$\mathcal{FRETTY}$

Förster Resonance Energy Transfer-Transition densitY cubes

short notes

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$\mathcal{FRETTY}$ code computes the excitation energy transfer (EET) rate (k_{EET}), according to Fermi Golden rule first order perturbation theory. It implements the expression known as Förster resonance energy transfer (FRET) rate[1]

$$k_{EET} = \frac{1}{\hbar^2 c}|V_{AD}^2|J. \tag{1}$$

V_{AD} is the electronic coupling between the donor and the acceptor states and J is the overlap between the emission lineshape of the donor (G_D) and the absorption lineshape (G_A) of the acceptor both normalized to unit area on a wavenumber ($\tilde{\nu}$) scale,

$$G_A(\tilde{\nu}) = \mathcal{N}_A \int \frac{\epsilon_A(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu} \tag{2}$$

$$G_D(\tilde{\nu}) = \mathcal{N}_D \int \frac{\Phi_D(\tilde{\nu})}{\tilde{\nu}^3} d\tilde{\nu} \tag{3}$$

$$J = \int G_A(\tilde{\nu}) G_D(\tilde{\nu}) d\tilde{\nu} \tag{4}$$

where ϵ_A is absorption spectrum of the acceptor expressed as molar absorptivity, Φ_D is the emission spectrum of the donor expressed as the number of emitted photons per unit of time and $\mathcal{N}_A$ and $\mathcal{N}_D$ are normalization constants.

$\mathcal{FRETTY}$ is written in Fortran 90 apart few routines that are written in Fortran 77. Different models are adopted to compute the electronic coupling V_{AD}: dipolar interaction, Coulomb interaction between transition charges and Coulomb interaction between transition densities. For the latter case, the code implements the transition density cube (TDC) method presented in ref.[1]. $\mathcal{FRETTY}$ therefore relies on data retrieved from external sources. Specifically, it has been tested employing transition charges and transition densities cubes provided by the freely-distributed `Multiwfn` code [2] which analyzes TD-DFT results obtained with `Gaussian 09`.[3] The overlap J must be provided from input and it can be either estimated from experiment or calculated with a code like *FCclasses*[4, 5, 6], able to compute spectral shapes including the vibronic contributions. Notice that also the contribution of polar broadening is fundamental. Methods to estimate such overlap from either implicit or explicit solvent models are reported for example in refs[7, 8].

1 "GLOB" and "FRAG" models for the computation of the electronic coupling

Let us assume that the DONOR and the ACCEPTOR are connected by a molecular bridge. Since now on the super-system comprising the DONOR, the ACCEPTOR and the bridge will be named "DIMER". Two different models can be followed to compute

V_{AD}. A possible route is to identify the excited electronic states of the DIMER that are essentially localized on the DONOR and on the ACCEPTOR and may exchange energy and to compute the Coulomb coupling between them. This option, that we name in the following "GLOB", has the advantage that the considered molecular states take into account the effect of the environment (and the bridge). Moreover, the computation is technically more straightforward since transition charges and cubes of the transition densities are directly generated in the correct relative orientation for computing V_{AD}. This model has however also a conceptual weakness since the selected excited states are actually eigenstates of the supersystem and therefore no coupling should exist among them.

The alternative route is to compute the transition charges and densities of the isolated donor and acceptor species. The underlying model of this option that we name "FRAG" is that fluctuations of the environment (and the bridge) dynamically lead the states of the DIMER to localize, creating "non-stationary" states that have a Coulomb coupling. These localized states are modelled by the states of the isolated DONOR and ACCEPTOR species. According to this model however no effect of the molecular bridge is taken into account. For instance, the bonds with the bridge are substituted with hydrogens or alchyl groups to saturate the valencies and perform meaningful electronic computations, but these substitutions must be carefully planned to avoid to introduce physically relevant differences in the excited states. The implementation of this model is also technically less straightforward since transition charges and densities generated for the isolated species need to be translated and rotated in order to resemble as much as possible those of the localized states in the DIMER. To explain how this is done, let us focus for example on the DONOR, the same steps will of course work also for the ACCEPTOR. As a preliminary step, it is necessary to identify the common subset of atoms of the DONOR that can be found both in the DIMER and in the isolated species; in the following this will be called a "fragment". Of course the DIMER is in general a molecule and therefore all its atoms are connected by covalent bonds to some other atoms of the system. The definition of the fragment therefore has some arbitrariness and it will be driven by the chemical intuition of the user. Of course the fragment in the DIMER should comprise all the donor atoms that are involved in the molecular excitation. This means for instance that all atoms that take part to the π system that is excited must be included, but long side chains might be cut to speed up the calculations. Clearly also the connection to the bridge must be truncated at a given point. The atoms of the fragment in the DIMER will be in general a subset of the atoms in the isolated DONOR, since, of course, the latter will also comprise either H atoms or alchyl groups that are necessary to saturate

