

NANCY_EX User Manual – Version 2.0

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NANCY_EX is a suite of codes developed in the “Théorie-Modélisation-Simulation” team of the University of Lorraine (SRSMC laboratory), France. It is designed to post-process Gaussian03 and Gaussian09 TDDFT (or CIS) outputs in order to get informations on the excited states nature. In particular analyses based on Detachment/Attachment density matrices and Natural Transition Orbitals are considered. Furthermore, a quantitative insight into the topology of excited states is provided by the assessment of various quantum mechanical descriptors.

All codes in NANCY_EX are produced under the term of the GPL license. The codes are free of charge and free to be distributed or modified under the terms of the GPL license. Codes come with absolutely no guarantee. Authors deny any responsibilities on every damage possibly occurring by the use of any of the present codes.

Every publication arising by using the NANCY_EX 2.0 code should appropriately cite the related literature:

- [1] Etienne, T., Assfeld, X., Monari, A., 2014. Toward a Quantitative Assessment of Electronic Transitions’ Charge-Transfer Character. *J. Chem. Theory Comput.* 10, 3896-3905.
- [2] Etienne, T., Assfeld, X., Monari, A., 2014. New Insight into the Topology of Excited States through Detachment/Attachment Density Matrices-Based Centroids of Charge. *J. Chem. Theory Comput.* 10, 3906-3914.
- [3] Etienne, T., 2015. Probing the Locality of Excited States with Linear Algebra. *J. Chem. Theory Comput.* doi:10.1021/ct501163b

The manual is organized as follows:

1. Theoretical Foundations

1.1. Detachment/Attachment Density Matrices

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1 Theoretical Foundations

We are dealing with the analysis of the excited states nature of a N -electron system in the framework of single reference quantum chemical methods, namely TDDFT and CIS, with a K -sized basis set¹. The canonical picture of an electronic transition consists in an expansion weighting the excitations from each occupied molecular orbital i to virtual molecular orbitals a . It may appear that multiple couples of i -to- a excitation have a consequent relative contribution, making the interpretation of the physical nature of the excited state rather cumbersome. Fortunately several transformations and tools can allow a more straightforward analysis. The subsequent paragraphs briefly relate in a qualitative manner the plot of these operations.

For more mathematical details we kindly invite the reader to consult the references [1] to [3].

1.1 Detachment/Attachment Density Matrices

This first class of analysis involves density matrices. Indeed, the first step consists in taking the difference between excited and ground states density matrices

$$\mathbf{\Delta} = \mathbf{P}_X - \mathbf{P}_0 \Rightarrow \sum_{k=1}^K (\mathbf{\Delta S})_{kk} = 0 \quad (1)$$

and to diagonalize the so-called difference density matrix $\mathbf{\Delta}$ into $\mathbf{\delta}$

$$\exists \mathbf{U} \mid \mathbf{\delta} = \mathbf{U}^\dagger \mathbf{\Delta} \mathbf{U} ; (\delta)_{ij} = 0 \quad \forall i \neq j \quad (2)$$

The entries of the diagonal matrix obtained after this first step are further split into two arrays σ_\pm according to their signs

$$(\sigma_\pm)_{kj} = \frac{1}{2} \left(\sqrt{(\delta)_{kk}^2} \pm (\delta)_{kk} \right) \times \delta_{kj} \mid \mathbf{\delta} = \sum_{\omega=+,-} \omega \sigma_\omega \quad (3)$$

¹For the sake of simplicity, we assume that there is no linear dependency in the basis set.

and the resulting two diagonal matrices are finally backtransformed in order to obtain the Detachment $\mathbf{\Gamma}$ and Attachment $\mathbf{\Lambda}$ Density Matrices

$$\left. \begin{aligned} \mathbf{\Delta} &= \mathbf{U}\delta\mathbf{U}^\dagger \\ \mathbf{\Gamma} &= \mathbf{U}\sigma_-\mathbf{U}^\dagger \\ \mathbf{\Lambda} &= \mathbf{U}\sigma_+\mathbf{U}^\dagger \end{aligned} \right\} \Rightarrow \mathbf{\Delta} = \mathbf{\Lambda} - \mathbf{\Gamma} \quad (4)$$

Detachment symbolizes the depletion of electron density occuring upon light-absorption. Conversely, Attachment depicts the electron density increment in the excited state. A proper plot of these density matrices in the real 3D-space gives the $\rho_{\mathbf{\Gamma}}$ and $\rho_{\mathbf{\Lambda}}$ densities and provides a qualitative depiction of the nature of the excited state.

