Electron correlation. Method of configuration interaction (CI)

Spinorbitals: occupied ϕ_a and virtual ϕ_r: $\epsilon_a \leq \epsilon_{\mathrm{HOMO}}, \quad \epsilon_r \geq \epsilon_{\mathrm{LUMO}}$

Operator of single excitations, $\hat{e}_a^r$ performs the substitution $\phi_a \to \phi_r$, e.g.,

$$\hat{e}_2^7 \,|\, \phi_1\, \phi_2\, \phi_3 \ldots \phi_N \,|=|\, \phi_1\, \phi_7\, \phi_3 \ldots \phi_N \,|$$

Operator of double excitations, $\hat{e}_{ab}^{rs} = \hat{e}_a^r\, \hat{e}_b^s$, performs a double substitution:

$$\hat{e}_{13}^{79} \,|\, \phi_1\, \phi_2\, \phi_3 \ldots \phi_N \,|=|\, \phi_7\, \phi_2\, \phi_9 \ldots \phi_N \,|$$

Singly excited determinants: $\Phi_a^r = \hat{e}_a^r\, \Phi_0$, where Φ_0 is a reference (HF) function

Doubly $\Phi_{ab}^{rs} = \hat{e}_{ab}^{rs}\, \Phi_0$ and triply $\Phi_{abc}^{rst} = \hat{e}_{abc}^{rst}\, \Phi_0$ excited determinants

The linear combination of Φ_0 and excited determinants Φ_I is the CI function:

$$\Psi = c_0 \Phi_0 + \sum_I c_I \Phi_I$$

In practice the CI function can include single excitations (CIS), single- and double excitations (CISD) as well as all excitations though triple (CISDT) and quadruple (CISDTQ) ones.

S=single, D=double, T=triple, Q=quadruple (excitations)

Most important variants of the CI method

CIS Method:

$$\Psi = c_0\Phi_0 + \sum_{ar} c_r^a \Phi_a^r$$

If Φ_0 is the HF determinant we obtain zero as the correlation energy because of the important **Brillouin Theorem**

$$\int \Phi_a^r \hat{H} \Phi_0 d\tau = 0 \quad \text{or} \quad \langle \Phi_a^r | \hat{H} \Phi_0 \rangle = 0, \quad \text{notation:} \quad \int \Psi_1^* \Psi_2 \, d\tau \equiv \langle \Psi_1 | \Psi_2 \rangle$$

However, the CIS method gives often quite good electronic excitation energies.

CISD Method:

$$\Psi = c_0\Phi_0 + \sum_{ar} c_r^a \Phi_a^r + \sum_{a<b} \sum_{r<s} c_{rs}^{ab} \Phi_{ab}^{rs}$$

Is today rather infrequently used because it is not size-consistent. The same applies to the slightly more accurate CISDT method and to much more accurate CISDTQ method.

Full CI (FCI) Method

$$\Psi = c_0\Phi_0 + \sum_{I} c_I \Phi_I$$

includes all determinants ($\sim M^N$) one can construct for N electrons using the basis of M orbitals. This method is most accurate but it is the most expensive.

Equations of the CI method

$$\Psi = c_0\Phi_0 + \sum_{ar} c_r^a\, \hat{e}_a^r\, \Phi_0 + \sum_{a<b}\sum_{r<s} c_{rs}^{ab}\, \hat{e}_{ab}^{rs}\, \Phi_0 + \cdots$$

We impose the intermediate normalization $\langle\Phi_0|\Psi\rangle = 1$. Then $c_0 = 1$ and

$$\Psi = (1 + \sum_{ar} c_r^a\, \hat{e}_a^r + \sum_{a<b}\sum_{r<s} c_{rs}^{ab}\, \hat{e}_{ab}^{rs} + \cdots)\, \Phi_0 = (1 + \hat{C})\Phi_0$$

where $\hat{C}$ is the CI operator:

$$\hat{C} = \sum_{ar} c_r^a\, \hat{e}_a^r + \sum_{a<b}\sum_{r<s} c_{rs}^{ab}\, \hat{e}_{ab}^{rs} + \cdots = \hat{C}_1 + \hat{C}_2 + \cdots$$

