

# QCEIMS 4.0 Installation Guide & Manual

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This manual gives a short overview on how to use QCEIMS. Please cite QCEIMS as S.Grimme, *Angew. Chem. Int. Ed.*, **2013**, *52*, 6306–6312. To obtain the qceims executables and the related tools and scripts, please contact [qceims@thch.uni-bonn.de](mailto:qceims@thch.uni-bonn.de)

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# 1 Installation

Untar the zipped archive:

```
tar -xvzf QCEIMS_4.0.tar.gz
```

The following files are being extracted:

1. `qceims` - main program (*executable*)
2. `plotms` - required for the generation of visualized spectra (*executable*)
3. `pqceims` - script that runs trajectories in parallel locally (*executable*)
4. `q-batch` - script that runs trajectories on a cluster with a queueing system (*executable*)
5. `getres` - script that gives the status of the parallel QCEIMS production run (*executable*)
6. `.mass.agr` - xmgrace template
7. `.XTBPARAM` - folder involving the xTB-parameterfiles `.param_gfn.xtb`, `.param_gfn2.xtb` and `.param_ipea.xtb`
8. `example` - folder hosting an example input and coordinate file.

- 1) Place the executables into your `$HOME/bin` directory or path.
- 2) Place the `.XTBPARAM` folder and `.mass.agr` file into your `$HOME` directory (these files can appear to be hidden).

For easy visualization of the calculated spectra we recommend the usage of **xmgrace**. Examples for an input file and coordinate file are to be found in the `examples` file.

**Hint:** If your queing system has a different name than `batch`, change this in the `q-batch` script.

## 1.1 Quantum Chemistry Codes Required

The low cost QC methods **GFN1-xTB** and **GFN2-xTB** are implemented in QCEIMS. No further rights or installations of third-party software is required and the methods can be called directly by the program. For this reason, using GFN1-xTB is set to run as **default**.

To run other QC methods, QCEIMS needs ORCA or TURBOMOLE to function. If available, place the following QC executables in `/usr/local/bin`:

- MND099
- DFTB+ - It is imperative that the Slater-Koster parameters `atom-atom.sp1`, which may or may not be included in your dftb+ version be placed in a directory called `/usr/local/dftb+`. Note that you need to have **root access** to your machine to place these files there.
- ORCA - All orca utilities must also be in your path.
- TURBOMOLE - The `ridft` and `rdgrad` programs of Turbomole 7.3 are used.

Please contact the development teams of these programs directly for executables since we do not have the right to distribute them.

## 2 Running QCEIMS

To obtain a QCEIMS simulated EI mass spectrum, please follow this protocol:

### 2.1 Setup

1. Prepare a file with the equilibrium structure of your desired molecule **M**.  
**Important:** This file has to be named **coord** and should have the **TURBOMOLE** coord format. In most cases you will have an **.xyz** file. This file can be easily converted by typing

```
x2t <xyzfile> > coord
```

if you have installed **TURBOMOLE**. If you do not have **TURBOMOLE**, you may have to write a script converting **.xyz** files to **TUROBOMOLE** coord files. Be advised that the coord file has to be in **atomic units**.

2. Prepare an input file called **qceims.in**. For the input options, see section 4 or the **qceims.in** file in the **examples** folder. If no such file is prepared, **default** options are: run GFN1-xTB with  $25 \times$  the number of atoms in the molecule trajectories (**ntraj**).

### 2.2 Preparing for Production Runs

3. Run QCEIMS for the first time. This will generate the first (ground state) trajectory from which information is taken for the production trajectories. Be aware that this already uses the QC method specified. After some steps for equilibration, the files **trjM** and **qceims.gs** are generated. It is highly recommended to conduct the initial run with a low-cost method, e.g. GFN-xTB (default) or OM2-D3.  
The implementation of an in-house force field for this purpose is planned for the near future.
4. When this is finished, run QCEIMS again. If the file **qceims.gs** exists, this will prepare the specifications for the parallel production run in the therefore created **TMPQCEIMS** folder.

### 2.3 Executing the Production Runs

5. If you use a computer cluster with a queing system, type **q-batch** for the execution of the batch script. This will initiate the production run with **ntraj** trajectories. For each trajectory this starts a single core calculation. **Reminder:** Look into the **q-batch** script, as it might need to be changed to match for your queing system.

