EOPDev
Version 1.0.0

Elimination of Electron Repulsion Integrals
from Fragment-Based Methods of Quantum Chemistry
A Plugin to Psi4

By

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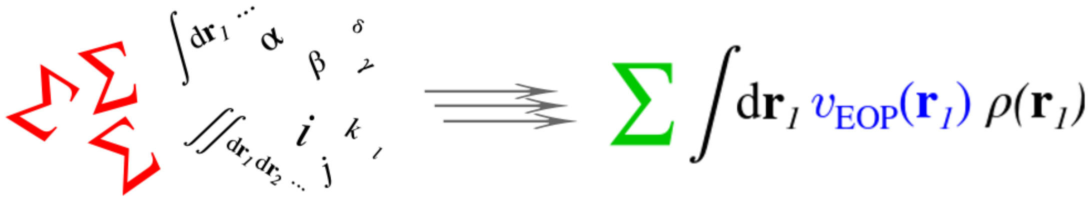
Contents



Effective one-electron operators can be systematically used to convert fragment-based methods into effective fragment potentials.

CHAPTER 1

Main Page

EOPDev

Generalized Effective One-Electron Potentials: Development Platform.

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Overview

Develop and test custom **Effective One-electron Potentials (EOP's)** for fragment-based methods of Quantum Chemistry of extended molecular aggregates.

EOPDev is a Psi4 plugin with extensive Python 3 interface. Currently, a few efficient methods that utilize EOP's and related approaches are implemented and tested against reference solutions:

1. Short-range components of interaction energy at Hartree-Fock level
2. Excitation energy transfer couplings at CIS level
3. Polarization of electronic density in non-uniform electric fields at any level

Places to go:

- EOPDev Code
- Current Issues
- Project Website

This wikipages might be updated in the future.

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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. Xu et al. [2018a] Tomasi et al. [2005] Despite many methodologies have been devised to describe energetic and dynamical properties of **extended molecular systems** efficiently and accurately, Warshel and Levitt [1976] Senn and Thiel [2009] Demerdash et al. [2014] Gordon et al. [2012] 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, Barbatti [2014] Szabla et al. [2015] Bednarska et al. [2017] Jedrzejewska et al. [2018]
- performing molecular dynamics at very high level of theory including dynamic electron correlation, Curchod and Martínez [2018]
- vibrational frequency calculations of particular normal mode in condensed phases Błasiak et al. [2017] Xu et al. [2018b] Lewis et al. [2016]

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 and potentials. On the other hand, it has been pointed out before that the one-electron density distributions are of particular importance in chemistry. Kohn and Sham [1965] Holas and March [1991] Thus, it can be 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. Roothaan [1951] Hohenberg and Kohn [1964] Kohn and Sham [1965] Otto and Ladik [1975] Holas and

March [1991] Weber and Thiel [2000] Neese [2005] Cisneros et al. [2005] Piquemal et al. [2006] Li et al. [2006] Błasiak et al. [2013] Błasiak et al. [2015]

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, ERIs. In a typical calculation, the amount of ERIs 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 ERIs 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 (EOPs) is developed. The main principle is to rewrite arbitrary sum of functions f of electron repulsion integrals (ERIs) by defining EOPs 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 ϕ_i is the i-th molecular orbital or basis function. Here, v_{kl}^B denotes the poeptypes *ab initio* "EOP matrix element". The above technique might be used in fragment-based *ab initio* methods including molecular dynamics protocols of new generation.

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

The proposed EOPs 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 EOPs, 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). Particularly, the EFP2 CT term is relatively time consuming and due to this reason it is sometimes omitted in the 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 evaluate when performing statistical averaging and applying to large molecular aggregates. Such Dexter effects could be computed by using EOPs in much more efficient manner without loosing high accuracy of state-of-the-art methods such as 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 EOPs 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 EOPs are implemented in the EOPDev code, along with the state-of-the-art benchmark and competiting methods. Written in C++ with an extensive Python interface, 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 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.

It can be shown that for a two-fragment system composed of fragments *A* and *B*

$$\sum_t \mathscr{F}_t \left[(BX|AA)\right] + \sum_s (B|\hat{o}_s^A|X) = \sum_{ij \in X} (B|\hat{v}^A|i) \left[\mathbf{S}^{-1}\right]_{ij} (j|X)$$

where $S_{ij} = (i|j)$, $\mathscr{F}_t$ is a certain linear functional of ERIs of type $(BX|AA)$, $\hat{o}_s^A$ is a one-electron operator associated with molecule A, and *X* = *A* or *B*. Błasiak et al. [2020a] Such elimination of ERIs is possible when either Coulomb-like or overlap-like interfragment ERIs are of importance. It is also possible to approximate the exchange-like ERIs and incorporate them into EOPs. Błasiak et al. [2020b] The above design offers subtantial gain of efficiency, since complicated contractions over ERIs are effectively removed and replaced by summations over one-electron integrals (OEIs).

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. By defining a (i) Solver class that handles such interaction, (ii) Wavefunction class, and (iii) 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 Classes of EOPs

There are many types of EOPs, but the underlying principle is the same and independent of the type of intermolecular interaction. Therefore, the EOPs should be implemented by using a multi-level class design. In turn, this design depends on the way EOPs 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. For illustrative purpose, distributed charge approximation is assumed for the DMTP form in this table. Note however, that higher multipoles can be also used for better accuracy. 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.

3.2 Density-fitting Specialized for EOPs

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 (ERIs) more efficiently. More detailed derivation and discussion of the results from this section can by found in the work of Błasiak et al. [2020a].

3.2.1 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

$$v_\eta^{(i)} = (\eta|vi)$$
$$S_{\eta\xi} = (\eta|\xi)$$

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.

3.2.2 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 an **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

$$b_\eta^{(i)} = (\eta||vi)$$
$$A_{\eta\xi} = (\eta||\xi)$$

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 oepdev::ERI_1_1).

3.2.3 Fitting in Incomplete Space - Alternative Approach

The above method of density fitting of EOPs in incomplete space might be still relatively costly since it requires two-centre ERIs. However, there exists alternative approach which requires only overlap integrals. The EOP matrix is then given by

$$\mathbf{G}_{\mathrm{m}}^{\dagger} = \mathbf{T}_{\mathrm{mX}} \mathbf{S}_{\mathrm{XX}'}^{-1} \mathbf{T}_{\mathrm{mX}}^{\dagger} \mathbf{S}_{\mathrm{ma}} \mathbf{G}_{\mathrm{a}}^{\dagger}$$

where $\mathbf{G}_{\mathrm{a}}$ and $\mathbf{G}_{\mathrm{m}}$ are the EOP matrices in complete and incomplete basis, respectively. The auxiliary matrices read

$$\begin{aligned}
\mathbf{T}_{\mathrm{mX}} &= \mathbf{S}_{\mathrm{mm}}^{-1} \mathbf{S}_{\mathrm{ma}} \mathbf{T}_{\mathrm{aX}} \mathbf{S}_{\mathrm{XX}'}^{-1} \\
\mathbf{S}_{\mathrm{XX}'}^{-1} &= \left(\mathbf{T}_{\mathrm{aX}}^{\dagger} \mathbf{S}_{\mathrm{am}} \mathbf{S}_{\mathrm{mm}}^{-1} \mathbf{S}_{\mathrm{ma}} \mathbf{T}_{\mathrm{aX}} \right)^{\frac{1}{2}} \\
\mathbf{T}_{\mathrm{aX}} &= \mathbf{S}_{\mathrm{aa}}^{-1} \mathscr{Q} \mathbf{U}_{\mathrm{aX}}
\end{aligned}$$

The similarity transformation matrix $\mathbf{T}_{\mathrm{aX}}$ is obtained from the eigenvectors of the co-variance matrix, i.e.,

$$\mathbf{C}_{\mathrm{aa}} = \mathbf{S}_{\mathrm{aa}}^{\frac{1}{2}} \mathbf{G}_{\mathrm{a}}^{\dagger} \mathbf{G}_{\mathrm{a}} \mathbf{S}_{\mathrm{aa}}^{\frac{1}{2}} = \mathbf{U}_{\mathrm{aX}} \mathbf{g}_{\mathrm{XX}} \mathbf{U}_{\mathrm{aX}}^{\dagger}$$

The operator $\mathscr{Q}$ selects only eigenvectors $\mathbf{U}_{\mathrm{aX}}$ associated with the non-vanishing eigenvalues stored in the diagonal matrix $\mathbf{g}_{\mathrm{XX}}$. In practice, the number of such eigenvalues is bounded by the number of rows in EOP matrix, i.e., the number of states on which the EOP operator acts. Thus, substantial reduction of the basis set size is achieved which further reduces computational cost.

CHAPTER 4

Implemented Models

4.1 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 method Błasiak 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)

4.2 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)
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 5

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**.

5.1 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.

5.2 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.

5.3 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.

5.4 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!

5.5 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`.

5.6 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.

5.7 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.

5.8 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

- **polymorphism** 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.

5.9 Implement Tests

When a computer code is updated by new features such as methods or algorithms, it becomes important to monitor its performance in order to ensure that it works correctly. To achieve this goal, a testing platform should be established, which contains a set of tests producing certain outputs and compare them with benchmark outputs. In EOPDev, `ctest` functionality is used as a testing platform for the C++ level code. Everytime you implement new feature in the code, it is very recommended to immediately supplement the testing platform with a new test. Remember to design tests carefully so that they address all potentially vulnerable aspects of added functionalities and a valid reference output can also be defined. See the tests in `oepdev/libtest` as well as `tests/oepdev` directories.

CHAPTER 6

Usage

EOPDev is addressed for developers.

Make sure you have first read the introduction and are familiar with the EOP-based ERI elimination technique before proceeding.

6.1 Installation

6.1.1 Preparing Psi4

EOPDev is a Psi4 plugin. It requires -`Psi4, version 1.2.1` (git commit `406f4de`). 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.

6.1.2 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).

6.1.3 Step-By-Step Installation

To summarize, follow these steps:

1. **Modify Psi4.** Create a copy of your Psi4 source, and in the directory containing the main directory of Psi4 run

```
./${EOPDEV_PATH}/misc/patch/run_patch-psi4-1.2.1_git.406f4de
```

where `EOPDEV_PATH` variable denotes here your local source directory of EOPDev. Subsequently, compile the modified Psi4.

2. **Install Eigen3**. Set the path to Eigen3:

```
export EIGEN3_INCLUDE_DIR=/your_path_to_eigen3
```

and add it to your `.bash.rc` file.

3. **Install EOPDev**. Go to your EOPDev source directory and run

```
./compile
./create_doc
evince ${EOPDEV_PATH}/doc/doxygen/latex/refman.pdf
```

The first script installs the EOPDev plugin. The second generates the HTML and documentations on your computer (e.g., see `refman.pdf` for documentation in PDF format). Generation of the documentation is optional but highly recommended.

4. **Install GEFP Python Package**. Run the following commands:

```
cd ${EOPDEV_PATH}/gefp
python setup.py install
```

Administrative priviledges might be necessary. Although installing GEFP is not necessary, it contains quite a few useful Python implementations of various quantum chemistry methods or handling with molecule and wavefunction objects. In particular, GEFP contains efficient and fully automatized implementation of the extended density fitting of EOPs.

5. **Test**. Run the tests:

```
cd ${EOPDEV_PATH}
ctest
```

If any of the tests do not work, resolve possible compilation issues (including Psi4).

6.2 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.

6.2.1 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.

6.2.2 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.

6.3 EOPDev Classes: Overview

6.3.1 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.

OEPotential

It is a container and computer class of EOP. Among others, the most important public method is `OEPotential::compute` which computes all the EOPs (by iterating over all possible EOP types within a chosen EOP subclass or category). EOPs 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.

GeneralizedDensityFit

Implements the density fitting schemes for EOPs.

6.3.2 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).

GenEffPar

Represents generalized effective fragment parameters.

GenEffParFactory

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

GenEffFrag

Represents one effective fragment.

6.3.3 EOPDev Solver Module

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

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`.

6.4 Developing EOPs

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.

EOPs are implemented in a suitable subclass of the `OEPotential` base. Due to the fact that EOPs 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 (OEIs) and the two-electron integrals (ERIs) 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 ERIs the `ShellCombinationsIterator` and `AOIntegralsIterator` classes. Transformations of OEIs 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 ERIs to MO basis can be performed by using the `psi4/libtrans/integraltransform.h` library.

It is recommended that the implementation of all the new EOPs 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 EOPs 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.

6.4.1 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 EOPs
    SampleOEPotential(SharedWavefunction wfn, Options& options);

