

## Approximate spherical wave thermal factors in XAFS

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We propose an approximate but rather accurate method to handle the thermal spherical wave (SW) effects in single and multiple scattering EXAFS spectra, and also in full multiple scattering XANES spectra. In contrast to EXAFS SW thermal factor, to resum the multiple scattering series, we assume the random cancellation for cross products of complicated multiple scattering terms which greatly simplifies the finite temperature XANES formula.

**Keywords:** EXAFS, XANES, spherical wave effects, Debye-Waller factors

### 1. Introduction

Spherical wave (SW) effects on Debye-Waller factors play an important role to study the temperature effects in EXAFS spectra. The previous theoretical works demonstrated the peak shift in Fourier transformed EXAFS spectra due to the SW thermal factors (Brouder, 1988; Rennert, 1992, 1993; Speder *et al.*, 1993; Fujikawa *et al.*, 1995; Yimagawa *et al.*, 1996). Those approaches are useful, however they are rather complicated and time consuming even for the single scattering EXAFS calculations. They are difficult to go beyond single scattering approximation. Here we propose a simple but rather accurate method to handle XAFS SW thermal factors due to atomic vibration in single and multiple scattering EXAFS, and also in XANES spectra.

### 2. Single-Scattering EXAFS Spherical Wave Thermal Factors

The single scattering K-edge EXAFS spherical wave (SW) formula is shown for randomly oriented samples,

$$\chi(k) = -k \sum_{\alpha} \text{Im} \left[ \sum_l t_l^{\alpha} \{ l h_{l-1}(kR_{\alpha})^2 + (l+1) h_{l+1}(kR_{\alpha})^2 \} \exp(2i\delta_l^{\alpha}) \right] \quad (1)$$

where  $\mathbf{k}$  is the wave vector of the scattering electrons excited from deep K shells by X-ray photons and  $\mathbf{R}_{\alpha}$  is the position of a surrounding atom  $\alpha$  measured from an excited atom A. In order to study the effects of thermal motion of atoms on EXAFS, we

should evaluate the ensemble average of  $\chi(k)$  for all possible positions. The procedure to average the thermal motion is first to replace  $\mathbf{R}_{\alpha}$  by  $\mathbf{R}_{\alpha}^0 + \mathbf{u}_{\alpha} - \mathbf{u}_A$  and retain all the leading term in  $|\mathbf{u}_{\alpha} - \mathbf{u}_A|/R_{\alpha}^0$ . Here  $\mathbf{u}_{\alpha}$  and  $\mathbf{u}_A$  are the displacement vector of the  $\alpha$ th atom and the X-ray absorbing atom,  $\mathbf{R}_{\alpha}^0$  is the position vector of the  $\alpha$ th atom in equilibrium measured from the atom A. We obtain, within this approximation, the relation between  $R_{\alpha}$  and  $R_{\alpha}^0$ ,  $R_{\alpha} = R_{\alpha}^0 + \Delta_{\alpha}$  ( $\Delta_{\alpha} = \hat{\mathbf{R}}_{\alpha}^0 \cdot (\mathbf{u}_{\alpha} - \mathbf{u}_A)$ ).

Instead of the exact SW expansion in displacement, we rather use an approximate formula for the spherical Hankel function (Rehr *et al.*, 1986; Rehr and Albers, 1990) and we obtain an approximate expression,

$$h_l(kR_{\alpha}^0 + k\Delta_{\alpha}) \sim i^{-l-1} \frac{\exp(ikR_{\alpha}^0)}{kR_{\alpha}^0} d_l^{\alpha} \exp\{il(l+1)/2kR_{\alpha}^0\} \times \exp(ik\Delta_{\alpha} p_l^{\alpha}) \quad (2)$$

$$p_l^{\alpha} = 1 - a_l^{\alpha} + \frac{2a_l^{\alpha} + 1}{a_l^{\alpha} + 1} \frac{i}{kR_{\alpha}^0} \quad (3)$$

