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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](#)

References

Chapter 2

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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 general 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 | $(I \hat{v}^A J)$ | $I \in A, J \in B$ |
| Type 2 | $(J \hat{v}^A L)$ | $J, L \in B$ |

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 |
|---------------------------------|--|--|
| $(\mu \hat{v}^{A[\mu]} \sigma)$ | $\sum_{I \in A} v_{\mu I}^A S_{I\sigma}$ | $\sum_{\alpha \in A} q_{\alpha}^{A[\mu]} V_{\mu\sigma}^{(\alpha)}$ |
| $(i \hat{v}^{A[i]} j)$ | $\sum_{I \in A} v_{ii}^A S_{Ij}$ | $\sum_{\alpha \in A} q_{\alpha}^{A[i]} V_{ij}^{(\alpha)}$ |

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

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 Potentials

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

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 Murrell'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:

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

Matrix forms:

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

4.2.2 Second-order contribution in overlap matrix expansion.

To be added here!

4.3 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.

4.3.1 ET contributions.

3D forms:

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

Matrix forms:

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

4.3.2 HT contributions.

Do be derived.

4.3.3 CT contributions.

To be derived.

4.4 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.

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

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

under the necessary assumption that the auxiliary basis set is *complete*. In that case, formally one can write the following identity

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

The matrix elements of the OEP operator in auxiliary space can be computed in the same way as the matrix elements with any other basis function. In reality, it is almost impossible to reach the completeness of the basis set, however, but it is possible to obtain the **effective** matrix elements of the OEP operator in auxiliary space, rather than compute them as they are in the above equation explicitly. 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:

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

The expansion coefficients are the effective matrix elements of the OEP operator in auxiliary basis set. Now, multiplying both sides by another auxiliary basis function and subsequently inverting the equation one obtains the expansion coefficients:

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

In this way, it is possible to approximately determine the matrix elements of the OEP operator with any other basis function in case the auxiliary basis set is not complete. **In particular**, when the other basis function 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.

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 and libraries

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. 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 specifying 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 blessing!

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 Use Object-Oriented Programming

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

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

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

Chapter 8

Namespace Index

8.1 Namespace List

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

| | | |
|------------------------|-----------------------------------|----|
| oepdev | Oepdev module namespace | ?? |
| psi | Psi4 package namespace | ?? |

Chapter 9

Hierarchical Index

9.1 Class Hierarchy

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

| | |
|--|----|
| oepdev::AllAOIntegralsIterator | ?? |
| oepdev::AllAOShellCombinationsIterator | ?? |
| oepdev::CPHF | ?? |
| CubicScalarGrid | |
| oepdev::CubePointsCollection3D | ?? |
| oepdev::DIISManager | ?? |
| enable_shared_from_this | |
| oepdev::OEPDevSolver | ?? |
| oepdev::ElectrostaticEnergySolver | ?? |
| oepdev::RepulsionEnergySolver | ?? |
| oepdev::OEPotential | ?? |
| oepdev::EETCouplingOEPotential | ?? |
| oepdev::ElectrostaticEnergyOEPotential | ?? |
| oepdev::RepulsionEnergyOEPotential | ?? |
| oepdev::ESPSolver | ?? |
| oepdev::Points3DIterator::Point | ?? |
| oepdev::Points3DIterator | ?? |
| oepdev::CubePoints3DIterator | ?? |
| oepdev::RandomPoints3DIterator | ?? |
| oepdev::PointsCollection3D | ?? |
| oepdev::CubePointsCollection3D | ?? |
| oepdev::RandomPointsCollection3D | ?? |
| PotentialInt | |
| oepdev::PotentialInt | ?? |
| oepdev::ScalarField3D | ?? |
| oepdev::ElectrostaticPotential3D | ?? |
| oepdev::OEPotential3D< T > | ?? |
| Wavefunction | |
| oepdev::WavefunctionUnion | ?? |

Chapter 10

Class Index

10.1 Class List

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

| | | |
|--|--|----|
| oepdev::AllAOIntegralsIterator | Loop over all possible ERI within a particular shell | ?? |
| oepdev::AllAOShellCombinationsIterator | Loop over all possible ERI shells | ?? |
| oepdev::CPHF | CPHF solver class | ?? |
| oepdev::CubePoints3DIterator | Iterator over a collection of points in 3D space. g09 Cube-like order | ?? |
| oepdev::CubePointsCollection3D | G09 cube-like ordered collection of points in 3D space | ?? |
| oepdev::DIISManager | DIIS manager | ?? |
| oepdev::EETCouplingOEPotential | Generalized One-Electron Potential for EET coupling calculations | ?? |
| oepdev::ElectrostaticEnergyOEPotential | Generalized One-Electron Potential for Electrostatic Energy calculations | ?? |
| oepdev::ElectrostaticEnergySolver | Compute the Coulombic interaction energy between unperturbed wavefunctions | ?? |
| oepdev::ElectrostaticPotential3D | Electrostatic potential of a molecule | ?? |
| oepdev::ESPSolver | Charges from Electrostatic Potential (ESP). A solver-type class | ?? |
| oepdev::OEPDevSolver | Solver of properties of molecular aggregates. Abstract base | ?? |
| oepdev::OEPotential | Generalized One-Electron Potential: Abstract base | ?? |
| oepdev::OEPotential3D< T > | Class template for OEP scalar fields | ?? |
| oepdev::Points3DIterator::Point | | ?? |
| oepdev::Points3DIterator | Iterator over a collection of points in 3D space. Abstract base | ?? |
| oepdev::PointsCollection3D | Collection of points in 3D space. Abstract base | ?? |
| oepdev::PotentialInt | Computes potential integrals | ?? |
| oepdev::RandomPoints3DIterator | Iterator over a collection of points in 3D space. Random collection | ?? |

| | |
|--|----|
| oepdev::RandomPointsCollection3D | |
| Collection of random points in 3D space | ?? |
| oepdev::RepulsionEnergyOEPotential | |
| Generalized One-Electron Potential for Pauli repulsion energy calculations | ?? |
| oepdev::RepulsionEnergySolver | |
| Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions | ?? |
| oepdev::ScalarField3D | |
| Scalar field in 3D space. Abstract base | ?? |
| oepdev::WavefunctionUnion | |
| Union of two Wavefunction objects | ?? |

Chapter 11

Namespace Documentation

11.1 oepdev Namespace Reference

oepdev module namespace.

