

Wavefunction-based Correlation Methods:

Perturbation Theory (PT) & Coupled-Cluster (CC) Theory

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Introduction

Recall the size-extensivity problem in CISD:

$$E_N^{\text{FCI}} = N \frac{1}{2} (\Delta - \sqrt{\Delta^2 + 4V^2}), \quad (1)$$

$$E_N^{\text{CISD}} = \frac{1}{2} (\Delta - \sqrt{\Delta^2 + 4NV^2}), \quad (2)$$

If $NV \leq \Delta$, by Taylor expansion we can get

$$E_N^{\text{FCI}} = -\frac{NV^2}{\Delta} + \frac{NV^4}{\Delta^3} - \frac{2NV^6}{\Delta^5} + \dots \quad (3)$$

$$E_N^{\text{CISD}} = -\frac{NV^2}{\Delta} + \frac{N^2V^4}{\Delta^3} - \frac{2N^3V^6}{\Delta^5} + \dots \quad (4)$$

This shows that we can get a size-extensive contribution from CISD by perturbative expansion. This in general leads to the second-order Møller-Plesset perturbation theory (MP2).

Introduction

MP n is the application of **nondegenerate** perturbation theory to the electron correlation problem.

We will just follow an elementary derivation of MP2. High-order PT can be derived using the resolvent technique¹² or time-dependent perturbation theory following Goldstone³. The latter proved a theorem called **linked-cluster theorem**, which implies that each order MP energy is size-extensive, that is, scales linearly as the number of electrons.

¹Ingvar Lindgren and John Morrison. *Atomic many-body theory*. Springer-Verlag Berlin Heidelberg, 1982.

²Isaiah Shavitt and Rodney J Bartlett. *Many-body methods in chemistry and physics: MBPT and coupled-cluster theory*. Cambridge university press, 2009.

³Jeffrey Goldstone. "Derivation of the Brueckner many-body theory". In: *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 239.1217 (1957), pp. 267–279.

MP2

The MP partition is

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad \hat{H}_0 = \sum_p \varepsilon_p a_p^\dagger a_p, \quad \hat{V} = \hat{H} - \hat{H}_0 \quad (5)$$

The zeroth-order problem is solved by

$$\hat{H}_0 |\Phi_0\rangle = E_0^{(0)} |\Phi_0\rangle, \quad E_0^{(0)} = \sum_i \varepsilon_i, \quad (6)$$

$$\hat{H}_0 |\Phi_i^a\rangle = (E^{(0)} + \varepsilon_i^a) |\Phi_0\rangle, \quad \varepsilon_i^a = \varepsilon_a - \varepsilon_i, \quad (7)$$

$$\hat{H}_0 |\Phi_{ij}^{ab}\rangle = (E^{(0)} + \varepsilon_{ij}^{ab}) |\Phi_0\rangle, \quad \varepsilon_{ij}^{ab} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j, \quad (8)$$

$$\dots \quad (9)$$

where $|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle$, $|\Phi_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle$, etc.

PT2

$$E_0^{(1)} = \langle 0|V|0\rangle, \quad \langle m|0^{(1)}\rangle = \frac{\langle m|V|0\rangle}{(E_0^{(0)} - E_m^{(0)})}, \quad E_0^{(2)} = \sum_{m>0} \frac{|\langle m|V|0\rangle|^2}{(E_0^{(0)} - E_m^{(0)})}. \quad (10)$$

Plugging the MP partition into these expressions:

$$E_0^{(1)} = \langle \Phi_0 | \hat{H} - \hat{H}_0 | \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle - E_0^{(0)} \quad (11)$$

that is

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = E_0^{(0)} + E_0^{(1)} \quad (12)$$

MP2

PT2

$$E_0^{(1)} = \langle 0|V|0\rangle, \quad \langle m|0^{(1)}\rangle = \frac{\langle m|V|0\rangle}{(E_0^{(0)} - E_m^{(0)})}, \quad E_0^{(2)} = \sum_{m>0} \frac{|\langle m|V|0\rangle|^2}{(E_0^{(0)} - E_m^{(0)})}. \quad (13)$$

