THE SCINE READUCT DEVELOPERS:

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USER MANUAL

SCINE READUCT 2.0.0

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Contents

Introduction

The SCINE project requires stable algorithms for the refinement of elementary-reaction paths and associated transition-state structures. The SCINE ReaDuct module was designed to serve this purpose and can be driven from SCINE Interactive and SCINE Chemoton. However, as with all SCINE modules it is a stand-alone program that can drive standard quantum chemical software.

SCINE ReaDuct is a command-line tool that allows to carry out structure optimizations, transition state searches and intrinsic reaction coordinate (IRC) calculations among other things. For these calculations, it relies on a backend program to provide the necessary quantum chemical properties (such as nuclear gradients). Currently, SCINE Sparrow[1], Gaussian[2], and ORCA[3] are supported as backend programs.

In this manual, we describe the installation of the software, an example calculation as a hands-on introduction to the program, and the most import functions and options.[4] A prospect on features in future releases and references for further reading are added at the end of this manual.

[1] Husch, T.; Vaucher, A. C.; Reiher, M. Semiempirical molecular orbital models based on the neglect of diatomic differential overlap approximation, *Int. J. Quantum Chem.* **2018,** *118,* e25799

[2] Frisch, M. J. *et al.* "Gaussian 09, revision D. 01", 2009 Gaussian, Inc., Wallingford CT

[3] Neese, F. The ORCA program system, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012,** *2,* 73–78

[4] Throughout this manual, the most import information is displayed in the main text, whereas useful additional information is given as a side note like this one.

Obtaining the Software

ReaDuct is distributed as open source software in the framework of the SCINE project (www.scine.ethz.ch). Visit our website (www.scine.ethz.ch/download/readuct) to obtain the software.

System Requirements

ReaDuct itself has only modest requirements regarding the hardware performance. However, the underlying quantum-chemical calculations might become resource intensive if extremely large systems are studied. We advise to first explore the software with the fast semiempirical methods provided in ReaDuct. This allows one to quickly understand what to expect from the software rather than being confused by possibly long times waiting for more involved quantum chemical calculations to finish.

Installation

ReaDuct is distributed as an open source code. In order to compile ReaDuct from this source code, you need

- a C++ compiler supporting the C++14 standard (we recommend gcc 7.3.0),
- cmake (we recommend version 3.9.0),
- the Boost library (we recommend version 1.64.0), and
- the Eigen3 library (we recommend version 3.3.2).

In order to compile the software, either directly clone the repository with git or extract the downloaded tarball, change to the source directory and execute the following steps:

```
git submodule init
git submodule update
mkdir build install
cd build
cmake -DCMAKE_BUILD_TYPE=Release -DBUILD_SPARROW=ON -DCMAKE_INSTALL_PREFIX=../install ..
make
make test
make install
export SCINE_MODULE_PATH=<source code directory>/install/lib
export PATH=$PATH:<source code directory>/install/bin
```

This will configure everything, compile your software, run the tests, and install the software into the folder "install". Finally, it will add the ReaDuct binary to your `PATH` such that you can use it without having to specify its full location. In this last command, you have to replace `<source code directory>` with the full path where you stored the source code of ReaDuct.

In case you need support with the setup of ReaDuct, please contact us by writing to scine@phys.chem.ethz.ch.

Using the Standalone Binary

ReaDuct is a command-line-only binary; there is no graphical user interface. Therefore, you always work with the ReaDuct binary on a command line such as the Gnome Terminal or KDE Konsole.

Almost all functionality is accessed via an input file following the YAML syntax. The program is then run with the command

```
readuct <input file>
```

where you have to give the actual filename of your input file for `<input file>`.

You can specify the verbosity of the log messages printed with the command line option `-l` or `--log`. For example, to only see log messages of "warning" severity and higher, you run readuct with the command

```
readuct -l warning <input file>
```

By default, the log severity is set to `info`. Available values are: `none`, `trace`, `debug`, `info`, `warning`, `error` and `fatal`.

General Structure of the Input File

The general structure of a ReaDuct input file is as follows:

```
systems:
  - name: [system name]
    path: [path to coordinates file]
    program: [program name]
    method_family: [method_family name]
    method: [method name]
    settings:
      [settings key]: [settings value]
      ...
```

```
tasks:
  - type: [task type name]
    input: [input system name]
    output: [output system name]
    settings:
      [settings key]: [settings value]
      ...
```

There are two major blocks, namely a `systems` block and a `tasks` block. You can define multiple systems in the `systems` block and multiple tasks in the `tasks` block (see also section Task Chaining).

