CH-452: Practical Research Projects

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Project 6. HF and post-HF calculation on small molecules

- The theoretical basis of these calculations $\rightarrow$ textbooks e.g., Jensen, Introduction to Computational Chemistry

- Using a computational chemistry software called Gaussian:
    ssh moghadda@fidis.epfl.ch
    module avail
    module load gaussian/g16-A.03
    module list
https://www.epfl.ch/research/facilities/scitas/getting-started
accounts-for-courses/

- VISUALIZATION SOFTWARE: GaussView (to be purchased), ChemDraw (to be purchased), molden (free), avogadro (free), molekel (free)

- Video TUTORIALS: search for "Avogadro with Gaussian Tutorial" in Youtube.

Input

- To start a calculation we basically need four things:

✓ The structure of the molecule of interest in (cartesian or internal) coordinates

✓ The overall charge and spin state of the system

✓ The method that will be used (Hartree-Fock (HF), Density Functional Theory (DFT), Moeller-Plesset perturbation theory (MPx), etc.)

✓ A basis set.

- The input can be done manually or come from another software, such as Chem-Draw (3D) or Avogadro.

- The input for G09 can have the following extensions:

- Gaussian Input File: .gjf
- Batch Control File: .bcf
- Avogadro Input File: .com
- Text File: .txt

Input

- G09s input file consists of the following parts:
e.g., Hydrogen molecule:

% section →   % chk=h2

Route section →   # RHF 3-21G Pop=Regular SCF=Tight

Title section →   Hydrogen molecule, 3-21G, R=0.734

Charge and multiplicity →   0 1

Molecular specification →   H
                                           H 1 0.734

- % chk=h2: keep the checkpoint file with the name h2. Orbitals are
stored on this file and can be visualized with e.g, Gaussview.

Input

- # RHF 3-21G Pop=Regular SCF=Tight:

RHF: Restricted Hartree-Fock calculation

3-21G: the basis set to be used in this calculation

Pop=Regular: how the program should provide output about populated and non-populated levels

SCF=Tight: requesting tight convergence criteria for the self-consistent field calculation.

- Hydrogen molecule, 3-21G, R=0.734:

The name of the job (for the users ease only)

- 0 1:

0: The total charge of the current molecule

1: The spin-multiplicity of the molecule, which is $2S + 1 = 1$ (a singlet state) in the present case

Input (Molecular Structure; to be calculated manually or using software such as Avogadro or ChemDraw)

- The molecular geometry (the Cartesian coordinates with Angstrom units, given in floating point format):

H 0.0 0.0 0.0
H 0.734 0.0 0.0

One hydrogen atom is taken to be at the origin and the other is a distance 0.734 along the x axis.

✓ An alternative way to provide the molecular configuration is by the Z-matrix:

H
H 1 R

R=0.734

In the case of a diatomic molecule, one needs to specify only the interatomic distance R, which is set at 0.734 Angstrom.

Example: Input File of a Polyatomic Molecule (Water):

RHF 3-21G Opt SCF=Tight   **Opt**: A geometry optimization

Water 3-21G RHF

0 1

O   **O**: First atom to be an oxygen atom
H 1 R
H 1 R 2 A

R=1.0   **R**: Set to 1.0 (Angstrom)
A=105.0   **A**: Set to 105.0 (degrees)

H 1 R: The distance between the second atom, H, and the first atom, O
H 1 R 2 A: The distance between the third atom, H, and the first atom, O
            The angle between the line connecting atoms 1 and 2 and the
line connecting atoms 1 and 3 (the angle 2-1-3)

The Electronic Structure Calculation:

g16 <inputfile> outputfile
e.g., g16 <h2.com> output.out

✓ Make sure that the execution was accomplished successfully:
The line "Normal termination of Gaussian" should appear at the end of the output file.

✓ In geometry optimization calculations make sure that convergence has been accomplished:

```
            Item                  Value     Threshold  Converged?
Maximum Force              0.000221      0.000450      YES
RMS      Force              0.000216      0.000300      YES
Maximum Displacement       0.000579      0.001800      YES
RMS      Displacement       0.000665      0.001200      YES
Predicted change in Energy=-2.382812D-07
Optimization completed.
```

Output File

The output file is huge, and contains:

- The license agreement

- The final SCF energy is the energy of the system with respect to its nuclei and electrons at infinite separation. The energy is given in atomic units (Hartree):

SCF Done: E(RHF) = -76.0250361479   A.U. after   10 cycles

Self consistent field (SCF) calculation: In the SCF method, an initial set of orbitals is used to generate a new set of orbitals and the procedure is repeated until some convergence criteria is met.