the valencies. Once the two fragments in the DIMER ($\text{FRAG}^D{}_{DIM}$) and in the isolated species ($\text{FRAG}^D{}_{IS}$) are defined, a one-to-one relation among their atoms must be established. This is in fact necessary to rotate $\text{FRAG}^D{}_{IS}$ in order to best superimpose to $\text{FRAG}^D{}_{DIM}$. Such a rotation is clearly preceded by a translation that makes their center of masses coincident. The same translation and rotation can be them applied to he transition charges and the transition density cubes.

$\mathcal{FRETTY}$ requires that the fragments in the DIMER are individuated by the user as well as the relation between the atoms of these fragments and those of the isolated donor an acceptors used for electronic calculations. It is worthy to notice that the general "FRAG" approach described above can clearly be applied also in the more easy case in which the DIMER is simply made of the DONOR and the ACCEPTOR and these are non covalently bound.

2 Distribution, Installation and execution

$\mathcal{FRETTY}$ is distributed as a tar.gz file. The main folder contains these short notes together with a copy of the GNU General Publica License and a script `link` for the installation of the code. The source codes are found in `source/` and after compilation the binary file `FRETTY.e` is found in `bin/`. The folder `TEST/` contains test calculations for a donor-acceptor system where donor is 7-nitrobenz-2-oxa-1,3-diazol-4-yl (NBD) and acceptor is a modified Nile Red (NR). The two dyes are bound to a common scaffold, a calix[4]arene and the system is simulated in acetonitrile (folder `NBD-NR-CALIXARENE_ACN`).

The system has been studied in ref. [9]. Two folders `FRAG/` and `GLOB/` contain examples of calculations with the two options "FRAG" and "GLOB" discussed in the previous Section. For "FRAG" option both medium-quality (MQ) and high-quality (HQ) transition density cubes were adopted. In each of these folders, `FROM-Multiwfn/` contains transition charges and transition density cubes computed with `Multiwfn` and examples of `Gaussian 09` input files adopted in the calculations. After executing `Gaussian 09`, the *.log and *fchk files were used as input files for `Multiwfn`.

Compilation of $\mathcal{FRETTY}$ has been tested with Fortran Compiler Intel.
Apart from the main program, the code is made up by few routines:

- `TRCH` computes V_{AD} from transition charges obtained from MultiWfn
- `TRDEGLOB` computes V_{AD} from transition densities cubes computed on the dimer.
- `TRDEFRAG` computes V_{AD} from transition densities cubes computed for the isolated donor and acceptors. In this case it is necessary to rotate the molecular structures

of the isolated species (and the corresponding transition densities) in order to best match their position with the position they have in the dimer. See discussion in the previous Section.

- `ROTATA` performs the displacement and rotation of the molecular structures described at the previous point. It is adapted from an analogous routine developed for the code *FCclasses* [4].

- `KRATE` computes the k_{EET}. Beyond the exciton coupling it requires J the overlap of absorption and emission lineshapes that must be provided in the input.

Notice that few routines that are simply used to declare and assign the value of a number of variables have not been listed for the sake of brevity.

The code is simply executed with the line command:

FRETTY.e<inputfile>outputfile

3 Input file format

The standard input "inputfile" has the following structure

- "n": The number of atoms of the structure that includes the donor the acceptor and the possible bridge. Since now on it is named the *dimer*.

- "filegeodim": A file reporting the atom dimer geometry. More specifically each line is "nn, nat, nchoice, x, y, z" where nn is the index, nat the atomic number, nchoice is "1" if the atom belongs to the donor, "2" if it belongs to the acceptor, "0" if it belongs to the bridge, and x, y, z are the Cartesian coordinates (in).

