

TDSCF in ReSpect tutorial

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1 Running ReSpect on stallo

Stallo can be accessed from Linux-based environment by invoking

```
ssh username@stallo.uit.no
```

where `username` is the (surprisingly) user's name. To be able to work in the graphical regime, one can use `-X` option:

```
ssh -X username@stallo.uit.no
```

For Windows you can download `Putty.exe` from [here](#).

If you want to run ReSpect directly on a login machine (for jobs shorter than 15 minutes or for tests), first add ReSpect to the list of available modules:

```
module use /global/home/uachstno/modulefiles/
```

Now it should be included in the available modules list, which can be displayed using `module avail` command. Then load it:

```
module load ReSpect
```

Now it can be seen in the list of active, loaded modules (shown when typing `module list`). Run ReSpect with:

```
respect --inp=file --scratch=/global/work/username/ --np=N
```

where `file` is a ReSpect input file (see later sections), `N` is the total number of processors to be used (should be no more than 4 or 8 on a login machine). *Always* use the `/global/work/username/` scratch directory!

2 Tutorial

This is a (hopefully) step by step tutorial that will guide you to photoabsorption spectrum of H_2O molecule. Some of the steps need only to be preformed once, other steps are repeated for all calculations.

2.1 Configure a submit script

An example of a submit script can be found attached to this tutorial. The script is called `submit_respect`. It provides stallo with some information about a calculation, e.g. number of CPUs. In principle, it only needs to be set up once, then it can be reused with small adjustments. **It is sufficient to change only 3 lines in this script.** First, line 7:

```
#PBS -l nodes=1:ppn=20,walltime=0:08:00,pmem=1600MB
```

Here:

- `nodes=1` means the total number of nodes to be used, each node has either 16 or 20 processors (CPUs)
- `ppn=20` is the number of processors per node – you can keep this on 20 or set it to 16. Note that it makes little sense using several nodes with not all CPUs allocated, so usually we change only the number of nodes.
- `walltime=HH:MM:SS` is the most important (and most often changed) parameter. It is the maximum time allocated for a calculation. When this time is exceeded, the calculation will terminate. On the other hand, the smaller the time is, the sooner the calculation starts¹. For information about how to estimate the walltime, see Section 4.

Then, line 8:

```
#PBS -M useremail@something.org
```

¹According to internal laws of the queue system.

change `useremail@something.org` to the email where you want to receive notifications about jobs you submit (when a job is finished, for instance). Finally, the last line (19):

```
respect --np=20 --inp=$inp --scratch=/global/work/username/
```

Here:

- `--np=20` is the **total number of processors** used. This number should equal to the number of nodes times the number of processors per node. So if you specified `nodes=2:ppn=20` above, then here you use `--np=40`.
- `--scratch=/global/work/username/` is the scratch directory to be used for temporary files (just as in Section 1). Remember to change `username` to your actual username for your account.

Good news: In most cases, after setting up the submit script, you only change the walltime parameter (and sometimes the number of processors).

2.2 Submit a calculation and monitor the progress

The tutorial folder contains examples of ReSpect input files for the real-time time-dependent SCF (RT-TDSCF), named `h2o_x.inp`, `h2o_y.inp` and `h2o_z.inp`. The three input files differ only in the orientation of an external electric field (denoted by the final letter), to obtain a photoabsorption spectrum for the water molecule, we need to perform calculations with all 3 orientations. To submit a job, execute:

```
qsub -v inp=/path/to/input_file /path/to/submit_respect
```

where `input_file` is a ReSpect input file without the `.inp` suffix. In our case, we execute 3 distinct commands to submit 3 jobs:

```
qsub -v inp=h2o_x submit_respect
qsub -v inp=h2o_y submit_respect
qsub -v inp=h2o_z submit_respect
```

Job status (running/completed/in queue) can be viewed using

```
qstat -u username
```

A job can be deleted from the queue (and/or terminated) by executing

```
qdel jobID
```

Our calculation can now be monitored by entering the scratch directory:

```
cd /global/work/username/tmpSomeNumbers
```

There is a temporary output file named conveniently `OUTPUT`. The file is updated every now and then, the tail of the file can be viewed using

```
tail -f OUTPUT
```

When the calculations are finished, files labeled `h2o_x.out`, `h2o_y.out` and `h2o_z.out` are generated, together with `.50` files.

