Electron Correlation Methods

HF method: electron-electron interaction is replaced by an average interaction

$$E_c^{HF} = E_0 - E_{HF}$$

E_0 – exact ground state energy
E_{HF} – HF energy for a given basis set

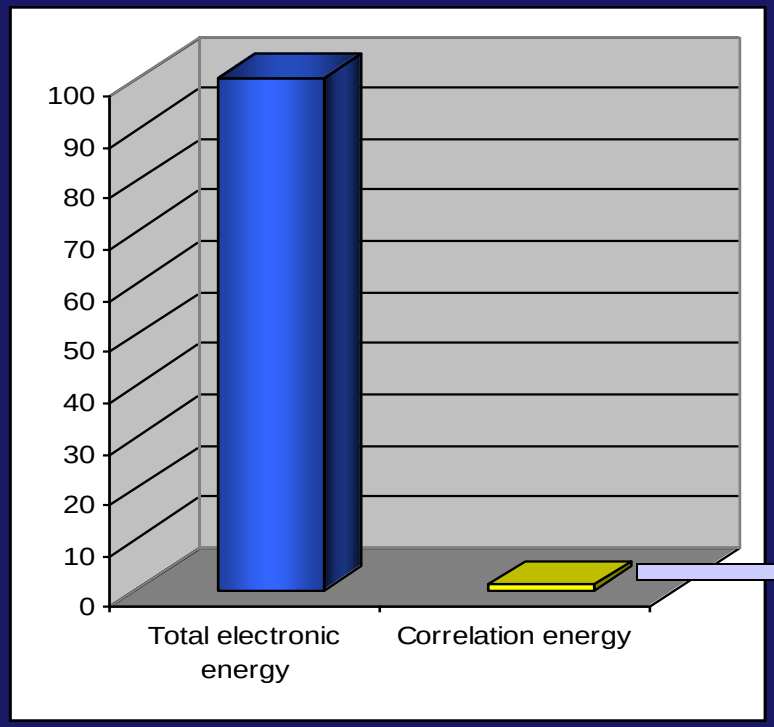
→ $E_c^{HF} < 0$ - represents a measure for the error introduced by the HF approximation

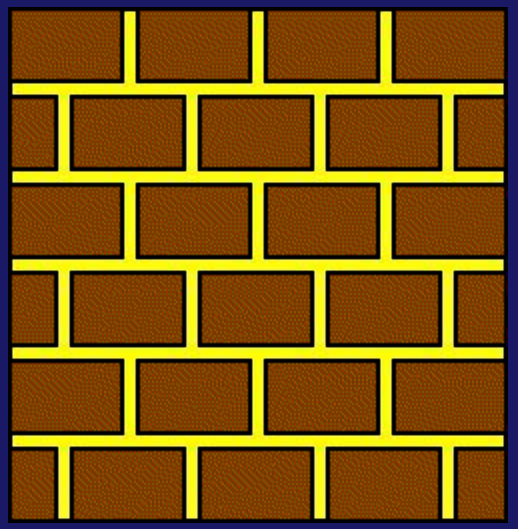
Dynamical correlation – related to the movements of the individual electrons
- short range effect
- due the overestimation of short-range electron repulsions in Hartree-Fock wavefunctions

Non-dynamical correlation - related to the fact that in certain circumstances the single reference ground state ψ^{SD} wave-function is inadequate to describe a given molecular state (i.e. in the case of near degeneracy between different configurations)
- long range effect

Frank Jensen, Introduction to Computational Chemistry, John Wiley and Sons, New York, 1999

Correlation Energy: Is it important?



