

Review

- Sources

- bend magnets
- wigglers
- undulators

} all are suitable for XAFS; narrow (~100eV) bandwidth of undulator requires either scanning or tapering of gap.

- detectors

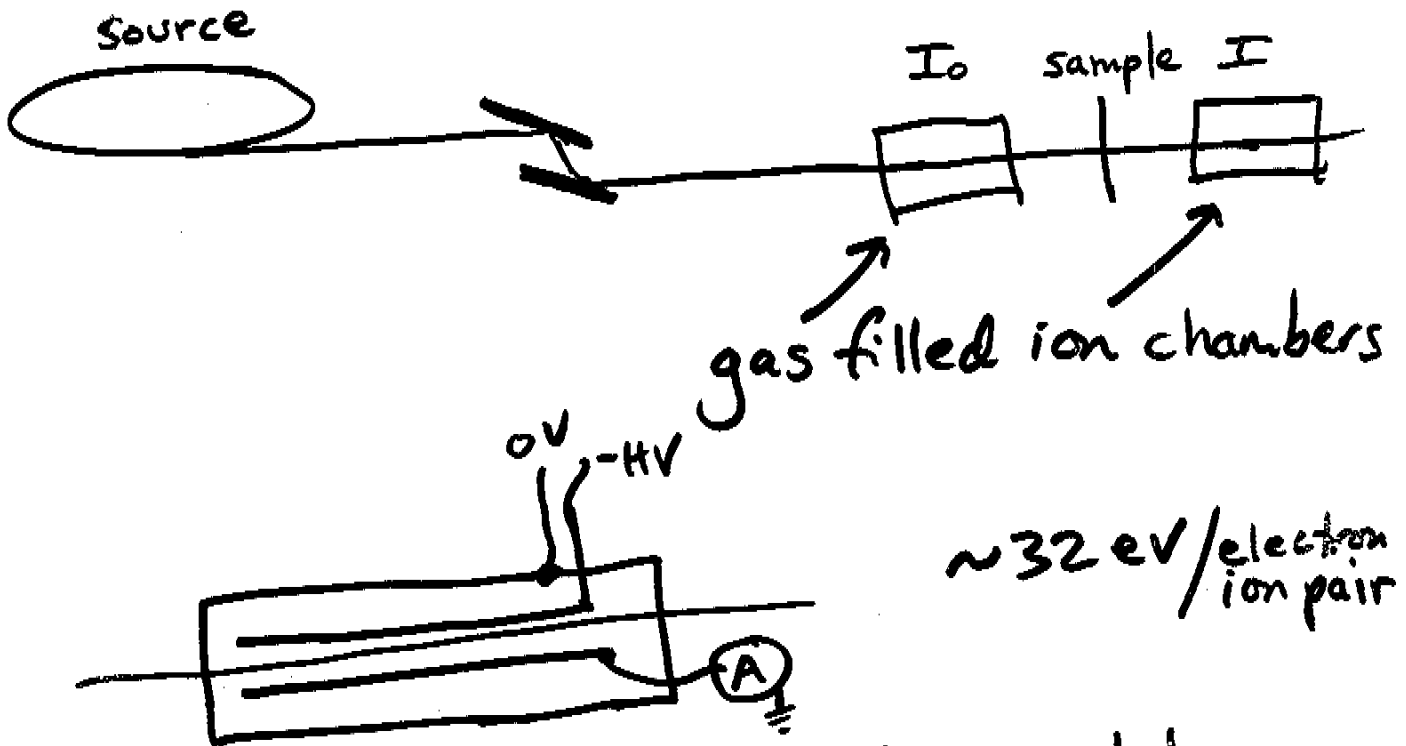
- ion chambers (transmission + fluorescence)
- PIN diodes

current

- Energy dispersive solid state detectors
- Avalanche Photodiodes
- PMTs with fast plastic scintillators
- electron yield

pulse counting

Transmission mode



energy deposited between plates:

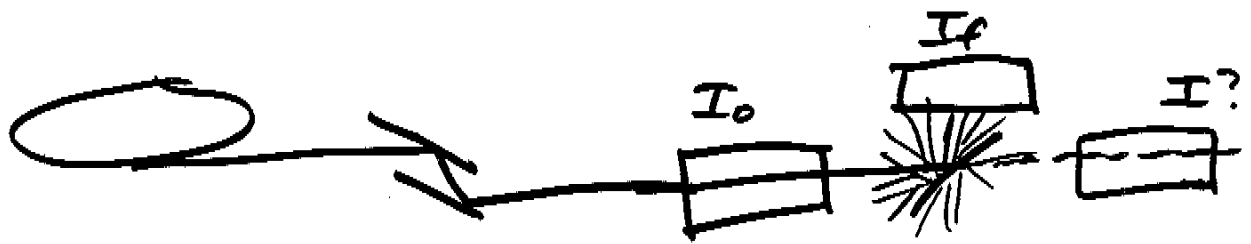
$$N_{\text{photons}} E (1 - \exp[-\mu_{\text{fill gas}}(E) l])$$

current

$$\sim \frac{\text{photons}}{\text{sec}} \frac{\text{Energy}}{\text{photon}} \frac{1 \text{ electron}}{32 \text{ eV}} (1 - e^{-\mu_{\text{fill gas}} l}) \times 1.6 \times 10^{-19} \frac{\text{coul}}{\text{electron}}$$

conversion factor ~ $3 \times 10^6 \frac{\text{photons}}{\text{sec}} / \text{volt} @ 10^{10} \text{ gain, Fe K}\alpha$

- Fluorescence mode



Why is detector placed at 90° in horizontal plane?

⇒

Scattered background minimum along X-ray polarization vector

- I_f detectors

- Stern/Heald-type ion chamber ("Lytle detector")
filters, slits reduce background before detection. (Biocat's multilayer analyzer better)
- Energy dispersive solid state detectors tend to get saturated by undesired background. Total counts/element/sec $1-4 \times 10^5$. ⇒ always do deadtime corrections!

— calculating absorption lengths
 $\frac{\text{photons absorbed}}{\text{time}}$

$$= \frac{\text{photons}}{\text{time} \cdot \text{area}} \times \text{cross section (area)}$$

↑

$$\frac{\text{cross section}}{\text{atom}} \times \text{atoms in beam}$$

cross section σ often expressed
 as $\frac{\text{area}}{\text{mass}}$:

— linear absorption coefficient

$$dN = -N (\mu dx)$$

$$\Rightarrow \ln N = -\mu x + \text{const}$$

↑ probability absorbed in dx

$$\frac{N}{N_0} = e^{-\mu x}$$

— μ "absorption length"

single species $\mu = \rho \sigma = \left[\frac{g}{\text{cm}^3} \right] \left[\frac{\text{cm}^2}{g} \right] = \text{cm}^{-1}$

multiple species $\mu = \sum_i \rho_i \sigma_i = \rho \sum_i \left(\frac{m_i}{M} \right) \sigma_i$

- Example: Fe_2O_3

Fe k-edge @ 7.1 keV

What is absorption at 7.2 keV?

⇒ use tables (e.g. McMaster, Intl tables
mucal, ...)

$$\begin{array}{ll} \text{Fe} & \sim 393 \frac{\text{cm}^2}{\text{g}} @ 7.2 \text{ keV} & 56 \text{ g/mol} \\ \text{O} & \sim 15 \frac{\text{cm}^2}{\text{g}} @ 7.2 \text{ keV} & 16 \text{ g/mol} \end{array}$$

$$\text{MW} = 2 \times 56 + 3 \times 16 = 160 \text{ g/mol}$$

$$\begin{aligned} \mu &= \rho \left(393 \times \frac{112}{160} + 15 \times \frac{48}{160} \right) \frac{\text{cm}^2}{\text{g}} \\ &\approx \rho \frac{280 \text{ cm}^2}{\text{g}} \quad \text{if } \rho = \frac{5 \text{ g}}{\text{cm}^3} \end{aligned}$$

$$\mu \approx \frac{1400}{\text{cm}}$$

$$\mu^{-1} \approx 7 \mu\text{m}$$

need particle sizes ≈ 7 micron!

- example: U metal

U L_{III} edge 17.2 KeV

photoelectric cross section $\frac{44 \text{ cm}^2}{\text{g}}$

$$\mu = \rho \sigma = 19 \frac{\text{g}}{\text{cm}^3} \times \frac{44 \text{ cm}^2}{\text{g}} = 838 / \text{cm}$$

$$\mu^{-1} \approx 11 \text{ micron}$$

- example: Ar gas at U L_{III} edge

$$\frac{13 \text{ cm}^2}{\text{g}}$$

$$40 \text{ g/mol}$$

$$\mu = \frac{13 \text{ cm}^2}{\text{g}} \frac{40 \text{ g}}{\text{mol}} \frac{\text{mol}}{24.5 \text{ L}} \frac{1 \text{ L}}{1000 \text{ cm}^3}$$

$$= .021 / \text{cm}$$

$$\mu^{-1} = 47 \text{ cm}$$

10cm ion chamber absorbs ~ 20% of beam, ok for I_0 .

