Tutorial: MOLMPS program

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Outline

1. Prerequisities
2. Naphthalene: effect of orbital choice and orbital ordering
3. Oligoacetylenes: DMRG, DMRG-SCF, and AC0
4. Extrapolation to FCI results: F_2 in DZ basis

Connection to the GPU cluster in Prague

- Connect using **ssh** to gpu.jh-inst.cas.cz with -**X** option
- User: **student1**
- Password: **TREX23@Heyr**

```
ssh student1@gpu.jh-inst.cas.cz -X
```

- ~~Connect to **g24**, **g30**, **g32**, or **g33** node (dependeng on to which group you belong)~~

~~ssh g24 ... for group 1~~
~~ssh g30 ... for group 2~~
~~ssh g32 ... for group 3~~
~~ssh g33 ... for group 4~~

- Connect to **g33**

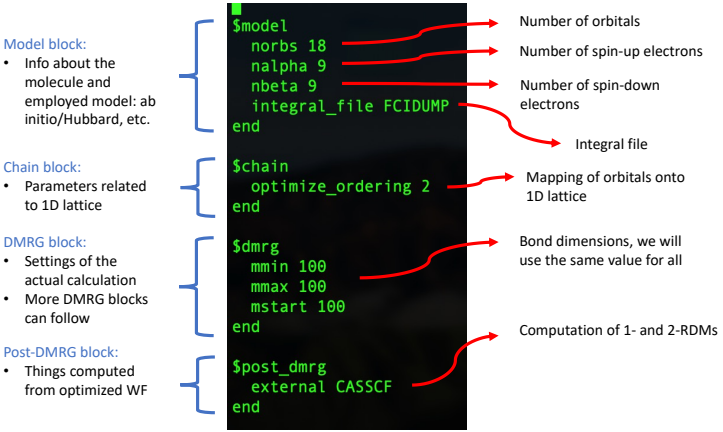
```
ssh g33 -X
```

- Go to the **/data/student1/student_X** directory (where X is your number)

```
cd /data/student1/student_X
```

Structure of MOLMPS input

- MOLMPS is not yet public on Github, but should be soon.
- Structure of input:



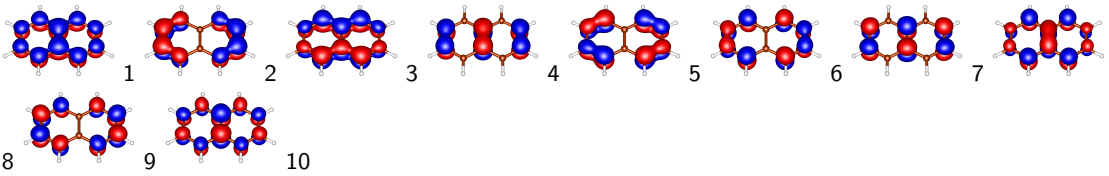
- You will run it locally using

```
molmps_run dmrg_input ncores > dmrg_output
```

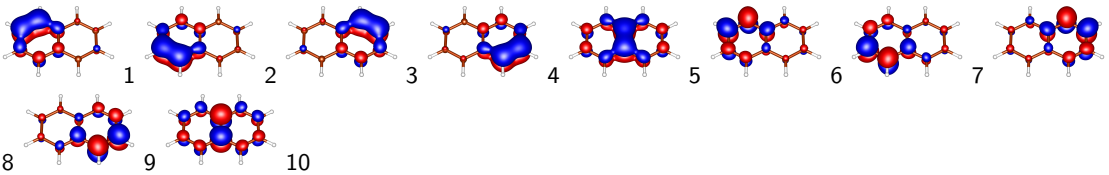
Naphthalene: effect of orbital choice and orbital ordering

- Go to subdirectory `naphthalene`
- We will compare DMRG performance in canonical HF orbitals and **split-localized orbitals**

