Solving Hartree Fock Equation

HF Roothaan Equation

For molecules numerical basis not efficient so use atom centered basis set to describe the molecular orbital

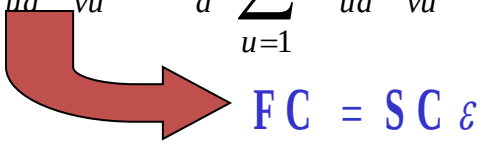
$$\phi_a(\mathbf{r}_1) = \sum_{u=1}^{Nbasis} C_{ua}\theta_u \qquad a = 1,2,...Nbasis$$

$$f(\mathbf{r}_1)\phi_a(\mathbf{r}_1) = \varepsilon_a\phi_a(\mathbf{r}_1)$$

$$f(\mathbf{r}_1)\sum_{u=1}^{Nbasis} C_{ua}\theta_u = \varepsilon_a \sum_{u=1}^{Nbasis} C_{ua}\theta_u \rightarrow$$

$$\sum_{u=1}^{Nbasis} C_{ua}\int \theta_v^*(\mathbf{r}_1) f(\mathbf{r}_1)\theta_u(\mathbf{r}_1)d\mathbf{r}_1 = \varepsilon_a \sum_{u=1}^{Nbasis} C_{ua}\int \theta_v^*(\mathbf{r}_1)\theta_u(\mathbf{r}_1)d\mathbf{r}_1$$

$$\sum_{u=1}^{Nbasis} C_{ua}F_{vu} = \varepsilon_a \sum_{u=1}^{Nbasis} C_{ua}S_{vu} \qquad a = 1,2,...Nbasis$$



Self Consistent Field

We just have to solve the fock equation:
PROBLEM FOCK OPERATOR HAS THE SOLUTION INSIDE

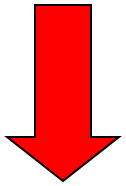
$$\mathbf{F}(\mathbf{C})\mathbf{C} = \mathbf{S}\mathbf{C}\varepsilon$$

So put in a guess $\mathbf{C}^{guess}$ this allows you to get $\mathbf{C}^{1}$

$$\mathbf{F}(\mathbf{C}^{guess})\mathbf{C}^{1} = \mathbf{S}\mathbf{C}^{1}\varepsilon$$

Then put in $\mathbf{C}^{1}$ this allows you to get $\mathbf{C}^{2}$

Continue the cycle until you get convergence on $\mathbf{C}^{input}$ and $\mathbf{C}^{output}$



Self consistent field (SCF) method

Fock Operator in Basis Representation

$$F_{vu} = \int \theta_v^*(\mathbf{r}_1) f(\mathbf{r}_1) \theta_u(\mathbf{r}_1) d\mathbf{r}$$

$$= \int \theta_v^*(\mathbf{r}_1) h(\mathbf{r}_1) \theta_u(\mathbf{r}_1) d\mathbf{r}$$

$$+ \int \theta_v^*(\mathbf{r}_1) \left(\sum_{b=1}^{n/2} \left(2J_b(\mathbf{r}_1) - K_b(\mathbf{r}_1) \right) \right) \theta_u(\mathbf{r}_1) d\mathbf{r}_1$$

Core Hamiltonian Matrix

$$h_{uv}^{core} = \int \theta_v^*(\mathbf{r}_1) h(\mathbf{r}_1) \theta_u(\mathbf{r}_1) d\mathbf{r}$$

$$h(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \sum_{I=1}^{N} \frac{Z_I}{|\mathbf{r}_{1I}|}$$

Calculated once in a SCF cycle

Two electron Matrix

$$\int \theta_v^*(\mathbf{r}_1) \left(\sum_{b=1}^{n/2} \left(2J_b(\mathbf{r}_1) - K_b(\mathbf{r}_1) \right) \right) \theta_u(\mathbf{r}_1) d\mathbf{r}_1$$

$$= \sum_{b=1}^{n/2} \left(2\langle vb|ub\rangle - \langle vb|bu\rangle \right)$$

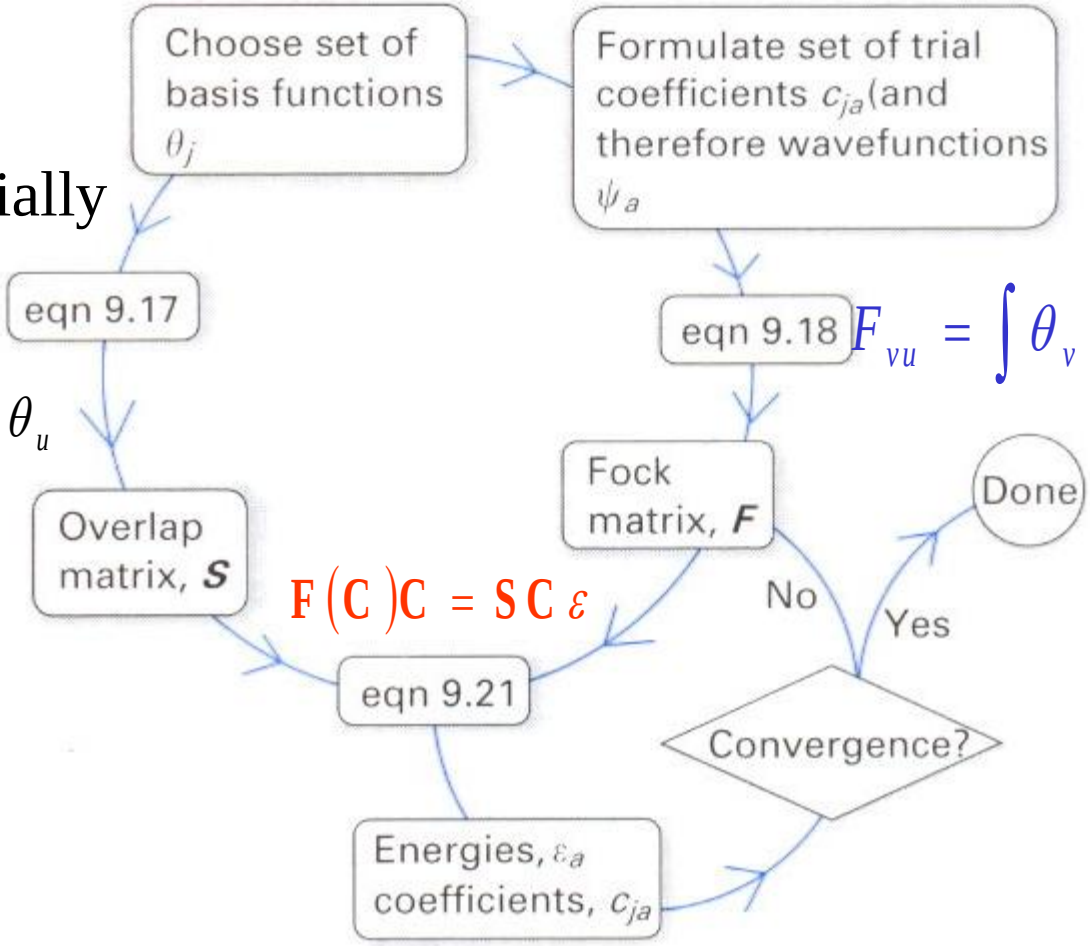
$$= \sum_{b=1}^{n/2} \sum_{w=1}^{Nbasis} \sum_{x=1}^{Nbasis} C_{wb}^* C_{xb} \left(2\langle vw|ux\rangle - \langle vw|xu\rangle \right)$$

Self Consistent Field Method

$$\langle vw|ux\rangle$$

$$= \iint \theta_v^*(\mathbf{r}_1)\theta_w^*(\mathbf{r}_2)|\mathbf{r}_{12}|^{-1}\theta_u(\mathbf{r}_1)\theta_x(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

