ABC of DFT: Hands-on session 1

Introduction into calculations on molecules

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Wo? KIT Campus Nord, Flachbau Physik, Geb. 30.22, Computerpool, Raum FE-6

Preliminary remarks (schedule)

- First 5 hands-on sessions (09.11; 16.11, 23.11, 30.11, 07.12): **TURBOMOLE package**
  - molecules: structure optimization, visualization of orbitals and charge densities, ionization energies & electron affinities, molecular vibrations, simulation of IR spectra, etc.
- Next 5 hands-on sessions (14.12, 18.01, 25.01, 01.02, 08.02): **FHI-aims package**
  - Periodic (3D & 2D) systems: density of states and band structure of metals & semiconductors, structure optimization, visualization of charge densities, ferromagnetic systems, graphene, work functions, defects and phonons, etc.

Overview

- Electronic structure methods for molecules
  - Reminder: Kohn-Sham formulation of DFT
  - Basis set approximation: Gaussian type orbitals

- TURBOMOLE
  - Functionality & usage philosophy

- Creating input, performing self-consistent calculation, geometry optimization
  - “Warm-up” examples: H atom, H_2 molecule
  - Do it yourself: N_2, O_2 molecules

Reminder: Kohn-Sham formulation of DFT

- Ansatz for the electron density:

$$n(\mathbf{r}) \overset{\text{def.}}{=} n_s(\mathbf{r}) = \sum_{i=1}^{N_{\text{el.}}} |\varphi_i(\mathbf{r})|^2$$

- Schrödinger like, Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$V_s(\mathbf{r}) = V_{\text{ext/ions}}(\mathbf{r}) + \int \frac{e^2 n_s(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' + V_{\text{XC}}[n_s(\mathbf{r})]$$

external potential

Hartree potential

“exchange & correlation” potential

Solving KS equations: basis set approximation

- Each Kohn-Sham molecular orbital φ_i (MO) is expanded in terms of atom-centered basis functions χ_α (“atomic orbitals”):

$$\varphi_i(\mathbf{r}) = \sum_{\alpha}^{M} \chi_\alpha(\mathbf{r}) C_{\alpha i}$$

- KS equations take form of the eigenvalue problem (many powerful algorithms exist to solve it):

$$\mathbf{HC} = \mathbf{SC}\varepsilon$$

$$H_{\alpha\beta} = \left\langle \chi_\alpha \middle| -\frac{\hbar^2}{2m}\nabla^2 + V_s(\mathbf{r}) \middle| \chi_\beta \right\rangle$$ → Hamiltonian

$$S_{\alpha\beta} = \langle \chi_\alpha | \chi_\beta \rangle$$ → Overlap integrals

Gaussian basis sets: typical choice in quant.chem.

- **Gaussian type orbitals (GTO)**

$$f^{\mathrm{GTO}}(r) = (2\alpha/\pi)^{3/4}\exp(-\alpha r^2)$$

- **Contracted GTOs (CGTOs)**

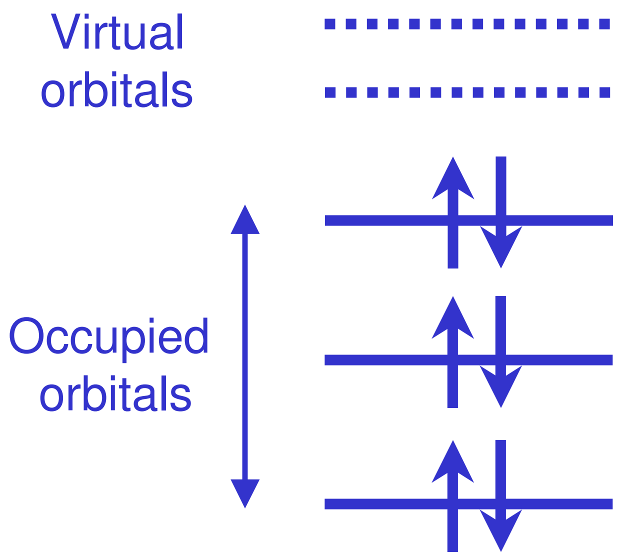
$$\chi_\alpha(\mathbf{r}) = \left[c_1 f^{\mathrm{GTO}}(\alpha_1, r) + c_2 f^{\mathrm{GTO}}(\alpha_2, r) + \ldots\right] Y_{lm}(\hat{\mathbf{r}})$$

