Los Alamos Computational Condensed Matter Summer School 2026

I. Theoretical X-ray Spectroscopy: Fundamentals and Applications

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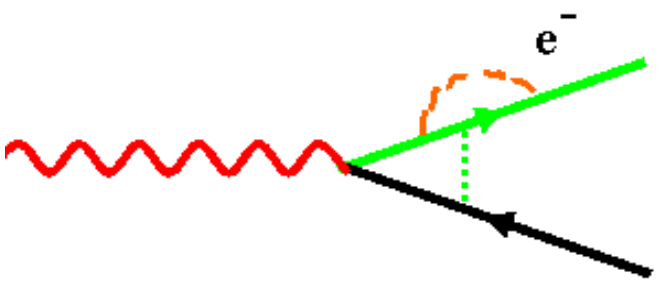

UNIVERSITY OF WASHINGTON
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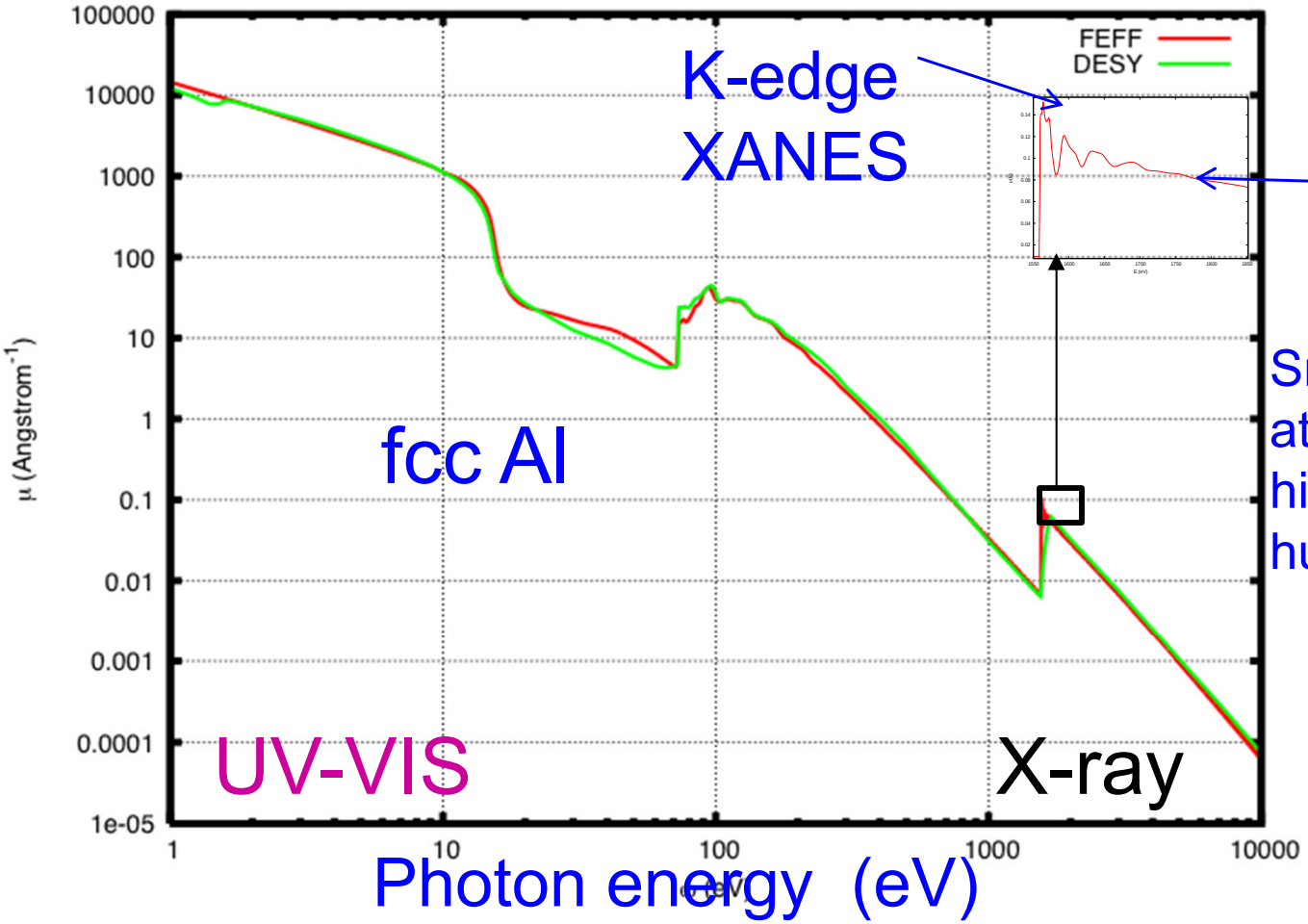
Theoretical X-ray Spectroscopy: Fundamentals and Applications

TALK

I. **Introduction – Challenge of x-ray spectra**
II. **Green's function theory of XAS**
III. **Implementation: FEFF codes**
IV. **Applications: EXAFS, XANES, EELS, etc.**
V. **Extensions**

I. Introduction : Challenges in X-ray Spectra

Full spectrum XAS Theory vs Experiment

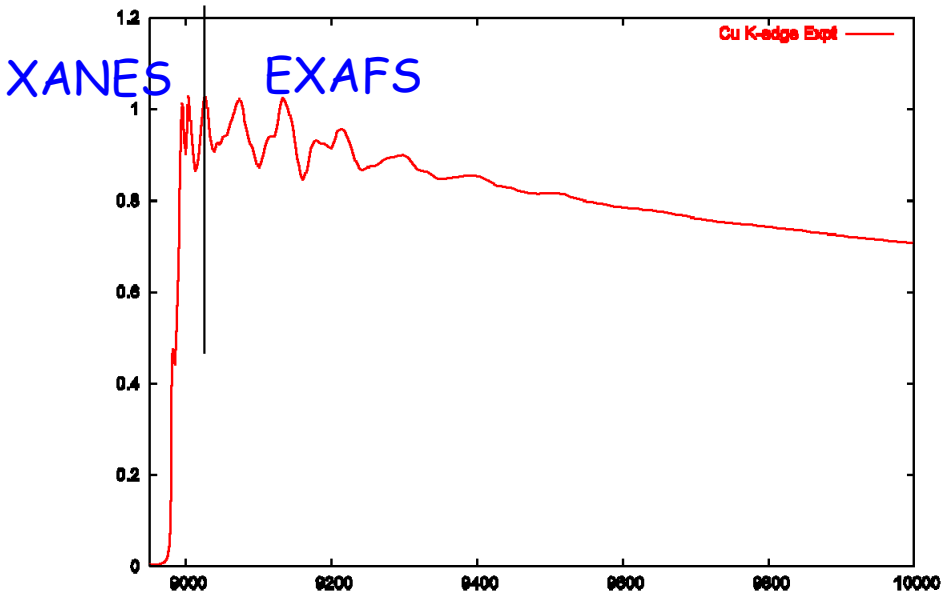


Small correction to atomic XAS – need high accuracy & huge energy range

"All of physics in a single experiment" ...

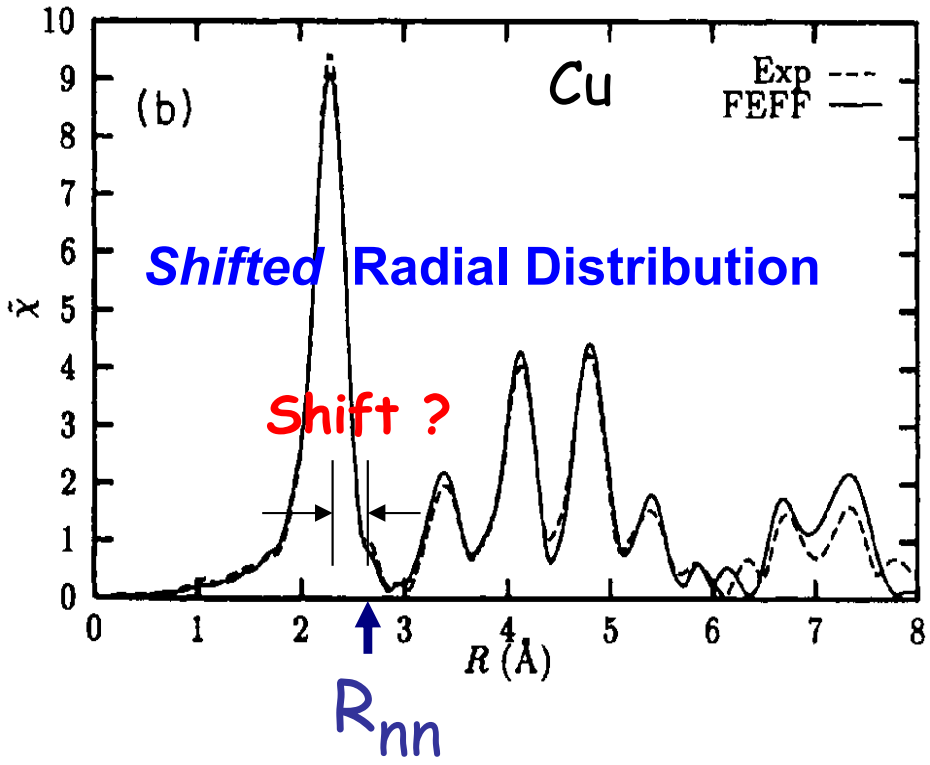
Historical Interpretation of XAS 1971*

EXAFS → Local structure



→ X-ray Microscope!

EXAFS Fourier Transform

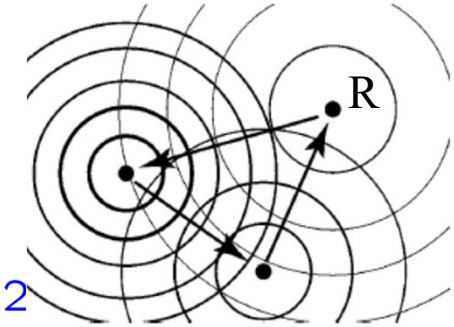


*Stern Sayers Lytle, UW 1971

BUT need to calibrate experiment with "Standard"

Challenge: Theory of EXAFS Equation*

Scattering picture of fine-structure in EXAFS



$$\chi(k) = S_0^2 \sum_R \frac{|f_{\text{eff}}(k)|}{kR^2} \sin(2kR + \Phi_k) e^{-2R/\lambda_k} e^{-2\sigma^2}$$

??? Several many-body effects observed in experiment

Mean free paths $\lambda_k \sim 5 - 20$ Å

Vibrational Debye Waller factors $e^{-2\sigma^2 k^2}$

Shakeup reduction factor S_0^2

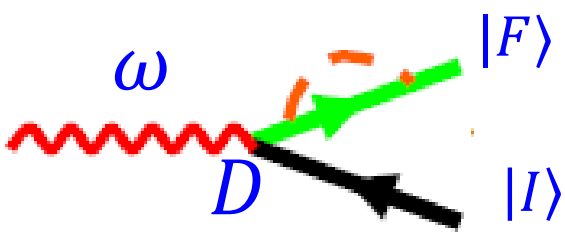
Need accurate scattering amplitudes $f_{\text{eff}}(k)$ phase shifts Φ_k and theory beyond independent electron approximation

*D.E. Sayers, E.A.Stern and F.W. Lytle, Phys. Rev. Lett. 27, 1204 (1971)

Exact Formal Theory: Fermi's golden rule ???

Fermi golden rule for XAS

$$\mu(\omega) \sim \sum_{IF} |\langle I|D|F\rangle|^2 \delta(\omega + E_I - E_F)$$



Need to calculate all **many-body** initial $|I\rangle$ and final $|F\rangle$ states and then sum over transition matrix elements

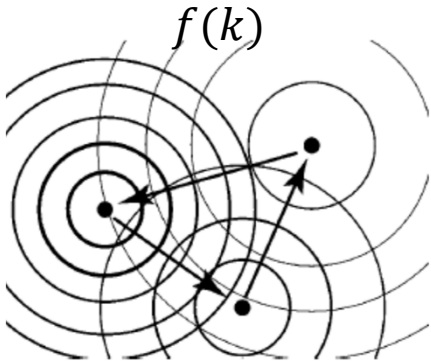
Computationally prohibitive for large $\omega \sim 10^3$ eV

➡ Sum over states computational bottleneck!

Plane wave approximation for back-scattering amplitude $f(k)$ *FAILS*

Textbook plane wave scattering amplitudes in EXAFS equation are inaccurate

$$f(k) = \sum_l (2l+1)(-1)^l e^{\delta_l} \sin \delta_l$$

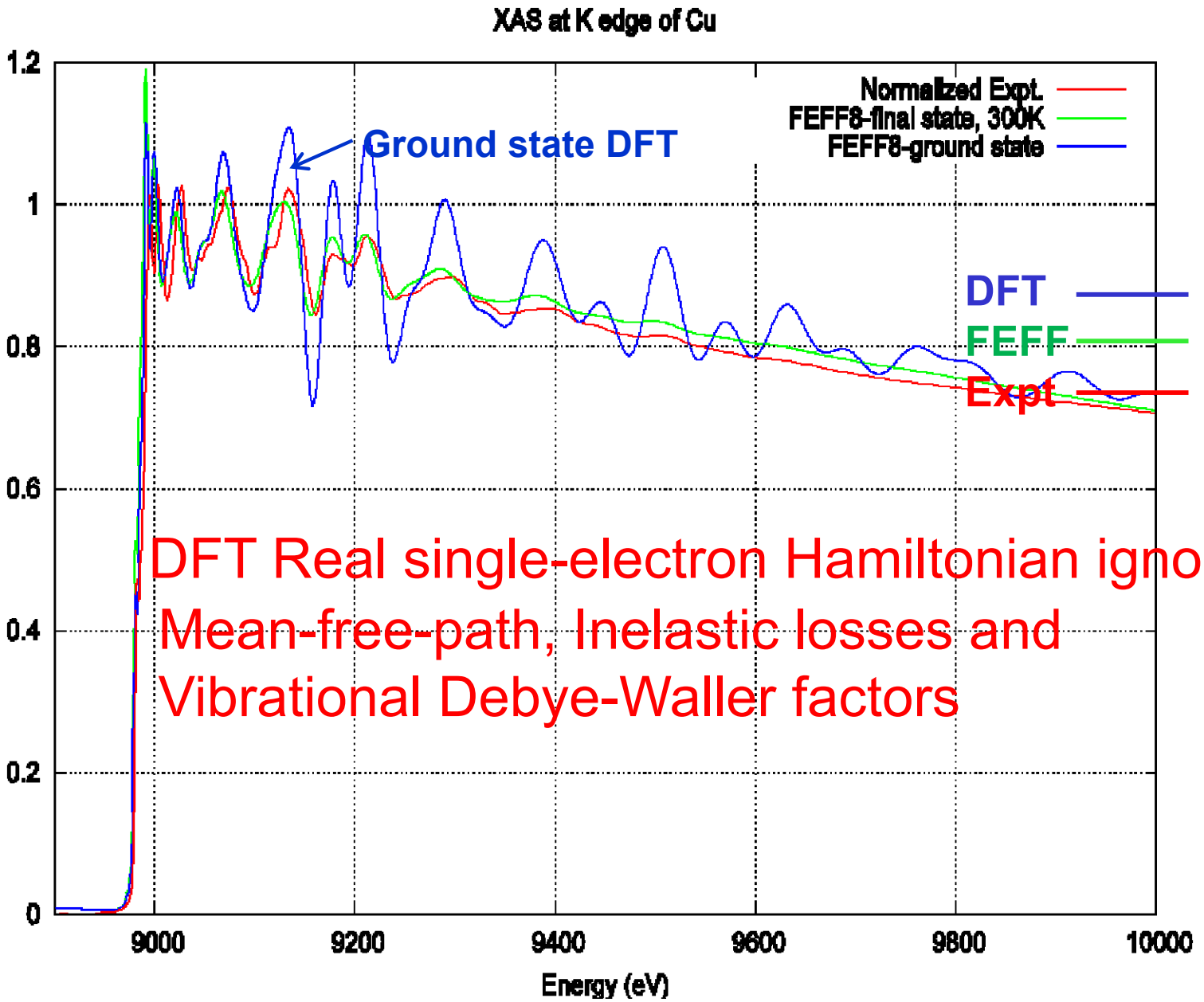


Large phase shift corrections $\sim e^{il(l+1)/2kR}$

Need curved-wave scattering theory f_{eff}

$$f_{\mathrm{eff}}(k) = \sum_l (2l+1)(-1)^l \, e^{\delta_l} \sin \delta_l \, C_l(kR)$$

Standard DFT *Fails*



”I always thought it was easier to

measure XAS than to calculate it.”

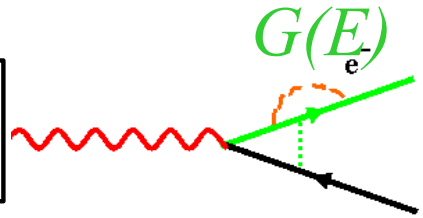
Hans Bethe

ca 1980

II Green's Function Theory of XAS

Golden rule via Green's Functions

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



$$G(E) \equiv \sum_f \frac{|f\rangle\langle f|}{E - E_f + i\delta} \quad E = \omega + E_i - E_f$$

Implicitly sums over final states

Equivalent to Fermi golden rule

$$\mu(E) = \Sigma_f \langle i|\hat{\epsilon}\cdot r'|f\rangle\langle f|\hat{\epsilon}\cdot r|i\rangle\delta(\omega + E_i - E_f)$$

What's a Green's function?

cf. Wave function in QM $(H - E)\,\Psi = 0$

$\Psi(r)$ = Amplitude to find particle at r

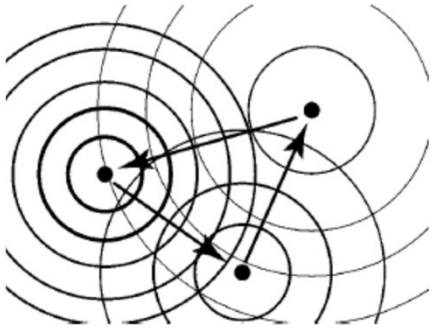
Green's function $(H - E)\,G = -\,\delta(r-r')$

$G(r,r',E)$ *aka Propagator*

= Amplitude to propagate particle from r to r'

$-\,\mathrm{Im}\,G = -\mathrm{Im}\,1/(E-H+i\,\delta) \sim$ density of states $\rho(E)$

R_x for EXAFS



Theory must explain EXAFS formula

$$\chi(k) = S_0^2 \sum_R \frac{|f_{\text{eff}}(k)|}{kR^2} \sin(2kR + \Phi_k) e^{-2R/\lambda_k} e^{-2\sigma^2 k^2}$$

Single and multiple scattering contributions R

Mean free paths $\lambda_k \sim 5 - 20$ Å

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

Curved wave scattering theory, $E \sim 10^4$ eV $l \sim 25$ f_{eff} Φ_k

Dirac-Fock Atomic core levels

Core-hole lifetime Γ and **core-hole potential** V_c

Basis: Local site - angular momentum states $|\, i\, L\,\rangle$

$$\mu(\omega) \propto \mathrm{Im} \sum_i \langle i | d^\dagger G(\omega + E_i) d | i \rangle \, \theta_\Gamma(\omega + E_i - E_{Fermi}) \; S_0^2$$

Insert complete set of states $1 = \sum_L |i,L\rangle\langle i,L|$ $L=(\kappa,\mu)$

Relativistic basis

Matrix elements

$$\mu(\omega) \propto \mathrm{Im} \sum_{iLL'} \langle i | d^\dagger | i,L \rangle \, G_{LL'}(\omega + E_i) \, \langle i,L' | d | i \rangle \, \theta_\Gamma(\omega + E_i + E_{Fermi}) \, S_0^2$$

Green's Function Matrix at site i

Breakthrough: Curved wave single scattering theory f_{eff}

PHYSICAL REVIEW B VOLUME 34, NUMBER 6 15 SEPTEMBER 1986

New high-energy approximation for x-ray-absorption near-edge structure

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(Received 14 April 1986)

Asymptotic high energy curved wave single scattering theory

0 ⟶ R

$$G^c t G^c = \Sigma_L G_{L_0 0,LR} t_{LR} G_{LR,L_0 0} \sim \frac{f(\pi,R)}{kR^2} e^{2ikR}$$

$$\tilde{f}(\pi,R) = \frac{1}{k}\sum_l (-1)^l (2l+1) t_l \times \left[\frac{(l+1)c_{l+1}^2(kR) + l c_{l-1}^2(kR)}{2l+1}\right] = \mathrm{f_{eff}}$$

Effective Backscattering Amplitude
Fixes errors in plane-wave approximation

Dirac-Fock Atomic Properties

Computer Physics Communications 98 (1996) 359–364

Single configuration Dirac–Fock atom code

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

[b] *Microsoft Corporation, Redmond, WA 98052, USA*

*Automated Desclaux Dirac-Fock atomic code for all atoms in periodic table with arbitrary electron configurations

Spinor-relativistic theory with spin-orbit built in

**Now includes all atoms up to $Z=138$, some undiscovered

*J.P. Desclaux, At. Data. Nucl. Data. Tables **12**, 311 (1973)

Z. Zhou et al., At. Data. Nucl. Data. Tables **114, 262 (2017)

Self-energy and Mean free paths

DFT fails $V_{xc} \rightarrow \Sigma(E)$ Complex electron self-energy

"Dynamically screened exchange -correlation potential"

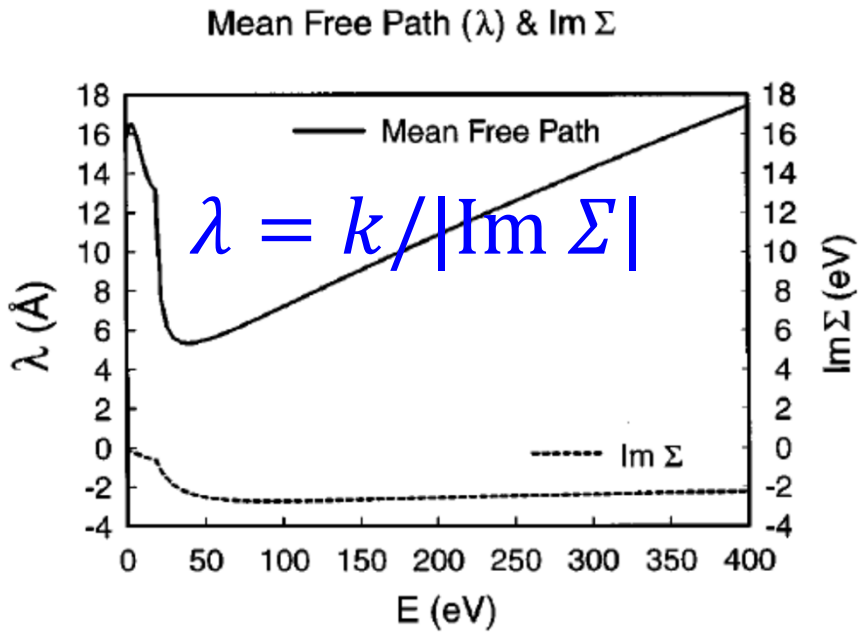
$$\Sigma(E) = \mathrm{i}\, G\, W = \mathrm{i}\, Gv/\epsilon$$

Standard approximation: Hedin-Lundqvist GW

plasmon pole model

$$\frac{1}{2}p^2 + \Sigma(E) = E, \qquad p = k + \frac{i}{\lambda}$$

$$MFP \;\; \boldsymbol{\lambda} = k/|\mathrm{Im}\, \boldsymbol{\Sigma}(\boldsymbol{E})|$$



Explains short range nature of EXAFS

EXAFS Debye Waller Factors

Phys. Rev. B **20**, 4908 (1979)

Extended x-ray absorption fine structure Debye-Waller factors. I. Monatomic crystals

E. Sevillano and H. Meuth
Aerospace and Energetics Research Laboratory, University of Washington, Seattle, Washington 98195

J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195

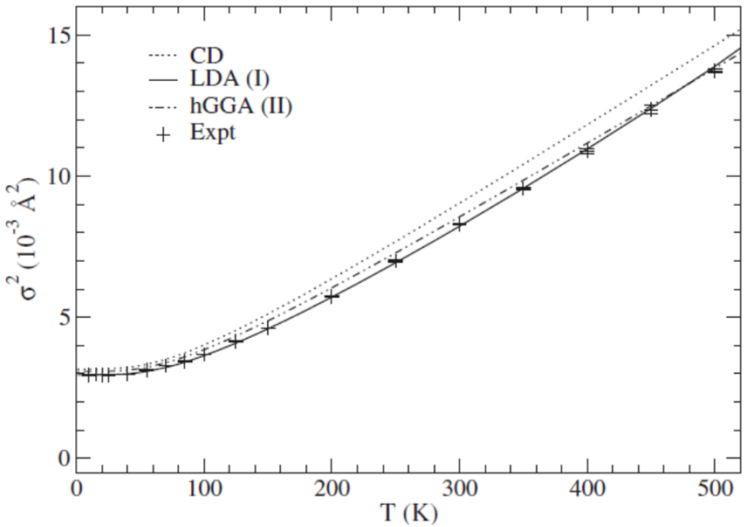
EXAFS DW Factor $e^{-2\sigma^2 k^2}$

Mean square radial disorder $\sigma^2 = \langle [(u_R - u_0) \cdot \hat{R}]^2 \rangle$

e.g.: Correlated Einstein model

$$\sigma^2 = \frac{\hbar}{M\omega_E} \coth\left(\frac{\beta\hbar\omega_E}{2}\right) \rightarrow \frac{k_B T}{\kappa}$$

➡ "EXAFS melts at high T"



Results: Accurate theoretical EXAFS phase shifts*

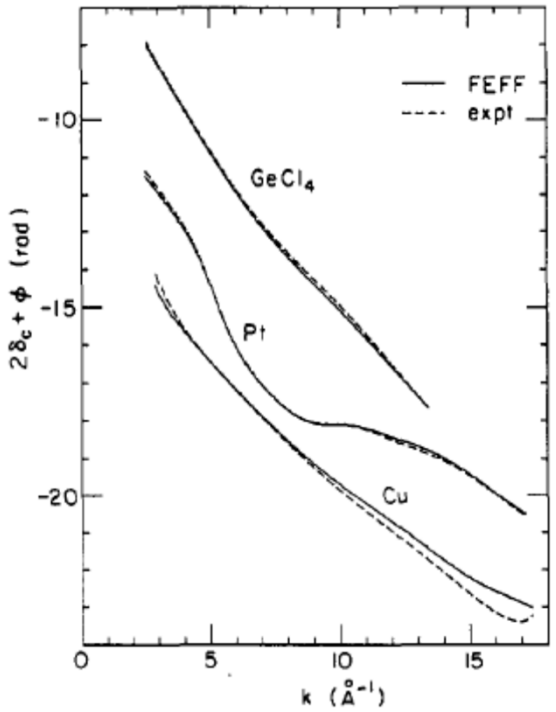
JACS **113**, 5136 **(1991)**

Theoretical X-ray Absorption Fine Structure Standards

J. J. Rehr,*,† J. Mustre de Leon,†,‡ S. I. Zabinsky,† and R. C. Albers§

Contribution from the Department of Physics, FM-15, University of Washington, Seattle, Washington 98195, and Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545. *Received November 13, 1990*

Abstract: Theoretical X-ray absorption fine structure (XAFS) standards are developed for arbitrary pairs of atoms throughout the periodic table ($Z \leq 94$). These standard XAFS spectra are obtained from *ab initio* single-scattering XAFS calculations, using an automated code, FEFF, which takes into account the most important features in current theories: (i) an exact treatment of curved-wave effects; (ii) approximate molecular potentials derived from relativistic atoms, (iii) a complex, energy-dependent self-energy; (iv) a well defined energy reference. FEFF also yields tables of XAFS phases and amplitudes as well as mean-free paths. Sample results are presented and compared with experimental results and with earlier work. We find that these theoretical standards are competitive with experimental standards, permitting XAFS analysis at lower wavenumbers and yielding distance determinations typically better than 0.02 Å and coordination numbers typically better than 20%. These standards also provide theoretical tests of chemical transferability in XAFS.

