CAT Documentation

Release 0.3.3

B. F. van Beek

Apr 11, 2019

Contents

Contents:

CHAPTER 1

Compound Attachment/Analysis Tool 0.3.3

CAT is a collection of tools designed for the construction, and subsequent analysis, of various chemical compounds. Further information is provided in the documentation.

1.1 Installation

- Download miniconda for python3: miniconda (also you can install the complete anaconda version).
- Install according to: installConda.
- Create a new virtual environment, for python 3.7, using the following commands:
  - `conda create --name CAT python`
- The virtual environment can be enabled and disabled by, respectively, typing:
  - Enable: `conda activate CAT`
  - Disable: `conda deactivate`

1.1.1 Dependencies installation

Using the conda environment the following packages should be installed:

- rdkit & HDF5: `conda install -y --name CAT --channel conda-forge rdkit h5py`

1.1.2 Package installation

Finally, install **CAT** using pip:

- **CAT**: `pip install git+https://github.com/nlesc-nano/CAT@master --upgrade`

Now you are ready to use **CAT**.

1.2 Input files

Running **CAT** and can be done with the following command: `init_cat my_settings.yaml`. The user merely has to provide a yaml file with the job settings, settings which can be tweaked and altered to suit ones purposes (see example1). Alternatively, **CAT** can be run like a regular python script, bypassing the command-line interface (*i.e.* `python input.py`, see example2).

An extensive description of the various available settings is available in the documentation.

CHAPTER 2

CAT Documentation

For a more detailed description of the **CAT** compound builder read the documentation. The documentation is divided into three parts: The basics, further details about the input cores & ligands and finally a more detailed look into the customization of the various jobs.

2.1 General Overview & Getting Started

A basic recipe for running **CAT**:

1. Create two directories named 'core' and 'ligand'. The 'core' directory should contain the input cores & the 'ligand' should contain the input ligands. The quantum dots will be exported to the 'QD' directory.

2. Customize the job settings to your liking, see CAT/examples/input_settings.yaml for an example. Note: everything under the `optional` section does **not** have to be included in the input settings. As is implied by the name, everything in `optional` is completely optional.

3. Run **CAT** with the following command: `init_cat input_settings.yaml`

4. Congratulations, you just ran **CAT**!

The default **CAT** settings, at various levels of verbosity, are provided below.

2.1.1 Default Settings

```yaml
path: None

input_cores:
    - Cd68Se55.xyz:
        guess_bonds: False

input_ligands:
    - OC(C)=O
    - OC(CC)=O
```

2.1.2 Verbose default Settings

```
path: None

input_cores:
    - Cd68Se55.xyz:
        guess_bonds: False

input_ligands:
    - OC(C)=O
    - OC(CC)=O

optional:
    database:
        dirname: database
        read: True
        write: True
        overwrite: False
        mol_format: [pdb, xyz]
        mongodb: False

    core:
        dirname: core
        dummy: Cl

    ligand:
        dirname: ligand
        optimize: True
        split: True
        cosmo-rs: False

    qd:
        dirname: QD
        optimize: False
        activation_strain: False
        dissociate: False
```

2.1.3 Maximum verbose default Settings

```
path: None

input_cores:
    - Cd68Se55.xyz:
        guess_bonds: False

input_ligands:
    - OC(C)=O
    - OC(CC)=O

optional:
    database:
        dirname: database
        read: True
        write: True
        overwrite: False
```

(continues on next page)

(continued from previous page)

```
        mol_format: [pdb, xyz]
        mongodb: False

    core:
        dirname: core
        dummy: Cl

    ligand:
        dirname: ligand
        optimize: True
        split: True
        cosmo-rs: False

    qd:
        dirname: QD
        optimize: False
        activation_strain: False
        dissociate:
            core_atom: Cd
            lig_count: 2
            core_core_dist: 5.0
            lig_core_dist: 5.0
            topology:
                6: vertice
                7: edge
                9: face

            job1: False
            s1: False
            job2: False
            s2: False
```

2.2 path

2.2.1 Default Settings

```
path: None
```

2.2.2 Arguments

path `None` or `str` = *None*

The path were all working directories are/will be stored. To use the current working directory, use one of the following values:

