

Turbomole HowTo

- ✓ Create directory, go into it: `mkdir mydirectory | cd mydirectory`
- ✓ Prepare initial geometry of molecule/cluster in. xyz format with your favorite molecule editor (Materials Studio, Mercury, GDIS etc.)
- ✓ Make coord file with `x2t` script: `x2t myfile.xyz > mycoordfile`
- ✓ Prepare input with `define` module.
- ✓ Run calculation by typing shell command or (more frequently) submit script with commands to queue.
- ✓ Check your results (or if calculations didn't crash:).
- ✓ You can prepare inputs, run calculations & analyze results with free graphical **Tmolex** client - I've never used it, so I will not help you much with this.

Making Your Own Input with `define`

`define` is an interactive input generator, running in txt mode & largely self-explanatory.

There are 4 main menus:

- ✓ **Geometry** - read geometry from external file, determine symmetry, define internal coordinates etc.
- ✓ **Atomic attributes** - assign basis sets and effective core potentials, nonstandard charges or atomic masses.
- ✓ **Start orbitals** - generating initial orbitals & their occupations, best done by extender Hückel theory.
- ✓ **General** - control parameters for various Turbomole modules (SCF parameters, RI on/off, XC functional in DFT, MP & CC settings etc.)

Huge amount of options, but take it easy, you don't have to use all at once, some of them you may never use in your life.

Push enter until you reach **Geometry** menu:

```
INPUT TITLE OR  
ENTER & TO REPEAT DEFINITION OF DEFAULT INPUT FILE
```

```
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>  
aa <file>         : ADD ATOMIC COORDINATES IN ANGSTROM UNITS FROM FILE <file>  
sub             : SUBSTITUTE AN ATOM BY A GROUP OF ATOMS  
▶ i               : INTERNAL COORDINATE MENU  
▶ ired           : REDUNDANT INTERNAL COORDINATES  
red_info        : DISPLAY REDUNDANT INTERNAL COORDINATES  
ff              : UFF-FORCEFIELD CALCULATION  
m               : MANIPULATE GEOMETRY  
▶ frag           : Define Fragments for BSSE calculation  
w <file>         : WRITE MOLECULAR COORDINATES TO FILE <file>  
r <file>         : RELOAD ATOMIC AND INTERNAL COORDINATES FROM FILE <file>  
name            : CHANGE ATOMIC IDENTIFIERS  
del             : DELETE ATOMS  
dis             : DISPLAY MOLECULAR GEOMETRY  
banal           : CARRY OUT BOND ANALYSIS  
*              : TERMINATE MOLECULAR GEOMETRY SPECIFICATION  
                  AND WRITE GEOMETRY DATA TO CONTROL FILE
```

```
IF YOU APPEND A QUESTION MARK TO ANY COMMAND AN EXPLANATION  
OF THAT COMMAND MAY BE GIVEN
```

By default Turbomole doesn't detect symmetry, all calc. are in *C1* point group. If you want detect symmetry use **desy** keyword (+ looser threshold for checking atomic positions, if necessary, in either decimal or exponential notation in atomic units, e. g. `desy 1d-2 = desy 0.01`).

Beware with symmetry! - it can speed up calculations & facilitate interpretation of results, but if you impose wrong point group in the beginning your system will stuck in it forever!

Atomic Attributes menu:

ATOMIC ATTRIBUTE DEFINITION MENU (#atoms=10 #bas=10 #ecp=0)