For $\hat{V} = \hat{H} - \hat{H}_0$, $|m\rangle \in \{|\Phi_i^a\rangle, |\Phi_{ij}^{ab}\rangle\}$,

$$\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle = \langle \Phi_i^a | \hat{H} | \Phi_0 \rangle = f_{ai} \quad (14)$$

$$\langle \Phi_{ij}^{ab} | \hat{V} | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle = \langle ab || ij \rangle \quad (15)$$

The MP1 wavefunction and MP2 energy are

$$|0^{(1)}\rangle = - \sum_{ia} |\Phi_i^a\rangle \frac{f_{ai}}{\varepsilon_i^a} - \sum_{i<j, a<b} |\Phi_{ij}^{ab}\rangle \frac{\langle ab || ij \rangle}{\varepsilon_{ij}^{ab}}, \quad (16)$$

$$E_0^{(2)} = - \sum_{ia} \frac{|f_{ai}|^2}{\varepsilon_i^a} - \sum_{i<j, a<b} \frac{|\langle ab || ij \rangle|^2}{\varepsilon_{ij}^{ab}} \quad (17)$$

For HF orbitals, singles do not contribute because $f_{ai} = 0$ (Brillouin condition).

MP2

Nowadays, MP2 is less widely used except for large systems. It is the cheapest electron correlation method, with a formal scaling of $O(N^5)$. The energy summation $E_0^{(2)} = - \sum_{i < j, a < b} \frac{|\langle ab || ij \rangle|^2}{\epsilon_{ij}^{ab}}$ is of $O(N^4)$. The computational cost of canonical MP2 is dominated by **integral transformation** of the two-electron integral $\langle ab || ij \rangle = [ai|bj] - [aj|bi]$.

$$[pq|rs] = \sum_{\mu\nu\kappa\lambda} [\mu\nu|\kappa\lambda] C_{\mu p}^* C_{\nu q} C_{\kappa r}^* C_{\lambda s} \quad (18)$$

which can be performed sequentially

$$[pq|rs] = \sum_{\mu} \left(\sum_{\nu} \left(\sum_{\kappa} \left(\sum_{\lambda} [\mu\nu|\kappa\lambda] C_{\mu p}^* \right) C_{\nu q} \right) C_{\kappa r}^* \right) C_{\lambda s} \quad (19)$$

Coupled cluster (CC) is a numerical technique used for describing many-body systems. The method was initially developed by Coester and Kümmel in the 1950s for studying nuclear-physics phenomena, but became more frequently used when in 1966 Čížek (and later together with Paldus) reformulated the method for electron correlation in atoms and molecules. It is now one of the most prevalent methods in quantum chemistry that includes electronic correlation.

The single-reference CC can be derived from various perspectives:

- Exponential ansatz for wavefunction⁴
- Diagrammatic summation for amplitudes⁵

We will just introduce the first method, which is the 'canonical' formulation.

⁴Isaiah Shavitt and Rodney J Bartlett. *Many-body methods in chemistry and physics: MBPT and coupled-cluster theory*. Cambridge university press, 2009.

⁵Ingvar Lindgren and John Morrison. *Atomic many-body theory*. Springer-Verlag Berlin Heidelberg, 1982.

CC wavefunction Ansatz

The distinct feature of CC is the exponential ansatz

$$|\Psi_{\text{CC}}\rangle = \Omega_{\text{CC}} |\Phi_{\text{HF}}\rangle, \quad (20)$$

$$\Omega_{\text{CC}} = e^{\hat{T}}, \quad \hat{T} = \sum_{n=1}^{\infty} \hat{T}_n \quad (21)$$

where \hat{T}_n is the n -body excitation operator. This ansatz naturally leads to size-extensivity. Considering two noninteracting subsystems, if $\hat{T} = \hat{T}_A + \hat{T}_B$, then

$$|\Psi_{\text{CC}}\rangle = e^{\hat{T}_A + \hat{T}_B} |\Psi_{\text{HF}}\rangle = e^{\hat{T}_A} e^{\hat{T}_B} |\Psi_{\text{HF}}^A\rangle |\Psi_{\text{HF}}^B\rangle = |\Psi_{\text{CC}}^A\rangle |\Psi_{\text{CC}}^B\rangle \quad (22)$$

such that

$$\hat{H} |\Psi_{\text{CC}}\rangle = (\hat{H}_A + \hat{H}_B) |\Psi_{\text{CC}}^A\rangle |\Psi_{\text{CC}}^B\rangle = (E_A + E_B) |\Psi_{\text{CC}}\rangle \quad (23)$$

This is for exact CC. But we will show that $\hat{T} = \hat{T}_A + \hat{T}_B$ and size-extensivity also hold for **truncated CC**!

