

# Quantum Chemistry

## Lecture 21

### Density Functional Theory

**NC State University**

# Introduction

Density functional theory is an approach for the description of ground state properties of metals, semiconductors, and insulators. The success of density functional theory (DFT) not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes.

The main idea of DFT is to describe an interacting system of fermions via its density and not via its many-body wave function. For  $N$  electrons in a solid, which obey the Pauli principle and repulse each other via the Coulomb potential, this means that the basic variable of the system depends only on three -- the spatial coordinates  $x$ ,  $y$ , and  $z$  -- rather than  $3N$  degrees of freedom.

# Basic Ideas Behind DFT

Knowledge of the density is all that is necessary for a complete determination of all ground state molecular properties.

If one knows the exact electron density,  $\rho(r)$ , then the cusps of this density would occur at the positions of the nuclei.

A knowledge of  $|\rho(r)|$  at the nuclei would give the effective nuclear charge.

Electron density is an observable.

Orbitals are just a mathematical construction.

# Significance

- (1). The wave function  $\phi$  of an N-electron system includes  $3N$  variables, while the density,  $\rho$  no matter how large the system is, has only three variables  $x$ ,  $y$ , and  $z$ . Moving from  $E[\phi]$  to  $E[\rho]$  in computational chemistry significantly reduces the computational effort needed to understand electronic properties of atoms, molecules, and solids.
- (2). Formulation along this line provides the possibility of the linear scaling algorithm currently in fashion, whose computational complexity goes like  $O(N\log N)$ , essentially linear in  $N$  when  $N$  is very large.
- (3). The other advantage of DFT is that it provides some chemically important concepts, such as electronegativity (chemical potential), hardness (softness), Fukui function, response function, etc..

# Definitions

**Function:** a prescription which maps one or more numbers to another number:  $y = f(x) = x^2$ .

**Operator:** a prescription which maps a function onto another function:

$$F = \frac{\partial^2}{\partial x^2} \Rightarrow F f(x) = \frac{\partial^2}{\partial x^2} f(x)$$

**Functional:** A functional takes a function as input and gives a number as output. An example is:

$$F[f(x)] = y$$

Here  $f(x)$  is a function and  $y$  is a number.

An example is the functional to integrate  $x$  from  $-\infty$  to  $\infty$ .

$$F[f] = \int_{-\infty}^{\infty} f(x) dx$$

# The Hohenberg-Kohn Theorems

The first Hohenberg-Kohn theorem asserts that the density of any system determines all **ground-state** properties of the system, that is,  $E = E[\rho]$ , where  $\rho$  is the ground-state density of the system.

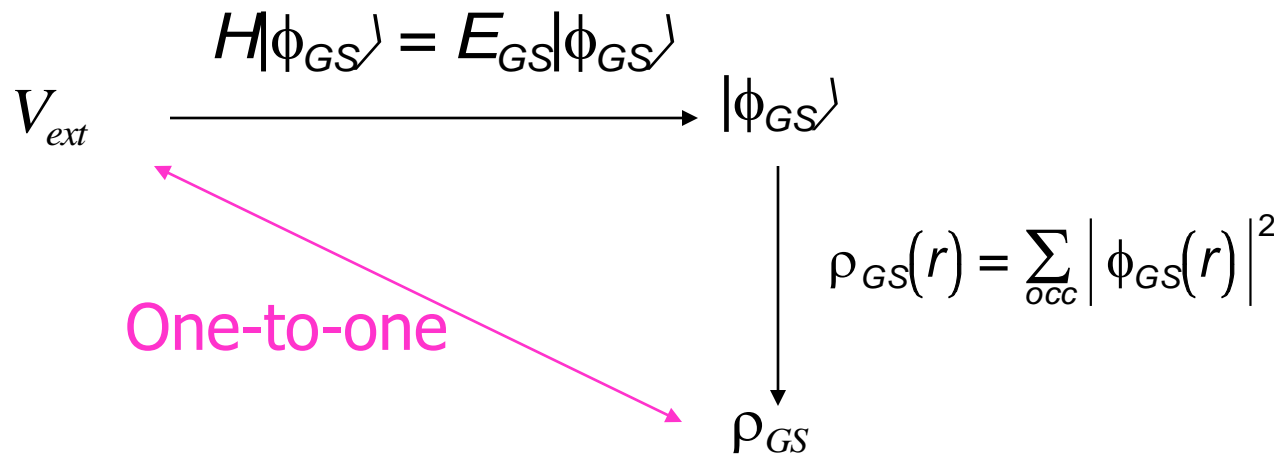
The second H-K theorem shows that there exists a **variational principle** for the above energy density functional  $E[\rho]$ . Namely, if  $\rho'$  is not the ground state density of the above system, then  $E[\rho'] > E[\rho]$ .