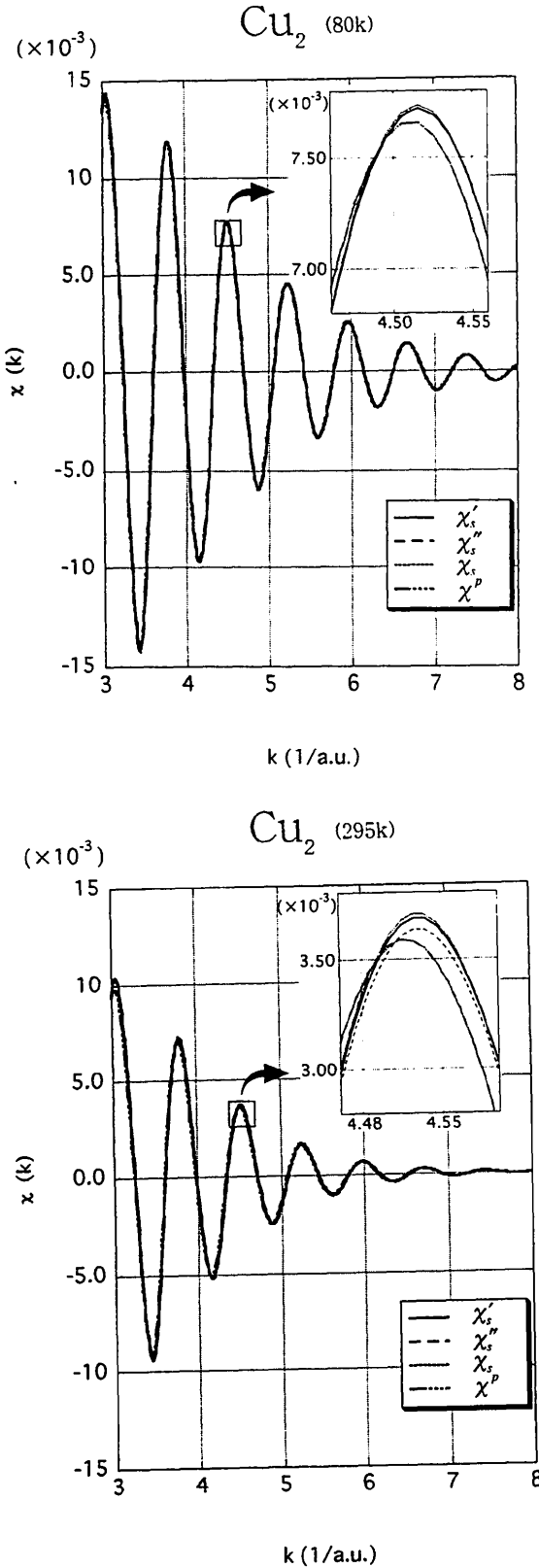
where  $a_l^{\alpha} = l(l+1)/2(kR_{\alpha}^0)^2$  and  $d_l^{\alpha} = (1 + a_l^{\alpha})^{1/2}$ . This approximation is quite accurate for large  $kR$  and  $l$ . By using eq. (2), the approximate expression for the thermal average of  $\chi(k)$  is obtained

$$\langle \chi(k) \rangle = - \sum_{\alpha} \text{Im} \left[ \frac{\exp(2ikR_{\alpha}^0)}{k(R_{\alpha}^0)^2} \sum_l (-1)^l t_l^{\alpha} \{ l (d_{l-1}^{\alpha})^2 \times \langle \exp(2ik\Delta_{\alpha} p_{l-1}^{\alpha}) \rangle + (l+1) (d_{l+1}^{\alpha})^2 \langle \exp(2ik\Delta_{\alpha} p_{l+1}^{\alpha}) \rangle \} \right] \quad (4)$$

The thermal averages  $\langle \dots \rangle$  in eq. (4) can be calculated by applying the cumulant expansion.

