

JACoPO

Just Another Coupling Program, Obviously

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1 Presentation

JACoPO is a program to calculate coulombic electronic couplings between two excited states according to various approaches. In particular, it is possible to calculate couplings with the Transition Density Cube method, with the monopole–monopole approximation and with the dipole–dipole approximation (also known as Point Dipole Approximation, PDA).

2 Requirements

JACoPO is a program written in Python and Fortran 90. A working installation of python and a fortran compiler (such as gfortran) are the only requirements.

3 Installation

To install JACoPO on your machine, few simple steps are needed. Get a copy of the program cloning the git repository:

```
$ git clone https://github.com/dpadula85/JACoPO
```

Alternatively, you could browse to the address <https://github.com/dpadula85/JACoPO> and download a .zip file with the appropriate button.

Install requirements by running

```
$ pip install -r requirements.txt
```

Finally, the package can be installed running

```
$ python setup.py install
```

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4 Running tests

In case you want to check whether everything is working properly, we suggest you run the tests distributed with the program. To do so, go in the `tests` directory and run the command

```
$ make &
```

The tests can take some time, but hopefully everything is working correctly! The result of the tests is summarized in the file `tests/logfile`, which is written on the fly while tests are running. You can check the progression of the tests in this file and which ones passed or failed by running

```
$ cat logfile
```

For more details about the tests, feel free to change directory to each test and have a look at the files, also for comparison with the instructions given in section 7.

5 Theory

Point Dipole Approximation (PDA)

This approximation is the one traditionally used to evaluate the coulombic term of electronic couplings. This description is based on a dipolar interaction.¹ Given two molecules D and A , the coulombic coupling between excited state a of molecule D and excited state b of molecule A is given by

$$V_{Da,Ab}^{coul} = \frac{1}{4\pi\epsilon_0} \left(\frac{\vec{\mu}_a \cdot \vec{\mu}_b}{r_{DA}^3} - \frac{3(\vec{\mu}_a \cdot \vec{r}_{DA})(\vec{\mu}_b \cdot \vec{r}_{DA})}{r_{DA}^5} \right) \quad (1)$$

where $\vec{\mu}_a$ is the transition electric dipole moment for excited state a of molecule D and r_{DA} is the distance between the two application points of the dipoles. Within this approximation, it is possible to define the orientation factor κ between the two chromophores as in

$$\kappa = \hat{\mu}_a \cdot \hat{\mu}_b - 3(\hat{\mu}_a \cdot \hat{r}_{DA})(\hat{\mu}_b \cdot \hat{r}_{DA}) \quad (2)$$

This approximation falls off when the distance between the two molecules is comparable to the molecular size or when the molecule has an elongated structure, such as a carotenoid.

More refined approaches have been developed to deal with these limitations.

Monopole–Monopole Approximation

In this approximation, the Transition Density of an excited state is expressed in terms of point charges on the atoms constituting the molecule.² There are many methods to evaluate these point charges,³ and the analysis of such methods goes beyond the scope of this manual. Once the set of charges is obtained with the method of choice, the coulombic term of the electronic coupling is calculated as

$$V_{Da,Ab}^{coul} = \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{q_D^a(i) \cdot q_A^b(j)}{r_{ij}} \quad (3)$$

where i runs over the coordinates of the atoms in molecule D and r_{ij} is the distance between atoms at positions i and j .

Within this approximation, the transition electric dipole moment associated to the charges can be obtained as

$$\vec{\mu}_a = \sum_i q^a(i) \vec{r}_i \quad (4)$$

thus the two transition electric dipole moments μ_a and μ_b can be retrieved by the two sets of charges and the coupling and the orientation factor can be estimated also according to the PDA.

Transition Density Cube method

This method was proposed in 1998 by Krueger *et al.*,⁴ and resulted in the development of a program for the calculation of electronic coupling according to this method (see http://www.chem.hope.edu/~krieg/TDC/TDC_home.htm).

