

# Nagual 1 user's manual

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# Chapter 1

## Introduction

The principal objective of this document is to serve as a first instance aid for the use of the software Nagual 1 [1]. Sometimes formulation details can be provided but it is no intended to serve as an exhaustive reference about the theory related to the methods implemented in Nagual 1. If you are interested on the foundations please refer to the bibliography of this document and the specific literature reference on the source code modules.

Nagual 1 is a multi-component Quantum Chemistry software bearing the following capabilities:

- Based on Cartesian Gaussian basis sets, both primary and auxiliary functions
- Effective core potentials
- Accepts Cartesian and z-matrix inputs (angstroms and bohrs)
- Multicomponent calculations simultaneously including electrons, protons, nucleons, etc.

- Hartree–Fock calculations [2, 3]
- Kohn–Sham [4] DFT calculations taking advantage of the variational fitting of Coulomb potential [5] and further use of the auxiliary densities for the computation of exchange–correlation energy functional [6].
  - Exchange functionals:
    - \* Dirac [7]
  - Correlation functionals:
    - \* Vosko–Wilk–Nusair (VWN) [8]
- MP2 calculations
- Possibility for re-initialization of an ongoing SCF
- Slater’s transition operator method [9].
- Generalized one-particle propagator calculations (G1PP) [9–12] applicable to electrons, protons and nucleons.

If you find any inconsistency between this manual and the actual behaviour of Nagual 1, please communicate it to Roberto Flores-Moreno ([r.flores@academicos.udg.mx](mailto:r.flores@academicos.udg.mx)). Likewise, if you have any suggestion or question related to the capabilities of Nagual 1 we will be happy to know about it.



# Chapter 2

## Installation

Nagual 1 is distributed together with a graphical user interface called GNagual [13]. Please, check that the full package is complete and your file system tree looks like the following:

```
ngl.1/  
    GNU_GPLv3.txt  
    LICENSE  
    README  
    Nagual.1.Manual.pdf  
    gnagual/  
        src/  
            gnagual.pro  
            *.h (header files)  
            *.cpp (source files)  
    nagual/
```

```
src/
  configure
  *.F90 (source files)
bin/
  nagual (script for running calculations)
lib/
  basis/
    electron/
      STO-3G
      ...
    proton/
      DZSPDH
      ...
  ecps/
    electron/
      LANL2DZ
      ...
```

If any file is missing stop here and contact us (see README file for contact details). Continuing with the installation without the complete list of files is at your own risk.

## 2.1 Compiling Nagual 1

Put yourself in the “nagual/src” directory and once there type the following:

1. ./configure

2. make

If everything goes fine the executable, named Nagual.1.exe, will be created and located on the “bin” directory. If NOT, look inside the configure file for adjustments of configuration. In particular check that libraries like LAPACK have the corresponding directory properly addressed.

## 2.2 Compiling GNagual 1

Put yourself in the “gnagual/src” directory and once there type the following:

1. qmake
2. make

If everything goes fine the executable, named GNagual.1.exe, will be created and located on the “bin” directory. If NOT, look inside the gnagual.pro file for adjustments of QT configuration. Additionally you will find useful to look into QT documentation.



# Chapter 3

## Input file

The following is an example input file for a multicomponent Hartree-Fock calculation on the hydrogen molecule:

```
#
# species_name    number_of_particles  basis_file
&Species
3
"electron"  1  "./lib/basis/electron/AUG-CC-PVDZ"
"electron"  1  "./lib/basis/electron/AUG-CC-PVDZ"
"proton"    2  "./lib/basis/proton/DZSPDH"
/

&scf
  guess="core"
  eris=4
```

```
nitmax=100
damping=0.3
tolerance=1.0e-6
diis=5
/

&Structure
H  0.00000  0.00000  -0.37747
H  0.00000  0.00000   0.37747
/
```

Reading of data from the input file follows a style based on fortran namelists. In fact, most data is read as a namelist. Blocks start with “&word” and close with “/”. Any line out of a block is considered as a comment only. Some of the most important blocks will be described in this chapter. Some others, that are more specific to a specialized type of calculation will be described in the chapter corresponding to those calculations.

### 3.1 Structure block

After the header the structure information comes either as a set of cartesian coordinates or as a Z-matrix description.

