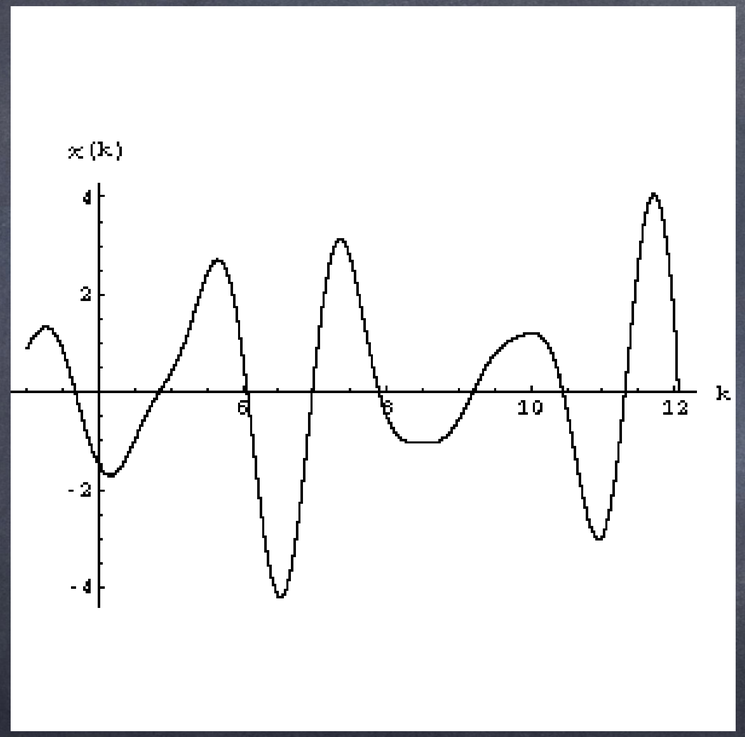


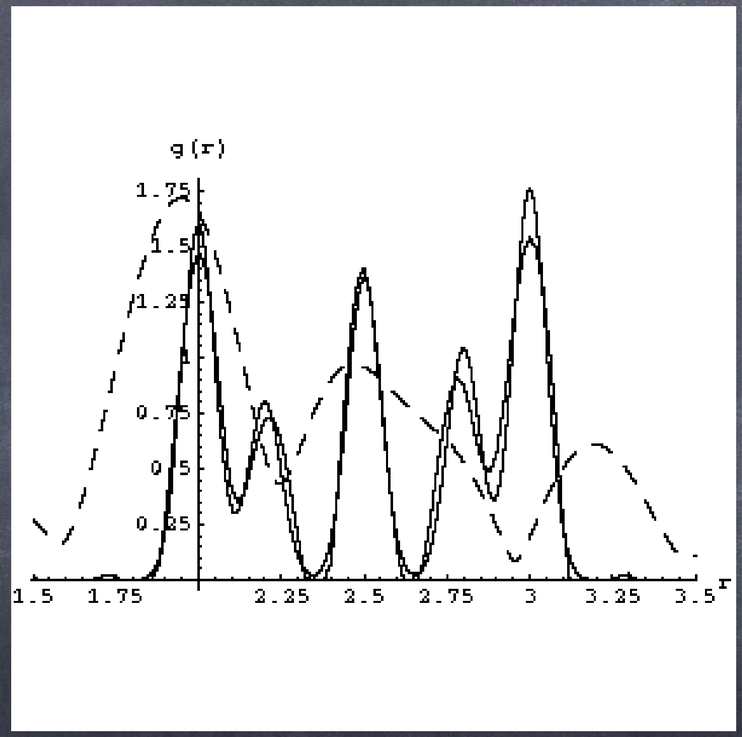




RDF determination by Regularization

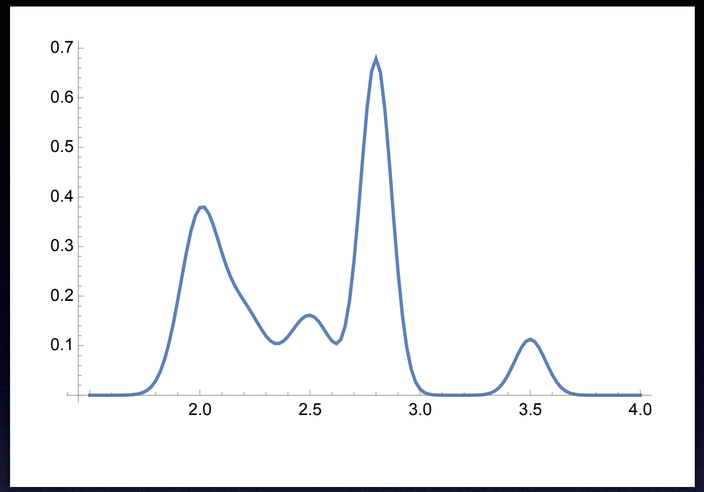
Direct method for determining radial distribution functions from EXAFS using Tikhonov and Projected Landweber-Friedman Regularization



