Lecture:

Introduction to the **ORCA** Program System

Frank Wennmohs

Max Planck Institute for
Chemical Energy Conversion
Stiftstr. 34-36
D-45470 Mülheim an der Ruhr
Germany

The Computational Environment

In order to run calculations with **ORCA**, three things are necessary:

1. Installation of the *ORCA* program

2. Using a text-editor to specify the calculation details, i. e. the ***input file***

3. Running the *ORCA* program (in a cluster environment possibly controlled by a batch system)

NOTE: **ORCA** is available for all popular platforms:
   - ★ Windows,
   - ★ MacOS,
   - ★ Linux

The Computational Environment

★ *ORCA* is available for the popular Windows, Mac OS X, and Linux platforms.

★ *ORCA* is distributed as an ***archive*** for all platforms. In this archive resides a **directory** with all **executables**. There are plenty of programs for extracting files from archives on all platforms (gzip, tar, zip/unzip,...).

★ On the following slides it will be shown how to run a calculation on Windows Vista/7, Mac OS X, and Linux.

★ It is assumed, that the orca executables reside in a directory '**orca**'

Configuring *ORCA* under Windows Vista / 7

Setting the **PATH variable** to the *ORCA* directory (with administrator rights)
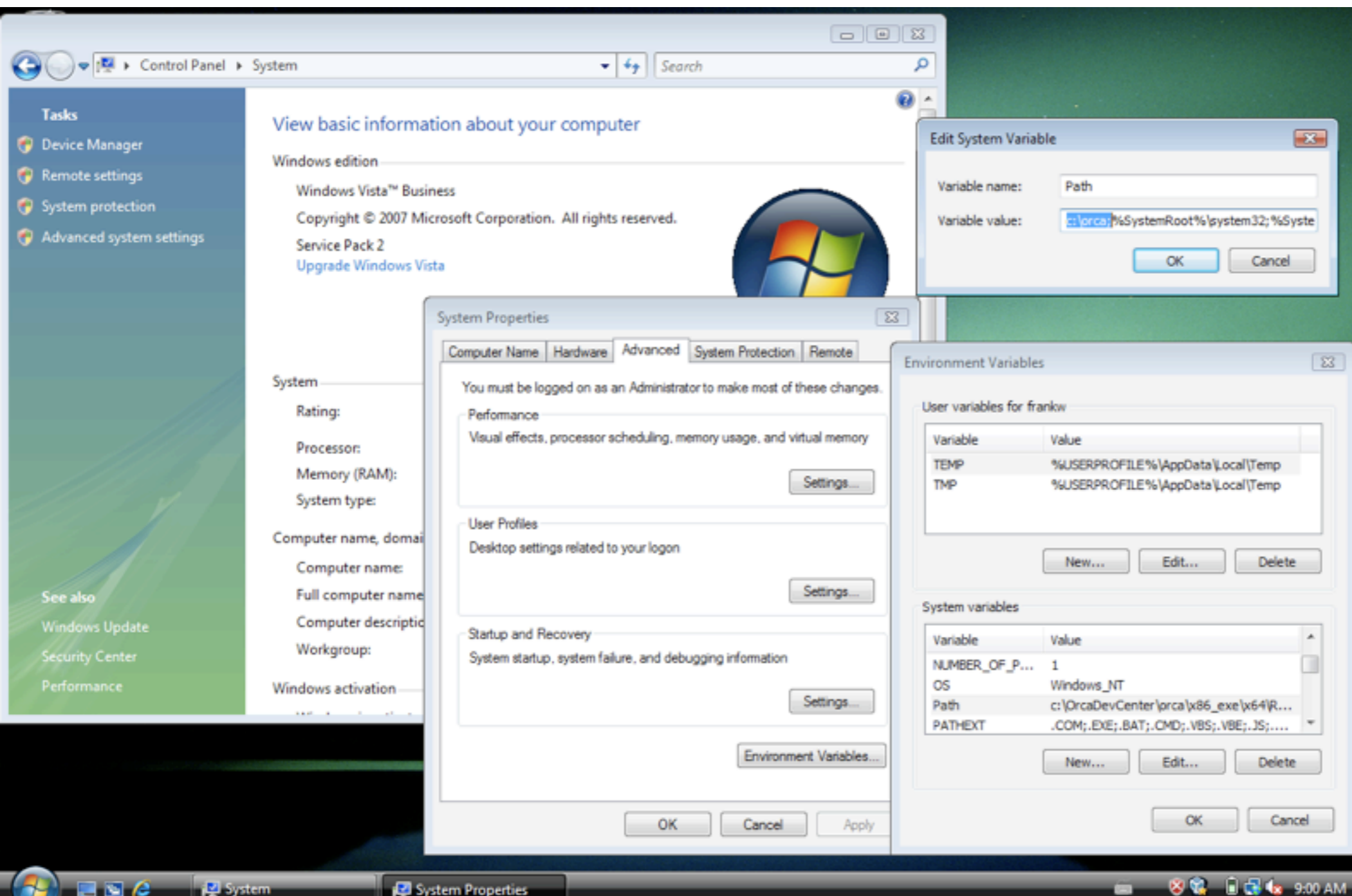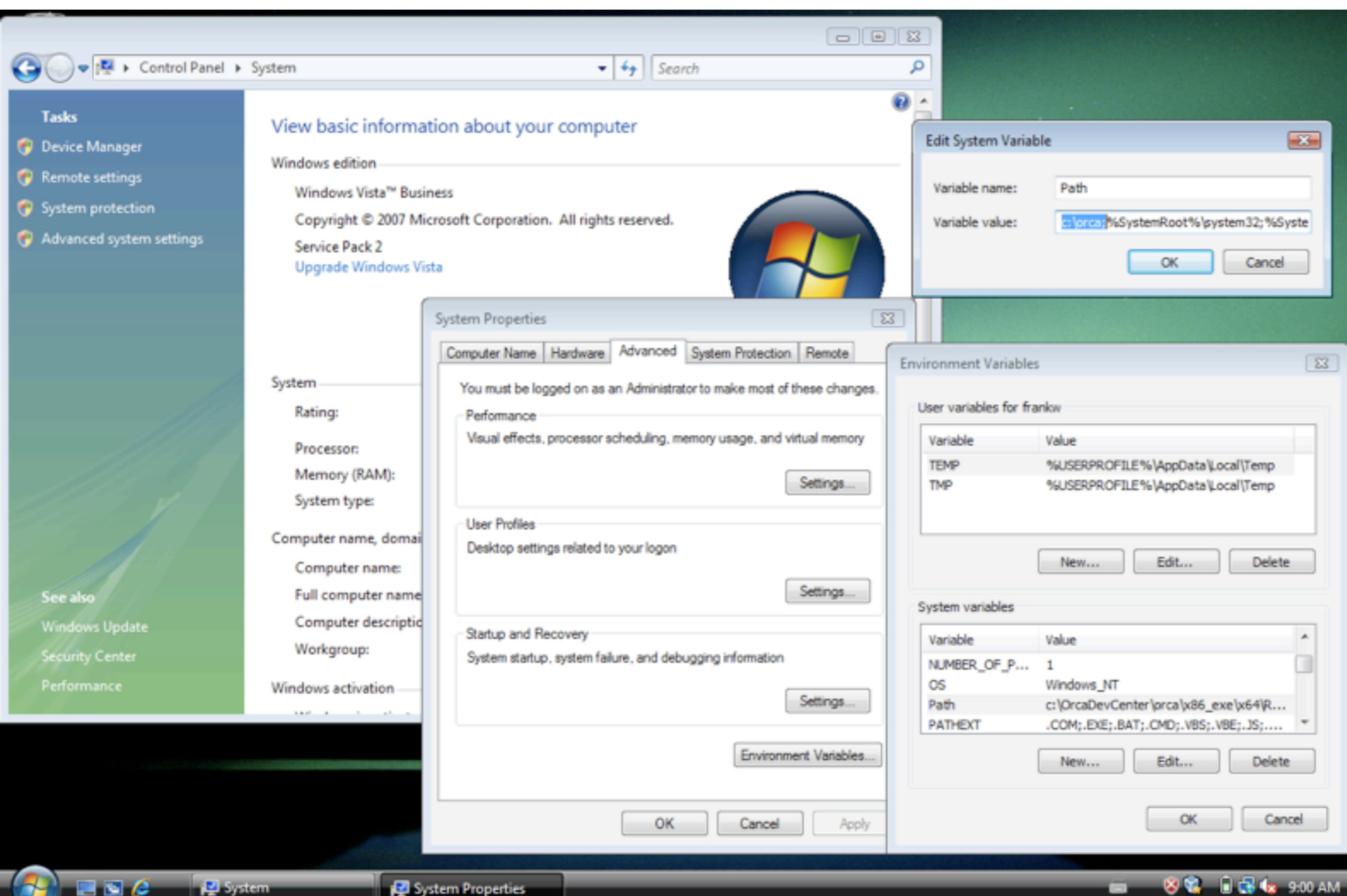

The Path Variable can be accessed via

Control Panel > System > Advanced system Settings

Here it is assumed that ORCA resides in **c:\orca**

Configuring *ORCA* under Windows Vista / 7

Setting the **PATH variable** to the *ORCA* directory (as normal user)

The Path Variable can be accessed via

Control Panel > User Accounts and Family Safety > User Accounts > Change my environment variables

Here it is assumed that ORCA resides in **c:\orca**

Editing Textfiles under Windows Vista / 7
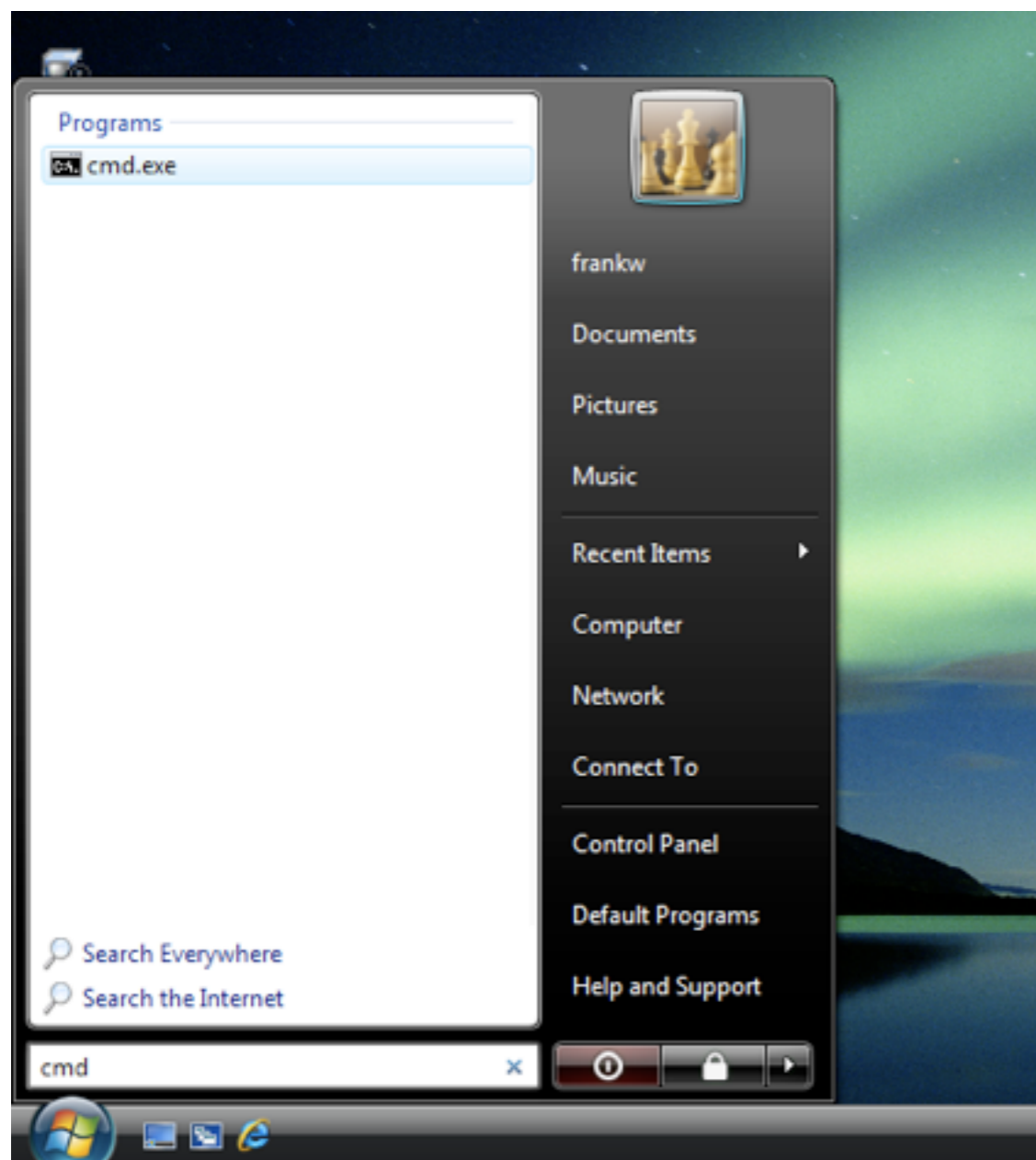
Editing Text using **Notepad**
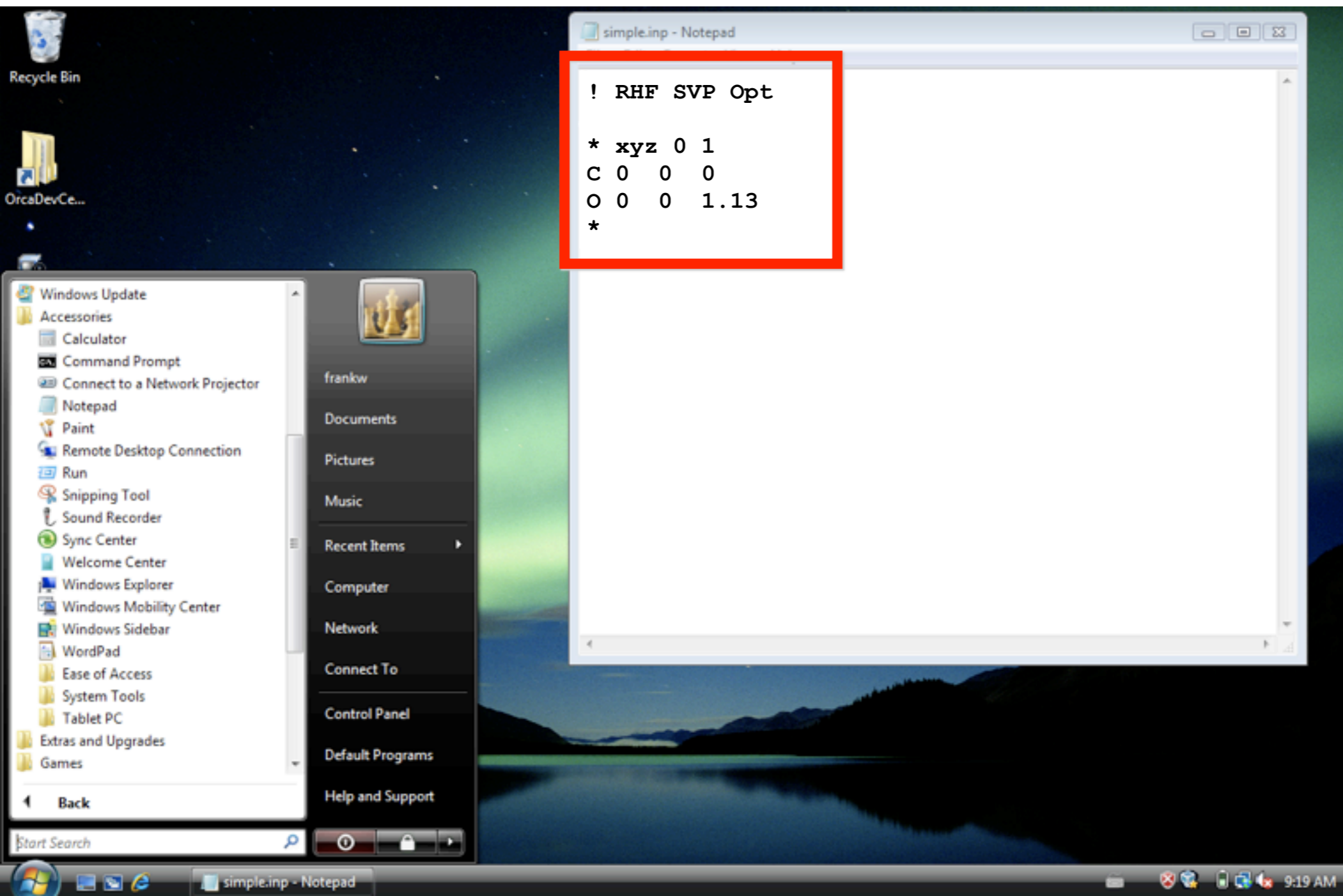
The **Notepad** application can be found under **Accessories**