    // GDF-based EOPs
    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  ");
```

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 EOPs need to create the `psi::Matrix` with EOP parameters and put them into `oepTypes_`. In the case of DMTP-based EOPs `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 EOPs 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)!

6.5 Examples

Exemplary demos of using the EOPDev code in C++ level can be found in the testing platform. Additional examples can also be found in `doc/examples` directory. However, the latter examples might not fully compile since they are only for illustrative purposes as the code constantly develops. They are constantly updated as much as possible.

CHAPTER 7

Module Index

7.1 Modules

Here is a list of all modules:

CHAPTER 8

Namespace Index

8.1 Namespace List

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

CHAPTER 9

Hierarchical Index

9.1 Class Hierarchy

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

CHAPTER 10

Class Index

10.1 Class List

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

CHAPTER 11

File Index

11.1 File List

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

CHAPTER 12

Module Documentation

12.1 The Generalized One-Electron Potentials Library

Implements the goal of this project: The Generalized One-Electron Potentials (EOPs). You will find here EOPs 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 >

12.1.1 Detailed Description

12.2 The EOPDev Solver Library

Implementations of various solvers for molecular properties as a functions of unperturbed monomeric wavefunctions. This is the place all target EOP-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.

12.2.1 Detailed Description

12.3 The Generalized Effective Fragment Potentials Library

Implements the GEFP method, the far goal of the EOPDev 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.

12.3.1 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, EOP-EFP2 as well as EOP-EET parameters. Fragments can be superimposed on target structures and the class contain methods that evaluate properties based on the fragments in the system.

12.4 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.

12.4.1 Detailed Description

Here, we define the primitive Gaussian type functions (GTOs)

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

in which $\mathbf{r}_A \equiv \mathbf{r} - \mathbf{A}$ and so on. $\mathbf{A}$ is the centre of the GTO, α_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 EOPDev 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 GTOs are denoted here as

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

12.4.2 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.

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

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

respectively. The first elements are given by

$$d_0^0 = 1$$
$$d_0^{00} = 1$$
$$d_0^{000} = 1$$

By using the above formalisms, it is strightforward to express the doublet of primitive GTOs 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 GTOs 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

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

12.4.3 One-Body Integrals over Hermite Functions

The fundamental Hermite integrals that appear during computations of any kind of one-body integrals over GTOs 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

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

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

12.4.4 Two-Body Integrals over Hermite Functions

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

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

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

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

12.4.5 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:

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

This scheme is implemented in EOPDev.

12.4.6 Function Documentation

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

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

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): • 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

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
buffer	- the McMurchie-Davidson-Hermite 5-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 n3+1 (0 to n3) • axis 4: dimension n1+n2+n3+1 (0 to n1+n2+n3)

See also

D3_INDEX

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

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

Parameters

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

12.5 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)

12.5.1 Detailed Description

12.5.2 Function Documentation

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

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

12.6 The Density Functional Theory Library

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

12.7 The EOPDev Utilities

Contains utility functions such as printing EOPDev 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 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)
- 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

12.7.1 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,

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

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

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

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.

12.7.2 Detailed Description

12.7.3 Function Documentation

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

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

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

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.

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.

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.

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

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.

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

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

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.

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

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

_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.

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

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

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

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

12.8 The EOPDev 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.

12.8.1 Detailed Description

CHAPTER 13

Namespace Documentation

13.1 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 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)
- 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);.

Rotation of AO Space

13.1.1 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

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

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 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]

13.1.2 Detailed Description

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

13.2 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)

13.2.1 Detailed Description

Contains all Psi4 functionalities.

13.2.2 Function Documentation

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

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)

CHAPTER 14

Class Documentation

14.1 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**

14.1.1 Detailed Description

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

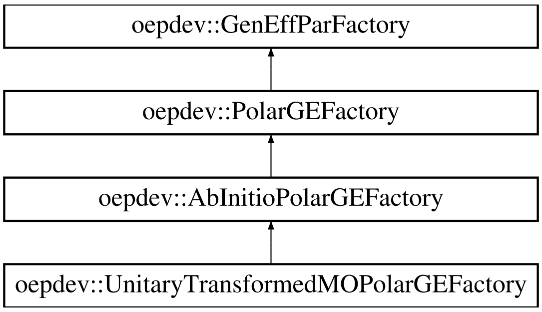
- oepdev/libutil/unitary_optimizer.h

14.2 oepdev::AbInitioPolarGEFactory Class Reference

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

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

Inheritance diagram for oepdev::AbInitioPolarGEFactory:



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

14.2.1 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

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

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

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

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

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

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:

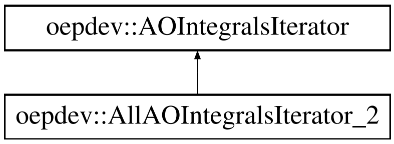
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_abinitio.cc

14.3 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

14.3.1 Detailed Description

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

See also

AllAOShellCombinationsIterator_2

14.3.2 Constructor & Destructor Documentation

AllAOIntegralsIterator_2() [1/2]

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

Parameters

shellIter	- shell iterator object

AllAOIntegralsIterator_2() [2/2]

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

Parameters

shellIter	- shell iterator object

14.3.3 Member Function Documentation

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:

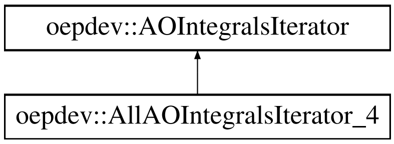
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

14.4 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

14.4.1 Detailed Description

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

See also

AllAOShellCombinationsIterator_4

14.4.2 Constructor & Destructor Documentation

AllAOIntegralsIterator_4() [1/2]

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

Parameters

shellIter	- shell iterator object

AllAOIntegralsIterator_4() [2/2]

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

Parameters

shellIter	- shell iterator object

14.4.3 Member Function Documentation

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:

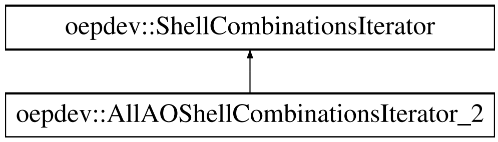
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

14.5 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:



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

14.5.1 Detailed Description

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

14.5.2 Constructor & Destructor Documentation

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

AllAOShellCombinationsIterator_2() [2/5]

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

Parameters

integrals	- OepDev integral factory object

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.

AllAOShellCombinationsIterator_2() [4/5]

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

Parameters

integrals	- Psi4 integral factory object

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.

14.5.3 Member Function Documentation

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:

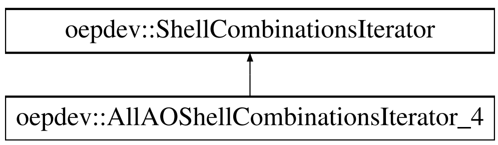
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

14.6 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:



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

14.6.1 Detailed Description

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

14.6.2 Constructor & Destructor Documentation

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

AllAOShellCombinationsIterator_4() [2/5]

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

Parameters

integrals	- OepDev integral factory object

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.

AllAOShellCombinationsIterator_4() [4/5]

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

Parameters

integrals	- OepDev integral factory object

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.

14.6.3 Member Function Documentation

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.

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:

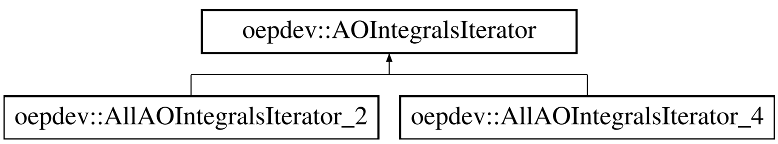
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

14.7 oepdev::AOIntegralsIterator Class Reference

Iterator for AO Integrals. Abstract Base.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::AOIntegralsIterator:



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.

14.7.1 Detailed Description

14.7.2 Member Function Documentation

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

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:

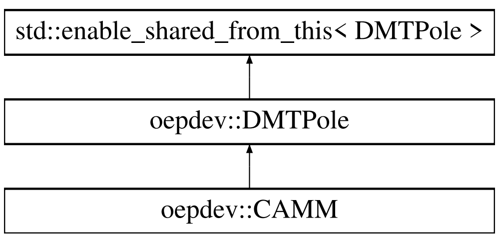
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

14.8 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

14.8.1 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:

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

where $M_{uw\ldots z}^{(A)}$ 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 $D_{\alpha\beta}^{\mathrm{OED}}$ 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:

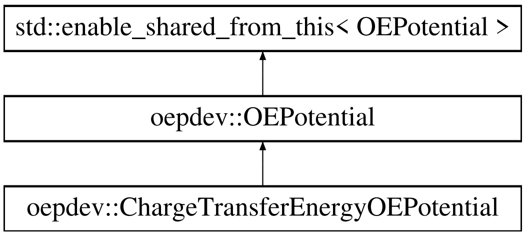
- oepdev/lib3d/dmtp.h
- oepdev/lib3d/dmtp_camm.cc

14.9 oepdev::ChargeTransferEnergyOEPotential Class Reference

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

`#include <oep.h>`

Inheritance diagram for 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

14.9.1 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:

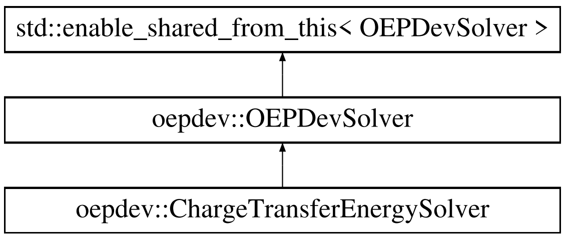
- oepdev/liboep/oep.h
- oepdev/liboep/oep_energy_ct.cc

14.10 oepdev::ChargeTransferEnergySolver Class Reference

Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::ChargeTransferEnergySolver:



Public Member Functions

- **ChargeTransferEnergySolver** (SharedWavefunctionUnion wfn_union)
- virtual double compute_oep_based (const std::string &method="DEFAULT")

  Compute property by using OEPs.
- virtual double compute_benchmark (const std::string &method="DEFAULT")

  Compute property by using benchmark method.

Additional Inherited Members

14.10.1 Detailed Description

The implemented methods are shown below

Table 14.15: 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 (ERIs) 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

$$\begin{aligned}V_{in} = V_{in}^B + 2\sum_{j\in B}^{\rm Occ_B}(in|jj) - \sum_{k\in A}^{\rm Occ_A} S_{kn}\left\{V_{ik}^B + 2\sum_{j\in B}^{\rm Occ_B}(ik|jj)\right\} \\ - \sum_{j\in B}^{\rm Occ_B}\left[S_{ij}\left\{V_{nj}^A + 2\sum_{k\in A}^{\rm Occ_A}(1-\delta_{ik})(nj|kk)\right\} + (nj|ij)\right] + \sum_{k\in A}^{\rm Occ_A}\sum_{j\in B}^{\rm Occ_B} S_{kj}(1-\delta_{ik})(ik|nj)\end{aligned}$$

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 OEPs, 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).

14.10.2 Member Function Documentation

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.

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.

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

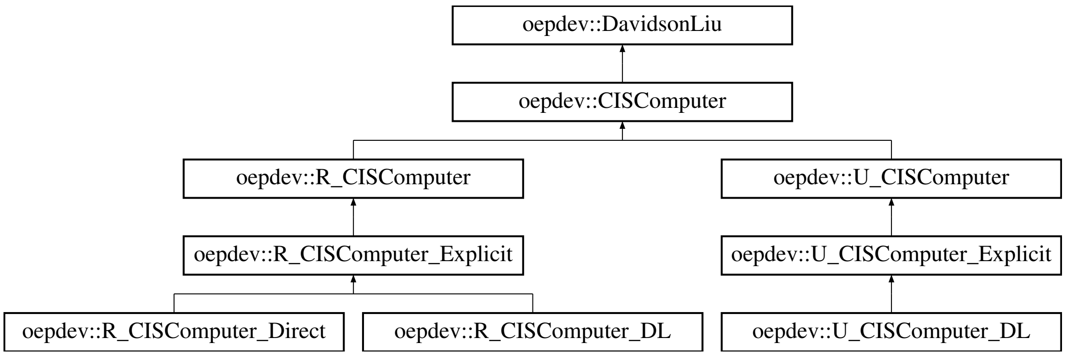
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_energy_ct.cc

14.11 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_**

14.11.1 Detailed Description

14.11.2 Member Function Documentation

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)

$$\left\langle \Phi_0 \middle| \mathscr{H} \middle| \Phi_i^a \right\rangle = 0$$
$$\left\langle \Phi_j^b \middle| \mathscr{H} \middle| \Phi_i^a \right\rangle = \delta_{ij}\delta_{ab}\left(\varepsilon_a - \varepsilon_i\right) + \left\langle aj \middle| ib \right\rangle - \left\langle aj \middle| bi \right\rangle$$

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 $i \to a$ 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

$$P_{\mu\nu}^{(g\to e)} = \sum_{i}^{\text{Occ}}\sum_{a}^{\text{Vir}} t_{i,e}^{a} C_{\nu i} C_{\mu a} + \sum_{\bar{i}}^{\text{Occ}}\sum_{\bar{a}}^{\text{Vir}} t_{\bar{i},e}^{\bar{a}} C_{\nu\bar{i}} C_{\mu\bar{a}}$$

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

$$P_{\mu\nu}^{(e)} = \sum_{pq} C_{\mu p} P_{pq}^{(e)} C_{\nu q} + \sum_{\bar{p}\bar{q}} C_{\mu\bar{p}} P_{\bar{p}\bar{q}}^{(e)} C_{\nu\bar{q}}$$

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

$$P_{pq}^{(e)} = \begin{cases} \delta_{pq} - \sum_a^{\mathrm{Vir}} t_{p,e}^a t_{q,e}^a & \text{for p,q } \in \mathrm{Occ} \\ \sum_i^{\mathrm{Occ}} t_{i,e}^p t_{i,e}^q & \text{for p,q } \in \mathrm{Vir} \\ 0 & \text{otherwise} \end{cases}$$

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.,

$$\left\langle \Phi_0 \middle| \hat{\mu}_u \middle| \Psi_e \right\rangle = \mathrm{Tr}\left[\mathbf{d}^{(u)} \cdot \mathbf{P}^{g\to e} \right]$$

Oscillator strength is computed from the transition dipole moment via

$$f^{g\to e} = \frac{2}{3} E_e \left| \left\langle \Phi_0 \middle| \hat{\boldsymbol{\mu}} \middle| \Psi_e \right\rangle \right|^2$$

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:

$$\begin{aligned}\left\langle \hat{S}^2 \right\rangle_{\mathrm{UCIS}} = \left\langle \hat{S}^2 \right\rangle_{\mathrm{UHF}} - \mathrm{Tr}\left[\mathbf{Q}_{\mathrm{Occ}}^{(\alpha)} \cdot \left\{ \mathbf{P}_{\mathrm{Occ}}^{(e,\alpha)} - \mathbf{1} \right\} \right] - \mathrm{Tr}\left[\mathbf{Q}_{\mathrm{Occ}}^{(\beta)} \cdot \left\{ \mathbf{P}_{\mathrm{Occ}}^{(e,\beta)} - \mathbf{1} \right\} \right] \\ - \mathrm{Tr}\left[\mathbf{Q}_{\mathrm{Vir}}^{(\alpha)} \cdot \mathbf{P}_{\mathrm{Vir}}^{(e,\alpha)} \right] - \mathrm{Tr}\left[\mathbf{Q}_{\mathrm{Vir}}^{(\beta)} \cdot \mathbf{P}_{\mathrm{Vir}}^{(e,\beta)} \right] - 2 \sum_i^{\mathrm{Occ}} \sum_a^{\mathrm{Vir}} \sum_{\bar{j}}^{\mathrm{Occ}} \sum_{\bar{b}}^{\mathrm{Vir}} \Delta_{i\bar{j}}^* \Delta_{a\bar{b}} t_{i,e}^a t_{\bar{j},e}^{\bar{b}}\end{aligned}$$

where

$$[\mathbf{Q}_{\mathrm{Occ}}^{(\alpha)}]_{ij} = \sum_{\bar{k}}^{\mathrm{Occ}} \Delta_{\bar{k}i}^* \Delta_{\bar{k}j}$$

$$[\mathbf{Q}_{\mathrm{Occ}}^{(\beta)}]_{\bar{i}\bar{j}} = \sum_{k}^{\mathrm{Occ}} \Delta_{k\bar{i}}^* \Delta_{k\bar{j}}$$

$$[\mathbf{Q}_{\mathrm{Vir}}^{(\alpha)}]_{ab} = \sum_{\bar{k}}^{\mathrm{Occ}} \Delta_{\bar{k}a}^* \Delta_{\bar{k}b}$$

$$[\mathbf{Q}_{\mathrm{Vir}}^{(\beta)}]_{\bar{a}\bar{b}} = \sum_{k}^{\mathrm{Occ}} \Delta_{k\bar{a}}^* \Delta_{k\bar{b}}$$

and

$$\Delta_{pq} = \sum_{\mu\nu} C_{\mu p} S_{\mu\nu} C_{\nu p}$$

The diagnostic for UHF spin contamination is given by

$$\langle \hat{S}^2 \rangle_{\rm UHF} = \langle \hat{S}^2 \rangle_{\rm exact} + N_\beta - \sum_i^{\rm Occ} \sum_{\bar{j}}^{\rm Occ} |\Delta_{i\bar{j}}|^2$$

with

$$\langle \hat{S}^2 \rangle_{\rm exact} = \frac{N_\alpha - N_\beta}{2} \left(\frac{N_\alpha - N_\beta + 2}{2} \right)$$

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

14.11.3 Member Data Documentation

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

14.12 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.

14.12.1 Detailed Description

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

- oepdev/libutil/cis.h
- oepdev/libutil/cis_base.cc

14.13 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.

14.13.1 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

14.13.2 Constructor & Destructor Documentation

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:

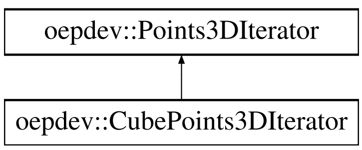
- oepdev/libutil/cphf.h
- oepdev/libutil/cphf.cc

14.14 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

14.14.1 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:

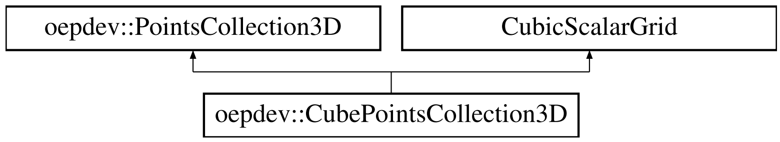
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

14.15 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

14.15.1 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:

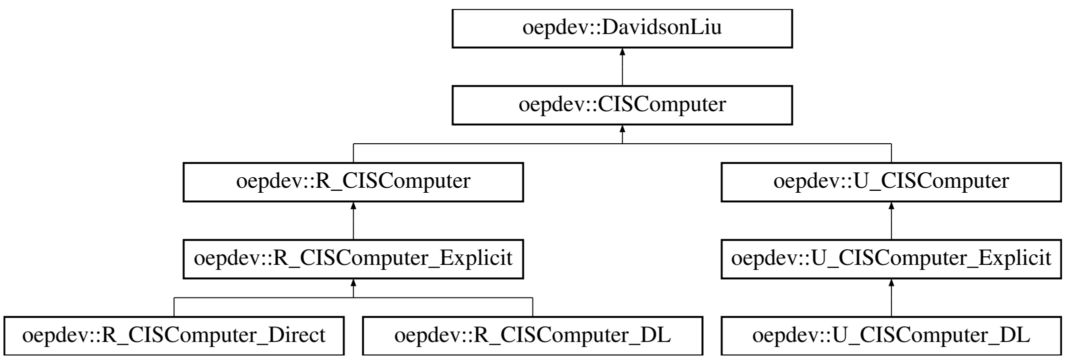
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

14.16 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.

14.16.1 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 σ 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

$$\mathbf{S} = \mathbf{HB}$$

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,

$$\mathbf{G} = \mathbf{UzU}^{\mathrm{T}}$$

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

$$\mathbf{C} = \mathbf{BA}$$

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

14.17 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)

14.17.1 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.

14.17.2 Constructor & Destructor Documentation

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

14.17.3 Member Function Documentation

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

compute()

