

Solving Hartree Fock Equation using a Basis Set HF Roothaan equation

HF Roothaan Equation

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

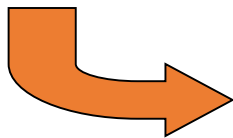
$$\phi_a(\mathbf{r}_1) = \sum_{u=1}^{Nbasis} C_{ua} \theta_u \quad a = 1, 2, \dots, Nbasis$$

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

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

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

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



$$\mathbf{FC} = \mathbf{SC}\epsilon$$

Self Consistent Field

We just have to solve the fock equation:

PROBLEM FOCK OPERATOR HAS THE SOLUTION INSIDE

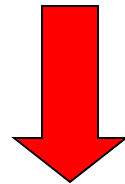
$$F(C)C = SC\epsilon$$

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

$$F(C^{\text{guess}})C^1 = SC^1\epsilon$$

Then put in C^1 this allows you to get C^2

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



SELF CONSISTENT FIELD (SCF) method

Fock Operator in Basis Representation

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

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

a, b are for spin orbitals
 u, v are for basis sets

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

Core Hamiltonian Matrix

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

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

Calculated once in a
 SCF cycle

Two electron Matrix

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

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

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

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 **density matrix** as

$$P_{wx} = \sum_{b=1}^{n/2} C_{wb}^* C_{xb}$$

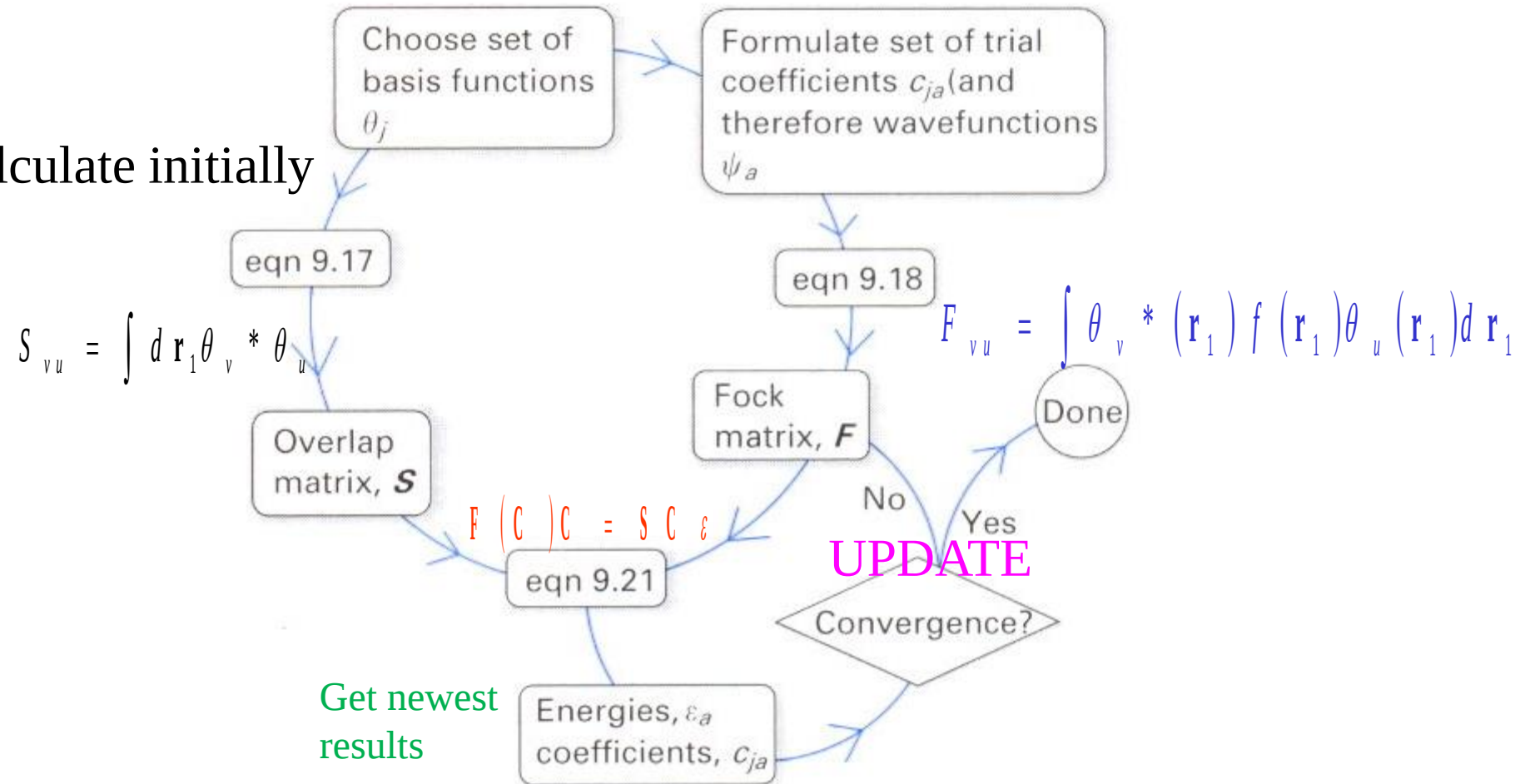
Since C changes every iteration this has to be recalculated every time