Classes

- class [OEPotential](#)
Generalized One-Electron Potential: Abstract base.
- class [ElectrostaticEnergyOEPotential](#)
Generalized One-Electron Potential for Electrostatic Energy calculations.
- class [RepulsionEnergyOEPotential](#)
Generalized One-Electron Potential for Pauli repulsion energy calculations.
- class [EETCouplingOEPotential](#)
Generalized One-Electron Potential for EET coupling calculations.
- class [PotentialInt](#)
Computes potential integrals.
- class [CPHF](#)
CPHF solver class.
- class [DIISManager](#)
DIIS manager.
- class [ESPSolver](#)
Charges from Electrostatic Potential (ESP). A solver-type class.
- class [AllAOShellCombinationsIterator](#)
Loop over all possible ERI shells.
- class [AllAOIntegralsIterator](#)
Loop over all possible ERI within a particular shell.
- 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 [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 [ScalarField3D](#)
Scalar field in 3D space. Abstract base.
- class [ElectrostaticPotential3D](#)
Electrostatic potential of a molecule.
- class [OEPotential3D](#)
Class template for OEP scalar fields.
- class [WavefunctionUnion](#)
Union of two Wavefunction objects.

Typedefs

- using **SharedWavefunction** = std::shared_ptr< Wavefunction >
- using **SharedBasisSet** = std::shared_ptr< BasisSet >
- using **SharedTensor** = std::shared_ptr< Tensor >
- using **SharedMatrix** = std::shared_ptr< Matrix >
- using **SharedVector** = std::shared_ptr< Vector >
- using **SharedScalarField3D** = std::shared_ptr< [ScalarField3D](#) >
- using **SharedIntegralFactory** = std::shared_ptr< IntegralFactory >
- using **SharedTwoBodyAOInt** = std::shared_ptr< TwoBodyAOInt >
- using **SharedWavefunctionUnion** = std::shared_ptr< [WavefunctionUnion](#) >
- using **SharedOEPotential** = std::shared_ptr< [OEPotential](#) >
- 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

- void [preamble](#) (void)
Print preamble 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.

11.1.1 Detailed Description

oepdev module namespace. Contains:

11.1.2 Function Documentation

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

Set up DFT functional.

Now it accepts only pure HF functional.

Parameters

| | |
|----------------|---|
| <i>name</i> | name of the functional ("HF" is now only available) |
| <i>options</i> | psi::Options object |

Returns

psi::SharedSuperFunctional object with functional.

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

Extract molecule from dimer.

Parameters

| | |
|-----------------------|---------------------------------------|
| <i>molecule_dimer</i> | psi::SharedMolecule object with dimer |
| <i>id</i> | index of a molecule (starts from 1) |

Returns

psi::SharedMolecule object with indicated monomer

11.1.2.3 `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

| | |
|-------------------|--|
| <i>molecule</i> | psi::SharedMolecule object with molecule |
| <i>primary</i> | shared primary basis set |
| <i>functional</i> | DFT functional |
| <i>options</i> | psi::Options object |
| <i>psio</i> | psi::PSIO object |

Returns

psi::SharedWavefunction SCF wavefunction of the molecule

11.2 psi Namespace Reference

Psi4 package namespace.

Typedefs

- using **SharedVetor** = std::shared_ptr< Vector >

- 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.

11.2.1 Detailed Description

Psi4 package namespace. Contains all Psi4 functionalities.

11.2.2 Function Documentation

11.2.2.1 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 exchange-repulsion 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). Detailed list of models is given below:

| | | Interaction Property | |
|------------------------|------------------------|----------------------|--------------|
| Pauli energy | | Induction energy | EET Coupling |
| Methods | | | |
| 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) |

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

| Target Model | Benchmarks | Competing Model |
|------------------------|------------------|----------------------|
| Murrel et al.'s | Murrel et al.'s | EFP2-Pauli |
| OEP-ET/HT | TrCAMM | Exact (Stone's) |
| Density Susceptibility | Exact (ESD) | TDFI-TI |
| | Exact (incl. CT) | FED |
| | | TDFI-TI |
| | | EFP2-Induced Dipoles |

Parameters of the plugin driver:

Parameters

| | |
|----------------|--------------------------------|
| <i>ref_wfn</i> | shared wavefunction of a dimer |
| <i>options</i> | psi::Options object |

Returns

psi::SharedWavefunction (as for now the same as ref_wfn)

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

Options for the OEPDEV plugin.

Parameters

| | |
|----------------|-------------------------|
| <i>name</i> | name of driver function |
| <i>options</i> | psi::Options object |

Returns

true

Chapter 12

Class Documentation

12.1 oepdev::AllAOIntegralsIterator Class Reference

Loop over all possible ERI within a particular shell.

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

Public Member Functions

- [AllAOIntegralsIterator](#) (const [AllAOShellCombinationsIterator](#) &shellIter)
Construct by shell iterator (const object)
- [AllAOIntegralsIterator](#) (std::shared_ptr< [AllAOShellCombinationsIterator](#) > shellIter)
Construct by shell iterator (pointed by shared pointer)
- void [first](#) ()
First iteration.
- void [next](#) ()
Next iteration.
- bool [is_done](#) ()
Check status of iterations.
- 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

12.1.1 Detailed Description

Loop over all possible ERI within a particular shell.

Constructed by providing a const reference or shared pointer to an [AllAOShellCombinationsIterator](#) object.

Suggested usage:

See Also

[AllAOShellCombinationsIterator](#)

12.1.2 Constructor & Destructor Documentation

12.1.2.1 oepdev::AllAOIntegralsIterator::AllAOIntegralsIterator (const AllAOShellCombinationsIterator & shellIter)

Construct by shell iterator (const object)

Parameters

| | |
|------------------|-------------------------|
| <i>shellIter</i> | - shell iterator object |
|------------------|-------------------------|

12.1.2.2 oepdev::AllAOIntegralsIterator::AllAOIntegralsIterator (std::shared_ptr< AllAOShellCombinationsIterator > shellIter)

Construct by shell iterator (pointed by shared pointer)

Parameters

| | |
|------------------|-------------------------|
| <i>shellIter</i> | - shell iterator object |
|------------------|-------------------------|

12.1.3 Member Function Documentation

12.1.3.1 int oepdev::AllAOIntegralsIterator::index () const [inline]

Grab the current index of integral value stored in the buffer

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

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

12.2 oepdev::AllAOShellCombinationsIterator Class Reference

Loop over all possible ERI shells.

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

Public Member Functions

- [AllAOShellCombinationsIterator](#) (SharedBasisSet [bs_1](#), SharedBasisSet [bs_2](#), SharedBasisSet [bs_3](#), SharedBasisSet [bs_4](#))
Construct by providing basis sets for each axis. The basis sets must be defined for the same molecule.
- [AllAOShellCombinationsIterator](#) (SharedIntegralFactory integrals)
Construct by providing integral factory.
- void [first](#) ()
First iteration.
- void [next](#) ()
Next iteration.
- bool [is_done](#) ()
Check status of iterations.
- 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.
- SharedBasisSet **bs_1** () const
Grab the basis set of axis 1.
- SharedBasisSet **bs_2** () const
Grab the basis set of axis 2.
- SharedBasisSet **bs_3** () const
Grab the basis set of axis 3.
- SharedBasisSet **bs_4** () const
Grab the basis set of axis 4.
- void **compute_shell** (SharedTwoBodyAOInt tei) const
Compute ERI's for the current shell. The eris are stored in the buffer of the argument object.

