oepdev

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Contents

1 Main Page 1

2 License 3

3 OEP Design. 5

- 3.1 OEP Classes 5
  - 3.1.1 Structure of possible OEP-based expressions and their unification 5

4 List of One-Electron Potentals 7

- 4.1 Electrostatic Energy OEP's 7
- 4.2 Pauli Repulsion OEP's 7
  - 4.2.1 First-order contribution in overlap matrix expansion. 7
  - 4.2.2 Second-order contribution in overlap matrix expansion. 8
- 4.3 Excitonic Energy Transfer OEP's 8
  - 4.3.1 ET contributions. 8
  - 4.3.2 HT contributions. 8
  - 4.3.3 CT contributions. 8
- 4.4 Full HF Interaction OEP's 8

5 Density-fitting specialized for OEP's 9

6 Implemented Models 11

- 6.1 Target Properties 11
- 6.2 Target, Benchmark and Competing Models 11

7 Contributing to oep-dev 13

- 7.1 Main routine and libraries 13
- 7.2 Header files in libraries 13
- 7.3 Environmental variables 14
- 7.4 Documenting the code 14
- 7.5 Naming conventions 14
- 7.6 Use Object-Oriented Programming 15

8 Namespace Index 17

8.1 Namespace List 17

9 Hierarchical Index 19

9.1 Class Hierarchy 19

10 Class Index 21

10.1 Class List 21

11 Namespace Documentation 23

11.1 oepdev Namespace Reference 23

11.1.1 Detailed Description 25

11.1.2 Function Documentation 25

11.1.2.1 create_superfunctional 25

11.1.2.2 extract_monomer 25

11.1.2.3 solve_scf 25

11.2 psi Namespace Reference 25

11.2.1 Detailed Description 26

11.2.2 Function Documentation 26

11.2.2.1 oepdev 26

11.2.2.2 read_options 27

12 Class Documentation 29

12.1 oepdev::AllAOIntegralsIterator Class Reference 29

12.1.1 Detailed Description 29

12.1.2 Constructor & Destructor Documentation 30

12.1.2.1 AllAOIntegralsIterator 30

12.1.2.2 AllAOIntegralsIterator 30

12.1.3 Member Function Documentation 30

12.1.3.1 index 30

12.2 oepdev::AllAOShellCombinationsIterator Class Reference 30

12.2.1 Detailed Description 31

12.2.2 Constructor & Destructor Documentation 31

12.2.2.1 AllAOShellCombinationsIterator 31

12.2.2.2 AllAOShellCombinationsIterator 31

12.2.3 Member Function Documentation 32

12.2.3.1 compute_shell 32

12.3 oepdev::ChargeTransferEnergyOEPotential Class Reference 32

12.3.1 Detailed Description 32

12.3.2 Member Function Documentation 33

12.3.2.1 compute_3D 33

12.4 oepdev::ChargeTransferEnergySolver Class Reference 33

12.4.1 Detailed Description 33
12.4.2 Member Function Documentation 35
12.4.2.1 compute_benchmark 35
12.4.2.2 compute_oep_based 35
12.5 oepdev::CPHF Class Reference 36
12.5.1 Detailed Description 37
12.5.2 Constructor & Destructor Documentation 37
12.5.2.1 CPHF 37
12.6 oepdev::CubePoints3DIterator Class Reference 37
12.6.1 Detailed Description 38
12.7 oepdev::CubePointsCollection3D Class Reference 38
12.7.1 Detailed Description 39
12.8 oepdev::DIISManager Class Reference 39
12.8.1 Detailed Description 39
12.8.2 Constructor & Destructor Documentation 39
12.8.2.1 DIISManager 39
12.8.3 Member Function Documentation 39
12.8.3.1 compute 39
12.8.3.2 put 40
12.8.3.3 update 40
12.9 oepdev::EETCouplingOEPotential Class Reference 40
12.9.1 Detailed Description 40
12.9.2 Member Function Documentation 41
12.9.2.1 compute_3D 41
12.10 oepdev::ElectrostaticEnergyOEPotential Class Reference 41
12.10.1 Detailed Description 41
12.10.2 Member Function Documentation 42
12.10.2.1 compute_3D 42
12.11 oepdev::ElectrostaticEnergySolver Class Reference 42
12.11.1 Detailed Description 42
12.11.2 Member Function Documentation 44
12.11.2.1 compute_benchmark 44
12.11.2.2 compute_oep_based 44
12.12 oepdev::ElectrostaticPotential3D Class Reference 44
12.12.1 Detailed Description 45
12.13 oepdev::ESPSolver Class Reference 45
12.13.1 Detailed Description 46
12.13.2 Constructor & Destructor Documentation 47
12.13.2.1 ESPSolver 47
12.13.2.2 ESPSolver 47

12.14 oepdev::OEPDevSolver Class Reference 47
12.14.1 Detailed Description 48
12.14.2 Constructor & Destructor Documentation 48
12.14.2.1 OEPDevSolver 48
12.14.3 Member Function Documentation 48
12.14.3.1 build 48
12.14.3.2 compute_benchmark 49
12.14.3.3 compute_oep_based 49
12.15 oepdev::OEPotential Class Reference 49
12.15.1 Detailed Description 51
12.15.2 Constructor & Destructor Documentation 51
12.15.2.1 OEPotential 51
12.15.2.2 OEPotential 51
12.15.3 Member Function Documentation 51
12.15.3.1 build 51
12.15.3.2 build 52
12.15.3.3 compute_3D 52
12.15.3.4 write_cube 52
12.16 oepdev::OEPotential3D< T > Class Template Reference 52
12.16.1 Detailed Description 53
12.16.2 Constructor & Destructor Documentation 53
12.16.2.1 OEPotential3D 53
12.16.2.2 OEPotential3D 54
12.17 oepdev::Points3DIterator::Point Struct Reference 54
12.18 oepdev::Points3DIterator Class Reference 54
12.18.1 Detailed Description 56
12.18.2 Constructor & Destructor Documentation 56
12.18.2.1 Points3DIterator 56
12.18.3 Member Function Documentation 56
12.18.3.1 build 56
12.18.3.2 build 56
12.18.3.3 build 57
12.19 oepdev::PointsCollection3D Class Reference 57
12.19.1 Detailed Description 58
12.19.2 Constructor & Destructor Documentation 58
12.19.2.1 PointsCollection3D 58
12.19.3 Member Function Documentation 58
12.19.3.1 build 58
12.19.3.2 build 59
12.19.3.3 build 59

