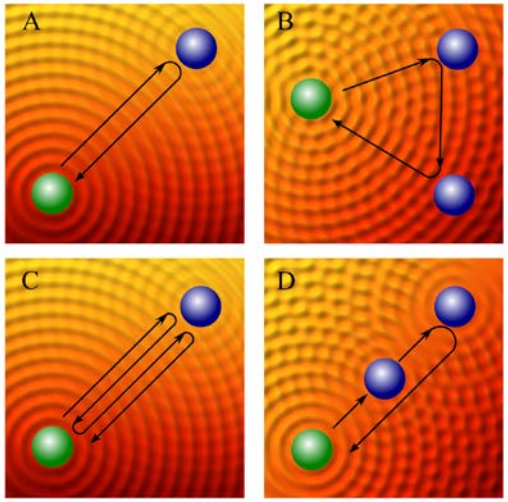
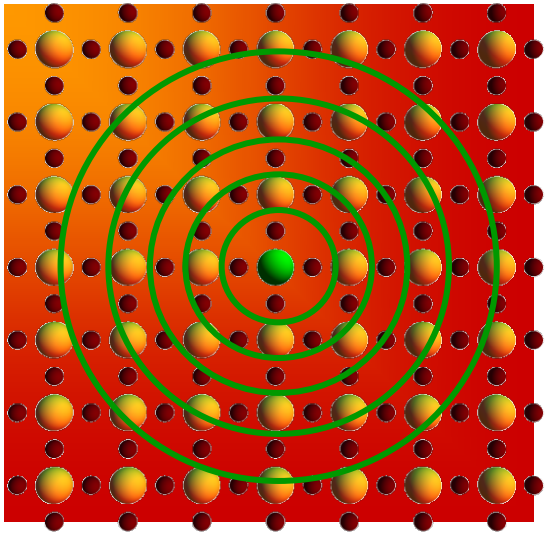
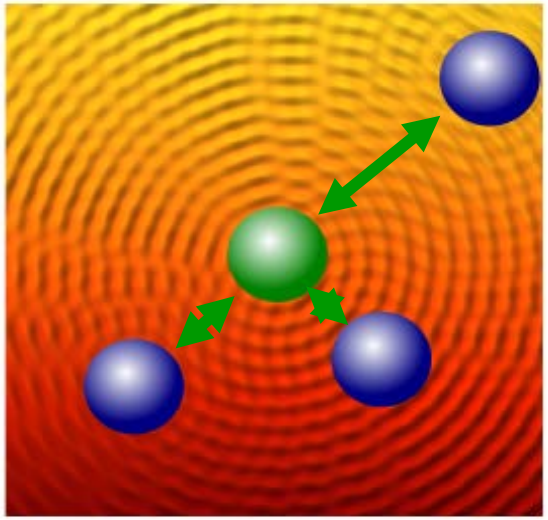
EXAFS data analysis by FEFF fitting



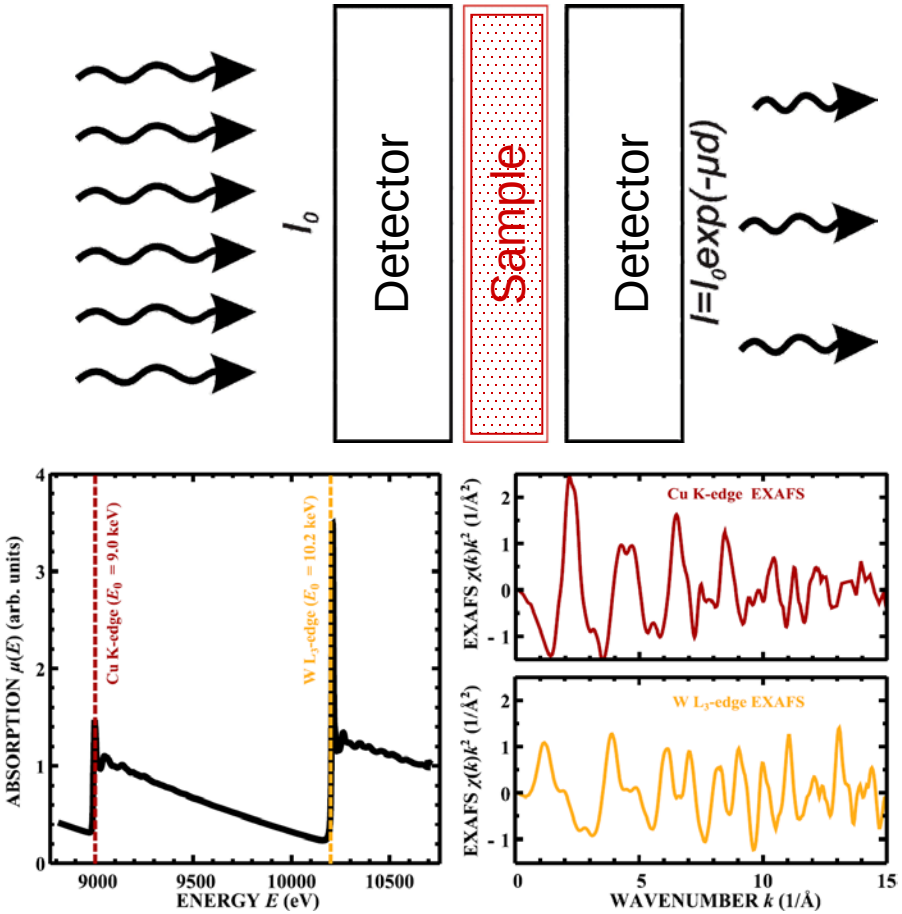


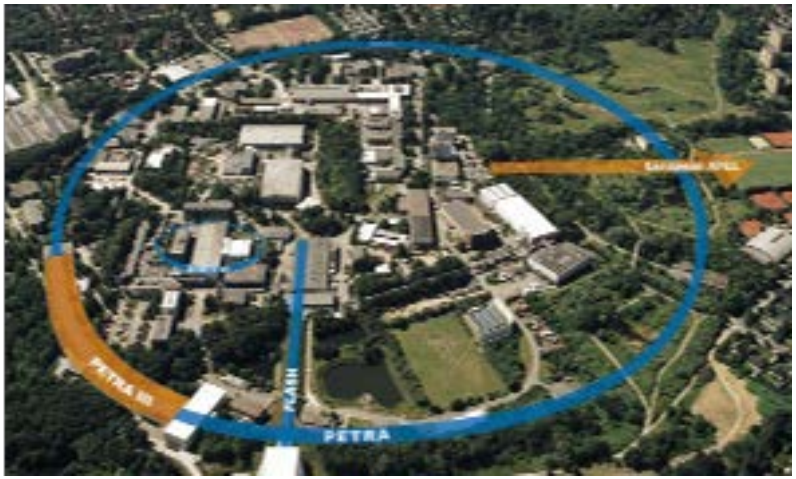


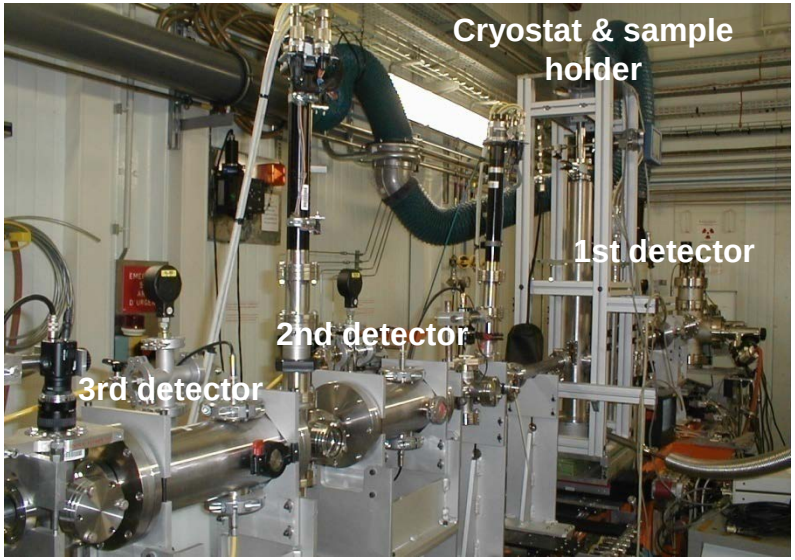
Janis Timoshenko

Materials Science and Chemical Engineering, Stony Brook University

EXAFS spectroscopy: experimental data

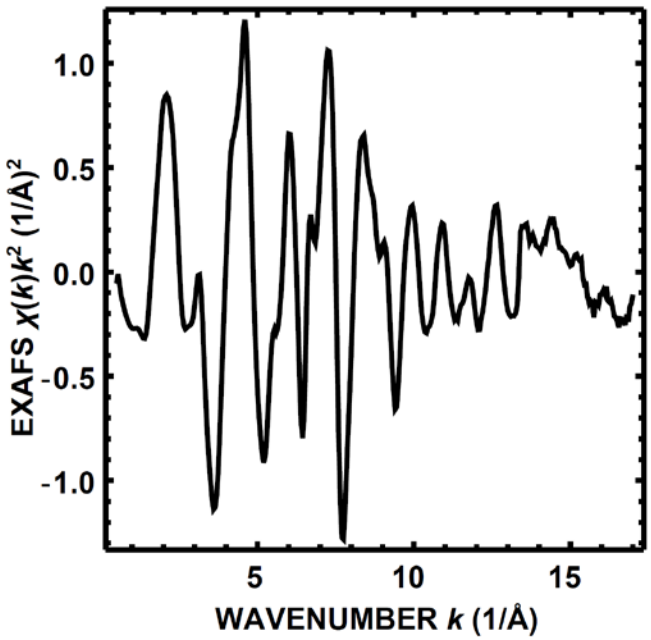


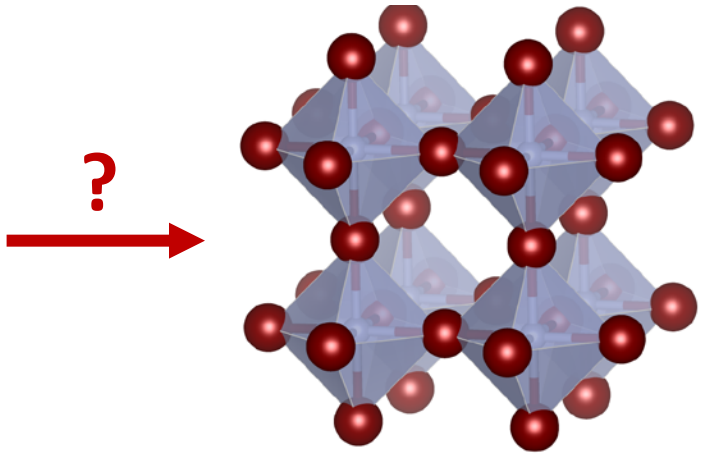




Objective of the analysis

Knowing EXAFS spectra of a material, how to obtain its structure?

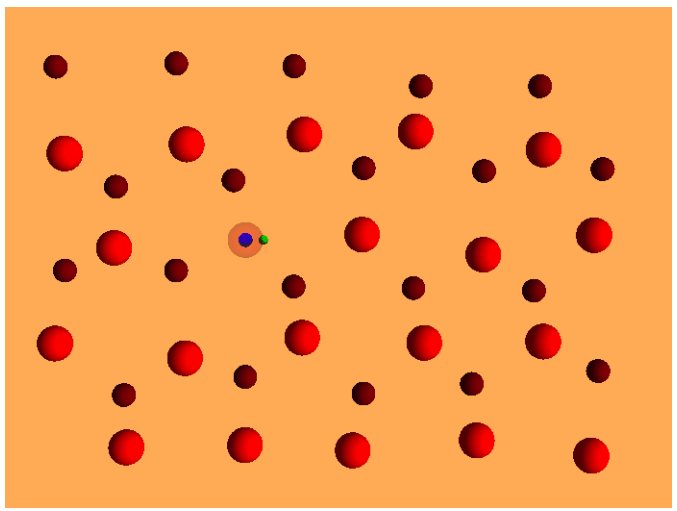




(Opposite is relatively easy)

Origin of EXAFS equation

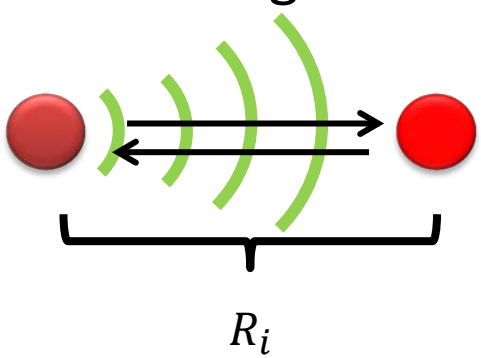
EXAFS: result of **interference** between orinal photolectron wave and backscattered wave



Photoelectron **wavenumber**:

$$k = \sqrt{2m\left(E_{photon} - E_0\right)/\hbar^2}$$

Contribution from a single backsattering atom:



$$\chi_i(k) = S_0^2 \frac{F_i(k) e^{-\frac{2R_i}{\lambda(k)}}}{kR_i^2} \sin(2kR_i + \phi_i(k))$$

