Molecular properties in quantum chemistry

Monika Musiał

Department of Theoretical Chemistry

Outline

1. Main computational schemes for correlated calculations
2. Development of the *ab initio* methods for the calculation of molecular properties.

Literature

- L. Piela, Idee Chemii Kwantowej, PWN, Warszawa, 2003.
- R. J. Bartlett, M. Musial, Rev. Mod. Phys., 79, 291-352 (2007).
- M. Musiał, Mol. Phys., 108, 2921 (2010).
- M. Jaworska, M. Musiał, T. Pluta, *Wybrane zagadnienia chemii kwantowej*, Uniwersytet Śląski (2009).
- J. F. Stanton, R. J. Bartlett, J. Chem. Phys., 98, 7029 (1993).
- J. F. Stanton, J. Chem. Phys., 99, 8840 (1993).

Computational methods of quantum chemistry based on the wave function – Ψ

Born-Oppenheimer approximation

Electronic Schrödinger equation:

$$\mathbf{H}\Psi = \mathbf{E}\Psi$$

Computational strategy in the wave function based calculations

Two-step approach to the solution of the Schrödinger equation:

1. construction of the wave function within the 1-electron approximation (independent particle model): Hartree-Fock method
2. post-Hartree-Fock approach: determination of electronic correlation

Computational strategy in the wave function based calculations

- **Hartree-Fock**
  (also known as a **mean field approach**)

Determination of (spin)orbitals

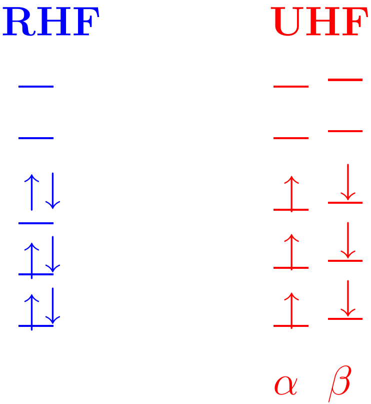
Self Consistent Field (SCF) method

$\mathbf{E_{HF} \sim 99\%}$ of total energy

RHF vs. UHF

- RHF(Restricted Hartree-Fock) - closed shell molecules, $\frac{N}{2}$ orbitals (doubly occupied)
- UHF(Unrestricted Hartree-Fock) - open shell molecules, l spinorbitals with the α spin and k spinorbitals with the β spin (DODS - Different Orbitals for Different Spins)

RHF vs. UHF



UHF

UHF cons:

- incorrect spin
- problems with convergence

UHF pros:

- size-consistent (extensive)

RHF

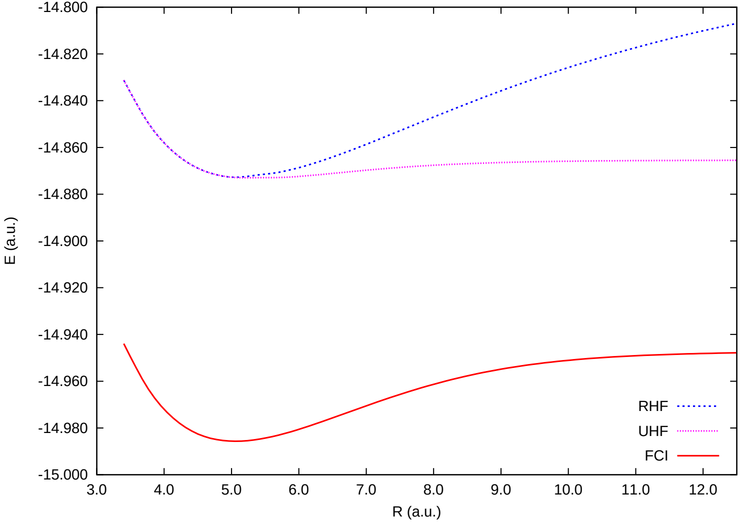
RHF cons:

- incorrect dissociation limit (in standard formulation)

RHF pros:

