EMSL

TDDFT

Daniel Mejia-Rodriguez,
Edoardo Aprà & Niri Govind

2023 CyberWorkshop

Time-Dependent DFT

Casida Formulation

Perturbed density → first-order correction

Linear response approach → frequency domain

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix}$$

$$1 = \left(X\middle|X\right) - \left(Y\middle|Y\right)$$

$$A_{ia,jb} = \delta_{ij}\delta_{ab}\left(\varepsilon_a - \varepsilon_i\right) + \left(ia\middle|F_H + F_{xc}\middle|jb\right)$$

$$B_{ia,jb} = \left(ia\middle|F_H + F_{xc}\middle|jb\right)$$

$$F_{xc}\left(r_1, r_2\right) = \frac{\partial^2 f}{\partial\rho\left(r_1\right)\partial\rho\left(r_2\right)}$$

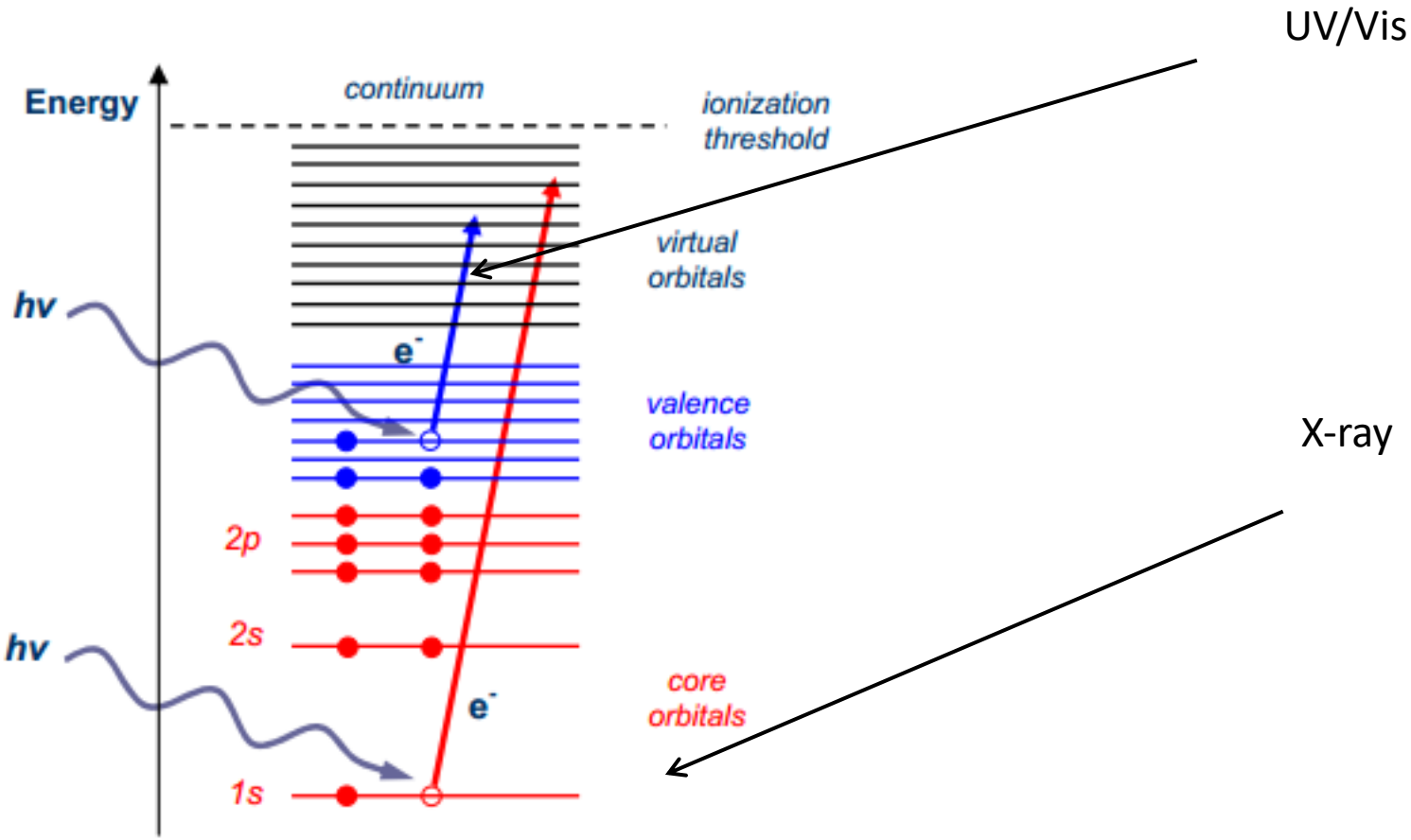
Cannot be used to describe excitations in intense fields

