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Recursion method for multiple-scattering XAFS Debye–Waller factors

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An efficient, finite temperature, recursion method (RM) is introduced for calculations of the mean-square relative displacements σ^2 in multiple scattering (MS) XAFS Debye-Waller factors. Instead of calculating total projected densities of modes, the calculations are based on a double δ-function representation. Results for the Debye-Waller factors are found to be in agreement with equation-of-motion (EM) method to within about 10% percent for all MS paths.

Keywords: Debye-Waller factors; XAFS; recursion method.

1. Introduction

In the weak disorder limit, or harmonic approximation, the mean square variation $\sigma_j^2 = \langle (r_j - R_j)^2 \rangle$ in the effective MS path length $R_j = \langle r_j \rangle$ controls the XAFS Debye-Waller (DW) factor. This damping parameter is crucial to the success of the modern theory of XAFS (Crozier *et al.*, 1988). We have shown in a previous publication (Poiarkova & Rehr, 1999) that σ_j^2 for a general MS path j can be calculated in terms of the local projected vibrational density of states (VDOS) $\rho_j(\omega)$,

$$\sigma_j^2(T) = \frac{\hbar}{2\mu_j} \int \frac{d\omega}{\omega} \rho_j(\omega) \coth \frac{\beta\hbar\omega}{2}, \tag{1}$$

where $\beta = 1/k_B T$ and μ_j is an effective reduced mass for path j that ensures normalized VDOS ρ_j,

$$\frac{1}{\mu_j} \equiv \sum_{i=1}^{n_j} \frac{1}{M_i} \left(\frac{\hat{R}_{ii-} + \hat{R}_{ii+}}{2} \right)^2. \tag{2}$$

Here $i+ \equiv i+1$, $i = n_j + 1$ corresponds to site $i = 1$, n_j is the number of scattering legs in the path, and $\hat{R}_{ii+}$ is the directing unit vector between scattering sites i and $i+$.

A number of techniques are being used for VDOS calculations. These include correlated Einstein (CE) and EM methods. The first one is an isotropic approach and requires knowledge of Einstein temperature (or frequency) for a given material. The CE model approximates the vibrational spectrum with a single delta-function centered at a path dependent effective vibrational frequency $\omega_E(R_j)$, $\rho_j(\omega) = \delta(\omega - \omega_E(R_j))$. The traditional single frequency CE approximation does not differentiate between acoustic and optical modes and can lead to poor agreement with experimental data. The EM approach (Rehr & Alben, 1977) is based on solving $3N_{at}$ equations of motion in real time given a few local force constants in an N_{at}-atom cluster. The EM method provides good agreement with experiment (e.g. 4% error for the first three shells in Cu crystal) but can be time consuming.

The purpose of this report is to present an improvement to the traditional CE model by using the recursion or Lanczos method (Haydock *et al.*, 1975) with a given set of microscopic force constants. We discuss our results in comparison with the CE and EM calculations. Further details will be presented elsewhere.

2. Formalism

The RM is a technique for determining local physical behavior by successive approximations, which involve more and more of a given system. We are interested in the projected density $\rho_j(\omega)$, but it is more convenient to deal with the distribution with respect to $\omega^2 = x$,

$$g_j(x) \equiv \langle Q_j | \delta(x - D) | Q_j \rangle = \frac{\rho_j(\omega)}{2\omega}. \tag{3}$$

Here $D_{\alpha,\beta}(l,m) = \Phi_{\alpha,\beta}(l,m)/\sqrt{M_l M_m}$ is the dynamical matrix of order $3N_{at} \times 3N_{at}$ with $\Phi_{l\alpha,m\beta}$ denoting the second derivatives of the potential energy V of the lattice deformation with respect to the atomic displacements $u_{l\alpha}$ and $u_{m\beta}$ taken in the equilibrium configuration, and $|Q_j\rangle \equiv |\sqrt{\mu_j/M_1}(\hat{R}_{1,n_j-} + \hat{R}_{1,2})/2, \ldots \sqrt{\mu_j/M_i}(\hat{R}_{ii-} + \hat{R}_{ii+})/2, \ldots 0\rangle$ $(i = 1, \ldots n_j)$ is a normalized initial displacement state for MS path j. If only the central interaction between the nearest neighbors is taken into account, $V = (1/2)\sum k_{lm}(\delta r_{lm})^2$ for bond stretches $\delta r_{lm} = (\vec{u}_l - \vec{u}_m) \cdot \hat{R}_{lm}$ and the matrix of the second derivatives can be written in the form

