

Discussion 2

Molecular orbital theory:

Born - Oppenheimer approximation:

$$\hat{H}[\{\vec{R}_a\}] \Psi[\{\vec{r}_i\}; \{\vec{R}_a\}] = E[\{\vec{R}_a\}] \Psi[\{\vec{r}_i\}; \{\vec{R}_a\}]$$

\vec{r}_i : electron coordinate

\vec{R}_a : nuclei coordinate

$E[\{\vec{R}_a\}]$: potential energy surface (PES)

$|\Psi|^2$ is interpreted as a probability distribution,
it needs to be normalized:

$$\int d\vec{r}_1 \dots d\vec{r}_n |\Psi|^2 = 1$$

electron density:

$$\rho(\vec{r}) = N \int d\vec{r}_1 \dots d\vec{r}_n \Psi^*(\vec{r}, \vec{r}_1 \dots \vec{r}_n; \{\vec{R}_a\}) \Psi(\vec{r}, \vec{r}_1 \dots \vec{r}_n; \{\vec{R}_a\})$$

Electronic Hamiltonian operator:

$$\hat{H} = \hat{T} + \hat{V}_{en} + \hat{V}_{ee} \leftarrow \begin{matrix} \text{electron - electron} \\ \text{repulsion} \end{matrix}$$

\nearrow \nearrow

electron kinetic energy electron-nuclei attraction

$$\hat{T} = \sum_{i=1}^n \frac{\hat{P}_i^2}{2m_e}$$

m_e : electron mass, in atomic unit, $m_e = 1$

From Q.M. momentum operator \hat{P} in coordinate space is represented as $\hat{P} = -i\hbar \frac{d}{dx}$, i.e.

$$\langle x | \hat{P} | \psi \rangle = -i\hbar \frac{d}{dx} \langle x | \psi \rangle$$

$\langle x | \psi \rangle : \psi(x)$ wavefunction

$$\Rightarrow \hat{T} = \sum_{i=1}^n \frac{\hat{P}_{xi}^2 + \hat{P}_{yi}^2 + \hat{P}_{zi}^2}{2} = -\frac{\hbar^2}{2} \sum_{i=1}^n \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \\ = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 \quad (\text{in atomic unit, } \hbar = 1)$$

$$\hat{V}_{en} = \sum_{i=1}^n \sum_{a=1}^A \frac{q_i Q_A}{R_{ia}} = \sum_{i=1}^n \sum_{a=1}^A \frac{-e \cdot z_a e}{R_{ia}} = -\sum_{i=1}^n \sum_{a=1}^A \frac{z_a e^2}{R_{ia}}$$

in atomic unit, $e = 1$

$$\Rightarrow \hat{V}_{en} = -\sum_{i=1}^n \sum_{a=1}^A \frac{z_a}{R_{ia}}$$

$$\hat{V}_{ee} = \sum_{i=1}^n \sum_{j>i}^n \frac{e^2}{r_{ij}} = \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} \quad (\text{in a.u.})$$

\hat{T} & \hat{V}_{en} are sums of 1-electron operators

\hat{V}_{ee} is a sum of two electron operators, this makes quantum chemistry hard!

How does the quantum state evolve?

Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{x}, t) = \hat{H} \Psi(\vec{x}, t)$$

if \hat{H} is time-independent, such as our electronic Hamiltonian, this can be solved by separation of variables:

$$\Psi(\vec{x}, t) = \phi(\vec{x}) X(t)$$

$$\Rightarrow i\hbar \phi(\vec{x}) \frac{\partial}{\partial t} X(t) = (\hat{H} \phi(\vec{x})) X(t)$$

if $\phi(\vec{x})$ is an eigenstate of \hat{H} :

$$\hat{H} \phi_i(\vec{x}) = E_i \phi_i(\vec{x})$$

$$\Rightarrow i\hbar \cancel{\phi(\vec{x})} \frac{\partial}{\partial t} X(t) = E_i \cancel{\phi(\vec{x})} X(t)$$

$$\Rightarrow \dot{\chi}(t) = -\frac{iE_i}{\hbar} \chi(t)$$

$$\chi(t) = \exp\left[-\frac{iE_it}{\hbar}\right]$$

thus, for an eigenstate of \hat{H} , its solution is

$$\psi_i(\vec{x}, t) = \phi_i(\vec{x}) \exp\left[-\frac{iE_it}{\hbar}\right]$$

How about a general state?