```
void oepdev::DIISManager::compute (
            void )
```

Perform DIIS interpolation.

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:

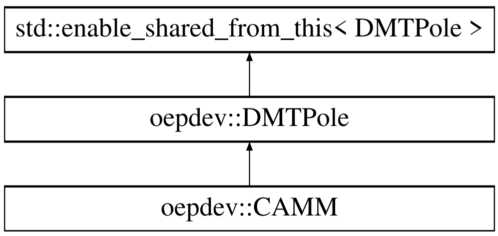
- oepdev/libutil/diis.h
- oepdev/libutil/diis.cc

14.18 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 ith distribution.
- virtual psi::SharedMatrix dipoles (int i) const
  Get the distributed dipoles for the ith distribution.
- virtual psi::SharedMatrix quadrupoles (int i) const
  Get the distributed quadrupoles for the ith distribution.
- virtual psi::SharedMatrix octupoles (int i) const
  Get the distributed octupoles for the ith distribution.
- virtual psi::SharedMatrix hexadecapoles (int i) const
  Get the distributed hexadecapoles for the ith 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 ith distribution.
- void set_dipoles (psi::SharedMatrix M, int i)
  Set the distributed dipoles for the ith distribution.
- void set_quadrupoles (psi::SharedMatrix M, int i)
  Set the distributed quadrupoles for the ith distribution.
- void set_octupoles (psi::SharedMatrix M, int i)

Set the distributed octupoles for the ith distribution.

- void set_hexadecapoles (psi::SharedMatrix M, int i)

  Set the distributed hexadecapoles for the ith 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.

14.18.1 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

14.18.2 Constructor & Destructor Documentation

DMTPole() `[1/2]`

```
oepdev::DMTPole::DMTPole (
          void )
```

Do not use this constructor. Use the DMTPole::empty method.

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.

14.18.3 Member Function Documentation

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.
wfn	- wavefunction
n	- number of DMTP sets

Returns

DMTP distribution

empty()

```
std::shared_ptr< DMTPole > oepdev::DMTPole::empty (
            std::string type ) [static]
```

Returns

Blank DMTP distribution with memory allocated by no data.

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

recenter()

```
void oepdev::DMTPole::recenter (
          psi::SharedMatrix new_origins ) [virtual]
```

Parameters

new_origins	- matrix with coordinates of the new origins $\{\mathbf{r}_{\text{new}}\}$.

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

$$\begin{aligned}
q_{\text{new}} &= q_{\text{old}} \\
\mu_{\text{new}} &= \mu_{\text{old}} - q_{\text{old}}\Delta^{(1)} \\
\Theta_{\text{new}} &= \Theta_{\text{old}} + q_{\text{old}}\Delta^{(2)} - \sum_{\mathscr{P}_2}\mathscr{P}_2\left[(q_{\text{old}}\mathbf{r}_{\text{old}} + \mu_{\text{old}})\otimes\Delta^{(1)}\right] \\
\Omega_{\text{new}} &= \Omega_{\text{old}} - q_{\text{old}}\Delta^{(3)} + \sum_{\mathscr{P}_3}\mathscr{P}_3\left[(q_{\text{old}}\mathbf{r}_{\text{old}} + \mu_{\text{old}})\otimes\Delta^{(2)}\right] - \sum_{\mathscr{P}_6}\mathscr{P}_6\left[\left(q_{\text{old}}\mathbf{r}^2_{\text{old}} + \mu_{\text{old}}\otimes\mathbf{r}_{\text{old}} + \Theta_{\text{old}}\right)\otimes\Delta^{(1)}\right] \\
\Xi_{\text{new}} &= \Xi_{\text{old}} + q_{\text{old}}\Delta^{(4)} - \sum_{\mathscr{P}_3}\mathscr{P}_3\left[(q_{\text{old}}\mathbf{r}_{\text{old}} + \mu_{\text{old}})\otimes\Delta^{(3)}\right] + \sum_{\mathscr{P}_3}\mathscr{P}_3\left[\left(q_{\text{old}}\mathbf{r}^2_{\text{old}} + \mu_{\text{old}}\otimes\mathbf{r}_{\text{old}} + \Theta_{\text{old}}\right)\otimes\Delta^{(2)}\right] \\
&\quad - \sum_{\mathscr{P}_3}\mathscr{P}_3\left[\left(q_{\text{old}}\mathbf{r}^3_{\text{old}} + \mu_{\text{old}}\otimes\mathbf{r}^2_{\text{old}} + \Theta_{\text{old}}\otimes\mathbf{r}_{\text{old}} + \Omega_{\text{old}}\right)\otimes\Delta^{(1)}\right]
\end{aligned}$$

where

$$\begin{aligned}
\Delta^{(1)} &\equiv \mathbf{r}_{\text{new}} - \mathbf{r}_{\text{old}} \\
\Delta^{(2)} &\equiv \mathbf{r}^2_{\text{new}} - \mathbf{r}^2_{\text{old}} \\
\Delta^{(3)} &\equiv \mathbf{r}^3_{\text{new}} - \mathbf{r}^3_{\text{old}} \\
\Delta^{(4)} &\equiv \mathbf{r}^4_{\text{new}} - \mathbf{r}^4_{\text{old}}
\end{aligned}$$

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!

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:

$$x_a^{(i)} \rightarrow \sum_{a'} x_{a'}^{(i)} r_{a'a}$$
$$o_a^{(i)} \rightarrow \sum_{a'} o_{a'}^{(i)} r_{a'a}$$
$$\mu_a^{(i)} \rightarrow \sum_{a'} \mu_{a'}^{(i)} r_{a'a}$$
$$\Theta_a^{(i)} \rightarrow \sum_{a'b'} \Theta_{a'b'}^{(i)} r_{a'a} r_{b'b}$$
$$\Omega_a^{(i)} \rightarrow \sum_{a'b'c'} \Omega_{a'b'c'}^{(i)} r_{a'a} r_{b'b} r_{c'c}$$
$$\Xi_a^{(i)} \rightarrow \sum_{a'b'c'd'} \Xi_{a'b'c'd'}^{(i)} r_{a'a} r_{b'b} r_{c'c} r_{d'd}$$

where the definition of $r_{a'a}$ is consistent with the Kabsch algorithm implemented in KabschSuperimposer.

See also

KabschSuperimposer

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

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

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.

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.

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.

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.

14.18.4 Friends And Related Function Documentation

MultipoleConvergence

```
friend class MultipoleConvergence [friend]
```

Convergence of multipole moment series.

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

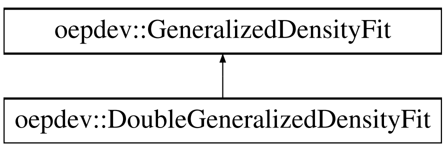
- oepdev/lib3d/dmtp.h
- oepdev/lib3d/dmtp_base.cc

14.19 oepdev::DoubleGeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme - Double Fit.