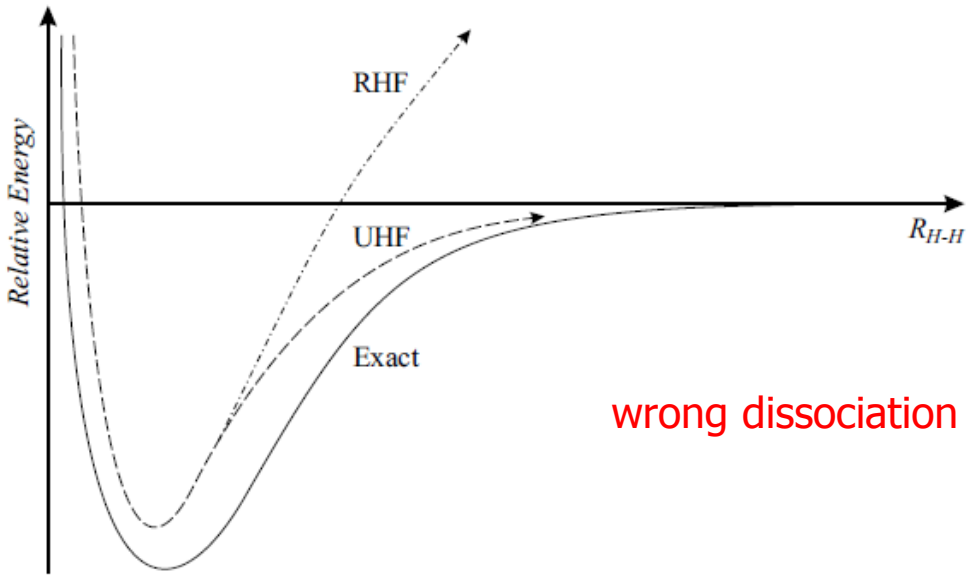


N_2 molecule:

CE ~ 0.5% of the EE

~ 50% of the binding energy!

Long-range correlation



wrong dissociation behavior for RHF wavefunction!

Potential energy curves for H_2 molecule

$$\Psi_X = \hat{\mathcal{A}}\sigma_g^\alpha(1)\sigma_g^\beta(2)$$

where $\sigma_g = N_g(s_A + s_b)$

Thus:

$$\Psi_X \sim \frac{1}{2}\hat{\mathcal{A}}\left(1s_A^\alpha 1s_B^\beta + 1s_B^\alpha 1s_A^\beta + 1s_A^\alpha 1s_A^\beta + 1s_B^\alpha 1s_B^\beta\right)$$

the first 2 terms: 2 neutral H atoms
last 2 terms: ionic terms; due to these terms the interaction energy is overestimated

Let' consider one of the excited state of H_2 in which the two electrons are in the antibonding σ_u orbital:

$$\Psi_E = \hat{\mathcal{A}}\sigma_u^\alpha(1)\sigma_u^\beta(2)$$

where: $\sigma_u = N_u(s_A - s_B)$

$$\Psi_E \sim \tfrac{1}{2}\hat{\mathcal{A}}\left(1s_A^\alpha 1s_B^\beta + 1s_B^\alpha 1s_A^\beta - 1s_A^\alpha 1s_A^\beta - 1s_B^\alpha 1s_B^\beta\right)$$

Ψ_E also contains the unphysical mixture of covalent and ionic terms.

Now, let's combine linearly Ψ_X with Ψ_E:

⇨ purely ionic or purely covalent wavefunctions:

For the $\Psi_X - \Psi_E = \sigma_g^2 - \sigma_u^2$, combination, the ionic terms cancel exactly, and the correct asymptotic wavefunction is obtained.

This is a configuration interaction whereby the wavefunction is considered as being a mixture of several Slater determinants. For H_2 at general internuclear separations, the form of the CI wavefunction is

$$\Psi = c_X\Psi_X + c_E\Psi_E$$

The coefficients specifying this linear combination must be allowed to vary, since it is known that near equilibrium, the RHF wavefunction is already a good approximation.

→ multideterminantal wave-function

$$\Psi = a_0\Psi^{HF} + \sum_i a_i\Psi_i$$

usually $a_0 \approx 1$

Short-range correlation

Consider the Hamiltonian for He atom:

$$\hat{H} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

Close to $r_{12} = 0$, the term $1/r_{12}$ becomes infinite; however, the energy is finite.

there must be an additional singularity in the Hamiltonian which cancels $1/r_{12}$ term for $r_{12} \approx 0$. The only candidate for this canceling term is the kinetic energy.

