n-body expansion for EXAFS analysis

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XAS cross section

The polarization averaged XAS cross-section for transitions to a dipole selected final state of angular momentum l_0 can be written as

$$\sigma(\omega) = \sigma_0 \left[\Im \frac{1}{\Im(t_0^{l_0})} \frac{1}{2l_0+1} \sum_{m_0} [T(I - GT)^{-1}]_{0,0}^{L_0,L_0} \right]$$

where σ_0 is the atomic cross-section, T and G are the atomic scattering (phase-shift) and photoelectron propagator matrices in a local basis, indexed by i, j running over the different atoms.

- Electron interaction (T) and structure (G) are decoupled
- Non-linear relationship between geometry and XAS signal: $\sigma \sim (I - GT)^{-1}$ mathematical consequence of the strong coupling of the photoelectron with the surrounding atoms (more difficulties in analyzing XAS data)

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

Multiple Scattering

- A first approach to this problem is to use the so-called MS expansion. Where the norm of the GT matrix (maximum modulus of its eigenvalues) satisfies $||GT|| < 1$ then the formal matrix expansion:

$$T(I - GT)^{-1} = T(I + GT + GTGT + GTGTGT + ...)$$

  is convergent and gives rise to the MS series. The above condition will certainly hold above a given energy since not only the elements of the G matrix decrease like $1/\sqrt{E}$ but also $||T|| = \max|t_i|$ tends to zero much more rapidly with energy.
- Writing down the series we obtain:

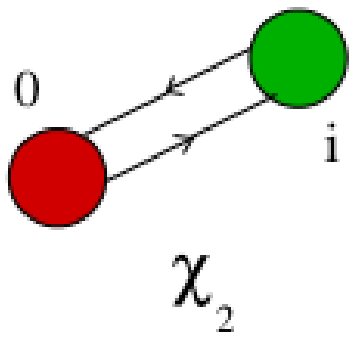
$$\sigma(\omega) = \sigma_0 \left[1 + \sum_{i \neq 0} \chi_2^{0i0} + \sum_{\substack{i \neq j \\ i \neq 0, j \neq 0}} \chi_3^{0ij0} + \sum_{\substack{i \neq j \neq k \\ i \neq 0, k \neq 0}} \chi_4^{0ijk0} + \cdots \right]$$

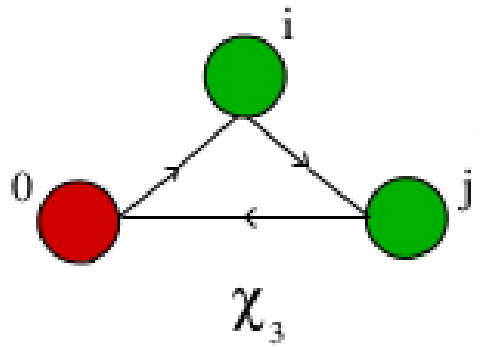
The χ_n signals are oscillating functions of the type:

$$\chi_n(k) = A(k, R)\sin(kR_p + \phi(k, R))$$

where A and ϕ are smooth functions of k and of the geometrical parameters R. The relevant frequency of the signal is the path length R_p.