```
#include <oep_gdf.h>
```

Inheritance diagram for 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

14.19.1 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.

14.19.2 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
- ξ denotes the auxiliary basis set element
- ε 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 $\hat{v}$.

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.

14.19.3 Member Function Documentation

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:

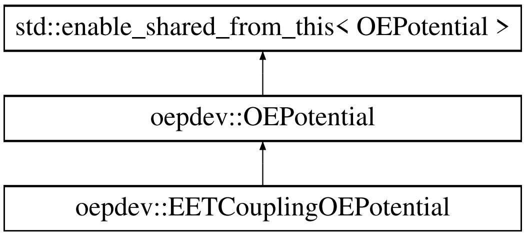
- oepdev/liboep/oep_gdf.h
- oepdev/liboep/oep_gdf.cc

14.20 oepdev::EETCouplingOEPotential Class Reference

Generalized One-Electron Potential for EET coupling calculations.

`#include <oep.h>`

Inheritance diagram for 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

14.20.1 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:

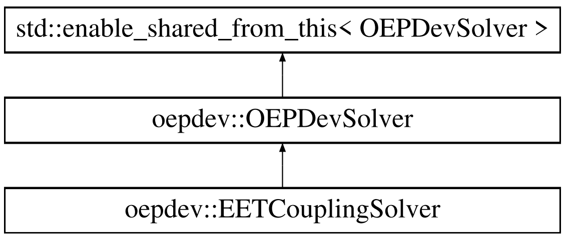
- oepdev/liboep/oep.h
- oepdev/liboep/oep_coupling_eet.cc

14.21 oepdev::EETCouplingSolver Class Reference

Compute the EET coupling energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::EETCouplingSolver:



Public Member Functions

- **EETCouplingSolver** (SharedWavefunctionUnion wfn_union)
- virtual double compute_oep_based (const std::string &method=”DEFAULT”)

  Compute property by using OEPs.
- virtual double compute_benchmark (const std::string &method=”DEFAULT”)

  Compute property by using benchmark method.

Additional Inherited Members

14.21.1 Detailed Description

The implemented methods are shown below

Table 14.32: 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 (ERIs) 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

$$\left\langle \Phi_1 \middle| \mathscr{H} - E_0 \middle| \Phi_1 \right\rangle \equiv E_1 = E^A_{e\rightarrow g} + \sum_{\mu\nu\in A} \left(P^{A(e)}_{\nu\mu} - P^{A(g)}_{\nu\mu} \right) \times \left\{ V^{B(\mathrm{nuc})}_{\mu\nu} + \sum_{\lambda\sigma\in B} P^{B(g)}_{\lambda\sigma} \left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu) \right] \right\}$$
$$\left\langle \Phi_2 \middle| \mathscr{H} - E_0 \middle| \Phi_2 \right\rangle \equiv E_2 = E^B_{e\rightarrow g} + \sum_{\mu\nu\in B} \left(P^{B(e)}_{\nu\mu} - P^{B(g)}_{\nu\mu} \right) \times \left\{ V^{A(\mathrm{nuc})}_{\mu\nu} + \sum_{\lambda\sigma\in A} P^{A(g)}_{\lambda\sigma} \left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu) \right] \right\}$$
$$\left\langle \Phi_3 \middle| \mathscr{H} - E_0 \middle| \Phi_3 \right\rangle \equiv E_3 = -\varepsilon^A_H + \varepsilon^B_L - \left(H^A H^A \middle| L^B L^B \right)$$
$$\left\langle \Phi_4 \middle| \mathscr{H} - E_0 \middle| \Phi_4 \right\rangle \equiv E_4 = \varepsilon^A_L - \varepsilon^B_H - \left(L^A L^A \middle| H^B H^B \right)$$

The associated off-diagonal Hamiltonian matrix elements can be defined as

$$\left\langle \Phi_1 \middle| \mathscr{H} \middle| \Phi_2 \right\rangle \equiv V^{\mathrm{Coul}} + V^{\mathrm{Exch}} + V^{\mathrm{Ovrl}}$$
$$\left\langle \Phi_1 \middle| \mathscr{H} \middle| \Phi_3 \right\rangle \equiv V^{\mathrm{ET1}}$$
$$\left\langle \Phi_2 \middle| \mathscr{H} \middle| \Phi_4 \right\rangle \equiv V^{\mathrm{ET2}}$$
$$\left\langle \Phi_1 \middle| \mathscr{H} \middle| \Phi_4 \right\rangle \equiv V^{\mathrm{HT1}}$$
$$\left\langle \Phi_2 \middle| \mathscr{H} \middle| \Phi_3 \right\rangle \equiv V^{\mathrm{HT2}}$$
$$\left\langle \Phi_3 \middle| \mathscr{H} \middle| \Phi_4 \right\rangle \equiv V^{\mathrm{CT}}$$

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

$$V^{\mathrm{Coul}} = \frac{V^{\mathrm{Coul},(0)}}{1 - S_{12}^2}$$
$$V^{\mathrm{Exch}} = \frac{V^{\mathrm{Exch},(0)}}{1 - S_{12}^2}$$
$$V^{\mathrm{Ovrl}} = -\frac{(E_1 + E_2) S_{12}}{2(1 - S_{12}^2)}$$

The overlap-corrected ET, HT and CT matrix elements read

$$V^{\mathrm{ET1}} = \left[1 - S_{13}^2\right]^{-1} \left\{ V^{\mathrm{ET1},(0)} - \frac{1}{2}(E_1 + E_2) S_{13} \right\}$$
$$V^{\mathrm{ET2}} = \left[1 - S_{24}^2\right]^{-1} \left\{ V^{\mathrm{ET2},(0)} - \frac{1}{2}(E_1 + E_2) S_{24} \right\}$$
$$V^{\mathrm{HT1}} = \left[1 - S_{14}^2\right]^{-1} \left\{ V^{\mathrm{HT1},(0)} - \frac{1}{2}(E_1 + E_2) S_{14} \right\}$$
$$V^{\mathrm{HT2}} = \left[1 - S_{23}^2\right]^{-1} \left\{ V^{\mathrm{HT2},(0)} - \frac{1}{2}(E_1 + E_2) S_{23} \right\}$$
$$V^{\mathrm{CT}} = \left[1 - S_{34}^2\right]^{-1} \left\{ V^{\mathrm{CT},(0)} - \frac{1}{2}(E_1 + E_2) S_{34} \right\}$$

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

$$
\begin{aligned}
V^{\text{Coul},(0)} &= \sum_{\mu\nu\in A}\sum_{\lambda\sigma\in B} P^{g\rightarrow e(A)}_{\nu\mu} P^{g\rightarrow e(B)}_{\lambda\sigma} (\mu\nu|\sigma\lambda) \\
V^{\text{Exch},(0)} &= -\frac{1}{2}\sum_{\mu\nu\in A}\sum_{\lambda\sigma\in B} P^{g\rightarrow e(A)}_{\nu\mu} P^{g\rightarrow e(B)}_{\lambda\sigma} (\mu\lambda|\sigma\nu) \\
V^{\text{ET1},(0)} &= t^{A}_{H\rightarrow L}\left\{ \left(L^A\middle|\mathscr{F}\middle|L^B\right) + 2\left(L^A H^A\middle|H^A L^B\right) - \left(L^A L^B\middle|H^A H^A\right) \right\} \\
V^{\text{ET2},(0)} &= t^{B}_{H\rightarrow L}\left\{ \left(L^A\middle|\mathscr{F}\middle|L^B\right) + 2\left(L^A H^B\middle|H^B L^B\right) - \left(L^A L^B\middle|H^B H^B\right) \right\} \\
V^{\text{HT1},(0)} &= t^{A}_{H\rightarrow L}\left\{ -\left(H^A\middle|\mathscr{F}\middle|H^B\right) + 2\left(H^A L^A\middle|L^A H^B\right) - \left(H^A H^B\middle|L^A L^A\right) \right\} \\
V^{\text{HT2},(0)} &= t^{B}_{H\rightarrow L}\left\{ -\left(H^A\middle|\mathscr{F}\middle|H^B\right) + 2\left(H^A L^B\middle|L^B H^B\right) - \left(H^A H^B\middle|L^B L^B\right) \right\} \\
V^{\text{CT},(0)} &= 2\left(H^A L^B\middle|L^A H^B\right) - \left(H^A H^B\middle|L^A L^B\right)
\end{aligned}
$$

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

$$
\begin{aligned}
S_{12} &\equiv \left(\Phi_1\middle|\Phi_2\right) \cong -\frac{1}{N^{AB}_{el}} \mathrm{Tr}\left[\mathbf{P}^{g\rightarrow e(A)}\mathbf{s}^{AB}\mathbf{P}^{g\rightarrow e(B)}\mathbf{s}^{BA}\right] \\
S_{13} &\equiv \left(\Phi_1\middle|\Phi_3\right) \cong -\frac{t^{A}_{H\rightarrow L}}{N^{AB}_{el}} S^{AB}_{LL} \\
S_{14} &\equiv \left(\Phi_1\middle|\Phi_4\right) \cong +\frac{t^{A}_{H\rightarrow L}}{N^{AB}_{el}} S^{AB}_{HH} \\
S_{24} &\equiv \left(\Phi_2\middle|\Phi_4\right) \cong -\frac{t^{B}_{H\rightarrow L}}{N^{AB}_{el}} S^{AB}_{LL} \\
S_{23} &\equiv \left(\Phi_2\middle|\Phi_3\right) \cong +\frac{t^{B}_{H\rightarrow L}}{N^{AB}_{el}} S^{AB}_{HH} \\
S_{34} &\equiv \left(\Phi_3\middle|\Phi_4\right) \cong -\frac{1}{N^{AB}_{el}} S^{AB}_{HH} S^{AB}_{LL}
\end{aligned}
$$

where the overlap between molecular orbitals U and W is given by

$$S^{AB}_{UW} \equiv \mathbf{s}^{AB} : \mathbf{c}^{A}_{U} \otimes \mathbf{c}^{B}_{W}$$

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

$$V \approx V^{\text{Direct}} + V^{\text{Inirect}}$$

where the overlap-corrected direct and indirect coupling constants are

$$
\begin{aligned}
V^{\text{Direct}} &= V^{\text{Coul}} + V^{\text{Exch}} + V^{\text{Ovrl}} \\
V^{\text{Indirect}} &= V^{\text{TI}-2} + V^{\text{TI}-3}
\end{aligned}
$$

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:

$$
F^{AB}_{\alpha\in A,\beta\in B} \approx T_{\alpha\beta} + V^{A(\mathrm{nuc})}_{\alpha\beta} + V^{B(\mathrm{nuc})}_{\alpha\beta} + \sum_{\mu\nu\in A} P^{A(g)}_{\nu\mu} G_{\alpha\beta,\mu\nu} + \sum_{\sigma\lambda\in B} P^{B(g)}_{\lambda\sigma} G_{\alpha\beta,\sigma\lambda}
$$

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 ERIs of type (AB,AB). It is instructive to approximate these contributions in terms of the Coulomb-like ERIs for the sake of testing of OEP-based approximations which are given in the next Section.

Application of the Mulliken 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

$$
\begin{aligned}
V^{\mathrm{Exch},(0)} &\approx -\frac{1}{8} \sum_{\mu\nu\in A} \sum_{\lambda\sigma\in B} P^{g\rightarrow e(A)}_{\nu\mu} P^{g\rightarrow e(B)}_{\lambda\sigma} S_{\mu\lambda} S_{\sigma\nu} \left[(\mu\mu|\sigma\sigma) + (\lambda\lambda|\nu\nu) + (\mu\mu|\nu\nu) + (\lambda\lambda|\sigma\sigma)\right] \\
V^{\mathrm{CT},(0)} &\approx \frac{1}{2} S^{AB}_{HL} S^{AB}_{LH} \left[r^A_{HL} + r^B_{HL} + \rho^A_H \odot \rho^B_H + \rho^A_L \odot \rho^B_L \right] \\
&\quad - \frac{1}{4} S^{AB}_{HH} S^{AB}_{LL} \left[r^A_{HL} + r^B_{HL} + \rho^A_H \odot \rho^B_L + \rho^A_L \odot \rho^B_H \right]
\end{aligned}
$$

The former can be rewritten in a more convenient to implement formula:

$$
\begin{aligned}
V^{\mathrm{Exch},(0)} \approx -\frac{1}{4} \sum_{\mu\in A} \sum_{\nu\in B} (\mu\mu|\sigma\sigma) [\mathbf{P}^A \mathbf{s}^{AB}]_{\mu\sigma} [\mathbf{P}^B \mathbf{s}^{BA}]_{\sigma\mu} - \frac{1}{8} \sum_{\mu\nu\in A} P^A_{\nu\mu} (\mu\mu|\nu\nu) [\mathbf{s}^{AB} \mathbf{P}^B \mathbf{s}^{BA}]_{\mu\nu} \\
- \frac{1}{8} \sum_{\sigma\lambda\in B} P^B_{\lambda\sigma} (\lambda\lambda|\sigma\sigma) [\mathbf{s}^{BA} \mathbf{P}^A \mathbf{s}^{AB}]_{\sigma\lambda}
\end{aligned}
$$

In the CT term,

$$r_{HL}^{A} \equiv \rho_H^A \odot \rho_L^A$$
$$r_{HL}^{B} \equiv \rho_H^B \odot \rho_L^B$$

where the effective Coulombic interaction energies are defined by

$$\rho_U^A \odot \rho_W^B \equiv \left(U^A U^A \middle| W^A W^A\right)$$

OEP-Based Methods

OEP method of interfragment ERI elimination applied to the direct Coulombic coupling yields the TrCAMM coupling. Direct exchange coupling requires using the Mulliken approximation. The TI contributions can be treated after certain fragmentation of the Fock operator of a dimer is assumed. In that case, OEP method yields the complete TI/CIS model. Błasiak et al. [2020b]

OEP-Based TI/CIS theory

Application of the OEP method yields the following expressions for the off-diagonal Hamiltonian matrix elements:

$$V^{\mathrm{ET1},(0)} = t_{H\to L}^{A} \left\{ \sum_{\zeta\in A} S_{\zeta L}^{AB} V_{\zeta;\mathrm{HL}}^{A;\mathrm{ET}} + \sum_{\eta\in B} S_{\eta L}^{BA} V_{\eta;\mathrm{L}}^{B;\mathrm{ET}} \right\}$$
$$V^{\mathrm{ET2},(0)} = t_{H\to L}^{B} \left\{ \sum_{\zeta\in A} S_{\zeta L}^{AB} V_{\zeta;\mathrm{L}}^{A;\mathrm{ET}} + \sum_{\eta\in B} S_{\eta L}^{BA} V_{\eta;\mathrm{HL}}^{B;\mathrm{ET}} \right\}$$
$$V^{\mathrm{HT1},(0)} = t_{H\to L}^{A} \left\{ \sum_{\zeta\in A} S_{\zeta H}^{AB} V_{\zeta;\mathrm{HL}}^{A;\mathrm{HT}} + \sum_{\eta\in B} S_{\eta H}^{BA} V_{\eta;\mathrm{H}}^{B;\mathrm{HT}} \right\}$$
$$V^{\mathrm{HT2},(0)} = t_{H\to L}^{B} \left\{ \sum_{\zeta\in A} S_{\zeta H}^{AB} V_{\zeta;\mathrm{H}}^{A;\mathrm{HT}} + \sum_{\eta\in B} S_{\eta H}^{BA} V_{\eta;\mathrm{HL}}^{B;\mathrm{HT}} \right\}$$
$$V^{\mathrm{CT},(0)} = \frac{1}{2} S_{HL}^{AB} S_{LH}^{AB} \left\{ r_{HL}^{A} + r_{HL}^{B} + \frac{1}{|\mathbf{r}_H^A - \mathbf{r}_H^B|} + \sum_{x\in A}\sum_{y\in B} \frac{q_{x;L}^{A} q_{y,L}^{B}}{|\mathbf{r}_x - \mathbf{r}_y|} \right\} - \frac{1}{4} S_{HH}^{AB} S_{LL}^{AB} \left\{ r_{HL}^{A} + r_{HL}^{B} - \sum_{y\in B} \frac{q_{y;L}^{B}}{|\mathbf{r}_H^A - \mathbf{r}_y|} - \sum_{x\in A} \frac{q_{x;L}^{A}}{|\mathbf{r}_H^B - \mathbf{r}_x|} \right\}$$

where the charge centroids are given by $\mathbf{r}_Y^X \equiv \left(Y^X|\hat{\mathbf{r}}|Y^X\right)$. The OEP matrices can be written in a density fitting form utilizing a nearly-complete auxiliary basis set as

$$V_{\zeta;\mathrm{N}}^{X;\mathrm{M}} = \sum_{\eta\in X} \left[\mathbf{S}^{-1}\right]_{\zeta\eta} a_{\eta;\mathrm{N}}^{X;\mathrm{M}}$$

for N = H, L or HL and M = ET1, ET2, HT1 or HT2, respectively. The explicit formulae for the auxiliary vectors **a** are as follows:

$$a^{X;\mathrm{ET}}_{\alpha;\mathrm{L}} = \sum_{\beta} C^X_{\beta L} Q^X_{\alpha\beta}$$

$$a^{X;\mathrm{ET}}_{\alpha;\mathrm{HL}} = a^{X;\mathrm{ET}}_{\alpha;\mathrm{L}} + \sum_{\beta\gamma\delta} (\alpha\beta|\gamma\delta) \left\{ 2C^X_{\beta H} C^X_{\gamma L} - C^X_{\beta L} C^X_{\gamma H} \right\} C^X_{\delta H}$$

$$a^{X;\mathrm{HT}}_{\alpha;\mathrm{H}} = -\sum_{\beta} C^X_{\beta H} Q^X_{\alpha\beta}$$

$$a^{X;\mathrm{HT}}_{\alpha;\mathrm{HL}} = a^{X;\mathrm{HT}}_{\alpha;\mathrm{H}} + \sum_{\beta\gamma\delta} (\alpha\beta|\gamma\delta) \left\{ 2C^X_{\beta L} C^X_{\gamma H} - C^X_{\beta H} C^X_{\gamma L} \right\} C^X_{\delta L}$$

The auxiliary matrix **Q** can be found by inverting the following matrix equation

$$\sum_{\beta} C^X_{\beta Y} Q^X_{\alpha\beta} = \sum_{\beta} C^X_{\beta Y} \left\{ \frac{1}{2} T_{\alpha\beta} + V^X_{\mathrm{nuc};\alpha\beta} \right\} + \sum_{\beta\gamma\delta} (\alpha\beta|\gamma\delta) \left\{ P^{X(g)}_{\delta\gamma} C^X_{\beta Y} - \frac{1}{2} P^{X(g)}_{\beta\gamma} C^X_{\delta Y} \right\}$$

The matrices **C** are the LCAO-MO matrices in primary AO basis.

Direct exchange

Neglecting interfragment ERIs from the Mulliken-approximated direct exchange coupling results in the following expression:

$$V^{\mathrm{Exch},(0)} \approx -\frac{1}{8} \sum_{\mu\nu\in A} P^A_{\nu\mu} (\mu\mu|\nu\nu) [\mathbf{s}^{AB}\mathbf{P}^B\mathbf{s}^{BA}]_{\mu\nu} - \frac{1}{8} \sum_{\sigma\lambda\in B} P^B_{\lambda\sigma} (\lambda\lambda|\sigma\sigma) [\mathbf{s}^{BA}\mathbf{P}^A\mathbf{s}^{AB}]_{\sigma\lambda}$$

which enables implementing it within the EFP methodology. Note that here, the ERIs $(\mu\mu|\nu\nu)$ refer only to one fragment, therefore they consitute a two-index EFP parameters which are relatively inexpensive to handle.

The OEP-based model also approximates the diagonal Hamiltonian matrix elements. The environmental contributions are usually small and are neglected here. The HOMO-LUMO interaction is approximated by using the DMTP approximation. Hence, the diagonal Hamiltonian matrix elements read approximately:

$$\left\langle \Phi_1 \middle| \mathscr{H} - E_0 \middle| \Phi_1 \right\rangle \equiv E_1 \cong E^A_{e\rightarrow g}$$

$$\left\langle \Phi_2 \middle| \mathscr{H} - E_0 \middle| \Phi_2 \right\rangle \equiv E_2 \cong E^B_{e\rightarrow g}$$

$$\left\langle \Phi_3 \middle| \mathscr{H} - E_0 \middle| \Phi_3 \right\rangle \equiv E_3 \cong -\varepsilon^A_H + \varepsilon^B_L - \rho^A_H \odot \rho^B_L$$

$$\left\langle \Phi_4 \middle| \mathscr{H} - E_0 \middle| \Phi_4 \right\rangle \equiv E_4 \cong \varepsilon^A_L - \varepsilon^B_H - \rho^A_L \odot \rho^B_H$$

where the ' $\odot$' symbol is treated via the CAMM expansion, Sokalski and Poirier [1983] or the LMTP expansion Etchebest et al. [1982] truncated on charges.

14.21.2 Member Function Documentation

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.

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.

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

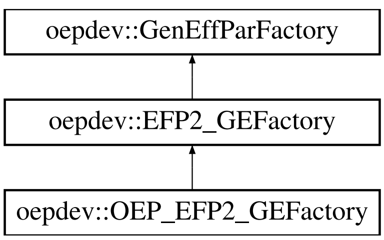
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_coupling_eet.cc

14.22 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

14.22.1 Detailed Description

Basic interface for the EFP2 parameters.

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

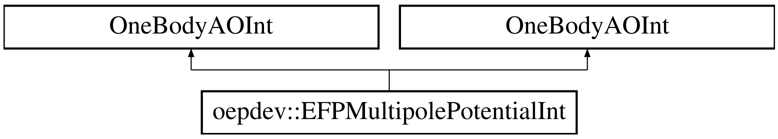
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_efp2.cc

14.23 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:

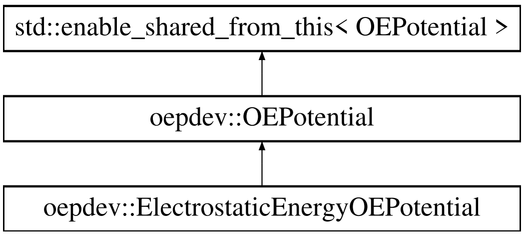
- oepdev/libpsi/bck/multipole_potential.h
- oepdev/libpsi/bck/multipole_potential.cc

14.24 oepdev::ElectrostaticEnergyOEPotential Class Reference

Generalized One-Electron Potential for Electrostatic Energy.

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

Inheritance diagram for 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

14.24.1 Detailed Description

Contains the following OEP types:

- V

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

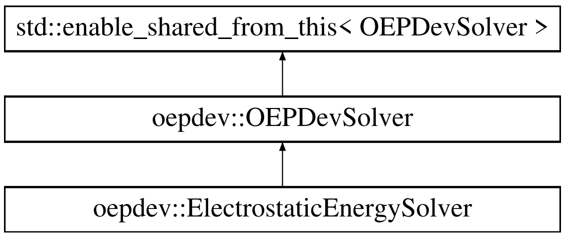
- oepdev/liboep/oep.h
- oepdev/liboep/oep_energy_coul.cc

14.25 oepdev::ElectrostaticEnergySolver Class Reference

Compute the Coulombic interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::ElectrostaticEnergySolver:



Public Member Functions

- **ElectrostaticEnergySolver** (SharedWavefunctionUnion wfn_union)
- virtual double compute_oep_based (const std::string &method="DEFAULT")

  Compute property by using OEPs.
- virtual double compute_benchmark (const std::string &method="DEFAULT")

  Compute property by using benchmark method.

Additional Inherited Members

14.25.1 Detailed Description

The implemented methods are shown in below

Table 14.35: 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

$$E^{\rm Nuc-El} = \sum_{x\in A}\sum_{\lambda\sigma\in B} Z_x V^{(x)}_{\lambda\sigma}\left(D^{(\alpha)}_{\lambda\sigma} + D^{(\beta)}_{\lambda\sigma}\right) + \sum_{y\in B}\sum_{\mu\nu\in A} Z_y V^{(y)}_{\mu\nu}\left(D^{(\alpha)}_{\mu\nu} + D^{(\beta)}_{\mu\nu}\right)$$

and the electron-electron repulsion energy is

$$E^{\rm El-El} = \sum_{\mu\nu\in A}\sum_{\lambda\sigma\in B}\left\{D^{(\alpha)}_{\mu\nu} + D^{(\beta)}_{\mu\nu}\right\}\left\{D^{(\alpha)}_{\lambda\sigma} + D^{(\beta)}_{\lambda\sigma}\right\}(\mu\nu|\lambda\sigma)$$

In the above equations,

$$V^{(x)}_{\lambda\sigma} \equiv \int \frac{\varphi^*_\lambda({\bf r})\varphi_\sigma({\bf r})}{|{\bf r} - {\bf r}_x|}d{\bf r}$$

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

$$E^{\mathrm{Nuc-El}} = 2\sum_{i\in A}\sum_{y\in B} V_{ii}^{(y)} + 2\sum_{j\in B}\sum_{x\in A} V_{jj}^{(x)}$$

and the electron-electron repulsion energy is

$$E^{\mathrm{El-El}} = 4\sum_{i\in A}\sum_{j\in B} (ii|jj)$$

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,

$$E^{\mathrm{Coul}} \approx \frac{1}{2}\left[\sum_{x\in A}\sum_{y\in B}\frac{Z_x q_y}{|\mathbf{r}_x - \mathbf{r}_y|} + \sum_{y\in B}\sum_{\mu\nu\in A} q_y V_{\mu\nu}^{(y)}\left(D_{\mu\nu}^{(\alpha)} + D_{\mu\nu}^{(\beta)}\right)\right.$$
$$\left. + \sum_{y\in B}\sum_{x\in A}\frac{q_x Z_y}{|\mathbf{r}_x - \mathbf{r}_y|} + \sum_{x\in A}\sum_{\lambda\sigma\in B} q_x V_{\lambda\sigma}^{(x)}\left(D_{\lambda\sigma}^{(\alpha)} + D_{\lambda\sigma}^{(\beta)}\right)\right]$$

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,

  $$E^{\mathrm{Coul,ESP}} \approx \sum_{x\in A}\sum_{y\in B}\frac{q_x q_y}{|\mathbf{r}_x - \mathbf{r}_y|}$$

  for reference purposes.
- In order to construct this solver, **always** use the `OEPDevSolver::build` static factory method.

14.25.2 Member Function Documentation

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.

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.

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

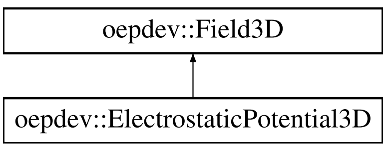
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_energy_coul.cc

14.26 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

14.26.1 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:

$$v(\mathbf{r}) = v_{\rm nuc}(\mathbf{r}) + v_{\rm el}(\mathbf{r})$$

where the nuclear and electronic contributions are defined accordingly as

$$\begin{aligned} v_{\rm nuc}(\mathbf{r}) &= \sum_x \frac{Z_x}{|\mathbf{r} - \mathbf{r}_x|} \\ v_{\rm el}(\mathbf{r}) &= \sum_{\mu\nu} \left\{ D_{\mu\nu}^{(\alpha)} + D_{\mu\nu}^{(\beta)} \right\} V_{\nu\mu}(\mathbf{r}) \end{aligned}$$

In the above equations, Z_x denotes the charge of xth nucleus, $D_{\mu\nu}^{(\omega)}$ is the one-particle (relaxed) density matrix element in AO basis associated with the ω 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:

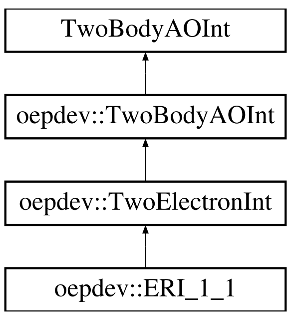
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

14.27 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)

14.27.1 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.

14.27.2 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:

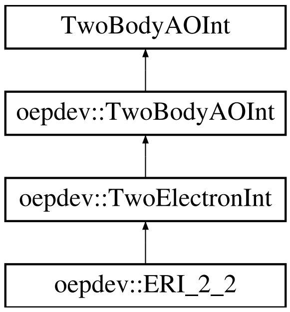
- oepdev/libints/eri.h
- oepdev/libints/eri.cc

14.28 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)

14.28.1 Detailed Description

ERI's are computed for a shell quartet (PQ|RS) and stored in the `target_full_` buffer, accessible through `buffer()` method:

$$\begin{aligned}
&\text{For each } (n_1,l_1,m_1) \in P:\\
&\quad\text{For each } (n_2,l_2,m_2) \in Q:\\
&\quad\quad\text{For each } (n_3,l_3,m_3) \in R:\\
&\quad\quad\quad\text{For each } (n_4,l_4,m_4) \in S:\\
&\quad\quad\quad\quad \mathrm{ERI} = (AB|CD)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}]
\end{aligned}$$

For detailed description of the McMurchie-Davidson scheme, refer to The Integral Package Library.

14.28.2 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

$$\begin{aligned}
(ij|kl)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}] &= E_{ij}(\alpha_1,\alpha_2)E_{kl}(\alpha_3,\alpha_4)\\
&\times \sum_{N_1=0}^{n_1+n_2}\sum_{L_1=0}^{l_1+l_2}\sum_{M_1=0}^{m_1+m_2}\sum_{N_2=0}^{n_3+n_4}\sum_{L_2=0}^{l_3+l_4}\sum_{M_2=0}^{m_3+m_4} d_{N_1}^{n_1n_2}d_{L_1}^{l_1l_2}d_{M_1}^{m_1m_2}d_{N_2}^{n_3n_4}d_{L_2}^{l_3l_4}d_{M_2}^{m_3m_4}[N_1L_1M_1|N_2L_2M_2]
\end{aligned}$$

In the above equation, the multiplicative constants are given as

$$\begin{aligned}
E_{ij}(\alpha_1,\alpha_2) &= \exp\left[-\frac{\alpha_1\alpha_2}{\alpha_1+\alpha_2}|\mathbf{A}-\mathbf{B}|^2\right]\\
E_{kl}(\alpha_3,\alpha_4) &= \exp\left[-\frac{\alpha_3\alpha_4}{\alpha_3+\alpha_4}|\mathbf{C}-\mathbf{D}|^2\right]
\end{aligned}$$

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

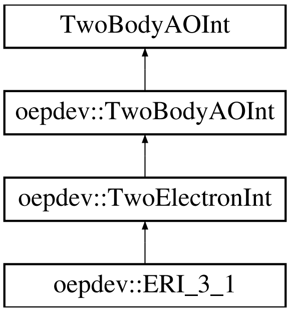
- oepdev/libints/eri.h
- oepdev/libints/eri.cc

14.29 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)

14.29.1 Detailed Description

ERI's are computed for a shell quartet (PQR|S) and stored in the `target_full_` buffer, accessible through `buffer()` method:

$$\begin{aligned}
&\text{For each } (n_1,l_1,m_1) \in P: \\
&\quad \text{For each } (n_2,l_2,m_2) \in Q: \\
&\quad\quad \text{For each } (n_3,l_3,m_3) \in R: \\
&\quad\quad\quad \text{For each } (n_4,l_4,m_4) \in S: \\
&\quad\quad\quad\quad \mathrm{ERI} = (ABC|D)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}]
\end{aligned}$$

For detailed description of the McMurchie-Davidson scheme, refer to The Integral Package Library.

14.29.2 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

14.30 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.

14.30.1 Detailed Description

Solves the least-squares problem to fit the generalized charges $q_{m;p}$, that reproduce the reference generalized potential $v_p^{\rm ref}(\mathbf{r})$ supplied by the `Field3D` object:

$$\int d\mathbf{r}' \left[v_p^{\rm ref}(\mathbf{r}') - \sum_m \frac{q_{m;p}}{|\mathbf{r}' - \mathbf{r}_m|} \right]^2 \rightarrow \text{minimize}$$

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

$$\begin{pmatrix} \mathbf{A} & 1 \\ 1 & 0 \end{pmatrix}^{-1} \cdot \begin{pmatrix} \mathbf{b}_p \\ Q_p \end{pmatrix} = \begin{pmatrix} \mathbf{q}_p \\ \lambda \end{pmatrix}$$

where the $\mathbf{A}$ matrix of dimension $(M+1) \times (M+1)$ and $\mathbf{b}_p$ vector or length $M+1$ are given as

$$A_{mn} = \sum_i \frac{1}{r_{im} r_{in}}$$

$$b_{m;p} = \sum_i \frac{v_p^{\rm ref}(\mathbf{r}_m)}{r_{im}}$$

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, $p_{\max}$). 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.]

14.30.2 Constructor & Destructor Documentation

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

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:

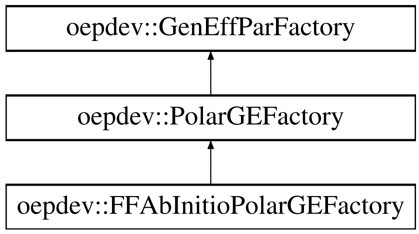
- oepdev/lib3d/esp.h
- oepdev/lib3d/esp.cc

14.31 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

14.31.1 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:

$$\delta D_{\alpha\beta} = \mathbf{B}^{(1)}_{\alpha\beta} \cdot \mathbf{F} + \mathbf{B}^{(2)}_{\alpha\beta} : \mathbf{F} \otimes \mathbf{F}$$

where $\mathbf{B}^{(1)}_{\alpha\beta}$ is the density matrix dipole polarizability defined as

$$\mathbf{B}^{(1)}_{\alpha\beta} = \frac{\partial D_{\alpha\beta}}{\partial \mathbf{F}}\bigg|_{\mathbf{F}=\mathbf{0}}$$

whereas $\mathbf{B}^{(2)}_{\alpha\beta}$ is the density matrix dipole-dipole hyperpolarizability,

$$\mathbf{B}^{(2)}_{\alpha\beta} = \frac{1}{2}\frac{\partial^2 D_{\alpha\beta}}{\partial \mathbf{F} \otimes \partial \mathbf{F}}\bigg|_{\mathbf{F}=\mathbf{0}}$$

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:

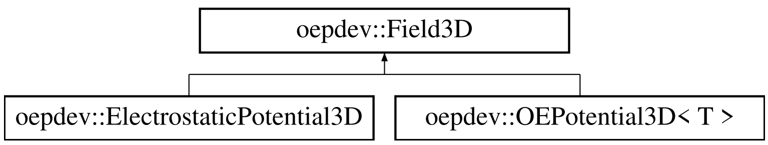
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_ffabinitio.cc

14.32 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?

14.32.1 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`

14.32.2 Constructor & Destructor Documentation

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);

14.32.3 Member Function Documentation

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

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

14.33 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**

14.33.1 Detailed Description

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

- oepdev/libutil/unitary_optimizer.h

14.34 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**

14.34.1 Detailed Description

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

- oepdev/libutil/unitary_optimizer.h

14.35 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.

14.35.1 Detailed Description

Implements interface of running fragment-based calculations on molecular systems defined in terms of independent but interacting fragments.

14.35.2 Member Function Documentation

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.

set_geometry()