Time-Dependent Density Functional Theory, Marques et al, Springer 2006

Excited State Calculations with TDDFT

- Optical properties (UV/Vis)
- Pre- and near-edge X-ray absorption (XANES)
- TDDFT Gradients/Optimization

UV/Vis & X-ray Spectroscopy



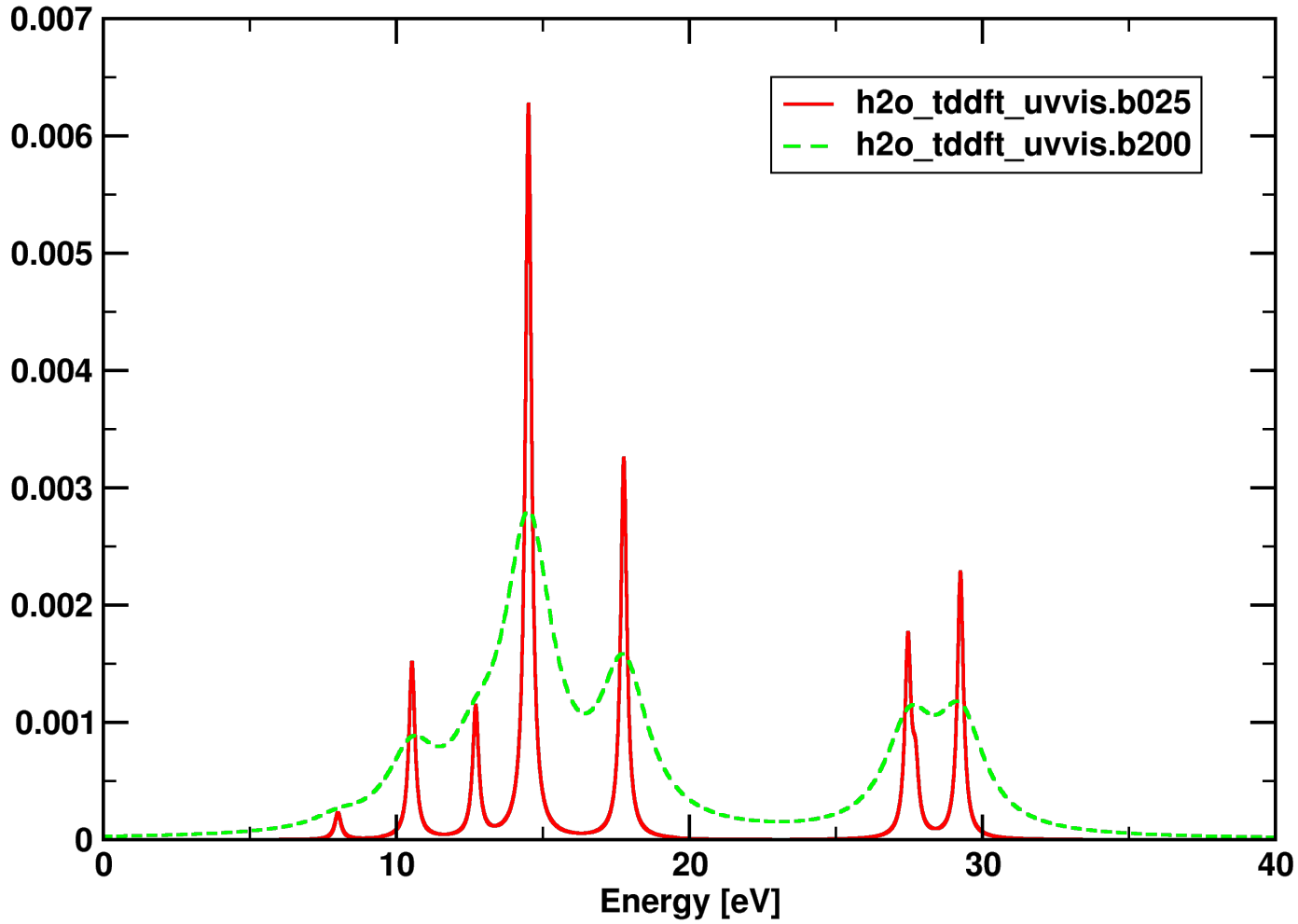
Basic UV/Vis Input

```
geometry
O      0.00000000     0.00000000      0.12982363
H      0.75933475     0.00000000     -0.46621158
H     -0.75933475     0.00000000     -0.46621158
end

basis
   O library 6-31G**
   H library 6-31G**
end

dft
  xc b3lyp
end

tddft
 nroots 10
end

task tddft energy
```