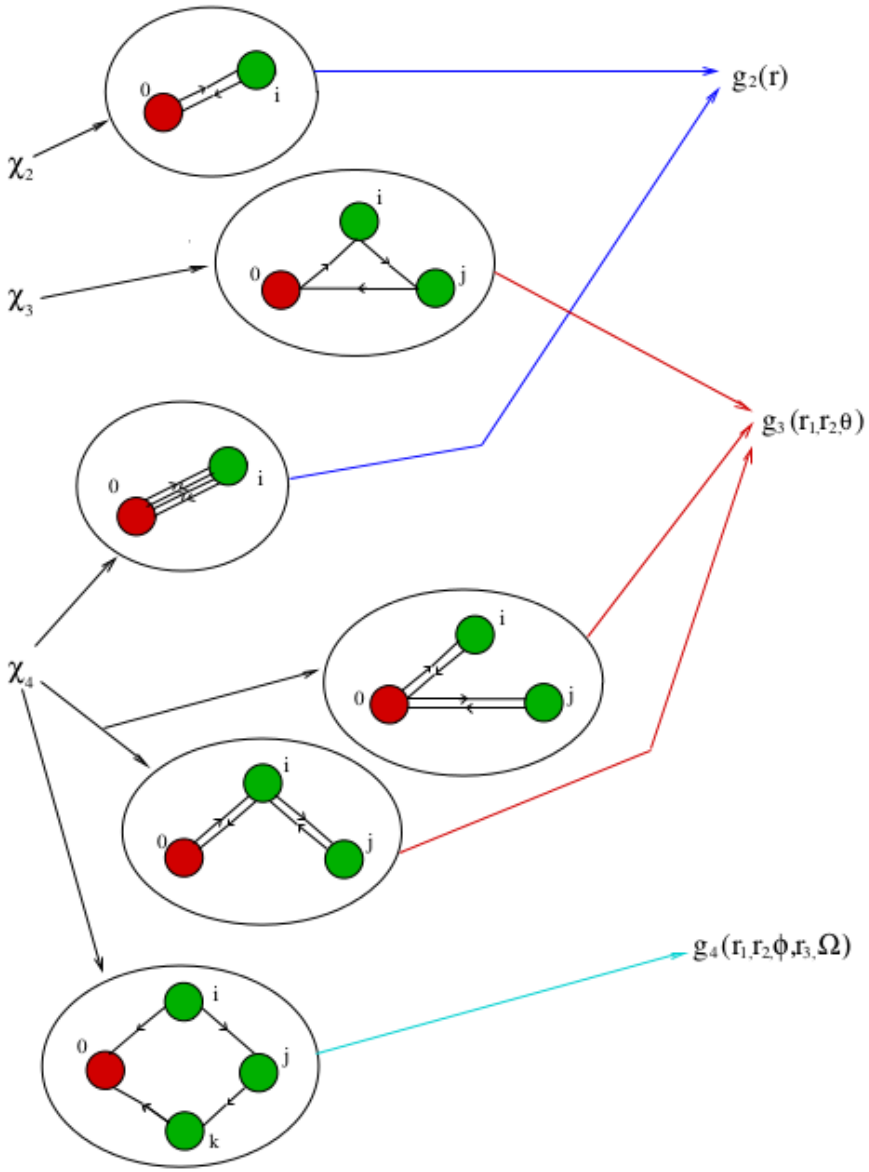
An important inconvenience of the MS expansion is that it has no simple relationship with the structure (geometry): χ_2 terms probe the relative position of atoms 0 and i, χ_3 terms probe the positions of the atoms 0, i and j. They are sensitive to the two-particle and three-particle distribution respectively.





Note: single scattering approximation (retain only the first χ_2 term) may be sufficient in some cases, but information limited to pair distributions

For χ_4 terms the situation becomes more complicated: a generic $0ijk0$ path probes four-particle correlations, but special paths like $0i0k0$ or $0iji0$ and $0i0i0$ probe lower order correlations. In general at order n, in χ_n there are paths involving all particle distributions from 2 to n if n is even or from 3 to n if n is odd.
A different and potentially more powerful approach to the solution of the XAS structural problem is based on a n-body decomposition of the cross-section. The main idea is to reduce the dimension of the problem to the actual local physical quantities of interest, related to n-atom properties where $n \ll N$ (N being the number of atoms of the system).



n-body expansion

The total x-ray absorption cross-section for n atoms $\sigma(0, i, j...n)$ can be expanded in terms of the irreducible n-body cross sections of lower order:

