Coordinate Systems and Model Building
座標系統與模型的建立

    In chemical calculation, the initial steps usually include the input of molecular structures. There are three major ways of providing the molecular structures:

(1) cartesian coordinates
(2) internal coordinates or Z-matrix
(3) graphic user interface (GUI)

   直角座標的方式是將分子中每一個原子的 xyz 座標分別列出，這是一種最簡單的結構指定方式，比如說二氧化碳的結構可以用以下的座標表示

In Cartesian coordinates, a molecular structure is written by x, y, z coordinates (in Å or bohrs) of every constituent atoms:

```
O  0.0  0.0  0.00
C  0.0  0.0  1.23
O  0.0  0.0  2.46
```

Cartesian coordinates is the most straightforward way of specifying a molecular structure. They are good choice for linear molecules, highly symmetric simple molecules (D_{4h}, O_h), very large molecules, and crystal structures. (xyz, pdb, cif format).

However, for small molecules the Cartesians might not be convenient for chemists since the bond lengths, bond angles are more familiar quantities. The **internal coordinates** use these familiar quantities to specify a molecular structure. For example, the structure of a water molecule can be specified uniquely by two bond lengths and one bond angle:

```
H
O  1  0.97
H  2  0.97  1  104.0
```

in the above, every row starts with an atomic symbol followed by the internal coordinates of the atom in the molecules. No particular information is needed for the first atom other than the atomic symbol. Then in the second row we need to provide bond distance (0.97 Å) between the first and the second atoms. In the third row, we specify the distance between the third and the second atoms (0.97 Å), and then the 3-2-1 bond angle (104.0 degrees).

When there are four or more atoms in a molecule, we usually need to specify the dihedral angles starting from the fourth atom, for example:

```
Cl
C   1  1.8
H   2  1.1  1  110.0
H   2  1.1  1  110.0  3   120.0
H   2  1.1  1  110.0  3  -120.0
```

The dihedral angles (120.0 degrees) at the end of the fourth line is the angle between the plane containing the 4-2-1 atoms and the plane containing the 2-1-3 atoms. The range of dihedral angles is usually defined from -180 degrees to 180 degrees. If we use A-B-C-D four atoms to define the dihedral angle of atom A (in the case just mentioned above, it would be 4-2-1-3 to define the dihedral angle of 4), the convention used by IUPAC is that looking along the B-C bond, the angle is defined as the clockwise rotation of the A-B bond to superimpose the C-D bonds. In the example above, we built a C_{3v} structure of CH_3Cl, and the dihedral angles of atom 4 and atom 5 are 120 and -120 degrees, respectively.

Another useful way of defining internal coordinates is to use one bond length and two angles. Using ammonia as an example:

```
N
H  1  R
H  1  R  2  A
H  1  R  2  A  3  A  1
```

```
R=0.95
A=100.0
```

The "1" in the last row means that the last A is the angle of 4-1-3, not the dihedral angle of 4-1-2-3. Sometimes, this is a more convenient way of defining molecular symmetry. In the example above, the method ensures a C_{3v} structure of an ammonia molecule.

When there are three or more atoms in a straight line, including dummy atoms makes it easier to define the internal coordinates. Using the acetylene as an example:

```
H
C  1  RCH
X  2  1.0  1  90.0
C  2  RCC  3  90.0  1  180.0
X  4  1.0  2  90.0  3   0.0
H  4  RCH  5  90.0  2  180.0
```

Where the X are dummy atoms. These atoms are there to simplify the definition of the internal coordinates, and do not make any effects in actual calculation.

The structure specification accepted by the Gaussian program can be found at:
https://gaussian.com/zmat/

Now, you can also the tools in graphic user interface (GUI) of various programs to build large

3-D molecular structures very quickly and easily by just a few clicks and drags of the mouse. For very complex molecules this might be the only sensible way. The calculated results can also be visualized conveniently using the GUI. Several commonly used programs include Spartan, Chem3D, and GaussView.

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