TURBOMOLE

Tutorial
# TURBOMOLE Tutorial

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1. TURBOMOLE Usage Philosophy

The usage of TURBOMOLE has been adapted to the way a UNIX user is working:

- Command line driven,
- Many different programs, each one specialized for methods and/or properties,
- Scripts are used to combine the functionalities and manage workflows,
- Input can be changed by text editors,
- Output processed by standard UNIX tools (editors, grep, awk, ...).

Hence: some UNIX skills are required!
The functionalities are not crammed into a single program, user interface, or tool, but they are separated in modules. The user has to know the most important modules and the way they interact via the input and output files and this is not the only difference to most other quantum chemistry programs:

<table>
<thead>
<tr>
<th>Most other programs:</th>
<th>TURBOMOLE:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a single input file per job like</strong></td>
<td><strong>one directory per job</strong></td>
</tr>
<tr>
<td><em>job1.inp</em></td>
<td></td>
</tr>
<tr>
<td><strong>containing:</strong></td>
<td><strong>containing:</strong></td>
</tr>
<tr>
<td>- coordinates</td>
<td>- coordinates</td>
</tr>
<tr>
<td>- basis set definition or basis sets</td>
<td>- basis sets</td>
</tr>
<tr>
<td>- method</td>
<td>- molecular orbitals</td>
</tr>
<tr>
<td>- kind of job (energy, structure, properties,...)</td>
<td>- old results and data</td>
</tr>
<tr>
<td><strong>start job by calling one program:</strong></td>
<td><strong>not containing:</strong></td>
</tr>
<tr>
<td><code>qcprog job1.inp &gt; job1.out</code></td>
<td>- method</td>
</tr>
<tr>
<td>- kind of job</td>
<td>- kind of job</td>
</tr>
<tr>
<td><strong>all calculations and prerequisites are done in one step</strong></td>
<td><strong>start job by calling one or a sequence of programs:</strong></td>
</tr>
<tr>
<td></td>
<td><code>dscf &gt; dscf.out</code></td>
</tr>
<tr>
<td></td>
<td><code>aoforce &gt; aoforce.out</code></td>
</tr>
<tr>
<td><strong>output contains the results</strong></td>
<td><strong>just one type of calculation per call,</strong> no automatic run of energy calculation or geometry optimization or any other kind of pre-step will be performed</td>
</tr>
<tr>
<td><strong>input file remains unchanged</strong></td>
<td><strong>control file and output contain the results</strong></td>
</tr>
<tr>
<td></td>
<td><strong>input files are overwritten,</strong> i.e. coordinates are changed, mos are changed,...</td>
</tr>
</tbody>
</table>
2. How to create the input

If \texttt{TURBOMOLE} is located at /my\_disk/my\_name/TURBOMOLE, you can get access to all scripts and programs by executing the following three commands in a (bash-like) shell:

\begin{verbatim}
export TURBODIR=/my_disk/my_name/TURBOMOLE
export PATH=$TURBODIR/scripts:$PATH
export PATH=$TURBODIR/bin/`sysname`:$PATH
\end{verbatim}

A shorter and alternative way is to source a script which sets $TURBODIR and does extend the PATH as described above (please make sure to use the complete path to the \texttt{TURBOMOLE} installation directory):

\begin{verbatim}
source /my_disk/my_name/TURBOMOLE/Config_turbo_env
\end{verbatim}

2.1. Coordinates

First of all, you need a 3D structure of your molecule:

1. Build

The \texttt{TURBOMOLE} module that interactively generates an input (details are described below), \texttt{define}, has some limited features to build a structure from scratch, but that is neither convenient nor intuitive, except for some small cases, especially if you apply symmetry. The graphical user interface TmoleX contains a molecular builder and is available for free from the COSMOflogic web site.

1. Use TmoleX to import structures, modify them or build from scratch, define a complete input for \texttt{TURBOMOLE}, submit jobs to the local machine or to remote systems, get back the results and analyze the data. See TmoleX tutorial (user manual).

2. Use an external builder and convert the structure to xyz format.

3. Get the structure from a database or the internet and modify it by \texttt{define} or the builder of your choice.

2. Convert

For xyz input files use the \texttt{TURBOMOLE} script \texttt{x2t} to convert xyz files to \texttt{TURBOMOLE} coordinates:

\begin{verbatim}
x2t struct.xyz > coord
\end{verbatim}

For SD input files (.sdf) use the \texttt{TURBOMOLE} script \texttt{sdf2coord} to write coord file to disk:

\begin{verbatim}
sdf2coord struct.sdf
\end{verbatim}

The script \texttt{calculate} can read in xyz, sdf, ml2, car, and cosmo files, while TmoleX is able to import a wide range of coordinate types.
2.2. From the structure to the calculation

There are several possibilities to obtain a complete control file and run a calculation. These are the most widely used:

1. **define**
   a) run **define**
   b) run any TURBOMOLE module (program or script).
      You have to start with a ground state energy calculation to get converged orbitals with dscf or ridft (exception: jobex performs an initial energy calculation by default).

2. **calculate**
   generates *.cosmo files for COSMOtherm input.
   a) make a list of molecules
   b) run COSMO calculations as a batch over all given molecules by using the script **calculate**

3. **TmoleX**
   TmoleX is a free add-on to TURBOMOLE by Dassault Systèmes. A version for Linux/PC, MacOSX, and Windows is available from the ftp server where the usual TURBOMOLE distribution is located (ask your TURBOMOLE administrator). There is also a free client version which can be used to build molecules, generate input files and submit TURBOMOLE jobs to remote machines. Check The BIOVIA home page for details about the client version.
   TmoleX can import coordinates, change structures, generate input files and run TURBOMOLE jobs. Results are shown in a panel within TmoleX. Structures, geometry optimizations and vibrational frequencies can be displayed and animated. See the web site: [TmoleX, the Turbomole GUI](#)

4. **Simplified Input**
   Since version 7.5 it is possible to write a simple control file in an editor and to skip the define step as described in point 1. The first module that has to be run must be either dscf, ridft or jobex. The rest of this tutorial can be used and only the first define step can be skipped in each example.

In this tutorial we are using **define** and the command line to be able to exploit all features of TURBOMOLE — all other types of input generation offer only a limited functionality.
3. The TURBOMOLE modules

See chapter 1.4 'Modules and Their Functionality' of the TURBOMOLE documentation for a description of each module and script. Please note that this is not a complete list of available modules.
4. The s[ai]mple input

4.1. Very basic input file(s)

The recommended way to generate TURBOMOLE input files is to call define and not to write the input file control manually. This has a lot of pros and avoids typical pitfalls like typos, inconsistent input files, contradictory keywords, etc.

define does generate a proper input, allows access to most known keywords without the need to be a TURBOMOLE expert or to search the documentation. It is interactive, offers options, provides suggestions, calculates some input properties and, in the end, provides an input which contains the most important keywords the user can change before, during or after the calculations.

There are, however, workflows and tasks which are highly non-interactive and do benefit from a simple approach using a minimal set of input data and accepting all or most defaults.

Since TURBOMOLE version 7.5 this can be done by using a new, simplified syntax for the input files. The basic requirements are:

1. A file named control which contains keywords in one of the forms:

   $keyword1
   $keyword2 options
   $keyword3
       options
   $keyword4 file=filename

   The first keyword is used like a flag (e.g. $uhf),
   the second keyword contains one or several options in the same line (e.g. $symmetry d4d),
   the third keyword has its options in the subsequent lines (note that for some keywords those options are used in a different way depending on their position – in the same line as the keyword or in the following lines, see e.g. $soes),
   the last keyword is a reference to an external file (usually in the same directory, but the filename can also contain a path, see e.g. $coord).

2. The coordinates in TURBOMOLE format. Those can be either added to the control file itself, defined by the keyword $coord, given in atomic units in the Cartesian format <x> <y> <z> <element>

   $coord
   2.62      0      0.142      c
However, it is much more convenient and also easier for scripting if the coordinates are not
directly stored in the control file. Note that the control file is not just an input file, so the
coordinates will change during a geometry optimization or a molecular dynamics
calculation. Hence, it is recommended to have two files as input:

a) control file with a reference to an external file (this is not yet a complete input):

```plaintext
$coord file=coord
[...]
$end
```

b) coord file with content:

```plaintext
$coord
  0.00000000000000  0.00000000000000  -0.12178983933899  o
  1.41713420892173  0.00000000000000  0.96657854674257  h
-1.41713420892173  0.00000000000000  0.96657854674257  h
$end
```

Note: It is good practice to put the keyword $end to each input file. And it is also convenient
to name the additional input files (like coord here) similar to the keyword they contain,
although this is not a must.

3. The basis set is also a prerequisite and there is no default if it is not given. So the minimal
input file in the simplified format also has to contain:

```plaintext
$atoms
  basis = def2-SV(P)
```

This assigns the basis set def2-SV(P) to all elements.

---

**Summary**

A complete minimal input for a job is therefore:

```
control file:

$coord file=coord
$atoms
  basis = def2-SV(P)
$end
```

```
coord file:

$coord
  0    0    -0.12    o
  1.41713 0    0.966    h
-1.41713 0    0.966    h
$end
```

This simple sample control file does not have to be changed if another
molecule is calculated.

The coord file will be changed during jobs that
alter the structure (optimization, etc.). The input
coord file simply contains the start structure. Can
also directly be integrated in control.
4.2. A more typical input file

The most simple input file as described in the section before will trigger Hartree-Fock calculations. This sounds like history, but this is also the default for `define` if nothing is changed in the last menu (see below).

The workhorse nowadays is DFT, most quantum chemistry program packages use RI or ‘density fitting’ for standard applications. Turbomole pioneered RI-DFT in the 90’ies and linear scaling methods like MARI-J (Multipole Accelerated RI-J, see documentation) are routinely used. Also basis sets have been developed to get a well-known average error for most cases and properties.

A simple input file for typical jobs like geometry optimizations is

```
control file:
$coord file=coord
$atoms
  basis = def2-TZVP
$dft
  functional b-p
$rij
$marij
$end
```

Remarks

- The coordinates are the same as in the first example.
- The file coord is therefore the same.
- The def2-TZVP basis set is a standard triple-zeta one with a good to very good accuracy for most properties.
- DFT is switched on by the $dft keyword, the functional here is BP86.
- $rij and $marij trigger a linear scaling RI-DFT calculation.

NOTE: As described earlier, the job type is not part of the input!

4.3. Input charge and symmetry

Different to all other ways to generate Turbomole input, the symmetry is actively checked by the first module which uses the simplified input format. If `$symmetry` is not present in the input, the symmetry will be detected and used. In the example given in the last section, C2v is automatically used. If you want to switch off the automatic detection, just add to the control file:

```
$symmetry c1
```

As `define` is not used to generate start orbitals the molecular charge and optionally the number of unpaired electrons (1 for doublet, 2 for triplet, etc.) can be added by using the `$eht` keyword:

```
$eht charge=<n>
$eht charge=<n> unpaired=<m>
```

Examples:

```
$eht charge=-1
$eht charge=2 unpaired=1
```
4. The sample input

4.4. Sample simple input files and job types

Three examples of input files and standard job tasks are shown below. Note that the coord file is not explicitly given here, please use the coord file for water from the example before. Only the control file has to be modified.

1. A RI-DFT geometry optimization, followed by a vibrational frequency calculation

   Use the following commands on the shell:
   
   ```
   $coord file=coord
   $atoms
   basis = def2-TZVP
   $dft
   functional b-p
   $rij
   $marij
   $end
   
   #geometry optimization:
   jobex &> jobex.out
   #vibrational analytical frequencies:
   aoforce &> force.out
   ```

2. A geometry optimization using RI-MP2

   Use the following commands on the shell:
   
   ```
   $coord file=coord
   $atoms
   basis = def2-TZVP
   $ricc2
   geoopt model=mp2
   $denconv 1d-7
   $end
   
   #geometry optimization:
   jobex -ri -level mp2 &> jobex.out
   ```

   MP2 and other post-Hartree-Fock methods need a well converged energy and density. It is therefore a prerequisite to add $denconv to the control file in order to get reasonable MP2 (and beyond) energies and properties.

3. A UV/Vis spectrum using TDDFT

   Use the following commands on the shell:
   
   ```
   $coord file=coord
   $atoms
   basis = def2-TZVP
   $dft
   functional pbe0
   $rij
   $marij
   $scfinstab rpas
   $soes all 5
   $end
   
   #a single-point energy calculation
   ridft &> ridft.out
   #a TDDFT excited state calculation
   escf &> uvvis.out
   ```

   The first flag ($scfinstab rpas) asks for a full TDDFT (RPA level) singlet excitation calculation (which also computes the oscillator and rotatory strength for UV/Vis and CD spectra), the second flag ($soes) asks for 5 excited states in all irreducible symmetry representations (IRREP, for C1 - no symmetry- there is only one IRREP).
5. The quick tour: How to run a calculation

Creating an input: The shortest way through define

As we have seen in the previous chapters, there is a special program that creates a complete Turbomole input: define

Most of the functionalities of define are not needed in your day-to-day work. In general, hitting <ENTER> will print out the current menu and * will proceed to the next step. And most of the time you may just accept all defaults.

In the first three menus, the geometry is loaded, basis sets are assigned and the start MOs together with the occupation is created. If you do not change anything in the last menu, you will get a nice Hartree-Fock input. Entering dft, ri, mp2, cc, ... in the last menu will switch on or off other methods.

So, the shortest way to an input is to get a structure, either in Turbomole coordinates (file coord), or in an xyz file (struct.xyz) and then let the x2t script of Turbomole convert it to a coord file:

```
x2t struct.xyz > coord
```

Then create a new empty directory and copy the coord file in there. Change to that directory and call define. First, you will be asked for a name of the input file, just hit <Enter> here, and then you can enter a title. The title can be just an empty line (it might be a good idea to give a title here, sometimes the fastest way to see what the input is about).

The most important commands in define are explained here. The * indicates where each one of the four main menus does end and the next one begins, since * or q are the commands to end a menu and proceed to the next (see below).

After that, you have a nice Turbomole input and you can run any of the Turbomole modules or scripts – depending on which property you want to calculate.
5. The quick tour: How to run a calculation

Creating the input and run a calculation

First exercise!

Instead of starting from an xyz file, we simply take one of the structures from the TURBOMOLE structure library, that is part of every TURBOMOLE distribution. We will do that for almost all other examples that will follow later...

1. Create the input with define:

   - start from a new or empty directory,
   - call define
   - and enter the following things:

   <Enter>
   This is the first exercise, where we do a HF calculation on benzene
   a ! benzene
   y
desy
ired
*
*
eht
<Enter>
<Enter>
<Enter>
*

All commands given above will be explained later in this tutorial. The (almost) same exercise is done in chapter 7.1 - with a detailed description of the in- and the output. If you have difficulties with this example, please try chapter 7.1 !!

Some notes:

You can skip the lengthy title, of course, or just hit <Enter> for not providing a title at all.