If you want to run QCEIMS locally, use the **pqceims** script. You might want to leave your work station and even log out in the meantime. In this case, type:

```
nohup pqceims <# proc> &
```

where <# proc> gives the number of CPUs you want to use.

6. Optionally, check the status of your QCEIMS run by changing to your working directory and typing `getres`, which will provide an output of the form:

```
XXX runs done and written to tmpqceims.res/out
```

## 2.4 Plotting Mass Spectra

The `plotms` utility and the `~/mass.agr` template file for `xmgrace` are provided in order to visualize your results. The following protocol should apply. Be advised that you can plot your spectra as soon as the production run has started. This may be useful to check for convergence in case you are running more trajectories than actually needed for good statistics.

1. Change into your working directory and run `plotms`. This should generate a `mass.agr` file.
2. Download an experimental EI-MS mass spectrum from the NIST database if available (JCAMP-DX format). Copy it to the working directory as `exp.dat`. This step is only necessary if you want to compare simulated and experimental spectra directly.
3. With the `mass.agr` file, visualize your QCEIMS spectrum with:

```
xmgrace mass.agr
```

If you have downloaded the experimental spectrum, `plotms` reads the `exp.dat` and compares your calculated spectrum directly to the experiment (*inverted*).

## 3 Visualization of Trajectories

Trajectories are saved in the `TMPQCEIMS/TMP.NUM` directories, where `NUM` is the first number of the specific trajectory track to be visualized. There are two programs that can easily display the trajectories, which are saved in the `trj.NUM.x` files. One is `(g)molden`, the other one is `VMD`. Obtaining a video (`.avi`) of a given trajectory is possibly most easily done by loading the trajectory of choice into `VMD` (file type `.xyz`).

## 4 Keywords for qceims.in

The `qceims.in` input file may have the following structure:

```
<method>
<program>
<qc method>
<ip method>
<mo method>
ntraj <integer>
tmax <real>
tinit <real>
ieeatm <real>
iseed <integer>
eimp0 <real>
poisson (<real> <real>) / gauss (<real> <real>)
```

Specifying nothing else will set all internal parameters to their default values. The specifications are (line by line):

1. MS method.  
**Default:** Electron Impact (EI) is used. DEA as a negative ionization method can be used alternatively.
2. QC program.  
**Default:** GFNn-xTB methods as implemented in QCEIMS will be used. Alternatively use `orca` or `tmol`.
3. QC method.  
**Default:** GFN1-xTB. Possible keywords are given in table 2. For DFT settings, please see section 4.1 below.
4. IP method.  
**Default:** Depending on the method used. Sets the method for ionization-potential calculations, see table 3.
5. MO method.  
**Default:** `mo-xtb`. The method used to calculate the MO spectrum. Only alternative is `mo-orca`.
6. `ntraj`: Number of trajectories for the production run. This is important for the statistics.  
**Default:**  $25 \times$  the number of atoms.
7. `tmax`: Maximum MD time for a given trajectory track. This number is given in **ps!**  
**Default:** 5 ps.
8. `tinit`: The initial temperature of the vaporized substrate  $T_{\text{init}}$ .  
**Default:** 500 K. Caution! The input reading routine is case-sensitive.
9. `ieeatm`: Impact excess energy (IEE)/atom.  
**Default:** 0.6 eV/atom.
10. `iseed`: random number initialization to start different runs.

11. `eimp0`: For special applications, e.g. photoionization experiments, where the ionization energy may be much lower, this can be changed.  
**Default:** Parameter is set to 70 eV.
12. `poisson/gauss`: The IEE distribution, which is generated from the MO spectrum of the molecule in question, is set to a Poisson distribution by default, with two parameters that may be entered manually. For low ionization energies and for large molecules, the Poisson distribution may sometimes not converge. It is then advisable to switch to the normal distribution by specifying the `gauss` keyword. Again, 2 parameters may be entered, which basically manipulate the shape of the distribution. One should note that by manipulating the IEE distribution in such a way that it becomes unphysical, one can obtain spectra with either over- or under-fragmentation of the parent molecule. So be cautious with these parameters.

