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Many-body effects and inelastic losses in x-ray spectra *

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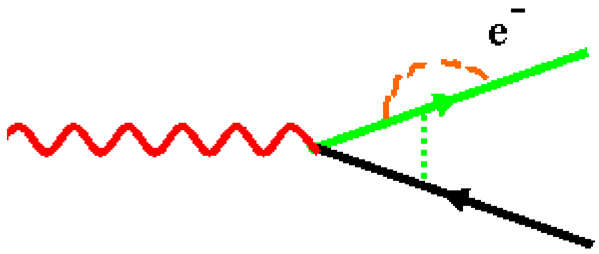
Many-body effects and inelastic losses in x-ray spectra

- **TALK:**

I.	Introduction	Many-body effects in XAS
II.	Inelastic losses & satellites	Cumulant expansion beyond GW
III.	Particle-hole theory: BSE Particle-hole cumulant	Intrinsic, extrinsic losses and interference

I. Introduction:
Many-body effects in x-ray spectra



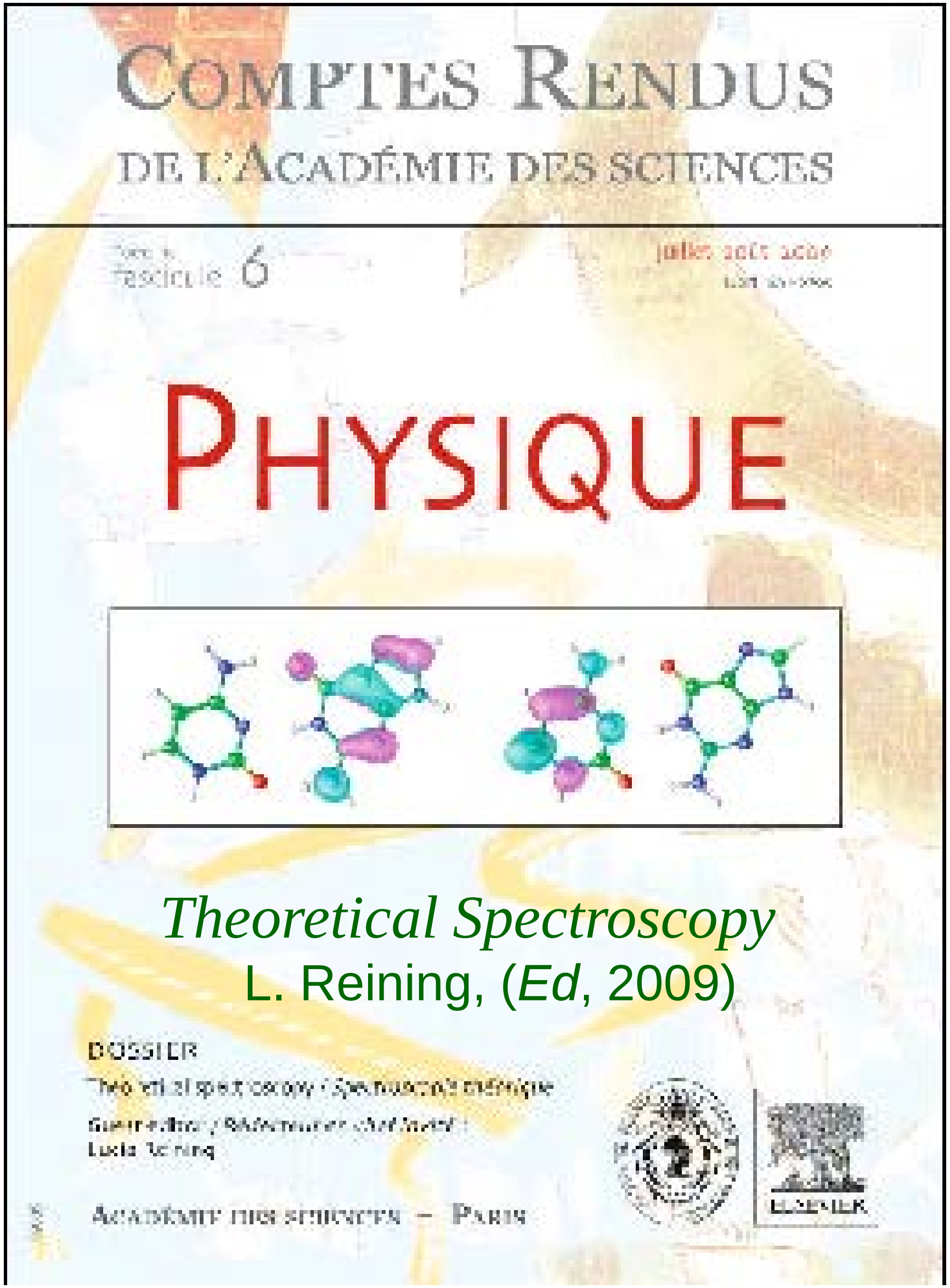
Key many-body effects

- Core-hole effects — Excitonic effects, Screening
- Self-energy $\Sigma(E)$ — Mean-free path, energy shifts
- Phonons, disorder — Debye-Waller factors
- Excitations — Inelastic losses & satellites

“ You can judge a many-body theory

by how it treats the satellites. ”

Lars Hedin (1995)

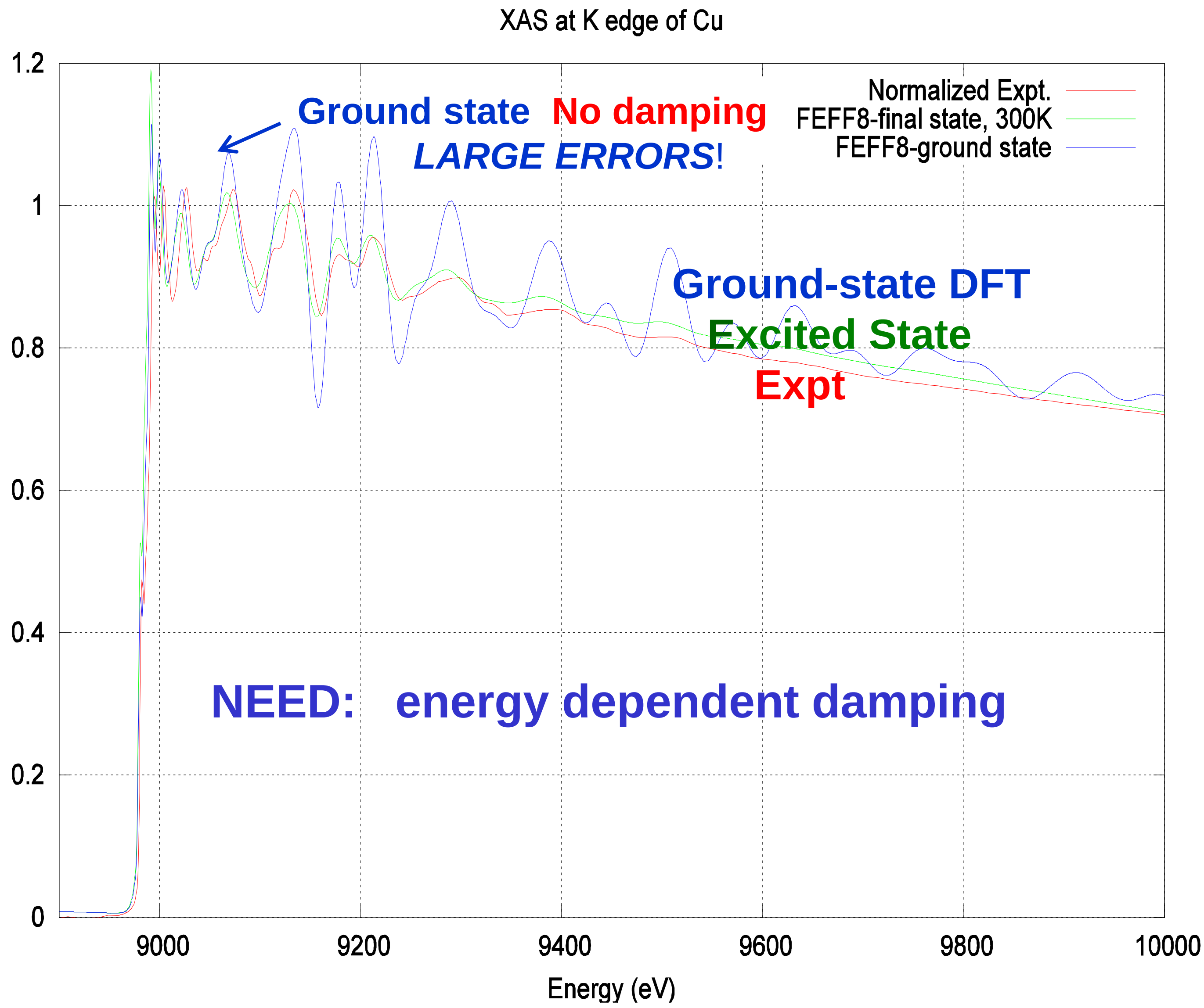


Quasi-particle theory of XAS

Mini-review

JJR et al., Comptes Rendus Physique **10**, 548 (2009)

Motivation: Failure of ground-state DFT in XAS; need for inelastic losses



Starting point for core-XAS calculations: Quasi-particle final state Green's function

~~Golden rule for XAS via Wave Functions~~

$$\mu(E) \sim \Sigma_f |\langle i|\hat{\epsilon}\cdot \mathbf{r}|f\rangle|^2 \delta(E - E_f)$$

Paradigm shift:

Golden rule via Green's Functions **G** = ***1/(E – h' – Σ)***

$$\mu(E) \sim -\frac{1}{\pi}\mathrm{Im}\,\langle \mathrm{i}|\,\hat{\epsilon}\cdot \mathbf{r}'\,\mathrm{G}(\mathbf{r}',\mathbf{r},\mathrm{E})\,\hat{\epsilon}\cdot\mathbf{r}\,|\mathrm{i}\rangle$$

Final state ***h'*** includes core-hole AND energy dependent self energy ***Σ(E)***

