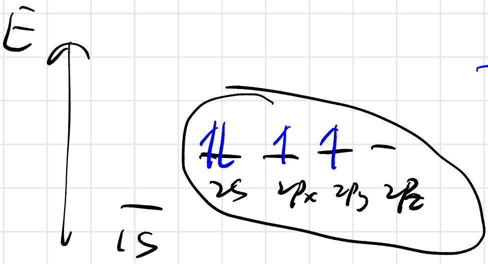
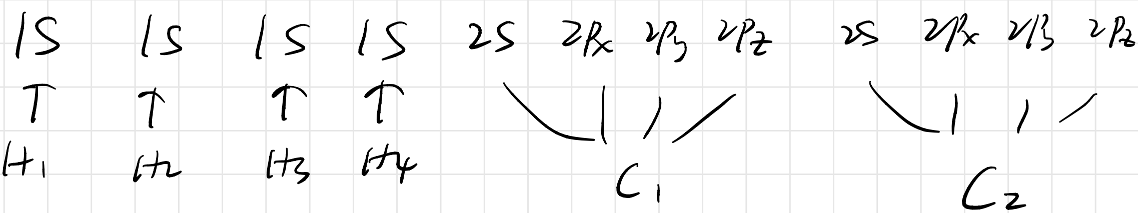


⇅ ⇅ ⇅ ⇅ ⇅ $10e^-$

4 electrons for C

Valent



$\langle \phi_a | \phi_b \rangle$

Gaussian function

$\langle \phi_\mu | \phi_\nu \rangle$

$$\underbrace{|\phi_\mu\rangle}_{\text{AO}} = \sum_a \underbrace{C_{a\mu}}_{\text{coefficient}} \underbrace{|\phi_a\rangle}_{\text{Gaussian}}$$

$$\langle \phi_\mu | \phi_\nu \rangle = C_{a\mu} C_{b\nu} \underbrace{\langle \phi_a | \phi_b \rangle}_{\text{obtained in HW2}}$$

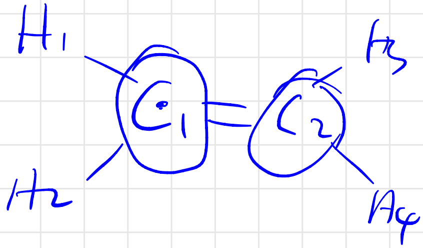
provided from HW3

$$\phi_\mu(\vec{r}) = 0.1543 \exp(-3.4253(\vec{r}-\vec{R}_A)^2) + 0.5353 \exp(-0.6239(\vec{r}-\vec{R}_A)^2) + 0.4446 \exp(-0.1689(\vec{r}-\vec{R}_A)^2)$$

$$2P_x(\vec{r}) = 0.1559162 \, 7(x-X_A)^1(y-Y_A)^0(z-Z_A)^0 \exp(-2.9412(\vec{r}-\vec{R}_A)^2) + 0.6077(x-X_A)^1(y-Y_A)^0(z-Z_A)^0 \exp(-0.6835(\vec{r}-\vec{R}_A)^2) + 0.3919(x-X_A)^1(y-Y_A)^0(z-Z_A)^0 \exp(-0.2223(\vec{r}-\vec{R}_A)^2)$$

$$2P_y(\vec{r}) = 0.1559162 \, 7(x-X_A)^0(y-Y_A)^1(z-Z_A)^0 \exp(-2.9412(\vec{r}-\vec{R}_A)^2) + 0.6077(x-X_A)^0(y-Y_A)^1(z-Z_A)^0 \exp(-0.6835(\vec{r}-\vec{R}_A)^2) + 0.3919(x-X_A)^0(y-Y_A)^1(z-Z_A)^0 \exp(-0.2223(\vec{r}-\vec{R}_A)^2)$$

$$2S(\vec{r}) = -0.0999^{H_1} \exp(-2.9412(\vec{r}-\vec{R}_A)^2) + 0.3995^{H_2} \exp(-0.6834(\vec{r}-\vec{R}_A)^2) + 0.7001^{H_3} \exp(-0.2222(\vec{r}-\vec{R}_A)^2)$$



