# OCEAN and AI2NBSE postprocessors of ABINIT for Core and Valence Spectra

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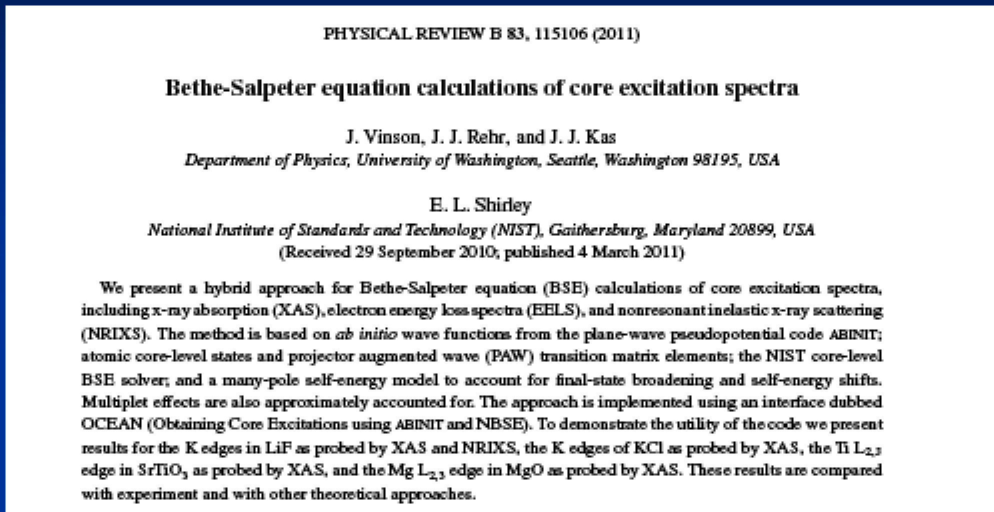
# aka SKWIGGLiE

Spectra from K-space Wave-functions with Interactions, Gradually Getting Like Experiment

# 1. OCEAN*



PHYSICAL REVIEW B 83, 115106 (2011)

**Bethe-Salpeter equation calculations of core excitation spectra**

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We present a hybrid approach for Bethe-Salpeter equation (BSE) calculations of core excitation spectra, including x-ray absorption (XAS), electron energy loss spectra (EELS), and nonresonant inelastic x-ray scattering (NRIXS). The method is based on *ab initio* wave functions from the plane-wave pseudopotential code ABINIT; atomic core-level states and projector augmented wave (PAW) transition matrix elements; the NIST core-level BSE solver; and a many-pole self-energy model to account for final-state broadening and self-energy shifts. Multiplet effects are also approximately accounted for. The approach is implemented using an interface dubbed OCEAN (Obtaining Core Excitations using ABINIT and NBSE). To demonstrate the utility of the code we present results for the K edges in LiF as probed by XAS and NRIXS, the K edges of KCl as probed by XAS, the Ti $L_{2,3}$ edge in $SrTiO_3$ as probed by XAS, and the Mg $L_{2,3}$ edge in MgO as probed by XAS. These results are compared with experiment and with other theoretical approaches.

**O**btaining
**C**ore
**E**xcitation
spectra using
**A**BINIT and
**N**BSE

- Hybrid approach to core spectroscopy
  - GW/BSE for XAS, NRIXS, EELS, …
  - PAW Pseudo-potential / planewave DFT
- Includes self energy damping, multiplets …

*Phys. Rev. B **83**, 115106 (2011)

# 2. Optical-UV Spectra AI2NBSE*

(ABINIT + NIST BSE)

PHYSICAL REVIEW B 78, 205108 (2008)

## Optical to UV spectra and birefringence of $SiO_2$ and $TiO_2$: First-principles calculations with excitonic effects

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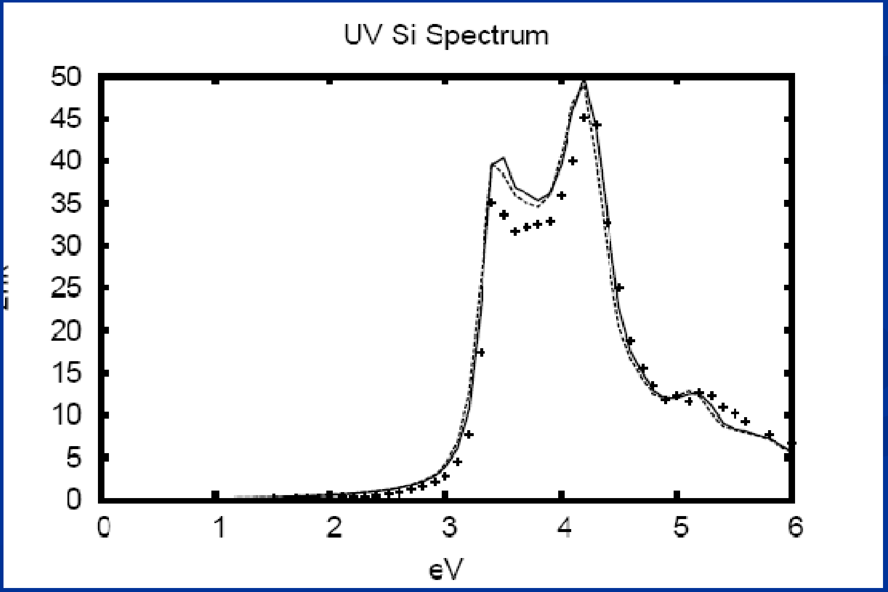
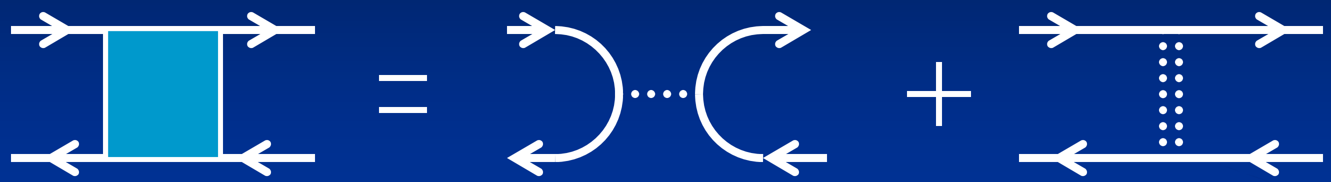
A first-principles approach is presented for calculations of optical, ultraviolet spectra including excitonic effects. The approach is based on Bethe-Salpeter equation calculations using the NBSE code combined with ground-state density-functional theory calculations from the electronic structure code ABINIT. Test calculations for bulk Si are presented, and the approach is illustrated with calculations of the optical spectra and birefringence of $\alpha$-phase $SiO_2$ and the rutile and anatase phases of $TiO_2$. An interpretation of the strong birefringence in $TiO_2$ is presented.