Of course all other Text-editors can be used on Windows.

(But not Word!) Textfiles have to be plain ASCII !

Running *ORCA* under Windows Vista / 7

Opening a command window:

Enter

'**cmd**'

into the **Search line,**

then cmd.exe will be executed
upon pressing **RETURN**.

Running *ORCA* under Windows Vista / 7

Executing the **ORCA** program
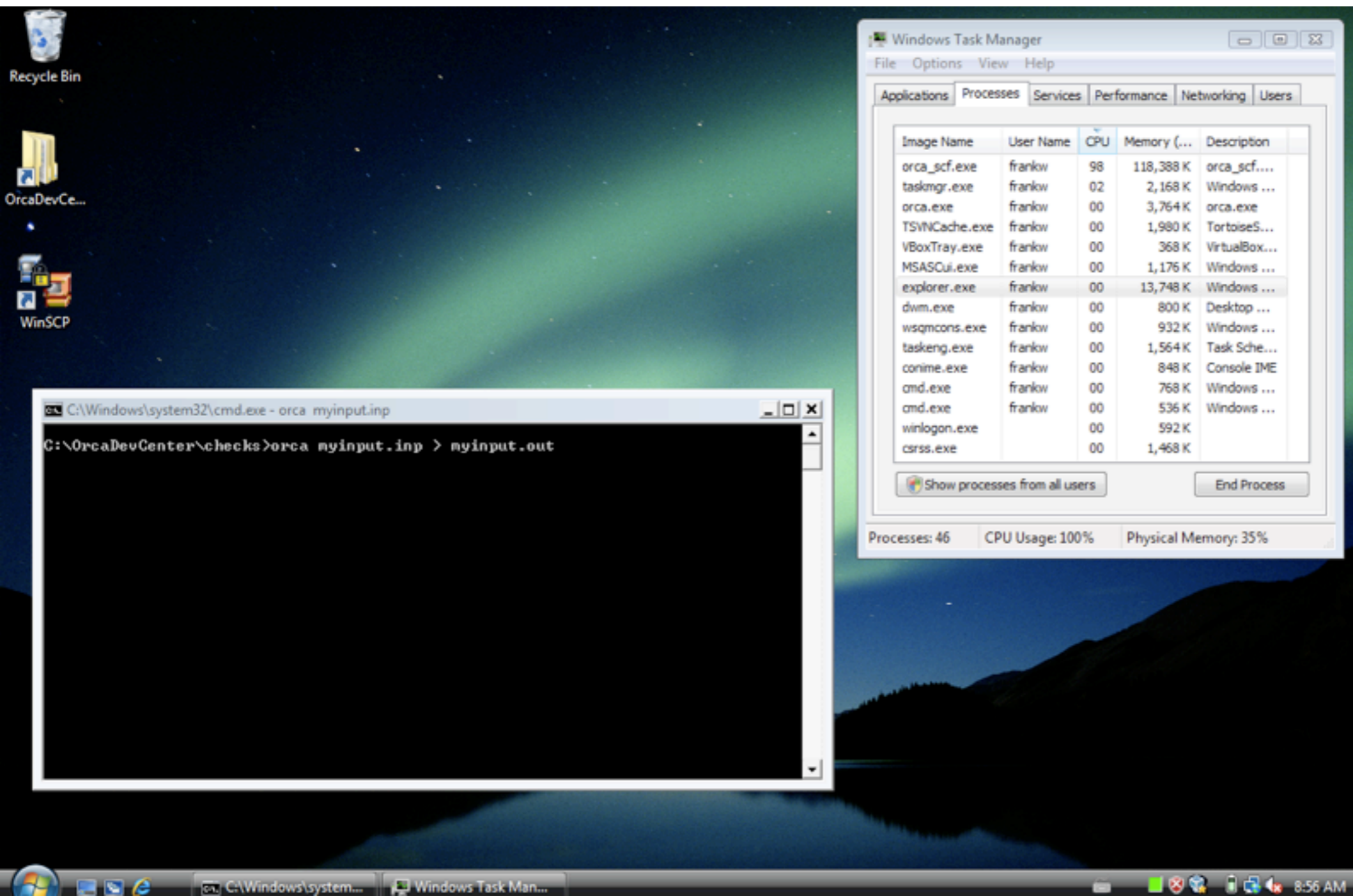
Once **ORCA** is in the **PATH**, you can run jobs from any directory you want

Using the sequence **orca myinput.inp > myinput.out'** the output will be put in a file named like that.

The **TaskManager** is a handy tool to check if the calculation is still running.

Getting Started with *ORCA* under Mac OS X
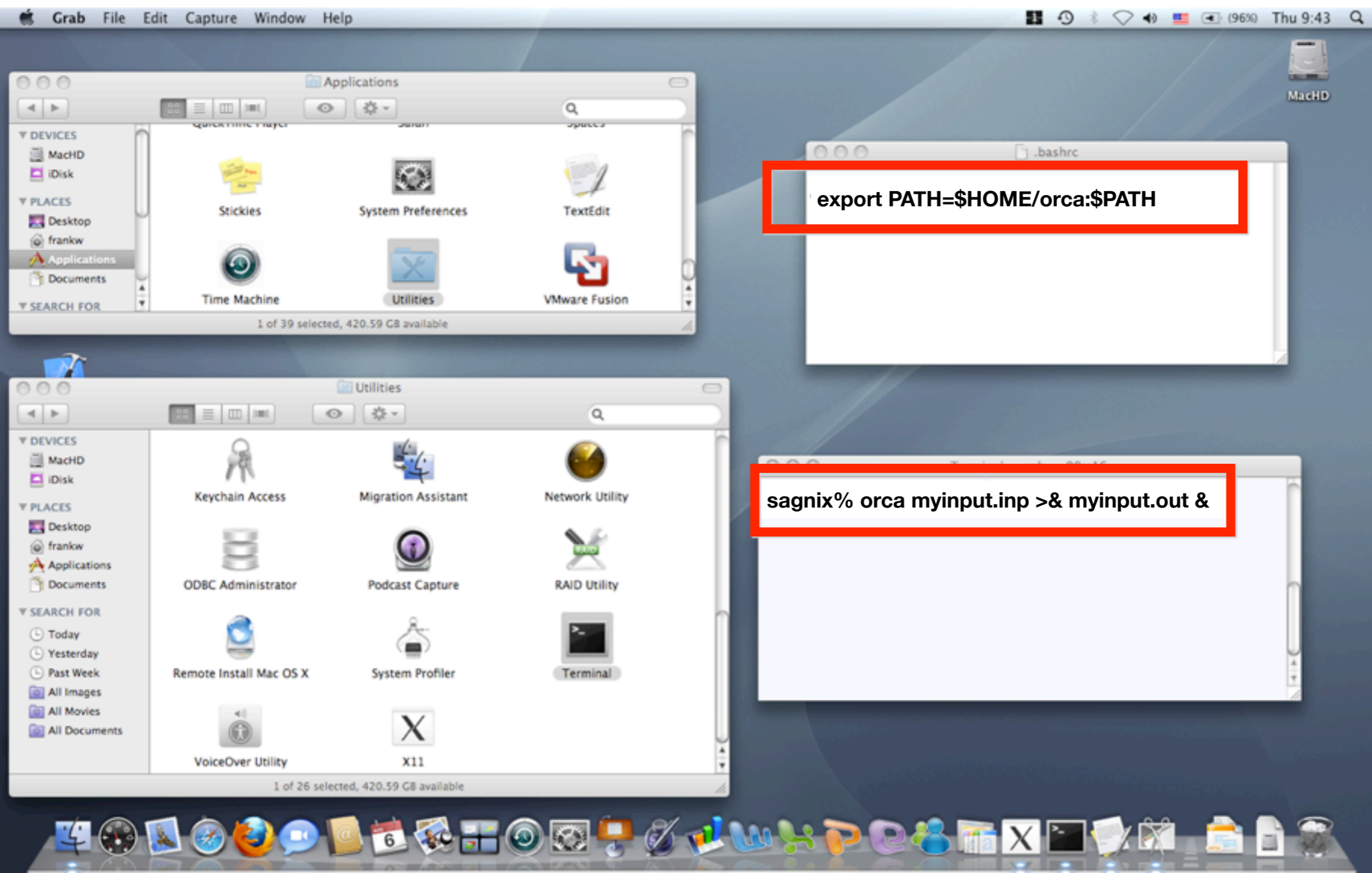
TextEdit & Terminal

Configuring *ORCA* under Mac OS X

TextEdit & Terminal
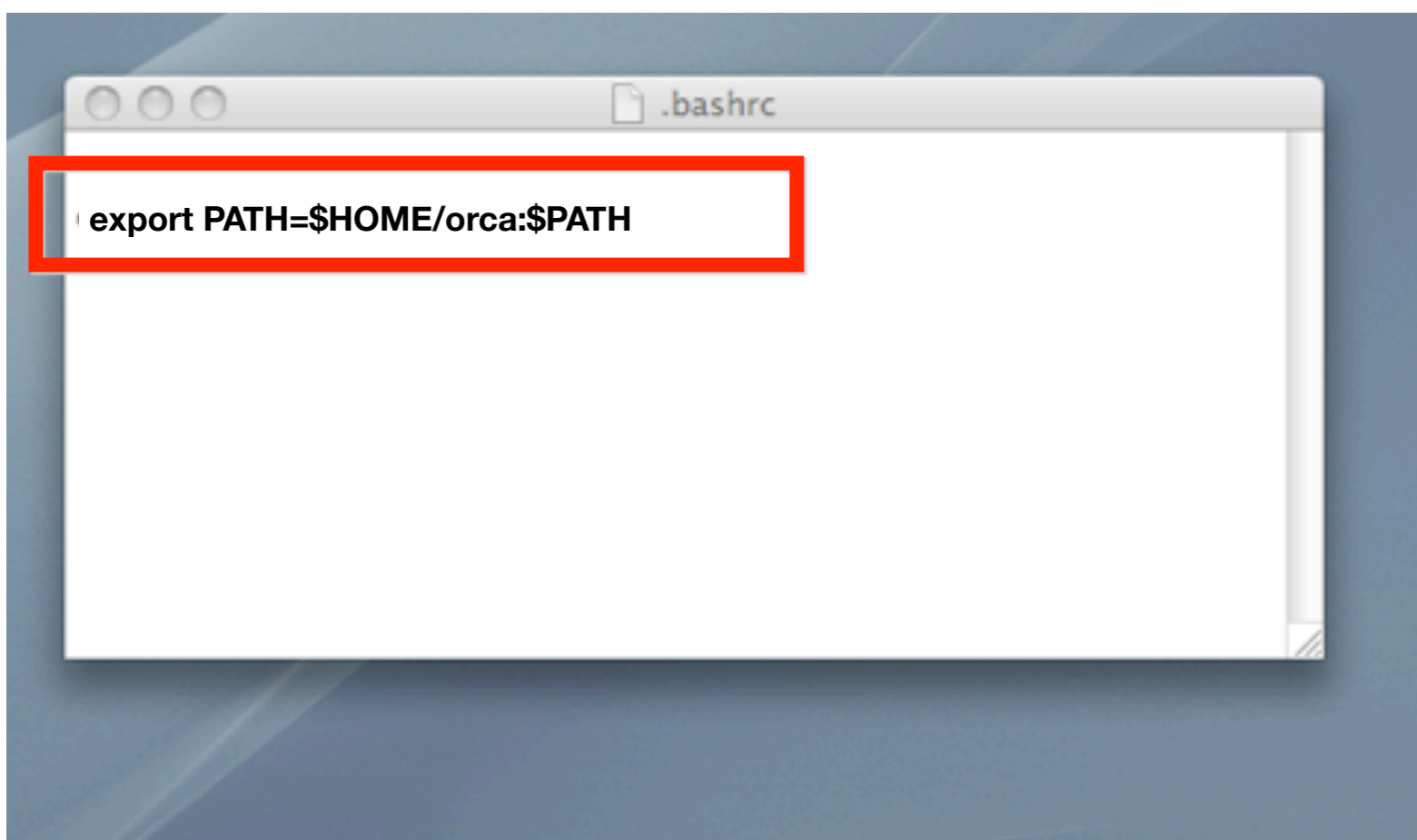
ORCA path entered in the file