# Consequences of the H-K Theorems

Each local one-particle potential corresponds exactly to one ground state density. This permits us to express the potential as a function of the density  $V[\rho]$ .

$E_{GS} \equiv$  ground state energy

$|\phi_{GS}\rangle \equiv$  non – degenerate ground state  $N$  – electron wave function



Ground state expectation values depend uniquely on  $\rho_{GS}$

$$\rho_{GS} \Rightarrow V_{ext} \Rightarrow H \Rightarrow |\phi[\rho_{GS}]\rangle \Rightarrow O[\rho_{GS}] = \langle \phi[\rho_{GS}] | O | \phi[\rho_{GS}] \rangle$$

$\rho_{GS}(x, y, z)$  and not  $\phi_{GS}(x_1, y_1, z_1, \dots, x_N, y_N, z_N)$  is the basic variable

# Beyond the Hartree-Fock Hamiltonian

We begin with the Hartree-Fock (HF) hamiltonian, but add a term that accounts for electron exchange in terms of the density. The HF hamiltonian in atomic units is:

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_{ext,i} + \sum_{i < j} \frac{1}{|r_i - r_j|} = T + V_{ext} + V_{coul} + V_{xc}$$

$V_{ext} \equiv$  external, local, electron–nuclear potentia

Recall that the major expense in the HF approach is the calculation of exchange (and even more so correlation). Instead of calculating using explicit exchange DFT uses an additional function of the density  $V_{xc}$  where the x stands for exchange and the c stands for correlation. The central problem in DFT is that there is no unique prescription for how to find the exchange and correlation functionals.



# Variational H-K Method

**Procedure:** Determine  $E_{GS}$  and  $\rho$  by means of a constrained energy minimization of the energy functional  $E[\rho]$

$N$  = total number of particles;

$\phi[\rho]$  is the functional of the density

$$E[\rho] = \langle \phi[\rho] | T + V_{ext} + V_{coul} + V_{xc} | \phi[\rho] \rangle \geq E_{GS}$$

$$E[\rho] = E_{GS}$$

The variational calculation is carried out using the Lagrange multiplier  $\mu$  as shown below.

$$\delta \left( E[\rho] - \mu \left( N - \int_v \rho(r) dr \right) \right) = 0$$

# The Kohn-Sham approach

Treat the electrons as  $N$  fictitious non-interacting particles moving in an effective potential.

$|\phi_i\rangle \equiv$  *independent particle wavefunction*

*density:*  $\rho_{KS} = \sum_{i=1}^N |\phi_i|^2$

*kinetic energy:*  $T_{KS} = -\frac{1}{2} \sum_{i=1}^N \langle \phi_i | \nabla^2 | \phi_i \rangle$

The Kohn-Sham assumption is that the K-S density  $\rho_{KS}$  is equal to the true density.

Kohn-Sham energy partitioning:

$$E[\rho] = T[\rho] + E_{\text{ext}}[\rho] + E_{\text{Coul}}[\rho] + E_{\text{xc}}[\rho]$$

# Energy evaluation in the K-S approach

The energies are calculated by:

$$E_{\text{Coul}} = \int \frac{\rho(r)\rho(r')}{r-r'} dr dr' , \text{ Coulomb integral (electron repulsion)}$$

$$E_{\text{ext}} = \int V_{\text{ext}}(r)\rho(r) dr , \quad V_{\text{ext}} = \sum_A \frac{Z_A e^2}{|r - R_A|} , \text{ elec - nucl attraction}$$

$$E_{\text{xc}} = \int V_{\text{xc}}(r)\rho(r) dr , \quad V_{\text{xc}} \text{ exchange and correlation potential}$$

The Kohn-Sham equations, variational minimization of  $E[\rho]$ :

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{Coul}}(\rho, r) + V_{\text{ext}}(\rho, r) + V_{\text{xc}}(\rho, r) \right] \phi_i(r) = \varepsilon_i \phi_i(r)$$

Note that wave functions are obtained. These are called Kohn-Sham wave functions. They do have a correspondence with HF molecular orbitals, but formally they have a different origin.