Origin of EXAFS equation

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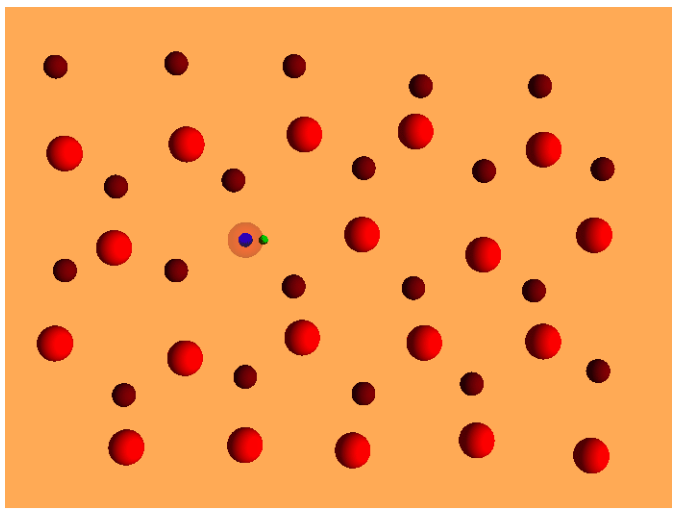

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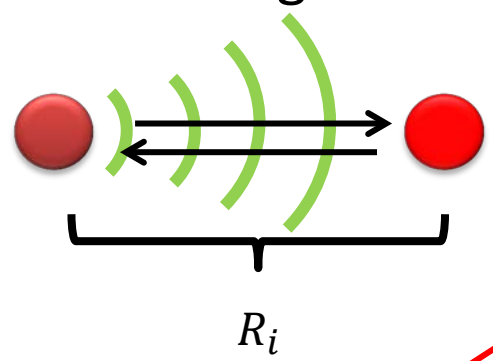
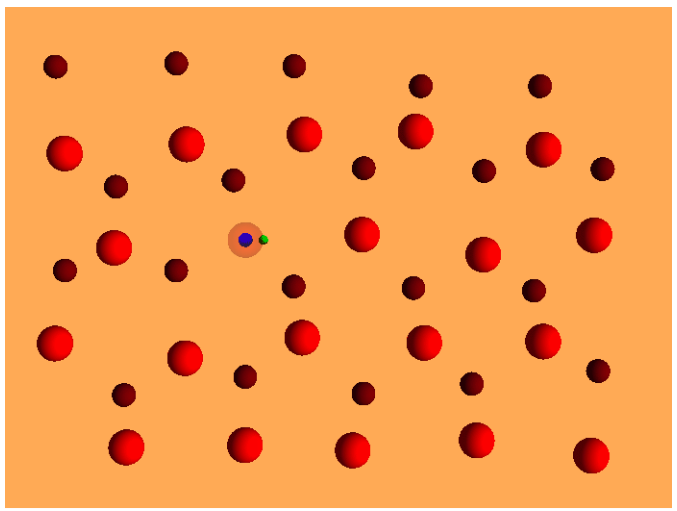


Interatomic distance

$$\chi_i(k) = S_0^2 \frac{F_i(k) e^{-\frac{2R_i}{\lambda(k)}}}{kR_i^2} \sin(2kR_i + \phi_i(k))$$

Origin of EXAFS equation

EXAFS: result of **interference** between orinal photolectron wave and backscattered wave



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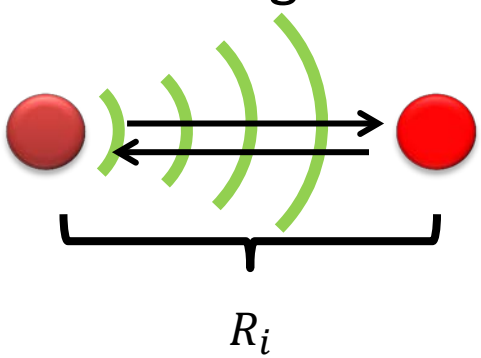
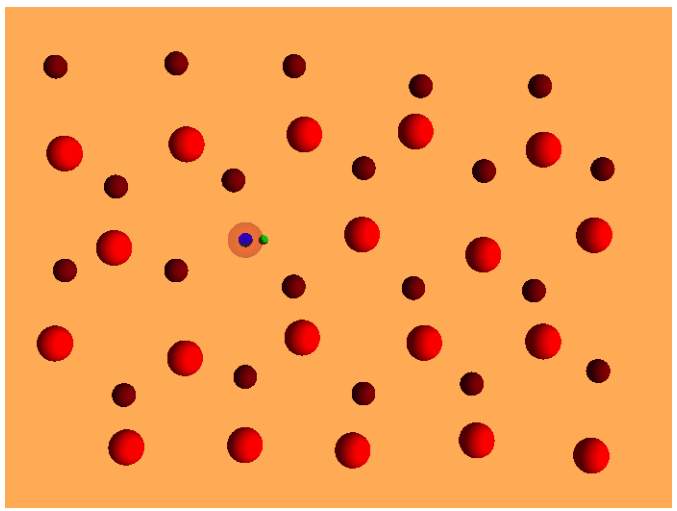


Effective mean-free path

$$\chi_i(k) = S_0^2 \frac{F_i(k) e^{-\frac{2R_i}{\lambda(k)}}}{kR_i^2} \sin(2kR_i + \phi_i(k))$$

Origin of EXAFS equation

EXAFS: result of **interference** between orinal photolectron wave and backscattered wave



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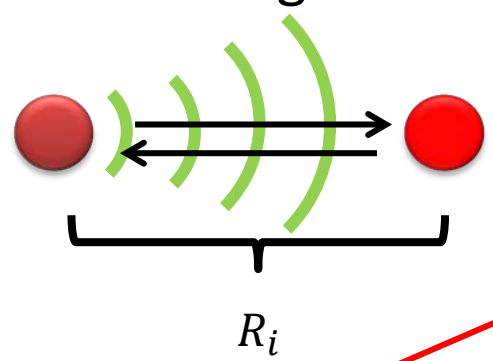
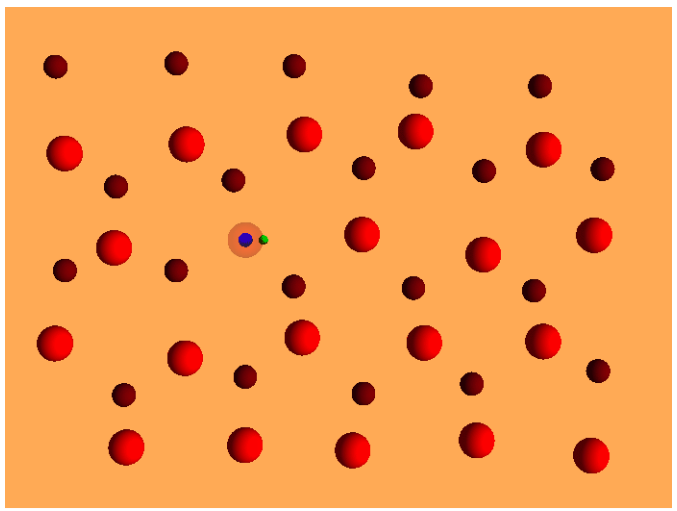


Scattering amplitude

$$\chi_i(k) = S_0^2 \frac{F_i(k) e^{-\frac{2R_i}{\lambda(k)}}}{kR_i^2} \sin(2kR_i + \phi_i(k))$$

Origin of EXAFS equation

EXAFS: result of **interference** between orinal photolectron wave and backscattered wave



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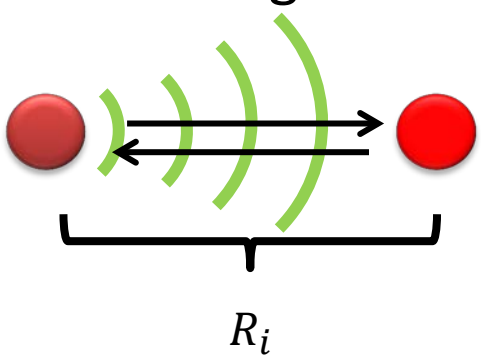
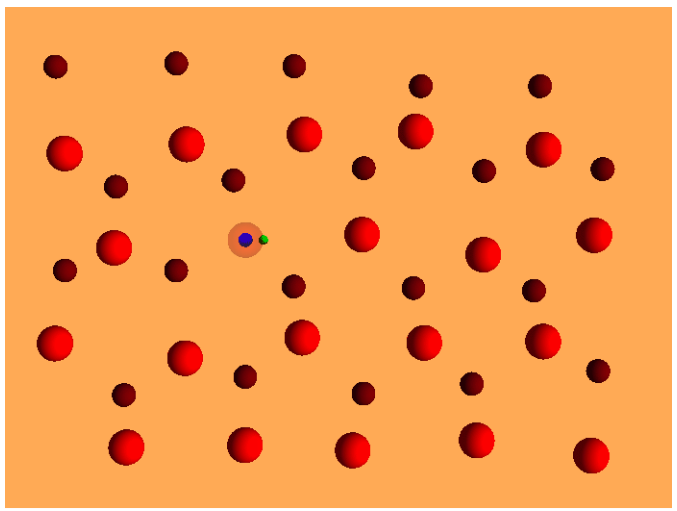


Scattering phase

$$\chi_i(k) = S_0^2 \frac{F_i(k) e^{-\frac{2R_i}{\lambda(k)}}}{kR_i^2} \sin(2kR_i + \phi_i(k))$$

Origins of EXAFS equation

EXAFS: result of **interference** between orinal photolectron wave and backscattered wave



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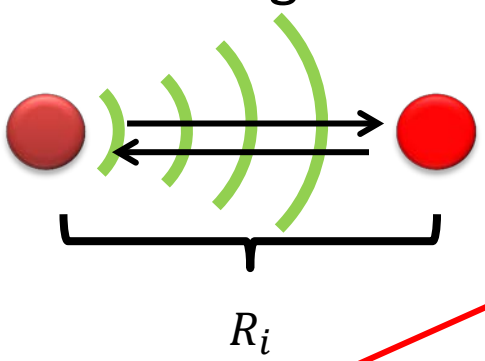
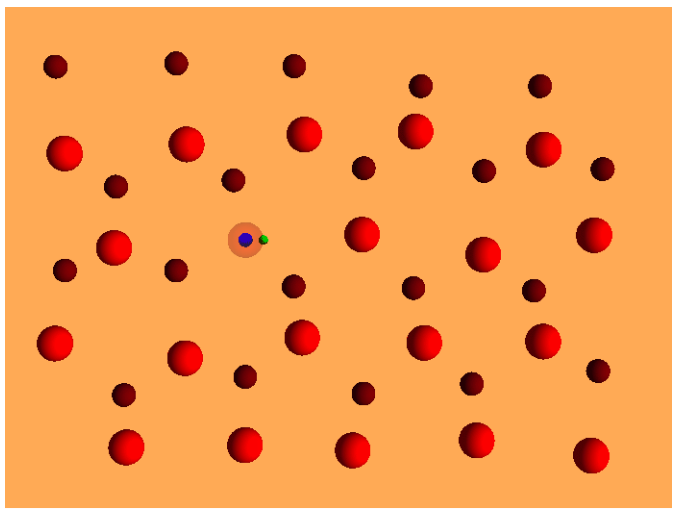


(Will use FEFF here!)

$$\chi_i(k) = S_0^2 \frac{F_i(k) e^{-\frac{2R_i}{\lambda(k)}}}{kR_i^2} \sin(2kR_i + \phi_i(k))$$

Origin of EXAFS equation

EXAFS: result of **interference** between orinal photolectron wave and backscattered wave



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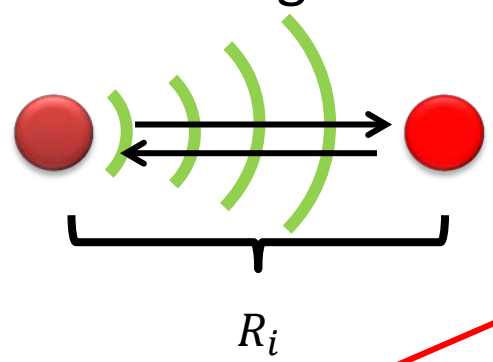
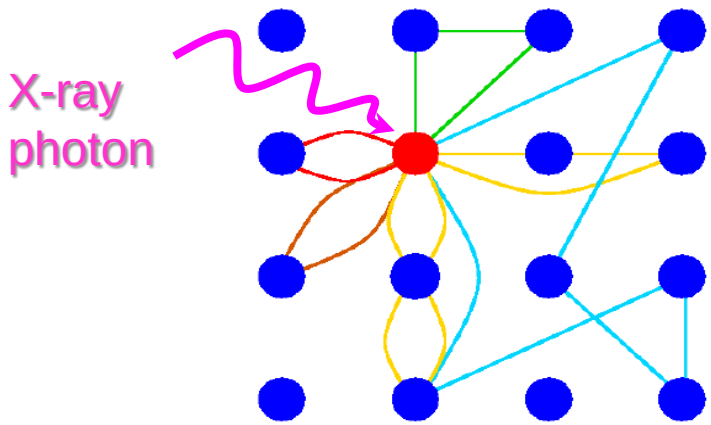


