- Clone GitHub repository with exercises:

```
git clone https://github.com/michalhapka/trex_workshop2023.git
```

1 Exercise: H_2-H_2 (static correlation)

Perform SAPT(CISD) calculations for the H_2-H_2 complex (Figure 1):

a) near the equilibrium geometry ($R = 1.44$ a.u.),

b) with a broken covalent bond in one of the monomers ($R = 7.20$ a.u.).

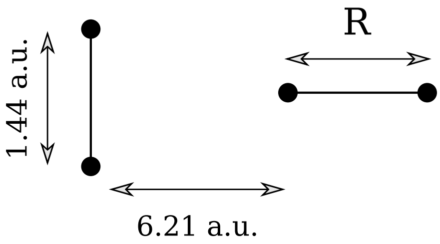

Figure 1: H_2-H_2 in T-shaped geometry.

The basis set is aug-cc-pVDZ.

1. Prepare `input.inp` file for SAPT. You will find the `xyz` files and `input.inp` templates in:
   - `trex_workshop2023/SAPT/h2_h2/cisd` .
2. Prepare a script to run CISD calculations (with Quantum Package) followed by SAPT calculation (with GammCor). You can find sample scripts at:
   - `https://qchem.gitlab.io/gammcor-manual/pages/calculation/sapt_methods/running_sapt_qpckg.html` .

If you do not have access to Quantum Package, you will find the necessary HDF5 files in `results` subfolders.

Answer the questions:

1. Which interaction energy components dominate for $R = 1.44$ a.u. and $R = 7.20$ a.u.?
2. How accurate is SAPT based on Hartree-Fock description of the monomers near the equilibrium and in the case of a stretched bond?
3. Table 1 shows also SAPT results obtained with CASSCF wave functions. What is the effect of increasing the active space?

Table 1: Results of SAPT calculations for H_2-H_2 dimer. CAS(m, n) denotes CASSCF calculation with m electrons occupying n active orbitals (for each monomer). Energy unit is microhartree.

	$E^{(1)}_{\text{elst}}$	$E^{(1)}_{\text{exch}}$	$E^{(2)}_{\text{ind}}$	$E^{(2)}_{\text{exch-ind}}$	$E^{(2)}_{\text{disp}}$	$E^{(2)}_{\text{exch-disp}}$	$E^{\text{SAPT}}_{\text{int}}$
$R = 1.44$ a.u.							
HF	-62.29	89.96	-5.169	1.706	-154.2	6.911	-123.0
CISD							
CAS(2,2)	-47.82	81.28	-4.030	1.637	-143.6	5.693	-106.8
CAS(2,8)	-52.61	88.43	-4.565	1.980	-151.7	6.094	-112.4
$R = 7.20$ a.u.							
HF	-185.4	445.0	-39.72	26.29	-320.6	33.55	-40.89
CISD							
CAS(2,2)	-44.87	201.1	-7.994	5.465	-161.1	10.15	2.748
CAS(2,8)	-47.17	209.4	-8.388	5.992	-165.9	10.43	4.335

2 Exercise: He-H_2* (excited states, ver 1)

Perform a SAPT(CISD)/aug-cc-pVDZ calculation for the He-H_2 complex (Figure 2):

a) both monomers are in the ground state and $R = 6.6$ a.u.,

b) He is in the ground state, H_2 is in the first singlet excited state ($^1\Sigma_u^+$), and $R = 4.0$ a.u.

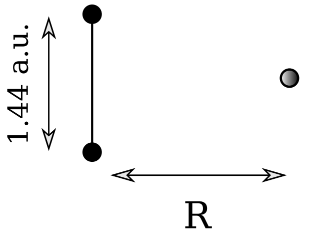

Figure 2: He-H_2 in T-shaped geometry.

1. Prepare `input.inp` file for SAPT. You will find the `xyz` files and `input.inp` templates in:
    - `trex_workshop2023/SAPT/he_h2` .
2. Prepare a script to run CISD calculations (with Quantum Package) followed by SAPT calculation (with GammCor). You can find sample scripts at:
    - `https://qchem.gitlab.io/gammcor-manual/pages/calculation/sapt_methods/running_sapt_qpckg.html`

Answer the questions:

1. What are the key interaction energy ingredients in the van der Waals minimum region in ground- and excited-state?
2. Which energy component dominates ground/exited-state interaction at $R = 4.0$ a.u.?

If you do not have access to Quantum Package, you will find the necessary HDF5 files in `/results` subfolders.

Table 2: Results of SAPT(CISD)/aug-cc-pVDZ calculations for He-H_2 and He-H_2* dimers. Energy unit is millihartree.

	$E^{(1)}_{\mathrm{elst}}$	$E^{(1)}_{\mathrm{exch}}$	$E^{(2)}_{\mathrm{ind}}$	$E^{(2)}_{\mathrm{exch-ind}}$	$E^{(2)}_{\mathrm{disp}}$	$E^{(2)}_{\mathrm{exch-disp}}$	$E^{\mathrm{SAPT}}_{\mathrm{int}}$
ground state							
$R = 4.0$ a.u.	-1.103	5.740	-0.375	0.395	-0.956	0.114	3.816
$R = 6.6$ a.u.							
excited state							
$R = 4.0$ a.u.							
$R = 6.6$ a.u.	-0.026	-0.060	-0.036	-0.003	-0.204	-0.005	-0.334

3 Computation of singlet-triplet gap of cyclobutadiene with ACn-CAS

- In `trex_workshop2023/C4H4` directories you will find all files needed to run ACn calculations with GammCor for singlet (S) and triplet (T) states using CAS(2,2) and CAS(4,4) reference wavefunctions.
- Input files for GammCor with electron integrals and 1,2-reduced density matrices have been generated with Dalton and are provided.

  If you want to learn how to use Dalton interfaced with GammCor see example in GammCor user manual:
  `https://qchem.gitlab.io/gammcor-manual/pages/calculation/correlation_methods/acn_dalton.html`
- To run GammCor, prepare the `job1` script for slurm (provide the correct path to gammcor in `GAMMCOR_EXEC="...."`) .

```
#!/bin/bash
#SBATCH -n 1
#SBATCH -c 1
#SBATCH --nodelist=cn08
#SBATCH -t 0:10:00
#SBATCH --mem=1GB

$GAMMCOR_EXEC="...."

srun $GAMMCOR_EXEC > "gammcor.out"
```

- Copy the script to CAS22/S, CAS22/T, CAS44/S, CAS44/T directories. In each directory submit the job.

```
sbatch job1
```

- Collect the results from `gammcor.out` files. Look for the line:
  `ECASSCF+ENuc, ACn-Corr, ACn-CASSCF`
  at the end of outputs.
- Compute S-T energy gaps for CASSCF (`ECASSCF+ENuc`) and ACn-CASSCF (`ACn-CASSCF`) from CAS(2,2) and CAS(4,4) models. Compare the numbers with the reference value of 0.18 eV from Stoneburner et al., J. Chem. Phys. 2017, 147, 164120.