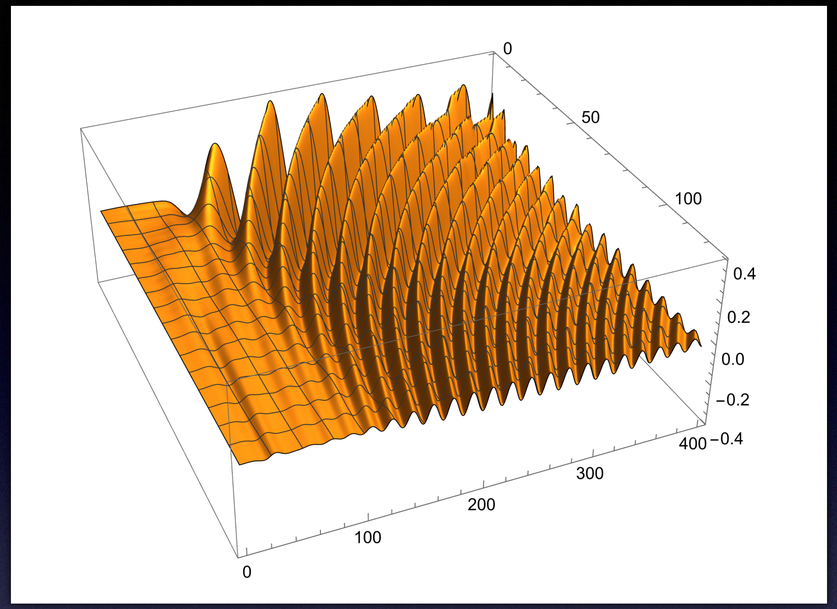


Gocha Khelashvili thesis 2000

Fe-Se synthetic RDF

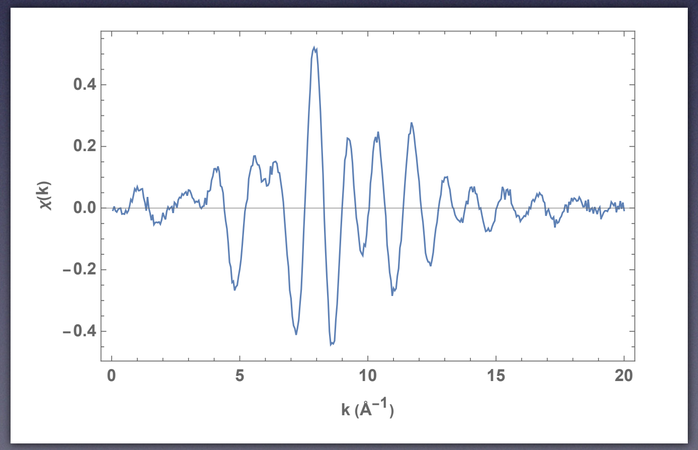


Fe-Se single scattering kernel constructed using FEFF8

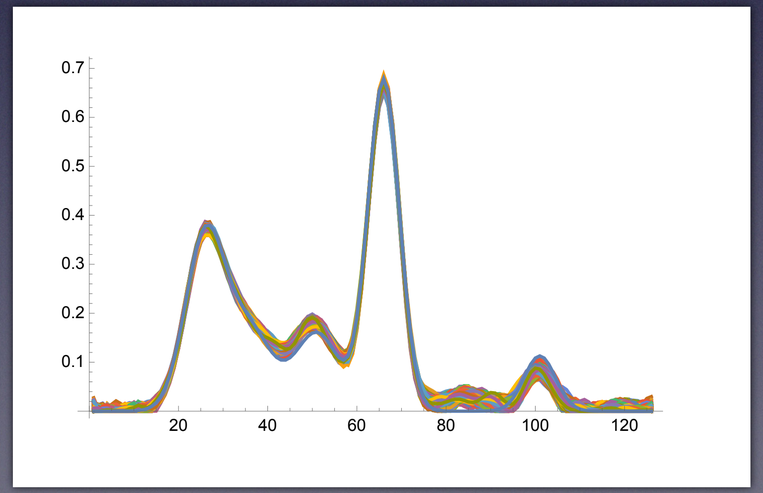


This also works well for 2-3 *different* elements, each with their own RDFs

corresponding $k^3\chi(k)$ +noise



True vs reconstructed RDFs



Caveat: SS only at this time

~Microfocus XAFS study of Hg and Se speciation in liver tissue of marine birds

C. Karanfil, K. Bischoff, G. Bunker (2013)