1.2 Natural Transition Orbitals & Canonical Transition Orbitals

If now instead of taking ground and excited states density matrices we rather use the so-called rectangular Transition Density Matrix \mathbf{T}' expressed in the molecular orbitals basis, we see that another possible analysis can be formally derived from its singular value decomposition. This operation can be performed with the help of two unitary matrices \mathbf{O} and \mathbf{V}

$$\mathbf{W} = \mathbf{O}^\dagger \mathbf{T}' \mathbf{V} \quad (\mathbf{W})_{ij} = w_i \delta_{ij} \quad (5)$$

Those are further used to perform a rotation over the canonical occupied and virtual spaces in order to derive the so-called Occupied and Virtual Natural Transition Orbitals (NTOs)

$$\psi_k^o = \sum_{i=1}^N (\mathbf{O})_{ik} \mathbf{c}^i \quad \psi_k^v = \sum_{i=1}^{K-N} (\mathbf{V})_{ik} \mathbf{c}^s \quad (k = 1, \dots, N) \quad (6)$$

The interesting advantage of NTOs analysis with respect to canonical orbitals lies in the fact that most often one couple of NTOs clearly prevails, which makes the excited state analysis really straightforward.

Note that in addition to its easy interpretation, NTOs analysis takes another advantage when compared for instance to Detachment/Attachment Density Matrices: the orbitals relative phase.

Moreover, it is possible to derive Occupied and Virtual Density Matrices from LCAO-NTOs coefficients and the singular values

$$(\mathbf{P}^o)_{ij} = \sum_{l=1}^N w_l^2 (\mathbf{C}^o)_{il} (\mathbf{C}^o)_{jl} \quad (\mathbf{P}^v)_{ij} = \sum_{l=1}^N w_l^2 (\mathbf{C}^v)_{il} (\mathbf{C}^v)_{jl} \quad (7)$$

These two novel density matrices actually have an interesting feature: their difference is, up to a sign, identical to the difference density matrix, which makes possible the derivation of NTOs-based $\mathbf{\Gamma}$ and $\mathbf{\Lambda}$ density matrices

$$\mathbf{P}_X - \mathbf{P}_0 = \mathbf{P}^v - \mathbf{P}^o \quad (8)$$

Alternatively, if instead of considering the Transition Density Matrix (based on additive representation of (de)excitation vector components in the case of TDHF/TDDFT-like methods, see the related literature on the transition density kernel) one considers the Canonical Transition Density Matrix, which components are constructed from the relative weight of each canonical orbital couple in the (de)excitation expansion, he/she obtains the so-called Canonical Transition Orbitals (CTO's). The general scheme remains identical to the one relative to the obtention of the NTO's, apart for the target matrix \mathbf{T}' being replaced by $\mathbf{\Gamma}'$. For more details about the CTOs, see reference [4].

[4] T. Etienne, *Transition Matrices and Orbitals from Reduced Density Matrix Theory*, Submitted.

1.3 Quantum Mechanical Descriptors

The charge-transfer ability of a chromophore can easily be quantitatively assessed through a simple quantum mechanical descriptor, the so-called ϕ_S index. This index consists in a measure of the Detachment/Attachment densities spatial overlap in the 3D-real space

$$\phi_S = \vartheta^{-1} \int_{\mathbb{R}^3} d^3\xi \sqrt{\varrho_{\mathbf{\Gamma}}(\xi) \varrho_{\mathbf{\Lambda}}(\xi)} \quad \vartheta \equiv \frac{1}{2} \left[\int_{\mathbb{R}^3} d^3\xi \sum_{\tau=\mathbf{\Gamma},\mathbf{\Lambda}} \varrho_{\tau}(\xi) \right] \quad \phi_S \in [0; 1] \quad (9)$$

As we previously saw, these densities can equivalently be obtained subsequently to a NTO analysis; so does the ϕ_S index.