12.2.1 Detailed Description

Loop over all possible ERI shells.

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

Suggested usage:

```
SharedIntegralFactory ints = std::make_shared<IntegralFactory>(bs1, bs2, bs3, bs4);
SharedTwoBodyAOInt tei(ints->eri());
AllAOShellCombinationsIterator shellIter(ints);
const double * buffer = tei->buffer();
for (shellIter.first(); shellIter.is_done()==false; shellIter.next())
{
    shellIter.compute_shell(tei);
    AllAOIntegralsIterator intsIter(shellIter);
    for (intsIter.first(); intsIter.is_done()==false; intsIter.next())
    {
        // Grab (ij|kl) integrals and indices here
        int i = intsIter.i();
        int j = intsIter.j();
        int k = intsIter.k();
        int l = intsIter.l();
        double integral = buffer[intsIter.index()];
    }
}
```

12.2.2 Constructor & Destructor Documentation

12.2.2.1 oepdev::AllAOShellCombinationsIterator::AllAOShellCombinationsIterator (SharedBasisSet *bs_1*, SharedBasisSet *bs_2*, SharedBasisSet *bs_3*, SharedBasisSet *bs_4*)

Construct by providing basis sets for each axis. The basis sets must be defined for the same molecule.

Parameters

| | |
|-------------|-----------------------|
| <i>bs_1</i> | - basis set of axis 1 |
| <i>bs_2</i> | - basis set of axis 2 |
| <i>bs_3</i> | - basis set of axis 3 |
| <i>bs_4</i> | - basis set of axis 4 |

12.2.2.2 oepdev::AllAOShellCombinationsIterator::AllAOShellCombinationsIterator (SharedIntegralFactory *integrals*)

Construct by providing integral factory.

Parameters

| | |
|------------------|---------------------------|
| <i>integrals</i> | - integral factory object |
|------------------|---------------------------|

12.2.3 Member Function Documentation

12.2.3.1 void oepdev::AllAOShellCombinationsIterator::compute_shell (SharedTwoBodyAOInt *tei*) const

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

Parameters

| | |
|------------|----------------------------|
| <i>tei</i> | - two electron AO integral |
|------------|----------------------------|

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

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

12.3 oepdev::CPHF Class Reference

[CPHF](#) solver class.

```
#include <cphf.h>
```

Public Member Functions

- [CPHF](#) (SharedWavefunction ref_wfn, Options &options)
orbital-associated polarizabilities tensors
- [~CPHF](#) ()
Destructor.
- void [compute](#) (void)
run the calculations
- void [print](#) (void) const
print to output file
- std::shared_ptr< Matrix > [get_molecular_polarizability](#) (void) const
retrieve the molecular (total) polarizability

Protected Attributes

- 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 > [_molecular_polarizability](#)
Total (molecular) polarizability tensor.

12.3.1 Detailed Description

[CPHF](#) solver class.

Solves [CPHF](#) equations (now only for RHF wavefunction). Computes molecular and orbital-associated polarizabilities.

Suggested usage:

```
std::shared_ptr<CPHF> cphf(new CPHF(ref_wfn, options)); cphf->compute(); std::shared_ptr<Matrix> polar-
izability = cphf->get_molecular_polarizability(); std::shared_ptr<Tensor> orbital_polars = cphf->get_orbital_-
polarizabilities();
```

12.3.2 Constructor & Destructor Documentation

12.3.2.1 oepdev::CPHF::CPHF (SharedWavefunction ref_wfn, Options & options)

orbital-associated polarizabilities tensors

Constructor

Parameters

| | |
|----------------|---------------------------|
| <i>ref_wfn</i> | reference HF wavefunction |
| <i>options</i> | set of Psi4 options |

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

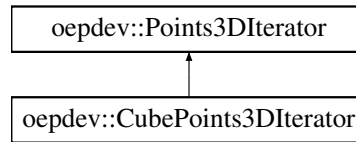
- oepdev/libutil/cphf.h
- oepdev/libutil/cphf.cc

12.4 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)
Initialize first iteration.
- 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

12.4.1 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:

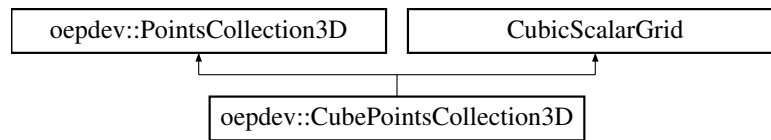
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.5 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)

Additional Inherited Members

12.5.1 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/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.6 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)

12.6.1 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.

12.6.2 Constructor & Destructor Documentation

12.6.2.1 oepdev::DIISManager::DIISManager (int *dim*, int *na*, int *nb*)

Constructor.

Parameters

| | |
|------------|----------------------------|
| <i>dim</i> | Size of DIIS subspace |
| <i>na</i> | Number of solution rows |
| <i>nb</i> | Number of solution columns |

12.6.3 Member Function Documentation

12.6.3.1 void oepdev::DIISManager::compute (void)

Perform DIIS interpolation.

12.6.3.2 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

| | |
|---------------|--|
| <i>error</i> | Shared matrix with current solution error |
| <i>vector</i> | Shared matrix with current solution vector |

12.6.3.3 void oepdev::DIISManager::update (std::shared_ptr< Matrix > & *other*)

Update solution vector. Pass the Shared pointer to current solution. Then it will be overridden by the updated DIIS solution.

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

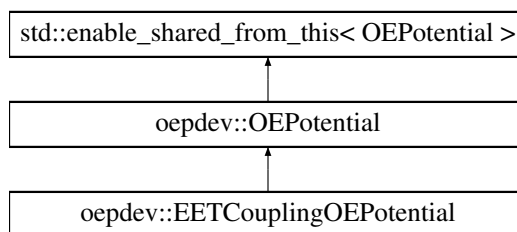
- oepdev/libutil/diis.h
- oepdev/libutil/diis.cc

12.7 oepdev::EETCouplingOEPotential Class Reference

Generalized One-Electron Potential for EET coupling calculations.

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

Inheritance diagram for oepdev::EETCouplingOEPotential:



Public Member Functions

- **EETCouplingOEPotential** (SharedWavefunction [wfn](#), SharedBasisSet auxiliary, Options &options)
- **EETCouplingOEPotential** (SharedWavefunction [wfn](#), Options &options)
- virtual void **compute** (const std::string &oepType) override
- virtual void [compute_3D](#) (const std::string &oepType, const double &x, const double &y, const double &z, double &v) override
- virtual void **print_header** () const override

Additional Inherited Members

12.7.1 Detailed Description

Generalized One-Electron Potential for EET coupling calculations.

