

Ab Initio Equation of Motion X-Ray Absorption Debye-Waller Factors

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An efficient equation of motion method is introduced for calculating the variance of the half scattering path lengths, σ_j^2 , which appear in multiple-scattering x-ray absorption fine-structure Debye-Waller factors. The approach is to obtain the correlation function via already existing implementations based on density functional theory which then makes it possible to calculate the projected vibrational density of states and finally σ_j^2 from first principles. A sample application is provided for germanium.

I. INTRODUCTION

In the recent years, x-ray absorption fine-structure (XAFS) has become a widely used technique for determining the local structure of complex materials. The physical origin of XAFS is the absorption of an x-ray photon by an atom leading to the excitation of a core-electron. The final state photoelectron wave will experience scattering off of the neighboring atoms, creating characteristic “wiggles” in absorption coefficient, μ , as a function of the photon energy. The structural information XAFS experiments provide include coordination number and interatomic distances. Thermal vibrations and structural disorder give rise to Debye-Waller factors, $e^{-W(T)}$, which dampen the XAFS spectra with respect to increasing temperature and energy of the photoelectron created in the absorption process. Because of this exponential decay, a first principles understanding of the Debye-Waller factors is crucial for a successful quantitative treatment of x-ray absorption spectra¹.

The Debye-Waller factors have conventionally been obtained using isotropic models which make use of experimental fitting or semi-empirical methods, e.g. the correlated Einstein and Debye models. In this paper, an *ab initio* equation of motion method (EM) is presented for calculating the Debye-Waller factors. This method is a significant improvement over the conventional methods. Also, since no diagonalization of huge matrices is required, it is applicable to large, aperiodic systems where solving the full eigenvalue problem would be very time-consuming.

In this work, results for crystal Germanium of the diamond space group is presented. It has previously been shown² that applying e.g. the correlated Debye model to a structure this anisotropic produces poor results. The equation of motion method however, reproduces experimental values satisfactorily.

II. FORMALISM

A. X-ray absorption fine-structure (XAFS)

In x-ray absorption spectroscopy the interesting experimental quantity is the absorption coefficient μ , mea-

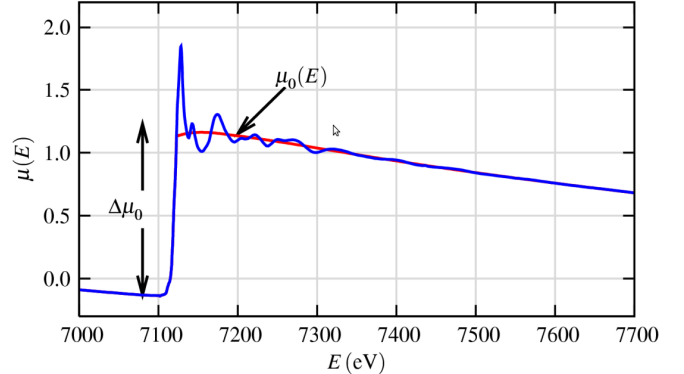


FIG. 1. The absorption coefficient $\mu(E)$ (blue), the smooth atomic-like background function $\mu_0(E)$ (red) and the edge-jump $\Delta\mu$. E is the x-ray photon energy.

sured as a function of the incoming x-ray photons. When plotting μ as a function of the incoming photon energy (Figure 1), the experimental data show two noticeable features. First of all, the absorption coefficient μ has a steep rise at certain energies, called edge energies. The position of these energies correspond to the excitation energy of a core-electron.

The second feature is the oscillatory behavior of $\mu(E)$ just above an edge. The origin of these oscillations can be found by considering an incoming photon getting absorbed by an atom, thereby exciting a core-electron and producing a photoelectron and a core-hole in the final state. The outgoing photoelectron, seen as a quantum wave, will scatter off neighboring atoms, creating an interference pattern (Figure 2). According to Fermi’s Golden Rule the transition probability, in this case μ , is proportional to a transition matrix element squared

$$\mu \propto |\langle f | H_{trans} | i \rangle|^2 \quad (1)$$

where f and i refer to final and initial states, respectively. The interference pattern modulates the matrix element thus shifting the value of μ . Since this interference pattern is energy dependent, μ will also be, hence giving rise to the oscillating fine-structure. This motivates the definition of the x-ray absorption fine-structure spectrum (XAFS) as the normalized, oscillatory part of μ