# Implications of the K-S approach

Local exchange-correlation functional contains all of the complexities of the many-electron system,

$$V_{xc}(\rho, r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \Big|_{\rho = \rho_{GS}}$$

or

$$E_{xc}[\rho] = \int dr \rho(r) V_{xc}(\rho, r)$$

Solve single-particle problem instead of many-electron problem. Except for  $\mu = \varepsilon_N$ ,  $\varepsilon_i$  are Lagrange parameters without physical meaning. The remaining issue is to find the appropriate exchange-correlation functional.

# The exchange-correlation potential

While DFT in principle gives a good description of ground state properties, practical applications of DFT are based on approximations for the so-called exchange-correlation potential. The exchange-correlation potential describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons.

Possessing the exact exchange-correlation potential means that we solved the many-body problem exactly.

A common approximation is the so-called local density approximation (LDA) which locally substitutes the exchange-correlation energy density of an inhomogeneous system by that of an electron gas evaluated at the local density.

# The Local Density Approximation (LDA)

The LDA approximation assumes that the density is slowly varying and the inhomogeneous density of a solid or molecule can be calculated using the homogeneous electron gas functional.

While many ground state properties (lattice constants, bulk moduli, etc.) are well described in the LDA, the dielectric constant is overestimated by 10-40% in LDA compared to experiment. This overestimation stems from the neglect of a polarization-dependent exchange correlation field in LDA compared to DFT.

The method can be improved by including the gradient of the density into the functional. The generalized gradient approximation GGA is an example of this type of approach.

# The free electron gas potential linear density vs. gradient functionals

The LDA approximation begins with the simplest potential. The free electron gas potential function is:

$$V_{X\alpha}(r) = -\frac{9}{2}\alpha\left(\frac{3}{8\pi}\right)^{1/3}\rho^{1/3}(r)$$

For a true electron gas  $\alpha = 2/3$ . Any potential that is a function of the density only is called a local density function.

When the gradient of the density.

$$\nabla\rho$$

is included the functional then the functional belongs to the class of gradient approximation functionals.

# The Slater exchange functional

The predecessor to modern DFT is Slater's  $X_\alpha$  method. This method was formulated in 1951 as an approximate solution to the Hartree-Fock equations. In this method the HF exchange was approximated by:

$$E_{X_\alpha}[\rho] = -\frac{9}{8}\alpha\left(\frac{3}{8\pi}\right)^{1/3}\int_0^\infty \rho^{4/3}(r)dr$$

The exchange energy  $E_{X_\alpha}$  is a fairly simple function of the electron density  $\rho$ .

The adjustable parameter  $\alpha$  was empirically determined for each atom in the periodic table. Typically  $\alpha$  is between 0.7 and 0.8.



# The VWN Correlation Functional

In ab initio calculations of the Hartree-Fock type electron correlation is also not included. However, it can be included by inclusion of configuration interaction (CI). In DFT calculations the correlation functional plays this role. The Vosko-Wilk-Nusair correlation function is often added to the Slater exchange function to make a combination exchange-correlation functional.

$$E_{xc} = E_x + E_c$$

The nomenclature here is not standardized and the correlation functionals themselves are very complicated functions. The correlation functionals can be seen on the MOLPRO website

<http://www.molpro.net/molpro2002.3/doc/manual/node146.html>

# Extensions of the LDA approach

Generalized gradient approximation (GGA). Take density gradient into account. Useful for molecules.

Spin density functional theory. Two independent variables: density and magnetization.

$$m(r) = -\mu_0(\rho_{\uparrow} - \rho_{\downarrow})$$

Exact exchange density functional theory. Calculate exchange exactly and correlation approximately using DFT.

Generalized density functional theory. Modify K-S energy partitioning to obtain a non-local hamiltonian.

# Generalized Gradient Approach (GGA)

The GGA approach takes into account variations in the density by including the gradient of the density in the functional. One commonly used GGA functional is that of Becke.

$$V_{xc}^B = -\beta\rho^{1/3} \frac{x^2}{\left(1 + 6\beta x \sinh^{-1}x\right)}, \quad x = \frac{|\nabla\rho|}{\rho^{4/3}}$$

This functional has only one adjustable parameter,  $\beta$ . The value of  $\beta = 0.0042$  was determined based on the best fit to the energies of six noble gas atoms using the sum of the LDA and GGA exchange terms.

The GGA option in DMol3 is that of Perdew and Wang.