Table 1: QC Programs that can be called by QCEIMS 4.0.

| keyword           | program   | comment   |
|-------------------|-----------|---|
| <code>xtb</code>  | QCEIMS    | built-in GFN1-xTB Hamiltonian                                       |
| <code>xtb2</code> | QCEIMS    | built-in GFN2-xTB Hamiltonian                                       |
| <code>mndo</code> | MNDO      | semiempirical QC program available from Walter Thiel.               |
| <code>dftb</code> | DFTB+     | semiempirical tight-binding QC program free for academic use.       |
| <code>tmol</code> | TURBOMOLE | The <code>ridft</code> and <code>rdgrad</code> programs are called. |
| <code>orca</code> | ORCA      | large QC program package free for academic use.                     |

The GFN1- and GFN2-xTB methods are available without any third-party software. All other semi-empirical methods have to be explicitly called with their corresponding program, that can be found in table 2:

Table 2: Semi-empirical QC methods available in QCEIMS 4.0.

| keyword           | semi-empirical method | comment                          | QC Program used   |
|-------------------|-----------------------|----------------------------------|-------------------|
| <code>xtb</code>  | GFN1-xTB              | D3-dispersion correction         | -                 |
| <code>xtb2</code> | GFN2-xTB              | <b>D4</b> -dispersion correction | -                 |
| <code>am1</code>  | AM1-D3                | D3-dispersion correction         | <code>mndo</code> |
| <code>om2</code>  | OM2-D3                | D3-dispersion correction         | <code>mndo</code> |
| <code>om3</code>  | OM3-D3                | D3-dispersion correction         | <code>mndo</code> |
| <code>pm3</code>  | PM3-D3                | D3-dispersion correction         | <code>mndo</code> |
| <code>dftb</code> | DFTB3-D3              | D3-dispersion correction         | <code>dftb</code> |

To decide which method should be used, **it is recommended to read the original publication<sup>1</sup> first!**

The usage of PM3 or AM1 are **not** recommended, due to their bad performances with QCEIMS!!! For using GFN1-xTB<sup>2</sup> and GFN2-xTB<sup>3</sup> with QCEIMS, refer to the publications<sup>4,5</sup>.

Table 3: Methods for IP-calculations QC methods available in QCEIMS 4.0.

|         |          |  |
|---------|----------|--|
| ip-xtb  | QCEIMS   | calculation of IPs/EAs with IPEA parameter ( <b>default</b> )          |
| ip-xtb2 | QCEIMS   | calculation of IPs/EAs with GFN2-xTB parameter ( <b>xtb2 default</b> ) |
| ip-mndo | MNDO     | calculation of IPs/EAs with OM2  |
| ip-orca | ORCA     | $\Delta$ SCF ORCA PBE0/SV(P) calculation of IPs/EAs                    |
| ip-tmol | TUBOMOLE | $\Delta$ SCF TM PBE0/SV(P) calculation of kIPs/EAs                     |

Default IP calculations are done with GFN1-xTB, using the IPEA parameterfiles (`.param_ipea.xtb`) or GFN2-xTB when using the `xtb2` keyword (`.param_gfn2.xtb`). To change this, write `ip-` and the desired method. It is **not** recommended to use IPEA-xTB for calculations of transition metal complexes.

#### 4.1 Functionals and Basis Sets Available with ORCA/TURBOMOLE

Table 4 gives the functional and basis set combinations that are available with TURBOMOLE 7.3 and/or ORCA 4.0. Automatic usage of the D3BJ dispersion correction is indicated.