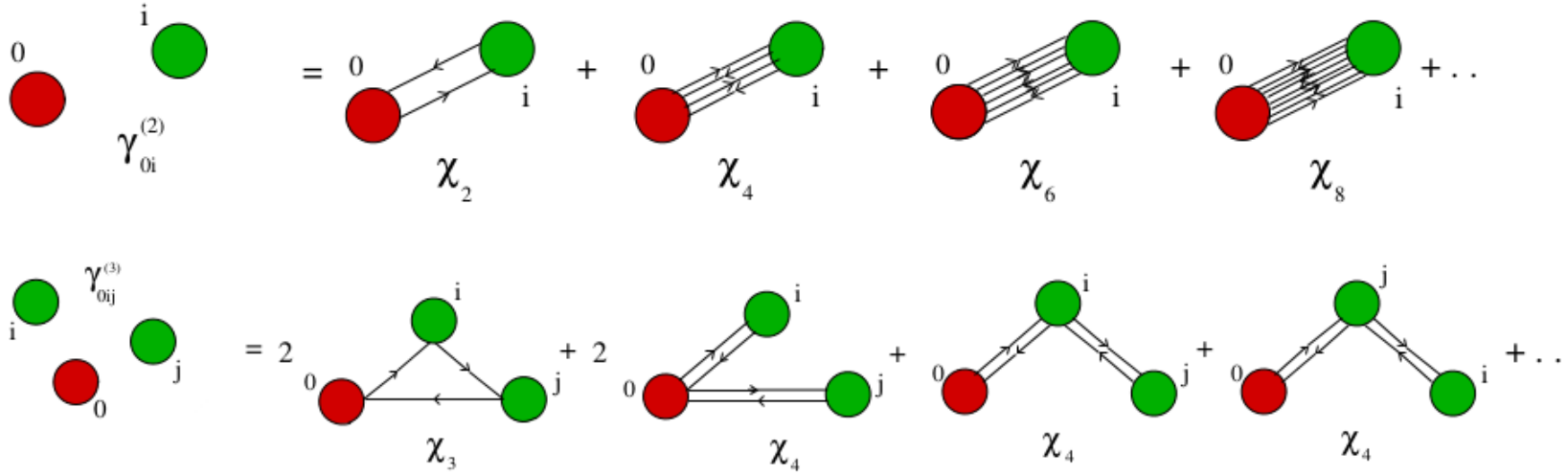
$$\sigma(0, i, j..., n) = \sigma_0 + \sum_i \sigma^{(2)}(0, i) + \sum_{(i,j)} \sigma^{(3)}(0, i, j) + \sum_{(i,j,k)} \sigma^{(4)}(0, i, j, k) + \cdots + \sigma^{(n)}(0, i, j, ..., n)$$

The dimensionless quantities $\gamma^{(n)} = \sigma^{(n)}/\sigma_0$, represent the irreducible n-body contributions to the structural XAS term $\chi(E) = \frac{\sigma(E)-\sigma_0(E)}{\sigma_0(E)}$. In this way we arrive to an equivalent expansion for the experimentally measurable structural signal $\chi(E)$ that differs substantially from the MS series:

$$\chi(0, i, j..., n) = \sum_i \gamma^{(2)}(0, i) + \sum_{(i,j)} \gamma^{(3)}(0, i, j) + \sum_{(i,j,k)} \gamma^{(4)}(0, i, j, k) + \cdots + \gamma^{(n)}(0, i, j, ..., n)$$

The irreducible n-body $\gamma^{(n)}$ signals are the central quantities in the GNXAS approach (`http://gnxas.unicam.it`) since they are associated with well defined n-body arrangements of the atoms.

- simple linear relationship among structure (expressed in terms of 2, 3, 4, ... n-body distributions) and signal is obtained;
- due to mean free path effects, the higher order n-body terms are generally smaller than the lower order ones, so that convergence with few terms is expected;



- hierarchical relationship between different n-body configurations: a n-body configuration contains several $n - m$-body sub-configurations that are not independent. This allows to reduce the number of n-body coordinates just to the independent ones.

Real XAS data: configurational average

Having defined the irreducible $\gamma^{(n)}$ MS signals, the general expression of the XAS structural term is given in terms of the n-body distribution functions $g_n(r)$ (r is a generic set of n-body coordinates):

$$\begin{aligned}\langle\chi(k)\rangle \;=\; & \int_0^\infty dr\; 4\pi r^2\rho\; g_2(r)\; \gamma^{(2)}(r,k) \;+\; \int dr_1 dr_2 d\phi\; 8\pi^2 r_1^2 r_2^2 \sin(\phi) \\ & \times \rho^2 g_3(r_1,r_2,\phi)\gamma^{(3)}(r_1,r_2,\phi,k) \;+\; \int dr_1 dr_2 d\phi dr_3 d\Omega\; 8\pi^2 r_1^2 r_2^2 r_3^2 \\ & \times \sin(\phi)\rho^3 g_4(r_1,r_2,\phi,r_3,\Omega)\gamma^{(4)}(r_1,r_2,\phi,r_3,\Omega,k) \;\cdots\end{aligned}$$