*Phys. Rev. B **78**, 205108 (2008)

# Bethe-Salpeter Equation




## Particle-Hole Hamiltonian

- $H = E_0 + V_c + W$

- Bubble $V_c$ is unscreened
- Ladder $W$ is screened

# Bethe-Salpeter Equation

$$H_{BSE} = H_h + H_e + H_{eh}$$

$$H_h = -\epsilon_h + L \cdot S$$

$$H_e = H_{KS}$$

$$H_{eh} = V(r) + g(i,j)$$

Central term

Multiplets

# Dielectric Response < BSE

$$-\mathrm{Im}\,\epsilon^{-1}(\mathbf{q},\omega) = \frac{4\pi}{q^2}\mathrm{Im}\,\langle\Psi_0|\hat{D}^\dagger \frac{1}{E_0+\omega-\hat{H}+i\gamma}\hat{D}|\Psi_0\rangle$$

***H*** particle-hole Hamiltonian including:

many-pole GW self-energy $\Sigma$

Algorithm: Haydock recursion

# Ground-state

- Standard Density-Functional Theory
  - Pseudopotential, Plane-wave, LDA
  - **ABINIT** (www.abinit.org)
- Well-documented shortcomings; improvements:
  - GW
  - XC + U
- Core to pseudo transitions with PAW
  - Following Blöchl, PRB 50, 17953 (1994)

# Kohn-Sham Wave-Functions

- **ABINIT** (Plane-wave, pseudo-potential)*
  - LDA (Ceperley-Alder) $V_{xc}$
  - Zero Temp / Frozen lattice

- Regular grid in $k$-space
  - Size required varies with BZ volume

- Core states from NIST HF atomic code

*Other PW/PP DFT codes may also work

# Electron-hole pair approximation

$$-\mathrm{Im}\,\epsilon^{-1}(\mathbf{q},\omega) = \frac{4\pi}{q^2}\mathrm{Im}\,\langle\Psi_0|\hat{D}^\dagger\frac{1}{E_0+\omega-\hat{H}+i\gamma}\hat{D}|\Psi_0\rangle$$

$$\cdots\sum_{\phi,\chi}\mathrm{Im}\left[\langle\Psi_0|\hat{D}^\dagger|\phi,\chi\rangle\times\langle\phi,\chi|\frac{1}{\omega-\hat{H}_{\mathrm{eff}}+i\gamma}|\cdots\right.$$

$$\phi=\phi_{n,\mathbf{k}}(\mathbf{r})$$ Conduction electron

$$\chi=\chi_{\alpha,\mathbf{r}}(\mathbf{r})$$ Core hole

$$\hat{D}=\begin{cases}\hat{e}\cdot\mathbf{r} & \mathrm{XAS}\\ e^{i\mathbf{q}\cdot\mathbf{r}} & \mathrm{NRIXS}\end{cases}$$

# PAW Matrix Elements

$$\phi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}}^{n,\mathbf{k}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$F^{ps} \rightleftharpoons F^{ae}$$

$$\phi_{n,\mathbf{k}}(\mathbf{r}+\tau) = \sum_{\nu l m} A_{\nu l m}^{n\mathbf{k}} F_{\nu l}^{ps}(r) Y_{lm}(\hat{\mathbf{r}})$$

$$A_{\nu l m}^{n\mathbf{k}} = 4\pi i^l \sum_{\mathbf{G}} C_{\mathbf{G}}^{n\mathbf{k}} e^{i(\mathbf{k}+\mathbf{G})\cdot\tau} Y_{lm}^*(\hat{\mathbf{k}}) \int_0^\infty dr r^2 j_l((k+G)r) F_{\nu l}^{ps}(r)$$

$$\langle \phi_{n,\mathbf{k}} | \hat{D}^{(1)} | \chi_\alpha \rangle = \int d^3r \sum_{\nu l m} A^{*\,n\mathbf{k}}_{\nu l m} F_{\nu l}^{ae}(r) Y_{lm}^*(\hat{r})\, \hat{D}^{(1)}\, \chi_\alpha(\mathbf{r})$$

# Core-Hole Screening

$$W(\mathbf{r}) = V_\alpha(\mathbf{r}) + \Delta V_\alpha(\mathbf{r}) + \Delta V_{val}(\mathbf{r})$$

- Core response from self-consistent HF
- Use neutralizing shell to divide valence
  - RPA for short range
  - Model dielectric for long range

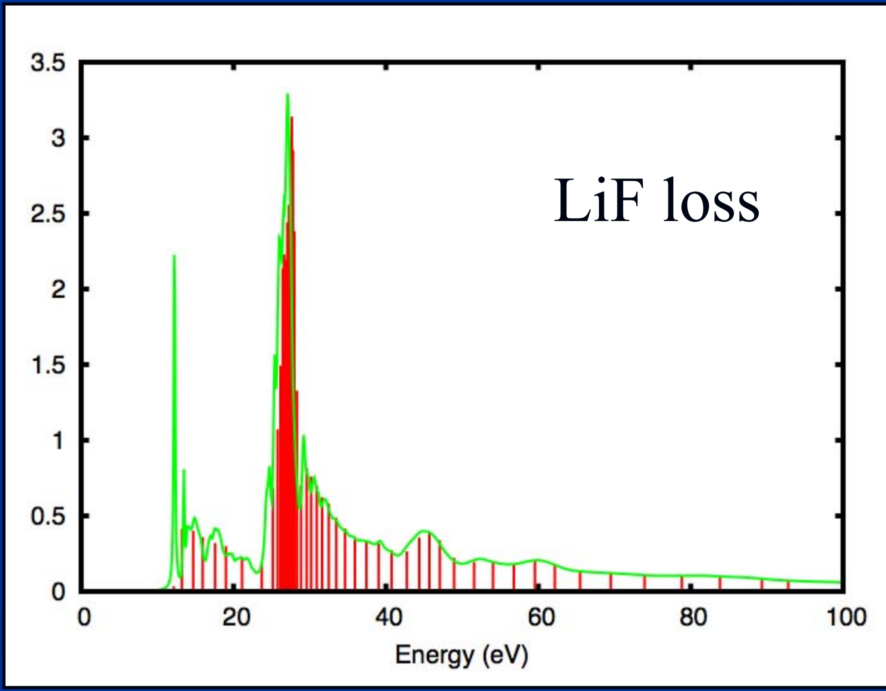
$$\Delta V_{val}(\mathbf{r}) = \int d^3\mathbf{r}'[\epsilon^{-1}(\mathbf{r},\mathbf{r}') - \delta^3(\mathbf{r}-\mathbf{r}')] \times [V_\alpha(\mathbf{r}') + \Delta V_\alpha(\mathbf{r}')]$$

