Niri Govind, Pacific Northwest National Laboratory

Real-Time (RT) TDDFT

Real-time TDDFT in a Nutshell

$$i\frac{\partial P'}{\partial t} = [F'(t), P'(t)]$$

Ground state P

Time-dependent observables

$\mu(t) = \text{Tr}[P(t)D]$ Dipole moment

$n_k(t) = C_k^\dagger P'(t) C_k$ Occupation of kth MO

$\rho(r,t) = \sum_p P_{pq}\phi_p(r)\phi_q^*(r)$ Charge density

$F[P(t)]$ Build Fock matrix in AO basis — Rate limiting step

$F(t) \to F'(t)$ Switch basis

Propagate density matrix in MO basis

F Fock matrix (AO basis)
F' Fock matrix (MO basis)
$P(t)$ Density matrix (AO basis)
$P'(t)$ Density matrix (MO basis)
C_k k^{th} eigenvector of F'
$\{\phi\}$ Atomic orbitals

Sophisticated propagators allow for larger time steps

Frequency domain data — Fourier transform — Linear or nonlinear absorption spectrum

Multi-component excitation

Time+space domain data — Real-time real-space visualization of charge density

Resonant excitation

- Full response beyond perturbation limit
- Real-time, real-space → full dynamical information
- Insight into ultrafast and nonlinear processes
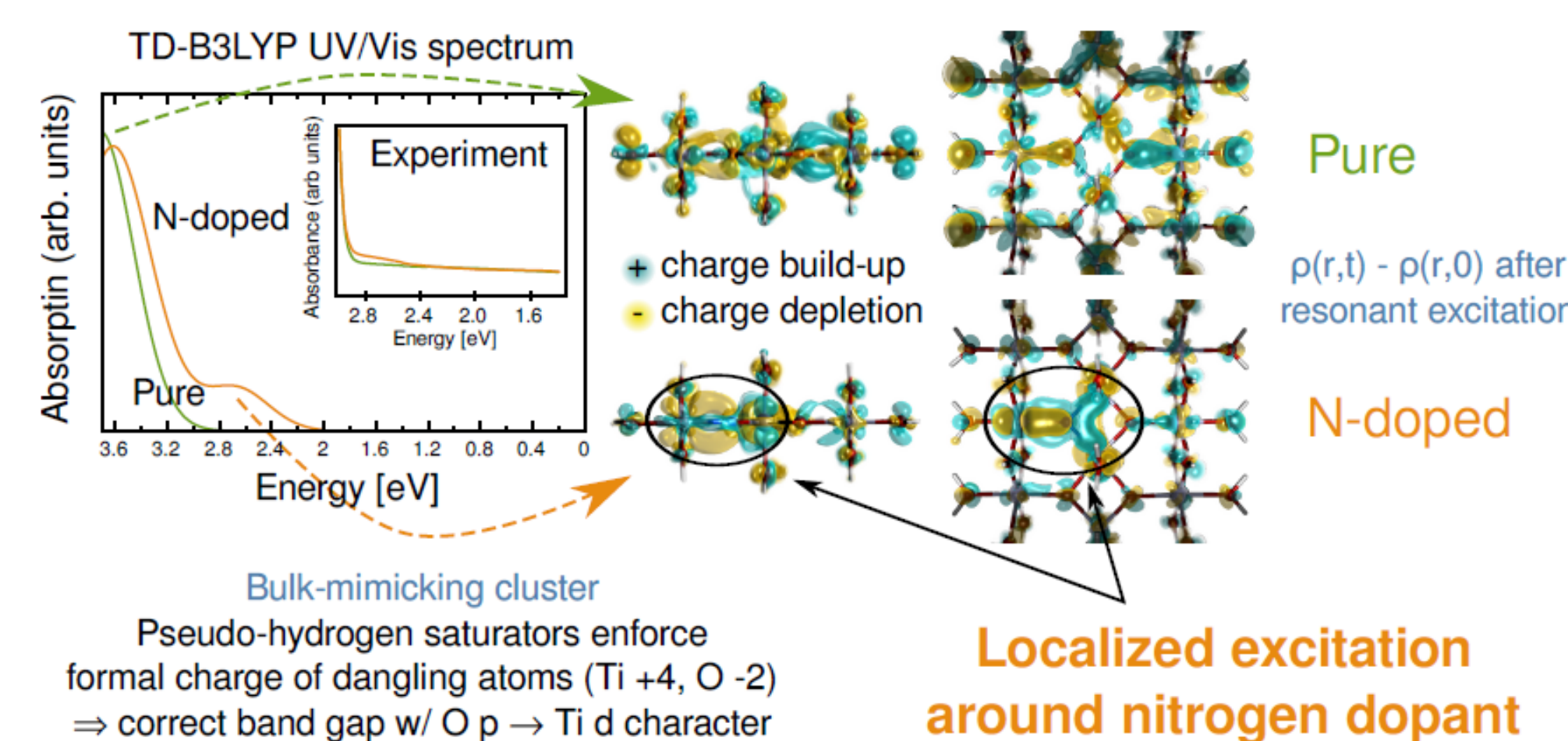- High harmonic generation
- Valence and core excitations