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



Basis Sets

Slater Type Orbital vs Gaussian Type Orbital

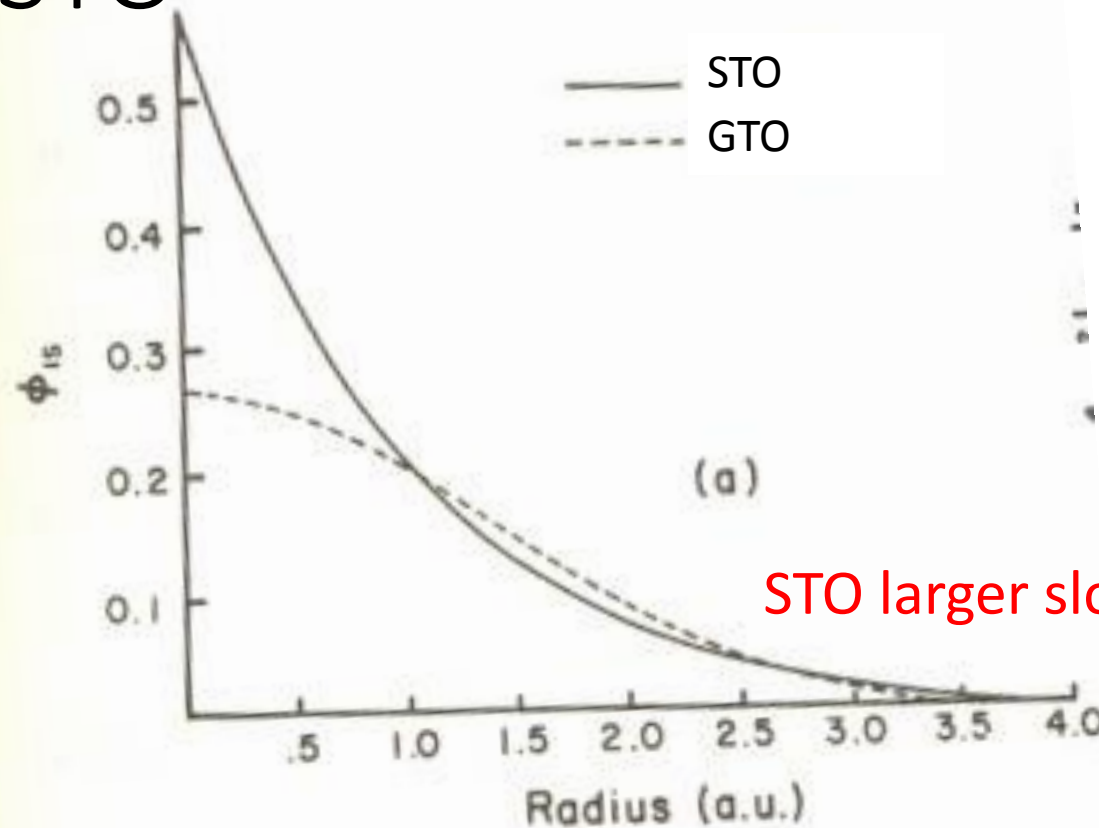
In the H_2 case we used Slater type orbitals for radial part where basis on H_A is given as

$$\theta_{1s}^{STO}(\xi, r - R_A) = \left(\xi^3 / \pi \right)^{1/2} e^{-\xi |r - R_A|}$$