Amplitude reduction factor (~ 0.7 - 1.0)

$$\chi_i(k) = S_0^2 \frac{F_i(k) e^{-\frac{2R_i}{\lambda(k)}}}{kR_i^2} \sin(2kR_i + \phi_i(k))$$

Multiple scattering expansion

A.L. Ankudinov et al, Phys. Rev. B 58 (1998) 7565.



$$\chi(k) = \sum_i \chi_i(k) =$$

$$= \sum_i S_0^2 \frac{f_i(k, R_i)}{kR_i^2} \sin(2kR_i + \phi_i(k))$$

$$(f_i(k, R_i) = F_i(R_i) e^{-\frac{2R_i}{\lambda_i(k)}})$$

Alternative: *N*-body expansion (GNXAS code):

$$\begin{aligned}
\chi(k) \;=\; & \int 4\pi R^2 \rho_0 g_2(R)(\chi_2^{oio}(k) + \chi_4^{oioio}(k) + \ldots)\mathrm{d}R \\
& + \iiint 8\pi^2 R_1^2 R_2^2 \sin(\theta) \rho_0^2 g_3(R_1, R_2, \theta) \\
& \times (2\chi_3^{oijo}(k) + 2\chi_4^{oiojo}(k) + \chi_4^{oijio}(k) + \chi_4^{ojijo}(k) + \ldots)\mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\theta \\
& + \iiiint\!\!\int 8\pi^2 R_1^2 R_2^2 R_3^2 \sin(\theta) \rho_0^3 g_4(R_1, R_2, \theta, R_3, \Omega) \\
& \times (2\chi_4^{oijko}(k) + 2\chi_4^{oikjo}(k) + 2\chi_4^{ojiko}(k) + \ldots)\mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\theta \mathrm{d}R_3 \mathrm{d}\Omega \\
& + \ldots
\end{aligned}$$

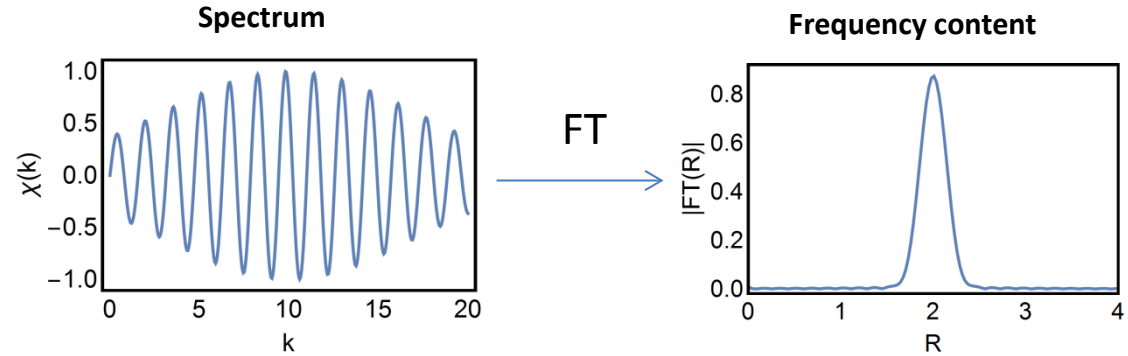
A. Filipponi, A. Di Cicco, C. R. Natoli, Phys. Rev. B 52 (1995) 15122-15134.

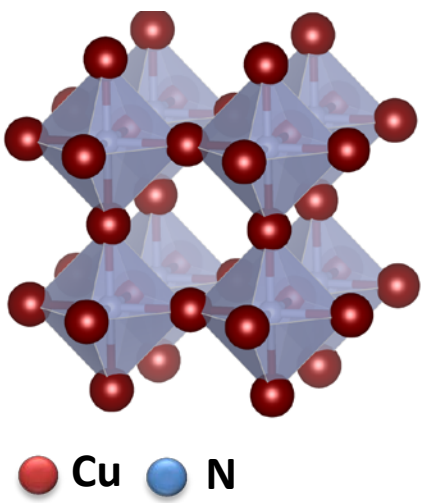
Fourier transform

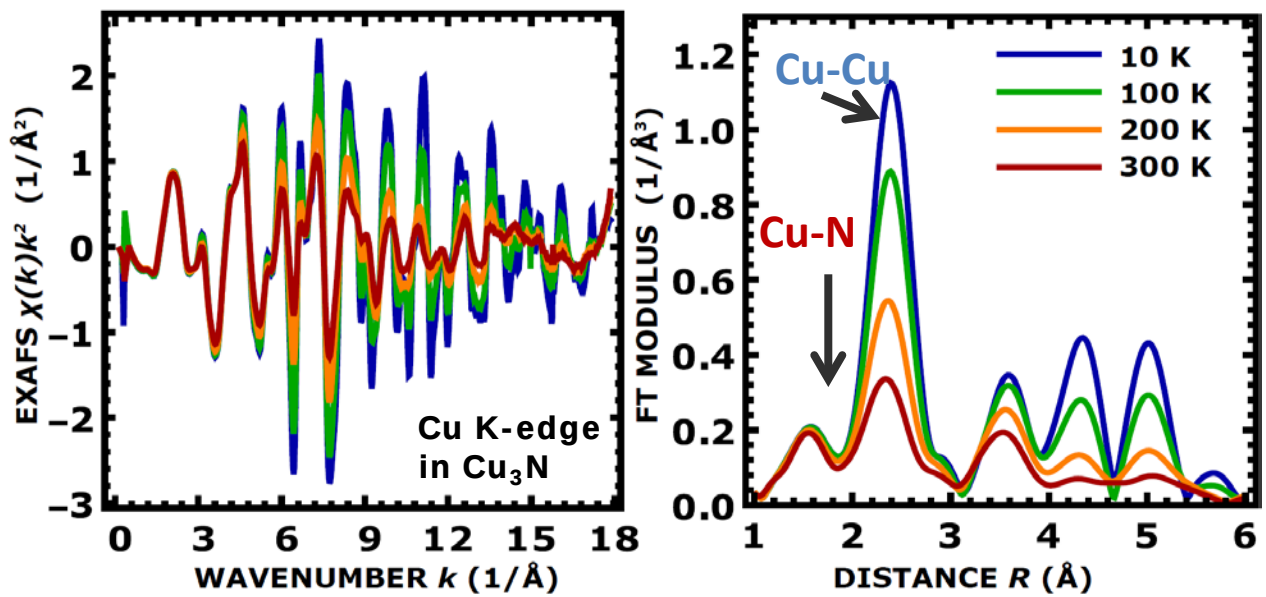
Interatomic distances are related to frequencies of EXAFS: one can use Fourier transform to separate different contributions and to select those of interest!

Fourier transform:

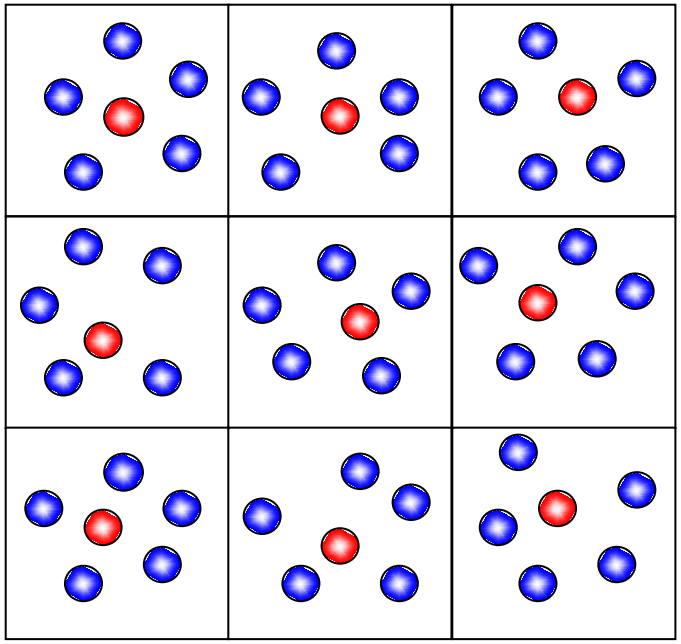
$$FT(r) = \int_{k_{\min}}^{k_{\max}} \chi(k) k^n \Omega(k) e^{-2ikr} dk$$





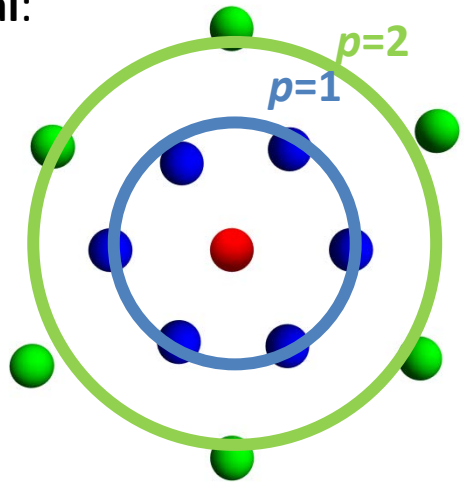


Radial distribution function



Even in perfect crystals atoms at given time-monent are rarely at their equilibrium positions: there is a lot of paths with slightly different lengths.

It makes sense to group them in **coordination shells** and replace summation over paths belonging to the same coordination shell with an **integral**:



$$\chi(k) = \sum_p \chi_p(k)$$

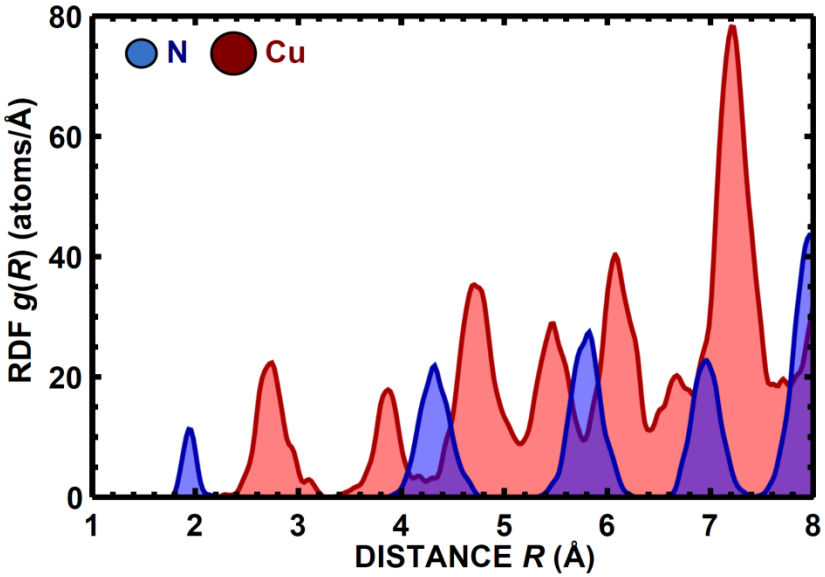
$$\chi_p(k) = S_0^2 \int_{-\infty}^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$

(for single-scattering path)

Radial distribution function

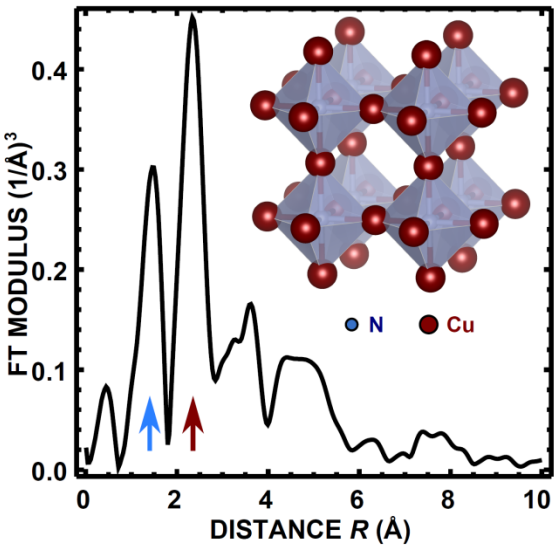
FT is not RDF!