Contains the following OEP types: "ET1" "ET2" "HT1" "HT1" "HT2" "CT1" "CT2"

12.7.2 Member Function Documentation

12.7.2.1 void EETCouplingOEPotential::compute_3D (const std::string & *oepType*, const double & *x*, const double & *y*, const double & *z*, double & *v*) [override],[virtual]

Compute value of potential in point x, y, z and save at v

Implements [oepdev::OEPotential](#).

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

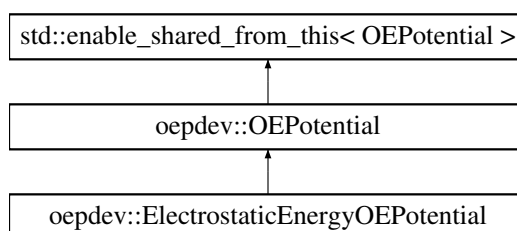
- oepdev/liboep/oep.h
- oepdev/liboep/oep.cc

12.8 oepdev::ElectrostaticEnergyOEPotential Class Reference

Generalized One-Electron Potential for Electrostatic Energy calculations.

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

Inheritance diagram for 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
- virtual void [compute_3D](#) (const std::string &oepType, const double &x, const double &y, const double &z, double &v) override
- virtual void **print_header** () const override

Additional Inherited Members

12.8.1 Detailed Description

Generalized One-Electron Potential for Electrostatic Energy calculations.

Contains the following OEP types: "V"

12.8.2 Member Function Documentation

12.8.2.1 void [ElectrostaticEnergyOEPotential::compute_3D](#) (const std::string & *oepType*, const double & *x*, const double & *y*, const double & *z*, double & *v*) [override], [virtual]

Compute value of potential in point x, y, z and save at v

Implements [oepdev::OEPotential](#).

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

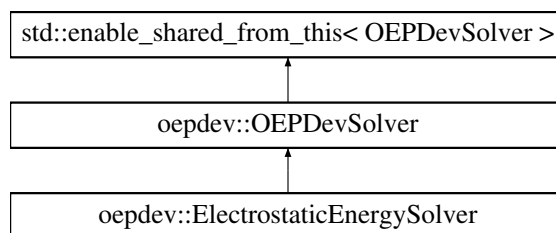
- oepdev/liboep/oep.h
- oepdev/liboep/oep.cc

12.9 oepdev::ElectrostaticEnergySolver Class Reference

Compute the Coulombic interaction energy between unperturbed wavefunctions.

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

Inheritance diagram for oepdev::ElectrostaticEnergySolver:



Public Member Functions

- **ElectrostaticEnergySolver** (SharedWavefunctionUnion wfn_union)
- virtual double [compute_oep_based](#) (const std::string &method="DEFAULT")
Compute property by using OEP's.
- virtual double [compute_benchmark](#) (const std::string &method="DEFAULT")
Compute property by using benchmark method.

Additional Inherited Members

12.9.1 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 12.1: 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

$$E^{\text{Coul}} = E^{\text{Nuc-Nuc}} + E^{\text{Nuc-El}} + E^{\text{El-El}}$$

where the nuclear-nuclear repulsion energy is

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

the nuclear-electronic attraction energy is

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

and the electron-electron repulsion energy is

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

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

$$E^{\text{Coul}} = E^{\text{Nuc-Nuc}} + E^{\text{Nuc-El}} + E^{\text{El-El}}$$

where the nuclear-nuclear repulsion energy is

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

the nuclear-electronic attraction energy is

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

and the electron-electron repulsion energy is

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

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,

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

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

Notes:

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

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

for reference purposes.

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

12.9.2 Member Function Documentation

12.9.2.1 `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

| | |
|---------------|--------------------|
| <i>method</i> | - benchmark method |
|---------------|--------------------|

Implements `oepdev::OEPDevSolver`.

12.9.2.2 `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

| | |
|---------------|------------------------|
| <i>method</i> | - flavour of OEP model |
|---------------|------------------------|

Implements [oepdev::OEPDevSolver](#).

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

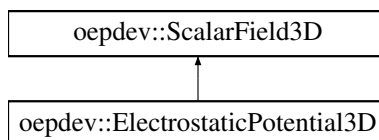
- oepdev/libutil/solver.h
- oepdev/libutil/solver.cc

12.10 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 double [compute_xyz](#) (const double &x, const double &y, const double &z)
Compute a value of scalar field at point (x, y, z)
- virtual void [print](#) () const
Print information of the object to Psi4 output.

Additional Inherited Members

12.10.1 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:

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

where the nuclear and electronic contributions are defined accordingly as

$$v_{\text{nuc}}(\mathbf{r}) = \sum_x \frac{Z_x}{|\mathbf{r} - \mathbf{r}_x|}$$

$$v_{\text{el}}(\mathbf{r}) = \sum_{\mu\nu} \left\{ D_{\mu\nu}^{(\alpha)} + D_{\mu\nu}^{(\beta)} \right\} V_{\nu\mu}(\mathbf{r})$$

In the above equations, Z_x denotes the charge of x th nucleus, $D_{\mu\nu}^{(\omega)}$ is the one-particle (relaxed) density matrix element in AO basis associated with the ω electron spin, and $V_{\mu\nu}(\mathbf{r})$ is the potential one-electron integral defined

by

$$V_{\nu\mu}(\mathbf{r}) \equiv \int d\mathbf{r}' \phi_{\nu}^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_{\mu}(\mathbf{r}')$$

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

- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.11 oepdev::ESPSolver Class Reference

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

```
#include <esp.h>
```

Public Member Functions

- [ESPSolver](#) (SharedScalarField3D field)
Construct from scalar field.
- [ESPSolver](#) (SharedScalarField3D field, psi::SharedMatrix [centres](#))
Construct from scalar field.
- virtual [~ESPSolver](#) ()
Destructor.
- virtual psi::SharedVector [charges](#) () const
Get the (fit) charges.
- virtual psi::SharedMatrix [centres](#) () const
Get the charge distribution centres.
- virtual void [compute](#) ()
Perform fitting of effective charges.

Protected Attributes

- const int [nCentres_](#)
Number of fit centres.
- SharedScalarField3D [field_](#)
Scalar field.
- psi::SharedVector [charges_](#)
Charges to be fit.
- psi::SharedMatrix [centres_](#)
Centres, at which fit charges will reside.

