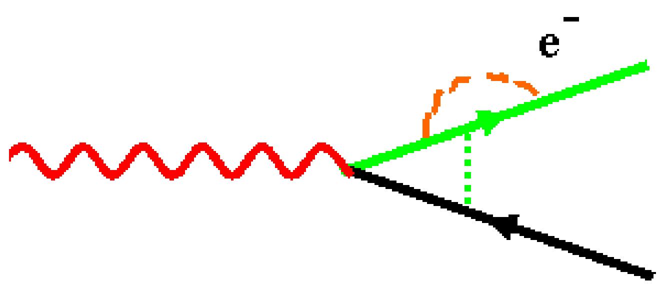
Summer School on Computational and Experimental Photoelectron Spectroscopy

Tartu, Estonia July 30, 2026

Cumulant Green's Function for Satellites in X-ray Spectra

J. J. Rehr

University of Washington and SLAC



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Talk: Cumulant Green's Function Approach

1. Satellites in Photoemission & XPS

2. Satellites in X-ray Spectra

3. Spectral function applications: Excited-states and finite T

“You can judge the quality

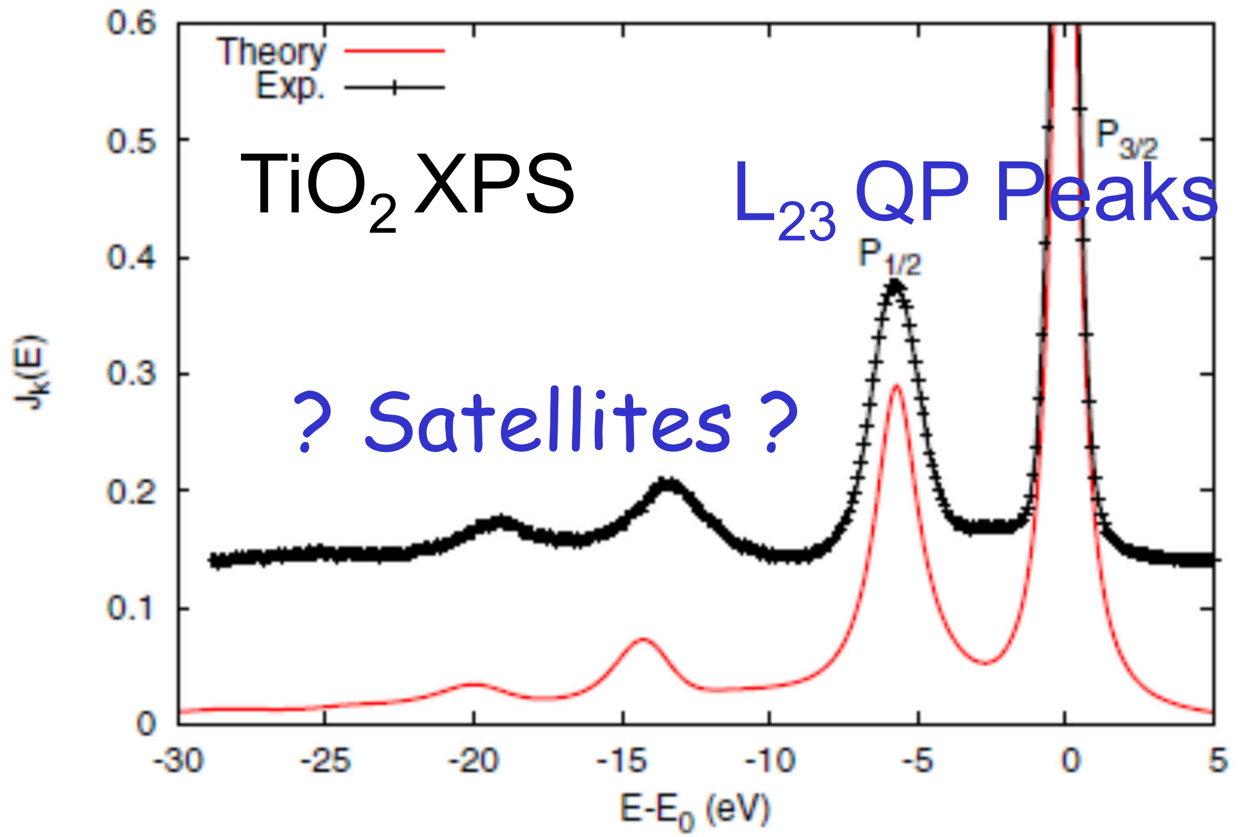
of a many-body theory by

how it treats the satellites”

Lars Hedin
ca 1994

1. Satellites in Photoemission & XPS*

Challenge: Calculations of satellites in XPS



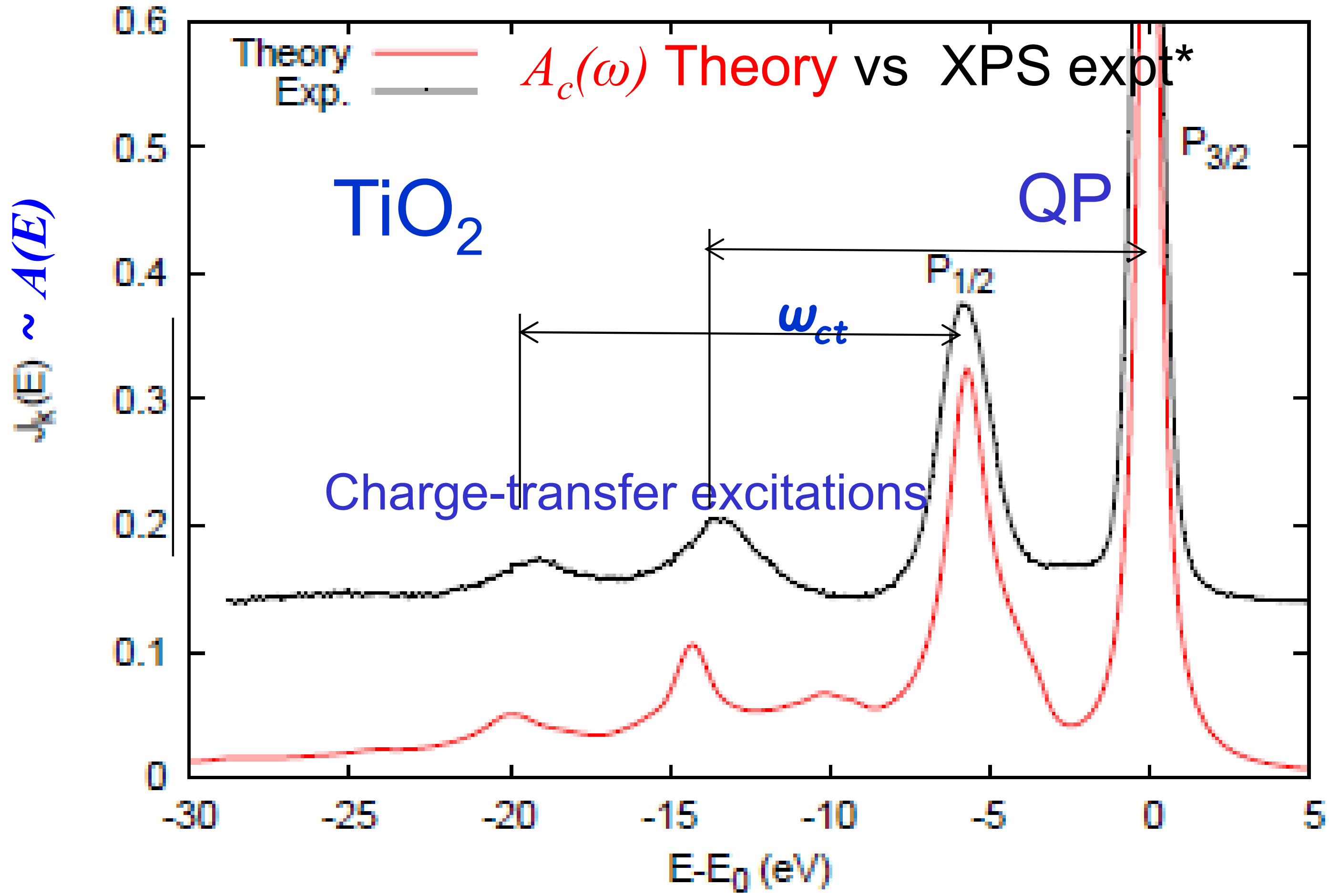
*S.A. Chambers, private communication (2011)

Theory: J. J. Kas, F. D. Vila, J. J. Rehr, and S. A. Chambers Phys Rev B **91**, 121112(R) (2015)

Spectral function interpretation of satellites*

XPS Photocurrent $J(E)$ ~ "Spectral function" $A_c(\omega)$

$A_c(\omega) = (1/\pi)\,|\mathrm{Im}\, G_c(\omega)|$ spectral density of state c



*Theory: . J. Kas, F. D. Vila, J. J. Rehr, and S. A. Chambers, PRB **91**, 121112(R) (2015)

Green's function approaches

Conventional approach vs Cumulant approach

GW + Dyson vs GW + Cumulant $C(t)$*

$$G(\omega) = G_0 + G_0 \Sigma G$$

$$\Sigma^{GW} = iGW$$

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

No vertex $\Gamma = 1$

Bad satellite struture

$$G_c(t) = G_0(t)\, e^{C(t)}$$

$$C(t) = \int d\omega\, \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}$$

$\beta(\omega)$ cumulant kernel

$$C(t) \sim |\mathrm{Im}\, \Sigma^{GW}|$$

Includes implicit vertex Γ

Improved satellite positions

*Landau representation: L. Landau, J. Phys. USSR **8**, 201 (1944)

Review: Green's function approaches

J. Phys.: Condens. Matter **11** (1999) R489–R528. Printed in the UK PII: S0953-8984(99)66997-1

REVIEW ARTICLE

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

Lars Hedin

Department of Theoretical Physics, Lund University, Sölvegatan 14A, 223 62 Lund, Sweden
and
Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

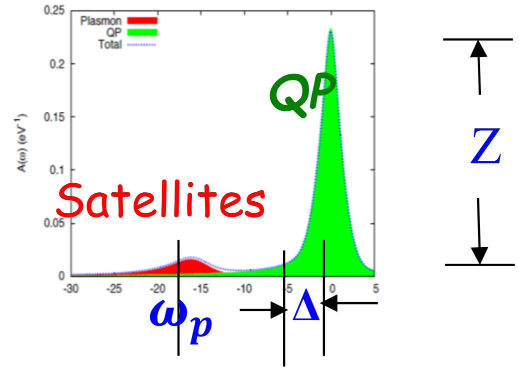
GW vs Cumulant Approaches for Green's function

Spectral Function properties $A(\omega) = \int d\omega\, e^{-i\omega t} e^{C(t)}$

Landau representation of cumulant*

$$C(t) = \int d\omega\, \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}$$

$$e^{C(t)} \approx Z e^{-i\Delta t}\left[1 + \int d\omega' [\frac{\beta(\omega')}{\omega'^2}] e^{i\omega' t} + \cdots \right]$$



Behavior QP peak + Satellites

$$A(\omega) = FT\, e^{C(t)} \approx Z\delta(\omega - \Delta) + Z\left[\frac{\beta(\omega-\Delta)}{(\omega-\Delta)^2}\right] + \ldots$$

Manne-Aberg Theorem

$$\omega_p a = Z\Delta$$

Renormalization constant $Z = e^{-a} \sim S_0^{\,2}$

$$a = \int d\omega \frac{\beta(\omega)}{\omega^2} \approx 0.2\, r_s^{3/4} > 0.2$$ satellite spectral weight

a Dimensionless measure of correlation
> 20% even in weakly correlated materials

*Landau representation: L. Landau, J. Phys. USSR **8**, 201 (1944)

Example: Langreth Cumulant

PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 197

Singularities in the X-Ray Spectra of Metals*

DAVID C. LANGRETH

$G(t) = G_0(t)e^{C(t)}$ $C(t) = \int d\omega\, \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}$

? How to calculate $C(t) \sim \beta(\omega)$?

Langreth: $\beta(\omega) = \sum_q V_q^2\, S(\boldsymbol{q},\omega) \sim |\mathrm{Im}\,\epsilon^{-1}(\omega)|$ Loss function

Hedin: GW approx $\beta_k(\omega) = \frac{1}{\pi}\,\mathrm{Im}\,\Sigma_{\mathrm{GW}}(\epsilon_k - \omega) \sim \mathrm{Im}\,W(\omega)$

Physical interpretation: density response function to suddenly turned on core-hole

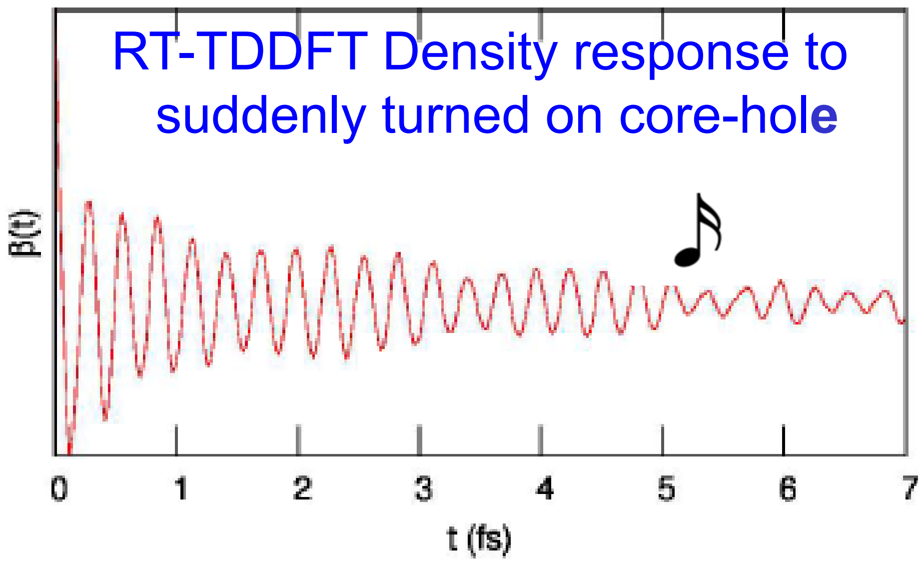
Equivalent form: Real-time Langreth cumulant*†