Note that a low value (close to zero) for the ϕ_S descriptor implies that the considered excited state has a long-ranged charge-transfer character. Conversely, a ϕ_S value close to one depicts a local nature for the target excited state.

Similarly, some other indices ζ and $\tilde{\zeta}_{\pm}$ (based on $\varrho_{\mathbf{\Gamma}}$ and $\varrho_{\mathbf{\Lambda}}$ centroids of charge analysis) together with a direct-space charge-transfer integral $\tilde{\chi}$ can be derived. Those are reported in Reference [2].

A more general descriptor, ψ , conciliating the formal origins of ϕ_S and a normalized variant of χ ($\tilde{\varphi}$) is also derivable in this suite of codes but has not been published yet. It is reported in the reference [3].

Note that the values of ϕ_S , $\tilde{\varphi}$, and ψ descriptors for a given molecular excited state can be approached through linear algebra, as reported in [3].

2 Installation

NANCY_EX is a Fortran90 code. In order to install it you will need to have a proper Fortran compiler. Intel Fortran compiler or gfortran are proved to be quite efficient. The code uses BLAS and LAPACK mathematical libraries in order to assure performance. You therefore need to have working LAPACK installed on your system. If you are using Intel Fortran compiler we recommend you to use the proper mkl libraries since the maximal performance is achieved. If you are reading this manual

it means you already had access to the repository web site. In order to use the code you should download on your system the source in a gzipped tar file. To proper compile the code you need to have a working gmake utility on your system. (The latter being provided by default in almost every linux/unix distribution). Once downloaded, unpack the sources

```
tar -zxvf nancy_ex_2.0.tgz
```

Move to the newly created directory NANCY_EX

```
cd NANCY_EX/src
```

You are now in the source directory, you can find a *makefile*, already working in case of a standard intel Fortran compiler plus mkl installation. If you want to change the compiler or the libraries open the file and change the values of the variables FC (compiler) and LFLAGS (libraries). Note that the values for gfortran are already given in a commented text line, if you want to use such a compiler and corresponding libraries, please uncomment the corresponding lines (and comment the ones referring to intel). Make sure that the tags \$() and -o are correctly placed according to the type of compiler you are using. Once you have edited the makefile simply type “make”. This will produce the executable Nex that will be placed in the directory main NANCY_EX directory, so you are now ready to use the code.

As usual if you want to clean the environment from binary fortran files just use the command

```
make clean
```

If you want to run the code on a Windows machine you should be aware that we performed no test on it. Anyway provided you dispose of the proper fortran compiler and library the executable should work also in that environment. In order to compile please set the appropriate path for compiler/library.

3 How to use it

3.1 Gaussian Input and Files

In order to use NANCY_EX 2.0 you need some informations and files provided by Gaussian (03 or 09) during CIS/TDA or TDHF/TDDFT calculation. The following keywords should be present in your Gaussian input file in order to properly use NANCY_EX

```
%chk = chk_filename.chk
```

```
%rwf = rwf_filename.rwf
```

```
X = (Nstates = N)
```

where X stands for “CIS” or “TD” or “TDA” and N is the number of states (minimum 3) to be computed.

After the Gaussian calculation has completed normally, the first three steps consists in processing the .rwf and .chk files with the help of rwdump and formchk utilities respectively to generate the basis

set overlap “overlap_filename” and density “density_filename” files, together with the formatted chk file with the extension “.fchk”

```
formchk chk_filename.chk
```

```
rwfdump rwf_filename.rwf overlap_filename 514r
```

```
rwfdump rwf_filename.rwf density_filename 633r
```

3.2 Input and Running

Input preparation

Depending on which calculation you wish to perform, your input should contain distinct informations. Note that in the following, the cubes to be used must have been generated with the cubegen utility and the proper keyword producing an ultrafine grid (option -3 or -4 are mandatory. For more informations, see the cubegen utility manual) for the sake of accuracy in the numerical integration that have to be performed.