Charge transfer excitation in adenine-thymine base pair

14.2 fs   14.3 fs   14.4 fs

Resonant excitation of zinc porphyrin

0.8 fs   2.5 fs   3.0 fs
9.7 fs   10.0 fs   10.3 fs
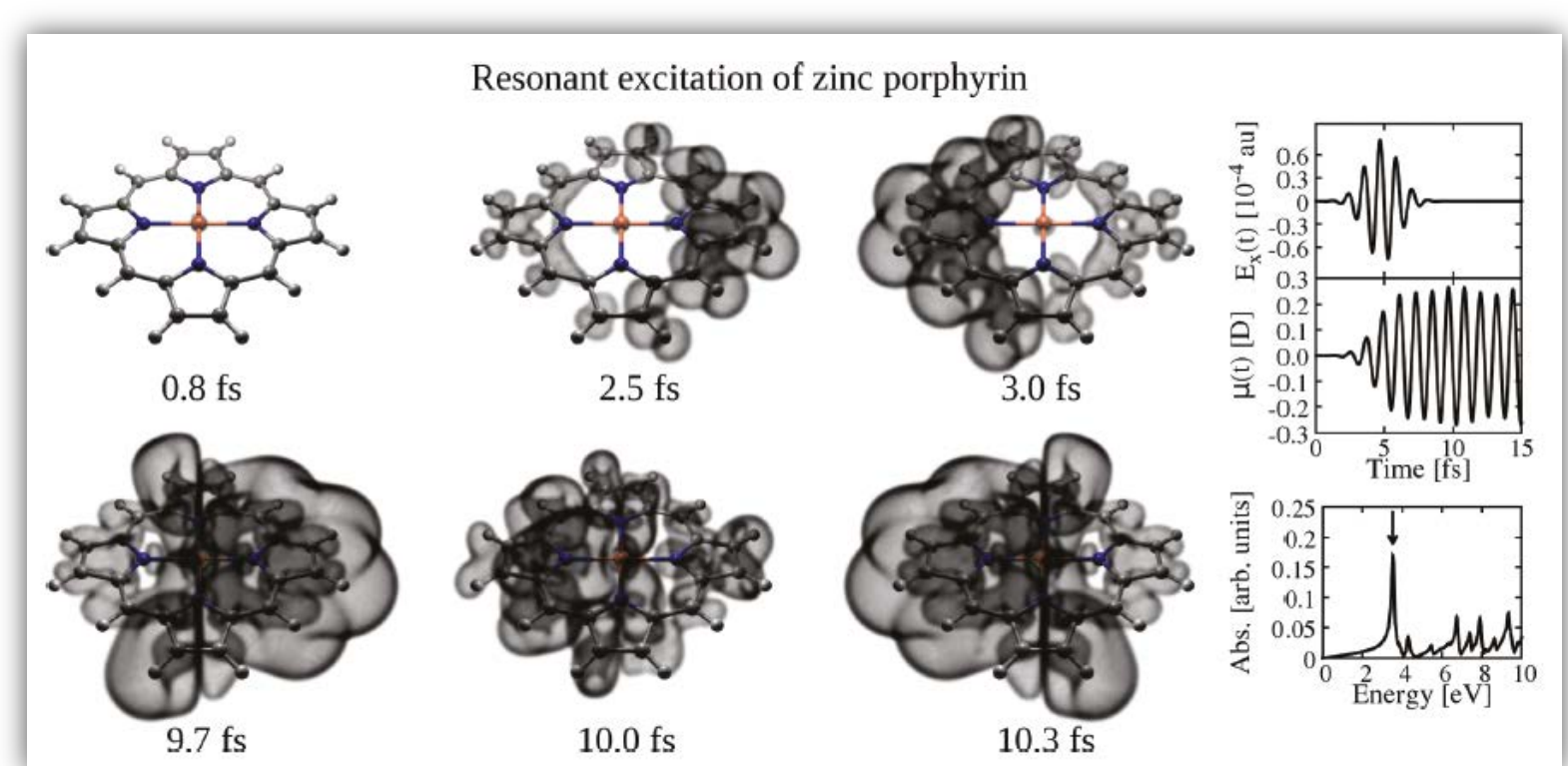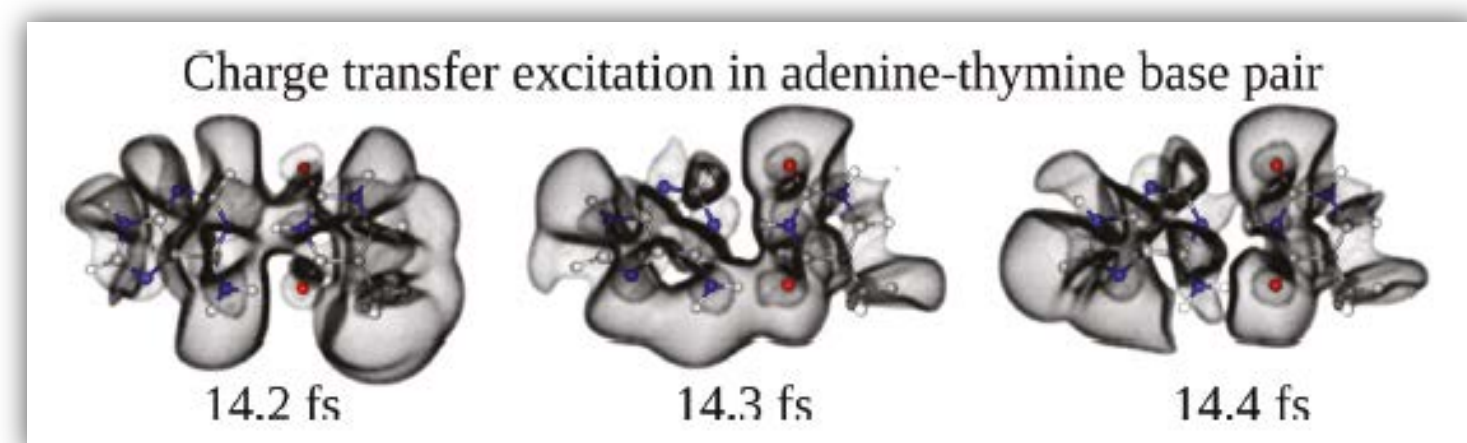
- Fully compatible with all XC functionals in NWChem
- **Optimized version released in NWChem 6.3 (May 2013)**
- Gradients in development