# Lee-Yang-Parr Correlation Functional

As was discussed above for the Slater exchange functional (no gradient), the VWN correlation functional provides a significant improvement in the calculation of the energies and properties such as bulk modulus, vibrational frequencies etc. In a similar manner the Becke exchange functional (including a gradient correlation) and the Lee-Yang-Parr functional are used together. The Lee-Yang-Parr or LYP correlation functional is quite complicated. It can be viewed on the MOLPRO website.

Thus, two of the most commonly used functionals are:  
S-VWN Slater exchange - VWN correlation (no gradients)  
B-LYP Becke exchange - LYP correlation (gradients)

# Example: H<sub>2</sub>O (the car file)

As a practical example of DFT methods we calculate the energy and electronic properties of the water molecule. In order to carry out the DFT calculation you will need a set of starting nuclear coordinates. I will use a set of coordinates that is clearly not correct (assuming a 90° H-O-H bond angle) for purposes of illustration. The coordinate file has the following appearance.

> vi h2o.car

```
!BIOSYM archive 3
PBC=OFF
```

```
!DATE      Jan 17 16:58:17 2004
O1         0.000000000    0.000000000    0.000000000  H2O1  1      o      O   -0.820
H2         0.000000000    1.000000000    0.000000000  H2O1  1      h      H    0.410
H3         1.000000000    0.000000000    0.000000000  H2O1  1      h      H    0.410
end
end
```

# Example: H<sub>2</sub>O (the input file)

Since we know the geometry is not correct the calculation type must be **optimize** or **optimize\_frequency**. The latter performs the frequency calculation once the geometry is optimized. If the molecule is smaller than 15 atoms it probably reasonable to select **optimize\_frequency** using DMol3 and running less than 4 processors. For now we can leave all other options in the input file as the default values.

> vi h2o.input

```
#Calculate          optimize
Calculate          energy
#Calculate          optimize_frequency
#Calculate          ts_search
#Calculate          frequency
#Calculate          gradient
#Calculate          Molecular_Dynamics
#Calculate          Simulated_Annealing
```

# Example: H<sub>2</sub>O (the input file)

Since we know the geometry is not correct the calculation type must be **optimize** or **optimize\_frequency**. The latter performs the frequency calculation once the geometry is optimized. If the molecule is smaller than 15 atoms it probably reasonable to select **optimize\_frequency** using DMol3 and running less than 4 processors. For now we can leave all other options in the input file as the default values.

> vi h2o.input

```
#Calculate optimize
#Calculate energy
Calculate optimize_frequency
#Calculate ts_search
#Calculate frequency
#Calculate gradient
#Calculate Molecular_Dynamics
#Calculate Simulated_Annealing
```

# Example: H<sub>2</sub>O (the input file)

Let's look at a few important options in the input file.

Use the search command and type

`/functional`

The functional selected is `gga` (i.e. GGA). Other common choices are `blyp` (BLYP) and `vwn` (SVWN) that were discussed earlier.

The search for `/basis`.

Here you will see that the default is `DNP`. This is the equivalent of a double-zeta quality basis set with one polarization function. The basis set in DMol3 is numerical. It does not use Gaussian functions. One aspect of DMol3 that is interesting is the ability to design and improve the basis set (but this is an advanced topic beyond our present objective).



# Example: H<sub>2</sub>O (the functional)

Functional

#Functional

#Functional

#Functional

#Functional

#Functional

#Functional

#Functional

#Functional\_Post\_LDA

#Functional\_Post\_LDA

gga

pwc

ks

jmw

vwn

vwn-bp

bp

blyp

off

BLYP

# Example: H<sub>2</sub>O (the basis set)

```
#Basis min
#Basis dn
#Basis dnd
Basis dnp
#Basis extended
#Basis all
#Basis user
# 1 7 0 0 0 0 2 2 2
# 6 11 0 0 0 0 0 0 0 2 2 2 2
# 7 11 0 0 0 0 0 0 0 2 2 2 2
# 8 11 0 0 0 0 0 0 0 2 2 2 2
# 44 15 0 0 0 0 0 0 0 0 0 0 0 0 0 0
```

# Example: H<sub>2</sub>O (the job file)

To launch the job we will use the following script:

```
> dft_input.job h2o DIRECTORY > h2o.job
```

The script tells the computer how many processors to use and how much memory to allocate Then you will submit the job.