1) Detachment/Attachment densities

```
dadens
```

```
fchk filename
```

```
overlap_filename (from rwfdump)
```

```
density_filename (from rwfdump)
```

```
Nstates state (Total number of states; State of interest)
```

```
‘T’ if relaxed density was computed (density = all in the Gaussian input file). ‘F’ if not.
```

2) NTO’s (CTO’s)

```
ntos (canonical)
```

```
gaussian version used (‘g03’ or ‘g09’)
```

```
.fchk filename
```

```
overlap_filename (from rwfdump)
```

```
density_filename (from rwfdump)
```

```
Nstates State (Total number of states; State of interest)
```

```
‘V’ if you want to print the first NTO (CTO) couple coefficients
```

```
(otherwise simply let an empty line at the end of your input)
```

3) ϕ_S index

This part of the code requires cube files generated with the cubegen utility, processing .fchk files produced by D/A, NTOs or CTOs subroutines. “phis” should be the first line of this input. The content of the following lines depends on which type of ϕ_S calculation you want to perform

- ‘dadens’ means that the cubes are generated from detachment/attachment density matrices (ddens.fchk and adens.fchk) and the cubegen utility using the fdensity = scf keyword. The whole input is

phis

dadens

detachment density cube filename

attachment density cube filename

- ‘ntoscouple’ (‘ctoscouple’) means that one couple of NTO’s (CTO’s) prevailed and that the ϕ_S index will be evaluated according to the square of occupied and virtual (Canonical) Natural Transition Orbitals moduli (see for instance ϕ'_S in [1]). The cube to use has therefore been generated from the nto.fchk (cto.fchk) file with cubegen and the option MO=1,2

phis

ntoscouple (ctoscouple)

nto (cto) cube filename

- ‘ntosdensity’ (‘ctosdensity’) means that all the couples of NTO’s (CTO’s) are used to express Occupied and Virtual density matrices (see for instance ϕ_S^{NTO} in [1]).

phis

ntosdensity (ctosdensity)

fchk filename

NTOs (CTOs) based detachment density cube filename (generated from occ**ddens***N.fchk* (occ**ddens***C.fchk*) with cubegen utility)

NTOs (CTOs) based attachment density cube filename (generated from virt**adens***N.fchk* (virt**adens***C.fchk*) with cubegen utility)

4) Centroid-based indices from GS/ES densities. The program requires ground and excited states densities .cube files.

gses

Ground state density cube filename

Excited state density cube filename

Using the code

Once your input file is ready, you can simply run the NANCY_EX processing by typing the following command in your terminal:

```
path_to_NANCY_EX_folder/Nex < input_filename
```

Other executable files

The executable files are located in a sub-directory named “executables”. Feel free to modify their contents according to your preferences and the location of your utilities.

- nto.sh, cto.sh and da.sh can be similarly used with the following arguments:

1. the name of the .fchk file
2. total number of states

3. state of interest
4. overlap filename
5. density filename

- highcube utility can be used to obtain a header that can further be provided to cubegen for enlarging an existing cube. First you should write in an individual file (“i-s” for instance) the percentage s of increase you want (each coordinate scale will be increased by this percentage - example: “27” for 27 percents of increase). For this purpose, use the following arguments:

1. the name of the original .cube file
2. i-s

The highcube utility will output a report in the terminal and will produce two files: “newheader-to-use” (the one to input to cubegen with the proper options - see cubegen manual) and “expected-newheader” (the one expected to be output by cubegen after cube enlargement). This utility is important when the integration over all the space of Detachment and Attachment densities is not identical (which usually means that one of the density cubes is not large enough, so that a fraction of the density is lost in the integration - the cube should be enlarged with the highcube and cubegen utilities to recover the correct spatial distribution).

- diffcubes and addcubes can be used to manipulate two cubes cube1 and cube2 in order to obtain a third one cube3 (diffcubes: $\text{cube3} = \text{cube1} - \text{cube2}$; addcubes: $\text{cube3} = \text{cube1} + \text{cube2}$). The arguments should be the filenames of cube1, cube2 and cube3 successively.

- phiS.sh can be used for the original definition of the ϕ_S index. The two arguments are simply the Detachment and Attachment cubes filenames.