2.3 Generate a photoabsorption spectrum

Photoabsorption spectra are generated with `spectrum.py` python program. The program creates new text files as output, so can be used directly on stallo, but can also generate a picture of a spectrum – in that case one must log on stallo in a graphical regime (see Section 1), or copy the files to a local computer (with python installed together with `matplotlib` library).

To generate a spectrum of the water molecule, execute

```
./spectrum.py --files=h2o
```

Note that we omitted suffixes `_x.out`, `_y.out` and `_z.out`, and used only `h2o` base — the program automatically processes all 3 files. In case of symmetry, fewer calculations are sufficient to be performed and then processed. If you also want a picture of the spectrum, run

```
./spectrum.py --files=h2o -p
```

The latter will open a python in-built GUI, which can intuitively be navigated. Additional parameters can also be provided for the program, type

```
./spectrum.py --help
```

for more information.

2.4 Output files

`spectrum.py` has produced `h2o_spectrum.out` and `h2o_peaks.out` output files. `h2o_spectrum.out` contains four columns; the first two columns represent energies or frequencies ω , the third column contains the imaginary part of the rotational averaged dynamic polarizability $\alpha(\omega)$, and the last column contains the dipole strength function

$$S(\omega) = \frac{4\pi\omega}{3c} \text{Im Tr} [\alpha(\omega)] \quad (1)$$

where c is the speed of light. You can use this file together with your favorite plotting tool (GNUplot, ...) to generate pictorial representation of absorption spectra (column 4 as a function of column 1 or 2), see Figure 1. `h2o_peaks.out` contains a list of “line shapes”. i.e. only resonant frequencies (and their intensities) selected from the whole spectrum. The data is arranged in the same way as in `h2o_spectrum.out`.

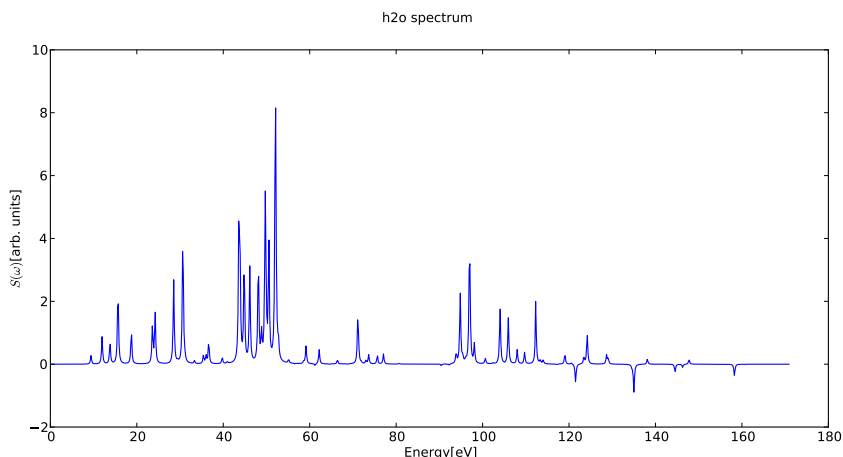


Figure 1: The photoabsorption spectrum of a water molecule.

3 Input file

3.1 Documentation

An example of an input file `h2o_x.inp` for the real-time time-dependent SCF (RT-TDSCF) can be found attached to this tutorial. All keywords (except the TDSCF section) are explained on the ReSpect homepage <http://rel-qchem.sav.sk/>, in the **DOCUMENTATION** section.

3.2 Available basis sets

A library of available basis sets will appear there in the future. Until then, it is possible to access the basis set library directory after loading ReSpect (see Section 1) by command

```
cd /global/home/uachstno/build/ReSpect_3.4.2_beta_x86_64_sequential/BAS/mdks/
```

The directory contains the basis set files with `.bas` suffix and `ao_` prefix, they can be viewed with standard text editors (like `vim`). Files beginning with `ax_` prefix are auxiliary basis sets, and are not required for our purposes. Note, that ReSpect only requires the stem of a basis set to be used in the input file. For example to use the basis set in the file `ao_aug-ucc-pvtz.bas`, use `aug-ucc-pvtz` in the input file. For all basis sets, letter `u` stands for an uncontracted basis set.

3.3 Brief TDSCF section documentation

The TDSCF section looks, for example, as follows:

```
SECTION    TDSCF
           EOM_SOLVER      MAGNUS
           ITERATIONS      1.0D-6 10
           TIME             0.5 2000
           FIELD            DELTA 0.001
           FIELD_DIRECTION  1.0 0.0 0.0
END
```

Meaning of keywords.