RDF



≠

FT-EXAFS



$$\chi(k) = \sum_p \chi_p(k)$$

$$\chi_p(k) = S_0^2 \int_{-\infty}^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$

Cumulant expansion

$$\chi_p(k) = \int_0^\infty \frac{g(R)}{kR^2} f(k,R)\sin(2kR+\phi(k))dR$$

$$= \int_0^\infty \frac{g(R)}{kR^2} F(k,R) e^{-\frac{2R}{\lambda(k)}} \sin(2kR+\phi(k))dR$$

The *effective distribution* $P(R,\lambda)$: $P(R,\lambda) = g(R)e^{-2R/\lambda(k)} / R^2$

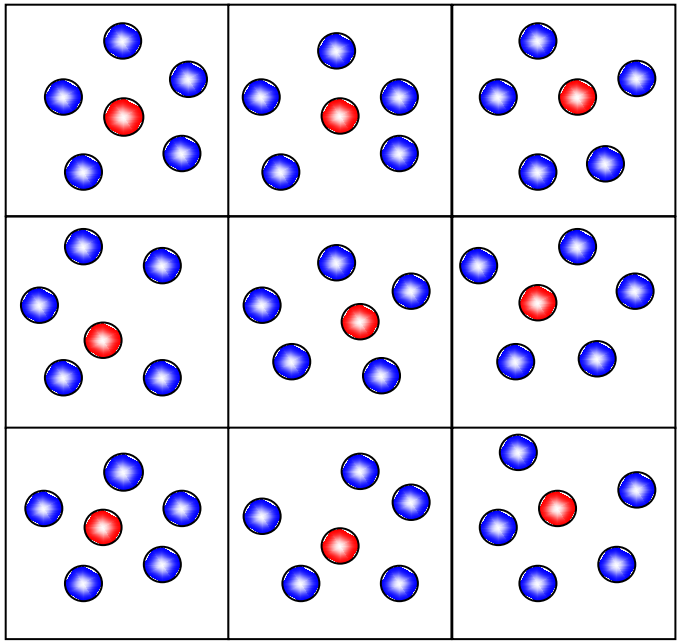
The *cumulant expansion* into a MacLaurin series: $\ln \int_0^\infty P(R,\lambda)\exp(2\mathrm{i}kR)\mathrm{d}R = \sum_{n=0}^{\infty} (2\mathrm{i}k)^n C_n / n!$

$$\chi_p(k) = S_0^2 \frac{1}{k} F(k) \exp(C_0 - 2C_2k^2 + \frac{2}{3}C_4k^4 - \frac{4}{45}C_6k^6)$$
$$\times \sin\left(2kC_1 - \frac{4}{3}C_3k^3 + \frac{4}{15}C_5k^5 + \phi(k)\right)$$

$\exp(C_0) \cong N\exp(-2C_1/\lambda)/C_1^2$

C_1 is the mean value of the distribution (**average distance**)
C_2 is the variance of the distribution (**MSRD factor**)
C_3 is the asymmetry of the distribution (**skewness**)
C_4 describes symmetric deviations from the Gaussian shape

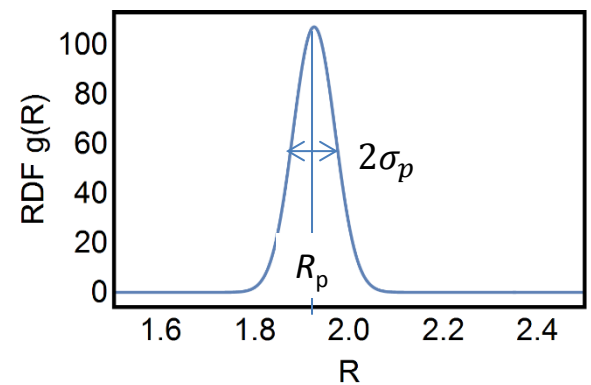
Gaussian approximation



In commonly used **Gaussian approximation**

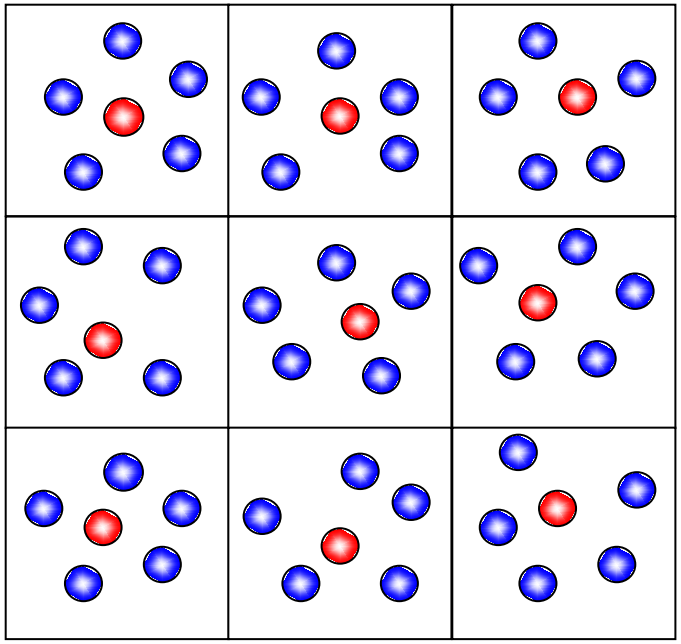
$$g_p(R) = N_p \frac{1}{\sqrt{2\pi\sigma_p^2}} \mathrm{e}^{-\frac{(R-R_p)^2}{2\sigma_p^2}}$$

and



$$\chi_p(k) = S_0^2 N_p \frac{f_p(k, R_p)}{kR_p^2} e^{-2k^2\sigma_p^2} \sin\left(2kR_p + \phi_p(k)\right)$$

Gaussian approximation



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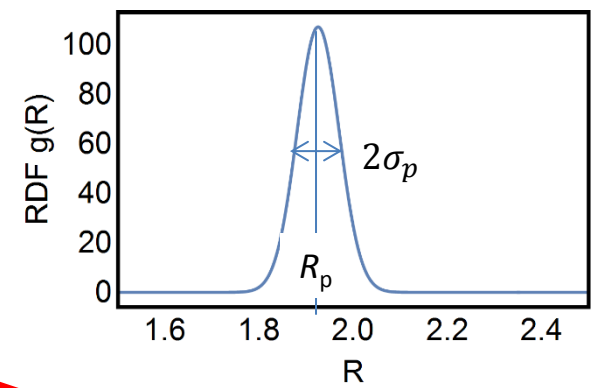
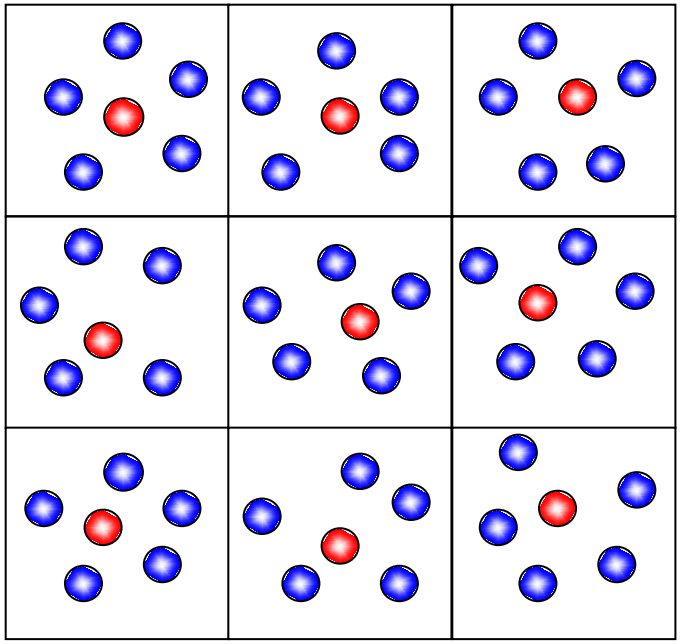


and

Average interatomic distance

$$\chi_p(k) = S_0^2 N_p \frac{f_p(k, R_p)}{kR_p^2} e^{-2k^2\sigma_p^2} \sin\left(2kR_p + \phi_p(k)\right)$$

Gaussian approximation



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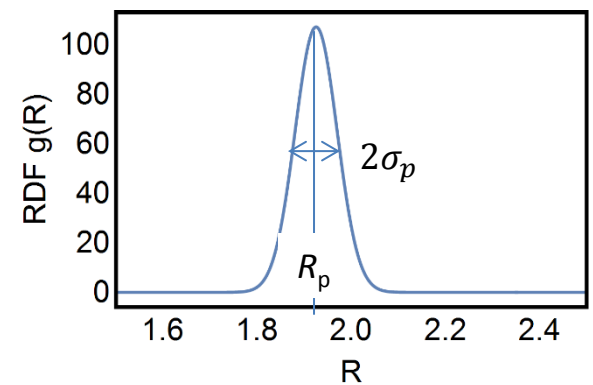
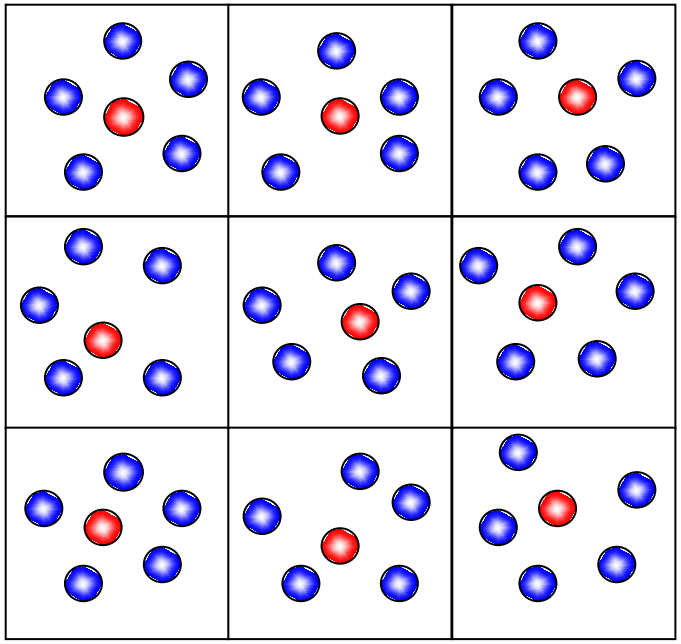
and



$$\chi_p(k) = S_0^2 N_p \frac{f_p(k, R_p)}{kR_p^2} e^{-2k^2\sigma_p^2} \sin\left(2kR_p + \phi_p(k)\right)$$

Coordination number

Gaussian approximation



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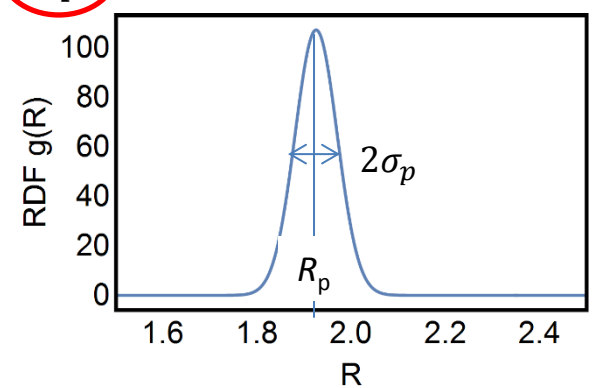
and



$$\chi_p(k) = S_0^2 N_p \frac{f_p(k, R_p)}{kR_p^2} e^{-2k^2\sigma_p^2} \sin\left(2kR_p + \phi_p(k)\right)$$

Disorder
(Debye-Waller or
MSRD factor)

Cumulant expansion

$$\chi_p(k) = \int_0^\infty \frac{g(R)}{kR^2} f(k,R)\sin(2kR+\phi(k))dR$$

$$= \int_0^\infty \frac{g(R)}{kR^2} F(k,R) e^{-\frac{2R}{\lambda(k)}} \sin(2kR+\phi(k))dR$$

This complex expansion will not save one, if the system is really disordered!

The *effective distribution* $P(R,\lambda)$: $P(R,\lambda) = g(R)e^{-2R/\lambda(k)} / R^2$

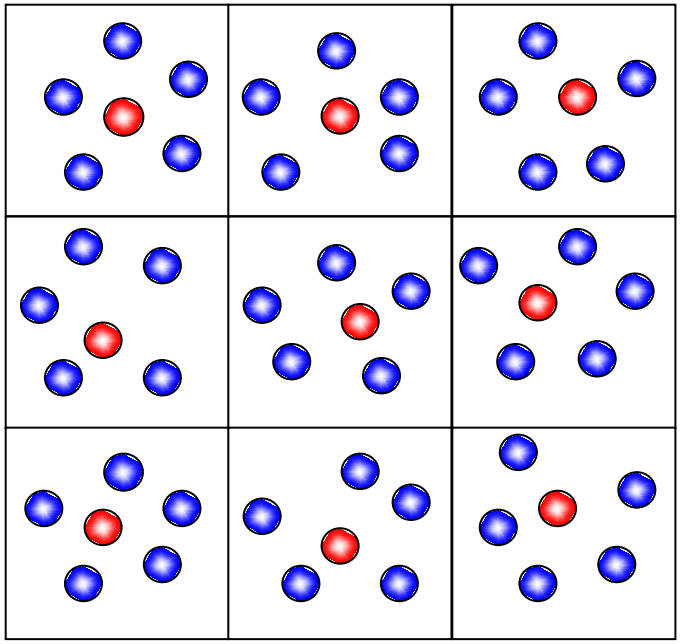
The *cumulant expansion* into a MacLaurin series: $\ln \int_0^\infty P(R,\lambda)\exp(2\mathrm{i}kR)\mathrm{d}R = \sum_{n=0}^{\infty} (2\mathrm{i}k)^n C_n / n!$

$$\chi_p(k) = S_0^2 \frac{1}{k} F(k) \exp(C_0 - 2C_2k^2 + \frac{2}{3}C_4k^4 - \frac{4}{45}C_6k^6)$$
$$\times \sin\left(2kC_1 - \frac{4}{3}C_3k^3 + \frac{4}{15}C_5k^5 + \phi(k)\right)$$

$\exp(C_0) \cong N\exp(-2C_1/\lambda)/C_1^2$

C_1 is the mean value of the distribution (**average distance**)
C_2 is the variance of the distribution (**MSRD factor**)
C_3 is the asymmetry of the distribution (**skewness**)
C_4 describes symmetric deviations from the Gaussian shape

Disorder



More about disorder – in the next lecture!

