Cumulant expansion approaches to excited state electronic structure and spectra

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Outline

- I. Cumulant expansion of the retarded GF
  - Motivation and theoretical background
  - Real systems: starting point and self-consistency
  - Example: Si
  - Effects of self-consistency: NiO
- II. Real-Time cumulant: charge transfer excitations in x-ray spectra
  - Theory and implementation
  - Results and analysis: TiO_2 XPS
  - Results: XAS
- Conclusions/Future directions

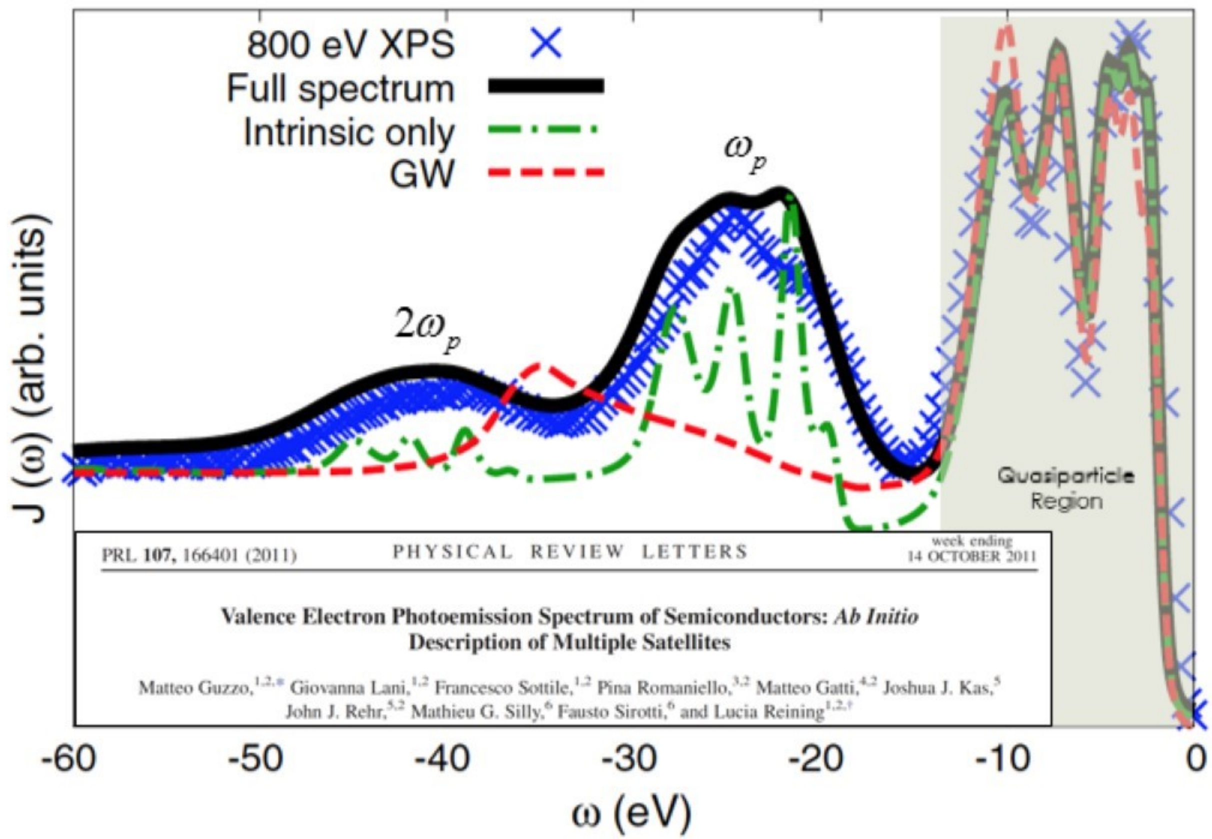
I. Motivation

- Exponential (cumulant) form gives improved XPS[1,2,3,4]

$$G_k(t) = G_k^0(t) e^{C_k(t)}$$

- Problem:
  TO occupation numbers wrong!

Multiple satellites in Si valence XPS



1. Langreth, Phys. Rev. B **1**, 471–477 (1970)
2. F. Aryasetiawan, L. Hedin, and K. Karlsson, Phys. Rev. Lett. **77**, 2268 (1996)
3. Guzzo et al, Phys. Rev. Lett. **107** 166401 (2011)
4. Johannes Lischner, Derek Vigil-Fowler, and Steven G. Louie, Phys. Rev. Lett. **110**, 146801 (2013)

I. Motivation

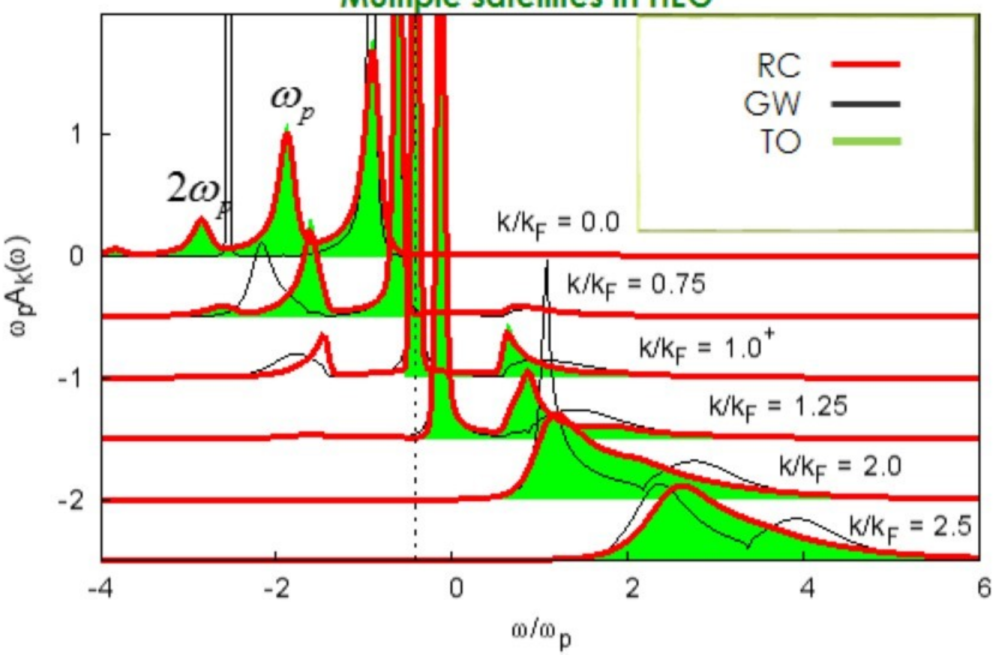
- Retarded cumulant provides consistent theory
  - Occupation numbers
  - Spectral function: Multiple plasmon satellites

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

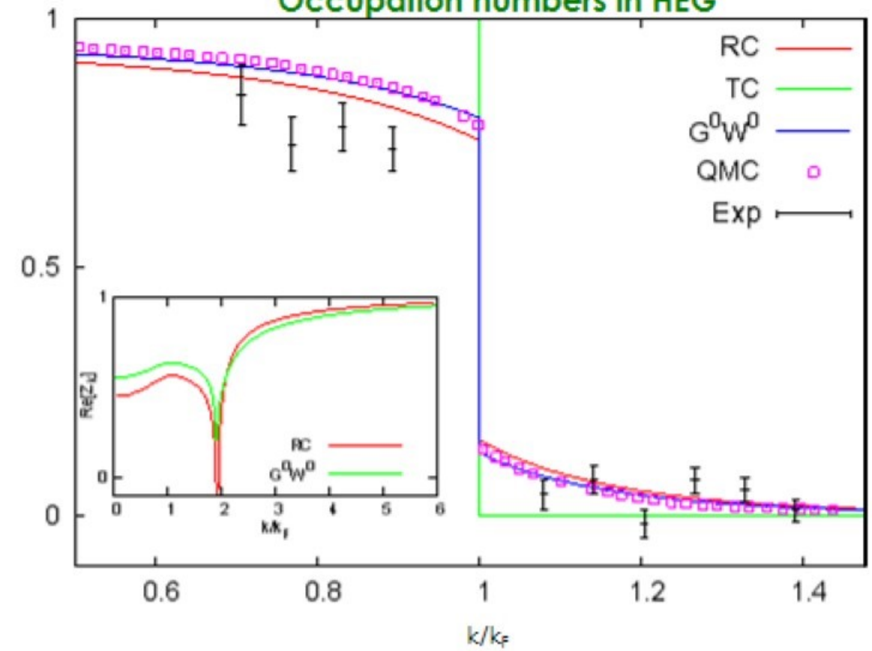
Cumulant expansion of the retarded one-electron Green function

J. J. Kas,[1,*] J. J. Rehr,[1,2,†] and L. Reining[3,2,‡]

Multiple satellites in HEG



Occupation numbers in HEG



- Need rigorous derivation for realistic systems!

I. Retarded cumulant expansion: homogeneous electron gas

- Green's function as exponential[1,2,3]

$$G_k(t) = G_k^0(t) e^{C_k(t)}; \qquad \mathrm{C}_k(t) = C_k^c(t) + iC_k^s t$$

- Cumulant to linear order in W

$$G_k(t) = G_k^0(t)[1 + C_k^{(1)}(t)] = G_k^0 + G_k^0(G_k^0 W)G_k^0$$

Equate to Dyson Eq.

$$C_k^c(t) = \int \frac{\beta_k(\omega)}{\omega^2}(e^{-i\omega t} + i\omega t - 1)d\omega; \qquad C_k^s = \Sigma_k^{xG^0W}$$

- Excitation spectrum related to GW self-energy

$$\beta_k(\omega) = \left|\mathrm{Im}[\Sigma_k^{G^0W}(\omega + \varepsilon_k)]\right| / \pi$$

"Quasi-boson" excitation spectrum

References:
1. Langreth, Phys. Rev. B **1**, 471–477 (1970)
2. P. Nozières and C. De Dominicis, Phys. Rev. **178**, 1097 (1969)
3. C.-O. Almbladh and L. Hedin, Handbook on Synchrotron Radiation (North-Holland, Amsterdam, 1983), Chap. 8.

I. Kohn-Sham starting-point: Problematic

- Green's function as exponential

$$G_k(t) = G_k^0(t)e^{C_k(t)}; \qquad \mathrm{C}_k(t) = C_k^c(t) + iC_k^s t$$

- Cumulant to linear order in W?

$$G(t) = G^{KS}(t)e^{C(t)} = G^{KS} + G^{KS}(\Sigma - V_{xc})G$$

$$G^{KS}(t)[1 + C(t)] = G^{KS} + G^{KS}(G^{KS}W - V_{xc})G^{KS}$$

$$+ G^{KS}V_{xc}G^{KS}V_{xc}G^{KS} - G^{KS}(G^{KS}W)G^{KS}V_{xc}G^{KS} + \dots$$

I. Quasiparticle starting-point: Good

- Green's function as exponential

$$G_k(t) = G_k^0(t) e^{C_k(t)}; \qquad \mathrm{C}_k(t) = C_k^c(t) + i C_k^s t$$

- Cumulant to linear order in W?