Hybersten and Louie, Phys Rev B **35**, 5585 (1987)

# GW Many-pole self-energy

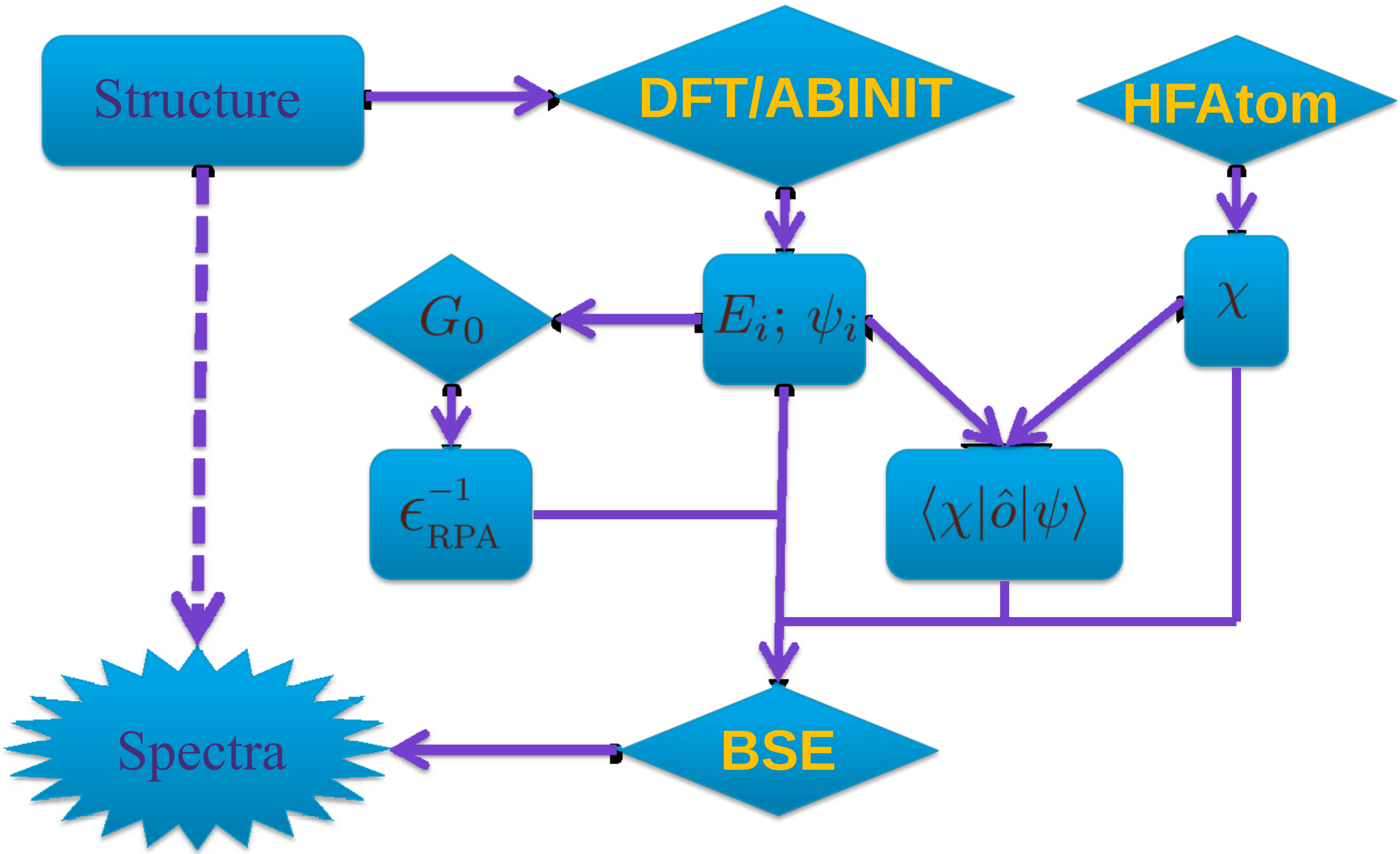
- Extension of Hedin-Lundqvist plasmon-pole

- MPSE (Kas et al.*)
  - Calculate loss function with AI2NBSE
  - Model as a series of (many) poles
  - Apply as convolution

