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Many-pole Model of X-ray Photoemission spectra

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Many-pole Model of X-ray Photoemission spectra

- **GOAL**: Calculate many-body effects in photoemission
  - *L. Hedin's* Quasi-boson method

- **TALK**:

1. Green's Function approach
2. Spectral function in Photoemission and XAS
3. Many-pole Self-energy
4. Satellites, Intrinsic and Extrinsic Losses

``If I can't calculate it,

I don't understand it."

R.P. Feynman

Formalism: Quasi-boson Approach

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

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Abstract. The *GW* approximation (GWA) extends the well-known Hartree–Fock approximation (HFA) for the self-energy (exchange potential), by replacing the bare Coulomb potential v by the *dynamically screened potential* W, e.g. $V_{ex} = iGv$ is replaced by $\Sigma_{GW} = iGW$. Here G is the one-electron Green's function. The GWA like the HFA is self-consistent, which allows for solutions beyond perturbation theory, like say spin-density waves. In a first approximation, iGW is a sum of a statically screened exchange potential plus a Coulomb hole (equal to the electrostatic energy associated with the charge pushed away around a given electron). The Coulomb hole part is larger in magnitude, but the two parts give comparable contributions to the dispersion of the quasi-particle energy. The GWA can be said to describe an *electronic polaron* (an electron surrounded by an electronic polarization cloud), which has great similarities to the ordinary polaron (an electron surrounded by a cloud of phonons). The dynamical screening adds new crucial features beyond the HFA. With the GWA not only bandstructures but also spectral functions can be calculated, as well as charge densities, momentum distributions, and total energies. We will discuss the ideas behind the GWA, and generalizations which are necessary to improve on the rather poor GWA satellite structures in the spectral functions. We will further extend the GWA approach to fully describe spectroscopies like photoemission, x-ray absorption, and electron scattering. Finally we will comment on the relation between the GWA and theories for strongly correlated electronic systems. In collecting the material for this review, a number of new results and perspectives became apparent, which have not been published elsewhere.

Excitations (plasmons, electron-hole pairs, ...)
represented by **bosons**

Wave-function vs Green's functions

Paradigm shift:

Use Green's functions *not* wave functions!

- Golden rule via Wave functions

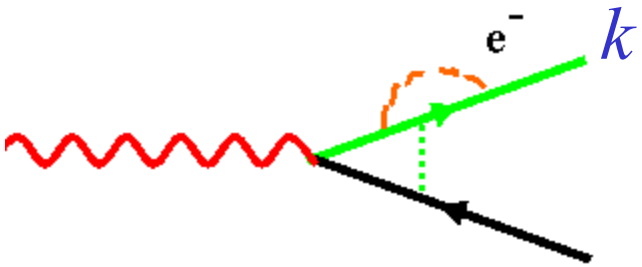
XAS $$\mu(E) \sim \Sigma_f |\langle i|\hat{\epsilon}\cdot\mathbf{r}|f\rangle|^2 \delta(E-E_f)$$

- Golden rule via Green's functions *Efficient!*

Theorem: $-\frac{1}{\pi}\mathrm{Im}\, G(\mathbf{r}',\mathbf{r},E) = \Sigma_f |f\rangle\delta(E-E_f)\langle f|$

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

Green's Function formalism



Key ingredients:

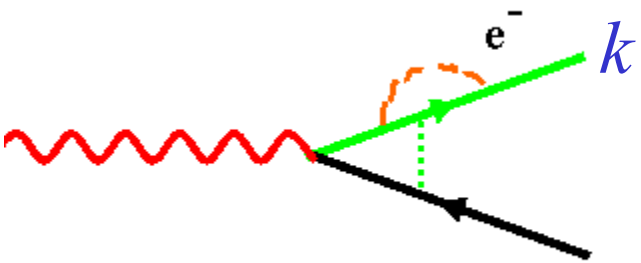
A. One-particle **Green's function**

$$G(\omega) = 1/[\omega - h - \Sigma(\omega)]$$

B. **Spectral Function** – beyond quasi-particle approx:

$$A(\omega) = \frac{1}{\pi} \operatorname{Im} G(\omega)$$

Spectral function and core-Photoemission



sudden approximation (intrinsic losses only):