Calculate initially



Slater Type Orbital
vs
Gaussian Type Orbital

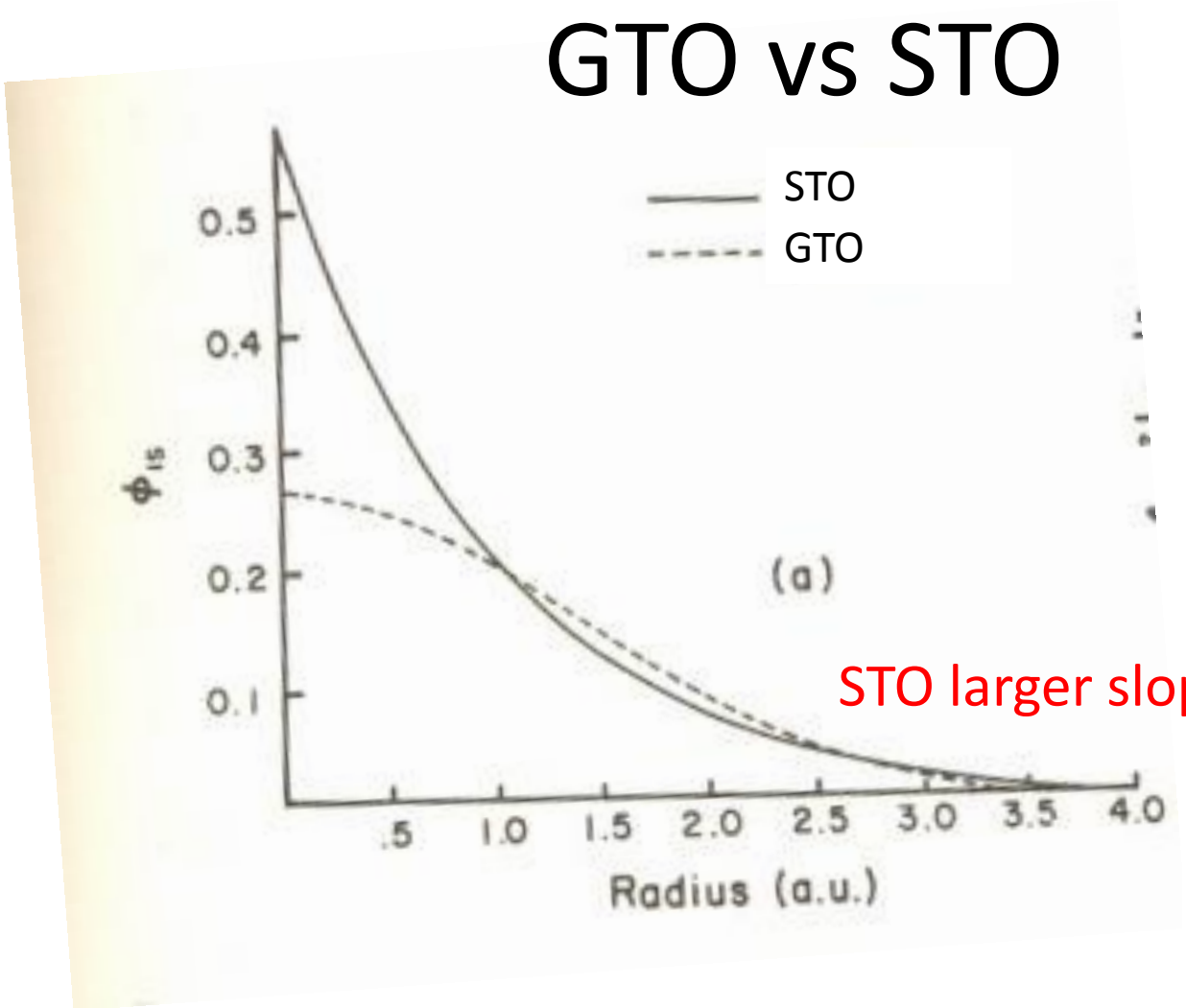
In the H_2 case we used Slater type orbitals for radial part where basis on H_A is given as

$$\theta_{1S}^{STO}\left(\xi, \mathbf{r}-\mathbf{R}_A\right)=\left(\xi^3/\pi\right)^{1/2} e^{-\xi|\mathbf{r}-\mathbf{R}_A|}$$

Another tye is a Gaussian type orbital for the radial part where basis on H_A is given as

$$\theta_{1S}^{GTO}\left(\alpha, \mathbf{r}-\mathbf{R}_A\right)=\left(2\alpha/\pi\right)^{3/4} e^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2}$$

GTO vs STO



STO larger slope near r=0

$$\left.\frac{d\theta_{1S}^{STO}(\xi,\mathbf{r}-\mathbf{R}_A)}{d\mathbf{r}}\right|_{\mathbf{r}=0} \neq 0 \qquad \left.\frac{d\theta_{1S}^{GTO}(\alpha,\mathbf{r}-\mathbf{R}_A)}{d\mathbf{r}}\right|_{\mathbf{r}=0} = 0$$

Solve the hydrogen atom by Gaussian Function

$$\hat{H} = \left[-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) + \left(-\frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2 l(l+1)}{2\mu r^2} \right) \right]$$

1S l=0, using atomic units

$$\hat{H} = \left[-\frac{1}{2r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r} \right]$$

$$E_{trial} = \frac{\left\langle \psi_{trial} \middle| \hat{H} \middle| \psi_{trial} \right\rangle}{\left\langle \psi_{trial} \middle| \psi_{trial} \right\rangle}$$

using $\psi_{trial} = Exp\left(-\alpha r^2\right)$

Solve for variational minimum of α and obtain the minimum energy. Compare the value with the exact one.

Hint: Gaussian Integrals

$$\left\langle \psi_{trial} \middle| \hat{H} \middle| \psi_{trial} \right\rangle = \int_0^\infty \exp\left(-\alpha r^2\right) \hat{H} \exp\left(-\alpha r^2\right) r^2 dr$$

$$\left\langle \psi_{trial} \middle| \psi_{trial} \right\rangle = \int_0^\infty \exp\left(-\alpha r^2\right) \exp\left(-\alpha r^2\right) r^2 dr$$

$$\left\langle r^n \right\rangle = \int_0^\infty r^n \exp\left(-2\alpha r^2\right) dr$$

$$\left\langle r^1 \right\rangle = \frac{1}{4\alpha}$$

$$\left\langle r^2 \right\rangle = \frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}}$$

$$\left\langle r^4 \right\rangle = \frac{3}{32\alpha^2}\sqrt{\frac{\pi}{2\alpha}}$$

(ans -0.424, 0.076 hartree off from the true value of -0.5)