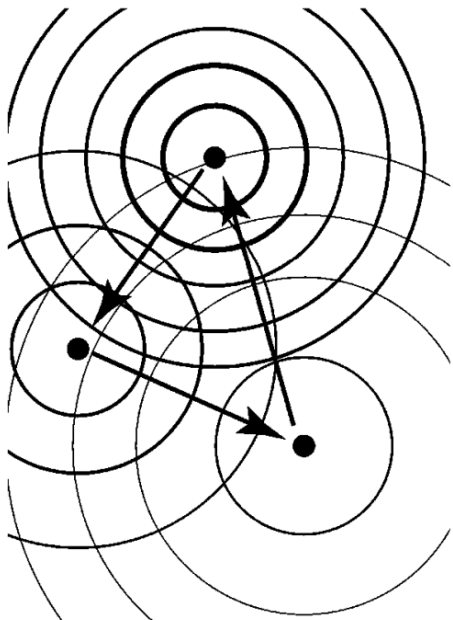


FIG. 2. Idealized picture of a photoelectron wave scattering of neighboring atoms creating an interference pattern. The upper atom is the absorbing atom, the source of the wave. The waves decay at long distances from the source, which is reflected in the thickness of the circles.

$$\chi \stackrel{\text{def}}{=} \frac{(\mu - \mu_0)}{\Delta\mu_0} \quad (2)$$

where μ_0 is an “atomic-like” absorption, i.e. the absorption that would be measured if one imagines turning off the effects due to the photoelectron scattering. $\Delta\mu_0$ is a normalization factor which is in principle energy-dependent but is in practice usually taken to be the jump in absorption at the energy edge.

For the extended XAFS (EXAFS) energy region and in the harmonic approximation, the XAFS spectrum can be parametrized by the so called standard XAFS equation

$$\chi(k) = \sum_j \frac{N_j S_0^2}{k R_j^2} |f_j^{\text{eff}}(k, R_j)| \times \sin(2kR_j + \phi_j(k)) e^{-2R_j/\lambda} e^{-2\sigma_j^2 k^2} \quad (3)$$

Here the sum runs over all unique (multiple or single) scattering paths j of degeneracy N_j . f_j^{eff} is the effective scattering amplitude for path j , S_0^2 is a many-body amplitude reduction factor, $\phi_j(k)$ is the net phase shift, $k = E - E_{\text{edge}}$ is a wavenumber measured relative to the edge energy, R_j is half the equilibrium scattering path length of path j . λ is the photoelectron mean free path. The Debye-Waller factor can be identified with $e^{-2\sigma_j^2 k^2}$, where σ_j^2 is defined as the variance of the scattering path length

$$\sigma_j^2 = \langle (r_j - R_j)^2 \rangle \quad (4)$$

where the brackets denote a thermal average and r_j is the instantaneous half path length. The general definition of the Debye-Waller factors e^{-W_j} is given by the configurational and thermal average

$$\langle e^{ikr_j} \rangle = e^{2ikR_j} e^{-W_j(k)} \quad (5)$$

In this paper, we focus only on thermal disorder since structural disorder is dependent on the sample preparation and history. For small vibrations, the average can be expressed in terms of the cumulant expansion

$$W_j(T) = - \sum_{n=1}^{\infty} \frac{(2ik)^n}{n!} \sigma_j^{(n)}(T) \quad (6)$$

where $\sigma_j^{(n)}(T)$ is the n -th cumulant average. Neglecting anharmonic terms, this reproduces the Debye-Waller factors of Equation (3).

B. The equation of motion method

The equation of motion (EM) method used in this paper was first introduced by Rehr and Alben³ and Beeman and Alben⁴ in order to calculate the total vibrational density of states and related quantities. The equation of motion method is efficient for large, complex systems in which the naïve way of solving the problem by diagonalizing huge matrices would be too time-consuming to be practical.