12.11.1 Detailed Description

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

Solves the least-squares problem to fit the generalized charges q_m , that reproduce the reference generalized potential $v^{\text{ref}}(\mathbf{r})$ supplied by the [ScalarField3D](#) object:

$$\int d\mathbf{r}' \left[v^{\text{ref}}(\mathbf{r}') - \sum_m \frac{q_m}{|\mathbf{r}' - \mathbf{r}_m|} \right]^2 \rightarrow \text{minimize}$$

The charges are subject to the following constraint:

$$\sum_m q_m = 0$$

Method description.

M generalized charges is found by solving the matrix equation

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

where the \mathbf{A} matrix of dimension $M \times M$ and \mathbf{b} vector of length M are given as

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

$$b_m = \sum_i \frac{v^{\text{ref}}(\mathbf{r}_m)}{r_{im}}$$

In the above equation, summations run over all sample points, at which reference potential is known.

12.11.2 Constructor & Destructor Documentation

12.11.2.1 oepdev::ESPSolver::ESPSolver (SharedScalarField3D *field*)

Construct from scalar field.

Assume that the centres are on atoms associated with the scalar field.

Parameters

| | |
|--------------|------------------------------|
| <i>field</i> | - oepdev scalar field object |
|--------------|------------------------------|

12.11.2.2 oepdev::ESPSolver::ESPSolver (SharedScalarField3D *field*, psi::SharedMatrix *centres*)

Construct from scalar field.

Solve ESP equations for a custom set of charge distribution centres.

Parameters

| | |
|----------------|--|
| <i>field</i> | - oepdev scalar field object |
| <i>centres</i> | - matrix with coordinates of charge distribution centres |

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

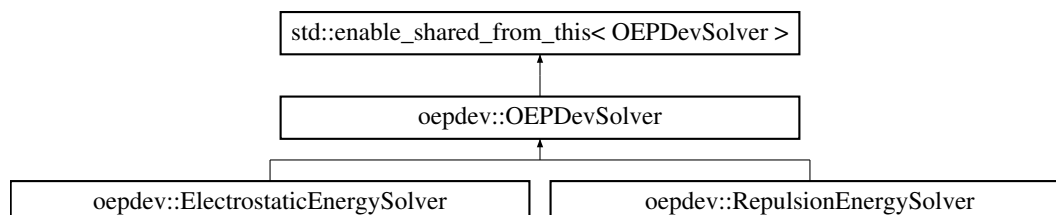
- oepdev/libutil/esp.h
- oepdev/libutil/esp.cc

12.12 oepdev::OEPDevSolver Class Reference

Solver of properties of molecular aggregates. Abstract base.

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

Inheritance diagram for oepdev::OEPDevSolver:



Public Member Functions

- [OEPDevSolver](#) (SharedWavefunctionUnion wfn_union)
Take wavefunction union and initialize the Solver.
- virtual [~OEPDevSolver](#) ()
Destructor.
- virtual double [compute_oeplib](#) (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_oeplib](#)
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.

12.12.1 Detailed Description

Solver of properties of molecular aggregates. Abstract base.

Uses only a wavefunction union object to initialize.

12.12.2 Constructor & Destructor Documentation

12.12.2.1 OEPDevSolver::OEPDevSolver (SharedWavefunctionUnion wfn_union)

Take wavefunction union and initialize the Solver.

Parameters

| | |
|------------------|--|
| <i>wfn_union</i> | - wavefunction union of isolated molecular wavefunctions |
|------------------|--|

12.12.3 Member Function Documentation

12.12.3.1 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

| | |
|------------------|--|
| <i>target</i> | - target property |
| <i>wfn_union</i> | - 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](#)

12.12.3.2 `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

| | |
|---------------|--------------------|
| <i>method</i> | - benchmark method |
|---------------|--------------------|

Implemented in [oepdev::RepulsionEnergySolver](#), and [oepdev::ElectrostaticEnergySolver](#).

12.12.3.3 `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

| | |
|---------------|------------------------|
| <i>method</i> | - flavour of OEP model |
|---------------|------------------------|

Implemented in [oepdev::RepulsionEnergySolver](#), and [oepdev::ElectrostaticEnergySolver](#).

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

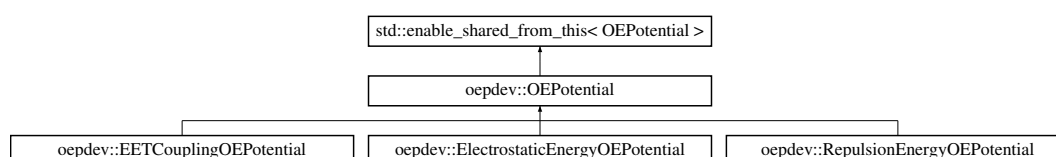
- `oepdev/libutil/solver.h`
- `oepdev/libutil/solver.cc`

12.13 oepdev::OEPotential Class Reference

Generalized One-Electron Potential: Abstract base.

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

Inheritance diagram for `oepdev::OEPotential`:



Public Member Functions

- **OEPotential** (SharedWavefunction [wfn](#), Options &options)
ESP-based OEP object.
- **OEPotential** (SharedWavefunction [wfn](#), SharedBasisSet auxiliary, Options &options)
DF-based OEP object.
- virtual **~OEPotential** ()
Destructor.
- 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.
- SharedMatrix **matrix** (const std::string &oeptype) const
Retrieve matrix potential.
- SharedWavefunction **wfn** () const
Retrieve wavefunction object.
- void **set_name** (const std::string &name)
- virtual void **print_header** () const =0

- virtual void **compute** (const std::string &oeptype)=0
- virtual void **compute** (void)

- virtual void **write_cube** (const std::string &oeptype, const std::string &fileName)
- virtual void **compute_3D** (const std::string &oeptype, const double &x, const double &y, const double &z, double &v)=0

Static Public Member Functions

- static std::shared_ptr
< **OEPotential** > **build** (const std::string &category, SharedWavefunction [wfn](#), Options &options)
Build ESP-based OEP object.
- static std::shared_ptr
< **OEPotential** > **build** (const std::string &category, SharedWavefunction [wfn](#), SharedBasisSet auxiliary, Options &options)
Build DF-based OEP object.

Public Attributes

- const bool **is_density_fitted**
Is this OEP density-fitted?
- const bool **is_esp_based**
Is this OEP ESP-based?

Protected Attributes

- Options [options_](#)
Psi4 options.
- SharedWavefunction [wfn_](#)
Wavefunction.
- SharedBasisSet [primary_](#)
Promary Basis set.
- SharedBasisSet [auxiliary_](#)
Auxiliary Basis set.
- std::string [name_](#)
Name of this OEP;.
- std::vector< std::string > [oepTypes_](#)
Types of OEP's within the scope of this object.
- std::map< std::string, SharedMatrix > [oepMatrices_](#)
OEP's matrix forms for each OEP type.
- 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.

12.13.1 Detailed Description

Generalized One-Electron Potential: Abstract base.