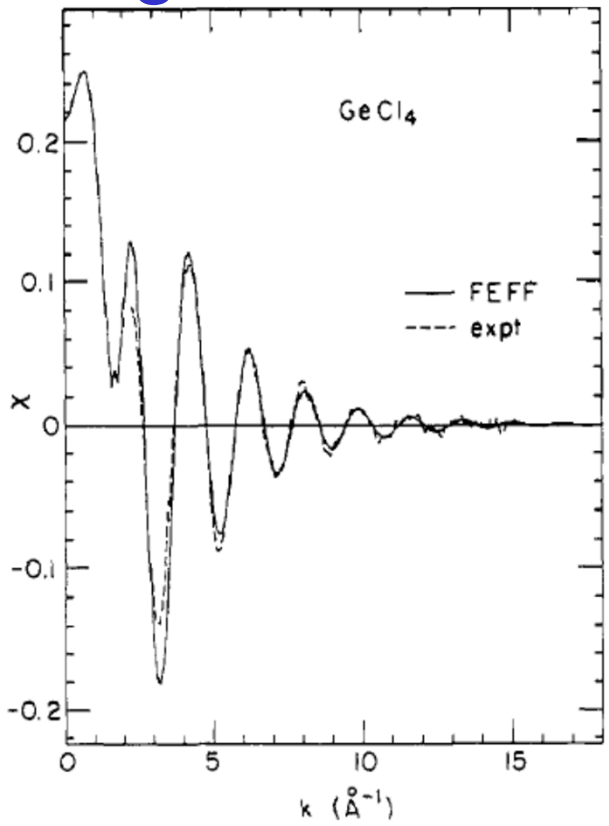


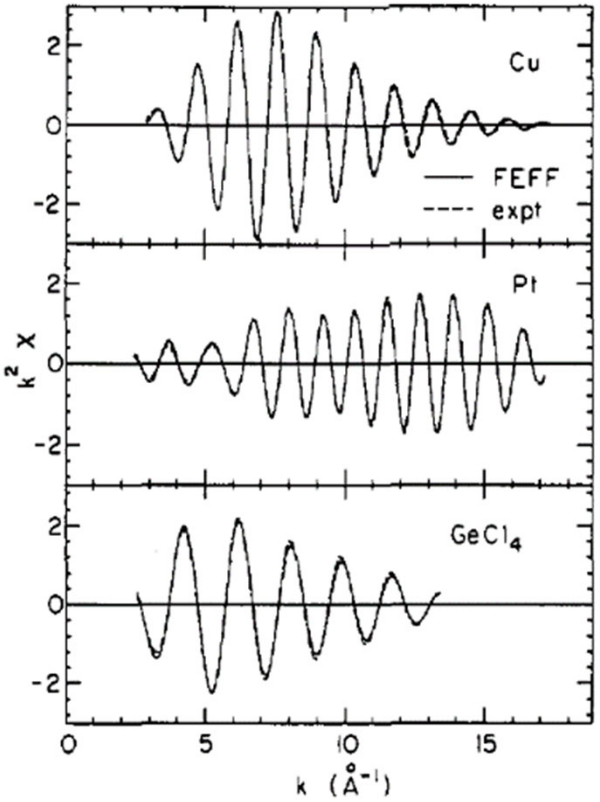
Explains distance shifts in EXAFS Fourier transforms

Eliminates need for empirical EXAFS standards

Results: Accurate single-scattering EXAFS

Good agreement of FEFF with experiment





Eliminates need for empirical EXAFS standards

Single scattering EXAFS mostly solved !

Next challenge: Multiple Scattering Theory

Three key steps

1) Separate V(r) into local e.g. muffin-tin potentials

$$V(r) = \sum v_R(r)$$

2) Calculate intra-atomic scattering to all orders, i.e. on-site scattering t-matrices:

$$t_R = v_R + v_R G^0 t_R = e^{i\delta_R} \sin(\delta_R)$$

3) Express G in terms of t_R and off site propagators

$$\overline{G}_{RR'} = G_{RR'}(1 - \delta_{RR'})$$

Real-space Multiple scattering Equations

Dyson's equation: $G = G^0 + G^0 V G$

Iterating: $G = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots$

Atomic pot. partition

$V = \sum_i v_i$

$G = G^0 + \sum_i G^0 v_i G^0 + \sum_{ij} G^0 v_i G^0 v_j G^0 + \ldots$

Site scatt. *t*-matrix

$t_i = v_i + v_i G_0 t_i$

~~$G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \ldots$~~

Large matrix dimensions of G and t at high energies

Breakthrough: Separable Green's function propagators

PHYSICAL REVIEW B VOLUME 41, NUMBER 12 15 APRIL 1990-II

Scattering-matrix formulation of curved-wave multiple-scattering theory: Application to x-ray-absorption fine structure

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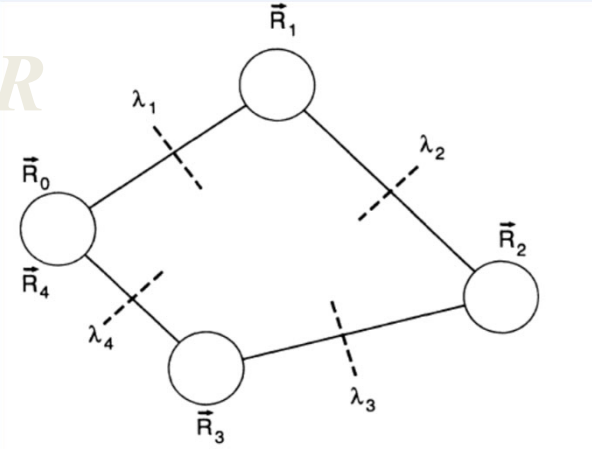
(Received 13 January 1989; revised manuscript received 4 January 1990)

$$G_{L,L'}(\boldsymbol{\rho}) = \frac{e^{i\rho}}{\rho} \sum_{\lambda} \tilde{\Gamma}^{L}_{\lambda}(\boldsymbol{\rho}) \Gamma^{L'}_{\lambda}(\boldsymbol{\rho})$$

$\rho = kR$



Fast, accurate separable GF and high-order real-space multiple-scattering *path expansion*

Cut diagrams

Exact for single-scattering

Curved wave multiple scattering amplitudes f_{eff}

MS Path amplitude

$$\chi_\Gamma(p) = \mathrm{Im}\, S_0^2 \frac{e^{i(\rho_1+\rho_2+\cdots\rho_N+2\delta_1)}}{\rho_1\rho_2\cdots\rho_N} e^{-\sigma_\Gamma^2 p^2/2} \times \mathrm{Tr}\, M_\ell F^N \cdots F^2 F^1 .$$

Fast accurate MS path approx. with 6x6 RA matrices

⇨ Effective scattering amplitude f_{eff} for any MS path Γ
Explains multiple-scattering EXAFS equation

$$\chi_\Gamma(k) = S_0^2\, \mathrm{Im} \frac{f_{\mathrm{eff}}}{kR^2} e^{2ikR+2i\delta_\ell} e^{-2\sigma^2 k^2}$$

*J.J. Rehr and R.C. Albers, Phys. Rev. B **41**, 8139 (1990)

RA Scattering-matrix theory

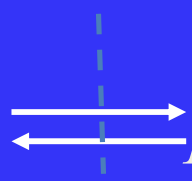
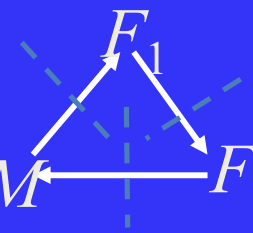
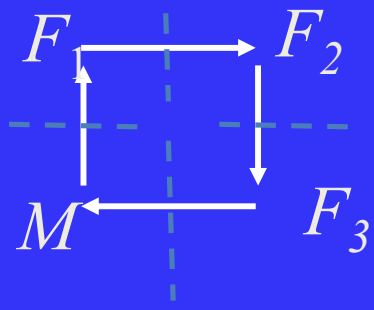
$$\mu = \mu_0 (1 + \chi)$$

χ = EXAFS

$$G = G_c + G_c T G_c + G_c T G^0 T G_c + G_c T G^0 T G^0 T G_c + \ldots$$

Efficient Rehr-Albers scattering matrix formulation

$$\chi = M F + M F_1 F_2 + M F_1 F_2 F_3 + \ldots$$

Fine Structure $\chi = M$  $F + M$  $F_2 +$ 

RA cut diagram expansion 6x6 F matrices

Anharmonic Debye Waller Factors

PHYSICAL REVIEW B VOLUME 48, NUMBER 1 1 JULY 199

Thermal expansion and x-ray-absorption fine-structure cumulants

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$\langle e^{2ikR} \rangle = \exp[\sum_n \frac{C_n (2ik)^n}{n!}]$ cumulants $C_n = \langle R^n \rangle_c$

$= e^{2ik\,(R+C_1)} + e^{-2k^2 C_2} + e^{-i\frac{4}{3} C_3 k^3} + \ldots$

$C_2 = \sigma^2$ $MSRD <$ Correlated Debye model*

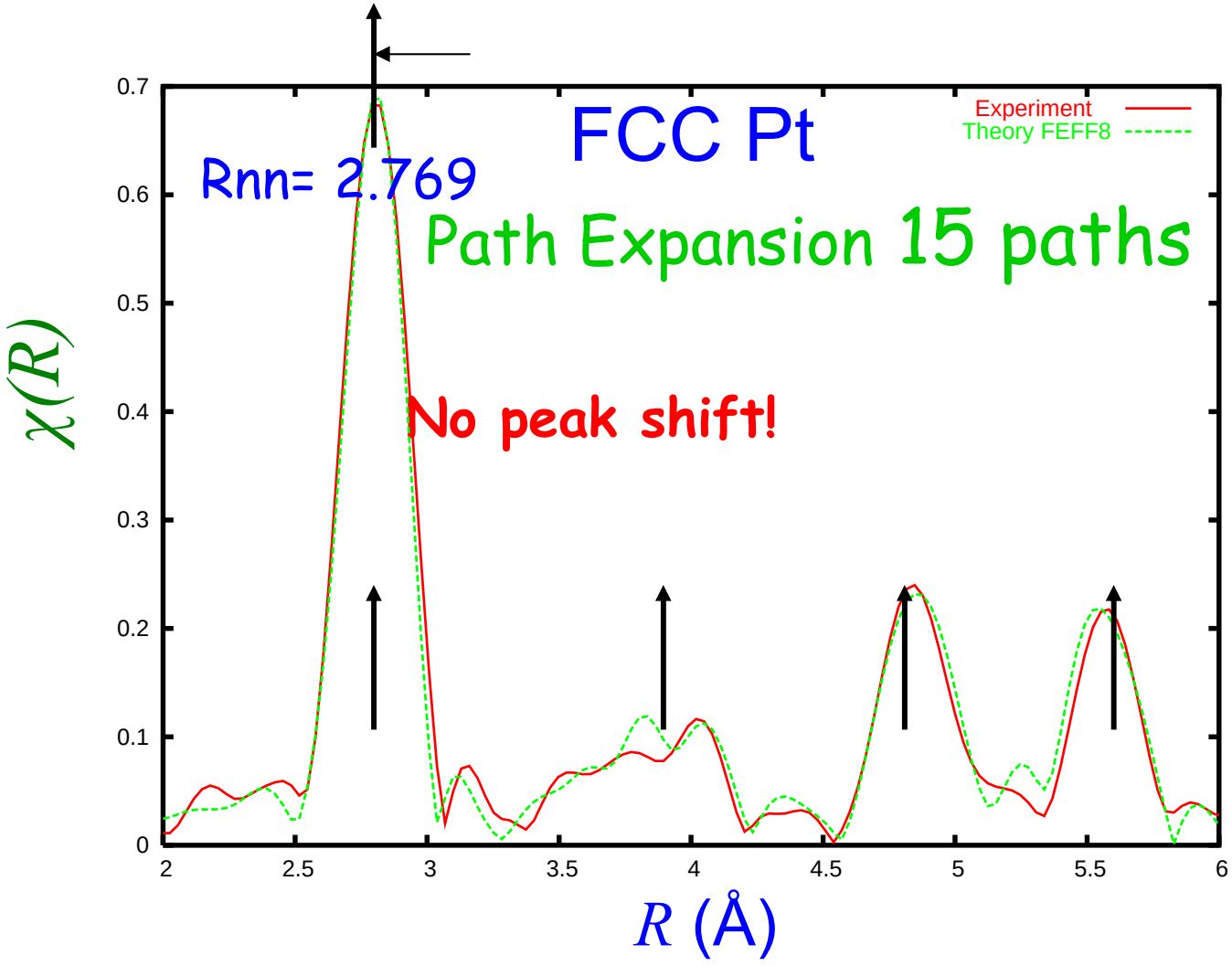
C_1 = thermal expansion Relations between C_i

C_3 = 3rd cumulant ~ *distance contraction* $\frac{C_3}{C_1 C_2} \approx 2$

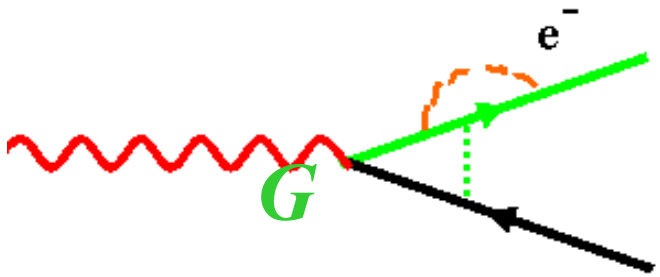
*E. Sevillano, H. Meuth and J.J.Rehr, Phys. Rev. B **20**, 4908 (1979)

Results: Accurate EXAFS Fourier Transforms

Phase Corrected EXAFS Fourier Transform



Next Challenge: R_x for XANES



Long MFP in XANES - need MS Paths to all orders

Green's function $G(E)$	Full multiple scattering
Screened core-hole V_c	Excitonic effects
Self-energy $\Sigma(E)$	Mean-free path, energy shifts
Debye-Waller factors σ^2	Thermal vibrations
Accuate Fermi energy E_F	SCF electronic structure

G: Full Multiple Scattering equations

$$G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \ldots$$

Total scatt. matrix

$$T^{ij}_{LL'} = t^i_{LL'} \delta_{ij}$$

$$G = G^0 + G^0 T G^0 + G^0 T G^0 T G^0 + \ldots$$

Sum to all orders by matrix inversion

XANES

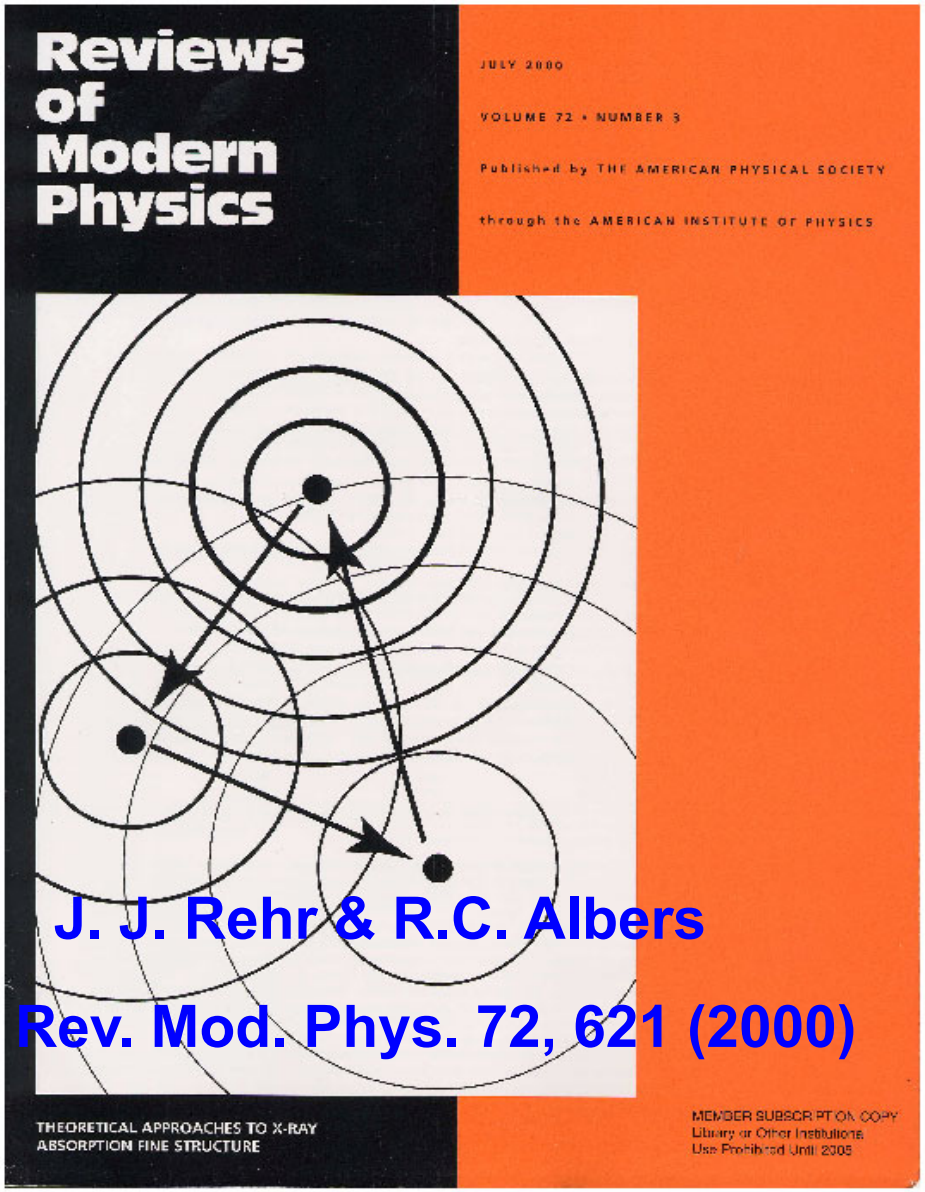
$$G = \left[1 - G^0 T\right]^{-1} G^0$$

Dimension: $N^* l_{max}^2$ x $N^* l_{max}^2$

$l_{max} \approx ka \approx E(ryd)^{1/2}$

Only practical for E < ~100 eV XANES

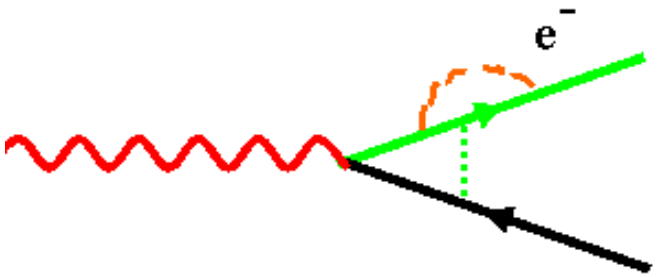
III. Implementation Real space Green's function* code



J. J. Rehr & R.C. Albers

Rev. Mod. Phys. 72, 621 (2000)

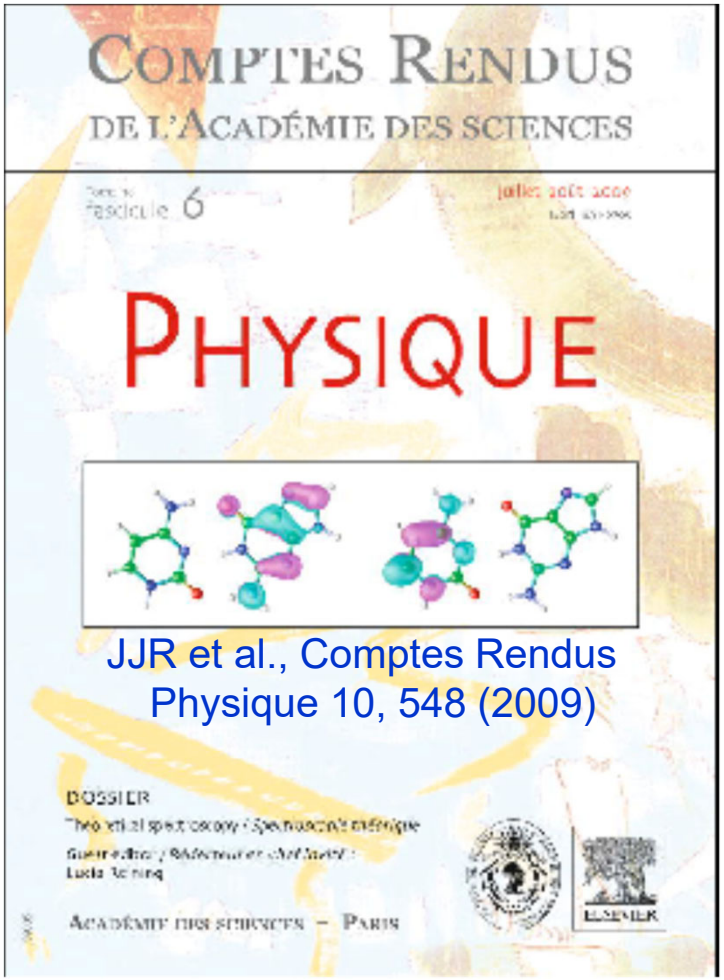
*aka Real-space multiple-scattering



FEFF

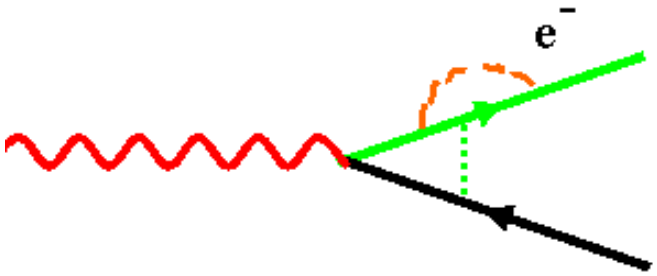
General approach for XAS
EXAFS, XANES, etc.