$$G(t) = G^{QP}(t) e^{C(t)} = G^{QP} + G^{QP}(\Sigma - \Sigma_{QP}) G$$

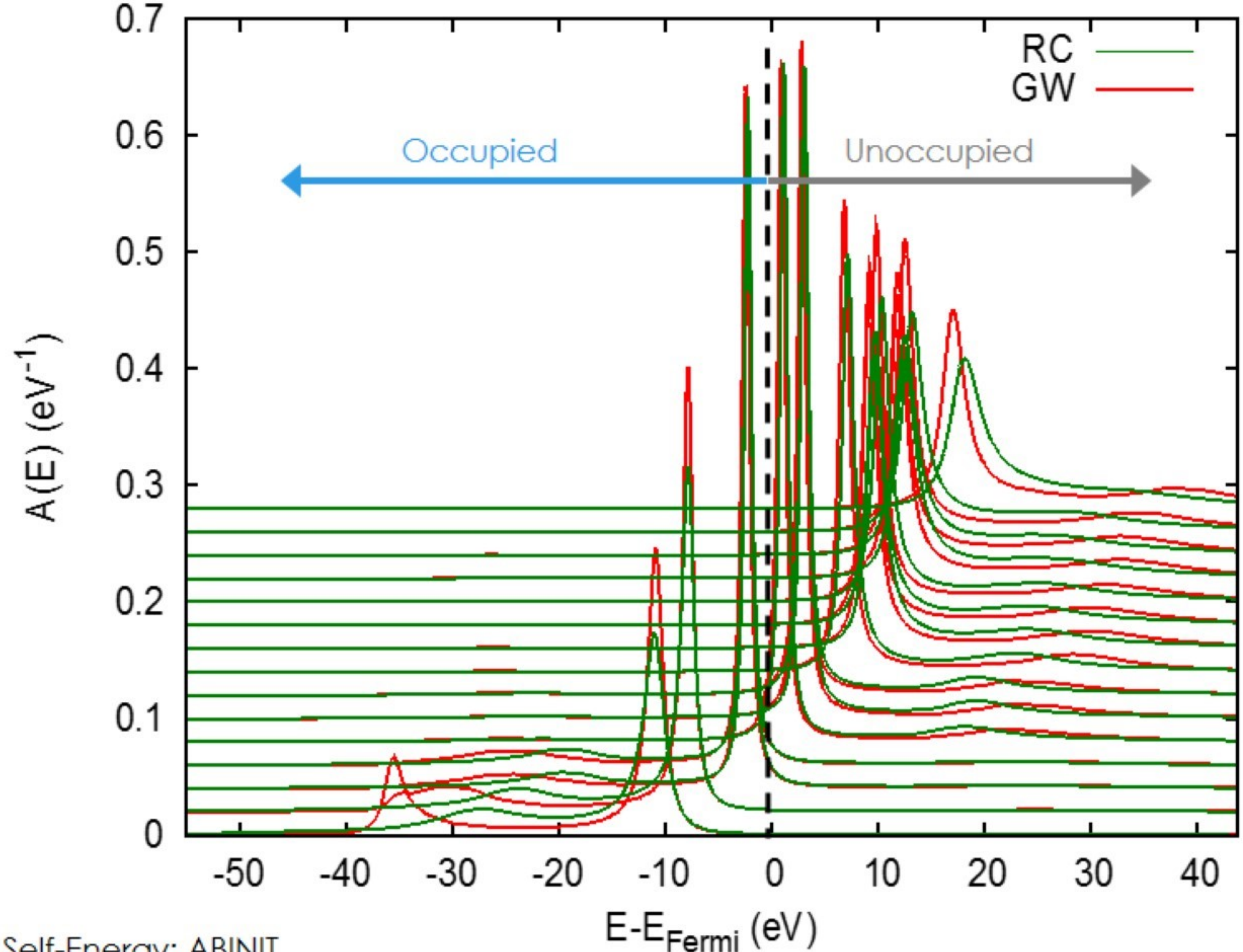
$$G^{QP}(t)[1 + C(t)] = G^{QP} + G^{QP}(G^{QP} W - \Sigma_{GW}^{QP}) G^{QP}$$

$$C_k^c(t) = \int \frac{\beta_k(\omega)}{\omega^2} (e^{-i\omega t} + i\omega t - 1) d\omega; \quad C_k^s = [\Sigma_k^x - \Sigma_k(E_k)] = -\Sigma_k^c(E_k)$$

$$\beta_k(\omega) = \left| \mathrm{Im}[\Sigma_k^{G^0 W}(\omega + \varepsilon_k)] \right| / \pi$$