Optical Excitations in Doped Metal Oxides

- ► Band gap engineering: Drive absorption into the visible
  - Light harvesting, photocatalysis, etc
  - Doping, solid solutions, etc
  - Inexpensive, abundant, environmentally friendly materials

- ► Computing **optical** (excited state) properties with TDDFT?
  - Bulk-mimicking finite clusters
  - Embedding with capping atoms and electrostatic potentials
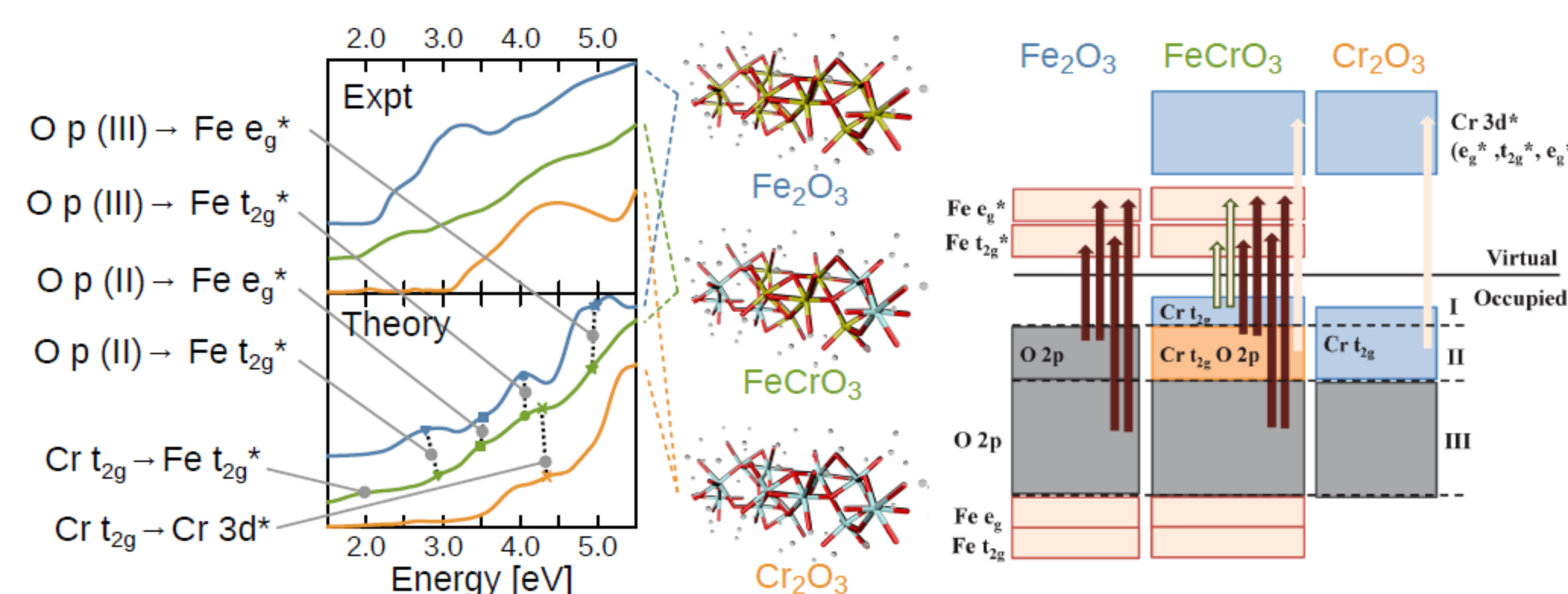 - Band-like: many 1000's of roots

N-doped TiO_2 Rutile

TD-B3LYP UV/Vis spectrum

Pure

N-doped

