

**VNU University of Science - Hanoi**  
**Faculty of Physics**  
**Computational Materials Science Laboratory**

# **Gaussian09 tutorials for molecular electronic structure calculations from first principles**

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# Single point energy calculations

- **H<sub>2</sub> bond length and orbitals**

- Aims:

- Get familiar with input and output file
    - Understand how the program works
    - Understand potential energy surface
    - Understand molecular orbital formation
    - Understand basis set size
    - See the effect of different methods on electronic structure and structure of molecule

# Single point energy calculations

- **H2 bond length and orbitals**

- Input file:

```
#P RHF/STO-3G Pop=full
```

Left a blank line

```
H2 single point energy calculation
```

Left a blank line

```
0 1
```

```
H 0.0 0.0 0.0
```

```
H 0.70 0.0 0.0
```

Left a blank line

Description for keywords: <https://gaussian.com/hf/>

Description for input file: text book or <http://gaussian.com/input/>

Specify calculations (methods, basis set, results to be printed out in the output file, calculation type)

Comment line, you can write whatever you want

Charge and spin state of the molecule

Structure of the molecule  
(Cartesian coordinates in Angstrom)

# Single point energy calculations

- **H<sub>2</sub> bond length and orbitals**

- Description for basis sets:

<http://gaussian.com/basissets/>

Chapter 5 and appendix in text book

[https://chem.libretexts.org/Textbook\\_Maps/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Map%3A\\_Physical\\_Chemistry\\_\(McQuarrie\\_and\\_Simon\)/11%3A\\_Computational\\_Quantum\\_Chemistry/11.1%3A\\_Gaussian\\_Basis\\_Sets](https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/Map%3A_Physical_Chemistry_(McQuarrie_and_Simon)/11%3A_Computational_Quantum_Chemistry/11.1%3A_Gaussian_Basis_Sets)

# Single point energy calculations

- **H2 bond length and orbitals**

- Description for basis sets:

STO: Hydrogenic Slater type orbital

$$R(r) = N r^{n-1} e^{-\zeta r}$$

XG: multiple zeta basis set

$$R_{2s}(r) = C_1 r e^{-\zeta_1 r} + C_2 r e^{-\zeta_2 r}$$

=> Instead of doing nonlinear variational calculation for zeta, doing linear variational calculation for coefficient (C1, C2 ...)

# Single point energy calculations

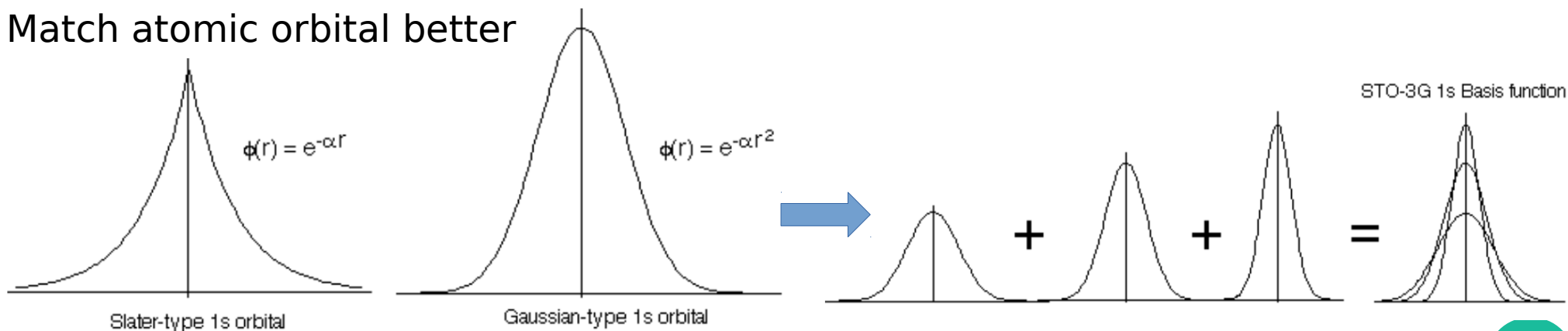
- **H2 bond length and orbitals**

- Description for basis sets:

GTO: Gaussian type orbital to simplify the integral calculations

$$G_{nlm}(r, \theta, \psi) = N_n \underbrace{r^{n-1} e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta, \psi)}_{\text{angular part}}$$

Match atomic orbital better



# Single point energy calculations

- **H2 bond length and orbitals**

- Description for basis sets:

GTO: Gaussian type orbital to simplify the integral calculations

$$G_{nlm}(r, \theta, \psi) = N_n \underbrace{r^{n-1} e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta, \psi)}_{\text{angular part}}$$

Pople type Gaussian basis set:

→ X-YZWVg(\*\* or d,p and ++ ...)