- "dip1": The components of the transition dipole of the electronic transition of the dimer that is localized on the donor (in atomic units).

- "dip2": The components of the transition dipole of the electronic transition of the dimer that is localized on the donor (in atomic units).

- "refindex": The refractive index of the medium.

- "ovl": The overlap J (in cm).

- "opztrch": Option for the calculation of the coupling from transition charges. It can take values SKIP (don't compute), FRAG (charges obtained from computations

on isolated DONOR and ACCEPTOR fragments), GLOB (charges obtained for transitions of the DIMER).

- "fitrchD": File where to read the cube of the transition charges of the DONOR state (for opztrd=FRAG,GLOB).
- "fitrchA": File where to read the cube of the transition charges of the ACCEPTOR state (for opztrd=FRAG,GLOB).
- "fifragD": Item only in case opztrch=FRAG; it is the name of the file that contains the information to connect the atoms of the fragment of the DONOR used to compute the charges with the atoms in the DIMER.
- "fifragA": Item only in case opztrch=FRAG; it is the name of the file that contains the information to connect the atoms of the fragment of the ACCEPTOR used to compute the charges with the atoms in the DIMER.
- "opztrd", "thshold": Opztrd can have the values SKIP, FRAG and GLOB. Thshold is a threshold. The value of the transition density is set to zero if it is lower than thshold$\times$MAX$_{TD}$, where MAX_{TD} is the absolute of the maximum value of the transition density. Few tests indicates that it cannot be given a too high value. 10^{-5} usually works fine.
- "rcut", "gammacut" (in bohr): If the distance r between the cells of the transition densities of the DONOR and the ACCEPTOR is lower than "rcut" a damping function $D(r) = \exp -(r - rcut)^2/gammacut^2$ is applied. If $D(r)$ is $> 10^{-10}$ at r=0.1 au, *gammacut* is automatically set to have $D(0.1) = 10^{-10}$. In order to avoid numerical instabilities, contributions to the Coulomb coupling are not computed for r <0.01 bohr.
- "fitrdD": File where to read the cube of the transition density of the DONOR (for opztrd=FRAG,GLOB).
- "fitrdA": File where to read the cube of the transition density of the ACCEPTOR (for opztrd=FRAG,GLOB).
- "fifragD": Item only in case opztrd=FRAG; it is the name of the file that contains the information to connect the atoms of the fragment of the DONOR used to compute the transition density with the atoms in the DIMER.

- "fifragA": Item only in case opztrd=FRAG; it is the name of the file that contains the information to connect the atoms of the fragment of the ACCEPTOR used to compute the transition density with the atoms in the DIMER.

An example of the input file is given below

Listing 1: Example input for an $\mathcal{FRETTY}$ calculation using the FRAG option.

```
168                                          no.  of atoms of the DIMER
 'geom_CONFCLOSED_ACN_Jexp'                  file with the geometry of the
     dimer and the indication of which atoms belong to donor=1 and
     acceptor=2
-1.5518      2.0469     -0.8459             transition dipole of the donor
    state in the dimer
-1.9470      2.8281      0.9253             transition dipole of the donor
    state in the dimer
1.344                                        refractive index
42.13                                        overlap of donor emission and
    acceptor absorption in au
'FRAG'                                        option transition charges
    'GLOB/FRAC/SKIP'
'FROM-Multiwfn/trans_charges_NBD_ACN_S1'     file transition charges Donor
'FROM-Multiwfn/trans_charges_NR_ACN_S1'      file transition charges
    Acceptor
'FRAG_D_SELECTION_NBD_CLOSED'                file that connects atoms of
    isolated donor and donor fragment in dimer
'FRAG_A_SELECTION_NR_CLOSED'                 file that connects atoms of
    isolated acceptor and acceptor fragment in dimer
'FRAG' 1.d-5                                 option transition density
    'GLOB/FRAC/SKIP' and threshold
5.d0 1.2247d0                                 rcut gammacut distance where
    the cut is activated and exp(-(rr-rcut)**2/gammacut**2)
'FROM-Multiwfn/NBD_ACN_transdens-S1-MQ.cub' file transition density Donor
'FROM-Multiwfn/NR_ACN_transdens-S1-MQ.cub'  file transition density
    Acceptor
'FRAG_D_SELECTION_NBD_CLOSED'                file that connects atoms of
    isolated donor and donor fragment in dimer
'FRAG_A_SELECTION_NR_CLOSED'                 file that connects atoms of
    isolated acceptor and acceptor fragment in dimer
```

The listing above shows an example input file, setting a calculation using the FRAG option for donor-acceptor system studied in ref. [9].

