Molecular Properties

Sample Input

```
echo
start ch3f
title ch3f

charge 0
geometry
c  0.0    0.0    0.0
f  0.0    0.0    1.383
h  1.028  0.0   -0.350
h -0.514  0.890 -0.350
h -0.514 -0.890 -0.350
end
basis
* library 6-311G
end
dft
 xc b3lyp
end
property
  mulliken
  dipole
  quadrupole
  octupole
  efieldgrad
  shielding
end
task dft property
```

```
property
  shielding  2 1 2
end
```

Output Snippet (1)

```
 -------------
 Dipole Moment
 -------------

Center of charge (in au) is the expansion point
      X =      0.0000000 Y =      0.0000000 Z =      0.0000000

 Dipole moment       0.8526960243 A.U.
        DMX      -0.0000003199 DMXEFC       0.0000000000
        DMY      -0.0000003199 DMYEFC       0.0000000000
        DMZ       0.8526960243 DMZEFC       0.0000000000
 -EFC- dipole       0.0000000000 A.U.
 Total dipole       0.8526960243 A.U.

 Dipole moment       2.1673534901 Debye(s)
        DMX      -0.0000008131 DMXEFC       0.0000000000
        DMY      -0.0000008130 DMYEFC       0.0000000000
        DMZ       2.1673534901 DMZEFC       0.0000000000
 -EFC- dipole       0.0000000000 DEBYE(S)
 Total dipole       2.1673534901 DEBYE(S)

1 a.u. = 2.541766 Debyes
```

Output Snippet (2)

EMSL

```
 ----------------------
 Electric field gradient
 ----------------------

1 a.u. = 0.324123 10**(16) esu/cm**3  ( or statvolts/cm**2 ) = 0.97174 10**(22) v/m**2


-------------------------------------------------------
 Atom     X        Y        Z
-------------------------------------------------------
  1 C   0.00000  0.00000  1.19651
-------------------------------------------------------

Electric field gradient in molecular frame (a.u.)
      XX          YY          ZZ          XY          XZ          YZ
-----------------------------------------------------------------------------------------
     0.280943    0.280943   -0.561885    0.000000    0.000000    0.000000

Principal components (a.u.) and orientation
of principal axis w.r.t. absolute frame                 Asymmetry parameter eta
-----------------------------------------------------------------------------------
    -0.561885    0.280943    0.280943                    0.000000

     0.000000    0.707453    0.706760
     0.000000   -0.706760    0.707453
     1.000000    0.000000    0.000000
```

Output Snippet (3)

```
Atom:    1  C
      Diamagnetic
   243.3437      0.0000      0.0000
     0.0000    243.3437      0.0000
     0.0000      0.0000    256.9231

      Paramagnetic
  -156.9102      0.0000      0.0000
     0.0000   -156.9102      0.0000
     0.0000      0.0000    -69.0429

      Total Shielding Tensor
    86.4335      0.0000      0.0000
     0.0000     86.4335      0.0000
     0.0000      0.0000    187.8802

         isotropic =    120.2491
        anisotropy =    101.4467

      Principal Components and Axis System
                1           2           3
          187.8802     86.4335     86.4335

   1        0.0000     -0.7065      0.7077
   2        0.0000      0.7077      0.7065
   3        1.0000      0.0000      0.0000
```

