

Vibrational normal mode sampling for computing x-ray spectra

Ryan Lau¹

Mentored by: Fernando D. Vila², John J. Rehr²

¹*Department of Physics, California Polytechnic State University, San Luis Obispo, California 93407, USA*

²*Department of Physics, University of Washington, Seattle, Washington 98195, USA*

A method to calculate and implement Debye-Waller factors more efficiently when computing x-ray spectra is proposed. Utilizing inverse sampling methods, we accurately produce Monte Carlo simulations of thermal motion allowing us to account for temperature dependencies in x-ray spectra. This eliminates the need for previous approximation and accounts for more spectral features such as symmetry-split peaks.

I. INTRODUCTION

X-ray absorption spectroscopy is a popular and powerful technique for probing condensed matter systems. It has successfully contributed to fields ranging from materials science to physical chemistry. Due to its importance as an experimental technique, it is of great interest to develop computational methods of producing accurate x-ray spectra to compare to experimental spectra. However, due to x-ray spectra probing many body interactions, there are many complex factors that must be considered when developing a computational model. In particular, damping coefficients known as Debye Waller (DW) factors characterize an x-ray spectra's temperature dependence as they are directly related to the thermal motions and vibrations of the sample. As opposed to DW factors for x-ray and neutron diffraction, which deals with the mean-square displacements of a given atom, DW factors for x-ray absorption near edge structures (XAFS) refer to the average over relative displacements[1]. By knowing a spectra's DW factors, a computed spectra would have the proper temperature dependence as well as proper intensity dampening compared to experimental result. Therefore it is essential to have an accurate and efficient method to include DW factors when computing an x-ray spectra.

Previously[2], XAFS DW factors were calculated using density functional theory calculations of the dynamical matrix of the system. Combining the calculations with a Lanczos algorithm for projected photon spectra within quasharmonic approximation, this method produces stable results of calculated DW factors typically within $\pm 10\%$. Although this method produces accurate DW factors, our current method requires these factors to be calculated over a variety of dimensions which becomes increasingly expensive to compute. Rather than compute the entirety of ranges required to produce the spectra, sampling the ranges to an accuracy specified is much more advantageous. Similar to how Monte-Carlo integration can converge to an answer faster than other numerical methods, given the integrated function is smooth, sampling coordinates with proper thermal distortions can converge to an accurate spectra faster than a spectra calculated from DW factors. In this project, we demonstrate that this sampling technique generates agreeable

DW factors to that of the DFT-Lanczos method for a variety of polyatomic atoms including F_2O , Br_2 , $OCCL_2$, and SF_6 . We also demonstrate that this new method is able to efficiently generate coordinates in accordance to the proper distribution. These coordinates will then be used to generate many spectra which will be averaged together to generate one complete, accurate, and averaged x-ray spectra with the proper thermal distortions.

II. THEORY

A. Inverse Transform Sampling

Inverse transform sampling is a popular technique to generate pseudo-random numbers on a known probability distribution. By generating a random sample, p , between 0 and 1, we are able to represent p as a probability and create an x on the domain $P(x)$ such that the sum between $P(-\infty)$ and $P(x)$ is equal to p .

Therefore, by integrating our probability density we are able to generate our cumulative density function which we use to map our uniform distribution to. This allows us to generate random samples according to any distribution, including a probability distribution that captures proper thermal motions.

Under the Born-Oppenheimer approximation, we are able to separate the wave-function of our molecules into vibrational and rotational components[4]. This means the electrons and nuclei movement are separate and can thus treat each movement independent. Therefore, when considering accurate depiction of thermal motion between our molecules, we need only consider vibrational normal modes. When our system is simply a diatomic molecule, the harmonic oscillator approximation with mode n fits exactly

$$\psi_n(x) = \left(\frac{\mu\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(x) e^{-\frac{\mu\omega}{2\hbar} x^2} \quad (1)$$

where μ is the reduced mass of the particles, ω is the frequency associated with the normal mode, \hbar is Planck's constant, and $H_n(x)$ are the hermite polynomials.

