Review

- Sources
  - bond magnets
  - wigglers
  - undulators

- detectors
  - ion chambers (transmission + fluorescence)
  - PIN diodes
  - Energy dispersive solid state detectors
  - Avalanche Photodiodes
  - PMTs with fast plastic scintillators

- electron yield

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

energy deposited between plates:
\[ N_{\text{photons}} E (1 - \exp \left[ -\frac{N_{\text{photons}} E}{N_{\text{gas}}} \right] ) \]

current
\[ \sim \frac{\text{photons}}{\text{sec}} \frac{\text{Energy}}{\text{photon}} \left( \frac{1}{\text{electron}} \right) \left( 1 - e^{-\frac{N_{\text{photons}} E}{N_{\text{gas}}}} \right) \]

conversion factor \( \sim 3 \times 10^6 \frac{\text{photons}}{\text{sec} / \text{volt} @ 10^6 \text{ gain}} \) Fe Kα
- Fluorescence mode

why is detector placed at 90° in horizontal plane?

Scattered background minimum along x-ray polarization vector

- If 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
\[ \text{photons absorbed} \quad \frac{\text{time}}{\text{time} \cdot \text{area}} = \frac{\text{photons}}{\text{time} \cdot \text{area}} \times \text{cross section (area)} \]
\[ \uparrow \]
\[ \text{cross section} \times \text{atoms} \quad \frac{\text{atom}}{\text{in beam}} \]
cross section \( \sigma \) often expressed as \( \frac{\text{area}}{\text{mass}} \):
— linear absorption coefficient
\[ dN = -N \, (\mu \, dx) \]
\[ \Rightarrow \ln N = -\mu x + \text{const} \quad \text{probability absorbed in } dx \]
\[ N = \frac{N_0}{e^{\mu x}} \]
— \( \mu \) "absorption length"
\[ \text{single species} = \varepsilon \sigma = \left[ \frac{g}{cm^2} \right] \left[ \frac{cm^2}{g} \right] = \text{cm}^{-1} \]
multiple species \( \mu = \sum_i \varepsilon_i \sigma_i = \varepsilon \sum_i \left( \frac{m_i}{M} \right) \sigma_i \)
Example: Fe$_2$O$_3$

Fe K-edge @ 7.1 keV

What is absorption at 7.2 keV?

$\Rightarrow$ use tables (e.g. McMaster, Int/tables, mical, ...)

Fe \[ \sim 393 \text{ cm}^2 \text{ g}^{-1} \text{ at 7.2 keV} \] 56 g/mol

O \[ \sim 15 \text{ cm}^2 \text{ g}^{-1} \text{ at 7.2 keV} \] 16 g/mol

MW = 2 \times 56 + 3 \times 16 = 160 g/mol

\[ \tau = \rho \left( \frac{393 \times 112}{160} + 15 \times \frac{48}{160} \right) \text{ cm}^2 \text{ g}^{-1} \]

\[ \approx \rho \, 280 \text{ cm}^2 \text{ g}^{-1} \text{ if } \rho = \frac{5 \text{ g}}{\text{ cm}^3} \]

\[ \mu \approx 1400 \text{ cm}^{-1} \]

\[ \mu' \approx 7 \mu \text{m} \]

need particle sizes \( \leq 7 \) micron!
Example: U metal

$U \ L_{III} \ edge \ 17.2 \ \text{keV}$

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

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

$1 / \mu = 11 \ \text{micron}$

Example: Ar gas at $U \ L_{III} \ edge$

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

$40 \text{g/mol}$

$\mu = 13 \text{cm}^2 / g \times \frac{40 \text{g}}{\text{mol}} \times \frac{\text{mol}}{24.58 \times 1000 \text{cm}^3} \times \frac{1}{14} = 0.021 / \text{cm}$

$1 / \mu = 47 \ \text{cm}$

10 cm ion chamber absorbs $\sim 20\%$ of beam, ok for Io.
- optics

- double crystal monochromator
  
  Si, Ge, C (diamond) \( n_A = 2d \sin \theta \)

  allowed reflections \( (hke) \)
  