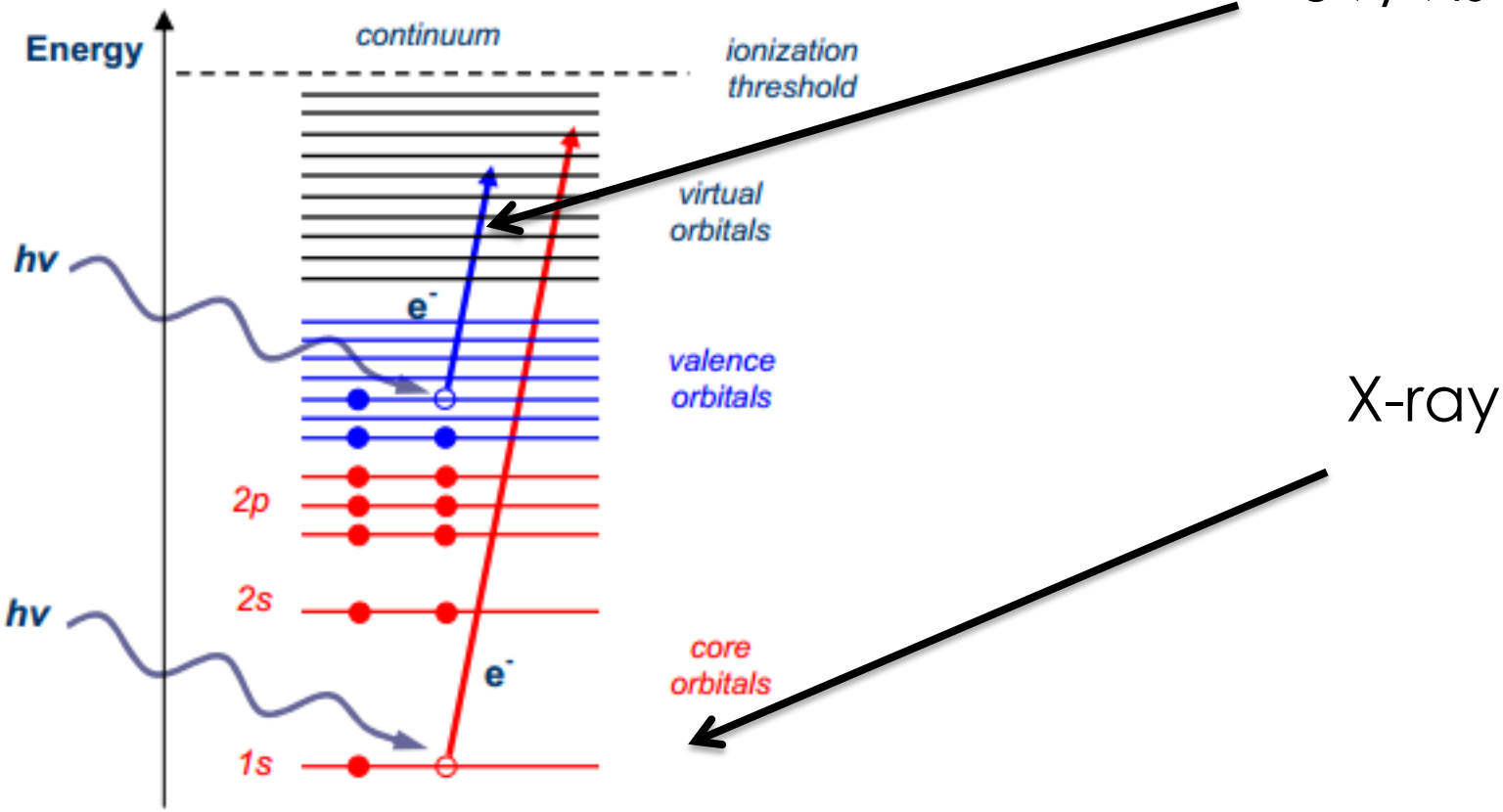
Excited State Calculations with TDDFT

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

See examples at:
https://github.com/nwchemgit/nwchem/wiki/Excited-State-Calculations

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

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 Output

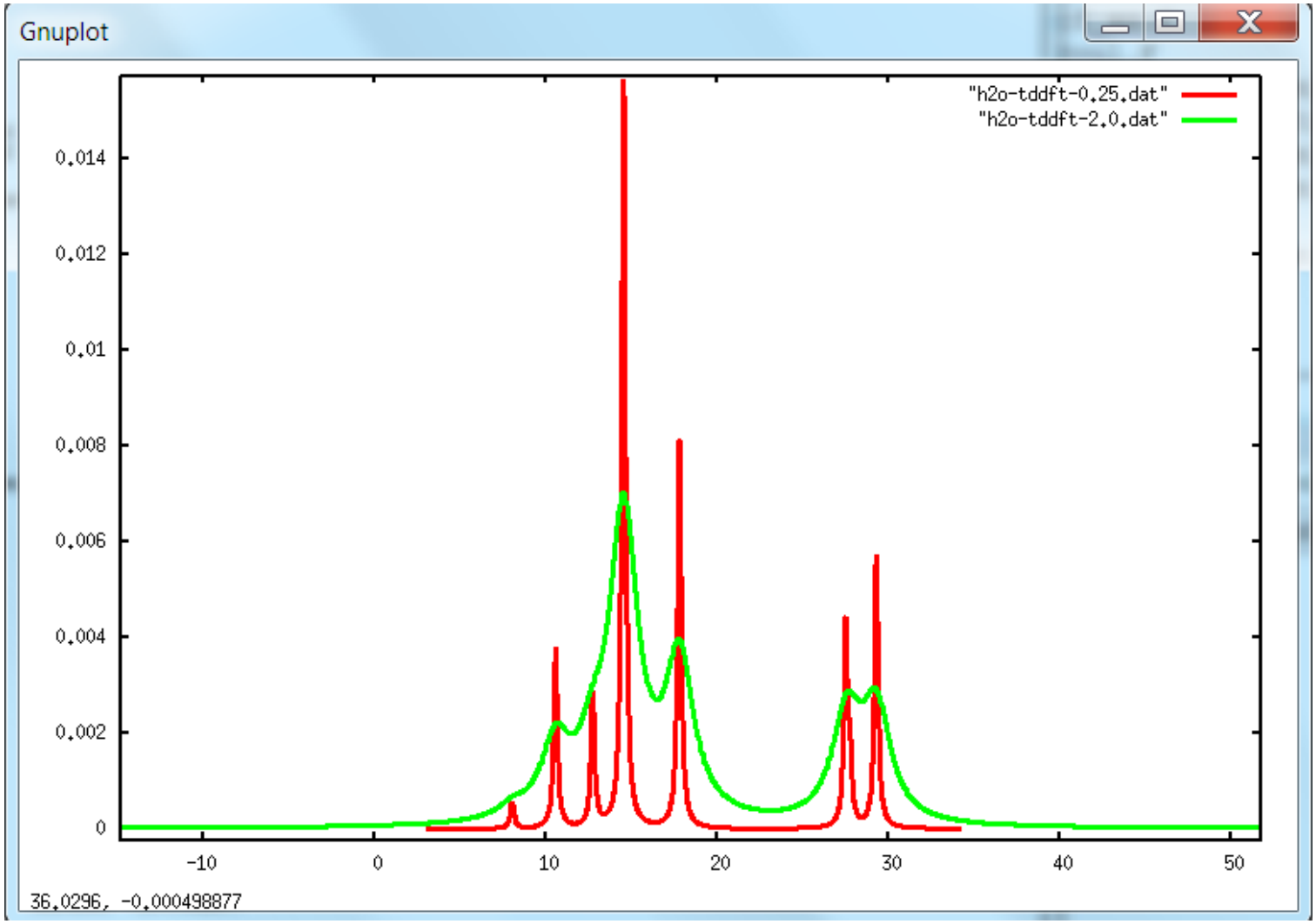
```
-----------------------------------------------------------------------
Root   1 singlet b2          0.294221372 a.u.          8.0062 eV
-----------------------------------------------------------------------
  Transition Moments    X  0.00000   Y  0.26890   Z  0.00000
  Transition Moments   XX  0.00000  XY  0.00000  XZ  0.00000
  Transition Moments   YY  0.00000  YZ -0.08066  ZZ  0.00000
  Dipole Oscillator Strength                0.01418

  Occ.    5  b2  ---  Virt.    6  a1   1.00002 X
-----------------------------------------------------------------------
Root   2 singlet a2          0.369097477 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                0.00000

  Occ.    5  b2  ---  Virt.    7  b1  -0.99936 X
-----------------------------------------------------------------------
Root   3 singlet a1          0.387064734 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
  Transition Moments   YY  0.09429  YZ  0.00000  ZZ  0.45941
  Dipole Oscillator Strength                0.09433

  Occ.    3  b1  ---  Virt.    7  b1   0.11875 X
  Occ.    4  a1  ---  Virt.    6  a1  -0.99241 X
```