Cormorants primarily eat fish, and in the Everglades bioaccumulate Hg and Se. Spatial fluorescence maps of liver tissue sections showed strong correlation between Hg and Se locations. Fe maps served as control.

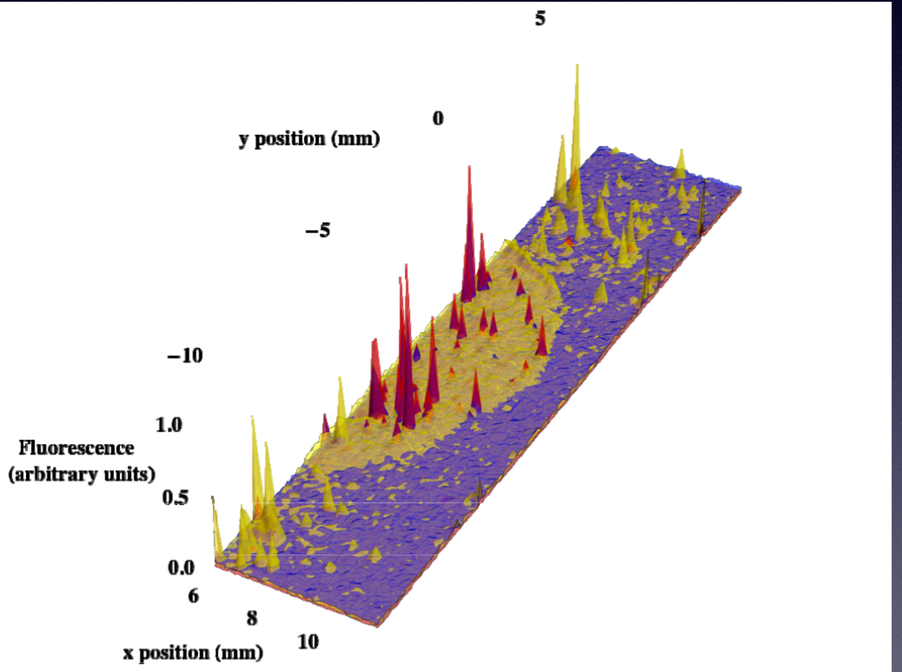


Figure 1: Spatial maps of fluorescence of Hg (red), Se (blue), and Fe (yellow). This shows the existence of "hot spots" of high concentration of both Hg and Se. The peaks corresponding to Hg and Se overlap so that they appear purple. The yellow Fe peaks are not spatially well-correlated with Hg and Se. The spatial resolution is approximately 100 micrometer.