Molecules from the structure library are loaded like any other coordinate files, the only difference is that there is an exclamation mark `!' between the command a and the name of the molecule.

We have let define determine the symmetry with desy, and define found D_{6h} point group.

Internal redundant coordinates are determined automatically with ired – this would not have been necessary here, but if ired is not called, you will be asked if you are sure not to use internal coordinates when exiting the geometry menu (the first *).

We have accepted the default basis set def-SV(P) – this is one of the TURBOMOLE default (def-) basis sets, SV(P) is a double zeta valence basis set with polarization at all non-Hydrogen atoms.

eht runs an extended Hückel calculation to create start orbitals and to determine the occupation/multiplicity, the rest of the <Enter> keys belong to questions that Hückel asks you. Note that one of those questions is the total charge of the molecule (default is 0 – neutral), and another question is if you accept the found occupation (closed shell system, trivial in this case).

Finally, the last * exits define, changing nothing at the last menu – hence we have a standard Hartree-Fock input.
2. Run a Hartree-Fock energy calculation:

```bash
dscf > dscf.out
```

After the calculation has finished (takes about 3 seconds), please look at the output file `dscf.out`:

You will see that 9 iterations have been done, the total energy is -230.51807365370 Hartree (convergence is \(10^{-7}\), so depending on your system/hardware, your result might differ from the one given here).

That's it.
See chapter 7 for details about single point calculations.

**Second exercise!**

Let us do the same thing as before – but this time we will do a geometry optimization with RI-DFT.

Now we have two different possibilities:

1. Start from scratch, i.e. from an empty directory, and go through `define` as before. But this time, do not enter the last `*`. So you will stay in the last, the general menu:

   ```
   GENERAL MENU : SELECT YOUR TOPIC
   scf    : SELECT NON-DEFAULT SCF PARAMETER
   mp2/cc2: OPTIONS AND DATA GROUPS FOR MP2, CC2, ETC.
   ex     : EXCITED STATE AND RESPONSE OPTIONS
   prop   : SELECT TOOLS FOR SCF-ORBITAL ANALYSIS
   ...
   ```

   Enter `dft` – and you will get in the DFT menu. Just enter `on` here and leave with `<Enter>` or `*`. Enter `ri` – and you will get in the RI-J menu. Like in the last menu, enter `on` here and leave again. Now enter `*` or `q` to leave `define`.

2. Rerun `define` in the same directory as before, keeping all files in there (including the output files like `dscf.out`, `energy` and the changed input files like `mos`).

   `define` will tell you that it found an input file which will be read in.

   Now you will be asked if you want to enter each of the three basic menus for geometry, atomic and molecular attributes. Just hit `<Enter>` all the time, since we do not want to change anything except the method.

   `define` will automatically stop in the last menu – no matter how often you are hitting `<Enter>` now...

   Here enter the same commands as given above (`dft` to `on` and `ri` to `on`) and leave `define` with `*` or `q`.

   We have an input for benzene, DFT (standard) B-P86 functional, using RI-J and D\(_h\) symmetry. You can have a look which density functional will be used with the `sdg` tool, that prints data groups of the `control` file.

   ```bash
   sdg dft
   ```

   gives:

   `$dft`
5. The quick tour: How to run a calculation

```
functional b-p
gridsize   m3
```

A single point calculation could be done by starting `ridft`, but we want a geometry optimization, so we enter:

```
jobex
```

`jobex` will do 4 geometry cycles until convergence. To learn more about `jobex` and structure optimizations please refer to chapter 8.

There are several ways to check the results, but the most common ones are:

1. look at the file `job.last` which contains the output of the last energy and gradient step
2. look at the file `GEO_OPT_CONVERGED` which contains some collected information about the run
3. look at the file `gradient`: it contains all geometries and gradients at each step of the optimization. A common shortcut is to do

   `grep cycle gradient`

   to check the convergence behavior during the optimization and to get the final result (last energy and gradient norm).
4. call

   `t2x > final_structure.xyz`

   and load the file `final_structure.xyz` in the molecular viewer of your choice (it is a multiple-xyz file)
5. or call `tm2molden` to get a `molden` input file that includes also the molecular orbitals.
6. at the command line, use `dist`, `bend`, or `tors` to get bond lengths, angles, dihedral angles, etc.

   `dist`

   gives:

   dist  1  c --  7  h =  2.0845 au = 110.30 pm
   dist  2  c --  8  h =  2.0845 au = 110.30 pm
   dist  3  c --  9  h =  2.0845 au = 110.30 pm
   dist  4  c -- 10  h =  2.0845 au = 110.30 pm
   dist  5  c -- 11  h =  2.0845 au = 110.30 pm
   dist  6  c -- 12  h =  2.0845 au = 110.30 pm
   dist  1  c --  2  c =  2.6570 au = 140.60 pm
   dist  1  c --  6  c =  2.6570 au = 140.60 pm
   dist  2  c --  3  c =  2.6570 au = 140.60 pm
   dist  3  c --  4  c =  2.6570 au = 140.60 pm
   dist  4  c --  5  c =  2.6570 au = 140.60 pm
   dist  5  c --  6  c =  2.6570 au = 140.60 pm
   etc.

   Call

   `dist -help`,
   `bend -help`, or
To see how a bond, a bending angle or a torsion changed during the geometry optimization, use the script evalgrad. Call evalgrad with two atom numbers for a bond length, three atom numbers for an angle and four atom numbers to see how a torsion has changed during optimization. The output shows three columns: the optimization step, the energy at this geometry and the value of the bond length, angle or torsion:

```
> evalgrad 1 2
1 -232.0725369223  1.3892
2 -232.0764471780  1.4034
3 -232.0765625911  1.4060
4 -232.0765631365  1.4061
```

### 6. DEFINE

**define** is an interactive input generator which creates the input file *control*:

1. Supports most basis sets in use, especially the only fully atom optimized consistent basis sets of SVP, TZV, and QZV quality available for the atoms H–Rn (including lanthanides and actinides up to Lawrencium for SVP and TZV),

2. Determines the molecular symmetry,

3. Determines the internal coordinates, allowing for efficient geometry optimization,

4. Allows to perform a geometry optimization at a force field level to pre-optimize the geometry and to calculate a Cartesian Hessian matrix,

5. Sets the keywords necessary for single point calculations and geometry optimizations for a variety of methods,


Just try and see how it works...

**Notes about how to proceed in this tutorial:**

The following chapter explains the usage of **define** to get a proper input for a calculation. Since **define** is not just a simple input preparation program but is also able to analyze, change, build, and compute properties of your input, the chapter is quite long – and you will not do a single real calculation until you have reached the near end of this chapter...

**For impatient users or users who want to know how to perform a certain calculation:**

Please read chapters 6.1 and 6.2 and then go directly to chapter 7: Single point calculations or to one of the other chapters...
6.1. The path through define

There are four major menus in define:

<table>
<thead>
<tr>
<th>1. Molecular Geometry Menu</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Atomic Attribute Definition Menu</td>
</tr>
<tr>
<td>3. Occupation Number &amp; Molecular Orbital Definition Menu</td>
</tr>
<tr>
<td>4. General Menu</td>
</tr>
</tbody>
</table>

But before you get to the first one, you will be asked for:

1. The name of the input file to read in and/or to be generated. The default is control
   
   Always accept the default here!

2. A title for the job you want to create an input for:
   
   That can be an arbitrary string, but it will be truncated to 80 characters automatically.

6.2. Navigation within define

Some general remarks:

1. You will always get the current menu printed on screen (enlarge your screen if you can not see everything).

2. The first line contains the most important data of your input for the current menu.

3. Most of the commands lead to sub-menus.

4. To finish the menu and proceed to the next one, enter:

    *

5. To go back to the previous menu, enter:

    &

    (but please do not do that too often...)

6. If you are in one of the four main menus, hitting <Enter> will just print out the menu you are in.

7. To quit define immediately (and prematurely), enter:

    qq

    which only gives proper input files if you have been reading in an existing input.
6.3. Making symmetric molecules with define

Skip this chapter if you are not going to build molecules with the define module of TURBOMOLE.

define is probably not the most convenient tool for coordinate inputs. For highly symmetric cases, however, it provides some nice features. Here are some examples:

- Cyclopentadienyl anion (Cp-, point group D$_{5h}$):

In the geometry menu of define, we start with defining the point group. Enter

```
sy d5h
```

Maybe you have to use the scroll bar of your window to see the following lines:

```
symmetry group of the molecule :   d5h
the group has the following generators :
c5(z)
c2(x)
mirror plane sigma(xy)
20 symmetry operations found
```

This tells us, that the molecule must lie in the xy-plane and the symmetry distinct atoms of Cp$^-$ should be on the x axis. To define the molecule, we enter the following commands

```
ai
c
1.2 0 0 A   # Angstrom units!
*h
2.3 0 0 A
```

Now we can have a look at the results with

- **disc**: displays the Cartesian coordinates
- **disb 1,6**: displays the bond distances for the two symmetry distinct atoms (1 c and 6 h)
- **disg**: calls a visualizer, needs some customizing by your system administrator; does probably not work properly if define runs on a remote machine.
- **disi**: displays internal coordinates (not yet defined, see next exercise).

We can save the current status of our project coordinates by typing

```
w coord.cp
```

(or any other file name, of course). If we don't like the results, we just delete everything by entering

```
del all
```

and confirming with y. The Cp$^-$ example continues in the next exercise.

- P$_4^-$ (point group T$_d$): Proceed as described above
- PF$_5$ (D$_{3h}$)
- B$_2$H$_6$- (I$_h$)
- C$_8$H$_8$, Cubane (O$_h$)

... Think of other examples.

Hint: Be always aware how the symmetry generators of the chosen point group are defined.
6.4. **Internal coordinates**

The definition of internal coordinates is extremely important for efficient structure optimizations.

If you are not interested in any property related to internal coordinates, it is usually safe to define the internal redundant coordinates automatically by `ired` and then proceed to the next menu with `*`. In that case, just keep in mind to call the `ired` option in the first `define` menu and go to the next chapter.

However, if you want to do constrained searches, or if you are looking for transition states, you need to know how to deal with internal non-redundant coordinates as well:

- **Non-redundant internal coordinates (manually):**

  Assume, we want to continue with our Cp` example – if you did skip the last menu, never mind... you can use the coordinates from the structure library.

  Call **define** in an empty directory and then type (ignore the comments behind and including the #):

  `<Enter>`
  `a ! cp-
  # load the coordinates from the structure library`

  restore the point group information by using the command

  `desy`

  We can now define the coordinates manually by issuing the following commands (ignore the comments):

  `i`  
  `idef`
  `k stre 1 2`  
  `k stre 1 6`

  After another two strokes on the return key, we are back in the internal coordinate menu. We can enter **imet** to find out whether the coordinates are complete and have a decent Wilson B-matrix. Now, also the **disi** command is working. We can play a little with internal coordinates and reshape the molecule (often the distances are not satisfyingly after input of guessed Cartesian coordinates). Use the **iman** command to change the bond lengths (but remember to reset them to chemically reasonable values before going to the next item of this exercise). If you are doing the „quick tour“ through the tutorial go to exercise 6.6.

- **Non-redundant internal coordinates (automatically):**

  Except for small cases, manual input of internal coordinates is a rather joyless task. Think of the internal coordinates necessary for Cp` in C1 symmetry. Delete the internal coordinates of the previous part of the exercise by typing

  `irem k`

  and reset the symmetry by

  `sy cl.`

  Now we can try an automatic assignment with
TURBOMOLE Tutorial 6. DEFINE

iaut

This will bring us to the „BOND ANALYSIS MAIN MENU“. Hitting the return key will display the automatically detected bonding information. Hit the return key another time and enter a

*  

to get back to them geometry main menu.
Use disi to view the result. After that we finish our define session prematurely by typing

  * # after this command we should be in the attributes menu
  qq

Now have a look at the control and coord files (with more, less, vim, etc.).

• Redundant internal coordinates (automatically):

The

  iaut

command fails for more complicated cases (cage molecules or sandwich complexes). Let us create a new directory and copy there the coord file containing the Cp' anion. We run define, load the molecule, detect the symmetry using desy and lower the symmetry to C₅ᵥ via the command susy. After that we add an aluminum atom:

  ai
  al 0 0 2 A
  *
  *

If we try to use iaut on this molecule, define will fail (you will see this, if you try imet). In cases like these we can use

  ired

which produces redundant internal coordinates. You can see the result by typing red_info (and using the scroll bar of you window). For the current molecule, due to its high symmetry, there still is a good solution using non-redundant internal coordinates (can you think of one?). However, if symmetry is lowered and/or the molecule becomes more complex, the Wilson B-matrix will become ill-defined for non-redundant internal coordinates.

Let's quit that project for a moment. Enter

  w coord
  qq

You can now have a look at the control file. It contains the redundant internal coordinates in the data group $redundant.

Note: you can delete files like tmp.input. They may remain after premature exits from define.
6.5. Detecting (unknown) symmetry

Crystal data or final structures from molecular dynamics runs (and even results of geometry optimizations) sometimes are only slightly distorted and will show high symmetry, if further optimized. define can help you to detect these „hidden“ symmetries. You have to use the

desy

option of the geometry main menu, together with a larger threshold:

desy 0.5

This threshold gives the size of a sphere around each atom (in Bohr units). If spheres overlap after a symmetry transformation, the two atoms are considered as symmetry equivalent. After a higher symmetry has been detected, the molecular framework is symmetrized.

There are three examples in the structure library.

1. Call define from an empty directory, and
2. hit <Enter> two times to get to the SPECIFICATION OF MOLECULAR GEOMETRY menu.
3. Add one of the example input coordinates with
   a ! name
   where name is one of c4h6.c2h (try to find C\textsubscript{2}h), ptcl4 (almost D\textsubscript{4}h), or mg17 (search for D\textsubscript{4d}),

Use desy to find the molecules secrets.

Hints: If the radius of the spheres was chosen too small such that only a subgroup of the full symmetry group was identified, the symmetrization may prevent define from finding the full symmetry. Sometimes, however, the reverse is true. Use the w <filename>, del all and a <filename> commands to save intermediate results, delete all atoms and to reload the coordinate files.

Of course, a too large value for the sphere is not very helpful, either. Best results are typically obtained with desy 1.0.

6.6. Assigning basis sets

Let’s resume with the Cp\textsuperscript{-} example (exercises 6.3, 6.4). Go to the previous directory and start define. If you left it in the status after the last exercise you might, after the title section, get a message like

SYMMETRY cl AND CARTESIAN COORDINATES FOR 10 ATOMS
HAVE BEEN READ FROM THE DEFAULT INPUT FILE control.
DEFINITIONS OF 24 INTERNAL COORDINATES HAVE BEEN READ.
SPECIFICATION OF BOND TOPOLOGY HAS BEEN READ.
DO YOU WANT TO CHANGE THE GEOMETRY DATA ? DEFAULT=n GOBACK=&

If it says SYMMETRY d5h everything is OK and we answer n.
Else we answer y and restore the symmetry with desy. After leaving that menu with * we find ourselves in the basis set menu. Automatically, define will assign the def-SV(P) basis sets. If we want something else, we may enter e.g.

b all def2-TZVP

All atoms now are assigned the def2-TZVP basis. Use the bl command to look at the current status. If we feel that we should rather use the def-SVP basis for the hydrogens, we enter
Use \texttt{bl} to check that this works.