Sample UV/Vis Output

```
-----------------------------------------------------------------------
Root   1 singlet b2              0.294221368 a.u.                 8.0062 eV
-----------------------------------------------------------------------
   Transition Moments    X -0.00000   Y  0.26890   Z  0.00000
   Transition Moments   XX -0.00000  XY  0.00000  XZ  0.00000
   Transition Moments   YY -0.00000  YZ -0.08066  ZZ -0.00000
   Dipole Oscillator Strength                     0.0141833591
   Electric Quadrupole                            0.0000000009
   Magnetic Dipole                                0.0000001219
   Total Oscillator Strength                      0.0141834819

   Occ.    5  b2  ---  Virt.    6  a1   1.00002 X
-----------------------------------------------------------------------
Root   2 singlet a2              0.369097480 a.u.                10.0437 eV
-----------------------------------------------------------------------
   Transition Moments    X -0.00000   Y  0.00000   Z -0.00000
   Transition Moments   XX -0.00000  XY  0.24936  XZ  0.00000
   Transition Moments   YY  0.00000  YZ -0.00000  ZZ -0.00000
   Dipole Oscillator Strength                     0.0000000000
   Electric Quadrupole                            0.0000000166
   Magnetic Dipole                                0.0000003348
   Total Oscillator Strength                      0.0000003515

   Occ.    5  b2  ---  Virt.    7  b1  -0.99936 X
-----------------------------------------------------------------------
Root   3 singlet a1              0.387064731 a.u.                10.5326 eV
-----------------------------------------------------------------------
   Transition Moments    X -0.00000   Y -0.00000   Z  0.60463
   Transition Moments   XX -0.62351  XY  0.00000  XZ  0.00000
```

UV/Vis Spectrum (different broadenings)




```
python3 nw_spectrum.py -b0.25 -p5000 < h2o_tddft_uvvis.out>h2o_tddft_uvvis.data.b025
python3 nw_spectrum.py -b2.00 -p5000 < h2o_tddft_uvvis.out>h2o_tddft_uvvis.data.b200
```

Basic XANES Input

```
geometry units angstrom noautosym nocenter
 O 0        0         0
 C 0        0.00      1.15
end
basis
  * library aug-cc-pvtz
end
dft
  xc b3lyp
end
task dft optimize
dft
  xc beckehandh
end
tddft
  cis
  ecut -15
  nroots 30
  notriplet
  thresh 1e-04
end
task tddft
```

Defines the initial state(s)
All (core) states below energy of -15 au are taken as initial states. No restriction on final states

Alternate input for XANES

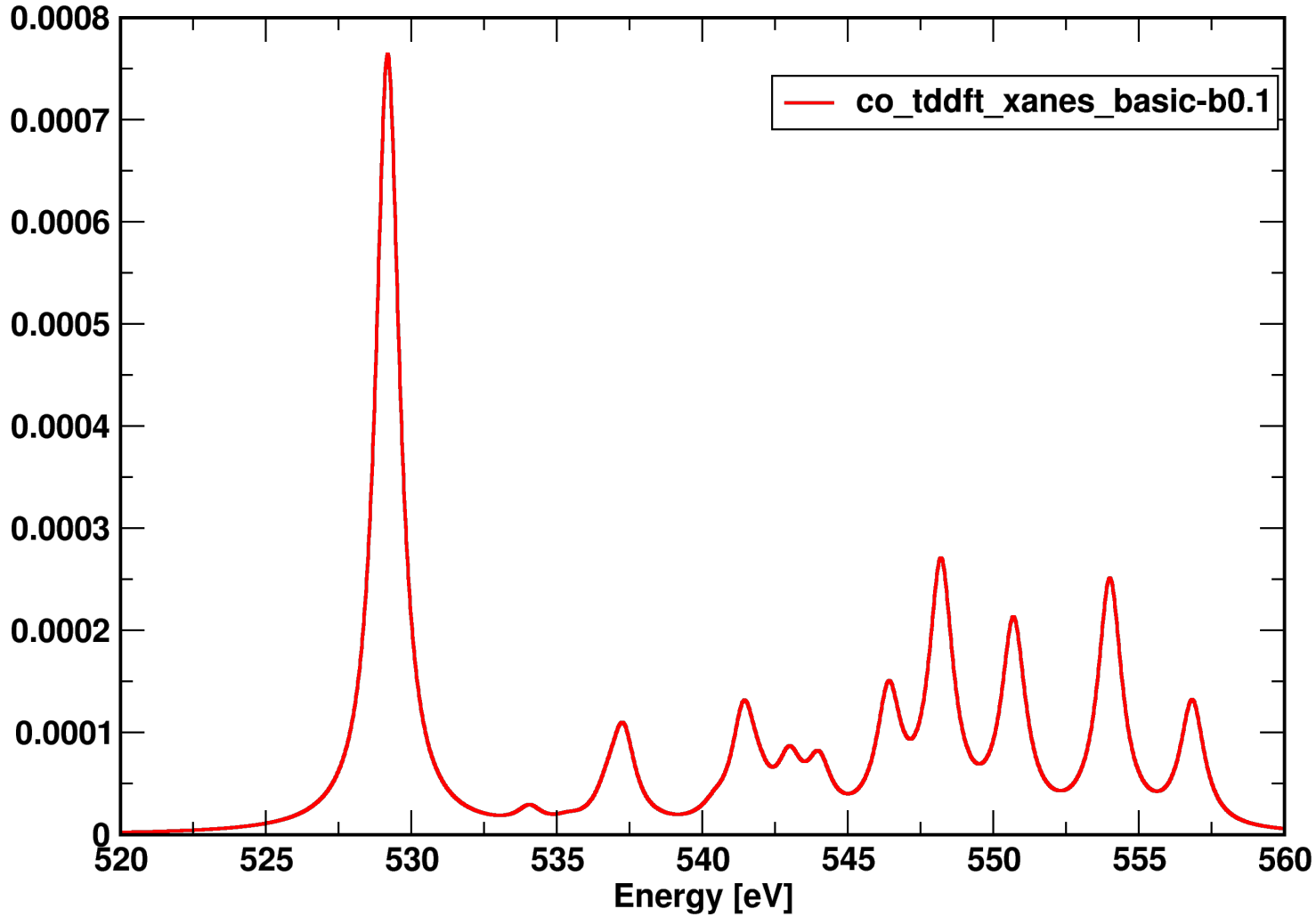
```
geometry units angstrom noautosym nocenter
 O 0        0         0
 C 0        0.00      1.15
end
basis
  * library aug-cc-pvtz
end
dft
  xc b3lyp
end
task dft optimize
dft
  xc beckehandh
end
tddft
  cis
  ewin -20.0 -10.0
  nroots 30
  notriplet
  thresh 1e-04
end
task tddft
```

