# EOP-Dev 1.0.2-alpha

Novel methods for Quantum Chemistry of Extended Molecular Aggregates

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## EOPDev

Generalized Effective One-Electron Potentials: Development Platform.

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### Overview

Test various models of the intermolecular interaction that is based on the application of the **Effective One-electron Potentials (EOP's)** technique.

Currently, the interaction between two molecules described by the Hartree-Fock-Roothaan-Hall theory or the configuration interaction with singles theory is considered. In particular, the plugin tests the models of:

1. the charge-transfer interaction energy (Project I )
2. the excitation energy transfer couplings (Project I )
3. the Pauli exchange-repulsion interaction energy (Project II )
4. the polarization of electronic density (Project III)

against reference solutions (exact or other approximations).

Places to go:

- EOP-Dev Code
- Current Issues

This wikipages might be updated in the future.

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## References

[1] B. Błasiak, "One-Particle Density Matrix Polarization Susceptibility Tensors", *J. Chem. Phys.* **149**, 164115 (2018)

# Chapter 2

# Introduction

Exploring biological phenomena at molecular scale is oftentimes indispensable to develop new drugs and intelligent materials.

Most of relevant system properties are affected by intermolecular interactions with nearby environment such as solvent or closely bound electronic chromophores. Studying such molecular aggregates requires rigorous and accurate quantum chemistry methods, the cost of which grows very fast with the number of electrons. Despite many methodologies have been devised to describe energetic and dynamical properties of **extended molecular systems** efficiently and accurately, there exist particularly difficult cases in which modelling is still challenging:

- describing electronic transitions in solution or
- when coupled with other electronic transition via resonance energy transfer,
- performing molecular dynamics at very high level of theory including dynamic electron correlation,
- vibrational frequency calculations of particular normal mode in condensed phases

and so on. The reason behind (sometimes prohibitively) high costs of fully *ab initio* calculations in the above areas is the complexity of mathematical models often based on wave functions rather then (conceptually more straightforward) electronic densities. On the other hand, it has been pointed out before that the one-electron density distributions are of particular importance in chemistry. It can be thus utilized as a means of developing a general model that re-expresses the physics of intermolecular interactions in terms of effective one-electron functions that are easier to handle in practice.

This Project focuses on finding a unified way to simplify various fragment-based approaches of Quantum Chemistry of extended molecular systems, i.e., molecular aggregates such as interacting chromophores and molecules solvated by water and other solvents. Indeed, one of the important difficulties encountered in Quantum Chemistry of large systems is the need of evaluation of special kind of numbers known as *electron repulsion integrals*, or in short, ERI's. In a typical calculation, the amount of ERI's can be as high as tens or even hundreds of millions (!) that unfortunately prevents from application of conventional methods when the number of particles in question is too large. In the Project, the complicated expressions involving ERI's shall be greatly simplified to reduce the computational costs as much as possible while introducing no or minor approximations to the original theories.

## 2.1 Research Project Methodology

In this Project the new theoretical protocol based on the effective one-electron potentials (EOP's) is developed. The main principle is to rewrite arbitrary sum of functions $f$ of electron repulsion integrals (ERI's) by defining EOP's according to the following general prescription:

$$\sum_f f\left[\left(\phi_i^A\phi_j^A||\phi_k^B\phi_l^B\right)\right] = \left(\phi_i^A|v_{kl}^B|\phi_j^A\right) \rightarrow \text{point charge or density fitting}$$
$$\sum_f f\left[\left(\phi_i^A\phi_j^B||\phi_k^B\phi_l^B\right)\right] = \left(\phi_i^A|v_{kl}^B|\phi_j^B\right) \rightarrow \text{density fitting,}$$

where $A$ and $B$ denote different molecules and $\phi_i$ is the $i$-th molecular orbital or basis function. Here, $v_{kl}^B$ denotes the poeptypes *ab initio* ”EOP matrix element”. The technique described above will be applied to simplify expressions for

- short-range excitation energy transfer couplings between chlorophyll subunits of reaction centres in photosynthesis
- Pauli interaction repulsion energy
- charge-transfer interaction energy
- electric field-induced charge density polarization of molecules.

The above developments might be used in fragment-based *ab initio* molecular dynamics protocols of new generation.

## 2.2 Expected Impact on the Development of Science, Civilization and Society

The proposed EOP's are expected to significantly develop the fragment-based methods that are widely used in physical chemistry and modelling of biologically important systems. Owing to universality of EOP's, they could find applications in many branches of chemical science: non-empirical$*$ molecular dynamics, short-range resonance energy transfer in photosynthesis, electronic and vibrational solvatochromism, multidimensional spectroscopy and so on. In particular:

- the EOP-based models of Pauli repulsion energy and charge-transfer (CT) energy could be used to improve the computational performance of the second generation effective fragment potential method (EFP2). At present, the CT term is very time consuming and due to this reasons it is not used in many of applications of EFP2 to perform molecular dynamics simulations.Błasiak et al. [2020a]
- the EOP-based model of EET couplings could significantly improve modelling of energy transfer in the light harvesting complexes. At present, short-range phenomena (Dexter mechanisms of EET) are very difficult to efficiently and quantitatively asses when performing statistical averaging and applying to large molecular aggregates. Such Dexter effects could be computed by using EOP's in much more efficient manner without loosing high accuracy of parent TDFI-TI method.Błasiak et al. [2020b]

- the density matrix polarization (DMS) tensors could be used in new generation fragment-based *ab initio* molecular dynamics protocols that rigorously take into consideration electron correlation effects.Błasiak [2018]

Therefore, we believe that the application of EOP's could have an indirect impact on the design of novel drugs and materials for industry.

## 2.3 The EOPDev Code

To pursue the above challenges in the field of computational quantum chemistry of extended molecular aggregates, the EOPDev platform is developed. Accurate and efficient *ab initio* models based on EOP's are implemented in the EOPDev code, along with the state-of-the-art benchmark and competiting methods. Written entirely in C++, EOPDev is a plugin to Psi4 quantum chemistry package. Therefore, compilation and running the EOPDev code is straightforward and follows the API interface similar to the one used in Psi4 with just a few specific programing conventions. The detailed discussion about using the EOPDev code can be found in advanced usage section.

**Note**

The ‘OEP' abbreviation, rather than the ‘EOP', is used throughout the code. It is because the earlier versions of EOPDev utilized the former abbreviation consecutively for the shared libraries, modules and class names. The abbreviation was changed to the latter in this public release of the code. Please treat these two abbreviations as synonyms within the project and code, both refering to the *effective one-electron potentials*.

# Chapter 3

# EOP Design.

EOP (One-Electron Potential) is associated with certain quantum one-electron operator $\hat{v}^A$ that defines the ability of molecule $A$ to interact in a particular way with other molecules.

Technically, EOP can be understood as a **container object** (associated with the molecule in question) that stores the information about the above mentioned quantum operator. Here, it is assumed that similar EOP object is also defined for all other molecules in a molecular aggregate.

In case of interaction between molecules $A$ and $B$, EOP object of molecule $A$ interacts directly with wavefunction object of the molecule $B$. Defining a Solver class that handles such interaction Wavefunction class and EOP class

the universal design of EOP-based approaches can be established and developed.

> **Important:** EOP and Wavefunction classes should not be restricted to Hartree-Fock (HF); in generall any correlated wavefunction and derived EOP‘s should be allowed to work with each other. However, in the current version of the project, only HF wavefunctions are considered.

## 3.1 EOP Classes

There are many types of EOP’s, but the underlying principle is the same and independent of the type of intermolecular interaction. Therefore, the EOP’s should be implemented by using a multi-level class design. In turn, this design depends on the way EOP’s enter the mathematical expressions, i.e., on the types of matrix elements of the one-electron effective operator $\hat{v}^A$.

### 3.1.1 Structure of possible EOP-based expressions and their unification

Structure of EOP-based mathematical expressions is listed below:

| Type | Matrix Element | Comment |
|---|---|---|
| Type 1 | $\left(I\vert\hat{v}^A\vert J\right)$ | $I \in A,\ J \in B$ |
| Type 2 | $\left(J\vert\hat{v}^A\vert L\right)$ | $J, L \in B$ |

In the above table, $I$, $J$ and $K$ indices correspond to basis functions or molecular orbitals. Basis functions can be primary or auxiliary EOP-specialized density-fitting. Depending on the type of function and matrix element, there are many subtypes of resulting matrix elements that differ in their dimensionality. Examples are given below:

| Matrix Element | DF-based form | DMTP-based form |
|---|---|---|
| $\left(\mu \vert \hat{v}^{A[\mu]} \vert \sigma\right)$ | $\sum_{\iota\in A} v^{A}_{\mu\iota} S_{\iota\sigma}$ | $\sum_{\alpha\in A} q_{\alpha}^{A[\mu]} V_{\mu\sigma}^{(\alpha)}$ |
| $\left(i \vert \hat{v}^{A[i]} \vert j\right)$ | $\sum_{\iota\in A} v^{A}_{i\iota} S_{\iota j}$ | $\sum_{\alpha\in A} q_{\alpha}^{A[i]} V_{ij}^{(\alpha)}$ |
| $\left(j \vert \hat{v}^{A[i]} \vert l\right)$ | $\sum_{\iota\kappa\in A} S_{j\iota} v^{A[i]}_{\iota\kappa} S_{\kappa l}$ | $\sum_{\alpha\in A} q_{\alpha}^{A[i]} V_{jl}^{(\alpha)}$ |

In the formulae above, the EOP-part (stored by EOP instances) and the Solver-part (to be computed by the Solver) are separated. It is apparent that all EOP-parts have the form of 2- or 3-index arrays with different class of axes (molecular orbitals, primary/auxiliary basis, atomic space). Therefore, they can be uniquely defined by a unified *tensor object* (storing double precision numbers) and unified *dimension object* storing the information of the axes classes.

In Psi4, a perfect candidate for the above is `psi4::Tensor` class declared in `psi4/libthce/thce.h`. Except from the numeric content its instances also store the information of the dimensions in a form of a vector of `psi4::Dimension` instances.

Another possibility is to use `psi::Matrix` objects, instead of `psi4::Tensor` objects, possibly putting them into a `std::vector` container in case there is more than two axes.

**Note**

Currently, the second possibility is used, i.e., matrices. For more complex data structures, other types of custom objects are defined.

# Chapter 4

# Density-fitting Specialized for EOP's

To get the ab-initio representation of a EOP, one can use a procedure similar to the typical density fitting or resolution of identity, both of which are nowadays widely used to compute electron-repulsion integrals (ERI's) more efficiently.

## 4.1 Fitting in Complete Space

An arbitrary one-electron potential of molecule *A* acting on any state vector associated with molecule *A* can be expanded in an *auxiliary space* centered on *A* as

$$v|i) = \sum_{\xi\eta} v|\xi)[\mathbf{S}^{-1}]_{\xi\eta}(\eta|i)$$

under the necessary assumption that the auxiliary basis set is *complete*. In a special case when the basis set is orthogonal (e.g., molecular orbitals) the above relation simplifies to

$$v|i) = \sum_{\xi} v|\xi)(\xi|i)$$

It can be easily shown that the above general and exact expansion can be obtained by performing a density fitting in the complete space. We expand the LHS of the first equation on this page in a series of the auxiliary basis functions scaled by the undetermined expansion coefficients:

$$v|i) = \sum_{\xi} G_{i\xi}|\xi)$$

which we shall refer here as to the matrix form of the EOP operator. By constructing the least-squares objective function

$$Z[\{G_{\xi}^{(i)}\}] = \int d\mathbf{r}_1 \left[ v(\mathbf{r}_1)\phi_i(\mathbf{r}_1) - \sum_{\xi} G_{\xi}^{(i)} \varphi_{\xi}(\mathbf{r}_1) \right]^2$$

and requiring that

$$\frac{\partial Z[\{G_{\xi}^{(i)}\}]}{\partial G_{\mu}^{(i)}} = 0 \text{ for all } \mu$$

we find the coefficients $G_\xi^{(i)}$ to be

$$\mathbf{G}^{(i)} = \mathbf{v}^{(i)} \cdot \mathbf{S}^{-1}$$

where

$$\begin{aligned} v_\eta^{(i)} &= (\eta|vi) \\ S_{\eta\xi} &= (\eta|\xi) \end{aligned}$$

or explitictly

$$G_{i\xi} = \sum_\eta [\mathbf{S}^{-1}]_{\xi\eta} (\eta|v|i)$$

identical to what we obtained from application of the resolution of identity in space spanned by non-orthogonal complete set of basis vectors.

Since matrix elements of an EOP operator in auxiliary space can be computed in the same way as the matrix elements with any other basis function, one can formally write the following identity

$$(X|v|i) = \sum_{\xi\eta} S_{X\xi} [\mathbf{S}^{-1}]_{\xi\eta} (\eta|v|i)$$

where $X$ is an arbitrary orbital. When the other orbital does not belong to molecule *A* but to the (changing) environment, it is straightforward to compute the resulting matrix element, which is simply given as

$$(j_{\in B}|v^A|i_{\in A}) = \sum_\xi S_{j\xi} G_{i\xi}$$

where *j* denotes the other (environmental) basis function.

In the above equation, the EOP-part (fragment parameters for molecule *A* only) and the Solver-part (subject to be computed by solver on the fly) are separated. This then forms a basis for fragment-based approach to solve Quantum Chemistry problems related to the extended molecular aggregates.

## 4.2 Fitting in Incomplete Space

Density fitting scheme from previous section has practical disadvantage of a nearly-complete basis set being usually very large (spanned by large amount of basis set vectors). Any non-complete basis set won't work in the previous example. Since most of basis sets used in quantum chemistry do not form a complete set, it is beneficial to design a modified scheme in which it is possible to obtain the **effective** matrix elements of the EOP operator in a **incomplete** auxiliary space. This can be achieved by minimizing the following objective function

$$Z[\{G_\xi^{(i)}\}] = \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\left[v(\mathbf{r}_1)\phi_i(\mathbf{r}_1) - \sum_\xi G_\xi^{(i)} \varphi_\xi(\mathbf{r}_1)\right] \left[v(\mathbf{r}_2)\phi_i(\mathbf{r}_2) - \sum_\xi G_\eta^{(i)} \varphi_\eta(\mathbf{r}_1)\right]}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Thus requesting that

$$\frac{\partial Z[\{G_\xi^{(i)}\}]}{\partial G_\mu^{(i)}} = 0 \text{ for all } \mu$$

we find the coefficients $G_\xi^{(i)}$ to be

$$\mathbf{G}^{(i)} = \mathbf{b}^{(i)} \cdot \mathbf{A}^{-1}$$

where

$$\begin{aligned} b_\eta^{(i)} &= (\eta||\nu i) \\ A_{\eta\xi} &= (\eta||\xi) \end{aligned}$$

The symbol $||$ is to denote the operator $r_{12}^{-1}$ and double integration over $\mathbf{r}_1$ and $\mathbf{r}_2$. Thus, in order to use this generalized density fitting scheme one must to compute two-centre electron repulsion integrals (implemented in ERI_1_1).

## 4.3 Fitting in Incomplete Space - Alternative Approach

TODO

# Chapter 5

# Implemented Models

## 5.1 Fragment-Based Methods

List of most important models implemented in the EOPDev project is given below. Among the interaction energy models are the second generation of the effective potential method (EFP2) Gordon et al. [2013] Li et al. [2006] Xu and Gordon [2013], perturbation theories of Murrel et al.Murrell et al. [1965], Otto and Ladik Otto and Ladik [1975] and Hayes and Stone Hayes and Stone [1984], density decomposition scheme (DDS) Mandado and Hermida-Ramón [2011], reduced variational space (RVS) method Stevens and Fink [1987]. Among the excitation energy transfer (EET) coupling methods are the TrCAMM methodBłasiak et al. [2015] and the transfer integral (TI) method Fujimoto [2012].

**Table 1.** Theoretical fragment-based models implemented in EOPDev.

| Pauli energy | CT energy | EET Coupling |
|---|---|---|
| EFP2 | EFP2 | TrCAMM |
| Murrel et al. | Otto-Ladik | TI |
| EOP-Murrel et al. | EOP-Otto-Ladik | EOP-TI |
| Otto-Ladik | | |
| EOP-Otto-Ladik | | |
| DDS | | |
| Hayes-Stone (exact) | RVS | Exact (ESD) |

## 5.2 Target, Benchmark and Competing Models

The target models introduced in the Project are tested against the following benchmarks and compared with the following state-of-the-art models:

**Table 2.** Target models vs benchmarks and competitor models.

| Target Model | Benchmarks | Competing Model |
|---|---|---|
| EOP-Murrel et al. (Pauli) | Murrel et al., DDS, Stone | EFP2 (Pauli) |
| EOP-Otto-Ladik (CT) | Otto-Ladik, RVS | EFP2 (CT) |

| Target Model | Benchmarks | Competing Model |
|---|---|---|
| EOP-TI | Exact (ESD), TI | TI |

The target models contain their EOP-based versions, that can be executed in the `OEPDevSolver::compute_oep_based`, and compared with the corresponding benchmark models `OEPDevSolver::compute_benchmark`.

# Chapter 6

# Contributing to EOPDev

EOPDev is a plugin to Psi4.

Therefore it should follow the programming etiquette of Psi4. Also, EOPDev has additional programming tips to make the code more versatile and easy to develop further. Here, I emphasise on most important aspects regarding the proposed **programming rules**.

## 6.1 Main routine and libraries

EOPDev has only *one* source file in the plugin base directory, i.e., `main.cc`. This is the main driver routine that handles the functionality of the whole EOP testing platform: specifies options for Psi4 input file and implements test routines based on the options. Include files directly related to `main.cc` are stored in the `include` directory, where only header files are present. Options are specified in `include/oepdev_options.h` whereas macros and defines in `include/oepdev_files.h`. Other sources are stored in `MODULE/libNAME*` directories where `NAME` is the name of the library with sources and header files, whereas `MODULE` is the directory of the EOPDev module.

Things to remember:

1. **No other sources in base directory.** It is not permitted to place any new source or other files in the plugin base directory (i.e., where `main.cc` resides).
2. **Sources in library directories.** Any additional source code has to be placed in `oepdev/libNAME*` directory (either existing one or a new one; in the latter case remember to add the new `*.cc` files to `CMakeLists.txt` in the plugin base directory.
3. **Miscellanea in special directories.** If you want to add additional documentation, put it in the `doc` directory. If you want to add graphics, put it in the `images` directory.

## 6.2 Header files in libraries

Header files are handy in obtaining a quick glimpse of the functionality within certain library. Each library directory should contain at least one header file in EOPDev. However, header files can be problematic if not managed properly.

Things to remember:

1. **Header preprocessor variable**. Define the preprocessor variable specyfying the existence of include of the particular header file. The format of such is

   ```
   #ifndef MODULE_LIBRARY_HEADER_h
   #define MODULE_LIBRARY_HEADER_h
   // rest of your code goes here
   #endif // MODULE_LIBRARY_HEADER_h
   ```

   Last line is the **end** of the header file. The preprocessor variables represents the directory tree `oepdev/MODULE/LIBRARY/HEADER.h` structure (where `oepdev` is the base plugin directory). `MODULE` is the plugin module name (e.g. `oepdev`, the name of the module directory) `LIBRARY` is the name of the library (e.g. `libutil`, should be the same as library directory name) `HEADER` is the name of the header in library directory (e.g. `diis` for `diis.h` header file)

2. **Set module namespace**. To prevent naming clashes with other modules and with Psi4 it is important to operate in separate namespace (e.g. for a module).

   ```
   namespace MODULE {
   // your code goes here
   } // EndNameSpace MODULE
   ```

   For instance, all classes and functions in `oepdev` module are implemented within the namespace of the same label. Considering addition of other local namespaces within a module can also be useful in certain cases.

## 6.3 Environmental variables

Defining the set of intrinsic environmental variables can help in code management and conditional compilation. The EOPDev environmental variables are defined in `include/oepdev_files.h` file. Remember also about psi4 environmental variables defined in `psi4/psifiles.h` header. As a rule, the EOPDev environmental variable should have the following format:

```
OEPDEV_XXXX
```

where `XXXX` is the descriptive name of variable.

## 6.4 Documenting the code

Code has to be documented (at best at a time it is being created). The place for documentation is always in header files. Additional documentation can be also placed in source files. Leaving a chunk of code for a production run without documentation is unacceptable.

Use Doxygen style for documentation all the time. Remember that it supports markdown which can make the documentation even more clear and easy to understand. Additionally you can create a nice `.rst` documentation file for Sphinx program. If you are coding equations, always include formulae in the documentation!

Things to remember:

1. **Descriptions of classes, structures, global functions, etc**. Each programming object should have a description.
2. **Documentation for function arguments and return object**. Usage of functions and class methods should be explained by providing the description of all arguments (use `\param` and `\return` Doxygen keywords).
3. **One-line description of class member variables**. Any class member variable should be preceded by a one-liner documentation (starting from `///`).
4. **Do not be afraid of long names in the code**. Self-documenting code is a bless!

## 6.5 Naming conventions

Naming is important because it helps to create more readable and clear self-documented code.

Some loose suggestions:

1. **Do not be afraid of long names in the code, but avoid redundancy**. Examples of good and bad names: good name: `get_density_matrix`; bad name: `get_matrix`. Unless there is only one type of matrix a particular objects can store, `matrix` is not a good name for a getter method. good name: `class Wavefunction`, bad name: `class WFN` good name: `int numberOfErrorVectors`, bad name: `int nvec`, bad name: `the_number_of_error_vectors` good name: `class EFPotential`, probably bad name: `class EffectiveFragmentPotential`. The latter might be understood by some people as a class that inherits from `EffectiveFragment` class. If it is not the case, compromise between abbreviation and long description is OK.
2. **Short names are OK in special situations**. In cases meaning of a particular variable is obvious and it is frequently used in the code locally, it can be named shortly. Examples are: `i` when iterating `no` number of occupied orbitals, `nv` number of virtual orbitals, etc.
3. **Clumped names for variables and dashed names for functions**. Try to distinguish between variable name like `sizeOfEOPTypeList` and a method name `get_matrix()` (neither `size_of_EOP_type_list`, nor `getMatrix()`). This is little bit cosmetics, but helps in managing the code when it grows.
4. **Class names start from capital letter**. However, avoid only capital letters in class names, unless it is obvious. Avoid also dashes in class names (they are reserved for global functions and class methods). Examples: good name: `DIISManager`, bad name: `DIIS`. good name: `EETCouplingSolver`, bad name: `EETSolver`, very bad: `EET`.

## 6.6 Track timing when evaluating the code

It is useful to track time elapsed for performing a particular task by a computer. For this, use for example `psi::timer_on` and `psi::timer_off` functions defined in `psi4/libqt/qt.h`. Psi4 always generates the report file `timer.dat` that contains all the defined timings. For example,

```
#include "psi/libqt/qt.h"
psi::timer_on("EOP    E(Paul) Murrell-etal S1  ");
// Your code goes here
psi::timer_off("EOP    E(Paul) Murrell-etal S1  ");
```

To maintain the printout in a neat form, the timing associated with the EOPDev code can be generated via `misc/python/timing.py` utility script.

## 6.7 Clean memory between independent jobs

If you use scratch disk space to store integrals, clean the scratch in between independent calculations. From C++ level invoke

```
#include "psi4/libpsio/psio.hpp"
// ...
psi::PSIOManager::shared_object()->psiclean();
```

whereas from the Python level use

```
import psi4
# ..
psi4.core.clean()
```

If the scratch space is not cleaned up before next independent task begins, certain computational routines might crash with `PSIOError` or continue without error, but produce wrong results.

## 6.8 Use Object-Oriented Programming

Try to organise your creations in objects having special relationships and data structures. Encapsulation helps in producing self-maintaining code and is much easier to use. Use:

- **factory design** for creating objects
- **container design** for designing data structures
- **polymorphysm** when dealing with various flavours of one particular feature in the data structure

  *Note:* In Psi4, factories are frequently implemented as static methods of the base classes, for example `psi::BasisSet::build` static method. It can be followed when building object factories in EOPDev too.

# Chapter 7

# Advanced Usage

This section is addressed for advanced users.

Make sure you have first read the introduction before proceeding.

## 7.1 Installation

### 7.1.1 Preparing Psi4

EOPDev is a Psi4 plugin. It requires

- Psi4, version 1.2.1 (git commit `9d4a61c`). Has to be modified (see below).
- Eigen3, any version.

**Note**

> Before compiling, make sure EFP is enabled in `CMakeLists.txt` (now it is not used in EOPDev but maybe in the future it would).

Recently, Psi4 introduced API visibility management. Only certain Psi4 classes and functions are *exposed* in the `core.so` library, that is further linked to Psi4 plugin shared library. Due to this reason, not all Psi4 functionalities can be directly used from outside Psi4. In order to access local API of Psi4 (also used in the EOPDev code) slight modification of Psi4 code and concomitant rebuild is necessary.

In order to expose local API used by EOPDev and hidden within Psi4 1.2, two types of small modifications are necessary:

- M1: add `PSI_API` macro after required class or function declaration in header file
- M2: add `#include "psi4/pragma.h"` line at the include section of an appropriate header file

Modification M1 is obligatory for all affected files whereas modification M2 needs to be done only in headers that do not have ”psi4/pragma.h” included explicitly or implicitly. The list of some Psi4 header files along with the respective changes that need to be done are listed in the table below:

| Psi4 Header File | Psi4 Class | Required Changes |
|---|---|---|
| `libfunctional/superfunctional.h` | `Superfunctional` | M1 |
| `libscf_solver/hf.h` | `HF` | M1 |
| `libscf_solver/rhf.h` | `RHF` | M1 |
| `libcubeprop/csg.h` | `CubicScalarGrid` | M1 |
| `libmints/onebody.h` | `OneBodyAOInt` | M1 |
| `libmints/potential.h` | `PotentialInt` | M1 |
| `libmints/multipoles.h` | `MultupoleInt` | M1 |
| `libmints/multipolesymmetry.h` | `MultipoleSymmetry` | M1 |
| `libmints/fjt.h` | `Taylor_Fjt` | M1 |
| `libmints/fjt.h` | `Fjt` | M1 |
| `libmints/oeprop.h` | `EOProp` | M1, M2 |
| `libmints/gshell.h` | `GaussianShell` | M1, M2 |

To quickly apply these and other required modifications, use the patch files stored in `misc/patch` directory. Please make sure to use a proper patch for a chosen Psi4 version.

### 7.1.2 Compiltation

After all the above changes have been done in Psi4 (followed by its rebuild) compile the EOPDev code by running `compile` script. Make sure Eigen3 path is set to environment variable `EIGEN3_INCLUDE_DIR` (instructions will appear on the screen). After compilation is successful, run `ctest` to check if the code works fine.

#### Note

It may happen that during code development there will be symbol lookup error when importing `oepdev.so` (in such case EOPDev compiles without error but Python cannot import the module `oepdev`). In such circumstance, probably there some local Psi4 feature that is needed in EOPDev is not exposed by `PSI_API` macro. To fix this, run `c++filt [name]` where `[name]` is the mangled undefined symbol. This will show you which Psi4 class or function is not exposed and requires `PSI_API` (change M1 and perhaps M2 too). Such change requires Psi4 rebuild and recompilation of EOPDev code. In any case, please contact me and report new undefined symbol (`blasiak.bartosz@gmail.com`).

## 7.2 EOPDev Code Structure

As a plugin to Psi4, EOPDev consists of the `main.cc` file with the plugin main routine, `include/oepdev_options.h` specifying the options of the plugin, `include/oepdev_files.h` defining all global macros and environmental variables, as well as the `oepdev` directory. The latter contains the actual EOPDev code that is divided into several subdirectories called modules.

### 7.2.1 Main Routine

Before the actual EOPDev calculations are started, the wavefunction of the input molecular aggregate is computed by Psi4. See the plugin driver script `pymodule.py` for more details on how the calculation environment is initialized. Subsequently, one out of four types of target operations can be performed by the program:

1. `OEP_BUILD` - Compute the EOP effective parameters for one molecule.
2. `DMATPOL` - Compute the generalized density matrix susceptibility tensors (DMS's) for one molecule.
3. `SOLVER` - Perform calculations for a molecular aggregate. As for now, only dimers are handled.
4. `TEST` - Perform the testing routine.

The first two modes are single molecule calculations. `OEP_BUILD` uses the `OEPotential::build` static factory to create EOP objects whereas `DMATPOL` uses the `GenEffParFactory::build` static factory to greate generalized effective fragment parameters (GEFP's) for polarization.

**Note**

> In the future, `OEP_BUILD` will be handled also by `GenEffParFactory::build` since EOP parameters are part of the GEFP's.

`SOLVER` requires at least molecular dimer and the `WavefunctionUnion` object (being the Hartree product of the unperturbed monomer wavefunctions) is constructed at the beginning, which is then passed to the `OEPDevSolver::build` static factory. `TEST` can refer to single- or multiple-molecule calculations, whereby each of the testing routines is listed in the `cmake/CTestTestfile.cmake.in` file.

### 7.2.2 Modules

The source code is distributed into directories called modules:

- `liboep`
- `libgefp`
- `libsolver`
- `libints`
- `libpsi`
- `lib3d`
- `libutil`
- `libtest`

See Modules for a detailed description of each of the modules.

## 7.3 EOPDev Classes: Overview

### 7.3.1 EOP Module

The EOP module located in `oepdev/liboep` consists of the following abstract bases:

- `OEPotential` implementing the EOP,
- `GeneralizedDensityFit` implementing the GDF technique.

Each of the bases contains static factory method called `build` that creates instances of chosen subclasses. The module contains also a structure `EOPType` which is a container storing all the data associated with a particular EOP: type name, dimensions, EOP coefficients and whether is density-fitted or not.

#### 7.3.1.1 OEPotential

It is a container and computer class of EOP. Among others, the most important public method is `OEPotential::compute` which computes all the EOP's (by iterating over all possible EOP types within a chosen EOP subclass or category). EOP's can be extracted by `OEPotential::oep` method, for instance. From protected attributes, each OEPotential instance stores blocks of the LCAO-MO matrices associated with the occupied (`cOcc_`) and virtual (`cVir_`) MO's. It also contains the pointers to the primary, auxiliary and intermediate basis sets (`primary_`, `auxiliary_` and `intermediate_`, accordingly). Usage example:

```
#include "oepdev/liboep/oep.h"
oep = oepdev::OEPotential::build("ELECTROSTATIC ENERGY", wfn, options);
oep->compute();
oep->write_cube("V", "oep_cube_file");
```

So far, four OEPotential subclasses are implemented, from which `ElectrostaticEnergyOEPotential` and `RepulsionEnergyOEPotential` are fully operative, while the rest is under development.

#### 7.3.1.2 GeneralizedDensityFit

Implements the density fitting schemes for EOP's.

### 7.3.2 GEFP Module

This module deals with the effective fragments consituting an extended molecular aggregate. It builds the platform to test various generalized effective fragment potentials (GEFP).

#### 7.3.2.1 GenEffPar

Represents generalized effective fragment parameters.

#### 7.3.2.2 GenEffParFactory

Implements routines of calculation of effective fragment parameters of various types.

#### 7.3.2.3 GenEffFrag

Represents one effective fragment.

### 7.3.3 EOPDev Solver Module

This module sets up a simple platform of comparing benchmark and EOP-based fragment-based methods.

#### 7.3.3.1 OEPDevSolver

This is the main solver which as for now assumes molecular dimers (or bi-fragment systems). It is based on a union of wavefunctions of unperturbed monomers, `WavefunctionUnion`.

## 7.4 Developing EOP's

**Note**

> This section is for illustrative purpose. The small details of the objects such as `OEPType` and others can change over the years due to development of the EOPDev code. However, the overal programing scheme remains unchanged and valid.

EOP's are implemented in a suitable subclass of the `OEPotential` base. Due to the fact that EOP's can be density-based or DMTP-based, the classes `GeneralizedDensityFit` as well as `ESPSolver` are usually necessary in the implementations. Handling the one-electron integrals (OEI's) and the two-electron integrals (ERI's) in AO basis is implemented in `IntegralFactory`. In particular, potential integrals evaluated at arbitrary centres can be accessed by using the `PotentialInt` instances. Useful iterators for looping over AO ERI's the `ShellCombinationsIterator` and `AOIntegralsIterator` classes. Transformations of OEI's to MO basis can be easily achieved by transforming AO integral matrices by `cOcc_` and `cVir_` members of `OEPotential` instances, e.g., by using the `psi::Matrix::doublet` or `psi::Matrix::triplet` static methods. Transformations of ERI's to MO basis can be performed by using the `psi4/libtrans/integraltransform.h` library.

It is recommended that the implementation of all the new EOP's follows the following steps:

1. **Write the class framework.** This includes choosing a proper name of a OEPotential subclass, sketching the constructors and a destructor, and all the necessary methods.
2. **Implement EOP types.** Each type of EOP is implemented, including the 3D vector field in case DMTP-based EOP's are of use.

3. **Update base factory method**. Add appropriate entries in the `OEPotential::build` static factory method.

Below, we shall go through each of these steps separately and discuss them in detail.

### 7.4.1 Drafting an EOP Subclass

This stage is the design of the overall framework of EOP subclass. The name should end with `OEPotential` to maintain the convention used so far. The template for the header file definition can be depicted as follows:

```
class SampleOEPotential : public OEPotential
{
  public:
    // Purely DMTP-based EOP's
    SampleOEPotential(SharedWavefunction wfn, Options& options);

    // GDF-based EOP's
    SampleOEPotential(SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate,
      Options& options);

    // Necessary destructor
    virtual ~SampleOEPotential();

    // Necessary computer
    virtual void compute(const std::string& oepType) override;

    // Necessary computer
    virtual void compute_3D(const std::string& oepType,
                            const double& x, const double& y, const double& z, std::shared_ptr<psi::Vector>
      & v) override;
    // Necessary printer
    virtual void print_header() const override;

  private:
    // Set defaults - good practice
    void common_init();

    // Auxilary computers - exemplary
    double compute_3D_sample_V(const double& x, const double& y, const double& z);
};
```

The constructors need to call the abstract base constructor and then specialized initializations. It is a good practice to put the specialized common initializers in a separate private method `common_init` (which is a convention in Psi4 and is adopted also in EOPDev). For instance, the exemplary constructor is show below:

```
SampleOEPotential::SampleOEPotential(SharedWavefunction wfn,
                                     SharedBasisSet auxiliary, SharedBasisSet intermediate, Options&
      options)
 : OEPotential(wfn, auxiliary, intermediate, options)
{
   common_init();
}

void SampleOEPotential::common_init()
{
   int n1 = wfn_->Ca_subset("AO","OCC")->ncol();
   int n2 = auxiliary_->nbf();
   int n3 = wfn_->molecule()->natom();

   psi::SharedMatrix mat_1 = std::make_shared<psi::Matrix>("G(S^{-1})", n2, n1);
   psi::SharedMatrix mat_2 = std::make_shared<psi::Matrix>("G(S^{-2})", n3, n1);

   OEPType type_1 = {"Murrell-etal.S1", true , n1, mat_1};
   OEPType type_2 = {"Otto-Ladik.S2"  , false, n1, mat_2};

   oepTypes_[type_1.name] = type_1;
   oepTypes_[type_2.name] = type_2;
}
```

Note that the `OEPotential::oepTypes_` attribute, which is a `std::map` of structures `OEPType`, is initialized here. All the EOP types need to be stated in the constructors. Destructors usually call nothing, unless dynamically allocated memory is also of use.

It is also a good practice to already sketch the `compute` method here by adding certain private computers, like in the example below:

```
void SampleOEPotential::compute(const std::string& oepType)
{
  if      (oepType == "Murrell-etal.S1") this->compute_murrell_etal_s1();  // calls private method
  else if (oepType ==   "Otto-Ladik.S2") this->compute_otto_ladik_s2();    // calls private method
  else throw psi::PSIEXCEPTION("EOPDEV: Error. Incorrect EOP type specified!\n"); // for safety
}
void SampleOEPotential::compute_murrell_etal_s1()
{
   psi::timer_on ("EOP    E(Paul) Murrell-etal S1  ");
   /* Your implementation goes here */
   psi::timer_off("EOP    E(Paul) Murrell-etal S1  ");
```

#### 7.4.1.1 Implementing EOP Types

Implementation of the inner body of `compute` method requires populating the members of `oepTypes_` with data. This means, that for each EOP type there has to be a specific implementation of EOP parameters. GDF-based EOP's need to create the `psi::Matrix` with EOP parameters and put them into `oepTypes_`. In the case of DMTP-based EOP's `compute_3D` method has to be additionally implemented before `compute` is fully functional. To implement `compute_3D`, `OEPotential::make_oeps3d` method is of high relevance: it creates `OEPotential3D<T>` instances, where `T` is the EOP subclass. These instances are `Field3D` objects that define EOP's in 3D Euclidean space. For example,

```
void SampleOEPotential::compute_otto_ladik_s2()
{
      // Switch on timer
      psi::timer_on("EOP    E(Paul) Otto-Ladik S2    ");

      // Create 3D field, automated through `make_oeps3d`. Requires `compute_3D` implementation.
      std::shared_ptr<OEPotential3D<OEPotential>> oeps3d = this->make_oeps3d("Otto-Ladik.S2");
      oeps3d->compute();

      // Perform ESP fit to get EOP effective charges
      ESPSolver esp(oeps3d);
      esp.set_charge_sums(0.5);
      esp.compute();

      // Put the EOP coefficients into `oepTypes_`
      for (int i=0; i<esp.charges()->nrow(); ++i) {
           for (int o=0; o<oepTypes_["Otto-Ladik.S2"].n; ++o) {
                oepTypes_["Otto-Ladik.S2"].matrix->set(i, o, esp.charges()->get(i, o));
           }
      }

      // Switch off timer
      psi::timer_off("EOP    E(Paul) Otto-Ladik S2    ");
}
// Necessary implementation for `make_oeps3d` to work
void SampleOEPotential::compute_3D(const std::string& oepType, const double& x, const double& y, const
      double& z, std::shared_ptr<psi::Vector>& v)
{
   // Loop over all possibilities for EOP types and exclude illegal names
   if (oepType == "Otto-Ladik.S2") {

       // this computes the actual values of EOP = v(x,y,z) and stores it in `vec_otto_ladik_s2_`
       this->compute_3D_otto_ladik_s2(x, y, z);

       // Assign final value to the buffer vector
       for (int o = 0; o < oepTypes_["Otto-Ladik.S2"].n; ++o) v->set(o, vec_otto_ladik_s2_[o]);

   }
   else if (oepType == "Murrell-etal.S1" ) {/* Even if it is not DMTP-based EOP, this line is necessary */}

   else {
      throw psi::PSIEXCEPTION("EOPDEV: Error. Incorrect EOP type specified!\n"); // Safety
   }
}
```

Note that `make_oeps3d` is not overridable and is fully defined in the base. Do not call `OEPotential3D` constructors in the OEPotential subclass (it can be done only from the level of the abstract base where all the pointers are dynamically converted to an appropriate data type due to polymorphism)!

# Chapter 8

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That's all there is to it!

# Chapter 9

# Module Index

## 9.1 Modules

Here is a list of all modules:

# Chapter 10

# Namespace Index

## 10.1 Namespace List

Here is a list of all documented namespaces with brief descriptions:

# Chapter 11

# Hierarchical Index

## 11.1 Class Hierarchy

This inheritance list is sorted roughly, but not completely, alphabetically:

# Chapter 12

# Class Index

## 12.1 Class List

Here are the classes, structs, unions and interfaces with brief descriptions:

# Chapter 13

# File Index

## 13.1 File List

Here is a list of all documented files with brief descriptions:

# Chapter 14

# Module Documentation

## 14.1 The Generalized One-Electron Potentials Library

Implements the goal of this project: The Generalized One-Electron Potentials (OEP's). You will find here OEP's for computation of Pauli repulsion energy, charge-transfer energy and others. The routines for the generalized density fitting are also implemented here. Located at `oepdev/liboep`.

### Classes

- struct oepdev::OEPType

  *Container to handle the type of One-Electron Potentials.*
- class oepdev::OEPotential

  *Generalized One-Electron Potential: Abstract base.*
- class oepdev::ElectrostaticEnergyOEPotential

  *Generalized One-Electron Potential for Electrostatic Energy.*
- class oepdev::RepulsionEnergyOEPotential

  *Generalized One-Electron Potential for Pauli Repulsion Energy.*
- class oepdev::ChargeTransferEnergyOEPotential

  *Generalized One-Electron Potential for Charge-Transfer Interaction Energy.*
- class oepdev::EETCouplingOEPotential

  *Generalized One-Electron Potential for EET coupling calculations.*
- class oepdev::GeneralizedDensityFit

  *Generalized Density Fitting Scheme. Abstract Base.*
- class oepdev::SingleGeneralizedDensityFit

  *Generalized Density Fitting Scheme - Single Fit.*
- class oepdev::DoubleGeneralizedDensityFit

  *Generalized Density Fitting Scheme - Double Fit.*
- class oepdev::OverlapGeneralizedDensityFit

  *Generalized Density Fitting Scheme - Single Fit Based on Minimal Overlap in MO Basis.*

### Typedefs

- using **oepdev::SharedOEPotential** = std::shared_ptr< OEPotential >

### 14.1.1 Detailed Description

## 14.2 The OEPDev Solver Library

Implementations of various solvers for molecular properties as a functions of unperturbed monomeric wavefunctions. This is the place all target OEP-based models are implemented and compared with benchmark and competitor models. Located at `oepdev/libsolver`.

### Classes

- class oepdev::OEPDevSolver

  *Solver of properties of molecular aggregates. Abstract base.*
- class oepdev::ElectrostaticEnergySolver

  *Compute the Coulombic interaction energy between unperturbed wavefunctions.*
- class oepdev::RepulsionEnergySolver

  *Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.*
- class oepdev::ChargeTransferEnergySolver

  *Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.*
- class oepdev::EETCouplingSolver

  *Compute the EET coupling energy between unperturbed wavefunctions.*
- class oepdev::TIData

  *Transfer Integral EET Data.*

### 14.2.1 Detailed Description

## 14.3 The Generalized Effective Fragment Potentials Library

Implements the GEFP method, the far goal of the OEPDev project. Here you will find the containers for GEFP parameters, the density matrix susceptibility tensors and GEFP solvers. Located at `oepdev/libgefp`.

### Classes

- class oepdev::GenEffPar

  *Generalized Effective Fragment Parameters. Container Class.*
- class oepdev::GenEffFrag

  *Generalized Effective Fragment. Container Class.*
- class oepdev::GenEffParFactory

  *Generalized Effective Fragment Factory. Abstract Base.*
- class oepdev::EFP2_GEFactory

  *EFP2 GEFP Factory.*
- class oepdev::OEP_EFP2_GEFactory

  *OEP-EFP2 GEFP Factory.*
- class oepdev::PolarGEFactory

  *Polarization GEFP Factory. Abstract Base.*
- class oepdev::AbInitioPolarGEFactory

  *Polarization GEFP Factory from First Principles. Hartree-Fock Approximation.*
- class oepdev::FFAbInitioPolarGEFactory

  *Polarization GEFP Factory from First Principles: Finite-Difference Model. Arbitrary level of theory.*
- class oepdev::GeneralizedPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::UniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::NonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::LinearUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::QuadraticUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::LinearNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::QuadraticNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::LinearGradientNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*

- class oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::UnitaryTransformedMOPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Scaling of MO Space.*
- class oepdev::FragmentedSystem

  *Molecular System for Fragment-Based Calculations.*

## Typedefs

- using oepdev::SharedGenEffPar = std::shared_ptr< GenEffPar >

  *GEFP Parameters container.*
- using oepdev::SharedGenEffParFactory = std::shared_ptr< GenEffParFactory >

  *GEFP Parameter factory.*
- using oepdev::SharedGenEffFrag = std::shared_ptr< GenEffFrag >

  *GEFP Fragment container.*
- using oepdev::SharedFragmentedSystem = std::shared_ptr< FragmentedSystem >

  *Fragmented system.*

### 14.3.1 Detailed Description

The objective is to implement the framework for the fragment-based (FB) calculations in which the system is divided into interacting fragments. The functionality relies on a few data structures:

- the `GenEffFrag` - Generalized Effective Fragment
- the `GenEffPar` - Generalized Effective Parameters
- the `GenEffParFactory` - Generalized Effective Parameters Factory Fragments can contain multiple types of parameters, e.g., ethylene fragment can have EFP2, OEP-EFP2 as well as OEP-EET parameters. Fragments can be superimposed on target structures and the class contain methods that evaluate properties based on the fragments in the system.

## 14.4 The Integral Package Library

Implementations of various two-, three- or four-centre two-body electron repulsion integrals via utilizing the McMurchie-Davidson recurrence scheme. Located at `oepdev/libints` and `oepdev/libpsi`.

### Classes

- class oepdev::TwoElectronInt

  *General Two Electron Integral.*
- class oepdev::ERI_1_1

  *2-centre ERI of the form (a|O(2)|b) where O(2) = 1/r12.*
- class oepdev::ERI_2_2

  *4-centre ERI of the form (ab|O(2)|cd) where O(2) = 1/r12.*
- class oepdev::ERI_3_1

  *4-centre ERI of the form (abc|O(2)|d) where O(2) = 1/r12.*
- class oepdev::EFPMultipolePotentialInt

  *Computes potential integrals.*
- class oepdev::TwoBodyAOInt
- class oepdev::IntegralFactory

  *Extended IntegralFactory for computing integrals.*
- class oepdev::ObaraSaikaTwoCenterEFPRecursion_New

  *Obara-Saika recursion formulae for improved EFP multipole potential integrals.*
- class oepdev::PotentialInt

  *Computes potential integrals.*

### Macros

- #define D1_INDEX(x, i, n) ((81∗(x))+(9∗(i))+(n))

  *Get the index of McMurchie-Davidson-Hermite D1 coefficient stored in the `mdh_buffer_`, that is attributed to the x Cartesian coordinate from angular momentum i of function 1, and the Hermite index n.*
- #define D2_INDEX(x, i, j, n) ((1377∗(x))+(153∗(i))+(17∗(j))+(n))

  *Get the index of McMurchie-Davidson-Hermite D2 coefficient stored in the `mdh_buffer_`, that is attributed to the x Cartesian coordinate from angular momenta i, j of function 1 and 2, and the Hermite index n.*
- #define D3_INDEX(x, i, j, k, n) ((18225∗(x))+(2025∗(i))+(225∗(j))+(25∗(k))+(n))

  *Get the index of McMurchie-Davidson-Hermite D3 coefficient stored in the `mdh_buffer_`, that is attributed to the x Cartesian coordinate from angular momenta i, j and k of function 1, 2 and 3, and the Hermite index n.*
- #define R_INDEX(n, l, m, j) ((14739∗(n))+(867∗(l))+(51∗(m))+(j))

  *Get the index of McMurchie-Davidson R coefficient stored in the `mdh_buffer_R_` from angular momenta n, l and m and the Boys index j.*

## Functions

- double oepdev::d_N_n1_n2 (int N, int n1, int n2, double PA, double PB, double aP)

  *Compute McMurchie-Davidson-Hermite (MDH) coefficient for binomial expansion.*
- void oepdev::make_mdh_D1_coeff (int n1, double aPd, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for monomial expansion.*
- void oepdev::make_mdh_D2_coeff (int n1, int n2, double aPd, double ∗PA, double ∗PB, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for binomial expansion.*
- void oepdev::make_mdh_D3_coeff (int n1, int n2, int n3, double aPd, double ∗PA, double ∗PB, double ∗PC, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for trinomial expansion.*
- void oepdev::make_mdh_D2_coeff_explicit_recursion (int n1, int n2, double aP, double ∗PA, double ∗PB, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for binomial expansion by explicit recursion. This function makes the same changes to buffers as oepdev::make_mdh_D2_coeff, but implements it through explicit recursion by calls to oepdev::d_N_n1_n2. Therefore, it is slightly slower. Here for debugging purposes.*
- void oepdev::make_mdh_R_coeff (int N, int L, int M, double alpha, double a, double b, double c, double ∗F, double ∗buffer)

  *Compute the McMurchie-Davidson R coefficients.*

### 14.4.1 Detailed Description

Here, we define the primitive Gaussian type functions (GTO's)

$$\begin{aligned}
\phi_i(\mathbf{r}) &\equiv x_A^{n_1} y_A^{l_1} z_A^{m_1} e^{-\alpha_1 r_A^2} \\
\phi_j(\mathbf{r}) &\equiv x_B^{n_2} y_B^{l_2} z_B^{m_2} e^{-\alpha_2 r_B^2} \\
\phi_k(\mathbf{r}) &\equiv x_C^{n_3} y_C^{l_3} z_C^{m_3} e^{-\alpha_3 r_C^2}
\end{aligned}$$

in which $\mathbf{r}_A \equiv \mathbf{r} - \mathbf{A}$ and so on. $\mathbf{A}$ is the centre of the GTO, $\alpha_1$ its exponent, whereas $n_1, l_1, m_1$ the Cartesian angular momenta, with the total angular momentum $\theta_1 = n_1 + l_1 + m_1$.

In OEPDev implementations, the following definition shall be in use:

$$\begin{aligned}
\mathbf{P} &\equiv \frac{\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B}}{\alpha_1 + \alpha_2} \\
\mathbf{Q} &\equiv \frac{\alpha_3 \mathbf{C} + \alpha_4 \mathbf{D}}{\alpha_3 + \alpha_4} \\
\mathbf{R} &\equiv \frac{\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B} + \alpha_3 \mathbf{C}}{\alpha_1 + \alpha_2 + \alpha_3} \\
\alpha_P &\equiv \alpha_1 + \alpha_2 \\
\alpha_Q &\equiv \alpha_3 + \alpha_4 \\
\alpha_R &\equiv \alpha_1 + \alpha_2 + \alpha_3
\end{aligned}$$

The unnormalized products of primitive GTO's are denoted here as

$$[ij] \equiv \phi_i(\mathbf{r})\phi_j(\mathbf{r})$$
$$[ijk] \equiv \phi_i(\mathbf{r})\phi_j(\mathbf{r})\phi_k(\mathbf{r})$$

### 14.4.2 Hermite Operators

It is convenient to define

$$\Lambda_j(x_P;\alpha_P) \equiv \left(\frac{\partial}{\partial P_x}\right)^j = \alpha_P^{j/2} H_j(\sqrt{\alpha_P} x_P)$$

where $H_j(x)$ is the Hermite polynomial of order *j* evaluated at *x* . Introduction of the above Hermite operator can be used by invoking the recurrence relationship due to Hermite polynomial properties:

$$x_A \Lambda_j(x_P;\alpha_P) = j\Lambda_{j-1} + |\mathbf{P}-\mathbf{A}|_x \Lambda_j + \frac{1}{2\alpha_P}\Lambda_{j+1}$$

This can be directly used to derive very useful McMurchie-Davidson-Hermite coefficients as expansion coefficients of the polynomial expansions.

#### 14.4.2.1 Polynomial Expansions as Hermite Series

By using the previous relation, it is possible to express the following expansions in Hermite series:

$$x_A^{n_1} = \sum_{N=0}^{n_1} d_N^{n_1} \Lambda_N(x_A;\alpha_A)$$
$$x_A^{n_1} x_B^{n_2} = \sum_{N=0}^{n_1+n_2} d_N^{n_1 n_2} \Lambda_N(x_P;\alpha_P)$$
$$x_A^{n_1} x_B^{n_2} x_C^{n_3} = \sum_{N=0}^{n_1+n_2+n_3} d_N^{n_1 n_2 n_3} \Lambda_N(x_R;\alpha_R)$$

The recurrence relationships can be easily found and they read

$$d_N^{n_1+1} = \frac{1}{2\alpha_A} d_{N-1}^{n_1} + (N+1) d_{N+1}^{n_1}$$

as well as

$$d_N^{n_1+1,n_2} = \frac{1}{2\alpha_P} d_{N-1}^{n_1 n_2} + |\mathbf{P}-\mathbf{A}|_x d_N^{n_1 n_2} + (N+1) d_{N+1}^{n_1 n_2}$$
$$d_N^{n_1,n_2+1} = \frac{1}{2\alpha_P} d_{N-1}^{n_1 n_2} + |\mathbf{P}-\mathbf{B}|_x d_N^{n_1 n_2} + (N+1) d_{N+1}^{n_1 n_2}$$

and

$$\begin{aligned} d_N^{n_1+1,n_2,n_3} &= \frac{1}{2\alpha_R} d_{N-1}^{n_1 n_2 n_3} + |\mathbf{R}-\mathbf{A}|_x d_N^{n_1 n_2 n_3} + (N+1) d_{N+1}^{n_1 n_2 n_3} \\ d_N^{n_1,n_2+1,n_3} &= \frac{1}{2\alpha_R} d_{N-1}^{n_1 n_2 n_3} + |\mathbf{R}-\mathbf{B}|_x d_N^{n_1 n_2 n_3} + (N+1) d_{N+1}^{n_1 n_2 n_3} \\ d_N^{n_1,n_2,n_3+1} &= \frac{1}{2\alpha_R} d_{N-1}^{n_1 n_2 n_3} + |\mathbf{R}-\mathbf{C}|_x d_N^{n_1 n_2 n_3} + (N+1) d_{N+1}^{n_1 n_2 n_3} \end{aligned}$$

respectively. The first elements are given by

$$\begin{aligned} d_0^0 &= 1 \\ d_0^{00} &= 1 \\ d_0^{000} &= 1 \end{aligned}$$

By using the above formalisms, it is strightforward to express the doublet of primitive GTO's as

$$[ij] = E_{ij} \sum_{N=0}^{n_1+n_2} \sum_{L=0}^{l_1+l_2} \sum_{M=0}^{m_1+m_2} d_N^{n_1 n_2} d_L^{l_1 l_2} d_M^{m_1 m_2} \Lambda_N(x_P) \Lambda_L(y_P) \Lambda_M(z_P) e^{-\alpha_P r_P^2}$$

Analogously, the triplet of primitive GTO's is given by

$$[ijk] = E_{ijk} \sum_{N=0}^{n_1+n_2+n_3} \sum_{L=0}^{l_1+l_2+l+3} \sum_{M=0}^{m_1+m_2+m_3} d_N^{n_1 n_2 n_3} d_L^{l_1 l_2 l_3} d_M^{m_1 m_2 m_3} \Lambda_N(x_R) \Lambda_L(y_R) \Lambda_M(z_R) e^{-\alpha_R r_R^2}$$

The multiplicative constants are given by

$$\begin{aligned} E_{ij}(\alpha_1,\alpha_2) &= \exp\left[-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}|\mathbf{A}-\mathbf{B}|^2\right] \\ E_{ijk}(\alpha_1,\alpha_2,\alpha_3) &= \exp\left[-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}|\mathbf{A}-\mathbf{B}|^2\right] \exp\left[-\frac{(\alpha_1+\alpha_2)\alpha_3}{\alpha_1+\alpha_2+\alpha_3}|\mathbf{P}-\mathbf{C}|^2\right] \end{aligned}$$

### 14.4.3 One-Body Integrals over Hermite Functions

The fundamental Hermite integrals that appear during computations of any kind of one-body integrals over GTO's are as follows

$$[NLM|\Theta(1)] \equiv \int d\mathbf{r}_1 \Theta(\mathbf{r}_1) \Lambda_N(x_{1P};\alpha_P) \Lambda_L(y_{1P};\alpha_P) \Lambda_M(z_{1P};\alpha_P) e^{-\alpha_P r_{1P}^2}$$

It immediately follows that the overlap, dipole, quadrupole and potential integrals are given as

$$\begin{aligned} [NLM|1] &= \delta_{N0}\delta_{L0}\delta_{M0}\left(\frac{\pi}{\alpha_P}\right)^{3/2} \\ [NLM|x_C] &= [\delta_{N1} + |\mathbf{PC}|_x \delta_{N0}]\,\delta_{L0}\delta_{M0}\left(\frac{\pi}{\alpha_P}\right)^{3/2} \\ \left[NLM|x_C^2\right] &= \left[2\delta_{N2} + 2|\mathbf{PC}|_x\delta_{N1} + \left(|\mathbf{PC}|_x^2 + \frac{1}{2\alpha_P}\right)\delta_{N0}\right]\delta_{L0}\delta_{M0}\left(\frac{\pi}{\alpha_P}\right)^{3/2} \\ [NLM|x_C y_C] &= (\delta_{N1} + |\mathbf{PC}|_x\delta_{N0})(\delta_{L1} + |\mathbf{PC}|_y\delta_{L0})\,\delta_{M0}\left(\frac{\pi}{\alpha_P}\right)^{3/2} \\ \left[NLM|r_C^{-1}\right] &= \frac{2\pi}{\alpha_P} R_{NLM} \end{aligned}$$

The coefficients $R_{NLM}$ are discussed in separate section below.

### 14.4.4 Two-Body Integrals over Hermite Functions

The fundamental Hermite integrals that appear during computations of any kind of two-electron integrals over GTO's are as follows

$$[N_1L_2M_2|N_2L_2M_2] \equiv \iint d\mathbf{r}_1 d\mathbf{r}_2 \Lambda_{N_1}(x_{1P};\alpha_P)\Lambda_{L_1}(y_{1P};\alpha_P)\Lambda_{M_1}(z_{1P};\alpha_P)\Lambda_{N_2}(x_{2Q};\alpha_Q)\Lambda_{L_2}(y_{2Q};\alpha_Q)\Lambda_{M_2}(z_{2Q};\alpha_Q$$

The above formula dramatically reduces to the following

$$[N_1L_2M_2|N_2L_2M_2] = \lambda(-)^{N2+L2+M2}R_{N1+N2,L1+L2,M1+M2}$$

with

$$\lambda \equiv \frac{2\pi^{5/2}}{\alpha_P\alpha_Q\sqrt{\alpha_P+\alpha_Q}}$$

To compute the $R_{N1+N2,L1+L2,M1+M2}$ coefficients, the parameter $T$ is given by

$$T = \frac{\alpha_P\alpha_Q}{\alpha_P+\alpha_Q}|\mathbf{P}-\mathbf{Q}|^2$$

### 14.4.5 The R(N,L,M) Coefficients

The *R* coefficients are defined as

$$R_{NLM} \equiv \left(\frac{\partial}{\partial a}\right)^N \left(\frac{\partial}{\partial b}\right)^L \left(\frac{\partial}{\partial c}\right)^M \int_0^1 e^{-Tu^2}\, du$$

with

$$T \equiv \alpha\left(a^2+b^2+c^2\right)$$

By extending the above definition to more general

$$R_{NLMj} \equiv \left(-\sqrt{\alpha}\right)^{N+L+M}(-2\alpha)^j \int_0^1 u^{N+L+M+2j} H_N(au\sqrt{\alpha})H_L(bu\sqrt{\alpha})H_M(cu\sqrt{\alpha})e^{-Tu^2}\, du$$

one can see that

$$R_{000j} = (-2\alpha)^j F_j(T)$$

The Boys function is here given by

$$F_j(T) \equiv \int_0^1 u^{2j} e^{-Tu^2}\, du$$

and its efficient implementation can be discussed elsewhere. In Psi4, `psi::Taylor_Fjt` class is used for this purpose.

Now, it is possible to show that the following recursion relationships are true:

$$\begin{aligned}
R_{0,0,M+1,j} &= cR_{0,0,M,j+1} + MR_{0,0,M-1,j+1} \\
R_{0,L+1,M,j} &= bR_{0,L,M,j+1} + LR_{0,L-1,M,j+1} \\
R_{N+1,L,M,j} &= aR_{N,L,M,j+1} + NR_{N-1,L,M,j+1}
\end{aligned}$$

This scheme is implemented in OEPDev.

### 14.4.6 Function Documentation

#### 14.4.6.1 d_N_n1_n2()

```
double oepdev::d_N_n1_n2 (
            int N,
            int n1,
            int n2,
            double PA,
            double PB,
            double aP )
```

**Parameters**

| | |
|---|---|
| *N* | - increment in the summation of MDH series |
| *n1* | - angular momentum of first function |
| *n2* | - angular momentum of second function |
| *PA* | - cartesian component of P-A distance |
| *PB* | - cartesian component of P-B distance |
| *aP* | - free parameter of MDH expansion |

**Returns**

the McMurchie-Davidson-Hermite coefficient

#### 14.4.6.2 make_mdh_D1_coeff()

```
void oepdev::make_mdh_D1_coeff (
            int n1,
            double aPd,
            double * buffer )
```

**Parameters**

| | |
|---|---|
| *n1* | - angular momentum of first function |
| *aPd* | - parameter equal to 0.500/Pa where Pa is exponent |
| *buffer* | - the McMurchie-Davidson-Hermite 3-dimensional array (raveled to vector): • axis 0: dimension 3 (x, y or z Cartesian component) • axis 1: dimension n1+1 (0 to n1) • axis 2: dimension n1+1 (0 to n1) |

**See also**

D1_INDEX

#### 14.4.6.3 make_mdh_D2_coeff()

```
void oepdev::make_mdh_D2_coeff (
            int n1,
            int n2,
            double aPd,
            double * PA,
            double * PB,
            double * buffer )
```

**Parameters**

| | |
|---|---|
| *n1* | - angular momentum of first function |
| *n2* | - angular momentum of second function |
| *aPd* | - parameter equal to 0.500/Pa where Pa is exponent |
| *PA* | - cartesian components of P-A distance |
| *PB* | - cartesian components of P-B distance |
| *buffer* | - the McMurchie-Davidson-Hermite 4-dimensional array (raveled to vector): <br>• axis 0: dimension 3 (x, y or z Cartesian component)<br>• axis 1: dimension n1+1 (0 to n1)<br>• axis 2: dimension n2+1 (0 to n2)<br>• axis 3: dimension n1+n2+1 (0 to n1+n2) |

**See also**

D2_INDEX

#### 14.4.6.4 make_mdh_D2_coeff_explicit_recursion()

```
void oepdev::make_mdh_D2_coeff_explicit_recursion (
            int n1,
            int n2,
            double aP,
            double * PA,
            double * PB,
            double * buffer )
```

**Parameters**

| | |
|---|---|
| *n1* | - angular momentum of first function |
| *n2* | - angular momentum of second function |
| *aPd* | - parameter equal to 0.500/Pa where Pa is exponent |
| *PA* | - cartesian components of P-A distance |
| *PB* | - cartesian components of P-B distance |
| *buffer* | - the McMurchie-Davidson-Hermite 4-dimensional array (raveled to vector): • axis 0: dimension 3 (x, y or z Cartesian component) • axis 1: dimension n1+1 (0 to n1) • axis 2: dimension n2+1 (0 to n2) • axis 3: dimension n1+n2+1 (0 to n1+n2) |

**See also**

D2_INDEX

#### 14.4.6.5 make_mdh_D3_coeff()

```
void oepdev::make_mdh_D3_coeff (
            int n1,
            int n2,
            int n3,
            double aPd,
            double * PA,
            double * PB,
            double * PC,
            double * buffer )
```

**Parameters**

| | |
|---|---|
| *n1* | - angular momentum of first function |
| *n2* | - angular momentum of second function |
| *n3* | - angular momentum of third function |
| *aPd* | - parameter equal to 0.500/Pa where Pa is exponent |
| *PA* | - cartesian components of P-A distance |
| *PB* | - cartesian components of P-B distance |
| *PC* | - cartesian components of P-C distance |

**Parameters**

| | |
|---|---|
| *buffer* | - the McMurchie-Davidson-Hermite 5-dimensional array (raveled to vector):<br>• axis 0: dimension 3 (x, y or z Cartesian component)<br>• axis 1: dimension n1+1 (0 to n1)<br>• axis 2: dimension n2+1 (0 to n2)<br>• axis 3: dimension n3+1 (0 to n3)<br>• axis 4: dimension n1+n2+n3+1 (0 to n1+n2+n3) |

**See also**

D3_INDEX

#### 14.4.6.6 make_mdh_R_coeff()

```
void oepdev::make_mdh_R_coeff (
            int N,
            int L,
            int M,
            double alpha,
            double a,
            double b,
            double c,
            double * F,
            double * buffer )
```

**Parameters**

| | |
|---|---|
| *N* | - increment in the summation of MDH series along *x* direction |
| *L* | - increment in the summation of MDH series along *y* direction |
| *M* | - increment in the summation of MDH series along *z* direction |
| *alpha* | - alpha parameter of R coefficient |
| *a* | - *x* component of PQ vector of R coefficient |
| *b* | - *y* component of PQ vector of R coefficient |
| *c* | - *z* component of PQ vector of R coefficient |
| *F* | - array of Boys function values for given alpha and PQ |

**Parameters**

| | |
|---|---|
| *buffer* | - the McMurchie-Davidson 4-dimensional array (raveled to vector):<br>• axis 0: dimension N+1<br>• axis 1: dimension L+1<br>• axis 2: dimension M+1<br>• axis 3: dimension N+L+M+1 (*j*-th element) |

## 14.5 The Three-Dimensional Vector Fields Library

Handles all sorts of scalar distributions in 3D Euclidean space, such as general vector potentials defined at particular collection of points. In this Module, you will also find handling both random and ordered points collections in a form of a G09 cube, as well as handling G09 Cube files. You will also find solvers used to fit the generalized multipole moments of a generalized density distribution, such as the electrostatic potential (ESP) fitting method. Located at `oepdev/lib3d`.

### Classes

- class oepdev::MultipoleConvergence

  *Multipole Convergence.*
- class oepdev::DMTPole

  *Distributed Multipole Analysis Container and Computer. Abstract Base.*
- class oepdev::CAMM

  *Cumulative Atomic Multipole Moments.*
- class oepdev::ESPSolver

  *Charges from Electrostatic Potential (ESP). A solver-type class.*
- class oepdev::Points3DIterator

  *Iterator over a collection of points in 3D space. Abstract base.*
- class oepdev::CubePoints3DIterator

  *Iterator over a collection of points in 3D space. g09 Cube-like order.*
- class oepdev::RandomPoints3DIterator

  *Iterator over a collection of points in 3D space. Random collection.*
- class oepdev::PointsCollection3D

  *Collection of points in 3D space. Abstract base.*
- class oepdev::RandomPointsCollection3D

  *Collection of random points in 3D space.*
- class oepdev::CubePointsCollection3D

  *G09 cube-like ordered collection of points in 3D space.*
- class oepdev::Field3D

  *General Vector Dield in 3D Space. Abstract base.*
- class oepdev::ElectrostaticPotential3D

  *Electrostatic potential of a molecule.*
- class oepdev::OEPotential3D< T >

  *Class template for OEP 3D fields.*

### Typedefs

- using oepdev::SharedDMTPole = std::shared_ptr< DMTPole >

  *DMTPole object.*
- using **oepdev::SharedField3D** = std::shared_ptr< oepdev::Field3D >

## Functions

- oepdev::OEPotential3D< T >::OEPotential3D (const int &ndim, const int &np, const double &padding, std::shared_ptr< T > oep, const std::string &oepType)

  *Construct random spherical collection of 3D field of type T.*
- oepdev::OEPotential3D< T >::OEPotential3D (const int &ndim, const int &nx, const int &ny, const int &nz, const double &px, const double &py, const double &pz, std::shared_ptr< T > oep, const std::string &oepType, psi::Options &options)

  *Construct ordered 3D collection of 3D field of type T.*
- virtual oepdev::OEPotential3D< T >::~OEPotential3D ()

  *Destructor.*
- virtual void oepdev::OEPotential3D< T >::print () const

  *Print information of the object to Psi4 output.*
- virtual std::shared_ptr< psi::Vector > oepdev::OEPotential3D< T >::compute_xyz (const double &x, const double &y, const double &z)

  *Compute a value of 3D field at point (x, y, z)*

### 14.5.1 Detailed Description

### 14.5.2 Function Documentation

#### 14.5.2.1 OEPotential3D() [1/2]

```
template<class T >
oepdev::OEPotential3D< T >::OEPotential3D (
            const int & ndim,
            const int & np,
            const double & padding,
            std::shared_ptr< T > oep,
            const std::string & oepType )
```

The points are drawn according to uniform distrinution in 3D space.

**Parameters**

| | |
|---|---|
| *ndim* | - dimensionality of 3D field (1: scalar field, >2: vector field) |
| *np* | - number of points to draw |
| *padding* | - spherical padding distance (au) |
| *oep* | - OEP object of type T |
| *oepType* | - type of OEP |

#### 14.5.2.2 OEPotential3D() [2/2]

```
template<class T >
oepdev::OEPotential3D< T >::OEPotential3D (
            const int & ndim,
            const int & nx,
            const int & ny,
            const int & nz,
            const double & px,
            const double & py,
            const double & pz,
            std::shared_ptr< T > oep,
            const std::string & oepType,
            psi::Options & options )
```

The points are generated according to Gaussian cube file format.

**Parameters**

| | |
|---|---|
| *ndim* | - dimensionality of 3D field (1: scalar field, >2: vector field) |
| *nx* | - number of points along x direction |
| *ny* | - number of points along y direction |
| *nz* | - number of points along z direction |
| *px* | - padding distance along x direction |
| *py* | - padding distance along y direction |
| *pz* | - padding distance along z direction |
| *oep* | - OEP object of type T |
| *oepType* | - type of OEP |
| *options* | - Psi4 options object |

## 14.6 The Density Functional Theory Library

Implements the OEPDev ab initio DFT methods. Located at `oepdev/libdft`. Currently, this library is empty.

## 14.7 The OEPDev Utilities

Contains utility functions such as printing OEPDev preambule to the output file, class for wavefunction union, DIIS converger, CPHF Solver, SCF solver for external electrostatic perturbations, and others. You will also find here various iterators to go through orbital shells while computing ERI, or iterators over ERI itself. Located at `oepdev/libutil`.

### Classes

- struct oepdev::CISData

  *CIS wavefunction parameters. Container structure.*
- class oepdev::CISComputer

  *CISComputer.*
- class oepdev::R_CISComputer
- class oepdev::U_CISComputer
- class oepdev::R_CISComputer_Explicit
- class oepdev::R_CISComputer_DL

  *CIS Computer with RHF reference: Davidson-Liu Solver.*
- class oepdev::R_CISComputer_Direct
- class oepdev::U_CISComputer_Explicit
- class oepdev::U_CISComputer_DL

  *CIS Computer with UHF reference: Davidson-Liu Solver.*
- class oepdev::CPHF

  *CPHF solver class.*
- class oepdev::DavidsonLiu

  *Davidson-Liu diagonalization method.*
- class oepdev::DIISManager

  *DIIS manager.*
- class oepdev::GramSchmidt

  *Gram-Schmidt orthogonalization method.*
- class oepdev::ShellCombinationsIterator

  *Iterator for Shell Combinations. Abstract Base.*
- class oepdev::AOIntegralsIterator

  *Iterator for AO Integrals. Abstract Base.*
- class oepdev::AllAOShellCombinationsIterator_4

  *Loop over all possible ERI shells in a shell quartet.*
- class oepdev::AllAOShellCombinationsIterator_2

  *Loop over all possible ERI shells in a shell doublet.*
- class oepdev::AllAOIntegralsIterator_4

  *Loop over all possible ERI within a particular shell quartet.*
- class oepdev::AllAOIntegralsIterator_2

*Loop over all possible ERI within a particular shell doublet.*

- class oepdev::KabschSuperimposer

  *Compute the Cartesian rotation matrix between two structures.*
- struct oepdev::QUAMBOData

  *Container to store the QUAMBO data.*
- class oepdev::QUAMBO

  *The Quasiatomic Minimal Basis Set Molecular Orbitals (QUAMBO)*
- struct oepdev::PerturbCharges

  *Structure to hold perturbing charges.*
- class oepdev::RHFPerturbed

  *RHF theory under electrostatic perturbation.*
- struct oepdev::ABCD

  *Simple structure to hold the Fourier series expansion coefficients.*
- struct oepdev::Fourier5

  *Simple structure to hold the Fourier series expansion coefficients for N=2.*
- struct oepdev::Fourier9

  *Simple structure to hold the Fourier series expansion coefficients for N=4.*
- class oepdev::UnitaryOptimizer

  *Find the optimim unitary matrix of quadratic matrix equation.*
- class oepdev::UnitaryOptimizer_4_2

  *Find the optimim unitary matrix for quartic-quadratic matrix equation with trace.*
- class oepdev::UnitaryOptimizer_2

  *Find the optimim unitary matrix for quadratic matrix equation with trace.*
- class oepdev::UnitaryOptimizer_2_1
- class oepdev::WavefunctionUnion

  *Union of two Wavefunction objects.*

## Macros

- #define OEPDEV_USE_PSI4_DIIS_MANAGER 0

  *Use DIIS from Psi4 (1) or OEPDev (0)?*
- #define OEPDEV_MAX_AM 8

  *L_max.*
- #define OEPDEV_N_MAX_AM 17

  *2L_max+1*
- #define OEPDEV_CRIT_ERI 1e-9

  *ERI criterion for E12, E34, E123 and lambda∗EXY coefficients.*
- #define OEPDEV_SIZE_BUFFER_R 250563

  *Size of R buffer (OEPDEV_N_MAX_AM∗OEPDEV_N_MAX_AM∗OEPDEV_N_MAX_AM∗OEPDEV_N_MAX_AM∗3)*
- #define OEPDEV_SIZE_BUFFER_D2 3264

*Size of D2 buffer (3∗(OEPDEV_MAX_AM+1)∗(OEPDEV_MAX_AM+1)∗OEPDEV_N_MAX_AM)*

- #define OEPDEV_AU_KcalPerMole 627.509

  *Energy converters.*
- #define **OEPDEV_AU_CMRec** 219474.63
- #define **OEPDEV_AU_EV** 27.21138

## Typedefs

- using oepdev::SharedCPHF = std::shared_ptr< CPHF >

  *CPHF object.*
- using oepdev::SharedShellsIterator = std::shared_ptr< ShellCombinationsIterator >

  *Iterator over shells as shared pointer.*
- using oepdev::SharedAOIntsIterator = std::shared_ptr< AOIntegralsIterator >

  *Iterator over AO integrals as shared pointer.*
- using **oepdev::SharedQUAMBOData** = std::shared_ptr< QUAMBOData >
- using oepdev::SharedQUAMBO = std::shared_ptr< QUAMBO >

  *Shared QUAMBO object.*
- using oepdev::SharedWavefunctionUnion = std::shared_ptr< WavefunctionUnion >

  *WavefunctionUnion.*

## Functions

- PSI_API void oepdev::preambule (void)

  *Print preambule for module OEPDEV.*
- template<typename... Args>
  std::string oepdev::string_sprintf (const char ∗format, Args... args)

  *Format string output. Example: std::string text = oepdev::string_sprinff("Test %3d, %13.5f", 5, -10.5425);.*
- PSI_API std::shared_ptr< SuperFunctional > oepdev::create_superfunctional (std::string name, Options &options)

  *Set up DFT functional.*
- PSI_API SharedBasisSet oepdev::create_basisset_by_copy (SharedBasisSet basis_ref, SharedMolecule molecule_target)

  *Build BasisSet by Copy.*
- PSI_API SharedBasisSet oepdev::create_atom_basisset_by_copy (SharedBasisSet basis_ref, SharedMolecule molecule_target, int idx_atom)

  *Build BasisSet by Copy for a Particular Atom.*
- PSI_API std::shared_ptr< Molecule > oepdev::extract_monomer (std::shared_ptr< const Molecule > molecule_dimer, int id)

  *Extract molecule from dimer.*
- PSI_API double oepdev::compute_distance (psi::SharedVector v1, psi::SharedVector v2)

*Compute distance between two points in nD space.*

- PSI_API std::shared_ptr< Wavefunction > oepdev::solve_scf (std::shared_ptr< Molecule > molecule, std::shared_ptr< BasisSet > primary, std::shared_ptr< BasisSet > auxiliary, std::shared_ptr< BasisSet > guess, std::shared_ptr< SuperFunctional > functional, Options &options, std::shared_ptr< PSIO > psio, bool compute_mints=false)

  *Solve RHF-SCF equations for a given molecule in a given basis set.*

- PSI_API std::shared_ptr< Wavefunction > oepdev::solve_scf_sad (std::shared_ptr< Molecule > molecule, std::shared_ptr< BasisSet > primary, std::shared_ptr< BasisSet > auxiliary, std::vector< std::shared_ptr< BasisSet >> sad, std::vector< std::shared_ptr< BasisSet >> sad_fit, std::shared_ptr< SuperFunctional > functional, Options &options, std::shared_ptr< PSIO > psio, bool compute_mints=false)

  *Solve RHF-SCF equations for a given molecule in a given basis set.*

- PSI_API double oepdev::average_moment (std::shared_ptr< psi::Vector > moment)

  *Compute the scalar magnitude of multipole moment.*

- PSI_API std::vector< std::shared_ptr< psi::Matrix > > oepdev::calculate_JK (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::Matrix > C)

  *Compute the Coulomb and exchange integral matrices in MO basis.*

- PSI_API double oepdev::calculate_idf_alpha_xc_energy (std::shared_ptr< psi::Wavefunction > wfn, std::vector< double > w, psi::SharedMatrix D, std::vector< psi::SharedMatrix > AI, std::vector< psi::SharedMatrix > BI)

  *Compute the IDF exchange-correlation energy.*

- PSI_API double oepdev::calculate_idf_xc_energy (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::Matrix > D, std::vector< std::shared_ptr< psi::Matrix >> f, std::vector< std::shared_ptr< psi::Matrix >> g, std::shared_ptr< psi::Vector > w, std::shared_ptr< psi::Vector > o, double N, double aN, double xiN, double AN, double wnorm)

  *Compute the IDF exchange-correlation energy.*

- PSI_API std::vector< std::shared_ptr< psi::Matrix > > **oepdev::calculate_JK_ints** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr)
- PSI_API std::vector< std::shared_ptr< psi::Matrix > > oepdev::calculate_JK_r (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > Dij)

  *Compute the Coulomb and exchange integral matrices in MO basis.*

- PSI_API std::vector< std::shared_ptr< psi::Matrix > > **oepdev::calculate_JK_rb** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > Dij)
- PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_der_D (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > C, std::vector< std::shared_ptr< psi::Matrix >> A)

  *Compute the derivative of exchange-correlation energy wrt the density matrix in MO-A basis.*

- PSI_API double oepdev::calculate_e_xc (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > f, std::shared_ptr< psi::Matrix > C)

*Compute the exchange-correlation energy from ERI in MO-SCF basis.*

- PSI_API double **oepdev::calculate_e_apsg** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > fJ, std::shared_ptr< psi::Matrix > fK, std::shared_ptr< psi::Matrix > C)
- PSI_API psi::SharedMatrix **oepdev::calculate_de_apsg** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Vector > P, std::shared_ptr< psi::Matrix > AJ, std::shared_ptr< psi::Matrix > AKL, std::shared_ptr< psi::Matrix > aJ, std::shared_ptr< psi::Matrix > aKL, std::shared_ptr< psi::Matrix > C)
- PSI_API psi::SharedMatrix **oepdev::calculate_de_apsg_new** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::Vector > P, std::shared_ptr< psi::Matrix > C, std::shared_ptr< psi::Matrix > A_J, std::shared_ptr< psi::Matrix > A_LK, std::shared_ptr< psi::Matrix > a_J, std::shared_ptr< psi::Matrix > a_LK)
- PSI_API psi::SharedMatrix **oepdev::calculate_unitary_uo_2** (psi::SharedVector Q, int n)
- PSI_API psi::SharedMatrix **oepdev::calculate_unitary_uo_2_1** (psi::SharedMatrix P, psi::SharedVector p)
- PSI_API std::shared_ptr< psi::Matrix > oepdev::matrix_power_derivative (std::shared_ptr< psi::Matrix > A, double g, double step)

  *Compute the contracted derivative of power of a square and symmetric matrix.*
- std::shared_ptr< psi::Matrix > oepdev::_calculate_DFI_Vel (std::shared_ptr< psi::IntegralFactory > f_aabb, std::shared_ptr< psi::IntegralFactory > f_abab, std::shared_ptr< psi::Matrix > d_b)

  *Compute the Effective DFI Potential Matrix Due To Electrons.*
- PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_DFI_Vel_JK (std::shared_ptr< psi::IntegralFactory > f_aabb, std::shared_ptr< psi::IntegralFactory > f_abab, std::shared_ptr< psi::Matrix > d_b)

  *Compute the Effective DFI Coulomb+Exchange Potential Matrix Due To Electrons.*
- PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_DFI_Vel_J (std::shared_ptr< psi::IntegralFactory > f_aabb, std::shared_ptr< psi::Matrix > d_b)

  *Compute the Effective DFI Coulomb Potential Matrix Due To Electrons.*
- PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_OEP_basisopt_V (const int &nt, std::shared_ptr< psi::IntegralFactory > f_pppt, std::shared_ptr< psi::Matrix > ca, std::shared_ptr< psi::Matrix > da)

  *Compute the 2-Electron Part of the Effective OEP Matrix for Auxiliary Basis Set Optimization.*
- PSI_API double oepdev::bs_optimize_projection (std::shared_ptr< psi::Matrix > ti, std::shared_ptr< psi::MintsHelper > mints, std::shared_ptr< psi::BasisSet > bsf_m, std::shared_ptr< psi::BasisSet > bsf_i)

  *Compute the objective function value for auxiliary basis set optimization of OEPs.*

## Rotation of AO Space

### 14.7.1 Theory

The objective is to find the formulae for rotation matrices of the AO spaces as functions of the Cartesian 3 x 3 rotation matrices. It is obvious that *p*-type functions transform as a usual

Cartesian vectors. However, higher angular momentum functions transform in a more complex way.