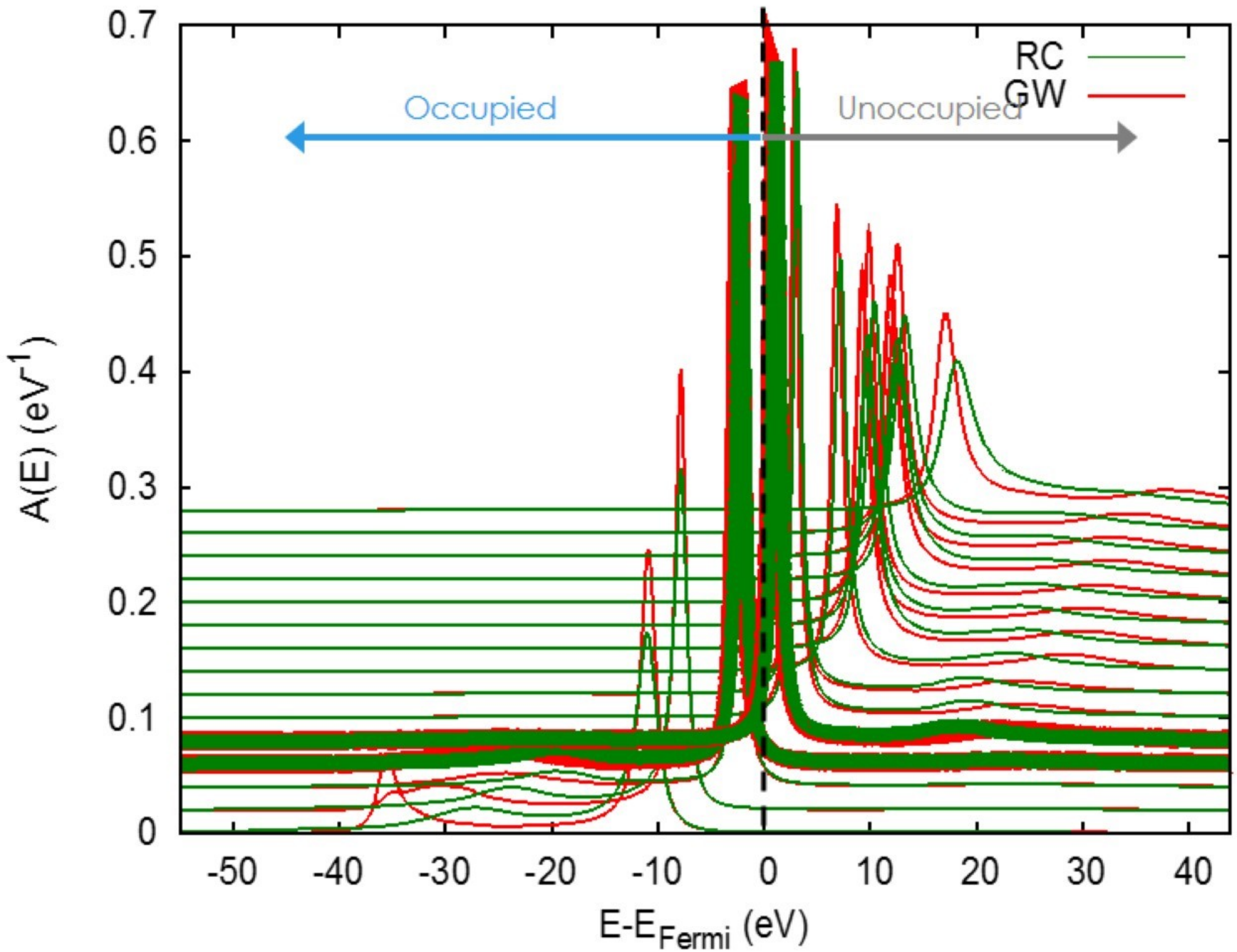
"Quasi-boson" excitation spectrum

I. Application to Si*

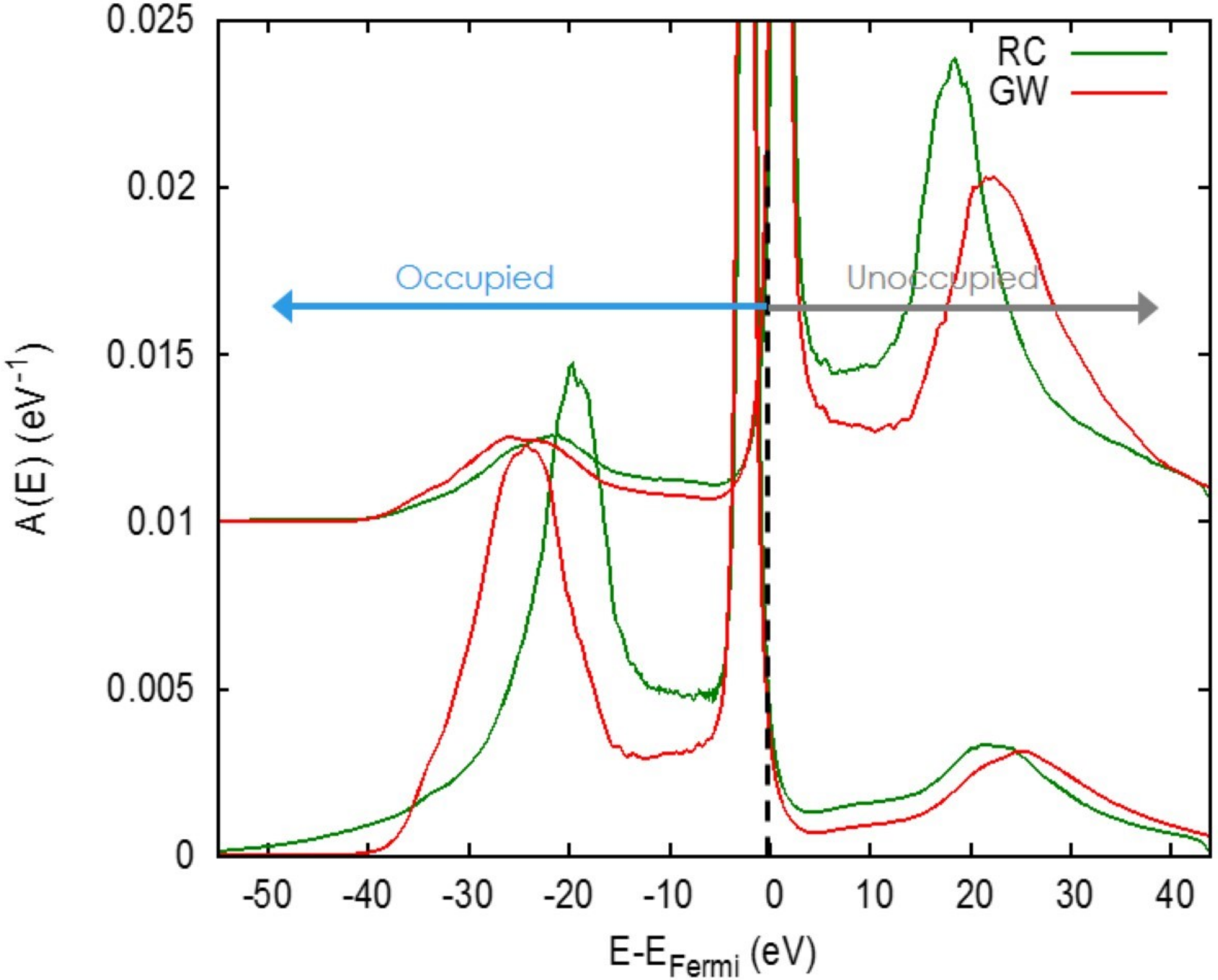


*G_0W_0 Self-Energy: ABINIT

I. Application to Si

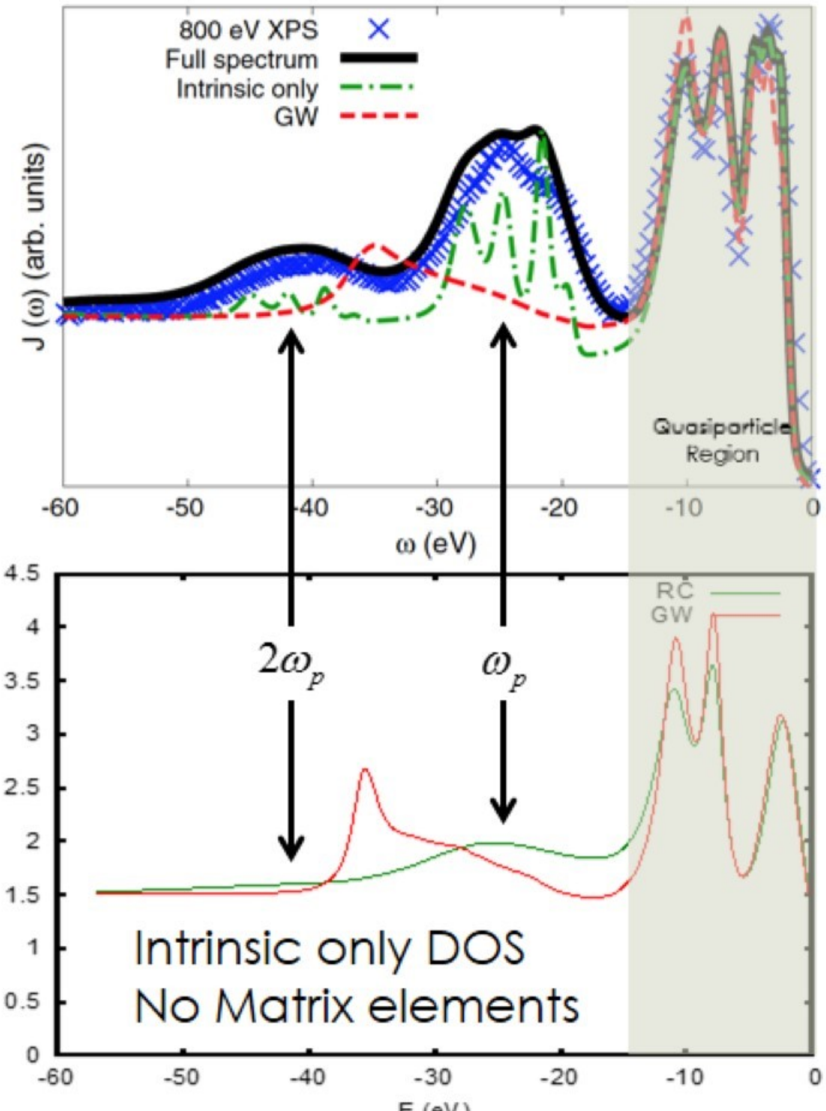


I. Application to Si

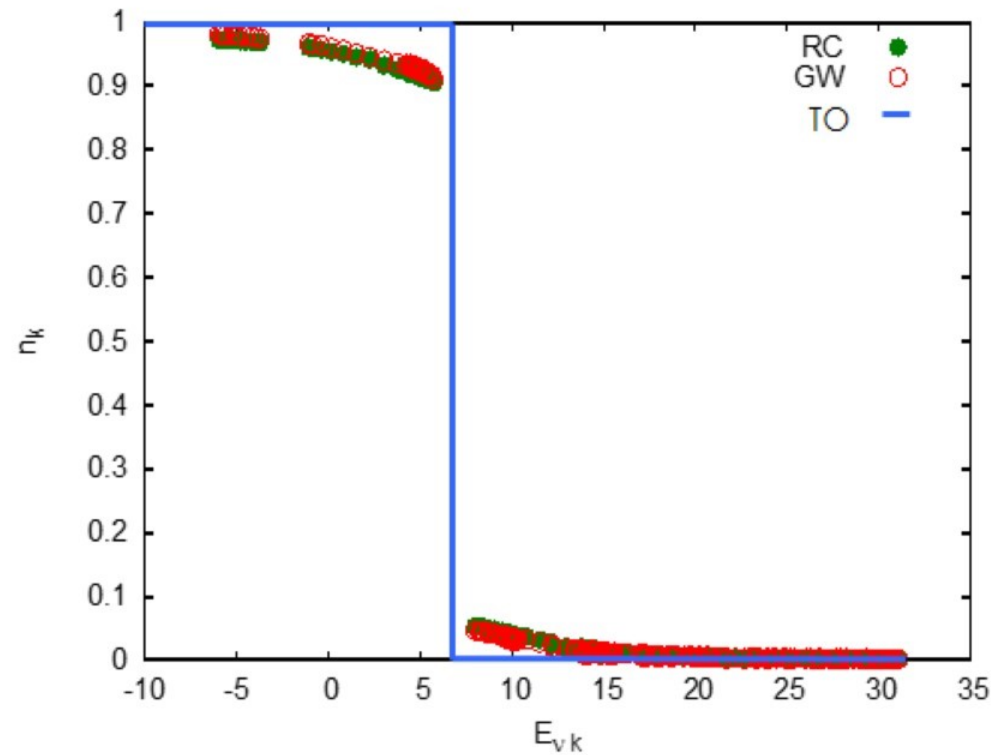


I. Application to Si

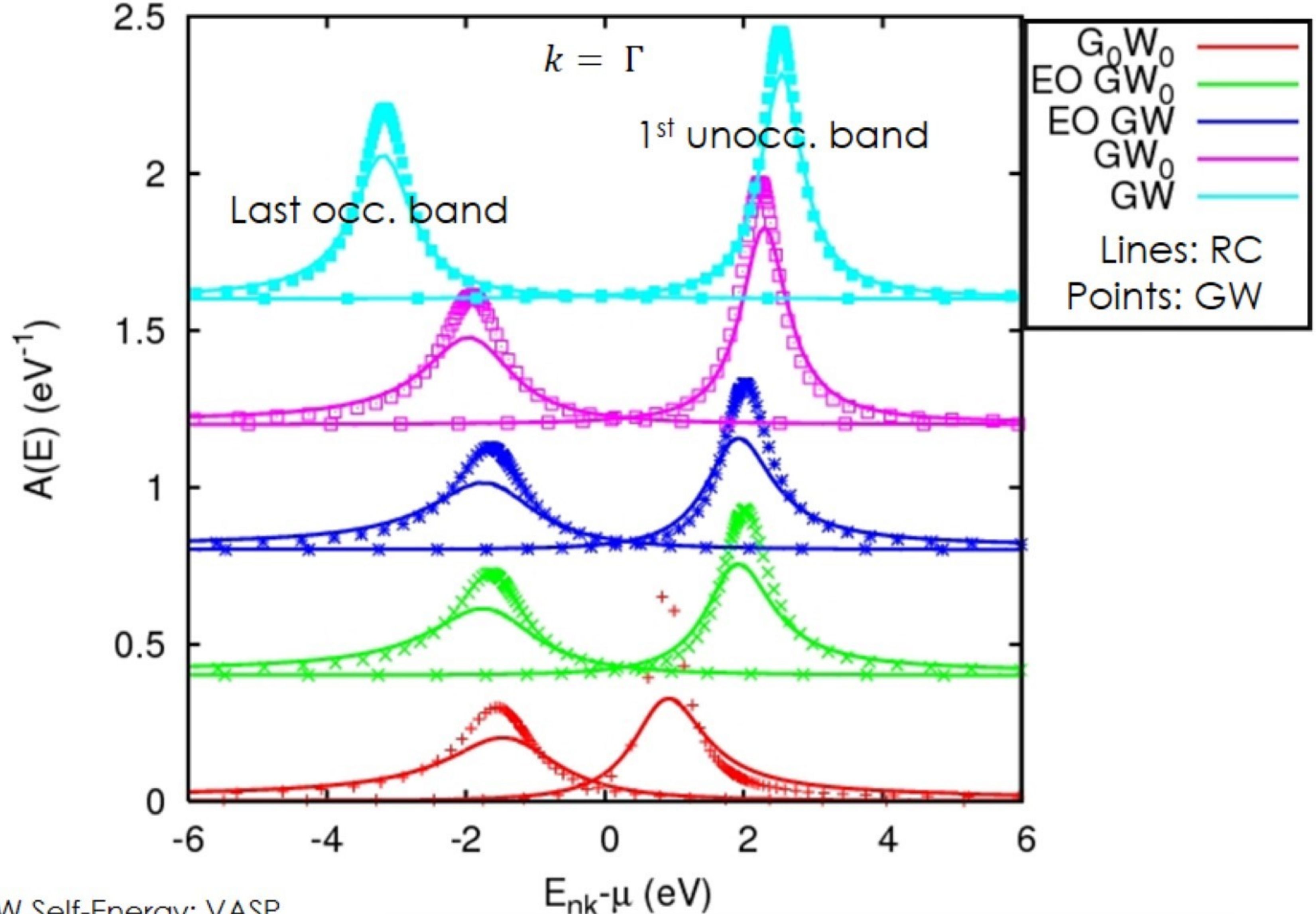
Plasmon Satellites: Si



Occupation numbers

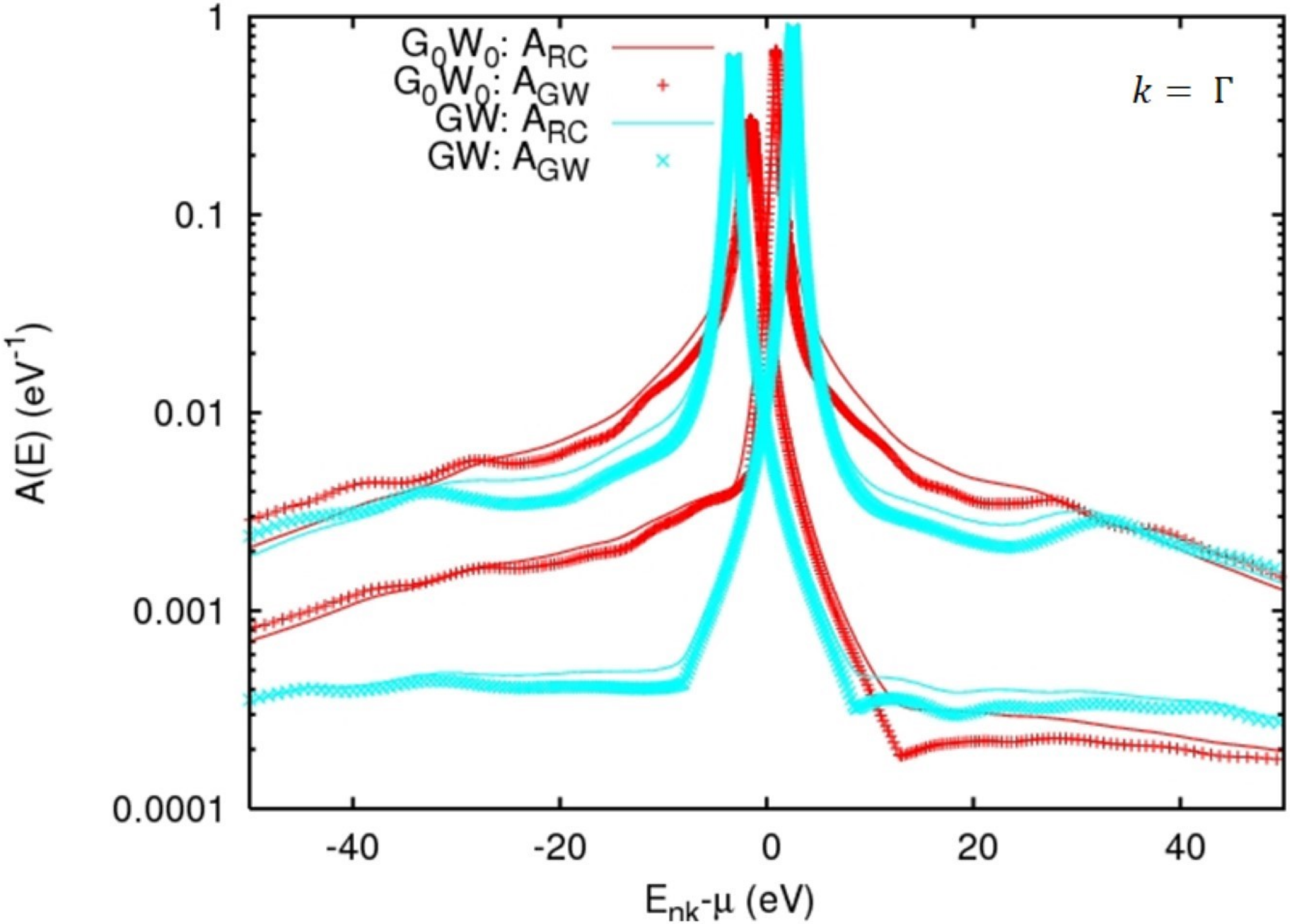


I. NiO Self-consistency: QP properties

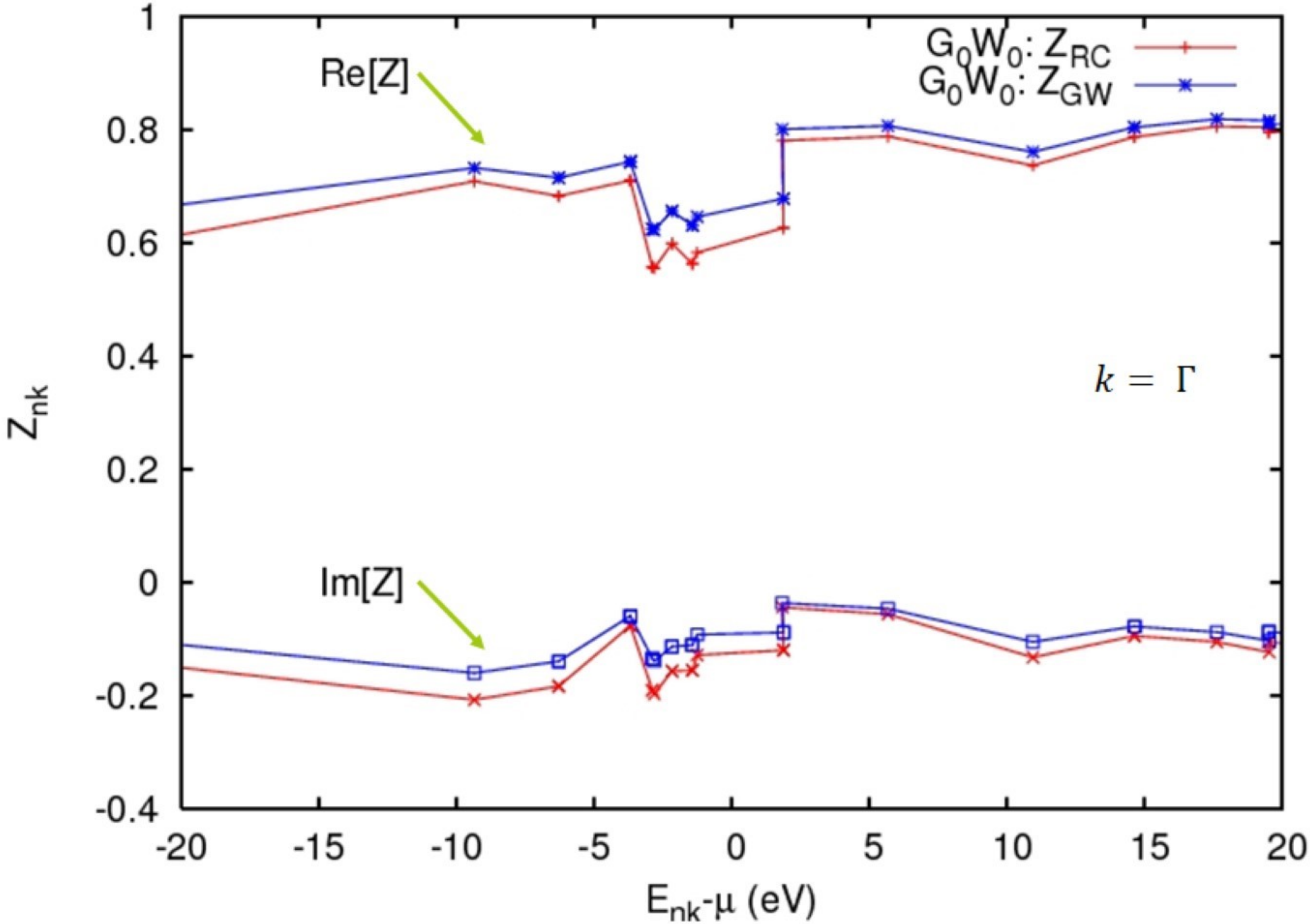


*GW Self-Energy: VASP

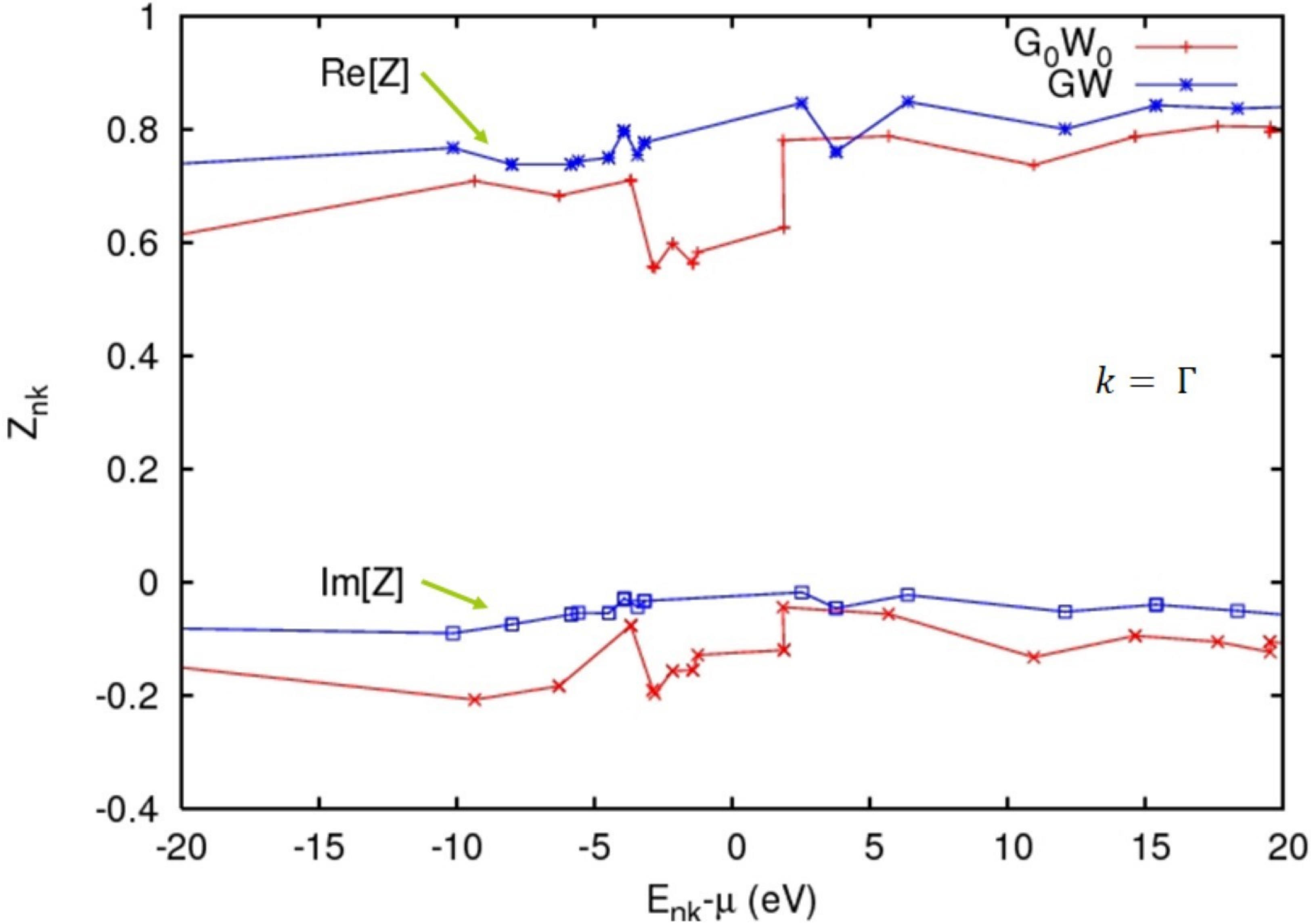
I. NiO Self-consistency: Satellites



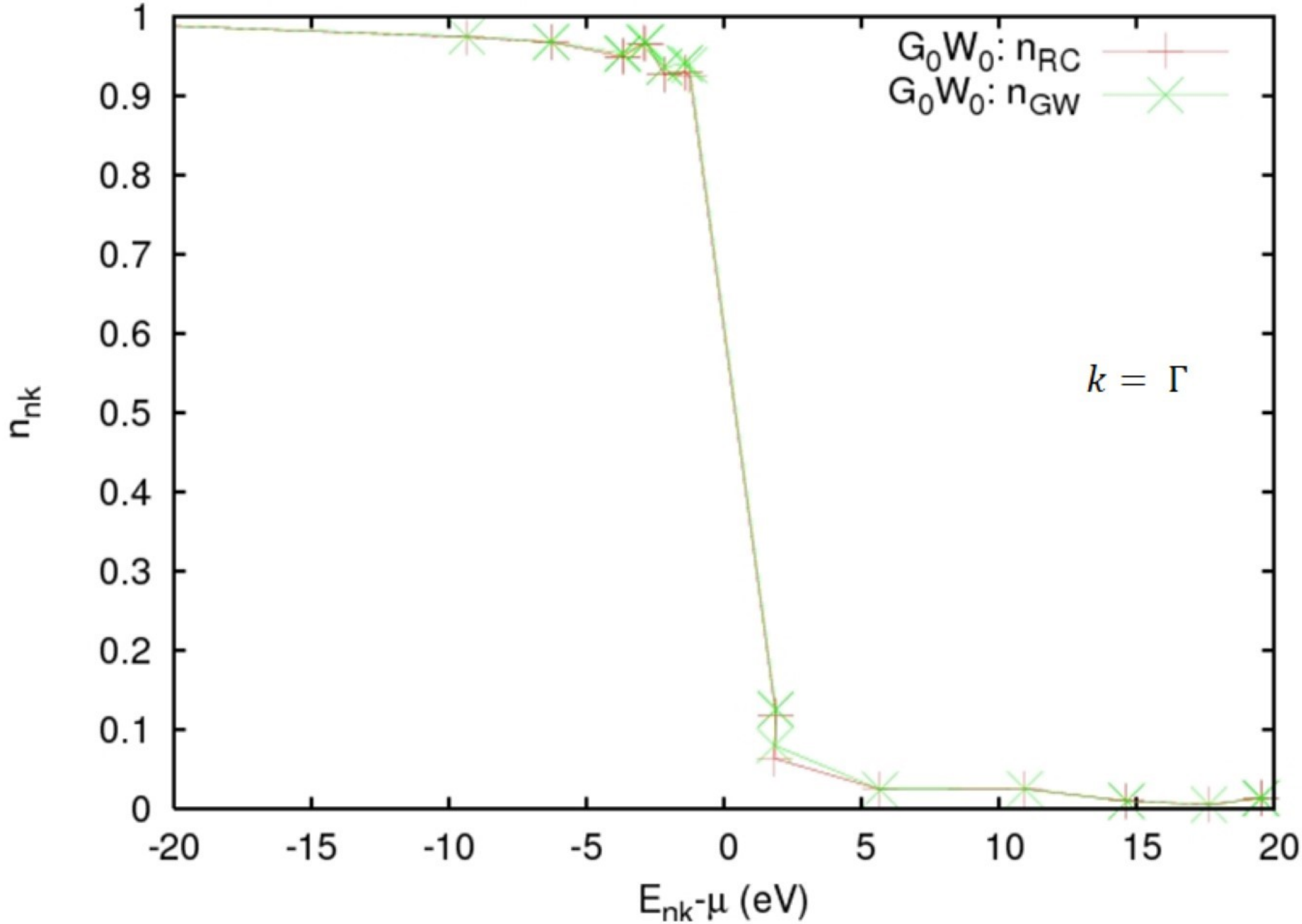
I. Renormalization constant Z: RC vs GW



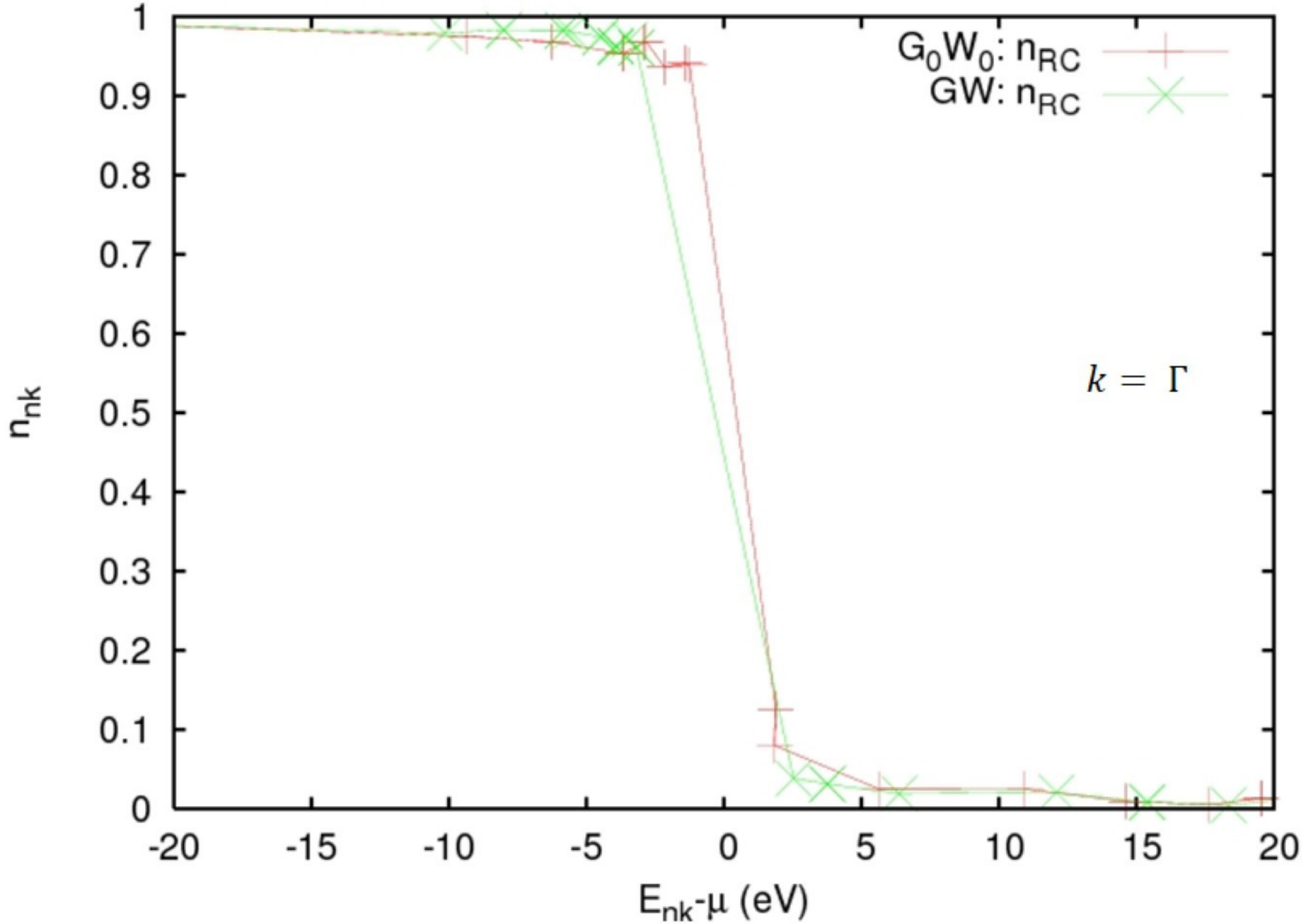
I. RC Renormalization: Self-consistency level



I. Occupation: RC vs GW

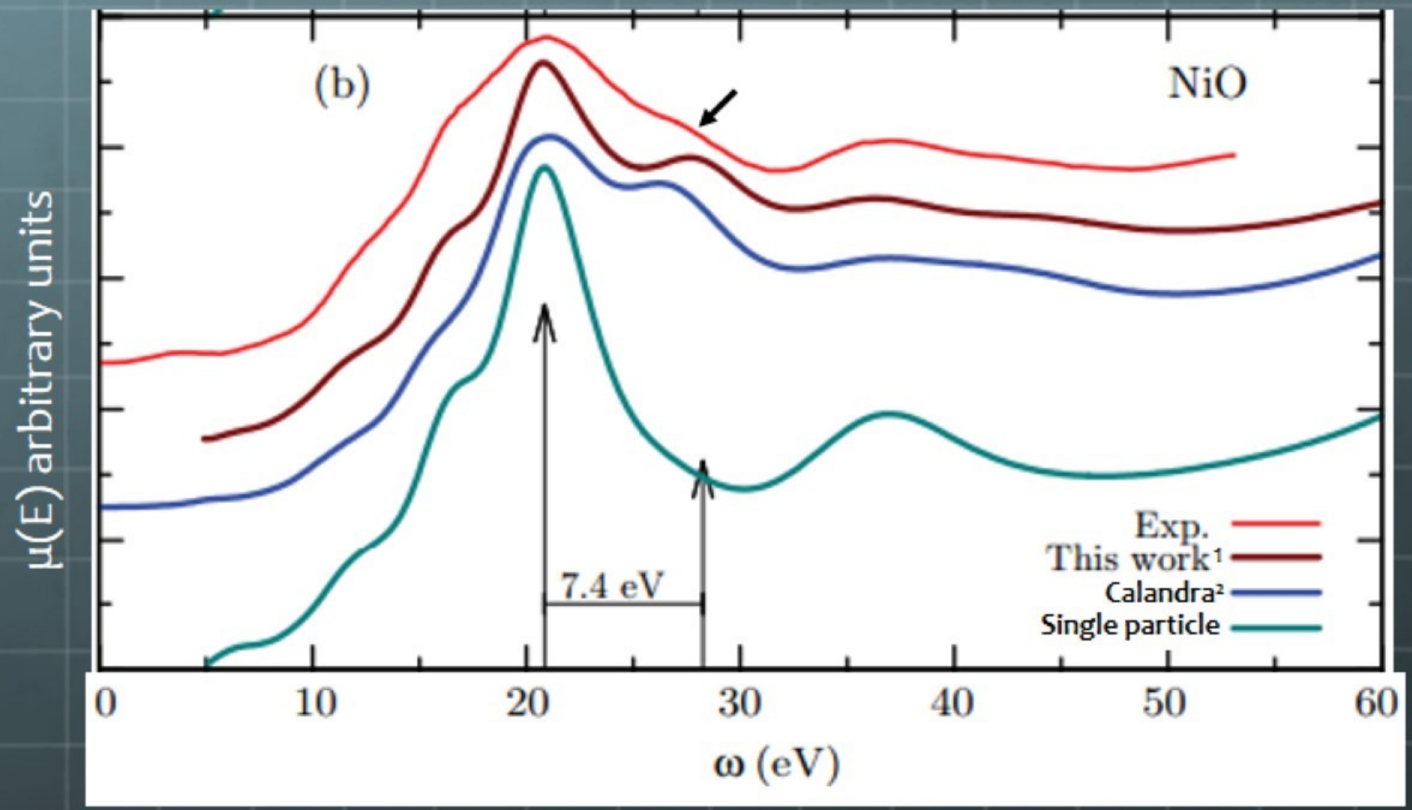


