

Overlap again

e.g. 1s, 1p

$$S = \begin{bmatrix} S & p_x & p_y & p_z \\ p_x & \times & 1 & \times \\ p_y & \times & 1 & \times \\ p_z & \times & \times & 1 \end{bmatrix}$$

calculated in part 2.

Also didn't count normalization constant.

Normalization.

$\rightarrow Hc = SCE$

Each shell is a contracted / primitive Gaussian.

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

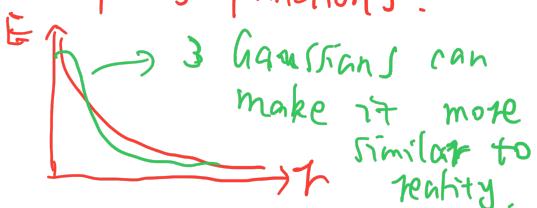
$$\vec{r} = \begin{bmatrix} x, y, z \end{bmatrix}$$

$$w_1 = N_1 (x-X)^0 (y-Y)^0 (z-Z)^0 \exp\left[-3.425 * (\vec{r} - \vec{R})^2\right]$$

$$w_2 = N_2 (x-X)^0 (y-Y)^0 (z-Z)^0 \exp\left[-0.6479 * (\vec{r} - \vec{R})^2\right]$$

$$w_3 = N_3 (x-X)^0 (y-Y)^0 (z-Z)^0 \exp\left[-0.16885 * (\vec{r} - \vec{R})^2\right]$$

Manually set to make it comprised of 3 functions.



Step 2: get N_1, N_2, N_3 .

$$S = 1 = \int_x \int_y \int_z w_1 w_2 d\vec{r} = \underbrace{N_1 * N_2}_{N_1^2} * \underbrace{\iiint w_1 w_2 d\vec{r}}_{\text{from HW 2.}}$$

$$\text{e.g. } S-S \approx 1.9$$

$$N_1 = \frac{1}{\sqrt{S_{w_1 w_2}}}$$

Now know primitives!

$$S = \begin{bmatrix} S_{H1} & S_{H12} \\ S_{H21} & S_{H2} \end{bmatrix}$$

$$S^{HH} = S^{SS}$$

$$S_{12} = S_{21} = \sum_k^3 \sum_l^3 d_{k \cdot SH_1} d_{l \cdot SH_2} N_{k \cdot SH_1} N_{l \cdot SH_2} S^{w_k w_l}$$

E.g. 1st sum $k=1, l=1 \Rightarrow 0.1543 \cdot 0.1543 \cdot N_1 \cdot N_1 \cdot S^{w_1 w_1}$

2nd sum $k=1, l=2 \Rightarrow 0.1543 \cdot 0.5353 \cdot N_1 \cdot N_1 \cdot S^{w_1 w_2}$

3rd sum $k=1, l=3 \Rightarrow 0.1543 \cdot 0.4446 \cdot N_1 \cdot N_2 \cdot S^{w_1 w_3}$

$k=2, l=1 \Rightarrow 0.5353 \cdot 0.1543 \cdot N_2 \cdot N_1 \cdot S^{w_2 w_1}$

$k=2, l=2$

$k=2, l=3$

$k=3, l=1$

$k=3, l=2$

$k=3, l=3,$

Final S in AO basis $S = \begin{bmatrix} 1 & 0.6599 \\ 0.6599 & 1 \end{bmatrix}$

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

$$H_{12} = H_{21} = \frac{1}{2} * 1.75 * (-13.6 - 13.6) * S \underbrace{\frac{H_{11} + H_{22}}{2}}_{0.6599}$$

$$= -15.705 \text{ eV}$$

We look for

$$H \underset{\uparrow}{C} = S \underset{\uparrow}{C} \underset{\uparrow}{E} \rightarrow \text{standard eigenvalue problem}$$

$$\rightarrow \text{orthogonalize} \rightarrow S = \mathbf{1}$$

Symmetric orthogonalization (could canonical)

1. diagonalize overlap matrix \rightarrow eigenvalues, eigenvectors

S vector U matrix

$$S^{-\frac{1}{2}} = \begin{bmatrix} S_1^{-\frac{1}{2}} & 0 \\ 0 & S_2^{-\frac{1}{2}} \end{bmatrix} \quad S_1, S_2 \text{ are eigenvalues}$$

Transformation matrix $X = US^{-\frac{1}{2}}U^\top$ check if your X

↪ transform Hamiltonian to orthonormal basis ↑ is correct.

$$H' = X^\top H X, \text{ and } \boxed{X^\top S X = \mathbb{I}}$$

$$\hookrightarrow H' C' = C' E$$

↪ in orthonormal basis

$$\text{Solve } H' C' = C' E$$

coeff matrix to build MO.

C' matrix → coeff. → transform back to AO, $C = XC'$

ϵ vector → list of energies of molecular orbitals.

$$\epsilon = \begin{bmatrix} -17.65 \\ 6.19 \end{bmatrix} \text{ orbital energies}$$

$$E = \sum_{i=1}^{\text{occ}} 2 \cdot \epsilon_i = 2 \cdot (-17.65 \text{ eV}) = -35.3 \text{ eV.}$$