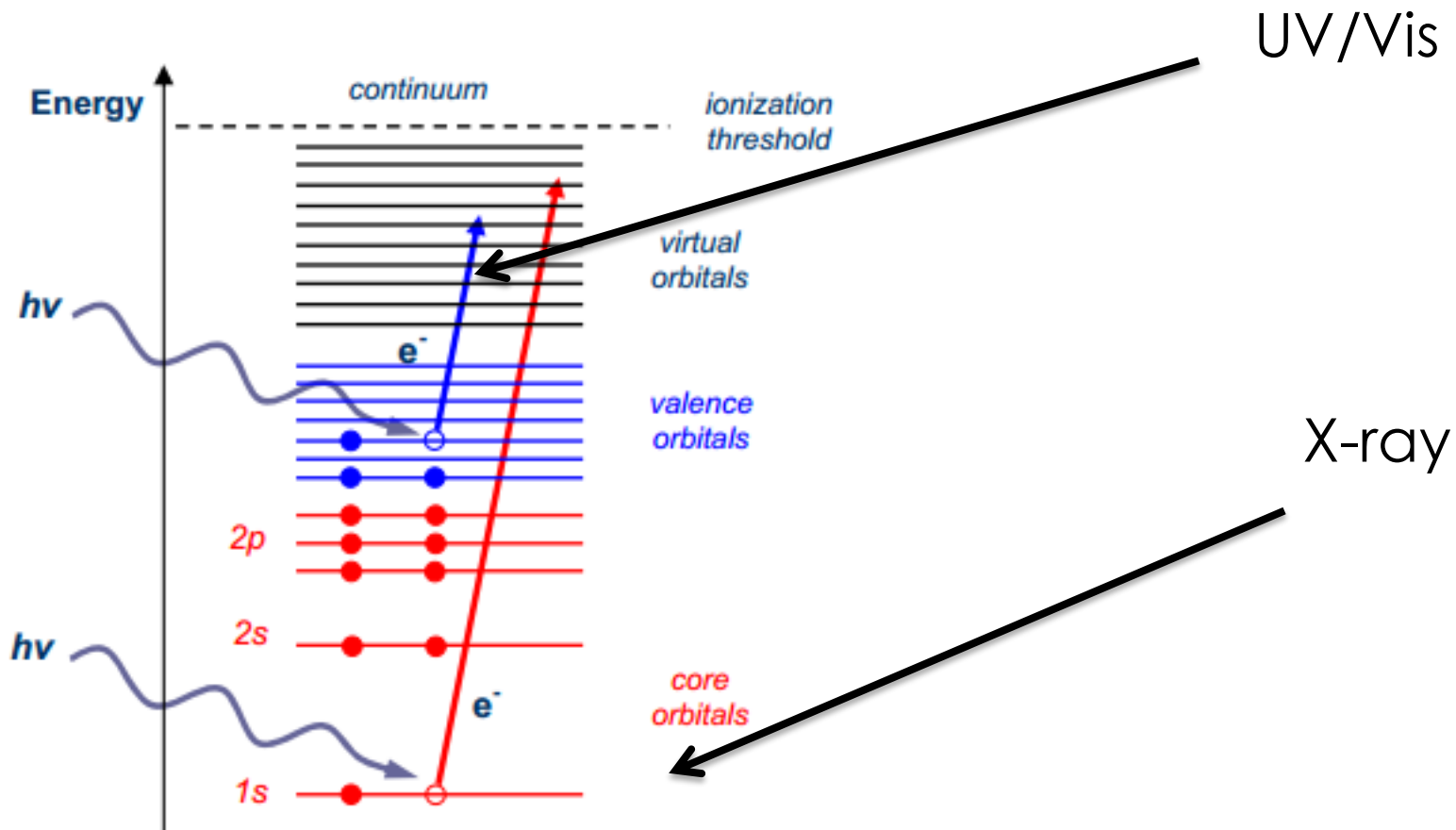


# Excited State Calculations with TDDFT

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



```
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  
-----

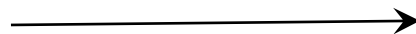
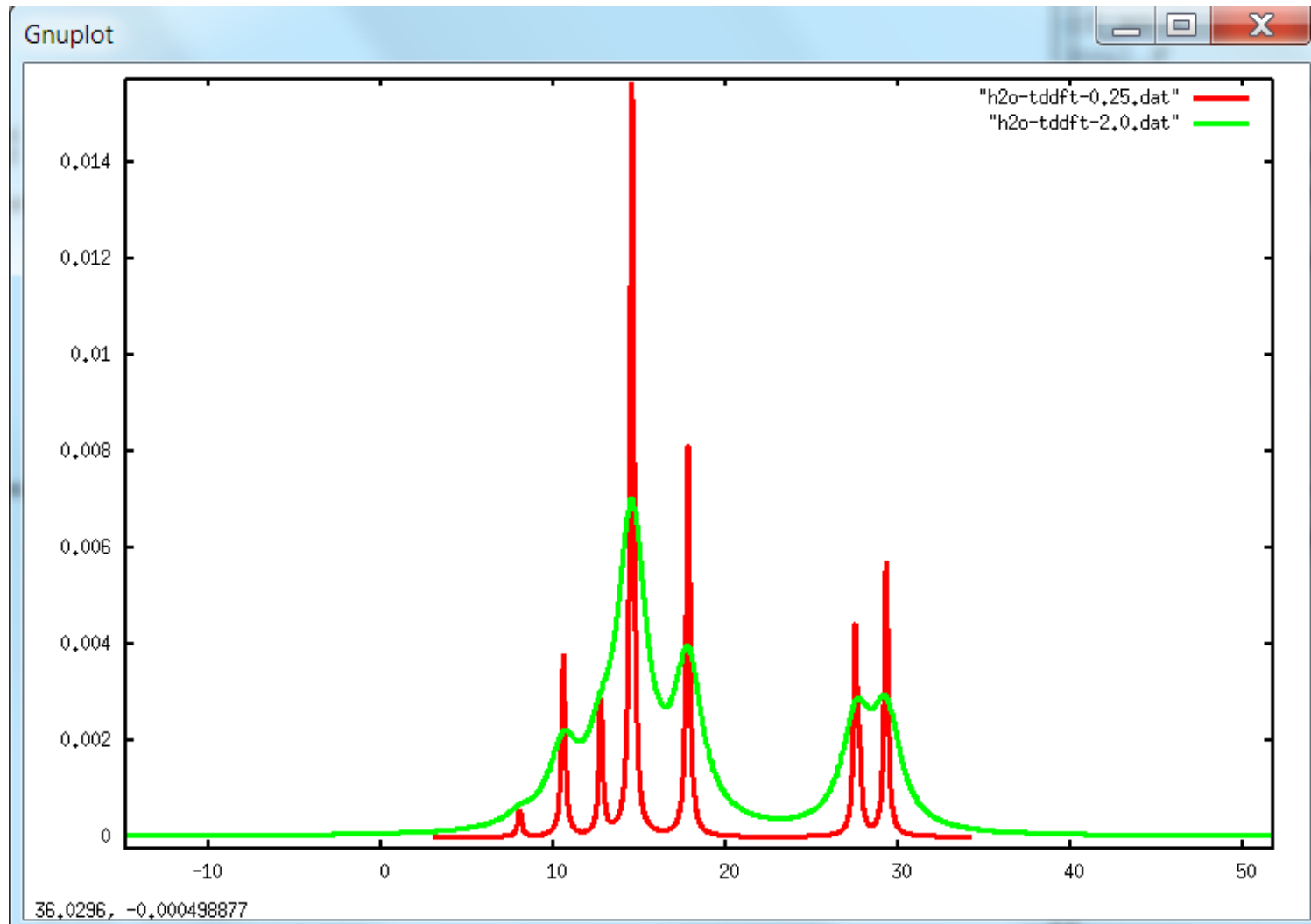