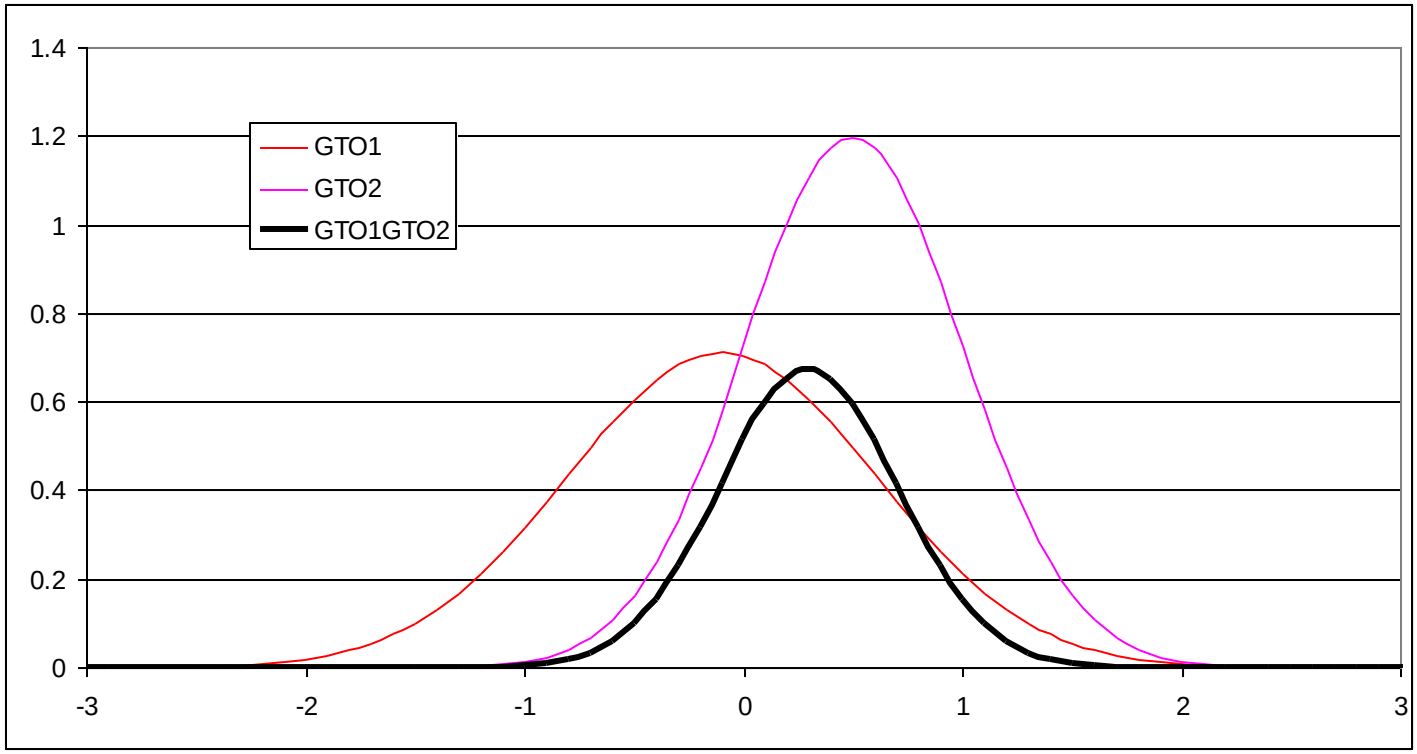
Why GTO

4 orbital integral, if the orbitals are on 4 different atoms

$$\langle vw|ux\rangle = \iint \theta_v^*(\mathbf{r}_1)\theta_w^*(\mathbf{r}_2)|\mathbf{r}_{12}|^{-1}\theta_u(\mathbf{r}_1)\theta_x(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

$$\theta_{1S}^{GTO}(\alpha,\mathbf{r}-\mathbf{R}_A)\theta_{1S}^{GTO}(\beta,\mathbf{r}-\mathbf{R}_B) = K_{AB}\theta_{1S}^{GTO}(\delta,\mathbf{r}-\mathbf{R}_D)$$

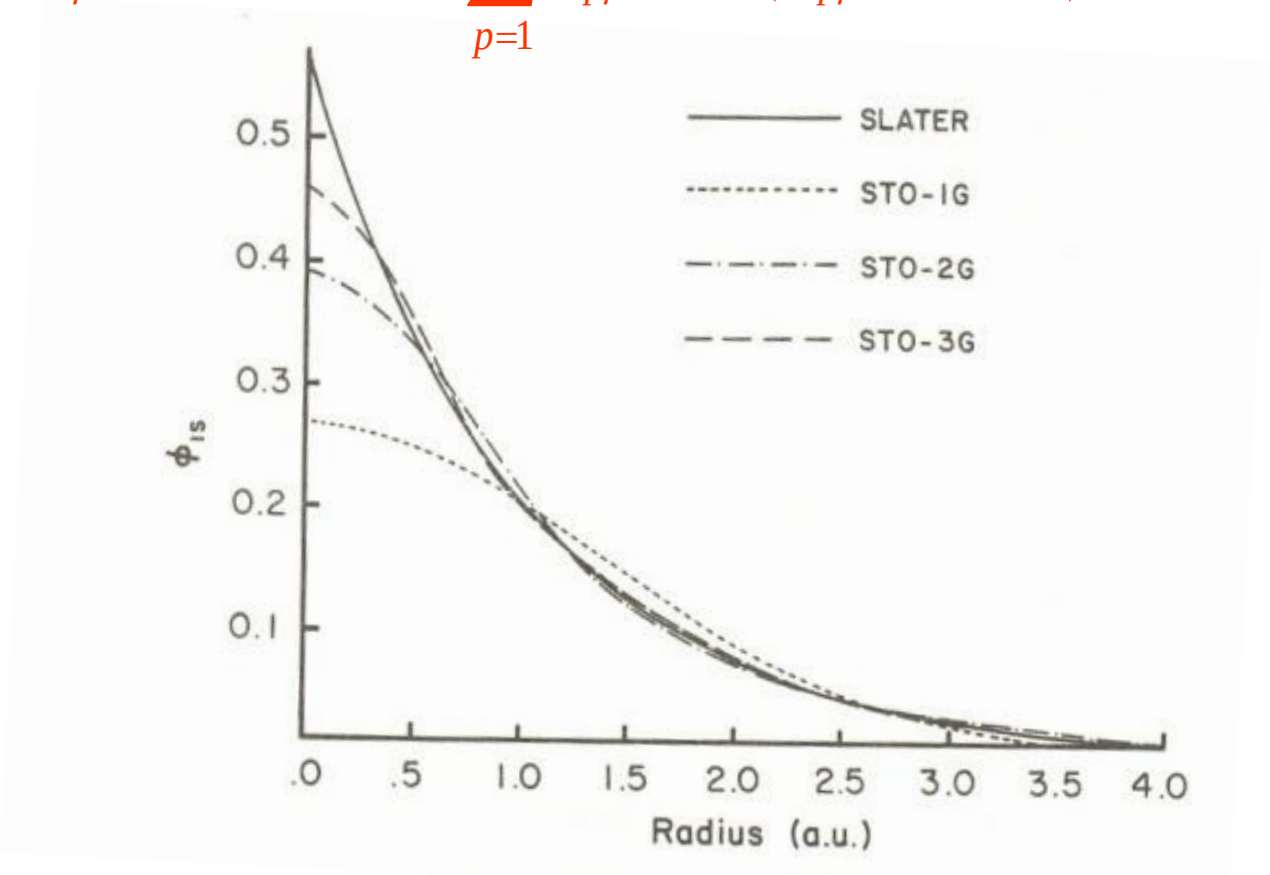
$$\mathbf{R}_D = \frac{(\alpha\mathbf{R}_A+\beta\mathbf{R}_\beta)}{(\alpha+\beta)};\quad K_{AB} = (2\alpha\beta/[(\alpha+\beta)\pi])^{3/4}\exp\left[-\frac{\alpha\beta}{(\alpha+\beta)}|\mathbf{R}_A-\mathbf{R}_B|^2\right]$$



Linear Combination of GTO

Contracted GTO: One GTO is not enough to describe the STO type orbital so lets use more than one GTO and add with correct coefficient (*d*) and exponent (α) value

$$\theta_{\mu}^{CGTO}\left(\mathbf{r}-\mathbf{R}_A\right)=\sum_{p=1}^{L} d_{p\mu}\,\theta^{GTO}\left(\alpha_{p\mu},\mathbf{r}-\mathbf{R}_A\right)$$