#### Problem

Define a vectorized AO space *M* of rank *r*>1 that is constructed from unique tensor components of fully symmetric *r*-th rank AO tensor populated in standard order,

$$M_{\{ab\ldots k\}} = M_{ab\ldots k} \quad \text{for} \quad a \le b \le \ldots \le k$$

Given a general rotation of Cartesian tensors

$$M_{ab\ldots k} = \sum_{a'b'\ldots k'} M_{a'b'\ldots k'} r_{a'a} r_{b'b} \cdots r_{k'k}$$

find closed expressions for the rotation matrix in reduced composite AO space obeying

$$M_{[ab\ldots k]} = \sum_{\{a'b'\ldots k'\}} M_{\{a'b'\ldots k'\}} R_{\{a'b'\ldots k'\},[ab\ldots k]}$$

In the derivations below the following identity of first-order partitioning will be of use:

$$\sum_{ab} M_{ab} \hat{s}_{ab} = \sum_{\{ab\}} M_{\{ab\}} \left( \hat{s}_{ab} + \Delta_{ab} \hat{s}_{ba} \right)$$

where

$$\Delta_{ab} \equiv 1 - \delta_{ab}$$

and the operator *s* of rank *r* acts as follows

$$s^{ab\ldots k}_{a'b'\ldots k'} \equiv \hat{s}_{a'b'\ldots k'} \underbrace{\mathbf{r} \otimes \mathbf{r} \otimes \cdots \otimes \mathbf{r}}_{r} = r_{a'a} r_{b'b} \cdots r_{k'k}$$

#### Rotation of 6D functions

The rotation of the full tensor AO space of rank 2 and dimensions (3,3) is given by

$$M_{ab} = \sum_{a'b'} M_{a'b'} r_{a'b} r_{b'b}$$

Applying the identity of first-order partitioning directly leads to the formula for a reduced 6D tensor rotation of rank 1 and dimension (6),

$$M_{[ab]} = \sum_{\{a'b'\}} M_{\{a'b'\}} R_{\{a'b'\},[ab]}$$

where the 6 x 6 rotation matrix is given by

$$R_{\{a'b'\},[ab]} = r_{a'a} r_{b'b} + \Delta_{a'b'} r_{b'a} r_{a'b}$$

**Rotation of 10F functions**

The rotation of the full tensor AO space of rank 3 and dimensions (3,3,3) is given by

$$M_{abc} = \sum_{a'b'c'} M_{a'b'c'} r_{a'b} r_{b'b} r_{c'c}$$

First of all, notice that one can perform the following partitioning

$$\sum_a \sum_{b\neq a} \sum_{c\neq b\neq a} M_{abc}\hat{s}_{abc} = \sum_{\{abc\}} M_{\{abc\}} \left(\hat{s}_{abc} + \hat{s}_{acb} + \hat{s}_{bac} + \hat{s}_{bca} + \hat{s}_{cab} + \hat{s}_{cba}\right)$$

Then, perform a partitioning of the triple sum,

$$\begin{aligned}\sum_{abc} M_{abc}\hat{s}_{abc} = \sum_a \sum_{b\neq a} \sum_{c\neq b\neq a} M_{abc}\hat{s}_{abc} \\ + \sum_a \sum_{b\geq a} M_{abb}\hat{s}_{abb} + \sum_a \sum_{b<a} M_{abb}\hat{s}_{abb} \\ + \sum_a \sum_{b>a} M_{aba}\hat{s}_{aba} + \sum_a \sum_{b<a} M_{aba}\hat{s}_{aba} \\ + \sum_a \sum_{b>a} M_{bba}\hat{s}_{bba} + \sum_a \sum_{b<a} M_{bba}\hat{s}_{bba}\end{aligned}$$

Using the first-order partitioning theorem and interchanging the dummy indices one finds that

$$M_{[abc]} = \sum_{\{a'b'c'\}} M_{\{a'b'c'\}} R_{\{a'b'c'\},[abc]}$$

where the 10 x 10 rotation matrix is given by

$$\begin{aligned}R_{\{a'b'c'\},[abc]} = \delta_{b'c'} \left(s^{abc}_{a'b'b'} + \Delta_{a'b'} \left\{s^{abc}_{b'a'b'} + s^{abc}_{b'b'a'}\right\}\right) \\ + \delta_{a'b'}\Delta_{b'c'} \left(s^{abc}_{c'a'a'} + s^{abc}_{a'c'a'} + s^{abc}_{a'a'c'}\right) \\ + \Delta_{a'b'}\Delta_{b'c'} \left(s'^{abc}_{a'b'c} + s^{abc}_{a'c'b'} + s^{abc}_{b'a'c'} + s^{abc}_{b'c'a'} + s^{abc}_{c'a'b'} + s^{abc}_{c'b'a'}\right)\end{aligned}$$

and

$$s^{abc}_{a'b'c'} \equiv \hat{s}_{a'b'c'} \mathbf{r} \otimes \mathbf{r} \otimes \mathbf{r} = r_{a'a} r_{b'b} r_{c'c}$$

- psi::SharedMatrix oepdev::r6 (psi::SharedMatrix r)

  *Compute the 6 x 6 rotation matrix of the 6D orbitals.*
- void oepdev::populate (double $**$R, double $**$r, std::vector$<$ int $>$ idx_am, const int &nam)

  *Compute the 6 x 6 rotation matrix of the 6D orbitals.*
- psi::SharedMatrix oepdev::ao_rotation_matrix (psi::SharedMatrix r, psi::SharedBasisSet b)

  *Compute the full rotation matrix of AO orbital space.*

## 14.7.2 Detailed Description

## 14.7.3 Function Documentation

#### 14.7.3.1 _calculate_DFI_Vel()

```
std::shared_ptr< psi::Matrix > oepdev::_calculate_DFI_Vel (
          std::shared_ptr< psi::IntegralFactory > f_aabb,
          std::shared_ptr< psi::IntegralFactory > f_abab,
          std::shared_ptr< psi::Matrix > d_b )
```

Potential is felt by molecule A and induced by electrons in molecule B.

**Parameters**

| | |
|---|---|
| *f_aabb* | - IntegralFactory of type (AA\|BB) |
| *f_abab* | - IntegralFactory of type (AB\|AB) |
| *d_b* | - one-particle density matrix in AO basis of B |

**Returns**

- V_el(B) matrix in AO basis set of A

If f_abab is nullptr, then only Coulomb matrix is computed. Otherwise, also exchange contribution is computed.

#### 14.7.3.2 ao_rotation_matrix()

```
psi::SharedMatrix oepdev::ao_rotation_matrix (
          psi::SharedMatrix r,
          psi::SharedBasisSet b )
```

**Parameters**

| | |
|---|---|
| *r* | - Cartesian 3 x 3 rotation matrix |
| *b* | - Basis set |

#### 14.7.3.3 average_moment()

```
PSI_API double oepdev::average_moment (
          std::shared_ptr< psi::Vector > moment )
```

**Parameters**

| | |
|---|---|
| *moment* | - multipole moment vector with unique matrix elements. Now supported only for dipole and quadrupole. |

**Returns**

- the average multipole moment value.

The magnitudes of multipole moments are defined here as follows:

- The dipole moment magnitude is just a norm

$$|\mu| \equiv \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$$

- The quadrupole moment magnitude refers to the traceless moment in Buckingham convention

$$|\Theta| \equiv \sqrt{\Theta_{zz}^2 + \frac{1}{3}\left(\Theta_{xx} - \Theta_{yy}\right)^2 + \frac{4}{3}\left(\Theta_{xy}^2 + \Theta_{xz}^2 + \Theta_{yz}^2\right)}$$

In the above equation, the quadrupole moment elements refer to its traceless form.

#### 14.7.3.4 bs_optimize_projection()

```
PSI_API double oepdev::bs_optimize_projection (
          std::shared_ptr< psi::Matrix > ti,
          std::shared_ptr< psi::MintsHelper > mints,
          std::shared_ptr< psi::BasisSet > bsf_m,
          std::shared_ptr< psi::BasisSet > bsf_i )
```

**Parameters**

| | |
|---|---|
| *ti* | - Ti matrix |
| *mints* | - integral helper (instantiated with bsf_i) |
| *bsf_m* | - auxiliary AO basis to optimize |
| *bsf_i* | - intermediate AO basis |

**Returns**

value of objective function equal to negative trace of overlap matrix

#### 14.7.3.5 calculate_der_D()

```
PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_der_D (
          std::shared_ptr< psi::Wavefunction > wfn,
          std::shared_ptr< psi::IntegralTransform > tr,
          std::shared_ptr< psi::Matrix > C,
          std::vector< std::shared_ptr< psi::Matrix >> A )
```

Reads the existing MO ERI's.

**Parameters**

| | |
|---|---|
| *wfn* | - Wavefunction object |
| *tr* | - IntegralTransform object |
| *C* | - Transformation matrix MO-B::MO-A (columns are MO-A basis) |
| *A* | - Vector of matrices A^(n)_{bd} |

**Returns**

- derivative matrix in MO-A basis

### 14.7.3.6 calculate_DFI_Vel_J()

```
PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_DFI_Vel_J (
            std::shared_ptr< psi::IntegralFactory > f_aabb,
            std::shared_ptr< psi::Matrix > d_b )
```

Potential is felt by molecule A and induced by electrons in molecule B.

**Parameters**

| | |
|---|---|
| *f_aabb* | - IntegralFactory of type (AA\|BB) |
| *d_b* | - one-particle density matrix in AO basis of B |

**Returns**

- V_el(B) matrix in AO basis set of A

### 14.7.3.7 calculate_DFI_Vel_JK()

```
PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_DFI_Vel_JK (
            std::shared_ptr< psi::IntegralFactory > f_aabb,
            std::shared_ptr< psi::IntegralFactory > f_abab,
            std::shared_ptr< psi::Matrix > d_b )
```

Potential is felt by molecule A and induced by electrons in molecule B.

**Parameters**

| | |
|---|---|
| *f_aabb* | - IntegralFactory of type (AA\|BB) |
| *f_abab* | - IntegralFactory of type (AB\|AB) |
| *d_b* | - one-particle density matrix in AO basis of B |

**Returns**

- V_el(B) matrix in AO basis set of A

#### 14.7.3.8 calculate_e_xc()

```
PSI_API double oepdev::calculate_e_xc (
          std::shared_ptr< psi::Wavefunction > wfn,
          std::shared_ptr< psi::IntegralTransform > tr,
          std::shared_ptr< psi::Matrix > f,
          std::shared_ptr< psi::Matrix > C )
```

Reads the existing MO ERI's.

**Parameters**

| | |
|---|---|
| *wfn* | - Wavefunction object |
| *tr* | - IntegralTransform object |
| *f* | - f_ij matrix in MO-NEW basis |
| *C* | - Transformation matrix MO-SCF::MO-NEW (columns are MO-A basis) |

**Returns**

- Exchange-correlation energy

#### 14.7.3.9 calculate_idf_alpha_xc_energy()

```
PSI_API double oepdev::calculate_idf_alpha_xc_energy (
          std::shared_ptr< psi::Wavefunction > wfn,
          std::vector< double > w,
          psi::SharedMatrix D,
          std::vector< psi::SharedMatrix > Al,
          std::vector< psi::SharedMatrix > Bl )
```

TODO Provide matrices in AO basis!

#### 14.7.3.10 calculate_idf_xc_energy()

```
PSI_API double oepdev::calculate_idf_xc_energy (
          std::shared_ptr< psi::Wavefunction > wfn,
          std::shared_ptr< psi::Matrix > D,
          std::vector< std::shared_ptr< psi::Matrix >> f,
          std::vector< std::shared_ptr< psi::Matrix >> g,
          std::shared_ptr< psi::Vector > w,
          std::shared_ptr< psi::Vector > o,
          double N,
          double aN,
          double xiN,
          double AN,
          double wnorm )
```

TODO Provide matrices in AO basis!

#### 14.7.3.11 calculate_JK()

```
PSI_API std::vector< std::shared_ptr< psi::Matrix > > oepdev::calculate_JK
(
          std::shared_ptr< psi::Wavefunction > wfn,
          std::shared_ptr< psi::Matrix > C )
```

Transforms the AO ERI's based on provided C matrix.

**Parameters**

| | |
|---|---|
| *wfn* | - Wavefunction object |
| *C* | - molecular orbital coefficients (AO x MO) |

**Returns**

- vector with J_ij and K_ij matrix

#### 14.7.3.12 calculate_JK_r()

```
PSI_API std::vector< std::shared_ptr< psi::Matrix > > oepdev::calculate_JK_r
(
          std::shared_ptr< psi::Wavefunction > wfn,
          std::shared_ptr< psi::IntegralTransform > tr,
          std::shared_ptr< psi::Matrix > Dij )
```

Reads the existing MO ERI's.

**Parameters**

| | |
|---|---|
| *wfn* | - Wavefunction object |
| *tr* | - IntegralTransform object |
| *D* | - density matrix in MO basis |

**Returns**

- vector with J_ij and K_ij matrix

#### 14.7.3.13 calculate_OEP_basisopt_V()

```
PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_OEP_basisopt_V (
            const int & nt,
            std::shared_ptr< psi::IntegralFactory > f_pppt,
            std::shared_ptr< psi::Matrix > ca,
            std::shared_ptr< psi::Matrix > da )
```

**Parameters**

| | |
|---|---|
| *nt* | - number of test basis functions |
| *f_pppt* | - IntegralFactory of type (PP\|PT) |
| *ca* | - target MOs |
| *da* | - one-particle density matrix in AO basis |

**Returns**

- V matrix

#### 14.7.3.14 compute_distance()

```
PSI_API double oepdev::compute_distance (
            psi::SharedVector v1,
            psi::SharedVector v2 )
```

**Parameters**

| | |
|---|---|
| *v1* | - vector 1 |
| *v2* | - vector 2 |

**Returns**

distance The vectors have to have the same length.

#### 14.7.3.15 create_atom_basisset_by_copy()

```
PSI_API SharedBasisSet oepdev::create_atom_basisset_by_copy (
          SharedBasisSet basis_ref,
          SharedMolecule molecule_target,
          int idx_atom )
```

**Parameters**

| | |
|---|---|
| *basis_ref* | - reference basis set |
| *molecule_target* | - target molecule (atom in this case) |
| *idx_atom* | - index of an atom in basis_ref->molecule() |

**Returns**

psi::SharedBasisSet object.

#### 14.7.3.16 create_basisset_by_copy()

```
PSI_API SharedBasisSet oepdev::create_basisset_by_copy (
          SharedBasisSet basis_ref,
          SharedMolecule molecule_target )
```

**Parameters**

| | |
|---|---|
| *basis_ref* | - reference basis set |
| *molecule_target* | - target molecule |

**Returns**

psi::SharedBasisSet object.

#### 14.7.3.17 create_superfunctional()

```
PSI_API std::shared_ptr< SuperFunctional > oepdev::create_superfunctional (
          std::string name,
          Options & options )
```

Now it accepts only pure HF functional.

**Parameters**

| | |
|---|---|
| *name* | name of the functional (”HF” is now only available) |
| *options* | psi::Options object |

**Returns**

psi::SharedSuperFunctional object with functional.

**Examples:**

example_scf_perturb.cc.

#### 14.7.3.18 extract_monomer()

```
PSI_API std::shared_ptr< Molecule > oepdev::extract_monomer (
          std::shared_ptr< const Molecule > molecule_dimer,
          int id )
```

**Parameters**

| | |
|---|---|
| *molecule_dimer* | psi::SharedMolecule object with dimer |
| *id* | index of a molecule (starts from 1) |

**Returns**

psi::SharedMolecule object with indicated monomer

#### 14.7.3.19 matrix_power_derivative()

```
PSI_API std::shared_ptr< psi::Matrix > oepdev::matrix_power_derivative (
          std::shared_ptr< psi::Matrix > A,
          double g,
          double step )
```

The contracted matrix derivative is defined here as

$$\mathbf{D} = \frac{d\mathbf{A}^{\gamma}}{\mathbf{A}} : \mathbb{I}$$

where $\mathbb{I}$ is the identity matrix. The derivative, which is the fourth-rank tensor, is computed by the forward 2-centre finite difference formula,

$$f' = \left(f(h) - f(0)\right)/h$$

- if $\gamma$ is non-integer, input matrix has to be positive-definite.

**Parameters**

| | |
|---|---|
| *A* | - Matrix |
| *g* | - Power |
| *step* | - Differentiation step $h$ |

**Returns**

- Contracted derivative (matrix)

### 14.7.3.20 populate()

```
void oepdev::populate (
          double ** R,
          double ** r,
          std::vector< int > idx_am,
          const int & nam )
```

Compute the 10 x 10 rotation matrix of the 10F orbitals.

**Parameters**

| | |
|---|---|
| *r* | - Cartesian 3 x 3 rotation matrix |

**Returns**

6 x 6 rotation matrix of the 6D orbitals

**Parameters**

| | |
|---|---|
| *r* | - Cartesian 3 x 3 rotation matrix |

**Returns**

10 x 10 rotation matrix of the 10F orbitals

### 14.7.3.21 r6()

```
psi::SharedMatrix oepdev::r6 (
          psi::SharedMatrix r )
```

Compute the 10 x 10 rotation matrix of the 10F orbitals.

**Parameters**

| | |
|---|---|
| *r* | - Cartesian 3 x 3 rotation matrix |

**Returns**

6 x 6 rotation matrix of the 6D orbitals

**Parameters**

|   |   |
|---|---|
| *r* | - Cartesian 3 x 3 rotation matrix |

**Returns**

10 x 10 rotation matrix of the 10F orbitals

#### 14.7.3.22 solve_scf()

```
PSI_API std::shared_ptr< Wavefunction > oepdev::solve_scf (
          std::shared_ptr< Molecule > molecule,
          std::shared_ptr< BasisSet > primary,
          std::shared_ptr< BasisSet > auxiliary,
          std::shared_ptr< BasisSet > guess,
          std::shared_ptr< SuperFunctional > functional,
          Options & options,
          std::shared_ptr< PSIO > psio,
          bool compute_mints = false )
```

**Parameters**

|   |   |
|---|---|
| *molecule* | psi::SharedMolecule object with molecule |
| *primary* | basis set |
| *auxiliary* | basis set |
| *guess* | basis set |
| *functional* | DFT functional |
| *options* | psi::Options object |
| *psio* | psi::PSIO object |
| *compute_mints* | Compute integrals (write IWL TOC entry - necessary when transforming integrals) |

**Returns**

psi::SharedWavefunction SCF wavefunction of the molecule

#### 14.7.3.23 solve_scf_sad()

```
PSI_API std::shared_ptr< Wavefunction > oepdev::solve_scf_sad (
std::shared_ptr< Molecule > molecule,
std::shared_ptr< BasisSet > primary,
std::shared_ptr< BasisSet > auxiliary,
std::vector< std::shared_ptr< BasisSet >> sad,
std::vector< std::shared_ptr< BasisSet >> sad_fit,
std::shared_ptr< SuperFunctional > functional,
Options & options,
std::shared_ptr< PSIO > psio,
bool compute_mints = false )
```

**Parameters**

| | |
|---|---|
| *molecule* | psi::SharedMolecule object with molecule |
| *primary* | shared primary basis set |
| *auxiliary* | shared auxiliary basis set |
| *sad* | SAD basis set list |
| *sad_fit* | SAD DF fitting basis set list |
| *functional* | DFT functional |
| *options* | psi::Options object |
| *psio* | psi::PSIO object |
| *compute_mints* | Compute integrals (write IWL TOC entry - necessary when transforming integrals) |

**Returns**

psi::SharedWavefunction SCF wavefunction of the molecule

## 14.8 The OEPDev Testing Platform Library

Testing platform at C++ level of code. You should add more tests here when developing new functionalities, theories or models. Located at `oepdev/libtest`.

### Classes

- class oepdev::test::Test

  *Manages test routines.*

### 14.8.1 Detailed Description

# Chapter 15

# Namespace Documentation

## 15.1 gefp.basis._util Namespace Reference

### Functions

- def **COMPARE** (a, b, i=None)

### 15.1.1 Detailed Description

```
Local utilities (protected interface)

BB, 29.07.2020, Gundelfingen
```

## 15.2 gefp.basis.edf Namespace Reference

### Functions

- def **compute_v** (Ca, Da, prim, left_axis)
- def **projection** (c_a, s_ab, s_bb)
- def **projected_t** (c_a, s_ab, s_bb)
- def **projected_o** (c_a, s_ab, s_bb)
- def **obj_numpy** (param, t_i, bsf_i, dfbasis)
- def **obj_oepdev** (param, t_i, bsf_i, dfbasis, mints)
- def **find_aux_mo_mini** (G, S, I=None, eps=0.0001)
- def **optimize_ao_mini** (t_i, bsf_i, dfbasis, opt_global, cpp=False, maxiter_micro=2000, maxiter_macro=10)

### Variables

- **matrix_power** = scipy.linalg.fractional_matrix_power

### 15.2.1 Detailed Description

```
Extended Density Fitting Helper Library.

Useful routines for AO basis set optimization can be found here.

BB, 29.07.2020, Gundelfingen
```

## 15.3 gefp.basis.optimize Namespace Reference

### Classes

- class DFBasis
- class DFBasisOptimizer
- class OEP
- class OEP_CT
- class OEP_FockLike
- class OEP_Pauli

### Functions

- def **make_bastempl** (templ, param)
- def **oepfitbasis** (mol, role='ORBITAL')
- def **removeComments** (string)
- def oep_ao_basis_set_optimizer (wfn, interm, test=None, exemplary=None, target="OCC", cpp=False, more_info=False, maxiter=2000, templ_file='templ.dat', param_file='param.dat', bound_file=None, constraints=(), outname='oepfit.gbs', opt_global=False, global_iter=10, standardized_input=None)

### 15.3.1 Detailed Description

```
Auxiliary Basis Set Optimization Library.

The auxiliary basis sets for generalized density fitting (GDF)
are here optimized.
```

### 15.3.2 Function Documentation

#### 15.3.2.1 oep_ao_basis_set_optimizer()

```
def gefp.basis.optimize.oep_ao_basis_set_optimizer (
            wfn,
            interm,
            test = None,
            exemplary = None,
            target = "OCC",
            cpp = False,
            more_info = False,
            maxiter = 2000,
            templ_file = 'templ.dat',
            param_file = 'param.dat',
            bound_file = None,
            constraints = (),
            outname = 'oepfit.gbs',
            opt_global = False,
            global_iter = 10,
            standardized_input = None )
```

```
Method that optimizes DF basis set.
This is currently the state-of-the-art and recommended.
```

## 15.4 gefp.basis.optimize_bcp Namespace Reference

### Classes

- class DFBasis
- class DFBasisOptimizer
- class OEP
- class OEP_CT
- class OEP_FockLike
- class OEP_Pauli

### Functions

- def **make_bastempl** (templ, param)
- def **oepfitbasis** (mol, role='ORBITAL')
- def **removeComments** (string)
- def **compute_error** (basis, oep, rms=False)
- def **objective_function** (param, oep)

### 15.4.1 Detailed Description

```
Auxiliary Basis Set Optimization Library.

The auxiliary basis sets for generalized density fitting (GDF)
are here optimized.
```

## 15.5 gefp.basis.parameters Namespace Reference

### Classes

- class StandardizedInput
- class TakeMyStandardSteps

### 15.5.1 Detailed Description

```
Parameters for Basis Set Optimization Module

Contains:
  o standard templates for auxiliary minimal AO basis set
  o guess parameters for auxiliary minimal AO basis set optimization
  o automatized basin hopping bound and step adjustment tools

BB, 30.07.2020, Gundelfingen
```

## 15.6 gefp.basis.template.extended Namespace Reference

### Variables

- dictionary **extended_template_by_row** = {}
- dictionary **extended_bounds_codes_by_row** = {}
- string **b1** = " E C E C E C"
- dictionary **extended_guess_parameters_by_atom** = {}
- float **s** = 0.3
- dictionary **extended_scales_by_row** = {}

### 15.6.1 Detailed Description

```
Extended Templates for AO Basis Set Optimization

BB, 04.08.2020, Gundelfingen
```

## 15.7 gefp.basis.template.standard Namespace Reference

### Variables

- dictionary **atoms_by_row** = {}
- dictionary **standard_template_by_row** = {}
- dictionary **standard_bounds_codes_by_row** = {}
- string **b1** = " E C E C E C"

- dictionary **standard_guess_parameters_by_atom** = {}
- dictionary **reference_symbol_by_row** = {}
- float **s** = 0.3
- dictionary **standard_scales_by_row** = {}

### 15.7.1 Detailed Description

```
Standard Templates for AO Basis Set Optimization

BB, 04.08.2020, Gundelfingen
```

## 15.8 gefp.density.dfi Namespace Reference

### Classes

- class DFI
- class DFI_J
- class DFI_JK
- class SCF

### Variables

- int **MAX_NBF** = 128

### 15.8.1 Detailed Description

```
 Demonstrates the use of Psi4 from Python level.
 Useful notes:
  o Use psi4.core module for most of the work
  o Useful modules within psi4.core:
     - MintsHelper
     - Molecule
     - BasisSet
     - ExternalPotential
     others
  o Psi4 defines its own matrix type (psi4.core.Matrix).
    Extracting numpy.array is easy:
       numpy_array = numpy.asarray(psi4_matrix)
    Creating Psi4 matrix from array is also easy:
       psi4_matrix = psi4.core.Matrix.from_array(numpy_array)
  o To compute 1-el potential matrix for a set of charges
    use ExternalPotential (charge positions are to be provided in Angstroms)
    unless charges are just nuclei within the basis set (in this case use of ao_potentia
    of MintsHelper is easier).
  o ao_potential method of MintsHelper is limited only for nuclei within the same basis
    (the nuclei are taken from the first basis set axis, for example:
      mints = MintsHelper(basis_X)
      mints.ao_potential()                 -> nuclei taken from basis of mints object (b
      mints.ao_potential(basis_1, basis_2) -> nuclei taken from basis_1
  o Psi4 has efficient and easy to use method of defining fragments within a molecule (u
    Defining ghost atoms and extracting fragment i in the multimer-centred basis set is
    (method extract_subsets(...) of psi4.core.Molecule)
```

## 15.9 gefp.density.population Namespace Reference

### Classes

- class Loc

### Functions

- def atomic_charges (wfn, kappa=0.0)

### 15.9.1 Detailed Description

```
Module for population analyses.
Bartosz B␣lasiak, Gundelfingen, September 2019

Notes:
  Copied from my QC Workshop.
  Reference: https://github.com/globulion/qc-workshop/tree/master/tutor/project_1#popul
```

### 15.9.2 Function Documentation

#### 15.9.2.1 atomic_charges()

```
def gefp.density.population.atomic_charges (
            wfn,
            kappa = 0.0 )
```

```
Compute atomic partial charges as a function of kappa parameter.

Input:
  wfn   - psi4.core.Wavefunction object
  kappa - parameter in the interval [0, 1]

Returns:
  numpy.ndarray of shape (wfn.molecule().natom(), ) with partial charges [A.U.]

Notes:
  o kappa = 0 corresponds to Mulliken charges
  o kappa = 1/2 corresponds to Lowdin charges
```

## 15.10 oepdev Namespace Reference

OEPDev module namespace.

### Classes

- struct ABCD

  *Simple structure to hold the Fourier series expansion coefficients.*
- class AbInitioPolarGEFactory

  *Polarization GEFP Factory from First Principles. Hartree-Fock Approximation.*
- class AllAOIntegralsIterator_2

  *Loop over all possible ERI within a particular shell doublet.*
- class AllAOIntegralsIterator_4

  *Loop over all possible ERI within a particular shell quartet.*
- class AllAOShellCombinationsIterator_2

  *Loop over all possible ERI shells in a shell doublet.*
- class AllAOShellCombinationsIterator_4

  *Loop over all possible ERI shells in a shell quartet.*
- class AOIntegralsIterator

  *Iterator for AO Integrals. Abstract Base.*
- class CAMM

  *Cumulative Atomic Multipole Moments.*
- class ChargeTransferEnergyOEPotential

  *Generalized One-Electron Potential for Charge-Transfer Interaction Energy.*
- class ChargeTransferEnergySolver

  *Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.*
- class CISComputer

  *CISComputer.*
- struct CISData

  *CIS wavefunction parameters. Container structure.*
- class CPHF

  *CPHF solver class.*
- class CubePoints3DIterator

  *Iterator over a collection of points in 3D space. g09 Cube-like order.*
- class CubePointsCollection3D

  *G09 cube-like ordered collection of points in 3D space.*
- class DavidsonLiu

  *Davidson-Liu diagonalization method.*
- class DIISManager

  *DIIS manager.*

- class DMTPole

  *Distributed Multipole Analysis Container and Computer. Abstract Base.*
- class DoubleGeneralizedDensityFit

  *Generalized Density Fitting Scheme - Double Fit.*
- class EETCouplingOEPotential

  *Generalized One-Electron Potential for EET coupling calculations.*
- class EETCouplingSolver

  *Compute the EET coupling energy between unperturbed wavefunctions.*
- class EFP2_GEFactory

  *EFP2 GEFP Factory.*
- class EFPMultipolePotentialInt

  *Computes potential integrals.*
- class ElectrostaticEnergyOEPotential

  *Generalized One-Electron Potential for Electrostatic Energy.*
- class ElectrostaticEnergySolver

  *Compute the Coulombic interaction energy between unperturbed wavefunctions.*
- class ElectrostaticPotential3D

  *Electrostatic potential of a molecule.*
- class ERI_1_1

  *2-centre ERI of the form (a|O(2)|b) where O(2) = 1/r12.*
- class ERI_2_2

  *4-centre ERI of the form (ab|O(2)|cd) where O(2) = 1/r12.*
- class ERI_3_1

  *4-centre ERI of the form (abc|O(2)|d) where O(2) = 1/r12.*
- class ESPSolver

  *Charges from Electrostatic Potential (ESP). A solver-type class.*
- class FFAbInitioPolarGEFactory

  *Polarization GEFP Factory from First Principles: Finite-Difference Model. Arbitrary level of theory.*
- class Field3D

  *General Vector Dield in 3D Space. Abstract base.*
- struct Fourier5

  *Simple structure to hold the Fourier series expansion coefficients for N=2.*
- struct Fourier9

  *Simple structure to hold the Fourier series expansion coefficients for N=4.*
- class FragmentedSystem

  *Molecular System for Fragment-Based Calculations.*
- class GenEffFrag

  *Generalized Effective Fragment. Container Class.*
- class GenEffPar

*Generalized Effective Fragment Parameters. Container Class.*
- class GenEffParFactory

  *Generalized Effective Fragment Factory. Abstract Base.*
- class GeneralizedDensityFit

  *Generalized Density Fitting Scheme. Abstract Base.*
- class GeneralizedPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class GramSchmidt

  *Gram-Schmidt orthogonalization method.*
- class IntegralFactory

  *Extended IntegralFactory for computing integrals.*
- class KabschSuperimposer

  *Compute the Cartesian rotation matrix between two structures.*
- class LinearGradientNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class LinearNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class LinearUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class MultipoleConvergence

  *Multipole Convergence.*
- class NonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class ObaraSaikaTwoCenterEFPRecursion_New

  *Obara-Saika recursion formulae for improved EFP multipole potential integrals.*
- class OEP_EFP2_GEFactory

  *OEP-EFP2 GEFP Factory.*
- class OEPDevSolver

  *Solver of properties of molecular aggregates. Abstract base.*
- class OEPotential

  *Generalized One-Electron Potential: Abstract base.*
- class OEPotential3D

  *Class template for OEP 3D fields.*
- struct OEPType

  *Container to handle the type of One-Electron Potentials.*
- class OverlapGeneralizedDensityFit

  *Generalized Density Fitting Scheme - Single Fit Based on Minimal Overlap in MO Basis.*
- struct PerturbCharges

  *Structure to hold perturbing charges.*
- class Points3DIterator

*Iterator over a collection of points in 3D space. Abstract base.*

- class PointsCollection3D

  *Collection of points in 3D space. Abstract base.*
- class PolarGEFactory

  *Polarization GEFP Factory. Abstract Base.*
- class PotentialInt

  *Computes potential integrals.*
- class QuadraticGradientNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class QuadraticNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class QuadraticUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class QUAMBO

  *The Quasiatomic Minimal Basis Set Molecular Orbitals (QUAMBO)*
- struct QUAMBOData

  *Container to store the QUAMBO data.*
- class R_CISComputer
- class R_CISComputer_Direct
- class R_CISComputer_DL

  *CIS Computer with RHF reference: Davidson-Liu Solver.*
- class R_CISComputer_Explicit
- class RandomPoints3DIterator

  *Iterator over a collection of points in 3D space. Random collection.*
- class RandomPointsCollection3D

  *Collection of random points in 3D space.*
- class RepulsionEnergyOEPotential

  *Generalized One-Electron Potential for Pauli Repulsion Energy.*
- class RepulsionEnergySolver

  *Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.*
- class RHFPerturbed

  *RHF theory under electrostatic perturbation.*
- class ShellCombinationsIterator

  *Iterator for Shell Combinations. Abstract Base.*
- class SingleGeneralizedDensityFit

  *Generalized Density Fitting Scheme - Single Fit.*
- class TIData

  *Transfer Integral EET Data.*
- class TwoBodyAOInt
- class TwoElectronInt

*General Two Electron Integral.*

- class U_CISComputer
- class U_CISComputer_DL

  *CIS Computer with UHF reference: Davidson-Liu Solver.*
- class U_CISComputer_Explicit
- class UniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class UnitaryOptimizer

  *Find the optimim unitary matrix of quadratic matrix equation.*
- class UnitaryOptimizer_2

  *Find the optimim unitary matrix for quadratic matrix equation with trace.*
- class UnitaryOptimizer_2_1
- class UnitaryOptimizer_4_2

  *Find the optimim unitary matrix for quartic-quadratic matrix equation with trace.*
- class UnitaryTransformedMOPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Scaling of MO Space.*
- class WavefunctionUnion

  *Union of two Wavefunction objects.*

## Typedefs

- using SharedDMTPole = std::shared_ptr< DMTPole >

  *DMTPole object.*
- using **SharedField3D** = std::shared_ptr< oepdev::Field3D >
- using **SharedOEPotential** = std::shared_ptr< OEPotential >
- using SharedGenEffPar = std::shared_ptr< GenEffPar >

  *GEFP Parameters container.*
- using SharedGenEffParFactory = std::shared_ptr< GenEffParFactory >

  *GEFP Parameter factory.*
- using SharedGenEffFrag = std::shared_ptr< GenEffFrag >

  *GEFP Fragment container.*
- using SharedFragmentedSystem = std::shared_ptr< FragmentedSystem >

  *Fragmented system.*
- using **SharedWavefunction** = std::shared_ptr< Wavefunction >
- using **SharedBasisSet** = std::shared_ptr< BasisSet >
- using **SharedMatrix** = std::shared_ptr< Matrix >
- using **SharedVector** = std::shared_ptr< Vector >
- using **SharedLocalizer** = std::shared_ptr< Localizer >
- using **SharedCISData** = std::shared_ptr< CISData >
- using SharedWavefunctionUnion = std::shared_ptr< WavefunctionUnion >

  *WavefunctionUnion.*

- using **SharedDMTPConvergence** = std::shared_ptr< oepdev::MultipoleConvergence >
- using **SharedMolecule** = std::shared_ptr< psi::Molecule >
- using **SharedMOSpace** = std::shared_ptr< psi::MOSpace >
- using **SharedMOSpaceVector** = std::vector< std::shared_ptr< psi::MOSpace > >
- using **SharedIntegralTransform** = std::shared_ptr< psi::IntegralTransform >
- using SharedCPHF = std::shared_ptr< CPHF >

  *CPHF object.*
- using **SharedIntegralFactory** = std::shared_ptr< IntegralFactory >
- using **SharedTwoBodyAOInt** = std::shared_ptr< TwoBodyAOInt >
- using SharedShellsIterator = std::shared_ptr< ShellCombinationsIterator >

  *Iterator over shells as shared pointer.*
- using SharedAOIntsIterator = std::shared_ptr< AOIntegralsIterator >

  *Iterator over AO integrals as shared pointer.*
- using **SharedQUAMBOData** = std::shared_ptr< QUAMBOData >
- using SharedQUAMBO = std::shared_ptr< QUAMBO >

  *Shared QUAMBO object.*
- using **SharedSuperFunctional** = std::shared_ptr< SuperFunctional >

## Functions

- double d_N_n1_n2 (int N, int n1, int n2, double PA, double PB, double aP)

  *Compute McMurchie-Davidson-Hermite (MDH) coefficient for binomial expansion.*
- void make_mdh_D2_coeff_explicit_recursion (int n1, int n2, double aP, double ∗PA, double ∗PB, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for binomial expansion by explicit recursion. This function makes the same changes to buffers as oepdev::make_mdh_D2_coeff, but implements it through explicit recursion by calls to oepdev::d_N_n1_n2. Therefore, it is slightly slower. Here for debugging purposes.*
- void make_mdh_D1_coeff (int n1, double aPd, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for monomial expansion.*
- void make_mdh_D2_coeff (int n1, int n2, double aPd, double ∗PA, double ∗PB, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for binomial expansion.*
- void make_mdh_D3_coeff (int n1, int n2, int n3, double aPd, double ∗PA, double ∗PB, double ∗PC, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for trinomial expansion.*
- void make_mdh_R_coeff (int N, int L, int M, double alpha, double a, double b, double c, double ∗F, double ∗buffer)

  *Compute the McMurchie-Davidson R coefficients.*
- double ∗∗∗ **init_box** (int a, int b, int c)
- void **zero_box** (double ∗∗∗box, int a, int b, int c)
- void **free_box** (double ∗∗∗box, int a, int b)

- psi::SharedMatrix **r10** (psi::SharedMatrix r3)
- constexpr std::complex< double > **operator""_i** (unsigned long long d)
- constexpr std::complex< double > **operator""_i** (long double d)
- PSI_API void preambule (void)

  *Print preambule for module OEPDEV.*
- PSI_API std::shared_ptr< SuperFunctional > create_superfunctional (std::string name, Options &options)

  *Set up DFT functional.*
- PSI_API SharedBasisSet create_basisset_by_copy (SharedBasisSet basis_ref, SharedMolecule molecule_target)

  *Build BasisSet by Copy.*
- PSI_API SharedBasisSet create_atom_basisset_by_copy (SharedBasisSet basis_ref, SharedMolecule molecule_target, int idx_atom)

  *Build BasisSet by Copy for a Particular Atom.*
- PSI_API std::shared_ptr< Molecule > extract_monomer (std::shared_ptr< const Molecule > molecule_dimer, int id)

  *Extract molecule from dimer.*
- PSI_API double compute_distance (psi::SharedVector v1, psi::SharedVector v2)

  *Compute distance between two points in nD space.*
- PSI_API std::shared_ptr< Wavefunction > solve_scf (std::shared_ptr< Molecule > molecule, std::shared_ptr< BasisSet > primary, std::shared_ptr< BasisSet > auxiliary, std::shared_ptr< BasisSet > guess, std::shared_ptr< SuperFunctional > functional, Options &options, std::shared_ptr< PSIO > psio, bool compute_mints=false)

  *Solve RHF-SCF equations for a given molecule in a given basis set.*
- PSI_API std::shared_ptr< Wavefunction > solve_scf_sad (std::shared_ptr< Molecule > molecule, std::shared_ptr< BasisSet > primary, std::shared_ptr< BasisSet > auxiliary, std::vector< std::shared_ptr< BasisSet >> sad, std::vector< std::shared_ptr< BasisSet >> sad_fit, std::shared_ptr< SuperFunctional > functional, Options &options, std::shared_ptr< PSIO > psio, bool compute_mints=false)

  *Solve RHF-SCF equations for a given molecule in a given basis set.*
- PSI_API double average_moment (std::shared_ptr< psi::Vector > moment)

  *Compute the scalar magnitude of multipole moment.*
- PSI_API std::vector< std::shared_ptr< psi::Matrix > > calculate_JK (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::Matrix > C)

  *Compute the Coulomb and exchange integral matrices in MO basis.*
- PSI_API double **calculate_idf_alpha_xc_energy** (std::shared_ptr< psi::Wavefunction > wfn, std::vector< double > w, std::shared_ptr< psi::Matrix > D, std::vector< std::shared_ptr< psi::Matrix >> AI, std::vector< std::shared_ptr< psi::Matrix >> BI)
- PSI_API double calculate_idf_xc_energy (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::Matrix > D, std::vector< std::shared_ptr< psi::Matrix >> f, std::vector< std::shared_ptr< psi::Matrix >> g, std::shared_ptr< psi::Vector > w, std::shared_ptr< psi::Vector > o, double N, double aN, double xiN, double AN, double wnorm)

  *Compute the IDF exchange-correlation energy.*

- PSI_API std::vector< std::shared_ptr< psi::Matrix > > **calculate_JK_ints** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr)
- PSI_API std::vector< std::shared_ptr< psi::Matrix > > calculate_JK_r (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > Dij)

    *Compute the Coulomb and exchange integral matrices in MO basis.*
- PSI_API std::vector< std::shared_ptr< psi::Matrix > > **calculate_JK_rb** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > Dij)
- PSI_API std::shared_ptr< psi::Matrix > calculate_der_D (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > C, std::vector< std::shared_ptr< psi::Matrix >> A)

    *Compute the derivative of exchange-correlation energy wrt the density matrix in MO-A basis.*
- PSI_API double calculate_e_xc (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > f, std::shared_ptr< psi::Matrix > C)

    *Compute the exchange-correlation energy from ERI in MO-SCF basis.*
- PSI_API double **calculate_e_apsg** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > fJ, std::shared_ptr< psi::Matrix > fK, std::shared_ptr< psi::Matrix > C)
- PSI_API psi::SharedMatrix **calculate_de_apsg** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Vector > P, std::shared_ptr< psi::Matrix > AJ, std::shared_ptr< psi::Matrix > AKL, std::shared_ptr< psi::Matrix > aJ, std::shared_ptr< psi::Matrix > aKL, std::shared_ptr< psi::Matrix > C)
- PSI_API psi::SharedMatrix **calculate_de_apsg_new** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::Vector > P, std::shared_ptr< psi::Matrix > C, std::shared_ptr< psi::Matrix > A_J, std::shared_ptr< psi::Matrix > A_LK, std::shared_ptr< psi::Matrix > a_J, std::shared_ptr< psi::Matrix > a_LK)
- PSI_API psi::SharedMatrix **calculate_unitary_uo_2** (psi::SharedVector Q, int n)
- PSI_API psi::SharedMatrix **calculate_unitary_uo_2_1** (psi::SharedMatrix P, psi::SharedVector p)
- PSI_API std::shared_ptr< psi::Matrix > matrix_power_derivative (std::shared_ptr< psi::Matrix > A, double g, double step)

    *Compute the contracted derivative of power of a square and symmetric matrix.*
- std::shared_ptr< psi::Matrix > _calculate_DFI_Vel (std::shared_ptr< psi::IntegralFactory > f_aabb, std::shared_ptr< psi::IntegralFactory > f_abab, std::shared_ptr< psi::Matrix > d_b)

    *Compute the Effective DFI Potential Matrix Due To Electrons.*
- PSI_API std::shared_ptr< psi::Matrix > calculate_DFI_Vel_JK (std::shared_ptr< psi::IntegralFactory > f_aabb, std::shared_ptr< psi::IntegralFactory > f_abab, std::shared_ptr< psi::Matrix > d_b)

    *Compute the Effective DFI Coulomb+Exchange Potential Matrix Due To Electrons.*
- PSI_API std::shared_ptr< psi::Matrix > calculate_DFI_Vel_J (std::shared_ptr< psi::IntegralFactory > f_aabb, std::shared_ptr< psi::Matrix > d_b)

    *Compute the Effective DFI Coulomb Potential Matrix Due To Electrons.*

- PSI_API std::shared_ptr< psi::Matrix > calculate_OEP_basisopt_V (const int &nt, std::shared_ptr< psi::IntegralFactory > f_pppt, std::shared_ptr< psi::Matrix > ca, std::shared_ptr< psi::Matrix > da)

  *Compute the 2-Electron Part of the Effective OEP Matrix for Auxiliary Basis Set Optimization.*
- PSI_API double bs_optimize_projection (std::shared_ptr< psi::Matrix > ti, std::shared_ptr< psi::MintsHelper > mints, std::shared_ptr< psi::BasisSet > bsf_m, std::shared_ptr< psi::BasisSet > bsf_i)

  *Compute the objective function value for auxiliary basis set optimization of OEPs.*
- template<typename... Args>
  std::string string_sprintf (const char ∗format, Args... args)

  *Format string output. Example: std::string text = oepdev::string_sprinff("Test %3d, %13.5f", 5, -10.5425);.*
- PSI_API double calculate_idf_alpha_xc_energy (std::shared_ptr< psi::Wavefunction > wfn, std::vector< double > w, psi::SharedMatrix D, std::vector< psi::SharedMatrix > AI, std::vector< psi::SharedMatrix > BI)

  *Compute the IDF exchange-correlation energy.*

**Rotation of AO Space**

### 15.10.1 Theory

*The objective is to find the formulae for rotation matrices of the AO spaces as functions of the Cartesian 3 x 3 rotation matrices. It is obvious that p-type functions transform as a usual Cartesian vectors. However, higher angular momentum functions transform in a more complex way.*

#### Problem

*Define a vectorized AO space M of rank r>1 that is constructed from unique tensor components of fully symmetric r-th rank AO tensor populated in standard order,*

$$M_{\{ab\ldots k\}} = M_{ab\ldots k} \quad \text{for} \quad a \le b \le \ldots \le k$$

*Given a general rotation of Cartesian tensors*

$$M_{ab\ldots k} = \sum_{a'b'\ldots k'} M_{a'b'\ldots k'} r_{a'a} r_{b'b} \cdots r_{k'k}$$

*find closed expressions for the rotation matrix in reduced composite AO space obeying*

$$M_{[ab\ldots k]} = \sum_{\{a'b'\ldots k'\}} M_{\{a'b'\ldots k'\}} R_{\{a'b'\ldots k'\},[ab\ldots k]}$$

*In the derivations below the following identity of first-order partitioning will be of use:*

$$\sum_{ab} M_{ab}\hat{s}_{ab} = \sum_{\{ab\}} M_{\{ab\}} \left(\hat{s}_{ab} + \Delta_{ab}\hat{s}_{ba}\right)$$

*where*

$$\Delta_{ab} \equiv 1 - \delta_{ab}$$

*and the operator s of rank r acts as follows*

$$s^{ab\ldots k}_{a'b'\ldots k'} \equiv \hat{s}_{a'b'\ldots k'} \underbrace{\mathbf{r} \otimes \mathbf{r} \otimes \cdots \otimes \mathbf{r}}_{r} = r_{a'a} r_{b'b} \cdots r_{k'k}$$

#### Rotation of 6D functions

*The rotation of the full tensor AO space of rank 2 and dimensions (3,3) is given by*

$$M_{ab} = \sum_{a'b'} M_{a'b'} r_{a'b} r_{b'b}$$

*Applying the identity of first-order partitioning directly leads to the formula for a reduced 6D tensor rotation of rank 1 and dimension (6),*

$$M_{[ab]} = \sum_{\{a'b'\}} M_{\{a'b'\}} R_{\{a'b'\},[ab]}$$

*where the 6 x 6 rotation matrix is given by*

$$R_{\{a'b'\},[ab]} = r_{a'a} r_{b'b} + \Delta_{a'b'} r_{b'a} r_{a'b}$$

#### Rotation of 10F functions

*The rotation of the full tensor AO space of rank 3 and dimensions (3,3,3) is given by*

$$M_{abc} = \sum_{a'b'c'} M_{a'b'c'} r_{a'b} r_{b'b} r_{c'c}$$

*First of all, notice that one can perform the following partitioning*

$$\sum_a \sum_{b \neq a} \sum_{c \neq b \neq a} M_{abc} \hat{s}_{abc} = \sum_{\{abc\}} M_{\{abc\}} \left( \hat{s}_{abc} + \hat{s}_{acb} + \hat{s}_{bac} + \hat{s}_{bca} + \hat{s}_{cab} + \hat{s}_{cba} \right)$$

*Then, perform a partitioning of the triple sum,*

$$\begin{aligned} \sum_{abc} M_{abc} \hat{s}_{abc} = & \sum_a \sum_{b \neq a} \sum_{c \neq b \neq a} M_{abc} \hat{s}_{abc} \\ & + \sum_a \sum_{b \geq a} M_{abb} \hat{s}_{abb} + \sum_a \sum_{b < a} M_{abb} \hat{s}_{abb} \\ & + \sum_a \sum_{b > a} M_{aba} \hat{s}_{aba} + \sum_a \sum_{b < a} M_{aba} \hat{s}_{aba} \\ & + \sum_a \sum_{b > a} M_{bba} \hat{s}_{bba} + \sum_a \sum_{b < a} M_{bba} \hat{s}_{bba} \end{aligned}$$

*Using the first-order partitioning theorem and interchanging the dummy indices one finds that*

$$M_{[abc]} = \sum_{\{a'b'c'\}} M_{\{a'b'c'\}} R_{\{a'b'c'\},[abc]}$$

*where the 10 x 10 rotation matrix is given by*

$$R_{\{a'b'c'\},[abc]} = \delta_{b'c'} \left( s^{abc}_{a'b'b'} + \Delta_{a'b'} \left\{ s^{abc}_{b'a'b'} + s^{abc}_{b'b'a'} \right\} \right) + \delta_{a'b'} \Delta_{b'c'} \left( s^{abc}_{c'a'a'} + s^{abc}_{a'c'a'} + s^{abc}_{a'a'c'} \right) + \Delta_{a'b'} \Delta_{b'c'} \left( s'^{abc}_{a'b'c} + s^{abc}_{a'c'b'} + s^{abc}_{b'a'c'} + s^{abc}_{b'c'a'} + s^{abc}_{c'a'b'} + s^{abc}_{c'b'a'} \right)$$

*and*

$$s^{abc}_{a'b'c'} \equiv \hat{s}_{a'b'c'} \mathbf{r} \otimes \mathbf{r} \otimes \mathbf{r} = r_{a'a} r_{b'b} r_{c'c}$$

- psi::SharedMatrix r6 (psi::SharedMatrix r)

  *Compute the 6 x 6 rotation matrix of the 6D orbitals.*
- void populate (double $**$R, double $**$r, std::vector$<$ int $>$ idx_am, const int &nam)

  *Compute the 6 x 6 rotation matrix of the 6D orbitals.*
- psi::SharedMatrix ao_rotation_matrix (psi::SharedMatrix r, psi::SharedBasisSet b)

  *Compute the full rotation matrix of AO orbital space.*

### Variables

- double **dfxxx** [MAX_DF]

### 15.10.2 Detailed Description

Contains all the functionalities for the development of the Generalized One-Electroc Potentials (OEP's).

## 15.11 psi Namespace Reference

Psi4 package namespace.

### Typedefs

- using **SharedBasisSet** = std::shared_ptr$<$ BasisSet $>$
- using **SharedMolecule** = std::shared_ptr$<$ Molecule $>$
- using **SharedMatrix** = std::shared_ptr$<$ Matrix $>$
- using **SharedWavefunction** = std::shared_ptr$<$ Wavefunction $>$

### Functions

- PSI_API int read_options (std::string name, Options &options)

  *Options for the OEPDev plugin.*
- void **export_dmtp** (py::module &)

- void **export_cphf** (py::module &)
- void **export_solver** (py::module &)
- void **export_util** (py::module &)
- void **export_oep** (py::module &)
- void **export_gefp** (py::module &)
- PSI_API SharedWavefunction oepdev (SharedWavefunction ref_wfn, Options &options)

  *Main routine of the OEPDev plugin.*
- **PYBIND11_MODULE** (oepdev, m)

## 15.11.1 Detailed Description

Contains all Psi4 functionalities.

## 15.11.2 Function Documentation

#### 15.11.2.1 oepdev()

```
PSI_API SharedWavefunction psi::oepdev (
          SharedWavefunction ref_wfn,
          Options & options )
```

Created with intention to test various models of the interaction energy between two molecules, described by the Hartree-Fock-Roothaan-Hall theory or the configuration interaction with singles theory.

In particular, the plugin tests the models of:

1. the Pauli repulsion and CT interaction energy (Project II )
2. the Induction interaction energy (Project III)
3. the excitation energy transfer couplings (Project I )

against benchmarks (exact or reference solutions). The list of implemented models can be found in Implemented Models .

**Parameters**

| | |
|---|---|
| *ref_wfn* | shared wavefunction of a dimer |
| *options* | psi::Options object |

**Returns**

psi::SharedWavefunction (either ref_wfn or wavefunction union)

#### 15.11.2.2 read_options()

```
PSI_API int psi::read_options (
          std::string name,
          Options & options )
```

**Parameters**

| | |
|---|---|
| *name* | name of driver function |
| *options* | psi::Options object |

**Returns**

true

# Chapter 16

# Class Documentation

## 16.1 oepdev::ABCD Struct Reference

Simple structure to hold the Fourier series expansion coefficients.

```
#include <unitary_optimizer.h>
```

### Public Attributes

- double **A**
- double **B**
- double **C**
- double **D**

### 16.1.1 Detailed Description

The documentation for this struct was generated from the following file:

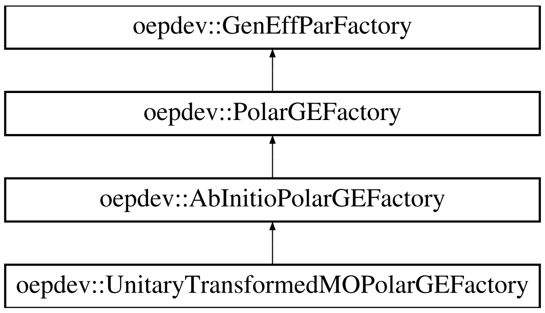
- oepdev/libutil/unitary_optimizer.h

## 16.2 oepdev::AbInitioPolarGEFactory Class Reference

Polarization GEFP Factory from First Principles. Hartree-Fock Approximation.

```
#include <gefp.h>
```

Inheritance diagram for oepdev::AbInitioPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::AbInitioPolarGEFactory
oepdev::UnitaryTransformedMOPolarGEFactory

## Public Member Functions

- **AbInitioPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- virtual std::shared_ptr< GenEffPar > compute (void)

  *Compute the density matrix susceptibility tensors.*

## Additional Inherited Members

### 16.2.1 Detailed Description

Implements creation of the density matrix susceptibility tensors for which $\mathbf{X} = \mathbf{1}$. Guarantees the idempotency of the density matrix up to first-order in LCAO-MO variation. The density matrix susceptibility tensor is represented by:

$$\delta D_{\alpha\beta} = \sum_i \mathbf{B}_{\alpha\beta}^{(i;1)} \cdot \mathbf{F}(\mathbf{r}_i)$$

where $\mathbf{B}_{\alpha\beta}^{(i;1)}$ is the density matrix dipole polarizability defined for the distributed LMO site at $\mathbf{r}_i$. Its explicit form is given by

$$\mathbf{B}_{\alpha\beta}^{(i;1)} = C_{\alpha i}^{(0)} \mathbf{b}_{\beta}^{(i;1)} C_{\beta i}^{(0)} \mathbf{b}_{\alpha}^{(i;1)} - \sum_{\gamma} \left( D_{\alpha\gamma}^{(0)} C_{\beta i}^{(0)} + D_{\beta\gamma}^{(0)} C_{\alpha i}^{(0)} \right) \mathbf{b}_{\gamma}^{(i;1)}$$

where the susceptibility of the LCAO-MO coefficient is given by

$$b_{\alpha;w}^{(i;1)} = \frac{1}{4} \sum_{u}^{x,y,z} [\alpha_i]_{uw} \left[ [\mathbf{L}_i]_{\text{Left}}^{-1} \right]_{u;\alpha}$$

for $w = x, y, z$. The auxiliary tensor $\mathbb{L}$ is defined as

$$\mathbb{L} = \mathbf{C}^{(0)\text{T}} \cdot \mathbb{M} \cdot \left( \mathbf{1} - \mathbf{D}^{(0)} \right)$$

where $\mathbb{M}$ is the dipole integral vector of matrices in AO representation. The left inverse of the $i$-th element is defined as

$$[\mathbf{L}_i]_{\text{Left}}^{-1} \equiv \left[ \mathbf{L}_i^{\text{T}} \cdot \mathbf{L}_i \right]^{-1} \cdot \mathbf{L}_i^{\text{T}}$$

Note that $\mathbf{L}_i \equiv [\mathbb{L}]_i$ is a $n \times 3$ matrix, whereas its left inverse is a $3 \times n$ matrix with $n$ being the size of the AO basis set.

The documentation for this class was generated from the following files:

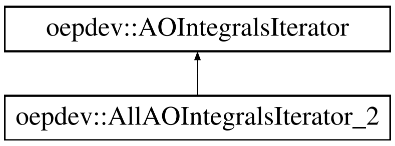
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_abinitio.cc

## 16.3 oepdev::AllAOIntegralsIterator_2 Class Reference

Loop over all possible ERI within a particular shell doublet.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::AllAOIntegralsIterator_2:



### Public Member Functions

- AllAOIntegralsIterator_2 (const ShellCombinationsIterator ∗shellIter)

  *Construct by shell iterator (const object)*
- AllAOIntegralsIterator_2 (std::shared_ptr< ShellCombinationsIterator > shellIter)

  *Construct by shell iterator (pointed by shared pointer)*
- void first ()

  *First iteration.*
- void next ()

  *Next iteration.*
- int i () const

  *Grab the current integral i index.*
- int j () const

  *Grab the current integral j index.*
- int index () const

### Additional Inherited Members

### 16.3.1 Detailed Description

Constructed by providing a const reference or shared pointer to an AllAOShellCombinationsIterator object.

**See also**

AllAOShellCombinationsIterator_2

### 16.3.2 Constructor & Destructor Documentation

#### 16.3.2.1 AllAOIntegralsIterator_2() [1/2]

```
AllAOIntegralsIterator_2::AllAOIntegralsIterator_2 (
            const ShellCombinationsIterator * shellIter )
```

**Parameters**

| | |
|---|---|
| *shellIter* | - shell iterator object |

#### 16.3.2.2 AllAOIntegralsIterator_2() [2/2]

```
AllAOIntegralsIterator_2::AllAOIntegralsIterator_2 (
            std::shared_ptr< ShellCombinationsIterator > shellIter )
```

**Parameters**

| | |
|---|---|
| *shellIter* | - shell iterator object |

### 16.3.3 Member Function Documentation

#### 16.3.3.1 index()

```
int oepdev::AllAOIntegralsIterator_2::index (
            void ) const [inline], [virtual]
```

Grab the current index of integral value stored in the buffer

Implements oepdev::AOIntegralsIterator.

The documentation for this class was generated from the following files:

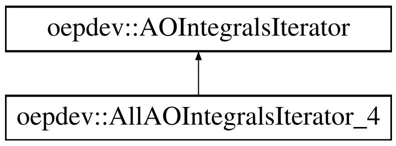
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

## 16.4 oepdev::AllAOIntegralsIterator_4 Class Reference

Loop over all possible ERI within a particular shell quartet.

```
#include <integrals_iter.h>
```

Inheritance diagram for oepdev::AllAOIntegralsIterator_4:



### Public Member Functions

- AllAOIntegralsIterator_4 (const ShellCombinationsIterator ∗shellIter)

  *Construct by shell iterator (const object)*
- AllAOIntegralsIterator_4 (std::shared_ptr< ShellCombinationsIterator > shellIter)

  *Construct by shell iterator (pointed by shared pointer)*
- void first ()

  *First iteration.*
- void next ()

  *Next iteration.*
- int i () const

  *Grab the current integral i index.*
- int j () const

  *Grab the current integral j index.*
- int k () const

  *Grab the current integral k index.*
- int l () const

  *Grab the current integral l index.*
- int index () const

### Additional Inherited Members

### 16.4.1 Detailed Description

Constructed by providing a const reference or shared pointer to an AllAOShellCombinationsIterator object.

**See also**

AllAOShellCombinationsIterator_4

### 16.4.2 Constructor & Destructor Documentation

#### 16.4.2.1 AllAOIntegralsIterator_4() [1/2]

```
AllAOIntegralsIterator_4::AllAOIntegralsIterator_4 (
            const ShellCombinationsIterator * shellIter )
```

**Parameters**

| | |
|---|---|
| *shellIter* | - shell iterator object |

#### 16.4.2.2 AllAOIntegralsIterator_4() [2/2]

```
AllAOIntegralsIterator_4::AllAOIntegralsIterator_4 (
            std::shared_ptr< ShellCombinationsIterator > shellIter )
```

**Parameters**

| | |
|---|---|
| *shellIter* | - shell iterator object |

### 16.4.3 Member Function Documentation

#### 16.4.3.1 index()

```
int oepdev::AllAOIntegralsIterator_4::index (
            void ) const [inline], [virtual]
```

Grab the current index of integral value stored in the buffer

Implements oepdev::AOIntegralsIterator.

The documentation for this class was generated from the following files:

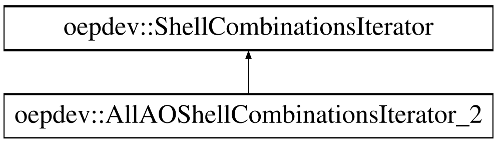
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

## 16.5 oepdev::AllAOShellCombinationsIterator_2 Class Reference

Loop over all possible ERI shells in a shell doublet.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::AllAOShellCombinationsIterator_2:


oepdev::ShellCombinationsIterator
oepdev::AllAOShellCombinationsIterator_2

## Public Member Functions

- AllAOShellCombinationsIterator_2 (SharedBasisSet bs_1, SharedBasisSet bs_2)

  *Iterate over shell doublets. Construct by providing basis sets for each axis. The basis sets must be defined for the same molecule.*
- AllAOShellCombinationsIterator_2 (std::shared_ptr< IntegralFactory > integrals)

  *Construct by providing integral factory.*
- AllAOShellCombinationsIterator_2 (const IntegralFactory &integrals)
- AllAOShellCombinationsIterator_2 (std::shared_ptr< psi::IntegralFactory > integrals)

  *Construct by providing integral factory.*
- AllAOShellCombinationsIterator_2 (const psi::IntegralFactory &integrals)
- void first ()

  *First iteration.*
- void next ()

  *Next iteration.*
- void compute_shell (std::shared_ptr< oepdev::TwoBodyAOInt > tei) const

  *Compute ERI's for the current shell. The eris are stored in the buffer of the argument object.*
- void **compute_shell** (std::shared_ptr< psi::TwoBodyAOInt > tei) const
- int P () const

  *Grab the current shell P index.*
- int Q () const

  *Grab the current shell Q index.*

## Additional Inherited Members

### 16.5.1 Detailed Description

Constructed by providing IntegralFactory object or shared pointers to two basis set spaces.

### 16.5.2 Constructor & Destructor Documentation

#### 16.5.2.1 AllAOShellCombinationsIterator_2() [1/5]

```
AllAOShellCombinationsIterator_2::AllAOShellCombinationsIterator_2 (
            SharedBasisSet bs_1,
            SharedBasisSet bs_2 )
```

**Parameters**

| | |
|---|---|
| *bs_1* | - basis set of axis 1 |
| *bs_2* | - basis set of axis 2 |

#### 16.5.2.2 AllAOShellCombinationsIterator_2() [2/5]

```
oepdev::AllAOShellCombinationsIterator_2::AllAOShellCombinationsIterator_2 (
            std::shared_ptr< IntegralFactory > integrals )
```

**Parameters**

| | |
|---|---|
| *integrals* | - OepDev integral factory object |

#### 16.5.2.3 AllAOShellCombinationsIterator_2() [3/5]

```
AllAOShellCombinationsIterator_2::AllAOShellCombinationsIterator_2 (
            const IntegralFactory & integrals )
```

This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.

#### 16.5.2.4 AllAOShellCombinationsIterator_2() [4/5]

```
AllAOShellCombinationsIterator_2::AllAOShellCombinationsIterator_2 (
            std::shared_ptr< psi::IntegralFactory > integrals )
```

**Parameters**

| | |
|---|---|
| *integrals* | - Psi4 integral factory object |

#### 16.5.2.5 AllAOShellCombinationsIterator_2() [5/5]

```
AllAOShellCombinationsIterator_2::AllAOShellCombinationsIterator_2 (
          const psi::IntegralFactory & integrals )
```

This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.

### 16.5.3 Member Function Documentation

#### 16.5.3.1 compute_shell()

```
void AllAOShellCombinationsIterator_2::compute_shell (
          std::shared_ptr< oepdev::TwoBodyAOInt > tei ) const  [virtual]
```

**Parameters**

| | |
|---|---|
| *tei* | - two electron AO integral |

Implements oepdev::ShellCombinationsIterator.

The documentation for this class was generated from the following files:

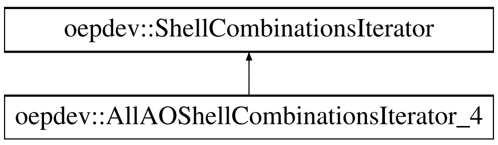
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

## 16.6 oepdev::AllAOShellCombinationsIterator_4 Class Reference

Loop over all possible ERI shells in a shell quartet.

```
#include <integrals_iter.h>
```

Inheritance diagram for oepdev::AllAOShellCombinationsIterator_4:


oepdev::ShellCombinationsIterator
oepdev::AllAOShellCombinationsIterator_4

### Public Member Functions

- AllAOShellCombinationsIterator_4 (SharedBasisSet bs_1, SharedBasisSet bs_2, SharedBasisSet bs_3, SharedBasisSet bs_4)

  *Iterate over shell quartets. Construct by providing basis sets for each axis. The basis sets must be defined for the same molecule.*
- AllAOShellCombinationsIterator_4 (std::shared_ptr< IntegralFactory > integrals)

*Construct by providing integral factory.*
- AllAOShellCombinationsIterator_4 (const IntegralFactory &integrals)
- AllAOShellCombinationsIterator_4 (std::shared_ptr< psi::IntegralFactory > integrals)

  *Construct by providing integral factory.*
- AllAOShellCombinationsIterator_4 (const psi::IntegralFactory &integrals)
- void first ()

  *Do the first iteration.*
- void next ()

  *Do the next iteration.*
- void compute_shell (std::shared_ptr< oepdev::TwoBodyAOInt > tei) const
- void compute_shell (std::shared_ptr< psi ::TwoBodyAOInt > tei) const
- int P () const

  *Grab the current shell P index.*
- int Q () const

  *Grab the current shell Q index.*
- int R () const

  *Grab the current shell R index.*
- int S () const

  *Grab the current shell S index.*

## Additional Inherited Members

### 16.6.1 Detailed Description

Constructed by providing IntegralFactory object or shared pointers to four basis set spaces.

### 16.6.2 Constructor & Destructor Documentation

#### 16.6.2.1 AllAOShellCombinationsIterator_4() [1/5]

```
AllAOShellCombinationsIterator_4::AllAOShellCombinationsIterator_4 (
            SharedBasisSet bs_1,
            SharedBasisSet bs_2,
            SharedBasisSet bs_3,
            SharedBasisSet bs_4 )
```

**Parameters**

| | |
|---|---|
| *bs_1* | - basis set of axis 1 |
| *bs_2* | - basis set of axis 2 |
| *bs_3* | - basis set of axis 3 |
| *bs_4* | - basis set of axis 4 |

#### 16.6.2.2 AllAOShellCombinationsIterator_4() [2/5]

```
oepdev::AllAOShellCombinationsIterator_4::AllAOShellCombinationsIterator_4 (
            std::shared_ptr< IntegralFactory > integrals )
```

**Parameters**

| | |
|---|---|
| *integrals* | - OepDev integral factory object |

#### 16.6.2.3 AllAOShellCombinationsIterator_4() [3/5]

```
AllAOShellCombinationsIterator_4::AllAOShellCombinationsIterator_4 (
            const IntegralFactory & integrals )
```

This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.

#### 16.6.2.4 AllAOShellCombinationsIterator_4() [4/5]

```
AllAOShellCombinationsIterator_4::AllAOShellCombinationsIterator_4 (
            std::shared_ptr< psi::IntegralFactory > integrals )
```

**Parameters**

| | |
|---|---|
| *integrals* | - OepDev integral factory object |

#### 16.6.2.5 AllAOShellCombinationsIterator_4() [5/5]

```
AllAOShellCombinationsIterator_4::AllAOShellCombinationsIterator_4 (
            const psi::IntegralFactory & integrals )
```

This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.

### 16.6.3 Member Function Documentation

#### 16.6.3.1 compute_shell() [1/2]

```
void AllAOShellCombinationsIterator_4::compute_shell (
          std::shared_ptr< oepdev::TwoBodyAOInt > tei ) const [virtual]
```

Compute integrals in a current shell. Works both for oepdev::TwoBodyAOInt and psi::TwoBodyAOInt

**Parameters**

| | |
|---|---|
| *tei* | - two body integral object |

Implements oepdev::ShellCombinationsIterator.

#### 16.6.3.2 compute_shell() [2/2]

```
void oepdev::AllAOShellCombinationsIterator_4::compute_shell (
          std::shared_ptr< psi ::TwoBodyAOInt > tei ) const [virtual]
```

Compute integrals in a current shell. Works both for oepdev::TwoBodyAOInt and psi::TwoBodyAOInt

**Parameters**

| | |
|---|---|
| *tei* | - two body integral object |

Implements oepdev::ShellCombinationsIterator.

The documentation for this class was generated from the following files:

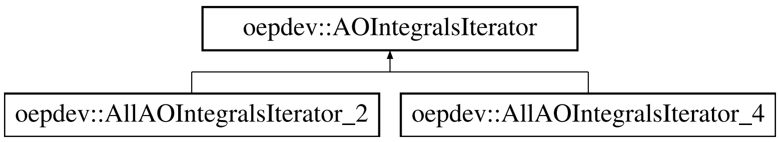
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

## 16.7 oepdev::AOIntegralsIterator Class Reference

Iterator for AO Integrals. Abstract Base.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::AOIntegralsIterator:


oepdev::AOIntegralsIterator
oepdev::AllAOIntegralsIterator_2
oepdev::AllAOIntegralsIterator_4

## Public Member Functions

- AOIntegralsIterator ()

  *Base Constructor.*
- virtual ∼AOIntegralsIterator ()

  *Base Destructor.*
- virtual void first (void)=0

  *Do the first iteration.*
- virtual void next (void)=0

  *Do the next iteration.*
- virtual int i (void) const

  *Grab i-th index.*
- virtual int j (void) const

  *Grab j-th index.*
- virtual int k (void) const

  *Grab k-th index.*
- virtual int l (void) const

  *Grab l-th index.*
- virtual int index (void) const =0

  *Grab index in the integral buffer.*
- virtual bool is_done (void)

  *Returns the status of an iterator.*

## Static Public Member Functions

- static std::shared_ptr< AOIntegralsIterator > build (const ShellCombinationsIterator ∗shellIter, std::string mode="ALL")
- static std::shared_ptr< AOIntegralsIterator > build (std::shared_ptr< ShellCombinationsIterator > shellIter, std::string mode="ALL")

## Protected Attributes

- bool done

  *The status of an iterator.*

### 16.7.1 Detailed Description

### 16.7.2 Member Function Documentation

#### 16.7.2.1 build() [1/2]

```
std::shared_ptr< AOIntegralsIterator > AOIntegralsIterator::build (
          const ShellCombinationsIterator * shellIter,
          std::string mode = "ALL" ) [static]
```

Build AO integrals iterator from current state of iterator over shells

**Parameters**

| | |
|---|---|
| *shellIter* | - iterator over shells - either ”ALL” or ”UNIQUE” (iterate over all or unique integrals) |

**Returns**

iterator over AO integrals

#### 16.7.2.2 build() [2/2]

```
std::shared_ptr< AOIntegralsIterator > AOIntegralsIterator::build (
          std::shared_ptr< ShellCombinationsIterator > shellIter,
          std::string mode = "ALL" ) [static]
```

This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.

The documentation for this class was generated from the following files:

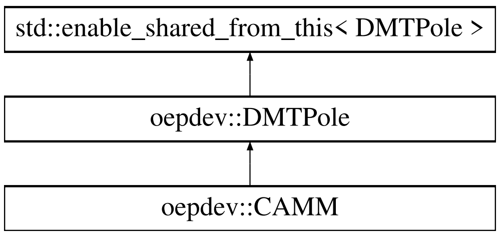
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

## 16.8 oepdev::CAMM Class Reference

Cumulative Atomic Multipole Moments.

`#include <dmtp.h>`

Inheritance diagram for oepdev::CAMM:



## Public Member Functions

- **CAMM** (psi::SharedWavefunction wfn, int n)
- **CAMM** (const CAMM $*$other)
- virtual void compute (psi::SharedMatrix D, bool transition, int n)

  *Compute DMTP's from the one-particle density matrix.*
- virtual void print_header (void) const

  *Print the header.*
- virtual std::shared_ptr$<$ DMTPole $>$ clone (void) const override

  *Make a deep copy (`wfn_`, `mol_`, and `primary_` are shallow-copied)*

## Additional Inherited Members

### 16.8.1 Detailed Description

Cumulative atomic multipole representation of the molecular charge distribution. Method of Sokalski and Poirier. Ref.: W. A. Sokalski and R. A. Poirier, *Chem. Phys. Lett.*, 98(1) **1983**

## Methodology.

The distributed multipole moments are computed in the following way:

- first the atomic additive multipole moments (AAMM's) with origins set to the global coordinate system origin are computed. AO basis set partitioning is used to dostribute the AAMM's onto the atomic centres.
- subsequently, the AAMM's origins are moved to the corresponding atomic site.

The computation of the AAMM's is performed according to the following prescription:

$$M^{(A)}_{uw\ldots z}(\mathbf{0}) = \sum_{\alpha\in A} \sum_{\beta\in\mathrm{allAO's}} D^{\mathrm{OED}}_{\alpha\beta} \langle\alpha|\mathscr{M}_{uw\ldots z}(\mathbf{0})|\beta\rangle$$

where $M^{(A)}_{uw\ldots z}$ denotes the $(uw\ldots z)$-th component of the multipole centered at atomic site $A$, the symbol $\mathscr{M}(\mathbf{0})$ is the associated quantum mechanical operator and $D^{\mathrm{OED}}_{\alpha\beta}$ is the (generalized) one-particle density matrx element in AO basis (Greek indices).

Recentering of the multipole moments is described in the documentation of oepdev::DMTPole::recenter.

The documentation for this class was generated from the following files:

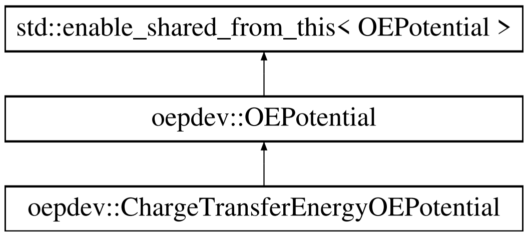
- oepdev/lib3d/dmtp.h
- oepdev/lib3d/dmtp_camm.cc

## 16.9 oepdev::ChargeTransferEnergyOEPotential Class Reference

Generalized One-Electron Potential for Charge-Transfer Interaction Energy.

```
#include <oep.h>
```

Inheritance diagram for oepdev::ChargeTransferEnergyOEPotential:


std::enable_shared_from_this< OEPotential >
oepdev::OEPotential
oepdev::ChargeTransferEnergyOEPotential

### Public Member Functions

- **ChargeTransferEnergyOEPotential** (SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate, Options &options)
- **ChargeTransferEnergyOEPotential** (SharedWavefunction wfn, Options &options)
- **ChargeTransferEnergyOEPotential** (const ChargeTransferEnergyOEPotential ∗f)
- virtual void compute (const std::string &oepType) override

  *Compute matrix forms of all OEP's within a specified OEP type.*
- virtual void compute_3D (const std::string &oepType, const double &x, const double &y, const double &z, std::shared_ptr< psi::Vector > &v) override

  *Compute value of potential in point x, y, z and save at v.*
- virtual void print_header () const override

  *Header information.*
- virtual std::shared_ptr< OEPotential > clone (void) const override

  *Make a deep copy of this object.*
- virtual void initialize () override

  *Initialize the object (expert)*

### Protected Member Functions

- virtual void **rotate_oep** (psi::SharedMatrix, psi::SharedMatrix, psi::SharedMatrix) override
- virtual void **translate_oep** (psi::SharedVector) override

### Additional Inherited Members

### 16.9.1 Detailed Description

Contains the following OEP types:

- `Otto-Ladik.V1.GDF` - DF-based term (group I)
- `Otto-Ladik.V3.CAMM-nj` - CAMM-based term (group III; truncated on distributed charges)

Group II terms do not require any particular OEP's due to great siplification of this term. Atomic numbers and LMO centroids are sufficient.

The documentation for this class was generated from the following files:

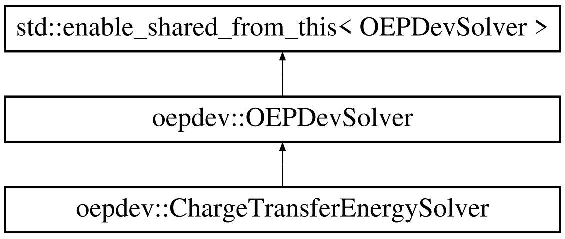
- oepdev/liboep/oep.h
- oepdev/liboep/oep_energy_ct.cc

## 16.10 oepdev::ChargeTransferEnergySolver Class Reference

Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::ChargeTransferEnergySolver:


std::enable_shared_from_this< OEPDevSolver >
oepdev::OEPDevSolver
oepdev::ChargeTransferEnergySolver

### Public Member Functions

- **ChargeTransferEnergySolver** (SharedWavefunctionUnion wfn_union)
- virtual double compute_oep_based (const std::string &method=”DEFAULT”)

  *Compute property by using OEP's.*
- virtual double compute_benchmark (const std::string &method=”DEFAULT”)

  *Compute property by using benchmark method.*

### Additional Inherited Members

### 16.10.1 Detailed Description

The implemented methods are shown below

Table 16.15: Methods available in the Solver

| Keyword | Method Description |
|---|---|
| **Benchmark Methods** | |
| `OTTO_LADIK` | *Default*. CT energy at HF level from Otto and Ladik (1975). |
| `EFP2` | CT energy at HF level from EFP2 model. |
| **OEP-Based Methods** | |
| `OTTO_LADIK` | *Default*. OEP-based Otto-Ladik expressions. |

In order to construct this solver, **always** use the `OEPDevSolver::build` static factory method.

Below the detailed description of the implemented equations is given for each of the above provided methods. In the formulae across, it is assumed that the orbitals are real. The Coulomb notation for electron repulsion integrals (ERI's) is adopted; i.e,

$$(ac|bd) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_1)\frac{1}{r_{12}}\phi_b(\mathbf{r}_2)\phi_d(\mathbf{r}_2)$$

Greek subscripts denote basis set orbitals whereas Italic subscripts denote the occupied molecular orbitals.

The CT energy between molecules *A* and *B* is given by

$$E^{\rm CT} = E^{\rm A^+B^-} + E^{\rm A^-B^+}$$

## Benchmark Methods

### CT energy at HF level by Otto and Ladik (1975).

For a closed-shell system, CT energy equation of Otto and Ladik becomes

$$E^{\rm A^+B^-} \approx 2\sum_{i\in A}^{\rm Occ_A}\sum_{n\in B}^{\rm Vir_B}\frac{V_{in}^2}{\varepsilon_i - \varepsilon_n}$$

where

$$V_{in} = V_{in}^B + 2\sum_{j\in B}^{\rm Occ_B}(in|jj) - \sum_{k\in A}^{\rm Occ_A} S_{kn}\left\{V_{ik}^B + 2\sum_{j\in B}^{\rm Occ_B}(ik|jj)\right\}$$
$$- \sum_{j\in B}^{\rm Occ_B}\left[S_{ij}\left\{V_{nj}^A + 2\sum_{k\in A}^{\rm Occ_A}(1-\delta_{ik})(nj|kk)\right\} + (nj|ij)\right] + \sum_{k\in A}^{\rm Occ_A}\sum_{j\in B}^{\rm Occ_B} S_{kj}(1-\delta_{ik})(ik|nj)$$

and analogously the twin term.

#### CT energy at HF level by EFP2.

In EFP2 method, CT energy is given as

$$E^{\mathrm{A^+B^-}} \approx 2 \sum_{i\in A}^{\mathrm{Occ_A}} \sum_{n\in B}^{\mathrm{Vir_B}} \frac{V_{in}^2}{F_{ii} - T_{nn}}$$

where

$$V_{in}^2 = \frac{V_{in}^{EF,B} - \sum_{m\in A}^{\mathrm{All_A}} V_{im}^{EF,B} S_{mn}^B}{1 - \sum_{m\in A}^{\mathrm{All_A}} S_{mn}^2} \left\{ V_{in}^{EF,B} - \sum_{m\in A}^{\mathrm{All_A}} V_{im}^{EF,B} S_{mn} + \sum_{j\in B}^{\mathrm{Occ_B}} S_{ij} \left( T_{nj} - \sum_{m\in A}^{\mathrm{All_A}} S_{nm} T_{mj} \right) \right\}$$

and analogously the twin term.

## OEP-Based Methods

### OEP-Based Otto-Ladik's theory

After introducing OEP's, the original Otto-Ladik's theory is reformulated *without* approximation as

$$E^{\mathrm{A^+B^-}} \approx 2 \sum_{i\in A}^{\mathrm{Occ_A}} \sum_{n\in B}^{\mathrm{Vir_B}} \frac{\left( V_{in}^{\mathrm{DF}} + V_{in}^{\mathrm{ESP,A}} + V_{in}^{\mathrm{ESP,B}} \right)^2}{\varepsilon_i - \varepsilon_n}$$

where

$$V_{in}^{\mathrm{DF}} = \sum_{\eta\in B}^{\mathrm{Aux_B}} S_{i\eta} G_{\eta n}^B$$

$$V_{in}^{\mathrm{ESP,A}} = \sum_{k\in A}^{\mathrm{Occ_A}} \sum_{j\in B}^{\mathrm{Occ_B}} S_{kj} \sum_{x\in A} V_{nj}^{(x)} q_{ik}^{(x)}$$

$$V_{in}^{\mathrm{ESP,B}} = - \sum_{k\in A}^{\mathrm{Occ_A}} S_{kn} V_{ik}^B$$

The OEP matrix for density fitted part is given by

$$G_{\eta n}^B = \sum_{\eta'\in B}^{\mathrm{Aux_B}} [\mathbf{S}^{-1}]_{\eta\eta'} \left\{ V_{\eta' n}^B + \sum_{j\in B}^{\mathrm{Occ_B}} \left[ 2(\eta' n|jj) - (\eta' j|nj) \right] \right\}$$

The OEP ESP-A charges are fit to reproduce the OEP potential

$$v_{ik}^A(\mathbf{r}) \equiv (1-\delta_{ik}) \int \frac{\phi_i(\mathbf{r}')\phi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' - \delta_{ik} \left( \sum_{x\in A} \frac{-Z_x}{|\mathbf{r}-\mathbf{r}_x|} + 2 \sum_{k\in A}^{\mathrm{Occ_A}} \int \frac{\phi_k(\mathbf{r}')\phi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' - 2 \int \frac{\phi_i(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \right)$$

so that

$$v_{ik}^A(\mathbf{r}) \cong \sum_{x\in A} \frac{q_{ik}^{(x)}}{|\mathbf{r}-\mathbf{r}_x|}$$

The OEP ESP-B charges are fit to reproduce the electrostatic potential of molecule *B* (they are standard ESP charges).