- **Split valence (SV) basis sets:** electrons are partitioned in core and valence types.
  - Each core electron: one contracted Gaussian orbital
  - For every valence electron: two, three, etc … contracted GTOs: so-called, double-ζ (SV), triple- ζ (TZV), … basis sets
- **Polarization effects** are accounted for by adding *polarization (P) basis functions*, which have larger angular momentum *l* numbers: SVP, TZVP, etc… basis sets

Closed shell and open shells systems

Even number of electrons:

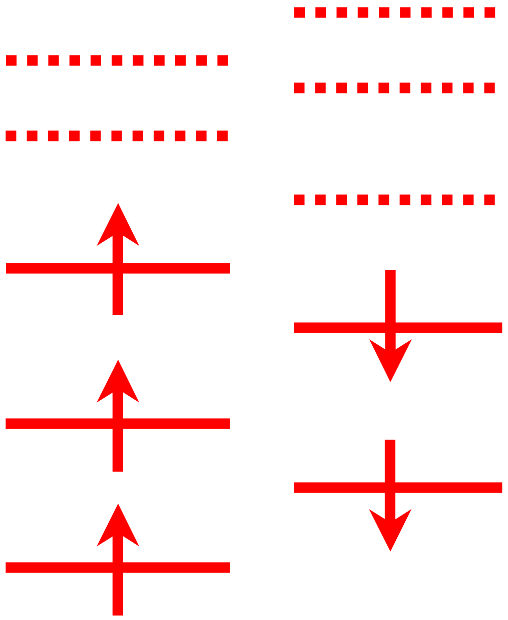
"closed shell"



Constrain: up-spin and down-spin orbitals are identical: $V_{xc}[n(\mathbf{r})]$

Odd number of electrons:

"open shell"



No constrain: up-spin and down-spin orbitals are optimized independently: $V_{xc}[n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r})]$

TURBOMOLE: functionality

- **One of the fastest quantum chemistry packages**
- developed by Prof. Ahlrichs group (Uni Karlsruhe)

- optimized Gaussian-type basis sets, real space formulation (molecules, clusters)
- all symmetry point groups

- DFT: various exchange-correlation (xc) functionals
- wave function methods: Hartree-Fock (HF) and post-HF levels of theory
- various ground and excited state properties: bond lenths & angles, excitation energies, vibrational spectra: infrared & Raman, NMR shieldings, response functions, etc …
- simulation of environment: solvation effects, ionic crystals
- parallel runs: simulations with hundreds of atoms

TURBOMOLE: usage philosophy

- The usage of TURBOMOLE is UNIX/Linux oriented:
  - command line driven
  - many different programs (modules), each one specialized for particular methods and/or properties
  - scripts are used to combine the functionalities and manage workflows
  - Input file(s) can be changed by Linux editors
  - output is processed by standard Linux tools (editors, grep, awk ...)

- **Hence: some (basic) Linux skills are required!**

Getting into practice …

- A user account is available for you on the Linux cluster (placed at INT) called intact: please, see a separate sheet given to you
- Required software (TURBOMOLE binaries and scripts, visualization tools, etc.) is accessible for you: `$PATH` variable is set in `.bashrc` file
- You can find a documentation (including this tutorial & TURBOMOLE manual, and also FHI-aims manual) at `~/ABC_of_DFT/hands-on-sessions/documentation`
- You can find set of basic exercises at `~/ABC_of_DFT/hands-on-sessions/session.1`
- Each basic exercise contains full output data (e.g, `.../example.2.h2/output.h2`), so that you'll be able to compare your results with expected ones

Example 1 – H atom

- We start with the simplest possible system: H atom
- Go to directory

```
cd ~/ABC_of_DFT/hands-on-
                    sessions/session.1/example.1.h
```

- Create your own directory where you are going to run a calculation:

```
cp -r structure.h my.h.atom
cd my.h.atom
```

