Real-time Approaches for Optical and X-ray Spectra

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KITP, UCSB Aug 30, 2010

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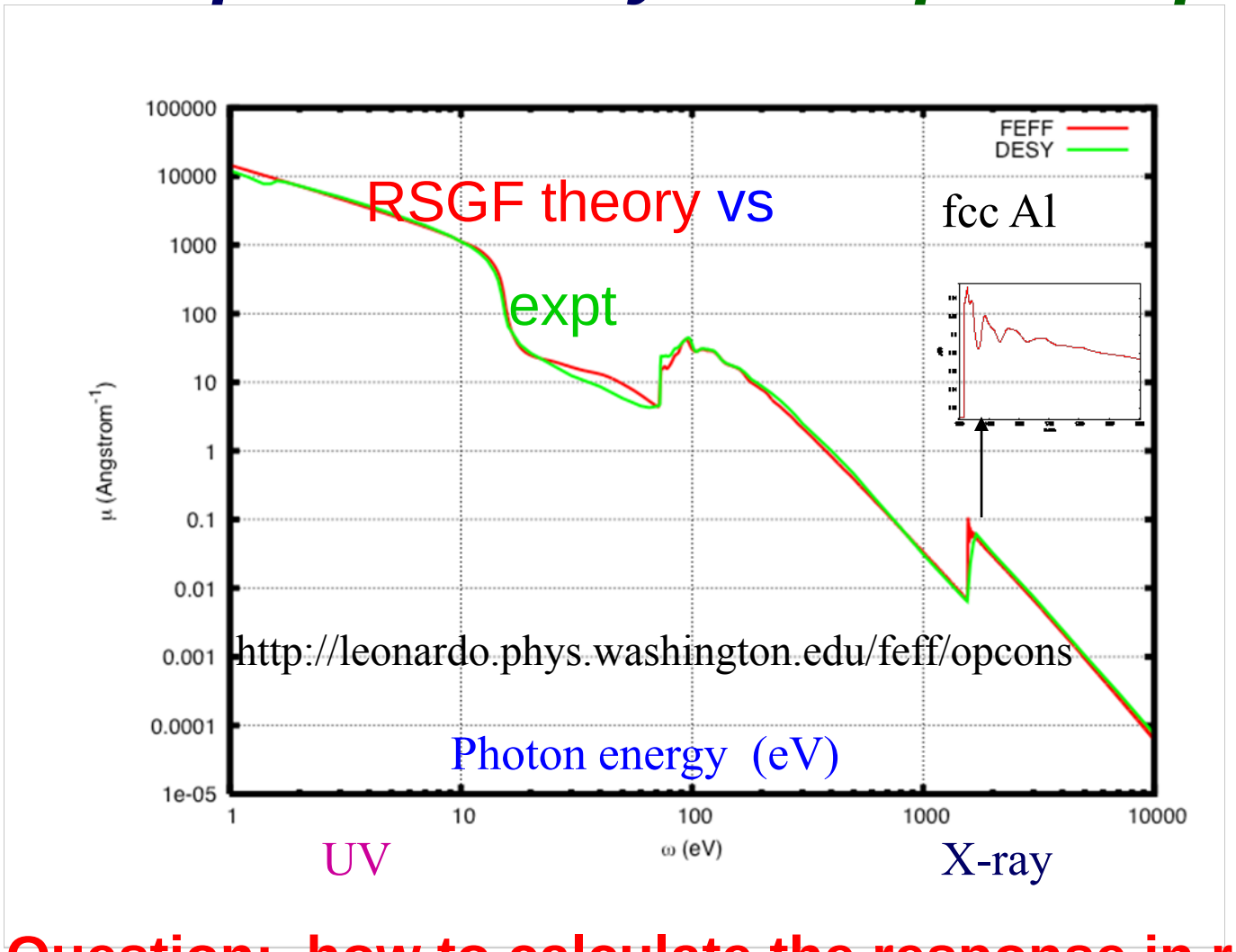
Goals: *Real-time response*

Talk:

- **I.** Linear & Non-linear Optical Response RT-TDDFT
- **II.** Real-time core-level XAS
- **III.** Many-body Effects

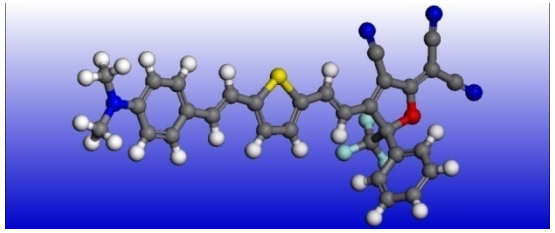
Experiment vs Theory: Full spectrum
Optical - X-ray Absorption Spectra



Question: how to calculate the response in real time??

I. *Real-Space & Real-Time*
Linear and Non-linear Optical Response

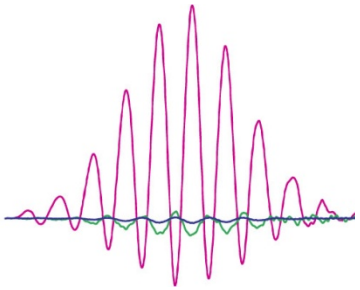
- Difficulty: frequency-space is computationally demanding **too-many** excited states



- Strategy: extend RT-TDDFT/ SIESTA *

*Sanchez-Portal, Tsolakidis, and Martin, Phys. Rev. B**66**, 235416 (2002)

Approach I*:* RT-TDDFT



THE JOURNAL OF CHEMICAL PHYSICS 127, 154114 (2007)

Real-time time-dependent density functional theory approach for frequency-dependent nonlinear optical response in photonic molecules

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(Received 11 July 2007; accepted 4 September 2007; published online 19 October 2007)

We present *ab initio* calculations of frequency-dependent linear and nonlinear optical responses based on real-time time-dependent density functional theory for arbitrary photonic molecules. This approach is based on an extension of an approach previously implemented for a linear response using the electronic structure program SIESTA. Instead of calculating excited quantum states, which can be a bottleneck in frequency-space calculations, the response of large molecular systems to time-varying electric fields is calculated in real time. This method is based on the finite field approach generalized to the dynamic case. To speed the nonlinear calculations, our approach uses Gaussian enveloped quasimonochromatic external fields. We thereby obtain the frequency-dependent second harmonic generation $\beta(-2\omega;\omega,\omega)$, the dc nonlinear rectification $\beta(0;-\omega,\omega)$, and the electro-optic effect $\beta(-\omega;\omega,0)$. The method is applied to nanoscale photonic nonlinear optical molecules, including *p*-nitroaniline and the FTC chromophore, i.e., 2-[3-Cyano-4-(2-{5-[2-(4-diethylamino-phenyl)-vinyl] - thiophen-2-yl] - vinyl)-5,5-dimethyl-5H-furan-2-ylidene]-malononitrile, and yields results in good agreement with experiment. © *2007 American Institute of Physics*.
[DOI: 10.1063/1.2790014]