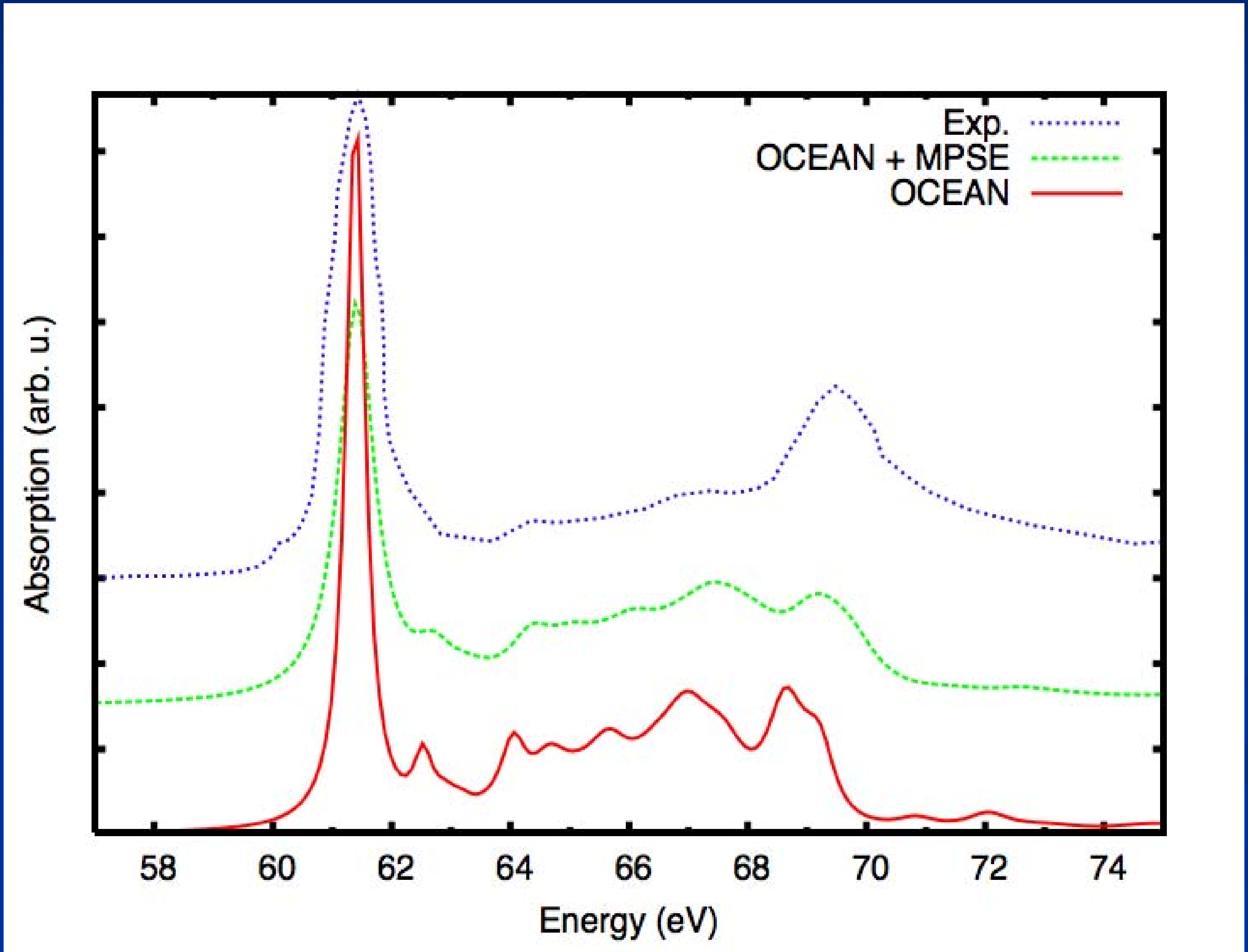



J.J. Kas et. al, Phys Rev B **76**, 195116 (2007)

# OCEAN Package



# Example: Li *K*-edge XAS of LiF



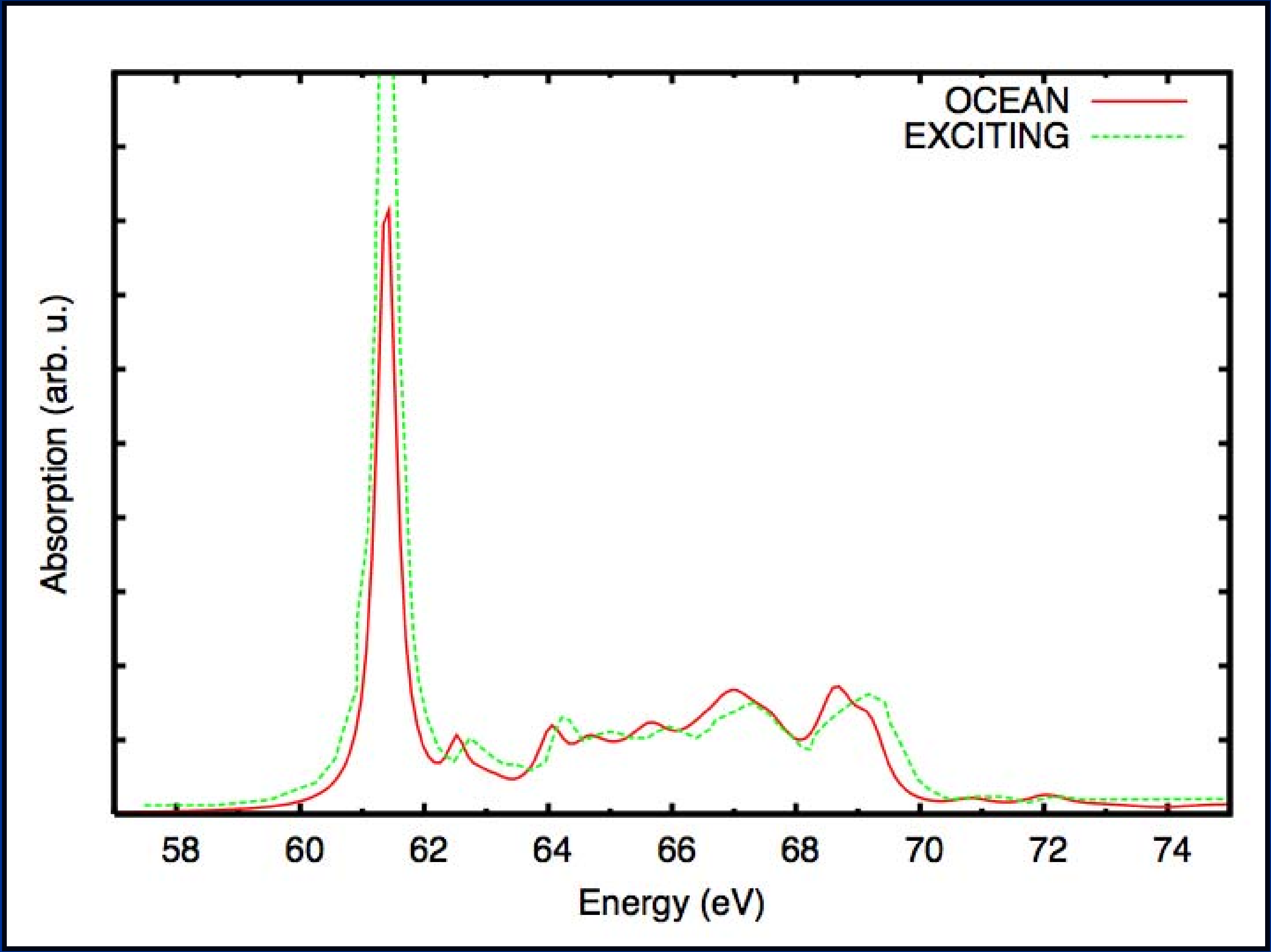

1000 k-points

100 Ha. cut-off

Expt. data from K. Handa et. al, Memoires Sr. Center Ritsumeika Univ **7** (2005)