Defines the initial state(s) with energy windows

Sample XANES Output

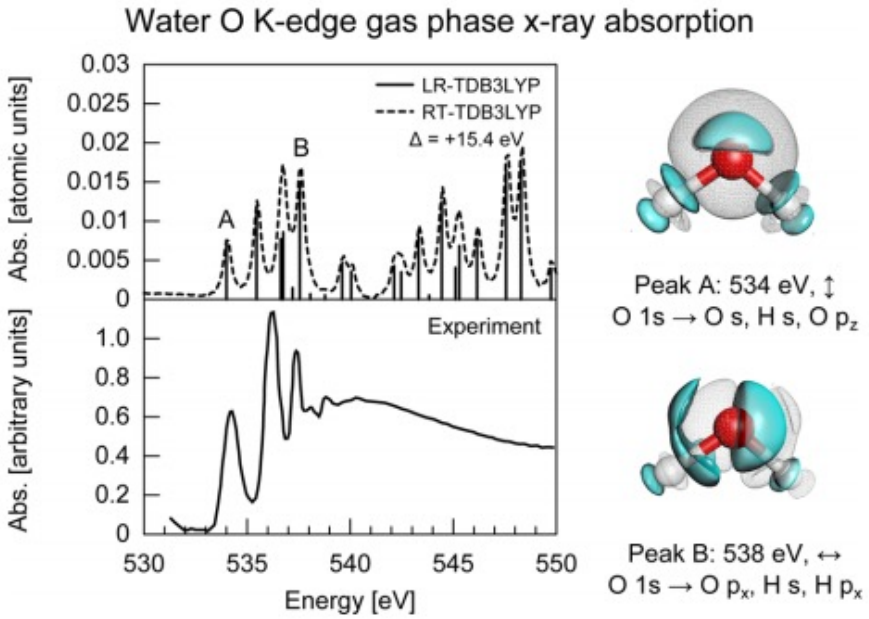
```
-----------------------------------------------------------------------
Root   1 singlet a              19.467775490 a.u.              529.7454 eV
-----------------------------------------------------------------------
   Transition Moments    X -0.05038   Y  0.00001   Z  0.00000
   Transition Moments   XX  0.00000  XY -0.00000  XZ  0.00222
   Transition Moments   YY  0.00000  YZ -0.00000  ZZ  0.00000
   Dipole Oscillator Strength                      0.0329382748
   Electric Quadrupole                             0.0000001929
   Magnetic Dipole                                 0.0000000133
   Total Oscillator Strength                       0.0329384810

   Occ.    1  a   ---  Virt.    8  a       -0.98992
   Occ.    1  a   ---  Virt.   16  a       -0.12916
-----------------------------------------------------------------------
Root   2 singlet a              19.467775490 a.u.              529.7454 eV
-----------------------------------------------------------------------
   Transition Moments    X -0.00001   Y -0.05038   Z -0.00000
   Transition Moments   XX -0.00000  XY -0.00000  XZ  0.00000
   Transition Moments   YY -0.00000  YZ  0.00222  ZZ  0.00000
   Dipole Oscillator Strength                      0.0329382748
   Electric Quadrupole                             0.0000001929
   Magnetic Dipole                                 0.0000000133
   Total Oscillator Strength                       0.0329384810

   Occ.    1  a   ---  Virt.    9  a       -0.98992
   Occ.    1  a   ---  Virt.   17  a       -0.12916
-----------------------------------------------------------------------
Root   3 singlet a              19.835495901 a.u.              539.7515 eV

….
```