Warnings and Notes

- When performing the NTOs (CTOs) calculation. The code first checks the orthonormality of the input Molecular Orbitals

$$\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1} \quad (10)$$

After performing the SVD, the code checks the outcome of different tests (this is also the case for CTO’s calculations): the first one checks the validity of relation (17) in [1]

$$\mathbf{O}^\dagger \mathbf{T}' \mathbf{T}'^\dagger \mathbf{O} = \mathbf{Y} \quad \mathbf{V}^\dagger \mathbf{T}'^\dagger \mathbf{T}' \mathbf{V} = \mathbf{Z} \quad \sum_{i=1}^N (\mathbf{Y})_{ii} = \sum_{j=1}^{K-N} (\mathbf{Z})_{jj} \equiv \sum_{kk}^N (\mathbf{W})_{kk} \quad (11)$$

the second one checks the validity of (38) in [1]

$$\mathbf{O} \mathbf{O}^\dagger = \mathbf{1}^o \quad (N \times N) \quad \mathbf{V} \mathbf{V}^\dagger = \mathbf{1}^v \quad (K - N \times K - N) \quad (12)$$

and the third test checks the reversibility of the SVD

$$\mathbf{W} = \mathbf{O}^\dagger \mathbf{T}' \mathbf{V} \Leftrightarrow \mathbf{T}' = \mathbf{O} \mathbf{W} \mathbf{V}^\dagger \quad (13)$$

- Values for ϕ_S , $\tilde{\chi}$, $\tilde{\varphi}$ and ψ reported after Detachment/Attachment or NTOs calculations are just approximations made from Linear Algebra.
- Please always check that the relations (1) and (5) of [1] are verified when computing Detachment/Attachment density matrices. For relation (5) the result should be higher or equal to one. So does the sum of squared singular values in NTOs computation.
- When computing ϕ_S from Detachment/Attachment density cubes, please cross-check that the integral over all the space of Detachment (Attachment) is exactly the trace of \mathbf{fS} (\mathbf{AS}). If not, see the highcube utility details above.
- If the code is supposed to post-process unrestricted calculations, it will automatically detect that the number of alpha and beta electrons is not equal.
- We highly recommend not to use the relaxed densities provided by Gaussian for densities analyses (Detachment/Attachment and ϕ_S).
- NTOs (CTOs) computation also outputs occupied and virtual density matrices in `occddensN.fchk` (`occddensC.fchk`) and `virtddensN.fchk` (`virtddensC.fchk`), the NTOs (CTOs)-based detachment and attachment density matrices in `occadensN.fchk` (`occadensC.fchk`), `virtadensN.fchk` (`virtadensC.fchk`) and the XT (X-T), YT (Y-T) and T (X2-Y2) files which respectively contain the X, Y vectors and the Transition Density Matrix (the $(\mathbf{X})_{ic}^2 - (\mathbf{Y})_{ic}^2$ entries, with $c = a - N$).
- When computing the ϕ_S index value, please cross-check that the integral over all the space of Detachment and Attachment densities are equal (up to 0.01).
- Due to the possibility of non-physical orbital occupations in the Mulliken Population Analysis, the outcome of the approximation to the charge-transfer integral from the Mulliken Detachment/Attachment Population Analysis may appear to be higher than one. Caution is therefore mandatory for the analysis of these results.
- CTO's are not aiming at exactly reproducing the results from NTO's analysis since their formal definition differs. It is indeed clear that the CTO's-derived ϕ_S , $\tilde{\chi}$, $\tilde{\varphi}$ and ψ indices values might be different than the NTO's-derived ones when the de-excitation processes become significant. However, the deviation of the CTOs with respect to the NTOs remains very low, so that the two analyses are exactly consistent.
- When using GS/ES densities with the `gses` keyword, please make sure that your cube is sufficiently large with a very high resolution in order to obtain the proper integral value of the densities.
- Relaxed density (density=all keyword in gaussian input) analyses are implemented, but their use (Detachment/Attachment densities; QM descriptors) is highly discouraged.