# Example: Li *K*-edge XAS of LiF

## Comparison with EXC!TING* (NO MPSE)



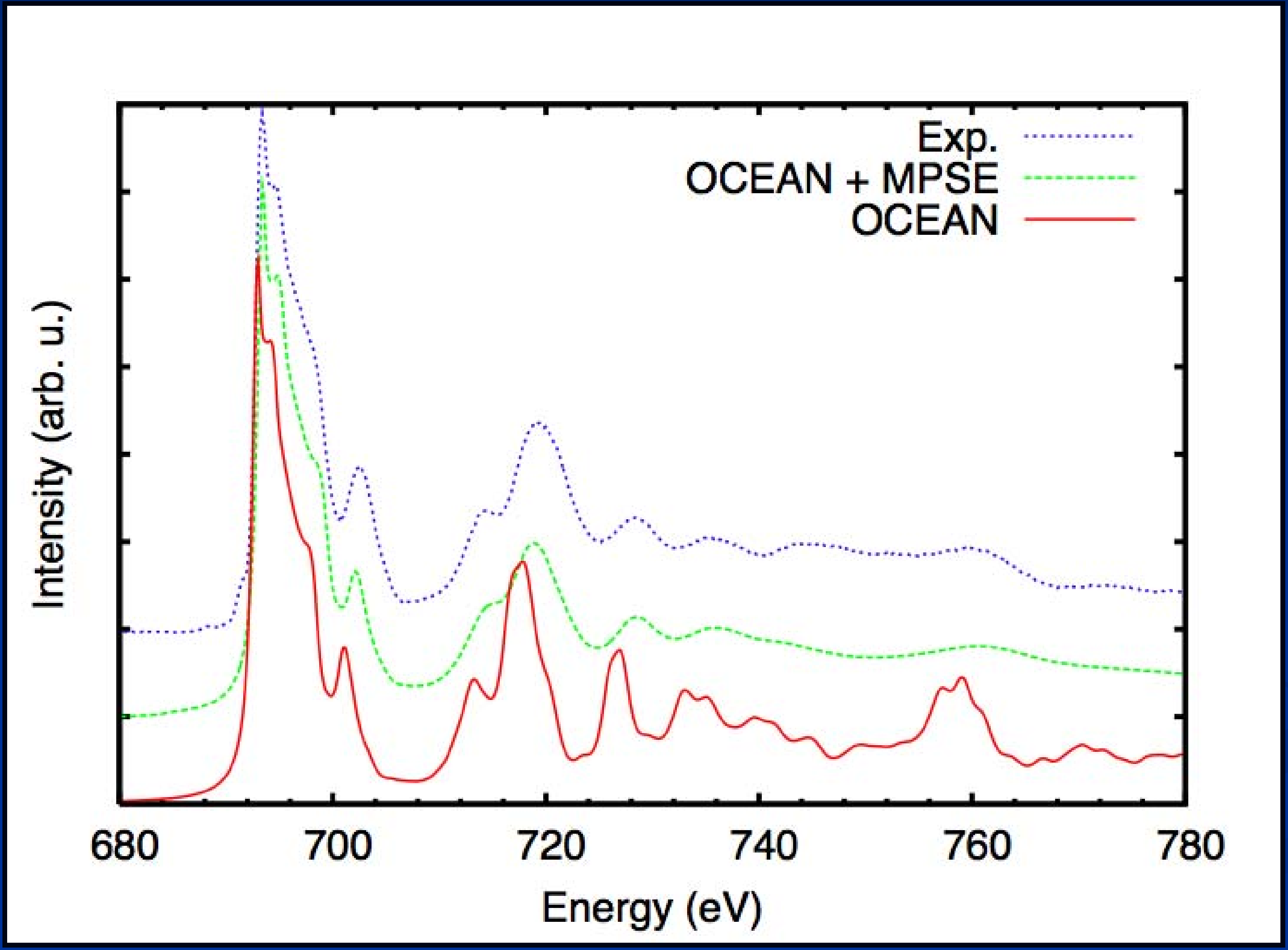

1000 k-points

100 Ha. cut-off

NO MPSE

*W. Olovsson et. al, Phys Rev B **79**, 041102(R) (2009)

