

Lecture FYS4480/9480,
September 26, 2024

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$$|\Psi_0\rangle = \sum_{\Phi H} C_H^P |\bar{\Phi}_H^P\rangle$$

$$\hat{H}_0 |\bar{\Phi}_H^P\rangle = E_H^P |\bar{\Phi}_H^P\rangle$$

C_H^P represents the overlap
 $\langle \Psi_0 | \bar{\Phi}_H^P \rangle$

$$H |\Psi_0\rangle = E_0 |\Psi_0\rangle$$

$$E_0 \leq \min_{\substack{C_H^P \\ C_H}} \frac{\sum_{PH}^{*P} C_H^P C_H^P \langle \Phi_H^P | H | \Phi_H^P \rangle}{\sum_{PH}^{*P} C_H^P C_H^P \langle \Phi_H^P | \Phi_H^P \rangle}$$

OND

$$\Rightarrow \det(H - \lambda I)$$

$$\sum_{PH} C_H^P | \Phi_H^P \rangle = \underbrace{1_P 1_H}_{\text{1}}$$

$$c_0 | \Phi_0 \rangle + \sum_{ai} c_i^a | \Phi_i^a \rangle + a_i^+ q_i | \Phi_c \rangle$$

$$\sum_{\substack{ab \\ ij}} c_{ij}^a \underbrace{a_a^\dagger q_i^\dagger q_j^\dagger q_i}_{} / \underline{\Phi_0} \rangle$$

$$| \underline{\Phi}_{ij}^{ab} \rangle$$

$z \rho z \hbar$

+ ...

+ $N \rho N \hbar$

$$\langle \underline{\Phi}_0 | H | \underline{\Phi}_i^a \rangle$$

$$\langle \underline{\Phi}_0 | H | \underline{\Phi}_{ij}^{ab} \rangle$$

$$\langle \underline{\Phi}_i^a | H | \underline{\Phi}_j^b \rangle$$

$$\langle \underline{\Phi}_i^a | H | \underline{\Phi}_{k\ell}^{cd} \rangle - \dots$$

Hamiltonian matrix

	E_0^{Ref}	$1p_1h$	$2p_2h$	$3p_3h$	\dots	$NpNh$
$0p0h$	$\langle \Phi_0 H \Phi_0 \rangle$	$\langle \Phi_1 H 1p_1h \rangle$	$\langle \Phi_2 H 2p_2h \rangle$	\dots	\dots	\dots
$1p1h$	$\langle 1p_1h H \Phi_0 \rangle$	$\langle 1p_1h H 1p_1h \rangle$	\times	\times	0	0
$2p2h$	$\langle 2p_2h H \Phi_0 \rangle$	$\langle 2p_2h H 1p_1h \rangle$	\times	\times	0	0
$3p3h$	0	\times	\times	\dots	\dots	\dots
\vdots	\vdots	\vdots	\vdots	\vdots	\vdots	\vdots
$NpNh$	0	0	0	0	\dots	\dots

$n = 8$ sp states

$N = 4$ particles

$P=4$ —

—

~~$\uparrow \downarrow$~~

$P=3$ —

~~$\uparrow \downarrow$~~

—

$P=2$ ~~$\uparrow \downarrow$~~

—

$|\psi_1\rangle$

$|\psi_2\rangle$

$P=1$ ~~$\uparrow \downarrow$~~

$|\psi_0\rangle$
opposite

~~$\uparrow \downarrow$~~

$2p^2 h$

~~$\uparrow \downarrow$~~

$2p^2 h$

~~$\uparrow \downarrow$~~

$|\psi_3\rangle$

~~$\uparrow \downarrow$~~

$|\psi_4\rangle$

~~$\uparrow \downarrow$~~

$|\psi_5\rangle$

$2p^2 h$

$2p^2 h$

$4p^4 h$

$$\langle \Psi_0 | H | \Psi_0 \rangle \quad \underbrace{\langle \Psi_0 | H | \Phi_1 \rangle - \langle \Psi_0 | H | \Phi_4 \rangle}_{\langle \Psi_0 | H | \Psi_2 \rangle} \quad \underbrace{\langle \Psi_0 | H | \Psi_5 \rangle}_{\langle \Phi_0 | H | \Psi_4 \rangle}$$

$$\langle \Phi_1 | H | \Psi_0 \rangle$$

$$\langle \Psi_2 | H | \Psi_0 \rangle \quad \times \quad \times \quad \times \quad \times$$