- *None*
- .
- *cwd*
- *$PWD*
- /path/to/my/current/working/directory

2.3 input_cores & input_ligands

Thia section related relates the importing and processing of cores and ligands. Ligand & cores can be imported from a wide range of different files and files types, which can roughly be divided into three categories:

1. Files containing coordinates of a single molecule: .xyz, .pdb & .mol files
2. Python objects: `plams.Molecule`, `rdkit.Chem.Mol` & (SMILES) `str`
3. Containers with one or multiple input molecules: directories & .txt files

In the later case, the container can consist of multiple SMILES strings or paths to .xyz, .pdb and/or .mol files. If necessary, containers are searched recursively. Both absolute and relative paths are explored.

2.3.1 Default Settings

```
input_cores:
    - Cd68Se55.xyz:
        guess_bonds: False

input_ligands:
    - OC(C)=O
    - OC(CC)=O
    - OC(CCC)=O
    - OC(CCCC)=O
```

2.3.2 Optional arguments

guess_bonds `bool` = *False*

Try to guess bonds and bond orders in a molecule based on the types atoms and the relative of atoms. Is set to False by default, with the exception of .xyz files.

column `int` = *0*

The column containing the to be imported molecules. Relevant when importing structures from .txt and .xlsx files with multiple columns. Numbering starts from 0.

row `int` = *0*

The first row in a column which contains a molecule. Useful for when, for example, the very first row contains the title of aforementioned row, in which case row = 1 would be a sensible choice. Relevant for .txt and .xlsx files. Numbering starts from 0.

indices `tuple` [`int`] = ()

For cores: Manually specify the atomic index of one ore more atom(s) in the core that will be replaced with ligands. If left empty, all atoms of a user-specified element (see `optional.cores.dummy = str or int`) will be replaced with ligands.

For ligands: Manually specify the atomic index of the ligand atom that will be attached to core (implying argument_dict: `optional.ligand.split = False`).If two atomic indices are rovided, the bond between `tuple` [0] and `tuple` [1] will be broken and the molecule containing `tuple` [0] is attached to the core, (implying argument_dict: `optional.ligand.split = True`). Serves as an alternative to the functional group based `CAT.attachment.ligand_anchoring.find_substructure()` function, which identifies the to be attached atom based on connectivity patterns (*i.e.* functional groups).

In both cases the numbering of atoms starts from 1, following the PLAMS [1, 2] convention.

2.4 Optional

There are a number of arguments which can be used to modify the functionality and behaviour of the quantum dot builder. Herein an overview is provided.

Note: Inclusion of this section in the input file is not required, assuming one is content with the default settings.

2.4.1 Default Settings

```
optional:
    database:
        dirname: database
        read: True
        write: True
        overwrite: False
        mol_format: [pdb, xyz]
        mongodb: False

    core:
        dirname: core
        dummy: Cl

    ligand:
        dirname: ligand
        optimize: True
        split: True
        cosmo-rs: False

    qd:
        dirname: QD
        optimize: False
        activation_strain: False
        dissociate: False
```

2.4.2 Arguments

Database

```
optional:
    database:
        dirname: database
        read: True
        write: True
        overwrite: False
        mol_format: [pdb, xyz]
        mongodb: False
```

database.dirname `str` = *database*

The name of the directory where the database will be stored. The database directory will be created (if it does not yet exist) at the path specified in *path*.

database.read `bool`, `str` or `list` [`str`] = *True*

Before optimizing a structure, check if a geometry is available from previous calculations. If a match is found, use that structure and avoid a geometry reoptimizations. If one wants more control then the boolean can be substituted for a list of strings (*i.e.* *core*, *ligand* and/or *QD*), meaning that structures will be read only for a specific subset.

For example:

```
optional:
    database:
        read: [core, ligand, QD]   # is equivalent to read: True
```

```
optional:
    database:
        read: ligand
```

database.write `bool`, `str` or `list` [`str`] = *True*

Export the optimized structures to the database of results. Previous results will **not** be overwritten unless `optional.database.overwrite = True`. If one wants more control then the boolean can be substituted for a list of strings (*i.e.* *core*, *ligand* and/or *QD*), meaning that structures written for for a specific subset.