Experiment

$\rho(r,t) - \rho(r,0)$ after resonant excitation
- charge build-up
- charge depletion

Pure

N-doped

Bulk-mimicking cluster
Pseudo-hydrogen saturators enforce formal charge of dangling atoms (Ti +4, O -2) ⇒ correct band gap w/ O p → Ti d character

Localized excitation around nitrogen dopant

- ► Red-shifting of rutile bulk absorption on nitrogen doping
- ► Bulk-mimicking (E_g = 3.0 eV) cluster
- ► Resonant excitation: study dopant band

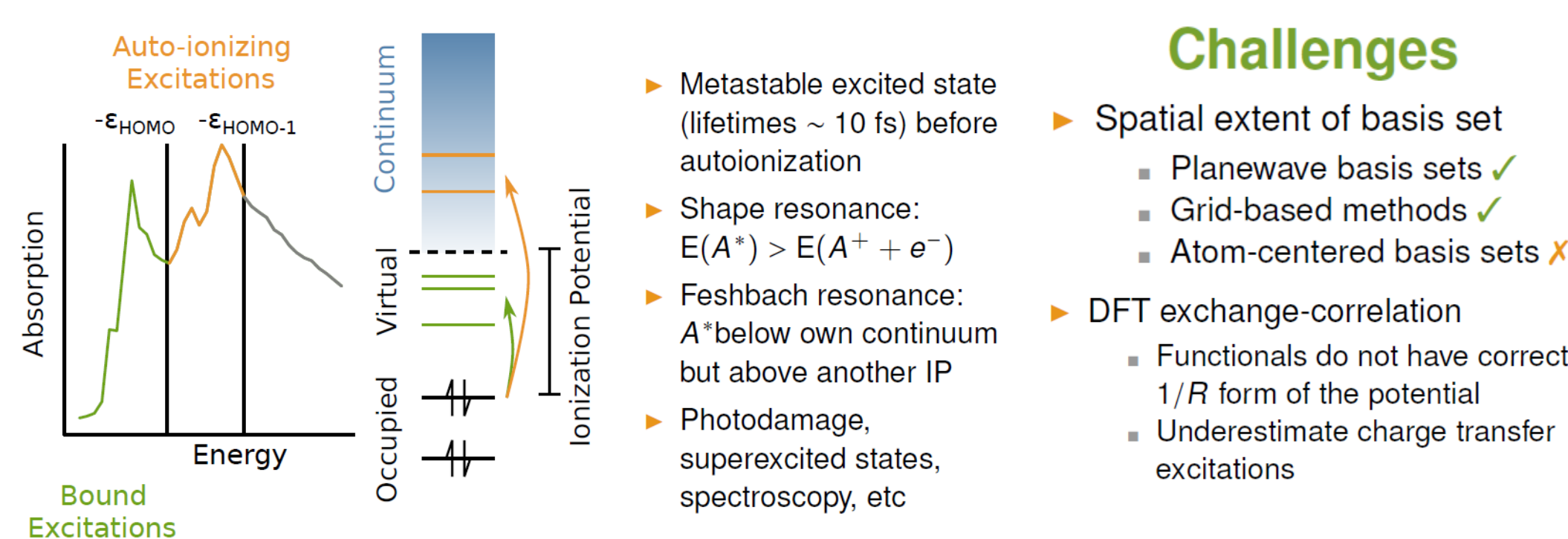### $(Fe_{1-x}Cr_x)_2O_3$ Solid Solutions

