

2017 by Roman Čurík

Method of Configuration InteractionSimple examples of HF failure

- dissociation of  $H_2$
- ionization of  $N_2$
- existence of  $H^-$

Correlation energy  $E_{cor} \equiv E - E^{HF}$  (nonrelativistic)

HF is a variational method with an exact nonrelativistic electronic Hamiltonian on a poor set of Slater determinands.

→ HF gives the upper guess of the energy →  $E_{cor} \leq 0$

(equality in a case of 1-electron system)

Idea of Configuration Interaction

- HF <sup>spin</sup> orbitals form a complete basis set in 1-electron Hilbert space  $H$  of dimension  $2K$ .  $N$ -tuple direct product of this basis forms a basis in  $\underbrace{H \times H \times \dots \times H}_{N \times}$ . Here  $N$  is the number of electrons.

- From this  $N$ -order direct product of the HF spin-orbitals we choose a subset satisfying the Pauli exclusion principle. Namely, the anti-symmetric basis set products without repeated 1-electron basis elements (spin-orbitals). These are exactly excited Slater

determinands of HF spinorbitals (occupied + virtual).

We have  $\binom{2K}{N}$  of such configurations.

- However, we define an "order of importance" on the product basis set elements. This order comes in form of groups according to the number of excitations.

$$\{B\}_N = |\psi_0\rangle \cup |\psi_a^r\rangle \cup |\psi_{ab}^{rs}\rangle \cup |\psi_{abc}^{rst}\rangle \cup \dots$$

reference
single excitations
double excitations
triple excitations
...

- Emphasize that CI uses 2 different ordering at different levels:

- Ordering of 1-electron basis according to 1-electron mean energy (in contrast to simple GS-orthogonalization)
- Ordering of N-products where we assume singly excited determinands more important than triply excited ...

- With this N-electron basis set the CI ground state can be written:

$$|\psi_0\rangle = c_0 |\psi_0\rangle + \sum_{ar} c_a^r |\psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst} |\psi_{abc}^{rst}\rangle + \dots$$

$$|\psi_0\rangle = c_0 |\psi_0\rangle + \sum_{ar} c_a^r |\psi_a^r\rangle + \left(\frac{1}{2!}\right)^2 \sum_{\substack{a,b \\ r,s}} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle + \left(\frac{1}{3!}\right)^2 \sum_{\substack{a,b,c \\ r,s,t}} c_{abc}^{rst} |\psi_{abc}^{rst}\rangle + \dots$$

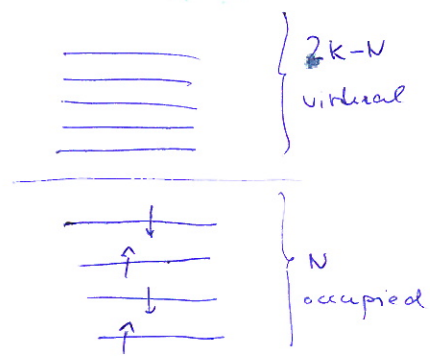
- How many of m-order excitations do we have?

(N = number of electrons, 2K basis spin-determinands)

$$= \binom{N}{m} \binom{2K-N}{m}$$

number of possibilities to choose m-electrons from N occupied orbitals

Number of possibilities to put m-electrons into 2K-N virtual orbitals



Method of CI  
(continued)

Variations with respect to  $c_0, c_a^r, c_{ab}^{rs}, c_{abc}^{rst}, \dots$  coefficients leads to diagonalization of the CI Hamiltonian matrix:

$$|\phi_0\rangle = c_0|0\rangle + c_s|S\rangle + c_D|D\rangle + c_T|T\rangle + \dots$$

CI Hamiltonian

HF theory	$\langle 0 H 0\rangle$	0	$\langle 0 H D\rangle$	0	0	0
CIS <small>only used for inaccurate excited states</small>	0	$\langle S H S\rangle$	$\langle S H D\rangle$	$\langle S H T\rangle$	0	0
CISD (most common CI method)	$\langle D H 0\rangle$	$\langle D H S\rangle$	$\langle D H D\rangle$	$\langle D H T\rangle$	$\langle D H R\rangle$	0
CISDT	0	$\langle T H S\rangle$	$\langle T H D\rangle$	$\langle T H T\rangle$	$\langle T H Q\rangle$	...
↓ Full CI	0	0	$\langle Q H D\rangle$	$\langle Q H T\rangle$	$\langle Q H Q\rangle$	
	0	0				

Two variants of the CI idea:

CAS CI and MCSCF

1.) CAS CI

one-electron basis (the set of HF orbitals) is severely reduced. This defines the active space. Then the FCI is carried out in the resulting active space.

CAS CI = complete active space CI.

2.) MCSCF (Multi-configuration self-consistent field)

$$|\Psi_{MCSCF}\rangle = \sum_I C_I |\Psi_I\rangle$$

$|\Psi_I\rangle$  are excited determinands in ~~an~~ <sup>the</sup> active space. Active space is again a reduced 1-electron set of HF orbitals. In contrast to CASCI, where the excited determinands are fixed, in MCSCF method also the ~~the~~ 1-electron basis <sup>forming</sup> ~~in~~ the active space is optimized.

- New  $C_I$  coefficients
- CI coefficients give HF equations
- New  $\varphi_i$  from HF
- New  $|\Psi_I\rangle$ , new FCI matrix
- New CI after the FCI diagonalization

Note: MCSCF has more applications:

- 1.) It gives decent results on its own
- 2.) It is used to generate reduced density matrix, that can be diagonalized  $\rightarrow$  natural orbitals. These orbitals can define a different excitation space (instead of the canonical HF orbitals) for a following CISD calculations. The convergence is usually faster in the natural orbitals.