UV/Vis Spectrum



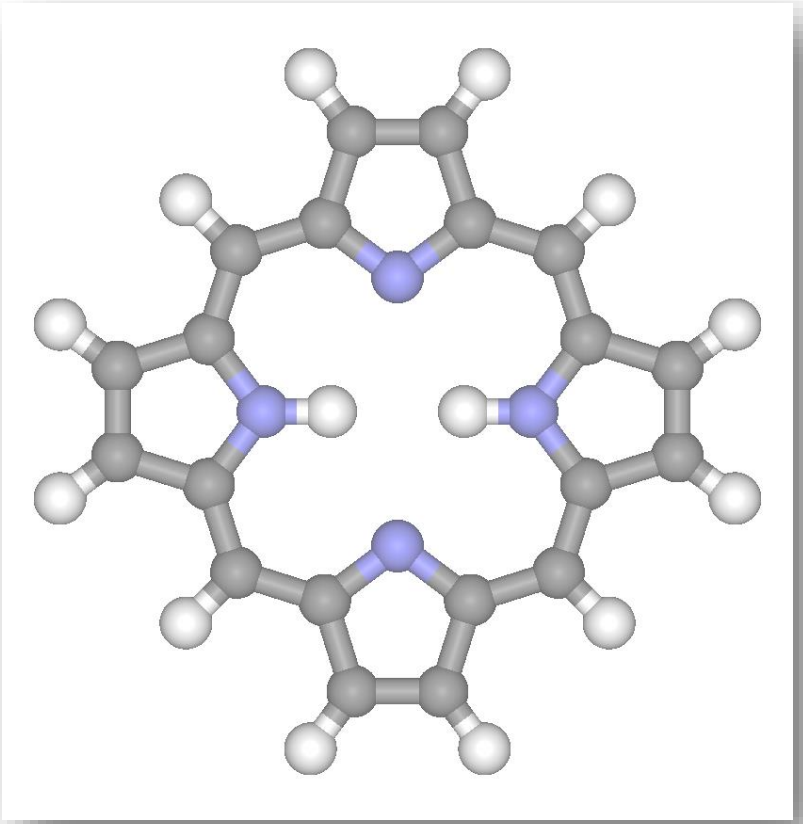
Energy (eV)

Free Base Porphyrin

TABLE III. Excitation energies (in eV) of 1^1B_{3u} and 1^1B_{2u} states of FBP. In all EOMCC calculations core electrons were kept frozen. The EOMCC calculations were performed for five basis sets: 6-31G, 6-31G*, cc-pVDZ, POL1, and cc-pVTZ. CAM-B3LYP: α=0.19, β=0.46, and $\alpha+\beta$=0.65; CAM-B3LYP(1): α=0.19, β=0.46, and $\alpha+\beta$=1.0; CAM-PBE0: α=0.25, β=0.75, and $\alpha+\beta$=1.0. The attenuation factor (γ) was set to 0.33 for the CAM-related calculations.

Method	1^1B_{3u}	1^1B_{2u}
B3LYP (POL1)	2.24	2.40
PBE0 (POL1)	2.27	2.43
CAM-B3LYP (POL1)	2.14	2.35
CAM-B3LYP(1) (POL1)	1.90	2.15
CAM-PBE0 (POL1)	1.92	2.18
CASPT2 (6-31G)	1.92[a]	2.16[a]
CASPT2 (6-31G*)	1.85[a]	2.18[a]
SAC-CI	1.75[b]	2.23[b]
STEOMCC	1.72[c]	2.61
EOMCCSD(6-31G)	2.16	2.77
CR-EOMCCSD(T) (6-31G)	1.90	2.52
EOMCCSD (6-31G*)	2.15	2.64
CR-EOMCCSD(T) (6-31G*)	1.85	2.35
EOMCCSD(cc-pVDZ)	2.15	2.61
CR-EOMCCSD(T) (cc-pVDZ)	1.86	2.32
EOMCCSd[−1.0,0.5] (POL1)	2.21	2.74
CR-EOMCCSd(t)-III[−1.0,0.5] (POL1)	2.01	2.56
CR-EOMCCSd(t)-II[−1.0,0.5] (POL1)	1.75	2.32
EOMCCSd[−1.0,1.0] (POL1)	2.21	2.66
CR-EOMCCSd(t)-III[−1.0,1.0] (POL1)	1.98	2.42
CR-EOMCCSd(t)-II[−1.0,1.0] (POL1)	1.83	2.29
EOMCCSd[−1.0,1.5] (POL1)	2.21	2.63
CR-EOMCCSd(t)-III[−1.0,1.5] (POL1)	1.97	2.37
CR-EOMCCSd(t)-II[−1.0,1.5] (POL1)	1.87	2.28
EOMCCSD (POL1)	2.15	2.55
CR-EOMCCSD(T) (POL1)	1.85	2.25
EOMCCSD (cc-pVTZ)	2.15	2.55
Experimental	1.98–2.02;[d] 1.91[a]	2.33–2.42;[d] 2.27[a]

[a]From Ref. 29.
[b]From Ref. 9.
[c]From Ref. 73.
[d]From Refs. 74–76.