Since \hat{H} is Hermitian

$$\psi(\vec{x}, 0) = \sum_j c_j \phi_j(\vec{x})$$

$$\text{then } \psi(\vec{x}, t) = \sum_j c_j \phi_j(\vec{x}) \exp\left[-\frac{iE_j t}{\hbar}\right]$$

let's check this satisfies S.E.

$$\begin{aligned} \text{LHS: } i\hbar \frac{\partial}{\partial t} \psi(\vec{x}, t) &= \sum_j c_j \phi_j(\vec{x}) i\hbar \frac{\partial}{\partial t} \exp\left[-\frac{iE_j t}{\hbar}\right] \\ &= \sum_j c_j \phi_j(\vec{x}) i\hbar \left(-\frac{iE_j}{\hbar}\right) \exp\left[-\frac{iE_j t}{\hbar}\right] \\ &= \sum_j c_j \phi_j(\vec{x}) E_j \exp\left[-\frac{iE_j t}{\hbar}\right] \end{aligned}$$

RHS:

$$\hat{H}(\Psi(\vec{x}, t)) = \sum_j C_j [\hat{H}(\phi_j(\vec{x}))] \exp\left(-\frac{iE_j t}{\hbar}\right)$$

$$= \sum_j C_j E_j \phi_j(\vec{x}) \exp\left(-\frac{iE_j t}{\hbar}\right)$$

$\Rightarrow \text{LHS} = \text{RHS}$, S.E. is satisfied!

So the problem is to get the spectrum of \hat{H} .

that's why we want to solve

$$\hat{H}(\{\vec{R}_a\}) \Psi(\{\vec{r}_i\}; \{\vec{R}_a\}) = E(\{\vec{R}_a\}) \Psi(\{\vec{r}_i\}; \{\vec{R}_a\})$$

we can't do it using grid based P.D.E method
(memory increases exponentially with number of electrons)

instead, use variational principle

Variational principle:

For a Hamiltonian \hat{H} with eigenvalues $\{E_i\}$ and eigenstates $\{|\psi_i\rangle\}$, and $E_0 < E_1 < E_2 \dots$
then for any normalized state $|\phi\rangle$,

$$\langle \phi | \hat{H} | \phi \rangle \geq E_0$$

Proof: Since \hat{H} is Hermitian, its eigenvectors form an orthonormal basis of the vector space

$$\Rightarrow |\psi\rangle = \sum_{i=0}^{\infty} c_i |\psi_i\rangle$$

$$\langle\psi|\psi\rangle = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} c_i^* \langle\psi_i| \psi_j \rangle$$

$$= \sum_{i,j=0}^{\infty} c_i^* c_j \underbrace{\langle\psi_i|\psi_j\rangle}_{\delta_{ij}} = \sum_{i=0}^{\infty} c_i^* c_i = 1$$

thus,

$$\begin{aligned} \langle\psi|\hat{H}|\psi\rangle &= \left[\sum_{i=0}^{\infty} c_i^* \langle\psi_i| \right] \hat{H} \underbrace{\sum_{j=0}^{\infty} c_j |\psi_j\rangle}_{\text{act on } |\psi_j\rangle} \\ &= \left(\sum_{i=0}^{\infty} c_i^* \langle\psi_i| \right) \sum_{j=0}^{\infty} c_j E_j |\psi_j\rangle \end{aligned}$$

$$= \sum_{i,j=0}^{\infty} c_i^* c_j E_j \underbrace{\langle\psi_i|\psi_j\rangle}_{\delta_{ij}}$$

$$= \sum_{i=0}^{\infty} c_i^* c_i E_i \geq \sum_{i=0}^{\infty} c_i^* c_i E_0 = E_0 \underbrace{\sum_{i=0}^{\infty} c_i^* c_i}_1 = E_0$$

$$\Rightarrow \langle\psi|\hat{H}|\psi\rangle \geq E_0 \quad \square$$

Molecular orbital theory:

approximate the many body wavefunction as a

single Slater determinant:

$$\Psi(\vec{x}_1, \vec{x}_2 \dots \vec{x}_n) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \psi_3(\vec{x}_1) & \dots & \psi_n(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \psi_3(\vec{x}_2) & \dots & \psi_n(\vec{x}_2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{x}_n) & \psi_2(\vec{x}_n) & \psi_3(\vec{x}_n) & \dots & \psi_n(\vec{x}_n) \end{vmatrix}$$
$$= \frac{1}{\sqrt{N!}} \sum_{\sigma} (-1)^{\delta} \psi_{\sigma(1)}(\vec{x}_1) \psi_{\sigma(2)}(\vec{x}_2) \psi_{\sigma(3)}(\vec{x}_3) \dots \psi_{\sigma(n)}(\vec{x}_n)$$

where $\langle \psi_i | \psi_j \rangle = d_{ij}$ i.e. $\int d\vec{x} \psi_i^*(\vec{x}) \psi_j(\vec{x}) = d_{ij}$

$\{|\psi_i\rangle\}$ are molecular orbitals

\vec{x} : spin coordinate, $\{x, y, z, w\}$

δ : permutation operator

$$(-1)^{\delta} = \begin{cases} 1 & \text{even permutation} \\ -1 & \text{odd permutation} \end{cases}$$

$$\text{e.g.: } \delta(1 \ 2 \ 3 \ 4) = (2 \ 3 \ 1 \ 4)$$

even permutation

$$\delta(1 \ 2 \ 3 \ 4) = (2 \ 1 \ 3 \ 4)$$

odd permutation

then, switch \vec{x}_1, \vec{x}_2 in $\Psi(\vec{x}_1, \vec{x}_2 \dots \vec{x}_n)$ is just to

switch the first two rows of the determinant, by the property of determinant, $\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) = -\Psi(\vec{x}_2, \vec{x}_1, \dots, \vec{x}_n)$
 this satisfies Pauli exclusion principle!

Let's check it's normalized:

$$\langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle$$

$$= \frac{1}{N!} \sum_{\sigma} \sum_{\epsilon} (-1)^{\sigma} (-1)^{\epsilon} \int d\vec{x}_1 d\vec{x}_2 \dots d\vec{x}_n \psi_{\sigma(1)}^*(\vec{x}_1) \psi_{\sigma(2)}^*(\vec{x}_2) \dots \psi_{\sigma(n)}^*(\vec{x}_n) \psi_{\epsilon(1)}(\vec{x}_1) \psi_{\epsilon(2)}(\vec{x}_2) \dots \psi_{\epsilon(n)}(\vec{x}_n)$$

$$= \frac{1}{N!} \sum_{\sigma} \sum_{\epsilon} (-1)^{\sigma} (-1)^{\epsilon} \int d\vec{x}_1 \psi_{\sigma(1)}^*(\vec{x}_1) \psi_{\epsilon(1)}(\vec{x}_1) \int d\vec{x}_2 \psi_{\sigma(2)}^*(\vec{x}_2) \psi_{\epsilon(2)}(\vec{x}_2) \dots$$

$$\int d\vec{x}_n \psi_{\sigma(n)}^*(\vec{x}_n) \psi_{\epsilon(n)}(\vec{x}_n)$$

$$= \frac{1}{N!} \sum_{\sigma} \sum_{\epsilon} (-1)^{\sigma} (-1)^{\epsilon} \underbrace{(\psi_{\sigma(1)} | \psi_{\epsilon(1)} \rangle \cdot (\psi_{\sigma(2)} | \psi_{\epsilon(2)} \rangle \dots (\psi_{\sigma(n)} | \psi_{\epsilon(n)} \rangle)}$$

non-zero unless

$$\sigma(1) = \epsilon(1), \sigma(2) = \epsilon(2), \dots, \sigma(n) = \epsilon(n)$$

this means the two permutations are equal!

$$\Rightarrow \langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle = \frac{1}{N!} \sum_{\sigma} \sum_{\epsilon} (-1)^{\sigma} (-1)^{\epsilon} \delta_{\sigma\epsilon}$$

$$= \frac{1}{N!} \sum_{\sigma} 1 = \frac{1}{N!} \times N! = 1$$

Hückel theory:

A mean field approximation, instead of using

$$\hat{H} = \sum_i -\frac{1}{2} D^2 + \sum_i \sum_A -\frac{Z_A}{4r_i - R_A} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_i - r_j}$$

assume each electron "feel" an effective potential field due to other electrons, so for single electron, we have

$$\hat{h}_{\text{eff}} = -\frac{1}{2} D^2 + V(r)$$

In a conjugate cyclic molecule, each P electron is equivalent so $\hat{H} = \sum_{i=1}^n \hat{h}_{\text{eff}}(i)$

acting on electron i

$$\text{System energy } E = \langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \hat{H} | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle$$

We want to minimize E by changing $\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n)$.