- well defined spin
- good convergence for HF equations

RHF vs. UHF


-14.800
-14.820
-14.840
-14.860
-14.880
-14.900
-14.920
-14.940
-14.960
-14.980
-15.000
E (a.u.)
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
R (a.u.)
RHF
UHF
FCI

Computational strategy in the wave function based calculations

- Determination of correlation energy

Perturbation theory (MPn)
Configuration Interaction (CI)
Coupled Cluster (CC)

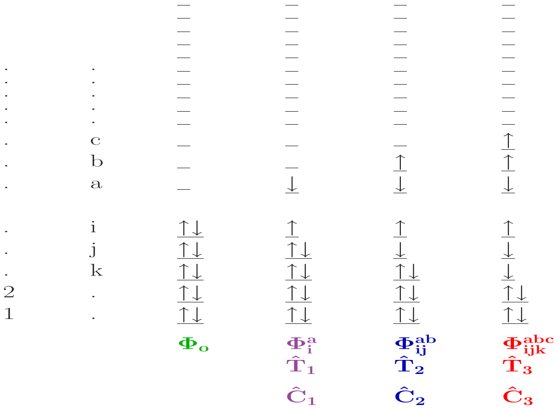
Correlation energy

$$\mathbf{H\Psi = E\Psi}$$

Expressing the wave function $\boldsymbol{\Psi}$ as a linear combination of (ground and excited) state configurations:

$$\begin{aligned}\boldsymbol{\Psi} &= \boldsymbol{\Phi_o} + \boldsymbol{\Sigma_{a,i} c_i^a \Phi_i^a} \\ &\quad + \boldsymbol{\Sigma_{a,b,i,j} c_{ij}^{ab} \Phi_{ij}^{ab}} \\ &\quad + \boldsymbol{\Sigma_{a,b,c,i,j,k} c_{ijk}^{abc} \Phi_{ijk}^{abc}} \\ &\quad + \ldots.\end{aligned}$$

Configurations



CCD, CCSD, CCSDT, CCSDTQ, ... , FULL CC

CID, CISD, CISDT, CISDTQ, ... , FULL CI

Expansion coefficients are obtained using:

1. perturbation theory ⟶ Moeller-Plesset corrections: MP2, MP3, ...

   $$V = \sum_{i>j} \frac{1}{r_{ij}} - \sum_q (J_q - K_q)$$

2. linear parametrization of the wave function

   $$\Psi = (1 + C)\Phi_o$$

   Configuration Interaction method

3. **exponential parametrization of the wave function**

   $$\boldsymbol{\Psi = \exp(T)\Phi_o}$$

   Coupled Cluster method

Coupled cluster method

exponential parametrization of the wave function

$$|\mathbf{\Psi_o}\rangle = \mathbf{e^T}|\mathbf{\Phi_o}\rangle$$

$$\mathbf{T} = \mathbf{T_1} + \mathbf{T_2} + \mathbf{T_3} ... + \mathbf{T_N}$$

where T_n – n-tuple excitation operator

$$\mathbf{T_n} = \mathbf{(n!)^{-2} \Sigma_{ab...} \Sigma_{ij...} t_{ij...}^{ab...} a^\dagger b^\dagger ... ji}$$

and $\mathbf{t_{ij...}^{ab...} a^\dagger b^\dagger ... ji}$ - coefficients (amplitudes) to be determined

Coupled cluster method

- amplitude equation:

$$\langle \Phi_{ij\ldots}^{ab\ldots} | e^{-T} H e^{T} | \Phi_o \rangle = \langle \Phi_{ij\ldots}^{ab\ldots} | \bar{H} | \Phi_o \rangle = 0$$

- energy expression:

$$E = \langle \Phi_o | e^{-T} H e^{T} | \Phi_o \rangle = \langle \Phi_o | \bar{H} | \Phi_o \rangle$$

where $\bar{H}$ – similarity transformed Hamiltonian.

