Discussion 3

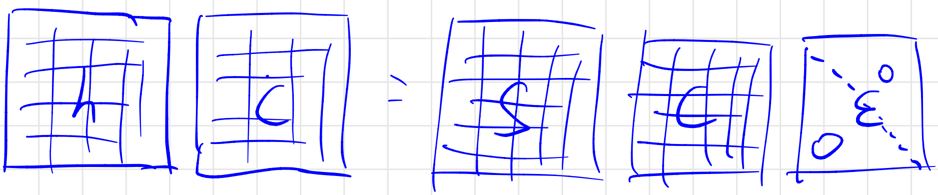
$$(|\psi_1\rangle, |\psi_2\rangle, |\psi_3\rangle, \cdots |\psi_n\rangle) = (|\phi_1\rangle, |\phi_2\rangle, |\phi_3\rangle \cdots |\phi_n\rangle) \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1n} \\ C_{21} & C_{22} & \cdots & C_{2n} \\ C_{31} & C_{32} & \cdots & C_{3n} \\ \vdots & \vdots & & \vdots \\ C_{n1} & C_{n2} & \cdots & C_{nn} \end{pmatrix}$$

minimize $\langle \Psi(x_1, x_2, \cdots x_n) | \hat{H} | \Psi(x_1, x_2, \cdots x_n) \rangle$

$$\iff \sum_i \langle \psi_i | \hat{h}_{eff} | \psi_i \rangle$$

$hC = C\varepsilon$

$$\iff hC = SC\varepsilon$$



$h_{\mu\nu} = \langle \phi_\mu | \hat{h}_{eff} | \phi_\nu \rangle$ $\qquad \underline{C_{\mu i}}$

$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$

In Hukel theory,

$h_{\mu\nu} = \frac{K}{2}[h_{\mu\mu} + h_{\nu\nu}]$

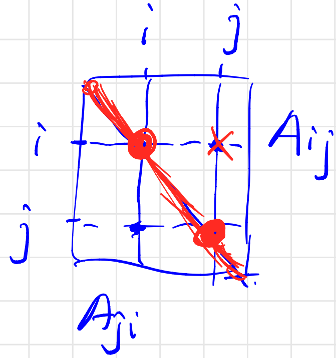
$$\hat{h}_{eff} = -\frac{1}{2}\nabla_i^2 + V_{eff}(\vec{r})$$

$$\langle \phi_\mu | \hat{h}_{eff} | \phi_\nu \rangle = \int d\vec{r}\, \phi_\mu(\vec{r}) \left[-\frac{1}{2}\frac{\partial^2}{\partial x^2}\phi_\nu(\vec{r}) - \frac{1}{2}\frac{\partial^2}{\partial y^2}\phi_\nu(\vec{r}) - \frac{1}{2}\frac{\partial^2}{\partial z^2}\phi_\nu(\vec{r}) + V_{eff}(\vec{r})\phi_\nu(\vec{r}) \right]$$

$$h_{\mu\nu} = \frac{K}{2}\left(h_{\mu\mu} + h_{\nu\nu}\right)$$

known

$$A_{ij} = A_{ji}$$



$$h_{\nu\mu} = \frac{K}{2}\left(h_{\nu\nu} + h_{\mu\mu}\right) = \frac{K}{2}\left(h_{\mu\mu} + h_{\nu\nu}\right) = h_{\mu\nu}$$

$$S_{\mu\nu} = \int d\vec{r}\, \phi_\mu(\vec{r})\phi_\nu(\vec{r}) = \int d\vec{r}\, \phi_\nu(\vec{r})\phi_\mu(\vec{r}) = S_{\nu\mu}$$

$$hC = SC\varepsilon \iff \underbrace{S^{-1}h}_{A}\, C = C\varepsilon$$

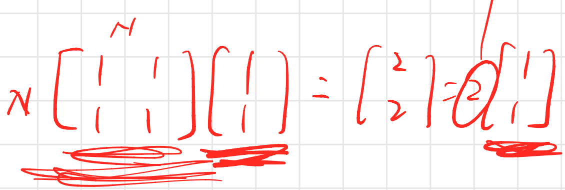
$$h^T = h, \quad S^T = S$$

$$Ac = c\varepsilon$$

$$A^T = (S^{-1}h)^T =$$

C

λ



$$hC = SC\varepsilon \quad ?$$

$$S^{-\frac{1}{2}} h C = S^{-\frac{1}{2}} S C \varepsilon$$

$$S^{-\frac{1}{2}} h S^{-\frac{1}{2}} S^{\frac{1}{2}} C = S^{\frac{1}{2}} C \varepsilon$$