A system is a combination of nuclear coordinates (given as an XYZ file), a calculation program (such as SCINE Sparrow or ORCA), a method family (such as DFT) and an actual method (such as PBEo). Depending on the program and method used, different settings (such as molecular charge, spin multiplicity, and convergence thresholds) can be given. A task specifies that a certain calculation type (such as a structure optimization) should be carried out with a given (input) system. Different tasks can have different settings. For every task, an output system can be assigned to be used in further tasks (for instance, the output system of a structure optimization task contains the optimized nuclear coordinates).

For example, in order to do a simple structure optimization, you can use the following input file:

```
systems:
  - name: 'water'
    path: 'h2o.xyz'
    program: 'Sparrow'
    method_family: 'PM6'
    settings:
      molecular_charge: 0
      spin_multiplicity: 1

tasks:
  - type: 'geoopt'
    input: ['water']
    output: ['water_opt']
    settings:
      optimizer: 'bfgs'
```

This specifies a system named `water`, the nuclear coordinates are

given by the XYZ file `h2o.xyz`. Any calculation performed on this system will use the PM6 method provided by SCINE Sparrow. For this system, a structure optimization will be carried out; the structure will be optimized with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.

Supported Programs and Methods

SCINE Sparrow

SCINE Sparrow is fully supported by SCINE ReaDuct. If built with the cmake option `-DBUILD_SPARROW=ON` as described in section Installation, it will be automatically downloaded and integrated into ReaDuct at compile time.

In order to use SCINE Sparrow with ReaDuct, specify `program: 'Sparrow'` in the respective system block and the desired calculation method or method family (such as `'PM6'`) in the `method_family` key. All semiempirical methods are considered their own family of methods. All options supported by Sparrow can be defined in the settings block. See the Sparrow manual for a complete list of these options (the option names are identical to the command line option names of the Sparrow standalone binary).

ORCA

Important note: Support for ORCA[5] is currently not fully tested. There might be specific calculation types and/or settings which do not work. Also, we cannot guarantee compatibility with any ORCA version different from 4.1.0 since we have no control over the output format of an external program. If you encounter any problems when using ORCA together with ReaDuct, please write a short message to scine@phys.chem.ethz.ch.

[5] Neese, F. The ORCA program system, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012,** *2*, 73–78

In order to use ORCA with ReaDuct, specify `program: 'ORCA'` in the respective system block and the desired calculation method family and method (e.g., 'DFT' and 'PBE') in the `method_family` and `method` key. Note that the name of the functional should match the string used in a typical ORCA input file.

The path to the ORCA binary must be set via the environment variable `ORCA_BINARY_PATH`.

You can specify the following settings in the settings block:

- `molecular_charge`: This specifies the molecular charge. It can take on values between -10 and 10; by default, it is zero.
- `spin_multiplicity`: This specifies the spin multiplicity. It can take on values between 1 and 10; by default, it is 1.
- `basis_set`: This specifies the basis set string. By default, it is `'def2-SVP'`. You can specify any valid ORCA basis set string (see the ORCA manual for a complete list).
- `self_consistence_criterion`: The threshold to which the electronic energy should be converged (given in hartree). By default, it is `1.0e-6` (*i.e.*, 10^{-6} hartree).
- `max_scf_iterations`: The maximum number of SCF iterations allowed by ORCA. By default, it is 100.
- `orca_nprocs`: The number of processors to use in the ORCA calculations. By default, it is one, *i.e.*, a serial calculation is carried out. Note that you have to specify the full ORCA binary path in case you want to do a parallel calculation.
- `external_program_memory`: The total amount of memory in MB that should be available for ORCA to use. By default set to `1024`.
- `orca_filename_base`: This specifies the basic filename (prefix) used for all files related to the ORCA calculations. By default, it is set to "orca_calc"; therefore, the generated input file will be named "orca_calc.inp".
- `base_working_directory`: This specifies the directory in which the files for the ORCA calculations will be stored. By default, this is set to the current directory. For each ORCA calculation a new directory will be created inside the directory specified by `base_working_directory` to keep the files related to that specific calculation.
- `delete_tmp_files`: Whether temporary files (i.e., all files with a ".tmp" extension) should be deleted in case the calculation fails. By default, this is set to `true`.

Gaussian

Important note: Support for Gaussian[6] is currently not fully tested. There might be specific calculation types and/or settings which do not work. Also, we cannot guarantee compatibility with any Gaussian version different from 09 Rev. D01 since we have no control over the output format of an external program. If you encounter any

[6] Frisch, M. J. *et al.* "Gaussian 09, revision D. 01", 2009 Gaussian, Inc., Wallingford CT

problems when using GAUSSIAN together with READUCT, please write a short message to scine@phys.chem.ethz.ch.

In order to use GAUSSIAN with READUCT, specify `program: 'GAUSSIAN'` in the respective system block and the desired calculation method family and method (e.g., `'DFT'` and `'PBEPBE'`) in the `method_family` and `method` key. Note that the name of the functional should match the string used in a typical GAUSSIAN input file.