Diffusion functions

Polarized functions

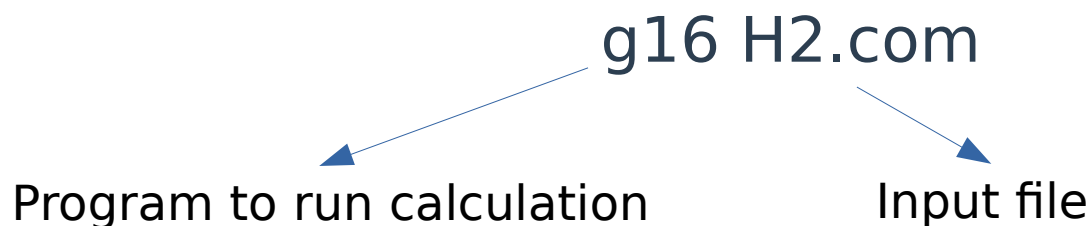
X primitive functions for each core shells

Split valence quadruple zeta basis set  
4 basis functions for each valence shell  
Y primitive functions for first, Z, W, V for second, third and forth basis function

# Single point energy calculations

- **H2 bond length and orbitals**

- Submit job:



- Look into output to understand how the program works:
    - Notice: Entering LinkX => Leave LinkX to understand how the program work: X=0 => 1 => 101 => 202 => 301 => 302 => 303 => 401=> 502 => 601
    - Check out:  
[http://wild.life.nctu.edu.tw/~jsyu/compchem/g09/g09ur/m\\_linklist.htm](http://wild.life.nctu.edu.tw/~jsyu/compchem/g09/g09ur/m_linklist.htm)



# Single point energy calculations

- **H2 bond length and orbitals**

- Convergence criteria:

Closed shell SCF:

Using DIIS extrapolation, IDIIS= 1040.

NGot= 104857600 LenX= 104856088 LenY= 104855206

Requested convergence on RMS density matrix=1.00D-08 within 128 cycles.

Requested convergence on MAX density matrix=1.00D-06.  $\Delta\rho=\sqrt{\langle\rho^2\rangle-\langle\rho\rangle^2}$

Requested convergence on energy=1.00D-06.

No special actions if energy rises.

- Convergence of the calculation:

RMSDP=0.00D+00 MaxDP=0.00D+00

CVMax= 0.00D+00

SCF Done: E(RHF) = -1.11734903500

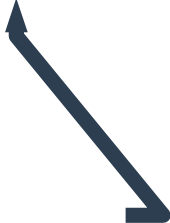
A.U. after 1 cycles

NFock= 1 Conv=0.00D+00

-V/T= 1.9221

KE= 1.211752380105D+00 PE= 3.767458393815D+00 EE= 6.823895345380D-01

Leave [Link](#) 502 at Wed Oct 3 12:33:46 2018, MaxMem= 104857600 cpu:

$$E=KE+PE+2*EE+NN$$


# Single point energy calculations

- **H2 bond length and orbitals**

- Convergence criteria:

Closed shell SCF:

Using DIIS extrapolation, IDIIS= 1040.

NGot= 104857600 LenX= 104856088 LenY= 104855206

Requested convergence on RMS density matrix=1.00D-08 within 128 cycles.

Requested convergence on MAX density matrix=1.00D-06.  $\Delta\rho=\sqrt{\langle\rho^2\rangle-\langle\rho\rangle^2}$

Requested convergence on energy=1.00D-06.

No special actions if energy rises.

- Convergence of the calculation: Change basis set to 3-21G => Need more cycles for SCF to converge  
=> Why???

# Single point energy calculations

STO-nG basis sets are minimal basis sets where n Gaussian type orbitals are fitted to a single Slater type orbital for both core and valence orbitals. Only a minimum number of atomic orbitals is used.

$$\psi_{STO-3G}(s) = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$$

$$\phi_1 = \left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2}$$

$$\phi_2 = \left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2}$$

$$\phi_3 = \left(\frac{2\alpha_3}{\pi}\right)^{3/4} e^{-\alpha_3 r^2}$$

The values of  $c_1$ ,  $c_2$ ,  $c_3$ ,  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  have to be determined by least squares fit of the three Gaussian orbitals to the single Slater-type orbitals.

