

Solving Hartree Fock Equation

HF Roothaan Equation

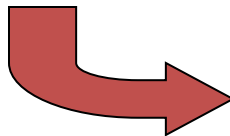
For molecules numerical basis not efficient so use atom centered basis set to describe the molecular orbital

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

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

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

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



$$\mathbf{F} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\varepsilon}$$

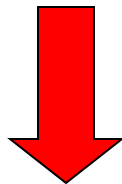
Self Consistent Field

We just have to solve the fock equation:

PROBLEM FOCK OPERATOR HAS THE SOLUTION INSIDE

$$F(C)C = SC\varepsilon$$

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



Self consistent field (SCF) method

Fock Operator in Basis Representation

$$\begin{aligned}
 F_{vu} &= \int \theta_v^*(\mathbf{r}_1) f(\mathbf{r}_1) \theta_u(\mathbf{r}_1) d\mathbf{r} \\
 &= \int \theta_v^*(\mathbf{r}_1) h(\mathbf{r}_1) \theta_u(\mathbf{r}_1) d\mathbf{r} \\
 &\quad + \int \theta_v^*(\mathbf{r}_1) \left(\sum_{b=1}^{n/2} (2J_b(\mathbf{r}_1) - K_b(\mathbf{r}_1)) \right) \theta_u(\mathbf{r}_1) d\mathbf{r}_1
 \end{aligned}$$

Core Hamiltonian Matrix

Two electron Matrix

Calculated once in a
SCF cycle

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

Fock Operator in Basis Representation

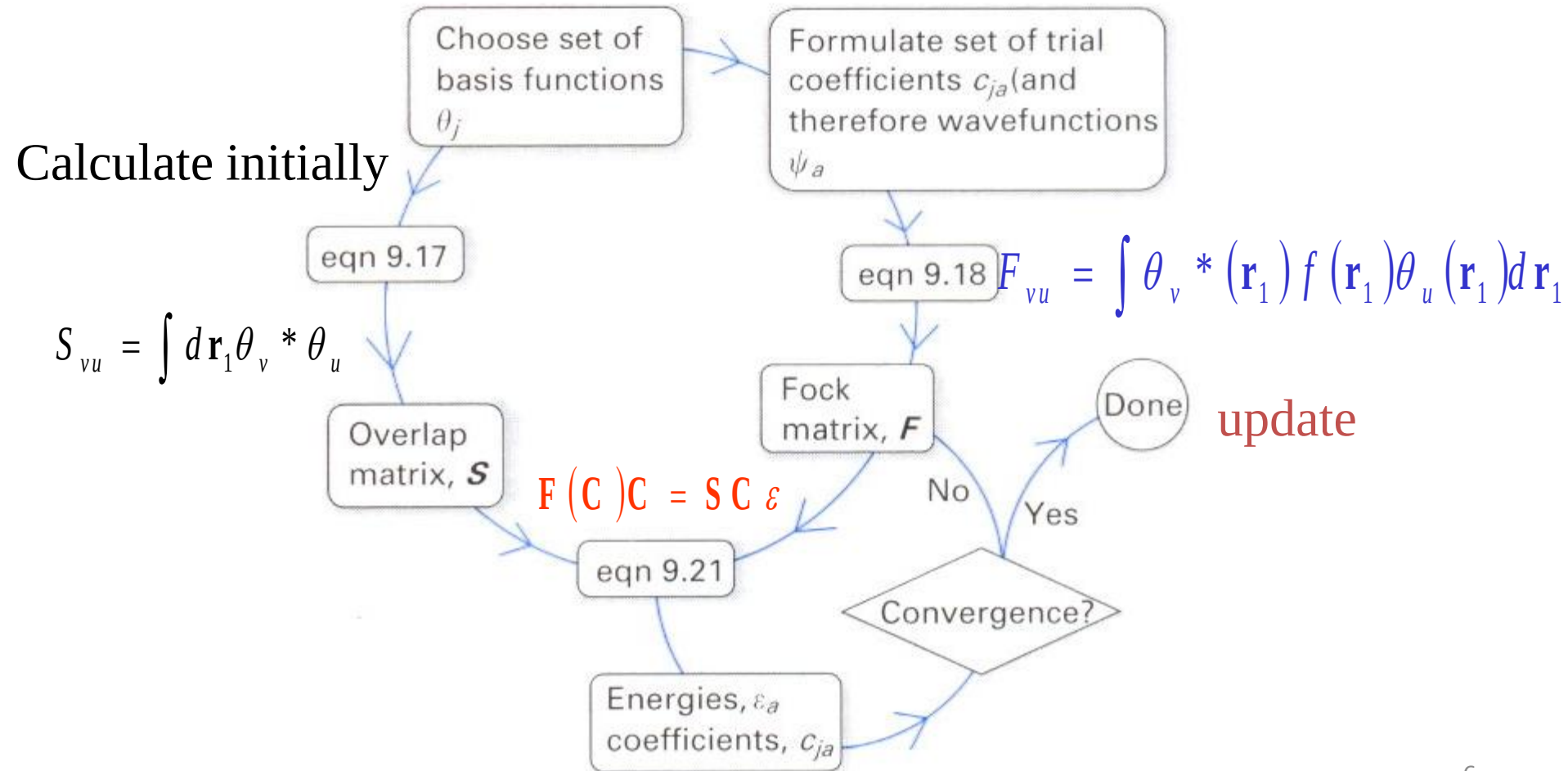
$$\begin{aligned} F_{vu} &= \int \theta_v^*(\mathbf{r}_1) f(\mathbf{r}_1) \theta_u(\mathbf{r}_1) d\mathbf{r} = \int \theta_v^*(\mathbf{r}_1) h(\mathbf{r}_1) \theta_u(\mathbf{r}_1) d\mathbf{r} \\ &+ \sum_{b=1}^{n/2} \sum_{w=1}^{Nbasis} \sum_{x=1}^{Nbasis} C_{wb}^* C_{xb} \left(2\langle vw | ux \rangle - \langle vw | xu \rangle \right) \\ &\rightarrow h_{vu} + \sum_{w=1}^{Nbasis} \sum_{x=1}^{Nbasis} P_{wx} \left(2\langle vw | ux \rangle - \langle vw | xu \rangle \right) \end{aligned}$$