# Example: F *K*-edge XAS in LiF

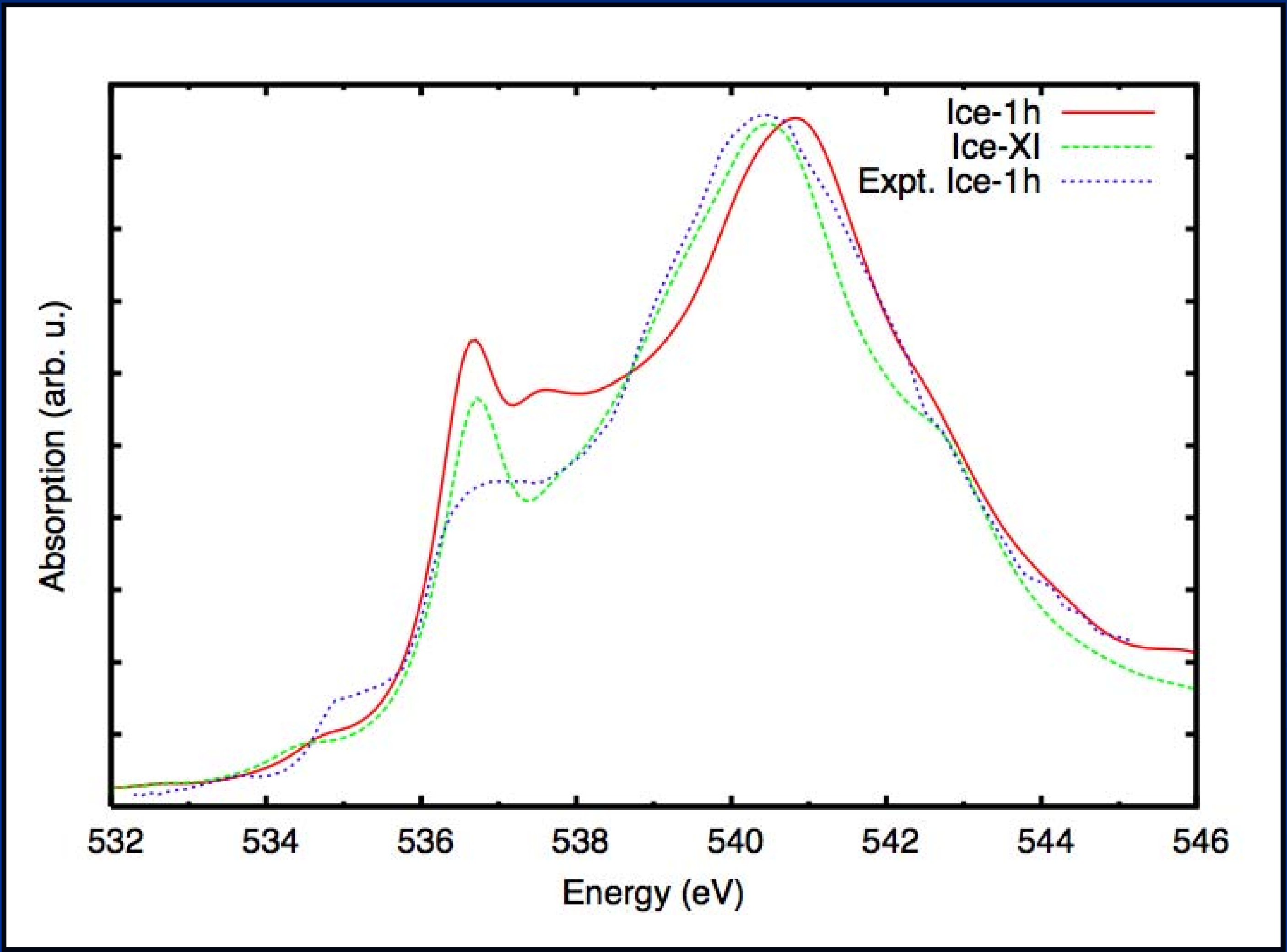



1000 k-points

100 Ha. cut-off

Expt. data from E. Hudson et. al, Phys. Rev. B **49**, 3701 (1994)

# Ice: O K edge XAS




Expt. data from P. Wernet et. al, Science **304**, 995 (2004)

8 molecule cells

216 k-points

50 Ha. cut-off

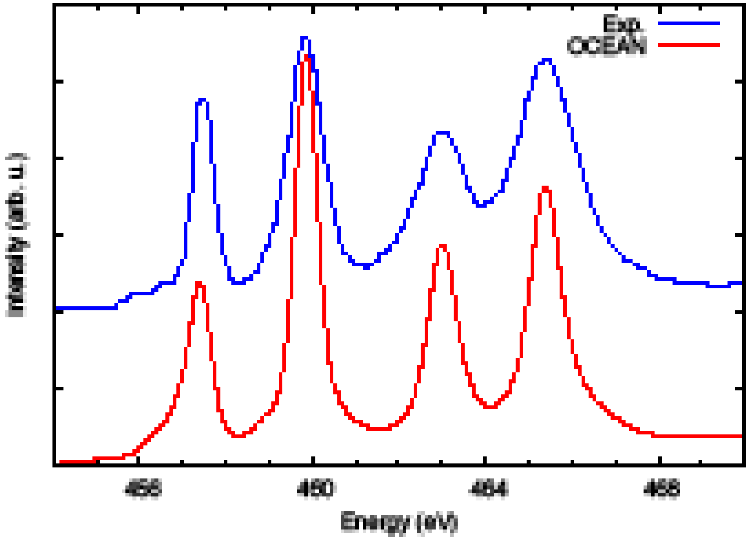
# Example: *L*-edge Spectra – Multiplet effects

Ti $L_{2,3}$ edge SrTiO3

Bethe–Salpeter treatment of X-ray absorption including core-hole multiplet effects

Eric L. Shirley*

*J. Elec.Spect. Rel. Phen. **144**, 1187(2005)