Projected Schrödinger equation

To determine the cluster excitation operator \hat{T} in $e^{\hat{T}}|\Phi_0\rangle$. One idea is to apply the variational principle as in CI. Unfortunately, the energy expression

$$E = \frac{\langle \Psi_{CC} | \hat{H} | \Psi_{CC} \rangle}{\langle \Psi_{CC} | \Psi_{CC} \rangle} = \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} \hat{H} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} \quad (24)$$

cannot be evaluated in closed form, namely, the expansion like $e^{\hat{T}^\dagger} e^{\hat{T}}$ does not terminate. Therefore, the conventional formulation of CC is to determine the excitation operator by projecting the Schrödinger equation into a subspace

$$\langle \Phi_\mu | (\hat{H} - E_{CC}) | \Psi_{CC} \rangle = 0 \quad (25)$$

By matching the number of unknowns in $|\Psi_{CC}\rangle$ with the dimension of the bra subspace, we can get a set of nonlinear equation for excitation amplitudes.

Excitation operators

More specifically, suppose \hat{T} can be expanded as

$$\hat{T} = \sum_{\mu} t_{\mu} \hat{\tau}_{\mu}, \quad (26)$$

with the excitation operator $\hat{\tau}_{\mu}$ chosen from $\hat{\tau}_{\mu} \in \{a_i^a, a_{ij}^{ab}, \dots\}$ (**not necessarily complete!**), such that

$$\hat{\tau}_{\mu}|\Phi_0\rangle \triangleq |\Phi_{\mu}\rangle, \quad \hat{\tau}_{\mu}^{\dagger}|\Phi_0\rangle = 0. \quad (27)$$

Then, the projected Schrödinger equation can be written as

$$\langle\Phi_0|(\hat{H} - E_{CC})|\Psi_{CC}\rangle = 0 \quad (\text{energy equation}) \quad (28)$$

$$\langle\Phi_0|\hat{\tau}_{\mu}^{\dagger}(\hat{H} - E_{CC})|\Psi_{CC}\rangle = 0 \quad (\text{amplitude equation}) \quad (29)$$

CC energy equation

Let us take a closer look at these two equations

$$\langle \Phi_0 | (\hat{H} - E_{CC}) | \Psi_{CC} \rangle = 0 \quad (\text{energy equation}) \quad (30)$$

$$\langle \Phi_0 | \hat{\tau}_\mu^\dagger (\hat{H} - E_{CC}) | \Psi_{CC} \rangle = 0 \quad (\text{amplitude equation}) \quad (31)$$

The energy equation can be rewritten as

$$E_{CC} = \langle \Phi_0 | \hat{H} | \Psi_{CC} \rangle = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle \triangleq \langle \Phi_0 | \bar{H} | \Phi_0 \rangle \quad (32)$$

where the **similarity transformed Hamiltonian** $\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$ can be written as

$$\bar{H} = \hat{H} + [\hat{H}, \hat{T}] + \dots \triangleq \hat{H} + (\hat{H} e^{\hat{T}})_c \quad (33)$$

The subscript 'c' means 'connected' (slightly different from definition in standard books). Then, the CC correlation energy is

$$E_{CC}^{\text{corr}} \triangleq E_{CC} - E_{\text{HF}} = \langle \Phi_0 | (\hat{H} e^{\hat{T}})_c | \Phi_0 \rangle \quad (34)$$

CC amplitude equation

The amplitude equation can be written as

$$\langle \Phi_\mu | \hat{H} | \Psi_{CC} \rangle = E_{CC} \langle \Phi_\mu | \Psi_{CC} \rangle \quad (35)$$

Recall $E_{CC} = \langle \Phi_0 | \hat{H} | \Psi_{CC} \rangle$, the goal is to remove E_{CC} from the amplitude equation. To this end, the LHS of Eq. (35) can be reformulated as

$$\text{LHS} = \langle \Phi_\mu | e^{\hat{T}} e^{-\hat{T}} \hat{H} | \Psi_{CC} \rangle = \sum_\nu \langle \Phi_\mu | e^{\hat{T}} | \nu \rangle \langle \nu | e^{-\hat{T}} \hat{H} | \Psi_{CC} \rangle = \sum_\nu \langle \Phi_\mu | e^{\hat{T}} | \nu \rangle \langle \nu | \bar{H} | \Phi_0 \rangle \quad (36)$$