3.3 Visualize Orbitals and Densities

From .fchk files, you can use the cubegen utility with the proper options in order to generate cubes (with orbitals (NTOs) using the option MO=1,2 for the first couple, MO=3,4 for the second one, etc. or densities (Detachment/Attachment) with the option fdensity=scf and the proper .fchk files) that may be exported and visualized with the help of a visualization software (GaussView or Avogadro for instance). Note that in the case of NTOs if you have performed an unrestricted calculation, you will obtain two sets of NTOs: alpha and beta. Therefore, their visualization requires a more specific keyword: AMO=1,2 for the first alpha NTOs couple or BMO=1,2 for the first NTOs couple.

4 Examples and Screenshots

We present here an example of a difficult situation in which the use of Detachment/Attachment densities or NTO's are of extreme importance to get a reliable analysis of an excited state. We consider a compound, **1**, which is a Ruthenium complex characterized by a bipyridinil moiety (bpy) and by a dipyridophenazine (dppz) unity as shown in Figure 1.

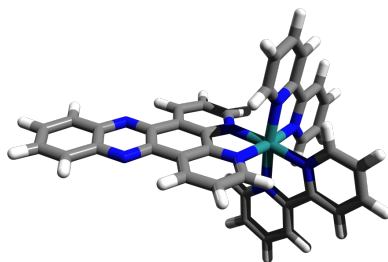


Figure 1 – The ruthenium-based complex structure **1**.

If one considers the excitation eight, it appears that this excited state is represented in the Kohn-Sham molecular orbital base by 6 orbitals (three occupied and three virtual) as shown in Figure 2. Moreover the weight coefficients are almost all of the same magnitude.

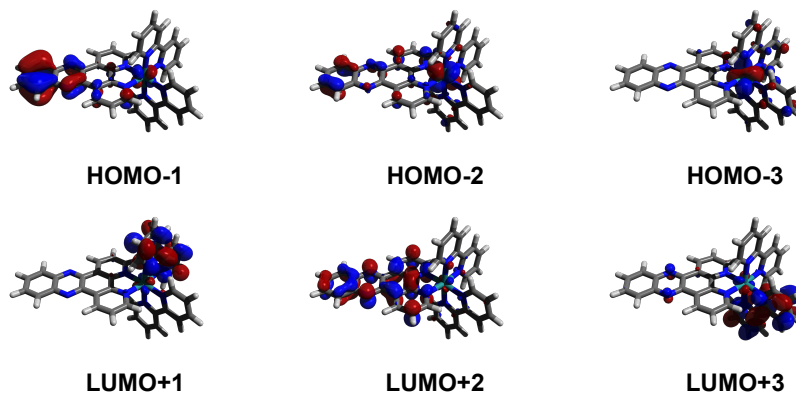


Figure 2 – The Kohn-Sham orbitals involved in the transition 8 of the ruthenium-based complex **1**.

If on the other hand one performs the NTO's analysis, the expansion NTO is found to be dominated by two singular values. The corresponding "Occupied" and "Virtual" NTO's are represented in Figure 3. It is evident that the transition has a MLCT character, and the excited state has an electron density

mostly concentrated on the dppz unit, with anyway a smaller but not negligible participation of the bpy moiety.

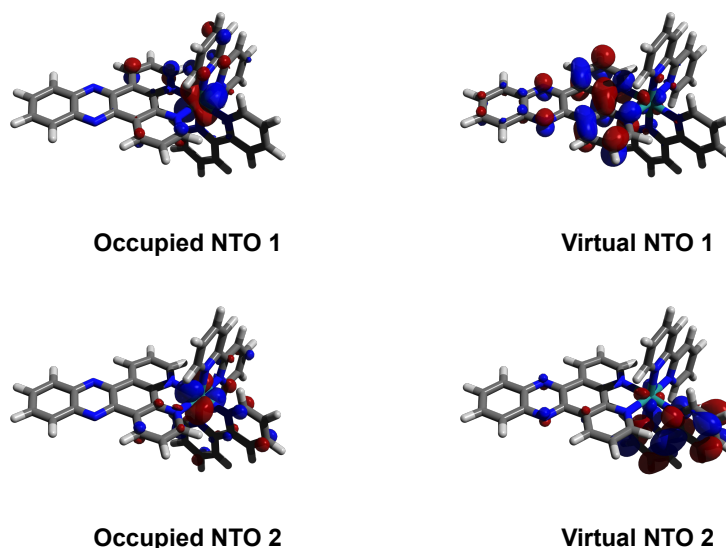


Figure 3 – Most important NTO's for transition 8 of compound **1**.