Coupled cluster method

SR

CCD	**(Bartlett, Purvis, 1978; Pople et al. 1978)**
CCSD	**(Purvis, Bartlett, 1982)**
CCSDT	**(Noga, Bartlett, 1987; Watts, Bartlett, 1989)**
CCSDTQ	**(Kucharski Bartlett, 1992)**
CCSDTQP	**(Musiał, Kucharski, Bartlett, 2002)**

S – Singles
D – Doubles
T – Triples
Q – Quadruples

P – Pentuples

Coupled cluster method

size-extensivity

Correct scaling of the energy with the size of the system $\Longrightarrow$ correct separation of the non-interacting fragments.

For the AB molecule composed of the non-interacting fragments A and B assuming that $\Phi_{AB} = \Phi_A \Phi_B$ we get:

$$\mathbf{\Psi_{AB} = \exp(T_{AB})|\Phi_{AB}\rangle = \exp(T_A)|\Phi_A\rangle \exp(T_B)|\Phi_B\rangle = \Psi_A \Psi_B}$$

$$\mathbf{E_{CC}^{AB} = E_{CC}^{A} + E_{CC}^{B}}$$

Important quantity in the CC theory:

$\bar{\mathbf{H}}$ - similarity transformed Hamiltonian

$$\boxed{\bar{\mathbf{H}} = \mathbf{e}^{-\mathbf{T}}\mathbf{H}\mathbf{e}^{\mathbf{T}} = (\mathbf{H}\mathbf{e}^{\mathbf{T}})_{\mathbf{c}}}$$

$\bar{\mathbf{H}}$ operator includes one-body, two-body and also higher (three, four, ...) -body elements.

How do we obtain $\bar{\mathbf{H}}$ operator?

- Get $\mathbf{T}$ amplitudes from the CC amplitude equations:

$$\langle \boldsymbol{\Phi}_{\mathbf{ij\ldots}}^{\mathbf{ab\ldots}} | \mathbf{e}^{-\mathbf{T}} \mathbf{H} \mathbf{e}^{\mathbf{T}} | \boldsymbol{\Phi}_{\mathbf{o}} \rangle = \mathbf{0}$$

- With $\mathbf{T}$ amplitudes construct $\bar{\mathbf{H}}$:

$$\bar{\mathbf{H}} = (\mathbf{H}\mathbf{e}^{\mathbf{T}})_{\mathbf{c}}$$

EOM-CC method

Equation-Of-Motion CC

(EOM-CC) method

EOM-CC method

EOM-CC method

- CI-like calculations for the $\bar{\mathrm{H}}$ operator

Reminder:

Standard CI are based on the regular Hamiltonian (H).

EOM-CC method

Wave function:

$$|\Psi_k\rangle \;=\; R(k)|\Psi_o\rangle \qquad k = 1, 2, \dots$$

Schrödinger equation:

$$\begin{aligned} HR(k)|\Psi_o\rangle &= E_k R(k)|\Psi_o\rangle \\ R(k)H|\Psi_o\rangle &= E_o R(k)|\Psi_o\rangle \end{aligned}$$

Equation-of-motion:

$$\boxed{[H, R(k)]|\Psi_o\rangle = \omega_k R(k)|\Psi_o\rangle}$$

EOM-CC method

Since $|\boldsymbol{\Psi}_{\mathbf{o}}\rangle = \mathbf{e}^{\mathbf{T}}|\boldsymbol{\Phi}_{\mathbf{o}}\rangle$ we obtain - after simple algebra - eigenvalue equation:

$$\boxed{(\bar{H}R(k))_c|\Phi_o\rangle = \omega_k R(k)|\Phi_o\rangle}$$

or in matrix form:

$$\boxed{\bar{\mathbf{H}}\mathbf{R}(\mathbf{k}) = \boldsymbol{\omega}_{\mathbf{k}}\mathbf{R}(\mathbf{k})}$$