EXAFS equation: summary

$$\chi(k) = S_0^2 \sum_{p=1}^{M} \frac{F_p(k, R_p) e^{-\frac{2R_p}{\lambda(k)}}}{k R_p^2} e^{-2k^2\sigma_p^2} \sin\left(2kR_p - \frac{4}{3} C_{3p} k^3 + \phi_p(k, R_p)\right)$$

	M	the number of scattering paths
Structural parameters	N_p	the coordination number for the *p*-th path
	R_p	the half-length of *p*-th path (the interatomic distance for SS paths)
	σ^2_p	the mean square radial displacement (a.k.a. Debye-Waller factor)
	C_{3p}	3rd cumulant of the distribution, which accounts for anharmonic effects,non-Gaussian disorder
	S_0^2	the scale factor, which accounts for the multielectron effects (≈ 0.7-1.0)
	$\lambda(k)$	photoelectron effective mean free path
	F_p	the backscattering amplitude
	ϕ_p	the backscattering phase

And one more parameter:

E_0 reference energy value ($k = \sqrt{2m\left(E_{photon} - E_0\right)/\hbar^2}$)

EXAFS equation: summary

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Fitting parameters

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$\lambda(k)$ photoelectron effective mean free path

F_p the backscattering amplitude

ϕ_p the backscattering phase

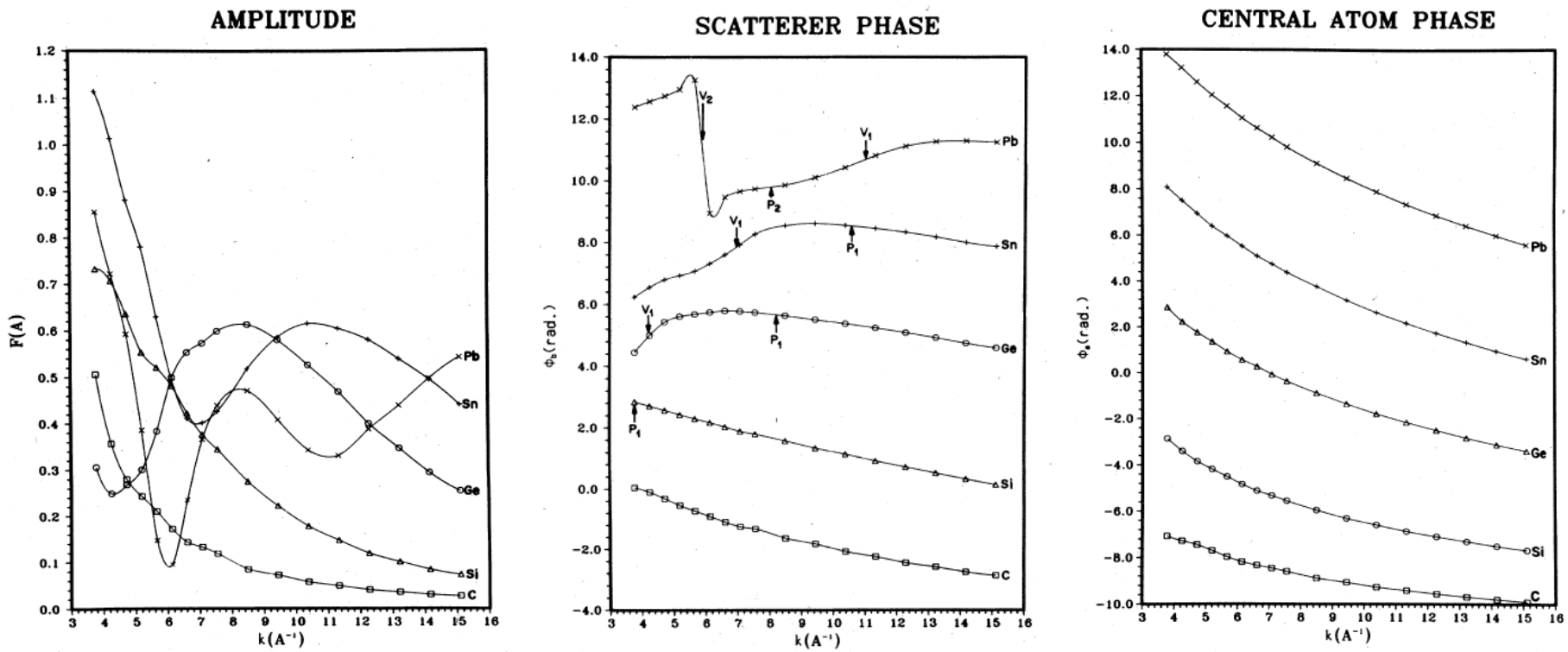
FEFF calculations

And one more parameter:

E_0 reference energy value ($k = \sqrt{2m(E_{photon} - E_0)/\hbar^2}$)

Chemical sensitivity: phases and amplitudes

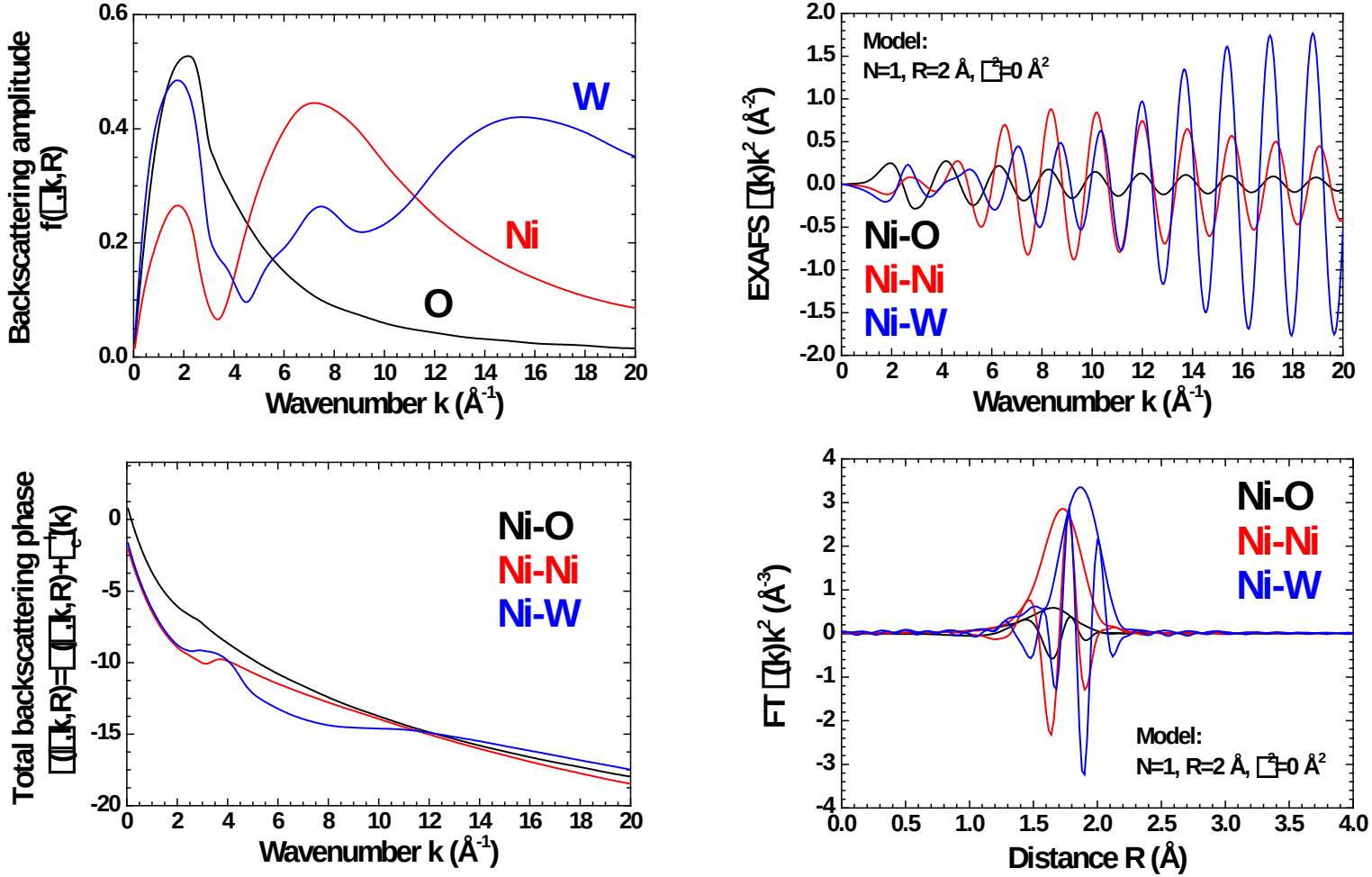
Scattering **amplitude** f and scattering **phase** $\phi(k) = \phi_{scatterer}(k) + \phi_{central\ atom}(k)$: different for different types of atoms and result in chemical sensitivity of EXAFS analysis



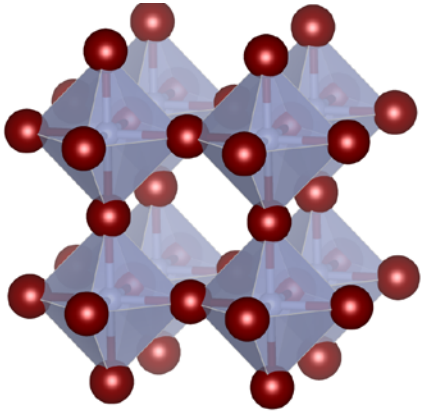
P. A. Lee, P. H. Citrin, P. Eisenberger, B. M. Kincaid, Rev. Mod. phys. 53 (1981) 769-806.

Chemical sensitivity: phases and amplitudes

Calculated contributions to the Ni K-edge EXAFS spectra for W, Ni and O atoms as backscatterers, assuming the same radial distribution (the same interatomic distances, disorder).



FEFF calculations



Initial, approximate structure model

feff.inp

```
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EDGE      K
S02       1.000000000000
*         pot    xsph  fms   paths genfmt ff2chi
CONTROL   1      1     1     1     1      1
PRINT     1      0     0     0     0      0
*         r_scf   [ l_scf  n_scf  ca ]
SCF       4.267535735058   0      30     0.100000000000
*         ixc  [ Vr  Vi ]
EXCHANGE  0      0   0
EXAFS 20.0
RPATH     7.000000000000
NLEGS     8
CRITERIA  0.0  0.500000000000
CFAVERAGE 2 1 7.000000000000
POTENTIALS
*   ipot   z [ label   l_scmt  l_fms  stoichiometry ]
      0   29    Cu      -1       -1       0
      1   7     N      -1       -1       1
      2   29    Cu      -1       -1       3
ATOMS
0.000000000000 1.908500000000 0.000000000000 2 Cu
0.000000000000 0.000000000000 0.000000000000 1 N
0.000000000000 3.817000000000 0.000000000000 1 N
-1.908500000000 3.817000000000 0.000000000000 2 Cu
-1.908500000000 0.000000000000 0.000000000000 2 Cu
```

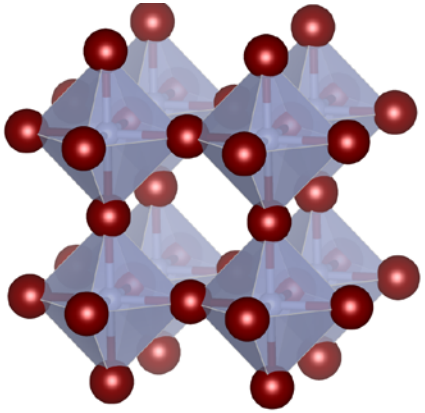
FEFF calculations

ments › 000_Cu3N › results › 2016 › feff_0

feff_win	atoms	feff
feff	fpf0	geom
global	log	mod1
mod2	mod3	mod4
mod5	mod6	s02
log1	misc	pot.bin
fort.38	fort.39	log2
log4	mpse	paths
phase.bin	xsect.bin	chi
feff.bin	feff	list
log5	log6	xmu
paths_fin	feff0001	feff0002
feff0003	feff0004	feff0005
feff0006	feff0007	feff0008
feff0009	feff0010	files