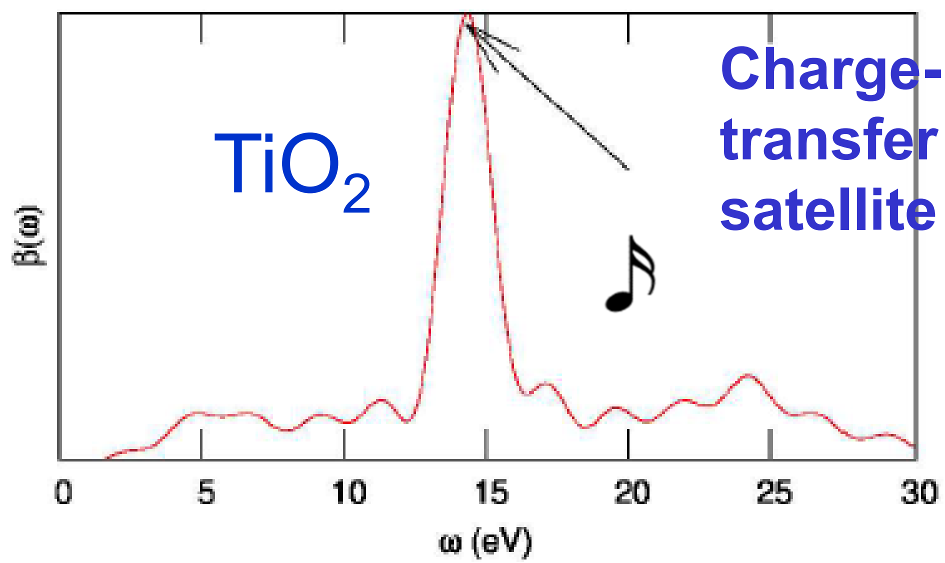
Langreth cumulant† $C(t)$ in time-domain*

$$C(t) = \int d\omega \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2} \qquad \beta(\omega) = \mathrm{FT}\,\beta(t)$$

$$\beta(t) = \frac{d^2 C(t)}{dt^2} = \int d^3 r V(\boldsymbol{r}) \delta\rho(\boldsymbol{r}, t)$$

Excitation spectrum – cumulant kernel



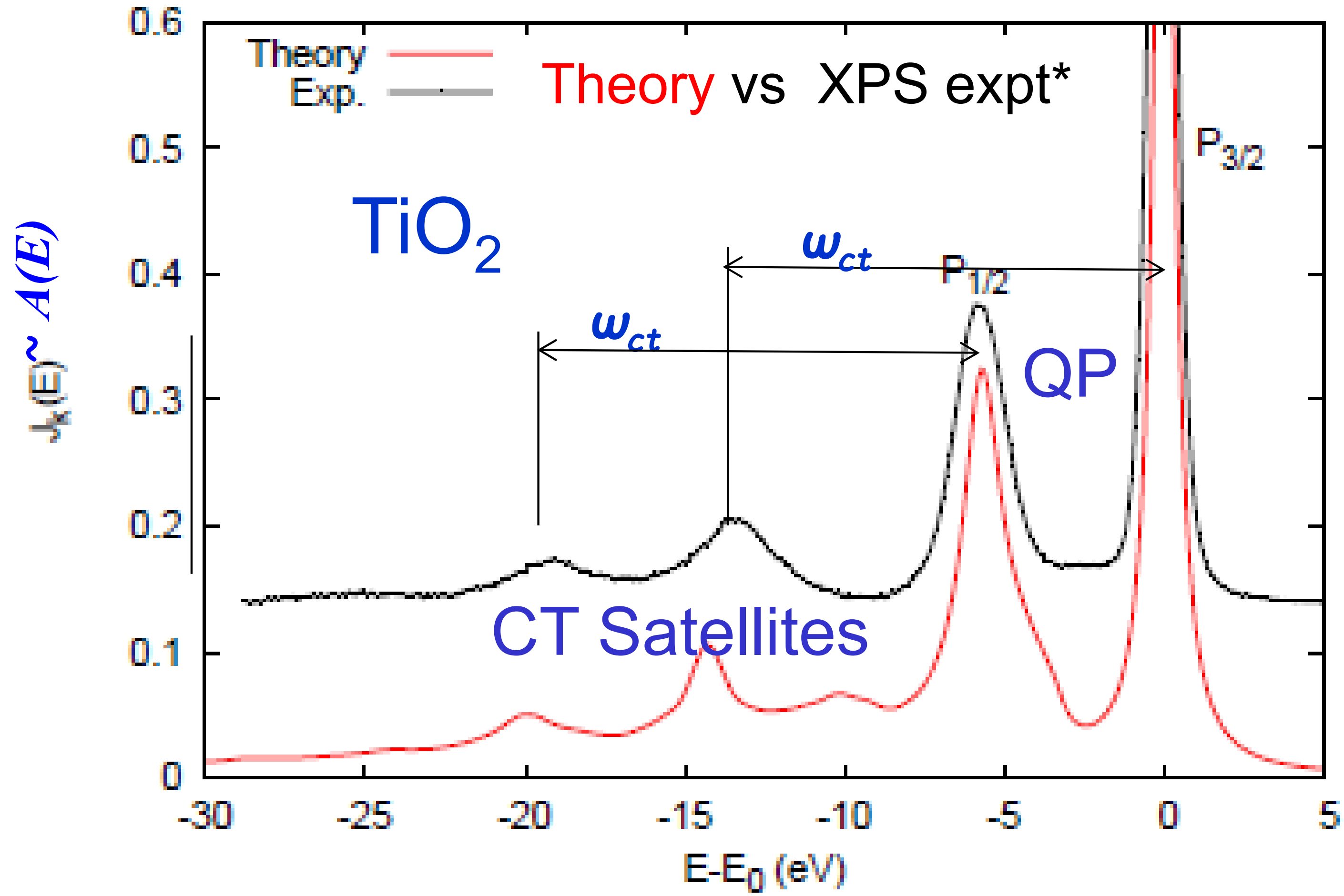


*J. J. Kas, F. D. Vila, J. J. Rehr, and S. A. Chambers, PRB **91**, 121112(R) (2015)

†D.C. Langreth, PRB **1**, 471 (1970)

Results: Good agreement with XPS experiment*

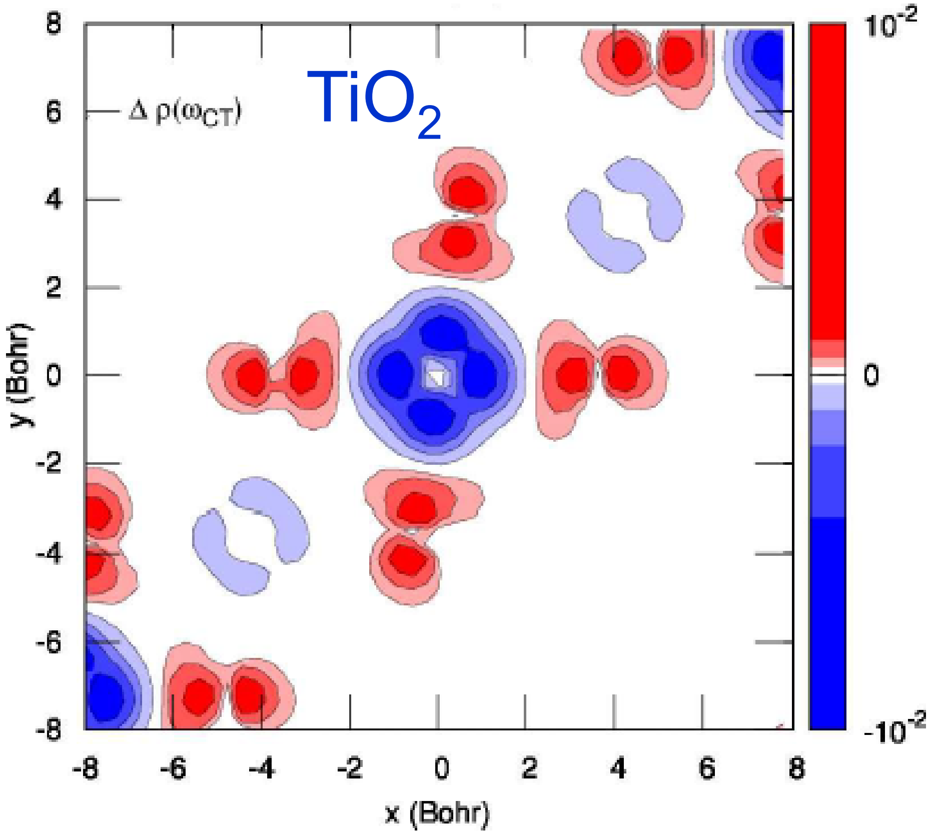
XPS $J(E)$ ~ Spectral function $A_c(\omega) = (1/\pi)\ |\mathrm{Im}\ G_c(\omega)|$



*J. J. Kas, F. D. Vila, J. J. Rehr, and S. A. Chambers, PRB **91**, 121112(R) (2015)

Real-space interpretation of satellites

Charge-transfer density fluctuations $\Delta\rho(r)$



$\Delta\rho(r)$

Interpretation: CT satellites arise from charge transfer between ligand O-$\boldsymbol{p}$ and Ti -$\boldsymbol{d}$ at frequency $\sim \omega_{CT}$ due to core-hole

Why does it work: Quasi-boson approximation

Physics: Neutral excitations - plasmons, phonons … are bosons

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

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

*D. C. Langreth, *Phys. Rev.* B **1,** 471 (1970)
B. I. Lundqvist, *Phys. Kondens. Mater.* **6 193 (1967)

Another equivalent: Real-space Langreth Cumulant

Real-space Green's function approximation for the Langreth cumulant*

J. J. Kas and J. J. Rehr
Dept. of Physics, Univ. of Washington Seattle, WA 98195
(Dated: July 3, 2022)

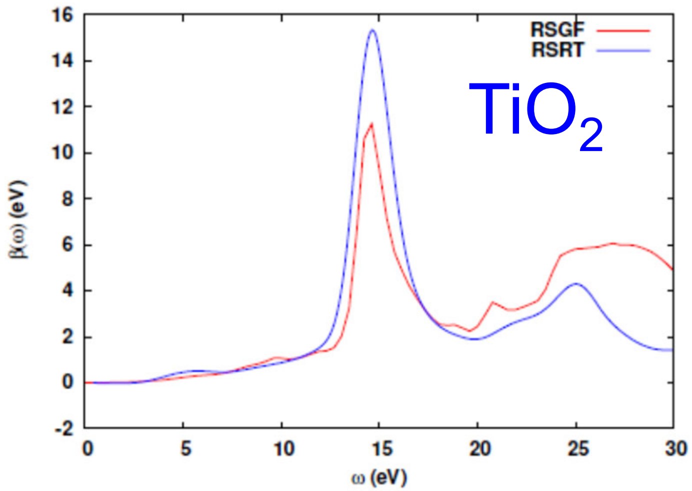
Langreth cumulant in Momentum space*

$$\beta(\omega) = \frac{1}{\pi}\sum_q |V_q|^2 \mathrm{Im}\,\chi(\mathbf{q},\omega)$$
$$\equiv \frac{1}{\pi}\sum_q |W_q(\omega)|^2 \mathrm{Im}\,\chi^0(\mathbf{q},\omega)$$
$$W_{\mathbf{q}}(\omega) = V_q/\epsilon(\mathbf{q},\omega)$$

Langreth cumulant in real space

$$\beta(\omega) = \frac{1}{\pi}\int d^3r d^3r'\, W_c^*(\mathbf{r},\omega) W_c(\mathbf{r}',\omega)\, \mathrm{Im}\,\chi^0(\mathbf{r},\mathbf{r}',\omega)$$
$$\mu_1(\omega) = \frac{4\pi}{V}\int d^3r d^3r'\, d(\mathbf{r}) d(\mathbf{r}')\, \mathrm{Im}\,\chi^0(\mathbf{r},\mathbf{r}',\omega)$$

Excitation spectrum $\beta(\omega)$



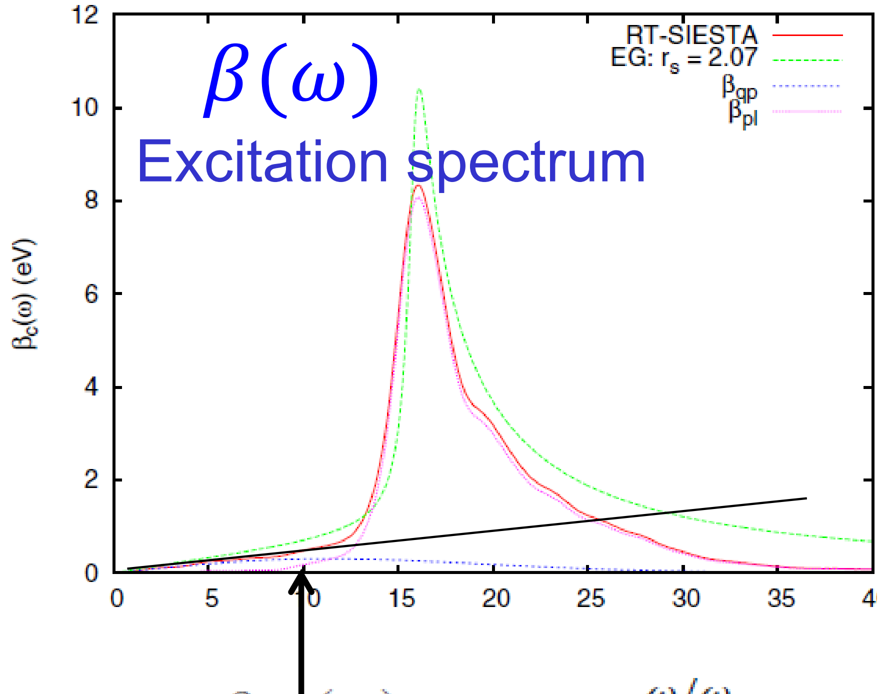
Dynamically screened core-hole potential W