▶ b : ASSIGN ATOMIC BASIS SETS
bb : b RESTRICTED TO BASIS SET LIBRARY
bl : LIST ATOMIC BASIS SETS ASSIGNED
bm : MODIFY DEFINITION OF ATOMIC BASIS SET
bp : SWITCH BETWEEN 5d/7f AND 6d/10f
lib : SELECT BASIS SET LIBRARY
ecp : ASSIGN EFFECTIVE CORE POTENTIALS
ecpb : ecp RESTRICTED TO BASIS SET LIBRARY
ecpi : GENERAL INFORMATION ABOUT EFFECTIVE CORE POTENTIALS
ecpl : LIST EFFECTIVE CORE POTENTIALS ASSIGNED
ecprm : REMOVE EFFECTIVE CORE POTENTIAL(S)
▶ c : ASSIGN NUCLEAR CHARGES (IF DIFFERENT FROM DEFAULTS)
cem : ASSIGN NUCLEAR CHARGES FOR EMBEDDING
m : ASSIGN ATOMIC MASSES (IF DIFFERENT FROM DEFAULTS)
dis : DISPLAY MOLECULAR GEOMETRY
dat : DISPLAY ATOMIC ATTRIBUTES YET ESTABLISHED
h : EXPLANATION OF ATTRIBUTE DEFINITION SYNTAX
* : TERMINATE THIS SECTION AND WRITE DATA OR DATA REFERENCES TO control
GOBACK=& (TO GEOMETRY MENU !)

■

By defaults Turbomole assigned *def-SV(P)* basis set &, for atoms $Z > 36$ (beyond Kr) relativistic effective core potentials.

Recommended basis set (type bi in this define section)

QUALITY:	exploratory	qualitative	quantitative	limit
DFT		def2-SV(P)	def2-TZVP	def2-QZVP
HF		def2-SV(P)	def2-TZVPP	def2-QZVPP
MP2	def2-SV(P)	def2-TZVPP	def2-QZVPP	

See: F. Weigend and R. Ahlrichs, PCCP, 7, 3297-3305 (2005).

Occupations & Start Orbitals menu:

OCCUPATION NUMBER & MOLECULAR ORBITAL DEFINITION MENU

CHOOSE COMMAND

```
infsao      : OUTPUT SAO INFORMATION
atb         : Switch for writing MOs in ASCII or binary format
▶ eht       : PROVIDE MOS && OCCUPATION NUMBERS FROM EXTENDED HUECKEL GUESS
▶ use <file> : SUPPLY MO INFORMATION USING DATA FROM <file>
man         : MANUAL SPECIFICATION OF OCCUPATION NUMBERS
hcore       : HAMILTON CORE GUESS FOR MOS
flip        : FLIP SPIN OF A SELECTED ATOM
&           : MOVE BACK TO THE ATOMIC ATTRIBUTES MENU
THE COMMANDS use OR eht OR * OR q(uit) TERMINATE THIS MENU !!!
FOR EXPLANATIONS APPEND A QUESTION MARK (?) TO ANY COMMAND
```

If you want to use old orbitals (*e. g.* calc. in smaller basis set) type path to directory with orbitals & control file: use mydirectorywithorbitals/control.

If you don't trust EHT occupations/want different spin state etc. type n & go to:

DO YOU ACCEPT THIS OCCUPATION ? DEFAULT=y

n

YOU HAVE TO ASSIGN OCCUPATION NUMBERS MANUALLY

>> UHF << : ALPHA AND BETA SHELLS (a,b)

>> RHF << : CLOSED AND OPEN SHELLS (c,o)

OCCUPATION NUMBER ASSIGNMENT MENU (#e=56 #c=0 #o=0)

```
s          : CHOOSE UHF SINGLET OCCUPATION
t          : CHOOSE UHF TRIPLET OCCUPATION
u <int>    : CHOOSE UHF WITH <int> UNPAIRED ELECTRONS
uf <int>   : AS u, BUT ALLOW FRACTIONAL OCCUPATION NUMBERS
l <list>   : PRINT MO'S FROM EHT IN <list>, (DEFAULT=ALL)
p <index>  : PRINT MO-COEFFICIENTS OF SHELL <index>
c <list>   : CHOOSE SHELLS IN <list> TO BECOME CLOSED SHELLS
o <index>  : CHOOSE SHELL <index> TO BECOME AN RHF OPEN SHELL
a <list>   : CHOOSE SHELLS IN <list> TO BECOME UHF ALPHA SHELLS
b <list>   : CHOOSE SHELLS IN <list> TO BECOME UHF BETA SHELLS
v <list>   : CHOOSE SHELLS IN <list> TO BECOME EMPTY SHELLS
&          : REPEAT THE EXTENDED HUECKEL CALCULATION
*          : SAVE OCCUPATION NUMBERS & GO TO NEXT ITEM
dis        : GEOMETRY DISPLAY COMMANDS
e          : CALCULATE EHT-ENERGY
f          : FURTHER ADVICE
<int>      = INTEGER
<index>    = INDEX OF MO-SHELL ACCORDING TO COMMAND s
<list>     = LIST OF MO-SHELL INDICES (LIKE 1-5,7-8,11)
ENTER COMMAND
```