J. Chem. Phys. **127**, 154114 (2007)

Real time *Linear* Response

$$\delta \mathbf{p}(t) = \mathbf{p}(t) - \vec{\mu}_0$$ Induced Dipole Moment

$$\delta p_i(t) = \int dt' \, \chi_{ij}^{(1)}(t - t') E_j(t')$$

$$\chi_{ij}^{(1)}(\omega) = \delta p_i(\omega) / E_j(\omega) = \alpha_{ij}(\omega)$$ Linear Response Function

$$\epsilon_{ij}(\omega) = 1 + 4\pi N \alpha_{ij}(\omega)$$ Linear Dielectric Function

$$\sigma(\omega) \sim \omega \, \langle \alpha(\omega) \rangle / E(\omega)$$ Optical Absorption

RT-TDDFT Formalism

- Yabana and Bertsch Phys. Rev. B**54**, 4484 (1996)

$$i\frac{\partial \Psi}{\partial t} = H(t)\,\Psi \qquad H = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r},t) + V_H[\rho](\mathbf{r},t) + V_{xc}[\rho](\mathbf{r},t)$$

- Direct numerical integration of TD Kohn-Sham equations

$$\Psi(t) = T\,\exp\left(-i\int_0^t H(t')dt'\right)\Psi(0)$$

- The response to external field is determined by applying a **time-dependent electric field** $\Delta H(t) = -\boldsymbol{E}(t)\cdot\boldsymbol{x}$.

- Optical properties determined from **total dipole moment**:

$$\mathbf{p}(t) = \int \rho(\mathbf{r},t)\,\mathbf{r}\,d^3\mathbf{r}$$

MORE EFFICIENT THAN FREQUENCY –SPACE METHODS !

Numerical Real-time Evolution

- Ground state density ρ_0, **overlap matrix *S*,** and ***H(t)*** at each time-step evaluated with SIESTA

$$i\frac{\partial c(t)}{\partial t} = S^{-1}H(t)c(t)$$

Coefficients of Orbitals

- Crank-Nicholson time-evolution: **unitary**, **time-reversible**

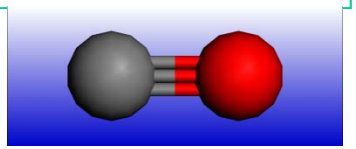
Stable for long time-steps !

$$c(t+\Delta t) = \frac{1 - iS^{-1}H(\bar{t})\Delta t/2}{1 + iS^{-1}H(\bar{t})\Delta t/2}c(t) + \mathcal{O}(\Delta t^2), \quad \bar{t} = t + \Delta t/2$$

- Adiabatic GGA exchange-correlation (PBE) functional

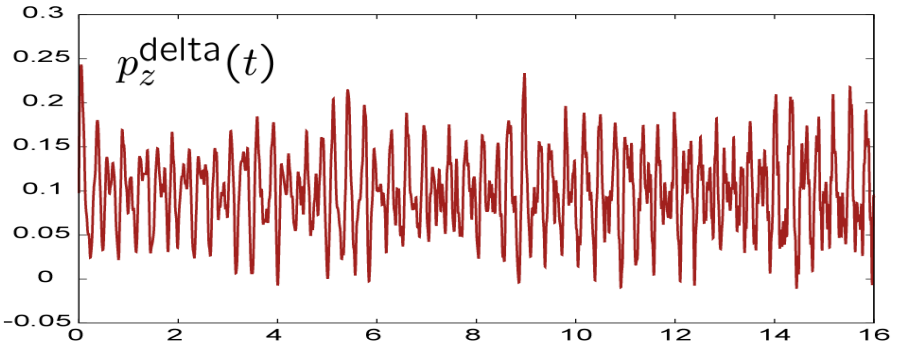
Example: CO Linear Response

$p_z(t)$ response due to applied $E_z(t)$

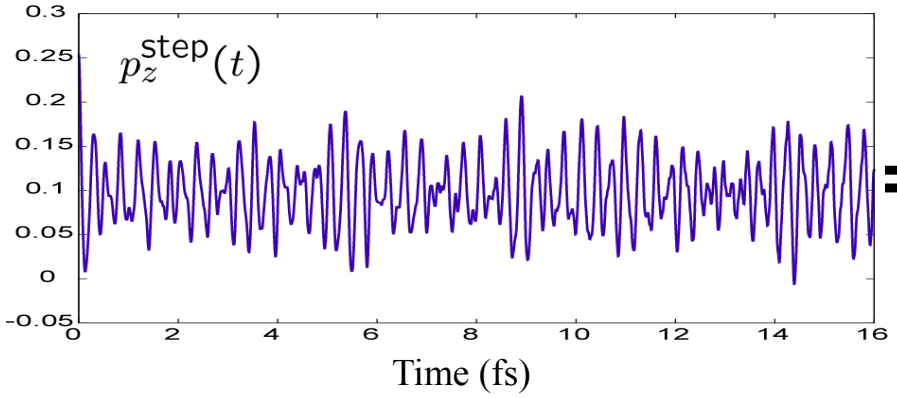


- Delta Function

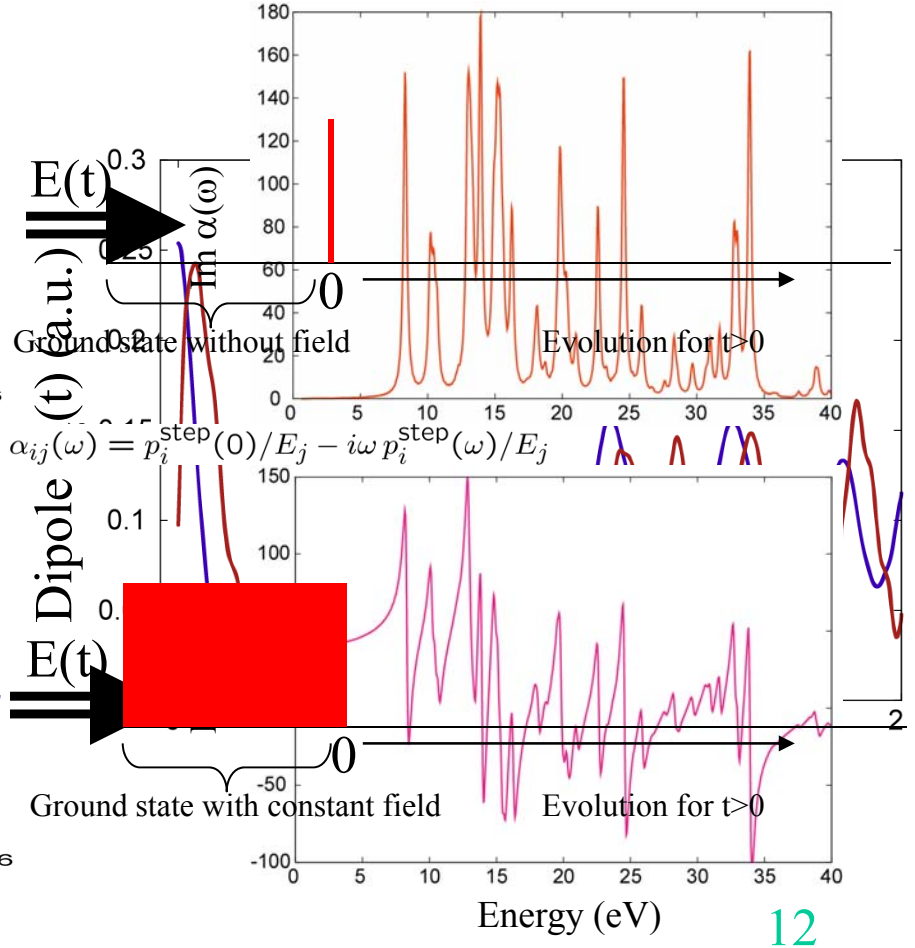
(Unit Impulse at *t=0*)



