Coupled Cluster (CC)

(1966 – Jiří Čížek, Josef Paldus)

$$|\Psi\rangle = e^{\hat{\mathbf{T}}} \,|\, \Psi_{HF}\rangle \qquad \hat{\mathbf{T}} = \hat{\mathbf{T}}_1 + \hat{\mathbf{T}}_2 + \hat{\mathbf{T}}_3 \ \ldots \ \hat{\mathbf{T}}_N \qquad e^{\hat{\mathbf{T}}} = 1 + \hat{\mathbf{T}} + (2!)^{-1}\hat{\mathbf{T}}^2 + (3!)^{-3}\hat{\mathbf{T}}^3 + \ldots = \sum_k^{\infty} \frac{\hat{\mathbf{T}}^k}{k!}$$

Wave function "Exponential Ansatz"

Excitation operator

Taylor expansion

$$|\Psi\rangle = (1 + \hat{\mathbf{T}} + \frac{1}{2}\hat{\mathbf{T}}^2 + \frac{1}{3!}\hat{\mathbf{T}}^3 + \ldots)\,|\,\Psi_{HF}\rangle$$

Eg., double excitation

$$\hat{\mathbf{T}}_2\Psi = \sum_i \sum_{j<i} \sum_a \sum_{b<a} t_{ij}^{ab} \Psi_{ij}^{ab}$$

$$\hat{\mathbf{T}}_2^2\Psi = \hat{\mathbf{T}}_2 \left(\sum_i \sum_{j<i} \sum_a \sum_{b<a} t_{ij}^{ab} \Psi_{ij}^{ab} \right)$$

$$= \sum_i \sum_{j<i} \sum_k \sum_{l<k} \sum_a \sum_{b<a} \sum_c \sum_{d<c} t_{ij}^{ab} t_{kl}^{cd} \Psi_{ijkl}^{abcd}$$

CID $\Phi^{CID} = (1 + \hat{T}_2)\Psi_{HF}$

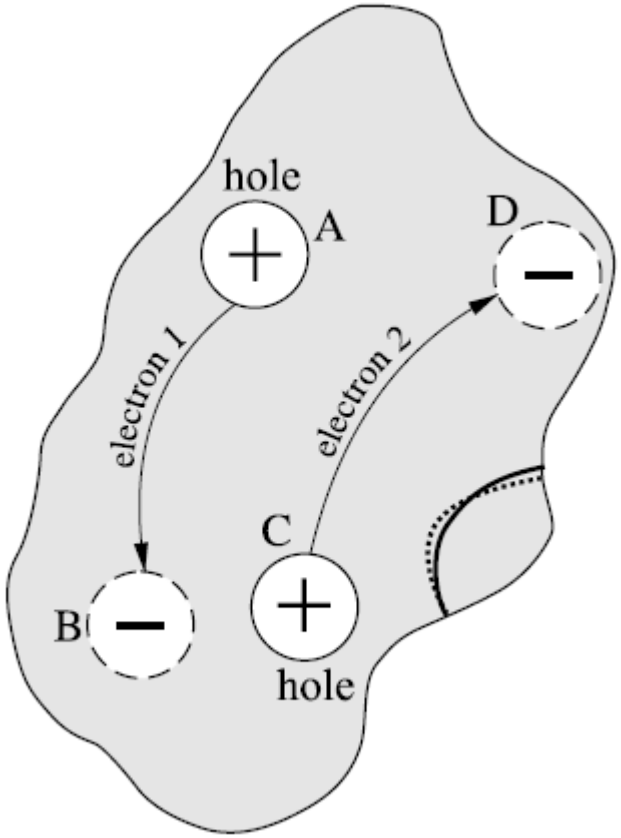
CCD $\Phi^{CCD} = (1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2)\Psi_{HF}$

Makes it size-consistent !

Pro systémy nekonečně vzdálené: $\hat{T} = \hat{T}_A + \hat{T}_B$

$$\left(\hat{T}_A + \hat{T}_B\right)\Phi_0$$

$$\left[\exp\left(\hat{T}_A + \hat{T}_B\right)\right]\Phi_0 = \exp(\hat{T}_A)\exp(\hat{T}_B)\Phi_0$$



Dominantní část elektronové korelace je v interakci mezi elektrony v rámci jednoho kanonického (HF) orbitalu.