- optics

- double crystal monochromator

Si, Ge, C (diamond) $n\lambda = 2d \sin\theta$

allowed reflections (hkl)

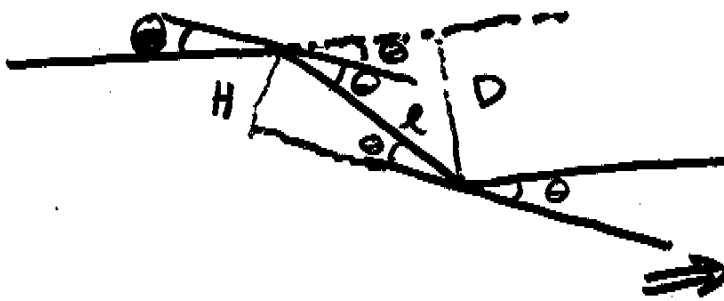
111, 220, 311, 331, 333,
400, 422, 440, 444, 511, 531,
533, 551, 553, 555, ...

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}; E = \frac{hc}{2d \sin\theta}$$

$$hc \cong 12398.6 \text{ eV \AA}$$

$$hc/2d(\text{Si } 111) \cong 1977.1 = E \sin\theta$$

(other Si lattice constants can be scaled from this)



$$\frac{H}{l} = \sin\theta; \frac{D}{l} = \sin 2\theta$$

$$D = H \sin(2\theta) / \sin\theta$$

$$D = 2H \cos\theta$$

displacement of beam
vs angle

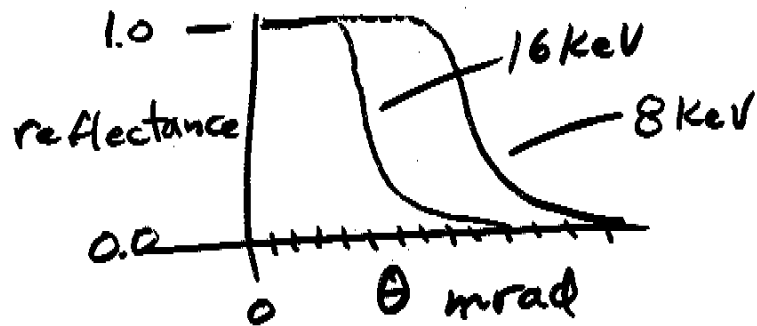
- crystal "tuning" + "detuning"

crystals must be parallel to
within rocking curve width
(~ 10 arcsec $\approx 50 \mu$ radian)

adjusted by a piezoelectric
transducer ("piezo")

because harmonics may be
diffracted as well as fundamental,
can minimize by "detuning":
deliberately misaligning second
crystal slightly. This kills harmonic
more than fundamental.

— Mirror for harmonic rejection



critical angle $\theta_c \sim \frac{\text{const (given material)}}{E \text{ (photon energy)}}$

Can find θ such that

$$\frac{\theta_c}{2} < \theta < \theta_c$$

so fundamental reflected
but 2nd harmonic is not.

— checklist:

Harmonics — get rid of them!

Alignment — ^{signal + reference} detector should see same beam (no clipping)

Linearity — detectors + electronics must be linear

Offsets — dark currents measured and subtracted correctly

$$\frac{I}{I_0} \neq \frac{I + \delta}{I_0 + \delta}$$

— you can eliminate 90% of your XAFS woes with "Halo".
Halo, are you listening?

- thin concentrated limit:

$$X_{max} \ll \left(\frac{\mu_r(E)}{\sin\theta} + \frac{\mu_r(E_f)}{\sin\varphi} \right)^{-1}$$

$$\Rightarrow \frac{\mu_s(E)(1 - e^{-\mu_s(E)x})}{L} \Rightarrow \mu_s(E)x \quad \checkmark$$

- thick dilute: $() X_{max} \Rightarrow \infty$

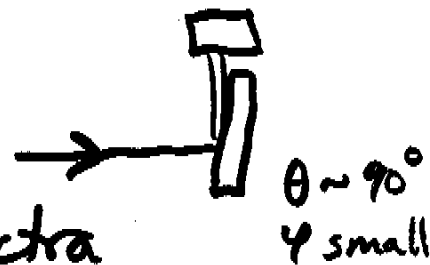
$$\frac{\mu_s(E)}{\left(\frac{\mu_r(E)}{\sin\theta} + \frac{\mu_r(E_f)}{\sin\varphi} \right)}$$

- concentrated but not thin:

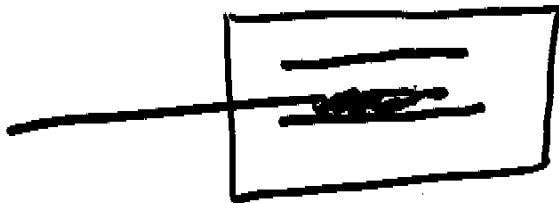
warning: distorted spectra
unless choose angle geometry

carefully. (low take-off angle)
(EXAFS correctable; XANES more difficult)

- alternatively use electron yield

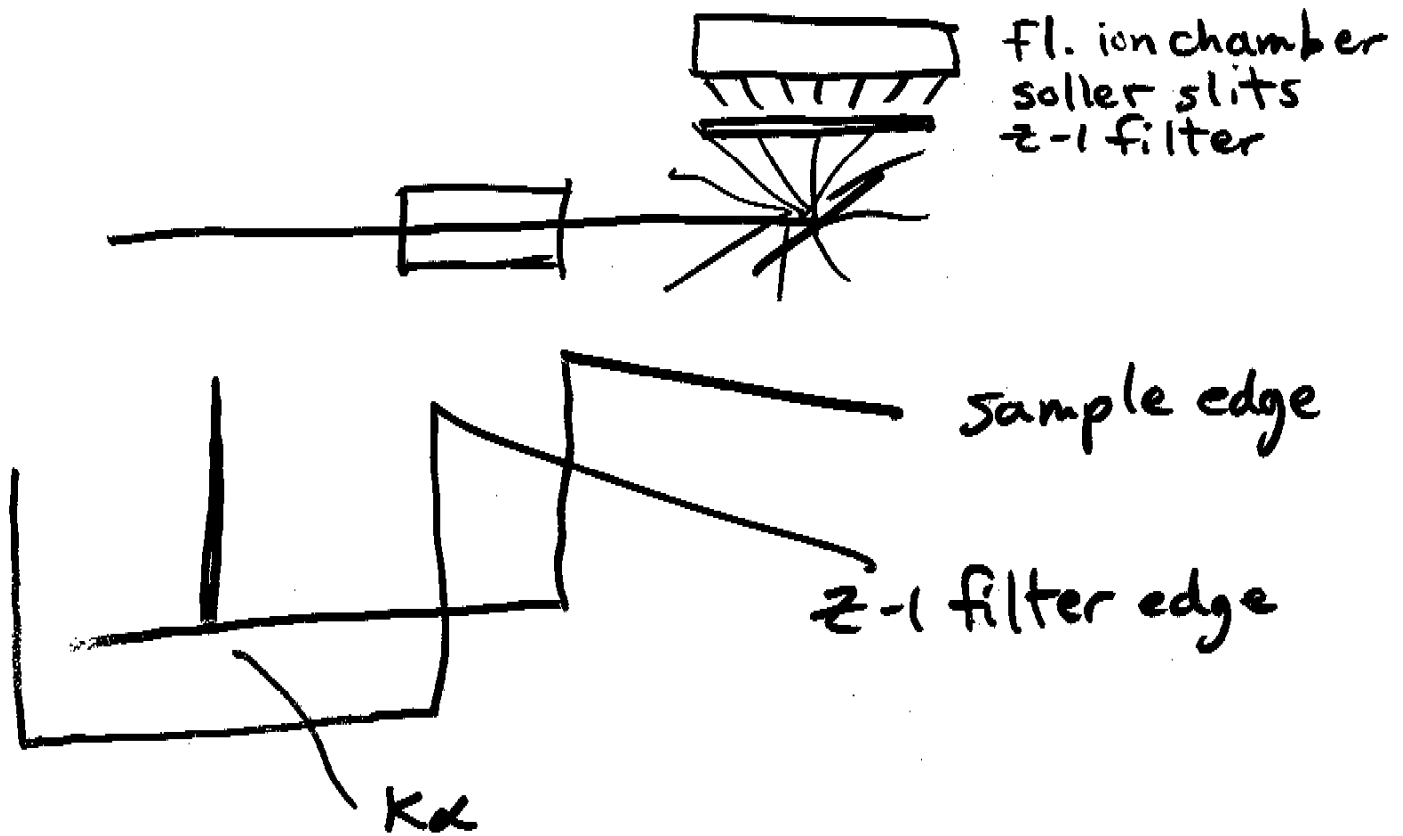


- electron yield
- fluorescence yield < 1
- radiationless transitions, auger electrons



- x-ray beam strikes sample which emits electrons
- electrons emitted within $\sim 1000 \text{ \AA}$ of surface can leave surface and excite He gas inside chamber
- ionization produced measured as in ion chamber
- only surface of sample is detected; always "thin" sample!

