Exercise Ex2

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Please use this template to submit your answers.
If you had to modify code from the notebook, please include the modified code in your submission either as screenshot or in a

```
\begin{lstlisting}[language=Python]
\end{lstlisting}
```

environment.
You only need to include the code cells that you modified.
Note, that references to other parts of the documents aren't resolved in this template and will show as **??**. Check the text of the exercises on website for the reference

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Exercise 1
A minimal basis set...
a) ...always gives the lowest energy.
b) ...is optimized for small molecules.
c) ...contains one basis function for each atomic orbital only.

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 c) ...contains one basis function for each atomic orbital only.

Exercise 2
A split-valence basis set...
a) ...contains two basis functions for each valence atomic orbital.
b) ...doubles the CPU time of the calculation.
c) ...attributes a different number of basis functions to valence and core orbtials.

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Exercise 3

Which of the following basis sets does not contain polarization functions?
a) 6-31G*
b) 6-31G(d,p)
c) 3-21+G
d) DZP

c) 3-21+G

Exercise 4

Diffuse functions are added to a basis set to...
a) ...save CPU time.
b) ...better represent electronic effects at larger distances from the nuclei.
c) ...take polarization into account.
d) ...enhance the description of core orbitals.

b) ...better represent electronic effects at larger distances from the nuclei.

Exercise 5

Using the information given about the 3-21G contraction coefficients:
a) Give the basis functions corresponding to the 1s, 2s and 2p orbitals of Carbon (**Hint**: use information from **Fig. 2.2**).
b) We wish to construct a single molecular orbital $\phi_m(\mathbf{r}_m)$ (which is a one-particle molecular orbital) for a carbon atom using the 3-21G basis set (so that our 1s, 2s, and 2p orbitals are all occupied with at least one electron and included in the construction of $\phi_m(\mathbf{r}_m)$). How many coefficients and exponents coming from contracted GTOs are unchanged during a Hartree Fock calculation (i.e. give the number of fixed coefficients, the ones that are not optimized)? Which expansion coefficients will vary for the calculation of the Hartree-Fock energy (i.e. explain the kind of coefficients that will be optimized during the calculation)?

a)
→ 1s orbital (core; one basis function from 3 GTOs):

$$\chi_{1s}(r) = 0.0617669\, e^{-172.256 r^2} + 0.3587940\, e^{-25.9109 r^2} + 0.7007130\, e^{-5.53335 r^2}$$

→ 2s orbital (valence; two basis functions):
- Inner (from 2 GTOs):

$$\chi_{2s}^{(2)}(r) = -0.3958970\, e^{-3.66498 r^2} + 1.2158400\, e^{-0.770545 r^2}$$

- Outer (from 1 GTO):

$$\chi_{2s}^{(1)}(r) = 1.0000000\, e^{-0.195857 r^2}$$

→ 2p orbitals (valence; two basis functions, we have the same thing for p_y and p_z):

- Inner (from 2 GTOs):

$$\chi_{2p_x}^{(2)}(r) = 0.2364600 \; e^{-3.66498r^2} + 0.8606190 \; e^{-0.770545r^2}$$

- Outer (from 1 GTO):

$$\chi_{2p_x}^{(1)}(r) = 1.0000000 \; e^{-0.195857r^2}$$

b) We know that an orbital can be expanded in the set of basis functions $\{\chi_n\}$ that we previously found such that :

$$\phi_m(\mathbf{r}_m) = \sum_n D_{mn}\chi_n(\mathbf{r}_m)$$

On the other hand, through our basis set, we found 9 different functions $(\chi_{1s}(r), \; \chi_{2s}^{(2)}(r), \; \chi_{2s}^{(1)}(r), \; \chi_{2p_x}^{(2)}(r), \; \chi_{2p_y}^{(2)}(r), \; \chi_{2p_z}^{(2)}(r), \; \chi_{2p_x}^{(1)}(r), \; \chi_{2p_y}^{(1)}(r), \; \chi_{2p_z}^{(1)}(r))$. This leads to a total of 9 coefficients D_{mn} to optimize for one 1-electron orbital function $\phi_m(\mathbf{r}_m)$.

Secondly, the number of coefficients that dont need to be optimize are the one fixed in the definition of the different basis functions χ. $\chi_{1s}(r)$ has 3 coefs $\alpha_{1s,k}$ and 3 $\zeta_{1s,k}$ which are fixed, while $\chi_{2s}^{(2)}$ has 2 coefs $\alpha_{2s,k}$ and 2 $\zeta_{2s,k}$ which are fixed, and $\chi_{2s}^{(1)}$ has 1 coefs $\alpha'_{2s,k}$ and 1 $\zeta'_{2s,k}$ which are fixed. We can proceed similarly for the $2p$ shell and find a total of 18 fixed coefficients that do not need to be optimized.

