

Example - He-H⁺

Step 1. Specify geometry

Instead of Slater functions, gaussian functions are used as the basis functions

Slater s-function

$$\phi = a \exp(-br)$$

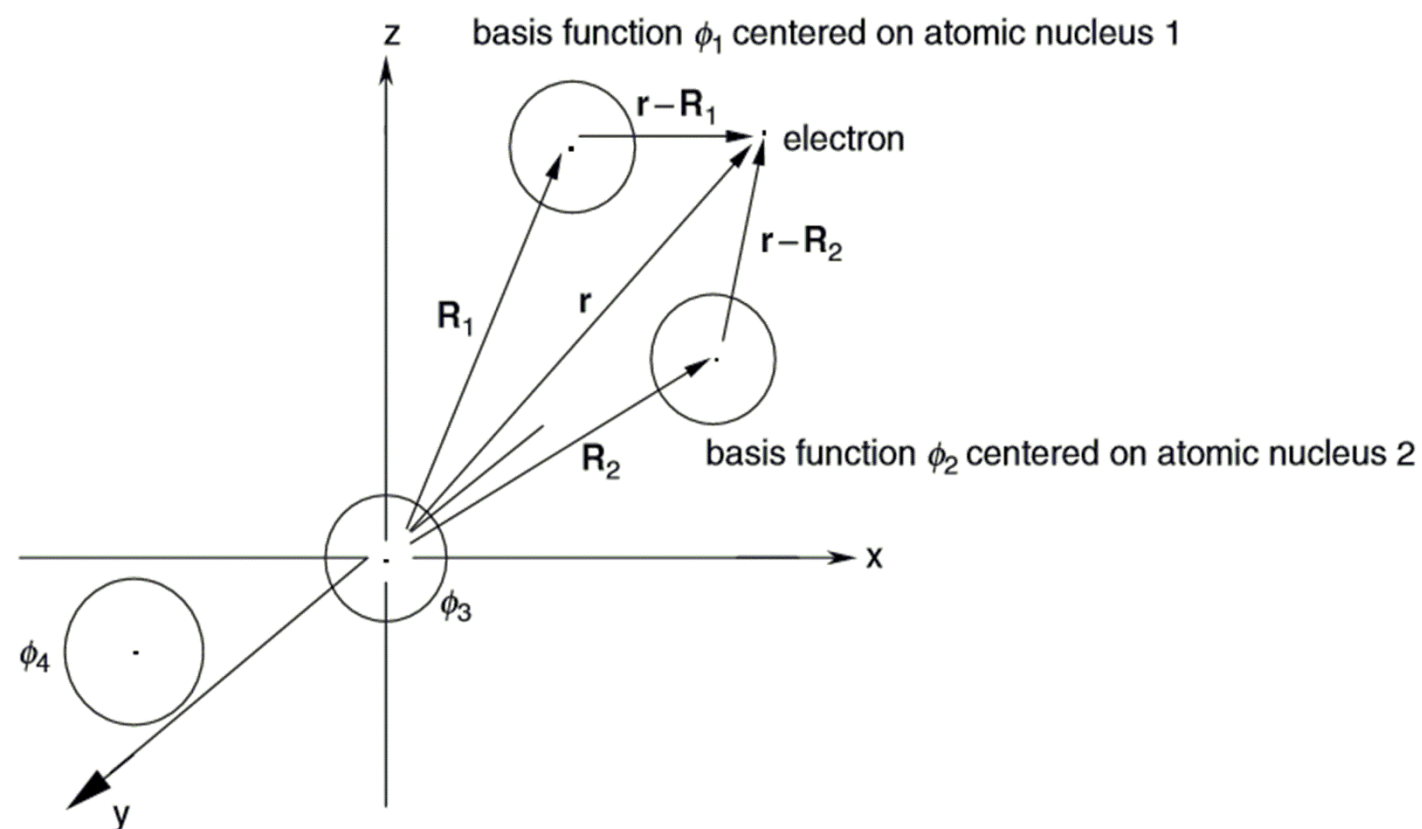
Gaussian s-function

$$\phi = a \exp(-br^2)$$

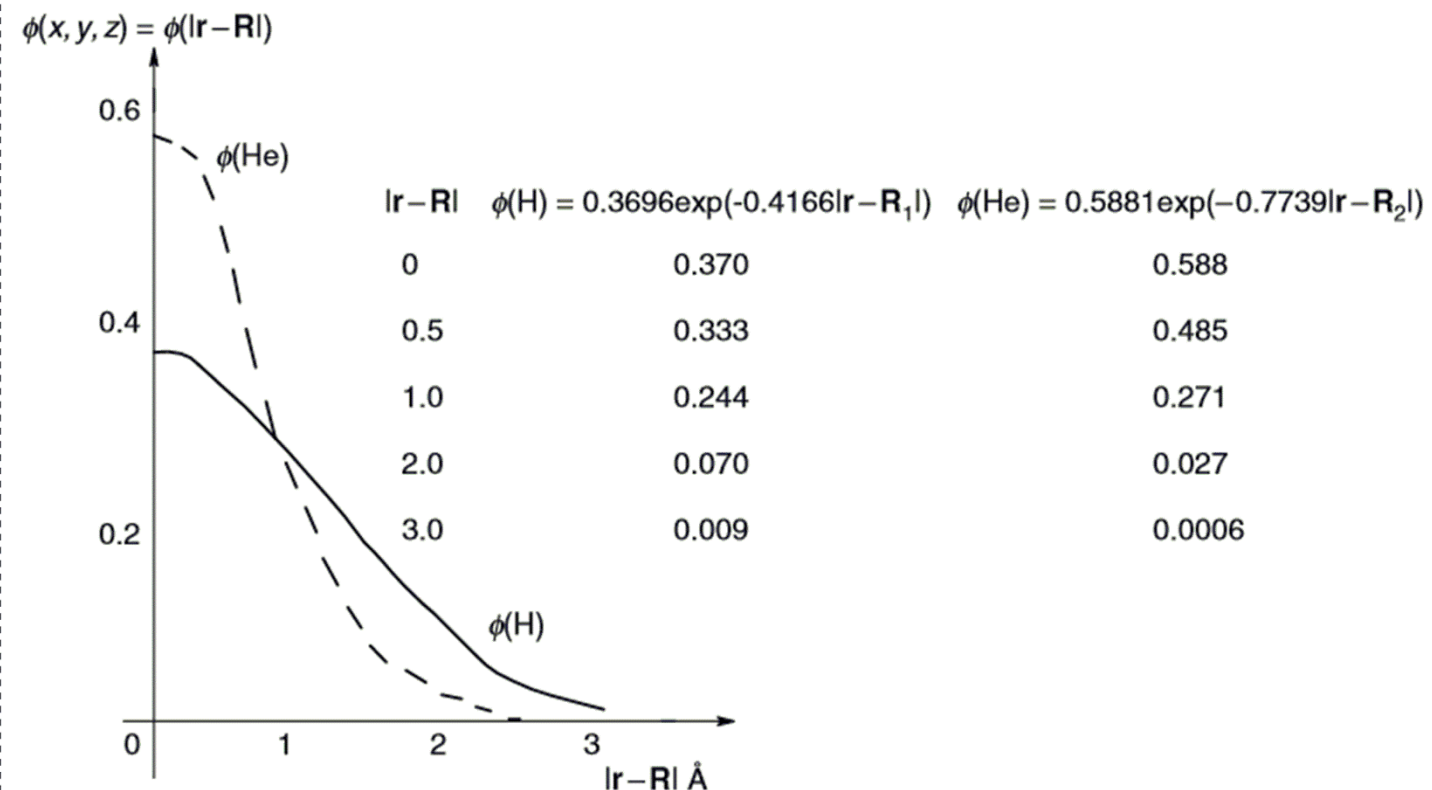
$$\phi(\text{H}) = \phi_1 = 0.3696 \exp(-0.4166|\mathbf{r} - \mathbf{R}_1|^2)$$