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

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

GTO vs STO



STO larger slope near $r=0$

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

Solve the hydrogen atom by Gaussian Function

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

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

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

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

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

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

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

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

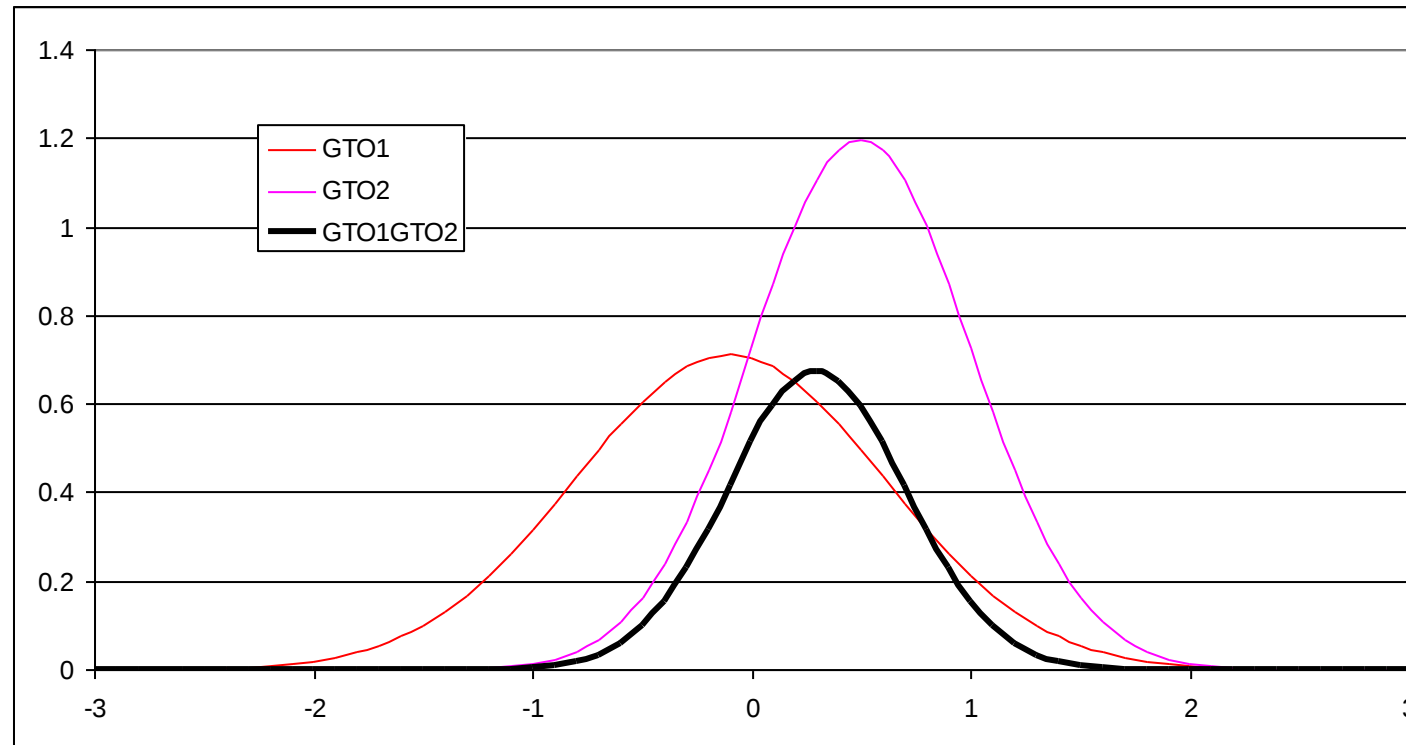
Why GTO?