(Turn-off Constant E at *t=0*)



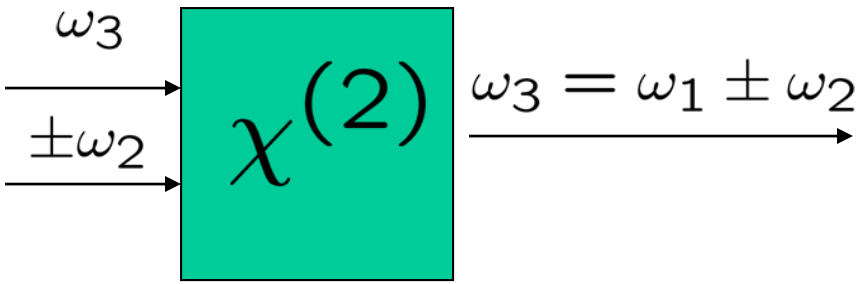
$\alpha_{ij}(\omega) = p_i^{\text{delta}}(\omega)/E_j$

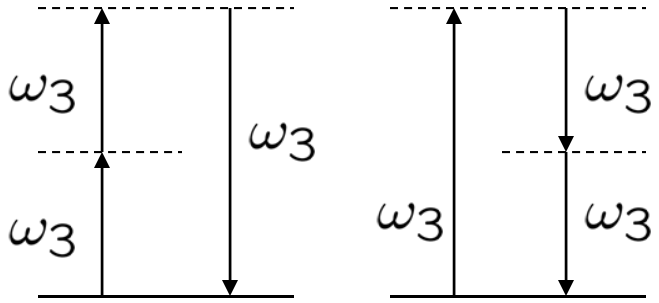


Nonlinear Polarizabilities

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots$$

- Second order nonlinearities





$\chi^{(2)}(-2\omega;\omega,\omega)$ Second Harmonic Generation (SHG)

$\chi^{(2)}(0;-\omega;\omega)$ Optical Rectification (OR)

$\chi^{(2)}(-\omega;0;\omega)$ Electro-Optic effect (Pockel's effect)

Extraction of Static Nonlinear Polarizabilities

- Standard technique: *static* nonlinearity

$$p_i = \mu_i^0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \cdots$$

Finite-difference or polynomial fitting $p_i(E)$ *e.g.,*

$$\beta_{ijj} = [-p_i(-2E_j) + 16p_i(-E_j) - 30p_i(0) + 16p_i(E_j) - p_i(2E_j)]/24E_j^2$$

Real time Dynamic Nonlinear Response

- The nonlinear expansion in field strength

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots$$

- Accounting for time lag in system response

$$\begin{aligned} p_i(t) = \quad & \mu_i^0 + \int dt_1\, \chi_{ij}^{(1)}(t-t_1)E_j(t_1) \\ & + \int dt_1 \int dt_2\, \chi_{ijk}^{(2)}(t-t_1, t-t_2)E_j(t_1)E_k(t_2) \\ & + \int dt_1 \int dt_2 \int dt_3\, \chi_{ijkl}^{(3)}(t-t_1, t-t_2, t-t_3)E_j(t_1)E_k(t_2)E_l(t_3) \\ & + \cdots \end{aligned}$$

¿ How can we invert the equation to get nonlinear response function?

Dynamic Nonlinear Polarizabilities

- Set $E_j(t) = F(t)E_j$ and define expansion $p_i(t)$

$$p_i(t) = \mu_i^0 + p_{ij}^{(1)}(t)E_j + p_{ijk}^{(2)}(t)E_jE_k + \cdots$$

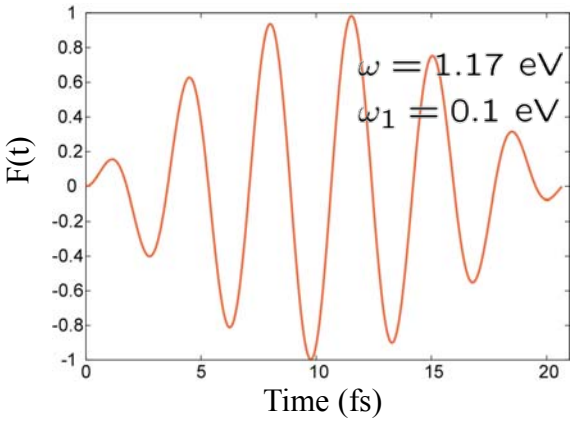
where $p^{(1)}$ yields linear response, $p^{(2)}$ first non-linear (quadratic) response, ….

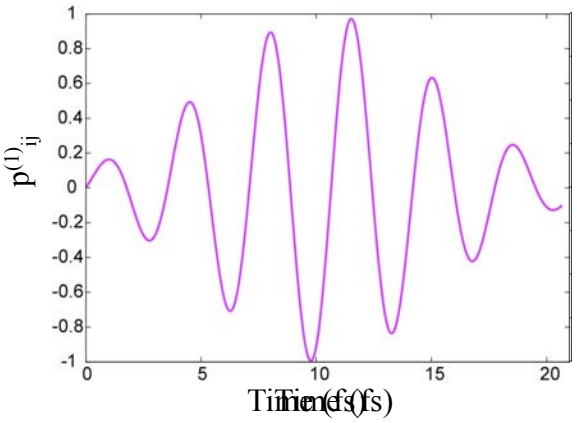
- Quadratic response $\chi^{(2)}$

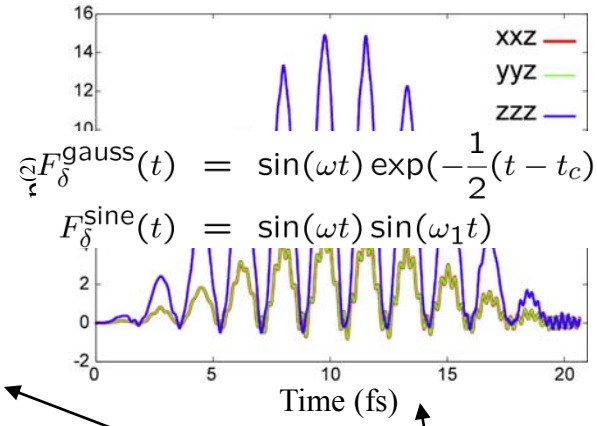
$$p_{ijk}^{(2)}(t) = \int dt_1 \int dt_2 \; \chi_{ijk}^{(2)}(t - t_1, t - t_2)F(t_1)F(t_2)$$

