INTERNAL COORDINATE SYSTEM

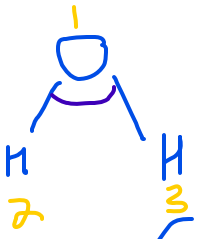
Molecular Geometry Input-

No:	Cartesian Coordinate system	Internal Coordinate system
1	Uses three mutually perpendicular axes x,y,z	bond lengths, valence angles and torsions are used
2	Cartesian coordinates are easy to define	Not so easily defined
3	The potential energy surface has very strong coupling between coordinates when represented in Cartesians.(Demerit)	more appropriate coordinates to describe the behavior of molecules
4	More coupling	They express the natural connectivity of chemical structures, there is much less coupling between these internal coordinates.

Z Matrix

- The Z-matrix is a way to represent a system built of atoms.
- It is also known as an internal coordinate representation.
- We write a Z-matrix in terms of bond lengths, angles, and dihedrals since this will preserve the actual bonding characteristics.
- *The name arises because the Z-matrix assigns the second atom along the Z axis from the first atom, which is at the origin.*
- They are used for creating input geometries for molecular systems in many molecular modelling and computational chemistry programs.
- Also, since Z-matrices can contain molecular connectivity information, quantum chemical calculations such as geometry optimization may be performed faster.
- The Z-matrix representation is often preferred, because this allows symmetry to be enforced upon the molecule (or parts thereof) by setting certain angles as constant.

Z matrix formulation



- Each line of a Z-matrix gives the internal coordinates for one of the atoms within the molecule. The most-used Z-matrix format uses the following syntax: for (a triatomic molecule)

Element-label

atom 1, bond-length,

atom 2, bond length ,bond-angle,

atom 3, bond length ,bond-angle, dihedral-angle

O
H 1 .9
H 1 .9 2 104

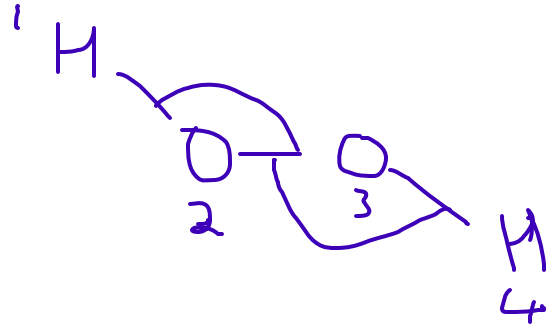
- Element-label is a character string consisting of either the chemical symbol for the atom or its atomic number. If the elemental symbol is used, it may be optionally followed by other alphanumeric characters to create an identifying label for that atom. A common practice is to follow the element name with a secondary identifying integer: C1, C2, etc.
- Atom1, atom2, atom3 are the labels for previously-specified atoms and are used to define the current atoms' position. Alternatively, the other atoms' line numbers within the molecule specification section may be used for the values of variables, where the charge and spin multiplicity line is line 0.
- 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 angle formed by the plane containing atom1, atom2 and atom3 with the plane containing the current atom, atom1 and atom2. Note that bond angles must be in the range 0° < angle < 180°. Dihedral angles may take on any value.

As an initial example, consider **hydrogen peroxide**. A Z-matrix for this structure would be:

H

O 1 0.9

O 2 1.4 1 105.0

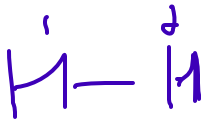


H 3 0.9 2 105.0 1 120.0

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.

Z MATRIX of Hydrogen Molecule

H



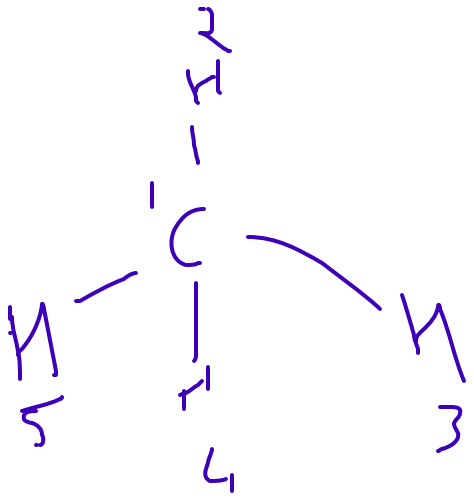
H 1 .75

Z matrix of water

O
H 1 0.952
H 1 0.952 2 104.5

Z matrix of Methane

C
H 1 1.083
H 1 1.083 2 109.471
H 1 1.083 2 109.471 3 120.0
H 1 1.083 2 109.471 4 120.0



Z matrix of Ammonia

N

H 1 1.0

H 1 1.0 2 110

H 1 1.0 2 110 3 120

Z MATRIX of Formaldehyde

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C
O 1 1.2
H 1 1.0 2 120
H 1 1.0 2 120 3 180
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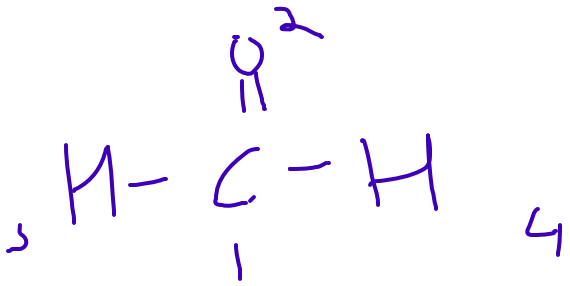


Z matrix of Acetaldehyde

C

O 1 1.2

H 1 1.0 2 120

C 1 1.5 2 120 3 180

H 4 1.1 1 110 2 0

H 4 1.1 1 110 2 120

H 4 1.1 1 110 2 -120

Z MATRIX of Ethane

C

C 1 1.53

H 1 1.09 2 112

H 1 1.09 2 112 3 120

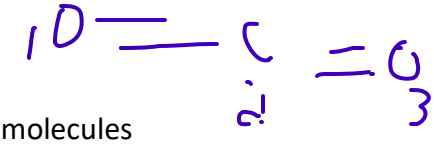
H 1 1.09 2 112 3 240

H 2 1.09 1 112 3 15

H 2 1.09 1 112 3 135

H 2 1.09 1 112 3 255

Z Matrix of Carbon dioxide -Dummy atoms



- Bond angles equal to 180 degrees are not accepted by Z matrix
- Therefore, we use dummy atoms when we are dealing with linear molecules
- When the input is read into a computer code, these dummy atoms are just used as reference points, and do not enter into any calculation

Z MATRIX of Carbon Dioxide

O

C 1 1.2

X 1 1.0 2 90

O 1 1.2 2 90 3 180