Where we define the

Self Consistent Field Method

$$\langle vw | ux \rangle$$

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

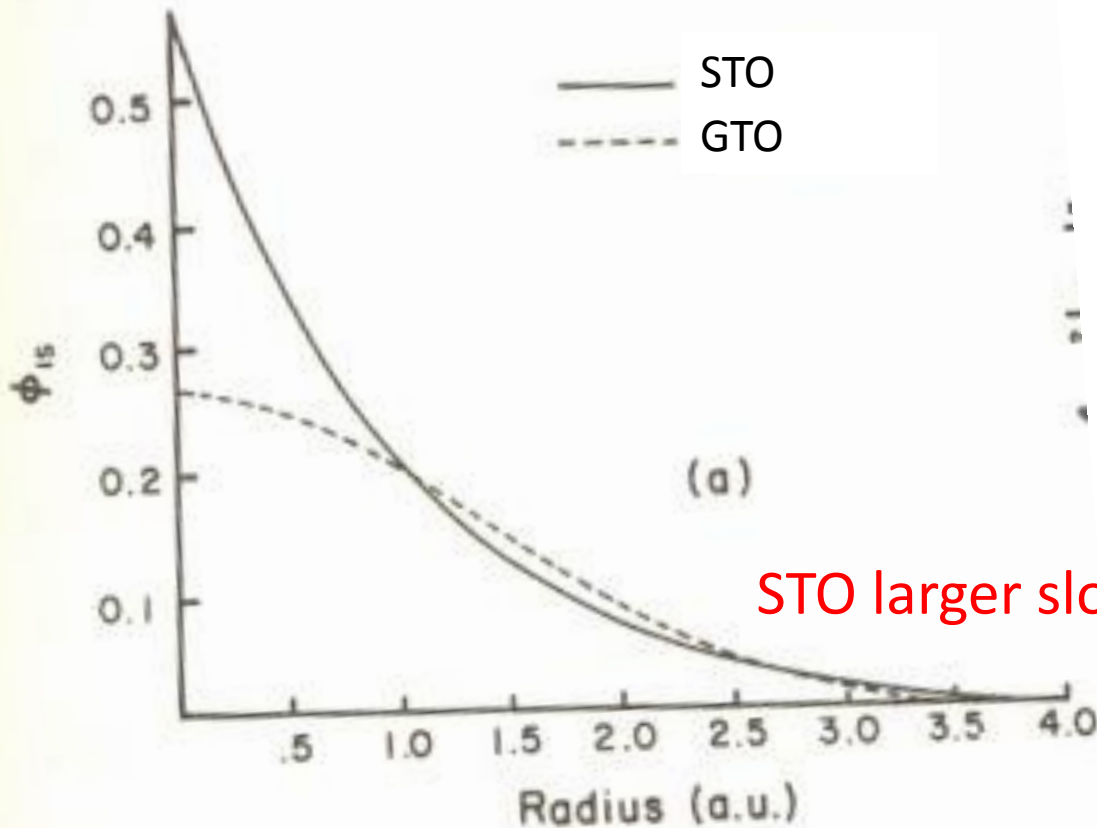


Slater Type Orbital vs Gaussian Type Orbital

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

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

GTO vs STO



STO larger slope near $r=0$

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

$$\left. \frac{d\theta_{1s}^{GTO}(\alpha, \mathbf{r} - \mathbf{R}_A)}{dr} \right|_{r=0} = 0$$

Solve the hydrogen atom by Gaussian Function

$$\hat{H} = \left[-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \left(-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2\mu r^2} \right) \right]$$