4 orbital basis integral: if the basis are on 4 different atoms

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

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

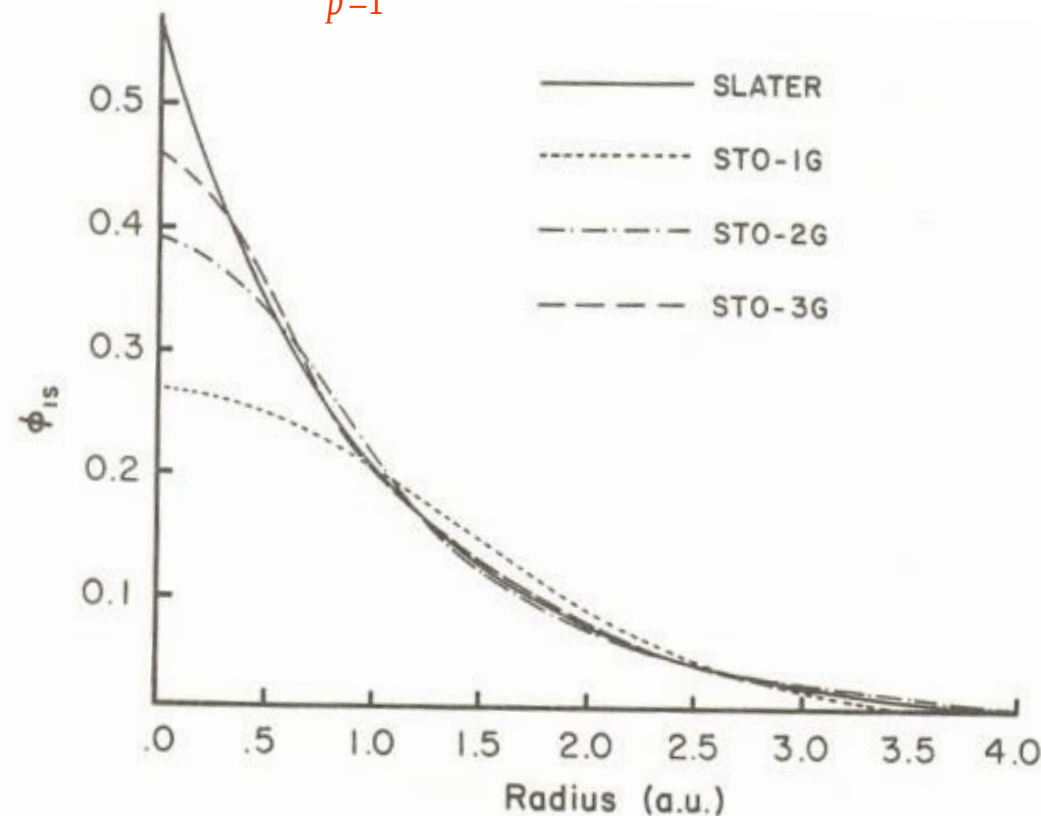
$$\mathbf{R}_D = \frac{(\alpha \mathbf{R}_A + \beta \mathbf{R}_B)}{(\alpha + \beta)}; \quad K_{AB} = (2\alpha\beta / [(\alpha + \beta)\pi])^{3/4} \exp\left[-\frac{\alpha\beta}{(\alpha + \beta)} |\mathbf{R}_A - \mathbf{R}_B|^2\right]$$