12.20 oepdev::PotentialInt Class Reference . . . 59
  12.20.1 Detailed Description . . . 60
  12.20.2 Constructor & Destructor Documentation . . . 60
    12.20.2.1 PotentialInt . . . 60
    12.20.2.2 PotentialInt . . . 60
    12.20.2.3 PotentialInt . . . 61
  12.20.3 Member Function Documentation . . . 61
    12.20.3.1 set_charge_field . . . 61
12.21 oepdev::RandomPoints3DIterator Class Reference . . . 61
  12.21.1 Detailed Description . . . 62
12.22 oepdev::RandomPointsCollection3D Class Reference . . . 63
  12.22.1 Detailed Description . . . 63
12.23 oepdev::RepulsionEnergyOEPotential Class Reference . . . 63
  12.23.1 Detailed Description . . . 64
  12.23.2 Member Function Documentation . . . 64
    12.23.2.1 compute_3D . . . 64
12.24 oepdev::RepulsionEnergySolver Class Reference . . . 64
  12.24.1 Detailed Description . . . 65
  12.24.2 Member Function Documentation . . . 68
    12.24.2.1 compute_benchmark . . . 68
    12.24.2.2 compute_oep_based . . . 69
12.25 oepdev::ScalarField3D Class Reference . . . 69
  12.25.1 Detailed Description . . . 71
  12.25.2 Member Function Documentation . . . 71
    12.25.2.1 build . . . 71
    12.25.2.2 build . . . 71
12.26 oepdev::WavefunctionUnion Class Reference . . . 72
  12.26.1 Detailed Description . . . 74
  12.26.2 Constructor & Destructor Documentation . . . 75
    12.26.2.1 WavefunctionUnion . . . 75
  12.26.3 Member Function Documentation . . . 76
    12.26.3.1 Ca_subset . . . 76
    12.26.3.2 Cb_subset . . . 76

Index **77**

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 generall any correlated wavefunction and derived OEP‘s should be allowed to work with each other.

3.1 OEP Classes

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

3.1.1 Structure of possible OEP-based expressions and their unification

Structure of OEP-based mathematical expressions is listed below:

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

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

Matrix Element	DF-based form	ESP-based form
$\left(\mu\middle|\hat{v}^{A[\mu]}\middle|\sigma\right)$	$\sum_{\iota\in A} v^A_{\mu\iota} S_{\iota\sigma}$	$\sum_{\alpha\in A} q_\alpha^{A[\mu]} V_{\mu\sigma}^{(\alpha)}$
$\left(i\middle|\hat{v}^{A[i]}\middle|j\right)$	$\sum_{\iota\in A} v^A_{i\iota} S_{\iota j}$	$\sum_{\alpha\in A} q_\alpha^{A[i]} V_{ij}^{(\alpha)}$

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

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

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

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

Chapter 4

List of One-Electron Potentals

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

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:

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

4.2 Pauli Repulsion OEP's

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

4.2.1 First-order contribution in overlap matrix expansion.

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

3D forms:

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

Matrix forms:

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

4.2.2 Second-order contribution in overlap matrix expansion.

To be added here!

4.3 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:

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

Matrix forms:

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

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 completness 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:

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

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 specyfying the existence of include of the particular header file. The format of such is

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

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

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

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

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

7.3 Environmental variables

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

```
OEPDEV_XXXX
```

where `XXXX` is the descriptive name of variable.

7.4 Documenting the code

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

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

Things to remember:

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

7.5 Naming conventions

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

Some loose suggestions:

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

7.6 Use Object-Oriented Programming

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

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

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

Chapter 8

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::ChargeTransferEnergySolver . . . . . **??**
    - oepdev::ElectrostaticEnergySolver . . . . . **??**
    - oepdev::RepulsionEnergySolver . . . . . **??**
  - oepdev::OEPotential . . . . . **??**
    - oepdev::ChargeTransferEnergyOEPotential . . . . . **??**
    - 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::ChargeTransferEnergyOEPotential
    Generalized One-Electron Potential for Charge-Transfer Interaction Energy . . . . **??**
oepdev::ChargeTransferEnergySolver
    Compute the Charge-Transfer interaction energy between unperturbed wavefunctions . . . . . **??**
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 . . . . **??**
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 . . . . ??
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.
- class RepulsionEnergyOEPotential

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

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

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

  Compute the Charge-Transfer 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 preambule (void)

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

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

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

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

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

name	name of the functional ("HF" is now only available)
options	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

molecule_dimer	psi::SharedMolecule object with dimer
id	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

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

Returns

psi::SharedWavefunction SCF wavefunction of the molecule

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 | +========================+========================+======================+ | 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 | +----------------------—+----------------------—+--------------------—+

Parameters of the plugin driver:

Parameters

ref_wfn	shared wavefunction of a dimer
options	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

name	name of driver function
options	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

shellIter	- shell iterator object

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

Construct by shell iterator (pointed by shared pointer)

Parameters

shellIter	- 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.
- **AllAOShellCombinationsIterator** (psi::IntegralFactory integrals)
- 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

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

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

Construct by providing integral factory.

Parameters

integrals	- 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

tei	- two electron AO integral

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

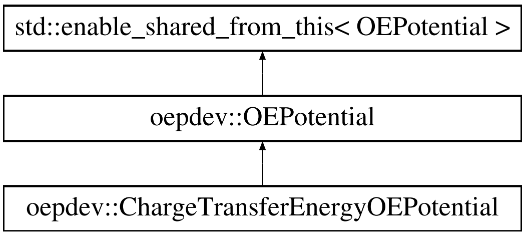
- oepdev/libutil/integrals_iter.h
- oepdev/libutil/integrals_iter.cc

12.3 oepdev::ChargeTransferEnergyOEPotential Class Reference

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

`#include <oep.h>`

Inheritance diagram for oepdev::ChargeTransferEnergyOEPotential:


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

Public Member Functions

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

12.3.1 Detailed Description

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

Contains the following OEP types:

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

12.3.2 Member Function Documentation

12.3.2.1 void ChargeTransferEnergyOEPotential::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:

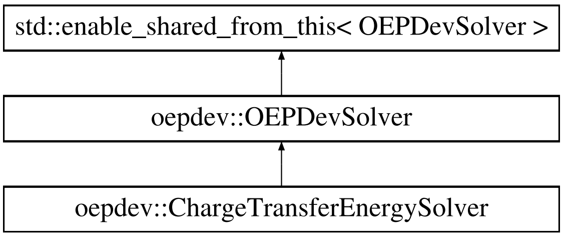
- oepdev/liboep/oep.h
- oepdev/liboep/oep.cc

12.4 oepdev::ChargeTransferEnergySolver Class Reference

Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::ChargeTransferEnergySolver:


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

Public Member Functions

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

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

  Compute property by using benchmark method.

Additional Inherited Members

12.4.1 Detailed Description

Compute the Charge-Transfer interaction energy between unperturbed wavefunctions.

The implemented methods are shown below

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

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

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

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

Keyword	**Method Description**
Benchmark Methods	
`OTTO_LADIK`	∗Default∗. CT energy at HF level from Otto and Ladik (1975).
`EFP2`	CT energy at HF level from EFP2 model.
OEP-Based Methods	
`OTTO_LADIK`	∗Default∗. OEP-based Otto-Ladik expressions.