You can see the queues typing:

```
> bqueues
```

To launch the job type:

```
> bsub < h2o.job
```

# Example: H<sub>2</sub>O (the outmol file)

For H<sub>2</sub>O you will not have long to wait. In about 1 minute the output (outmol) file appears. You can see it by typing

```
> vi h2o.outmol
```

Go to the bottom by typing `<shift>G`. You will see how long the job took. Go back to top by typing `:1`. Let's check the job. Searching for the text `/electrons` (and then following that with the letter `n` to find the second occurrence) you will see the number of basis functions and electrons in the calculation.

```
Symmetry orbitals
```

```
   n  norb  representation
   1   24         a
```

```
total number of valence orbitals:      24
```

```
molecule charge=      0.0  active electron number=      10.0
including core=      10.0  (without charge=      10.0)
```

# Example: H<sub>2</sub>O (the basis set)

Just above you will see the description of the numerical basis set.

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## Specifications for Basis Set Selection

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atomic cutoff radius 6.00 au

Hydrogen	nbas= 1	z= 1.	3 radial functions, e_ref= -0.0461310Ha	
n=1 L=0	occ= 1.00	e=	-0.222910Ha	-6.0657eV
n=1 L=0	occ= 0.00	e=	-0.844526Ha	-22.9807eV
n=2 L=1	occ= 0.00	e=	-1.999912Ha	-54.4204eV
Oxygen	nbas= 2	z= 8.	7 radial functions, e_ref= -0.0607807Ha	
n=1 L=0	occ= 2.00	e=	-18.896548Ha	-514.2014eV
n=2 L=0	occ= 2.00	e=	-0.868840Ha	-23.6424eV
n=2 L=1	occ= 4.00	e=	-0.322562Ha	-8.7774eV
n=2 L=0	occ= 0.00	e=	-2.144678Ha	-58.3597eV
n=2 L=1	occ= 0.00	e=	-1.593751Ha	-43.3682eV
n=3 L=2	occ= 0.00	e=	-2.722082Ha	-74.0717eV
n=3 L=2	occ= 0.00	e=	-1.383811Ha	-37.6554eV eliminated

---

# Example: H<sub>2</sub>O (the SCF cycles)

From this point search for the text **/SCF** and you will see the how the energy of the calculation is altered as the variational principle is applied to find the best coefficients. Convergence is set in the input file to  $10^{-6}$  Hartrees.

~~~~~ Start Computing SCF Energy/Gradient ~~~~~

|    | Total E (au) | Binding E (au) | Convergence | Time (m) | Iter |
|----|--------------|----------------|-------------|----------|------|
| Ef | -76.4907801  | -0.4371008     | 0.16E+00    | 0.021    | 1    |
| Ef | -76.4409749  | -0.3872957     | 0.91E-01    | 0.024    | 2    |
| Ef | -76.4308187  | -0.3771395     | 0.61E-01    | 0.026    | 3    |
| Ef | -76.4309567  | -0.3772774     | 0.25E-01    | 0.028    | 4    |
| Ef | -76.4296483  | -0.3759690     | 0.32E-02    | 0.030    | 5    |
| Ef | -76.4296274  | -0.3759482     | 0.13E-02    | 0.032    | 6    |
| Ef | -76.4296135  | -0.3759343     | 0.27E-03    | 0.034    | 7    |
| Ef | -76.4296117  | -0.3759324     | 0.62E-04    | 0.036    | 8    |
| Ef | -76.4296120  | -0.3759327     | 0.36E-04    | 0.038    | 9    |
| Ef | -76.4296122  | -0.3759329     | 0.11E-05    | 0.040    | 10   |
| Ef | -76.4296122  | -0.3759329     | 0.76E-06    | 0.042    | 11   |

# Example: H<sub>2</sub>O (the energy states)

Once convergence is reached the energies of the molecular orbitals is calculated. Only one unoccupied orbital is listed here. The others are occupied. More detailed output can be requested. The MOs can be output as shown on the website.

Energy of Highest Occupied Molecular Orbital -0.24970Ha -6.795eV

| state |   |   |   | eigenvalue |          | occupation |
|-------|---|---|---|------------|----------|------------|
|       |   |   |   | (au)       | (ev)     |            |
| 1     | + | 1 | a | -18.762994 | -510.567 | 2.000      |
| 2     | + | 2 | a | -0.912899  | -24.841  | 2.000      |
| 3     | + | 3 | a | -0.434975  | -11.836  | 2.000      |
| 4     | + | 4 | a | -0.354427  | -9.644   | 2.000      |
| 5     | + | 5 | a | -0.249700  | -6.795   | 2.000      |
| 6     | + | 6 | a | 0.027694   | 0.754    | 0.000      |

# Example: H<sub>2</sub>O (the geometry optimization)

At this point the program starts the geometry optimization. Notice that the molecule has been transformed so the symmetry axis is coincident with z axis, but otherwise the geometry is not changed yet. Search on the word */Cycle* (case must right!) and track the progress of the optimization.