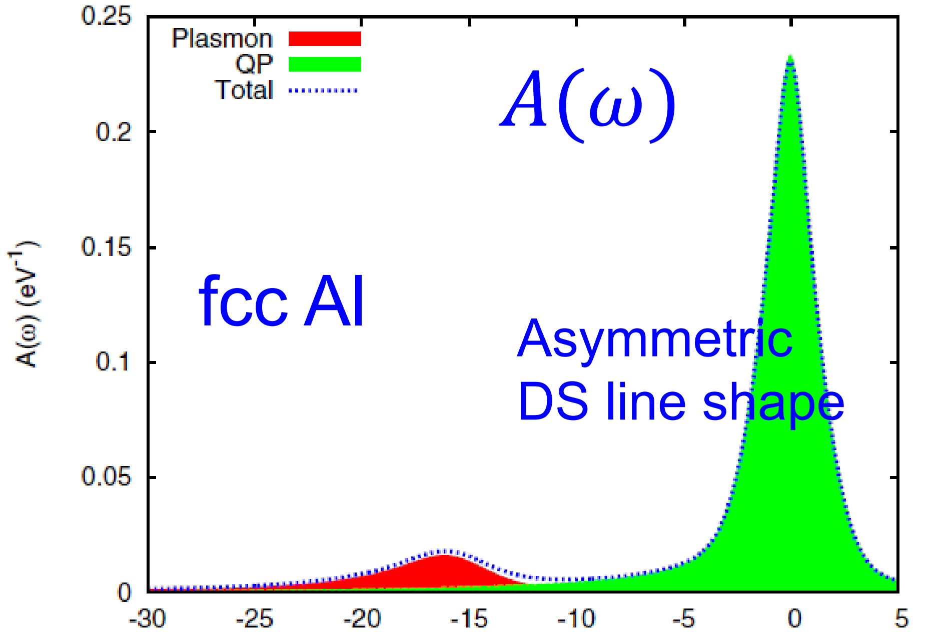
Langreth cumulant **similar** to XAS $\mu(\omega)$
but with $W_c(\boldsymbol{r},\omega)$ replacing dipole $d(r)$
Can calculate $C(t)$ with FEFF codes
in parallel with QP XAS

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

Bonus: X-ray Edge Singularities in Metals

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





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

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

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

cf Doniach-Sunjic line-shape in XPS

Yet another formalism: RT EOM-CC cumulant

Equation of motion coupled-cluster cumulant approach for intrinsic losses in x-ray spectra

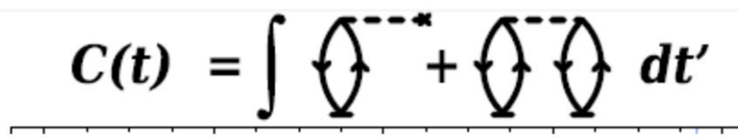
Cite as: J. Chem. Phys. 152, 174113 (2020); doi: 10.1063/5.0004865
Submitted: 17 February 2020 • Accepted: 14 April 2020 •
Published Online: 6 May 2020

View Online Export Citation CrossMark

J. J. Rehr,[1,a)] F. D. Vila,[1] J. J. Kas,[1] N. Y. Hirshberg,[1] K. Kowalski,[2] and B. Peng[2]

Exact non-perturbative cumulant including non-linear terms from coupled 1st order differential equations

JCTC Journal of Chemical Theory and Computation



$$= i \int_0^t \langle \phi | \bar{H}_N(t') | \phi \rangle \mathrm{d}t'$$

pubs.acs.org/JCTC Article

Real-Time Coupled-Cluster Approach for the Cumulant Green's Function

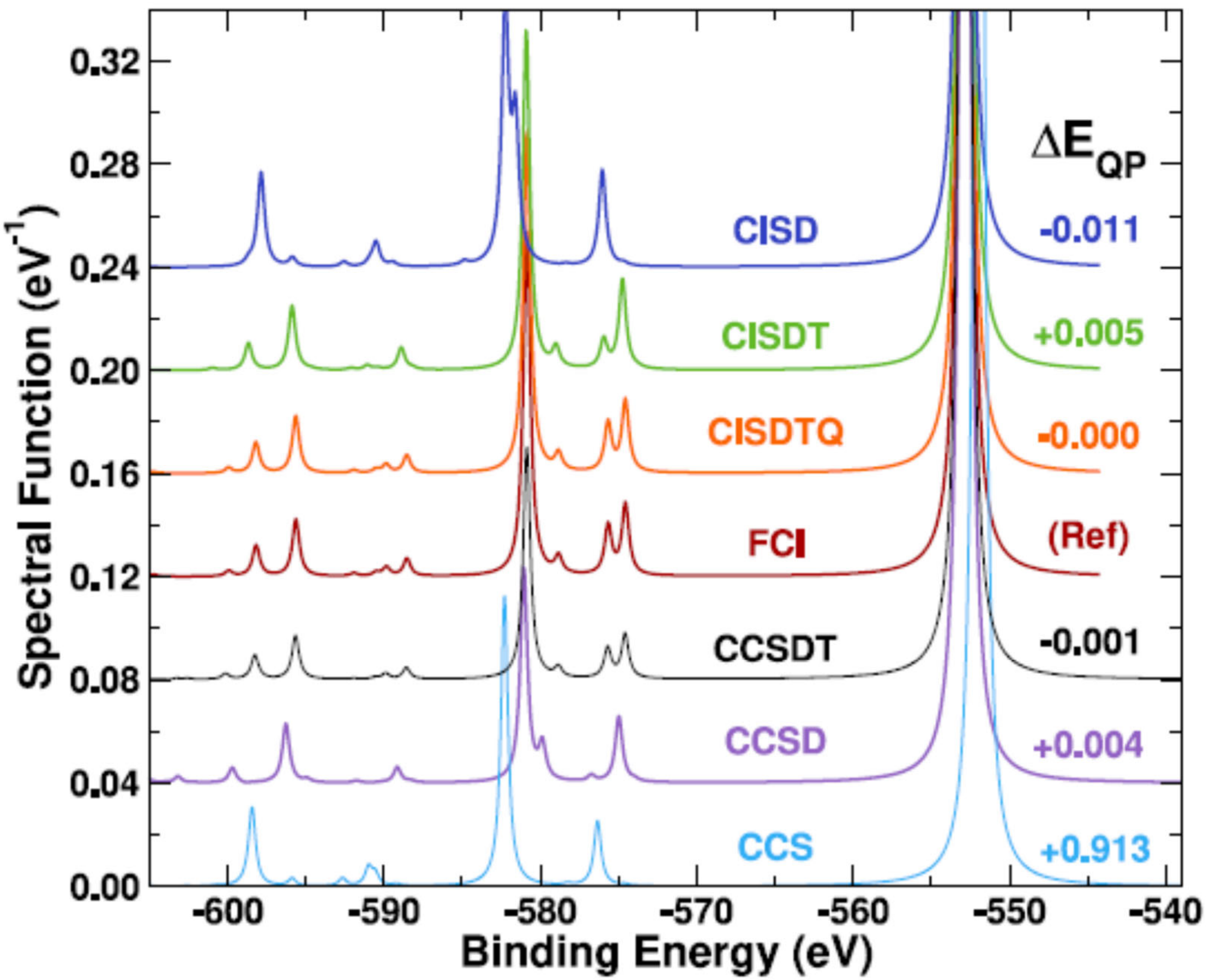
F. D. Vila,* J. J. Rehr, J. J. Kas, K. Kowalski, and B. Peng

Cite This: J. Chem. Theory Comput. 2020, 16, 6983–6992 Read Online

$$G_c^R(t) = -i\Theta(t) e^{-i\epsilon_c t} e^{C_c^R(t)}$$

Computationally challenging – small *N* systems

RT-EOM-CC SDTQ vs CI*



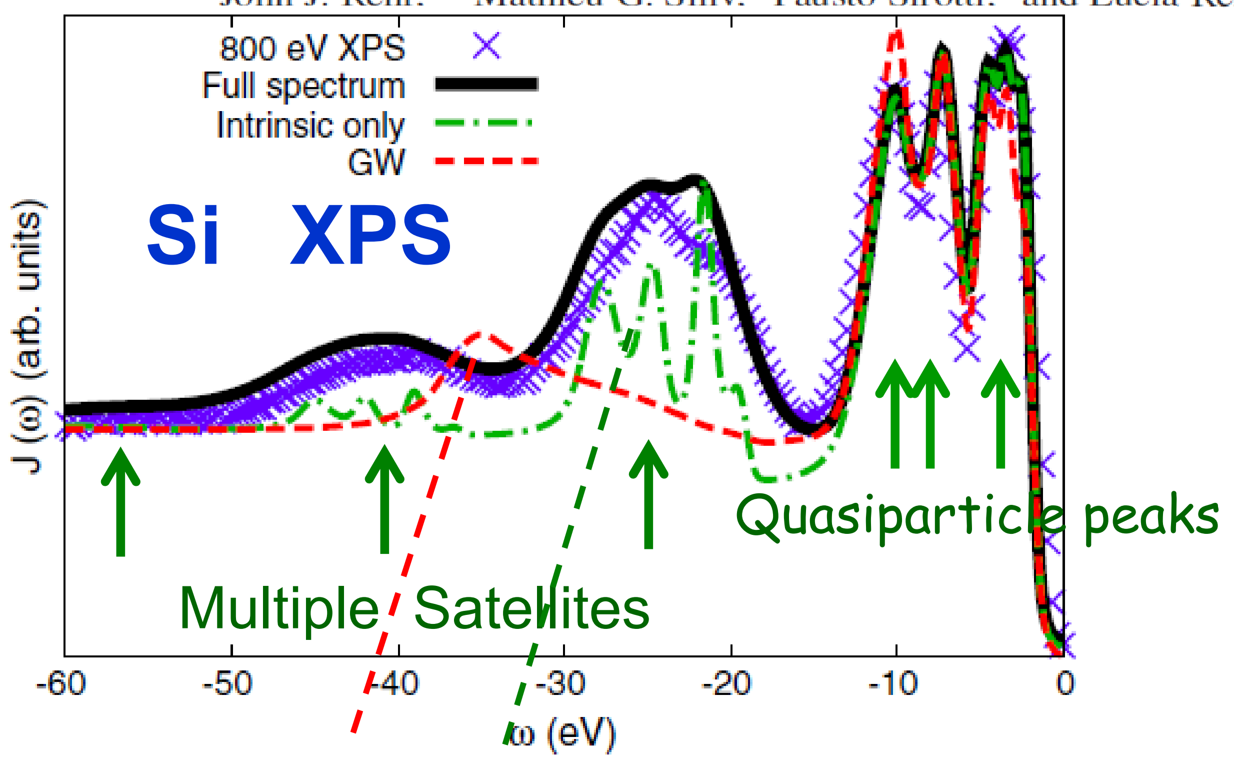
F.D. Vila et al, *J. Chem. Theory Comput.* 2025, 21, 5771–5777

New challenge: 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 has one broad satellite at the wrong place

Intrinsic cumulant has multiple satellites BUT intensity too small

Fix: Particle-hole Cumulant Green's function

$$G_K(t) = G_K^0(t) e^{C_K(t)} \qquad K = (k, c)$$

Particle-hole spectral function includes interference

$$A_K(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\, G_K(\omega) = A_{ext} + A_{int} + A_{inter}$$

Includes intrinsic, extrinsic & *interference* effects on satellites

interference *missing* in Intrinsic Cumulant GF

Extrinsic **+** Intrinsic - 2 x Interference

*J.J. Kas, J.J. Rehr and J.B.Curtis, Phys Rev B **94**,034156 (2016)

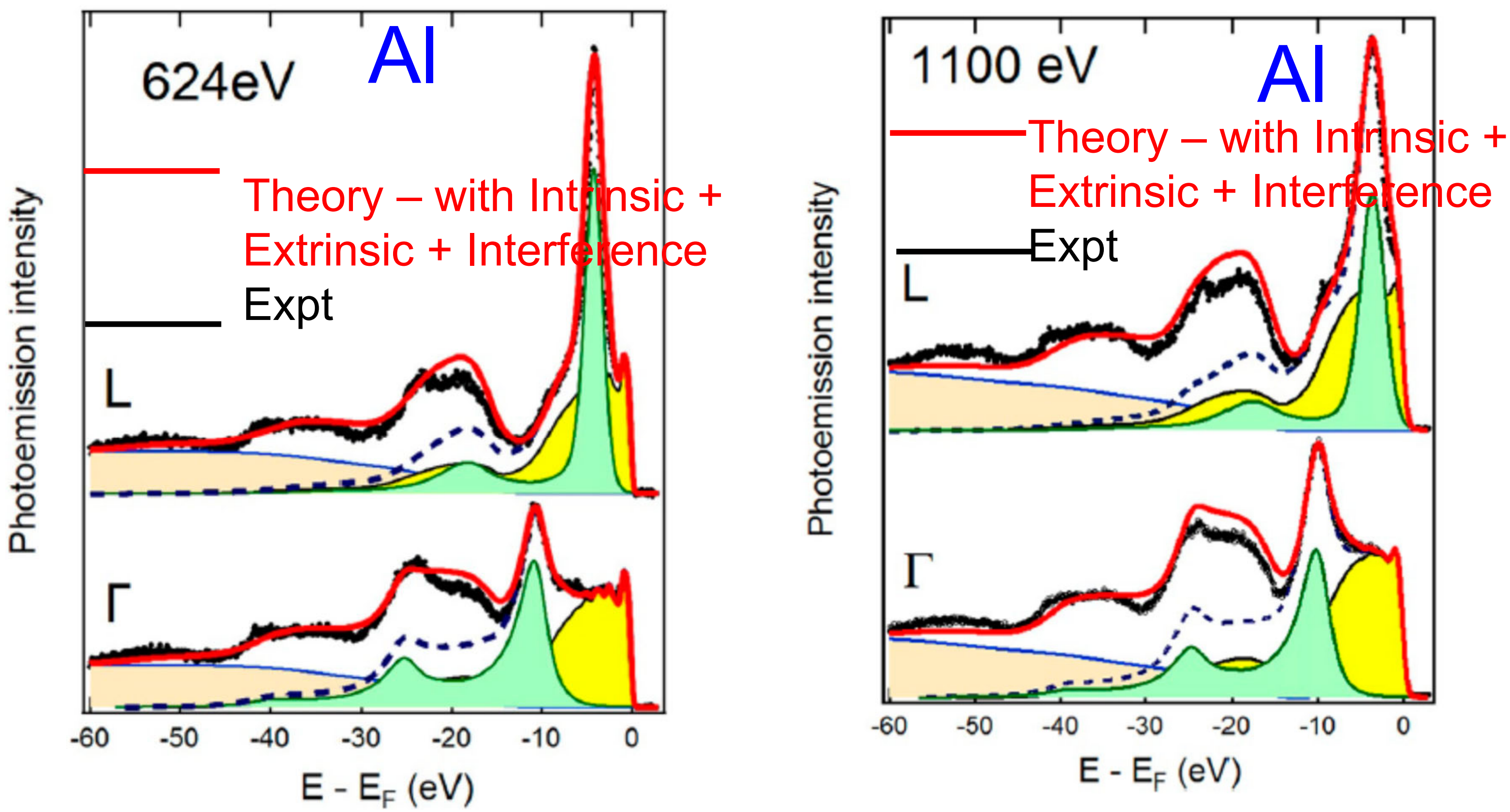
Also: L. Hedin, J. Michiels and J. Inglesfield, Phys Rev B **58**, 15565 (1998)