Phases & amplitudes for different paths

FEFF calculations



feff.inp

```
TITLE    Cu3N_example
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S02       1.000000000000
*         pot    xsph  fms   paths genfmt ff2chi
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PRINT     1      0     0     0     0      0
*         r_scf   [ l_scf  n_scf  ca ]
SCF       4.267535735058   0      30     0.100000000000
*         ixc  [ Vr  Vi ]
EXCHANGE  0      0   0
EXAFS 20.0
RPATH     7.000000000000
NLEGS     8
CRITERIA  0.0  0.500000000000
CFAVERAGE 2 1 7.000000000000
POTENTIALS
*   ipot   z [ label   l_scmt  l_fms  stoichiometry ]
      0   29    Cu      -1       -1       0
      1   7     N      -1       -1       1
      2   29    Cu      -1       -1       3
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0.000000000000 1.908500000000 0.000000000000 2 Cu
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0.000000000000 3.817000000000 0.000000000000 1 N
-1.908500000000 3.817000000000 0.000000000000 2 Cu
-1.908500000000 0.000000000000 0.000000000000 2 Cu
```

Initial, approximate structure model

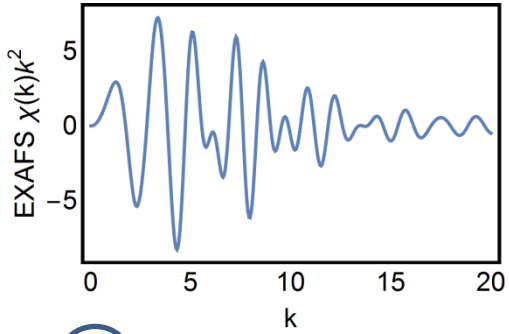
FEFF calculations

ments › 000_Cu3N › results › 2016 › feff_0

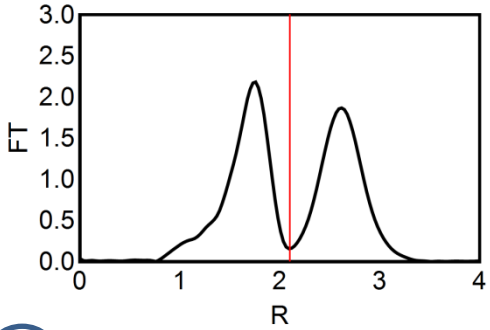
feff_win	atoms	feff
feff	fpf0	geom
global	log	mod1
mod2	mod3	mod4
mod5	mod6	s02
log1	misc	pot.bin
fort.38	fort.39	log2
log4	mpse	paths
phase.bin	xsect.bin	chi
feff.bin	feff	list
log5	log6	[illegible]
paths_fin	feff0001	feff0002
feff0003	feff0004	feff0005
feff0006	feff0007	feff0008
feff0009	feff0010	files

Phases & amplitudes for different paths

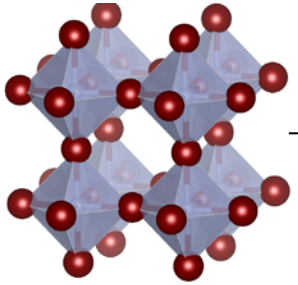
Fitting data!



1 Experimental data

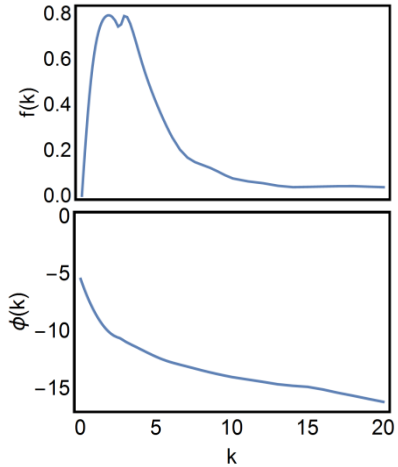


2 Fourier transform

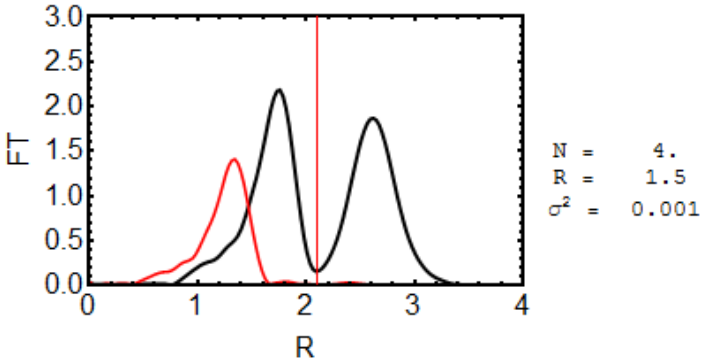


3 Initial model

4 FEFF



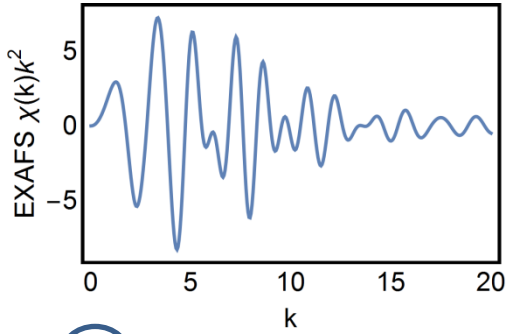
5 Scattering phases/amplitudes



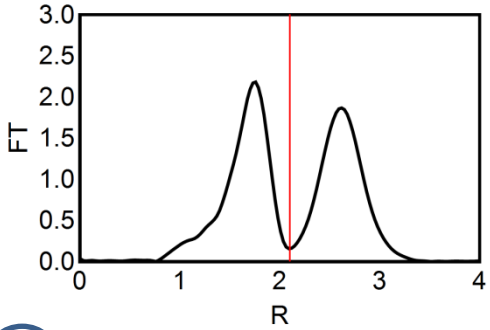
6 Non-linear least-squares fitting

Packages for FEFF-based analysis:
IFEFFIT, EXAFSPAK, WINXAS, XDAP, XFIT, EDA, LASE, MAC

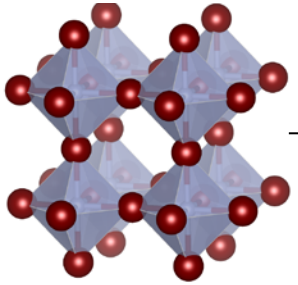
Fitting data!



1 Experimental data

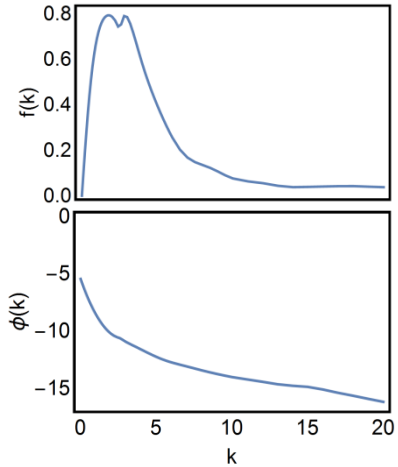


2 Fourier transform



3 Initial model

4 FEFF



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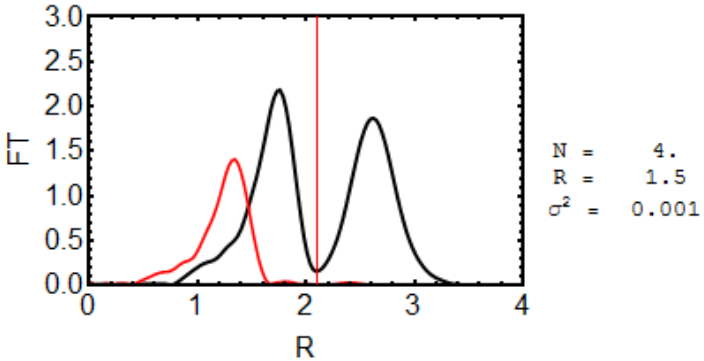


6 Non-linear least-squares fitting

Packages for FEFF-based analysis:
IFEFFIT, EXAFSPAK, WINXAS, XDAP, XFIT, EDA, LASE, MAC

What can go wrong?

☹ **Non-linear problem: many possible solutions, result will depend on the starting values for fitting parameters**

☹ **Correlation between parameters**

in the amplitude of EXAFS function: S_0^2N, σ^2, C_4

in the phase of EXAFS function: R, C_3, ΔE_0

Example:

$\Delta E_0 = 1$ eV $\Rightarrow \Delta R \approx 0.005$ Å

$\Delta E_0 = 5$ eV $\Rightarrow \Delta R \approx 0.025$ Å

$\Delta E_0 = 10$ eV $\Rightarrow \Delta R \approx 0.048$ Å

$\Delta N = 0.5 \Rightarrow \Delta\sigma^2 \approx 0.001$ Å^2

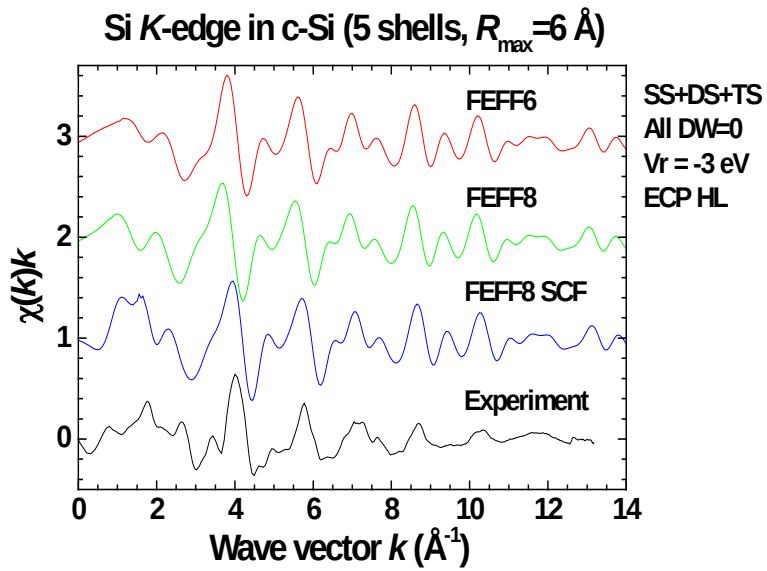
$\Delta N = 1.0 \Rightarrow \Delta\sigma^2 \approx 0.002$ Å^2

1. Fix E_0
2. Fix N

☹ **Some shape (Gaussian, quasi-Gaussian…) of the RDF needs to be assumed: not well-defined problem for disordered materials**

What can go wrong?

☹ **FEFF phases and amplitudes are not 100% accurate**



In some cases other EXAFS data analysis methods may give better accuracy (e.g ratio method, splice method)

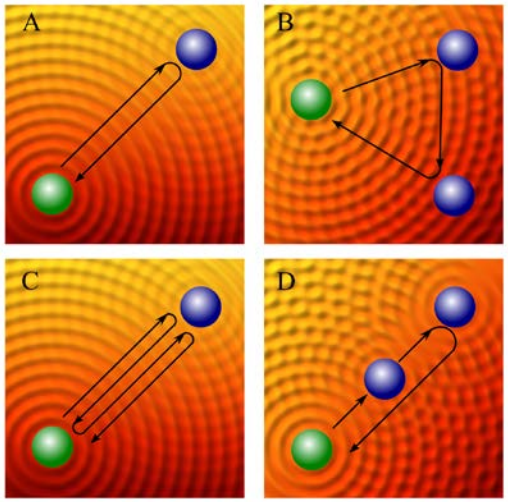
$$\ln \frac{AMPL(k)}{AMPL_{et}(k)} = \ln \frac{NR_{et}^2}{N_{et}R^2} - 2k^2(\sigma^2 - \sigma_{et}^2) + \frac{2}{3}k^4 \Delta C_4$$

$$PHASE(k) - PHASE_{et}(k) = 2k(R - R_{et}) - \frac{4}{3}k^3 \Delta C_3.$$

Stern et al, Phys. Rev. B 46 687 (1992)
Frenkel et al, Phys. Rev. B 54 884 (1996)

What can go wrong?