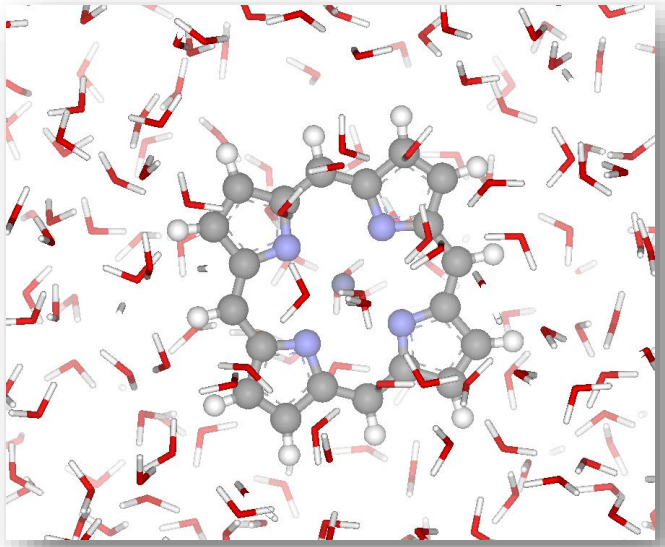


JCP, 132, 154103 (2010)

Zinc Porphyrin in Aqueous Solution

	Q		B		N	
method	2^1A	3^1A	4^1A	5^1A	6^1A	7^1A
B3LYP (G)	2.40	2.40	3.52	3.52	3.65	3.66
	(0.001)	(0.001)	(0.861)	(0.896)	(0.004)	(0.043)
B3LYP (S)	2.40	2.41	3.51	3.51	3.36	3.38
	(0.001)	(0.002)	(0.795)	(0.808)	(0.009)	(0.022)
PBE0 (G)	2.44	2.44	3.58	3.58	3.79	3.79
	(0.001)	(0.001)	(0.943)	(0.957)	(0.003)	(0.022)
PBE0 (S)	2.44	2.44	3.57	3.58	3.50	3.52
	(0.001)	(0.002)	(0.878)	(0.735)	(0.065)	(0.102)
CAM-B3LYP-A (G)	2.34	2.34	3.66	3.66	4.17	4.18
	(0.004)	(0.004)	(1.071)	(1.075)	(0.002)	(0.006)
CAM-B3LYP-A (S)	2.35	2.35	3.65	3.66	3.89	3.92
	(0.003)	(0.006)	(1.023)	(1.039)	(0.004)	(0.013)
CAM-B3LYP-B (G)	2.14	2.14	3.75	3.75	4.55	4.55
	(0.006)	(0.006)	(1.152)	(1.158)	(0.003)	(0.005)
CAM-B3LYP-B (S)	2.15	2.17	3.75	3.76	4.27	4.30
	(0.006)	(0.009)	(1.123)	(1.129)	(0.001)	(0.005)
CAM-PBE0 (G)	2.17	2.17	3.79	3.79	4.62	4.62
	(0.007)	(0.007)	(1.179)	(1.186)	(0.003)	(0.005)
CAM-PBE0 (S)	2.18	2.20	3.78	3.80	4.35	4.38
	(0.006)	(0.010)	(1.149)	(1.154)	(0.002)	(0.005)
SAC-CI	1.84	1.84	3.50	3.50	3.92	3.92
EOMCCSD	2.49	2.50	4.01	4.02	4.29	4.32
CR-EOMCCSD(T)	2.25	2.26	3.74	3.75	4.18	4.20

JPCA, 113, 6041 (2009)



QM/MM approach
ZnP embedded in water

Basis:
6-31G* (C,H,N)
Ahlrichs VTZ basis (Zn)

xc: B3LYP (optimization)
Cubic Box: 30 Å, 869 H_2O
Equilibration: 60ps (298.15K)

X-ray Absorption Spectroscopy (XAS)