$$\phi(\text{He}) = \phi_2 = 0.5881 \exp(-0.7739|\mathbf{r} - \mathbf{R}_2|^2)$$

Coordinate System for Four Atoms



Slater vs Gaussian



Step 2. Calculate Integrals

$$F_{rs} = H_{rs}^{\text{core}}(1) + \sum_{t=1}^m \sum_{u=1}^m P_{tu} \left[(rs|tu) - \frac{1}{2} (ru|ts) \right]$$

$$= T_{rs} + V_{rs}(\text{H}) + V_{rs}(\text{He}) + G_{rs}$$

Kinetic Energy Terms

$$T_{rs}(1) = \int \phi_r \left(-\frac{1}{2} \nabla_1^2 \right) \phi_s dv$$

$$= \int \phi_r \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \right] \phi_s dv$$

Potential Energy Nuclear-Electron Attraction

$$V_{rs}(\text{H}, 1) = \int \phi_r \left(\frac{Z_{\text{H}}}{r_{\text{H}1}} \right) \phi_s dv \quad V_{rs}(\text{He}, 1) = \int \phi_r \left(\frac{Z_{\text{He}}}{r_{\text{He}1}} \right) \phi_s dv$$

T and **V** matrix elements

$$T_{11} = 0.6249 \quad T_{12} = T_{21} = 0.2395 \quad T_{22} = 1.1609$$

$$V_{11}(\text{H}) = -1.0300 \quad V_{12}(\text{H}) = V_{21}(\text{H}) = -0.4445 \quad V_{22}(\text{H}) = -0.6563$$

$$V_{11}(\text{He}) = -1.2555 \quad V_{12}(\text{He}) = V_{21}(\text{He}) = -1.1110 \quad V_{22}(\text{He}) = -2.8076$$

Two-electron Contributions

$$G_{rs} = \sum_{t=1}^m \sum_{u=1}^m P_{tu} \left[(rs|ts) - \frac{1}{2} (ru|ts) \right]$$

We need G_{11} , $G_{12}=G_{21}$, G_{22}

$$G_{11} = \sum_{t=1}^2 \sum_{u=1}^2 P_{tu} \left[(11|tu) - \frac{1}{2} (1u|t1) \right]$$

$$\begin{aligned} G_{11} &= \sum_{t=1}^2 \left[P_{t1} \left[(11|t1) - \frac{1}{2} (11|t1) \right] + P_{t2} \left[(11|t2) - \frac{1}{2} (12|t1) \right] \right] \\ &= P_{11} \left[(11|11) - \frac{1}{2} (11|11) \right] + P_{12} \left[(11|12) - \frac{1}{2} (12|11) \right] \\ &\quad + P_{21} \left[(11|21) - \frac{1}{2} (11|21) \right] + P_{22} \left[(11|22) - \frac{1}{2} (12|21) \right] \end{aligned}$$

$$G_{12} = G_{21} = \sum_{t=1}^2 \sum_{u=1}^2 P_{tu} \left[(12|tu) - \frac{1}{2} (1u|t2) \right]$$

$$\begin{aligned} G_{12} = G_{21} &= \sum_{t=1}^2 \left[P_{t1} \left[(12|t1) - \frac{1}{2} (11|t2) \right] + P_{t2} \left[(12|t2) - \frac{1}{2} (12|t2) \right] \right] \\ &= P_{11} \left[(12|11) - \frac{1}{2} (11|12) \right] + P_{12} \left[(12|12) - \frac{1}{2} (12|12) \right] \\ &\quad + P_{21} \left[(12|21) - \frac{1}{2} (11|22) \right] + P_{22} \left[(12|22) - \frac{1}{2} (12|22) \right] \end{aligned}$$

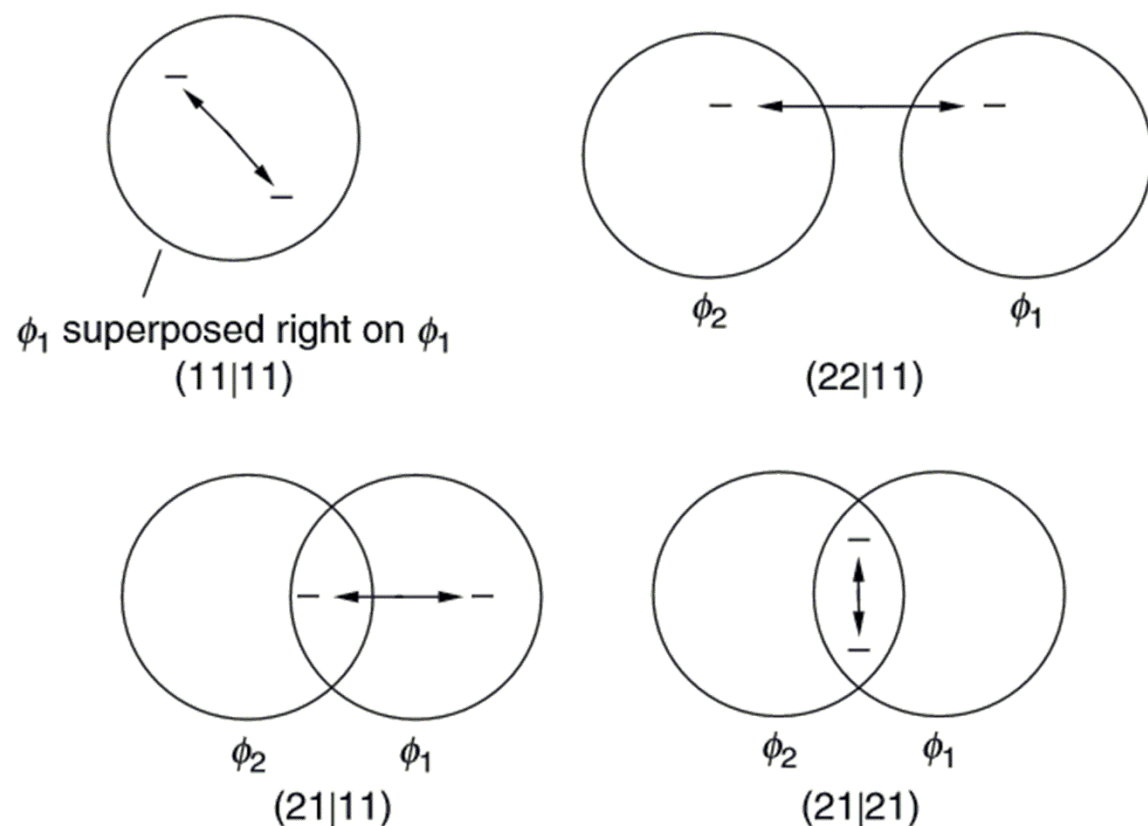
$$G_{22} = \sum_{t=1}^2 \sum_{u=1}^2 P_{tu} \left[(22|tu) - \frac{1}{2} (2u|t2) \right]$$