```
** GEOMETRY OPTIMIZATION IN CARTESIAN COORDINATES **  
Searching for a Minimum
```

```
Optimization Cycle: 1
```

```
Input Coordinates (Angstroms)
```

```
-----  
      ATOM      X      Y      Z  
1      O      0.000000  0.000000 -0.471405  
2      H      0.707107  0.000000  0.235702  
3      H     -0.707107  0.000000  0.235702  
-----
```



# Example: H<sub>2</sub>O (convergence)

It took 6 cycles in the present example. The final cycle had the appearance:

|       | Cycle | Total Energy | Energy change | Max Gradient | Max Displacement |
|-------|-------|--------------|---------------|--------------|------------------|
| opt== | 6     | -76.4352059  | -0.0000006    | 0.000588     | 0.001194         |

Again the criteria for convergence are set in the input file. Note that minimization of the energy is one criterion for convergence. Keep in mind that a set of iterations to find the SCF coefficient is carried for each geometry (i.e. 6 times in the present case). If you look at the car file you will find the updated geometry (original car file is overwritten).

```
!BIOSYM archive 3
PBC=OFF
```

```
!DATE      Jan 22 02:24:58 2004
O1         0.000000000    0.000000000   -0.400578191 H2O1 1      o      O   -0.820
H2         0.760530176    0.000000000    0.200289095 H2O1 1      h      H    0.410
H3        -0.760530176    0.000000000    0.200289095 H2O1 1      h      H    0.410
end
end
```

# Example: H<sub>2</sub>O (charges and dipole)

The properties are calculated next.

```
+++ Entering Properties Section +++
```

```
Charge partitioning by Hirshfeld method:
```

```
O      1 charge      -0.3008
H      2 charge       0.1503
H      3 charge       0.1503
```

Gas phase water  
experimental value  
is 1.86 Debye.

```
symmetry unique atoms:   1   2   3
```

```
dipole moment vector (au):    0.00000    0.00000    0.76730
dipole magnitude:             0.76730 au    1.9503 debye
```

```
Mulliken Population analysis
```

```
Mulliken atomic charges:
```

```
charge    spin
O( 1)  -0.487  0.000
H( 2)   0.243  0.000
H( 3)   0.243  0.000
```

# Example: H<sub>2</sub>O (esp fitting)

Electrostatic potential fitting is considered more accurate than Hirshfeld or Mulliken charge.

Limits of the ESP box:

```
-6.850260 -6.377828 -6.963917  
6.850260 6.377828 5.791740
```

=====

Summary of ESP fitting calculations

```
Number of points:      6288.76  
Spacing between:      0.25Ang  
Sigma:                0.2059E-02  
RMS of V(exact):     0.1703E-01  
RRMS fit:            12.09%
```

ESP-fitted charges:

| n | Elem | chg    | vdW(in) | vdW(ex) |
|---|------|--------|---------|---------|
| 1 | O    | -0.704 | 1.72    | 3.22    |
| 2 | H    | 0.352  | 1.30    | 2.80    |
| 3 | H    | 0.352  | 1.30    | 2.80    |

=====

TIP3P water used in MD force fields has

O -0.82

H 0.41

H 0.41

However, this is a gas phase calculation. We would need to model a water cluster or in periodic boundaries to obtain comparable values.

# Example: H<sub>2</sub>O (frequencies)

Searching on the text `/freq` you will find the calculated vibrational frequencies.

```
vibrational frequencies, intensities
mode      au_amu      cm-1      km/mol
  7      0.315034    1619.4    69.54
  8      0.721257    3707.6     6.72
  9      0.743767    3823.3    43.56
```

| Experimental values are: | Error                    |
|--------------------------|--------------------------|
| bending mode             | 1654 cm <sup>-1</sup> 2% |
| asymmetric stretch       | 3825 cm <sup>-1</sup> 8% |
| symmetric stretch        | 3935 cm <sup>-1</sup> 3% |