### 16.10.2 Member Function Documentation

#### 16.10.2.1 compute_benchmark()

```
double ChargeTransferEnergySolver::compute_benchmark (
            const std::string & method = "DEFAULT" )  [virtual]
```

Each solver object has one `DEFAULT` benchmark method

**Parameters**

|  |  |
|---|---|
| *method* | - benchmark method |

Implements oepdev::OEPDevSolver.

#### 16.10.2.2 compute_oep_based()

```
double ChargeTransferEnergySolver::compute_oep_based (
            const std::string & method = "DEFAULT" )  [virtual]
```

Each solver object has one `DEFAULT` OEP-based method.

**Parameters**

|  |  |
|---|---|
| *method* | - flavour of OEP model |

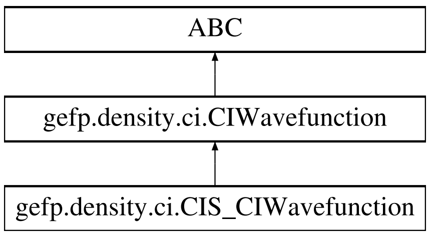
Implements oepdev::OEPDevSolver.

The documentation for this class was generated from the following files:

- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_energy_ct.cc

## 16.11 gefp.density.ci.CIS_CIWavefunction Class Reference

Inheritance diagram for gefp.density.ci.CIS_CIWavefunction:


ABC
gefp.density.ci.CIWavefunction
gefp.density.ci.CIS_CIWavefunction

### Public Member Functions

- def __**init**__ (self, ref_wfn, E, W)
- def **make_ci_I** (self)

### Additional Inherited Members

The documentation for this class was generated from the following file:

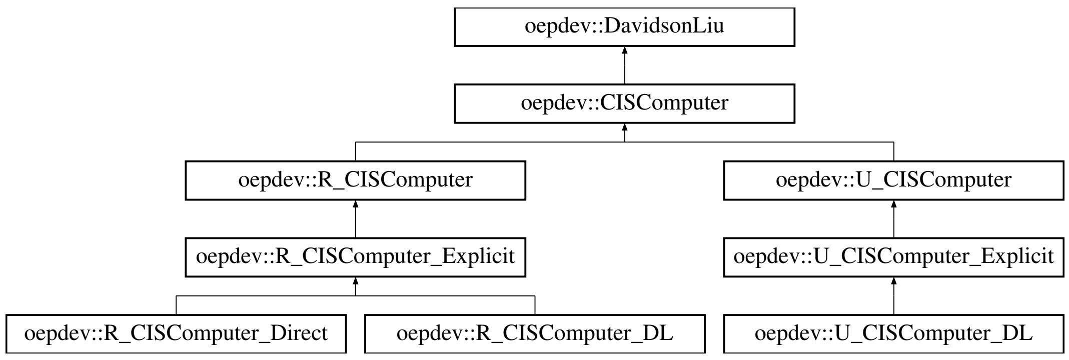
- gefp/gefp/density/ci.py

## 16.12 oepdev::CISComputer Class Reference

CISComputer.

```
#include <cis.h>
```

Inheritance diagram for oepdev::CISComputer:



### Public Member Functions

- virtual ~CISComputer ()

  *Destructor.*
- virtual void compute (void)

  *Solve the CIS problem.*
- virtual void clear_dpd (void)

  *Clear DPD instance.*
- int nstates (void) const

  *Get the total number of excited states.*
- psi::SharedVector eigenvalues () const

  *Get the CIS eigenvalues.*
- psi::SharedVector **E** () const
- psi::SharedMatrix eigenvectors () const

*Get the CIS eigenvectors.*

- psi::SharedMatrix **U** () const
- std::pair< double, double > U_homo_lumo (int I, int h=0, int l=0) const

  *Get the HOMO+*h*->LUMO+*l* CIS coefficient for a given excited state I for spin alpha and beta.*
- SharedMatrix Da_mo (int i) const

  *Compute MO one-particle alpha density matrix for state i*
- SharedMatrix Db_mo (int i) const

  *Compute MO one-particle beta density matrix for state i*
- SharedMatrix Da_ao (int i) const

  *Compute AO one-particle alpha density matrix for state i*
- SharedMatrix Db_ao (int i) const

  *Compute AO one-particle beta density matrix for state i*
- SharedDMTPole camm (int j, bool symmetrize=false) const

  *Compute CAMM for j excited state.*
- SharedMatrix Ta_ao (int j) const

  *Compute MO one-particle alpha 0->*j* transition density matrix.*
- SharedMatrix Tb_ao (int j) const

  *Compute MO one-particle beta 0->*j* transition density matrix.*
- SharedMatrix Ta_ao (int i, int j) const

  *Compute MO one-particle alpha i->*j* transition density matrix.*
- SharedMatrix Tb_ao (int i, int j) const

  *Compute MO one-particle beta i->*j* transition density matrix.*
- SharedDMTPole trcamm (int j, bool symmetrize=true) const

  *Compute TrCAMM for 0->*j* transition.*
- SharedDMTPole trcamm (int i, int j, bool symmetrize=true) const

  *Compute TrCAMM for i->*j* transition.*
- SharedVector transition_dipole (int j) const

  *Compute transition dipole moment for 0->*j* transition.*
- SharedVector transition_dipole (int i, int j) const

  *Compute transition dipole moment for i->*j* transition.*
- double oscillator_strength (int j) const

  *Compute oscillator strength for 0->*j* transition.*
- double oscillator_strength (int i, int j) const

  *Compute oscillator strength for i->*j* transition.*
- double s2 (int i) const

  *Compute <S2> expectation value for the *i*th state.*
- void determine_electronic_state (int &I)

  *Determine electronic state.*
- std::shared_ptr< CISData > data (int I, int h, int l, bool symmetrize_trcamm=false)

  *Return CIS data structure for a given excited state I*

## Static Public Member Functions

- static std::shared_ptr< CISComputer > build (const std::string &type, std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt, const std::string &reference="")

    *Build CIS Computer.*

## Static Public Attributes

- static const std::vector< std::string > reference_types = {"RHF", "UHF"}

    *Slater determinant possible references, that are implemented.*

## Protected Member Functions

- **CISComputer** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt, psi::IntegralTransform::Tran
trans_type)
- virtual void **print_header_** (void)
- virtual void **set_nstates_** (void)
- virtual void **allocate_memory** (void)
- virtual void **allocate_hamiltonian_** (void)
- virtual void **prepare_for_cis_** (void)
- virtual void **build_hamiltonian_** (void)=0
- virtual void **diagonalize_hamiltonian_** (void)
- virtual void **standardize_amplitudes_** (void)
- virtual void **print_excited_states_** (void)
- virtual void **print_excited_state_character_** (int I)=0
- virtual void **set_beta_** (void)=0
- virtual void **transform_integrals_** (void)
- virtual void **davidson_liu_compute_diagonal_hamiltonian** (void)
- virtual void **davidson_liu_compute_sigma** (void)

## Protected Attributes

- std::shared_ptr< psi::Wavefunction > ref_wfn_

    *Reference wavefunction.*

- const int nmo_

    *Psi4 Options.*

- const int naocc_

    *Number of alpha occupied MO's.*

- const int nbocc_

    *Number of beta occupied MO's.*

- const int navir_

    *Number of alpha virtual MO's.*

- const int nbvir_

  *Number of beta virtual MO's.*
- int ndets_

  *Number of excited determinants.*
- int nstates_

  *Number of excited states.*
- SharedMatrix H_

  *CIS Excited State Hamiltonian in Slater determinantal basis.*
- SharedMatrix **U_**
- SharedVector **E_**
- std::shared_ptr< psi::JK > jk_

  *Computer of generalized JK objects.*
- SharedVector **eps_a_o_**
- SharedVector **eps_a_v_**
- SharedVector **eps_b_o_**
- SharedVector **eps_b_v_**
- const psi::IntegralTransform::TransformationType transformation_type_

  *MO Integral Transformation Type.*
- std::shared_ptr< psi::IntegralTransform > **inttrans_**

### 16.12.1 Detailed Description

### 16.12.2 Member Function Documentation

#### 16.12.2.1 build()

```
std::shared_ptr< CISComputer > oepdev::CISComputer::build (
            const std::string & type,
            std::shared_ptr< psi::Wavefunction > wfn,
            psi::Options & opt,
            const std::string & reference = "" )  [static]
```

**Parameters**

| | |
|---|---|
| *type* | - Type of computer |
| *wfn* | - Psi4 wavefunction |
| *opt* | - Psi4 options |
| *reference* | - Reference Slater determinant (`RHF`, `UHF` available). |

Available computer types:

- `RESTRICTED` or `RCIS` - RHF wavefunction is used as reference state
- `UNRESTRICTED` or `UCIS` - UHF wavefunction is used as reference state

## Implementation

The CIS Hamiltonian in the basis space of singly-excited Slater determinants is constructed from canonical molecular orbitals (CMO's)

$$\begin{aligned}
\left\langle \Phi_0 \middle| \mathscr{H} \middle| \Phi_i^a \right\rangle &= 0 \\
\left\langle \Phi_j^b \middle| \mathscr{H} \middle| \Phi_i^a \right\rangle &= \delta_{ij}\delta_{ab}\left(\varepsilon_a - \varepsilon_i\right) + \left\langle aj \middle| ib \right\rangle - \left\langle aj \middle| bi \right\rangle
\end{aligned}$$

where *i* labels the occupied CMO's whereas *a* labels the virtual CMO's. In the above equation, $\left\langle aj \middle| ib \right\rangle$ is the 2-electron 4-centre integral in physicist's notation. After integrating out the spin coordinate, four blocks of Hamiltonian are explicitly given as

$$\begin{aligned}
\left\langle \Phi_j^b \middle| \mathscr{H} \middle| \Phi_i^a \right\rangle &= \delta_{ij}\delta_{ab}\left(\varepsilon_a - \varepsilon_i\right) + \left[ ia \middle| jb \right] - \left[ ab \middle| ij \right] \\
\left\langle \Phi_{\bar{j}}^{\bar{b}} \middle| \mathscr{H} \middle| \Phi_{\bar{i}}^{\bar{a}} \right\rangle &= \delta_{\bar{i}\bar{j}}\delta_{\bar{a}\bar{b}}\left(\varepsilon_{\bar{a}} - \varepsilon_{\bar{i}}\right) + \left[ \bar{i}\bar{a} \middle| \bar{j}\bar{b} \right] - \left[ \bar{a}\bar{b} \middle| \bar{i}\bar{j} \right] \\
\left\langle \Phi_{\bar{j}}^{\bar{b}} \middle| \mathscr{H} \middle| \Phi_i^a \right\rangle &= \left[ ia \middle| \bar{j}\bar{b} \right] \\
\left\langle \Phi_j^b \middle| \mathscr{H} \middle| \Phi_{\bar{i}}^{\bar{a}} \right\rangle &= \left[ \bar{i}\bar{a} \middle| jb \right]
\end{aligned}$$

where the $\left[ ia \middle| jb \right]$ is the 2-electron 4-centre integral in the chemist's (Coulomb) notation.

Such matrix is diagonalized yelding the excitation energies (wrt HF ground state) as well as the CIS coefficients

$$\sum_{ij}\sum_{ab} t_{i,I}^{a} H_{ij}^{ab} t_{j,J}^{b} = E_I \delta_{IJ}$$

where the summations above extend over alpha and beta electron spin labels and $t_{i,I}^a$ is the CIS amplitude for the $*$I$*$th excited state, associated with the $i \rightarrow a$ excitation with respect to the HF reference determinant. Note that $E_I$ is *not* the excited state energy, but the energy relative the the HF reference energy.

### See also

For Davidson-Liu solution to CIS problem, see oepdev::R_CISComputer_DL and oepdev::U_CISComputer_DL.

### Transition density matrix

AO basis transition density from ground (HF) to excited (CIS) state is given by

$$P_{\mu\nu}^{(g\rightarrow e)} = \sum_{i}^{\text{Occ}}\sum_{a}^{\text{Vir}} t_{i,e}^{a} C_{\nu i} C_{\mu a} + \sum_{\bar{i}}^{\text{Occ}}\sum_{\bar{a}}^{\text{Vir}} t_{\bar{i},e}^{\bar{a}} C_{\nu\bar{i}} C_{\mu\bar{a}}$$

### Excited state density matrix

CMO basis excited state density matrix for alpha spin is given by

Analogous expression is given for the beta spin.

AO representation of the CMO excited state density matrix is

$$P^{(e)}_{\mu\nu} = \sum_{pq} C_{\mu p} P^{(e)}_{pq} C_{\nu q} + \sum_{\overline{pq}} C_{\mu\overline{p}} P^{(e)}_{\overline{pq}} C_{\nu\overline{q}}$$

which is the sum of alpha and beta density matrices in CMO basis transformed to AO basis.

The CMO excited state density matrix for spin alpha is given by

$$P^{(e)}_{pq} = \begin{cases} \delta_{pq} - \sum_a^{\mathrm{Vir}} t^a_{p,e} t^a_{q,e} & \text{for p,q } \in \mathrm{Occ} \\ \sum_i^{\mathrm{Occ}} t^p_{i,e} t^q_{i,e} & \text{for p,q } \in \mathrm{Vir} \\ 0 & \text{otherwise} \end{cases}$$

The beta spin density matrix is generated analogously as above.

The cumulative atomic multipole moments (CAMM) are computed from the excited state density matrices in AO basis. The nuclear contribution is included.

### Transition multipole moments

The transition dipole moment is computed from the AO transition density matrix and the dipole integrals in AO basis, i.e.,

$$\left\langle \Phi_0 \middle| \hat{\mu}_u \middle| \Psi_e \right\rangle = \mathrm{Tr}\left[ \mathbf{d}^{(u)} \cdot \mathbf{P}^{g\rightarrow e} \right]$$

Oscillator strength is computed from the transition dipole moment via

$$f^{g\rightarrow e} = \frac{2}{3} E_e \left| \left\langle \Phi_0 \middle| \hat{\mu} \middle| \Psi_e \right\rangle \right|^2$$

Transition cumulative atomic multipole moments (TrCAMM) are computed from the transition density matrices in AO basis. The nuclear contribution is not included.

### Spin angular momentum

The expectation value of the $\hat{S}^2$ operator is calculated from the CIS amplitudes and MOs of the reference wavefunction according to D. Maurice and M. Head-Gordon, *Int. J. Quant. Chem.*, **1995**, 95, 010361-10:

$$\begin{aligned} \left\langle \hat{S}^2 \right\rangle_{\mathrm{UCIS}} = \left\langle \hat{S}^2 \right\rangle_{\mathrm{UHF}} &- \mathrm{Tr}\left[ \mathbf{Q}^{(\alpha)}_{\mathrm{Occ}} \cdot \left\{ \mathbf{P}^{(e,\alpha)}_{\mathrm{Occ}} - \mathbf{1} \right\} \right] - \mathrm{Tr}\left[ \mathbf{Q}^{(\beta)}_{\mathrm{Occ}} \cdot \left\{ \mathbf{P}^{(e,\beta)}_{\mathrm{Occ}} - \mathbf{1} \right\} \right] \\ &- \mathrm{Tr}\left[ \mathbf{Q}^{(\alpha)}_{\mathrm{Vir}} \cdot \mathbf{P}^{(e,\alpha)}_{\mathrm{Vir}} \right] - \mathrm{Tr}\left[ \mathbf{Q}^{(\beta)}_{\mathrm{Vir}} \cdot \mathbf{P}^{(e,\beta)}_{\mathrm{Vir}} \right] - 2 \sum_i^{\mathrm{Occ}} \sum_a^{\mathrm{Vir}} \sum_{\overline{j}}^{\mathrm{Occ}} \sum_{\overline{b}}^{\mathrm{Vir}} \Delta^*_{i\overline{j}} \Delta_{a\overline{b}} t^a_{i,e} t^{\overline{b}}_{\overline{j},e} \end{aligned}$$

where

$$[\mathbf{Q}^{(\alpha)}_{\rm Occ}]_{ij} = \sum_{\bar{k}}^{\rm Occ} \Delta^*_{\bar{k}i}\Delta_{\bar{k}j}$$

$$[\mathbf{Q}^{(\beta)}_{\rm Occ}]_{\bar{i}\bar{j}} = \sum_{k}^{\rm Occ} \Delta^*_{k\bar{i}}\Delta_{k\bar{j}}$$

$$[\mathbf{Q}^{(\alpha)}_{\rm Vir}]_{ab} = \sum_{\bar{k}}^{\rm Occ} \Delta^*_{\bar{k}a}\Delta_{\bar{k}b}$$

$$[\mathbf{Q}^{(\beta)}_{\rm Vir}]_{\bar{a}\bar{b}} = \sum_{k}^{\rm Occ} \Delta^*_{k\bar{a}}\Delta_{k\bar{b}}$$

and

$$\Delta_{pq} = \sum_{\mu\nu} C_{\mu p} S_{\mu\nu} C_{\nu p}$$

The diagnostic for UHF spin contamination is given by

$$\left\langle \hat{S}^2 \right\rangle_{\rm UHF} = \left\langle \hat{S}^2 \right\rangle_{\rm exact} + N_\beta - \sum_i^{\rm Occ} \sum_{\bar{j}}^{\rm Occ} |\Delta_{i\bar{j}}|^2$$

with

$$\left\langle \hat{S}^2 \right\rangle_{\rm exact} = \frac{N_\alpha - N_\beta}{2} \left( \frac{N_\alpha - N_\beta + 2}{2} \right)$$

and is also printed out to the output file.

**Note**

Useful options:

- `CIS_TYPE` - Algorithm of CIS. Available: `DAVIDSON_LIU` (Default), `DIRECT_EXPLICIT` (only RHF reference), `EXPLICIT`.
- `CIS_SCHWARTZ_CUTOFF` - Cutoff for Schwartz ERI screening. Default: 0.0. Relevant if `DAVIDSON_LIU` or `DIRECT_EXPLICIT` are chosen as CIS type.
- `CIS_STANDARDIZE_AMPLITUDES` - If true, CIS amplitudes of each excited state are rephased so that the leading amplitude is positive. Default: true.
- `OEPDEV_AMPLITUDE_PRINT_THRESHOLD` - Control threshold how many CIS amplitudes to print to the output. Default: 0.1.
- For UHF references, SAD guess might lead to triplet instabilities. It is then better to set `CORE` as the UHF guess

### 16.12.3 Member Data Documentation

#### 16.12.3.1 nmo_

```
const int oepdev::CISComputer::nmo_ [protected]
```

Number of MO's

The documentation for this class was generated from the following files:

- oepdev/libutil/cis.h
- oepdev/libutil/cis_base.cc

## 16.13 oepdev::CISData Struct Reference

CIS wavefunction parameters. Container structure.

```
#include <cis.h>
```

### Public Member Functions

- CISData (void)=default

  *Null Constructor.*
- CISData (const CISData ∗)

  *Copy Constructor.*

### Public Attributes

- double E_ex

  *Excitation energy.*
- double t_homo_lumo

  *CIS HOMO-LUMO amplitude.*
- SharedMatrix Pe

  *Excited state density matrix (sum of alpha and beta)*
- SharedMatrix Peg

  *Transition ground-to-excited state density matrix (sum of alpha and beta)*
- SharedDMTPole trcamm

  *TrCAMM.*
- SharedDMTPole camm_homo

  *CAMM for HOMO orbital.*
- SharedDMTPole camm_lumo

  *CAMM for LUMO orbital.*

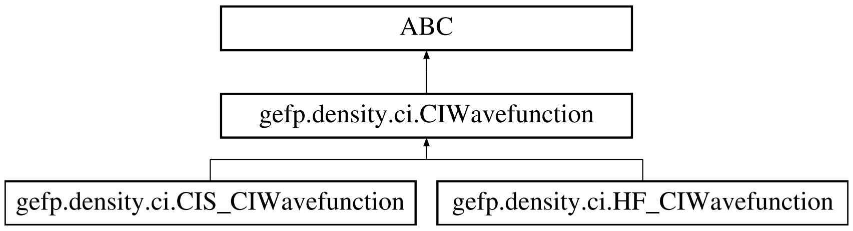
### 16.13.1 Detailed Description

The documentation for this struct was generated from the following files:

- oepdev/libutil/cis.h
- oepdev/libutil/cis_base.cc

## 16.14 gefp.density.ci.CIWavefunction Class Reference

Inheritance diagram for gefp.density.ci.CIWavefunction:


ABC
gefp.density.ci.CIWavefunction
gefp.density.ci.CIS_CIWavefunction
gefp.density.ci.HF_CIWavefunction

### Public Member Functions

- def **__init__** (self, ref_wfn, E, W)
- def **make_ci_l** (self)
- def **overlap** (self, other)

### Public Attributes

- **ref_wfn**
- **ci_e**
- **ci_c**
- **ca_o**
- **cb_o**
- **ca_v**
- **cb_v**
- **bfs**
- **naocc**
- **nbocc**
- **nmo**
- **navir**
- **nbvir**
- **ci_l**
- **ndet**

The documentation for this class was generated from the following file:

- gefp/gefp/density/ci.py

## 16.15 oepdev::CPHF Class Reference

CPHF solver class.

`#include <cphf.h>`

### Public Member Functions

#### Constructor and Destructor

- CPHF (SharedWavefunction ref_wfn, Options &options)
  *Constructor.*
- ∼CPHF ()
  *Desctructor.*

#### Executor

- void compute (void)
  *run the calculations*

#### Printer

- void print (void) const
  *print to output file*

#### Accessors

- int nocc (void) const
  *get the number of occupied orbitals*
- std::shared_ptr< Wavefunction > wfn (void) const
  *grab the wavefunction*
- Options & options (void) const
  *grab the Psi4 options*
- std::shared_ptr< Matrix > polarizability (void) const
  *retrieve the molecular (total) polarizability*
- std::shared_ptr< Matrix > polarizability (int i) const
  *retrieve the i-th orbital-associated polarizability*
- std::shared_ptr< Matrix > polarizability (int i, int j) const
  *retrieve the charge-transfer polarizability associated with orbitals i and j*
- std::shared_ptr< Matrix > X (int x) const
  *retrieve the X operator O-V perturbation matrix in AO basis for x-th component*
- std::vector< std::shared_ptr< Matrix > > X (void) const

*retrieve the X operator O-V perturbation matrix in AO basis for all three Cartesian components*
- std::shared_ptr< Matrix > X_mo (int x) const

  *retrieve the X operator O-V perturbation matrix in MO basis for x-th component*
- std::vector< std::shared_ptr< Matrix > > X_mo (void) const

  *retrieve the X operator O-V perturbation matrix in MO basis for all three Cartesian components*
- std::shared_ptr< Matrix > F_mo (int x) const

  *retrieve the F operator O-V perturbation matrix in MO basis for x-th component*
- std::vector< std::shared_ptr< Matrix > > F_mo (void) const

  *retrieve the F operator O-V perturbation matrix in MO basis for all three Cartesian components*
- std::shared_ptr< Matrix > T (void) const

  *retrieve the transformation from old to new MO's*
- std::shared_ptr< Matrix > Cocc (void) const

  *retrieve the Cocc (always Canonical)*
- std::shared_ptr< Matrix > Cvir (void) const

  *retrieve the Cvir*
- std::shared_ptr< Vector > epsocc (void) const

  *retrieve the epsocc (always Canonical)*
- std::shared_ptr< Vector > epsvir (void) const

  *retrieve the epsvir*
- std::shared_ptr< Vector > lmo_centroid (int i) const

  *retrieve the i-th orbital (LMO) centroid*
- std::shared_ptr< Localizer > localizer (void) const

  *retrieve the orbital localizer*

## Protected Attributes

### Basic Data

- std::shared_ptr< psi::Wavefunction > _wfn

  *Wavefunction object.*
- Options & _options

  *Options.*
- std::shared_ptr< BasisSet > _primary

  *Primary Basis Set.*
- std::shared_ptr< Localizer > _localizer

  *Orbital localizer.*

### Sizing Information

- const int _no

  *Number of occupied orbitals.*
- const int _nv

  *Number of virtual orbitals.*
- const int _nn

  *Number of basis functions.*

- long int _memory
  *Memory.*

### Parameters of CPHF Calculations

- int _maxiter
  *Maximum number of iterations.*
- double _conv
  *CPHF convergence threshold.*
- bool _with_diis
  *whether use DIIS or not*
- const int _diis_dim
  *Size of subspace.*

### Molecular Orbitals

- std::shared_ptr< Matrix > _cocc
  *Occupied orbitals.*
- std::shared_ptr< Matrix > _cvir
  *Virtual orbitals.*
- std::shared_ptr< Vector > _eps_occ
  *Occupied orbital energies.*
- std::shared_ptr< Vector > _eps_vir
  *Virtual orbital energies.*
- std::shared_ptr< psi::Matrix > _T
  *Transformation from old to new MO's.*

### DIIS Manager

- std::vector< std::shared_ptr< oepdev::DIISManager > > _diis
  *the DIIS managers for each perturbation operator x, y and z*

### Response Properties

- std::shared_ptr< Matrix > _molecularPolarizability
  *Total (molecular) polarizability tensor.*
- std::vector< std::shared_ptr< Vector > > _orbitalCentroids
  *LMO centroids.*
- std::vector< std::shared_ptr< Matrix > > _orbitalPolarizabilities
  *orbital-associated polarizability tensors*
- std::vector< std::vector< std::shared_ptr< Matrix > > > _orbitalChargeTransferPolarizabilities
  *orbital-orbital charge-transfer polarizability tensors*
- std::vector< std::shared_ptr< Matrix > > _X_OV_ao_matrices
  *Perturbation X Operator O->V matrices in AO basis.*
- std::vector< std::shared_ptr< Matrix > > _X_OV_mo_matrices
  *Perturbation X Operator O->V matrices in MO basis.*
- std::vector< std::shared_ptr< Matrix > > _F_OV_mo_matrices
  *Electric Field Operator O->V matrices in MO basis.*

### 16.15.1 Detailed Description

Solves CPHF equations (now only for RHF wavefunction). Computes molecular and polarizabilities associated with the localized molecular orbitals (LMO).

**Note**

Useful options:

- `CPHF_CONVER` - convergence of CPHF. Default: `1e-8` (au)
- `CPHF_CONVER` - maximum numberof iterations. Default: `50`
- `CPHF_DIIS` - wheather use DIIS or not. Default: `true`
- `CPHF_DIIS_DIM` - dimension of iterative subspace. Default: `3`
- `CPHF_LOCALIZE` - localize the molecular orbitals? Default: `true`
- `CPHF_LOCALIZER` - set orbital localization method. Available: `BOYS` and `PIPEK_MEZEY`. Default: `BOYS`

### 16.15.2 Constructor & Destructor Documentation

#### 16.15.2.1 CPHF()

```
oepdev::CPHF::CPHF (
            SharedWavefunction ref_wfn,
            Options & options )
```

**Parameters**

| | |
|---|---|
| *ref_wfn* | reference HF wavefunction |
| *options* | set of Psi4 options |

The documentation for this class was generated from the following files:

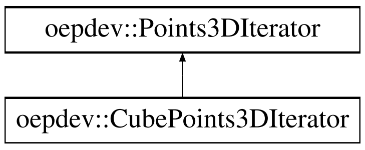
- oepdev/libutil/cphf.h
- oepdev/libutil/cphf.cc

## 16.16 oepdev::CubePoints3DIterator Class Reference

Iterator over a collection of points in 3D space. g09 Cube-like order.

`#include <space3d.h>`

Inheritance diagram for oepdev::CubePoints3DIterator:



## Public Member Functions

- **CubePoints3DIterator** (const int &nx, const int &ny, const int &nz, const double &dx, const double &dy, const double &dz, const double &ox, const double &oy, const double &oz)
- virtual void first ()

    *Initialize first iteration.*
- virtual void next ()

    *Step to next iteration.*

## Protected Attributes

- const int **nx_**
- const int **ny_**
- const int **nz_**
- const double **dx_**
- const double **dy_**
- const double **dz_**
- const double **ox_**
- const double **oy_**
- const double **oz_**
- int **ii_**
- int **jj_**
- int **kk_**

## Additional Inherited Members

### 16.16.1 Detailed Description

**Note:** Always create instances by using static factory method from Points3DIterator. Do not use constructor of this class.

The documentation for this class was generated from the following files:

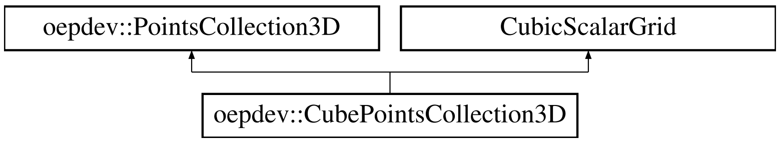
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

## 16.17 oepdev::CubePointsCollection3D Class Reference

G09 cube-like ordered collection of points in 3D space.

`#include <space3d.h>`

Inheritance diagram for oepdev::CubePointsCollection3D:



### Public Member Functions

- **CubePointsCollection3D** (Collection collectionType, const int &nx, const int &ny, const int &nz, const double &px, const double &py, const double &pz, psi::SharedBasisSet bs, psi::Options &options)
- virtual void print () const

  *Print the information to Psi4 output file.*
- virtual void **write_cube_file** (psi::SharedMatrix v, const std::string &name, const int &col=0)

### Additional Inherited Members

### 16.17.1 Detailed Description

**Note:** Do not use constructors of this class explicitly. Instead, use static factory methods of the superclass to create instances.

The documentation for this class was generated from the following files:

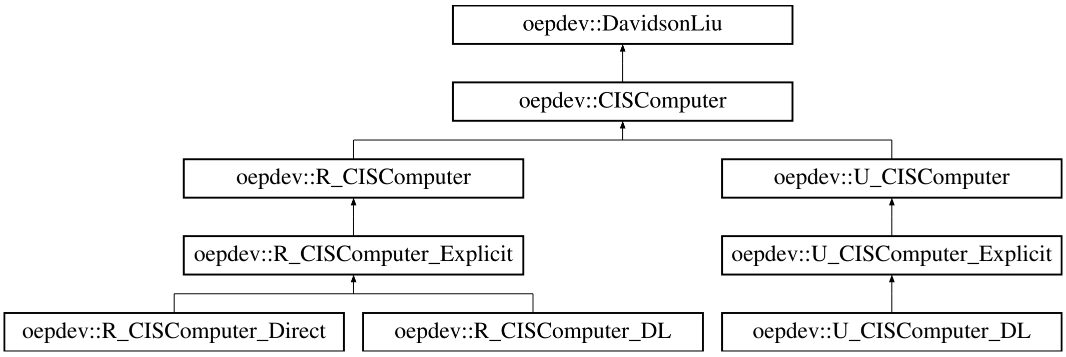
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

## 16.18 oepdev::DavidsonLiu Class Reference

Davidson-Liu diagonalization method.

`#include <davidson_liu.h>`

Inheritance diagram for oepdev::DavidsonLiu:



## Public Member Functions

- DavidsonLiu (psi::Options &opt)

    *Constructor.*
- virtual ∼DavidsonLiu ()

    *Destructor.*
- virtual void run_davidson_liu ()

    *Run the Davidson-Liu solver.*
- psi::SharedVector eigenvalues_davidson_liu () const

    *Get the eigenvalues.*
- psi::SharedVector **E_davidson_liu** () const
- psi::SharedMatrix eigenvectors_davidson_liu () const

    *Get the eigenvectors.*
- psi::SharedMatrix **U_davidson_liu** () const

## Protected Member Functions

- virtual void davidson_liu_initialize (int N, int L, int M)

    *Helper interface.*
- virtual void **davidson_liu_initialize_guess_vectors** ()
- virtual void **davidson_liu_initialize_guess_vectors_by_random** ()
- virtual void **davidson_liu_initialize_guess_vectors_by_custom** ()
- virtual void **davidson_liu_compute_diagonal_hamiltonian** ()=0
- virtual void **davidson_liu_compute_sigma** ()=0
- virtual void **davidson_liu_add_guess_vectors** ()
- virtual double **davidson_liu_compute_convergence** ()
- virtual void **davidson_liu_finalize** (bool)

## Protected Attributes

- int N_davidson_liu_

  *Dimensionality of Hamiltonian.*
- int L_davidson_liu_

  *Number of guess vectors.*
- int M_davidson_liu_

  *Number of roots of interest.*
- psi::Options & options_

  *Psi4 options.*
- psi::SharedVector E_davidson_liu_

  *Eigenvalues.*
- psi::SharedMatrix U_davidson_liu_

  *Eigenvectors.*
- psi::SharedVector H_diag_davidson_liu_

  *Diagonal elements of the matrix to diagonalize.*
- psi::SharedVector E_old_davidson_liu_

  *Old estimation of eigenvalues.*
- bool davidson_liu_initialized_

  *Is Davidson-Liu computer ready for calculations?*
- bool davidson_liu_finalized_

  *Is Davidson-Liu computer finished with calculations?*
- int **davidson_liu_n_sigma_computed_**
- std::vector< psi::SharedVector > sigma_vectors_davidson_liu_

  *Sigma vectors stored.*
- std::shared_ptr< oepdev::GramSchmidt > guess_vectors_davidson_liu_

  *Object storing guess vectors.*

### 16.18.1 Detailed Description

Find the lowest *M* eigenvalues and associated eigenvectors of the real, symmetric (square) matrix **H**.

Associated options:

- `DAVIDSON_LIU_NROOTS` - number of roots of interest. Default: 1.
- `DAVIDSON_LIU_CONVER` - convergence of the iterative procedure as RMS of old and current eigenvalues. Default: 1.0E-10.
- `DAVIDSON_LIU_MAXITER` - maximum number of iterations. Default: 500.
- `DAVIDSON_LIU_GUESS` - Type of guess vectors. Default: `RANDOM`, which is constructing ranrom vectors.

- `DAVIDSON_LIU_THRESH_LARGE` - Small correction vector threshold (see description below). Default: 1.0E-03.
- `DAVIDSON_LIU_THRESH_SMALL` - Small correction vector threshold (see description below). Default: 1.0E-06.
- `DAVIDSON_LIU_SPACE_MAX` - Maximum number of guess vectors. Default: 200.
- `DAVIDSON_LIU_SPACE_START` - Starting amount of guess vectors. Must be larger or equal to number of roots. Default: -1, which means that number of roots is taken.
- `DAVIDSON_LIU_STOP_WHEN_UNCONVERGED` - Raise error when iterations do not converge. Default: True.

## Usage in C++ programming

This class is an abstract base. In order to use the Davidson-Liu method fully implemented here, one must define a child class inheriting from oepdev::DavidsonLiu and implementing two of the pure methods:

- `davidson_liu_compute_diagonal_hamiltonian` - method specifying the calculation of the $\sigma$ vectors, which are stored in the `std::vector<psi::SharedVector> sigma_vectors_davidson_liu_`;
- `davidson_liu_compute_diagonal_hamiltonian` - method specifying the calculation of the diagonal elements of the Hamiltonian, stored in the `psi::SharedVector H_diag_davidson_liu_`.

### See also

Examples for demo use.

## Implementation

The implementation follows Figure 5, Section 3.2.1 in Ref.[1]. Dimensionality:

- `N` - number of rows/collumns of matrix to diagonalize
- `L` - current number of guess vectors
- `M` - number of roots of interest

Sigma vectors are defined to be

$$\mathbf{S} = \mathbf{H}\mathbf{B}$$

where **B** are the guess vectors stored as a matrix of size (N, L) in core memory. Subspace Hamiltonain is then given by

$$\mathbf{G} = \mathbf{B}^{\mathrm{T}}\mathbf{S}$$

and is diagonalized using standard diagonalization technique,

$$\mathbf{G} = \mathbf{U}\mathbf{z}\mathbf{U}^{\mathrm{T}}$$

where **z** are the eigenvalues. First *M* lowest eigenvalues and associated eigenvectors are saved in **E** and **A**, respectively (with the latter having size of (L, M)). The current eigenvector matrix **C** containing roots is given by

$$\mathbf{C} = \mathbf{B}\mathbf{A}$$

Once this step is completed, the correction vectors are computed for each eigenvalue according to

$$\delta_{Ik} = \frac{1}{E_k - H_{II}} \left[ -E_k C_{Ik} + \sum_{l}^{L} \sigma_{Il} A_{lk} \right]$$

and they are orthonormalized against all the collumns of **B** by using the Gram-Schmidt procedure. If the norm of such orthonormalized correction vector is larger than threshold value, it is appended to **B** as new guess vector.

**Note**

Note that the current implementation uses the original Davidson's preconditioner, which might have problems with breaking spin symmetry of the solution.

### Treatment of correction vector threshold.

In the current implementation, two threshold values are defined:

- larger threshold, controlled by `DAVIDSON_LIU_THRESH_LARGE` Psi4 option, is used for the first lowest eigenvalue.
- smaller threshold, controlled by `DAVIDSON_LIU_THRESH_SMALL` Psi4 option, is used for the next eigenvalues if $M > 1$.

## References

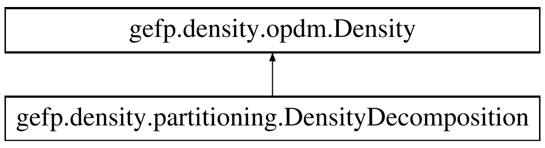
[1] C. David Sherrillt and Henry F. Schaefer III, *Adv. Quant. Chem.* **1999** (34), pp. 94720-1460.

The documentation for this class was generated from the following files:

- oepdev/libutil/davidson_liu.h
- oepdev/libutil/davidson_liu.cc

## 16.19 gefp.density.opdm.Density Class Reference

Inheritance diagram for gefp.density.opdm.Density:


gefp.density.opdm.Density
gefp.density.partitioning.DensityDecomposition

## Public Member Functions

- def **__init__** (self, D=None, jk=None)
- def **matrix** (self)
- def **set_D** (self, D)
- def **set_jk** (self, jk)
- def **compute_1el_energy** (self, D, Hcore)
- def **compute_2el_energy** (self, D_left, D_right, type='j')
- def **generalized_JK** (self, D, type='j')
- def natural_orbitals (cls, D, S=None, C=None, orthogonalize_mo=True, order='descending', return_ao_orthogonal=False, renormalize=False, no_cutoff=False, ignore_large_n=False, n_eps=5.0E-5)
- def **generalized_density** (cls, n, c, g=1.0)
- def **orthogonalize_OPDM** (cls, D, S)
- def **deorthogonalizer** (cls, S)
- def **orthogonalizer** (cls, S)

## 16.19.1 Detailed Description

```
--------------------------------------------------------------------------------------
                                           Electron Density

Handles the Electron Density Distribution.

--------------------------------------------------------------------------------------

Usage as container class:

 1) Initialize container object:

density = Density(D = None, jk = None)

where:
  o D  - the density matrix in AO or MO basis
  o jk - the psi4::JK object for AO basis JK calculations

 2) Grab the density matrix

D = density.matrix()

 3) Computations in AO basis:

o compute 1-electron energy (does not require JK object to be set)

  e_1 = density.compute_1el_energy(D, V1)

The below require jk to be set:

o compute 2-electron energy (J-type expression)

  e_2j = density.compute_2el_energy(D_left, D_right, type='j')
o compute 2-electron energy (K-type expression)

  e_2k = density.compute_2el_energy(D_left, D_right, type='k')

o compute J matrix (or K matrix if type=='k'):

  J = density.generalized_JK(D, type='j')

-----------------------------------------------------------------------------------------

Usage as method class.

Using 'Density' as a class of methods do not require object initialization.
The list of class methods is given below:

  o Density.natural_orbitals      - compute natural orbitals
  o Density.generalized_density   - compute generalized OPDM
  o Density.orthogonalize_OPDM    - compute orthogonalized OPDM
  o Density.orthogonalizer        - compute orthogonalizer matrix
  o Density.deorthogonalizer      - compute deorthogonalizer rmatrix

Usage:
  result = Density.'class method name'

See respective documentation for each of them for further details.

-----------------------------------------------------------------------------------------
                                                                             Last Revis
```

### 16.19.2 Member Function Documentation

#### 16.19.2.1 natural_orbitals()

```
def gefp.density.opdm.Density.natural_orbitals (
            cls,
            D,
            S = None,
            C = None,
            orthogonalize_mo = True,
            order = 'descending',
            return_ao_orthogonal = False,
            renormalize = False,
            no_cutoff = False,
            ignore_large_n = False,
            n_eps = 5.0E-5 )
```

```
 -----------------------------------------------------------------------------------------
 Compute the Natural Orbitals from a given OPDM

 -----------------------------------------------------------------------------------------
```

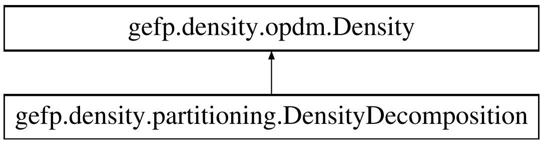
```
Usage:

n, c = Density.natural_orbitals(D, S = None, C = None,
                   orthogonalize_mo     = True,
                   order                = 'descending',
                   return_ao_orthogonal = False,
                   renormalize          = False,
                   no_cutoff            = False,
                   ignore_large_n       = False,
                   n_eps                = 5.0E-5)

where:
 o D - OPDM in AO or MO basis
 o S - overlap integrals in AO or MO basis
 o C - LCAO-MO transformation matrix
 o orthogonalize_mo     - whether to transform D from AO to certain MO basis and diagon
 o order                - order in which eigenvalues (occupancies) are sorted. Eigenval
 o return_ao_orthogonal - whether to return NO's in oAO basis set or not
 o renormalize          - renormalize to integer number of electrons
 o no_cutoff            - cut-off threshold for occupancies
 o ignore_large_n       - raise ValueError if (1.0 + n_eps) < n < (0.0 - n_eps)
 o n_eps                - tolerance for occupancy deviation

-------------------------------------------------------------------------------------------

Examples:

 1) NO's in AO (non-orthogonal, original) basis from D in AO basis

    n, c = Density.natural_orbitals(D, S, C, orthogonalize_mo = True, n_eps = 0.001)

    D: ndarray of shape (AO x AO)
    S: ndarray of shape (AO x AO)
    C: ndarray of shape (AO x MO)

    --> transformation D (MO x MO) = C.T S D S C and its diagonalization
    --> transformation of transformation matrix from MO to AO basis

    n: ndarray of shape (NO)
    c: ndarray of shape (AO x NO)

 2) NO's in certain orthogonal MO basis from D in the same MO basis

    n, c = Density.natural_orbitals(D, None, None, orthogonalize_mo = False, n_eps = 0.

    D: ndarray of shape (MO x MO)

    --> diagonalization of D

    n: ndarray of shape (NO)
    c: ndarray of shape (MO x NO)

-------------------------------------------------------------------------------------------
                                                                   Last Revision: Gundelf
```

The documentation for this class was generated from the following file:

- gefp/gefp/density/opdm.py

## 16.20 gefp.density.partitioning.DensityDecomposition Class Reference

Inheritance diagram for gefp.density.partitioning.DensityDecomposition:


gefp.density.opdm.Density
gefp.density.partitioning.DensityDecomposition

### Public Member Functions

- def **__init__** (self, aggregate, method='hf', acbs=True, jk_type='direct', no_cutoff=0.000, xc_scale=1.0, l_dds=True, cc_relax=True, verbose=False, n_eps=5.0E-5, kwargs)
- def compute (self, polar_approx=True)
- def deformation_density (self, name)
- def **compute_monomers** (self)
- def **compute_full_QM** (self)
- def **compute_densities** (self)
- def **compute_coulomb** (self)
- def **compute_pauli** (self)
- def **compute_polar** (self)
- def **compute_polar_approx** (self)
- def **__repr__** (self)
- def **print_out** (self)
- def **doublet** (self, A, B)
- def **triplet** (self, A, B, C)
- def **matrix_power** (self, M, x, eps=1.0e-6)
- def **rms** (self, m1, m2)

### Public Attributes

- **aggregate**
- **method**
- **data**
- **matrix**
- **vars**
- **xc_recommended**
- **kwargs**
- **acbs**

- **no_cutoff**
- **n_eps**
- **cc_relax**
- **l_dds**
- **verbose**
- **xc_scale**
- **monomers_computed**
- **densities_computed**
- **energy_coulomb_computed**
- **energy_pauli_computed**
- **energy_polar_computed**
- **energy_polar_approx_computed**
- **energy_ind_computed**
- **energy_disp_computed**
- **energy_ct_compute**
- **energy_full_QM_computed**
- **dms_ind_computed**
- **dms_disp_computed**
- **dms_ct_computed**
- **bfs**
- **global_jk**
- **nmo_t**
- **nbf_t**

### 16.20.1 Detailed Description

```
-----------------------------------------------------------------------------------------------------------

Density-Based Decomposition Scheme of Mandado and Hermida-Ramon
with partitioning of polarization deformation density into induction,
dispersion and charge-transfer contributions.

                      --> DDS <--
          --> Density Decomposition Scheme <--

References:
 * Mandado and Hermida-Ramon, J. Chem. Theory Comput. 2011, 7, 633-641. (JCTC 2011)
 * B␣lasiak, J. Chem. Phys. 2018 149 (16), 164115. (JCP 2018)

-----------------------------------------------------------------------------------------------------------

Constructor arguments and options:

 o aggregate - Psi4 molecular aggregate with at least two fragments
 o method    - QM method (hf, mp2, cc2, ccsd)
 o acbs      - use aggregate-centred basis set for calculations of wavefunctions.
           Otherwise use monomer-centred basis sets and composite Hadamard
           addition of AO spaces. ACBS=False result in no correction for BSSE.
```

```
  o jk_type    - type of Psi4 JK object.
  o no_cutoff - cutoff for natural occupancies threshold. All natural orbitals
          with occupancies less or equal to the threshold will be neglected.
  o xc_scale  - scaling parameter for exchange-correlation density
  o l_dds     - compute also linear DDS total interaction energy
  o kwargs    - additional Psi4-relevant options.

 -------------------------------------------------------------------------------------------------

 Usage example:

   solver = DensityDecomposition(aggr, method='hf',
                                 acbs=True,
                                 jk_type='direct',
                                 no_cutoff=0.000,
                                 xc_scale=1.0,
                                 l_dds=True,
                                 n_eps=5.0E-5,
                                 cc_relax=True,
                                 verbose=True,
                                 **kwargs)
   solver.compute(polar_approx=False)

   dD_pauli = solver.deformation_density('pau')
   dD_pol   = solver.deformation_density('pol')
   dD       = solver.deformation_density('fqm')

   # dictionaries:
   # 1. accessing variables
   solver.vars
   # 2. accessing aggregate data
   solver.matrix
   # 3. accessing unperturbed fragment data (expert)
   solver.data


   print(solver)
   solver.print_out()

 -------------------------------------------------------------------------------------------------
                                                                            Created      : Gundelf
                                                                            Last Revision: Gundelf
```

### 16.20.2 Member Function Documentation

#### 16.20.2.1 compute()

```
def gefp.density.partitioning.DensityDecomposition.compute (
            self,
            polar_approx = True )
```

\

```
 Perform the full density and interaction energy decompositions.

 Options:
  o polar_approx - in addition to exact polarization energy, compute
    also the approximated polarization energy using
    NO-expansion of exchange-correlation 2-electron density
    and exact Pauli, polarization and unperturbed 1-electron densities.
    Default: True

 Notes:
  o Exact polarization energy is always computed as a difference between
    the full QM interaction energy and all the remaining energies (Coulombic,
    exchange and repulsion energies).
```

#### 16.20.2.2 deformation_density()

```
def gefp.density.partitioning.DensityDecomposition.deformation_density (
            self,
            name )
```

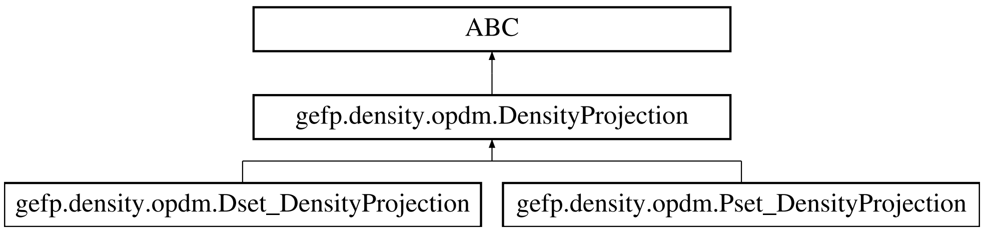
```
\
 Compute the deformation 1-particle density matrix.
 Returns density matrix in AO basis of entire molecular aggregate.

 Possible <name> entries:
  o fqm      - full QM deformation density
  o pau      - Pauli-repulsion denformation density
  o pol      - polarization deformation density
  o ind      - induction part of polarization deformation density
  o dis      - dispersion part of polarization deformation density
  o ct       - charge-transfer part of polarization deformation density
```

The documentation for this class was generated from the following file:

- gefp/gefp/density/partitioning.py

## 16.21 gefp.density.opdm.DensityProjection Class Reference

Inheritance diagram for gefp.density.opdm.DensityProjection:


ABC
gefp.density.opdm.DensityProjection
gefp.density.opdm.Dset_DensityProjection
gefp.density.opdm.Pset_DensityProjection

### Public Member Functions

- def **__init__** (self, np, S)
- def **compute** (self, n, c, perfect_pairing=False)

### Static Public Member Functions

- def **create** (np, dtype='p', S=None)

### 16.21.1 Detailed Description

```
\
 Gradient Projection Algorithms.
 Ref.: Pernal, Cances, J. Chem. Phys. 2005

 Usage:
  proj = DensityProjection.create(np, dtype='p', S=None)
  n, c = proj.compute(n, c, S)
```

The documentation for this class was generated from the following file:

- gefp/gefp/density/opdm.py

## 16.22 gefp.basis.optimize.DFBasis Class Reference

### Public Member Functions

- def **__init__** (self, mol, templ_file='templ.dat', param_file='param.dat', bounds_file=None, constraints=(), standardized_input=None)
- def **basisset** (self, param=None)
- def **print** (self, param=None, misc=None)
- def **save** (self, out='oepfit.gbs', param=None, misc=None)
- def **__repr__** (self)

### Public Attributes

- **mol**
- **templ**
- **param**
- **n_param**
- **bounds**
- **constraints**
- **scales**
- **basis**

### Static Public Attributes

- float **exp_lower_bound** = 0.01
- float **exp_upper_bound** = 10000.0
- float **ctr_lower_bound** = -2.0
- float **ctr_upper_bound** = 2.0

### 16.22.1 Detailed Description

```
Basis set object to be optimized.

Notes:

o Default bounds can be modified by resetting static variables
  DFBasis.exp_lower_bound
  DFBasis.exp_upper_bound
  DFBasis.ctr_lower_bound
  DFBasis.ctr_upper_bound
prior to calling DFBasis if not using the driver.gdf_basis_optimizer.
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize.py

## 16.23 gefp.basis.optimize_bcp.DFBasis Class Reference

### Public Member Functions

- def **__init__** (self, mol, templ_file='templ.dat', param_file='param.dat', bounds_file=None, constraints=())
- def **basisset** (self, param=None)
- def **print** (self, param=None)
- def **save** (self, out='oepfit.gbs', param=None)

### Public Attributes

- **mol**
- **templ**
- **param**
- **n_param**
- **bounds**
- **constraints**
- **basis**

### Static Public Attributes

- float **exp_lower_bound** = 0.01
- float **exp_upper_bound** = 10000.0
- float **ctr_lower_bound** = -2.0
- float **ctr_upper_bound** = 2.0

### 16.23.1 Detailed Description

```
Basis set object to be optimized.

Notes:

o Default bounds can be modified by resetting static variables
  DFBasis.exp_lower_bound
  DFBasis.exp_upper_bound
  DFBasis.ctr_lower_bound
  DFBasis.ctr_upper_bound
prior to calling DFBasis if not using the driver.gdf_basis_optimizer.
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize_bcp.py

## 16.24 gefp.basis.optimize_bcp.DFBasisOptimizer Class Reference

### Public Member Functions

- def **__init__** (self, oep)
- def **fit** (self, maxiter=1000, tolerance=1e-9, method='slsqp', opt_global=False, temperature=500, stepsize=500, take_step=None, accept_test=None)

### Public Attributes

- **oep**
- **basis_fit**
- **param**
- **mints**

### 16.24.1 Detailed Description

```
Method that optimizes DF basis set.
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize_bcp.py

## 16.25 gefp.basis.optimize.DFBasisOptimizer Class Reference

### Public Member Functions

- def **__init__** (self, oep)
- def **fit** (self, maxiter=1000, tolerance=1e-9, method='slsqp', opt_global=False, temperature=500, stepsize=500, take_step=None, accept_test=None)
- def **compute_error** (self, basis, rms=False)

### Public Attributes

- **oep**
- **basis_fit**
- **param**

### 16.25.1 Detailed Description

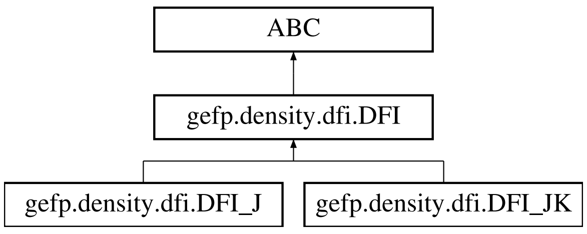
```
Method that optimizes DF basis set.
This is currently not recommended.
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize.py

## 16.26 gefp.density.dfi.DFI Class Reference

Inheritance diagram for gefp.density.dfi.DFI:



### Public Member Functions

- def **__init__** (self, frags)
- def run (self, maxit=100, conv=1.0e-5, verbose_scf=False, conv_scf=1.0e-5, maxit_scf=100, damp_scf=0.14, ndamp_scf=0)
- def **aggregate** (self)
- def **wfn** (self, i)

- def **epsilon** (self, i)
- def **Cocc** (self, i)
- def **C** (self, i)
- def **D** (self, i)
- def **F** (self, i)
- def **V** (self, i)
- def **E** (self, i)

### Static Public Member Functions

- def **create** (frags, j_only=False)

### Public Attributes

- **enuc**
- **en_0**

## 16.26.1 Detailed Description

```
 -----------------------------------------------------------------------------------------------
                               Density Fragment Interaction (DFI) Method
 -----------------------------------------------------------------------------------------------

 Demo for SCF-DFI method (closed shells).

 Usage:
dfi = DFI(fragment_1, fragment_2, [...])  # OR: dfi = DFI(fragments)
dfi.run(maxit=30, conv=1.0e-5, verbose_scf=False, conv_scf=1.0e-5, maxit_scf=100, damp_s

 Notes:
o fragmet_i is a psi4.core.Molecule wit one Psi4 Fragment
o fragments is a psi4.core Molecule with multiple Psi4 Fragments ('--' separator in inpu
o SCF of unperturbed molecule is solved by Psi4, while the subsequent SCF's in DFI itera
  by SCF class instances of this Demo.
 -----------------------------------------------------------------------------------------------
                                                                          Last Revision: Gund
```

## 16.26.2 Member Function Documentation

#### 16.26.2.1 run()

```
def gefp.density.dfi.DFI.run (
            self,
            maxit = 100,
            conv = 1.0e-5,
            verbose_scf = False,
            conv_scf = 1.0e-5,
            maxit_scf = 100,
            damp_scf = 0.14,
            ndamp_scf = 0 )
```

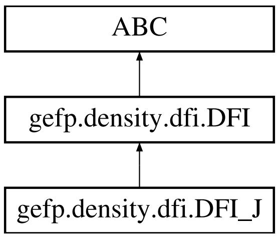
```
Runs DFI iterations
```

The documentation for this class was generated from the following file:

- gefp/gefp/density/dfi.py

## 16.27 gefp.density.dfi.DFI_J Class Reference

Inheritance diagram for gefp.density.dfi.DFI_J:



### Public Member Functions

- def **__init__** (self, frags)

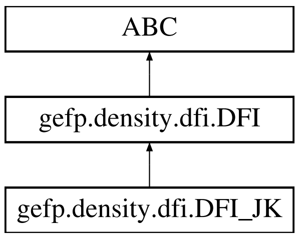
### Additional Inherited Members

The documentation for this class was generated from the following file:

- gefp/gefp/density/dfi.py

## 16.28 gefp.density.dfi.DFI_JK Class Reference

Inheritance diagram for gefp.density.dfi.DFI_JK:



### Public Member Functions

- def __**init**__ (self, frags)

### Additional Inherited Members

The documentation for this class was generated from the following file:

- gefp/gefp/density/dfi.py

## 16.29 oepdev::DIISManager Class Reference

DIIS manager.

```
#include <diis.h>
```

### Public Member Functions

- DIISManager (int dim, int na, int nb)
- ∼DIISManager ()

    *Destructor.*
- void put (const std::shared_ptr< const Matrix > &error, const std::shared_ptr< const Matrix > &vector)
- void compute (void)
- void update (std::shared_ptr< Matrix > &other)

### 16.29.1 Detailed Description

Instance can interact directly with the process of solving vector quantities in iterative manner. One needs to pass the dimensions of solution vector as well as the DIIS subspace size. The iterative procedure requires providing the current vector and also an estimate of the error vector. The updated DIIS vector can be copied to an old vector through the Instance.

### 16.29.2 Constructor & Destructor Documentation

#### 16.29.2.1 DIISManager()

```
oepdev::DIISManager::DIISManager (
            int dim,
            int na,
            int nb )
```

Constructor.

**Parameters**

| | |
|---|---|
| *dim* | Size of DIIS subspace |
| *na* | Number of solution rows |
| *nb* | Number of solution columns |

### 16.29.3 Member Function Documentation

#### 16.29.3.1 compute()

```
void oepdev::DIISManager::compute (
          void  )
```

Perform DIIS interpolation.

#### 16.29.3.2 put()

```
void oepdev::DIISManager::put (
          const std::shared_ptr< const Matrix > & error,
          const std::shared_ptr< const Matrix > & vector )
```

Put the current solution to the DIIS manager.

**Parameters**

| | |
|---|---|
| *error* | Shared matrix with current solution error |
| *vector* | Shared matrix with current solution vector |

#### 16.29.3.3 update()

```
void oepdev::DIISManager::update (
          std::shared_ptr< Matrix > & other )
```

Update solution vector. Pass the Shared pointer to current solution. Then it will be overriden by the updated DIIS solution.

The documentation for this class was generated from the following files:

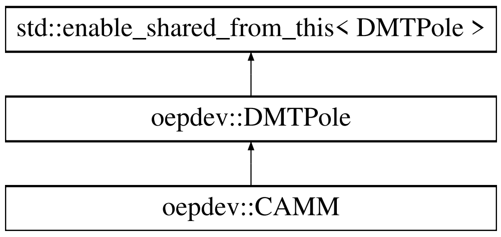
- oepdev/libutil/diis.h
- oepdev/libutil/diis.cc

## 16.30 oepdev::DMTPole Class Reference

Distributed Multipole Analysis Container and Computer. Abstract Base.

`#include <dmtp.h>`

Inheritance diagram for oepdev::DMTPole:



### Public Member Functions

#### Accessors

- virtual bool has_charges () const
  *Has distributed charges?*
- virtual bool has_dipoles () const
  *Has distributed dipoles?*
- virtual bool has_quadrupoles () const
  *Has distributed quadrupoles?*
- virtual bool has_octupoles () const
  *Has distributed octupoles?*
- virtual bool has_hexadecapoles () const
  *Has distributed hexadecapoles?*
- virtual psi::SharedMatrix centres () const
  *Get the positions of distribution centres.*
- virtual psi::SharedMatrix origins () const
  *Get the positions of distribution origins.*
- virtual psi::SharedVector centre (int x) const
  *Get the position of the ∗x∗th distribution centre.*
- virtual psi::SharedVector origin (int x) const
  *Get the position of the ∗x∗th distribution origin.*
- virtual std::vector< psi::SharedMatrix > charges () const
  *Get the distributed charges.*
- virtual std::vector< psi::SharedMatrix > dipoles () const
  *Get the distributed dipoles.*
- virtual std::vector< psi::SharedMatrix > quadrupoles () const
  *Get the distributed quadrupoles.*
- virtual std::vector< psi::SharedMatrix > octupoles () const
  *Get the distributed octupoles.*
- virtual std::vector< psi::SharedMatrix > hexadecapoles () const
  *Get the distributed hexadecapoles.*

- virtual psi::SharedMatrix charges (int i) const
  *Get the distributed charges for the $i$th distribution.*
- virtual psi::SharedMatrix dipoles (int i) const
  *Get the distributed dipoles for the $i$th distribution.*
- virtual psi::SharedMatrix quadrupoles (int i) const
  *Get the distributed quadrupoles for the $i$th distribution.*
- virtual psi::SharedMatrix octupoles (int i) const
  *Get the distributed octupoles for the $i$th distribution.*
- virtual psi::SharedMatrix hexadecapoles (int i) const
  *Get the distributed hexadecapoles for the $i$th distribution.*
- virtual int n_sites () const
  *Get the number of distributed sites.*
- virtual int n_dmtp () const
  *Get the number of distributions.*

### Mutators

- void set_charges (std::vector< psi::SharedMatrix > M)
  *Set the distributed charges.*
- void set_dipoles (std::vector< psi::SharedMatrix > M)
  *Set the distributed dipoles.*
- void set_quadrupoles (std::vector< psi::SharedMatrix > M)
  *Set the distributed quadrupoles.*
- void set_octupoles (std::vector< psi::SharedMatrix > M)
  *Set the distributed octupoles.*
- void set_hexadecapoles (std::vector< psi::SharedMatrix > M)
  *Set the distributed hexadecapoles.*
- void set_charges (psi::SharedMatrix M, int i)
  *Set the distributed charges for the $i$th distribution.*
- void set_dipoles (psi::SharedMatrix M, int i)
  *Set the distributed dipoles for the $i$th distribution.*
- void set_quadrupoles (psi::SharedMatrix M, int i)
  *Set the distributed quadrupoles for the $i$th distribution.*
- void set_octupoles (psi::SharedMatrix M, int i)
  *Set the distributed octupoles for the $i$th distribution.*
- void set_hexadecapoles (psi::SharedMatrix M, int i)
  *Set the distributed hexadecapoles for the $i$th distribution.*

### Transformators

- virtual void recenter (psi::SharedMatrix new_origins)
  *Change origins of the distributed multipole moments of all sets.*
- void translate (psi::SharedVector transl)
  *Translate the DMTP sets.*
- void rotate (psi::SharedMatrix rotmat)
  *Rotate the DMTP sets.*
- double superimpose (psi::SharedMatrix ref_xyz, std::vector< int > suplist={})

*Superimpose the DMTP sets.*

#### Computers

- void compute (std::vector< psi::SharedMatrix > D, std::vector< bool > t)
  *Compute DMTP's from the set of the one-particle density matrices.*
- void compute (void)
  *Compute ground state DMTP.*
- std::shared_ptr< MultipoleConvergence > energy (std::shared_ptr< DMTPole > other, MultipoleConvergence::ConvergenceLevel max_clevel=MultipoleConvergence::R5)
  *Evaluate the generalized interaction energy.*
- std::shared_ptr< MultipoleConvergence > potential (const double &x, const double &y, const double &z, MultipoleConvergence::ConvergenceLevel max_clevel=MultipoleConvergence::R5)
  *Evaluate the generalized potential at a given point.*
- std::shared_ptr< MultipoleConvergence > field (const double &x, const double &y, const double &z, MultipoleConvergence::ConvergenceLevel max_clevel=MultipoleConvergence::R5)
  *Evaluate the generalized field at a given point.*

#### Printers

- virtual void print_header () const =0
  *Print the header.*
- void print () const
  *Print the contents.*

### Static Public Member Functions

- static MultipoleConvergence::ConvergenceLevel determine_dmtp_convergence_level (const std::string &option)

### Protected Member Functions

#### Protected Interface

- DMTPole (std::shared_ptr< psi::Wavefunction > wfn, int n)
  *Construct an empty DMTP object from the wavefunction.*
- virtual void compute (psi::SharedMatrix D, bool transition, int i)
  *Compute DMTP's from the one-particle density matrix.*
- void compute_integrals ()
  *Compute multipole integrals.*
- void compute_order ()
  *Compute maximum order of the integrals.*
- virtual void recenter (psi::SharedMatrix new_origins, int i)
  *Change origins of the distributed multipole moments of ith set.*
- virtual void allocate ()
  *Initialize and allocate memory.*
- virtual void copy_from (const DMTPole ∗)
  *Deep-copy the matrix and DMTP data.*

## Protected Attributes

### Basic

- std::string name_
  *Name of the distribution method.*
- psi::SharedMolecule mol_
  *Molecule associated with this DMTP.*
- psi::SharedWavefunction wfn_
  *Wavefunction associated with this DMTP.*
- psi::SharedBasisSet primary_
  *Basis set (primary)*
- std::vector< psi::SharedMatrix > mpInts_
  *Multipole integrals.*

### Sizing

- int nDMTPs_
  *Number of DMTP's.*
- int nSites_
  *Number of DMTP sites.*
- int order_
  *Maximum order of the multipole.*

### Descriptors

- bool hasCharges_
  *Has distributed charges?*
- bool hasDipoles_
  *Has distributed dipoles?*
- bool hasQuadrupoles_
  *Has distributed quadrupoles?*
- bool hasOctupoles_
  *Has distributed octupoles?*
- bool hasHexadecapoles_
  *Has distributed hexadecapoles?*

### Geometry

- psi::SharedMatrix centres_
  *DMTP centres.*
- psi::SharedMatrix origins_
  *DMTP origins.*

### Multipoles

- std::vector< psi::SharedMatrix > charges_

*DMTP charges.*

- std::vector< psi::SharedMatrix > dipoles_

  *DMTP dipoles.*
- std::vector< psi::SharedMatrix > quadrupoles_

  *DMTP quadrupoles.*
- std::vector< psi::SharedMatrix > octupoles_

  *DMTP octupoles.*
- std::vector< psi::SharedMatrix > hexadecapoles_

  *DMTP hexadecapoles.*

## Friends

- class MultipoleConvergence

## Constructors and Destructor

- static std::shared_ptr< DMTPole > build (const std::string &type, std::shared_ptr< psi::Wavefunction > wfn, int n=1)

  *Build an empty DMTP object from the wavefunction.*
- static std::shared_ptr< DMTPole > empty (std::string type)

  *Build an empty DMTP object of no type.*
- DMTPole (void)

  *Construct an empty DMTP object of no type.*
- DMTPole (const DMTPole ∗)

  *Copy constructor.*
- virtual std::shared_ptr< DMTPole > clone (void) const =0

  *Make a deep copy (`wfn_`, `mol_`, and `primary_` are shallow-copied)*
- virtual ∼DMTPole ()

  *Destructor.*

### 16.30.1 Detailed Description

Handles the distributed multipole expansions up to hexadecapoles. Distributed centres as well as DMTP origins are allowed to be located in arbitrary points in space. The object describes a set of $N$ DMTP's, that can be generated by providing one-particle density matrices in AO basis. Nuclear contributions can be switched on or off separately for each DMTP within a set. The following operations on the DMTP sets are available through the API:

- translation
- rotation
- superimposition

- recentering the origins
- computing the generalized property from another DMTP set

**See also**

MultipoleConvergence

## 16.30.2 Constructor & Destructor Documentation

### 16.30.2.1 DMTPole() [1/2]

```
oepdev::DMTPole::DMTPole (
          void  )
```

Do not use this constructor. Use the DMTPole::empty method.

### 16.30.2.2 DMTPole() [2/2]

```
oepdev::DMTPole::DMTPole (
          std::shared_ptr< psi::Wavefunction > wfn,
          int n )  [protected]
```

**Parameters**

| | |
|---|---|
| *wfn* | - wavefunction |
| *n* | - number of DMTP sets |

Do not use this constructor. Use the DMTPole::build method.

## 16.30.3 Member Function Documentation

### 16.30.3.1 build()

```
std::shared_ptr< DMTPole > oepdev::DMTPole::build (
          const std::string & type,
          std::shared_ptr< psi::Wavefunction > wfn,
          int n = 1 )  [static]
```

**Parameters**

| | |
|---|---|
| *type* | - DMTP method. Available: CAMM. |

**Parameters**

| | |
|---|---|
| *wfn* | - wavefunction |
| *n* | - number of DMTP sets |

**Returns**

DMTP distribution

### 16.30.3.2 compute() [1/2]

```
void oepdev::DMTPole::compute (
          std::vector< psi::SharedMatrix > D,
          std::vector< bool > t )
```

**Parameters**

| | |
|---|---|
| *D* | - list of one-particle density matrices |
| *t* | - list of flags determining if density is of transition type or not |

### 16.30.3.3 compute() [2/2]

```
void oepdev::DMTPole::compute (
          void )
```

Compute DMTP's from the *sum* of the ground-state alpha and beta one-particle density matrices (t=false, i=0). Results in a usual DMTP analysis of a molecule's charge density distribution.

### 16.30.3.4 determine_dmtp_convergence_level()

```
MultipoleConvergence::ConvergenceLevel oepdev::DMTPole::determine_dmtp_convergence_level
(
          const std::string & option ) [static]
```

Determine the CAMM convergence for a given global option

**Parameters**

| | |
|---|---|
| *option* | - string for option |

### 16.30.3.5 empty()

```
std::shared_ptr< DMTPole > oepdev::DMTPole::empty (
          std::string type ) [static]
```

**Returns**

Blank DMTP distribution with memory allocated by no data.

### 16.30.3.6 energy()

```
std::shared_ptr< MultipoleConvergence > oepdev::DMTPole::energy (
          std::shared_ptr< DMTPole > other,
          MultipoleConvergence::ConvergenceLevel max_clevel = MultipoleConvergence::R5
)
```

**Parameters**

| | |
|---|---|
| *other* | - interacting DMTP distribution. |
| *max_clevel* | - maximum convergence level (see below). |

**Returns**

The generalized interaction energy convergence (A.U. units)

The following convergence levels are available:

- `MultipoleConvergence::R1`: includes qq terms.
- `MultipoleConvergence::R2`: includes dq terms and above.
- `MultipoleConvergence::R3`: includes qQ, dd terms and above.
- `MultipoleConvergence::R4`: includes qO, dQ terms and above.
- `MultipoleConvergence::R5`: includes qH, dO, QQ terms and above.

### 16.30.3.7 field()

```
std::shared_ptr< MultipoleConvergence > oepdev::DMTPole::field (
          const double & x,
          const double & y,
          const double & z,
          MultipoleConvergence::ConvergenceLevel max_clevel = MultipoleConvergence::R5
)
```

**Parameters**

| | |
|---|---|
| *x* | - location *x*-th Cartesian component |
| *y* | - location *y*-th Cartesian component |
| *z* | - location *z*-th Cartesian component |
| *max_clevel* | - maximum convergence level (see below). |

**Returns**

The generalized field convergence (A.U. units)

The following convergence levels are available:

- `MultipoleConvergence::R1`: includes qq terms.
- `MultipoleConvergence::R2`: includes dq terms and above.
- `MultipoleConvergence::R3`: includes qQ, dd terms and above.
- `MultipoleConvergence::R4`: includes qO, dQ terms and above.
- `MultipoleConvergence::R5`: includes qH, dO, QQ terms and above.

#### 16.30.3.8 potential()

```
std::shared_ptr< MultipoleConvergence > oepdev::DMTPole::potential (
            const double & x,
            const double & y,
            const double & z,
            MultipoleConvergence::ConvergenceLevel max_clevel = MultipoleConvergence::R5
)
```

**Parameters**

| | |
|---|---|
| *x* | - location *x*-th Cartesian component |
| *y* | - location *y*-th Cartesian component |
| *z* | - location *z*-th Cartesian component |
| *max_clevel* | - maximum convergence level (see below). |

**Returns**

The generalized potential convergence (A.U. units)

The following convergence levels are available:

- `MultipoleConvergence::R1`: includes qq terms.

- `MultipoleConvergence::R2`: includes dq terms and above.
- `MultipoleConvergence::R3`: includes qQ, dd terms and above.
- `MultipoleConvergence::R4`: includes qO, dQ terms and above.
- `MultipoleConvergence::R5`: includes qH, dO, QQ terms and above.

#### 16.30.3.9 recenter()

```
void oepdev::DMTPole::recenter (
          psi::SharedMatrix new_origins )  [virtual]
```

**Parameters**

| | |
|---|---|
| *new_origins* | - matrix with coordinates of the new origins $\{\mathbf{r}_{\rm new}\}$. |

**Note**

The number of origins has to be equal to the number of distributed centres.

Recentering of the multipoles affects the distributed dipoles and higher moments. The moments are given as

$$\begin{aligned}
q_{\rm new} &= q_{\rm old} \\
\mu_{\rm new} &= \mu_{\rm old} - q_{\rm old}\Delta^{(1)} \\
\Theta_{\rm new} &= \Theta_{\rm old} + q_{\rm old}\Delta^{(2)} - \sum_{\mathscr{P}_2}\mathscr{P}_2\left[\left(q_{\rm old}\mathbf{r}_{\rm old} + \mu_{\rm old}\right)\otimes\Delta^{(1)}\right] \\
\Omega_{\rm new} &= \Omega_{\rm old} - q_{\rm old}\Delta^{(3)} + \sum_{\mathscr{P}_3}\mathscr{P}_3\left[\left(q_{\rm old}\mathbf{r}_{\rm old} + \mu_{\rm old}\right)\otimes\Delta^{(2)}\right] - \sum_{\mathscr{P}_6}\mathscr{P}_6\left[\left(q_{\rm old}\mathbf{r}^2_{\rm old} + \mu_{\rm old}\otimes\mathbf{r}_{\rm old} + \Theta_{\rm old}\right)\otimes\Delta^{(1)}\right] \\
\Xi_{\rm new} &= \Xi_{\rm old} + q_{\rm old}\Delta^{(4)} - \sum_{\mathscr{P}_3}\mathscr{P}_3\left[\left(q_{\rm old}\mathbf{r}_{\rm old} + \mu_{\rm old}\right)\otimes\Delta^{(3)}\right] + \sum_{\mathscr{P}_3}\mathscr{P}_3\left[\left(q_{\rm old}\mathbf{r}^2_{\rm old} + \mu_{\rm old}\otimes\mathbf{r}_{\rm old} + \Theta_{\rm old}\right)\otimes\Delta^{(2)}\right] - \sum
\end{aligned}$$

where

$$\begin{aligned}
\Delta^{(1)} &\equiv \mathbf{r}_{\rm new} - \mathbf{r}_{\rm old} \\
\Delta^{(2)} &\equiv \mathbf{r}^2_{\rm new} - \mathbf{r}^2_{\rm old} \\
\Delta^{(3)} &\equiv \mathbf{r}^3_{\rm new} - \mathbf{r}^3_{\rm old} \\
\Delta^{(4)} &\equiv \mathbf{r}^4_{\rm new} - \mathbf{r}^4_{\rm old}
\end{aligned}$$

In the above equations, the distributed centre label was omitted (redundant) as each distributed site of multipoles is independent of the others. TODO - Finish for octupoles and hexadecapoles! -> define the permutation operators!

#### 16.30.3.10 rotate()

```
void oepdev::DMTPole::rotate (
          psi::SharedMatrix rotmat )
```

**Parameters**

| | |
|---|---|
| *rotmat* | - Cartesian rotation matrix $\mathbf{r}$ |

Centers and origins, as well as dipole, quadrupole, octupole and hexadecapole moments are transformed according to:

$$
\begin{aligned}
x_a^{(i)} &\rightarrow \sum_{a'} x_{a'}^{(i)} r_{a'a} \\
o_a^{(i)} &\rightarrow \sum_{a'} o_{a'}^{(i)} r_{a'a} \\
\mu_a^{(i)} &\rightarrow \sum_{a'} \mu_{a'}^{(i)} r_{a'a} \\
\Theta_a^{(i)} &\rightarrow \sum_{a'b'} \Theta_{a'b'}^{(i)} r_{a'a} r_{b'b} \\
\Omega_a^{(i)} &\rightarrow \sum_{a'b'c'} \Omega_{a'b'c'}^{(i)} r_{a'a} r_{b'b} r_{c'c} \\
\Xi_a^{(i)} &\rightarrow \sum_{a'b'c'd'} \Xi_{a'b'c'd'}^{(i)} r_{a'a} r_{b'b} r_{c'c} r_{d'd}
\end{aligned}
$$

where the definition of $r_{a'a}$ is consistent with the Kabsch algorithm implemented in KabschSuperimposer.

**See also**

KabschSuperimposer

#### 16.30.3.11 superimpose()

```
double oepdev::DMTPole::superimpose (
          psi::SharedMatrix ref_xyz,
          std::vector< int > suplist = {} )
```

**Parameters**

| | |
|---|---|
| *ref_xyz* | - target geometry to superimpose |
| *suplist* | - superimposition list |

**Returns**

the RMS of superimposition Kabsch algorithm is used for superimposition.

**See also**

KabschSuperimposer

### 16.30.4 Friends And Related Function Documentation

#### 16.30.4.1 MultipoleConvergence

`friend class MultipoleConvergence [friend]`

Convergence of multipole moment series.

The documentation for this class was generated from the following files:

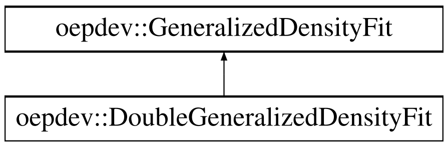
- oepdev/lib3d/dmtp.h
- oepdev/lib3d/dmtp_base.cc

## 16.31 oepdev::DoubleGeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme - Double Fit.

`#include <oep_gdf.h>`

Inheritance diagram for oepdev::DoubleGeneralizedDensityFit:


oepdev::GeneralizedDensityFit
oepdev::DoubleGeneralizedDensityFit

### Public Member Functions

- **DoubleGeneralizedDensityFit** (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::BasisSet > bs_intermediate, std::shared_ptr< psi::Matrix > v_vector)
- std::shared_ptr< psi::Matrix > compute (void)

  *Perform the generalized density fit.*

### Additional Inherited Members

### 16.31.1 Detailed Description

The density fitting map projects the OEP onto an arbitrary (not necessarily complete) auxiliary basis set space through application of the self energy minimization technique. The resulting three-electron repulsion integrals are computed by utilizing the resolution of identity in an intermediate, nearly-complete basis set space, hence performing an internal density fitting in nearly complete basis. Refer to density fitting specialized for OEP's for more details.

### 16.31.2 Determination of the OEP matrix

Coefficients $\mathbf{G}$ are computed by using the following relation

$$\mathbf{G} = \mathbf{A}^{-1} \cdot \mathbf{R} \cdot \mathbf{H}$$

where the intermediate projection matrix is given by

$$\mathbf{H} = \mathbf{S}^{-1} \cdot \mathbf{V}$$

In the above equations,

$$\begin{aligned} A_{\xi\xi'} &= (\xi||\xi') \\ R_{\xi\varepsilon} &= (\xi||\varepsilon) \\ S_{\varepsilon\varepsilon'} &= (\varepsilon|\varepsilon') \\ V^{\varepsilon i} &= (\varepsilon|\hat{v}i) \end{aligned}$$

The following labeling convention is used here:

- $i$ denotes the arbitrary state vector
- $\xi$ denotes the auxiliary basis set element
- $\varepsilon$ denotes the intermediate (nearly complete) basis set element

In the above, $|$ denotes the single integration over electron coordinate, i.e.,

$$(a|b) \equiv \int d\mathbf{r} \phi_a^*(\mathbf{r}) \phi_b(\mathbf{r})$$

whereas $||$ acts as shown below:

$$(a||b) \equiv \iint d\mathbf{r}' d\mathbf{r}'' \frac{\phi_a^*(\mathbf{r}') \phi_b(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|}$$

The spatial form of the potential operator $\hat{v}$ can be expressed by

$$v(\mathbf{r}) \equiv \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}$$

with $\rho(\mathbf{r})$ being the effective one-electron density associated with $\hat{v}$.

#### 16.31.2.1 Theory behind the double GDF scheme

In order to perform the generalized density fitting in an incomplete auxiliary basis set, one must apply the following formula:

$$\mathbf{G} = \mathbf{A}^{-1} \cdot \mathbf{B}$$

where one encounters the need of evaluation of the following *three-electron integrals*

$$B_{\xi i} = (\xi || \hat{v} i) \equiv \iiint d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \phi_{\xi}^{*}(\mathbf{r}') \frac{1}{|\mathbf{r}' - \mathbf{r}''|} \rho(\mathbf{r}''') \frac{1}{|\mathbf{r}''' - \mathbf{r}''|} \phi_i(\mathbf{r}'')$$

Computation of all the necessery integrals of this kind is very costly and impractical for larger molecules. However, one can use the same trick that is a kernel of the OEP technique introduced in the OEPDev project, i.e., introduce the effective potential in order to get rid of one integration. This can be done by performing the generalized density fitting in the nearly complete intermediate basis

$$\hat{v}|i) \cong \sum_{\varepsilon} H_{\varepsilon i} |\varepsilon)$$

Note that this is done just for the sake of factorizing the triple integral and computing the OEP matrix for the incomplete auxiliary basis. Therefore, the intermediate basis set is used just for a while during density fitting and is no longer necessary later on. By inserting the above identity to the triple integral one can transform it into a sum of the two-electron integrals that are much easier to evaluate. This leads to equations given in the beginning of this section.

### 16.31.3 Member Function Documentation

#### 16.31.3.1 compute()

```
std::shared_ptr< psi::Matrix > DoubleGeneralizedDensityFit::compute (
          void  )  [virtual]
```

**Returns**

The OEP coefficients $G_{\xi i}$

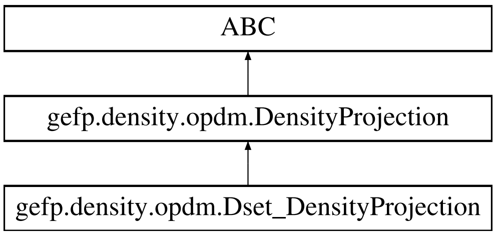
Implements oepdev::GeneralizedDensityFit.