The path to the GAUSSIAN binary must be set via the environment variable `GAUSSIAN_BINARY_PATH`.

You can specify the following settings in the settings block:

- `molecular_charge`: This specifies the molecular charge. It can take on values between -10 and 10; by default, it is zero.

- `spin_multiplicity`: This specifies the spin multiplicity. It can take on values between 1 and 10; by default, it is 1.

- `basis_set`: This specifies the basis set string. By default, it is `'def2SVP'`. You can specify any valid GAUSSIAN basis set string (see the GAUSSIAN manual for a complete list).

- `gaussian_nprocs`: The number of processors to use in the GAUSSIAN calculations. By default, it is one, *i.e.*, a serial calculation is carried out.

- `external_program_memory`: The total amount of memory in MB that should be available for GAUSSIAN to use. By default set to `1024`.

- `gaussian_filename_base`: This specifies the basic filename (prefix) used for all files related to the GAUSSIAN calculations. By default, it is set to "gaussian_calc"; therefore, the generated input file will be named "gaussian_calc.inp".

- `base_working_directory`: This specifies the directory in which the files for the GAUSSIAN calculations will be stored. By default, this is set to the current directory. For each GAUSSIAN calculation a new directory will be created inside the directory specified by `base_working_directory` to keep the files related to that specific calculation.

Tasks

Single Point Calculation

The single point task can be used to obtain the electronic energy of a given system. In order to carry out this task, specify any of the following in the respective task block: `type: 'single_point'`, `type: 'singlepoint'`, `type: 'sp'`, or `type: 'energy'`. The single point task will print partial atomic charges if the given model provides any. If charges are required the keyword `'require_charges': true` can be given in the tasks settings. In this case the program will abort if a method that does not provide charges is requested.

Bond Order Analysis

Depending on the chosen method it is possible to generate Mayer bond orders for a given system. In order to carry out this task, specify any of the following in the respective task block: `type: 'bond_orders'`, `type: 'bondorders'`, `type: 'bonds'`, `type: 'bos'`, or `type: 'bo'`. This task also generates and states the electronic energy.

Hessian Calculation

This task calculates the Hessian of a given system and outputs the vibrational frequencies as well as thermochemical data. In order to carry out this task, specify any of the following in the respective task block: `type: 'hessian'`, `type: 'frequency_analysis'`, `type: 'frequencyanalysis'`, `type: 'frequencies'`, `type: 'frequency'`, or `type: 'freq'`.

Structure Optimization

This task is used in order to optimize the structure of a given system to a minimum on the potential energy surface. In order to carry out this task, specify any of the following in the respective task block: `type: 'geometry_optimization'`, `type: 'geometryoptimization'`, `type: 'geoopt'`, or `type: 'opt'`.

The task works without the specification of any additional settings; the default settings work usually fine. However, if desired, the following settings can always be set:

- `optimizer`: This sets the desired optimization algorithm. You can set `'bfgs'` for the BFGS algorithm including G-DIIS, `'lbfgs'` for the L-BFGS algorithm, `'steepestdescent'` or `'sd'` for a steepest descent algorithm, and `'newtonraphson'` or `'nr'` for a Newton–Raphson algorithm. By default, it is set to `'bfgs'`.
- `convergence_step_max_coefficient`: The convergence threshold for the maximum absolute element of the last step taken. By default set to `2.0e-3`.
- `convergence_step_rms`: The convergence threshold for the root mean square of the last step taken. By default set to `1.0e-3`.
- `convergence_gradient_max_coefficient`: The convergence threshold for the maximum absolute element of the gradient. By default set to `2.0e-4`.
- `convergence_gradient_rms`: The convergence threshold for the root mean square of the gradient. By default set to `1.0e-4`.
- `convergence_delta_value`: The convergence threshold for the change in the functional value. By default set to `1.0e-6`.
- `convergence_max_iterations`: The maximum number of iterations. By default set to `150`.
- `convergence_requirement`: The number of criteria that have to converge besides the value criterion. This has to be between `0` and `4`; by default it is set to `3`.
- `geoopt_transform_coordinates`: Transform the coordinates into internal ones and carry out the optimization in the internal coordinate system. This will first try to use redundant internal coordinates[7] and fall back to the removal of translation and rotation if unsuccessful; by default it is set to `true`.
- `allow_unconverged`: Allows the calculation to finish correctly even if the optimization did not converge, *i.e.*, no exception is thrown and the final result structure is stored anyways. By default it is set to `false`.

[7] Meli, R. "IRC", `https://github.com/RMeli/irc`, 2019

If you specified `optimizer: 'bfgs'`, you can also set the following options:

- `bfgs_use_gdiis`: Switch to enable the use of a G-DIIS possibly accelerating convergence. By default set to `true`.
- `bfgs_gdiis_max_store`: The maximum number of old steps used in the G-DIIS. By default set to `5`.