The integrals, because of the short range nature of the kernels $\gamma^{(n)}$, are actually limited to a region of linear dimensions of the order of few Å . This is due to the strong electron interaction (mean free path).
This equation should be compared with the well known expression for the static structure factor (disordered system) which can be measured by using x-ray or neutron diffraction:

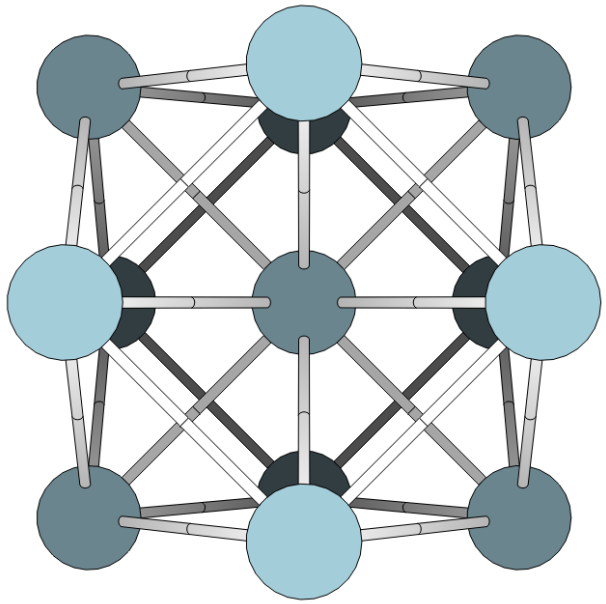
$$S(k) = 1 + \frac{4\pi\rho}{k}\int_0^\infty (g_2(r)-1) r \sin(kr) dr.$$

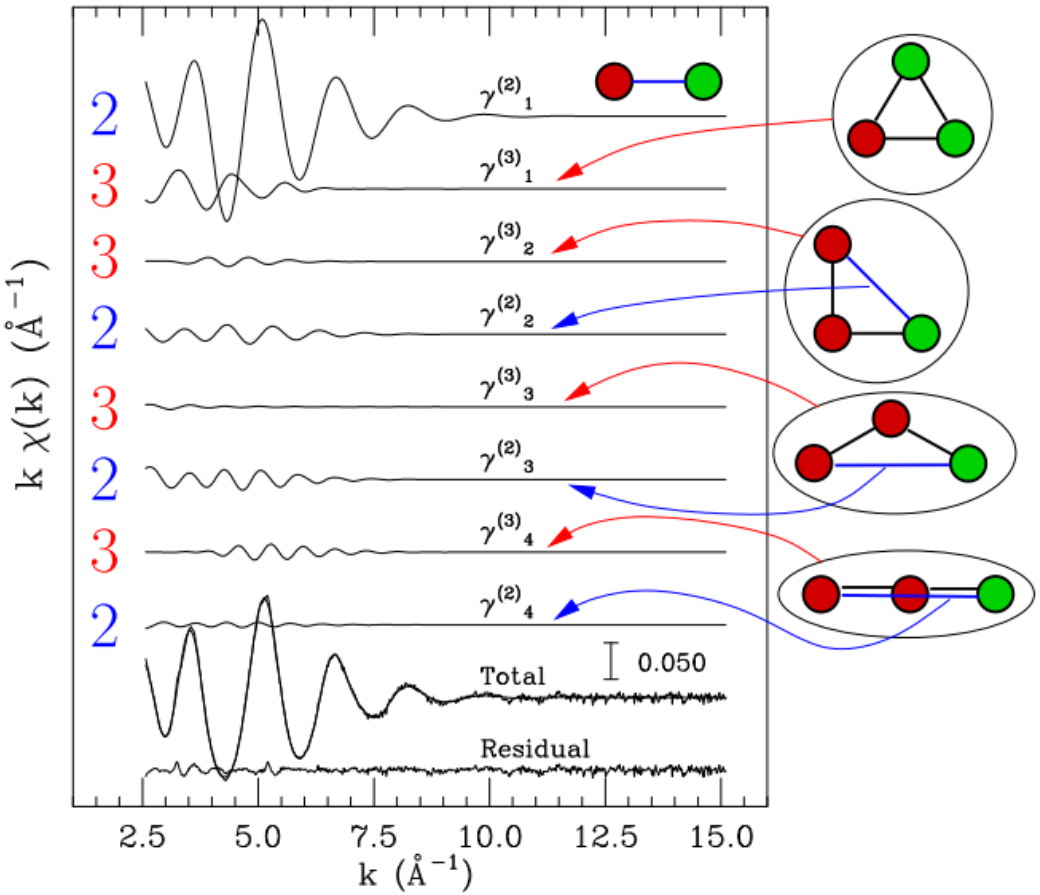
The different nature of the kernels makes the structural information on the $g_2(r)$ obtainable in the two cases largely complementary (short vs. medium range information). Moreover, XAS can give information beyond the pair distribution. For crystals, where diffraction gives obviously a richer information about atomic positions, XAS can provide unique data about local correlated vibrations.