The documentation for this class was generated from the following files:

- oepdev/liboep/oep_gdf.h
- oepdev/liboep/oep_gdf.cc

## 16.32 gefp.density.opdm.Dset_DensityProjection Class Reference

Inheritance diagram for gefp.density.opdm.Dset_DensityProjection:


ABC
gefp.density.opdm.DensityProjection
gefp.density.opdm.Dset_DensityProjection

## Public Member Functions

- def **__init__** (self, np, S)

## Additional Inherited Members

### 16.32.1 Detailed Description

```
\
 Gradient Projection Algorithm on D-sets.
 Ref.: Pernal, Cances, J. Chem. Phys. 2005

 Notes:
  o Appropriate only for HF functional.
```

The documentation for this class was generated from the following file:

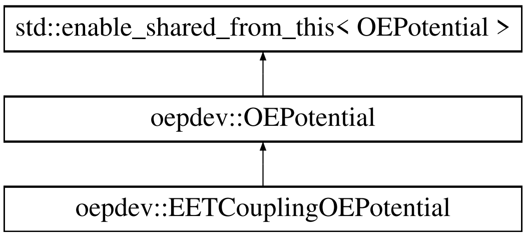
- gefp/gefp/density/opdm.py

## 16.33 oepdev::EETCouplingOEPotential Class Reference

Generalized One-Electron Potential for EET coupling calculations.

`#include <oep.h>`

Inheritance diagram for oepdev::EETCouplingOEPotential:


std::enable_shared_from_this< OEPotential >
oepdev::OEPotential
oepdev::EETCouplingOEPotential

## Public Member Functions

- **EETCouplingOEPotential** (SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate, Options &options)

- **EETCouplingOEPotential** (SharedWavefunction wfn, Options &options)
- **EETCouplingOEPotential** (const EETCouplingOEPotential *f)
- virtual void compute (const std::string &oepType) override

  *Compute matrix forms of all OEP's within a specified OEP type.*
- virtual void compute_3D (const std::string &oepType, const double &x, const double &y, const double &z, std::shared_ptr< psi::Vector > &v) override

  *Compute value of potential in point x, y, z and save at v.*
- virtual void print_header () const override

  *Header information.*
- virtual std::shared_ptr< OEPotential > clone (void) const override

  *Make a deep copy of this object.*
- virtual void initialize () override

  *Initialize the object (expert)*

### Protected Member Functions

- virtual void **rotate_oep** (psi::SharedMatrix, psi::SharedMatrix, psi::SharedMatrix) override
- virtual void **translate_oep** (psi::SharedVector) override

### Additional Inherited Members

### 16.33.1 Detailed Description

Contains the following OEP types:

- `Fujimoto.GDF` - Joint OEP type for ET(L), ET(HL), HT(H) and HT(HL)
- `Fujimoto.CIS` - CIS data
- `Fujimoto.EXCH`- Pure-exchange coupling matrix $G_{\mu\nu} \equiv (\mu\mu|\nu\nu)$
- `Fujimoto.CT_M`- $(HH|LL)$ integral for the H_34 Hamiltonian matrix elements (CT)

The documentation for this class was generated from the following files:

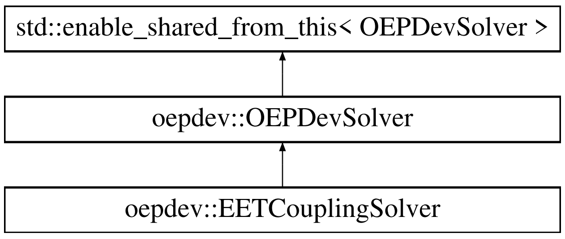
- oepdev/liboep/oep.h
- oepdev/liboep/oep_coupling_eet.cc

## 16.34 oepdev::EETCouplingSolver Class Reference

Compute the EET coupling energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::EETCouplingSolver:


std::enable_shared_from_this< OEPDevSolver >
oepdev::OEPDevSolver
oepdev::EETCouplingSolver

## Public Member Functions

- **EETCouplingSolver** (SharedWavefunctionUnion wfn_union)
- virtual double compute_oep_based (const std::string &method="DEFAULT")

  *Compute property by using OEP's.*
- virtual double compute_benchmark (const std::string &method="DEFAULT")

  *Compute property by using benchmark method.*

## Additional Inherited Members

### 16.34.1 Detailed Description

The implemented methods are shown below

Table 16.32: Methods available in the Solver

| Keyword | Method Description |
|---|---|
| **Benchmark Methods** | |
| `FUJIMOTO_TI_CIS` | *Default.* EET Coupling by Fujimoto JPC 2012. |
| **OEP-Based Methods** | |
| `FUJIMOTO_TI_CIS` | *Default.* OEP-based TI/CIS expressions. |

In order to construct this solver, **always** use the `OEPDevSolver::build` static factory method.

Below the detailed description of the implemented equations is given for each of the above provided methods. In the formulae across, it is assumed that the orbitals are real. The Coulomb notation for electron repulsion integrals (ERI's) is adopted; i.e,

$$(ac|bd) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_1)\frac{1}{r_{12}}\phi_b(\mathbf{r}_2)\phi_d(\mathbf{r}_2)$$

Greek subscripts denote basis set orbitals whereas Italic subscripts denote the occupied molecular orbitals.

## Benchmark Methods

### TI/CIS Method (Fujimoto JPC 2012).

In the simplest version of TI/CIS approach, the Hamiltonian of the molecular aggregate (dimer) is constructed from the CIS approximation and 4 basis functions constructed as follows:

$$\begin{aligned}
\left|\Phi_1\right\rangle &= \left|\Psi_A^{(e)} \otimes \Psi_B^{(g)}\right\rangle \\
\left|\Phi_2\right\rangle &= \left|\Psi_A^{(g)} \otimes \Psi_B^{(e)}\right\rangle \\
\left|\Phi_3\right\rangle &= \left|\Psi_A^{(+)} \otimes \Psi_B^{(-)}\right\rangle \\
\left|\Phi_4\right\rangle &= \left|\Psi_A^{(-)} \otimes \Psi_B^{(+)}\right\rangle
\end{aligned}$$

where *g* and *e* superscripts denote the ground and excited state of a molecule, + and − label the cationic and anionic state, respectively, whereas $\left|\Psi_X \otimes \Psi_Y\right\rangle$ denotes the antisymmetrized Hartree product of the monomer wavefunctions. The associated diagonal Hamiltonian matrix elements can be defined as

$$\begin{aligned}
\left\langle\Phi_1\middle|\mathscr{H} - E_0\middle|\Phi_1\right\rangle &\equiv E_1 = E^A_{e\to g} + \sum_{\mu\nu\in A}\left(P^{A(e)}_{\nu\mu} - P^{A(g)}_{\nu\mu}\right) \times \left\{V^{B(\text{nuc})}_{\mu\nu} + \sum_{\lambda\sigma\in B} P^{B(g)}_{\lambda\sigma}\left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right]\right\} \\
\left\langle\Phi_2\middle|\mathscr{H} - E_0\middle|\Phi_2\right\rangle &\equiv E_2 = E^B_{e\to g} + \sum_{\mu\nu\in B}\left(P^{B(e)}_{\nu\mu} - P^{B(g)}_{\nu\mu}\right) \times \left\{V^{A(\text{nuc})}_{\mu\nu} + \sum_{\lambda\sigma\in A} P^{A(g)}_{\lambda\sigma}\left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right]\right\} \\
\left\langle\Phi_3\middle|\mathscr{H} - E_0\middle|\Phi_3\right\rangle &\equiv E_3 = -\varepsilon^A_H + \varepsilon^B_L - \left(H^A H^A\middle|L^B L^B\right) \\
\left\langle\Phi_4\middle|\mathscr{H} - E_0\middle|\Phi_4\right\rangle &\equiv E_4 = \varepsilon^A_L - \varepsilon^B_H - \left(L^A L^A\middle|H^B H^B\right)
\end{aligned}$$

The associated off-diagonal Hamiltonian matrix elements can be defined as

$$\begin{aligned}
\left\langle\Phi_1\middle|\mathscr{H}\middle|\Phi_2\right\rangle &\equiv V^{\text{Coul}} + V^{\text{Exch}} + V^{\text{Ovrl}} \\
\left\langle\Phi_1\middle|\mathscr{H}\middle|\Phi_3\right\rangle &\equiv V^{\text{ET1}} \\
\left\langle\Phi_2\middle|\mathscr{H}\middle|\Phi_4\right\rangle &\equiv V^{\text{ET2}} \\
\left\langle\Phi_1\middle|\mathscr{H}\middle|\Phi_4\right\rangle &\equiv V^{\text{HT1}} \\
\left\langle\Phi_2\middle|\mathscr{H}\middle|\Phi_3\right\rangle &\equiv V^{\text{HT2}} \\
\left\langle\Phi_3\middle|\mathscr{H}\middle|\Phi_4\right\rangle &\equiv V^{\text{CT}}
\end{aligned}$$

where the Forster-type Coulombic (Coul), Dexter-type exchange (Exch), remaining overlap correction (Ovrl), as well as the electron, hole and charge (ET, HT, CT) transfer contributions are defined. The exchange-Coulomb coupling takes the form

$$
\begin{aligned}
V^{\rm Coul} &= \frac{V^{\rm Coul,(0)}}{1-S_{12}^2} \\
V^{\rm Exch} &= \frac{V^{\rm Exch,(0)}}{1-S_{12}^2} \\
V^{\rm Ovrl} &= -\frac{(E_1+E_2)S_{12}}{2(1-S_{12}^2)}
\end{aligned}
$$

The overlap-corrected ET, HT and CT matrix elements read

$$
\begin{aligned}
V^{\rm ET1} &= \left[1-S_{13}^2\right]^{-1}\left\{V^{\rm ET1,(0)} - \frac{1}{2}(E_1+E_2)S_{13}\right\} \\
V^{\rm ET2} &= \left[1-S_{24}^2\right]^{-1}\left\{V^{\rm ET2,(0)} - \frac{1}{2}(E_1+E_2)S_{24}\right\} \\
V^{\rm HT1} &= \left[1-S_{14}^2\right]^{-1}\left\{V^{\rm HT1,(0)} - \frac{1}{2}(E_1+E_2)S_{14}\right\} \\
V^{\rm HT2} &= \left[1-S_{23}^2\right]^{-1}\left\{V^{\rm HT2,(0)} - \frac{1}{2}(E_1+E_2)S_{23}\right\} \\
V^{\rm CT} &= \left[1-S_{34}^2\right]^{-1}\left\{V^{\rm CT,(0)} - \frac{1}{2}(E_1+E_2)S_{34}\right\}
\end{aligned}
$$

In the above equatons, the superscript (0) denotes that the matrix elements are not affected by the overlap between molecular wavefunctions, and are given by

$$
\begin{aligned}
V^{\rm Coul,(0)} &= \sum_{\mu\nu\in A}\sum_{\lambda\sigma\in B} P_{\nu\mu}^{g\rightarrow e(A)} P_{\lambda\sigma}^{g\rightarrow e(B)} (\mu\nu|\sigma\lambda) \\
V^{\rm Exch,(0)} &= -\frac{1}{2}\sum_{\mu\nu\in A}\sum_{\lambda\sigma\in B} P_{\nu\mu}^{g\rightarrow e(A)} P_{\lambda\sigma}^{g\rightarrow e(B)} (\mu\lambda|\sigma\nu) \\
V^{\rm ET1,(0)} &= t_{H\rightarrow L}^{A}\left\{\left(L^A|\mathscr{F}|L^B\right) + 2\left(L^AH^A|H^AL^B\right) - \left(L^AL^B|H^AH^A\right)\right\} \\
V^{\rm ET2,(0)} &= t_{H\rightarrow L}^{B}\left\{\left(L^A|\mathscr{F}|L^B\right) + 2\left(L^AH^B|H^BL^B\right) - \left(L^AL^B|H^BH^B\right)\right\} \\
V^{\rm HT1,(0)} &= t_{H\rightarrow L}^{A}\left\{-\left(H^A|\mathscr{F}|H^B\right) + 2\left(H^AL^A|L^AH^B\right) - \left(H^AH^B|L^AL^A\right)\right\} \\
V^{\rm HT2,(0)} &= t_{H\rightarrow L}^{B}\left\{-\left(H^A|\mathscr{F}|H^B\right) + 2\left(H^AL^B|L^BH^B\right) - \left(H^AH^B|L^BL^B\right)\right\} \\
V^{\rm CT,(0)} &= 2\left(H^AL^B|L^AH^B\right) - \left(H^AH^B|L^AL^B\right)
\end{aligned}
$$

In the above, $\mathscr{F}$ is the Fock operator whereas $H$ and $L$ denote the HOMO and LUMO orbitals, respectively. The overlap integrals between the basis states are approximated by

$$\begin{aligned}
S_{12} &\equiv \left(\Phi_1\middle|\Phi_2\right) \cong -\frac{1}{N_{el}^{AB}}\mathrm{Tr}\left[\mathbf{P}^{g\rightarrow e(A)}\mathbf{s}^{AB}\mathbf{P}^{g\rightarrow e(B)}\mathbf{s}^{BA}\right]\\
S_{13} &\equiv \left(\Phi_1\middle|\Phi_3\right) \cong -\frac{t_{H\rightarrow L}^{A}}{N_{el}^{AB}}S_{LL}^{AB}\\
S_{14} &\equiv \left(\Phi_1\middle|\Phi_4\right) \cong +\frac{t_{H\rightarrow L}^{A}}{N_{el}^{AB}}S_{HH}^{AB}\\
S_{24} &\equiv \left(\Phi_2\middle|\Phi_4\right) \cong -\frac{t_{H\rightarrow L}^{B}}{N_{el}^{AB}}S_{LL}^{AB}\\
S_{23} &\equiv \left(\Phi_2\middle|\Phi_3\right) \cong +\frac{t_{H\rightarrow L}^{B}}{N_{el}^{AB}}S_{HH}^{AB}\\
S_{34} &\equiv \left(\Phi_3\middle|\Phi_4\right) \cong -\frac{1}{N_{el}^{AB}}S_{HH}^{AB}S_{LL}^{AB}
\end{aligned}$$

where the overlap between molecular orbitals $U$ and $W$ is given by

$$S_{UW}^{AB} \equiv \mathbf{s}^{AB} : \mathbf{c}_U^A \otimes \mathbf{c}_W^B$$

and $\mathbf{s}^{AB}$ is the AO overlap matrix between molecule A and B atomic basis functions.

For a closed-shell system, the EET coupling constant for two electronic transitions can be given approximately by

$$V \approx V^{\mathrm{Direct}} + V^{\mathrm{Inirect}}$$

where the overlap-corrected direct and indirect coupling constants are

$$\begin{aligned}
V^{\mathrm{Direct}} &= V^{\mathrm{Coul}} + V^{\mathrm{Exch}} + V^{\mathrm{Ovrl}}\\
V^{\mathrm{Indirect}} &= V^{\mathrm{TI-2}} + V^{\mathrm{TI-3}}
\end{aligned}$$

with

$$\begin{aligned}
V^{\mathrm{TI-2}} &= -\frac{V^{\mathrm{ET1}}V^{\mathrm{HT2}}}{E_3 - E_1} - \frac{V^{\mathrm{ET2}}V^{\mathrm{HT1}}}{E_4 - E_1}\\
V^{\mathrm{TI-3}} &= \frac{V^{\mathrm{CT}}\left(V^{\mathrm{ET1}}V^{\mathrm{ET2}} + V^{\mathrm{HT1}}V^{\mathrm{HT2}}\right)}{(E_3 - E_1)(E_4 - E_1)}
\end{aligned}$$

### Fock matrix in AB space

In the current implementation, Fock matrix in the AB space, that is necessary to evaluate ET and HT matrix elements, can be defined as

1. the AB block of full Hartree-Fock SCF Fock matrix for entire system;

2. the zeroth-order Fock matrix that is composed of monomer's unperturbed ground-state 1-particle density matrices.

In the latter case, the Fock matrix in AO representation is given by:

$$F^{AB}_{\alpha\in A,\beta\in B} \approx T_{\alpha\beta} + V^{A(\rm nuc)}_{\alpha\beta} + V^{B(\rm nuc)}_{\alpha\beta} + \sum_{\mu\nu\in A} P^{A(g)}_{\nu\mu} G_{\alpha\beta,\mu\nu} + \sum_{\sigma\lambda\in B} P^{B(g)}_{\lambda\sigma} G_{\alpha\beta,\sigma\lambda}$$

where

$$G_{\alpha\beta,\gamma\delta} \equiv (\alpha\beta|\gamma\delta) - \frac{1}{2}(\alpha\delta|\gamma\beta)$$

#### Mulliken approximated exchange-like contributions.

Exchange and CT contributions require ERI's of type (AB,AB). It is instructive to approximate these contributions in terms of the Coulomb-like ERI's for the sake of testing of OEP-based approximations which are given in the next Section.

Application of the Mullipen approximation

$$(ij|kl) \approx \frac{1}{4} S_{ij} S_{kl} \left[ (ii|kk) + (jj|kk) + (ii|ll) + (jj|ll) \right]$$

results in the following approximations to the exchange-like terms

$$V^{\rm Exch,(0)} \approx -\frac{1}{8} \sum_{\mu\nu\in A} \sum_{\lambda\sigma\in B} P^{g\rightarrow e(A)}_{\nu\mu} P^{g\rightarrow e(B)}_{\lambda\sigma} S_{\mu\lambda} S_{\sigma\nu} \left[ (\mu\mu|\sigma\sigma) + (\lambda\lambda|\nu\nu) + (\mu\mu|\nu\nu) + (\lambda\lambda|\sigma\sigma) \right]$$

$$\begin{aligned} V^{\rm CT,(0)} &\approx \frac{1}{2} S^{AB}_{HL} S^{AB}_{LH} \left[ r^A_{HL} + r^B_{HL} + \rho^A_H \odot \rho^B_H + \rho^A_L \odot \rho^B_L \right] \\ &\quad - \frac{1}{4} S^{AB}_{HH} S^{AB}_{LL} \left[ r^A_{HL} + r^B_{HL} + \rho^A_H \odot \rho^B_L + \rho^A_L \odot \rho^B_H \right] \end{aligned}$$

The former can be rewritten in a more convenient to implement formula:

$$V^{\rm Exch,(0)} \approx -\frac{1}{4} \sum_{\mu\in A} \sum_{\nu\in B} (\mu\mu|\sigma\sigma) [\mathbf{P}^A \mathbf{s}^{AB}]_{\mu\sigma} [\mathbf{P}^B \mathbf{s}^{BA}]_{\sigma\mu} - \frac{1}{8} \sum_{\mu\nu\in A} P^A_{\nu\mu} (\mu\mu|\nu\nu) [\mathbf{s}^{AB} \mathbf{P}^B \mathbf{s}^{BA}]_{\mu\nu} - \frac{1}{8} \sum_{\sigma\lambda\in B} P^B_{\lambda\sigma} (\lambda\lambda|\sigma$$

In the CT term,

$$\begin{aligned} r^A_{HL} &\equiv \rho^A_H \odot \rho^A_L \\ r^B_{HL} &\equiv \rho^B_H \odot \rho^B_L \end{aligned}$$

where the effective Coulombic interaction energies are defined by

$$\rho^A_U \odot \rho^B_W \equiv \left( U^A U^A \middle| W^A W^A \right)$$

### OEP-Based Methods

TODO

#### OEP-Based TI/CIS theory

After introducing OEP's, the original TI/CIS theory by Fujimoto is reformulated *without* approximation as TODO

### 16.34.2 Member Function Documentation

#### 16.34.2.1 compute_benchmark()

```
double EETCouplingSolver::compute_benchmark (
            const std::string & method = "DEFAULT" )  [virtual]
```

Each solver object has one `DEFAULT` benchmark method

**Parameters**

| | |
|---|---|
| *method* | - benchmark method |

Implements oepdev::OEPDevSolver.

#### 16.34.2.2 compute_oep_based()

```
double EETCouplingSolver::compute_oep_based (
            const std::string & method = "DEFAULT" )  [virtual]
```

Each solver object has one `DEFAULT` OEP-based method.

**Parameters**

| | |
|---|---|
| *method* | - flavour of OEP model |

Implements oepdev::OEPDevSolver.

The documentation for this class was generated from the following files:

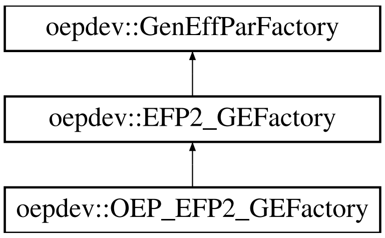
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_coupling_eet.cc

## 16.35 oepdev::EFP2_GEFactory Class Reference

EFP2 GEFP Factory.

`#include <gefp.h>`

Inheritance diagram for oepdev::EFP2_GEFactory:



## Public Member Functions

- EFP2_GEFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

  *Construct from Psi4 options.*
- virtual ∼EFP2_GEFactory ()

  *Destruct.*
- virtual std::shared_ptr< GenEffPar > compute (void)

  *Compute the EFP2 parameters.*

## Protected Member Functions

- virtual std::shared_ptr< oepdev::DMTPole > **compute_dmtp** (void)
- virtual void **compute_lmoc** (void)
- virtual std::shared_ptr< oepdev::CPHF > **compute_cphf** (void)
- virtual std::shared_ptr< oepdev::QUAMBO > **compute_quambo** (void)
- virtual void **assemble_efp2_parameters** (void)
- virtual void **assemble_geometry_data** (void)
- virtual void **assemble_dmtp_data** (void)
- virtual void **assemble_lmo_centroids** (void)
- virtual void **assemble_fock_matrix** (void)
- virtual void **assemble_canonical_orbitals** (void)
- virtual void **assemble_distributed_polarizabilities** (void)

## Protected Attributes

- std::shared_ptr< oepdev::GenEffPar > **EFP2Parameters_**

## Additional Inherited Members

### 16.35.1 Detailed Description

Basic interface for the EFP2 parameters.

The documentation for this class was generated from the following files:

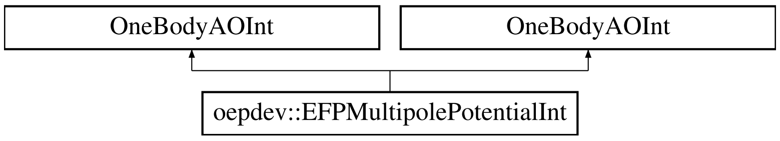
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_efp2.cc

## 16.36 oepdev::EFPMultipolePotentialInt Class Reference

Computes potential integrals.

`#include <multipole_potential.h>`

Inheritance diagram for oepdev::EFPMultipolePotentialInt:



### Public Member Functions

- EFPMultipolePotentialInt (std::vector< psi::SphericalTransform > &, std::shared_ptr< psi::BasisSet >, std::shared_ptr< psi::BasisSet >, int max_k=3, int deriv=0)

  *Constructor. Do not call directly use an IntegralFactory.*
- ∼EFPMultipolePotentialInt () override

  *Virtual destructor.*
- EFPMultipolePotentialInt (std::vector< psi::SphericalTransform > &, std::shared_ptr< psi::BasisSet >, std::shared_ptr< psi::BasisSet >, int max_k=3, int deriv=0)

  *Constructor. Do not call directly use an IntegralFactory.*
- ∼EFPMultipolePotentialInt () override

  *Virtual destructor.*

### Protected Member Functions

- void compute_pair (const psi::GaussianShell &, const psi::GaussianShell &) override

  *Computes the electric field between two gaussian shells.*
- void compute_pair (const psi::GaussianShell &, const psi::GaussianShell &) override

  *Computes the electric field between two gaussian shells.*

### Protected Attributes

- oepdev::ObaraSaikaTwoCenterMultipolePotentialRecursion **mvi_recur_**
- int **max_k_**
- oepdev::ObaraSaikaTwoCenterEFPRecursion_New **mvi_recur_**
- bool **do_octupoles_**
- int **nchunk_**

The documentation for this class was generated from the following files:

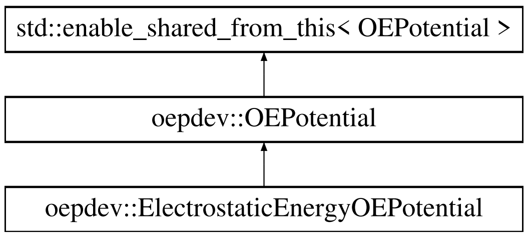
- oepdev/libpsi/bck/multipole_potential.h
- oepdev/libpsi/bck/multipole_potential.cc

## 16.37 oepdev::ElectrostaticEnergyOEPotential Class Reference

Generalized One-Electron Potential for Electrostatic Energy.

```
#include <oep.h>
```

Inheritance diagram for oepdev::ElectrostaticEnergyOEPotential:


std::enable_shared_from_this< OEPotential >
oepdev::OEPotential
oepdev::ElectrostaticEnergyOEPotential

### Public Member Functions

- ElectrostaticEnergyOEPotential (SharedWavefunction wfn, Options &options)

  *Only ESP-based potential is worth implementing.*
- **ElectrostaticEnergyOEPotential** (const ElectrostaticEnergyOEPotential ∗f)
- virtual void compute (const std::string &oepType) override

  *Compute matrix forms of all OEP's within a specified OEP type.*
- virtual void compute_3D (const std::string &oepType, const double &x, const double &y, const double &z, std::shared_ptr< psi::Vector > &v) override

  *Compute value of potential in point x, y, z and save at v.*
- virtual void print_header () const override

  *Header information.*
- virtual std::shared_ptr< OEPotential > clone (void) const override

  *Make a deep copy of this object.*
- virtual void initialize () override

  *Initialize the object (expert)*

### Protected Member Functions

- virtual void **rotate_oep** (psi::SharedMatrix r, psi::SharedMatrix R_prim, psi::SharedMatrix R_aux) override
- virtual void **translate_oep** (psi::SharedVector t) override

### Additional Inherited Members

### 16.37.1 Detailed Description

Contains the following OEP types:

- V

The documentation for this class was generated from the following files:

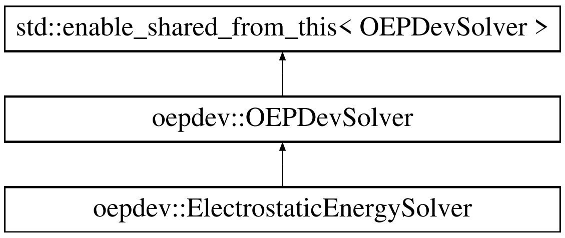
- oepdev/liboep/oep.h
- oepdev/liboep/oep_energy_coul.cc

## 16.38 oepdev::ElectrostaticEnergySolver Class Reference

Compute the Coulombic interaction energy between unperturbed wavefunctions.

```
#include <solver.h>
```

Inheritance diagram for oepdev::ElectrostaticEnergySolver:


std::enable_shared_from_this< OEPDevSolver >
oepdev::OEPDevSolver
oepdev::ElectrostaticEnergySolver

### Public Member Functions

- **ElectrostaticEnergySolver** (SharedWavefunctionUnion wfn_union)
- virtual double compute_oep_based (const std::string &method="DEFAULT")

  *Compute property by using OEP's.*
- virtual double compute_benchmark (const std::string &method="DEFAULT")

  *Compute property by using benchmark method.*

### Additional Inherited Members

### 16.38.1 Detailed Description

The implemented methods are shown in below

Table 16.35: Methods available in the Solver

| Keyword | Method Description |
|---|---|
| **Benchmark Methods** | |
| `AO_EXPANDED` | *Default.* Exact Coulombic energy from atomic orbital expansions. |
| `MO_EXPANDED` | Exact Coulombic energy from molecular orbital expansions |

| Keyword | Method Description |
|---|---|
| | **OEP-Based Methods** |
| ESP_SYMMETRIZED | *Default*. Coulombic energy from ESP charges interacting with nuclei and electronic density. Symmetrized with respect to monomers. |
| CAMM | Coulombic energy from CAMM distributions. |

Below the detailed description of the above methods is given.

## Benchmark Methods

### Exact Coulombic energy from atomic orbital expansions.

The Coulombic interaction energy is given by

$$E^{\rm Coul} = E^{\rm Nuc-Nuc} + E^{\rm Nuc-El} + E^{\rm El-El}$$

where the nuclear-nuclear repulsion energy is

$$E^{\rm Nuc-Nuc} = \sum_{x\in A}\sum_{y\in B} \frac{Z_xZ_y}{|{\bf r}_x - {\bf r}_y|}$$

the nuclear-electronic attraction energy is

$$E^{\rm Nuc-El} = \sum_{x\in A}\sum_{\lambda\sigma\in B} Z_x V_{\lambda\sigma}^{(x)} \left( D_{\lambda\sigma}^{(\alpha)} + D_{\lambda\sigma}^{(\beta)} \right) + \sum_{y\in B}\sum_{\mu\nu\in A} Z_y V_{\mu\nu}^{(y)} \left( D_{\mu\nu}^{(\alpha)} + D_{\mu\nu}^{(\beta)} \right)$$

and the electron-electron repulsion energy is

$$E^{\rm El-El} = \sum_{\mu\nu\in A}\sum_{\lambda\sigma\in B} \left\{ D_{\mu\nu}^{(\alpha)} + D_{\mu\nu}^{(\beta)} \right\} \left\{ D_{\lambda\sigma}^{(\alpha)} + D_{\lambda\sigma}^{(\beta)} \right\} (\mu\nu|\lambda\sigma)$$

In the above equations,

$$V_{\lambda\sigma}^{(x)} \equiv \int \frac{\varphi_\lambda^*({\bf r})\varphi_\sigma({\bf r})}{|{\bf r} - {\bf r}_x|} d{\bf r}$$

### Exact Coulombic energy from molecular orbital expansion.

This approach is fully equivalent to the atomic orbital expansion shown above. For the closed shell case, the Coulombic interaction energy is given by

$$E^{\rm Coul} = E^{\rm Nuc-Nuc} + E^{\rm Nuc-El} + E^{\rm El-El}$$

where the nuclear-nuclear repulsion energy is

$$E^{\rm Nuc-Nuc} = \sum_{x\in A}\sum_{y\in B} \frac{Z_xZ_y}{|{\bf r}_x - {\bf r}_y|}$$

the nuclear-electronic attraction energy is

$$E^{\rm Nuc-El} = 2\sum_{i\in A}\sum_{y\in B} V_{ii}^{(y)} + 2\sum_{j\in B}\sum_{x\in A} V_{jj}^{(x)}$$

and the electron-electron repulsion energy is

$$E^{\rm El-El} = 4\sum_{i\in A}\sum_{j\in B} (ii|jj)$$

### OEP-Based Methods

#### Coulombic energy from ESP charges interacting with nuclei and electronic density.

In this approach, nuclear and electronic density of either species is approximated by ESP charges. In order to achieve symmetric expression, the interaction is computed twice (ESP of A interacting with density matrix and nuclear charges of B and vice versa) and then divided by 2. Thus,

$$E^{\rm Coul} \approx \frac{1}{2}\left[\sum_{x\in A}\sum_{y\in B}\frac{Z_x q_y}{|\mathbf{r}_x-\mathbf{r}_y|} + \sum_{y\in B}\sum_{\mu\nu\in A} q_y V_{\mu\nu}^{(y)}\left(D_{\mu\nu}^{(\alpha)}+D_{\mu\nu}^{(\beta)}\right) + \sum_{y\in B}\sum_{x\in A}\frac{q_x Z_y}{|\mathbf{r}_x-\mathbf{r}_y|} + \sum_{x\in A}\sum_{\lambda\sigma\in B} q_x V_{\lambda\sigma}^{(x)}\left(D_{\lambda\sigma}^{(\alpha)}+D_{\lambda\sigma}^{(\beta)}\right.\right.$$

If the basis set is large and the number of ESP centres $q_{x(y)}$ is sufficient, the sum of first two contributions equals the sum of the latter two contributions.

*Notes:*

- This solver also computes and prints the ESP-ESP point charge interaction energy,

  $$E^{\rm Coul,ESP} \approx \sum_{x\in A}\sum_{y\in B}\frac{q_x q_y}{|\mathbf{r}_x-\mathbf{r}_y|}$$

  for reference purposes.

- In order to construct this solver, **always** use the `OEPDevSolver::build` static factory method.

## 16.38.2 Member Function Documentation

### 16.38.2.1 compute_benchmark()

```
double ElectrostaticEnergySolver::compute_benchmark (
           const std::string & method = "DEFAULT" )  [virtual]
```

Each solver object has one `DEFAULT` benchmark method

**Parameters**

| | |
|---|---|
| *method* | - benchmark method |

Implements oepdev::OEPDevSolver.

#### 16.38.2.2 compute_oep_based()

```
double ElectrostaticEnergySolver::compute_oep_based (
          const std::string & method = "DEFAULT" )  [virtual]
```

Each solver object has one `DEFAULT` OEP-based method.

**Parameters**

| | |
|---|---|
| *method* | - flavour of OEP model |

Implements oepdev::OEPDevSolver.

The documentation for this class was generated from the following files:

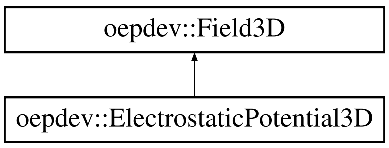
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_energy_coul.cc

## 16.39 oepdev::ElectrostaticPotential3D Class Reference

Electrostatic potential of a molecule.

`#include <space3d.h>`

Inheritance diagram for oepdev::ElectrostaticPotential3D:



### Public Member Functions

- **ElectrostaticPotential3D** (const int &np, const double &padding, psi::SharedWavefunction wfn, psi::Options &options)
- **ElectrostaticPotential3D** (const int &nx, const int &ny, const int &nz, const double &px, const double &py, const double &pz, psi::SharedWavefunction wfn, psi::Options &options)
- virtual std::shared_ptr< psi::Vector > compute_xyz (const double &x, const double &y, const double &z)

*Compute a value of 3D field at point (x, y, z)*

- virtual void print () const

  *Print information of the object to Psi4 output.*

## Additional Inherited Members

### 16.39.1 Detailed Description

Computes the electrostatic potential of a molecule directly from the wavefunction. The electrostatic potential $v(\mathbf{r})$ at point $\mathbf{r}$ is computed from the following formula:

$$v(\mathbf{r}) = v_{\text{nuc}}(\mathbf{r}) + v_{\text{el}}(\mathbf{r})$$

where the nuclear and electronic contributions are defined accordingly as

$$v_{\text{nuc}}(\mathbf{r}) = \sum_x \frac{Z_x}{|\mathbf{r}-\mathbf{r}_x|}$$
$$v_{\text{el}}(\mathbf{r}) = \sum_{\mu\nu} \left\{ D_{\mu\nu}^{(\alpha)} + D_{\mu\nu}^{(\beta)} \right\} V_{\nu\mu}(\mathbf{r})$$

In the above equations, $Z_x$ denotes the charge of $x$th nucleus, $D_{\mu\nu}^{(\omega)}$ is the one-particle (relaxed) density matrix element in AO basis associated with the $\omega$ electron spin, and $V_{\mu\nu}(\mathbf{r})$ is the potential one-electron integral defined by

$$V_{\nu\mu}(\mathbf{r}) \equiv \int d\mathbf{r}' \varphi_\nu^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \varphi_\mu(\mathbf{r}')$$

The documentation for this class was generated from the following files:

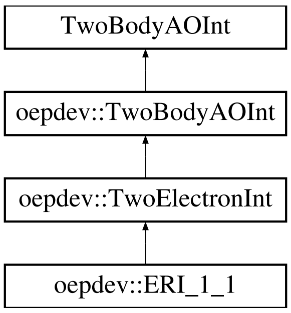
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

## 16.40 oepdev::ERI_1_1 Class Reference

2-centre ERI of the form (a|O(2)|b) where O(2) = 1/r12.

```
#include <eri.h>
```

Inheritance diagram for oepdev::ERI_1_1:



### Public Member Functions

- ERI_1_1 (const IntegralFactory ∗integral, int deriv=0, bool use_shell_pairs=false)

  *Constructor. Use oepdev::IntegralFactory to generate this object.*
- ∼ERI_1_1 ()

  *Destructor.*

### Protected Member Functions

- size_t compute_doublet (int, int)

  *Compute ERI's between 2 shells.*

### Protected Attributes

- double ∗ mdh_buffer_1_

  *Buffer for McMurchie-Davidson-Hermite coefficents for monomial expansion (shell 1)*
- double ∗ mdh_buffer_2_

  *Buffer for McMurchie-Davidson-Hermite coefficents for monomial expansion (shell 2)*

## 16.40.1 Detailed Description

ERI's are computed for a shell doublet (P|Q) and stored in the `target_full_` buffer, accessible through `buffer()` method:

$$
\begin{aligned}
&\text{For each } (n_1,l_1,m_1) \in P:\\
&\quad \text{For each } (n_2,l_2,m_2) \in Q:\\
&\qquad \mathrm{ERI} = (A|B)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}]
\end{aligned}
$$

For detailed description of the McMurchie-Davidson scheme, refer to The Integral Package Library.

## 16.40.2 Implementation

A set of ERI's in a shell is decontracted as

$$(A|B)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}] = \sum_{ij} c_i(\alpha_1)c_j(\alpha_2)(i|j)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}]$$

where the primitive ERI is given by

$$(i|j)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}] = \sum_{N_1=0}^{n_1}\sum_{L_1=0}^{l_1}\sum_{M_1=0}^{m_1}\sum_{N_2=0}^{n_2}\sum_{L_2=0}^{l_2}\sum_{M_2=0}^{m_2} d_{N_1}^{n_1} d_{L_1}^{l_1} d_{M_1}^{m_1} d_{N_2}^{n_2} d_{L_2}^{l_2} d_{M_2}^{m_2} [N_1L_1M_1|N_2L_2M_2]$$

The documentation for this class was generated from the following files:

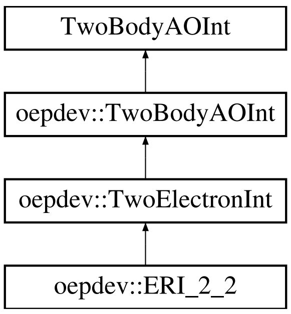
- oepdev/libints/eri.h
- oepdev/libints/eri.cc

## 16.41 oepdev::ERI_2_2 Class Reference

4-centre ERI of the form (ab|O(2)|cd) where O(2) = 1/r12.

`#include <eri.h>`

Inheritance diagram for oepdev::ERI_2_2:



### Public Member Functions

- ERI_2_2 (const IntegralFactory ∗integral, int deriv=0, bool use_shell_pairs=false)

  *Constructor. Use oepdev::IntegralFactory to generate this object.*
- ∼ERI_2_2 ()

  *Destructor.*

### Protected Member Functions

- size_t compute_quartet (int, int, int, int)

  *Compute ERI's between 4 shells.*

### Protected Attributes

- double ∗ mdh_buffer_12_

  *Buffer for McMurchie-Davidson-Hermite coefficents for binomial expansion (shells 1 and 2)*
- double ∗ mdh_buffer_34_

  *Buffer for McMurchie-Davidson-Hermite coefficents for binomial expansion (shells 3 and 4)*

### 16.41.1 Detailed Description

ERI's are computed for a shell quartet (PQ|RS) and stored in the `target_full_` buffer, accessible through `buffer()` method:

```
For each $(n_1,l_1,m_1) \in P$ :
  For each $(n_2,l_2,m_2) \in Q$ :
    For each $(n_3,l_3,m_3) \in R$ :
      For each $(n_4,l_4,m_4) \in S$ :
        $\mathrm{ERI} = (AB|CD)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}]$
```

For detailed description of the McMurchie-Davidson scheme, refer to The Integral Package Library.

### 16.41.2 Implementation

A set of ERI's in a shell is decontracted as

$$(AB|CD)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}] = \sum_{ijkl} c_i(\alpha_1)c_j(\alpha_2)c_k(\alpha_3)c_l(\alpha_4)(ij|kl)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}]$$

where the primitive ERI is given by

$$(ij|kl)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}] = E_{ij}(\alpha_1,\alpha_2)E_{kl}(\alpha_3,\alpha_4)$$
$$\times \sum_{N_1=0}^{n_1+n_2}\sum_{L_1=0}^{l_1+l_2}\sum_{M_1=0}^{m_1+m_2}\sum_{N_2=0}^{n_3+n_4}\sum_{L_2=0}^{l_3+l_4}\sum_{M_2=0}^{m_3+m_4} d_{N_1}^{n_1n_2}d_{L_1}^{l_1l_2}d_{M_1}^{m_1m_2}d_{N_2}^{n_3n_4}d_{L_2}^{l_3l_4}d_{M_2}^{m_3m_4}[N_1L_1M_1|N_2L_2M_2]$$

In the above equation, the multiplicative constants are given as

$$E_{ij}(\alpha_1,\alpha_2) = \exp\left[-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}|\mathbf{A}-\mathbf{B}|^2\right]$$
$$E_{kl}(\alpha_3,\alpha_4) = \exp\left[-\frac{\alpha_3\alpha_4}{\alpha_3+\alpha_4}|\mathbf{C}-\mathbf{D}|^2\right]$$

The documentation for this class was generated from the following files:

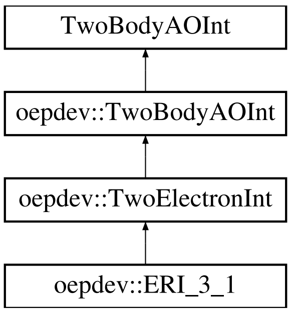
- oepdev/libints/eri.h
- oepdev/libints/eri.cc

## 16.42 oepdev::ERI_3_1 Class Reference

4-centre ERI of the form (abc|O(2)|d) where O(2) = 1/r12.

`#include <eri.h>`

Inheritance diagram for oepdev::ERI_3_1:



## Public Member Functions

- ERI_3_1 (const IntegralFactory ∗integral, int deriv=0, bool use_shell_pairs=false)

  *Constructor. Use oepdev::IntegralFactory to generate this object.*
- ∼ERI_3_1 ()

  *Destructor.*

## Protected Member Functions

- size_t compute_quartet (int, int, int, int)

  *Compute ERI's between 4 shells.*

## Protected Attributes

- double ∗ mdh_buffer_123_

  *Buffer for McMurchie-Davidson-Hermite coefficents for trinomial expansion (shells 1, 2 and 3)*
- double ∗ mdh_buffer_4_

  *Buffer for McMurchie-Davidson-Hermite coefficents for monomial expansion (shell 4)*

### 16.42.1 Detailed Description

ERI's are computed for a shell quartet (PQR|S) and stored in the `target_full_` buffer, accessible through `buffer()` method:

```
For each $(n_1,l_1,m_1) \in P$ :
  For each $(n_2,l_2,m_2) \in Q$ :
    For each $(n_3,l_3,m_3) \in R$ :
      For each $(n_4,l_4,m_4) \in S$ :
        $\mathrm{ERI} = (ABC|D)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}]$
```

For detailed description of the McMurchie-Davidson scheme, refer to The Integral Package Library.

### 16.42.2 Implementation

A set of ERI's in a shell is decontracted as

$$(ABC|D)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}] = \sum_{ijkl} c_i(\alpha_1)c_j(\alpha_2)c_k(\alpha_3)c_l(\alpha_4)(ijk|l)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}]$$

where the primitive ERI is given by

$$(ijk|l)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}] = E_{ijk}(\alpha_1,\alpha_2,\alpha_3)$$
$$\times \sum_{N_1=0}^{n_1+n_2+n_3} \sum_{L_1=0}^{l_1+l_2+l_3} \sum_{M_1=0}^{m_1+m_2+m_3} \sum_{N_2=0}^{n_4} \sum_{L_2=0}^{l_4} \sum_{M_2=0}^{m_4} d_{N_1}^{n_1n_2n_3} d_{L_1}^{l_1l_2l_3} d_{M_1}^{m_1m_2m_3} d_{N_2}^{n_4} d_{L_2}^{l_4} d_{M_2}^{m_4} [N_1L_1M_1|N_2L_2M_2]$$

In the above equation, the multiplicative constants are given as

$$E_{ijk}(\alpha_1,\alpha_2,\alpha_3) = \exp\left[-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}|\mathbf{A}-\mathbf{B}|^2\right]\exp\left[-\frac{(\alpha_1+\alpha_2)\alpha_3}{\alpha_1+\alpha_2+\alpha_3}|\mathbf{P}-\mathbf{C}|^2\right]$$

The documentation for this class was generated from the following files:

- oepdev/libints/eri.h
- oepdev/libints/eri.cc

## 16.43 oepdev::ESPSolver Class Reference

Charges from Electrostatic Potential (ESP). A solver-type class.

```
#include <esp.h>
```

### Public Member Functions

- ESPSolver (SharedField3D field)

  *Construct from 3D vector field.*
- ESPSolver (SharedField3D field, psi::SharedMatrix centres)

  *Construct from 3D vector field.*
- virtual ∼ESPSolver ()

  *Destructor.*
- virtual psi::SharedMatrix charges () const

  *Get the (fit) charges.*
- virtual psi::SharedMatrix centres () const

  *Get the charge distribution centres.*
- virtual void set_charge_sums (psi::SharedVector s)

  *Set the charge sums $Q_p$.*
- virtual void set_charge_sums (const double &s)

  *Set the charge sums $Q_p$ (equal to all fields)*
- virtual void compute ()

  *Perform fitting of effective charges.*

## Protected Attributes

- const int nCentres_

    *Number of fit centres.*
- const int nFields_

    *Number of fields to fit.*
- SharedField3D field_

    *Scalar field.*
- psi::SharedMatrix charges_

    *Charges to be fit.*
- psi::SharedMatrix centres_

    *Centres, at which fit charges will reside.*
- psi::SharedVector charge_sums_

    *Vector of sums of partial charges.*

## 16.43.1 Detailed Description

Solves the least-squares problem to fit the generalized charges $q_{m;p}$, that reproduce the reference generalized potential $v_p^{\rm ref}({\bf r})$ supplied by the `Field3D` object:

$$\int d{\bf r}' \left[ v_p^{\rm ref}({\bf r}') - \sum_m \frac{q_{m;p}}{|{\bf r}' - {\bf r}_m|} \right]^2 \rightarrow \text{minimize}$$

The charges are subject to the following constraint:

$$\sum_m q_{m;p} = Q_p \text{ for all } p$$

### Method description.

$M$ generalized charges is found by solving the matrix equation

$$\begin{pmatrix} {\bf A} & 1 \\ 1 & 0 \end{pmatrix}^{-1} \cdot \begin{pmatrix} {\bf b}_p \\ Q_p \end{pmatrix} = \begin{pmatrix} {\bf q}_p \\ \lambda \end{pmatrix}$$

where the ${\bf A}$ matrix of dimension $(M+1) \times (M+1)$ and ${\bf b}_p$ vector or length $M+1$ are given as

$$A_{mn} = \sum_i \frac{1}{r_{im} r_{in}}$$
$$b_{m;p} = \sum_i \frac{v_p^{\rm ref}({\bf r}_m)}{r_{im}}$$

In the above equation, summations run over all sample points, at which reference potential is known. The solution is stored in the $M \times N$ matrix, where $N$ is the dimensionality of the 3D vector field (i.e., the number of potentials supplied, $p_{\rm max}$). As a default, $Q_p = 0$ for all potentials. This can be set by `oepdev::ESPSolver::set_charge_sums` method.

**Note**

Useful options:

- `ESP_PAD_SPHERE` - Padding spherical radius for random points selection. Default: `10.0` [A.U.]
- `ESP_NPOINTS_PER_ATOM` - Number of random points per atom in a molecule. Default: `1500`
- `ESP_VDW_RADIUS_C` - The vdW radius for carbon atom. Default: `3.0` [A.U.]
- `ESP_VDW_RADIUS_H` - The vdW radius for hydrogen atom. Default: `4.0` [A.U.]
- `ESP_VDW_RADIUS_N` - The vdW radius for nitrogen atom. Default: `2.4` [A.U.]
- `ESP_VDW_RADIUS_O` - The vdW radius for oxygen atom. Default: `5.6` [A.U.]
- `ESP_VDW_RADIUS_F` - The vdW radius for fluorium atom. Default: `2.3` [A.U.]
- `ESP_VDW_RADIUS_CL` - The vdW radius for chlorium atom. Default: `2.9` [A.U.]

## 16.43.2 Constructor & Destructor Documentation

### 16.43.2.1 ESPSolver() `[1/2]`

```
oepdev::ESPSolver::ESPSolver (
          SharedField3D field )
```

Assume that the centres are on atoms associated with the 3D vector field.

**Parameters**

| | |
|---|---|
| *field* | - oepdev 3D vector field object |

### 16.43.2.2 ESPSolver() `[2/2]`

```
oepdev::ESPSolver::ESPSolver (
          SharedField3D field,
          psi::SharedMatrix centres )
```

Solve ESP equations for a custom set of charge distribution centres.

**Parameters**

| | |
|---|---|
| *field* | - oepdev 3D vector field object |
| *centres* | - matrix with coordinates of charge distribution centres |

The documentation for this class was generated from the following files:

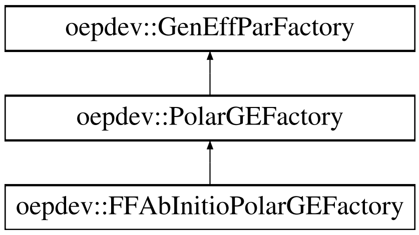
- oepdev/lib3d/esp.h
- oepdev/lib3d/esp.cc

## 16.44 oepdev::FFAbInitioPolarGEFactory Class Reference

Polarization GEFP Factory from First Principles: Finite-Difference Model. Arbitrary level of theory.

```
#include <gefp.h>
```

Inheritance diagram for oepdev::FFAbInitioPolarGEFactory:



### Public Member Functions

- **FFAbInitioPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- virtual std::shared_ptr< GenEffPar > compute (void)

  *Compute the density matrix susceptibility tensors.*

### Additional Inherited Members

### 16.44.1 Detailed Description

Implements creation of the density matrix susceptibility tensors. Does not guarantee the idempotency of the density matrix in LCAO-MO variation, but for weak electric fields the idempotency is to be expected up to first order. The density matrix susceptibility tensor is represented by:

$$\delta D_{\alpha\beta} = \mathbf{B}_{\alpha\beta}^{(1)} \cdot \mathbf{F} + \mathbf{B}_{\alpha\beta}^{(2)} : \mathbf{F} \otimes \mathbf{F}$$

where $\mathbf{B}_{\alpha\beta}^{(1)}$ is the density matrix dipole polarizability defined as

$$\mathbf{B}_{\alpha\beta}^{(1)} = \frac{\partial D_{\alpha\beta}}{\partial \mathbf{F}}\bigg|_{\mathbf{F}=\mathbf{0}}$$

whereas $\mathbf{B}_{\alpha\beta}^{(2)}$ is the density matrix dipole-dipole hyperpolarizability,

$$\mathbf{B}_{\alpha\beta}^{(2)} = \frac{1}{2}\frac{\partial^2 D_{\alpha\beta}}{\partial \mathbf{F} \otimes \partial \mathbf{F}}\bigg|_{\mathbf{F}=\mathbf{0}}$$

The first derivative is evaluated numerically from central finite-field 3-point formula,

$$f' = \frac{f(h) - f(-h)}{2h} + \mathfrak{O}(h^2)$$

where $h$ is the differentiation step. Second derivatives are evaluated from the following formulae:

$$f_{uu} = \frac{f(h) + f(-h) - 2f(0)}{h^2} + \mathfrak{O}(h^2)$$

$$f_{uw} = \frac{f(h,h) + f(-h,-h) + 2f(0) - f(h,0) - f(-h,0) - f(0,h) - f(0,-h)}{2h^2} + \mathfrak{O}(h^2)$$

As long as the second-order susceptibility is considered, this susceptibility model works well for uniform weak, moderate and strong electric fields.

The documentation for this class was generated from the following files:

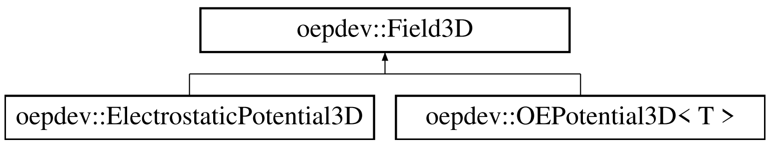
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_ffabinitio.cc

## 16.45 oepdev::Field3D Class Reference

General Vector Dield in 3D Space. Abstract base.

```
#include <space3d.h>
```

Inheritance diagram for oepdev::Field3D:



### Public Member Functions

- Field3D (const int &ndim, const int &np, const double &pad, psi::SharedWavefunction wfn, psi::Options &options)

    *Construct potential on random grid by providing wavefunction. Excludes space within vdW volume.*

- Field3D (const int &ndim, const int &nx, const int &ny, const int &nz, const double &px, const double &py, const double &pz, std::shared_ptr< psi::Wavefunction > wfn, psi::Options &options)

    *Construct potential on cube grid by providing wavefunction.*

- virtual ∼Field3D ()

    *Destructor.*

- virtual int npoints () const

    *Get the number of points at which the 3D field is defined.*

- virtual std::shared_ptr< PointsCollection3D > points_collection () const

  *Get the collection of points.*
- virtual std::shared_ptr< psi::Matrix > data () const

  *Get the data matrix in a form { [x, y, z, f_1(x, y, z), f_2(x, y, z), ... , f_n(x, y, z) ] } where n = ndim.*
- virtual std::shared_ptr< psi::Wavefunction > wfn () const

  *Get the wavefunction.*
- virtual bool is_computed () const

  *Get the information if data is already computed or not.*
- int dimension () const

  *Get the number of fields.*
- virtual void compute ()

  *Compute the 3D field in each point from the point collection.*
- virtual std::shared_ptr< psi::Vector > compute_xyz (const double &x, const double &y, const double &z)=0

  *Compute a value of 3D field at point (x, y, z)*
- virtual void write_cube_file (const std::string &name)

  *Write the cube file (only for Cube collections, otherwise does nothing)*
- virtual void print () const =0

  *Print information of the object to Psi4 output.*

## Static Public Member Functions

- static shared_ptr< Field3D > build (const std::string &type, const int &np, const double &pad, psi::SharedWavefunction wfn, psi::Options &options, const int &ndim=1)

  *Build 3D field of random points. vdW volume is excluded.*
- static shared_ptr< Field3D > build (const std::string &type, const int &nx, const int &ny, const int &nz, const double &px, const double &py, const double &pz, psi::SharedWavefunction wfn, psi::Options &options, const int &ndim=1)

  *Build 3D field of points on a g09-cube grid.*

## Protected Attributes

- std::shared_ptr< PointsCollection3D > pointsCollection_

  *Collection of points at which the 3D field is to be computed.*
- std::shared_ptr< psi::Matrix > data_

  *The data matrix in a form { [x, y, z, f_1(x, y, z), f_2(x, y, z), ..., f_n(x, y, z) ] } where n = nDim_.*
- std::shared_ptr< psi::Wavefunction > wfn_

  *Wavefunction.*
- psi::Matrix geom_

  *Geometry of a molecule.*
- std::shared_ptr< psi::IntegralFactory > fact_

*Integral factory.*
- std::shared_ptr< psi::Matrix > pot_

  *Matrix of potential one-electron integrals.*
- std::shared_ptr< psi::OneBodyAOInt > oneInt_

  *One-electron integral shared pointer.*
- std::shared_ptr< PotentialInt > potInt_

  *One-electron potential shared pointer.*
- std::shared_ptr< psi::BasisSet > primary_

  *Basis set.*
- int nbf_

  *Number of basis functions.*
- int nDim_

  *Dimensionality of the 3D field (1: scalar field, 2>: vector field)*
- bool isComputed_

  *Has data already computed?*

### 16.45.1 Detailed Description

Create vector field defined at points distributed randomly or as an ordered g09 cube-like collection. Currently implemented fields are:

- Electrostatic potential - computes electrostatic potential (requires wavefunction)
- Template of generic classes - compute custom vector fields (requires generic object that is able to compute the field in 3D space)

**Note:** Always create instances by using static factory methods `build`. The following types of 3D vector fields are currently implemented:

- `ELECTROSTATIC POTENTIAL`

### 16.45.2 Constructor & Destructor Documentation

#### 16.45.2.1 Field3D()

```
oepdev::Field3D::Field3D (
            const int & ndim,
            const int & nx,
            const int & ny,
            const int & nz,
            const double & px,
            const double & py,
            const double & pz,
            std::shared_ptr< psi::Wavefunction > wfn,
            psi::Options & options )
```

Construct potential on random grid by providing molecule. Excludes space within vdW volume Field3D(const int& ndim, const int& np, const double& pad, psi::SharedMolecule mol, psi::Options& options);

### 16.45.3 Member Function Documentation

#### 16.45.3.1 build() [1/2]

```
std::shared_ptr< Field3D > oepdev::Field3D::build (
            const std::string & type,
            const int & np,
            const double & pad,
            psi::SharedWavefunction wfn,
            psi::Options & options,
            const int & ndim = 1 )  [static]
```

**Parameters**

| | |
|---|---|
| *ndim* | - dimensionality of 3D field (1: scalar field, >2: vector field) |
| *type* | - type of 3D field |
| *np* | - number of points |
| *pad* | - radius padding of a minimal sphere enclosing the molecule |
| *wfn* | - Psi4 Wavefunction containing the molecule |
| *options* | - Psi4 options |

#### 16.45.3.2 build() [2/2]

```
std::shared_ptr< Field3D > oepdev::Field3D::build (
            const std::string & type,
            const int & nx,
            const int & ny,
            const int & nz,
            const double & px,
            const double & py,
            const double & pz,
            psi::SharedWavefunction wfn,
            psi::Options & options,
            const int & ndim = 1 )  [static]
```

**Parameters**

| | |
|---|---|
| *ndim* | - dimensionality of 3D field (1: scalar field, >2: vector field) |
| *type* | - type of 3D field |
| *nx* | - number of points along x direction |
| *ny* | - number of points along y direction |
| *nz* | - number of points along z direction |
| *px* | - padding distance along x direction |
| *py* | - padding distance along y direction |
| *pz* | - padding distance along z direction |
| *wfn* | - Psi4 Wavefunction containing the molecule |
| *options* | - Psi4 options |

The documentation for this class was generated from the following files:

- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

## 16.46 oepdev::Fourier5 Struct Reference

Simple structure to hold the Fourier series expansion coefficients for *N*=2.

`#include <unitary_optimizer.h>`

### Public Attributes

- double **a0**
- double **a1**
- double **a2**
- double **b1**
- double **b2**

### 16.46.1 Detailed Description

The documentation for this struct was generated from the following file:

- oepdev/libutil/unitary_optimizer.h

## 16.47 oepdev::Fourier9 Struct Reference

Simple structure to hold the Fourier series expansion coefficients for *N*=4.

```
#include <unitary_optimizer.h>
```

### Public Attributes

- double **a0**
- double **a1**
- double **a2**
- double **a3**
- double **a4**
- double **b1**
- double **b2**
- double **b3**
- double **b4**

### 16.47.1 Detailed Description

The documentation for this struct was generated from the following file:

- oepdev/libutil/unitary_optimizer.h

## 16.48 oepdev::FragmentedSystem Class Reference

Molecular System for Fragment-Based Calculations.

```
#include <gefp.h>
```

### Public Member Functions

#### Mutators

- void set_geometry (std::vector< psi::SharedMolecule > aggregate)

  *Set the current atomic coordinates of the system.*
- void set_primary (std::vector< psi::SharedBasisSet > p)

  *Set the current atomic coordinates of the system.*
- void set_auxiliary (std::vector< psi::SharedBasisSet > a)

  *Set the auxiliary basis sets (TO BE DEPRECATED)*

#### Transformators

- void superimpose ()

  *Superimpose all the fragments onto the current atomic coordinates.*

#### Computers

- double compute_energy (std::string theory)

    *Compute a total energy.*
- double compute_energy_term (std::string theory, bool manybody)

    *Compute a single energy term.*

## Protected Attributes

### Working Attributes

- std::vector< std::shared_ptr< GenEffFrag > > bsm_

    *List of Base Fragments (BSMs)*
- std::vector< int > ind_

    *List of fragment assignment indices.*
- const int nfrag_

    *Number of all fragments in the system.*
- std::vector< std::shared_ptr< GenEffFrag > > fragments_

    *List of all fragments in the system.*
- std::vector< psi::SharedMolecule > aggregate_

    *List of molecules currently representing all fragments in the system.*
- std::vector< psi::SharedBasisSet > basis_prim_

    *List of current primary basis sets (TO BE DEPRECATED)*
- std::vector< psi::SharedBasisSet > basis_aux_

    *List of current auxiliary basis sets (TO BE DEPRECATED)*

## Constructors and Destructor.

- static std::shared_ptr< FragmentedSystem > build (std::vector< std::shared_ptr< GenEffFrag >> bsm, std::vector< int > ind)

    *Build from the list of base molecules (BSM) and fragment assignment vector.*
- FragmentedSystem (std::vector< std::shared_ptr< GenEffFrag >> bsm, std::vector< int > ind)

    *Constructor.*
- virtual ∼FragmentedSystem ()

    *Destructor.*

## 16.48.1 Detailed Description

Implements interface of running fragment-based calculations on molecular systems defined in terms of independent but interacting fragments.

## 16.48.2 Member Function Documentation

#### 16.48.2.1 build()

```
oepdev::SharedFragmentedSystem oepdev::FragmentedSystem::build (
          std::vector< std::shared_ptr< GenEffFrag >> bsm,
          std::vector< int > ind ) [static]
```

**Parameters**

| | |
|---|---|
| *bsm* | - list of base molecules |
| *ind* | - list of fragment assignments indices |

**Returns**

system of fragments

After initialization, the list of fragments $f_i$ is created within the object, where the *i*-th fragment is given by

$$f_i = \text{copy}\left(m_{d_i}\right)$$

In the above, *m* and *d* denote the lists of BSMs and fragment assignment indices, respectively.

#### 16.48.2.2 compute_energy()

```
double oepdev::FragmentedSystem::compute_energy (
          std::string theory )
```

**Parameters**

| | |
|---|---|
| *theory* | - theory to use for calculations |

**Returns**

energy in a.u.

#### 16.48.2.3 compute_energy_term()

```
double oepdev::FragmentedSystem::compute_energy_term (
          std::string theory,
          bool manybody )
```

**Parameters**

| | |
|---|---|
| *theory* | - theory to use for calculations |
| *manybody* | - whether to use many body routines. |

**Returns**

energy in a.u.

### 16.48.2.4 set_auxiliary()

```
void oepdev::FragmentedSystem::set_auxiliary (
            std::vector< psi::SharedBasisSet > a )  [inline]
```

**Parameters**

| | |
|---|---|
| *a* | - list of all auxiliary basis sets in the system |

**Note**

This will be deprecated once basis sets can be rotated and embedded in oepdev::GenEffFrag.

### 16.48.2.5 set_geometry()

```
void oepdev::FragmentedSystem::set_geometry (
            std::vector< psi::SharedMolecule > aggregate )  [inline]
```

**Parameters**

| | |
|---|---|
| *aggregate* | - list of all molecules in the system |

### 16.48.2.6 set_primary()

```
void oepdev::FragmentedSystem::set_primary (
            std::vector< psi::SharedBasisSet > p )  [inline]
```

**Parameters**

| | |
|---|---|
| *aggregate* | - molecule object of the whole systemSet the current atomic coordinates of the system. |
| *aggregate* | - molecule object of the whole systemSet the primary basis sets (TO BE DEPRECATED) |
| *p* | - list of all primary basis sets in the system |

**Note**

This will be deprecated once basis sets can be rotated and embedded in oepdev::GenEffFrag.

The documentation for this class was generated from the following files:

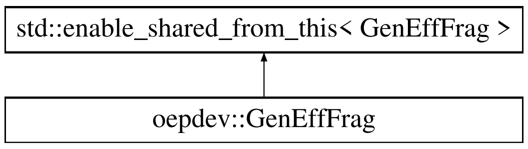
- oepdev/libgefp/gefp.h
- oepdev/libgefp/fragmented_system.cc

## 16.49 oepdev::GenEffFrag Class Reference

Generalized Effective Fragment. Container Class.

`#include <gefp.h>`

Inheritance diagram for oepdev::GenEffFrag:



### Public Member Functions

#### Transformators

- void rotate (std::shared_ptr< psi::Matrix > R)
  *Rotate.*
- void translate (std::shared_ptr< psi::Vector > T)
  *Translate.*
- void superimpose (std::shared_ptr< psi::Matrix > targetXYZ, std::vector< int > supList)
  *Superimpose.*
- void superimpose (psi::SharedMolecule targetMol, std::vector< int > supList)
  *Superimpose.*
- void superimpose (void)
  *Superimpose to the structure held in* `frag_`

#### Mutators

- void set_parameters (const std::string &type, std::shared_ptr< GenEffPar > par)
  *Set the parameters.*
- void set_ndocc (int n)
  *Set the number of doubly occupied MOs.*
- void set_nbf (int n)
  *Set the number of primary basis functions.*
- void set_molecule (const psi::SharedMolecule mol)

*Set the fragment molecule.*
- void set_basisset (std::string key, psi::SharedBasisSet basis)

  *Set the basis set.*
- void set_gefp_polarization (const std::shared_ptr< GenEffPar > &par)

  *Set the Density Matrix Susceptibility Tensor Object.*
- void set_dmat_dipole_polarizability (const std::vector< std::vector< std::shared_ptr< psi::Matrix >>> &susc)

  *Set the Density Matrix Dipole Polarizability.*
- void set_dmat_dipole_dipole_hyperpolarizability (const std::vector< std::vector< std::shared_ptr< psi::Matrix >>> &susc)

  *Set the Density Matrix Dipole-Dipole Hyperpolarizability.*
- void set_dmat_quadrupole_polarizability (const std::vector< std::vector< std::shared_ptr< psi::Matrix >>> &susc)

  *Set the Density Matrix Quadrupole Polarizability.*

#### Accessors

- int nbf (void) const

  *Grab the number of primary basis functions.*
- int natom (void) const

  *Grab the number of atoms.*
- int ndocc (void) const

  *Grab the number of doubly occupied molecular orbitals.*
- psi::SharedMolecule molecule (void) const

  *Grab the molecule attached to this fragment.*
- std::shared_ptr< psi::Matrix > susceptibility (int fieldRank, int fieldGradientRank, int i, int x) const

  *Grab the Density Matrix Susceptibility.*
- std::vector< std::shared_ptr< psi::Matrix > > susceptibility (int fieldRank, int fieldGradientRank, int i) const

  *Grab the Density Matrix Susceptibility.*
- std::vector< std::vector< std::shared_ptr< psi::Matrix > > > susceptibility (int fieldRank, int fieldGradientRank) const

  *Grab the Density Matrix Susceptibility.*

## Public Attributes

#### Parameters

- std::map< std::string, std::shared_ptr< GenEffPar > > parameters

  *Dictionary of All GEF Parameters.*
- std::map< std::string, psi::SharedBasisSet > basissets

  *Dictionary of All Basis Sets.*

## Protected Member Functions

- psi::SharedVector extract_xyz (psi::SharedMolecule) const

  *Extract XYZ.*
- psi::SharedVector extract_dmtp (std::shared_ptr< oepdev::DMTPole >) const

  *Extract DMTP.*
- psi::SharedVector compute_u_vector (psi::SharedMatrix rmo_1, psi::SharedMatrix rmo_2, psi::SharedMolecule mol_2) const

  *Compute u vector for OEP-CT calculations.*
- psi::SharedMatrix compute_w_matrix (psi::SharedMolecule mol_1, psi::SharedMolecule mol_2, psi::SharedMatrix rmo_1) const

  *Compute w matrix for OEP-CT calculations.*
- double compute_ct_component (psi::SharedVector eps_occ_X, psi::SharedVector eps_vir_Y, psi::SharedMatrix V) const

  *Compute OEP-CT energy component.*

### Interface Computers

- double **compute_pairwise_energy** (std::string theory, std::shared_ptr< GenEffFrag > other) const
- double **compute_pairwise_energy_efp2_coul** (std::shared_ptr< GenEffFrag > other) const
- double **compute_pairwise_energy_efp2_exrep** (std::shared_ptr< GenEffFrag > other) const
- double **compute_pairwise_energy_efp2_ind** (std::shared_ptr< GenEffFrag > other) const
- double **compute_pairwise_energy_efp2_ct** (std::shared_ptr< GenEffFrag > other) const
- double **compute_pairwise_energy_efp2_disp** (std::shared_ptr< GenEffFrag > other) const
- double **compute_pairwise_energy_oep_efp2_exrep** (std::shared_ptr< GenEffFrag > other) const
- double **compute_pairwise_energy_oep_efp2_ct** (std::shared_ptr< GenEffFrag > other) const

## Protected Attributes

- std::string name_

  *Name of GEFP.*
- psi::SharedMolecule frag_

  *Structure.*
- int nbf_

  *Number of primary basis functions.*
- int natom_

*Number of atoms.*

- int ndocc_

  *Number of doubly occupied MOs.*

- std::shared_ptr< GenEffPar > **densityMatrixSusceptibilityGEF_**

### Constructors and Destructor

- GenEffFrag ()

  *Initialize with default name of GEFP (Default)*

- GenEffFrag (std::string name)

  *Initialize with custom name of GEFP.*

- GenEffFrag (const GenEffFrag ∗)

  *Copy Constructor.*

- std::shared_ptr< GenEffFrag > clone (void) const

  *Make a deep copy.*

- ∼GenEffFrag ()

  *Destruct.*

- static std::shared_ptr< GenEffFrag > build (std::string name)

  *Create an empty fragment.*

### Computers

- double energy_term (std::string theory, std::shared_ptr< GenEffFrag > other) const

  *Compute interaction energy between this and other fragment.*

- static double compute_energy (std::string theory, std::vector< std::shared_ptr< GenEffFrag >> fragments)

  *Compute the total interaction energy term in a cluster of fragments.*

- static double compute_energy_term (std::string theory, std::vector< std::shared_ptr< GenEffFrag >> fragments, bool manybody)

  *Compute a single interaction energy term in a cluster of fragments.*

- static double compute_many_body_energy_term (std::string theory, std::vector< std::shared_ptr< GenEffFrag >> fragments)

  *Compute a single interaction energy term in a cluster of fragments by using manybody routine.*

## 16.49.1 Detailed Description

Describes the GEFP fragment that is in principle designed to work at correlated levels of theory.

**See also**

GenEffPar, GenEffParFactory

### 16.49.2 Member Function Documentation

#### 16.49.2.1 compute_energy()

```
double oepdev::GenEffFrag::compute_energy (
          std::string theory,
          std::vector< std::shared_ptr< GenEffFrag >> fragments )  [static]
```

**Parameters**

| | |
|---|---|
| *theory* | - theory used to compute energy |
| *fragments* | - list of fragments in the system |

**Returns**

interaction energy in [A.U.]

#### 16.49.2.2 compute_energy_term()

```
double oepdev::GenEffFrag::compute_energy_term (
          std::string theory,
          std::vector< std::shared_ptr< GenEffFrag >> fragments,
          bool manybody )  [static]
```

**Parameters**

| | |
|---|---|
| *theory* | - theory used to compute energy |
| *fragments* | - list of fragments in the system |
| *manybody* | - use the manybody routine? If not, pairwise routine is utilized. |

**Returns**

interaction energy in [A.U.]

#### 16.49.2.3 compute_many_body_energy_term()

```
double oepdev::GenEffFrag::compute_many_body_energy_term (
          std::string theory,
          std::vector< std::shared_ptr< GenEffFrag >> fragments )  [static]
```

**Parameters**

| | |
|---|---|
| *theory* | - theory used to compute energy |
| *fragments* | - list of fragments in the system |

**Returns**

interaction energy in [A.U.]

#### 16.49.2.4 energy_term()

```
double oepdev::GenEffFrag::energy_term (
          std::string theory,
          std::shared_ptr< GenEffFrag > other ) const
```

**Parameters**

| | |
|---|---|
| *theory* | - theory used to compute energy |
| *other* | - other fragment |

**Returns**

interaction energy in [A.U.]

#### 16.49.2.5 susceptibility() [1/3]

```
std::shared_ptr<psi::Matrix> oepdev::GenEffFrag::susceptibility (
          int fieldRank,
          int fieldGradientRank,
          int i,
          int x ) const [inline]
```

**Parameters**

| | |
|---|---|
| *fieldRank* | - power dependency with respect to the electric field |
| *fieldGradientRank* | - power dependency with respect to the electric field gradient |
| *i* | - id of the distributed site |
| *x* | - id of the composite Cartesian component |

#### 16.49.2.6 susceptibility() [2/3]

```
std::vector<std::shared_ptr<psi::Matrix> > oepdev::GenEffFrag::susceptibility
(
            int fieldRank,
            int fieldGradientRank,
            int i ) const [inline]
```

**Parameters**

| | |
|---|---|
| *fieldRank* | - power dependency with respect to the electric field |
| *fieldGradientRank* | - power dependency with respect to the electric field gradient |
| *i* | - id of the distributed site |

#### 16.49.2.7 susceptibility() [3/3]

```
std::vector<std::vector<std::shared_ptr<psi::Matrix> > > oepdev::GenEffFrag::susceptib
(
            int fieldRank,
            int fieldGradientRank ) const [inline]
```

**Parameters**

| | |
|---|---|
| *fieldRank* | - power dependency with respect to the electric field |
| *fieldGradientRank* | - power dependency with respect to the electric field gradient |

The documentation for this class was generated from the following files:

- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_frag.cc

## 16.50 oepdev::GenEffPar Class Reference

Generalized Effective Fragment Parameters. Container Class.

```
#include <gefp.h>
```

### Public Member Functions

#### Transformators

- void rotate (psi::SharedMatrix R)
  *Rotate the parameters in 3D Euclidean space.*

- void translate (psi::SharedVector t)

  *Translate the parameters in 3D Euclidean space.*
- void superimpose (psi::SharedMatrix targetXYZ, std::vector< int > supList)

  *Superimpose the parameters in 3D Euclidean space onto a target geometry.*

### Mutators

- void set_vector (std::string key, psi::SharedVector mat)

  *Set the vector data.*
- void set_matrix (std::string key, psi::SharedMatrix mat)

  *Set the matrix data.*
- void set_dmtp (std::string key, std::shared_ptr< oepdev::DMTPole > mat)

  *Set the DMTP data.*
- void set_oep (std::string key, oepdev::SharedOEPotential oep)

  *Set the OEP data.*
- void set_dpol (std::string key, std::vector< psi::SharedMatrix > mats)

  *Set the DPOL data.*
- void set_basisset (std::string key, psi::SharedBasisSet basis)

  *Set the basis set data.*
- void set_susceptibility (int fieldRank, int fieldGradientRank, const std::vector< std::vector< std::shared_ptr< psi::Matrix >>> &susc)

  *Set the Density Matrix Susceptibility.*
- void set_dipole_polarizability (const std::vector< std::vector< std::shared_ptr< psi::Matrix >>> &susc)

  *Set The Density Matrix Dipole Polarizability.*
- void set_dipole_dipole_hyperpolarizability (const std::vector< std::vector< std::shared_ptr< psi::Matrix >>> &susc)

  *Set The Density Matrix Dipole-Dipole Hyperpolarizability.*
- void set_quadrupole_polarizability (const std::vector< std::vector< std::shared_ptr< psi::Matrix >>> &susc)

  *Set The Density Matrix Quadrupole Polarizability.*
- void set_centres (const std::vector< std::shared_ptr< psi::Vector >> &centres)

  *Set the distributed centres' positions.*

### Allocators

- void allocate (int fieldRank, int fieldGradientRank, int nsites, int nbf)

  *Allocate the Density Matrix Susceptibility.*
- void allocate_dipole_polarizability (int nsites, int nbf)

  *Allocate The Density Matrix Dipole Polarizability.*
- void allocate_dipole_dipole_hyperpolarizability (int nsites, int nbf)

  *Allocate The Density Matrix Dipole-Dipole Hyperpolarizability.*
- void allocate_quadrupole_polarizability (int nsites, int nbf)

  *Allocate The Density Matrix Quadrupole Polarizability.*

### Descriptors

- std::string type () const
  *Type of Parameters.*
- std::string name () const
  *Name of Parameters.*
- bool hasDensityMatrixDipolePolarizability () const
  *Does it has dipole polarizability DMS?*
- bool hasDensityMatrixDipoleDipoleHyperpolarizability () const
  *Does it has dipole-dipole hyperpolarizability DMS?*
- bool hasDensityMatrixQuadrupolePolarizability () const
  *Does it has quadrupole polarizability DMS?*

### Accessors

- psi::SharedVector vector (std::string key) const
  *Get the vector data.*
- psi::SharedMatrix matrix (std::string key) const
  *Get the matrix data.*
- std::shared_ptr< oepdev::DMTPole > dmtp (std::string key) const
  *Get the DMTP data.*
- oepdev::SharedOEPotential oep (std::string key) const
  *Get the OEP data.*
- std::vector< psi::SharedMatrix > dpol (std::string key) const
  *Get the DPOL data.*
- psi::SharedBasisSet basisset (std::string key) const
  *Get the basis set data.*
- std::shared_ptr< psi::Matrix > susceptibility (int fieldRank, int fieldGradientRank, int i, int x) const
  *Grab the Density Matrix Susceptibility.*
- std::vector< std::shared_ptr< psi::Matrix > > susceptibility (int fieldRank, int fieldGradientRank, int i) const
  *Grab the Density Matrix Susceptibility.*
- std::vector< std::vector< std::shared_ptr< psi::Matrix > > > susceptibility (int fieldRank, int fieldGradientRank) const
  *Grab the Density Matrix Susceptibility.*
- std::vector< std::vector< std::shared_ptr< psi::Matrix > > > dipole_polarizability () const
  *Grab the density matrix dipole polarizability tensor.*
- std::vector< std::shared_ptr< psi::Matrix > > dipole_polarizability (int i) const
  *Grab the density matrix dipole polarizability tensor's x-th component.*
- std::shared_ptr< psi::Matrix > dipole_polarizability (int i, int x) const
  *Grab the density matrix dipole polarizability tensor's x-th component of the i-th distributed site.*
- std::vector< std::vector< std::shared_ptr< psi::Matrix > > > dipole_dipole_hyperpolarizability () const
  *Grab the density matrix dipole-dipole hyperpolarizability tensor.*
- std::vector< std::shared_ptr< psi::Matrix > > dipole_dipole_hyperpolarizability (int i) const

*Grab the density matrix dipole-dipole hyperpolarizability tensor's x-th component.*
- std::shared_ptr< psi::Matrix > dipole_dipole_hyperpolarizability (int i, int x) const

  *Grab the density matrix dipole-dipole hyperpolarizability tensor's x-th component of the i-th distributed site.*
- std::vector< std::vector< std::shared_ptr< psi::Matrix > > > quadrupole_polarizability () const

  *Grab the density matrix quadrupole polarizability tensor.*
- std::vector< std::shared_ptr< psi::Matrix > > quadrupole_polarizability (int i) const

  *Grab the density matrix quadrupole polarizability tensor's x-th component.*
- std::shared_ptr< psi::Matrix > quadrupole_polarizability (int i, int x) const

  *Grab the density matrix quadrupole polarizability tensor's x-th component of the i-th distributed site.*
- std::vector< std::shared_ptr< psi::Vector > > centres () const

  *Grab the centres' positions.*
- std::shared_ptr< psi::Vector > centre (int i) const

  *Grab the position of the i-th distributed site.*

### DMS Computers

- std::shared_ptr< psi::Matrix > compute_density_matrix (std::shared_ptr< psi::Vector > field)

  *Compute the density matrix due to the uniform electric field perturbation.*
- std::shared_ptr< psi::Matrix > compute_density_matrix (double fx, double fy, double fz)

  *Compute the density matrix due to the uniform electric field perturbation.*
- std::shared_ptr< psi::Matrix > compute_density_matrix (std::vector< std::shared_ptr< psi::Vector >> fields)

  *Compute the density matrix due to the non-uniform electric field perturbation.*
- std::shared_ptr< psi::Matrix > compute_density_matrix (std::vector< std::shared_ptr< psi::Vector >> fields, std::vector< std::shared_ptr< psi::Matrix >> grads)

  *Compute the density matrix due to the non-uniform electric field perturbation.*

## Protected Attributes

### Qualifiers

*Compute the interaction energy between this and other EFP2 fragment.*

**Parameters**

| | |
|---|---|
| par | *- other parameters object* |

- std::string name_

  *The Name of Parameter.*
- std::string type_

  *The Type of Parameter.*
- bool hasDensityMatrixDipolePolarizability_

  *The Name of Parameter.*

- bool hasDensityMatrixDipoleDipoleHyperpolarizability_

  *The Name of Parameter.*
- bool hasDensityMatrixQuadrupolePolarizability_

  *The Name of Parameter.*

### Matrices and Multipoles

- std::vector< std::shared_ptr< psi::Vector > > distributedCentres_

  *The Positions of the Distributed Centres.*
- std::map< std::string, psi::SharedVector > data_vector_

  *Data for Vector Types by Keyword.*
- std::map< std::string, psi::SharedMatrix > data_matrix_

  *Data for Matrix Types by Keyword.*
- std::map< std::string, std::shared_ptr< oepdev::DMTPole > > data_dmtp_

  *Data for DMTP Types by Keyword.*
- std::map< std::string, oepdev::SharedOEPotential > data_oep_

  *Data for OEP Types by Keyword.*
- std::map< std::string, std::vector< psi::SharedMatrix > > data_dpol_

  *Data for DMTP Types by Keyword.*
- std::map< std::string, psi::SharedBasisSet > data_basisset_

  *Data for AO Basis Set by Keyword.*

### Density Matrix Susceptibility

- std::vector< std::vector< std::shared_ptr< psi::Matrix > > > densityMatrixDipolePolarizability_

  *The Density Matrix Dipole Polarizability.*
- std::vector< std::vector< std::shared_ptr< psi::Matrix > > > densityMatrixDipoleDipoleHyperpolarizability_

  *The Density Matrix Dipole-Dipole Hyperpolarizability.*
- std::vector< std::vector< std::shared_ptr< psi::Matrix > > > densityMatrixQuadrupolePolarizability_

  *The Density Matrix Quadrupole Polarizability.*

## Constructor and Destructor

- GenEffPar (std::string name)

  *Create with name of this parameter.*
- GenEffPar (const GenEffPar ∗)

  *Copy Constructor.*
- std::shared_ptr< GenEffPar > clone (void) const

  *Make a deep copy.*
- ∼GenEffPar ()

  *Destruct.*
- virtual void copy_from (const GenEffPar ∗)

  *Deep-copy the matrix and DMTP data.*

### 16.50.1 Detailed Description

**See also**

GenEffFrag, GenEffParFactory

### 16.50.2 Member Function Documentation

#### 16.50.2.1 allocate()

```
void oepdev::GenEffPar::allocate (
            int fieldRank,
            int fieldGradientRank,
            int nsites,
            int nbf )  [inline]
```

**Parameters**

| | |
|---|---|
| *fieldRank* | - power dependency with respect to the electric field $\mathbf{F}$ |
| *fieldGradientRank* | - power dependency with respect to the electric field gradient $\nabla \otimes \mathbf{F}$ |
| *nsites* | - number of distributed sites |
| *nbf* | - number of basis functions in the basis set |

The following susceptibilities are supported (fieldRank, fieldGradientRank):

- (1, 0) - dipole polarizability, interacts with $\mathbf{F}$
- (2, 0) - dipole-dipole hyperpolarizability, interacts with $\mathbf{F} \otimes \mathbf{F}$
- (0, 1) - quadrupole polarizability, interacts with $\nabla \otimes \mathbf{F}$

#### 16.50.2.2 basisset()

```
psi::SharedBasisSet oepdev::GenEffPar::basisset (
            std::string key ) const  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a basis set |

**Returns**

basis set data type

### 16.50.2.3 compute_density_matrix() [1/4]

```
std::shared_ptr<psi::Matrix> oepdev::GenEffPar::compute_density_matrix (
          std::shared_ptr< psi::Vector > field )
```

**Parameters**

| | |
|---|---|
| *field* | - the uniform electric field vector (A.U.) |

### 16.50.2.4 compute_density_matrix() [2/4]

```
psi::SharedMatrix oepdev::GenEffPar::compute_density_matrix (
          double fx,
          double fy,
          double fz )
```

**Parameters**

| | |
|---|---|
| *fx* | - *x*-th Cartesian component of the uniform electric field vector (A.U.) |
| *fy* | - *y*-th Cartesian component of the uniform electric field vector (A.U.) |
| *fz* | - *z*-th Cartesian component of the uniform electric field vector (A.U.) |

### 16.50.2.5 compute_density_matrix() [3/4]

```
std::shared_ptr<psi::Matrix> oepdev::GenEffPar::compute_density_matrix (
          std::vector< std::shared_ptr< psi::Vector >> fields )
```

**Parameters**

| | |
|---|---|
| *fields* | - the list of non-uniform electric field vector (A.U.) evaluated at the distributed DMatPol sites |

#### 16.50.2.6 compute_density_matrix() [4/4]

```
std::shared_ptr<psi::Matrix> oepdev::GenEffPar::compute_density_matrix (
            std::vector< std::shared_ptr< psi::Vector >> fields,
            std::vector< std::shared_ptr< psi::Matrix >> grads )
```

**Parameters**

| | |
|---|---|
| *fields* | - the list of electric field vectors (A.U.) evaluated at the distributed DMatPol sites |
| *grads* | - the list of electric field gradient matrices (A.U.) evaluated at the distributed DMatPol sites |

#### 16.50.2.7 dmtp()

```
std::shared_ptr<oepdev::DMTPole> oepdev::GenEffPar::dmtp (
            std::string key ) const  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a DMTP |

**Returns**

DMTP data type

#### 16.50.2.8 dpol()

```
std::vector<psi::SharedMatrix> oepdev::GenEffPar::dpol (
            std::string key ) const  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a DPOL |

**Returns**

DPOL data type

#### 16.50.2.9 matrix()

```
psi::SharedMatrix oepdev::GenEffPar::matrix (
          std::string key ) const  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a matrix |

**Returns**

matrix data type

#### 16.50.2.10 oep()

```
oepdev::SharedOEPotential oepdev::GenEffPar::oep (
          std::string key ) const  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a OEP |

**Returns**

OEP data type

#### 16.50.2.11 rotate()

```
void oepdev::GenEffPar::rotate (
          psi::SharedMatrix R )
```

**Parameters**

| | |
|---|---|
| *R* | - the rotation matrix |

#### 16.50.2.12 set_basisset()

```
void oepdev::GenEffPar::set_basisset (
          std::string key,
          psi::SharedBasisSet basis )  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a matrix |
| *mat* | - matrix |

This sets the item in the map `data_basisset_`.