Output File

- Population analysis using the SCF density:
- Different symmetries of the MOs
- The number of each orbital
- **O**: Occupied   **V**: Virtual
- Eigenvalues: energy of each orbital
- Distribution of energy for each orbital
- HOMO: highest occupied molecular orbital $\rightarrow$ **the last O**
- LUMO: lowest unoccupied molecular orbital $\rightarrow$ **the first V**

```
                      1          2          3          4          5
                      O          O          O          O          O
      Eigenvalues --  -20.54974  -1.32646   -0.70133  -0.55415   -0.49034
  1 1   O   1S        0.99710    -0.20933   0.00000   -0.06665    0.00000
  2         2S        0.01523    0.44412    0.00000   0.14316     0.00000
  3         3S        -0.00275   0.38860    0.00000   0.33098     0.00000
  4         4PX       0.00000    0.00000    0.48561   0.00000     0.00000
  5         4PY       -0.00167   -0.07241   0.00000   0.55048     0.00000
  6         4PZ       0.00000    0.00000    0.00000   0.00000     0.63091
  7         5PX       0.00000    0.00000    0.21728   0.00000     0.00000
```

Output File

- Density Matrix:

- Full Mulliken population analysis:

- Orbital energies and kinetic energies in short:

```
Orbital energies and kinetic energies (alpha):
                                    1                2
    1        O            -20.549737        29.201186
    2        O             -1.326464         2.617826
    3        O             -0.701334         1.715900
    4        O             -0.554151         2.155153
    5        O             -0.490342         2.276570
    6        V              0.184112         0.792360
    7        V              0.253864         0.763000
    8        V              0.798112         1.955305
    9        V              0.819672         2.137855
   10        V              1.162252         3.071468
```

Plotting Molecular Orbitals

Drawing HOMO and LUMO orbitals in GaussView using Gaussian output file:
https://www.youtube.com/watch?v=vMt7x7IEG1g

Drawing HOMO and LUMO orbitals in Avogadro using Gaussian output file:
https://www.youtube.com/watch?v=WpyqqDwspoo&t=33s

Some Useful Materials:

https://www.cup.uni-muenchen.de/oc/zipse/teaching/
computational-chemistry-2/topics/
a-typical-gaussian-output-file/

https://www.tau.ac.il/~ephraim/glab-1.pdf

http://wwwuser.gwdg.de/~ggroenh/exercise_H2/h2.html

https:
//barrett-group.mcgill.ca/tutorials/Gaussian%20tutorial.pdf

http://www.ccl.net/cca/documents/dyoung/topics-orig/
gaussian.html

Project 8. Phonon calculation in a crystal using DFPT

- The coordinates of lattice sites in a cubic crystal:

$$R = (n_x, n_y, n_z)a, \qquad n_\mu = 0, \pm 1, \pm 2, \ldots \qquad \mu = x, y, z$$

- The position of an atom at site R is characterized by the following vector:

$$r(R) = R + U(R)$$

- In the Debye-Einstein model, the energy for atoms in a crystal is

$$E = \sum_R \frac{P^2(R)}{2M} + \frac{1}{2} M\omega^2 \sum_{\langle RR' \rangle} |U(R) - U(R')|^2$$

The second sum is over all neighboring sites.

Introduction to Phonons

- The Fourier transform of $W(R)$ in general is

$$W(R) = \frac{1}{\sqrt{V_L}} \sum_Q W(Q) \exp(iQ.R)$$

V_L: the number of lattice sites in a crystal
- Introducing

$$U(R) = \frac{1}{\sqrt{V_L}} \sum_Q U(Q) \exp(-iQ.R) \ \& \ P(R) = \frac{1}{\sqrt{V_L}} \sum_Q P(Q) \exp(iQ.R)$$

one gets

$$\frac{1}{2} M \omega^2 \sum_{\langle RR' \rangle} |U(R) - U(R')|^2 = \sum_Q \frac{1}{2} M \Omega^2(Q) U^2(Q)$$

i.e., a set of decoupled harmonic oscillators.