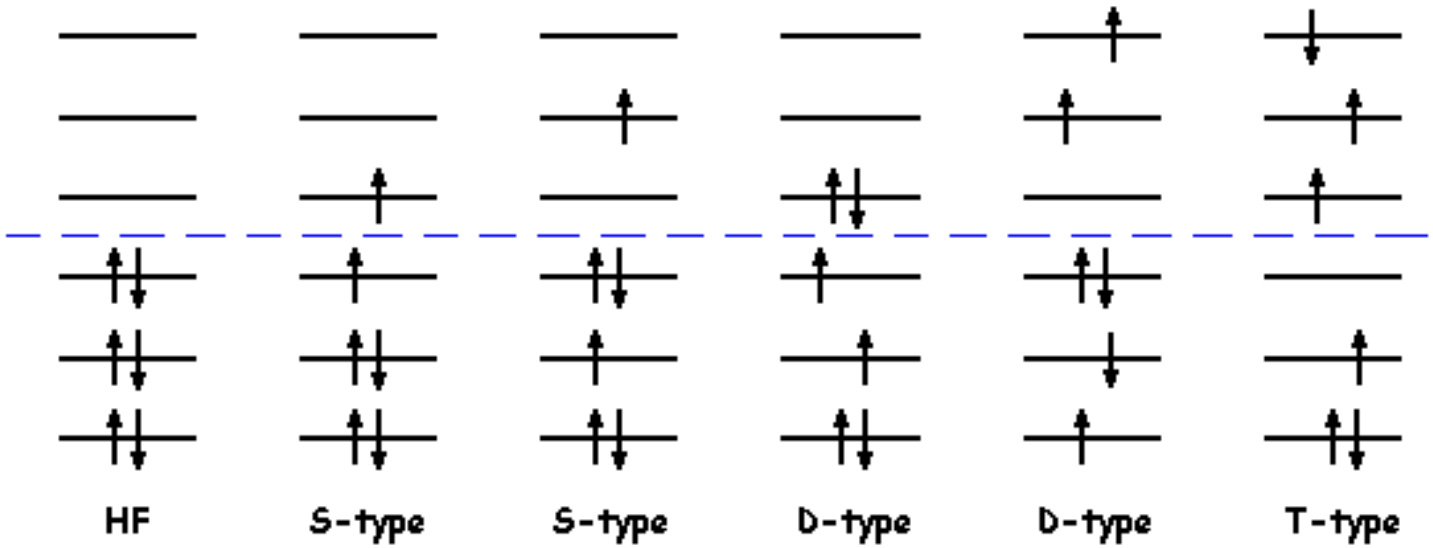
The RHF wavefunction overestimates the probability of finding the two electrons close together (the electrons are avoided to get too close to each other because the electrostatic interaction is treated in only an average manner), and this in turn implies an overestimate of the electron repulsion energy.
This is a **dynamical effect** (related to the electron movements) characteristic for short range distances and the corresponding energy is called correlation energy.
For electrons with parallel spins, the exchange interaction (Fermi hole) contributes significantly to the reduction of the overestimation of $1/r_{12}$; the electrons are already kept apart by the Pauli principle, and the effects of electron correlation neglect are fairly minor.

Excited Slater Determinants (ESD)

Suppose we have N electrons and K basis functions used to expand the MOs

→ RHF formalism will give N/2 occupied MOs and K-N/2 virtual MOs

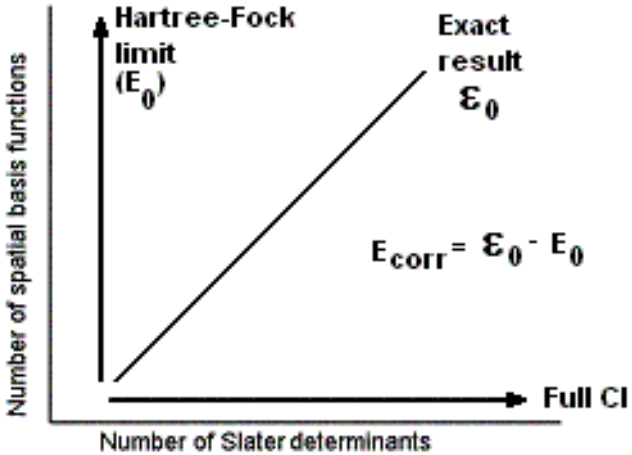
ESD – obtained by replacing MOs which are occupied in the HF determinant by unoccupied MOs
- singly, doubly, triply, quadruply, etc. excited relative to the HF determinant



Total number of ESD depends on the size of the basis set
If all the possible ESD (in a given basis set) are included then all the electron correlation energy is recovered

↓

Methods including electron correlation are two-dimensional !!