- ► Finite QM cluster embedded in classical background
  - Point charge (non-polarizable) background
  - Electrostatic potential ≃ potential of infinite periodic lattice
  - ∼ 100 atoms, ∼ 700 e^-, ∼ 1200 basis functions, open shell
- ► Linear-response (frequency domain) TDDFT
  - Spectrum spanning $0-5$ eV: ∼ 5000 roots (!!!)
  - Painstaking "windowing" procedure
- ► Real-time TDDFT
  - Three simulations (x, y, z) per cluster

O p (III) → Fe e_g^*
O p (III) → Fe t_{2g}^*
O p (II) → Fe e_g^*
O p (II) → Fe t_{2g}^*
Cr t_{2g} → Fe t_{2g}^*
Cr t_{2g} → Cr 3d*

Expt

Theory

Fe_2O_3 $FeCrO_3$ Cr_2O_3

- ► Optical band gap in $FeCrO_3$ (∼ 2 eV): Cr t_{2g} → Fe t_{2g}^*

J. Phys: Condensed Matter (Fast Track Communication) submitted (July 2013)
J. Phys. Chem. C submitted (July 2013)

Modeling Above Ionization Excitations

Auto-ionizing Excitations

Bound Excitations

Challenges

- ► Metastable excited state (lifetimes ∼ 10 fs) before autoionization
  - Shape resonance: $E(A^*) > E(A^+ + e^-)$
  - Feshbach resonance: A^* below own continuum but above another IP
  - Photodamage, superexcited states, spectroscopy, etc

- ► Spatial extent of basis set
  - Planewave basis sets ✓
  - Grid-based methods ✓
  - Atom-centered basis sets ✗
- ► DFT exchange-correlation
  - Functionals do not have correct $1/R$ form of the potential
 - Underestimate charge transfer excitations

- ► **Range-separated functionals**: Fix incorrect DFT exchange-correlation asymptote by spliting exchange into short (DFT) and long range (Hartree-Fock) terms

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\gamma r_{12})}{r_{12}} + \frac{\text{erf}(\gamma r_{12})}{r_{12}}$$

- ► But how to pick γ? E.g., Want: enforce Koopmans'
- ► Tune γ to minimize object function:

$$J(\gamma) = |IP_{SCF}(\gamma) - IP_{Koopmans}(\gamma)|$$
$$= |E_{SCF}^{cation}(\gamma) - E_{SCF}^{neutral}(\gamma) + \epsilon_{HOMO}^{neutral}|$$

- ► "First principles" tuning (no inputs from experiment)
- ► Typically brings Koopmans' IP and SCF IP within ≤ 1%, and within ≤ 5% of experimental IP