Manages OEP's in matrix and 3D forms.

12.13.2 Constructor & Destructor Documentation

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

ESP-based OEP object.

Parameters

| | |
|----------------|----------------|
| <i>wfn</i> | - wavefunction |
| <i>options</i> | - Psi4 options |

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

DF-based OEP object.

Parameters

| | |
|------------------|--|
| <i>wfn</i> | - wavefunction |
| <i>auxiliary</i> | - basis set for density fitting of OEP's |
| <i>options</i> | - Psi4 options |

12.13.3 Member Function Documentation

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

Build ESP-based OEP object.

Parameters

| | |
|----------------|----------------|
| <i>type</i> | - OEP category |
| <i>wfn</i> | - wavefunction |
| <i>options</i> | - Psi4 options |

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

Build DF-based OEP object.

Parameters

| | |
|------------------|--|
| <i>type</i> | - OEP category |
| <i>wfn</i> | - wavefunction |
| <i>auxiliary</i> | - basis set for density fitting of OEP's |
| <i>options</i> | - Psi4 options |

12.13.3.3 `void OEPotential::compute_3D (const std::string & oepType, const double & x, const double & y, const double & z, double & v) [pure virtual]`

Compute value of potential in point x, y, z and save at v

Implemented in [oepdev::EETCouplingOEPotential](#), [oepdev::RepulsionEnergyOEPotential](#), and [oepdev::ElectrostaticEnergyOEPotential](#).

12.13.3.4 `void OEPotential::write_cube (const std::string & oepType, const std::string & fileName) [virtual]`

Write potential to a cube file

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

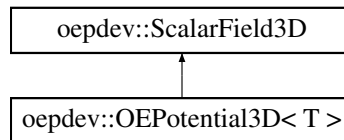
- oepdev/liboep/oep.h
- oepdev/liboep/oep.cc

12.14 oepdev::OEPotential3D< T > Class Template Reference

Class template for OEP scalar fields.

```
#include <space3d.h>
```

Inheritance diagram for oepdev::OEPotential3D< T >:



Public Member Functions

- [OEPotential3D](#) (const int &np, const double &padding, std::shared_ptr< T > oep, const std::string &oepType)
Construct random spherical collection of scalar field of type T.
- [OEPotential3D](#) (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 scalar field of type T.
- virtual [~OEPotential3D](#) ()
Destructor.
- virtual double [compute_xyz](#) (const double &x, const double &y, const double &z)
Compute a value of scalar 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 scalar field type stored in instance of T

Additional Inherited Members

12.14.1 Detailed Description

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

Class template for OEP scalar 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,
                  double& v);

    shared_ptr<psi::Wavefunction> wfn() const {return wfn_;}
};
  
```

with the `descriptor` of a certain scalar field type, `x`, `y`, `z` the points in 3D space in which the scalar 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

| | |
|----------|---|
| <i>T</i> | the compatible class (e.g. <code>oepdev::OEPotential</code>) |
|----------|---|

12.14.2 Constructor & Destructor Documentation

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

Construct random spherical collection of scalar field of type T.

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

Parameters

| | |
|----------------|-----------------------------------|
| <i>np</i> | - number of points to draw |
| <i>padding</i> | - spherical padding distance (au) |
| <i>oep</i> | - OEP object of type T |
| <i>oepType</i> | - type of OEP |

12.14.2.2 `template<class T> oepdev::OEPotential3D< T>::OEPotential3D (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 scalar field of type T.

The points are generated according to Gaussian cube file format.

Parameters

| | |
|----------------|--------------------------------------|
| <i>nx</i> | - number of points along x direction |
| <i>ny</i> | - number of points along y direction |
| <i>nz</i> | - number of points along z direction |
| <i>px</i> | - padding distance along x direction |
| <i>py</i> | - padding distance along y direction |
| <i>pz</i> | - padding distance along z direction |
| <i>oep</i> | - OEP object of type T |
| <i>oepType</i> | - type of OEP |
| <i>options</i> | - Psi4 options object |

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

- `oepdev/libutil/space3d.h`

12.15 `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:

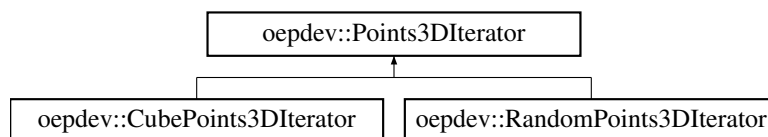
- `oepdev/libutil/space3d.h`

12.16 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_`

12.16.1 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.

12.16.2 Constructor & Destructor Documentation

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

Plain constructor. Initializes the abstract features.

Parameters

| | |
|-----------------|---|
| <code>np</code> | - number of points this iterator is constructed for |
|-----------------|---|

12.16.3 Member Function Documentation

12.16.3.1 `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

| | |
|-----------------|--------------------------------------|
| <code>nx</code> | - number of points along x direction |
| <code>ny</code> | - number of points along y direction |
| <code>nz</code> | - number of points along z direction |
| <code>dx</code> | - spacing distance along x direction |
| <code>dy</code> | - spacing distance along y direction |
| <code>dz</code> | - spacing distance along y direction |
| <code>ox</code> | - coordinate x of cube origin |
| <code>oy</code> | - coordinate y of cube origin |
| <code>oz</code> | - coordinate z of cube origin |

12.16.3.2 `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 distribution in 3D space.

Parameters

| | |
|---------------|---|
| <i>np</i> | - number of points to draw |
| <i>radius</i> | - sphere radius inside which points are to be drawn |
| <i>cx</i> | - coordinate x of sphere's centre |
| <i>cy</i> | - coordinate y of sphere's centre |
| <i>cz</i> | - coordinate z of sphere's centre |

12.16.3.3 `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 distribution in 3D space enclosing a molecule given. All drawn points lie outside the van der Waals volume.

Parameters

| | |
|------------|---|
| <i>np</i> | - number of points to draw |
| <i>pad</i> | - radius padding of a minimal sphere enclosing the molecule |
| <i>mol</i> | - Psi4 molecule object |

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

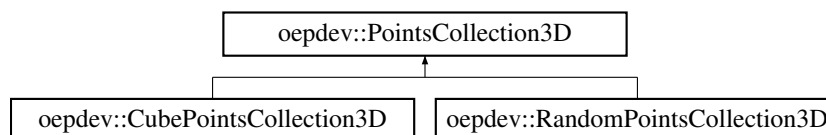
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.17 oepdev::PointsCollection3D Class Reference

Collection of points in 3D space. Abstract base.