The EM method is based on solving $3N$ coupled Newton’s equations of motion, where N is the number of atoms in the cluster. Regarding the potential energy V of the system as a function of the atomic displacements from equilibrium, $\mathbf{u}_i = \mathbf{r}_i - \mathbf{R}_i$, and keeping only terms of second order in u , one obtains the equations of motion⁵

$$\frac{d^2 Q_{i\alpha}(t)}{dt^2} = - \sum_{k\beta} D_{i\alpha, k\beta} Q_{k\beta} \quad (7)$$

where $Q_{i\alpha}(t) = u_{i\alpha}/\sqrt{M_i}$ and M_i is the mass of atom at site i . The force constants of the system is contained in the $3N \times 3N$ dynamical matrix $D_{i\alpha, k\beta}$ defined by

$$D_{i\alpha, k\beta} = \frac{\partial^2 V}{\partial u_{i\alpha} \partial u_{k\beta}} \quad (8)$$

Making an ansatz of oscillatory solutions, $Q_{i\alpha}(t) = \epsilon_{i\alpha}(\lambda) e^{-i\omega_\lambda t}$, Equation (7) reduces to an eigenvalue problem for the $3N$, $3N$ -dimensional eigenvectors $|\lambda\rangle$ with elements $\epsilon_{i\alpha}(\lambda)$, each with a corresponding eigenfrequency ω_λ

$$\omega_\lambda^2 \epsilon_{i\alpha}(\lambda) = \sum_{k\beta} D_{i\alpha, k\beta} \epsilon_{k\beta}(\lambda) \quad (9)$$

We can thus expand the displacements $Q_{i\alpha}$ in terms of the normal modes

$$Q_{i\alpha} = \sum_{\lambda} \epsilon_{i\alpha}(\lambda) q_0(\lambda) e^{-i\omega_{\lambda} t} \quad (10)$$

where the eigenmodes are here chosen orthonormal, $\langle \lambda | \lambda' \rangle = \delta_{ij}$ and $q_0(\lambda)$ is a constant amplitude factor for each mode λ .

By Taylor expanding σ_j^2 using Equation (4), assuming small vibrations around the equilibrium positions, σ_j^2 can be written as a function of the displacement vectors

$$\sigma_j^2 = \frac{1}{4} \left\langle \left[\sum_{i=1}^{n_j} (\mathbf{u}_i - \mathbf{u}_{i+}) \cdot \hat{\mathbf{R}}_{ii+} \right]^2 \right\rangle \quad (11)$$

where n_j is the number of participating atoms in scattering path j . Using the normal mode expansion of Equation (10), evaluating the thermal average using Bose-Einstein statistics, we can rewrite σ_j^2 in terms of the normal modes λ ,

$$\sigma_j^2 = \frac{\hbar}{2\mu_j} \sum_{\lambda} \frac{1}{\omega_{\lambda}} \coth \frac{\beta \hbar \omega}{2} \times \left[\sum_i \sqrt{\frac{\mu_j}{M_i}} \left(\frac{\hat{\mathbf{R}}_{ii-} + \hat{\mathbf{R}}_{ii+}}{2} \right) \cdot \epsilon_i(\lambda) \right]^2 \quad (12)$$

By setting the initial conditions of the problem to be in the direction of

$$|Q_j(0)\rangle \stackrel{\text{def}}{=} \begin{pmatrix} \frac{1}{2} \sqrt{\frac{\mu_j}{M_1}} (\hat{\mathbf{R}}_{1,n_j} + \hat{\mathbf{R}}_{1,2}) \\ \vdots \\ \frac{1}{2} \sqrt{\frac{\mu_j}{M_1}} (\hat{\mathbf{R}}_{1,i-} + \hat{\mathbf{R}}_{i,i+}) \\ \vdots \\ 0 \end{pmatrix} \quad (13)$$

and defining the projected vibrational density of states (VDOS) to be

$$\rho_j(\omega) \stackrel{\text{def}}{=} \sum_{\lambda} |\langle \lambda | Q_j(0) \rangle|^2 \delta_{\Delta}(\omega - \omega_{\lambda}) \quad (14)$$

where $\delta_{\Delta}(\omega)$ is a delta-like function of width Δ , one obtains a normal mode integral expression for σ_j^2

$$\sigma_j^2(T) = \frac{\hbar}{2\mu_j} \int_0^{\omega_{max}} \frac{d\omega}{\omega} \rho_j(\omega) \coth \frac{\beta \hbar \omega}{2} \quad (15)$$

