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

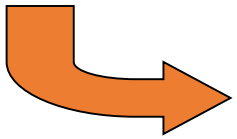
$$\phi_a(\mathbf{r}_1) = \sum_{u=1}^{Nbasis} C_{ua}\theta_u \qquad a = 1,2,\ldots Nbasis$$

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

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

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

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



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

Self Consistent Field

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

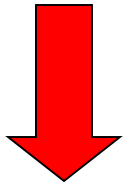
$$F(C)C = SC\varepsilon$$

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

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

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

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

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

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

a, b are for spin orbitals

u, v are for basis sets

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

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

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

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

Fock Operator in Basis Representation

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

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

$$\rightarrow h_{vu} + \sum_{w=1}^{Nbasis} \sum_{x=1}^{Nbasis} P_{wx} \left(2\langle vw | ux \rangle - \langle vw | xu \rangle \right)$$

Where we define the density matrix as

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

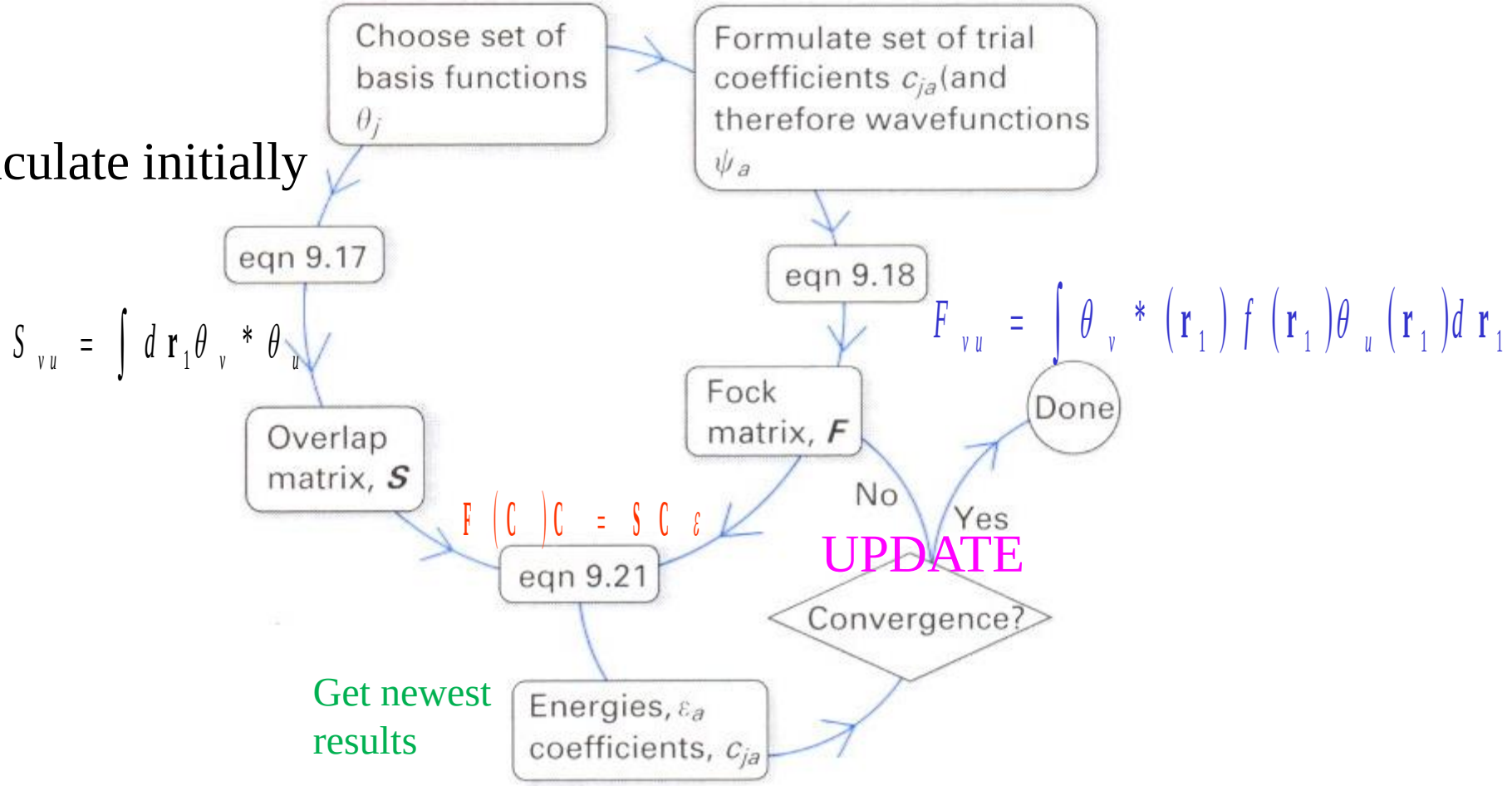
Since C changes every iteration this has to be recalculated every time

