

- Clone GITHUB repository with exercises:  
`git clone https://github.com/michalhapka/trex_workshop2023.git`

## 1 Exercise: H<sub>2</sub>-H<sub>2</sub> (static correlation)

Perform SAPT(HF) and SAPT(CISD) calculations for the H<sub>2</sub>-H<sub>2</sub> complex (Figure 1):

- near the equilibrium geometry ( $R = 1.44$  a.u.),
- with a broken covalent bond in one of the monomers ( $R = 7.20$  a.u.).

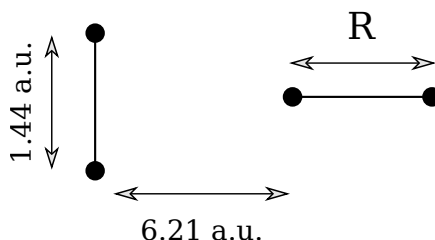


Figure 1: H<sub>2</sub>-H<sub>2</sub> in T-shaped geometry.

The basis set is aug-cc-pVDZ. First, use Quantum Package to run Hartree-Fock/CISD calculations. Then, use GammCor to run SAPT. You will find the xyz files in:

- `trex_workshop2023/h2_h2/hartree-fock` ,
- `trex_workshop2023/h2_h2/cisd` .

If you do not have access to Quantum Package, you will find the necessary HDF5 files in `/results` subfolders. For sample SAPT inputs, see:

- `trex_workshop2023/h2_h2/cisd/results` ,
- [https://qchem.gitlab.io/gammcor-manual/pages/calculation/sapt\\_methods/running\\_sapt\\_qpckg.html](https://qchem.gitlab.io/gammcor-manual/pages/calculation/sapt_methods/running_sapt_qpckg.html) .

**Answer the questions:**

1. How accurate is SAPT based on Hartree-Fock description of the monomers near the equilibrium and in the case of a stretched bond?
2. Which interaction energy components dominate for  $R = 1.44$  a.u. and  $R = 7.20$  a.u.?
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<sub>2</sub>-H<sub>2</sub> dimer. CAS( $m, n$ ) denotes CASSCF calculation with  $m$  electrons occupying  $n$  active orbitals (for each monomer). Energy unit is microhartree.

	$E_{\text{elst}}^{(1)}$	$E_{\text{exch}}^{(1)}$	$E_{\text{ind}}^{(2)}$	$E_{\text{exch-ind}}^{(2)}$	$E_{\text{disp}}^{(2)}$	$E_{\text{exch-disp}}^{(2)}$	$E_{\text{int}}^{\text{SAPT}}$
$R = 1.44$ a.u.							
HF							
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							
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<sub>2</sub>\* (excited states, ver 1)

Perform a SAPT(CISD)/aug-cc-pVDZ calculation for the He-H<sub>2</sub> complex (Figure 2):

- both monomers are in the ground state and  $R = 6.6$  a.u.,
- He is in the ground state, H<sub>2</sub> is in the first singlet excited state ( $^1\Sigma_u^+$ ), and  $R = 4.0$  a.u.

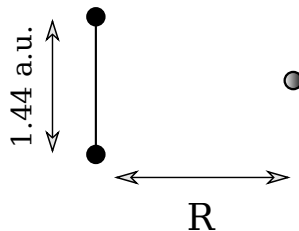


Figure 2: He-H<sub>2</sub> in T-shaped geometry.

First, use Quantum Package to run Hartree-Fock/CISD calculations. Then, use GammCor to run SAPT. You will find the xyz files in `trex_workshop2023/he_h2` directory (see also Table 2).

### Answer the questions:

- What are the key interaction energy ingredients in the van der Waals minimum region in ground- and excited-state?
- Which energy component dominates ground/exited-state interaction at  $R = 4.4$  a.u.?

If you do not have access to Quantum Package, you will find the necessary HDF5 files in `/results` subfolders. For sample SAPT jobs, see:

- [https://qchem.gitlab.io/gammcor-manual/pages/calculation/sapt\\_methods/running\\_sapt\\_qpckg.html](https://qchem.gitlab.io/gammcor-manual/pages/calculation/sapt_methods/running_sapt_qpckg.html) ,
- [https://quantum-package.readthedocs.io/en/dev/users\\_guide/excited\\_states.html](https://quantum-package.readthedocs.io/en/dev/users_guide/excited_states.html)

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

	$E_{\text{elst}}^{(1)}$	$E_{\text{exch}}^{(1)}$	$E_{\text{ind}}^{(2)}$	$E_{\text{exch-ind}}^{(2)}$	$E_{\text{disp}}^{(2)}$	$E_{\text{exch-disp}}^{(2)}$	$E_{\text{int}}^{\text{SAPT}}$
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