$$\begin{aligned} G_{22} &= \sum_{t=1}^2 \left[P_{t1} \left[(22|t1) - \frac{1}{2} (21|t2) \right] + P_{t2} \left[(22|t2) - \frac{1}{2} (22|t2) \right] \right] \\ &= P_{11} \left[(22|11) - \frac{1}{2} (21|12) \right] + P_{12} \left[(22|12) - \frac{1}{2} (22|12) \right] \\ &\quad + P_{21} \left[(22|21) - \frac{1}{2} (21|22) \right] + P_{22} \left[(22|22) - \frac{1}{2} (22|22) \right] \end{aligned}$$

Two-electron Integrals

$$\begin{aligned} (11|11) &= 0.7283 & (21|21) &= 0.2192 \\ (21|11) &= 0.3418 & (22|21) &= 0.4368 \\ (22|11) &= 0.5850 & (22|22) &= 0.9927 \end{aligned}$$

Repulsion Integrals Visually



Overlap Integrals

$$S_{11} = 1.0000 \quad S_{12} = S_{21} = 0.5017 \quad S_{22} = 1.0000$$

$$\mathbf{S} = \begin{pmatrix} 1.0000 & 0.5017 \\ 0.5017 & 1.0000 \end{pmatrix}$$

Step 3. Calculate orthogonalizing matrix $\mathbf{S}^{-1/2}$

$$\mathbf{S} = \begin{pmatrix} 0.7071 & 0.7071 \\ 0.7071 & -0.7071 \end{pmatrix} \begin{pmatrix} 1.5017 & 0.0000 \\ 0.0000 & 0.4983 \end{pmatrix} \begin{pmatrix} 0.7071 & 0.7071 \\ 0.7071 & -0.7071 \end{pmatrix}$$

$\mathbf{P} \qquad \qquad \mathbf{D} \qquad \qquad \mathbf{P}^{-1}$

$$\mathbf{D}^{-1/2} = \begin{pmatrix} 1.5017^{-1/2} & 0.0000 \\ 0.0000 & 0.4983^{-1/2} \end{pmatrix} = \begin{pmatrix} 0.8160 & 0.0000 \\ 0.0000 & 1.4166 \end{pmatrix}$$

$$\mathbf{S}^{-1/2} = \mathbf{PD}^{-1/2}\mathbf{P}^{-1} = \begin{pmatrix} 1.1163 & -0.3003 \\ -0.3003 & 1.1163 \end{pmatrix}$$

Step 4. Calculate Fock Matrix

$$\mathbf{F} = \mathbf{T} + \mathbf{V}(\text{H}) + \mathbf{V}(\text{He}) + \mathbf{G} = \mathbf{H}^{\text{core}} + \mathbf{G}$$

Calculate one-electron matrices $\mathbf{T}$ and $\mathbf{V}$

$$\mathbf{T} = \begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix} = \begin{pmatrix} 0.6249 & 0.2395 \\ 0.2395 & 1.1609 \end{pmatrix}$$

$$\mathbf{V}(\text{H}) = \begin{pmatrix} V_{11}(\text{H}) & V_{12}(\text{H}) \\ V_{21}(\text{H}) & V_{22}(\text{H}) \end{pmatrix} = \begin{pmatrix} -1.0300 & -0.4445 \\ -0.4445 & -0.6563 \end{pmatrix}$$

$$\mathbf{V}(\text{He}) = \begin{pmatrix} V_{11}(\text{He}) & V_{12}(\text{He}) \\ V_{21}(\text{He}) & V_{22}(\text{He}) \end{pmatrix} = \begin{pmatrix} -1.2555 & -1.1110 \\ -1.1110 & -2.8076 \end{pmatrix}$$

$$\mathbf{H}^{\text{core}} = \mathbf{T} + \mathbf{V}(\text{H}) + \mathbf{V}(\text{He}) = \begin{pmatrix} -1.6606 & -1.3160 \\ -1.3160 & -2.3030 \end{pmatrix}$$

Calculate two-electron matrix $\mathbf{G}$

Density Matrix

$$P_{tu} = 2 \sum_{j=1}^n c_{tj}^* c_{uj} \quad t = 1, 2, \dots, m \quad \text{and} \quad u = 1, 2, \dots, m$$

Initial c's are obtained from EHT

$$c_{11} = 0.249, \quad c_{21} = 0.867$$

$$P_{11} = 2c_{11}c_{11} = 2(0.249)0.249 = 0.1240$$

$$P_{12} = 2c_{11}c_{21} = 2(0.249)0.867 = 0.4318$$

$$P_{22} = 2c_{21}c_{21} = 2(0.867)0.867 = 1.5034$$

Proceed to calculate $\mathbf{G}$

$$G_{11} = P_{11} \left[(11|11) - \frac{1}{2} (11|11) \right] + P_{12} \left[(11|12) - \frac{1}{2} (12|11) \right] \\ + P_{21} \left[(11|21) - \frac{1}{2} (11|21) \right] + P_{22} \left[(11|22) - \frac{1}{2} (12|21) \right] \\ = 0.1240(0.3642) + 0.4318(0.1709) \\ + 0.4318(0.1709) + 1.5034(0.4754) = 0.9075$$

$$G_{12} = G_{21} = P_{11} \left[(12|11) - \frac{1}{2} (11|12) \right] + P_{12} \left[(12|12) - \frac{1}{2} (12|12) \right] \\ + P_{21} \left[(12|21) - \frac{1}{2} (11|22) \right] + P_{22} \left[(12|22) - \frac{1}{2} (12|22) \right] \\ = 0.1240(0.1709) + 0.4318(0.1096) \\ + 0.4318(-0.0733) + 1.5034(0.2184) = 0.3652$$

$$G_{22} = P_{11} \left[(22|11) - \frac{1}{2} (21|12) \right] + P_{12} \left[(22|12) - \frac{1}{2} (22|12) \right] \\ + P_{21} \left[(22|21) - \frac{1}{2} (21|22) \right] + P_{22} \left[(22|22) - \frac{1}{2} (22|22) \right] \\ = 0.1240(0.4754) + 0.4318(0.2184)$$

Initial $\mathbf{G}$ matrix

$$\mathbf{G}_0 = \begin{pmatrix} 0.9075 & 0.3652 \\ 0.3652 & 0.9938 \end{pmatrix}$$