### 16.50.2.13 set_dmtp()

```
void oepdev::GenEffPar::set_dmtp (
            std::string key,
            std::shared_ptr< oepdev::DMTPole > mat )  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a DMTP |
| *dmtp* | - DMTP object |

This sets the item in the map `data_dmtp_`.

### 16.50.2.14 set_dpol()

```
void oepdev::GenEffPar::set_dpol (
            std::string key,
            std::vector< psi::SharedMatrix > mats )  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a DPOL |
| *dmtp* | - DPOL object |

This sets the item in the map `data_dpol_`.

### 16.50.2.15 set_matrix()

```
void oepdev::GenEffPar::set_matrix (
            std::string key,
            psi::SharedMatrix mat )  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a matrix |
| *mat* | - matrix |

This sets the item in the map `data_matrix_`.

### 16.50.2.16 set_oep()

```
void oepdev::GenEffPar::set_oep (
          std::string key,
          oepdev::SharedOEPotential oep ) [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a OEP |
| *oep* | - OEP object |

This sets the item in the map `data_oep_`.

### 16.50.2.17 set_susceptibility()

```
void oepdev::GenEffPar::set_susceptibility (
          int fieldRank,
          int fieldGradientRank,
          const std::vector< std::vector< std::shared_ptr< psi::Matrix >>>
& susc ) [inline]
```

**Parameters**

| | |
|---|---|
| *fieldRank* | - power dependency with respect to the electric field $\mathbf{F}$ |
| *fieldGradientRank* | - power dependency with respect to the electric field gradient $\nabla \otimes \mathbf{F}$ |
| *susc* | - the susceptibility tensor |

The following susceptibilities are supported (fieldRank, fieldGradientRank):

- (1, 0) - dipole polarizability, interacts with $\mathbf{F}$
- (2, 0) - dipole-dipole hyperpolarizability, interacts with $\mathbf{F} \otimes \mathbf{F}$
- (0, 1) - quadrupole polarizability, interacts with $\nabla \otimes \mathbf{F}$

### 16.50.2.18 set_vector()

```
void oepdev::GenEffPar::set_vector (
          std::string key,
          psi::SharedVector mat ) [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a vector |
| *mat* | - vector |

This sets the item in the map `data_vector_`.

#### 16.50.2.19 superimpose()

```
void oepdev::GenEffPar::superimpose (
          psi::SharedMatrix targetXYZ,
          std::vector< int > supList )
```

**Parameters**

| | |
|---|---|
| *targetXYZ* | - the target geometry |
| *suplist* | - the superimposition list |

#### 16.50.2.20 susceptibility() [1/3]

```
std::shared_ptr<psi::Matrix> oepdev::GenEffPar::susceptibility (
          int fieldRank,
          int fieldGradientRank,
          int i,
          int x ) const [inline]
```

**Parameters**

| | |
|---|---|
| *fieldRank* | - power dependency with respect to the electric field |
| *fieldGradientRank* | - power dependency with respect to the electric field gradient |
| *i* | - id of the distributed site |
| *x* | - id of the composite Cartesian component |

The following susceptibilities are supported (fieldRank, fieldGradientRank):

- (1, 0) - dipole polarizability, interacts with $\mathbf{F}$
- (2, 0) - dipole-dipole hyperpolarizability, interacts with $\mathbf{F}\otimes\mathbf{F}$
- (0, 1) - quadrupole polarizability, interacts with $\nabla\otimes\mathbf{F}$

The distributed sites are assumed to be atomic sites or molecular orbital centroids (depending on the polarization factory used). For the electric field, the composite Cartesian index is just an ordinary Cartesian index. For the electric field gradient and electric field squared, the composite Cartesian index is given as

$$I(x,y) = 3x + y$$

where the values of 0, 1 and 2 correspond to *x*, *y* and *z* Cartesian components, respectively. Therefore, in the latter case, there is 9 distinct composite Cartesian components.

#### 16.50.2.21 susceptibility() [2/3]

```
std::vector<std::shared_ptr<psi::Matrix> > oepdev::GenEffPar::susceptibility
(
          int fieldRank,
          int fieldGradientRank,
          int i ) const  [inline]
```

**Parameters**

| | |
|---|---|
| *fieldRank* | - power dependency with respect to the electric field |
| *fieldGradientRank* | - power dependency with respect to the electric field gradient |
| *i* | - id of the distributed site |

The following susceptibilities are supported (fieldRank, fieldGradientRank):

- (1, 0) - dipole polarizability, interacts with $\mathbf{F}$
- (2, 0) - dipole-dipole hyperpolarizability, interacts with $\mathbf{F}\otimes\mathbf{F}$
- (0, 1) - quadrupole polarizability, interacts with $\nabla\otimes\mathbf{F}$

The distributed sites are assumed to be atomic sites or molecular orbital centroids (depending on the polarization factory used).

#### 16.50.2.22 susceptibility() [3/3]

```
std::vector<std::vector<std::shared_ptr<psi::Matrix> > > oepdev::GenEffPar::susceptibil
(
          int fieldRank,
          int fieldGradientRank ) const  [inline]
```

**Parameters**

| | |
|---|---|
| *fieldRank* | - power dependency with respect to the electric field |
| *fieldGradientRank* | - power dependency with respect to the electric field gradient |

The following susceptibilities are supported (fieldRank, fieldGradientRank):

- (1, 0) - dipole polarizability, interacts with $\mathbf{F}$
- (2, 0) - dipole-dipole hyperpolarizability, interacts with $\mathbf{F}\otimes\mathbf{F}$
- (0, 1) - quadrupole polarizability, interacts with $\nabla\otimes\mathbf{F}$

#### 16.50.2.23 translate()

```
void oepdev::GenEffPar::translate (
          psi::SharedVector t )
```

**Parameters**

| | |
|---|---|
| *t* | - the translation vector |

#### 16.50.2.24 vector()

```
psi::SharedVector oepdev::GenEffPar::vector (
          std::string key ) const  [inline]
```

**Parameters**

| | |
|---|---|
| *key* | - keyword for a vector |

**Returns**

vector data type

The documentation for this class was generated from the following files:

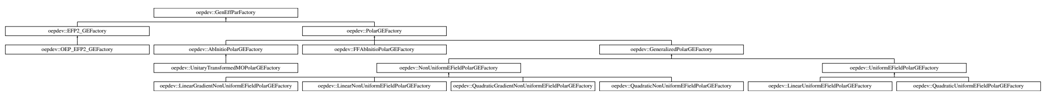
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp.cc

## 16.51 oepdev::GenEffParFactory Class Reference

Generalized Effective Fragment Factory. Abstract Base.

`#include <gefp.h>`

Inheritance diagram for oepdev::GenEffParFactory:


oepdev::GenEffParFactory
oepdev::EFP2_GEFactory
oepdev::PolarGEFactory
oepdev::OEP_EFP2_GEFactory
oepdev::AbInitioPolarGEFactory
oepdev::FFAbInitioPolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UnitaryTransformedMOPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

### Public Member Functions

**Executor of the Factory**

- virtual std::shared_ptr< GenEffPar > compute (void)=0

*Compute the fragment parameters.*

### Accessors

- virtual std::shared_ptr< psi::Wavefunction > wfn (void) const
  *Grab wavefunction.*
- virtual psi::Options & options (void) const
  *Grab options.*
- std::shared_ptr< oepdev::CPHF > cphf_solver () const
  *Grab the CPHF object.*
- std::shared_ptr< oepdev::DMTPole > dmtp () const
  *Grab the DMTP object.*

## Protected Attributes

### Basic data

- std::shared_ptr< psi::Wavefunction > wfn_
  *Wavefunction.*
- psi::Options & options_
  *Psi4 Options.*
- const int nbf_
  *Number of basis functions.*

### Padding of box

- double cx_
  *Centre-of-mass coordinates.*
- double cy_
  *Centre-of-mass coordinates.*
- double cz_
  *Centre-of-mass coordinates.*
- double radius_
  *Radius of padding sphere around the molecule.*

### Container objects

- std::shared_ptr< oepdev::CPHF > cphfSolver_
  *The CPHF object.*
- std::shared_ptr< oepdev::DMTPole > dmtpSolver_
  *The DMTP object.*
- std::shared_ptr< oepdev::QUAMBO > quamboSolver_
  *The QUAMBO object.*

### Other Factories

- std::shared_ptr< oepdev::GenEffParFactory > abInitioPolarizationSusceptibilitiesFactory_
  *Ab initio polarization susceptibility factory.*

### Constructors and Desctructor

- static std::shared_ptr< GenEffParFactory > build (const std::string &type, std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

  *Build Density Matrix Susceptibility Generalized Factory.*
- static std::shared_ptr< GenEffParFactory > build (const std::string &type, std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt, psi::SharedBasisSet aux, psi::SharedBasisSet intermed)

  *Build Density Matrix Susceptibility Generalized Factory.*
- GenEffParFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

  *Construct from wavefunction and Psi4 options.*
- virtual ~GenEffParFactory ()

  *Destruct.*

### Random number generation

- std::default_random_engine randomNumberGenerator_

  *Draw random number.*
- std::uniform_real_distribution< double > randomDistribution_

  *Draw random number.*
- virtual double random_double ()

  *Draw random number.*
- virtual std::shared_ptr< psi::Vector > draw_random_point ()

  *Draw random point in 3D space, excluding the vdW region.*

### Van der Waals region

- std::shared_ptr< psi::Matrix > excludeSpheres_

  *Matrix with vdW sphere information.*
- std::map< std::string, double > vdwRadius_

  *Map with vdW radii.*
- virtual bool is_in_vdWsphere (double x, double y, double z) const

  *Is the point inside a vdW region?*

### 16.51.1 Detailed Description

Describes the GEFP fragment that is in principle designed to work at correlated levels of theory.

**See also**

GenEffPar, GenEffFrag

### 16.51.2 Member Function Documentation

#### 16.51.2.1 build() [1/2]

```
static std::shared_ptr<GenEffParFactory> oepdev::GenEffParFactory::build (
          const std::string & type,
          std::shared_ptr< psi::Wavefunction > wfn,
          psi::Options & opt ) [static]
```

**Parameters**

| | |
|---|---|
| *type* | - Type of factory |
| *wfn* | - Psi4 wavefunction |
| *opt* | - Psi4 options |

Available factory types:

- `POLARIZATION` - creates the polarization generalized effective fragment parameters' factory Factory subtype is specified in Psi4 options (input file).

**Note**

Useful options:

- `POLARIZATION` factory type:
  - `DMATPOL_TRAINING_MODE` - training mode. Default: `EFIELD`
  - `DMATPOL_NSAMPLES` - number of random samples (field or test charges sets). Default: `30`
  - `DMATPOL_FIELD_SCALE` - electric field scale factor (relevant if training mode is `EFIELD`). Default: `0.01` [au]
  - `DMATPOL_NTEST_CHARGE` - number of test charges per sample (relevant if training mode is `CHARGES`). Default: `1`
  - `DMATPOL_TEST_CHARGE` - test charge value (relevant if training mode is `CHARGES`). Default: `0.001` [au]
  - `DMATPOL_FIELD_RANK` - electric field rank. Default: `1`
  - `DMATPOL_GRADIENT_RANK` - electric field gradient rank. Default: `0`
  - `DMATPOL_TEST_FIELD_X` - test electric field in X direction. Default: `0.000` [au]
  - `DMATPOL_TEST_FIELD_Y` - test electric field in Y direction. Default: `0.000` [au]
  - `DMATPOL_TEST_FIELD_Z` - test electric field in Z direction. Default: `0.008` [au]
  - `DMATPOL_OUT_STATS` - output file name for statistical evaluation results. Default: `dmatpol.stats.dat`

  - `DMATPOL_DO_AB_INITIO` - compute ab initio susceptibilities and evaluate statistics for it. Default: `false`
  - `DMATPOL_OUT_STATS_AB_INITIO` - output file name for statistical evaluation results of ab initio model. Default: `dmatpol.stats.abinitio.dat`

#### 16.51.2.2 build() [2/2]

```
static std::shared_ptr<GenEffParFactory> oepdev::GenEffParFactory::build (
          const std::string & type,
          std::shared_ptr< psi::Wavefunction > wfn,
          psi::Options & opt,
          psi::SharedBasisSet aux,
          psi::SharedBasisSet intermed )  [static]
```

**Parameters**

| | |
|---|---|
| *type* | - Type of factory |
| *wfn* | - Psi4 wavefunction |
| *opt* | - Psi4 options |

Available factory types:

- `POLARIZATION` - creates the polarization generalized effective fragment parameters' factory Factory subtype is specified in Psi4 options (input file).

**Note**

Useful options:

- `POLARIZATION` factory type:
  - `DMATPOL_TRAINING_MODE` - training mode. Default: `EFIELD`
  - `DMATPOL_NSAMPLES` - number of random samples (field or test charges sets). Default: `30`
  - `DMATPOL_FIELD_SCALE` - electric field scale factor (relevant if training mode is `EFIELD`). Default: `0.01` [au]
  - `DMATPOL_NTEST_CHARGE` - number of test charges per sample (relevant if training mode is `CHARGES`). Default: `1`
  - `DMATPOL_TEST_CHARGE` - test charge value (relevant if training mode is `CHARGES`). Default: `0.001` [au]
  - `DMATPOL_FIELD_RANK` - electric field rank. Default: `1`
  - `DMATPOL_GRADIENT_RANK` - electric field gradient rank. Default: `0`
  - `DMATPOL_TEST_FIELD_X` - test electric field in X direction. Default: `0.000` [au]
  - `DMATPOL_TEST_FIELD_Y` - test electric field in Y direction. Default: `0.000` [au]

- DMATPOL_TEST_FIELD_Z - test electric field in Z direction. Default: 0.008 [au]
- DMATPOL_OUT_STATS - output file name for statistical evaluation results. Default: dmatpol.stats.dat
- DMATPOL_DO_AB_INITIO - compute ab initio susceptibilities and evaluate statistics for it. Default: false
- DMATPOL_OUT_STATS_AB_INITIO - output file name for statistical evaluation results of ab initio model. Default: dmatpol.stats.abinitio.dat

The documentation for this class was generated from the following files:

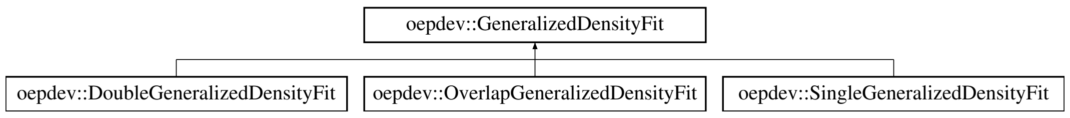
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp.cc

## 16.52 oepdev::GeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme. Abstract Base.

```
#include <oep_gdf.h>
```

Inheritance diagram for oepdev::GeneralizedDensityFit:


oepdev::GeneralizedDensityFit
oepdev::DoubleGeneralizedDensityFit
oepdev::OverlapGeneralizedDensityFit
oepdev::SingleGeneralizedDensityFit

### Public Member Functions

- GeneralizedDensityFit ()

  *Constructor. Initializes the pointers.*
- virtual ~GeneralizedDensityFit ()

  *Destructor.*
- virtual std::shared_ptr< psi::Matrix > compute (void)=0

  *Perform the generalized density fit.*
- std::shared_ptr< psi::Matrix > G (void) const

  *Extract the $G_{\xi i}$ coefficients.*

### Static Public Member Functions

- static std::shared_ptr< GeneralizedDensityFit > build (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::Matrix > v_vector)

  *Factory for Single GDF Computer.*

- static std::shared_ptr< GeneralizedDensityFit > build (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::BasisSet > bs_intermediate, std::shared_ptr< psi::Matrix > v_vector)

  *Factory for Double GDF Computer.*
- static std::shared_ptr< GeneralizedDensityFit > build (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::BasisSet > bs_intermediate, std::shared_ptr< psi::Matrix > v_vector, int dummy)

  *Factory for Overlap GDF Computer.*

## Protected Member Functions

- void invert_matrix (std::shared_ptr< psi::Matrix > &M)

  *Invert a square matrix and check if the inverse is acceptable.*

## Protected Attributes

- std::shared_ptr< psi::Matrix > G_

  *The OEP coefficients* $G_{\xi i}$.
- std::shared_ptr< psi::Matrix > H_

  *The intermediate DF coefficients for* $\hat{v}|i)$.
- std::shared_ptr< psi::Matrix > V_

  *The V matrix* $(\xi|\hat{v}i)$.
- int n_a_

  *Number of auxiliary basis set functions.*
- int n_i_

  *Number of intermediate basis set functions.*
- int n_o_

  *Number of OEP's.*
- std::shared_ptr< psi::BasisSet > bs_a_

  *Basis set: auxiliary.*
- std::shared_ptr< psi::BasisSet > bs_i_

  *Basis set: intermediate.*
- std::shared_ptr< oepdev::IntegralFactory > ints_aa_

  *Integral factory: aux - aux.*
- std::shared_ptr< oepdev::IntegralFactory > ints_ai_

  *Integral factory: aux - int.*
- std::shared_ptr< oepdev::IntegralFactory > ints_ii_

  *Integral factory: int - int.*

### 16.52.1 Detailed Description

Performs the following map:

$$\hat{v}|i) \cong \sum_{\eta} G_{\eta i} |\eta)$$

where $\hat{v}$ is the effective one-electron potential (OEP) operator, $|i)$ is an arbitrary state vector and $|\eta)$ is an auxiliary basis vector. The coefficients $G_{\eta i}$ are stored and define the OEP acting on the state $i$. The mapping onto the auxiliary space can be done in two ways:

- **Single Density Fit.** This method requires the auxiliary basis set to be nearly complete.
- **Double Density Fit.** This method can be used to arbitrary auxiliary basis sets.

### 16.52.2 Member Function Documentation

#### 16.52.2.1 build() [1/3]

```
std::shared_ptr< GeneralizedDensityFit > GeneralizedDensityFit::build (
          std::shared_ptr< psi::BasisSet > bs_auxiliary,
          std::shared_ptr< psi::Matrix > v_vector ) [static]
```

**Parameters**

| | |
|---|---|
| *bs_auxiliary* | - auxiliary basis set |
| *v_vector* | - the matrix with $V_{\xi i}$ elements |

**Returns**

Generalized Density Fit Computer.

#### 16.52.2.2 build() [2/3]

```
std::shared_ptr< GeneralizedDensityFit > GeneralizedDensityFit::build (
          std::shared_ptr< psi::BasisSet > bs_auxiliary,
          std::shared_ptr< psi::BasisSet > bs_intermediate,
          std::shared_ptr< psi::Matrix > v_vector ) [static]
```

**Parameters**

| | |
|---|---|
| *bs_auxiliary* | - auxiliary basis set |
| *bs_intermediate* | - intermediate basis set |
| *v_vector* | - the matrix with $V_{\varepsilon i}$ elements |

**Returns**

Generalized Density Fit Computer.

#### 16.52.2.3 build() [3/3]

```
std::shared_ptr< GeneralizedDensityFit > GeneralizedDensityFit::build (
          std::shared_ptr< psi::BasisSet > bs_auxiliary,
          std::shared_ptr< psi::BasisSet > bs_intermediate,
          std::shared_ptr< psi::Matrix > v_vector,
          int dummy ) [static]
```

**Parameters**

| | |
|---|---|
| *bs_auxiliary* | - auxiliary basis set |
| *bs_intermediate* | - intermediate basis set |
| *v_vector* | - the matrix with $V_{\varepsilon i}$ elements |
| *dummy* | - a dummy variable (not used) |

**Returns**

Generalized Density Fit Computer.

#### 16.52.2.4 compute()

```
std::shared_ptr< psi::Matrix > GeneralizedDensityFit::compute (
          void ) [pure virtual]
```

**Returns**

The OEP coefficients $G_{\xi i}$

Implemented in oepdev::OverlapGeneralizedDensityFit, oepdev::DoubleGeneralizedDensityFit, and oepdev::SingleGeneralizedDensityFit.

The documentation for this class was generated from the following files:

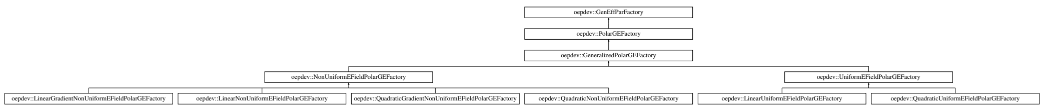
- oepdev/liboep/oep_gdf.h
- oepdev/liboep/oep_gdf.cc

## 16.53 oepdev::GeneralizedPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

```
#include <gefp.h>
```

Inheritance diagram for oepdev::GeneralizedPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

## Classes

- struct StatisticalSet

  *A structure to handle statistical data.*

## Public Member Functions

- GeneralizedPolarGEFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

  *Construct from Psi4 wavefunction and options.*
- virtual ∼GeneralizedPolarGEFactory ()

  *Destruct.*
- virtual std::shared_ptr< GenEffPar > compute (void)

  *Pefrorm Least-Squares Fit.*
- bool has_dipole_polarizability () const

  *Dipole Polarizability (interacting with $\mathbf{F}$)*
- bool has_dipole_dipole_hyperpolarizability () const

  *Dipole-Dipole Hyperpolarizability (interacting with $\mathbf{F}^2$)*
- bool has_quadrupole_polarizability () const

  *Quadrupole Polarizability (interacting with $\nabla \otimes \mathbf{F}$)*
- bool has_ab_initio_dipole_polarizability () const

  *Ab Initio Dipole Polarizability (interacting with $\mathbf{F}$)*
- double Zinit () const

  *Grab initial summaric Z value.*
- double Z () const

  *Grab final summaric Z value.*

## Protected Member Functions

- void allocate (void)

  *Allocate memory.*
- void invert_hessian (void)

  *Invert Hessian (do also the identity test)*

- void compute_electric_field_sums (void)

  *Compute electric field sum set.*
- void compute_electric_field_gradient_sums (void)

  *Compute electric field gradient sum set.*
- void compute_statistics (void)

  *Run the statistical evaluation of results.*
- void set_distributed_centres (void)

  *Set the distributed centres.*
- void compute_parameters (void)

  *Compute the parameters.*
- void fit (void)

  *Perform least-squares fit.*
- void compute_ab_initio (void)

  *Compute ab initio parameters.*
- void save (int i, int j)

  *Save susceptibility tensors associated with the i-th and j-th basis set function.*
- virtual void compute_samples (void)=0

  *Compute samples of density matrices and select electric field distributions.*
- virtual void compute_gradient (int i, int j)=0

  *Compute Gradient vector associated with the i-th and j-th basis set function.*
- virtual void compute_hessian (void)=0

  *Compute Hessian matrix (independent on the parameters)*

## Protected Attributes

- int nBlocks_

  *Number of parameter blocks.*
- int nSites_

  *Number of distributed sites.*
- int nSitesAbInitio_

  *Number of distributed sites of Ab Initio model (FF - single site (com); distributed: LMO sites)*
- int nParameters_

  *Dimensionality of entire parameter space.*
- std::vector< int > nParametersBlock_

  *Dimensionality of parameter space per block.*
- const int nSamples_

  *Number of statistical samples.*
- const double symmetryNumber_ [6]

  *Symmetry number for matrix susceptibilities.*
- std::shared_ptr< psi::Matrix > Gradient_

*Gradient.*

- std::shared_ptr< psi::Matrix > Hessian_

  *Hessian.*
- std::shared_ptr< psi::Matrix > Parameters_

  *Parameters.*
- std::shared_ptr< oepdev::GenEffPar > PolarizationSusceptibilities_

  *Density Matrix Susceptibility Tensors Object.*
- std::shared_ptr< oepdev::GenEffPar > abInitioPolarizationSusceptibilities_

  *Density Matrix Susceptibility Tensors Object for Ab Initio Model.*
- bool hasDipolePolarizability_

  *Has Dipole Polarizability?*
- bool hasDipoleDipoleHyperpolarizability_

  *Has Dipole-Dipole Hyperpolarizability?*
- bool hasQuadrupolePolarizability_

  *Has Quadrupole Polarizability?*
- bool hasAbInitioDipolePolarizability_

  *Has Ab Initio Dipole Polarizability?*
- StatisticalSet referenceStatisticalSet_

  *Reference statistical data.*
- StatisticalSet referenceDpolStatisticalSet_

  *Multipole reference statistical data.*
- StatisticalSet modelStatisticalSet_

  *Model statistical data.*
- StatisticalSet abInitioModelStatisticalSet_

  *Ab Initio Model statistical data.*
- std::vector< std::shared_ptr< psi::Matrix > > VMatrixSet_

  *Potential matrix set.*
- std::vector< std::vector< std::shared_ptr< Vector > > > electricFieldSet_

  *Electric field set.*
- std::vector< std::vector< std::shared_ptr< Matrix > > > electricFieldGradientSet_

  *Electric field gradient set.*
- std::vector< std::vector< double > > electricFieldSumSet_

  *Electric field sum set.*
- std::vector< std::vector< std::shared_ptr< psi::Vector > > > electricFieldGradientSum-Set_

  *Electric field gradient sum set.*
- std::vector< std::vector< std::shared_ptr< Vector > > > abInitioModelElectricFieldSet_

  *Electric field set for Ab Initio Model (LMO-distributed)*
- const double mField_

  *Level shifters for Hessian blocks.*

- double Zinit_

  *Initial summaric Z value.*
- double Z_

  *Final summaric Z value.*
- std::shared_ptr< psi::JK > jk_

  *Computer of generalized JK objects.*

### Additional Inherited Members

### 16.53.1 Detailed Description

Implements a general class of methods for the density matrix susceptibility tensors represented by:

$$\delta D_{\alpha\beta} = \sum_i \left\{ \mathbf{B}_{i;\alpha\beta}^{(10)} \cdot \mathbf{F}(\mathbf{r}_i) + \mathbf{B}_{i;\alpha\beta}^{(20)} : \mathbf{F}(\mathbf{r}_i) \otimes \mathbf{F}(\mathbf{r}_i) + \mathbf{B}_{i;\alpha\beta}^{(01)} : \nabla_i \otimes \mathbf{F}(\mathbf{r}_i) + \ldots \right\}$$

where:

- $\mathbf{B}_{i;\alpha\beta}^{(10)}$ is the density matrix dipole polarizability
- $\mathbf{B}_{i;\alpha\beta}^{(20)}$ is the density matrix dipole-dipole hyperpolarizability
- $\mathbf{B}_{i;\alpha\beta}^{(01)}$ is the density matrix quadrupole polarizability

all defined for the generalized distributed site at $\mathbf{r}_i$.

Available models:

1. Training against uniform electric fields
   - oepdev::LinearUniformEFieldPolarGEFactory - linear with respect to electric field
   - oepdev::QuadraticUniformEFieldPolarGEFactory - quadratic with respect to electric field
2. Training against non-uniform electric fields
   - oepdev::LinearNonUniformEFieldPolarGEFactory - linear with respect to electric field, distributed site model
   - oepdev::QuadraticNonUniformEFieldPolarGEFactory - quadratic with respect to electric field, distributed site model
   - oepdev::LinearGradientNonUniformEFieldPolarGEFactory - linear with respect to electric field and linear with respect to electric field gradient, distributed site model. This model does not function now.
   - oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory - linear with respect to electric field and linear with respect to electric field gradient, distributed site model. This model does not function now.

For the non-linear field training, a set of point charges in each training sample is assumed. Distributed models use atomic centers as expansion points.

### Determination of the generalized susceptibilities

Let $\left\{\mathbf{F}^{(1)}(\mathbf{r}), \mathbf{F}^{(2)}(\mathbf{r}), \ldots, \mathbf{F}^{(N)}(\mathbf{r}), \ldots\right\}$ be a set of $N_{\max}$ distinct and randomly sampled spatial distributions of electric field. It is assumed that the exact difference one-particle density matrices (with respect to the unperturbed state) defined as

$$\delta\overline{\mathbf{D}}^{(N)} \equiv \overline{\mathbf{D}}^{(N)} - \overline{\mathbf{D}}^{(0)}$$

are known for each sample (overline symbolizes the exact estimate). Now, for each pair of the AO indices the following parameterization is constructed:

$$\delta D^{(N)} = \sum_{i}^{M} \left\{ \sum_{u}^{x,y,z} s_{iu}^{[1]} F_{iu}^{(N)} + \sum_{u}^{x,y,z} \sum_{w<u} r_{uw} s_{iuw}^{[2]} F_{iu}^{(N)} F_{iw}^{(N)} + \ldots \right\}$$

(the Greek subscripts were omitted here for notational simplicity). In the above equation, $B_u^{(i;1)} = s_{iu}^{[1]}$ and $B_{uw}^{(i;2)} = r_{uw} s_{iuw}^{[2]}$, where $r_{uw}$ is the symmetry factor equal to 1 for diagonal elements and 2 for off-diagonal elements of $B_{uw}^{(i;2)}$. The multiple parameter blocks ( $\mathbf{s}^{[1]}$, $\mathbf{s}^{[2]}$ and so on) appear in the first power, allowing for linear least-squares regression. The square bracket superscripts denote the block of the parameter space.

To determine the optimum set, $\mathbf{s} = \begin{pmatrix}\mathbf{s}^{[1]} & \mathbf{s}^{[2]} & \cdots\end{pmatrix}^{\mathrm{T}}$, a loss function $Z$ that is subject to the least-squares minimization, is defined as

$$Z(\mathbf{s}) = \sum_{N}^{N_{\max}} \left(\delta D^{(N)} - \delta\overline{D}^{(N)}\right)^2 .$$

The Hessian of $Z$ computed with respect to the parameters is parameter-independent (constant) and generally non-singular as long as the electric fields on all distributed sites are different. Therefore, the exact solution for the optimal parameters is given by the Newton equation

$$\mathbf{s} = -\mathbf{H}^{-1} \cdot \mathbf{g} ,$$

where $\mathbf{g}$ and $\mathbf{H}$ are the gradient vector and the Hessian matrix, respectively. Note that in this case the dimensions of parameter space for the block 1 and 2 are equal to $3M$ and $6M$, respectively. The explicit forms of the gradient and Hessian up to second-order are given in the next section.

### Explicit Formulae for Gradient and Hessian Blocks in Linear Regression DMS Model

The gradient vector $\mathbf{g}$ and the Hessian matrix $\mathbf{H}$ are built from blocks associated with a particular type of parameters, i.e.,

$$\mathbf{g} = \begin{pmatrix}\mathbf{g}^{[1]} \\ \mathbf{g}^{[2]}\end{pmatrix}, \quad \mathbf{H} = \begin{pmatrix}\mathbf{H}^{[11]} & \mathbf{H}^{[12]} \\ \mathbf{H}^{[21]} & \mathbf{H}^{[22]}\end{pmatrix} ,$$

where the block indices 1 and 2 correspond to the first- and second-order susceptibilities, respectively. Note that the second derivatives of $\delta D^{(N)}$ with respect to the adjustable parameters vanish due to the linear functional form of the parameterization formula given in the previous section. Thus, the gradient element of the $r$-th block and Hessian element of the $(rs)$-th block read

$$g^{[r]} \equiv \frac{\partial Z}{\partial s^{[r]}} = -2\sum_{N} \overline{\delta D}^{(N)} \frac{\partial \left[\delta D^{(N)}\right]}{\partial s^{[r]}} ,$$

$$H^{[rs]} \equiv \frac{\partial^2 Z}{\partial s^{[r]} \partial s^{[s]}} = 2\sum_{N} \frac{\partial \left[\delta D^{(N)}\right]}{\partial s^{[r]}} \frac{\partial \left[\delta D^{(N)}\right]}{\partial s^{[s]}} .$$

The explicit formulae for the gradient are

$$g_{ku}^{[1]} = -2\sum_N \overline{\delta D}^{(N)} F_{ku}^{(N)} \ ,$$
$$g_{kuw}^{[2]} = -2r_{uw}\sum_N \overline{\delta D}^{(N)} F_{ku}^{(N)} F_{kw}^{(N)} \ .$$

The Hessian subsequently follows to be %

$$H_{ku,lw}^{[11]} = 2\sum_N F_{ku}^{(N)} F_{lw}^{(N)} \ ,$$
$$H_{ku,lu'w'}^{[12]} = 2r_{u'w'}\sum_N F_{ku}^{(N)} F_{lu'}^{(N)} F_{lw'}^{(N)} \ ,$$
$$H_{kuw,lu'w'}^{[22]} = 2r_{uw}r_{u'w'}\sum_N F_{ku}^{(N)} F_{kw}^{(N)} F_{lu'}^{(N)} F_{lw'}^{(N)} \ .$$

Note that due to the symmetry of the Hessian matrix, the block 21 is a transpose of the block 12. The composite indices $ku$ and $kuw$ are constructed from the distributed site index $k$ and the appropriate symmetry-adapted ( $w < u$) Cartesian component of a particular DMS tensor: $u$ for the first-order, and $uw$ for the second-order susceptibility tensor, respectively. The method described above can be easily extended to third and higher orders.

The documentation for this class was generated from the following files:

- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_base.cc

## 16.54 gefp.math.orthonorm.GrammSchmidt Class Reference

### Public Member Functions

- def __**init**__ (self, V)
- def **normalize** (self)
- def **orthonormalize** (self)
- def **orthogonalize** (self)
- def **orthogonalize_vector** (self, d, normalize=False)
- def **append** (self, d)
- def **proj** (self, u, v)

### Public Attributes

- **V**
- **n**

The documentation for this class was generated from the following file:

- gefp/gefp/math/orthonorm.py

## 16.55 oepdev::GramSchmidt Class Reference

Gram-Schmidt orthogonalization method.

`#include <gram_schmidt.h>`

### Public Member Functions

- GramSchmidt ()

  *Construct the blank Gram-Schmidt Orthonormalizer.*
- GramSchmidt (std::vector< psi::SharedVector > vectors)

  *Construct the Gram-Schmidt Orthonormalizer.*
- virtual ∼GramSchmidt ()

  *Destructor.*
- virtual std::vector< psi::SharedVector > V (void) const

  *Retrieve all the vectors.*
- virtual int L (void) const

  *Retrieve the number of vectors.*
- virtual psi::SharedVector V (int i) const

  *Retrieve the ∗i∗th vector.*
- void normalize (void)

  *Normalize all the vectors.*
- void orthonormalize (void)

  *Orthonormalize all the vectors.*
- void orthogonalize (void)

  *Orthogonalize all the vectors.*
- void orthogonalize_vector (psi::SharedVector &d, bool normalize=false) const

  *Orthogonalize vector with respect to the vector set. Modifies **d**.*
- psi::SharedVector projection (psi::SharedVector u, psi::SharedVector v) const
- void append (psi::SharedVector d)

  *Append new vector to the list.*
- void reset (std::vector< psi::SharedVector > V)

  *Reset by providing new vectors.*
- void reset (void)

  *Reset to empty state.*

### Protected Attributes

- std::vector< psi::SharedVector > V_

  *Vectors stored.*
- int L_

  *Number of vectors.*

### 16.55.1 Detailed Description

Orthonormalize a set of $L$ vectors, i.e.,

$$\{\mathbf{v}_k\} \rightarrow \{\mathbf{u}_k\} \text{ for } k = 1, 2, \ldots, L$$

### Implementation

The orthogonalized vectors are generated according to

$$\mathbf{u}_k = \left[ 1 - \sum_{i=1}^{k-1} \hat{P}_{\mathbf{u}_i} \right] \mathbf{v}_k$$

where the projection operator is given by

$$\hat{P}_{\mathbf{u}} = \frac{1}{u^2} \mathbf{u} [\square \cdot \mathbf{u}]$$

### 16.55.2 Constructor & Destructor Documentation

#### 16.55.2.1 GramSchmidt() [1/2]

```
oepdev::GramSchmidt::GramSchmidt ( )
```

#### 16.55.2.2 GramSchmidt() [2/2]

```
oepdev::GramSchmidt::GramSchmidt (
          std::vector< psi::SharedVector > vectors )
```

**Parameters**

| | |
|---|---|
| *vectors* | - list of vectors to be orthogonalized. |

### 16.55.3 Member Function Documentation

#### 16.55.3.1 projection()

```
psi::SharedVector oepdev::GramSchmidt::projection (
          psi::SharedVector u,
        psi::SharedVector v ) const
```

Compute the projection vector.

**Parameters**

| | |
|---|---|
| *u* | - projected direction |
| *v* | - projected vector |

**Returns**

a new vector $\mathbf{v}'$ such that

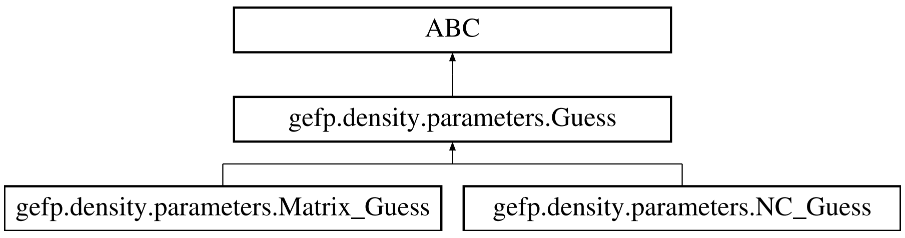
$$\mathbf{v}' = \hat{P}_{\mathbf{u}}\mathbf{v}$$

The documentation for this class was generated from the following files:

- oepdev/libutil/gram_schmidt.h
- oepdev/libutil/gram_schmidt.cc

## 16.56 gefp.density.parameters.Guess Class Reference

Inheritance diagram for gefp.density.parameters.Guess:


ABC
gefp.density.parameters.Guess
gefp.density.parameters.Matrix_Guess
gefp.density.parameters.NC_Guess

### Public Member Functions

- def __**init**__ (self, n=None, c=None, matrix=None)
- def **create** (cls, n=None, c=None, matrix=None, t='matrix')
- def **update** (self, S=None, C=None)
- def **matrix** (self)
- def **copy** (self)
- def **pack** (self)
- def **unpack** (self)
- def __**add**__ (self, other)
- def __**sub**__ (self, other)
- def __**rmul**__ (self, other)

### 16.56.1 Detailed Description

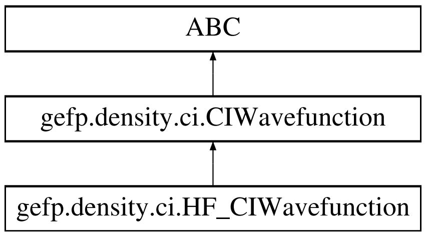
```
\
 Container for handling density matrix guesses for DMFT calculations.
 Contains functionalities for working with occupation numbers,
 natural orbitals and density matrices.
```

The documentation for this class was generated from the following file:

- gefp/gefp/density/parameters.py

## 16.57 gefp.density.ci.HF_CIWavefunction Class Reference

Inheritance diagram for gefp.density.ci.HF_CIWavefunction:


ABC
gefp.density.ci.CIWavefunction
gefp.density.ci.HF_CIWavefunction

### Public Member Functions

- def __**init**__ (self, ref_wfn, E)
- def **make_ci_l** (self)

### Additional Inherited Members

The documentation for this class was generated from the following file:

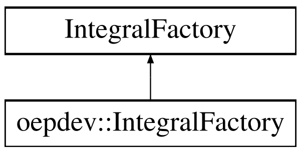
- gefp/gefp/density/ci.py

## 16.58 oepdev::IntegralFactory Class Reference

Extended IntegralFactory for computing integrals.

`#include <integral.h>`

Inheritance diagram for oepdev::IntegralFactory:



## Public Member Functions

- IntegralFactory (std::shared_ptr< psi::BasisSet > bs1, std::shared_ptr< psi::BasisSet > bs2, std::shared_ptr< psi::BasisSet > bs3, std::shared_ptr< psi::BasisSet > bs4)

  *Initialize integral factory given a BasisSet for each center. Becomes (bs1 bs2 | bs3 bs4).*
- IntegralFactory (std::shared_ptr< psi::BasisSet > bs1, std::shared_ptr< psi::BasisSet > bs2)

  *Initialize integral factory given a BasisSet for two centres. Becomes (bs1 bs2 | bs1 bs2).*
- IntegralFactory (std::shared_ptr< psi::BasisSet > bs1)

  *Initialize integral factory given a BasisSet for two centres. Becomes (bs1 bs1 | bs1 bs1).*
- virtual ~IntegralFactory ()

  *Destructor.*
- virtual psi::OneBodyAOInt ∗ ao_efp_multipole_potential_new (int max_k=3, int deriv=0)

  *Returns an improved EFPMultipolePotentialInt.*
- virtual oepdev::TwoBodyAOInt ∗ eri_1_1 (int deriv=0, bool use_shell_pairs=false)

  *Returns an ERI_1_1 integral object.*
- virtual oepdev::TwoBodyAOInt ∗ eri_2_1 (int deriv=0, bool use_shell_pairs=false)

  *Returns an ERI_2_1 integral object.*
- virtual oepdev::TwoBodyAOInt ∗ eri_2_2 (int deriv=0, bool use_shell_pairs=false)

  *Returns an ERI_2_2 integral object.*
- virtual oepdev::TwoBodyAOInt ∗ eri_3_1 (int deriv=0, bool use_shell_pairs=false)

  *Returns an ERI_3_1 integral object.*

### 16.58.1 Detailed Description

In addition to integrals available in Psi4, oepdev::IntegralFactory enables to compute also:

- OEI's:
  - none at that moment
- ERI's:
  - integrals of type (a|b) - `oepdev::ERI_1_1`
  - integrals of type (ab|c) - `oepdev::ERI_2_1`
  - integrals of type (abc|d) - `oepdev::ERI_3_1`
  - integrals of type (ab|cd) - `oepdev::ERI_2_2` (also in Psi4 as `psi::ERI`)

The documentation for this class was generated from the following files:

- oepdev/libpsi/integral.h
- oepdev/libpsi/integral.cc

## 16.59 oepdev::KabschSuperimposer Class Reference

Compute the Cartesian rotation matrix between two structures.

`#include <kabsch_superimposer.h>`

### Public Member Functions

- KabschSuperimposer ()
  *Constructor.*
- ∼KabschSuperimposer ()
  *Destructor.*
- void compute (psi::SharedMatrix initial_xyz, psi::SharedMatrix final_xyz)
  *Run the Kabsch algorithm.*
- void compute (psi::SharedMolecule initial_mol, psi::SharedMolecule final_mol)
  *Run the Kabsch algorithm.*
- psi::SharedMatrix get_transformed (void)
  *Return transformed coordinates $\mathbf{X}'$.*
- double rms (void)
  *Compute RMS or superimposition.*
- void clear (void)
  *Clear all previous calculations.*

### Public Attributes

- psi::SharedMatrix rotation
  *Rotation matrix $\mathbf{r}$.*
- psi::SharedVector translation
  *Translation vector $\mathbf{t}$.*
- psi::SharedMatrix initial_xyz
  *Initial xyz $\mathbf{X}$.*
- psi::SharedMatrix final_xyz
  *Final xyz $\mathbf{X}_0$.*

### 16.59.1 Detailed Description

The superimposition is defined as:

$$\mathbf{X}' = \mathbf{t} + \mathbf{X} \cdot \mathbf{r} \approx \mathbf{X}_0$$

where $X_{iu}$ is the *u*-th Cartesian component of the *i*-th atom's position, $\mathbf{t}$ is the superimposition translation vector, $\mathbf{r}$ is the superimposition rotation matrix, and prime denotes transformed coordinates.

The superimposition uses the Kabsch algorithm.

### The Kabsch Algorithm.

Rotation matrix is calculated from
$$\mathbf{r} = \mathbf{U} \cdot \mathbf{V}^{\mathrm{T}}$$
where
$$\mathbf{A} = \mathbf{U} \cdot \mathbf{S} \cdot \mathbf{V}^{\mathrm{T}}$$
is the singular value decomposition of the covariance matrix
$$\mathbf{A} = [\mathbf{X} - \langle \mathbf{X} \rangle]^{\mathrm{T}} \cdot [\mathbf{X}_0 - \langle \mathbf{X}_0 \rangle]$$
The average of position is given by
$$\langle \mathbf{X} \rangle_u = \frac{1}{N} \sum_i X_{iu}$$
where *N* is the number of atoms. If determinant of rotation matrix is negative (indicating inversion), rotation matrix is recomputed by inverting the sign of the third column of $\mathbf{V}$.

The translation vector is then calculated by
$$\mathbf{t} = \langle \mathbf{X}_0 \rangle - \langle \mathbf{X} \rangle \cdot \mathbf{r}$$

## 16.59.2 Member Function Documentation

### 16.59.2.1 compute() [1/2]

```
void oepdev::KabschSuperimposer::compute (
          psi::SharedMatrix initial_xyz,
          psi::SharedMatrix final_xyz )
```

**Parameters**

| | |
|---|---|
| *initial_xyz* | - position vectors $\mathbf{X}$ |
| *final_xyz* | - position vectors $\mathbf{X}_0$ |

### 16.59.2.2 compute() [2/2]

```
void oepdev::KabschSuperimposer::compute (
          psi::SharedMolecule initial_mol,
          psi::SharedMolecule final_mol )  [inline]
```

**Parameters**

| | |
|---|---|
| *initial_mol* | - molecule with atomic positions at $\mathbf{X}$ |
| *final_mol* | - molecule with atomic positions at $\mathbf{X}_0$ |

The documentation for this class was generated from the following files:

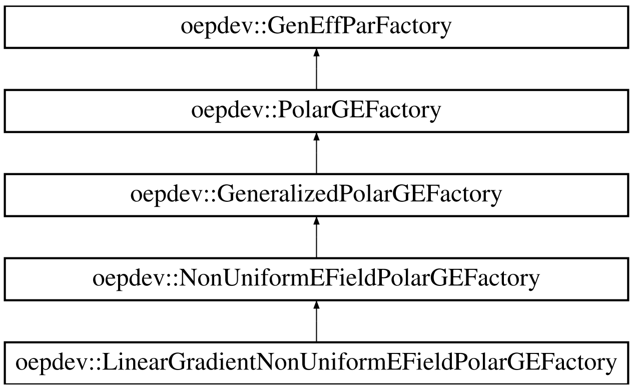
- oepdev/libutil/kabsch_superimposer.h
- oepdev/libutil/kabsch_superimposer.cc

## 16.60 oepdev::LinearGradientNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

```
#include <gefp.h>
```

Inheritance diagram for oepdev::LinearGradientNonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory

### Public Member Functions

- **LinearGradientNonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  *Compute Gradient vector associated with the i-th and j-th basis set function.*
- void compute_hessian (void)

  *Compute Hessian matrix (independent on the parameters)*

### Additional Inherited Members

### 16.60.1 Detailed Description

Implements the generalized density matrix susceptibility model of the form

$$\delta D_{\alpha\beta} \approx \sum_i \left\{ \mathbf{B}^{(10)}_{i;\alpha\beta} \cdot \mathbf{F}(\mathbf{r}_i) + \mathbf{B}^{(01)}_{i;\alpha\beta} : \nabla_i \otimes \mathbf{F}(\mathbf{r}_i) \right\}$$

where:

- $\mathbf{B}^{(10)}_{i;\alpha\beta}$ is the density matrix dipole polarizability
- $\mathbf{B}^{(01)}_{i;\alpha\beta}$ is the density matrix quadrupole polarizability all defined for the distributed site at $\mathbf{r}_i$.

**Note**

This model is not available now and probably will be deprecated in the future.

The documentation for this class was generated from the following files:

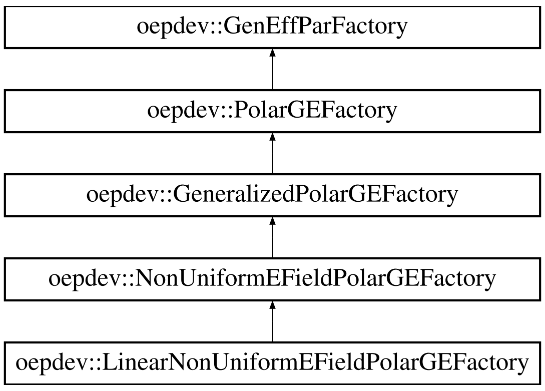
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_1_grad_1.cc

## 16.61 oepdev::LinearNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

```
#include <gefp.h>
```

Inheritance diagram for oepdev::LinearNonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory

### Public Member Functions

- **LinearNonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  *Compute Gradient vector associated with the i-th and j-th basis set function.*
- void compute_hessian (void)

  *Compute Hessian matrix (independent on the parameters)*

### Additional Inherited Members

### 16.61.1 Detailed Description

Implements the generalized density matrix susceptibility model of the form

$$\delta D_{\alpha\beta} \approx \sum_i \mathbf{B}_{i;\alpha\beta}^{(10)} \cdot \mathbf{F}(\mathbf{r}_i)$$

where:

- $\mathbf{B}_{i;\alpha\beta}^{(10)}$ is the density matrix dipole polarizability defined for the distributed site at $\mathbf{r}_i$.

The documentation for this class was generated from the following files:

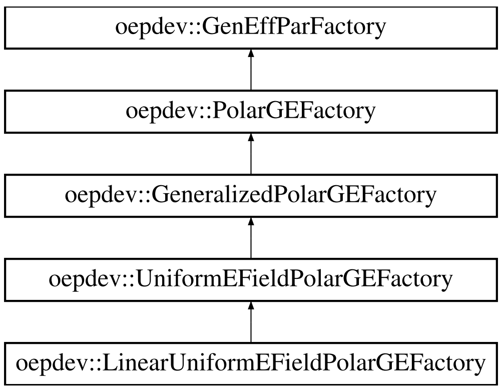
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_1.cc

## 16.62 oepdev::LinearUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::LinearUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory

### Public Member Functions

- **LinearUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  *Compute Gradient vector associated with the i-th and j-th basis set function.*
- void compute_hessian (void)

  *Compute Hessian matrix (independent on the parameters)*

### Additional Inherited Members

### 16.62.1 Detailed Description

Implements the generalized density matrix susceptibility model of the form

$$\delta D_{\alpha\beta} \approx \mathbf{B}_{\alpha\beta}^{(10)} \cdot \mathbf{F}$$

where:

- $\mathbf{B}_{\alpha\beta}^{(10)}$ is the density matrix dipole polarizability

The documentation for this class was generated from the following files:

- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_uniform_field_1.cc

## 16.63 gefp.density.population.Loc Class Reference

### Public Member Functions

- def **__init__** (self, wfn, method='BOYS')
- def **lmoc** (self)
- def **el_charges** (self)
- def **el_dipoles** (self)
- def **el_quadrupoles** (self)
- def **__repr__** (self)

### Public Attributes

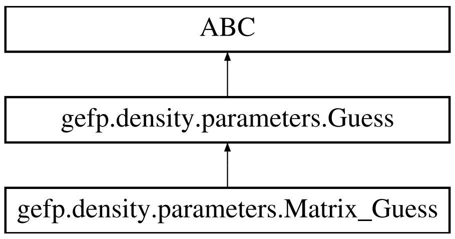
- **wfn**
- **method**
- **La**
- **Lb**
- **Ua**
- **Ub**

The documentation for this class was generated from the following file:

- gefp/gefp/density/population.py

## 16.64 gefp.density.parameters.Matrix_Guess Class Reference

Inheritance diagram for gefp.density.parameters.Matrix_Guess:


ABC
gefp.density.parameters.Guess
gefp.density.parameters.Matrix_Guess

### Public Member Functions

- def **__init__** (self, n=None, c=None, matrix=None)
- def **pack** (self)

The documentation for this class was generated from the following file:

- gefp/gefp/density/parameters.py

## 16.65 oepdev::MultipoleConvergence Class Reference

Multipole Convergence.

```
#include <dmtp.h>
```

### Public Types

- enum ConvergenceLevel {
  **R1**, **R2**, **R3**, **R4**,
  **R5** }
- enum Property { **Energy**, **Potential**, **Field** }

### Public Member Functions

- MultipoleConvergence (std::shared_ptr< DMTPole > dmtp1, std::shared_ptr< DMTPole > dmtp2, ConvergenceLevel max_clevel=R5)

  *Construct from two shared DMTPole objects.*
- virtual ~MultipoleConvergence ()

  *Destructor.*
- void compute (Property property=Energy)
- void compute (const double &x, const double &y, const double &z, Property property=Potential)
- std::shared_ptr< psi::Matrix > level (ConvergenceLevel clevel=R5)

## Protected Member Functions

- void compute_energy ()

  *Compute the generalized energy.*
- void compute_potential (const double &x, const double &y, const double &z)

  *Compute the generalized potential.*
- void compute_field (const double &x, const double &y, const double &z)

  *Compute the generalized field potential.*

## Protected Attributes

- ConvergenceLevel max_clevel_

  *Maximum allowed convergence level.*
- std::shared_ptr< DMTPole > dmtp_1_

  *First DMTP set.*
- std::shared_ptr< DMTPole > dmtp_2_

  *Second DMTP set.*
- std::map< std::string, std::shared_ptr< psi::Matrix > > convergenceList_

  *Dictionary of available convergence level results.*
- std::map< std::string, std::shared_ptr< psi::Matrix > > energyConvergencePairs_

  *Dictionary of available energy convergence pairs.*

### 16.65.1 Detailed Description

Handles the convergence of the distributed multipole expansions up to hexadecapole. Takes shared pointers to existing DMTPole objects and computes the generalized property:

- energy
- potential from the DMTP sets. The results are stored in matrix of size (N1, N2) where N1 and N2 are equal to the number of DMTP's in a set decribed by according DMTPole object given.

**Note**

Useful options:

- `DMTP_CONVER` - level of multipole series convergence (available: `R1`, `R2`, `R3`, `R4` and `R5`). Default: `R5`.

**See also**

DMTPole

### 16.65.2 Member Enumeration Documentation

#### 16.65.2.1 ConvergenceLevel

`enum oepdev::MultipoleConvergence::ConvergenceLevel`

Convergence level of the multipole expansion:

**Parameters**

| | |
|---|---|
| *R1* | - qq term |
| *R2* | - qd and sum of the above |
| *R3* | - qQ, dd and sum of the above |
| *R4* | - qO, dQ and sum of the above |
| *R5* | - qH, dO, QQ and sum of the above |

#### 16.65.2.2 Property

`enum oepdev::MultipoleConvergence::Property`

Property to be evaluated from DMTP's:

**Parameters**

| | |
|---|---|
| *Energy* | - generalized energy |
| *Field* | - generalized field |
| *Potential* | - generalized potential |

### 16.65.3 Constructor & Destructor Documentation

#### 16.65.3.1 MultipoleConvergence()

```
oepdev::MultipoleConvergence::MultipoleConvergence (
            std::shared_ptr< DMTPole > dmtp1,
            std::shared_ptr< DMTPole > dmtp2,
            MultipoleConvergence::ConvergenceLevel max_clevel = R5 )
```

**Parameters**

| | |
|---|---|
| *dmtp1* | - first DMTPole object |

**Parameters**

| | |
|---|---|
| *dmtp2* | - second DMTPole object |
| *max_clevel* | - maximul allowed convergence level |

### 16.65.4 Member Function Documentation

#### 16.65.4.1 compute() [1/2]

```
void oepdev::MultipoleConvergence::compute (
            MultipoleConvergence::Property property = Energy )
```

Compute the generalized interaction property

**Parameters**

| | |
|---|---|
| *property* | - generalized Property |

#### 16.65.4.2 compute() [2/2]

```
void oepdev::MultipoleConvergence::compute (
            const double & x,
            const double & y,
            const double & z,
            MultipoleConvergence::Property property = Potential )
```

Compute the generalized generator property

**Parameters**

| | |
|---|---|
| *x* | - location *x*-th Cartesian component |
| *y* | - location *y*-th Cartesian component |
| *z* | - location *z*-th Cartesian component |
| *property* | - generalized Property |

#### 16.65.4.3 level()

```
std::shared_ptr< psi::Matrix > oepdev::MultipoleConvergence::level (
            MultipoleConvergence::ConvergenceLevel clevel = R5 )
```

Grab the generalized property at specified level of convergence

**Parameters**

|  |  |
|---|---|
| *clevel* | - ConvergenceLevel |

**Returns**

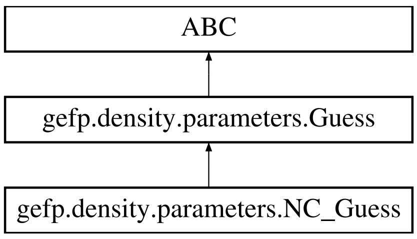
vector of results (each element corresponds to each DMTP pair in a set)

The documentation for this class was generated from the following files:

- oepdev/lib3d/dmtp.h
- oepdev/lib3d/dmtp_base.cc

## 16.66 gefp.density.parameters.NC_Guess Class Reference

Inheritance diagram for gefp.density.parameters.NC_Guess:


ABC
gefp.density.parameters.Guess
gefp.density.parameters.NC_Guess

### Public Member Functions

- def **__init__** (self, n=None, c=None, matrix=None)
- def **pack** (self)

The documentation for this class was generated from the following file:

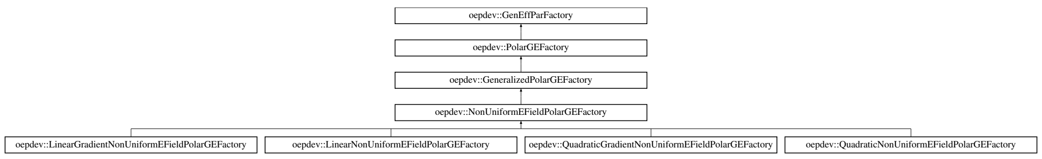
- gefp/gefp/density/parameters.py

## 16.67 oepdev::NonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

```
#include <gefp.h>
```

Inheritance diagram for oepdev::NonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory

### Public Member Functions

- **NonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_samples (void)

  *Compute samples of density matrices and select electric field distributions.*
- virtual void compute_gradient (int i, int j)=0

  *Compute Gradient vector associated with the i-th and j-th basis set function.*
- virtual void compute_hessian (void)=0

  *Compute Hessian matrix (independent on the parameters)*

### Additional Inherited Members

### 16.67.1 Detailed Description

Implements a class of density matrix susceptibility models for parameterization in the non-uniform electric field generated by point charges.

The documentation for this class was generated from the following files:

- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_base.cc

## 16.68 oepdev::ObaraSaikaTwoCenterEFPRecursion_New Class Reference

Obara-Saika recursion formulae for improved EFP multipole potential integrals.

```
#include <osrecur.h>
```

### Public Member Functions

- ObaraSaikaTwoCenterEFPRecursion_New & **operator=** (const ObaraSaikaTwoCenterEFPRecursion_New &)
- ObaraSaikaTwoCenterEFPRecursion_New (int max_am1, int max_am2, int max_k)
- double $***$ q () const

  *Returns the potential integral 3D matrix.*
- double $***$ **x** () const

- double ∗∗∗ **y** () const
- double ∗∗∗ **z** () const
- double ∗∗∗ **xx** () const
- double ∗∗∗ **yy** () const
- double ∗∗∗ **zz** () const
- double ∗∗∗ **xy** () const
- double ∗∗∗ **xz** () const
- double ∗∗∗ **yz** () const
- double ∗∗∗ **xxx** () const
- double ∗∗∗ **yyy** () const
- double ∗∗∗ **zzz** () const
- double ∗∗∗ **xxy** () const
- double ∗∗∗ **xxz** () const
- double ∗∗∗ **xyy** () const
- double ∗∗∗ **yyz** () const
- double ∗∗∗ **xzz** () const
- double ∗∗∗ **yzz** () const
- double ∗∗∗ **xyz** () const
- virtual void compute (double PA[3], double PB[3], double PC[3], double zeta, int am1, int am2)

  *Computes the potential integral 3D matrix using the data provided.*

## Protected Member Functions

- void **calculate_f** (double ∗F, int n, double t)

## Protected Attributes

- int **max_am1_**
- int **max_am2_**
- int **size_**
- bool **do_octupoles_**
- double ∗∗∗ **q_**
- double ∗∗∗ **x_**
- double ∗∗∗ **y_**
- double ∗∗∗ **z_**
- double ∗∗∗ **xx_**
- double ∗∗∗ **xy_**
- double ∗∗∗ **xz_**
- double ∗∗∗ **yy_**
- double ∗∗∗ **yz_**
- double ∗∗∗ **zz_**

- double ∗∗∗ **xxx_**
- double ∗∗∗ **xxy_**
- double ∗∗∗ **xxz_**
- double ∗∗∗ **xyy_**
- double ∗∗∗ **xyz_**
- double ∗∗∗ **xzz_**
- double ∗∗∗ **yyy_**
- double ∗∗∗ **yyz_**
- double ∗∗∗ **yzz_**
- double ∗∗∗ **zzz_**

### 16.68.1 Constructor & Destructor Documentation

#### 16.68.1.1 ObaraSaikaTwoCenterEFPRecursion_New()

```
oepdev::ObaraSaikaTwoCenterEFPRecursion_New::ObaraSaikaTwoCenterEFPRecursion_New
(
            int max_am1,
            int max_am2,
            int max_k )
```

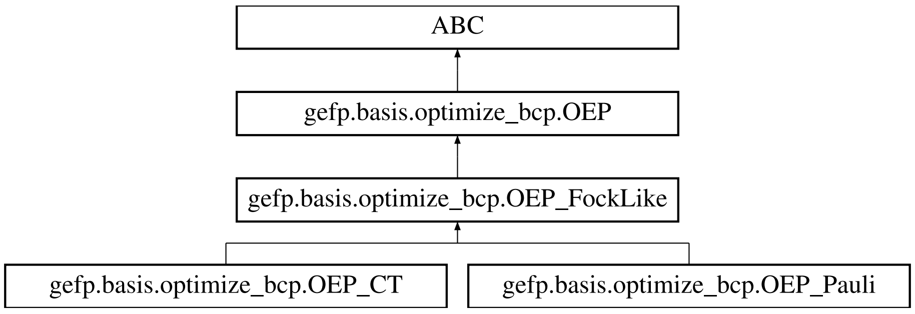
Constructor, max_am1 and max_am2 are the max angular momentum on center 1 and 2. Needed to allocate enough memory.

The documentation for this class was generated from the following files:

- oepdev/libpsi/osrecur.h
- oepdev/libpsi/osrecur.cc

## 16.69 gefp.basis.optimize_bcp.OEP Class Reference

Inheritance diagram for gefp.basis.optimize_bcp.OEP:


ABC
gefp.basis.optimize_bcp.OEP
gefp.basis.optimize_bcp.OEP_FockLike
gefp.basis.optimize_bcp.OEP_CT
gefp.basis.optimize_bcp.OEP_Pauli

### Public Member Functions

- def **__init__** (self, wfn, dfbasis)
- def **create** (cls, name, wfn, dfbasis)
- def **compute** (self)
- def **compute_and_save_V** (self, name='vints.dat')

### Public Attributes

- **wfn**
- **dfbasis**
- **basis_test**
- **basis_prim**
- **basis_aux**
- **V**

### Static Public Attributes

- bool **read_vints** = True

### 16.69.1 Detailed Description

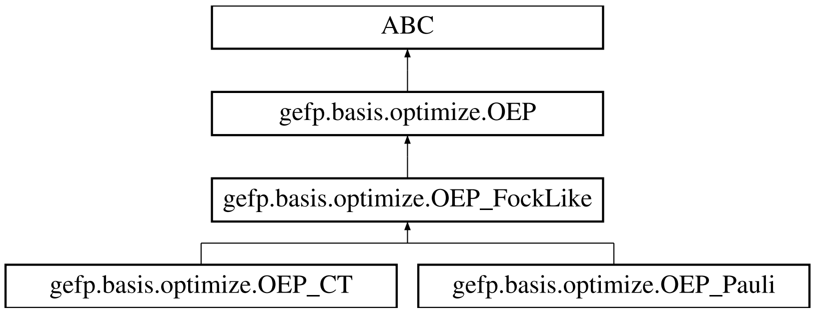
```
OEP object that defines the V matrix necessary for GDF.
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize_bcp.py

## 16.70 gefp.basis.optimize.OEP Class Reference

Inheritance diagram for gefp.basis.optimize.OEP:


ABC
gefp.basis.optimize.OEP
gefp.basis.optimize.OEP_FockLike
gefp.basis.optimize.OEP_CT
gefp.basis.optimize.OEP_Pauli

### Public Member Functions

- def **__init__** (self, wfn, dfbasis)
- def **create** (cls, name, wfn, dfbasis)
- def **compute** (self)
- def **compute_and_save_V** (self, name='vints.dat')

### Public Attributes

- **wfn**
- **dfbasis**
- **basis_test**
- **basis_prim**
- **basis_aux**
- **V**

### Static Public Attributes

- bool **read_vints** = True

### 16.70.1 Detailed Description

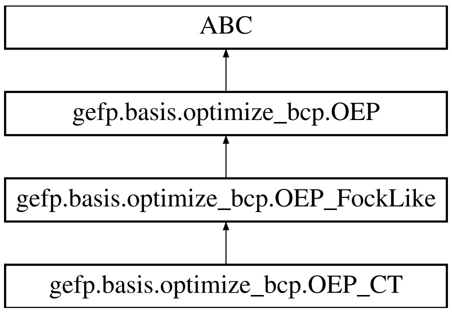
```
OEP object that defines the V matrix necessary for GDF.
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize.py

## 16.71 gefp.basis.optimize_bcp.OEP_CT Class Reference

Inheritance diagram for gefp.basis.optimize_bcp.OEP_CT:


ABC
gefp.basis.optimize_bcp.OEP
gefp.basis.optimize_bcp.OEP_FockLike
gefp.basis.optimize_bcp.OEP_CT

### Public Member Functions

- def __**init**__ (self, wfn, dfbasis)

### Additional Inherited Members

### 16.71.1 Detailed Description

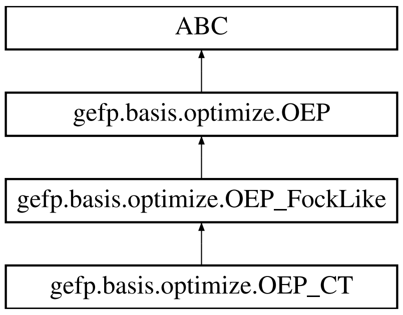
```
OEP for Group-(i) term of Otto-Ladik's theory of Charge-Transfer Energy
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize_bcp.py

## 16.72 gefp.basis.optimize.OEP_CT Class Reference

Inheritance diagram for gefp.basis.optimize.OEP_CT:



### Public Member Functions

- def __**init**__ (self, wfn, dfbasis)

### Additional Inherited Members

### 16.72.1 Detailed Description

```
OEP for Group-(i) term of Otto-Ladik's theory of Charge-Transfer Energy
```

The documentation for this class was generated from the following file:

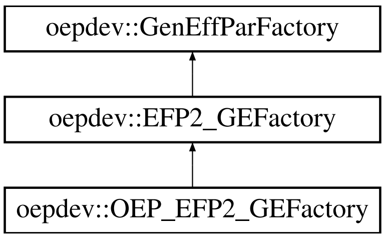
- gefp/gefp/basis/optimize.py

## 16.73 oepdev::OEP_EFP2_GEFactory Class Reference

OEP-EFP2 GEFP Factory.

`#include <gefp.h>`

Inheritance diagram for oepdev::OEP_EFP2_GEFactory:



### Public Member Functions

- OEP_EFP2_GEFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

    *Construct from Psi4 options.*
- OEP_EFP2_GEFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt, psi::SharedBasisSet aux, psi::SharedBasisSet intermed)

    *Construct from Psi4 options and additional basis sets.*
- virtual ∼OEP_EFP2_GEFactory ()

    *Destruct.*
- virtual std::shared_ptr< GenEffPar > compute (void)

    *Compute the OEP-EFP2 parameters.*

### Protected Member Functions

- virtual void **assemble_canonical_orbitals** (void) override
- virtual void **assemble_oep_efp2_parameters** (void)
- virtual void **assemble_oep_lmo_centroids** (void)

### Protected Attributes

- psi::SharedBasisSet **auxiliary_**
- psi::SharedBasisSet **intermediate_**
- oepdev::SharedOEPotential **oep_rep_**
- oepdev::SharedOEPotential **oep_ct_**

### Additional Inherited Members

### 16.73.1 Detailed Description

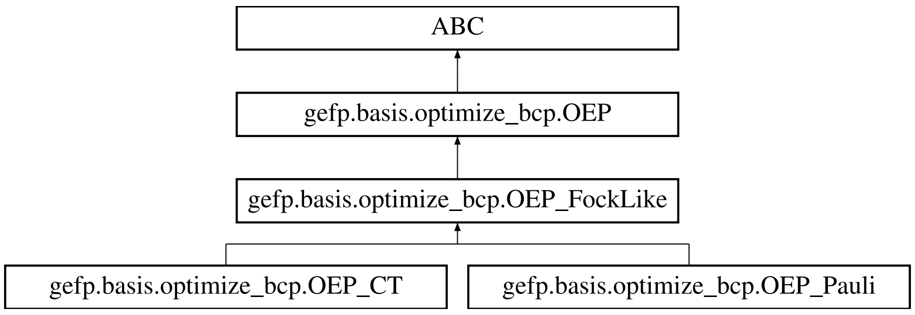
Basic interface for the OEP-EFP2 parameters.