$$\Phi_{\alpha,\beta}(l,m) = \sum_{i=1}^{N_m} k_{im} \hat{R}_{im}^{\alpha} \hat{R}_{im}^{\beta} \delta_{lm} - k_{lm} \hat{R}_{lm}^{\alpha} \hat{R}_{lm}^{\beta}, \tag{4}$$

where k_{lm} is a bond-stretching force constant for nearest neighbors l and m, N_m is a number of the nearest neighbors of atom m, and $\hat{R}_{lm}^{\alpha}$ is the αth cartesian component of the directing unit vector between atoms l and m.

The RM yields a continued fraction representation of $g_j(x)$, i.e.

$$g_j(x) = -\frac{1}{\pi} \operatorname{Im} \cfrac{1}{x - a_0 - \cfrac{b_0}{x - a_1 - \cfrac{b_1}{x - a_2 - \ldots}}} \tag{5}$$

in which $\operatorname{Im} x \to 0^+$. The coefficients a_n and b_n determine a 3-term recursion relation which defines new orthogonal basis states $|n\rangle$,

$$\begin{aligned} &|n+1\rangle = (D - a_n)|n\rangle - b_{n-1}|n-1\rangle, \\ &|0\rangle \equiv |Q_j\rangle, \; |-1\rangle \equiv 0. \end{aligned} \tag{6}$$

One can picture these states roughly as "shell states" since their largest components are typically on the nth shell of neighbors to the atoms in the path. If one truncates the fraction after N tiers, the continued fraction can be unfolded as an $[N/N+1]$ Padé approximate, $Q_N(x)/P_{N+1}(x)$, the polynomials in which may be generated by recurrence relations similar to Eq. (6). Taking the imaginary part then yields an N-point δ-function representation,

$$\rho_j(\omega) \approx \sum_{i=1}^{N} w_i \delta(\omega - x_i^{1/2}), \tag{7}$$

where w_i and x_i are respectively residues and poles of $Q_N(x)/P_{N+1}(x)$. This approximant yields exactly the leading $2N$ power moments m_n of the spectrum $g_j(x)$, and also gives an N-point Gaussian quadrature formula for σ_j^2,

$$\sigma_j^2(T) = \frac{\hbar}{2\mu_j} \sum_{i=1}^{N} \frac{w_i}{x_i^{1/2}} \coth \frac{\beta\hbar x_i^{1/2}}{2}. \quad (8)$$

From the leading term of the continued fraction (Eq. 3), the result for a single tier is $g_j(x) = 1/(1 - a_0)$ which corresponds to the CE approximation with $\omega_E^2 \equiv a_0 = \langle Q_j|D|Q_j\rangle$ which is equal to the second moment m_2.

In the present study we limit the continued fraction to the second tier. Thus, the vibrational spectrum is approximated with two δ-functions centered at the effective frequencies $\omega_{1,2} = \sqrt{x_{1,2}}$ with the corresponding weight factors $w_1 = (a_1 - x_2)/(x_1 - x_2)$ and $w_2 = (x_1 - a_1)/(x_1 - x_2)$, where

$$x_{1,2} = \frac{1}{2}\left[a_0 + a_1 \pm \sqrt{(a_0 - a_1)^2 + 4b_0}\right]. \quad (9)$$

In this, case the lowest frequency represents an effective acoustic mode whereas the highest one corresponds to an effective optical mode.

3. Calculation and results

The model structure used in the calculation is a 225-atom cluster (11 shells, $R_{max} = 8.47$ Å) of fcc Cu crystal without periodic boundary conditions. Following the model of Rehr and Alben (Rehr & Alben, 1977), only a single central interaction between the first nearest neighbors with force constant $k = 27.9$ N/m was taken into account. The MS σ_j^2 at 295 K calculated using the RM in comparison with results obtained from the EM method and a single frequency CE model with ω_E based on the second moment of the dynamical matrix are presented in Fig. 1 versus scattering paths index j listed in order of increasing path length as generated by FEFF7 (also see Table 1). For example, path number 1 corresponds to first shell single scattering (SS), 2 to second shell SS, 3 to 111 triangular MS path, 4 to triangular 211 MS path, 5 to third shell SS, 12 to double scattering from the first neighbor ($\sigma_{12}^2 = 4\sigma_1^2$) *etc.*