10 years later: *Ab initio* XAS Calculations*



Ab initio Green's function theory
with SCF Electronic Structure

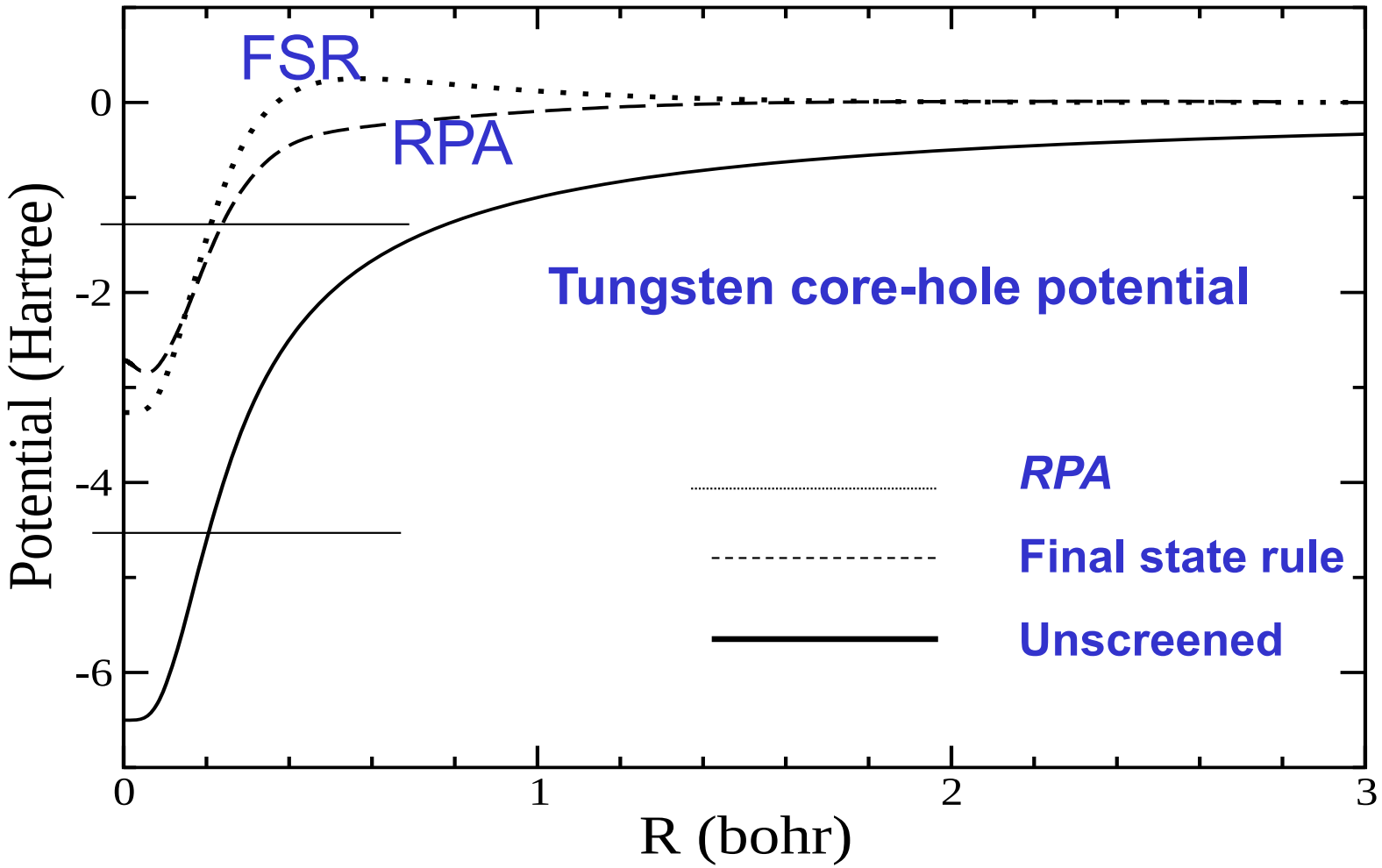
FEFF9



*Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure

AL Ankudinov (LANL), B Ravel (NIST), JJ Rehr(UW), SD Conradson (LANL), Phys. Rev. B **58,** 7565 (1998)

RPA and FSR Screened core-hole potentials



RPA improves on FSR, half-core hole, etc

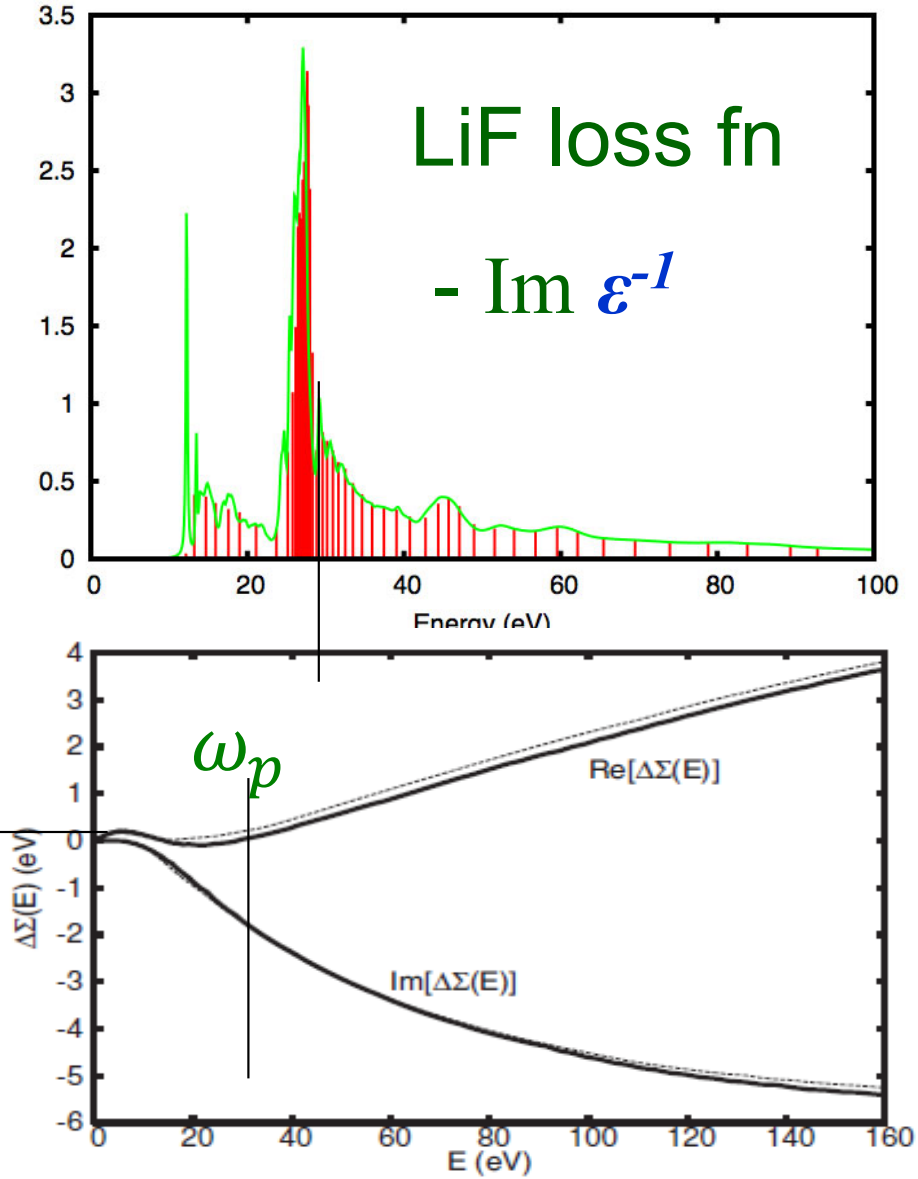
Many-pole *GW* Self-energy $\Sigma(E)$*

Efficient GW approximation for self-energy Σ & mean free path λ

Sum of plasmon-pole models matched to loss function

Improves on HL PP model

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



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

Ab initio Debye Waller factors

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

DMDW

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

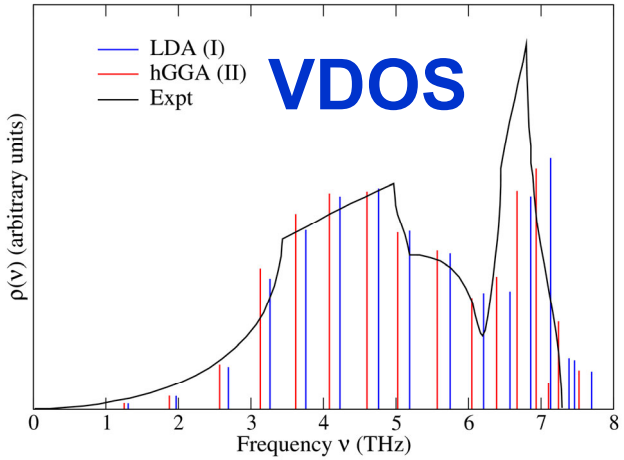
$e^{-2\sigma^2 k^2}$

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

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

Many pole model for phonons

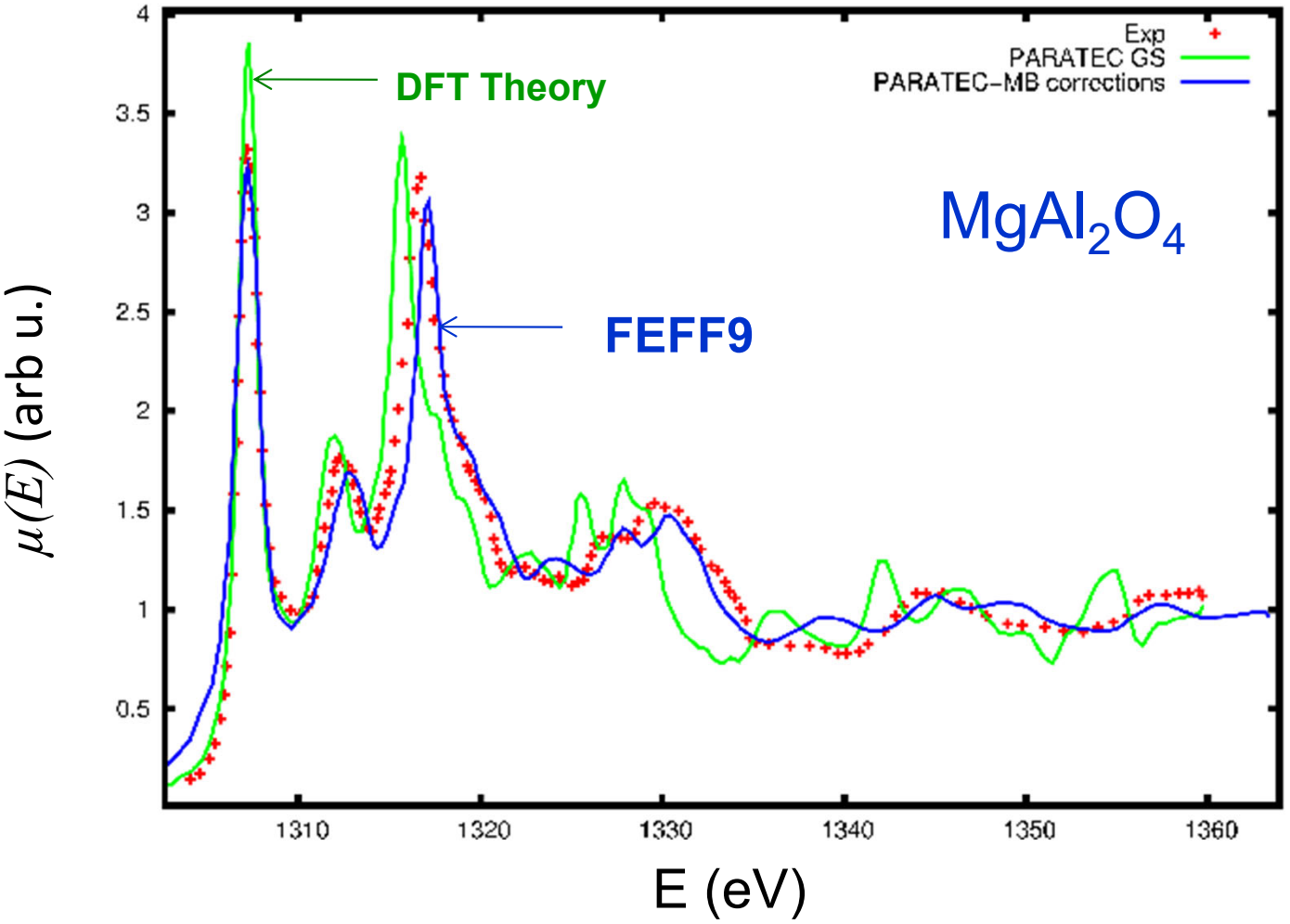
D dynamical matrix < ABINIT, VASP
Improves on correlated Debye model



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

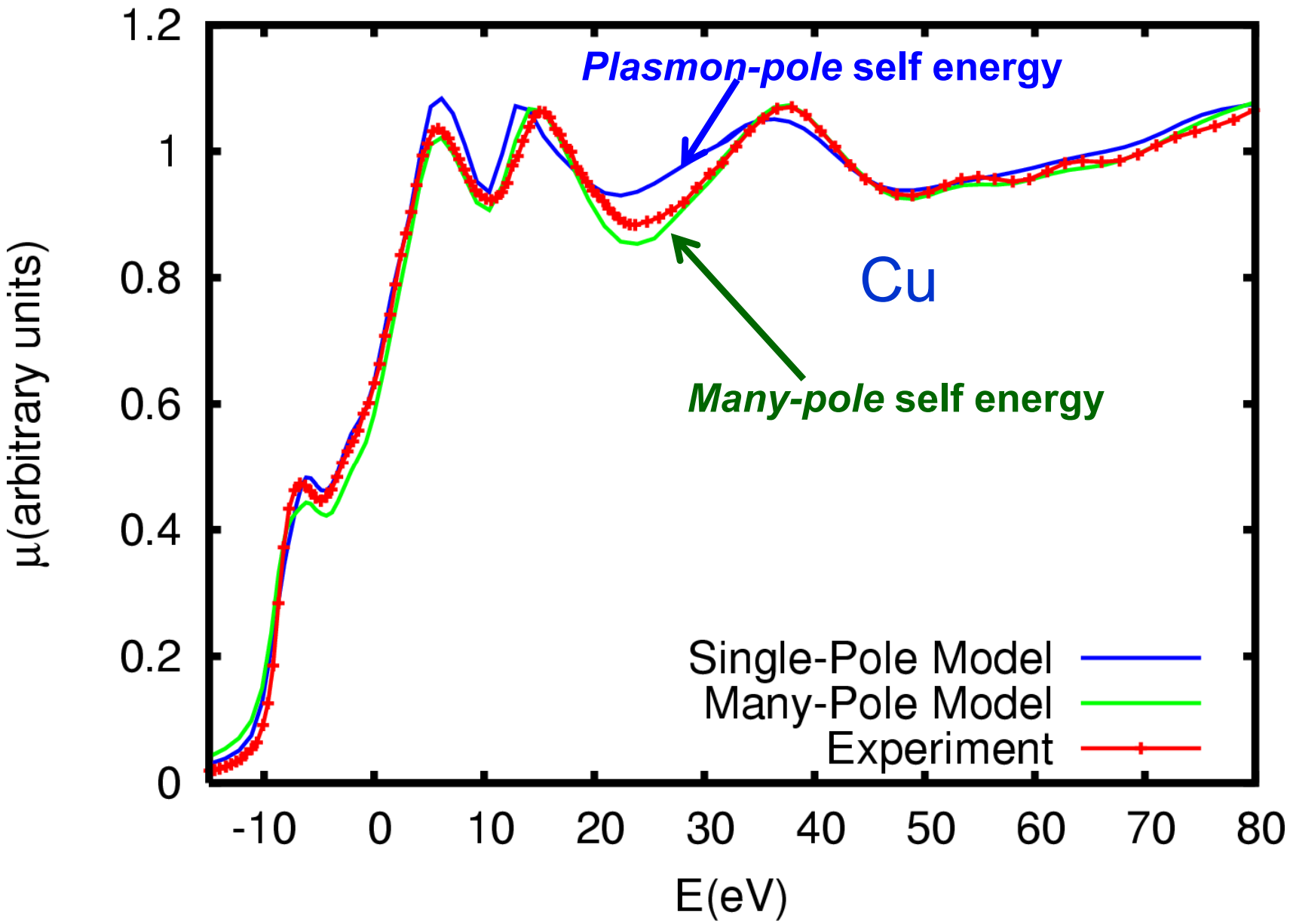
Results: Accurate *ab initio* XANES

Self-energy & DW factors fix DFT



*J. J. Kas et al. J. Phys.: Conference Series **190**, 012009 (2009)

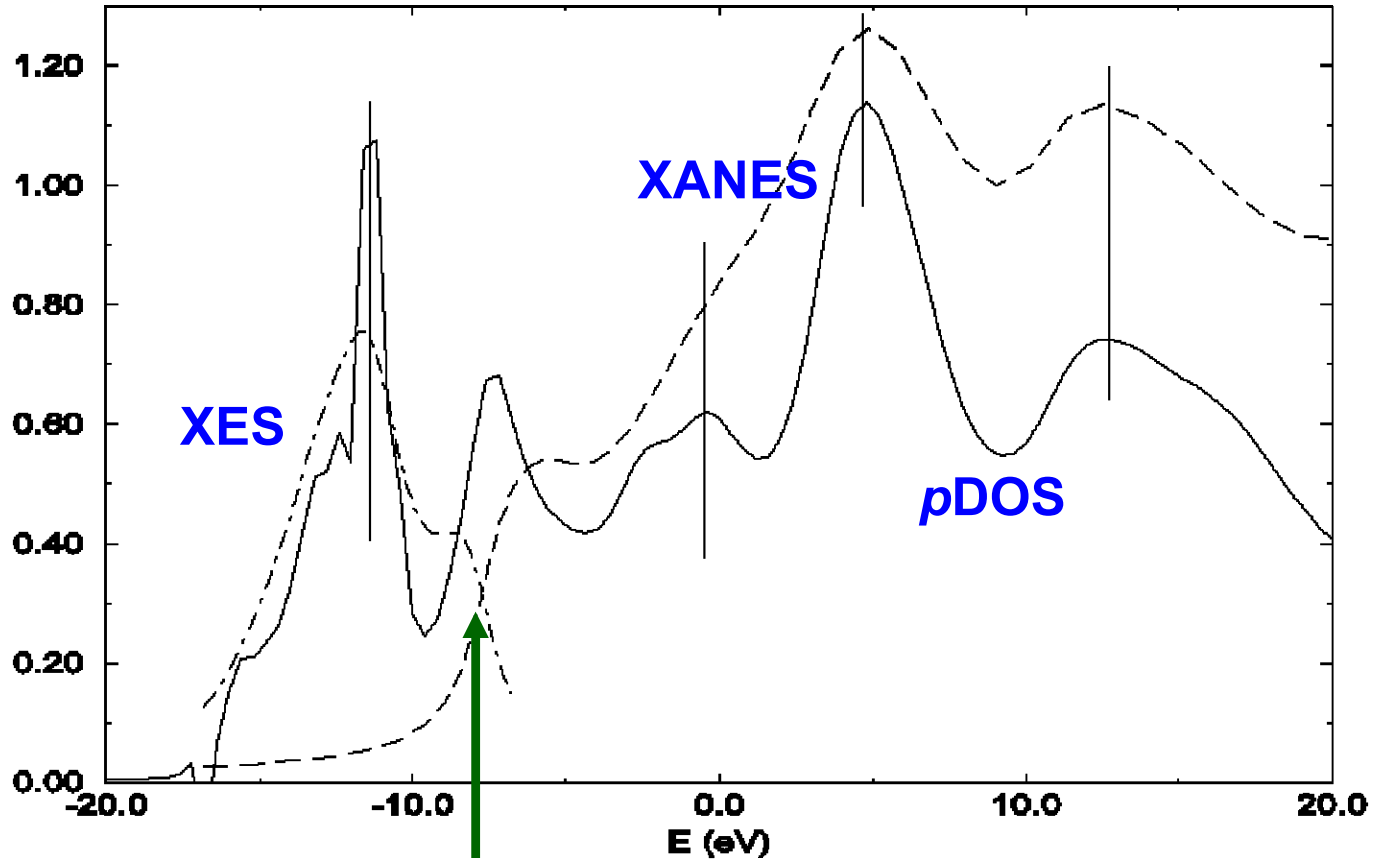
Results: Accurate self energy in XANES



Interpretation of XANES ~ Projected density of states

`LDOS emin emax eimag`

Cu *p*DOS vs XANES and XES



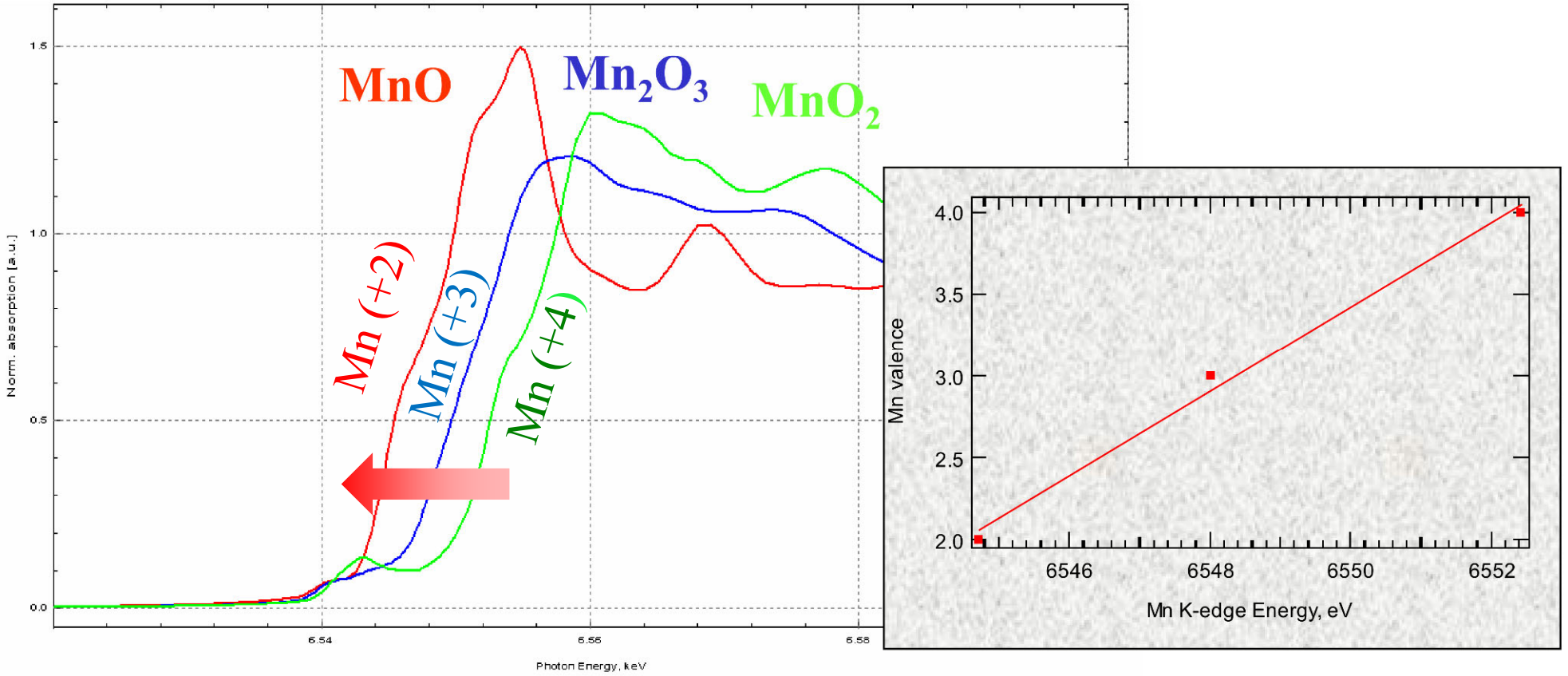
Fermi energy E_F

Photoelectron energy E

Interpretation: Oxidation state vs edge position

electronic charge on Mn

Mn (+4) Mn (+3) Mn (+2)



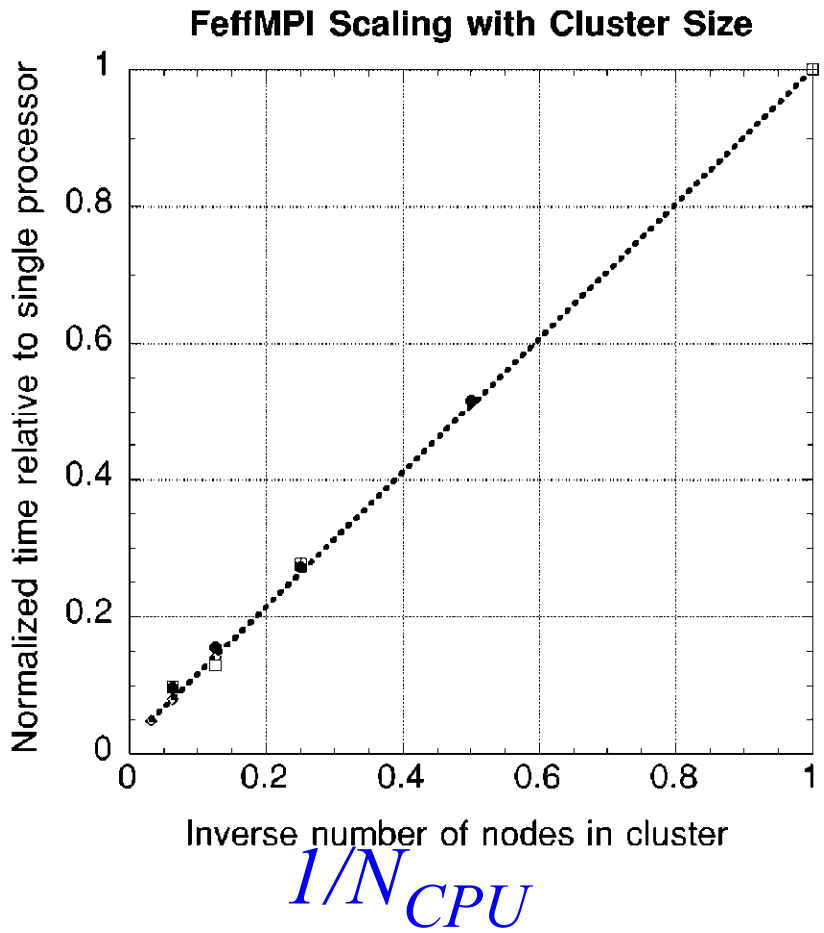
Mn K-edge blue shifts with higher oxidation state

Green's Functions & Parallel Computations*

PHYSICAL REVIEW B, VOLUME 65, 104107

Parallel calculation of electron multiple scattering using Lanczos algorithms

A. L. Ankudinov,[1] C. E. Bouldin,[2] J. J. Rehr,[1] J. Sims,[2] and H. Hung[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195*
[2]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899*



$1/N_{CPU}$

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

Energy E
is a parameter !

