Koopmansův ~~Hartreeho~~ ~~věta~~ teorém

~~Brillouinův teorém~~ ~~Brillouinův teorém~~

$$\varepsilon_i = \langle \chi_i | f | \chi_i \rangle = \langle i | h | i \rangle + \sum_b [ii|bb] - \sum_b [ib|bi]$$

$$\langle i | h | i \rangle + \sum_b [ii||bb]$$

Pro obsazený orbital

$$\varepsilon_a = \langle a | h | a \rangle + \sum_{b(\neq a)} [aa||bb]$$

Pro virtuální orbital

$$\varepsilon_r = \langle r | h | r \rangle + \sum_b [\cancel{aa} rr|bb]$$

$$\sum_a \varepsilon_a = \sum_a^N \langle a | h | a \rangle + \sum_{ab}^N [aa|bb] \Rightarrow \boxed{E_0 \neq \sum_a \varepsilon_a}$$

$$\boxed{E_0 = \sum_a [a|h|a] + \frac{1}{2} \sum_{ab} [aa||bb] = \sum_a \varepsilon_a - \frac{1}{2} \sum_{ab} [aa|bb]}$$

Ionizační potenciál $\boxed{IP = {}^{N-1}E_c - {}^{N}E_0}$ (kladný)

$${}^{N}E_0 = \sum_a [a|h|a] + \frac{1}{2} \sum_{a,b} [aa||bb]$$

$${}^{N-1}E_c = \sum_{a \neq c} [a|h|a] + \frac{1}{2} \sum_{a,b \neq c} [aa||bb]$$

$$IP = -[c|h|c] - \frac{1}{2} \sum_b [cc||bb] - \frac{1}{2} \sum_a [aa||cc] = -[c|h|c] - \cancel{\tfrac{1}{2}} \sum_b [cc|bb]$$

$$\boxed{IP = -\varepsilon_b}\ !$$

Elektronová afinita $\boxed{EA = {}^{N}E_0 - {}^{N+1}E_r}$

${}^{N+1}E_r$

$$\boxed{EA = -\cancel{\tfrac{1}{2}} [r|h|r] - \sum_b [rr|bb] = -\varepsilon_r}$$

Koopmansův teorém

Maticové elementy

$$\Psi_a^r = \frac{1}{\sqrt{N!}} |\chi_1(1) \ldots \chi_r(a) \ldots \chi_N(N)|$$

$$\Psi_{ab}^{rs} = \frac{1}{\sqrt{N!}} |\chi_1(1) \ldots \chi_r(a) \ldots \chi_s(b) \ldots \chi_N(N)|$$

(1) $\sum_i h(i) = \mathcal{O}_1$

(Může být libovolný 1-el. ham.!)

A) $\langle \Psi_0 | \sum_i h(i) | \Psi_0 \rangle = \sum_{a=1}^{N} \langle a | h | a \rangle$

B) $\langle \Psi_0 | \sum_i h(i) | \Psi_a^r \rangle = \frac{1}{N!} \langle \chi_1(1) \ldots \chi_a(a) \ldots \chi_N(N) | \sum_i h(i) | \chi_1(1) \ldots \chi_r(a) \ldots \chi_N(N) \rangle = \langle a | h | r \rangle$

C) $\langle \Psi_0 | \sum_i h(i) | \Psi_{ab}^{rs} \rangle = \frac{1}{N!} \langle \chi_1(1) \ldots \chi_a(a) \ldots \chi_b(b) \ldots \chi_N(N) | \sum_i h(i) | \chi_1(1) \ldots \chi_r(a) \ldots \chi_s(b) \ldots \chi_N(N) \rangle = 0$

(2) $\mathcal{O}_2 = \frac{1}{2} \sum_{ij} \frac{1}{r_{ij}}$

A) $\langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle = \frac{1}{2} \sum_{ab} [aa||bb]$ ... odvození HF rovnic

B) $\langle \Psi_0 | \mathcal{O}_2 | \Psi_a^r \rangle = \frac{1}{N!} \langle \chi_1(1) \ldots \chi_a(a) \ldots \chi_N(N) | \mathcal{O}_2 | \chi_1(1) \ldots \chi_r(a) \ldots \chi_N(N) \rangle = \sum_b [ar||bb] \cdot \frac{N(N-1)(N-2)!}{N!}$