- optimizing filters



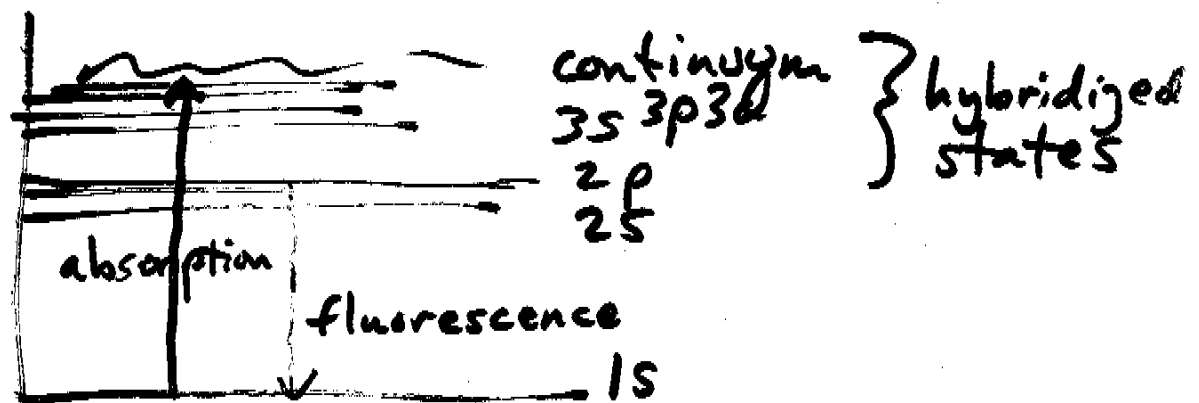
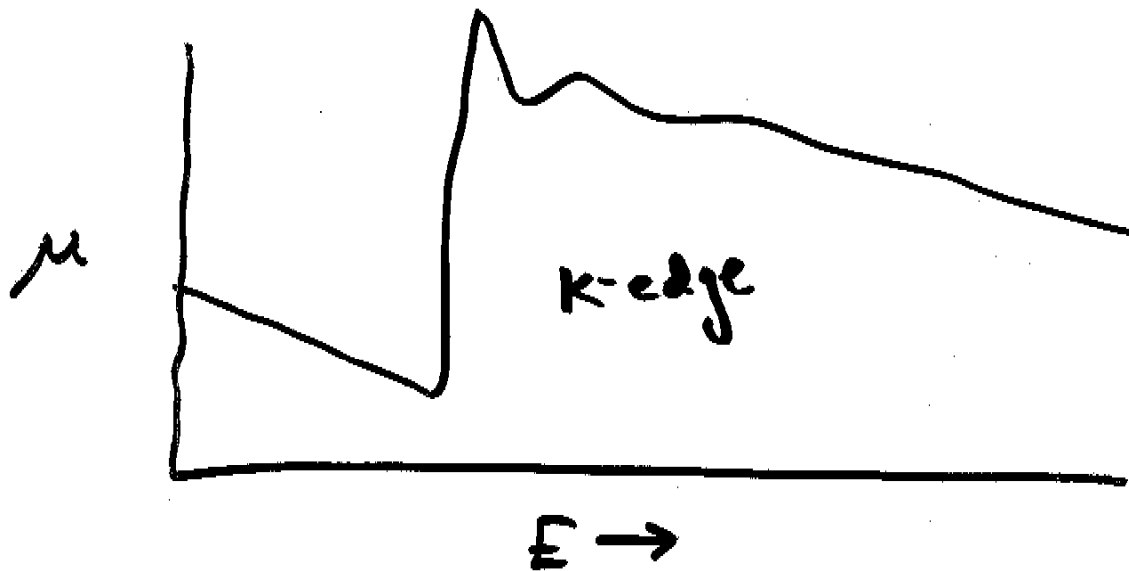
- filter absorbs scattered background

- slits reject fluorescence from filter

⇒ this technology should work well at APS if done right

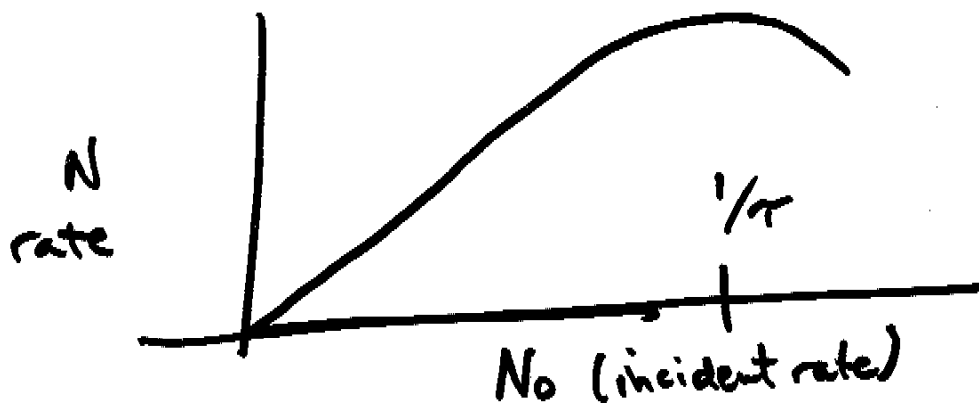
⇒ { see plots + tutorials by GB }

XAFS phenomenon



transition occurs if energy sufficient to raise electron to unfilled state of appropriate symmetry (e.g. $s \rightarrow p$; $p \rightarrow s, d$)

- characterize dead time



$$N = N_0 e^{-N_0 T}$$

or

$$N = N_0 (1 - N_0 T)$$

or

etc (depends on electronics)

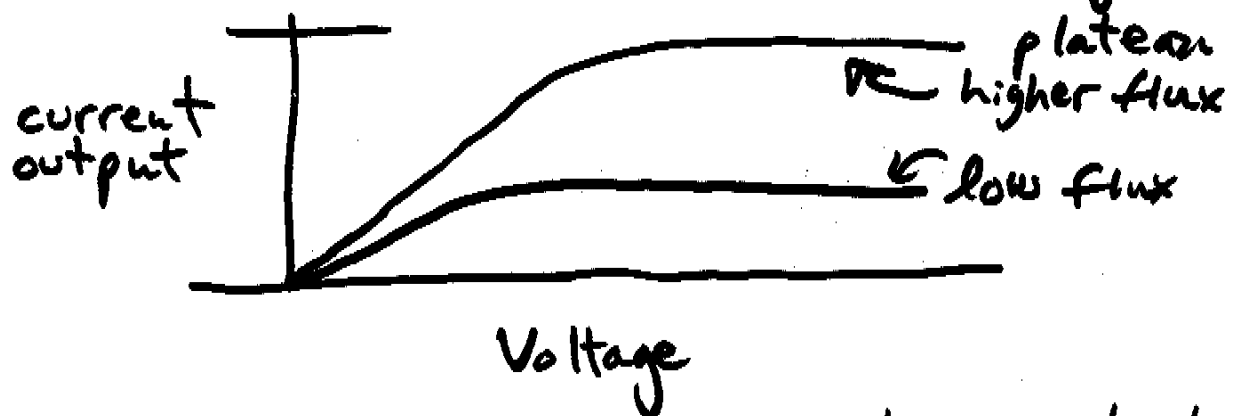
- deadtime usually several times
shaping time

- Know your detector system's dead time
characteristics

- limited by bunch rep rate of ring

- detector linearity is essential
far above edge, oscillations
may be $\sim 10^{-3}$ or 10^{-4} of edge step.
A factor of 2 drop in I chamber
intensity (as encountered over edge)
should have no effect on $\ln\left(\frac{I_0}{I}\right)$
to within $\sim 10^{-3}$ or better

- ion chamber plateau voltage



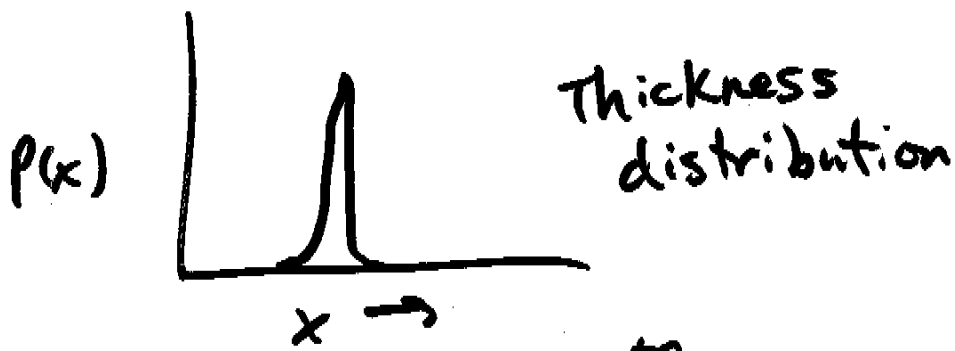
- ⇒ check linearity of detectors!
- ⇒ holding I_0 constant doesn't
do it because I still varies a lot
even when I_0 doesn't (edges!)

- considerations for exptal design
 - what edges are of interest?
 - beamline capabilities
 - how thick is sample you can get light through? (x)
 - what is the $\Delta\mu x$ of element of interest for sample thickness x ?
 - if $\Delta\mu x \lesssim .1$ consider fluorescence
 - also consider fluor. if sample inhomogeneous: Thickness effects less of a problem for fluorescence
- watch out for:
 - Thickness effects (transmission)
 - particle size effects (all)
 - self absorption (fluorescence)

- thickness effects

uniform sample (no harmonics)

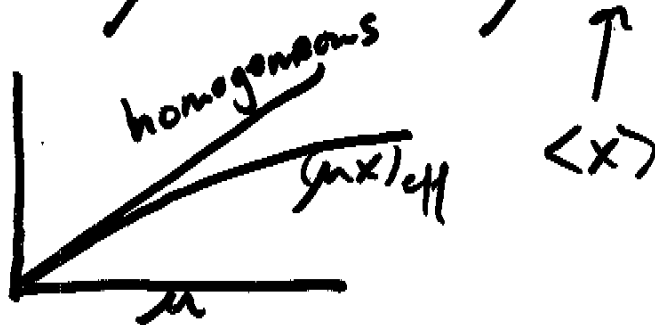
μx is just there



$$e^{-(\mu x)_{\text{eff}}} = \int_0^{\infty} P(x) e^{-\mu x} dx$$

$$-(\mu x)_{\text{eff}} = \sum_{n=1}^{\infty} \frac{C_n}{n!} (-\mu)^n \quad \text{cumulants}$$

$$(\mu x)_{\text{eff}} = \mu C_1 - \frac{1}{2} \mu^2 C_2 \dots$$



$\langle (x - \bar{x})^2 \rangle$
 { see mathematical notebook }

— "effective counts"

$$\frac{\text{Signal}}{\text{Noise}} = \frac{N_s}{\sqrt{N_s + N_B}}$$

what ~~count~~ count rate has this same S/N ratio in absence of background?

$$S/N = \sqrt{N_{\text{eff}}} = \frac{N_s}{\sqrt{N_s + N_B}}$$

$$\Rightarrow N_{\text{eff}} = \frac{N_s}{1 + \frac{N_B}{N_s}}$$

large background to signal ratio kills your effective counts.