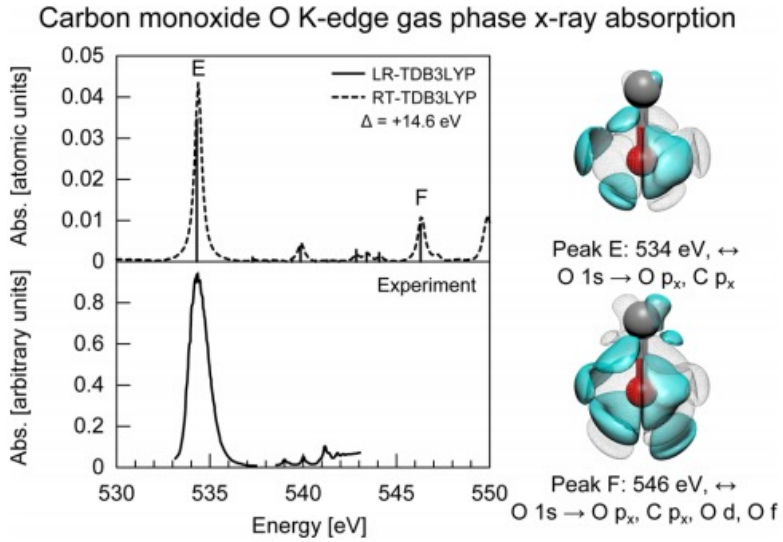
Pre- & Near-Edge X-ray Spectrum

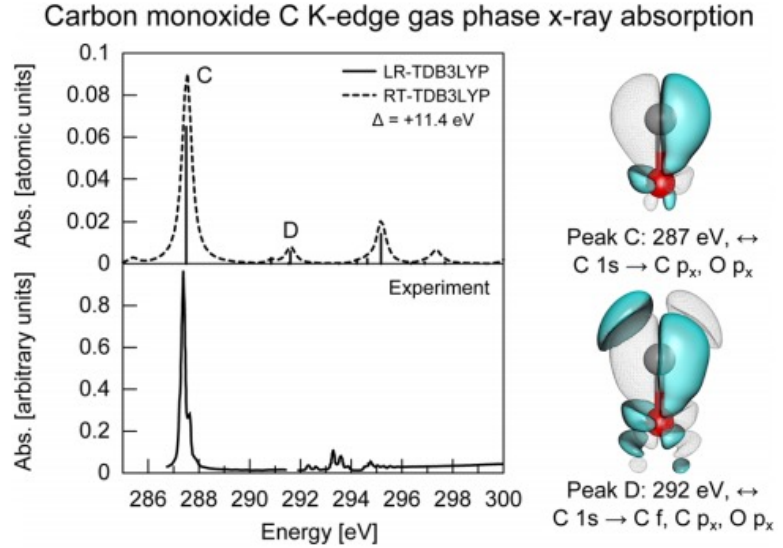



```
python3 nw_spectrum.py -b0.1 -p5000
<co_tddft_xanes_basic.out>co_tddft_xanes_basic-b0.1
```