In many cases the interest is only in calculating the correlation energy associated with the valence electrons

➡ Frozen Core Approximation (FCA)

= limiting the number of ESD to only those which can be generated by exciting the valence electrons

- it is not justified in terms of total energy because the correlation of core electrons gives substantial contribution. However, it is essentially a constant factor which drops out when relative energies are calculated

Methods for taking the electron correlation into account:

Configuration Interaction (CI)
Many Body Perturbation Theory (MBPT) → Moller-Plesset (MP) Theory
Coupled Cluster (CC)

Configuration Interaction (CI)

-**based on the variational principle**, the trial wave-function being expressed as a linear combination of Slater determinants

The expansion coefficients are determined by imposing that the energy should be a minimum. The MOs used for building the excited determinants are taken from HF calculation and held fixed

$$\Psi_{CI} = a_0\Psi_{SCF} + \sum_S a_S\Psi_S + \sum_D a_D\Psi_D + \sum_T a_T\Psi_T + \ldots$$

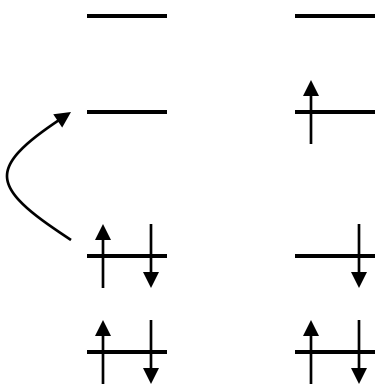
In the large basis set limit, all electron correlation methods scale at least as K^5

Example
Molecule: H_2O
Basis set: 6-31G(d) => 19BF => 38 spin MOs (10 occupied, 28 virtual)

The total number of excited determinants will be $C_{38}^{10} = 398637556$
Many of them will have different spin multiplicity and can therefore be left out in the calculation.
Generating only the singlet Configurational State Functions (CSF) we still obtain 1002001 determinants!!!

→ **Full CI method is only feasible for quite small systems!!!**

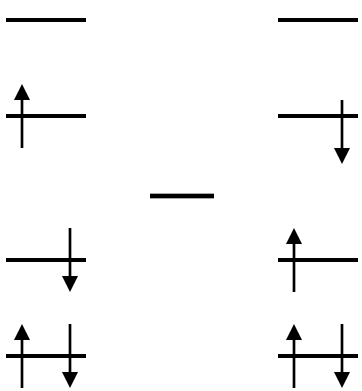
Configuration State Functions



Φ_{RHF} $\Phi^{(1)}$

Consider a single excitation from the RHF reference.

Both Φ_{RHF} and $\Phi^{(1)}$ have S_z=0, but $\Phi^{(1)}$ is <u>not</u> an eigenfunction of S^2.



Singlet CSF

Linear combination of singly excited determinants <u>is</u> an eigenfunction of S^2.

<u>Configuration State Function, CSF</u>
(Spin Adapted Configuration, SAC)

Only CSFs that have the <u>same multiplicity</u> as the HF reference

$$\Phi(1,2) = \phi_1\alpha(1)\phi_2\beta(2) - \phi_1\alpha(2)\phi_2\beta(1)$$

Truncated CI methods

$$\Psi_{CI} = a_0 \Psi_{SCF} + \sum_{S} a_S \Psi_S + \sum_{D} a_D \Psi_D + \sum_{T} a_T \Psi_T + \ldots$$

Truncating the expansion given above at level one =>

CIS - CI with only single excited determinants
CID - CI with only doubly excited determinants
CISD - CI with Singles and Doubles (scales as K^6)
CISDT - CI with Singles, Doubles and Triples (scales as K^8)
CISDTQ - CI with Singles, Doubles, Triples and Quadruples (scales as K^{10})
- gives results close to the full CI
- can only be applied to small molecules and small basis sets

CISD - the only CI method which is generally feasible for a large variety of systems
- recovers 80-90% of the available correlation energy

Multi-Configuration Self-Consistent Field Method (MCSCF)

- is the CI method in which the MOs are also varied, along with the coefficients of the CI expansion