The constant μ_j in these above equations is the reduced mass of scattering path j . It is defined by requiring that the initial value displacement vectors of Equation (13) are unit normalized, $|\langle Q_j(0) | Q_j(0) \rangle| = 1$. Obtaining $\rho_j(\omega)$ via Equation(14) would involve an expensive diagonalization of the dynamical matrix D in order to get all the normal modes. Thus, it is preferable to instead obtain it using the correlation function, $\langle Q_j(t) | Q_j(0) \rangle$. Fourier

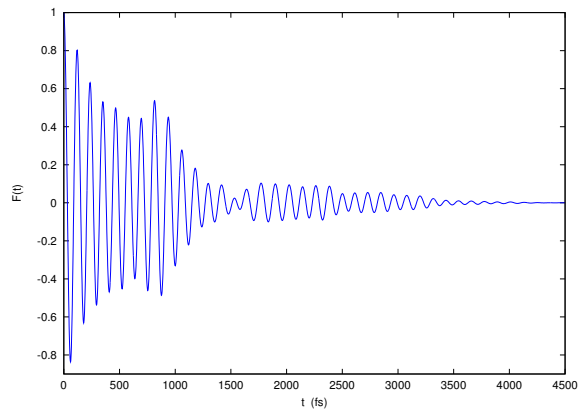


FIG. 3. The damped correlation function of germanium, $\langle Q(t) | Q(0) \rangle e^{-\epsilon t^2}$.

transforming this function extracts the normal modes involved for scattering path j

$$\rho_j(\omega) = \frac{2}{\pi} \int_0^{t_{max}} \langle Q_j(t) | Q_j(0) \rangle e^{-\epsilon t^2} \cos(\omega t) dt \quad (16)$$

where $e^{-\epsilon t^2}$ is a damping factor included for computational efficiency.

The correlation function can be calculated using available implementations based on density functional theory.

III. APPLICATIONS

A. Germanium

The crystal considered in our study was a 64-atom cluster of Ge of the diamond space group with enforced periodic boundary conditions. Calculations were made for the single scattering nearest neighbour path at a temperature of 300 K.

The correlation function was obtained using the density functional theory based implementation VASP. The result is illustrated in Figure 3. The oscillating system was iterated forward 4500 fs in time. From the figure, one can note the presence of a dominating frequency and the period of those oscillations is around 117 fs. This leaves us with about 38 full vibrational cycles. In practice however, one would probably only include ~ 10 cycles or less for computational efficiency.

The calculated projected and total VDOS is presented in Figure 4 in comparison with experimental data for the total VDOS⁶. Just as with the correlation function, one can note the presence of a dominating frequency at about 53 T rad/s, in all three spectra. Also, the calculated versus experimental total VDOS compare reasonably well considering the general features of the plots. The larger width of the calculated total VDOS compared to the projected one, is most likely a time length effect, since for

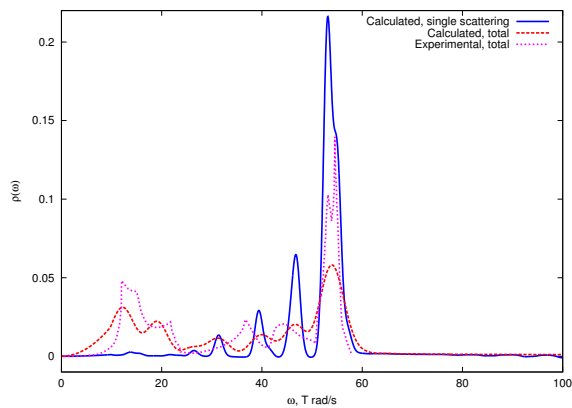


FIG. 4. Calculated single-scattering nearest neighbor (blue), calculated total (red) and experimental total (pink) VDOS.