See **database.read** for a similar relevant example.

database.overwrite `bool`, `str` or `list` [`str`] = *False*

Allows previous results in the database to be overwritten. Only apllicable if `optional.database.write = True`. If one wants more control then the boolean can be substituted for a list of strings (*i.e.* *core*, *ligand* and/or *QD*), meaning that structures written for for a specific subset.

See **database.read** for a similar relevant example.

database.mol_format `bool`, `str` or `list` [`str`] = [*pdb*, *xyz*]

The file format(s) for storing moleculair structures. By default all structures are stored in the .hdf5 format as (partially) de-serialized .pdb files. Additional formats can be requisted with this keyword. Accepted values: *pdb* and/or *xyz*.

database.mongodb `bool` = *False*

Handles convertion of the database to the mongoDB format. Not implemented as of yet, this keyword is a placeholder.

Core

```
optional:
    core:
        dirname: core
        dummy: Cl
```

core.dirname `str` = *core*

The name of the directory where all cores will be stored. The core directory will be created (if it does not yet exist) at the path specified in *path*.

core.dummy `str` or `int` = *Cl*

The atomic number or atomic symbol of the atoms in the core which are to be replaced with ligands. Alternatively, dummy atoms can be manually specified with the core_indices variable.

Ligand

```
optional:
    ligand:
        dirname: ligand
        optimize: True
        split: True
        cosmo-rs: False
```

ligand.dirname `str` = *ligand*

The name of the directory where all ligands will be stored. The ligand directory will be created (if it does not yet exist) at the path specified in *path*.

ligand.optimize `bool` = *True*

Optimize the geometry of the to be attached ligands. The ligand is split into one or multiple (more or less) linear fragments, which are subsequently optimized (RDKit UFF [1, 2, 3]) and reassembled while checking for the optimal dihedral angle. The ligand fragments are biased towards more linear conformations to minimize inter-ligand repulsion once the ligands are attached to the core.

ligand.split `bool` = *True*

If *False*: The ligand in its entirety is to be attached to the core.

- N^+R_4 -> N^+R_4
- O_2CR -> O_2CR
- HO_2CR -> HO_2CR
- H_3CO_2CR -> H_3CO_2CR

If *True*: A proton, counterion or functional group is to be removed from the ligand before attachment to the core.

- $X^-.N^+R_4$ -> N^+R_4
- HO_2CR -> $O^-{}_2CR$
- $Na^+.O^-{}_2CR$ -> $O^-{}_2CR$
- H_3CO_2CR -> $O^-{}_2CR$

ligand.cosmo-rs `bool` = *False*

Perform a property calculation with COSMO-RS [4, 5, 6, 7]; the COSMO surfaces are constructed using ADF MOPAC [8, 9, 10].

The solvation energy of the ligand and its activity coefficient are calculated in the following solvents: acetone, acetonitrile, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), ethyl acetate, ethanol, *n*-hexane, toluene and water.

QD

```
optional:
    qd:
        dirname: QD
        optimize: False
        activation_strain: False
        dissociate: False
```

qd.dirname `str` = *QD*

The name of the directory where all quantum dots will be stored. The quantum dot directory will be created (if it does not yet exist) at the path specified in *path*.

qd.optimize `bool` = *False*

Optimize the quantum dot (i.e. core + all ligands) with ADF UFF [3, 11]. The geometry of the core and ligand atoms directly attached to the core are frozen during this optimization.

qd.activation_strain `bool` = *False*

Perform an activation strain analyses [12, 13, 14] (kcal mol^{-1}) on the ligands attached to the quantum dot surface with RDKit UFF [1, 2, 3].

The core is removed during this process; the analyses is thus exclusively focused on ligand deformation and inter-ligand interaction. Yields three terms:

1. dE_{strain} : The energy required to deform the ligand from their equilibrium geometry to the geometry they adopt on the quantum dot surface. This term is, by definition, destabilizing. Also known as the preperation energy (dE_{prep}).

2. dE_{int} : The mutual interaction between all deformed ligands. This term is characterized by the non-covalent interaction between ligands (UFF Lennard-Jones potential) and, depending on the inter-ligand distances, can be either stabilizing or destabilizing.

