Exercise 1 Dimensionality of PES

- What is the dimensionality of the PES of H_2O?
- And of HOF?
- And of H_2O_2?
- We assumed that the two bond lengths of water are equal. Must an acyclic molecule AB_2 have equal AB bond lengths? What about a cyclic molecule AB_2? (Chapter 2 Harder question 4)

Exercise 2 Constructing a Z-matrix for H_2CO

For a nonlinear molecule of N atoms, there are $p = 3N - 6$ vibrational degrees of freedom, that can be varied during a geometry optimization. The Z-matrix describes a molecule with p coordinates in term of bond lengths, bond angles and dihedral angles. The most-used Z-matrix format uses the following syntax:

*ElementLabel atom*1 ;*bondLength atom*2 *bondAngle atom*3 *dihedralAngle*

ElementLabel is a character string consisting of either the chemical symbol for the atom or its atomic number. If the elemental symbol is used, it may be optionally followed by other alphanumeric characters to create an identifying label for that atom. A common practice is to follow the element name with a secondary identifying integer: C1, C2, etc.

atom1, *atom2*, *atom3* are the labels for previously-specified atoms. The position of the current atom is then specified by giving the length of the bond joining it to *atom1*, the angle formed by this bond and the bond joining *atom1* and *atom2*, and the dihedral (torsion) angle formed by the plane containing *atom1*, *atom2* and *atom3* with the plane containing the current atom, *atom1* and *atom2*. The bond angles must be in the range $0° < angle < 180°$. Dihedral angles may take on any value.

```
H
O 1 0.9
O 2 1.4 1 105.0
H 3 0.9 2 105.0 1 120.0
```

The first line of the Z-matrix simply specifies a hydrogen. The next line lists an oxygen atom and specifies the internuclear distance between it and the hydrogen as 0.9 Angstroms. The third line defines another oxygen with an O-O distance of 1.4 Angstroms (i.e., from atom 2, the other oxygen) and having an O-O-H angle (with atoms 2 and 1) of 105 degrees. The fourth and final line is the only one for which all three internal coordinates need be given. It defines the other hydrogen as bonded to the second oxygen with an H-O distance of 0.9 Angstroms, an H-O-O angle of 105 degrees and a H-O-O-H dihedral angle of 120 degrees.

Variables may be used to specify some or all of the values within the Z-matrix. Here is another version of the previous Z-matrix:

```
H
O 1 R1
O 2 R2 1 A
H 3 R1 2 A 1 D
  Variables:
R1 0.9
R2 1.4
A 105.0
D 120.0
```

Symmetry constraints on the molecule are reflected in the internal coordinates. The two H-O distances are specified by the same variable, as are the two H-O-O bond angles. When such a Z-matrix is used for a geometry optimization in internal coordinates, the values of the variables will be optimized to locate the lowest energy structure. One therefore has to be careful that the variables given in the Z-matrix coincide with the $p = 3N - 6$ vibrational degrees of freedom. A frequent cause of problems in optimizations was (and still is) the specification of too many or too few coordinates. Using all Cartensian coordinates obvious leads to too many degrees of freedom and this was the initial reason to use a Z-matrix. Too few coordinates (by setting too many symmetry constraints) correspond to a constraint on the geometry and means that the full surface is not searched. Too many coordinates result in a redundancy.

In the early days of geometry optimizations it was usual to take all kinds of shortcuts in order to save computer resources. For example, the C-H bonds length would be taken equal in substituted benzenes, yet there are subtle, systematic differences. Computer resources are much cheaper than they once were, and the assumptions of constant bond length, etc. are no longer needed.

a) What are the number of internal coordinates for formaldehyde?

b) Construct a Z-matrix for formaldehyde. You will need this Z-matrix for the first computer exercise.

c) Do the number of parameters in the Z-matrix correspond to your answer at (a)?

Exercise 3 Importance of gravitational energy in chemistry.

This question is taken from Chapter 2 Harder questions 2+3

a) How high would you have to lift a mole of water for its gravitational potential energy to be equivalent to the energy needed to dissociate it completely into hydroxyl radicals and hydrogen atoms? The strength of the O–H bond is about 400 kJ mol^{-}1; the gravitational acceleration g at the Earths surface (and out to hundreds of km) is about 10 ms^{-2}.

b) What does this indicate about the role of gravity in chemistry?

c) If gravity plays no role in chemistry, why are vibrational frequencies different for, say, C–H and C–D bonds?