'**.bashrc**'
or
'**.bash_profile**'

using TextEdit

Running *ORCA* under Mac OS X

sagnix% orca simple.inp >& simple.out &

Configuring *ORCA* under Linux

Linux (Ubuntu 9.10): Setting the PATH variable
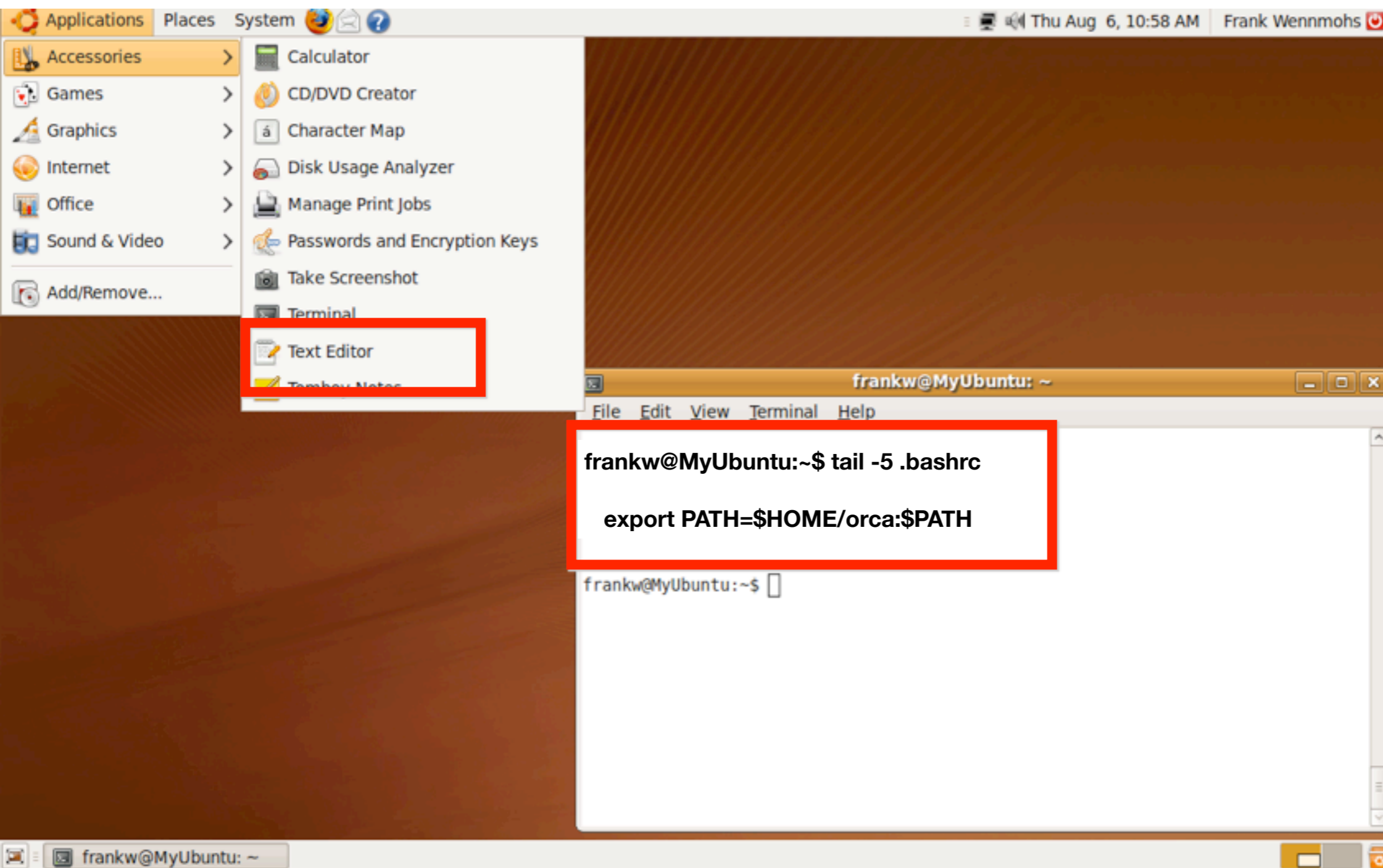
Setting the **PATH** variable is done in the file

'.**bashrc**'

You can use the '**Text Editor**'

to add the line shown.

Running *ORCA* under Linux

Linux (Ubuntu 9.10): Text Editor (gedit) & ORCA execution
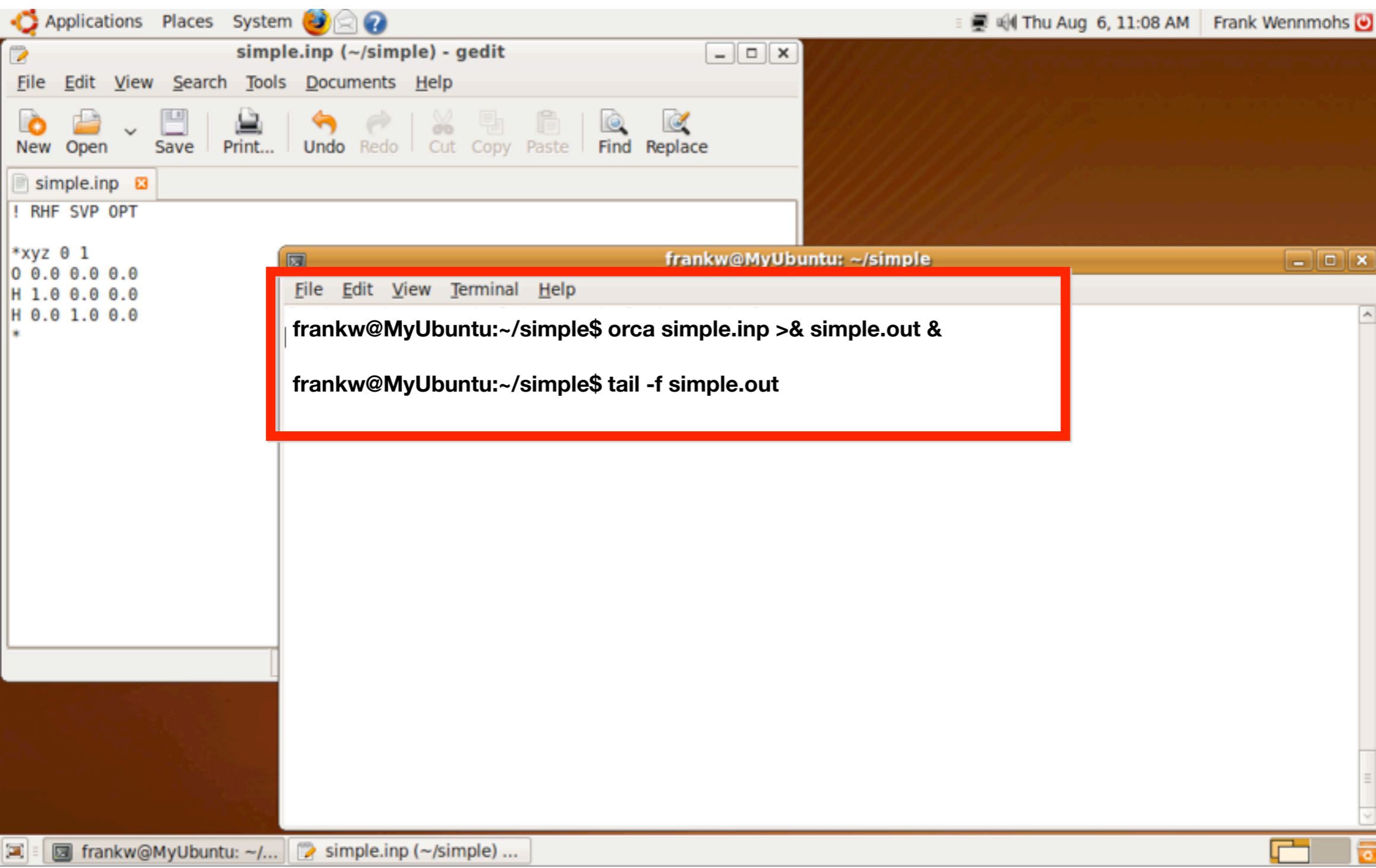
Especially under Linux there is an uncountable number of text-editors.

Very popular ones are **Vim**, **Emacs**, **NEdit**, **Kate**, etc.

The *ORCA* Project

Philosophy of the *ORCA* Project

General goal: Create a powerful tool to allow connection between theory and experiment. → Observables! (Spectra, Structures, Energies)

Design principles:

1. The program should be as flexible as possible
2. The program should be as efficient as possible (parallel, efficient algorithms, BLAS libraries)
3. The program should be as comprehensive as possible
4. The program should be as user friendly as possible
5. The program should be easily extendable (highly modular)
6. The source code should be as clean and well structured as possible (C++ rather than Fortran).
7. The program should be platform independent

Tasks to be Performed

- Calculation of single point energies
  - Hartree-Fock calculations: RHF, UHF and ROHF
  - Density functional calculations
- Optimization of molecular structures
  - Equilibrium geometries
  - Transition states and reaction rates
- Calculation of vibrational frequencies
  - Characterization of stationary points
  - Thermodynamic properties
  - Vibrational spectra
- Calculation of ground state properties
  - Looking at charge distributions and orbitals
  - IR+Raman spectra
  - NMR spectra
  - EPR spectra and exchange couplings
  - Mössbauer spectra
- Calculation of excited states and their properties
  - DFT calculation of absorption and CD spectra
  - *Ab initio* calculation of absorption and CD spectra
  - Advanced: Resonance-Raman, X-Ray absorption, forbidden transitions, MCD, Excited state geometry optimizations, ...

Common Jobs in Computational Chemistry

- Energy Calculations

- Geometry Optimizations

- Frequency Calculations

- Transition States

Common Jobs in Computational Chemistry

- Energy Calculations

- Geometry Optimizations

90%
Of all Calculations!

- Frequency Calculations

- Transition States

First Stop: Energy Calculations

A First *ORCA* Job

DFT Functional   The basis set

A comment line

Start a keyword line

```
# A simple single point DFT calculation
! RKS B3LYP SVP LARGEPRINT

* xyz 0 1
C 0 0 0
O 0 0 1.128
*
```

Restricted (closed-shell) Calculation

Start of coordinate definition

Coordinates are defined as cartesian coordinates

End of coordinate definition

Total Charge is zero and Multiplicity (2*S+1) is one (no unpaired electrons)

One atom each line:
atomic symbol x y z coordinates in Angström

Output of Single Points

We first echo the input file and some references to the basis sets used. Then you get information on the job-type, the input coordinates in various formats and the basis set

```
*****************************
* Single Point Calculation *
*****************************


------------------------------------
CARTESIAN COORDINATES (ANGSTROEM)
------------------------------------
  C      0.000000    0.000000    0.000000
  O      0.000000    0.000000    1.130000


----------------------
BASIS SET INFORMATION
----------------------
There are 2 groups of distinct atoms

 Group   1 Type C  : 7s4p1d contracted to 3s2p1d pattern {511/31/1}
 Group   2 Type O  : 7s4p1d contracted to 3s2p1d pattern {511/31/1}
```

Next the one-electron integrals are calculated (and perhaps also the two-electron integrals if **conv** if requested for "conventional SCF")

```
--------------------------------------------------------------------------
                    ORCA GTO INTEGRAL CALCULATION
--------------------------------------------------------------------------

               BASIS SET STATISTICS AND STARTUP INFO

# of primitive gaussian shells          ...    24
# of primitive gaussian functions       ...    48
# of contracted shell                    ...    12
# of contracted basis functions          ...    28
Highest angular momentum                 ...     2
Maximum contraction depth                ...     5
Integral threshhold          Thresh  ... 1.000e-010
Primitive cut-off            TCut    ... 3.000e-012
```

Next the SCF program is taking over and commences with giving all details about the SCF settings

```
------------
SCF SETTINGS
------------
Hamiltonian:
 Density Functional     Method       .... DFT(GTOs)
 Exchange Functional    Exchange     .... B88
   X-Alpha parameter    XAlpha       .... 0.666667
   Becke's b parameter  XBeta        .... 0.004200
 Correlation Functional Correlation  .... LYP
 LDA part of GGA corr.  LDAOpt       .... VWN-5
 Gradients option       PostSCFGGA   .... off
 Hybrid DFT is turned on
   Fraction HF Exchange ScalHFX      .... 0.200000
   Scaling of DF-GGA-X  ScalDFX      .... 0.720000
   Scaling of DF-GGA-C  ScalDFC      .... 0.810000


General Settings:
 Integral files         IntName      .... JOB-01
 Hartree-Fock type      HFTyp        .... RHF
 Total Charge           Charge       ....    0
 Multiplicity           Mult         ....    1
 Number of Electrons    NEL          ....   14
 Basis Dimension        Dim          ....   28
 Nuclear Repulsion      ENuc         ....     22.4778902655 Eh


Convergence Tolerance:
 Energy Change          TolE         .... 1.000e-008 Eh
 Max Density Change     TolMaxP      .... 1.000e-007
 RMS Density Change     TolRMSP      .... 1.000e-008
 DIIS Error             TolErr       .... 1.000e-007


Diagonalization of the overlap matrix:
Smallest eigenvalue                   ... 1.911e-002
Time for diagonalization              ...      0.010 sec
Time for construction of square roots ...      0.030 sec
Total time needed                     ...      0.040 sec
```