$\gamma = 0.415\ a_0^{-1}$
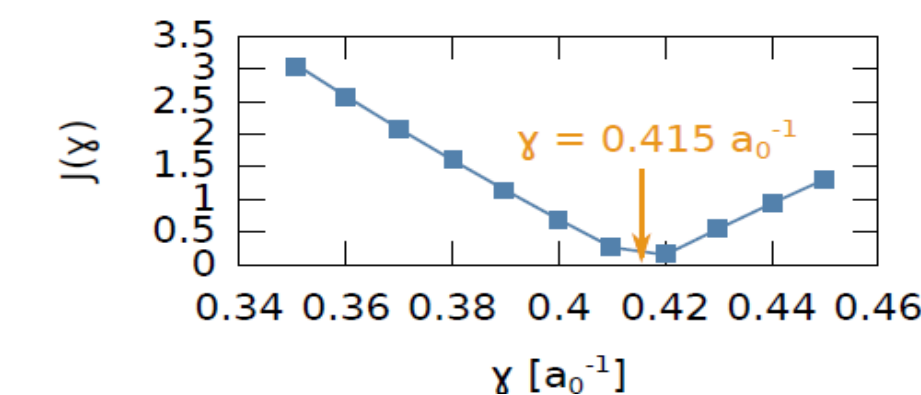
Imaginary Absorbing Potentials

$$|\psi_i(t)\rangle = \exp[iHt]|\psi_i(0)\rangle = \exp[iH_0 t - \Gamma t]|\psi_i(0)\rangle$$

- ► Natural for planewaves or grids ✓
- ► Atom-centered basis sets ✗

Molecular Orbital-Based Absorb. Potential

- ► Instead build Γ directly in the MO space:

$$D = \begin{pmatrix} \beta_1 & 0 & \cdots & 0 \\ 0 & \beta_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \beta_M \end{pmatrix}$$

- ► β_i: phenomenological damping parameter for the ith MO
- ► Project onto TD Fock matrix via TD eigenvectors $C'(t)$

$$\Gamma'(t) = C'(t) D C'^\dagger(t)$$

- ► Exponential damping acting on MO's in the continuum:

$$\beta_i = \begin{cases} 0, & \tilde{\epsilon}_i \leq 0 \\ \beta_0 [\exp(\xi \tilde{\epsilon}_i) - 1], & \tilde{\epsilon}_i > 0 \end{cases}$$

- ► $\tilde{\epsilon}_i = \epsilon_i - \epsilon_0$: energy of ith MO above vacuum cutoff energy ϵ_0
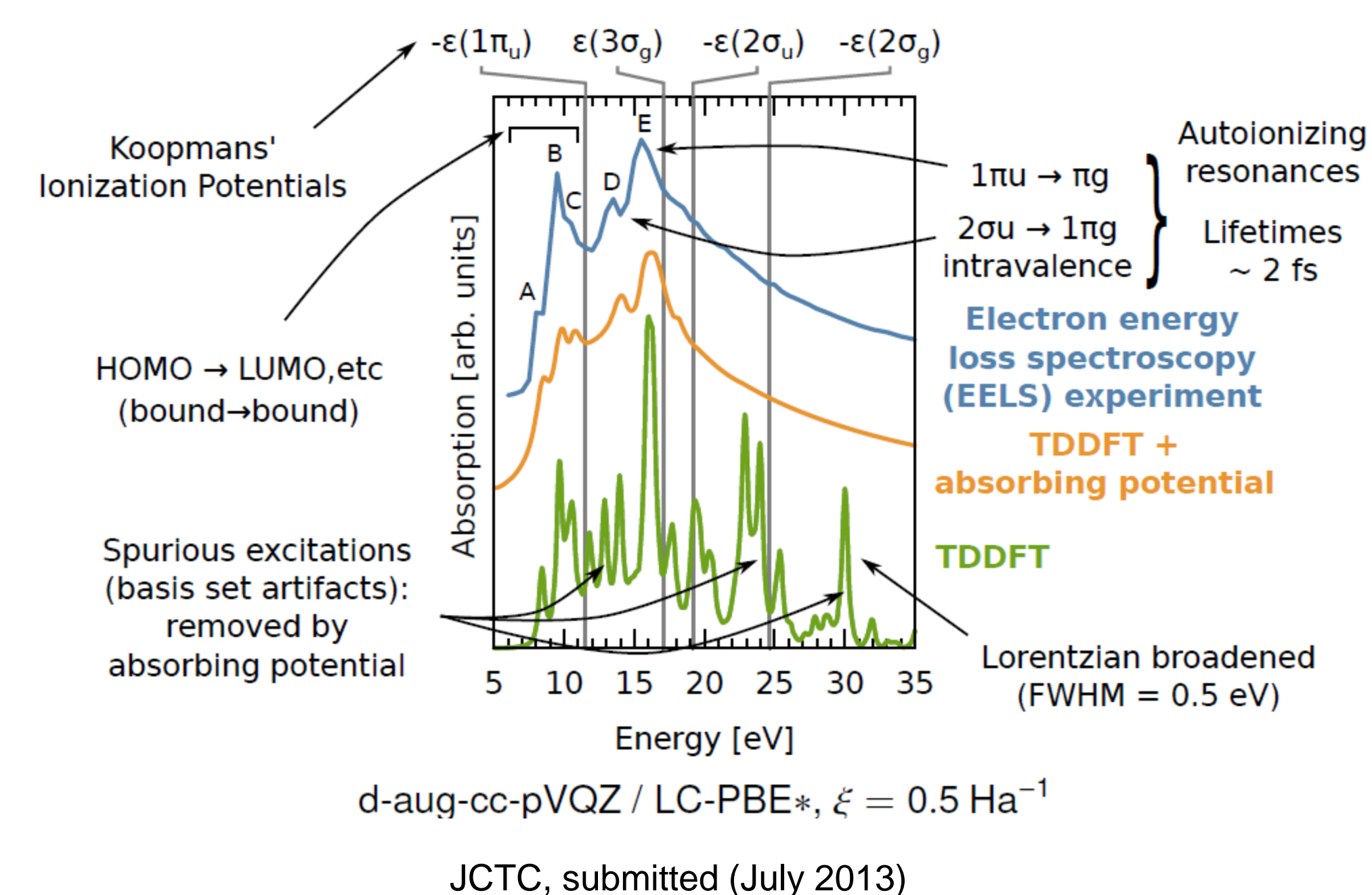 - Virtuals unreliable in DFT, so use "relaxed" orbitals (e.g., electron affinities)