Briefly, this method evaluates the coulombic interaction between the transition densities of two molecules. The coulombic term of the coupling is given by

$$V_{Da,Ab}^{coul} = \frac{1}{4\pi\epsilon_0} \int \frac{\rho_D^a(\vec{r}_i)\rho_A^b(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} d\vec{r}_i d\vec{r}_j \quad (5)$$

where $\rho_D^a(\vec{r}_i)$ is the transition density of excited state a of molecule D .

Computationally speaking, the transition density is expressed by an array of finite-size volume elements, which is called Transition Density Cube, from which the method takes the name. To obtain $V_{Da,Ab}^{coul}$ we calculate the sum of the interactions of every couple of elements on the two Cubes, as in

$$V_{Da,Ab}^{coul} = \sum_{i,j} \frac{\rho_D^a(i) \cdot \rho_A^b(j)}{r_{ij}} \quad (6)$$

where i denotes the set of 3D coordinates of the i -th point of the Cube of molecule D and r_{ij} is the distance between the two elements on the two cubes. To avoid discontinuous behaviour at low distances between two volume elements, we introduced a Gaussian distribution of charge in each volumen element, according to the literature.⁵

Within this approximation, the transition electric dipole moment associated to the Cube can be obtained as

$$\vec{\mu}_a = \sum_i \rho^a(i) \vec{r}_i \quad (7)$$

thus the two transition electric dipole moments μ_a and μ_b can be retrieved from the two Cubes and the coupling and the orientation factor can be estimated also according to the PDA.

6 Additional Information

The data needed to run JACoPO are transition charges and transition density cubes. If you don't know how to obtain these data from quantum calculations with your favorite package, we suggest you read the manual of your program, have a look at the Multiwfn package (<https://multiwfn.codeplex.com/>) or contact the developers of your program for information.

7 Features and Options

A short help including the list of options is available by running the command

```
$ compute_coupling -h
```

Let's have a quick look at all these options and what they require as arguments.

- **--coup**: this option specifies the approach you want to use for the coupling calculation. You can choose between **chgs** and **den** for the Monopole-Monopole approximation or the TDC method respectively. The default value is not specified and calculation with both methods will be attempted.

- **--chg1,chg2**: these two options want filenames as argument. The file you should give is constituted by 5 columns. The first column contains the atomic symbols, the second to the fourth column contain the (x, y, z) coordinates of the atom (in Å), the last column contains the value of the charge of the atom (in a.u.). As default, these files are not specified. If those files are not found, calculation with the Monopole–Monopole approximation will be skipped.
- **--cub1,cub2**: these two options want filenames as argument. You should specify the transition density cube (Gaussian cube) files needed for the calculation with the TDC method. For general information regarding the structure of these files, have a look at http://www.gaussian.com/g_tech/g_ur/u_cubegen.htm. Please, make sure the coordinates of the structure specified in the appropriate section of the .cub files are expressed in atomic units. The default choice for these options are **mon1.cub** and **mon2.cub**, respectively.
- **--fac1,fac2**: these two options allow to scale the Transition Density Cubes in input by some factor. This can be used to achieve exact correspondence between the transition dipole moment calculated from a cube and the one from *ab initio* simulations.¹
- **--thresh**: this is a threshold to speed up TDC calculations. Elements of the cubes lower than this threshold will be ignored in the calculation of the coupling. For a more accurate, but slower, result, decrease this parameter.
- **-o,--output**: this is the name of the logfile JACoP0 will write. The default is **Coup.out**.

Before explaining the other options, all related to the TDC method, a small digression is needed. A situation that could occur is that you want to evaluate the coupling for two equivalent molecules in different positions in space. The value of the transition density is the same for these two molecules, what changes is just its position. What you need is a *reference* cube file that you want to project on the real geometry of the molecule in space.

The **--geo1,geo2** options allow doing this. More specifically, you should specify a file that is constituted by 4 columns: the first column contains the atomic symbols, the second to the fourth column contain the (x, y, z) coordinates of the atom (in Å). These files are basically Gaussian input files without the route section, and we assign them a .inc extension. If these files are specified, the cube selected with the **--cub1,cub2** option will be transformed in space to match the geometries specified with the **--geo1,geo2** option. If no other option is specified, JACoP0 will assume that the atom order in the cube files is the same as in the geometry files. The option **--savecube** simply allows to save the cube files after the geometrical transformation occurred.² In case you want to skip the coupling calculation to only obtain the transformed cube files, you can do so activating the option **--nocoup**.