☹ **Information content in experimental EXAFS is limited, but number of scattering paths growths exponentially with the increase of *R*: analysis beyond the first coordination shell is challenging**



Nyquist criterion:

The total number of parameters M_{max} used in the model must be less than that given by the Nyquist theorem:

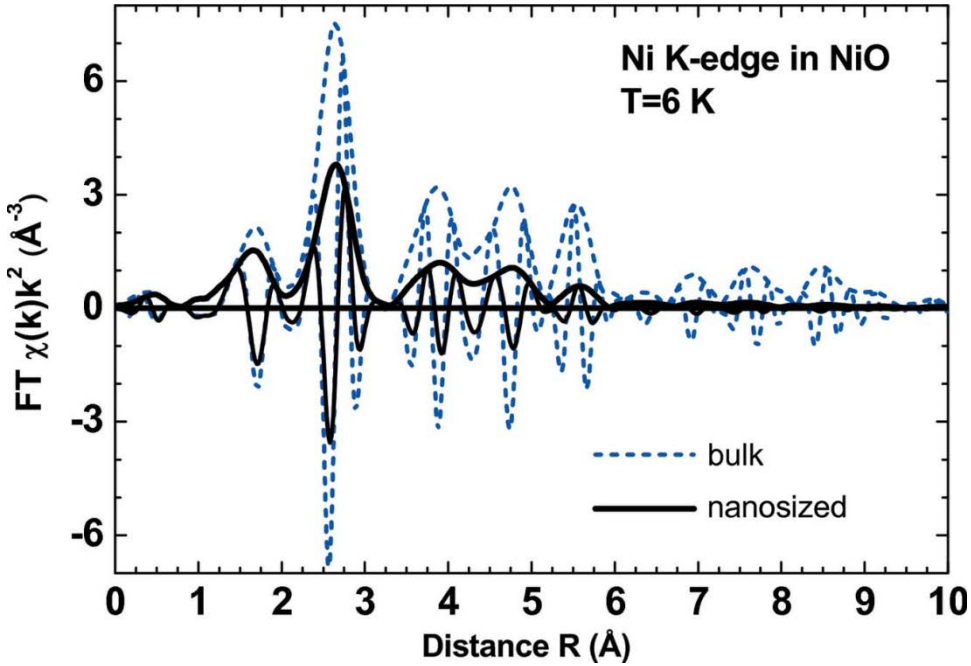
$$M_{\max} = \frac{2\Delta k \Delta R}{\pi} + 2$$

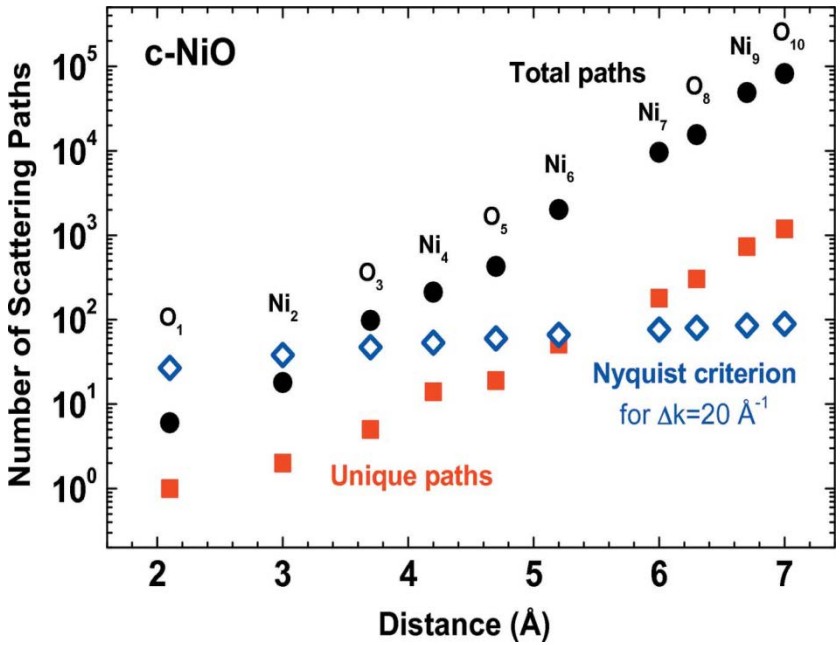
For a single shell, $\Delta k = k_{max} - k_{min} = 15$ Å^{-1} and $\Delta R = R_{max} - R_{min} = 1$ Å, then $M_{max} \approx 11.5$.

E.O. Brigham, The Fast Fourier Transform (Prentice Hall, Englewood Cliffs, New Jersey, 1974).
E.A. Stern, Phys. Rev. B 48 (1993) 9825.

Nyquist criterion:

Information from atoms at distances up to 10 Å can sometimes be encoded in experimental EXAFS. Our ability to access this information, however, is very limited.





A. Kuzmin and J. Chaboy, IUCrJ 1 (2014) 571-589.

List of paths, included in the analysis, should be very carefully considered

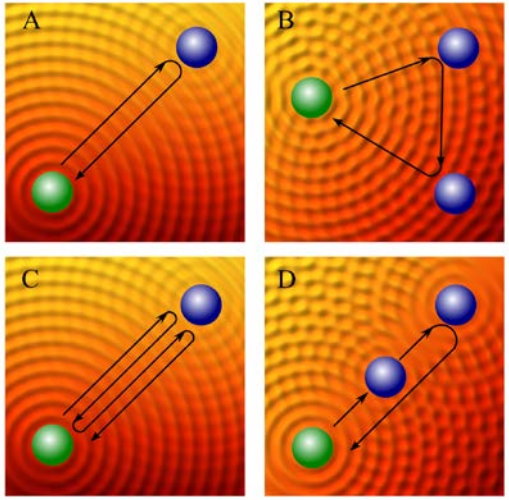
Can multiple scattering effects be neglected?

Problems with MS paths:

☹ There is a lot of them!

☹ Many paths have the same frequency – constructive/destructive interference is common

☹ Scattering amplitude $f(\theta, k)$ depends not only on k, but also on angle!!



A. Kuzmin and J. Purans, J. Phys.: Condensed Matter 5 (1993) 9423-9430.

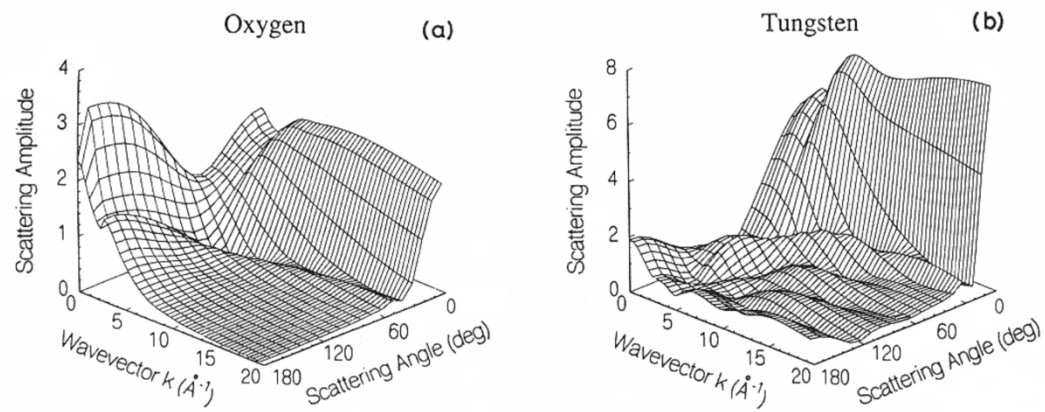
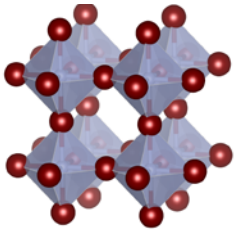
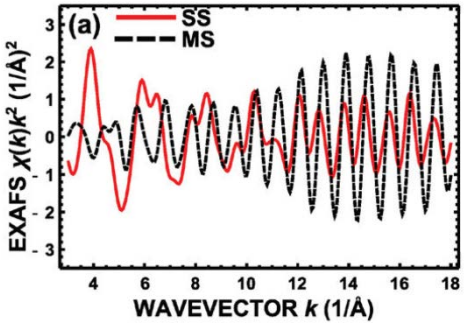


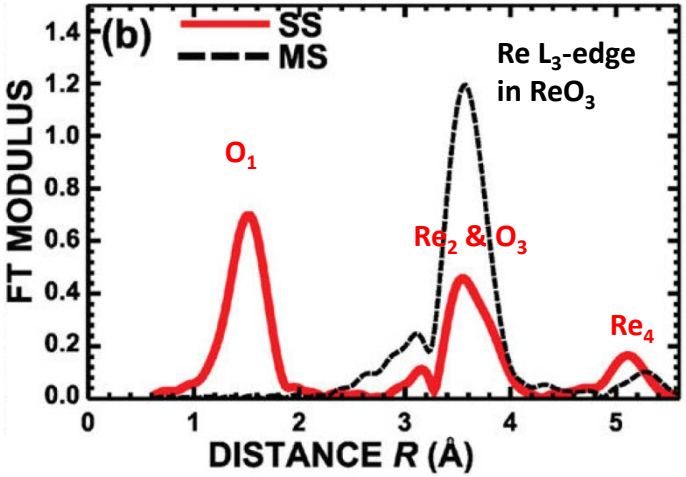
Figure 1. The angular dependence of the atomic scattering amplitude for oxygen and tungsten atoms. The angle $\theta = 0°$ corresponds to the back-scattering process and θ=180° to the forward-scattering process.

MS paths: focusing effect

Perovskites:

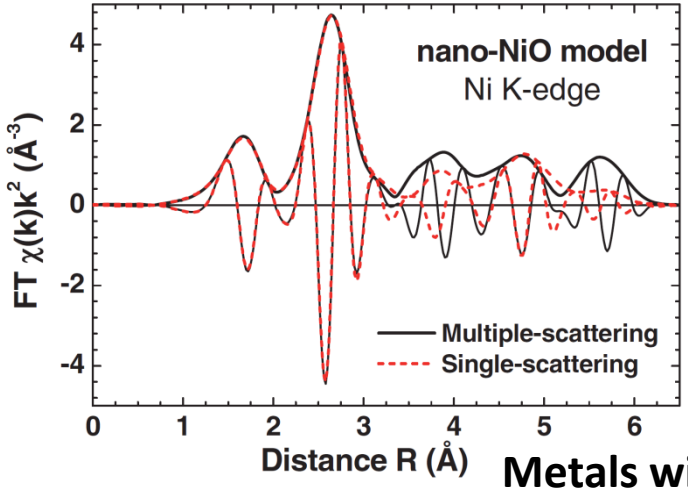


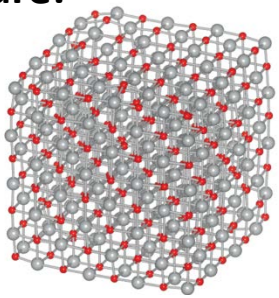




J. Timoshenko, A. Kuzmin, and J. Purans., J. Phys.: Condensed Matter 26 (2014) 055401.

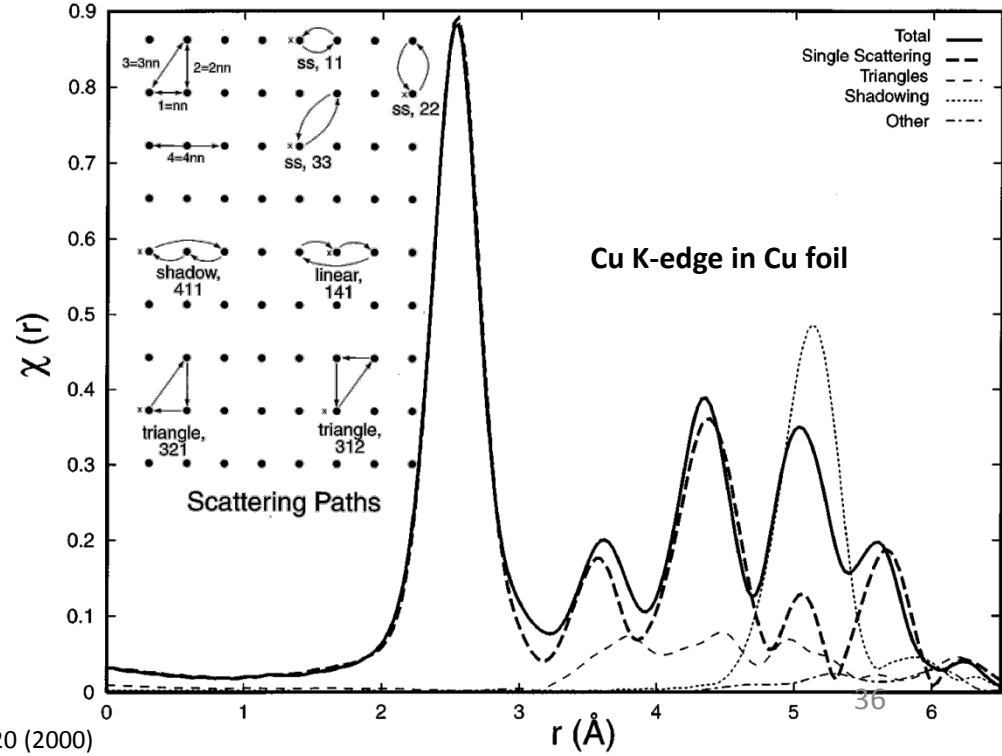
Materials with rock-salt structure:

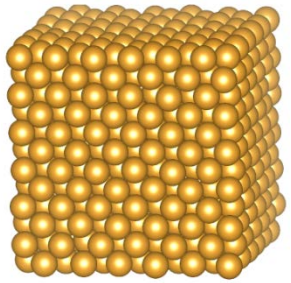




A. Anspoks et al, Phys. Rev. B 86, 174114 (2012)

Metals with fcc structure:





J.Rehr et al, Rev. Mod. Phys 72 620 (2000)