General menu:

```
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
senex    : seminumeric exchange parameters
hybno    : hybrid Noga/Diag parameters
dsp      : DFT dispersion correction
trunc    : USE TRUNCATED AUXBASIS DURING ITERATIONS
marij    : MULTIPOLE 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
```

If interested just in DFT - adjust `dft`, `ri` (& `marij` for large molecules), `scf`, maybe `dsp` (Grimme correction for van der Waals).

Under `stp` there are options for searching for transition states.

`ex` is for time dependent-DFT & familiar techniques to deal with response properties (excitations energies, polarizabilities etc.).

`mp2` & `cc` is for MP2 & CC (not suprisingly).

After finishing `define` run you should have in your directory the following files:

(i) `control` (general I/O), (ii) `coord` (with geometry, will be overwritten), (iii) basis sets file(s) - basis, possibly `auxbasis` with auxiliary basis sets for RI, (iv) orbital files - `mos` for restricted calculations or `alpha` & `beta` for unrestricted ones.

Turbomole Lifehacks

- ✓ If you want to keep all initial files make copy after closing `define` (e. g. `mkdir stardirectory | cp * stardirectory`). `coord` file can be overwritten even during `define` manipulation, so to keep initial geometry name it somehow else (e. g. `coord1`).
- ✓ Doing RI-DFT for systems > 2000 basis set functions always turn on `MARIJ`.
- ✓ Calculation of response properties (e. g. with `aoforce`, `escf`) takes a lot of memory, set `$maxcor/$rpacor` to ~80% of available RAM. Diminish `$ricore` value, if necessary.
- ✓ To save disk space you can gzip the largest files: orbitals (`mos` or `alpha/beta`) & `gradient` (contains history of optimizations), if temporary unused.
- ✓ If Turbomole crashes check directory & remove large temporary files dumped.
- ✓ If you get really lost in `define`, you can always terminate with `Ctrl+C`. `tmp.input` file will be dumped & if you rerun `define`, there should be already filled these parts of `control` file, for which you accomplished `define` sections.
- ✓ If you want to keep Cartesian coordinates of given atom frozen during optimization add 'f' letter in the end of line in `coord` file.
- ✓ Dummy atoms can be introduced to `coord` file with letter 'q' in the place of element symbol (may be useful if you want to add point charges to your system, you can assign to them charges in Atomic Attributes menu of `define`).

Energy Units:

1 hartree = 27.2114 eV = 627.51 kcal/mol = 2625.50 kJ/mol

1 eV = 23.061 kcal/mol = 96.4853 kJ/mol

1 kcal/mol = 4.1840 kJ/mol

The Most Important/Commonly Used Turbomole Modules

- ✓ `define` - input generator (text mode, largely self-explanatory)
- ✓ `dscf/ridft` - SCF HF/DFT (energy & wavefunctions) without/with RI.
- ✓ `grad/rdgrad` - HF/DFT gradients without/with RI. Converged `dscf/ridft` run required.
- ✓ `mpgrad` - MP2 energy & gradient. Requires successful `dscf` run.
- ✓ `ricc2` - MP & CC energies, gradients & excited states properties employing RI. Successful `dscf` run required.
- ✓ `escf` - time dependent & dielectric properties. Well converged SCF `dscf/ridft` run required.
- ✓ `egrad` - gradients & 1st order excited states properties. Well converged `dscf/ridft` & usually `escf` runs needed.
- ✓ `mpshift` - NMR shieldings for closed shell systems. `dscf/ridft` ...
- ✓ `relax` - geometry optimizer, proposes new structures on the base of gradients & updates Hessian. Gradients from either `grad/rdgrad/`
`mpgrad/ricc2/egrad` mandatory.
- ✓ `frog` - molecular dynamics run. Gradients demanded as in `relax`.
- ✓ `statpt` - another geometry optimizer, can search for transition states (for the latter usually accurate Hessian needed).