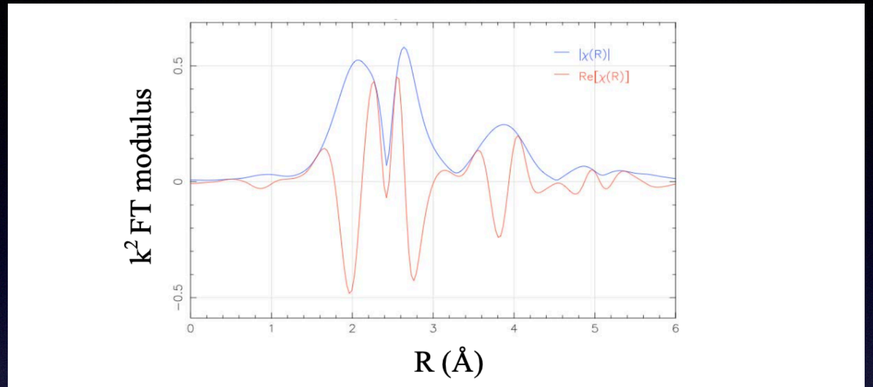


Figure 2: Fourier Transform of theoretical spectrum of Tiemannite, with DWFs calculated by FEFF8 in Debye approximation at sample temp 300K and Debye temperature 200K. The nearest neighbor peaks are due to 4 Hg atoms at 2.63 Å, and the peak at 3.8 Å is Se. The first shell peak splitting is due to a Ramsauer-Townsend-type resonance in the backscattering amplitude of Hg.

EXAFS of "hot spots" revealed HgSe (Tiemannite-like) deposits. Suggests Hg detoxification mechanism by Se.

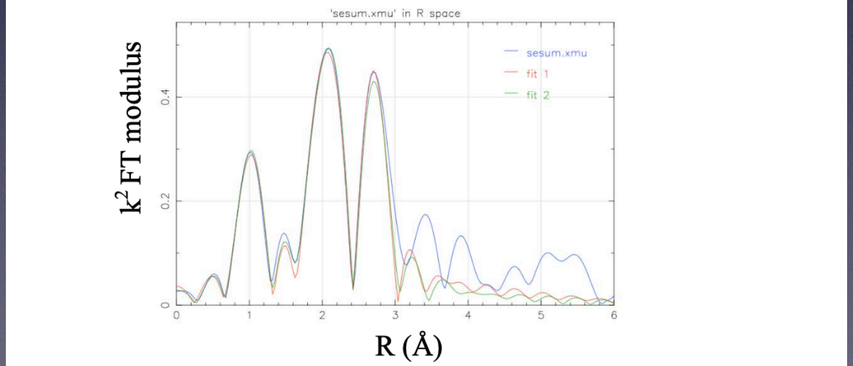


Figure 3: Magnitude of k^2 Fourier transform of summed Se data and two R-space fits to data fit between R=1.6-3.2 Å. The (background-fitted) peak at R=1.0 Å is due to Hg EXAFS extending into the Se transform range, and is of no consequence. The data within the fit range correspond to a single shell of 4 Hg at 2.61 Å; the peak splitting is due to the shape of the Hg scattering amplitude function.