The Debye-Einstein Model for Phonons

✓ $\Omega(Q)$ is a function of ω, a, and Q

✓ The linear dispersion relation at small $|Q|$

$$\Omega(Q) = v_s |Q|$$

v_s: the speed of sound

- The Debye-Einstein Hamiltonian:

$$H = \sum_Q \left(\frac{P^2(Q)}{2M} + \frac{1}{2} M \Omega^2(Q) U^2(Q) \right)$$

with

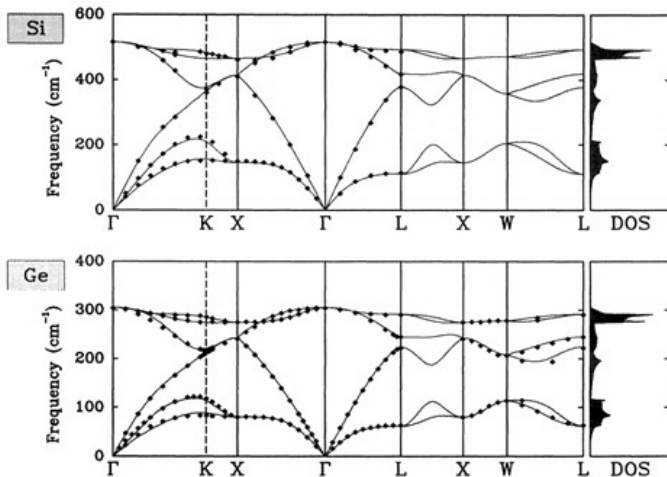$$[P_\mu(Q), U_\nu(Q')] = i\hbar \delta_{Q,Q'} \delta_{\mu\nu}$$

Reference: https://phas.ubc.ca/~feizhou/phys455/P455L5.pdf

Phonon Dispersions and Density of States

FIG. 1. Calculated phonon dispersions and densities of state of elemental semiconductors, Si and Ge. Experimental data are denoted by diamonds (from Refs. 28 and 29).

PHonon Package of Quantum Espresso

- Install QUANTUM ESPRESSO according to its general user guide (Doc/user_guide.pdf) or http://www.quantum-espresso.org.

- You can see the "PHonon" package in the main directory of QUANTUM ESPRESSO.

- Structure of the PHonon package:
    - **Doc/**: contains the user_guide and input data description
    - **examples/**: some running examples
    See Example 02 for a complete calculation of phonon dispersions in AlAs.
    - **PH/**: source files for phonon calculations and analysis
    - **Gamma/**: source files for Gamma-only phonon calculations
    - **FD/**: source files for FInite-Difference calculations

Reference: https://www.quantum-espresso.org/Doc/ph_user_guide.pdf

Different Types of Calculations Performed by the PHonon Package

- Phonon frequencies and eigenvectors at a generic wave vector, using Density-Functional Perturbation Theory.

- Effective charges and dielectric tensors.

- Electron-phonon interaction coefficients for metals.

- Interatomic force constants in real space.

- Infrared and Raman (nonresonant) cross section.

Reference:
https://www.quantum-espresso.org/Doc/ph_user_guide.pdf

Compilation of the PHonon Package

Phonon calculation is a two-step process:
1) Finding the ground-state atomic and electronic configuration;
2) Calculating phonons using Density Functional Perturbation Theory.

- **pw.x**: produces data files with a simple SCF calculation.

- **PH/ph.x**: calculates phonon frequencies and displacement patterns, dielectric tensors, effective charges (uses data produced by *pw.x*).

- **PH/q2r.x**: calculates Interatomic Force Constants (IFC) in real space from dynamical matrices produced by *ph.x* on a regular **q**-grid.

- **PH/matdyn.x**: produces phonon frequencies at a generic wave vector using the IFC file calculated by *q2r.x*; may also calculate phonon DOS. Reference:
https://www.quantum-espresso.org/Doc/ph_user_guide.pdf

Batch Systems:

#!/bin/bash -l
#SBATCH –nodes 1
#SBATCH –ntasks 1
#SBATCH –cpus-per-task 1
#SBATCH –mem 4096
#SBATCH –time 12:30:00

sbatch job.run

Submitted batch job [job-ID]

Sjob [job-ID]

module purge
module load gcc mvapich2 openblas
module load quantum-espresso/6.4-mpi-hdf5
echo STARTING AT 'date'
pw.x <nacl.scf.in> naclSlurm2.scf.out
ph.x <nacl.freq.in> naclSlurm2.freq.out
echo FINISHED at 'date'

https:
//scitas-data.epfl.ch/confluence/display/DOC/Using+the+clusters

Some Useful Resources:

- Phonon Theory:
https://www.youtube.com/watch?v=SsknqM0gCB4
https://www.youtube.com/watch?v=Qsa9eXAoh_o&t=1s
https://www.youtube.com/watch?v=ZhRk5WltxcU
https://www.youtube.com/watch?v=qCJD6NUEpmg&t=314s

N. W. Ashcroft and N. D Mermin: Solid state physics (Saunders College, 1976)

- QUANTUM ESPRESSO:
https://www.quantum-espresso.org/Doc/INPUT_PH.html

https://www.youtube.com/watch?v=9jD1KY426EM

https://www.youtube.com/watch?v=cCCTm5og9lw&t=33s

Thank you for your attention.