Exercise 6

You wish to calculate the wavefunction of acetylene C_2H_2 using the 6-31G* basis.

Indicate the number of basis functions and the number of Gaussian primitives that will be used in the calculation.

- For carbon (C) atoms:

    - $\chi(1s)$: 1 function $\rightarrow$ 6 primitives (core orbital, single contracted function).

    - $\chi(2s)$: 2 functions $\rightarrow$ 4 primitives (3 inner + 1 outer, split-valence with 2 contracted functions).

    - $\chi(2p)$: 6 functions $\rightarrow$ 12 primitives (3 inner $\times$ 3 directions + 1 outer $\times$ 3 directions, 2 contracted functions per direction).

    - $\chi_{\text{polarization}}$: 6 functions $\rightarrow$ 6 primitives (polarization functions, uncontracted, typically Cartesian components).

- For hydrogen (H) atoms:

    - $\chi(1s)$: 2 functions $\rightarrow$ 4 primitives (3 inner + 1 outer, split-valence with 2 contracted functions). This is because $(1s)$ is directly considered to be valence and no core is considered

Total Calculation

- Total basis functions: 34 (15 per C × 2 + 2 per H × 2).

- Total primitives: 64 (28 per C × 2 + 4 per H × 2).

Exercise 7

Include a table of the the calculated energies using the three different basis sets, specifying for each of them the number of basis functions used. Compare the energies with the analytical value for the H atom, given by the analytical expression:

$$E = -\frac{1}{2}m_e c^2 \alpha^2, \tag{1}$$

where α is the fine structure constant.

$$m_e = 0.910953 \cdot 10^{-30} kg \tag{2}$$
$$c = 2.99792458 \cdot 10^8 ms^{-1} \tag{3}$$
$$\alpha = 7.2973525376 \cdot 10^{-3} \tag{4}$$
$$N_A = 6.0221367 \cdot 10^{23} mol^{-1} \tag{5}$$

Pay attention to the units - use atomic units or kcal·mol^{-1} throughout!

Thoeritical value in J: $E = -2.179907351 \cdot 10^{-18}[J]$

Thoeritical value in $J \cdot mol^{-1}$: $E = -1'312'770.006[J \cdot mol^{-1}]$

Thoeritical value in kcal·mol^{-1} : $E = \frac{-1'312'770.006[J\cdot mol^{-1}]}{4184} = -313.7595617[$kcal·mol$^{-1}]$

Theoritcal in (ua or Hartree) : $E = \frac{-2.179907351\cdot 10^{-18}[J]}{4.3597482\cdot 10^{-18}[J]} = -0.5[ua]$

Table 1: Calculated energies for the Hydrogen atom with different basis sets

Basis Set	Number of Basis Functions	Computed Energy (au)	Deviation from Analytical (au)
STO-3G	1	-0.4665818495572754	+0.03341815044
6-31G	2	-0.4982329107290698	+0.001767089271
6-311G	3	-0.4998098152732825	+0.0001901847267

Exercise 8

What is the influence of the basis set size on the accuracy of the result? How do the split-valence bases compare to STO-3G?

Increasing the number of basis functions leads to higher accuracy since we are closer to $E = -0.5[$ua$]$. We also notice that the split-valence bases outperform

STO-3G. This is due to the fact that STO-3G is a minimum type basis where the exponents of the PGTO are determined by fitting to the STO, rather than optimizing them by a variational principal such as done for split-valence bases. The latter have coefficient to be optimized and allow more flexibility to the valence orbitals even though a great amount of the energy is concentrated in the core, leading to higher accuracies.

Exercise 9

How does the resulting relative energies for helium compare to the hydrogen case? And why?

We can see that Hartree-Fock energies of Helium are significantly lower (e.g., -2.859918 vs. -0.499810 for 6-311G) than the one of hydrogen. We can deduce that this is likely due to its higher nuclear charge ($Z = 2$ vs. $Z = 1$), which leads to binding electrons more tightly. We also observe that energies of Hydrogen are closer to its exact value (-0.5) because its single electron lacks correlation effects. Then this leads to faster convergence (1–2 iterations) compared to helium's slower convergence (4–5 iterations) likely due to electron-electron repulsion. On the other hand we can say that larger basis sets like 6-31G or 6-311G improve helium's energy more than hydrogen's, as helium's two-electron system benefits more from enhanced wavefunction flexibility. Indeed even small basis set performs well for the simplicity of Hydrogen. Also H_2 has two electrons in his valence shell making him more stable than Hydrogen. This leads to lower energy since it would not be favorable to give one his electrons (high ionization energy required as obtained)

Exercise 10

Include in your report the coordinates you set for your water molecules and a screenshot of how it looks like in 3D representation.

```
1  h2o = psi4.geometry("""
2  0 1
3  O
4  H 1 0.9572
5  H 1 0.9572 2 104.5
6  """)
```

Exercise 11

How do you calculate the spin multiplicity of a species? Compare the case of the water molecule to the previous examples of the hydrogen atom and the helium atom.