"*Natural parallelization*"

Each CPU does few energies

*Need MPI, multicore CPU

Interpretation of EXAFS vs XANES

PHYSICAL REVIEW B, VOLUME 65, 104107 (2002)

Parallel calculation of electron multiple scattering using Lanczos algorithms

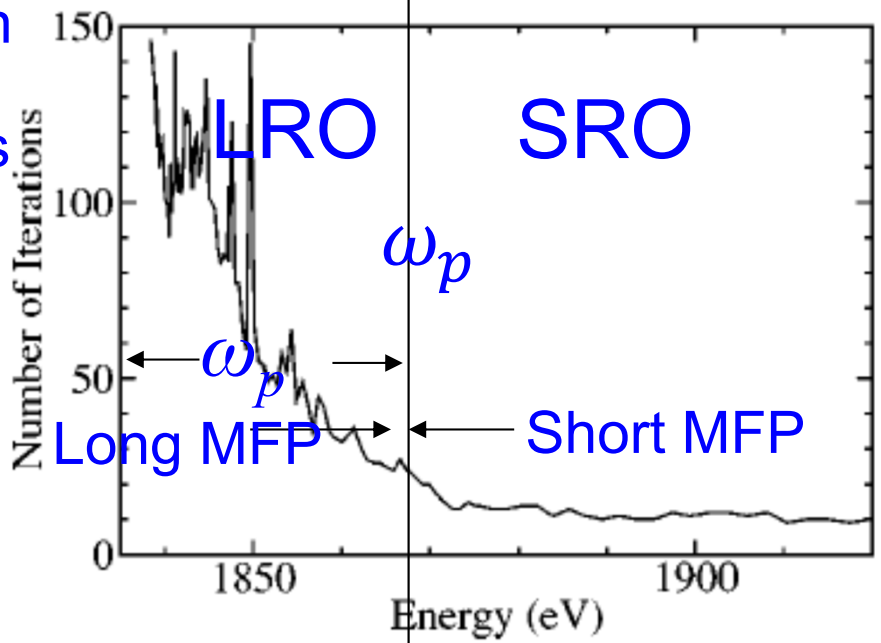
A. L. Ankudinov,[1] C. E. Bouldin,[2] J. J. Rehr,[1] J. Sims,[2] and H. Hung[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195*
[2]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

XANES EXAFS $E\text{-}E_0 > \omega_p \sim 30$ eV

Lanczos matrix inversion

Lanczos G^0T iterations explains crossover from XANES to EXAFS

ω_p Onset of excitations



$\lambda \sim k/[\Gamma + |\ \mathrm{Im}\ \Sigma\ |]$
$\sim [\ 5 - 20\ ]$ Å

FMS Path expansion

Reciprocal Space XAS and EELS Calculations

PHYSICAL REVIEW B 81, 245124 (2010)

Calculations of electron energy loss and x-ray absorption spectra in periodic systems without a supercell

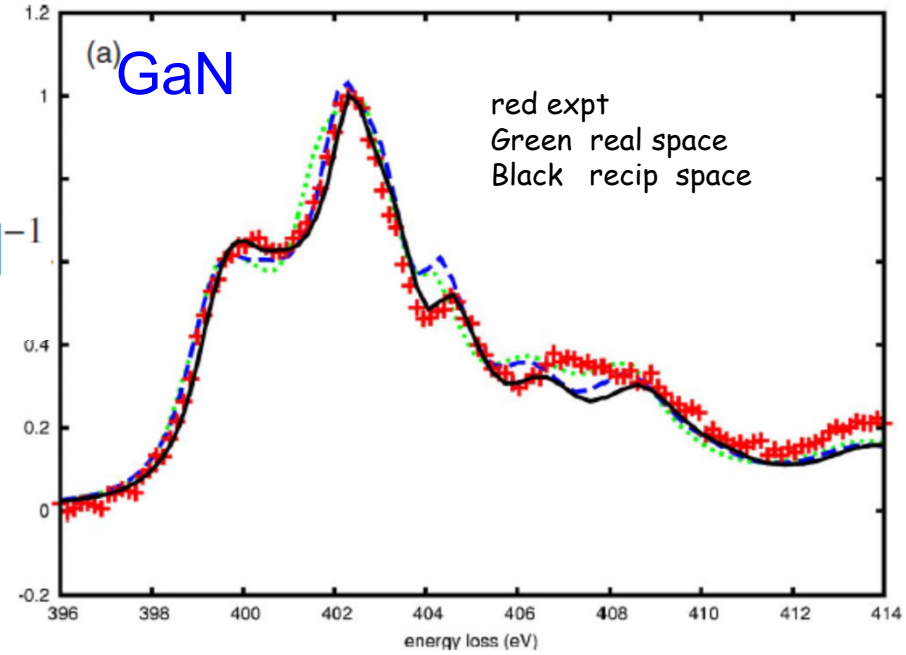
K. Jorissen and J. J. Rehr*

Alternative **Reciprocal space** calculations of FMS XAS and EELS with Green's functions transformed to *k*-space $G(k)$

No core hole: **KKR Equations**

$$G = G_0[1 - tG_0]^{-1} = \int_{BZ} dk G_0(k)[1 - tG_0(k)]^{-1}$$

With core hole $G_{ch} = G[1 - \Delta t_{ch} G]^{-1}$



Other applications

RIXS

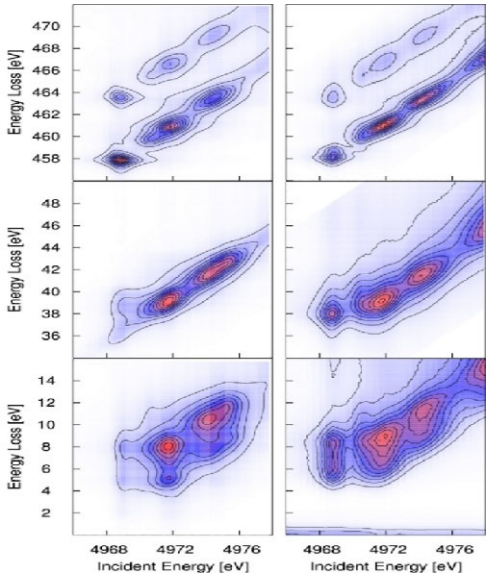
PHYSICAL REVIEW B **83**, 235114 (2011)

Real-space Green's function approach to resonant inelastic x-ray scattering

J. J. Kas,[1] J. J. Rehr,[1,*] J. A. Soininen,[2] and P. Glatzel[3]
[1]*Department of Physics, Box 351560, University of Washington, Seattle, Washington 98195-1560, USA*
[2]*Department of Physics, P.O. Box 64, University of Helsinki, FI-00014 Helsinki, Finland*
[3]*European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble, France*
(Received 21 January 2011; revised manuscript received 7 April 2011; published 8 June 2011)

We present an *ab initio* theory of core and valence resonant inelastic x-ray scattering (RIXS) based on a real-space multiple-scattering Green's function formalism and a quasiboson model Hamiltonian. Simplifying assumptions are made that lead to an approximation of the RIXS spectrum in terms of a convolution of an effective x-ray absorption signal with the x-ray emission cross section. Additional many-body corrections are incorporated in terms of an effective energy-dependent spectral function. Example calculations of RIXS are found to give qualitative agreement with experimental data. Our approach also yields simulations of lifetime-broadening suppressed x-ray absorption, as observed in high-energy resolution fluorescence detection experiment. Finally, possible improvements to our approach are briefly discussed.

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{\omega}{\Omega}\int d\omega_1 \frac{\mu_e(\omega_1)\bar{\mu}(\Omega,\Omega-\omega-\omega_1+E_b)}{|\omega-\omega_1+i\Gamma_b|^2}$$



COMPTON

PHYSICAL REVIEW B **85**, 115135 (2012)

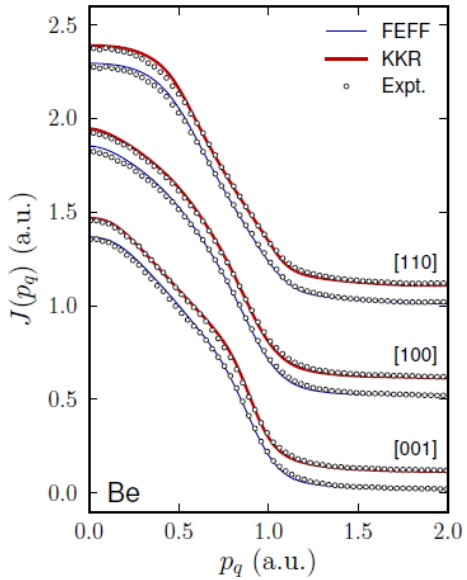
Real-space Green's function calculations of Compton profiles

Brian A. Mattern, Gerald T. Seidler,* Joshua J. Kas, Joseph I. Pacold, and John J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA
(Received 2 February 2012; revised manuscript received 16 March 2012; published 29 March 2012)

We report the development of a first-principles, real-space Green's function method for calculation of Compton profiles in the impulse approximation. For crystalline Be, we find excellent agreement with prior theoretical treatments requiring periodicity, with prior experimental measurements of the Compton profile, and with present measurements of the dynamical structure factor via nonresonant inelastic x-ray scattering (often also called x-ray Thomson scattering in the plasma physics community). We also find good agreement with prior experimental results for the Compton profile of Cu. This approach can be extended to disordered and very high-temperature systems, such as "warm dense matter," where theories presently used for the interpretation of inelastic x-ray scattering include condensed phase effects only at a perturbative level.

$$J(p_q) = \int dx\, dy\, dz\, dz'\, e^{ip_q(z-z')}\rho(\mathbf{r},\mathbf{r}'),$$

$$\rho(\mathbf{r},\mathbf{r}') = -\frac{2}{\pi}\mathrm{Im}\int_{E_c}^{\infty} dE\, G(\mathbf{r},\mathbf{r}',E) f_T(E)$$



And still others

Similar RSGF formalism also explains

XES - transitions to occupied states
NIXS - transition operator $e^{iq\cdot r}$
XMCD – spin dependent absorption
Optical Constants – dielectric properties
DAFS - Fine structure in x-ray scattering
Two-photon Absorption – nonlinear abs
etc.

V. Extensions Corvus Workflow Manager

JOURNAL OF SYNCHROTRON RADIATION
ISSN 1600-5775

Advanced calculations of X-ray spectroscopies with *FEFF10* and Corvus

J. J. Kas,[a,b]* F. D. Vila,[a,b] C. D. Pemmaraju,[b] T. S. Tan[a] and J. J. Rehr[a,b]

CORVUS "Intelligent" python workflow manager for complex calculations

Example: Corvus workflow for Optical constants

```
target_list { opcons }
usehandlers { Feff }
opcons.usesaved{ True }
cif_input{CIF_symm.cif}
feff.scf{ 3.2350952042425325 0 30 0.1 0 }
feff.fms{ 5.075798356336175 0 0 0.0 0.0 40.0 }
feff.debye{ 298.0 416.52459701743817 0 }

# The lines below should set the parallel settings
...
```

Fig. 8. Typical template Corvus [opcons] input generated by the crv_mp_mk_set

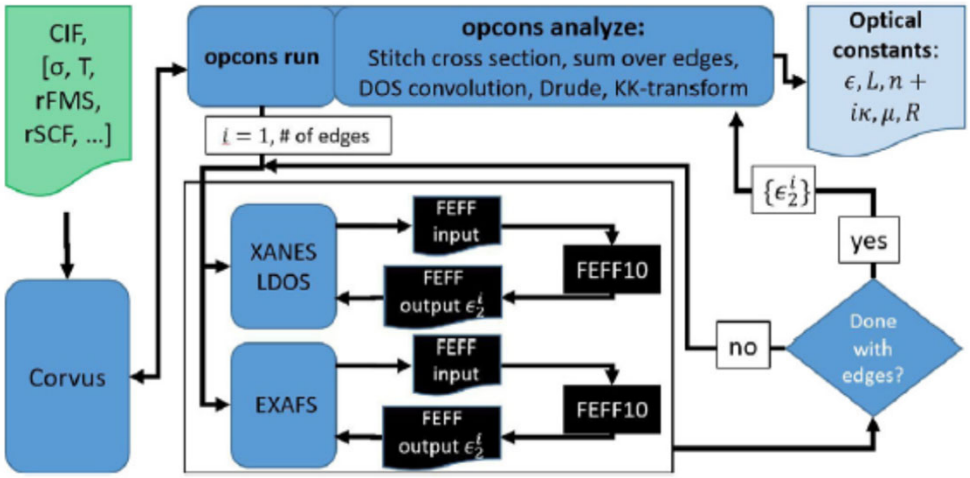
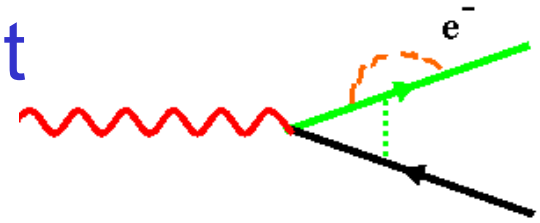
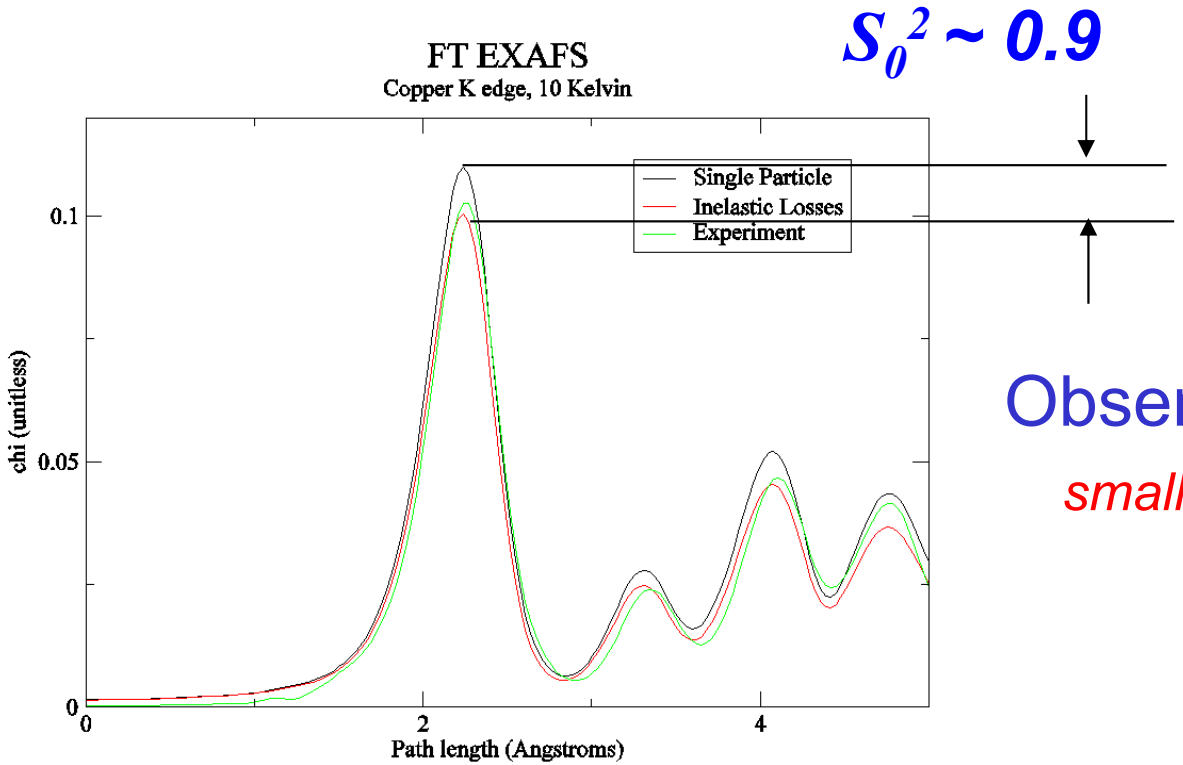


Fig. 6. Schematic of the Corvus workflow for optical constants. User input is shown

Remaining Challenge: Inelastic losses in XAS - S_0^2

Theory over estimates XAS experiment



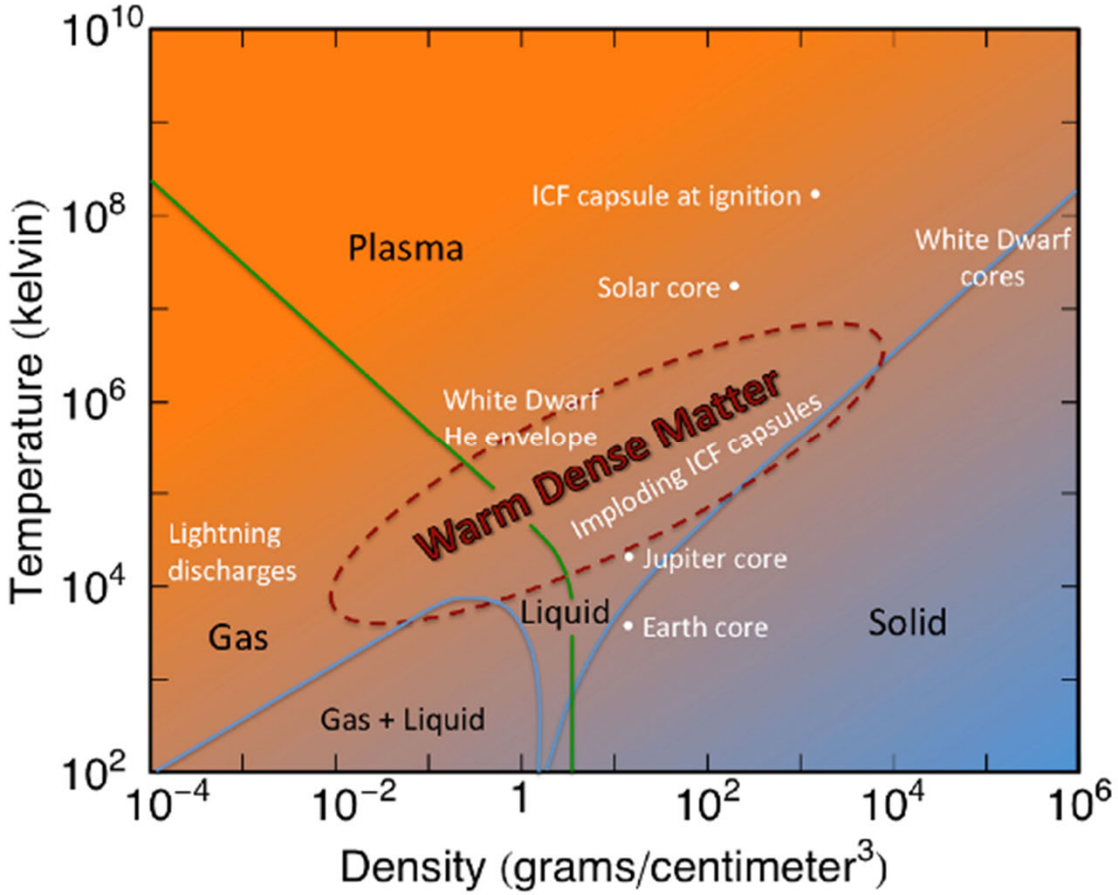


$S_0^2 \sim 0.9$

Observed fine structure *smaller* than QP theory

Remaining challenge: XAS in extreme conditions

Broad ranges of temperature & density



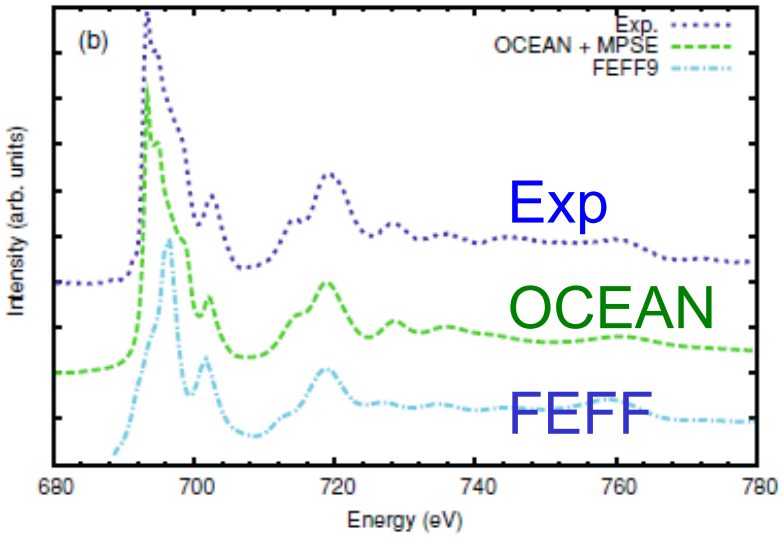
Remaining challenge: Full potential & excitonic effects

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



Full-potential GW/BSE code

Computer Physics Communications 197 (2015) 109–117

Contents lists available at ScienceDirect

Computer Physics Communications

journal homepage: www.elsevier.com/locate/cpc

Efficient implementation of core-excitation Bethe–Salpeter equation calculations

K. Gilmore [a,b,*], John Vinson [c], E.L. Shirley [c], D. Prendergast [d], C.D. Pemmaraju [d], J.J. Kas [e], F.D. Vila [e], J.J. Rehr [e]

*J. Vinson et al. Phys. Rev. B**83**, 115106 (2011); K. Gilmore et al. CPC **197**,109 (2015)

Summary & Conclusions I

Automated real-space Green's approach for x-ray spectra from the UV-VIS to hard x-rays

Implemented in *ab initio* FEFF10 codes

User-friendly for novice & expert users alike

Applicable to molecules, solids and aperiodic systems throughout the periodic table

Acknowledgments

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Special thanks to LANL for supporting the initial phase of this work and to all of our collaborators:

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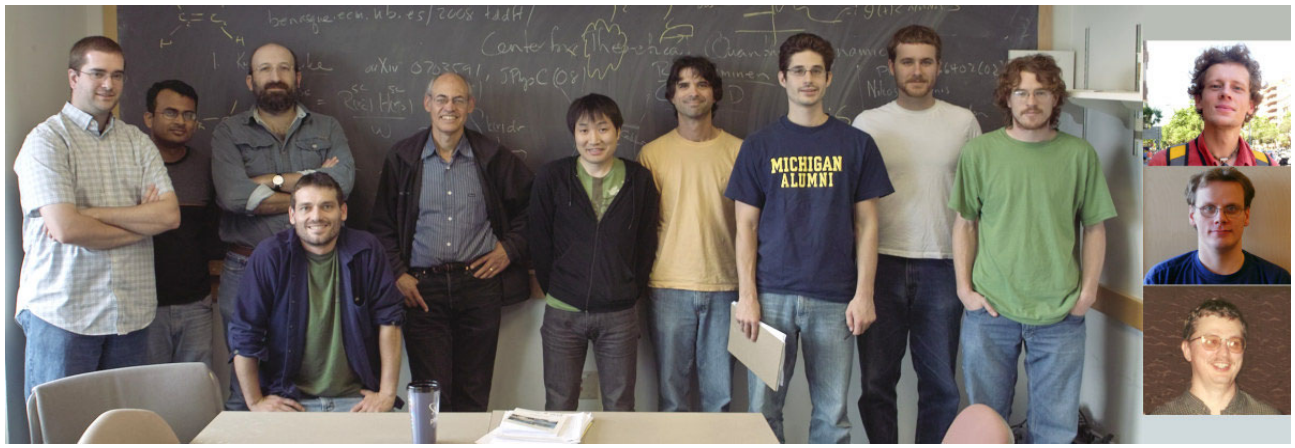
G. Bertsch
J. Sky Zhou
F. Aryasetiwan
and many others
E. Shirley
S. Story
T. Fujikawa

Rehr Group
ca 2010



UNIVERSITY OF WASHINGTON

TIMES

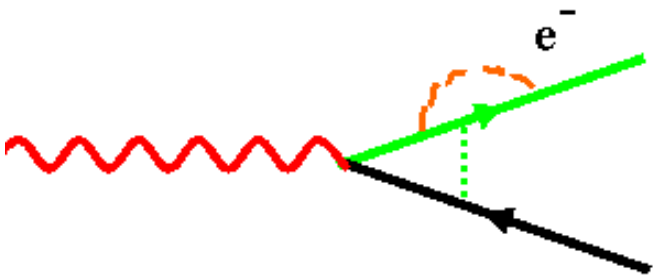
U.S. DEPARTMENT OF ENERGY | Office of Science

Los Alamos Computational Condensed Matter Summer School June 23, 2026

Advances in Theoretical X-ray spectroscopy

J. J. Rehr

University of Washington and SLAC



UNIVERSITY OF WASHINGTON TIMES Pacific Northwest NATIONAL LABORATORY SPEC U.S. DEPARTMENT OF ENERGY Office of Science

Advances in Theoretical X-ray spectroscopy

Talk:

Remaining Challenges in X-ray Theory:

Many-body physics beyond the quasi-particle approximation:
S_0^2 Satellites, Correlated systems, Finite *T* & extreme conditions

Advances:

Cumulant Green's Function method
Multiplet + Cumulant
Finite T Two-photon absorption

Common theme: Cumulant Green's functions

"You can judge the quality

of a many-body theory by

how it treats the satellites"

Lars Hedin
ca 1994

Recent Review & References

PCCP

ROYAL SOCIETY OF CHEMISTRY

PERSPECTIVE

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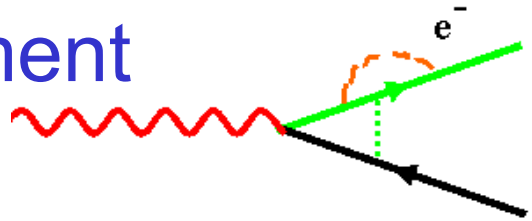
Cite this: *Phys. Chem. Chem. Phys.*, 2022, **24**, 13461

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

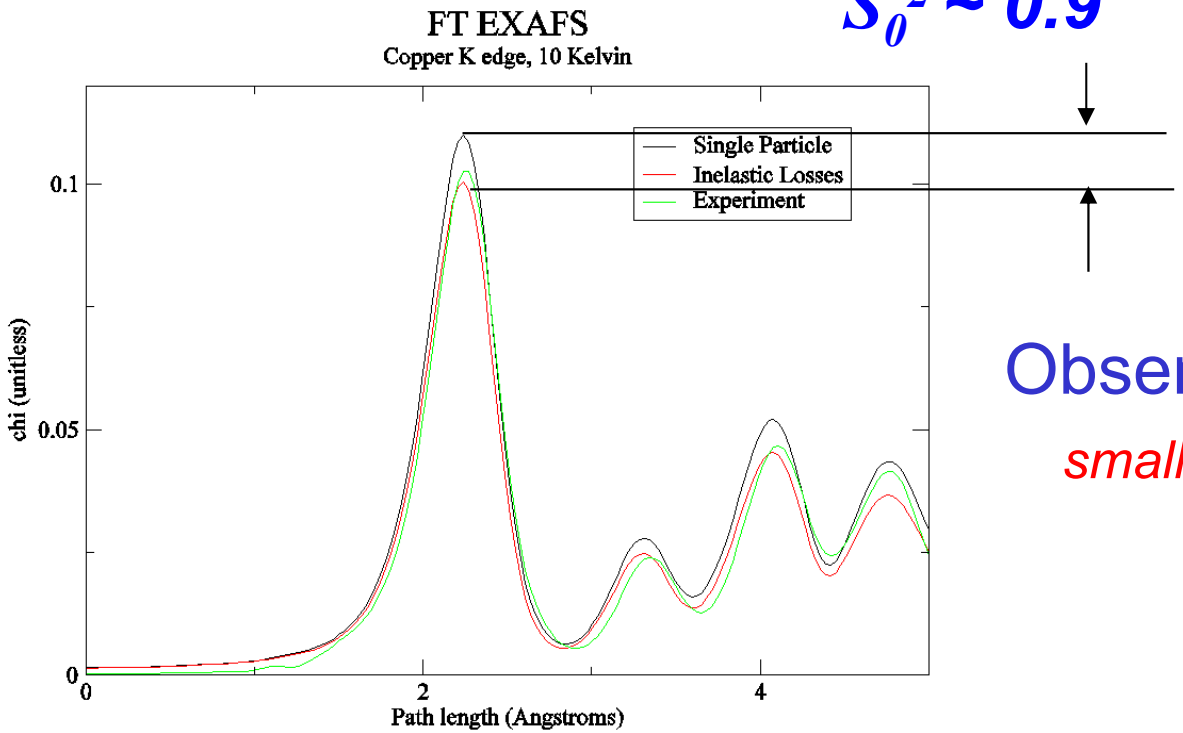
Joshua J. Kas, * Fernando D. Vila, Tun S. Tan and John J. Rehr

I. Inelastic losses in XAS - S_0^2

QP Theory over estimates XAS experiment



$S_0^2 \sim 0.9$



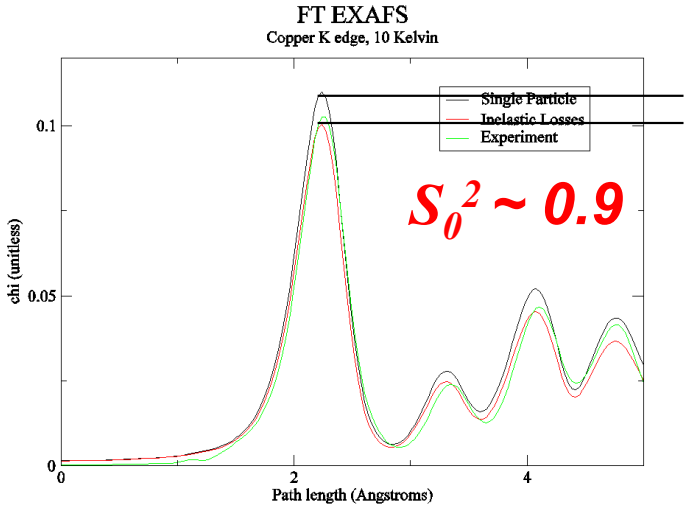
Observed fine structure *smaller* than QP theory

Hedin suggestion: Add intrinsic inelastic 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.