Initial Fock matrix

$$\mathbf{F}_0 = \mathbf{T} + \mathbf{V}(\text{H}) + \mathbf{V}(\text{He}) + \mathbf{G}_0 = \mathbf{H}^{\text{core}} + \mathbf{G}_0 \\ = \begin{pmatrix} -1.6606 & -1.3160 \\ -1.3160 & -2.3030 \end{pmatrix} + \begin{pmatrix} 0.9095 & 0.3652 \\ 0.3652 & 0.9938 \end{pmatrix} = \begin{pmatrix} -0.7511 & -0.9508 \\ -0.9508 & -1.3092 \end{pmatrix}$$

Step 5. Transform $\mathbf{F}$ to $\mathbf{F}'$

$$\mathbf{F}'_0 = \begin{pmatrix} 1.1163 & -0.3003 \\ -0.3003 & 1.1163 \end{pmatrix} \begin{pmatrix} -0.7511 & -0.9508 \\ -0.9508 & -1.3092 \end{pmatrix} \begin{pmatrix} 1.1163 & -0.3003 \\ -0.3003 & 1.1163 \end{pmatrix} \\ \mathbf{S}^{-1/2} \qquad \qquad \mathbf{F}_0 \qquad \qquad \mathbf{S}^{-1/2} \\ = \begin{pmatrix} -0.4166 & -0.5799 \\ -0.5799 & -1.0617 \end{pmatrix} \\ \mathbf{F}'_0$$

Step 6. Diagonalize $\mathbf{F}'$ to get ε 's

$$\mathbf{F}'_0 = \begin{pmatrix} 0.5069 & 0.8620 \\ 0.8620 & -0.5069 \end{pmatrix} \begin{pmatrix} -1.4027 & 0.0000 \\ -0.0000 & -0.0756 \end{pmatrix} \begin{pmatrix} 0.5069 & 0.8620 \\ 0.8620 & -0.5069 \end{pmatrix} \\ \mathbf{C}'_1 \qquad \qquad \mathbf{\varepsilon}_1 \qquad \qquad \mathbf{C}'_1{}^{-1}$$

MO's in orthonormal basis

$$\mathbf{v}'_1 = \begin{pmatrix} 0.5069 \\ 0.8620 \end{pmatrix} \quad \text{and} \quad \mathbf{v}'_2 = \begin{pmatrix} 0.8620 \\ -0.5069 \end{pmatrix}$$

$$\psi_1 = 0.5069\phi'_1 + 0.8620\phi'_2 \quad \text{and} \quad \psi_2 = 0.8620\phi'_1 - 0.5069\phi'_2$$

Step 7. Transform $\mathbf{C}'$ to $\mathbf{C}$

Coefficients

$$\mathbf{C}_1 = \begin{pmatrix} 1.1163 & -0.3003 \\ -0.3003 & 1.1163 \end{pmatrix} \begin{pmatrix} 0.5069 & 0.8620 \\ 0.8620 & -0.5069 \end{pmatrix} = \begin{pmatrix} 0.3070 & 1.1145 \\ 0.8100 & -0.8247 \end{pmatrix}$$

$\mathbf{S}^{-1/2} \qquad \mathbf{C}'_1 \qquad \mathbf{C}_1$

MO energies

$$\varepsilon_1 = -1.4027 \quad \text{and} \quad \varepsilon_2 = -0.0756$$

MO's in original basis

$$\psi_1 = 0.3070\phi_1 + 0.8100\phi_2 \quad \text{and} \quad \psi_2 = 1.1145\phi_1 - 0.8247\phi_2$$

Step 8. Comparing Density Matrix with prior Density matrix

New density matrix

$$P_{11} = 2c_{11}c_{11} = 2(0.3070)0.3070 = 0.1885$$

$$P_{12} = 2c_{11}c_{21} = 2(0.3070)0.8100 = 0.4973$$

$$P_{22} = 2c_{21}c_{21} = 2(0.8100)0.8100 = 1.3122$$

Difference between old $\mathbf{P}$ and new $\mathbf{P}$

$$|(1.312 - 1.503)/1.503| = 0.127$$

Our convergence criteria is for the largest difference to be < 0.001 .

Another SCF cycle is needed due to lack of convergence.

Step 9. Starting next SCF cycle

one-electron and two-electron integrals do not need to be recalculated

New $\mathbf{G}$ matrix from new $\mathbf{P}$

$$\begin{aligned} G_{11} &= P_{11} \left[(11|11) - \frac{1}{2}(11|11) \right] + P_{12} \left[(11|12) - \frac{1}{2}(12|11) \right] \\ &\quad + P_{21} \left[(11|21) - \frac{1}{2}(11|21) \right] + P_{22} \left[(11|22) - \frac{1}{2}(12|21) \right] \\ &= 0.1885(0.3642) + 0.4973(0.1709) \\ &\quad + 0.4973(0.1709) + 1.3122(0.4754) = 0.8624 \end{aligned}$$

$$\begin{aligned} G_{12} = G_{21} &= P_{11} \left[(12|11) - \frac{1}{2}(11|12) \right] + P_{12} \left[(12|12) - \frac{1}{2}(12|12) \right] \\ &\quad + P_{21} \left[(12|21) - \frac{1}{2}(11|22) \right] + P_{22} \left[(12|22) - \frac{1}{2}(12|22) \right] \\ &= 0.1885(0.1709) + 0.4973(0.1096) \\ &\quad + 0.4973(-0.0733) + 1.3122(0.2184) = 0.3369 \end{aligned}$$

$$\begin{aligned} G_{22} &= P_{11} \left[(22|11) - \frac{1}{2}(21|12) \right] + P_{12} \left[(22|12) - \frac{1}{2}(22|12) \right] \\ &\quad + P_{21} \left[(22|21) - \frac{1}{2}(21|22) \right] + P_{22} \left[(22|22) - \frac{1}{2}(22|22) \right] \\ &= 0.1885(0.4754) + 0.4973(0.2184) \\ &\quad + 0.4973(0.2184) + 1.3122(0.4964) = 0.9582 \end{aligned}$$

$$\mathbf{G}_1 = \begin{pmatrix} 0.8624 & 0.3369 \\ 0.3369 & 0.9582 \end{pmatrix}$$

New Fock matrix

$$\mathbf{F}_1 = \mathbf{H}^{\text{core}} + \mathbf{G}_1 = \begin{pmatrix} -1.6606 & -1.3160 \\ -1.3160 & -2.3030 \end{pmatrix} + \begin{pmatrix} 0.8624 & 0.3369 \\ 0.3369 & 0.9582 \end{pmatrix}$$
$$= \begin{pmatrix} -0.7982 & -0.9791 \\ -0.9791 & -1.3448 \end{pmatrix}$$

Step 10. Transform **F** to **F'**

$$\mathbf{F}'_1 = \begin{pmatrix} 1.1163 & -0.3003 \\ -0.3003 & 1.1163 \end{pmatrix} \begin{pmatrix} -0.7982 & -0.9791 \\ -0.9791 & -1.3448 \end{pmatrix} \begin{pmatrix} 1.1163 & -0.3003 \\ -0.3003 & 1.1163 \end{pmatrix}$$