Transition Moments   X -0.00000   Y 0.00000   Z -0.00000  
Transition Moments   XX -0.00000   XY 0.24936   XZ 0.00000  
Transition Moments   YY 0.00000   YZ -0.00000   ZZ -0.00000  
Dipole Oscillator Strength            0.0000000000  
Electric Quadrupole            0.0000000166  
Magnetic Dipole            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)



Energy (eV)

# 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

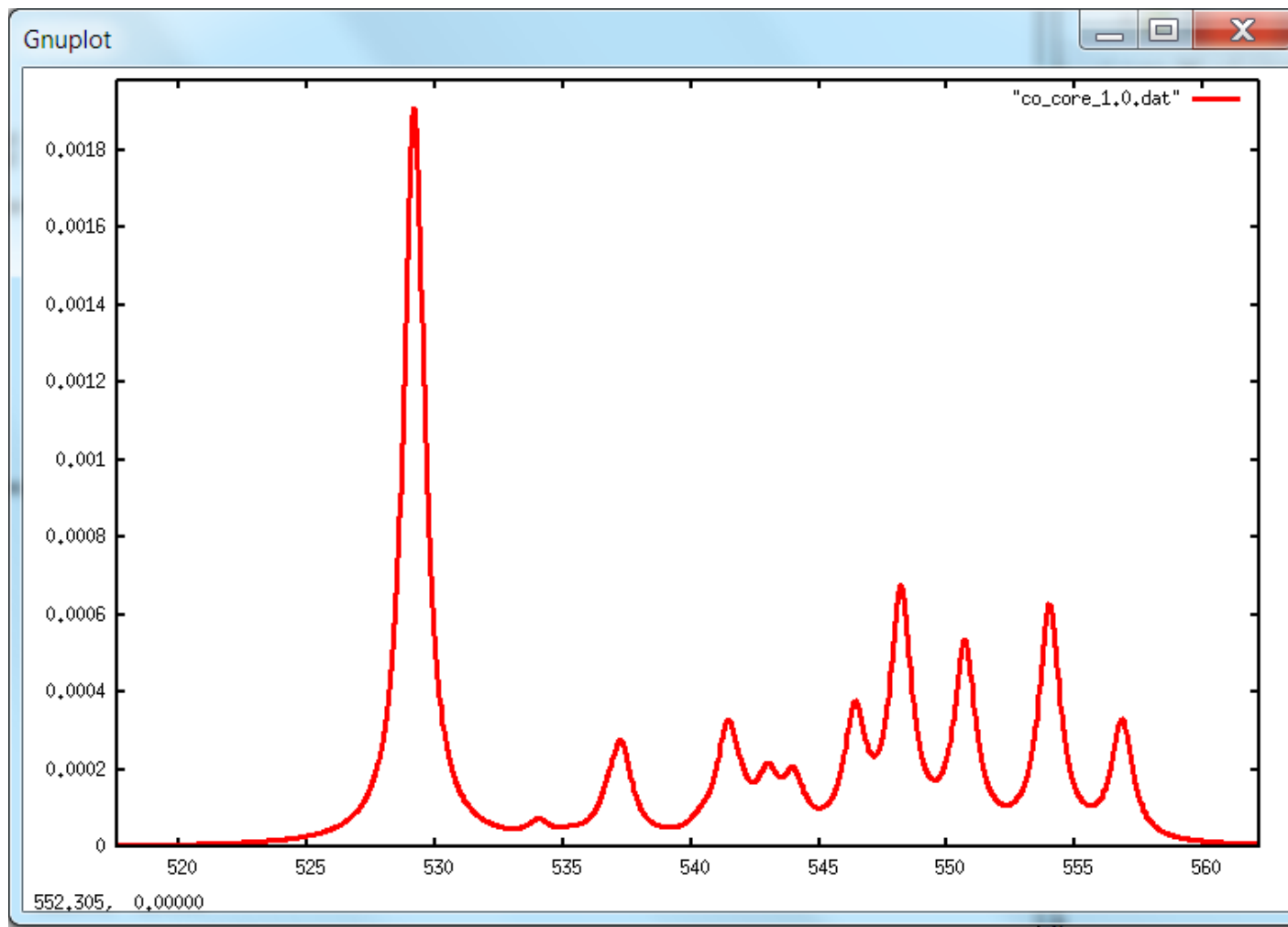
Occ. 1 a --- Virt. 9 a -0.98992  
Occ. 1 a --- Virt. 17 a -0.12916

-----  
Root 3 singlet a 19.835495901 a.u. 539.7515 eV  
-----

....