- A file `coord` is reserved for atomic positions. In our case, there is a single H atom. Type:

```
cat coord
```

```
$coord
  0.00000000000000   0.00000000000000   0.00000000000000   h
$end
```

- Remark: atomic positions are given in atomic units (1 a.u. = 0.529 Å)

Example 1 – H atom: creating an input (step 1)

- Interactive module **define** is used to set-up system specific parameters for the calculation. Type from the command line: `define`

```
  ...
DATA WILL BE WRITTEN TO THE NEW FILE control
IF YOU WANT TO READ DEFAULT-DATA FROM ANOTHER control-TYPE FILE,
THEN ENTER ITS LOCATION/NAME OR OTHERWISE HIT >return<.
```

- Hit `<Enter>` for the name of input file
-

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

  Type e.g. `h atom` for the title, followed by `<Enter>`

- You will get the „molecular geometry“ menu

```
SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=0     SYMMETRY=c1  )
YOU MAY USE ONE OF THE FOLLOWING COMMAND
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>
 ....
```

Type `a coord <Enter>` to append a single H atom

Example 1 – H atom: creating an input (step 2)

- You will see that 1 atom has been added:

```
CARTESIAN COORDINATES FOR  1 ATOMS HAVE SUCCESSFULLY
BEEN ADDED.
   ....
SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=1     SYMMETRY=c1  )
YOU MAY USE ONE OF THE FOLLOWING COMMAND
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>
 ....
*                : 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
```

- Nothing to be done any more in the “molecular geometry” menu.
  To proceed, type
  `* <Enter>`

Example 1 – H atom: creating an input (step 3)

- We come to „atomic attributes“ menu:

```
ATOMIC ATTRIBUTE DEFINITION MENU  ( #atoms=1     #bas=1     #ecp=0     )

b     : ASSIGN ATOMIC BASIS SETS
bb    : b RESTRICTED TO BASIS SET LIBRARY
bl    : LIST ATOMIC BASIS SETS ASSIGNED

....

*     : TERMINATE THIS SECTION AND WRITE DATA OR DATA REFERENCES TO control
GOBACK=& (TO GEOMETRY MENU !)
```

- You may check that a default basis set def-SV(P) is assigned:

```
 bl <Enter>
```

```
 -----------------------------------------------------------------------
 INDEX | BASIS SET NICKNAME
 -----------------------------------------------------------------------
    1  | h def-SV(P)
 -----------------------------------------------------------------------
```

- To proceed for the next menu, type

```
* <Enter>
```

Example 1 – H atom: creating an input (step 4)

- Within next menu **define** provides initial molecular orbitals (in our case, atomic orbitals) with, e.g., an extended Hückel guess.

```
OCCUPATION NUMBER & MOLECULAR ORBITAL DEFINITION MENU

CHOOSE COMMAND
infsao     : OUTPUT SAO INFORMATION
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
&          : 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
```

To choose the Hückel guess, type

`eht <Enter>`

- You will be asked further questions: accept all defaults (among them are default zero charge & occupation of one orbital with one spin)

Example 1 – H atom: creating an input (step 5)

- You will come to the last, “general menu”:

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

- Choose DFT, by entering `dft <Enter>` , and then `on <Enter>`

```
STATUS OF DFT_OPTIONS:
DFT is used
  functional b-p
   ....
Just <ENTER>, q or '*' terminate this menu.
```

Default “b-p” functional is GGA BP86 by Becke and Perdew

Type `q <Enter>` to quit and go back to the “general menu”

- Nothing to be done any more for H atom, type `q <Enter>` to finish your session with define

Example 1 – H atom: creating an input (remarks)

- After **define** session is finished, you'll find several files in your directory: `control, basis, alpha, beta.`

- File `control` contains all settings to control over your calculation.

  If required, changes to it can be done using standard UNIX editors (like `vim` or `emacs`).

- File `basis` contains information about basis functions (contracted Gaussian type orbitals) to be used for the expansion of the wave functions.

- Files `alpha & beta` contain energies and expansion coefficients of atomic orbitals over the basis functions, for up- and down-spin electrons (in case of molecules, molecular orbitals & their energies).

