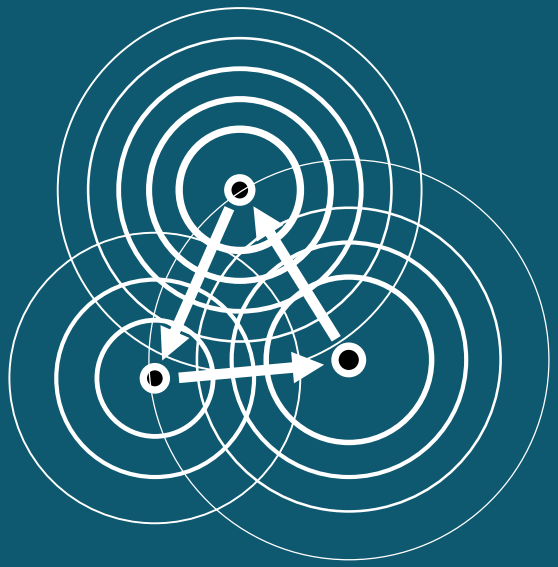
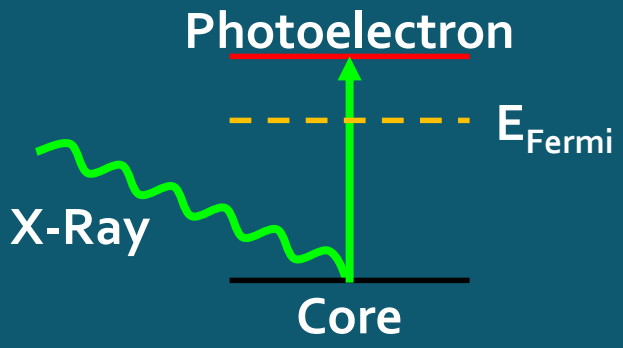
Real-Time and Finite Temperature Green's Function Approaches for Excited States, Response Functions, and Thermodynamics

F. D. Vila, J. J. Kas and J. J. Rehr





DOE Office of Science grants DE-FG02-03ER15476 (FDV) and DE-FG02-97ER45623 (JJK, JJR), with computer support from DOE - NERSC.

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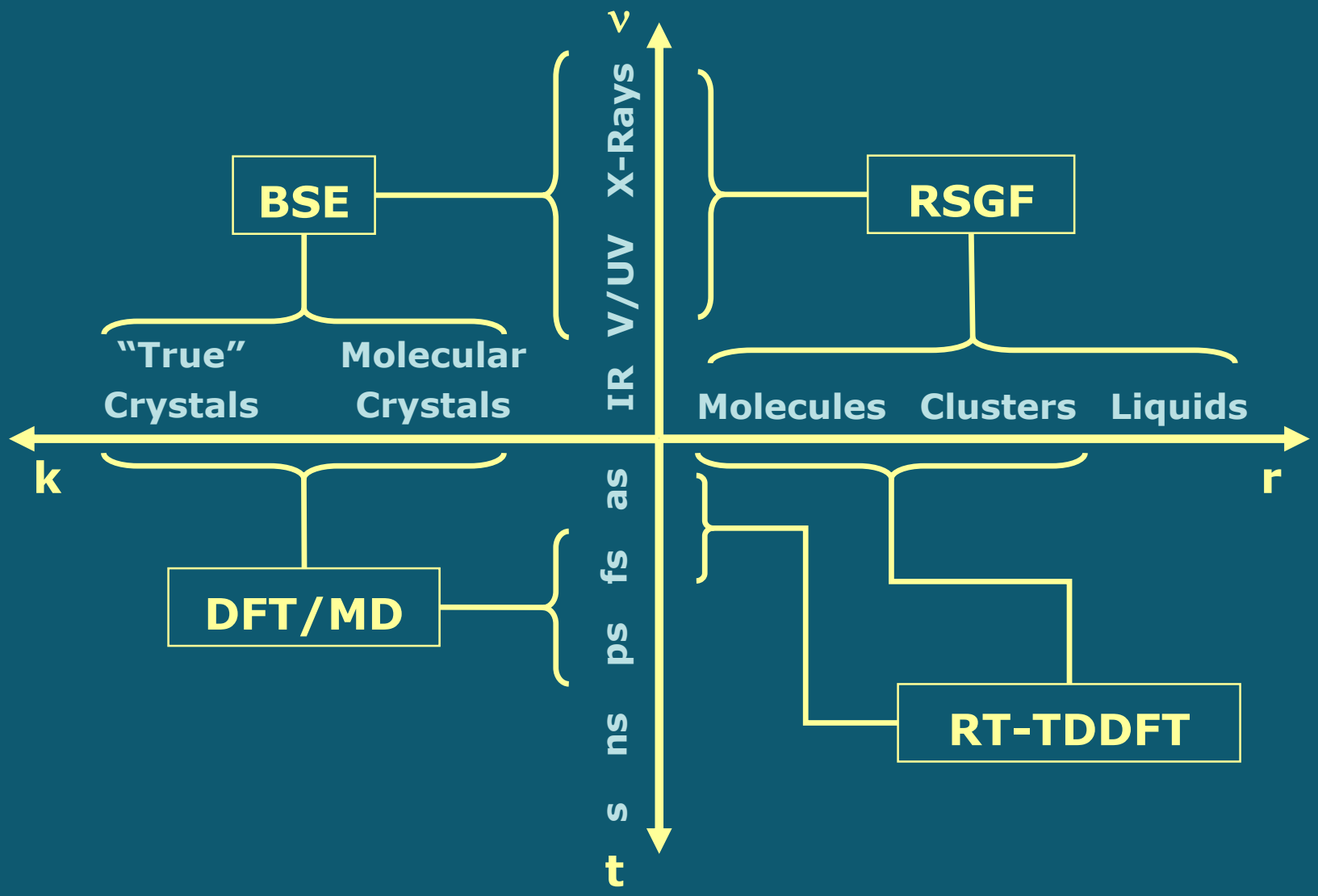
Experimental/Theoretical Landscape



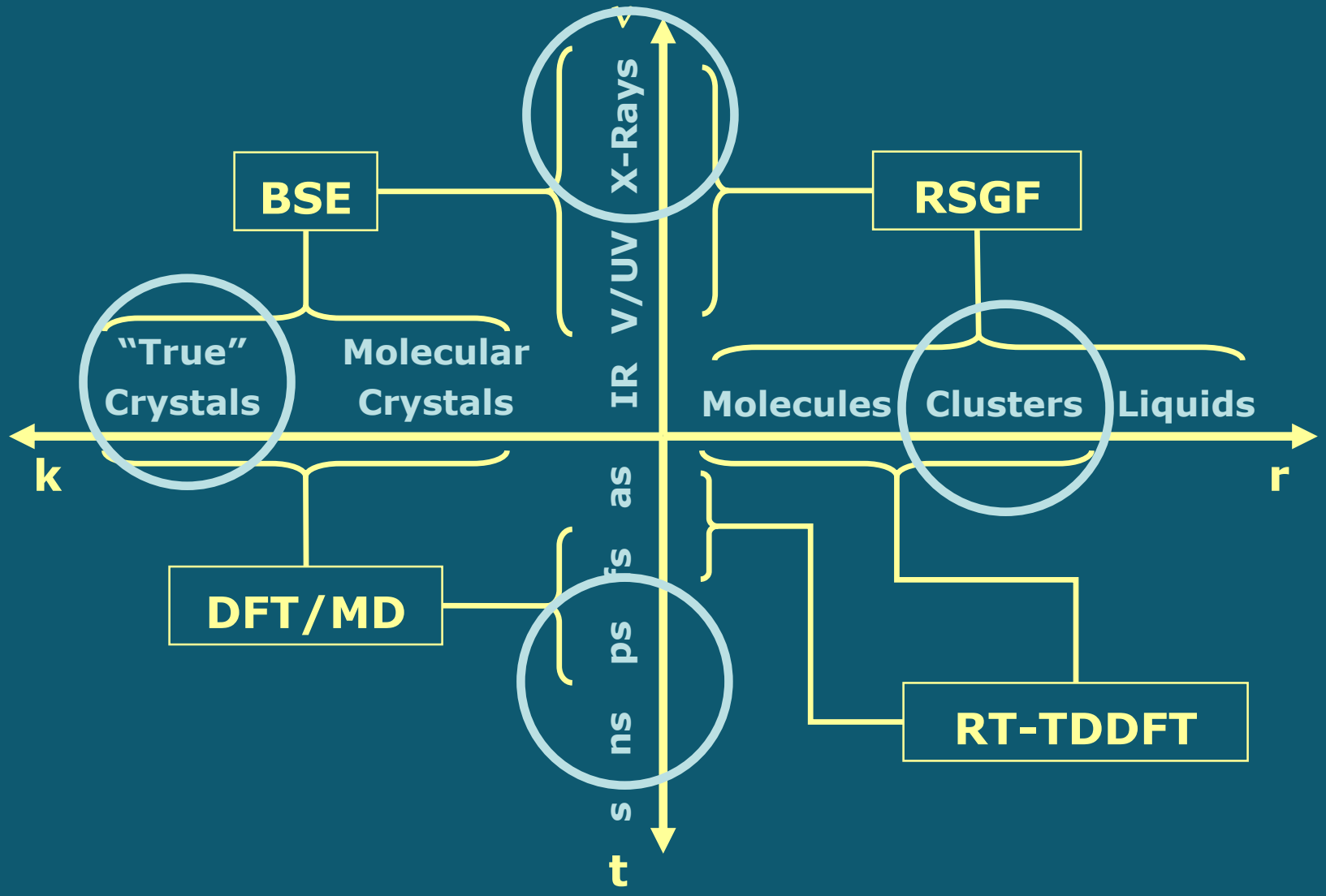
Motivation

Why real-time and finite temperature?

