DALTON 2011: Practical Hands-on Materials

CECAM workshop "High Performance Computing in Computational Chemistry and Molecular Biology: Challenges and Solutions provided by ScalaLife project"

Oct. 3 and 5, CECAM-HQ-EPFL, Lausanne, Switzerland

Modeling of linear and non-linear optical properties: charge transfer systems

This part of hands-on session covers computations of various linear and non-linear properties using RESPONSE module of DALTON 2011 program, and it is divided into four separate exercises. Each of these exercises is designed to demonstrate the different aspects of optical properties modeling using DALTON 2011 program, as well as to draw your attention to limitations of various *ab initio* and time dependent density functional theory methods (TD-DFT) employed in these projects. More specifically, this hands-on session includes exercises in computation of following optical properties: 1) one-photon absorption using TD-DFT and CC2 methods; 2) two-photon absorption using TD-DFT methods; 3) dynamic second hyperpolarizability using TD-DFT methods; 4) excited state polarizability using TD-DFT methods. All above enumerated calculations will be carried out simplest possible model of charge transfer dye (see Fig. 1) constructed from ethylene by substituting one hydrogen with electron donor group (-NH_2) and other hydrogen with electron acceptor group (-CN). Assuming that most of you have attended lecture on DALTON 2011 program and thus are already familiar with basic structure of DALTON 2011 input files, here we will give molecular geometry input file used by DALTON 2011 program for this model system without any additional explanations:

```
BASIS
aug-cc-pVDZ
NH2HC=CHCN.A Model charge transfer
system.
-------------------------------------------------------------
Atomtypes=3 Angstrom
Charge=7.0 Atoms=2
N     1.188678    0.000000   -2.031876
N    -0.003855    0.000000    2.621171
Charge=6.0 Atoms=3
C    -0.030196    0.000000    0.051264
C    -0.005603    0.000000    1.464112
C     1.107517    0.000000   -0.677869
Charge=1.0 Atoms=4
H    -1.004085    0.000000   -0.425110
H     2.065741    0.000000   -0.171351
H     2.078067    0.000000   -2.494811
H     0.364244    0.000000   -2.607206
```

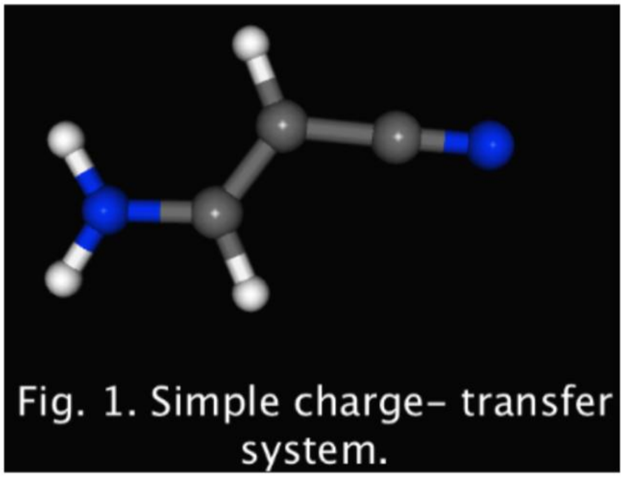

Fig. 1. Simple charge- transfer system.

Above described model system has C_s symmetry, which is automatically detected by DALTON 2011 program, all TD-DFT as well as CC2 calculations are carried taking advantage of molecular symmetry (symmetry adapted atomic and molecular orbitals are used, Fock and other operators partitioned according to irreducible representations of this symmetry group). Before, we proceed to description of each exercise, we would like to draw your attention to electronic structure as well as to localization and composition of lowest occupied and unoccupied molecular orbitals in our model system, as the familiarity with these features of model system is a key for understanding optical processes in this system. Ground state of our model system is closed-shell singlet (1^1A’, with 15 doubly occupied orbitals of a’ symmetry and 3 occupied orbitals of a’’ symmetry), and is well described by single Slater determinant (static electron correlation in ground state is negligible). According to B3LYP/cc-pVTZ calculations, HOMO and LUMO orbitals (a’’ symmetry) are delocalized over whole molecule (see Fig. 2), and thus one can expect that lowest excited state to be of A’ symmetry.

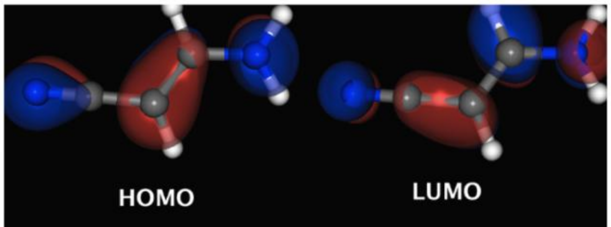

Figure 2. HOMO and LUMO orbitals.