- For additional information and details about the keywords, see Section 4.
- For theoretical background and method details, see Ref. [1].
- For application of this method to X-ray spectroscopy (photoabsorption cross-section), see Ref. [2].

```
EOM_SOLVER      MAGNUS
```

– time-dependent equation of motion solver, should not be changed.

```
ITERATIONS      1.0D-6 10
```

- first number: TDSCF convergence threshold (per time step). The smaller the threshold is, the more expensive each time step becomes (but also more accurate).
- second number: maximum number of microiterations allowed per time step, does not need to be changed.

```
TIME            0.5 2000
```

- first number: time step length (in a.u.). **Remember: This is the most important numerical parameter entering the simulation!**
- second number: total number of time steps

```
FIELD           DELTA 0.001
```

- external (homogeneous electric) field specification. The second number is the magnitude of the field in a.u.

```
FIELD_DIRECTION 1.0 0.0 0.0
```

- direction of the external field given by a vector in cartesian coordinates x, y, z .

4 Useful tips when setting up a calculation

Here are the most important relations (in atomic units) when determining the time step length Δt and the number of time steps N :

$$\Delta\omega = \frac{2\pi}{N\Delta t} \qquad \omega_{\max} = \frac{\pi}{\Delta t} \qquad (2)$$

where $\Delta\omega$ is the frequency (energy) *resolution*, i.e. the distance between two adjacent points in the frequency domain (it is the frequency domain equivalent of the time step Δt , which is the distance between two adjacent point in time domain)². ω_{\max} is the upper frequency cutoff (the lower cutoff is always zero), meaning that the output frequency window is always between 0 and ω_{\max} . Some tips:

1. Before starting a calculation, it is important to consider the energy range you want to look at (a type of spectroscopy): Is it just 10-20 eV for valence spectroscopy or thousands of eV (X-ray, core excitations)? Koopman's theorem can give you a good guess (using the ground state orbitals). Although ω_{\max} determines the time step Δt , I still recommend using a smaller time step than the one obtained from Eq. (2), at least by a factor 2.
2. The desired resolution $\Delta\omega$ determines the total simulation time from Eq. (2), and thus the number of time points. The longer a simulation is, the finer frequency points you get. Longer simulations are required to achieve a reasonable precision, especially when the excited states (peaks) are too dense. A typical situation that occurs when the resolution is insufficient is that multiple peaks appear as one single peak. This may sometimes not be enough to observe various smaller effects responsible for multiple peaks, but it depends on the situation.
3. Another restriction to the time step length comes from the numerical implementation of the solver – to keep a reasonable precision and stability of the time evolution. Generally, larger time steps result in more microiterations per time step, but not necessarily with the same precision.
4. The number of microiterations should usually be between 2-6 (and not more than 8). In case of too many microiterations, it may be better to rerun the calculation with a smaller time step. Alternatively, it is also possible to reduce the convergence threshold (keyword `ITERATIONS`) – but this will affect the number of correct digits in the result; or use smaller external field strength (keyword `FIELD`) – this will affect the number of significant digits in the result.
5. In case you observe negative intensity peaks in the energy region of your interest, reduce the time step (by at least factor 2).
6. In all cases you should check if the ground state optimization SCF procedure converged successfully (search for `dE` or `max[F,D]` of the last iteration). Running TDSCF with an ill-converged ground state is almost pointless.
7. It is a very good practice to tune the parameters of a calculation by running the first 100 time steps to observe the number of microiterations per time step, the number of significant digits on dipole moments, oscillations of energy, etc. . . This will also give you an estimate of how long the full simulation will run (on a given number of CPUs), so this information can be used as walltime.

²Note that the product $N\Delta t$ is the total simulation time.

References

- [1] M. Repisky, L. Konecny, M. Kadek, S. Komorovsky, O. L. Malkin, V. G. Malkin, and K. Ruud, “Excitation energies from real-time propagation of the four-component Dirac–Kohn–Sham equation,” *J. Chem. Theory Comput.*, vol. 11, no. 3, pp. 980–991, 2015.
- [2] M. Kadek, L. Konecny, B. Gao, M. Repisky, and K. Ruud, “X-ray absorption resonances near L 2, 3-edges from real-time propagation of the Dirac–Kohn–Sham density matrix,” *Phys. Chem. Chem. Phys.*, vol. 17, no. 35, pp. 22566–22570, 2015.