EOM-CC method

$$\begin{aligned}\mathbf{R^{EE}(k)} &= \mathbf{r_o(k)} + \mathbf{\Sigma_a \Sigma_i r_i^a(k) a^\dagger i} + \mathbf{\frac{1}{4} \Sigma_{ab} \Sigma_{ij} r_{ij}^{ab}(k) a^\dagger b^\dagger j i} \\ &+ \mathbf{\frac{1}{36} \Sigma_{abc} \Sigma_{ijl} r_{ijl}^{abc}(k) a^\dagger b^\dagger c^\dagger l j i} + \ldots\end{aligned}$$

$$\begin{aligned}\mathbf{R^{IP}(k)} &= \mathbf{\Sigma_i r_i(k) i} + \mathbf{\frac{1}{2} \Sigma_a \Sigma_{ij} r_{ij}^a(k) a^\dagger j i} \\ &+ \mathbf{\frac{1}{12} \Sigma_{ab} \Sigma_{ijl} r_{ijl}^{ab}(k) a^\dagger b^\dagger l j i} + \ldots\end{aligned}$$

$$\begin{aligned}\mathbf{R^{EA}(k)} &= \mathbf{\Sigma_a r^a(k) a^\dagger} + \mathbf{\frac{1}{2} \Sigma_{ab} \Sigma_i r_i^{ab}(k) a^\dagger b^\dagger i} \\ &+ \mathbf{\frac{1}{12} \Sigma_{abc} \Sigma_{ij} r_{ij}^{abc}(k) a^\dagger b^\dagger c^\dagger j i} + \ldots\end{aligned}$$

EOM-CC method

$$\mathbf{R^{DIP}(k) \;=\; \frac{1}{2}\sum_{ij} r_{ij}(k) j i + \frac{1}{6}\sum_{a}\sum_{ijl} r^{a}_{ijl}(k) a^{\dagger} l j i + \ldots}$$

$$\mathbf{R^{DEA}(k) \;=\; \frac{1}{2}\sum_{ab} r^{ab}(k) a^{\dagger} b^{\dagger} + \frac{1}{6}\sum_{abc}\sum_{i} r^{abc}_{i}(k) a^{\dagger} b^{\dagger} c^{\dagger} i + \ldots}$$

EOM-CC method

EOM-CCSD model

$$\bar{\mathbf{H}} = \begin{bmatrix} \langle \mathbf{S}|\bar{\mathbf{H}}|\mathbf{S}\rangle & \langle \mathbf{S}|\bar{\mathbf{H}}|\mathbf{D}\rangle \\ \langle \mathbf{D}|\bar{\mathbf{H}}|\mathbf{S}\rangle & \langle \mathbf{D}|\bar{\mathbf{H}}|\mathbf{D}\rangle \end{bmatrix}$$

S$\equiv \mathbf{\Phi_j}$	D$\equiv \mathbf{\Phi^a_{ij}}$	Ionization potential (IP)
S$\equiv \mathbf{\Phi^b}$	D$\equiv \mathbf{\Phi^{ab}_i}$	Electron affinity (EA)
S$\equiv \mathbf{\Phi^a_i}$	D$\equiv \mathbf{\Phi^{ab}_{ij}}$	Excitation energy (EE)

EOM-CC method

EOM-CCSDT model

$$\mathbf{\bar{H}} = \begin{bmatrix} \langle \mathbf{S}|\mathbf{\bar{H}}|\mathbf{S}\rangle & \langle \mathbf{S}|\mathbf{\bar{H}}|\mathbf{D}\rangle & \langle \mathbf{S}|\mathbf{\bar{H}}|\mathbf{T}\rangle \\ \langle \mathbf{D}|\mathbf{\bar{H}}|\mathbf{S}\rangle & \langle \mathbf{D}|\mathbf{\bar{H}}|\mathbf{D}\rangle & \langle \mathbf{D}|\mathbf{\bar{H}}|\mathbf{T}\rangle \\ \langle \mathbf{T}|\mathbf{\bar{H}}|\mathbf{S}\rangle & \langle \mathbf{T}|\mathbf{\bar{H}}|\mathbf{D}\rangle & \langle \mathbf{T}|\mathbf{\bar{H}}|\mathbf{T}\rangle \end{bmatrix}$$