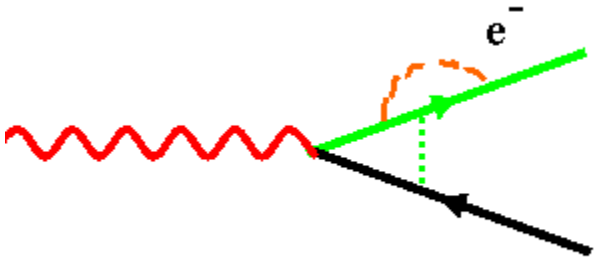
$$J_k(\omega) = \sum_i M_{ki} A_{ii}(\epsilon_k - \omega) M_{ik}$$

independent particle approximation

$$\approx \sum_i |M_{ki}|^2 \delta(\epsilon_k - \epsilon_i - \omega)$$

? What about extrinsic losses and satellites ?

XAS vs Photoemission



XAS ~ XPS summed over all final states k

(time-reversed scattering states)

$$\mu(\omega) = \sum_k J_k(\omega)$$

$$\approx \sum_{ik} |M_{ik}|^2 \delta(\epsilon_k - \epsilon_i - \omega)$$

GW Self-energy (L. Hedin 67)

- GW Approximation

$$\Sigma(E) = i \int \frac{d\omega}{2\pi} G(E-\omega) W(\omega) e^{-i\delta\omega}$$

- Screened Coulomb Interaction W

$$W = \epsilon^{-1}(\omega) V$$

- Ingredient: Dielectric Response $\epsilon^{-1}(\omega)$

Quasi-boson Hamiltonian

(Mapping of full many-body Hamiltonian)

$$h = \sum_k \epsilon_k c_k^\dagger c_k$$

electrons

$$H_v = \sum_n \omega_n a_n^\dagger a_n$$

valence excitations

bosons

electron-boson coupling

$$V_{ev} = \sum_{nkk'} c_k^\dagger c_{k'} [V_{kk'}^n a_n^\dagger + hc]$$

core-hole-boson coupling

$$V_{vc} = -\sum_n V_{cc}^n (a_n^\dagger + a_n)$$

Self-energy Algorithm: Many-pole Dielectric Function*

Map boson couplings V^q to loss function*

"fluctuation potentials"