If the atom order in the cube and the geometry files is not the same, you can specify the atom correspondence with the **--selcub1,selcub2** and **--selgeo1,selgeo2** options. These options expect a list of atoms or a file, containing the list of atoms as it would be written if you were passing it directly. The rules to specify atom selections are simple and intuitive. Atoms should be separated by commas. For a more compact notation a group of consecutive atoms could be written in compact form (*e.g.* 3, 4, 5, 6 can be specified as 3-6).

Another realistic scenario is that your chromophore is included in a molecule, and the vicinities of the portion you are interested in are not UV active, *i. e.* they do not participate in the electronic excitations on your chromophore. In this case you want to project your cube on the chromophore, which is part of a bigger molecule. You can use the **--selcub1,selcub2** and **--selgeo1,selgeo2** options to specify the atoms you want to use for the transformation.

Examples of the files to be passed for each option are available in the **tests** folder.

¹This factor can also be used to correct possible problems with cubes obtained from some QM software. For example, we found out that cubes obtained from NWChem should be scaled by a factor $\sqrt{2}$ to reproduce the TDDFT transition dipole moment.

²Concerning cube files generated by JACoP0 we experienced problems in visualizing them with software such as VMD, because the plugin that allows VMD to read cube files aligns the axes of the grid to the main axes. On the contrary, we obtained a correct visualization of the transformed cube file with GaussView or UCSF Chimera.

8 Output

Examples of output files from JACoPO are in the `tests` folder. The first section of the output is a title and credits section.

```
#####  
## JACoPO ##  
#####
```

```
JACoPO: Just Another COupling Program, Obviously  
JACoPO.py Copyright (C) 2016 Daniele Padula, Marco Campetella
```

After this section, JACoPO writes information only on the calculations that have been chosen from the command line options. For the Monopole–Monopole approximation, an example is as follows.

```
#####  
## Coupling Transition Charges ##  
#####
```

```
Coupling calculated from transition charges according to  
J. Phys. Chem. B, 2006, 110, 17268
```

Donor Structure and Charges:

C	0.000000	1.394991	2.000000	0.095611
C	1.208097	0.697495	2.000000	0.047806
C	1.208097	-0.697495	2.000000	-0.047806
C	0.000000	-1.394991	2.000000	-0.095611
C	-1.208097	-0.697495	2.000000	-0.047806
C	-1.208097	0.697495	2.000000	0.047806
H	0.000000	2.494601	2.000000	0.063673
H	2.160388	1.247300	2.000000	0.031832
H	2.160388	-1.247300	2.000000	-0.031832
H	0.000000	-2.494601	2.000000	-0.063673
H	-2.160388	-1.247300	2.000000	-0.031832
H	-2.160388	1.247300	2.000000	0.031832

Donor Electric Transition Dipole Moment from Transition Charges in a.u.:

x	y	z	norm
0.0000	1.6566	0.0000	1.6566

Acceptor structure and Charges:

C	0.000000	1.394991	-2.000000	0.095611
C	1.208097	0.697495	-2.000000	0.047806
C	1.208097	-0.697495	-2.000000	-0.047806
C	0.000000	-1.394991	-2.000000	-0.095611
C	-1.208097	-0.697495	-2.000000	-0.047806
C	-1.208097	0.697495	-2.000000	0.047806
H	0.000000	2.494601	-2.000000	0.063673
H	2.160388	1.247300	-2.000000	0.031832
H	2.160388	-1.247300	-2.000000	-0.031832
H	0.000000	-2.494601	-2.000000	-0.063673
H	-2.160388	-1.247300	-2.000000	-0.031832
H	-2.160388	1.247300	-2.000000	0.031832

Acceptor Electric Transition Dipole Moment from Transition Charges in a.u.:

x	y	z	norm
0.0000	1.6566	-0.0000	1.6566

Orientation Factor:

1.00

Electronic Coupling according to PDA from Dipoles from Transition Charges in cm-1:

1394.54

Electronic Coupling in cm-1:

793.57

There is a small title section to remind you of the calculation that has been performed, followed by a reference containing the formula used. A recapitulation of the file specified with the `--chg1` option is reported, followed by the result of the calculation of the transition electric dipole moment for the geometry and charges you specified (see Eq. 4). An analogous section for the option `--chg2` is written.