Figure 1 (a) shows different EXAFS functions in the region  $k=3-8$  a.u.<sup>-1</sup> for Cu<sub>2</sub> diatomic system where Cu-Cu distance is fixed at the measured one (2.545 Å) in metals. The temperature is 80K; here we use lowest order (up to 3rd) cumulants estimated by Yokoyama *et al.* (1989) for Cu metals. EXAFS function  $\chi^p$  is the SW EXAFS function with the PW thermal factor, and  $\chi_s$  is the full SW EXAFS function previously discussed by Fujikawa *et al.* (1995). EXAFS function  $\chi'_s$  is the approximate SW EXAFS function by using an approximation,  $p_l^{\alpha} \sim 1 - a_l^{\alpha}$  in eq. (4).  $\chi'_s$  is the more accurate but simple SW EXAFS function defined by eq. (4). As it is difficult to distinguish these functions in the usual scale, the expanded EXAFS oscillations are shown in the insert. At this low temperature the difference between  $\chi'_s$  and  $\chi_s$  is too small which cannot be seen even in the insert, and they are close to  $\chi_s$ . Those three thermal SW EXAFS functions have different phase from the thermal PW EXAFS function  $\chi^p$  as observed in the previous papers. (Brouder, 1988; Rennert, 1992; Fujikawa *et al.*, 1995). Figure 1 (b) shows the same one but at  $T=295$ K. In this case we can observe the difference between  $\chi'_s$  and  $\chi_s$  in the insert, however  $\chi'_s$  is still very close to  $\chi_s$ . It is interesting to note that the phase difference between

$\chi_s'$  and  $\chi_s$ , is quite small even at 295K.



**Fig. 1** SW EXAFS functions for Cu, at 80K (a) and 295K (b).  $\chi^p$  has the PW thermal factor,  $\chi_s$  has the full SW thermal factor whereas  $\chi_s'$  and  $\chi_s''$  are the SW EXAFS function with the approximate SW thermal factors.

### 3. Full Multiple Scattering XANES Thermal Factors

First we consider the plane wave multiple scattering thermal factors within the harmonic approximation. The  $N$ th order multiple scattering factor is calculated from the thermal average,

$$\langle \exp(ik \sum_{n=1}^{N+1} \Delta_n) \rangle \quad (5)$$

where  $\Delta_n = \hat{\mathbf{R}}_{n,n-1} \cdot (\mathbf{u}_n - \mathbf{u}_{n-1})$  and  $\mathbf{R}_{n,n-1} = \mathbf{R}_n^0 - \mathbf{R}_{n-1}^0$ . By applying Mermin's theorem (Mermin, 1966), the average (5) is rewritten as

$$\begin{aligned} & \exp(-k^2 \langle (\sum_{n=1}^{N+1} \Delta_n)^2 \rangle / 2) \\ & = \exp\left[-\frac{k^2}{2} \left( \sum_{n=1}^{N+1} \langle \Delta_n^2 \rangle + 2 \sum_{n>m} \langle \Delta_n \Delta_m \rangle \right)\right]. \end{aligned} \quad (6)$$

We can expect that the second term  $\sum_{n>m} \langle \Delta_n \Delta_m \rangle$  is quite small because of the random phase cancellation for complicated systems such as solids. In this approximation the plane wave thermal factor can be given by  $\exp\left[-\frac{k^2}{2} \left( \sum_{n=1}^{N+1} \langle \Delta_n^2 \rangle \right)\right]$ .

In the case where SW multiple scattering contribution is important, that is low energy scattering, the approximation (2) does not work any more. In the XANES region the temperature effects are not so pronounced (Farges, 1997), and it is enough only to include the second cumulant whereas the SW thermal factor should carefully be taken into account. As an example, we consider a double scattering path  $A \rightarrow \alpha \rightarrow \beta \rightarrow A$ . Here we use the expansion formula for the Green's function (Brouder and Goulon, 1989; Rennert, 1992)

$$G_{LL}(k\mathbf{R}^0 + k\mathbf{u}) = \sum_{L'} G_{L'L}(k\mathbf{R}^0) J_{L'L}(k\mathbf{u}), \quad (7)$$