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

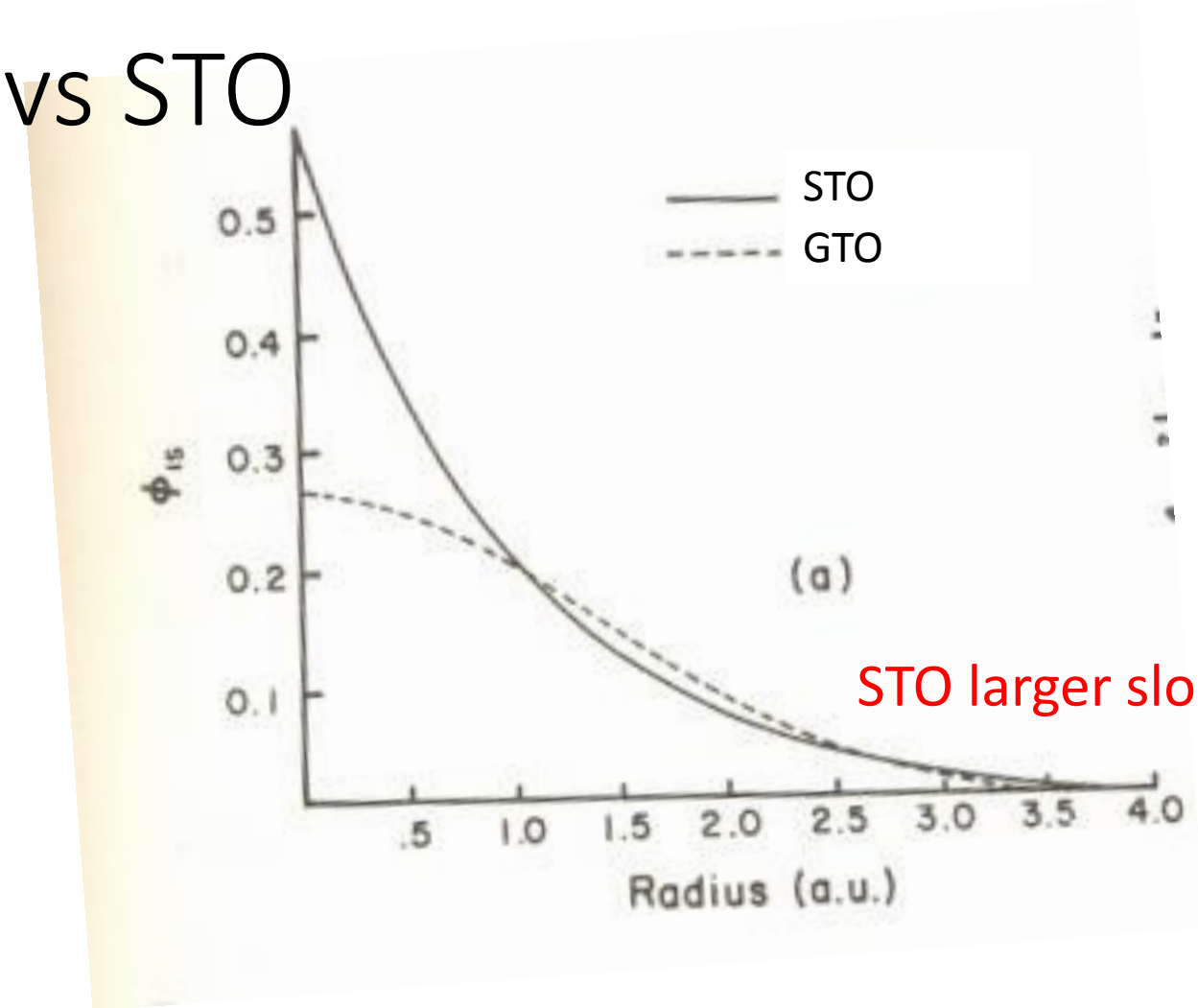
In the H_2 case we used Slater type orbitals for radial part where basis on H_A is given as

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

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

$$\hat{H} = \left[-\frac{1}{2r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r} \right] \qquad E_{trial} = \frac{\left\langle \psi_{trial} \middle| \hat{H} \middle| \psi_{trial} \right\rangle}{\left\langle \psi_{trial} \middle| \psi_{trial} \right\rangle}$$