Table 12.1: Methods available in the Solver

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

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

Benchmark Methods

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

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

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

where

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

and analogously the twin term.

CT energy at HF level by EFP2.

In EFP2 method, CT energy is given as

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

where

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

and analogously the twin term.

OEP-Based Methods

OEP-Based Otto-Ladik's theory

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

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

where

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

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

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

The OEP matrix for density fitted part is given by

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

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

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

so that

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

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

12.4.2 Member Function Documentation

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

Compute property by using benchmark method.

Each solver object has one `DEFAULT` benchmark method

Parameters

method	- benchmark method

Implements oepdev::OEPDevSolver.

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

Compute property by using OEP's.

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

Parameters

method	- flavour of OEP model

Implements oepdev::OEPDevSolver.

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

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

12.5 oepdev::CPHF Class Reference

CPHF solver class.

`#include <cphf.h>`

Public Member Functions

- CPHF (SharedWavefunction ref_wfn, Options &options)

  orbital-associated polarizabilities tensors
- ∼CPHF ()

  Desctructor.
- 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.

12.5.1 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> polarizability = cphf->get_molecular_polarizability(); std::shared_ptr<Tensor> orbital_polars = cphf->get_orbital_polarizabilities();

12.5.2 Constructor & Destructor Documentation

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

orbital-associated polarizabilities tensors

Constructor

Parameters

ref_wfn	reference HF wavefunction
options	set of Psi4 options

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

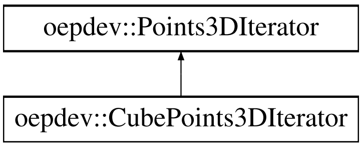
- oepdev/libutil/cphf.h
- oepdev/libutil/cphf.cc

12.6 oepdev::CubePoints3DIterator Class Reference

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

`#include <space3d.h>`

Inheritance diagram for oepdev::CubePoints3DIterator:



Public Member Functions

- **CubePoints3DIterator** (const int &nx, const int &ny, const int &nz, const double &dx, const double &dy, const double &dz, const double &ox, const double &oy, const double &oz)
- virtual void first ()

  Initialize first iteration.
- virtual void next ()

  Step to next iteration.

Protected Attributes

- const int **nx_**
- const int **ny_**
- const int **nz_**
- const double **dx_**
- const double **dy_**
- const double **dz_**
- const double **ox_**
- const double **oy_**
- const double **oz_**
- int **ii_**
- int **jj_**
- int **kk_**

Additional Inherited Members

12.6.1 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:

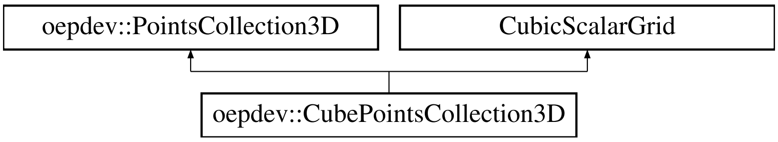
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.7 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

12.7.1 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

12.8 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)

12.8.1 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.

12.8.2 Constructor & Destructor Documentation

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

Constructor.

Parameters

dim	Size of DIIS subspace
na	Number of solution rows
nb	Number of solution columns

12.8.3 Member Function Documentation

12.8.3.1 void oepdev::DIISManager::compute (void)

Perform DIIS interpolation.

12.8.3.2 void oepdev::DIISManager::put (const std::shared_ptr$<$ const Matrix $>$ & *error,* const std::shared_ptr$<$ const Matrix $>$ & *vector*)

Put the current solution to the DIIS manager.

Parameters

error	Shared matrix with current solution error
vector	Shared matrix with current solution vector

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

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

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

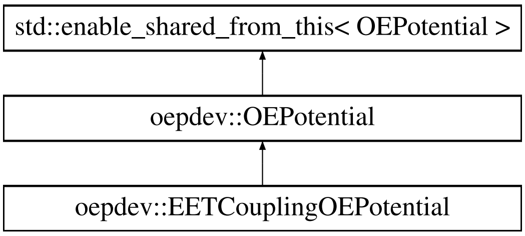
- oepdev/libutil/diis.h
- oepdev/libutil/diis.cc

12.9 oepdev::EETCouplingOEPotential Class Reference

Generalized One-Electron Potential for EET coupling calculations.

`#include <oep.h>`

Inheritance diagram for oepdev::EETCouplingOEPotential:


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

Public Member Functions

- **EETCouplingOEPotential** (SharedWavefunction wfn, SharedBasisSet auxiliary, 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

12.9.1 Detailed Description

Generalized One-Electron Potential for EET coupling calculations.

Contains the following OEP types:

- `Fujimoto.ET1`

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

12.9.2 Member Function Documentation

12.9.2.1 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:

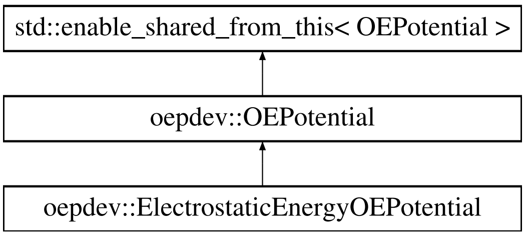
- oepdev/liboep/oep.h
- oepdev/liboep/oep.cc

12.10 oepdev::ElectrostaticEnergyOEPotential Class Reference

Generalized One-Electron Potential for Electrostatic Energy.

`#include <oep.h>`

Inheritance diagram for oepdev::ElectrostaticEnergyOEPotential:


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

Public Member Functions

- ElectrostaticEnergyOEPotential (SharedWavefunction wfn, Options &options)
  Only ESP-based potential is worth implementing.
- virtual void **compute** (const std::string &oepType) override
- 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

12.10.1 Detailed Description

Generalized One-Electron Potential for Electrostatic Energy.

Contains the following OEP types:

- `V`

12.10.2 Member Function Documentation

12.10.2.1 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:

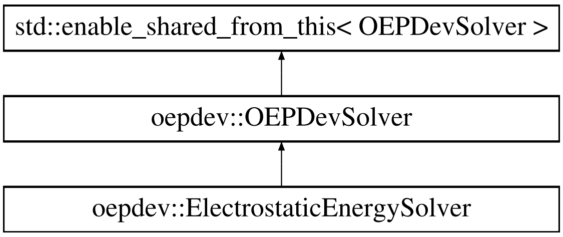
- oepdev/liboep/oep.h
- oepdev/liboep/oep.cc

12.11 oepdev::ElectrostaticEnergySolver Class Reference

Compute the Coulombic interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::ElectrostaticEnergySolver:


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

Public Member Functions

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

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

  Compute property by using benchmark method.

Additional Inherited Members

12.11.1 Detailed Description

Compute the Coulombic interaction energy between unperturbed wavefunctions.