Other Examples: O K-edge in Water and O, C K-edges in CO



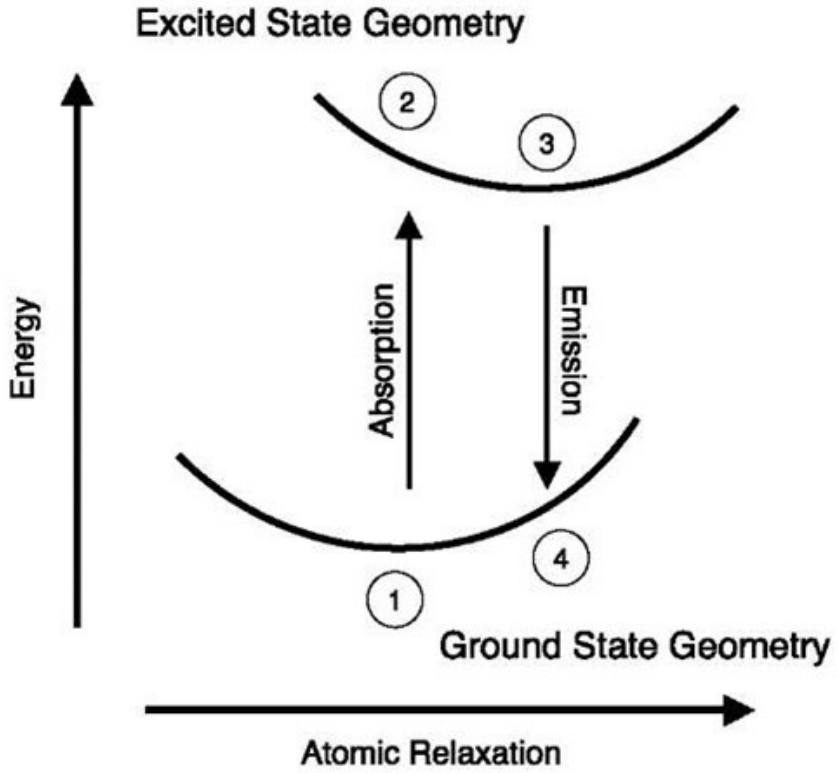


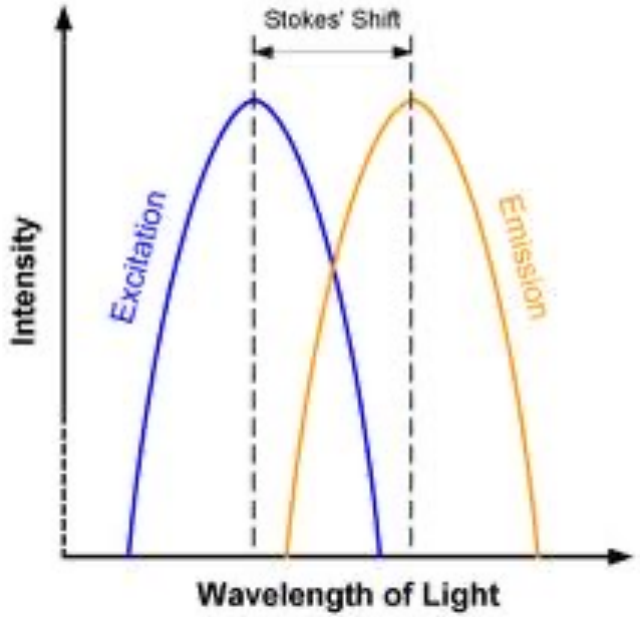


Details: JCTC, 8, 3284 (2012)

Excited-State Optimization

Optimization on the excited state





Analytic TDDFT Gradients/Opt in NWChem

Available functionals for TDDFT gradients/optimization/dynamics

Table 1. Definitions of the XC Functionals[a]

functional	definition
LDA	Slater + VWN 5
BP86	Becke 88 + Perdew 86
PBE	PBEx + PBEc
BLYP	Becke 88 + LYP
B3LYP	Slater (80%) + Becke 88 (nonlocal, 72%) + HF Exchange (20%) + LYP (81%) + VWN 1 RPA (19%)
PBE0	PBEx (75%) + HF Exchange (25%) + PBEc
BHLYP	Slater (50%) + Becke 88 (nonlocal, 50%) + HF Exchange (50%) + LYP
CAM-B3LYP	CAM-Becke 88 (α = 0.19, β = 0.46, ω = 0.33) + LYP
LC-PBE	CAM-PBE (α = 0.00, β = 1.00, ω = 0.30) + PBEc
LC-PBE0	CAM-PBE (α = 0.25, β = 0.75, ω = 0.30) + PBEc
BNL	Baer–Neuhauser–Livshits (α = 0.00, β = 1.00, ω = 0.33) + LYP
LC-ωPBE	LC-ωPBE (α = 0.00, β = 1.00, ω = 0.30) + PBEc
LC-ωPBEh	LC-ωPBE (α = 0.20, β = 0.80, ω = 0.20) + PBEc
LC-BLYP	CAM-Becke 88 (α = 0.00, β = 1.00, ω = 0.33) + LYP

Details: J. Chem. Theory Comput., **2013**, 9 (12), pp 5490–5503

Basic TDDFT Optimization Input

```
geometry units angstrom noautosym nocenter
 O 0        0         0
 C 0        0.00      1.15
end
basis
  * library 6-31G*
end
dft
  xc pbe0
end
task dft optimize

tddft
  nroots 2
  notriplet
  civecs
  grad
    root 1
  end
end
task tddft optimize
```