The integration grid is produced and the initial guess performed

```
-------------------
DFT GRID GENERATION
-------------------

General Integration Accuracy     IntAcc     ...     4.010

Total number of grid points                ...      5057

-------------------------------
INITIAL GUESS: MODEL POTENTIAL
-------------------------------
Loading Hartree-Fock densities                 ... done
....etc
Now organizing SCF variables                   ... done
                    -------------------
                     INITIAL GUESS DONE
                    -------------------
```

Now we are ready to start the SCF iterations

```
--------------
SCF ITERATIONS
--------------
            ***  Starting incremental Fock matrix formation  ***
                     ***Turning on DIIS***

                   ----------------------------
                   !       ITERATION    0   !
                   ----------------------------
     Total Energy       :     -112.951951547431 Eh
     Energy Change      :     -112.951951547431 Eh
     MAX-DP             :        0.674569966353
     RMS-DP             :        0.053899776162
     Actual Damping     :        0.0000
     Int. Num. El.      :       14.00002071 (UP=      7.00001035
     Exchange           :      -10.98287769
     Correlation        :       -0.58429246
     DIIS-Error         :        0.450135783168
```

Which hopefully eventually converge and:

```
      ******************************************************
      *                     SUCCESS                        *
      *          SCF CONVERGED AFTER  11 CYCLES            *
      ******************************************************
```

The total energy and its components are printed

```
----------------
TOTAL SCF ENERGY
----------------

Total Energy       :         -113.17273851 Eh         -3079.50944 eV

Components:
Nuclear Repulsion  :           22.47789027 Eh           611.63913 eV
Electronic Energy  :         -135.65062877 Eh         -3691.14856 eV

One Electron Energy:         -198.09397475 Eh         -5390.27572 eV
Two Electron Energy:           62.44334598 Eh          1699.12715 eV

Virial components:
Potential Energy   :         -225.62136955 Eh         -6139.31540 eV
Kinetic Energy     :          112.44863104 Eh          3059.80596 eV
Virial Ratio       :            2.00643945
```

Next you get the orbital energies printed:

```
----------------
ORBITAL ENERGIES
----------------

  NO   OCC         E(Eh)            E(eV)
   0   2.0000    -19.243280       -523.6231
   1   2.0000    -10.301611       -280.3141
   2   2.0000     -1.152619        -31.3636
   3   2.0000     -0.568518        -15.4698
   4   2.0000     -0.476766        -12.9731
   5   2.0000     -0.476766        -12.9731
   6   2.0000     -0.373742        -10.1698
   7   0.0000     -0.026298         -0.7156
   8   0.0000     -0.026298         -0.7156
   9   0.0000      0.221613          6.0303
  10   0.0000      0.400346         10.8937
  11   0.0000      0.457384         12.4458
  12   0.0000      0.457384         12.4458
...
```

Now comes the "soft science" (e.g. population analysis of the SCF density matrix

The Löwdin analysis contains a detailed breakdown of the MOs in terms of angular momentum components of each atom. This helps a lot when you select the orbitals for plotting.

```
        ********************************
        * MULLIKEN POPULATION ANALYSIS *
        ********************************


-----------------------
MULLIKEN ATOMIC CHARGES
-----------------------
   0 C :    0.016669
   1 O :   -0.016669
Sum of atomic charges:   -0.0000000


-----------------------------------
MULLIKEN REDUCED ORBITAL CHARGES
-----------------------------------
  0 C s      :     3.834569  s :     3.834569
      pz     :     1.009723  p :     2.073008
      px     :     0.531642
      py     :     0.531642
      dz2    :     0.027088  d :     0.075754
      dxz    :     0.024333
      dyz    :     0.024333
      dx2y2  :     0.000000
      dxy    :     0.000000
  1 O s      :     3.737862  s :     3.737862
      pz     :     1.381818  p :     4.256855
      px     :     1.437518
      py     :     1.437518
      dz2    :     0.008940  d :     0.021953
      dxz    :     0.006506
      dyz    :     0.006506
      dx2y2  :     0.000000
      dxy    :     0.000000


-----------------------
MULLIKEN OVERLAP CHARGES
-----------------------
B( 0-C , 1-O ) :    1.3340
```

```
        *******************************
        * LOEWDIN POPULATION ANALYSIS *
        *******************************


-----------------------
LOEWDIN ATOMIC CHARGES
-----------------------
   0 C :   -0.050462
   1 O :    0.050462

  etc.
-------------------------------------------
LOEWDIN REDUCED ORBITAL POPULATIONS PER MO
-------------------------------------------
THRESHOLD FOR PRINTING IS 0.1%
                     0         1         2         3         4         5
ORB-EN         -19.24328 -10.30161  -1.15262  -0.56852  -0.47677  -0.47677
OCC              2.00000   2.00000   2.00000   2.00000   2.00000   2.00000
                --------  --------  --------  --------  --------  --------
 0 C  s            0.0      99.5      18.6      11.5       0.0       0.0
 0 C  pz           0.1       0.0      16.7       4.8       0.0       0.0
 0 C  px           0.0       0.0       0.0       0.0       6.9      20.9
 0 C  py           0.0       0.0       0.0       0.0      20.9       6.9
 0 C  dz2          0.1       0.0       2.4       0.0       0.0       0.0
 0 C  dxz          0.0       0.0       0.0       0.0       0.5       1.5
 0 C  dyz          0.0       0.0       0.0       0.0       1.5       0.5
 1 O  s           99.8       0.1      54.7      20.8       0.0       0.0
 1 O  pz           0.0       0.4       7.3      62.3       0.0       0.0
 1 O  px           0.0       0.0       0.0       0.0      17.4      52.4
 1 O  py           0.0       0.0       0.0       0.0      52.4      17.4
 1 O  dz2          0.0       0.1       0.3       0.6       0.0       0.0
 1 O  dxz          0.0       0.0       0.0       0.0       0.1       0.3
 1 O  dyz          0.0       0.0       0.0       0.0       0.3       0.1

                     6         7         8         9        10        11
               -0.37374  -0.02630  -0.02630   0.22161   0.40035   0.45738
                2.00000   0.00000   0.00000   0.00000   0.00000   0.00000
                --------  --------  --------  --------  --------  --------
 0 C  s           49.2       0.0       0.0      33.5      60.9       0.0
 0 C  pz          39.3       0.0       0.0      46.5      35.3       0.0
 0 C  px           0.0      15.2      54.7       0.0       0.0      15.5
 0 C  py           0.0      54.7      15.2       0.0       0.0      81.4
 0 C  dz2          0.8       0.0       0.0       7.8       1.2       0.0
 0 C  dxz          0.0       0.4       1.5       0.0       0.0       0.1
 0 C  dyz          0.0       1.5       0.4       0.0       0.0       0.3
 1 O  s            2.0       0.0       0.0      12.0       0.6       0.0
 1 O  pz           8.8       0.0       0.0       0.2       1.0       0.0
 1 O  px           0.0       5.9      21.2       0.0       0.0       0.3
 1 O  py           0.0      21.2       5.9       0.0       0.0       1.5
 1 O  dz2          0.0       0.0       0.0       0.0       0.9       0.0
 1 O  dxz          0.0       0.2       0.9       0.0       0.0       0.1
 1 O  dyz          0.0       0.9       0.2       0.0       0.0       0.7
```

Looking at Orbitals

There is a utility program `orca_plot` which lets you generate graphics information. The information about the MOs, the geometry and the basis set is stored in the so called gbw-File (‚geometry-basis-wavefunction').

To generate the plot information interactively use:

```
orca_plot myjob.gw -i
```

You will get a „stone-age" menu which you can use to generate the necessary files.

1. Press 5 ENTER to choose the output formation. (press 7 ENTER for gaussian cube, the preferred format)
2. Press 4 ENTER to choose the number of grid intervals. Something like 40 will be o.k. For high resolution on larger molecules choose 65-75.
3. To plot an orbital from a closed shell calculation press 3 ENTER and choose 0 ENTER. For spin-up from UHF/UKS the same. For spin down from UHF/UKS choose 1 ENTER.
4. Press 2 ENTER and enter the number of the MO that you want to plot. NOTE THAT COUNTING STARTS WITH 0!!!
5. Press 10 ENTER to generate the output file.
6. Repeat steps 4 and 5 until all desired files are produced

The `orca_plot` program automatically produces an **,xyz' file** which contains the molecular coordinates.

We presently like the ***Chimera*** program for vizualization. There are many free alternatives such as *Molekel, gOpenMol, Molden*,... any program that reads .xyz and .cube files

With **Chimera**, do the following:

1. Start Chimera
2. Choose „**File Open**" and navigate to open the .xyz file of interest
3. Choose „**Presets → Publication 1**"
4. Choose „**Actions → Atoms&Bonds → ball & stick**"
5. Choose „**Actions → Color → By element**"
6. Choose „**Tools → Volume Data → Volume Viewer**"
7. Choose „**File → Open Map**" and **Gaussian Cube format** and open the cube file of interest
8. Enter in „**Level**" 0.03 and press ENTER. Then click on **Color** and choose red (or whatever you like)
9. Hold the Ctrl-key and click on the negative part of the contours. Enter in „**Level**" -0.03 and press ENTER, then go to **color** and choose yellow (or whatever you like)
10. Orient the contour in the way you like and go to „**File → Save Image**". Choose PovRay „true" and go ahead.
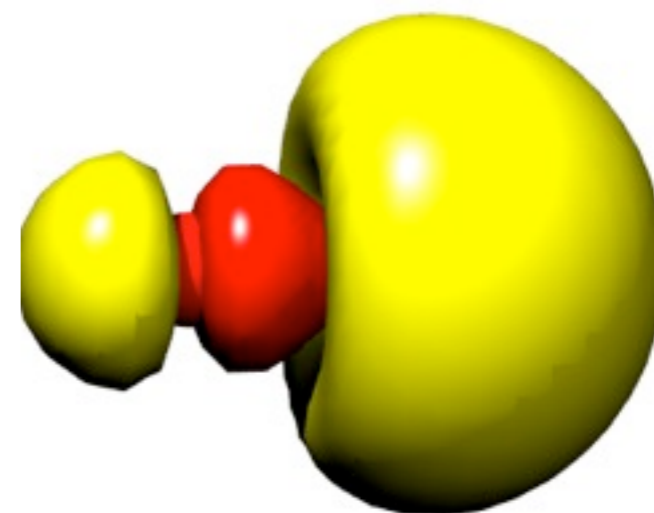
HOMO (MO#6) of CO
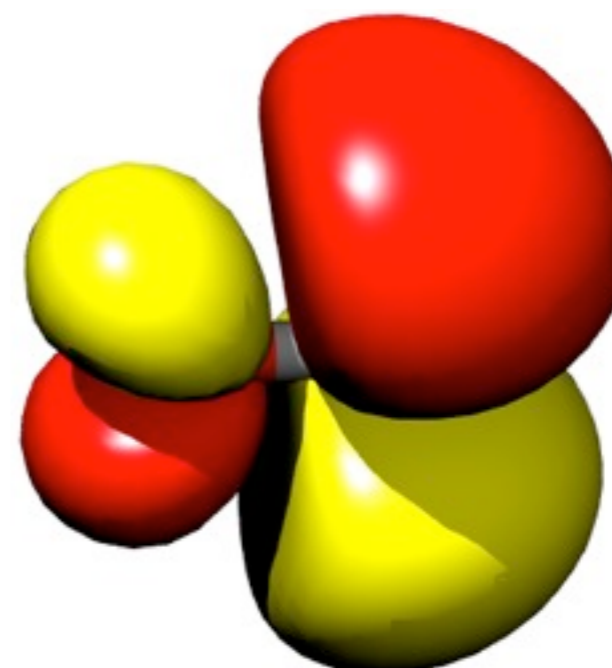
LUMO (MO#7) of CO

What You Need for an Energy Calculation

Energy calculations make up the simplest computational task available

To actually start a calculation three things have to be determined before:

- Method
- Basis set
- Coordinates

Method: Ab initio wavefunction based or DFT?

Accuracy versus Computing Time Tradeoff

Hartree Fock	Fast, but not accurate enough. Usually only as a basis for higher methods
DFT	Fast, *usually* good accuracy. But is the accuracy also good in my case? Very dependent on the Functional
Correlated, wavefunction based methods	Very high accuracy, with Coupled Pair Theories up to Chemical Accuracy. BUT: Calculation scales formally at least with the size of the basis set to N^5

Method: Ab initio wavefunction based or DFT?

Roughly there are three main branches available:

Method	Keyword
Hartree Fock	RHF, UHF, ROHF
DFT	RKS, UKS, ROKS
	MP2
Correlated, wavefunction based methods	Coupled Pair Theories (Single & Double Excitations, CEPA, (N)CPF, CCSD) Coupled Pair Theories + Linearized Triple Excitations (CCSD(T))

But I just want CCSD(T), because it's the best, right?

