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Ab Initio XAS Debye-Waller Factors Beyond the Harmonic Approximation

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Introduction

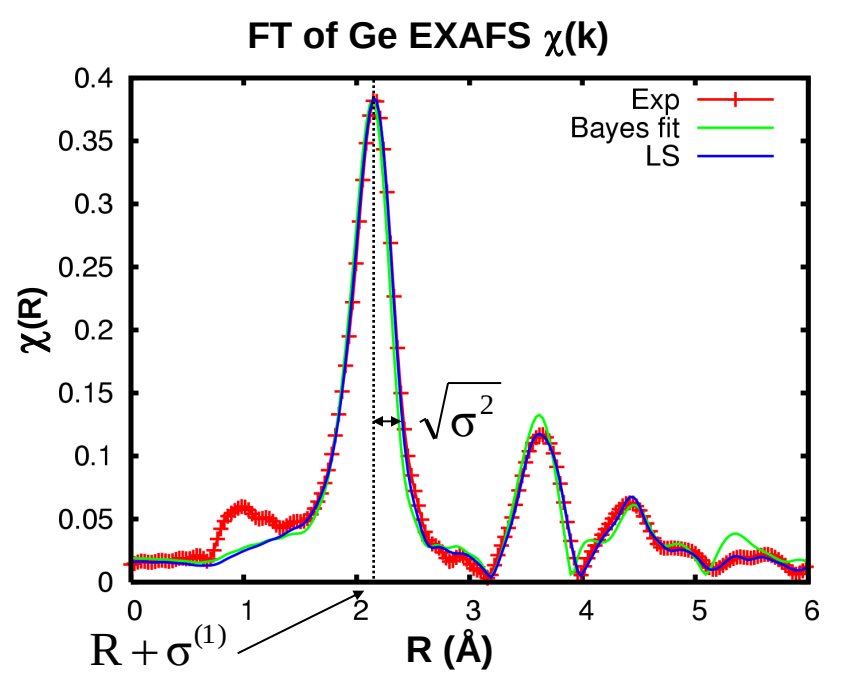
XAFS Debye-Waller (DW) Factor

$$\left\langle e^{i2kr} \right\rangle \equiv e^{2ikR_0} e^{-W(T)}$$

- **Originate from thermal and configurational disorder**
- **Crucial for a quantitative treatment of XAS**

Average commonly expressed in terms of the cumulant expansion:

$$W(T) = -\sum_{n=1}^{\infty} \frac{(2ik)^n}{n!} \sigma^{(n)}(T)$$



J. Kas *et al.* (2007)

First cumulants:

$$\begin{cases} \sigma^{(1)} = \langle r - R_0 \rangle \\ \sigma^{(2)} = \left\langle (r - \bar{r})^2 \right\rangle \equiv \sigma^2(T) \\ \sigma^{(3)} = \left\langle (r - \bar{r})^3 \right\rangle \end{cases}$$

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Lanczos Recursion Algorithm

XAFS DW Factor for path *R*:

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

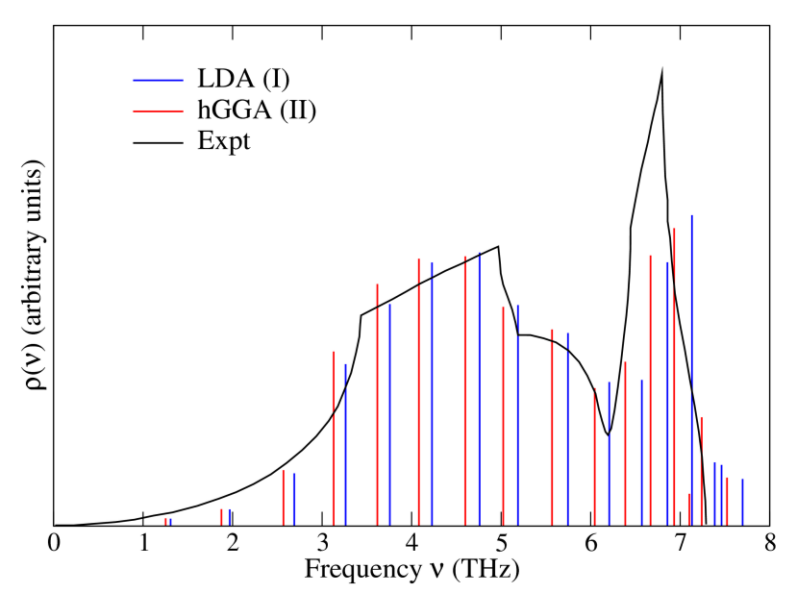
- Originally developed by Poiarkova and Rehr
- Extended by Krappe and Rossner