$$J_{LL}(k\mathbf{u}) = \exp(ik\mathbf{u} \cdot \mathbf{M})_{LL} = \int Y_L'(\hat{\mathbf{k}}) \exp(i\hat{\mathbf{k}} \cdot \mathbf{u}) Y_L(\hat{\mathbf{k}}) d\hat{\mathbf{k}}, \quad (8)$$

where  $\mathbf{M}$  is a vector matrices whose explicit formulas are shown elsewhere (Brouder and Goulon, 1989). By including the lowest order SW correction for  $J(k\mathbf{u})$  we have

$$\begin{aligned} J(k\mathbf{u}) & = \exp(ik\mathbf{u} \cdot \hat{\mathbf{R}}) \{1 + ik\mathbf{u} \cdot (\mathbf{M} - \hat{\mathbf{R}}) + \dots\} \\ & = \{1 + (\mathbf{M} - \hat{\mathbf{R}}) \cdot \frac{\partial}{\partial \hat{\mathbf{R}}} + \dots\} \exp(ik\mathbf{u} \cdot \hat{\mathbf{R}}). \end{aligned} \quad (9)$$

By using this expansion, we can write the thermal average of the double scattering path  $A \rightarrow \alpha \rightarrow \beta \rightarrow A$ ,

$$\begin{aligned} & \sum_{\alpha,\beta} G(-\mathbf{R}_\beta^0) \left\{1 - (\mathbf{M} + \hat{\mathbf{R}}_\beta^0) \cdot \frac{\partial}{\partial \hat{\mathbf{R}}_\beta^0}\right\} X^{\beta\alpha} \left\{1 + (\mathbf{M} - \hat{\mathbf{R}}_\alpha^0) \cdot \frac{\partial}{\partial \hat{\mathbf{R}}_\alpha^0}\right\} \\ & \times \langle \exp\{-k(\mathbf{u}_{\alpha\beta} \cdot \hat{\mathbf{R}}_\beta^0 - \mathbf{u}_{\beta\alpha} \cdot \hat{\mathbf{R}}_{\beta\alpha} - \mathbf{u}_{\alpha\alpha} \cdot \hat{\mathbf{R}}_\alpha^0)\} \rangle. \end{aligned} \quad (10)$$

This formula shows an interesting feature of the SW thermal factor, which can be calculated from the PW thermal factor. In eq. (10) we introduced the matrix  $X$  defined by

$$X_{LL}^{\alpha\beta} = t_i^\alpha G_{LL}(\mathbf{R}_\alpha - \mathbf{R}_\beta)(1 - \delta_{\alpha\beta}). \quad (11)$$

Within the harmonic approximation, we have a compact form for the  $A \rightarrow a \rightarrow b \rightarrow A$  double scattering loop,

$$\sum_{\alpha,\beta} G^{A\alpha}(T) X^{\alpha\beta}(T) X^{\beta A}(T) = \{G(T)X(T)\}^{AA} \quad (12)$$

where the temperature dependent propagator  $G(T)$  is defined by

$$G^{A\alpha}(T) = G(-\mathbf{R}_\alpha^0) \{1 + k^2(\mathbf{M} + \hat{\mathbf{R}}_\alpha^0) \cdot U^{A\alpha} \hat{\mathbf{R}}_\alpha^0\} \\ \times \exp\left(-\frac{k^2}{2} \hat{\mathbf{R}}_\alpha^0 \cdot U^{A\alpha} \hat{\mathbf{R}}_\alpha^0\right) \quad (13)$$

and the related matrix  $X(T)$  is defined by use of the temperature independent matrix  $X$  given by eq. (11),

$$X^{\alpha\beta}(T) = X^{\alpha\beta} \{1 - k^2(\mathbf{M} - \hat{\mathbf{R}}_{\alpha\beta}^0) \cdot U^{\alpha\beta} \hat{\mathbf{R}}_{\alpha\beta}^0\} \\ \times \exp\left(-\frac{k^2}{2} \hat{\mathbf{R}}_{\alpha\beta}^0 \cdot U^{\alpha\beta} \hat{\mathbf{R}}_{\alpha\beta}^0\right) \quad (14)$$

