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MPD Quickstart Guide

The Maximum Probability Domains (MPD) program was developed by Osvaldo Mafra Lopez Jr. during his PhD thesis at the Laboratoire de Chimie Théorique. It is written in FORTRAN 90, interfaced with Gaussian (via a *.wfn* file for molecules described by a single determinant wavefunction) and the Quantum Monte Carlo program CHAMP. It allows a probability analysis, the generation and manipulation of volumes of differents forms and the optimization of a given volume to maximize the probability to find a given number of electrons in it. MPD program is based in three subprograms:

1. ***ProbaDomain***: domain generation and transformation
2. ***ProbaCpt***: single probabilities calculation
3. ***ProbaOpt***: domain optimization

Two different optimization algorithms are available:

1. *Discrete Optimization Method*: make some perturbations on the surface of the volume by adding or deleting small cubes, the step being accepted if the probability of the new domain increase.
2. *Steepest Descent Method*: make use of the availability of *shape derivatives*. The derivative indicates if small cubes should be added or deleted at each point in order to increase probability.

Here, it is presented some basics options of the MPD program. It is divided in the three parts of which the MPD program consists of.

The words marked in bold and italic refer to commands and/or parameters and values and/or file names respectively.

ProbaDomain

Generation and manipulation of domains in *.cube* format, which is recognized by several visualization programs as Molekel, Jmol ...

- **ExtractAtoms** *file_name.wfn*
  To extract the atoms' positions from the .wfn file. This command must be executed at least one time during a *ProbaDomain* calculation.
- **New Grid** \ **End New**
  To generate a new cuboidal grid without domain with the following parameters:
  xmin, ymin, zmin, xmax, ymax, zmax: limits of the grid
  nbX, nbY, nbZ: steps' number of the grid in each direction
- **Read Domain** \ **End Read**
  To read the grid and the domain of a .cube file.
  File *domain_file_name.cube*

- **Save Domain \ End Save**
  To save the current domain.
  File *domain_file_name.cube*

- **Join Cuboid \ End Join**
  To join a new domain to the grid.
  xmin, ymin, zmin, xmax, ymax, zmax: limits of the new domain

- **Join Domain \ End Join**
  To join an already built domain.
  File *domain_file_name.cube*

- **Complement Domain**
  To make a complementary operation, so the final domain created will be the whole space minus the domain complemented. This operation does not need more parameters.

- **Rotate Domain \ End Rotate**
  To make a rotation on a domain respect to the x, y or z direction by the angle value given in *radians*.
  Angle *value*
  Axis x, y *or* z

- **Reflect Domain \ End Reflect**
  To reflect a domain by respect to the perpendicular plane given by x, y or z direction.
  Axis x, y *or* z

- **Intersect Domain \ End Intersect**
  To make the intersection of the current domain with another one given by
  File *domain_file_name.cube*

- **Minus Domain \ End Minus**
  To substract from the current domain a second one given by
  File *domain_file_name.cube*

- **MinusFrom Domain \ End MinusFrom**
  To substract the current domain from a second one given by
  File *domain_file_name.cube*

The *Complement*, *Rotate*, *Reflect*, *Intersect*, *Minus*, *MinusFrom* and *Save* commands act on the final domain read, built or joined following the order of the input file.

⋆ Two little examples of *ProbaDomain* input file:

```
ExtractAtoms file_name.wfn

New Grid
   xmin -5.
   ymin -5.
   zmin -5.
   xmax  5.
   ymax  5.
   zmax  5.
   nbX 100
   nbY 100
   nbZ 100
End New

Join Cuboid
   xmin -0.5
   ymin -0.6
   zmin -0.4
   xmax  0.7
   ymax  0.6
   zmax  0.8
End Join

Save Domain
  File domain_file_name.cube
End Save
```

```
ExtractAtoms file_name.wfn

New Grid
   xmin -6.
   ymin -6.
   zmin -6.
   xmax  6.
   ymax  6.
   zmax  6.
   nbX  80
   nbY  80
   nbZ  80
End New

Read Domain
  File domain_file_name.cube
End Read

Rotate Domain
  Angle 3.1415
  Axis x
End Rotate

Save Domain
  File domain_file_name.cube
End Save
```

The left blank spaces at the beginning of the lines inside each command and the separation among commands are not mandatory.

The *New Grid* \ *End New* command can be omitted (at least one time should be executed), but attention should be paid when interacting with several domains. Domains created with differents $nbi, i = X, Y, Z$ values (the size of the grid does not matter) can not be manipulated together because of their incompatible sizes.

ProbaCpt

Single probabilities calculation. The *.wfn* and *.cube* files are needed.

- **DomainFile** *domain_file_name.cube*
  Name of the file containing the domain for which the probability will be calculated.
- **WFNFile** *file_name.wfn*
  Name of the file containing the wavefunction.
- **WFNFormatFile** *Gaussian*
  Wavefunction file format. The *.wfn* format of Gaussian.
- **BaseType** *CartesianGaussian*
  Type of the basis functions used.

These four commands are mandatory. For a single probability calculation, no more commands are needed.

ProbaOpt

Optimization of a given domain in order to maximize the probability of finding a given number of electrons in it. The four lines of the *ProbaCpt* input file must be added in the *ProbaOpt* input file with some other commands.

- **DomainFile** *domain_file_name*
- **WFNFile** *file_name.wfn*
- **WFNFormatFile** *Gaussian*
- **BaseType** *CartesianGaussian*
- **Spin** *ON* or *OFF*
  To take into account if the maximized probability is spin-dependent or not.
  - OFF
    nu *value*: number of electrons
  - ON
    na *value*: number of α electrons
    nb *value*: number of β electrons

The next commands are optional:

- **PrintCriter** *value*
  Number of optimization steps to write the calculated quantities (probabilities, populations . . .). By default, the value is 1 (at each optimization step the quantities are written).

- **SavingCriter** *value*
  Number of optimization steps in order to save an intermediate domain. The default value is 1 (saving an intermediate domain at each optimization step).

- **OptimizationOrder** *0* or *1*
  To define the optimization type algorithm. By default, the value is 0.
  $\longrightarrow$ *0* : Discrete Optimization Method
  $\longrightarrow$ *1* : Steepest Descent Method

Spin ON
na 1
nb 1

Contraint ON
ContraintFile constr-2dom_sig_compl.cube

CompressMode PConst
P_ext 0.0000001

⋆ Examples of *ProbaCpt* input file:

```
DomainFile domain_file_name.cube

WFNFile file_name.wfn

WFNFormatFile Gaussian

BaseType CartesianGaussian
```

⋆ Example of *ProbaOpt* input file:

```
DomainFile domain_file_name.cube

WFNFile file_name.wfn

WFNFormatFile Gaussian

BaseType CartesianGaussian

Spin OFF
   nu 2

PrintCriter  10

SavingCriter 50

OptimizationOrder 1
```

The left blank spaces at the beginning of the lines inside each command and the separation among commands are not mandatory.