VDOS expressed as imaginary part of the phonon propagator:

$$\rho_R(\omega) = -\frac{2\omega}{\pi}\mathrm{Im}\left\langle 0\left|\frac{1}{\omega^2 - \mathbf{D} + i\varepsilon}\right|0\right\rangle$$

Seed state: Displacement along path

Total VDOS of Cu



Dynamical Matrix: Calculated using the Density Functional Theory (DFT) of Response implemented in ABINIT (Gonze et al., 2002)

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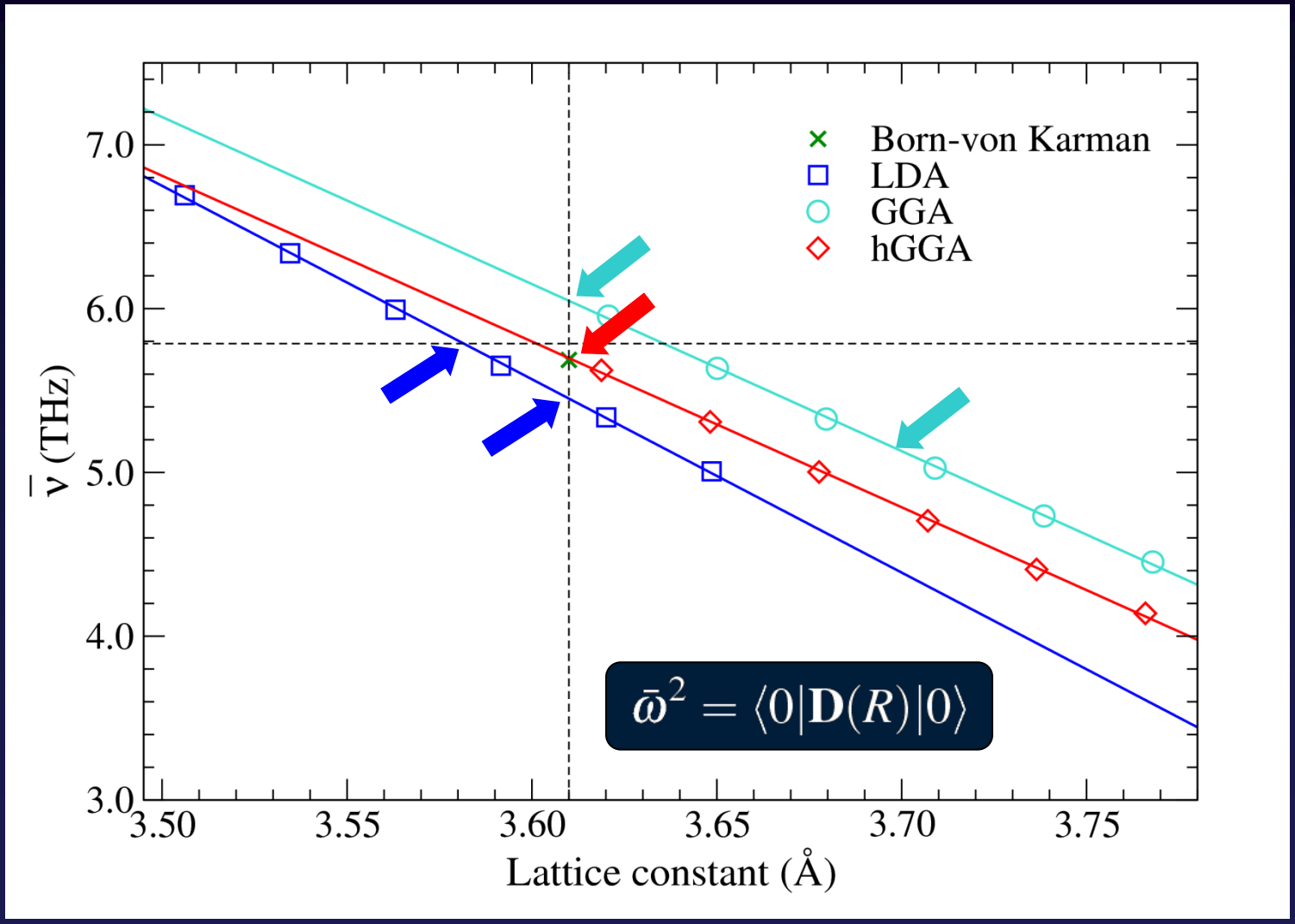
Anharmonicity Effects on the Einstein Freq. of Cu