Exercise I: One-photon absorption calculations

In this exercise you will compute two lowest excited states of each symmetry in our model system using TD-DFT (B3LYP and CAM-B3LYP exchange-correlation functionals) and approximate second order coupled cluster (CC2) methods. In DALTON 2011 program both types of calculations can be carried out using direct algorithm without storing two-electron integrals on disk, but only TD-TDFT calculation can be performed in parallel. Below we provide DALTON.INP files for both types of calculations. In order to run CAM-B3LYP calculations you should uncomment .CAMB3LYP keyword and comment out B3LYP keyword in exchange-correlation functional definition section.

*Input file for TD-DFT B3LYP/CAM-B3LYP calculation*s:

```
**GENERAL
.RUN RESPONSE
.DIRECT
#.PARALLEL              ! Uncomment for running in parallel
**WAVE FUNCTION
.DFT
B3LYP                   ! Comment out for running CAM-B3LYP
#CAMB3LYP               ! Uncomment for running CAM-B3LYP
**RESPONS
*LINEAR
.DIPLEN
.SINGLE
.PRINT                  ! Comment out for reducing output size
4                       ! Comment out for reducing output size
```

```
.ROOTS
 2 2
*END OF
```

Correct TD-DFT results

B3LYP (1 A'' – 4.69 eV, 2 A'' – 5.33 eV, 2 A' -5.49 eV, 3 A' - 6.80 eV)

CAM-B3LYP (1 A'' – 5.13 eV, 2 A'' – 5.71 eV, 2 A' -5.60 eV, 3 A' – 7.07 eV)

Input file for CC2 calculations:

```
**GENERAL
.RUN WAVE FUNCTIONS
**WAVE FUNCTIONS
.CC
*CC INPUT
.CC2                                    ! Change for different coupled cluster model (CCSD, CC3)
.NSYM
  2
*CCEXCI
.NCCEXCI
 2 2
 0 0
*END OF
```

Correct CC2 results

CC2 (1 A'' – 5.06 eV, 2 A'' – 5.72 eV, 2 A' -5.68 eV, 3 A' – 7.01 eV)

Exercise II: Two-photon absorption calculations

In this exercise you will compute two-photon absorption cross-section for two lowest excited states of each symmetry in our model system using TD-DFT method. Similarly, to previous exercise we will employ B3LYP and CAM-B3LYP exchange-correlation functionals in these calculations. In DALTON 2011 program all types of TD-DFT calculations can be carried out using direct and parallel approach, and thus similar strategy can be used as in previous exercise. Below we provide DALTON.INP file for two-photon absorption calculations.

Input file for TD-DFT B3LYP/CAM-B3LYP calculations:

```
**GENERAL
.RUN RESPONSE
.DIRECT
.PARALLEL
**WAVE FUNCTION
.DFT
B3LYP                    ! Comment out for running CAM-B3LYP
#CAMB3LYP                ! Uncomment for running CAM-B3LYP
**RESPONS
*QUADRATIC
.SINGLE
.TWO-PHOTON
.ROOTS
 2 2
*END OF
```

Exercise III: Dynamic second hyperpolarizability calculations

In this exercise you will compute static and dynamic (at 0.03 a.u. incoming photons energy) second hyperpolarizability corresponding to third harmonic generation using cubic TD-DFT response code, which is unique feature of DALTON 2011 program. Currently, this type of nonlinear optical processes can be properly modelled only using DALTON 2011 program. Below we provide DALTON.INP file for second hyperpolarizability calculations.

Input file for TD-DFT B3LYP/CAM-B3LYP calculations:

```
**GENERAL
.RUN RESPONSE
.DIRECT
.PARALLEL
**WAVE FUNCTION
.DFT
B3LYP                    ! Comment out for running CAM-B3LYP
#CAMB3LYP                ! Uncomment for running CAM-B3LYP
**RESPONS
*CUBIC
.DIPLEN
.THG
.FREQUE
 2
0.00 0.03
*END OF
```

Exercise IV: Excited state polarizability calculations

In this exercise you will compute polarizability of lowest excited state in our model system using single residue of cubic TD-DFT response function. Similarly to previous exercise, in this last exercise you will again be using cubic TD-DFT code, which is unique to DALTON 2011 program. Below we provide DALTON.INP file for lowest excited state polarizability calculations.

*Input file for TD-DFT B3LYP/CAM-B3LYP calculation*s:

```
**GENERAL
.RUN RESPONSE
.DIRECT
.PARALLEL
**WAVE FUNCTION
.DFT
B3LYP                   ! Comment out for running CAM-B3LYP
#CAMB3LYP               ! Uncomment for running CAM-B3LYP
**RESPONS
*CUBIC
.DOUBLE RESIDUE
.DIPLEN
.BFREQ
 1
0.00
.ROOTS
  0 1
.MAXITO
 100
.MAX IT
 100
.MAXITP
 100
*END OF
```