  \( 111, 220, 311, 331, 333, 900, 422, 440, 444, 511, 531, 533, 551, 553, 555, \ldots \)

  \[
  d_{hke} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}; \quad E = \frac{hc}{2d \sin \theta} \]

  \( hc \approx 12398.6 \text{ ev} \text{A} \)

  \[
  \frac{hc}{2d(511)} \approx 1977.1 = E \sin \theta
  \]

  (other Si lattice constants can be scaled from this)

  \[
  \frac{H}{2} = \sin \theta; \quad \frac{D}{2} = \sin 2\theta
  \]

  \[
  D = H \sin (2\theta)/\sin \theta
  \]

  \[
  D = 2H \cos \theta
  \]

  displacement of beam vs angle
- crystal "tuning" and "detuning"
  crystals must be parallel to
  within rocking curve width
  $\sim 10\,\text{arcsec} \approx 0.05\,\text{rad}$
  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

\[ \text{Reflectance} \begin{cases} \text{1.0} & \text{16 keV} \\ \text{0.2} & \text{8 keV} \end{cases} \]

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

Can find \( \theta \) such that \( \theta_c < \theta < \theta_c \frac{\pi}{2} \)

so fundamental reflected but 2nd harmonic is not.
- checklist:

Harmonics — get rid of them!

Alignment — detector should see same beam (no clipping)

Linearity — detectors + electronics must be linear

Offsets — dark currents measured and subtracted correctly

\[ \frac{I}{I_0} \neq \frac{I+8}{I_0+8} \]

- you can eliminate 90% of your XAPS woes with "Halo."

Halo, are you listening?
--- thin concentrated limit:

\[
x_{\text{max}} \ll \left( \frac{\mu_r(E) + \mu_t(E_F)}{\sin \theta} \right)^{-1}
\]

\[
\Rightarrow \frac{\mu_s(E)}{1 - e^{-\frac{1}{x}}} \Rightarrow \mu_s(E)x
\]

--- thick dilute:

\[
x_{\text{max}} \gg \infty
\]

--- concentrated but not thin:

\[
\frac{\mu_s(E)}{\left( \frac{\mu_r(E) + \mu_t(E_F)}{\sin \theta} \right)}
\]

--- concentrated but not thin: warning: distorted spectra unless choose angle geometry carefully. (law take-off angle) (EXAFS correctable, XANES more difficult)

--- alternatively use electron yield

\[\theta \sim 90^\circ\ y \text{ small}\]
- electron yield
- fluorescence yield < 1
- radiationless transitions, auger electrons

- x-ray beam strikes sample which emits electrons
- electrons emitted within ~1000 Å 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 CB
XAFS phenomenon

\[ \mu \]

K-edge

\[ E \rightarrow \]

continuum

3p, 3d

hybridized states

transition occurs if energy sufficient to raise electron to unfulfilled state of appropriate symmetry (e.g. s → p; p → s, d)
- Characterize dead time

\[ N = N_0 e^{-No \tau} \]

or

\[ N = N_0 (1 - No \tau) \]

or

etc. (depends on electronics)

- dead time 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 $\ln (\frac{I_0}{E})$ to within $\sim 10^{-3}$ or better.

- Ion chamber plateau voltage

```
\begin{center}
\begin{tikzpicture}
\draw[thick] (0,0) -- (2,0) -- (2,1) -- (0,1) -- cycle;
\draw[thick] (0,0) -- (0,1);
\draw[thick] (2,0) -- (2,1);
\draw[thick] (1,0) -- (1,1);
\draw[thick] (0.5,0) -- (0.5,1);
\draw[thick] (1.5,0) -- (1.5,1);
\draw[thick] (1,0.5) -- (1,1);
\draw[thick] (0.5,0.5) -- (0.5,1);
\draw[thick] (1.5,0.5) -- (1.5,1);
\node at (0.5,0.5) {current output};
\node at (1.5,0.5) {plateau};
\node at (1,0.5) {higher flux};
\node at (0,0.5) {low flux};
\end{tikzpicture}
\end{center}
```

Voltage

$\Rightarrow$ check linearity of detectors.