The implemented methods are shown in below

Below the detailed description of the above methods is given.

Benchmark Methods

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 12.2: Methods available in the Solver

Exact Coulombic energy from atomic orbital expansions.

The Coulombic interaction energy is given by

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

where the nuclear-nuclear repulsion energy is

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

the nuclear-electronic attraction energy is

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

and the electron-electron repulsion energy is

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

In the above equations,

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

Exact Coulombic energy from molecular orbital expansion.

This approach is fully equivalent to the atomic orbital expansion shown above. For the closed shell case, the Coulombic interaction energy is given by

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

where the nuclear-nuclear repulsion energy is

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

the nuclear-electronic attraction energy is

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

and the electron-electron repulsion energy is

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

OEP-Based Methods

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

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

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

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

Notes:

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

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

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

12.11.2 Member Function Documentation

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

Compute property by using benchmark method.

Each solver object has one `DEFAULT` benchmark method

Parameters

method	- benchmark method

Implements oepdev::OEPDevSolver.

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

Compute property by using OEP's.

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

Parameters

method	- flavour of OEP model

Implements oepdev::OEPDevSolver.

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

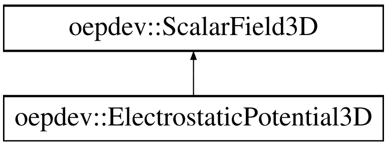
- oepdev/libutil/solver.h
- oepdev/libutil/solver.cc

12.12 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

12.12.1 Detailed Description

Electrostatic potential of a molecule.

Computes the electrostatic potential of a molecule directly from the wavefunction. The electrostatic potential $v(\mathbf{r})$ at point $\mathbf{r}$ is computed from the following formula:

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

where the nuclear and electronic contributions are defined accordingly as

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

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

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

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

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

12.13 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.

12.13.1 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 $v^{\rm ref}(\mathbf{r})$ supplied by the `ScalarField3D` object:

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

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 b} vector or length M are given as

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

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

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

12.13.2 Constructor & Destructor Documentation

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

Construct from scalar field.

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

Parameters

field	- oepdev scalar field object

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

Construct from scalar field.

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

Parameters

field	- oepdev scalar field object
centres	- matrix with coordinates of charge distribution centres

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

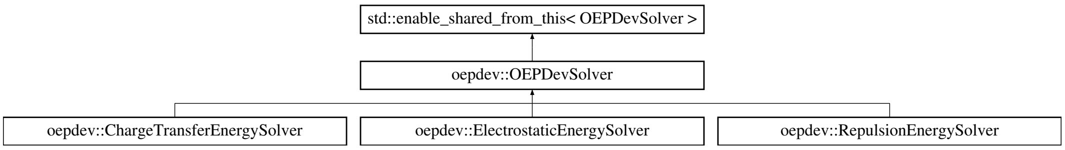
- oepdev/libutil/esp.h
- oepdev/libutil/esp.cc

12.14 oepdev::OEPDevSolver Class Reference

Solver of properties of molecular aggregates. Abstract base.

`#include <solver.h>`

Inheritance diagram for oepdev::OEPDevSolver:


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

Public Member Functions

- OEPDevSolver (SharedWavefunctionUnion wfn_union)

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

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

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

  Compute property by using benchmark method.

Static Public Member Functions

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

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

Protected Attributes

- SharedWavefunctionUnion wfn_union_

  Wavefunction union.
- std::vector< std::string > methods_oepBased_

  Names of all OEP-based methods implemented for a solver.
- std::vector< std::string > methods_benchmark_

  Names of all benchmark methods implemented for a solver.

12.14.1 Detailed Description

Solver of properties of molecular aggregates. Abstract base.

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

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

12.14.2 Constructor & Destructor Documentation

12.14.2.1 OEPDevSolver::OEPDevSolver (SharedWavefunctionUnion *wfn_union*)

Take wavefunction union and initialize the Solver.

Parameters

wfn_union	- wavefunction union of isolated molecular wavefunctions

12.14.3 Member Function Documentation

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

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

Parameters

target	- target property
wfn_union	- wavefunction union of isolated molecular wavefunctions

Implemented target properties:

- `ELECTROSTATIC_ENERGY` - Coulombic interaction energy between unperturbed wavefunctions.
- `REPULSION_ENERGY` - Pauli repulsion interaction energy between unperturbed wavefunctions.

See Also

ElectrostaticEnergySolver

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

Compute property by using benchmark method.

Each solver object has one `DEFAULT` benchmark method

Parameters

method	- benchmark method

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

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

Compute property by using OEP's.

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

Parameters

method	- flavour of OEP model

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

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

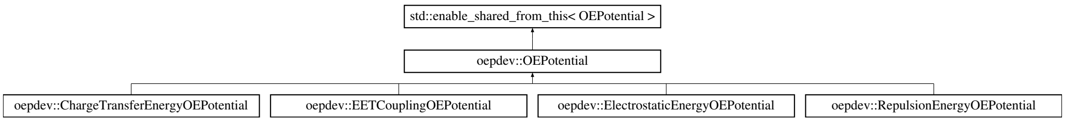
- oepdev/libutil/solver.h
- oepdev/libutil/solver.cc

12.15 oepdev::OEPotential Class Reference

Generalized One-Electron Potential: Abstract base.

`#include <oep.h>`

Inheritance diagram for oepdev::OEPotential:


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

Public Member Functions

- OEPotential (SharedWavefunction wfn, Options &options)

  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.

12.15.1 Detailed Description

Generalized One-Electron Potential: Abstract base.

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

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

12.15.2 Constructor & Destructor Documentation

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

ESP-based OEP object.

Parameters

wfn	- wavefunction
options	- Psi4 options

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

DF-based OEP object.

Parameters

wfn	- wavefunction
auxiliary	- basis set for density fitting of OEP's
options	- Psi4 options

12.15.3 Member Function Documentation

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

Build ESP-based OEP object.

Parameters

type	- OEP category
wfn	- wavefunction
options	- Psi4 options

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

Build DF-based OEP object.

Parameters

type	- OEP category
wfn	- wavefunction
auxiliary	- basis set for density fitting of OEP's
options	- Psi4 options

12.15.3.3 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::ChargeTransferEnergyOEPotential, oepdev::RepulsionEnergyOEPotential, and oepdev::ElectrostaticEnergyOEPotential.

12.15.3.4 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:

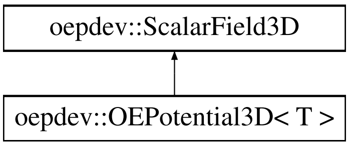
- oepdev/liboep/oep.h
- oepdev/liboep/oep.cc

12.16 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

12.16.1 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

T	the compatible class (e.g. `oepdev::OEPotential`)

12.16.2 Constructor & Destructor Documentation

12.16.2.1 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 distrinution in 3D space.