$$N_1 = \left\{ \int \underline{d\vec{r}} \left[\underbrace{\exp\left(-2.9412(\vec{r}-\vec{R}_A)^2\right)}_{w_1(\vec{r})} \right]^2 \right\}^{-\frac{1}{2}}$$

$$N_2 = \left\{ \int d\vec{r} \left[\underbrace{\exp\left(-0.6834(\vec{r}-\vec{R}_A)^2\right)}_{w_2(\vec{r})} \right]^2 \right\}^{-\frac{1}{2}}$$

$$N_3 = \left\{ \int d\vec{r} \left[\underbrace{\exp\left(-0.2222(\vec{r}-\vec{R}_A)^2\right)}_{w_3(\vec{r})} \right]^2 \right\}^{-\frac{1}{2}}$$

$$2S(\vec{r}) = -0.0999\, N_1 w_1(\vec{r}) + 0.3995\, N_2\, w_2(\vec{r}) + 0.7001\, N_3 w_3(\vec{r})$$

$d_{k\mu}$

normalization factor

$$\phi_\mu(\vec{r}) = \sum_i C_{\mu i} \underbrace{N_i \, \overset{\text{primitive gaussian}}{w_i(\vec{r})}}_{\text{normalized primitive gaussian}}$$

$$N_i^2 \langle w_i | w_i \rangle = 1 \Rightarrow N_i = \left(\langle w_i | w_i \rangle\right)^{-\frac{1}{2}}$$

$$\phi'_\mu(\vec{r}) = N \sum_i C_{\mu i} N_i w_i(\vec{r})$$

$$\phi'_\mu(\vec{r})$$

$$\underbrace{\int d\vec{r} \, d\vec{r} \, (x - X_A) \exp(-\alpha |\vec{r} - \vec{R}_A|^2) \exp(-\beta |\vec{r} - \vec{R}_B|^2)}_{S_{ij}}$$

primitive gaussian

$$\hat{P} = \sum_i^{MO} |\phi_i\rangle\langle\phi_i|$$

AO

$$\underbrace{\langle \phi_\mu | \hat{P} | \phi_\nu \rangle}_{\text{density matrix}} = \sum_i^{MO} \langle \phi_\mu | \underbrace{\phi_i \rangle \langle \phi_i}_{MO} | \phi_\nu \rangle = \sum_i^{MO} \underbrace{C_{\mu i} C_{\nu i}}_{\text{MO coefficient}}$$

Discussion 4

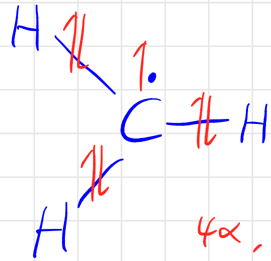
CNDO/2 SCF

α : spin up

β : spin down

Coupled SCF equation:

$$\begin{cases} \sum_{\nu}^{AO} f_{\mu\nu}^{\alpha} C_{\nu i}^{\alpha} = C_{\mu i}^{\alpha} \varepsilon_i^{\alpha} \\ \sum_{\nu}^{AO} f_{\mu\nu}^{\beta} C_{\nu i}^{\beta} = C_{\mu i}^{\beta} \varepsilon_i^{\beta} \end{cases}$$



4α, 3β

in matrix form:

$$\begin{cases} \underbrace{\begin{bmatrix} f_{\mu\nu}^{\alpha} \end{bmatrix}}_{AO \times AO} \underbrace{\begin{bmatrix} C^{\alpha} \end{bmatrix}}_{AO \times AO} = \underbrace{\begin{bmatrix} C^{\alpha} \end{bmatrix}}_{AO \times AO} \underbrace{\begin{bmatrix} \varepsilon_1^{\alpha} & & & & 0 \\ & \varepsilon_2^{\alpha} & & & \\ & & \varepsilon_3^{\alpha} & & \\ & & & \ddots & \\ 0 & & & & \varepsilon_n^{\alpha} \end{bmatrix}}_{AO \times AO} \\ \underbrace{\begin{bmatrix} f_{\mu\nu}^{\beta} \end{bmatrix}}_{AO \times AO} \underbrace{\begin{bmatrix} C^{\beta} \end{bmatrix}}_{AO \times AO} = \underbrace{\begin{bmatrix} C^{\beta} \end{bmatrix}}_{AO \times AO} \underbrace{\begin{bmatrix} \varepsilon_1^{\beta} & & & & 0 \\ & \varepsilon_2^{\beta} & & & \\ & & \varepsilon_3^{\beta} & & \\ & & & \ddots & \\ 0 & & & & \varepsilon_n^{\beta} \end{bmatrix}}_{AO \times AO} \end{cases}$$