The documentation for this class was generated from the following files:

- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_oep_efp2.cc

## 16.74 gefp.basis.optimize_bcp.OEP_FockLike Class Reference

Inheritance diagram for gefp.basis.optimize_bcp.OEP_FockLike:


ABC
gefp.basis.optimize_bcp.OEP
gefp.basis.optimize_bcp.OEP_FockLike
gefp.basis.optimize_bcp.OEP_CT
gefp.basis.optimize_bcp.OEP_Pauli

### Public Member Functions

- def **__init__** (self, wfn, dfbasis)

### Additional Inherited Members

### 16.74.1 Detailed Description

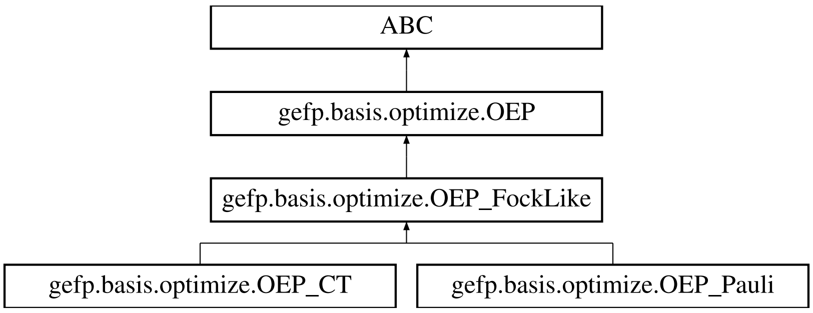
```
OEP for S1 term in Murrell et al.'s theory of Pauli repulsion
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize_bcp.py

## 16.75 gefp.basis.optimize.OEP_FockLike Class Reference

Inheritance diagram for gefp.basis.optimize.OEP_FockLike:


ABC
gefp.basis.optimize.OEP
gefp.basis.optimize.OEP_FockLike
gefp.basis.optimize.OEP_CT
gefp.basis.optimize.OEP_Pauli

### Public Member Functions

- def __**init**__ (self, wfn, dfbasis)

### Additional Inherited Members

### 16.75.1 Detailed Description

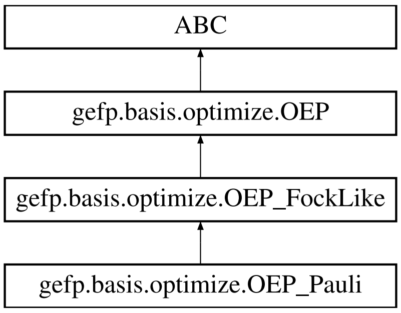
```
OEP for S1 term in Murrell et al.'s theory of Pauli repulsion
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize.py

## 16.76 gefp.basis.optimize.OEP_Pauli Class Reference

Inheritance diagram for gefp.basis.optimize.OEP_Pauli:


ABC
gefp.basis.optimize.OEP
gefp.basis.optimize.OEP_FockLike
gefp.basis.optimize.OEP_Pauli

### Public Member Functions

- def __**init**__ (self, wfn, dfbasis)

### Additional Inherited Members

### 16.76.1 Detailed Description

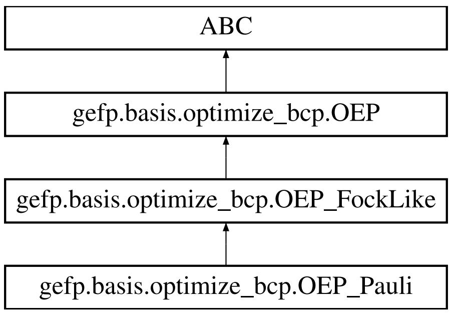
```
OEP for S1 term in Murrell et al.'s theory of Pauli repulsion
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/optimize.py

## 16.77 gefp.basis.optimize_bcp.OEP_Pauli Class Reference

Inheritance diagram for gefp.basis.optimize_bcp.OEP_Pauli:


ABC
gefp.basis.optimize_bcp.OEP
gefp.basis.optimize_bcp.OEP_FockLike
gefp.basis.optimize_bcp.OEP_Pauli

### Public Member Functions

- def **__init__** (self, wfn, dfbasis)

### Additional Inherited Members

### 16.77.1 Detailed Description

```
OEP for S1 term in Murrell et al.'s theory of Pauli repulsion
```

The documentation for this class was generated from the following file:

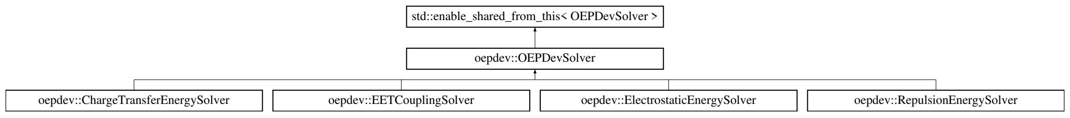
- gefp/gefp/basis/optimize_bcp.py

## 16.78 oepdev::OEPDevSolver Class Reference

Solver of properties of molecular aggregates. Abstract base.

`#include <solver.h>`

Inheritance diagram for oepdev::OEPDevSolver:


std::enable_shared_from_this< OEPDevSolver >
oepdev::OEPDevSolver
oepdev::ChargeTransferEnergySolver
oepdev::EETCouplingSolver
oepdev::ElectrostaticEnergySolver
oepdev::RepulsionEnergySolver

## Public Member Functions

- OEPDevSolver (SharedWavefunctionUnion wfn_union)

  *Take wavefunction union and initialize the Solver.*
- virtual ∼OEPDevSolver ()

  *Destroctor.*
- virtual double compute_oep_based (const std::string &method="DEFAULT")=0

  *Compute property by using OEP's.*
- virtual double compute_benchmark (const std::string &method="DEFAULT")=0

  *Compute property by using benchmark method.*

## Static Public Member Functions

- static std::shared_ptr< OEPDevSolver > build (const std::string &target, SharedWavefunctionUnion wfn_union)

  *Build a solver of a particular property for given molecular cluster.*

## Protected Attributes

- SharedWavefunctionUnion wfn_union_

  *Wavefunction union.*
- psi::Options & options_

  *Options.*
- std::vector< std::string > methods_oepBased_

  *Names of all OEP-based methods implemented for a solver.*
- std::vector< std::string > methods_benchmark_

  *Names of all benchmark methods implemented for a solver.*

## 16.78.1 Detailed Description

Uses only a wavefunction union object to initialize.

## Available solvers

- `ELECTROSTATIC ENERGY`
- `REPULSION ENERGY`
- `CHARGE TRANSFER ENERGY`
- `EET COUPLING CONSTANT`

## Options

### Interaction Property Method

- `OEPDEV_SOLVER_EINT_COUL_AO` - Coulombic energy: AO expanded
- `OEPDEV_SOLVER_EINT_COUL_MO` - Coulombic energy: MO expanded
- `OEPDEV_SOLVER_EINT_COUL_ESP` - Coulombic energy: ESP
- `OEPDEV_SOLVER_EINT_COUL_CAMM` - Coulombic energy: CAMM
- `OEPDEV_SOLVER_EINT_REP_HS` - Exchange-repulsion energy: Hayes-Stone
- `OEPDEV_SOLVER_EINT_REP_DDS` - Exchange-repulsion energy: DDS
- `OEPDEV_SOLVER_EINT_REP_MRW` - Exchange-repulsion energy: Murrell et al.
- `OEPDEV_SOLVER_EINT_REP_OL` - Exchange-repulsion energy: Otto-Ladik
- `OEPDEV_SOLVER_EINT_REP_OEP1` - Exchange-repulsion energy: OEP (S1: GDF, S2: ESP)
- `OEPDEV_SOLVER_EINT_REP_OEP2` - Exchange-repulsion energy: OEP (S1: GDF, S2: CAMM)
- `OEPDEV_SOLVER_EINT_REP_EFP2` - Exchange-repulsion energy: EFP2
- `OEPDEV_SOLVER_EINT_CT_OL` - Charge-transfer energy: Otto-Ladik
- `OEPDEV_SOLVER_EINT_CT_OEP` - Charge-transfer energy: OEP
- `OEPDEV_SOLVER_EINT_CT_EFP2` - Charge-transfer energy: EFP2

### Generalized density fitting (GDF) options:

- `OEPDEV_DF_TYPE` - type of the GDF. Default: `DOUBLE`. Other: `SINGLE`.
- `DF_BASIS_OEP` - auxiliary basis set. Default: `sto-3g`.
- `DF_BASIS_INT` - intermediate basis set. Relevant only if double GDF is used. Default: `aug-cc-pVDZ-jkfit`. Note that intermediate basis set should be nearly complete.

#### EFP2 Charge transfer energy options:

- `EFP2_CT_POTENTIAL_INTS` - Type of potential one-electron operator. Default: 'DMTP'. Other: 'ERI'.
- `EFP2_CT_NO_OCTUPOLES` - Ignore octupole moments from potential integrals? Default: `True`.

#### Excited States

- `EXCITED_STATE` - ID of state for all monomers to consider. If `-n`, then the ∗n∗th bright state is taken. Default: `-1`.
- `EXCITED_STATE_A` - ID of state for monomer A to consider. If `-n`, then the ∗n∗th bright state is taken. Default: `-1`.
- `EXCITED_STATE_B` - ID of state for monomer B to consider. If `-n`, then the ∗n∗th bright state is taken. Default: `-1`.
- `OSCILLATOR_STRENGTH_THRESHOLD` - Threshold for oscillator strength for bright states selection. Default: `0.01`.
- `TrCAMM_SYMMETRIZE` - Whether to use the 'symmetrized transition density' or not. Default: `true`.
- `TI_CIS_SCF_FOCK_MATRIX` - Whether to compute the full SCF Fock matrix for the dimer or approximate it from monomer OPDM's. Default: `false`.
- `TI_CIS_PRINT_FOCK_MATRIX` - Whether to print the Fock matrix (AB block in AO basis) or not. Default: `false`.

### Environmental variables

One can easily access those variables from Python level by calling

```
psi4.get_variable("name of variable")
```

in your Python script.

Table 16.95: Environmental variables in the OEPDev solver.

| Keyword | Description |
|---|---|
| **Coulombic Interaction Energy** | |
| ***Distributed Multipole Series*** | |
| `EINT COUL CAMM R-1` | CAMM charge-charge terms |

| Keyword | Description |
|---|---|
| `EINT COUL CAMM R-2` | CAMM charge-dipole terms + all above |
| `EINT COUL CAMM R-3` | CAMM charge-quadrupole, dipole-dipole + all above |
| `EINT COUL CAMM R-4` | CAMM charge-octupole, dipole-quadrupole + all above |
| `EINT COUL CAMM R-5` | CAMM charge-hexadecapole, dipole-octupole, quadrupole-quadrupole + all above |
| `EINT COUL ESP` | ESP charge-charge terms |
| ***Exact First-Order Perturbation Theory*** | |
| `EINT COUL EXACT` | MO or AO expanded Coulombic energy. Both give same results but MO is much faster. |
| **Exchange-Repulsion Interaction Energy** | |
| ***Density Decomposition Scheme*** | |
| `EINT REP DDS KCAL` | Pauli repulsion |
| `EINT EXC DDS KCAL` | DDS exchange |
| `EINT EXR DDS KCAL` | Sum of the above |
| ***Hayes-Stone model*** | |
| `EINT REP HAYES-STONE KCAL` | Pauli repulsion |
| `EINT EXC HAYES-STONE KCAL` | Pure exchange |
| `EINT EXR HAYES-STONE KCAL` | Sum of the above |
| ***Murrell et al. model*** | |
| `EINT REP MURRELL-ETAL KCAL` | Pauli repulsion |
| `EINT EXC MURRELL-ETAL KCAL` | Pure exchange (same as Hayes-Stone) |
| `EINT EXR MURRELL-ETAL KCAL` | Sum of the above |
| `EINT REP MURRELL-ETAL:S1 KCAL` | Pauli repulsion: S^{-1} term |
| `EINT REP MURRELL-ETAL:S2 KCAL` | Pauli repulsion: S^{-2} term |
| ***Otto-Ladik model*** | |
| `EINT REP OTTO-LADIK KCAL` | Pauli repulsion |
| `EINT EXC OTTO-LADIK KCAL` | Pure exchange (same as Hayes-Stone) |
| `EINT EXR OTTO-LADIK KCAL` | Sum of the above |
| `EINT REP OTTO-LADIK:S1 KCAL` | Pauli repulsion: S^{-1} term |

| Keyword | Description |
|---|---|
| `EINT REP OTTO-LADIK:S2 KCAL` | Pauli repulsion: S^{-2} term |
| ***EFP2 model*** | |
| `EINT REP EFP2 KCAL` | Pauli repulsion |
| `EINT EXC EFP2 KCAL` | Exchange: SGO approximation of Jensen |
| `EINT EXR EFP2 KCAL` | Sum of the above |
| `EINT REP EFP2:S1 KCAL` | Pauli repulsion: S^{-1} term |
| `EINT REP EFP2:S2 KCAL` | Pauli repulsion: S^{-2} term |
| ***OEP-based models*** | |
| `EINT REP OEP-MURRELL-ETAL-1 KCAL` | Pauli repulsion: S1 term using GDF, S2 term using CAMM |
| `EINT REP OEP-MURRELL-ETAL-1 S1 KCAL` | S^{-1} term of the above total term |
| `EINT REP OEP-MURRELL-ETAL-1 S2 KCAL` | S^{-2} term of the above total term |
| `EINT REP OEP-MURRELL-ETAL-2 KCAL` | Pauli repulsion: S1 term using GDF, S2 term using ESP |
| `EINT REP OEP-MURRELL-ETAL-2 S1 KCAL` | S^{-1} term of the above total term |
| `EINT REP OEP-MURRELL-ETAL-2 S1 KCAL` | S^{-2} term of the above total term |
| **Charge-Transfer Interaction Energy** | |
| ***EFP2 Model*** | |
| `EINT CT EFP2 KCAL` | Total charge-transfer energy (kcal/mole) |
| ***Otto-Ladik Model*** | |
| `EINT CT OTTO-LADIK KCAL` | Total charge-transfer energy (kcal/mole) |
| ***OEP-Based Otto-Ladik Model*** | |
| `EINT CT OEP-OTTO-LADIK KCAL` | Total charge-transfer energy (kcal/mole) |
| **EET Coupling Constant** | |

| Keyword | Description |
|---|---|
| ***TrCAMM Model*** | |
| `EET V0 TRCAMM R1 CM-1` | Overlap-uncorrected, converged to R1 (cm-1) |
| `EET V TRCAMM R1 CM-1` | Overlap-corrected, converged to R1 (cm-1) |
| `EET V0 TRCAMM R2 CM-1` | Overlap-uncorrected, converged to R2 (cm-1) |
| `EET V TRCAMM R2 CM-1` | Overlap-corrected, converged to R2 (cm-1) |
| `EET V0 TRCAMM R3 CM-1` | Overlap-uncorrected, converged to R3 (cm-1) |
| `EET V TRCAMM R3 CM-1` | Overlap-corrected, converged to R3 (cm-1) |
| `EET V0 TRCAMM R4 CM-1` | Overlap-uncorrected, converged to R4 (cm-1) |
| `EET V TRCAMM R4 CM-1` | Overlap-corrected, converged to R4 (cm-1) |
| `EET V0 TRCAMM R5 CM-1` | Overlap-uncorrected, converged to R5 (cm-1) |
| `EET V TRCAMM R5 CM-1` | Overlap-corrected, converged to R5 (cm-1) |
| ***TI/CIS Model*** | |
| `EET V0 COUL CM-1` | Overlap-uncorrected Coulomb (Forster) coupling (cm-1) |
| `EET V0 EXCH CM-1` | Overlap-uncorrected exchange (Dexter) coupling (cm-1) |
| `EET V COUL CM-1` | Overlap-corrected Coulomb (Forster) coupling (cm-1) |
| `EET V EXCH CM-1` | Overlap-corrected exchange (Dexter) coupling (cm-1) |
| `EET V OVRL CM-1` | Remaining overlap correction to direct coupling(cm-1) |
| `EET V0 ET1 CM-1` | Overlap-uncorrected H_13 matrix element (cm-1) |
| `EET V0 ET2 CM-1` | Overlap-uncorrected H_24 matrix element (cm-1) |
| `EET V0 HT1 CM-1` | Overlap-uncorrected H_14 matrix element (cm-1) |
| `EET V0 HT2 CM-1` | Overlap-uncorrected H_23 matrix element (cm-1) |
| `EET V0 CT CM-1` | Overlap-uncorrected H_34 matrix element (cm-1) |
| `EET V ET1 CM-1` | Overlap-corrected H_13 matrix element (cm-1) |
| `EET V ET2 CM-1` | Overlap-corrected H_24 matrix element (cm-1) |
| `EET V HT1 CM-1` | Overlap-corrected H_14 matrix element (cm-1) |
| `EET V HT2 CM-1` | Overlap-corrected H_23 matrix element (cm-1) |

| Keyword | Description |
|---|---|
| `EET V CT CM-1` | Overlap-corrected H_34 matrix element (cm-1) |
| `EET V0 TI-2 CM-1` | Approximate 2nd-order indirect coupling (cm-1) |
| `EET V0 TI-3 CM-1` | Approximate 3rd-order indirect coupling (cm-1) |
| `EET V TI-2 CM-1` | 2nd-order indirect coupling (cm-1) |
| `EET V TI-3 CM-1` | 3rd-order indirect coupling (cm-1) |
| `EET V0 DIRECT CM-1` | Approximate direct coupling (cm-1) |
| `EET V0 INDIRECT CM-1` | Approximate indirect coupling (cm-1) |
| `EET V DIRECT CM-1` | Direct coupling (cm-1) |
| `EET V INDIRECT CM-1` | Indirect coupling (cm-1) |
| `EET V0 TI-CIS CM-1` | Approximate total coupling (cm-1) |
| `EET V TI-CIS CM-1` | Total coupling (cm-1) |
| `EET V0 EXCH-M CM-1` | Overlap-uncorrected exchange (Dexter) coupling in Mulliken approximation (cm-1) |
| `EET V EXCH-M CM-1` | Overlap-corrected exchange (Dexter) coupling in Mulliken approximation (cm-1) |
| `EET V0 CT-M CM-1` | Overlap-uncorrected H_34 matrix element in Mulliken approximation (cm-1) |
| `EET V CT-M CM-1` | Overlap-corrected H_34 matrix element in Mulliken approximation (cm-1) |
| ***OEP-Based TI/CIS Model*** | |
| `EET V OEP:COUL CM-1` | Overlap-corrected Coulomb (Forster) coupling (TrCAMM; cm-1) |
| `EET V OEP:EXCH CM-1` | Overlap-corrected exchange (Dexter) coupling (Mulliken approximation of AO ERI's; cm-1) |
| `EET V OEP:OVRL CM-1` | Remaining overlap correction to direct coupling (cm-1) |
| `EET V0 OEP:ET1 CM-1` | Overlap-uncorrected H_13 matrix element (cm-1) |
| `EET V0 OEP:ET2 CM-1` | Overlap-uncorrected H_24 matrix element (cm-1) |
| `EET V0 OEP:HT1 CM-1` | Overlap-uncorrected H_14 matrix element (cm-1) |
| `EET V0 OEP:HT2 CM-1` | Overlap-uncorrected H_23 matrix element (cm-1) |
| `EET V0 OEP:CT:CAMM CM-1` | Overlap-uncorrected H_34 matrix element: CAMM approximation of ionic interaction (cm-1) |

| Keyword | Description |
|---|---|
| `EET V0 OEP:CT:CC CM-1` | Overlap-uncorrected H_34 matrix element: Point-charge approximation of ionic interaction (cm-1) |
| `EET V OEP:ET1 CM-1` | Overlap-corrected H_13 matrix element (cm-1) |
| `EET V OEP:ET2 CM-1` | Overlap-corrected H_24 matrix element (cm-1) |
| `EET V OEP:HT1 CM-1` | Overlap-corrected H_14 matrix element (cm-1) |
| `EET V OEP:HT2 CM-1` | Overlap-corrected H_23 matrix element (cm-1) |
| `EET V OEP:CT:CAMM CM-1` | Overlap-corrected H_34 matrix element: CAMM approximation of ionic interaction (cm-1) |
| `EET V OEP:CT:CC CM-1` | Overlap-corrected H_34 matrix element: Point-charge approximation of ionic interaction (cm-1) |
| `EET V OEP:TI-2 CM-1` | 2nd-order indirect coupling (cm-1) |
| `EET V OEP:TI-3:CAMM CM-1` | 3rd-order indirect coupling with CAMM approximation for V_CT (cm-1) |
| `EET V OEP:TI-3:CC CM-1` | 3rd-order indirect coupling with point-charge approximation for V_CT (cm-1) |
| `EET V OEP:DIRECT CM-1` | Direct coupling (cm-1) |
| `EET V OEP:INDIRECT:CAMM CM-1` | Indirect coupling with CAMM approximation for V_CT (cm-1) |
| `EET V OEP:INDIRECT:CC CM-1` | Indirect coupling with point-charge approximation for V_CT (cm-1) |
| `EET V OEP:TI-CIS:CAMM CM-1` | Total coupling with CAMM approximation for V_CT (cm-1) |
| `EET V OEP:TI-CIS:CC CM-1` | Total coupling with point-charge approximation for V_CT (cm-1) |

### 16.78.2 Constructor & Destructor Documentation

#### 16.78.2.1 OEPDevSolver()

```
OEPDevSolver::OEPDevSolver (
          SharedWavefunctionUnion wfn_union )
```

**Parameters**

| | |
|---|---|
| *wfn_union* | - wavefunction union of isolated molecular wavefunctions |

### 16.78.3 Member Function Documentation

#### 16.78.3.1 build()

```
std::shared_ptr< OEPDevSolver > OEPDevSolver::build (
          const std::string & target,
          SharedWavefunctionUnion wfn_union )  [static]
```

**Parameters**

| | |
|---|---|
| *target* | - target property |
| *wfn_union* | - wavefunction union of isolated molecular wavefunctions |

Implemented target properties:

- `ELECTROSTATIC_ENERGY` - Coulombic interaction energy between unperturbed wavefunctions.
- `REPULSION_ENERGY` - Pauli repulsion interaction energy between unperturbed wavefunctions.

**See also**

ElectrostaticEnergySolver

#### 16.78.3.2 compute_benchmark()

```
double OEPDevSolver::compute_benchmark (
          const std::string & method = "DEFAULT" )  [pure virtual]
```

Each solver object has one `DEFAULT` benchmark method

**Parameters**

| | |
|---|---|
| *method* | - benchmark method |

Implemented in oepdev::EETCouplingSolver, oepdev::ChargeTransferEnergySolver, oepdev::RepulsionEnergy
and oepdev::ElectrostaticEnergySolver.

#### 16.78.3.3 compute_oep_based()

```
double OEPDevSolver::compute_oep_based (
            const std::string & method = "DEFAULT" )  [pure virtual]
```

Each solver object has one `DEFAULT` OEP-based method.

**Parameters**

| | |
|---|---|
| *method* | - flavour of OEP model |

Implemented in oepdev::EETCouplingSolver, oepdev::ChargeTransferEnergySolver, oepdev::RepulsionEnergy
and oepdev::ElectrostaticEnergySolver.

The documentation for this class was generated from the following files:

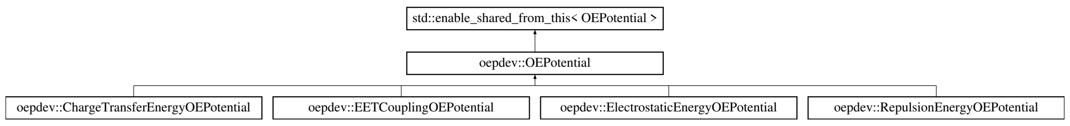
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_base.cc

## 16.79 oepdev::OEPotential Class Reference

Generalized One-Electron Potential: Abstract base.

`#include <oep.h>`

Inheritance diagram for oepdev::OEPotential:


std::enable_shared_from_this< OEPotential >
oepdev::OEPotential
oepdev::ChargeTransferEnergyOEPotential
oepdev::EETCouplingOEPotential
oepdev::ElectrostaticEnergyOEPotential
oepdev::RepulsionEnergyOEPotential

### Public Member Functions

- OEPotential (SharedWavefunction wfn, Options &options)

  *Fully ESP-based OEP object.*
- OEPotential (SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate, Options &options)

  *General OEP object.*
- OEPotential (const OEPotential $*$)

  *Copy constructor.*
- virtual std::shared_ptr$<$ OEPotential $>$ clone (void) const =0

  *Make a deep copy of this object.*
- virtual ∼OEPotential ()

  *Destructor.*
- virtual void compute (void)

*Compute matrix forms of all OEP's within all OEP types.*

- virtual void compute (const std::string &oepType)=0

  *Compute matrix forms of all OEP's within a specified OEP type.*

- virtual void compute_3D (const std::string &oepType, const double &x, const double &y, const double &z, std::shared_ptr< psi::Vector > &v)=0

  *Compute value of potential in point x, y, z and save at v.*

- std::shared_ptr< OEPotential3D< OEPotential > > make_oeps3d (const std::string &oep-Type)

  *Create 3D vector field with OEP.*

- virtual void write_cube (const std::string &oepType, const std::string &fileName)

  *Write potential to a cube file.*

- virtual void localize (void)

  *Localize Occupied MO's.*

- virtual std::vector< psi::SharedVector > mo_centroids (psi::SharedMatrix C)

  *Compute MO centroids from LCAO-MO matrix.*

- virtual void rotate (psi::SharedMatrix r, psi::SharedMatrix R_prim, psi::SharedMatrix R_aux)

  *Rotate.*

- virtual void translate (psi::SharedVector t)

  *Translate.*

- virtual void superimpose (const Matrix &refGeometry, const std::vector< int > &supList, const std::vector< int > &reordList)

  *Superimpose.*

- std::string name () const

  *Retrieve name of this OEP.*

- OEPType oep (const std::string &oepType) const

  *Retrieve the potentials.*

- SharedMatrix matrix (const std::string &oepType) const

  *Retrieve the potentials of a particular OEP type in a matrix form.*

- int n (const std::string &oepType) const

  *Retrieve the number of a particular OEP type.*

- SharedWavefunction wfn () const

  *Retrieve wavefunction object.*

- SharedMatrix cOcc () const

  *Retrieve Canonical occupied MOs.*

- SharedMatrix cVir () const

  *Retrieve Canonical virtual MOs.*

- SharedVector epsOcc () const

  *Retrieve Canonical occupied MO energies.*

- SharedVector epsVir () const

  *Retrieve Canonical virtual MO energies.*

- SharedMatrix lOcc () const

  *Retrieve Localized occupied MOs.*
- SharedMatrix T () const

  *Retrieve Canonical to Localized occupied MO transformation matrix.*
- SharedLocalizer localizer () const

  *Retrieve MO Localizer.*
- std::vector< std::shared_ptr< psi::Vector > > lmoc () const

  *Retrieve LMO Centroids.*
- void set_name (const std::string &name)

  *Set the name of this OEP.*
- void set_localized_orbitals (std::shared_ptr< psi::Localizer > localizer)

  *Set the localized molecular orbitals in OEP calculation.*
- void set_localized_orbitals (std::shared_ptr< OEPotential > oep)

  *Set the localized molecular orbitals in OEP calculation.*
- void set_occupied_canonical_orbitals (std::shared_ptr< OEPotential > oep)

  *Set the occupied canonical orbitals in OEP calculations.*
- virtual void print_header () const

  *Header information.*
- void print () const

  *Print the contents (OEP data)*
- virtual void initialize ()=0

  *Initialize the object (expert)*

## Static Public Member Functions

- static std::shared_ptr< OEPotential > build (const std::string &category, SharedWavefunction wfn, Options &options)

  *Build fully ESP-based OEP object.*
- static std::shared_ptr< OEPotential > build (const std::string &category, SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate, Options &options)

  *Build general OEP object.*

## Public Attributes

- bool use_localized_orbitals

  *Whether to use localized molecular orbitals in OEP calculation; Default: False.*
- bool use_quambo_orbitals

  *Whether to use QUAMBO orbitals to construct VVOs; Default: False.*

## Protected Member Functions

- virtual void copy_from (const OEPotential ∗)

    *Deep-copy the data.*
- virtual void rotate_basic (psi::SharedMatrix r, psi::SharedMatrix R_prim, psi::SharedMatrix R_aux)

    *Rotate basic data.*
- virtual void translate_basic (psi::SharedVector t)

    *Translate basic data.*
- virtual void **rotate_oep** (psi::SharedMatrix r, psi::SharedMatrix R_prim, psi::SharedMatrix R_aux)
- virtual void **translate_oep** (psi::SharedVector t)
- virtual void compute_molecular_orbitals ()

    *Compute MOs (used in initialization stage)*

## Protected Attributes

- Options options_

    *Psi4 options.*
- SharedWavefunction wfn_

    *Wavefunction.*
- SharedBasisSet primary_

    *Promary Basis set.*
- SharedBasisSet auxiliary_

    *Auxiliary Basis set.*
- SharedBasisSet intermediate_

    *Intermediate Basis set.*
- SharedLocalizer localizer_

    *Molecular Orbital Localizer.*
- std::string name_

    *Name of this OEP;.*
- std::map< std::string, OEPType > oepTypes_

    *Types of OEP's within the scope of this object.*
- std::shared_ptr< psi::IntegralFactory > intsFactory_

    *Integral factory.*
- psi::SharedMatrix potMat_

    *Matrix of potential one-electron integrals.*
- std::shared_ptr< psi::OneBodyAOInt > OEInt_

    *One-electron integral shared pointer.*
- std::shared_ptr< oepdev::PotentialInt > potInt_

    *One-electron potential shared pointer.*

- psi::SharedMatrix cOcc_

  *Occupied orbitals: Canonical (CMO)*
- psi::SharedMatrix cVir_

  *Virtual orbitals (Canonical or Valence)*
- psi::SharedVector epsOcc_

  *Occupied orbital energies: Canonical (CMO)*
- psi::SharedVector epsVir_

  *Virtual orbital energies (Canonical or Valence)*
- psi::SharedMatrix lOcc_

  *Occupied orbitals: Localized (LMO)*
- psi::SharedMatrix T_

  *Canonical to Occupied orbitals transformation.*
- std::vector< psi::SharedVector > lmoc_

  *LMO Centroids.*
- bool initialized_

  *Is the object initialized? (MOs computed)*

## 16.79.1 Detailed Description

Manages OEP's in matrix and 3D forms. Available OEP categories:

- `ELECTROSTATIC ENERGY`
- `REPULSION ENERGY`
- `CHARGE TRANSFER ENERGY`
- `EET COUPLING CONSTANT`

## 16.79.2 Constructor & Destructor Documentation

### 16.79.2.1 OEPotential() [1/2]

```
OEPotential::OEPotential (
            SharedWavefunction wfn,
            Options & options )
```

**Parameters**

| | |
|---|---|
| *wfn* | - wavefunction |
| *options* | - Psi4 options |

#### 16.79.2.2 OEPotential() [2/2]

```
OEPotential::OEPotential (
            SharedWavefunction wfn,
            SharedBasisSet auxiliary,
            SharedBasisSet intermediate,
            Options & options )
```

**Parameters**

| | |
|---|---|
| *wfn* | - wavefunction |
| *auxiliary* | - auxiliary basis set for density fitting of OEP's |
| *intermediate* | - intermediate basis set for density fitting of OEP's |
| *options* | - Psi4 options |

### 16.79.3 Member Function Documentation

#### 16.79.3.1 build() [1/2]

```
std::shared_ptr< OEPotential > OEPotential::build (
            const std::string & category,
            SharedWavefunction wfn,
            Options & options ) [static]
```

**Parameters**

| | |
|---|---|
| *type* | - OEP category |
| *wfn* | - wavefunction |
| *options* | - Psi4 options |

#### 16.79.3.2 build() [2/2]

```
std::shared_ptr< OEPotential > OEPotential::build (
            const std::string & category,
            SharedWavefunction wfn,
            SharedBasisSet auxiliary,
            SharedBasisSet intermediate,
            Options & options ) [static]
```

**Parameters**

| | |
|---|---|
| *type* | - OEP category |
| *wfn* | - wavefunction |
| *auxiliary* | - auxiliary basis set for density fitting of OEP's |
| *intermediate* | - intermediate basis set for density fitting of OEP's |
| *options* | - Psi4 options |

#### 16.79.3.3 make_oeps3d()

```
std::shared_ptr< OEPotential3D< OEPotential > > OEPotential::make_oeps3d (
         const std::string & oepType )
```

**Parameters**

| | |
|---|---|
| *oepType* | - type of OEP. ESP-based OEP is assumed. |

**Returns**

Vector field 3D with the OEP values.

The documentation for this class was generated from the following files:

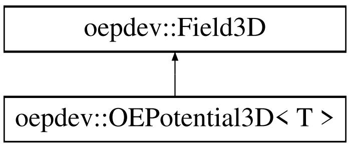
- oepdev/liboep/oep.h
- oepdev/liboep/oep_base.cc

## 16.80 oepdev::OEPotential3D< T > Class Template Reference

Class template for OEP 3D fields.

```
#include <space3d.h>
```

Inheritance diagram for oepdev::OEPotential3D< T >:



### Public Member Functions

- OEPotential3D (const int &ndim, const int &np, const double &padding, std::shared_ptr< T > oep, const std::string &oepType)

*Construct random spherical collection of 3D field of type T.*
- OEPotential3D (const int &ndim, const int &nx, const int &ny, const int &nz, const double &px, const double &py, const double &pz, std::shared_ptr< T > oep, const std::string &oepType, psi::Options &options)

  *Construct ordered 3D collection of 3D field of type T.*
- virtual ~OEPotential3D ()

  *Destructor.*
- virtual std::shared_ptr< psi::Vector > compute_xyz (const double &x, const double &y, const double &z)

  *Compute a value of 3D field at point (x, y, z)*
- virtual void print () const

  *Print information of the object to Psi4 output.*

## Protected Attributes

- std::shared_ptr< T > oep_

  *Shared pointer to the instance of class* `T`
- std::string oepType_

  *Descriptor of the 3D field type stored in instance of* `T`

## Additional Inherited Members

### 16.80.1 Detailed Description

**template<class T>**
**class oepdev::OEPotential3D< T >**

Used for special type of classes T that contain following public member functions:

```
class T : public std::enable_shared_from_this<T> {

  public:
     void compute_3D(const std::string& descriptor,
                     const double& x, const double& y, const double& z,
                     std::shared_ptr<psi::Vector> &v);

     shared_ptr<psi::Wavefunction> wfn() const {return wfn_;}

};
```

with the `descriptor` of a certain 3D field type, `x`, `y`, `z` the points in 3D space in which the scalar or vector field has to be computed and stored at `v`. Instances of `T` should store shared pointer to wavefunction object. List of classes `T` that are compatible with this class template and are currently implemented in oepdev is given below:

- `oepdev::OEPotential` abstract base (do not use derived classes as `T`)

Template parameters:

**Template Parameters**

| | |
|---|---|
| *T* | the compatible class (e.g. `oepdev::OEPotential`) |

The documentation for this class was generated from the following file:

- oepdev/lib3d/space3d.h

## 16.81 oepdev::OEPType Struct Reference

Container to handle the type of One-Electron Potentials.

`#include <oep.h>`

### Public Member Functions

- OEPType ()=default

  *Initializer.*
- OEPType (std::string, bool, int, SharedMatrix, SharedDMTPole, SharedCISData)

  *Initializer from list.*
- OEPType (const OEPType ∗)

  *Copy constructor.*

### Public Attributes

- std::string name

  *Name of this type of OEP.*
- bool is_density_fitted

  *Is this OEP DF-based?*
- int n

  *Number of OEP's within a type.*
- SharedMatrix matrix

  *All OEP's of this type gathered in a matrix form.*
- SharedDMTPole dmtp

  *Distributed Multipole Object.*
- SharedCISData cis_data

  *CIS data.*

The documentation for this struct was generated from the following files:

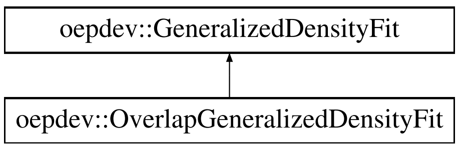
- oepdev/liboep/oep.h
- oepdev/liboep/oep_base.cc

## 16.82 oepdev::OverlapGeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme - Single Fit Based on Minimal Overlap in MO Basis.

`#include <oep_gdf.h>`

Inheritance diagram for oepdev::OverlapGeneralizedDensityFit:


oepdev::GeneralizedDensityFit
oepdev::OverlapGeneralizedDensityFit

### Public Member Functions

- **OverlapGeneralizedDensityFit** (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::BasisSet > bs_intermediate, std::shared_ptr< psi::Matrix > v_vector)
- std::shared_ptr< psi::Matrix > compute (void)

  *Perform the generalized density fit.*

### Additional Inherited Members

### 16.82.1 Detailed Description

The density fitting map projects the OEP onto an arbitrary (not necessarily complete) auxiliary basis set space through application of the basis projection technique. Refer to density fitting specialized for OEP's for more details.

### 16.82.2 Determination of the OEP matrix

Coefficients $\mathbf{G}$ are computed by using the following relation

$$\mathbf{G} = \mathbf{T}_{\rm m\tilde{B}} \cdot \mathbf{S}^{-1}_{\rm \tilde{B}\tilde{B}} \cdot \mathbf{T}^{\dagger}_{\rm m\tilde{B}} \cdot \mathbf{S}_{\rm mi} \cdot \mathbf{G}_{\rm i}$$

where the intermediate projection matrix is given by

$$\mathbf{G}_{\rm i} = \mathbf{S}^{-1}_{\rm ii} \cdot \mathbf{V}_{\rm i}$$

In the above equations, TODO

The spatial form of the potential operator $\hat{v}$ can be expressed by

$$v(\mathbf{r}) \equiv \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}$$

with $\rho(\mathbf{r})$ being the effective one-electron density associated with $\hat{v}$.

### 16.82.3 Member Function Documentation

#### 16.82.3.1 compute()

```
std::shared_ptr< psi::Matrix > OverlapGeneralizedDensityFit::compute (
          void  ) [virtual]
```

**Returns**

The OEP coefficients $G_{\xi i}$

Implements oepdev::GeneralizedDensityFit.

The documentation for this class was generated from the following files:

- oepdev/liboep/oep_gdf.h
- oepdev/liboep/oep_gdf.cc

## 16.83 oepdev::PerturbCharges Struct Reference

Structure to hold perturbing charges.

`#include <scf_perturb.h>`

### Public Attributes

- std::vector< double > charges

  *Vector of charge values.*
- std::vector< std::shared_ptr< psi::Vector > > positions

  *Vector of charge position vectors.*

### 16.83.1 Detailed Description

The documentation for this struct was generated from the following file:

- oepdev/libutil/scf_perturb.h

## 16.84 oepdev::Points3DIterator::Point Struct Reference

### Public Attributes

- double **x**

- double **y**
- double **z**
- int **index**

The documentation for this struct was generated from the following file:

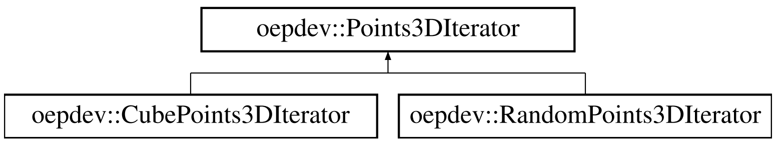
- oepdev/lib3d/space3d.h

## 16.85 oepdev::Points3DIterator Class Reference

Iterator over a collection of points in 3D space. Abstract base.

`#include <space3d.h>`

Inheritance diagram for oepdev::Points3DIterator:



### Classes

- struct Point

### Public Member Functions

- Points3DIterator (const int &np)

  *Plain constructor. Initializes the abstract features.*
- virtual ∼Points3DIterator ()

  *Destructor.*
- virtual bool is_done ()

  *Check if iteration is finished.*
- virtual void first ()=0

  *Initialize first iteration.*
- virtual void next ()=0

  *Step to next iteration.*
- virtual void rewind ()

  *Rewind to the beginning.*

- virtual double **x** () const
- virtual double **y** () const
- virtual double **z** () const
- virtual int **index** () const

### Static Public Member Functions

- static shared_ptr< Points3DIterator > build (const int &nx, const int &ny, const int &nz, const double &dx, const double &dy, const double &dz, const double &ox, const double &oy, const double &oz)

  *Build G09 Cube collection iterator.*
- static shared_ptr< Points3DIterator > build (const int &np, const double &radius, const double &cx, const double &cy, const double &cz)

  *Build random collection iterator.*
- static shared_ptr< Points3DIterator > build (const int &np, const double &pad, psi::SharedMolecule mol)

  *Build random collection iterator.*

### Protected Attributes

- const int np_

  *Number of points.*
- bool done_

  *Status of the iterator.*
- int index_

  *Current index.*

- Point **current_**

## 16.85.1 Detailed Description

Points3DIterators are constructed either as iterators over:

- a random collections or
- an ordered (g09 cube-like) collections. **Note:** Always create instances by using static factory methods.

## 16.85.2 Constructor & Destructor Documentation

#### 16.85.2.1 Points3DIterator()

```
oepdev::Points3DIterator::Points3DIterator (
          const int & np )
```

**Parameters**

| | |
|---|---|
| *np* | - number of points this iterator is constructed for |

### 16.85.3 Member Function Documentation

#### 16.85.3.1 build() [1/3]

```
std::shared_ptr< Points3DIterator > oepdev::Points3DIterator::build (
          const int & nx,
          const int & ny,
          const int & nz,
          const double & dx,
          const double & dy,
          const double & dz,
          const double & ox,
          const double & oy,
          const double & oz )  [static]
```

The points are generated according to Gaussian cube file format.

**Parameters**

| | |
|---|---|
| *nx* | - number of points along x direction |
| *ny* | - number of points along y direction |
| *nz* | - number of points along z direction |
| *dx* | - spacing distance along x direction |
| *dy* | - spacing distance along y direction |
| *dz* | - spacing distance along y direction |
| *ox* | - coordinate x of cube origin |
| *oy* | - coordinate y of cube origin |
| *oz* | - coordinate z of cube origin |

#### 16.85.3.2 build() [2/3]

```
std::shared_ptr< Points3DIterator > oepdev::Points3DIterator::build (
            const int & np,
            const double & radius,
            const double & cx,
            const double & cy,
            const double & cz )  [static]
```

The points are drawn according to uniform distrinution in 3D space.

**Parameters**

| | |
|---|---|
| *np* | - number of points to draw |
| *radius* | - sphere radius inside which points are to be drawn |
| *cx* | - coordinate x of sphere's centre |
| *cy* | - coordinate y of sphere's centre |
| *cz* | - coordinate z of sphere's centre |

### 16.85.3.3 build() [3/3]

```
shared_ptr< Points3DIterator > oepdev::Points3DIterator::build (
            const int & np,
            const double & pad,
            psi::SharedMolecule mol )  [static]
```

The points are drawn according to uniform distrinution in 3D space enclosing a molecule given. All drawn points lie outside the van der Waals volume.

**Parameters**

| | |
|---|---|
| *np* | - number of points to draw |
| *pad* | - radius padding of a minimal sphere enclosing the molecule |
| *mol* | - Psi4 molecule object |

The documentation for this class was generated from the following files:

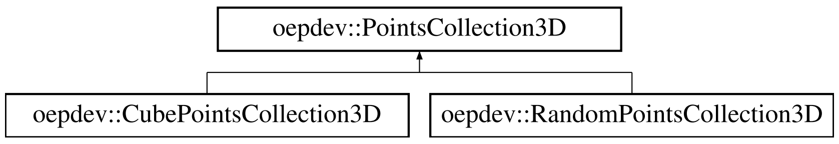
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

## 16.86 oepdev::PointsCollection3D Class Reference

Collection of points in 3D space. Abstract base.

```
#include <space3d.h>
```

Inheritance diagram for oepdev::PointsCollection3D:


oepdev::PointsCollection3D
oepdev::CubePointsCollection3D
oepdev::RandomPointsCollection3D

## Public Types

- enum Collection { **Random**, **Cube** }

  *Public descriptior of collection type.*

## Public Member Functions

- PointsCollection3D (Collection collectionType, int &np)

  *Initialize abstract features.*
- **PointsCollection3D** (Collection collectionType, const int &np)
- virtual ∼PointsCollection3D ()

  *Destructor.*
- virtual int npoints () const

  *Get the number of points.*
- virtual shared_ptr< Points3DIterator > points_iterator () const

  *Get the iterator over this collection of points.*
- virtual Collection get_type () const

  *Get the collection type.*
- virtual void print () const =0

  *Print the information to Psi4 output file.*

## Static Public Member Functions

- static shared_ptr< PointsCollection3D > build (const int &npoints, const double &radius, const double &cx=0.0, const double &cy=0.0, const double &cz=0.0)

  *Build random collection of points.*
- static shared_ptr< PointsCollection3D > build (const int &npoints, const double &padding, psi::SharedMolecule mol)

  *Build random collection of points.*
- static shared_ptr< PointsCollection3D > build (const int &nx, const int &ny, const int &nz, const double &px, const double &py, const double &pz, psi::SharedBasisSet bs, psi::Options &options)

  *Build G09 Cube collection of points.*

## Protected Attributes

- const int np_

    *Number of points.*
- Collection collectionType_

    *Collection type.*
- shared_ptr< Points3DIterator > pointsIterator_

    *iterator over points collection*

### 16.86.1 Detailed Description

Create random or ordered (g09 cube-like) collections of points in 3D space.

**Note:** Always create instances by using static factory methods.

### 16.86.2 Constructor & Destructor Documentation

#### 16.86.2.1 PointsCollection3D()

```
oepdev::PointsCollection3D::PointsCollection3D (
            Collection collectionType,
            int & np )
```

**Parameters**

| | |
|---|---|
| *np* | - number of points to be created |

### 16.86.3 Member Function Documentation

#### 16.86.3.1 build() [1/3]

```
std::shared_ptr< PointsCollection3D > oepdev::PointsCollection3D::build (
            const int & npoints,
            const double & radius,
            const double & cx = 0.0,
            const double & cy = 0.0,
            const double & cz = 0.0 ) [static]
```

Points uniformly span a sphere.

**Parameters**

| | |
|---|---|
| *npoints* | - number of points to draw |
| *radius* | - sphere radius inside which points are to be drawn |
| *cx* | - coordinate x of sphere's centre |
| *cy* | - coordinate y of sphere's centre |
| *cz* | - coordinate z of sphere's centre |

### 16.86.3.2 build() [2/3]

```
std::shared_ptr< PointsCollection3D > oepdev::PointsCollection3D::build (
            const int & npoints,
            const double & padding,
            psi::SharedMolecule mol ) [static]
```

Points uniformly span space inside a sphere enclosing a molecule. exluding the van der Waals volume.

**Parameters**

| | |
|---|---|
| *np* | - number of points to draw |
| *padding* | - radius padding of a minimal sphere enclosing the molecule |
| *mol* | - Psi4 molecule object |

### 16.86.3.3 build() [3/3]

```
std::shared_ptr< PointsCollection3D > oepdev::PointsCollection3D::build (
            const int & nx,
            const int & ny,
            const int & nz,
            const double & px,
            const double & py,
            const double & pz,
            psi::SharedBasisSet bs,
            psi::Options & options ) [static]
```

The points span a parallelpiped according to Gaussian cube file format.

**Parameters**

| | |
|---|---|
| *nx* | - number of points along x direction |
| *ny* | - number of points along y direction |
| *nz* | - number of points along z direction |

**Parameters**

| | |
|---|---|
| *px* | - padding distance along x direction |
| *py* | - padding distance along y direction |
| *pz* | - padding distance along z direction |
| *bs* | - Psi4 basis set object |
| *options* | - Psi4 options object |

The documentation for this class was generated from the following files:

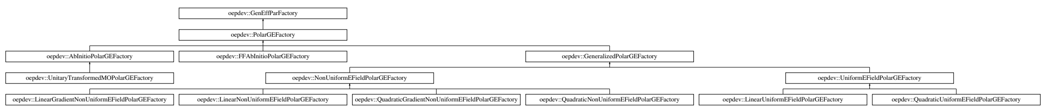
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

## 16.87 oepdev::PolarGEFactory Class Reference

Polarization GEFP Factory. Abstract Base.

`#include <gefp.h>`

Inheritance diagram for oepdev::PolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::AbInitioPolarGEFactory
oepdev::FFAbInitioPolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UnitaryTransformedMOPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

### Public Member Functions

- PolarGEFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

  *Construct from Psi4 options.*
- virtual ∼PolarGEFactory ()

  *Destruct.*
- virtual std::shared_ptr< GenEffPar > compute (void)=0

  *Compute the density matrix susceptibility tensors.*

### Protected Member Functions

- std::shared_ptr< psi::Vector > draw_field ()

  *Randomly draw electric field value.*
- double draw_charge ()

  *Randomly draw charge value.*
- std::shared_ptr< oepdev::RHFPerturbed > perturbed_state (const std::shared_ptr< psi::Vector > &field)

  *Solve SCF equations to find perturbed state due to uniform electric field.*

- std::shared_ptr< oepdev::RHFPerturbed > perturbed_state (const std::shared_ptr< psi::Vector > &pos, const double &charge)

    *Solve SCF equations to find perturbed state due to point charge.*
- std::shared_ptr< oepdev::RHFPerturbed > perturbed_state (const std::shared_ptr< psi::Matrix > &charges)

    *Solve SCF equations to find perturbed state due to set of point charges.*
- std::shared_ptr< psi::Vector > field_due_to_charges (const std::shared_ptr< psi::Matrix > &charges, const double &x, const double &y, const double &z)

    *Evaluate electric field at point (x,y,z) due to point charges.*
- std::shared_ptr< psi::Vector > **field_due_to_charges** (const std::shared_ptr< psi::Matrix > &charges, const std::shared_ptr< psi::Vector > &pos)
- std::shared_ptr< psi::Matrix > field_gradient_due_to_charges (const std::shared_ptr< psi::Matrix > &charges, const double &x, const double &y, const double &z)

    *Evaluate electric field gradient at point (x,y,z) due to point charges.*
- std::shared_ptr< psi::Matrix > **field_gradient_due_to_charges** (const std::shared_ptr< psi::Matrix > &charges, const std::shared_ptr< psi::Vector > &pos)

### Additional Inherited Members

### 16.87.1 Detailed Description

Basic interface for the polarization density matrix susceptibility parameters.

The documentation for this class was generated from the following files:

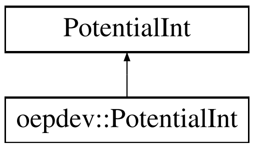
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_base.cc

## 16.88 oepdev::PotentialInt Class Reference

Computes potential integrals.

```
#include <potential.h>
```

Inheritance diagram for oepdev::PotentialInt:



### Public Member Functions

- PotentialInt (std::vector< psi::SphericalTransform > &st, std::shared_ptr< psi::BasisSet > bs1, std::shared_ptr< psi::BasisSet > bs2, int deriv=0)

*Constructor. Initialize identically like in psi::PotentilInt.*

- PotentialInt (std::vector< psi::SphericalTransform > &st, std::shared_ptr< psi::BasisSet > bs1, std::shared_ptr< psi::BasisSet > bs2, std::shared_ptr< psi::Matrix > Qxyz, int deriv=0)

  *Constructor. Takes an arbitrary collection of charges.*
- PotentialInt (std::vector< psi::SphericalTransform > &, std::shared_ptr< psi::BasisSet >, std::shared_ptr< psi::BasisSet >, const double &x, const double &y, const double &z, const double &q=1.0, int deriv=0)

  *Constructor. Computes potential for one point x, y, z for a test particle of charge q.*
- void set_charge_field (const double &x, const double &y, const double &z, const double &q=1.0)

  *Mutator. Set the charge field to be a x, y, z point of charge q.*

## 16.88.1 Constructor & Destructor Documentation

### 16.88.1.1 PotentialInt() [1/3]

```
oepdev::PotentialInt::PotentialInt (
            std::vector< psi::SphericalTransform > & st,
            std::shared_ptr< psi::BasisSet > bs1,
            std::shared_ptr< psi::BasisSet > bs2,
            int deriv = 0 )
```

**Parameters**

| | |
|---|---|
| *st* | - Spherical transform object |
| *bs1* | - basis set for first space |
| *bs2* | - basis set for second space |
| *deriv* | - derivative level |

### 16.88.1.2 PotentialInt() [2/3]

```
oepdev::PotentialInt::PotentialInt (
            std::vector< psi::SphericalTransform > & st,
            std::shared_ptr< psi::BasisSet > bs1,
            std::shared_ptr< psi::BasisSet > bs2,
            std::shared_ptr< psi::Matrix > Qxyz,
            int deriv = 0 )
```

**Parameters**

| | |
|---|---|
| *st* | - Spherical transform object |
| *bs1* | - basis set for first space |
| *bs2* | - basis set for second space |
| *Qxyz* | - matrix with charges and their positions |
| *deriv* | - derivative level |

#### 16.88.1.3 PotentialInt() [3/3]

```
oepdev::PotentialInt::PotentialInt (
          std::vector< psi::SphericalTransform > & st,
          std::shared_ptr< psi::BasisSet > bs1,
          std::shared_ptr< psi::BasisSet > bs2,
          const double & x,
          const double & y,
          const double & z,
          const double & q = 1.0,
          int deriv = 0 )
```

**Parameters**

| | |
|---|---|
| *st* | - Spherical transform object |
| *bs1* | - basis set for first space |
| *bs2* | - basis set for second space |
| *x* | - x coordinate of q |
| *y* | - y coordinate of q |
| *z* | - z coordinate of q |
| *q* | - value of the probe charge |
| *deriv* | - derivative level |

### 16.88.2 Member Function Documentation

#### 16.88.2.1 set_charge_field()

```
void oepdev::PotentialInt::set_charge_field (
          const double & x,
          const double & y,
          const double & z,
          const double & q = 1.0 )
```

**Parameters**

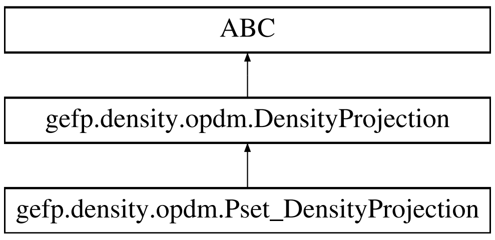
| | |
|---|---|
| *x* | - x coordinate of q |
| *y* | - y coordinate of q |
| *z* | - z coordinate of q |
| *q* | - value of the probe charge |

The documentation for this class was generated from the following files:

- oepdev/libpsi/potential.h
- oepdev/libpsi/potential.cc

## 16.89 gefp.density.opdm.Pset_DensityProjection Class Reference

Inheritance diagram for gefp.density.opdm.Pset_DensityProjection:


ABC
gefp.density.opdm.DensityProjection
gefp.density.opdm.Pset_DensityProjection

### Public Member Functions

- def __**init**__ (self, np, S)

### Additional Inherited Members

### 16.89.1 Detailed Description

```
\
 Gradient Projection Algorithm on P-sets.
 Ref.: Pernal, Cances, J. Chem. Phys. 2005

 Notes:
  o Appropriate for any DMFT functional.
```

The documentation for this class was generated from the following file:

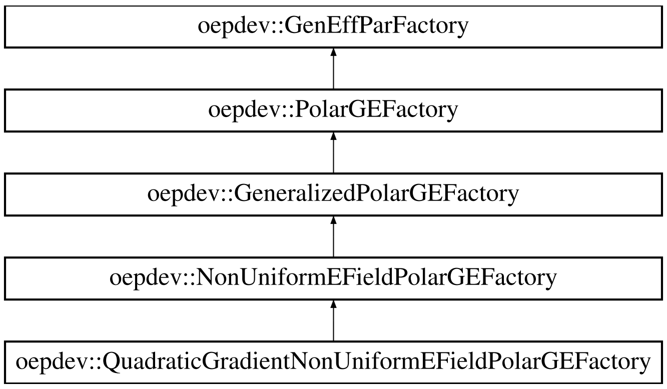
- gefp/gefp/density/opdm.py

## 16.90 oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory

### Public Member Functions

- **QuadraticGradientNonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  *Compute Gradient vector associated with the i-th and j-th basis set function.*
- void compute_hessian (void)

  *Compute Hessian matrix (independent on the parameters)*

### Additional Inherited Members

### 16.90.1 Detailed Description

Implements the generalized density matrix susceptibility model of the form

$$\delta D_{\alpha\beta} \approx \sum_i \left\{ \mathbf{B}_{i;\alpha\beta}^{(10)} \cdot \mathbf{F}(\mathbf{r}_i) + \mathbf{B}_{i;\alpha\beta}^{(20)} : \mathbf{F} \otimes \mathbf{F}(\mathbf{r}_i) + \mathbf{B}_{i;\alpha\beta}^{(01)} : \nabla_i \otimes \mathbf{F}(\mathbf{r}_i) \right\}$$

where:

- $\mathbf{B}_{i;\alpha\beta}^{(10)}$ is the density matrix dipole polarizability
- $\mathbf{B}_{i;\alpha\beta}^{(20)}$ is the density matrix dipole-dipole hyperpolarizability
- $\mathbf{B}_{i;\alpha\beta}^{(01)}$ is the density matrix quadrupole polarizability all defined for the distributed site at $\mathbf{r}_i$.

The documentation for this class was generated from the following files:

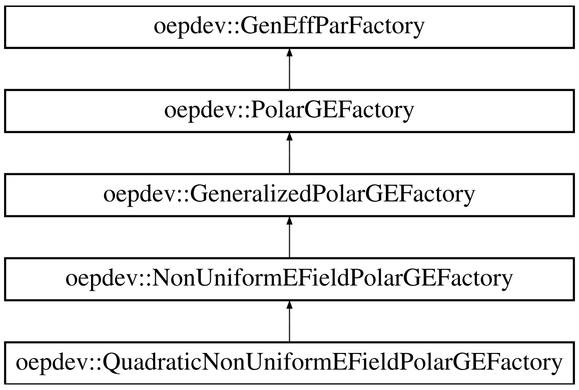
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_2_grad_1.cc

## 16.91 oepdev::QuadraticNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

```
#include <gefp.h>
```

Inheritance diagram for oepdev::QuadraticNonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory

### Public Member Functions

- **QuadraticNonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  *Compute Gradient vector associated with the i-th and j-th basis set function.*
- void compute_hessian (void)

  *Compute Hessian matrix (independent on the parameters)*

### Additional Inherited Members

### 16.91.1 Detailed Description

Implements the generalized density matrix susceptibility model of the form

$$\delta D_{\alpha\beta} \approx \sum_i \left\{ \mathbf{B}^{(10)}_{i;\alpha\beta} \cdot \mathbf{F}(\mathbf{r}_i) + \mathbf{B}^{(20)}_{i;\alpha\beta} : \mathbf{F}(\mathbf{r}_i) \otimes \mathbf{F}(\mathbf{r}_i) \right\}$$

where:

- $\mathbf{B}^{(10)}_{i;\alpha\beta}$ is the density matrix dipole polarizability
- $\mathbf{B}^{(20)}_{i;\alpha\beta}$ is the density matrix dipole-dipole hyperpolarizability all defined for the distributed site at $\mathbf{r}_i$.

The documentation for this class was generated from the following files:

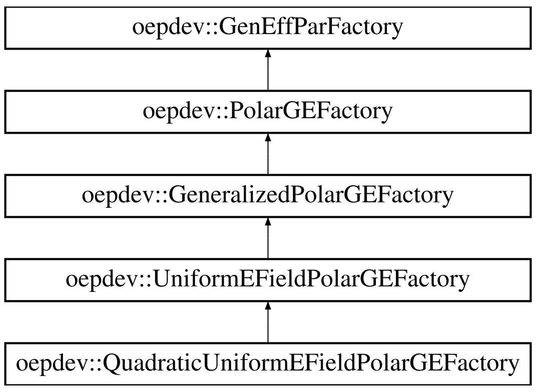
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_2.cc

## 16.92 oepdev::QuadraticUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::QuadraticUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

### Public Member Functions

- **QuadraticUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  *Compute Gradient vector associated with the i-th and j-th basis set function.*
- void compute_hessian (void)

  *Compute Hessian matrix (independent on the parameters)*

### Additional Inherited Members

#### 16.92.1 Detailed Description

Implements the generalized density matrix susceptibility model of the form

$$\delta D_{\alpha\beta} \approx \mathbf{B}^{(10)}_{\alpha\beta} \cdot \mathbf{F} + \mathbf{B}^{(20)}_{\alpha\beta} : \mathbf{F} \otimes \mathbf{F}$$

where:

- $\mathbf{B}^{(10)}_{\alpha\beta}$ is the density matrix dipole polarizability
- $\mathbf{B}^{(20)}_{\alpha\beta}$ is the density matrix dipole-dipole hyperpolarizability

The documentation for this class was generated from the following files:

- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_uniform_field_2.cc

## 16.93 oepdev::QUAMBO Class Reference

The Quasiatomic Minimal Basis Set Molecular Orbitals (QUAMBO)

```
#include <quambo.h>
```

### Public Member Functions

- QUAMBO (psi::SharedWavefunction wfn, bool acbs=true)

  *Constructor.*
- virtual ∼QUAMBO ()

  *Destructor.*
- void compute (void)

  *Compute QUAMBOs and VVOs.*
- psi::SharedMatrix quambo (const std::string &spin, const std::string &type="ORTHOGONAL")

  *Get the QUAMBOs in AO representation (AOs: rows, QUAMBOs: columns)*
- psi::SharedVector epsilon_a_subset (const std::string &space, const std::string &subset)

  *Get SCF alpha orbital energies in minimal MO basis.*
- psi::SharedVector epsilon_b_subset (const std::string &space, const std::string &subset)

  *Get SCF beta orbital energies in minimal MO basis.*
- psi::SharedMatrix Ca_subset (const std::string &space, const std::string &subset)

  *Get SCF alpha orbitals in minimal MO basis.*
- psi::SharedMatrix Cb_subset (const std::string &space, const std::string &subset)

  *Get SCF beta orbitals in minimal MO basis.*
- int nbas () const

  *Size of QUAMBO basis.*
- int naocc () const

  *Number of Alpha occupied MOs in minimal basis (same as in original basis)*
- int nbocc () const

  *Number of Beta occupied MOs in minimal basis (same as in original basis)*
- int navir () const

*Number of Alpha virtual MOs in minimal basis (number of Alpha VVOs)*

- int nbvir () const

  *Number of Beta virtual MOs in minimal basis (number of Beta VVOs)*

## Static Public Member Functions

- static std::shared_ptr< QUAMBO > build (psi::SharedWavefunction wfn, bool acbs=true)

  *Static factory method.*

## Public Attributes

- const bool acbs

  *Is ACBS mode selected?*

## Protected Member Functions

- double **compute_error_between_two_vectors_** (psi::SharedVector a, psi::SharedVector b)
- int **calculate_nbas_mini_** (void)
- std::vector< psi::SharedMolecule > **atomize_** (void)
- SharedQUAMBOData **compute_quambo_data_** (psi::SharedMatrix, psi::SharedMatrix, psi::SharedVector, psi::SharedVector, psi::SharedMatrix, psi::SharedMatrix, psi::SharedMatrix, int, int, std::string)
- psi::SharedVector **epsilon_subset_helper_** (psi::SharedVector C_full, const std::string &label, const int &n, const std::string &space, const std::string &subset)
- psi::SharedMatrix **C_subset_helper_** (psi::SharedMatrix C_full, const std::string &label, const int &n, const std::string &space, const std::string &subset)

## Protected Attributes

- psi::Options & options_

  *Psi4 options.*

- psi::SharedMolecule mol_

  *Molecule.*

- psi::SharedWavefunction wfn_

  *Wavefunction.*

- std::map< std::string, int > nbas_atom_mini_

  *numbers of minimal basis functions of free atoms*

- std::map< std::string, int > unpe_atom_

  *numbers of unpaired electrons in free atoms*

- psi::SharedMatrix Sao_

*AO Overlap Matrix.*

- psi::SharedMatrix quambo_a_nonorthogonal_

  *QUAMBO (Alpha, non-orthogonal)*
- psi::SharedMatrix quambo_a_orthogonal_

  *QUAMBO (Alpha, orthogonal)*
- psi::SharedMatrix quambo_b_nonorthogonal_

  *QUAMBO (Beta, non-orthogonal)*
- psi::SharedMatrix quambo_b_orthogonal_

  *QUAMBO (Beta, orthogonal)*
- psi::SharedMatrix c_a_mini_vir_

  *Virtual Valence Molecular Orbitals (Alpha, VVO)*
- psi::SharedMatrix c_b_mini_vir_

  *Virtual Valence Molecular Orbitals (Beta, VVO)*
- psi::SharedVector e_a_mini_vir_

  *VVO Energies (Alpha)*
- psi::SharedVector e_b_mini_vir_

  *VVO Energies (Beta)*
- psi::SharedMatrix c_a_mini_

  *All Molecular orbitals (Alpha, OCC + VVO)*
- psi::SharedMatrix c_b_mini_

  *All Molecular orbitals (Beta, OCC + VVO)*
- psi::SharedVector e_a_mini_

  *Energies of All Molecular Orbitals (Alpha)*
- psi::SharedVector e_b_mini_

  *Energies of All Molecular Orbitals (Beta)*
- int nbas_mini_

  *Size of QUAMBO basis per orbital group (Alpha, Beta)*
- int naocc_mini_

  *Number of Alpha occupied MOs.*
- int nbocc_mini_

  *Number of Beta occupied MOs.*
- int navir_mini_

  *Number of Alpha virtual MOs.*
- int nbvir_mini_

  *Number of Beta virtual MOs.*
- int nbf_

  *Number of AO basis functions.*

### 16.93.1 Detailed Description

TODO

### Calculation Algorithm.

TODO

References:

[1] W. C. Lu, C. Z. Wang, M.W. Schmidt, L. Bytautas, K. M. Ho, K. Reudenberg, J. Chem. Phys. 120, 2629 (2004) [original QUAMBO paper] [2] P. Xu, M. S. Gordon, J. Chem. Phys. 139, 194104 (2013) [application of QUAMBO in EFP2 CT term]

The documentation for this class was generated from the following files:

- oepdev/libutil/quambo.h
- oepdev/libutil/quambo.cc

## 16.94 gefp.basis.quambo.QUAMBO Class Reference

### Public Member Functions

- def **__init__** (self, mol, options, acbs=False)
- def **quambo** (self, spin="alpha", type="orthogonal")
- def **mo** (self, spin="alpha", space="all")
- def **eps** (self, spin="alpha", space="all")
- def **overlap** (self, spin="alpha", type="nonorthogonal")
- def **compute** (self)

### Public Attributes

- **acbs**

### 16.94.1 Detailed Description

```
 Quasiatomic Minimal Basis Set Molecular Orbitals

 Usage:

 solve = QUAMBO(molecule, psi4.core.get_options(), acbs=False)
 solve.compute()
 c_vir = solve.mo(space='vir')
 e_all = solve.eps(space='all')
 quambo_b_nonorthogonal = solve.quambo(type='nonorthogonal', spin='beta')

 Notes:
o first argument to QUAMBO constructor can also be Wavefunction object
  with the SCF solution of a molecule. In this case, SCF is not run
  for the molecule.

 References:
```

```
[1] W. C. Lu, C. Z. Wang, M.W. Schmidt, L. Bytautas, K. M. Ho, K. Reudenberg,
    J. Chem. Phys. 120, 2629 (2004) [original QUAMBO paper]
[2] P. Xu, M. S. Gordon, J. Chem. Phys. 139, 194104 (2013) [application
    of QUAMBO in EFP2 CT term]
```

The documentation for this class was generated from the following file:

- gefp/gefp/basis/quambo.py

## 16.95 oepdev::QUAMBOData Struct Reference

Container to store the QUAMBO data.

`#include <quambo.h>`

### Public Attributes

- psi::SharedMatrix quambo_nonorthogonal

  *QUAMBO (non-orthogonal)*
- psi::SharedMatrix quambo_orthogonal

  *QUAMBO (orthogonal)*
- psi::SharedMatrix c_mini_vir

  *Virtual Valence Molecular Orbitals (VVO)*
- psi::SharedVector e_mini_vir

  *VVO Energies.*
- psi::SharedMatrix c_mini

  *All Molecular orbitals (OCC + VVO)*
- psi::SharedVector e_mini

  *Energies of All Molecular Orbitals.*

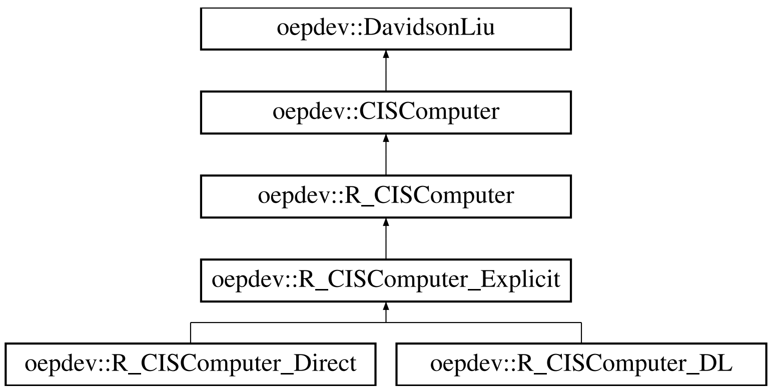
### 16.95.1 Detailed Description

The documentation for this struct was generated from the following file:

- oepdev/libutil/quambo.h

## 16.96 oepdev::R_CISComputer Class Reference

Inheritance diagram for oepdev::R_CISComputer:



## Public Member Functions

- **R_CISComputer** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

## Protected Member Functions

- virtual void **print_excited_state_character_** (int I)

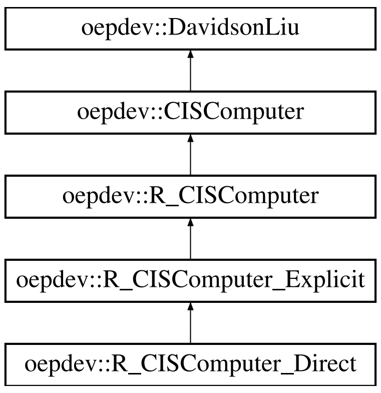
## Additional Inherited Members

The documentation for this class was generated from the following files:

- oepdev/libutil/cis.h
- oepdev/libutil/cis_rhf.cc

## 16.97 oepdev::R_CISComputer_Direct Class Reference

Inheritance diagram for oepdev::R_CISComputer_Direct:



### Public Member Functions

- **R_CISComputer_Direct** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

### Protected Member Functions

- virtual void **build_hamiltonian_** (void)
- virtual void **transform_integrals_** (void)

### Additional Inherited Members

The documentation for this class was generated from the following files:

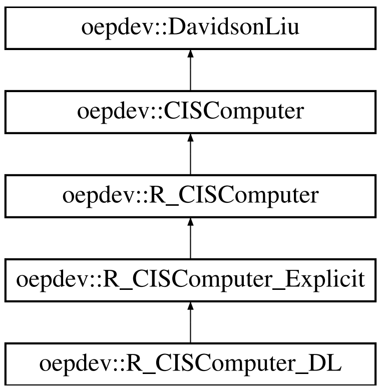
- oepdev/libutil/cis.h
- oepdev/libutil/cis_rhf_direct.cc

## 16.98 oepdev::R_CISComputer_DL Class Reference

CIS Computer with RHF reference: Davidson-Liu Solver.

```
#include <cis.h>
```

Inheritance diagram for oepdev::R_CISComputer_DL:



### Public Member Functions

- **R_CISComputer_DL** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

### Protected Member Functions

- virtual void **set_nstates_** (void)
- virtual void **transform_integrals_** (void)

- virtual void **allocate_hamiltonian_** (void)
- virtual void **build_hamiltonian_** (void)
- virtual void **diagonalize_hamiltonian_** (void)
- virtual void **davidson_liu_compute_diagonal_hamiltonian** (void)
- virtual void **davidson_liu_compute_sigma** (void)

## Additional Inherited Members

### 16.98.1 Detailed Description

Associated options:

- `CIS_TYPE` - must be set to `DAVIDSON_LIU` (Default).
- `CIS_SCHWARTZ_CUTOFF` - Cutoff for Schwartz ERI screening. Default: 0.0.

## Implementation

### Diagonal Hamiltonian elements

They are computed by using direct method with Schwartz screening of AO ERI's. The implementation formula is

$$H_{ii}^{aa} = \varepsilon_a - \varepsilon_i + \sum_{\alpha\beta\gamma\delta} (\alpha\beta|\gamma\delta) C_{\alpha i} C_{\delta a} \left( C_{\beta a} C_{\gamma i} - C_{\beta i} C_{\gamma a} \right)$$

The block associated with beta spin is equal to alpha block.

### Sigma vectors

The sigma vectors are computed from

$$\sigma_i^{a,k} = (\varepsilon_a - \varepsilon_i) b_i^{a,k} + J_i^a(\mathbf{T}^{(k)}) + J_i^a(\overline{\mathbf{T}^{(k)}}) - K_i^a(\mathbf{T}^{(k)})$$
$$\sigma_{\bar{i}}^{\bar{a},k} = (\varepsilon_a - \varepsilon_i) b_{\bar{i}}^{\bar{a},k} + J_i^a(\mathbf{T}^{(k)}) + J_i^a(\overline{\mathbf{T}^{(k)}}) - K_i^a(\overline{\mathbf{T}^{(k)}})$$

where *k* labels the vectors and where the generalized one-particle density matrices are defined by

$$T_{\gamma\delta}^{(k)} = \sum_{jb} C_{\delta b} b_j^{b,k} C_{\gamma j}$$
$$\overline{T}_{\gamma\delta}^{(k)} = \sum_{\bar{j}\bar{b}} C_{\delta\bar{b}} b_{\bar{j}}^{\bar{b},k} C_{\gamma\bar{j}}$$

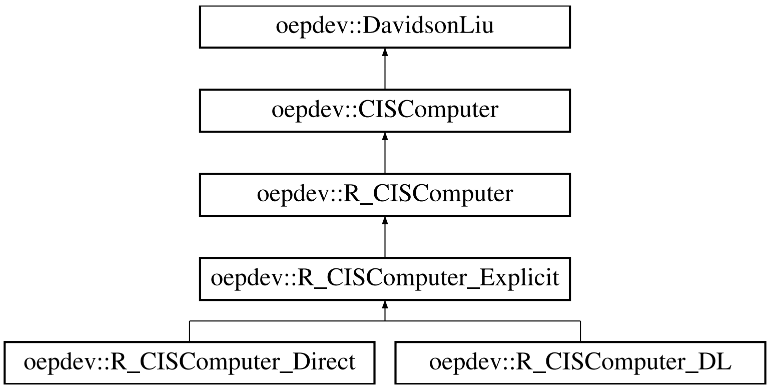
The **J** and **K** matrices in AO basis are computed by using the `psi::JK` object, and subsequently transformed to CMO's.

The documentation for this class was generated from the following files:

- oepdev/libutil/cis.h
- oepdev/libutil/cis_rhf_dl.cc

## 16.99 oepdev::R_CISComputer_Explicit Class Reference

Inheritance diagram for oepdev::R_CISComputer_Explicit:



### Public Member Functions

- **R_CISComputer_Explicit** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

### Protected Member Functions

- virtual void **set_beta_** (void)
- virtual void **build_hamiltonian_** (void)

### Additional Inherited Members

The documentation for this class was generated from the following files:

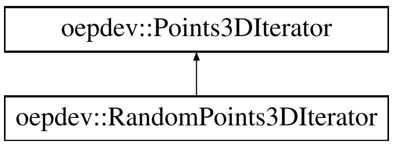
- oepdev/libutil/cis.h
- oepdev/libutil/cis_rhf_explicit.cc

## 16.100 oepdev::RandomPoints3DIterator Class Reference

Iterator over a collection of points in 3D space. Random collection.

`#include <space3d.h>`

Inheritance diagram for oepdev::RandomPoints3DIterator:



### Public Member Functions

- **RandomPoints3DIterator** (const int &np, const double &radius, const double &cx, const double &cy, const double &cz)
- **RandomPoints3DIterator** (const int &np, const double &pad, psi::SharedMolecule mol)
- virtual void first ()

  *Initialize first iteration.*
- virtual void next ()

  *Step to next iteration.*

### Protected Member Functions

- virtual double **random_double** ()
- virtual void **draw_random_point** ()
- virtual bool **is_in_vdWsphere** (double x, double y, double z) const

### Protected Attributes

- double **cx_**
- double **cy_**
- double **cz_**
- double **radius_**
- double **r_**
- double **phi_**
- double **theta_**
- double **x_**
- double **y_**
- double **z_**
- psi::SharedMatrix **excludeSpheres_**
- std::map< std::string, double > **vdwRadius_**
- std::default_random_engine **randomNumberGenerator_**
- std::uniform_real_distribution< double > **randomDistribution_**

### Additional Inherited Members

### 16.100.1 Detailed Description

**Note:** Always create instances by using static factory method from Points3DIterator. Do not use constructors of this class.

The documentation for this class was generated from the following files:

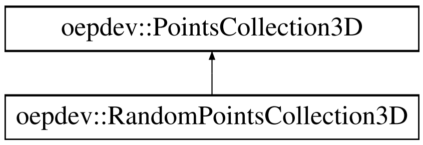
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

## 16.101 oepdev::RandomPointsCollection3D Class Reference

Collection of random points in 3D space.

`#include <space3d.h>`

Inheritance diagram for oepdev::RandomPointsCollection3D:



### Public Member Functions

- **RandomPointsCollection3D** (Collection collectionType, const int &npoints, const double &radius, const double &cx, const double &cy, const double &cz)
- **RandomPointsCollection3D** (Collection collectionType, const int &npoints, const double &padding, psi::SharedMolecule mol)
- virtual void print () const

  *Print the information to Psi4 output file.*

### Additional Inherited Members

### 16.101.1 Detailed Description

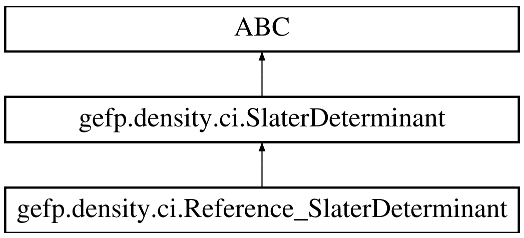
**Note:** Do not use constructors of this class explicitly. Instead, use static factory methods of the superclass to create instances.

The documentation for this class was generated from the following files:

- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

## 16.102 gefp.density.ci.Reference_SlaterDeterminant Class Reference

Inheritance diagram for gefp.density.ci.Reference_SlaterDeterminant:


ABC
gefp.density.ci.SlaterDeterminant
gefp.density.ci.Reference_SlaterDeterminant

### Public Member Functions

- def **__init__** (self, nao, nbo, nmo)

### Public Attributes

- **is_reference**

The documentation for this class was generated from the following file:

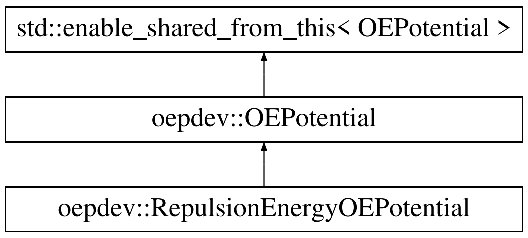
- gefp/gefp/density/ci.py

## 16.103 oepdev::RepulsionEnergyOEPotential Class Reference

Generalized One-Electron Potential for Pauli Repulsion Energy.

```
#include <oep.h>
```

Inheritance diagram for oepdev::RepulsionEnergyOEPotential:


std::enable_shared_from_this< OEPotential >
oepdev::OEPotential
oepdev::RepulsionEnergyOEPotential

### Public Member Functions

- **RepulsionEnergyOEPotential** (SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate, Options &options)
- **RepulsionEnergyOEPotential** (SharedWavefunction wfn, Options &options)
- **RepulsionEnergyOEPotential** (const RepulsionEnergyOEPotential ∗f)
- virtual void compute (const std::string &oepType) override

  *Compute matrix forms of all OEP's within a specified OEP type.*
- virtual void compute_3D (const std::string &oepType, const double &x, const double &y, const double &z, std::shared_ptr< psi::Vector > &v) override

  *Compute value of potential in point x, y, z and save at v.*
- virtual void print_header () const override

  *Header information.*
- virtual std::shared_ptr< OEPotential > clone (void) const override

  *Make a deep copy of this object.*
- virtual void initialize () override

  *Initialize the object (expert)*

### Protected Member Functions

- virtual void **rotate_oep** (psi::SharedMatrix r, psi::SharedMatrix R_prim, psi::SharedMatrix R_aux) override
- virtual void **translate_oep** (psi::SharedVector t) override

### Additional Inherited Members

### 16.103.1 Detailed Description

Contains the following OEP types:

- `Murrell-etal.S1`
- `Otto-Ladik.S2`

The documentation for this class was generated from the following files:

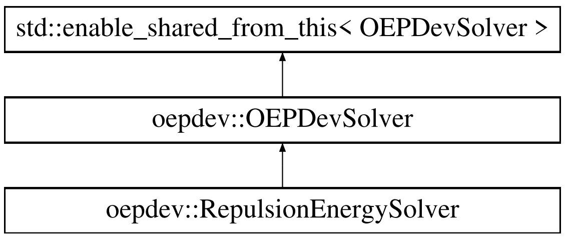
- oepdev/liboep/oep.h
- oepdev/liboep/oep_energy_pauli.cc

## 16.104 oepdev::RepulsionEnergySolver Class Reference

Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::RepulsionEnergySolver:


std::enable_shared_from_this< OEPDevSolver >
oepdev::OEPDevSolver
oepdev::RepulsionEnergySolver

### Public Member Functions

- **RepulsionEnergySolver** (SharedWavefunctionUnion wfn_union)
- virtual double compute_oep_based (const std::string &method="DEFAULT")

  *Compute property by using OEP's.*
- virtual double compute_benchmark (const std::string &method="DEFAULT")

  *Compute property by using benchmark method.*

## Additional Inherited Members

### 16.104.1 Detailed Description

The implemented methods are shown below

Table 16.118: Methods available in the Solver

| Keyword | Method Description |
|---|---|
| | **Benchmark Methods** |
| `HAYES_STONE` | *Default.* Pauli Repulsion energy at HF level from Hayes and Stone (1984). |
| `DDS` | Pauli Repulsion energy at HF level from Mandado and Hermida-Ramon (2012). |
| `MURRELL_ETAL` | Approximate Pauli Repulsion energy at HF level from Murrell et al (1967). |
| `OTTO_LADIK` | Approximate Pauli Repulsion energy at HF level from Otto and Ladik (1975). |
| `EFP2` | Approximate Pauli Repulsion energy at HF level from EFP2 model. |
| | **OEP-Based Methods** |
| `MURRELL_ETAL_GDF_ESP` | *Default.* OEP-Murrell et al's: S1 term via DF-OEP, S2 term via ESP-OEP. |
| `MURRELL_ETAL_GDF_CAMM` | OEP-Murrell et al's: S1 term via DF-OEP, S2 term via CAMM-OEP. |
| `MURRELL_ETAL_ESP` | OEP-Murrell et al's: S1 and S2 via ESP-OEP (not implemented) |

*Note:*

- This solver also computes and prints the exchange energy at HF level (formulae are given below) for reference purposes.
- In order to construct this solver, **always** use the `OEPDevSolver::build` static factory method.

Below the detailed description of the implemented equations is given for each of the above provided methods. In the formulae across, it is assumed that the orbitals are real. The Coulomb notation for electron repulsion integrals (ERI's) is adopted; i.e,

$$(ac|bd) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_1)\frac{1}{r_{12}}\phi_b(\mathbf{r}_2)\phi_d(\mathbf{r}_2)$$

Greek subscripts denote basis set orbitals whereas Italic subscripts denote the occupied molecular orbitals.

## Benchmark Methods

### Pauli Repulsion energy at HF level by Hayes and Stone (1984).

For a closed-shell system, equation of Hayes and Stone (1984) becomes

$$E^{\rm Rep} = 2\sum_{kl}\left(V^A_{kl} + V^B_{kl} + T_{kl}\right)\left[[\mathbf{S}^{-1}]_{lk} - \delta_{lk}\right] + \sum_{klmn}(kl|mn)\left\{2[\mathbf{S}^{-1}]_{kl}[\mathbf{S}^{-1}]_{mn} - [\mathbf{S}^{-1}]_{kn}[\mathbf{S}^{-1}]_{lm} - 2\delta_{kl}\delta_{mn} + \delta_{kn}\delta\right.$$

where $\mathbf{S}$ is the overlap matrix between the doubly-occupied orbitals. The exact, pure exchange energy is for a closed shell case given as

$$E^{\rm Ex,pure} = -2\sum_{a\in A}\sum_{b\in B}(ab|ba)$$

Similarity transformation of molecular orbitals does not affect the resulting energies. The overall exchange-repulsion interaction energy is then (always net repulsive)

$$E^{\rm Ex-Rep} = E^{\rm Ex,pure} + E^{\rm Rep}$$

### Repulsion energy of Mandado and Hermida-Ramon (2011)

At the Hartree-Fock level, the exchange-repulsion energy from the density-based scheme of Mandado and Hermida-Ramon (2011) is fully equivalent to the method by Hayes and Stone (1984). However, density-based method enables to compute exchange-repulsion energy at any level of theory. It is derived based on the Pauli deformation density matrix,

$$\Delta\mathbf{D}^{\rm Pauli} \equiv \mathbf{D}^{oo} - \mathbf{D}$$

where $\mathbf{D}^{oo}$ and $\mathbf{D}$ are the density matrix formed from mutually orthogonal sets of molecular orbitals within the entire aggregate (formed by symmetric orthogonalization of MO's) and the density matrix of the unperturbed system (that can be understood as a Hadamard sum $\mathbf{D} \equiv \mathbf{D}^A \oplus \mathbf{D}^B$).

At HF level, the Pauli deformation density matrix is given by

$$\Delta\mathbf{D}^{\rm Pauli} = \mathbf{C}\left[\mathbf{S}^{-1} - \mathbf{1}\right]\mathbf{C}^\dagger$$

whereas the density matrix constructed from mutually orthogonal orbitals is

$$\mathbf{D}^{oo} = \mathbf{C}\mathbf{S}^{-1}\mathbf{C}^\dagger$$

In the above equations, $\mathbf{S}$ is the overlap matrix between doubly occupied molecular orbitals of the entire aggregate.

Here, the expressions for the exchange-repulsion energy at any level of theory are shown for the case of open-shell system. The net repulsive energy is given as

$$E^{\rm Ex-Rep} = E^{\rm Rep,1} + E^{\rm Rep,2} + E^{\rm Ex}$$

where the one- and two-electron part of the repulsion energy is

$$E^{\rm Rep,1} = E^{\rm Rep,Kin} + E^{\rm Rep,Nuc}$$
$$E^{\rm Rep,2} = E^{\rm Rep,el-\Delta} + E^{\rm Rep,\Delta-\Delta}$$

The kinetic and nuclear contributions are

$$\begin{aligned} E^{\text{Rep,Kin}} &= 2 \sum_{\alpha\beta\in A,B} \Delta D^{\text{Pauli}}_{\alpha\beta} T_{\alpha\beta} \\ E^{\text{Rep,Nuc}} &= 2 \sum_{\alpha\beta\in A,B} \Delta D^{\text{Pauli}}_{\alpha\beta} \sum_{z\in A,B} V^{(z)}_{\alpha\beta} \end{aligned}$$

whereas the electron-deformation and deformation-deformation interaction contributions are

$$\begin{aligned} E^{\text{Rep,el}-\Delta} &= 4 \sum_{\alpha\beta\gamma\delta\in A,B} \Delta D^{\text{Pauli}}_{\alpha\beta} D_{\gamma\delta} (\alpha\beta|\gamma\delta) \\ E^{\text{Rep},\Delta-\Delta} &= 2 \sum_{\alpha\beta\gamma\delta\in A,B} \Delta D^{\text{Pauli}}_{\alpha\beta} \Delta D^{\text{Pauli}}_{\gamma\delta} (\alpha\beta|\gamma\delta) \end{aligned}$$

The associated exchange energy is given by

$$E^{\text{Ex}} = - \sum_{\alpha\beta\gamma\delta\in A,B} \left[ D^{oo}_{\alpha\delta} D^{oo}_{\beta\gamma} - D^{A}_{\alpha\delta} D^{A}_{\beta\gamma} - D^{B}_{\alpha\delta} D^{B}_{\beta\gamma} \right] (\alpha\beta|\gamma\delta)$$

It is important to emphasise that, although, at HF level, the particular 'repulsive' and 'exchange' energies computed by using either Hayes and Stone or Mandado and Hermida-Ramon methods are not equal to each other, they sum up to exactly the same exchange-repulsion energy, $E^{\text{Ex}-\text{Rep}}$. Therefore, these methods at HF level are fully equivalent but the nature of partitioning of repulsive and exchange parts is different. It is also noted that the orbital localization does *not* affect the resulting energies, as opposed to the few approximate methods described below (Otto-Ladik and EFP2 methods).

#### Approximate Pauli Repulsion energy at HF level from Murrell et al.

By expanding the overlap matrix in a Taylor series one can show that the Pauli repulsion energy is approximately given as

$$E^{\text{Rep}} = E^{\text{Rep}}(\mathscr{O}(S)) + E^{\text{Rep}}(\mathscr{O}(S^2))$$

where the first-order term is

$$E^{\text{Rep}}(\mathscr{O}(S)) = -2 \sum_{a\in A} \sum_{b\in B} S_{ab} \left\{ V^{A}_{ab} + \sum_{c\in A} \left[ 2(ab|cc) - (ac|bc) \right] + V^{B}_{ab} + \sum_{d\in B} \left[ 2(ab|dd) - (ad|bd) \right] \right\}$$

whereas the second-order term is

$$E^{\text{Rep}}(\mathscr{O}(S^2)) = 2 \sum_{a\in A} \sum_{b\in B} S_{ab} \left\{ \sum_{c\in A} S_{bc} \left[ V^{B}_{ac} + 2 \sum_{d\in B} (ac|dd) \right] + \sum_{d\in B} S_{ad} \left[ V^{A}_{bd} + 2 \sum_{x\in A} (bd|cc) \right] - \sum_{c\in A} \sum_{d\in B} S_{cd} (ac|bd$$

Thus derived repulsion energy is invariant with respect to transformation of molecular orbitals, similarly as Hayes-Stone's method and density-based method. By using OEP technique, the above theory can be exactly re-cast *without* any further approximations.

**Approximate Pauli Repulsion energy at HF level from Otto and Ladik (1975).**

The Pauli repulsion energy is approximately given as

$$E^{\rm Rep} = E^{\rm Rep}(\mathcal{O}(S)) + E^{\rm Rep}(\mathcal{O}(S^2))$$

where the first-order term is

$$E^{\rm Rep}(\mathcal{O}(S)) = -2\sum_{a\in A}\sum_{b\in B} S_{ab} \left\{ V^A_{ab} + 2\sum_{c\in A}(ab|cc) - (ab|aa) + V^B_{ab} + 2\sum_{d\in B}(ab|dd) - (ab|bb) \right\}$$

whereas the second-order term is

$$E^{\rm Rep}(\mathcal{O}(S^2)) = 2\sum_{a\in A}\sum_{b\in B} S^2_{ab} \left\{ V^B_{aa} + V^A_{bb} + 2\sum_{c\in A}(cc|bb) + 2\sum_{d\in B}(aa|dd) - (aa|bb) \right\}$$

Thus derived repulsion energy is *not* invariant with respect to transformation of molecular orbitals, in contrast to Hayes-Stone's method and density-based method. It was shown that good results are obtained when using localized molecular orbitals, whereas using canonical molecular orbitals brings poor results. By using OEP technique, the above theory can be exactly re-cast *without* any further approximations.

**Approximate Pauli Repulsion energy at HF level from Jensen and Gordon (1996).**

The Pauli repulsion energy used within the EFP2 approach is approximately given as

$$E^{\rm Rep} = E^{\rm Rep}(\mathcal{O}(S)) + E^{\rm Rep}(\mathcal{O}(S^2))$$

where the first-order term is

$$E^{\rm Rep}(\mathcal{O}(S)) = -2\sum_{a\in A}\sum_{b\in B} S_{ab} \left\{ \sum_{c\in A} F^A_{ac}S_{cb} + \sum_{d\in B} F^B_{bd}S_{da} - 2T_{ab} \right\}$$

whereas the second-order term is

$$E^{\rm Rep}(\mathcal{O}(S^2)) = 2\sum_{a\in A}\sum_{b\in B} S^2_{ab} \left\{ \sum_{x\in A}\frac{-Z_x}{R_{xb}} + \sum_{y\in B}\frac{-Z_y}{R_{ya}} + \sum_{c\in A}\frac{2}{R_{bc}} + \sum_{d\in B}\frac{2}{R_{ad}} - \frac{1}{R_{ab}} \right\}$$

Thus derived repulsion energy is *not* invariant with respect to transformation of molecular orbitals, in contrast to Hayes-Stone's method and density-based method. It was shown that good results are obtained when using localized molecular orbitals, whereas using canonical molecular orbitals brings poor results.

In EFP2, exchange energy is approximated by spherical Gaussian approximation (SGO). The result of this is the following formula for the exchange energy:

$$E^{\rm Ex} \approx -4\sum_{a\in A}\sum_{b\in B} \sqrt{\frac{-2\ln|S_{ab}|}{\pi}\frac{S^2_{ab}}{R_{ab}}}$$

In all the above formulas, $R_{ij}$ are distances between position vectors of $*$i$*$th and $*$j$*$th point. The LMO centroids are defined by

$$\mathbf{r}_a = (a|\mathbf{r}|a)$$

where *a* denotes the occupied molecular orbital.

### OEP-Based Methods

The Murrell et al's theory of Pauli repulsion for S-1 term and the Otto-Ladik's theory for S-2 term is here re-cast by introducing OEP's. The S-1 term is expressed via DF-OEP, whereas the S-2 term via ESP-OEP.

#### S-1 term (Murrell et al.)

The OEP reduction without any approximations leads to the following formula

$$E^{\rm Rep}(\mathscr{O}(S^1)) = -2 \sum_{a\in A} \sum_{b\in B} S_{ab} \left\{ \sum_{\xi\in A} S_{b\xi} G^A_{\xi a} + \sum_{\eta\in B} S_{a\eta} G^B_{\eta b} \right\}$$

where the OEP matrices are given as

$$G^A_{\xi a} = \sum_{\xi'\in A} [\mathbf{S}^{-1}]_{\xi\xi'} \sum_{\alpha\in A} \left\{ C_{\alpha a} V^A_{\alpha\xi'} + \sum_{\mu\nu\in A} \left[ 2C_{\alpha a} D_{\mu\nu} - C_{\nu a} D_{\alpha\mu} \right] (\alpha\xi'|\mu\nu) \right\}$$

and analogously for molecule *B*. Here, the nuclear attraction integrals are denoted by $V^A_{\alpha\xi'}$.

#### S-2 term (Otto-Ladik)

After the OEP reduction, this contribution under Otto-Ladik approximation has the following form:

$$E^{\rm Rep}(\mathscr{O}(S^2)) = 2 \sum_{a\in A} \sum_{b\in B} S^2_{ab} \left\{ \sum_{x\in A} q_{xa} V^{(x)}_{bb} + \sum_{y\in B} q_{yb} V^{(y)}_{aa} \right\}$$

where the ESP charges associated with each occupied molecular orbital reproduce the *effective potential* of molecule in question, i.e.,

$$\sum_{x\in A} \frac{q_{xa}}{|\mathrm{r} - \mathrm{r}_x|} \cong v^A_a(\mathbf{r})$$

where the potential is given by

$$v^A_a(\mathbf{r}) = \sum_{x\in A} \frac{-Z_x}{|\mathrm{r} - \mathrm{r}_x|} + 2\sum_{c\in A} \int \frac{\phi_c(\mathrm{r}')\phi_c(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|}\, d\mathbf{r}' - \frac{1}{2} \int \frac{\phi_a(\mathrm{r}')\phi_a(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|}\, d\mathbf{r}'$$

## 16.104.2 Member Function Documentation

### 16.104.2.1 compute_benchmark()

```
double RepulsionEnergySolver::compute_benchmark (
            const std::string & method = "DEFAULT" )  [virtual]
```

Each solver object has one `DEFAULT` benchmark method

**Parameters**

| | |
|---|---|
| *method* | - benchmark method |

Implements oepdev::OEPDevSolver.

#### 16.104.2.2 compute_oep_based()

```
double RepulsionEnergySolver::compute_oep_based (
          const std::string & method = "DEFAULT" )  [virtual]
```

Each solver object has one `DEFAULT` OEP-based method.

**Parameters**

| | |
|---|---|
| *method* | - flavour of OEP model |

Implements oepdev::OEPDevSolver.

The documentation for this class was generated from the following files:

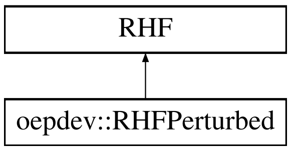
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_energy_pauli.cc

## 16.105 oepdev::RHFPerturbed Class Reference

RHF theory under electrostatic perturbation.

`#include <scf_perturb.h>`

Inheritance diagram for oepdev::RHFPerturbed:



### Public Member Functions

- RHFPerturbed (std::shared_ptr< psi::Wavefunction > ref_wfn, std::shared_ptr< psi::SuperFunctional > functional)

  *Build from wavefunction and superfunctional.*
- RHFPerturbed (std::shared_ptr< psi::Wavefunction > ref_wfn, std::shared_ptr< psi::SuperFunctional > functional, psi::Options &options, std::shared_ptr< psi::PSIO > psio)

*Build from wavefunction and superfunctional + options and psio.*

- virtual ∼RHFPerturbed ()

  *Clear memory.*

- virtual double compute_energy ()

  *Compute total energy.*

- virtual void set_perturbation (std::shared_ptr< psi::Vector > field)

  *Perturb the system with external electric field.*

- virtual void set_perturbation (const double &fx, const double &fy, const double &fz)

  *This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.*

- virtual void set_perturbation (std::shared_ptr< psi::Vector > position, const double &charge)

  *Perturb the system with a point charge.*

- virtual void set_perturbation (const double &rx, const double &ry, const double &rz, const double &charge)

  *This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.*

- std::shared_ptr< psi::Matrix > Vpert () const

  *Get a copy of the perturbation potential one-electron matrix.*

- double nuclear_interaction_energy () const

  *Get the interaction energy of the nuclei with the perturbing potential.*

## Protected Member Functions

- virtual void perturb_Hcore ()

  *Add the electrostatic perturbation to the Hcore matrix.*

## Protected Attributes

- std::shared_ptr< psi::Vector > perturbField_

  *Perturbing electric field.*

- std::shared_ptr< PerturbCharges > perturbCharges_

  *Perturbing charges.*

- std::shared_ptr< psi::Matrix > Vpert_

  *Perturbation potential one-electron matrix.*

- double nuclearInteractionEnergy_

  *Electrostatic interaction energy due to nuclei.*

### 16.105.1 Detailed Description

Compute RHF wavefunction under the following conditions:

- external uniform electric field
- set of point charges The mixed conditions can also be used.

#### Theory

The electrostatic perturbation is here understood as a distribution of external (generally non-uniform) electric field. It is assumed that this perturbation is one-electron in nature. Therefore, the one-electron Hamiltonian is changed according to the following

$$\mathbf{H}^{\rm core} \rightarrow \mathbf{H}^{\rm core} + \sum_n q_n \mathbf{V}^{(n)} - \mathbb{M}\cdot\mathbf{F}$$

where $q_n$ is the external classical point charge, $\mathbf{V}^{(n)}$ is the associated matrix of potential integrals, $\mathbb{M}$ is the vector of dipole integrals and $\mathbf{F}$ is an external uniform electric field. The total energy is then computed by performing an SCF procedure on the above one-electron Hamiltonian. The contribution due to nuclei is included, i.e.,

$$E_{\rm Nuc} \rightarrow E_{\rm Nuc-Nuc} + \sum_{In} \frac{q_n Z_I}{r_{In}} - \mu_{\rm Nuc}\cdot\mathbf{F}$$

where $\mu_{\rm Nuc}$ is the nuclear dipole moment and $Z_I$ is the atomic number of the $I$th nucleus. It is added in the nuclear repulsion energy $E_{\rm Nuc-Nuc}$ (note that the resulting energy can be negative as well depending on the electric field direction and configuration of point charges.

The documentation for this class was generated from the following files:

- oepdev/libutil/scf_perturb.h
- oepdev/libutil/scf_perturb.cc

## 16.106 gefp.density.rvs.RVS Class Reference

### Public Member Functions

- def **__init__** (self, wfn)
- def **run_dimer** (self, conver=1.0e-7, maxiter=100, ndamp=10)
- def **__repr__** (self)

### Public Attributes

- **vars**

### 16.106.1 Detailed Description

```
-----------------------------------------------------------------------------
Reduced Variational Scheme (RVS)
Ref.: Stevens & Fink, Chem. Phys. Lett., Vol. 139, pp. 15-22 (1987)

Implementation for closed-shell systems.
-----------------------------------------------------------------------------

Notes:

o This code contains general implementation of the RVS-SCF method.
Currently, only dimers are automatically analyzed. To use for
multimers, define a subclass and redefine the `run` method
to include n-mers for n>2.

o Projection of frozen orbitals is achieved by transforming
Fock matrix to orthogonal MO basis of entire n-fragment
aggregate, and setting all the off-diagonal matrix elements
that are associated to the frozen orbitals to zero
[Kairys & Jensen, J. Phys. Chem. A, Vol. 104, No. 28, 2000].

o Orthogonal MO basis is constructed from the original
mutually non-orthogonal MOs of isolated fragments by
GrammSchmidt orthogonalization with respect to the frozen
MOs. If no frozen MOs are requested, symmetric Lowdin
orthogonalization is performed instead.