# Single point energy calculations

- **H<sub>2</sub> bond length and orbitals**

- Look at MO symmetry: notice that number of MO = total number of AO included in calculation

STO-3G => 1 AO for each H atom => 2 MOs were calculated

3-21G => 2 AO for each H atom => 4 MOs were calculated

6-311G => 3 AO for each H atom => 6 MOs were calculated

- Notation of MO symmetry:
  - A, when rotation around the principal axis is symmetrical
  - B, when rotation around the principal axis is asymmetrical
  - E and T are doubly and triply degenerate representations, respectively
  - when the point group has an inversion center, the subscript g (German: gerade or even) signals no change in sign, and the subscript u (ungerade or uneven) a change in sign, with respect to inversion.

# Single point energy calculations

## • H2 bond length and orbitals

- Visualize MO orbitals:

1) Generate wavefunction file in form of .chk file (checkpoint file)

```
%Chk=H2
#P RHF/STO-3G Pop=full

H2 single point energy calculation
```

```
0 1
H 0.0 0.0 0.0
H 0.70 0.0 0.0
```

2) Generate H2.chk file => H2.fchk file which is readable by cubgen program in Gaussian package:

```
formchk H2.chk H2.fchk
```

3) Generate .cub files which contain orbital data and readable by visualization program such as Molden, VESTA:

```
cubegen 0 MO=HOMO H2.fchk H2_HOMO.cub
```

<http://www.somewhereville.com/2014/06/07/generating-molecular-orbitals-and-visualizing-assorted-properties-with-the-gaussian09-cubegen-utility/>

# Single point energy calculations

- **H2 bond length and orbitals**

**Assignment 4:** 1) Use HF/STO-3G and HF/3-21G methods to scan total energy of H<sub>2</sub> molecule with respect to H<sub>2</sub> bondlength. Plot the E(bondlength) graph and show what is the calculated H<sub>2</sub> bondlength. Compare with experiment value.

2) Change basis set size (STO-3G, 6-21G, 6-31G, 4-31G, 6-311G) and show which basis set can reproduce experimental bondlength value the best.

3) Use that basis set, change from HF to LDA (SVWN), GGA (BLYP) and hybrid (B3LYP) functionals to see effect of methods on bondlength and HOMO-LUMO gap. Show which method can reproduce experimental HOMO-LUMO gap the best. Compare you results with attached paper for H<sub>2</sub> molecule case.