```
#include <space3d.h>
```

Inheritance diagram for oepdev::PointsCollection3D:



Public Types

- enum [Collection](#) { **Random**, **Cube** }
- Public descriptor 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

12.17.1 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.

12.17.2 Constructor & Destructor Documentation

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

Initialize abstract features.

Parameters

| | |
|-----------|----------------------------------|
| <i>np</i> | - number of points to be created |
|-----------|----------------------------------|

12.17.3 Member Function Documentation

12.17.3.1 `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

| | |
|----------------|---|
| <i>npoints</i> | - number of points to draw |
| <i>radius</i> | - sphere radius inside which points are to be drawn |
| <i>cx</i> | - coordinate x of sphere's centre |
| <i>cy</i> | - coordinate y of sphere's centre |
| <i>cz</i> | - coordinate z of sphere's centre |

12.17.3.2 `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. excluding the van der Waals volume.

Parameters

| | |
|----------------|---|
| <i>np</i> | - number of points to draw |
| <i>padding</i> | - radius padding of a minimal sphere enclosing the molecule |
| <i>mol</i> | - Psi4 molecule object |

12.17.3.3 `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 parallelepiped according to Gaussian cube file format.

Parameters

| | |
|----------------|--------------------------------------|
| <i>nx</i> | - number of points along x direction |
| <i>ny</i> | - number of points along y direction |
| <i>nz</i> | - number of points along z direction |
| <i>px</i> | - padding distance along x direction |
| <i>py</i> | - padding distance along y direction |
| <i>pz</i> | - padding distance along z direction |
| <i>bs</i> | - Psi4 basis set object |
| <i>options</i> | - Psi4 options object |

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

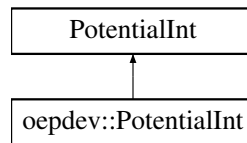
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.18 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::Potentillnt.
- [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.

12.18.1 Detailed Description

Computes potential integrals.

12.18.2 Constructor & Destructor Documentation

12.18.2.1 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::Potentillnt.

Parameters

| | |
|--------------|------------------------------|
| <i>st</i> | - Spherical transform object |
| <i>bs1</i> | - basis set for first space |
| <i>bs2</i> | - basis set for second space |
| <i>deriv</i> | - derivative level |

12.18.2.2 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

| | |
|-----------|------------------------------|
| <i>st</i> | - Spherical transform object |
|-----------|------------------------------|

| | |
|--------------|---|
| <i>bs1</i> | - basis set for first space |
| <i>bs2</i> | - basis set for second space |
| <i>Qxyz</i> | - matrix with charges and their positions |
| <i>deriv</i> | - derivative level |

12.18.2.3 `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

| | |
|--------------|------------------------------|
| <i>st</i> | - Spherical transform object |
| <i>bs1</i> | - basis set for first space |
| <i>bs2</i> | - basis set for second space |
| <i>x</i> | - x coordinate of <i>q</i> |
| <i>y</i> | - y coordinate of <i>q</i> |
| <i>z</i> | - z coordinate of <i>q</i> |
| <i>q</i> | - value of the probe charge |
| <i>deriv</i> | - derivative level |

12.18.3 Member Function Documentation

12.18.3.1 `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

| | |
|----------|-----------------------------|
| <i>x</i> | - x coordinate of <i>q</i> |
| <i>y</i> | - y coordinate of <i>q</i> |
| <i>z</i> | - z coordinate of <i>q</i> |
| <i>q</i> | - value of the probe charge |

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

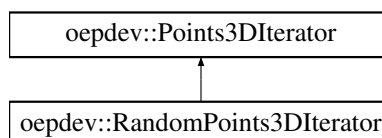
- `oepdev/libpsi/potential.h`
- `oepdev/libpsi/potential.cc`

12.19 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

12.19.1 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:

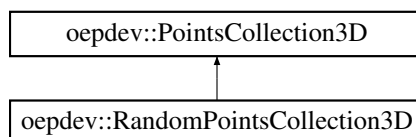
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.20 oepdev::RandomPointsCollection3D Class Reference

Collection of random points in 3D space.

```
#include <space3d.h>
```

Inheritance diagram for oepdev::RandomPointsCollection3D:



Public Member Functions

- **RandomPointsCollection3D** ([Collection](#) collectionType, const int &npoints, const double &radius, const double &cx, const double &cy, const double &cz)
- **RandomPointsCollection3D** ([Collection](#) collectionType, const int &npoints, const double &padding, psi::SharedMolecule mol)
- virtual void [print](#) () const

Print the information to Psi4 output file.

Additional Inherited Members

12.20.1 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:

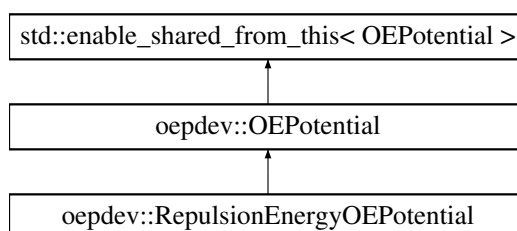
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.21 oepdev::RepulsionEnergyOEPotential Class Reference

Generalized One-Electron Potential for Pauli repulsion energy calculations.

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

Inheritance diagram for oepdev::RepulsionEnergyOEPotential:



Public Member Functions

- **RepulsionEnergyOEPotential** (SharedWavefunction [wfn](#), SharedBasisSet auxiliary, Options &options)
- **RepulsionEnergyOEPotential** (SharedWavefunction [wfn](#), Options &options)
- virtual void **compute** (const std::string &oepType) override
- virtual void **compute_3D** (const std::string &oepType, const double &x, const double &y, const double &z, double &v) override
- virtual void **print_header** () const override

Additional Inherited Members

12.21.1 Detailed Description

Generalized One-Electron Potential for Pauli repulsion energy calculations.

Contains the following OEP types:

12.21.2 Member Function Documentation

12.21.2.1 void RepulsionEnergyOEPotential::compute_3D (const std::string & oepType, const double & x, const double & y, const double & z, double & v) [override],[virtual]

Compute value of potential in point x, y, z and save at v

Implements [oepdev::OEPotential](#).

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

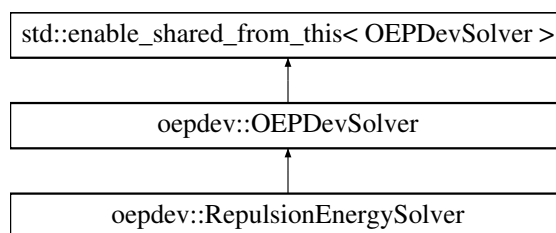
- oepdev/liboep/oep.h
- oepdev/liboep/oep.cc

12.22 oepdev::RepulsionEnergySolver Class Reference

Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.

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

Inheritance diagram for oepdev::RepulsionEnergySolver:



Public Member Functions

- **RepulsionEnergySolver** (SharedWavefunctionUnion wfn_union)
- virtual double **compute_oep_based** (const std::string &method="DEFAULT")
Compute property by using OEP's.
- virtual double **compute_benchmark** (const std::string &method="DEFAULT")
Compute property by using benchmark method.

Additional Inherited Members

12.22.1 Detailed Description

Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.

The implemented methods are shown below

| Keyword | Method Description |
|--------------------------|---|
| Benchmark Methods | |
| HAYES_STONE | *Default*. Exact Pauli Repulsion energy at HF level from Hayes and Stone (1984). |
| DENSITY_BASED | Approximate 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. |
| 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 12.2: Methods available in the Solver

Below the detailed description of the above methods is given. In the formulae, the Coulomb notation for electron repulsion integrals (ERI's) in MO basis is adopted; i.e,

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

It is also assumed that the orbitals are real.

Benchmark Methods

Exact Pauli Repulsion energy at HF level.

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

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

where \mathbf{S} is the overlap matrix between the doubly-occupied orbitals. The exact exchange energy is for a closed shell case given as

$$E^{\text{Ex}} = -2 \sum_{a \in A} \sum_{b \in B} (ab|ba)$$

Similarity transformation of molecular orbitals does not affect the resulting energies.

Approximate Pauli Repulsion energy at HF level from Murrell et al.

By expanding the overlap matrix in a Taylor series one can show that the Pauli repulsion energy is approximately given as

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

where the first-order term is

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

whereas the second-order term is

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

By using OEP technique, the above theory can be exactly re-cast *without* any further approximations.

OEP-Based Methods

The Murrell et al's theory of Pauli repulsion is here re-cast by introducing OEP's.

S1 term via DF-OEP, S2 term via ESP-OEP.

S1 and S2 terms via ESP-OEP.

Notes:

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

12.22.2 Member Function Documentation

12.22.2.1 `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

| | |
|---------------|--------------------|
| <i>method</i> | - benchmark method |
|---------------|--------------------|

Implements [oepdev::OEPDevSolver](#).

12.22.2.2 `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

| | |
|---------------|------------------------|
| <i>method</i> | - flavour of OEP model |
|---------------|------------------------|

Implements [oepdev::OEPDevSolver](#).

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

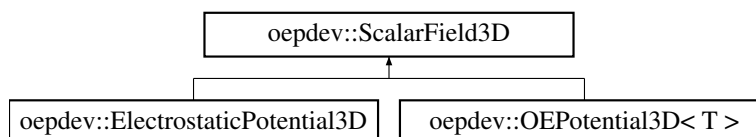
- `oepdev/libutil/solver.h`
- `oepdev/libutil/solver.cc`

12.23 oepdev::ScalarField3D Class Reference

Scalar field in 3D space. Abstract base.