Please, consider the following critical items:

- Empty lines are forbidden in this block

- Closing character ‘/’ must be the first in its line

### 3.1.1 Cartesian coordinates

Each line contains element symbol, x coordinate, y coordinate, and z coordinate. By default cartesian coordinates are assumed to be given in angstroms. However, if you wish to provide a structure in bohrs just add the word `bohr` after `structure`, in the same line.

### 3.1.2 Z matrix

Z-matrix format is also accepted, using variables for bond lengths, angles and dihedrals. In order to use it you must ensure that the ‘z’ character is present in the header line. It really does not matter if it is part of a word or not. Thus, you could also use `Z-matrix` or `matriz Z`, etc. After completing the description of atoms, the symbol `#` is used to notify that description of variables will start, see the following example for normal butane:

```
&structure z
H1
C2 H1 rHC
C3 C2 rCC H1 wHCC
C4 C3 rCC C2 wCCC H1 180.0
C5 C4 rCC C3 wCCC C2 180.0
H6 C5 rHC C4 wCCC C3 180.0
H7 C2 rHC C3 wHCC H1 120.0
```

```

H8  C2 rHC C3 wHCC H1 240.0
H9  C3 rHC C2 wHCC H1 300.0
H10 C3 rHC C2 wHCC H1 60.0
H11 C4 rHC C3 wHCC C2 300.0
H12 C4 rHC C3 wHCC C2 60.0
H13 C5 rHC C4 wHCC C3 300.0
H14 C5 rHC C4 wHCC C3 60.0
#
rCC  1.54
rHC  1.00
wCCC 109.467
wHCC 109.467
/

```

Notice that variable values are assigned after the `#` sign. No equal sign should be written. By default bond lengths are expected in angstroms, and angles in degrees. Just like in the case of cartesian coordinates, if you wish to provide a structure in bohrs just add the word `bohr` after structure, in the same line.

## 3.2 Interactions block

It serves to control types of interactions considered for the SCF process. This block is **optional**, by default a Hartree–Fock calculation is assumed. However if you wish to perform a Kohn–Sham DFT calculation Hartree–Fock exchange can be disabled and other functionals can be activated using this block. For example, for running



local density approximation with Dirac exchange and VWN correlation functionals the following block is required:

```
&Interactions
electron electron exchange=fock 0.0
electron electron exchange=dirac 1.0
electron electron correlation=vwn 1.0
/
```

where the first two words in each line identify the types of particles for each species in the binary interaction being defined. The numerical value at the end is the weight of this functional. A value of zero deactivates that specific functional. Notice that this also can be applied to particles other than electrons but functionals are usually not available for any kind of particles. Furthermore, some species could have a given functional, different to the one used in others. A mixed Hartree–Fock/Kohn–Sham calculation is also feasible. Of course exchange functionals involve a single species at a time. Correlation functionals involve pairs of species at most (in the current implementation).

### 3.3 Species block

Specifies number of species in the first line. After that, each line provides information for a given species, including the name for the particles in that species, number of particles, basis set to be loaded for each atomic center. Please, notice that the full path to data files should be provided (assuming that a file contains basis sets of a

given name only). Notice also that the basis or potential file should contain an entry for each kind of atom included in the structure description. If no basis set is to be loaded (like in proton basis for heavy atoms) then the number basis blocks in the data file should be zero.

### 3.4 SCF block

Every item of the SCF (Self-Consistent Field procedure) block is explained here:

- **guess**: This text variable specifies the type of guess to be used. Only two options are available: “core” for initial approximation of non-interacting particles or “restart” for continuation of calculations. The “restart” option uses “.bas” files from a previous calculation for loading a guess (initial MOs), one file per species.
- **eris**: This integer variable specifies the type of ERIs (electron repulsion integrals in regular electronic structure calculations) to be used. A value of 4 points to exact 4-index integrals. A value of 3 points to 3-index integrals. Notice that current implementation uses always 4 for Hartree-Fock calculations and 3 for DFT calculations.
- **nitmax**: This integer variable specifies the maximum number of iterations allowed for the SCF iterative process.
- **damping**: This real variable should get a positive value lower or equal to one. One corresponding to no damping at all. Do not use zero because that would

result in no progress on the convergence of the SCF. A value between 0.1 and 0.5 is good for most systems.