The Functional Zoo

Name	Type	Comments
BLYP	GGA	One of the earliest GGA functionals. Usually inferior to BP86 and PBE. Predicts too long bonds.
BP86	GGA	Excellent geometries and vibrational frequencies. Energetics is usually not highly accurate but performs often well in spectroscopic investigations.
PW91	GGA	One of the older GGA functionals with excellent accuracy for exchange couplings.
PBE	GGA	A GGA version designed to replace PW91. Very popular in physics. Often similar to BP86.
OLYP	GGA	Violates the uniform electron gas limit but gives improved results for molecules
B3LYP	Hybrid	De facto standard in chemistry for structures, energies and properties. See discussion in the text.
PBE0	Hybrid	Excellent accuracy; competitive with B3LYP
TPSS	Meta-GGA	Improvement over PBE. Includes the kinetic energy density and obeys more constraints known from rigorous theory.
TPSSh	Hybrid meta-GGA	Probably improvement over PBE0; perhaps increase fraction of HF to 25% (TPSS0)
B2PLYP	Double hybrid	First (and prototypical) member of the double hybrid class of functionals. So far been proven excellent for energies and geometries. More exploration needed.

Efficient DFT: The RI Approximation

As long as there is NO Hartree-Fock exchange present (no hybrid functionals), a very efficient approximation can be used to speed up (factor 10-100) DFT calculations: the **RI approximation** (also called **density fitting** method)

In this method the electron density is fit to an auxiliary basis set which must be provided by the user. The effect of the approximation on structures and frequencies is barely visible. Absolute energies are affected to a few kcal/mol, relative energies much less.

```
! RKS BP86 RI SV(P) SV/J TightSCF Opt

* int 0 1
C 0 0 0  0        0    0
O 1 0 0  1.15     0    0
H 1 2 0  1.00  115     0
H 1 2 3  1.00  115  180
*
```

Auxiliary basis appropriate for SV(P) (equivalently **Def-2** uses SV(P) and SV/J together; **Def-3** is equivalent to TZVP and TZV/J)

Use the RI approximation

The job leads to an energy of **–114.37494125 Eh**

Without RI and SV/J **–114.37466595 Eh**

Error **0.00028 Eh = 0.17 kcal/mol**

TIP: For geometry and frequency calculations the BP86 and PBE functionals together with the RI approximation is recommended. Basis sets of TZVP quality are appropriate for good accuracy! SV(P) is already good enough for a first orientation. Use keywords **QuickOpt, NormalOpt or GoodOpt**!
For energy calculations I recommend the B3LPY or PBE0 functionals and larger basis sets (TZVPP if possible or even aug-TZVPP). Use Keyword **DFTEnergy**

Efficient HF and Hybrid DFT: RIJCOSX

Unfortunately, RI does not smoothly carry over to Hartree-Fock and hybrid DFT calculations. One attempt to do so is the **RI-JK** approximation that needs to be invoked together with ‚JK' fitting bases. RI-JK cannot be used for optimizations

```
! B3LYP RI-JK def2-SVP def2-SVP/JK TightSCF
```

A more efficient approximation that leads to large speedups is the **RIJCOSX** approximation. it uses **RI-J** for the Coulomb part and a special approximation ‚**COSX**' for the exchange part. It is available throughout the program and leads to large speedups at very little loss in accuracy

```
! B3LYP RIJCOSX def2-SVP def2-SVP/J TightSCF
```

If combined with **RI-MP2** you need to give two auxiliary basis sets for optimal speed and accuracy:

```
! RI-MP2 RIJCOSX def2-SVP def2-SVP/J def2-SVP/C TightSCF
```

Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. (**2009**) *Chem. Phys*., 356, 98–109

The Crux of DFT: Which Functional to Choose?

Always first thing to do:

RI BP86

The BP86 functional in combination with the Resolution of Identity approximation (RI) is the fastest way to calculate by far, with reasonable results with respect to geometries, etc.

For a more quantitative result, for example, the calculation of energy differences, the following hybrid functionals are known to provide good results:

B3LYP RIJCOSX
(PBE0 RIJCOSX)

To keep in mind:
Usually the results are good, but this does not rule out the possibility, that it might produce wrong results in other cases!

Modern DFT: Double Hybrid Functionals

★ A Special feature of ORCA are ‚**double hybrid functionals**‘ proposed in 2006 by **Stefan Grimme**. Here part of the DFT correlation is replaced by a MP2 like term and part of the DFT exchange by Hartree-Fock exchange.

★ For main group thermodynamics and kinetics it is more accurate than standard functionals

★ ORCA is the only program to have analytic gradients and excited states for these functionals

★ The prototypical member is „**B2PLYP**“

```
! RI-B2PLYP def2-SVP def2-SVP/C TightSCF Opt
```

★ It can be combined with RIJCOSX

```
! RI-B2PLYP RIJCOSX def2-SVP def2-SVP/J def2-SVP/C TightSCF Opt
```

★ And together with empirical **van der Waals corrections** (also proposed by Stefan Grimme) it is particularly accurate:

```
!  RI-B2PLYP  D3BJ  RIJCOSX  def2-SVP  def2-SVP/J  def2-SVP/C
TightSCF Opt
```

Choice of Basis Set

6-31G
6-31G*
6-31G**
6-31++G**
6-3111++G**

DZP
TZP

Ahlrichs SVP
Ahlrichs TZVP

cc-pVDZ
cc-pVTZ
aug-cc-pVTZ

Lots of basis sets to choose from

Which one is the best for one's purpose?

Choice of Basis Set

Pople basis sets: (most popular)

polarization functions on heavy atoms

N_{core} – valence – diffuse **G**(polar. heavy, polar. hydrogen)

\# of primitives
in core orbitals

+ for additional
diffuse orbitals on
heavy atoms

polarization functions on
hydrogen atoms

contraction pattern
for valence orbitals

++ for additional
diffuse orbitals on hydrogen
atoms (→ anions!)

example: 6-31++G(d,p):

➡ Core orbitals are represented by a contraction of six primitive gaussian functions. The valence shell is double- ζ with 3 primitives in first contraction, one in second.

➡ There is a set of diffuse orbitals (p,d) on heavy atoms as well as on hydrogen atoms (diffuse s-orbitals).There is one additional set of d-functions on heavy atoms and one additional set of p-polarization functions on hydrogen atoms.

note: Core orbitals have the lowest energy. Thus, an accurate description is necessary (otherwise the variational principle makes the valence orbitals "core like").
→ Deep contraction for core orbitals, but only one function per AO (because the core-radial function does not change much in the molecule)!

Choice of Basis Set

6-31G
6-31G*
6-31G**
6-31++G**
6-3111++G**

DZP
TZP

Ahlrichs SVP
Ahlrichs TZVP

cc-pVDZ
cc-pVTZ
aug-cc-pVTZ

These Pople style basis sets are very popular in the English-speaking community. They are also very popular due to their availability in the Gxx series of programs.

Better:
The Ahlrichs basis sets provide better results at the same computational cost.

Tip:
Always start calculations at the SVP level, especially geometry optimizations. Only when precise energies are requested, switch to TZVP (or even: def2-TZVPP)

Generation of Coordinates

In principle:

Only a texteditor is needed to enter a molecule's coordinates

Small molecules can be entered by specification of internal coordinates and their values. This is usually called a

Z-Matrix

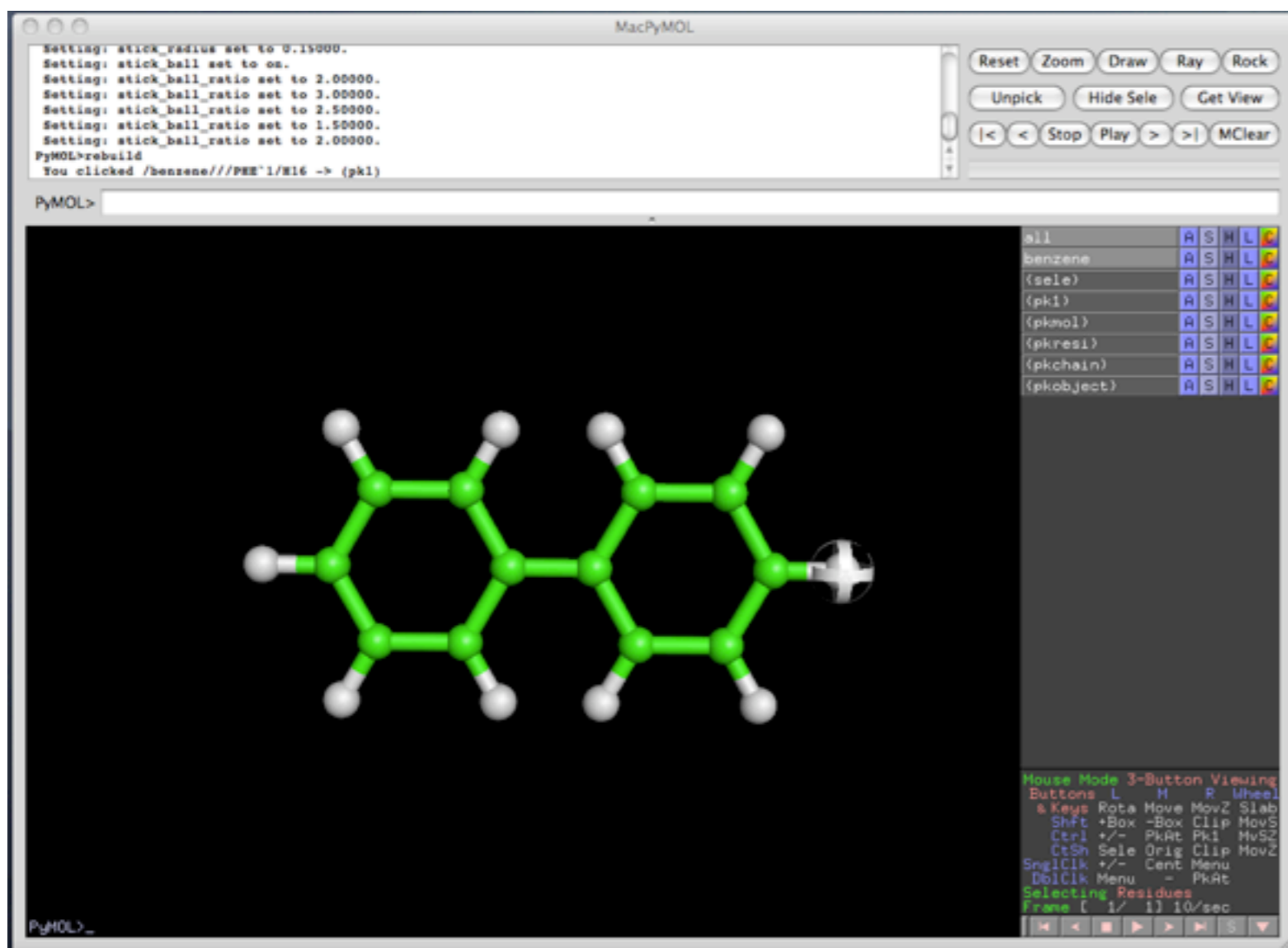But this is only feasible for molecules of a few (<5) atoms.

Today

Molecules are created with full specification in an xyz space using common programs.

Generation of Coordinates

Today

Molecules are created with full specification in an xyz space
using common programs.

Building molecules
using PyMol

Generation of Coordinates

Today

Molecules are created with full specification in an xyz space
using common programs.
(Molden, PyMol, GaussView, etc.)

There are two ways to get coordinates into ORCA, once those
have been created and exported into an .xyz file:

1. Copy the contents of the .xzy file into the ORCA input file, using copy/

   paste facilities of the texteditor or operating system

2. Read in the .xyz file via ORCA input, using the *xyzfile command

Generation of Coordinates

Today

Molecules are created with full specification in an xyz space
using common programs.

There are two ways to get coordinates into ORCA, once those
have been created and exported into an .xyz file:

1. Copy the contents of the .xzy file into the ORCA input file, using copy/

   paste facilities of the texteditor or operating system

2. Read in the .xyz file via ORCA input, using the *xyzfile command

Although the first method looks somewhat more cumbersome at first,
it usually is the safer way:
By this, all information reside in your input file, reducing the error margin and making
the file more easily transportable.

Other Sources of Molecular Structures

Today there are many more sources for acquiring the molecular structure of molecules. It is quite easy, to generate a small organic molecule from scratch. This is definitely not the case with large biomolecular structures like proteins or DNA !

The structures deposited in publicly available databanks might have different origins:

- Crystal Structures:
  Structures generated by analyzing X-Ray diffraction patterns.
  Very good resolution with organic/inorganic molecules, varying with large biomolecules

- NMR Structures:
  Structures, or usually an ensemble of structures, by applying NMR structural information into the generation of structures.
  Very good for accessing structures in solution.

- Theoretical Models
  Sometimes there are neither X-Ray nor NMR information available. In that case people try to come up with a theoretical model, which is usually refined by techniques like simulated annealing etc. to make certain the overall structure reaches a state of low energy.
  It can be hard to assess the quality of these structures at time. The difficulty of generating good theoretical models gets worse with increasing molecular size.

SCF Convergence

Sooner or later it happens:
The SCF cycles does not converge!

What now?

There are serveral reasons causing the SCF not to converge.

- Molecular Structure contains errors
  For example, missing atoms, the electronic state is wrong, etc.

- Very Large Systems
  Due to the accumulation of numerical noise the SCF might not converge

- Difficult Chemical Bonding
  Bonding situations containing transition metals might be hard to converge
  due, especially if the specified state is far away from the ground state

SCF Convergence

What now?

There are many ways to influence the SCF convergence, for example:

- Damping

- Level Shift

- DIIS

- SOSCF

- Newton - Raphson

SCF Convergence

What now?

There are many ways to influence the SCF
convergence, for example:

- Damping

- Level Shift

- DIIS

- SOSCF

- Newton - Raphson

First thing to try:
Specifying `!slowconv`

Otherwise:
- Increase Level Shift
- Increase DIIS Length

(For the whole list, see ORCA manual)

Transition Metal Calculations

For open-shell transition metals convergence of the SCF is often a problem. There are a few ways in ORCA to help this process:

```
# Help a transition metal calculation to converge
! UKS B3LYP SV(P) TightSCF SlowConv

%scf   shift shift 0.1 erroff 0 end
       damp fac 0.80 erroff 0.001 end
       end


* xyz -2 2
Cu   0 0 0
F    1.9 0 0
F   -1.9 0 0
F    0   1.9 0
F    0  -1.9 0
*
```

This tells the program that you expect slow-convergence

Use level-shifting. Never turn it off

Use damping. Turn it off after convergence of the DIIS procedure to 0.001 has been achieved

... Actually, this particular job converges without any damping or shifting. However, in many situations, the damping and shifting is necessary as you will undoubtedly find out yourself once you start calculations in the „real world".