-----------------------------------------------------------------------------
Usage for dimers:

e, wfn = psi4.energy('scf', return_wfn=True)
rvs = RVS(wfn)
rvs.run_dimer(conver=1.0e-7, maxiter=100, ndamp=10)
print(rvs)
# access variables:
print(rvs.vars.keys())

-----------------------------------------------------------------------------
Example for redefining for multimers:

class Trimer_RVS(RVS):
 def __init__(self, wfn):
     super(RVS, self).__init__(wfn)

 def run_trimer(self, conver, maxiter, ndamp):
     "Here there is your implementation for trimer"

     # example for A-B-C (0-1-2) trimer:

     # energy of Hartree product
     #                        frozen_occ active_vir exclude_occ
     E_Ao_Bo_Co        = self._scf([ ], [   ], [ ], conver, maxiter, damp=0.0, ndamp=nd

     # energy of Bocc frozen, virtual space composed of Cvir and Bvir, and A molecule e
     E_fBo_Bv_Cv       = self._scf([1], [1,2], [0], conver, maxiter, damp=0.0, ndamp=nd

     # energy of Bocc and Cocc frozen and all virtual space included, Aocc active
```

```
        E_fBo_fCo_Av_Bv_Cv= self._scf([1,2], [0,1,2], [ ], conver, maxiter, damp=0.0, ndam

    def __repr__(self):
        "Print the contents"
        log = ''
        # ...
        return str(log)

 -----------------------------------------------------------------------------
 B. B␣lasiak                                         Gundelfingen, 14.02.2020
```

The documentation for this class was generated from the following file:

- gefp/gefp/density/rvs.py

## 16.107 gefp.density.dfi.SCF Class Reference

### Public Member Functions

- def __**init**__ (self, mol, bfs=None)
- def **run** (self, maxit=30, conv=1.0e-7, guess=None, damp=0.01, ndamp=10, verbose=True, v_ext=None)

### Public Attributes

- e_nuc

  *Accessors nuclear repulsion energy.*
- **E**
- **D**
- **Co**
- **C**
- **F**
- **eps**
- **H**
- **S**
- **X**

### 16.107.1 Detailed Description

```
 ------------------------------------------------------------------------------------
                            Self-Consistent Field (SCF) Procedure for Hartree-Fock Model
 ------------------------------------------------------------------------------------

 Demo for RHF-SCF method (closed shells). Implements SCF algorithm
 with primitive damping of the AO Fock matrix.
 Usage:
scf = SCF(molecule)
scf.run(maxit=30, conv=1.0e-7, guess=None, damp=0.01, ndamp=10, verbose=True)

 The above example runs SCF on 'molecule' psi4.core.Molecule object
 starting from core Hamiltonian as guess (guess=None)
 and convergence 1.0E-7 A.U. in total energy with 30 maximum iterations
 (10 of which are performed by damping of the Fock matrix with damping coefficient of 0.
 The SCF iterations are printed to standard output (verbose=True).
 ----------------------------------------------------------------------------------------
                                                                  Last Revision: Gund
```

The documentation for this class was generated from the following file:

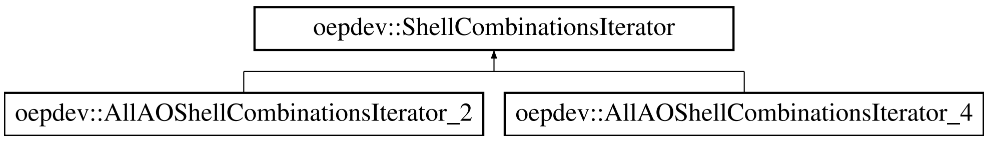
- gefp/gefp/density/dfi.py

## 16.108 oepdev::ShellCombinationsIterator Class Reference

Iterator for Shell Combinations. Abstract Base.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::ShellCombinationsIterator:


oepdev::ShellCombinationsIterator
oepdev::AllAOShellCombinationsIterator_2
oepdev::AllAOShellCombinationsIterator_4

### Public Member Functions

- ShellCombinationsIterator (int nshell)

  *Constructor.*
- virtual ∼ShellCombinationsIterator ()

  *Destructor.*
- virtual void first (void)=0

  *First iteration.*
- virtual void next (void)=0

  *Next iteration.*
- virtual std::shared_ptr< psi::BasisSet > bs_1 (void) const

  *Grab the basis set of axis 1.*
- virtual std::shared_ptr< psi::BasisSet > bs_2 (void) const

  *Grab the basis set of axis 2.*
- virtual std::shared_ptr< psi::BasisSet > bs_3 (void) const

  *Grab the basis set of axis 3.*

- virtual std::shared_ptr< psi::BasisSet > bs_4 (void) const

  *Grab the basis set of axis 4.*
- virtual int P (void) const

  *Grab the current shell P index.*
- virtual int Q (void) const

  *Grab the current shell Q index.*
- virtual int R (void) const

  *Grab the current shell R index.*
- virtual int S (void) const

  *Grab the current shell S index.*
- virtual bool is_done (void)

  *Return status of an iterator.*
- virtual int nshell (void) const

  *Return number of shells this iterator is for.*
- virtual std::shared_ptr< AOIntegralsIterator > ao_iterator (std::string mode="ALL") const
- virtual void compute_shell (std::shared_ptr< oepdev::TwoBodyAOInt > tei) const =0
- virtual void compute_shell (std::shared_ptr< psi ::TwoBodyAOInt > tei) const =0

## Static Public Member Functions

- static std::shared_ptr< ShellCombinationsIterator > build (const IntegralFactory &ints, std::string mode="ALL", int nshell=4)

  *Build shell iterator from oepdev::IntegralFactory.*
- static std::shared_ptr< ShellCombinationsIterator > build (std::shared_ptr< IntegralFactory > ints, std::string mode="ALL", int nshell=4)

  *This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.*
- static std::shared_ptr< ShellCombinationsIterator > build (const psi::IntegralFactory &ints, std::string mode="ALL", int nshell=4)

  *Build shell iterator from psi::IntegralFactory.*
- static std::shared_ptr< ShellCombinationsIterator > build (std::shared_ptr< psi::IntegralFactory > ints, std::string mode="ALL", int nshell=4)

  *This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.*

## Protected Attributes

- SharedBasisSet bs_1_

  *Basis set of axis 1.*
- SharedBasisSet bs_2_

  *Basis set of axis 2.*
- SharedBasisSet bs_3_

  *Basis set of axis 3.*
- SharedBasisSet bs_4_

  *Basis set of axis 4.*
- const int nshell_

  *Number of shells this iterator is for.*
- bool done

  *Status of an iterator.*

## 16.108.1 Detailed Description

**Date**

2018/03/01 17:22:00

## 16.108.2 Constructor & Destructor Documentation

### 16.108.2.1 ShellCombinationsIterator()

```
ShellCombinationsIterator::ShellCombinationsIterator (
            int nshell )
```

**Parameters**

| | |
|---|---|
| *nshell* | - number of shells this iterator is for |

## 16.108.3 Member Function Documentation

### 16.108.3.1 ao_iterator()

```
std::shared_ptr< AOIntegralsIterator > ShellCombinationsIterator::ao_iterator
(
          std::string mode = "ALL" ) const  [virtual]
```

Make an AO integral iterator based on current shell

**Parameters**

| | |
|---|---|
| *mode* | - either "ALL" or "UNIQUE" (iterate over all or unique integrals) |

**Returns**

iterator over AO integrals

### 16.108.3.2 build() [1/2]

```
std::shared_ptr< ShellCombinationsIterator > ShellCombinationsIterator::build
(
          const IntegralFactory & ints,
          std::string mode = "ALL",
          int nshell = 4 )  [static]
```

**Parameters**

| | |
|---|---|
| *ints* | - integral factory |
| *mode* | - mode of iteration (either `ALL` or `UNIQUE`) |
| *nshell* | - number of shells to iterate through |

**Returns**

shell iterator

**Examples:**

example_integrals_iter.cc.

### 16.108.3.3 build() [2/2]

```
std::shared_ptr< ShellCombinationsIterator > ShellCombinationsIterator::build
(
          const psi::IntegralFactory & ints,
          std::string mode = "ALL",
          int nshell = 4 )  [static]
```

**Parameters**

| | |
|---|---|
| *ints* | - integral factory |
| *mode* | - mode of iteration (either `ALL` or `UNIQUE`) |
| *nshell* | - number of shells to iterate through |

**Returns**

shell iterator

#### 16.108.3.4 compute_shell() [1/2]

```
void ShellCombinationsIterator::compute_shell (
          std::shared_ptr< oepdev::TwoBodyAOInt > tei ) const  [pure virtual]
```

Compute integrals in a current shell. Works both for oepdev::TwoBodyAOInt and psi::TwoBodyAOInt

**Parameters**

| | |
|---|---|
| *tei* | - two body integral object |

Implemented in oepdev::AllAOShellCombinationsIterator_2, and oepdev::AllAOShellCombinationsIterator_4.

#### 16.108.3.5 compute_shell() [2/2]

```
void ShellCombinationsIterator::compute_shell (
          std::shared_ptr< psi ::TwoBodyAOInt > tei ) const  [pure virtual]
```

Compute integrals in a current shell. Works both for oepdev::TwoBodyAOInt and psi::TwoBodyAOInt

**Parameters**

| | |
|---|---|
| *tei* | - two body integral object |

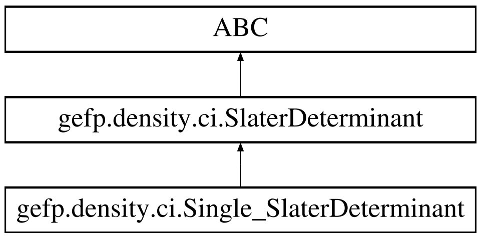
Implemented in oepdev::AllAOShellCombinationsIterator_4.

The documentation for this class was generated from the following files:

- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

## 16.109 gefp.density.ci.Single_SlaterDeterminant Class Reference

Inheritance diagram for gefp.density.ci.Single_SlaterDeterminant:


ABC
gefp.density.ci.SlaterDeterminant
gefp.density.ci.Single_SlaterDeterminant

### Public Member Functions

- def **__init__** (self, nao, nbo, nmo, rule)

### Public Attributes

- **is_single**
- **change_alpha**

The documentation for this class was generated from the following file:

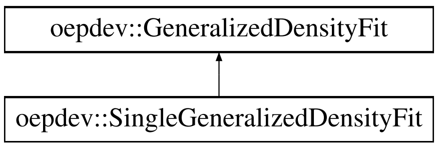
- gefp/gefp/density/ci.py

## 16.110 oepdev::SingleGeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme - Single Fit.

`#include <oep_gdf.h>`

Inheritance diagram for oepdev::SingleGeneralizedDensityFit:


oepdev::GeneralizedDensityFit
oepdev::SingleGeneralizedDensityFit

### Public Member Functions

- **SingleGeneralizedDensityFit** (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::Matrix > v_vector)
- std::shared_ptr< psi::Matrix > compute (void)

  *Perform the generalized density fit.*

## Additional Inherited Members

### 16.110.1 Detailed Description

The density fitting map projects the OEP onto the auxiliary, nearly complete basis set space through application of the resolution of identity. Refer to density fitting in complete space for more details.

### 16.110.2 Determination of the OEP matrix

Coefficients $\mathbf{G}$ are computed by using the following relation

$$\mathbf{G}^{(i)} = \mathbf{v}^{(i)} \cdot \mathbf{S}^{-1}$$

where

$$S_{\xi\eta} = (\xi|\eta)$$
$$v_{\xi}^{(i)} = (\xi|\hat{v}i)$$

In the above, $|$ denotes the single integration over electron coordinate, i.e.,

$$(a|b) \equiv \int d\mathbf{r}\phi_a^*(\mathbf{r})\phi_b(\mathbf{r})$$

whereas the spatial form of the potential operator $\hat{v}$ can be expressed by

$$v(\mathbf{r}) \equiv \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}$$

with $\rho(\mathbf{r})$ being the effective one-electron density associated with $\hat{v}$.

### 16.110.3 Member Function Documentation

#### 16.110.3.1 compute()

```
std::shared_ptr< psi::Matrix > SingleGeneralizedDensityFit::compute (
            void ) [virtual]
```

**Returns**

The OEP coefficients $G_{\xi i}$

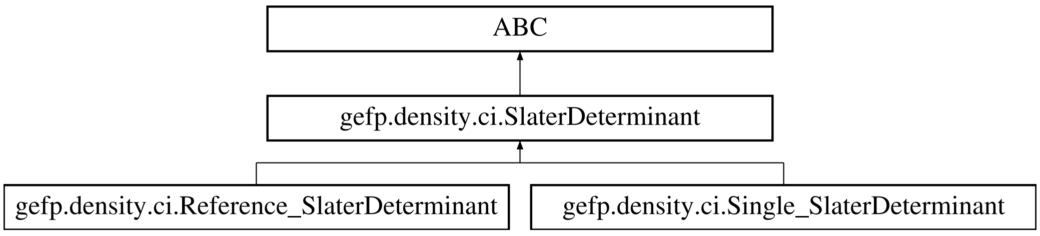
Implements oepdev::GeneralizedDensityFit.

The documentation for this class was generated from the following files:

- oepdev/liboep/oep_gdf.h
- oepdev/liboep/oep_gdf.cc

## 16.111 gefp.density.ci.SlaterDeterminant Class Reference

Inheritance diagram for gefp.density.ci.SlaterDeterminant:


ABC
gefp.density.ci.SlaterDeterminant
gefp.density.ci.Reference_SlaterDeterminant
gefp.density.ci.Single_SlaterDeterminant

### Public Member Functions

- def **__init__** (self, nao, nbo, nmo, rule)

### Public Attributes

- **is_reference**
- **is_single**
- **is_double**
- **is_triple**
- **rule**
- **nao**
- **nbo**
- **nav**
- **nbv**
- **nmo**

The documentation for this class was generated from the following file:

- gefp/gefp/density/ci.py

## 16.112 gefp.basis.parameters.StandardizedInput Class Reference

### Public Member Functions

- def **__init__** (self, mol, oep_type, standard='standard')
- def **prepare_standard_template_and_starting_parameters** (self)
- def **get_constraints** (self, scales)
- def **get_row** (self, symbol)
- def **get_atom_symbols** (self)

### Public Attributes

- **mol**
- **oep_type**
- **standard**
- **template**
- **parameters**
- **constraints**
- **bounds_codes**
- **scales**

The documentation for this class was generated from the following file:

- gefp/gefp/basis/parameters.py

## 16.113 oepdev::GeneralizedPolarGEFactory::StatisticalSet Struct Reference

A structure to handle statistical data.

```
#include <gefp.h>
```

### Public Attributes

- std::vector< double > InducedInteractionEnergySet

  *Interaction energy set.*
- std::vector< std::shared_ptr< psi::Matrix > > DensityMatrixSet

  *Density matrix set.*
- std::vector< std::shared_ptr< psi::Vector > > InducedDipoleSet

  *Induced dipole moment set.*
- std::vector< std::shared_ptr< psi::Vector > > InducedQuadrupoleSet

  *Induced quadrupole moment set.*
- std::vector< std::shared_ptr< psi::Matrix > > JKMatrixSet

  *Sum of J and K matrix set.*

The documentation for this struct was generated from the following file:

- oepdev/libgefp/gefp.h

## 16.114 gefp.math.matrix.Superimposer Class Reference

### Public Member Functions

- def __init__ (self)

  *SVDSuperimposer from BIOPYTHON PACKAGE Copyright (C) 2002, Thomas Hamelryck (thamelry@vub.ac.be) This code is part of the Biopython distribution and governed by its license.*
- def set (self, reference_coords, coords)
- def **run** (self)
- def **get_transformed** (self)
- def **get_rotran** (self)
- def **get_init_rms** (self)
- def **get_rms** (self)

### Public Attributes

- **reference_coords**
- **coords**
- **transformed_coords**
- **rot**
- **tran**
- **rms**
- **init_rms**
- **n**

### 16.114.1 Detailed Description

```
\
 SVDSuperimposer finds the best rotation and translation to put
 two point sets on top of each other (minimizing the RMSD). This is
 eg. useful to superimpose crystal structures.

 SVD stands for Singular Value Decomposition, which is used to calculate
 the superposition.

 Reference:

 Matrix computations, 2nd ed. Golub, G. & Van Loan, CF., The Johns
 Hopkins University Press, Baltimore, 1989
```

### 16.114.2 Constructor & Destructor Documentation

#### 16.114.2.1 __init__()

```
def gefp.math.matrix.Superimposer.__init__ (
            self )
```

Please see the LICENSE file that should have been included as part of this package.

### 16.114.3 Member Function Documentation

#### 16.114.3.1 set()

```
def gefp.math.matrix.Superimposer.set (
            self,
            reference_coords,
            coords )
```

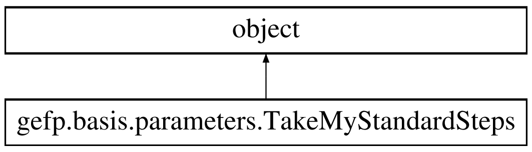
```
Set the coordinates to be superimposed.
coords will be put on top of reference_coords.

o reference_coords: an NxDIM array
o coords: an NxDIM array

DIM is the dimension of the points, N is the number
of points to be superimposed.
```

The documentation for this class was generated from the following file:

- gefp/gefp/math/matrix.py

## 16.115 gefp.basis.parameters.TakeMyStandardSteps Class Reference

Inheritance diagram for gefp.basis.parameters.TakeMyStandardSteps:



### Public Member Functions

- def __**init**__ (self, scales, stepsize=1.0)
- def __**call**__ (self, x)

### Public Attributes

- **stepsize**

The documentation for this class was generated from the following file:

- gefp/gefp/basis/parameters.py

## 16.116 oepdev::test::Test Class Reference

Manages test routines.

`#include <test.h>`

### Public Member Functions

- Test (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &options)

  *Construct the tester.*
- ∼Test ()

  *Destructor.*
- double run (void)

  *Pefrorm the test.*

### Protected Member Functions

- double test_basic (void)

  *Test the basic functionalities of OEPDev.*
- double test_basis_rotation (void)

  *Test the AO basis set rotation from oepdev::ao_rotation_matrix.*
- double test_cis_rhf (void)

  *Test the CIS(RHF) method.*
- double test_cis_uhf (void)

  *Test the CIS(UHF) method.*
- double test_cis_rhf_dl (void)

  *Test the CIS(RHF) method with Davidson-Liu algorithm.*
- double test_cis_uhf_dl (void)

  *Test the CIS(UHF) method with Davidson-Liu algorithm.*
- double test_cphf (void)

  *Test the CPHF method.*
- double test_dmatPol (void)

  *Test the density matrix susceptibility (X = 1)*

- double test_dmatPolX (void)

  *Test the density matrix susceptibility.*
- double test_eri_1_1 (void)

  *Test the oepdev::ERI_1_1 class against psi::ERI.*
- double test_eri_2_2 (void)

  *Test the oepdev::ERI_2_2 class against psi::ERI.*
- double test_eri_3_1 (void)

  *Test the oepdev::ERI_3_1 class against psi::ERI.*
- double test_unitaryOptimizer (void)

  *Test the oepdev::UnitaryOptimizer class.*
- double test_unitaryOptimizer_2 (void)

  *Test the oepdev::UnitaryOptimizer_2 class.*
- double test_unitaryOptimizer_4_2 (void)

  *Test the oepdev::UnitaryOptimizer_4_2 class.*
- double test_scf_perturb (void)

  *Test the oepdev::RHFPerturbed class.*
- double test_quambo (void)

  *Test the oepdev::QUAMBO class.*
- double test_camm (void)

  *Test the oepdev::CAMM class.*
- double test_dmtp_pot_field (void)

  *Test the oepdev::MultipoleConvergence class: potential and field calculations.*
- double test_dmtp_energy (void)

  *Test the oepdev::DMTP class for energy calculations.*
- double test_efp2_energy (void)

  *Test the oepdev::EFP2_GenEffPar and oepdev::EFP2_Computer classes.*
- double test_oep_efp2_energy (void)

  *Test the oepdev::EFP2_GenEffPar and oepdev::EFP2_Computer classes.*
- double test_kabsch_superimposition (void)

  *Test the oepdev::KabschSuperimposer.*
- double test_dmtp_superimposition (void)

  *Test the oepdev::DMTP class for superimposition.*
- double test_esp_solver (void)

  *Test the oepdev::ESPSolver.*
- double test_points_collection3d (void)

  *Test the cube file generation (oepdev::Field3D electrostatic potential and oepdev::Points3DIterator for cube collection)*
- double test_ct_energy_benchmark_ol (void)

  *Test the Charge-transfer Energy Solver (benchmark method Otto-Ladik)*
- double test_ct_energy_oep_based_ol (void)

*Test the Charge-transfer Energy Solver (oep-based method Otto-Ladik)*
- double test_rep_energy_benchmark_hs (void)

  *Test the Repulsion Energy Solver: (benchmark method Hayes-Stone)*
- double test_rep_energy_benchmark_dds (void)

  *Test the Repulsion Energy Solver: (benchmark method Density-Based - DDS/HF)*
- double test_rep_energy_benchmark_murrell_etal (void)

  *Test the Repulsion Energy Solver: (benchmark method Murrell-etal)*
- double test_rep_energy_oep_based_murrell_etal (void)

  *Test the Repulsion Energy Solver: (OEP-based method Murrell-etal)*
- double test_rep_energy_benchmark_ol (void)

  *Test the Repulsion Energy Solver: (benchmark method Otto-Ladik)*
- double test_rep_energy_benchmark_efp2 (void)

  *Test the Repulsion Energy Solver: (benchmark method EFP2)*
- double test_custom (void)

  *Test the custom code (to be deprecated)*

## Protected Attributes

- std::shared_ptr< psi::Wavefunction > wfn_

  *Wavefunction object.*
- psi::Options & options_

  *Psi4 Options.*

The documentation for this class was generated from the following files:

- oepdev/libtest/test.h
- oepdev/libtest/basic.cc
- oepdev/libtest/basis_rotation.cc
- oepdev/libtest/camm.cc
- oepdev/libtest/cis_rhf_dl.cc
- oepdev/libtest/cis_rhf_explicit.cc
- oepdev/libtest/cis_uhf_dl.cc
- oepdev/libtest/cis_uhf_explicit.cc
- oepdev/libtest/cphf.cc
- oepdev/libtest/ct_energy_benchmark_ol.cc
- oepdev/libtest/ct_energy_oep_based_ol.cc
- oepdev/libtest/dmatpol.cc
- oepdev/libtest/dmatpolX.cc
- oepdev/libtest/dmtp_energy.cc
- oepdev/libtest/dmtp_pot_field.cc
- oepdev/libtest/dmtp_superimposition.cc
- oepdev/libtest/efp2_energy.cc

- oepdev/libtest/eri_1_1.cc
- oepdev/libtest/eri_2_2.cc
- oepdev/libtest/eri_3_1.cc
- oepdev/libtest/esp_solver.cc
- oepdev/libtest/kabsch_superimposition.cc
- oepdev/libtest/oep_efp2_energy.cc
- oepdev/libtest/points_collection3d.cc
- oepdev/libtest/quambo.cc
- oepdev/libtest/rep_energy_benchmark_dds.cc
- oepdev/libtest/rep_energy_benchmark_efp2.cc
- oepdev/libtest/rep_energy_benchmark_hs.cc
- oepdev/libtest/rep_energy_benchmark_murrell_etal.cc
- oepdev/libtest/rep_energy_benchmark_ol.cc
- oepdev/libtest/rep_energy_oep_based_murrell_etal.cc
- oepdev/libtest/scf_perturb.cc
- oepdev/libtest/test.cc
- oepdev/libtest/test_custom.cc
- oepdev/libtest/unitary_optimizer.cc
- oepdev/libtest/unitary_optimizer_2.cc
- oepdev/libtest/unitary_optimizer_4_2.cc

## 16.117 oepdev::TIData Class Reference

Transfer Integral EET Data.

```
#include <ti_data.h>
```

### Public Member Functions

- TIData ()

  *Constructor.*
- virtual ∼TIData ()

  *Destroctor.*
- void set_s (double, double, double, double, double, double)

  *Set the overlap integrals between basis states, $S_{ij}$, for ij=12,13,14,23,24,34.*
- void set_e (double, double, double, double)

  *Set the diagonal exciton Hamiltonian matrix elements $E_n$ for n=1,2,3,4.*
- void set_de (double, double)

  *Set environmental corrections $\Delta E_1$ and $\Delta E_2$.*
- void set_trcamm_coupling (oepdev::SharedDMTPConvergence)

  *Set the convergence object for TrCAMM-based $V^{\rm Coul,(0)}$.*
- virtual double coupling_trcamm (const std::string &rn)

- virtual double coupling_direct (void)
- virtual double coupling_direct_coul (void)
- virtual double coupling_direct_exch (void)
- virtual double coupling_indirect (void)
- virtual double coupling_indirect_ti2 (void)
- virtual double coupling_indirect_ti3 (void)
- virtual double coupling_total (void)
- virtual double overlap_corrected (const std::string &type)
- virtual double overlap_corrected_direct (void)
- virtual double overlap_corrected_direct (double v)
- virtual double overlap_corrected_indirect (double v, double s)

## Public Attributes

- oepdev::MultipoleConvergence::ConvergenceLevel trcamm_convergence

  *Convergence object for Coulombic coupling under TrCAMM approximation.*
- bool diagonal_correction

  *Environmental correction activated?*
- bool mulliken_approximation

  *Mulliken approximation activated?*
- bool overlap_correction

  *Overlap correction acrivatved?*
- bool trcamm_approximation

  *TrCAMM approximation activated?*
- std::map< std::string, double > v0
- oepdev::SharedDMTPConvergence v0_trcamm

  *V0_Coul multipole convergence.*

- double s12

  *Overlap matrix element between basis functions.*
- double s13

  *Overlap matrix element between basis functions.*
- double s14

  *Overlap matrix element between basis functions.*
- double s23

  *Overlap matrix element between basis functions.*
- double s24

  *Overlap matrix element between basis functions.*
- double s34

*Overlap matrix element between basis functions.*

- double e1

  *Diagonal Hamiltonian matrix element.*
- double e2

  *Diagonal Hamiltonian matrix element.*
- double e3

  *Diagonal Hamiltonian matrix element.*
- double e4

  *Diagonal Hamiltonian matrix element.*

- double de1

  *Environmental correction to the $E_n$ for n =1,2.*
- double de2

  *Environmental correction to the $E_n$ for n =1,2.*

### Protected Attributes

- double c_

  *Conversion factor (unused now)*

### 16.117.1 Detailed Description

Container for storing and managing TI data for EET coupling calculations, according to Fujimoto JCP 2012:

- exciton Hamiltonian matrix elements
- overlap integrals between basis states
- TrCAMM EET coupling convergence object

Contains useful methods to process exciton Hamiltonian matrix elements:

- compute direct and indirect EET coupling constants
- compute overlap-corrected exciton Hamiltonian off-diagonal matrix elements
- include or exclude environmental correction in the diagonal exciton Hamiltonian
- activate TrCAMM approximation of $V^{\mathrm{Coul},(0)}$

- activate Mulliken approximation for $V^{\mathrm{Exch},(0)}$ and $V^{\mathrm{CT},(0)}$

To activate/deactivate the various approximations and corrections listed above, set the following attributes

- `diagonal_correction`
- `mulliken_approximation`
- `overlap_correction`
- `trcamm_approximation`

to `true`/`false`, accroding to your need.

### Example of usage.

```
{c++}
  // Set up exciton Hamiltonian
  TIData data = TIData();
  data.set_s(S12, S13, S14, S32, S42, S34);
  data.set_e(E1, E2, E3, E4);
  data.set_de(E1 - E01, E2 - E02);
  data.v0["COUL"]= V0_Coul;
  data.v0["EXCH"]= V0_Exch;
  data.v0["ET1"] = V0_ET1;
  data.v0["ET2"] = V0_ET2;
  data.v0["HT1"] = V0_HT1;
  data.v0["HT2"] = V0_HT2;
  data.v0["CT" ] = V0_CT;
  data.v0["EXCH_M"]= V0_Exch_M;
  data.v0["CT_M"] = V0_CT_M;

  // Set up appriximations and corrections
  data.diagonal_correction = true;
  data.mulliken_approximation= false;
  data.trcamm_approximation = false;
  data.overlap_correction = true;

  // Compute overlap-corrected indirect coupling matrix elements
  double V_ET1 = data.overlap_corrected("ET1");
  double V_ET2 = data.overlap_corrected("ET2");
  double V_HT1 = data.overlap_corrected("HT1");
  double V_HT2 = data.overlap_corrected("HT2");
  double V_CT  = data.overlap_corrected("CT") ;
  double V_CT_M= data.overlap_corrected("CT_M");

  // Compute final coupling contributions
  double V_Coul = data.overlap_corrected("COUL");
  double V_Exch = data.overlap_corrected("EXCH");
  double V_Ovrl = data.overlap_corrected("OVRL");

  double V_Exch_M= data.overlap_corrected("EXCH_M");

  double V_TI_2 = data.coupling_indirect_ti2();
  double V_TI_3 = data.coupling_indirect_ti3();

  data.diagonal_correction = false;
  double V0_TI_2 = data.coupling_indirect_ti2();
  double V0_TI_3 = data.coupling_indirect_ti3();

  data.mulliken_approximation = true;
  double V0_TI_3_M = data.coupling_indirect_ti3();
  data.diagonal_correction = true;
  double V_TI_3_M = data.coupling_indirect_ti3();
  double V_direct = V_Coul + V_Exch + V_Ovrl;
  double V_indirect = V_TI_2 + V_TI_3;
```

**See also**

oepdev::EETCouplingSolver

### 16.117.2 Member Function Documentation

#### 16.117.2.1 coupling_direct()

```
double TIData::coupling_direct (
            void ) [virtual]
```

Compute the direct EET coupling constant.

**Returns**

$V^{\text{Dir}} = V^{\text{Coul}} + V^{\text{Exch}} + V^{\text{Ovrl}}$

Overlap and diagonal corrections as well as TrCAMM and Mulliken approximations for Coulomb and pure exchange parts can be set.

#### 16.117.2.2 coupling_direct_coul()

```
double TIData::coupling_direct_coul (
            void ) [virtual]
```

Compute the direct EET coupling constant in Forster limit (Coulombic approximation)

**Returns**

$V^{\text{Dir}} = V^{\text{Coul}}$

Overlap correction as well as TrCAMM approximation for Coulomb coupling can be set.

#### 16.117.2.3 coupling_direct_exch()

```
double TIData::coupling_direct_exch (
            void ) [virtual]
```

Compute the direct EET coupling constant due to pure exchange.

**Returns**

$V^{\text{Dir}} = V^{\text{Exch}}$

Overlap correction as well Mulliken approximation for pure exchange coupling can be set.

#### 16.117.2.4 coupling_indirect()

```
double TIData::coupling_indirect (
          void  )  [virtual]
```

Compute the indirect EET coupling constant.

**Returns**

$$V^{\text{Indir}} = V^{\text{TI},(2)} + V^{\text{TI},(3)}$$

Overlap and diagonal corrections as well as Mulliken approximations for $V^{\text{CT},(0)}$ can be set.

#### 16.117.2.5 coupling_indirect_ti2()

```
double TIData::coupling_indirect_ti2 (
          void  )  [virtual]
```

Compute the indirect EET coupling constant in second-order with respect to TI.

**Returns**

$$V^{\text{TI},(2)} = -\frac{V^{\text{ET1}}V^{\text{HT2}}}{E_3-E_1} - \frac{V^{\text{ET2}}V^{\text{HT1}}}{E_4-E_1}$$

Overlap and diagonal corrections can be set.

#### 16.117.2.6 coupling_indirect_ti3()

```
double TIData::coupling_indirect_ti3 (
          void  )  [virtual]
```

Compute the indirect EET coupling constant in third-order with respect to TI.

**Returns**

$$V^{\text{TI},(3)} = \frac{V^{\text{CT}}\left(V^{\text{ET1}}V^{\text{ET2}}+V^{\text{HT1}}V^{\text{HT2}}\right)}{(E_3-E_1)(E_4-E_1)}$$

Overlap and diagonal corrections as well as Mulliken approximations for $V^{\text{CT},(0)}$ can be set.

#### 16.117.2.7 coupling_total()

```
double TIData::coupling_total (
          void  )  [virtual]
```

Compute the *total* EET coupling constant.

**Returns**

$$V^{\text{Total}} = V^{\text{Dir}} + V^{\text{Indir}}$$

Overlap and diagonal corrections, TrCAMM approximation for Coulomb coupling, and Mulliken approximations for pure exchange coupling and $V^{\text{CT},(0)}$ can be set.

#### 16.117.2.8 coupling_trcamm()

```
double TIData::coupling_trcamm (
          const std::string & rn ) [virtual]
```

Compute Coulombic coupling approximated by TrCAMM.

**Parameters**

| | |
|---|---|
| *rn* | - convergence of TrCAMM coupling. Can be from `R1` to `R5`, which corresponds to the $R^{-n}$ series expansion of distributed multipoles. |

**Returns**

$V^{\mathrm{Coul},(0)} \approx V^{\mathrm{TrCAMM},(0)}\left(R^{-n}\right)$

#### 16.117.2.9 overlap_corrected()

```
double TIData::overlap_corrected (
          const std::string & type ) [virtual]
```

Compute overlap corrected matrix elements.

**Parameters**

| | |
|---|---|
| *type* | - matrix element $V^{\text{type},(0)}$ subject to overlap correction, where type is one of the following:<br>• `COUL` - $V^{\text{Coul},(0)}$,<br>• `EXCH` - $V^{\text{Exch},(0)}$,<br>• `TrCAMM_R1` - $V^{\text{TrCAMM},(0)}(R^{-1})$,<br>• `TrCAMM_R2` - $V^{\text{TrCAMM},(0)}(R^{-2})$,<br>• `TrCAMM_R3` - $V^{\text{TrCAMM},(0)}(R^{-3})$,<br>• `TrCAMM_R4` - $V^{\text{TrCAMM},(0)}(R^{-4})$,<br>• `TrCAMM_R5` - $V^{\text{TrCAMM},(0)}(R^{-5})$,<br>• `ET1` - $V^{\text{ET1},(0)}$,<br>• `ET2` - $V^{\text{ET2},(0)}$,<br>• `HT1` - $V^{\text{HT1},(0)}$,<br>• `HT2` - $V^{\text{HT2},(0)}$,<br>• `CT` - $V^{\text{CT},(0)}$,<br>• `CT_M` - Mulliken-approximated $V^{\text{CT},(0)}$,<br>• `EXCH_M` - Mulliken-approximated $V^{\text{Exch},(0)}$. |

If type = `OVRL`, the overlap-correction to the direct EET coupling constant is returned, $V^{\text{Ovrl}}$.

**Returns**

overlap-corrected exciton Hamiltonian matrix element contribution of selected type

Diagonal correction can be set.

#### 16.117.2.10 overlap_corrected_direct() [1/2]

```
double TIData::overlap_corrected_direct (
          void ) [virtual]
```

Compute overlap-corrected direct EET coupling constant.

**Returns**

$V^{\text{Dir}} = V^{\text{Coul}} + V^{\text{Exch}} + V^{\text{Ovrl}}$

Diagonal correction, TrCAMM approximation and Mulliken approximation can be set.

#### 16.117.2.11 overlap_corrected_direct() [2/2]

```
double TIData::overlap_corrected_direct (
          double v ) [virtual]
```

Compute overlap-corrected direct EET coupling constant from value *v*.

**Returns**

$\frac{v}{1-S_{12}^2}$

#### 16.117.2.12 overlap_corrected_indirect()

```
double TIData::overlap_corrected_indirect (
          double v,
          double s ) [virtual]
```

Compute overlap-corrected coupling constant from value *v* and associated overlap integral *s*.

**Returns**

$\frac{1}{1-s^2}\left(v-\frac{(E_1+E_2)s}{2}\right)$

Diagonal correction can be set.

### 16.117.3 Member Data Documentation

#### 16.117.3.1 v0

```
std::map<std::string, double> oepdev::TIData::v0
```

Dictionary of all zeroth-order off-diagonal matrix elements.

Use only the following keywords:

- `COUL` - $V^{\rm Coul,(0)}$,
- `EXCH` - $V^{\rm Exch,(0)}$,
- `TrCAMM_R1` - $V^{\rm TrCAMM,(0)}(R^{-1})$,
- `TrCAMM_R2` - $V^{\rm TrCAMM,(0)}(R^{-2})$,
- `TrCAMM_R3` - $V^{\rm TrCAMM,(0)}(R^{-3})$,
- `TrCAMM_R4` - $V^{\rm TrCAMM,(0)}(R^{-4})$,

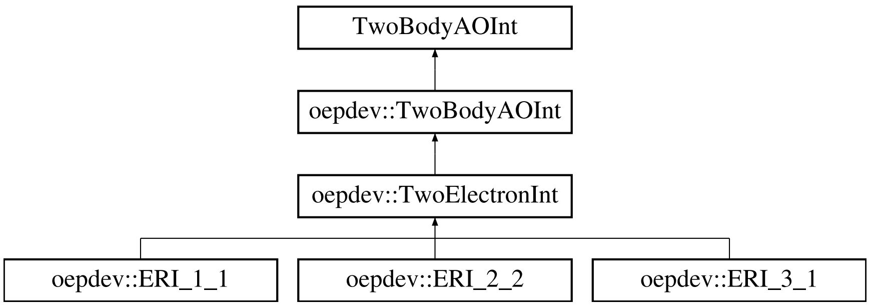
- `TrCAMM_R5` - $V^{\mathrm{TrCAMM},(0)}(R^{-5})$,
- `ET1` - $V^{\mathrm{ET1},(0)}$,
- `ET2` - $V^{\mathrm{ET2},(0)}$,
- `HT1` - $V^{\mathrm{HT1},(0)}$,
- `HT2` - $V^{\mathrm{HT2},(0)}$,
- `CT` - $V^{\mathrm{CT},(0)}$,
- `CT_M` - Mulliken-approximated $V^{\mathrm{CT},(0)}$,
- `EXCH_M` - Mulliken-approximated $V^{\mathrm{Exch},(0)}$,
- `OVRL` - $V^{\mathrm{Ovrl}}$.

The documentation for this class was generated from the following files:

- oepdev/libsolver/ti_data.h
- oepdev/libsolver/ti_data.cc

## 16.118 oepdev::TwoBodyAOInt Class Reference

Inheritance diagram for oepdev::TwoBodyAOInt:



### Public Member Functions

- virtual void compute (std::shared_ptr< psi::Matrix > &result, int ibs1=0, int ibs2=2)

  *Compute two-body two-centre integral and put it into matrix.*
- virtual void compute (psi::Matrix &result, int ibs1=0, int ibs2=2)
- virtual size_t **compute_shell** (int, int, int, int)=0
- virtual size_t **compute_shell** (int, int, int)=0
- virtual size_t **compute_shell** (int, int)=0
- virtual size_t **compute_shell_deriv1** (int, int, int, int)=0
- virtual size_t **compute_shell_deriv2** (int, int, int, int)=0

- virtual size_t **compute_shell_deriv1** (int, int, int)=0
- virtual size_t **compute_shell_deriv2** (int, int, int)=0
- virtual size_t **compute_shell_deriv1** (int, int)=0
- virtual size_t **compute_shell_deriv2** (int, int)=0

## Protected Member Functions

- **TwoBodyAOInt** (const IntegralFactory ∗intsfactory, int deriv=0)
- **TwoBodyAOInt** (const TwoBodyAOInt &rhs)

## 16.118.1 Member Function Documentation

### 16.118.1.1 compute() [1/2]

```
void oepdev::TwoBodyAOInt::compute (
          std::shared_ptr< psi::Matrix > & result,
          int ibs1 = 0,
          int ibs2 = 2 )  [virtual]
```

**Parameters**

| | |
|---|---|
| *result* | - matrix where to store (i\|\|j) two-body integrals |
| *ibs1* | - first basis set axis |
| *ibs2* | - second basis set axis |

### 16.118.1.2 compute() [2/2]

```
void oepdev::TwoBodyAOInt::compute (
          psi::Matrix & result,
          int ibs1 = 0,
          int ibs2 = 2 )  [virtual]
```

This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.

The documentation for this class was generated from the following files:

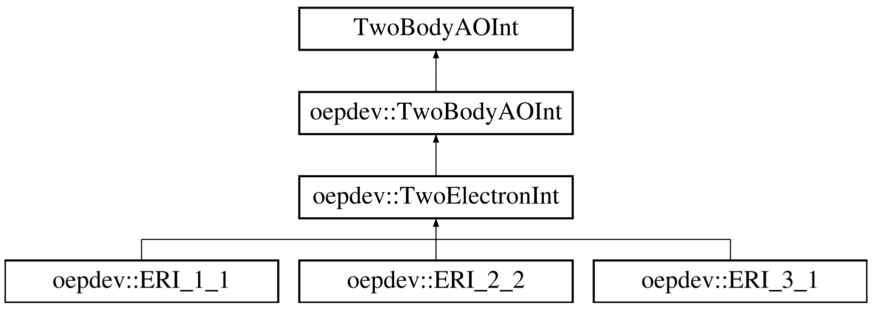
- oepdev/libpsi/integral.h
- oepdev/libpsi/integral.cc

## 16.119 oepdev::TwoElectronInt Class Reference

General Two Electron Integral.

`#include <eri.h>`

Inheritance diagram for oepdev::TwoElectronInt:



### Public Member Functions

- **TwoElectronInt** (const IntegralFactory ∗integral, int deriv, bool use_shell_pairs)
- virtual size_t compute_shell (int, int)

  *Compute ERI's between 2 shells. Result is stored in buffer.*
- virtual size_t compute_shell (int, int, int)

  *Compute ERI's between 3 shells. Result is stored in buffer.*
- virtual size_t compute_shell (int, int, int, int)

  *Compute ERI's between 4 shells. Result is stored in buffer.*
- virtual size_t compute_shell (const psi::AOShellCombinationsIterator &)
- virtual size_t compute_shell_deriv1 (int, int)

  *Compute first derivatives of ERI's between 2 shells.*
- virtual size_t compute_shell_deriv2 (int, int)

  *Compute second derivatives of ERI's between 2 shells.*
- virtual size_t compute_shell_deriv1 (int, int, int)

  *Compute first derivatives of ERI's between 3 shells.*
- virtual size_t compute_shell_deriv2 (int, int, int)

  *Compute second derivatives of ERI's between 3 shells.*
- virtual size_t compute_shell_deriv1 (int, int, int, int)

  *Compute first derivatives of ERI's between 4 shells.*
- virtual size_t compute_shell_deriv2 (int, int, int, int)

  *Compute second derivatives of ERI's between 4 shells.*

### Protected Member Functions

- int get_cart_am (int am, int n, int x)

    *Get the angular momentum per Cartesian component.*
- double get_R (int N, int L, int M)

    *Get the (N,L,M)th McMurchie-Davidson coefficient.*
- virtual size_t compute_doublet (int, int)

    *Computes the ERI's between three shells.*
- virtual size_t compute_triplet (int, int, int)

    *Computes the ERI's between three shells.*
- virtual size_t compute_quartet (int, int, int, int)

    *Computes the ERI's between four shells.*

### Protected Attributes

- const int max_am_

    *Maximum angular momentum.*
- const int n_max_am_

    *Maximum number of angular momentum functions.*
- psi::Fjt ∗ fjt_

    *Computes the fundamental: Boys function value at T for degree v.*
- bool use_shell_pairs_

    *Should we use shell pair information?*
- const double cartMap_ [60]

    *Map of Cartesian components per each am.*
- const double df_ [8]

    *Double factorial array.*
- double ∗ mdh_buffer_R_

    *Buffer for the McMurchie-Davidson-Hermite R coefficents.*

### 16.119.1 Detailed Description

Implements the McMurchie-Davidson recursive scheme for all integral types. The integral can be defined for any number of Gaussian centres, thus it is not limited to 2-by-2 four-centre ERI. Currently implemented subtypes are:

- oepdev::ERI_1_1 - 2-centre electron-repulsion integral (i|j)
- oepdev::ERI_2_2 - 4-centre electron-repulsion integral (ij|kl)
- oepdev::ERI_3_1 - 4-centre electron-repulsion integral (ijk|l)

**See also**

The Integral Package Library

### 16.119.2 Member Function Documentation

#### 16.119.2.1 compute_shell()

```
size_t oepdev::TwoElectronInt::compute_shell (
            const psi::AOShellCombinationsIterator & shellIter )  [virtual]
```

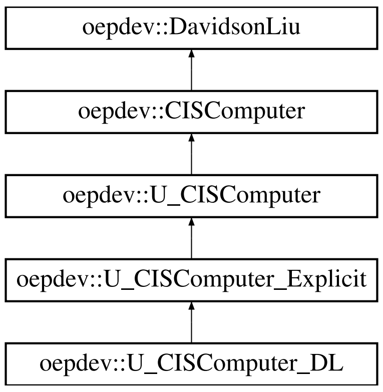
Compute ERIs between 4 shells. Result is stored in buffer. Only for use with ERI_2_2 and the same basis sets, otherwise shell pairs won't be compatible.

The documentation for this class was generated from the following files:

- oepdev/libints/eri.h
- oepdev/libints/eri.cc

## 16.120 oepdev::U_CISComputer Class Reference

Inheritance diagram for oepdev::U_CISComputer:



### Public Member Functions

- **U_CISComputer** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

### Protected Member Functions

- virtual void **print_excited_state_character_** (int I)

### Additional Inherited Members

The documentation for this class was generated from the following files:

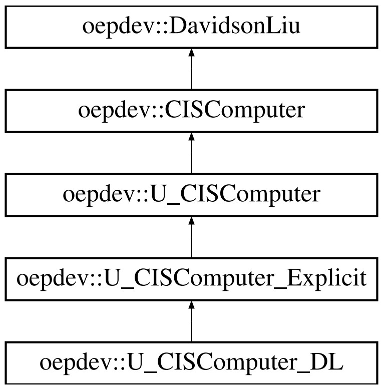
- oepdev/libutil/cis.h
- oepdev/libutil/cis_uhf.cc

## 16.121 oepdev::U_CISComputer_DL Class Reference

CIS Computer with UHF reference: Davidson-Liu Solver.

`#include <cis.h>`

Inheritance diagram for oepdev::U_CISComputer_DL:



### Public Member Functions

- **U_CISComputer_DL** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

### Protected Member Functions

- virtual void **set_nstates_** (void)
- virtual void **transform_integrals_** (void)
- virtual void **allocate_hamiltonian_** (void)
- virtual void **build_hamiltonian_** (void)
- virtual void **diagonalize_hamiltonian_** (void)
- virtual void **davidson_liu_compute_diagonal_hamiltonian** (void)
- virtual void **davidson_liu_compute_sigma** (void)

### Additional Inherited Members

### 16.121.1 Detailed Description

Associated options:

- `CIS_TYPE` - must be set to `DAVIDSON_LIU` (Default).
- `CIS_SCHWARTZ_CUTOFF` - Cutoff for Schwartz ERI screening. Default: 0.0.

## Implementation

### Diagonal Hamiltonian elements

They are computed by using direct method with Schwartz screening of AO ERI's. The implementation formula is

$$H_{ii}^{aa} = \varepsilon_a - \varepsilon_i + \sum_{\alpha\beta\gamma\delta} (\alpha\beta|\gamma\delta) C_{\alpha i} C_{\delta a} \left( C_{\beta a} C_{\gamma i} - C_{\beta i} C_{\gamma a} \right)$$
$$H_{\bar{i}\bar{i}}^{\bar{a}\bar{a}} = \varepsilon_{\bar{a}} - \varepsilon_{\bar{i}} + \sum_{\alpha\beta\gamma\delta} (\alpha\beta|\gamma\delta) C_{\alpha\bar{i}} C_{\delta\bar{a}} \left( C_{\beta\bar{a}} C_{\gamma\bar{i}} - C_{\beta\bar{i}} C_{\gamma\bar{a}} \right)$$

### Sigma vectors

The sigma vectors are computed from

$$\sigma_i^{a,k} = (\varepsilon_a - \varepsilon_i) b_i^{a,k} + J_i^a(\mathbf{T}^{(k)}) + J_i^a(\overline{\mathbf{T}^{(k)}}) - K_i^a(\mathbf{T}^{(k)})$$
$$\sigma_{\bar{i}}^{\bar{a},k} = (\varepsilon_{\bar{a}} - \varepsilon_{\bar{i}}) b_{\bar{i}}^{\bar{a},k} + J_{\bar{i}}^{\bar{i}}(\mathbf{T}^{(k)}) + J_{\bar{i}}^{\bar{i}}(\overline{\mathbf{T}^{(k)}}) - K_{\bar{i}}^{\bar{i}}(\overline{\mathbf{T}^{(k)}})$$

where *k* labels the vectors and where the generalized one-particle density matrices are defined by

$$T_{\gamma\delta}^{(k)} = \sum_{jb} C_{\delta b} b_j^{b,k} C_{\gamma j}$$
$$\overline{T}_{\gamma\delta}^{(k)} = \sum_{\bar{j}\bar{b}} C_{\delta\bar{b}} b_{\bar{j}}^{\bar{b},k} C_{\gamma\bar{j}}$$

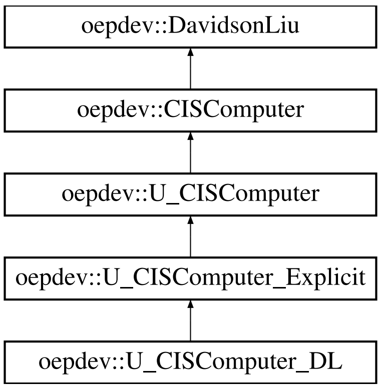
The **J** and **K** matrices in AO basis are computed by using the `psi::JK` object, and subsequently transformed to CMO's.

The documentation for this class was generated from the following files:

- oepdev/libutil/cis.h
- oepdev/libutil/cis_uhf_dl.cc

## 16.122 oepdev::U_CISComputer_Explicit Class Reference

Inheritance diagram for oepdev::U_CISComputer_Explicit:



### Public Member Functions

- **U_CISComputer_Explicit** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

### Protected Member Functions

- virtual void **set_beta_** (void)
- virtual void **build_hamiltonian_** (void)

### Additional Inherited Members

The documentation for this class was generated from the following files:

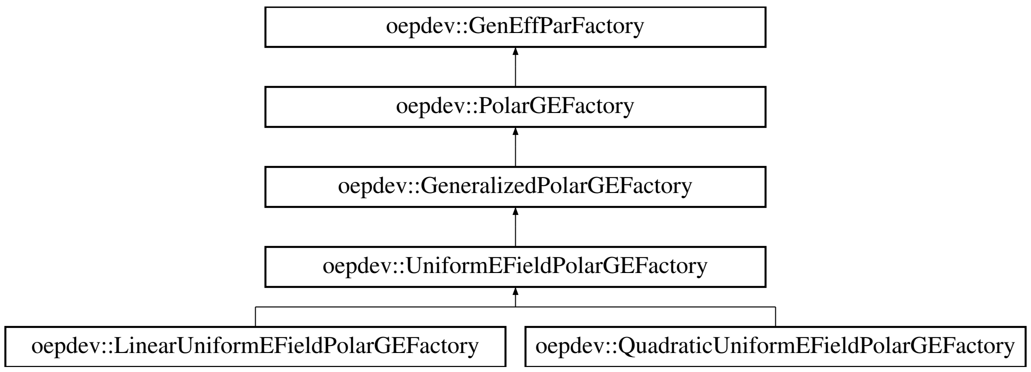
- oepdev/libutil/cis.h
- oepdev/libutil/cis_uhf_explicit.cc

## 16.123 oepdev::UniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

```
#include <gefp.h>
```

Inheritance diagram for oepdev::UniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

### Public Member Functions

- **UniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_samples (void)

  *Compute samples of density matrices and select electric field distributions.*
- virtual void compute_gradient (int i, int j)=0

  *Compute Gradient vector associated with the i-th and j-th basis set function.*
- virtual void compute_hessian (void)=0

  *Compute Hessian matrix (independent on the parameters)*

### Additional Inherited Members

### 16.123.1 Detailed Description

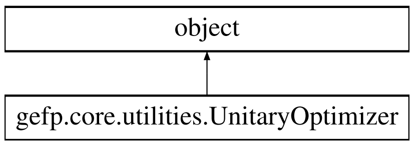
Implements a class of density matrix susceptibility models for parameterization in the uniform electric field.

The documentation for this class was generated from the following files:

- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_uniform_base.cc

## 16.124 gefp.core.utilities.UnitaryOptimizer Class Reference

Inheritance diagram for gefp.core.utilities.UnitaryOptimizer:



### Public Member Functions

- def __init__ (self, R, P, conv=1.0e-8, maxiter=100, verbose=True)
- def maximize (self)
- def minimize (self)
- def run (self, opt='minimize')
- def Z (self)

## Public Attributes

- **X**
- **conv**
- **maxiter**
- **verbose**

### 16.124.1 Detailed Description

```
--------------------------------------------------------------------------------

Finds the unitary matrix X that optimizes the following function:

Z(X) = \sum_{ijkl} X_{ij}X_{kl} R_{jl} - \sum_{ij} X_{ij}P_{j}

where
* X is a square unitary matrix of size N x N
* R is a square, in general non-symmetric matrix of size N x N
* P is a vector of length N

Usage:
optimizer = UnitaryOptimizer(R, P, conv=1.0e-8, maxiter=100, verbose=True)
optimizer.maximize() #or minimize()
X = optimizer.X
Z = optimizer.Z

--------------------------------------------------------------------------------
                                                    Last Revision: 25.03.2018
```

### 16.124.2 Constructor & Destructor Documentation

#### 16.124.2.1 __init__()

```
def gefp.core.utilities.UnitaryOptimizer.__init__ (
            self,
            R,
            P,
            conv = 1.0e-8,
            maxiter = 100,
            verbose = True )
```

```
Initialize with R and P matrix, as well as optimization options
```

### 16.124.3 Member Function Documentation

#### 16.124.3.1 maximize()

```
def gefp.core.utilities.UnitaryOptimizer.maximize (
            self )
```

```
Maximize the Z function under unitary constraint for X
```

#### 16.124.3.2 minimize()

```
def gefp.core.utilities.UnitaryOptimizer.minimize (
            self )
```

```
Minimize the Z function under unitary constraint for X
```

#### 16.124.3.3 run()

```
def gefp.core.utilities.UnitaryOptimizer.run (
            self,
            opt = 'minimize' )
```

```
Perform the optimization
```

#### 16.124.3.4 Z()

```
def gefp.core.utilities.UnitaryOptimizer.Z (
            self )
```

```
Return the current value of objective function
```

The documentation for this class was generated from the following file:

- gefp/gefp/core/utilities.py

## 16.125 oepdev::UnitaryOptimizer Class Reference

Find the optimim unitary matrix of quadratic matrix equation.

`#include <unitary_optimizer.h>`

## Public Member Functions

- UnitaryOptimizer (double ∗R, double ∗P, int n, double conv=1.0e-6, int maxiter=100, bool verbose=true)

  *Create from R and P matrices and optimization options.*
- UnitaryOptimizer (std::shared_ptr< psi::Matrix > R, std::shared_ptr< psi::Vector > P, double conv=1.0e-6, int maxiter=100, bool verbose=true)

  *Create from R and P matrices and optimization options.*
- ∼UnitaryOptimizer ()

  *Clear memory.*
- bool maximize ()

  *Run the minimization.*
- bool minimize ()

  *Run the maximization.*
- std::shared_ptr< psi::Matrix > X ()

  *Get the unitary matrix (solution)*
- double ∗ get_X () const

  *Get the unitary matrix (pointer to solution)*
- double Z ()

  *Get the actual value of Z function.*
- bool success () const

  *Get the status of the optimization.*

## Protected Member Functions

- UnitaryOptimizer (int n, double conv, int maxiter, bool verbose)

  *Initialize the basic memory.*
- void common_init_ ()

  *Prepare the optimizer.*
- void run_ (const std::string &opt)

  *Run the optimization (intermediate interface)*
- void optimize_ (const std::string &opt)

  *Run the optimization (inner interface)*
- void refresh_ ()

  *Restore the initial state of the optimizer.*
- void update_conv_ ()

  *Update the convergence.*
- void update_iter_ ()

  *Update the iterates.*
- void update_Z_ ()

  *Update Z value.*

- void update_RP_ ()

  *Uptade R and P matrices.*
- void update_X_ ()

  *Update the solution matrix X.*
- double eval_Z_ (double ∗X, double ∗R, double ∗P)

  *Evaluate the objective Z function.*
- double **eval_Z_** ()
- double eval_dZ_ (double g, double ∗R, double ∗P, int i, int j)

  *Evaluate the change in Z.*
- double eval_Z_trial_ (int i, int j, double gamma)

  *Evaluate the trial Z value.*
- void form_X0_ ()

  *Create identity matrix.*
- void form_X_ (int i, int j, double gamma)

  *Form unitary matrix X (store in buffer Xnew_)*
- void form_next_X_ (const std::string &opt)

  *Form the next unitary matrix X.*
- ABCD get_ABCD_ (int i, int j)

  *Retrieve ABCD parameters for root search.*
- void find_roots_boyd_ (const ABCD &abcd)

  *Solve for all roots of equation A∗sin(g) + B∗cos(g) + C∗sin(2∗g) + D∗cos(2∗g) = 0 -> implements Boyd's method.*
- double find_root_halley_ (double x0, const ABCD &abcd)

  *Solve for root of equation A∗sin(g) + B∗cos(g) + C∗sin(2∗g) + D∗cos(2∗g) = 0 -> implements Halley's method.*
- double find_gamma_ (const ABCD &abcd, int i, int j, const std::string &opt)

  *Compute gamma from roots of base equations.*
- bool lt_ (double a, double b)

  *less-than function*
- bool gt_ (double a, double b)

  *greater-than function*
- double func_0_ (double g, const ABCD &abcd)

  *Function f(gamma) = d(dZ)/dgamma.*
- double func_1_ (double g, const ABCD &abcd)

  *Gradient of f(gamma)*
- double func_2_ (double g, const ABCD &abcd)

  *Hessian of f(gamma) - used only for Halley method (not implemented since Boyd method is more suitable here)*
- std::shared_ptr< psi::Matrix > psi_X_ ()

  *Form the Psi4 matrix with the transformation matrix.*

## Protected Attributes

- const int n_

  *Dimension of the problem.*
- const double conv_

  *Convergence.*
- const int maxiter_

  *Maximum number of iterations.*
- const bool verbose_

  *Verbose mode.*
- double ∗ R_

  *R matrix.*
- double ∗ P_

  *P vector.*
- double ∗ R0_

  *Reference R matrix.*
- double ∗ P0_

  *Reference P vector.*
- double ∗ X_

  *X Matrix (accumulated solution)*
- double ∗ W_

  *Work place.*
- double ∗ Xold_

  *Temporary X matrix.*
- double ∗ Xnew_

  *Temporary X matrix.*
- int niter_

  *Current number of iterations.*
- double S_ [4]

  *Current solutions.*
- double Zinit_

  *Initial Z value.*
- double Zold_

  *Old Z value.*
- double Znew_

  *New Z value.*
- double conv_current_

  *Current convergence.*
- bool success_

  *Status of optimization.*

### 16.125.1 Detailed Description

The objective function of the orthogonal matrix $\mathbf{X}$

$$Z(\mathbf{X}) \equiv \sum_{ijkl} X_{ij} X_{kl} R_{jl} - \sum_{ij} X_{ij} P_j$$

is optimized by using the Jacobi iteration algorithm. In the above equation, $\mathbf{R}$ is a square, general real matrix of size $N \times N$ whereas $\mathbf{P}$ is a real vector of length $N$.

#### Algorithm.

Optimization of $\mathbf{X}$ is factorized into a sequence of 2-dimensional rotations with one real parameter $\gamma$:

$$\mathbf{X}^{\text{New}} = \mathbf{U}(\gamma) \cdot \mathbf{X}^{\text{Old}}$$

where

$$\mathbf{U}(\gamma) \equiv \begin{pmatrix} \ddots & & & & \\ & \cos(\gamma) & \cdots & \sin(\gamma) & \\ & \vdots & \ddots & \vdots & \\ & -\sin(\gamma) & \cdots & \cos(\gamma) & \\ & & & & \ddots \end{pmatrix}$$

is the Jacobi transformation matrix constructed for the $I$th and $J$th element from the entire $N$-dimensional set. For the sake of algirithmic simplicity, every iteration after $\mathbf{U}(\gamma)$ has been formed, $\mathbf{X}^{\text{Old}}$ is for a while assumed to be an identity matrix and the $\mathbf{R}$ matrix and $\mathbf{P}$ vector are transformed according to the following formulae

$$\mathbf{R} \rightarrow \mathbf{U}\mathbf{R}\mathbf{U}^T$$
$$\mathbf{P} \rightarrow \mathbf{U}\mathbf{P}$$

The full transformation matrix is accumulated in the memory buffer until convergence.

In each iteration, the optimum angle $\gamma$ is found as follows: First, the roots of the finite Fourier series

$$A\sin(\gamma) + B\cos(\gamma) + C\sin(2\gamma) + D\cos(2\gamma) = 0$$

are found. In the above equations, the expansion coefficients are given as

$$A = P_I + P_J - \sum_{k \neq I,J} (R_{Ik} + R_{Jk} + R_{kI} + R_{kJ})$$
$$B = P_I - P_J - \sum_{k \neq I,J} (R_{Ik} - R_{Jk} + R_{kI} - R_{kJ})$$
$$C = -2(R_{IJ} + R_{JI})$$
$$D = -2(R_{II} - R_{JJ})$$

and $I, J$ are the chosen indices in the Jacobi iteration subspace. The roots are evaluated by applying the Boyd's method[1], in which they are given as

$$\gamma_n = \Re\left[-i\ln(\lambda_n)\right]$$

where $\lambda_n$ is an eivenvalue of the following 4 by 4 complex matrix:

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -\frac{D+iC}{D-iC} & -\frac{B+iC}{D-iC} & 0 & -\frac{B-iC}{D-iC} \end{pmatrix}$$

Once the four roots of the Fourier series equation are found, one solution out of four is chosen which satisfies the global optimum condition, i.e., the largest increase/decrease in the objective function given by

$$\delta Z = A(1-\cos(\gamma)) + B\sin(\gamma) + C\sin^2(\gamma) + \frac{D}{2}\sin(2\gamma)$$

The discrimination between the minimae/maximae is performed based on the evaluation of the Hessian of $Z$ with respect to $\gamma$,

$$\frac{\partial^2 Z}{\partial \gamma^2} = A\cos(\gamma) - B\sin(\gamma) + 2C\cos(2\gamma) - 2D\sin(2\gamma)$$

All the $N(N-1)/2$ unique pairs of molecular orbitals are checked and the optimal set of $\gamma, I, J$ is chosen to construct $\mathbf{X}^{\rm New}$.

**References:**

[1] Boyd, J.P.; J. Eng. Math. (2006) 56, pp. 203-219

### 16.125.2 Constructor & Destructor Documentation

#### 16.125.2.1 UnitaryOptimizer() [1/3]

```
oepdev::UnitaryOptimizer::UnitaryOptimizer (
            double * R,
            double * P,
            int n,
            double conv = 1.0e-6,
            int maxiter = 100,
            bool verbose = true )
```

**Parameters**

| | |
|---|---|
| *R* | - $\mathbf{R}$ matrix |
| *P* | - $\mathbf{P}$ vector |
| *n* | - dimensionality of the problem ( $N$) |
| *conv* | - convergence in the $Z$ function |
| *maxiter* | - maximum number of iterations |
| *verbose* | - whether print information of iteration process or not Sets up the optimizer. |

#### 16.125.2.2 UnitaryOptimizer() [2/3]

```
oepdev::UnitaryOptimizer::UnitaryOptimizer (
            std::shared_ptr< psi::Matrix > R,
            std::shared_ptr< psi::Vector > P,
            double conv = 1.0e-6,
            int maxiter = 100,
            bool verbose = true )
```

**Parameters**

| | |
|---|---|
| *R* | - $\mathbf{R}$ matrix |
| *P* | - $\mathbf{P}$ vector |
| *conv* | - convergence in the $Z$ function |
| *maxiter* | - maximum number of iterations |
| *verbose* | - whether print information of iteration process or not Sets up the optimizer. |

#### 16.125.2.3 UnitaryOptimizer() [3/3]

```
oepdev::UnitaryOptimizer::UnitaryOptimizer (
            int n,
            double conv,
            int maxiter,
            bool verbose )  [protected]
```

**Parameters**

| | |
|---|---|
| *n* | - dimensionality of the problem ( $N$) |
| *conv* | - convergence in the $Z$ function |
| *maxiter* | - maximum number of iterations |
| *verbose* | - whether print information of iteration process or not Sets up the optimizer. |

The documentation for this class was generated from the following files:

- oepdev/libutil/unitary_optimizer.h
- oepdev/libutil/unitary_optimizer.cc

## 16.126 oepdev::UnitaryOptimizer_2 Class Reference

Find the optimim unitary matrix for quadratic matrix equation with trace.