! `relax/statpt/frog` in practice are called with `jobex` script - shell command:

`jobex -relax` (-other options) (see next page)

- ✓ `aoforce` - analytical force constants, harmonic vibrational freqs. & IR intensities. Needs converged `dscf/ridft` (& for vibrational analysis well optimized geometry!).

If analytical Hessian not available for given method you can always calc. numerical 2nd derivatives with `NumForce` script, type `NumForce -h` for details.

Geometry optimization with jobex

jobex manages geometry optimization, namely calculation of energy & energy gradients by given Turbomole modules, approximating Hessian & moving atoms according to forces acting on them.

```
nohup jobex & or (nohup jobex > jobex.out) 2> errors &
```

You can use jobex with many arguments: `jobex -argument1 -argument2 ...`

The most important arguments:

- ✓ `-c integer` - no. of energy optimization cycles (default 100 - safer to increase it)
- ✓ `-energy integer` (default 6) - converge total energy up to to $10^{-integer}$ hartree
- ✓ `-gcart integer` (default 3) - converge max. norm of cartesian gradient up to $10^{-integer}$ hartree/bohr; if you want accurate geometry, like for calc. of vibrational frequencies, it is safer to increase it to 4
- ✓ `-level level` - define the level of methods, `level = mp2, cc2, rirpa, uff, scf`; default is `scf`, i. e. HF or DFT
- ✓ `-ri` - use energy/gradient modules with RI acceleration (proper RI flags must be set in control file!)
- ✓ `-relax` - use relax for force relaxation
- ✓ `-trans` - search for transition state (some additional entries in control must be prepared with `stp` submenu in define)
- ✓ `-ex` - excited state optimization with egrad (some additional entries in control must be prepared with `ex` submenu in define)
- ✓ `-help` - list all options with short explanations

In this course we use: `jobex -relax -ri -c 300 -energy 6 -gcart 4`

After running jobex you will have files: (i) `job.start`, with info about current options, (ii) `job.integer`, with data from the current step no. `integer`, & (iii) `job.last` with data from the last accomplished step. If optimization converged, there should be `converged` file.

Wavefunction Analysis

Atomic charges - concept, that one can assigned no. of electrons connected to given atom in molecules, hence charge. Remember - atomic charge is not an observable, it is just a kind of 'useful fiction'.

Several ways of calc. of atomic charges (all somewhat arbitrary!), like (i) population analysis - partitioning of wavefunction (Mulliken, Löwdin, NAO), (ii) partitioning of electron density in real space, (iii) fitting of electrostatic potential produced by molecule to a system of point charges in positions of nuclei.

In Turbomole you can calc. Mulliken charges by adding `$pop` keyword to `control` & running SCF. Another choice is `$pop nbo AO` - it produces Natural Bond Orbital charges in atomic orbitals basis set. NBO are less basis set dependent than Mullikens & more 'physical', it gives also occupations of orbitals of specific angular momentum.

Plots of isosurface

To produce plots of orbitals, electron densities add `$pointval` keyword to `control`. By default it produce plot electron densities (`td. file`), & spin densities (`sd.`) for unrestricted calc. You can (among other) plot electrostatic potential with extension `pot` and molecular orbitals in given range (`mo list`), e. g.:

Format is `.plt`, read by Gopenmole software, you can change it to `fmt=xyz/cub`, which is general grid of points in Cartesian coord. or Gaussian cube format (read by `molden`).

e. g. `$pointval dens pot mo 10-12 fmt=cub` instructs to prepare file with grids of isosurfaces for electron density, electrostatic potential & MO in range 10-12 in cube format.