Parameters

np	- number of points to draw
padding	- spherical padding distance (au)
oep	- OEP object of type T
oepType	- type of OEP

12.16.2.2 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

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

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

- oepdev/libutil/space3d.h

12.17 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:

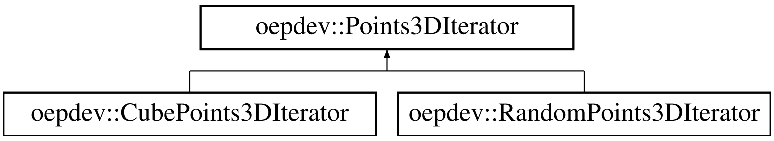
- oepdev/libutil/space3d.h

12.18 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_**

12.18.1 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.

12.18.2 Constructor & Destructor Documentation

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

Plain constructor. Initializes the abstract features.

Parameters

np	- number of points this iterator is constructed for

12.18.3 Member Function Documentation

12.18.3.1 std::shared_ptr< **Points3DIterator** > oepdev::Points3DIterator::build (const int & *nx,* const int & *ny,* const int & *nz,* const double & *dx,* const double & *dy,* const double & *dz,* const double & *ox,* const double & *oy,* const double & *oz*) `[static]`

Build G09 Cube collection iterator.

The points are generated according to Gaussian cube file format.

Parameters

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

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

Build random collection iterator.

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

Parameters

np	- number of points to draw
radius	- sphere radius inside which points are to be drawn
cx	- coordinate x of sphere's centre

cy	- coordinate y of sphere's centre
cz	- coordinate z of sphere's centre

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

Build random collection iterator.

The points are drawn according to uniform distrinution in 3D space enclosing a molecule given. All drawn points lie outside the van der Waals volume.

Parameters

np	- number of points to draw
pad	- radius padding of a minimal sphere enclosing the molecule
mol	- Psi4 molecule object

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

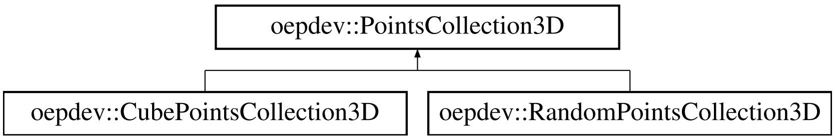
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.19 oepdev::PointsCollection3D Class Reference

Collection of points in 3D space. Abstract base.

`#include <space3d.h>`

Inheritance diagram for oepdev::PointsCollection3D:


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

Public Types

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

  Public 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

12.19.1 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.

12.19.2 Constructor & Destructor Documentation

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

Initialize abstract features.

Parameters

np	- number of points to be created

12.19.3 Member Function Documentation

12.19.3.1 std::shared_ptr< PointsCollection3D > oepdev::PointsCollection3D::build (const int & *npoints,* const double & *radius,* const double & *cx* = `0.0`, const double & *cy* = `0.0`, const double & *cz* = `0.0`) `[static]`

Build random collection of points.

Points uniformly span a sphere.

Parameters

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

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

Build random collection of points.

Points uniformly span space inside a sphere enclosing a molecule. exluding the van der Waals volume.

Parameters

np	- number of points to draw
padding	- radius padding of a minimal sphere enclosing the molecule
mol	- Psi4 molecule object

12.19.3.3 std::shared_ptr< PointsCollection3D > oepdev::PointsCollection3D::build (const int & *nx*, const int & *ny*, const int & *nz*, const double & *px*, const double & *py*, const double & *pz*, psi::SharedBasisSet *bs*, psi::Options & *options*) `[static]`

Build G09 Cube collection of points.

The points span a parallelpiped according to Gaussian cube file format.

Parameters

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

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

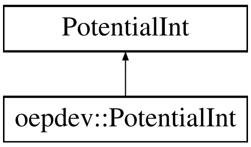
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.20 oepdev::PotentialInt Class Reference

Computes potential integrals.

`#include <potential.h>`

Inheritance diagram for oepdev::PotentialInt:



Public Member Functions

- PotentialInt (std::vector< psi::SphericalTransform > &st, std::shared_ptr< psi::BasisSet > bs1, std::shared_ptr< psi::BasisSet > bs2, int deriv=0)

  Constructor. Initialize identically like in psi::PotentilInt.
- PotentialInt (std::vector< psi::SphericalTransform > &st, std::shared_ptr< psi::BasisSet > bs1, std::shared_ptr< psi::BasisSet > bs2, std::shared_ptr< psi::Matrix > Qxyz, int deriv=0)

  Constructor. Takes an arbitrary collection of charges.
- PotentialInt (std::vector< psi::SphericalTransform > &, std::shared_ptr< psi::BasisSet >, std::shared_ptr< psi::BasisSet >, const double &x, const double &y, const double &z, const double &q=1.0, int deriv=0)

  Constructor. Computes potential for one point x, y, z for a test particle of charge q.
- void set_charge_field (const double &x, const double &y, const double &z, const double &q=1.0)

  Mutator. Set the charge field to be a x, y, z point of charge q.

12.20.1 Detailed Description

Computes potential integrals.

12.20.2 Constructor & Destructor Documentation

12.20.2.1 oepdev::PotentialInt::PotentialInt (std::vector< psi::SphericalTransform > & *st*, std::shared_ptr< psi::BasisSet > *bs1*, std::shared_ptr< psi::BasisSet > *bs2*, int *deriv* = 0)

Constructor. Initialize identically like in psi::PotentilInt.

Parameters

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

12.20.2.2 oepdev::PotentialInt::PotentialInt (std::vector< psi::SphericalTransform > & *st*, std::shared_ptr< psi::BasisSet > *bs1*, std::shared_ptr< psi::BasisSet > *bs2*, std::shared_ptr< psi::Matrix > *Qxyz*, int *deriv* = 0)

Constructor. Takes an arbitrary collection of charges.

Parameters

st	- Spherical transform object
bs1	- basis set for first space
bs2	- basis set for second space
Qxyz	- matrix with charges and their positions

deriv	- derivative level

12.20.2.3 oepdev::PotentialInt::PotentialInt (std::vector< psi::SphericalTransform > & *st*, std::shared_ptr< psi::BasisSet > *bs1*, std::shared_ptr< psi::BasisSet > *bs2*, const double & *x*, const double & *y*, const double & *z*, const double & *q* = `1.0`, int *deriv* = `0`)

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

Parameters

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

12.20.3 Member Function Documentation

12.20.3.1 void oepdev::PotentialInt::set_charge_field (const double & *x*, const double & *y*, const double & *z*, const double & *q* = `1.0`)

Mutator. Set the charge field to be a x, y, z point of charge q.