```
#include <unitary_optimizer.h>
```

## Public Member Functions

- UnitaryOptimizer_2 (double ∗P, int n, double conv=1.0e-6, int maxiter=100, bool verbose=true)

    *Create from P tensor and optimization options.*
- ∼UnitaryOptimizer_2 ()

    *Clear memory.*
- bool maximize ()

    *Run the minimization.*
- bool minimize ()

    *Run the maximization.*
- std::shared_ptr< psi::Matrix > X ()

    *Get the unitary matrix (solution)*
- double ∗ get_X () const

    *Get the unitary matrix (pointer to solution)*
- double Z ()

    *Get the actual value of Z function.*
- bool success () const

    *Get the status of the optimization.*

## Protected Member Functions

- UnitaryOptimizer_2 (int n, double conv, int maxiter, bool verbose)

    *Initialize the basic memory.*
- void common_init_ ()

    *Prepare the optimizer.*
- void run_ (const std::string &opt)

    *Run the optimization (intermediate interface)*
- void optimize_ (const std::string &opt)

    *Run the optimization (inner interface)*
- void refresh_ ()

    *Restore the initial state of the optimizer.*
- void update_conv_ ()

    *Update the convergence.*
- void update_iter_ ()

    *Update the iterates.*
- void update_Z_ ()

    *Update Z value.*
- void update_P_ ()

    *Uptade P tensor.*
- void update_X_ ()

*Update the solution matrix X.*
- double eval_Z_ (double ∗X, double ∗P)

  *Evaluate the objective Z function.*
- double **eval_Z_** ()
- double eval_dZ_ (double g, double ∗P, int I, int J)

  *Evaluate the change in Z.*
- double eval_Z_trial_ (int I, int J, double gamma)

  *Evaluate the trial Z value.*
- void form_X0_ ()

  *Create identity matrix.*
- void form_X_ (int I, int J, double gamma)

  *Form unitary matrix X (store in buffer Xnew_)*
- void form_next_X_ (const std::string &opt)

  *Form the next unitary matrix X.*
- Fourier5 get_fourier_ (int I, int J)

  *Retrieve ABCD parameters for root search.*
- void find_roots_boyd_ (const Fourier5 &abcd)

  *Solve for all roots of equation A∗sin(g) + B∗cos(g) + C∗sin(2∗g) + D∗cos(2∗g) + E = 0 -> implements Boyd's method.*
- double find_root_halley_ (double x0, const Fourier5 &abcd)

  *Solve for root of equation A∗sin(g) + B∗cos(g) + C∗sin(2∗g) + D∗cos(2∗g) = 0 -> implements Halley's method.*
- double find_gamma_ (const Fourier5 &abcd, int i, int j, const std::string &opt)

  *Compute gamma from roots of base equations.*
- bool lt_ (double a, double b)

  *less-than function*
- bool gt_ (double a, double b)

  *greater-than function*
- std::shared_ptr< psi::Matrix > psi_X_ ()

  *Form the Psi4 matrix with the transformation matrix.*

## Protected Attributes

- const int n_

  *Dimension of the problem.*
- const double conv_

  *Convergence.*
- const int maxiter_

  *Maximum number of iterations.*
- const bool verbose_

  *Verbose mode.*

- double ∗ P_

  *P tensor.*
- double ∗ P0_

  *Reference P tensor.*
- double ∗ X_

  *X Matrix (accumulated solution)*
- double ∗ W_

  *Work place.*
- double ∗ Xold_

  *Temporary X matrix.*
- double ∗ Xnew_

  *Temporary X matrix.*
- int niter_

  *Current number of iterations.*
- double S_ [4]

  *Current solutions.*
- double Zinit_

  *Initial Z value.*
- double Zold_

  *Old Z value.*
- double Znew_

  *New Z value.*
- double conv_current_

  *Current convergence.*
- bool success_

  *Status of optimization.*

### 16.126.1 Detailed Description

The objective function of the orthogonal matrix $\mathbf{X}$

$$Z(\mathbf{X}) \equiv \sum_{ijk} X_{ji} X_{ki} P_{ijk}$$

is optimized by using the Jacobi iteration algorithm. In the above equation, $\mathbf{P}$ is a general real third-rank tensor of size $N^3$. The solver is equivalent to UnitaryOptimizer_4_2 in mathematical sense, in which the sixth-rank tensor is zero, hence costly $N^6$ memory alocation is avoided.

**Algorithm.**

Optimization of $\mathbf{X}$ is factorized into a sequence of 2-dimensional rotations with one real parameter $\gamma$:

$$\mathbf{X}^{\rm New} = \mathbf{X}^{\rm Old} \cdot \mathbf{U}(\gamma)$$

where

$$\mathbf{U}(\gamma) \equiv \begin{pmatrix} \ddots & & & & \\ & \cos(\gamma) & \cdots & \sin(\gamma) & \\ & \vdots & \ddots & \vdots & \\ & -\sin(\gamma) & \cdots & \cos(\gamma) & \\ & & & & \ddots \end{pmatrix}$$

is the Jacobi transformation matrix constructed for the $I$th and $J$th element from the entire $N$-dimensional set. For the sake of algorithmic simplicity, every iteration after $\mathbf{U}(\gamma)$ has been formed, $\mathbf{X}^{\rm Old}$ is for a while assumed to be an identity matrix and the $\mathbf{P}$ tensor are transformed according to the following formulae

$$P_{ijk} \rightarrow \sum_{j'k'} P_{ij'k'} X_{j'j} X_{k'k}$$

The full transformation matrix is accumulated in the memory buffer until convergence.

In each iteration, the optimum angle $\gamma$ is found as follows: First, the roots of the finite Fourier series

$$a_0 + \sum_{p=1}^{2} \left\{ a_p \cos(px) + b_p \sin(px) \right\} = 0$$

are found. In the above equations, the expansion coefficients are calculated analytically as a function of $I, J$ - the chosen indices in the Jacobi iteration subspace. The roots are evaluated by applying the Boyd's method[1], in which they are given as

$$\gamma_n = \Re\left[ -i \ln(\lambda_n) \right]$$

where $\lambda_n$ is an eivenvalue of the following 4 by 4 complex matrix:

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -\frac{a_2+ib_2}{a_2-ib_2} & -\frac{a_1+ib_1}{a_2-ib_2} & -\frac{2a_0}{a_2-ib_2} & -\frac{a_1-ib_1}{a_2-ib_2} \end{pmatrix}$$

Once the four roots of the Fourier series equation are found, one solution out of four is chosen which satisfies the global optimum condition, i.e., the largest increase/decrease in the objective function given by

$$\delta Z = Z\left(\mathbf{U}(\gamma)\right) - Z(\mathbf{1})$$

The Hessian is not computed. All the $N(N-1)/2$ unique pairs of molecular orbitals are checked and the optimal set of $\gamma, I, J$ is chosen to construct $\mathbf{X}^{\rm New}$.

**References:**

[1] Boyd, J.P.; J. Eng. Math. (2006) 56, pp. 203-219

### 16.126.2 Constructor & Destructor Documentation

#### 16.126.2.1 UnitaryOptimizer_2() [1/2]

```
oepdev::UnitaryOptimizer_2::UnitaryOptimizer_2 (
            double * P,
            int n,
            double conv = 1.0e-6,
            int maxiter = 100,
            bool verbose = true )
```

**Parameters**

| | |
|---|---|
| *P* | - $\mathbf{P}$ tensor (flattened row-wise) |
| *n* | - dimensionality of the problem ( $N$) |
| *conv* | - convergence in the $Z$ function |
| *maxiter* | - maximum number of iterations |
| *verbose* | - whether print information of iteration process or not Sets up the optimizer. |

#### 16.126.2.2 UnitaryOptimizer_2() [2/2]

```
oepdev::UnitaryOptimizer_2::UnitaryOptimizer_2 (
            int n,
            double conv,
            int maxiter,
            bool verbose ) [protected]
```

**Parameters**

| | |
|---|---|
| *n* | - dimensionality of the problem ( $N$) |
| *conv* | - convergence in the $Z$ function |
| *maxiter* | - maximum number of iterations |
| *verbose* | - whether print information of iteration process or not Sets up the optimizer. |

The documentation for this class was generated from the following files:

- oepdev/libutil/unitary_optimizer.h
- oepdev/libutil/unitary_optimizer.cc

## 16.127 oepdev::UnitaryOptimizer_2_1 Class Reference

## Public Member Functions

- UnitaryOptimizer_2_1 (psi::SharedMatrix P, psi::SharedVector p, double conv=1.0e-6, int maxiter=100, bool verbose=true)

  *Create from P matrix and p vector and optimization options.*
- ∼UnitaryOptimizer_2_1 ()

  *Clear memory.*
- bool maximize ()

  *Run the minimization.*
- bool minimize ()

  *Run the maximization.*
- psi::SharedMatrix X ()

  *Get the unitary matrix (solution)*
- double ∗∗ get_X () const

  *Get the unitary matrix (pointer to solution)*
- double Z ()

  *Get the actual value of Z function.*
- bool success () const

  *Get the status of the optimization.*

## Protected Member Functions

- UnitaryOptimizer_2_1 (int n, double conv, int maxiter, bool verbose)

  *Initialize the basic memory.*
- void common_init_ ()

  *Prepare the optimizer.*
- void run_ (const std::string &opt)

  *Run the optimization (intermediate interface)*
- void optimize_ (const std::string &opt)

  *Run the optimization (inner interface)*
- void refresh_ ()

  *Restore the initial state of the optimizer.*
- void update_conv_ ()

  *Update the convergence.*
- void update_iter_ ()

  *Update the iterates.*
- void update_Z_ ()

  *Update Z value.*
- void update_P_ ()

  *Uptade P tensor.*
- void update_X_ ()

*Update the solution matrix X.*

- double eval_Z_ (psi::SharedMatrix X, psi::SharedMatrix P)

  *Evaluate the objective Z function.*
- double **eval_Z_** ()
- double eval_dZ_ (double g, psi::SharedMatrix, int I, int J)

  *Evaluate the change in Z.*
- double eval_Z_trial_ (int I, int J, double gamma)

  *Evaluate the trial Z value.*
- void form_X0_ ()

  *Create identity matrix.*
- void form_X_ (int I, int J, double gamma)

  *Form unitary matrix X (store in buffer Xnew_)*
- void form_next_X_ (const std::string &opt)

  *Form the next unitary matrix X.*
- Fourier5 get_fourier_ (int I, int J)

  *Retrieve ABCD parameters for root search.*
- void find_roots_boyd_ (const Fourier5 &abcd)

  *Solve for all roots of equation A∗sin(g) + B∗cos(g) + C∗sin(2∗g) + D∗cos(2∗g) + E = 0 -> implements Boyd's method.*
- double find_root_halley_ (double x0, const Fourier5 &abcd)

  *Solve for root of equation A∗sin(g) + B∗cos(g) + C∗sin(2∗g) + D∗cos(2∗g) = 0 -> implements Halley's method.*
- double find_gamma_ (const Fourier5 &abcd, int i, int j, const std::string &opt)

  *Compute gamma from roots of base equations.*
- bool lt_ (double a, double b)

  *less-than function*
- bool gt_ (double a, double b)

  *greater-than function*
- psi::SharedMatrix psi_X_ ()

  *Form the Psi4 matrix with the transformation matrix.*

## Protected Attributes

- const int n_

  *Dimension of the problem.*
- const double conv_

  *Convergence.*
- const int maxiter_

  *Maximum number of iterations.*
- const bool verbose_

  *Verbose mode.*

- psi::SharedMatrix P_

  *P tensor.*
- psi::SharedMatrix P0_

  *Reference P tensor.*
- psi::SharedVector p_

  *p vector*
- psi::SharedMatrix X_

  *X Matrix (accumulated solution)*
- psi::SharedMatrix W_

  *Work place 1.*
- psi::SharedMatrix Y_

  *Work place 2.*
- psi::SharedMatrix Xold_

  *Temporary X matrix.*
- psi::SharedMatrix Xnew_

  *Temporary X matrix.*
- int niter_

  *Current number of iterations.*
- double S_ [4]

  *Current solutions.*
- double Zinit_

  *Initial Z value.*
- double Zold_

  *Old Z value.*
- double Znew_

  *New Z value.*
- double conv_current_

  *Current convergence.*
- bool success_

  *Status of optimization.*

### 16.127.1 Constructor & Destructor Documentation

#### 16.127.1.1 UnitaryOptimizer_2_1() [1/2]

```
oepdev::UnitaryOptimizer_2_1::UnitaryOptimizer_2_1 (
          psi::SharedMatrix P,
          psi::SharedVector p,
          double conv = 1.0e-6,
          int maxiter = 100,
          bool verbose = true )
```

**Parameters**

| | |
|---|---|
| *P* | - $\mathbf{P}$ matrix |
| *p* | - $\mathbf{p}$ vector |
| *conv* | - convergence in the $Z$ function |
| *maxiter* | - maximum number of iterations |
| *verbose* | - whether print information of iteration process or not Sets up the optimizer. |

#### 16.127.1.2 UnitaryOptimizer_2_1() [2/2]

```
oepdev::UnitaryOptimizer_2_1::UnitaryOptimizer_2_1 (
          int n,
          double conv,
          int maxiter,
          bool verbose )  [protected]
```

**Parameters**

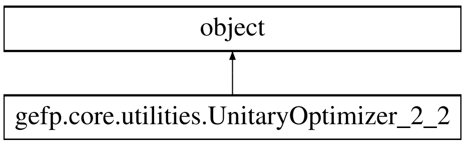
| | |
|---|---|
| *n* | - dimensionality of the problem ( $N$) |
| *conv* | - convergence in the $Z$ function |
| *maxiter* | - maximum number of iterations |
| *verbose* | - whether print information of iteration process or not Sets up the optimizer. |

The documentation for this class was generated from the following files:

- oepdev/libutil/unitary_optimizer.h
- oepdev/libutil/unitary_optimizer.cc

## 16.128 gefp.core.utilities.UnitaryOptimizer_2_2 Class Reference

Inheritance diagram for gefp.core.utilities.UnitaryOptimizer_2_2:



### Public Member Functions

- def __init__ (self, R, P, conv=1.0e-8, maxiter=100, verbose=True)
- def maximize (self)

- def minimize (self)
- def run (self, opt='minimize')
- def Z (self)

## Public Attributes

- **X**
- **conv**
- **maxiter**
- **verbose**

## 16.128.1 Detailed Description

```
---------------------------------------------------------------------------------

Finds the unitary matrix X that optimizes the following function:

Z(X) = \sum_{ijk} X_{ij}X_{ik} A_{jk} - \sum_{ij} X_{ij}B_{ji}

where
* X is a square unitary matrix of size N x N
* A is a square, in general non-symmetric matrix of size N x N
* B is a square, in general non-symmetric matrix of size N x N

Usage:
optimizer = UnitaryOptimizer_2_2(A, B, conv=1.0e-8, maxiter=100, verbose=True)
optimizer.maximize() #or minimize()
X = optimizer.X
Z = optimizer.Z

---------------------------------------------------------------------------------
                                                    Last Revision: 25.03.2018
```

## 16.128.2 Constructor & Destructor Documentation

### 16.128.2.1 __init__()

```
def gefp.core.utilities.UnitaryOptimizer_2_2.__init__ (
            self,
            R,
            P,
            conv = 1.0e-8,
            maxiter = 100,
            verbose = True )
```

```
Initialize with R and P matrix, as well as optimization options
```

## 16.128.3 Member Function Documentation

### 16.128.3.1 maximize()

```
def gefp.core.utilities.UnitaryOptimizer_2_2.maximize (
            self )
```

```
Maximize the Z function under unitary constraint for X
```

### 16.128.3.2 minimize()

```
def gefp.core.utilities.UnitaryOptimizer_2_2.minimize (
            self )
```

```
Minimize the Z function under unitary constraint for X
```

### 16.128.3.3 run()

```
def gefp.core.utilities.UnitaryOptimizer_2_2.run (
            self,
            opt = 'minimize' )
```

```
Perform the optimization
```

### 16.128.3.4 Z()

```
def gefp.core.utilities.UnitaryOptimizer_2_2.Z (
            self )
```

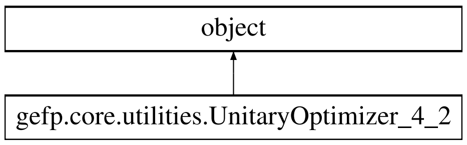
```
Return the current value of objective function
```

The documentation for this class was generated from the following file:

- gefp/gefp/core/utilities.py

## 16.129 gefp.core.utilities.UnitaryOptimizer_4_2 Class Reference

Inheritance diagram for gefp.core.utilities.UnitaryOptimizer_4_2:



### Public Member Functions

- def __init__ (self, R, P, conv=1.0e-8, maxiter=100, verbose=True)
- def maximize (self)
- def minimize (self)
- def run (self, opt='minimize')
- def Z (self)

### Public Attributes

- **X**
- **conv**
- **maxiter**
- **verbose**

### 16.129.1 Detailed Description

```
---------------------------------------------------------------------------------

Finds the unitary matrix X that optimizes the following function:

Z(X) = \sum_{ijklmn} X_{ki} X_{lj} X_{mi} X_{nj} R_{ijklmn}
   + \sum_{ijk}    X_{ji} X_{ki}               P_{ijk}

where
* X is a square unitary matrix of size N x N
* R is a general real 6-th rank tensor of size N^6
* P is a general real 3-rd rank tensor of size N^3

Usage:
optimizer = UnitaryOptimizer(R, P, conv=1.0e-8, maxiter=100, verbose=True)
optimizer.maximize() #or minimize()
X = optimizer.X
Z = optimizer.Z

---------------------------------------------------------------------------------
                                                    Last Revision: 07.04.2018
```

## 16.129.2 Constructor & Destructor Documentation

### 16.129.2.1 __init__()

```
def gefp.core.utilities.UnitaryOptimizer_4_2.__init__ (
            self,
            R,
            P,
            conv = 1.0e-8,
            maxiter = 100,
            verbose = True )
```

```
Initialize with R and P matrix, as well as optimization options
```

## 16.129.3 Member Function Documentation

### 16.129.3.1 maximize()

```
def gefp.core.utilities.UnitaryOptimizer_4_2.maximize (
            self )
```

```
Maximize the Z function under unitary constraint for X
```

### 16.129.3.2 minimize()

```
def gefp.core.utilities.UnitaryOptimizer_4_2.minimize (
            self )
```

```
Minimize the Z function under unitary constraint for X
```

### 16.129.3.3 run()

```
def gefp.core.utilities.UnitaryOptimizer_4_2.run (
            self,
            opt = 'minimize' )
```

```
Perform the optimization
```

#### 16.129.3.4 Z()

```
def gefp.core.utilities.UnitaryOptimizer_4_2.Z (
            self )
```

```
Return the current value of objective function
```

The documentation for this class was generated from the following file:

- gefp/gefp/core/utilities.py

## 16.130 oepdev::UnitaryOptimizer_4_2 Class Reference

Find the optimim unitary matrix for quartic-quadratic matrix equation with trace.

`#include <unitary_optimizer.h>`

### Public Member Functions

- UnitaryOptimizer_4_2 (double ∗R, double ∗P, int n, double conv=1.0e-6, int maxiter=100, bool verbose=true)

  *Create from R and P matrices and optimization options.*
- ∼UnitaryOptimizer_4_2 ()

  *Clear memory.*
- bool maximize ()

  *Run the minimization.*
- bool minimize ()

  *Run the maximization.*
- std::shared_ptr< psi::Matrix > X ()

  *Get the unitary matrix (solution)*
- double ∗ get_X () const

  *Get the unitary matrix (pointer to solution)*
- double Z ()

  *Get the actual value of Z function.*
- bool success () const

  *Get the status of the optimization.*

### Protected Member Functions

- UnitaryOptimizer_4_2 (int n, double conv, int maxiter, bool verbose)

  *Initialize the basic memory.*
- void common_init_ ()

*Prepare the optimizer.*

- void run_ (const std::string &opt)

  *Run the optimization (intermediate interface)*
- void optimize_ (const std::string &opt)

  *Run the optimization (inner interface)*
- void refresh_ ()

  *Restore the initial state of the optimizer.*
- void update_conv_ ()

  *Update the convergence.*
- void update_iter_ ()

  *Update the iterates.*
- void update_Z_ ()

  *Update Z value.*
- void update_RP_ ()

  *Uptade R and P matrices.*
- void update_X_ ()

  *Update the solution matrix X.*
- double eval_Z_ (double ∗X, double ∗R, double ∗P)

  *Evaluate the objective Z function.*
- double **eval_Z_** ()
- double eval_dZ_ (double g, double ∗R, double ∗P, int I, int J)

  *Evaluate the change in Z.*
- double eval_Z_trial_ (int I, int J, double gamma)

  *Evaluate the trial Z value.*
- void form_X0_ ()

  *Create identity matrix.*
- void form_X_ (int I, int J, double gamma)

  *Form unitary matrix X (store in buffer Xnew_)*
- void form_next_X_ (const std::string &opt)

  *Form the next unitary matrix X.*
- Fourier9 get_fourier_ (int I, int J)

  *Retrieve ABCD parameters for root search.*
- void find_roots_boyd_ (const Fourier9 &abcd)

  *Solve for all roots of equation A∗sin(g) + B∗cos(g) + C∗sin(2∗g) + D∗cos(2∗g) = 0 -> implements Boyd's method.*
- double find_root_halley_ (double x0, const Fourier9 &abcd)

  *Solve for root of equation A∗sin(g) + B∗cos(g) + C∗sin(2∗g) + D∗cos(2∗g) = 0 -> implements Halley's method.*
- double find_gamma_ (const Fourier9 &abcd, int i, int j, const std::string &opt)

  *Compute gamma from roots of base equations.*
- bool lt_ (double a, double b)

*less-than function*

- bool gt_ (double a, double b)

  *greater-than function*

- std::shared_ptr< psi::Matrix > psi_X_ ()

  *Form the Psi4 matrix with the transformation matrix.*

## Protected Attributes

- const int n_

  *Dimension of the problem.*

- const double conv_

  *Convergence.*

- const int maxiter_

  *Maximum number of iterations.*

- const bool verbose_

  *Verbose mode.*

- double * R_

  *R tensor.*

- double * P_

  *P tensor.*

- double * R0_

  *Reference R tensor.*

- double * P0_

  *Reference P tensor.*

- double * X_

  *X Matrix (accumulated solution)*

- double * W_

  *Work place.*

- double * Xold_

  *Temporary X matrix.*

- double * Xnew_

  *Temporary X matrix.*

- int niter_

  *Current number of iterations.*

- double S_ [8]

  *Current solutions.*

- double Zinit_

  *Initial Z value.*

- double Zold_

  *Old Z value.*

- double Znew_

  *New Z value.*
- double conv_current_

  *Current convergence.*
- bool success_

  *Status of optimization.*

### 16.130.1 Detailed Description

The objective function of the orthogonal matrix $\mathbf{X}$

$$Z(\mathbf{X}) \equiv \sum_{ijklmn} X_{ki}X_{lj}X_{mi}X_{nj}R_{ijklmn} + \sum_{ijk} X_{ji}X_{ki}P_{ijk}$$

is optimized by using the Jacobi iteration algorithm. In the above equation, $\mathbf{R}$ is a general real sixth-rank tensor of size $N^6$ whereas $\mathbf{P}$ is a general real third-rank tensor of size $N^3$.

#### Algorithm.

Optimization of $\mathbf{X}$ is factorized into a sequence of 2-dimensional rotations with one real parameter $\gamma$:

$$\mathbf{X}^{\rm New} = \mathbf{X}^{\rm Old} \cdot \mathbf{U}(\gamma)$$

where

$$\mathbf{U}(\gamma) \equiv \begin{pmatrix} \ddots & & & & \\ & \cos(\gamma) & \cdots & \sin(\gamma) & \\ & \vdots & \ddots & \vdots & \\ & -\sin(\gamma) & \cdots & \cos(\gamma) & \\ & & & & \ddots \end{pmatrix}$$

is the Jacobi transformation matrix constructed for the $I$th and $J$th element from the entire $N$-dimensional set. For the sake of algirithmic simplicity, every iteration after $\mathbf{U}(\gamma)$ has been formed, $\mathbf{X}^{\rm Old}$ is for a while assumed to be an identity matrix and the $\mathbf{R}$ as well as $\mathbf{P}$ tensors are transformed according to the following formulae

$$\begin{aligned} R_{ijklmn} &\rightarrow \sum_{k'l'm'n'} R_{ijk'l'm'n'}X_{k'k}X_{l'l}X_{m'm}X_{n'n} \\ P_{ijk} &\rightarrow \sum_{j'k'} P_{ij'k'}X_{j'j}X_{k'k} \end{aligned}$$

The full transformation matrix is accumulated in the memory buffer until convergence.

In each iteration, the optimum angle $\gamma$ is found as follows: First, the roots of the finite Fourier series

$$a_0 + \sum_{p=1}^{4} \left\{ a_p \cos(px) + b_p \sin(px) \right\} = 0$$

are found. In the above equations, the expansion coefficients are calculated analytically as a function of $I,J$ - the chosen indices in the Jacobi iteration subspace. The roots are evaluated by applying the Boyd's method[1], in which they are given as

$$\gamma_n = \Re\left[-i\ln(\lambda_n)\right]$$

where $\lambda_n$ is an eivenvalue of the following 8 by 8 complex matrix:

$$\begin{pmatrix}
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
-\frac{a_4+ib_4}{a_4-ib_4} & -\frac{a_3+ib_3}{a_4-ib_4} & -\frac{a_2+ib_2}{a_4-ib_4} & -\frac{a_1+ib_1}{a_4-ib_4} & -\frac{2a_0}{a_4-ib_4} & -\frac{a_1-ib_1}{a_4-ib_4} & -\frac{a_2-ib_2}{a_4-ib_4} & -\frac{a_3-ib_3}{a_4-ib_4}
\end{pmatrix}$$

Once the eight roots of the Fourier series equation are found, one solution out of eight is chosen which satisfies the global optimum condition, i.e., the largest increase/decrease in the objective function given by

$$\delta Z = Z\left(\mathbf{U}(\gamma)\right) - Z(\mathbf{1})$$

The Hessian is not computed. All the $N(N-1)/2$ unique pairs of molecular orbitals are checked and the optimal set of $\gamma, I, J$ is chosen to construct $\mathbf{X}^{\rm New}$.

**References:**

[1] Boyd, J.P.; J. Eng. Math. (2006) 56, pp. 203-219

### 16.130.2 Constructor & Destructor Documentation

#### 16.130.2.1 UnitaryOptimizer_4_2() [1/2]

```
oepdev::UnitaryOptimizer_4_2::UnitaryOptimizer_4_2 (
            double * R,
            double * P,
            int n,
            double conv = 1.0e-6,
            int maxiter = 100,
            bool verbose = true )
```

**Parameters**

| | |
|---|---|
| *R* | - $\mathbf{R}$ tensor (flattened row-wise) |
| *P* | - $\mathbf{P}$ tensor (flattened row-wise) |
| *n* | - dimensionality of the problem ( $N$) |
| *conv* | - convergence in the $Z$ function |
| *maxiter* | - maximum number of iterations |
| *verbose* | - whether print information of iteration process or not Sets up the optimizer. |

#### 16.130.2.2 UnitaryOptimizer_4_2() [2/2]

```
oepdev::UnitaryOptimizer_4_2::UnitaryOptimizer_4_2 (
            int n,
            double conv,
            int maxiter,
            bool verbose )  [protected]
```

**Parameters**

| | |
|---|---|
| *n* | - dimensionality of the problem ( $N$) |
| *conv* | - convergence in the $Z$ function |
| *maxiter* | - maximum number of iterations |
| *verbose* | - whether print information of iteration process or not Sets up the optimizer. |

The documentation for this class was generated from the following files:

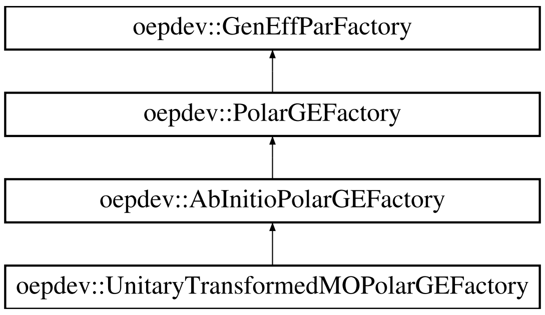
- oepdev/libutil/unitary_optimizer.h
- oepdev/libutil/unitary_optimizer.cc

## 16.131 oepdev::UnitaryTransformedMOPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Scaling of MO Space.

```
#include <gefp.h>
```

Inheritance diagram for oepdev::UnitaryTransformedMOPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::AbInitioPolarGEFactory
oepdev::UnitaryTransformedMOPolarGEFactory

### Public Member Functions

- UnitaryTransformedMOPolarGEFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

    *Construct from CPHF object and Psi4 options.*
- virtual ~UnitaryTransformedMOPolarGEFactory ()

*Destruct.*

- std::shared_ptr< GenEffPar > compute (void)

  *Pefrorm Least-Squares Fit.*

### Additional Inherited Members

### 16.131.1 Detailed Description

Implements creation of the density matrix susceptibility tensors for which $\mathbf{X} \neq \mathbf{1}$. Guarantees the idempotency of the density matrix up to first-order in LCAO-MO variation.

**Note**

> This method does not give better results than the X=1 method and is extremely time and memory consuming. Therefore, it is placed here only for future reference about solving unitary optimization problem in case it occurs.

The documentation for this class was generated from the following files:

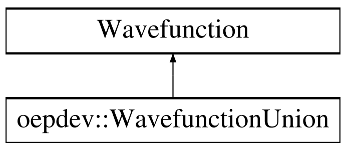
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_abinitio.cc

## 16.132 oepdev::WavefunctionUnion Class Reference

Union of two Wavefunction objects.

```
#include <wavefunction_union.h>
```

Inheritance diagram for oepdev::WavefunctionUnion:



### Public Member Functions

- WavefunctionUnion (SharedWavefunction ref_wfn, Options &options)

  *Constructor.*

- WavefunctionUnion (SharedMolecule dimer, SharedBasisSet primary, SharedBasisSet auxiliary_df, SharedBasisSet guess, SharedBasisSet primary_1, SharedBasisSet primary_2, SharedBasisSet auxiliary_1, SharedBasisSet auxiliary_2, SharedBasisSet auxiliary_df_1, SharedBasisSet auxiliary_df_2, SharedBasisSet intermediate_1, SharedBasisSet intermediate_2, SharedBasisSet guess_1, SharedBasisSet guess_2, SharedWavefunction wfn_1, SharedWavefunction wfn_2, Options &options)

*Constructor.*

- virtual ∼WavefunctionUnion ()

  *Destructor.*
- virtual double compute_energy ()

  *Compute Energy (now blank)*
- virtual double nuclear_repulsion_interaction_energy ()

  *Compute Nuclear Repulsion Energy between unions.*
- void localize_orbitals ()

  *Localize Molecular Orbitals.*
- void transform_integrals ()

  *Transform Integrals (2- and 4-index transformations)*
- void clear_dpd ()

  *Close the DPD instance.*
- int l_nmo (int n) const

  *Get number of molecular orbitals of the ∗n∗th fragment.*
- int l_nso (int n) const

  *Get number of symmetry orbitals of the ∗n∗th fragment.*
- int l_ndocc (int n) const

  *Get number of doubly occupied orbitals of the ∗n∗th fragment.*
- int l_nvir (int n) const

  *Get number of virtual orbitals of the ∗n∗th fragment.*
- int l_nalpha (int n) const

  *Get the number of the alpha electrons of the ∗n∗th fragment.*
- int l_nbeta (int n) const

  *Get the number of the beta electrons of the ∗n∗th fragment.*
- int l_nbf (int n) const

  *Get number of basis functions of the ∗n∗th fragment.*
- int l_noffs_ao (int n) const

  *Get the basis set offset of the ∗n∗th fragment.*
- double l_energy (int n) const

  *Get the reference energy of the ∗n∗th fragment.*
- SharedMolecule l_molecule (int n) const

  *Get the molecule object of the ∗n∗th fragment.*
- SharedBasisSet l_primary (int n) const

  *Get the primary basis set object of the ∗n∗th fragment.*
- SharedBasisSet l_auxiliary (int n) const

  *Get the auxiliary basis set object of the ∗n∗th fragment.*
- SharedBasisSet l_intermediate (int n) const

  *Get the intermediate basis set object of the ∗n∗th fragment.*
- SharedBasisSet l_guess (int n) const

*Get the guess basis set object of the ∗n∗th fragment.*

- SharedWavefunction l_wfn (int n) const

  *Get the wavefunction object of the ∗n∗th fragment.*
- SharedMOSpace l_mospace (int n, const std::string &label) const

  *Get the MO space named `label` (either `OCC` or `VIR`) of the ∗n∗th fragment.*
- SharedLocalizer l_localizer (int n) const

  *Get the orbital localizer object of the ∗n∗th fragment.*
- psi::SharedMatrix l_ca_occ (int n) const

  *Get the occupied molecular orbitals of the ∗n∗th fragment.*
- psi::SharedMatrix l_ca_vir (int n) const

  *Get the virtual molecular orbitals of the ∗n∗th fragment.*
- psi::SharedVector l_eps_a_occ (int n) const

  *Get the occupied molecular orbital energies of the ∗n∗th fragment.*
- psi::SharedVector l_eps_a_vir (int n) const

  *Get the virtual molecular orbital energies of the ∗n∗th fragment.*
- SharedIntegralTransform integrals (void) const

  *Get the integral transform object of the entire union.*
- bool has_localized_orbitals (void) const

  *If union got its molecular orbital localized or not.*
- SharedBasisSet primary (void) const

  *Get the primary basis set for the entire union.*
- SharedMOSpace mospace (const std::string &label) const

  *Get the MO space named `label` (either `OCC` or `VIR`)*
- SharedMatrix Ca_subset (const std::string &basis="SO", const std::string &subset="ALL")
- SharedMatrix Cb_subset (const std::string &basis="SO", const std::string &subset="ALL")
- SharedMatrix C_subset_helper (SharedMatrix C, const Dimension &noccpi, SharedVector epsilon, const std::string &basis, const std::string &subset)

  *Helpers for Ca_ and Cb_ matrix transformers.*
- SharedVector epsilon_subset_helper (SharedVector epsilon, const Dimension &noccpi, const std::string &basis, const std::string &subset)

  *Helper for epsilon transformer.*
- void print_header (void)

  *Print information about this wavefunction union.*
- void print_mo_integrals (void)

  *Print the MO ingegrals.*

## Protected Attributes

- int nIsolatedMolecules_

    *Number of isolated molecules.*
- SharedWavefunction dimer_wavefunction_

    *The wavefunction for a dimer (electrons relaxed in the field of monomers)*
- SharedIntegralTransform integrals_

    *Integral transform object (2- and 4-index transformations)*
- bool hasLocalizedOrbitals_

    *whether orbitals of the union were localized (or not)*
- std::map< const std::string, SharedMOSpace > mospacesUnion_

    *Dictionary of MO spaces for the entire union (`OCC` and `VIR`)*
- std::vector< SharedMolecule > l_molecule_

    *List of molecules.*
- std::vector< SharedBasisSet > l_primary_

    *List of primary basis functions per molecule.*
- std::vector< SharedBasisSet > l_auxiliary_

    *List of auxiliary basis functions per molecule.*
- std::vector< SharedBasisSet > l_intermediate_

    *List of intermediate basis functions per molecule.*
- std::vector< SharedBasisSet > l_guess_

    *List of guess basis functions per molecule.*
- std::vector< SharedWavefunction > l_wfn_

    *List of original isolated wavefunctions (electrons unrelaxed)*
- std::vector< std::string > l_name_

    *List of names of isolated wavefunctions.*
- std::vector< int > l_nbf_

    *List of basis function numbers per molecule.*
- std::vector< int > l_nmo_

    *List of numbers of molecular orbitals (MO's) per molecule.*
- std::vector< int > l_nso_

    *List of numbers of SO's per molecule.*
- std::vector< int > l_ndocc_

    *List of numbers of doubly occupied orbitals per molecule.*
- std::vector< int > l_nvir_

    *List of numbers of virtual orbitals per molecule.*
- std::vector< int > l_noffs_ao_

    *List of basis set offsets per molecule.*
- std::vector< double > l_energy_

    *List of energies of isolated wavefunctions.*
- std::vector< double > l_efzc_

*List of frozen-core energies per isolated wavefunction.*

- std::vector< bool > l_density_fitted_

  *List of information per wfn whether it was obtained using DF or not.*
- std::vector< int > l_nalpha_

  *List of numbers of alpha electrons per isolated wavefunction.*
- std::vector< int > l_nbeta_

  *List of numbers of beta electrons per isolated wavefunction.*
- std::vector< int > l_nfrzc_

  *List of numbers of frozen-core orbitals per isolated molecule.*
- std::vector< psi::SharedMatrix > l_ca_occ_

  *List of occupied orbitals.*
- std::vector< psi::SharedMatrix > l_ca_vir_

  *List of virtual orbitals.*
- std::vector< psi::SharedVector > l_eps_a_occ_

  *List of occupied orbital energies.*
- std::vector< psi::SharedVector > l_eps_a_vir_

  *List of virtual orbital energies.*
- std::vector< SharedLocalizer > l_localizer_

  *List of orbital localizers.*
- std::vector< std::map< const std::string, SharedMOSpace > > l_mospace_

  *List of dictionaries of MO spaces.*
- std::shared_ptr< psi::OEProp > oeprop_

  *One-Electron Property.*

### 16.132.1 Detailed Description

The WavefunctionUnion is the union of two unperturbed Wavefunctions.

**Notes:**

1. Works only for C1 symmetry! Therefore `this->nirrep() = 1`.
2. Does not set `reference_wavefunction_`
3. Sets `oeprop_` for the union of uncoupled molecules

1. Performs Hadamard sums on `H_`, `Fa_`, `Da_`, `Ca_` and `S_` based on uncoupled wavefunctions.
2. Since it is based on shallow copy of the original Wavefunction, it **changes** contents of this wavefunction. Reallocate and copy if you want to keep the original wavefunction.

**Warnings:**

1. Gradients, Hessians and frequencies are not touched, hence they are **wrong**!
2. Lagrangian (if present) is not touched, hence its **wrong**!
3. Ca/Cb and epsilon subsets were reimplemented from psi::Wavefunction to remove sorting of orbitals. However, the corresponding member functions are not virtual in psi::Wavefunction. This could bring problems when upcasting.

The following variables are *shallow* copies of variables inside the Wavefunction object, that is created for the *whole* molecule cluster:

- `basissets_` (DF/RI/F12/etc basis sets)_
- `basisset_` (ORBITAL basis set)
- `sobasisset_` (Primary basis set for SO integrals)
- `AO2SO_` (AO2SO conversion matrix (AO in rows, SO in cols)
- `molecule_` (Molecule that this wavefunction is run on)
- `options_` (Options object)
- `psio_` (PSI file access variables)
- `integral_` (Integral factory)
- `factory_` (Matrix factory for creating standard sized matrices)
- `memory_` (How much memory you have access to)
- `nalpha_`, `nbeta_` (Total alpha and beta electrons)
- `nfrzc_` (Total frozen core orbitals)
- `doccpi_` (Number of doubly occupied per irrep)
- `soccpi_` (Number of singly occupied per irrep)
- `frzcpi_` (Number of frozen core per irrep)
- `frzvpi_` (Number of frozen virtuals per irrep)
- `nalphapi_` (Number of alpha electrons per irrep)
- `nbetapi_` (Number of beta electrons per irrep)
- `nsopi_` (Number of so per irrep)
- `nmopi_` (Number of mo per irrep)
- `nso_` (Total number of SOs)
- `nmo_` (Total number of MOs)
- `nirrep_` (Number of irreps; must be equal to 1 due to symmetry reasons)
- `same_a_b_dens_` and `same_a_b_orbs_` The rest is altered so that the Wavefunction parameters reflect a cluster of non-interacting (uncoupled, isolated, unrelaxed) molecular electron densities.

### 16.132.2 Constructor & Destructor Documentation

#### 16.132.2.1 WavefunctionUnion() [1/2]

```
oepdev::WavefunctionUnion::WavefunctionUnion (
          SharedWavefunction ref_wfn,
          Options & options )
```

Provide wavefunction with molecule containing at least 2 fragments.

**Parameters**

| | |
|---|---|
| *ref_wfn* | - reference wavefunction |
| *options* | - Psi4 options |

This constructor is used for C++ internal interface.

#### 16.132.2.2 WavefunctionUnion() [2/2]

```
oepdev::WavefunctionUnion::WavefunctionUnion (
          SharedMolecule dimer,
          SharedBasisSet primary,
          SharedBasisSet auxiliary_df,
          SharedBasisSet guess,
          SharedBasisSet primary_1,
          SharedBasisSet primary_2,
          SharedBasisSet auxiliary_1,
          SharedBasisSet auxiliary_2,
          SharedBasisSet auxiliary_df_1,
          SharedBasisSet auxiliary_df_2,
          SharedBasisSet intermediate_1,
          SharedBasisSet intermediate_2,
          SharedBasisSet guess_1,
          SharedBasisSet guess_2,
          SharedWavefunction wfn_1,
          SharedWavefunction wfn_2,
          Options & options )
```

Provide molecule dimer and all the required monomer basis sets and wavefunctions.

**Parameters**

| | |
|---|---|
| *dimer* | - molecule object |
| *primary* | - basis set object: dimer (primary) |
| *auxiliary_df* | - basis set object: dimer (DF SCF) |
| *guess* | - basis set object: dimer (guess) |

**Parameters**

| | |
|---|---|
| *primary_1* | - basis set object for 1st monomer |
| *primary_2* | - basis set object for 2nd monomer |
| *auxiliary_1* | - basis set object for 1st monomer |
| *auxiliary_2* | - basis set object for 2nd monomer |
| *auxiliary_df_1* | - basis set object for 1st monomer |
| *auxiliary_df_2* | - basis set object for 2nd monomer |
| *intermediate_1* | - basis set object for 1st monomer |
| *intermediate_2* | - basis set object for 2nd monomer |
| *guess_1* | - basis set object for 1st monomer |
| *guess_2* | - basis set object for 2nd monomer |
| *wfn_1* | - unperturbed wavefunction object |
| *wfn_2* | - unperturbed wavefunction object |
| *options* | - Psi4 options |

This constructor is for interface with Python level.

### 16.132.3 Member Function Documentation

#### 16.132.3.1 Ca_subset()

```
SharedMatrix oepdev::WavefunctionUnion::Ca_subset (
          const std::string & basis = "SO",
          const std::string & subset = "ALL" )
```

Return a subset of the Ca matrix in a desired basis

**Parameters**

| | |
|---|---|
| *basis* | the symmetry basis to use AO, SO |
| *subset* | the subset of orbitals to return ALL, ACTIVE, FROZEN, OCC, VIR, FROZEN_OCC, ACTIVE_OCC, ACTIVE_VIR, FROZEN_VIR |

**Returns**

the matrix in Pitzer order in the desired basis

#### 16.132.3.2 Cb_subset()

```
SharedMatrix oepdev::WavefunctionUnion::Cb_subset (
            const std::string & basis = "SO",
            const std::string & subset = "ALL" )
```

Return a subset of the Cb matrix in a desired basis

**Parameters**

| | |
|---|---|
| *basis* | the symmetry basis to use AO, SO |
| *subset* | the subset of orbitals to return ALL, ACTIVE, FROZEN, OCC, VIR, FROZEN_OCC, ACTIVE_OCC, ACTIVE_VIR, FROZEN_VIR |

**Returns**

the matrix in Pitzer order in the desired basis

The documentation for this class was generated from the following files:

- oepdev/libutil/wavefunction_union.h
- oepdev/libutil/wavefunction_union.cc

# Chapter 17

# File Documentation

## 17.1 include/oepdev_files.h File Reference

### Macros

- #define OEPDEV_USE_PSI4_DIIS_MANAGER 0

  *Use DIIS from Psi4 (1) or OEPDev (0)?*
- #define OEPDEV_MAX_AM 8

  *L_max.*
- #define OEPDEV_N_MAX_AM 17

  *2L_max+1*
- #define OEPDEV_CRIT_ERI 1e-9

  *ERI criterion for E12, E34, E123 and lambda∗EXY coefficients.*
- #define OEPDEV_SIZE_BUFFER_R 250563

  *Size of R buffer (OEPDEV_N_MAX_AM∗OEPDEV_N_MAX_AM∗OEPDEV_N_MAX_AM∗OEPDEV_N_MAX_AM∗3)*
- #define OEPDEV_SIZE_BUFFER_D2 3264

  *Size of D2 buffer (3∗(OEPDEV_MAX_AM+1)∗(OEPDEV_MAX_AM+1)∗OEPDEV_N_MAX_AM)*
- #define OEPDEV_AU_KcalPerMole 627.509

  *Energy converters.*
- #define **OEPDEV_AU_CMRec** 219474.63
- #define **OEPDEV_AU_EV** 27.21138

## 17.2 include/oepdev_options.h File Reference

### Namespaces

- psi

  *Psi4 package namespace.*

### Functions

- PSI_API int psi::read_options (std::string name, Options &options)

  *Options for the OEPDev plugin.*

## 17.3 main.cc File Reference

```
#include <string>
#include "include/oepdev_files.h"
#include "psi4/liboptions/liboptions.h"
#include "psi4/libmints/wavefunction.h"
#include "include/oepdev_options.h"
#include "oepdev/liboep/oep.h"
#include "oepdev/libgefp/gefp.h"
#include "oepdev/libsolver/solver.h"
#include "oepdev/libtest/test.h"
#include <pybind11/pybind11.h>
```

### Namespaces

- psi

  *Psi4 package namespace.*

### Typedefs

- using **SharedWavefunction** = std::shared_ptr< psi::Wavefunction >
- using **SharedUnion** = std::shared_ptr< oepdev::WavefunctionUnion >
- using **SharedOEPotential** = std::shared_ptr< oepdev::OEPotential >
- using **SharedGEFPFactory** = std::shared_ptr< oepdev::GenEffParFactory >
- using **SharedGEFPParameters** = std::shared_ptr< oepdev::GenEffPar >

### Functions

- void **psi::export_dmtp** (py::module &)
- void **psi::export_cphf** (py::module &)
- void **psi::export_solver** (py::module &)
- void **psi::export_util** (py::module &)
- void **psi::export_oep** (py::module &)
- void **psi::export_gefp** (py::module &)
- PSI_API SharedWavefunction psi::oepdev (SharedWavefunction ref_wfn, Options &options)

*Main routine of the OEPDev plugin.*

- **psi::PYBIND11_MODULE** (oepdev, m)

## 17.4 oepdev/lib3d/dmtp.h File Reference

```
#include "psi4/libmints/wavefunction.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/molecule.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/vector.h"
```

### Classes

- class oepdev::MultipoleConvergence

  *Multipole Convergence.*
- class oepdev::DMTPole

  *Distributed Multipole Analysis Container and Computer. Abstract Base.*
- class oepdev::CAMM

  *Cumulative Atomic Multipole Moments.*

### Namespaces

- psi

  *Psi4 package namespace.*
- oepdev

  *OEPDev module namespace.*

### Typedefs

- using **psi::SharedBasisSet** = std::shared_ptr< BasisSet >
- using oepdev::SharedDMTPole = std::shared_ptr< DMTPole >

  *DMTPole object.*

## 17.5 oepdev/lib3d/esp.h File Reference

```
#include "space3d.h"
```

### Classes

- class oepdev::ESPSolver

  *Charges from Electrostatic Potential (ESP). A solver-type class.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Typedefs

- using **oepdev::SharedField3D** = std::shared_ptr< oepdev::Field3D >

## 17.6 oepdev/libgefp/gefp.h File Reference

```
#include <vector>
#include <string>
#include <random>
#include <cmath>
#include <map>
#include "psi4/libpsi4util/PsiOutStream.h"
#include "psi4/libpsi4util/process.h"
#include "psi4/libmints/wavefunction.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/vector3.h"
#include "../liboep/oep.h"
#include "../libutil/util.h"
#include "../libutil/cphf.h"
#include "../libutil/scf_perturb.h"
#include "../libutil/quambo.h"
#include "../libpsi/integral.h"
```

### Classes

- class oepdev::GenEffPar

  *Generalized Effective Fragment Parameters. Container Class.*
- class oepdev::GenEffFrag

  *Generalized Effective Fragment. Container Class.*
- class oepdev::GenEffParFactory

  *Generalized Effective Fragment Factory. Abstract Base.*

- class oepdev::EFP2_GEFactory

  *EFP2 GEFP Factory.*
- class oepdev::OEP_EFP2_GEFactory

  *OEP-EFP2 GEFP Factory.*
- class oepdev::PolarGEFactory

  *Polarization GEFP Factory. Abstract Base.*
- class oepdev::AbInitioPolarGEFactory

  *Polarization GEFP Factory from First Principles. Hartree-Fock Approximation.*
- class oepdev::FFAbInitioPolarGEFactory

  *Polarization GEFP Factory from First Principles: Finite-Difference Model. Arbitrary level of theory.*
- class oepdev::GeneralizedPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- struct oepdev::GeneralizedPolarGEFactory::StatisticalSet

  *A structure to handle statistical data.*
- class oepdev::UniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::NonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::LinearUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::QuadraticUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::LinearNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::QuadraticNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::LinearGradientNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Parameterization.*
- class oepdev::UnitaryTransformedMOPolarGEFactory

  *Polarization GEFP Factory with Least-Squares Scaling of MO Space.*
- class oepdev::FragmentedSystem

  *Molecular System for Fragment-Based Calculations.*

## Namespaces

- oepdev

  *OEPDev module namespace.*

### Typedefs

- using **oepdev::SharedOEPotential** = std::shared_ptr< OEPotential >
- using oepdev::SharedGenEffPar = std::shared_ptr< GenEffPar >

  *GEFP Parameters container.*
- using oepdev::SharedGenEffParFactory = std::shared_ptr< GenEffParFactory >

  *GEFP Parameter factory.*
- using oepdev::SharedGenEffFrag = std::shared_ptr< GenEffFrag >

  *GEFP Fragment container.*
- using oepdev::SharedFragmentedSystem = std::shared_ptr< FragmentedSystem >

  *Fragmented system.*

## 17.7 oepdev/libints/eri.h File Reference

```
#include "psi4/libpsi4util/exception.h"
#include "psi4/libmints/integral.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/fjt.h"
#include "../libpsi/integral.h"
#include "recurr.h"
```

### Classes

- class oepdev::TwoElectronInt

  *General Two Electron Integral.*
- class oepdev::ERI_1_1

  *2-centre ERI of the form (a|O(2)|b) where O(2) = 1/r12.*
- class oepdev::ERI_2_2

  *4-centre ERI of the form (ab|O(2)|cd) where O(2) = 1/r12.*
- class oepdev::ERI_3_1

  *4-centre ERI of the form (abc|O(2)|d) where O(2) = 1/r12.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

## 17.8 oepdev/libints/recurr.h File Reference

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Macros

- #define D1_INDEX(x, i, n) ((81∗(x))+(9∗(i))+(n))

  *Get the index of McMurchie-Davidson-Hermite D1 coefficient stored in the* `mdh_buffer_`*, that is attributed to the x Cartesian coordinate from angular momentum i of function 1, and the Hermite index n.*
- #define D2_INDEX(x, i, j, n) ((1377∗(x))+(153∗(i))+(17∗(j))+(n))

  *Get the index of McMurchie-Davidson-Hermite D2 coefficient stored in the* `mdh_buffer_`*, that is attributed to the x Cartesian coordinate from angular momenta i, j of function 1 and 2, and the Hermite index n.*
- #define D3_INDEX(x, i, j, k, n) ((18225∗(x))+(2025∗(i))+(225∗(j))+(25∗(k))+(n))

  *Get the index of McMurchie-Davidson-Hermite D3 coefficient stored in the* `mdh_buffer_`*, that is attributed to the x Cartesian coordinate from angular momenta i, j and k of function 1, 2 and 3, and the Hermite index n.*
- #define R_INDEX(n, l, m, j) ((14739∗(n))+(867∗(l))+(51∗(m))+(j))

  *Get the index of McMurchie-Davidson R coefficient stored in the* `mdh_buffer_R_` *from angular momenta n, l and m and the Boys index j.*

### Functions

- double oepdev::d_N_n1_n2 (int N, int n1, int n2, double PA, double PB, double aP)

  *Compute McMurchie-Davidson-Hermite (MDH) coefficient for binomial expansion.*
- void oepdev::make_mdh_D1_coeff (int n1, double aPd, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for monomial expansion.*
- void oepdev::make_mdh_D2_coeff (int n1, int n2, double aPd, double ∗PA, double ∗PB, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for binomial expansion.*
- void oepdev::make_mdh_D3_coeff (int n1, int n2, int n3, double aPd, double ∗PA, double ∗PB, double ∗PC, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for trinomial expansion.*
- void oepdev::make_mdh_D2_coeff_explicit_recursion (int n1, int n2, double aP, double ∗PA, double ∗PB, double ∗buffer)

  *Compute the McMurchie-Davidson-Hermite coefficients for binomial expansion by explicit recursion. This function makes the same changes to buffers as oepdev::make_mdh_D2_coeff, but implements it through explicit recursion by calls to oepdev::d_N_n1_n2. Therefore, it is slightly slower. Here for debugging purposes.*

- void oepdev::make_mdh_R_coeff (int N, int L, int M, double alpha, double a, double b, double c, double ∗F, double ∗buffer)

  *Compute the McMurchie-Davidson R coefficients.*

## 17.9 oepdev/liboep/oep.h File Reference

```
#include <cstdio>
#include <string>
#include <vector>
#include <map>
#include "psi4/liboptions/liboptions.h"
#include "psi4/libpsi4util/PsiOutStream.h"
#include "psi4/libmints/wavefunction.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/local.h"
#include "../libutil/cis.h"
#include "../libpsi/integral.h"
#include "../libpsi/potential.h"
#include "../lib3d/space3d.h"
#include "../lib3d/dmtp.h"
```

### Classes

- struct oepdev::OEPType

  *Container to handle the type of One-Electron Potentials.*
- class oepdev::OEPotential

  *Generalized One-Electron Potential: Abstract base.*
- class oepdev::ElectrostaticEnergyOEPotential

  *Generalized One-Electron Potential for Electrostatic Energy.*
- class oepdev::RepulsionEnergyOEPotential

  *Generalized One-Electron Potential for Pauli Repulsion Energy.*
- class oepdev::ChargeTransferEnergyOEPotential

  *Generalized One-Electron Potential for Charge-Transfer Interaction Energy.*
- class oepdev::EETCouplingOEPotential

  *Generalized One-Electron Potential for EET coupling calculations.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Typedefs

- using **oepdev::SharedWavefunction** = std::shared_ptr< Wavefunction >
- using **oepdev::SharedBasisSet** = std::shared_ptr< BasisSet >
- using **oepdev::SharedMatrix** = std::shared_ptr< Matrix >
- using **oepdev::SharedVector** = std::shared_ptr< Vector >
- using **oepdev::SharedLocalizer** = std::shared_ptr< Localizer >
- using **oepdev::SharedCISData** = std::shared_ptr< CISData >

## 17.10 oepdev/liboep/oep_gdf.h File Reference

```
#include <cstdio>
#include <string>
#include "psi4/liboptions/liboptions.h"
#include "psi4/libmints/wavefunction.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/matrix.h"
#include "../libpsi/integral.h"
```

### Classes

- class oepdev::GeneralizedDensityFit

  *Generalized Density Fitting Scheme. Abstract Base.*
- class oepdev::SingleGeneralizedDensityFit

  *Generalized Density Fitting Scheme - Single Fit.*
- class oepdev::DoubleGeneralizedDensityFit

  *Generalized Density Fitting Scheme - Double Fit.*
- class oepdev::OverlapGeneralizedDensityFit

  *Generalized Density Fitting Scheme - Single Fit Based on Minimal Overlap in MO Basis.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

## 17.11 oepdev/libpsi/integral.h File Reference

```
#include "psi4/libmints/integral.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/matrix.h"
```

```
#include "multipole_potential.h"
```

### Classes

- class oepdev::TwoBodyAOInt
- class oepdev::IntegralFactory

  *Extended IntegralFactory for computing integrals.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

## 17.12 oepdev/libpsi/osrecur.h File Reference

### Classes

- class oepdev::ObaraSaikaTwoCenterEFPRecursion_New

  *Obara-Saika recursion formulae for improved EFP multipole potential integrals.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Macros

- #define **MAX_DF** 500
- #define **MAX_FAC** 100

### Functions

- double $***$ **oepdev::init_box** (int a, int b, int c)
- void **oepdev::zero_box** (double $***$box, int a, int b, int c)
- void **oepdev::free_box** (double $***$box, int a, int b)

## 17.13 oepdev/libpsi/potential.h File Reference

```
#include <vector>
#include "psi4/psi4-dec.h"
#include "psi4/liboptions/liboptions.h"
#include "psi4/libpsio/psio.h"
#include "psi4/libmints/typedefs.h"
#include "psi4/libmints/onebody.h"
#include "psi4/libmints/potential.h"
#include "psi4/libmints/sointegral_onebody.h"
#include "psi4/libmints/osrecur.h"
```

### Classes

- class oepdev::PotentialInt

    *Computes potential integrals.*

### Namespaces

- oepdev

    *OEPDev module namespace.*

## 17.14 oepdev/libsolver/solver.h File Reference

```
#include <cstdio>
#include <string>
#include <map>
#include "psi4/psi4-dec.h"
#include "psi4/liboptions/liboptions.h"
#include "psi4/libpsio/psio.h"
#include "psi4/libmints/potential.h"
#include "psi4/libmints/integral.h"
#include "psi4/libpsi4util/PsiOutStream.h"
#include "../libutil/wavefunction_union.h"
#include "../libutil/integrals_iter.h"
#include "../libpsi/integral.h"
#include "../liboep/oep.h"
#include "../../include/oepdev_files.h"
```

### Classes

- class oepdev::OEPDevSolver

*Solver of properties of molecular aggregates. Abstract base.*
- class oepdev::ElectrostaticEnergySolver

  *Compute the Coulombic interaction energy between unperturbed wavefunctions.*
- class oepdev::RepulsionEnergySolver

  *Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.*
- class oepdev::ChargeTransferEnergySolver

  *Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.*
- class oepdev::EETCouplingSolver

  *Compute the EET coupling energy between unperturbed wavefunctions.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Typedefs

- using oepdev::SharedWavefunctionUnion = std::shared_ptr< WavefunctionUnion >

  *WavefunctionUnion.*

## 17.15 oepdev/libsolver/ti_data.h File Reference

```
#include <cstdio>
#include <string>
#include <map>
#include "../lib3d/dmtp.h"
```

### Classes

- class oepdev::TIData

  *Transfer Integral EET Data.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Typedefs

- using **oepdev::SharedDMTPConvergence** = std::shared_ptr< oepdev::MultipoleConvergence >

## 17.16 oepdev/libtest/test.h File Reference

```
#include <vector>
#include "psi4/psi4-dec.h"
#include "psi4/liboptions/liboptions.h"
#include "psi4/libpsio/psio.h"
#include "psi4/libpsi4util/PsiOutStream.h"
#include "psi4/libmints/integral.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/wavefunction.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libqt/qt.h"
#include "../libpsi/integral.h"
#include "../libutil/integrals_iter.h"
#include "../../include/oepdev_files.h"
```

### Classes

- class oepdev::test::Test

    *Manages test routines.*

### Namespaces

- oepdev

    *OEPDev module namespace.*

## 17.17 oepdev/libutil/basis_rotation.h File Reference

```
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/basisset.h"
```

### Namespaces

- psi

    *Psi4 package namespace.*

- oepdev

  *OEPDev module namespace.*

## Functions

**Rotation of AO Space**

### 17.17.1 Theory

*The objective is to find the formulae for rotation matrices of the AO spaces as functions of the Cartesian 3 x 3 rotation matrices. It is obvious that p-type functions transform as a usual Cartesian vectors. However, higher angular momentum functions transform in a more complex way.*

#### Problem

*Define a vectorized AO space M of rank r>1 that is constructed from unique tensor components of fully symmetric r-th rank AO tensor populated in standard order,*

$$M_{\{ab\ldots k\}} = M_{ab\ldots k} \quad \text{for} \quad a \leq b \leq \ldots \leq k$$

*Given a general rotation of Cartesian tensors*

$$M_{ab\ldots k} = \sum_{a'b'\ldots k'} M_{a'b'\ldots k'} r_{a'a} r_{b'b} \cdots r_{k'k}$$

*find closed expressions for the rotation matrix in reduced composite AO space obeying*

$$M_{[ab\ldots k]} = \sum_{\{a'b'\ldots k'\}} M_{\{a'b'\ldots k'\}} R_{\{a'b'\ldots k'\},[ab\ldots k]}$$

*In the derivations below the following identity of first-order partitioning will be of use:*

$$\sum_{ab} M_{ab}\hat{s}_{ab} = \sum_{\{ab\}} M_{\{ab\}} \left(\hat{s}_{ab} + \Delta_{ab}\hat{s}_{ba}\right)$$

*where*

$$\Delta_{ab} \equiv 1 - \delta_{ab}$$

*and the operator s of rank r acts as follows*

$$s^{ab\ldots k}_{a'b'\ldots k'} \equiv \hat{s}_{a'b'\ldots k'} \underbrace{\mathbf{r} \otimes \mathbf{r} \otimes \cdots \otimes \mathbf{r}}_{r} = r_{a'a} r_{b'b} \cdots r_{k'k}$$

#### Rotation of 6D functions

*The rotation of the full tensor AO space of rank 2 and dimensions (3,3) is given by*

$$M_{ab} = \sum_{a'b'} M_{a'b'} r_{a'b} r_{b'b}$$

*Applying the identity of first-order partitioning directly leads to the formula for a reduced 6D tensor rotation of rank 1 and dimension (6),*

$$M_{[ab]} = \sum_{\{a'b'\}} M_{\{a'b'\}} R_{\{a'b'\},[ab]}$$

*where the 6 x 6 rotation matrix is given by*

$$R_{\{a'b'\},[ab]} = r_{a'a} r_{b'b} + \Delta_{a'b'} r_{b'a} r_{a'b}$$

#### Rotation of 10F functions

*The rotation of the full tensor AO space of rank 3 and dimensions (3,3,3) is given by*

$$M_{abc} = \sum_{a'b'c'} M_{a'b'c'} r_{a'b} r_{b'b} r_{c'c}$$

*First of all, notice that one can perform the following partitioning*

$$\sum_a \sum_{b\neq a} \sum_{c\neq b\neq a} M_{abc} \hat{s}_{abc} = \sum_{\{abc\}} M_{\{abc\}} \left( \hat{s}_{abc} + \hat{s}_{acb} + \hat{s}_{bac} + \hat{s}_{bca} + \hat{s}_{cab} + \hat{s}_{cba} \right)$$

*Then, perform a partitioning of the triple sum,*

$$\begin{aligned}
\sum_{abc} M_{abc} \hat{s}_{abc} = \sum_a \sum_{b\neq a} \sum_{c\neq b\neq a} & M_{abc} \hat{s}_{abc} \\
& + \sum_a \sum_{b\geq a} M_{abb} \hat{s}_{abb} + \sum_a \sum_{b<a} M_{abb} \hat{s}_{abb} \\
& + \sum_a \sum_{b>a} M_{aba} \hat{s}_{aba} + \sum_a \sum_{b<a} M_{aba} \hat{s}_{aba} \\
& + \sum_a \sum_{b>a} M_{bba} \hat{s}_{bba} + \sum_a \sum_{b<a} M_{bba} \hat{s}_{bba}
\end{aligned}$$

*Using the first-order partitioning theorem and interchanging the dummy indices one finds that*

$$M_{[abc]} = \sum_{\{a'b'c'\}} M_{\{a'b'c'\}} R_{\{a'b'c'\},[abc]}$$

*where the 10 x 10 rotation matrix is given by*

$$\begin{aligned}
R_{\{a'b'c'\},[abc]} = \delta_{b'c'} & \left( s^{abc}_{a'b'b'} + \Delta_{a'b'} \left\{ s^{abc}_{b'a'b'} + s^{abc}_{b'b'a'} \right\} \right) \\
& + \delta_{a'b'} \Delta_{b'c'} \left( s^{abc}_{c'a'a'} + s^{abc}_{a'c'a'} + s^{abc}_{a'a'c'} \right) \\
& + \Delta_{a'b'} \Delta_{b'c'} \left( s^{abc}_{\prime a'b'c} + s^{abc}_{a'c'b'} + s^{abc}_{b'a'c'} + s^{abc}_{b'c'a'} + s^{abc}_{c'a'b'} + s^{abc}_{c'b'a'} \right)
\end{aligned}$$

*and*

$$s^{abc}_{a'b'c'} \equiv \hat{s}_{a'b'c'} \mathbf{r} \otimes \mathbf{r} \otimes \mathbf{r} = r_{a'a} r_{b'b} r_{c'c}$$

- psi::SharedMatrix oepdev::r6 (psi::SharedMatrix r)

  *Compute the 6 x 6 rotation matrix of the 6D orbitals.*
- void oepdev::populate (double **R, double **r, std::vector< int > idx_am, const int &nam)

  *Compute the 6 x 6 rotation matrix of the 6D orbitals.*
- psi::SharedMatrix oepdev::ao_rotation_matrix (psi::SharedMatrix r, psi::SharedBasisSet b)

  *Compute the full rotation matrix of AO orbital space.*

## 17.18 oepdev/libutil/cis.h File Reference

```
#include <string>
#include <utility>
#include "psi4/liboptions/liboptions.h"
#include "psi4/libpsio/psio.h"
#include "psi4/libpsio/psio.hpp"
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/molecule.h"
#include "psi4/libmints/wavefunction.h"
#include "psi4/libtrans/integraltransform.h"
#include "psi4/libtrans/mospace.h"
#include "psi4/libdpd/dpd.h"
#include "psi4/libfock/jk.h"
#include "../lib3d/dmtp.h"
#include "davidson_liu.h"
```

### Classes

- struct oepdev::CISData

  *CIS wavefunction parameters. Container structure.*
- class oepdev::CISComputer

  *CISComputer.*
- class oepdev::R_CISComputer
- class oepdev::U_CISComputer
- class oepdev::R_CISComputer_Explicit
- class oepdev::R_CISComputer_DL

  *CIS Computer with RHF reference: Davidson-Liu Solver.*
- class oepdev::R_CISComputer_Direct
- class oepdev::U_CISComputer_Explicit
- class oepdev::U_CISComputer_DL

  *CIS Computer with UHF reference: Davidson-Liu Solver.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Typedefs

- using **oepdev::SharedMolecule** = std::shared_ptr< psi::Molecule >
- using **oepdev::SharedMOSpace** = std::shared_ptr< psi::MOSpace >
- using **oepdev::SharedMOSpaceVector** = std::vector< std::shared_ptr< psi::MOSpace > >
- using **oepdev::SharedIntegralTransform** = std::shared_ptr< psi::IntegralTransform >

## 17.19 oepdev/libutil/davidson_liu.h File Reference

```
#include "psi4/liboptions/liboptions.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/matrix.h"
#include "gram_schmidt.h"
```

### Classes

- class oepdev::DavidsonLiu

  *Davidson-Liu diagonalization method.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

## 17.20 oepdev/libutil/diis.h File Reference

```
#include <cstdio>
#include <string>
#include <vector>
#include "psi4/libciomr/libciomr.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libqt/qt.h"
#include "psi4/libpsi4util/PsiOutStream.h"
```

### Classes

- class oepdev::DIISManager

    *DIIS manager.*

### Namespaces

- oepdev

    *OEPDev module namespace.*

## 17.21 oepdev/libutil/gram_schmidt.h File Reference

```
#include "psi4/libmints/vector.h"
```

### Classes

- class oepdev::GramSchmidt

    *Gram-Schmidt orthogonalization method.*

### Namespaces

- oepdev

    *OEPDev module namespace.*

## 17.22 oepdev/libutil/integrals_iter.h File Reference

```
#include <cstdio>
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/integral.h"
#include "../libpsi/integral.h"
```

### Classes

- class oepdev::ShellCombinationsIterator

    *Iterator for Shell Combinations. Abstract Base.*
- class oepdev::AOIntegralsIterator

    *Iterator for AO Integrals. Abstract Base.*
- class oepdev::AllAOShellCombinationsIterator_4

*Loop over all possible ERI shells in a shell quartet.*
- class oepdev::AllAOShellCombinationsIterator_2

  *Loop over all possible ERI shells in a shell doublet.*
- class oepdev::AllAOIntegralsIterator_4

  *Loop over all possible ERI within a particular shell quartet.*
- class oepdev::AllAOIntegralsIterator_2

  *Loop over all possible ERI within a particular shell doublet.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Typedefs

- using **oepdev::SharedIntegralFactory** = std::shared_ptr< IntegralFactory >
- using **oepdev::SharedTwoBodyAOInt** = std::shared_ptr< TwoBodyAOInt >
- using oepdev::SharedShellsIterator = std::shared_ptr< ShellCombinationsIterator >

  *Iterator over shells as shared pointer.*
- using oepdev::SharedAOIntsIterator = std::shared_ptr< AOIntegralsIterator >

  *Iterator over AO integrals as shared pointer.*

## 17.23 oepdev/libutil/kabsch_superimposer.h File Reference

```
#include <string>
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/molecule.h"
```

### Classes

- class oepdev::KabschSuperimposer

  *Compute the Cartesian rotation matrix between two structures.*

### Namespaces

- oepdev

  *OEPDev module namespace.*

## 17.24 oepdev/libutil/quambo.h File Reference

```
#include <string>
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/molecule.h"
#include "psi4/libmints/wavefunction.h"
```

### Classes

- struct oepdev::QUAMBOData

  *Container to store the QUAMBO data.*
- class oepdev::QUAMBO

  *The Quasiatomic Minimal Basis Set Molecular Orbitals (QUAMBO)*

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Typedefs

- using oepdev::SharedQUAMBO = std::shared_ptr< QUAMBO >

  *Shared QUAMBO object.*

## 17.25 oepdev/libutil/scf_perturb.h File Reference

```
#include "psi4/libmints/vector.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libscf_solver/rhf.h"
```

### Classes

- struct oepdev::PerturbCharges

  *Structure to hold perturbing charges.*
- class oepdev::RHFPerturbed

  *RHF theory under electrostatic perturbation.*

### Namespaces

- oepdev

    *OEPDev module namespace.*

## 17.26 oepdev/libutil/unitary_optimizer.h File Reference

```
#include <string>
#include <complex>
#include "psi4/libmints/vector.h"
#include "psi4/libmints/matrix.h"
```

### Classes

- struct oepdev::ABCD

    *Simple structure to hold the Fourier series expansion coefficients.*
- struct oepdev::Fourier5

    *Simple structure to hold the Fourier series expansion coefficients for N=2.*
- struct oepdev::Fourier9

    *Simple structure to hold the Fourier series expansion coefficients for N=4.*
- class oepdev::UnitaryOptimizer

    *Find the optimim unitary matrix of quadratic matrix equation.*
- class oepdev::UnitaryOptimizer_4_2

    *Find the optimim unitary matrix for quartic-quadratic matrix equation with trace.*
- class oepdev::UnitaryOptimizer_2

    *Find the optimim unitary matrix for quadratic matrix equation with trace.*
- class oepdev::UnitaryOptimizer_2_1

### Namespaces

- oepdev

    *OEPDev module namespace.*

### Macros

- #define **IDX**(i, j, n) ((n)∗(i)+(j))
- #define **IDX3**(i, j, k) (n2_∗(i)+n_∗(j)+(k))
- #define **IDX6**(i, j, k, l, m, n) (n5_∗(i)+n4_∗(j)+n3_∗(k)+n2_∗(l)+n_∗(m)+(n))

### Functions

- constexpr std::complex< double > **oepdev::operator""_i** (unsigned long long d)
- constexpr std::complex< double > **oepdev::operator""_i** (long double d)

## 17.27 oepdev/libutil/util.h File Reference

```
#include <cstdio>
#include <string>
#include <cmath>
#include <map>
#include <cassert>
#include "psi4/psi4-dec.h"
#include "psi4/liboptions/liboptions.h"
#include "psi4/libpsio/psio.h"
#include "psi4/libciomr/libciomr.h"
#include "psi4/libpsio/psio.hpp"
#include "psi4/libiwl/iwl.h"
#include "psi4/libqt/qt.h"
#include "psi4/libmints/molecule.h"
#include "psi4/libmints/writer.h"
#include "psi4/libmints/writer_file_prefix.h"
#include "psi4/libmints/wavefunction.h"
#include "psi4/libmints/mintshelper.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/oeprop.h"
#include "psi4/libmints/local.h"
#include "psi4/libfunctional/superfunctional.h"
#include "psi4/libtrans/mospace.h"
#include "psi4/libtrans/integraltransform.h"
#include "psi4/libscf_solver/rhf.h"
#include "psi4/libdpd/dpd.h"
```

### Namespaces

- oepdev

  *OEPDev module namespace.*

### Typedefs

- using **oepdev::SharedSuperFunctional** = std::shared_ptr< SuperFunctional >

## Functions

- PSI_API void oepdev::preambule (void)

  *Print preambule for module OEPDEV.*
- template<typename... Args>
  std::string oepdev::string_sprintf (const char *format, Args... args)

  *Format string output. Example: std::string text = oepdev::string_sprinff("Test %3d, %13.5f", 5, -10.5425);.*
- PSI_API std::shared_ptr< SuperFunctional > oepdev::create_superfunctional (std::string name, Options &options)

  *Set up DFT functional.*
- PSI_API SharedBasisSet oepdev::create_basisset_by_copy (SharedBasisSet basis_ref, SharedMolecule molecule_target)

  *Build BasisSet by Copy.*
- PSI_API SharedBasisSet oepdev::create_atom_basisset_by_copy (SharedBasisSet basis_ref, SharedMolecule molecule_target, int idx_atom)

  *Build BasisSet by Copy for a Particular Atom.*
- PSI_API std::shared_ptr< Molecule > oepdev::extract_monomer (std::shared_ptr< const Molecule > molecule_dimer, int id)

  *Extract molecule from dimer.*
- PSI_API double oepdev::compute_distance (psi::SharedVector v1, psi::SharedVector v2)

  *Compute distance between two points in nD space.*
- PSI_API std::shared_ptr< Wavefunction > oepdev::solve_scf (std::shared_ptr< Molecule > molecule, std::shared_ptr< BasisSet > primary, std::shared_ptr< BasisSet > auxiliary, std::shared_ptr< BasisSet > guess, std::shared_ptr< SuperFunctional > functional, Options &options, std::shared_ptr< PSIO > psio, bool compute_mints=false)

  *Solve RHF-SCF equations for a given molecule in a given basis set.*
- PSI_API std::shared_ptr< Wavefunction > oepdev::solve_scf_sad (std::shared_ptr< Molecule > molecule, std::shared_ptr< BasisSet > primary, std::shared_ptr< BasisSet > auxiliary, std::vector< std::shared_ptr< BasisSet >> sad, std::vector< std::shared_ptr< BasisSet >> sad_fit, std::shared_ptr< SuperFunctional > functional, Options &options, std::shared_ptr< PSIO > psio, bool compute_mints=false)

  *Solve RHF-SCF equations for a given molecule in a given basis set.*
- PSI_API double oepdev::average_moment (std::shared_ptr< psi::Vector > moment)

  *Compute the scalar magnitude of multipole moment.*
- PSI_API std::vector< std::shared_ptr< psi::Matrix > > oepdev::calculate_JK (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::Matrix > C)

  *Compute the Coulomb and exchange integral matrices in MO basis.*
- PSI_API double oepdev::calculate_idf_alpha_xc_energy (std::shared_ptr< psi::Wavefunction > wfn, std::vector< double > w, psi::SharedMatrix D, std::vector< psi::SharedMatrix > AI, std::vector< psi::SharedMatrix > BI)

  *Compute the IDF exchange-correlation energy.*

- PSI_API double oepdev::calculate_idf_xc_energy (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::Matrix > D, std::vector< std::shared_ptr< psi::Matrix >> f, std::vector< std::shared_ptr< psi::Matrix >> g, std::shared_ptr< psi::Vector > w, std::shared_ptr< psi::Vector > o, double N, double aN, double xiN, double AN, double wnorm)

    *Compute the IDF exchange-correlation energy.*
- PSI_API std::vector< std::shared_ptr< psi::Matrix > > **oepdev::calculate_JK_ints** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr)
- PSI_API std::vector< std::shared_ptr< psi::Matrix > > oepdev::calculate_JK_r (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > Dij)

    *Compute the Coulomb and exchange integral matrices in MO basis.*
- PSI_API std::vector< std::shared_ptr< psi::Matrix > > **oepdev::calculate_JK_rb** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > Dij)
- PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_der_D (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > C, std::vector< std::shared_ptr< psi::Matrix >> A)

    *Compute the derivative of exchange-correlation energy wrt the density matrix in MO-A basis.*
- PSI_API double oepdev::calculate_e_xc (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > f, std::shared_ptr< psi::Matrix > C)

    *Compute the exchange-correlation energy from ERI in MO-SCF basis.*
- PSI_API double **oepdev::calculate_e_apsg** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Matrix > fJ, std::shared_ptr< psi::Matrix > fK, std::shared_ptr< psi::Matrix > C)
- PSI_API psi::SharedMatrix **oepdev::calculate_de_apsg** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::IntegralTransform > tr, std::shared_ptr< psi::Vector > P, std::shared_ptr< psi::Matrix > AJ, std::shared_ptr< psi::Matrix > AKL, std::shared_ptr< psi::Matrix > aJ, std::shared_ptr< psi::Matrix > aKL, std::shared_ptr< psi::Matrix > C)
- PSI_API psi::SharedMatrix **oepdev::calculate_de_apsg_new** (std::shared_ptr< psi::Wavefunction > wfn, std::shared_ptr< psi::Vector > P, std::shared_ptr< psi::Matrix > C, std::shared_ptr< psi::Matrix > A_J, std::shared_ptr< psi::Matrix > A_LK, std::shared_ptr< psi::Matrix > a_J, std::shared_ptr< psi::Matrix > a_LK)
- PSI_API psi::SharedMatrix **oepdev::calculate_unitary_uo_2** (psi::SharedVector Q, int n)
- PSI_API psi::SharedMatrix **oepdev::calculate_unitary_uo_2_1** (psi::SharedMatrix P, psi::SharedVector p)
- PSI_API std::shared_ptr< psi::Matrix > oepdev::matrix_power_derivative (std::shared_ptr< psi::Matrix > A, double g, double step)

    *Compute the contracted derivative of power of a square and symmetric matrix.*
- std::shared_ptr< psi::Matrix > oepdev::_calculate_DFI_Vel (std::shared_ptr< psi::IntegralFactory > f_aabb, std::shared_ptr< psi::IntegralFactory > f_abab, std::shared_ptr< psi::Matrix > d_b)

    *Compute the Effective DFI Potential Matrix Due To Electrons.*

- PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_DFI_Vel_JK (std::shared_ptr< psi::IntegralFactory > f_aabb, std::shared_ptr< psi::IntegralFactory > f_abab, std::shared_ptr< psi::Matrix > d_b)

  *Compute the Effective DFI Coulomb+Exchange Potential Matrix Due To Electrons.*
- PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_DFI_Vel_J (std::shared_ptr< psi::IntegralFactory > f_aabb, std::shared_ptr< psi::Matrix > d_b)

  *Compute the Effective DFI Coulomb Potential Matrix Due To Electrons.*
- PSI_API std::shared_ptr< psi::Matrix > oepdev::calculate_OEP_basisopt_V (const int &nt, std::shared_ptr< psi::IntegralFactory > f_pppt, std::shared_ptr< psi::Matrix > ca, std::shared_ptr< psi::Matrix > da)

  *Compute the 2-Electron Part of the Effective OEP Matrix for Auxiliary Basis Set Optimization.*
- PSI_API double oepdev::bs_optimize_projection (std::shared_ptr< psi::Matrix > ti, std::shared_ptr< psi::MintsHelper > mints, std::shared_ptr< psi::BasisSet > bsf_m, std::shared_ptr< psi::BasisSet > bsf_i)

  *Compute the objective function value for auxiliary basis set optimization of OEPs.*

## 17.28 oepdev/libutil/wavefunction_union.h File Reference

```
#include <cstdio>
#include <string>
#include <map>
#include "psi4/psi4-dec.h"
#include "psi4/liboptions/liboptions.h"
#include "psi4/libpsio/psio.h"
#include "psi4/libciomr/libciomr.h"
#include "psi4/libpsio/psio.hpp"
#include "psi4/libqt/qt.h"
#include "psi4/libmints/molecule.h"
#include "psi4/libmints/writer.h"
#include "psi4/libmints/writer_file_prefix.h"
#include "psi4/libmints/wavefunction.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/oeprop.h"
#include "psi4/libmints/local.h"
#include "psi4/libfunctional/superfunctional.h"
#include "psi4/libtrans/mospace.h"
#include "psi4/libtrans/integraltransform.h"
#include "psi4/libscf_solver/rhf.h"
#include "psi4/libdpd/dpd.h"
```

## Classes

- class oepdev::WavefunctionUnion

  *Union of two Wavefunction objects.*

## Namespaces

- oepdev

  *OEPDev module namespace.*

# Chapter 18

# Example Documentation

## 18.1 example_cphf.cc

Shows how to use the oepdev::CPHF solver to compute molecular and LMO-distributed polarizabilities at RHF level of theory.

```
void example_cphf(std::shared_ptr<psi::Wavefunction> wfn, psi::Options& opt){

  // build the solver
  std::shared_ptr<oepdev::CPHF> solver = std::make_shared<oepdev::CPHF>(wfn, opt);

  // run the solver to converge CPHF equations
  solver->compute();

  // print the LMO-distributed polarizabilities
  for (int i=0; i<solver->nocc(); i++) {
       solver->polarizability(i)->print();
  }

  // print the molecular polarizability
  solver->polarizability()->print();

  // grab 4th LMO-distributed polarizability and its associated LMO centroid
  psi::SharedMatrix pol_4 = solver->polarizability(3);
  psi::SharedVector rmo_4 = solver->lmo_centroid(3);
};
```

## 18.2 example_davidson_liu.cc

This example is a trivial demo to use `oepdev::DavidsonLiu` in order to diagonalize a real, symmetric matrix **H**, stored in a `psi::SharedMatrix H`. This can help you to construct more complicated classes that need to solve eigenpairs for very large, sparse matrices such as CI Hamiltonians.

#### Note

This example might need compile properly (it's only a draft). Debug if necessary.

```
// Define a class that inherits from DavidsonLiu
class Diagonalize : public DavidsonLiu {

 public:
  Diagonalize(psi::SharedMatrix H, psi::Options& opt, int M);
  virtual void ~Diagonalize() {};

 protected:
  // Desired number of roots to be found
  int M_;
  // Matrix to be diagonalized (explicitly stored)
  psi::SharedMatrix matrix_;

  // Implementation of pure methods must be declared
  void davidson_liu_compute_diagonal_hamiltonian();
  void davidson_liu_compute_sigma();
};

Diagonalize::Diagonalize(psi::SharedMatrix H, psi::Options& opt, int M) :
  DavidsonLiu(opt) , matrix_(nullptr), M_(M)
{
  matrix_ = std::make_shared<psi::Matrix>(H);
  int N = H->ncol();
  int L = M_;

  // Must be run in order to allocate memory
  this->davidson_liu_initialize(N, L, M_);
}

// Implementation of pure methods
void Diagonalize::davidson_liu_compute_diagonal_hamiltonian() {
 for (int i=0; i<this->matrix_->ncol(); ++i) {
      double v = matrix_->get(i, i);
      this->H_diag_davidson_liu_->set(i, v);
 }
}

void Diagonalize::davidson_liu_compute_sigma() {
 for (int k=this->davidson_liu_n_sigma_computed_; k<this->L_davidson_liu_; ++k) {
      psi::SharedVector Sigma = std::make_shared<psi::Vector>("", this->N_davidson_liu_);
      Sigma->gemv(false, 1.0, *this->matrix_, *Sigma, 0.0);
      this->sigma_vectors_davidson_liu_.push_back(Sigma);
 }
}

// Testing function
void example_davidson_liu(psi::SharedMatrix H, int M, psi::Options& opt){

  // Construct the solver object
  Diagonalize solver(H, opt, M);

  // Find *M* lowest eigenpairs of a given matrix **H**
  solver.run_davidson_liu();
};
```

## 18.3 example_gefp.cc

### Working with GenEffFrag objects

At the moment, `psi::Molecule` and `psi::BasisSet` objects do not have Cartesian rotation implemented which prohibits using them as containers in OEPDev. On the other hand, many calculations in FB approaches require molecule and basis set rotation. Therefore, to temporarily overcome this technical difficulty, molecule and basis set objects need to be supplied for each fragment in the system by building them from scratch. Below, the guideline for fragment generation and manipulation is given:

```
// Create empty fragment
SharedGenEffFrag fragment = oepdev::GenEffFrag::build("Ethylene");
// Set the parameters
```

```
fragment->parameters["efp2"] = par_efp2;
fragment->parameters["eet"] = par_eet;
// Set the number of doubly occupied MOs and number of primary basis functions at the end
fragment->set_ndocc(ndocc);
fragment->set_nbf(nbf);
// Set the current molecule and basis set
fragment->set_molecule(mol);
fragment->set_basisset("primary", basis_prim);
fragment->set_basisset("auxiliary", basis_aux);
```

Creating the parameters can be done by using an appropriate factory

```
SharedGenEffParFactory factory = GenEffParFactory::build("OEP-EFP2", wfn, options,
      auxiliary, intermediate);
SharedGenEffPar parameters = factory->compute();
```

Currently, parameters are not created with allocated basis set objects due to the above mentioned problem in Psi4 regarding lack of functionality of basis set rotation. Therefore, **it is important to first set the parameters before setting the basis set** when constructing the fragments. It is because using the `set_basisset` method for the fragment sets the basis set for all parameters as well, and if the parameters were set after the basis set, they would not have any basis sets allocated leading to errors in FB calculations. This problem will not emerge once a rotation of `psi::BasisSet` is implemented (either in Psi4 or in OEPDev).

```
void example_gefp() {
//TODO
}
```

## 18.4 example_integrals_iter.cc

Iterations over electron repulsion integrals in AO basis. This is an example of how to use

- the oepdev::ShellCombinationsIterator class
- the oepdev::AOIntegralsIterator class.

```
void iterate(std::shared_ptr<oepdev::IntegralFactory> ints)
{
  // Prepare for direct calculation of ERI's (shell by shell)
  std::shared_ptr<psi::TwoBodyAOInt> tei(ints->eri());

  // Grab the buffer where the integrals for a current shell will be placed
  const double* buffer = tei->buffer();

  // Create iterator to go through all shell quartet combinations
  oepdev::SharedShellsIterator shellIter =
      oepdev::ShellCombinationsIterator::build(ints, "ALL", 4);

  // Iterate over shells, and then over all integrals in each shell quartet
  for (shellIter->first(); shellIter->is_done() == false; shellIter->next())
  {
       // Compute all integrals between shells in the current quartet
       shellIter->compute_shell(tei);

       // Create iterator to go through all integrals within a shell quartet
       oepdev::SharedAOIntsIterator intsIter = shellIter->ao_iterator("ALL");

       for (intsIter->first(); intsIter->is_done() == false; intsIter->next())
       {
```

```
                // Grab current (ij|kl) indices here
                int i = intsIter->i();
                int j = intsIter->j();
                int k = intsIter->k();
                int l = intsIter->l();

                // Grab the (ij|kl) integral
                double integral = buffer[intsIter->index()];
            }
        }
    }
```

## 18.5 example_scf_perturb.cc

Perturb HF Hamiltonian with external electrostatic potential. This is an example of how to use the oepdev::RHFPerturbed class.

```
void scf_perturb(std::shared_ptr<psi::Wavefunction> wfn, psi::Options& opt)
{
   // Set up HF superfunctional
   std::shared_ptr<psi::SuperFunctional> func = oepdev::create_superfunctional
      ("HF", opt);

   // Initialize the perturbed wavefunction
   std::shared_ptr<oepdev::RHFPerturbed> scf = std::make_shared<oepdev::RHFPerturbed>(wfn, func, opt, wfn->
      psio());

   /* Perturb the system with the uniform electric field [Fx, Fy, Fz].
      Then, add two point charges of charge qi placed at [Rxi, Ryi, Rzi].
      Provide all these values in atomic units! */
   const double Fx = 0.04, Fy = 0.05, Fz = -0.09;
   const double Rx1= 0.00, Rx2= 1.30, Rx3= -1.00;
   const double Rx1= 0.10, Rx2=-0.30, Rx3=  3.50;
   const double q1 = 0.30, q2 =-0.09;

   scf->set_perturbation(Fx, Fy, Fz);        /* set it only once, setting it again will overwrite the
       field, not add */
   scf->set_perturbation(Rx1, Ry1, Rz1, q1);
   scf->set_perturbation(Rx2, Ry2, Rz2, q2); /* more charges can be added */

   // Solve perturbed SCF equations
   scf->compute_energy();

   // Grab some data
   double energy = scf->reference_energy();      // Total energy of the system
   std::shared_ptr<psi::Matrix> Da = scf->Da();  // One-particle density matrix

   /* Note that the external field and charges perturb only one-electron Hamiltonian.*/
}
```

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