

KOOPMAN'S THEOREMS

Back to HF equations

$$(\hat{h} + \hat{J} - \hat{K}) |\varphi_i\rangle = \epsilon_i |\varphi_i\rangle$$

$$\langle \vec{r} | \hat{J} | \varphi_i \rangle = \sum_{j=1}^N \int d^3r' \frac{\varphi_j(\vec{r}') \varphi_j^*(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad \rho_i(\vec{r}) = \int d^3r' \frac{|\varphi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} \varphi_i(\vec{r})$$

If  $j=i$  we have a term that describes self-repulsion!

$$\rho(\vec{r}') = \sum_{j=1}^N |\varphi_j(\vec{r}')|^2$$

Density contains contribution of the orbital  $\varphi_i$

$$\langle \vec{r} | \hat{J} | \varphi_i \rangle = \sum_{j=1}^N \langle \vec{r} | \hat{J}_j | \varphi_i \rangle, \text{ where } \hat{J}_j = \int d^3r' \frac{|\varphi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|}$$

The self-repulsion is removed by the exchange term

$$\langle \vec{r} | \hat{K} | \varphi_i \rangle = \sum_{j=1}^N \int d^3r' \frac{\varphi_i(\vec{r}') \varphi_j^*(\vec{r}')}{|\vec{r} - \vec{r}'|} \varphi_j(\vec{r}) \delta_{i,j}$$

for  $j=i$  we have  $\int d^3r' \frac{|\varphi_i(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} \varphi_i(\vec{r})$

Koopman's theorems

$$|i\rangle \equiv |\varphi_i\rangle$$

$$\epsilon_i = \langle i | \hat{f} | i \rangle = \langle i | \hat{h} + \hat{J} - \hat{K} | i \rangle = \langle i | \hat{h} | i \rangle + \underbrace{\sum_j [i i | j j] - \sum_j [i j | j i]}_{\sum_j [i i || j j]}$$

Occupied orbitals : a, b, c, d, ...

Virtual orbitals : r, s, t, u, ...

HF energy

$$\sum_a \epsilon_a = \sum_{a=1}^N \langle a | \hat{h} | a \rangle + \sum_{a,b=1}^N [a a || b b] \Rightarrow E_0 + \sum_a \epsilon_a$$

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

Why?

2-electron interaction is counted twice in the sum of the orbital energies  $\sum_a \epsilon_a$

# Ionization potential

Definition

$$IP = E_{c}^{N-1} - E_0^N$$

taking the electron from the occupied orbital  $\psi_c$

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

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

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

$$IP = -\epsilon_c$$

The term  $[cc||cc]$  is not counted twice (wrongly), but luckily  $[cc||cc] = 0$

# Electron affinity

Definition

$$EA = E_0^N - E_r^{N+1}$$

Positive if the anion is more stable

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

$$E_r^{N+1} = \sum_a \langle a|h|a \rangle + \langle r|h|r \rangle + \frac{1}{2} \sum_{a,b} [aa||bb] + \frac{1}{2} \sum_b [rr||bb] + \frac{1}{2} \sum_a [aa||rr]$$

$$EA = -\langle r|h|r \rangle - \sum_b [rr||bb] = -\epsilon_r$$

$$EA = -\epsilon_r$$

by Roman Čurík

SLATER - CONDON RULES

Matrix elements of 1-electron (1-body) and 2-electron (2-body) operators and HF, single-, double- excited wave-functions

Single excitation  $\Psi_a^r \equiv \frac{1}{\sqrt{N!}} |\varphi_1(1) \dots \varphi_{a-1}(a-1) \varphi_r(a) \varphi_{a+1}(a+1) \dots \varphi_N(N)|$

Double excitation  $\Psi_{ab}^{rs} \equiv \frac{1}{\sqrt{N!}} |\varphi_1(1) \dots \varphi_r(a) \dots \varphi_s(b) \dots \varphi_N(N)|$

① 1-electron operator:  $\hat{\sigma}_1 = \sum_{i=1}^N f(i)$

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

B.)  $\langle \Psi_0 | \sum_{i=1}^N f(i) | \Psi_a^r \rangle = \frac{1}{N!} \langle \varphi_1(1) \dots \varphi_a(a) \dots \varphi_N(N) | \sum_{i=1}^N f(i) | \varphi_1(1) \dots \varphi_r(a) \dots \varphi_N(N) \rangle = \langle a | f | r \rangle$