Symmetry is maintained in this section of \texttt{define}, so

\begin{verbatim}
bb 7 def2-TZVP
\end{verbatim}

has the effect of assigning the \texttt{def2-TZVP} basis to all symmetry equivalent hydrogen atoms.

At this point we leave this menu by entering *. To immediately quit \texttt{define}, enter \texttt{qq}.

If you want to continue with exercising, please go to chapter 6.11. To learn more about basis sets and basis set assignments, simply continue.

If you are interested in some more advanced features like basis set modifications, entering \texttt{h} will provide some help.

### 6.7. Which basis set should I take?

The question which basis set is the best for your purposes depends on which method you apply and what you are going to do. First of all, we recommend to use the Karlsruhe (Ahlrichs) basis sets – not just for \texttt{TURBOMOLE}. There is a complete set of highly optimized basis sets at double zeta (split valence – SV), triple zeta (TZV), and quadruple zeta (QZV) quality available.

The default basis set which \texttt{define} sets automatically is \texttt{def-SV(P)}, i.e. \texttt{def-SVP} for all non-hydrogen elements and \texttt{def-SV} for the H's (no polarization function P there). This basis set is sufficient for ground state DFT structures and some properties, but should be set to a higher level (\texttt{def2-TZVP}) for DFT single point energy calculations or Hartree—Fock and MP2/CC2 calculations.

A short note about the names and the quality of each basis set for the methods implemented in \texttt{TURBOMOLE} is given, when you call the basis set information sub-menu (bi) in the \texttt{ATOMIC ATTRIBUTE DEFINITION MENU}. Enter \texttt{bi} and you will get this message on screen:

\begin{verbatim}
bi

==============================================================================
Information about improved TURBOMOLE basis sets:
Balanced basis sets for H-Rn of types SV, TZV and QZV (plus polarization sets) were developed in 2005, partly by modifying previous bases. The resulting bases, def2-SV(P)/SVP/TZVP/TZVPP/QZVP/QZVPP, were tested at more than 300 representatively chosen systems. We thus may give some rough recommendations:
QUALITY: exploratory-----qualitative-----quantitative-------limit
DFT        def2-SV(P)  def2-TZVP  def2-QZVP
HF         def2-SVP    def2-TZVPP  def2-QZVPP
MP2        def2-SVP    def2-TZVPP  def2-QZVPP

For further details see: F. Weigend and R. Ahlrichs, PCCP, 7, 3297-3305 (2005).

==============================================================================
\end{verbatim}
Note that the former standard basis sets for Turbomole are still in the basis set library, just replace def2- by def-, e.g. def-SVP instead of def2-SVP.

Another set of basis sets, typically used for correlated methods like Coupled Cluster calculations, are Dunning’s basis sets. Those are included in the standard Turbomole basis set library, denoted as usual: cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z. And the augmented ones: aug-cc-pVDZ, aug-cc-pVTZ, etc.

To get an overview about the quality of each basis function compared to the other ones, choose an element and look at the file STURBODIR/basen/<element name>. At the beginning of the file, the names of the basis sets are given together with the total energy of an unrestricted Hartree-Fock calculation. The lower the energy, the better the basis set.

### 6.8. How to get a list of available basis sets

There is (quite hidden) an option in define that prints out all available basis sets, letting you choose the one you like. It was thought as a help, so you get there only if you do the assignment step by step.

- In the basis set menu enter
  
  b all

- then you will be asked for a nickname. If you have no idea what to take, enter something like (it does not matter):
  
  help

- `define` will now search for the string 'help' and gives an error output:

  THERE ARE NO DATA SETS CATALOGUED IN FILE
  /usr/local/TURBOMOLE/basen/c
  CORRESPONDING TO NICKNAME c help

  USE ONE OF THE FOLLOWING OPTIONS :
  nick    - REPEAT NICKNAME INPUT
  ...

- Enter `nick` to get to the nick name section

- `define` now asks for a nick name:

  INPUT NICKNAME

- Enter a question mark here:

  ?

- you will first get the list of available basis functions (the header of the files in the basis set library), and then `define` goes through all basis set nicknames, asking if you want the current entry or not.

- If you just remember the beginning of the name, or if you want to use one of the default basis sets, you can also enter as nick name:
6. DEFINE

def-?

or

def2-?

And you will get just the basis sets from the library that start with def- or def2-, resp.

Unfortunately, define will take the first name of a basis set if several names are given, which might prevent the automatic assignment of auxiliary basis sets for RI later on. But there, you will be able to go through the available auxiliary basis sets either.

6.9. A basis set library of your own

In your home directory, you can create a .definerc file (the leading dot is important!). The contents of .definerc may look like that:

```
basis=/home/me/PROG/TURBOMOLE/basen
basis=/home/me/BASISSETS
```

Each line defines an alternative basis set library. The user defined basis set library should look like the TURBOMOLE library (have a short look at $TURBODIR/basen): The directory must contain files having the name of the element, which in their turn contain the various basis sets. Create such a directory in your home directory. Load one or two basis sets of your choice for carbon and hydrogen from the EMSL basis set library http://bse.pnl.gov/bse/portal

and copy the basis set information into files named C and H. Make sure that you selected the TURBOMOLE format. There should be only one $basis at the beginning and one $end at the end of each library file. Then create a .definerc in your home directory and enter the full path of your new basis set library in the format shown above.

To check whether it is working, go to the directory where you last edited the Cp anion and run define. In the basis set menu, enter lib and choose your new library. Now you can specify the basis sets that you have just downloaded.

6.10. Geometry manipulation with define

If you feel that your molecule builder is much better, you can simply skip this exercise.

Get a copy of the Cp- ring, which you hopefully succeeded to create in the previous exercise and turn it into Cp- (i.e. Substitute the hydrogens by methyl groups). This can be accomplished as follows:

- Create a new directory and call define. Enter two times <Enter> until you reach the Molecular Geometry Menu.
- Enter a \texttt{!cp-} and then \texttt{desy}
- If the displayed symmetry group is not $D_{6h}$ use \texttt{desy 0.5}. Then use the \texttt{susy} command to lower the symmetry group to $C_5$ (you have to go to $C_5$, first).
- Still in the geometry menu, enter \texttt{sub}. Then you have to specify the atom index of one of the hydrogens. Use the \texttt{disc} command if you do not remember. The program will ask you whether you want to replace all symmetry equivalent atoms (provided the symmetry was set correctly). Answer \texttt{y}.
- Now we have to define a molecular fragment that should replace hydrogen. We use the little structure library

25
of TURBOMOLE again and enter
\texttt{!ch4}. We accept the first offered structured and choose one arbitrary hydrogen of methane to be taken away, thus defining the way the fragments are linked together. For the following question, you can accept the defaults.

- After entering the basis set menu, we can simply leave define by entering \texttt{qq}.

Use the \texttt{t2x} or the \texttt{tm2molden} tool to get the input for a visualizer. Copy this file via FTP to your local machine and hope, that there is something installed to view the result.
6.11. Providing an initial guess for molecular orbitals

This menu serves for the definition of occupation numbers (and thereby the charge of the molecule) and the start orbitals for the SCF calculation. For well-behaved molecules (like our Cp-anion), the procedure is very easy. Just choose the option

\texttt{eht}

to perform an extended Hückel calculation. Accept the 'DEFAULT PARAMETERS' and enter the charge (-1 for Cp, of course). The program will propose occupation numbers which for most cases are correct. If the HOMO/LUMO separation is small, you will get a warning. For Cp, we can accept the assignment and go on to chapter 6.13.

If you don't like the assignment, entering

\texttt{n}

brings you to a menu for manual assignment of orbitals. You will get this menu automatically, if \texttt{define} cannot establish occupation numbers because of degeneracies of the frontier orbitals. The most important options are:

- \texttt{l} to list the MOs (ordering according to their EHT energies).
- \texttt{t} to choose a UHF triplet occupation
- \texttt{u} to choose a UHF multiplet with $n$ unpaired electrons
  \hspace{1cm} e.g. \texttt{u 3} for a (high-spin) quartet.
- \texttt{c} to declare a list of closed shells,
  \hspace{1cm} e.g. \texttt{c 1-20,22}.
- \texttt{a} and \texttt{b} to declare a list of occupied alpha and beta orbitals (for UHF).
- \texttt{o} declares open shells for ROHF (!) runs.

Do not use this option if you actually want to declare the occupation for a UHF run.

6.12. Reusing old mos

All \texttt{TURBOMOLE} jobs are restart jobs as default. So you will always reuse the old molecular orbitals that are present in your working directory. In some cases those are not valid any more and \texttt{define} provides the \texttt{use} option to recycle MOs when

- you have changed the symmetry (without changing the structure!),
- you have changed the basis set.

The \texttt{use} command will need an unchanged copy of the \texttt{control}, \texttt{basis} and \texttt{mos} files; therefore make a copy of the contents of your working directory (e.g. in the subdirectory \texttt{save}: \texttt{mkdir save ; cp * save}).

- Run \texttt{define} in the working directory and change the symmetry to C$_2$ (use \texttt{susy})

Leave the geometry menu and skip the attributes menu; you will automatically end up in the molecular orbital section of \texttt{define}.

Enter the command

\texttt{use save/control}

(you have to modify the path name, of course) to obtain transformed orbitals.

Quit \texttt{define} and use the \texttt{eiger} command to view the result.
6. DEFINE

- Restore the old control and coord files (symmetry $D_{sd}$) by copying them back from the subdirectory and rerun define.
  
  This time you change the basis set to TZVPP.
  
  The command
  
  use save/control
  
  will generate projected orbitals.
  
  Run ridft and compare with a run which starts from EHT Mos.

6.13. The general menu of define

Here, you can choose additional parameters for your calculation. Depending on the type of calculation you wish to start you have to visit some sub menus:

- Hartree-Fock SCF:
  
  This is the default with a convergence threshold for the energy of $10^{-7}$ Hartree.
  
  If you want to change some options, go to the scf sub menu. Most options concern convergence acceleration. They are normally OK for most cases.

- MP2/RI-MP2/RI-CC2/PNO-CC:
  
  In this menu you can set all RI-MP2 and RI-CC2 related settings – i.e. assigning auxiliary basis sets with cbas, freezing orbitals with freeze, setting the memory that should be used for the calculation with memory, and denconv to get accurate Hartree-Fock densities as input for MP2 and CC2.
  
  In general, you can use the ricc2 program for both MP2 and CC2 calculations. Call cc2 instead of mp2 in the general menu and choose the method by entering ricc2. With list models you get a list of available wave function models.

- DFT:
  
  Enter the dft sub menu, switch it on and select a functional and a grid (if the default is not satisfactory).
  
  If you want to switch on dispersion correction for DFT, use the dsp submenu to switch it on or off.

- RI-DFT:
  
  Enter the dft sub menu and make your changes as described above. Subsequently, go to the ri sub menu and switch on this option. You should also increase the core memory; the default is 200 MB. In general, you can use up to about 80-90% of the net memory available per processor (ask your system administrator and check the run time behavior of the program with top).
  
  To switch on the multipole accelerated version of RI-J, just got to the marij menu (see chapter 7.7 for details about MARI-J).

Some other options will be described later in the tutorial.

Coming back to our Cp' example: Try to set up the input the input for the following calculations and run a single point energy calculation.

1. Hartree-Fock SCF (scfconv 8).
   Run the dscf module.

2. DFT (try e.g. B3-LYP [func b3-lyp]).
   Run the dscf module.

3. RI-DFT (try e.g. PBE [func pbe]).
   Run the ridft module.

4. RI-MP2 (with cc2, ricc2, mp2, *, cbas, *, ...)
   Run dscf and then ricc2.

Have a look at your working directory before and after the run. Also inspect the files control, coord, basis, energy.

Once the control file has been set up, many changes to it can also be done using standard UNIX editors (like vim or emacs).

7. Single Point Calculations

7.1. How to perform a single point calculation

Let us do a Hartree-Fock energy calculation of benzene:

1. Start with a new and/or empty directory.

2. Call define.

3. Hit <Enter> when being asked for the name of the input file, enter a title for the input file you are going to create, this can be an arbitrary text like:

   benzene, Hartree-Fock calculation, with symmetry and def-TZVP basis set

4. Now you will get the first menu of define (here only the first few lines are printed):

    SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=0     SYMMETRY=c1     )
    YOU MAY USE ONE OF THE FOLLOWING COMMANDS :
      sy <group> <eps> : DEFINE MOLECULAR SYMMETRY (default for eps=3d-1)
      desy <eps>       : DETERMINE MOLECULAR SYMMETRY AND ADJUST COORDINATES (default for eps=1d-6)
      susy             : ADJUST COORDINATES FOR SUBGROUPS
      ai               : ADD ATOMIC COORDINATES INTERACTIVELY
      a <file>         : ADD ATOMIC COORDINATES FROM FILE <file>
    ...

    make sure that your terminal window is large enough to see the first line with the most important data.

5. As you can see in the first line, there are no atoms yet, symmetry is C1.

6. Load benzene from the structure library (located in STURBODIR/structures)

   a !benzene

   Usually, you would say

   a coord

   here at this point, assuming that your coordinates in Turbomole format are in the file coord in the local directory. A complete path to a coord file can be given here either, like: a /home/me/infiles/projectA/coord
7. **define** will scan through the structure library and ask you if you want to take the proposed molecule:

```
****** STRUCTURE LIBRARY UTILITY ******
ENTRY NO.  1 MATCHING SEARCH STRING benzene :

formula=c6h6
file=benzene
name=benzene
name=benzol
# benzene optimized at SCF-level with basis sets of dz quality.
# max. internal gradient is 2.1d-05 (stre 1 7), total energy is 230.601994.
# the molecule lies in the xy-plane (for d6h-symmetry)
# Note: there is one more entry for benzene in this library.

DO YOU WANT THIS STRUCTURE (DEFAULT=n) ?
```

just say

```
y
```

here to accept the structure.

8. The main menu is printed again, and if you look at the first line, you will see that 12 atoms have been added:

```
SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=12 SYMMETRY=c1 )
YOU MAY USE ONE OF THE FOLLOWING COMMANDS :
```

9. Switch on the symmetry detection by entering:

```
desy
```

10. Symmetry detection prints out the Schönflies symbol, the generators, and much more. Scroll up your window if you want to see the details.