Parameters

x	- x coordinate of q
y	- y coordinate of q
z	- z coordinate of q
q	- value of the probe charge

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

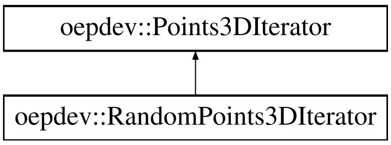
- oepdev/libpsi/potential.h
- oepdev/libpsi/potential.cc

12.21 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

12.21.1 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:

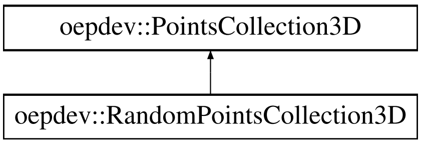
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.22 oepdev::RandomPointsCollection3D Class Reference

Collection of random points in 3D space.

`#include <space3d.h>`

Inheritance diagram for oepdev::RandomPointsCollection3D:


oepdev::PointsCollection3D
oepdev::RandomPointsCollection3D

Public Member Functions

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

  Print the information to Psi4 output file.

Additional Inherited Members

12.22.1 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:

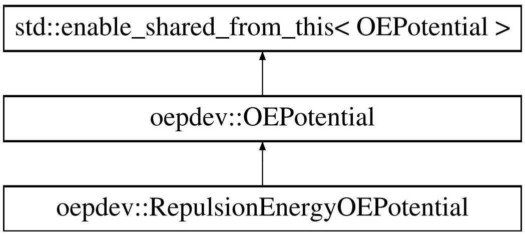
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.23 oepdev::RepulsionEnergyOEPotential Class Reference

Generalized One-Electron Potential for Pauli Repulsion Energy.

`#include <oep.h>`

Inheritance diagram for oepdev::RepulsionEnergyOEPotential:


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

Public Member Functions

- **RepulsionEnergyOEPotential** (SharedWavefunction wfn, SharedBasisSet auxiliary, 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

12.23.1 Detailed Description

Generalized One-Electron Potential for Pauli Repulsion Energy.

Contains the following OEP types:

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

12.23.2 Member Function Documentation

12.23.2.1 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:

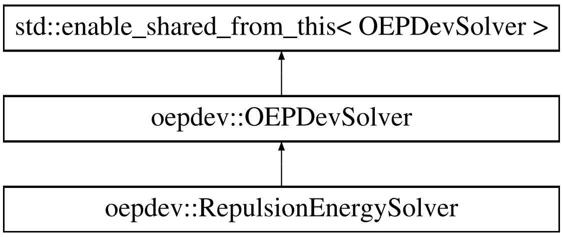
- oepdev/liboep/oep.h
- oepdev/liboep/oep.cc

12.24 oepdev::RepulsionEnergySolver Class Reference

Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.

`#include <solver.h>`

Inheritance diagram for oepdev::RepulsionEnergySolver:


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

Public Member Functions

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

Compute property by using OEP's.

- virtual double compute_benchmark (const std::string &method="DEFAULT")

  Compute property by using benchmark method.

Additional Inherited Members

12.24.1 Detailed Description

Compute the Pauli-Repulsion interaction energy between unperturbed wavefunctions.

The implemented methods are shown below *Note:*

Keyword	**Method Description**
Benchmark Methods	
`HAYES_STONE`	∗Default∗. Pauli Repulsion energy at HF level from Hayes and Stone (1984).
`DENSITY_BASED`	Pauli Repulsion energy at HF level from Mandado and Hermida-Ramon (2012).
`MURRELL_ETAL`	Approximate Pauli Repulsion energy at HF level from Murrell et al (1967).
`OTTO_LADIK`	Approximate Pauli Repulsion energy at HF level from Otto and Ladik (1975).
`EFP2`	Approximate Pauli Repulsion energy at HF level from EFP2 model.
OEP-Based Methods	
`MURRELL_ETAL_MIX`	∗Default∗. OEP-Murrell et al's: S1 term via DF-OEP, S2 term via ESP-OEP.
`MURRELL_ETAL_ESP`	OEP-Murrell et al's: S1 and S2 via ESP-OEP

Table 12.3: Methods available in the Solver

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

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

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

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

Benchmark Methods

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

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

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

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

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

Similarity transformation of molecular orbitals does not affect the resulting energies. The overall exchange-repulsion interaction energy is then (always net repulsive)

$$E^{\text{Ex}-\text{Rep}} = E^{\text{Ex,pure}} + E^{\text{Rep}}$$

Repulsion energy of Mandado and Hermida-Ramon (2011)

At the Hartree-Fock level, the exchange-repulsion energy from the density-based scheme of Mandado and Hermida-Ramon (2011) is fully equivalent to the method by Hayes and Stone (1984). However, density-based method enables to compute exchange-repulsion energy at any level of theory. It is derived based on the Pauli deformation density matrix,

$$\Delta\mathbf{D}^{\text{Pauli}} \equiv \mathbf{D}^{oo} - \mathbf{D}$$

where $\mathbf{D}^{oo}$ and $\mathbf{D}$ are the density matrix formed from mutually orthogonal sets of molecular orbitals within the entire aggregate (formed by symmetric orthogonalization of MO's) and the density matrix of the unperturbed system (that can be understood as a Hadamard sum $\mathbf{D} \equiv \mathbf{D}^A \oplus \mathbf{D}^B$).

At HF level, the Pauli deformation density matrix is given by

$$\Delta\mathbf{D}^{\text{Pauli}} = \mathbf{C}\left[\mathbf{S}^{-1} - \mathbf{1}\right]\mathbf{C}^{\dagger}$$

whereas the density matrix constructed from mutually orthogonal orbitals is

$$\mathbf{D}^{oo} = \mathbf{C}\mathbf{S}^{-1}\mathbf{C}^{\dagger}$$

In the above equations, $\mathbf{S}$ is the overlap matrix between doubly occupied molecular orbitals of the entire aggregate.

Here, the expressions for the exchange-repulsion energy at any level of theory are shown for the case of open-shell system. The net repulsive energy is given as

$$E^{\text{Ex}-\text{Rep}} = E^{\text{Rep,1}} + E^{\text{Rep,2}} + E^{\text{Ex}}$$

where the one- and two-electron part of the repulsion energy is

$$E^{\text{Rep,1}} = E^{\text{Rep,Kin}} + E^{\text{Rep,Nuc}}$$
$$E^{\text{Rep,2}} = E^{\text{Rep,el}-\Delta} + E^{\text{Rep},\Delta-\Delta}$$

The kinetic and nuclear contributions are

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

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

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

The associated exchange energy is given by

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

It is important to emphasise that, although, at HF level, the particular 'repulsive' and 'exchange' energies computed by using either Hayes and Stone or Mandado and Hermida-Ramon methods are not equal to each other, they sum up to exactly the same exchange-repulsion energy, $E^{\text{Ex}-\text{Rep}}$. Therefore, these methods at HF level are fully equivalent but the nature of partitioning of repulsive and exchange parts is different. It is also noted that the orbital localization does *not* affect the resulting energies, as opposed to the few approximate methods described below (Otto-Ladik and EFP2 methods).