$\Rightarrow$ holding $I_0$ constant doesn't do it because $I_0$ still varies a lot even when $I_0$ doesn't (edges!)
- considerations for experimental design
  - what edges are of interest?
  - beamline capabilities
  - how thick is sample you can get light through? (x)
  - what is the alpha of element of interest for sample thickness x?
  - if alpha ≤ 1 consider fluorescence
  - also consider fluor if sample inhomogeneous: Thickness effects lead of a problem for fluorescence
- watch out for:
  - Thickness effects (transmission)
  - particle size effects (all)
  - self absorption (fluorescence)
- thickness effects

uniform sample (no harmonics)

\[ \mu x \text{ is just there} \]

\[
p(x) \xrightarrow{\text{Thickness distribution}}
\]

\[
- (\mu x)_\text{eff} = \int_{-\infty}^{\infty} p(x) e^{-\mu x} \, dx
\]

\[-(\mu x)_\text{eff} = \sum_{n=1}^{\infty} \frac{c_n}{n!} (-\mu)^n \text{ cumulants} \]

\[
(\mu x)_\text{eff} = \mu c_1 - \frac{1}{2} \mu^2 c_2 \ldots
\]

\text{homogeneous}

\[ \langle x \rangle \quad \langle x - \bar{x} \rangle \]

\[ \text{See mathematics notebook} \]
"effective counts"

\[
\frac{Signal}{Noise} = \frac{N_s}{\sqrt{N_s + N_B}}
\]

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

\[
S/N = \sqrt{N_{eff}} = \frac{N_s}{\sqrt{N_s + N_B}}
\]

\[\Rightarrow \quad N_{eff} = \frac{N_s}{1 + \frac{N_B}{N_s}}\]

large background to signal ratio kills your effective counts.

\[\Rightarrow \quad \text{optimize conditions to improve } N_{eff}\]

\[\Rightarrow \quad \text{filters, slits, ...} \]
\[-\mu_t(E) x / \sin \theta \]
\[
\frac{m_{5}(E)}{e} \int_{0}^{x_{\text{max}}} -\left(\frac{\mu_t(E) + \mu_t(E_f)}{\sin \theta + \sin \phi}\right) x \, \frac{dx}{\sin \theta}
\]
\[
= \frac{\mu_s(E) \sin \theta \left(1 - e^{-\left(\frac{x_{\text{max}}}{\mu_s(E) \sin \theta + \mu_t(E_f) \sin \phi}\right)}\right)}{\left(\frac{\mu_t(E) + \mu_t(E_f)}{\sin \theta + \sin \phi}\right)}
\]

(include factors for solid angle -2/4\pi
and fluorescence yield \varepsilon for absolute number)
EXAFS is simpler to interpret quantitatively than optical spectroscopy
- initial state simple (is, 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 midcycle of vibrations

we always measure ensemble average of absorbing atoms

\( \Rightarrow \) have to average theoretical expressions appropriately

\( \Rightarrow \) Core hole broadening \( \Delta E \sim \frac{\hbar}{\tau} \)
\( \sim 1 \) ev \( \Rightarrow \) increases for high \( Z \)
$\hbar^2 k^2 = E - E_0$

$\frac{1}{2m} \Rightarrow$ edge energy

$x$-ray energy

Scanning $E$

literally records interferogram of environment of absorbing atom
XAFS is inherently a quantum effect, time dependent perturbation theory absorption.\[ \alpha \propto \left| \langle f | H^{\dagger} | i \rangle \right|^2 \delta (E+E_i-E_f) \] per probability/time.

Fermi's "golden rule":

\[ H \approx \sum_y H_{xy} \approx f \] expresses energy conservation interaction between incident x-ray and electron.

\[ H' \propto \frac{\hbar}{m} \overrightarrow{A} \cdot \overrightarrow{p} \] \overrightarrow{A} is vector potential of x-ray, \overrightarrow{p} is momentum of electron.