$\mathbf{S}^{-1/2} \qquad \qquad \mathbf{F}_1 \qquad \qquad \mathbf{S}^{-1/2}$

$$= \begin{pmatrix} -0.4595 & -0.5900 \\ -0.5900 & -1.0913 \end{pmatrix}$$

$\mathbf{F}'_1$

Step 11. Diagonalize **F'**

$$\mathbf{F}'_1 = \begin{pmatrix} 0.5138 & 0.8579 \\ 0.8579 & -0.5138 \end{pmatrix} \begin{pmatrix} -1.4447 & 0.0000 \\ 0.0000 & -0.1062 \end{pmatrix} \begin{pmatrix} 0.5138 & 0.8579 \\ 0.8579 & -0.5138 \end{pmatrix}$$

$\mathbf{C}'_2 \qquad \qquad \boldsymbol{\epsilon}_2 \qquad \qquad \mathbf{C}'_2{}^{-1}$

Step 12. Transform **C'** to **C**

$$\mathbf{C}_2 = \begin{pmatrix} 1.1163 & -0.3003 \\ -0.3003 & 1.1163 \end{pmatrix} \begin{pmatrix} 0.5138 & 0.8579 \\ 0.8579 & -0.5138 \end{pmatrix} = \begin{pmatrix} 0.3159 & 1.1120 \\ 0.8034 & -0.8319 \end{pmatrix}$$

$\mathbf{S}^{-1/2} \qquad \qquad \mathbf{C}'_2 \qquad \qquad \mathbf{C}_2$

New MO energies and coefficients

$\epsilon_1 = -1.4447 \quad \text{and} \quad \epsilon_2 = -0.1062$

$\psi_1 = 0.3159\phi_1 + 0.8034\phi_2 \quad \text{and} \quad \psi_2 = 1.1120\phi_1 - 0.8319\phi_2$

Step 13. Compare new Density matrix to prior Density Matrix

New Density matrix

$$P_{11} = 2c_{11}c_{11} = 2(0.3159)0.3159 = 0.1996$$
$$P_{12} = 2c_{11}c_{21} = 2(0.3159)0.8034 = 0.5076$$
$$P_{22} = 2c_{21}c_{21} = 2(0.8034)0.8034 = 1.2909$$

Take the difference.

$$(0.1996 - 0.1885)/0.1885 = 0.059$$

$0.059 > 0.001$

Need a few more cycles, but we're getting closer

Three more cycles reaches convergence

$$E_{\text{HF}} = \sum_{i=1}^n \epsilon_i + \frac{1}{2} \sum_{r=1}^m \sum_{s=1}^m P_{rs} H_{rs}^{\text{core}} \qquad V_{NN} = \sum_{\text{all } \mu, \nu} \frac{Z_{\mu} Z_{\nu}}{r_{\mu \nu}}$$

SCF Summary

	Initial guess (zeroth cycle)	First cycle	Second cycle	Third cycle	Fourth cycle	Fifth cycle
$\epsilon_1, \epsilon_2,$	–	–1.4027, –0.0756	–1.4447, –0.1062	–1.4466, –0.1054	–1.4473, –0.1056	–1.4470, –0.1051
c_{11}, c_{21}	0.249, 0.867	0.3070, 0.8100	0.3159, 0.8034	0.3175, 0.8022	0.3177, 0.8021	0.3178, 0.8020
c_{12}, c_{22}	–	1.1145, –0.8247	1.1120, –0.8319	1.1115, –0.8323	1.1115, –0.8325	1.1114, –0.8325
P_{11}	0.1240	0.1885	0.1996	0.2010	0.2019	0.2020
P_{12}	0.4318	0.4973	0.5076	0.5094	0.5097	0.5097
P_{22}	1.5034	1.3122	1.2909	1.2870	1.2867	1.2864
$E_{\text{HF}}^{\text{total}}$	–	–2.3992	–2.4419	–2.4428	–2.4443	–2.4438

Total Energy Calculation

$$E_{\text{HF}}^{\text{total}} = E_{\text{HF}} + V_{\text{NN}} = \sum_{i=1}^n \varepsilon_i + \frac{1}{2} \sum_{r=1}^m \sum_{s=1}^m P_{rs} H_{rs}^{\text{core}} + V_{\text{NN}}$$

$$\begin{aligned} E_{\text{HF}} &= \varepsilon_1 + \frac{1}{2} \sum_{r=1}^2 \sum_{s=1}^2 P_{rs} H_{rs}^{\text{core}} \\ &= \varepsilon_1 + \frac{1}{2} \sum_{r=1}^2 [P_{r1} H_{r1}^{\text{core}} + P_{r2} H_{r2}^{\text{core}}] \\ &= \varepsilon_1 + \frac{1}{2} [P_{11} H_{11}^{\text{core}} + P_{12} H_{12}^{\text{core}} + P_{21} H_{21}^{\text{core}} + P_{22} H_{22}^{\text{core}}] \\ &= -1.4027 \text{ h} + \frac{1}{2} [0.1885(-1.6606) + 0.4973(-1.3160) \\ &\quad + 0.4973(-1.3160) + 1.3122(-2.3030)] \text{ h} \\ &= -3.7222 \text{ h} \end{aligned}$$

Internuclear repulsion term is added at the end of the SCF calculation.

