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Ab Initio X-Ray Absorption Fine Structure Cumulants

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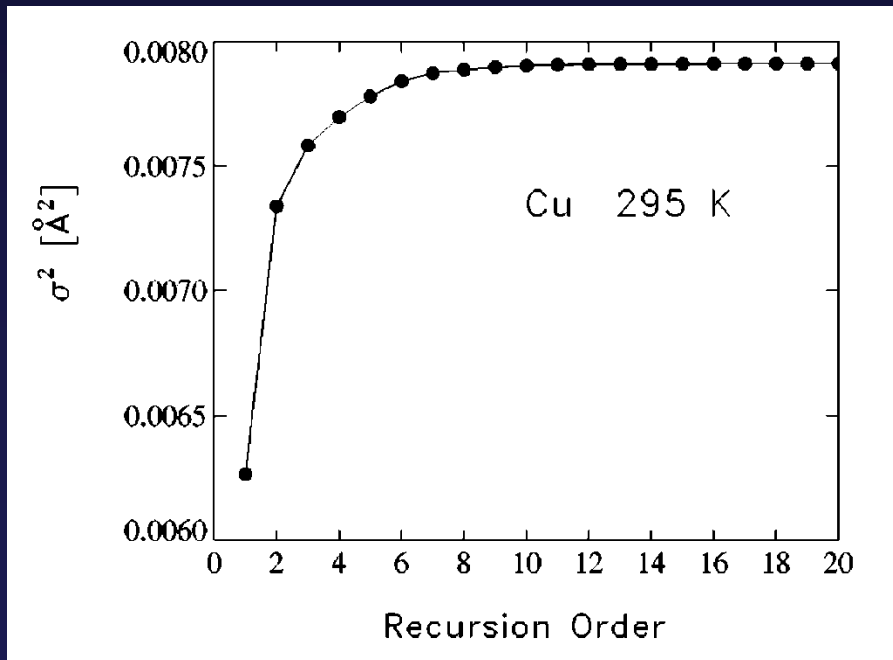*[2] Hahn-Meitner-Institut, Berlin, Germany*

Introduction

- **Method originally developed by Poiarkova and Rehr**
- **Used two tier representation of the vibrational density of states**

$$\sigma_j^2 = \frac{\hbar}{2\mu_j} \int_0^\infty \frac{1}{\omega} \coth \frac{\beta\hbar\omega}{2} \rho_j(\omega) \, d\omega \qquad \rho_j(\omega)\,d\omega = \sum_\gamma |\langle 0|\gamma\rangle|^2 \delta(\omega - \omega_\gamma)\,d\omega$$

$$= -\frac{1}{\pi} \mathrm{Im} \left\langle 0 \left| \frac{1}{z - \Phi + i\epsilon} \right| 0 \right\rangle dz := w(z)\,dz,$$

Cu   295 K

- **Extended to higher recursion order by Krappe and Rossner**

The Dynamical Matrix/Hessian

$$\Phi_{jl\alpha,j'l'\beta} = \frac{1}{(m_j m j')^{1/2}} \frac{\partial^2 E}{\partial u_{jl\alpha} \partial u_{j'l'\beta}}$$

- Can be obtained (at least partially) from experiment:

    - Neutron Scattering

    - Vibrational Spectrosopy

- Here we use first principles electronic structure theory to determine it:

    - For crystalline materials we use the Density Functional Theory (DFT) of Response implemented in ABINIT

    - For molecular or amorphous systems we use the Hessians implemented in Gaussian03

    - All calculations are done with DFT using both local (LDA) and gradient corrected (GGA) functionals

Born-von Karman parameters Φ_{ij}^{m} for some selected metals (in N/m)

Cu

m	ij	LDA	GGA	Exp. (49 K)
	xx	11.55	14.73	13.278
110	zz	-1.12	-1.71	-1.351
	xy	12.56	16.49	14.629
200	xx	1.82	1.74	-0.041
	yy	-0.67	-0.65	-0.198