Table 4: DFT methods and basis-sets available with ORCA 4.0/TURBOMOLE 7.3

| keyword      | method      | DFT type  | available with |
|--------------|-------------|---|----------------|
| pbe          | PBE-D3BJ    | GGA   | ORCA/TM        |
| pbe0         | PBE0-D3BJ   | global hybrid   | ORCA/TM        |
| pbeh3c       | PBEh3-c     | global hybrid   | ORCA           |
| revpbe       | REVPBE-D3BJ | GGA   | ORCA           |
| blyp         | BLYP-D3BJ   | GGA   | ORCA/TM        |
| b3lyp        | B3LYP-D3BJ  | global hybrid   | ORCA/TM        |
| tpss         | TPSS-D3BJ   | meta-GGA  | ORCA/TM        |
| b97d         | B97-D3BJ    | GGA   | ORCA/TM        |
| bp86         | BP86-D3BJ   | GGA   | ORCA/TM        |
| b3pw91       | B3PW91-D3BJ | global hybrid   | ORCA           |
| m062x        | M062X       | meta-GGA global hybrid                                | ORCA/TM        |
| pw6b95       | PW6B95-D3BJ | meta-GGA global hybrid                                | ORCA/TM        |
| keyword      | basis set   | basis set type  | available with |
| SV           | SV          | Karlsruhe split valence (double $\zeta$ )             | ORCA/TM        |
| SVx          | SV+pol.     | same as above, polarization functions on O, N         | ORCA           |
| SV(P)        | SV+pol.     | same as above, polarization functions on all except H | ORCA/TM        |
| SVP          | SV+pol.     | same as above, polarization functions on all          | ORCA/TM        |
| TZVP         | TZ+pol.     | triple $\zeta$ , polarization functions on all        | ORCA/TM        |
| def2-SVP     | DZ+pol.     | Karlsruhe double $\zeta$                              | ORCA/TM        |
| def2-TZVP    | TZ+pol.     | Karlsruhe triple $\zeta$                              | ORCA/TM        |
| ma-def2-SVP  | DZ+pol.+aug | Karlsruhe double $\zeta$ , minimally augmented        | ORCA           |
| ma-def2-TZVP | TZ+pol.+aug | Karlsruhe triple $\zeta$ , minimally augmented        | ORCA           |

## 4.2 Command Line Options

Command line options of QCEIMS, version 3.7

| argument      | effect   |
|---------------|--|
| -c            | check IEE but do nothing (requires ground state trajectory). Writes IEE distribution in file <code>eimp.dat</code>                         |
| -p            | normal production (fragmentation) mode. Possible in any existing <code>TMPCCEIMS/TMP.XXX</code> directory.                                 |
| -only         | use the requested QC (as specified in <code>qceims.in</code> ) and do a single-point energy  |
| -e0           | same as above, charge = 0  |
| -e1           | same as above, charge = 1  |
| -qcp <string> | string = path to the QC code <code>/usr/local/bin</code> is default  |
| -unity        | enforces uniform velocity scaling during the vibrational heating phase, which is automatically done if the system is larger than 35 atoms. |

## 5 Various MS Methods

### 5.1 EI - Electron Impact

For default, the EI method for mass spectroscopy is used. To be sure to use this in the future, type `ei` into the `qceims.in` file.

### 5.2 DEA - Negative Ion Mode

Negative ion mode simulations can be executed by the following keywords in `qceims.in`:

```
dea
scan 1
upper 15
lower 0
<program>
<functional>
<basis>
```

The `dea` keyword switches on the negative ion mode. Instead of the IEE distribution, the excess energy is scanned by switching on the `scan` keyword, with `upper/lower` bounds in eV. The negative ion mode is enabled with the `xtb` method or the `orca` program for DFT methods. The `ma-def2-SVP/ma-def2-TZVP` basis sets are recommended for anion calculations. The `xtb` negative ion simulations are not recommended for production level for accuracy reasons.



## 6 Making Trajectory Movies Using VMD

The `msmovie` and `movie.tcl` scripts for VMD generate a visualization using the dynamic bonds graphical representations setting. This allows for movie generation employing the VMD movie maker plug-in. Simply type `msmovie X Y` in the working directory to load the trajectory `TMPQCEIMS/TMP.X/trj.X.Y`. For instance, `msmovie 1 1` loads the first trajectory of the first folder. Some adjustments according to personal preferences for movie-making may have to be made in these scripts.

### References

- [1] Grimme, S. Towards First Principles Calculation of Electron Impact Mass Spectra of Molecules. *Angew. Chem. Int. Ed.* **2013**, *52*, 6306 – 6312.
- [2] Grimme, S.; Bannwarth, C.; Shushkov, P. A Robust and Accurate Tight-Binding Quantum Chemical Method for Structures, Vibrational Frequencies, and Noncovalent Interactions of Large Molecular Systems Parametrized for All spd-Block Elements ( $Z = 1-86$ ). *J. Chem. Theory Comput.* **2017**, *13*, 1989–2009.
- [3] Bannwarth, C.; Ehlert, S.; Grimme, S. GFN2-xTB - An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019**, *15*, 1652–1671.
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