```
void oepdev::FragmentedSystem::set_geometry (
            std::vector< psi::SharedMolecule > aggregate ) [inline]
```

Parameters

aggregate	- list of all molecules in the system

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.

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.

compute_energy()

```
double oepdev::FragmentedSystem::compute_energy (
          std::string theory )
```

Parameters

theory	- theory to use for calculations

Returns

energy in a.u.

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.

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

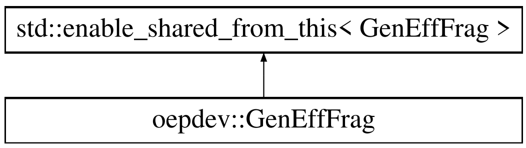
- oepdev/libgefp/gefp.h
- oepdev/libgefp/fragmented_system.cc

14.36 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.

14.36.1 Detailed Description

Describes the GEFP fragment that is in principle designed to work at correlated levels of theory.

See also

GenEffPar, GenEffParFactory

14.36.2 Member Function Documentation

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

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

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

Parameters

fieldGradientRank	- power dependency with respect to the electric field gradient

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.]

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.]

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.]

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.]

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

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

14.37 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.

14.37.1 Detailed Description

See also

GenEffFrag, GenEffParFactory

14.37.2 Member Function Documentation

rotate()

```
void oepdev::GenEffPar::rotate (
            psi::SharedMatrix R )
```

Parameters

R	- the rotation matrix

translate()

```
void oepdev::GenEffPar::translate (
            psi::SharedVector t )
```

Parameters

t	- the translation vector

superimpose()

```
void oepdev::GenEffPar::superimpose (
            psi::SharedMatrix targetXYZ,
            std::vector< int > supList )
```

Parameters

targetXYZ	- the target geometry
suplist	- the superimposition list

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_`.

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_`.

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_`.

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_`.

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_`.

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_`.

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 $\nabla \otimes \mathbf{F}$

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 $\nabla \otimes \mathbf{F}$

vector()

```
psi::SharedVector oepdev::GenEffPar::vector (
          std::string key ) const [inline]
```

Parameters

key	- keyword for a vector

Returns

vector data type

matrix()

```
psi::SharedMatrix oepdev::GenEffPar::matrix (
          std::string key ) const  [inline]
```

Parameters

key	- keyword for a matrix

Returns

matrix data type

dmtp()

```
std::shared_ptr<oepdev::DMTPole> oepdev::GenEffPar::dmtp (
          std::string key ) const  [inline]
```

Parameters

key	- keyword for a DMTP

Returns

DMTP data type

oep()

```
oepdev::SharedOEPotential oepdev::GenEffPar::oep (
          std::string key ) const  [inline]
```

Parameters

key	- keyword for a OEP

Returns

OEP data type

dpol()

```
std::vector<psi::SharedMatrix> oepdev::GenEffPar::dpol (
          std::string key ) const [inline]
```

Parameters

key	- keyword for a DPOL

Returns

DPOL data type

basisset()