BvK: Nicklow *et al.* (1967)

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Prescriptions for the Calculation of the Dynamical Matrix

I. Calculate *D* with the LDA at the theoretical estimate of *a(T)*

- Fully *ab initio*
- Provides lattice expansion directly
- Computationally demanding

$$F(a,T) = E(a) + 3k_B T \int_0^\infty d\omega \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]\rho_a(\omega)$$

$$D_{jl\alpha,j'l'\beta} = A_{jl\alpha,j'l'\beta} + B_{jl\alpha,j'l'\beta}\,\Delta a$$

II. Calculate *D* with the hGGA at the experimental estimate of *a(T)*

- Uses a new functional (hGGA): 50% LDA + 50% GGA
- Requires experimental input
- Lattice expansion from Correlated Einstein model
- Less computationally demanding

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Debye-Waller factors (in 10^{-3} Å^2) for Pt and GaAs

	n	CD	LDA(I)	hGGA(II)	Expt
Pt (190 K)	1	3.55	3.23	3.23	3.22 ± 0.05
	2	4.38	4.64	4.78	4.7 ± 0.3
	3	4.50	4.44	4.49	4.3 ± 0.4
	4	4.56	4.60	4.66	4.5 ± 0.4
Pt (300 K)	1	5.41	4.98	4.90	4.83 ± 0.05
	2	6.69	7.23	7.34	6.8 ± 0.5
	3	6.91	6.92	6.89	6.7 ± 0.6
	4	7.01	7.17	7.16	7.0 ± 0.6
GaAs (295 K)	1	5.17	3.97	3.86	4.2 ± 0.1
	2	7.75	12.70	12.01	11.7 ± 0.14
	3	7.69	14.91	14.01	
GaAs (295 K)	1	5.15	3.96	3.86	4.2 ± 0.1
	2	7.20	10.80	10.19	9.6 ± 0.11
	3	7.68	14.83	14.00	

Expt: Stern *et al.* (1980)