$A^T = A$

eigenvector matrix

$$A = U \Lambda U^T$$

$$\begin{bmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & & \lambda_3 \\ & & & \ddots \end{bmatrix}$$

$U^T U = I$

$\langle 1s \mid 2p \rangle$

$$\begin{array}{c|cc} & 1s & 2p \\ \hline 1s & & \\ 2p & & \end{array}$$

$$f(A) = U f(\Lambda) U^T$$

matrix vector

$$U = \begin{pmatrix} u_1 & u_2 & u_3 & \cdots & u_n \end{pmatrix}$$

$$f(\Lambda) = \begin{bmatrix} f(\lambda_1) & & 0 \\ & f(\lambda_2) & \\ 0 & & f(\lambda_3) \\ & & & \ddots \end{bmatrix}$$

$S u_i = s_i u_i$ ← vector

number

$$S = U \begin{pmatrix} s_1 & & & 0 \\ & s_2 & & \\ & & \ddots & \\ 0 & & & s_n \end{pmatrix} U^T$$

$n \times n$ matrix

$$S^{-\frac{1}{2}} = U \begin{bmatrix} s_1^{-\frac{1}{2}} & & 0 \\ & s_2^{-\frac{1}{2}} & \\ 0 & & \ddots \\ & & & s_n^{-\frac{1}{2}} \end{bmatrix} U^T$$

where $S = U s U^T$

eigenvalues of S

$$hC = SC\varepsilon$$

$$S^{-\frac{1}{2}} h C = S^{-\frac{1}{2}} S C \varepsilon \qquad S^{-\frac{1}{2}} S = S^{\frac{1}{2}}$$

solved known

$$\underbrace{S^{-\frac{1}{2}} h S^{-\frac{1}{2}}}_{h'} \underbrace{S^{\frac{1}{2}} C}_{C'} = \underbrace{S^{\frac{1}{2}} C}_{C'} \varepsilon$$

set $\rightarrow h'$

answer solved solved

$$C = S^{-\frac{1}{2}} C'$$

$$\Rightarrow \boxed{h' C' = C' \varepsilon} \leftarrow \text{solving } C', \varepsilon$$

$2 \text{tr}(\varepsilon) = E$

$$h' = S^{-\frac{1}{2}} h S^{-\frac{1}{2}} \qquad C' = S^{\frac{1}{2}} C$$

$$\begin{bmatrix} \varepsilon_1 & & 0 \\ & \varepsilon_2 & \\ 0 & & \varepsilon_n \end{bmatrix}$$

$$h'^T = (S^{-\frac{1}{2}} h S^{-\frac{1}{2}})^T$$
$$= (S^{-\frac{1}{2}})^T h^T (S^{-\frac{1}{2}})^T$$
$$= S^{-\frac{1}{2}} h S^{-\frac{1}{2}} = h'$$

solve solve

$$h' C' = C' \varepsilon$$

$$C = S^{-\frac{1}{2}} C'$$

① construct S, h

② arma::vec S_eval; arma::mat S_evec;

arma::eig_sym(S_eval, S_evec, S)

arma::mat $S^{-\frac{1}{2}}$ = S_evec * S_eval$^{-\frac{1}{2}}$ * transpose(S_evec)

$$S^{\frac{1}{2}} = S\_evec * S\_eval^{\frac{1}{2}} * transpose(S\_evec)$$

③ arma h_prime = $S^{-\frac{1}{2}} * h * S^{-\frac{1}{2}}$

eig_sym(ε, C_prime, h_prime)