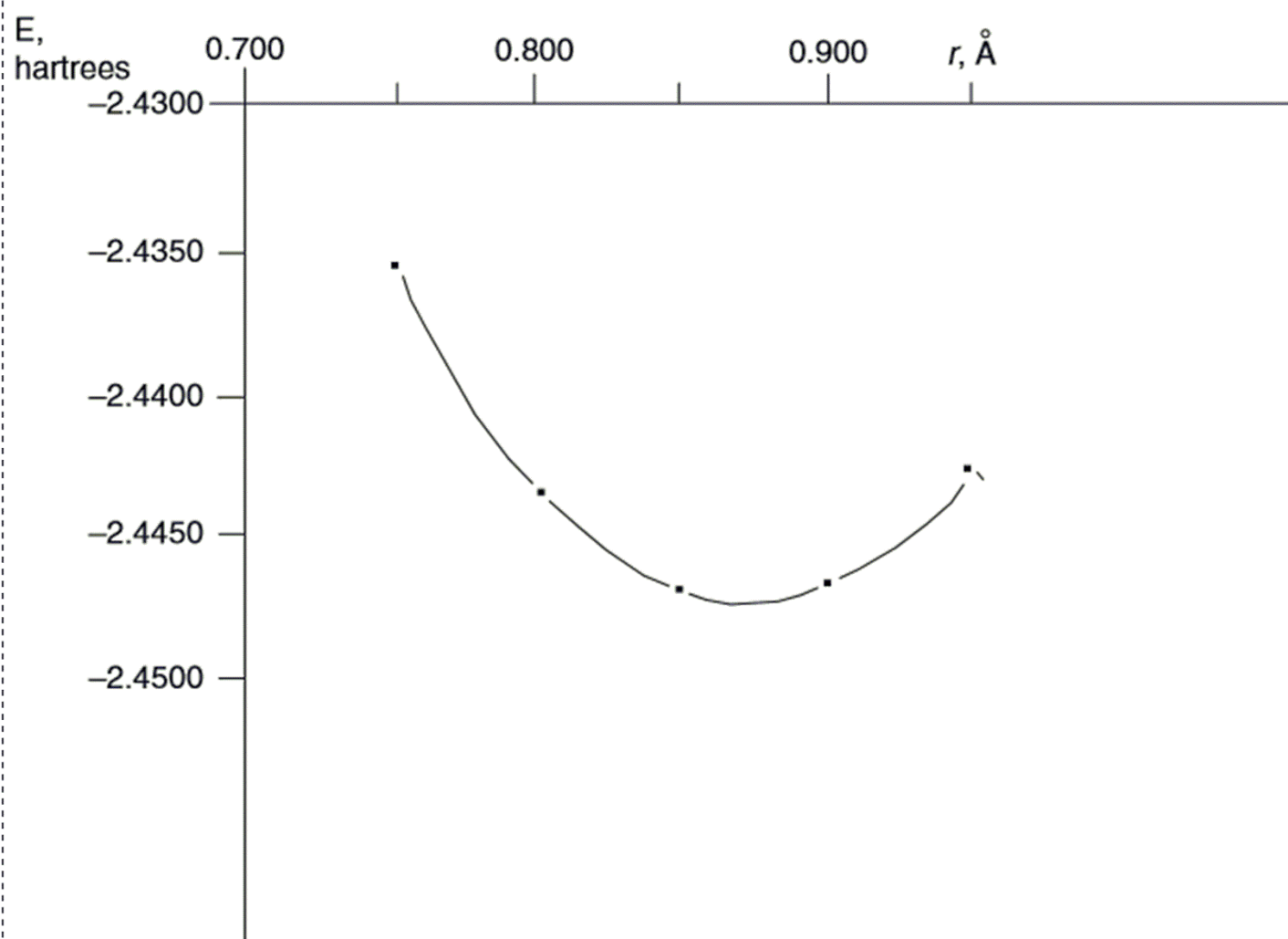
$$\begin{aligned} V_{\text{NN}} &= \frac{Z_{\text{H}} Z_{\text{He}}}{r_{\text{HHe}}} \\ &= \frac{1(2)}{1.5117} \text{ h} = 1.3230 \text{ h} \end{aligned}$$

$$E_{\text{HF}}^{\text{total}} = E_{\text{HF}} + V_{\text{NN}} = -3.7222 \text{ h} + 1.3230 \text{ h} = -2.3992 \text{ h}$$

Consider how much higher is the energy calculated from only the occupied MO.

$$E = 2\varepsilon_1 = 2(-1.4027) = -2.894$$

Geometry Optimization. What is the HF predicted optimal He⁻H⁺ bond length?



Optimal bond length is 0.86 Å

H-F SCF Procedure Review

1. Specify geometry, basis set, and orbital occupancy.
2. Calculate all integrals; T_{rs} , V_{rs} , $(rs|tu)$, S_{rs}
3. Calculate orthogonalizing matrix $\mathbf{S}^{-1/2}$; T_{rs} , V_{rs} , $(rs|tu)$, S_{rs}
 - $\mathbf{S} = \mathbf{PDP}^{-1}$
 - $\mathbf{D}^{-1/2}$ from inverse square root of the diagonal elements
 - $\mathbf{S}^{-1/2} = \mathbf{PD}^{-1/2}\mathbf{P}^{-1}$
4. Calculate the Fock matrix $\mathbf{F}$
 - $\mathbf{H}^{\text{core}} = \mathbf{T} + \mathbf{V}_1 + \mathbf{V}_2 + \dots$
 - Calculate two-electron matrix $\mathbf{G}$ using density matrix determined initially from guess coefficients
 - $\mathbf{F} = \mathbf{H}^{\text{core}} + \mathbf{G}$
5. Transform $\mathbf{F}$ to $\mathbf{F}'$
 - $\mathbf{F}' = \mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2}$
6. Diagonalize $\mathbf{F}'$ to get MO energies and $\mathbf{C}'$
 - $\mathbf{F}' = \mathbf{C}'\epsilon\mathbf{C}'^{-1}$
7. Transform $\mathbf{C}'$ to $\mathbf{C}$ to get coefficients in the original basis
 - $\mathbf{C} = \mathbf{S}^{-1/2}\mathbf{C}'$
8. Compare density matrix elements to those of the previous step to test convergence.

Mathematica Demonstration

Basis Sets

- Slater functions the natural choice for basis functions.
- Why Gaussian functions over Slater functions?
The two-electron integrals using Gaussian functions take much less time to compute than the integrals using Slater functions.
The product of two Gaussians is a Gaussian on a third center.

s-type Gaussians centered on atoms **A** and **B**

$$g_A = a_A e^{-\alpha_A |\mathbf{r} - \mathbf{r}_A|^2}, \quad g_B = a_B e^{-\alpha_B |\mathbf{r} - \mathbf{r}_B|^2}$$

$$|\mathbf{r} - \mathbf{r}_A|^2 = (x - x_A)^2 + (y - y_A)^2 + (z - z_A)^2$$

$$|\mathbf{r} - \mathbf{r}_B|^2 = (x - x_B)^2 + (y - y_B)^2 + (z - z_B)^2$$

Product of two Gaussians leads to a new Gaussian centered on **C**

$$g_A g_B = a_C e^{-\alpha_C |\mathbf{r} - \mathbf{r}_C|^2} = g_C$$

The three and four center two-electron integrals....

$$(rs|tu) = \int \int \frac{\phi_r^*(1)\phi_s(1)\phi_t^*(2)\phi_u(2)}{r_{12}} dv_1 dv_2$$

...simplify to two-center integrals

$$(v/w) = \int \int \frac{\phi_v(1)\phi_w(2)}{r_{12}} dv_1 dv_2$$

Unfortunately one Gaussian poorly describes a Slater function. How can this deficiency be addressed?

H-F SCF Procedure Review

1. Specify geometry, basis set, and orbital occupancy.
2. Calculate all integrals; T_{rs} , V_{rs} , $(rs|tu)$, S_{rs}
3. Calculate orthogonalizing matrix $\mathbf{S}^{-1/2}$; T_{rs} , V_{rs} , $(rs|tu)$, S_{rs}
 - $\mathbf{S} = \mathbf{PDP}^{-1}$
 - $\mathbf{D}^{-1/2}$ from inverse square root of the diagonal elements
 - $\mathbf{S}^{-1/2} = \mathbf{PD}^{-1/2}\mathbf{P}^{-1}$
4. Calculate the Fock matrix $\mathbf{F}$
 - $\mathbf{H}^{\text{core}} = \mathbf{T} + \mathbf{V}_1 + \mathbf{V}_2 + \dots$
 - Calculate two-electron matrix $\mathbf{G}$ using density matrix determined initially from guess coefficients
 - $\mathbf{F} = \mathbf{H}^{\text{core}} + \mathbf{G}$
5. Transform $\mathbf{F}$ to $\mathbf{F}'$
 - $\mathbf{F}' = \mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2}$
6. Diagonalize $\mathbf{F}'$ to get MO energies and $\mathbf{C}'$
 - $\mathbf{F}' = \mathbf{C}'\epsilon\mathbf{C}'^{-1}$
7. Transform $\mathbf{C}'$ to $\mathbf{C}$ to get coefficients in the original basis
 - $\mathbf{C} = \mathbf{S}^{-1/2}\mathbf{C}'$
8. Compare density matrix elements to those of the previous step to test convergence.