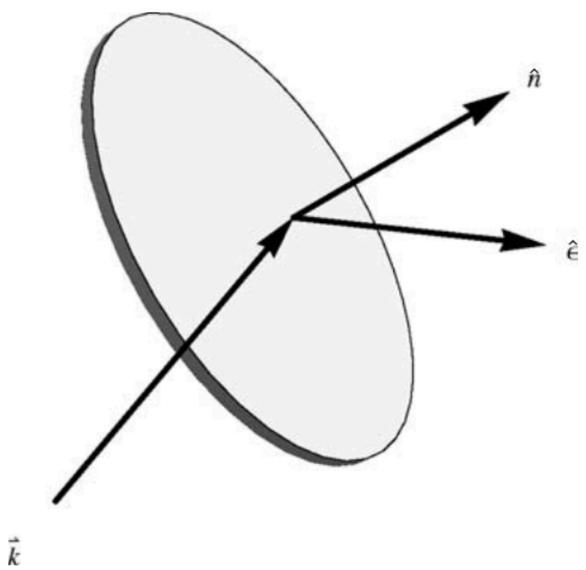
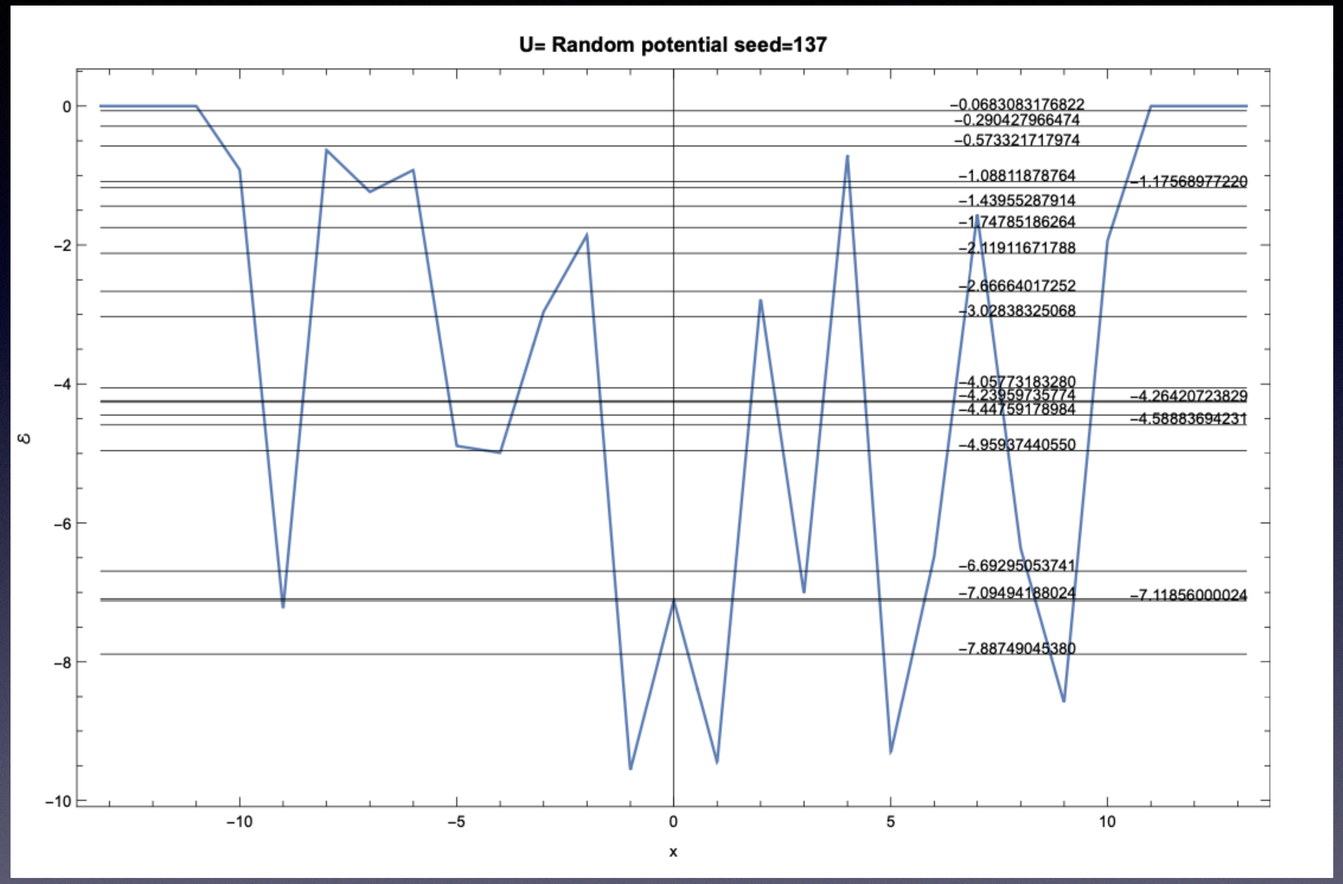


