
بسم الله الرحمن الرحيم

Introduction to Computational Chemistry

Lecture # 02

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Key Concepts

- In this lecture we ‘ll learn:
- Nobel Recognition of Computational Chemistry
- Advantages of Computational Chemistry
- Disadvantages of Computational Chemistry
- Theoretical Model
- Molecular Structure

Nobel Recognition of Computational Chemistry

- The 1998 Nobel Prize in Chemistry was awarded to ***Walter Kohn*** “for his development of the density functional theory” and ***John Pople*** “for his development of computational methods in quantum chemistry”.
- In 2013, ***Martin Karplus***, ***Michael Levitt***, and ***Arieh Warshel*** have been awarded the Nobel Prize in Chemistry for the development of computer-based methods to model complex systems.

Advantages of Computational Chemistry

- Calculations are *easy to perform*, whereas experiments are often difficult.
- Calculations are becoming *less costly*, whereas experiments are becoming more expensive.
- Calculations can be *performed on any system*, even those that don’t exist, whereas many experiments are limited to relatively stable molecules.
- Calculations are *safe*, whereas many experiments have an intrinsic danger associated with them.

Disadvantages of Computational Chemistry

- Calculations can be *very expensive* in terms of the amount of time required.
- Calculations can be performed on any system, even those that don't exist!

Computational chemistry is not a replacement for experimental studies, but plays an important role in enabling chemists to:

- Explain and rationalize known chemistry
- Explore new or unknown chemistry

Theoretical Model

- The theoretical foundation for computational chemistry is the time-independent Schrodinger wave equation:
$$\hat{\mathrm{H}}\Psi = \mathrm{E}\Psi$$
- Ψ is the wavefunction. It is a function of the positions of all the fundamental particles (electrons and nuclei) in the system.
- $\hat{\mathrm{H}}$ is the Hamiltonian operator. It is the operator associated with the observable energy.
- E is the total energy of the system. It is a scalar (number).
- The wave equation is a postulate of quantum mechanics.

The Hamiltonian

- The Hamiltonian, $\widehat{\mathrm{H}}$, is an operator. It contains all the terms that contribute to the energy of a system:

$$\widehat{\mathrm{H}} = \widehat{\mathrm{T}} + \widehat{\mathrm{V}}$$

- $\widehat{\mathrm{T}}$ is the kinetic energy operator:

$$\hat{\mathrm{T}} = \hat{\mathrm{T}}_{\mathrm{e}} + \hat{\mathrm{T}}_{\mathrm{n}}$$

$$\hat{\mathrm{T}}_{\mathrm{e}} = -\frac{1}{2}\sum_{i} \nabla_{i}^{2} \qquad \hat{\mathrm{T}}_{\mathrm{n}} = -\frac{1}{2M_A}\sum_{A} \nabla_{A}^{2}$$

- ∇^2 is the Laplacian given by:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The Hamiltonian

- $\hat{V}$ is the potential energy operator::

$$\hat{V} = \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}$$

- $\hat{V}_{nn}$ is the nuclear-nuclear repulsion term:

$$\hat{V}_{\mathrm{nn}} = \sum_{A<B} \frac{Z_A Z_B}{R_{AB}}$$

- $\hat{V}_{ne}$ is the nuclear-electron attraction term:

$$\hat{V}_{\mathrm{ne}} = -\sum_{iA} \frac{Z_A}{R_{iA}}$$

- $\hat{V}_{ee}$ is the electron-electron repulsion term: $$\hat{V}_{\mathrm{ee}} = \sum_{i<j} \frac{1}{r_{ij}}$$

Atomic Units

- All quantum chemical calculations use a special system of units which, while not part of the SI, are very natural and greatly simplify expressions for various quantities.
  - The length unit is the ***bohr*** ($a_0 = 5.29 \times 10^{-11}$m)
  - The mass unit is the ***electron mass*** ($m_e = 9.11 \times 10^{-31}$kg)
  - The charge unit is the ***electron charge*** ($e = 1.60 \times 10^{-19}$C)
  - The energy unit is the ***hartree*** ($E_h = 4.36 \times 10^{-18}$ J)

- For example, the energy of the H atom is -0.5 hartree. In more familiar units this is −1, 313 kJ/mol

The Born-Oppenheimer approximation

- The Born-Oppenheimer Approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions and nuclear positions.
- Nuclei are much heavier than electrons (the mass of a proton ≈ 2000 times that of an electron) and therefore travel much more slowly.
- The electronic wavefunction depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.