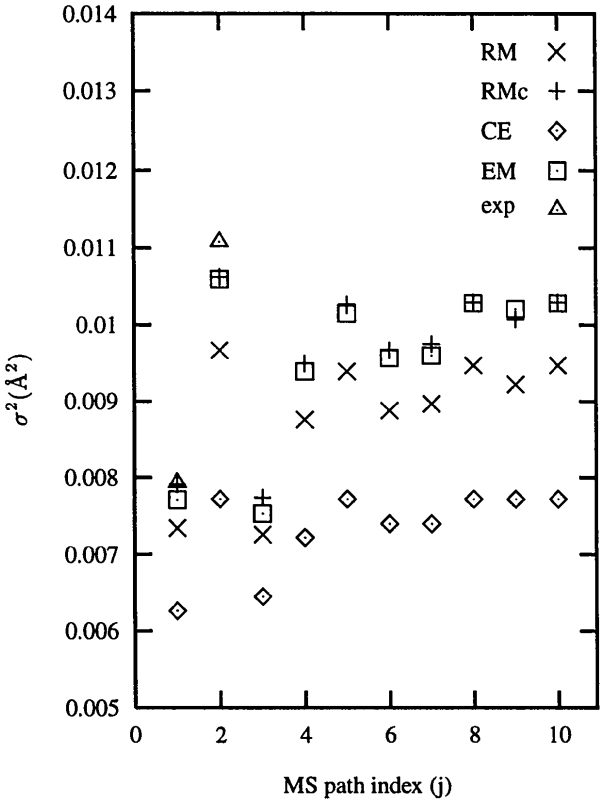

Figure 1
MS XAFS σ_j^2 for Cu at 295 K as calculated with a single force constant ($k = 27.9$ N/m) with RM, RM corrected with the 9/8 factor (RMc), EM and CE methods vs MS path index. Two experimental values (Stern *et al.*, 1980) corresponding to the first and second shell SS are given for comparison.

Table 1
Values of MS $\sigma_j^2 \times 10^{-3}$Å^2 at 295 K for a 225-atom cluster of Cu as calculated with a single force constant ($k = 27.9$ N/m) model using RM (σ_{RM}^2) and CE (σ_{CE}^2) approximation vs MS path index j. Two experimental values (Stern *et al.*, 1980) corresponding to the first and second shell SS are given for comparison. Also, given are Einstein frequencies ω_E, effective frequencies $\omega_{1,2}$ (all in THz), and the corresponding weight factors $w_{1,2}$ (dimensionless).

j	σ_{RM}^2	σ_{CE}^2	σ_{exp}^2	ω_E	ω_1	ω_2	w_1	w_2
1	7.34	6.26	7.93	36.4	27.5	41.9	.434	.566
2	9.67	7.72	11.08	32.5	24.9	41.2	.592	.408
3	7.26	6.45		38.1	28.9	42.2	.349	.651
4	8.76	7.22		35.5	26.3	41.7	.458	.542
5	9.39	7.72		32.5	25.0	39.8	.550	.450

The σ_j^2 calculated via the RM appear to be within about 9% of the corresponding EM values which are in a good agreement with experiment (2.7 % for the 1st shell and 4.4 % for the 2nd), whereas the CE values are typically 15-27% off in comparison with EM. These results indicate that the RM provides a much better agreement with the EM method and experiment than the CE model for all MS paths.

Typically, the RM somewhat underestimates the σ^2 values for Cu due to insufficient weight at the lower part of the spectrum. In cases when VDOS contains low frequency acoustic modes (e.g. in crystals), in order to account for these modes it is sufficient to multiply the weight of the lowest effective frequency by a factor of 9/8. This factor is calculated in such a way that it weights low frequency modes as they would be in the correlated Debye model. For example, in case of Cu at 295 K this correction brings σ_1^2 and σ_2^2 up to 7.91 and 10.62 $\times 10^{-3}$Å^2, in closer agreement with EM method and experiment.

4. Conclusion

The RM presented in the paper provides an efficient and general approach for the calculation of MS XAFS DW within the harmonic approximation from a few local force constants. This approach takes into account both effective optical and effective acoustic modes which is an improvement over the traditional CE model. Although, the RM yields accuracy comparable to the EM method, it requires less computation time and can be easily used for ionic crystals, in which case EM approach can be unstable unless proper boundary conditions applied. Additional temperature dependence from anharmonic and other corrections will be considered elsewhere.

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