I. Occupation: Self-consistency level



II. Real time cumulant approach: Motivation

- Charge-transfer satellites: XPS, XAS, …



- **Can we calculate these excitations *ab initio*?**

[1]E. Klevak, J. J. Kas, and J. J. Rehr, Phys. Rev. B **89**, 085123 (2014)
[2]Calandra et al., Phys. Rev. B **86**, 165102 (2012)

II. XAS: Product of Green's functions

- **Absorption in real time**

$$\mu(\omega) = \Im \frac{1}{\pi} \int_0^{\infty} dt e^{i\omega t} F(t)$$

$$F(t) = g_c(t) \langle \psi_x'(0) | \psi_x'(t) \rangle$$

Time correlation funtion

$$g_c(t)$$

Core-hole Green's function

$$G(t) \approx \langle \psi_x'(0) | \psi_x'(t) \rangle$$

Transient Green's function

P. Nozieres and C. T. De Dominicis, Phys. Rev. **178**, 1097 (1969)

II. Core-hole Green's function

- Cumulant form[1,2]

$$g_c(t) \;=\; g_c^0(t)e^{C(t)}, \quad g_c^0 = -\theta(-t)e^{-i\epsilon_c t}$$

- Cumulant from linear response to transient potential[2,3]

$$C(t) = \sum_{\boldsymbol{q},\boldsymbol{q}'} V_{\boldsymbol{q}}^* V_{\boldsymbol{q}'} \int d\omega \, \mathrm{Im}[\chi(\boldsymbol{q},\boldsymbol{q}',\omega)] \, \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}$$

- Response function from RT-TDDFT

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

$$\frac{\beta(\omega)}{\omega} = \mathrm{Re}\{\mathrm{FT}[\Delta_c(t)]\}; \qquad \Delta_c(t) = \int d^3r \, V(\boldsymbol{r})\delta\rho(\boldsymbol{r},t)$$

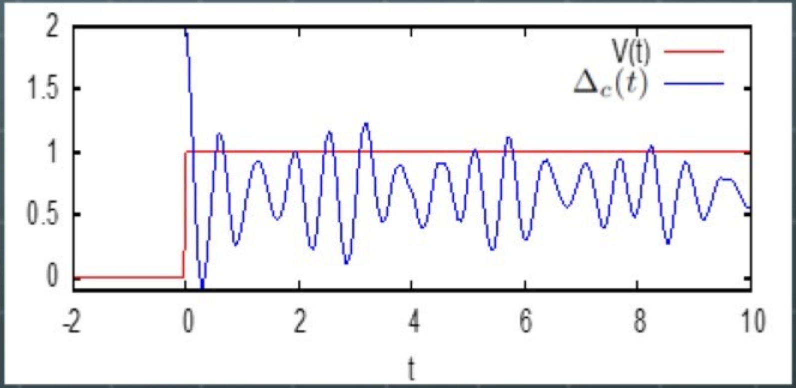
[1] P. Nozières and C. T. de Dominicis, Phys. Rev. **178**, 1097 (1969).
[2] D. C. Langreth, Phys. Rev. B **1**, 471–477 (1970)
[3] Rehr et al., Preprint

II. Implementation

- Extension of RT-SIESTA/RT-GPAW real time TDDFT
  - Non-Linear optical response[1,2], core-level XAS[2]
  - Inspired by Bertsch and Yabana[3]
- $\Delta_c(t)$: Response to core-hole perturbation