Old approaches not well suited for new science:

- XFEL pulsed x-ray sources (FLASH, LCLS)
- Pump-probe experiments (with finite electronic T)
- Interest in time-dependent response
- Direct access to time-domain
- Importance of non-equilibrium states
- Interest in exotic states (warm dense matter)

The Challenge



This talk:

Green's Functions and DFT/MD Approaches in X-Ray Excited States and Structural Disorder

Real-Time Approaches for Optical and Core Response

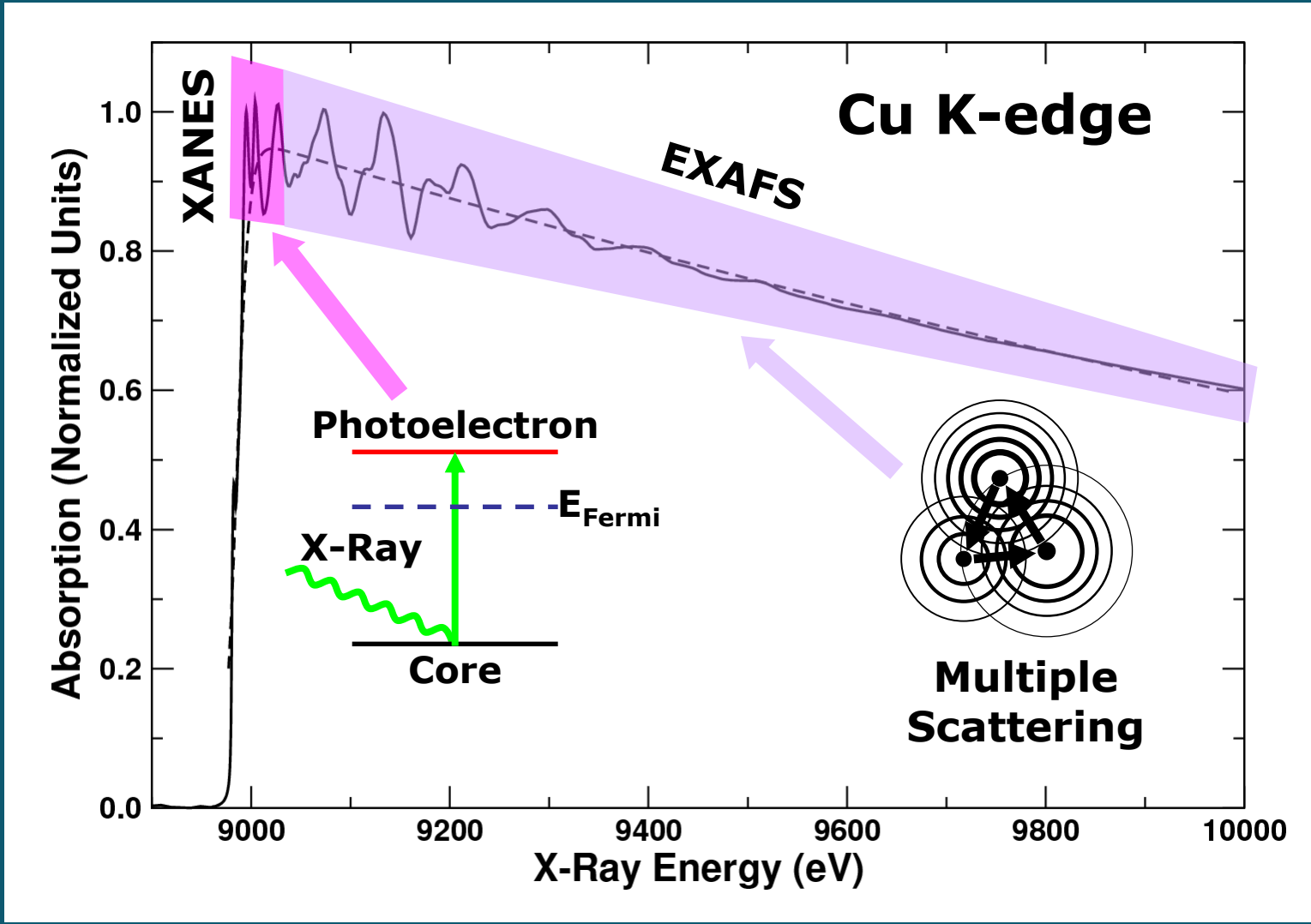
Finite Temperature Green's Functions

Green's Functions and DFT/MD Approaches in X-Ray Excited States and Structural Disorder

Real-Time Approaches for Optical and Core Response

Finite Temperature Green's Functions

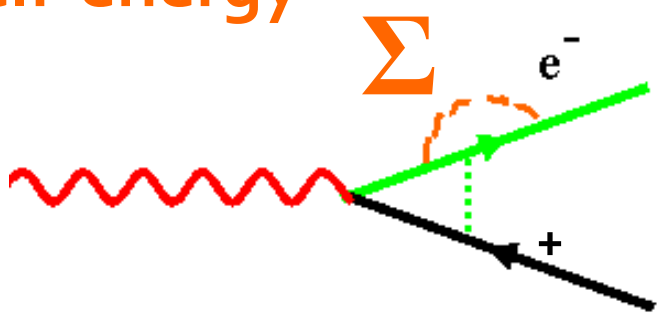
XAS: XANES and EXAFS



FEFF Quantitative XANES Theory in One Picture

Inelastic Losses
Self-energy

Real-Space
Green's Function



x-ray

Screened
core-hole

Many-body to Effective Single Particle

XAS absorption coefficient

Many-body Fermi's Golden Rule

$$\mu(\omega) \propto \sum_F |\langle I|\Delta|F\rangle|^2 \, \delta\left(E_F - E_I - \omega\right)$$

Effective Single particle Fermi's Golden Rule

$$\mu(\omega) \propto \sum_{i,f} |\langle i|d|f\rangle|^2 \, \delta\left(E_f - E_i - \omega\right)$$

$$H = -(1/2)\nabla^2 + V$$

$$H' = H + V_{ch} + \Sigma(E)$$

FEFF: From Sum-Over-States to Green's Function

Effective Single particle Fermi's Golden Rule

$$\mu(\omega) \propto \sum_{cf} \langle c | d^{\dagger} | f \rangle \langle f | d | c \rangle \, \delta(E_f - E_c - \omega)$$

$$\rho(r, r', E) = \sum_f |f\rangle\langle f| \, \delta(E_f - E)$$

$$\mathrm{Im}\left[G(r, r', E)\right] = -\frac{1}{\pi}\rho(r, r', E)$$

$$G = [E - H + i\Gamma]^{-1}$$

Substitute sum over final states with Green's function

$$\mu(\omega) \propto \mathrm{Im} \sum_c \langle c | d^{\dagger} G(\omega + E_c) d | c \rangle \, \theta_{\Gamma}(\omega + E_c + E_{Fermi})$$

FEFF: Local basis and Matrix elements

$$\mu(\omega) \propto \mathrm{Im} \sum_c \langle c | d^\dagger G(\omega + E_c) d | c \rangle \, \theta_\Gamma(\omega + E_c + E_{Fermi})$$

Insert complete set of site states $1 = \sum_L |i,L\rangle\langle i,L|$

Matrix elements

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

Green's function matrix

Getting G: Path Expansion and Full Multiple Scattering

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., site scat., central atom, etc.

