oepdev 1.0.0-alpha

Novel methods for Quantum Chemistry of Extended Molecular Aggregates

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Chapter 1

Main Page

oep-dev

Generalized One-Electron Potentials: Development Platform.

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Overview

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

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

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

against reference solutions (exact or other approximations).

Places to go:

- https://github.com/globulion/oepdev/blob/master/doc/git/doc_oep_design.md "OEP Design"
- https://github.com/globulion/oepdev/blob/master/doc/git/doc_implemented_models.md "Implemented Models"
- https://github.com/globulion/oepdev/blob/master/doc/git/doc_programming_etiquette.md "Programming Etiquette"
- Current Issues

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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. Despite many methodologies have been devised to describe energetic and dynamical properties of **extended molecular systems** efficiently and accurately, there exist particularly difficult cases in which modelling is still challenging:

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

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

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

2.1 Research Project Methodology

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

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

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

where A and B denote different molecules and ϕ_i is the i-th molecular orbital or basis function. Here, v_{kl}^B denotes the List of One-Electron Potentals *ab initio* "OEP matrix element". The technique described above will be applied to simplify expressions for

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

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

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

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

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

Therefore, it is strongly believed that the OEP's could have an indirect impact on the design of novel drugs and materials for industry.

2.3 The OEPDev Code

To pursue the above challenges in the field of computational quantum chemistry of extended molecular aggregates, the OEPDev platform is developed. Accurate and efficient *ab initio* models based on OEP's are implemented in the OEPDev code, along with the state-of-the-art benchmark and competiting methods. Written entirely in C++, OEPDev is a plugin to Psi4 quantum chemistry package. Therefore, compilation and running the OEPDev 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 OEPDev code can be found in advanced usage section.

Chapter 3

OEP Design.

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

Technically, OEP 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 OEP object is also defined for all other molecules in a molecular aggregate.

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

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

> **Important:** OEP and Wavefunction classes should not be restricted to Hartree-Fock; in generall any correlated wavefunction and derived OEP‘s should be allowed to work with each other.

3.1 OEP Classes

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

3.1.1 Structure of possible OEP-based expressions and their unification

Structure of OEP-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 OEP-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	ESP-based form
$\left(\mu\vert\hat{v}^{A[\mu]}\vert\sigma\right)$	$\sum_{\iota\in A} v^A_{\mu\iota} S_{\iota\sigma}$	$\sum_{\alpha\in A} q_\alpha^{A[\mu]} V_{\mu\sigma}^{(\alpha)}$
$\left(i\vert\hat{v}^{A[i]}\vert j\right)$	$\sum_{\iota\in A} v^A_{i\iota} S_{\iota j}$	$\sum_{\alpha\in A} q_\alpha^{A[i]} V_{ij}^{(\alpha)}$

$\left(j\lvert\hat{v}^{A[i]}\rvert l\right)$	$\sum_{\iota\kappa\in A} S_{j\iota} v_{\iota\kappa}^{A[i]} S_{\kappa l}$	$\sum_{\alpha\in A} q_{\alpha}^{A[i]} V_{jl}^{(\alpha)}$

In the formulae above, the OEP-part (stored by OEP instances) and the Solver-part (to be computed by the Solver) are separated. It is apparent that all OEP-parts have the form of 2nd- or 3rd-rank tensors 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.

Chapter 4

List of One-Electron Potentals

Here I provide the list of OEP's that have been already derived within the scope of the OEPDev project.

Note

> Add here a table with all the OEP types along with their symbols used in the OEPDev code (e.g., `Murrell.-etal-S1` etc).

4.1 Electrostatic Energy OEP's

For electrostatic energy calculations, OEP is simply the electrostatic potential due to nuclei and electrons.

3D form:

$$v(\mathbf{r}) = \sum_x \frac{Z_x}{|\mathbf{r}-\mathbf{r}_x|} + \sum_{\mu\nu\in A} P_{\nu\mu} \int d\mathbf{r}' \frac{\phi_\mu^*(\mathbf{r}')\phi_\nu(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Matrix form:

$$v_{ik} = \sum_{x\in A} Z_x V_{ik}^{(x)} + \sum_{\mu\nu\in A} P_{\nu\mu}\,(\mu\nu|ik)$$

4.2 Pauli Repulsion OEP's

The following potentials are derived for the evaluation of the Pauli repulsion energy based on Murrel's expressions.

4.2.1 First-order contribution in overlap matrix expansion.

This contribution is simply the electrostatic potential coming from all nuclei and electron density except$*$ from electron density from molecular orbital i that interacts with the generalized overlap density between i of molecule A and j of molecule B.

3D forms:

$$v(\mathbf{r})^{A[i]}_{S^{-1}} = -\sum_{x\in A} \frac{Z_x}{|\mathbf{r}-\mathbf{r}_x|} + \sum_{\mu\nu\in A} \left\{D_{\nu\mu} - C_{\mu i}^* C_{\nu i}\right\} \int d\mathbf{r}' \frac{\phi_\mu^*(\mathbf{r}')\phi_\nu(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Matrix forms:

$$v_{\xi i}(S^{-1}) = \sum_{\kappa \in A} C_{i\kappa} \left\{ - \sum_{x \in A} V_{\kappa\xi}^{(x)} + \sum_{\mu\nu \in A} \left\{ D_{\nu\mu} - C_{\mu i}^{*} C_{\nu i} \right\} (\mu\nu|\xi\kappa) \right\}$$

4.2.2 Second-order contribution in overlap matrix expansion.

To be added here!

4.3 Charge-Transfer Energy OEP's

To be added here!

4.4 Excitonic Energy Transfer OEP's

The following potentials are derived for the evaluation of the short-range EET couplings based on Fujimoto's TDFI-TI method.

4.4.1 ET contributions.

3D forms:

$$\begin{aligned}
v(\mathbf{r})_1^{A[\mu]} &= -C_{\mu L}^{*} \sum_{x \in A} \frac{Z_x}{|\mathbf{r} - \mathbf{r}_x|} + \sum_{\nu\kappa \in A} \left\{ C_{\mu L}^{*} D_{\nu\kappa} - \frac{1}{2} C_{\nu L}^{*} D_{\mu\kappa} \right\} \int d\mathbf{r}' \frac{\phi_\nu^{*}(\mathbf{r}')\phi_\kappa(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
v(\mathbf{r})_2^{A[\mu]} &= C_{\kappa H} \sum_{\nu\kappa \in A} \left\{ 2C_{\nu L}^{*} C_{\mu H}^{*} - C_{\nu H}^{*} C_{\mu L}^{*} \right\} \int d\mathbf{r}' \frac{\phi_\nu^{*}(\mathbf{r}')\phi_\kappa(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
v(\mathbf{r})_3^{A[\mu]} &= v(\mathbf{r})_1^{A[\mu]} + v(\mathbf{r})_1^{A[\mu]}
\end{aligned}$$

Matrix forms:

$$\begin{aligned}
v_{\mu\xi}(1) &= -C_{\mu L}^{*} \sum_{x \in A} V_{\mu\xi}^{x} + \sum_{\nu\kappa \in A} \left\{ C_{\mu L}^{*} D_{\nu\kappa} - \frac{1}{2} C_{\nu L}^{*} D_{\mu\kappa} \right\} (\nu\kappa|\mu\xi) \\
v_{\mu\xi}(2) &= C_{\kappa H} \sum_{\nu\kappa \in A} \left\{ 2C_{\nu L}^{*} C_{\mu H}^{*} - C_{\nu H}^{*} C_{\mu L}^{*} \right\} (\nu\kappa|\mu\xi) \\
v_{\mu\xi}(3) &= v_{\mu\xi}(1) + v_{\mu\xi}(2)
\end{aligned}$$

4.4.2 HT contributions.

Do be derived.

4.4.3 CT contributions.

To be derived.

4.5 Full HF Interaction OEP's

The following potentials are derived for the evaluation of the full Hartree-Fock interaction energy based on the OEPDev equations.

Chapter 5

Density-fitting Specialized for OEP's

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

5.1 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 OEP 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 OEP 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 OEP-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.

5.2 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 OEP operator in a **incomplete** auxiliary space. This can be achieved by minimizing the following objective function

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

Thus requesting that

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

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

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

where

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

The symbol $||$ is to denote the operator r_{12}^{-1} and double integration over $\mathbf{r}_1$ and $\mathbf{r}_2$. Thus, it is clear that in order to use this generalized density fitting scheme one must to compute two-centre electron repulsion integrals (implemented in oepdev::ERI_1_1) as well as four-centre asymmetric electron repulsion integrals of the type $(\alpha\beta\gamma||\eta)$ (implemented in oepdev::ERI_3_1).

Chapter 6

Implemented Models

6.1 Target Properties

Detailed list of models which is to be implemented in the OEPDev project is given below:

Table 1. Models subject to be implemented and analyzed within oep-dev.

Pauli energy	Induction energy	EET Coupling
EFP2-Pauli	EFP2-Induced Dipoles	TrCAMM
Murrel et al.'s theory	Density Susceptibility	OEP-ET/HT
OEP-Murrel et al.'s		TDFI-TI
		FED
Exact (Stone's)	Exact (incl. CT)	Exact (ESD)

6.2 Target, Benchmark and Competing Models

The target models introduced in the Project shall be 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
OEP-Murrel et al.'s	Murrel et al.'s	EFP2-Pauli
	Exact (Stone's)	
OEP-ET/HT + TrCAMM	Exact (ESD)	TDFI-TI
	FED	FED
	TDFI-TI	
Density Susceptibility	Exact (incl. CT)	EFP2-Induced Dipoles

Chapter 7

Contributing to oep-dev

OepDev is a plugin to Psi4.

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

7.1 Main Routine

Oep-dev 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 OEP 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 oep-dev 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.

7.2 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 oep-dev. 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.

7.3 Environmental variables

Defining the set of intrinsic environmental variables can help in code management and conditional compilation. The oep-dev 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 oep-dev environmental variable should have the following format:

```
OEPDEV_XXXX
```

where `XXXX` is the descriptive name of variable.

7.4 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!

7.5 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 `sizeOfOEPTypeList` and a method name `get_matrix()` (neither `size_of_OEP_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`.

7.6 Track timing when evaluating the code

It is useful to track time elapsed for performing a particular task by a computer. For this, use `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("OEP    E(Paul) Murrell-etal S1  ");
// Your code goes here
psi::timer_off("OEP    E(Paul) Murrell-etal S1  ");
```

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

7.7 Use Object-Oriented Programming

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

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

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

Chapter 8

Advanced Usage

This section is addressed for advanced users.

Make sure you have first read the introduction before proceeding.

8.1 OEPDev Code Structure

As a plugin to Psi4, OEPDev 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 OEPDev code that is divided into several subdirectories called modules.

8.1.1 Main Routine

Before the actual OEPDev 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 OEP 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 `oepdev::OEPotential::build` static factory to create OEP objects whereas `DMATPOL` uses the `oepdev::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 `oepdev::GenEffParFactory::build` since OEP parameters are part of the GEFP's.

`SOLVER` requires at least molecular dimer and the `oepdev::WavefunctionUnion` object (being the Hartree product of the unperturbed monomer wavefunctions) is constructed at the beginning, which is then passed to the `oepdev::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.

8.1.2 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.

8.2 OEPDev Classes: Overview

8.2.1 OEP Module

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

- `oepdev::OEPotential` implementing the OEP,
- `oepdev::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 `oepdev::OEPType` which is a container storing all the data associated with a particular OEP: type name, dimensions, OEP coefficients and whether is density-fitted or not.

8.2.1.1 OEPPotential

It is a container and computer class of OEP. Among others, the most important public method is `oepdev::OEPotential::compute` which computes all the OEP's (by iterating over all possible OEP types within a chosen OEP subclass or category). OEP's can be extracted by `oepdev::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 `oepdev::ElectrostaticEnergyOEPotential` and `oepdev::RepulsionEnergyOEPotential` are fully operative, while the rest is under development.

8.2.1.2 GeneralizedDensityFit

8.2.2 GEFP Module

8.2.2.1 GenEffPar

8.2.2.2 GenEffParFactory

8.2.2.3 GenEffFrag

8.2.3 OEPDev Solver Module

8.2.3.1 OEPDevSolver

8.3 Developing OEP's

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

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

1. **Write the class framework.** This includes choosing a proper name of a OEPotential subclass, sketching the constructors and a destructor, and all the necessary methods.
2. **Implement OEP types.** Each type of OEP is implemented, including the 3D vector field in case ESP-based OEP's are of use.
3. **Update base factory method**. Add appropriate entries in the `oepdev::OEPotential::build` static factory method.

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

8.3.1 Drafting an OEP Subclass

This stage is the design of the overall framework of OEP 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 ESP-based OEP's
    SampleOEPotential(SharedWavefunction wfn, Options& options);

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

    // Necessary destructor
    virtual ~SampleOEPotential();

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

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

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

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

The constructors need to call the abstract base constructor and then specialized initializations. It is a good practice to put the specialized common initializers in a separate private method `common_init` (which is a convention in Psi4 and is adopted also in OEPDev). 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();

   SharedMatrix mat_1 = std::make_shared<psi::Matrix>("G(S^{-1})", n2, n1);
   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 `oepdev::OEPotential::oepTypes_` attribute, which is a `std::map` of structures `oepdev::OEPType`, is initialized here. All the OEP 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("OEPDEV: Error. Incorrect OEP type specified!\n"); // for safety
}
void SampleOEPotential::compute_murrell_etal_s1()
{
   psi::timer_on ("OEP    E(Paul) Murrell-etal S1  ");
   /* Your implementation goes here */
   psi::timer_off("OEP    E(Paul) Murrell-etal S1  ");
```