The resolution-of-identity (RI) $\sum_\nu |\nu\rangle\langle\nu| = \hat{I}$ is applied in the Hilbert space. We can separate $\hat{I} = P_0 + P_t + Q$, then the RHS becomes

$$\langle \Phi_\mu | e^{\hat{T}} | \Phi_0 \rangle \langle \Phi_0 | \bar{H} | \Phi_0 \rangle + \sum_\nu \langle \Phi_\mu | e^{\hat{T}} | \Phi_\nu \rangle \langle \Phi_\nu | \bar{H} | \Phi_0 \rangle + \sum_{\nu_Q} \langle \Phi_\mu | e^{\hat{T}} | \Phi_{\nu_Q} \rangle \langle \Phi_{\nu_Q} | \bar{H} | \Phi_0 \rangle \quad (37)$$

The first term is just the RHS of Eq. (35).

CC amplitude equation

Now the CC amplitude equation becomes

$$\sum_{\nu} \langle \Phi_{\mu} | e^{\hat{T}} | \Phi_{\nu} \rangle \langle \Phi_{\nu} | \bar{H} | \Phi_0 \rangle + \sum_{\nu_Q} \langle \Phi_{\mu} | e^{\hat{T}} | \Phi_{\nu_Q} \rangle \langle \Phi_{\nu_Q} | \bar{H} | \Phi_0 \rangle = 0 \quad (38)$$

The matrix $[\mathbf{S}]_{\mu\nu} = [\langle \Phi_{\mu} | e^{\hat{T}} | \Phi_{\nu} \rangle]$ can be made as a lower triangular matrix with diagonal elements all equal to one by properly ordering $\{|\Phi_{\nu}\rangle\}$, which means that it is invertible. Then,

$$\langle \Phi_{\nu} | \bar{H} | \Phi_0 \rangle + \sum_{\mu} [\mathbf{S}^{-1}]_{\nu\mu} \sum_{\nu_Q} \langle \Phi_{\mu} | e^{\hat{T}} | \Phi_{\nu_Q} \rangle \langle \Phi_{\nu_Q} | \bar{H} | \Phi_0 \rangle = 0 \quad (39)$$

Hierarchical truncation: if the excitation operators are selected hierarchically, viz. CCS, CCSD, CCSDT, etc., then $\langle \Phi_{\mu} | e^{\hat{T}} | \Phi_{\nu_Q} \rangle = 0$, which leads to

$$\langle \Phi_{\nu} | \bar{H} | \Phi_0 \rangle = 0. \quad (40)$$

CC by similarity transformation

There is another more usual formulation of CC in term of similarity transformation. Starting with

$$\hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{CC}e^{\hat{T}}|\Phi_0\rangle, \quad (41)$$

then multiplying both sides by $e^{-\hat{T}}$,

$$\bar{H}|\Phi_0\rangle = E_{CC}|\Phi_0\rangle. \quad (42)$$

The projection naturally leads to

$$\langle\Phi_0|\bar{H}|\Phi_0\rangle = E_{CC} \quad (43)$$

$$\langle\Phi_\mu|\bar{H}|\Phi_0\rangle = 0 \quad (44)$$

We can take these equations as the starting point to make further approximation, such as the selection/truncation of excitation operators. These two formulations reveal the subtlety that **making the same approximation in equivalent formulations can lead to different results!**

CC by similarity transformation

The advantages of the similarity transformation is that \bar{H} terminates

$$\bar{H} = \hat{H} + (\hat{H}\hat{T} + \frac{1}{2!}\hat{H}\hat{T}^2 + \frac{1}{3!}\hat{H}\hat{T}^3 + \frac{1}{4!}\hat{H}\hat{T}^4)_c \quad (45)$$

because \hat{H} contains at most four-indexed operators. The energy equation is simple

$$\begin{aligned} E_{CC}^{\text{corr}} &= \langle \Phi_0 | (\hat{H}e^{\hat{T}})_c | \Phi_0 \rangle = \langle \Phi_0 | (\hat{H}\hat{T} + \frac{1}{2}\hat{H}\hat{T}^2)_c | \Phi_0 \rangle \\ &= \sum_{ia} f_{ia} t_i^a + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab} + \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b \end{aligned} \quad (46)$$