- `bfgs_use_trust_radius`: Whether to use the trust radius. By default set to `false`.
- `bfgs_trust_radius`: The maximum size of a taken step. By default set to `0.1`.

If you specified `optimizer: 'lbfgs'`, you can also set the following options:

- `lbfgs_maxm`: The number of parameters and gradients from previous iterations to keep. By default set to `10`.
- `lbfgs_linesearch`: Whether to use a line search or not. By default set to `true`.
- `lbfgs_c1`: The first parameter of the Wolfe conditions. This option is only relevant if line search is used (see above). By default set to `0.0001`.
- `lbfgs_c2`: The second parameter of the Wolfe conditions. This option is only relevant if line search is used (see above). By default set to `0.9`.
- `lbfgs_step_length`: The initial step length. By default set to `1.0`.
- `lbfgs_use_trust_radius`: Whether to use the trust radius. By default set to `false`.
- `lbfgs_trust_radius`: The maximum size of a taken step. By default set to `0.1`.

If you specified `optimizer: 'steepestdescent'` or `optimizer: 'sd'`, you can also set the following options:

- `sd_factor`: The scaling factor to be used in the steepest descent algorithm. By default set to `0.1`.

If you specified `optimizer: 'newtonraphson'` or `optimizer: 'nr'`, you can also set the following options:

- `nr_trust_radius`: The trust radius (maximum root mean square) of a taken step. By default set to `0.5`.
- `nr_svd_threshold`: The threshold for the singular value decomposition of the Hessian. By default set to `1.0e-12`.

Transition State Optimization

This task is used to optimize the structure of a given system to a transition state on the potential energy surface. In order to carry out this

task, specify any of the following in the respective task block: `type: 'transition_state_optimization'`, `type: 'transitionstate_optimization'`, `type: 'tsopt'`, or `type: 'ts'`.

The task works without the specification of any additional settings; the default settings work usually fine. However, if desired, the following settings can always be set:

- `optimizer`: This sets the desired optimization algorithm. You can set `'bofill'` for Bofill's algorithm[8], or any of `'eigenvector_following'`, `'eigenvectorfollowing'`, `ef`, `evf`, or `ev` for a eigenvector following algorithm, or `'dimer'` for the Dimer algorithm [9]. By default, it is set to `'bofill'`.
- `convergence_step_max_coefficient`: The convergence threshold for the maximum absolute element of the last step taken. By default set to `2.0e-3`.
- `convergence_step_rms`: The convergence threshold for the root mean square of the last step taken. By default set to `1.0e-3`.
- `convergence_gradient_max_coefficient`: The convergence threshold for the maximum absolute element of the gradient. By default set to `2.0e-4`.
- `convergence_gradient_rms`: The convergence threshold for the root mean square of the gradient. By default set to `1.0e-4`.
- `convergence_delta_value`: The convergence threshold for the change in the functional value. By default set to `1.0e-6`.
- `convergence_max_iterations`: The maximum number of iterations. By default set to `150`.
- `convergence_requirement`: The number of criteria that have to converge besides the value criterion (`convergence_delta_value`). This has to be between `0` and `4`; by default it is set to `3`.
- `allow_unconverged`: Allows the calculation to finish correctly even if the optimization did not converge, *i.e.*, no exception is thrown and the final result structure is stored anyways. By default it is set to `false`.

If you specified `optimizer: 'bofill'`, you can also set the following options:

- `bofill_trust_radius`: The maximum root mean square of a taken step. By default set to `0.1`.
- `bofill_hessian_update`: The number of iterations using the Bofill

[8] Bofill, J. M. Updated Hessian Matrix and the Restricted Step Method for Locating Transition Structures, *J. Comput. Chem.* **1994,** *15,* 1-11; and Farkas, O.; Schlegel, H. B. Methods for optimizing large molecules, *Phys. Chem. Chem. Phys.* **2002,** *4,* 11–15

[9] Henkelman, G.; Jónsson, H. A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives, *J. Chem. Phys.* **1999,** *111,* 7010–7022; Kästner, J.; Sherwood, P. Superlinearly converging dimer method for transition state search, *J. Chem. Phys* **2008,** *128,* 014106; and Shang, C.; Liu, Z.-P. Constrained Broyden minimization combined with the dimer method for locating transition state of complex reactions, *J. Chem. Theory Comput.* **2010,** *6,* 1136–1144

update scheme in between full hessian calculations. By default set to `5`.

If you specified `optimizer: 'eigenvector_following', 'eigenvectorfollowing', ef, evf`, or `ev`, you can also set the following option:

- `ev_trust_radius`: The maximum root mean square of a taken step. By default set to `0.1`.