Example: Cumulant GF for satellites in ARPES

PNAS **117**, 28596 (2020)

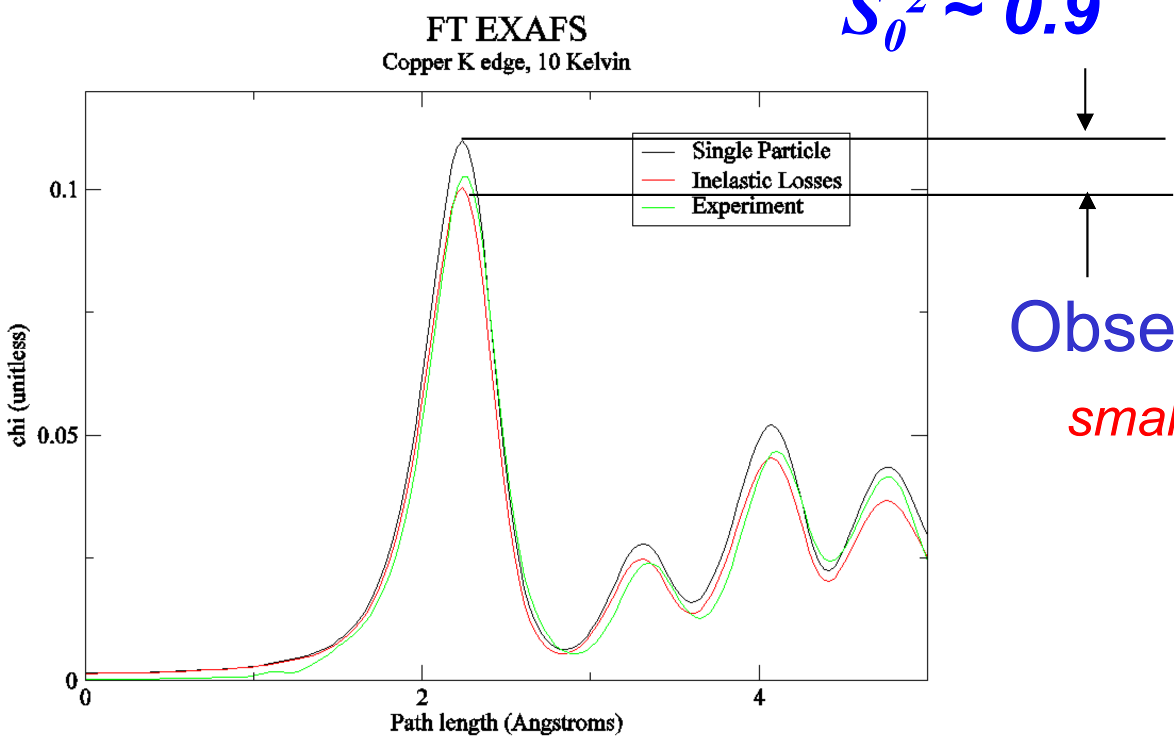
Unraveling intrinsic correlation effects with angle-resolved photoemission spectroscopy

Jianqiang Sky Zhou[a,b,c], Lucia Reining[a,b,1], Alessandro Nicolaou[d], Azzedine Bendounan[d], Kari Ruotsalainen[d,2], Marco Vanzini[a,b,e], J. J. Kas[f], J. J. Rehr[f], Matthias Muntwiler[g], Vladimir N. Strocov[g], Fausto Sirotti[h,1], and Matteo Gatti[a,b,d,1]



2. Satellites in X-ray Spectra

Observe: QP Theory of XAS over estimates experiment



$S_0^2 \sim 0.9$

Observed fine structure *smaller* than QP theory

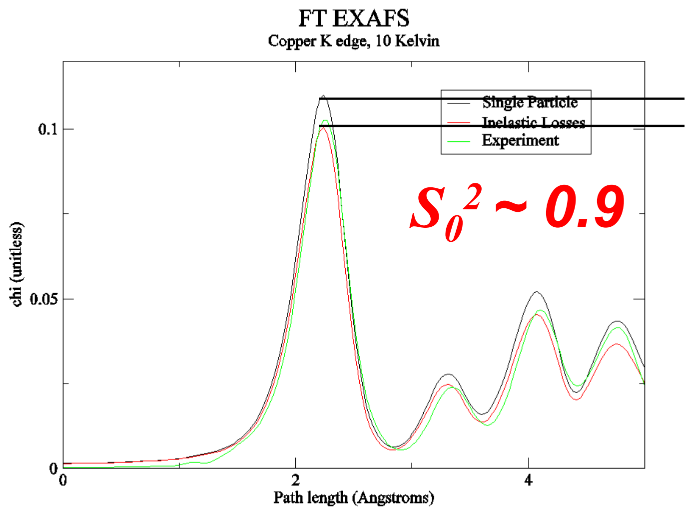
Hedin suggestion: Intrinsic losses

Important to include intrinsic and extrinsic losses

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.



Ad hoc fix: Convolution XPS ⊗ QP-XAS

Observation: Satellites in XAS are embedded in XPS

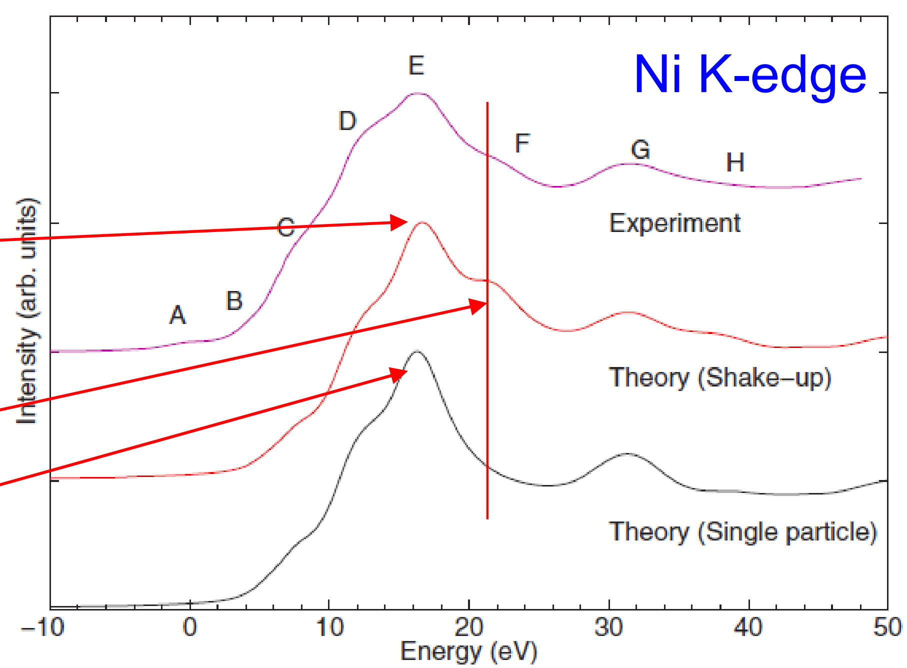
PHYSICAL REVIEW B **86**, 165102 (2012)

K-edge x-ray absorption spectra in transition-metal oxides beyond the single-particle approximation: Shake-up many-body effects

M. Calandra,[1] J. P. Rueff,[2,3] C. Gougoussis,[1] D. Céolin,[2] M. Gorgoi,[4] S. Benedetti,[5] P. Torelli,[6] A. Shukla,[1] D. Chandesris,[7] and Ch. Brouder[1]

$$\sigma_{\mathrm{XAS}}(\omega) = \int d\epsilon\, \sigma^{\mathrm{exp.}}_{\mathrm{XPS}}(\epsilon)\sigma^{\mathrm{sp}}_{\mathrm{XAS}}(\omega-\epsilon)$$

Shake-up satellites in NiO XAS



Many body reduction in edge peak S_0^2

XPS Excitation spectrum includes shake satellites; & reduces single particle theory

Cumulant Green's function Approach

Cumulant GF in time-domain factorizes $G_c(t) \equiv G_{qp}(t)e^{C(t)}$

Cumulant $C(t)$ includes many-body corrections to quasi-particle theory

- builds in inelastic losses S_0^2 & satellites via Spectral function

Factorization explains *ad hoc* convolution formula for satellites in XAS

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

Spectral function $\tilde{A}(\omega,\omega')$

Includes satellites & S_0^2

$\tilde{A}(\omega,\omega') = FT\ e^{C(t)}$ ~ XPS

Quasi-particle XAS μ_{qp}

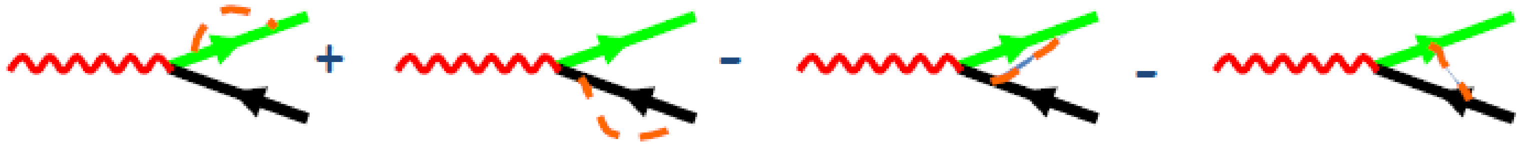
Includes core-hole V_c

Mean-free path λ

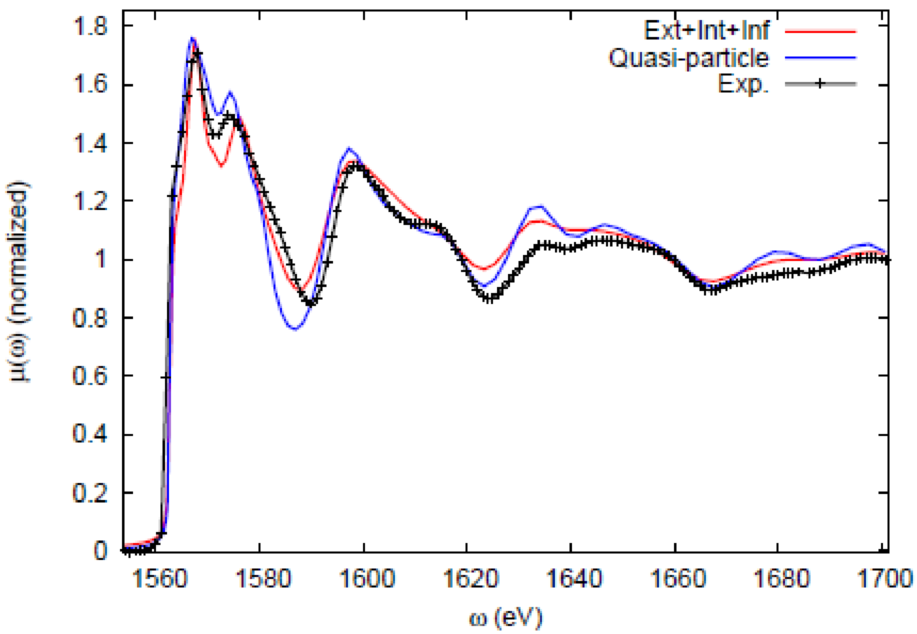
DW factor $e^{-2\sigma^2 k^2}$

*J.J. Kas, J.J. Rehr and J.B.Curtis, Phys Rev B **94**,034156 (2016)

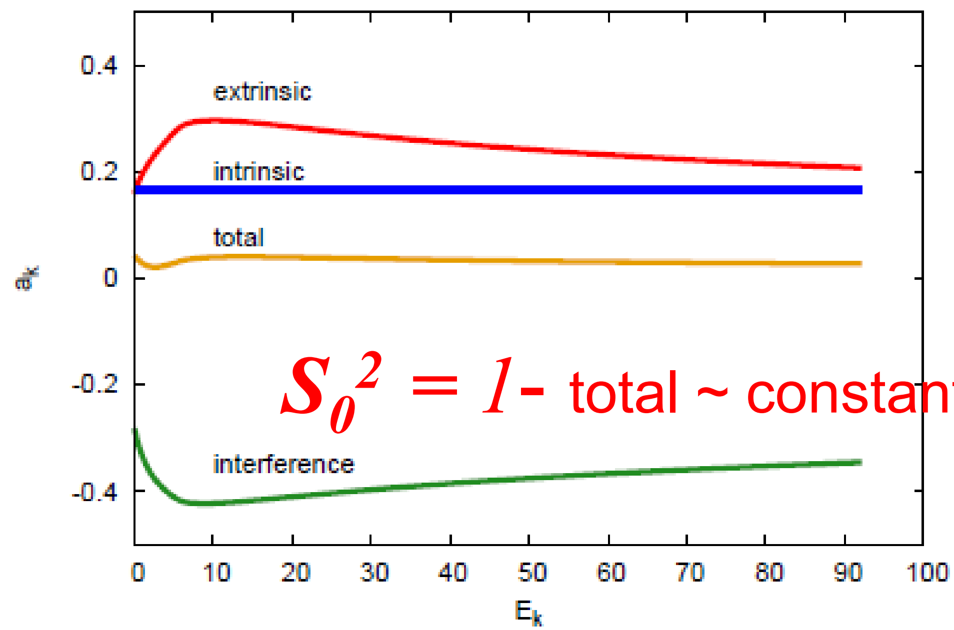
Extension: Particle-hole cumulant in XAS