Full spectrum loss function < FEFF8

$-\mathrm{Im}\, \varepsilon^{-1}(\omega) \longrightarrow$ *many-pole* model

$\sim \Sigma_i g_i \delta(\omega - \omega_i)$

$\longrightarrow$ *many-pole* self-energy

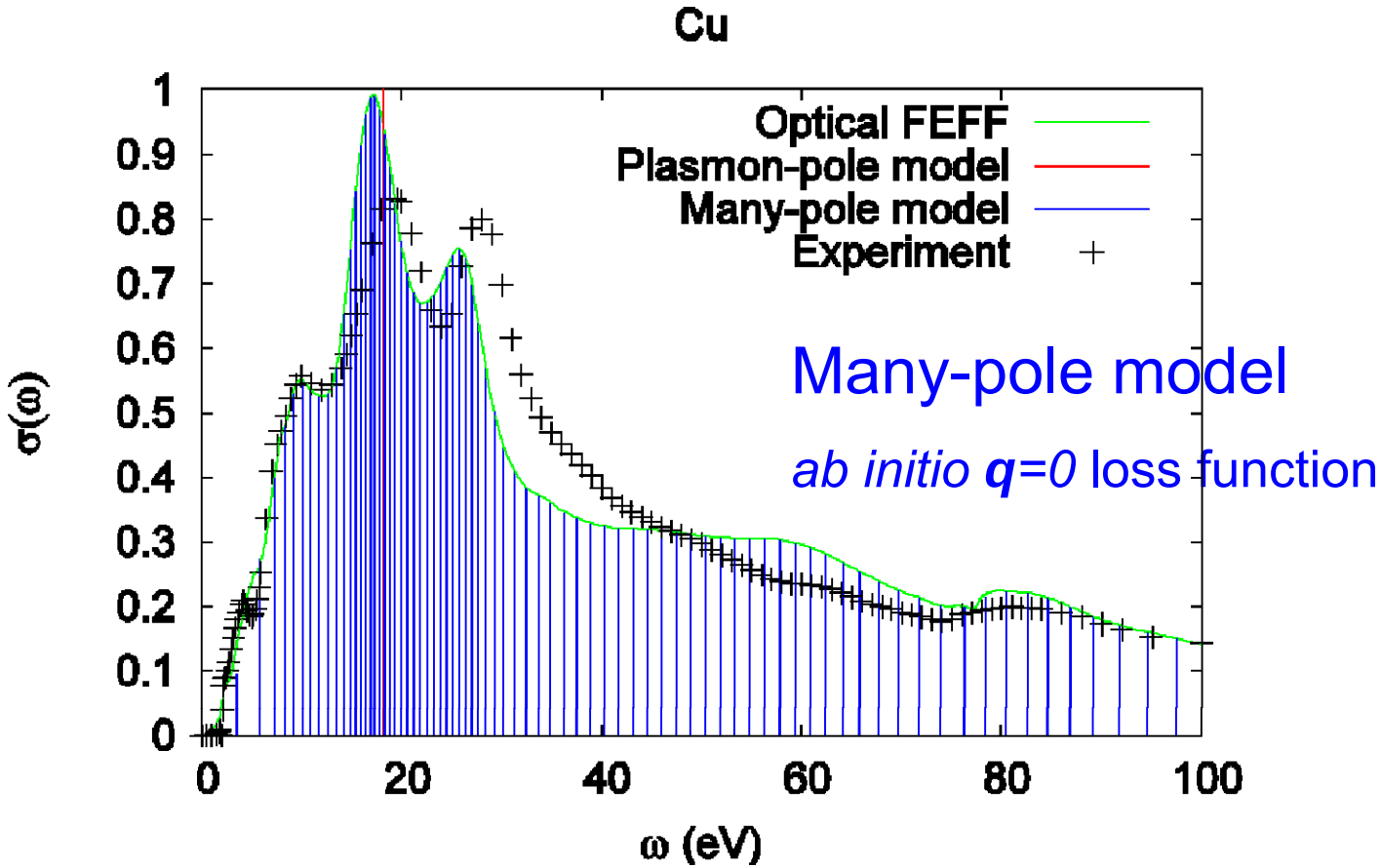
Improvement on plasmon-pole model:

* J. Kas et al. PRB **76**, 195116(2008)

J.A. Soininen et al. J. Phys. CM **15**, 2573 (2003)