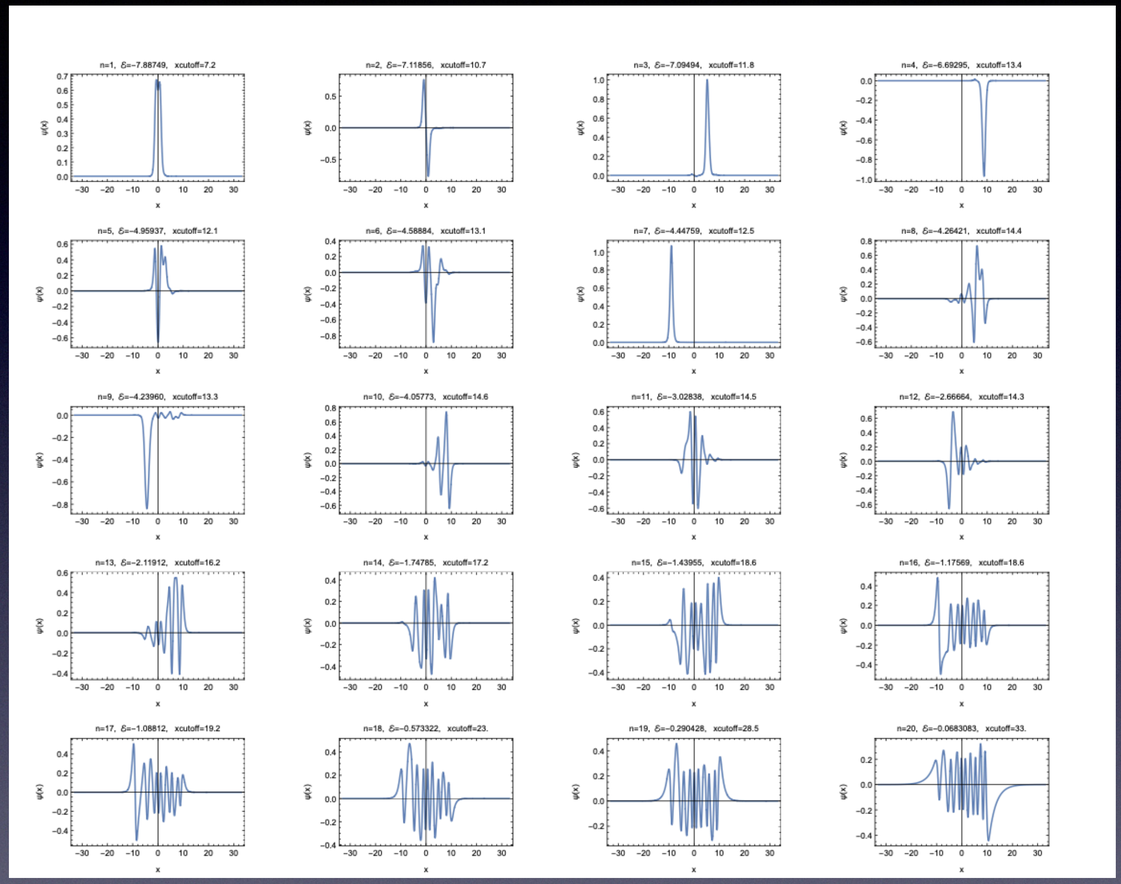
Fig. 3.29 Magic angle spinning geometry: $\vec{k}$ is the incident beam direction; $\hat{\epsilon}$ is the x-ray polarization; $\hat{n}$ is the normal vector about which the sample spins. The angle between $\hat{\epsilon}$ and $\hat{n}$ should be $\theta^* \approx 54.7°$ to average out the dichroism.