This can be achieved by changing $\psi_i(\vec{x})$ (MOs)

How to change $\psi_i(\vec{x})$?

LCAO (linear combination of atomic orbitals)

expand MOs as linear combinations of a set of basis functions

$$|\Psi_i\rangle = \sum_m C_{mi} |\phi_m\rangle$$

K: number of basis
 $K \gg n$

$$E = \langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \hat{H} | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle$$

$$= \sum_{i=1}^n \langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \hat{h}_{\text{eff}}(i) | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle$$

let's first look at $\langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \hat{h}_{\text{eff}}(1) | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle$

$$\langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \hat{h}_{\text{eff}}(1) | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle$$

$$= \frac{1}{N!} \sum_{\sigma} \sum_{\tau} (-1)^{\sigma} (-1)^{\tau} \int d\vec{x}_1 d\vec{x}_2 \dots d\vec{x}_n \psi_{\sigma(1)}^*(\vec{x}_1) \psi_{\sigma(2)}^*(\vec{x}_2) \dots \psi_{\sigma(n)}^*(\vec{x}_n) \hat{h}_{\text{eff}}(1) \psi_{\tau(1)}(\vec{x}_1) \psi_{\tau(2)}(\vec{x}_2)$$

$$= \frac{1}{N!} \sum_{\sigma} \sum_{\tau} (-1)^{\sigma} (-1)^{\tau} \int d\vec{x}_1 \psi_{\sigma(1)}^*(\vec{x}_1) \hat{h}_{\text{eff}}(1) \psi_{\tau(1)}(\vec{x}_1) \int d\vec{x}_2 \psi_{\sigma(2)}^*(\vec{x}_2) \psi_{\tau(2)}(\vec{x}_2) \dots \int d\vec{x}_n \psi_{\sigma(n)}^*(\vec{x}_n) \psi_{\tau(n)}(\vec{x}_n)$$

$$= \frac{1}{N!} \sum_{\sigma} \sum_{\tau} (-1)^{\sigma} (-1)^{\tau} (\psi_{\sigma(1)} | \hat{h}_{\text{eff}} | \psi_{\tau(1)}) \underbrace{(\psi_{\sigma(2)} | \psi_{\tau(2)} \rangle - (\psi_{\sigma(2)} | \psi_{\tau(2)} \rangle)}$$

non-zero unless

$$\sigma(2) = \tau(2), \sigma(3) = \tau(3), \dots, \sigma(n) = \tau(n)$$

$$\Rightarrow \sigma = \tau$$

$$\Rightarrow \langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \hat{h}_{\text{eff}}(1) | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle$$

$$= \frac{1}{N!} \sum_{\sigma} \sum_{\tau} (-1)^{\sigma} (-1)^{\tau} (\psi_{\sigma(1)} | \hat{h}_{\text{eff}} | \psi_{\sigma(1)}) \delta_{\sigma\tau}$$

$$= \frac{1}{N!} \sum_{\sigma} (\psi_{\sigma(1)} | \hat{h}_{\text{eff}} | \psi_{\sigma(1)})$$

we have $(N-1)!$ permutations s.t. $\sigma(1) = 1$
 $(N-1)! - - - - \sigma(1) = 2$

$$(N-1)! - \text{---} \quad \text{s.t. } \delta(i) = n$$

$$\Rightarrow \langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \hat{h}_{\text{eff}}(1) | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle \\ = \frac{1}{N!} \sum_{i=1}^n (N-1)! \langle \psi_i | \hat{h}_{\text{eff}} | \psi_i \rangle = \frac{1}{N} \sum_{i=1}^n \langle \psi_i | \hat{h}_{\text{eff}} | \psi_i \rangle$$

this result doesn't depend on electron 1, so

$$\langle \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) | \hat{h}_{\text{eff}}(i) | \Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) \rangle \text{ is the same for all electrons} \Rightarrow$$

$$E = N \cdot \frac{1}{N} \sum_{i=1}^n \langle \psi_i | \hat{h}_{\text{eff}} | \psi_i \rangle = \sum_{i=1}^n \langle \psi_i | \hat{h}_{\text{eff}} | \psi_i \rangle$$