8.3.1.1 Implementing OEP Types

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

```
void SampleOEPotential::compute_otto_ladik_s2()
{
      // Switch on timer
      psi::timer_on("OEP    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 OEP effective charges
      ESPSolver esp(oeps3d);
      esp.set_charge_sums(0.5);
      esp.compute();

      // Put the OEP 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("OEP    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 OEP types and exclude illegal names
   if (oepType == "Otto-Ladik.S2") {

       // this computes the actual values of OEP = 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 ESP-based OEP, this line is necessary */}

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

Note that `make_oeps3d` is not overridable and is fully defined in the base. Do not call `oepdev::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)!

8.3.1.2 Abstract Base

Chapter 9

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Chapter 10

Module Index

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Chapter 15

Module Documentation

15.1 The Generalized One-Electron Potentials Library

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

Classes

- struct oepdev::OEPType

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

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

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

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

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

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

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

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

  Generalized Density Fitting Scheme - Double Fit.

15.1.1 Detailed Description

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

15.2 The OEPDev Solver Library

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

Classes

- class oepdev::OEPDevSolver

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

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

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

  Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.

15.2.1 Detailed Description

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

15.3 The Generalized Effective Fragment Potentials Library

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

Classes

- class oepdev::GenEffPar

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

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

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

15.3.1 Detailed Description

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

15.4 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::TwoBodyAOInt
- class oepdev::IntegralFactory

  Extended IntegralFactory for computing 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.

15.4.1 Detailed Description

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

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

in which $\mathbf{r}_A \equiv \mathbf{r} - \mathbf{A}$ and so on. $\mathbf{A}$ is the centre of the GTO, 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 OEPDev implementations, the following definition shall be in use:

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

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

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

15.4.2 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.

15.4.2.1 Polynomial Expansions as Hermite Series

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

$$\begin{aligned} x_A^{n_1} &= \sum_{N=0}^{n_1} d_N^{n_1} \Lambda_N(x_A;\alpha_A) \\ x_A^{n_1} x_B^{n_2} &= \sum_{N=0}^{n_1+n_2} d_N^{n_1n_2} \Lambda_N(x_P;\alpha_P) \\ x_A^{n_1} x_B^{n_2} x_C^{n_3} &= \sum_{N=0}^{n_1+n_2+n_3} d_N^{n_1n_2n_3} \Lambda_N(x_R;\alpha_R) \end{aligned}$$

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

$$\begin{aligned} d_N^{n_1+1,n_2} &= \frac{1}{2\alpha_P} d_{N-1}^{n_1n_2} + |\mathbf{P}-\mathbf{A}|_x d_N^{n_1n_2} + (N+1) d_{N+1}^{n_1n_2} \\ d_N^{n_1,n_2+1} &= \frac{1}{2\alpha_P} d_{N-1}^{n_1n_2} + |\mathbf{P}-\mathbf{B}|_x d_N^{n_1n_2} + (N+1) d_{N+1}^{n_1n_2} \end{aligned}$$

and

$$\begin{aligned} d_N^{n_1+1,n_2,n_3} &= \frac{1}{2\alpha_R} d_{N-1}^{n_1n_2n_3} + |\mathbf{R}-\mathbf{A}|_x d_N^{n_1n_2n_3} + (N+1) d_{N+1}^{n_1n_2n_3} \\ d_N^{n_1,n_2+1,n_3} &= \frac{1}{2\alpha_R} d_{N-1}^{n_1n_2n_3} + |\mathbf{R}-\mathbf{B}|_x d_N^{n_1n_2n_3} + (N+1) d_{N+1}^{n_1n_2n_3} \\ d_N^{n_1,n_2,n_3+1} &= \frac{1}{2\alpha_R} d_{N-1}^{n_1n_2n_3} + |\mathbf{R}-\mathbf{C}|_x d_N^{n_1n_2n_3} + (N+1) d_{N+1}^{n_1n_2n_3} \end{aligned}$$

respectively. The first elements are given by

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

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

$$[ij] = E_{ij} \sum_{N=0}^{n_1+n_2} \sum_{L=0}^{l_1+l_2} \sum_{M=0}^{m_1+m_2} d_N^{n_1n_2} d_L^{l_1l_2} d_M^{m_1m_2} \Lambda_N(x_P) \Lambda_L(y_P) \Lambda_M(z_P) e^{-\alpha_P r_P^2}$$

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

$$[ijk] = E_{ijk} \sum_{N=0}^{n_1+n_2+n_3} \sum_{L=0}^{l_1+l_2+l+3} \sum_{M=0}^{m_1+m_2+m_3} d_N^{n_1n_2n_3} d_L^{l_1l_2l_3} d_M^{m_1m_2m_3} \Lambda_N(x_R) \Lambda_L(y_R) \Lambda_M(z_R) e^{-\alpha_R r_R^2}$$

The multiplicative constants are given by

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

15.4.3 One-Body Integrals over Hermite Functions

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

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

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

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

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

15.4.4 Two-Body Integrals over Hermite Functions

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

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

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

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

15.4.5 The R(N,L,M) Coefficients

The *R* coefficients are defined as

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

with

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

By extending the above definition to more general

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

one can see that

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

The Boys function is here given by

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

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

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

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

This scheme is implemented in OEPDev.

15.4.6 Function Documentation

15.4.6.1 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.

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

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

Compute the McMurchie-Davidson-Hermite coefficients for monomial expansion.

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

15.4.6.3 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.

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

15.4.6.4 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.

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

15.4.6.5 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.

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

15.4.6.6 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.

Parameters

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

15.5 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::DMTPole

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

15.5.1 Detailed Description

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`.

15.5.2 Function Documentation

15.5.2.1 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*)

Construct random spherical collection of 3D field of type T.

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

15.5.2.2 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*)

Construct ordered 3D collection of 3D field of type T.

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

15.6 The Density Functional Theory Library

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

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

15.7 The OEPDev Utilities

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

Classes

- class oepdev::CPHF

  CPHF solver class.
- class oepdev::DIISManager

  DIIS manager.
- 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.
- 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::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::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)

Typedefs

- 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.

Functions

- 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);.
- std::shared_ptr< SuperFunctional > oepdev::create_superfunctional (std::string name, Options &options)

  Set up DFT functional.
- std::shared_ptr< Molecule > oepdev::extract_monomer (std::shared_ptr< const Molecule > molecule_dimer, int id)

  Extract molecule from dimer.
- std::shared_ptr< Wavefunction > oepdev::solve_scf (std::shared_ptr< Molecule > molecule, std::shared_ptr< BasisSet > primary, std::shared_ptr< SuperFunctional > functional, Options &options, std::shared_ptr< PSIO > psio)

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

  Compute the scalar magnitude of multipole moment.

15.7.1 Detailed Description

Contains utility functions such as printing OEPDev preamble 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`.

15.7.2 Function Documentation

15.7.2.1 double oepdev::average_moment (std::shared_ptr< psi::Vector > *moment*)

Compute the scalar magnitude of multipole 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.

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

Set up DFT functional.

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.

15.7.2.3 std::shared_ptr< Molecule > oepdev::extract_monomer (std::shared_ptr< const Molecule > *molecule_dimer,* int *id*)

Extract molecule from dimer.

Parameters

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

Returns

psi::SharedMolecule object with indicated monomer

15.7.2.4 std::shared_ptr< Wavefunction > oepdev::solve_scf (std::shared_ptr< Molecule > *molecule,* std::shared_ptr< BasisSet > *primary,* std::shared_ptr< SuperFunctional > *functional,* Options & *options,* std::shared_ptr< PSIO > *psio*)

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

Parameters

molecule	psi::SharedMolecule object with molecule
primary	shared primary basis set
functional	DFT functional
options	psi::Options object
psio	psi::PSIO object

Returns

psi::SharedWavefunction SCF wavefunction of the molecule

15.8 The OEPDev Testing Platform Library

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

Classes

- class oepdev::test::Test

  Manages test routines.

15.8.1 Detailed Description

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

Chapter 16

Namespace Documentation

16.1 oepdev Namespace Reference

OEPDev module namespace.

Classes

- class DMTPole

  Distributed Multipole Analysis Container and Computer. Abstract Base.
- class CAMM
- class ESPSolver

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

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

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

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

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

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

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

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

  Electrostatic potential of a molecule.
- class OEPotential3D

  Class template for OEP 3D fields.
- class GenEffPar

  Generalized Effective Fragment Parameters. Container Class.
- class GenEffFrag

  Generalized Effective Fragment. Container Class.
- class GenEffParFactory

  Generalized Effective Fragment Factory. Abstract Base.
- class PolarGEFactory

Polarization GEFP Factory. Abstract Base.
- class AbInitioPolarGEFactory

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

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

  Polarization GEFP Factory with Least-Squares Parameterization.
- class UniformEFieldPolarGEFactory

  Polarization GEFP Factory with Least-Squares Parameterization.
- class NonUniformEFieldPolarGEFactory

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

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

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

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

  Polarization GEFP Factory with Least-Squares Parameterization.
- class LinearGradientNonUniformEFieldPolarGEFactory

  Polarization GEFP Factory with Least-Squares Parameterization.
- class QuadraticGradientNonUniformEFieldPolarGEFactory

  Polarization GEFP Factory with Least-Squares Parameterization.
- class UnitaryTransformedMOPolarGEFactory

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

  General Two Electron Integral.
- 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.
- struct OEPType

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

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

  Generalized One-Electron Potential for Electrostatic Energy.
- class RepulsionEnergyOEPotential

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

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

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

  Generalized Density Fitting Scheme. Abstract Base.
- class SingleGeneralizedDensityFit

  Generalized Density Fitting Scheme - Single Fit.
- class DoubleGeneralizedDensityFit

  Generalized Density Fitting Scheme - Double Fit.

- class TwoBodyAOInt
- class IntegralFactory

  Extended IntegralFactory for computing integrals.
- class PotentialInt

  Computes potential integrals.
- class OEPDevSolver

  Solver of properties of molecular aggregates. Abstract base.
- class ElectrostaticEnergySolver

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

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

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

  CPHF solver class.
- class DIISManager

  DIIS manager.
- class ShellCombinationsIterator

  Iterator for Shell Combinations. Abstract Base.
- class AOIntegralsIterator

  Iterator for AO Integrals. Abstract Base.
- class AllAOShellCombinationsIterator_4

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

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

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

  Loop over all possible ERI within a particular shell doublet.
- struct PerturbCharges

  Structure to hold perturbing charges.
- class RHFPerturbed

  RHF theory under electrostatic perturbation.
- struct ABCD

  Simple structure to hold the Fourier series expansion coefficients.
- struct Fourier9

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

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

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

  Union of two Wavefunction objects.

Typedefs

- using **SharedField3D** = std::shared_ptr< oepdev::Field3D >
- 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 **SharedWavefunctionUnion** = std::shared_ptr< WavefunctionUnion >
- using **SharedOEPotential** = std::shared_ptr< OEPotential >
- 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 **SharedMolecule** = std::shared_ptr< Molecule >
- using **SharedSuperFunctional** = std::shared_ptr< SuperFunctional >
- using **SharedMOSpace** = std::shared_ptr< MOSpace >
- using **SharedMOSpaceVector** = std::vector< std::shared_ptr< MOSpace >>
- using **SharedIntegralTransform** = std::shared_ptr< IntegralTransform >
- using **SharedLocalizer** = std::shared_ptr< Localizer >

Functions

- **dipoles_** ({})
- **quadrupoles_** ({})
- **octupoles_** ({})
- **hexadecapoles_** ({})
- **n_max_am_** (2 ∗max_am_+1)
- 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.
- constexpr std::complex< double > **operator""_i** (unsigned long long d)
- constexpr std::complex< double > **operator""_i** (long double d)
- void preamble (void)

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

  Set up DFT functional.
- std::shared_ptr< Molecule > extract_monomer (std::shared_ptr< const Molecule > molecule_dimer, int id)

Extract molecule from dimer.

- std::shared_ptr< Wavefunction > solve_scf (std::shared_ptr< Molecule > molecule, std::shared_ptr< BasisSet > primary, std::shared_ptr< SuperFunctional > functional, Options &options, std::shared_ptr< PSIO > psio)

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

  Compute the scalar magnitude of multipole moment.
- 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);.

16.1.1 Detailed Description

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

16.2 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

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

  Options for the OEPDev plugin.
- SharedWavefunction oepdev (SharedWavefunction ref_wfn, Options &options)

  Main routine of the OEPDev plugin.

16.2.1 Detailed Description

Psi4 package namespace. Contains all Psi4 functionalities.

16.2.2 Function Documentation

16.2.2.1 SharedWavefunction psi::oepdev (SharedWavefunction *ref_wfn*, Options & *options*)

Main routine of the OEPDev plugin.

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)

16.2.2.2 int psi::read_options (std::string *name*, Options & *options*)

Options for the OEPDev plugin.

Parameters

name	name of driver function
options	psi::Options object

Returns

true

Chapter 17

Class Documentation

17.1 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**

17.1.1 Detailed Description

Simple structure to hold the Fourier series expansion coefficients.

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

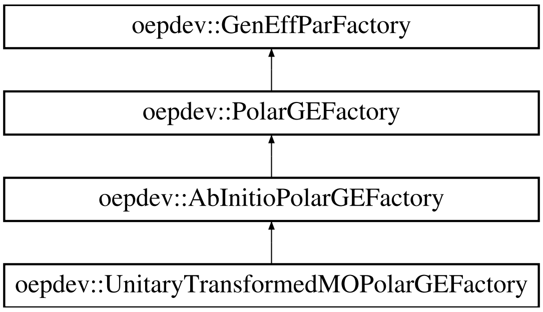
- oepdev/libutil/unitary_optimizer.h

17.2 oepdev::AbInitioPolarGEFactory Class Reference

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

`#include <gefp.h>`

Inheritance diagram for oepdev::AbInitioPolarGEFactory:


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

Public Member Functions

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

  Compute the density matrix susceptibility tensors.

Additional Inherited Members

17.2.1 Detailed Description

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

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:

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

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

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

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

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

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

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

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:

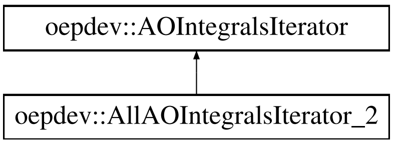
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_abinitio.cc

17.3 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

17.3.1 Detailed Description

Loop over all possible ERI within a particular shell doublet.

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

See Also

AllAOShellCombinationsIterator_2

17.3.2 Constructor & Destructor Documentation