Example: energy loss function of Cu

Calculated -Im $\varepsilon^{-1}(\omega)$ FEFF8OP - M. Prange

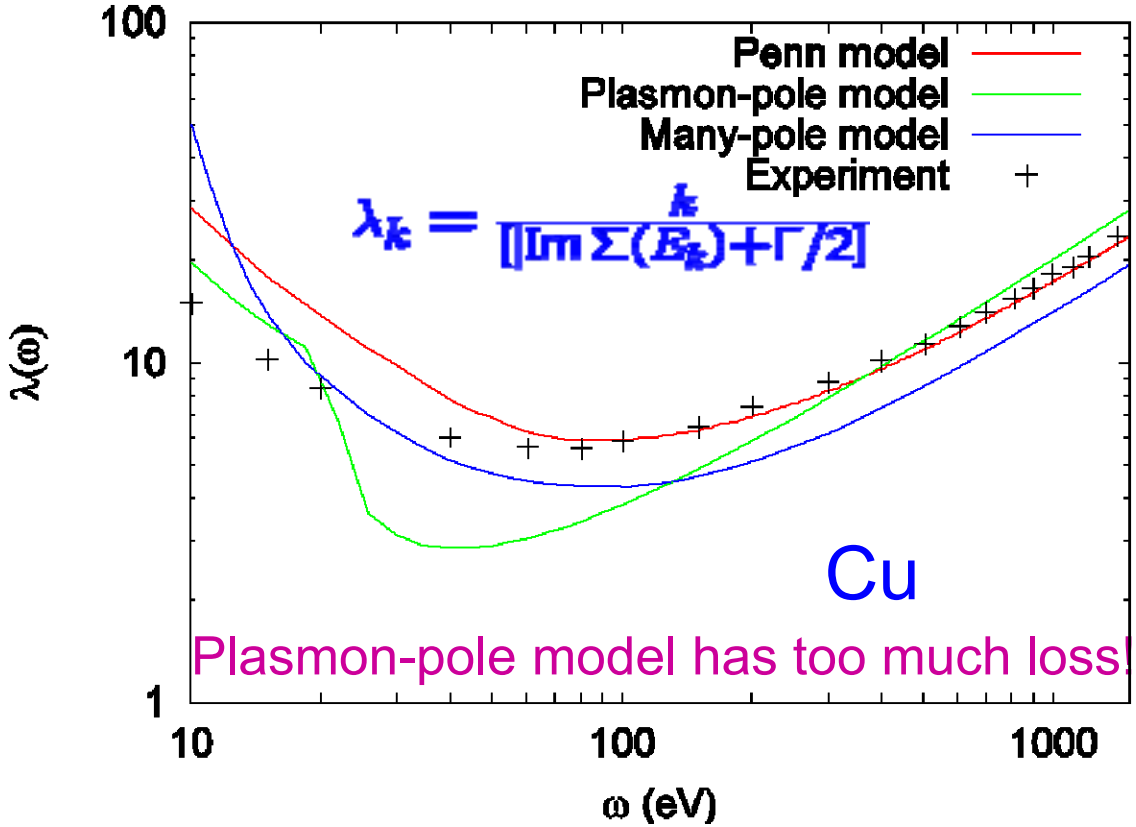


J. Kas et al. PRB **76**, 195116(2008)

Example: *ab initio* Inelastic Mean Free Paths

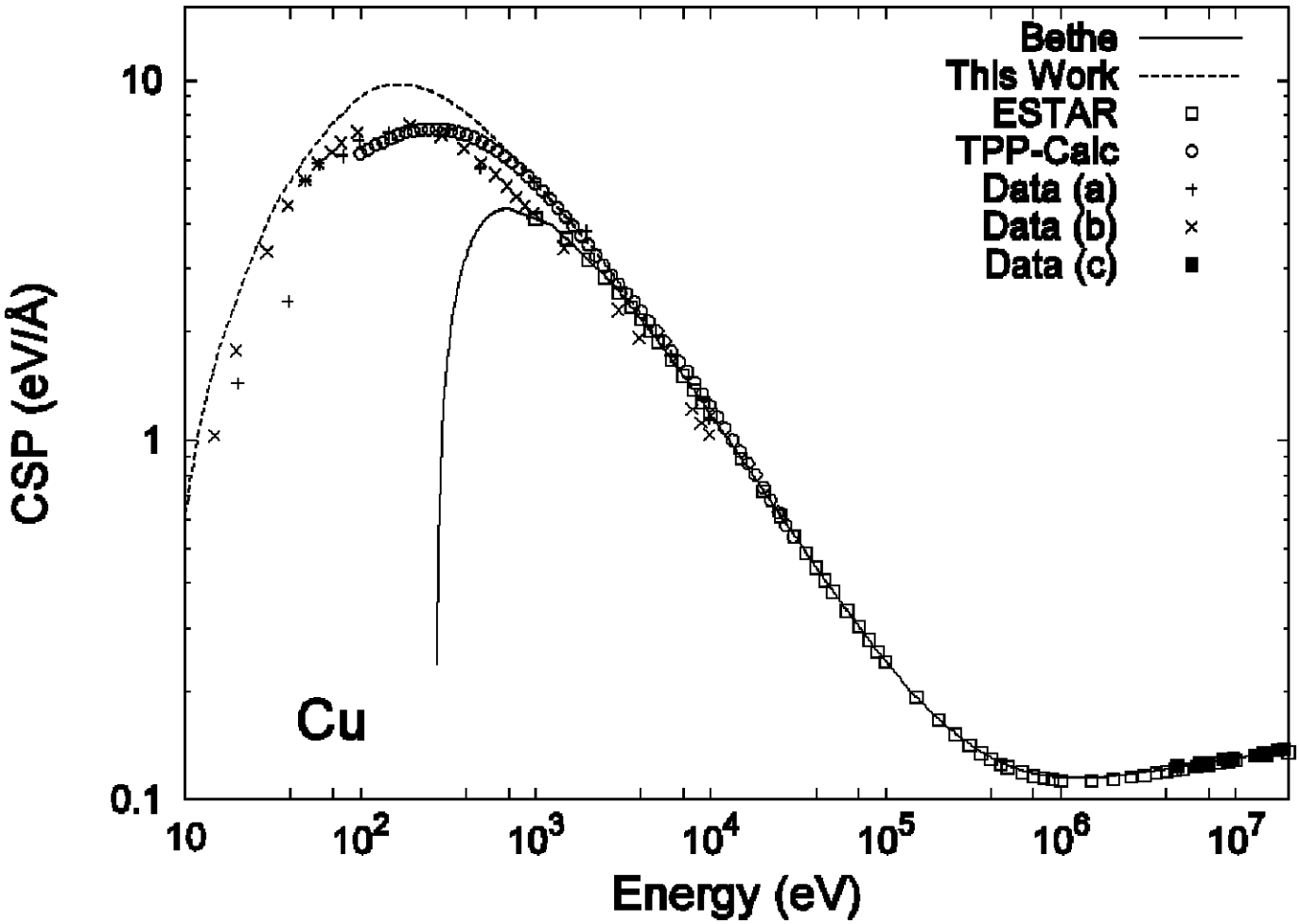
Plasmon-pole model → ***many-pole*** model