3. dE : The sum of dE_{strain} and dE_{int}. Accounts for both the destabilizing ligand deformation and (de-)stabilizing interaction between all ligands in the absence of the core.

qd.dissociate `bool` = *False*

Calculate the bond dissociation energy (BDE) of ligands attached to the surface of the core. See *Bond Dissociation Energy* for more details. The calculation consists of five distinct steps:

1. Dissociate all combinations of n ligandsand an atom from the core within a radius r from aforementioned core atom. General structure: XY_n.

2. Optimize the geometry of XY_n at the first level of theory (lvl1): ADF MOPAC [1, 2, 3].

3. Calculate the "electronic" contribution to the BDE (dE) at the first level of theory (lvl1): ADF MOPAC [1, 2, 3]. This step consists of single point calculations of the complete quantum dot, XY_n and all XY_n-dissociated quantum dots.

4. Calculate the thermalchemical contribution to the BDE (dd$G$) at the second level of theory (lvl2): ADF UFF [4, 5]. This step consists of geometry optimizations and frequency analyses of the same compounds used for step 3.

5. $dG = dE_{lvl1} + ddG_{lvl2} = dE_{lvl1} + (dG_{lvl2} - dE_{lvl2})$.

2.5 Bond Dissociation Energy

Calculate the bond dissociation energy (BDE) of ligands attached to the surface of the core. The calculation consists of five distinct steps:

1. Dissociate all combinations of n ligands (Y, see **qd.dissociate.lig_count**) and an atom from the core (X, see **qd.dissociate.core_atom**) within a radius r from aforementioned core atom (see **qd.dissociate.lig_core_dist** and **qd.dissociate.core_core_dist**). The dissociated compound has the general structure of XY_n.

2. Optimize the geometry of XY_n at the first level of theory (lvl1): ADF MOPAC [1, 2, 3].

3. Calculate the "electronic" contribution to the BDE (dE) at the first level of theory (lvl1): ADF MOPAC [1, 2, 3]. This step consists of single point calculations of the complete quantum dot, XY_n and all XY_n-dissociated quantum dots.

4. Calculate the thermalchemical contribution to the BDE (dd$G$) at the second level of theory (lvl2): ADF UFF [4, 5]. This step consists of geometry optimizations and frequency analyses of the same compounds used for step 3.

5. $dG = dE_{lvl1} + ddG_{lvl2} = dE_{lvl1} + (dG_{lvl2} - dE_{lvl2})$.

2.5.1 Default Settings

```
optional:
    qd:
        dissociate:
            core_atom: Cd
            lig_count: 2
            core_core_dist: 5.0
            lig_core_dist: 5.0
            topology:
                7: vertice
```

(continues on next page)

(continued from previous page)

```
                8: edge
                10: face

            job1: AMSJob
            s1: True
            job2: AMSJob
            s2: True
```

2.5.2 Arguments

qd.dissociate.core_atom `str` or `int` = *Cd*

The atomic number or atomic symbol of the core atoms (X) which are to be dissociated. The core atoms are dissociated in combination with *n* ligands (Y, see **qd.dissociate.lig_count**). Yields a compound with the general formula XY_n.

qd.dissociate.lig_count `int` = *2*

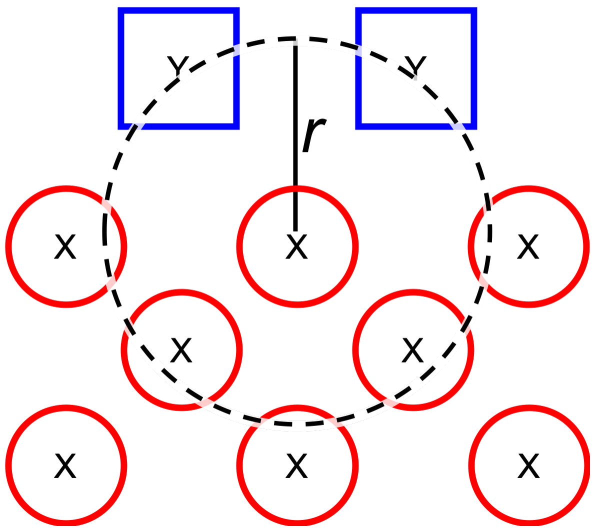
The number of ligands, *n*, which is to be dissociated in combination with a single core atom (X, see **qd.dissociate.core_atom**). Yields a compound with the general formula XY_n.