Satellites and S_0^2

Observation: many-body amplitude reduction & satellites in XAS *are absent* in quasiparticle theory

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]

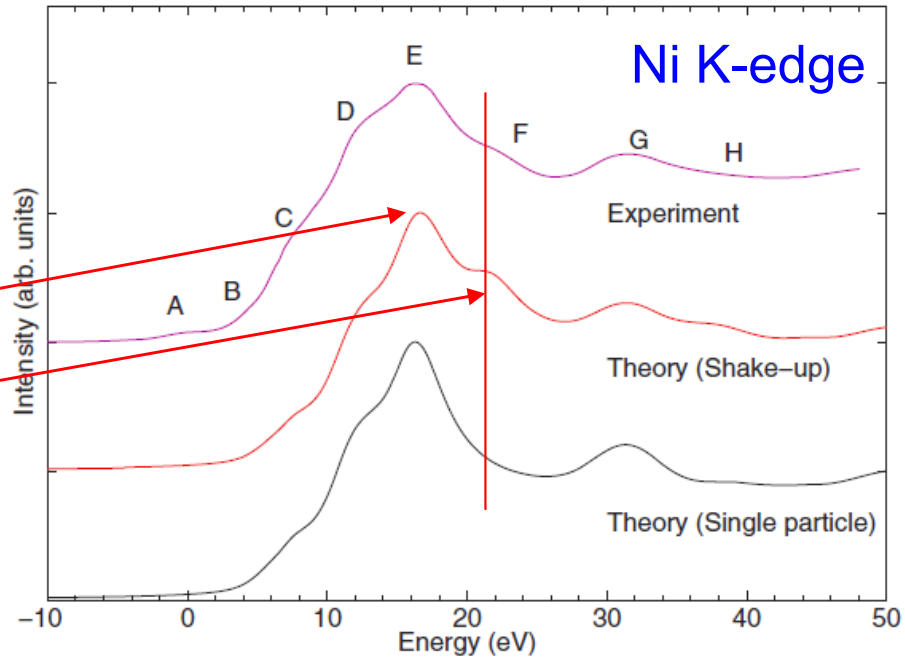
***Ad hoc* fix** : Convolution XPS ⊗ XAS

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

Many body reduction in edge peak S_0^2

XPS Excitation spectrum includes shake satellites

Shake-up satellites in NiO XAS



Advance: Cumulant Green's function theory

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

Factorization explains *ad hoc* convolution formula of XAS of Colandra et al

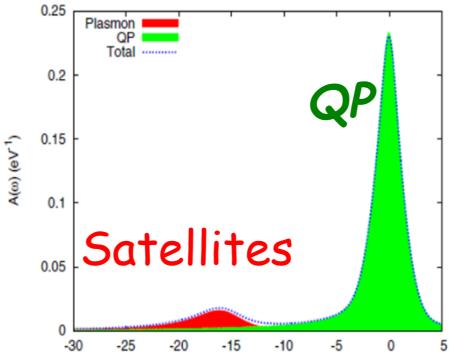
$$\mu(\omega) = \int_0^\infty d\omega' \, \tilde{A}(\omega, \omega')\mu_{qp}(\omega - \omega') \equiv \langle \mu_{qp}(\omega) \rangle$$

Spectral function

Includes satellites & S_0^2

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

~ XPS



Quasi-particle XAS μ_{qp}

Includes core-hole Vc

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)

Reference: Cumulant Green's function approach

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

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

Lars Hedin

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

aka Quasi-boson approximation

Cumulant GF alternative to Dyson Equation

GW + Dyson

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

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

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

No vertex $\Gamma = I$

vs

Cumulant $C(t)$*

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

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

All excitations in $C(t)$

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

Includes implicit vertex Γ

***Recent review and new derivation,**

J. Zhou et al. J. Chem. Phys. **143**, 184109 (2015).

Cumulant Green's Function Properties*

Retarded Cumulant Green's function in time domain

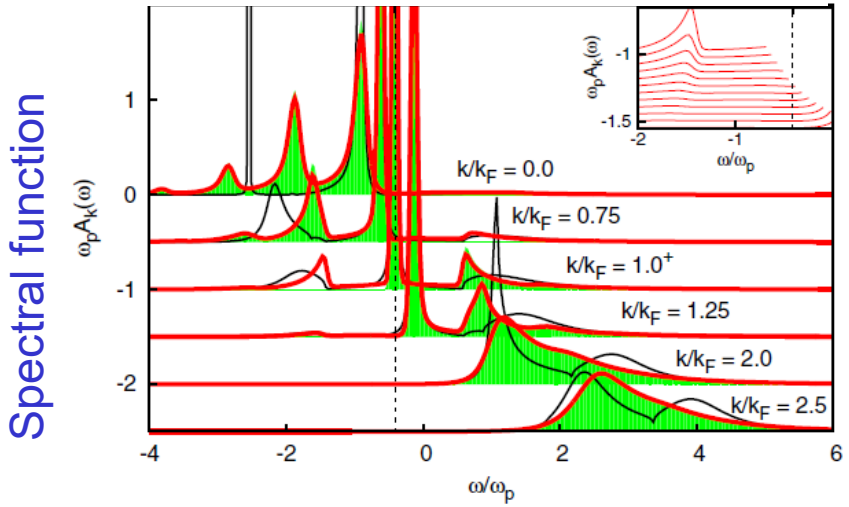
$$G_k(t) = -i\theta(t)e^{-i\varepsilon_k^x t}e^{\tilde{C}_k(t)}$$

Natural separation of QP, exchange, & correlation parts

Landau form of cumulant (1944)

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

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



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

Why does it work: Quasi-boson approximation

IDEA: Neutral excitations - plasmons, phonons, etc. are **bosons**

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

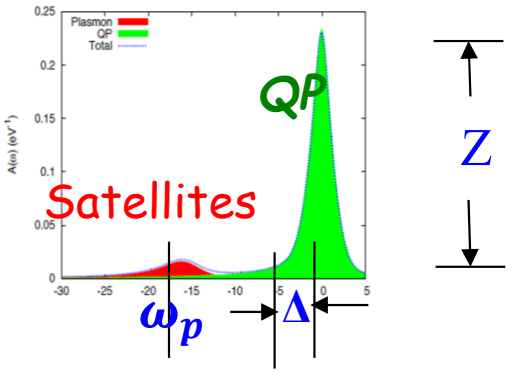
B. I. Lundqvist, *Phys. Kondens. Mater.* **6 193 (1967)

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

Landau form of cumulant

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

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



Spectral function 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 $Z = e^{-a} \sim {S_0}^2$

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

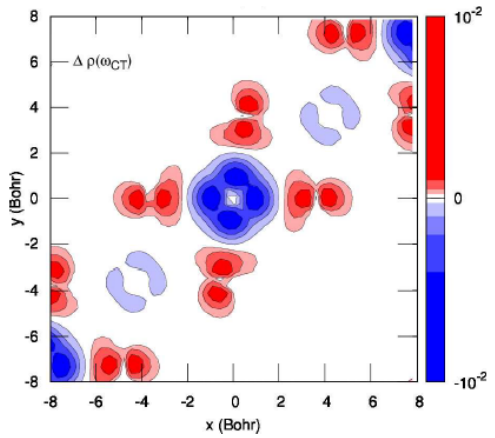
Dimensionless measure of correlation
significant even in weakly correlated materials

Calculation: Real-time Langreth cumulant†

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

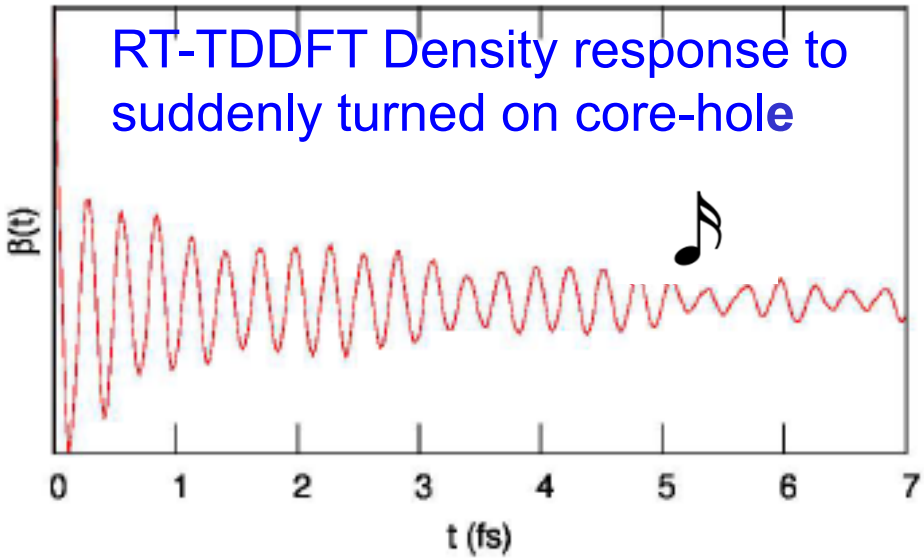
$$C(t) = \int d\omega \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}$$

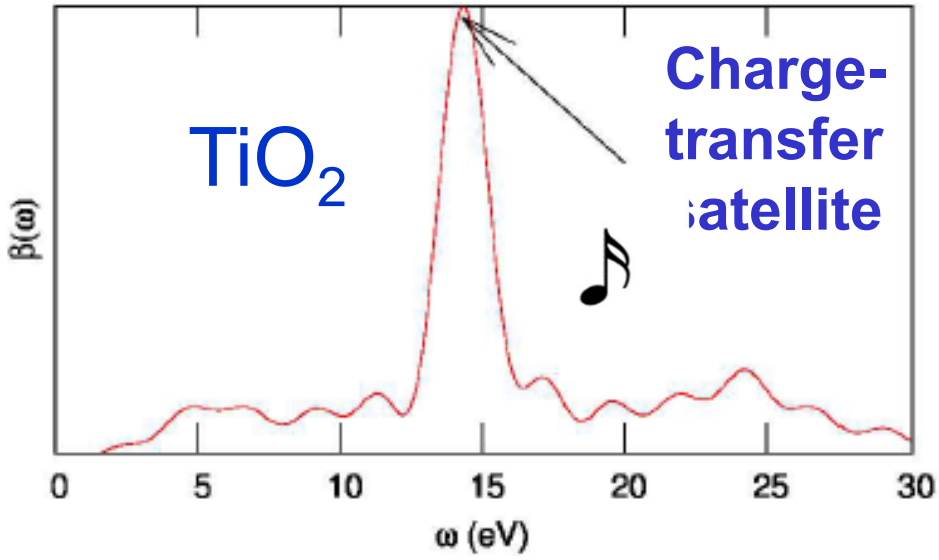
$$\beta(t) = \frac{d^2 C(t)}{dt^2} = \int d^3 r V(r) \delta\rho(r,t)$$



$$\beta(\omega) = \mathrm{FT}\, \beta(t)$$

Excitation spectrum – cumulant kernel



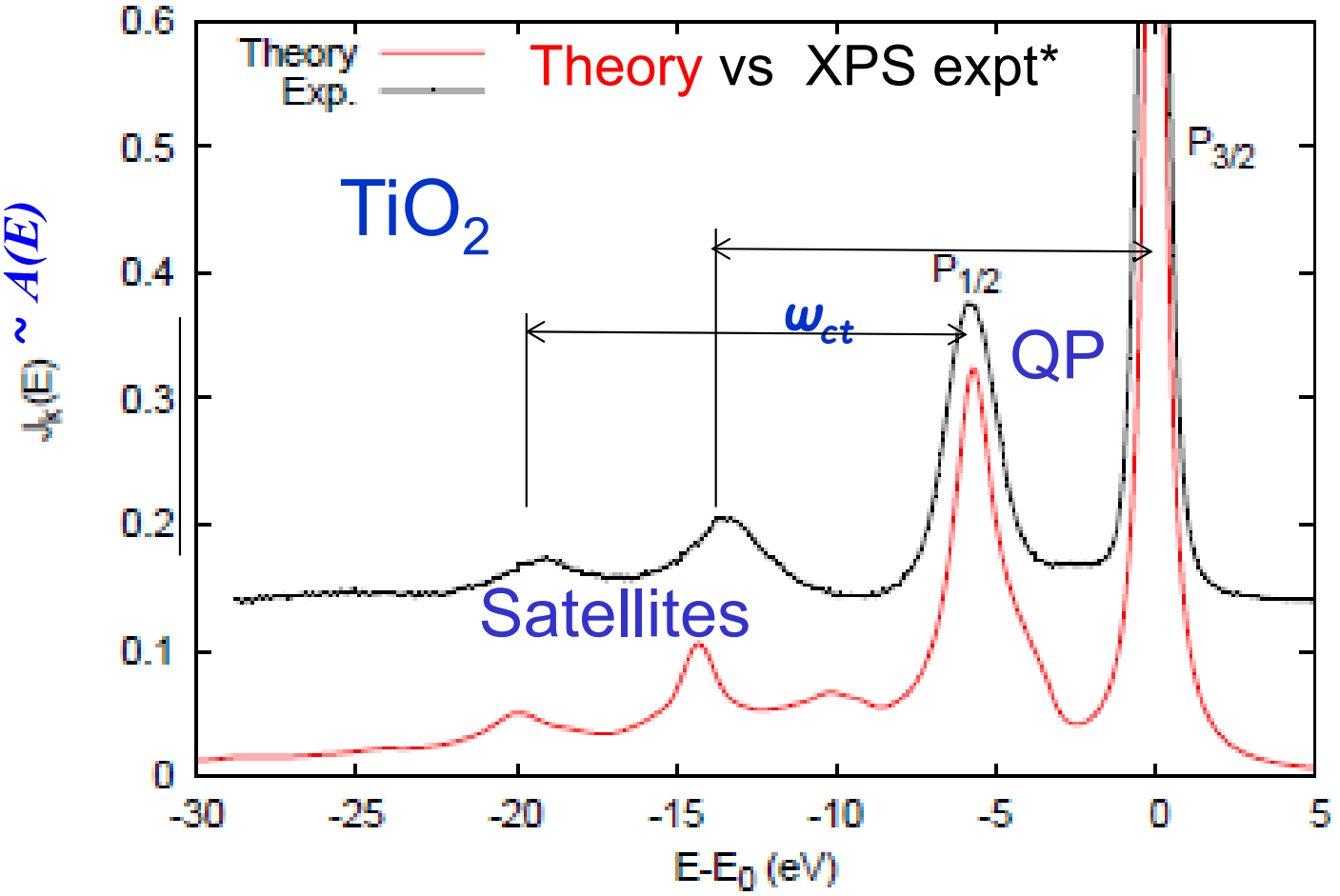


*J. J. Kas, F. D. Vila, J. J. Rehr, and S. A. Chambers, PRB **91**, 121112(R) (2015)

†D.C. Langreth, PRB **1**, 471 (1970)

Results: Multiple-satellites in XPS*

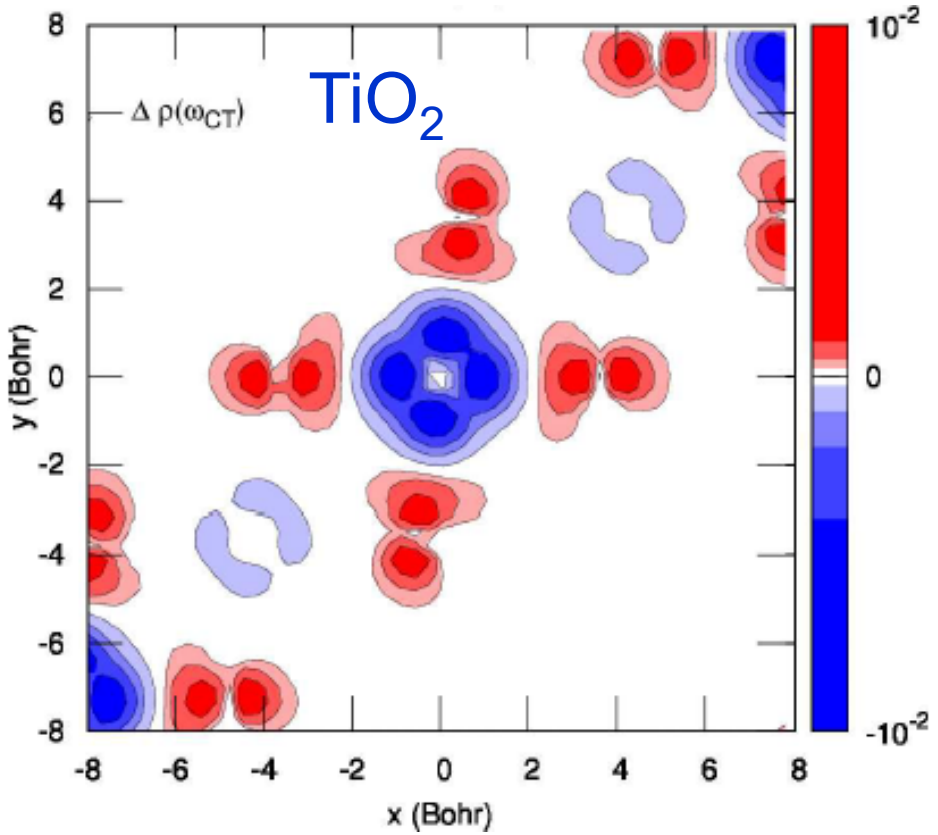
Spectral function $A_c(\omega) = (1/\pi)\,|\mathrm{Im}\,G_c(\omega)|$ ~ XPS $J_k(E)$



*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 $\Delta\rho(r)$

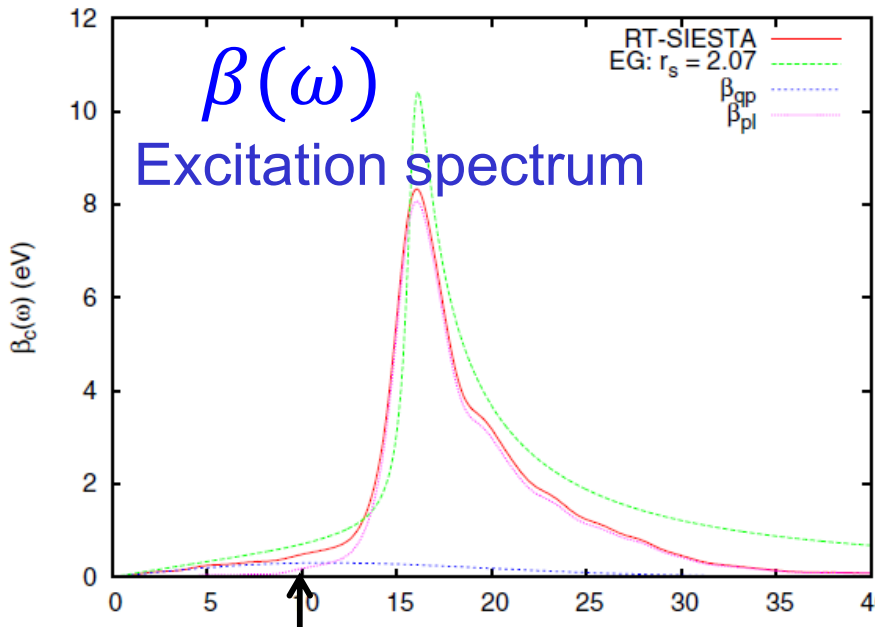


$\Delta\rho(r)$

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

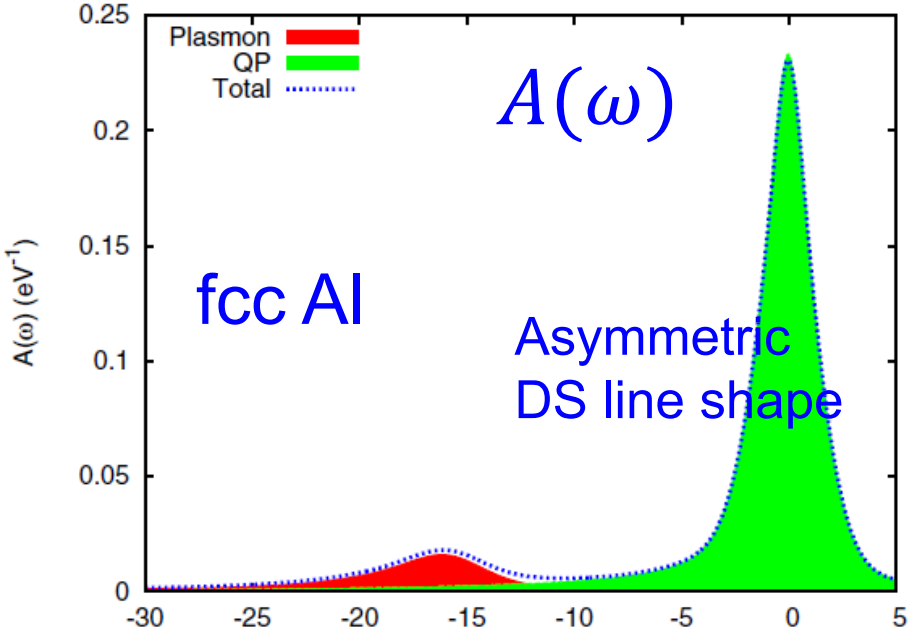
Bonus: X-ray Edge Singularities in Metals

Low energy particle-hole excitations in cumulant **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

Example: Bethe-Salpeter Eq + Cumulant*

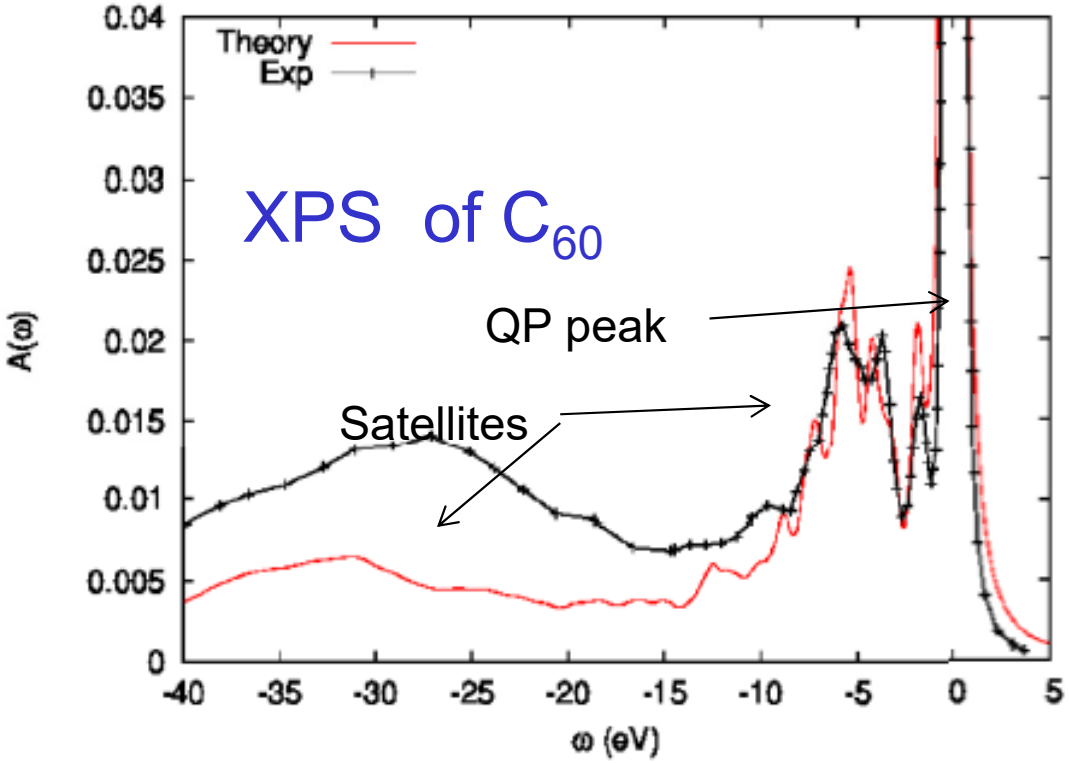
Phys Rev B **95**,115112(2017)

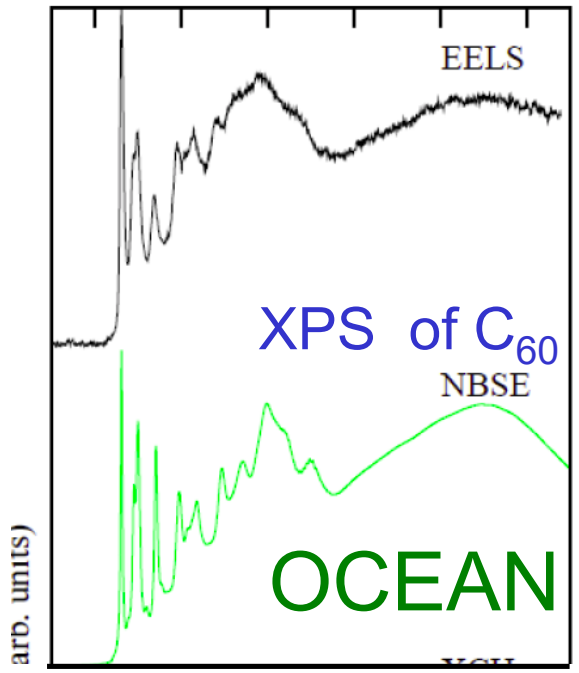
High-resolution valence and core excitation spectra of solid C_{60}

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

BSE (particle-hole GF) Improves on quasi-particle theory





*E. L. Shirley, J. Vinson, and K. Gilmore, The **OCEAN** suite: IUCr 2020 vol 1.