11. **desy** does its work and the main menu is printed again, now with the right symmetry D_{6h}:

```
SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=12 SYMMETRY=d6h )
YOU MAY USE ONE OF THE FOLLOWING COMMANDS :
```

12. Next typical step is to provide internal coordinates. That is not needed for single point calculations, but since we are already here, and since one never knows if a geometry optimization will follow, and (finally) since you will be asked if you really do not want to use internal coordinates when leaving this menu afterwards, a simple

```
ired
```

is something you should get used to do at this point.

13. Now we are done with this menu and proceed to the next one by entering

```
*
```

14. Next menu is the atomic attributes menu, here you usually will just change the basis set. The default basis set,
which is assigned automatically, is def-SV(P) – see chapter 6.7 about basis sets and their quality.

As you can see in the first line of the menu

ATOMIC ATTRIBUTE DEFINITION MENU ( #atoms=12 #bas=12 #ecp=0 )

all 12 atoms have a basis set assigned.

We wrote in the title, that we are going to use def-TZVP. To change the basis set accordingly, enter:

`b all def-TZVP`

this will assign 'all' elements the basis set 'def-TZVP'.

That is it for this menu, so let us proceed to the next one by entering

`*`

15. The third menu where we are in now is the one where `define` determines the start molecular orbitals with (e.g.) an extended Hückel guess.

To do the guess and to choose the correct occupation, just call

`eht`

and you will be asked a lot of questions. Just accept all defaults.

There are TWO important questions during this procedures:

ENTER THE MOLECULAR CHARGE (DEFAULT=0)

If you have a charged system, you have to tell define that at this point! For now, we accept the neutral benzene by hitting simply <Enter>.

and

```
AUTOMATIC OCCUPATION NUMBER ASSIGNMENT ESTABLISHED !
FOUND CLOSED SHELL SYSTEM !
HOMO/LUMO-SEPARATION : 0.167139
```

```
ORBITAL (SHELL) SYMMETRY TYPE ENERGY DEFAULT OCCUPATION
11 3e1u -0.51863 4
12 1blu -0.50821 2
13 1elg -0.48203 4
14 3e2g -0.43095 4
15 1e2u -0.26381 0
16 1blg -0.08611 0
17 4elu 0.39013 0
```

DO YOU ACCEPT THIS OCCUPATION ? DEFAULT=y

Here define suggests a certain occupation, which also determines the multiplicity and the choice between restricted and unrestricted calculations. In this case it is a restricted singlet calculation which is just fine.

16. `eht` automatically terminates the occupation menu, so we get directly to the last menu which is called 'general
menu'. Here the settings for the methods (HF, DFT, MP2/CC2, excited states, RI, ...) can be done:

```
GENERAL MENU : SELECT YOUR TOPIC
scf : SELECT NON-DEFAULT SCF PARAMETER
mp2 : OPTIONS AND DATA GROUPS FOR rimp2 and mpgrad
cc : OPTIONS AND DATA GROUPS FOR ricc2
pnocc : OPTIONS AND DATA GROUPS FOR pnoccsd
ex : EXCITED STATE AND RESPONSE OPTIONS
prop : SELECT TOOLS FOR SCF-ORBITAL ANALYSIS
DRV : SELECT NON-DEFAULT INPUT PARAMETER FOR EVALUATION
     OF ANALYTICAL ENERGY DERIVATIVES
     (GRADIENTS, FORCE CONSTANTS)
rex : SELECT OPTIONS FOR GEOMETRY UPDATES USING RELAX
stp : SELECT NON-DEFAULT STRUCTURE OPTIMIZATION PARAMETER
E : DEFINE EXTERNAL ELECTROSTATIC FIELD
DFT : DFT Parameters
RI : RI Parameters
RIJK : RI-JK-HF Parameters
RIRPA : RIRPA Parameters
GW : OPTIONS AND DATA GROUPS FOR GW (escf)
SEINEX : seminumeric exchange parameters
HYBNO : hybrid Noga/Diag parameters
DSP : DFT dispersion correction
NMR : NMR shift parameters
NCouple : NMR coupling parameters
TRUNC : USE TRUNCATED AUXBASIS DURING ITERATIONS
MARIJ : MULTIPOLAR ACCELERATED RI-J
DIS : DISPLAY MOLECULAR GEOMETRY
LIST : LIST OF CONTROL FILE
& : GO BACK TO OCCUPATION/ORBITAL ASSIGNMENT MENU
* or q : END OF DEFINE SESSION
```

The default is a Hartree-Fock calculation, and therefore we do not have to change anything here. Simply enter:

```
*
```

17. define ends now and you will find several files in your directory, containing all important settings and data.

18. To run a Hartree-Fock single point energy calculation, call

```
dscf > dscf.out
```

19. after the run, look in the output and/or the energy file. The energy file should give:

```
$energy       SCF      SCFKIN      SCFPOT
 1  -230.773367010  230.6595606167  -461.4328973177
$end
```

The converged energy is given in the SCF column, kinetic and potential energies are also given.

20. Look in the output `dscf.out` and search for the dipole and quadrupole moment, the number of basis functions, and whatever you like to know.

21. We get more details about the orbitals, the HOMO-LUMO gap and the occupation with the Turbomole own tool
Just call it and see what it prints out.

To run a DFT calculation, call define again and accept all defaults – it will read in the existing control file, so you will not have to change anything at the first three menus (coordinates, basis sets, molecular orbitals).

In the last menu, enter dft and then on to switch on this method:

STATUS OF DFT_OPTIONS:
  DFT is used
    functional b-p
    gridsize m3

ENTER DFT-OPTION TO BE MODIFIED
  func    : TO CHANGE TYPE OF FUNCTIONAL
  grid    : TO CHANGE GRIDSIZE
  off:  TO SWITCH OFF DFT

Just <ENTER>, q or '*' terminate this menu.

With <Enter> you will get back to the general menu.

End define and run dscf again. The energy is now:

$energy     SCF         SCFKIN           SCFPOT
  1 -230.7733366808  230.6595789619  -461.4329156428
  2 -232.3278889602  231.4444536342  -463.7723425944
$end

Note that energies are always appended to the list of energies!

Next, switch on RI the same way: enter ri and then on. define will automatically assign the auxiliary basis set if you have chosen a basis set where optimized auxiliary basis sets exist (all def- and def2- basis sets).

Run ridft and check the energy:

$energy     SCF         SCFKIN           SCFPOT
  1 -230.7733366808  230.6595789619  -461.4329156428
  2 -232.3278889602  231.4444536342  -463.7723425944
  3 -232.3286314547  231.4468598575  -463.7754913122
$end

Note that the RI and non-RI energies differ: Never compare absolute energies of RI with non-RI calculations!!
7.2. Semi-direct runs with dscf

Semi-direct runs are optimal for medium-sized SCF calculations (up to 500-1000 basis functions). This example gives you an idea of the computational savings.

1. Get the coordinates of P_{10} from the structure library:
   - call define from an empty directory
   - hit two times the <Enter> key
   - say a !p10 to load the coordinates from the structure library
   - call desy and ired for symmetry and internal redundant coordinates, resp.
   - and then * or q to go to the next, the basis set menu
   - enter `all def-TZVP` here to assign the default triple zeta valence basis set
   - then end this menu with * and call eht in the next menu. Now hit <Enter> many times to accept all defaults...
   - skip the final menu and end define with * or q.

   Save the start Mos (cp mos mos.save) in an extra file and run dscf.

2. After the first run, rename the file statistics and copy back the start Mos (cp mos.save mos).

   Run define to change to a semi-direct run. In order to accomplish that, choose the scf option in the last define menu and select the ints sub option.

   Enter maximum size (e.g. 2000 MB) and name of the two-electron integral file (e.g. twoint). Please note that entering multiple integral files is neither necessary - since there is no file size limit on all machines TURBOMOLE runs on – nor possible with define.

   Make sure, that the scratch directory is located on a fast (!) access file system. You can give the whole path if the two-electron integral file should be in a directory other than the control file (e.g. /scratchdir/myusername/twoint, provided that the directory /scratchdir/myusername/ exists).

   Start another dscf run and compare the timings (have a look at the two statistics files, as well).

Notes and hints:

1. The selection of integrals to be stored on disk is controlled by the two keywords $thime (threshold for estimated time consumption of integral batch evaluation; idea: we only need to store expensive integrals) and $thize (threshold for integral value; idea: only large integrals will contribute in subsequent iterations). The default values of the integrals work well, normally. If the given size of the two-electron integral file becomes too small you get error messages like

   <put> : FILE SPACE EXHAUSTED -- switching to 'direct' mode!
   written (= 2560) + newbuffer > max (= 2560)

   but the program will continue, nevertheless. Either increase the disk space or use larger values for $thime and $thize. For highly contracted basis sets like the Dunning series, $thime 20 will still give some savings for larger cases.

2. Specifying an integral file will also improve the Z-vector equations in rimp2 and ricc2 runs.
3. NMR chemical shielding calculations using hybrid functionals like B3-LYP do also require a non-zero value for the integral file size.

It is also possible to let \texttt{dscf} calculate the size of the integral file for the given settings of $\text{thime}$ and $\text{thize}$:

1. Prepare your input as usual with \texttt{define}.

2. On the command line, call

\texttt{stati dscf}

\texttt{stati} is a \textsc{turbomole} own script that will do nothing but adding the keyword \texttt{$\text{statistics <option>}$} to the control file.

3. Run \texttt{dscf} as usual. It will perform a statistics run only and change the value of \texttt{size} of the keyword \texttt{$\text{scfintunit}$} accordingly.

4. Now you can edit the control file and check if the size is reasonable. If it is too large for your system, change it to an arbitrary value – as mentioned above, \texttt{dscf} will fill the file and then continue the calculation in the direct mode.

### 7.3. Check for convergence

After a single point energy calculation has been done, you can check if and how the energy has converged:

1. The converged energy is written to the file \texttt{energy} – however, if there has been such a file before, the energy is appended to the existing ones. You might have to check the date and time of the file to find out if it has been written lately.

2. The header of the MOs (either file \texttt{mos} or \texttt{alpha} for RHF or UHF cases resp.) gives a hint about the status of the MOs. Do a \texttt{head mos} or \texttt{head alpha} and check if you can find one of the entries in the first line:

   - \texttt{scfconv=6} \quad # converged MOs with energy convergence of 1d-6
   - \texttt{expanded} \quad # start MOs from an extended Hückel guess
   - \texttt{scfdump=23} \quad # non-converged MOs after 23 SCF iterations

3. If you have \texttt{gnuplot} installed, you can call \texttt{cgnce <output file>} to get a graphical plot of the convergence behaviour, with the output file of the energy run as option. If no output file is given, \texttt{cgnce} takes \texttt{job.last}, i.e. the last energy run of a geometry calculation (see chapter 8.1).
7. Single Point Calculations

7.4. RI-MP2 is much faster than MP2

Create two new subdirectories and copy to each the coordinates of C₈H₈ (from exercise 6.3). If you do not have the coordinates, use the ones from the structure library (see below).

Make sure that the working directory, from which the runs are started later on, is located on a file system with fast access (i.e. directly connected to the node you are running on and shared by as few processors as possible).

- In both directories, run `define` and set up the input for (semi-direct, if you like) SCF calculations with a def-SVP (in one directory) and a def-TZVPP basis set (in the other directory), respectively. Don't forget to set the symmetry-information (desy)! To add the coordinates, use either a `coord` if you have copied the file, or a `!c8h8` if you do not have the coordinates (any more?).

Enter `mp2` at the general menu and then assign the auxiliary basis sets with `cbas`. You should get:

```
AUXILIARY BASIS SET DEFINITION MENU
( #atoms=16    #cbas=16    )
```

And then `other` and `emp2` to do a MP2 energy only calculation.

- accept all defaults but change the core memory to some larger value (should be 70 to 80 % of the RAM per CPU, some memory should be left to the system for I/O cache). `define` will automatically set the keyword `$denconv .1d-6` thus requesting a tighter convergence threshold. All post-SCF programs will terminate, if this keyword is not found in `control`.

- Run `dscf`.

- Prepare also the conventional MP2 run. Issue the command

```
mp2prep -e -p 2000 -m 700
```

   to prepare a run with a maximum disk usage of 2000 MB and a maximum memory usage of 700 MB (adapt these values as necessary). The script `mp2prep` works only properly, if the file `mos` has been created by a converged SCF run (this is the reason, why we ran `dscf` before).

- Now, we can start the MP2 calculations (`rimp2/ricc2` and `mpgrad`)

   Note that those two programs do not disturb each other. There is no need to run them in different directories. However, save the output from both runs, because the energy is not appended to the energy file (no geometry optimization, so both energies are written to the 1st cycle and hence, the second program overwrites the energies of the first one).

Calculate the RI-error in the correlation energy in percent:

\[
\Delta RI = (E_{corr}^{RIMP2} - E_{corr}^{MP2})/E_{corr}^{MP2} \times 100
\]

and compare to the change in the correlation energy between def-SVP and def-TZVPP.
7.5. **RI-SCF works best for large basis sets**

Make three subdirectories. Call `define` in each directory, and load the coordinates of BF from the structure library (a `!bf`). Prepare semi-direct (!) `dscf` runs, employing the cc-pVTZ, cc-pVQZ and cc-pV5Z basis sets respectively (see chapter 7.2 to see how semi-direct runs are prepared). Keep copies of the initial `mos` files and run the calculations. Then, prepare the RI-SCF calculations. To do that, just run through `define` until you reach the last menu. Enter the `rijk` sub menu and switch on this option. This will automatically load the appropriate auxiliary basis sets. Choose a sufficiently large value for the core memory. Compare the computation times.

7.6. **Don’t get confused by auxiliary basis sets**

To speed up calculations using the Resolution-of-the-identity (RI) approximation, `TURBOMOLE` currently provides three kinds of auxiliary basis sets, which you should not mix up.

1. **Coulomb-Fitting** ($\text{jbas}$). Basis sets declared in this data-group are needed for RI-DFT calculations, where only the Coulomb part of the Fock operator is approximated. They can be kept rather small.

2. **Coulomb- and Exchange-Fitting** ($\text{jkbas}$). If additionally the exchange part of the Fock operator needs to be approximated (RI-SCF calculations), a larger fitting basis is needed. It also can be used for RI-DFT runs (if the accuracy of the $\text{jbas}$ auxiliary basis is not satisfactory for you).

3. **Correlation-Fitting** ($\text{cbas}$). These basis sets are needed for RI-MP2 and RI-CC2 calculations. They contain basis functions with high angular momentum.

Have a look at the three different kinds of fitting basis sets by doing the following:

- Run `define` and input just one atom (e.g. carbon).
- Choose the def-TZVPP basis set and provide dummy start orbitals.
- In the last menu, enter the `ri` section and switch RI on. This will automatically make the program write the $\text{jbas}$ data group. Then enter the `rijk` menu and leave it again. This causes the $\text{jkbas}$ data group to be written.
- In the last menu, go to the `mp2` menu to get the $\text{cbas}$ data group by entering `cbas`.
- Have a look at the `auxbasis` file. It contains the three data groups $\text{jbas}$, $\text{jkbas}$ and $\text{cbas}$. Try to find out the differences.