1S $l=0$, using atomic units

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

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

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

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

Hint: Gaussian Integrals

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

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

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

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

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

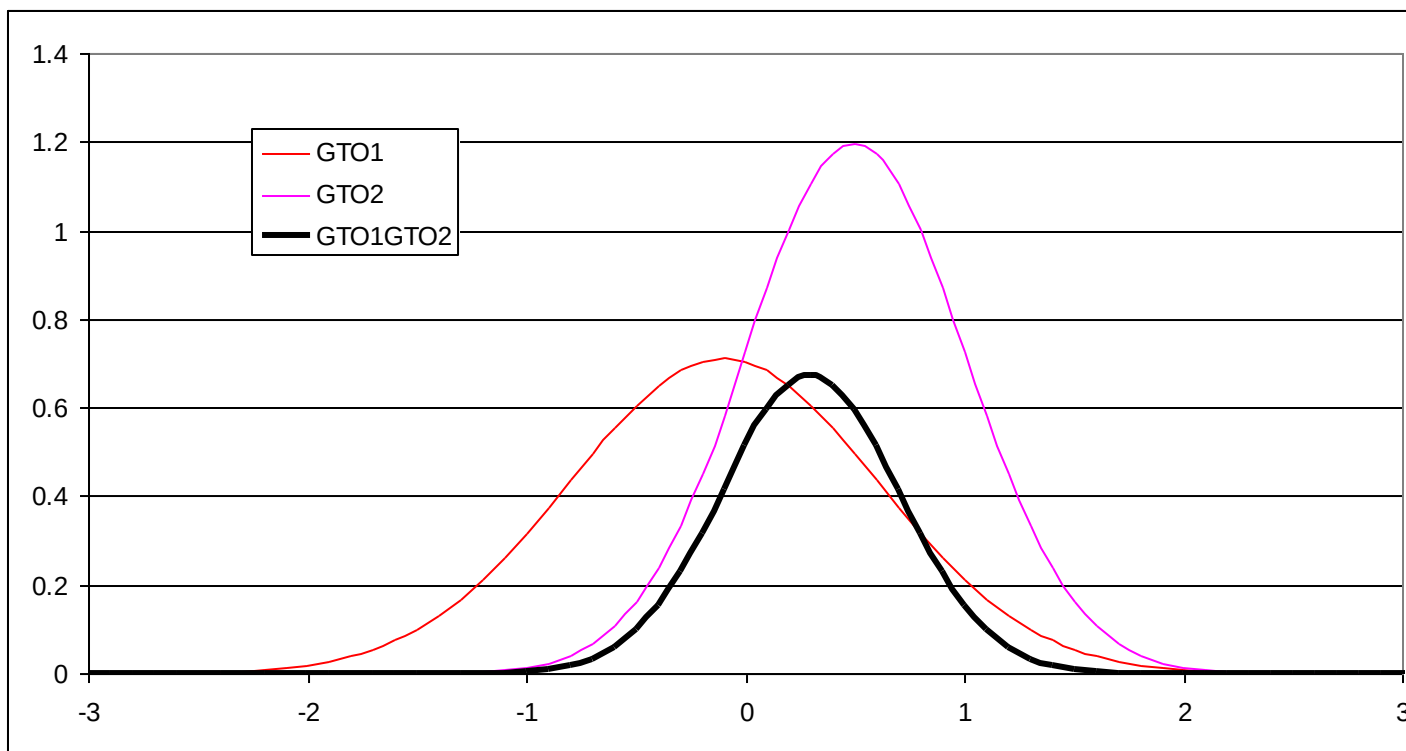
$$\langle r^4 \rangle = \frac{3}{32\alpha^2} \sqrt{\frac{\pi}{2\alpha}}$$