Now let's minimize E : (assuming real orbitals)

$$E = \sum_{i=1}^n \sum_{m=1}^K \sum_{v=1}^K C_{mi} \underbrace{\langle \phi_m | \hat{h}_{\text{eff}} | \phi_v \rangle}_{h_{mv}} C_{vi}$$

$$= \sum_{i=1}^n \sum_{m=1}^K \sum_{v=1}^K C_{mi} h_{mv} C_{vi}$$

We want to minimize E under constraint

$$\langle \psi_i | \psi_j \rangle = \sum_{m=0}^K C_{mi} \underbrace{\langle \phi_m | \phi_v \rangle}_{S_{mv}} C_{vj} = \delta_{ij}$$

use Lagrange multiplier: S_{mv}

$$\mathcal{L} = \sum_{i=1}^n \sum_{m=1}^K \sum_{v=1}^K C_{mi} h_{mv} C_{vi} - \sum_{i=1}^n \sum_{j=1}^n \epsilon_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij})$$

$$= \sum_{i=1}^n \sum_{\mu\nu} C_{\mu i} h_{\mu\nu} C_{\nu i} - \sum_{ij} \sum_{\mu\nu} \left(\sum_{\mu\nu} C_{\mu i} S_{\mu\nu} C_{\nu j} - \delta_{ij} \right)$$

$$\begin{cases} \frac{\partial L}{\partial C_{\alpha k}} = 0 & \textcircled{1} \\ \frac{\partial L}{\partial \varepsilon_{ij}} = 0 & \textcircled{2} \end{cases}$$

$$\textcircled{1} \Rightarrow \frac{\partial L}{\partial C_{\alpha k}} = \sum_{i=1}^n \sum_{\mu\nu} \left(\delta_{\mu\alpha} \delta_{ik} h_{\mu\nu} C_{\nu i} + C_{\mu i} h_{\mu\nu} \delta_{\nu\alpha} \delta_{ik} \right)$$

$$- \sum_{ij} \varepsilon_{ij} \left[\sum_{\mu\nu} \left(\delta_{\mu\alpha} \delta_{ik} S_{\mu\nu} C_{\nu j} + C_{\mu i} S_{\mu\nu} \delta_{\nu\alpha} \delta_{ik} \right) \right]$$

$$= \sum_{\nu=1}^K h_{\alpha\nu} C_{\nu k} + \sum_{\mu=1}^K C_{\mu k} h_{\mu\alpha}$$

$$- \sum_{j=1}^n \sum_{\nu=1}^K \varepsilon_{kj} S_{\alpha\nu} C_{\nu j} - \sum_{i=1}^n \sum_{\mu=1}^K \varepsilon_{ik} C_{\mu i} S_{\mu\alpha}$$

$$= \sum_{\mu=1}^K h_{\alpha\mu} C_{\mu k} + \sum_{\nu=1}^K h_{\nu\alpha} C_{\nu k}$$

$$- \sum_{i=1}^n \sum_{\mu=1}^K S_{\mu i} C_{\mu i} \varepsilon_{ki} - \sum_{\nu=1}^n \sum_{\mu=1}^K S_{\mu\alpha} C_{\mu i} \varepsilon_{ik}$$

In real orbital, $h_{\mu\nu} = h_{\nu\mu}$, $S_{\mu\nu} = S_{\nu\mu}$, $\varepsilon_{ij} = \varepsilon_{ji}$

$$\Rightarrow 2(hC)_{\alpha k} - 2(SCE)_{\alpha k} = 0$$

$$\Rightarrow hC = SCE \quad *$$

after solving *, the energy is

$$\begin{aligned} E &= \sum_i \langle \psi_i | \hat{h} | \psi_i \rangle = \sum_i \sum_{\mu\nu} C_{\mu i} h_{\mu\nu} C_{\nu i} \\ &= \sum_i \sum_{\mu} C_{\mu i} (hC)_{\mu i} \\ &= \sum_i \sum_{\mu} C_{\mu i} (SCE)_{\mu i} \\ &= \sum_i (C^T SCE)_{ii} \end{aligned}$$

$$\text{But } \langle \psi_i | \psi_j \rangle = \sum_{\mu\nu} C_{\mu i} S_{\mu\nu} C_{\nu j} = (C^T SC)_{ij} = \delta_{ij}$$

$$\Rightarrow C^T SC = I$$

$$\Rightarrow E = \sum_i \varepsilon_{ii}$$

How to solve *?