If you specified `optimizer: 'dimer'`, you can also set the following options:

- Options to initialize the dimer:
  - `dimer_calculate_hessian_once`: Calculate the Hessian matrix in the beginning to create the dimer along the lowest frequency eigenvector and skip first rotation. By default set to `false`.
  - `dimer_guess_vector_file`: File name in which a row vector is stored. It will be read and used as a guess for the dimer axis. By default the dimer is still rotated before the first translation. The B-Spline task allows to write out the tangent at the maximum of the spline for this purpose (see below).
  - `dimer_discrete_guesses`: Calculate the vector between two structures given as XYZ files to create the dimer. A list of file names of structures has to be provided. This vector then forms the dimer axis. By default the dimer is rotated before the first translation.

    If none of these three options is given, a random vector is used for the initialization of the dimer. If more than one of these three options is set, only one will be used, because there can only be one dimer axis. The options will be preferred according to the above list from top to bottom.
- `dimer_skip_first_rotation`: Skip the first rotation. Recommended if a very reliable guess vector is available. By default set to `false`. If the option to calculate the hessian for the first step was set to `true`, this option is automatically set to `true`.
- `dimer_decrease_rotation_gradient_threshold`: Option to decrease the threshold for the gradient in the rotation after certain number of cycles. By default set to `false`.
- `dimer_gradient_interpolation`: Option to estimate the gradient during the rotation [10]. By default set to `false`.
- `dimer_only_one_rotation`: Only rotate the dimer in the first step. By default set to `false`.

[10] Kästner, J.; Sherwood, P. Superlinearly converging dimer method for transition state search, *J. Chem. Phys* **2008,** *128*, 014106

- `dimer_rotation_lbfgs`: Option to use L-BFGS in the rotation. By default set to `true` and automatically set to `false` if `dimer_rotation_conjugate_gradient` is set. If both are set to false, a steepest descent is performed.
- `dimer_rotation_conjugate_gradient`: Option to use conjugate gradient method in the rotation. By default set to `false`.
- `dimer_projection_trust_radius`: Option to use a stepsize scaling based on the change of projection of the modified force onto the dimer axis in the translation step. By default set to `true` and automatically set to `false` if `dimer_gdiis` is set. If both are set to false, a steepest descent is performed.
- `dimer_gdiis`: Option to use G-DIIS in the translation. This uses a stepsize scaling based on the change of the projection of the modified force onto the dimer axis. By default set to `false`.
- `dimer_multi_scale`: Option to apply step size scaling onto the scaled step of the previous step. By default set to `true`.
- `dimer_radius`: Radius of the dimer. By default set to `0.01`.
- `dimer_phi_tolerance`: Threshold for convergence of rotation with ϕ method [11]. By default set to `1.0e-3`.
- `dimer_rotation_gradient_first`: Threshold for convergence of rotation in the first cycle. By default set to `1.0e-7`.
- `dimer_rotation_gradient_other`: Threshold for convergence of rotation in all cycles but the first. By default set to `1.0e-4`.
- `dimer_lowered_rotation_gradient`: Threshold for convergence of rotation, if lowered by `dimer_decrease_rotation_gradient_threshold`. By default set to `1.0e-3`.
- `dimer_grad_rmsd_threshold`: Threshold for applying stepsize scaling. By default set to `1.0e-3`.
- `dimer_trust_radius`: The maximum root mean square of a taken step. By default set to `0.5`.
- `dimer_default_translation_step`: Scaling factor for steepest descent translation. By default set to `1.0`.
- `dimer_max_rotations_first_cycle`: Maximum number of allowed individual rotations in first rotation. By default set to `100`.
- `dimer_max_rotations_other_cycle`: Maximum number of allowed individual rotations in all rotations except the first. By default set to `100`.

[11] Kästner, J.; Sherwood, P. Superlinearly converging dimer method for transition state search, *J. Chem. Phys* **2008,** *128,* 014106

- `dimer_interval_of_rotations`: Number of translation steps after which it is checked whether a rotation should be performed. By default set to `5`.
- `dimer_cycle_of_rotation_gradient_decrease`: Number of rotation cycles after which the rotation gradient threshold is decreased. By default set to `5`.
- `dimer_max_backtracking`: Number of saved steps in L-BFGS. By default set to `5`.

Intrinsic Reaction Coordinate Calculation

This task is used to perform an intrinsic reaction coordinate (IRC) calculation. In order to carry out this task, specify any of the following in the respective task block: `type: 'ircopt'`, or `type: 'irc'`. Note that for this task you have to specify two output systems. The first one will contain the results of the forward IRC calculation while the second on will contain the result of the backward IRC calculation.

You usually want to set the following settings:

- `irc_mode`: This sets the normal mode which should be used for the IRC calculation. By default set to zero (designates the first normal mode).