Inelastic mean free path



J. Kas et al. Phys Rev B. **76**, 195116 (2008)

Example *Ab initio* Collision Stopping Powers



A. Sorini et al. Phys Rev B 74, 165111 (2006)

Satellites: beyond the sudden approximation in photoemission

PHYSICAL REVIEW B VOLUME 58, NUMBER 23 15 DECEMBER 1998-I

Transition from the adiabatic to the sudden limit in core-electron photoemission

Quasi-boson Model

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(Received 17 July 1998; revised manuscript received 3 September 1998)

Experimental results for core-electron photoemission $J_k(\omega)$ are often compared with the one-electron spectral function $A_c(e_k-\omega)$, where ω is the photon energy, e_k is the photoelectron energy, and the optical transition matrix elements are taken as constant. Since $J_k(\omega)$ is nonzero only for $e_k>0$, we must actually compare it with $A_c(e_k-\omega)\theta(e_k)$. For metals $A_c(\omega)$ is known to have a quasiparticle (QP) peak with an asymmetric power-law [theories of Mahan, Nozières, de Dominicis, Langreth, and others (MND)] singularity due to low-energy particle-hole excitations. The QP peak starts at the core-electron energy e_c, and is followed by an extended satellite (shakeup) structure at smaller ω. For photon energies ω just above threshold, $\omega_{th}=-e_c$, $A_c(e_k-\omega)\theta(e_k)$ as a function of e_k (ω constant) is cut just behind the quasiparticle peak, and neither the tail of the MND line nor the plasmon satellites are present. The sudden (high-energy) limit is given by a convolution of $A_c(\omega)$ and a loss function, i.e., by the Berglund-Spicer two-step expression. Thus $A_c(\omega)$ alone does not give the correct photoelectron spectrum, neither at low nor at high energies. We present an extension of the quantum-mechanical (QM) models developed earlier by Inglesfield, and by Bardyszewski and Hedin to calculate $J_k(\omega)$. It includes recoil and damping, as well as shakeup effects and extrinsic losses, is exact in the high-energy limit, and allows calculations of $J_k(\omega)$ including the MND line and multiple plasmon losses. The model, which involves electrons coupled to quasibosons, is motivated by detailed arguments. As an illustration we have made quantitative calculations for a semi-infinite jellium with the density of aluminum metal and an embedded atom. The coupling functions (fluctuation potentials) between the electron and the quasibosons are related to the random-phase-approximation dielectric function, and different levels of approximations are evaluated numerically. The differences in the predictions for the photoemission spectra are found small. We confirm the finding by Langreth that the BS limit is reached only in the keV range. At no photon energy are the plasmon satellites close to being either purely intrinsic or extrinsic. For photoelectron energies larger than a few times the plasmon energy, a semiclassical approximation gives results very close to our QM model. At lower energies the QM model gives a large peak in the ratio between the total intensity in the first plasmon satellite and the main peak, which is not reproduced by the SC expression. This maximum has a simple physical explanation in terms of different dampings of the electrons in the QP peak and in the satellite. For the MND peak $J_k(\omega)$ and $A_c(e_k-\omega)$ agree well for a range of a few eV, and experimental data can thus be used to extract the MND singularity index. For an embedded atom at a small distance from the surface there are, however, substantial deviations from the large-distance limit. Our model is simple enough to perform quantitative calculations allowing for band-structure and surface details. [S0163-1829(98)03847-8]