7.7. **DFT versus RI-DFT versus MARI-DFT**

For large RI-DFT calculations (more than 2000 basis functions), the multipole-accelerated RI-J approximation (MARI-J) leads to a considerable speed-up. The loss in numerical precision is much lower than that due to the RI-approximation. The multipole acceleration produces almost no overhead, so it can be used for any large DFT calculation.

In `$\text{TURBODIR/structures/c216h36/}$` you can find the coordinates of a graphite sheet ($\text{C}_{216}\text{H}_{32}$). For a system of this size, the multipole approximation is faster by nearly a factor of 2.

Setting up the input is rather easy. Prepare a RI-DFT run as usual. In the final menu of `define` - additionally to the sub menus `ri` and `dft` - you also have to visit `marij`. Just switch on this option and accept the defaults. Only if your calculation contains basis functions with higher angular momenta (f-functions), you will have to use higher maximum multipole moments.

For comparison, you may start a conventional DFT run. It will take ages!
7.8. Finding occupation numbers

Dealing with transition metal clusters one is often faced with the problem that the extended Hückel (EHT) guess does not provide the correct occupation. Playing around with occupation numbers often makes the user feel like Sisyphus. Fractional occupation numbers (FON) which are automatically determined in a Fermi-distribution motivated manner (actually an error function is used) can improve convergence in these cases (see manual, keyword $fermi$).

- Create a new directory and run `define`, read in the coordinates of Pd$_4$ from the structure library (a !pd4) and detect the symmetry (should be D$_{2d}$). As basis set accept the default def-SV(P) basis.
- In the “OCCUPATION NUMBER & MOLECULAR ORBITAL DEFINITION MENU” choose `eht` and answer no to the next question. This chooses EHT parameters for d$^4$s$^1$ occupation instead of d$^{10}$.

Answer with no the question: 'DO YOU ACCEPT THIS OCCUPATION ?'.
This provides you a menu for assignment of occupation numbers. Choose the quintet state by entering u 4
(alternatively you may choose a singlet by entering s or u 0).
- In the final `define` menu choose a RI-DFT calculation using the BP86 functional.
- Enter the menu of “NON-DEFAULT SCF PARAMETER” and select `fermi`
Set the final temperature to 25 K, the annealing factor to 0.90, and the HOMO-LUMO gap criterion to 1.0.
- In the same “NON-DEFAULT SCF PARAMETER” menu select `damp`
Set the start value for damping to 3.0 and the final value to 1.0.
- Finally, open `control` file and increase value of `$scfiterlimit` to 50.
- Run the `ridft` calculation.

Save the output and the energy file, then try to do a few calculations with different occupations and start orbitals, but without using $fermi$. Check how close you can get in the total energy compared to the previous run.

**Warning:** Fermi pseudo smearing is a very nice feature to get an occupation you would not have expected to be the lowest one... But if you leave $fermi$ in the control file and then start a geometry optimization, `ridft` or `dscf` will redo the occupation in each geometry cycle! That might be what you want, but the run has the possibility to switch from one hyper surface to another, leading to a completely different minimum structure with a completely different occupation than you might have expected. This minimum does not have to be lower in energy than the one with the fixed occupation numbers...
7.9. **SCF convergence**

If your energy did not converge after a first run, you can change all the keywords that are responsible for the convergence behavior in the control file:

1. `$scfiterlimit` # sets the maximum number of SCF iterations
2. `$scfdamp` # sets the damping of the DIIS, damping starts with the start value # and will either be decreased or increased by step and decreased # only to the limit of min.
3. `$fermi` # use it to let dscf or ridft determine the occupation automatically. # Check at the end of the run if your occupation numbers are all close # to an integer value. Values between 0.2 and 0.8 indicate either a not # fully converged SCF step or possibly a multi reference case (which can # not be treated in TURBOMOLE)
4. `$scforbitalshift` # helps to get a better convergence by shifting the virtual and/or occupied # orbitals up or down, resp. - please refer to the manual (keywords section)

7.10. **Counterpoise calculations**

The basis set superposition error (BSSE) can be corrected for using the counterpoise method. The following example explains how to perform a counterpoise calculation with TURBOMOLE.

Note that this example is a simple BSSE case for a dimer. More complicated BSSE calculations for up to three fragments and counterpoise corrected geometry optimizations can be done with the module `jobbsse`. Please read chapter 3.6 of the manual if you want to use that tool.

The coordinates of the dimer of H\(_2\)O in C\(_s\) symmetry are available from the structure library. The structure has already been optimized.

First of all the energy of the dimer has to be evaluated at the MP2-level:

1. Crate a new working directory and run `define` as for a SCF run. Load the coordinates of the water dimer from the structure library (`a !h2o_2`). Choose the basis sets def-SV(P) and create start-MOs for `dscf` from Hückel guess.

2. Go to the `mp2` section in the last menu
   1. Let `define` choose an appropriate auxiliary basis set by entering `cbas`.
   2. Enter `freeze`
      to get in the frozen core assignment menu and choose `core 0`
      in order not to have frozen electrons.
   3. Run a `dscf`-run first and a `rimp2`-run afterwards to get the energy of the dimer at the MP2 level (E\(_{\text{DIM}}\)).
Next, you can evaluate the energy of each water molecule, in the presence of the basis set of the second one:

1. Create a new directory and copy in it the `control` and the `coord` files.

2. In the control file change the symmetry group of the system to $C_1$ and the $\$\text{atoms}$ keyword, so that one of the two water molecules displays charge zero:

   ```
   $\$\text{atoms}
   o 1 \n   cbas=o def-SV(P) \n   basis =o def-SV(P) \n   h 2-3 \n   cbas=h def-SV(P) \n   basis =h def-SV(P) \n   o 4 \n   charge =0.000000 \n   cbas=o def-SV(P) \n   basis =o def-SV(P) \n   h 5-6 \n   charge =0.000000 \n   cbas=h def-SV(P) \n   basis =h def-SV(P)
   ```

3. Alternatively (and that is the easier way to do it), start `define` with the input and change the charge of the elements in question to zero by entering in the Atomic Attributes Menu:

   ```
   c 4-6 0.000
   ```

4. Run `define` to get start-MOs and to switch off the frozen core approximation as shown above.

5. Run a `dscf`-run first and a `rimp2`-run afterwards, to get the energy of the monomer, already corrected for the BSSE ($E_{1B}$).

6. Repeat the same procedure for the second molecule of water, to get the energy of the monomer $E_{2B}$.

You can evaluate the dissociation energy, corrected for the BSSE, in the following way:

$$
\Delta E_B = E_{\text{DIM}} - E_{1B} - E_{2B}
$$

Furthermore, you can calculate the energies of the molecules of water in the geometry of the complex:

1. Create a new directory and copy in it the `coord` file.

2. Delete in the `coord` file the coordinates of one of the two water molecules.

3. Run `define` as usual.

4. Run a `dscf` and a `rimp2` step, to get the energy of the monomer $E_1$.

5. Repeat the same procedure for the other water molecule, to get the energy of the monomer $E_2$.

Now you can estimate the dissociation energy (without structure relaxation effect) in the following way:

$$
\Delta E = E_{\text{DIM}} - E_1 - E_2
$$

The BSSE is usually defined as the difference between the two dissociation energies:

$$
BSSE = \Delta E - \Delta E_B
$$
7.11. Parallel runs

The procedure to set up and run parallel jobs depends much on the computer architecture and the queuing-system.

There are different parallelization methods implemented in the current version of Turbomole, but for their usage no additional keywords or settings are needed. The user just has to tell Turbomole whether a parallel job will be running on a single system with many CPUs or cores (SMP) or on a cluster using several (different) nodes connected by a network interface:

1. **MPI** – parallel versions of dscf, grad, rdft, rdgrad, escf, aoforce, mpgrad, rice2, pnoccsd

2. **SMP** – parallel versions for shared memory systems of almost all time demanding modules are available

In general, the parallel version can be used the same way the serial one is used. All you have to do is to set the environment variable **PARA_ARCH** to MPI for the MPI parallelization or to SMP for the multi-core version, and, if you do not want to do the calculations on the default 2 nodes, set **PARNODES** to the number of CPUs you would like to use.

For the SMP version, which is the recommended way to run post SCF calculations on a multi-core system, the binaries will be called by wrapper scripts named like the serial binaries. Hence, calling this version does not differ from calling the serial binaries.

**MPI version for parallel jobs over a network using different nodes:**

- set **PARA_ARCH**=MPI
  the sysname script will append a _mpi to its output:
  ```
  export PARA_ARCH=MPI
  ```

- set **PARNODES** to the number of CPUs you like to use:
  ```
  export PARNODES=4
  ```

- to run parallel single-point jobs, it is recommended to reset the **PATH**:
  ```
  export PATH=$TURBODIR/bin/`sysname`/:$PATH
  ```
  since now sysname prints out a different name.

- The name of the nodes where the parallel job will run is also needed. If you use a supported queuing system (PBS, LSF, SGE, SLURM), Turbomole will automatically find the right nodes from the provided settings.

  Otherwise write the names of the machines in a file (each line just one name, so for using several CPUs or cores on one node, add additional lines with the same name) and set the environment variable **HOSTS_FILE** to this file. Turbomole will process this list and use either just as many nodes as provided or just the number which has been set with **PARNODES** – depending on which number is larger.
SMP version to run on a single machine, using many cores:

- set PARA_ARCH=SMP
  the sysname script will append a _smp to its output.
- set number of threads with PARNODES and the PATH just in the same way as for the MPI version.

The most common way to run jobs is to have a queuing system like PBS, LSF, SLURM or SGE/Univa Grid engine. For those queuing systems, TURBOMOLE will use the information about the available nodes directly, so it will automatically start the jobs where they are supposed to run. For other queuing systems: please ask your system administrator.

In general, if no PBS/LSF/SGE/SLURM is used, TURBOMOLE will check if it finds an environment variable HOSTS_FILE containing the name of a file with a list of available machine names. Otherwise the node where the job is started will be used.

The input has to be in a directory that can be accessed on each node, having the same path name. Usually one starts parallel calculations from an NFS disk.

**Note**: avoid the usage of the shared NFS disk as much as possible !! Otherwise this might dramatically slow down the calculation. See the hints below and carefully read Hints in the Turbomole User Forum.

Some hints:

1. When using **ridft** for larger inputs, do not forget to switch on $marij. Multipole accelerated RI-J can be more than a factor of 6 and more faster than usual RI-J calculations for big systems. You get that for free and without additional errors, **so it is always safe to turn it on**.

2. **NumForce** can also be run in parallel, but here it is much more efficient to run the serial binaries at a time instead of the parallel version – all single-point jobs can be run independently. To run it in parallel, add the -mfile option with the name of a file which contains a list of nodes (just like $HOSTS_FILE):

   \[
   \text{NumForce -mfile $HOSTS\_FILE [...]}
   \]

## 7.12. **CCSD(T) with OpenMP**

Let us now try a single point energy calculation of Water on CCSD(T)/cc-pVTZ level.

1. start in an empty directory

2. assuming TURBODIR is already set, now we set the path to the SMP version.
   ```bash
   export PARA_ARCH=SMP
   export PATH=$TURBODIR/bin/`sysname`:PATH
   ```

3. call **define** and type in the following:
   ```
   <Enter>
   This is an example of a CCSD(T) calculation
   a ! h2o
   y
desy
ired
   ```
+ bb all cc-pVTZ + eht <Enter> <Enter> <Enter> cc freeze + cbas + ricc2 ccsd(t) + + 4. run a Hartree-Fock energy calculation:
dscf > dscf.out 5. run the Coupled-Cluster energy calculation:
csdf12 > ccsdt.out 6. look at the output.
At the beginning of dscf.out and csdf12 you will the line: ‘OpenMP run-time library returned nthreads = 2’.
At the end of ccsdt.out the final energies of MP2, SCS-MP2, SOS-MP2, CCSD, and CCSD(T) are summarized.
8. Structure Optimizations

8.1. Getting in contact with jobex

jobex is a shell script that drives the geometry optimization. Here, we will have a look at a HF/SV(P) geometry optimization of C₆H₆:

- Create a new input for this molecule, just the way it has been done in chapter 7.1. Note that the input itself does not contain the information about the kind of job you want to run: Single point or structure optimization.

- In order to see how the optimization is working, we first proceed step by step. First, we carry out the energy calculation (run dscf). This will create a file called energy (and converged MOs in mos, of course).

After that, we shall run the gradient program. Run the module grad. It will produce the file gradient.

Finally, the module statpt will estimate new coordinates. You can monitor the current structure with the help of the command dist. Try this command before and after the statpt run.

- jobex will carry out these three steps automatically. On the command line, type
  
  jobex -h

to get some further information. Then just run jobex without any further command line arguments. After completion, inspect the energy and gradient files. A useful command for the latter is

  grep cyc gradient

Note, that there is one more energy in the energy file. The reason is that for a SCF (and DFT) optimization, jobex tests the convergence after each energy calculation.

- A RI-DFT optimization would need:
  
  jobex -ri

- In another directory, set up a RI-MP2 calculation and start the optimization by typing
  
  jobex -ri -level cc2

8.2. Optimize at Hartree-Fock, DFT, MP2, CC2, TD-DFT, … level?

The method that is used during a geometry optimization is determined by two things:
1. the keywords in the control file, and
2. the options you use when calling jobex.
8.3. Did it converge?

Jobex finishes after the calculation did converge, but it also stops if the maximum number of cycles (default is 20) has been reached. Now, how do we get more informations about the job that has just finished?

1. Make two new directories.

2. Call define there and load acrolein from the structure library:

   - hit <Enter> and then give a title
   - enter a !acrolein
   - then desy and ired, as usual

3. Prepare a RI-DFT calculation, accepting all defaults (basis set, functional, occupation, etc.). Hence, you can just say <Enter> and * all the time – just remember set dft to on as well as setting ri to on in the last, the general menu.

4. Copy the input to the other directory.

5. In one directory call

   jobex -ri -c 5

6. And in the other directory

   jobex -ri -c 100

7. Compare the two directories.

8. To check what jobex was about to do, look at the file job.start. There you will find the information about the options that have been given, the method that has been chosen and the convergence criteria that have been applied.

9. You will find a file called converged in the second directory and a file not.converged in the first directory.

10. Open not.converged in an editor. You can see the criterias given from jobex in $convcrit and the current criteria in $convinfo.