C.)  $\langle \Psi_0 | \sum_{i=1}^N f(i) | \Psi_{ab}^{rs} \rangle = \frac{1}{N!} \langle \varphi_1(1) \dots \varphi_a(a) \dots \varphi_b(b) \dots \varphi_N(N) | \sum_{i=1}^N f(i) | \varphi_1(1) \dots \varphi_r(a) \dots \varphi_s(b) \dots \varphi_N(N) \rangle = 0$

② 2-electron operator:  $\hat{\sigma}_2 \equiv \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$

A)  $\langle \Psi_0 | \hat{\sigma}_2 | \Psi_0 \rangle = \frac{1}{2} \sum_{a,b} [aa || bb]$  ... Derivation of the energy functional & HF equations

B.)  $\langle \Psi_0 | \hat{\sigma}_2 | \Psi_a^r \rangle = \frac{1}{N!} \langle \varphi_1(1) \dots \varphi_a(a) \dots \varphi_N(N) | \sum_{\substack{i < j \\ i \neq j}} \frac{1}{r_{ij}} | \varphi_1(1) \dots \varphi_r(a) \dots \varphi_N(N) \rangle = \sum_b [ar || bb] \frac{N(N-1)(N-2)!}{N!}$

C.)  $\langle \Psi_0 | \hat{\sigma}_2 | \Psi_{ab}^{rs} \rangle = \frac{1}{N!} \langle \varphi_1(1) \dots \varphi_a(a) \dots \varphi_b(b) \dots \varphi_N(N) | \sum_{\substack{i < j \\ i \neq j}} \frac{1}{r_{ij}} | \varphi_1(1) \dots \varphi_r(a) \dots \varphi_s(b) \dots \varphi_N(N) \rangle = [ar || bs] \frac{N(N-1)(N-2)!}{N!}$

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

BRILLOIN'S THEOREM

$\langle \Psi_0 | \underbrace{\sum_{i=1}^N h(i)}_{H_{el}} + \sum_{i < j} \frac{1}{r_{ij}} | \Psi_a^r \rangle = \langle a | h | r \rangle + \sum_b [ar || bb] = \langle a | f | r \rangle = 0$

Basics of the perturbation theory

Full Hamiltonian  $H = H_0 + V$  — perturbation

↑  
unperturbed  
Hamiltonian

Unperturbed eigenstates  $\psi_n^{(0)}$ :

$$H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$$

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

$$|\psi\rangle = |\psi^{(0)}\rangle + |\psi^{(1)}\rangle + |\psi^{(2)}\rangle + \dots$$

$$H|\psi\rangle = E|\psi\rangle$$

Known results

- $E^{(1)} = \langle \psi^{(0)} | V | \psi^{(0)} \rangle$  with  $\langle \psi^{(0)} | \psi^{(0)} \rangle = 1$
- $E^{(2)} = \sum_{n \neq 0} \frac{|\langle \psi_n^{(0)} | V | \psi^{(0)} \rangle|^2}{E^{(0)} - E_n^{(0)}} \leq 0!$
- $|\psi^{(1)}\rangle = \sum_{n \neq 0} \frac{\langle \psi_n^{(0)} | V | \psi^{(0)} \rangle}{E^{(0)} - E_n^{(0)}} |\psi_n^{(0)}\rangle$