1

$$\langle \Psi_4 | H | \Psi_0 \rangle \quad \times$$

0

×

$$\langle \Psi_4 | H | \Phi_4 \rangle$$

+

$$\langle \Psi_5 | H | \Phi_5 \rangle$$

$$\langle \Phi_0 | H | \Phi_{ij}^{ab} \rangle = \langle ab | v | ij \rangle_{AS}$$

$$= \langle ab | v | ij \rangle - \langle ab | v | ji \rangle$$

$$\langle \Phi_0 | H | \psi \rangle \Rightarrow$$

$$\langle \Phi_0 | H | \Phi_i^a \rangle = \langle alg | i \rangle$$

$$| \Phi_i^a \rangle = q_a^\dagger q_i | \Phi_0 \rangle$$

$$\langle alg | i \rangle = \langle alhol | i \rangle + \sum_{j \leq F} \langle aj | v | ij \rangle_{AS}$$

$$(H - E_0) |\psi_0\rangle = 0$$

$$(H - E_0) \sum_{HP} C_H^P |\Phi_H^P\rangle = 0$$

$$(HC_i = E_i C_i)$$

First row of Hamiltonian matrix

$$\langle \Phi_C | H - E_0 | \psi_0 \rangle = 0$$

$$\langle \Phi_C | H - E_0 | \Phi_0 \rangle + \sum_{ai} C_i^a \langle \Phi_0 | H - E_0 | \Phi_i^a \rangle$$

$$+ \sum_{\substack{ab \\ ij}} C_{ij}^{ab} \langle \Phi_0 | H - E_0 | \Psi_{ij}^{ab} \rangle =$$

$$\underbrace{\langle \Phi_0 | H | \Phi_0 \rangle}_{E_0^{\text{Ref}}} - E_0$$

$$+ \sum_{ai} c_i^a \langle \alpha | g | i \rangle$$

$$+ \sum_{\substack{ab \\ ij'}} C_{ij}^{ab} \langle \alpha b | \alpha l | ij' \rangle_{AS} = 0$$

$$\Delta E = E_0 - E_0^{\text{Ref}} = \sum_{ai} c_i^a \langle \alpha | g | i \rangle + \sum_{\substack{ab \\ ij}} C_{ij}^{ab} \langle \alpha b | \alpha l | ij \rangle_{AS}$$

$$\langle \Phi_i^a | H - E_0 | \psi_0 \rangle = 0$$

$$= \underbrace{\langle \Phi_i^a | H | \Phi_0 \rangle}_{\sum_j c_j^b c_j^b} + \sum_{kj} c_j^b c_j^b \langle \Phi_i^a | H - E_0 | \Phi_j^b \rangle$$

$$+ \sum_{\substack{bc \\ jk}} c_{jk}^{bc} \langle \Phi_i^a | H | \Phi_{jk}^{bc} \rangle$$

$$+ \sum_{\substack{bcd \\ jke}} c_{jke}^{bcd} \langle \Phi_i^a | H | \Phi_{jke}^{bcd} \rangle = 0$$

3P3L

\Rightarrow

$$\langle i | f(a) \rangle + c_i^a \langle \Phi_i^a | H - E_0 | \Phi_i^a \rangle$$

$$+ \sum_{\substack{b \neq a \\ j \neq i}} \langle \Phi_j^b | H | \Phi_j^b \rangle c_j^b$$

$$+ \dots = 0$$

$$\langle \Phi_i^a | H - E_0 | \Phi_i^a \rangle c_i^a =$$

$$\langle \Phi_i^a | H | \Phi_i^a \rangle - c_i^a E_0$$

$$\langle c | g | a \rangle + [\langle a | g | a \rangle - \langle c | g | i \rangle$$

$$+ \langle a_i | v | a_i \rangle_{AS}] c_i^a$$

$$\rightarrow \sum_{\substack{b \neq a \\ j \neq i}} c_j^b \underbrace{\langle \sum_n | H(\phi_j^n) }_{\langle a_j | v | t_i \rangle_{AS}}$$

$$+ \dots = E_0 c_i^a$$

Solve iteratively with a
guess $c_i^a(0), c_{ij}^{av}(0), \dots$

$$\text{in } MBPT(2) : C_i^a(0) = \frac{\langle i | g | a \rangle}{\varepsilon_i - \varepsilon_a}$$

$$C_{ij}^{av}(0) = \frac{\langle ij | v | ab \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$\text{guess : } C_{ijk}^{abc}(0) \dots = 0$$