For our purposes, sufficient to take \overrightarrow{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 $E = -\frac{1}{2} \alpha^2 (mc^2)$

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

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

fine structure constant

\[
\chi = \frac{e^2}{\hbar c} \approx \frac{1}{137}
\]

\[
\begin{array}{c}
\sqrt{E} \\
\text{virial thm} \quad E = \frac{1}{2} V = \frac{1}{2} \frac{e^4}{\alpha_0 d} = \frac{me^4}{\hbar^2} \\
\Rightarrow \alpha_0 = \frac{\hbar^2}{me^4} \quad \text{(Bohr radius)}
\end{array}
\]
\[ \mu \propto | \langle \psi_f | e^{-i \mathbf{H} \cdot \mathbf{r}} | \psi_i \rangle |^2 \]

\[ \mathbf{H} \quad \text{x-ray wavevector} \]

\[ k \quad \text{electron wavenumber} \]

\[ | \psi_i \rangle \quad \text{is initial state (I5)} \]

\[ | \psi_f \rangle \quad \text{is final state w.f.} \]

(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, \( \mu \) depends on interference pattern at center of absorber.
atomic units \( m, e, \hbar \rightarrow 1 \)
(wonderful invention!)

\[ E = -\frac{1}{2} \frac{m e^4}{\hbar^2} \rightarrow -\frac{1}{2} \]

\( \Rightarrow \) energy unit = 2 Rydberg

"Hartree" \( \approx \) 27.2 eV

\[ a_0 = \frac{\hbar^2}{me^2} \rightarrow 1 \]

\( \Rightarrow \) length unit = 1 bohr radius

"Bohr" \( \approx 0.529 \) Å

for nuclear charge \( Z \)

\[ e^2 \rightarrow Ze^2 \]

\( \Rightarrow E \rightarrow -\frac{Ze^2}{2} \) (a.u.) (remember \( Z \approx 2.17 \) empirically)

\[ a_0 \rightarrow \frac{1}{Z \frac{e^2}{2}} \) (a.u.)
\[ |\langle f | \varepsilon \cdot \mathbf{r} | \ell \rangle |^2 \]

because the state \( |\ell \rangle \) extends only over radius \( \sim \frac{\hbar}{\varepsilon} \) (Bohr), we can estimate the importance of the term \( e^{i \mathbf{H} \cdot \mathbf{r}} \) in a.u.

\[
\langle \mathbf{r} \cdot \mathbf{r} \rangle \approx \frac{E}{\hbar c} \frac{a_0}{2} \sim \frac{\hbar}{\varepsilon} \frac{m e}{2} \frac{\hbar}{\hbar c} \frac{\hbar}{m e c^2} \\
= \frac{\hbar^2}{2} \frac{e^2}{\hbar c} \frac{\hbar}{m e c^2} = \frac{\hbar}{2} \times \alpha = \frac{\alpha}{2 \cdot 137}
\]

Note that \( \langle \mathbf{r} \rangle \) is not the atomic size (on the order of \( \AA \)); if it were we would not be able to consider \( \langle \mathbf{r} \cdot \mathbf{r} \rangle \) small, since \( |\ell \rangle \sim \mathbf{R}^{-1} \frac{2 \pi}{\lambda_{\text{photon}}} \).
\[ e^{-i \mathbf{R} \cdot \mathbf{r}} = 1 + (i \mathbf{R} \cdot \mathbf{r}) + \frac{(i \mathbf{R} \cdot \mathbf{r})^2}{2} + \ldots \]

\[ \langle f | \mathbf{r} e^{i \mathbf{R} \cdot \mathbf{r}} | i \rangle = \langle f | \mathbf{r} | i \rangle + i \langle f | (\mathbf{R} \cdot \mathbf{r}) | i \rangle \]

\[ \uparrow \quad \text{dipole} \quad \uparrow \quad \text{quadrupole} \]