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

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

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

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

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

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

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

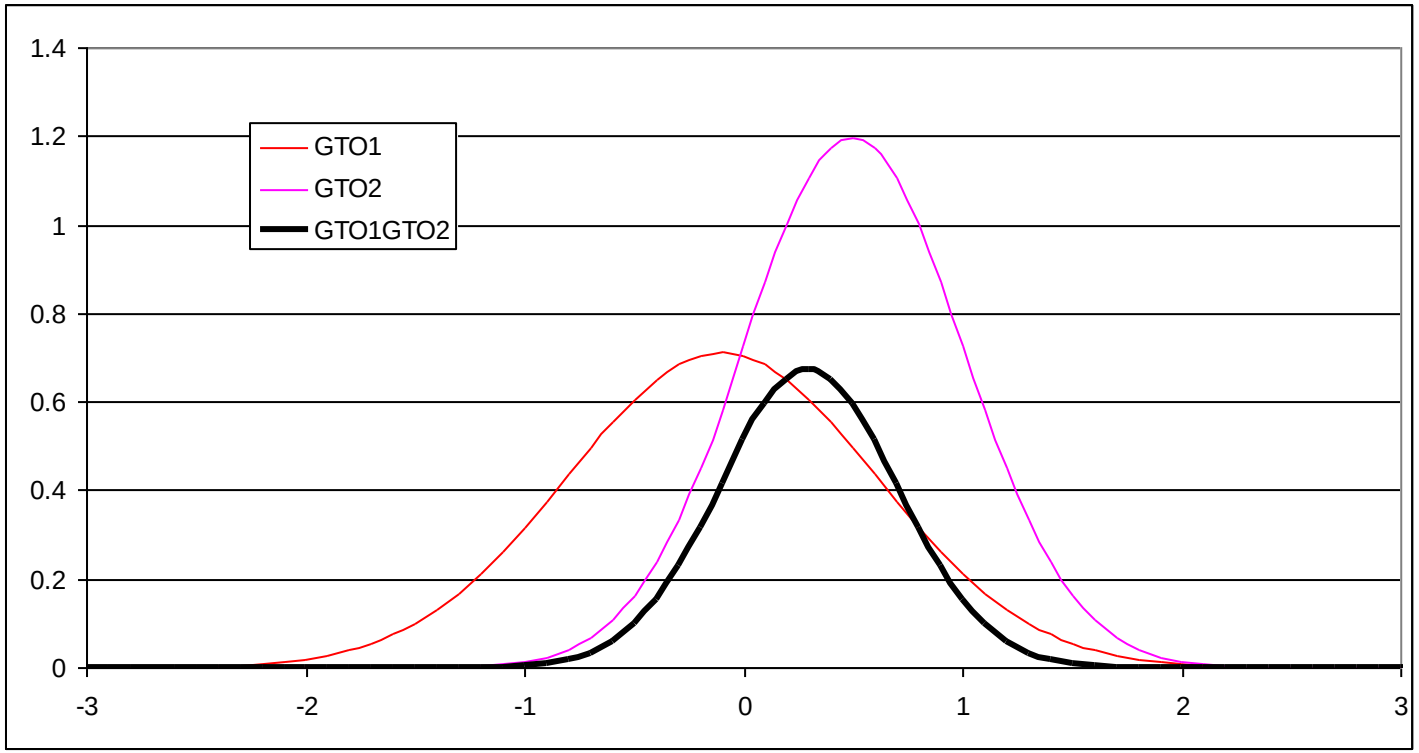
Why GTO?