When we elevate to a polyatomic system we justify that vibrational normal modes are still in this harmonic

oscillator approximation so long as we are within the binding energy region of our atomic Morse Potential. [4] It becomes more convenient to write equation 1 in a way that is mass-dependent to avoid any confusion with what a polyatomic reduced weight may be. Substituting $q = \sqrt{\mu}x$, equation 1 can be rewritten as

$$\psi(x)_n = \mu^{\frac{1}{4}} \left(\frac{\omega}{\pi\hbar} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n \left(\sqrt{\frac{\omega}{\hbar}} q \right) e^{-\frac{\omega}{2\hbar} q^2} \quad (2)$$

This way there is no mass-dependence when constructing our probability amplitudes and we are sampling in mass-weighted coordinates q . In order to sample in real-space coordinates, we will utilize a dynamical matrix with the proper weighting to calculate displacements in real-space.

In order to account for the thermal properties of our probability distribution, we use a Bose-Einstein distribution to determine the occupancy levels at which our system will occupy [4].

$$q_{vib} = \frac{e^{-\beta\hbar\nu/2}}{1 - e^{-\beta\hbar\nu}} \quad (3)$$

This allows us to determine the proportion of our atoms' occupancy levels and multiply these proportions to construct a full probability density. As temperature varies, our atoms will have a different probability to occupy various n levels which correspond to different wave-functions. Summing and normalizing these wave-functions and squaring our wave-functions will generate the proper probability distribution of atoms' positions. Integrating this probability density can be done numerically generating the cumulative density function needed to perform the inverse sampling.

B. Dynamical Matrix

Using the inverted transform sampling method, we are able to generate pseudo-random probability amplitudes according to an atom's probability distribution. These distributions correspond directly with the vibrational normal modes needed to simulate proper DW factor when constructing x-ray spectra. We then construct a matrix of force constants for each atom in our system [2]. These force constants correspond to various normal modes of motion, including vibrational normal modes, and are constructed in detail by [5]. The dynamical matrix can then be used to generate the vibrational normal mode frequencies of our system. [2] These frequencies are used in equation 2 to calculate the proper probability amplitudes, p , used. The dynamical matrix also allows us to generate displacement vectors \vec{d} that follow the path of vibration and when multiplied by our probability amplitude, simulates random vibrations of our particle. Summarized below, we are able to generate sampled coordinates \vec{Q}' if we add our sampled displacements to some original coordinate \vec{Q} also generated by the dynamical matrix.

$$\vec{Q}' = \vec{Q} + \vec{d}p \quad (4)$$

By randomly generating a large number of p , we can generate a large number of sampled coordinates. These coordinates, per particle, will represent new positions of an atomic system that can be used to generate a large number of XANES spectra. We can thus average the intensities of our XANES spectra to simulate a XANES spectra of a vibrationally averaged system generating more accurate spectra.

III. METHOD

Although Monte-Carlo simulation of thermal motion can generate spectra quicker than other methods that try to simulate thermal motion, it would not be of any use if they were not accurate. In order to ensure accuracy, we will generate DW factors using our randomly generated coordinates and compare them to computationally calculated DW factors [2]. DW factors in XAS arise from a thermal and configurational average of the spectra over the pair distribution function. If the effect of the vibrations on a normalized XAS spectra is dominated by the average over the oscillatory behavior of the multiple scattering path, the DW factors depend only on the path-length distribution. Detailed in [2], we can then model our DW factors as

$$\sigma^{(2)} = \langle (r - \bar{r})^2 \rangle \equiv \sigma^2(T) \quad (5)$$

where r is the relative bond length between our atoms. This is easily achieved as we are generating coordinates representing our atoms' positions. We then simply have to find the distance between the two atoms and we do this for each pair of atoms to generate DW factors per path. Using the previous DFT-Lanczos method, DW factors were calculated using the Debye integral

$$\sigma_R^2(T) = \frac{\hbar}{2\mu_R} \int_0^\infty \frac{1}{\omega} \coth \left(\frac{\beta\hbar\omega}{2} \right) \rho_R(\omega) d\omega \quad (6)$$

where μ_R is the reduced mass associated with that path, $\beta = 1/k_bT$, and $\rho_R(\omega)$ is the vibrational density of states projected on R . Comparing these two methods should generate DW factors that agree with each other. The former being a new method taking advantage of our sampled coordinate and will have an error of \sqrt{N} , where N is the number of samples we take and the latter being the method used by DFT-Lanczos formulation.