17.3.2.1 AllAOIntegralsIterator_2::AllAOIntegralsIterator_2 (const ShellCombinationsIterator ∗ *shellIter*)

Construct by shell iterator (const object)

Parameters

shellIter	- shell iterator object

17.3.2.2 AllAOIntegralsIterator_2::AllAOIntegralsIterator_2 (std::shared_ptr< ShellCombinationsIterator > *shellIter*)

Construct by shell iterator (pointed by shared pointer)

Parameters

shellIter	- shell iterator object

17.3.3 Member Function Documentation

17.3.3.1 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:

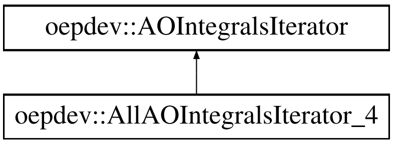
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

17.4 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

17.4.1 Detailed Description

Loop over all possible ERI within a particular shell quartet.

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

See Also

AllAOShellCombinationsIterator_4

17.4.2 Constructor & Destructor Documentation

17.4.2.1 AllAOIntegralsIterator_4::AllAOIntegralsIterator_4 (const **ShellCombinationsIterator** ∗ *shellIter*)

Construct by shell iterator (const object)

Parameters

shellIter	- shell iterator object

17.4.2.2 AllAOIntegralsIterator_4::AllAOIntegralsIterator_4 (std::shared_ptr< ShellCombinationsIterator > *shellIter*)

Construct by shell iterator (pointed by shared pointer)

Parameters

shellIter	- shell iterator object

17.4.3 Member Function Documentation

17.4.3.1 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:

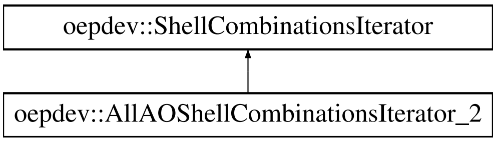
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

17.5 oepdev::AllAOShellCombinationsIterator_2 Class Reference

Loop over all possible ERI shells in a shell doublet.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::AllAOShellCombinationsIterator_2:


oepdev::ShellCombinationsIterator
oepdev::AllAOShellCombinationsIterator_2

Public Member Functions

- AllAOShellCombinationsIterator_2 (SharedBasisSet bs_1, SharedBasisSet bs_2)

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

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

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

  First iteration.
- void next ()

  Next iteration.

- void compute_shell (std::shared_ptr< oepdev::TwoBodyAOInt > tei) const

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

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

  Grab the current shell Q index.

Additional Inherited Members

17.5.1 Detailed Description

Loop over all possible ERI shells in a shell doublet.

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

17.5.2 Constructor & Destructor Documentation

17.5.2.1 AllAOShellCombinationsIterator_2::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.

Parameters

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

17.5.2.2 oepdev::AllAOShellCombinationsIterator_2::AllAOShellCombinationsIterator_2 (std::shared_ptr< IntegralFactory > *integrals*)

Construct by providing integral factory.

Parameters

integrals	- OepDev integral factory object

17.5.2.3 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.

17.5.2.4 AllAOShellCombinationsIterator_2::AllAOShellCombinationsIterator_2 (std::shared_ptr< psi::IntegralFactory > *integrals*)

Construct by providing integral factory.

Parameters

integrals	- Psi4 integral factory object

17.5.2.5 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.

17.5.3 Member Function Documentation

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

Compute ERI's for the current shell. The eris are stored in the buffer of the argument object.

Parameters

tei	- two electron AO integral

Implements oepdev::ShellCombinationsIterator.

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

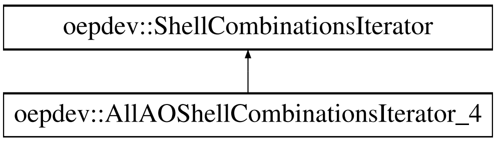
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

17.6 oepdev::AllAOShellCombinationsIterator_4 Class Reference

Loop over all possible ERI shells in a shell quartet.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::AllAOShellCombinationsIterator_4:


oepdev::ShellCombinationsIterator
oepdev::AllAOShellCombinationsIterator_4

Public Member Functions

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

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

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

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

  Do the first iteration.
- void next ()

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

- int P () const

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

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

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

  Grab the current shell S index.

Additional Inherited Members

17.6.1 Detailed Description

Loop over all possible ERI shells in a shell quartet.

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

17.6.2 Constructor & Destructor Documentation

17.6.2.1 AllAOShellCombinationsIterator_4::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.

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

17.6.2.2 oepdev::AllAOShellCombinationsIterator_4::AllAOShellCombinationsIterator_4 (std::shared_ptr< IntegralFactory > *integrals*)

Construct by providing integral factory.

Parameters

integrals	- OepDev integral factory object

17.6.2.3 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.

17.6.2.4 AllAOShellCombinationsIterator_4::AllAOShellCombinationsIterator_4 (std::shared_ptr< psi::IntegralFactory > *integrals*)

Construct by providing integral factory.

Parameters

integrals	- OepDev integral factory object

17.6.2.5 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.

17.6.3 Member Function Documentation

17.6.3.1 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.

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

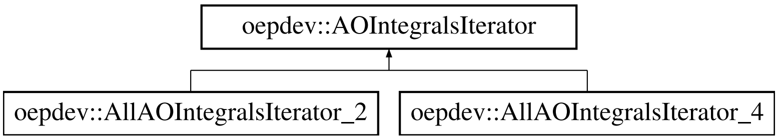
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

17.7 oepdev::AOIntegralsIterator Class Reference

Iterator for AO Integrals. Abstract Base.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::AOIntegralsIterator:


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

Public Member Functions

- AOIntegralsIterator ()

  Base Constructor.
- virtual ~AOIntegralsIterator ()

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

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

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

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

Grab j-th index.

- virtual int k (void) const

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

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

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

  Returns the status of an iterator.

Static Public Member Functions

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

Protected Attributes

- bool done

  The status of an iterator.

17.7.1 Detailed Description

Iterator for AO Integrals. Abstract Base.

17.7.2 Member Function Documentation

17.7.2.1 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

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

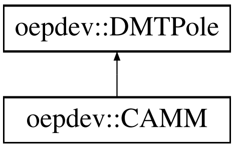
This is an overloaded member function, provided for convenience. It differs from the above function only in what argument(s) it accepts.

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

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

17.8 oepdev::CAMM Class Reference

Inheritance diagram for oepdev::CAMM:



Public Member Functions

- **CAMM** (psi::SharedWavefunction wfn, int n)
- virtual void compute (psi::SharedMatrix D, int n)

    Compute from the one-particle density matrix.

Additional Inherited Members

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

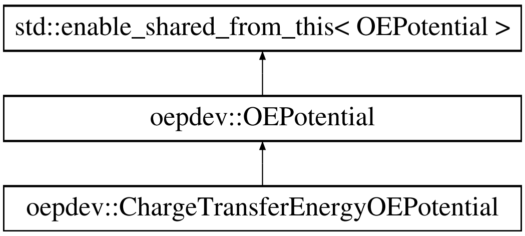
- oepdev/lib3d/dmtp.h
- oepdev/lib3d/dmtp_camm.cc

17.9 oepdev::ChargeTransferEnergyOEPotential Class Reference

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

`#include <oep.h>`

Inheritance diagram for oepdev::ChargeTransferEnergyOEPotential:


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

Public Member Functions

- **ChargeTransferEnergyOEPotential** (SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate, Options &options)
- **ChargeTransferEnergyOEPotential** (SharedWavefunction wfn, Options &options)
- 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

Additional Inherited Members

17.9.1 Detailed Description

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

Contains the following OEP types:

- `Otto-Ladik.V1` - DF-based term
- `Otto-Ladik.V2` - ESP-based term
- `Otto-Ladik.V3` - ESP-based term

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

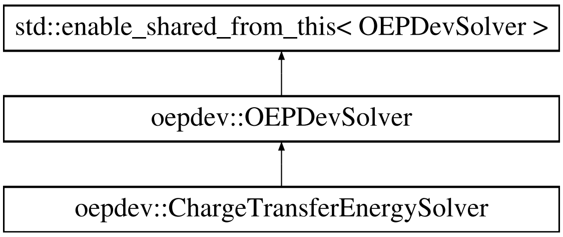
- oepdev/liboep/oep.h
- oepdev/liboep/oep_energy_ct.cc

17.10 oepdev::ChargeTransferEnergySolver Class Reference

Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::ChargeTransferEnergySolver:


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

Public Member Functions

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

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

  Compute property by using benchmark method.

Additional Inherited Members

17.10.1 Detailed Description

Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.

The implemented methods are shown below

> In order to construct this solver, **always** use the `OEPDevSolver::build` static factory method.

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.

Table 17.1: Methods available in the Solver

Below the detailed description of the implemented equations is given for each of the above provided methods. In the formulae across, it is assumed that the orbitals are real. The Coulomb notation for electron repulsion integrals (ERI's) is adopted; i.e,

$$(ac|bd) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_1)\frac{1}{r_{12}}\phi_b(\mathbf{r}_2)\phi_d(\mathbf{r}_2)$$

Greek subscripts denote basis set orbitals whereas Italic subscripts denote the occupied molecular orbitals.

The CT energy between molecules *A* and *B* is given by

$$E^{\rm CT} = E^{\rm A^+B^-} + E^{\rm A^-B^+}$$

Benchmark Methods

CT energy at HF level by Otto and Ladik (1975).

For a closed-shell system, CT energy equation of Otto and Ladik becomes

$$E^{\rm A^+B^-} \approx 2\sum_{i\in A}^{\rm Occ_A}\sum_{n\in B}^{\rm Vir_B}\frac{V_{in}^2}{\varepsilon_i - \varepsilon_n}$$

where

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

and analogously the twin term.

CT energy at HF level by EFP2.

In EFP2 method, CT energy is given as

$$E^{\rm A^+B^-} \approx 2\sum_{i\in A}^{\rm Occ_A}\sum_{n\in B}^{\rm Vir_B}\frac{V_{in}^2}{F_{ii} - T_{nn}}$$

where

$$V_{in}^2 = \frac{V_{in}^B - \sum_{m\in A}^{\rm All_A} V_{im}S_{mn}^B}{1 - \sum_{m\in A}^{\rm All_A} S_{mn}^2}\left\{V_{in}^B - \sum_{m\in A}^{\rm All_A} V_{im}^B S_{mn} + \sum_{j\in B}^{\rm Occ_B} S_{ij}\left(T_{nj} - \sum_{m\in A}^{\rm All_A} S_{nm}T_{mj}\right)\right\}$$

and analogously the twin term.

OEP-Based Methods

OEP-Based Otto-Ladik's theory

After introducing OEP's, the original Otto-Ladik's theory is reformulated *without* approximation as

$$E^{\mathrm{A^+B^-}} \approx 2 \sum_{i\in A}^{\mathrm{Occ_A}} \sum_{n\in B}^{\mathrm{Vir_B}} \frac{\left(V_{in}^{\mathrm{DF}} + V_{in}^{\mathrm{ESP,A}} + V_{in}^{\mathrm{ESP,B}}\right)^2}{\varepsilon_i - \varepsilon_n}$$

where

$$V_{in}^{\mathrm{DF}} = \sum_{\eta\in B}^{\mathrm{Aux_B}} S_{i\eta} G_{\eta n}^{B}$$

$$V_{in}^{\mathrm{ESP,A}} = \sum_{k\in A}^{\mathrm{Occ_A}} \sum_{j\in B}^{\mathrm{Occ_B}} S_{kj} \sum_{x\in A} V_{nj}^{(x)} q_{ik}^{(x)}$$

$$V_{in}^{\mathrm{ESP,B}} = -\sum_{k\in A}^{\mathrm{Occ_A}} S_{kn} V_{ik}^{B}$$

The OEP matrix for density fitted part is given by

$$G_{\eta n}^{B} = \sum_{\eta'\in B}^{\mathrm{Aux_B}} [\mathbf{S}^{-1}]_{\eta\eta'} \left\{ V_{\eta' n}^{B} + \sum_{j\in B}^{\mathrm{Occ_B}} \left[2(\eta' n|jj) - (\eta' j|nj) \right] \right\}$$

The OEP ESP-A charges are fit to reproduce the OEP potential

$$v_{ik}^{A}(\mathbf{r}) \equiv (1-\delta_{ik}) \int \frac{\phi_i(\mathbf{r}')\phi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' - \delta_{ik} \left(\sum_{x\in A} \frac{-Z_x}{|\mathbf{r}-\mathbf{r}_x|} + 2\sum_{k\in A}^{\mathrm{Occ_A}} \int \frac{\phi_k(\mathbf{r}')\phi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' - 2\int \frac{\phi_i(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' \right)$$

so that

$$v_{ik}^{A}(\mathbf{r}) \cong \sum_{x\in A} \frac{q_{ik}^{(x)}}{|\mathbf{r}-\mathbf{r}_x|}$$

The OEP ESP-B charges are fit to reproduce the electrostatic potential of molecule *B* (they are standard ESP charges).

17.10.2 Member Function Documentation

17.10.2.1 double ChargeTransferEnergySolver::compute_benchmark (const std::string & *method* = "DEFAULT") [virtual]

Compute property by using benchmark method.

Each solver object has one `DEFAULT` benchmark method

Parameters

method	- benchmark method

Implements oepdev::OEPDevSolver.

17.10.2.2 double ChargeTransferEnergySolver::compute_oep_based (const std::string & *method* = "DEFAULT") [virtual]

Compute property by using OEP's.

Each solver object has one `DEFAULT` OEP-based method.

Parameters

method	- flavour of OEP model

Implements oepdev::OEPDevSolver.

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

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

17.11 oepdev::CPHF Class Reference

CPHF solver class.

`#include <cphf.h>`

Public Member Functions

- CPHF (SharedWavefunction ref_wfn, Options &options)

  Constructor.
- ∼CPHF ()

  Desctructor.
- void compute (void)

  run the calculations
- void print (void) const

  print to output file
- 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::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

- std::shared_ptr
  < psi::Wavefunction > _wfn

  Wavefunction object.
- std::shared_ptr< Localizer > _localizer

Orbital localizer.

- 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.

- 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.

- std::shared_ptr< BasisSet > _primary

  Primary Basis Set.

- 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::vector< std::shared_ptr
  < oepdev::DIISManager > > _diis

  the DIIS managers for each perturbation operator x, y and z

- Options & _options

  Options.

- 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.

17.11.1 Detailed Description

CPHF solver class.

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`

17.11.2 Constructor & Destructor Documentation

17.11.2.1 oepdev::CPHF::CPHF (SharedWavefunction *ref_wfn*, Options & *options*)

Constructor.

Parameters

ref_wfn	reference HF wavefunction
options	set of Psi4 options

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

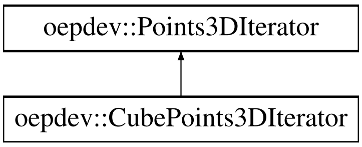
- oepdev/libutil/cphf.h
- oepdev/libutil/cphf.cc

17.12 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

17.12.1 Detailed Description

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

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:

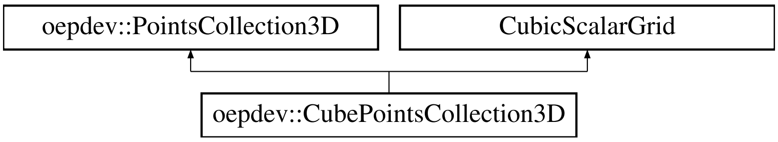
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

17.13 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

17.13.1 Detailed Description

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

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

17.14 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)

17.14.1 Detailed Description

DIIS manager.

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.

17.14.2 Constructor & Destructor Documentation

17.14.2.1 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

17.14.3 Member Function Documentation

17.14.3.1 void oepdev::DIISManager::compute (void)

Perform DIIS interpolation.

17.14.3.2 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

17.14.3.3 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:

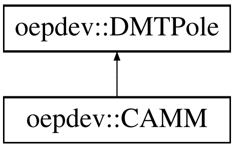
- oepdev/libutil/diis.h
- oepdev/libutil/diis.cc

17.15 oepdev::DMTPole Class Reference

Distributed Multipole Analysis Container and Computer. Abstract Base.

`#include <dmtp.h>`

Inheritance diagram for oepdev::DMTPole:



Public Member Functions

- DMTPole (std::shared_ptr< psi::Molecule > mol, int n)

  Construct an empty DMTP object from the molecule.
- DMTPole (std::shared_ptr< psi::Wavefunction > wfn, int n)

  Construct an empty DMTP object from the wavefunction.
- virtual ~DMTPole ()

  Destructor.
- virtual bool **has_hexadecapoles** () const
- virtual psi::SharedMatrix centres () const

  Get the distribution centres.
- virtual psi::SharedMatrix origins () const

  Get the origins.
- virtual std::vector
  < psi::SharedMatrix > charges () const

  Get the distributed charges, dipoles, quadrupoles, octupoles and hexadecapoles.
- virtual std::vector
  < psi::SharedMatrix > **dipoles** () const
- virtual std::vector
  < psi::SharedMatrix > **quadrupoles** () const

- virtual std::vector
  < psi::SharedMatrix > **octupoles** () const
- virtual std::vector
  < psi::SharedMatrix > **hexadecapoles** () const
- virtual psi::SharedMatrix **charges** (int n) const
- virtual psi::SharedMatrix **dipoles** (int n) const
- virtual psi::SharedMatrix **quadrupoles** (int n) const
- virtual psi::SharedMatrix **octupoles** (int n) const
- virtual psi::SharedMatrix **hexadecapoles** (int n) const
- void **set_charges** (std::vector< psi::SharedMatrix > M)
- void **set_dipoles** (std::vector< psi::SharedMatrix > M)
- void **set_quadrupoles** (std::vector< psi::SharedMatrix > M)
- void **set_octupoles** (std::vector< psi::SharedMatrix > M)
- void **set_hexadecapoles** (std::vector< psi::SharedMatrix > M)
- void **set_charges** (psi::SharedMatrix M, int n)
- void **set_dipoles** (psi::SharedMatrix M, int n)
- void **set_quadrupoles** (psi::SharedMatrix M, int n)
- void **set_octupoles** (psi::SharedMatrix M, int n)
- void **set_hexadecapoles** (psi::SharedMatrix M, int n)
- virtual void compute (psi::SharedMatrix D, int n)=0

  Compute from the one-particle density matrix.
- void compute (std::vector< psi::SharedMatrix > D)

  Compute from the set of the one-particle density matrices.

Static Public Member Functions

- static std::shared_ptr< DMTPole > build (std::shared_ptr< psi::Wavefunction > wfn, const std::string &type="CAMM", int n=1)

  Construct an empty DMTP object from the wavefunction.

Protected Member Functions

- virtual void allocate ()

  Initialize and allocate memory.

Protected Attributes

- std::string name_

  Name.
- psi::SharedMolecule mol_

  Molecule associated with this DMTP.
- psi::SharedWavefunction wfn_

  Wavefunction associated with this DMTP.
- int nDMTPs_

  Number of DMTP's.
- int nCentres_

  Number of distribution centres.
- int nOrigins_

  Number of origins.
- bool **hasHexadecapoles_**
- psi::SharedMatrix centres_

DMTP centres.

- psi::SharedMatrix origins_

  DMTP origins.
- std::vector< psi::SharedMatrix > charges_

  DMTP Multipoles.
- std::vector< psi::SharedMatrix > **dipoles_**
- std::vector< psi::SharedMatrix > **quadrupoles_**
- std::vector< psi::SharedMatrix > **octupoles_**
- std::vector< psi::SharedMatrix > **hexadecapoles_**

17.15.1 Detailed Description

Distributed Multipole Analysis Container and Computer. Abstract Base.

17.15.2 Constructor & Destructor Documentation

17.15.2.1 oepdev::DMTPole::DMTPole (std::shared_ptr< psi::Molecule > *mol*, int *n*)