Many-pole GW Self-energy $\Sigma(E)$*

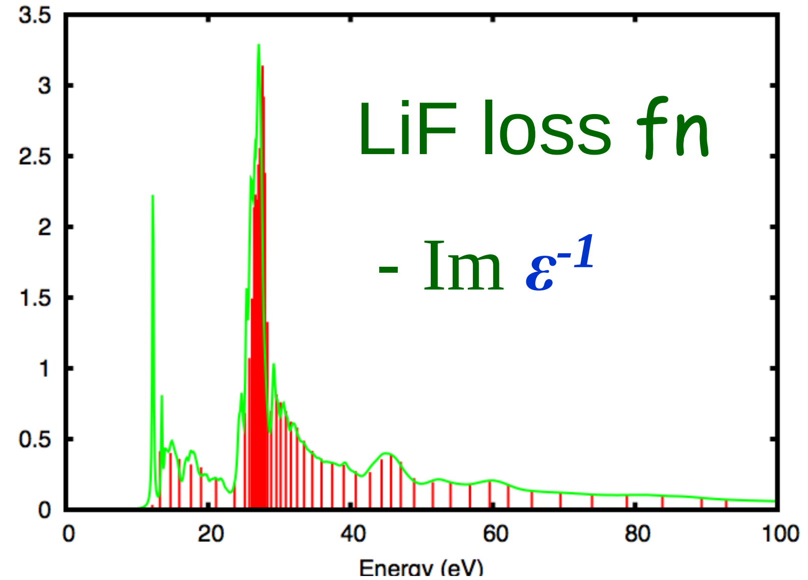
Extension of Hedin-Lundqvist GW plasmon-pole

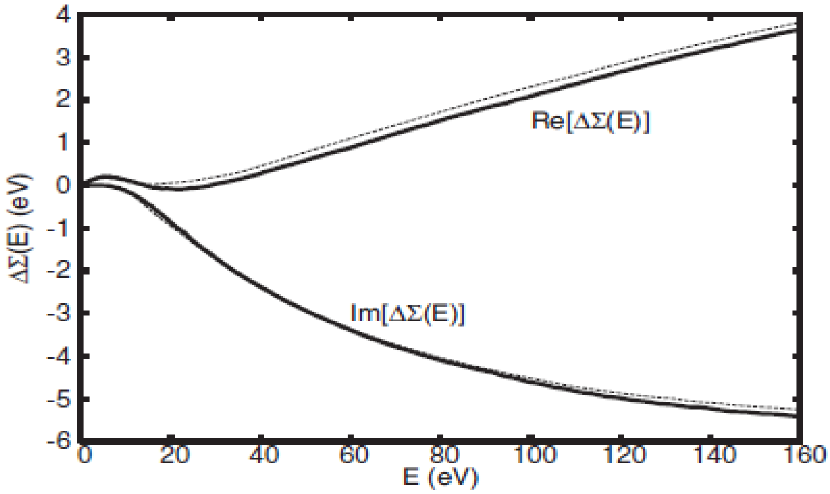
$$W = \varepsilon^{-1} v$$

Sum of plasmon-pole models matched to loss function

Efficient GW method

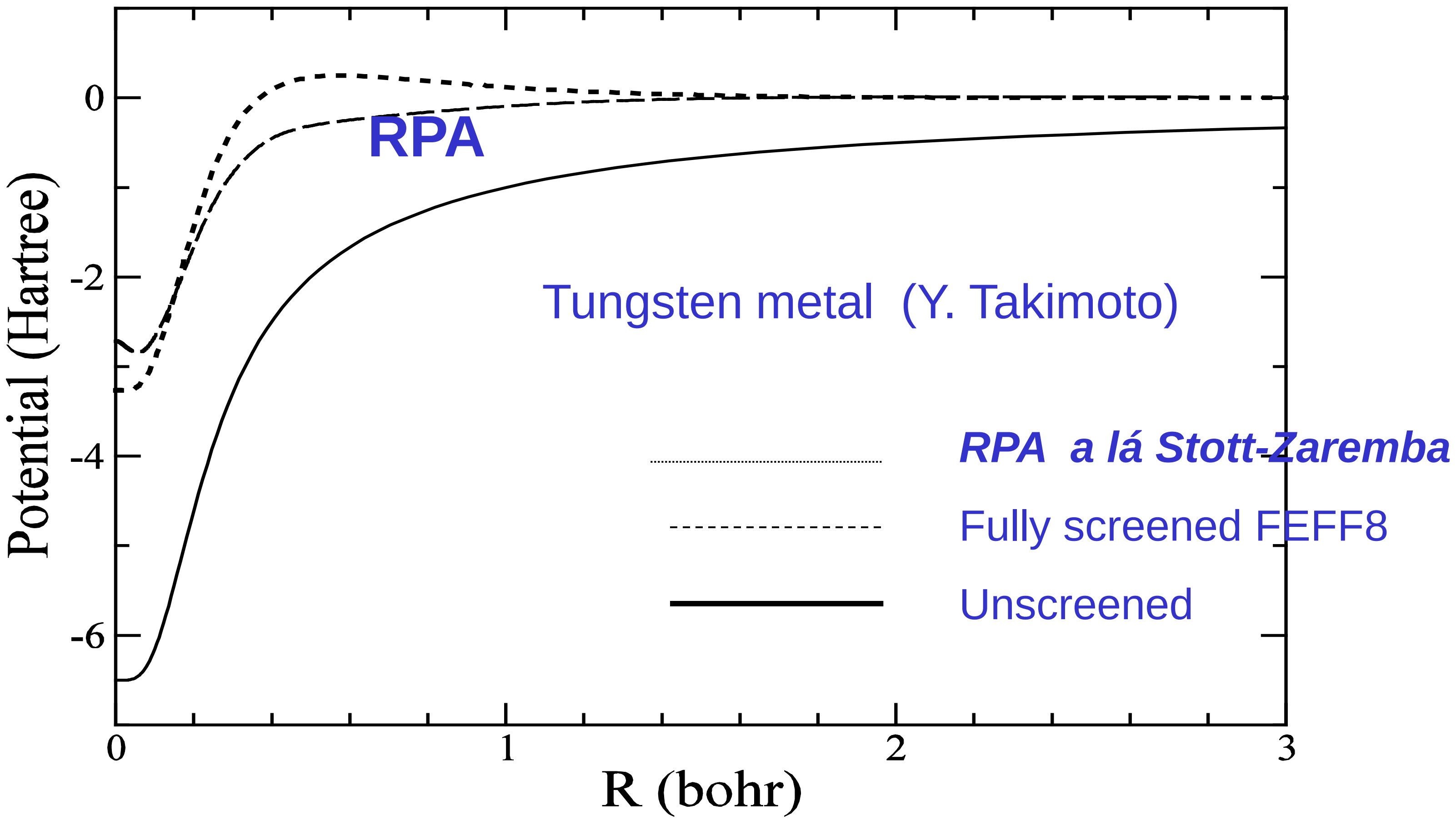
$$\Sigma(E) = iGW = \Sigma' - i\,\Gamma$$





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

Core-hole potential - RPA *W*



cf. Screened core hole *W* in Bethe-Salpeter Eq

Improves on final state rule, *Z+1*, half-core hole

Phonon effects: Debye Waller Factors in XAS

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

Fernando D. Vila, G. Shu, and John J. Rehr
Department of Physics, University of Washington, Seattle, WA 98195

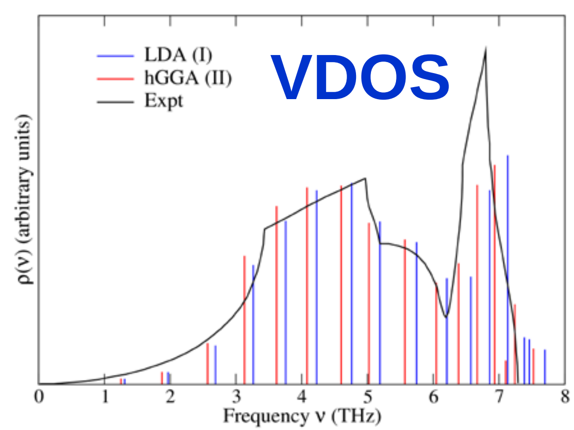
H. H. Rossner and H. J. Krappe
Hahn-Meitner-Institut Berlin, Glienicker Strasse 100, D-14109 Berlin, Germany
(Dated: August 23, 2005)