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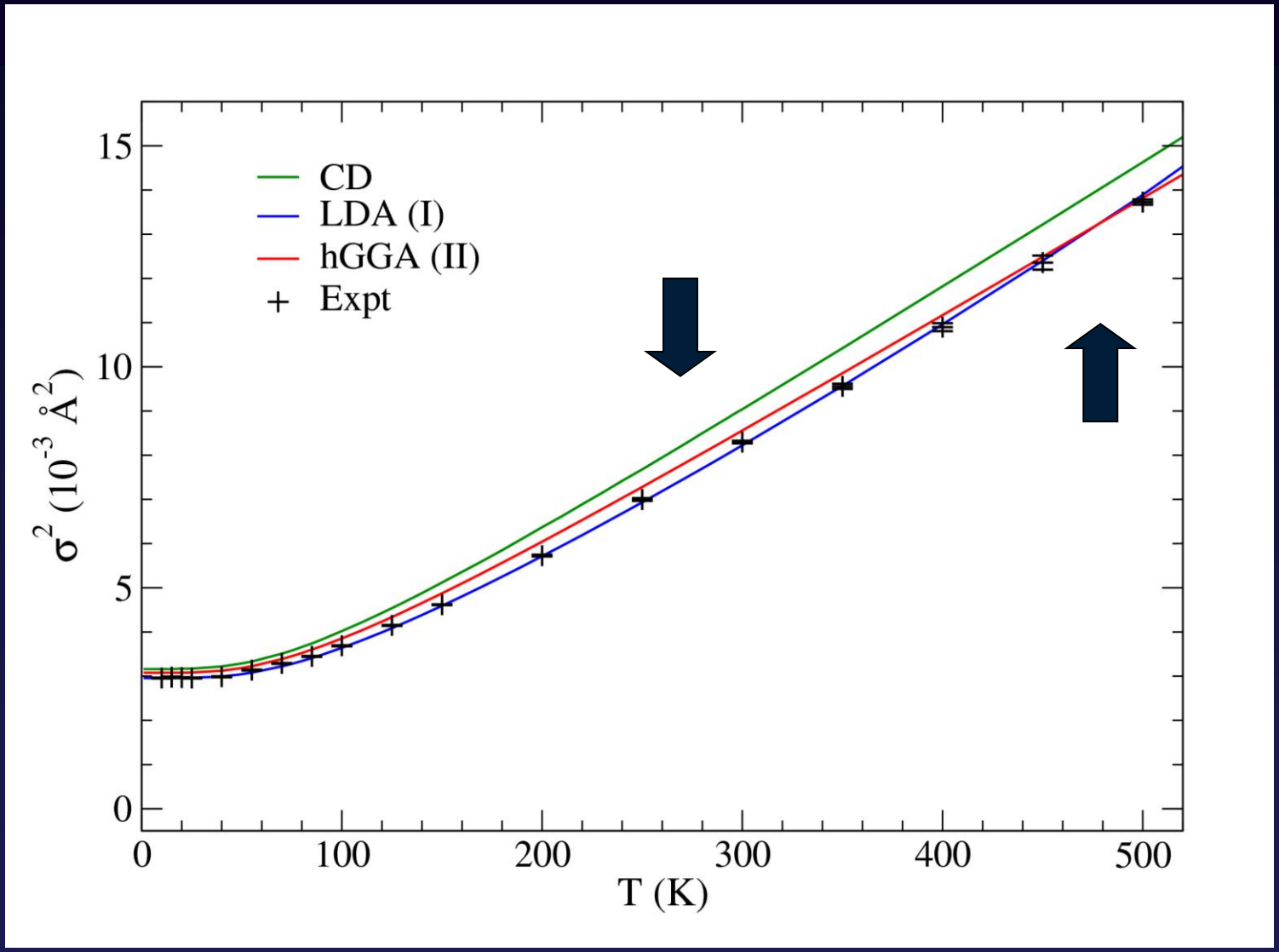
XAFS Debye-Waller Factor of Cu



Expt: Fornasini *et al.* (2004)