Dynamic Nonlinear Response with Quasi-monochromatic Field $F_\delta(t)$

- Sine wave enveloped by another sine wave or Gaussian



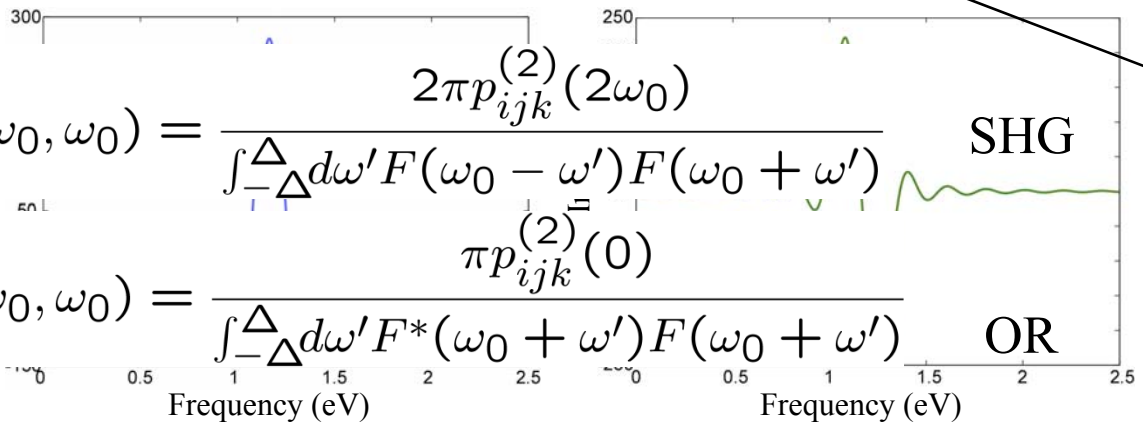




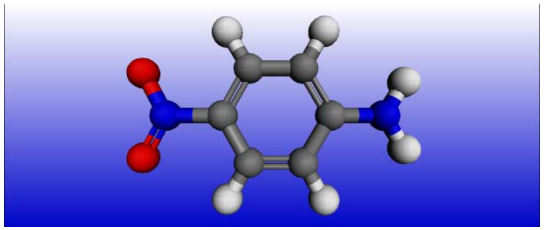
Linear and Nonlinear response of CO

$$\chi^{(2)}_{ijk}(-2\omega_0;\omega_0,\omega_0) = \frac{2\pi p^{(2)}_{ijk}(2\omega_0)}{\int_{-\Delta}^{\Delta} d\omega' F(\omega_0-\omega')F(\omega_0+\omega')}$$ SHG

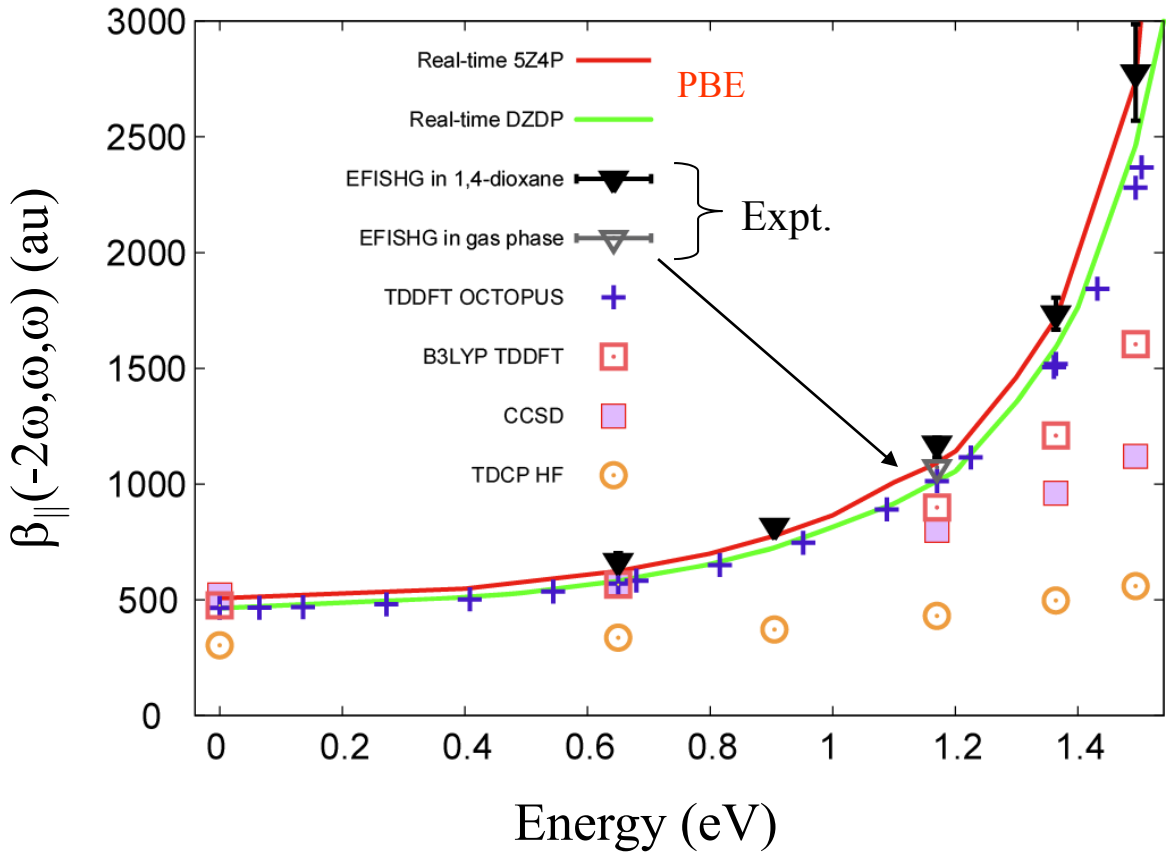
$$\chi^{(2)}_{ijk}(0;-\omega_0,\omega_0) = \frac{\pi p^{(2)}_{ijk}(0)}{\int_{-\Delta}^{\Delta} d\omega' F^*(\omega_0+\omega')F(\omega_0+\omega')}$$ OR