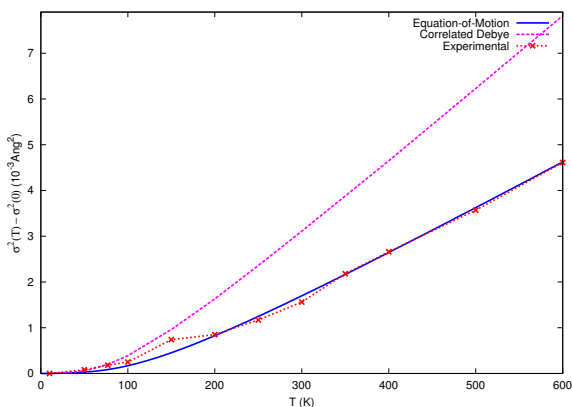


FIG. 5. Temperature dependence of $\sigma^2(T) - \sigma^2(0)$ for the equation of motion method (blue), the correlated Debye model (pink) in comparison with experimental data (red).

this calculation the correlation function was only determined for about 1200 fs. The more confined the correlation function is in time, the more its transform will spread out in frequency space.

The important quantity for obtaining the Debye-Waller factors, σ_j^2 , was determined to be $3.23 \cdot 10^{-3} \text{ \AA}^2$. The experimental value available is $3.50 \cdot 10^{-3} \text{ \AA}^2$ ⁷. Seeing as our accuracy requirements lie in the 10-20% range, this deviation of less than 10% is considered to be a successful result.

We can also study the temperature dependence of our result. Figure 5 shows the temperature dependence of σ^2 at temperature T relative to σ^2 at 0 K, which is the quantity that can usually be extracted from experiment. The pink line shows results using the correlated Debye model and the blue line contains experimental data. It is clear how poorly the correlated Debye model performs compared to the EM method, shown in blue.

The effect of the time length and time step length of the correlation function was also studied. The effect of changing the time length from 4500 fs to 700 fs was to

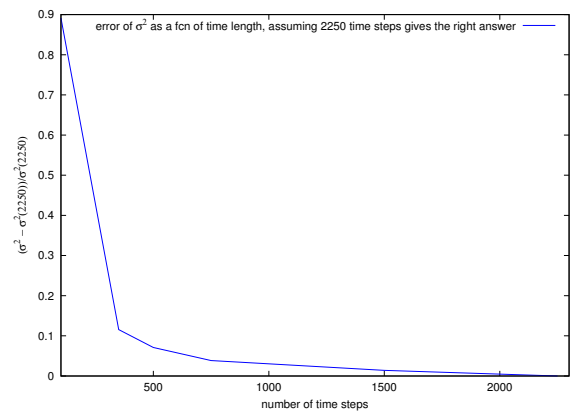


FIG. 6. The change in σ^2 relative to $\sigma^2(2250)$, where 2250 is the maximum number of time steps used in the calculation.

change σ^2 from $3.23 \cdot 10^{-3} \text{ \AA}^2$ to $3.60 \cdot 10^{-3} \text{ \AA}^2$. Doubling the time step length from 2 fs to 4 fs changed σ^2 from $3.23 \cdot 10^{-3} \text{ \AA}^2$ to $3.46 \cdot 10^{-3} \text{ \AA}^2$, while a tripling resulted in $3.66 \cdot 10^{-3} \text{ \AA}^2$. The relative shift in σ^2 due to time length effects is illustrated in Figure 6. Here, the y-axis is the relative “error” in σ^2 that is introduced due to decreased time length. Note that the x-axis shows the number of time steps and not the actual time.

IV. CONCLUSIONS

Debye-Waller factors were calculated with the equation of motion method using the correlation function approach. The calculations were performed for the single scattering, nearest neighbor path of crystalline germanium. Our results show that this method produces satisfactory results for germanium in comparison with available experimental data, while the correlated Debye model does not. The traditional methods are therefore deficient when it comes to more complex and nonisotropic structures. It is hence important for the development of x-ray absorption spectroscopy that better models such as the equation of motion method is investigated further. Future studies might include:

- Validate the equation of motion method for multiple scattering paths, e.g. for germanium.
- Apply the equation of motion method to other more complex structures.
- Analyze in more detail how time length, time step length and other computational factors affect the final result for σ^2 .

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