Nomenclature

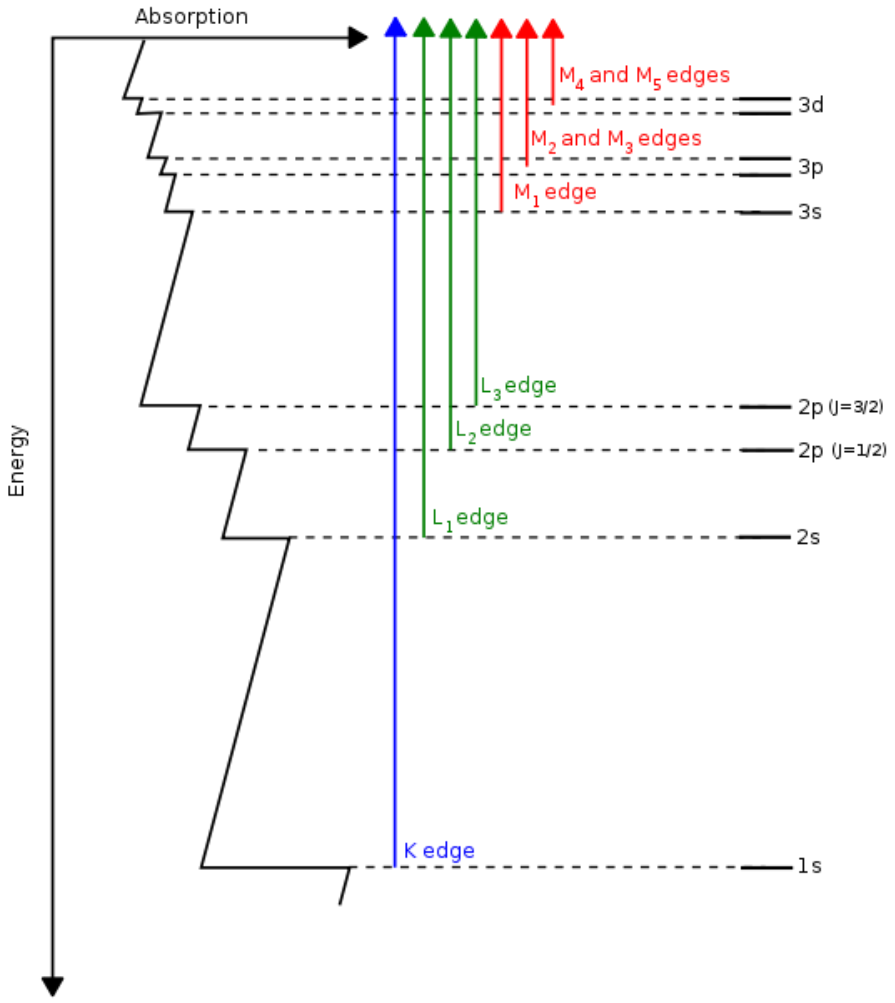
K-, L-, M- → n= 1, 2, 3

K-edge: 1s, 1s → np
L-edge: 2s, 2p
L_3-edge : 2p → nd

L_2, L_3 → spin-orbit splitting of the p states

Near-edge x-ray absorption (XANES)

- Core → unoccupied states
- Sub-ionization threshold
- Probes chemical env around absorbing center
- Requires full treatment of electronic structure of absorbing center and neighbors (nearest, next-nearest)



http://en.wikipedia.org/wiki/X-ray_absorption_spectroscopy

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
```

Sample XANES Output

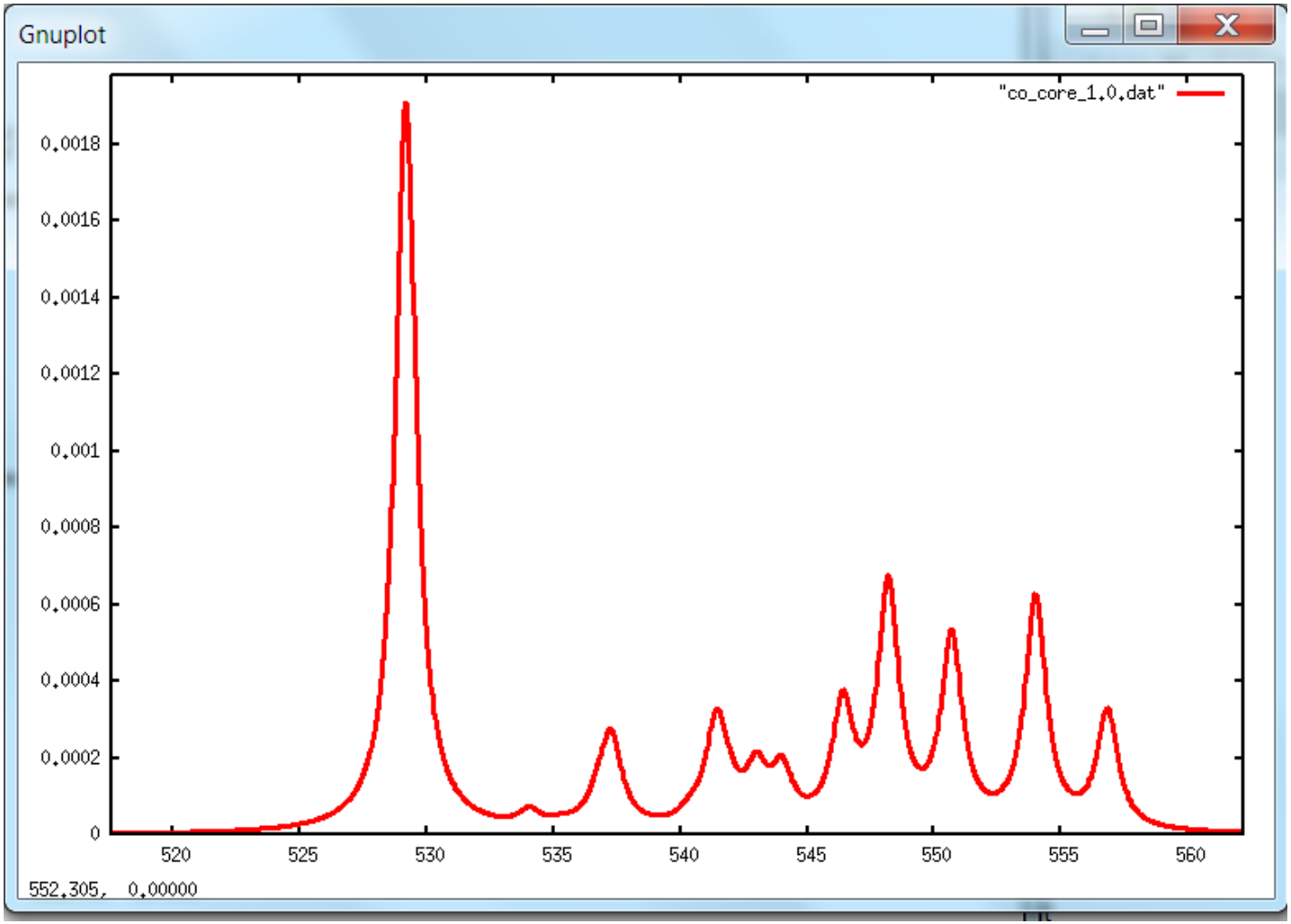
EMSL