Mathematica Demonstration

Basis Sets

- Slater functions the natural choice for basis functions.
- Why Gaussian functions over Slater functions?
The two-electron integrals using Gaussian functions take much less time to compute than the integrals using Slater functions.
The product of two Gaussians is a Gaussian on a third center.

s-type Gaussians centered on atoms **A** and **B**

$$g_A = a_A e^{-\alpha_A |\mathbf{r} - \mathbf{r}_A|^2}, \quad g_B = a_B e^{-\alpha_B |\mathbf{r} - \mathbf{r}_B|^2}$$

$$|\mathbf{r} - \mathbf{r}_A|^2 = (x - x_A)^2 + (y - y_A)^2 + (z - z_A)^2$$

$$|\mathbf{r} - \mathbf{r}_B|^2 = (x - x_B)^2 + (y - y_B)^2 + (z - z_B)^2$$

Product of two Gaussians leads to a new Gaussian centered on **C**

$$g_A g_B = a_C e^{-\alpha_C |\mathbf{r} - \mathbf{r}_C|^2} = g_C$$

The three and four center two-electron integrals....

$$(rs|tu) = \int \int \frac{\phi_r^*(1)\phi_s(1)\phi_t^*(2)\phi_u(2)}{r_{12}} dv_1 dv_2$$

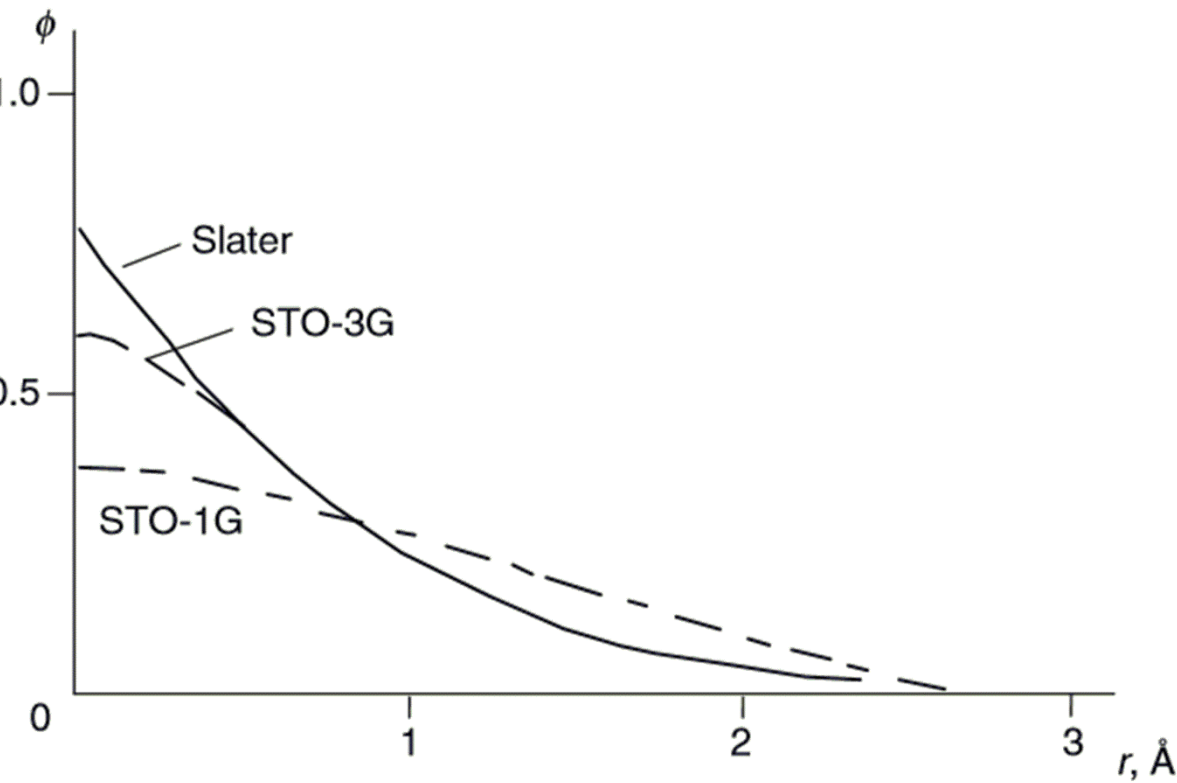
...simplify to two-center integrals

$$(v/w) = \int \int \frac{\phi_v(1)\phi_w(2)}{r_{12}} dv_1 dv_2$$

Unfortunately one Gaussian poorly describes a Slater function. How can this deficiency be addressed?

Use several Gaussians to approximate a Slater function

Slater and Gaussian distributions



$$\phi(\text{Slater}) = \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta r} = 0.7790 e^{-1.24r}$$

$$\phi(\text{STO-1G}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2} = 0.3696 e^{-0.4166r^2}$$

$$\phi(\text{STO-3G}) = 0.4446 \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2} + 0.5353 \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2} + 0.1543 \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$
$$= 0.0835 e^{-0.1689r^2} + 0.2678 e^{-0.6239r^2} + 0.2769 e^{-3.4253r^2}$$

- one primitive Gaussian function: STO-1G basis
- three primitive Gaussian functions: STO-3G basis
- a basis function contains a coefficient that is optimized in the SCF process
- a primitive Gaussian function contains a coefficient defined by the basis set that remains unchanged during the SCF process

For each basis function

$$\phi_r = d_{1r}g_{1r} + d_{2r}g_{2r} + d_{3r}g_{3r}$$

the two-electron integrals evaluate to

$$(rs|tu) = \int \int d_{1r}d_{1s}g_{1r1s} \frac{1}{r_{12}} d_{1t}d_{1u}g_{1t1u} dv_1 dv_2$$
$$+ \int \int d_{1r}d_{1s}g_{1r1s} \frac{1}{r_{12}} d_{1t}d_{2u}g_{1t2u} dv_1 dv_2 + \dots$$
$$+ \int \int d_{3r}d_{3s}g_{3r3s} \frac{1}{r_{12}} d_{3t}d_{3u}g_{3t3u} dv_1 dv_2$$

Consider H₂O as an example

- STO-3G basis set
- 1 basis function on each H
- 5 basis functions on O; 1s, 2s, 2p_x, 2p_y, 2p_z
- Fock matrix is 7x7 with 49 elements

$$G_{11} = \sum_{t=1}^7 \sum_{u=1}^7 P_{tu} \left[(11|tu) - \frac{1}{2} (1u|t1) \right]$$