In the present example the convergence „aids" acctually strongly slow down convergence. It is quite uniform since the energy is always decreasing. Thus, these „helpers" more or less „babysit" the job to a converged solution.

Restarting Calculations

In many cases it is a very good idea to start from the convergence MOs of a previous job.

```
# Start calculation from MOs of a previous one
! UKS B3LYP TZVP TightSCF SlowConv
! moread
%moinp "JOB-02.gbw"

%scf   guessmode cmatrix
       end

* xyz -2 2
Cu   0 0 0
F    1.9 0 0
F   -1.9 0 0
F    0   1.9 0
F    0  -1.9 0
*
```

Use previous MOs

Name of the GBW file
NOTE: must not have the same
name as your present input file!

Large basis set calculation started from MOs of a small basis set calculation

„Play safe" if restarting calculations on anions

Note that the calculation can be started from a gbw file which is from a nearby geometry, uses a different basis set of theoretical method or HFType (UHF,RHF or ROHF). The program will take care to translate the orbitals to the present situation.

Second Stop: Geometry Optimizations

Geometry Optimizations
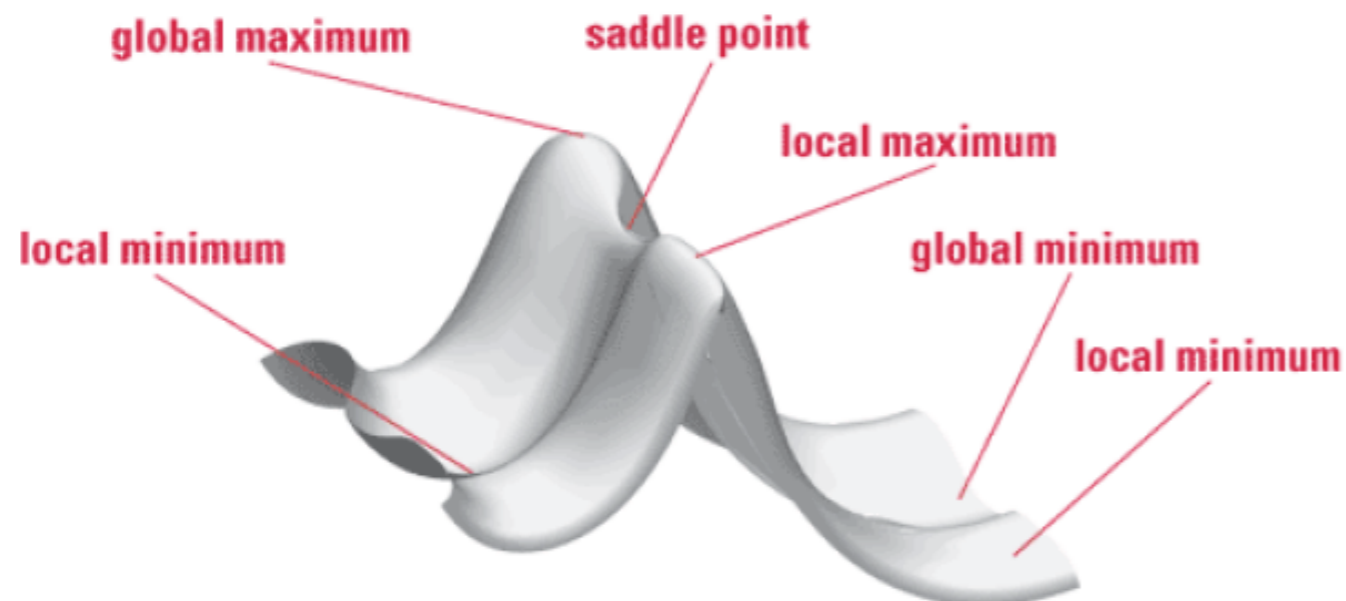
From a formal point of view:

A geometry optimizations minimizes the overall energy of the system by changing the atomic coordinates.

Minimum: All gradients have to vanish

$$f_i = \left. \frac{\partial E(\mathbf{R})}{\partial R_i} \right|_{\mathbf{R}=\mathbf{R}^{(k)}}$$

Problem:
Leads to the *nearest* local minimum, not the *global* minimum of the system!

global maximum saddle point local maximum local minimum global minimum local minimum

Geometry Optimizations

Things to keep in mind when performing geometry optimizations:

- The SCF wavefunction has to be quite precise to generate a smooth potential surface without 'bumps'

- Geometry optimizations might be tough if the molecule contains many soft potentials, for example dihedrals with very low barriers

Geometry Optimization

To optimize the geometry of the molecule, simply include the keyword `Opt`

```
! RKS SV(P) B3LYP TightSCF Opt

* int 0 1
C 0 0 0  0        0    0
O 1 0 0  1.15     0    0
H 1 2 0  1.00 115    0
H 1 2 3  1.00 115 180
*
```

The program will first produce a set of „redundant internal coordinates" which are used in the calculation.

```
-----------------------------------------------------------------
                    Redundant Internal Coordinates

-----------------------------------------------------------------
        Defintion                  Initial Value    Approx d2E/dq
-----------------------------------------------------------------
    1. B(O    1,C    0)                  1.1500          1.351281
    2. B(H    2,C    0)                  1.0000          0.501167
    3. B(H    3,C    0)                  1.0000          0.501167
    4. A(H    2,C    0,O    1)         115.0000          0.425466
    5. A(H    3,C    0,O    1)         115.0000          0.425466
    6. A(H    3,C    0,H    2)         130.0000          0.323418
    7. I(O    1,H    3,H    2,C    0)    0.0000          0.151694
-----------------------------------------------------------------
```

TIP: Always use **TightSCF** or **VeryTightSCF** in geometry optimizations. Otherwise the gradients are somewhat noisy.

After calculating the SCF energy and the gradient of the energy, a relaxation is step is carried out:

```
-------------------------------------------------------------------
                    ORCA GEOMETRY RELAXATION STEP
-------------------------------------------------------------------
Number of atoms                       ....    4
Number of internal coordinates        ....    7
Current Energy                        ....  -114.317745134 Eh
Current gradient norm                 ....     0.207887808 Eh/bohr
Maximum allowed component of the step ....  0.300
Current trust radius                  ....  0.300
Evaluating the initial hessian        ....  (Almloef) done
Projecting the Hessian                ....  done
Forming the augmented Hessian         ....  done
Diagonalizing the augmented Hessian   ....  done
Last element of RFO vector            ....  0.957975075
Lowest eigenvalues of augmented Hessian:
 -0.057174708  0.151693870  0.360949845  0.425465740  0.501166791
Length of the computed step           ....  0.299435193
The final length of the internal step ....  0.299435193
Converting the step to cartesian space:
Transforming coordinates:
 Iter   0:  RMS(Cart)=    0.0824560429 RMS(Int)=    0.1127292561
 Iter   1:  RMS(Cart)=    0.0024951498 RMS(Int)=    0.0033197589
 Iter   2:  RMS(Cart)=    0.0002432861 RMS(Int)=    0.0003067902
 Iter   3:  RMS(Cart)=    0.0000185328 RMS(Int)=    0.0000231161
 Iter   4:  RMS(Cart)=    0.0000012690 RMS(Int)=    0.0000015779
 Iter   5:  RMS(Cart)=    0.0000000832 RMS(Int)=    0.0000001034
 Iter   6:  RMS(Cart)=    0.0000000054 RMS(Int)=    0.0000000067
done
Storing new coordinates                ....  Done
```

The status of the geometry convergence is printed:

```
                        .--------------------.
----------------------|Geometry convergence|---------------------
Item                value            Tolerance    Converged
------------------------------------------------------------------
RMS gradient        0.07883145       0.00010000       NO
MAX gradient        0.14233649       0.00030000       NO
RMS step            0.11317586       0.00200000       NO
MAX step            0.18511086       0.00400000       NO
...............................................
Max(Bonds)    0.0980      Max(Angles)    4.89
Max(Dihed)    0.00        Max(Improp)    0.00
------------------------------------------------------------------

The optimization has not yet converged - more geometry cycles are needed
```

And a new geometry is proposed:

```
-------------------------------------------------------------------
                    Redundant Internal Coordinates
                        (Angstroem and degrees)

    Definition                      Value    dE/dq    Step    New-Value
-------------------------------------------------------------------
 1. B(O    1,C    0)                1.1500 -0.142336  0.0535    1.2035
 2. B(H    2,C    0)                1.0000 -0.103355  0.0980    1.0980
 3. B(H    3,C    0)                1.0000 -0.103355  0.0980    1.0980
 4. A(H    2,C    0,O    1)       115.00 -0.017685    2.44    117.44
 5. A(H    3,C    0,O    1)       115.00 -0.017685    2.44    117.44
 6. A(H    3,C    0,H    2)       130.00  0.035370   -4.89    125.11
 7. I(O    1,H    3,H    2,C    0)  0.00 -0.000000    0.00      0.00
-------------------------------------------------------------------


  *************************************************************
  *            GEOMETRY OPTIMIZATION CYCLE    2            *
  *************************************************************
```

Then the next SCF is done and the next gradient calculated, a new geometry is proposed until (hopefully) finally:

```
  ***********************HURRAY********************
  ***           THE OPTIMIZATION HAS CONVERGED       ***
  *************************************************
```

Following this statement one more energy calculation is performed in order to make sure that the energy and properties are really done at the stationary point of the PES.

Constraints and Relaxed Scans

You can „freeze" certain geometrical parameters in an optimization:

```
! RKS B3LYP/G SV(P) TightSCF Opt
%geom Constraints
        { B 0 1 1.25 C }
        { A 2 0 3 120.0 C }
        end
      end

* int 0 1
    C  0 0 0 0.0000    0.000      0.00
    O  1 0 0 1.2500    0.000      0.00
    H  1 2 0 1.1075  122.016      0.00
    H  1 2 3 1.1075  122.016    180.00
*
```

... Or freeze some and vary others (one frequently used possibility is to only optimize hydrogen positions **OptimizeHydrogens true**). Constrained surfaces are calculated as:

```
%geom Scan
      B 0 1 = 1.35, 1.10, 12 # C-O distance that will be scanned
      end
    end
```

Third Stop: Frequency Calculations

Frequencies? What Frequencies?

Behind the simple term 'Frequency Calculation' quite a few useful properties are hidden.

Calculation of the mass weighted Hessian matrix, i. e. the second derivative of the energy with

respect to all coordinates

$$H_{AB} = \frac{\partial^2 E^{(I)}}{\partial X_A \partial X_B}\bigg|_{X_A = X_B = \ldots \bar{X}}$$

Upon diagonalization we get the frequencies of the normal modes:

$$\omega = \frac{1}{2\pi c}\sqrt{\frac{k}{m}}$$

Following the strict meaning, it describes the calculation of frequencies, usually in the domain of Infrared, in the harmonic approximation of all coordinates of the molecule.

?

Transition State?

At times the geometry optimization might not lead to a minimum on the PES, but to a transition state.
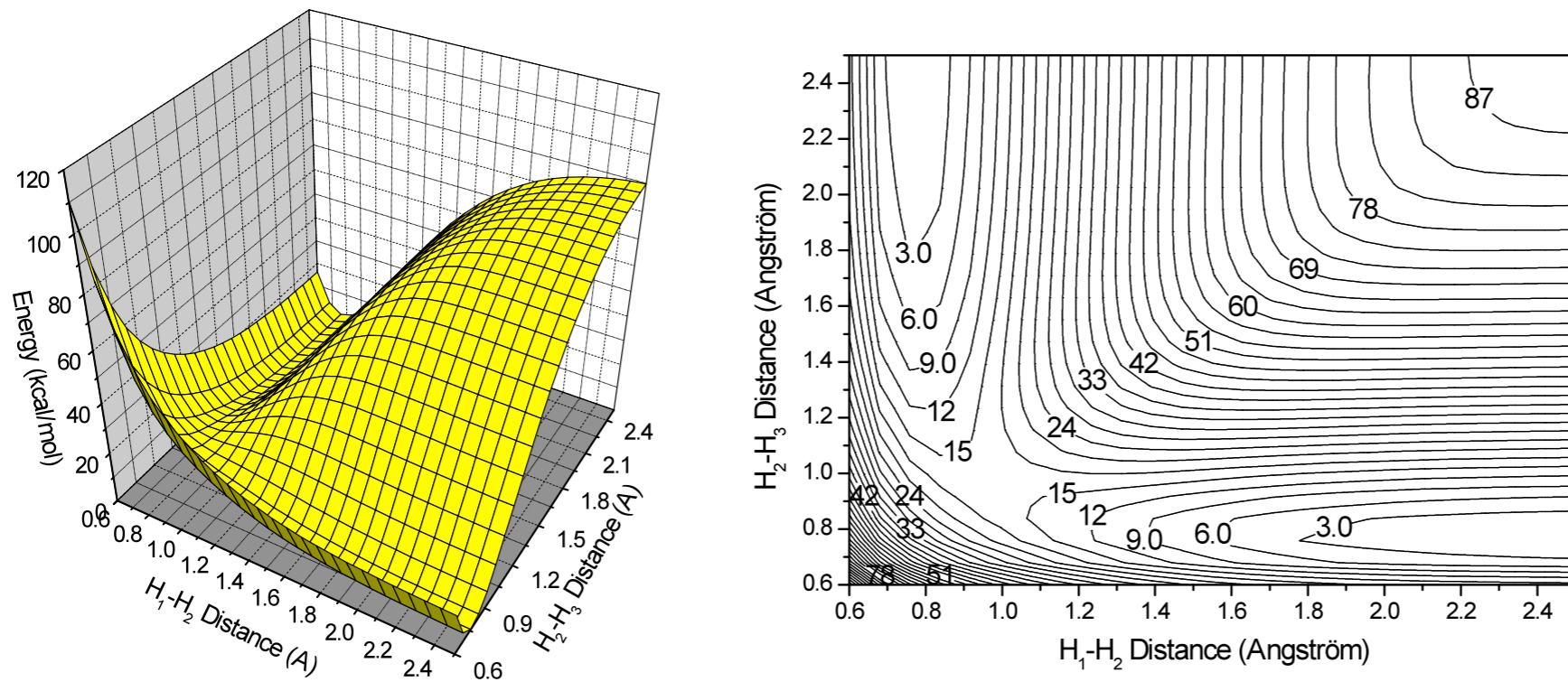
Two-dimensional potential energy surface for the system H-H-H in a linear arrangement. A transition state is observed around the H_1-H_2 and H_2-H_3 distances being both 1.0 Angström.