Defines root on which the excited state gradient/optimization is performed

Linear-Response Time-Dependent DFT

Casida Formulation

Cannot be used to describe excitations in intense fields

Perturbed density → first-order correction

Linear response approach → frequency domain

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix}$$

$$1 = \left(X \middle| X\right) - \left(Y \middle| Y\right)$$

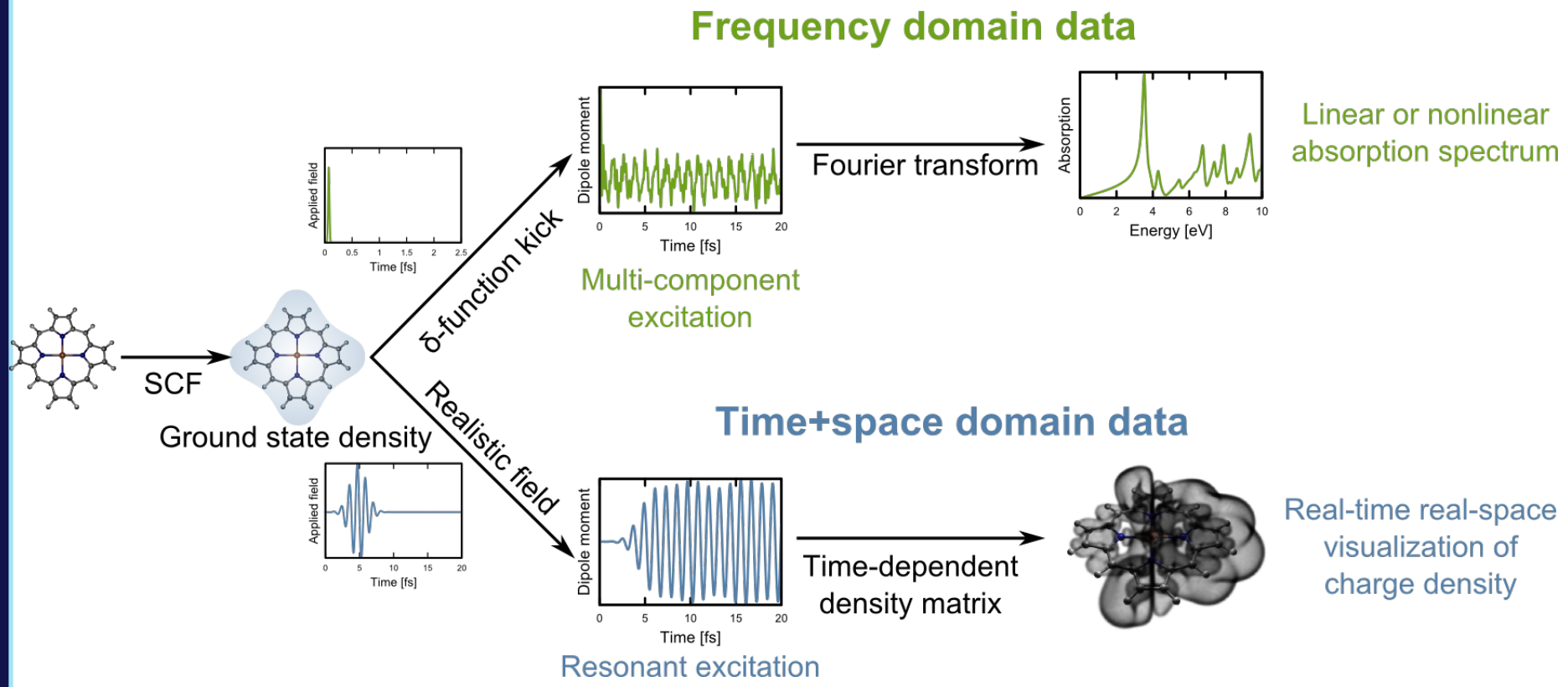
$$A_{ia,jb} = \delta_{ij}\delta_{ab}\left(\varepsilon_a - \varepsilon_i\right) + \left(ia \middle| F_H + F_{xc} \middle| jb\right)$$

$$B_{ia,jb} = \left(ia \middle| F_H + F_{xc} \middle| jb\right)$$

$$F_{xc}\left(r_1, r_2\right) = \frac{\partial^2 f}{\partial\rho\left(r_1\right)\partial\rho\left(r_2\right)}$$