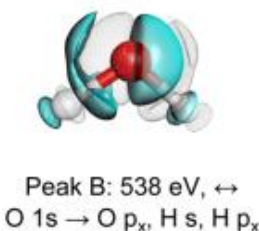
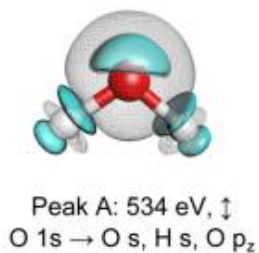
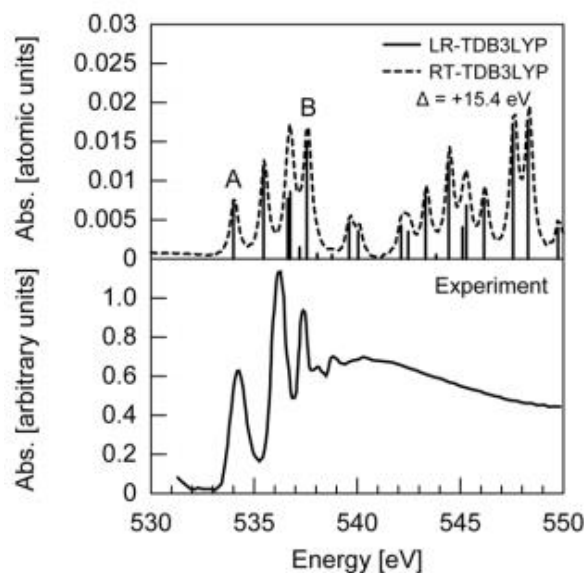
# Pre- & Near-Edge X-ray Spectrum



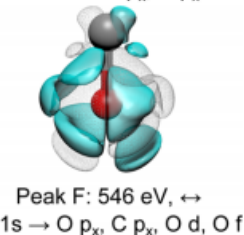
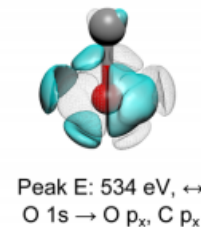
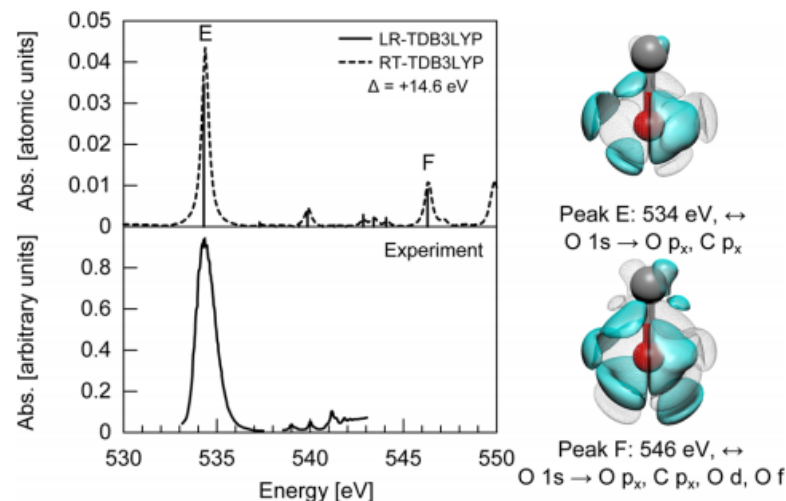
Energy (eV)

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

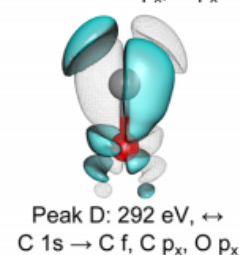
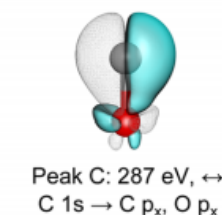
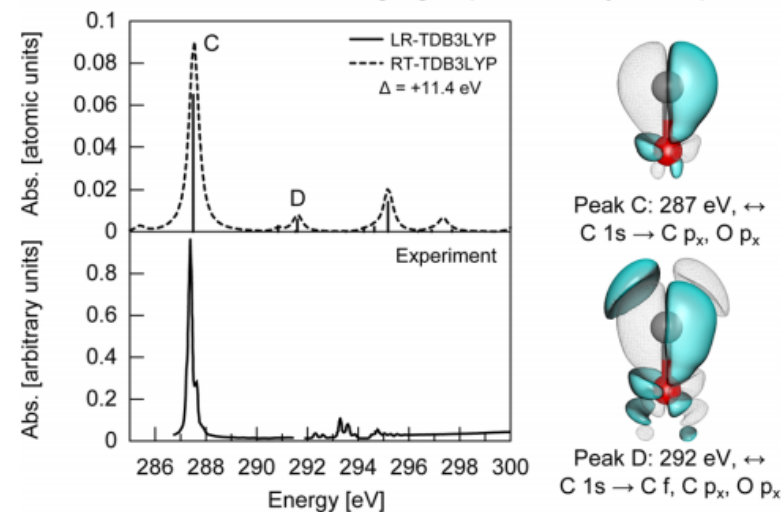
Water O K-edge gas phase x-ray absorption



Carbon monoxide O K-edge gas phase x-ray absorption

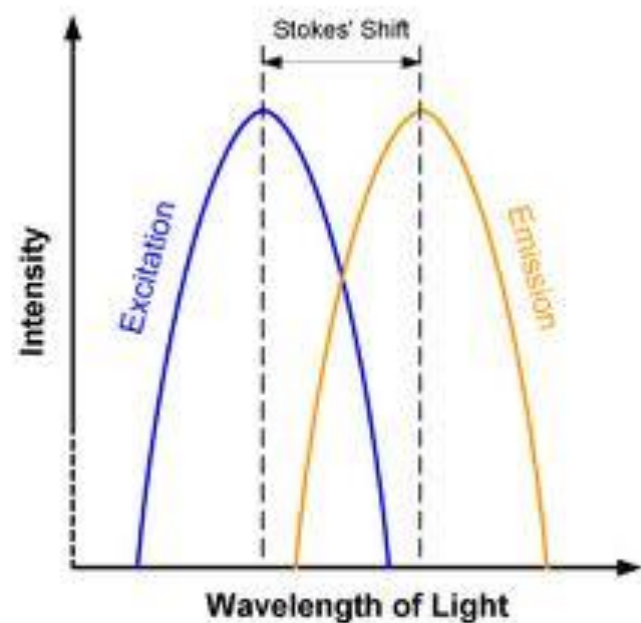
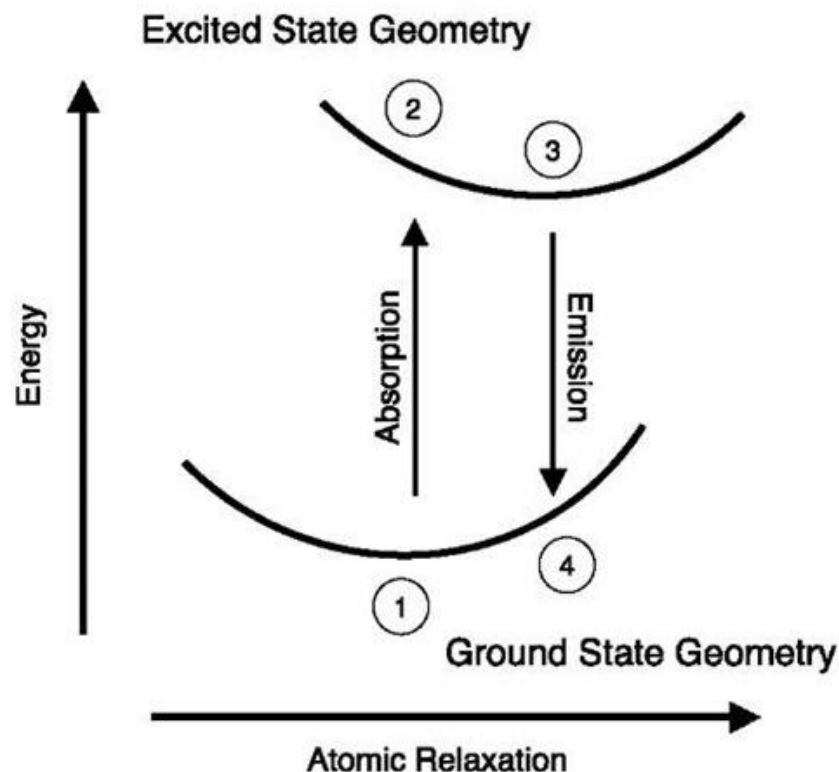


Carbon monoxide C K-edge gas phase x-ray absorption