11. Do a grep cyc gradient in both directories.

12. Look at the end of the files job.last

8.4. Preoptimization

1. The probably best option to pre-optimize a structure is to use xTB-GFN2 tight binding method from the Grimme group. For this purpose, only a coord file is needed, and jobex can be started with the option

   jobex -level xtb

2. P:H₃ is a rather nice cage molecule (its point group we naively assume to be C₃ᵥ, in exercise 9 we will examine this), set up the input for a RIDFT structure optimization (def-SV(P) basis and B-P functional).
Create a new working directory, call `define` and load P·H$_3$ from the structure library:

- hit <Enter> and then give a title
- enter
  a !p7h3
- then desy and ired, as usual.
- enter two * until you reach the Molecular Orbital menu and generate start MOs with eht
- accept all defaults by hitting <Enter> many times...
- now you should be in the General Menu
- switch on dft and ri
- end `define`

Start `jobex -ri`

Create another subdirectory and start again by reading in the coordinates of P·H$_3$.

After symmetrization, try the `ff` command to pre-optimize the structure using the force field program (intuitive usage). Run a RIDFT geometry optimization starting from this pre-optimized structure. Document the number of optimization cycles with and without pre-optimization. Note that the structure stored in the structure library of TURBOMOLE is closer to the DFT minimum already.

3. Starting from the RIDFT/SV(P) structure, optimize the geometry at the RIDFT/TZVP level. Create two subdirectories.
   1. Copy the `coord` file into the first directory, set up the input and run `jobex`.
   2. For the second run which you prepare in the other directory, use as well the `coord` file as well as the `hessapprox` file from the SV(P) calculation (make sure, that a line saying `$hessapprox file=hessapprox` is contained in the control file before starting `jobex`).

Compare the convergence of the two structure optimizations.

### 8.5. Constrained optimization

In the structure library, you will find the converged ground state structure of H$_3$CBr (RI-MP2/TZVPP). Assume, we are interested in the energy path upon approach of a chlorine anion.

- Load the coordinates into `define (a !h3cbr)`, get the symmetry (via good old `desy`) and add a chlorine atom at an appropriate position (somewhere on the negative z-axis).
Define a bond between chlorine and carbon by entering the command sequence

```plaintext
ifdef
f stre 1 6  # defines a [f]ixed bond between atom 1 c and 6 cl
```

After several blank lines you are back in the geometry menu. Test the quality of the B-matrix with `imet`. Find out the number of that newly defined internal coordinate (enter `dis`). Then use the command

```plaintext
imanat <$# of int coord>
```

to change this distance to 250 pm (actually, you have to enter 2.5 Å since only Ås are supported). Now we are ready to leave the geometry menu.
8. Structure Optimizations

- Assign def-TZVPP basis sets to the atoms. In the molecular orbital menu, remember to set the total charge to -1.

- The input preparation is finished by running through the mp2 options in the last define menu.
  We ignore the warning concerning the too small gap between frozen and active orbitals (it is due to the rather high-lying d-orbitals of bromine).

- Now you can start the RIMP2 optimization by
  
  \texttt{jobex -ri -level cc2}

- Inspect the results. If you liked it, you can decrease the carbon-chlorine distance (use \texttt{man in define}) and look for an estimate of the transition structure.

Before sending the results to JACS, please consider two things:

  a) Freezing the d-orbitals of 3\textsuperscript{rd} row elements may be problematic, larger basis set like def-QZVPP are adequate basis sets for including them.
  b) We should have tested the effect of diffuse functions on chlorine and bromine (anions!).

For more complex structures, the automatic generation of internal coordinates might fail. In that case, just proceed as written above and define the fixed coordinates by using the command

\texttt{idef}

After that, go back to the geometry menu of \texttt{define} and do

\texttt{ired}

The automatic definition of redundant internal coordinates ignores the non-redundant coordinate definitions.
\textbf{But:} fixed internal coordinates will be taken into account, building redundant internal coordinates around the given fixed ones.

The more fixed internal coordinates you have, the more difficult it is to find the remaining set of redundant internal coordinates – and the higher the possibility that the set of redundant internal coordinates will get linear dependent during the optimization!

8.6. Molecular dynamics - simulated annealing

Simulated annealing serves for finding new structures on complex hyper surfaces, e.g. for metal clusters. Here, we chose a more obvious example: the PtCl$_4^{2-}$ complex.

The coordinates of that molecule, but with a distorted tetrahedral structure are available in the structure library.

1. Run \texttt{define} as for a RI-DFT run, but the group symmetry of the complex should remain C\textsubscript{1h}.
   Load PtCl\textsubscript{4} by entering \texttt{!ptcl4}. Choose basis sets (def-SVP) and create start MOs (do not forget that the charge is +2).
   In the 'GENERAL MENU', choose \texttt{dft} (default functional and grid size are appropriate) and \texttt{ri} options.
   Adjust the option \texttt{ricore} according to the available RAM per processor.
   Set the maximum number of SCF iterations to 100 ($\texttt{scfiterlimit}$) and the damping to a start value of 3 ($\texttt{scfdamp start=3.0 step=0.050 min=0.050}$).
2. Run **mdprep**. Most default parameters are appropriate, change only the following ones:
   1. request 150 MD steps in the section 'NUMBER OF MD STEPS';
   2. in the section 'USER-DEFINED ACTIONS' choose a simulated annealing calculation;
   3. in the sub-menu 'SIMULATED ANNEALING / QUENCHING' choose the anneal option;
   4. enter an annealing rate of 0.985 and a time of 1000, from which the anneal will start to occur.

3. The program **mdprep** creates two files: *mdmaster* and *mdlog*. The first is a command file, which contains the keywords for the module **frog**, while the latter is an output file. Be curious and inspect these files.

In order to run the structure optimization, you have to use the command:

```
jobex -ri -md
```

The procedure consists of a **ridft** step, followed by a gradient and by a molecular dynamics step. In the file *gradient* the total energy, the coordinates and the gradient for each interaction are collected. In the file *mdlog* information on the time and the displacements are dumped. The file *job.last* contains the output of the gradient, of the **ridft** and of the MD steps of the last complete iteration. There should be a script **log2egy** which accomplishes that.

In order to understand the output, you should **grep** from the *gradient* file the numbers of the cycles versus the total energy and perhaps plot a graphic. Then you can choose the coordinates of the geometry with the minimal energy and run a conventional optimization to refine the structure.

### 8.7. Transition states

Searching transition state is usually a highly non-trivial task, simply because there are many of them while you are searching for the one with the lowest barrier. Usually, you have already the reactant and product structures when looking for the transition state.

There are two different steps needed to get a transition state:

1. you first have to guess an approximate transition state somewhere between the reactant and product structures,
2. if you have a guess structure for the transition state (like the one from 1.), and if that one is within the quadratic region around the real state, you can apply a procedures like quasi–Newton–Josephson methods. They are based on the restricted second-order method, which employs Hessian shift parameters. The program **statpt** is doing that for you.

While step 2 is more or less straight forward and can be done in a similar way a geometry optimization (search for minima) is performed, step 1 requires a lot of work, chemical intuition, experience, and time – at least if you want to find the transition state rather than a transition state. Some remarks and details can be found in the **TURBOMOLE** documentation, chapter 3.2 and 3.2.4.

Let's start with step 2:

If you like to see how step 2 works (i.e. if you have a guess for a transition state structure), get the coordinates of acrolein from structure library, and execute the following steps:

- Run **define**, load the coordinates (a !acrolein) and leave the geometry menu without specifying internal coordinates (answer no after leaving the menu).
As basis set specify 3-21g hondo.
Provide Hückel MOs and continue until the last menu where you enter the

stp

section and set the index of the transition vector (itvc) to 1. Please note that in statpt, the six zero
eigenvalues of rotation and translation are not between the negative and positive values as usual, but shifted
away. So itvec 4 is the 4th eigenvalue, counted from minus infinity upwards, leaving out the zeros.

- Run the dscf, grad and aoforce modules in order to provide the start information for the transition state
search. Please see chapter 9 for a detailed description of the module aoforce and how to perform force
constant calculations.

- Run the command

    jobex -trans

to start the transition state search.

- Run aoforce again to check, whether a transition state has been reached.

Here you did a full force constant calculation (see chapter 9) with the input you are using for finding the transition state. For real life applications, the input for this is usually a bit different:

1. The system in question is much bigger,
2. The basis set is a bigger one, usually at least def-SVP for (RI-)DFT and def-TZVP for MP2/CC2 calculations,
   to get reasonable results.
3. The symmetry is set to C1 only, otherwise you are doing a constrained search.

For such realistic inputs, getting the full Hessian can be the by far most time consuming step of the calculation.
Generally, the quality of the eigenvector for a transition state search does not have to be too high, using a lower and
cheaper method might just take a few geometry steps more, but saving much time at the initial Hessian calculation.

Doing the force constant calculation at RI-DFT/B-P86/def-SV(P) level is usually good enough. In addition, if the
system is big, a LES search can be done at this level (see chapter 9.2 about how to perform such a calculation).

Now to step 1:

There is no black box method in TURBOMOLE that finds a good guess structure for the transition state. However, some of
the features can be of great help:

a) Constraint minimization by freezing internal, internal redundant, or Cartesian coordinates.

Fixing internal coordinates is described in chapter 8.5. Freeze the internal coordinates which you think are
involved in the transition and run a usual geometry optimization.

Change the value of the internal coordinates with define by using iman in the internal coordinate menu,
and redo this steps for a few structures.

Use the structure with the highest total energy to get as close to the transition state as possible.

Note about fixing Cartesian coordinates:

To fix a Cartesian coordinate, open the coord file and append an f to each line of the atoms that should
b) Scanning the potential energy surface (PES) along an internal (z-matrix) coordinate using the \texttt{tmole} script.

This step is very similar to a), but here you do not have to distort anything yourself. \texttt{tmole} is able to read in z-matrix coordinates with parameters. The additional \texttt{%scan} option in the \texttt{tmole} input file determines along which coordinate is scanned. An example input can be found in the Manual of \texttt{tmole}.

To run the calculation, simply call

\begin{verbatim}
tmole tmole.in
\end{verbatim}

at the command line. \texttt{tmole} prints the results in a file called \texttt{potentialcurve.molden} which can be opened and viewed in \texttt{molden} or directly in an editor.

c) Distortion of the structure along an imaginary mode using the script \texttt{screwer}.

If your first crude guess gives more than one imaginary frequency, you can distort the structure along one of the (negative) modes. To do that, make sure that you have converged MOs from an energy run, the gradients from a gradient run and the Hessian and the vibrational modes from an \texttt{aoforce} run. Then, just call

\begin{verbatim}
screwer
\end{verbatim}

and follow the instructions. You will be asked for the number of the mode along which the coordinates will be changed. Please look at the output (scroll up the window if necessary) and choose one of the imaginary frequencies. Next you will be asked for the step length, given as a temperature in Kelvin. If the value is too low, \texttt{statpt} might optimize the structure back to the initial guess – and if it is too high, you might get to the other side of the hill on the PES...

d) Most convenient is the usage of TmoleX for scan jobs. The builder within TmoleX can define bond lengths, angles and torsions as fixed, and this can be used to scan along one or along several of the internal coordinates. See the TmoleX manual for details.

\textbf{A jobex of your own?}

\texttt{jobex}, like many other \textsc{Turbomole} tools, is a shell script. If you know something about shell programming, why not have a look at it? Just get a local copy and customize it.
9. Vibrational normal modes

9.1. aoforce: Analytical force constant calculations for HF and DFT (ground states)

The calculation of HF and DFT force constants is quite easy: After having performed a single point energy calculation or a geometry optimization, just start the program aoforce.

- Retrieve the geometry-optimized BP86/SV(P) calculation of P₂H₇ from exercise 8.4, or redo the input generation and the jobex calculation. Perform a force constant calculation with the program aoforce:

  aoforce > force.out

  Check the file force.out and the control file.

  While force.out contains the detailed data about the vibrational spectrum, the zero point energy, etc., the keyword $vibrational spectrum in the control file contains a list of the modes:

<table>
<thead>
<tr>
<th>#</th>
<th>mode</th>
<th>symmetry</th>
<th>wave number cm**(-1)</th>
<th>IR intensity km/mol</th>
<th>selection rules</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a2</td>
<td>-768.31</td>
<td>0.0000</td>
<td>NO NO</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>e</td>
<td>-667.21</td>
<td>0.0000</td>
<td>YES YES</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>e</td>
<td>-667.21</td>
<td>0.0000</td>
<td>YES YES</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.00</td>
<td>0.0000</td>
<td>- -</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.00</td>
<td>0.0000</td>
<td>- -</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.00</td>
<td>0.01127</td>
<td>- -</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>0.00</td>
<td>0.00379</td>
<td>- -</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>0.00</td>
<td>0.01826</td>
<td>- -</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>208.36</td>
<td>0.0000</td>
<td>NO NO</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>a2</td>
<td>247.39</td>
<td>0.52958</td>
<td>YES YES</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>e</td>
<td>247.39</td>
<td>0.52958</td>
<td>YES YES</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>e</td>
<td>268.18</td>
<td>0.01352</td>
<td>YES YES</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>268.18</td>
<td>0.01352</td>
<td>YES YES</td>
<td></td>
</tr>
</tbody>
</table>

  There are three negative eigenvalues: The C₃ᵥ-structure is found to be a transition state!

- Run the module vibration to lower the symmetry of the molecule along the “most imaginary” normal mode with the number 1. The default value for the displacement (i.e. “room temperature”) should be fine.

  After vibration has finished, copy the coordinates from the control file, found in the keyword $newcoord to the coordinate file coord – replace the coordinates and rerun

  define

  Now, define will find that the coordinates do not fit to the former symmetry, that is still given in the control file:
COORDINATES REFERENCED BY CONTROL INPUT FILE control DO NOT COMPLY WITH
SCHOENFLIES SYMBOL c3v .
THESE COORDINATES AND SCHOENFLIES SYMBOL ARE IGNORED !
HIT >return< TO CONTINUE WITH STANDARD GEOMETRY MENU

So you have to reload the coordinates simply by saying:

    a coord

To check for the new symmetry with

    desy

which will find C3 symmetry.

    ired

will redo the internal coordinates according to the new structure (if you forget that here, jobex will fail to run
properly later on. If that happens, just recall define, say y when being asked for changes of the structure and
call ired now – accept the rest of the input until you reach the end of define).

And, you will also have to redo the start mos with eht.

- Before we continue, save the energy file:

  cp energy energy.c3v

- Perform a geometry-optimization of the molecule in the new symmetry (C3) also on the BP86/SV(P)-level.

  The energy lowering by going from C3v- to C3-symmetry should be about 341.8 kJ/mol (or 0.13018 Hartree):

  tail -n 2 energy.c3v energy

  ==> energy.c3v <==
  7 -2390.781033598      2383.424468007     -4774.205501605
  $end

  ==> energy <==
  25 -2390.911215563      2383.657356328     -4774.568571890
  $end

Please note:

1. Small force constant calculations, like this example, work well with the default core memory. In case of larger
molecules, however, huge matrices have to be stored, and it is advantageous to process several of them at the
same time. For this purpose, add

    $maxcor <N>

to the control file, where N specifies the core memory given in MB - but remember that some additional
quantities, e.g. the core memory for RI-matrices, cause further memory requirements. Depending on the total
size of the available memory, approximately 50% of it might be a good choice.