Ag

m	ij	LDA	GGA	Exp. (296 K)
	xx	11.72	14.35	10.71
110	zz	-2.88	-3.32	1.75
	xy	13.72	17.02	12.32
200	xx	0.98	0.90	0.06
	yy	-0.31	-0.30	-0.23

Au

m	ij	LDA	GGA	Exp. (295 K)
	xx	18.40	21.42	16.43
110	zz	-6.44	-6.91	-6.54
	xy	21.44	25.25	19.93
200	xx	3.32	3.28	4.04
	yy	-0.65	-0.64	-1.27

Pt

m	ij	LDA	GGA	Exp. (90 K)
	xx	26.40	30.84	25.681
110	zz	-7.04	-7.83	-7.703
	xy	29.88	35.32	30.830
200	xx	8.36	8.36	5.604
	yy	-2.19	-2.19	-1.337

Pb

m	ij	LDA	GGA	Exp. (80 K)
	xx	3.16	4.34	4.3243
110	zz	-1.14	-1.37	-2.4881
	xy	3.67	5.23	4.6730
200	xx	1.06	1.03	1.4083
	yy	-0.30	-0.31	0.0719

Mo

m	ij	LDA	GGA	Exp. (296 K)
111	xx	15.55	18.67	16.51
	xy	5.88	11.55	11.78
200	xx	40.23	46.83	44.57
	yy	-5.25	-6.15	-2.69