④ arma C = $S^{-\frac{1}{2}}$ * C_prime ;

$$S^{-\frac{1}{2}} S^{\frac{1}{2}} = I$$

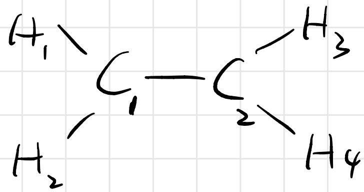
$$S^{-\frac{1}{2}} S^{\frac{1}{2}} = U \begin{pmatrix} s_1^{-\frac{1}{2}} & & 0 \\ & s_2^{-\frac{1}{2}} & \\ 0 & & \ddots \; s_n^{-\frac{1}{2}} \end{pmatrix} \underbrace{U^T U}_{I} \begin{pmatrix} s_1^{\frac{1}{2}} & & 0 \\ & s_2^{\frac{1}{2}} & \\ 0 & & \ddots \; s_n^{\frac{1}{2}} \end{pmatrix} U^T$$

$$= U \begin{pmatrix} s_1^{-\frac{1}{2}} & & 0 \\ & s_2^{-\frac{1}{2}} & \\ 0 & & \ddots \; s_n^{-\frac{1}{2}} \end{pmatrix} \begin{pmatrix} s_1^{\frac{1}{2}} & & 0 \\ & s_2^{\frac{1}{2}} & \\ 0 & & \ddots \; s_n^{\frac{1}{2}} \end{pmatrix} U^T$$

$$= U \begin{pmatrix} s_1^{-\frac{1}{2}} s_1^{\frac{1}{2}} & & 0 \\ & s_2^{-\frac{1}{2}} s_2^{\frac{1}{2}} & \\ 0 & & \ddots \; s_n^{-\frac{1}{2}} s_n^{\frac{1}{2}} \end{pmatrix} U^T$$

$$= U \underbrace{\begin{pmatrix} 1 & & 0 \\ & 1 & \\ 0 & & \ddots \end{pmatrix}}_{I} U^T = U U^T = U U^{-1} = I$$

$$U^T U = I \iff U^T = U^{-1}$$



C : valence electron : 2S, $2P_x$, $2P_y$, $2P_z$

H : – ——— -- 1S

# of AO for C_2H_4 = 4 × 2 + 1 × 4 = 8 + 4 = 12

#of C   #of H

1s
H

$1s^2$
He

Li Be   B C N O F Ne

Na Mg   Al Si P S Cl Ar

K Ca - - Si Ti - - -

H : $1s^1$

He : $1s^2$

Li : $1s^2 2s^1$

Be : $1s^2 2s^2$

B : $1s^2 2s^2 2p^1$

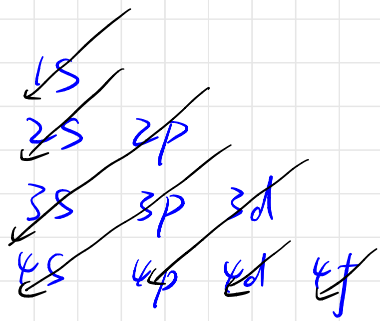
C : $1s^2 2s^2 2p^2$

O : $1s^2 2s^2 2p^4$

F : $1s^2 2s^2 2p^5$

2S   2P

n = 2



S orbital nondenerate :

1s ⇅

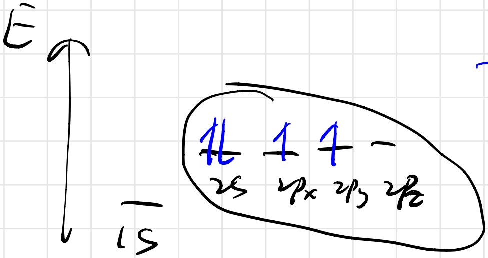
S orbital can have 2 e^-

P orbital 3-denegrate

⇅ ⇅ ⇅
$2P_x$ $2P_y$ $2P_z$

6 e^-

d orbital 5 – degenerate



$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $10e^-$

4 electrons for C

$\uparrow$

Valent

1s	1s	1s	1s	2s 2px 2py 2pz	2s 2px 2py 2pz
$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$		
H_1	H_2	H_3	H_4	C_1	C_2

$$\langle \varphi_a | \varphi_b \rangle$$

$\nearrow$ Gaussian function

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

$$\underset{\text{AO}}{|\phi_\mu\rangle} = \sum_a \underset{\text{coefficient}}{C_{a\mu}} \underset{\text{Gaussian}}{|\varphi_a\rangle}$$

$$\langle \phi_\mu | \phi_\nu \rangle = \underbrace{C_{a\mu} C_{b\nu}}_{\text{provided from HW3}} \underbrace{\langle \varphi_a | \varphi_b \rangle}_{\text{obtained in HW2}}$$