```
#include <space3d.h>
```

Inheritance diagram for oepdev::ScalarField3D:



Public Member Functions

- [ScalarField3D](#) (const int &np, const double &pad, psi::SharedWavefunction [wfn](#), psi::Options &options)
Construct potential on random grid by providing wavefunction.
- [ScalarField3D](#) (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 [~ScalarField3D](#) ()
Destructor.
- virtual int [npoints](#) () const
Get the number of points at which the scalar 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(x, y, z)] }.
- 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.
- virtual void [compute](#) ()
Compute the scalar field in each point from the point collection.
- virtual double [compute_xyz](#) (const double &x, const double &y, const double &z)=0
Compute a value of scalar 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< [ScalarField3D](#) > [build](#) (const std::string &type, const int &np, const double &pad, psi::SharedWavefunction [wfn](#), psi::Options &options)
Build scalar field of random points.
- static shared_ptr< [ScalarField3D](#) > [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)
Build scalar field of points on a g09-cube grid.

Protected Attributes

- `std::shared_ptr`
`< PointsCollection3D > pointsCollection_`
Collection of points at which the scalar field is to be computed.
- `std::shared_ptr< psi::Matrix >` `data_`
The data matrix in a form $\{ [x, y, z, f(x, y, z)] \}$.
- `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.
- `bool` `isComputed_`
Has data already computed?

12.23.1 Detailed Description

Scalar field in 3D space. Abstract base.

Create scalar field defined at points distributed randomly or as an ordered g09 cube-like collection. Currently implemented scalar fields are:

- Electrostatic potential - computes electrostatic potential (requires wavefunction)
- Template of generic classes - compute custom scalar 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 scalar field are currently implemented:

- ELECTROSTATIC POTENTIAL

12.23.2 Member Function Documentation

12.23.2.1 `std::shared_ptr< ScalarField3D > oepdev::ScalarField3D::build (const std::string & type, const int & np, const double & pad, psi::SharedWavefunction wfn, psi::Options & options) [static]`

Build scalar field of random points.

Parameters

| | |
|----------------|---|
| <i>type</i> | - type of scalar field |
| <i>np</i> | - number of points |
| <i>pad</i> | - radius padding of a minimal sphere enclosing the molecule |
| <i>wfn</i> | - Psi4 Wavefunction containing the molecule |
| <i>options</i> | - Psi4 options |

12.23.2.2 `std::shared_ptr< ScalarField3D > oepdev::ScalarField3D::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) [static]`

Build scalar field of points on a g09-cube grid.

Parameters

| | |
|----------------|---|
| <i>type</i> | - type of scalar field |
| <i>nx</i> | - number of points along x direction |
| <i>ny</i> | - number of points along y direction |
| <i>nz</i> | - number of points along z direction |
| <i>px</i> | - padding distance along x direction |
| <i>py</i> | - padding distance along y direction |
| <i>pz</i> | - padding distance along z direction |
| <i>wfn</i> | - Psi4 Wavefunction containing the molecule |
| <i>options</i> | - Psi4 options |

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

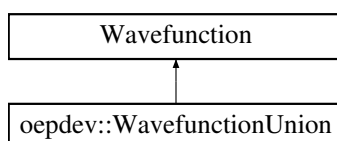
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.24 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.*
- 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 &noccp, 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 &noccp, 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 integrals.

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< 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.

12.24.1 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)
- `frzvp_` (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.

12.24.2 Constructor & Destructor Documentation

12.24.2.1 `oepdev::WavefunctionUnion::WavefunctionUnion (SharedWavefunction ref_wfn, Options & options)`

Constructor.

Provide wavefunction with molecule containing at least 2 fragments.

Parameters

| | |
|----------------|--------------------------|
| <i>ref_wfn</i> | - reference wavefunction |
| <i>options</i> | - Psi4 options |

12.24.3 Member Function Documentation

12.24.3.1 `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

| | |
|---------------|--|
| <i>basis</i> | the symmetry basis to use AO, SO |
| <i>subset</i> | 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

12.24.3.2 `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

| | |
|---------------|--|
| <i>basis</i> | the symmetry basis to use AO, SO |
| <i>subset</i> | 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

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- oepdev/libutil/wavefunction_union.h
- oepdev/libutil/wavefunction_union.cc

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