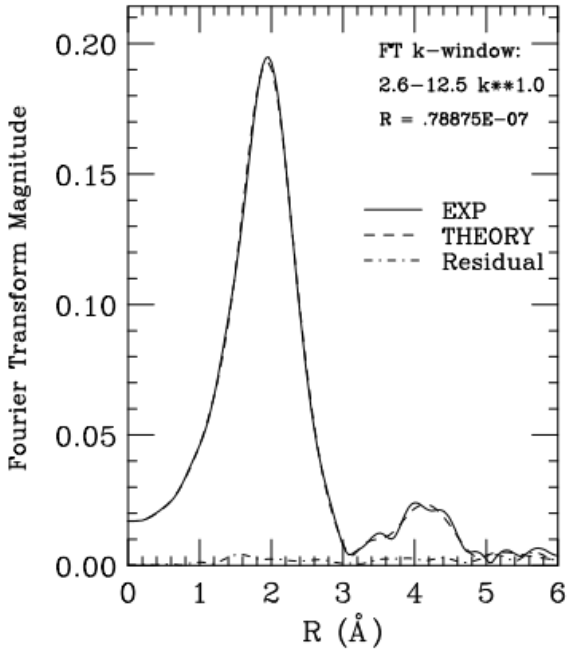
Example: fcc Ni

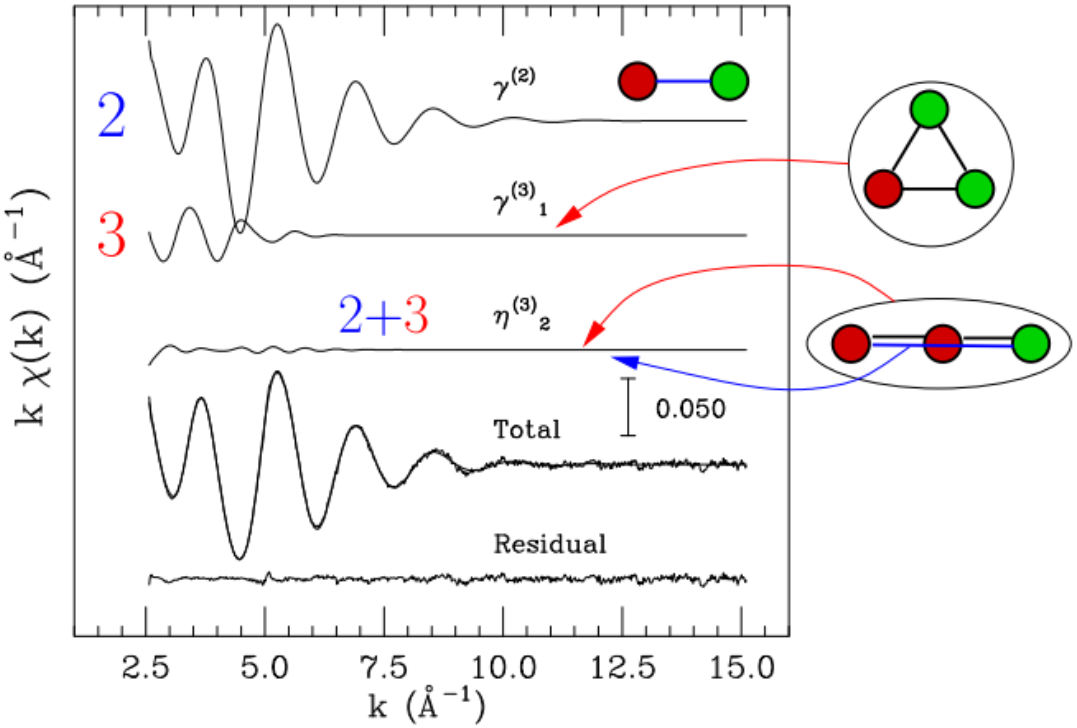
TABLE VI. Pair and triplet contributions in the fcc structure. The distances are reported in units of the nearest-neighbor distance R, the angles are in degrees. The degeneracy (Deg.) is specified for each configuration. The photoabsorber position for the triplet configurations is also specified (Pos.).