ε is symmetric, so can be diagonalized as

$$\varepsilon = U^T \varepsilon' U \quad \text{where } U^T U = I, \varepsilon' \text{ is diagonal}$$

$$\Rightarrow hC = SCE \Rightarrow \underbrace{hCU}_{C'} = \underbrace{SCU}_{C'} \underbrace{U^T \varepsilon U}_{\varepsilon'}$$

$$\Rightarrow hC' = SC'\varepsilon' \quad \text{generalized eigenvalue problem}$$

notice, $|4'_i\rangle = \sum_m C_{mi} |\phi_m\rangle$ is the rotated MOs

and $\langle 4'_i | 4'_j \rangle = C^T S C' = U^T \underline{C^T S C} U = U^T U = I$

they are also orthonormal! we will use them as MOs instead!

How to solve $hC' = SC'\epsilon'$?

S is symmetric, so $S = V \circ V^T$

where $V^T V = I$, S is diagonal

$$\Rightarrow S^{\frac{1}{2}} = V S^{\frac{1}{2}} V^T, S^{-\frac{1}{2}} = V S^{-\frac{1}{2}} V^T$$

$$hC' = SC'\epsilon'$$

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

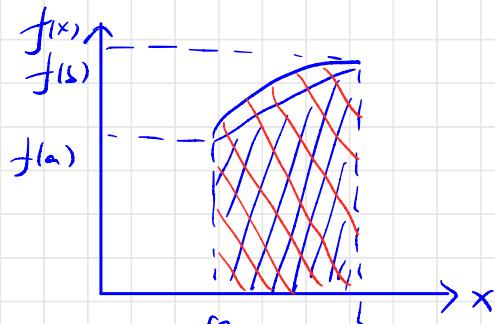
$$\Rightarrow h' C'' = C'' \epsilon' \quad \text{eigenvalue problem}$$

$h' = S^{-\frac{1}{2}} h C^{-\frac{1}{2}}$ is still symmetric and its eigenvalue & eigenvectors can be easily solved

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

We now have a nice theory, to use it, we need the matrix elements $h_{\mu\nu}$, $S_{\mu\nu}$. So we need to do numerical integration.

1d integration:



Trapezoidal rule:

$$I = \frac{b-a}{2} [f(a) + f(b)] \quad \text{exact if } f(x) \text{ is linear in } [a,b]$$

error analysis:

$$f(a+x) \approx f(a) + f'(a)x + \frac{1}{2}f''(a)x^2 + \dots$$

$$\text{so } I = \int_a^b f(x) dx \quad \text{let } x = a+y \Rightarrow dx = dy$$

$$= \int_0^{b-a} f(a+y) dy = \int_0^{b-a} \left[f(a) + f'(a)y + \frac{1}{2}f''(a)y^2 + \dots \right] dy$$

approximate $f'(a)$ as $\frac{f(b) - f(a)}{b-a}$

$$\Rightarrow I = f(a)(b-a) + \frac{f(b) - f(a)}{b-a} \cdot \frac{(b-a)^2}{2} + \frac{f''(a)}{2} \cdot \frac{(b-a)^3}{3} + \dots$$

$$= f(a) \frac{\delta-a}{2} + f(\delta) \frac{\delta-a}{2} + O((\delta-a)^3) + \dots$$

$$= \frac{\delta-a}{2} [f(a) + f(\delta)] + O((\delta-a)^3) + \dots$$

How about divide $[a, \delta]$ into n equal pieces?

on each piece, the error is $\sim O\left(\left(\frac{\delta-a}{n}\right)^3\right)$ and
accumulation of error is $\sim O\left[n \cdot \left(\frac{\delta-a}{n}\right)^3\right] \sim O\left(\frac{(\delta-a)^3}{n^2}\right)$

if we increase n , error reduce quadratically!

$$I = (\delta-a) \frac{f(a) + 2 \sum_{k=0}^{n-1} f(a+kh) + f(\delta)}{2n}$$

$$h = \frac{\delta-a}{n}$$