**alá E. Shirley: BSE**
**+ KS crystal potential**
***ab initio* – no parameters**

$$H_{BSE} = H_h + H_e + H_{eh}$$

$$H_h = -\epsilon_\alpha + L \cdot S(p)$$

$$H_e = \frac{p^2}{2m} + L \cdot S(d) + H_{KS}^{xtal}$$

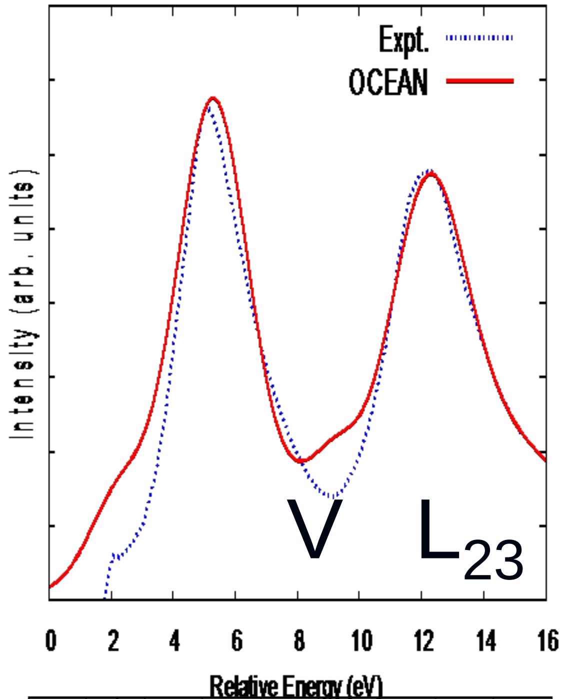
$$H_{eh} = V_\alpha(r) + g(i,j)$$

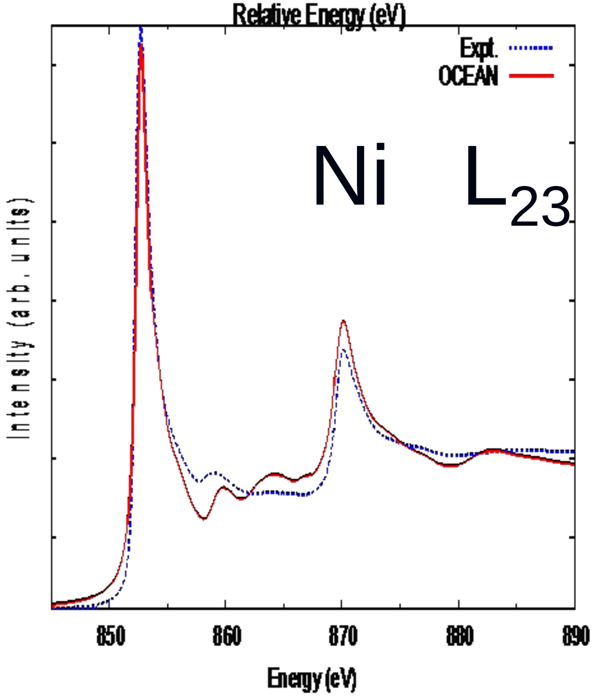
**cf. De Groot et al – Atomic model + crystal-field parameters**

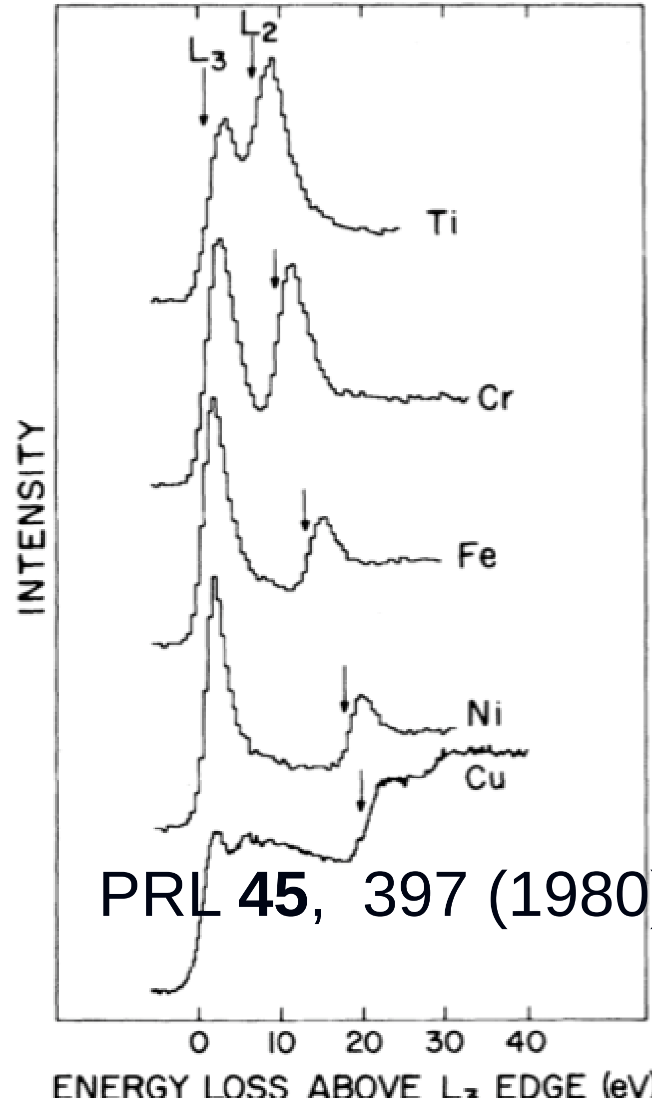
$$H_{at} = H_{av} + L \cdot S(p)$$

$$+L \cdot S(d) + H_{xtalfield} + g(i,j)$$

# $L_{23}$ Transition Elements




PRL **45**, 397 (1980)

# 3. *Ab initio* XAS Debye Waller Factors $e^{-2\sigma^2 k^2}$

**An Initio Determination of Extended X-Ray Absorption Fine Structure Debye-Waller Factors**

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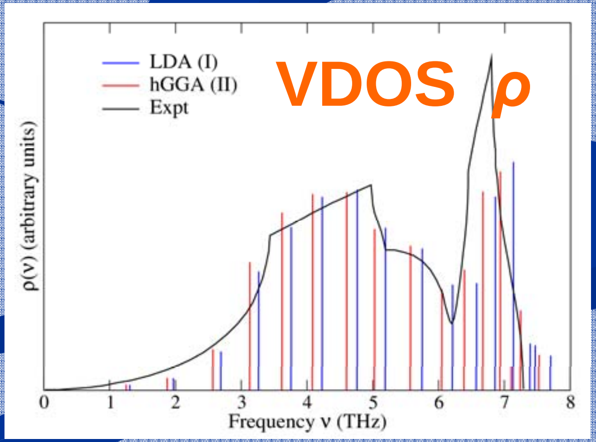
*Hahn-Meitner-Institut Berlin, Glienicker Strasse 100, D-14109 Berlin, Germany*
(Dated: August 23, 2005)

Many Pole model for phonons

$$\sigma^2 = \frac{\hbar}{\mu_i}\int_0^\infty \rho(\omega^2)\coth\frac{\beta\hbar\omega}{2}\,d\omega$$