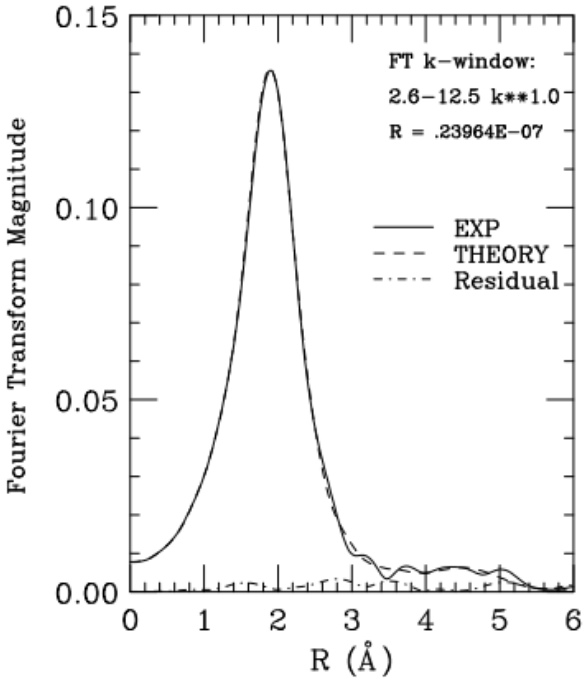
Peak	R_1/R	R_2/R	θ (°)	Deg.	Pos.	$R_{path}/2R$
1	1			12		1
2	$\sqrt{2}$			6		$\sqrt{2}$
3	$\sqrt{3}$			24		$\sqrt{3}$
4	2			12		2
5	$\sqrt{5}$			24		$\sqrt{5}$
6	$\sqrt{6}$			8		$\sqrt{6}$
1	1	1	60	24	1	1.5
2	1	1	90	12	1	1.707
				24	2	1.707
3	1	1	120	24	1	1.866
				48	2	1.866
4	1	1	180	6	1	2
				12	2	2
5	1	$\sqrt{2}$	90	24	1	2.073
				24	2	2.073
				24	3	2.073
6	1	$\sqrt{3}$	73.22	48	1	2.232
				24	3	2.232
7	1	$\sqrt{2}$	135.00	24	1	2.325
				24	2	2.325
				24	3	2.325




k χ(k) (Å^{-1})
2
3
3
2
3
2
3
2
$\gamma^{(2)}_1$
$\gamma^{(3)}_1$
$\gamma^{(3)}_2$
$\gamma^{(2)}_2$
$\gamma^{(3)}_3$
$\gamma^{(2)}_3$
$\gamma^{(3)}_4$
$\gamma^{(2)}_4$
Total
0.050
Residual
2.5
5.0
7.5
10.0
12.5
15.0
k (Å^{-1})


Fourier Transform Magnitude
0.20
0.15
0.10
0.05
0.00
FT k−window:
2.6−12.5 k**1.0
R = .78875E−07
EXP
THEORY
Residual
0
1
2
3
4
5
6
R (Å)


2
3
2+3
$\gamma^{(2)}$
$\gamma^{(3)}_1$
$\eta^{(3)}_2$
Total
Residual
0.050
k χ(k) (Å^{-1})
2.5
5.0
7.5
10.0
12.5
15.0
k (Å^{-1})


FT k−window:
2.6−12.5 k**1.0
R = .23964E−07
EXP
THEORY
Residual
Fourier Transform Magnitude
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
R (Å)