The task works without the specification of any additional settings; the default settings work usually fine. However, if desired, the following settings can always be set:

- `optimizer`: This sets the desired optimization algorithm. You can set `'bfgs'` for the BFGS algorithm including G-DIIS, `'lbfgs'` for the L-BFGS algorithm, and `'steepestdescent'` or `'sd'` for a steepest descent algorithm. By default, it is set to `'sd'`.
- `convergence_step_max_coefficient`: The convergence threshold for the maximum absolute element of the last step taken. By default set to `5.0e-3`.
- `convergence_step_rms`: The convergence threshold for the root mean square of the last step taken. By default set to `1.0e-3`.
- `convergence_gradient_max_coefficient`: The convergence threshold for the maximum absolute element of the gradient. By default set to `5.0e-4`.
- `convergence_gradient_rms`: The convergence threshold for the root mean square of the gradient. By default set to `1.0e-4`.

- `convergence_delta_value`: The convergence threshold for the change in the functional value. By default set to `1.0e-6`.
- `convergence_max_iterations`: The maximum number of iterations. By default set to `150`.
- `convergence_requirement`: The number of criteria that have to converge besides the value criterion. This must be between `0` and `4`; by default it is set to `3`.
- `irc_transform_coordinates`: Transform the coordinates into internal ones and carry out the optimization in the internal coordinate system. This will first try to use redundant internal coordinates[12] and fall back to the removal of translation and rotation if unsuccessful; by default it is set to `true`.
- `allow_unconverged`: Allows the calculation to finish correctly even if the optimization did not converge, *i.e.*, no exception is thrown and the final result structures are stored anyways. Especially when using a SD type optimizer this option can be helpful. By default it is set to `false`.

[12] Meli, R. "IRC", https://github.com/RMeli/irc, 2019

If you specified `optimizer: 'bfgs'`, you can also set the following options:

- `bfgs_use_gdiis`: Switch to enable the use of a G-DIIS possibly accelerating convergence. By default set to `true`.
- `bfgs_gdiis_max_store`: The maximum number of old steps used in the G-DIIS. By default set to `5`.
- `bfgs_use_trust_radius`: Whether to use the trust radius. By default set to `false`.
- `bfgs_trust_radius`: The maximum size of a taken step. By default set to `0.1`.

If you specified `optimizer: 'lbfgs'`, you can also set the following options:

- `lbfgs_maxm`: The number of parameters and gradients from previous iterations to keep. By default set to `10`.
- `lbfgs_linesearch`: Whether to use a line search or not. By default set to `true`.
- `lbfgs_c1`: The first parameter of the Wolfe conditions. This option is only relevant if line search is used (see above). By default set to `0.0001`.

- `lbfgs_c2`: The second parameter of the Wolfe conditions. This option is only relevant if line search is used (see above). By default set to `0.9`.
- `lbfgs_step_length`: The initial step length. By default set to `1.0`.
- `lbfgs_use_trust_radius`: Whether to use the trust radius. By default set to `false`.
- `lbfgs_trust_radius`: The maximum size of a taken step. By default set to `0.1`.

If you specified `optimizer: 'steepestdescent'` or `optimizer: 'sd'`, you can also set the following options:

- `sd_factor`: The scaling factor to be used in the steepest descent algorithm. By default set to `0.1`.

Artificial Force Induced Reaction Calculation

This task is used in order to do an artificial force induced reaction (AFIR[13]) calculation. In order to carry out this task, specify any of the following in the respective task block: `type: 'afir_optimization'`, `type: 'afiroptimization'`, `type: 'afiropt'`, or `type: 'afir'`. The energy given in the output includes the artifical force term.

[13] Maeda, S.; Morokuma, K. Communications: A systematic method for locating transition structures of A+B $\rightarrow$ X type reactions, *J. Chem. Phys.* **2010,** *132*, 241102; and Maeda, S.; Morokuma, K. Finding Reaction Pathways of Type A + B $\rightarrow$ X: Toward Systematic Prediction of Reaction Mechanisms, *J. Chem. Theory Comput.* **2011,** *7*, 2335–2345

You usually want to set the following settings:

- `afir_rhs_list`: This specifies list of indices of atoms to be artificially forced onto or away from those in the LHS list (see below). By default, this list is empty. Note that the first atom has the index zero.
- `afir_lhs_list`: This specifies list of indices of atoms to be artificially forced onto or away from those in the RHS list (see above). By default, this list is empty. Note that the first atom has the index zero.

The task works without the specification of any additional settings; the default settings work usually fine. However, if desired, the following settings can always be set:

- `afir_weak_forces`: This activates an additional, weakly attractive force applied to all atom pairs. By default set to `false`.
- `afir_attractive`: Specifies whether the artificial force is attractive or repulsive. By default set to `true`, which means that the force is attractive.