\Rightarrow optimize conditions to improve N_{eff}

\Rightarrow filters, slits, ...



Fluorescence

$$e^{-\mu_T(E)x/\sin\theta}$$

prob gets to depth x

$$\mu_s(E) dx$$

prob absorbed

$$e^{-\mu_T(E_f)x/\sin\phi}$$

prob fluorescence gets out

$$\int_0^{x_{max}} \mu_s(E) e^{-\left(\frac{\mu_T(E)}{\sin\theta} + \frac{\mu_T(E_f)}{\sin\phi}\right)x} dx / \sin\theta$$

$$= \frac{\mu_s(E) / \sin\theta (1 - e^{-\left(\frac{\mu_T(E)}{\sin\theta} + \frac{\mu_T(E_f)}{\sin\phi}\right)x_{max}})}{\left(\frac{\mu_T(E)}{\sin\theta} + \frac{\mu_T(E_f)}{\sin\phi}\right)}$$

(include factors for solid angle $\Omega/4\pi$ and fluorescence yield ϵ for absolute number)

EXAFS is simpler to interpret quantitatively than optical spectroscopy

- initial state simple (1s, localized)
- above edge, not too sensitive to chemistry
(basically just scattering)

How long does it take?

EXAFS takes a snapshot

$\sim 10^{-15}$ sec core hole lifetime
before deexcitation
(faster for high Z)

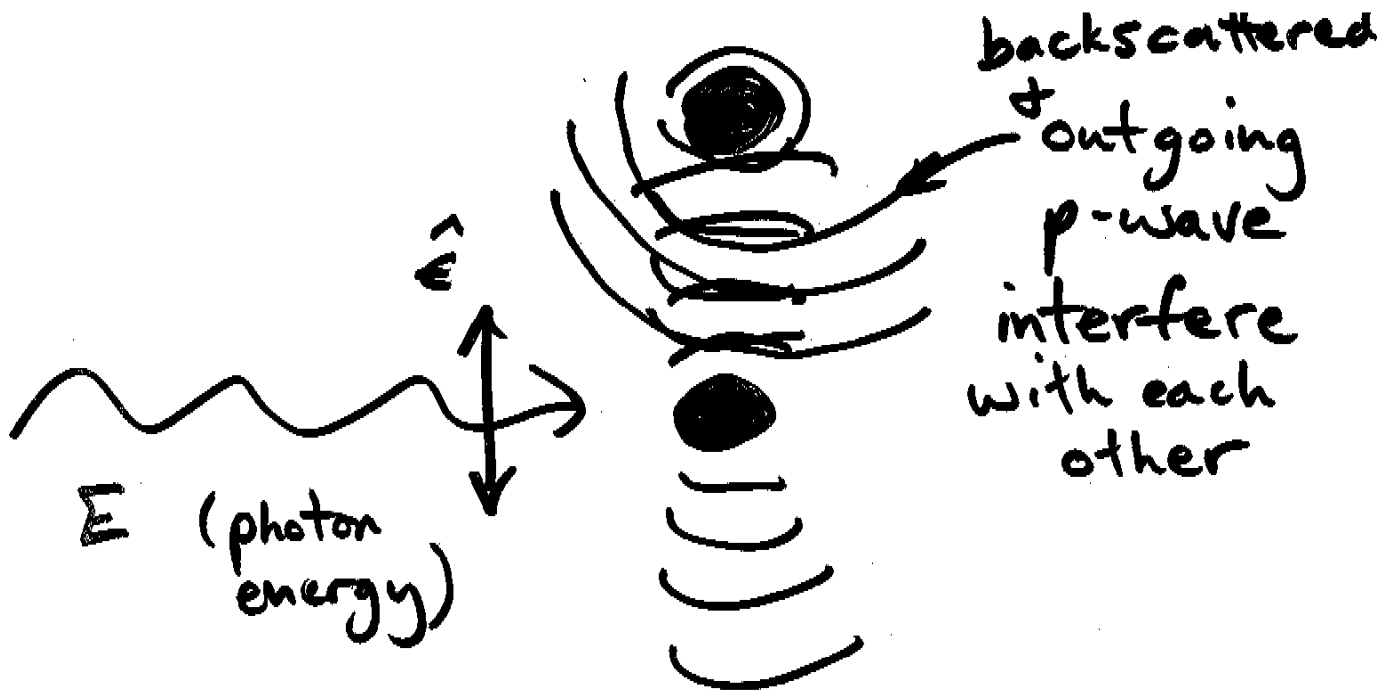
vibrational periods $\sim 10^{-12}, 10^{-13}$ sec

atoms are frozen in mid cycle
of vibrations

we always measure ensemble
average of absorbing atoms

\Rightarrow have to average theoretical
expressions appropriately

\Rightarrow Core hole broadening $\Delta E \sim \frac{\hbar}{\tau}$
 $\sim 1\text{eV} \Rightarrow$ increases for high Z



$$\frac{\hbar^2 k^2}{2m} = E - E_0$$

↑ edge energy

↑ x-ray energy

↑ $k =$ electron wavenumber

$$k = \frac{2\pi}{\lambda_{\text{electron}}} = \frac{p}{\hbar}$$

Scanning E literally records interferogram of environment of absorbing atom

XAFS is inherently a quantum effect
time dependent perturbation theory

absorption prob/time $\propto |\langle f | H' | i \rangle|^2 \delta(E_f - E_i)$

Fermi's
'golden
rule'

$\equiv \left| \int \psi_f^* H' \psi_i \right|^2 \delta(E_f - E_i)$

H' expresses interaction between incident x-ray and electron

↑
energy conservation

$H' \propto \frac{e\vec{A} \cdot \vec{p}}{m}$

\vec{A} is vector potential of x-ray

\vec{p} is momentum of electron

for our purposes sufficient to take \vec{A} as applied field. (Quantizing field doesn't change result significantly.)

How big is 1s state? Estimate!

(who cares? need to justify dipole approximation)

1s state sees unscreened nuclear charge (all other electrons at larger radius)

Approximate as hydrogenic atom (nuclear) charge Ze

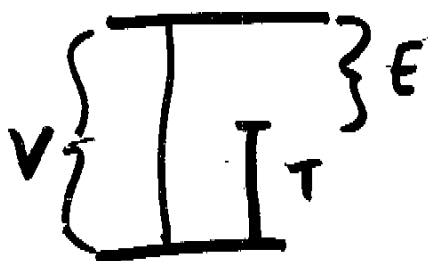
hydrogen atom $E = -\frac{1}{2} \alpha^2 (mc)^2$

$$E = -\frac{1}{2} \frac{e^4}{\hbar^2 c^2} mc^2$$

$$= -\frac{1}{2} \frac{me^4}{\hbar^2} \text{ (rydberg)}$$

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

fine structure constant



virial thm \sim

$$E = \frac{1}{2} V = \frac{1}{2} \frac{e}{a_0} = \frac{me^4}{\hbar^2}$$

$$\Rightarrow a_0 = \frac{\hbar^2}{me^2} \text{ (Bohr radius)}$$

$$\mu \propto |\langle f | \vec{E} \cdot \vec{r} e^{i\vec{k} \cdot \vec{r}} | i \rangle|^2$$

\vec{k} x-ray wavevector

k electron wavenumber

$|i\rangle$ is initial state (1s)

$|f\rangle$ is final state w.f.

(mixture of outgoing + scattered waves)

They interfere.