Also: W. Bardyszewski and L. Hedin, Phys. Scr. 32, 439 (1985)

Intrinsic and Extrinsic Losses in XPS

Contributions to photocurrent from
single boson excitations

$$J_k^n = |\tau_n(k)|^2 \delta(\omega - \epsilon_k - \omega_n)$$

Amplitude for extrinsic and intrinsic losses

$$\tau_n = \langle k; n | [V^n G(\epsilon_k - \omega_n) - \frac{V_{cc}^n}{\omega_n}] d | c \rangle$$

Beyond the sudden approximation in XAS

Quasi-boson Model

PHYSICAL REVIEW B, VOLUME 65, 064107

Interference between extrinsic and intrinsic losses in x-ray absorption fine structure

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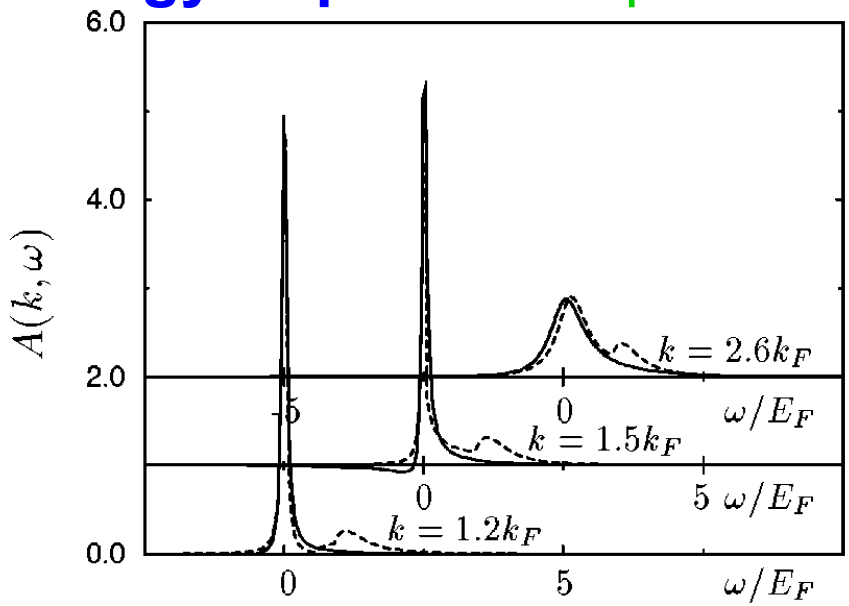
Energy Dependent Spectral Function $A(k,\omega)$



Beyond quasiparticles!