From GB book “Introduction to XAFS”:
Magic angle spinning to eliminate unintended dichroism from preferred orientation in sample.

Current project: “Phase Method” for numerically solving Schrödinger eigenvalue problems in arbitrary 1D/central/separable potentials. Example: Random Linear Potential, no Airy functions needed



potential and eigenvalues



wavefunctions

Automatically calculated in minutes on laptop; nearly degenerate eigenvalues resolved;
no discretization or matrix methods; no guessing of eigenvalues needed; *no matching of boundary conditions;*
eigenvalues are typically accurate to 15 digits or better using 30 digit extended precision

Closing Remarks

Some Enabling Factors for Growth of XAFS

currently, new papers published at ~ 17K/year

- Theory (RSGF, many body theory-> accuracy)
- Analysis Software, Algorithms
- Software Languages and Platforms
- Beamlines and X-ray Optics
- Insertion Devices
- Accelerator Technology
- Detector & Electronics Technology
- Computing Power/$ (~10^7 increase)
- Data Storage/$ (~10^7 increase)

- Government Funding of Facilities
- Government Funding of Internet
- Free and Open Source Software
- World Wide Web
- IXAS/XAFS conferences/workshops
- International Science and XAFS Community
- Standards and Criteria/Education
- Commercialization of Components
- Industrial Investment in Facilities

A large collective effort

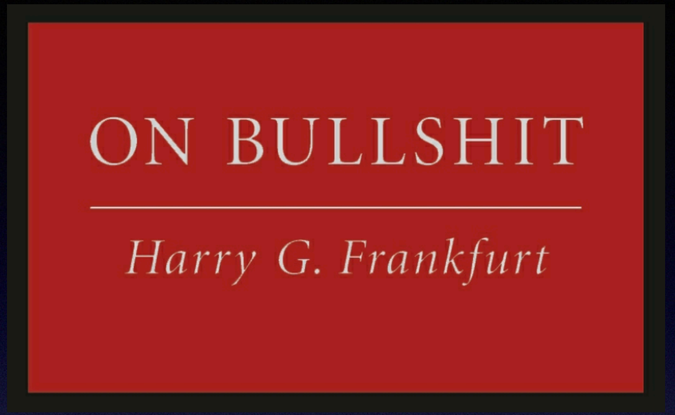
Obvious Extrapolations for XAFS

- Coherent beams, expanded use of compact sources, FELs
- Improved space and time resolution
- Expanded use of HERFD, IXS/XES
- Integrated modeling using multiple techniques simultaneous refinement
- Self-consistent theory (electronic+vibrational from same model) Integrated with modeling/analysis software (or not)
- Canned analysis environments e.g. Docker, Kubernetes for simplified distribution and support
- Increased use of Laboratory-based XAFS
- Rapid growth of AI/ML methods, integrating with modeling/ODE methods
- Organizations to specifically support packages
- High throughput data analysis, increased parallel and GPU use
    - eventually cloud-based quantum, eventually desktop (trapped ions or other etc)
- High throughput data acquisition
- Improved detectors and analyzers, perhaps based on new principles
- *New* experimental modalities
- More *rigorous* experimental modalities
- Combinatorial materials synthesis using AI
- …