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

Why GTO

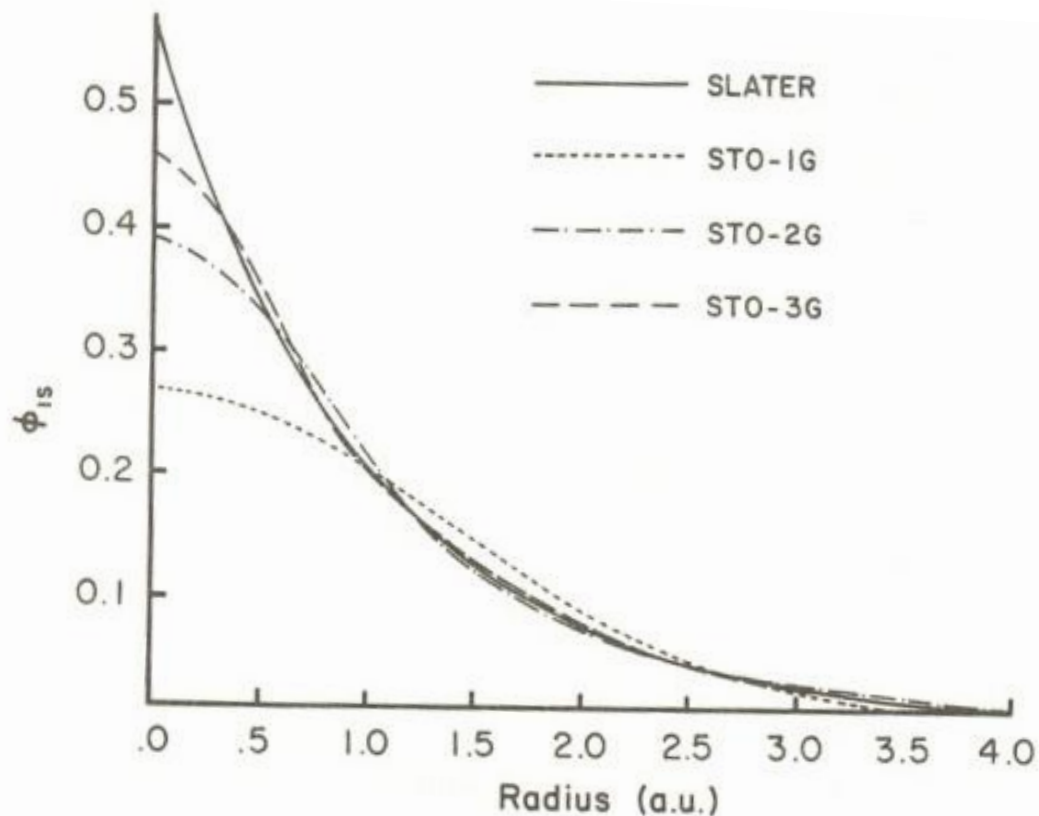
4 orbital integral, if the orbitals are on 4 different atoms