XAS of Al



Satellite strengths



$S_0^2 = 1$- total ~ constant

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

AND crossover: **adiabatic**

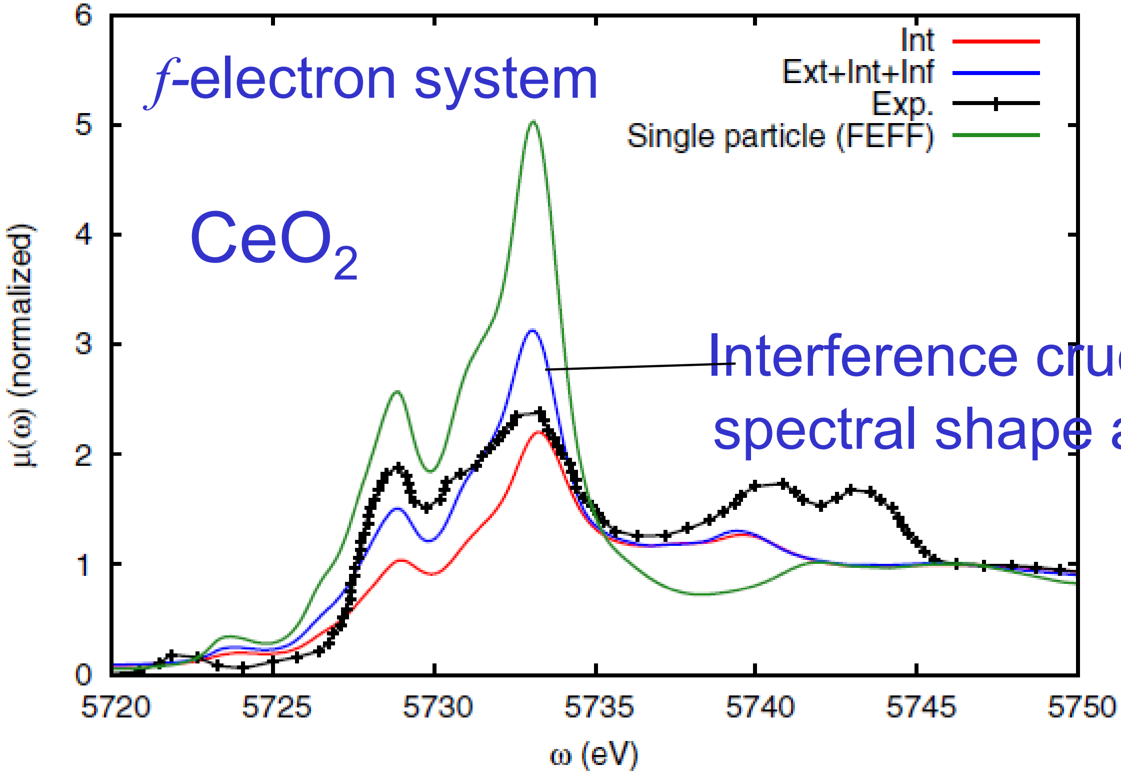
to **sudden** approximations

Example: XAS in *f*-electron systems

Observe: strong correlation & interference in *f*-electron systems

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

Particle-hole cumulant yields improved agreement in XANES



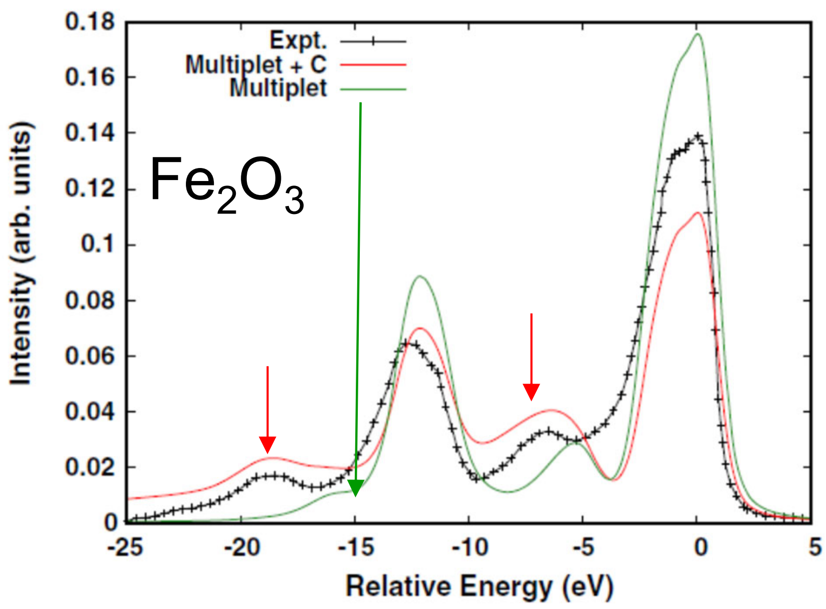
Extension: Multiplet + Cumulant Approach

PHYSICAL REVIEW LETTERS **128,** 216401 (2022)

Ab Initio **Multiplet-Plus-Cumulant Approach for Correlation Effects in X-Ray Photoelectron Spectroscopy**

J. J. Kas,[1,*] J. J. Rehr,[1,2] and T. P. Devereaux[3,4]

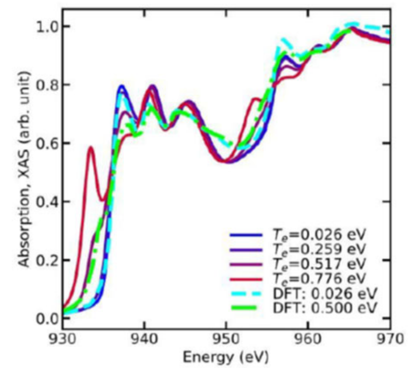
Cumulant spectral function accounts for long ranged charge-transfer satellites missing in LFMT with local atomic multiplet Hamiltonians



Ab initio theory: Slater-Condon parameters from FEFF10 + real-time cumulant spectral function *C(t)*

Improved treatment of CT satellites, amplitudes, and tails in XPS

3. Cumulant GF at finite T and Extreme conditions



Challenge: Theory of excited states at T up to WDM $T \sim T_F \sim 10^5$ K

Approach: Cumulant Green's function for excited states, high T thermodynamics, & x-ray spectra

Alternative to FT-DFT[1], RPIMC[2], & dielectric methods[3]

[1]FT DFT: N.D. Mermin, Phys. Rev. **137,** 1 (1965); V.V. Karasiev et al. Phys. Rev. Lett. **112**, 076403 (2014)

[2]PIMC: E. W. Brown et al., Phys. Rev. Lett. **110**, 146405 (2013); T. Dornheim et al; Phys. Rept. **744**, 1 (2018)

[3]Dielectric: T. Sjostrom & J. Dufty, Phys. Rev. B **88**, 115123 (2013)

Thermodynamics from Cumulant Spectral function

Phys Rev Lett **109**, 176403 (2017)

Finite temperature Green's function approach for excited state and thermodynamic properties of cool to warm dense matter

J. J. Kas and J. J. Rehr
Dept. of Physics, Univ. of Washington Seattle, WA 98195
(Dated: May 23, 2017)

Theory: Galitskii-Migdal-Koltun sum rules*

Example: density sum-rule* $n(\mu,T) \equiv n \Rightarrow \mu(n,T)$

$$n(\mu,T) \equiv n = \frac{1}{V}\sum_k \int d\omega\, A_k(\omega) f(\omega)$$

Cumulant spectral function $A_k(\omega) = (1/\pi)|\mathrm{Im}\, G_k(\omega)|$

Fermi function $f(\omega) = 1/[e^{\beta(\omega-\mu)}+1]$

*P. Martin & J. Schwinger, Phys. Rev. **115**, (1959)

History: Martin & Schwinger 1959

PHYSICAL REVIEW VOLUME 115, NUMBER 6 SEPTEMBER 15, 1959

Theory of Many-Particle Systems. I*†

Paul C. Martin and Julian Schwinger
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts

(Received March 20, 1959)

$$\frac{E}{V}=\int\frac{d\mathbf{p}}{(2\pi)^3}\frac{1}{2}\left(\omega+\frac{\mathbf{p}^2}{2m}\right)\frac{\operatorname{tr}A^{\alpha\beta}(\mathbf{p}\omega)}{e^{\alpha+\beta\omega}\mp1}. \quad (3.69)$$

$$\frac{N}{V}=\int\frac{d\mathbf{p}}{(2\pi)^3}\int\frac{d\omega}{2\pi}\frac{\operatorname{tr}A^{\alpha\beta}(\mathbf{p}\omega)}{e^{\alpha+\beta\omega}\mp1}. \quad (3.67)$$

$$A(p,\omega)=|\mathrm{Im}\,\boldsymbol{G}(p,\omega)|$$

[1] The many-body problem has been studied with the aid of perturbation theory by many authors. This paper will not draw on any results of these works but has various points of contact with them. We mention the work of T. Matsubara, Progr. Theoret. Phys. (Kyoto) **14**, 351 (1955); K. M. Watson, Phys. Rev. **103**, 489 (1956); W. Riesenfeld and K. M. Watson, Phys. Rev. **104**, 492 (1956), **108**, 518 (1957), and other articles; K. Brueckner, Phys. Rev. **100**, 36 (1955), and other articles; K. Brueckner and S. L. Gammel, Phys. Rev. **109**, 1038 (1958); J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957); L. Van Hove, Physica **22**, 343 (1956), and other articles; N. M. Hugenholz, Physica **23**, 481 (1957), and other articles; Huang, Lee, and Yang, Lecture at Stevens Institute Conference on Many-Body Problems, 1957 (to be published); Lee, Huang, and Yang, Phys. Rev. **106**, 1135 (1957); T. D. Lee and C. N. Yang, Phys. Rev. **112**, 1419 (1958), and **113**, 1406 (1959); Schafroth, Butler, and Blatt, Helv. Phys. Acta **30**, 93 (1957); E. Montroll and J. Ward, Phys. Fluids **1**, 55 (1958); J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957), and other articles; J. Lindhardt, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **28**, No. 8 (1954); P. Nozières and D. Pines, Nuovo cimento **9**, 470 (1958); A. Klein and R. Prange, Phys. Rev. **112**, 994, 1008 (1958); C. DeDominicis and C. Bloch, Nuclear Phys. **7**, 459 (1958), and other articles; R. H. Kraichnan, Phys. Rev. **112**, 1054 (1958); S. T. Beliaev, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 417 (1958) [translation: Soviet Phys. JETP **7**, 289 (1958)]. A spirit similar to ours occurs in the work of V. M. Galitskii and A. B. Migdal, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 139 (1958) [translation: Soviet Phys. JETP **7**, 96 (1958)]; the note of L. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 262 (1958) [translation: Soviet Phys. JETP **7**, 182 (1958)]; and in E. S. Fradkin, J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 951, 1286 (1959).

Spectral function properties at $T=0$*

Retarded Cumulant Green's function in time domain

$$G_k(t) \;=\; -i\theta(t)e^{-i\varepsilon_k^x t}e^{\tilde{C}_k(t)}$$

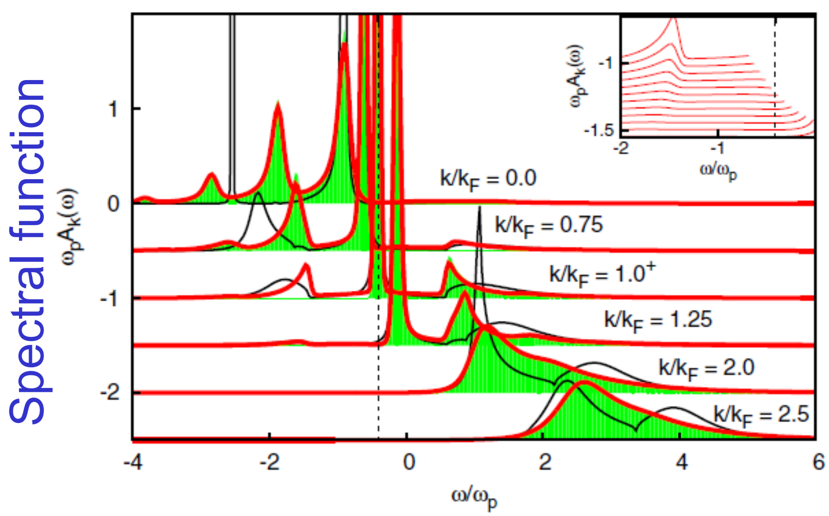
Natural separation of QP & exchange-correlation parts

Landau form of cumulant (1944)

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

$$A_k(\omega) \;=\; -\frac{1}{\pi}\mathrm{Im}\int d\omega e^{i\omega t}G_k(t)$$

Electron gas $r_s = 4$



* L. Hedin, J. Phys.: Condens. Matter **11** R489 (1999)
J.J. Kas, J. J. Rehr, and L. Reining, Phys. Rev. B **90**, 085112 (2014)

Ingredients at Finite T: GW Self-energy $\Sigma^{GW}(\omega,T)$

FT GW Self-energy*

$$\Sigma^{GW}(\omega,T) = \int d\omega' \frac{d^3q}{(2\pi)^3} |\mathrm{Im}\, W(q,\omega')| \times$$
$$\times \left[\frac{f(\varepsilon_{k-q}) + N(\omega')}{\omega + \omega' - \varepsilon_{k-q} + i\delta} + \frac{1 - f(\varepsilon_{k-q}) + N(\omega')}{\omega - \omega' - \varepsilon_{k-q} + i\delta} \right]$$

Bose & Fermi factors $N(\omega) = 1/(e^{\beta\omega} - 1)$ $f(\varepsilon) = 1/(e^{\beta(\varepsilon-\mu)} + 1)$