\[ \frac{\mu_{\text{quad}}}{\mu_{\text{dipole}}} \sim \langle \mathbf{R} \cdot \mathbf{r} \rangle^2 \sim \left( \frac{2 \kappa}{\zeta} \right)^2 \]

\[ \begin{align*}
K\text{-edge} & \sim 0.5 \% \quad \zeta = 20 \text{ (Ca)} \\
& \sim 10 \% \quad \zeta = 92 \text{ (U)}
\end{align*} \]

radius of initial state larger yet
\(~4\times\text{times}) \text{ for } L\text{-edges.} \quad \Rightarrow \text{quadrupole not always negligible for high } \zeta
7.11 keV

3d hybridized levels (transitions dipole forbidden in inversion symmetric environment)

Can map out quadrupole from angle dependence (Hahn et al.) (Pomer-Hahn)

Therefore you can see quadrupole transitions if not masked by dipole
approximate potential
as spherically symmetric scatterers with flat (constant potential) interstitial region.
→ W.f.s separate into radial dependence ↔ spherical harmonics inside muffin tin
→ Propagating waves in flat region
→ Match boundary conditions to get soln.
EXAFS: normally assume dipole approx

\[ \mu(E) = \frac{4\pi^{2} \alpha \omega}{f} \langle i | \hat{\varepsilon} \cdot \hat{\alpha} \cdot \hat{\varepsilon} \cdot \hat{\alpha} \cdot \delta(E-E_{\text{F}}) \rangle \]

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

\[ \mu \propto -\frac{1}{\pi} \text{Im} <i|\hat{\varepsilon} \cdot \hat{\alpha} \cdot G(\varepsilon_{\text{F}}, \varepsilon) \hat{\alpha} \cdot \hat{\varepsilon} |i> \theta(E-E_{\text{F}}) \]

\[ G = (E-H+i\eta)^{-1} \text{ single particle hamiltonian} \]

\[ H = H_{0} + V \]

\[ \theta(E) = \frac{1}{\pi} \arctan \left( \frac{E_{\text{F}}}{E_{\text{F}}-E} \right) \]

\[ H_{0} = -\frac{\nabla^{2}}{2} + V_{\text{int}} - \text{ interstitial potential} \]

\[ H = H_{0} + V \]

\[ \delta V = V - V_{\text{int}} \text{ Scattering potential} \]
MS expansion follows from expanding Green's function in Dyson series:

\[ G = G^0 + G^0 T G \]

\[ G^0 = (E - H_0 + i\eta)^{-1} \quad \text{G.F. system no scatterers} \]
\[ G = (E - H + i\eta)^{-1} \quad \text{total G.F.} \]
\[ G^c = (E - H_c + i\eta)^{-1} \quad \text{central atom G.F.} \]

\[ G = G^c + \sum \hat{G}^c + \hat{G}^c + \sum \hat{G}^c \]
\[ \hat{i} \not= 0 \]
\[ \hat{i} \not= j \]
\[ \hat{i}, \hat{j} \not= 0 \]

\[ \equiv \sum_{\Gamma} G_\Gamma \]

(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 \( \Gamma \) begin and 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, Zabinisky, Ankudinov et al. have shown this MS expansion can be expressed as

\[
\mu(E) = \mu_0(E) (1 + \sum_{\Delta} \sum_{\gamma} \chi_{\Delta\gamma}(E))
\]

\[
\chi_{\Delta\gamma} = \frac{2 i}{F} \left[ e^{-\frac{2 i}{F} (E_1 + E_2 - E_n + 2s_i)} \right]
\]

\[
\chi_{\Delta\gamma} = \text{Im} \sum_{\Delta} e^{i \sum_{\gamma} \chi_{\Delta\gamma}(E)} \times \text{Tr} \text{M}_{\Delta\gamma} F \text{e}^{i \sum_{\gamma} \chi_{\Delta\gamma}(E)}
\]

scattering matrix
or in more conventional notation

\[ X^r(k) = \sum_i \frac{S_{ii}}{k^2} \left( \int_0^\infty f_i^r(k) \sin(2kR + \phi^r_i(k) + \Delta^r_i(k)) \right) \]

\[ \times \exp \left( -2k^2 \sigma^2 - 2k/\Delta^r_i(k) \right) \]

average

\[ 2R = \text{length of path} \]

\[ \sigma^2 = \langle (R - \langle R \rangle)^2 \rangle \] 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 amplitudes and phases: \( \text{feff} \).