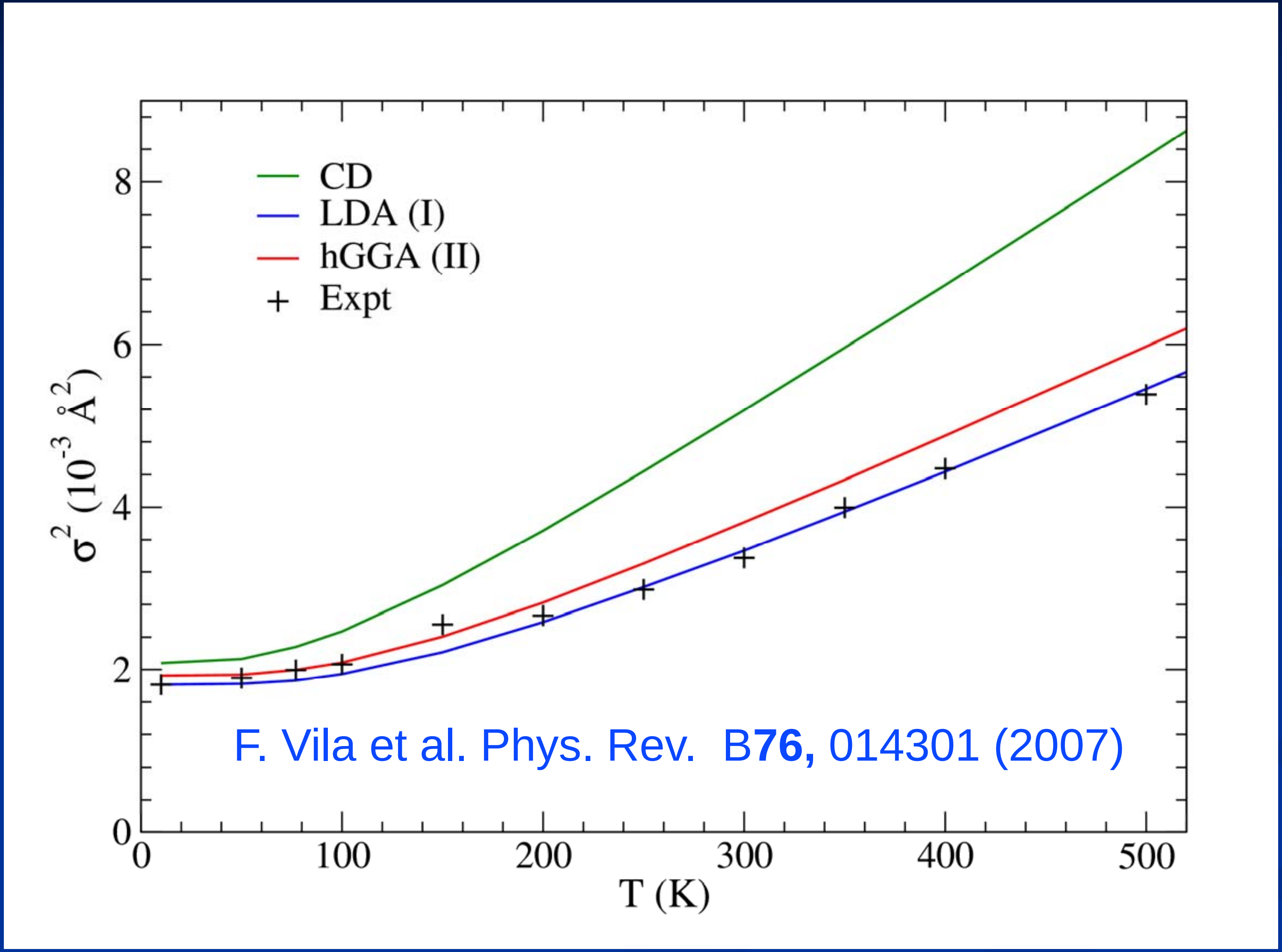
$$\rho(\omega^2) = \langle Q_i|\delta(\omega^2 - D)|Q_i\rangle = \{6-\text{step Lanczos recursion}\}$$




**D ynamical matrix $D$ from ABINIT**

*Phys. Rev. B **76,** 014301 (2007)

# Example: XAFS Debye-Waller Factor of Ge




**Expt: Dalba *et al.* (1999)**

# Conclusions

- Core & Valence BSE+GW packages

  OCEAN & AI2NBSE

- NRIXS, EELS, XAS,

- Includes GW self-energy, multiplets, ..

- Future: RIXS, XPS, DW factors, etc.

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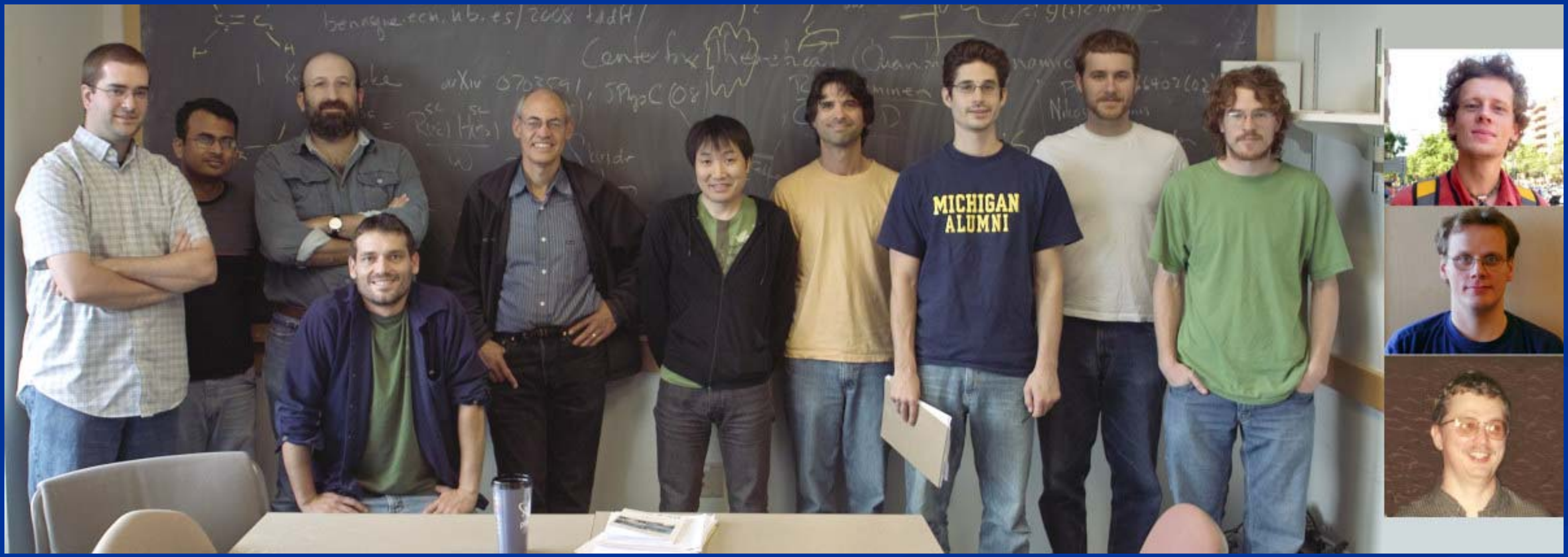


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