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



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



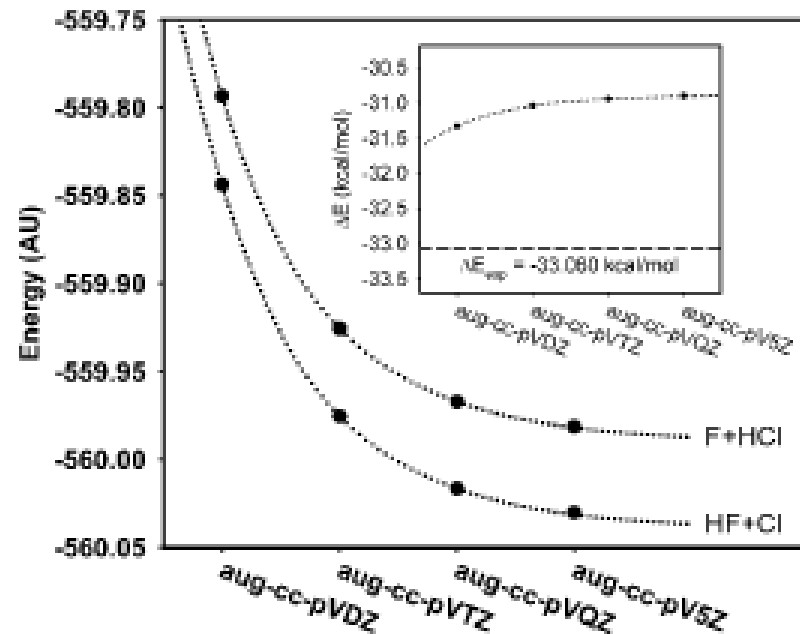
Basis Sets

- 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 valence electrons, electrons in the core do not contribute to important reactions use

Hay-Wadt: LANL2DZ LANL2TZ, Dolg

In bulk simulation like VASP it is called Pseudo potential

Basis Set Library

(https://bse.pnl.gov/bse/portal)

EMSL Basis Set Exchange - Mozilla Firefox

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All

3-21++G

3-21++G*

3-21G

3-21G*

3-21G* Polarization

3-21GSP

4-22GSP

4-31G

6-31++G

6-31++G*

6-31++G**

6-31++G*

6-311++G(2d,2p)

6-311++G(3df,3pd)

6-311++G**

Search Basis Set Name

Total: 439 published basis sets

H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo				
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu						
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr						

Format: NWChem ☒ Optimized General Contractions [Get Basis Set](#)

"3-21++G" Basis Set Information

Summary:

Primary Developer:

Last Modified:

VDZD Valence Double Zeta + Diffuse Functions on All Atoms

N/A

Mon, 15 Jan 2007 23:47:08 GMT

Contributor:

Curation Status:

Dr. David Feller

published

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[User annotations...](#)

When publishing results obtained from use of the Basis Set Exchange (BSE) software and the EMSL Basis Set Library, please cite:

The Role of Databases in Support of Computational Chemistry Calculations

Feller, D., J. Comp. Chem., 17(13), 1571-1586, 1996.

Basis Set Exchange: A Community Database for Computational Sciences

Schuchardt, K.L., Didier, B.T., Elsethagen, T., Sun, L., Gurnamoorhi, V., Chase, J., Li, J., and Windus, T.L.
J. Chem. Inf. Model., 47(3), 1045-1052, 2007, doi:10.1021/ci600510j.

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SCIENTIFIC ANNOTATION MIDDLEWARE



KnECS v1.0 | SAM v2.1.4b8 | CHEF v1.1.01 [build #307231] | Jetspeed v1.4b2[cvs08oct2002p]