$$e^{-2\sigma^2 k^2}$$

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

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

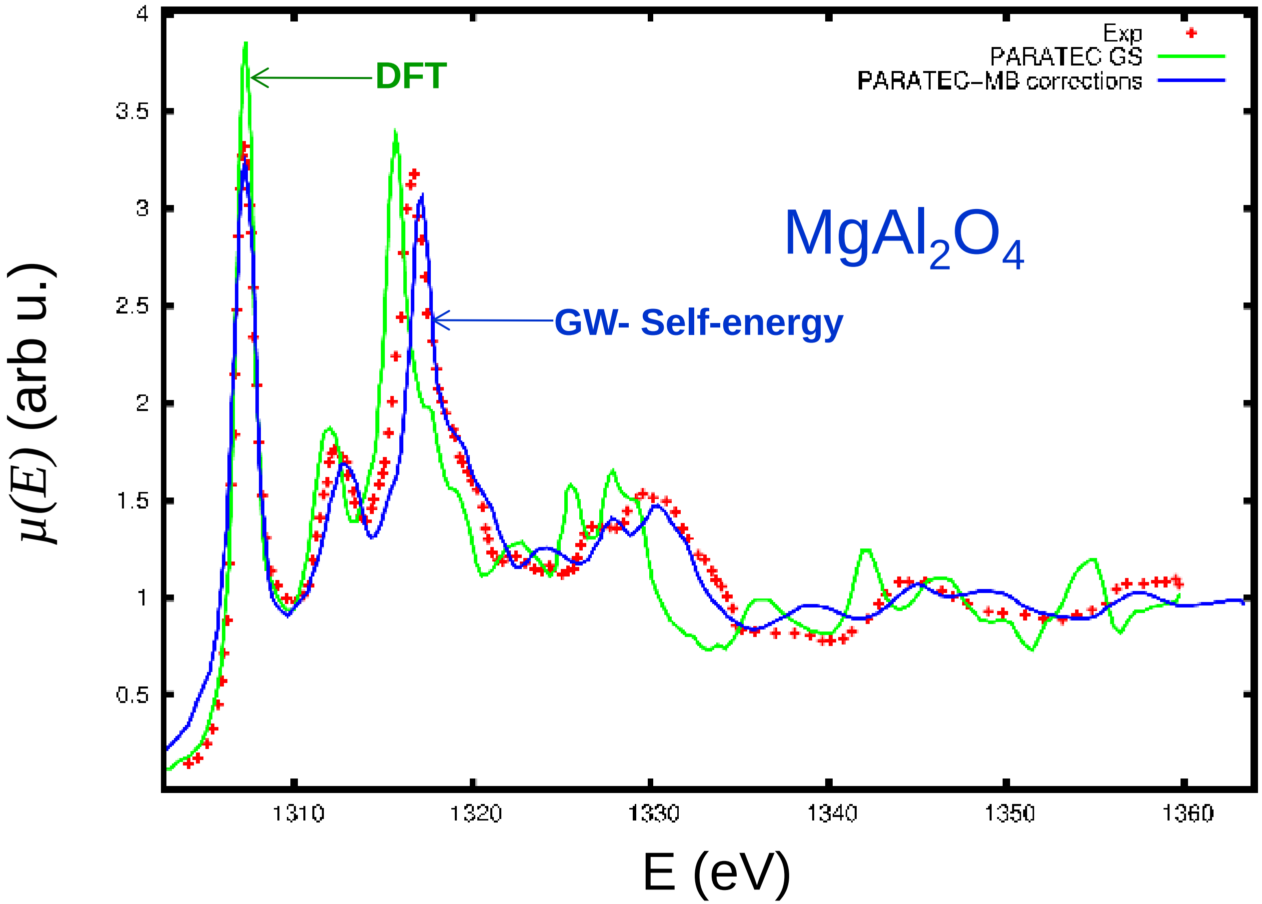
Many pole model for phonons



D dynamical matrix **< ABINIT**

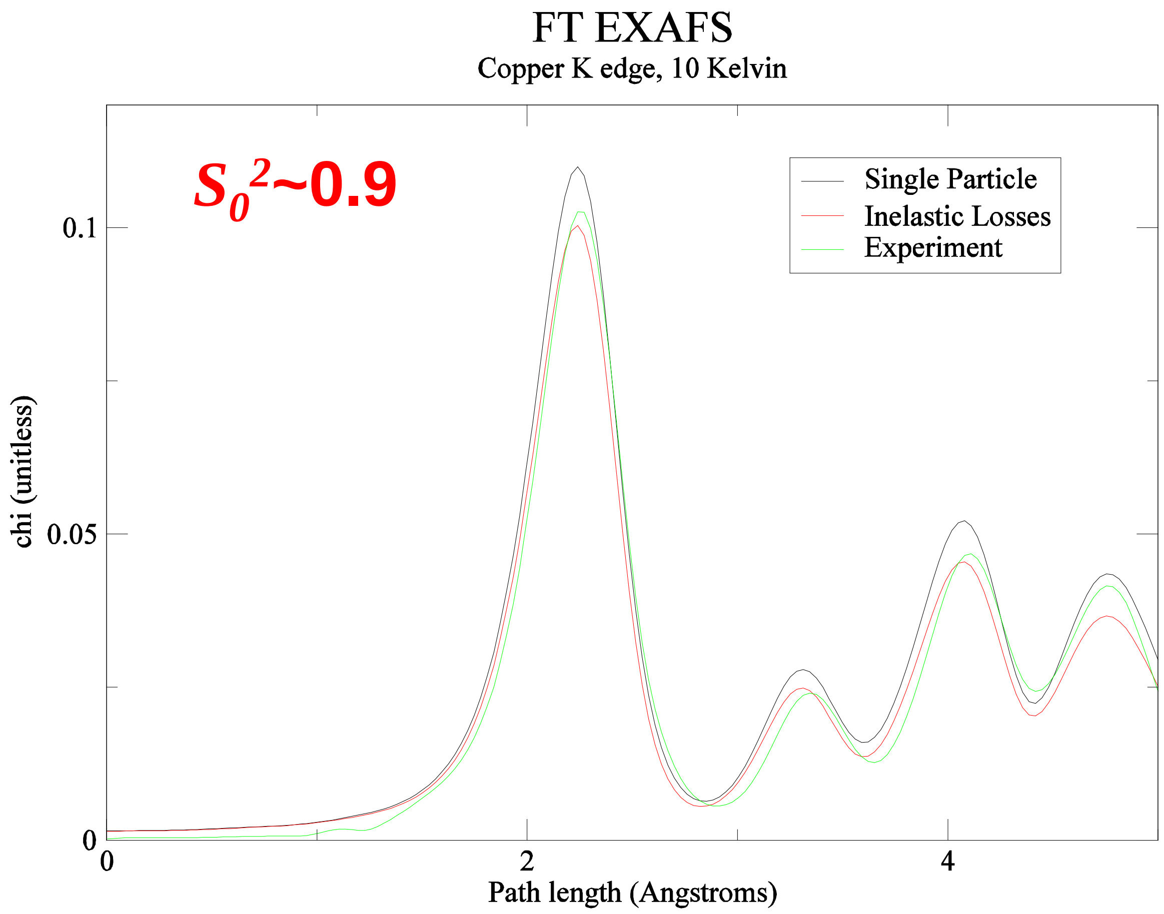
*Phys. Rev. B **76,** 014301 (2007)

Self-energy largely fixes systematic errors due to self-energy in XAS



*J. J. Kas, J. Vinson, N. Trcera, D. Cabaret, E. L. Shirley, and J. J. Rehr, Journal of Physics: Conference Series **190**, 012009 (2009)

PROBLEM: Amplitude discrepancy - observed fine structure smaller than QP theory by factor S_0^2~0.9 - inelastic losses, multi-electron excitations



Theoretical mysteries

? Why does quasi-particle approx work well in XAS (~90%) ?
? Why are multi-electron excitations small in XAS (~10%) ?

Failure of the Quasiparticle Picture of X-ray Absorption?

J. J. Rehr[1]

Foundations of Physics, Vol. 33, No. 12, December 2003 (© 2003)

Received December 20, 2002; revised February 7, 2003

? Why mysterious ?

Corrections to QP approx are **large** in electron gas

$Z \sim \exp(-n) \approx 0.7$ $\quad \bar{n} = 0.201 r_s^{3/4} \approx 0.3$

II. Inelastic losses and satellites

Q How to treat losses beyond the GW-quasi-particle approximaton ?

Approach: Improved treatment of $G(E)$ including satellites in spectral function

$$A(\omega) = (1/\pi)\, \mathrm{Im}\, G(E)$$

Two methods: GW + Dyson Eq.
Cumulant expansion

Which is better? *GW* + **Dyson** vs Cumulant*

GW	**Cumulant**
$G(\omega) = G_0 + G_0 \Sigma G$	$G(t) = G_0(t)\, e^{C(t)}$
$\Sigma^{GW} = iGW$	$C \sim \vert \mathrm{Im}\, \Sigma^{GW} \vert$
$W = \epsilon^{-1} v$	
No vertex $\Gamma = 1$	**Implicit vertex**

***Recent review and new derivation, see J. Zhou et al. J. Chem. Phys. 143, 184109 (2015).**

Answer: from XPS

Phys Rev Lett **77**, 2268 (1996)

Multiple Plasmon Satellites in Na and Al Spectral Functions from *Ab Initio* Cumulant Expansion

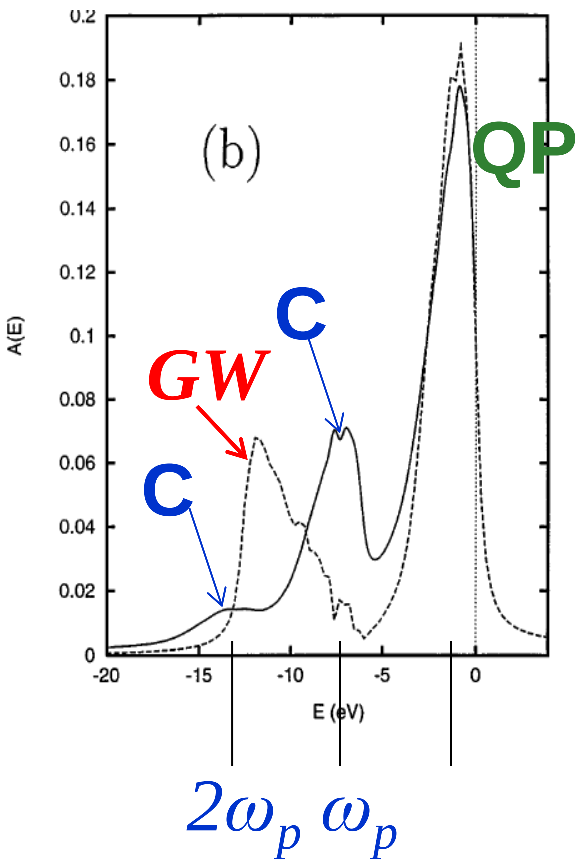
F. Aryasetiawan,[1,2] L. Hedin,[1] and K. Karlsson[3]

Quasi-particle peaks of **both** GW and *C* agrees with XPS expt

GW fails for satellites: only ***one*** satellite at wrong energy

C: Cumulant model has multiple satellites ω_p apart in agreement with expt

Na XPS



Cumulant expansion properties*

$$G_k(t) = e^{i\epsilon_k^0 t} e^{C(t)}$$

$$C(t) = \int d\omega' \beta(\omega') \frac{e^{i\omega' t} - i\omega' t - 1}{\omega'^2}$$

Landau formula for ***C(t)***

Excitation spectra (GW *Σ*)

$$\beta_k(\omega) = \frac{1}{\pi} |\mathrm{Im}\,\Sigma_k(\omega + \epsilon_k)|$$

Spectral Function

$$A_k(\omega) = \int \frac{dt}{2\pi} e^{i(\omega - \epsilon_k)t} \exp\left\{ \int d\omega' \beta(\omega') \frac{e^{i\omega' t} - i\omega' t - 1}{\omega'^2} \right\}$$