2. aoforce will always compute the Hessian, and from it the vibrational modes, even if your gradients are not
3. TmoleX can be used to visualize the vibrational modes, and also to distort a structure along a mode.

9.2. **Lowest Eigenvalue Search**

One of the most common applications of the calculation of vibrational modes is a check for the minimum or transition state of an optimized structure. Hence, it is not necessary to compute the complete Hessian and vibrational spectrum, since already the lowest eigenvalue determines the kind of a stationary point. A negative eigenvalue, i.e., an imaginary frequency, indicates a transition state of (at least) first order, whereas a positive lowest eigenvalue is a proof for a (local) minimum structure.

For larger systems, a Hessian calculation can be more expensive than the complete geometry optimization. `aoforce` scales with $N^3$, where $N$ is the number of basis functions.

The Lowest Eigenvalue Search (LES) approach calculates only the lowest $N$ eigenvalues and eigenvectors numerically (Davidson iteration scheme). This reduces the scaling behavior to $N^2$ and gets thus more efficient compared to the full run, the bigger your input is.

The setup of an LES calculation is the same as for the full one, the keyword `$les` switches on the LES mode of `aoforce`.

1. Load the coordinates of the P$_4$H$_3$ exercise from chapter 8.4, do an SCF energy calculation and then add

   `$les all 2`

   to the control file.

2. Run `aoforce` as before and compare the frequencies with the full run.

Note:

- LES is not faster than the calculation of the full spectrum if:
  1. The system is small to medium sized (as in the example here),
  2. The number of eigenvalues that shall be computed is too large,
  3. The order of the symmetry group is very high (reducing the 'largeness' of your system, see 1.).

- Since LES will calculate the eigenvector, it can also be used to generate an input Hessian matrix for a transition state search (see chapter 8.7) using `statpt`:

  1. You have to add (by hand) two more keywords to the control file:

     `$h0hessian`
     `$nomw`

  2. `statpt` will use the full Hessian instead of the one from the LES search if both are found.
9.3. **NumForce: RI-MP2 force constant calculation on methane**

**NumForce** enables numerical force constant calculations for all levels of theory with a gradient implemented.

As an example, we will perform a numerical RI-MP2/TZVP force constant calculation for methane with the **NumForce** script.

- Prepare an RI-MP2 calculation (energy and gradient calculation of MP2).
- Run **dscf** and **ricc2**.
- To run **NumForce** just issue the command

```
NumForce -level cc2 -central
```

This chooses RI-MP2 (options `-ri` and `-level mp2`) and additionally the use of central differences (better numerical stability) is ensured by the option `-central`.

Please note:

The default increment for numerical differentiation is 0.02 au. To get more accurate results, you may have to lower this value, but only, if you increase the quality of the wave function employing stricter convergence criteria (i.e. modify `$scfconv` and `$denconv` in `control`).

**NumForce** actually is a shell script. If you know some shell script programming, you can have a look at it and maybe improve it for your own purposes (of course you should copy it first).

If you have forgotten the options of **NumForce**, just call **NumForce -help** to get a short overview.

9.4. **Analysis of Normal Modes in Terms of Internal Coordinates**

A frequently asked question is which internal coordinate (bond, angle, ...) is involved in which mode of the vibrational spectrum. This can be answered by an analysis of the normal modes in terms of internal (non-redundant!) coordinates.

Chapter 8.1 of the TURBOMOLE documentation gives a nice description about how to perform such a calculation.

9.5. **Thermodynamic data from vibrational frequencies**

From a full vibrational spectrum (not from a lowest eigenvalue calculation), it is possible to get various thermodynamic functions at various temperatures and pressures.

After an **aoforce** or **NumForce** run, just call the 'free enthalpy' program:

```
freeh
```

in the directory of your input. **freeh** is an interactive program:

1. After calling it, **freeh** will first print out the normal modes from the control file. From the coordinates and the point group it finds out the symmetry number \( \sigma \) needed in the quasi-classical rotational partition sum. Just
accept the proposed $\sigma$ and go ahead.

2. Next, you will be asked for a scaling factor for the frequencies:

    wave numbers calculated by scf theory tend to be
    1-10% too large and may be corrected by scaling
    -----------------------------------------------
    default value of scaling factor (BP/SVP):   0.9914
    enter new value for corr, if you want to change
    -----------------------------------------------

This scaling factor should be chosen depending on the applied method. The proposed scaling factor is the one that is recommended for BP/SVP calculations. Other usual scaling factors\(^1\) are, for a small SVP or 6-31G(d) like basis set:

<table>
<thead>
<tr>
<th>Method</th>
<th>Scaling Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.8953</td>
</tr>
<tr>
<td>DFT: B-P86</td>
<td>0.9914</td>
</tr>
<tr>
<td>DFT: B-LYP</td>
<td>0.9945</td>
</tr>
<tr>
<td>DFT: B3-LYP</td>
<td>0.9614</td>
</tr>
<tr>
<td>MP2</td>
<td>0.9434</td>
</tr>
</tbody>
</table>

3. Next, you will be asked for a range of temperatures and pressures:

    enter the range of temperatures (K) and pressures (MPa)
    at which you want to calculate partition sums and free enthalpies :

    tstart=<real> tend=<real> numt=<integer> pstart=<real> pend=<real> nump=<integer>

    default values are :
    tstart=298.15 tend=298.15 numt=1 pstart=0.1 pend=0.1 nump=1

    or enter  q  or  *  to quit

You do not have to write the complete line every time. If you accept the default temperature and pressure (298.15 K and 0.1 MPa), just hit <Enter>. Otherwise, just change the values of the temperatures or pressures:

    tend=350 numt=2 pend=0.5 nump=4

The input above will let the start temperature and the start pressure at the default values while changing the end temperature to 350K and the end pressure to 0.5 MPa. numt and nump are the number of temperatures and pressures between the start and end values that will be evaluated.

\(^1\) Taken from Scott, A. P., Radom, L., Harmonic Vibrational Frequencies: An Evaluation of Hartree-Fock, Møller-Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors, J. Phys. Chem. A, 1996, **100**, 16502

and

4. **freeh** will print out a list of several properties for the given range of temperature and pressure. Here an example for benzene, RI-DFT calculation using def-SV(P) basis set and C1 symmetry for the input given above (tstart is default, tend is 350, number of temperatures numt is 2, pressure is from default 0.1 MPa to pend of 0.5 MPa, number of pressures numt is 4):

```
zero point vibrational energy
----------------------------
zpe= 260.9 kJ/mol

<table>
<thead>
<tr>
<th>T</th>
<th>p</th>
<th>ln(qtrans)</th>
<th>ln(qrot)</th>
<th>ln(qvib)</th>
<th>chem.pot. Energy</th>
<th>entropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(MPa)</td>
<td></td>
<td></td>
<td></td>
<td>(kJ/mol)</td>
<td>(kJ/mol/K)</td>
</tr>
<tr>
<td>298.15</td>
<td>0.1000000</td>
<td>17.14</td>
<td>11.41</td>
<td>0.83</td>
<td>188.07</td>
<td>273.65</td>
</tr>
<tr>
<td>298.15</td>
<td>0.2333333</td>
<td>16.29</td>
<td>11.41</td>
<td>0.83</td>
<td>190.17</td>
<td>273.65</td>
</tr>
<tr>
<td>298.15</td>
<td>0.3666667</td>
<td>15.84</td>
<td>11.41</td>
<td>0.83</td>
<td>191.29</td>
<td>273.65</td>
</tr>
<tr>
<td>298.15</td>
<td>0.5000000</td>
<td>15.53</td>
<td>11.41</td>
<td>0.83</td>
<td>192.06</td>
<td>273.65</td>
</tr>
<tr>
<td>350.00</td>
<td>0.1000000</td>
<td>17.54</td>
<td>11.65</td>
<td>1.23</td>
<td>172.36</td>
<td>278.22</td>
</tr>
<tr>
<td>350.00</td>
<td>0.2333333</td>
<td>16.69</td>
<td>11.65</td>
<td>1.23</td>
<td>174.82</td>
<td>278.22</td>
</tr>
<tr>
<td>350.00</td>
<td>0.3666667</td>
<td>16.24</td>
<td>11.65</td>
<td>1.23</td>
<td>176.14</td>
<td>278.22</td>
</tr>
<tr>
<td>350.00</td>
<td>0.5000000</td>
<td>15.93</td>
<td>11.65</td>
<td>1.23</td>
<td>177.04</td>
<td>278.22</td>
</tr>
</tbody>
</table>

You might have to scroll up the windows to see the output since **freeh** prints out a detailed explanation of the used formulas and some hints.
10. Excited states

10.1. escf: UV/Vis and CD Spectrum of Pentahelicene

- Starting from the coordinates in the structure library (a !pentahelicene), set up the input for an RIDFT/SV(P) run (and please switch on symmetry by calling desy).

- Before leaving define, enter the

  ex

submenu of the “GENERAL MENU”. Here you can see the properties and methods escf and egrad are capable of. If you have switched dft on, then e.g. rpas will do a singlet excitation at TDDFT level, otherwise it would be a TDHF (RPA) calculation.

Specify a TDDFT calculation of singlet excited states by typing

  rpas

Go to the next question by entering

  *

and enter

  a 3
  and
  b 3

to calculate 3 states of each A and B symmetry (if there is only symmetry A, you have probably forgotten poor desy). You can leave the other options unchanged. For larger calculations you may consider to increase rpacor which determines the number of vectors to be treated simultaneously (saves much time!).

- Run ridft and – subsequently – escf. Have a look at the results.

Note:

1. The irrep given in $soes is the one for the excited state vector, i.e. the direct product of the irreps of the ground state and the excited state.
2. Add $spectrum <unit> and/or $cdspectrum <unit> to the control file, and you will get the files spectrum and cdspectrum with a table containing the excitation energies (in the given unit) and the oscillator and/or rotatory strengths. Possible units are eV, nm, au, or 1/cm.
3. Do not forget that you have to apply the selection rules yourself. The calculated oscillator strengths for the triplet excitations from a singlet ground state are of equal size than the ones for the singlet excitations. Keep in mind which excitations are suppressed because of the selection rules (spin).

After a calculation, the converged excitation vectors are saved in files (sing_* , trip_*) . A following run with a larger number of excitations will read in and use the already converged eigenvectors.
10.2. **egrad**: Excited state structure of CH₂O

To optimize the structure of an excited state with TDDFT, one has to specify which excited state should be followed. Load the coordinates of CH₂O from the structure library.

- Let the symmetry at C₄, since we do not know right now how the excited state will look like,

- Start from a new or empty directory and call **define**
  - hit <Enter> and then give a title
  - enter
    `a !ch2o`
  - and accept the found structure with `y` – then do `ired`
  - enter two `*` until you reach the Molecular Orbital menu and generate start MOs with
    `eht`
  - accept all defaults by hitting <Enter> many times...
  - now you should be in the General Menu
  - switch on `dft` and `ri`

- Go to the `ex` menu and choose `rpas` for singlet.

- For gradient calculations, only one irrep is allowed – here it is much easier to edit the **control** file directly, rather than using **define**. Look at `$soes` if only one irrep is given as option.

- If no additional option is given, the highest number of the entry in `$soes` will be taken to compute the excited state gradient and structure.
  Sometimes, when two excitations are lying close in energy, the algorithm is more stable if you include some higher excitation vectors in addition. In that case, if the highest number in `$soes` is not the one you want to use, add the keyword
    `$exopt <N>`
  with `<N>` as the number of the excited state you have in mind.

- The module **egrad** does the energy and the gradient calculation. For single point runs, just start **egrad** instead of **escf** and look at the output.

- To optimize the excited state structure, run

  `jobex -ri -ex`  
  # and other options like `-c 100` if needed

- Look at the excited state structure. Call

  `t2x > exstate.xyz`

  and load the file `exstate.xyz` in a viewer that is able to plot multiple xyz structures (`molden`, `jmol`, ...).

10.3. **TDDFT excited state vibrational spectrum**

Since the module **egrad** of **TURBOMOLE** calculates the gradients of the excited states analytically, second derivatives can be done numerically by using the script **NumForce** (see chapter 9.3).
We will now calculate the vibrational spectrum of the first excited (singlet) state of CH$_2$O at TDDFT level.

1. Use the directory of the last chapter with the converged excited state structure of CH$_2$O.

2. Since we have already specified which excited state we want to use for the gradient/structure calculation, we do not have to change the input file.

3. Just start **NumForce** with the option `-ex <number of state>` in addition to the usual options:

```
NumForce -ex 1 -ri
```

Note that you have to tell **NumForce** here which excited state in $C_1$ you want to follow. **NumForce** has to distort the geometry to do the numerical second derivatives for each of its steps. Hence, the symmetry for the calculation will automatically be lowered to $C_1$. The `ssoes` keyword contains an irrep different than $a$, so we have to choose the right excitation in $C_1$ ourselves (by looking at the output of `jobex`, counting all excitations).

Got a transition state? Then check why:

- DFT grid? Set gridsize to 4 and redo the calculation from scratch (!).
- Basis set too small? Redo the calculation with def-TZVP.
- Convergence criteria? Call `jobex` with `-energy 6 -gcart 4` in addition and start again from scratch (default is `-energy 6 -gcart 3`).

## 10.4. **ricc2**: Excited states of HCP

1. Start to make a usual input with **define** using the coordinates of HCP from the structure library (`a !hcp`). Choose cc2 in the General Menu and there:

```
ricc2
c2  *
cbas *

exci
list irrep
```

`list irrep` gives you the syntax of the `irrep` command in this submenu (unlike most other submenus, you have to specify a line just the way you would add the keyword to the control file).

It also prints out the irreps of the chosen point group and possible multiplicities.

```
irrep=a1  nexc=1
irrep=a2  nexc=3
  *
  *
```

2. After that, you can run the **ricc2** module. Note that this module currently knows Abelian point groups only if used for excited state calculations, therefore the symmetry group given in the `control` file is $C_{2v}$. Look
carefully at the output (D1-diagnostic, %T of the excitations). Note that CC2 excitation energies are optimized in three steps.

3. You can also specify more than one method. Try:

```plaintext
$ricc2
  ccs
cis(d)
cc2
$excitations
  irrep=a2  nexc=1
```

**Important General Note about restarts of rcc2:**

Remove the `restart.cc, alles.cc, syminfo` files and all `CC*` files before rerunning rcc2 if you have changed the input - the program would try a CC2 restart and thus skip methods, fails to converge, stops with error messages or produces nonsense results!

4. You certainly are also interested in properties of the excited states. Try e.g.