Example pNA: *Nonlinear SHG*



- Comparison with other methods



Core-level x-ray Response

1. Time-correlation function approach
2. Dynamic response: adiabatic vs sudden
3. Many-body corrections

II. Real-time core-level XAS

Local time-correlation approach for x-ray absorption spectra*

J. J. Rehr[1]

[1] *Dept. of Physics, Univ. of Washington Seattle, WA 98195*

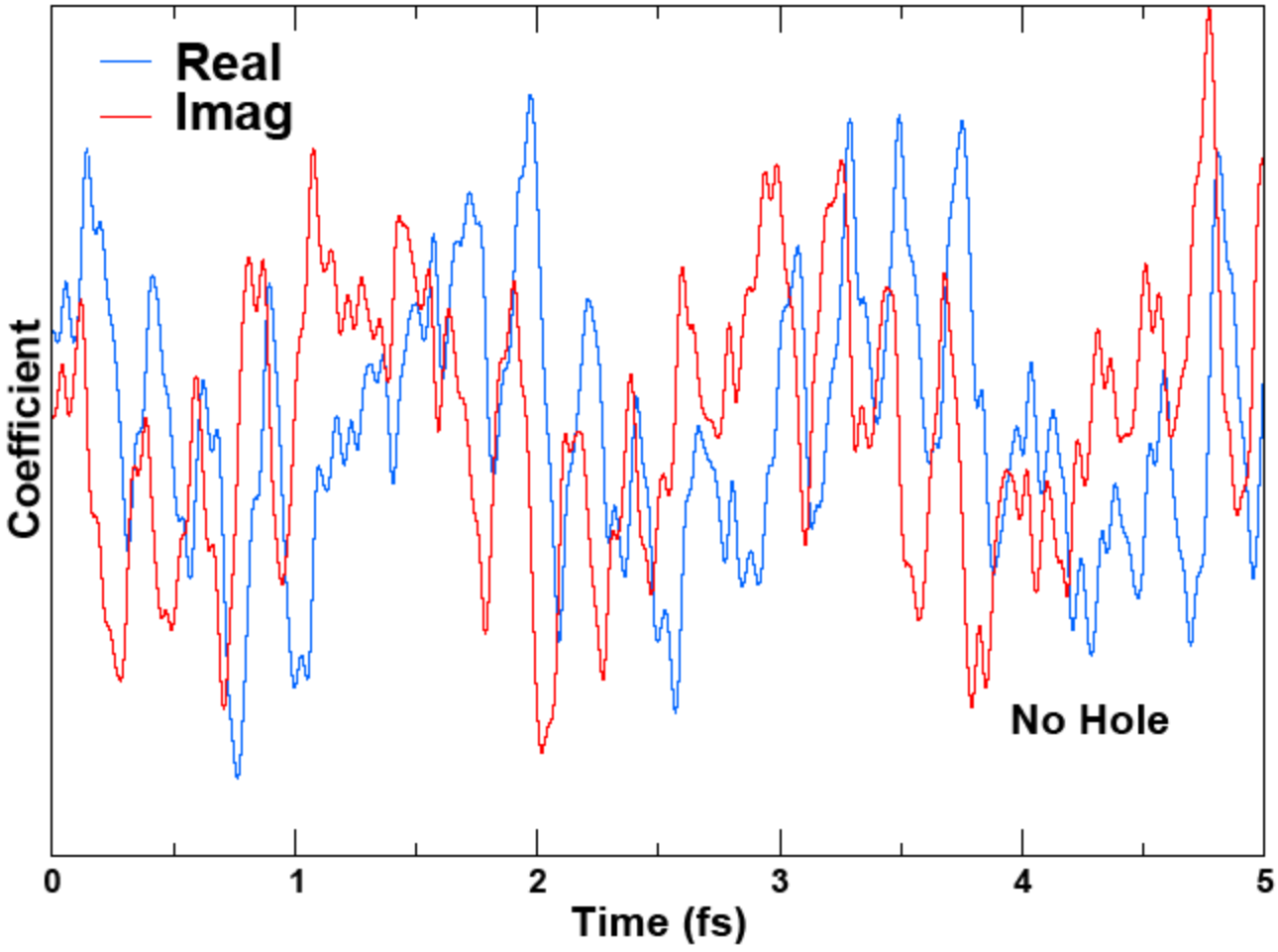
(Dated: August 12, 2010)

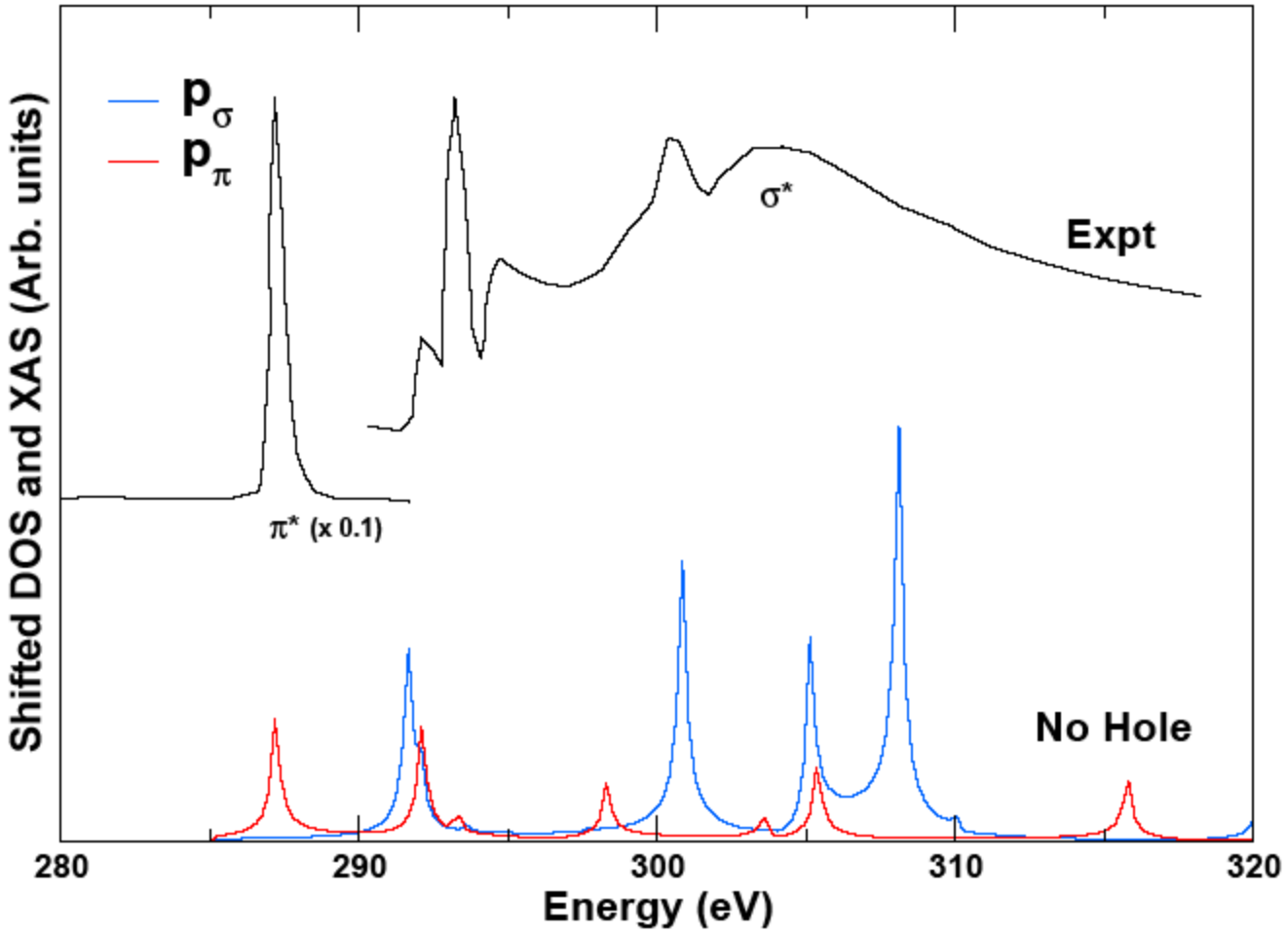
We present an approach for calculations of core level x-ray absorption spectra based on local time-correlation functions of the response function, which is formally equivalent to a Fermi golden rule calculation. The approach is implemented in a local orbital basis using a Crank-Nicholson time-evolution algorithm and projector augmented wave (PAW) atomic transition matrix elements. Illustrative calculations are presented based on a real-time extension of the SIESTA code.