Hartree-Fock theory (unjustified approximation)

$$H \cdot C = E C$$

standard approach:

$$U^+ H U = D = \begin{bmatrix} \lambda_0 & & & \\ & \ddots & \ddots & \lambda_{d-1} \\ & & \ddots & \\ & & & \lambda_d \end{bmatrix}$$

$$U^+ U = U U^+ = \mathbf{1} \quad U = U^{-1}$$

$$U_M^+ U_{M-1}^+ \cdots U_1^+ H U_1 U_2 \cdots U_M$$

$$= D$$

$$U_{2 \times 2} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

$$U^T H U = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$$

choose ϵ so that the non-diagonal elements to
are zero

$$H = \begin{bmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{bmatrix}$$

$$U^T H U = \begin{bmatrix} h_{11} & 0 \\ 0 & h_{22} \end{bmatrix}$$

$$= \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$$

specify a whole tensor
out $\langle \text{PIK} | H | \Psi_0 \rangle$

$$u + u =$$

Ciphre

A hand-drawn diagram illustrating atomic orbitals (AOs) for a molecule. The diagram shows a grid of AOs arranged in rows and columns, representing different atomic species.

- Rows:**
 - The first row contains four AOs labeled **open**, **1p1h**, **2p2h**, and **3p3h.. NpNh**.
 - The second row contains three AOs labeled **2p2h**, **3p3h**, and **- - -**.
 - The third row contains two AOs labeled **1p1h** and **2p2h**.
 - The fourth row contains one AO labeled **3p3h**.
 - The fifth row contains one AO labeled **open**.
- Columns:**
 - The first column contains three AOs labeled **open**, **2p2h**, and **3p3h**.
 - The second column contains three AOs labeled **1p1h**, **3p3h**, and **- - -**.
 - The third column contains two AOs labeled **2p2h** and **1p1h**.
 - The fourth column contains one AO labeled **2p2h**.
- AO Labels:**
 - open**: Represented by an empty circle.
 - 1p1h**: Represented by a circle with a cross inside.
 - 2p2h**: Represented by a circle with a tilde (~) above it.
 - 3p3h.. NpNh**: Represented by a circle with a tilde (~) above it and a dash (-) below it.
 - 3p3h**: Represented by a circle with a tilde (~) above it and a dash (-) below it.
 - 1p1h**: Represented by a circle with a tilde (~) above it and a dash (-) below it.
 - 2p2h**: Represented by a circle with a tilde (~) above it and a dash (-) below it.
 - 3p3h**: Represented by a circle with a tilde (~) above it and a dash (-) below it.
 - open**: Represented by an empty circle.
- Red Boxes:**
 - A red box encloses the first four AOs in the first column (labeled **open**, **2p2h**, **3p3h**, and **1p1h**).
 - A red box encloses the first three AOs in the second column (labeled **1p1h**, **3p3h**, and **- - -**).
 - A red box encloses the first two AOs in the third column (labeled **2p2h** and **1p1h**).
 - A red box encloses the single AO in the fourth column (labeled **2p2h**).

$$\text{new } E_d^{\text{ref}} \leq \text{old } E_d^{\text{ref}}$$

$$\langle \Phi_C | H | \text{IP(4)} \rangle = \langle \Phi_C | H | \Phi_A^a \rangle$$

$$\langle \psi_0 | + | \psi_r \rangle = \langle \alpha | g | i \rangle$$

$$= \langle \alpha | h_0 | i \rangle + \sum_{j \leq F} \langle \alpha_j | v | i \rangle_{AS}$$

= 0

Standard Hartree-Fock

$$\langle \alpha | g | \alpha \rangle = \epsilon_\alpha^{HF}$$

$$\langle i | g | i \rangle = \epsilon_i^{HF}$$

$$\langle i | g | a \rangle = 0 \Rightarrow h_{|P\rangle}^{HF} = \epsilon_P^{HF}$$

$$\hat{h}^{HF} = \underbrace{\hat{h}_0}_{(\hat{t} + \hat{u}^{\text{ext}})} + \hat{u}^{HF}$$

$$\langle p | \hat{u}^{HF} | q \rangle =$$

$$\sum_{i \in F} \langle p_i | v | q_i \rangle$$

The new basis $|p\rangle$ defines a new Ref state

$$|\psi_0\rangle \Rightarrow |\psi_0^{HF}\rangle$$

$$\langle \psi_0^{HF} | H | \psi_0^{HF} \rangle \geq E_0$$

$$\langle \psi_0^{HF} | H | \psi_0^{HF} \rangle \leq$$

$$\langle \psi_0 | H | \psi_0 \rangle$$

How do we find $|P\rangle$?

Variational calculus

(i) coordinate space variation

$$|\Psi_\alpha(x)\rangle \rightarrow |\Psi_\alpha(x)\rangle +$$

$$|\delta\Psi_\alpha(x)\rangle$$

\rightarrow coupled integro-differential equations.

(ii)

variation of coefficients

$$|P\rangle = \sum_{\lambda} c_{\lambda} |\lambda\rangle$$

(iii) HF im 2nd quantization