Example 1 – H atom: running calculation

- To run a DFT calculation, call a dscf module: `dscf`
- Scroll up output data: you'll find, a calculation is finished within 5 iterations
- Data post-processing script `eiger` provides information about orbital energies and occupations. Type: `eiger > atomic.levels.dat` and afterwards: `cat atomic.levels.dat`

```
 h atom
Total energy =     -0.4989430987 H =       -13.5769402 eV
 HOMO-LUMO Separation
   HOMO:     1. a   1 a     -0.27623884 H =     -7.51685 eV
   LUMO:     2. b   1 a     -0.04813878 H =     -1.30992 eV
   Gap :                    +0.22810006 H =     +6.20692 eV

Number of MOs=      4, Electrons=      1.00, Symmetry: c1
   Nr.   Orbital    Occupation       Energy
    4. b   2 a                     +0.624165 H =       +16.984 eV
    3. a   2 a                     +0.383478 H =       +10.435 eV
    2. b   1 a                     -0.048139 H =        -1.310 eV
    1. a   1 a        1.000        -0.276239 H =        -7.517 eV
```

- Compare the energy of a single occupied orbital with the ionization potential for H atom (-13.6 eV). Why there is a difference?

Example 2 – H_2 molecule: creating input

- Structure of a hydrogen molecule can be found at

```
cd ~/ABC_of_DFT/hands-on-
                    sessions/session.1/example.2.h2
```

- Create a new directory:

```
cp -r structure.h2 h2.molecule
cd h2.molecule
```

- Positions (in atomic units) of two H hydrogen atoms are written to file `coord` (type, `cat coord`):

```
$coord
  0.00000000000000   0.00000000000000   0.00000000000000   h
  0.00000000000000   0.00000000000000   1.40000000000000   h
$end
```

Example 2 – H_2 molecule: creating input

- Run **define** module, create an input for H2, similar to that for H atom
- In the “molecular geometry menu”, append your structure with

  `a coord <Enter>`

```
 CARTESIAN COORDINATES FOR   2 ATOMS HAVE SUCCESSFULLY
 BEEN ADDED.
    ....
 SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=2     SYMMETRY=c1  )
 YOU MAY USE ONE OF THE FOLLOWING COMMAND
 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 ANGSTROEM UNITS FROM FILE <file>
 sub              : SUBSTITUTE AN ATOM BY A GROUP OF ATOMS
 i                : INTERNAL COORDINATE MENU
 ired             : REDUNDANT INTERNAL COORDINATES
    ....
```

- To make possible atomic structure relaxations, switch on “internal coordinates”:

  `ired <Enter>`

Example 2 – H_2 molecule: creating input

- You’ll see a message like that:

```
    GEOSPY: NBDIM:       1  NDEGR:       1
     Lowest Eigenvalue of BmBt is:          2.0000000000
     GEOSPY: ATTENTION!
     natural internals not linearly independent?
      Decoupling with "globtry"=    0.9999999999000000
     Lowest Eigenvalue of projected BBt           2.0000000000 No:     1
     Quotient of Eigenvalues           1.0000000000
    OCCUPATION OF BLOCKS:    1    0    0    0    0

SPECIFICATION OF MOLECULAR GEOMETRY ( #ATOMS=2     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
  ...
```

- To proceed, type

  `* <Enter>`

- Continue a define session, following instructions at slides 14-16.

Example 2 – H_2 molecule: running calculation

- Perform a DFT calculation, analyze your output. Type

```
dscf <Enter>
eiger > molecular.levels.dat <Enter>
cat molecular.levels.dat <Enter>
```

- Your results will look like:

```
  h2 molecule
Total energy =     -1.1693659559 H =       -31.8200848 eV

 HOMO-LUMO Separation
   HOMO:     1.      1 a      -0.38338626 H =    -10.43248 eV
   LUMO:     2.      2 a      +0.05883434 H =     +1.60096 eV
   Gap :                      +0.44222060 H =    +12.03344 eV

Number of MOs=      4, Electrons=      2.00, Symmetry: c1

   Nr.    Orbital    Occupation       Energy
    4.      4 a                    +0.737992 H =      +20.082 eV
    3.      3 a                    +0.313745 H =       +8.537 eV
    2.      2 a                    +0.058834 H =       +1.601 eV
    1.      1 a       2.000        -0.383386 H =      -10.432 eV
```

Example 2 – H_2 molecule: remarks

- A default basis set, def-SV(P), which we have used, ascribes two basis functions (per spin) per H atom : in case of H_2 molecule, we get four spin-degenerate molecular orbitals: one being occupied by two electrons, and three virtual, empty orbitals.