4 Other files

4.1 Auxiliary input files

As discussed in the previous section a number of auxiliary files is read. Here we give some detail and suggestion more on how they should be prepared.

- "figeodim". Each line is composed by 6 items "nn, nat, nchoice, x, y, z", where "nn" is the index, "nat" the atomic number, "nchoice" is "1" if the atom belongs to the donor, "2" if it belongs to the acceptor, "0" if it belongs to the bridge, and x, y, z are the Cartesian coordinates (in). It is easily generated cutting a part of G09 output.

- "fitrchD" and "fitrchA". Files where the code reads the transition charges of the electronic states localized on the DONOR and the ACCEPTOR (if opztrch=GLOB) or computed separately considering the DONOR and the ACCEPTOR isolated species, obtained removing the bridge and saturating the valencies. The code expects these data are generated by the code `Multiwfn`.

- "fitrdD" and "fitrdA". Files where the code reads the transition densities of the electronic states localized on the DONOR and the ACCEPTOR (if opztrch=GLOB) or computed separately considering the DONOR and the ACCEPTOR isolated species, obtained removing the bridge and saturating the valencies. $\mathcal{FRETTY}$ has been tested reading data generated by the code `Multiwfn`. In principle the format of a cube file is rather standard so cubes generated with other codes may work as well, but no test has been performed.

- "fifragD" and "fifragA". As reported above, these files contain the information to connect one-by-one the atoms of the isolated DONOR and the ACCEPTOR used to compute the transition densities with those of the fragments in the DIMER. Although, these files can in principle be different for the calculation either transition charges or transition densities, usually they coincide in the two cases.

  - The first line of the file reports "NAT" the number of atoms in the DONOR/ACCEPTOR isolated species. Notice in fact that since valencies must be saturated for a meaningful electronic calculation, the number of atoms of the "isolated species " is usually larger than the number of atoms of the DONOR and ACCEPTOR fragments in the DIMER defined by file "figeodim".

– For each of the "NAT" atoms of the isolated species, the following lines report two numbers: the atom they correspond to in the fragment defined in "figeodim" and the atomic number. For instance, as reported in the example in the following section, if line 2 of the file is "9 8" it means that the 1st atom in the isolated species is an oxygen (8) and corresponds to the 9th atom in the fragment defined in "figeodim".

4.2 Output files

Beyond the standard output "outputfile" $\mathcal{FRETTY}$ writes few files, with the format of a Gaussian input file, that are essentially used to visualize the fragments defined from input and check that the selection was right.

- `reference_dimer.com`. It is the DIMER geometry defined in the input file "figeodim"
- `def_donor.com` and `def_acceptor.com`. They give the geometries of the DONOR and ACCEPTOR fragments defined in the input file "figeodim"
- `def_donor_frag_shifted.com` and `def_acceptor_frag_shifted.com`. They give the geometries of the DONOR and ACCEPTOR fragments, $\mathrm{FRAG}^D{}_{IS}$ and $\mathrm{FRAG}^A{}_{IS}$ (see Section 2) obtained from the DONOR and ACCEPTOR isolated molecules defined by the cube files, after cutting the atoms that were only introduced to saturate the valencies but are not present in the fragments defined in file "figeodim" ($\mathrm{FRAG}^D{}_{DIM}$ and $\mathrm{FRAG}^A{}_{DIM}$. The structures $\mathrm{FRAG}^D{}_{IS}$ and $\mathrm{FRAG}^A{}_{IS}$ are translated in order to have the same center of mass of $\mathrm{FRAG}^D{}_{DIM}$ and $\mathrm{FRAG}^A{}_{DIM}$. Only printed if the "FRAG" option for the transition density is selected.
- `def_donor_frag_rotated.com`, `def_acceptor_frag_rotated.com`. They give the same structures $\mathrm{FRAG}^D{}_{IS}$ and $\mathrm{FRAG}^A{}_{IS}$ discussed above but rotated in order to minimize the root mean square distance with $\mathrm{FRAG}^D{}_{DIM}$ and $\mathrm{FRAG}^A{}_{DIM}$ respectively. Only printed if the "FRAG" option for the transition density is selected.

