Manual for nemo and mp2 programs in MADNESS

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1 Intro

The nemo program computes molecular HF and DFT energies and gradients using a nuclear correlation factor (ncf) as well as vibrational frequencies.[1] In contrast, the moldft program does the same without using an ncf.

The mp2 program computes the MP2 energies on top of either the nemo or the moldft HF reference wave function.[2, 3]

2 Input sections

2.1 nemo

The nemo program uses the same input parameters as moldft, with only a few restrictions and extensions. In addition to the regular moldft input parameters there are the following options (all are optional)

nuclear_corrfac: [*slater x, gausssslater, polynomialN, none*]
with $x > 1$ recommended $x = 2.0$, and $3 < N < 11$, recommended $N = 8$. Default is "none".

hessian if present computes the hessian matrix and vibrational frequencies

read_cphf if present read in the solutions to the CPHF equations from a prior hessian calculation

There is no open-shell/spin-polarized version of nemo available.

Note there is a inconsistency with the `eprec` keyword in the geometry section. Because there is no singular potential in the nemo calculation, the `eprec` keyword is used to smoothen the derivatives of the nuclear correlation factor (It is a step function). Typically a factor of 1e-3 to 1.e-4 will give you micro-Hartree accuracy with respect to the energy of the (regularized) nuclear potential, and about 1 cm-1 accuracy with respect to vibrational frequencies.

2.2 mp2

On top of the HF reference wave function (from nemo or moldft) a MP2 calculation may be performed. The relevant input is contained in the mp2 input section with the following keywords:

econv *val* energy convergence threshold for the correlation energy. Recommended is 1.e-3 or 1.e-4.

dconv *val* [optional] residual for the convergence of the MP1 wave function. Default is sqrt(econv)*0.1;

freeze *val* number of frozen core electrons. Default is 0.

maxsub *val* size of the subspace of the KAIN solver for the MP1 wave function. Default is 3.

Other options like k, L, or the nuclear correlation factor are taken from the reference input section. For 6D calculations the polynomial order k must be chosen small to keep calculations reasonably fast, i.e. k=5,6. The `econv` keyword of the 3D reference will be overriden by mp2 to be 100 times tighter than the 6D correlation. Local orbitals may be used.

3 Example input

```
dft
xc hf
canon
k 5
econv 1.00e-05
dconv 1.00e-04
maxiter 20
L 20
nuclear_corrfac slater 2.0
end

mp2
econv 1.00e-03
dconv 3.16e-03
maxsub 3
freeze 1
end

geometry
eprec 1.e-3
O 0.0 0.0 0.0
H 1.4375 0.0 1.15
```

H -1.4375 0.0 1.15
end

References

[1] F. A. Bischoff, J. Chem. Phys. **141**, 184105 (2014).

[2] F. A. Bischoff, J. Chem. Phys. **141**, 184106 (2014).

[3] F. A. Bischoff and E. F. Valeev, J. Chem. Phys. **139**, 114106 (2013).