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

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

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

where the first-order term is

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

whereas the second-order term is

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

Thus derived repulsion energy is invariant with respect to transformation of molecular orbitals, similarly as Hayes--Stone's method and density-based method. By using OEP technique, the above theory can be exactly re-cast *without* any further approximations.

Approximate Pauli Repulsion energy at HF level from Otto and Ladik (1975).

The Pauli repulsion energy is approximately given as

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

where the first-order term is

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

whereas the second-order term is

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

Thus derived repulsion energy is *not* invariant with respect to transformation of molecular orbitals, in contrast to Hayes-Stone's method and density-based method. It was shown that good results are obtained when using localized molecular orbitals, whereas using canonical molecular orbitals brings poor results. By using OEP technique, the above theory can be exactly re-cast *without* any further approximations.

Approximate Pauli Repulsion energy at HF level from Jensen and Gordon (1996).

The Pauli repulsion energy used within the EFP2 approach is approximately given as

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

where the first-order term is

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

whereas the second-order term is

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

Thus derived repulsion energy is *not* invariant with respect to transformation of molecular orbitals, in contrast to Hayes-Stone's method and density-based method. It was shown that good results are obtained when using localized molecular orbitals, whereas using canonical molecular orbitals brings poor results.

In EFP2, exchange energy is approximated by spherical Gaussian approximation (SGO). The result of this is the following formula for the exchange energy:

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

In all the above formulas, R_{ij} are distances between position vectors of ∗i∗th and ∗j∗th point. The LMO centroids are defined by

$$\mathbf{r}_a = (a|\mathbf{r}|a)$$

where *a* denotes the occupied molecular orbital.

OEP-Based Methods

The Murrell et al's theory of Pauli repulsion for S-1 term and the Otto-Ladik's theory for S-2 term is here re-cast by introducing OEP's. The S-1 term is expressed via DF-OEP, whereas the S-2 term via ESP-OEP.

S-1 term (Murrell et al.)

The OEP reduction without any approximations leads to the following formula

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

where the OEP matrices are given as

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

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

S-2 term (Otto-Ladik)

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

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

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

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

where the potential is given by

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

12.24.2 Member Function Documentation

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

Compute property by using benchmark method.

Each solver object has one `DEFAULT` benchmark method

Parameters

method	- benchmark method

Implements oepdev::OEPDevSolver.

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

Compute property by using OEP's.

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

Parameters

method	- flavour of OEP model

Implements oepdev::OEPDevSolver.

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

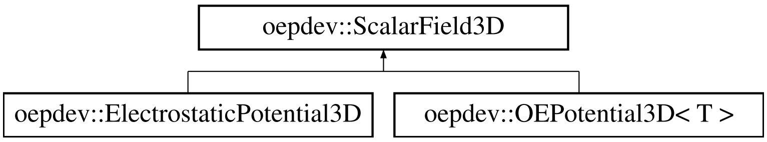
- oepdev/libutil/solver.h
- oepdev/libutil/solver.cc

12.25 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?

12.25.1 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`

12.25.2 Member Function Documentation

12.25.2.1 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

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

12.25.2.2 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

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

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

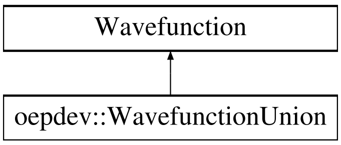
- oepdev/libutil/space3d.h
- oepdev/libutil/space3d.cc

12.26 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 &noccpi, SharedVector epsilon, const std::string &basis, const std::string &subset)

  Helpers for Ca_ and Cb_ matrix transformers.
- SharedVector epsilon_subset_helper (SharedVector epsilon, const Dimension &noccpi, const std::string &basis, const std::string &subset)

  Helper for epsilon transformer.
- void print_header (void)

  Print information about this wavefunction union.
- void print_mo_integrals (void)

  Print the MO ingegrals.

Protected Attributes

- int nIsolatedMolecules_

  Number of isolated molecules.
- SharedWavefunction dimer_wavefunction_

  The wavefunction for a dimer (electrons relaxed in the field of monomers)
- SharedIntegralTransform integrals_

  Integral transform object (2- and 4-index transformations)
- bool hasLocalizedOrbitals_

  whether orbitals of the union were localized (or not)
- std::map< const std::string,
  SharedMOSpace > mospacesUnion_

  Dictionary of MO spaces for the entire union (`OCC` *and* `VIR`*)*
- std::vector< SharedMolecule > l_molecule_

  List of molecules.
- std::vector< SharedBasisSet > l_primary_

  List of primary basis functions per molecule.
- std::vector< SharedBasisSet > l_auxiliary_

  List of auxiliary basis functions per molecule.
- std::vector< 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.

12.26.1 Detailed Description

Union of two Wavefunction objects.

The WavefunctionUnion is the union of two unperturbed Wavefunctions.

Notes:

1. Works only for C1 symmetry! Therefore `this->nirrep() = 1`.
2. Does not set `reference_wavefunction_`
3. Sets `oeprop_` for the union of uncoupled molecules
4. Performs Hadamard sums on `H_`, `Fa_`, `Da_`, `Ca_` and `S_` based on uncoupled wavefunctions.
5. Since it is based on shallow copy of the original Wavefunction, it **changes** contents of this wavefunction. Reallocate and copy if you want to keep the original wavefunction.

Warnings:

1. Gradients, Hessians and frequencies are not touched, hence they are **wrong**!
2. Lagrangian (if present) is not touched, hence its **wrong**!
3. Ca/Cb and epsilon subsets were reimplemented from psi::Wavefunction to remove sorting of orbitals. However, the corresponding member functions are not virtual in psi::Wavefunction. This could bring problems when upcasting.

The following variables are *shallow* copies of variables inside the Wavefunction object, that is created for the *whole* molecule cluster:

- `basissets_` (DF/RI/F12/etc basis sets)_
- `basisset_` (ORBITAL basis set)
- `sobasisset_` (Primary basis set for SO integrals)
- `AO2SO_` (AO2SO conversion matrix (AO in rows, SO in cols)
- `molecule_` (Molecule that this wavefunction is run on)
- `options_` (Options object)
- `psio_` (PSI file access variables)
- `integral_` (Integral factory)
- `factory_` (Matrix factory for creating standard sized matrices)
- `memory_` (How much memory you have access to)
- `nalpha_`, `nbeta_` (Total alpha and beta electrons)
- `nfrzc_` (Total frozen core orbitals)
- `doccpi_` (Number of doubly occupied per irrep)
- `soccpi_` (Number of singly occupied per irrep)
- `frzcpi_` (Number of frozen core per irrep)
- `frzvpi_` (Number of frozen virtuals per irrep)
- `nalphapi_` (Number of alpha electrons per irrep)
- `nbetapi_` (Number of beta electrons per irrep)
- `nsopi_` (Number of so per irrep)
- `nmopi_` (Number of mo per irrep)
- `nso_` (Total number of SOs)
- `nmo_` (Total number of MOs)
- `nirrep_` (Number of irreps; must be equal to 1 due to symmetry reasons)
- `same_a_b_dens_` and `same_a_b_orbs_` The rest is altered so that the Wavefunction parameters reflect a cluster of non-interacting (uncoupled, isolated, unrelaxed) molecular electron densities.