Finally if Detachment/Attachment densities are considered (Figure 4) one can get a complete picture of the transition, note that the Detachment/Attachment picture bears a strong similarity with the union of the two dominant NTO couples.



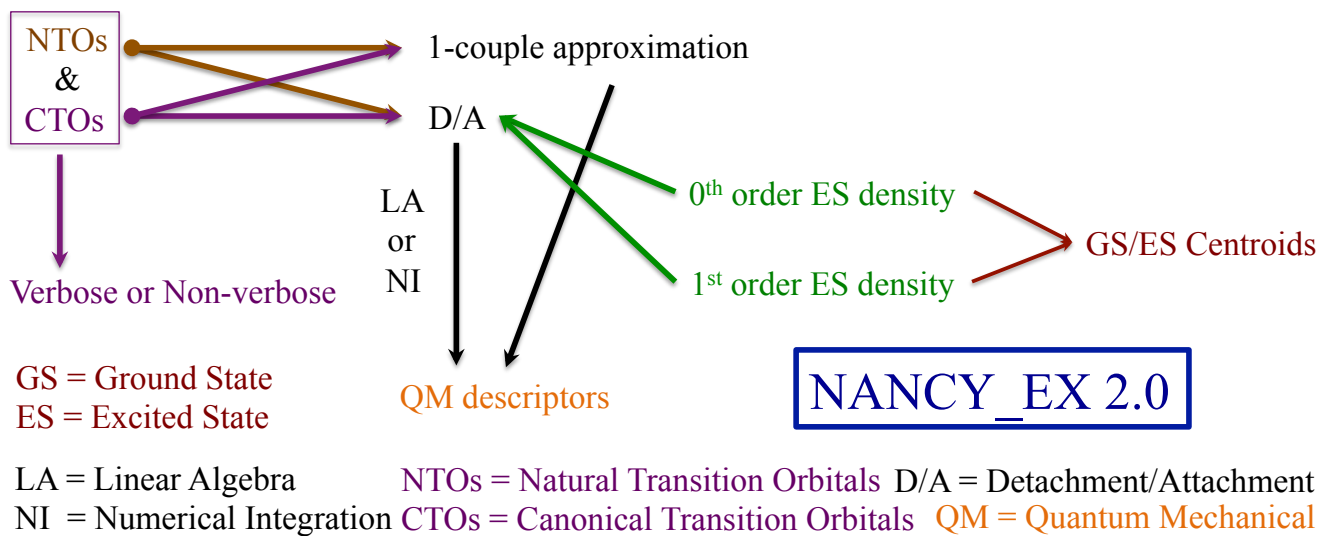
Figure 4 – Detachment/Attachment densities plot in real space for the eighth transition of complex **1**.

In the TEST folder, you will find two inputs (for CIS and TDDFT calculations) to compute the excited states of an organic compound (a push-pull molecule, with a nitro group and a cyanoacrylic moiety spaced by a single thiophene), together with a series of files. Those files are some inputs for the use of NANCY_EX program and the expected outputs. Note that since the molecule used for the TEST is relatively small, a perfect match between numerical integration and linear algebra is not expected in this special case, since the linear algebraic approximation to the numerical integration process was designed especially for large molecules.

Excited States calculations were performed with Gaussian 09 (revision B01), and the equilibrium molecular geometry was preliminarily obtained with the PBE0/6-311G(d,p). The overlap and density files were assumed to be simply given the name “overlap” and “density” when dumping the rwf file.

Simply run the Gaussian input and use the files with the “i-” prefix in the TEST folder for computing NTOs, Detachment/Attachment density matrices and the ϕ_S index value.

Figure 5 presents a schematic view of the possibilities offered by NANCY_EX 2.0.



NANCY_EX 2.0 is fully RSCF & USCF compatible

Figure 5 – Summary of the NANCY_EX 2.0 structure.