Construct an empty DMTP object from the molecule.

Type of the DMTP distribution.

Based on this qualifier the number and positions of the distribution centres and origins are determined. `CAMM` - The Cumulative Atomic Multipole Moments `MMM` - The Molecular Multipole Moments `LMTP` - `DMA` - The Distributed Multipole Analysis of Stone `ESP` - Electrostatic potential charges Whether it contains nuclear part or not.

`NucleiIncluded` - Nuclei are included and atomic numbers are added to distributed charges at atomic locations. `NucleiExcluded` - Nuclei are excluded.

17.15.2.2 oepdev::DMTPole::DMTPole (std::shared_ptr< psi::Wavefunction > *wfn*, int *n*)

Construct an empty DMTP object from the wavefunction.

17.15.3 Member Function Documentation

17.15.3.1 std::shared_ptr< DMTPole > oepdev::DMTPole::build (std::shared_ptr< psi::Wavefunction > *wfn*, const std::string & *type* = "CAMM", int *n* = 1) [static]

Construct an empty DMTP object from the wavefunction.

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

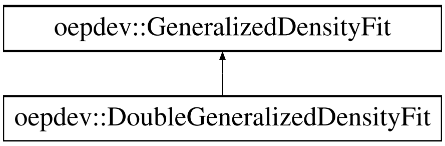
- oepdev/lib3d/dmtp.h
- oepdev/lib3d/dmtp_base.cc

17.16 oepdev::DoubleGeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme - Double Fit.

`#include <oep_gdf.h>`

Inheritance diagram for oepdev::DoubleGeneralizedDensityFit:


oepdev::GeneralizedDensityFit
oepdev::DoubleGeneralizedDensityFit

Public Member Functions

- **DoubleGeneralizedDensityFit** (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::BasisSet > bs_intermediate, std::shared_ptr< psi::Matrix > v_vector)
- std::shared_ptr< psi::Matrix > compute (void)

  Perform the generalized density fit.

Additional Inherited Members

17.16.1 Detailed Description

Generalized Density Fitting Scheme - Double Fit.

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.

17.16.2 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 $\hat{v}$.

17.16.2.1 Theory behind the double GDF scheme

In order to perform the generalized density fitting in an incomplete auxiliary basis set, one must apply the following formula:

$$\mathbf{G} = \mathbf{A}^{-1} \cdot \mathbf{B}$$

where one encounters the need of evaluation of the following *three-electron integrals*

$$B_{\xi i} = (\xi || \hat{v} i) \equiv \iiint d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \phi^*_{\xi}(\mathbf{r}') \frac{1}{|\mathbf{r}' - \mathbf{r}''|} \rho(\mathbf{r}''') \frac{1}{|\mathbf{r}''' - \mathbf{r}''|} \phi_i(\mathbf{r}'')$$

Computation of all the necessery integrals of this kind is very costly and impractical for larger molecules. However, one can use the same trick that is a kernel of the OEP technique introduced in the OEPDev project, i.e., introduce the effective potential in order to get rid of one integration. This can be done by performing the generalized density fitting in the nearly complete intermediate basis

$$\hat{v}|i) \cong \sum_{\varepsilon} H_{\varepsilon i} |\varepsilon)$$

Note that this is done just for the sake of factorizing the triple integral and computing the OEP matrix for the incomplete auxiliary basis. Therefore, the intermediate basis set is used just for a while during density fitting and is no longer necessary later on. By inserting the above identity to the triple integral one can transform it into a sum of the two-electron integrals that are much easier to evaluate. This leads to equations given in the beginning of this section.

17.16.3 Member Function Documentation

17.16.3.1 std::shared_ptr< psi::Matrix > DoubleGeneralizedDensityFit::compute (void) [virtual]

Perform the generalized density fit.

Returns

The OEP coefficients $G_{\xi i}$

Implements oepdev::GeneralizedDensityFit.

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

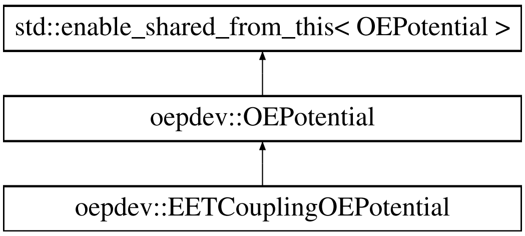
- oepdev/liboep/oep_gdf.h
- oepdev/liboep/oep_gdf.cc

17.17 oepdev::EETCouplingOEPotential Class Reference

Generalized One-Electron Potential for EET coupling calculations.

`#include <oep.h>`

Inheritance diagram for oepdev::EETCouplingOEPotential:


std::enable_shared_from_this< OEPotential >
oepdev::OEPotential
oepdev::EETCouplingOEPotential

Public Member Functions

- **EETCouplingOEPotential** (SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate, Options &options)
- **EETCouplingOEPotential** (SharedWavefunction wfn, Options &options)
- 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

Additional Inherited Members

17.17.1 Detailed Description

Generalized One-Electron Potential for EET coupling calculations.

Contains the following OEP types:

- `Fujimoto.ET1`
- `Fujimoto.ET2`
- `Fujimoto.HT1`
- `Fujimoto.HT1`
- `Fujimoto.HT2`
- `Fujimoto.CT1`
- `Fujimoto.CT2`

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

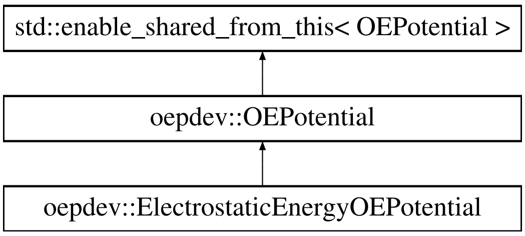
- oepdev/liboep/oep.h
- oepdev/liboep/oep_coupling_eet.cc

17.18 oepdev::ElectrostaticEnergyOEPotential Class Reference

Generalized One-Electron Potential for Electrostatic Energy.

`#include <oep.h>`

Inheritance diagram for oepdev::ElectrostaticEnergyOEPotential:


std::enable_shared_from_this< OEPotential >
oepdev::OEPotential
oepdev::ElectrostaticEnergyOEPotential

Public Member Functions

- ElectrostaticEnergyOEPotential (SharedWavefunction wfn, Options &options)

  Only ESP-based potential is worth implementing.
- 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

Additional Inherited Members

17.18.1 Detailed Description

Generalized One-Electron Potential for Electrostatic Energy.

Contains the following OEP types:

- `V`

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

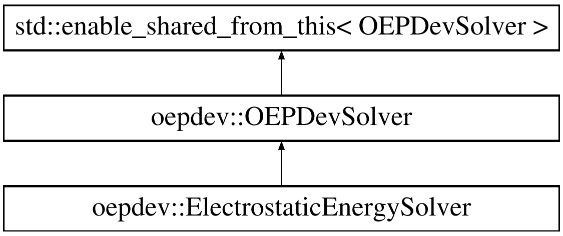
- oepdev/liboep/oep.h
- oepdev/liboep/oep_energy_coul.cc

17.19 oepdev::ElectrostaticEnergySolver Class Reference

Compute the Coulombic interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::ElectrostaticEnergySolver:


std::enable_shared_from_this< OEPDevSolver >
oepdev::OEPDevSolver
oepdev::ElectrostaticEnergySolver

Public Member Functions

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

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

  Compute property by using benchmark method.

Additional Inherited Members

17.19.1 Detailed Description

Compute the Coulombic interaction energy between unperturbed wavefunctions.

The implemented methods are shown in below

Keyword	Method Description
Benchmark Methods	
`AO_EXPANDED`	∗Default∗. Exact Coulombic energy from atomic orbital expansions.
`MO_EXPANDED`	Exact Coulombic energy from molecular orbital expansions
OEP-Based Methods	
`ESP_SYMMETRIZED`	∗Default∗. Coulombic energy from ESP charges interacting with nuclei and electronic density. Symmetrized with respect to monomers.

Table 17.2: Methods available in the Solver

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

$$E^{\rm Nuc-Nuc} = \sum_{x\in A}\sum_{y\in B} \frac{Z_x Z_y}{|\mathbf{r}_x - \mathbf{r}_y|}$$

the nuclear-electronic attraction energy is

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

and the electron-electron repulsion energy is

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

In the above equations,

$$V_{\lambda\sigma}^{(x)} \equiv \int \frac{\varphi_\lambda^*(\mathbf{r})\varphi_\sigma(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_x|} d\mathbf{r}$$

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

$$E^{\rm Nuc-Nuc} = \sum_{x\in A}\sum_{y\in B}\frac{Z_xZ_y}{|\mathbf{r}_x-\mathbf{r}_y|}$$

the nuclear-electronic attraction energy is

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

and the electron-electron repulsion energy is

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

OEP-Based Methods

Coulombic energy from ESP charges interacting with nuclei and electronic density.

In this approach, nuclear and electronic density of either species is approximated by ESP charges. In order to achieve symmetric expression, the interaction is computed twice (ESP of A interacting with density matrix and nuclear charges of B and vice versa) and then divided by 2. Thus,

$$E^{\rm Coul} \approx \frac{1}{2}\left[\sum_{x\in A}\sum_{y\in B}\frac{Z_xq_y}{|\mathbf{r}_x-\mathbf{r}_y|} + \sum_{y\in B}\sum_{\mu\nu\in A} q_yV_{\mu\nu}^{(y)}\left(D_{\mu\nu}^{(\alpha)}+D_{\mu\nu}^{(\beta)}\right) + \sum_{y\in B}\sum_{x\in A}\frac{q_xZ_y}{|\mathbf{r}_x-\mathbf{r}_y|} + \sum_{x\in A}\sum_{\lambda\sigma\in B} q_xV_{\lambda\sigma}^{(x)}\left(D_{\lambda\sigma}^{(\alpha)}+D_{\lambda\sigma}^{(\beta)}\right)\right]$$

If the basis set is large and the number of ESP centres $q_{x(y)}$ is sufficient, the sum of first two contributions equals the sum of the latter two contributions.

Notes:

- This solver also computes and prints the ESP-ESP point charge interaction energy,

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

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

17.19.2 Member Function Documentation

17.19.2.1 double ElectrostaticEnergySolver::compute_benchmark (const std::string & *method* = `"DEFAULT"`) `[virtual]`

Compute property by using benchmark method.

Each solver object has one `DEFAULT` benchmark method

Parameters

method	- benchmark method

Implements oepdev::OEPDevSolver.

17.19.2.2 double ElectrostaticEnergySolver::compute_oep_based (const std::string & *method* = `"DEFAULT"`) `[virtual]`

Compute property by using OEP's.

Each solver object has one `DEFAULT` OEP-based method.

Parameters

method	- flavour of OEP model

Implements oepdev::OEPDevSolver.

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

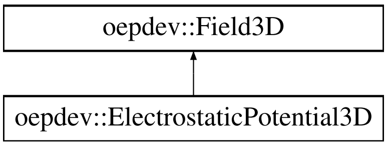
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_energy_coul.cc

17.20 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

17.20.1 Detailed Description

Electrostatic potential of a molecule.

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:

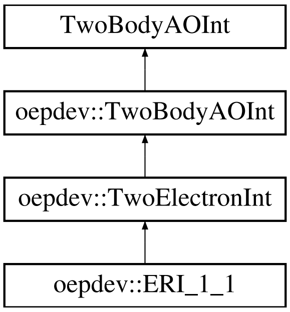
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

17.21 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)

17.21.1 Detailed Description

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

ERI's are computed for a shell doublet (P|Q) and stored in the `target_full_` buffer, accessible through `buffer()` method:

$$\begin{aligned}&\text{For each } (n_1,l_1,m_1)\in P:\\ &\quad\text{For each } (n_2,l_2,m_2)\in Q:\\ &\quad\quad \text{ERI} = (A|B)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}]\end{aligned}$$

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

17.21.2 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:

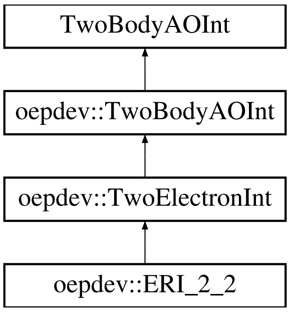
- oepdev/libints/eri.h
- oepdev/libints/eri.cc

17.22 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)

17.22.1 Detailed Description

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

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.

17.22.2 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:

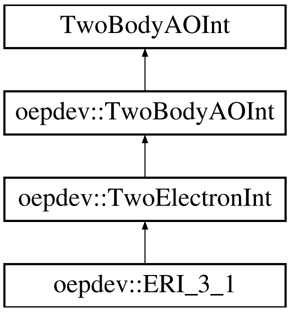
- oepdev/libints/eri.h
- oepdev/libints/eri.cc

17.23 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)

17.23.1 Detailed Description

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

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.

17.23.2 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

$$\begin{aligned}(ijk|l)[\{\alpha\},\mathbf{n},\mathbf{l},\mathbf{m}] &= E_{ijk}(\alpha_1,\alpha_2,\alpha_3)\\ &\times \sum_{N_1=0}^{n_1+n_2+n_3}\sum_{L_1=0}^{l_1+l_2+l_3}\sum_{M_1=0}^{m_1+m_2+m_3}\sum_{N_2=0}^{n_4}\sum_{L_2=0}^{l_4}\sum_{M_2=0}^{m_4} d_{N_1}^{n_1n_2n_3} d_{L_1}^{l_1l_2l_3} d_{M_1}^{m_1m_2m_3} d_{N_2}^{n_4} d_{L_2}^{l_4} d_{M_2}^{m_4} [N_1L_1M_1|N_2L_2M_2]\end{aligned}$$

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

17.24 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.

17.24.1 Detailed Description

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

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

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

The charges are subject to the following constraint:

$$\sum_m q_{m;p} = Q_p \text{ for all } p$$

Method description.

M generalized charges is found by solving the matrix equation

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

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

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

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

In the above equation, summations run over all sample points, at which reference potential is known. The solution is stored in the $M\times N$ matrix, where N is the dimensionality of the 3D vector field (i.e., the number of potentials supplied, $p_{\rm max}$). As a default, $Q_p = 0$ for all potentials. This can be set by `oepdev::ESPSolver::set_charge_sums` method.

Note

Useful options:

- `ESP_PAD_SPHERE` - Padding spherical radius for random points selection. Default: `10.0` [A.U.]
- `ESP_NPOINTS_PER_ATOM` - Number of random points per atom in a molecule. Default: `1500`
- `ESP_VDW_RADIUS_C` - The vdW radius for carbon atom. Default: `3.0` [A.U.]
- `ESP_VDW_RADIUS_H` - The vdW radius for hydrogen atom. Default: `4.0` [A.U.]
- `ESP_VDW_RADIUS_N` - The vdW radius for nitrogen atom. Default: `2.4` [A.U.]
- `ESP_VDW_RADIUS_O` - The vdW radius for oxygen atom. Default: `5.6` [A.U.]
- `ESP_VDW_RADIUS_F` - The vdW radius for fluorium atom. Default: `2.3` [A.U.]
- `ESP_VDW_RADIUS_CL` - The vdW radius for chlorium atom. Default: `2.9` [A.U.]

17.24.2 Constructor & Destructor Documentation

17.24.2.1 oepdev::ESPSolver::ESPSolver (SharedField3D *field*)

Construct from 3D vector field.

Assume that the centres are on atoms associated with the 3D vector field.

Parameters

field	- oepdev 3D vector field object

17.24.2.2 oepdev::ESPSolver::ESPSolver (SharedField3D *field,* psi::SharedMatrix *centres*)

Construct from 3D vector field.

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:

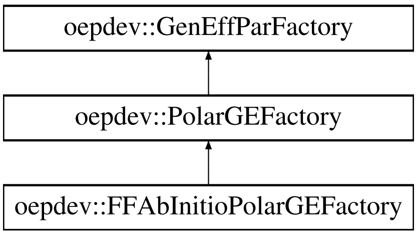
- oepdev/lib3d/esp.h
- oepdev/lib3d/esp.cc

17.25 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

17.25.1 Detailed Description

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

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

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

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

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

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:

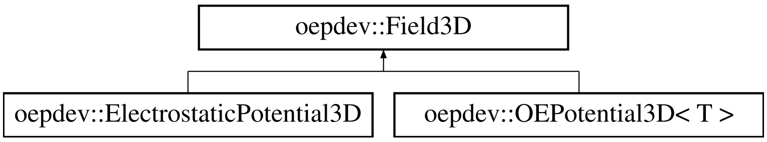
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_ffabinitio.cc

17.26 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?

17.26.1 Detailed Description

General Vector Dield in 3D Space. Abstract base.

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`

17.26.2 Constructor & Destructor Documentation

17.26.2.1 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 cube grid by providing wavefunction.

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);

17.26.3 Member Function Documentation

17.26.3.1 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]`

Build 3D field of random points. vdW volume is excluded.

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

17.26.3.2 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]`

Build 3D field of points on a g09-cube grid.

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

17.27 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**

17.27.1 Detailed Description

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

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

- oepdev/libutil/unitary_optimizer.h

17.28 oepdev::GenEffFrag Class Reference

Generalized Effective Fragment. Container Class.

`#include <gefp.h>`

Public Member Functions

- GenEffFrag ()

  Initialize with default name of GEFP (Default)
- GenEffFrag (std::string name)

  Initialize with custom name of GEFP.
- ∼GenEffFrag ()

  Destruct.
- 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 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.
- 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

- std::map< std::string,
  std::shared_ptr< GenEffPar > > parameters

  Dictionary of All GEF Parameters.

Protected Attributes

- std::string name_

  Name of GEFP.
- std::shared_ptr< GenEffPar > densityMatrixSusceptibilityGEF_

  Density Matrix Susceptibility Tensor.
- std::shared_ptr< GenEffPar > electrostaticEnergyGEF_

  Electrostatic Energy Effective One-Electron Potential.
- std::shared_ptr< GenEffPar > repulsionEnergyGEF_

  Exchange-Repulsion Effective One-Electron Potential.
- std::shared_ptr< GenEffPar > chargeTransferEnergyGEF_

  Charge-Transfer Effective One-Electron Potential.
- std::shared_ptr< GenEffPar > EETCouplingConstantGEF_

  EET Coupling Effective One-Electron Potential.

17.28.1 Detailed Description

Generalized Effective Fragment. Container Class.

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

17.28.2 Member Function Documentation

17.28.2.1 std::shared_ptr<psi::Matrix> oepdev::GenEffFrag::susceptibility (int *fieldRank*, int *fieldGradientRank*, int *i*, int *x*) const [inline]

Grab the Density Matrix Susceptibility.

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

17.28.2.2 std::vector<std::shared_ptr<psi::Matrix> > oepdev::GenEffFrag::susceptibility (int *fieldRank*, int *fieldGradientRank*, int *i*) const [inline]

Grab the Density Matrix Susceptibility.

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

17.28.2.3 std::vector<std::vector<std::shared_ptr<psi::Matrix> > > oepdev::GenEffFrag::susceptibility (int *fieldRank*, int *fieldGradientRank*) const [inline]

Grab the Density Matrix Susceptibility.

Parameters

fieldRank	- power dependency with respect to the electric field
fieldGradientRank	- power dependency with respect to the electric field gradient

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

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

17.29 oepdev::GenEffPar Class Reference

Generalized Effective Fragment Parameters. Container Class.

`#include <gefp.h>`

Public Member Functions

- GenEffPar (std::string name)

  Create with name of this parameter type.
- ∼GenEffPar ()

  Destruct.
- 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.
- 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.
- bool **hasDensityMatrixDipolePolarizability** () const
- bool **hasDensityMatrixDipoleDipoleHyperpolarizability** () const
- bool **hasDensityMatrixQuadrupolePolarizability** () const
- 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.
- 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

- std::string name_

  The Name of Parameter Type.
- 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.
- std::vector< std::shared_ptr
  < psi::Vector > > distributedCentres_

  The Positions of the Distributed Centres.
- bool **hasDensityMatrixDipolePolarizability_**
- bool **hasDensityMatrixDipoleDipoleHyperpolarizability_**
- bool **hasDensityMatrixQuadrupolePolarizability_**

17.29.1 Detailed Description

Generalized Effective Fragment Parameters. Container Class.

17.29.2 Member Function Documentation

17.29.2.1 void oepdev::GenEffPar::allocate (int *fieldRank*, int *fieldGradientRank*, int *nsites*, int *nbf*) [inline]

Allocate the Density Matrix Susceptibility.

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 $\nabla \otimes \mathbf{F}$