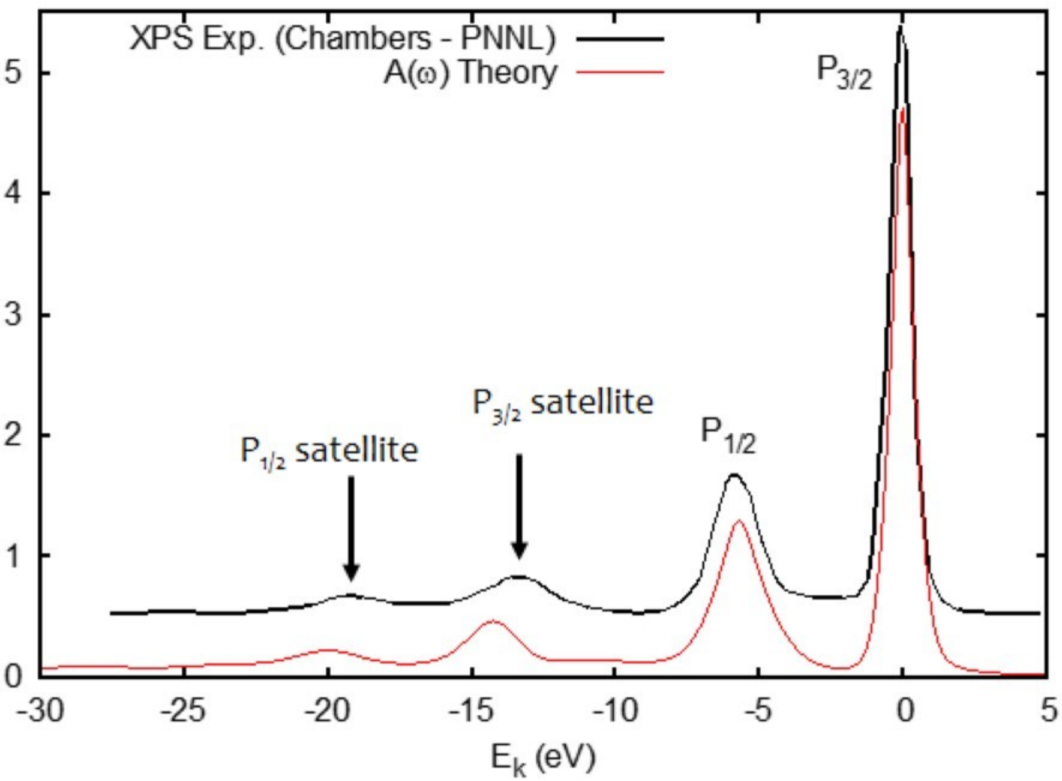
$$V(t) = v_c(\mathbf{r})\theta(t)$$

$$\Delta_c(t) = \int d^3r\, V(\boldsymbol{r})\delta\rho(\boldsymbol{r},t)$$



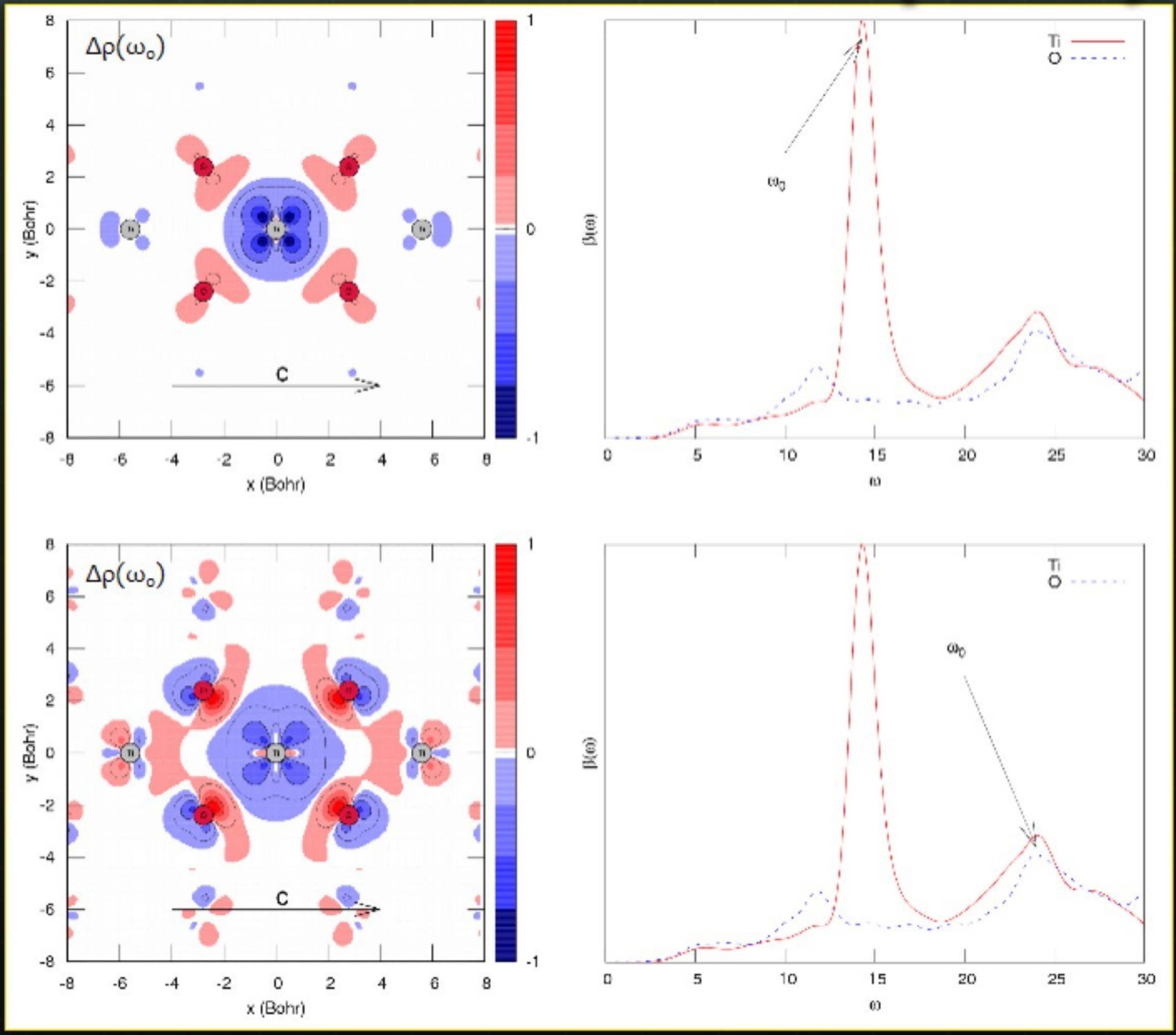
[1]Y. Takimoto, F. D. Vila, and J. J. Rehr, J. Chem. Phys. **127**, 154114 (2007)
[2]A. J. Lee, F. D. Vila, and J. J. Rehr, Phys. Rev. B **86**, 115107 (2012)
[3]K. Yabana, T. Nakatsukasa, J.-I. Iwata, and G. Bertsch, physica status sol. **243**, 1121 (2006)

II. Results: Ti 2P XPS of Rutile vs CH spectral function

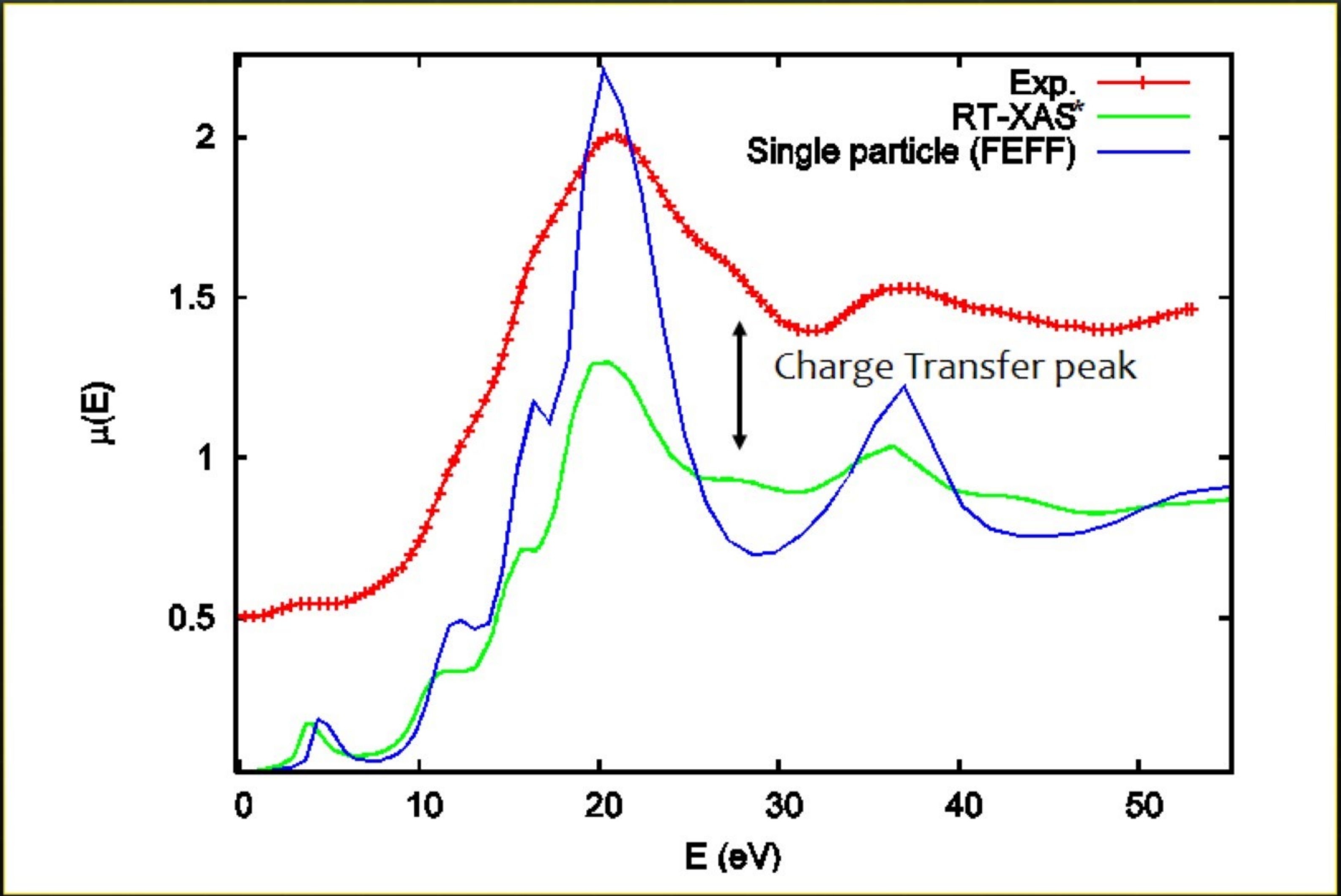


J. J. Kas, F. D. Vila, J. J. Rehr, and S. A. Chambers, Phys. Rev. B **91**, 121112(R) (2015)

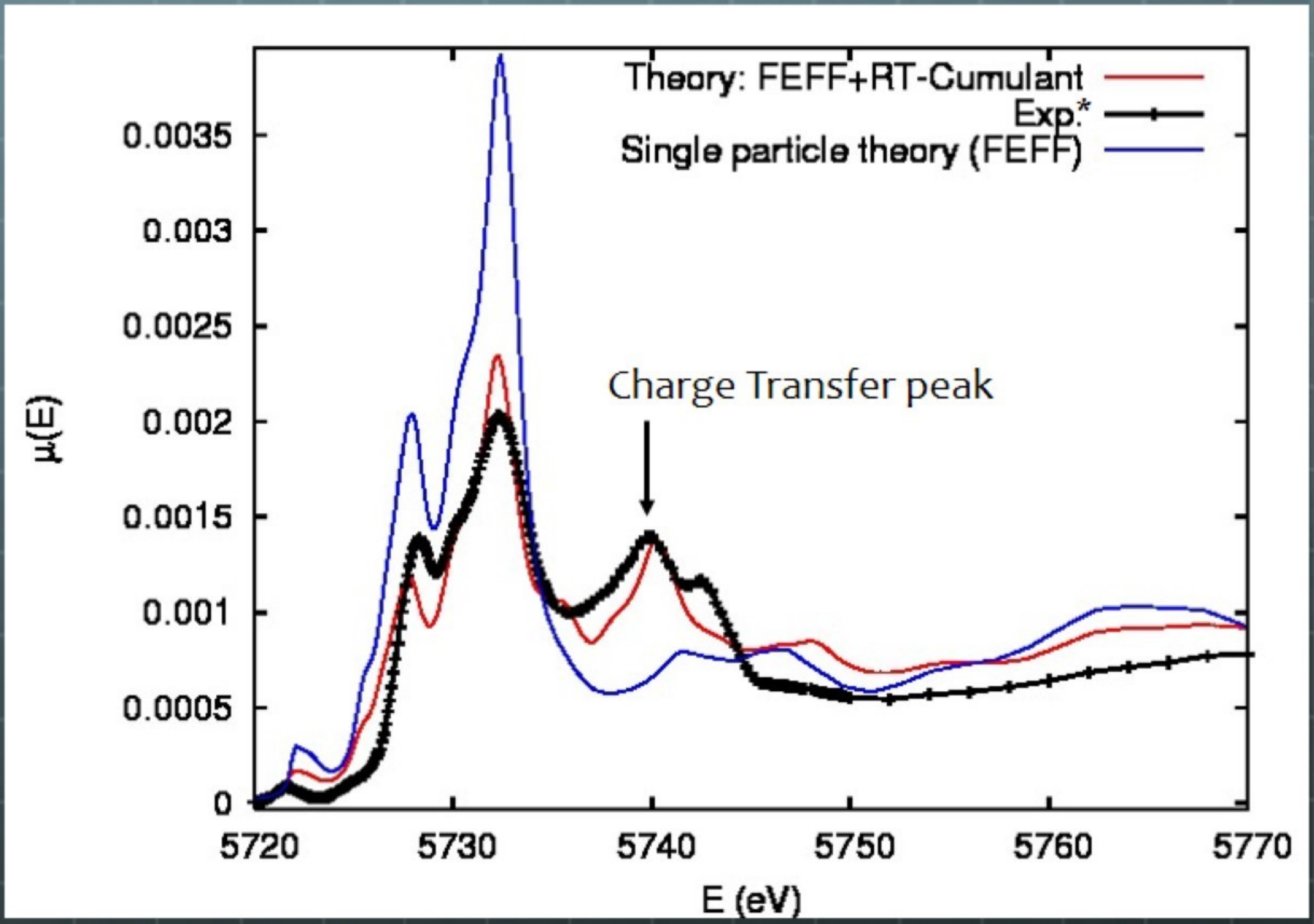
II. Excitations in frequency



II. Results: Ni K XAS of NiO



II. Results: Ce L3 XAS of CeO_2



*Measured by Y.Li (Yeshiva U.), A.Frenkel, O.Kraynis and I.Lubomirsky at SSRL beamline 6-2

Summary/Conclusions

- Cumulant expansion: Retarded one electron Green's function
  - SCQP starting point provides theoretical justification
  - Self-consistency in NiO
    - Decreases effects on occupation/renormalization
    - Effect on total energies
- Real time cumulant approach to core-level spectra
  - Metal-Ligand Charge transfer excitations in XPS/XAS
  - Qualitative agreement with experiment for TiO_2, NiO, CeO_2
  - Future: pump-probe, multiplet effects, extrinsic effects