Because it's an integral of the product of w.f.s, and the initial state is localized around the nucleus of the absorbing atom,

μ depends on interference pattern at center of absorber.

atomic units $m, e, \hbar \rightarrow 1$
(wonderful invention!)

$$E = -\frac{1}{2} \frac{me^4}{\hbar^2} \Rightarrow -\frac{1}{2}$$

\Rightarrow energy unit = 2 Rydberg
"Hartree" $\approx 27.2 \text{ eV}$

$$a_0 = \frac{\hbar^2}{me^2} \Rightarrow 1$$

\Rightarrow length unit = 1 bohr radius
"Bohr" $\approx 0.529 \text{ \AA}$

for nuclear charge Z

$$e^2 \Rightarrow Ze^2$$

$$\Rightarrow E \Rightarrow -\frac{Z^2}{2} \quad (\text{a.u.})$$

$$a_0 \Rightarrow \frac{1}{Z} \quad (\text{a.u.})$$

(remember $E \sim Z^{2.17}$ empirically?)

$$|\langle f | \vec{\epsilon} \cdot \vec{r} e^{i\vec{k} \cdot \vec{r}} | i \rangle|^2$$

because the state $|i\rangle$ extends only over radius $\sim \frac{1}{z}$ (Bohr) we can estimate the importance of the term $e^{i\vec{k} \cdot \vec{r}}$ ($\frac{z}{2c}$ in a.u.)

$$\begin{aligned} \langle \vec{k} \cdot \vec{r} \rangle &\sim \frac{E}{\hbar c} \frac{a_0}{z} \sim \frac{z}{2} \frac{m e^4}{\hbar^2 \hbar c} \frac{\hbar^2}{m z e^2} \\ &= \frac{1}{2} z \frac{e^2}{\hbar c} = \frac{z}{2} \alpha = \frac{z}{2 \cdot 137} \end{aligned}$$

note that $\langle r \rangle$ is not the atomic size (on the order of \AA); if it were we would not be able to consider $\langle \vec{k} \cdot \vec{r} \rangle$ small, since $|\vec{k}| \sim \frac{2\pi}{\lambda_{\text{photon}}}$

$$e^{i\vec{k}\cdot\vec{r}} \approx 1 + (i\vec{k}\cdot\vec{r}) + \frac{(\vec{k}\cdot\vec{r})^2}{2} + \dots$$

$$\langle f | \hat{\epsilon}\cdot\vec{r} e^{i\vec{k}\cdot\vec{r}} | i \rangle$$

$$\approx \langle f | \hat{\epsilon}\cdot\vec{r} | i \rangle + i \langle f | (\hat{\epsilon}\cdot\vec{r})(\vec{k}\cdot\vec{r}) | i \rangle + \dots$$

↑
dipole

↑ + ...
quadrupole

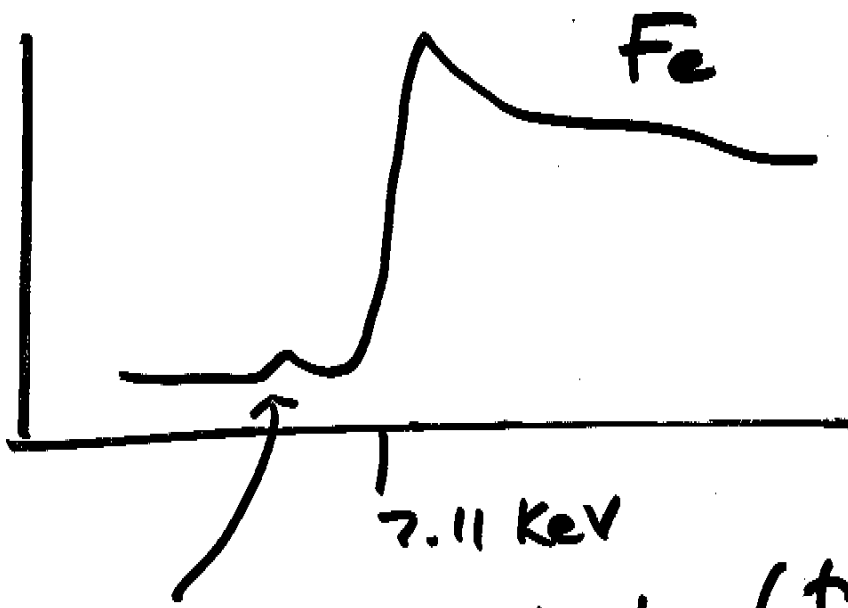
$$\frac{\mu_{\text{quad}}}{\mu_{\text{dipole}}} \sim \langle \vec{k}\cdot\vec{r} \rangle^2 \sim \left(\frac{z\alpha}{2}\right)^2$$

K-edge	~ 0.5%	z = 20 (Ca)
	~ 10%	z = 92 (U)

radius of initial state larger yet

(~ 4 times) for L-edges.

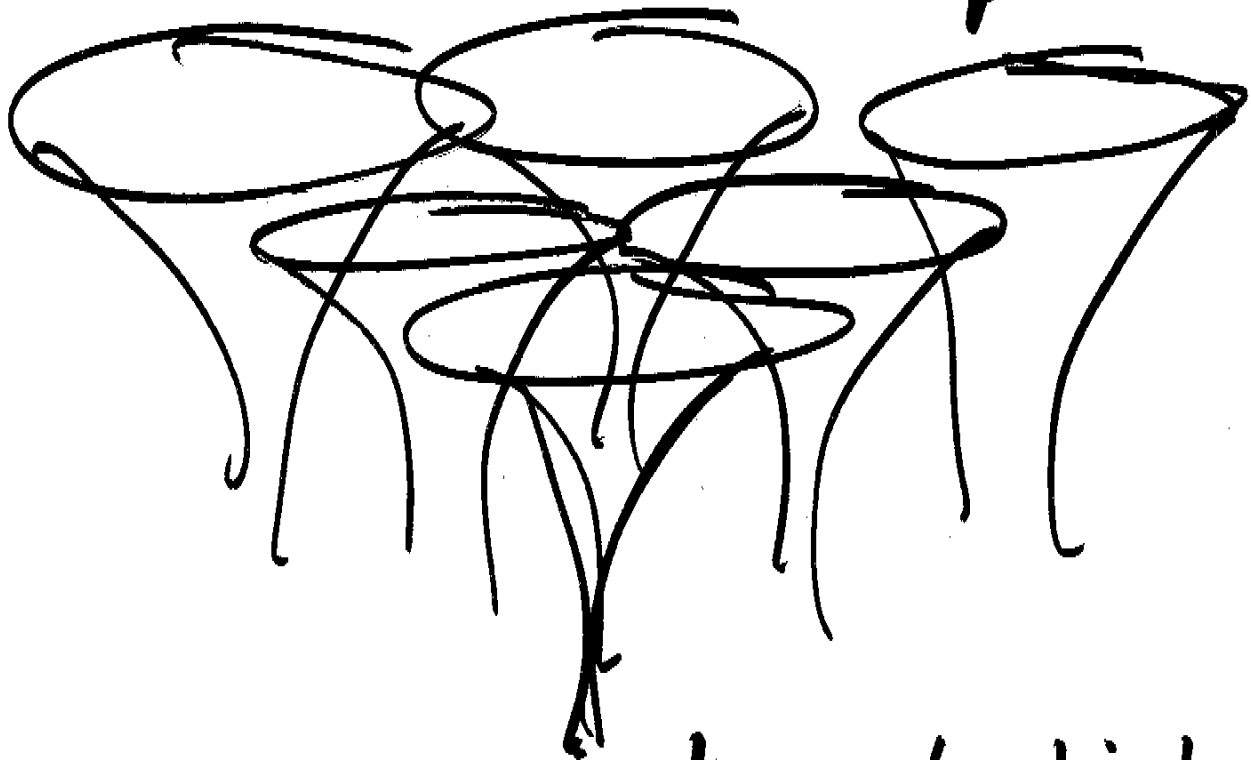
⇒ quadrupole not always negligible for high z



3d hybridized levels (transitions dipole forbidden in inversion symmetric environment)
 can map out quadrupole from angle dependence
 (Hahn et al)
 (Pinner-Hahn)

⇒ you can see quadrupole transitions if not masked by dipole

"muffin tin potential"



- ⇒ approximate potential as spherically symmetric scatterers with flat (constant potential) interstitial region.
- ⇒ w.f.s separate into radial dependence * spherical harmonics inside muffin tins
- propagating waves in flat region
- match boundary conditions to get soln.

EXAFS: normally assume
dipole approx

$$\mu(E) = 4\pi^2 \alpha \omega \sum_f |\langle f | \hat{\mathbf{E}} \cdot \vec{r} | i \rangle|^2 \delta(E - E_f)$$

(in atomic units $e = \hbar = m = 1$)

$$\mu \propto -\frac{1}{\pi} \text{Im} \langle i | \hat{\mathbf{E}} \cdot \vec{r} G(\vec{r}, \vec{r}'; E) \hat{\mathbf{E}} \cdot \vec{r} | i \rangle \theta(E - E_f)$$

$$G = (E - H + i\eta)$$

$$H = H_0 + V$$

H
single
particle
hamiltonian
+ Green's
function

$$\theta(E) = \frac{1}{\pi} \arctan\left(\frac{\Gamma_e}{E_f - E}\right)$$

$$H_0 = -\frac{\nabla^2}{2} + V_{\text{int}} \quad \text{--- interstitial potential}$$

$$H = H_0 + V$$

$$S_V = V - V_{\text{int}}$$

S_V is
scattering
potential

MS expansion follows from expanding Green's function in Dyson series

$$G = G^0 + G^0 T G \quad *$$

$$G^0 \equiv (E - H_0 + i\eta)^{-1} \quad \text{G.F. system no scatterers}$$

$$G \equiv (E - H + i\eta)^{-1} \quad \text{total G.F.}$$

$$G^c \equiv (E - H_c + i\eta)^{-1} \quad \text{central atom G.F.}$$

$$G = G^c + \sum_{i \neq 0} G^c t_i G^c + \sum_{\substack{i \neq j \\ i, j \neq 0}} G^c t_i G^0 t_j G^c + \dots$$

$$\equiv \sum_{\Gamma} G^{\Gamma}$$

↑ sum over paths

* follows from operator identity

$$A^{-1} = B^{-1} + B^{-1} (B - A) A^{-1}$$

(confirm by multiplying both sides by A)