```
psi::SharedBasisSet oepdev::GenEffPar::basisset (
          std::string key ) const [inline]
```

Parameters

key	- keyword for a basis set

Returns

basis set data type

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

Parameters

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.

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).

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 $\nabla \otimes \mathbf{F}$

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.)

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.)

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

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

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

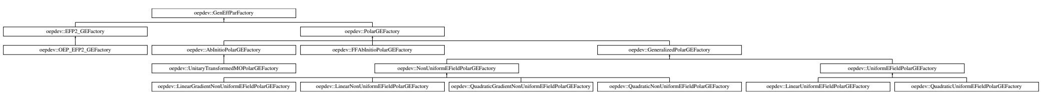
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp.cc

14.38 oepdev::GenEffParFactory Class Reference

Generalized Effective Fragment Factory. Abstract Base.

`#include <gefp.h>`

Inheritance diagram for oepdev::GenEffParFactory:



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?

14.38.1 Detailed Description

Describes the GEFP fragment that is in principle designed to work at correlated levels of theory.

See also

GenEffPar, GenEffFrag

14.38.2 Member Function Documentation

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`

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:

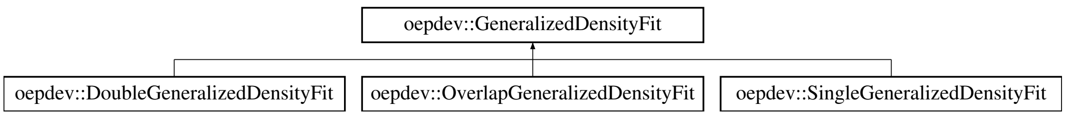
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp.cc

14.39 oepdev::GeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme. Abstract Base.

`#include <oep_gdf.h>`

Inheritance diagram for oepdev::GeneralizedDensityFit:



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.

14.39.1 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.

14.39.2 Member Function Documentation

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.

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.

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.

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:

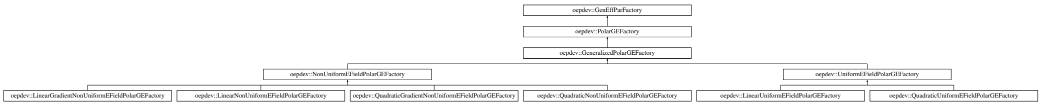
- oepdev/liboep/oep_gdf.h
- oepdev/liboep/oep_gdf.cc

14.40 oepdev::GeneralizedPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

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

Inheritance diagram for oepdev::GeneralizedPolarGEFactory:



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 > > > electricFieldGradientSumSet_

  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

14.40.1 Detailed Description

Implements a general class of methods for the density matrix susceptibility tensors represented by:

$$\delta D_{\alpha\beta} = \sum_i \left\{ \mathbf{B}^{(10)}_{i;\alpha\beta} \cdot \mathbf{F}(\mathbf{r}_i) + \mathbf{B}^{(20)}_{i;\alpha\beta} : \mathbf{F}(\mathbf{r}_i) \otimes \mathbf{F}(\mathbf{r}_i) + \mathbf{B}^{(01)}_{i;\alpha\beta} : \nabla_i \otimes \mathbf{F}(\mathbf{r}_i) + \dots \right\}$$

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
- $\mathbf{B}^{(01)}_{i;\alpha\beta}$ 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 $N_{\rm max}$ 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, $\mathbf{s} = \begin{pmatrix}\mathbf{s}^{[1]} & \mathbf{s}^{[2]} & \cdots\end{pmatrix}^{\rm T}$, a loss function Z that is subject to the least-squares minimization, is defined as

$$Z(\mathbf{s}) = \sum_N^{N_{\rm max}} \left(\delta D^{(N)} - \delta\overline{D}^{(N)}\right)^2 .$$

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

14.41 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.

14.41.1 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

$$\hat{P}_{\mathbf{u}} = \frac{1}{u^2} \mathbf{u} [\Box \cdot \mathbf{u}]$$

14.41.2 Constructor & Destructor Documentation

GramSchmidt() [1/2]

```
oepdev::GramSchmidt::GramSchmidt ( )
```

GramSchmidt() [2/2]

```
oepdev::GramSchmidt::GramSchmidt (
          std::vector< psi::SharedVector > vectors )
```

Parameters

vectors	- list of vectors to be orthogonalized.

14.41.3 Member Function Documentation

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:

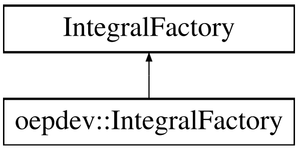
- oepdev/libutil/gram_schmidt.h
- oepdev/libutil/gram_schmidt.cc

14.42 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.

14.42.1 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

14.43 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 $\mathbf{X}_0$.

14.43.1 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

$$\mathbf{A} = \left[\mathbf{X} - \langle \mathbf{X} \rangle\right]^{\mathrm{T}} \cdot \left[\mathbf{X}_0 - \langle \mathbf{X}_0 \rangle\right]$$

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

$$\mathbf{t} = \langle \mathbf{X}_0 \rangle - \langle \mathbf{X} \rangle \cdot \mathbf{r}$$

14.43.2 Member Function Documentation

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 $\mathbf{X}_0$

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:

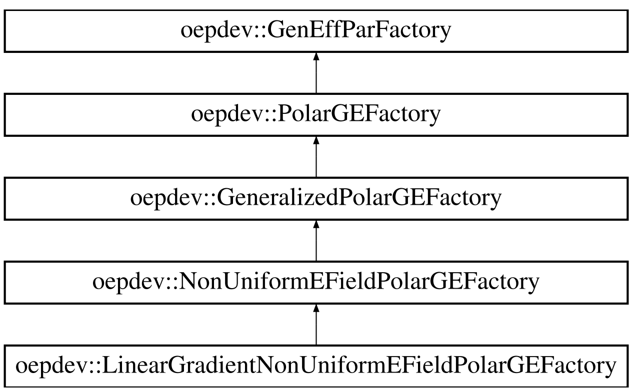
- oepdev/libutil/kabsch_superimposer.h
- oepdev/libutil/kabsch_superimposer.cc

14.44 oepdev::LinearGradientNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for 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

14.44.1 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:

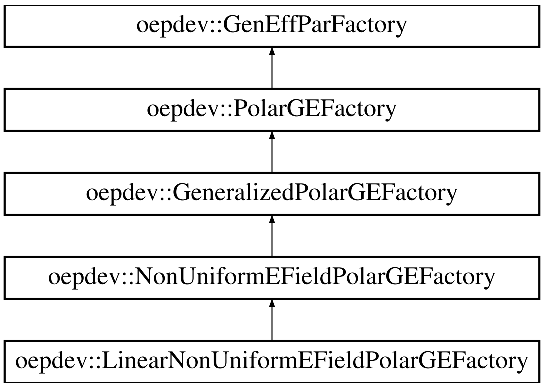
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_1_grad_1.cc

14.45 oepdev::LinearNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for 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

14.45.1 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:

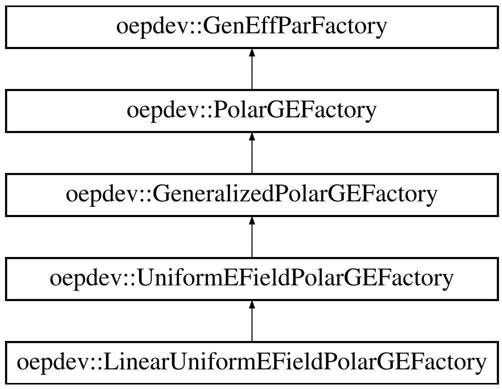
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_1.cc

14.46 oepdev::LinearUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

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

Inheritance diagram for 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

14.46.1 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

14.47 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.

14.47.1 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

14.47.2 Member Enumeration Documentation

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

Property

`enum oepdev::MultipoleConvergence::Property`

Property to be evaluated from DMTP's:

Parameters

Energy	- generalized energy
Field	- generalized field
Potential	- generalized potential

14.47.3 Constructor & Destructor Documentation

MultipoleConvergence()

```
oepdev::MultipoleConvergence::MultipoleConvergence (
            std::shared_ptr< DMTPole > dmtp1,
            std::shared_ptr< DMTPole > dmtp2,
            MultipoleConvergence::ConvergenceLevel max_clevel = R5 )
```

Parameters

dmtp1	- first DMTPole object
dmtp2	- second DMTPole object
max_clevel	- maximul allowed convergence level

14.47.4 Member Function Documentation

compute() [1/2]

```
void oepdev::MultipoleConvergence::compute (
            MultipoleConvergence::Property property = Energy )
```

Compute the generalized interaction property

Parameters

property	- generalized Property

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

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:

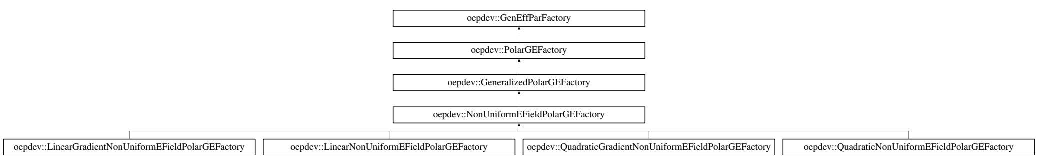
- oepdev/lib3d/dmtp.h
- oepdev/lib3d/dmtp_base.cc

14.48 oepdev::NonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

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

Inheritance diagram for oepdev::NonUniformEFieldPolarGEFactory:



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

14.48.1 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

14.49 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_**

14.49.1 Constructor & Destructor Documentation

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:

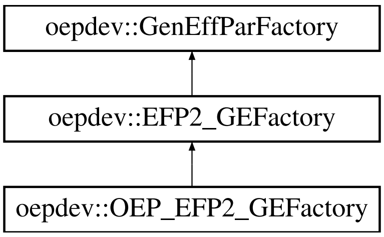
- oepdev/libpsi/osrecur.h
- oepdev/libpsi/osrecur.cc

14.50 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

14.50.1 Detailed Description

Basic interface for the OEP-EFP2 parameters.

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

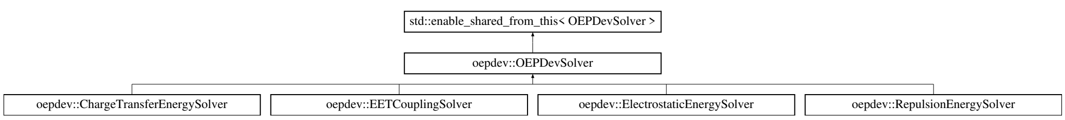
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_oep_efp2.cc

14.51 oepdev::OEPDevSolver Class Reference

Solver of properties of molecular aggregates. Abstract base.

```
#include <solver.h>
```

Inheritance diagram for oepdev::OEPDevSolver:



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 OEPs.
- 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.

14.51.1 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 14.95: Environmental variables in the OEPDev solver.

Keyword	Description
Coulombic Interaction Energy	
Distributed Multipole Series	
`EINT COUL CAMM R-1`	CAMM charge-charge terms
`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

Keyword	Description
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
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

Keyword	Description
`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	
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)

Keyword	Description
`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)
`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)

Keyword	Description
`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 ERIs; 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)
`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)

Keyword	Description
`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)

14.51.2 Constructor & Destructor Documentation

OEPDevSolver()

```
OEPDevSolver::OEPDevSolver (
        SharedWavefunctionUnion wfn_union )
```

Parameters

wfn_union	- wavefunction union of isolated molecular wavefunctions

14.51.3 Member Function Documentation

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

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::RepulsionEnergyS
and oepdev::ElectrostaticEnergySolver.

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::RepulsionEnergyS
and oepdev::ElectrostaticEnergySolver.

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

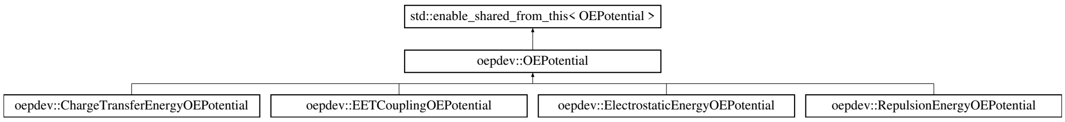
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_base.cc

14.52 oepdev::OEPotential Class Reference

Generalized One-Electron Potential: Abstract base.

`#include <oep.h>`

Inheritance diagram for oepdev::OEPotential:



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 &oepType)

  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)

14.52.1 Detailed Description

Manages OEP's in matrix and 3D forms. Available OEP categories:

- `ELECTROSTATIC ENERGY`
- `REPULSION ENERGY`
- `CHARGE TRANSFER ENERGY`
- `EET COUPLING CONSTANT`

14.52.2 Constructor & Destructor Documentation

OEPotential() [1/2]

```
OEPotential::OEPotential (
          SharedWavefunction wfn,
          Options & options )
```

Parameters

wfn	- wavefunction
options	- Psi4 options

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

14.52.3 Member Function Documentation

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

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

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:

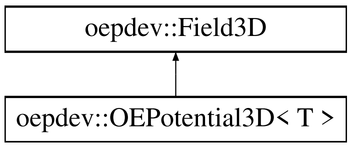
- oepdev/liboep/oep.h
- oepdev/liboep/oep_base.cc

14.53 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

14.53.1 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

14.54 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:

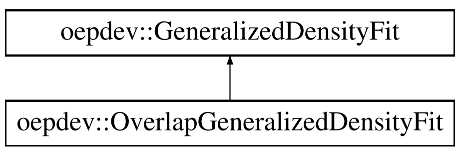
- oepdev/liboep/oep.h
- oepdev/liboep/oep_base.cc

14.55 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:



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

14.55.1 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.

14.55.2 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

$$\mathbf{G}_{\rm i} = \mathbf{S}^{-1}_{\rm ii} \cdot \mathbf{V}_{\rm i}$$

See density fitting of OEPs for more details regarding the matrices involved in the above expressions.

14.55.3 Member Function Documentation

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

14.56 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.

14.56.1 Detailed Description

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

- oepdev/libutil/scf_perturb.h

14.57 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:

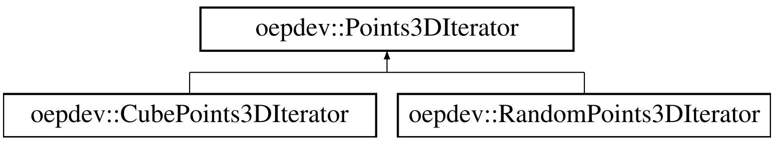
- oepdev/lib3d/space3d.h

14.58 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_**

14.58.1 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.

14.58.2 Constructor & Destructor Documentation

Points3DIterator()

```
oepdev::Points3DIterator::Points3DIterator (
        const int & np )
```

Parameters

np	- number of points this iterator is constructed for

14.58.3 Member Function Documentation

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

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

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:

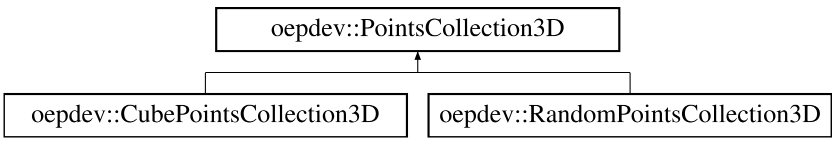
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

14.59 oepdev::PointsCollection3D Class Reference

Collection of points in 3D space. Abstract base.

`#include <space3d.h>`

Inheritance diagram for oepdev::PointsCollection3D:



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

14.59.1 Detailed Description

Create random or ordered (g09 cube-like) collections of points in 3D space.

Note: Always create instances by using static factory methods.

14.59.2 Constructor & Destructor Documentation

PointsCollection3D()