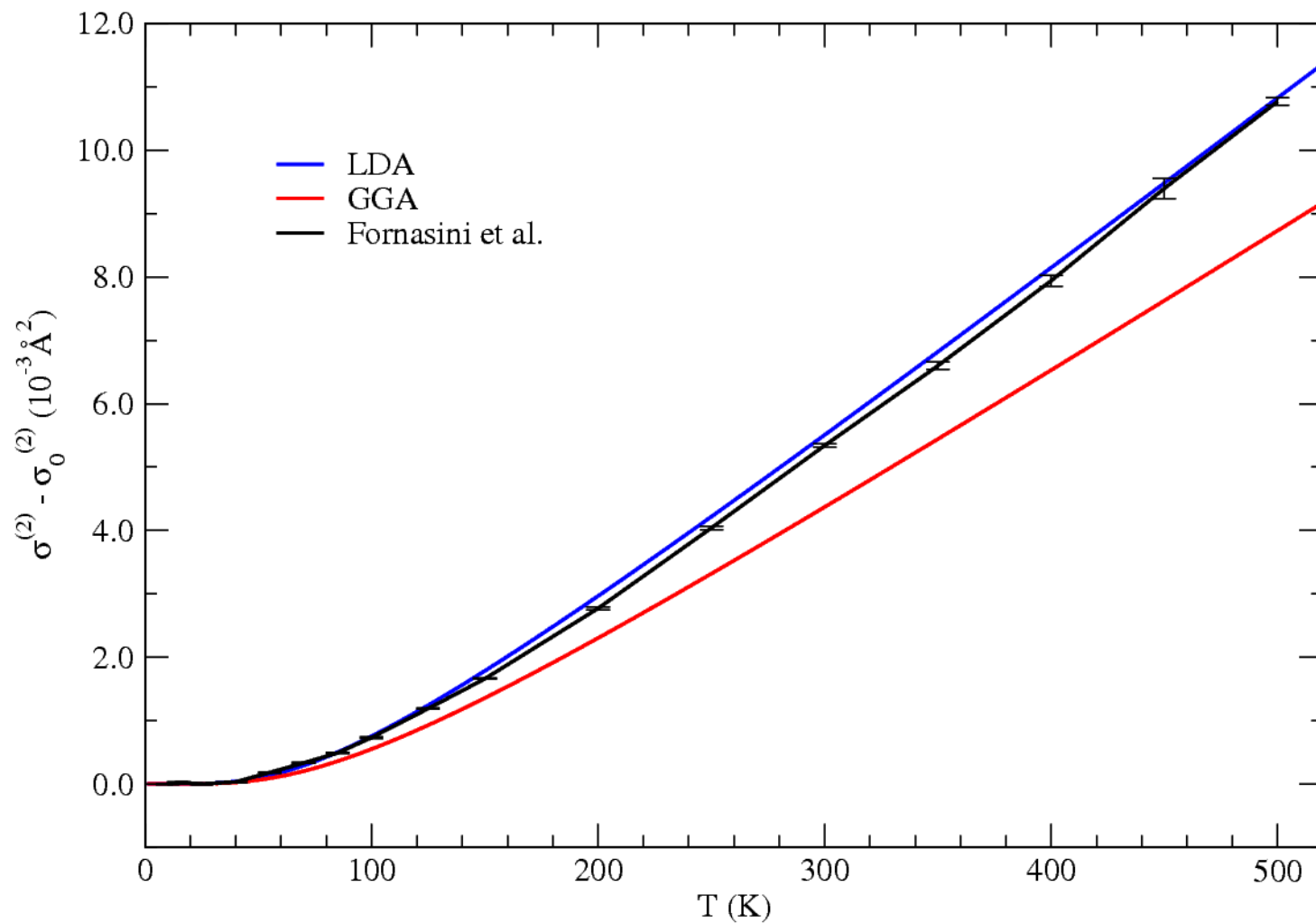# Vibrational Density of States of Cu

First Cumulant (Linear Expansion) of Cu
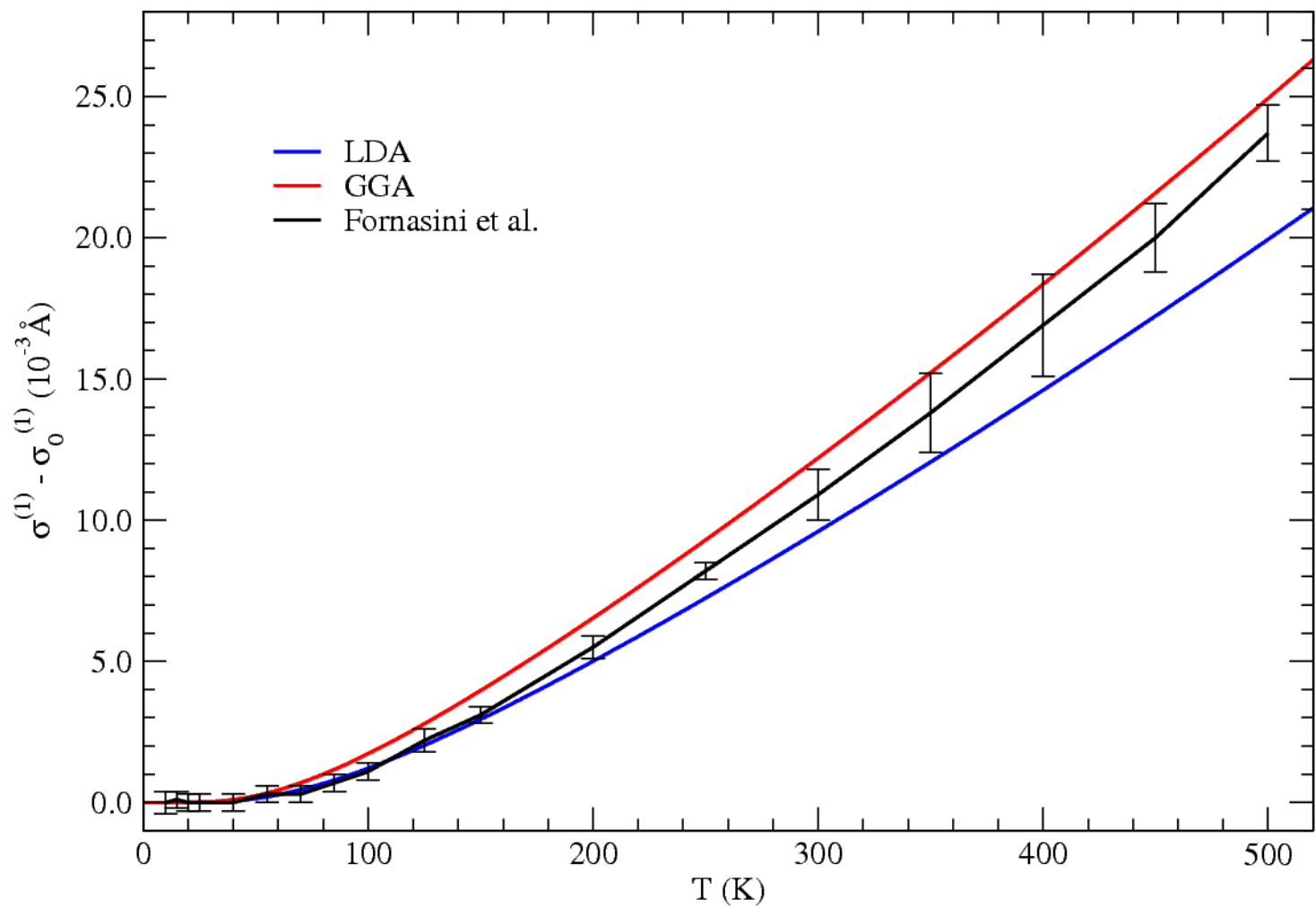
Second Cumulant (DW factor) of Cu