$$V = \sum_i v_i \qquad t_i = v_i + v_i G_0 t_i$$

$$G_c = G_0 + G_0 t_c G_0 \qquad T_{LL'}^{ij} = t_{LL'}^{i} \delta_{ij}$$

EXAFS

Path expansion

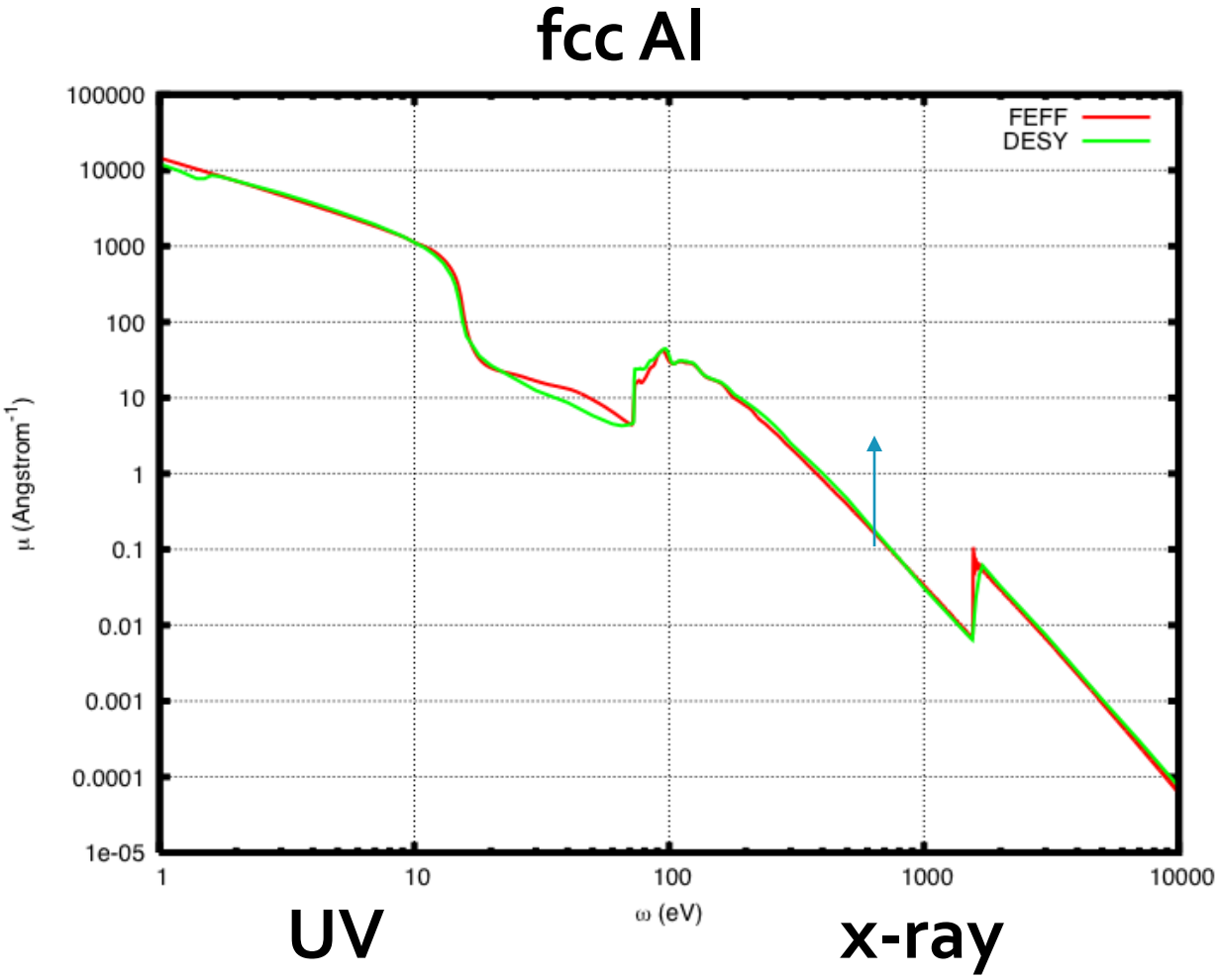
$$G = G_c + G_c T G_c + G_c T G^0 T G_c + G_c T G^0 T G^0 T G_c + \ldots$$

XANES

Full Multiple Scattering

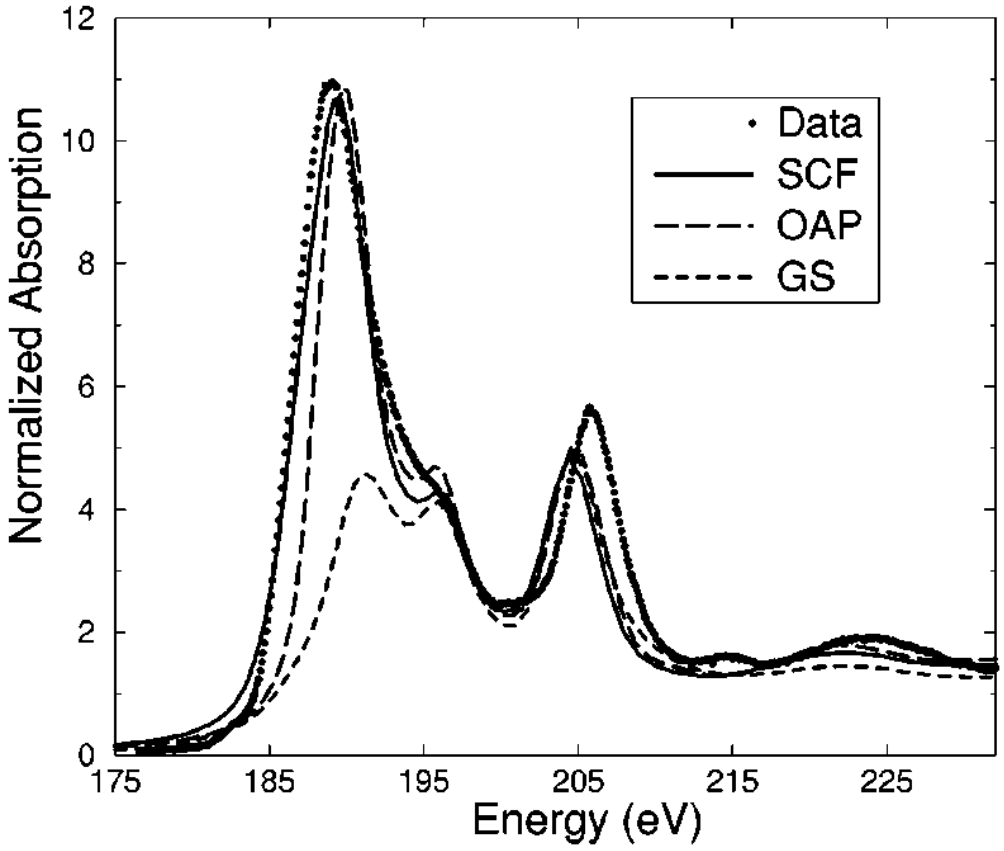
$$G = \left[1 - G^0 T\right]^{-1} G^0$$

Full spectrum: Expt. Vs Theory



Beyond DFT: Quasi-particle Self-Energy Effects

Quasi-particle (QP) effects: $G = [E - H - \Sigma]^{-1}$



BN 89 atom cluster

Ground state potential:

Usually insufficient

Need QP effects

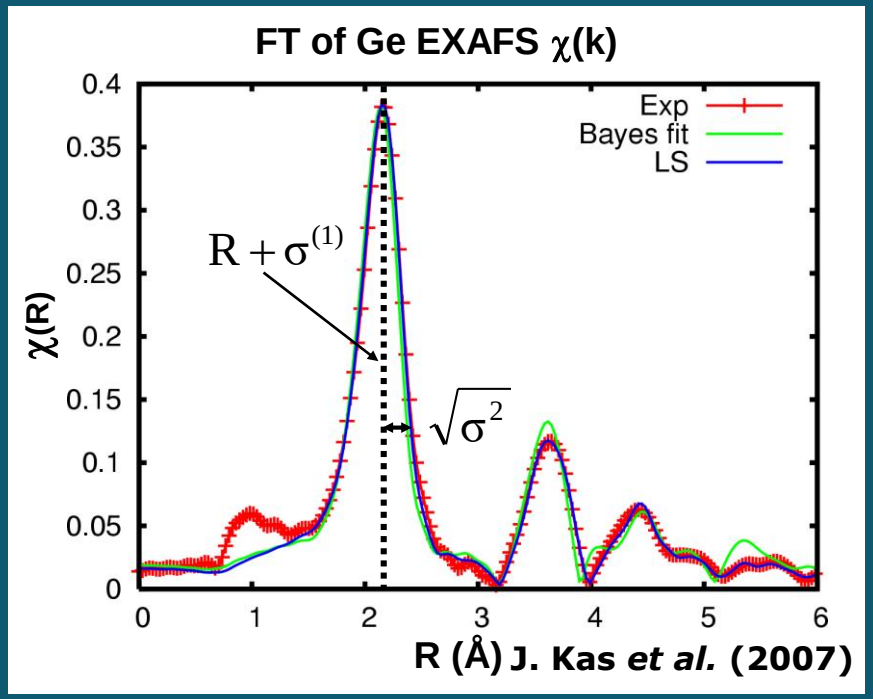
Debye-Waller Factors in EXAFS

Multiple Scattering Path XAFS DW Factor

Average commonly expressed in terms of the cumulant expansion

$$\left\langle e^{i2kr} \right\rangle \equiv e^{2ikR_0} e^{-W(T)}$$

$$W(T) = -\sum_{n=1}^{\infty} \frac{(2ik)^n}{n!} \sigma^{(n)}(T)$$



First cumulants

$$\begin{cases} \sigma^{(1)} = \langle r - R_0 \rangle \\ \sigma^{(2)} = \left\langle (r - \bar{r})^2 \right\rangle \equiv \sigma^2(T) \\ \sigma^{(3)} = \left\langle (r - \bar{r})^3 \right\rangle \end{cases}$$