qd.dissociate.core_core_dist `float` = *5.0*

The maximum to be considered distance (Ångström) between atoms in **qd.dissociate.core_atom**. Used for determining the topology of the core atom (see **qd.dissociate.topology**) and whether it is exposed to the surface of the core or not. It is recommended to use a radius which encapsulates a single (complete) shell of neighbours.

qd.dissociate.lig_core_dist `float` = *5.0*

Dissociate all possible combinations of *n* ligands and a single core atom (see **qd.dissociate.core_atom**) within a given radius (Ångström) from aforementioned core atom. The number of ligands dissociated in combination with a single core atom is controlled by **qd.dissociate.lig_count**.



qd.dissociate.topology `dict` = {*7*: *vertice*, *8*: *edge*, *10*: *face*}

A dictionary which translates the number neighbouring core atoms (see **qd.dissociate.core_atom** and **qd.dissociate.core_core_dist**) into a topology. Keys represent the number of neighbours, values represent the matching topology.

Note: values can take on any user-specified value (*e.g.* Miller indices) and are thus not limited to *vertice*, *edge* and/or *face*.

2.5.3 Arguments - Job Customization

qd.dissociate.job1 `type`, `str` or `bool` = *AMSJob*

A `type` object of a `Job` subclass, used for calculating the “electronic” component (dE_{lvl1}) of the bond dissociation energy. Involves single point calculations.

Alternatively, an alias (`str`) can be provided for a specific job type (see *Type Aliases*).

Setting it to *True* (`bool`) will default to `type` (`AMSJob`), while *False* (`bool`) is equivalent to `optional.qd.dissociate = False`.

qd.dissociate.s1 `Settings`, `str` or `bool` =

```
s1:
    input:
        mopac:
```

(continues on next page)

(continued from previous page)

```
            model: PM7
        ams:
            system:
                charge: 0
```

The job Settings used for calculating the "electronic" component (dE_{lvl1}) of the bond dissociation energy.

Alternatively, a path (str) can be provided to .json or .yaml file containing the job settings.

Setting it to *True* (bool) will default to the *MOPAC* block in CAT/data/templates/qd.yaml, while *False* (bool) is equivalent to `optional.qd.dissociate = False`.

qd.dissociate.job2 type, str or bool = *AMSJob*

A type object of a Job subclass, used for calculating the thermal component (ddG_{lvl2}) of the bond dissociation energy. Involves a geometry reoptimizations and frequency analyses.

Alternatively, an alias (str) can be provided for a specific job type (see *Type Aliases*).

Setting it to *True* (bool) will default to type (AMSJob), while *False* (bool) will skip the thermochemical analysis completely.

qd.dissociate.s2 Settings, str or bool =

```
s2:
    input:
        uff:
            library: uff
        ams:
            system:
                charge: 0
                bondorders:
                    _1: null
```

The job Settings used for calculating the thermal component (ddG_{lvl2}) of the bond dissociation energy.

Alternatively, a path (str) can be provided to .json or .yaml file containing the job settings.

Setting it to *True* (bool) will default to the the *MOPAC* block in CAT/data/templates/qd.yaml, while *False* (bool) will skip the thermochemical analysis completely.

2.6 Type Aliases

Aliases are available for a large number of job types, allowing one to pass a `str` instead of a `type` object, thus simplifying the input settings for **CAT**. Aliases are insensitive towards capitalization (or lack thereof).

A comprehensive list of `Job` subclasses and their respective aliases (`str`) is presented below.

2.6.1 Aliases

- `ADFJob` = *adf* = *adfjob*
- `AMSJob` = *ams* = *amsjob*
- `UFFJob` = *uff* = *uffjob*
- `BANDJob` = *band* = *bandjob*
- `DFTBJob` = *dftb* = *dftbjob*
- `MOPACJob` = *mopac* = *mopacjob*
- `ReaxFFJob` = *reaxff* = *reaxffjob*
- `Cp2kJob` = *cp2k* = *cp2kjob*
- `ORCAJob` = *orca* = *orcajob*
- `DiracJob` = *dirac* = *diracjob*
- `GamessJob` = *gamess* = *gamessjob*
- `DFTBPlusJob` = *dftbplus* = *dftbplusjob*
- `CRSJob` = *crs* = *cosmo-rs* = *crsjob*