The spin multiplicity (M) of a species is calculated using the formula $M = 2S+1$, where $S = N_{\text{unpaired}}/2$. For the water molecule, O has 6 valence electrons while the two H have one 1 contributing to the pairing. Therefore the system has 0 unpaired electron leading to $S_{H_2O} = 0$ and $M_{H_2O} = 2S + 1 = 1$. On the other hand for hydrogene alone, there is one unpaired electron. Therefore
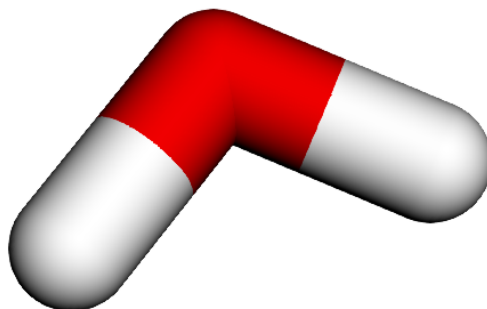
Figure 1: H_2O molecule via psi4

$N_\text{unpaired} = 1$, $S_H = 1/2$ and $M_H = 2 \cdot \frac{1}{2} + 1 = 2$. For Helium which has an electronic configuration $1s^2$, it has no unpaired electron, therefore $N_\text{unpaired} = 0$, $S_{He} = 0$ and $M_{He} = 2 \cdot 0 + 1 = 1$.

Exercise 12

Compute energy calculations for the different basis sets indicated below with a loop similar to the one used before. Include a table of the the calculated energies. Specify what is the difference between the basis sets that we used.

Bonus: which of the additional functions introduced with respect to the `6-31G` basis set are more reasonable for the present case, i.e. a water molecule? Why?

Basis Set	Energy (Hartree)	Number of Basis Functions	Dipole Magnitude (au)
6-31G	$-75.983\,974\,744\,631\,41$	13	$1.034\,894\,3$
6-311G	$-76.009\,385\,726\,536\,66$	19	$1.033\,308\,0$
6-31+G	$-75.991\,265\,839\,113\,38$	17	$1.080\,042\,9$
6-31G**	$-76.023\,127\,185\,732\,14$	25	$0.859\,640\,3$
6-31++G**	$-76.030\,744\,652\,767\,42$	31	$0.899\,585\,8$

Table 2: Properties of H_2O calculations with different basis sets: UHF energies, number of basis functions, and dipole moments.

The size of the basis set (M) directly impacts computational cost. Larger sets like 6-31++G** (with diffuse and polarization functions) increase the number of functions to better represent the wavefunction, while minimal sets like 6-31G use fewer for efficiency.

The energies decrease (become more negative, more stable) with larger basis sets, converging toward the Hartree-Fock limit. Indeed finite basis sets approximate the complete basis; split-valence bases like 6-311G (triple-zeta) and those with polarization (**) or diffuse (+) functions improve accuracy by better spanning the molecular orbital space

Concerning what we added compared to basis sets considered for Hydrogen, we added diffuse functions (+) which increases the dipole (e.g., 6-31G to 6-31+G: 1.03 to 1.08 au) by better describing long-range electron density, as STOs/GTOs with low exponents capture diffuse tails. Polarization functions (**) decrease it (e.g., 6-31G to 6-31G**: 1.03 to 0.86 au) by allowing orbital distortion for better angular flexibility. Combined (++G**), they yield values closer to experiment ($\approx$ 0.73 au), reducing finite basis error.

Bonus: For H_2O, polarization functions (d on O, p on H) in 6-31G** and 6-31++G** are more reasonable than diffuse functions. They improve bond polarity and directional electron distribution, aligning with H_2O's covalent O-H bonds, as seen in lower energies and better dipole values ($\approx$0.86-0.90 au vs. experimental $\approx$0.73 au). Diffuse functions, useful for anions or tails, are less critical for neutral H_2O where electrons are not far away.

Exercise 13

What can you say about the relative energies and stability of a linear water molecule compared to our original bent case? And why?

We can see that the bent H_2O configuration is more stable than the linear one with convergence towards a lower energy. On the other hand it requires more SCF iterations (8 vs. 7), showing a relative energy decreasing slower for the bent configuration vs the linear one. We also know that the bent geometry (configuration of water found in nature) minimizes the electron repulsion due to the two lone pairs which bend the molecule.

Exercise 14

What can you say about the stability of the bent and linear beryllium hydride conformations? How does it compare to the water case and why?

The linear BeH_2 configuration is more stable than the bent one. Indeed it has a lower energy(-15.619552752773998 vs -15.557525851835333, and converges faster (5 vs. 6 iterations). Unlike H_2O, where the bent form is favored which comes from the lone pair repulsion, BeH_2 has a linear stability since there is no lone pairs.