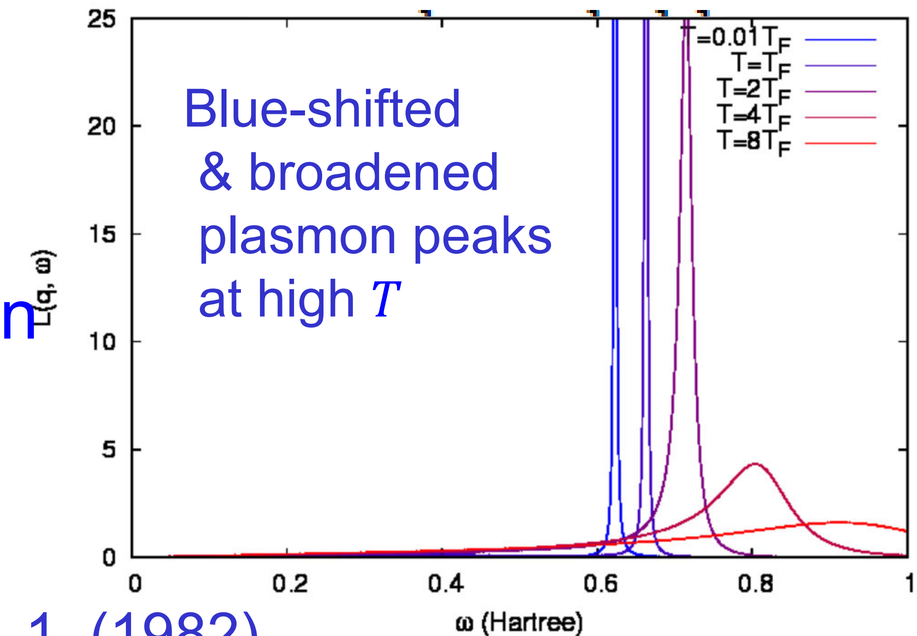
Screened Coulomb interaction $W(q,\omega)$

$$|\mathrm{Im}\, \epsilon^{-1}(q,\omega)|$$

$$|\mathrm{Im}\, W(q,\omega')| \sim |\mathrm{Im}\, \epsilon^{-1}(q,\omega)|$$

$\epsilon(q,\omega,T)$ FT RPA Dielectric function

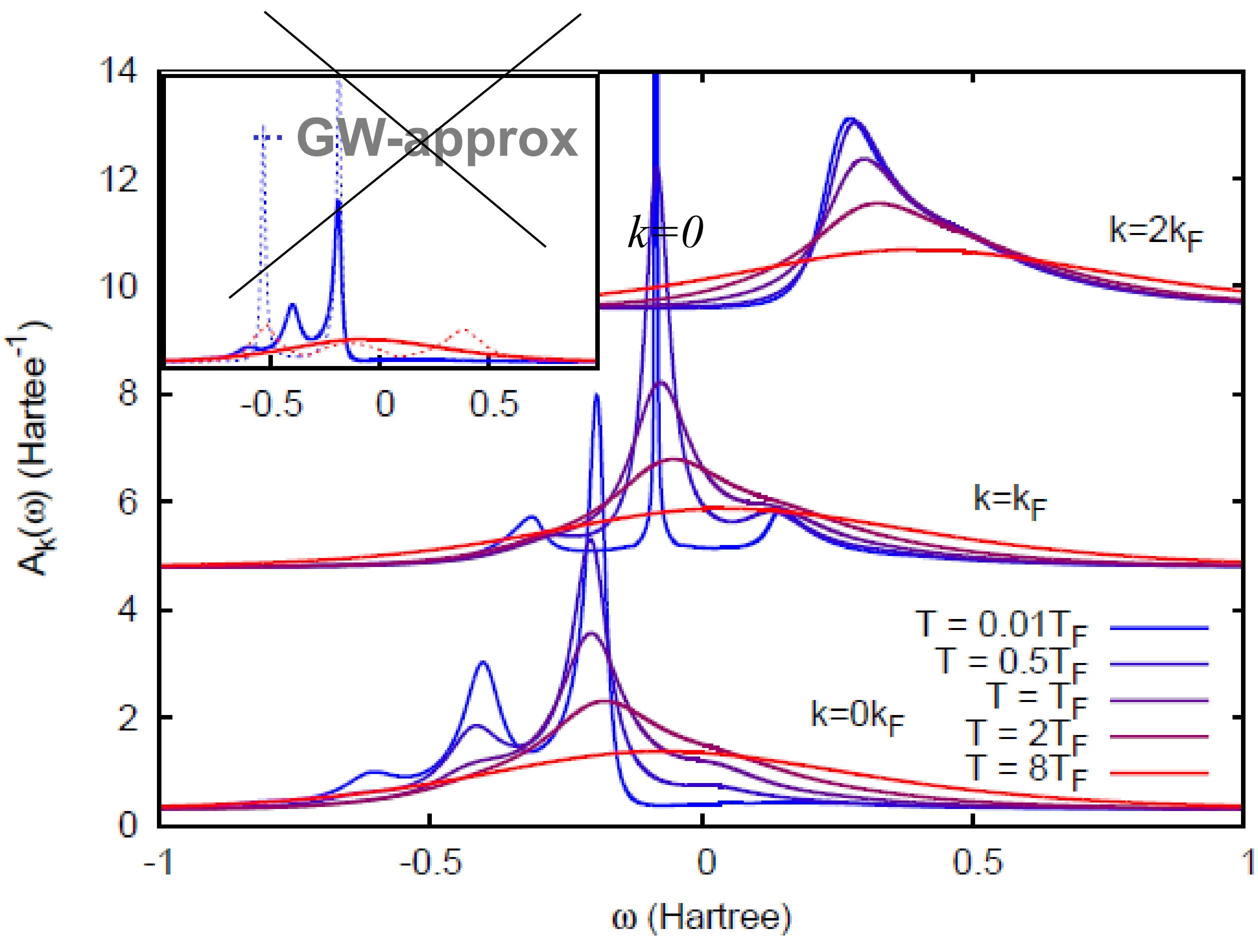
$$\epsilon(q,\omega) = 1 + 2v_q \int \frac{d^3k}{(2\pi)^3} \frac{f_{k+q} - f_k}{\omega - \varepsilon_{k+q} + \varepsilon_k}$$



*P.B. Allen & B. Mitrovic, Sol. St. Phys **37**, 1 (1982).

Finite-T Spectral-function $A_k(\omega, T)$

$$A_k(\omega, T) = -\frac{1}{\pi}\,\mathrm{Im}\; G_k(\omega, T)$$ ~ finite T XPS



Single broad peaks at high T above k_F

Blurred QP peaks and satellites at k_F

Calculations simplify at high T - no sharp satellite structure

Chemical potential & occupation numbers

Chemical potential $\mu(T)$ fixed by charge neutrality

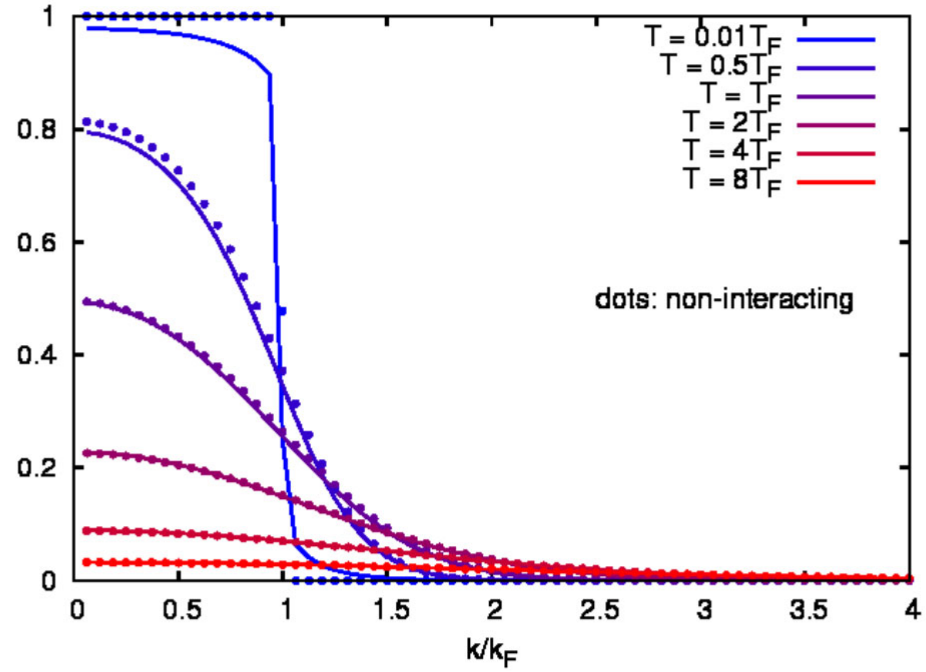
$$\boxed{\Sigma_{\mathbf{k}}\, n_k = \langle N(T) \rangle}$$

$$n_k(\mu, T) = \int_{-\infty}^{\infty} d\omega\, A_k(\omega) f(\omega)$$

$$f(\varepsilon) = 1/(e^{\beta(\varepsilon-\mu)} + 1)$$

QP Occupation number

n_k

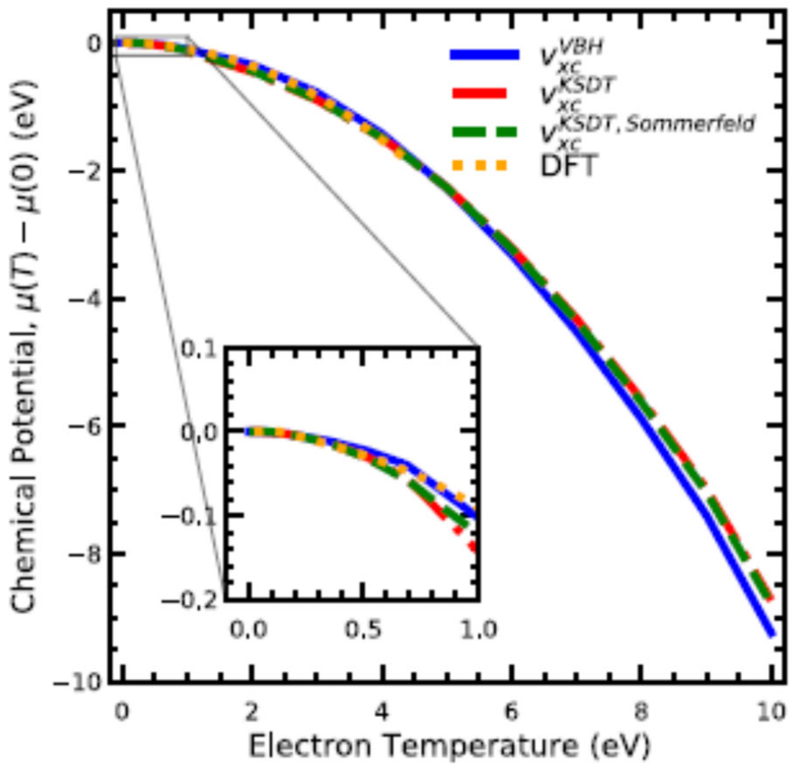


Increasingly metallic (plasmonic) behavior at high T

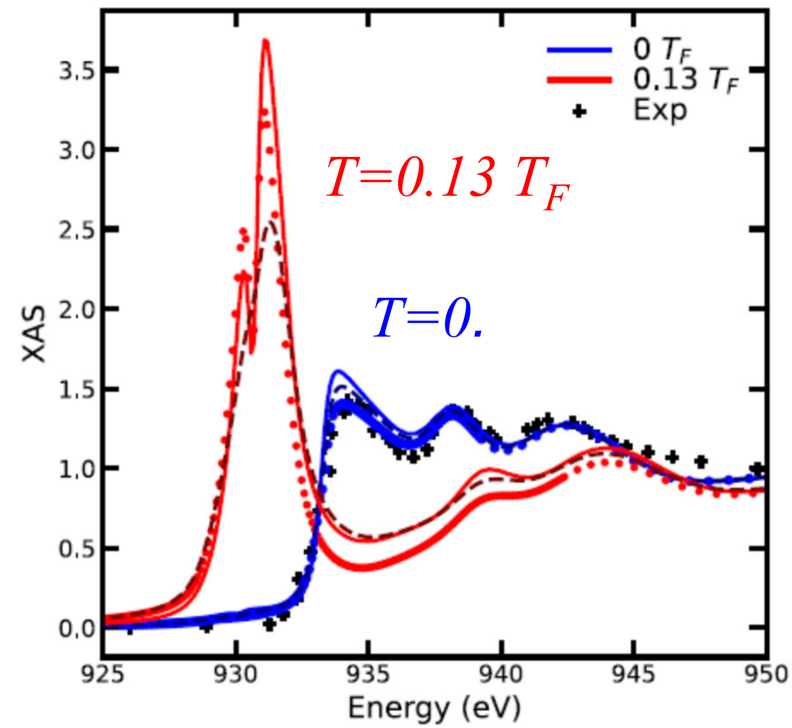
Finite T Chemical Potential* $\mu(n,T)$

"Continuum lowering "
edge-shifts to lower E

Chemical Potential $\boldsymbol{\mu(n,T)}$



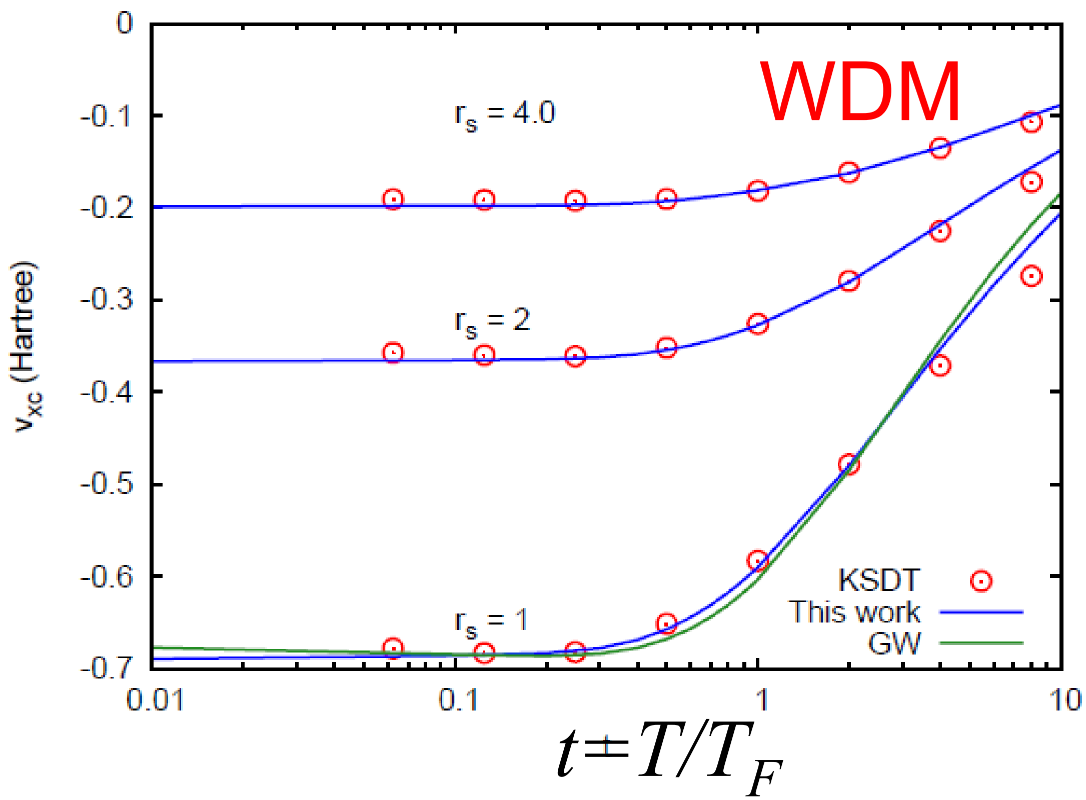
Cu-L XAS



*Tun S. Tan et al. Phys Rev. B **104**, 035104 (2021)