Construction of $f_{\mu\nu}^{\omega}$ $(\omega = \alpha, \beta)$:

atomic number of atom

$$\begin{cases} f_{\mu\mu}^{\omega} = -\frac{1}{2}(I_\mu + A_\mu) + \left[(P_{AA}^{tot} - Z_A) - (P_{\mu\mu}^{\omega} - \frac{1}{2}) \right] \gamma_{AA} \\ \qquad + \sum_{B \neq A}^{atoms} (P_{BB}^{tot} - Z_B) \gamma_{AB} \end{cases}$$

$$t^{w}_{\mu\nu} = -\frac{1}{2}(\beta_A + \beta_B) S_{\mu\nu} - P^{w}_{\mu\nu}\gamma_{AB} \qquad (\mu \neq \nu)$$

I_μ, A_μ : parameter for orbitals

β_A : parameter for atoms

t depends on P,
P depends on C,
C depends on t
need to be solved self-consistently

$$P^{\alpha}_{\mu\nu} = \sum_{i=1}^{n^{\alpha}_{occ}} C^{\alpha}_{\mu i} C^{\alpha}_{\nu i} \qquad P^{\beta}_{\mu\nu} = \sum_{i=1}^{n^{\beta}_{occ}} C^{\beta}_{\mu i} C^{\beta}_{\nu i}$$

$$P^{tot}_{\mu\nu} = P^{\alpha}_{\mu\nu} + P^{\beta}_{\mu\nu} \qquad P^{tot}_{AA} = \sum_{\mu \in A} P^{tot}_{\mu\mu}$$

$S_{\mu\nu}$: AO overlap, same thing as in HW3

$$\gamma_{AB} = \int d\vec{r}_1 d\vec{r}_2 \, [S_A(\vec{r}_1)]^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} [S_B(\vec{r}_2)]^2$$

s orbital located on atom A

s orbital located on atom B

$$S_A(\vec{r}) = \sum_{k=1}^{3} \underbrace{(d_{k,S_A} N^{s}_{k})}_{d'_{k,S_A}} \underbrace{\omega^{s}_{k}(\vec{r} - \vec{R}_A)}_{\exp(-\alpha_k(\vec{r} - \vec{R}_A)^2)}$$

$$= \sum_{k=1}^{3} d'_{k,S_A} \exp(-\alpha_k (\vec{r} - \vec{R}_A)^2)$$

$$\Rightarrow \gamma_{AB} = \sum_{k=1}^{3}\sum_{k'=1}^{3}\sum_{l=1}^{3}\sum_{l'=1}^{3} d'_{k,S_A} d'_{k',S_A} d'_{l,S_B} d'_{l',S_B} [0]^{(0)}$$

$$[0]^{(0)} = \frac{U_A U_B}{\sqrt{(\vec{R}_A - \vec{R}_B)^2}} \, \mathrm{erf}(\sqrt{T})$$

$$U_A = \left(\frac{\pi}{\alpha_k + \alpha_k'}\right)^{\frac{3}{2}} \qquad U_B = \left(\frac{\pi}{\beta_l + \beta_{l'}}\right)^{\frac{3}{2}}$$

primitive gaussian exponents on A

primitive gaussian exponents on B

$$\exp\left(-\beta_l (\vec{r} - \vec{R}_B)^2\right)$$

$$T = (\sigma_A + \sigma_B)^{-1} (\vec{R}_A - \vec{R}_B)^2$$

$$\sigma_A = (\alpha_k + \alpha_{k'})^{-1} \qquad \sigma_B = (\beta_l + \beta_{l'})^{-1}$$

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

(built in C++, just do
#include <cmath>
the function can be called as
erf(x))