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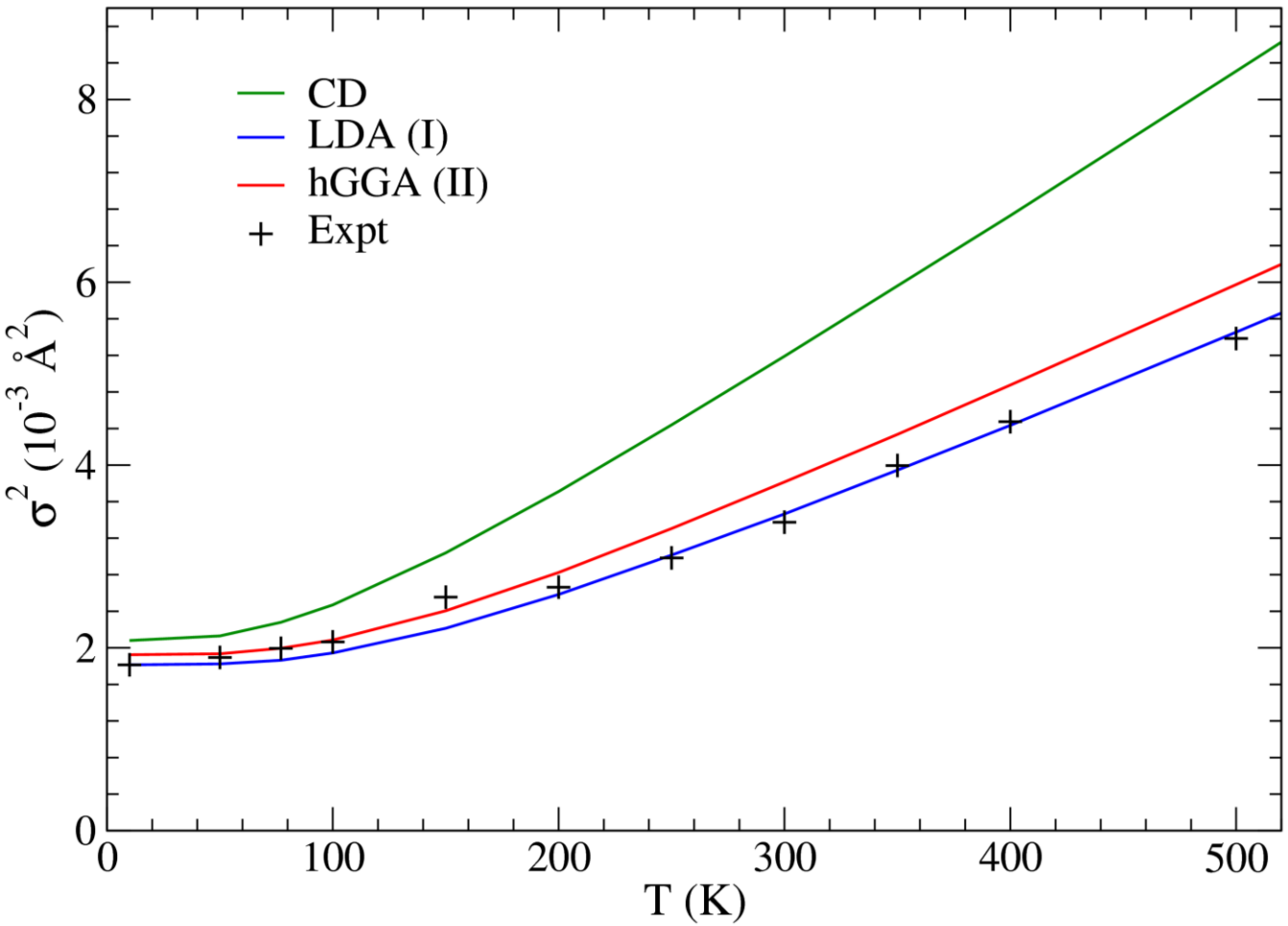