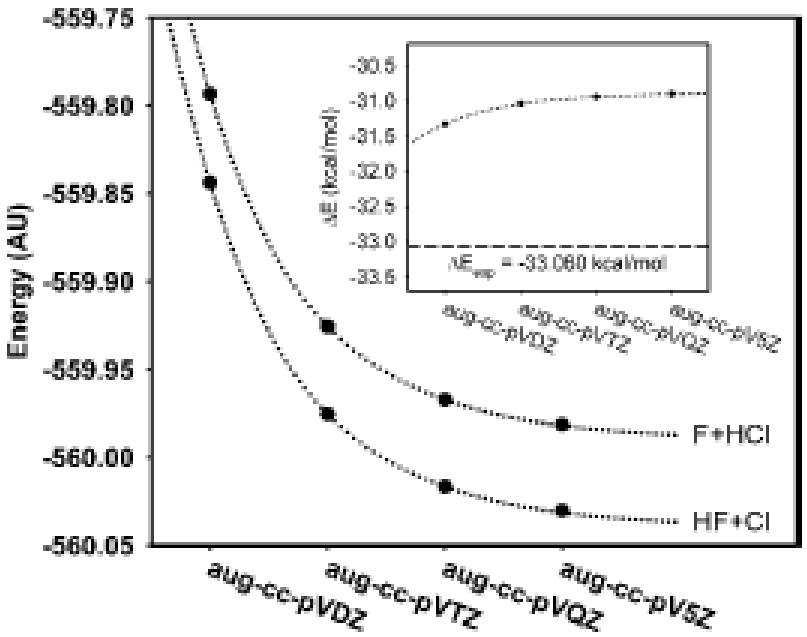
Basis Sets

- Minimal Basis: only those in atomic orbital so one 1S orbital for hydrogen, one 1S, 2S, 2P for carbon, oxygen
    - STO-3G
- Split Valence: valence orbital has two, for hydrogen two 1S orbital, one 1S and two 2S, 2P for carbon oxygen
    - 6-31G, 3-21G
- Diffuse: large version of valence orbital
    - +, ++
- Polarization: higher angular momentum add 2P for hydrogen, add 3D for carbon, oxygen
    - *,**, (d), (d,p)

Dunning Correlation Consistent Basis Set

T. Dunning decided on defining the contraction coefficient and exponential coefficient to maximize electron correlation

aug-cc-pVDZ (X=2)
aug-cc-pVTZ (X=4)
aug-cc-pVQZ (X=4)
aug-cc-pV5Z (X=5)



$$E(X) = E_{CBS} + B\exp[-(X-1)] + C\exp[-(X-1)^2]$$

Basis Set Effective Core Potential

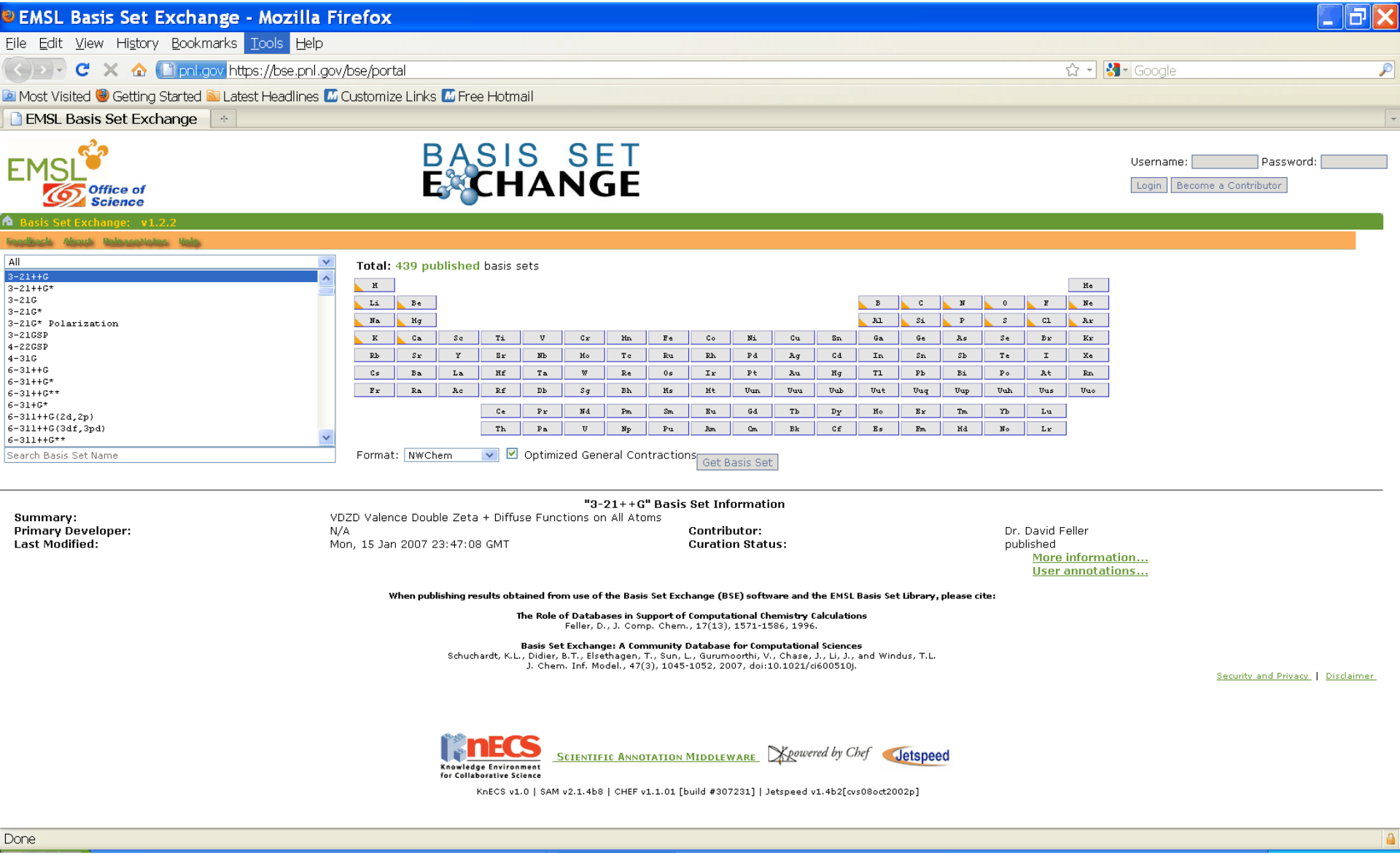
- Most Chemistry occurs between valance electrons, electrons in the core do not contribute to important reactions use EFFECTIVE POTENTIAL FOR THE CORE ELECTRONS:

Effective Core Potential (ECP) used for many electron systems. Relativistic Effect become important for heavy transition metal systems so use relativistic ECP (RECP)

Hay-Wadt: LANL2DZ LANL2TZ, Dolg

In bulk simulation like VASP it is called Psuedo potential

Basis Set Library (https://bse.pnl.gov/bse/portal)



Pick Basis Set Convergence

Dipole moment of H_2O

Method	# of basis	Debye
HF/STO-3G	7	1.7076
HF/6-31G	13	2.5006
HF/6-31+G	17	2.5824
HF/6-31+G(d,p)	29	2.2339
HF/6-311G	19	2.4881
HF/6-311++G	25	2.5536
HF/6-311++G(d,p)	37	2.1959
HF/6-311++G(3d,3p)	61	1.9744
HF/6-311++G(3df,3pd)	83	1.9681
HF/aug-cc-pVTZ	105	1.9394
HF/aug-cc-pVQZ	215	1.9361
Exp		1.8550

Computational time ~ (# of basis)^2

Using the Gaussian 09 Program

Making INPUT 1

- First lines are input of method and basis set
  - #P HF/STO-3G pop=reg
- Empty line
- Title of the calculation: Anything is OK
- Empty line
- Charge and spin multiplicity: usually we consider neutral molecule so charge 0, multiplicity is number of unpaired electrons +1, usually we consider filled electron so 1