DW factors from Phonon Green's Function

XAFS DW Factor for path R:

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

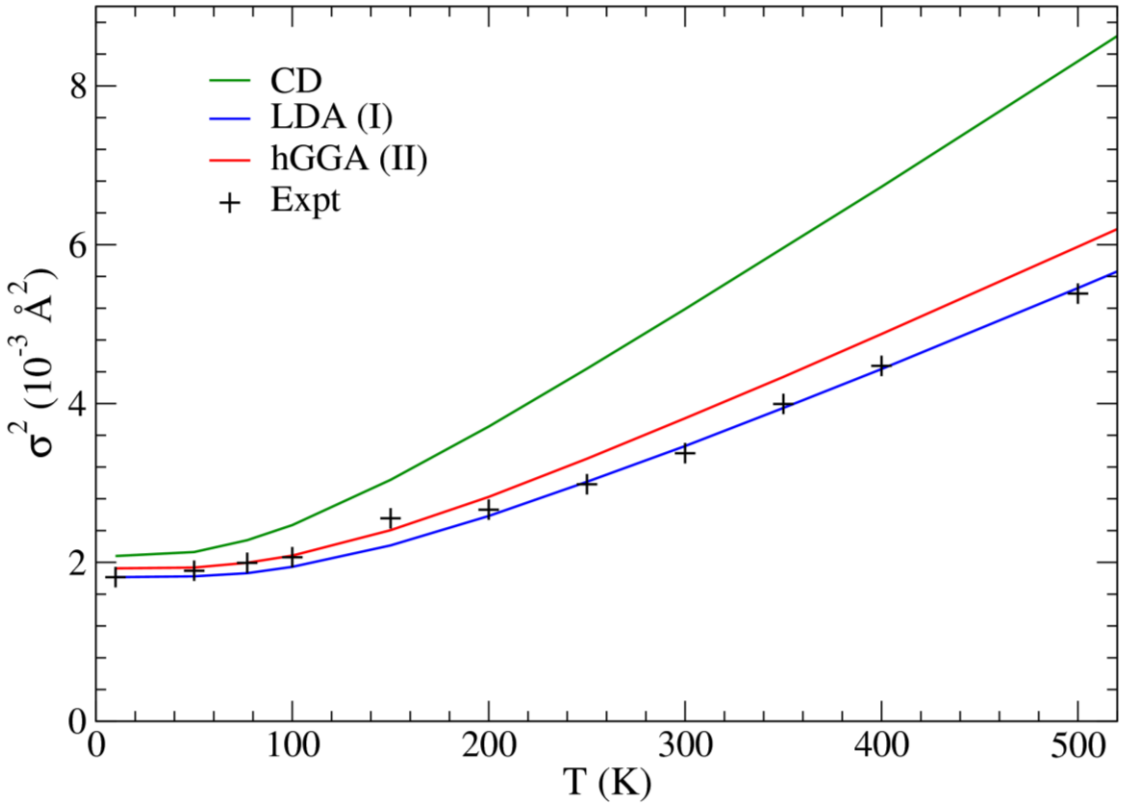
VDOS expressed as imaginary part of the phonon Green's function

$$\rho_R(\omega) = -\frac{2\omega}{\pi}\mathrm{Im}\left\langle 0\left|\frac{1}{\omega^2 - \mathbf{D} + i\varepsilon}\right|0\right\rangle$$

Seed state: Displacement along path

Dynamical Matrix: Calculated using ab initio methods (Abinit, Gaussian, VASP, NWChem, etc)

EXAFS near-neighbor DW Factor of Ge



CD (Correlated Debye):
Standard FEFF

LDA, hGGA:
Ab initio DW

Directional bonding:
Needs AIDW

Expt: Dalba et al. (1999)

Dynamic Structural Disorder In XANES

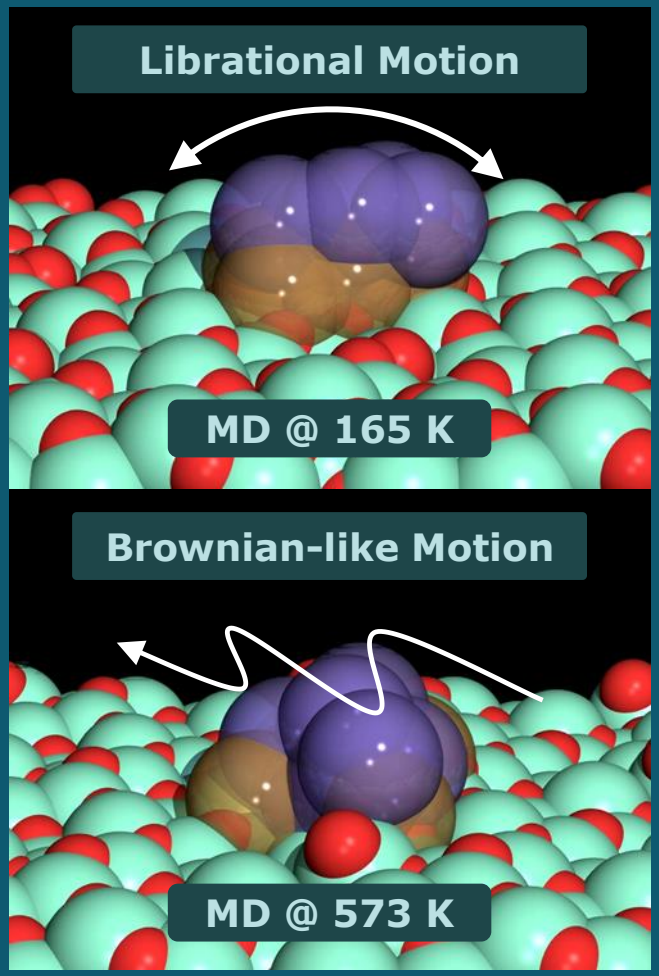
Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

F. D. Vila, J. J. Rehr, J. Kas, R. G. Nuzzo, A. I. Frenkel

Physical Review B **78**, 121404(R), 2008

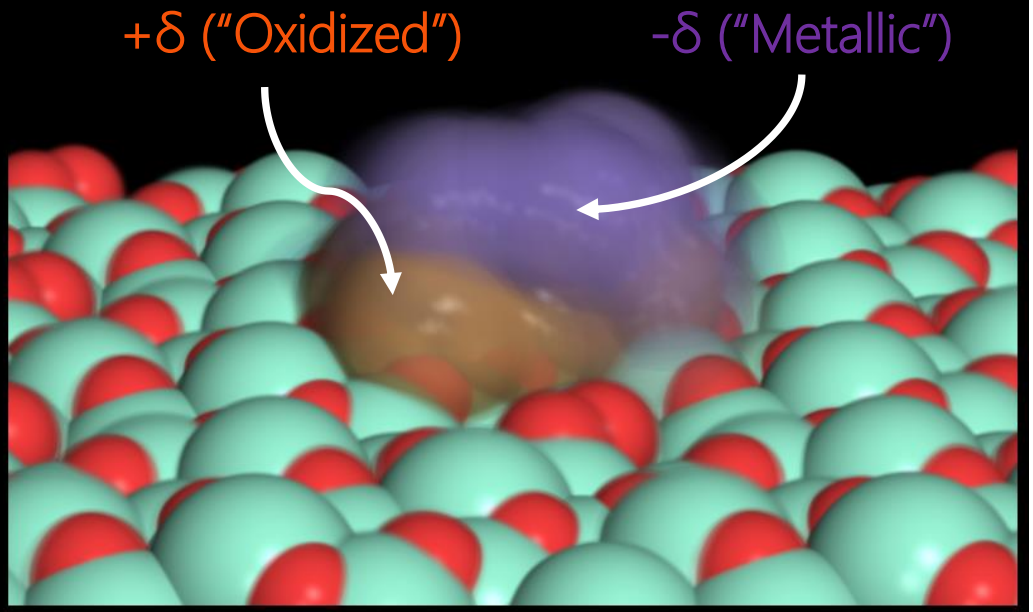
Complex dynamics:
multiple-time scales, librational motion, fluctuating bonding

Simulations explain:
large structural disorder, Negative Thermal Expansion (NTE).