- A measured ionization energy of H_2 molecule is 15.4 eV. For the exact (but unknown!) XC functional, the HOMO (highest occupied molecular orbital) energy would give the value of the ionization potential (up to minus sign): statement known as Koopman's theorem.

  Our value (10.4 eV) significantly underestimates the ionization energy: that is a common problem with all approximate DFT XC-functionals, which are based on the local density approximation (LDA) and its gradient corrections (GGA).

Example 2 – H_2 molecule: potential energy surface

- Computing the energy of H-H dimer as function of a distance between H atoms gives us a potential energy surface and allows to estimate the H-H bond length. Let us check, how DFT performs in this case.

- Make a new directory, say

```
cd ~/ABC_of_DFT/hands-on-
                  sessions/session.1/example.2.h2
mkdir h2.energy
```

- A script `h2` (located at your `~/bin` directory) creates automatically an input and runs the DFT calculation for several H-H distances. Simply type from a command line: `h2`, and read a short description.

- As input, the script takes an abbreviation of the TURBOMOLE basis set. Accepted sets are: def-SVP (2 basis functions per H atom), def-TZVP (6 basis functions), and def-QZVP (30 basis functions).

Example 2 – H_2 molecule: potential energy surface

- Perform calculations with different basis sets. Type

  `h2 def-SVP` (output will follow up …)

  `h2 def-TZVP`

  `h2 def-QZVP`

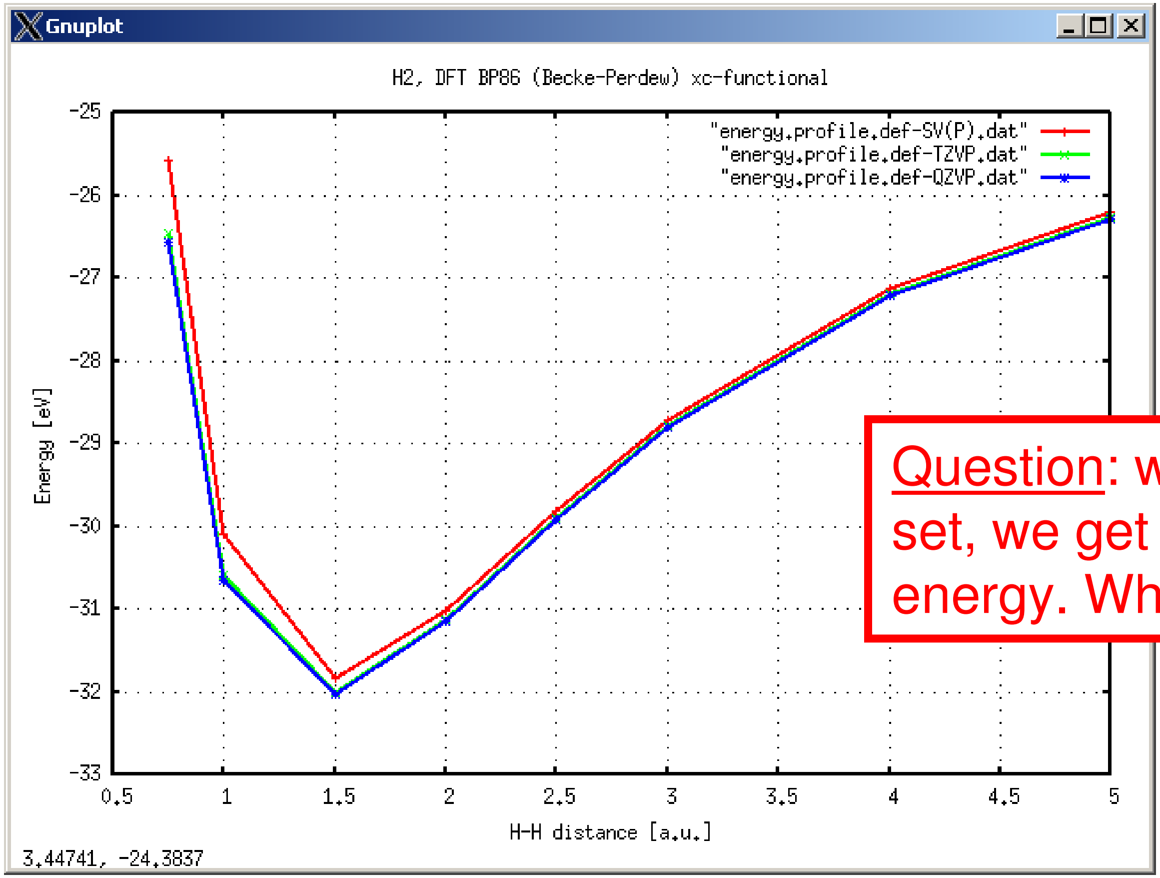
- Results of your calculations will be sorted into three different directories and three output .dat-files. Check any of them, type

```
cat energy.profile.def-SV\(P\).dat
#dist[a.u.]   E[eV].def-SV(P)
   .75         -25.5655107
   1.0         -30.0952703
   1.5         -31.8268463
   2.0         -31.0131306
   2.5         -29.8140698
   3.0         -28.7179669
   4.0         -27.1254815
   5.0         -26.2018811
#end
```