Details: JCTC, 8, 3284 (2012)

## Optimization on the excited state



## Available functionals for TDDFT gradients/optimization/dynamics

**Table 1. Definitions of the XC Functionals<sup>a</sup>**

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 ( $\alpha = 0.19$ , $\beta = 0.46$ , $\omega = 0.33$ ) + LYP
LC-PBE	CAM-PBE ( $\alpha = 0.00$ , $\beta = 1.00$ , $\omega = 0.30$ ) + PBEc
LC-PBE0	CAM-PBE ( $\alpha = 0.25$ , $\beta = 0.75$ , $\omega = 0.30$ ) + PBEc
BNL	Baer-Neuhauser-Livshits ( $\alpha = 0.00$ , $\beta = 1.00$ , $\omega = 0.33$ ) + LYP
LC- $\omega$ PBE	LC- $\omega$ PBE ( $\alpha = 0.00$ , $\beta = 1.00$ , $\omega = 0.30$ ) + PBEc
LC- $\omega$ PBEh	LC- $\omega$ PBE ( $\alpha = 0.20$ , $\beta = 0.80$ , $\omega = 0.20$ ) + PBEc
LC-BLYP	CAM-Becke 88 ( $\alpha = 0.00$ , $\beta = 1.00$ , $\omega = 0.33$ ) + 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



## Casida Formulation

Perturbed density  $\rightarrow$  first-order correction

Linear response approach  $\rightarrow$  frequency domain

Cannot be used to describe excitations in intense fields

- Working equations have  $N_{\text{occ}} * N_{\text{virt}}$  solutions
- Dimension  $\rightarrow$  tetradic ( $N^2 * N^2$ )
- Every root  $\rightarrow$  cost of a HF or hybrid DFT calculation
- Note that the vectors are normalized but differently so than your usual wavefunction