Whence the famous program "FEFF" (up to FEFF7 at this time)
\[ X(k) = \sum \left[ 3 \cos \theta_i f_i(k) \right] \frac{1}{k R_i^2} \sin(2kR_i + 2\pi k) + \text{Arg} \{ f_i(k) \} \]

\[ \cos \theta_i = \hat{e} \cdot \hat{r}_i \]

Plane, average, shells

\[ X(k) = \sum \sum \left[ 3 \cos \theta_i \right] N_i f_i(k) \frac{1}{k R_i^2} \sin(2kR_i + \delta_j(k)) \]

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

If \( f(k) \rightarrow \text{Effective } (k,r) \) this traditional plane wave formula is of same form as more rigorous modern form (no accident!)
what you do to calculate

*make atoms
  (self consistent, preferably relativistic)

*superimpose charge densities
  by putting atoms in right place (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 $S_2(k)$ for each atom
  (also calc $mu$ for central atom)

*construct $T$ matrices & propagators

*simmer until done, season to taste

$\Rightarrow K : \text{ Guess what?}$

$\Rightarrow K : \text{ Feff does it all for you!}$
Disorder
(when is a shell a shell?)
(after G.B. 1983)
consider a single shell (1 atom type)

\[ X(k) = N B(k) \int e^{-2r/\lambda} \frac{P(r)}{r^2} e^{i 2kr + s(k)} dk \]

\[ B(k) = \frac{s_0 F(k)}{k} \]

\[ = N \text{Im} \int_0^\infty P(r) e^{i 2kr} dr \]

(\text{fourier transform})

\[ P(r) = \frac{p(r)}{r^2} e^{-2r/\lambda} \]

"effective distribution"

\[ X(k) = A(k) e^{i Y(k)} \]

\[ X(k) = \text{Im} \hat{X}(k) \]
\[ \ln \hat{X}(k) = \ln A(k) + i \Psi(k) \]
\[ \ln A(k) = \text{Re} \ln \hat{X}(k) \]
\[ \Psi(k) = \text{Im} \ln \hat{X}(k) \]

Can expand
\[ \ln \hat{X}(k) \text{ in power series in } k \]
\[ \ln \hat{X}(k) = \sum_{n=0}^{\infty} \frac{C_n}{n!} (2i k)^n \]

Cn are "cumulants" of effective distribution \( P(r) \)
\[ \frac{\ln (A(k))}{NB(k)} = C_0 - 2k^2 C_2 + \frac{2}{3} k^4 C_4 \ldots \]
\[ \Psi(k) - \delta(k) = 2 k C_1 - \frac{4}{3} k^3 C_3 + \ldots \]
\[ \exp[C_0] = \langle 1 \rangle \leq e^{\langle H \rangle / \hbar^2} \]

\[ C_1 = \langle r \rangle \quad ; \quad \langle h(r) \rangle = \int_{\mathbb{R}}^f \langle h(r) \rangle \exp[-\frac{r^2}{2\hbar^2}] \text{ any } h(r) \]

\[ C_2 = \langle r^2 \rangle \]

\[ C_3 = \langle r^3 \rangle \]

\[ C_4 = \langle r^4 \rangle - 3\langle r^2 \rangle^2 \]

- for a gaussian effective distr.,
\[ C_n = 0 \quad \text{for } n > 2 \]

- if you convolote two distributions, their cumulants just add

- \( C_n \) are independent of origin

\[ \text{for } n > 1 \]
single shell

\[ X(k) = NB(k) e^{c_0 - \frac{2}{3} k^2 c_2 + \frac{2}{3} k^4 c_4 \ldots} \]

\[ \times \sin \left( 2 k c_1 - \frac{4}{3} k^3 c_3 + \ldots + \delta(k) \right) \]

ratio method

\[ \ln \left( \frac{X}{NB} \right) \]