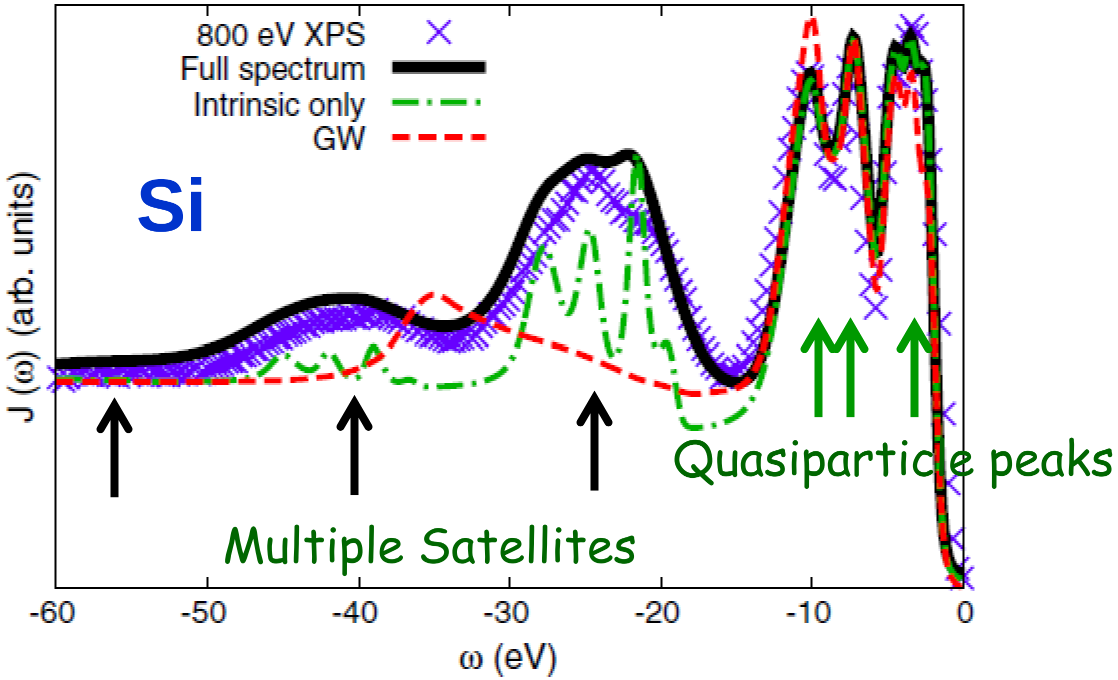
*For diagrammatic expansion of higher order terms, see e.g.
O. Gunnarsson et al., Phys. Rev. B **50**, 10462 (1994)

Example: Multiple Satellites in XPS of Si

PRL 107, 166401 (2011) PHYSICAL REVIEW LETTERS week ending 14 OCTOBER 2011

Valence Electron Photoemission Spectrum of Semiconductors: *Ab Initio* Description of Multiple Satellites

Matteo Guzzo,[1,2,*] Giovanna Lani,[1,2] Francesco Sottile,[1,2] Pina Romaniello,[3,2] Matteo Gatti,[4,2] Joshua J. Kas,[5] John J. Rehr,[5,2] Mathieu G. Silly,[6] Fausto Sirotti,[6] and Lucia Reining[1,2,†]



Lucia Reining

Problems: **GW: only one broad satellite at wrong position**
C: **position ok but intensity too small**

Quasi-boson approximation

Theorem:* Cumulant representation of core-hole Green's function is EXACT for electrons coupled to bosons

*D. C. Langreth, *Phys. Rev.* B **1,** 471 (1970)

Corollary: also valid for valence with recoil approximation.

IDEA: Neutral excitations - plasmons, phonons, etc. can be represented as **bosons**

Physics:** GW approximation describes an electronic-polaron: electrons coupled to density fluctuations modeled as bosons

B. I. Lundqvist, *Phys. Kondens. Mater.* **6 193 (1967)

Reviews/references for cumulant model

J. Phys.: Condens. Matter 11 (1999) R489–R528

On correlation effects in electron spectroscopies and the *GW* approximation

Lars Hedin

Department of Theoretical Physics, Lund University, Sölvegatan 14A, 223 62 Lund, Sweden

THE JOURNAL OF CHEMICAL PHYSICS 143, 184109 (2015)

Dynamical effects in electron spectroscopy

Jianqiang Sky Zhou,[1,2,a)] J. J. Kas,[2,3] Lorenzo Sponza,[4] Igor Reshetnyak,[1,2] Matteo Guzzo,[5] Christine Giorgetti,[1,2] Matteo Gatti,[1,2,6] Francesco Sottile,[1,2] J. J. Rehr,[2,3] and Lucia Reining[1,2]

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[2]*European Theoretical Spectroscopy Facility (ETSF)*

[3]*Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA*

[4]*Department of Physics, King's College London, London WC2R 2LS, United Kingdom*

[5]*Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, D-12489 Berlin, Germany*

[6]*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette, France*

cf. Retarded Cumulant Approximation*

PHYSICAL REVIEW B **90**, 085112 (2014)

Cumulant expansion of the retarded one-electron Green function

J. J. Kas,[1,*] J. J. Rehr,[1,2,†] and L. Reining[3,2,‡]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195, USA*
[2]*European Theoretical Spectroscopy Facility (ETSF)*
[3]*Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, F-91128 Palaiseau, France*

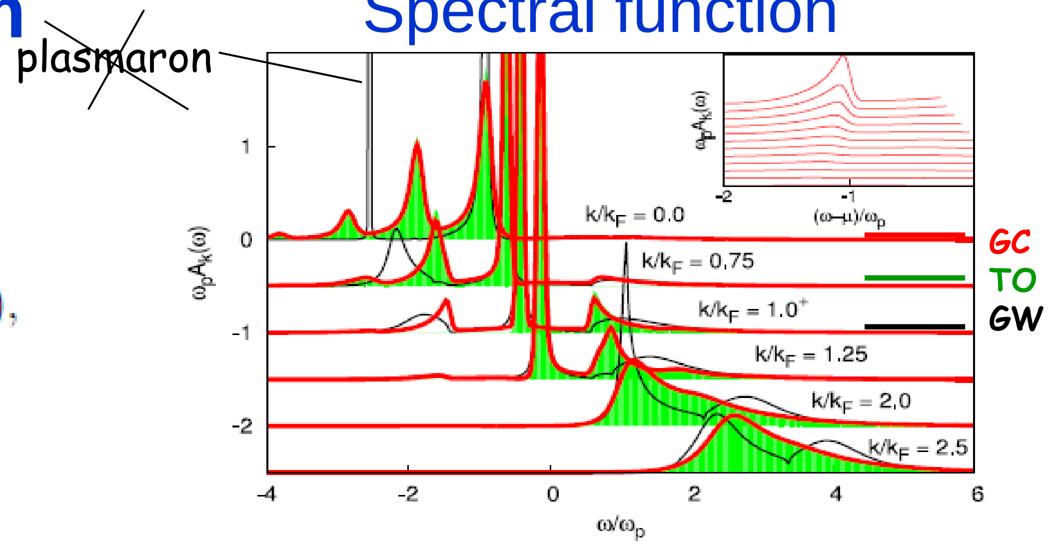
Retarded GF formalism

$$G_k^R(t) = -i\theta(t)e^{-i\epsilon_k^{HF}t}e^{\tilde{C}_k^R(t)},$$

$$\tilde{C}_k^R(t) = \int d\omega \frac{\beta_k(\omega)}{\omega^2}(e^{-i\omega t} + i\omega t - 1),$$

$$\beta_k(\omega) = \frac{1}{\pi}\left|\mathrm{Im}\,\Sigma_k^R(\omega + \epsilon_k)\right|,$$

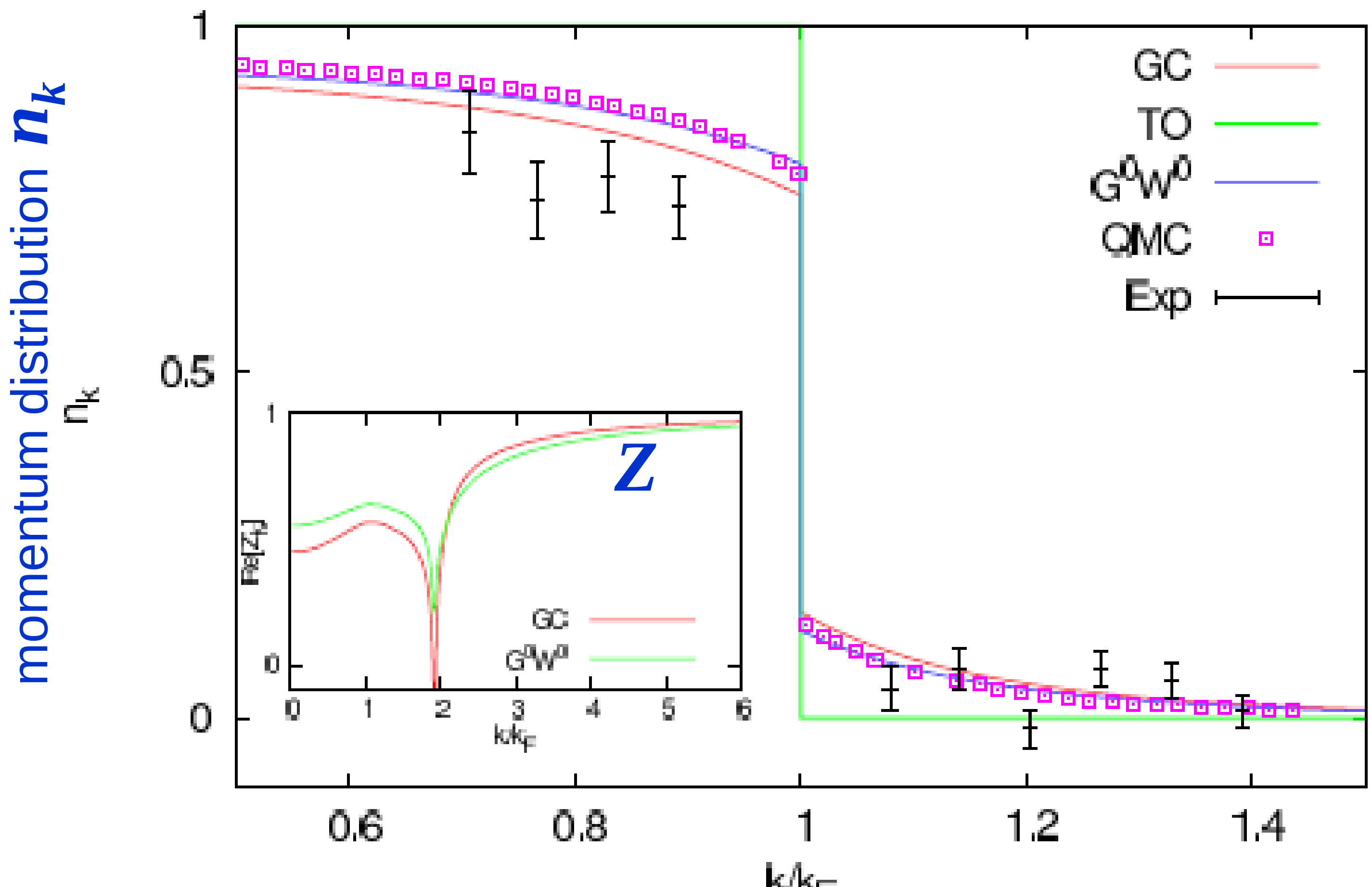
Spectral function



Builds in particle-hole symmetry

Electron-gas quasi-particle properties

Retarded cumulant has good n_k *and Z*,
& pretty good correlation energies



Retarded cumulant for phonons*

Generalized cumulant expansion for phonon contributions to the electron spectral function