17.29.2.2 std::shared_ptr< psi::Matrix > oepdev::GenEffPar::compute_density_matrix (std::shared_ptr< psi::Vector > *field*)

Compute the density matrix due to the uniform electric field perturbation.

Parameters

field	- the uniform electric field vector (A.U.)

17.29.2.3 std::shared_ptr< psi::Matrix > oepdev::GenEffPar::compute_density_matrix (double *fx*, double *fy*, double *fz*)

Compute the density matrix due to the uniform electric field perturbation.

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.)

17.29.2.4 std::shared_ptr< psi::Matrix > oepdev::GenEffPar::compute_density_matrix (std::vector< std::shared_ptr< psi::Vector >> *fields*)

Compute the density matrix due to the non-uniform electric field perturbation.

Parameters

fields	- the list of non-uniform electric field vector (A.U.) evaluated at the distributed DMatPol sites

17.29.2.5 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*)

Compute the density matrix due to the non-uniform electric field perturbation.

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

17.29.2.6 void oepdev::GenEffPar::set_susceptibility (int *fieldRank,* int *fieldGradientRank,* const std::vector< std::vector< std::shared_ptr< psi::Matrix >>> & *susc*) [inline]

Set the Density Matrix Susceptibility.

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 $\nabla \otimes \mathbf{F}$

17.29.2.7 std::shared_ptr<psi::Matrix> oepdev::GenEffPar::susceptibility (int *fieldRank,* int *fieldGradientRank,* int *i,* int *x*) const [inline]

Grab the Density Matrix Susceptibility.

Parameters

fieldRank	- power dependency with respect to the electric field
fieldGradientRank	- power dependency with respect to the electric field gradient

i	- id of the distributed site
x	- id of the composite Cartesian component

The following susceptibilities are supported (fieldRank, fieldGradientRank):

- (1, 0) - dipole polarizability, interacts with $\mathbf{F}$
- (2, 0) - dipole-dipole hyperpolarizability, interacts with $\mathbf{F} \otimes \mathbf{F}$
- (0, 1) - quadrupole polarizability, interacts with $\nabla \otimes \mathbf{F}$

The distributed sites are assumed to be atomic sites or molecular orbital centroids (depending on the polarization factory used). For the electric field, the composite Cartesian index is just an ordinary Cartesian index. For the electric field gradient and electric field squared, the composite Cartesian index is given as

$$I(x,y) = 3x + y$$

where the values of 0, 1 and 2 correspond to *x*, *y* and *z* Cartesian components, respectively. Therefore, in the latter case, there is 9 distinct composite Cartesian components.

17.29.2.8 std::vector<std::shared_ptr<psi::Matrix> > oepdev::GenEffPar::susceptibility (int *fieldRank,* int *fieldGradientRank,* int *i*) const [inline]

Grab the Density Matrix Susceptibility.

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).

17.29.2.9 std::vector<std::vector<std::shared_ptr<psi::Matrix> > > oepdev::GenEffPar::susceptibility (int *fieldRank,* int *fieldGradientRank*) const [inline]

Grab the Density Matrix Susceptibility.

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 $\nabla \otimes \mathbf{F}$

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

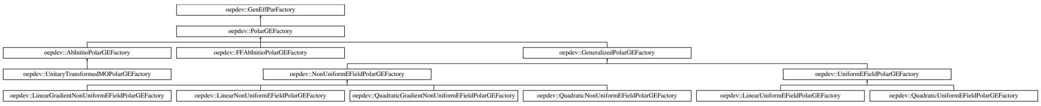
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp.cc

17.30 oepdev::GenEffParFactory Class Reference

Generalized Effective Fragment Factory. Abstract Base.

`#include <gefp.h>`

Inheritance diagram for oepdev::GenEffParFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::AbInitioPolarGEFactory
oepdev::FFAbInitioPolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UnitaryTransformedMOPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

Public Member Functions

- GenEffParFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

  Construct from wavefunction and Psi4 options.
- virtual ∼GenEffParFactory ()

  Destruct.
- virtual std::shared_ptr
  < GenEffPar > compute (void)=0

  Compute the fragment parameters.
- virtual std::shared_ptr
  < psi::Wavefunction > wfn (void) const

  Grab wavefunction.
- virtual psi::Options & options (void) const

  Grab options.
- std::shared_ptr< CPHF > cphf_solver () const

  Grab the CPHF object.

Static Public Member Functions

- 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.

Protected Member Functions

- 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.
- virtual bool is_in_vdWsphere (double x, double y, double z) const

  Is the point inside a vdW region?

Protected Attributes

- std::shared_ptr
  < psi::Wavefunction > wfn_

  Wavefunction.

- psi::Options & options_

  Psi4 Options.
- std::default_random_engine randomNumberGenerator_

  Random number generators.
- std::uniform_real_distribution
  < double > **randomDistribution_**
- std::shared_ptr< psi::Matrix > excludeSpheres_

  Matrix with vdW sphere information.
- std::map< std::string, double > vdwRadius_

  Map with vdW radii.
- double cx_

  Centre-of-mass coordinates.
- double **cy_**
- double **cz_**
- double radius_

  Radius of padding sphere around the molecule.
- const int nbf_

  Number of basis functions.
- std::shared_ptr< CPHF > cphfSolver_

  The CPHF object.
- std::shared_ptr
  < oepdev::GenEffParFactory > abInitioPolarizationSusceptibilitiesFactory_

  Ab initio polarization susceptibility factory.

17.30.1 Detailed Description

Generalized Effective Fragment Factory. Abstract Base.

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

17.30.2 Member Function Documentation

17.30.2.1 std::shared_ptr< **oepdev::GenEffParFactory** > oepdev::GenEffParFactory::build (const std::string & *type*, std::shared_ptr< psi::Wavefunction > *wfn*, psi::Options & *opt*) `[static]`

Build Density Matrix Susceptibility Generalized Factory.

Parameters

type	- Type of factory
wfn	- Psi4 wavefunction
opt	- Psi4 options

Available factory types:

- `POLARIZATION` - creates the polarization generalized effective fragment parameters' factory Factory sub-type 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:

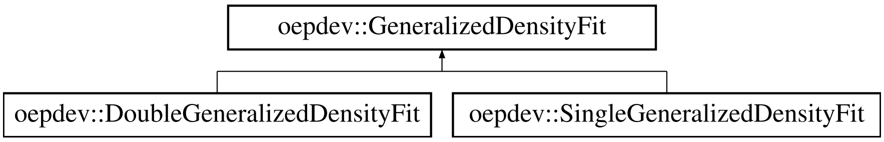
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp.cc

17.31 oepdev::GeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme. Abstract Base.

`#include <oep_gdf.h>`

Inheritance diagram for oepdev::GeneralizedDensityFit:


oepdev::GeneralizedDensityFit
oepdev::DoubleGeneralizedDensityFit
oepdev::SingleGeneralizedDensityFit

Public Member Functions

- GeneralizedDensityFit ()

  Constructor. Initializes the pointers.
- virtual ∼GeneralizedDensityFit ()

  Destructor.
- virtual std::shared_ptr
  < psi::Matrix > compute (void)=0

  Perform the generalized density fit.
- std::shared_ptr< psi::Matrix > G (void) const

  Extract the $G_{\xi i}$ coefficients.

Static Public Member Functions

- static std::shared_ptr
  < GeneralizedDensityFit > build (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::Matrix > v_vector)

  Factory for Single GDF Computer.
- static std::shared_ptr
  < GeneralizedDensityFit > build (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::BasisSet > bs_intermediate, std::shared_ptr< psi::Matrix > v_vector)

  Factory for Double GDF Computer.

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.

17.31.1 Detailed Description

Generalized Density Fitting Scheme. Abstract Base.

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.

17.31.2 Member Function Documentation

17.31.2.1 std::shared_ptr< **GeneralizedDensityFit** > GeneralizedDensityFit::build (std::shared_ptr< psi::BasisSet > *bs_auxiliary*, std::shared_ptr< psi::Matrix > *v_vector*) `[static]`

Factory for Single GDF Computer.

Parameters

bs_auxiliary	- auxiliary basis set
v_vector	- the matrix with $V_{\xi i}$ elements

Returns

Generalized Density Fit Computer.

17.31.2.2 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]`

Factory for Double GDF Computer.

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.

17.31.2.3 std::shared_ptr< psi::Matrix > GeneralizedDensityFit::compute (void) `[pure virtual]`

Perform the generalized density fit.

Returns

The OEP coefficients $G_{\xi i}$

Implemented in oepdev::DoubleGeneralizedDensityFit, and oepdev::SingleGeneralizedDensityFit.

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

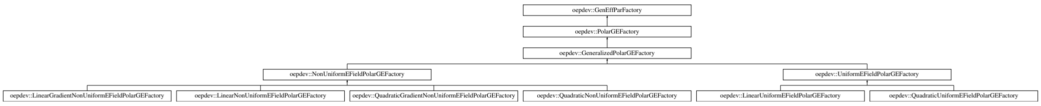
- oepdev/liboep/oep_gdf.h
- oepdev/liboep/oep_gdf.cc

17.32 oepdev::GeneralizedPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::GeneralizedPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

Classes

- struct StatisticalSet

  A structure to handle statistical data.

Public Member Functions

- GeneralizedPolarGEFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

  Construct from Psi4 wavefunction and options.
- virtual ~GeneralizedPolarGEFactory ()

  Destruct.
- virtual std::shared_ptr
  < GenEffPar > compute (void)

  Pefrorm Least-Squares Fit.
- bool has_dipole_polarizability () const

  Dipole Polarizability (interacting with $\mathbf{F}$*)*
- bool has_dipole_dipole_hyperpolarizability () const

  Dipole-Dipole Hyperpolarizability (interacting with $\mathbf{F}^2$*)*
- bool has_quadrupole_polarizability () const

  Quadrupole Polarizability (interacting with $\nabla \otimes \mathbf{F}$*)*
- bool has_ab_initio_dipole_polarizability () const

  Ab Initio Dipole Polarizability (interacting with $\mathbf{F}$*)*
- double Zinit () const

  Grab initial summaric Z value.
- double Z () const

  Grab final summaric Z value.

Protected Member Functions

- void allocate (void)

  Allocate memory.
- void invert_hessian (void)

  Invert Hessian (do also the identity test)
- void compute_electric_field_sums (void)

  Compute electric field sum set.
- void compute_electric_field_gradient_sums (void)

  Compute electric field gradient sum set.
- void compute_statistics (void)

  Run the statistical evaluation of results.
- void set_distributed_centres (void)

  Set the distributed centres.
- void compute_parameters (void)

  Compute the parameters.
- void fit (void)

Perform least-squares fit.
- void compute_ab_initio (void)

  Compute ab initio parameters.
- void save (int i, int j)

  Save susceptibility tensors associated with the i-th and j-th basis set function.
- virtual void compute_samples (void)=0

  Compute samples of density matrices and select electric field distributions.
- virtual void compute_gradient (int i, int j)=0

  Compute Gradient vector associated with the i-th and j-th basis set function.
- virtual void compute_hessian (void)=0

  Compute Hessian matrix (independent on the parameters)

Protected Attributes

- int nBlocks_

  Number of parameter blocks.
- int nSites_

  Number of distributed sites.
- int nSitesAbInitio_

  Number of distributed sites of Ab Initio model (FF - single site (com); distributed: LMO sites)
- int nParameters_

  Dimensionality of entire parameter space.
- std::vector< int > nParametersBlock_

  Dimensionality of parameter space per block.
- const int nSamples_

  Number of statistical samples.
- const double symmetryNumber_ [6]

  Symmetry number for matrix susceptibilities.
- std::shared_ptr< psi::Matrix > Gradient_

  Gradient.
- std::shared_ptr< psi::Matrix > Hessian_

  Hessian.
- std::shared_ptr< psi::Matrix > Parameters_

  Parameters.
- std::shared_ptr
  < oepdev::GenEffPar > PolarizationSusceptibilities_

  Density Matrix Susceptibility Tensors Object.
- std::shared_ptr
  < oepdev::GenEffPar > abInitioPolarizationSusceptibilities_

  Density Matrix Susceptibility Tensors Object for Ab Initio Model.
- bool hasDipolePolarizability_

  Has Dipole Polarizability?
- bool hasDipoleDipoleHyperpolarizability_

  Has Dipole-Dipole Hyperpolarizability?
- bool hasQuadrupolePolarizability_

  Has Quadrupole Polarizability?
- bool hasAbInitioDipolePolarizability_

  Has Ab Initio Dipole Polarizability?
- StatisticalSet referenceStatisticalSet_

  Reference statistical data.
- StatisticalSet referenceDpolStatisticalSet_

Multipole reference statistical data.

- StatisticalSet modelStatisticalSet_

  Model statistical data.

- StatisticalSet abInitioModelStatisticalSet_

  Ab Initio Model statistical data.

- std::vector< std::shared_ptr < psi::Matrix > > VMatrixSet_

  Potential matrix set.

- std::vector< std::vector < std::shared_ptr< Vector > > > electricFieldSet_

  Electric field set.

- std::vector< std::vector < std::shared_ptr< Matrix > > > electricFieldGradientSet_

  Electric field gradient set.

- std::vector< std::vector < double > > electricFieldSumSet_

  Electric field sum set.

- std::vector< std::vector < std::shared_ptr< psi::Vector > > > 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

17.32.1 Detailed Description

Polarization GEFP Factory with Least-Squares Parameterization.

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

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

where:

- $\mathbf{B}_{i;\alpha\beta}^{(10)}$ is the density matrix dipole polarizability
- $\mathbf{B}_{i;\alpha\beta}^{(20)}$ is the density matrix dipole-dipole hyperpolarizability
- $\mathbf{B}_{i;\alpha\beta}^{(01)}$ is the density matrix quadrupole polarizability

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

Available models:

1. Training against uniform electric fields
    - oepdev::LinearUniformEFieldPolarGEFactory - linear with respect to electric field
    - oepdev::QuadraticUniformEFieldPolarGEFactory - quadratic with respect to electric field
2. Training against non-uniform electric fields
    - oepdev::LinearNonUniformEFieldPolarGEFactory - linear with respect to electric field, distributed site model
    - oepdev::QuadraticNonUniformEFieldPolarGEFactory - quadratic with respect to electric field, distributed site model
    - oepdev::LinearGradientNonUniformEFieldPolarGEFactory - linear with respect to electric field and linear with respect to electric field gradient, distributed site model. This model does not function now.
    - oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory - linear with respect to electric field and linear with respect to electric field gradient, distributed site model. This model does not function now.

For the non-linear field training, a set of point charges in each training sample is assumed. Distributed models use atomic centers as expansion points.

Determination of the generalized susceptibilities

Let $\left\{\mathbf{F}^{(1)}(\mathbf{r}),\mathbf{F}^{(2)}(\mathbf{r}),\ldots,\mathbf{F}^{(N)}(\mathbf{r}),\ldots\right\}$ be a set of $N_{\rm max}$ 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, $\mathbf{s} = \left(\mathbf{s}^{[1]} \quad \mathbf{s}^{[2]} \quad \cdots\right)^{\rm T}$, 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

$$
\begin{aligned}
g^{[r]} &\equiv \frac{\partial Z}{\partial s^{[r]}} = -2\sum_N \overline{\delta D}^{(N)} \frac{\partial \left[\delta D^{(N)}\right]}{\partial s^{[r]}} \; , \\
H^{[rs]} &\equiv \frac{\partial^2 Z}{\partial s^{[r]} \partial s^{[s]}} = 2\sum_N \frac{\partial \left[\delta D^{(N)}\right]}{\partial s^{[r]}} \frac{\partial \left[\delta D^{(N)}\right]}{\partial s^{[s]}} \; .
\end{aligned}
$$

The explicit formulae for the gradient are

$$
\begin{aligned}
g^{[1]}_{ku} &= -2\sum_N \overline{\delta D}^{(N)} F^{(N)}_{ku} \; , \\
g^{[2]}_{kuw} &= -2 r_{uw} \sum_N \overline{\delta D}^{(N)} F^{(N)}_{ku} F^{(N)}_{kw} \; .
\end{aligned}
$$

The Hessian subsequently follows to be %

$$
\begin{aligned}
H^{[11]}_{ku,lw} &= 2\sum_N F^{(N)}_{ku} F^{(N)}_{lw} \; , \\
H^{[12]}_{ku,lu'w'} &= 2 r_{u'w'} \sum_N F^{(N)}_{ku} F^{(N)}_{lu'} F^{(N)}_{lw'} \; , \\
H^{[22]}_{kuw,lu'w'} &= 2 r_{uw} r_{u'w'} \sum_N F^{(N)}_{ku} F^{(N)}_{kw} F^{(N)}_{lu'} F^{(N)}_{lw'} \; .
\end{aligned}
$$

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:

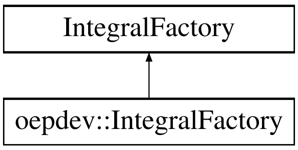
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_base.cc

17.33 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 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.

17.33.1 Detailed Description

Extended IntegralFactory for computing integrals.

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:

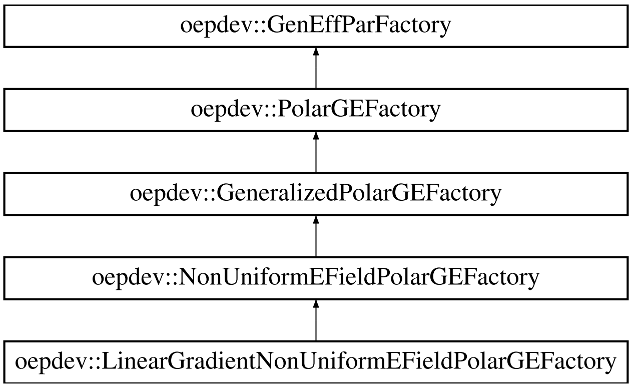
- oepdev/libpsi/integral.h
- oepdev/libpsi/integral.cc

17.34 oepdev::LinearGradientNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::LinearGradientNonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory

Public Member Functions

- **LinearGradientNonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  Compute Gradient vector associated with the i-th and j-th basis set function.
- void compute_hessian (void)

  Compute Hessian matrix (independent on the parameters)

Additional Inherited Members

17.34.1 Detailed Description

Polarization GEFP Factory with Least-Squares Parameterization.

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:

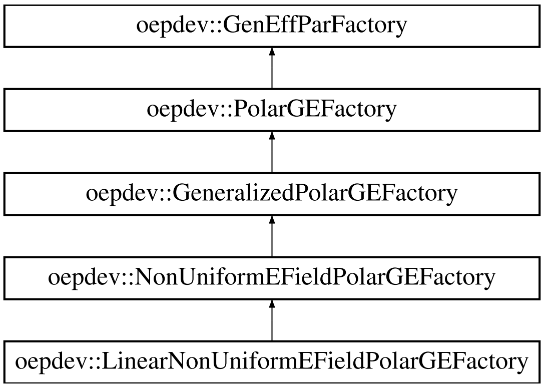
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_1_grad_1.cc

17.35 oepdev::LinearNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::LinearNonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory

Public Member Functions

- **LinearNonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  Compute Gradient vector associated with the i-th and j-th basis set function.
- void compute_hessian (void)

  Compute Hessian matrix (independent on the parameters)

Additional Inherited Members

17.35.1 Detailed Description

Polarization GEFP Factory with Least-Squares Parameterization.

Implements the generalized density matrix susceptibility model of the form

$$\delta D_{\alpha\beta} \approx \sum_i \mathbf{B}^{(10)}_{i;\alpha\beta} \cdot \mathbf{F}(\mathbf{r}_i)$$

where:

- $\mathbf{B}^{(10)}_{i;\alpha\beta}$ 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:

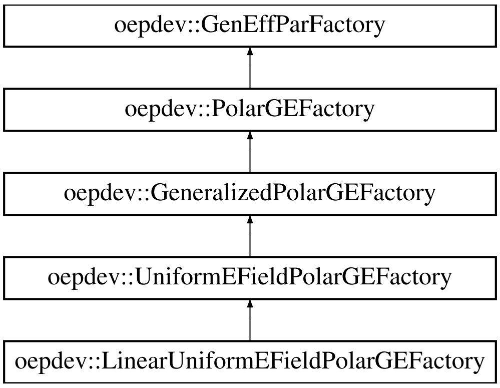
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_1.cc

17.36 oepdev::LinearUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::LinearUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory

Public Member Functions

- **LinearUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  Compute Gradient vector associated with the i-th and j-th basis set function.
- void compute_hessian (void)

  Compute Hessian matrix (independent on the parameters)

Additional Inherited Members

17.36.1 Detailed Description

Polarization GEFP Factory with Least-Squares Parameterization.

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:

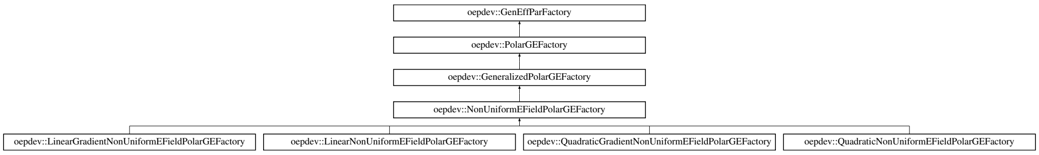
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_uniform_field_1.cc

17.37 oepdev::NonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::NonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory

Public Member Functions

- **NonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_samples (void)

  Compute samples of density matrices and select electric field distributions.
- virtual void compute_gradient (int i, int j)=0

  Compute Gradient vector associated with the i-th and j-th basis set function.
- virtual void compute_hessian (void)=0

  Compute Hessian matrix (independent on the parameters)

Additional Inherited Members

17.37.1 Detailed Description

Polarization GEFP Factory with Least-Squares Parameterization.

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:

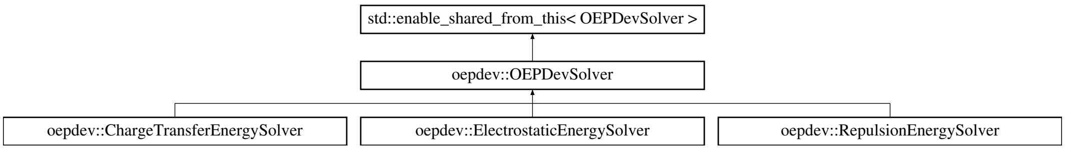