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  - F. D. Vila
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  - F. Sirotti
  - G. Bertsch
  - And many more …

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XAS: Time Correlation function

- **Absorption in real time**

$$\mu(\omega) = \Im \frac{1}{\pi} \int_0^\infty dt e^{i\omega t} F(t)$$

$$-iF(t) = e^{iE_0 t} \langle \Psi_x(0) | \Psi_x(t) \rangle$$

Time correlation funtion

$$|\Psi_x(t)\rangle = \det\{ |\psi_x'(t)\rangle, |\psi_i'(t)\rangle \}$$

Valence plus photoelectron

$$|\psi_x'(0)\rangle = (1 - \mathcal{P}) d |c(0)\rangle$$

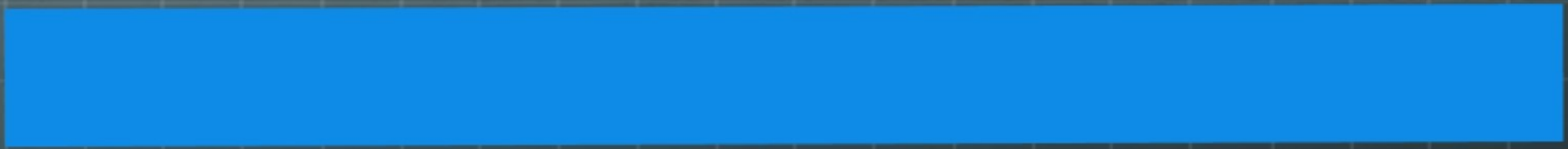
Photoelectron state:
dipole acting on core state

A. J. Lee, F. D. Vila, and J. J. Rehr, Phys. Rev. B **86**, 115107 (2012)
G. F. Bertsch and A. J. Lee., Phys. Rev. B **89**, 075135 (2014)
A. J. Lee, Thesis, University of Washington (2015)