A transition state is defined as the point, where all coordinates are at a minimum level, with the exception of one, which is at its maximum.

Transition State?

At times the geometry optimization might not lead to a minimum on the PES, but to a transition state.

Two-dimensional potential energy surface for the system H-H-H in a linear arrangement. A transition state is observed around the H_1-H_2 and H_2-H_3 distances being both 1.0 Angström.
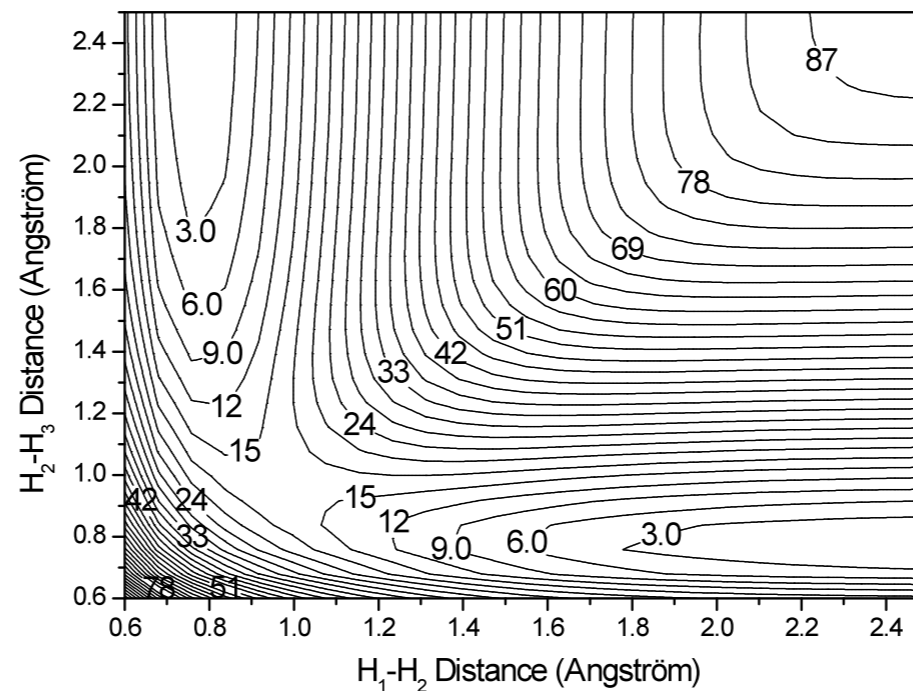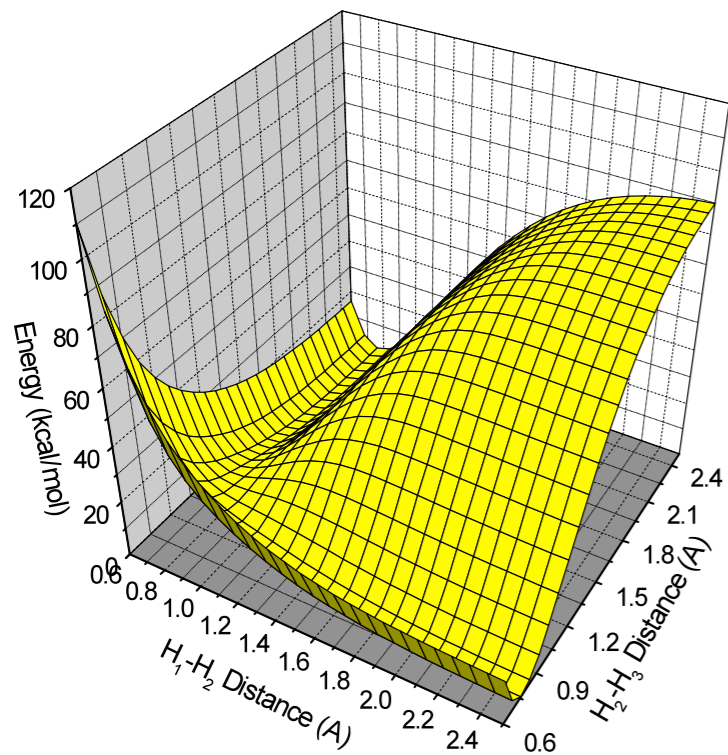
Analyzing the Normal Modes and Frequencies:

A Transition State has exactly one negative frequency!

A transition state is defined as the point, where all coordinates are at a minimum level, with the exception of one, which is at its maximum.

Zero Point Energy (ZPE)

As known from basic Physical Chemistry, even at 0K a molecule still has some vibrational energy.

Having calculated all normal modes of the molecule, as well as the frequency of vibration, it is fairly easy to calculate the zero point energy using the harmonic approximation.

In addition, taking into account a finite Temperature, the vibrational part of the ZPE accounts to

For the translational and rotational degrees of freedom, the statistical equipartition of energy is applied, meaning

$$H_{trans} = H_{rot} = 3/2 \text{ RT}$$

$$H_{vib} = R \sum_{i=1}^{3N-6(7)} \left(\frac{h\nu_i}{2k_B} + \frac{h\nu_i}{k_B} \cdot \frac{1}{e^{h\nu_i/k_B T} - 1} \right)$$

Frequency Calculations

There are several good reasons for calculating the harmonic frequencies:

1. Characterize stationary points as minima (no negative frequencies), transition states (one negative frequency) or higher-order saddle point (more negative frequencies
2. Predict vibrational spectra (IR, Raman)
3. Calculate thermodynamic properties (zero-point energy, finite temperature correction)

ORCA presently calculates harmonic frequencies through (one- or two-sided) numeric differentiation of analytic frequencies

```
! RKS BP86 RI SV(P) SV/J Grid4 TightSCF SmallPrint
! TightOpt NumFreq

%freq CentralDiff true
      Increment 0.005
      end

* xyz 0 1
 C   0.000000    0.000000   -0.533905
 O   0.000000    0.000000    0.682807
 H   0.000000    0.926563   -1.129511
 H   0.000000   -0.926563   -1.129511
*
```

Run a numerical frequency calculation

Two sided differences (twice as expensive but more accurate! Be careful – numerical frequencies can be quite noisy)

Increment for displacements (in Bohrs)

The first thing that is printed are the vibrational frequencies. The first six modes are translations and rotations and these are zero because they are projected out.

```
-------------------------
VIBRATIONAL FREQUENCIES
-------------------------

  0:          0.00 cm**-1
  1:          0.00 cm**-1
  2:          0.00 cm**-1
  3:          0.00 cm**-1
  4:          0.00 cm**-1
  5:          0.00 cm**-1
  6:       1140.72 cm**-1
  7:       1230.49 cm**-1
  8:       1498.92 cm**-1
  9:       1812.75 cm**-1
 10:       2773.72 cm**-1
 11:       2805.59 cm**-1
```

Then the program prints the normal modes. This is usually not very revealing. The program produces a **BaseName.hess** file which you can run through **orca_vib** to get additional information.
XYZ files to be used for animation of vibrational modes are produces by the program **orca_pltvib**.
Then you get the IR spectrum:

```
-----------
IR SPECTRUM
-----------

Mode     freq (cm**-1)     T**2        TX          TY         TZ
-------------------------------------------------------------------------
   6:       1140.72      1.465985  ( -1.210739  -0.008963  -0.004000)
   7:       1230.49     10.082152  (  0.004428  -3.175237  -0.001184)
   8:       1498.92      4.648016  ( -0.000197   0.001760  -2.155925)
   9:       1812.75    105.821353  ( -0.000043   0.002847 -10.286950)
  10:       2773.72     73.358541  (  0.000042  -0.020336  -8.564936)
  11:       2805.59    205.230431  ( -0.000359 -14.325864   0.007790)
```

The IR spectrum can be plotted through the orca_mapspc utility (**orca_mapspc BaseName.out IR**)
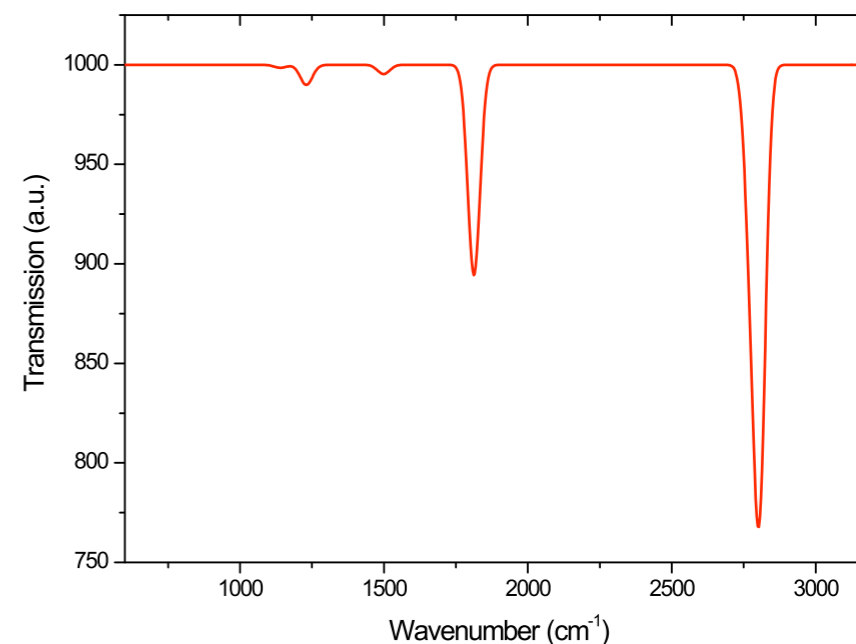
Finally, the thermodynamic properties at 298.15 K are printed (assuming ideal gas behaviour)

```
Electronic energy                   ... -114.41435858 Eh
Zero point energy                   ...    16.10 kcal/mol
Thermal vibrational correction      ...     0.03 kcal/mol
Thermal rotational correction       ...     0.89 kcal/mol
Thermal translational correction ...       0.89 kcal/mol
------------------------------------------------------------
Total thermal energy                    -114.38582646 Eh
```

Then enthalpy+entropy and finally the free energy:

```
Total enthalpy             -114.38488225 Eh
Total entropy correction    -15.36 kcal/mol
--------------------------------------------
Final Gibbs free enthalpy -114.40935858 Eh
G-E(el) = 0.00500000 Eh = 3.14 kcal/mol
```

Solvation

★ The effects of solvation can be quite important for many properties (and in particular for charged molecules – for cations less than for anions).

★ Solvation effects can be (relatively crudely) modelled by polarizable continuum models. In **ORCA** the Conductor Like Screening (COSMO) model by Klamt is implemented in an efficient way for energies and structures (don't do frequencies!)
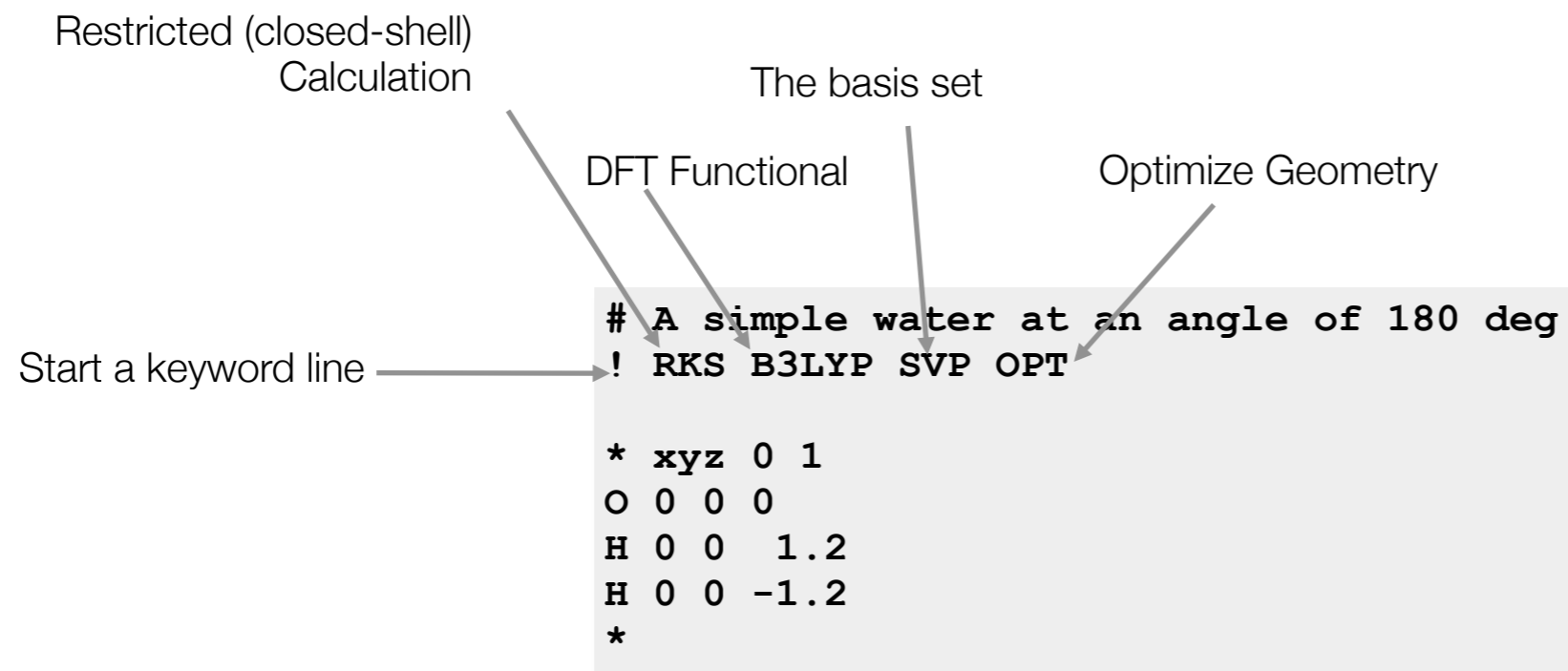
```
! RKS DFTEnergy COSMO(water)

%cosmo epsilon 80
       refrac 1.33
       end

* int 0 1
 C     0    0    0    0.000000     0.000      0.000
 O     1    0    0    1.200371     0.000      0.000
 H     1    2    0    1.107372   121.941      0.000
 H     1    2    3    1.107372   121.941    180.000
*
```

Shortcut is COSMO(solvent)

Alternatively: the dielectric constant and refractive index can be input as needed

TIP: Solvation can be quite important in the prediction of optical and magnetic spectroscopic properties. Consider using it!