12.26.2 Constructor & Destructor Documentation

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

Constructor.

Provide wavefunction with molecule containing at least 2 fragments.

Parameters

ref_wfn	- reference wavefunction
options	- Psi4 options

12.26.3 Member Function Documentation

12.26.3.1 SharedMatrix oepdev::WavefunctionUnion::Ca_subset (const std::string & *basis* = `"SO"`, const std::string & *subset* = `"ALL"`)

Return a subset of the Ca matrix in a desired basis

Parameters

basis	the symmetry basis to use AO, SO
subset	the subset of orbitals to return ALL, ACTIVE, FROZEN, OCC, VIR, FROZEN_OCC, ACTIVE_OCC, ACTIVE_VIR, FROZEN_VIR

Returns

the matrix in Pitzer order in the desired basis

12.26.3.2 SharedMatrix oepdev::WavefunctionUnion::Cb_subset (const std::string & *basis* = `"SO"`, const std::string & *subset* = `"ALL"`)

Return a subset of the Cb matrix in a desired basis

Parameters

basis	the symmetry basis to use AO, SO
subset	the subset of orbitals to return ALL, ACTIVE, FROZEN, OCC, VIR, FROZEN_OCC, ACTIVE_OCC, ACTIVE_VIR, FROZEN_VIR

Returns

the matrix in Pitzer order in the desired basis

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

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

Index

AllAOIntegralsIterator
    oepdev::AllAOIntegralsIterator, 30
AllAOShellCombinationsIterator
    oepdev::AllAOShellCombinationsIterator, 31

build
    oepdev::OEPDevSolver, 48
    oepdev::OEPotential, 51, 52
    oepdev::Points3DIterator, 56, 57
    oepdev::PointsCollection3D, 58, 59
    oepdev::ScalarField3D, 71

CPHF
    oepdev::CPHF, 37
Ca_subset
    oepdev::WavefunctionUnion, 76
Cb_subset
    oepdev::WavefunctionUnion, 76
compute
    oepdev::DIISManager, 39
compute_3D
    oepdev::ChargeTransferEnergyOEPotential, 33
    oepdev::EETCouplingOEPotential, 41
    oepdev::ElectrostaticEnergyOEPotential, 42
    oepdev::OEPotential, 52
    oepdev::RepulsionEnergyOEPotential, 64
compute_benchmark
    oepdev::ChargeTransferEnergySolver, 35
    oepdev::ElectrostaticEnergySolver, 44
    oepdev::OEPDevSolver, 48
    oepdev::RepulsionEnergySolver, 68
compute_oep_based
    oepdev::ChargeTransferEnergySolver, 35
    oepdev::ElectrostaticEnergySolver, 44
    oepdev::OEPDevSolver, 49
    oepdev::RepulsionEnergySolver, 69
compute_shell
    oepdev::AllAOShellCombinationsIterator, 32
create_superfunctional
    oepdev, 25

DIISManager
    oepdev::DIISManager, 39

ESPSolver
    oepdev::ESPSolver, 47
extract_monomer
    oepdev, 25

index
    oepdev::AllAOIntegralsIterator, 30

OEPDevSolver
    oepdev::OEPDevSolver, 48
OEPotential
    oepdev::OEPotential, 51
OEPotential3D
    oepdev::OEPotential3D, 53, 54
oepdev, 23
    create_superfunctional, 25
    extract_monomer, 25
    psi, 26
    solve_scf, 25
oepdev::AllAOIntegralsIterator, 29
    AllAOIntegralsIterator, 30
    index, 30
oepdev::AllAOShellCombinationsIterator, 30
    AllAOShellCombinationsIterator, 31
    compute_shell, 32
oepdev::CPHF, 36
    CPHF, 37
oepdev::ChargeTransferEnergyOEPotential, 32
    compute_3D, 33
oepdev::ChargeTransferEnergySolver, 33
    compute_benchmark, 35
    compute_oep_based, 35
oepdev::CubePoints3DIterator, 37
oepdev::CubePointsCollection3D, 38
oepdev::DIISManager, 39
    compute, 39
    DIISManager, 39
    put, 39
    update, 40
oepdev::EETCouplingOEPotential, 40
    compute_3D, 41
oepdev::ESPSolver, 45
    ESPSolver, 47
oepdev::ElectrostaticEnergyOEPotential, 41
    compute_3D, 42
oepdev::ElectrostaticEnergySolver, 42
    compute_benchmark, 44
    compute_oep_based, 44
oepdev::ElectrostaticPotential3D, 44
oepdev::OEPDevSolver, 47
    build, 48
    compute_benchmark, 48
    compute_oep_based, 49
    OEPDevSolver, 48
oepdev::OEPotential, 49
    build, 51, 52
    compute_3D, 52

    OEPotential, 51
    write_cube, 52
oepdev::OEPotential3D
    OEPotential3D, 53, 54
oepdev::OEPotential3D$<$ T $>$, 52
oepdev::Points3DIterator, 54
    build, 56, 57
    Points3DIterator, 56
oepdev::Points3DIterator::Point, 54
oepdev::PointsCollection3D, 57
    build, 58, 59
    PointsCollection3D, 58
oepdev::PotentialInt, 59
    PotentialInt, 60, 61
    set_charge_field, 61
oepdev::RandomPoints3DIterator, 61
oepdev::RandomPointsCollection3D, 63
oepdev::RepulsionEnergyOEPotential, 63
    compute_3D, 64
oepdev::RepulsionEnergySolver, 64
    compute_benchmark, 68
    compute_oep_based, 69
oepdev::ScalarField3D, 69
    build, 71
oepdev::WavefunctionUnion, 72
    Ca_subset, 76
    Cb_subset, 76
    WavefunctionUnion, 75

Points3DIterator
    oepdev::Points3DIterator, 56
PointsCollection3D
    oepdev::PointsCollection3D, 58
PotentialInt
    oepdev::PotentialInt, 60, 61
psi, 25
    oepdev, 26
    read_options, 27
put
    oepdev::DIISManager, 39

read_options
    psi, 27

set_charge_field
    oepdev::PotentialInt, 61
solve_scf
    oepdev, 25

update
    oepdev::DIISManager, 40

WavefunctionUnion
    oepdev::WavefunctionUnion, 75
write_cube
    oepdev::OEPotential, 52