In order to generate our x-ray spectra, we will create FEFF9 input files using extracted subroutines from CORVUS [7]. FEFF currently uses real space Green's functions approach and calculated DW factors to produce x-ray spectra. If we provide FEFF with our sampled coordinates, there shouldn't be a need to provide calculated DW factors as our sampled coordinates will be used to create a vibrationally averaged spectra that has DW factors built into the coordinates. Our main results will therefore be the comparisons between the two methods of calculating DW factors, and the qualitative comparison of x-ray spectra produced by both methods.

IV. RESULTS

A. Calculated DW Factors

Results produced from this method are compared against theoretical DW factor calculations. Shown in table I, are DW factors calculated using both methods as well as the corresponding paths used to compute them. All ranges of temperatures calculated match within the margin of error suggesting our method to calculate DW factors is correct. Furthermore, with this Monte-Carlo sampling method, we can increase our number of samples to have as fine of an accuracy as we want.

	10^{-3} \AA^2	DWF (DFT)	DWF (Expt)
OCCl ₂ T = 1K		1.320	1.384
		2.675	2.777
		2.675	2.760
		2.516	2.525
		2.516	2.545
	2.858	2.958	
OCCl ₂ T = 300.75K		1.320	1.377
		3.242	3.315
		3.242	3.203
		2.764	2.825
		2.764	2.778
	4.457	4.452	
OCCl ₂ T = 1200K		1.638	1.712
		9.143	9.312
		9.143	9.055
		6.586	6.686
		6.586	6.586
	15.060	14.784	
F ₂ O T = 1K		2.079	2.134
		2.079	2.118
		3.484	3.288
F ₂ O T = 300.75K		2.134	2.125
		2.134	2.169
		3.924	3.937
F ₂ O T = 1200K		3.583	3.848
		3.583	3.616
		9.367	9.296

TABLE I. Theoretical calculations of DW factors. While DFT-Lanczos method has roughly $\pm 10\%$ error, our method has an error of $1/\sqrt{N}$ where N for each trial is 1000 samples.

We show both OCCl₂ and F₂O as representative samples for this method because demonstrating this technique on diatomic molecules is too simple to demonstrate we operate in the quasi-harmonic region. Furthermore, if we calculate DW factors on polyatomic atoms and these factors do not vary in accuracy, we can eventually apply this technique to large atom structures such as copper lattice structures or a zirconium tungstate sample. It also appears that as we increase in temperature range, our results show some deviancy as this may be explained that such a high temperature no longer allows

us to assume the atom remains in its Morse Potential. This would negate our harmonic approximation as the sampling would capture outside of this region. Overall, however, our DW factors calculated from this sampling method agree with previous DW factor calculations ratifying our sampled coordinates as an accurate way to produce x-ray spectra.

B. X-ray Spectra

Using sampled coordinates produced by our Monte-Carlo simulation is run through FEFF-9 XANES calculation to produce the spectra shown in figure 1. We produced 500 different spectra which are then averaged together to produce a final, vibrationally averaged, spectra which is then compared to a spectra produced using the DW factors calculated by [2].

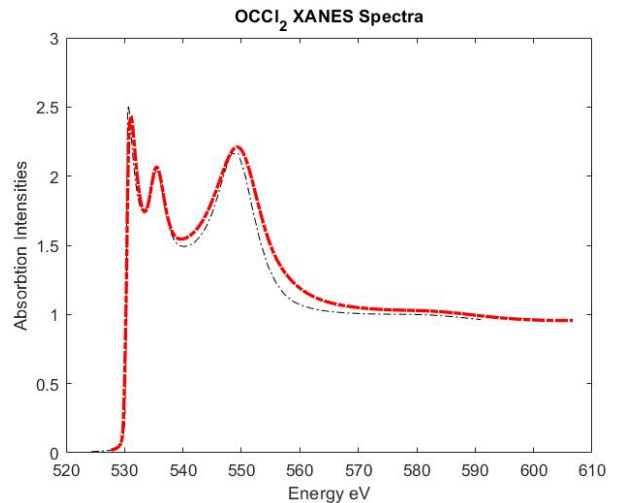


FIG. 1. An averaged OCCl₂ spectra produced with randomly sampled coordinates [red] and an OCCl₂ spectra calculation from Debye-Waller factors.