The Chemical Connection

- So far, we have focused mainly on obtaining the ***total energy*** of our system.
- Many chemical properties can be obtained from *derivatives* of the energy with respect to some *external parameter*
- Examples of external parameters include:
  - Geometric parameters (bond lengths, angles etc.)
  - External electric field (for example from a solvent or other molecule in the system)
  - External magnetic field (NMR experiments)

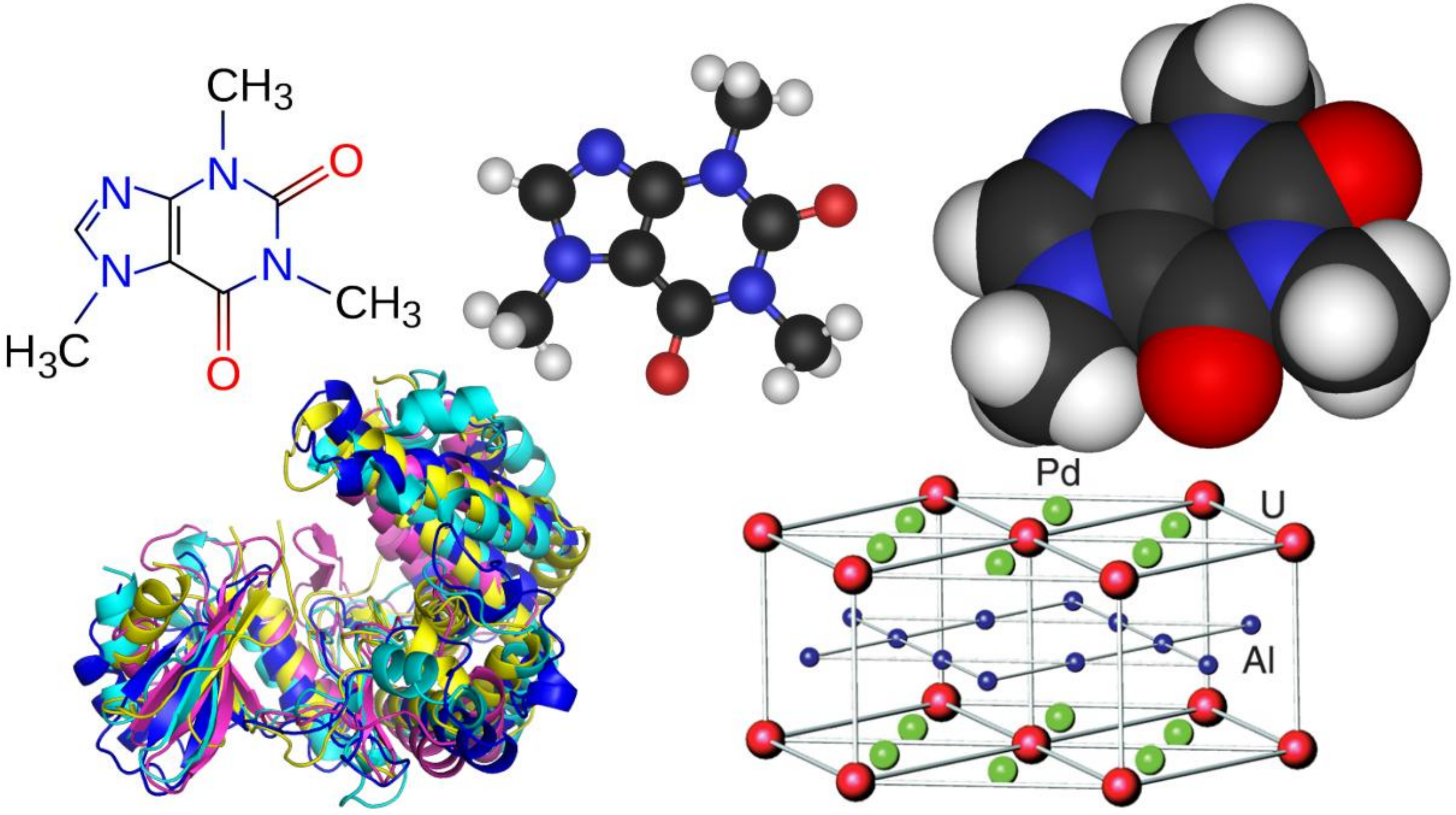
Computable Properties

Many molecular properties can be computed, these include:

- Bond energies and reaction energies
- Structures of ground-, excited- and transition-states
- Atomic charges and electrostatic potentials
- Vibrational frequencies (IR and Raman)
- Transition energies and intensities for UV and IR spectra
- NMR chemical shifts
- Dipole moments, polarizabilities and hyperpolarizabilities
- Reaction pathways and mechanisms

Molecular Structure

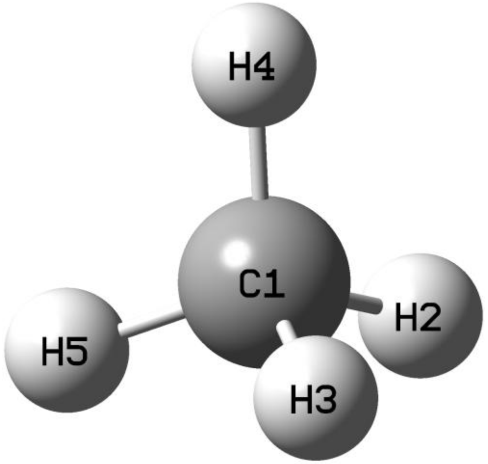
- The first thing most chemists think about when they hear the name of a compound is the structure.



Molecular Structure

Every atom has three cartesian coordinates, methane:

C	-1.69999999	1.55000011	0.00000000
H	-1.34334556	0.54119011	0.00000000
H	-1.34332715	2.05439830	0.87365150
H	-1.34332715	2.05439830	-0.87365150
H	-2.76999999	1.55001330	0.00000000



Or, we only describe the internal relationships between the atoms:

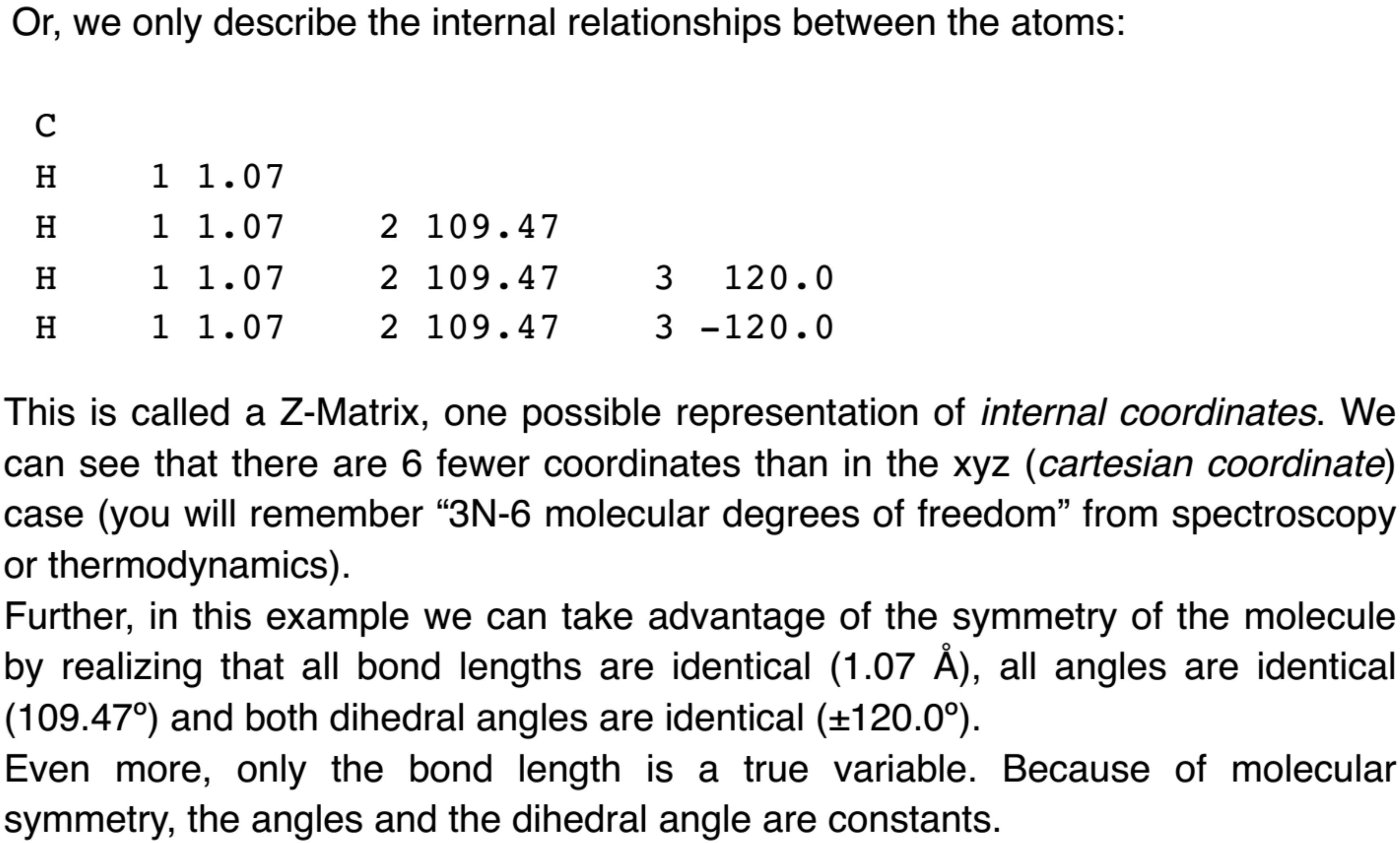
C						
H	1	1.07				
H	1	1.07	2	109.47		
H	1	1.07	2	109.47	3	120.0
H	1	1.07	2	109.47	3	-120.0

distance of this atom to atom #1 = 1.07 Å

angle between this atom, the atoms to which the distance is defined (#1) and atom #2 = 109.47°

dihedral angle between this atom, the atoms to which distance and angle are defined (#1 & #2) and atom #3 = 120.0°

Molecular Structure



Or, we only describe the internal relationships between the atoms:

```
C
H     1 1.07
H     1 1.07    2 109.47
H     1 1.07    2 109.47    3  120.0
H     1 1.07    2 109.47    3 -120.0
```