```plaintext
$ricc2
  cc2
$excitations
  irrep=a2  nexc=1
  expval operators=diplen,qudlen
$response
  expval operators=diplen,qudlen
```

The `$response` keyword switches on the calculation of ground state properties. Inspect the output file carefully.

**10.5. Circular dichroism and UV/Vis spectra calculations at CC2 level**

If you want to calculate optical spectra, the oscillator and rotator strength have to be requested. An input looks like this:

```plaintext
$ricc2
  cc2
$excitations
  irrep=a  nexc=2
  spectrum operators=diplen,dipvel,angmom
$spectrum ev
$cdspectrum ev
```

When given the `$spectrum` and the `$cdspectrum` flags the output is parsed in individual files, which can directly be loaded in plot programs, like e.g. gnuplot.

**10.6. Excited state frequency analysis at CC2 level**

NumForce (see chapter 9.3) can also be used to calculate the vibrational frequencies of excited states. We will try that for Ammonia and R1-CC2:
1. Prepare the input and load the coordinates from the structure library (a !ammonia).

2. Do not apply symmetry, so this time try to avoid entering desy and keep C\textsubscript{1} symmetry.

3. Accept the default def-SV(P) basis (yes, it is much too small, so please do not publish the results).

4. Go to cc2 in the last menu and do:
   1. cbas # assign auxiliary basis sets, accept the ones \texttt{define} chooses for you
   2. ricc2 and then cc2 # switch on CC2 as method
   3. geoopt cc2 (a 1) # to get the vibrational spectrum of the first excited state, we need gradients
   4. *
   5. exci # go the the excitation menu
   6. irrep=a nexc=1 # switch on the excited state calculation, otherwise the (a 1)
      # option of geoopt will not work!
   7. * and * and *

5. End define and run a geometry optimization at CC2 level:
   \texttt{jobex -level cc2}

6. Since we have chosen the gradients and the energy of the excited states, \texttt{jobex} will do a geometry optimization of the first excited state. If you delete the keyword $\texttt{excitations}$, you will get the ground state.

7. Run
   \texttt{NumForce -level cc2 > force.out}

8. Take a look at force.out and numforce/aoforce.out.

\textbf{Note:} do not call NumForce with the -ex option! This does only work for TDDFT excited state calculations, whereas the CC2 part always is completely controlled by the keywords $\texttt{ricc2}$ and $\texttt{excitations}$. 
11. COSMO: dealing with solvation effects

Solvation effects can be treated by the COSMO (COnductorlike Screening MOdel). If you want to know more about COSMO, please read chapter 11 of the TURBOMOLE documentation or visit www.cosmologic.de

Briefly: COSMO is a continuum solvation model, almost identical to the CPCM called method in many other quantum chemistry programs. COSMO builds a metal cavity around the molecule, corresponding to an electrostatically ideal solvent of $e=\infty$.

The cavity construction starts with a union of spheres of radii $R_i + RSOLV$ for all atoms $i$. So the most important input parameter for COSMO is the radius for each element that should be taken for the cavity construction.

This is done interactively by the script

`cosmoprep`

that can be called in a directory containing a usual gas phase input.

Here we just do a geometry optimization with DFT (Hartree-Fock can be used the same way). To learn how to do vibrational frequency calculations or how to use COSMO with MP2, please see chapter 12.2.6 of the TURBOMOLE documentation.

Now, let us calculate the structure of benzene in a solute:

1. Start with define, load benzene from the structure library with

   ```
a !benzene
   ```

2. Let the symmetry at C$_1$ and define internal redundant coordinates (ired and *).

3. Choose def-TZVP basis set (b all def-TZVP and *)

4. Do a eht and accept the occupation for charge=0 (eht and many times <Enter>).

5. Switch on dft an ri

6. Get define to an end with q or * and start

   ```
cosmoprep
   ```

7. Accept all defaults until you get to the

   ```
   ****************************************************
   ***           radius definition menu             ***
   ****************************************************
   ( #atoms= 12 --- #radius= 0 )
   **
   ```

8. Here you have to tell cosmoprep which radius for each element you want to use. Unless you have your own radii, there are two possibilities:

   1. optimized radius – for a limited set of elements, optimized radii have been determined by fitting the
results of many calculations to experiments,

2. bondii radius – unoptimized radii for all elements

A good approach is to use optimized radii for all elements available, and the bondii for the rest.
Enter

```
r all o
```
to assign optimized radii to all atoms.
In case of benzene, all atoms have got a radius now:

```
( #atoms= 12 --- #radius= 12 )
```

9. For elements where optimized radii are missing, e.g. Si in SiMe₃, you would get something like:

```
( #atoms= 13 --- #radius= 12 )
```

so for one of your 25 atoms the optimized radius is missing and you have to assign bondii radii.
Scroll up your windows and search for one or more lines like:

```
no optimized radius available for atom     1 (si)
```

and then tell cosmoprep to use bondii for Si:

```
r "si" b
```

and check if the number of atoms is now equal to the number of radii.

10. Exit the radius assignment with * and enter a name of the cosmo file in the next section – or use the default by hitting <Enter>.

11. Now check the control file and search for cosmo. With those keywords in the control file, energy and gradient calculations at Hartree-Fock and DFT level will include solvation effects – you do not have to specify any additional option with jobex:

```
jobex -ri > jobex.out
```

12. Check the job_last file and look at the energy output there.
12. Calculation of NMR chemical shifts

12.1. At the HF or DFT level

Please refer to chapter 9 and section 12.2.18 (Keywords for Module mpshift) of the documentation for an overview of the capabilities and the usability of mpshift.

Prepare an input for a calculation of the shieldings of tetramethylsilane, a typical reference molecule for $^{13}$C shifts:

1. DFT, non-hybrid functional, without RI
   1. Call define and load the minimum structure of TMS from the structure library by entering
      
      a !sime4
      
      at the geometry menu. Let desy determine the symmetry of the coordinates ($T_d$).
   2. Accept the default basis set def-SV(P). Usually a basis set of SVP quality is sufficient for DFT calculations when non-hybrid functionals are used, as long as no transition state elements with non-$d^0$ or $d^10$ occupation are involved.
   3. Do an extended Hückel guess with eht, switch on dft in the last menu and accept the defaults (B-P functional with m3 grid).
   4. Call dscf to get converged Mos.
   5. Call mpshift or the script chemshift.
   6. The total, the isotropic, and the anisotropic shieldings of all nuclei can be found at the keyword $^{nmr}$ dft shielding constants in the control file if you have called mpshift, or in the file shieldings if you have called chemshift.

2. DFT, non-hybrid functional, with RI
   1. Just repeat the last calculation, but do an ridft input and start it before running mpshift.
   2. mpshift does not use the RI-J approximation itself, but it can do NMR shielding calculations starting either from a conventional DFT run or from an RI-DFT run.

3. HF or hybrid functionals (B3-LYP, PBE0, ...)
   1. Prepare the input as in the DFT case, but choose the def-TZVP basis set this time and select b3-lyp as functional (or switch off DFT for a Hartree-Fock calculation). For HF and DFT with hybrid functionals, a TZVP basis set is recommended.
   2. For a fully direct calculation just continue with point 4, but it can be faster to use some disk space. You can either set the maximum file size of the twoint file to an arbitrary number (in MB, as usual), or let a statistics run determine the maximum file size needed for this input: Call stati dscf to add the $statistics$ keyword to the control file and call dscf to start the statistics calculation.
   3. Edit the control file and add a path to a local directory at the keyword $scfintunit$ at file=twoint
     
      If the twoint file is too big for your system, set it to a smaller number. mpshift (just like dscf) will use only as much space as provided by the keyword and computes the rest of the integrals directly.
4. Call `dscf` and then `chemshift`

5. Note that HF results are written to the keyword
   
   `$nmr\ rhf\ shielding\ constants$
   
   while DFT ones to
   
   `$nmr\ dft\ shielding\ constants$

12.2. At MP2 level

1. Create a usual `dscf` input like the one in the section before.

2. MP2 chemical shieldings need a very well converged density, so you have to do a single-point `dscf`
   calculation with at least `$denconv .1d-6`. This keyword is added by the script `mp2prep` when preparing
   usual MP2 energy or gradient calculations, but not when preparing MP2 chemical shifts. It can not be set
   within define, so you have to add it 'by hand' if you do just a `mpshift` calculation after a single-point HF
   run.

3. Do a statistics run for `dscf`, add `$denconv .1d-6` to the control file and run `dscf`.

4. `mp2prep -c` prepares the input for the NMR shieldings calculation at MP2 level. On many systems,
   `mp2prep` has got problems determining the free disk space, so it is highly recommended to use the `-p <MB>`
   option of `mp2prep`
   
   ```
   mp2prep -c -p 400
   ```

5. Start `mpshift`. It will do the SCF and the MP2 calculation of the nuclear magnetic shieldings.

12.3. Hints

- Only RHF calculations can be done.
- Do not use ECPs. The electrons in the core potential will not be taken into account during the calculation, so
  the results will just be nonsense.
13. Visualization of orbitals and densities

13.1. TmoleX

The easiest way to visualize surfaces of orbitals, densities and much more is to use TmoleX. Choose the property which you like to see in the Result section of TmoleX (e.g. by reading in the control file of a completed calculation) by clicking on the button called '3D Surfaces'.

13.2. Using molden or molekel

Just call the TURBOMOLE program tm2molden after a calculation. You will be asked about the data that should be included in the molden input file. If the basis set and the molecular orbitals are written to the input file, molden (or molekel) will be able to plot the orbitals and the density by calculating those properties itself.

13.3. Using gOpenMol

The TURBOMOLE modules dscf, ridft, ricc2, and egrad are evaluating the new keywords for property and visualization purposes (see chapter 10 of the documentation).

If you have an old calculation, you can add one of those keywords and call

\[ \text{dscf -proper} \]

or any other of the programs mentioned above. Only the property/visualization step will be done in such a case.

To plot, say, the total density of water, just do a usual input and add

\[ \$\text{pointval dens} \]

to the control file and run the calculation.

After the run, start gOpenMol:

1. Load in the coordinates by using the Menus of gOpenMol:
   
   File -> Import -> Coords...

You will get a menu where you can select the coordinates from. The TURBOMOLE programs will automatically write out an xyz file, so usually you can just load in the file coord.xyz and click on the <Apply> button.

Note:

gOpenMol can also read in directly the Turbomole coordinate file coord, but in the current version it expects it with .txt
3. The Contour Control Window will expand, writing out the minimum and maximum value of the density that has been read in.

For each of the 10 fields, called Value 1 to Value 10, you can now enter a value of the density that shall define the iso-density surface of the contour that will be plotted.

With Colour... and Details.. you can change the colour and the opacity of each contour.

Do not forget to click on Apply each time you change something in the menu.
Here is an example of two iso-density surfaces of Water, one at a value of 0.1 a.u. in blue, and one at a value of 0.03 in red.
To plot MOs, it is recommended to do a single point calculation first and then look at the orbitals and the occupation by calling the script

```
eiger
```

You will get a list of the orbitals together with the occupation and the energy. This gives a hint about the MOs which might be interesting to have a look at.

Let us make an input for benzene (`!benzene` from the structure library), call `desy` for the symmetry, choose `def-SVP` and `RI/DFT-BP86`. Run `ridft` and call `eiger`:

```
Total energy =   -232.0860361135 H =     -6315.3859631 eV

HOMO-LUMO Separation
HOMO:    14.     1 e1g   -0.23205215 H =     -6.31446 eV
LUMO:    15.     1 e2u   -0.03843656 H =     -1.04591 eV
Gap :                    +0.19361560 H =     +5.26855 eV

Number of MOs=     76, Electrons=     42.00, Symmetry: d6h
```

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Orbital</th>
<th>Occupation</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.</td>
<td>1 b1g</td>
<td></td>
<td>+0.107418 H</td>
</tr>
<tr>
<td>17.</td>
<td>4 e1u</td>
<td></td>
<td>+0.085010 H</td>
</tr>
<tr>
<td>16.</td>
<td>4 a1g</td>
<td></td>
<td>+0.042434 H</td>
</tr>
<tr>
<td>15.</td>
<td>1 e2u</td>
<td></td>
<td>-0.038437 H</td>
</tr>
<tr>
<td>14.</td>
<td>1 e1g</td>
<td>4.000</td>
<td>-0.232052 H</td>
</tr>
<tr>
<td>13.</td>
<td>3 e2g</td>
<td>4.000</td>
<td>-0.303729 H</td>
</tr>
<tr>
<td>12.</td>
<td>1 a2u</td>
<td>2.000</td>
<td>-0.333745 H</td>
</tr>
<tr>
<td>11.</td>
<td>3 e1u</td>
<td>4.000</td>
<td>-0.377379 H</td>
</tr>
<tr>
<td>10.</td>
<td>1 b1u</td>
<td>2.000</td>
<td>-0.402110 H</td>
</tr>
</tbody>
</table>

As you can see, the HOMO is MO number 14 and the LUMO is MO number 15. So to plot the HOMO and the LUMO, add

```
$pointval mo 14-15
```

to the control file and call

```
ridft -proper
```

If you look at the output, you will see which file name is associated to which orbital – usually that is quite clear from the file name anyway.

Start `gOpenMol`, load in the coordinates as shown above, go to the Plot/Contour menu and load the HOMO file. Import it and specify two different contours – one with a positive value and one with a negative. Change the color of one of them and let them plot by clicking on `Apply`.

Now you can load the LUMO in addition, import it and plot again two contours with different colors.

Play a bit with the values and colours. Below is a screen shot of such a plot. Red and blue is the HOMO and green and grey is the LUMO.
Look at the Turbomole documentation about how to plot differential densities of excited states, MP2 densities, spin densities, ...
13. Visualization of orbitals and densities

13.4. Using an arbitrary program to plot 3D grids

To choose a simple xyz format instead of the one for OpenMol, add

```
$pointval mo 13-14 fmt=xyz
```

to the control file and run an energy calculation.

This will write out the grid and the value of the MO in a file using the format:

```
x  y  z  f(x,y,z)
```

and, in addition, some lines at the beginning that contain the most interesting data of this plot:

```
#origin           0.000000      0.000000      0.000000
#vector1          1.000000      0.000000      0.000000
#vector2          0.000000      1.000000      0.000000
#vector3          0.000000      0.000000      1.000000
#grid1  start   -8.037772  delta    0.203488  points     80
#grid2  start   -8.662417  delta    0.201452  points     87
#grid3  start   -4.000000  delta    0.205128  points     40
#title for this grid
#amplitude of MO    1e1g 1         -0.23205a.u.
#plotdata
# cartesian coordinates x,y,z and f(x,y,z)
-8.03777189       -8.66241737        -4.00000000        0.00000002
-7.83428399       -8.66241737        -4.00000000        0.00000002
-7.63079610       -8.66241737        -4.00000000        0.00000003
-7.42730820       -8.66241737        -4.00000000        0.00000004
-7.22382031       -8.66241737        -4.00000000        0.00000006
-7.02033241       -8.66241737        -4.00000000        0.00000008
-6.81684451       -8.66241737        -4.00000000        0.00000011
```

Load this in your favorite spread sheet or statistics program.

Since Turbomole V6.0 it is also possible to write out the 3D grid information in the commonly used cube format, just set fmt=cub.