$$EA_1 = E^{anion} - E^{neutral}$$
$$EA_k \simeq EA_1 + \nu_{k-1}, \quad k = 2, 3, \dots$$
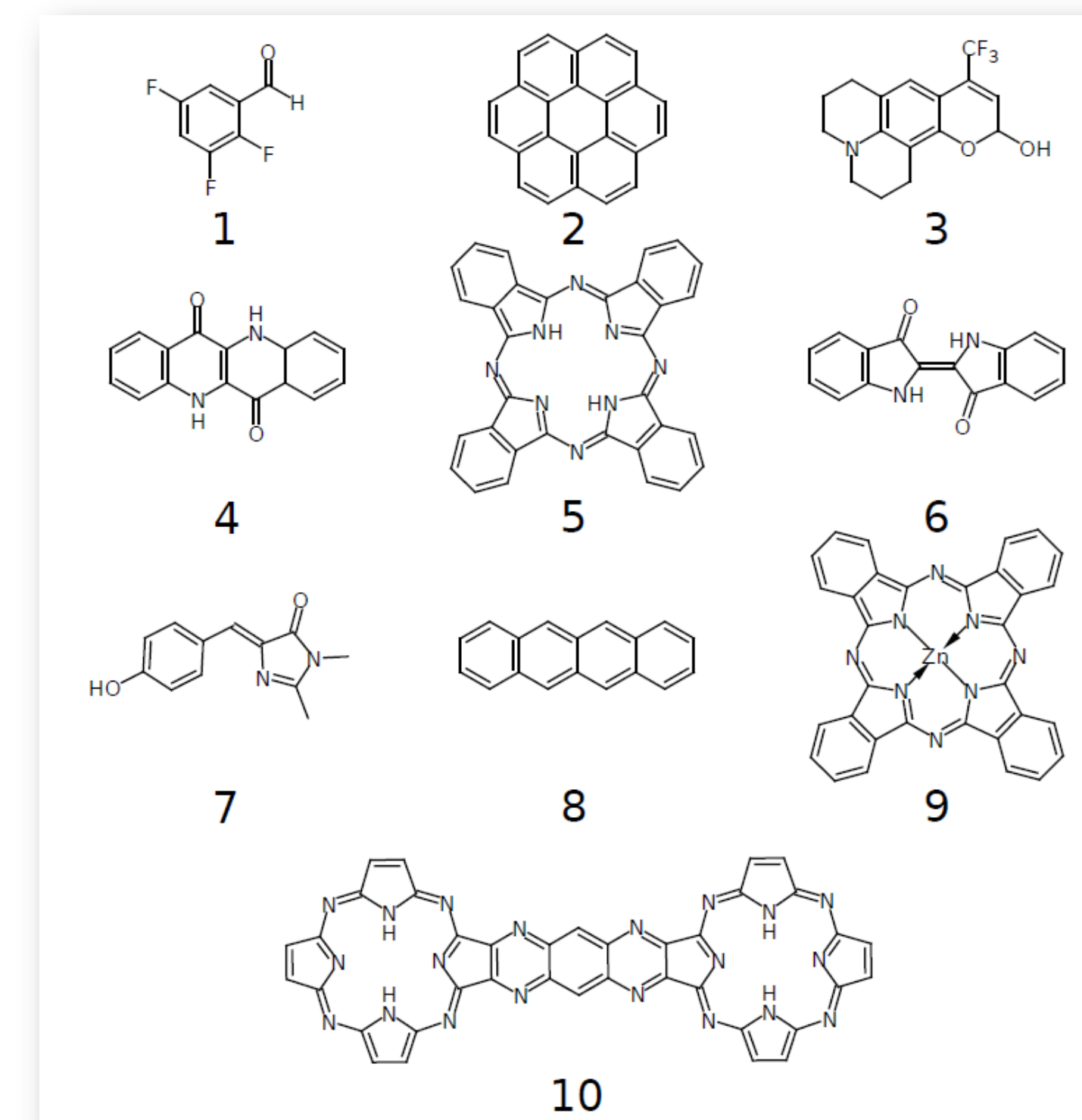
ν_k: k^{th} TDDFT excitation of the anion