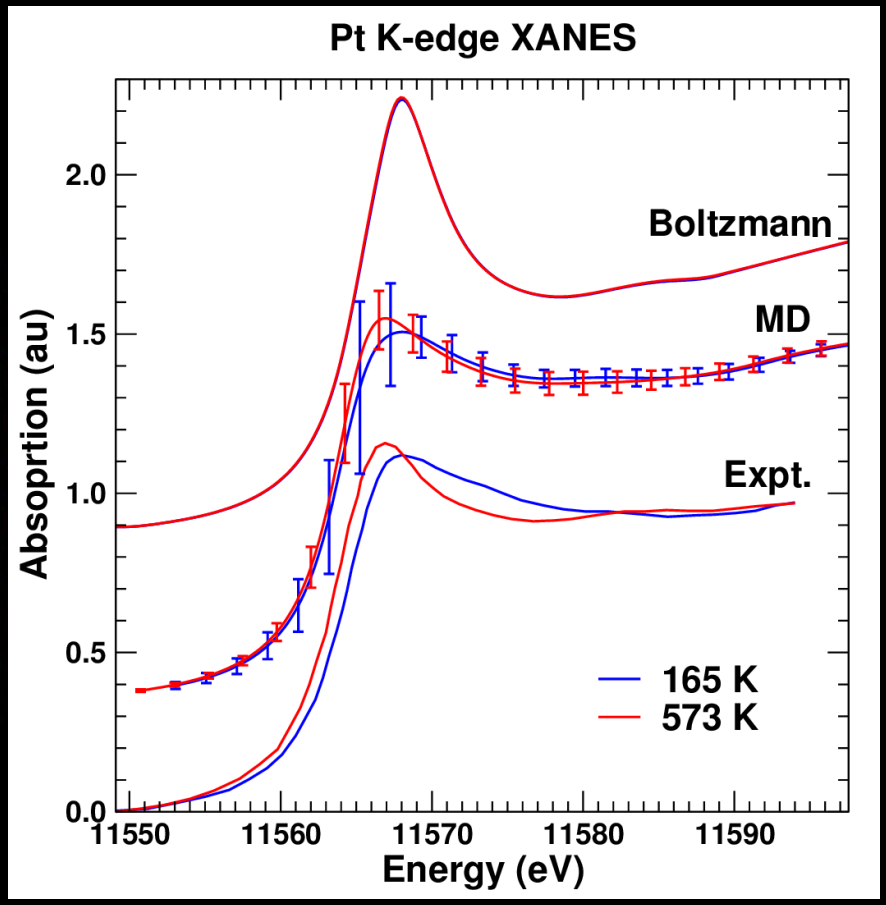


Pt_{10} on γ-Al_2O_3

Theory: Static Simulations are Inadequate



Pt_{10} on γ-Al_2O_3 @ 165 K



MD simulations reproduce experiment

Vila *et al.* Physical Review B **78**, 121404(R), 2008

Green's Functions and DFT/MD Approaches in X-Ray Excited States and Structural Disorder

Real-Time Approaches for Optical and Core Response

Finite Temperature Green's Functions

Real-Time TDDFT Advantages

Can be more efficient than frequency space (large systems)

Very versatile (pulses, transport, etc)

More “physical/realistic”

Easy access to NLO properties

Real-Time Time Dependent DFT

Direct numerical integration of the time-dependent Kohn-Sham equations in a time-dependent external electric field:

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

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

Optical properties are determined from the total dipole moment:

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

$$\chi^{(1)}_{ij}(\omega) = \delta p_i(\omega)/E_j(\omega) = \alpha_{ij}(\omega) \qquad \sigma(\omega) \sim \omega\,\mathbf{Im}\,\langle\alpha(\omega)\rangle$$

Linear Response

Absorption

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

Numerical Real-Time Evolution

The ground state density ρ_0, overlap matrix S and Hamiltonian matrix $H(t)$ evaluated at each time-step using SIESTA:

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

Orbital coefficients

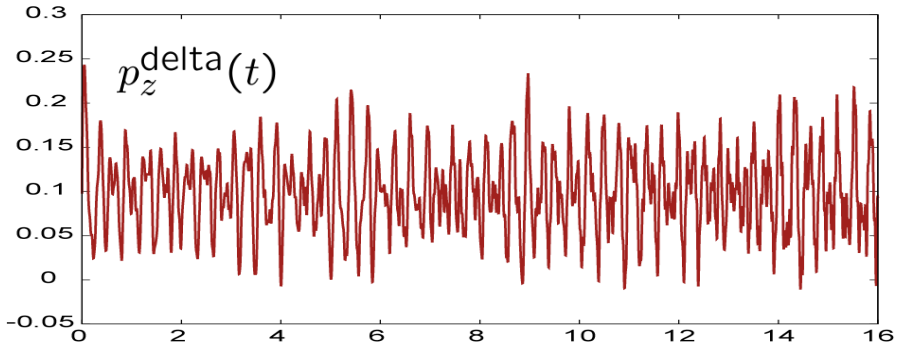
Accurate and stable evolution using Crank-Nicolson propagator:

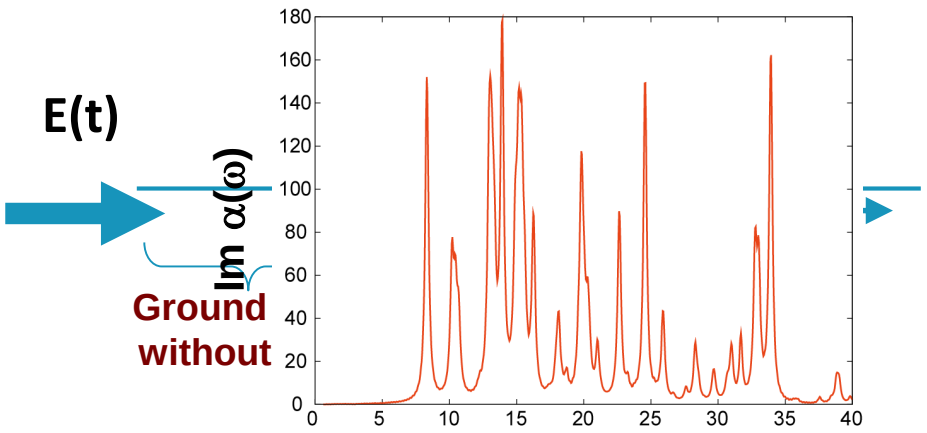
$$c(t+\Delta t) = \frac{1 - iS^{-1}H(\bar{t})\Delta t/2}{1 + iS^{-1}H(\bar{t})\Delta t/2}c(t) + \mathcal{O}(\Delta t^2)$$

Soler et al. J. Phys.: Condens. Matter 14, 2745 (2002)
Tsolakidis et al. Phys. Rev. B 66, 235416 (2002)

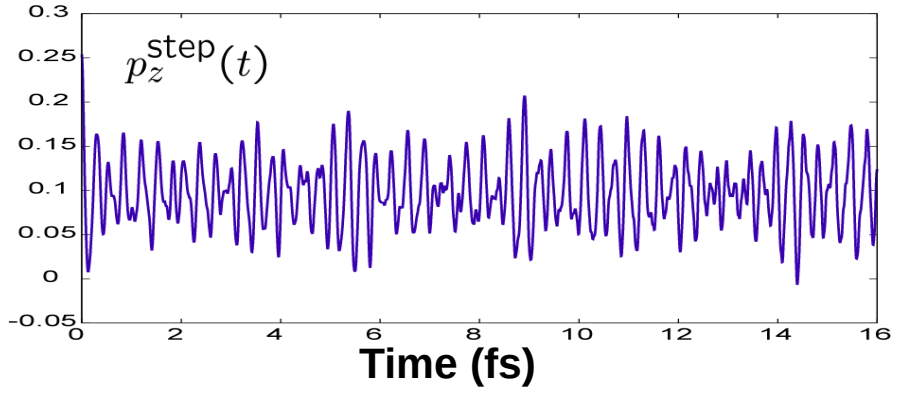
Optical Absorption in CO

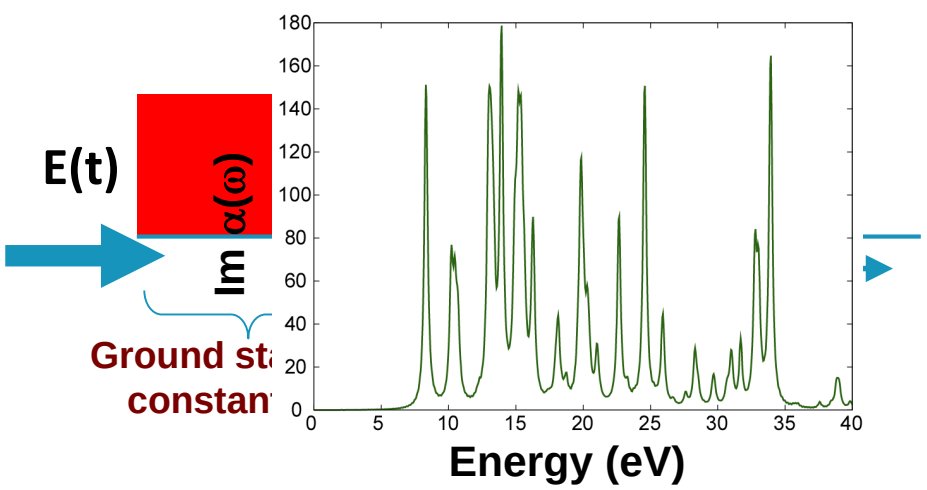
Delta Function (Unit Impulse at t=0)