MS paths:angular information

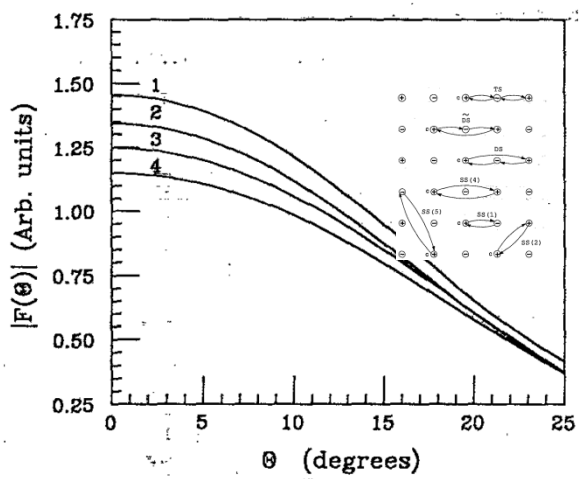
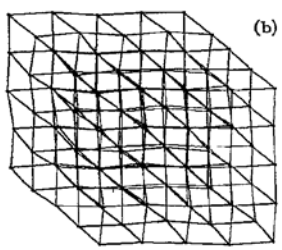


FIG. 4. $F(k,\Theta)$ ($k = 8\,\text{Å}^{-1}$) of nearly collinear DS paths: (1) Br-Rb^1-Br^4-Br; (2) Rb-Br^1-Rb^4-Rb; (3) Br-K^1-Br^4-Br; (4) Rb-Cl^1-Rb^4-Rb. Superscripts indicate the coordination shell.

$$\langle F(k,\Theta)\rangle \approx F(k,0)[1 - b(k)\langle\Theta^2\rangle],$$



Frenkel et al, Phys. Rev. Lett. 71, 3485 (1993)
Frenkel et al, Phys. Rev. B. 48, 12449 (1993)
Frenkel et al, Phys. Rev. B. 49, 11662 (1994)

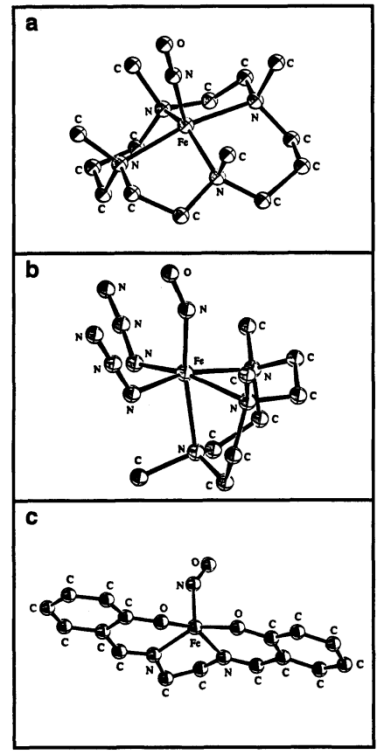
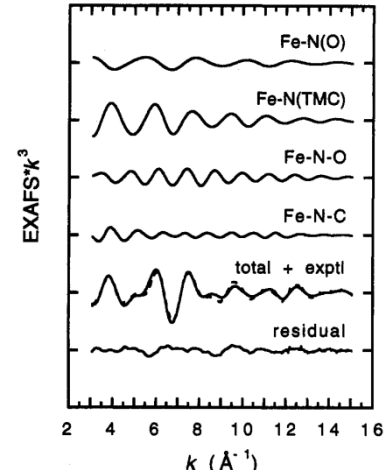
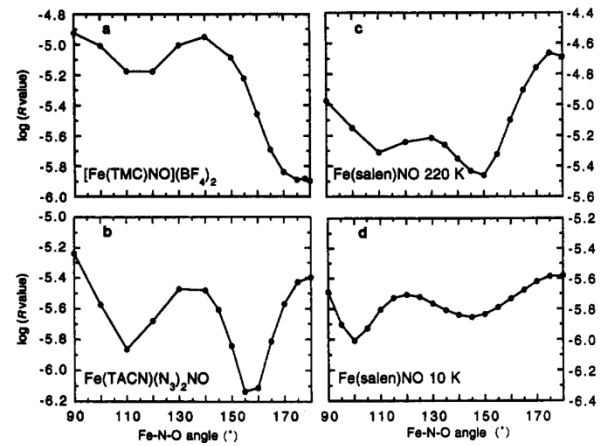


Figure 1. The molecular structure of (a) [Fe(TMC)NO](BF$_4$)$_2$, (b) Fe(TACN)(N$_3$)$_2$NO, and (c) Fe(salen)NO at 23 °C.





Vestre et al, J. Am. Chem. Soc. 116 6757 (1994)

J.Rehr et al, Rev. Mod. Phys 72 620 (2000)

Which paths to include?

FEFF provides estimates, how important is each path:

list.dat | paths.dat

```
PATH  Rmax= 7.000,  Keep_limit= 0.00, Heap_limit 0.00  Pwcrit= 0.50%
 ----------------------------------------------------------------------
  pathindex     sig2   amp ratio    deg    nlegs  r effective
        1     0.00000     0.1000E+03     2.000     2   1.9085
        2     0.00000     0.1519E+03     8.000     2   2.6990
        3     0.00000     0.3518E+02    16.000     3   3.2580
        4     0.00000     0.5060E+02     6.000     2   3.8170
        5     0.00000     0.1985E+02     2.000     3   3.8170
        6     0.00000     0.5150E+02     4.000     3   3.8170
        7     0.00000     0.8260E+01     2.000     4   3.8170
```

A good fitting strategy **– to start with small number of the most important paths** and, if necessary, to add some other paths afterwards, if they improve fit.

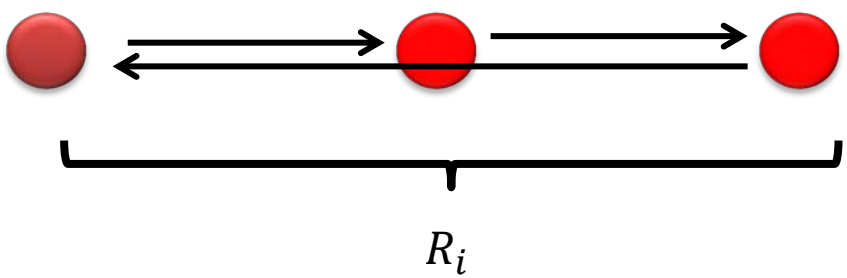
list.dat | paths.dat

```
PATH  Rmax= 7.000,  Keep_limit= 0.00, Heap_limit 0.00  Pwcrit= 0.50%
 ----------------------------------------------------------------------
     1    2   2.000  index, nleg, degeneracy, r=  1.9085
      x           y           z     ipot  label      rleg      beta        eta
    0.000000    1.908500    0.000000   1 'N     '     1.9085  180.0000    0.0000
    0.000000    0.000000    0.000000   0 'Cu    '     1.9085  180.0000    0.0000
     2    2   8.000  index, nleg, degeneracy, r=  2.6990
      x           y           z     ipot  label      rleg      beta        eta
    0.000000    1.908500   -1.908500   2 'Cu    '     2.6990  180.0000    0.0000
    0.000000    0.000000    0.000000   0 'Cu    '     2.6990  180.0000    0.0000
     3    3  16.000  index, nleg, degeneracy, r=  3.2580
      x           y           z     ipot  label      rleg      beta        eta
    0.000000    1.908500    1.908500   2 'Cu    '     2.6990  135.0000    0.0000
    0.000000    1.908500    0.000000   1 'N     '     1.9085   90.0000    0.0000
    0.000000    0.000000    0.000000   0 'Cu    '     1.9085  135.0000    0.0000
     4    2   6.000  index, nleg, degeneracy, r=  3.8170
      x           y           z     ipot  label      rleg      beta        eta
    0.000000   -3.817000    0.000000   2 'Cu    '     3.8170  180.0000    0.0000
    0.000000    0.000000    0.000000   0 'Cu    '     3.8170  180.0000    0.0000
     5    3   2.000  index, nleg, degeneracy, r=  3.8170
      x           y           z     ipot  label      rleg      beta        eta
    0.000000    1.908500    0.000000   1 'N     '     1.9085  180.0000    0.0000
    0.000000   -1.908500    0.000000   1 'N     '     3.8170  180.0000    0.0000
    0.000000    0.000000    0.000000   0 'Cu    '     1.9085    0.0000    0.0000
     6    3   4.000  index, nleg, degeneracy, r=  3.8170
      x           y           z     ipot  label      rleg      beta        eta
    0.000000   -3.817000    0.000000   2 'Cu    '     3.8170  180.0000    0.0000
    0.000000   -1.908500    0.000000   1 'N     '     1.9085    0.0000    0.0000
    0.000000    0.000000    0.000000   0 'Cu    '     1.9085  180.0000    0.0000
```

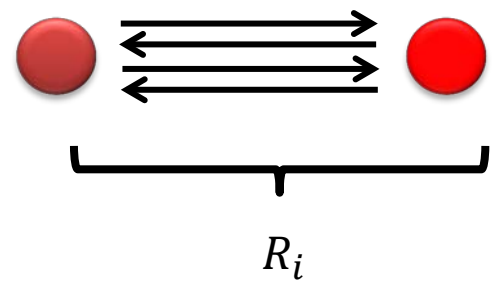
Reducing number of variables: constraints

Constraints - another important way how to minimize the total number of fitting variables and stabilize the fit:

- E_0 value is (most likely) the same for all scattering paths
- **Coordination numbers *N*** for crystals are often known in advance
- **Geometric constraints:**



R_i and σ_i^2 for linear double-scattering path should be the same as for corresponding single-scattering path



R_i is 2 times larger and σ_i^2 is 4 times larger for this tripple-scattering path than for corresponding single-scattering path

- **Isotropic expansion model:** $R_i = R_i(\mathrm{eq})(1+\varepsilon)$, where $R_i(\mathrm{eq})$ - corresponding distance in reference structure (e.g., crystallographic structure, known from diffraction) and ε is a fitting parameter.
- **Stoichiometry:** ratio of partial coordination numbers *N*(M-A)/N(M-B) may correspond to the ratio of A and B atoms in the sample

Constraints: fitting multiple data sets

- EXAFS data acquired **at two (or more) absorption edges** for the same sample can be fit simultaneously to find a single structure model that agrees with all experimental information. In this case
  - R(A-B) = R(B - A)
  - σ^2(A-B) = σ^2 (B - A)
  - N(A-B) = N (B - A) n (B) / n(A), where n(A) and n(B) – concentrations of atoms A and B

- **Temperature dependent data:**
  - $R_i(T) = R_i(T_0)(1 + \alpha(T - T_0))$, where $R_i(T_0)$ and α are fitting parameters
  - $\sigma^2(T)$ follows Einstein or Debye model (see the next lecture)

- **Concentration-dependent data*:***
  - R(A-B) may follow Veggard's law

- …

It may be a good idea **to start with very constrained model with only a few degrees of freedom**.

Additional choices

- Different ***n* values** can be used for the analysis of EXAFS data $\chi(k)k^n$ to highlight contributions at low or high *k* values.
  - **Simultaneous fitting** of EXAFS data $\chi(k)k^n$ with different *n* values (1, 2, 3, …) may help to minimize the correlation between *N* and σ^2 values.

- Different *k*-ranges, used for Fourier transform and analysis, may increase or reduce the influence of **experimental noise** (dominates at high *k*-values) and influence of **imprecisions of FEFF theory, background subtraction artifacts, multiple-scattering effects** (dominates at low *k*-values)

Fit quality. How to compare two fits

Goodness of fit:

$$\chi^2 = \frac{M_{max}}{N} \sum_i \left(\frac{\left| f_i^{exp} - f_i^{model} \right|}{\varepsilon_i} \right)^2$$

N – number of points, M_{max} – number of independent measurements (number in Nyquist theorem), ε_i - uncertainty.

For good fit χ^2 should be around 1, if random error dominates. However, in our case systematic errors are significant and ε_i is hard to estimate. Typically χ^2>10.

The actual χ^2 value is not very useful, but by comparing χ^2 obtained in two different fits, one can judge, which fit is better.

Fit quality. How to compare two fits?

R-factor:

$$R = \frac{\sum_i \left(\left|f_i^{exp} - f_i^{model}\right|\right)^2}{\sum_i \left|f_i^{exp}\right|^2}$$

R factor is proportional to χ^2. Fit is bad, if R is larger than a few percents (unless the data are very noisy).

Statistical tests can be sometimes used to determine if the fit given by more complicated model is substantially better fit

e.g., **F-test** or **Hamilton test** (see, for example, [*Downward, L., Booth, C. H., Lukens, W. W., & Bridges, F. (2006). A variation of the F-test for determining statistical relevance of particular parameters in EXAFS fit.*])

Indications that something is wrong

- Unphysical values of non-structural parameters (S_0^2 larger than 1 or smaller than 0.5, E_0 very far from the absorption edge value).

- Unphysical values of structural parameters (*R* values substantially (e.g., more than by 0.1 Å) different from crystallographic values, σ^2 values negative or very large (e.g., larger than 0.1 Å^2), *N* values in nanomaterial larger than that in corresponding bulk material, …).

- Very unstable fit – small changes in the initial values of structure parameters or in the fitting range result in dramatic changes in the fit results.

Thank you for your attention!