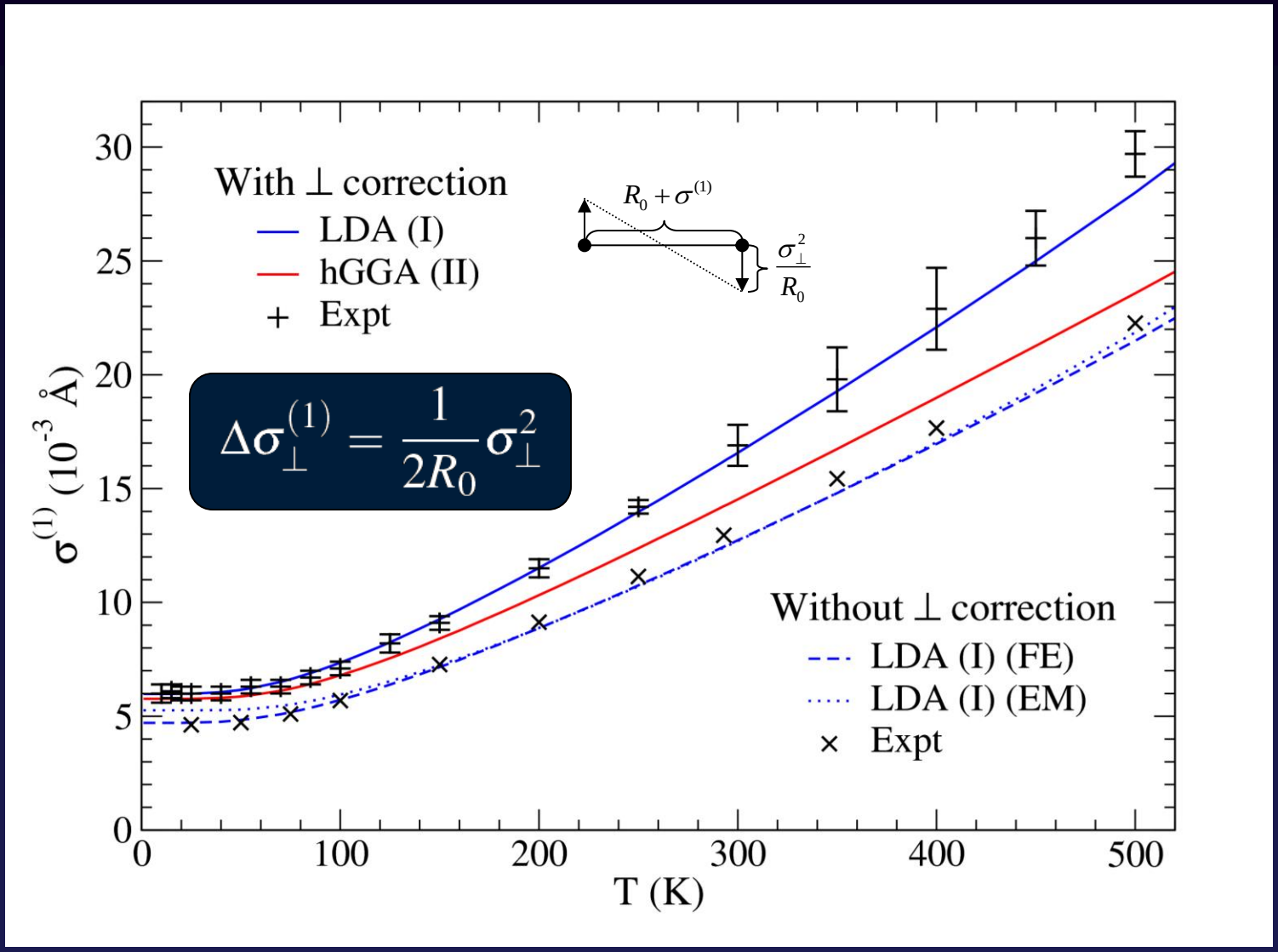
XAFS Debye-Waller Factor of Ge