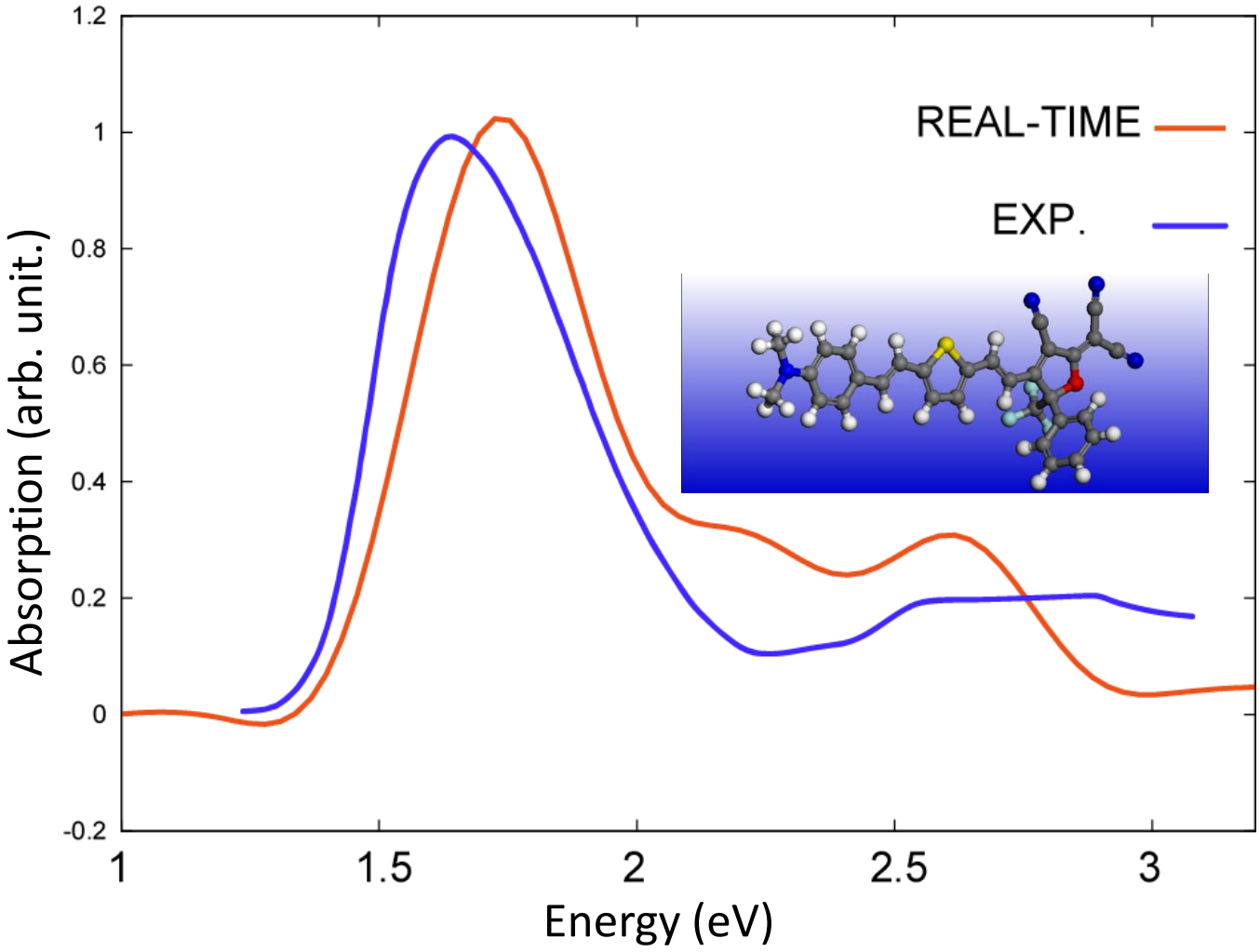
Step Function (Turn-off Constant E at t=0)





Takimoto et al. J. Chem. Phys. 127, 154114 (2007)

Linear Response: Chromophore YLD_156



Real-time (gas) absorption peak

ω_0 = 1.72 eV

(λ_0 = 721 nm)

Expt. ($CHCl_3$) absorption peak

ω_0 = 1.65 eV

(λ_0 = 753 nm)

Real time Nonlinear Response

Nonlinear expansion:

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

Must take into account response time:

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

How do we invert to get nonlinear response function?

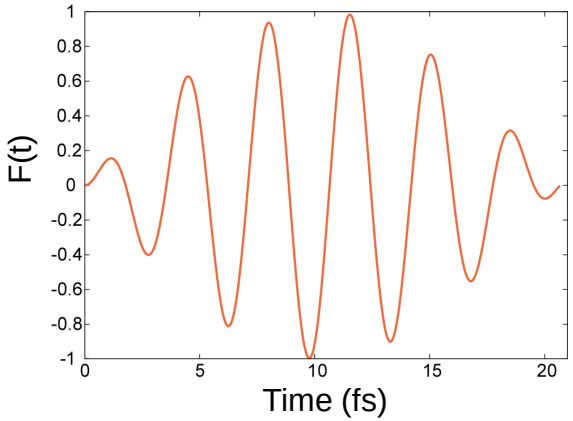
Dynamic NLO with Quasi-Monochromatic Field F_δ

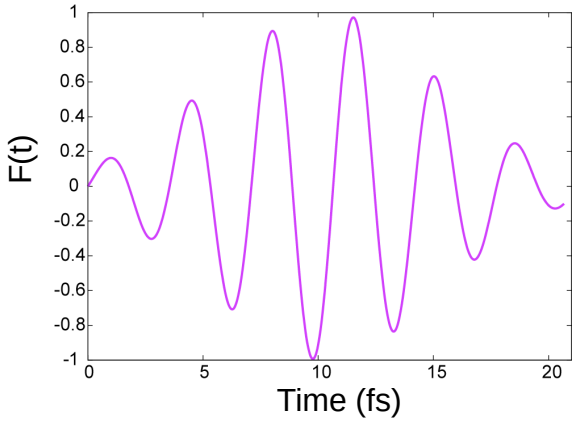
F_δ: Sine wave with sine or Gaussian envelope