The amplitude equations $\langle \Phi_\mu | \hat{H} | \Phi_0 \rangle + \langle \Phi_\mu | (\hat{H}e^{\hat{T}})_c | \Phi_0 \rangle = 0$ are also nonlinear equations, which can be solved by iterative methods introduced before. The detailed forms can be derived using Wick's theorem/diagrammatic tools, see Ref.⁶.

⁶T Daniel Crawford and Henry F Schaefer. "An introduction to coupled cluster theory for computational chemists". In: *Reviews in computational chemistry* 14 (2000), pp. 33–136.

Size extensivity in truncated CC

Now we come back to the problem of size extensivity in truncated CC. The size extensivity is most obvious from the perspective of **connected diagrams**. Here, we try to illustrate it from an algebraic perspective. For a system composed of two noninteracting subsystems $\hat{H} = \hat{H}_A + \hat{H}_B$,

$$|\Phi_0\rangle = |0_A 0_B\rangle, \quad \hat{T} = \hat{T}_A + \hat{T}_B + \hat{T}_{AB}, \quad e^{\hat{T}} = e^{\hat{T}_A} e^{\hat{T}_B} e^{\hat{T}_{AB}} \quad (47)$$

Here, \hat{T}_{AB} refer to operators with mixed indices. Recall the action of commutator

$$[a_q^p, a_s^r] = \delta_q^r a_s^p - \delta_s^p a_q^r \quad (48)$$

then we have the following identities

$$[a_{q_A}^{p_A}, a_{s_A}^{r_B}] = \delta_{s_A}^{p_A} a_{q_A}^{r_B}, \quad [a_{q_A}^{p_A}, a_{s_B}^{r_A}] = \delta_{q_A}^{r_A} a_{s_B}^{p_A}, \quad [a_{q_A}^{p_A}, a_{s_B}^{r_B}] = 0 \quad (49)$$

Thus, the B -operators in a mixed operator (e.g., $a_{s_A}^{r_B}$) remain intact for commutators with pure A -operators.

Size extensivity in truncated CC

The energy equation for the total system is

$$\begin{aligned} E_{CC}^{\text{corr}} &= \langle \Phi_0 | (\hat{H} e^{\hat{T}})_c | \Phi_0 \rangle = \langle 0_A 0_B | (\hat{H} e^{\hat{T}})_c | 0_A 0_B \rangle \\ &= \langle 0_A 0_B | (\hat{H}_A e^{\hat{T}})_c | 0_A 0_B \rangle + \langle 0_A 0_B | (\hat{H}_B e^{\hat{T}})_c | 0_A 0_B \rangle \end{aligned} \quad (50)$$

Note that $(\hat{H}_A e^{\hat{T}})_c = (\hat{H}_A e^{\hat{T}_A + \hat{T}_{AB}})_c = (\hat{H}_A e^{\hat{T}_A})_c + \hat{\Upsilon}_{AB}^A$, where $\hat{\Upsilon}_{AB}^A$ is the operators that contain **at least one** \hat{T}_{AB} .

Because there is no operators in \hat{H}_A to contract with (particle or hole) creation B -operators in \hat{T}_{AB} , each term in $\hat{\Upsilon}_{AB}^A$ will retain at least one particle creation $a_{a_B}^\dagger$ or one hole creation a_{i_B} originated from in \hat{T}_{AB} . This implies $\langle 0_B | \hat{\Upsilon}_{AB}^A | 0_B \rangle = 0$, such that $E_{CC}^{\text{corr}} = \langle 0_A | (\hat{H}_A e^{\hat{T}_A})_c | 0_A \rangle + \langle 0_B | (\hat{H}_B e^{\hat{T}_B})_c | 0_B \rangle$.

This does not prove the extensivity yet, since we still need to show that \hat{T}_A is the same as the one determined from the subsystem alone.