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_base.cc

17.38 oepdev::OEPDevSolver Class Reference

Solver of properties of molecular aggregates. Abstract base.

`#include <solver.h>`

Inheritance diagram for oepdev::OEPDevSolver:


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

Public Member Functions

- OEPDevSolver (SharedWavefunctionUnion wfn_union)

  Take wavefunction union and initialize the Solver.
- virtual ∼OEPDevSolver ()

  Destructor.
- virtual double compute_oep_based (const std::string &method="DEFAULT")=0

  Compute property by using OEP's.
- virtual double compute_benchmark (const std::string &method="DEFAULT")=0

  Compute property by using benchmark method.

Static Public Member Functions

- static std::shared_ptr
  < OEPDevSolver > build (const std::string &target, SharedWavefunctionUnion wfn_union)

  Build a solver of a particular property for given molecular cluster.

Protected Attributes

- SharedWavefunctionUnion wfn_union_

  Wavefunction union.
- 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.

17.38.1 Detailed Description

Solver of properties of molecular aggregates. Abstract base.

Uses only a wavefunction union object to initialize. Available solvers:

- `ELECTROSTATIC ENERGY`
- `REPULSION ENERGY`
- `CHARGE TRANSFER ENERGY`

Options controlling the generalized density fitting (GDF):

- `OEPDEV_DF_TYPE` - type of the GDF. Default: `DOUBLE`.
- `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.

17.38.2 Constructor & Destructor Documentation

17.38.2.1 OEPDevSolver::OEPDevSolver (SharedWavefunctionUnion *wfn_union*)

Take wavefunction union and initialize the Solver.

Parameters

wfn_union	- wavefunction union of isolated molecular wavefunctions

17.38.3 Member Function Documentation

17.38.3.1 std::shared_ptr< **OEPDevSolver** > OEPDevSolver::build (const std::string & *target*, SharedWavefunctionUnion *wfn_union*) `[static]`

Build a solver of a particular property for given molecular cluster.

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

17.38.3.2 double OEPDevSolver::compute_benchmark (const std::string & *method* = `"DEFAULT"`) `[pure virtual]`

Compute property by using benchmark method.

Each solver object has one `DEFAULT` benchmark method

Parameters

method	- benchmark method

Implemented in oepdev::ChargeTransferEnergySolver, oepdev::RepulsionEnergySolver, and oepdev::ElectrostaticEnergySolver.

17.38.3.3 double OEPDevSolver::compute_oep_based (const std::string & *method* = `"DEFAULT"`) `[pure virtual]`

Compute property by using OEP's.

Each solver object has one `DEFAULT` OEP-based method.

Parameters

method	- flavour of OEP model

Implemented in oepdev::ChargeTransferEnergySolver, oepdev::RepulsionEnergySolver, and oepdev::ElectrostaticEnergySolver.

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

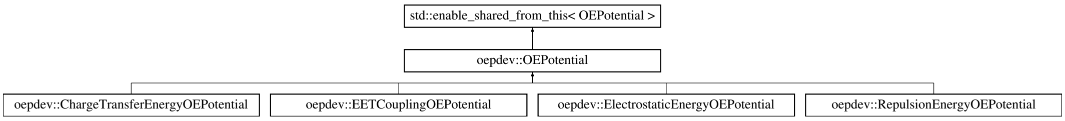
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_base.cc
- oepdev/libsolver/solver_energy_pauli.cc

17.39 oepdev::OEPotential Class Reference

Generalized One-Electron Potential: Abstract base.

`#include <oep.h>`

Inheritance diagram for oepdev::OEPotential:


std::enable_shared_from_this< OEPotential >
oepdev::OEPotential
oepdev::ChargeTransferEnergyOEPotential
oepdev::EETCouplingOEPotential
oepdev::ElectrostaticEnergyOEPotential
oepdev::RepulsionEnergyOEPotential

Public Member Functions

- OEPotential (SharedWavefunction wfn, Options &options)

  Fully ESP-based OEP object.
- OEPotential (SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate, Options &options)

  General OEP object.
- 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 rotate (const Matrix &rotmat)

  Rotate.
- virtual void translate (const Vector &trans)

  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 in a matrix form.
- SharedWavefunction wfn () const

  Retrieve wavefunction object.
- void **set_name** (const std::string &name)
- virtual void **print_header** () const =0

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.

Protected Attributes

- Options options_

  Psi4 options.
- SharedWavefunction wfn_

  Wavefunction.
- SharedBasisSet primary_

  Promary Basis set.
- SharedBasisSet auxiliary_

  Auxiliary Basis set.
- SharedBasisSet intermediate_

  Intermediate Basis set.
- 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.
- std::shared_ptr< psi::Matrix > potMat_

  Matrix of potential one-electron integrals.
- std::shared_ptr
  < psi::OneBodyAOInt > OEInt_

  One-electron integral shared pointer.
- std::shared_ptr< PotentialInt > potInt_

  One-electron potential shared pointer.
- std::shared_ptr< psi::Matrix > cOcc_

  Occupied orbitals.
- std::shared_ptr< psi::Matrix > cVir_

  Virtual orbitals.

17.39.1 Detailed Description

Generalized One-Electron Potential: Abstract base.

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

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

17.39.2 Constructor & Destructor Documentation

17.39.2.1 OEPotential::OEPotential (SharedWavefunction *wfn,* Options & *options*)

Fully ESP-based OEP object.

Parameters

wfn	- wavefunction
options	- Psi4 options

17.39.2.2 OEPotential::OEPotential (SharedWavefunction *wfn,* SharedBasisSet *auxiliary,* SharedBasisSet *intermediate,* Options & *options*)

General OEP object.

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

17.39.3 Member Function Documentation

17.39.3.1 std::shared_ptr< OEPotential > OEPotential::build (const std::string & *category,* SharedWavefunction *wfn,* Options & *options*) `[static]`

Build fully ESP-based OEP object.

Parameters

type	- OEP category
wfn	- wavefunction
options	- Psi4 options

17.39.3.2 std::shared_ptr< OEPotential > OEPotential::build (const std::string & *category,* SharedWavefunction *wfn,* SharedBasisSet *auxiliary,* SharedBasisSet *intermediate,* Options & *options*) `[static]`

Build general OEP object.

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

17.39.3.3 std::shared_ptr< **OEPotential3D**< **OEPotential** > > OEPotential::make_oeps3d (const std::string & *oepType*)

Create 3D vector field with OEP.

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:

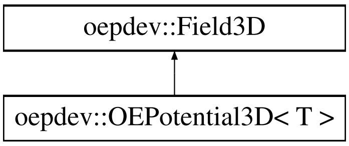
- oepdev/liboep/oep.h
- oepdev/liboep/oep_base.cc

17.40 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

17.40.1 Detailed Description

template<class T>class oepdev::OEPotential3D< T >

Class template for OEP 3D fields.

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

17.41 oepdev::OEPType Struct Reference

Container to handle the type of One-Electron Potentials.

`#include <oep.h>`

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.

17.41.1 Detailed Description

Container to handle the type of One-Electron Potentials.

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

- oepdev/liboep/oep.h

17.42 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.

17.42.1 Detailed Description

Structure to hold perturbing charges.

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

- oepdev/libutil/scf_perturb.h

17.43 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:

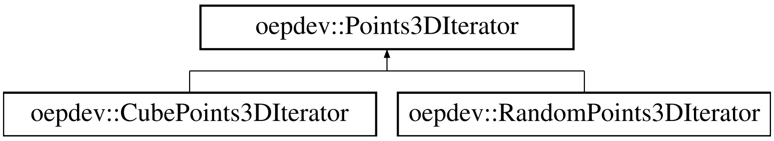
- oepdev/lib3d/space3d.h

17.44 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 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_**

17.44.1 Detailed Description

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

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.

17.44.2 Constructor & Destructor Documentation

17.44.2.1 oepdev::Points3DIterator::Points3DIterator (const int & *np*)

Plain constructor. Initializes the abstract features.

Parameters

np	- number of points this iterator is constructed for

17.44.3 Member Function Documentation

17.44.3.1 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]`

Build G09 Cube collection iterator.

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

17.44.3.2 std::shared_ptr< Points3DIterator > oepdev::Points3DIterator::build (const int & *np,* const double & *radius,* const double & *cx,* const double & *cy,* const double & *cz*) `[static]`

Build random collection iterator.

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

17.44.3.3 shared_ptr< Points3DIterator > oepdev::Points3DIterator::build (const int & *np*, const double & *pad*, psi::SharedMolecule *mol*) `[static]`

Build random collection iterator.

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:

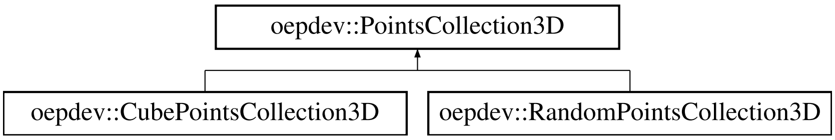
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

17.45 oepdev::PointsCollection3D Class Reference

Collection of points in 3D space. Abstract base.

`#include <space3d.h>`

Inheritance diagram for oepdev::PointsCollection3D:


oepdev::PointsCollection3D
oepdev::CubePointsCollection3D
oepdev::RandomPointsCollection3D

Public Types

- enum Collection { **Random**, **Cube** }

  Public descriptior of collection type.

Public Member Functions

- PointsCollection3D (Collection collectionType, int &np)

  Initialize abstract features.
- **PointsCollection3D** (Collection collectionType, const int &np)
- virtual ∼PointsCollection3D ()

  Destructor.
- virtual int npoints () const

  Get the number of points.
- virtual shared_ptr
  < Points3DIterator > points_iterator () const

  Get the iterator over this collection of points.
- virtual Collection get_type () const

Get the collection type.

- virtual void print () const =0

  Print the information to Psi4 output file.

Static Public Member Functions

- static shared_ptr
  < PointsCollection3D > build (const int &npoints, const double &radius, const double &cx=0.0, const double &cy=0.0, const double &cz=0.0)

  Build random collection of points.
- static shared_ptr
  < PointsCollection3D > build (const int &npoints, const double &padding, psi::SharedMolecule mol)

  Build random collection of points.
- static shared_ptr
  < PointsCollection3D > build (const int &nx, const int &ny, const int &nz, const double &px, const double &py, const double &pz, psi::SharedBasisSet bs, psi::Options &options)

  Build G09 Cube collection of points.

Protected Attributes

- const int np_

  Number of points.
- Collection collectionType_

  Collection type.
- shared_ptr< Points3DIterator > pointsIterator_

  iterator over points collection

17.45.1 Detailed Description

Collection of points in 3D space. Abstract base.

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

Note: Always create instances by using static factory methods.

17.45.2 Constructor & Destructor Documentation

17.45.2.1 oepdev::PointsCollection3D::PointsCollection3D (**Collection** *collectionType*, int & *np*)

Initialize abstract features.

Parameters

np	- number of points to be created

17.45.3 Member Function Documentation

17.45.3.1 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]`

Build random collection of points.

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

17.45.3.2 std::shared_ptr< **PointsCollection3D** > oepdev::PointsCollection3D::build (const int & *npoints,* const double & *padding,* psi::SharedMolecule *mol*) `[static]`

Build random collection of points.

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

17.45.3.3 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]`

Build G09 Cube collection of points.

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:

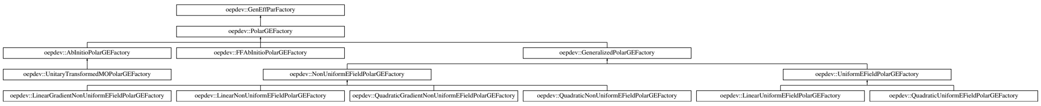
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

17.46 oepdev::PolarGEFactory Class Reference

Polarization GEFP Factory. Abstract Base.

`#include <gefp.h>`

Inheritance diagram for oepdev::PolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::AbInitioPolarGEFactory
oepdev::FFAbInitioPolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UnitaryTransformedMOPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearGradientNonUniformEFieldPolarGEFactory
oepdev::LinearNonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

Public Member Functions

- PolarGEFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

  Construct from Psi4 options.
- virtual ∼PolarGEFactory ()

  Destruct.
- virtual std::shared_ptr
  < GenEffPar > compute (void)=0

  Compute the density matrix susceptibility tensors.

Protected Member Functions

- std::shared_ptr< psi::Vector > draw_field ()

  Randomly draw electric field value.
- double draw_charge ()

  Randomly draw charge value.
- std::shared_ptr
  < oepdev::RHFPerturbed > perturbed_state (const std::shared_ptr< psi::Vector > &field)

  Solve SCF equations to find perturbed state due to uniform electric field.
- std::shared_ptr
  < oepdev::RHFPerturbed > perturbed_state (const std::shared_ptr< psi::Vector > &pos, const double &charge)

  Solve SCF equations to find perturbed state due to point charge.
- std::shared_ptr
  < oepdev::RHFPerturbed > perturbed_state (const std::shared_ptr< psi::Matrix > &charges)

  Solve SCF equations to find perturbed state due to set of point charges.
- std::shared_ptr< psi::Vector > field_due_to_charges (const std::shared_ptr< psi::Matrix > &charges, const double &x, const double &y, const double &z)

  Evaluate electric field at point (x,y,z) due to point charges.
- std::shared_ptr< psi::Vector > **field_due_to_charges** (const std::shared_ptr< psi::Matrix > &charges, const std::shared_ptr< psi::Vector > &pos)
- std::shared_ptr< psi::Matrix > field_gradient_due_to_charges (const std::shared_ptr< psi::Matrix > &charges, const double &x, const double &y, const double &z)

  Evaluate electric field gradient at point (x,y,z) due to point charges.
- std::shared_ptr< psi::Matrix > **field_gradient_due_to_charges** (const std::shared_ptr< psi::Matrix > &charges, const std::shared_ptr< psi::Vector > &pos)

Additional Inherited Members

17.46.1 Detailed Description

Polarization GEFP Factory. Abstract Base.

Basic interface for the polarization density matrix susceptibility parameters.

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

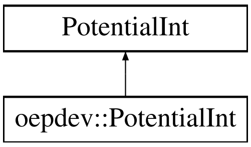
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_base.cc

17.47 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.

17.47.1 Detailed Description

Computes potential integrals.

17.47.2 Constructor & Destructor Documentation

17.47.2.1 oepdev::PotentialInt::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.

Parameters

st	- Spherical transform object
bs1	- basis set for first space
bs2	- basis set for second space
deriv	- derivative level

17.47.2.2 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)

Constructor. Takes an arbitrary collection of charges.

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

17.47.2.3 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`)

Constructor. Computes potential for one point x, y, z for a test particle of charge q.

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

17.47.3 Member Function Documentation

17.47.3.1 void oepdev::PotentialInt::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.

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:

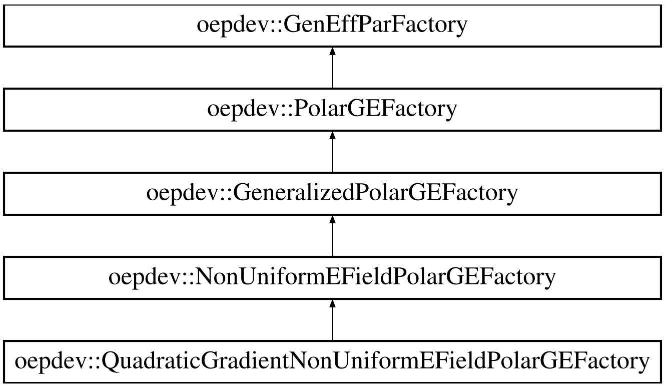
- oepdev/libpsi/potential.h
- oepdev/libpsi/potential.cc

17.48 oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::QuadraticGradientNonUniformEFieldPolarGEFactory

Public Member Functions

- **QuadraticGradientNonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  Compute Gradient vector associated with the i-th and j-th basis set function.
- void compute_hessian (void)

  Compute Hessian matrix (independent on the parameters)

Additional Inherited Members

17.48.1 Detailed Description

Polarization GEFP Factory with Least-Squares Parameterization.

Implements the generalized density matrix susceptibility model of the form

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

where:

- $\mathbf{B}^{(10)}_{i;\alpha\beta}$ is the density matrix dipole polarizability
- $\mathbf{B}^{(20)}_{i;\alpha\beta}$ is the density matrix dipole-dipole hyperpolarizability
- $\mathbf{B}^{(01)}_{i;\alpha\beta}$ is the density matrix quadrupole polarizability all defined for the 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:

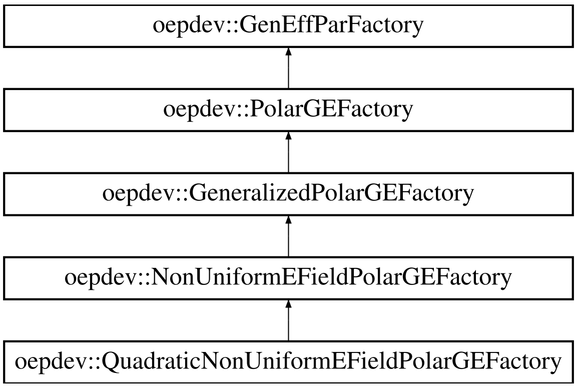
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_2_grad_1.cc

17.49 oepdev::QuadraticNonUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::QuadraticNonUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::NonUniformEFieldPolarGEFactory
oepdev::QuadraticNonUniformEFieldPolarGEFactory

Public Member Functions

- **QuadraticNonUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  Compute Gradient vector associated with the i-th and j-th basis set function.
- void compute_hessian (void)

  Compute Hessian matrix (independent on the parameters)

Additional Inherited Members

17.49.1 Detailed Description

Polarization GEFP Factory with Least-Squares Parameterization.

Implements the generalized density matrix susceptibility model of the form

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

where:

- $\mathbf{B}^{(10)}_{i;\alpha\beta}$ is the density matrix dipole polarizability
- $\mathbf{B}^{(20)}_{i;\alpha\beta}$ is the density matrix dipole-dipole hyperpolarizability all defined for the distributed site at $\mathbf{r}_i$.

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

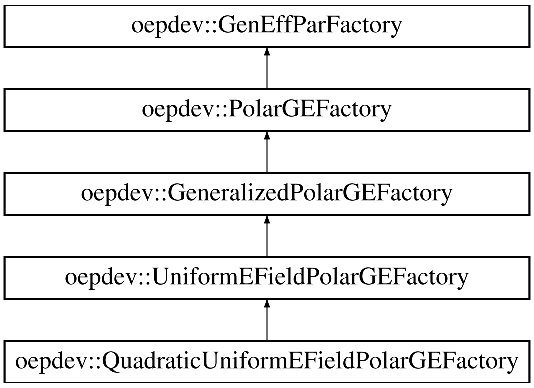
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_nonuniform_field_2.cc

17.50 oepdev::QuadraticUniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::QuadraticUniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

Public Member Functions

- **QuadraticUniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_gradient (int i, int j)

  Compute Gradient vector associated with the i-th and j-th basis set function.
- void compute_hessian (void)

  Compute Hessian matrix (independent on the parameters)

Additional Inherited Members

17.50.1 Detailed Description

Polarization GEFP Factory with Least-Squares Parameterization.

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:

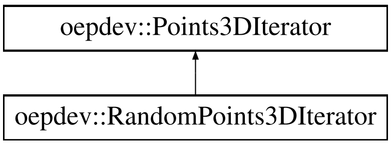
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_uniform_field_2.cc

17.51 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

17.51.1 Detailed Description

Iterator over a collection of points in 3D space. Random collection.

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:

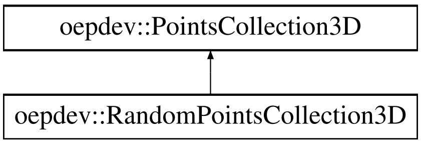
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

17.52 oepdev::RandomPointsCollection3D Class Reference

Collection of random points in 3D space.

`#include <space3d.h>`

Inheritance diagram for oepdev::RandomPointsCollection3D:


oepdev::PointsCollection3D
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

17.52.1 Detailed Description

Collection of random points in 3D space.

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:

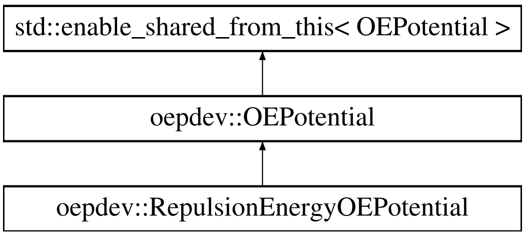
- oepdev/lib3d/space3d.h
- oepdev/lib3d/space3d.cc

17.53 oepdev::RepulsionEnergyOEPotential Class Reference

Generalized One-Electron Potential for Pauli Repulsion Energy.

`#include <oep.h>`

Inheritance diagram for oepdev::RepulsionEnergyOEPotential:


std::enable_shared_from_this< OEPotential >
oepdev::OEPotential
oepdev::RepulsionEnergyOEPotential

Public Member Functions

- **RepulsionEnergyOEPotential** (SharedWavefunction wfn, SharedBasisSet auxiliary, SharedBasisSet intermediate, Options &options)