```
-------------------------------------------------------------------------
Root   1 singlet a          19.446988682 a.u.          529.1797 eV
-------------------------------------------------------------------------
  Transition Moments    X -0.03998   Y  0.04263   Z  0.00000
  Transition Moments   XX  0.00000  XY  0.00000  XZ  0.00048
  Transition Moments   YY  0.00000  YZ -0.00052  ZZ  0.00000
  Dipole Oscillator Strength                0.04429

  Occ.   1  a   ---  Virt.   8  a    -0.89542
  Occ.   1  a   ---  Virt.  12  a    -0.29239
  Occ.   1  a   ---  Virt.  13  a     0.20379
  Occ.   1  a   ---  Virt.  15  a     0.12786
  Occ.   1  a   ---  Virt.  16  a    -0.13234
  Occ.   1  a   ---  Virt.  22  a    -0.10334
  Occ.   1  a   ---  Virt.  23  a     0.10010
  Occ.   1  a   ---  Virt.  31  a    -0.05352
  Occ.   1  a   ---  Virt.  34  a    -0.06341
  Occ.   1  a   ---  Virt.  35  a     0.06832
-------------------------------------------------------------------------
Root   2 singlet a          19.446988682 a.u.          529.1797 eV
-------------------------------------------------------------------------
  Transition Moments    X  0.04263   Y  0.03998   Z  0.00000
  Transition Moments   XX  0.00000  XY  0.00000  XZ -0.00052
  Transition Moments   YY  0.00000  YZ -0.00048  ZZ  0.00000
  Dipole Oscillator Strength                0.04429