```
oepdev::PointsCollection3D::PointsCollection3D (
          Collection collectionType,
          int & np )
```

Parameters

np	- number of points to be created

14.59.3 Member Function Documentation

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

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

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
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:

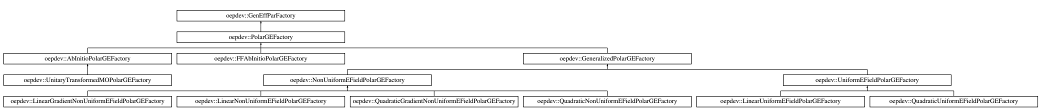
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

14.60 oepdev::PolarGEFactory Class Reference

Polarization GEFP Factory. Abstract Base.

`#include <gefp.h>`

Inheritance diagram for oepdev::PolarGEFactory:



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

14.60.1 Detailed Description

Basic interface for the polarization density matrix susceptibility parameters.

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

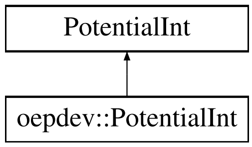
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_base.cc

14.61 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.

14.61.1 Constructor & Destructor Documentation

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

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

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

14.61.2 Member Function Documentation

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:

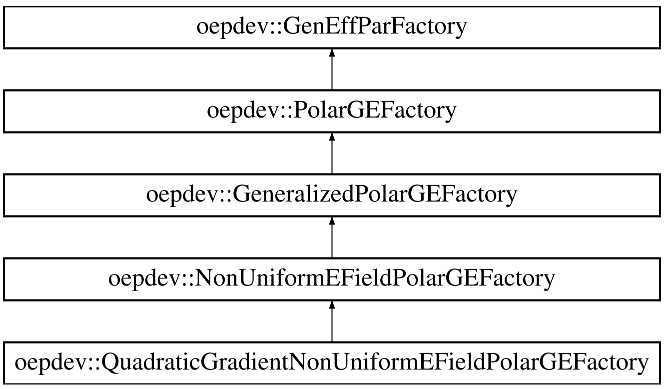
- oepdev/libpsi/potential.h
- oepdev/libpsi/potential.cc

14.62 oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

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

Inheritance diagram for 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

14.62.1 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:

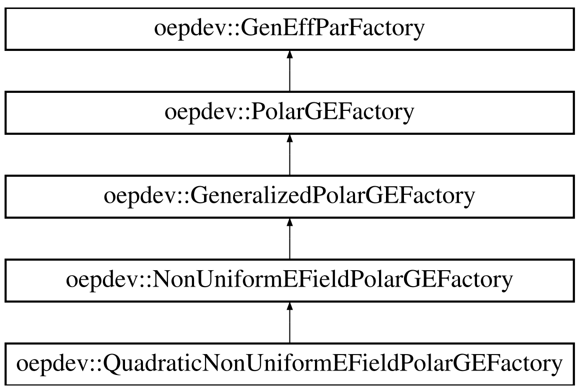
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_2_grad_1.cc

14.63 oepdev::QuadraticNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

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

Inheritance diagram for 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

14.63.1 Detailed Description

Implements the generalized density matrix susceptibility model of the form

$$\delta D_{\alpha\beta} \approx \sum_i \left\{ \mathbf{B}_{i;\alpha\beta}^{(10)} \cdot \mathbf{F}(\mathbf{r}_i) + \mathbf{B}_{i;\alpha\beta}^{(20)} : \mathbf{F}(\mathbf{r}_i) \otimes \mathbf{F}(\mathbf{r}_i) \right\}$$

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 all defined for the distributed site at $\mathbf{r}_i$.

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

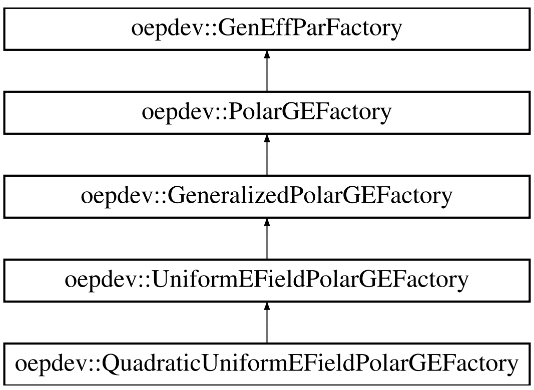
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_2.cc

14.64 oepdev::QuadraticUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

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

Inheritance diagram for 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

14.64.1 Detailed Description

Implements the generalized density matrix susceptibility model of the form

$$\delta D_{\alpha\beta} \approx \mathbf{B}_{\alpha\beta}^{(10)} \cdot \mathbf{F} + \mathbf{B}_{\alpha\beta}^{(20)} : \mathbf{F} \otimes \mathbf{F}$$

where:

- $\mathbf{B}_{\alpha\beta}^{(10)}$ is the density matrix dipole polarizability
- $\mathbf{B}_{\alpha\beta}^{(20)}$ 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

14.65 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.

14.65.1 Detailed Description

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

14.66 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.

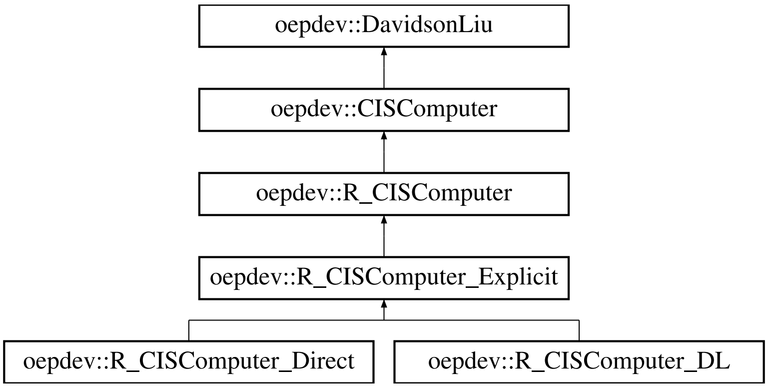
14.66.1 Detailed Description

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

- oepdev/libutil/quambo.h

14.67 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)

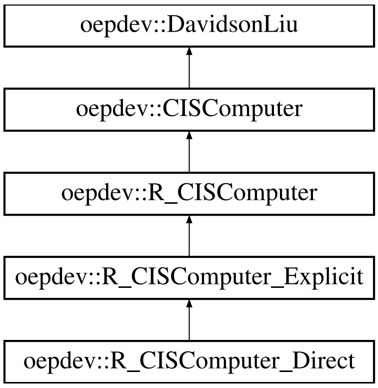
Additional Inherited Members

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

- oepdev/libutil/cis.h
- oepdev/libutil/cis_rhf.cc

14.68 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:

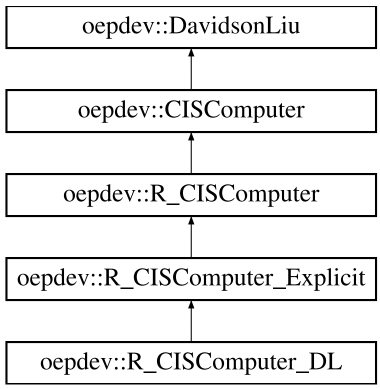
- oepdev/libutil/cis.h
- oepdev/libutil/cis_rhf_direct.cc

14.69 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

14.69.1 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

$$T_{\gamma\delta}^{(k)} = \sum_{jb} C_{\delta b} b_j^{b,k} C_{\gamma j}$$
$$\overline{T}_{\gamma\delta}^{(k)} = \sum_{\bar{j}\bar{b}} C_{\delta \bar{b}} b_{\bar{j}}^{\bar{b},k} C_{\gamma \bar{j}}$$

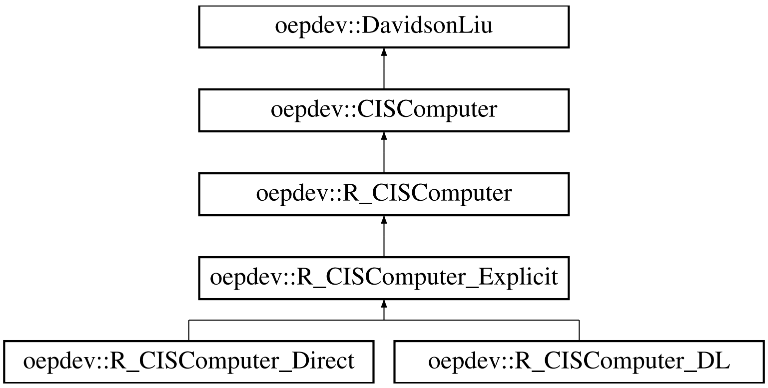
The **J** and **K** matrices in AO basis are computed by using the `psi::JK` object, and subsequently transformed to CMO's.

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

- oepdev/libutil/cis.h
- oepdev/libutil/cis_rhf_dl.cc

14.70 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:

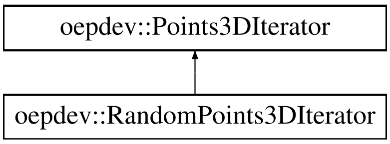
- oepdev/libutil/cis.h
- oepdev/libutil/cis_rhf_explicit.cc

14.71 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

14.71.1 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:

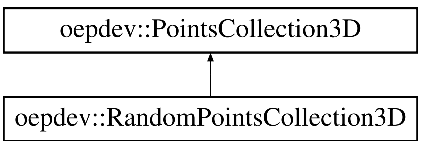
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

14.72 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

14.72.1 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:

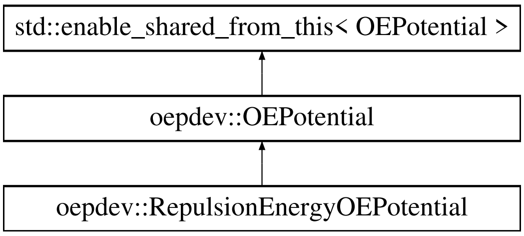
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

14.73 oepdev::RepulsionEnergyOEPotential Class Reference

Generalized One-Electron Potential for Pauli Repulsion Energy.

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

Inheritance diagram for 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

14.73.1 Detailed Description

Contains the following OEP types:

- `Murrell-etal.S1`
- `Otto-Ladik.S2`

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

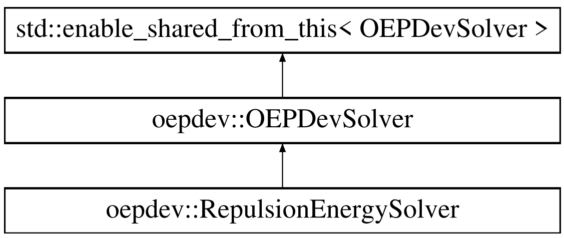
- oepdev/liboep/oep.h
- oepdev/liboep/oep_energy_pauli.cc

14.74 oepdev::RepulsionEnergySolver Class Reference

Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.

```
#include <solver.h>
```

Inheritance diagram for oepdev::RepulsionEnergySolver:



Public Member Functions

- **RepulsionEnergySolver** (SharedWavefunctionUnion wfn_union)
- virtual double compute_oep_based (const std::string &method="DEFAULT")

  Compute property by using OEPs.
- virtual double compute_benchmark (const std::string &method="DEFAULT")

  Compute property by using benchmark method.

Additional Inherited Members

14.74.1 Detailed Description

The implemented methods are shown below

Table 14.118: 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 (ERIs) 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

$$E^{\rm Rep} = 2\sum_{kl}\left(V_{kl}^A + V_{kl}^B + T_{kl}\right)\left[[\mathbf{S}^{-1}]_{lk} - \delta_{lk}\right] + \sum_{klmn}(kl|mn)\left\{2[\mathbf{S}^{-1}]_{kl}[\mathbf{S}^{-1}]_{mn} - [\mathbf{S}^{-1}]_{kn}[\mathbf{S}^{-1}]_{lm} - 2\delta_{kl}\delta_{mn} + \delta_{kn}\delta_{lm}\right\}$$

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

$$E^{\rm Rep,Kin} = 2 \sum_{\alpha\beta\in A,B} \Delta D^{\rm Pauli}_{\alpha\beta} T_{\alpha\beta}$$
$$E^{\rm Rep,Nuc} = 2 \sum_{\alpha\beta\in A,B} \Delta D^{\rm Pauli}_{\alpha\beta} \sum_{z\in A,B} V^{(z)}_{\alpha\beta}$$

whereas the electron-deformation and deformation-deformation interaction contributions are

$$E^{\rm Rep,el-\Delta} = 4 \sum_{\alpha\beta\gamma\delta\in A,B} \Delta D^{\rm Pauli}_{\alpha\beta} D_{\gamma\delta} (\alpha\beta|\gamma\delta)$$
$$E^{\rm Rep,\Delta-\Delta} = 2 \sum_{\alpha\beta\gamma\delta\in A,B} \Delta D^{\rm Pauli}_{\alpha\beta} \Delta D^{\rm Pauli}_{\gamma\delta} (\alpha\beta|\gamma\delta)$$

The associated exchange energy is given by

$$E^{\rm Ex} = - \sum_{\alpha\beta\gamma\delta\in A,B} \left[D^{oo}_{\alpha\delta} D^{oo}_{\beta\gamma} - D^{A}_{\alpha\delta} D^{A}_{\beta\gamma} - D^{B}_{\alpha\delta} D^{B}_{\beta\gamma} \right] (\alpha\beta|\gamma\delta)$$

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, $E^{\rm Ex-Rep}$. 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

$$E^{\rm Rep} = E^{\rm Rep}(\mathscr{O}(S)) + E^{\rm Rep}(\mathscr{O}(S^2))$$

where the first-order term is

$$E^{\rm Rep}(\mathscr{O}(S)) = -2 \sum_{a\in A} \sum_{b\in B} S_{ab} \left\{ V^A_{ab} + \sum_{c\in A} \left[2(ab|cc) - (ac|bc) \right] + V^B_{ab} + \sum_{d\in B} \left[2(ab|dd) - (ad|bd) \right] \right\}$$

whereas the second-order term is

$$E^{\rm Rep}(\mathscr{O}(S^2)) = 2 \sum_{a\in A} \sum_{b\in B} S_{ab} \left\{ \sum_{c\in A} S_{bc} \left[V^B_{ac} + 2 \sum_{d\in B} (ac|dd) \right] + \sum_{d\in B} S_{ad} \left[V^A_{bd} + 2 \sum_{x\in A} (bd|cc) \right] \right.$$
$$\left. - \sum_{c\in A} \sum_{d\in B} S_{cd} (ac|bd) \right\}$$

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

$$E^{\rm Rep} = E^{\rm Rep}(\mathscr{O}(S)) + E^{\rm Rep}(\mathscr{O}(S^2))$$

where the first-order term is

$$E^{\rm Rep}(\mathscr{O}(S)) = -2\sum_{a\in A}\sum_{b\in B} S_{ab}\left\{V_{ab}^A + 2\sum_{c\in A}(ab|cc) - (ab|aa) + V_{ab}^B + 2\sum_{d\in B}(ab|dd) - (ab|bb)\right\}$$

whereas the second-order term is

$$E^{\rm Rep}(\mathscr{O}(S^2)) = 2\sum_{a\in A}\sum_{b\in B} S_{ab}^2\left\{V_{aa}^B + V_{bb}^A + 2\sum_{c\in A}(cc|bb) + 2\sum_{d\in B}(aa|dd) - (aa|bb)\right\}$$

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

$$E^{\rm Rep} = E^{\rm Rep}(\mathscr{O}(S)) + E^{\rm Rep}(\mathscr{O}(S^2))$$

where the first-order term is

$$E^{\rm Rep}(\mathscr{O}(S)) = -2\sum_{a\in A}\sum_{b\in B} S_{ab}\left\{\sum_{c\in A} F_{ac}^A S_{cb} + \sum_{d\in B} F_{bd}^B S_{da} - 2T_{ab}\right\}$$

whereas the second-order term is

$$E^{\rm Rep}(\mathscr{O}(S^2)) = 2\sum_{a\in A}\sum_{b\in B} S_{ab}^2\left\{\sum_{x\in A}\frac{-Z_x}{R_{xb}} + \sum_{y\in B}\frac{-Z_y}{R_{ya}} + \sum_{c\in A}\frac{2}{R_{bc}} + \sum_{d\in B}\frac{2}{R_{ad}} - \frac{1}{R_{ab}}\right\}$$

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:

$$E^{\rm Ex} \approx -4\sum_{a\in A}\sum_{b\in B}\sqrt{\frac{-2\ln|S_{ab}|}{\pi}}\frac{S_{ab}^2}{R_{ab}}$$

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 OEPs. 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

$$v^A_a(\mathbf{r}) = \sum_{x\in A} \frac{-Z_x}{|\mathrm{r} - \mathrm{r}_x|} + 2\sum_{c\in A} \int \frac{\phi_c(\mathrm{r}')\phi_c(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|}\, d\mathbf{r}' - \frac{1}{2} \int \frac{\phi_a(\mathrm{r}')\phi_a(\mathrm{r}')}{|\mathrm{r} - \mathrm{r}'|}\, d\mathbf{r}'$$

14.74.2 Member Function Documentation

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.

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.

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

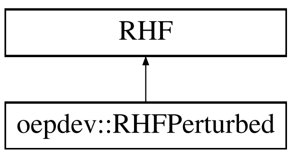
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_energy_pauli.cc

14.75 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.

14.75.1 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 Hamiltionian. 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 Ith 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:

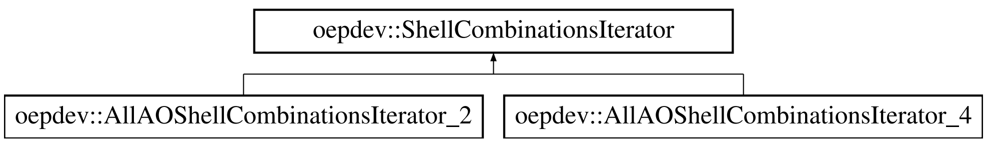
- oepdev/libutil/scf_perturb.h
- oepdev/libutil/scf_perturb.cc

14.76 oepdev::ShellCombinationsIterator Class Reference

Iterator for Shell Combinations. Abstract Base.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::ShellCombinationsIterator:



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.

14.76.1 Detailed Description

Date

2018/03/01 17:22:00

14.76.2 Constructor & Destructor Documentation

ShellCombinationsIterator()

```
ShellCombinationsIterator::ShellCombinationsIterator (
          int nshell )
```

Parameters

nshell	- number of shells this iterator is for

14.76.3 Member Function Documentation

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.

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

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.

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.

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

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

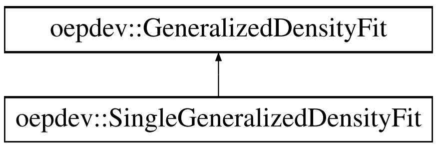
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

14.77 oepdev::SingleGeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme - Single Fit.