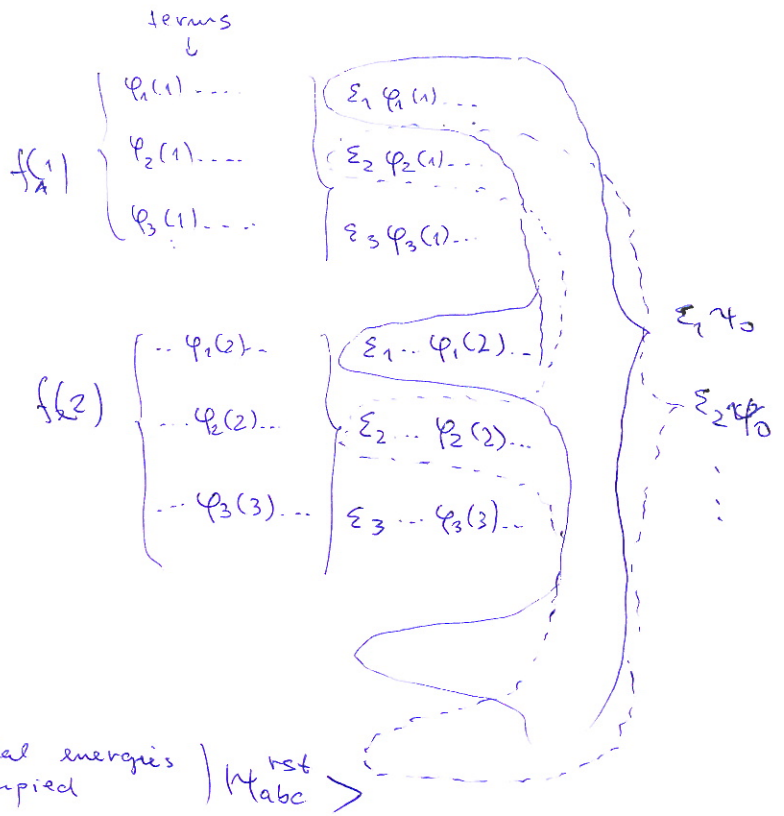
Our goal is to apply this perturbation theory to obtain "a correction to HF energy". This correction is defined as "correlation energy" as it accounts for an error brought by the product of 1-electron spinorbitals. For the perturbation theory we need eigenstates of the unperturbed Hamiltonian  $H_0$ . HF theory gives approximate states to the exact Hamiltonian  $H$ . Is there an exact Hamiltonian  $H_0$  with eigenstates formed by the Slater determinants?

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

- It is not trivial to see that

$$H_0 |\psi_0\rangle = \left( \sum_a \epsilon_a \right) \psi_0$$

Proof:  $\sum_{i=1}^N f(i) |\varphi_1(i) \dots \varphi_n(i)\rangle =$



- Generally  $H_0 |\psi_{abc}^{rst}\rangle = \left( \sum_{\text{occupied}} \text{orbital energies} \right) |\psi_{abc}^{rst}\rangle$

- Single, Double, Triple ... excitations form the excited space of  $H_0$

$$H = H_0 + V$$

$$\Rightarrow V = H - H_0 = \sum_{i=1}^N h(i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} - \sum_i f(i)$$

$$= \frac{1}{2} \sum_{i \neq j} \left( \sum_{\mu} J_{\mu}(ij) + \sum_{\mu} K_{\mu}(ij) \right)$$

Zeroth order

$$E^{(0)} = \sum_{a=1}^N \epsilon_a \neq \text{HF energy!}$$

First order

$$E^{(1)} = \langle \psi^{(0)} | V | \psi^{(0)} \rangle = \frac{1}{2} \sum_{ij} [i i || j j] - \textcircled{A}$$

$$\textcircled{A} = \langle \psi^{(0)} | \sum_{i=1}^N \sigma_i^{ii} | \psi^{(0)} \rangle = \sum_{j=1}^N \langle j | J | j \rangle - \langle j | K | j \rangle = \sum_{ij} [i i || j j]$$

$$\left( E^{(1)} = -\frac{1}{2} \sum_{ij} [i i || j j] \right) \Rightarrow E^{(0)} + E^{(1)} = \text{HF energy}$$

## Second order

$$E^{(2)} = \sum_{n \neq 0} \frac{|\langle \psi_n^{(0)} | V | \psi_0^{(0)} \rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$

What excited states <sup>of  $H_0$</sup>  contribute to the sum "n" over the excited states?

A.) Single excited determinants

$$\langle \psi^{(0)} | H - H_0 | \psi_a^r \rangle =$$

$$= \underbrace{\langle \psi^{(0)} | H | \psi_a^r \rangle}_0 \text{ from } B^\dagger - \underbrace{\langle \psi_0 | H_0 | \psi_a^r \rangle}_{\langle a | f | r \rangle} = 0$$

B.) Double excitations

$$\sum_{\substack{a < b \\ r < s}} \frac{|\langle \psi^{(0)} | \sum_{i,j,r,s} \frac{1}{i!j!r!s!} + \dots | \psi_{ab}^{rs} \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} = \sum_{\substack{a < b \\ r < s}} \frac{[a_r || b_s]^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

C.) Triple excitations

= 0 ; Two-electron operator does not couple triple excitations and the ground state

$$E^{(2)} = \sum_{\substack{a < b \\ r < s}} \frac{[a_r || b_s]^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$