S. M. Story, J. J. Kas, F. D. Vila, and J. J. Rehr
Department of Physics, University of Washington Seattle, WA 98195

M. J. Verstraete
Institut de Physique, Université de Liège B-4000 Sart Tilman, Belgium
(Dated: March 7, 2014)

$$G_k^R(t) = -i\, e^{-i\varepsilon_k^0 t} e^{C_k^R(t)} \theta(t)$$

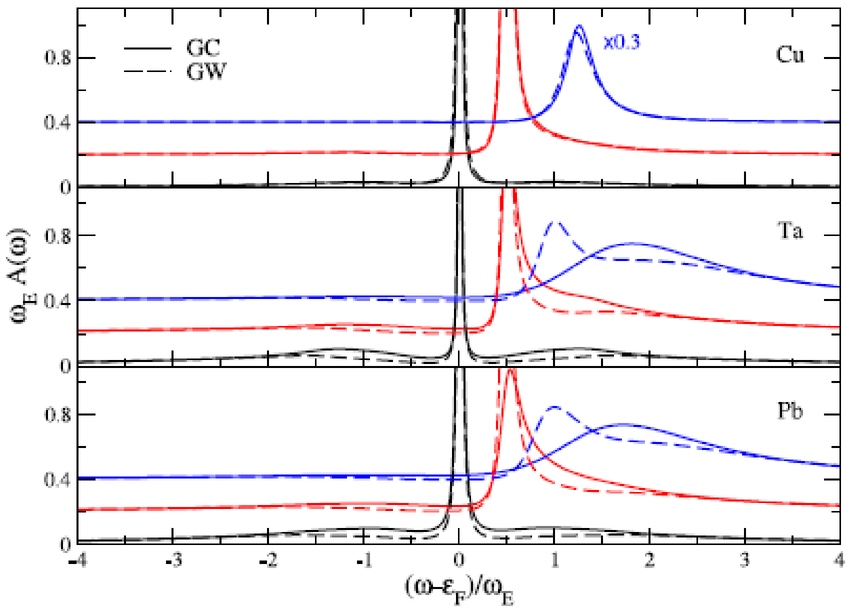
$$C_k^R(t) = \int_{-\infty}^{\infty} d\omega\, \beta_k(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}$$

$$\beta_k(\omega) = \frac{1}{\pi} \left| \mathrm{Im}\, \Sigma_k^R\left(\omega + \varepsilon_k^0\right) \right|$$

$$\Sigma_k(\omega, T) = \int d\omega'\, 2\tilde{\Sigma}^{\mathrm{Ei}}(\omega, \omega', T)\, \alpha^2 F_k(\omega')$$

cf **A. Eiguren and C. Draxl, Phys. Rev. Lett. 101, 036402 (2008)**

Spectral function

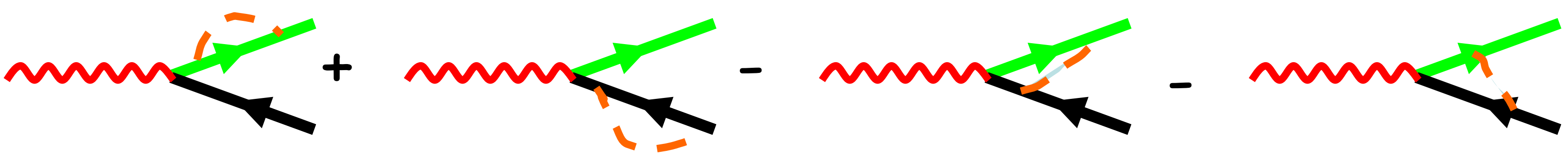


Corrections to Migdal's theorem visible at low *T*

III. Particle-hole cumulant theory

Q: How to calculate all inelastic losses and satellites in x-ray spectra ?

Single-particle cumulant in XPS (XAS) only has intrinsic (extrinsic) losses.

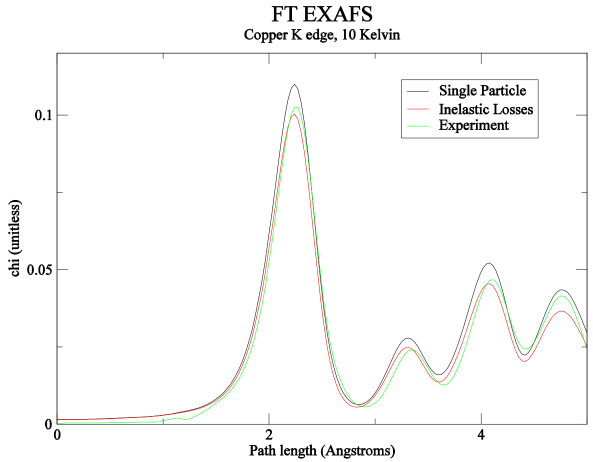


Extrinsic + Intrinsic - 2 x Interference

Suggestion from Hedin (1989): quasi-boson method for intrinsic, extrinsic, and interference terms

Explanation of XAFS many-body amplitude factor:* $\chi_{exp} = \chi_{th} * S_0^2$

EXTRINSIC AND INTRINSIC PROCESSES IN EXAFS
Lars Hedin, Dept of Theoretical Physics, University of Lund, Sweden



Physica B 158 (1989) 344–346
North-Holland, Amsterdam

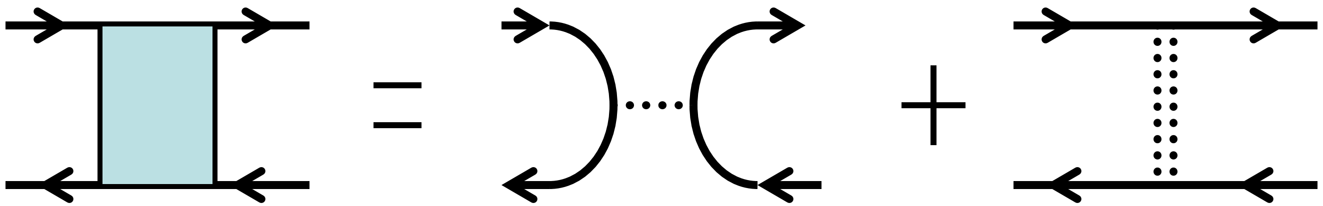
The importance of correlation effects in spectroscopies like EXAFS and photoemission is well recognized. The two main mechanisms are shake-off (in which we include skake-up) when the photoelectron is created, and energy loss of the propagating electron. Shake-off is clearly impossible at threshold, due to lack of energy. For photoemission often the "Spicer three-step model" is used, (1) creation of the photoelectron (including shake-off), (2) propagation to the surface (including losses), and (3) passage through the surface (including losses). Langreth [1] has pointed out that one should add the amplitudes for (2) and (3), and not, as in the Spicer model, convolute their squares, the probabilities. This effect is important primarely at threshold.

***J.J. Rehr, E.A. Stern, R.L. Martin, and E.R. Davidson, Phys. Rev. B 17,560 (1978)**

GW/Bethe-Salpeter Equation*

- Particle-hole Green's function w/o satellites

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



Ingredients: Particle-Hole Hamiltonian

$$H = h_e - h_h + V_{eh} \qquad h_{e/h} = \varepsilon_{nk} + \Sigma_{nk}$$

Σ GW self-energy

$V_{eh} = V_x + W$ Particle-hole interaction

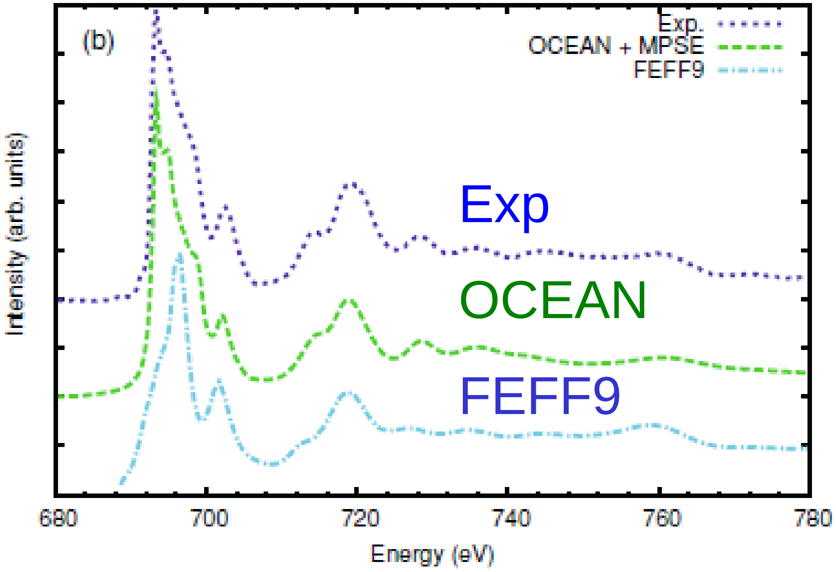
OCEAN* Core-GW/BSE Code

PHYSICAL REVIEW B 83, 115106 (2011)

Bethe-Salpeter equation calculations of core excitation spectra

J. Vinson, J. J. Rehr, and J. J. Kas
Department of Physics, University of Washington, Seattle, Washington 98195, USA

E. L. Shirley
National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, USA



*Obtaining Core Excitations from ABINIT and NBSE

PW-PP + PAW
+ MPSE + NBSE

*J. Vinson et al. Phys. Rev. B83, 115106 (2011)

Quasi-boson method for Particle-hole GF*

Many-body Model: $|N\rangle = |e^-, h, \gamma\rangle$

- Excitations: $H_v = \Sigma_n \omega_n a_n^\dagger a_n$
- Electrons: $h' = \Sigma_k \epsilon_k c_k^\dagger c_k$
- e-boson coupling $V_{pv} = \Sigma_{nkk'} \left[V_{kk'}^n a_n^\dagger + (V_{kk'}^n)^* a_n\right] c_k^\dagger c_{k'}$
- Core-hole-boson coupling: $V_{vc} = -\Sigma_n V_{bb}^n \left(a_n^\dagger + a_n\right)$

$V^n \rightarrow -\mathrm{Im}\, \varepsilon^{-1}(\omega_n, q_n)$

fluctuation potentials*

Partition contributions into Intrinsic + Extrinsic + Interference

$$\gamma_K(\omega) = \sum_q \left| V^q \tilde{g}(\omega - \omega_q) - \frac{V_{cc}^q}{\omega_q} \right|^2 \delta(\omega - \omega_q) = \gamma_c(\omega) + \gamma_k(\omega) + \gamma_{ck}(\omega)$$