---> A value being close to the H-H bond length (1.40 a.u.)

Example 2 – H_2 molecule: potential energy surface

- With another script `h2plot`, you can view results of calculations for the three different basis sets.
- Type from a command line: `h2plot`. A window will appear:



Question: with larger basis set, we get lower values of energy. Why?

Example 2 – H_2 molecule: structure optimization

- An automatic structure optimization is possible with help of shell script `jobex`, which calls subsequently modules for the electronic energy calculation, gradient and, based on that, estimates the new coordinates.

- To perform a geometry optimization of H_2, take one of your calculations [say, with *d*(H-H)=2.0 a.u.] and make a new directory:

```
cd results.def-SV\(P\)
cp -r d_2.0 h2.relaxed
cd h2.relaxed
```

Example 2 – H_2 molecule: structure optimization

- Structure optimization is controlled by the script jobex ; type from a command line: `jobex`

- Few steps are required, until the energy gradient approaches zero. Type: `grep cycle gradient`
  Do you understand results?

- Optimized geometry of the molecule is saved to file `coord.`
  Check it: what is the equilibrium H-H bond length which you've got?

Example 2 – H_2 molecule: structure optimization

- Print out the orbital energies. Type:

```
eiger > molecular.levels.relaxed.dat
cat molecular.levels.relaxed.dat
```

Compare your results for the relaxed H_2 molecule with data in the file `molecular.levels.h2_2.0.def-SV(P).dat` corresponding to the H-H distance of 2.0 a.u.

Question: how did the energies of HOMO (highest occupied molecular level) and LUMO (lowest unoccupied molecular level) change? Why?

- Perform similar calculations with other basis sets (def-TZVP,def-QZVP).
  What are the equilibrium H-H bond lengths? Do results converge to the experimental value of 1.40 a.u.?

Further examples: try to do yourself!

- Following introduced strategy, compute potential energy profiles and equilibrium interatomic distances *d* of diatomic molecules, N_2 and O_2:

  (i) modify script h2 accordingly, create new scripts, say n2 and o2, and compute energy profiles (choose *d* in the range 1.75…6.0 a.u.)

  (ii) take energy minimum point, and invoke a script jobex to even better relax your molecule, compare your optimized interatomic distance with known experimental data (Google for it!)

- Remark: ground state of N_2 is closed shell (spin singlet, S=0), while the ground state of O_2 is a spin triplet (S=1, open shell)

Ask questions if you have problems, and enjoy!