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

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

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

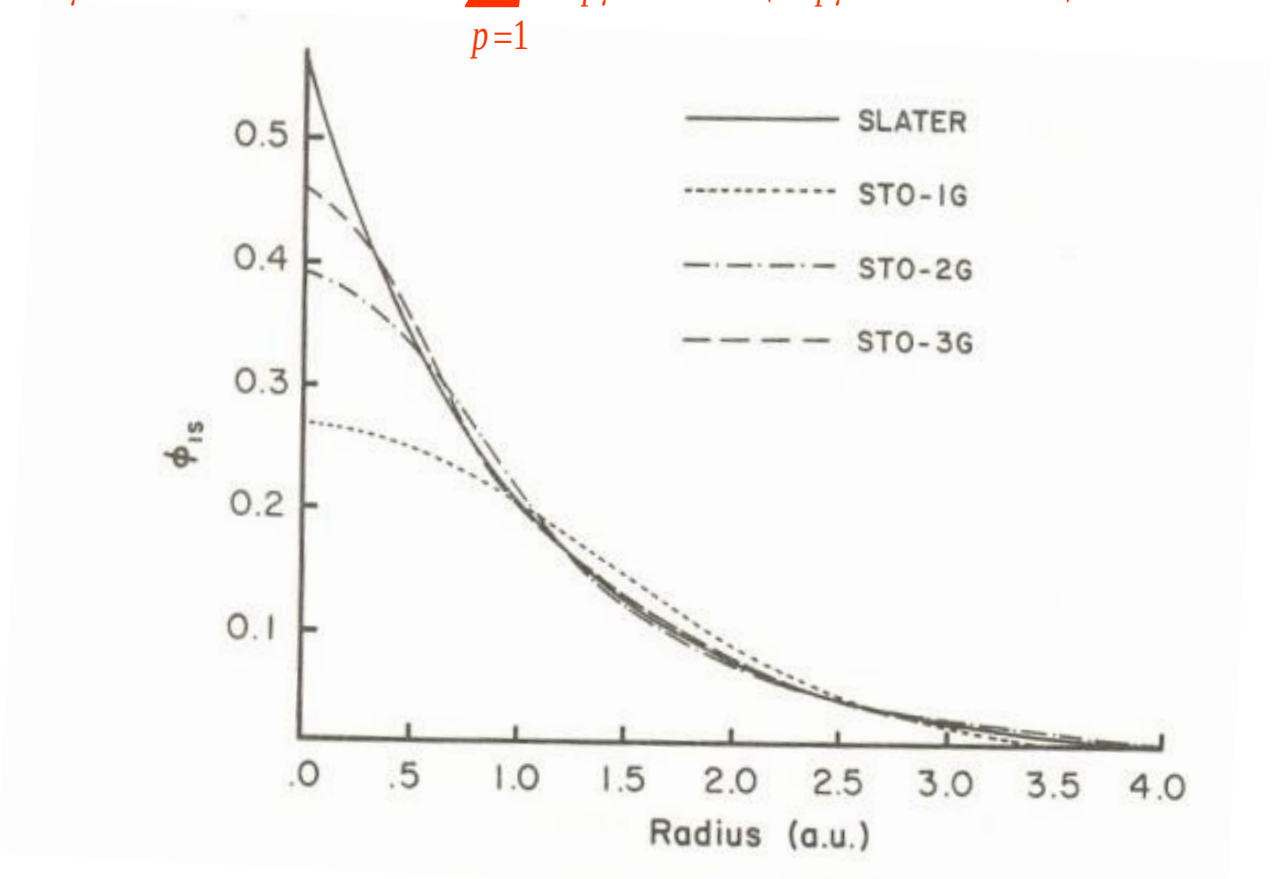
$$\mathbf{R}_D = \frac{(\alpha\mathbf{R}_A+\beta\mathbf{R}_\beta)}{(\alpha+\beta)};\quad K_{AB} = (2\alpha\beta/[(\alpha+\beta)\pi])^{3/4}\exp\left[-\frac{\alpha\beta}{(\alpha+\beta)}|\mathbf{R}_A-\mathbf{R}_B|^2\right]$$



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 (a) value

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



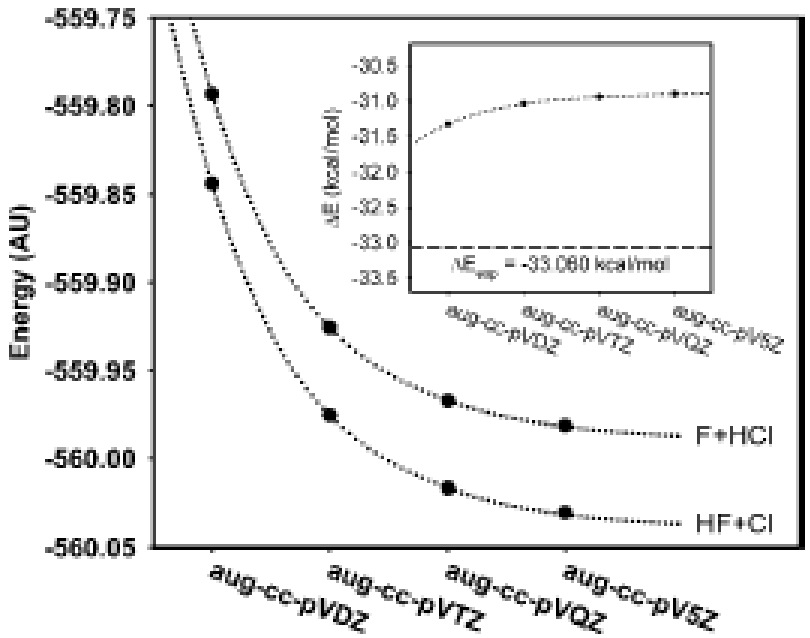
Basis Sets

- 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)