  Occ.   1  a   ---  Virt.   9  a     0.89542
  Occ.   1  a   ---  Virt.  12  a    -0.20379
  Occ.   1  a   ---  Virt.  13  a    -0.29239
  Occ.   1  a   ---  Virt.  15  a     0.13234
  Occ.   1  a   ---  Virt.  16  a     0.12786
  Occ.   1  a   ---  Virt.  22  a    -0.10010
  Occ.   1  a   ---  Virt.  23  a    -0.10334
  Occ.   1  a   ---  Virt.  30  a    -0.05352
  Occ.   1  a   ---  Virt.  34  a     0.06832
  Occ.   1  a   ---  Virt.  35  a     0.06341
```

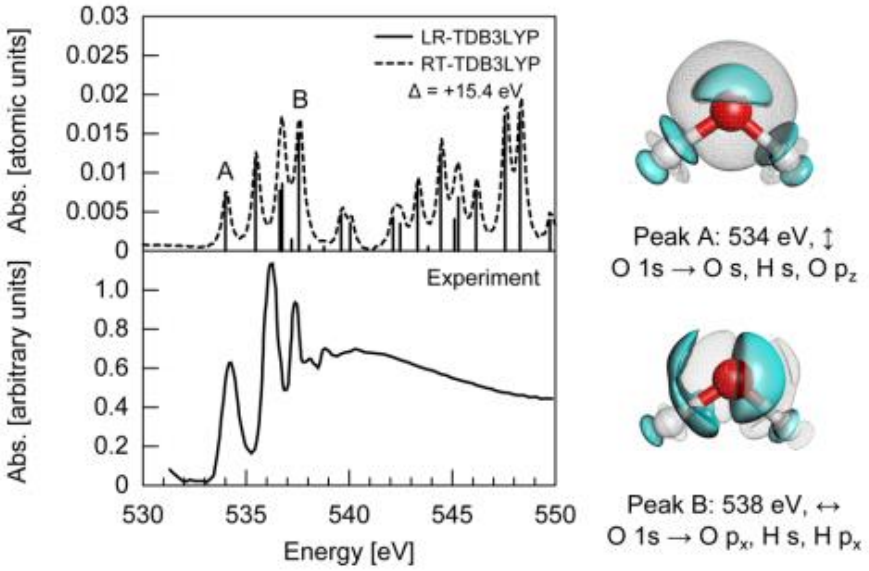
Pre- & Near-Edge X-ray Spectrum



Energy (eV)

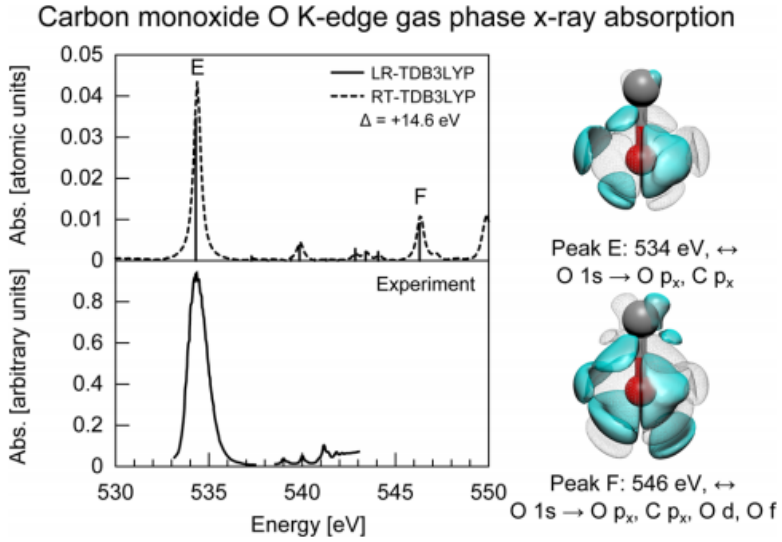
O K-edge in Water and O, C K-edges in CO

EMSL



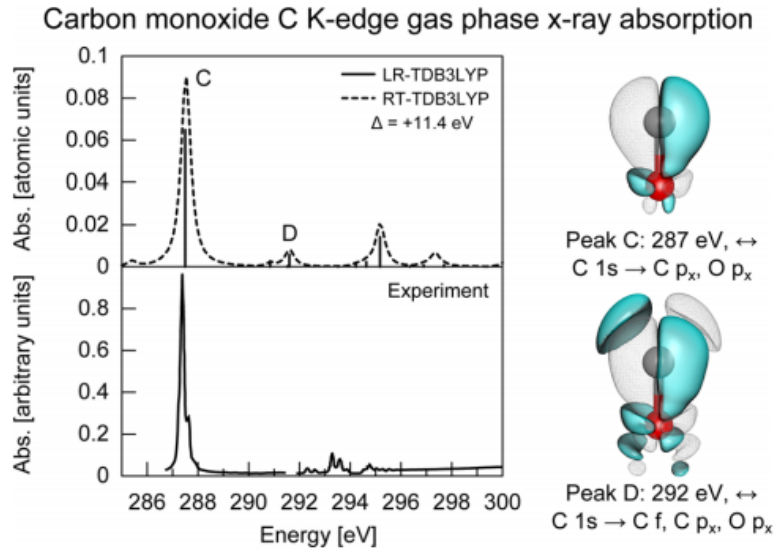
Peak A: 534 eV, ↕
O 1s → O s, H s, O p_z

Peak B: 538 eV, ↔
O 1s → O p_x, H s, H p_x



Peak E: 534 eV, ↔
O 1s → O p_x, C p_x

Peak F: 546 eV, ↔
O 1s → O p_x, C p_x, O d, O f

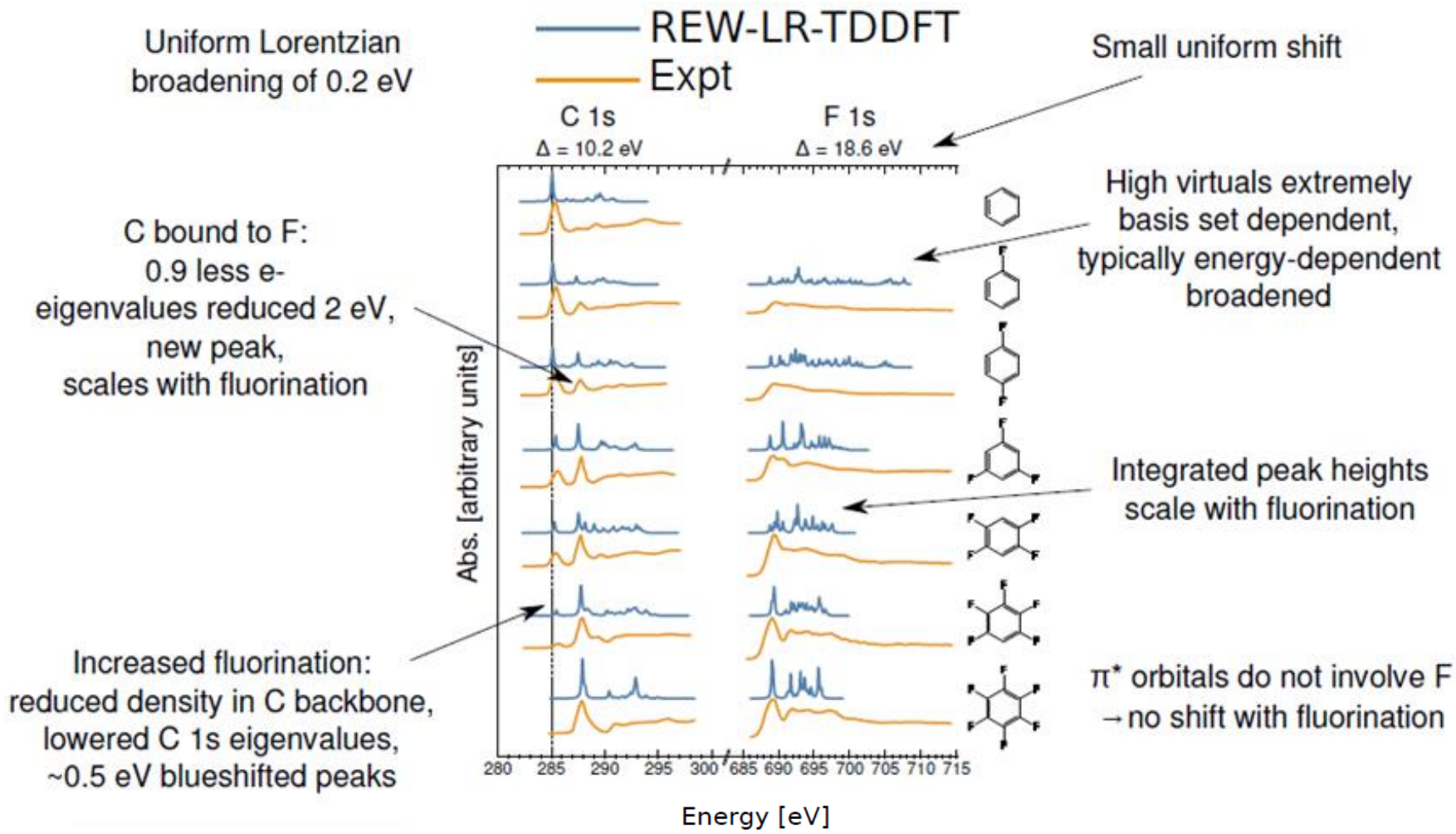


Peak C: 287 eV, ↔
C 1s → C p_x, O p_x

Peak D: 292 eV, ↔
C 1s → C f, C p_x, O p_x

JCTC, 8, 3284 (2012)

C & F K-edge in Fluorobenzenes

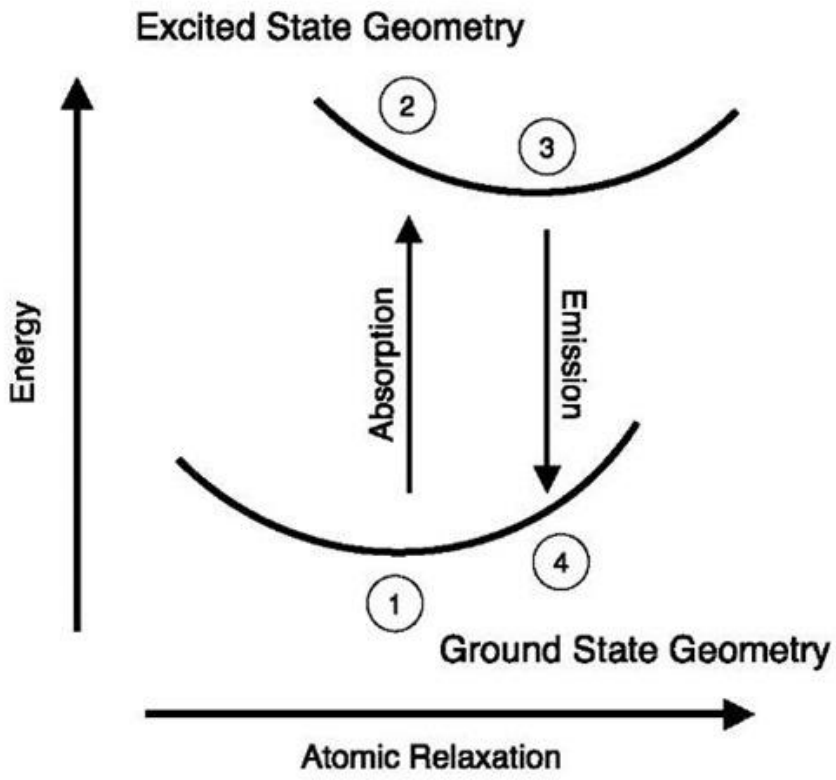


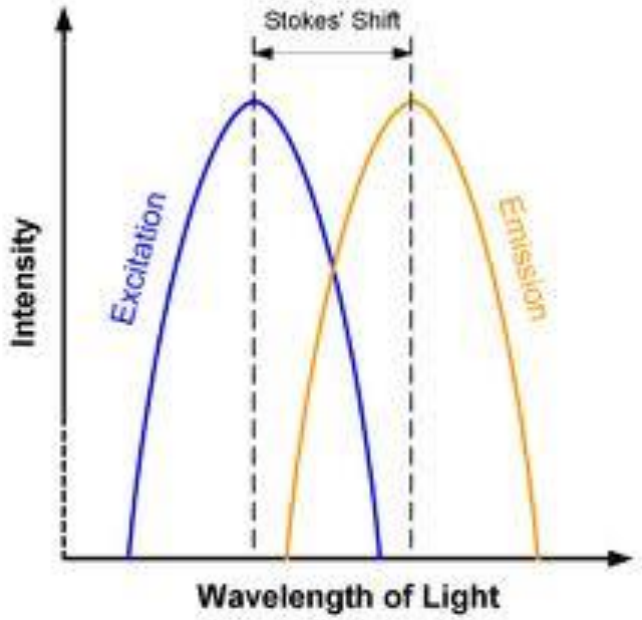
JCTC, 8, 3284 (2012)

TDDFT Excited-State Gradients

EMSL