- \[ c_2 \text{ always } \geq 0 + \frac{2}{3} k^4 c_4 \text{ in } \]
- \[ c_4 \text{ can be positive or negative } \]
- \[ c_3 \text{ measures weight in tails of dist.} \]
- \[ -\frac{4}{3} k^3 c_3 \text{ in } \]

\[ \psi(k) - \delta(k) \]

\[ 2 k c_1 \]

\[ k \]

\[ c_3 \text{ measures skewing of dist.} \]
at a beat, $\phi_1 \neq \phi_2$ phases differ by $180^\circ (\pi)$ on $(2n+1)\pi$

$A^2 = \phi_1^2 + \phi_2^2 + 2\phi_1\phi_2 \cos(\pi)$

$A = |\phi_1 - \phi_2|$

$\Delta \phi = (2n+1)\pi$ if same type of atom

$2\kappa \Delta r = (2n+1)\pi$ if different types of atom in two shells

(approximately)

_doesn't matter - error is small_
\[ X_1(k) = NB(k)e^{c_0 - \frac{2}{3}k^2 c_2 + \frac{2}{3}k^4 c_4 \ldots} \]

\[ \times \sin\left(2kC_1 - \frac{4}{3}k^3 C_3 + \ldots + \delta(k)\right) \]

**Ratio Method**

\[ \ln\left(\frac{X}{NB}\right) \]

- \( C_2 \) always \( \geq 0 \)
- \( \frac{2}{3}k^4 C_4 \) in growth
- \( C_4 \) can be positive or negative
- \( C_4 \) measures weight in tails of distribution

\[ \phi(k) - \delta(k) \]

- \( -\frac{4}{3}k^3 C_3 \) in skewing
- \( C_3 \) measures skewing of distribution
Cumulants cannot generally be neglected unless \( k_{\text{max}} \Delta < < 1 \) presence of additional terms in phase and amplitude can cause erroneous distances and 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 $C_1 \sim 2 \sigma^2 F$ 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, $\frac{A_1}{A_2}$

phases differ by $180^\circ (\pi)$ on $(2n+1)\pi$

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

$A = |A_1 - A_2|$

- $\Delta \gamma = (2n+1)\pi$

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

$2K\alpha r = (2n+1)\pi$

$\Rightarrow \angle r = \frac{\pi}{2K\alpha \text{beat}}$ etc

- $2K\alpha r = (2n+1)\pi - \Delta \delta$ if different types of atom

in two shells
Beats

\[ A e^{i\gamma} = A_1 e^{i\gamma_1} + A_2 e^{i\gamma_2} \]

\[ A \cos \gamma = A_1 \cos \gamma_1 + A_2 \cos \gamma_2 \]

\[ A \sin \gamma = A_1 \sin \gamma_1 + A_2 \cos \gamma_2 \]

\[ \Rightarrow \tan \gamma = \frac{\sum A_i \sin \gamma_i}{\sum A_j \cos \gamma_j} \]

\[ \Rightarrow A^2 = A_1^2 + A_2^2 + 2A_1 A_2 \cos (\gamma_1 - \gamma_2) \]

Each contribution \( \vec{\gamma} \) has a magnitude \( A \) (and phase \( \gamma \)).

As \( A \) increases, imagine vectors rotating—speed of rotation proportional to \( F \) (approximately).
at a beat, phase jumps too

\[ K < K_{\text{beat}} \quad K > K_{\text{beat}} \]

- if smaller amplitude shell is larger distance, phase jump negative

\[ K < K_{\text{beat}} \quad K > K_{\text{beat}} \]

- if smaller amp shell is smaller dist, phase jump positive

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

positive skewness

$C_3 > 0$

phase curvature

negative phase jump at beat

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 $k_{00} = \pi/2n$