- předpokládáme že orbitaly jsou (částečně) lokalizovány
- excitace z orbital *i* do *r* odpovídá přenosu náboje
- vytvoření páru elektron-díra
- monoexcitace – korelační energii nepřinese
- diexcitace – tak jak znázorněno – rozhodující vliv
- obdobně pro tetraexcitace – elektronový pár z A do B a zároveň druhý elektronový pár z C do D
- coupled clusters – vybírají právě takovéto zpřažené excitace

L. Piela: Ideas of Quantum Chemistry

CCSD
CCSD(T), CCSDT

- quite precise
- size consistent
- best routine method for description of dynamic el. correlation

QCISD(T) - neglects some of T_1T_2 cross-terms - only small computer saving, lost of accuracy

PERTURBATION THEORY

Rayleigh-Schrödinger formulation (non-degenerate systems)

System of interest: $\hat{H}\Psi_n = E_n\Psi_n$

"Reference" (known) system: $\hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$

Perturbation (small !): $\hat{V} \equiv \hat{H}' = \hat{H} - \hat{H}_0$

Introducing an ordering parameter λ and expand eigenfunctions and eigenvalues in Taylor series:

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

$$\Psi_n = \Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} + \cdots$$

$$\Psi_n^{(k)} = \frac{1}{k!}\frac{\partial^k \Psi_n}{\partial\lambda^k}\Big|_{\lambda=0} \qquad E_n^{(k)} = \frac{1}{k!}\frac{\partial^k E_n}{\partial\lambda^k}\Big|_{\lambda=0}$$

$$\hat{H}_0\Psi_n^{(0)} + \lambda(\hat{H}'\Psi_n^{(0)} + \hat{H}_0\Psi_n^{(1)}) + \lambda^2(\hat{H}'\Psi_n^{(1)} + \hat{H}_0\Psi_n^{(2)}) + \cdots =$$
$$= E_n^{(0)}\Psi_n^{(0)} + \lambda(E_n^{(1)}\Psi_n^{(0)} + E_n^{(0)}\Psi_n^{(1)}) + \lambda^2(E_n^{(2)}\Psi_n^{(0)} + E_n^{(1)}\Psi_n^{(1)} + E_n^{(0)}\Psi_n^{(2)}) + \cdots$$

Results cannot depend on λ ⟶ independent equations for each λ^k

Using "intermediate normalization" + additional manipulation:

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$$

$$E_n^{(1)} = \left\langle \Psi_n^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| \left\langle \Psi_m^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)} + \Psi_n^{(2)} + \cdots$$

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| \hat{H}' \middle| \Psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} \Psi_m^{(0)}$$

PT for electron correlation - Moller-Plesset formulation

$$\hat{H}^0 = \sum_{i=1} \hat{F}(i) = \sum_{i=1}^{n} \left(h(i) + v^{HF}(i) \right)$$

$$\Psi_0^{(0)} \equiv \Psi^{HF}$$

$\Psi_n^{(0)}$ … all possible Slater det. From Fock orbitals

Perturbation $\hat{H}' = \sum_{i<j} r_{ij}^{-1} - \sum_i v^{HF}(i)$

Limited to double excitations !

$$E_0^{(0)} = \sum_{i=1} \varepsilon_i \qquad E_0^{(0)} + E_0^{(1)} = E_{HF}$$

$$E^{MP2} = \underbrace{E^{(0)} + E^{(1)}}_{=E^{HF}} + E^{(2)} = E^{HF} + \sum_a^{occ} \sum_b^{occ} \sum_r^{virt} \sum_s^{virt} \frac{\left| \langle ab \mid rs \rangle - \langle ab \mid sr \rangle \right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

Size-consistent (*linked-cluster theorem*), nonvariational
MP2, MP3, MP4
MP2 - cheapest post-HF method for electron correlation
Most popular method

Can be close to 0 !