Making INPUT 2

- Then define the molecule either using XYZ or Z-matrix input

```
O1      0.000000   0.754227  -0.058812
O2      0.000000  -0.754227  -0.058812
H3     -0.742068  -1.085986   0.470499
H4      0.742068   1.085986   0.470499
```

```
O1
O2   1,  RO1O2
H3,  2,  RO2H3,  1,  AO1O2H3
H4,  1,  RO1H4,  2,  AO2O1H4,  3,  DH3O2O1H4

RO1O2=1.50845307
RO2H3=0.97
RO1H4=0.97
AO1O2H3=110.0
AO2O1H4=110.0
DH3O2O1H4=109.
```

- Then end with one blank line

Single Point Calculation SCF

- Check how many cycles is needed to converge the result, what happens when you add SCF=tight keyword
- Check the viral condition should be close to 2 (this is not satisfied when you use Effective Core Potential)

Gaussian Input of H2

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```
 the Gaussian(R) 98 system (copyright 1998, Gaussian, Inc.),
 the Gaussian(R) 94 system (copyright 1995, Gaussian, Inc.),
 the Gaussian 92(TM) system (copyright 1992, Gaussian, Inc.),
 the Gaussian 90(TM) system (copyright 1990, Gaussian, Inc.),
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 used, copied, transmitted, or stored only in accord with that
 written license.

kaito@master:/lustre/lwork/kaito/kaito/G09/h2/hf> more h2.com
#P HF/6-31G pop=reg

Title

0 1
H1
H2,  H1,  RH1H2

RH1H2=0.75


kaito@master:/lustre/lwork/kaito/kaito/G09/h2/hf>
```

Gaussian Output 1of H2

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```
 Cycle   1  Pass 1  IDiag  1:
 E= -1.12430148486308
 DIIS: error= 1.80D-02 at cycle   1 NSaved=   1.
 NSaved= 1 IEnMin= 1 EnMin= -1.12430148486308     IErMin= 1 ErrMin= 1.80D-02
 ErrMax= 1.80D-02 EMaxC= 1.00D-01 BMatC= 1.30D-03 BMatP= 1.30D-03
 IDIUse=3 WtCom= 8.20D-01 WtEn= 1.80D-01
 Coeff-Com:  0.100D+01
 Coeff-En:   0.100D+01
 Coeff:      0.100D+01
 Gap=     0.834 Goal=   None    Shift=    0.000
 GapD=    0.834 DampG=2.000 DampE=0.500 DampFc=1.0000 IDamp=-1.
 RMSDP=8.37D-03 MaxDP=1.37D-02              0VMax= 0.00D+00

 Cycle   2  Pass 1  IDiag  1:
 E= -1.12649426159182     Delta-E=       -0.002192776729 Rises=F Damp=F
 DIIS: error= 2.72D-03 at cycle   2 NSaved=   2.
 NSaved= 2 IEnMin= 2 EnMin= -1.12649426159182     IErMin= 2 ErrMin= 2.72D-03
 ErrMax= 2.72D-03 EMaxC= 1.00D-01 BMatC= 2.96D-05 BMatP= 1.30D-03
 IDIUse=3 WtCom= 9.73D-01 WtEn= 2.72D-02
 Coeff-Com: -0.178D+00 0.118D+01
 Coeff-En:   0.000D+00 0.100D+01
 Coeff:     -0.173D+00 0.117D+01
 Gap=     0.829 Goal=   None    Shift=    0.000
 RMSDP=1.46D-03 MaxDP=2.34D-03 DE=-2.19D-03 0VMax= 0.00D+00

 Cycle   3  Pass 1  IDiag  1:
 E= -1.12654503027512     Delta-E=       -0.000050768683 Rises=F Damp=F
 DIIS: error= 6.67D-06 at cycle   3 NSaved=   3.
 NSaved= 3 IEnMin= 3 EnMin= -1.12654503027512     IErMin= 3 ErrMin= 6.67D-06
h2.log lines 206-234/363 63%
```

Gaussian Input of H2

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```
ErrMax= 6.67D-06 EMaxC= 1.00D-01 BMatC= 1.78D-10 BMatP= 2.96D-05
IDIUse=1 WtCom= 1.00D+00 WtEn= 0.00D+00
Large coefficients: NSaved=  3 BigCof=    0.00 CofMax=   10.00 Det= 0.00D+00
Inversion failed.  Reducing to  2 matrices.
Coeff-Com: -0.246D-02 0.100D+01
Coeff:     -0.246D-02 0.100D+01
Gap=     0.829 Goal=   None    Shift=    0.000
RMSDP=3.59D-06 MaxDP=5.73D-06 DE=-5.08D-05 OVMax= 0.00D+00

Cycle   4  Pass 1  IDiag  1:
E= -1.12654503058015     Delta-E=       -0.000000000305 Rises=F Damp=F
DIIS: error= 1.60D-09 at cycle   4 NSaved=   3.
NSaved= 3 IEnMin= 3 EnMin= -1.12654503058015     IErMin= 3 ErrMin= 1.60D-09
ErrMax= 1.60D-09 EMaxC= 1.00D-01 BMatC= 1.02D-17 BMatP= 1.78D-10
IDIUse=1 WtCom= 1.00D+00 WtEn= 0.00D+00
Large coefficients: NSaved=  3 BigCof=    0.00 CofMax=   10.00 Det=-2.58D-26
Inversion failed.  Reducing to  2 matrices.
Coeff-Com:  0.240D-03 0.100D+01
Coeff:      0.240D-03 0.100D+01
Gap=     0.829 Goal=   None    Shift=    0.000
RMSDP=8.60D-10 MaxDP=1.37D-09 DE=-3.05D-10 OVMax= 0.00D+00

SCF Done:  E(RHF) =  -1.12654503058     A.U. after    4 cycles
           Convg  =    0.8599D-09             -V/T =  2.0100
KE= 1.115390962782D+00 PE=-3.594021281515D+00 EE= 6.465156766989D-01
Leave Link  502 at Mon Mar 21 13:29:44 2011, MaxMem=   33554432 cpu:       0.0
(Enter /home/software/g09-i7/g09/l601.exe)
Copying SCF densities to generalized density rwf, IOpCl= 0 IROHF=0.
```

h2.log lines 235-263/363 71%

Diatomic Molecule Calculate Potential energy Curve

- Calculate the energy of H_2 at different bond length, plot the energy versus bond length and find the equilbrium point, lowest energy bond length

Potential Energy Curve Input

```
"h2scan.com" 11L, 94C written
kaito@master:/lustre/lwork/kaito/kaito/G09/h2/hf> qsub run
226693.master.cluster
kaito@master:/lustre/lwork/kaito/kaito/G09/h2/hf> more h2scan.com
#P HF/6-31G pop=reg scan IOP(2/12=1)