(right and left multiply both check out) ✓

- all paths Γ begin + end at central atom
- no scatterer repeated twice in a row
 (e.g. 1-2-3-1 allowed but 1-2-2-1 is not)

Rehr, Albers, Zabinsky, Ankudinov et al have shown this MS expansion can be expressed as

$$\mu(E) = \mu_0(E) \left(1 + \sum_{\alpha\beta} \epsilon_\alpha \epsilon_\beta \chi_{\alpha\beta}(E) \right)$$

$$\chi_{\alpha\beta} = \sum_{\Gamma} \chi_{\alpha\beta}^{\Gamma}$$

$$\chi_{\alpha\beta}^{\Gamma} = \text{Im} S_0 \frac{e^{2i(\rho_1 + \rho_2 - \rho_n + 2\delta_1)}}{\rho_1 \rho_2 \dots \rho_n}$$

$l = K r_n$
 $\xrightarrow{\text{length of } \Gamma}$ path
 $\rho_1 \dots \rho_n$ nth
 $\times \text{Tr} M_{\alpha\beta} F \dots F e$
 \downarrow
 scattering matrices

or in more conventional notation

$$\chi^{\Gamma}(\mathbf{k}) = \sum_{\Gamma} \frac{S_0}{KR^2} |f_{\Gamma}^{\Gamma}(\mathbf{k})| \sin(2kR + \phi^{\Gamma}(\mathbf{k}) + 2\delta_{\Gamma}^{\Gamma}(\mathbf{k}))$$

$$\times e^{-2k^2 \sigma_r^2 - 2R/\lambda(\mathbf{k})}$$

$2R = \overset{\text{average}}{\text{length of path}}$

$\sigma_r^2 = \langle (R - \langle R \rangle)^2 \rangle$ mean
square
variation in
path length

Note this is of same form as
Sayers, Stern + Lytle's original ~~single~~
scattering formula, but with
effective scattering amplitude &
phases: f_{eff} .

whence the famous program
"FEFF"

(up to FEFF7 at this time)

K-edge, plane wave, oriented, sum over atoms

$$\chi(k) = \sum_i^{\text{atoms}} 3 \cos^2 \theta_i \frac{|f_i(k)|}{k r_i^2} e^{-2r_i/\lambda(k)} \sin(2k r_i + 2\delta_i(k) + \text{Arg } f_i(k))$$

$$\cos \theta_i = \hat{e} \cdot \hat{r}_i$$

central atom phase shift (l=1 shown)
 phase of complex scattering amplitude

Plane, angle average, shells

$$\chi(k) \approx S_0 \sum_j^{\text{shells}} \langle 3 \cos^2 \theta_j \rangle \frac{N |f_j(k)|}{k R_j^2} e^{-2k R_j} \sin(2k R_j + \delta_j(k))$$

this averages to 1 for isotropic average (no preferred orientation of sample)

If $f(k) \rightarrow F_{\text{effective}}(k,r)$ this traditional plane wave formula is of same form as more rigorous modern form (no accident!)

what you do to calculate ab initio XAFS spectra

- make atoms
(self consistent, preferably relativistic)
 - superimpose charge densities
by putting atoms in right places (approx)
 - Spherically average within muffin tins,
average interstitial potential
(add energy dependent self energy)
 - At each energy, integrate out radial
w.f.'s, match b.c.'s to get scattering
phase shifts $\delta_l(k)$ for each atom
(also calc μ_0 for central atom)
 - construct T matrices + propagators
 - simmer until done, season to taste
- ⇒ χ : Guess what?
Feff does it all for you!

Disorder

(when is a shell a shell?)
 (after G.B. 1983)

consider a single shell (1 atom type)

$$\chi(k) = N B(k) \int_0^{\infty} \frac{p(r)}{r^2} e^{-2r/\lambda} \sin(2kr + \delta(k)) dk$$

$$B(k) \equiv \frac{S_0^2 F(k)}{k}$$

$$2\delta(k) + \delta_1(k)$$

$$= N \operatorname{Im} \left[e^{i\delta} \int_0^{\infty} p(r) e^{2ikr} dr \right] \quad (\text{fourier transform})$$

$$p(r) \equiv \frac{p(r)}{r^2} e^{-2r/\lambda} \quad \text{"effective distribution"}$$

$$\hat{\chi}(k) = A(k) e^{i\varphi(k)}$$

$$\chi(k) = \operatorname{Im} \hat{\chi}(k)$$

$$\ln \hat{X}(k) = \ln A(k) + i\varphi(k)$$

$$\ln A(k) = \operatorname{Re} \ln \hat{X}(k)$$

$$\varphi(k) = \operatorname{Im} \ln \hat{X}(k)$$

can expand

$\ln \hat{X}(k)$ in power series in k

$$\ln \hat{X}(k) = \sum_{n=0}^{\infty} \frac{C_n}{n!} (2ik)^n$$

C_n are "cumulants" of
effective distribution $P(r)$

$$\ln \left(\frac{A(k)}{NB(k)} \right) = C_0 - 2k^2 C_2 + \frac{2}{3} k^4 C_4 \dots$$

$$\varphi(k) - \delta(k) = 2k C_1 - \frac{4}{3} k^3 C_3 + \dots$$

$$\exp[C_0] = \langle 1 \rangle \equiv e^{-2\sigma^2/\lambda^2}$$

$$C_1 = \langle r \rangle ; \quad \langle h(r) \rangle \equiv \int \frac{p(r)}{r^2} e^{-2r/\lambda} h(r) dr$$

any $h(r)$

$$C_2 = \langle (r - \bar{r})^2 \rangle$$

$$C_3 = \langle (r - \bar{r})^3 \rangle$$

$$C_4 = \langle (r - \bar{r})^4 \rangle - 3 \langle (r - \bar{r})^2 \rangle^2$$

⋮

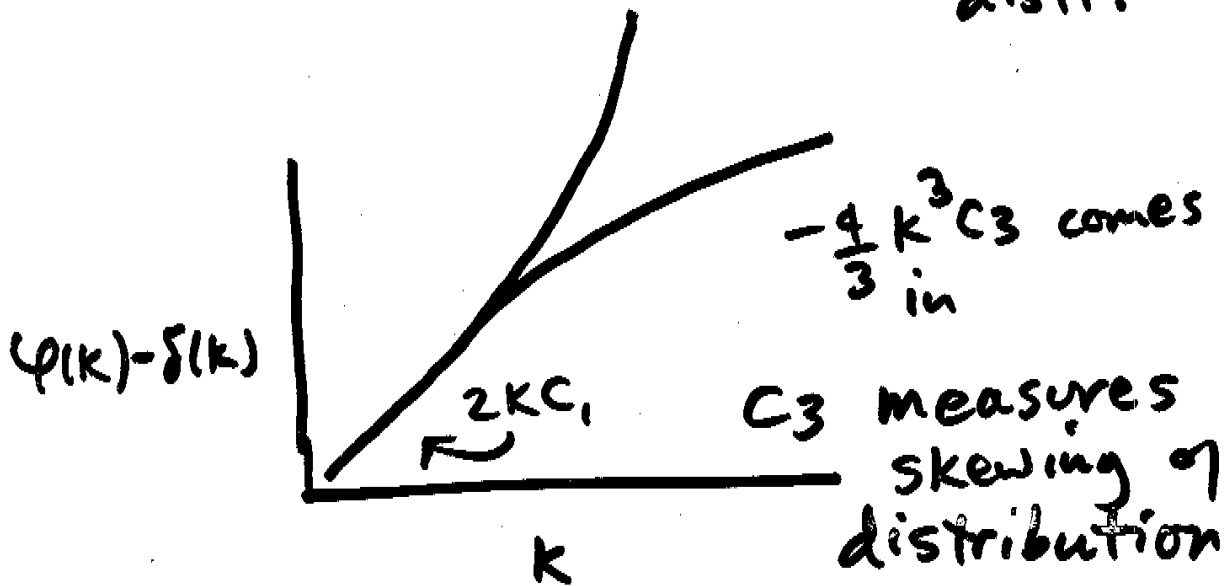
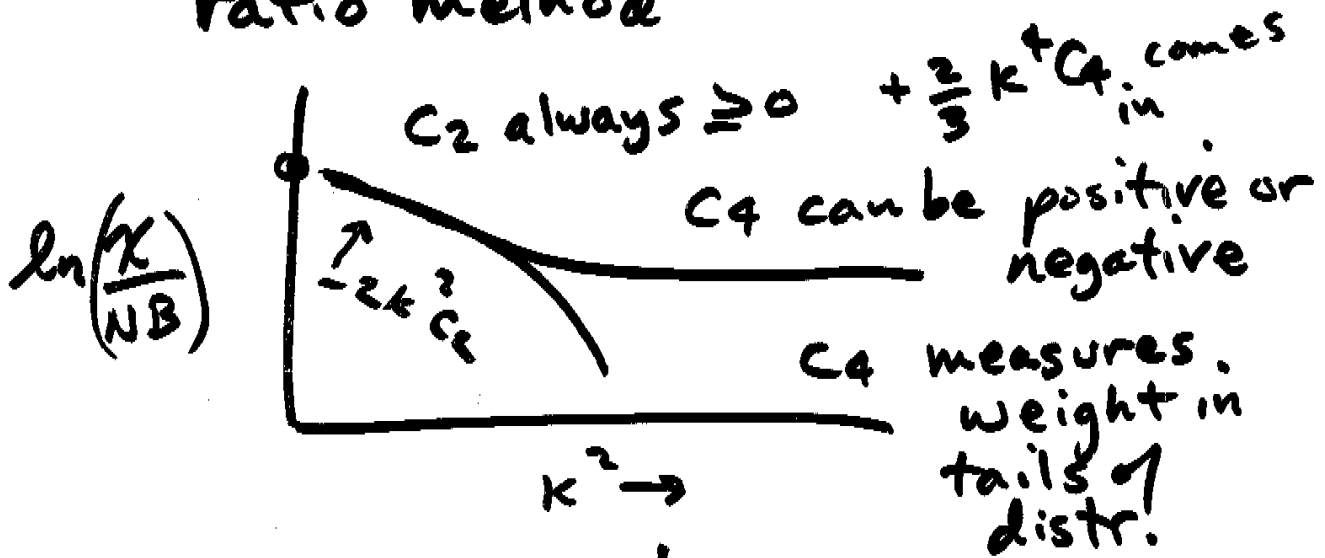
- for a gaussian effective distr.,
 $C_n = 0$ for $n > 2$
- if you convolute two distributions,
 their cumulants just add
- C_n are independent of origin
 for $n > 1$