- ► ξ: steepness of absorbing potential
  - E.g., if $\xi = 0.5$ Ha^{-1} a MO 1 eV above ϵ_0 would have a lifetime of 1.3 fs, and thus FWHM of ∼ 1 eV in the spectrum

Acetylene (C_2H_2) Extreme UV Absorption

Koopmans' Ionization Potentials

HOMO → LUMO, etc (bound→bound)

$1\pi_u \to \pi g$
$2\sigma_u \to 1\pi g$ intravalence

Autoionizing resonances Lifetimes ∼ 2 fs

Electron energy loss spectroscopy (EELS) experiment

TDDFT + absorbing potential

Spurious excitations (basis set artifacts): removed by absorbing potential

TDDFT

Lorentzian broadened (FWHM = 0.5 eV)

d-aug-cc-pVQZ / LC-PBE*, ξ = 0.5 Ha^{-1}

JCTC, submitted (July 2013)

Implementation of Analytic LR-TDDFT Gradients

Organic Dyes

1   2   3   4   5   6   7   8   9   10

| Dye | BLYP | | | LC-BLYP | | | B3LYP | | | CAM-B3LYP | | | Exp. |
	Abs.	Em.	S.S.	Abs.	Em.	S.S.	Abs.	Em.	S.S.	Abs.	Em.	S.S.	S.S.
1	3.09	2.12	0.97	3.72	3.04	0.68	3.55	2.72	0.83	3.79	3.07	0.72	0.86[a]
2	3.68	3.62	0.06	5.00	4.79	0.21	4.16	4.06	0.10	4.73	4.56	0.17	0.23[b]
3	2.84	2.16	0.68	4.00	3.54	0.46	3.36	2.85	0.51	3.85	3.48	0.37	0.44[c]
4	2.63	2.49	0.14	3.71	3.34	0.37	3.11	2.90	0.21	3.58	3.26	0.32	0.19[d]
5	1.94	1.87	0.07	1.97	1.77	0.20	2.09	2.01	0.08	2.08	1.94	0.14	0.02[e]
6	1.99	1.26	0.73	2.70	2.45	0.25	2.31	2.09	0.22	2.64	2.41	0.23	0.10[d]
7	3.16	(I)	–	3.97	3.31	0.66	3.54	2.93	0.61	3.88	3.29	0.59	0.68[f]
8	2.14	1.90	0.14	3.15	2.60	0.55	2.49	2.16	0.33	2.78	2.45	0.33	0.36[g]
9	1.94	1.89	0.05	1.96	1.83	0.13	2.09	2.02	0.07	2.07	1.97	0.10	0.02[e]
10	1.47	1.29	0.18	1.97	1.94	0.03	1.94	1.76	0.18	2.13	2.11	0.02	–
ME	0.07			0.08			0.01			0.02			
MAE	0.18			0.10			0.06			0.08			
RMSD	0.26			0.12			0.07			0.09			

JCTC, in preparation (2013)

Collaborators: K. Lopata, H. van Dam (PNNL), D. Silverstein, L. Jensen (PennState), D. Truhlar, C. Cramer (Minnesota), **Experiment:** Scott Chambers (PNNL)

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