- `afir_energy_allowance`: The maximum amount of energy to be added by the artifical force, in kJ/mol. By default set to `1000`.
- `afir_phase_in`: The number of steps over which the full attractive force is gradually applied. By default set to `30`.
- `afir_transform_coordinates`: Whether to transform the coordinates from a Cartesian basis into an internal space. By default set to `true`.
- `optimizer`: This sets the desired optimization algorithm. You can set `'bfgs'` for the BFGS algorithm including G-DIIS, `'lbfgs'` for the L-BFGS algorithm, and `'steepestdescent'` or `'sd'` for a steepest descent algorithm. By default, it is set to `'bfgs'`.
- `convergence_step_max_coefficient`: The convergence threshold for the maximum absolute element of the last step taken. By default set to `2.0e-3`.
- `convergence_step_rms`: The convergence threshold for the root mean square of the last step taken. By default set to `1.0e-3`.
- `convergence_gradient_max_coefficient`: The convergence threshold for the maximum absolute element of the gradient. By default set to `2.0e-4`.
- `convergence_gradient_rms`: The convergence threshold for the root mean square of the gradient. By default set to `1.0e-4`.
- `convergence_delta_value`: The convergence threshold for the change in the functional value. By default set to `1.0e-6`.
- `convergence_max_iterations`: The maximum number of iterations. By default set to `150`.
- `convergence_requirement`: The number of criteria that have to converge besides the value criterion. This has to be between `0` and `4`; by default it is set to `3`.
- `allow_unconverged`: Allows the calculation to finish correctly even if the optimization did not converge, *i.e.*, no exception is thrown and the final result structure is stored anyways. By default it is set to `false`.

If you specified `optimizer: 'bfgs'`, you can also set the following options:

- `bfgs_use_gdiis`: Switch to enable the use of a G-DIIS possibly accelerating convergence. By default set to `true`.

- `bfgs_gdiis_max_store`: The maximum number of old steps used in the G-DIIS. By default set to `5`.
- `bfgs_use_trust_radius`: Whether to use the trust radius. By default set to `true`.
- `bfgs_trust_radius`: The maximum size of a taken step. By default set to `0.1`.

If you specified `optimizer: 'lbfgs'`, you can also set the following options:

- `lbfgs_maxm`: The number of parameters and gradients from previous iterations to keep. By default set to `10`.
- `lbfgs_linesearch`: Whether to use a line search or not. By default set to `true`.
- `lbfgs_c1`: The first parameter of the Wolfe conditions. This option is only relevant if line search is used (see above). By default set to `0.0001`.
- `lbfgs_c2`: The second parameter of the Wolfe conditions. This option is only relevant if line search is used (see above). By default set to `0.9`.
- `lbfgs_step_length`: The initial step length. By default set to `1.0`.
- `lbfgs_use_trust_radius`: Whether to use the trust radius. By default set to `true`.
- `lbfgs_trust_radius`: The maximum size of a taken step. By default set to `0.1`.

If you specified `optimizer: 'steepestdescent'` or `optimizer: 'sd'`, you can also set the following options:

- `sd_factor`: The scaling factor to be used in the steepest descent algorithm. By default set to `0.1`.

B-Spline Interpolation and Optimization

This task is used in order to approximate a reaction path between a given start and end structure by means of an interpolation based on B-splines[14]. This interpolated path can be optimized to yield a better approximation to the true reaction path. Furthermore, from the optimized path, a guess for the transition state structure can be extracted. In order to carry out this task, specify any of the following

[14] Vaucher, A. C.; Reiher, M. Minimum Energy Paths and Transition States by Curve Optimization, *J. Chem. Theory Comput.* **2018,** *14,* 3091–3099

in the respective task block: `type: 'bspline_interpolation'`, `type: 'bsplineinterpolation'`, or `type: 'bspline'`.

The task works without the specification of any additional settings; the default settings work usually fine. However, if desired, the following settings can always be set:

- `optimizer`: This sets the desired optimization algorithm. You can set `'lbfgs'` for the L-BFGS algorithm, and `'steepestdescent'` or `'sd'` for a steepest descent algorithm. By default, it is set to `'lbfgs'`.
- `optimize`: Whether the interpolated path should be optimized. By default set to `true`.
- `trajectory_guess`: A list of possibly concatenated XYZ files that should be added as data points when interpolating the initial spline. The files may, but do not need to, include the start and end structures as first and last structure.
- `extract_ts_guess`: Whether a guess for the transition state structure should be extracted from the optimized path. By default set to `false`. If set to true, the structure is written into the file `<output_name>_tsguess.xyz`.
- `extract_threshold`: Specifies the threshold for the extraction of the maximum energy structure from a reaction profile. For the extraction, the part of the spline around its maximum is discretized to five grid points. These points are refined until the energy difference between the two points neighboring the point with maximal energy is less than two times this threshold. By default this threshold is set to `1e-3` (hartree).
- `extract_ts_guess_neighbours`: Whether the structures before and after the transition state structure should be extracted from the optimized path. By default set to `false`. If set to true, the structures are written into the file `<output_name>_tsguess-1.xyz` and `<output_name>_tsguess+1.xyz`.
- `tangent_file`: The name of the file in which the tangent of the spline at the TS guess will be stored as a row vector. This can be used for a single ended TS optimization. If a relative path is given, it is interpreted relative to the output directory of the B-spline interpolation task. By default no tangent is written out.
- `align_structures`: Whether to remove the overall rotation and translation of the end structure. By default set to `true`.