The agreement between the two spectra greatly suggests that the sampled coordinate method produces a similar amount of accuracy to the spectra calculated with DWF. Furthermore, this spectra was produced with only 500 points leaving an error of roughly a %5 error on every point. With more sampled points we would have a finer level of accuracy and would be able to calculate more points with the same level of accuracy.

C. GeCl₄ Spectra

Another simple molecule that we compared to was GeCl₄. There is significant documentation on GeCl₄ and serves as a standard example when calculating theoretical XANES spectra.

Both the spectra calculated from sampled coordinates and the spectra calculated using DWF agree with ex-

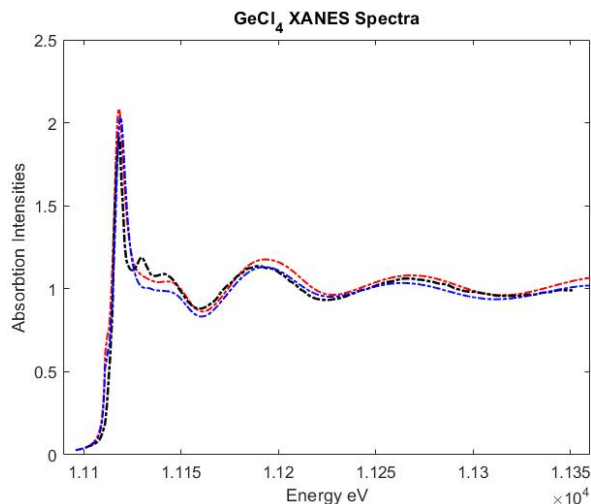


FIG. 2. A spectra of GeCl_4 where blue shows a calculation using sampled coordinates while red shows a calculation using DWF. An experimental spectra in black is also overlaid.

perimental data [6] when both spectra intensities were aligned with the experimental version. Particularly, the sampled coordinate spectra agrees extremely well with experimental data at higher energies when approaching EXAFS region. Again both spectra greatly capture the peak near the K-edge, however it appears the sampled coordinate misaligns a few eV after the edge. Both theoretical spectra miss a small feature shown in the experimental data. This small peak may be due to a many-body cascading effect in the x-ray spectra which becomes difficult to capture with the calculation shown here. Furthermore, it appears that the difference in energy between the small and large peaks is roughly 11.6 eV which happens to be the ionization energy of GeCl_4 indicating a feature that might be caused by this many-body effect. Further investigation into this feature would be needed to help improve the ability of our sampled coordinate approach. Regardless, our sampled coordinate method still produces a greatly agreeing spectra to both experimental data and previous methods of XANES calculation.

D. SF_6 Spectra

While OCCl_2 provides a good base demonstration of the utility of the sampling method, we hypothesize that this method should be able to capture some additional local atomic displacement XANES peaks that were not captured previously. In particular, experimental SF_6 spectra shows these additional features [9]. By producing a proper SF_6 dynamical matrix, we can use the inverse transform sampling methods to produce new coordinates that, when averaged, contain proper thermal distortions. This should account for peaks that are caused by local atomic displacements as we are able to directly capture this motion in our spectra.

As discussed in [8], we performed an average over many displacements from the equilibrium position to produce the spectra in figure 3. Although we had expected the appearance of many peaks that are caused by vibronic coupling, we could still only produce a single absorption peak similar to a potential calculation with no shifting of the absorber. Even over a variety of temperature we see no strong indication of additional peaks and little agreement to spectra in [9].

