

Koopmans'ska teorema ~~je~~ korisna | III - 1
~~Brillouinova~~ Brillouinova teorema

$$\epsilon_i = \langle \chi_i | \hat{H} | \chi_i \rangle = \langle a | \hat{H} | a \rangle + \sum_b [a | \hat{H} | b] - \sum_b [a | b | b] \\
\langle a | \hat{H} | a \rangle + \sum_b [a | \hat{H} | b] b$$

Pro obscureni orbital

$$\epsilon_a = \langle a | \hat{H} | a \rangle + \sum_{b \neq a} [a a | b b]$$

Pro virtuelni orbital

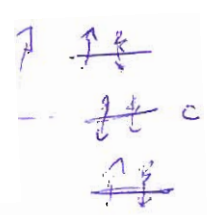
$$\epsilon_b = \langle b | \hat{H} | b \rangle + \sum_b [a a | b b]$$

$$\sum_a \epsilon_a = \sum_a \langle a | \hat{H} | a \rangle + \sum_{a,b} [a a | b b] \Rightarrow \boxed{E_0 + \sum_a \epsilon_a}$$

$$\boxed{E_0 = \sum_a [a | \hat{H} | a] + \frac{1}{2} \sum_{a,b} [a a | b b] = \sum_a \epsilon_a - \frac{1}{2} \sum_{a,b} [a a | b b]}$$

Ionska potencijal $IP = \left[\begin{matrix} N-1 \\ E_c \end{matrix} - \begin{matrix} N \\ E_0 \end{matrix} \right]$ (kladno)

$$E_0 = \sum_a [a | \hat{H} | a] + \frac{1}{2} \sum_{a,b} [a a | b b]$$

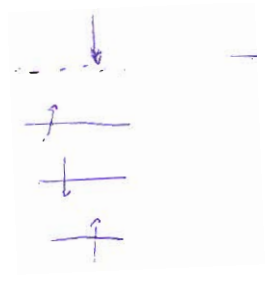


$$E_c = \sum_{a \neq c} [a | \hat{H} | a] + \frac{1}{2} \sum_{a,b,c} [a a | b b]$$

$$IP = - [c | \hat{H} | c] - \frac{1}{2} \sum_b [c c | b b] - \frac{1}{2} \sum_a [a a | c c] = - [c | \hat{H} | c] - \sum_b [c c | b b]$$

$$\rightarrow IP = - \epsilon_b$$

Elektronski afinitet $EA = \left[\begin{matrix} N \\ E_0 \end{matrix} - \begin{matrix} N+1 \\ E_r \end{matrix} \right]$



$$\rightarrow EA = - [r | \hat{H} | r] - \sum_b [r r | b b] = - \epsilon_r$$

Koopmans'ska teorema

Kalibrose' elementy

$$\Psi_a^r = \frac{1}{N!} |\chi_1(i), \chi_r(a), \dots, \chi_N(N)|$$

$$(1) \sum_i h(i) = \sigma_1$$

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

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

(Může být libovolný 1-el. ham.)

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

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

$$(2) \sigma_2 = \frac{1}{2} \sum_{ij} \frac{1}{r_{ij}}$$

$$(1) \langle \Psi_0 | \sigma_2 | \Psi_0 \rangle = \frac{1}{2} \sum_{a,b} [a a | b b] \quad \text{odvození HF rovnice}$$

$$B) \langle \Psi_0 | \sigma_2 | \Psi_a^r \rangle = \frac{1}{N!} \langle \chi_1(i), \chi_a(a), \dots, \chi_N(N) | \sigma_2 | \chi_1(i), \dots, \chi_r(a), \dots, \chi_N(N) \rangle = \sum_b [a r | b b] \cdot \frac{N(N-1)(N-2)!}{N!}$$

$$C) \langle \Psi_0 | \sigma_2 | \Psi_{ab}^{rs} \rangle = \frac{1}{N!} \langle \chi_1(i), \chi_a(a), \chi_b(b), \dots, \chi_N(N) | \sigma_2 | \chi_1(i), \chi_r(a), \chi_s(b), \dots, \chi_N(N) \rangle = [a r | b s] \cdot \frac{N(N-1)(N-2)!}{N!}$$

$$D) \langle \Psi_0 | \sigma_2 | \Psi_{abc}^{rst} \rangle = 0$$

Brilloinův teorém

$$\langle \Psi_0 | \sigma_1 + \sigma_2 \equiv H | \Psi_a^r \rangle = \langle a | h | r \rangle + \sum_b [a r | b b] = \langle a | f | r \rangle = 0$$

$$H = H_0 + V$$

$$H_0 | \Psi_0^{(0)} \rangle = E_0^{(0)} | \Psi_0^{(0)} \rangle$$

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

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

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

Co bude H_0 ?

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

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

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

Ne máme ještě nějakou funkci Ψ , která minimalizuje energii na prostoru Slaterových determinantů. Takže otázka zní: „Existuje hamiltonián H_0 , kterého vlastními jsou Ψ ?“ Odpověď: „Ano“.

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

- Φ_0 je vlastní funkce s vlastním číslem $\sum_a \epsilon_a$
- Existenci determinantu $|\Psi_{HF}^{(0)}\rangle$ jsou d. slaj s il. čísly = \sum orbitálních energií

$$H = H_0 + V$$

$$\Rightarrow V = \sum_i h(i) + \frac{1}{2} \sum_{i,j} \frac{1}{r_{ij}} - \sum_j f(j)$$

$$= \frac{1}{2} \sum_{i,j} \frac{1}{r_{ij}} - \sum_j \frac{1}{r_{HF}(j)} \quad \text{--- } \sum_j \frac{1}{r_{HF}(j)}$$

$$V_{HF}^{(0)} = \sum_j J_j(i) - K_j(i)$$

$$E_0^{(1)} = \langle \Psi_0 | V | \Psi_0 \rangle = \frac{1}{2} \sum_{ij} [u_i | v_j] - \textcircled{A}$$

①

$$\langle \Psi_0 | \sum_{ij} J_{ij}(\hat{n}_i) | \Psi_0 \rangle = \frac{1}{N!} = \frac{N(N-1)!}{N!} \sum_{ij} \langle \Psi_0 | J_{ij} | \Psi_0 \rangle = \sum_{ij} [u_i | v_j] = \sum_{ij} [v_j | u_i]$$

$$E_0^{(1)} = - \frac{1}{2} \sum_{ij} [u_i | v_j]$$

! kompenzace 2-měsítnou částou repulze

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

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

Single excitation ... $\langle \Psi_0 | H - H_0 | \Psi_a^v \rangle =$
 $= \langle \Psi_0 | H | \Psi_a^v \rangle - \langle \Psi_0 | H_0 | \Psi_a^v \rangle = 0$
 0 (BT) < a | f | b >

Triple excitation ... ne

Double excitation

$$E_0^{(2)} = \sum_{\substack{a < b \\ r < s}} \frac{K \Psi_0 | \frac{1}{E_2} | \Psi_{ab}^{rs} \rangle^2}{E_r + E_s - E_a - E_b} = \dots \frac{[a | f | b]^2}{E_r + E_s - E_a - E_b}$$

Møller - Plessetova ~~per~~ pertrubační teorie (MP2)