* L. Hedin, J. Michiels, and J. Inglesfield, Phys. Rev. B **58**, 15 565 (1998)

cf Particle-hole Cumulant in XPS*

Europhys J. J. B **85**, 324 (2012)

Plasmon Satellites in Valence-band Photoemission Spectroscopy

Ab Initio study of the photon-energy dependence in semiconductors

Matteo Guzzo[1,2], Joshua J. Kas[3], Francesco Sottile[1,2], Mathieu G. Silly[4], Fausto Sirotti[4], John J. Rehr[3], and Lucia Reining[1,2]

$$\langle J_k(\omega)\rangle = \sum_i |M_{ik_0}|^2 \int_0^\infty e^{-a} \int_{-\infty}^\infty e^{i(\omega_0-\epsilon_k+\epsilon_i)t} \times \exp\left[\int \gamma_{ik}(\omega)(e^{-i\omega t}-1)\, d\omega\right] dt\, dz_c$$

Kernel $\gamma(\omega)$ *with* extrinsic, intrinsic and interference terms

$$\gamma_{ik}(\omega) = \sum_{\mathbf{q}} |g_{\mathbf{q}}|^2 \delta(\omega-\omega_q) = \gamma_i^{int} + \gamma_k^{ext} + \gamma_{ik}^{inf}$$

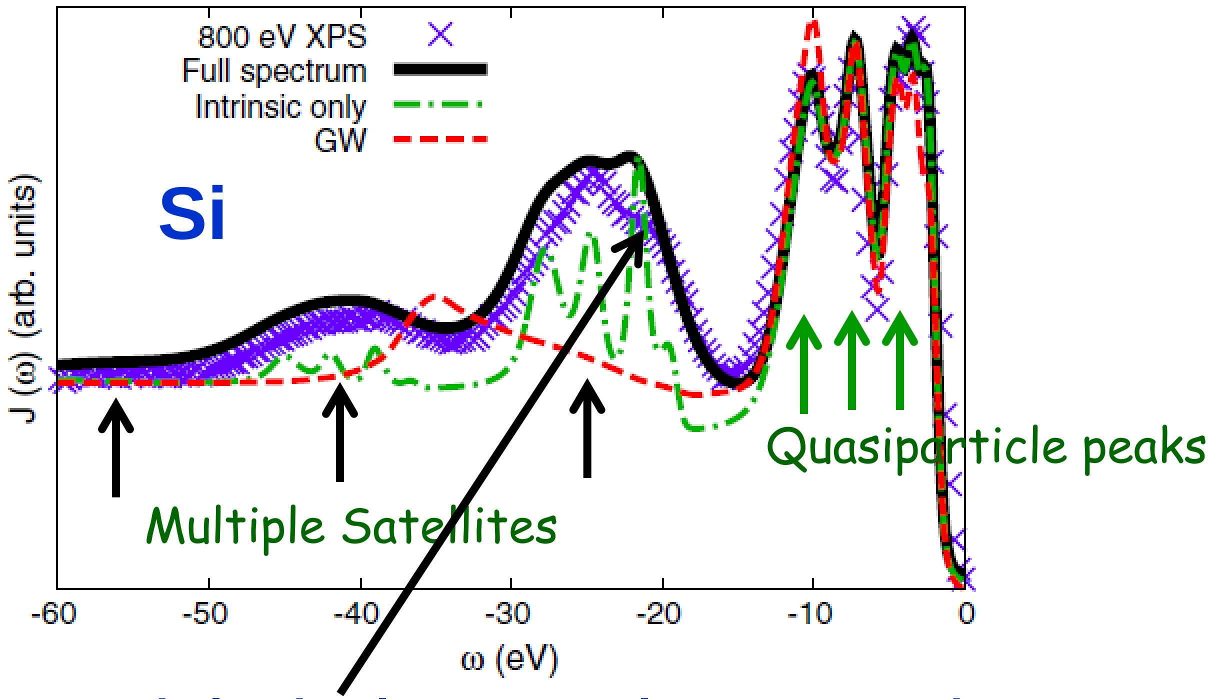
*L. Hedin, J. Michiels, and J. Inglesfield, Phys. Rev. B 58, 15 565 (1998).

Example: Satellites in XPS of Si again

PRL 107, 166401 (2011) PHYSICAL REVIEW LETTERS week ending 14 OCTOBER 2011

Valence Electron Photoemission Spectrum of Semiconductors: *Ab Initio* Description of Multiple Satellites

Matteo Guzzo,[1,2,*] Giovanna Lani,[1,2] Francesco Sottile,[1,2] Pina Romaniello,[3,2] Matteo Gatti,[4,2] Joshua J. Kas,[5] John J. Rehr,[5,2] Mathieu G. Silly,[6] Fausto Sirotti,[6] and Lucia Reining[1,2,†]



Success for particle-hole cumulant: good agreement when extrinsic and interference terms are included

Particle-hole cumulant for XAS*

PHYSICAL REVIEW B **94**, 035156 (2016)

Particle-hole cumulant approach for inelastic losses in x-ray spectra

J. J. Kas,[1] J. J. Rehr,[1] and J. B. Curtis[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA*
[2]*Department of Physics, University of Rochester, Rochester, New York 14927, USA*

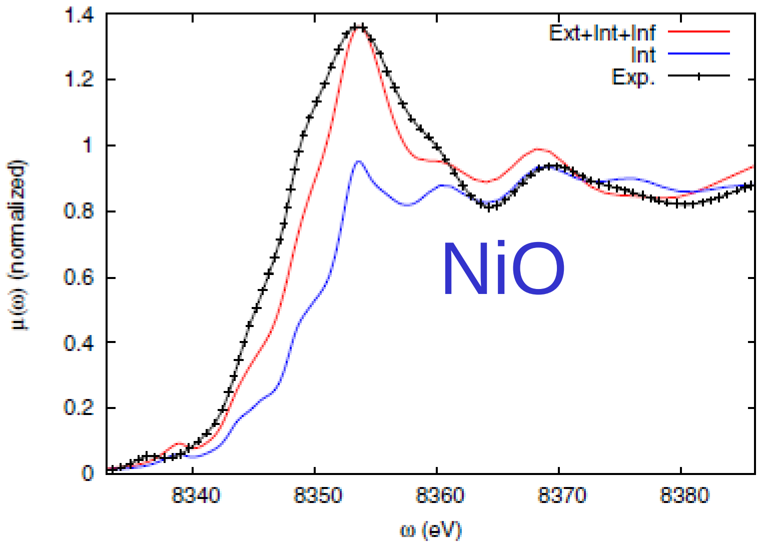
$$\tilde{G}_K(t) = \tilde{G}^0_K(t)e^{\tilde{C}_K(t)}$$

$$\tilde{C}_K(t) = \int d\omega\, \gamma_K(\omega)(e^{i\omega t} - i\omega t - 1)$$

$$\tilde{C}_K(t) = C_c(t) + C_k(t) + C_{ck}$$

All losses in particle-hole spectral function A_K

$$\mu(\omega) = \int d\omega'\, \tilde{A}_K(\omega')\mu_K(\omega - \omega')$$



* cf. L. Campbell, L. Hedin, J. J. Rehr, and W. Bardyszewski, Phys. Rev. B **65**, 064107 (2002)

Many-body amplitudes $S_0^2(\omega)$ in XAS

- Many-body XAS ≈ Convolution

$$\mu(\omega) = \int_0^\infty d\omega' \tilde{A}(\omega,\omega')\mu_{qp}(\omega-\omega')$$

$$\equiv \langle \mu_{qp}(\omega) \rangle \approx \mu_{qp}(\omega)\, S_0^2(\omega)$$

- Explains crossover: **adiabatic** $S_0^2(\omega) = 1$

to sudden transition $S_0^2(\omega) \approx 0.9$

$$|g_q|^2 = |g_q^{ext}|^2 + |g_q^{intrin}|^2 - 2\, g_q^{ext}\, g_q^{intrin}$$

Interference reduces loss!

Intrinsic losses: real-time TDDFT cumulant

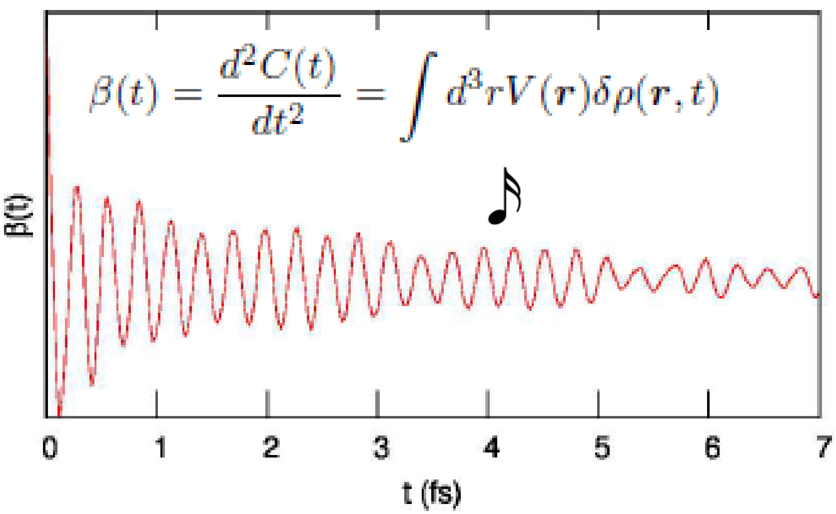
PHYSICAL REVIEW B **91**, 121112(R) (2015)

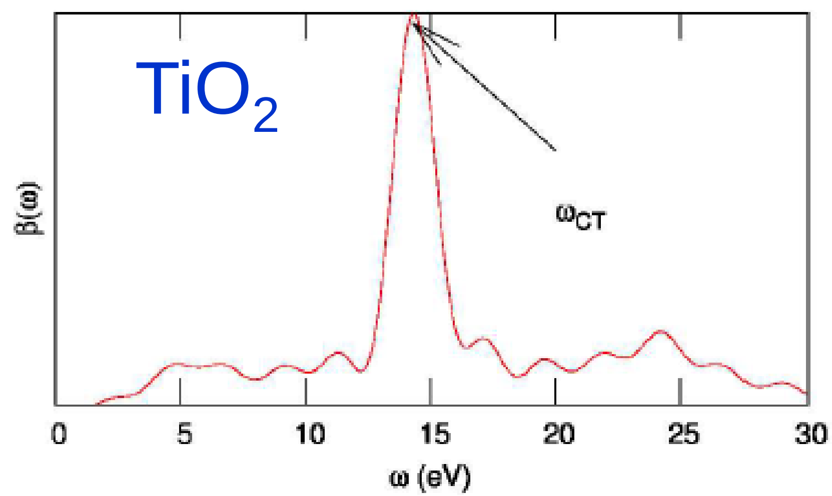
Real-time cumulant approach for charge-transfer satellites in x-ray photoemission spectra