Basis functions and number of integrals

		Basis functions		Two-electron integrals			
		STO-3G	3-21G(*)	From $m^4/8$	From G92 ^a	From $m^4/8$	From G92
HHe+	C _{∞v}	2	4	2	6	32	55
H ₂ O	C _{2v}	7	13	300	144	3,570	1,314
H ₂ O ₂	C _{2h}	12	22	2,592	738	29,282	7,713
H ₂ O ₂	C ₁ [*]	12	22	2,592	2,774	29,282	28,791
H ₂ O ₃	C _{2v}	17	31	10,440	3,421	115,440	31,475
H ₂ O ₃	C ₁	17	31	10,440	11,046	115,440	107,869

Types of Basis Sets

General Form of a GTO

$$\psi_{\zeta,l_x,l_y,l_z}^{CGTO}(x,y,z) = N \sum_{i=1}^n c_i x^{l_x} y^{l_y} z^{l_z} e^{-\zeta_i r^2}$$

STO-3G

- *minimal basis set* (each atomic orbital is assigned one basis function)

^1H 1s 1 function	^2He 1s 1 function	$^3\text{Li}-^{10}\text{Ne}$ 1s 5 functions	$^{11}\text{Na}-^{18}\text{Ar}$ 1s 9 functions	$^{19}\text{K}-^{20}\text{Ca}$ 1s 13 functions	$^{21}\text{Sc}-^{30}\text{Zn}$ 1s 18 functions
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- each basis function is constructed from a linear combination of three primitive GTOs with their corresponding contraction coefficients

$$\begin{aligned} \phi(2s) &= d_{1s}e^{-\alpha_{1s}r} + d_{2s}e^{-\alpha_{2s}r} + d_{3s}e^{-\alpha_{3s}r} \\ \phi(2p_x) &= d_{1p}xe^{-\alpha_{1p}r} + d_{2p}xe^{-\alpha_{2p}r} + d_{3p}xe^{-\alpha_{3p}r} \\ \phi(2p_y) &= d_{1p}ye^{-\alpha_{1p}r} + d_{2p}ye^{-\alpha_{2p}r} + d_{3p}ye^{-\alpha_{3p}r} \\ \phi(2p_z) &= d_{1p}ze^{-\alpha_{1p}r} + d_{2p}ze^{-\alpha_{2p}r} + d_{3p}ze^{-\alpha_{3p}r} \end{aligned}$$

Basis function format can be retrieved from <https://bse.pnl.gov/bse/portal>.

STO-3G (Hydrogen)

\$basis		
*		
h	STO-3G	
*		
	3 s	
	3.42525091	0.15432897
	0.62391373	0.53532814
	0.16885540	0.44463454
*		
	exponents	contraction coefficients

STO-3G (Carbon)

c	STO-3G	
*		
	3 s	
	71.6168370	0.15432897
	13.0450960	0.53532814
	3.5305122	0.44463454
	3 s	
	2.9412494	-0.09996723
	0.6834831	0.39951283
	0.2222899	0.70011547
	3 p	
	2.9412494	0.15591627
	0.6834831	0.60768372
	0.2222899	0.39195739

- The STO-3G basis set generally gives inaccurate geometries due to its poorer Slater function description than slightly larger basis sets (3-21G)
- Lacks *polarization functions*



6-31G, 6-31G*			
- split valence with and without polarization			
- valence shell has an inner with 3 Gaussians and an outer with 1 Gaussian			
- Core orbitals are desribed by 6 primitive Gaussians (H and He have 3 Gaussians)			
- For elements past He, a set of polarization functions with one greater orbital angular momentum are added.			
1H	3Li-10Ne	11Na-18Ar	
1s'	1s	1s	
1s''	2s' 2p' 2p' 2p'	2s 2p 2p 2p	
2 functions	2s'' 2p'' 2p'' 2p''	3s' 3p' 3p' 3p'	
	3d 3d 3d 3d 3d 3d	3s'' 3p'' 3p'' 3p''	
	15 functions	3d 3d 3d 3d 3d 3d	
		19 functions	
		h	6-31G**
		*	
		3 s	
		18.7311370	0.03349460
		2.8253937	0.23472695
		0.6401217	0.81375733
		1 s	
		0.1612778	1.00000000
		1 p	
		1.10000000	1.00000000
		c	6-31G*
		*	
		6 s	
		3047.5249000	0.0018347
		457.3695100	0.0140373
		103.9486900	0.0688426
		29.2101550	0.2321844
		9.2866630	0.4679413
		3.1639270	0.3623120
		3 s	
		7.8682724	-0.1193324
		1.8812885	-0.1608542
		0.5442493	1.1434564
		1 s	
		0.1687144	1.00000000
		3 p	
		7.8682724	0.0689991
		1.8812885	0.3164240
		0.5442493	0.7443083
		1 p	
		0.1687144	1.00000000
		1 p	
		0.0438000	1.00000000
		1 d	
		0.8000000	1.00000000

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Correlation-Consistent Basis Sets

- From STO-3G to 6-311++G(3df,3pd) are the Pople basis sets
- The Pople basis sets were optimized for H-F calculations
- Basis sets have been introduced that were optimized for methods beyond H-F that include electron correlation (correlation-consistent or "cc" basis sets)
- cc basis sets are designated as cc-pVXZ
 - p: polarization; V: valence; X: for number of split shells for the valence shell; Z: for zeta.

cc-pVDZ - cc polarized valence doubly-split zeta

cc-pVTZ - cc polarized valence triply-split zeta

cc-pVQZ - cc polarized valence quadruply-split zeta

cc-pV5Z - cc polarized valence five-fold-split zeta

- can be augmented with diffuse functions using "aug" (eg. aug-cc-pVTZ)

Example for H-C-H

cc-pVDZ $14 + 5 + 5 = 24$ functions

cc-pVTZ $30 + 14 + 14 = 58$ functions

cc-pVQZ $55 + 30 + 30 = 115$ functions

cc-pV5Z $91 + 55 + 55 = 201$ functions

Effective Core Potentials

- As we go down the periodic table, the number of core electrons increases and the resulting two-electron integrals increase dramatically.
- Since the core electrons do not engage in electronic reorganization to a significant extent, they can be treated in an average way how they interact with the valence electrons using a separately defined Hamiltonian (Fock operator). This Hamiltonian is called an effective core potential (ECP).
- ECP's can also be designed to account for relativistic effects that are particularly important with heavy metals

Choosing a Basis set

- a split valence double-zeta basis set (6-31G*, cc-pVDZ) are sufficient for exploratory work
- All non-hydrogen atoms should have at least one set of polarization functions (l+1)
- If an H-bond is being broken or formed then p-functions should be added to H's
- If a lone pair is involved in bonding and bond forming or breaking, then diffuse functions should be used.
- If there is a negative charge, then diffuse functions are usually required for accurate results

Example. Different results depending on basis set and theory level