Time-Dependent Density Functional Theory, Marques et al, Springer 2006

Real-Time TDDFT

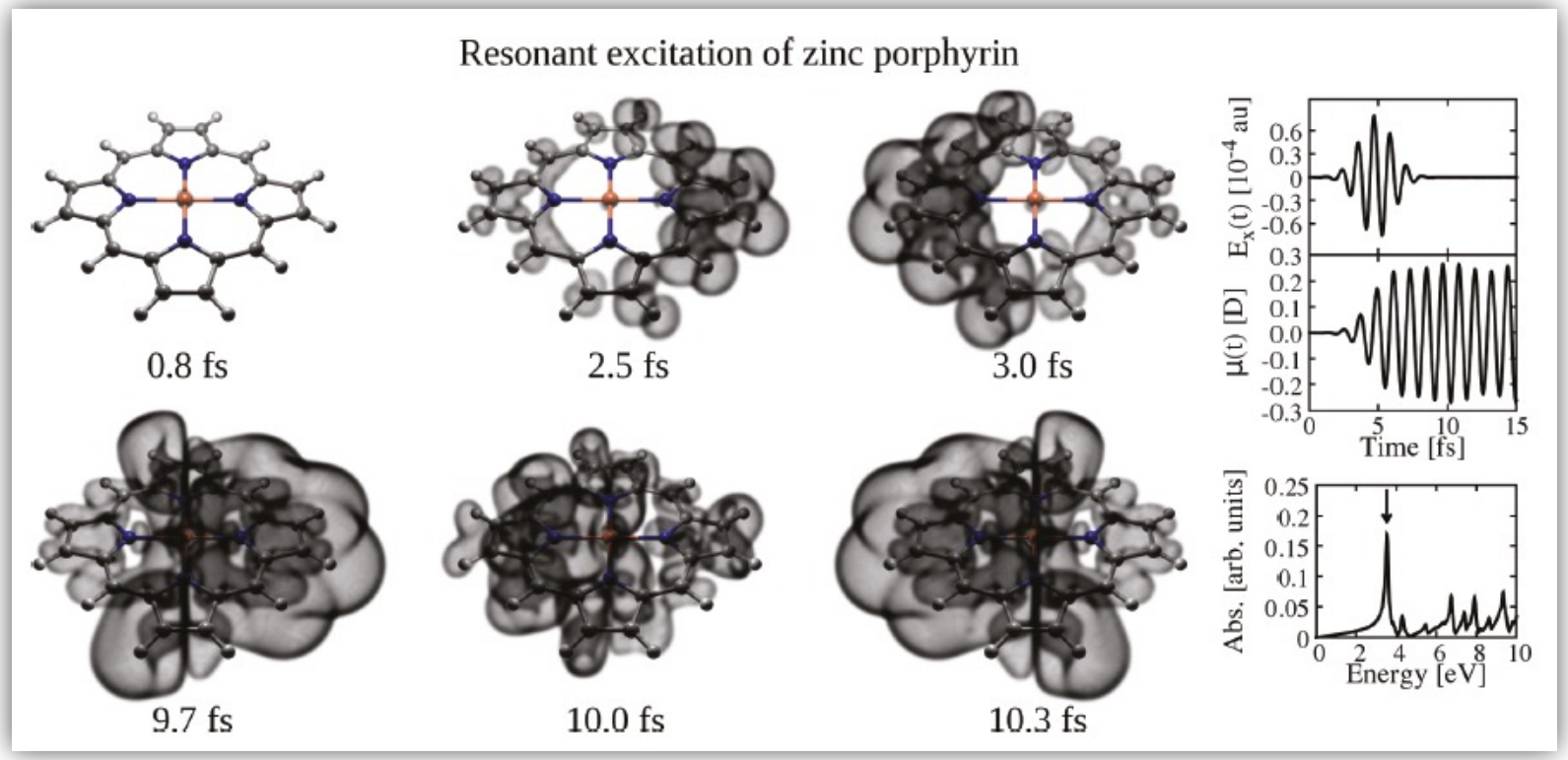


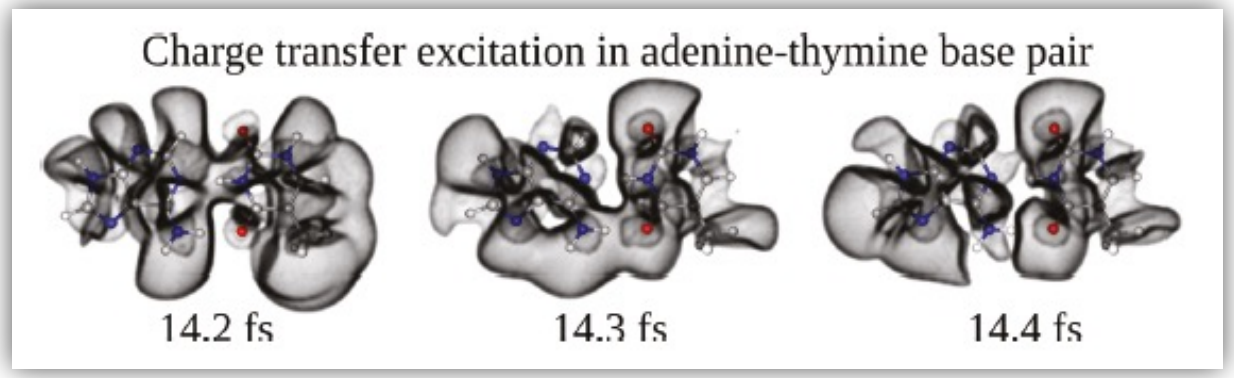
- Response beyond perturbation limit, anharmonic effects
- Depends only on the XC potential
- Real-time, real-space → full dynamical information
- Insight into ultrafast and nonlinear processes

JCTC 7, 1344 (2011)

Ultrafast Electron Dynamics

K.Lopata
N. Govind





JCTC 7, 1344 (2011)

Questions?

Thank you