Title

0 1
H1
H2,  H1,  RH1H2

RH1H2=0.25  S  20 0.10


kaito@master:/lustre/lwork/kaito/kaito/G09/h2/hf>
```

Potential Energy Curve

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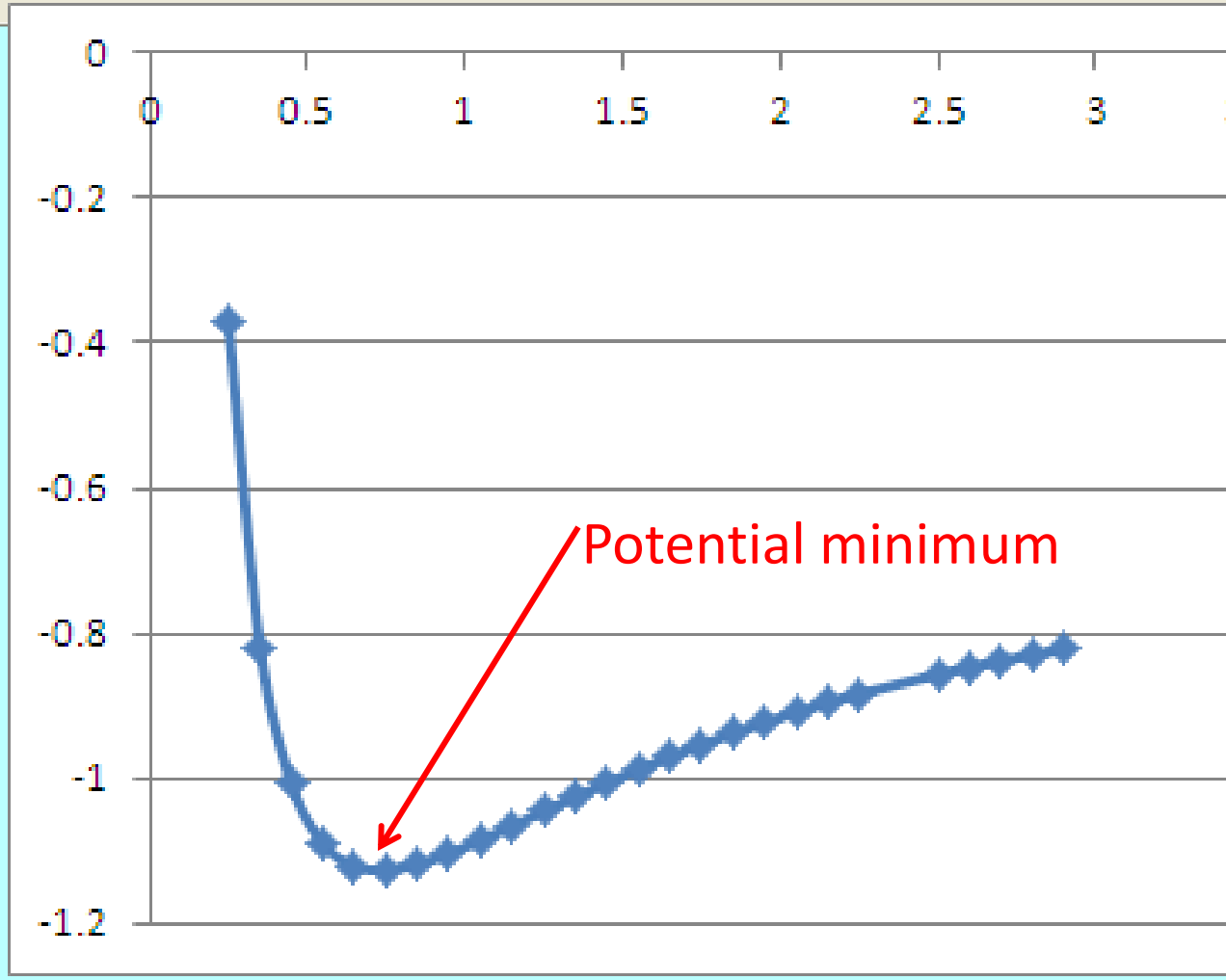
File Edit Setup Control Window Resize Help

Scan completed.

Summary of the potential surface

N	RH1H2	SCF
1	0.2500	-0.37196
2	0.3500	-0.81916
3	0.4500	-1.00834
4	0.5500	-1.09016
5	0.6500	-1.12120
6	0.7500	-1.12655
7	0.8500	-1.11854
8	0.9500	-1.10365
9	1.0500	-1.08542
10	1.1500	-1.06576
11	1.2500	-1.04576
12	1.3500	-1.02600
13	1.4500	-1.00682
14	1.5500	-0.98838
15	1.6500	-0.97078
16	1.7500	-0.95407
17	1.8500	-0.93827
18	1.9500	-0.92338
19	2.0500	-0.90939
20	2.1500	-0.89628
21	2.2500	-0.88403



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h2scan.log lines 3718-3746/3766 99%

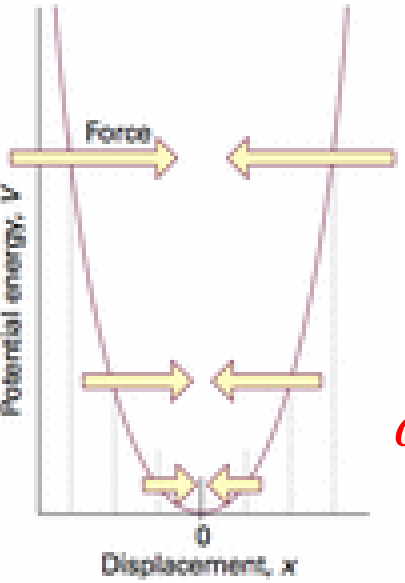
How to quantify Minimum?

- At the minimum the first derivative is zero and the second derivative is always positive

  Check the Hessian (second derivative)

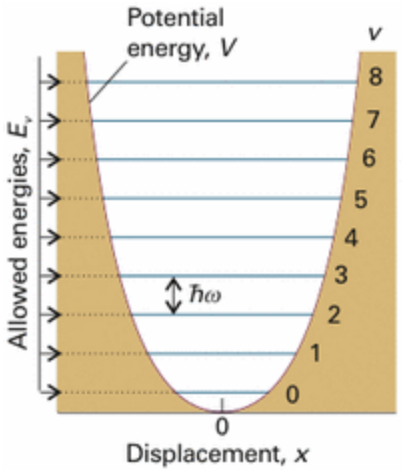
  In Gaussian you can use the freq keyword

Harmonic Oscillator



$$F = m\frac{d^2x}{dt^2} = -kx \qquad k\text{: force constant}$$

$$\omega = \sqrt{\frac{k}{m}} \qquad E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad n = 0,1,2,\ldots$$



Optimization and Vibrational Frequency

- Add in opt and freq keyword to the line of command
- Compare criteria of optimization opt, opt=tight, opt=verytight
- Compare frequency results with experiment

140.109.112.238:22 - Tera Term VT

File Edit Setup Control Window Resize Help

Optimize Geometry Input

```
#P HF/6-31G pop=reg opt=verytight freq

Title

0 1
H1
H2,  H1,  RH1H2

RH1H2=0.75


kaito@master:/lustre/lwork/kaito/kaito/G09/h2/hf>
```

Optimize Geometry 1

140.109.112.238:22 - Tera Term VT

File Edit Setup Control Window Resize Help

```
    Eigenvalues ---    0.37819
RFO step:  Lambda=-5.64143898D-04 EMin= 3.78189209D-01
Linear search not attempted -- first point.
Iteration  1 RMS(Cart)=  0.02728989 RMS(Int)=  0.00000000
Iteration  2 RMS(Cart)=  0.00000000 RMS(Int)=  0.00000000
ClnCor:  largest displacement from symmetrization is 2.22D-16 for atom     2.
Variable       Old X    -DE/DX   Delta X   Delta X   Delta X     New X
                                 (Linear)    (Quad)   (Total)
   R1         1.41729  -0.01462   0.00000  -0.03859  -0.03859   1.37870
         Item               Value     Threshold  Converged?
Maximum Force            0.014618     0.000002     NO
RMS     Force            0.014618     0.000001     NO
Maximum Displacement     0.019297     0.000006     NO
RMS     Displacement     0.027290     0.000004     NO
Predicted change in Energy=-2.824921D-04
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

Leave Link  103 at Mon Mar 21 18:00:53 2011, MaxMem=   33554432 cpu:       0.0
(Enter /home/software/g09-i7/g09/l202.exe)
                         Input orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type              X           Y           Z
---------------------------------------------------------------------
     1          1           0        0.000000    0.000000    0.010211
     2          1           0        0.000000    0.000000    0.739789
---------------------------------------------------------------------
Stoichiometry    H2
Framework group  D*H[C*(H.H)]
h2opt.log lines 425-453/1505 28%
```

$$F = -\frac{dV(x)}{dx}$$

Optimize Geometry 2

140.109.112.238:22 - Tera Term VT

File Edit Setup Control Window Resize Help