Finite T DFT Exchange-correlation Potential $v_{xc}(T)$

$$v_{xc}(T) \equiv \mu_{xc}(T) = \mu(T) - \mu_0(T)$$



Nearly constant $v_{xc}(T)$ $T < .3T_F$

Smaller in WDM

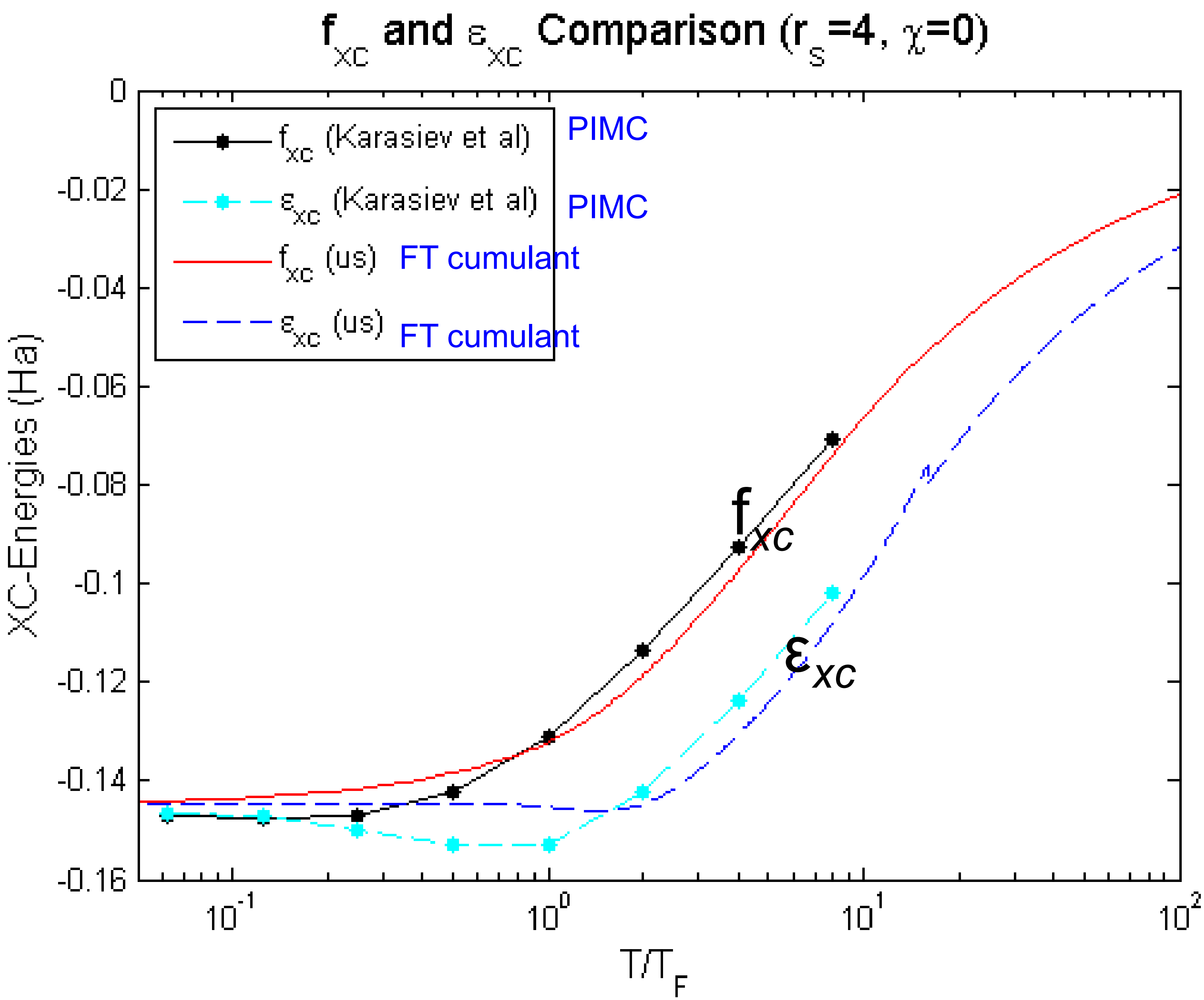
Finite T cumulant♦ $v_{xc}(T)$ in good agreement with Finite T DFT* functionals○

*N.D. Mermin, Phys. Rev. **137,** 1 (1965)

○ **KSDT** V.V. Karasiev, T.Sjostrom, J. Duffy and S.B. Trickey, Phys. Rev. Lett. **112**, 076403 (2014)

♦Retarded Cumulant (RC) JJ Kas et al, Phys. Rev. B **100**, 195144 (2019)

FT Exchange-correlation energy and free energy

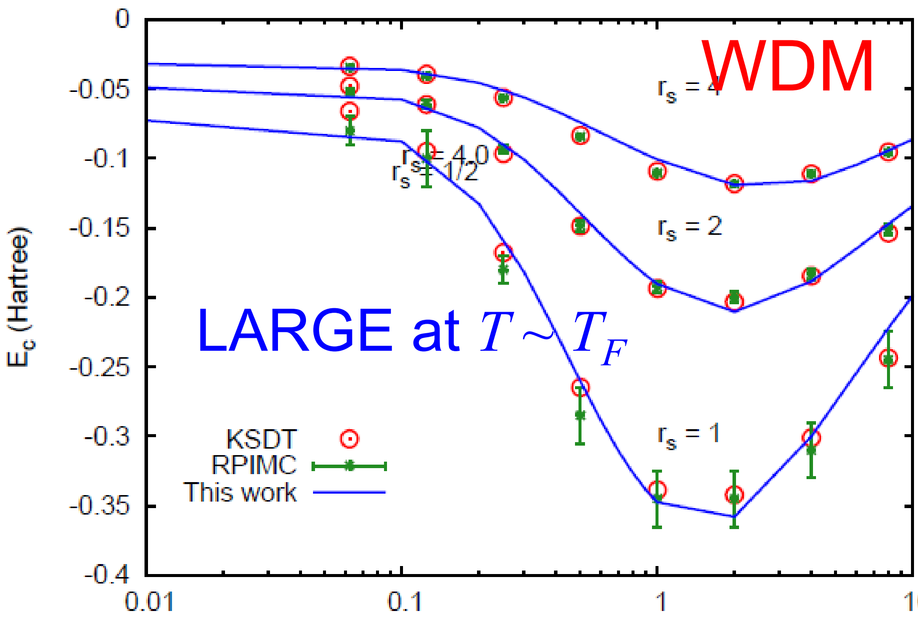


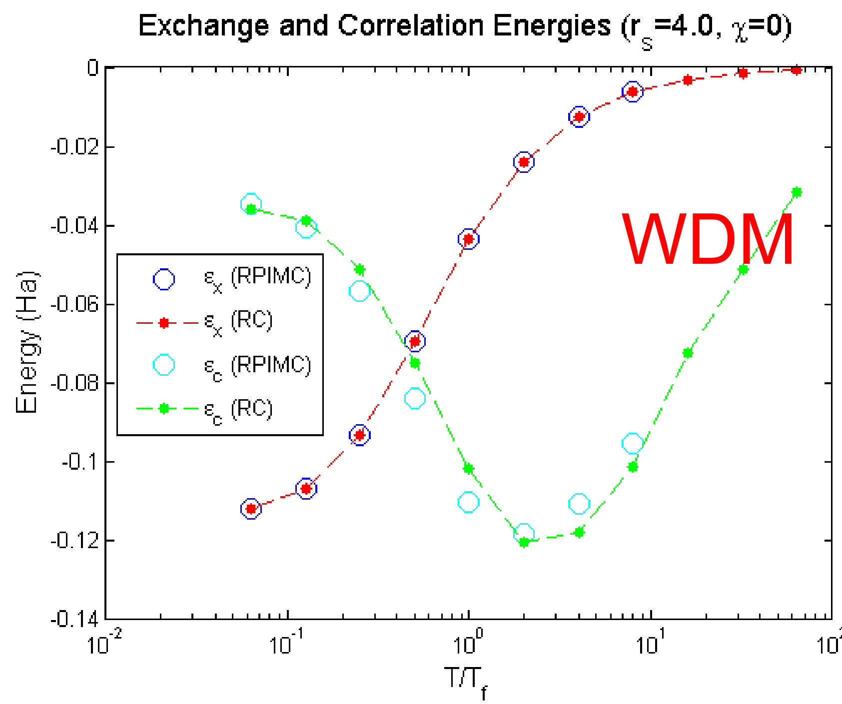
Finite T Correlation Energy*

Exchange-correlation ***crossover***
Weak temperature dependence $T < T_F$

Exchange **disappears** at high T
Correlation increases near T_F

$$\varepsilon_c = \varepsilon_{xc} - \varepsilon_x$$



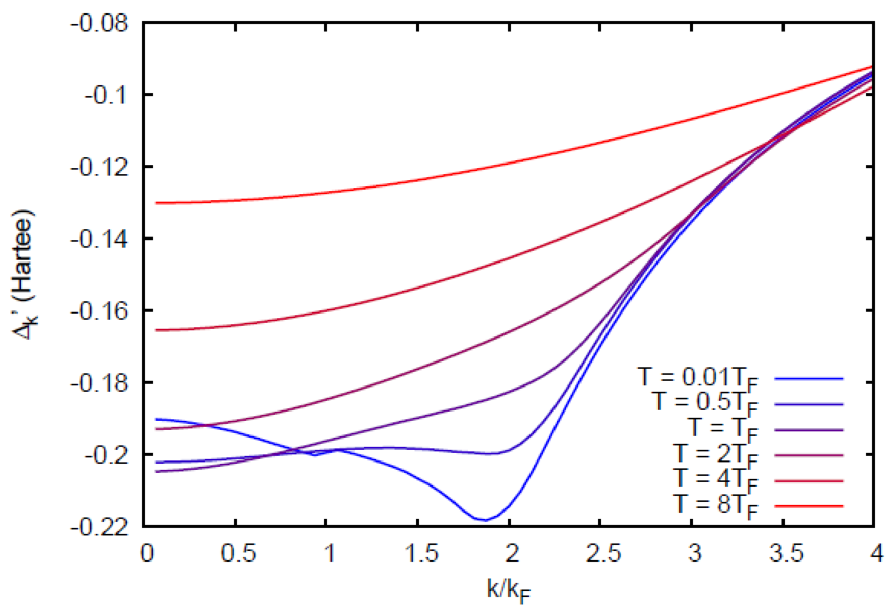


*RPIMC: W. Brown, D. Ceperley et al. Phys Rev Lett **110**, 146405 (2014)
◦ KSDT: V.V. Karasiev, et al, Phys. Rev. Lett. **112**, 076403 (2014)

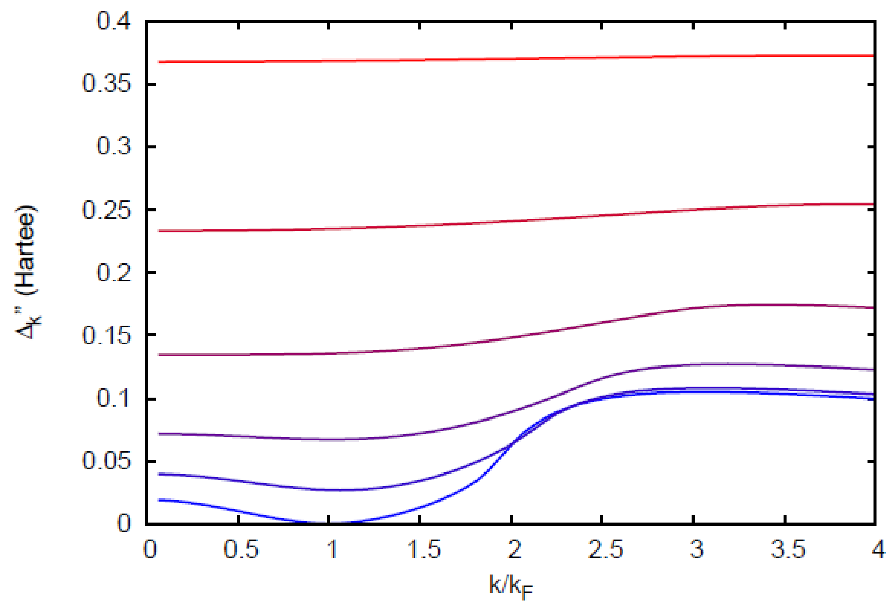
Quasi-particle energies & damping

$$\varepsilon_k^{qp} = \varepsilon_k + \Delta_k \qquad \Delta_k = \Sigma_k^x + \int d\omega \, \frac{\gamma_k(\omega)}{(\omega - i\delta)}$$

Energy shift Δ_k



Damping Δ_k''



Δ' decreases **BUT** Damping Δ'' increases with T

Band gaps & band structure *smeared* out at high T

Cross-over to *m*etallic - short-ranged plasma-like behavior

Corollary: Finite- T TDDFT kernel $f_{xc}\,(T)$

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Eur. Phys. J. B (2018) 91: 153 DOI: 10.1140/epjb/e2018-90063-3

Exchange and correlation in finite-temperature TDDFT*

John J. Rehr[a] and Joshua J. Kas

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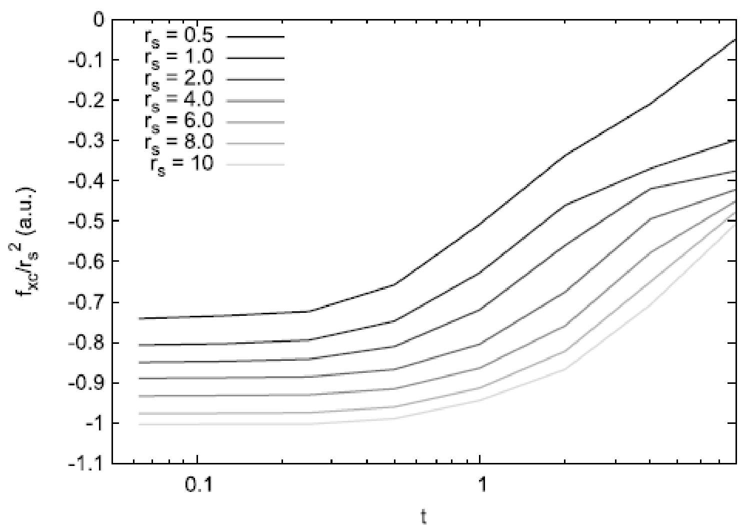
$$
\begin{aligned}
f_{\mathrm{xc}}(T,n) &= \frac{\partial \mu_{\mathrm{xc}}(T,n)}{\partial n}\delta(\mathbf{r}-\mathbf{r}'), \\
&= \frac{\partial^2[n a_{\mathrm{xc}}(T,n)]}{\partial n^2}\delta(\mathbf{r}-\mathbf{r}')
\end{aligned}
$$