Electrostatic moments

By default Turbomole calc. dipoles & quadrupoles, if you want octupoles specify `$moment 3rd`.

To calc. above rerun SCF in directory with converged wavefunction with:
`ridft/dscf -proper` - it will reuse converged orbitals.

Overview of Planned Exercises

Ex. 1

Build small closed shell molecule (e. g. ethanol) with `Tmolex` graphical interface, write geometry in `.xyz` format, convert it into Turbomole format with `x2t` script, prepare input with `define`: DFT calculations, PBE0 hybrid xc functional, def2-TZVP basis set. Run geometry optimization with `jobex` & then harmonic frequencies calculation with `aoforce`, check if local minimum of energy was found - if not, modify initial geometry & run calculation again.

Watch results (geometry, IR spectrum, orbitals) with `molden` graphical interface, `molden` input files prepared with `tm2molden` utility. Use `$pointval` keyword to produce external files with grids read by external programs.

Ex. 2

Perform DFT calculations on $[\text{Co}(\text{Im})_6]^{2+}$ complex - initial structure taken from exp. geometry Zhang et al. *Chin. J. Chem.* **2006**, 24, 51. Prepare Turbomole input with `define`, both for low spin (doublet) & high spin (quartet) state, change orbital occupations suggested by extended Hückel method, if necessary, run SCF calculations & check HOMO-LUMO gap with `eiger` script.

Perform geometry optimization with PBE gradient xc functional, check geometry & compare stability of spin states, perform single point energy calculations with PBE0 hybrid xc functional.

Ex. 3

Perform DFT & MP2 geometry optimizations for ethylene dimer, initial structure taken from <http://www.begdb.com/index.php?action=oneMolecule&state=show&id=90>. def2-TZVPP basis set, PBE0 c functional in DFT case, with & without Grimme dispersion correction ('-D'), calc. frequencies at DFT-D level.

Calculate dissociation energy of ethylene dimer for DFT/DFT-D & MP2 calculation, correct it with zero point (vibrational) energy (ZPE) from DFT-D calculation,

calculate basis set superposition error.

Dissociation energy - 'naive definition':

$$\Delta E' = E_{AB} - (E_A + E_B) \text{ (should be negative for bound system)}$$

Calc. with respect to zero order vibrational levels:

$$\Delta E'' = \Delta E' + (ZPE_{AB} - (ZPE_A + ZPE_B)) = \Delta E' + \Delta ZPE$$

Basis set superposition error - computational artifact occurring for atom centered (incomplete) basis sets, like Gaussian basis sets used by Turbomole & majority of quantum chemistry codes.

Dimer is calc. in larger (thus more complete) basis set than monomers, thus dimer's energy is somewhat lower (more accurate) than subsystems, which influences our $\Delta E'$.

One has to calc. energy of each monomers in the same basis set as dimers, i. e. with 'ghost functions', centered in the positions where the atoms of dimer would be.

In 'counterpoise method' BSSE is estimated as:

$$\text{BSSE} \approx [E_A(A \text{ bs}, AB \text{ geom}) - E_A(AB \text{ bs}, AB \text{ geom})] + \\ + [E_B(B \text{ bs}, AB \text{ geom}) - E_B(AB \text{ bs}, AB \text{ geom})] \quad (\text{BSSE} > 0)$$

'Correct' dissociation energy (well, at 0 K):

$$\Delta E = E_{AB} - (E_A + E_B) + \Delta ZPE + \text{BSSE}$$

Ex. 4

Optimize geometry of glyoxal $(\text{CHO})_2$ at DFT/PBE0 level, initial geometry taken from NIST Webbook database. Calculate vertical excitation energies for transitions with specific symmetry (only those transforming as x, y, z are electrically dipole allowed) with `escf` module, compare to exp. spectrum. Check the orbital contribution to excitation, calculate differential densities with `$pointval` keyword with `egrad` module, compare exc. energies with orbital energies difference.

For more infos on excitation in time dependent DFT see e. g. Neese paper in *Coord. Chem. Rev.* Generally time dependent-DFT has problems with Rydberg state, charge transfer excitations, double excitations.

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