Debye-Waller factors (in 10^{-3} Å^2) for fcc and bcc metals.

Shell	Cu				Ag			
	CD	LDA	GGA	Exp.	CD	LDA	GGA	Exp.
1	8.91	8.55	7.15	7.83	11.11	10.07	8.36	10.5
2	10.99	11.06	9.50	11.08	13.73	14.42	12.14	
3	11.32	10.80	9.14	9.58	14.17	12.55	10.44	

Shell	Au				Pt			
	CD	LDA	GGA	Exp.	CD	LDA	GGA	Exp.
1	8.62	8.20	6.76	8.10	5.37	4.29	3.75	5.72
2	10.67	12.61	10.36	12.03	6.65	5.68	5.06	6.78
3	11.02	11.76	9.57	10.93	6.86	5.66	4.97	6.65

Shell	Pb				Mo			
	CD	LDA	GGA	Exp.	CD	LDA	GGA	Exp.
1	33.86	30.98	24.76	29.7	4.06	4.50	3.79	
2	41.98	39.57	33.30		4.60	4.04	3.57	
3	43.40	37.65	30.70		5.32	5.25	4.46	

Debye-Waller factors (in 10^{-3} Å^2) for some semiconductors with diamond crystal structure.

Shell	Ge				GaAs			
	CD	LDA	GGA	Exp.	CD	LDA	GGA	Exp.
1	5.12	3.77	3.41	3.5	5.22	3.97	3.63	4.1
2	7.43	10.21	11.59	9.3	7.82	12.11	13.22	11.1

Debye-Waller factors (in 10^{-3} Å^2) for some simple molecules.

Shell	N_2			C_6H_6		
	LDA	GGA	Exp.	LDA	GGA	Exp.
1	1.003	0.983	1.033	2.240	2.230	2.009
2				2.770	2.730	2.942
3				2.970	2.900	3.856

Shell	$GeCl_4$			GeH_3Cl		
	LDA	GGA	Exp.	LDA	GGA	Exp.
1	2.040	2.160	2.070	2.200	2.300	3.000

Conclusions

- General, applicable to crystalline and amorphous systems

- Can be improved systematically

- Accuracy dependent only on electronic structure calculation

- Can provide rough estimates useful as initial guesses in fitting procedures

The (near) future