IP: T$\equiv \mathbf{\Phi_{ijl}^{ab}}$
EA: T$\equiv \mathbf{\Phi_{ij}^{abc}}$
EE: T$\equiv \mathbf{\Phi_{ijl}^{abc}}$

EOM-CC method

EOM-CCSD for DIP and DEA

$$\mathbf{\bar{H}} = \left[\ \langle \mathbf{D} | \mathbf{\bar{H}} | \mathbf{D} \rangle\ \right]$$

D $\equiv \mathbf{\Phi_{ij}}$ Double ionization potential (DIP)
D $\equiv \mathbf{\Phi^{ab}}$ Double electron affinity (DEA)

EOM-CC method

EOM-CCSDT for DIP and DEA

$$\mathbf{\bar{H}} = \left[\begin{array}{cc} \langle \mathbf{D}|\mathbf{\bar{H}}|\mathbf{D}\rangle & \langle \mathbf{D}|\mathbf{\bar{H}}|\mathbf{T}\rangle \\ \langle \mathbf{T}|\mathbf{\bar{H}}|\mathbf{D}\rangle & \langle \mathbf{T}|\mathbf{\bar{H}}|\mathbf{T}\rangle \end{array} \right]$$

DIP: $\mathrm{T} \equiv \mathbf{\Phi^{a}_{ijk}}$

DEA: $\mathrm{T} \equiv \mathbf{\Phi^{abc}_{i}}$

EOM-CC method

Efficient technique used to diagonalize large matrices:

Davidson method generalized for non-Hermitian matrices.

EOM-CC method

A crucial step in the Davidson procedure is taking product of the amplitude vector **R** and the matrix - to be diagonalized - $\bar{\mathrm{H}}$

$$\mathbf{x_k} = \bar{\mathbf{H}}\mathbf{R_k}$$

EOM-CC method

The product $\bar{\mathrm{H}}\mathrm{R}_{\mathrm{k}}$ cannot be taken directly as a matrix product.

Why?

Rank of $\bar{\mathrm{H}}$ goes into milions.

We know $\bar{\mathrm{H}}$ operator but we do not construct $\bar{\mathrm{H}}$ matrix.
Thus our equations can be seen as:

EOM-CC method

EE-EOM-CCSDT equations

$$\mathbf{R(k)} = \mathbf{R_o(k)} + \mathbf{R_1(k)} + \mathbf{R_2(k)} + \mathbf{R_3(k)}$$

$$x_i^a(k) = \langle \mathbf{\Phi_i^a} | (\mathbf{\bar{H}_N R(k)})_\mathbf{c} | \mathbf{\Phi_o} \rangle$$

$$x_{ij}^{ab}(k) = \langle \mathbf{\Phi_{ij}^{ab}} | (\mathbf{\bar{H}_N R(k)})_\mathbf{c} | \mathbf{\Phi_o} \rangle$$

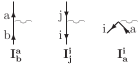
$$x_{ijl}^{abc}(k) = \langle \mathbf{\Phi_{ijl}^{abc}} | (\mathbf{\bar{H}_N R(k)})_\mathbf{c} | \mathbf{\Phi_o} \rangle$$

x_i^a, x_{ij}^{ab}, x_{ijl}^{abc} – elements of the $\mathbf{x_k}$ vector

EOM-CC method

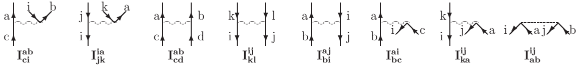
The diagrammatic representation of the elements of $\bar{H}_N$ used in derivation of the EE-EOM-CCSDT equations.

one-body I^1 : $I^1_1 + I^1_2$



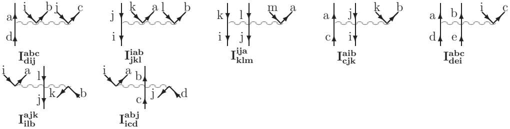
I^a_b I^i_j I^i_a

two-body I^2 : $I^2_1 + I^2_2 + I^2_3 + I^2_4$



I^{ab}_{ci} I^{ia}_{jk} I^{ab}_{cd} I^{ij}_{kl} I^{aj}_{bi} I^{ai}_{bc} I^{ij}_{ka} I^{ij}_{ab}