C) $\langle \Psi_0 | \mathcal{O}_2 | \Psi_{ab}^{rs} \rangle = \frac{1}{N!} \langle \chi_1(1) \ldots \chi_a(a) \ldots \chi_b(b) \ldots \chi_N(N) | \mathcal{O}_2 | \chi_1(1) \ldots \chi_r(a) \ldots \chi_s(b) \ldots \chi_N(N) \rangle = [ar||bs] \frac{N(N-1)(N-2)!}{N!}$

D) $\langle \Psi_0 | \mathcal{O}_2 | \Psi_{abc}^{rst} \rangle = 0$

Brillouinův teorém

$$\langle \Psi_0 | \mathcal{O}_1 + \mathcal{O}_2 \equiv H | \Psi_a^r \rangle = \langle a | h | r \rangle + \sum_b [ar||bb] = \langle a | f | r \rangle = 0$$

Poruchová teorie a $H_0 - H_{HF}$

$H = H_0 + V \qquad H_0|\Psi_*^{(0)}\rangle = E^{(0)}|\Psi^{(0)}\rangle$

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \dots$$

$E_0^{(1)} = \langle\Psi^{(0)}|V|\Psi^{(0)}\rangle$; ~~$E^{(2)} =$~~ $\quad |\Psi_0^{(1)}\rangle = \sum_{n\neq 0} \frac{\langle\Psi_n^{(0)}|V|\Psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}$

$$\boxed{E_0^{(2)} = \sum_{n\neq 0} \frac{|\langle\Psi_n^{(0)}|V|\Psi_0^{(0)}\rangle|^2}{E_0^{(0)}-E_n^{(0)}} \qquad E_0^{(2)} \le 0 \ !}$$

Co bude H_0?

Hartree-Fockův hamiltonián. Máme přesný H, ale nemáme přesnou vlnovou fci Ψ. Nevyřešili jsme Schrödingerovu rovnici

$$\cancel{H|\Phi_0\rangle = E_0|\Phi_0\rangle}$$

$$H|\Phi_0\rangle = E_0|\Phi_0\rangle$$

Ale našli jsme fci Ψ, která minimalizuje energii na prostoru Slaterových determinantů. Takže otázka zní: „Existuje hamiltonián H_0, jehož vlastní fcí je Ψ?" Odpověď: „Ano".

$$H_0 = \sum_{i=1}^{N} f(i)$$

- Ψ_0 je vlastní fce s vlastním číslem $\sum_a \varepsilon_a$
- Excitované determinanty $|\Psi_{ab\dots}^{rs\dots}\rangle$ jsou vl. stavy s vl. čísly = $\sum$ orbitálních energií

$$\boxed{H = H_0 + V} \implies V = \sum_i h(i) + \frac{1}{2}\sum_{ij}\frac{1}{r_{ij}} - \sum_i f(i)$$

$$= \frac{1}{2}\sum_{ij}\frac{1}{r_{ij}} - \sum_j v_{HF}(j)$$

$$v_{HF}(i) = \sum_j J_j(i) - K_j(i)$$

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$$E_0^{(1)} = \langle \Psi | V | \Psi \rangle = \frac{1}{2} \sum_{ij} [ii|jj] - (A)$$

(A)

$$\langle \chi_1 \chi_2 | \sum_i J_i(i) | \chi_1 \ldots \chi_N \rangle \frac{1}{N} = \frac{N(N-1)!}{N!} \sum_i \langle \chi_i | J | i \rangle = \sum_{ij} [ii|jj]$$

K

$$= \sum \sum_{ij} [ij|ji]$$

$$\boxed{E_0^{(1)} = -\frac{1}{2} \sum_{ij} [ii|jj]}$$

! kompenzuje 2-násobnou ~~elektron~~ repulzi

$$E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle \Psi_0^{(0)} | V | \Psi_n^{(0)} \rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$

Jaké $|\Psi_n^{(0)}\rangle$ přispívají ?

Single excitace .. $\langle \Psi_0 | H - H_0 | \Psi_a^r \rangle =$

$$= \underbrace{\langle \Psi_0 | H | \Psi_a^r \rangle}_{0 \ (BT)} - \underbrace{\langle \Psi_0 | H_0 | \Psi_a^r \rangle}_{\langle a | f | r \rangle} = 0$$

Triple excitace .. ne

Double excitace

$$E_0^{(2)} = \sum_{\substack{a<b \\ r<s}} \frac{|\langle \Psi_0 | \frac{1}{r_{12}} | \Psi_{ab}^{rs} \rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b} = \sum_{\substack{a<b \\ r<s}} \frac{[ar|bs]^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$

Møller - Plessetova ~~[illegible]~~ perturbační teorie

(MP2)