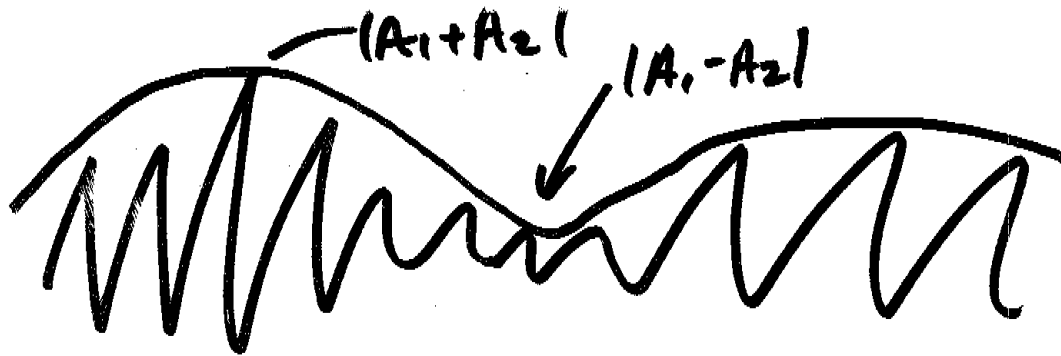
single shell

$$\chi(k) = NB(k) e^{C_0 - 2k^2 C_2 + \frac{2}{3} k^4 C_4 \dots}$$

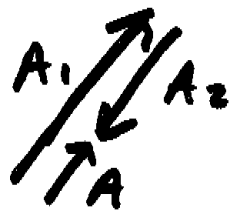
$$\times \sin(2kC_1 - \frac{4}{3} k^3 C_3 + \dots + \delta(k))$$

ratio method





- at a beat, A_1 and A_2 phases differ by 180° (π) on $(2n+1)\pi$



$$- A^2 = A_1^2 + A_2^2 + 2A_1A_2 \cos(\pi)$$

$$A = |A_1 - A_2|$$

$$- \Delta\varphi = (2n+1)\pi \quad \pm(\pi, 3\pi, \dots)$$

$$n = 0, \pm 1, \dots$$

$$2k\Delta r = (2n+1)\pi$$

$$\Rightarrow \Delta r = \frac{\pi}{2k_{\text{beat}}} \text{ etc}$$

if same type of atom

$$- 2k\Delta r = (2n+1)\pi - \Delta\delta \text{ if different types of atom in two shells}$$

(approximately)

doesn't matter - effect is same

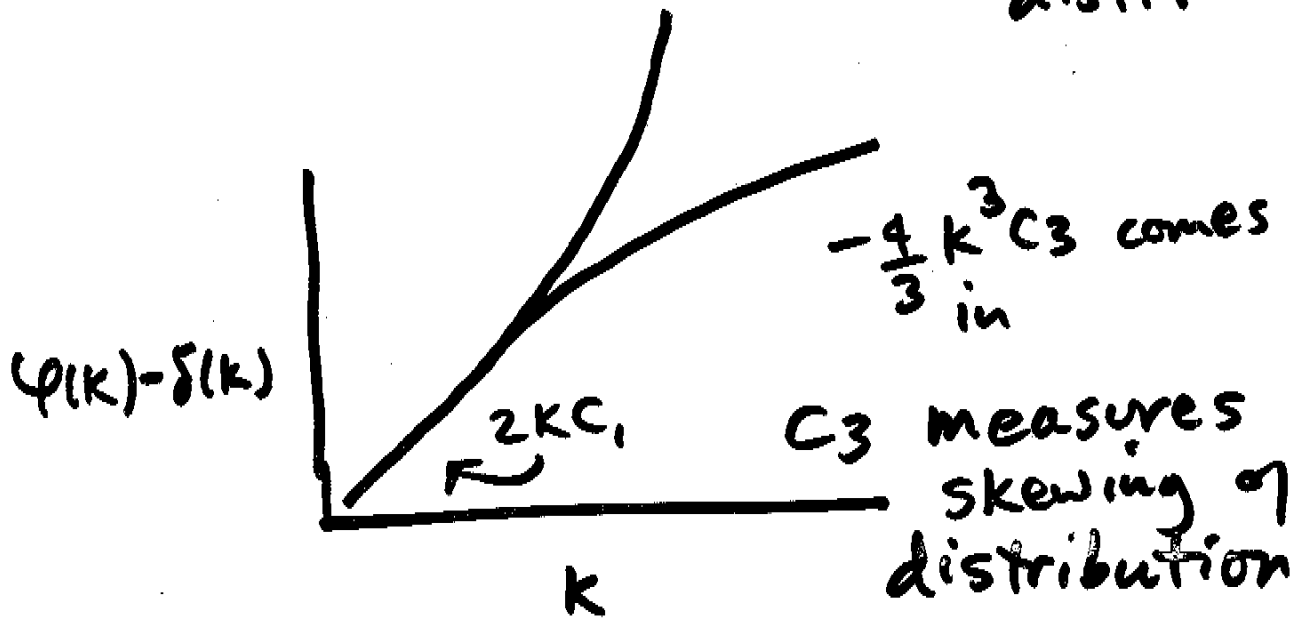
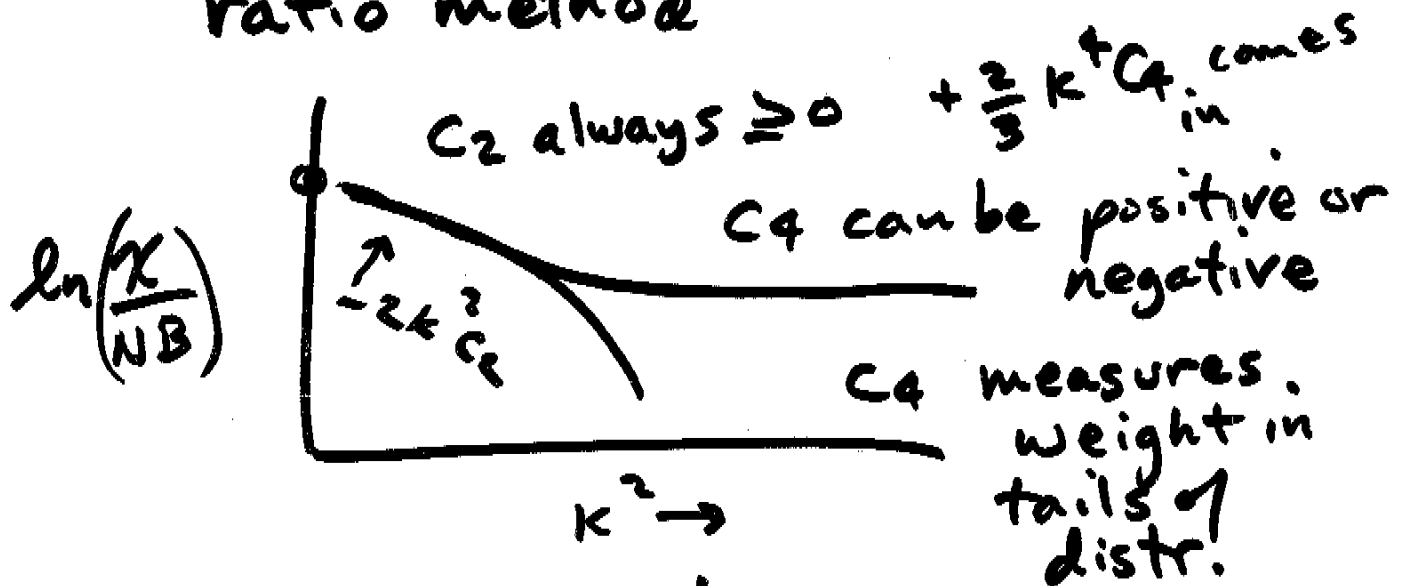
END

single shell

$$\chi(k) = NB(k) e^{C_0 - 2k^2 C_2 + \frac{2}{3} k^4 C_4 \dots}$$

$$\times \sin(2kC_1 - \frac{4}{3} k^3 C_3 + \dots + \delta(k))$$


ratio method



$n \geq 2$ Cumulants cannot generally be neglected unless $k_{max} \sigma \ll 1$

presence of additional terms in phase & amplitude can cause erroneous distances & coordination numbers if neglected.

e.g. for $C_3 > 0$ (positive skewness)

 average phase slope reduced, causing peaks in FT to shift to lower r .