Multi-electron excitations

$\longrightarrow$ satellites in $A(k,\omega)$

Explains intrinsic losses

$$s_0^2 = 0.9$$

Intrinsic and Extrinsic Losses in XAS

$$G_{\text{eff}} = e^{-a}[G(\omega)$$ extrinsic

intrinsic - sudden approx

$$+\sum_n (\frac{V_{cc}^n}{\omega_n})^2 G(\omega - \omega_n)$$

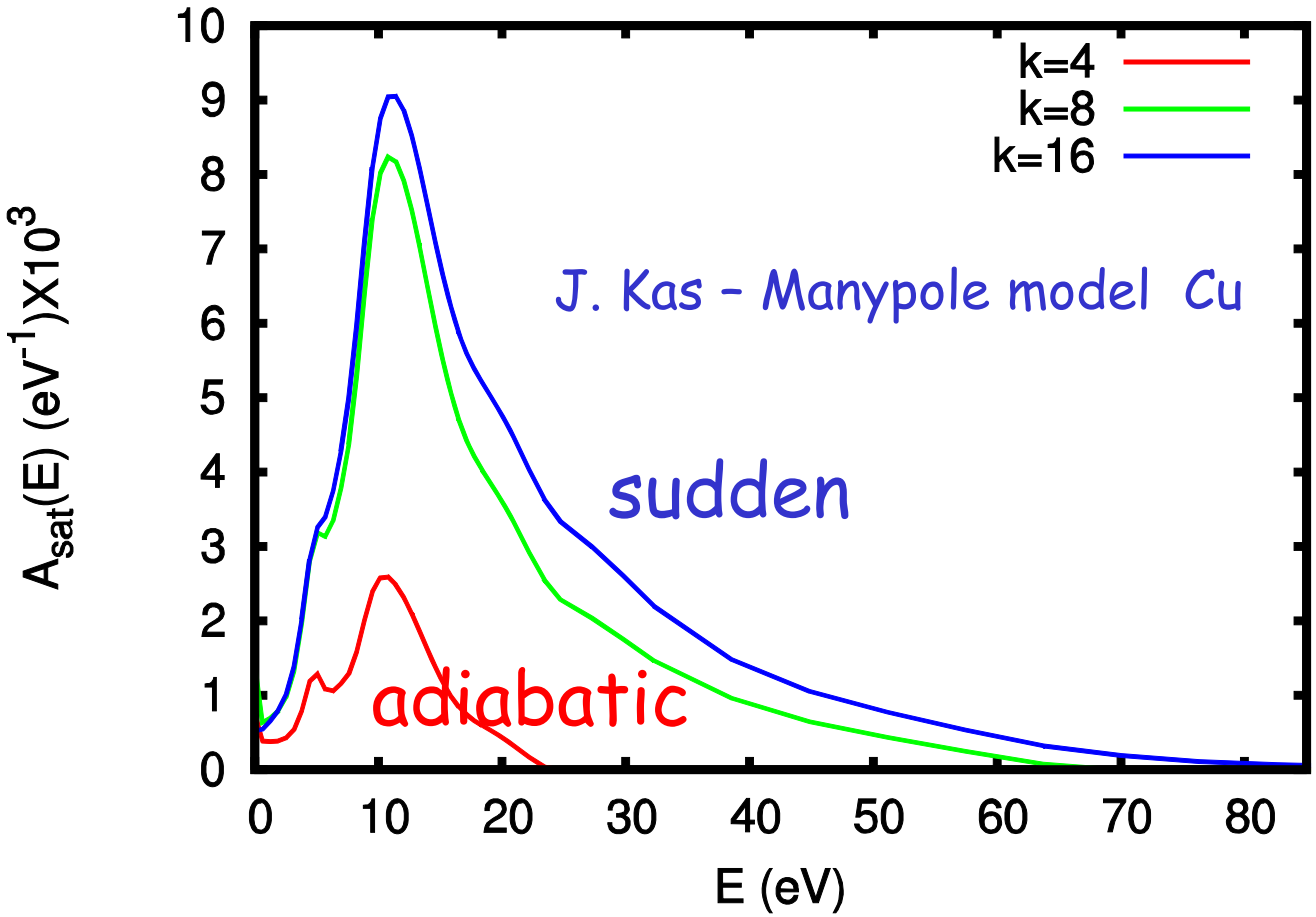
interference

$$-2\sum_n (\frac{V_{cc}^n}{\omega_n}) G(\omega - \omega_n) V^n G(\omega)]\text{-}$$