J. J. Kas,[1] F. D. Vila,[1] J. J. Rehr,[1] and S. A. Chambers[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA*
[2]*Physical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, USA*

Langreth cumulant in time-domain*

$$C(t) = \sum_{\mathbf{q},\mathbf{q}'} V_{\mathbf{q}}^{*} V_{\mathbf{q}'} \int d\omega S(\mathbf{q},\mathbf{q}',\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2} = \int d\omega \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}$$



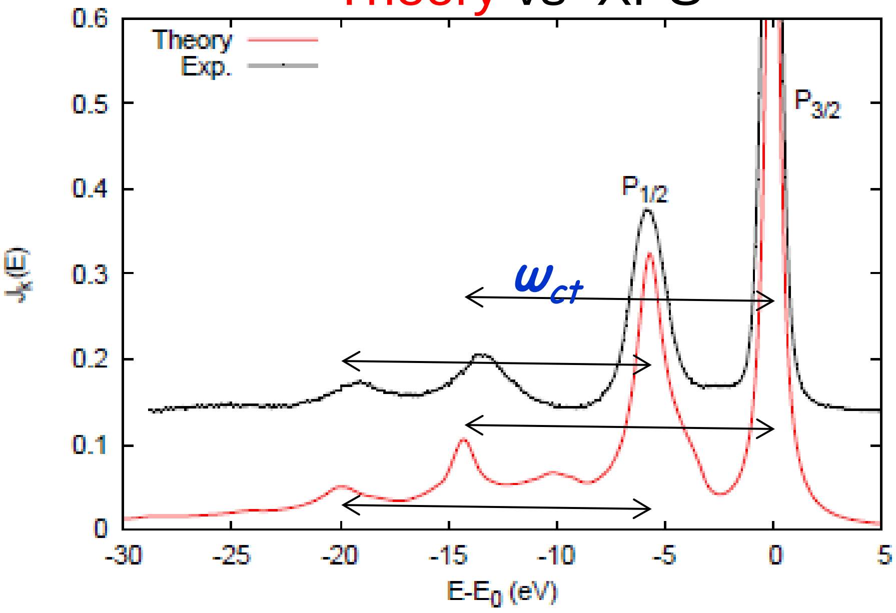


*D. C. Langreth, Phys. Rev. B **1**, 471 (1970)

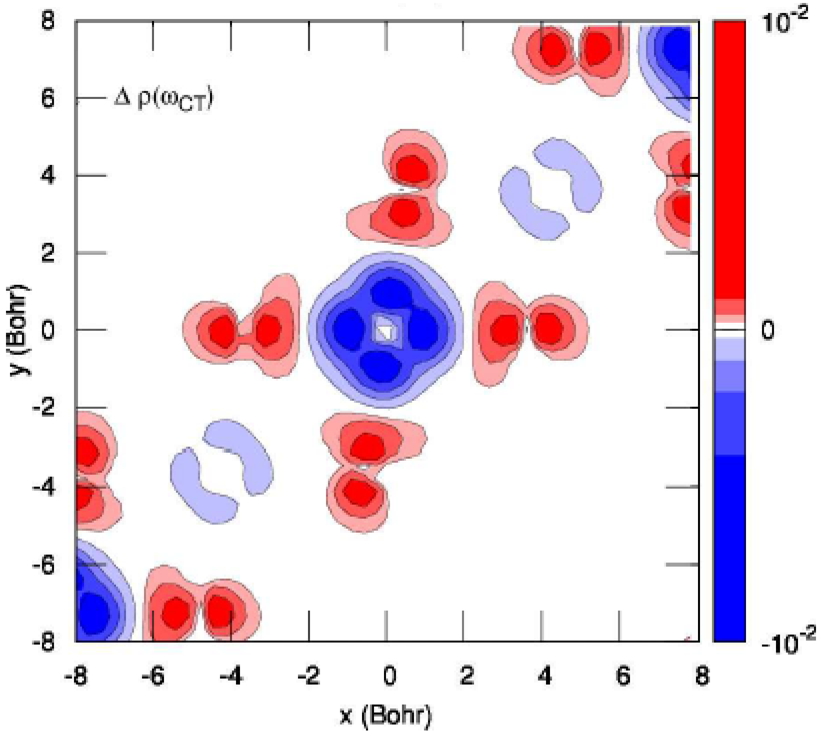
Real-space interpretation: RT-TDDFT cumulant explains intrinsic excitations in TiO_2

RT TDDFT Cumulant

Theory vs XPS



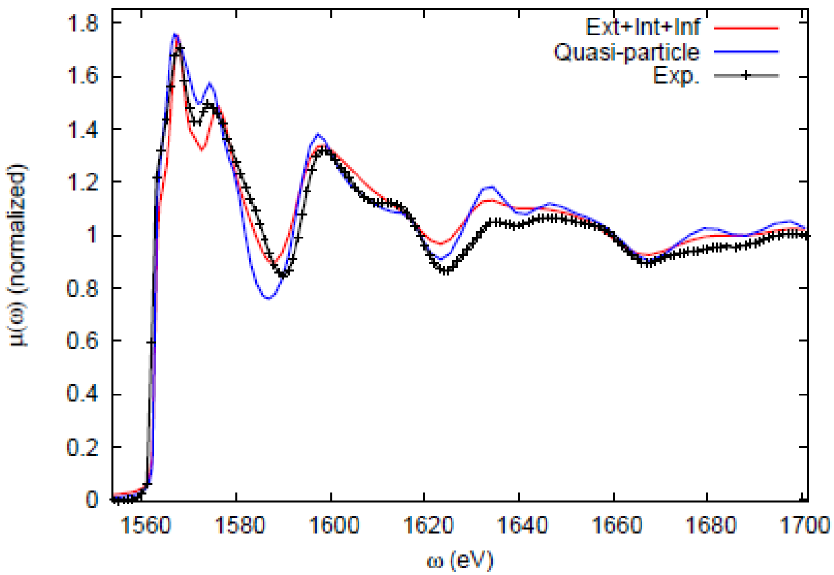
Charge transfer fluctuations



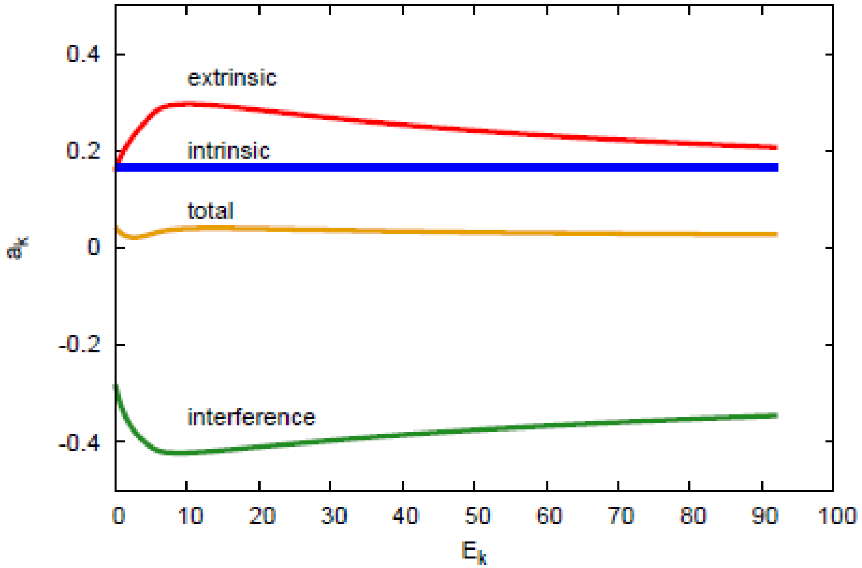
Interpretation: satellites arise from oscillatory charge density fluctuations between ligand and metal at frequency ~ ω_{CT} due to turned-on core-hole

Extrinsic losses and Interference

XAS of Al



Satellite strengths



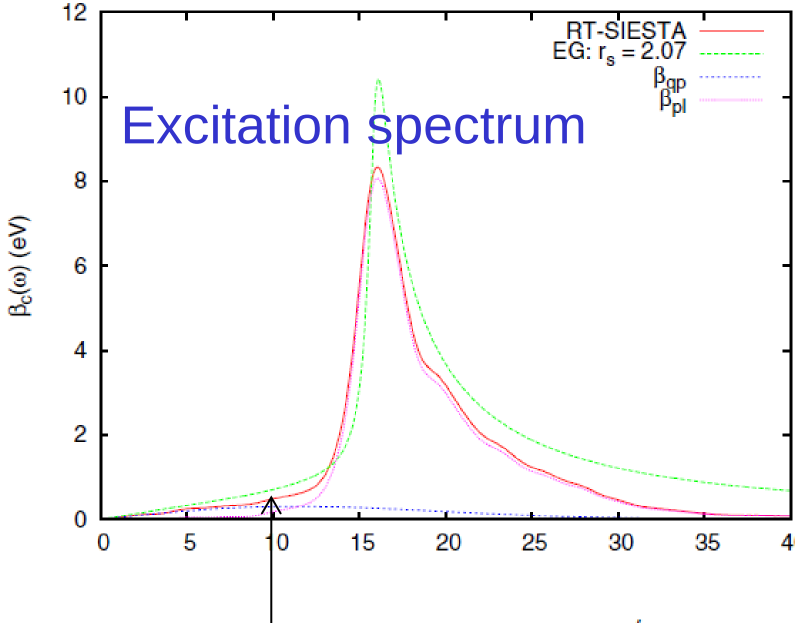
Particle-hole cumulant explains **cancellation** of extrinsic and intrinsic losses at threshold and