XAS: Qualitative picture

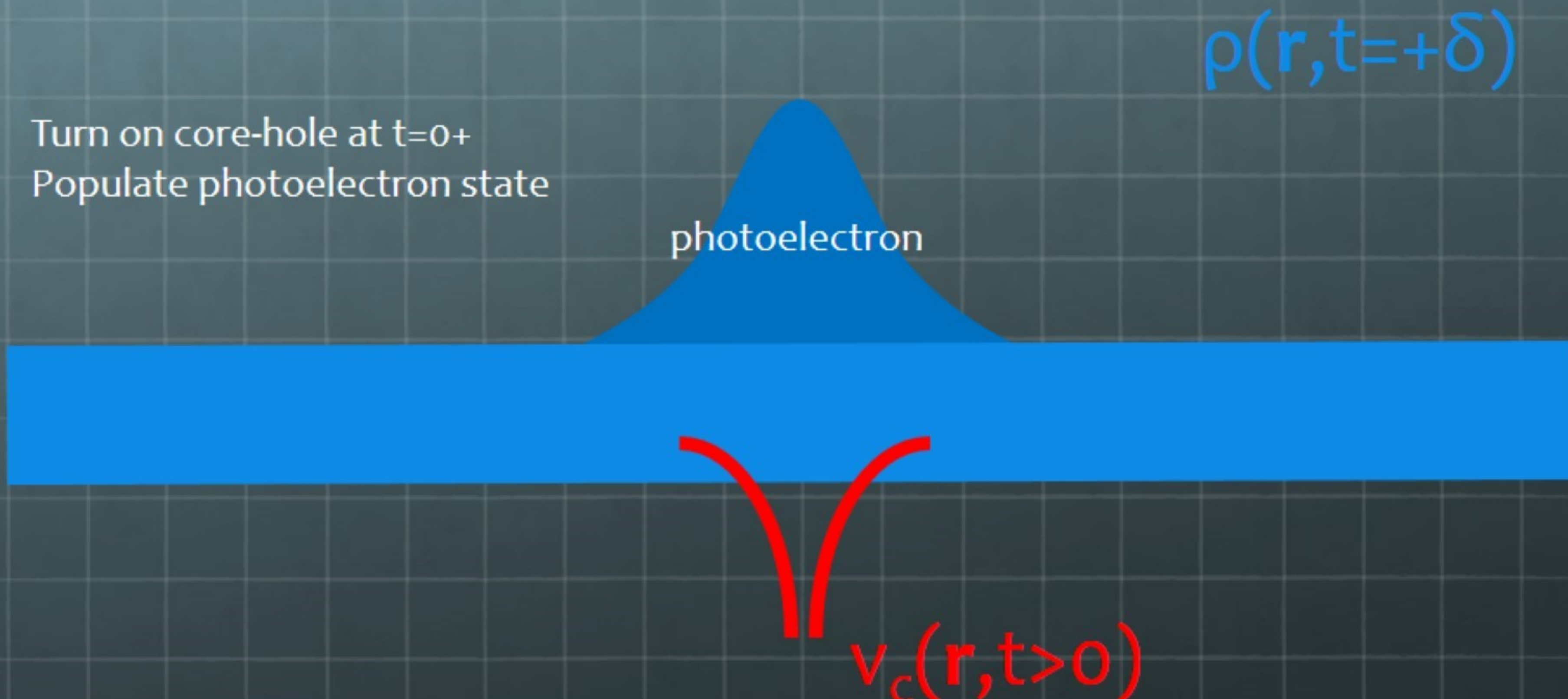
$\rho(\mathbf{r},t=-\delta)$

Relaxed Ground State



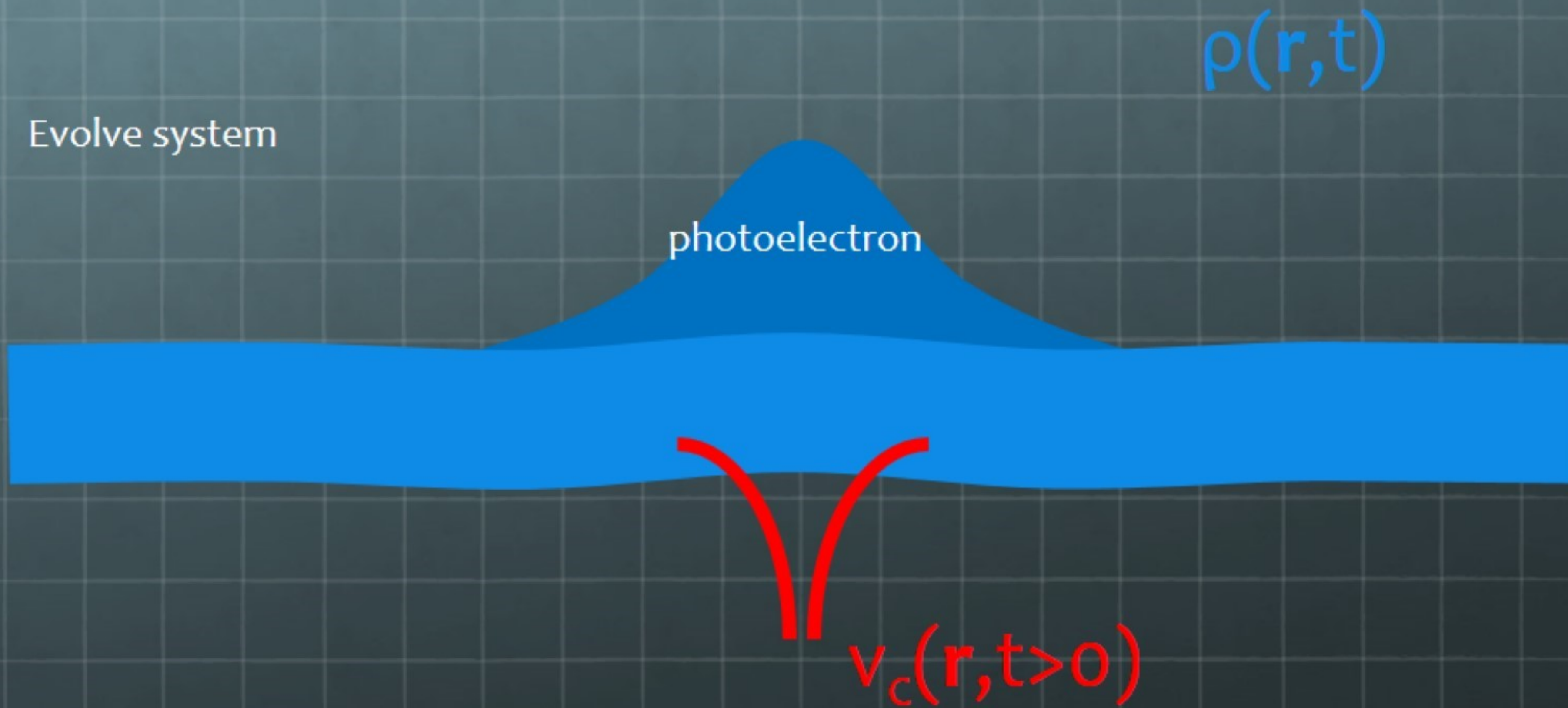
XAS: Qualitative picture

Turn on core-hole at t=0+
Populate photoelectron state



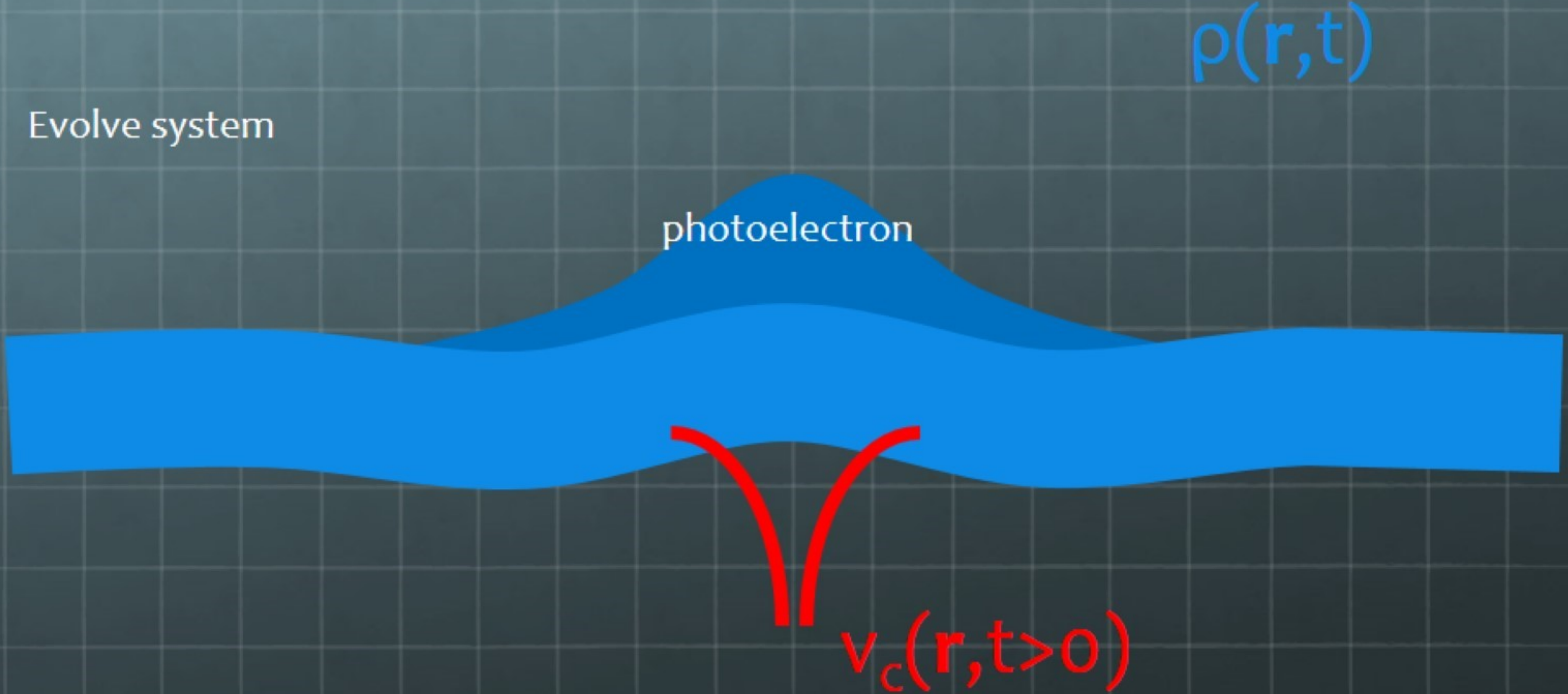
XAS: Qualitative picture

Evolve system



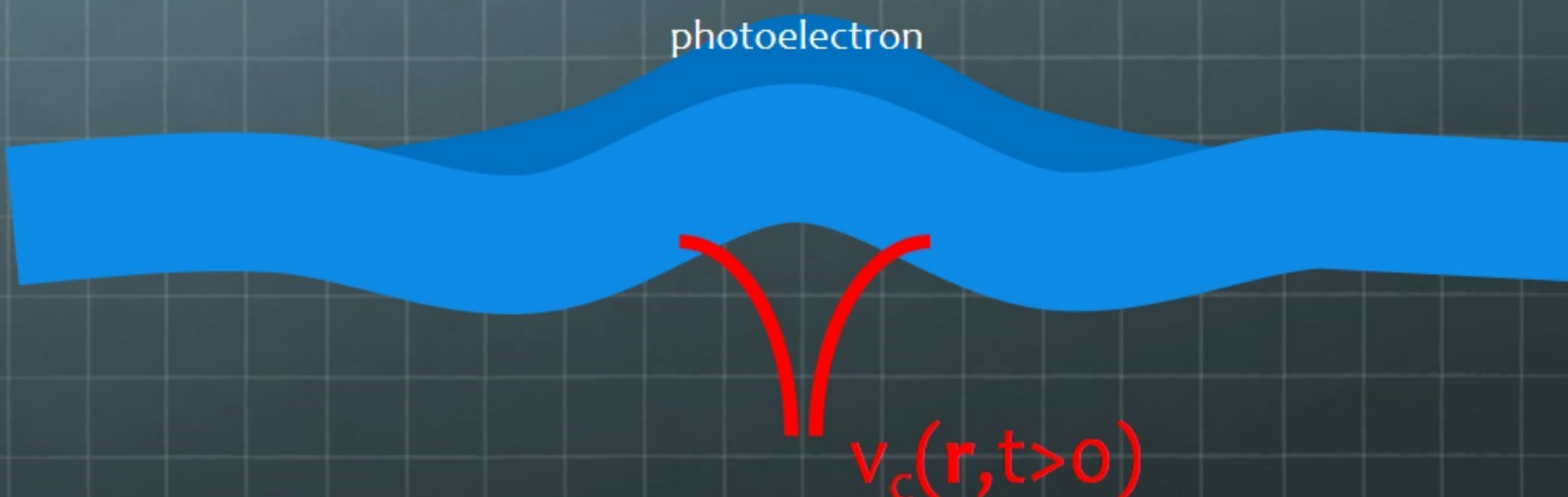
XAS: Qualitative picture

Evolve system



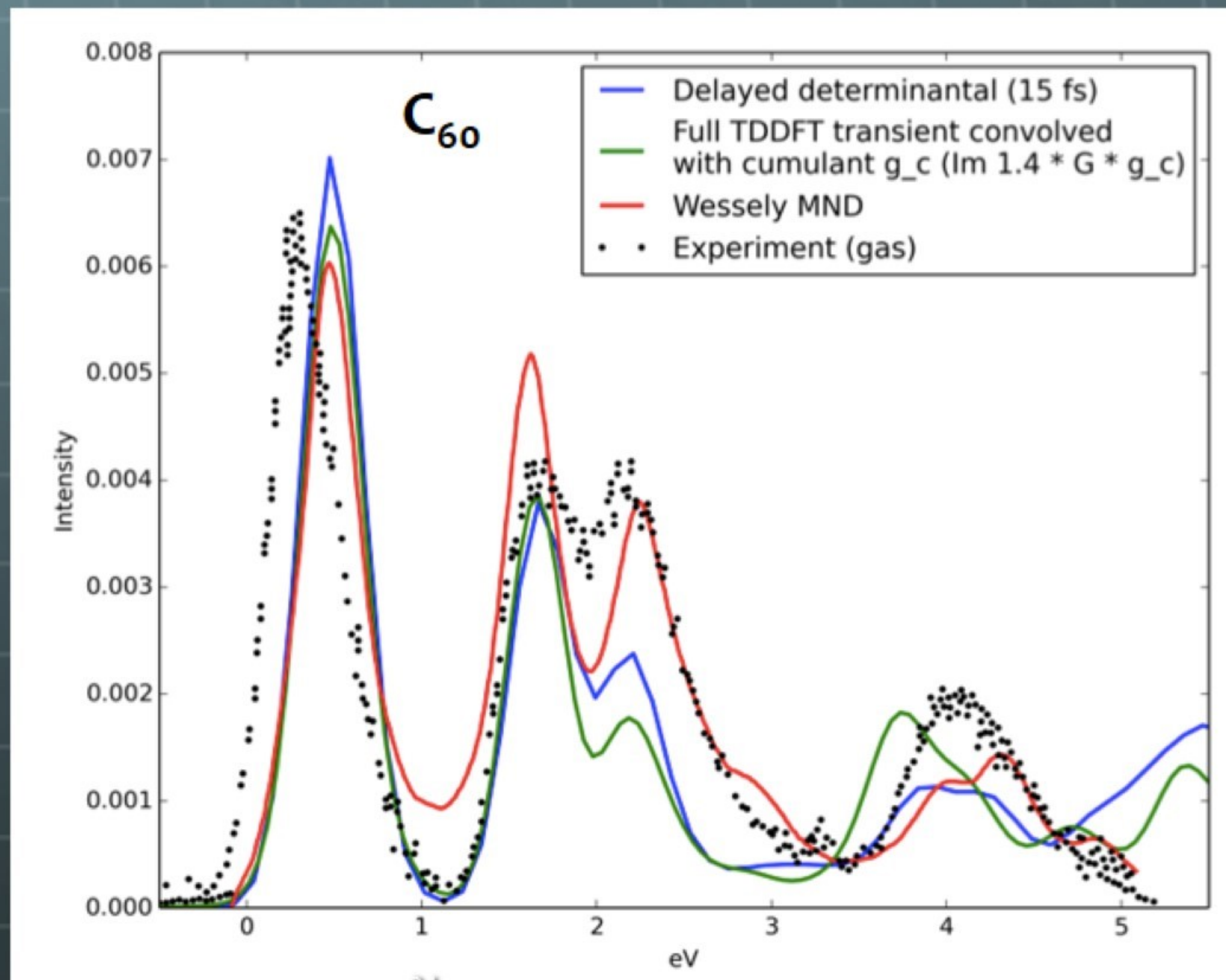
XAS: Qualitative picture

Evolve system



XAS, det vs convolution

- Includes intrinsic, extrinsic, interference effects!



I. Quasiparticle starting-point: Sum rules

- Sum rules of spectral function

$$\left\langle \omega^n \right\rangle_k = \int \omega^n A_k(\omega) d\omega$$

- Same as GW to n=2

$$\left\langle \omega^0 \right\rangle_k = 1$$

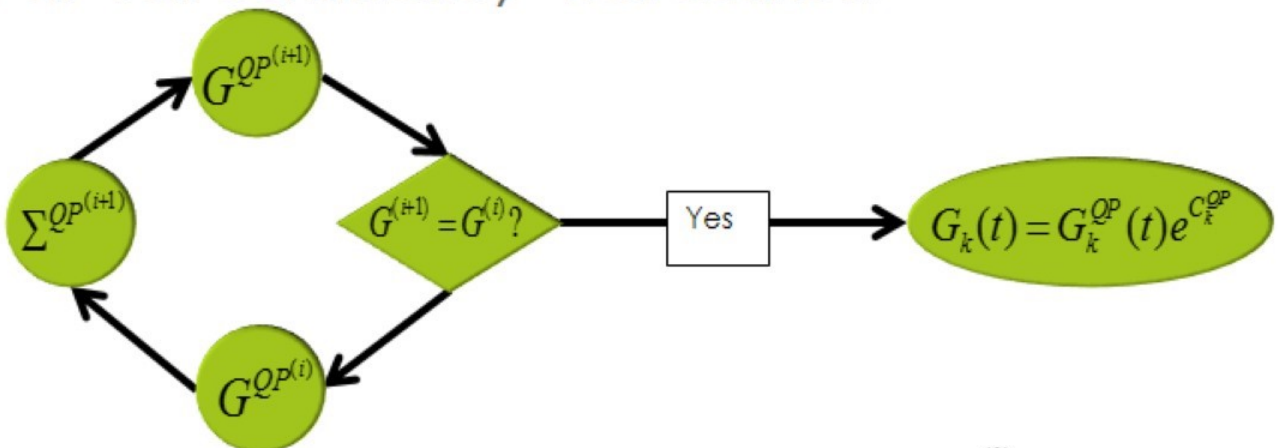
$$\left\langle \omega^1 \right\rangle_k = \varepsilon_k + \Sigma_k^x$$

$$\left\langle \omega^2 \right\rangle_k = (\varepsilon_k + \Sigma_k^x)^2 + \int \beta_k(\omega)$$

I. Quasiparticle starting-point: Benefits

- Reproduces exact Green's function in principle
  ➡ higher order corrections

- QP Self-consistency* well defined



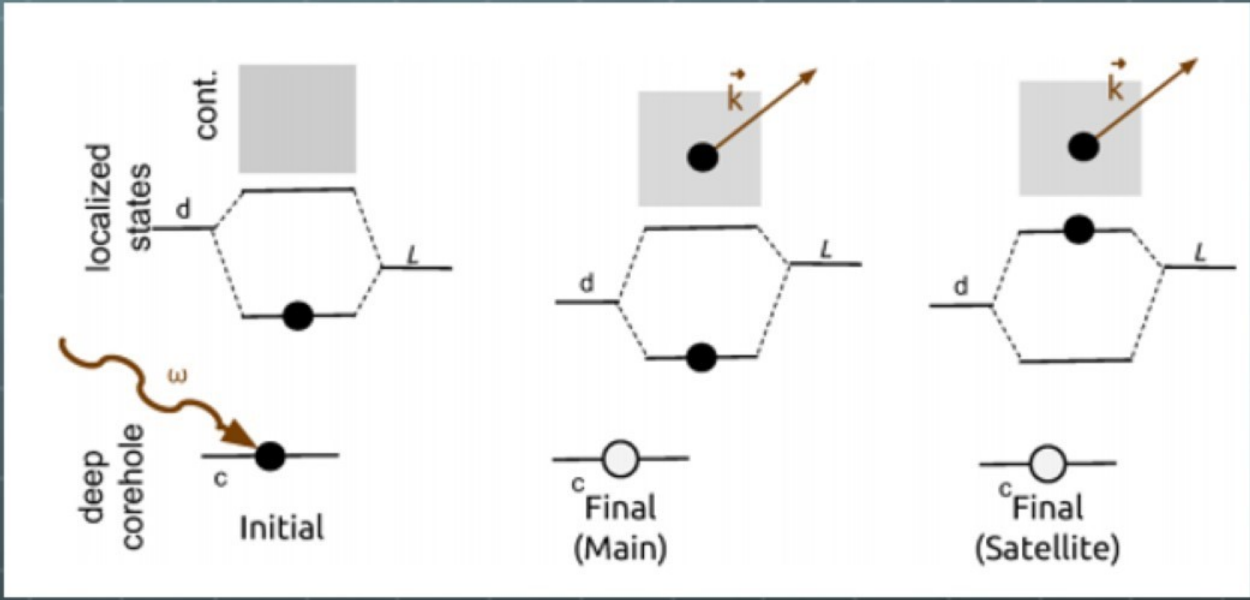
- Simple single step approximation: $G_k^{QP^{(0)}} = G_k^{KS}; \quad \Sigma^{(1)} = G_k^{KS}W \Rightarrow G_k^{QP^{(1)}}, C_k^{(1)}$

$$G_k(t) = G_k^{QP^{(1)}}(t)e^{C_k^{(1)}}$$

*M. van Schilfgaarde, Takao Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006)

II. Real time cumulant approach: Motivation

- Charge-transfer satellites: XPS, XAS, …



- **Can we calculate these excitations *ab initio*?**

J. D. Lee, O. Gunnarsson, and L. Hedin, Phys. Rev. B **60**, 8034 (1999)

II. Rutile TiO_2 – transient response to core-hole