

# MADNESS Molecular electronic structure calculations

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# Chapter 1

## Overview

### 1.1 Capabilities

### 1.2 Current status

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### 1.3 Input structure

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### 1.4 Reproducibility

g



## Chapter 2

# Geometry specification



## Chapter 3

# Ground state molecular DFT and HF

**nopen value** — E.g., **nopen 3** — The number of unpaired spin orbitals,  $n_\alpha - n_\beta$  (default 0)

**unrestricted** — Selects a spin-unrestricted calculation (default is spin restricted)

**xc value** — E.g., **xc HF** — Selects the exchange correlation potential (default is LDA). See XC section for more details.

**aobasis value** — E.g., **aobasis sto-3g** — Sets the atomic orbital basis used for the initial guess. Options are **sto-3g** (down to Iodine) or **6-31g** (down to Zinc, default).

**charge value** — E.g., **charge -1.0** — Total charge (default 0) on the molecule. Atomic units.

**nvalpha value** — E.g., **nvalpha 2** — The number of alpha spin virtual orbitals to solve for (default 0) — is this working now?

**nvbeta value** — E.g., **nvbeta 2** — The number of beta spin virtual orbitals to solve for (default 0) — is this working now?

**no-orient** — Do not reorient/translate the molecule to orientation/center.

**core\_type value** — E.g., **What is available?** Selects the pseudopotential to be used on all atoms (can also do mixed all-electron/pseudopotential calculation). Not heavily tested and unoptimized. (default is all electron).



**psp\_calc** — Perform pseudopotential calculation on all atoms. Not heavily tested and unoptimized. (default is all-electron)

**L value** — E.g., **L 50** — Sets the computational box size to  $[-L, L]^3$  atomic units (mostly for testing). Default is to find cube that contains all nuclei and to add 50 atomic units.

## 3.1 XC — DFT exchange correlation

Without LIBXC, the code just provides either Hartree-Fock (**xc HF**) or local (spin) density approximation (**xc LDA**, the default).

With LIBXC, in addition to HF and LDA (default) there are wide variety of GGA and hybrid functionals available — the ones that have been tested to some extent include

- PBE — **xc GGA\_X\_PBE 1. GGA\_C\_PBE 1.**
- PBE0 — **xc GGA\_X\_PBE .75 GGA\_C\_PBE 1. HF\_X .25**
- PW91 — ???
- B3LYP — ????

We have not yet implemented the near linear-scaling algorithm for HF exchange, which as a consequence is fairly slow.

## 3.2 Restarting

At completion of an HF or DFT calculation, the molecular orbitals are saved in the files **restartdata.\*** (with one file per I/O server process). The projection of the orbitals onto the **sto-3G** AO basis set is saved into the file **restartaodata**.

**restart** — Restart from numerical orbitals from a previous calculation (default is no)

**restartao** — Restart from projection of orbitals onto AO basis set from a previous calculation (default is no unless doing geometry optimization). If a restart file is not found, or the file contains incompatible data then the default atomic guess is used.

**save value** — E.g., **save false** — Boolean flag to save (or not) orbitals at completion (default is true).

### 3.3 Controlling convergence and accuracy

The default convergence test is on both the 2-norm of change in density per atom (separately for each spin) between iterations and the residual error in each wave function.

```
converged = (da < dconv * molecule.natom()) &&
            (db < dconv * molecule.natom()) &&
            (conv_only_dens || (max_residual < 5.0 * dconv))
```

**dconv value** — E.g., `dconv 1e-5` — SCF convergence criterion (default 1e-4 atomic units). Suggest decreasing this to 1e-5 for geometry optimization or property calculations.

**canon** — Solves for canonical orbitals or eigenfunctions (default is localized orbitals except for atoms and diatomics).