$$F_\delta^{\text{sine}}(t) = \sin(\omega t)\sin(\omega_1 t)$$

$$F_\delta^{\text{gauss}}(t) = \sin(\omega t)\exp(-\frac{1}{2}(t-t_c)\delta)$$

$\omega = 1.17$ eV
$\omega_1 = 0.1$ eV

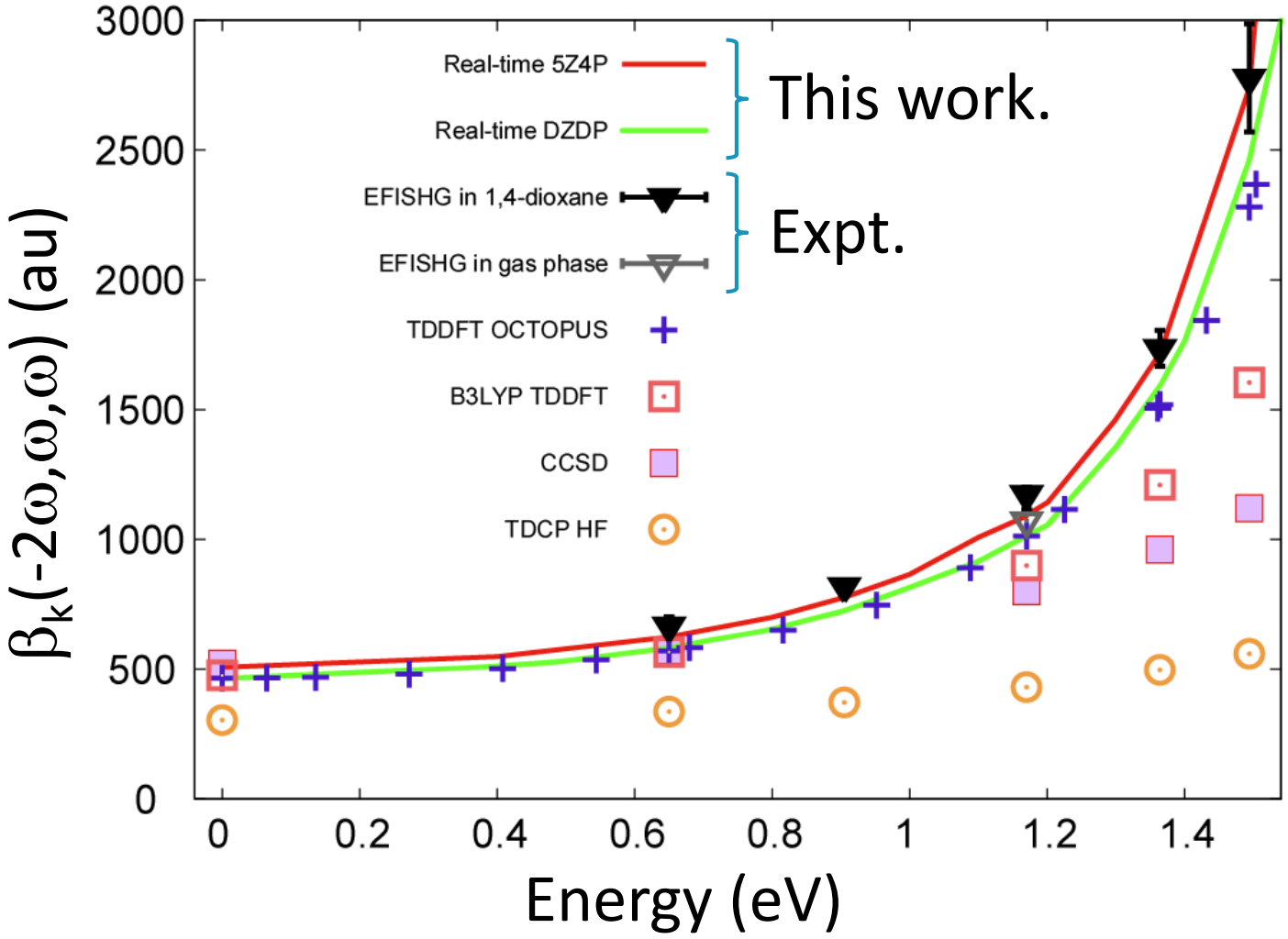


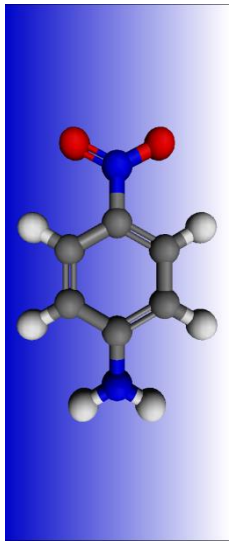


$$\chi^{(2)}_{ijk}(-2\omega_0;\omega_0,\omega_0) = \frac{2\pi p^{(2)}_{ijk}(2\omega_0)}{\int_{-\Delta}^{\Delta} d\omega' F(\omega_0-\omega')F(\omega_0+\omega')}$$ **SHG**

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

Second Harmonic Generation (SHG) in pNA





Real-Time X-Ray Spectroscopy (RTXS)

XAS Absorption (FGR, ΔSCF, FSR)

$$\mu(\omega) = \sum_k |\langle c|d|k\rangle|^2 \delta_\Gamma(\omega + \varepsilon_c - \varepsilon_k)\theta(E - E_F)$$

FT

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

Core Hole Green's Function

$$G_c(t) = i\exp[i(\varepsilon_c + i\Gamma)t]$$

Autocorrelation Function

$$\langle\psi(t)|\psi(0)\rangle = \sum_{jj'}\langle c|d^\dagger|j\rangle U_{jj'}(t,0)\langle\tilde{j}'|d|c\rangle$$

$$\langle\psi(0)|\psi(t)\rangle \begin{cases} |\psi(0)\rangle = d|c\rangle \\ |\psi(t)\rangle = U(t,0)|\psi(0)\rangle \end{cases} \rightarrow U(t,0) = T\exp\left[-i\int_0^t dt\, H(t)\right]$$

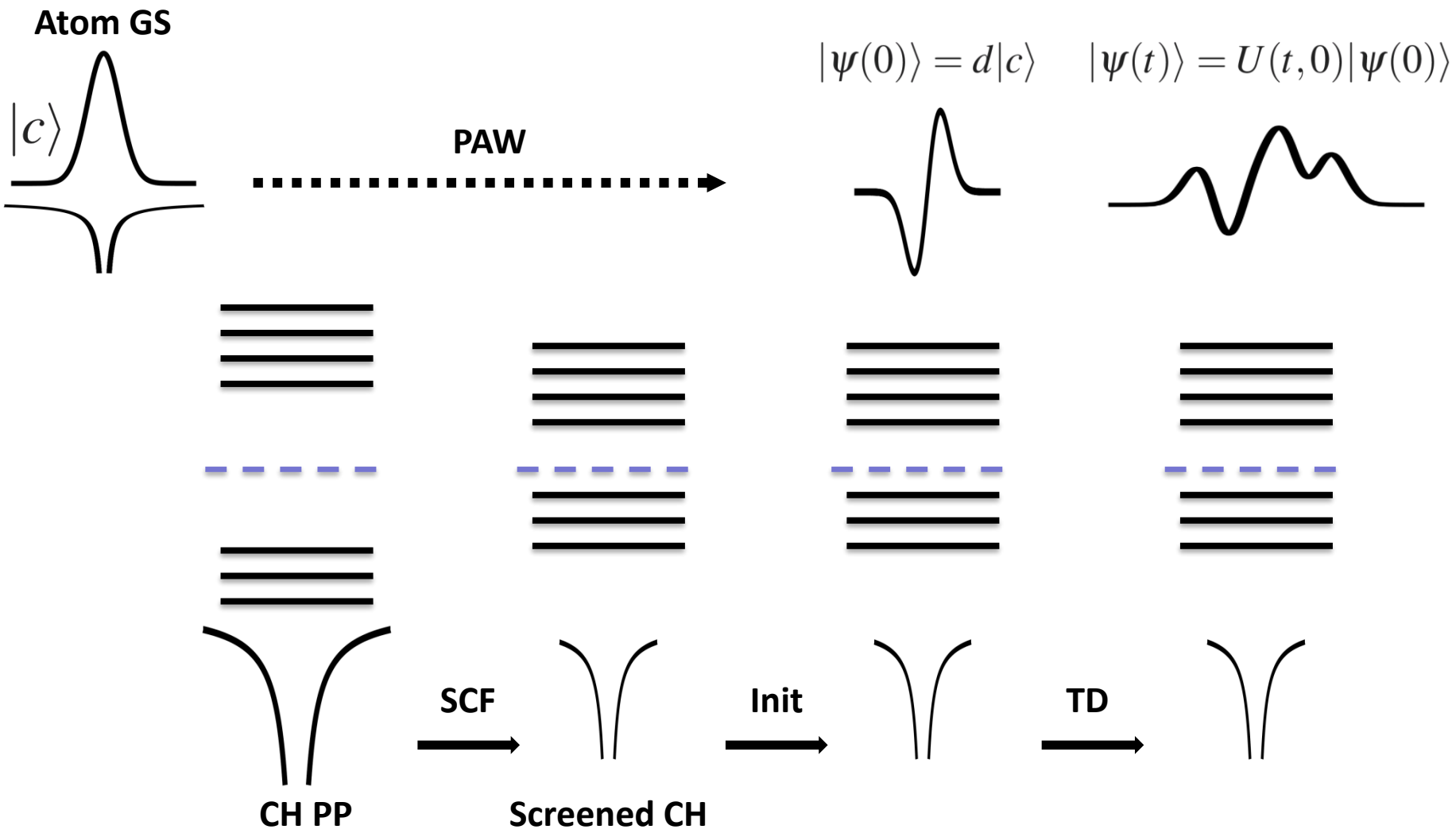
$$|\psi(t)\rangle = \sum_j |j\rangle c_j(t)$$