Importance of Open Source XAFS Software

- Well-integrated automated theory/analysis/modeling packages can offer productivity gains
- Free and open source analysis software has been in UW XAFS tradition since 1970's
  - Free (or low cost) is important for dissemination and outreach
  - Ongoing support should be a distributed effort or supported institutionally
    - too demanding for a single individual to support over decades, risky
    - example: EXCURV
      - SS+MS analysis with integrated 3D modeling.
      - went commercial -> became less accessible to global XAFS community
      - didn't keep up with theoretical advances
- Matt Newville's open Python-dialect "X-ray Larch" DSL seems a good platform to build on

- **I have some concerns about *uncritical* adoption of "Oracular" neural network models**
  - Oracles (e.g. GPTx) confabulate, and they *don't care*: HAL 9000 on magic mushrooms
  - at present, one can't predict precisely when they will fail
  - not logic-based, so verifiability has to be done by exhaustion
  - results may be no better than an intelligently done parameterization and inversion
  - who will be able to create and use them?
    - If commercial, they unexpectedly may be put behind a paywall and fenced off
    - everyone in the world has a brain, but not everyone has resources to train large network models
  - data analysts may lose contact with data and physical understanding of spectra
- ***Having Said That***, neural network models inevitably will be of growing use and importance
  - Cambrian explosion of network types
  - as a generalized function when traditional parameterized models not obvious
  - for generating possible candidate solutions for further vetting and error analysis
  - learning patterns in large parameter spaces e.g. combinatorial materials



"It is just this lack of connection to a concern with truth—this indifference to how things really are—that I regard as of the essence of bullshit"
Harry Frankfurt,
Philosopher,
Princeton U.

thanks for your attention

Questions?

postscript on AI

- Inverse problem: inverse mapping from *spectrum* to *structure*
- “solving” by “deep learning”
  - Vast data sets and very large compute time needed for training
  - AlexNet - importance of large data sets
  - Alpha-Fold - harvested vast number of Protein Data Bank structure, lots of human input/work
    - large vetted experimental data sets are not currently available for XAFS
    - might be doable with calculated data if the forward calculation is efficient enough and training structures are chosen appropriately. Materials Project might provide.
    - Calculating MS DWFs for structures (e.g. proteins) with heterogeneous bonds to generate training data may be a bottleneck (but see Dimakis).

Artificial Intelligence/Machine Learning

- Not so new: Neural Networks have been around since the 1960's
  - Multilayer Neural Nets were proved to be universal function approximators in 1980's.
  - Backpropagation/automatic differentiation was developed for efficient training
- In XAFS we have been using AI/ML for decades, but have generally not called it that
- Code that adapts its execution depending on the data stream
  - (e.g. AutoBK, LSODA ODE solver, Mathematica …)
  - Mathematica has *always* employed "Artificial Intelligence", but without calling it that. Wolfram "Neural Net Repository" has been around for years
  - Since 2017 all iPhones, iPads, and since 2020 Apple Silicon Macs have shipped with "Neural Engine" integrated into SOC, for ML inferencing. These are used behind the scenes by the OS and accessible via CoreML API. Intel and AMD are planning similar things.

- What *is* new is:
  - *massive* investment by Venture Capital (*surely out of the good of their hearts*)
  - *massive* compute GPUs + CUDA
  - *massive* data (harvested from the internet commons, often without attribution or consent)
  - *Generative Pretrained Transformers*
- “You can fit an elephant with enough parameters” (old saying regarding overfitting data)
  - You can *model* an elephant with enough parameters (we’re getting there with GPT3-> 10^11 parameters, and GPT4->10^12)
  - giga: 10^9; tera: 10^12; peta: 10^15; exa: 10^18; I suggest another: “lotta” -> 10^11:
    - how many neurons in a human brain? (a *lotta* ~10^11); how many stars in a galaxy (a *lotta*); how many galaxies are there that we can we see (a *lotta*); how many parameters does GPT3 have (a *lotta*) - and GPT-4 supposed has an order of magnitude more