$$\mu(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\, e^{i\omega t} G_c(t)\langle\psi(t)|\psi(0)\rangle\theta(\omega+\epsilon_c-E_F).$$

$$|\psi(0)\rangle = d|b\rangle$$

* UW pre-preprint Aug 2010


Real
Imag
Coefficient
No Hole
0
1
2
3
4
5
Time (fs)


Shifted DOS and XAS (Arb. units)
p$_\sigma$
p$_\pi$
π* (x 0.1)
σ*
Expt
No Hole
280
290
300
310
320
Energy (eV)

III. Many-body Effects

Dynamic core-hole screening algorithm

PHYSICAL REVIEW B 73, 075402 (2006)

Dynamical core-hole screening in the x-ray absorption spectra of graphite, C_{60}, and carbon nanotubes: A first-principles electronic structure study

O. Wessely and O. Eriksson
Department of Physics, Uppsala University, Box 530, SE-75121, Uppsala, Sweden

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Institute for Molecules and Materials, Radboud University Nijmegen, NL-6525 ED Nijmegen, The Netherlands

(Received 14 September 2005; revised manuscript received 23 November 2005; published 1 February 2006)

alá Nozieres & De Dominicis

$$I(\omega) \sim \mathrm{Re} \int_0^\infty dt \int_\mu^\infty \frac{d\epsilon}{\pi} e^{it(\omega-\epsilon+\epsilon_c)+\Delta(-t)} \times \sum_{ij} t_i [\mathrm{Im}\, g^R(\epsilon)\bar{\varphi}(\epsilon,t)]_{ij} t_j^*, \quad (8)$$

$$\Delta(t) = i\,\mathrm{Tr}\, V \int_0^{-t} dt_1 \int_{-\infty}^{\mu} \frac{d\epsilon}{\pi} \mathrm{Im}\, g^R(\epsilon)\bar{\varphi}(\epsilon,t_1), \quad (9)$$

where $\bar{\varphi}(\epsilon,t)$ can be found from the matrix integral equation

$$\bar{\varphi}(\epsilon,t) = 1 + V \int_\mu^\infty \frac{d\epsilon_1}{\pi} \mathrm{Im}\, g^R(\epsilon_1) L^+(\epsilon,\epsilon_1,t)\bar{\varphi}(\epsilon_1,t),$$

$$L^+(\epsilon,\epsilon_1,t) = \frac{I^*(\epsilon_1,t) - e^{i(\epsilon-\epsilon_1)t} I^*(\epsilon,t)}{\epsilon_1 - \epsilon},$$

$$I(\epsilon,t) = 1 + V \int_{-\infty}^{\infty} \frac{d\epsilon_1}{\pi} \frac{e^{i(\epsilon-\epsilon_1)t} - 1}{\epsilon - \epsilon_1} \mathrm{Im}\, G^R(\epsilon_1). \quad (10)$$

Also: Grebennikov, Babanov and Sololov, Phys. Stat. Sol. **79**, 423 (1977)
and Privalov, Gel'mukhanov & Agren: Phys Rev. B **64,** 165115 (2001)

Intrinsic Satellites

PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Singularities in the X-Ray Spectra of Metals*

Dexter C. Langreth
Rutgers University, New Brunswick, New Jersey 08903

(Received 4 August 1969)

Recently, Nozières *et al.* have shown that Mahan's x-ray-edge singularity, coupling between the deep hole and electron-hole excitations, could be solved exactly in the singular exponents. Here, it is shown that Landqvist's model, x-ray probe-like coupling between the deep hole and plasmons, may also be solved exactly. Furthermore, an exact solution for the singular exponents can be obtained for the more general problem of coupling to both electron-hole pairs and plasmons simultaneously. Finally, a perturbation method is developed to treat band effects and to apply theory to actual photoemission experiments.