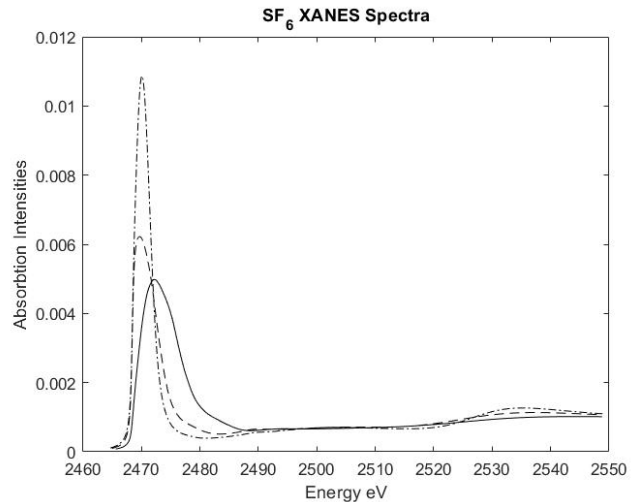


FIG. 3. An averaged SF_6 spectra produced with randomly sampled coordinates where dotted-dashed spectra is $T = 300\text{K}$, dashed spectra is $T = 3000\text{K}$, and solid spectra is $T = 9234\text{K}$.

The spectra in [8] was produced by displacing the sulfur atom (0.1, 0.1, 0.1) angstroms and running a XANES calculation. This decision was motivated as this is the amplitude consistent with measured Debye-Waller factors for the sulfur atom. Using our method for calculating DW factors, we see that our DW factors for SF_6 agree with the DW factors used in [8]. However, if we were to weight all of the DW factors into to the displacement of the S atom, we only see a displacement of 0.042 angstroms instead of the 0.173 angstrom displacement used. This is an overestimation by over a factor of four and could account for the differences between the two spectra.

We estimate a very high temperature, on the order of 16000 K, would be needed to achieve a displacement of 0.173 angstroms for the sulfur atom. Although running a spectra calculation at 16000 K is possible, it becomes unrealistic as a result because our quasi-harmonic approximation begins to see failure. Furthermore, at 16000K, the sulfur atom is not the only atom in the molecule that is shifted. This affects the calculation, despite using the sulfur atom as the absorber, as DWF rely on the average bond length between other atoms as well. Figure 4 compares the three different spectra. Although both the spectra calculated with DWF and sampled coordinates do not capture the small peak at 2490 eV, the sampled

coordinate spectra shows a slight increased trend indicating the presence of these peaks. We are unsure why a displacement of 0.173 angstroms generates these features, but the sampled coordinate method, with an average displacement of the same amount, does not generate these features.

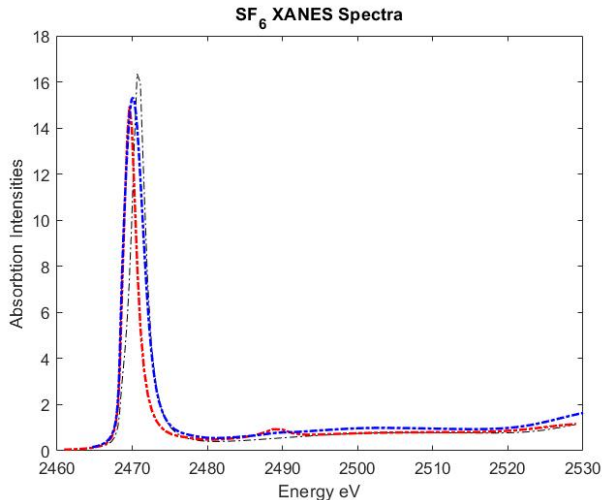


FIG. 4. A spectra calculated with DWF (black), a spectra calculated with sampled coordinates (blue), and a spectra calculated with only the S atom perturbed by 0.173 angstroms (red) are overlaid together.

V. CONCLUSION

We demonstrated that the inverse transform sampling technique produces accurate Debye Waller factors which are essential in producing accurate x-ray spectra. With just 1000 samples, our technique matches that of previous calculations [2] of DW factors and that it can be used to produce accurate spectra. Overall, there is now no longer a need to separately calculate DW factors as we can simply calculate XANES spectra using vibrationally averaged coordinates. These coordinates should have the vibrational effects factored in automatically and we simply have to generate a larger sample size for a higher degree of accuracy.

Future plans include a more detailed analysis in the discrepancy of the XANES spectra for SF₆. If the extra peaks produced in experimental SF₆ are caused by vibrational effects, the proper sampling technique should be able to capture these effects. Regardless, this project demonstrates great promise from its accurate ability to calculate and incorporate Debye-Waller factors into XANES spectra.

VI. ACKNOWLEDGMENTS

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