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

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



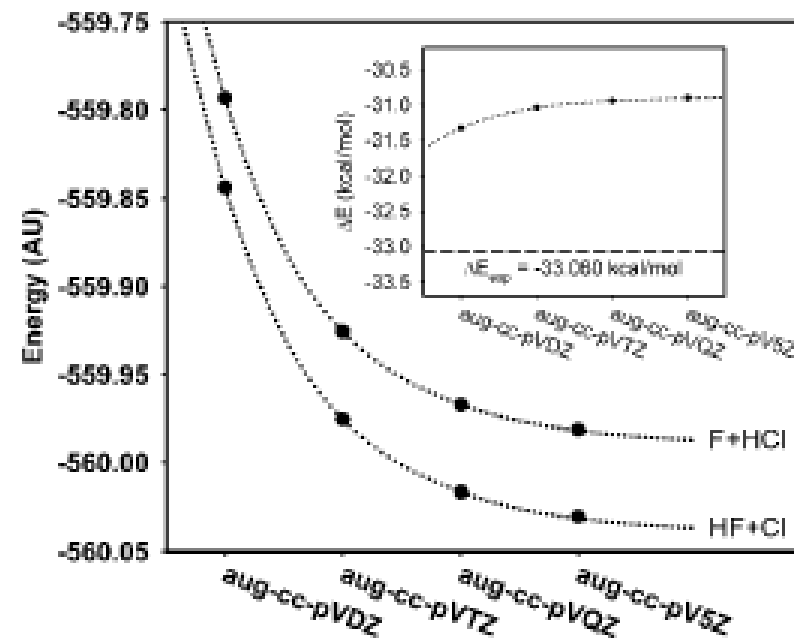
Basis Sets

- 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 **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 Pseudo potential

Basis Set Library

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

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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: ☒ Optimized General Contractions

Summary:

Primary Developer:

Last Modified:

VDZD Valence Double Zeta + Diffuse Functions on All Atoms
N/A
Mon, 15 Jan 2007 23:47:08 GMT

"3-21++G" Basis Set Information

Contributor:

Curation Status:

Dr. David Feller
published
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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., Gurunoorathi, 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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KnECS v1.0 | SAM v2.1.4b8 | CHEF v1.1.01 [build #307231] | Jetspeed v1.4b2[cvs08oct2002p]

Done

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 $\sim (\# \text{ of basis})^2$

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

$$\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = \int \exp(-\alpha r^2) \left[-\frac{1}{r} \frac{\partial}{\partial r} - \frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{1}{r} \right] \exp(-\alpha r^2) r^2 dr$$

$$\frac{\partial}{\partial r} \exp(-\alpha r^2) = -2\alpha r \exp(-\alpha r^2)$$

$$\frac{\partial^2}{\partial r^2} \exp(-\alpha r^2) = (-2\alpha + 4\alpha^2 r^2) \exp(-\alpha r^2)$$

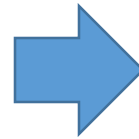
$$\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = \int \exp(-\alpha r^2) \left[2\alpha + \alpha - 2\alpha^2 r^2 - \frac{1}{r} \right] \exp(-\alpha r^2) r^2 dr$$

$$= 3\alpha \langle r^2 \rangle - 2\alpha^2 \langle r^4 \rangle - \langle r^1 \rangle$$

$$\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle = 3\alpha \langle r^2 \rangle - 2\alpha^2 \langle r^4 \rangle - \langle r^1 \rangle = \frac{3}{8} \sqrt{\frac{\pi}{2\alpha}} - \frac{3}{16} \sqrt{\frac{\pi}{2\alpha}} - \frac{1}{4\alpha}$$

$$= \frac{3}{16} \sqrt{\frac{\pi}{2\alpha}} - \frac{1}{4\alpha}$$

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



$$\frac{\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle} = \frac{\frac{3}{16} \sqrt{\frac{\pi}{2\alpha}} - \frac{1}{4\alpha}}{\frac{1}{8\alpha} \sqrt{\frac{\pi}{2\alpha}}}$$

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

$$= \frac{3}{2} \alpha - 2 \sqrt{\frac{2\alpha}{\pi}}$$

Derivative with respect to α

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

$$\frac{dE(\alpha)}{d\alpha} = \frac{3}{2} - \sqrt{\frac{2}{\pi}} \sqrt{\frac{1}{\alpha}} = 0 \rightarrow \sqrt{\alpha} = \frac{2}{3} \sqrt{\frac{2}{\pi}}$$

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

$$E\left(\alpha = \frac{8}{9\pi}\right) = \frac{24}{18\pi} - 2 \sqrt{\frac{16}{9\pi^2}}$$

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

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