Alternative: 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*

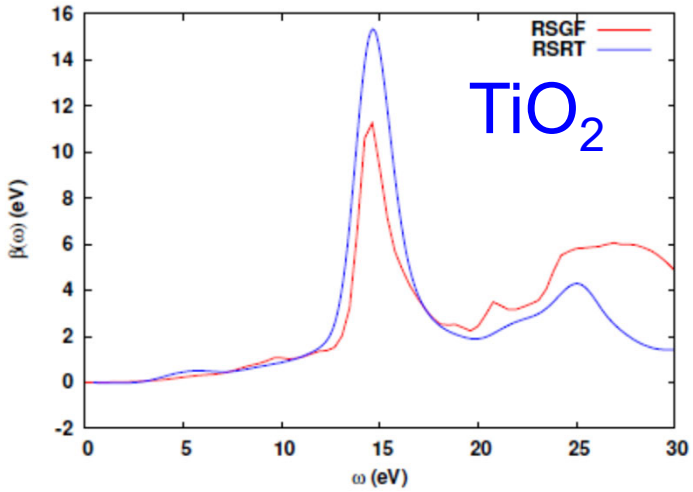
$$\beta(\omega) = \frac{1}{\pi}\sum_q |V_q|^2 \mathrm{Im}\,\chi(\mathbf{q},\omega)$$
$$\equiv \frac{1}{\pi}\sum_q |W_q(\omega)|^2 \mathrm{Im}\,\chi^0(\mathbf{q},\omega)$$
$$W_\mathbf{q}(\omega) = V_q/\epsilon(\mathbf{q},\omega)$$

Langreth cumulant in real space

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

Dynamically screened core-hole potential W

Excitation spectrum $\beta(\omega)$

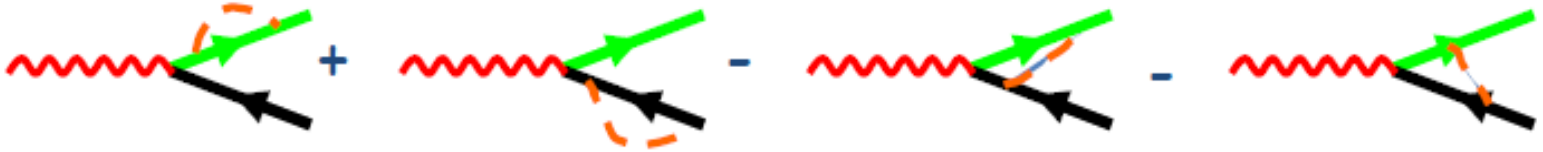


Langreth cumulant similar to XAS $\mu(\omega)$
but with $W_c(\boldsymbol{r},\omega)$ replacing dipole $d(r)$
Can calculate $C(t)$ with FEFF codes
in parallel with QP XAS

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

Extension: Particle-hole Cumulant GF

Includes intrinsic, extrinsic & *interference* effects on satellites
interference *missing* in single-particle Cumulant GF



Extrinsic + Intrinsic - 2 x Interference

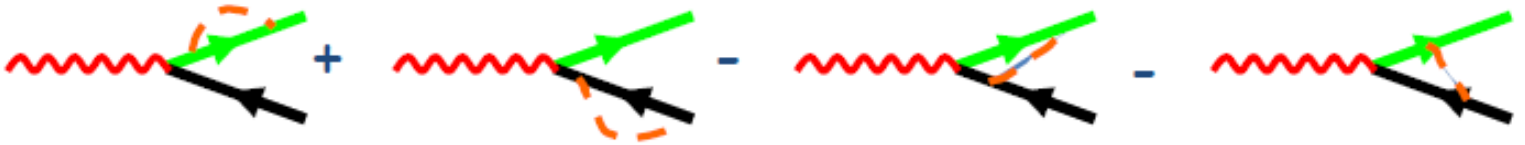
$$\mu(\omega) = \int d\omega' \, \tilde{A}_K(\omega') \mu_K(\omega - \omega')$$

$A_K(\omega)$ particle-hole spectral function

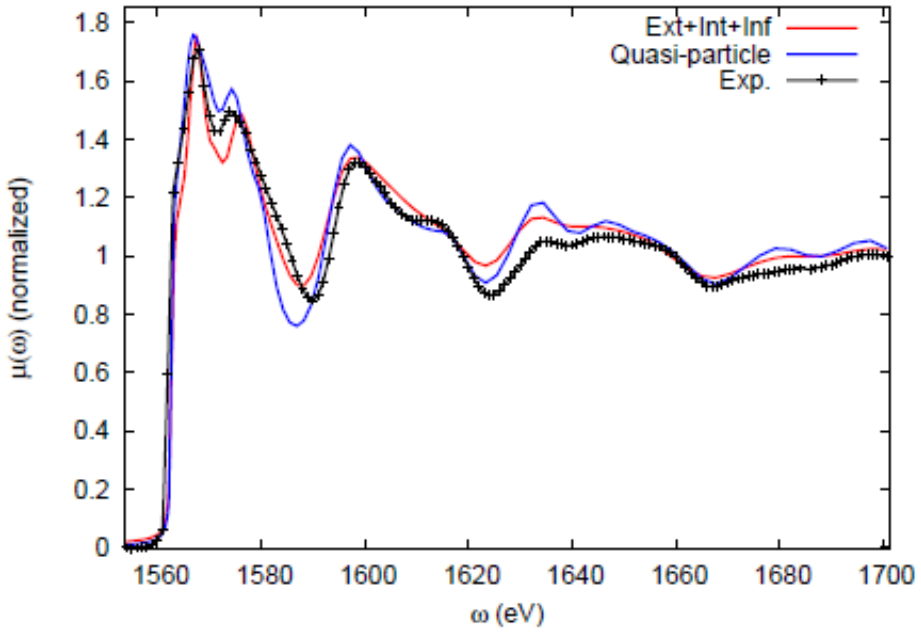
$\mu_K(\omega)$ Quasi-particle XAS from final-state rule or BSE

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

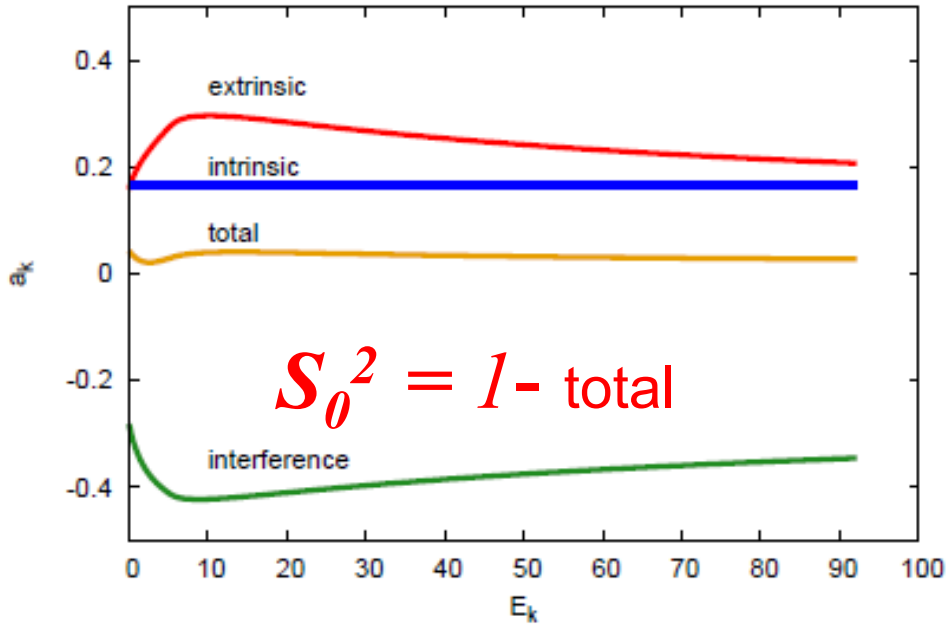
Example: particle-hole cumulant in XAS



XAS of Al



Satellite strengths



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

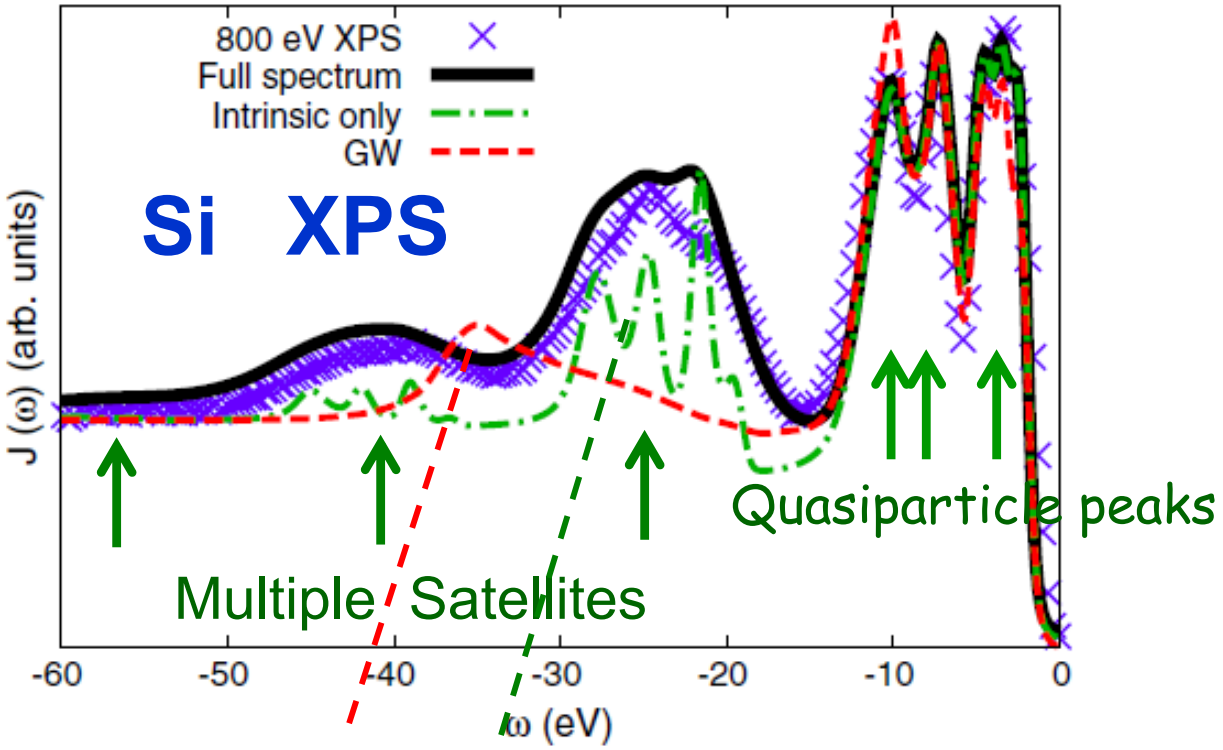
AND crossover: **adiabatic** to **sudden** approximation

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 has one broad satellite at the wrong place

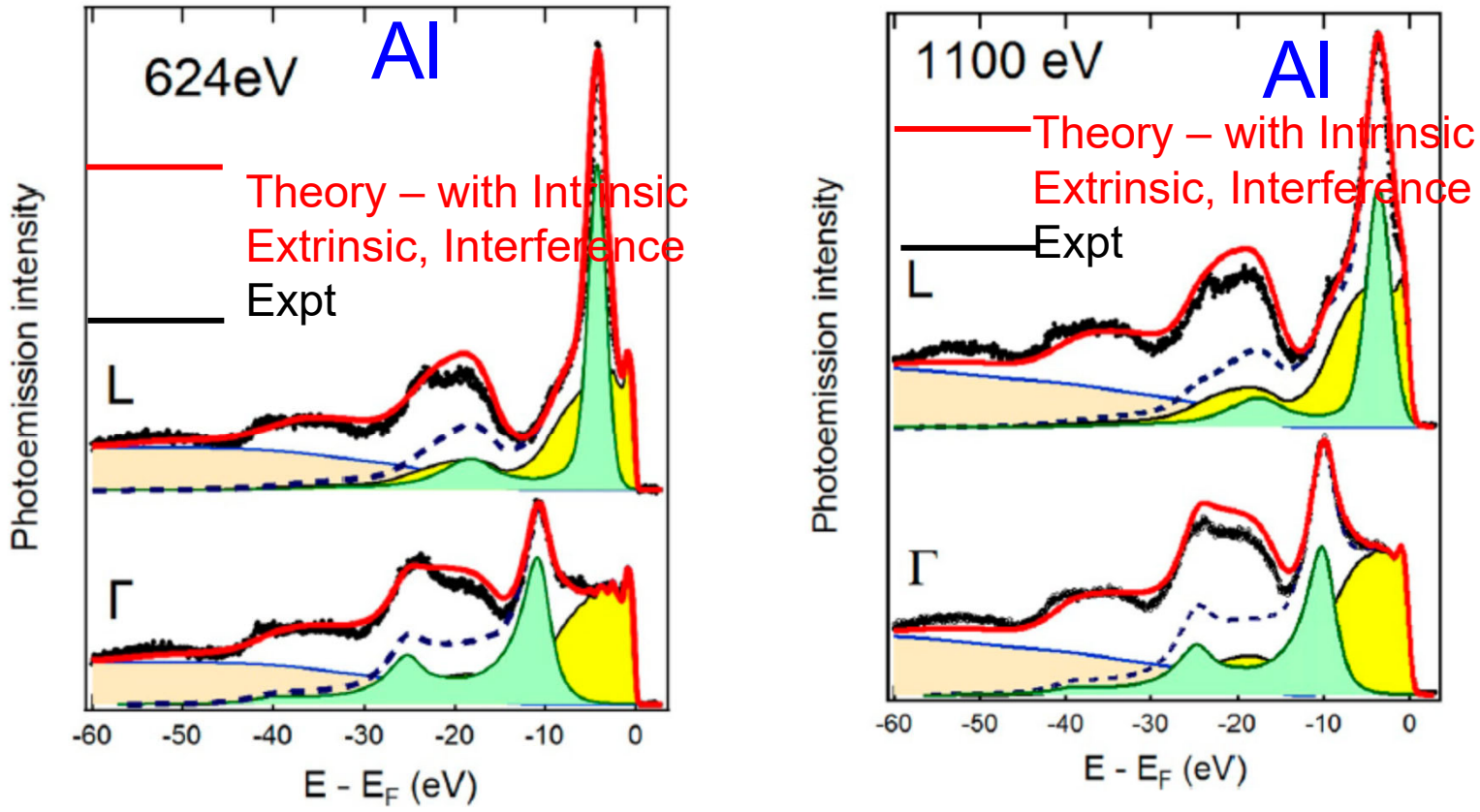
Retarded cumulant has multiple satellites BUT intensity too small

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]



? Correlated systems ?

Question: Can the particle-hole cumulant GF apply to correlated d- and f-electron systems ?

Hedin's answer* **MAYBE**

"Calculation similar … not a question of principle, but of computational work..."

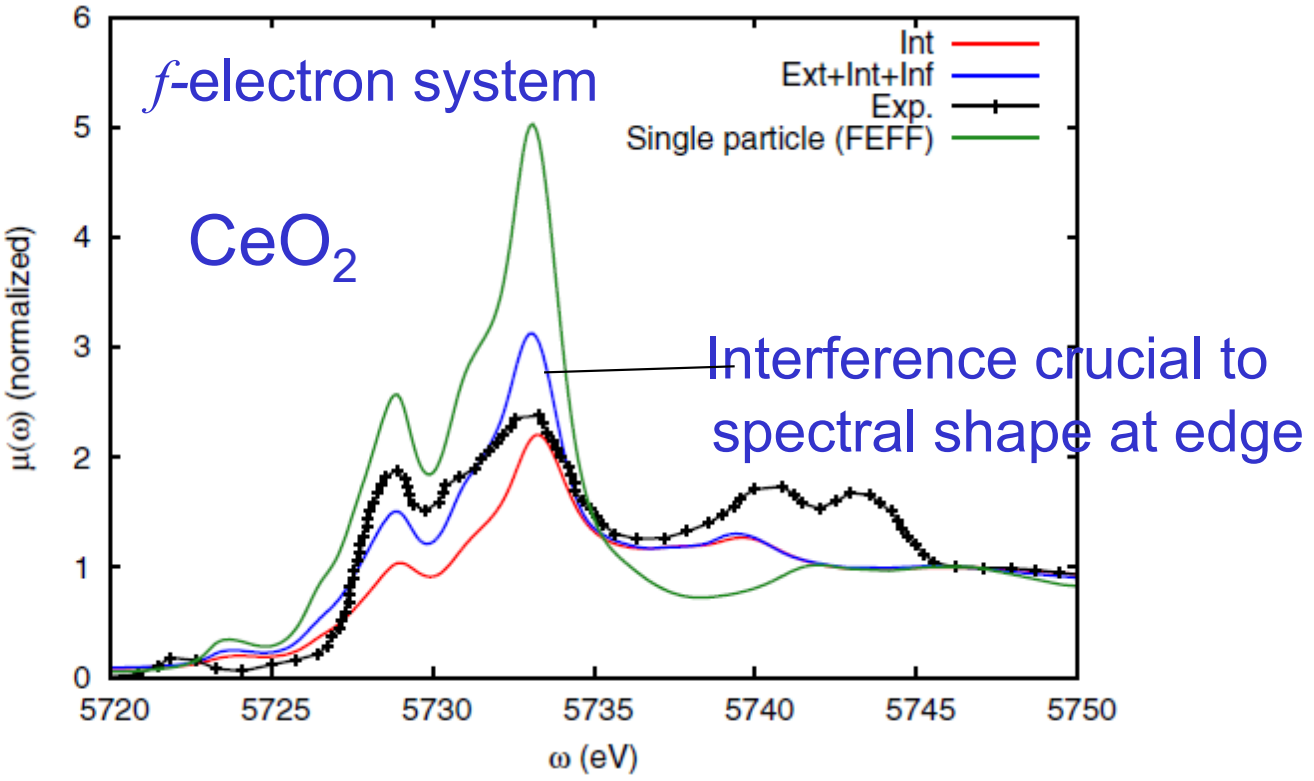
* L. Hedin, J. Phys.: Condens. Matter **11,** R489 (1999)

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



Interference crucial to spectral shape at edge

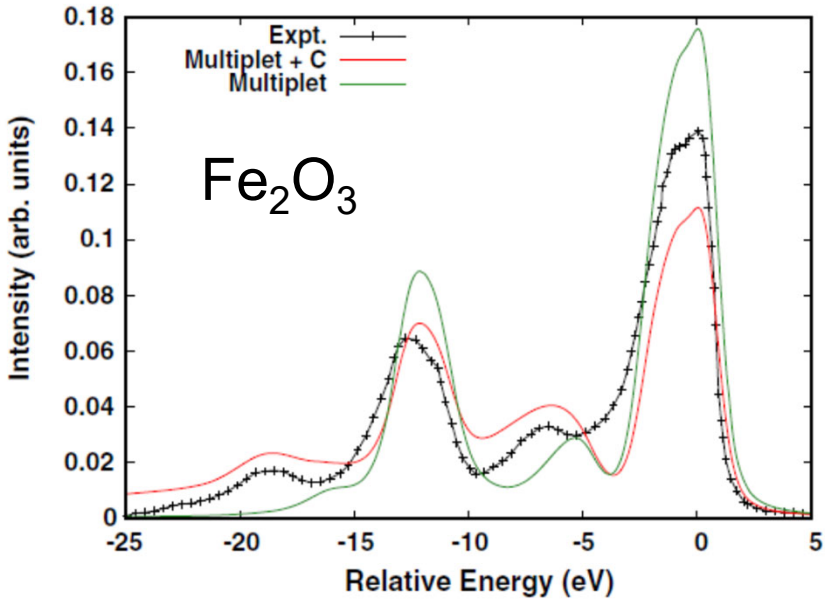
Extension: Multiplet + Cumulant Approach

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 of XPS

Extension: EOM-CC for correlated molecular systems

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

$$C(t) = \int \; + \; dt' \quad = i \int_0^t \langle \phi | \bar{H}_N(t') | \phi \rangle \mathrm{d}t'$$

pubs.acs.org/JCTC

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

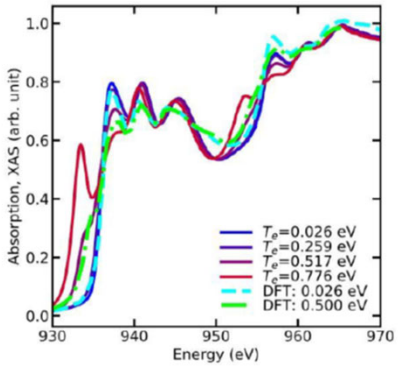
Cite This: J. Chem. Theory Comput. 2020, 16, 6983–6992

Read Online

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

III. High 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

Ab initio 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)

Hi T Properties from Cumulant Green's 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)

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

$$\frac{N}{V}=\int\frac{d\mathbf{p}}{(2\pi)^3}\int\frac{d\omega}{2\pi}\frac{\mathrm{tr}\,A^{\alpha\beta}(\mathbf{p}\omega)}{e^{\alpha+\beta\omega}\mp 1}. \qquad (3.67)$$

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

[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).