Cumulant expansion

$$G_c^+(t) = e^{i\epsilon_c t} e^{C(t)} \theta(t)$$

$$C(t) = \sum_q |V_q|^2 \int_{-\infty}^{\infty} d\omega S(q,\omega) \times (1 + e^{i\omega t} - e^{i\epsilon_c t} e^{-i\omega t}), \quad (44)$$

where $S(q,\omega)$ is the dynamic form factor for the electron gas. That is,

$$S(q,\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} \langle \rho_q(t) \rho_{-q}(0) \rangle, \quad (45)$$

INSTITUTE OF PHYSICS PUBLISHING

J. Phys.: Condens. Matter 15 (2003) 2573–2586

JOURNAL OF PHYSICS: CONDENSED MATTER

PII: S0953-8984(03)59657-6

Many-pole Self-energy Algorithm*

Electron self-energy calculation using a general multi-pole approximation

J A Soininen[1], J J Rehr[1] and Eric L Shirley[2]

[1] Department of Physics, University of Washington, Seattle, WA 98195, USA
[2] Optical Technology Division, Physics Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

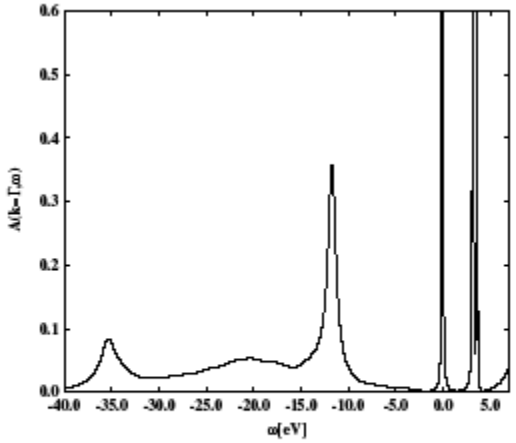


Figure 5. The spectral function for Si at the Γ point. This result was calculated using a 1.0 eV HWHM Gaussian broadening. A small imaginary part (0.005 eV) was added to the self-energy to give a finite width to the quasiparticle peak for the highest valence band states, for purposes of presentation. The energy scale was shifted so that the valence band maximum energy was at 0 eV.

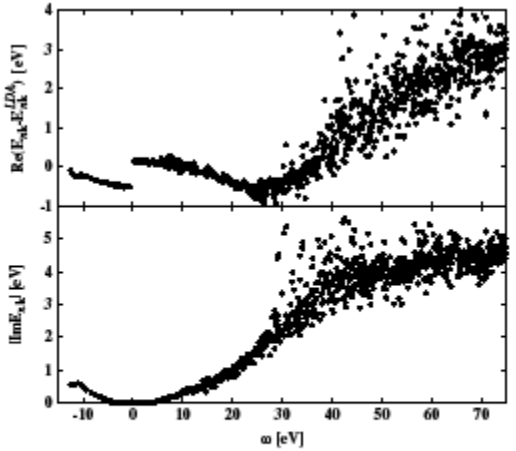


Figure 4. Quasiparticle corrections for Si as a function of the LDA band energy. The upper panel shows the real part of the quasiparticle correction, and the lower panel, the imaginary part of the quasiparticle energy. The result was calculated using a 1.0 eV HWHM Gaussian broadening.

*Many-pole Self-energy Algorithm**

Plasmon-pole model ⟶ many-pole model

-Im $\varepsilon^{-1}(\omega)$ *Many-pole* Dielectric Function

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

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

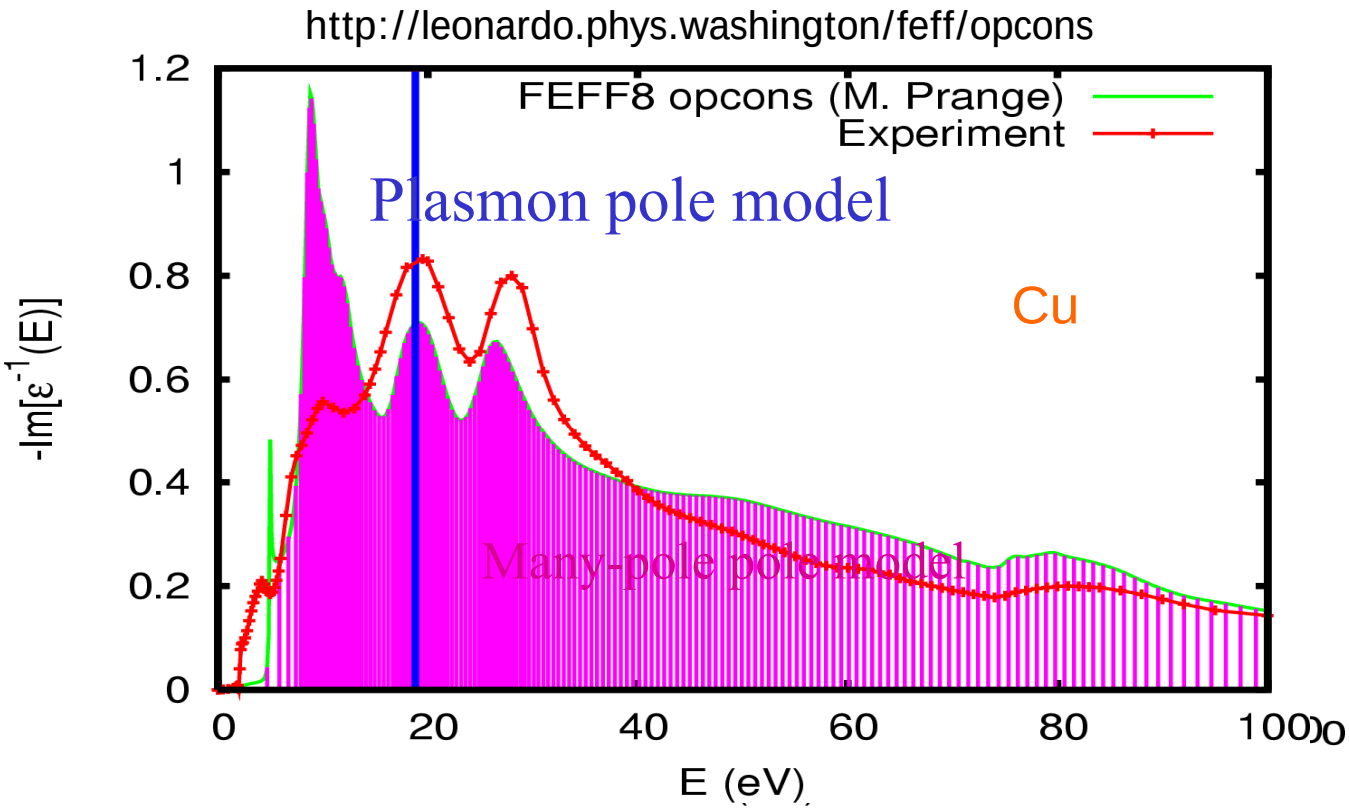
* J. Kas et al. PRB **76**, 195116(2008)

Example: Many-pole model for Cu*

- *ab initio* **q**=0 loss function

  $-\mathrm{Im}\ \varepsilon^{-1}(\omega)$

- Sum of single pole self-energies



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

Extension to: Extrinsic and Intrinsic losses:

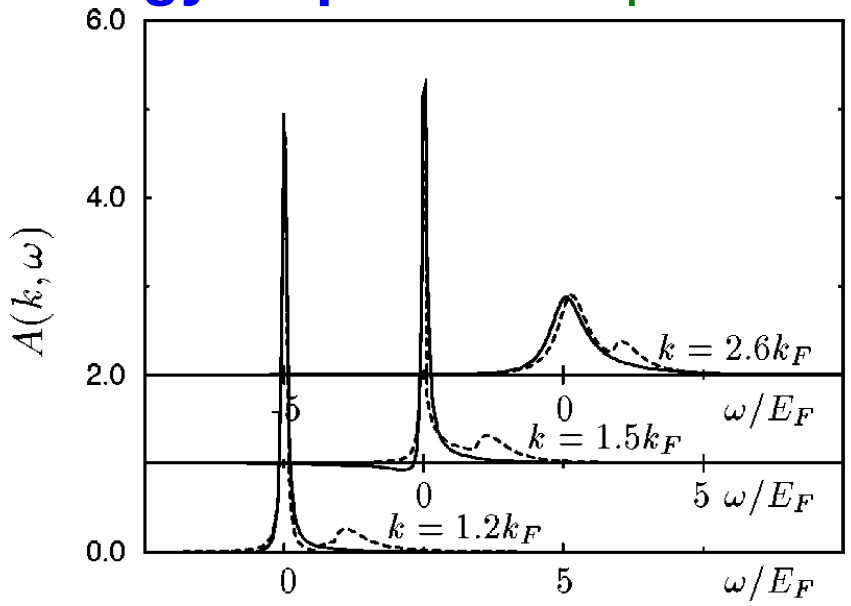
Quasi-boson Model

PHYSICAL REVIEW B, VOLUME 65, 064107

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

L. Campbell,[1] L. Hedin,[2] J. J. Rehr,[1] and W. Bardyszewski[3]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195-1560*
[2]*Department of Physics, Lund University, Lund, S22362 Sweden*
and MPI-FKF, Stuttgart, D70569 Germany
[3]*Department of Physics, Institute of Theoretical Physics, 00-681 Warsaw, Poland*

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



Question: How to *extend* theory to real-time approach?

Quasi-Boson Theory of Inelastic Loss*

Excitations - plasmons, electron-hole pairs ... are **bosons**

Many-body Model: $|e^-, h, \text{bosons}\rangle$

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

"GW++" Same ingredients as GW self-energy

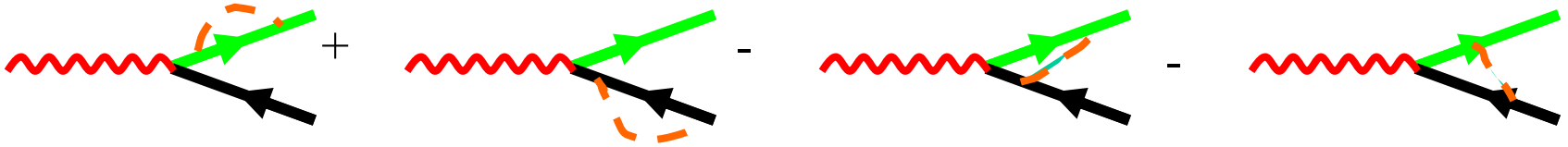
$V^n \rightarrow$ **-Im** $\varepsilon^{-1}(\omega_n, q_n)$ fluctuation potentials

*W. Bardyszewski and L. Hedin, Physica Scripta **32**, 439 (1985)

Effective GW++ Green's Function $g_{eff}(\omega)$

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

$$g_{eff}(\omega) = e^{-a}\left[g'(\omega) + \Sigma_n \left(\frac{V^n_{bb}}{\omega_n}\right)^2 g'(\omega-\omega_n) - 2\Sigma_n \frac{V^n_{bb}}{\omega_n} g'(\omega-\omega_n) V^n g'(\omega)\right]$$



Extrinsic + Intrinsic - 2 x Interference

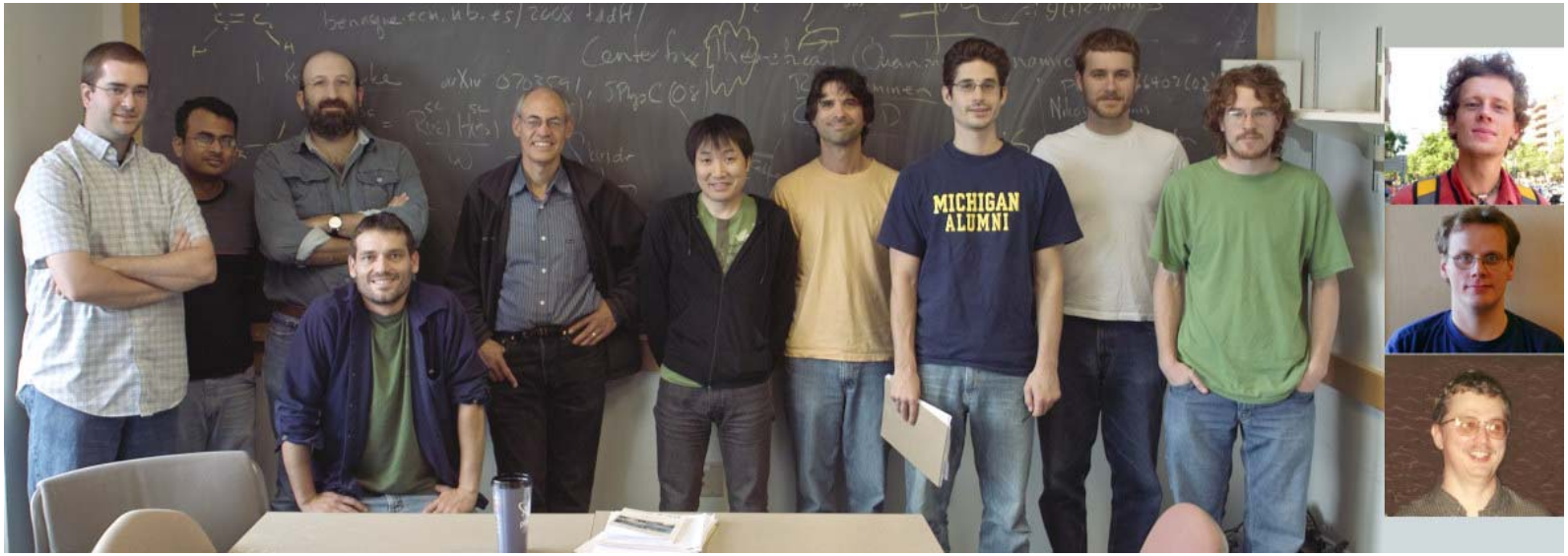
Damped ***qp*** Green's function $g'(\omega) \equiv [\omega - h' - \Sigma(\omega) + i\gamma]^{-1}$

Spectral function: $A(\omega) = -(1/\pi)\ \mathrm{Im}\ g_{eff}(\omega)$

Acknowledgments

Rehr Group

- J. Kas (UW)
- F. Vila (UW)
- Y. Takimoto (ISSP,UW)
- J. Vinson (UW)



Supported by DOE-BES and NSF