4.3 Some additional notes

- `Multiwfn` can generated cube files of low, medium and high quality (increasing the density of the grid) and $\mathcal{FRETTY}$ is able to read any of these files. However calculation time rises at the increase of the density of the grid.

- Please check for warnings in the "outputfile" and monitor the transition dipoles recomputed with different strategies during the calculations. If they are very different from those computed for the DIMER state and provided by input, inaccuracies should be expected. For instance, few tests indicate that transition charges on the (side-)atoms added in the isolated species to saturate valencies might be non negligible; discarding them the approximate transition dipole might be significantly different from what expected. This warning should not apply to transition density cubes since they implicitly include the effect of these side-atoms.

- The TDC method is based on the hypothesis that there is no appreciable overlap between the DONOR and ACCEPTOR orbitals (and therefore between the transition densities).[1]. In practical implementations, since cubes are defined on large grids, it can happen that some cells of the TDCs of the DONOR and the ACCEPTOR are actually very close each other. In order to avoid numerical instabilities, $\mathcal{FRETTY}$ neglects contributions from cells that are closer than 0.01 bohr and it applies a damping factor when the distance is smaller than "rcut". In the output file the contributions of these terms to the coupling, with and without the damping, is explicitly reported. It is clear that such contribution (without damping) is a significant fraction of the computed coupling the accuracy of the results should be considered with care.

- In order to show how the fragments for a "FRAG" calculation can be defined we consider again the system investigated in ref. [9] for which the "inputfile" was reported in Section 3. The molecular structure of the DIMER (as given by file "figeodim", and reported in the output file `reference_dimer.com`) is reported in Figure 1. The molecular structures of the DONOR (NBD, 7-nitrobenz-2-oxa-1,3-diazol-4-yl) and ACCEPTOR (NR, modified Nile Red) fragments extracted from the DIMER are reported in the upper panels of Figure 2. They are given respectively in files `def_donor.com` and `def_acceptor.com`. The molecular structures adopted in electronic calculations to obtain transition charges and transition densities are given in the lower panels of Figure 2.

Listing 2: Example input file to relate the atoms of $\text{FRAG}^{D}{}_{IS}$ to the atoms of $\text{FRAG}^{D}{}_{DIM}$

```
20                    no.  atoms isolated species (from cube)
     9          8     For each of the 20 lines:
    10          7     1st col:  corr atom in DIMER fragment
     2          6     if zero then the atom was added to saturate
     1          6     valencies and has no counterpart in the DIMER
    11          7     2nd col:atomic number for double-checking
     6          6
     5          6
     4          6
     3          6
    17          7
    12          7
    14          8
    13          8
    16          1
     7          1
     8          1
    15          6
     0          1
     0          1
     0          1
```