Effective spectral function

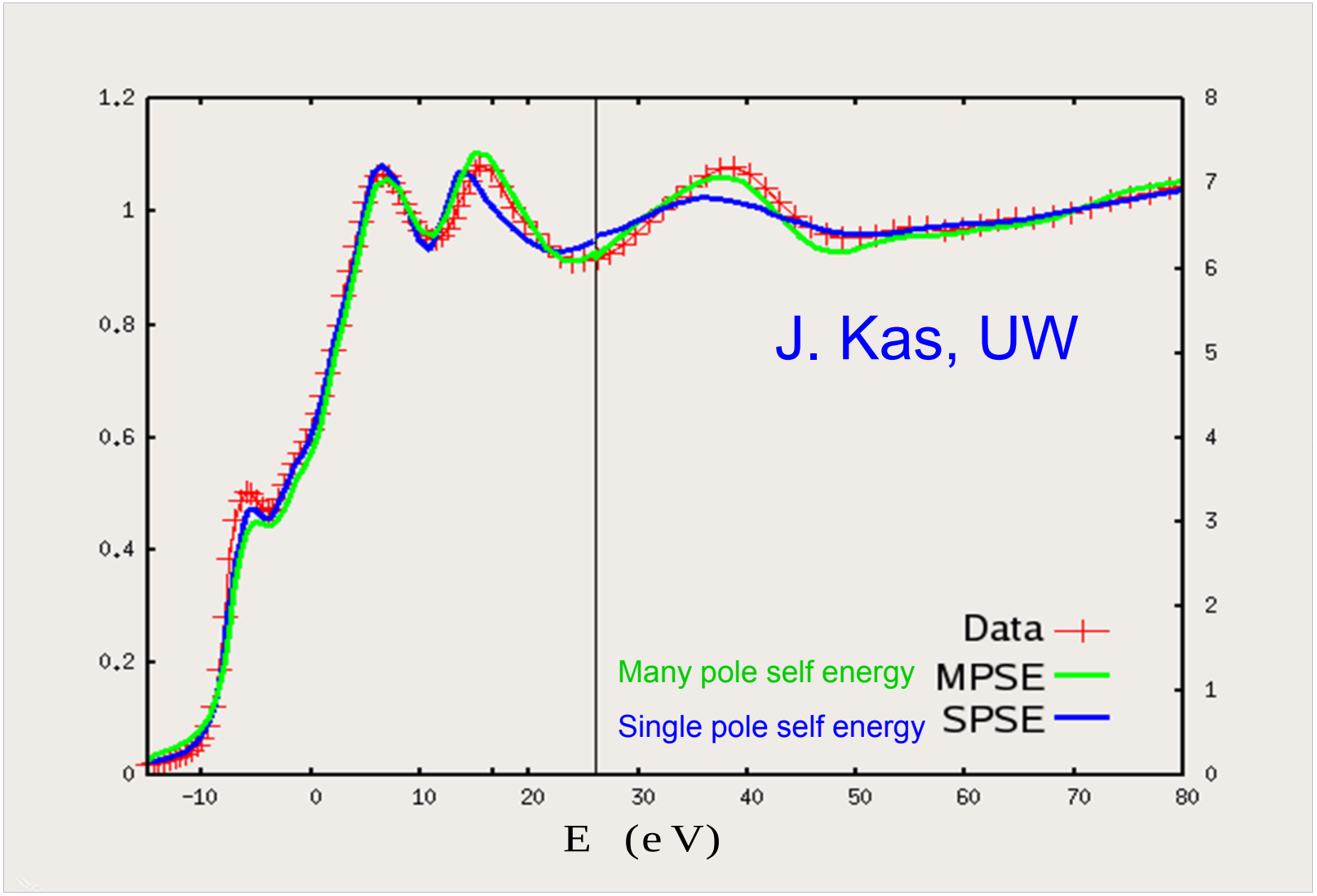
$$A = \frac{1}{\pi} \mathrm{Im} G_{\text{eff}}$$

Satellite spectral function including intrinsic & extrinsic losses & interference



Note: crossover between sudden/adiabatic limits

Many-body Corrections to XAS of Cu



Conclusion

Many-pole model for effects of excitations

- extension of GW approximation

- explains inelastic losses, satellites

Can be used in XAS, XPS, …

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That's all folks