Overlap again:

ex. 1s 1p

$$S = \begin{array}{c} \\ s \\ p_x \\ p_y \\ p_z \end{array} \begin{array}{cccc} s & p_x & p_y & p_z \\ \hline 1 & \times & \times & \times \\ \times & 1 & & \\ \times & & 1 & \\ \times & & & 1 \end{array}$$

← normalization

1. step: build each of the primitive Gaussians w/ the normalization constant

← your code from hw 2

$\vec{r} = \{x, y, z\}$

H - 1s function

$$\omega_1 = N_1 (x-X)^0 (y-Y)^0 (z-Z)^0 \exp(-3.425 \cdot (\vec{r}-\vec{R})^2)$$

$$\omega_2 = N_2 (x-X)^0 (y-Y)^0 (z-Z)^0 \exp(-0.6239 \cdot (\vec{r}-\vec{R})^2)$$

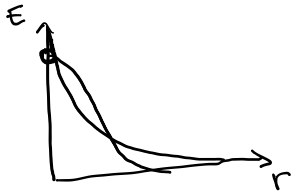
$$\omega_3 = N_3 (x-X)^0 (y-Y)^0 (z-Z)^0 \exp(-0.1688 \cdot (\vec{r}-\vec{R})^2)$$

2. step get N_1, N_2, N_3

$$S = 1 = \int_x \int_y \int_z \omega_1 \omega_1 \, d\vec{r} = \underbrace{N_1 \cdot N_1}_{N_1^2} \cdot \underbrace{\iiint \omega_1 \omega_1 \, d\vec{r}}_{\text{from hw 2}}$$

ex. s-s ≈ 1.9

$$N_1 = \frac{1}{\sqrt{S_{\omega_1 \omega_1}}}$$



now know primitives!

$$S^{HH} = S^{ss}$$

$$S = \begin{array}{c} \\ S_{H1} \\ S_{H2} \end{array} \begin{array}{cc} S_{H1} & S_{H2} \\ \hline 1 & S_{12} \\ S_{21} & 1 \end{array} \qquad S_{12} = S_{21} = \sum_k^3 \sum_l^3 d_{k S_{H1}} d_{l S_{H2}} N_{k S_{H1}} N_{l H2} S^{\omega_k \omega_l}$$

ex. 1st sum $k=1, l=1 \to 0.1543 \cdot 0.1543 \cdot N_1 \cdot N_1 \cdot S^{\omega_1 \omega_1}$

2nd sum $k=1, l=2 \to 0.1543 \cdot 0.5353 \cdot N_1 \cdot N_2 \cdot S^{\omega_1 \omega_2}$

3rd sum $k=1, l=3 \to 0.1543 \cdot 0.4446 \cdot N_1 \cdot N_3 \cdot S^{\omega_1 \omega_3}$

$k=2, l=1$

$k=2, l=2$

⋮

Final S in AO basis $S = \begin{bmatrix} 1 & 0.6599 \\ 0.6599 & 1 \end{bmatrix}$ ← I'll send this

Build Hamiltonian $H = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} = \begin{bmatrix} -13.6 & -15.705 \\ -15.705 & -13.6 \end{bmatrix}$

0.6599

$$H_{12} = H_{21} = \frac{1}{2} \cdot 1.75 (-13.6 - 13.6) \cdot S^{H_{1s} H_{2s}}$$

$$= -15.705 \quad \leftarrow \text{unit is eV}$$

we look for

$Hc = Sc\epsilon$ → standard eigenvalue problem $Hc = c\epsilon$

→ orthogonalize → $S = \underline{\mathbb{1}}$

symmetric orthogonalization (could canonical)

1. diagonalize Overlap matrix → eigenvalues, eigenvectors

s vector $\qquad$ U matrix

$s^{-1/2} = \begin{pmatrix} s_1^{-1/2} & 0 \\ 0 & s_2^{-1/2} \end{pmatrix}$ s_1, s_2 are eigenvalues

transformation matrix $X = U s^{-1/2} U^T$

check if your X is correct

→ transform Hamiltonian $H' = X^T H X$, and $X^{+} S X = \mathbb{1}$

→ $H' c' = c' \varepsilon$

in orthonormal basis

solve $H' c' = c' \varepsilon$

c' matrix → coeff. → transform back to AO $C = X c'$

coeff to build MO

ε vector → list of energies of molecular orbitas

$$\varepsilon = \begin{bmatrix} -17.65 \\ 6.19 \end{bmatrix} \qquad E = \sum_{i=1}^{occ} 2 \cdot \varepsilon_i = 2 \cdot (-17.65\ eV)$$

$$= -35.3\ eV$$