```
Iteration  1 RMS(Cart)=  0.00051163 RMS(Int)=  0.00000000
Iteration  2 RMS(Cart)=  0.00000000 RMS(Int)=  0.00000000
ClnCor:  largest displacement from symmetrization is 5.55D-17 for atom     1.
Variable       Old X    -DE/DX   Delta X   Delta X   Delta X     New X
                                 (Linear)    (Quad)   (Total)
   R1         1.37870   0.00030   0.00072   0.00000   0.00072   1.37942
         Item               Value     Threshold  Converged?
Maximum Force            0.000298     0.000002     NO
RMS     Force            0.000298     0.000001     NO
Maximum Displacement     0.000362     0.000006     NO
RMS     Displacement     0.000512     0.000004     NO
Predicted change in Energy=-1.144811D-07
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

Leave Link  103 at Mon Mar 21 18:00:53 2011, MaxMem=   33554432 cpu:       0.0
(Enter /home/software/g09-i7/g09/l202.exe)
                         Input orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type              X           Y           Z
---------------------------------------------------------------------
     1          1           0        0.000000    0.000000    0.010020
     2          1           0        0.000000    0.000000    0.739980
---------------------------------------------------------------------
Stoichiometry    H2
Framework group  D*H[C*(H.H)]
Deg. of freedom     1
Full point group                 D*H     NOp   8
Largest Abelian subgroup         D2H     NOp   8
```

$$F = -\frac{dV(x)}{dx}$$

Optimize Geometry 3

140.109.112.238:22 - Tera Term VT

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```
The second derivative matrix:
                          R1
          R1           0.41217
    Eigenvalues ---    0.41217
En-DIIS/RFO-DIIS IScMMF=        0 using points:     3    2
RFO step:  Lambda=-5.61772850D-14.
Iteration  1 RMS(Cart)=  0.00000033 RMS(Int)=  0.00000000
ClnCor:  largest displacement from symmetrization is 1.41D-23 for atom     2.
Variable       Old X    -DE/DX   Delta X   Delta X   Delta X     New X
                                  (DIIS)     (GDIIS)  (Total)
   R1         1.37942   0.00000   0.00000   0.00000   0.00000   1.37942
         Item               Value     Threshold  Converged?
Maximum Force            0.000000     0.000002     YES
RMS     Force            0.000000     0.000001     YES
Maximum Displacement     0.000000     0.000006     YES
RMS     Displacement     0.000000     0.000004     YES
Predicted change in Energy=-4.377425D-14
Optimization completed.
   -- Stationary point found.
                          ----------------------------
                          !   Optimized Parameters   !
                          ! (Angstroms and Degrees)  !
--------------------------                            --------------------------
! Name  Definition              Value          Derivative Info.                !
--------------------------------------------------------------------------------
! R1    R(1,2)                  0.73           -DE/DX =    0.0                 !
--------------------------------------------------------------------------------
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

n2opt.log lines 815-843/1505 55%
```

$$F = -\frac{dV(x)}{dx}$$

Optimize Geometry 4 Frequency

140.109.112.238:22 - Tera Term VT

File Edit Setup Control Window Resize Help

```
                4.55421818D-14
Full mass-weighted force constant matrix:
Low frequencies ---   -0.0002    0.0001    0.0001    2.6873    2.6873 4646.1741
Diagonal vibrational polarizability:
       0.0000000       0.0000000       0.0000000
Diagonal vibrational hyperpolarizability:
       0.0000000       0.0000000       0.0000000
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
activities (A**4/AMU), depolarization ratios for plane and unpolarized
incident light, reduced masses (AMU), force constants (mDyne/A),
and normal coordinates:
                     1
                   SGG
Frequencies --  4646.1741
Red. masses --     1.0078
Frc consts  --    12.8182
IR Inten    --     0.0000
Raman Activ --    89.3384
Depolar (P) --     0.3333
Depolar (U) --     0.5000
 Atom  AN      X      Y      Z
    1   1     0.00   0.00   0.71
    2   1     0.00   0.00  -0.71

-------------------
- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
 Atom     1 has atomic number  1 and mass   1.00783
h2opt.log lines 1351-1379/1505 91%
```

Koopmans' Theorem and Unrestricted Hartree Fock

HF Roothaan Equation

For molecules numerical basis not efficient so use atom centered basis set to describe the molecular orbital

$$\phi_a(\mathbf{r}_1) = \sum_{u=1}^{Nbasis} C_{ua}\theta_u \qquad a = 1,2,...Nbasis$$

$$f(\mathbf{r}_1)\phi_a(\mathbf{r}_1) = \varepsilon_a\phi_a(\mathbf{r}_1)$$

$$f(\mathbf{r}_1)\sum_{u=1}^{Nbasis} C_{ua}\theta_u = \varepsilon_a \sum_{u=1}^{Nbasis} C_{ua}\theta_u \rightarrow$$

$$\sum_{u=1}^{Nbasis} C_{ua}\int \theta_v^*(\mathbf{r}_1) f(\mathbf{r}_1)\theta_u(\mathbf{r}_1)d\mathbf{r}_1 = \varepsilon_a \sum_{u=1}^{Nbasis} C_{ua}\int \theta_v^*(\mathbf{r}_1)\theta_u(\mathbf{r}_1)d\mathbf{r}_1$$

$$\sum_{u=1}^{Nbasis} C_{ua}F_{vu} = \varepsilon_a \sum_{u=1}^{Nbasis} C_{ua}S_{vu} \qquad a = 1,2,...Nbasis$$

$$FC = SC\varepsilon$$

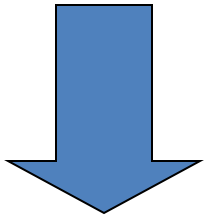
Nbasis is usually more than the total number of orbitals needed n/2

For a closed shell system

Occupied Orbital, Unoccupied/Virtual Orbital

The first n orbitals of a spin orbital (n/2 spacial orbital* alpha, n/2 spacial orbital * beta) is called occupied orbitals because the electron are occupying that orbital

The rest of 2*Nbasis-n orbitals (Nbasis-n/2 spacial * alpha, and Nbasis-n/2 spacial* beta) are called unoccupied or virtual orbitals



Is there any physical meaning to these orbitals

Orbital Energy and Total Hartree Fock Energy

$$\left[h(\mathbf{r}_1)+\sum_{j=1}^{n}\left(J_j(\mathbf{x}_1)-K_j(\mathbf{x}_1)\right)\right]\psi_i(\mathbf{x}_1)=\varepsilon_i\psi_i(\mathbf{x}_1) \qquad i=1,2,\ldots n$$

$$f(1)\psi_i(\mathbf{x}_1)=\varepsilon_i\psi_i(\mathbf{x}_1) \qquad i=1,2,\ldots n$$

ε_i : orbital energy $\quad \varepsilon_i=\langle\psi_i|f|\psi_i\rangle=h_{ii}+\sum_{j=1}^{n}\left(J_{ij}-K_{ij}\right)$

Sum of orbital energy

$$\sum_{i=1}^{n}\varepsilon_i=\sum_{i=1}^{n}h_{ii}+\sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij}-K_{ij}\right)$$

$$\left\langle\psi_1\psi_2\ldots\psi_n\left|\hat{H}^0\right|\psi_1\psi_2\ldots\psi_n\right\rangle=\sum_{i=1}^{n}\langle\psi_i|h_1|\psi_i\rangle+\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(\langle ij\,|\,ij\rangle-\langle ij\,|\,ji\rangle\right)$$

$$=\sum_{i=1}^{n}h_{ii}+\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij}-K_{ij}\right)$$

Double Counting by Orbital energy

Sum of orbital energy has excess energy of $\frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij}-K_{ij}\right)$

What does orbital energy mean?