TDDFT optimization on the excited state





TDDFT Excited-State Gradients -Sample

```
dft
 maxiter 500
 xc b3lyp
 direct
end

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

See examples at:
https://github.com/nwchemgit/nwchem/wiki/Excited-State-Calculations

TDDFT Transition Density -Sample

```
tddft
  nroots 5
  notriplet
  civecs
end
task tddft energy

dplot
 civecs h2o-td.civecs_singlet
 root 2
 LimitXYZ
-3.74335 2.47044 50
-2.23369 3.35028 50
-2 3.06035 50
 gaussian
 output root-2.cube
end
task dplot
```

See examples at:
https://github.com/nwchemgit/nwchem/wiki/Excited-State-Calculations

Real-Time TDDFT (RT-TDDFT)

EMSL

RT-TDDFT is a DFT-based approach to calculate electronic excited states based on integrating the time-dependent Kohn-Sham (TDKS) equations in time

RT-TDDFT calculation steps:

- Compute ground state density matrix with DFT module
- Propagate density matrix using RT-TDDFT
- Post-process resulting time-dependent observables (e.g., dipole moment)

See worked examples and post-process scripts:

- Absorption spectrum of water
- Resonant ultraviolet excitation of water
- Charge transfer between TCNE dimer

https://github.com/nwchemgit/nwchem/wiki/RT-TDDFT