Pick Basis Set Convergence

Dipole moment of H₂O

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 $\sim$ (# 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
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.
```

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

- 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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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 1 of 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 OVMMax= 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 OVMMax= 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
Conv = 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/l60l.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 equilibrium 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

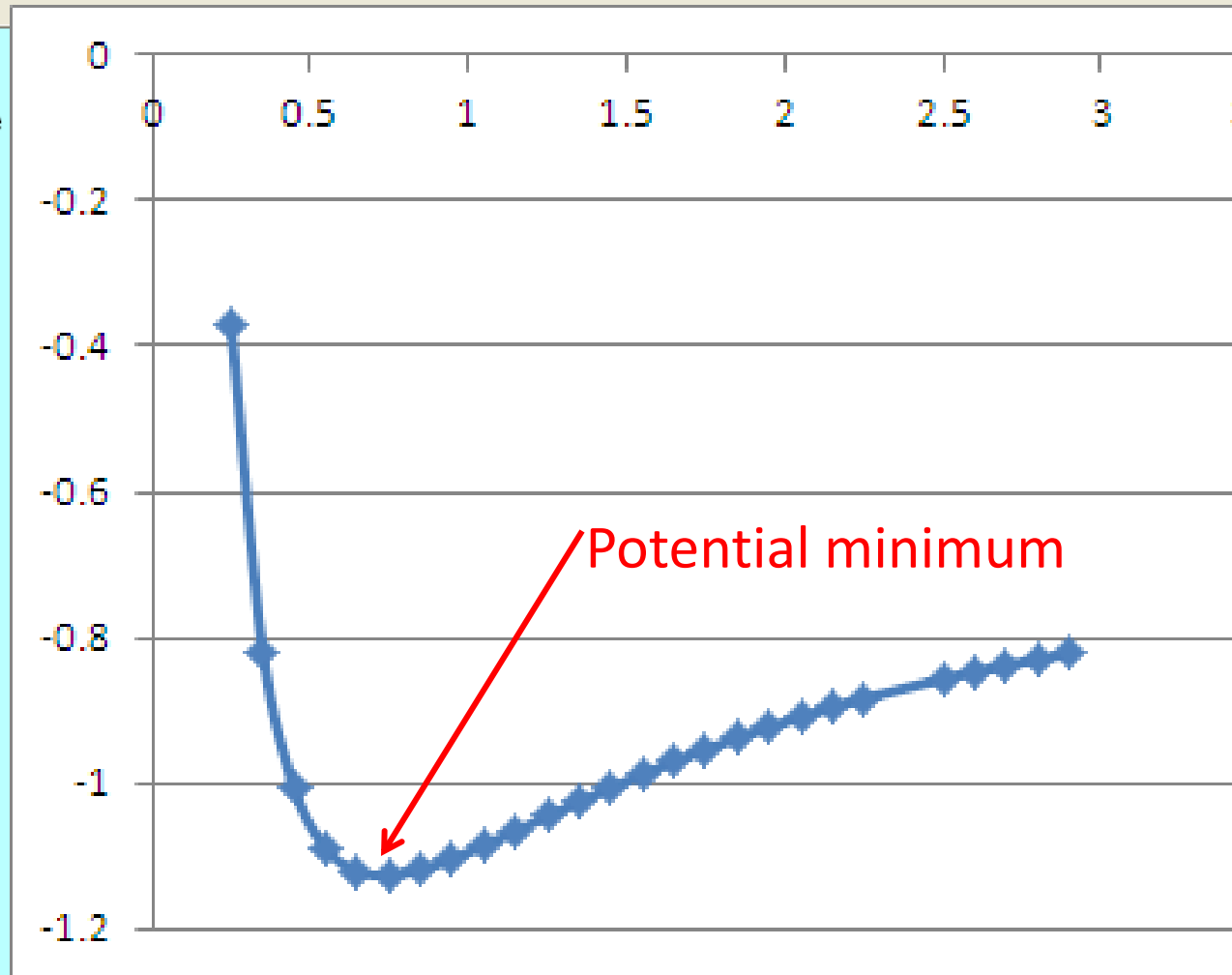
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File Edit Setup Control Window Resize Help

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



Leave Link 108 at Mon Mar 21 17:55:19 2011, MaxMem= 33554432 cpu: 0.0
h2scan.log lines 3718-3746/3766 99%

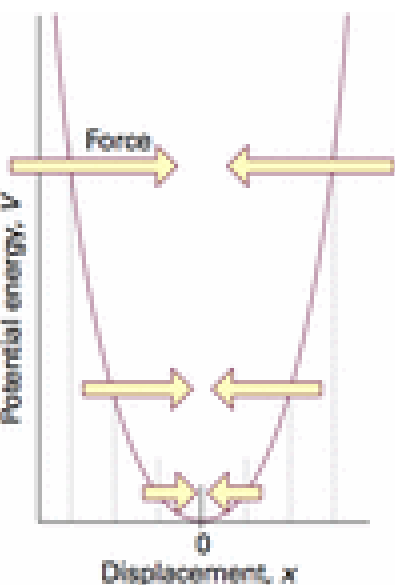
How to quantify Minimum?

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

Check the Hessian (second derivative)

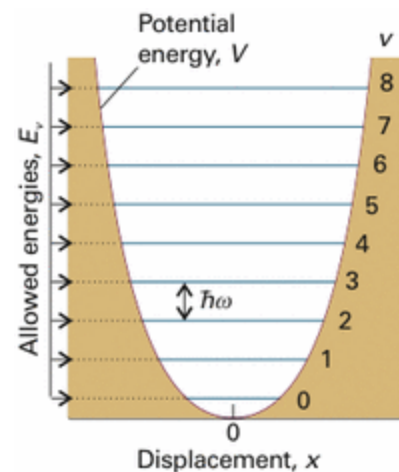
In Gaussian you can use the freq keyword

Harmonic Oscillator



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

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



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

Optimize Geometry Input

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