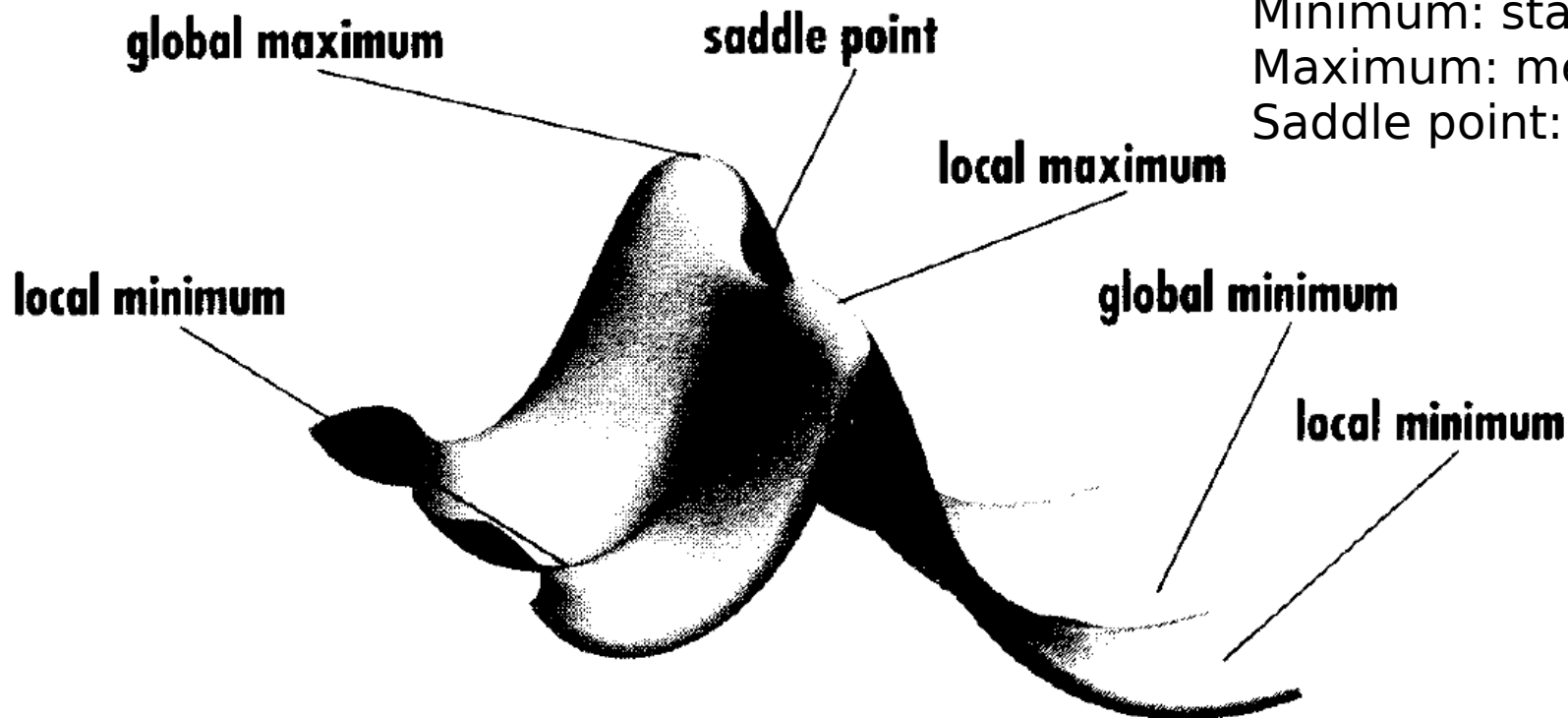
4) At the best set of methods, plot the change of HOMO-LUMO gap with respect to H-H bondlength. Explain this. Plot HOMO and LUMO of H<sub>2</sub> molecule at optimal bondlength. Give your comments on those orbitals.

# Structural optimization

- Calculate electronic structures of H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub> molecules

- Potential energy surface: stationary points:  $\text{Grad } E \text{ with all coordinates} = 0$

Minimum: stable structure  
Maximum: meta-stable structure  
Saddle point: transition state



# Structural optimization

- **Calculate electronic structures of H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub> molecules**

- Potential energy surface: stationary points: Grad E with all coordinates=0
- Mathematical language:

$$\vec{F} = -\vec{\nabla} E = 0$$

$$\frac{\partial^2 E}{\partial R^2} > 0$$

$$\frac{\partial^2 E}{\partial R^2} < 0$$

$$k \sim \frac{\partial^2 E}{\partial R^2}$$

$$f \sim \sqrt{k}$$

Minimum in R direction, frequency is real

Maximum in R direction, frequency is imaginary



# Structural optimization

- **Calculate electronic structures of H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub> molecules**

- Convergence criteria for structure optimizations:
  - ◆ The forces must be essentially 0. Specifically the maximum component of the force must be below the cutoff value of 0.00045 (interpreted as 0).
  - ◆ The root-mean-square of the forces must be essentially 0 (below the defined tolerance of 0.0003).
  - ◆ The calculated displacement for the next step must be smaller than the defined cutoff value of 0.0018 (again, meaning essentially 0).
  - ◆ The root-mean-square of the displacement for the next step must also be below its cutoff value of 0.0012.

# Structural optimization

- **Calculate electronic structures of H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub> molecules**

- **Assignment 5:** 1) Use Avogadro or Molden to build structure of H<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub>

- 2) Optimize their molecular structures (use “opt” keyword in route session of input file), calculate HOMO-LUMO gaps using B3LYP functional and various Pople type basis sets. Compare your results (HOMO-LUMO gaps, structure parameters) with experiments as well as attached paper. Which basis set is the best?

- 3) Plot energy diagrams of H<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub> of 5 orbitals below HOMO (HOMO to HOMO-5) and 5 orbitals above LUMO (LUMO to LUMO+5) with corresponding MOs. Give your comments about the formation of bonds in these molecules. (The energy diagrams have the form similar to figure in next slide)

# Structural optimization

- Calculate electronic structures of H<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub> molecules