- The orbital energy difference is a main term in the excitation energy
- In the case of pure DFT with large molecules most of the integrals involving  $F_{xc}$  vanish as this is a local kernel

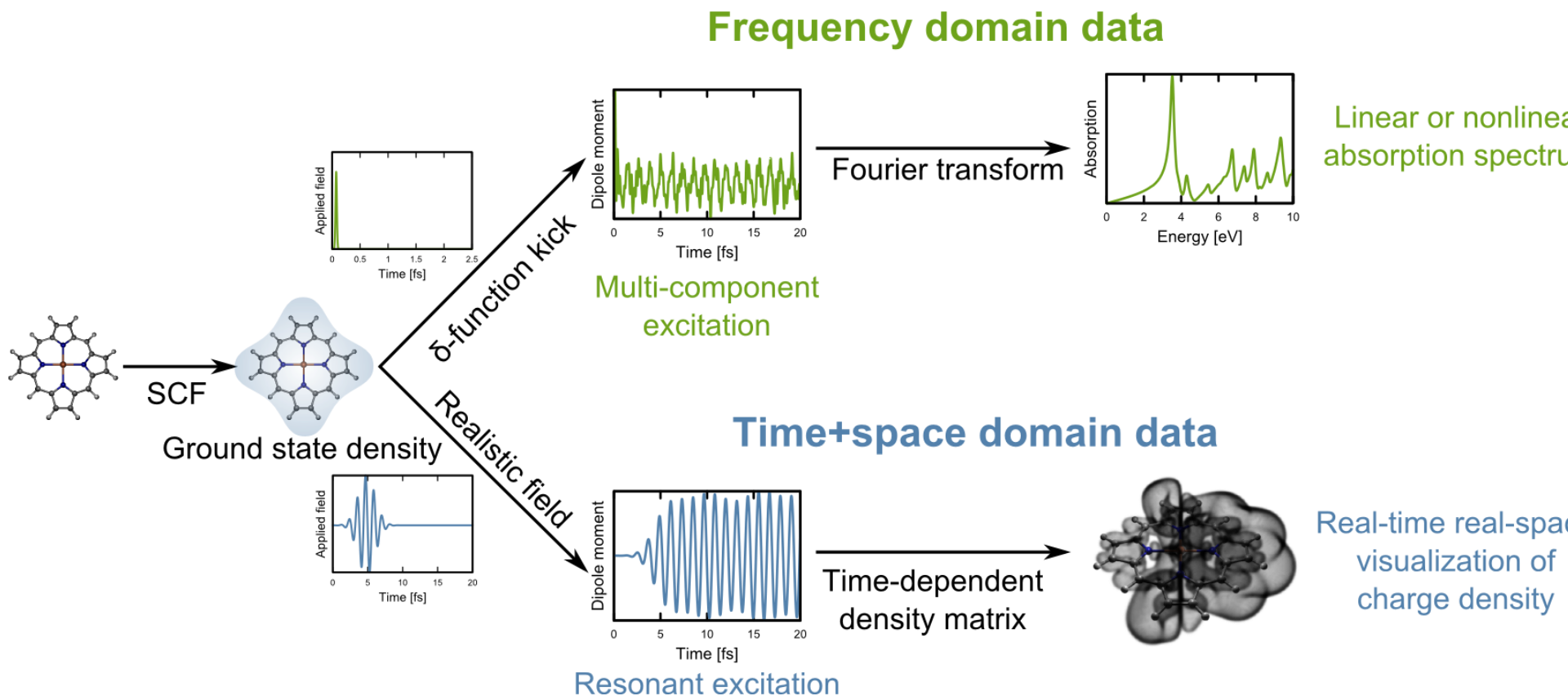
$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}$$

$$1 = (X | X) - (Y | Y)$$

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

$$B_{ia,jb} = (ia | F_H + F_{xc} | jb)$$

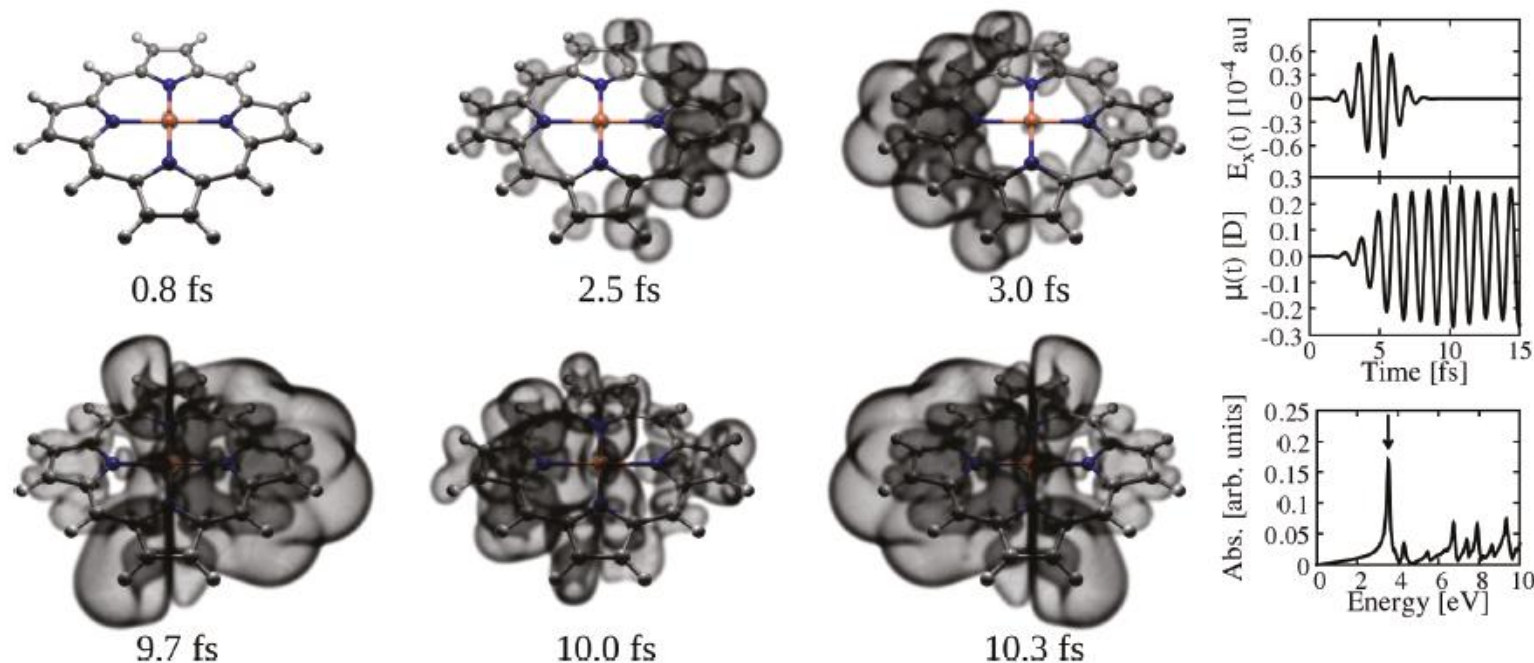
$$F_{xc}(r_1, r_2) = \frac{\partial^2 f}{\partial \rho(r_1) \partial \rho(r_2)}$$



- 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



## Resonant excitation of zinc porphyrin



## Charge transfer excitation in adenine-thymine base pair