The $\hat{C}$ operator should satisfy the Schrödinger equation:

$$(\hat{H} - E)(1 + \hat{C})\Phi_0 = 0,$$

This is not possible, therefore we use the Galerkin-Pietrow method, that is we equate to zero the projections of the l.h.s. on the basis functions Φ_I:

$$\langle\Phi_I|(\hat{H} - E)(1 + \hat{C})\Phi_0\rangle = 0$$

$$E = \langle\Phi_0|\hat{H}(1 + \hat{C})\Phi_0\rangle$$

Equations of the CI method, continued

The final CI equations (for the $\hat{C}$ operator) are

$$\langle \Phi_I | (\hat{H} - E)\hat{C})\Phi_0 \rangle = -\langle \Phi_I | \hat{H}\Phi_0 \rangle$$

where

$$E = E_{\mathrm{HF}} + \langle \Phi_0 | \hat{H}\hat{C}_2\Phi_0 \rangle$$

and

$$\hat{C} = \hat{C}_1 + \hat{C}_2 + \cdots + \hat{C}_K.$$

Accuracy of the variants of the CI method

Metoda CI	Operator $\hat{C}$	Cost	Error FH	Error H_2O
CID	$\hat{C}_2$	n^6	10.3	13.7
CISD	$\hat{C}_1 + \hat{C}_2$	n^6	9.4	12.9
CISDT	$\hat{C}_1 + \hat{C}_2 + \hat{C}_3$	n^8	7.0	10.6
CISDTQ	$\hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \hat{C}_4$	n^{10}	0.3	0.4
FCI	$\hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \cdots + \hat{C}_N$	n^N	0.0	0.0

DZP Basis. Errors in millihartree, 1 mhartree = 0.627 kcal/mol.

Møller-Plesset Perturbation Theory (MP Theory)

Problems with the CI:

- slow convergence when the multiplicity of the excitations K increases
- lack of the size consistency when $K < N$
- lack of the extensivity of the correlation energy for crystals and polymers (the correlation energy grows as $\sqrt{L}$, where L is the number of atoms in the system)

The MP theory is free from these problems. In this theory the Hamiltonian is partitioned as:

$$\hat{H} = \hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{W}$$

where

$$\hat{H}_0 = \sum_{i=1}^{N} \hat{f}(\vec{r}_i)$$

is the sum of the Fock operators for all electrons and $\hat{W} = \hat{H} - \hat{H}_0$.
It is essential that:

$$\hat{H}_0\Phi_0 = E_0\Phi_0$$

where Φ_0 is the HF function and E_0 is the sum of the occupied orbital energies $E_0 = \sum_a \epsilon_a$. The perturbation $\hat{W}$ is a two-body operator $\hat{W} = \sum_{ij} g(\vec{r}_i, \vec{r}_j)$.

MP Theory, continued

After substituting $\hat{H} \to \hat{H}(\lambda)$ in the FCI equations the operator $\hat{C}$ and the energy E become functions of λ and can be expanded as the power series:

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

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

Inserting these expansions to the FCI equations one can easily show that:

$$\hat{C}^{(0)} = 0$$

$$E^{(0)} + E^{(1)} = \langle \Phi_0 | \hat{H} \Phi_0 \rangle = E_{\mathrm{HF}}$$

$$E^{(2)} = \langle \Phi_0 | \hat{W} \, \hat{C}^{(1)} \Phi_0 \rangle$$

$$\hat{C}^{(1)} = \sum_{a<b} \sum_{r<s} \frac{\langle ab || rs \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \hat{e}_{ab}^{rs}$$

where $\langle pq || rs \rangle = \langle pq | rs \rangle - \langle pq | sr \rangle$ stands for the antisymmetrized two-electron integral and

$$\langle pq | rs \rangle = \int \int \phi_p^*(\vec{r}_1) \, \phi_q^*(\vec{r}_2) \, \frac{1}{|\vec{r}_1 - \vec{r}_2|} \, \phi_r(\vec{r}_1) \, \phi_s \, (\vec{r}_2) \, d\tau_1 d\tau_2$$

MP Theory (MPPT lub MBPT), the third, last slide

Inserting the $\hat{C}^{(1)}$ operator into the expression for $E^{(2)}$ we obtain:

$$E^{(2)} = \sum_{a<b} \sum_{r<s} \frac{|\langle ab||rs\rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

This is the expression for the MP2 energy - the simplest and most important correlation energy expression.

The MP2 and higher-order MP energies are size-consistent and size-extensive

MP2 theory was introduced by physicists - Møller and Plesset in 1930, but higher-order ones by quantum chemists: MP3 - by Bartlett i Silver in 1974, MP4 - Wilson and Silver in 1979, MP5 by Kucharski and Bartlett in 1986 r.