Expt: Dalba *et al.* (1999)

First XAFS Cumulant of Cu



Expt: Fornasini *et al.* (2004), AIP Handbook (1972)

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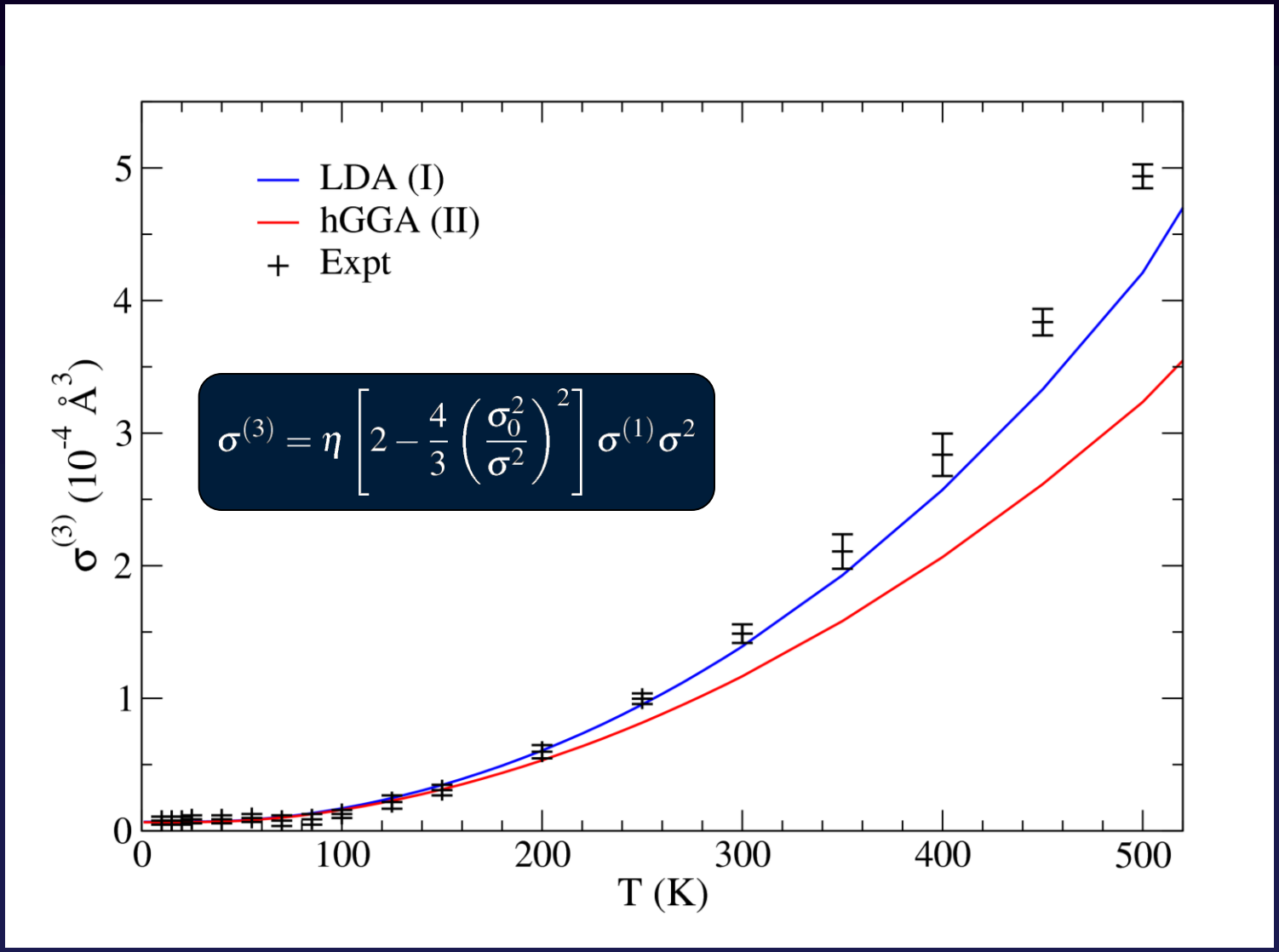
Third XAFS Cumulant of Cu



Expt: Fornasini *et al.* (2004)

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Conclusions

- Developed two prescriptions for the calculation of XAFS cumulants
- Can determine lattice expansion from:
  - Free energy minimization
  - Correlated Einstein model
- New Lanczos seed states provide:
  - Total VDOS
  - Perpendicular correction to first cumulant
  - Crystallographic Debye-Waller factors
- Developed new functional (hGGA): 50% LDA + 50% GGA

Future Prospects

- Implementation for arbitrary crystals
- Better form of hGGA functional ("Diminished functionals", *cf.* Perdew *et al.*)
- "Black Box" implementation for FEFF XAFS
- Tables of Debye-Waller factors for most common substances

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