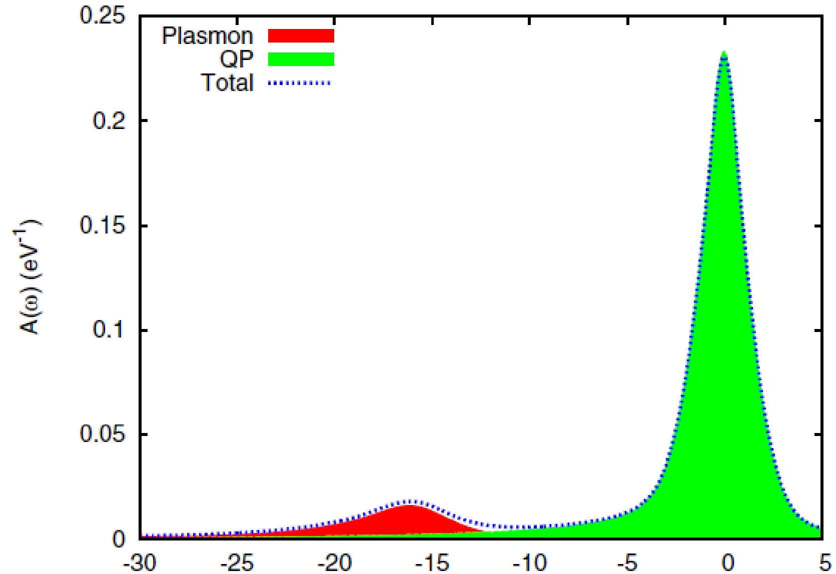
crossover: adiabatic

to sudden approximation

X-ray Edge Singularities

Low energy particle-hole excitations in cumulant **explain** edge singularities in XPS and XAS of metals





$$\beta_{ph}(\omega) = \alpha\omega e^{-\omega/\omega_p}$$

$$C_{ph}(t) = -i\alpha\omega_p t - \alpha\ln(1 - i\omega_p t)$$

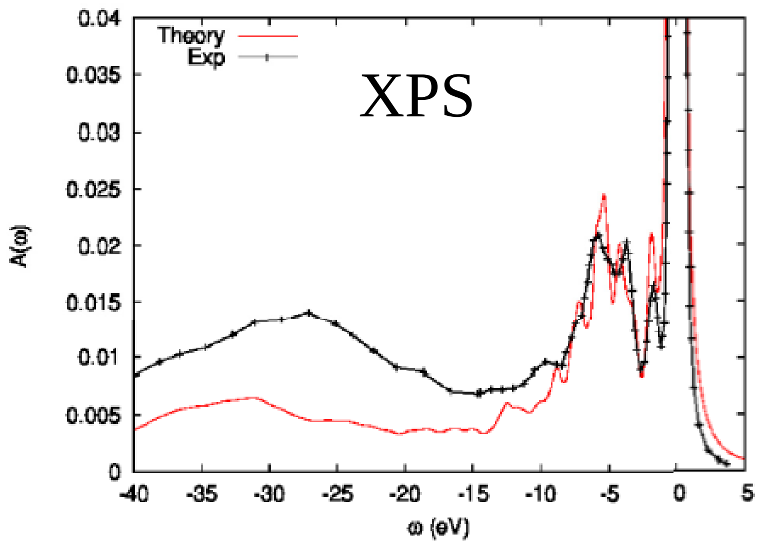
$$A_{ph}(\omega) = e^{-a_{pl}} \frac{e^{-\tilde{\omega}/\omega_p}}{\Gamma(\alpha)} \frac{\omega_p^{-\alpha}}{\tilde{\omega}^{1-\alpha}}$$

NIST Preprint; submitted to PRB 2016

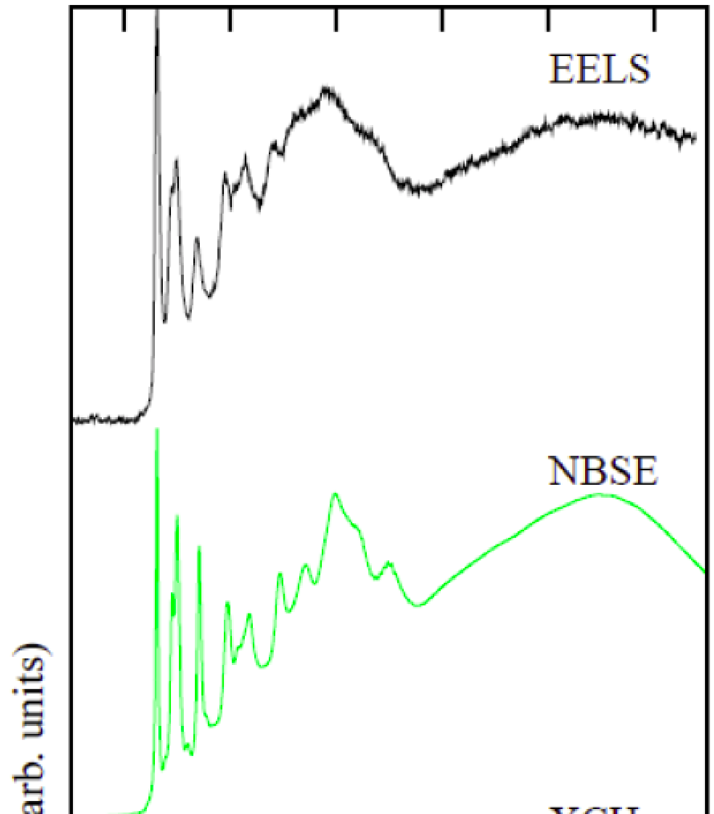
High-resolution valence and core excitation spectra of solid C_{60} via first-principles calculations and experiment

F. Fossard, K. Gilmore, G. Hug, J J. Kas, J J Rehr, E L Shirley and F D Vila

RT-TDDFT cumulant



Particle-hole cumulant



Question: Does the cumulant method work for correlated systems ?

Hedin's answer * MAYBE

"Calculation similar to core case … but with more complicated fluctuation potentials …

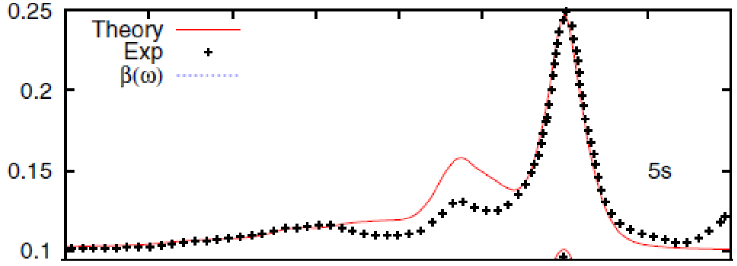
$$V^n \to -\mathrm{Im}\, \varepsilon^{-1}(\omega_n, q_n)$$

… not question of principle, but of computational work..."

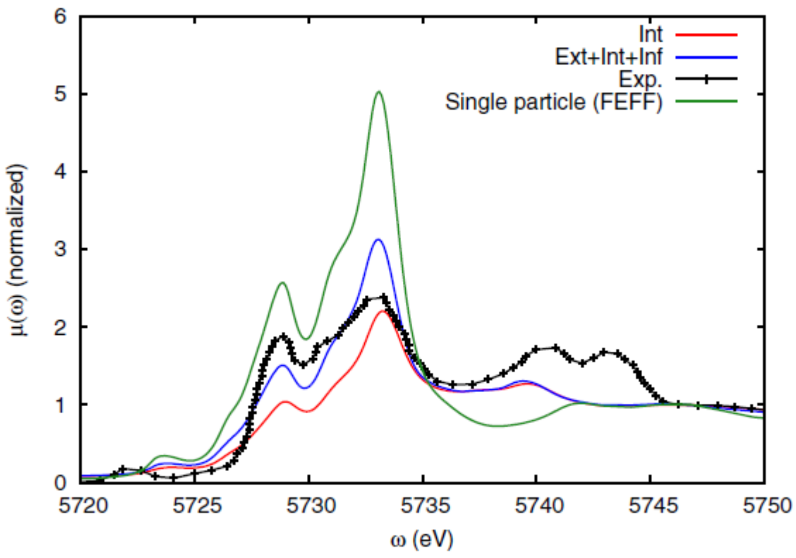
* L. Hedin, J. Phys.: Condens. Matter **11,** R489 (1999)

Particle-hole cumulant for CeO_2

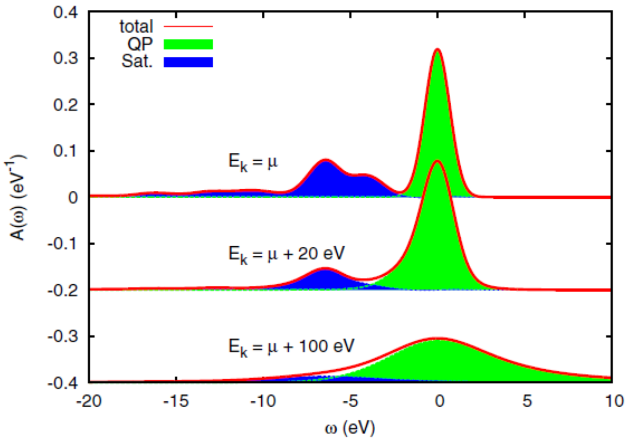
Ce *5s* XPS of CeO_2



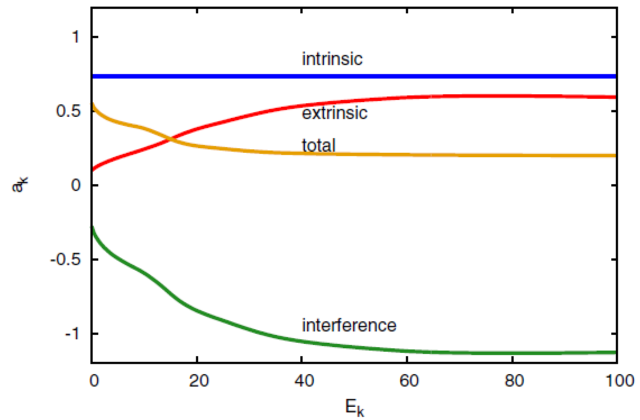
Ce L_3 XAS of CeO_2



Spectral function



Spectral weights



Conclusions

Particle-hole cumulant theory yields reasonable approximation for inelastic losses in XPS & XAS

$$\mu(\omega) = \int d\omega' \, \tilde{A}_K(\omega')\mu_K(\omega - \omega')$$

All losses (intrinsic, extrinsic and interference) in spectral function $\boldsymbol{A_K(\omega)}$ – *can be added ex post facto*

Interference terms explain mysteries in amplitudes and energy dependence: adiabatic- sudden transition

Theory also applicable to some *d*- and *f*-systems.

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S. Story	S. Biermann	M Guzzo
M. Verstraete	J. Sky Zhou	C. Draxl

et al.

& especially the ETSF