- `num_control_points`: The number of control points for the B-spline representing the reaction path. This number is directly proportional to the number of parameters to optimize. By default set to `5`.
- `num_integration_points`: The number of integration points used during the optimization of the B-spline. A higher number of integration points increases the accuracy but also the computational cost. By default set to `21`.
- `num_structures`: Sets the number of structures into which a reaction path is discretized for the final output (*i.e.,* when writing it to a XYZ trajectory file). By default set to `10`.

If you specified `optimizer: 'lbfgs'`, you can also set the following options:

- `lbfgs_maxm`: The number of parameters and gradients from previous iterations to keep. By default set to `10`.
- `lbfgs_linesearch`: Whether to use a line search or not. By default set to `false`.
- `lbfgs_c1`: The first parameter of the Wolfe conditions. This option is only relevant if line search is used (see above). By default set to `0.0001`.
- `lbfgs_c2`: The second parameter of the Wolfe conditions. This option is only relevant if line search is used (see above). By default set to `0.9`.
- `lbfgs_step_length`: The initial step length. By default set to `1.0`.
- `lbfgs_use_trust_radius`: Whether to use the trust radius. By default set to `false`.
- `lbfgs_trust_radius`: The maximum size of a taken step. By default set to `0.1`.

If you specified `optimizer: 'steepestdescent'` or `optimizer: 'sd'`, you can also set the following options:

- `sd_factor`: The scaling factor to be used in the steepest descent algorithm. By default set to `0.1`.

Task Chaining

You can specify multiple tasks to be executed after each other. Tasks are processed in the order in which they are given in the input file.

For example, the following input file would first carry out a structure optimization, and then calculate the vibrational frequencies of the optimized structure:

```
systems:
  - name: 'water'
    path: 'h2o.xyz'
    program: 'Sparrow'
    method: 'PM6'

tasks:
  - type: 'geoopt'
    input: ['water']
    output: ['water_opt']
  - type: 'hessian'
    input: ['water_opt']
```

Using the Python Library

ReaDuct provides Python bindings such that all functionality of ReaDuct can be accessed also via the Python programming language. In order to build the Python bindings, you need to specify `-DSCINE_BUILD_PYTHON_BINDINGS=ON` when running cmake (see also chapter Installation).

In order to use the Python bindings, you need to specify the path to the Python library in the environment variable `PYTHONPATH`, *e.g.*, you have to run the command

```
export PYTHONPATH=$PYTHONPATH:<source code directory>/install/lib/python<version>/site-packages
```

where `<version>` is the Python version you are using (*e.g.*, 3.6). Now, you can simply import the library and use it as any other Python library. For example, in order to carry out a structure optimization, you could use the following Python script:

```
import scine_readuct

system1 = scine_readuct.load_system('h2o.xyz', 'PM6', program='Sparrow',
                                    molecular_charge=0, spin_multiplicity=1)

systems = {}
systems['water'] = system1

systems, success = scine_readuct.run_opt_task(systems, ['water'], output=['water_opt'],
                                    optimizer='bfgs')

if success:
    systems['water_opt'].positions
```

Note that we use a dictionary called "systems" to store all systems we deal with in one central data structure. As second argument, the structure optimization task accepts a list of the systems which should be optimized, *i.e.*, the dictionary "systems" can contain more systems

but these will not be optimized (all other tasks work with the same concept). The output system(s) will be automatically added to the systems dictionary.

A detailed list of all the functions provided by the ReaDuct Python library can be found by running

```
import scine_readuct

help(scine_readuct)
```

Extensions Planned in Future Releases

- Interfaces to other quantum chemical packages such as SERENITY[15]

[15] Unsleber, J. P.; Dresselhaus, T.; Klahr, K.; Schnieders, D.; Böckers, M.; Barton, D.; Neugebauer, J. SERENITY: A subsystem quantum chemistry program, *J. Comput. Chem.* **2018,** *39,* 788–798

Important References

Please consult the following references for more details on ReaDuct. We kindly ask you to cite the following reference in any publication of results obtained with ReaDuct.

A. C. Vaucher, M. Reiher "Minimum Energy Paths and Transition States by Curve Optimization", *J. Chem. Theory Comput.*, **2018**, *16*, 3091.

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