**pm** — Selects use of the Pipek-Mezy localized orbitals (default).

**boys** — Selects use of the Boys localized orbitals.

**maxrotn value** — E.g., `maxrotn 0.1` — Used to restrict maximum rotation of orbitals (default 0.25)

**maxiter value** — E.g., `maxiter 20` — The maximum number of iterations (default is 20)

**maxsub value** — E.g., `maxsub 5` — The size of the iterative subspace (default is 5). Sometimes it helps to make this larger.

**protocol valuelist** — E.g., `protocol 1e-4 1e-6 1e-8` — Sets the solution protocol. The default is '1e-4 1e-6' which means solve first using a truncation threshold of 1e-4 (using  $k = 6$ ) and with a threshold of 1e-6 (using  $k = 8$ ).

**orbitalshift ---** E.g., `orbitalshift 0.1 ---` Shifts the occupied orbitals down in energy by the given amount (default 0). Is this working?

**k value ---** E.g., `k 8 ---` Sets the wavelet order to a fixed value (mostly only used for testing)

**convonlydens ---** Just test on the change in the density for convergence.

### 3.4 Geometry optimization

By default geometry optimization is performed using the BFGS Hessian update algorithm. The convergence test is on all of the 2-norm of

the gradient, the change in the energy between iterations, and the maximum change in Cartesian coordinates (all in atomic units). The

For geometry optimization it is recommended to select dconv 1e-5 to obtain more accurate gradients.

gopt --- Requests optimization of the geometry

gtol value --- E.g., gtol 1e-4 --- Sets the convergence threshold for the 2-norm of the gradient (default 1e-3).

gtest value --- E.g., gtest 1e-4 --- Sets the convergence threshold for the maximum change in Cartesian coordinates (default 1e-3 atomic units).

gval value --- E.g., gval 1e-6 --- Sets the available precision in the energy (default is 1e-5 atomic units).

gprec value --- E.g., gtest 1e-6 --- Sets the available precision in the gradient (default is 1e-5 atomic units).

gmaxiter value --- E.g., gmaxiter 100 --- Sets the maximum number of geometry optimization iterations (default is 20).

algopt value --- E.g., algopt SR1 --- Selects the quasi-Newton update method (default is ). Options are BFGS (default) or SR1 (not heavily tested). Case sensitive.

## 3.5 Properties

derivatives --- Compute the derivatives (default is false).

dipole --- Compute the molecular dipole moment (default is false --- why?).

response --- TBD

response\_freq --- TBD

response\_axis --- TBD

rconv --- TBD

efield --- TBD

efield\_axis x y z --- TBD

print\_dipole\_moments --- TBD

## 3.6 Plotting

Plots are generated to OpenDX files. In the moldft source directory are two useful files

- vizit.net --- An OpenDX visual program that displays a molecule (from file molecule.dx) along with positive+negative isosurfaces (with adjustable value) for a scalar field read from a file.
- moldx.py --- A Python program you can run with your *output* file as standard input to produce a molecule.dx file. It is important to use your output file since moldft will (by default) translate and rotate the molecular coordinates.

plotmos lo hi --- E.g., plotmos 10 12 --- Plots the molecular orbitals in the given inclusive range (default is none). Orbitals are numbered from zero. Seems like this needs extending to accomodate unrestricted calculations.

plotdens --- Plots the total electronic charge density and, if spin unrestricted, the spin density (default is off).

plotcoul --- Plots the total (electronic + nuclear) electrostatic potential (default is off).

plotnpt value --- E.g., plotnpt 501 --- Sets the number of plots used per dimension in the cube of points (default 101).

plotcell xlo xhi ylo yhi zlo zhi --- E.g., plotcell -10 10 -15 15 -10 5 --- Sets the cell (in atomic units) used for plotting (default is the entire simulation cell).

## 3.7 Parallel execution

loadbal vnucfac parts --- E.g., loadbal 12 2 --- Adjusts data/loadbalance when running in parallel with MPI. vnucfac (default 12) is extra weight associated with nuclear potential and parts (default 2) is the number of partitions (or subtrees) per node. SCF

nio value --- E.g., nio 10 --- The number of MPI processes to use as I/O servers (default is 1)