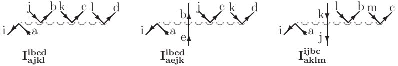
three-body I^3 : $I^3_1 + I^3_2 + I^3_3$



I^{abc}_{dij} I^{iab}_{jkl} I^{ija}_{klm} I^{aib}_{cjk} I^{abc}_{dei}

I^{ajk}_{ilb} I^{abj}_{icd}

four-body I^4 : $I^4_2 + I^4_3$



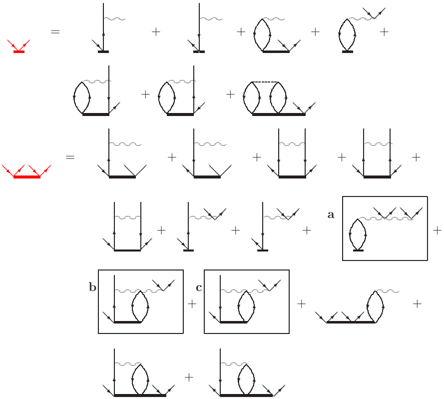
I^{ibcd}_{ajkl} I^{ibcd}_{aejk} I^{ijbc}_{aklm}

EOM-CC method

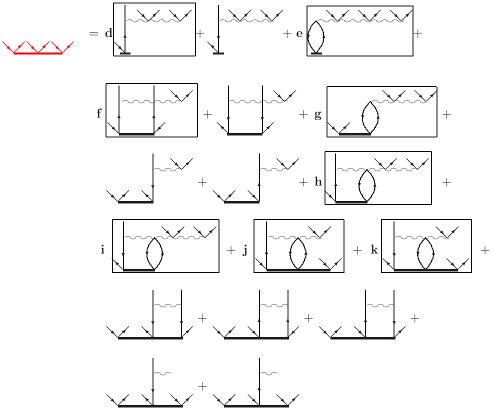
	S	**D**	**T**
S	I_1^1 $I_2^{2'}$	I_2^1 I_3^2	I_4^2
D	I_1^2 $I_2^{3'}$	I_1^1 I_2^2 I_3^3	I_2^1 I_3^2
T	I_1^3 $I_2^{4'}$ I_3^4	I_1^2 I_2^3 I_3^3	I_1^1 I_2^2

EOM-CC method

Diagrammatic form of the standard EE-EOM-CCSDT equations.



EOM-CC method



EOM-CC method

$\bar{\mathrm{H}}$ operator

1. $\bar{\mathrm{H}}$ is non-Hermitian
2. It includes three-, four- and higher-body elements

$$\bar{\mathbf{H}} = \mathbf{e}^{-\mathbf{T}}\mathbf{H}\mathbf{e}^{\mathbf{T}} = (\mathbf{H}\mathbf{e}^{\mathbf{T}})_{\mathbf{c}}$$

Expanding $\bar{\mathbf{H}}_{\mathbf{N}}$ into one-body, two-body, three-body, ... etc. contributions we get:

$$\bar{\mathbf{H}}_{\mathbf{N}} = \mathbf{I}^{\mathbf{o}} + \sum_{\mathbf{k}=0}^{2} \mathbf{I}^{1}_{\mathbf{k}} + \sum_{\mathbf{k}=0}^{4} \mathbf{I}^{2}_{\mathbf{k}} + \sum_{\mathbf{k}=0}^{3} \mathbf{I}^{3}_{\mathbf{k}} + \sum_{\mathbf{k}=0}^{3} \mathbf{I}^{4}_{\mathbf{k}} + \cdots$$

EOM-CC

Computational strategy

Steps applied in the standard EOM-CC method:

- solve the standard CCSD (or CCSDT) equations for the ground state problem
- using the converged T_1, T_2 (or T_3) amplitudes construct all $\bar{H}$ elements
- apply a generalized Davidson diagonalization procedure to obtain eigenvalues of the $\bar{\mathbf{H}}$ matrix.