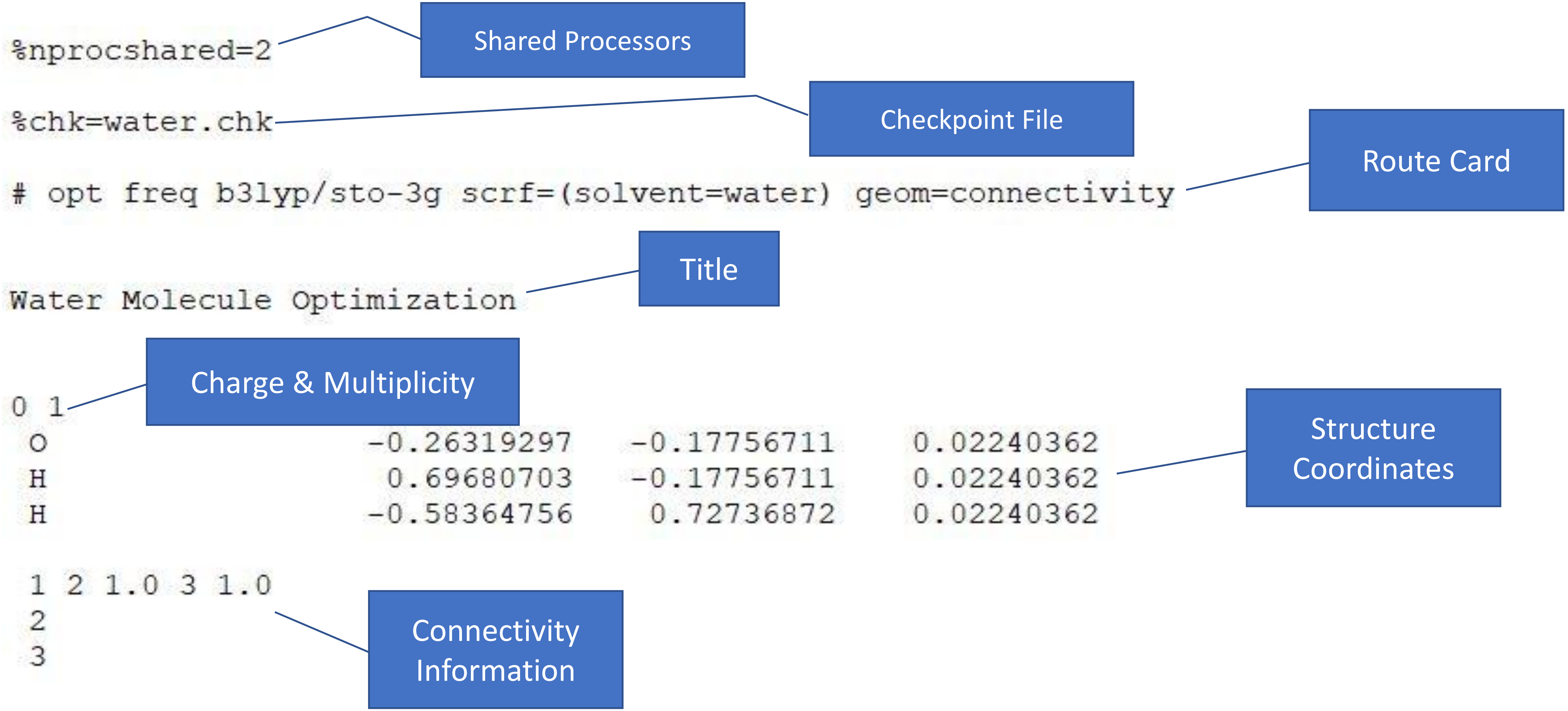
This is called a Z-Matrix, one possible representation of *internal coordinates*. We can see that there are 6 fewer coordinates than in the xyz (*cartesian coordinate*) case (you will remember "3N-6 molecular degrees of freedom" from spectroscopy or thermodynamics).

Further, in this example we can take advantage of the symmetry of the molecule by realizing that all bond lengths are identical (1.07 Å), all angles are identical (109.47º) and both dihedral angles are identical (±120.0º).

Even more, only the bond length is a true variable. Because of molecular symmetry, the angles and the dihedral angle are constants.

Molecular Structure

- Following are different parts of a *Gaussian* calculation:



```
%nprocshared=2

%chk=water.chk

# opt freq b3lyp/sto-3g scrf=(solvent=water) geom=connectivity

Water Molecule Optimization

0 1
 O                -0.26319297   -0.17756711    0.02240362
 H                 0.69680703   -0.17756711    0.02240362
 H                -0.58364756    0.72736872    0.02240362

 1 2 1.0 3 1.0
 2
 3
```

Gaussian Input File

1. Link 0 Commands: -set up memory limits, etc. Line starts with %. (Optional).

2. Route Section: -specifies the details of the calculation
-can be multiple lines with max. 80 characters
-each line in Route Section must start with #

3. Blank Line: -tells program Route Section is done

4. Title

5. Blank Line: -tells program Title is done

6. Charge and Multiplicity

7. Molecular Geometry: -provide the atomic coordinates
-Cartesian or Z-matrix format

8. Blank Line: -tells program the input file is done

Route Card / Route Line

- The route line contains (but not limited to) the following information:
- Property to be calculated (Energy, Optimization, Frequency, UV, NMR, Scan etc.)
- Functional (Theory, like DFT, Hartree Fock etc.)
- Basis Set
- Solvation Information (Solvent to be used)
- Other parameters (SCF tightness, convergence criterion, etc.)

What is a basis set? We ‘ll understand it in the upcoming discussion.