FT-TDDFT $f_{xc}\,/r_s^{\,2}$



Needed for finite T optical spectra, inelastic losses

Example: Finite T XAS

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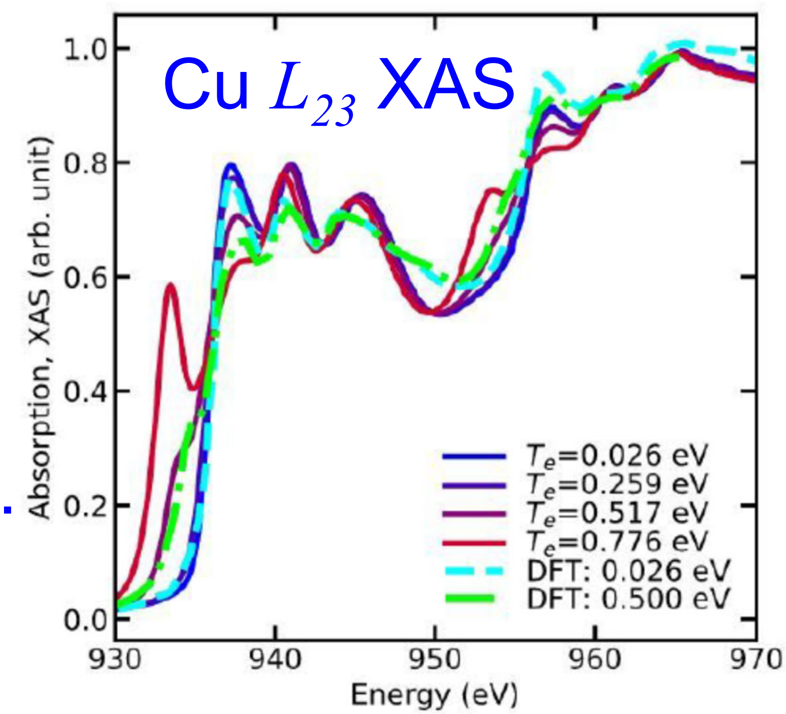
Ab initio **calculation of X-ray and related core-level spectroscopies: Green's function approaches**

Joshua J. Kas, * Fernando D. Vila, Tun S. Tan and John J. Rehr

Useful probe of finite-T structure temperature and excitations

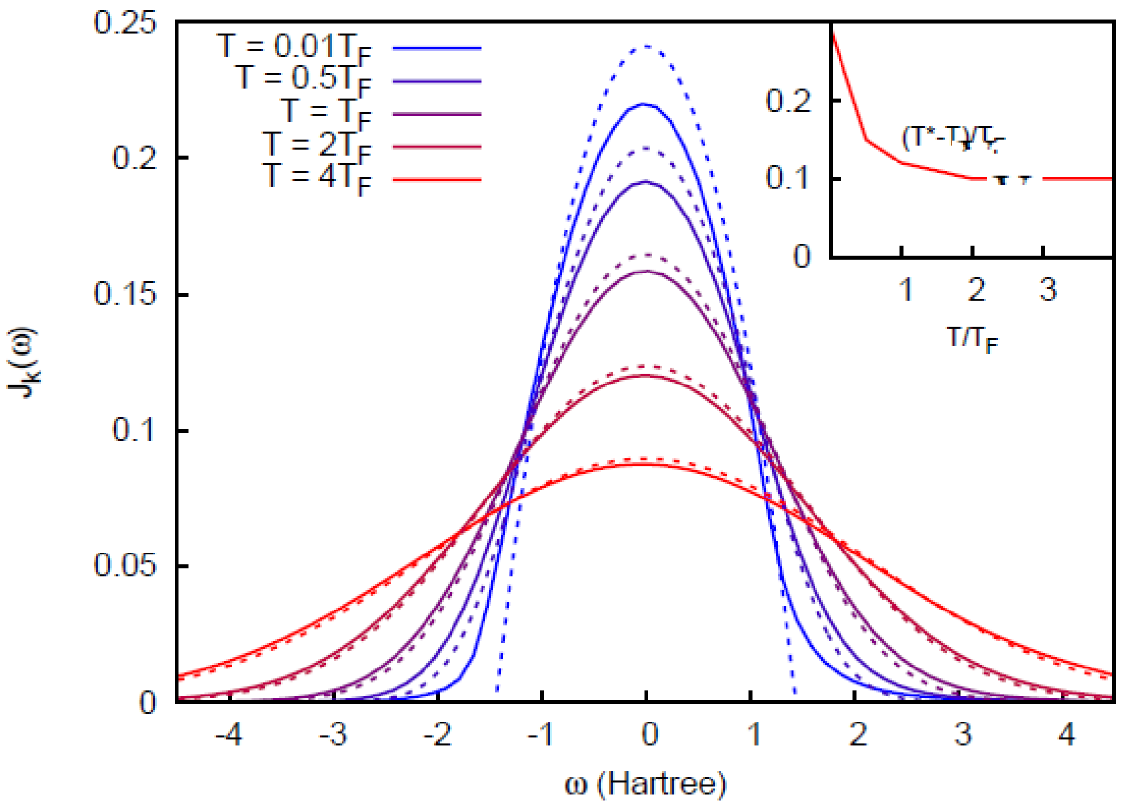
Large T-dependence in XAS *red-shifted edges*, broadening, …



Example: Finite-temperature Compton Profile*

$$J_q(\omega) = \int d^3k\, d\omega' A_{\mathbf{k}}(\omega') A_{\mathbf{k+q}}(\omega+\omega') f(\omega') f(\omega+\omega')$$

Comparison of cumulant (solid) vs free electron (dotted)



Many-body effects give "effective temp" T^* correction

Useful thermometer for WDM

*W. Schulke, G. Stutz, F.Wohlert, and A. Kaprolat, Phys. Rev. B **54**, 14381 (1996)

Example: Transient XAS of Warm Dense Matter

Nature Physics ***20***, 1564-1569 (2024).

EU XFEL Expt

Transient Absorption of Warm Dense Matter Created by an X-ray Free-Electron Laser

Laurent Mercadier,[1,*] Andrei Benediktovitch,[2] Špela Krušič,[3] Justine Schlappa,[1] Marcus Agåker,[4] Robert Carley,[1] Giuseppe Fazio,[6] Natalia Gerasimova,[1] Young Yong Kim,[1] Loïc Le Guyader,[1] Giuse Mercurio,[1] Sergii Parchenko,[1] Jan-Erik Rubensson,[4] Svitozar Serkez,[1] Michal Stransky,[1,7] Martin Teichmann,[1] Zhong Yin,[1] Matjaž Žitnik,[3] Andreas Scherz,[1] Beata Ziaja,[2,7,†] and Nina Rohringer[2]

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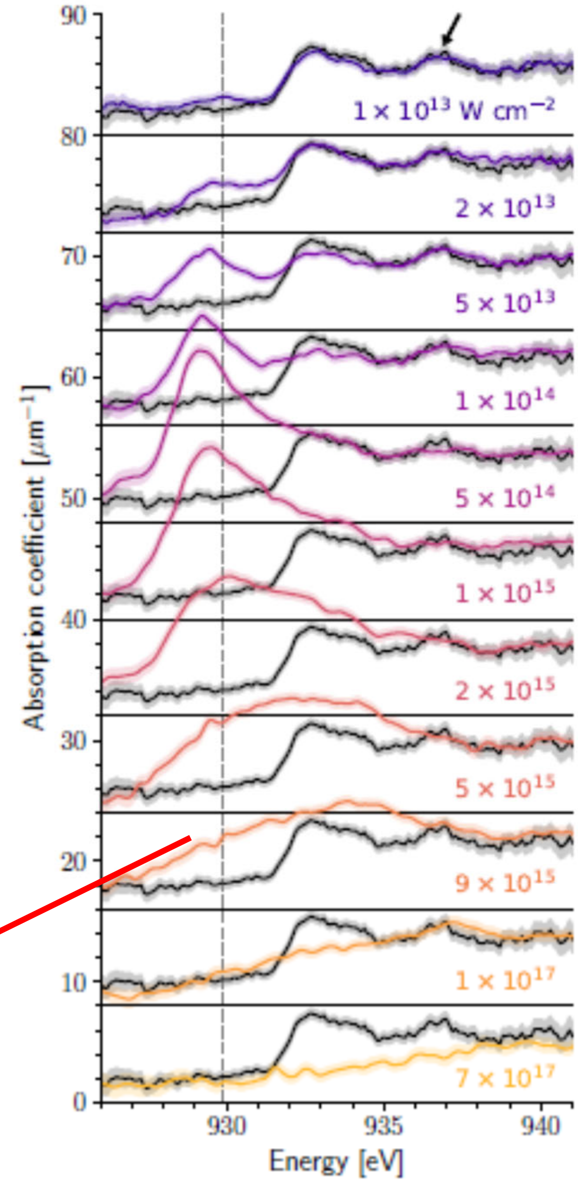


Experiment:
L-edge XAS of Cu from ultra-short 15 fs, 932 eV XFEL X-ray pulses vs pulse intensity (red)

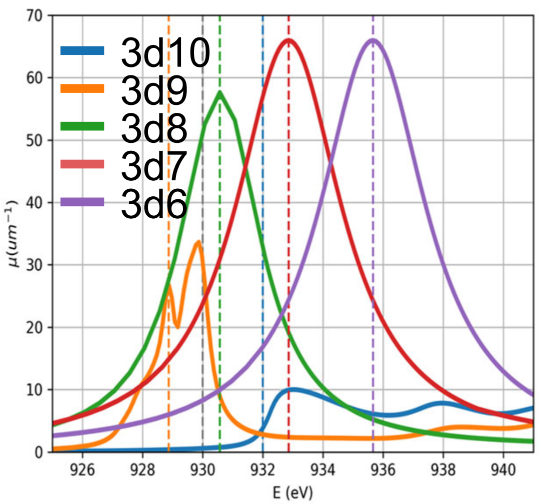
Cross-over: RSA to SA with increased intensity

Transient high fluence XAS theory vs expt

Theory*

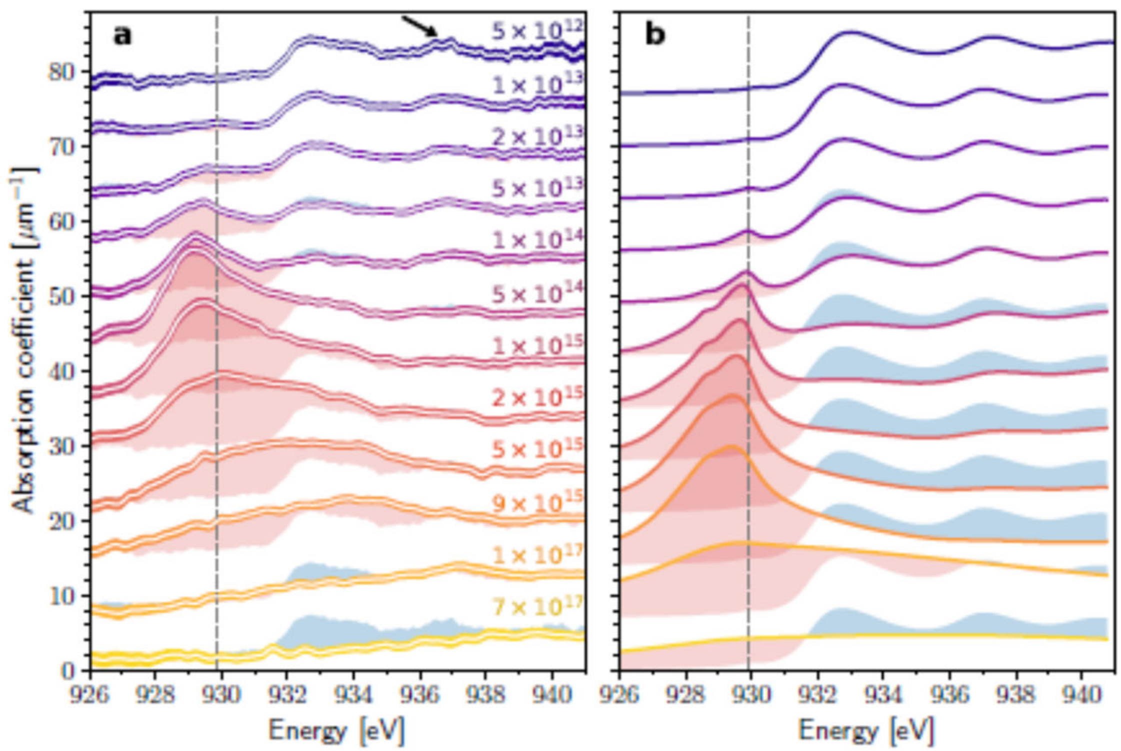
SCF FEFF10 results averaged over Boltzmann weighted $3d$ * configurations vs pulse intensity

XAS vs 3d occupation



Experiment

Theory*



Cross-over: RSA to SA with increased intensity

RSMS Theory - A. Benediktovitch & J.J. Kas

Boltzmann equations simulations - B. Ziaja

FEFF10: J.J. Kas et al. PCCP **24,** 13461 (2022)

Summary and Conclusions

- Theory of XPS, XAS, etc. from Cumulant-spectral function

- Cumulant spectral function explains quasi-particle line-shapes and satellites in XPS beyond QP theory

- Convolution with Spectral function explains satellites & inelastic losses in X-ray spectra

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

- Many extensions: particle-hole GF finite-T, thermodynamic properties, extreme conditions

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B. Peng	T. Devereaux	G. Hug	S. Vimolchaleo
R. C. Albers	and many others		

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That's all folks