- **RepulsionEnergyOEPotential** (SharedWavefunction wfn, Options &options)
- 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

Additional Inherited Members

17.53.1 Detailed Description

Generalized One-Electron Potential for Pauli Repulsion Energy.

Contains the following OEP types:

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

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

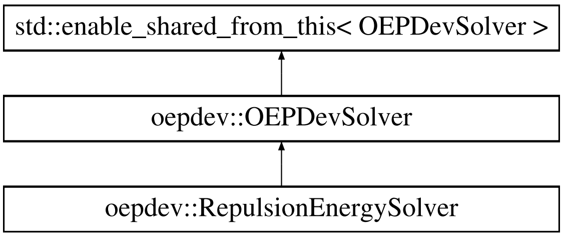
- oepdev/liboep/oep.h
- oepdev/liboep/oep_energy_pauli.cc

17.54 oepdev::RepulsionEnergySolver Class Reference

Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::RepulsionEnergySolver:


std::enable_shared_from_this< OEPDevSolver >
oepdev::OEPDevSolver
oepdev::RepulsionEnergySolver

Public Member Functions

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

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

  Compute property by using benchmark method.

Additional Inherited Members

17.54.1 Detailed Description

Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.

The implemented methods are shown below *Note:*

Keyword	Method Description
Benchmark Methods	
`HAYES_STONE`	∗Default∗. Pauli Repulsion energy at HF level from Hayes and Stone (1984).
`DENSITY_BASED`	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_MIX`	∗Default∗. OEP-Murrell et al's: S1 term via DF-OEP, S2 term via ESP-OEP.
`MURRELL_ETAL_ESP`	OEP-Murrell et al's: S1 and S2 via ESP-OEP

Table 17.3: Methods available in the Solver

- This solver also computes and prints the exchange energy at HF level (formulae are given below) for reference purposes.
- In order to construct this solver, **always** use the `OEPDevSolver::build` static factory method.

Below the detailed description of the implemented equations is given for each of the above provided methods. In the formulae across, it is assumed that the orbitals are real. The Coulomb notation for electron repulsion integrals (ERI's) is adopted; i.e,

$$(ac|bd) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_1)\frac{1}{r_{12}}\phi_b(\mathbf{r}_2)\phi_d(\mathbf{r}_2)$$

Greek subscripts denote basis set orbitals whereas Italic subscripts denote the occupied molecular orbitals.

Benchmark Methods

Pauli Repulsion energy at HF level by Hayes and Stone (1984).

For a closed-shell system, equation of Hayes and Stone (1984) becomes

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

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

$$\begin{aligned} E^{\rm Rep,1} &= E^{\rm Rep,Kin} + E^{\rm Rep,Nuc} \\ E^{\rm Rep,2} &= E^{\rm Rep,el-\Delta} + E^{\rm Rep,\Delta-\Delta} \end{aligned}$$

The kinetic and nuclear contributions are

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

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

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

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

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

whereas the second-order term is

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

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

$$E^{\mathrm{Rep}} = E^{\mathrm{Rep}}(\mathcal{O}(S)) + E^{\mathrm{Rep}}(\mathcal{O}(S^2))$$

where the first-order term is

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

whereas the second-order term is

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

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

$$E^{\mathrm{Rep}} = E^{\mathrm{Rep}}(\mathcal{O}(S)) + E^{\mathrm{Rep}}(\mathcal{O}(S^2))$$

where the first-order term is

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

whereas the second-order term is

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

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:

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

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 OEP's. The S-1 term is expressed via DF-OEP, whereas the S-2 term via ESP-OEP.

S-1 term (Murrell et al.)

The OEP reduction without any approximations leads to the following formula

$$E^{\rm Rep}(\mathscr{O}(S^1)) = -2\sum_{a\in A}\sum_{b\in B} S_{ab}\left\{\sum_{\xi\in A} S_{b\xi} G^A_{\xi a} + \sum_{\eta\in B} S_{a\eta} G^B_{\eta b}\right\}$$

where the OEP matrices are given as

$$G^A_{\xi a} = \sum_{\xi'\in A} [\mathbf{S}^{-1}]_{\xi\xi'} \sum_{\alpha\in A}\left\{C_{\alpha a} V^A_{\alpha\xi'} + \sum_{\mu\nu\in A}\left[2C_{\alpha a} D_{\mu\nu} - C_{\nu a} D_{\alpha\mu}\right](\alpha\xi'|\mu\nu)\right\}$$

and analogously for molecule *B*. Here, the nuclear attraction integrals are denoted by $V^A_{\alpha\xi'}$.

S-2 term (Otto-Ladik)

After the OEP reduction, this contribution under Otto-Ladik approximation has the following form:

$$E^{\rm Rep}(\mathscr{O}(S^2)) = 2\sum_{a\in A}\sum_{b\in B} S^2_{ab}\left\{\sum_{x\in A} q_{xa} V^{(x)}_{bb} + \sum_{y\in B} q_{yb} V^{(y)}_{aa}\right\}$$

where the ESP charges associated with each occupied molecular orbital reproduce the *effective potential* of molecule in question, i.e.,

$$\sum_{x\in A}\frac{q_{xa}}{|\mathrm{r}-\mathrm{r}_x|} \cong v^A_a(\mathbf{r})$$

where the potential is given by

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

17.54.2 Member Function Documentation

17.54.2.1 double RepulsionEnergySolver::compute_benchmark (const std::string & *method* = `"DEFAULT"`) `[virtual]`

Compute property by using benchmark method.

Each solver object has one `DEFAULT` benchmark method

Parameters

method	- benchmark method

Implements oepdev::OEPDevSolver.

17.54.2.2 double RepulsionEnergySolver::compute_oep_based (const std::string & *method* = `"DEFAULT"`) `[virtual]`

Compute property by using OEP's.

Each solver object has one `DEFAULT` OEP-based method.

Parameters

method	- flavour of OEP model

Implements oepdev::OEPDevSolver.

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

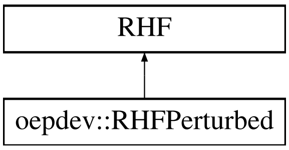
- oepdev/libsolver/solver.h
- oepdev/libsolver/solver_energy_pauli.cc

17.55 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.

17.55.1 Detailed Description

RHF theory under electrostatic perturbation.

Compute RHF wavefunction under the following conditions:

- external uniform electric field
- set of point charges The mixed conditions can also be used.

Theory

The electrostatic perturbation is here understood as a distribution of external (generally non-uniform) electric field. It is assumed that this perturbation is one-electron in nature. Therefore, the one-electron Hamiltonian is changed according to the following

$$\mathbf{H}^{\rm core} \rightarrow \mathbf{H}^{\rm core} + \sum_n q_n \mathbf{V}^{(n)} - \mathbb{M}\cdot\mathbf{F}$$

where q_n is the external classical point charge, $\mathbf{V}^{(n)}$ is the associated matrix of potential integrals, $\mathbb{M}$ is the vector of dipole integrals and $\mathbf{F}$ is an external uniform electric field. The total energy is then computed by performing an SCF procedure on the above one-electron Hamiltonian. The contribution due to nuclei is included, i.e.,

$$E_{\rm Nuc} \rightarrow E_{\rm Nuc-Nuc} + \sum_{In} \frac{q_n Z_I}{r_{In}} - \mu_{\rm Nuc}\cdot\mathbf{F}$$

where $\mu_{\rm Nuc}$ is the nuclear dipole moment and Z_I is the atomic number of the 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:

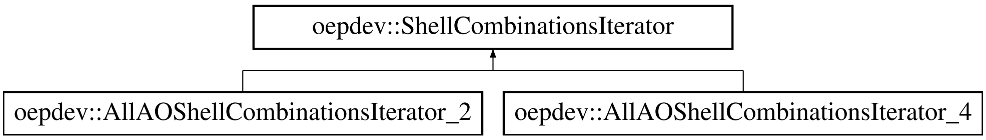
- oepdev/libutil/scf_perturb.h
- oepdev/libutil/scf_perturb.cc

17.56 oepdev::ShellCombinationsIterator Class Reference

Iterator for Shell Combinations. Abstract Base.

`#include <integrals_iter.h>`

Inheritance diagram for oepdev::ShellCombinationsIterator:


oepdev::ShellCombinationsIterator
oepdev::AllAOShellCombinationsIterator_2
oepdev::AllAOShellCombinationsIterator_4

Public Member Functions

- ShellCombinationsIterator (int nshell)

  Constructor.
- virtual ∼ShellCombinationsIterator ()

  Destructor.
- virtual void first (void)=0

  First iteration.
- virtual void next (void)=0

  Next iteration.
- virtual std::shared_ptr
  < psi::BasisSet > bs_1 (void) const

  Grab the basis set of axis 1.
- virtual std::shared_ptr
  < psi::BasisSet > bs_2 (void) const

  Grab the basis set of axis 2.
- virtual std::shared_ptr
  < psi::BasisSet > bs_3 (void) const

  Grab the basis set of axis 3.
- virtual std::shared_ptr
  < psi::BasisSet > bs_4 (void) const

  Grab the basis set of axis 4.
- virtual int P (void) const

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

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

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

  Grab the current shell S index.
- virtual bool is_done (void)

  Return status of an iterator.
- virtual const 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.

17.56.1 Detailed Description

Iterator for Shell Combinations. Abstract Base.

Date

2018/03/01 17:22:00

17.56.2 Constructor & Destructor Documentation

17.56.2.1 ShellCombinationsIterator::ShellCombinationsIterator (int *nshell*)

Constructor.

Parameters

nshell	- number of shells this iterator is for

17.56.3 Member Function Documentation

17.56.3.1 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

17.56.3.2 std::shared_ptr< **ShellCombinationsIterator** > ShellCombinationsIterator::build (const **IntegralFactory** & *ints*, std::string *mode* = `"ALL"`, int *nshell* = `4`) `[static]`

Build shell iterator from oepdev::IntegralFactory.

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.

17.56.3.3 std::shared_ptr< **ShellCombinationsIterator** > ShellCombinationsIterator::build (const psi::IntegralFactory & *ints*, std::string *mode* = `"ALL"`, int *nshell* = `4`) `[static]`

Build shell iterator from psi::IntegralFactory.

Parameters

ints	- integral factory
mode	- mode of iteration (either `ALL` or `UNIQUE`)
nshell	- number of shells to iterate through

Returns

shell iterator

17.56.3.4 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.

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

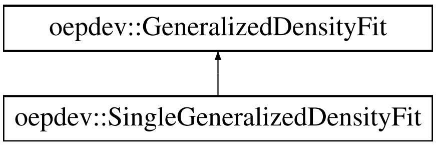
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

17.57 oepdev::SingleGeneralizedDensityFit Class Reference

Generalized Density Fitting Scheme - Single Fit.

`#include <oep_gdf.h>`

Inheritance diagram for oepdev::SingleGeneralizedDensityFit:


oepdev::GeneralizedDensityFit
oepdev::SingleGeneralizedDensityFit

Public Member Functions

- **SingleGeneralizedDensityFit** (std::shared_ptr< psi::BasisSet > bs_auxiliary, std::shared_ptr< psi::Matrix > v_vector)
- std::shared_ptr< psi::Matrix > compute (void)

  Perform the generalized density fit.

Additional Inherited Members

17.57.1 Detailed Description

Generalized Density Fitting Scheme - Single Fit.

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.

17.57.2 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 $\hat{v}$.

17.57.3 Member Function Documentation

17.57.3.1 std::shared_ptr< psi::Matrix > SingleGeneralizedDensityFit::compute (void) `[virtual]`

Perform the generalized density fit.

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

17.58 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.

17.58.1 Detailed Description

A structure to handle statistical data.

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

- oepdev/libgefp/gefp.h

17.59 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_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_4_2 (void)

  Test the oepdev::UnitaryOptimizer_4_2 class.
- double test_scf_perturb (void)

  Test the oepdev::RHFPerturbed class.

Protected Attributes

- std::shared_ptr
  < psi::Wavefunction > wfn_

  Wavefunction object.
- psi::Options & options_

  Psi4 Options.

17.59.1 Detailed Description

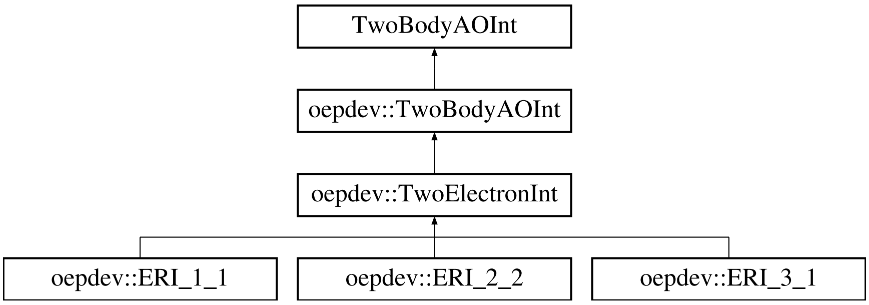
Manages test routines.

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

- oepdev/libtest/test.h
- oepdev/libtest/test.cc

17.60 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)

17.60.1 Member Function Documentation

17.60.1.1 void oepdev::TwoBodyAOInt::compute (std::shared_ptr< psi::Matrix > & *result*, int *ibs1* = 0, int *ibs2* = 2) [virtual]

Compute two-body two-centre integral and put it into matrix.

Parameters

result	- matrix where to store (i||j) two-body integrals
ibs1	- first basis set axis
ibs2	- second basis set axis

17.60.1.2 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:

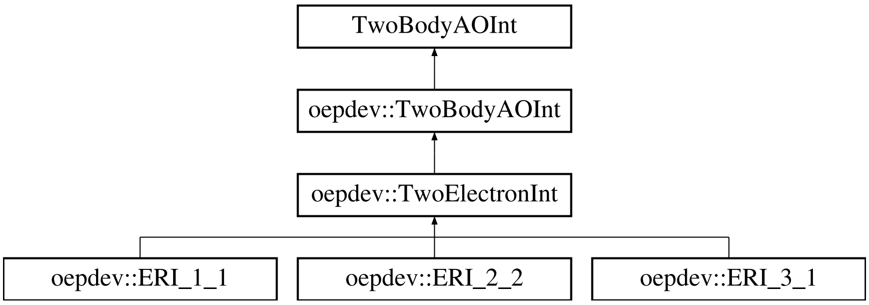
- oepdev/libpsi/integral.h
- oepdev/libpsi/integral.cc

17.61 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.

17.61.1 Detailed Description

General Two Electron Integral.

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

17.61.2 Member Function Documentation

17.61.2.1 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:

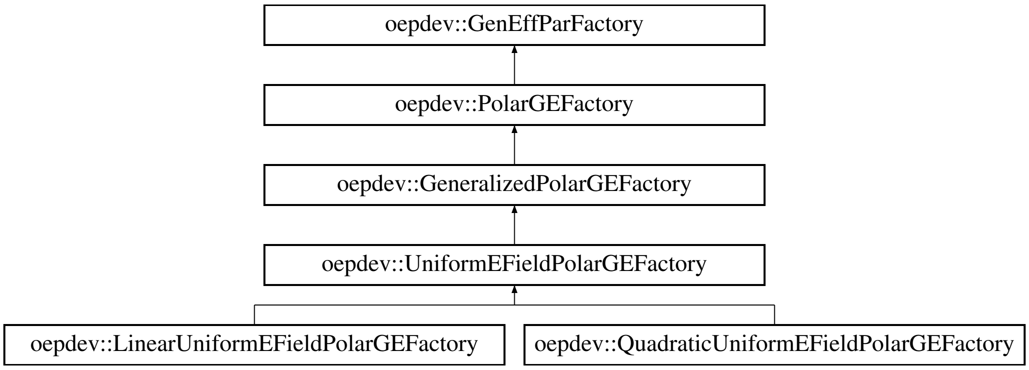
- oepdev/libints/eri.h
- oepdev/libints/eri.cc

17.62 oepdev::UniformEFieldPolarGEFactory Class Reference

Polarization GEFP Factory with Least-Squares Parameterization.

`#include <gefp.h>`

Inheritance diagram for oepdev::UniformEFieldPolarGEFactory:


oepdev::GenEffParFactory
oepdev::PolarGEFactory
oepdev::GeneralizedPolarGEFactory
oepdev::UniformEFieldPolarGEFactory
oepdev::LinearUniformEFieldPolarGEFactory
oepdev::QuadraticUniformEFieldPolarGEFactory

Public Member Functions

- **UniformEFieldPolarGEFactory** (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)
- void compute_samples (void)

  Compute samples of density matrices and select electric field distributions.
- virtual void compute_gradient (int i, int j)=0

  Compute Gradient vector associated with the i-th and j-th basis set function.
- virtual void compute_hessian (void)=0

  Compute Hessian matrix (independent on the parameters)

Additional Inherited Members

17.62.1 Detailed Description

Polarization GEFP Factory with Least-Squares Parameterization.

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

17.63 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.

17.63.1 Detailed Description

Find the optimim unitary matrix of quadratic matrix equation.

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:

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

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, $\mathbf{X}^{\mathrm{Old}}$ is for a while assumed to be an identity matrix and the $\mathbf{R}$ matrix and $\mathbf{P}$ vector are transformed according to the following formulae

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

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

In each iteration, the optimum angle 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 $\mathbf{X}^{\rm New}$.

References:

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

17.63.2 Constructor & Destructor Documentation

17.63.2.1 oepdev::UnitaryOptimizer::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.

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.

17.63.2.2 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`)

Create from R and P matrices and optimization options.

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.

17.63.2.3 oepdev::UnitaryOptimizer::UnitaryOptimizer (int *n*, double *conv*, int *maxiter*, bool *verbose*) `[protected]`

Initialize the basic memory.

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

17.64 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.

17.64.1 Detailed Description

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

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:

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

where

$$\mathbf{U}(\gamma) \equiv \begin{pmatrix} \ddots & & & & \\ & \cos(\gamma) & \cdots & \sin(\gamma) & \\ & \vdots & \ddots & \vdots & \\ & -\sin(\gamma) & \cdots & \cos(\gamma) & \\ & & & & \ddots \end{pmatrix}$$

is the Jacobi transformation matrix constructed for the 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, $\mathbf{X}^{\rm Old}$ is for a while assumed to be an identity matrix and the $\mathbf{R}$ as well as $\mathbf{P}$ tensors are transformed according to the following formulae

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

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

In each iteration, the optimum angle 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 $\mathbf{X}^{\rm New}$.

References:

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

17.64.2 Constructor & Destructor Documentation

17.64.2.1 oepdev::UnitaryOptimizer_4_2::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.

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.

17.64.2.2 oepdev::UnitaryOptimizer_4_2::UnitaryOptimizer_4_2 (int *n*, double *conv*, int *maxiter*, bool *verbose*) `[protected]`

Initialize the basic memory.

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:

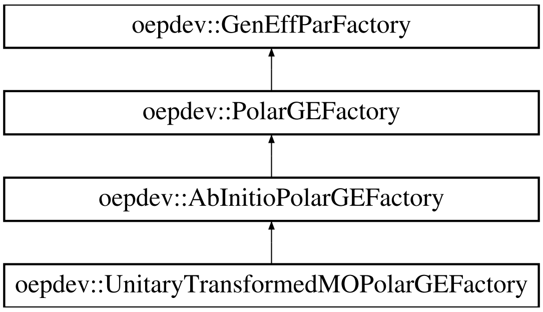
- oepdev/libutil/unitary_optimizer.h
- oepdev/libutil/unitary_optimizer.cc

17.65 oepdev::UnitaryTransformedMOPolarGEFactory Class Reference

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

`#include <gefp.h>`

Inheritance diagram for oepdev::UnitaryTransformedMOPolarGEFactory:


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

Public Member Functions

- UnitaryTransformedMOPolarGEFactory (std::shared_ptr< psi::Wavefunction > wfn, psi::Options &opt)

  Construct from CPHF object and Psi4 options.
- virtual ∼UnitaryTransformedMOPolarGEFactory ()

  Destruct.
- std::shared_ptr< GenEffPar > compute (void)

  Pefrorm Least-Squares Fit.

Additional Inherited Members

17.65.1 Detailed Description

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

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:

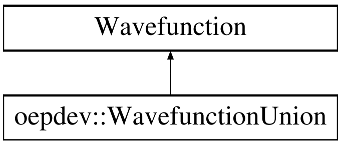
- oepdev/libgefp/gefp.h
- oepdev/libgefp/gefp_polar_abinitio.cc

17.66 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.
- 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)
- 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.
- 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.
- 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< 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< SharedLocalizer > l_localizer_

    List of orbital localizers.
- std::vector< std::map< const std::string, SharedMOSpace > > l_mospace_

    List of dictionaries of MO spaces.

17.66.1 Detailed Description

Union of two Wavefunction objects.

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
4. Performs Hadamard sums on `H_`, `Fa_`, `Da_`, `Ca_` and `S_` based on uncoupled wavefunctions.
5. 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.

17.66.2 Constructor & Destructor Documentation

17.66.2.1 oepdev::WavefunctionUnion::WavefunctionUnion (SharedWavefunction *ref_wfn,* Options & *options*)

Constructor.

Provide wavefunction with molecule containing at least 2 fragments.

Parameters

ref_wfn	- reference wavefunction
options	- Psi4 options

17.66.3 Member Function Documentation

17.66.3.1 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

17.66.3.2 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 18

File Documentation

18.1 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)

18.2 include/oepdev_options.h File Reference

Namespaces

- psi

  Psi4 package namespace.

Functions

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

  Options for the OEPDev plugin.

18.3 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"
```