- **tolerance:** This real variable specifies the error tolerance for the SCF testing of convergence. Values of 1.0e-6 are frequently enough. More accurate requirements motivate some people to use 1.0e-8 sometimes.
- **diis:** This integer variable if positive corresponds to the number of matrices to be stored for the direct inversion of iterative space (DIIS) method. Negative value corresponds to no use of DIIS at all. Notice that activation of DIIS automatically disables damping.



# Chapter 4

## Running calculations

### 4.1 Using script for customized input file names

Nagual distribution comes with a bash script named `nagual`, located in the `bin` directory. After preparing your input file properly, running the calculation will require a command as simple as the following

```
nagual test.inp
```

On successful calculations a number of files will be returned: one with extension `.scf`, one with extension `.out` and a few files with extension `bas.n`, being  $n$  an positive integer lower or equal to the number of species in the calculation. Files with extension `bas.n` are required whenever you wish to run a calculation using `restart` density. In case of failure there will be a file with extension `.log`. For understanding each of these files read the following chapter.

## 4.2 Running with primitive executable

After compilation the executable will be found in the `bin` subdirectory. This executable will always read input data from an ASCII file named `Nagual.inp`. Output will be written to `Nagual.scf` and `Nagual.out`. In general all files have a root name `Nagual`. This mode of running is usually employed by developers or during the initial installation in order to test the program.

# Chapter 5

## Output files

### 5.1 Main output file

The principal output file bears the extension `.out`. It contains only final report of results. No SCF information is found here, for example.

### 5.2 SCF file

The SCF output file bears the extension `.scf`. This file contains a copy of the basis set used in the calculation. It also lists the kinds of interactions considered for each couple of species. Energies and errors obtained on each step of the iterative process are also printed. After termination of the SCF orbital information will be printed including orbital energies and coefficients.

### 5.3 NGL file

This file is prepared by Nagual 1 for GNagual 1. To a great extent this may look similar to the `.scf` file. However, GNagual 1 is only able to handle `.ngl` file.

The following is a list of instructions for opening Nagual 1 `.ngl` files with GNagual 1:

1. Open GNagual 1 graphic user interface by running GNagual 1 executable.
2. Go to the **File** menu and select **Read** submenu. This will open a dialog box for selecting the file to be open.
3. Select the desired Nagual 1 `.ngl` file.
4. Once loaded the `.ngl` file you can use **Plotter** subwindow to generate isosurfaces and other types of plots for molecular orbitals, density, basis functions and others.

### 5.4 Error report file

The error report file bears the extension `.log`. Whenever you get an **Internal STOP** message look inside the `.log` file for more details.

### 5.5 Restart files

Files with extension `bas.n` are binary. They contain MO matrices for each species and, therefore, are useful for restarting SCF process, resulting in considerable time



savings.



# Chapter 6

## Self-consistent field calculations

### 6.1 Regular electronic structure of atoms

Virtually, all calculations performed with Nagual 1 will include a self-consistent field calculation. Most of the information associated to the SCF process is reported on the file with extension `.scf`.

#### 6.1.1 Hartree-Fock results

Table 6.1 lists a few Hartree-Fock results obtained with Nagual 1 using cc-pVTZ basis set. Since these are atomic calculations it will be straightforward for users to reproduce these results up to six digits.

Table 6.1: SCF energy results obtained with cc-pVTZ basis set

System	Energy (a.u.)
Li	-7.432706
B	-24.532104

### 6.1.2 Kohn–Sham results

Table 6.2 lists a few Kohn–Sham/Dirac–VWN results obtained with Nagual 1 using cc-pVTZ basis set. Since these are atomic calculations it will be straightforward for users to reproduce these results up to four or five digits. However, notice that auxiliary density is being used in the exchange–correlation energy functional [6].