Theory	Operator $\hat{C}$	Scaling	Error FH	Error H_2O
MP2	$\hat{C}_2$	n^5	7.8	13.0
MP3	$\hat{C}_2$	n^6	5.4	7.2
MP4 -E$^{(4)}(\hat{C}_3)$	$\hat{C}_1$, $\hat{C}_2$	n^6	2.8	4.4
MP4	$\hat{C}_1$, $\hat{C}_2$, $\hat{C}_3$	n^7	-0.3	0.9
MP5	$\hat{C}_1$, $\hat{C}_2$, $\hat{C}_3$	n^8	0.8	0.7
MP6	$\hat{C}_1$, $\hat{C}_2$, $\hat{C}_3$, $\hat{C}_4$	n^9	0.2	0.1

Coupled-cluster (CC) theory - Coester-Kümmel-Cizek theory

In some cases the MP theory may be divergent. Thus, we need a non-perturbative theory better than CI. CC theory is the desired solution.

CI theory is not extensive since the operator $1 + \hat{C}$ is not extensive.

It turns out, that the logarithm of the $1 + \hat{C}$ operator is extensive! The main idea of the CC theory is that we do not compute $\hat{C}$ but directly $\hat{T} = \ln(1+\hat{C})$.

$$\hat{T} = \ln(1 + \hat{C}) = \hat{C} - \frac{1}{2}\hat{C}^2 + \frac{1}{3}\hat{C}^3 + \cdots$$

$\hat{T}$ is well defined because this series is always convergent (since $\hat{C}^{N+1} = 0$).

$$1 + \hat{C} = \exp(\hat{T}) = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \cdots$$

Obviously

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N = \sum_{ar} t_r^a \, \hat{e}_a^r + \sum_{a<b}\sum_{r<s} t_{rs}^{ab} \, \hat{e}_{ab}^{rs} + \cdots + \hat{T}_N$$

Since $\Psi = (1 + \hat{C})\,\Phi_0$ we can write

$$\boxed{\Psi = e^{\hat{T}}\,\Phi_0}$$

This is the exponential form of the wave function (the "exponential Ansatz")

Coupled-cluster theory, continued

Inserting the wave function $e^{\hat{T}}\,\Phi_0$ into the Schrödinger equation we get:

$$(\hat{H} - E)\,e^{\hat{T}}\,\Phi_0 = 0$$

Multiplying by $e^{-\hat{T}}$ we further obtain:

$$e^{-\hat{T}}\,(\hat{H} - E)\,e^{\hat{T}}\,\Phi_0 = 0$$

This equation is solved using the Galerkin-Pietrov method, i.e. by projecting it on all excited determinants Φ_I. One obtains then:

$$\langle \Phi_I | e^{-\hat{T}}\hat{H}e^{\hat{T}}\,\Phi_0\rangle = 0$$

All levels of the CC theory are size-consistent and size-extensive. The most important levels are CCSD ($\hat{T} = \hat{T}_1+\hat{T}_2$) and CCSD(T) when the contribution of triple excitations ($\hat{T}_3$) is included via the MP4 expression and added to the CCSD energy (the so called "gold standard" of quantum chemistry).

Theory	Operator $\hat{T}$	Scaling	Error FH	Error H_2O
CCD	$\hat{T}_2$	n^6	3.76	5.01
CCSD	$\hat{T}_1+\hat{T}_2$	n^6	3.01	4.12
CCSD(T)	$\hat{T}_1+\hat{T}_2$, $\hat{T}_3$	n^7	0.40	0.72
CCSDT	$\hat{T}_1+\hat{T}_2+\hat{T}_3$	n^8	0.27	0.53
CCSDTQ	$\hat{T}_1+\hat{T}_2+\hat{T}_3+\hat{T}_4$	n^{10}	0.02	0.02

Multi-reference configuration interaction theory - MRCI

One starts by computing the MCSCF wave function

$$\Psi_0 = \sum_L c_L \, \Phi_L$$

and subsequently includes all single and double excitations (for the MRCISD theory) from each reference determinant Φ_L:

$$\Psi = \Psi_0 + \sum_L \hat{C}_L \, \Phi_L,$$

(the operator $\hat{C}_L$ generates excitations form the determinant Φ_L).

We include each Slater determinant only once and diagonalize the Hamiltonian in the basis such obtained (without re-optimization of orbitals).

The MRCISD energies are not size-consistent but are often very accurate.

The MRCISD method is particularly suitable for for the study of excited states and for the reactive potential energy surfaces.

MRCISD calculations are expensive and difficult to converge.