$$H_{jj'} = \langle j|h_H + v_{ch} + \Sigma|j'\rangle$$

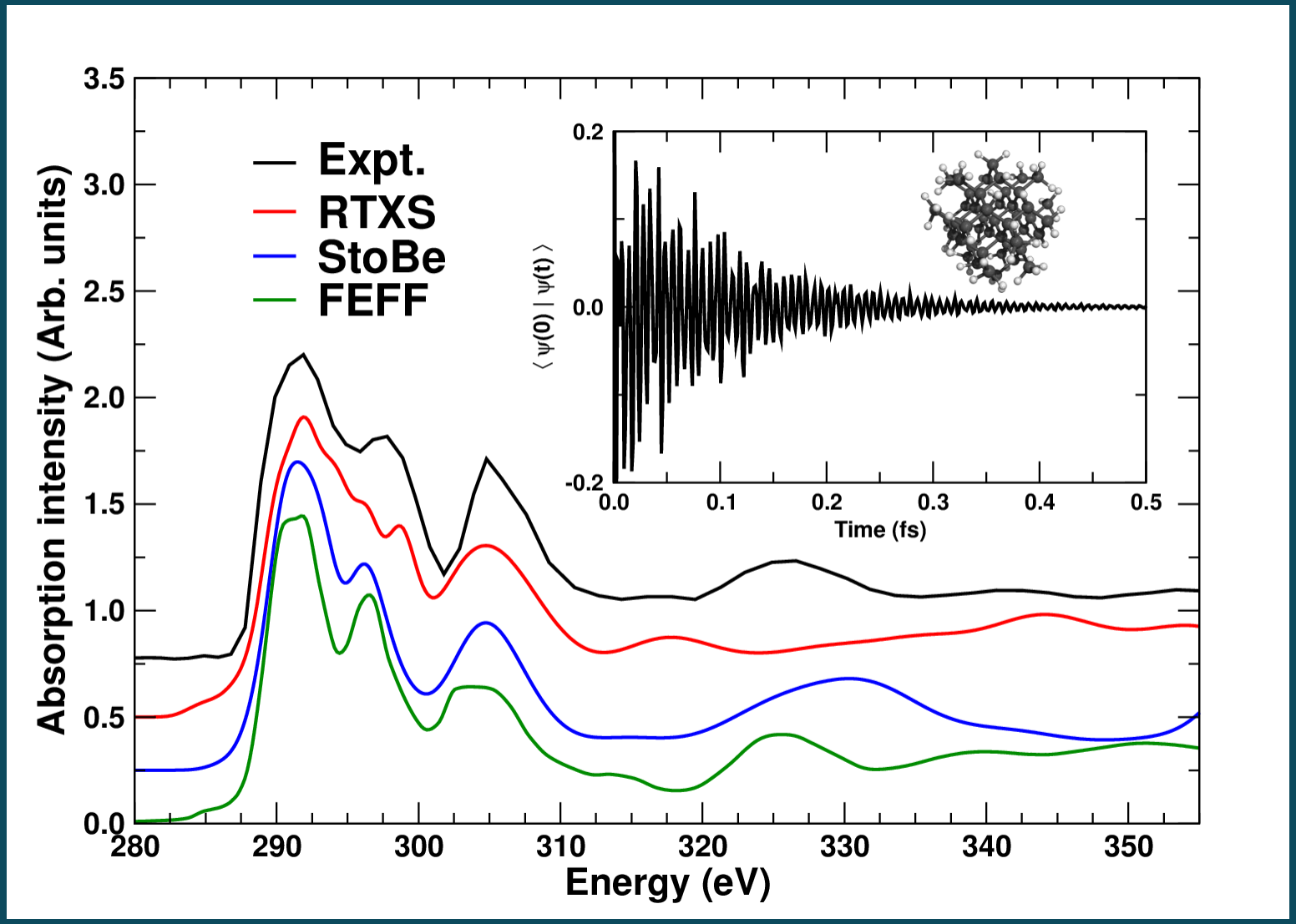
Crank-Nicolson

$$\bar{t} = t + \Delta/2 \qquad \mathbf{U}(t+\Delta,t) = \frac{\mathbf{1} - \mathbf{S}^{-1}\mathbf{H}(\bar{t})\Delta/2}{\mathbf{1} + \mathbf{S}^{-1}\mathbf{H}(\bar{t})\Delta/2}$$

RTXS in “Pictures”



C K-Edge XAS of Diamond ($C_{47}H_{60}$ cluster)



Expt: Fister et al., Phys. Rev. B 75, 174106 (2007)

Green's Functions and DFT/MD Approaches in X-Ray Excited States and Structural Disorder

Real-Time Approaches for Optical and Core Response

Finite Temperature Green's Functions

Green's Functions at Finite-T

Motivation:

For excited states & thermodynamics at finite-T and extreme conditions (WDM, $T \sim T_F$) we need methods beyond 0 K DFT

Starting point: Sum-rules for energy and density

$$E(T)/N = \sum_k \int d\omega \, [\omega + \varepsilon_k] \, A_k(\omega) f(\omega) \qquad n = \frac{1}{V} \sum_k \int d\omega \, A_k(\omega) f(\omega)$$

Key ingredient: Spectral function from Green's function

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

J. J. Kas and J. J. Rehr Phys. Rev. Lett. 109, 176403 (2017)

Which Green's Function? *GW* vs Cumulant

GW

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

$$\Sigma^{GW} = iGW \qquad W = \varepsilon^{-1} v$$

No vertex: $\Gamma = 1$

Cumulant*

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

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

Implicit vertex

We choose the cumulant *G*: Better than *GW*

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

Finite T Cumulant Green's Function

Similar to T=0 [1] with implicit temperature dependence [2]

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

Retarded Green's function
Matsubara formalism

Natural separation into independent particle and correlation parts

$$\tilde{C}_k(t) = \int d\omega \frac{\gamma_k(\omega)}{\omega^2}(e^{-i\omega t} + i\omega t - 1) \qquad \gamma_k(\omega) = \frac{1}{\pi}\left|\mathrm{Im}\,\Sigma_k(\omega + \varepsilon_k)\right|.$$

FT Cumulant

[1] Kas et al., Phys. Rev. B 90, 085112 (2014)

[2] Kas el al., Phys. Rev. Lett. 109, 176403 (2017)

Thermodynamics from *G*

Thermodynamics of the homogeneous electron gas from the cumulant Green's function approach

T. Blanton, J. J. Kas, and J. J. Rehr
Dept. of Physics, Univ. of Washington Seattle, WA 98195
(Dated: January 5, 2018)

UW Preprint Jan 2018

Chemical potential $\mu(n,T)$: solution of $n(\mu,T) = n$

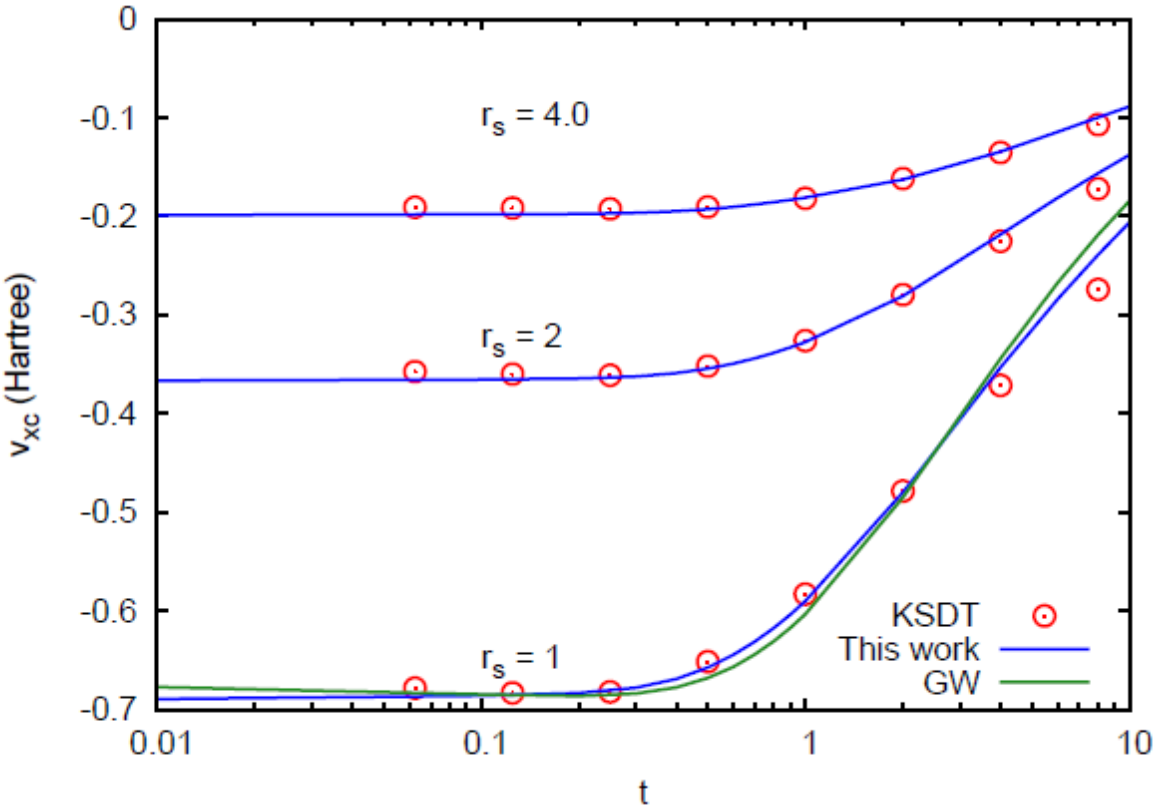
$$n = \frac{1}{V}\sum_k \int d\omega\, A_k(\omega) f(\omega) \qquad f(\omega) = \frac{1}{e^{\beta(\omega-\mu)}+1}$$

Can always separate into independent particle + xc parts:

$$\mu(n,T) = \mu_0(n,T) + \mu^{xc}(n,T)$$

Exchange-Correlation Potential

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



Good agreement with finite T DFT functionals

KSDT: VV Karasiev, T Sjostrom, J Duffy and SB Trickey, Phys. Rev. Lett. 112, 076403 (2014)

Summary

Green's Functions:

Provide an efficient and versatile approach to:

- X-Ray Excited States
- Structural Disorder
- Finite Temperature Effects

Real-Time Approaches:

RT-TDDFT:

- Alternative to frequency-space simulations
- Fast implementation, highly adaptable
- Both linear and non-linear response
- Access to core response

DFT/MD:

- Crucial for systems with dynamic disorder/bond breaking

Real-time and finite temperature Green's function approaches for excited states, response functions, and thermodynamics

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