MCSCF methods - are mainly used for generating a qualitatively correct wave-function
- recover the static part of the correlation (the energy lowering is due to the greater flexibility in the wave-function)

dynamic correlation – the correlation of the electrons' motions

In MCSCF methods the necessary configurations must be selected

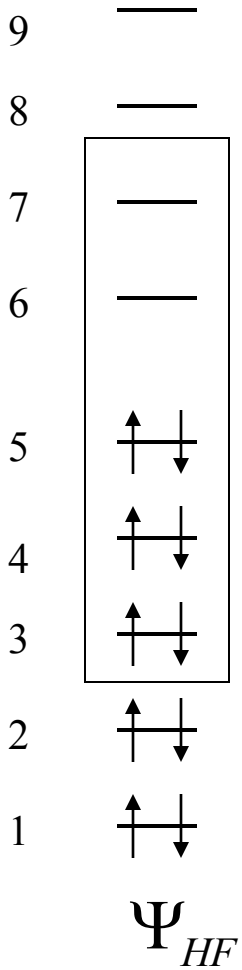
→ CASSCF (Complete Active Space SCF)

- the selection of the configurations is done by partitioning the MOs into active and inactive spaces

active MOs - some of the highest occupied and some of the lowest unoccupied MOs

Within the active MOs a full CI is performed

A more complete notation for this kind of methods is:
[n,m]-CASSCF
- n electrons are distributed in all possible ways in m orbitals



H_2O MOs

Carry out Full CI ***and*** orbital optimization within a <u>small</u> active space.

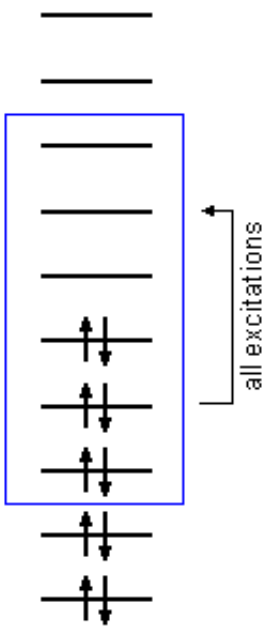
Six-electron in six-orbital MCSCF is shown (written as [6,6]-CASSCF)

<u>Complete Active Space Self-consistent Field (CASSCF)</u>

Why?

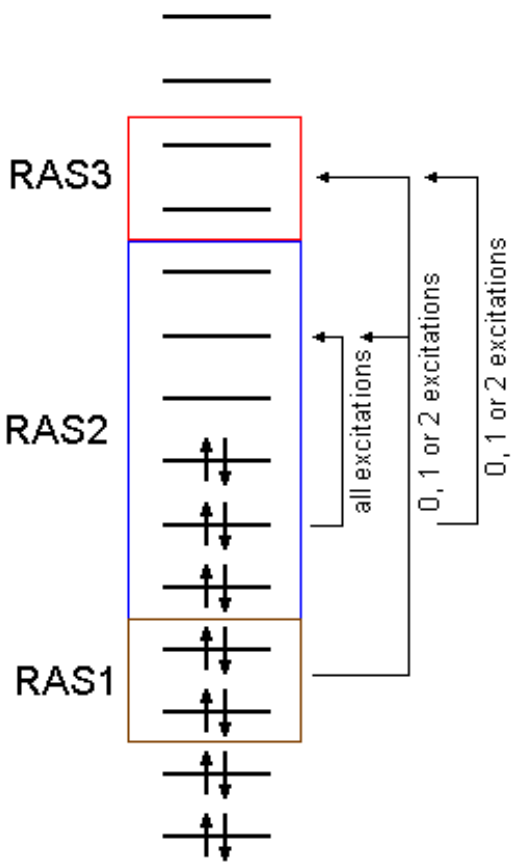
1. To have a better description of the ground or excited state. Some molecules are not well-described by a single Slater determinant, e.g. O_3.
2. To describe bond breaking/formation; Transition States.
3. Open-shell system, especially low-spin.
4. Low lying energy level(s); mixing with the ground state produces a better description of the electronic state.

CAS



Alternative to CASSCF → Restricted Active Space SCF (RASSCF)

RASSCF – the active MOs are further divided into three sections: RAS1, RAS2 and RAS3



RAS1 space – MOs doubly occupied in the HF reference determinant

RAS2 space – both occupied and virtual MOs in the HF reference determinant

RAS3 space – MOs empty in the HF reference determinant

Configurations in RAS2 are generated by a full CI
Additional configurations are generated by allowing for example a maximum of two electrons to be excited from RAS1 and a maximum of two electrons to be excited to RAS3

RASSCF combines a full CI in a small number of MOs (RAS2) and a CISD in a larger MO space (RAS1 and RAS3)