ε_i includes coulomb and exchange energy of electron in orbital ψ_i and electrons in all other occupied spin orbitals (particularly ψ_j).

ε_j includes coulomb and exchange energy of electron in orbital ψ_j and electrons in all other occupied spin orbitals (particularly ψ_i).

Add ε_i and ε_j we have twice the electron interaction

If the sum of the orbital energies is not total energy what physical significance can we say about the orbital energy?

Koopmans' Theorem

$$\left|{}^{n}\Psi_0\right\rangle = \left|\psi_1\psi_2..\psi_k.\psi_n\right\rangle, {}^{n}E_0 = \sum_{i=1}^{n} h_{ii} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij} - K_{ij}\right)$$

Let's consider taking an electron away from orbital k to make an n-1 electron system

$$\left|{}^{n-1}\Psi_k\right\rangle = \left|\psi_1\psi_2...\psi_n\right\rangle, {}^{n-1}E_k = \sum_{i\neq k}^{n} h_{ii} + \frac{1}{2}\sum_{i\neq k}^{n}\sum_{j\neq k}^{n}\left(J_{ij} - K_{ij}\right)$$

Ionization Potential $= {}^{n-1}E_k - {}^{n}E_0$

$$= -h_{kk} - \frac{1}{2}\sum_{i=1}^{n}\left(J_{ik} - K_{ik}\right) - \frac{1}{2}\sum_{j=1}^{n}\left(J_{kj} - K_{kj}\right)$$

$$= -h_{kk} - \sum_{j=1}^{n}\left(J_{kj} - K_{kj}\right) = -\varepsilon_k$$

Remember symmetry?

$$J_{ij} = \langle ij \mid ij\rangle = \langle ji \mid ji\rangle = J_{ji}$$

$$K_{ij} = \langle ij \mid ji\rangle = \langle ji \mid ij\rangle = K_{ji}$$

Ionization energy given by the negative of orbital energy that electron ionizes from.

Koopmans' Theorem

$$\left|{}^{n}\Psi_0\right\rangle = \left|\psi_1\psi_2..\psi_k.\psi_n\right\rangle, {}^{n}E_0 = \sum_{i=1}^{n} h_{ii} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(J_{ij} - K_{ij}\right)$$

Let's consider adding an electron to orbital r to make an n+1 electron system

$$\left|{}^{n+1}\Psi_r\right\rangle = \left|\psi_1\psi_2..\psi_k.\psi_n\psi_r\right\rangle, {}^{n+1}E_r = \sum_{i=1}^{n} h_{ii} + h_{rr} + \frac{1}{2}\sum_{i=1}^{n+1}\sum_{j=1}^{n+1}\left(J_{ij} - K_{ij}\right)$$

$$\text{Electron Affinity} = {}^{n}E_0 - {}^{n+1}E_r$$

$$= -h_{rr} - \frac{1}{2}\sum_{i=1}^{n}\left(J_{ir} - K_{ir}\right) - \frac{1}{2}\sum_{j=1}^{n}\left(J_{rj} - K_{rj}\right) = -h_{rr} - \sum_{j=1}^{n}\left(J_{rj} - K_{rj}\right) = -\varepsilon_r$$

Electron affinity is given by the negative of orbital energy that the electron occupies

Since the n-1/n+1 electron system is different from n electron system you can not assume that spin orbitals are equivalent!!!
But orbital energies give a good estimate

Unrestricted Hartree Fock

$$\left|\psi_1\psi_2\ldots\psi_n\right\rangle = \left|\phi_1\bar{\phi}_1..\phi_i\bar{\phi}_i\ldots\phi_{n/2}\right\rangle$$

$$\psi_1(\mathbf{x}_1) = \phi_1(\mathbf{r}_1)\alpha(s_1) \rightarrow \phi_1$$

$$\psi_2(\mathbf{x}_1) = \phi_1(\mathbf{r}_1)\beta(s_1) \rightarrow \bar{\phi}_1$$

Different Spin Different (spacial) Orbital calculation
(RHF is different spin same orbital calculation)

$$\left[h(\mathbf{r}_1) + \sum_{b=1}^{n_a}\left(J_b{}^{\alpha}(\mathbf{r}_1) - K_b{}^{\alpha}(\mathbf{r}_1)\right) + \sum_{b=1}^{n_\beta}\left(J_b{}^{\beta}(\mathbf{r}_1)\right)\right]\phi_a{}^{\alpha}(\mathbf{r}_1) = \varepsilon_a{}^{\alpha}\phi_a{}^{\alpha}(\mathbf{r}_1) \qquad a = 1,2,\ldots n_\alpha$$

$$f^{\alpha}(\mathbf{r}_1)\phi_a{}^{\alpha}(\mathbf{r}_1) = \varepsilon_a{}^{\alpha}\phi_a{}^{\alpha}(\mathbf{r}_1)$$

$$\left[h(\mathbf{r}_1) + \sum_{b=1}^{n_\beta}\left(J_b{}^{\beta}(\mathbf{r}_1) - K_b{}^{\beta}(\mathbf{r}_1)\right) + \sum_{b=1}^{n_\alpha}\left(J_b{}^{\alpha}(\mathbf{r}_1)\right)\right]\phi_a{}^{\beta}(\mathbf{r}_1) = \varepsilon_a{}^{\beta}\phi_a{}^{\beta}(\mathbf{r}_1) \qquad a = 1,2,\ldots n_\beta$$

$$f^{\beta}(\mathbf{r}_1)\phi_a{}^{\beta}(\mathbf{r}_1) = \varepsilon_a{}^{\beta}\phi_a{}^{\beta}(\mathbf{r}_1)$$

Virial Theorem Classical

$$2T = \sum_{i=1}^{n} \vec{v}_i \bullet \vec{p}_i = \frac{d}{dt}\left(\sum_{i=1}^{n} \vec{r}_i \bullet \vec{p}_i\right) - \sum_{i=1}^{n} \vec{r}_i \bullet \dot{\vec{p}}_i = \frac{d}{dt}\left(\sum_{i=1}^{n} \vec{r}_i \bullet \vec{p}_i\right) + \sum_{i=1}^{n} \vec{r}_i \bullet \frac{dV}{d\vec{r}_i}$$

If you take an average of a time derivative of a quantity that is bound (has some finite maximum and minimum values)

$$\bar{f} = \lim_{\tau\to\infty} \frac{1}{\tau}\int_0^{\tau} \frac{dF}{dt}\,dt = \lim_{\tau\to\infty} \frac{F(\tau) - F(0)}{\tau} = 0$$

Position and momentum can only take certain values that is bound by the energy so average of first term in left hand is zero

$$2\overline{T} = \text{time average}\left[\sum_{i=1}^{n} \vec{r}_i \bullet dV / d\vec{r}_i\right]$$

If potential is given as $V = \sum_{i=1}^{n} k\vec{r}_i^{\,s} \rightarrow \vec{r}_i \bullet \frac{dV}{d\vec{r}_i} = \vec{r}_i \bullet s\sum_{i=1}^{n} k\vec{r}_i^{\,s-1} = sV$

$$2\overline{T} = s\overline{V}$$

For coulombic interactio s=-1

For harmonic oscillator s=2

Projects Hartree Fock Calculations

- Energy of H (different basis sets) compare with exact answer, binding energy of H_2 (different basis set), extrapolation compare distance
- HF, HCl, HBr, binding energy, charge distribution, compare bond length
- F_2, Cl_2, Br_2 binding energy, bond length, vibrational frequency
- Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, which spin state is most stable