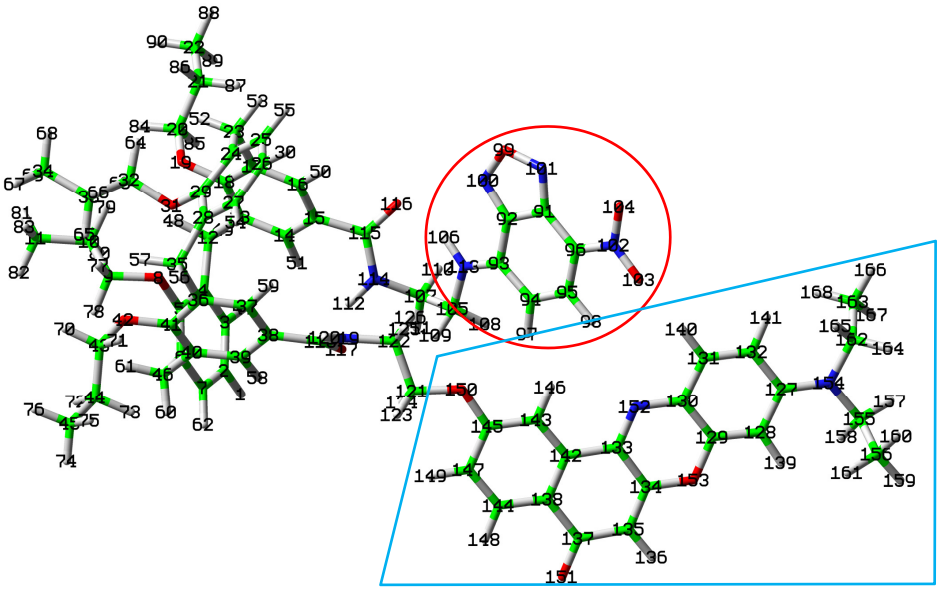

Figure 1: The molecular structure of the donor-acceptor system investigated in ref.[9]. The donor NBD is highlighted in red and the acceptor in blue

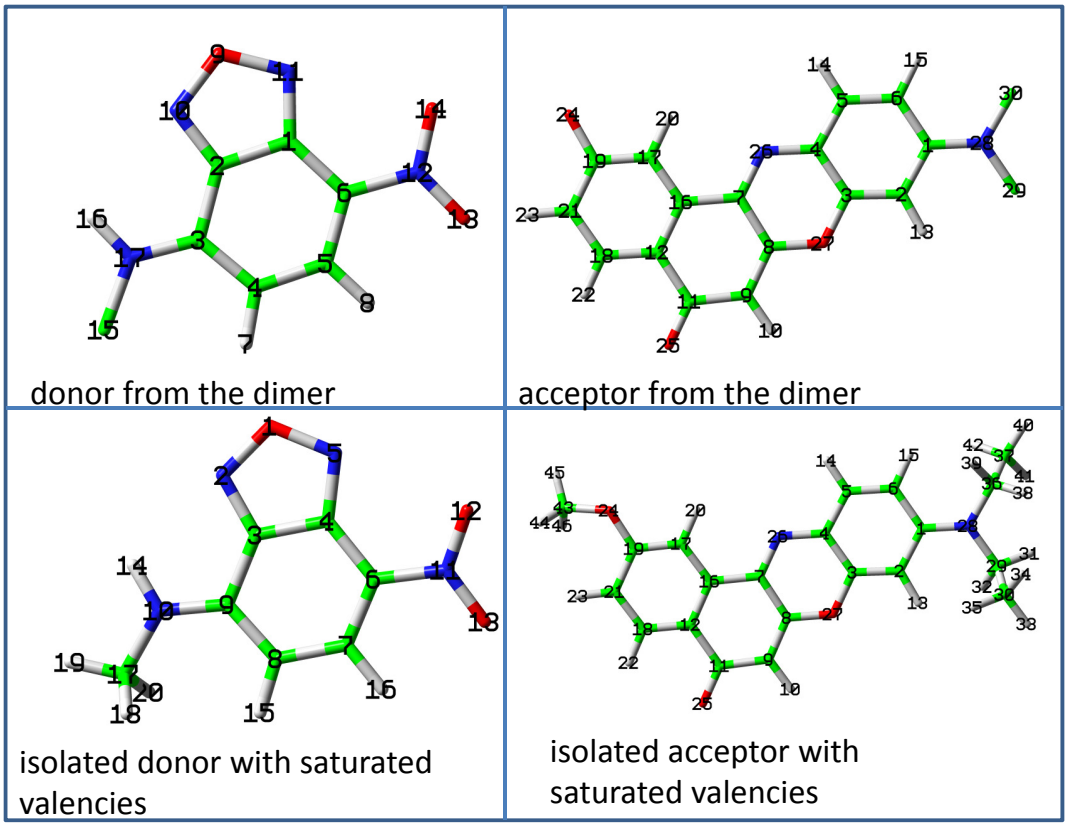

Figure 2: Upper panels: the donor (left) and acceptor (right) fragments extracted from the DIMER structure (see Figure 1). Lower panels: the donor (left) and acceptor (right) isolated species employed to compute transition charges and densities with a "FRAG" option.

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