MADNESS: CIS Excitation Energies

The Tutorial was written for the Git commit *f03a51fbe4f5a30d870c28772e5960ae39502da9* which you can checkout before compiling via:
git checkout f03a51fbe4f5a30d870c28772e5960ae39502da9
If you experience any sort of trouble please feel free to contact me at:
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1 Built LRCCS

Detailed information can be found in the MADNESS wiki on Github: https://github.com/m-a-d-n-e-s-s/madness/wiki

- Make shure you have Git installed
- Make shure you have (see also the MADNESS wiki):
  - C++11 Compiler: Clang-3.8 or later (Mac OS), GCC-4.8 or later (Linux)
  - Corresponding MPICH
  - GNU Autotools (autoconf 2.59 or later, automake 1.11 or later)
- Get the MADNESS source Code from Github
  git clone https://github.com/m-a-d-n-e-s-s/madness.git madness-source
- Execute *autogen.sh* in the madness-source directory
- Configure MADNESSS in your compile directory like this (use the correct paths):
  /path-to-source/madness-source/configure 'CC=/usr/bin/clang' 'CXX=/usr/bin/clang++' 'MPICC=/opt/local/bin/mpicc-mpich-clang38' 'MPICXX=/opt/local/bin/mpicxx-mpich-clang38'
- Compile the MADNESS libraries in your compile directory
  make -C /path-to-madness-compile/madness-compile/ libraries
- Compile LRCCS in the MADNESS examples directory
  make -C /path-to-madness-compile/madness-compile/src/examples lrccs

2 Run LRCCS

After compiling you can execute *lrccs* in the *madness-compile/src/examples* directory. For the calculation it is necessary that an input file with the name *input* is present in the directory from which you call lrccs.

3 Quick Tutorial

The programm *LRCCS* [2] will solve the linear-response equations for excitation energies in the CIS approximation via the following steps.

1. Solve Hartree-Fock (HF) ground state
2. Create guess vectorfunctions $\{x_i\}$ from the HF orbitals $\{\phi_i\}$ via
$$x_i = f \cdot \phi_i$$
where f is constructed from polynomials (see Keyword section)
3. Iterate the guess vectorfunctions
4. Iterate the lowest guess vectorfunctions further
5. Iterate sequentially untill convergence

Detailed information can be found in [2].

3.1 Input File Structure

The input file has four main sections.

Ground-State section: Begins with *dft* and ends with *end*

Mandatory Keywords:

- xc value: *value* is the exchange correlation potential. To solve the CIS equations this has to be always *hf*
- k value: *value* is the order of polynomials for the MRA representation (usually around 6-9)
- econv value: *value* is the MRA:threshold for the HF orbitals and at the same time the convergence threshold for the energy

Optional Keywords:

- L value: *value* it the size of the cubic simulation box in atomic units. Each dimension of the box runs rum -L to L (default is 50.0)
- dconv value: *value* convergence threshold for the orbitals (does not affect MRA threshold)
- nuclear_corrfac value: *value* is the nuclear correlation factor which is used (default is *none*, other options are *slater*, *GradientalGaussSlater*, *GaussSlater*, *LinearSlater* and *Polynomial*). For more information see [1].
- no_compute or restart: Load the HF equations from the file *restartdata.00000* which has to be present in the same directory. If *restart* is chosen the HF orbitals will be re-iterated

Response Section: Begins with *cc2* and ends with *end*

Mandatory Keywords

- thresh_3D value: *value* is the MRA threshold for the response vectorfunctions (default is 5)

Optional Keywords

- tda_econv_hard value: *value* is the final convergence threshold for the excitation energies
- tda_dconv_hard value: *value* is the final convergence threshold for the response vectorfunctions
- tda_excitations value: *value* is the number of excitation energies which shall be calculated
- tda_guess_excitations value: *value* is the number of guess excitations which is iterated in the beginning
- tda_iterating_excitations value: *value* is the number of excitation vectors which are iterated together (change if you have memory problems)
- freeze value: *value* is the number of frozen core orbitals
- tda_guess value: *value* is the guess that is used (default is a big guess from a perturbed fock matrix). Possible entries are: *dipole*, *dipole+*, *quadrupole*, *big_fock_3*, *big_fock_4*, *c2v*, *c2v_big* and *custom*). The polynomials which are used for the specific guesses will be displayed in the output. The *custom* valueword has to be used together with the *exop* valueword.
- exop value: *value* is a custom polynomial to create a guess vectorfunction from the HF orbitals. Example: *exop x 1.0 y 2.0, x 3.0 z 1.0 c -2.0* corresponds to $xy^2 + -2.0 \cdot x^3 z$. To calculate more than one guess the exop keyword can used more than one time. Example: The following line would be equivalent with the *tda_guess dipole+* keyword:
  tda_guess custom
  exop x 1.0
  exop y 1.0
  exop z 1.0
  exop x 2.0, y 2.0, z 2.0

Geometry section: Begins with *geometry* and ends with *end*. Contains the molecular coordinates in atomic units

Plot section: Begins with *plot* and ends with *end*. Contains plotting information. Can in principle be empty but should be present.

3.2 Example Input

The example input File should also be found in the madness-source/src/examples directory with the name *input_example_lrccs*. Note that it has to be renamed to *input*

```
dft
xc hf
econv 1.e-5
dconv 1.e-4
end

cc2
thresh_3D 1.e-4
tda_econv_hard 1.e-4
tda_dconv_hard 1.e-3
tda_guess dipole+
end

geometry
he 0.0 0.0 0.0
end

plot
plane x1 x2
origin 0.0 0.0 0.0
zoom 1.0
end
```

References

[1] Florian A. Bischoff. Regularizing the molecular potential in electronic structure calculations. I. SCF methods. *The Journal of Chemical Physics*, 141(18), 2014.

[2] Jakob S. Kottmann, Sebastian Höfener, and Florian A. Bischoff. Numerically accurate linear response-properties in the configuration-interaction singles (CIS) approximation. *Physical Chemistry Chemical Physics*, 17:31453–31462, 2015.