Canonical



Split-localized



Naphthalene: effect of orbital choice and orbital ordering

- Go to subdirectory `canonical`
- Take a look at FCIDUMP and dmrg.inp files
- Run DMRG: `molmps_run dmrg.inp 4 > dmrg.out`
- Analyze the results with `mmps_ext dmrg.out` and `mmps_ext dmrg.out swp`
- Do the same in the subdirectory `split_localized`, record the final energies
- Probe the effect of ordering optimization, record the energy

```
$chain
optimize_ordering 1
optimize_bond_dims [50 50 50]
end
```

- Try `moltools correls_5.moltools`, imrove manually the ordering and re-run DMRG

Naphthalene: effect of orbital choice and orbital ordering

- Try very cheap optimization based on the exchange integrals $\langle ij||ji\rangle$

```
$chain
optimize_ordering 2
end
```

Take-home message

1. Split-localized basis is the best suitable for DMRG (exploits locality).
2. Ordering optimization based on the exchange integrals is in most cases good-enough.

Naphthalene: effect of orbital choice and orbital ordering

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```
$chain
optimize_ordering 2
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Take-home message

1. Split-localized basis is the best suitable for DMRG (exploits locality).
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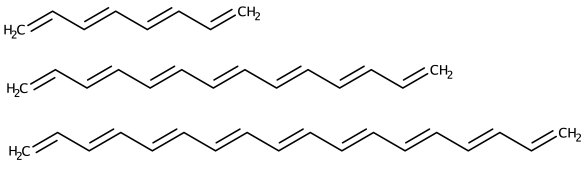
Oligoacetylenes

- For pre-DMRG stuff, we will use Orca
- **Orca counts orbitals from 0!**
- We will compute singlet-triplet (S-T) gaps for the following three examples:

4 units, CAS(8,8), DMRG(-SCF)-AC0

7 units, CAS(14,14), DMRG(-SCF)-AC0

9 units, CAS(18,18), DMRG



- Go to directory `/data/student1/student_X/oligoacetylenes`

Oligoacetylenes ($n = 4$): DMRG, DMRG-SCF, AC0

- Go to subdirectory `units_4`
- According to instructions run HF calculation
- Select which orbitals to rotate, copy the `rhf.gbw` file to `2_rot/inputOrbs.gbw` and rotate them
- Split-localize the active space (in `3_loc` directory)
- Dump the `FCIDUMP` file (in `4_dump` directory)
- Run the singlet and triplet state DMRG calculations (in `5_dmrg/singlet` and `5_dmrg/triplet`)
- Use `dump.gbw` as an initial guess for DMRG-SCF, i.e. copy it to `inputOrbs.gbw`
- Run the DMRG-SCF singlet and triplet state calculations
- In order to compute DMRG-SCF-AC0, copy the RDMs (`G1.bin` and `G2.bin`) and orbitals from the next-to-last iteration (rename them to `inputOrbs.gbw`) to `7_dmrgscf_ac0`
- Compute also DMRG-AC0, try to sort out what files do you need.

Oligoacetylenes ($n = 7$): DMRG, DMRG-SCF, AC0

- Go to subdirectory `units_7`
- Not to waste your time, MO integrals have already been dumped, check the orbitals with Molden
- Compute the singlet and triplet states by means of DMRG and DMRG-SCF, notice that this time DMRG-SCF employes the resolution of identity for integral transformation
- Compute DMRG-AC0 for the singlet state (group 1), DMRG-AC0 for the triplet state (group 2), DMRG-SCF-AC0 for the singlet state (group 3), and DMRG-SCF-AC0 for the triplet state (group 4), it will take a while.

Oligoacetylenes ($n = 9$): DMRG, DMRG-SCF

- Go to subdirectory `units_9`
- Not to waste your time, MO integrals have already been dumped, no need to check the orbitals with Molden
- Run the DMRG and possibly also DMRG-SCF calculations of the singlet and triplet states
- Analyze all the S-T gaps of oligoacetylenes obtained by different computational methods

Extrapolation to FCI results: F_2 in DZ basis

- Go to directory `/data/student1/student_X/f2`
- Check the DMRG input file `f2.inp` - several DMRG blocks with increasing bond dimensions
- Run the DMRG calculation
- Use a linear function to extrapolate the energy w.r.t. the truncation error. You can find both values below the lines `Final energy:` in the output file