Can often see effect in ratio plot but comes out in fitting if done right

Cumulant approach provides model independent description of distribution of distances

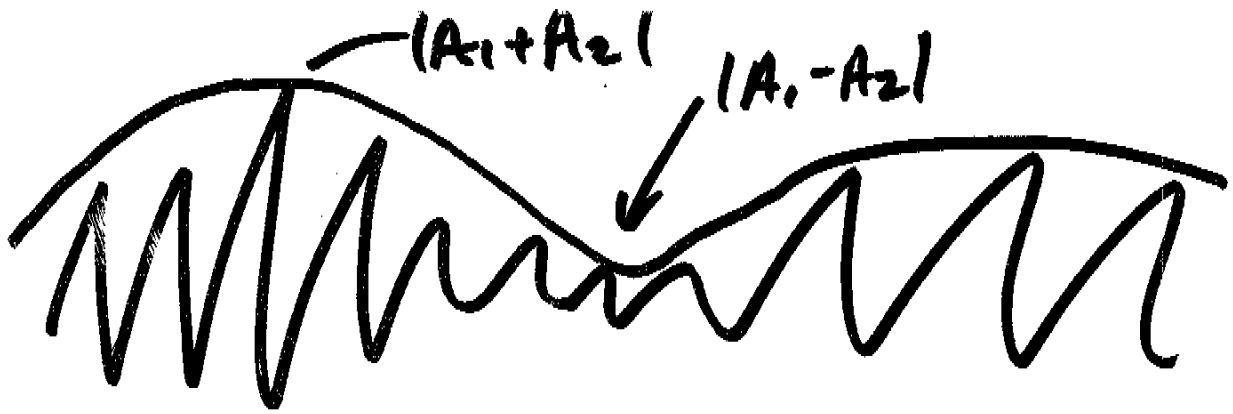
$C_1 \sim \frac{2\sigma^2}{F}$ shorter than centroid of real distribution

(see GB thesis for general formulae)

(usually only C_1 shift matters)

Cumulant expansion useful when small to moderate disorder present $K_{\max} \sigma \ll 1$

Breaks down completely at a "beat"



- at a beat, A_1 and A_2 phases differ by $180^\circ (\pi)$ on $(2n+1)\pi$

$$- A^2 = A_1^2 + A_2^2 + 2A_1A_2 \cos(\pi)$$

$$A = |A_1 - A_2|$$

$$- \Delta\varphi = (2n+1)\pi \quad \pm(\pi, 3\pi, \dots)$$

$n = 0, \pm 1, \dots$

$$2k\Delta r = (2n+1)\pi$$

$$\Rightarrow \Delta r = \frac{\pi}{2k_{\text{beat}}} \text{ etc}$$

if same type of atom

$$- 2k\Delta r = (2n+1)\pi - \Delta\delta \text{ if different types of atom in two shells}$$

Beats

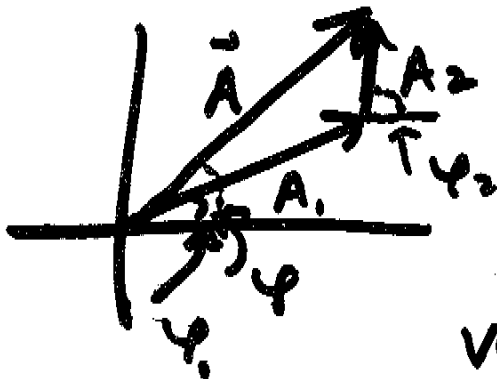
$$A e^{i\varphi} = A_1 e^{i\varphi_1} + A_2 e^{i\varphi_2}$$

$$A \cos \varphi = A_1 \cos \varphi_1 + A_2 \cos \varphi_2$$

$$A \sin \varphi = A_1 \sin \varphi_1 + A_2 \cos \varphi_2$$

$$\Rightarrow \tan \varphi = \frac{\sum_j A_j \sin \varphi_j}{\sum_j A_j \cos \varphi_j}$$

$$\Rightarrow A^2 = A_1^2 + A_2^2 + 2A_1 A_2 \cos(\varphi_1 - \varphi_2)$$

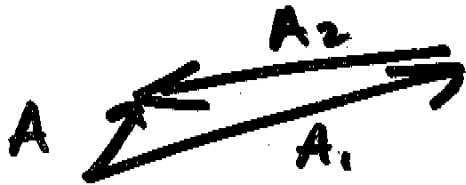


each contribution

\hat{x} has a magnitude $A(k)$ and phase $\varphi(k)$

As k increases, imagine vectors rotating - speed of rotation proportional to \bar{v} (approximately)

at a beat, phase jumps too



$K < K_{beat}$

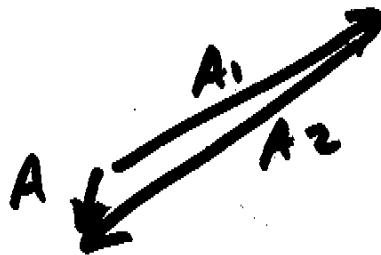


$K > K_{beat}$

— if smaller amplitude shell is larger distance, phase jump negative ↙



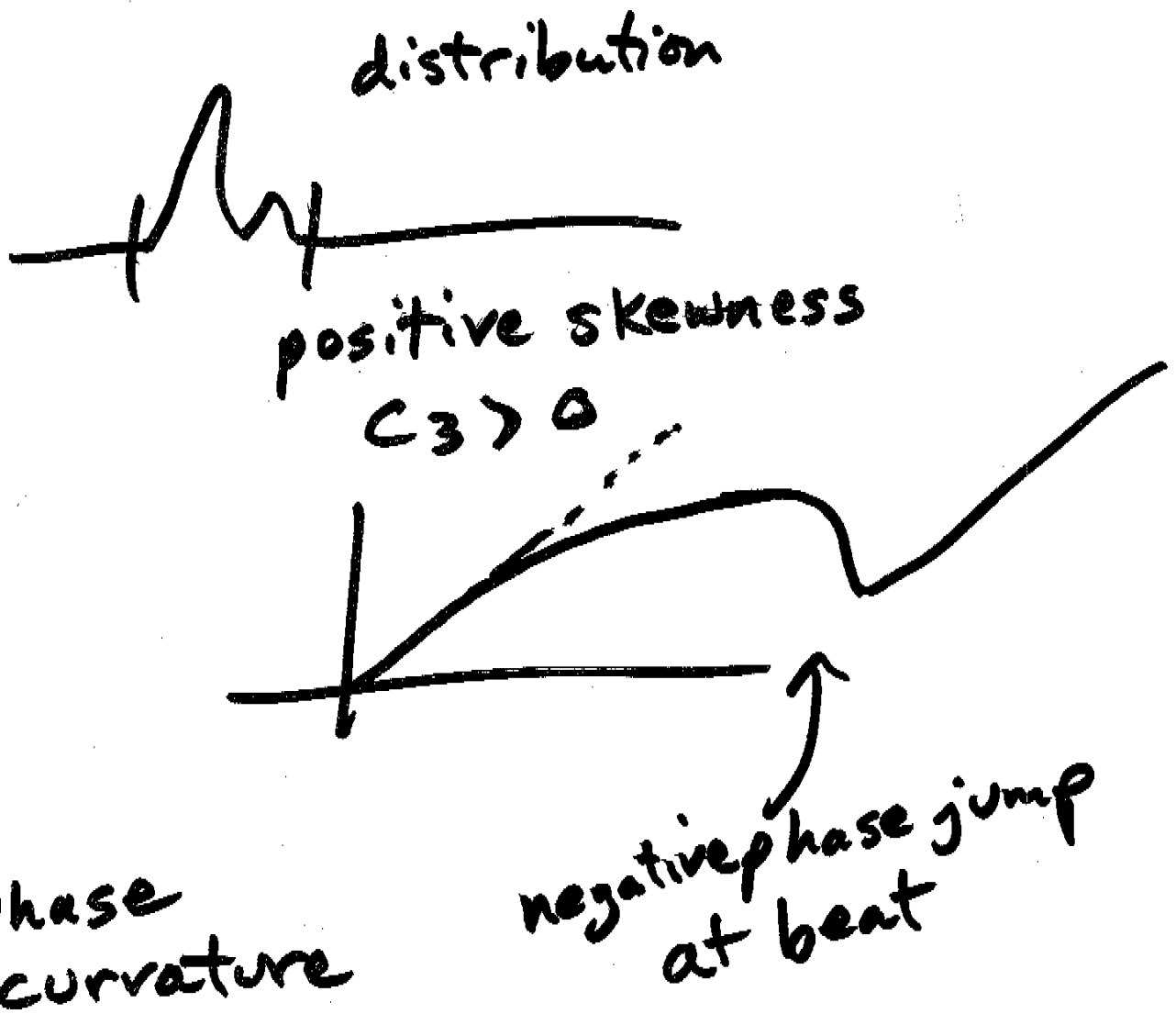
$K < K_{beat}$



$K > K_{beat}$

— if smaller amp shell is smaller dist, phase jump positive ↘

(if they're equal, phase jump is π so doesn't matter - effect is same)



from cumulant C_3
is prelude to a beat

- if $A_1 = A_2$, discontinuity at beat is sharp \Rightarrow need all orders in cumulant expansion.
- cum. exp not useful close to beat
 $k_{beat} = \pi/2\omega$