```
Title
```

```
O 1
```

```
H1
```

```
H2, H1, RH1H2
```

```
RH1H2=0.75
```

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

Optimize Geometry 1

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```

Eigenvalues ---      0.37819
RF0 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
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGrad

```

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

```

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 Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			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%

Optimize Geometry 2

140.109.112.238:22 - Tera Term VT

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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 (Linear)	Delta X (Quad)	Delta X (Total)	New X
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 Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			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

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

140.109.112.238:22 - Tera Term VT

The second derivative matrix:

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

! Name	Definition	Value	Derivative Info.	!
! R1	R(1,2)	0.73	-DE/DX = 0.0	!

```
in2opt.log lines 815-843/1505 55%
```

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

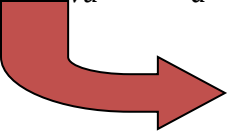
$$\phi_a(\mathbf{r}_1) = \sum_{u=1}^{Nbasis} C_{ua} \theta_u \quad a = 1, 2, \dots, Nbasis$$

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

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

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

$$\sum_{u=1}^{Nbasis} C_{ua} F_{vu} = \epsilon_a \sum_{u=1}^{Nbasis} C_{ua} S_{vu} \quad a = 1, 2, \dots, Nbasis$$

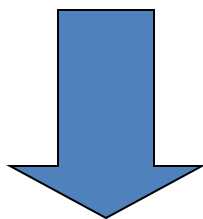
 $\mathbf{F} \mathbf{C} = \mathbf{S} \mathbf{C} \epsilon$

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 * α , $n/2$ spacial orbital * β) is called

The rest of $2*N_{\text{basis}} - n$ orbitals ($N_{\text{basis}} - n/2$ spacial * α , and $N_{\text{basis}} - n/2$ spacial * β)



Is there any physical meaning to these orbitals

Orbital Energy and Total Hartree Fock Energy

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

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

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

Sum of orbital energy

Double Counting by Orbital energy

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

What does orbital energy mean?

ϵ_i

ϵ_j

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

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

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

$$\left| {}^{n-1}\Psi_k \right\rangle = \left| \psi_1 \psi_2 \dots \psi_n \right\rangle,$$

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

=

=

Remember symmetry?

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

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

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

Koopmans' Theorem

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

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

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

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

=

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

Unrestricted Hartree Fock

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

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

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

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

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

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

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

Virial Theorem Classical

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

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

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

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

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

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

Virial Theorem Quantum

$$\frac{d}{dt} \left\langle \sum_{i=1}^n \vec{r}_i \cdot \vec{p}_i \right\rangle = \frac{i}{\hbar} \left[H, \sum_{i=1}^n \vec{r}_i \cdot \vec{p}_i \right]$$

First lets do this for one particle in the x-direction

Therefore

Virial Theorem Quantum

Time average of $\frac{d}{dt} \langle xp_x \rangle$

$$\frac{1}{\tau} \int_0^\tau \frac{d}{dt} \langle xp_x \rangle dt = \frac{1}{\tau} \int_0^\tau \left[2\langle T \rangle - \left\langle x \frac{dV}{dx} \right\rangle \right] dt$$



$$\frac{1}{\tau} \langle xp_x \rangle \Big|_0^\tau = -2\langle T \rangle - \left\langle x \frac{dV}{dx} \right\rangle = 0$$



If $V = \alpha x^s$

For coulombic interactio $s=-1$

For harmonic oscillator $s=2$

Take a look at your gaussian outputs

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