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

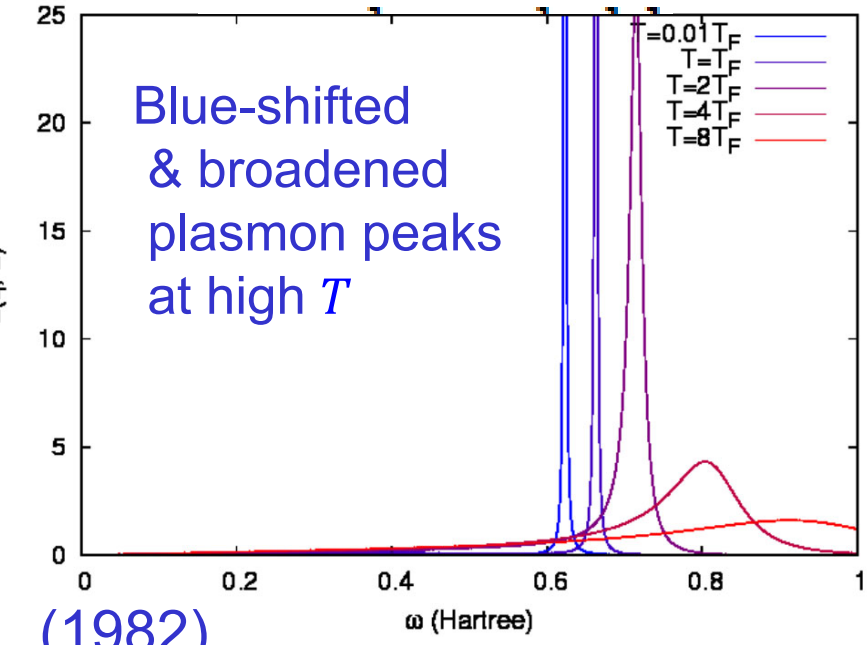
Screened Coulomb interaction $W(q,\omega)$

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

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

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

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



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

Chemical potential & occupation numbers

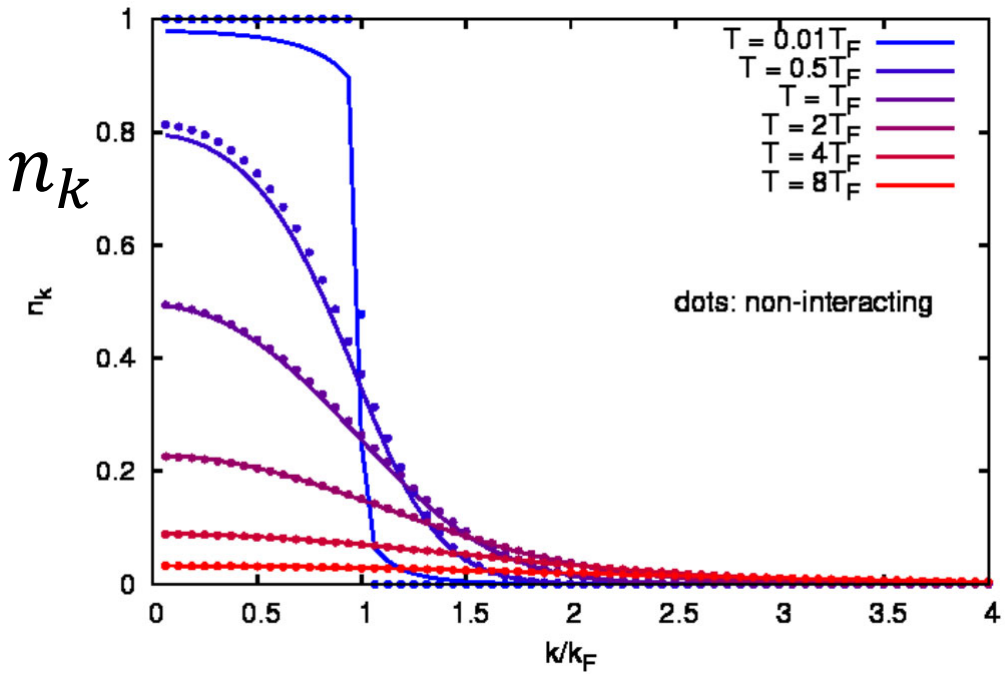
Chemical potential $\mu(T)$ fixed by charge neutrality

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

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

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

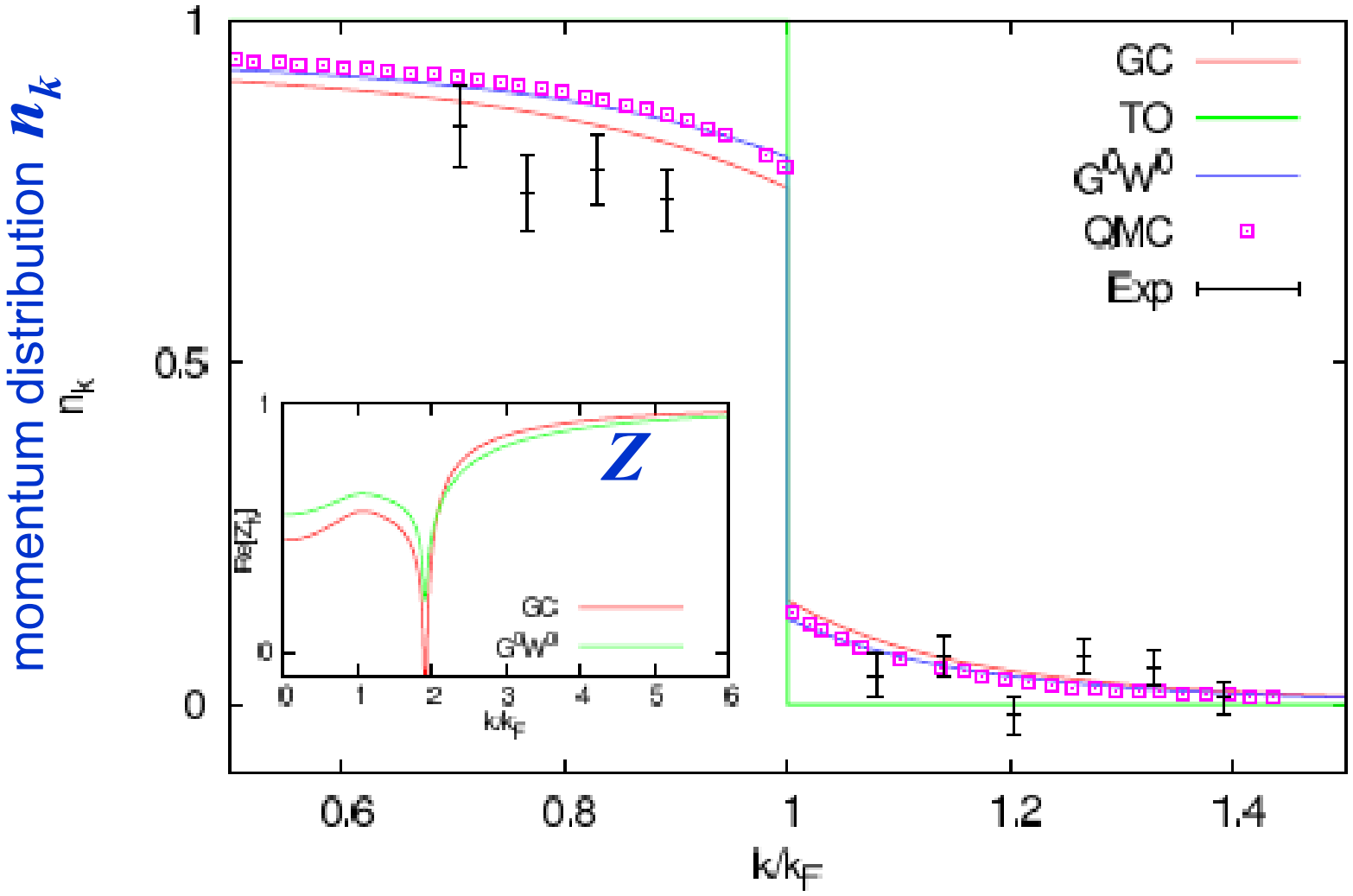
QP Occupation number



Increasingly metallic behavior at high T

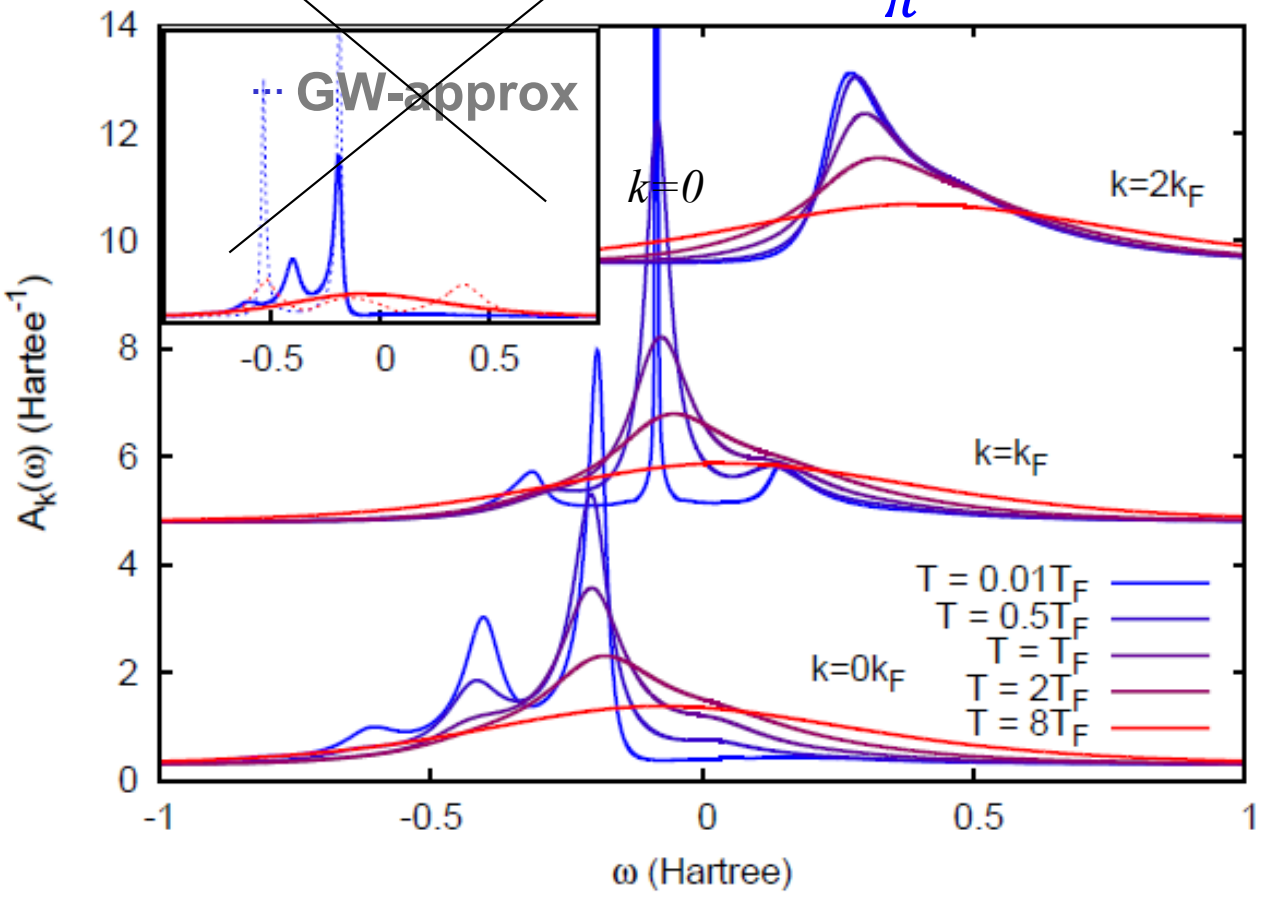
Electron-gas quasi-particle properties*

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



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

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



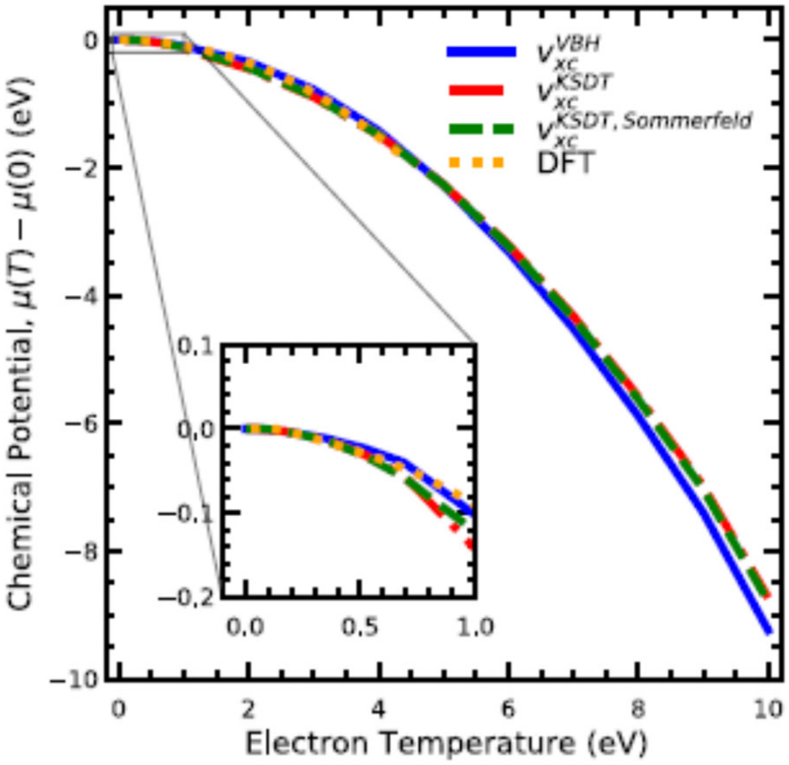
Single broad peaks at high T above k_F

Blurred QP peaks and satellites at k_F

Calculations simplify at high T
- no sharp satellite structure

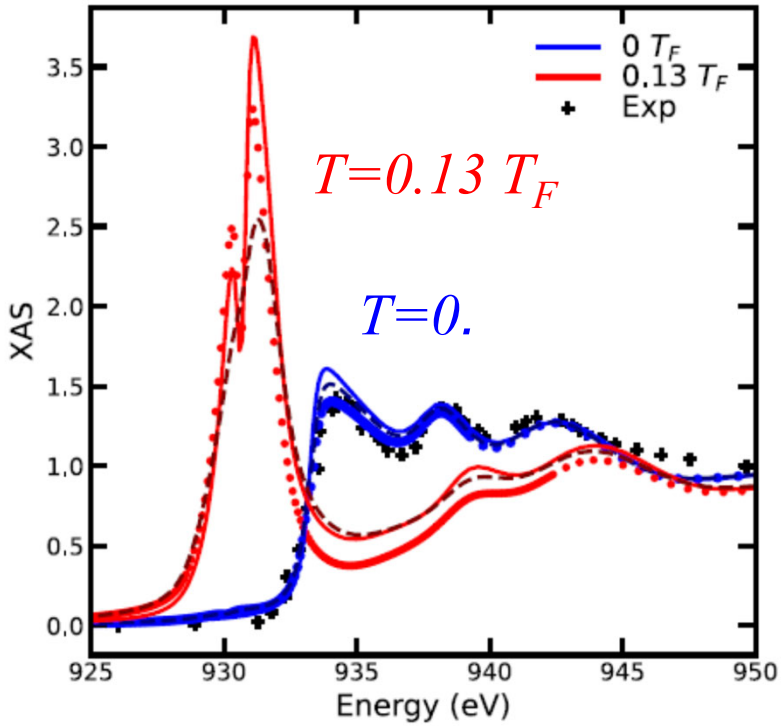
Finite T Chemical Potential* $\mu(n,T)$

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



"Continuum lowering "
edge-shifts to lower E

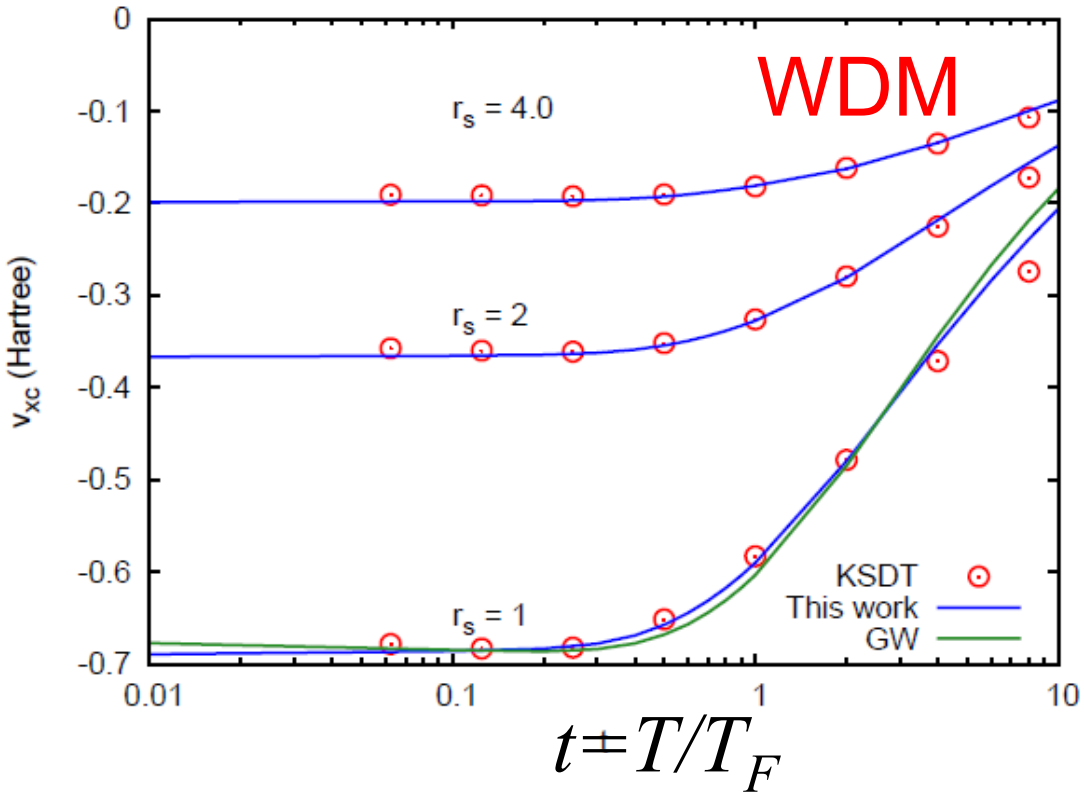
Cu-L XAS



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

Bonus: 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

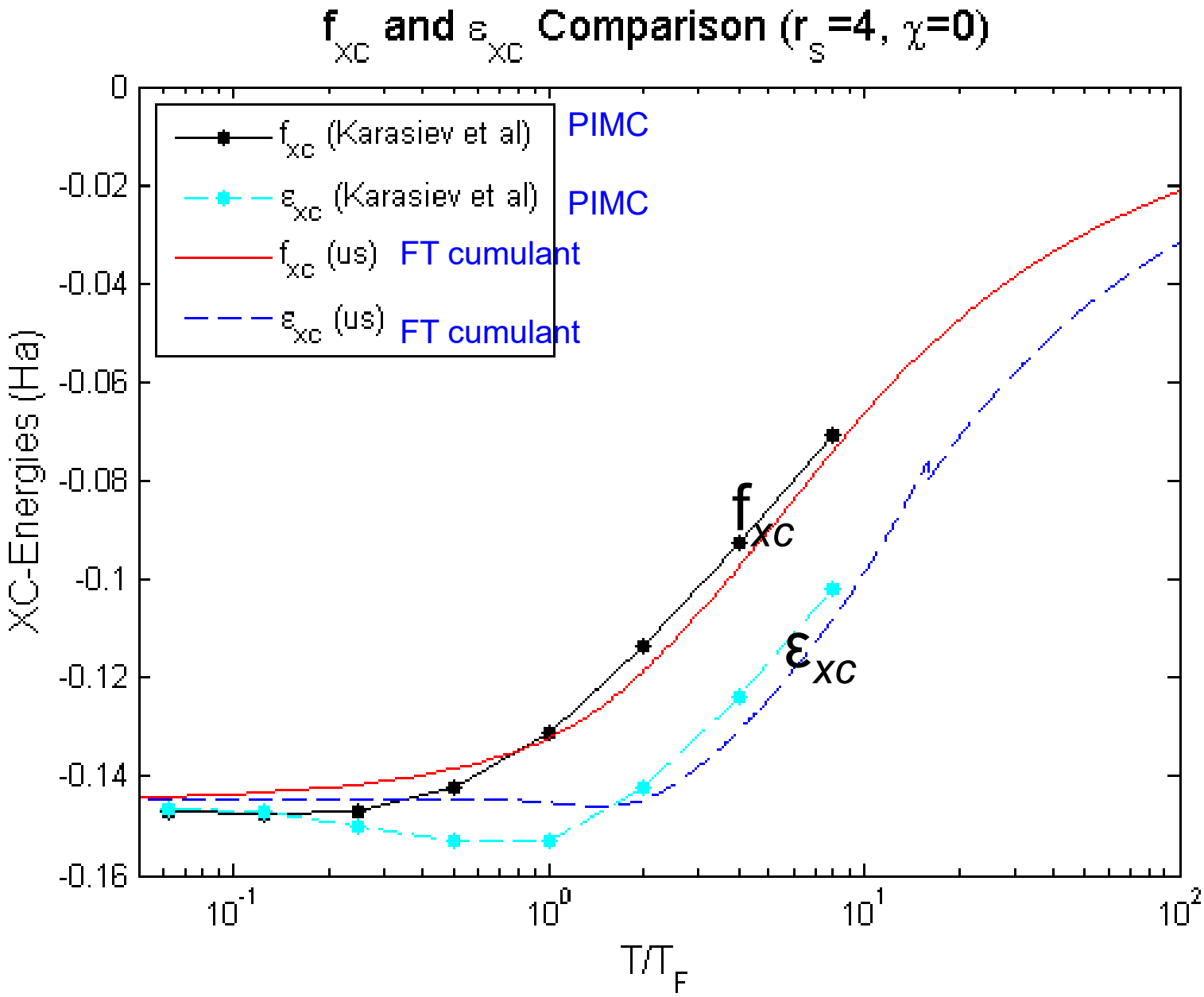
Finite T cumulant♦ $v_{xc}(T)$ in good agreement with Finite T DFT* functionals○

*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)

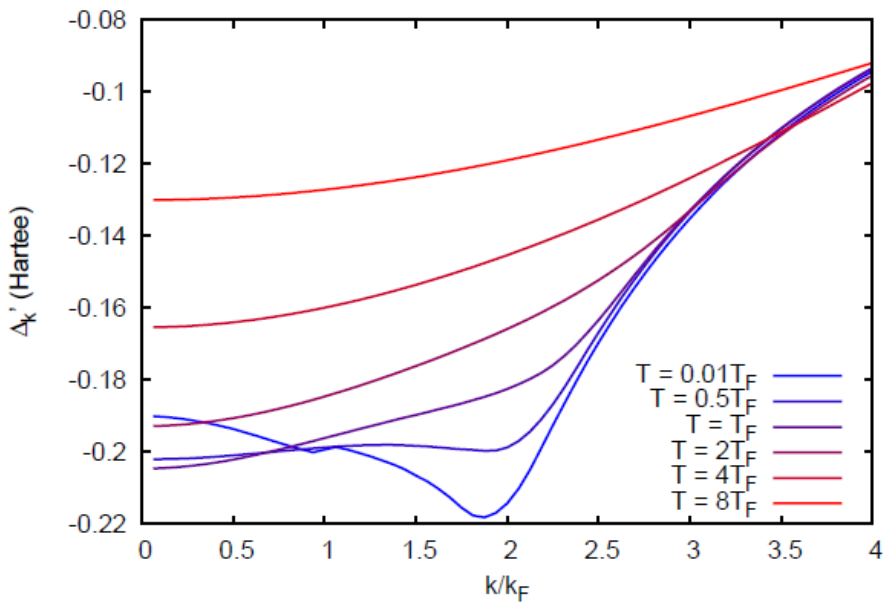
FT Exchange-correlation energy and free energy



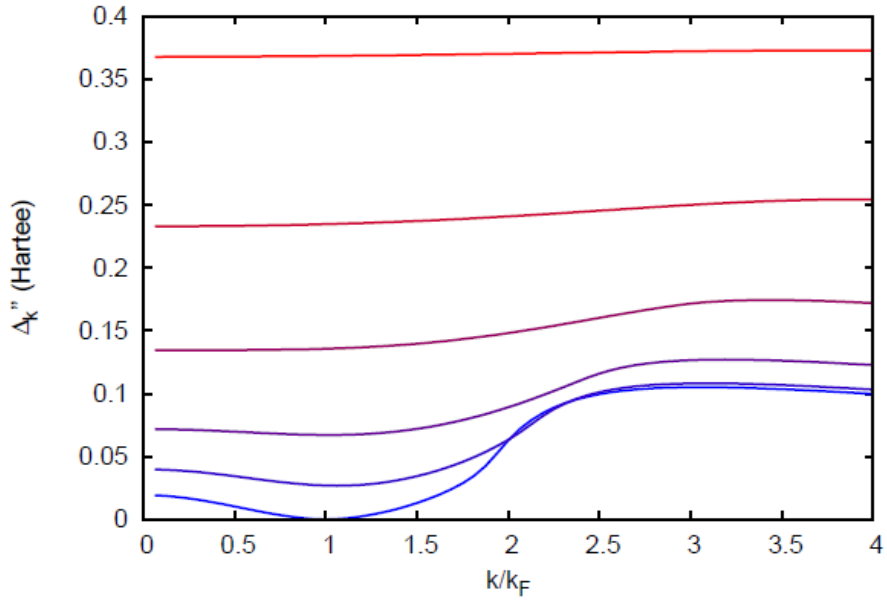
Quasi-particle energies & damping

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

Energy shift Δ_k



Damping Δ_k''



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

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

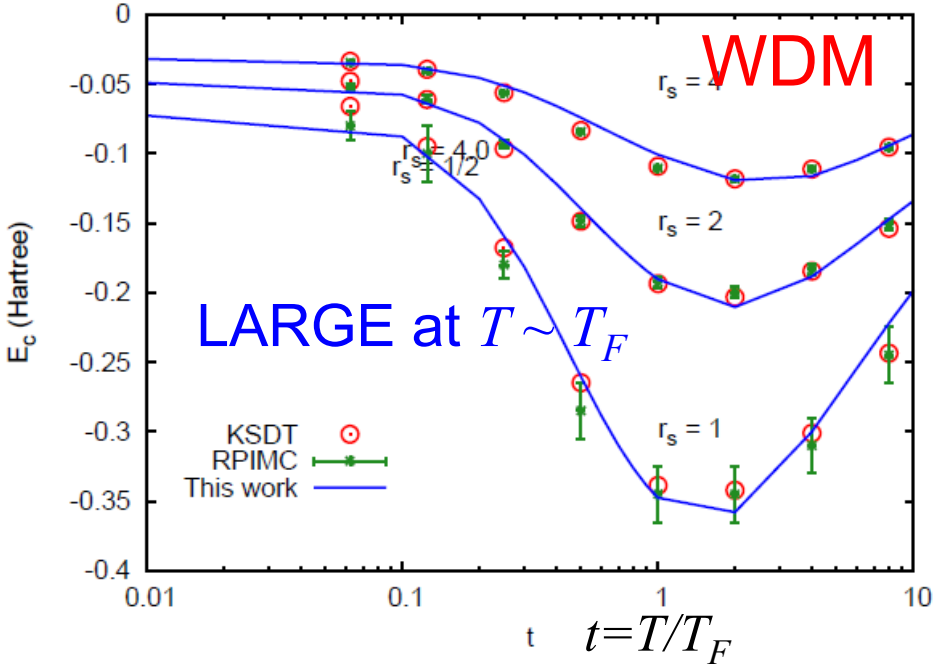
Cross-over to *m*etallic - short-ranged plasma-like behavior

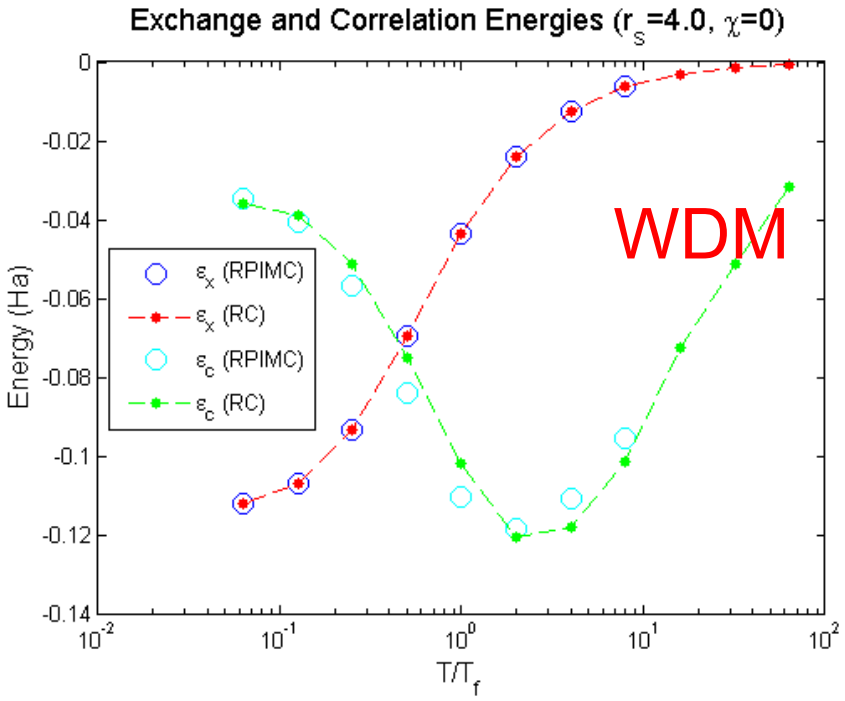
Finite T Correlation Energy*

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)

Efficient static finite-T COHSEX Approximation

Coulomb-hole and screened-exchange in the electron-self energy at finite temperature