The temperature dependent tensor  $U^{\alpha\beta}$  is defined by the thermal average  $U^{\alpha\beta}_{ij} = \langle (\mathbf{u}_\alpha - \mathbf{u}_\beta)_i (\mathbf{u}_\alpha - \mathbf{u}_\beta)_j \rangle$ , ( $i, j = x, y, z$ ). The use of the approximation shown by eq. (14) enable us to renormalize the full multiple scattering series as usual. (Fujikawa, 1993) We obtain the temperature dependent XANES formula excitation from a core orbital  $c$  at site  $A$ ,

$$\sigma(T) = -\frac{8}{3} \text{Im} \left[ \sum_m \sum_{LL'} i^{l-l'} \exp\{i(\delta_l^A + \delta_{l'}^A)\} \rho_c(l) \rho_c(l') \right] \\ \times G(L_c 10 | L) G(L_c 10 | L') (t^{-1})_{LL}^{AA} \{1 - X(T)\}^{-1}_{LL} \quad (15)$$

where  $G(L_c 10 | L)$  is the Gaunt's integral,  $\rho_c(l)$  is the radial dipole integral between the radial part of core orbital  $c$  and the  $l$ th partial wave of a photoelectron.

For the isotropic systems the thermal factor in eq. (13) is further simplified, and we obtain an approximate formula,

$$X^{\alpha\beta}(T) = X^{\alpha\beta} \{1 - k^2 \Delta_{\alpha\beta}^2 (\mathbf{M} \cdot \hat{\mathbf{R}}_{\alpha\beta}^0 - 1)\} \exp(-k^2 \Delta_{\alpha\beta}^2 / 2). \quad (16)$$

As an example, we study the temperature dependence of Br K-edge XANES spectra of bromonaphthalene solved in supercritical xenon, which are recently measured by Murata *et al.* (1998). For simplicity we consider the situation in which there exists one Xe atom near a Br atom. Here we use the Debye-Waller factor  $\Delta^2$  only for the Br-Xe pair; the distance is fixed at 5Å. Figure 2 shows the calculated XANES spectra for different  $\Delta^2$  by use of eqs. (15) and (16). The spectrum with large  $\Delta^2$  ( $\Delta^2 = 0.4 \text{Å}^2$ ) is similar to the one for free bromonaphthalene, because the information on the Br-Xe pair is lost as understood from eqs.

(13) and (14). Large  $\Delta^2$  gives rise to the suppression of the near edge structures as well as the peak shift as observed at 10~15 eV above the edge.

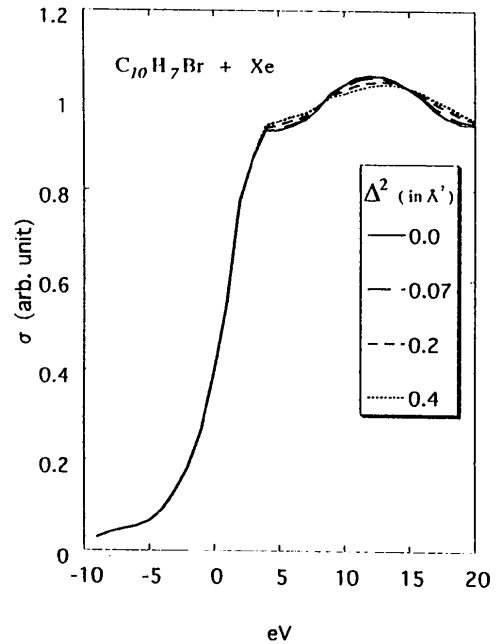


Fig. 2 The  $\Delta$  dependence of the calculated Br K-edge XANES spectra for bromonaphthalene in Xe. The relative thermal vibration is taken into account only for the Br-Xe pair.

#### 4. Conclusion

As demonstrated in this work, SW thermal effects should be carefully taken into account in different ways in EXAFS and XANES analyses.

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