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

- SharedWavefunction psi::oepdev (SharedWavefunction ref_wfn, Options &options)

  Main routine of the OEPDev plugin.

18.4 oepdev/lib3d/dmtp.h File Reference

```
#include "psi4/libmints/wavefunction.h"
#include "psi4/libmints/molecule.h"
#include "psi4/libmints/matrix.h"
```

Classes

- class oepdev::DMTPole

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

Namespaces

- oepdev

  OEPDev module namespace.

18.5 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 >

18.6 oepdev/libgefp/gefp.h File Reference

```
#include <vector>
#include <string>
#include <random>
#include <cmath>
#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"
```

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::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.

Namespaces

- oepdev

  OEPDev module namespace.

18.7 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.

18.8 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.

18.9 oepdev/liboep/oep.h File Reference

```
#include <cstdio>
#include <string>
#include <vector>
#include <map>
#include "psi4/libparallel/parallel.h"
#include "psi4/liboptions/liboptions.h"
#include "psi4/libmints/wavefunction.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libmints/vector.h"
#include "../libpsi/integral.h"
#include "../libpsi/potential.h"
#include "../lib3d/space3d.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 >

18.10 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.

Namespaces

- oepdev

  OEPDev module namespace.

18.11 oepdev/libpsi/integral.h File Reference

```
#include "psi4/libmints/integral.h"
#include "psi4/libmints/basisset.h"
#include "psi4/libmints/matrix.h"
```

Classes

- class oepdev::TwoBodyAOInt
- class oepdev::IntegralFactory

  Extended IntegralFactory for computing integrals.

Namespaces

- oepdev

  OEPDev module namespace.

18.12 oepdev/libpsi/potential.h File Reference

```
#include <vector>
#include "psi4/psi4-dec.h"
#include "psi4/libparallel/parallel.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.

18.13 oepdev/libsolver/solver.h File Reference

```
#include <cstdio>
#include <string>
#include <map>
#include "psi4/psi4-dec.h"
#include "psi4/libparallel/parallel.h"
#include "psi4/liboptions/liboptions.h"
#include "psi4/libpsio/psio.h"
#include "psi4/libmints/potential.h"
#include "psi4/libmints/integral.h"
#include "../libutil/wavefunction_union.h"
#include "../libutil/integrals_iter.h"
#include "../libpsi/integral.h"
#include "../liboep/oep.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.

Namespaces

- oepdev

  OEPDev module namespace.

Typedefs

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

18.14 oepdev/libtest/test.h File Reference

```
#include <vector>
#include "psi4/psi4-dec.h"
#include "psi4/libparallel/parallel.h"
#include "psi4/liboptions/liboptions.h"
#include "psi4/libpsio/psio.h"
#include "psi4/libmints/integral.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"
```

Classes

- class oepdev::test::Test

  Manages test routines.

Namespaces

- oepdev

  OEPDev module namespace.

18.15 oepdev/libutil/diis.h File Reference

```
#include <cstdio>
#include <string>
#include <vector>
#include "psi4/libparallel/parallel.h"
#include "psi4/libciomr/libciomr.h"
#include "psi4/libmints/vector.h"
#include "psi4/libmints/matrix.h"
#include "psi4/libqt/qt.h"
```

Classes

- class oepdev::DIISManager

  DIIS manager.

Namespaces

- oepdev

  OEPDev module namespace.

18.16 oepdev/libutil/integrals_iter.h File Reference

```
#include <cstdio>
#include "psi4/libparallel/parallel.h"
#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.

18.17 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.

18.18 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::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.

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)

18.19 oepdev/libutil/util.h File Reference

```
#include <cstdio>
#include <string>
#include <cmath>
#include <map>
#include "psi4/psi4-dec.h"
#include "psi4/libparallel/parallel.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/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::SharedMolecule** = std::shared_ptr< Molecule >
- using **oepdev::SharedSuperFunctional** = std::shared_ptr< SuperFunctional >
- using **oepdev::SharedMOSpace** = std::shared_ptr< MOSpace >
- using **oepdev::SharedMOSpaceVector** = std::vector< std::shared_ptr< MOSpace >>
- using **oepdev::SharedIntegralTransform** = std::shared_ptr< IntegralTransform >
- using **oepdev::SharedLocalizer** = std::shared_ptr< Localizer >

Functions

- 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);.

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

  Set up DFT functional.

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

    Extract molecule from dimer.
- std::shared_ptr< Wavefunction > oepdev::solve_scf (std::shared_ptr< Molecule > molecule, std::shared_ptr< BasisSet > primary, std::shared_ptr< SuperFunctional > functional, Options &options, std::shared_ptr< PSIO > psio)

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

    Compute the scalar magnitude of multipole moment.

18.20 oepdev/libutil/wavefunction_union.h File Reference

```
#include <cstdio>
#include <string>
#include <map>
#include "psi4/psi4-dec.h"
#include "psi4/libparallel/parallel.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 19

Example Documentation

19.1 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);
};
```

19.2 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()];
       }
  }
}
```

19.3 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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