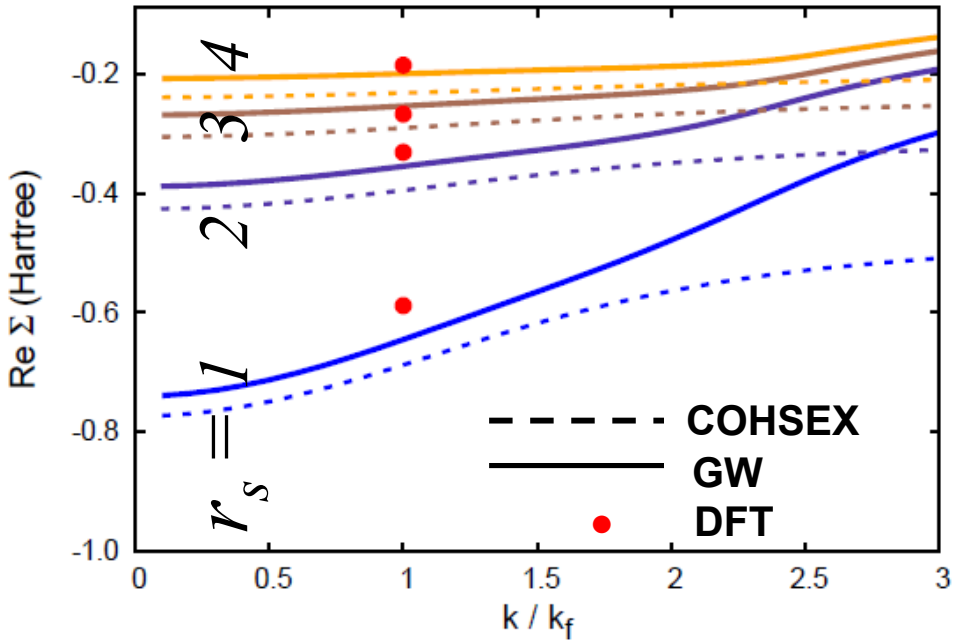
Tun S. Tan, J. J. Kas, and J.J. Rehr
Dept. of Physics, Univ. of Washington, Seattle, WA 98195-1560
(Dated: August 3, 2018)

$$\Sigma_k^{COHSEX} \equiv \Sigma_k^{COH} + \Sigma_k^{SEX}$$ = poles of W + poles of G

$$\mathrm{Re}\left[\Sigma_k^{COH}(T)\right] = \frac{1}{2}\int \frac{d^3q}{(2\pi)^3} W_p^M(q,0)$$

$$\Sigma_k^{SEX}(T) = -\int \frac{d^3q}{(2\pi)^3} f(\varepsilon_{\mathbf{k}-\mathbf{q}}) W^M(q,0)$$

COHSEX accurate to ~ *10%*



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

EPJ B
Condensed Matter and Complex Systems
EPJ.org
your physics journal

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

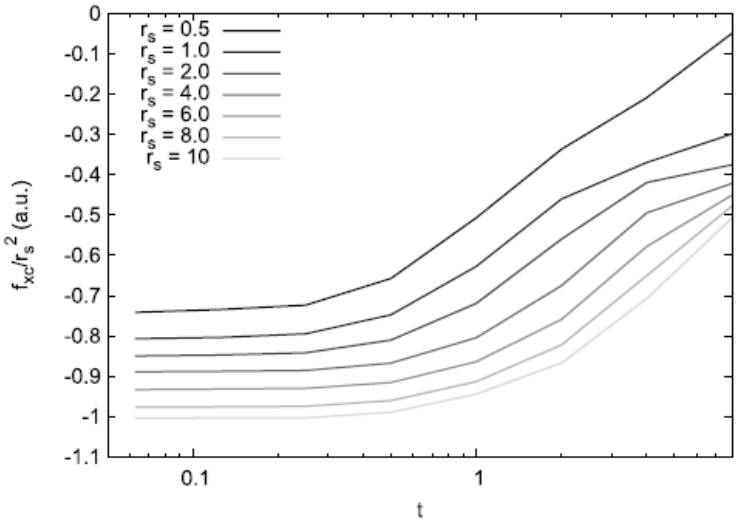
Exchange and correlation in finite-temperature TDDFT*

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

Dept. of Physics, BOX 351560, Univ. of Washington, Seattle, WA 98195-1560, USA

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

FT-TDDFT f_{xc}/r_s^2



Needed for finite T optical spectra, inelastic losses

Example: Finite T XAS

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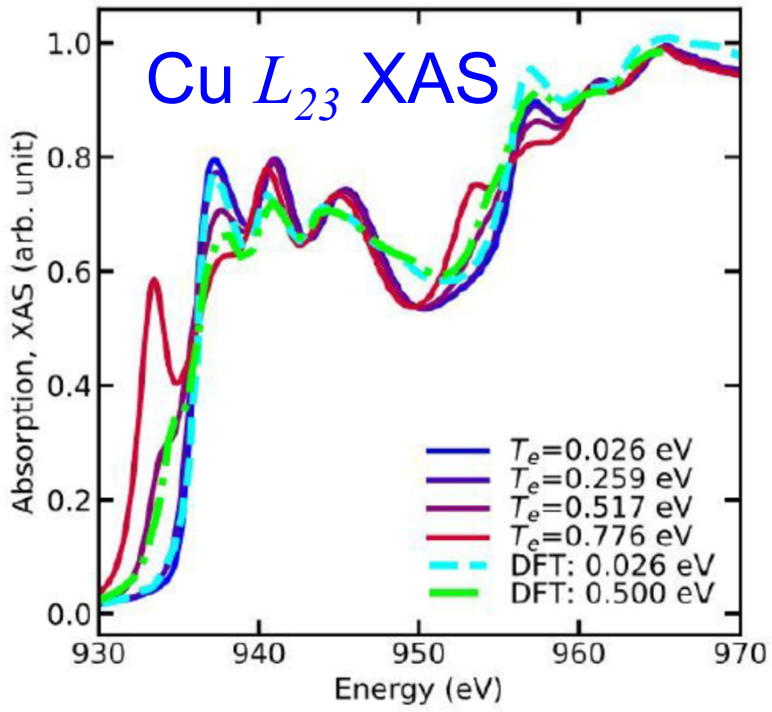
Cite this: *Phys. Chem. Chem. Phys.*, 2022, **24**, 13461

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

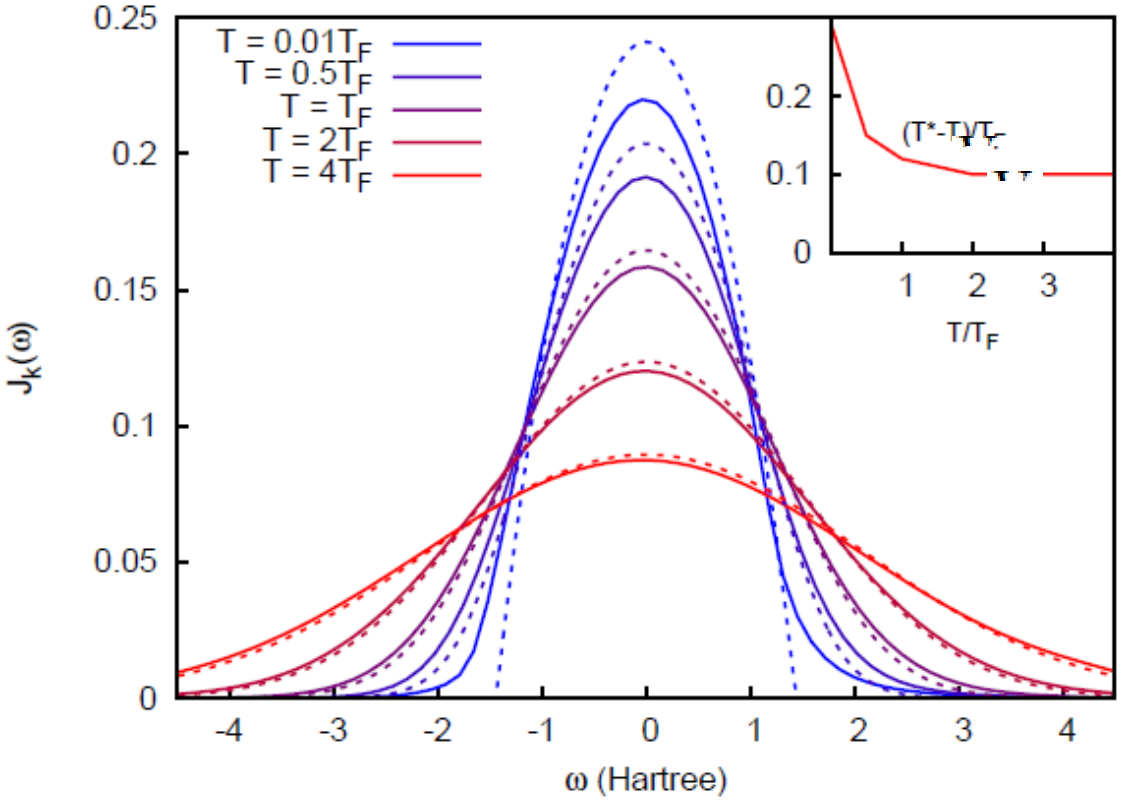
Large T-dependence in XAS edge-shifts, broadening, …



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) & free electron (dotted)



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

Suggested 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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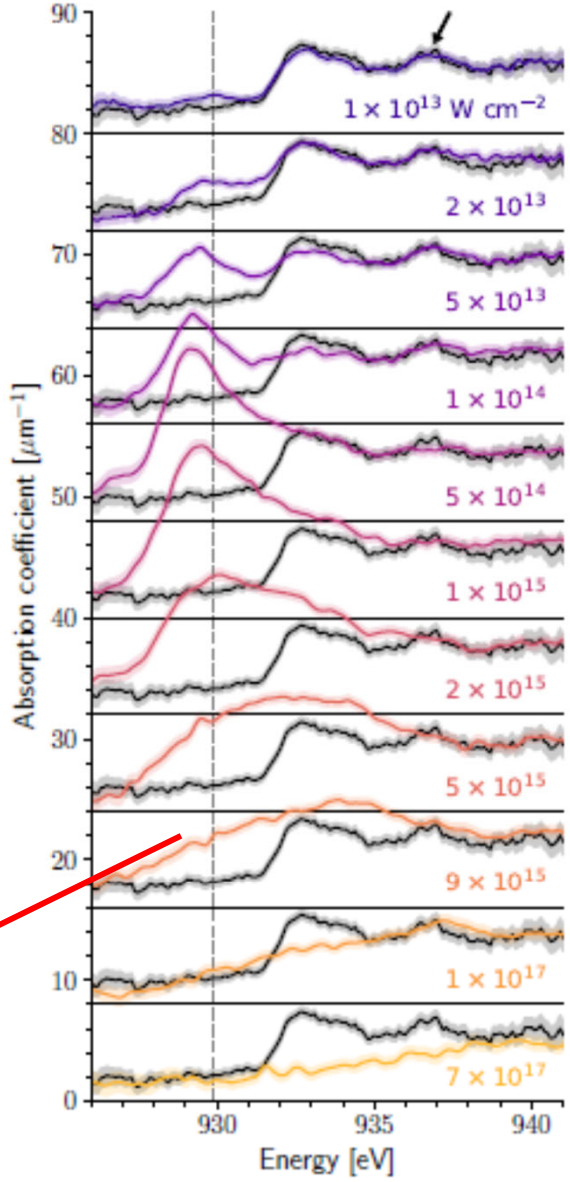


Experiment:
L-edge XAS of Cu from ultra-short 15 fs, 932 eV XFEL X-ray pulses vs pulse intensity (red)

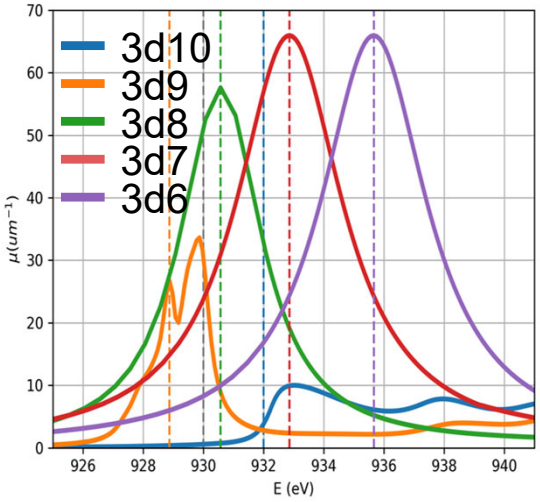
Cross-over: RSA to SA with increased intensity

Transient high fluence XAS theory vs expt

Theory*

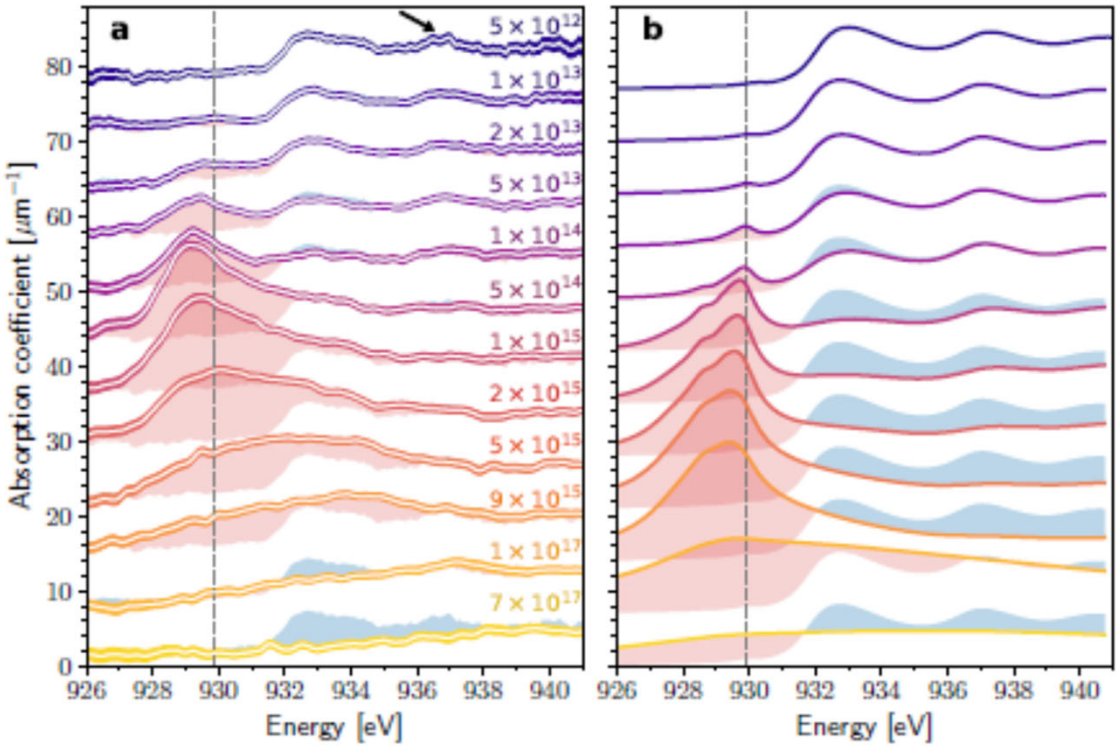
SCF FEFF10 results averaged over Boltzmann weighted 3d * configurations vs pulse intensity

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

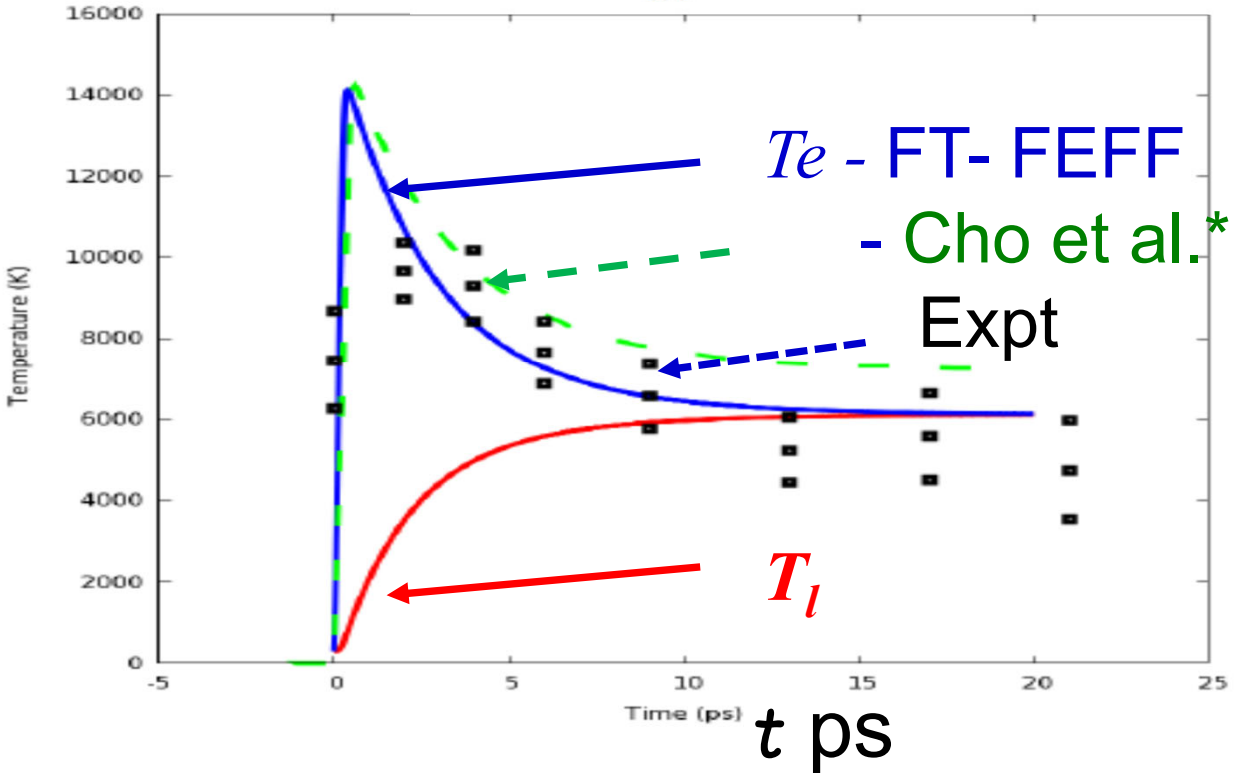
FEFF10: J.J. Kas et al. PCCP **24,** 13461 (2022)

Example: Non-equilibrium Pump-Probe Expt

2-T Models: Electron and lattice T vs time

$$C_e(T_e)\frac{dT_e(t)}{dt} = -G(T_e)[T_e(t) - T_i(t)] + S_L(t)$$

$$C_i\frac{dT_i(t)}{dt} = G(T_e)[T_e(t) - T_i(t)].$$



Electronic temperature Te (blue) vs Lattice temperature T_l (red) for Cu
For comparison Te (green) from Cho et al. PRL **106**, 167601 (2011)
and Expt (black dashes).

Last example: Non-resonant Two Photon Absorption*

PRB **112**, 045116 (2025)

Non-resonant two-photon x-ray absorption in Cu

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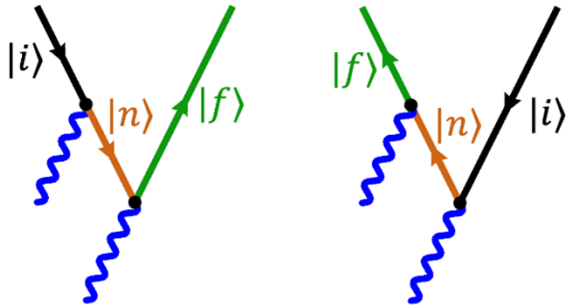


Kramers-Heisenberg Eq.

$$\sigma^{2P}_{\mathrm{XAS}}(\omega) = 8\pi^3\alpha^2\omega^2 \times \sum_F |M_{IF}(\omega)|^2 \delta_{\Gamma_F}(2\omega + E_I - E_F)$$

$$M_{IF}(\omega) = \sum \frac{\langle F|\hat{d}|X\rangle\langle X|\hat{d}|I\rangle}{\omega + E_I - E_X + i\Gamma_X}.$$

Über Elementarakte mit zwei Quantensprüngen

Von Maria Göppert-Mayer

Translation: ***Elementary processes with two quantum transitions***

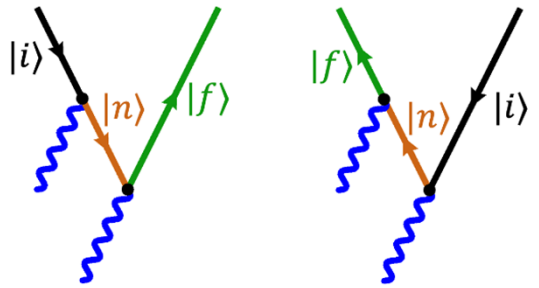
*Ann. Phys. **18**, 466 (1930) DOI 10.1002/andp.200910358

Green's function Theory of TPA*

Independent electron Kramers-Heisenberg Equation

$$\sigma^{2P}_{\mathrm{XAS}}(\omega) = 8\pi^3\alpha^2\omega^2 \sum_{f}^{unocc} |M_{if}(\omega)|^2 \delta(2\omega + \epsilon_i - \epsilon_f)$$

$$M_{if}(\omega) = \langle f | d\, G_{l=1}(\omega + \epsilon_{1s}) d | i \rangle$$



$$d\, G_{l=1} d \approx -\frac{\boldsymbol{Q}}{\omega}$$ Effective static TPA quadrupole op.

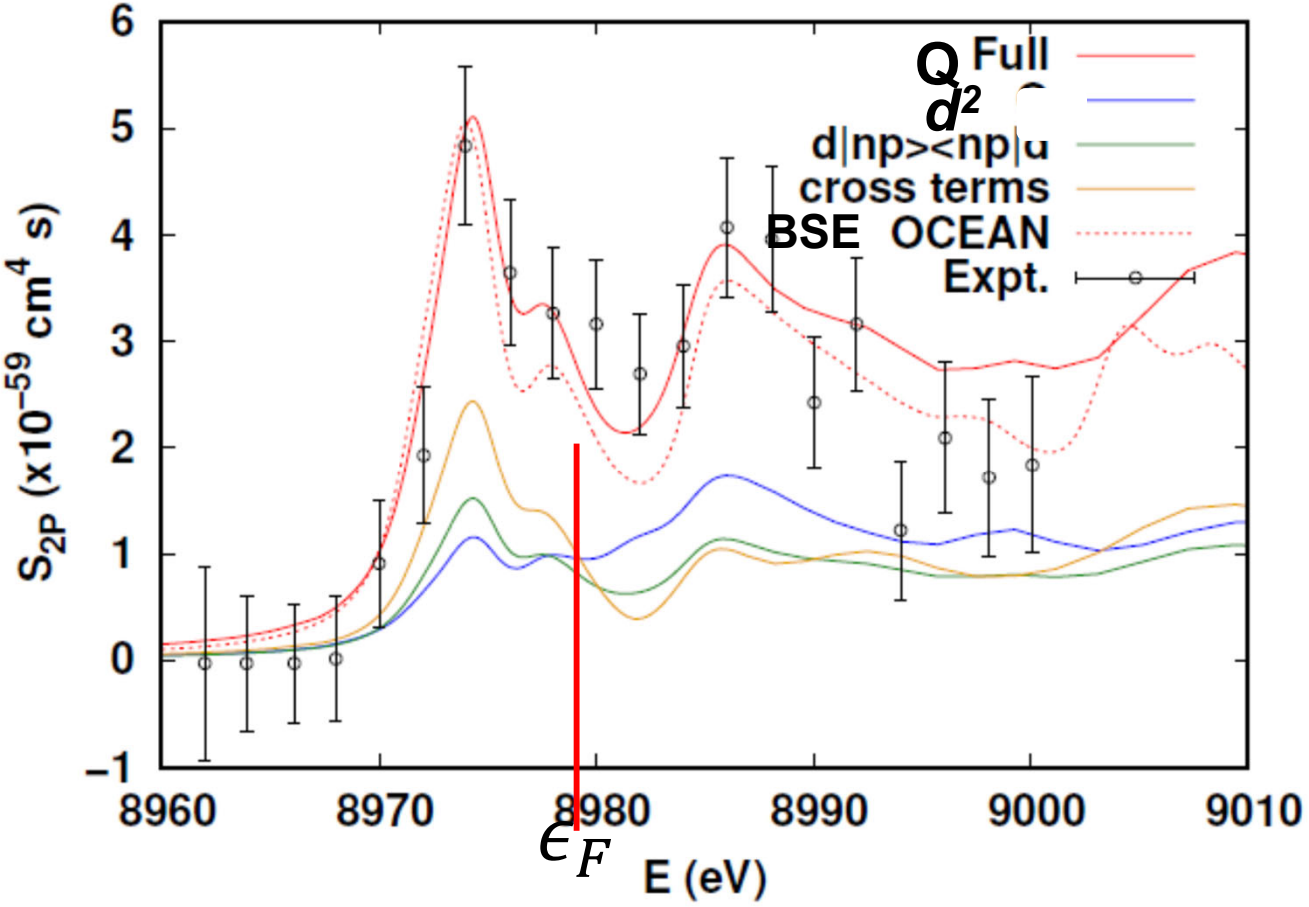
Calculation of TPA similar to OPA with dipole operator $\boldsymbol{d}$ replaced by $\boldsymbol{Q}$ in FEFF calculation

*J. J. Kas et al. Phys. Rev. B **112**, 045116 (2025)

Real-space Green's Function TPA Calculations*

XFEL effects modeled by *depleted* d-band occupation $g(\epsilon)$ & well screened core-hole

No-hole approximation



Quantitative agreement with XFEL TPA experiment & Bethe Salpeter Equation TPA calculations

*J. J. Kas et al. Phys. Rev. B **112**, 045116 (2025)

Summary and Conclusions

- Advances in theory based on Cumulant GF explain several many body effects ~ 10-20% corrections to quasiparticle theory

- Convolution formula for XAS explains satellites, inelastic losses & long-range corrections to atomic multiplet theory

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

- Extensions & codes for satellites, multiplets & finite-T, extreme conditions all based on cumulant GF

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J. Sky Zhou
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S. Vimolchaleo

That's all folks