MØller-Plesset Perturbation Theory

- **a perturbational method** in which the unperturbed Hamiltonian is chosen as a sum over Fock operators

$$H_0 = \sum_{i=1}^{N} F_i = \sum_{i=1}^{N} \left(h_i + \sum_{j=1}^{N} (J_{ij} - K_{ij}) \right) = \sum_{i=1}^{N} h_i + 2\langle V_{ee} \rangle$$

The sum of Fock operators counts the average electron-electron repulsion twice and the perturbation is chosen the difference:

$V_{ee} - 2\langle V_{ee} \rangle$ where V_{ee} represents the exact operator for the electron-electron repulsion

It can be shown (Jensen, pag.127) that the zero order wave-function is the HF determinant while the zero order energy is just the sum of MO energies. Also, the first order energy is exactly the HF energy so that in this approach
the correlation energy is recovered starting with the second order correction (MP2 method)

In addition, the first contribution to the correlation energy involves a sum over doubly excited determinants which can be generated by promoting two electrons from occupied MOs *i* and *j* to virtual MOs *a* and *b.* The explicit formula for the second order Moller-Plesset correction is:

$$E(MP2) = \sum_{i<j}^{occ} \sum_{a<b}^{vir} \frac{\left[\langle \Phi_i \Phi_j \mid \Phi_a \Phi_b \rangle - \langle \Phi_i \Phi_j \mid \Phi_b \Phi_a \rangle \right]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

MP2 method

- scales as K^5
- accounts for cca. 80-90% of the correlation energy
- is fairly inexpensive (from the computational resources perspective) for systems with reasonable number of basis functions (100-200)

Coupled Cluster (CC) Methods

The idea in CC methods is to include all corrections of a given type to infinite order.
The wave-function is written as:

$$\Psi_{cc} = e^{\mathrm{T}}\Psi_0$$

where: $$e^{\mathrm{T}} = 1 + \mathrm{T} + \mathrm{T}^2 + \ldots = \sum_{k=0}^{\infty} \frac{1}{k!}\mathrm{T}^k$$

with the cluster operator given by:

$$\mathrm{T} = \mathrm{T}_1 + \mathrm{T}_2 + \mathrm{T}_3 + \ldots + \mathrm{T}_N$$

Acting on the HF reference wave function, the $\mathbf{T_i}$ operator generates all i-th excited Slater determinants:

$$\mathrm{T}_1\Psi_0 = \sum_{i}^{occ}\sum_{a}^{vir} t_i^a \Psi_i^a$$

$$\mathrm{T}_2\Psi_0 = \sum_{i<j}^{occ}\sum_{a<b}^{vir} t_{ij}^{ab} \Psi_{ij}^{ab}$$

...

The exponential operator may be rewritten as:

$$e^{\mathrm{T}} = 1 + \mathrm{T}_1 + \left(\mathrm{T}_2 + \frac{1}{2}\mathrm{T}_1^2\right) + \left(\mathrm{T}_3 + \mathrm{T}_1\mathrm{T}_2 + \frac{1}{6}\mathrm{T}_1^3\right) + \ldots$$

First term generates the reference HF wave-function
Second term generates all singly excited determinants
First parentheses generates all doubly excited states (true doubly excited states by $\mathbf{T_2}$ or product of singly excited states by the product $\mathbf{T_1T_1}$

The second parentheses generates all triply excited states, true (**T_3**) or products triples (**T_1T_2, $T_1T_1T_1$**)

The energy is given by:

$$E_{cc} = E_0 + \sum_{i<j}^{occ} \sum_{a<b}^{vir} \left(t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a \right) \left(\left\langle \Phi_i \Phi_j \mid \Phi_a \Phi_b \right\rangle - \left\langle \Phi_i \Phi_j \mid \Phi_b \Phi_a \right\rangle \right)$$

So, the coupled cluster correlation energy is determined completely by the singles and doubles amplitudes and the two-electron MO integrals

Truncated Coupled Cluster Methods

If all **T_N** operators are included in **T** the CC wave-function is equivalent to full CI wave-function, but this is possible only for the smallest systems.

→ Truncation of **T**

Including only the **T_1** operator there will be no improvement over HF, the lowest level of approximation being **T**=**T_2** (→ CCD=Coupled Cluster Doubles)

If **T**=**T_1**+**T_2** → CCSD → scales as K^6 the only generally applicable model

If **T**=**T_1**+**T_2**+**T_3** → CCSDT → scales as K^8