A Second *ORCA* Job

Restricted (closed-shell)
Calculation

The basis set

DFT Functional

Optimize Geometry

Start a keyword line

```
# A simple water at an angle of 180 deg
! RKS B3LYP SVP OPT

* xyz 0 1
O 0 0 0
H 0 0  1.2
H 0 0 -1.2
*
```

A Second *ORCA* Job

1. Create a folder / directory named '**water**'
2. Open your text-editor
   (Windows: Notepad, MacOS: TextEdit)
3. Enter the 'water' example in the text-editor
4. Save the water example as '**water.inp**' in the '**water**' folder
   that has been created before
5. Open the command-line window
   On Windows: Type '**cmd.exe**' in the program-search field
   On MacOS: Open the 'Terminal' program from
                   'Application' -> 'Utilities'
6. In the command-line window, move to the water folder/directory:
   Windows: cd C:\Documents\water
   MacOS: cd /Users/MyUSERNAME/Documents/water
7. Execute the ORCA program with the water example, type:
   orca water.inp

```
# A simple water
! RKS B3LYP SVP OPT

* xyz 0 1
O 0 0  0
H 0 0  1.2
H 0 0 -1.2
*
```

A Second *ORCA* Job

.
.
.

```
Timings for individual modules:

Sum of individual times         ...        13.587 sec (=    0.226 min)
GTO integral calculation        ...         1.927 sec (=    0.032 min)  14.2 %
SCF iterations                  ...         9.339 sec (=    0.156 min)  68.7 %
SCF Gradient evaluation         ...         2.097 sec (=    0.035 min)  15.4 %
Geometry relaxation             ...         0.224 sec (=    0.004 min)   1.7 %
                        ****ORCA TERMINATED NORMALLY****
TOTAL RUN TIME: 0 days 0 hours 0 minutes 13 seconds 767 msec


C:\Documents\water>
```

```
# A simple water
! RKS B3LYP SVP OPT

* xyz 0 1
O 0 0 0
H 0 0  1.2
H 0 0 -1.2
*
```

Where did my output go?

A Second *ORCA* Job

```
.
.
.

Timings for individual modules:

Sum of individual times          ...        13.587 sec (=    0.226 min)
GTO integral calculation         ...         1.927 sec (=    0.032 min)  14.2 %
SCF iterations                   ...         9.339 sec (=    0.156 min)  68.7 %
SCF Gradient evaluation          ...         2.097 sec (=    0.035 min)  15.4 %
Geometry relaxation              ...         0.224 sec (=    0.004 min)   1.7 %
                       ****ORCA TERMINATED NORMALLY****
TOTAL RUN TIME: 0 days 0 hours 0 minutes 13 seconds 767 msec


C:\Documents\water>
```

```
# A simple water
! RKS B3LYP SVP OPT

* xyz 0 1
O 0 0 0
H 0 0  1.2
H 0 0 -1.2
*
```

Where did my output go?

Starting ORCA for the advanced user:
orca water.inp > water.out

This will put the *output* of the calculation into the file '**water.out**'.
This file can be opened with the text-editor and examined at leisure.

Where is my result?
(Or is water really linear?)

Look for '**HURRAY**':
Below it you will find
the optimized structure

The step convergence is overachieved with
reasonable convergence on the gradient
Convergence will therefore be signaled now

```
************************HURRAY********************
***           THE OPTIMIZATION HAS CONVERGED     ***
*************************************************
```

```
--------------------------------------------------
            Redundant Internal Coordinates

            --- Optimized Parameters ---
               (Angstroem and degrees)

    Definition              OldVal   dE/dq     Step    FinalVal
--------------------------------------------------
 1. B(H   1,0   0)          0.9378  0.000333 -0.0003   0.9375
 2. B(H   2,0   0)          0.9378  0.000333 -0.0003   0.9375
 3. L(H   1,0   0,H   2, 2) 180.00  0.000000  -0.00    180.00
 4. L(H   1,0   0,H   2, 1) 180.00  0.000000  -0.00    180.00
--------------------------------------------------
```

```
*************************************************
*** FINAL ENERGY EVALUATION AT THE STATIONARY POINT ***
***              (AFTER    6 CYCLES)            ***
*************************************************
```

```
----------------------------------------
CARTESIAN COORDINATES (ANGSTROEM)
----------------------------------------
  O      0.000000   -0.000000   -0.000000
  H     -0.000000    0.000000    0.937514
  H     -0.000000    0.000000   -0.937514


----------------------------------------
CARTESIAN COORDINATES (A.U.)
----------------------------------------

 NO LB    ZA     FRAG    MASS       X               Y               Z
  0 O   8.0000    0     15.999    0.000000030868530   -0.000000034755270   -0.000000002434515
  1 H   1.0000    0      1.008   -0.000000015434265    0.000000017377635    1.771645136378302
  2 H   1.0000    0      1.008   -0.000000015434265    0.000000017377635   -1.771645133943787


----------------------------------------
INTERNAL COORDINATES (ANGSTROEM)
----------------------------------------

  O     0   0   0   0.000000      0.000     0.000
  H     1   0   0   0.937514      0.000     0.000
  H     1   2   0   0.937514    180.000     0.000


----------------------------------------
INTERNAL COORDINATES (A.U.)
----------------------------------------

  O     0   0   0   0.000000      0.000     0.000
  H     1   0   0   1.771645      0.000     0.000
  H     1   2   0   1.771645    180.000     0.000
```

A Second *ORCA* Job

Sometimes it might be difficult to imagine the structure by looking at the xyz coordinates...

water.out

The step convergence is overachieved with
reasonable convergence on the gradient
Convergence will therefore be signaled now

```
***************************HURRAY*********************
***         THE OPTIMIZATION HAS CONVERGED      ***
*****************************************************
```

```
--------------------------------------------------------------
                  Redundant Internal Coordinates

                    --- Optimized Parameters ---
                      (Angstroem and degrees)

    Definition                    OldVal   dE/dq    Step    FinalVal
--------------------------------------------------------------
 1. B(H   1,0   0)                 0.9378  0.000333 -0.0003   0.9375
 2. B(H   2,0   0)                 0.9378  0.000333 -0.0003   0.9375
 3. L(H   1,0   0,H   2, 2)       180.00  0.000000   -0.00   180.00
 4. L(H   1,0   0,H   2, 1)       180.00  0.000000   -0.00   180.00
--------------------------------------------------------------
```

```
        **********************************************************
        *** FINAL ENERGY EVALUATION AT THE STATIONARY POINT ***
        ***            (AFTER    6 CYCLES)               ***
        **********************************************************
```

```
---------------------------------
CARTESIAN COORDINATES (ANGSTROEM)
---------------------------------
  O      0.000000   -0.000000   -0.000000
  H     -0.000000    0.000000    0.937514
  H     -0.000000    0.000000   -0.937514
```

```
-------------------------------
CARTESIAN COORDINATES (A.U.)
-------------------------------
  NO LB    ZA    FRAG    MASS        X                Y                Z
   0 O   8.0000    0    15.999    0.000000030868530   -0.000000034755270   -0.000000002434515
   1 H   1.0000    0     1.008   -0.000000015434265    0.000000017377635    1.771645136378302
   2 H   1.0000    0     1.008   -0.000000015434265    0.000000017377635   -1.771645133943787
```

```
--------------------------------
INTERNAL COORDINATES (ANGSTROEM)
--------------------------------
  O   0   0   0   0.000000    0.000    0.000
  H   1   0   0   0.937514    0.000    0.000
  H   1   2   0   0.937514  180.000    0.000
```

```
-----------------------------
INTERNAL COORDINATES (A.U.)
-----------------------------
  O   0   0   0   0.000000    0.000    0.000
  H   1   0   0   1.771645    0.000    0.000
  H   1   2   0   1.771645  180.000    0.000
```

1.) Copy the cartesian coordinates to a new and empty text-editor window:

Untitled

```
3
  O      0.000000   -0.000000   -0.000000
  H     -0.000000    0.000000    0.937514
  H     -0.000000    0.000000   -0.937514
```

2.) Place the numer of atoms in the first line, followed by an empty line

3.) Save it as '**water_opt.xyz**'

Open the molecule with a molecule-viewer, e.g. Chimera…

Open the molecule with a molecule-viewer, e.g. Chimera...
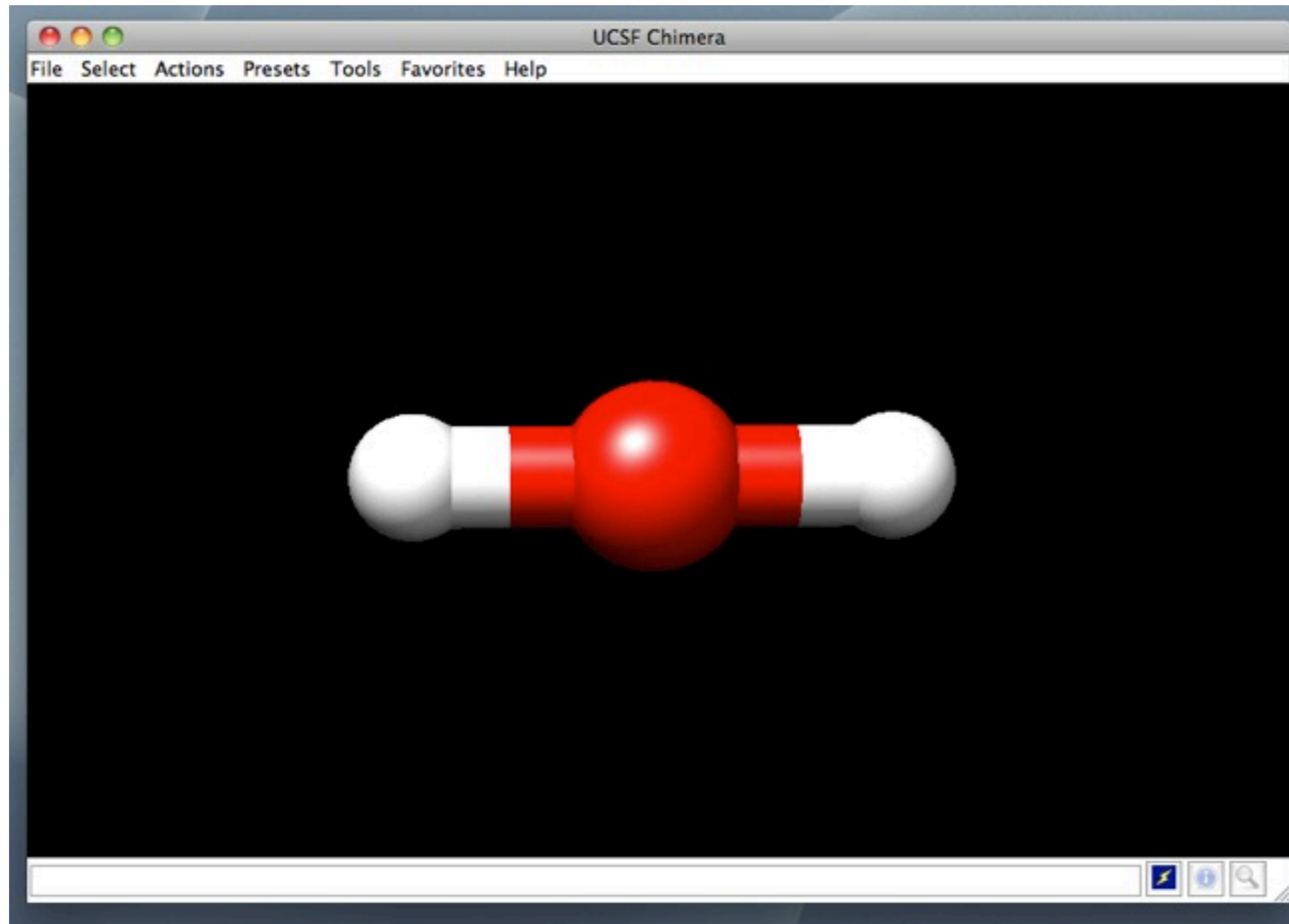
Ahm..... what happened?!

A Second *ORCA* Job

Slight modification:

```
# A simple water
! RKS B3LYP SVP TightOPT Freq

* xyz 0 1
O 0 0 0
H 0 0  1.2
H 0 0 -1.2
*
```

This will result on the calculation of vibrational frequencies

Negative frequencies:
The optimization has converged to a **saddle-point**!!!

A Second *ORCA* Job

Solution: Start from a different structure

```
# A simple water, 90 degrees
! RKS B3LYP SVP TightOPT Freq

* xyz 0 1
O 0    0     0
H 0    0   1.2
H 0 1.2      0
*
```

Same procedure as before...
water is **not** linear!

The End