Table 6.2: SCF energy results obtained with cc-pVTZ basis set

System	Energy (a.u.)
Li	-7.338429
B	-24.354860

## 6.2 Nuclear structure

### 6.2.1 Hartree–Fock results

Nagual 1 is able to perform Hartree–Fock calculations for nucleons (protons and neutrons) using Yukawa’s effective potential for recovering residual interaction. Nucleons use the same basis sets, usually stored on the `basis/nucleons` directory. In the input file of Nagual 1 the structure for this type of calculations is just one atom

corresponding to the desired nucleus. This is required to address the corresponding basis set. All nuclear structure calculations assume a single center configuration. By default Nagual 1 uses a pre-loaded effective potential. If this potential has to be modified `nmintegrals.F90` should be edited and the program recompiled. The following is an input example for deuteron

```
#Deuteron
&Species
2
"nucleonp" 1  "./lib/basis/nucleon/N-T15S"
"nucleonn" 1  "./lib/basis/nucleon/N-T15S"
/

&scf
  guess="core"
  eris=4
  diis=-5
  nitmax=200
  damping=0.4
  tolerance=1.0e-6
/

&Structure
H  0.000000      0.00000      0.000000
```

/

Usually nucleon densities range on the scale of femtometers. For this reason basis sets employed will have exponents much larger than those found in regular electronic structure.

### 6.2.2 Kohn–Sham calculations

Although DFT could be used in principle, in practice no functional is available currently.

# Chapter 7

## Generalized one-particle propagator

The generalized one-particle propagator (G1PP) is the extension of electron propagator theory to the multi-component orbital calculations. General particle binding energies can be calculated with this methodology. This is one of the distinctive features of Nagual 1 with respect to other software packages used in Quantum Chemistry.

In order to perform a G1PP calculation input should include a block like the following one:

```
&g1pp
  species_id=2
  orbital_id=8
  method="d2"
  memory=1000
```

/

Here, `species_id` is the number of the row in the species block that corresponds to the species of which a particle will be removed. Likewise, `orbital_id` is the number of the occupied orbital out of which the particle is taken. The maximum amount of memory for the G1PP calculations is also specified in the block together with the method. Currently Nagual 1 handles only diagonal approximation of orders 1 (corresponding to Koopmans' theorem) and 2. The last one can be used to produce results of second order electron or proton propagator, depending on the species selected.

## 7.1 Electron propagator

Table 7.1 lists results obtained with Nagual for atoms of the main groups, first and second row.

## 7.2 Proton propagator

Proton propagator calculations should reproduce results reported in the literature [12].



Table 7.1: G1PP results (eV) obtained with cc-pVTZ basis set

System	Transition	KT	G1PP2	Expt.
Li	$^2S \rightarrow ^1S$	5.343	5.356	5.39
Be	$^1S \rightarrow ^2S$	8.415	8.898	9.32
B	$^2P \rightarrow ^1S$	8.655	8.396	8.30
C	$^3P \rightarrow ^2P$	11.918	11.300	11.26
N	$^4S \rightarrow ^3P$	15.490	14.437	14.53
O	$^3P \rightarrow ^4S$	14.151	12.926	13.62
F	$^2P \rightarrow ^3P$	18.410	16.375	17.42
Ne	$^1S \rightarrow ^2P$	23.013	20.133	21.56
Na	$^2S \rightarrow ^1S$	4.957	4.983	5.14
Mg	$^1S \rightarrow ^2S$	6.886	7.348	7.65
Al	$^2P \rightarrow ^1S$	5.926	5.910	5.98
Si	$^3P \rightarrow ^2P$	8.181	8.111	8.05
P	$^4S \rightarrow ^3P$	10.649	10.488	10.49
S <sup>a</sup>	$^3P \rightarrow ^4S$	10.288	10.001	10.36
Cl	$^2P \rightarrow ^3P$	13.051	12.579	12.97
Ar	$^1S \rightarrow ^2P$	16.059	15.389	15.76

<sup>a</sup> Ref. [9] has error for S(3  $\rightarrow$  4)



## Chapter 8

# Geometry optimizations

Nagual 1 is able to compute molecular gradients for Kohn–Sham/Dirac–VWN calculations. It also includes a primitive module for local geometry optimizations. The only algorithm available for this purpose is the steepest descent with backtracking line search based only on energy. It is rather expensive but seems to be working properly. For activating a geometry optimization an extra block should be added. The following is a verbatim example for a local optimization with a maximum of 100 optimization cycles (updates of configuration):

```
&opt
  algorithm="local"
  cycles=100
/
```

computed by Nagual 1.



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