Finally, the orientation factor (see Eq. 2) and two electronic couplings are reported. The first, is the result of the PDA applied on the dipoles calculated (see Eq. 1). The application points of the dipoles are the centers of mass of the geometries. The second is the coupling calculated with the Monopole-Monopole approximation (see Eq. 3). Please, be aware that the charges that you use for your input determine the quality of this calculation.

An example of a complete section for the TDC method is as follows.

```
#####
## Coupling Transition Densities ##
#####
```

Coupling calculated from transition densities according to
J. Phys. Chem. B, 1998, 102, 5378

Structure and Transition Density Cube in temp.cub moved to match geometry in 1.inc
RMSD (Ang): 0.0019

Donor Electric Transition Dipole Moment from Transition Density in a.u.:

x	y	z	norm
1.2234	1.7318	1.4028	2.5424

Structure and Transition Density Cube in temp.cub moved to match geometry in 2.inc
Atom correspondence between the cub and the geometry file, respectively:

1	2	3	7	8	4	5	18	9	16	6	17	19	20	14	12	10	15	13	11	21
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21

RMSD (Ang): 0.0019

Acceptor Electric Transition Dipole Moment from Transition Density in a.u.:

x	y	z	norm
-1.2234	1.7318	-1.4028	2.5424

Orientation Factor:

0.80

Electronic Coupling according to PDA from Dipoles from Transition Densities in cm-1:
595.87

Electronic Coupling in cm-1:
538.58

There is a small title section to remind you of the calculation that has been performed, followed by a reference containing the formula used. The first section refers to the cube specified with the option `--cub1`. When the `--geo1` option is specified, a reminder of this option is printed and the RMSD (in Å, up to the 4th decimal digit) for the transformation is printed, to give you a rough idea of the quality of the transformation. If the RMSD is too high, maybe the selection of atoms is wrong, and you should check that. After this section, the result of the transition electric dipole calculation is reported (see Eq. 7).

Similar sections are present for the cube specified with the `--cub2` option. In this case, since `--selcub2` and `--selgeo2` options have been specified, a summary of atom correspondence according to the options specified is also reported.

Finally, two electronic couplings are reported. The first, is the result of the PDA applied on the dipoles calculated (see Eq. 1). The application points of the dipoles are the centers of mass of the geometries. The second is the coupling calculated with the TDC method (see Eq. 6). Please, be aware that the cubes that you use for your input determine the quality of this calculation. In particular, for a better evaluation of the coupling, we recommend using thicker grids in the generation of the cube files.

At the end of the output file, a short summary of the calculations performed is reported.

```
#####
## Results Table ##
#####

Calculation time: 00:01:16

# Method          Coupling (cm-1)
#-----
Tr Chgs           793.57
PDA Dip Chgs      1394.54
Tr Den            1405.30
PDA Dip Den       1578.42
```

The calculation time and the results of calculations according to the required methods are summarized in a table.

Useful Commands

If you are not interested in reading the whole output file, the most straightforward command that you could use to have a quick look at the results is

```
$ tail Coup.out
#####

Calculation time: 00:01:16

# Method          Coupling (cm-1)
```

```
#-----
Tr Chgs          793.57
PDA Dip Chgs     1394.54
Tr Den           1405.30
PDA Dip Den      1578.42
```

If you are interested in extracting directly a number out of the output, you could use the command

```
$ grep "Tr Den" Coup.out | awk '{print $NF}'
1405.30
```

Substituting the string to search in the **grep** command gives you access to the result obtained with the method you prefer. This last command is useful for incorporation into shell scripts.

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