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

Basis Set Effective Core Potential

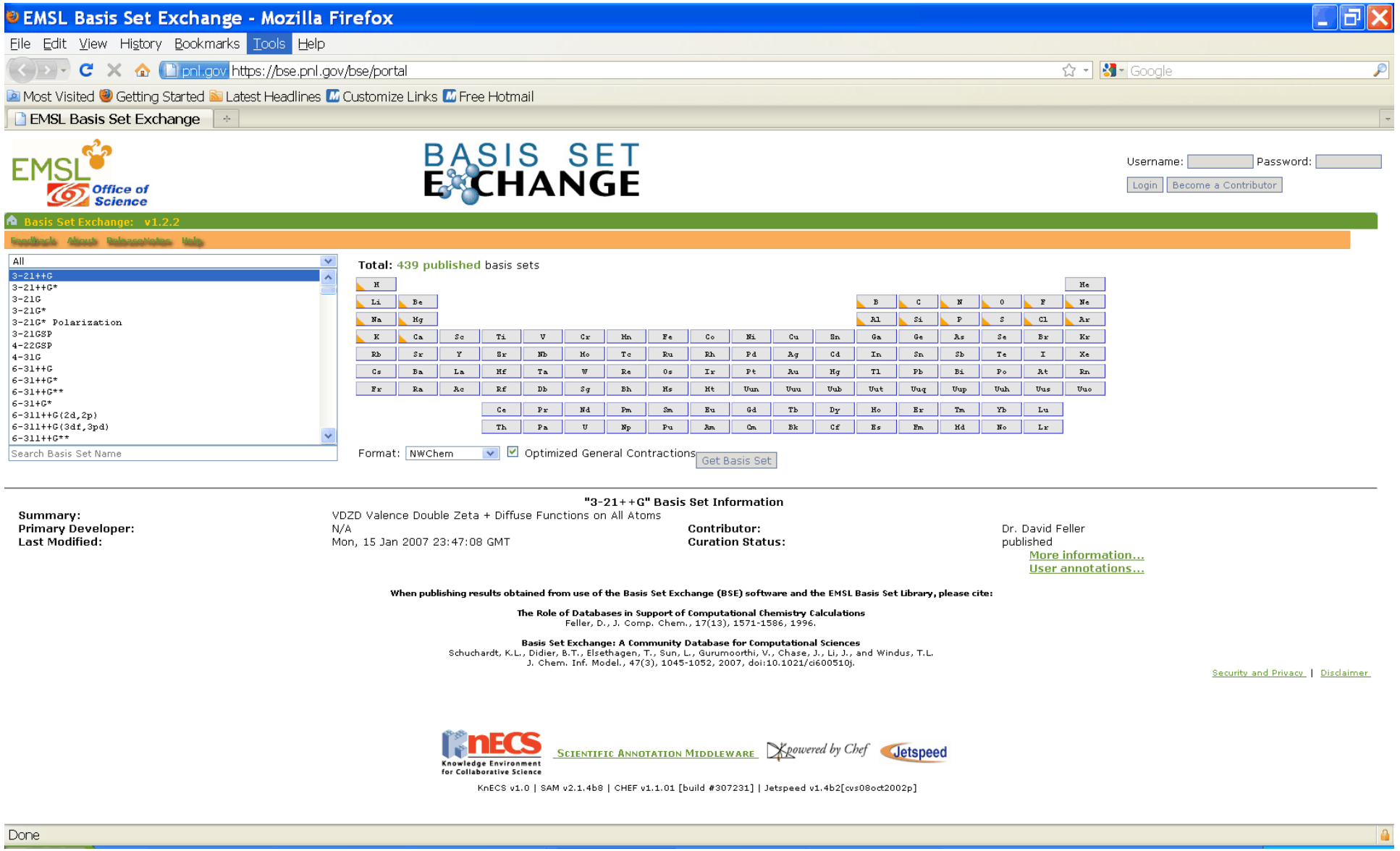
- Most Chemistry occurs between valance electrons, electrons in the core do not contribute to important reactions use EFFECTIVE POTENTIAL FOR THE CORE ELECTRONS:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Derivative with respect to α

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

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

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