```
#include <oep_gdf.h>
```

Inheritance diagram for 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

14.77.1 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.

14.77.2 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 $\hat{v}$.

14.77.3 Member Function Documentation

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

14.78 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

14.79 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

14.80 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 ΔE_1 and ΔE_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)

14.80.1 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

14.80.2 Member Function Documentation

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

$V^{\mathrm{Coul},(0)} \approx V^{\mathrm{TrCAMM},(0)}(R^{-n})$

coupling_direct()

```
double TIData::coupling_direct (
          void ) [virtual]
```

Compute the direct EET coupling constant.

Returns

$V^{\mathrm{Dir}} = V^{\mathrm{Coul}} + V^{\mathrm{Exch}} + V^{\mathrm{Ovrl}}$

Overlap and diagonal corrections as well as TrCAMM and Mulliken approximations for Coulomb and pure exchange parts can be set.

coupling_direct_coul()

```
double TIData::coupling_direct_coul (
          void ) [virtual]
```

Compute the direct EET coupling constant in Forster limit (Coulombic approximation)

Returns

$V^{\mathrm{Dir}} = V^{\mathrm{Coul}}$

Overlap correction as well as TrCAMM approximation for Coulomb coupling can be set.

coupling_direct_exch()

```
double TIData::coupling_direct_exch (
          void ) [virtual]
```

Compute the direct EET coupling constant due to pure exchange.

Returns

$V^{\mathrm{Dir}} = V^{\mathrm{Exch}}$

Overlap correction as well Mulliken approximation for pure exchange coupling can be set.

coupling_indirect()

```
double TIData::coupling_indirect (
          void ) [virtual]
```

Compute the indirect EET coupling constant.

Returns

$V^{\mathrm{Indir}} = V^{\mathrm{TI},(2)} + V^{\mathrm{TI},(3)}$

Overlap and diagonal corrections as well as Mulliken approximations for $V^{\mathrm{CT},(0)}$ can be set.

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.

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.

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.

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: • `COUL` - $V^{\text{Coul},(0)}$, • `EXCH` - $V^{\text{Exch},(0)}$, • `TrCAMM_R1` - $V^{\text{TrCAMM},(0)}(R^{-1})$, • `TrCAMM_R2` - $V^{\text{TrCAMM},(0)}(R^{-2})$, • `TrCAMM_R3` - $V^{\text{TrCAMM},(0)}(R^{-3})$, • `TrCAMM_R4` - $V^{\text{TrCAMM},(0)}(R^{-4})$, • `TrCAMM_R5` - $V^{\text{TrCAMM},(0)}(R^{-5})$, • `ET1` - $V^{\text{ET1},(0)}$, • `ET2` - $V^{\text{ET2},(0)}$, • `HT1` - $V^{\text{HT1},(0)}$, • `HT2` - $V^{\text{HT2},(0)}$, • `CT` - $V^{\text{CT},(0)}$, • `CT_M` - Mulliken-approximated $V^{\text{CT},(0)}$, • `EXCH_M` - Mulliken-approximated $V^{\text{Exch},(0)}$.

If type = `OVRL`, the overlap-correction to the direct EET coupling constant is returned, V^{Ovrl}.

Returns

overlap-corrected exciton Hamiltonian matrix element contribution of selected type

Diagonal correction can be set.

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.

overlap_corrected_direct() [2/2]

```
double TIData::overlap_corrected_direct (
          double v ) [virtual]
```

Compute overlap-corrected direct EET coupling constant from value *v*.

Returns

$\frac{v}{1-S_{12}^2}$

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.

14.80.3 Member Data Documentation

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` - $V^{\rm TrCAMM,(0)}(R^{-4})$,

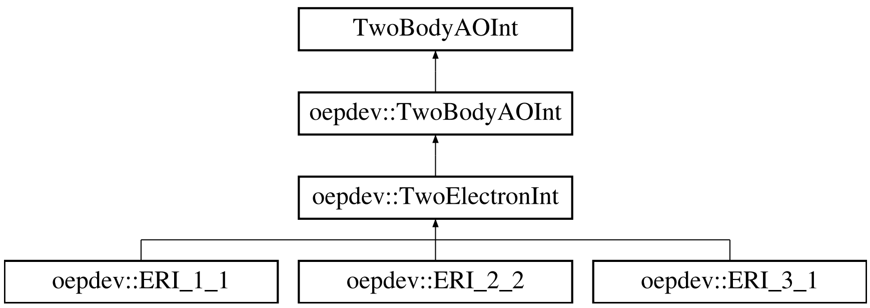
- TrCAMM_R5 - $V^{\mathrm{TrCAMM},(0)}(R^{-5})$,
- ET1 - $V^{\mathrm{ET1},(0)}$,
- ET2 - $V^{\mathrm{ET2},(0)}$,
- HT1 - $V^{\mathrm{HT1},(0)}$,
- HT2 - $V^{\mathrm{HT2},(0)}$,
- CT - $V^{\mathrm{CT},(0)}$,
- CT_M - Mulliken-approximated $V^{\mathrm{CT},(0)}$,
- EXCH_M - Mulliken-approximated $V^{\mathrm{Exch},(0)}$,
- OVRL - V^{Ovrl}.

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

- oepdev/libsolver/ti_data.h
- oepdev/libsolver/ti_data.cc

14.81 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)

14.81.1 Member Function Documentation

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

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:

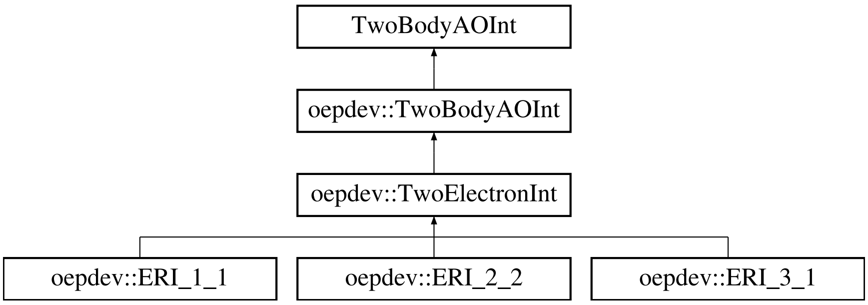
- oepdev/libpsi/integral.h
- oepdev/libpsi/integral.cc

14.82 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.

14.82.1 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

14.82.2 Member Function Documentation

compute_shell()

```
size_t oepdev::TwoElectronInt::compute_shell (
        const psi::AOShellCombinationsIterator & shellIter ) [virtual]
```

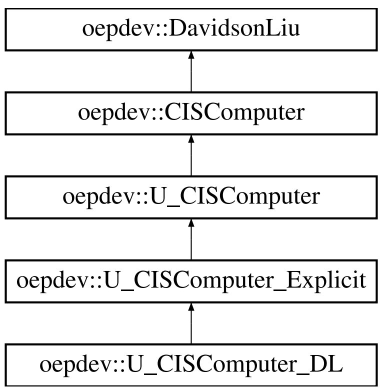
Compute ERIs between 4 shells. Result is stored in buffer. Only for use with ERI_2_2 and the same basis sets, otherwise shell pairs won't be compatible.

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

- oepdev/libints/eri.h
- oepdev/libints/eri.cc

14.83 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:

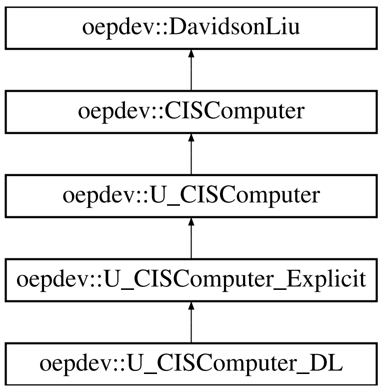
- oepdev/libutil/cis.h
- oepdev/libutil/cis_uhf.cc

14.84 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

14.84.1 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

$$T_{\gamma\delta}^{(k)} = \sum_{jb} C_{\delta b} b_j^{b,k} C_{\gamma j}$$
$$\overline{T}_{\gamma\delta}^{(k)} = \sum_{\bar{j}\bar{b}} C_{\delta\bar{b}} b_{\bar{j}}^{\bar{b},k} C_{\gamma\bar{j}}$$

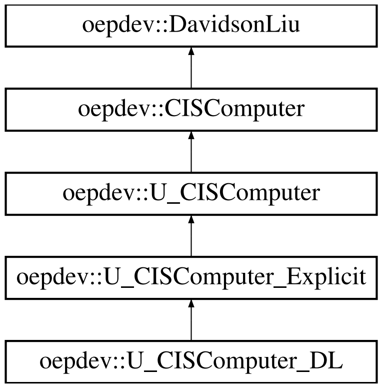
The **J** and **K** matrices in AO basis are computed by using the psi::JK object, and subsequently transformed to CMO's.

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

- oepdev/libutil/cis.h
- oepdev/libutil/cis_uhf_dl.cc

14.85 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:

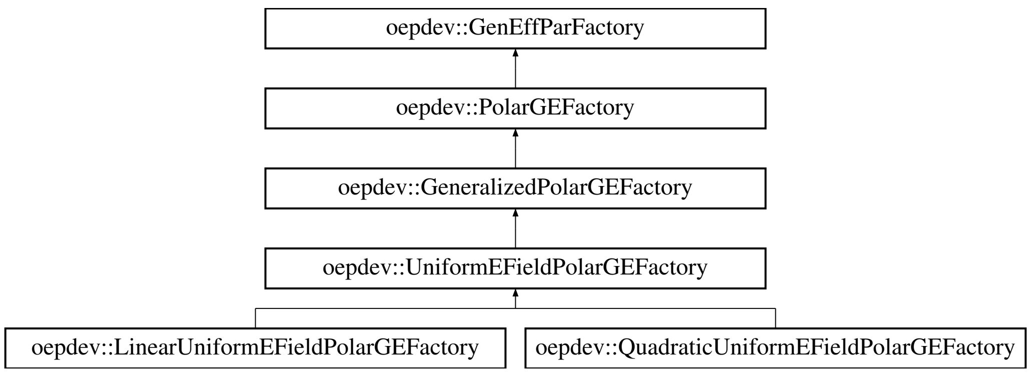
- oepdev/libutil/cis.h
- oepdev/libutil/cis_uhf_explicit.cc

14.86 oepdev::UniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::UniformEFieldPolarGEFactory:



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

14.86.1 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

14.87 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.

14.87.1 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 γ:

$$\mathbf{X}^{\text{New}} = \mathbf{U}(\gamma) \cdot \mathbf{X}^{\text{Old}}$$

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 Ith and Jth 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

$$\mathbf{R} \to \mathbf{U}\mathbf{R}\mathbf{U}^T$$
$$\mathbf{P} \to \mathbf{U}\mathbf{P}$$

The full transformation matrix is accumulated in the memory buffer until convergence.

In each iteration, the optimum angle γ 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

$$\begin{aligned} A &= P_I + P_J - \sum_{k \neq I,J} (R_{Ik} + R_{Jk} + R_{kI} + R_{kJ}) \\ B &= P_I - P_J - \sum_{k \neq I,J} (R_{Ik} - R_{Jk} + R_{kI} - R_{kJ}) \\ C &= -2(R_{IJ} + R_{JI}) \\ D &= -2(R_{II} - R_{JJ}) \end{aligned}$$

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 λ_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 γ,

$$\frac{\partial^2 Z}{\partial \gamma^2} = A\cos(\gamma) - B\sin(\gamma) + 2C\cos(2\gamma) - 2D\sin(2\gamma)$$

All the $N(N-1)/2$ unique pairs of molecular orbitals are checked and the optimal set of γ, I, J is chosen to construct $\mathbf{X}^{\text{New}}$.

References:

[1] Boyd, J.P.; J. Eng. Math. (2006) 56, pp. 203-219

14.87.2 Constructor & Destructor Documentation

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.

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.

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

14.88 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.

14.88.1 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 γ:

$$\mathbf{X}^{\mathrm{New}} = \mathbf{X}^{\mathrm{Old}} \cdot \mathbf{U}(\gamma)$$

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 Ith and Jth 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 γ 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 λ_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 γ, I, J is chosen to construct $\mathbf{X}^{\rm New}$.

References:

[1] Boyd, J.P.; J. Eng. Math. (2006) 56, pp. 203-219

14.88.2 Constructor & Destructor Documentation

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.

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

14.89 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.

14.89.1 Constructor & Destructor Documentation

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.

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

14.90 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.

14.90.1 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 γ:

$$\mathbf{X}^{\mathrm{New}} = \mathbf{X}^{\mathrm{Old}} \cdot \mathbf{U}(\gamma)$$

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 Ith and Jth element from the entire N-dimensional set. For the sake of algirithmic simplicity, every iteration after $\mathbf{U}(\gamma)$ has been formed,

$\mathbf{X}^{\mathrm{Old}}$ 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

$$R_{ijklmn} \rightarrow \sum_{k'l'm'n'} R_{ijk'l'm'n'} X_{k'k} X_{l'l} X_{m'm} X_{n'n}$$
$$P_{ijk} \rightarrow \sum_{j'k'} P_{ij'k'} X_{j'j} X_{k'k}$$

The full transformation matrix is accumulated in the memory buffer until convergence.

In each iteration, the optimum angle γ 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 λ_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 γ, I, J is chosen to construct $\mathbf{X}^{\mathrm{New}}$.

References:

[1] Boyd, J.P.; J. Eng. Math. (2006) 56, pp. 203-219

14.90.2 Constructor & Destructor Documentation

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.

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:

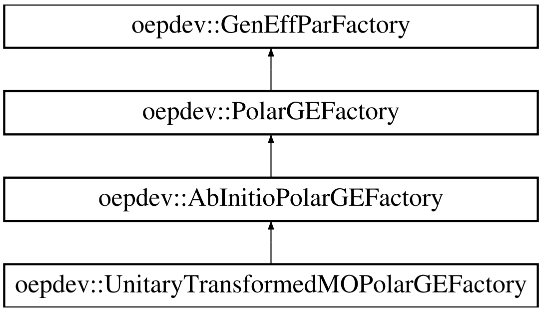
- oepdev/libutil/unitary_optimizer.h
- oepdev/libutil/unitary_optimizer.cc

14.91 oepdev::UnitaryTransformedMOPolarGEFactory Class Reference

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

`#include <gefp.h>`

Inheritance diagram for 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

14.91.1 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:

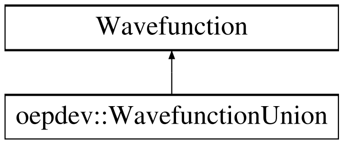
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_abinitio.cc

14.92 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.

14.92.1 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.

14.92.2 Constructor & Destructor Documentation

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.

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)
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.

14.92.3 Member Function Documentation

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

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 15

File Documentation

15.1 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

15.2 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.

15.3 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)

15.4 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.

15.5 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 >

15.6 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.

15.7 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.

15.8 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.

15.9 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 >

15.10 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.

15.11 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.

15.12 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)

15.13 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.

15.14 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.

15.15 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 >

15.16 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.

15.17 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

15.17.1 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,

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

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.

15.18 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 >

15.19 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.

15.20 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.

15.21 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.

15.22 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.

15.23 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.

15.24 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.

15.25 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.

15.26 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)

15.27 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::preamble (void)

  Print preamble 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 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)
- 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.

15.28 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 16

Example Documentation

16.1 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);
};
```

16.2 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();
};
```

16.3 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
}
```

16.4 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()];
      }
  }
}
```

16.5 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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Index