Size extensivity in truncated CC

Likewise, the amplitude equation can be written as

$$\langle \mu_A \nu_B | \bar{H} | 0_A 0_B \rangle = \langle \mu_A \nu_B | \bar{H}_A + \hat{\Upsilon}_{AB}^A + \bar{H}_B + \hat{\Upsilon}_{AB}^B | 0_A 0_B \rangle = 0 \quad (51)$$

where $\bar{H}_A = e^{-\hat{T}_A} \hat{H}_A e^{\hat{T}_A}$. It simplifies to

$$\begin{aligned} \langle \mu_A | \bar{H}_A | 0_A \rangle \delta_{\nu_B 0_B} + \langle \mu_A \nu_B | \hat{\Upsilon}_{AB}^A | 0_A 0_B \rangle (1 - \delta_{\nu_B 0_B}) + \\ \langle \nu_B | \bar{H}_B | 0_B \rangle \delta_{\mu_A 0_A} + \langle \mu_A \nu_B | \hat{\Upsilon}_{AB}^B | 0_A 0_B \rangle (1 - \delta_{\mu_A 0_A}) = 0 \end{aligned} \quad (52)$$

For three classes of excited configurations ($|\mu_A 0_B\rangle$, $|0_A \nu_B\rangle$, $|\mu_A \nu_B\rangle$, $\mu, \nu > 0$),

$$\langle \mu_A | \bar{H}_A | 0_A \rangle + \langle \mu_A 0_B | \hat{\Upsilon}_{AB}^B | 0_A 0_B \rangle = 0 \quad (53)$$

$$\langle 0_A \nu_B | \hat{\Upsilon}_{AB}^A | 0_A 0_B \rangle + \langle \nu_B | \bar{H}_B | 0_B \rangle = 0 \quad (54)$$

$$\langle \mu_A \nu_B | \hat{\Upsilon}_{AB}^A | 0_A 0_B \rangle + \langle \mu_A \nu_B | \hat{\Upsilon}_{AB}^B | 0_A 0_B \rangle = 0 \quad (55)$$

The last equation has an obvious solution $\hat{T}_{AB} = 0$, and hence coupling terms $\hat{\Upsilon}_{AB}^X = 0$. The first two eqs reduce to $\langle \mu_X | \bar{H}_X | 0_X \rangle = 0$ for individual subsystem. This proves that $\hat{T} = \hat{T}_A + \hat{T}_B$, if \hat{T} is obtained by solving the 'connected' amplitude equation. Therefore, (arbitrarily **truncated**) CC is size-extensive.

Summary

We have introduced the basic idea of CC.

In practice, **CCSD(T)**⁷ [coupled-cluster singles and doubles with perturbative triples] is referred as the 'gold-standard', which emerged as a compromise between accuracy and efficiency. (T) indicates that the connected triples \hat{T}_3 is estimated in a non-iterative way using many-body perturbation theory arguments.

However, keep in mind that CC methods are not expected to work well for multi-configurational problems!

⁷Krishnan Raghavachari et al. "A fifth-order perturbation comparison of electron correlation theories". In: *Chemical Physics Letters* 157 (1989), pp. 479–483.

Excited states: EOM-CC

Equation-of-motion CC ansatz:

$$|\Psi_I\rangle = \hat{R}_I e^{\hat{T}} |\Phi_0\rangle = e^{\hat{T}} \hat{R}_I |\Phi_0\rangle \quad (56)$$

Using the Schrödinger equation,

$$\hat{H} |\Psi_I\rangle = E_I |\Psi_I\rangle \quad (57)$$

Left multiplying $e^{-\hat{T}}$ on both sides and using $[e^{\hat{T}}, \hat{R}_I] = 0$,

$$e^{-\hat{T}} \hat{H} \hat{R}_I e^{\hat{T}} |\Phi_0\rangle = E_I \hat{R}_I |\Phi_0\rangle, \quad (58)$$

which leads to a CI-like equation but with \bar{H} ,

$$\boxed{\bar{H} \hat{R}_I |\Phi_0\rangle = E_I \hat{R}_I |\Phi_0\rangle} \quad (59)$$

Further subtracting $\hat{R}_I \bar{H} |\Phi_0\rangle = E_0 \hat{R}_I |\Phi_0\rangle$ leads to the EOM form

$$\boxed{[\bar{H}, \hat{R}_I] |\Phi_0\rangle = \omega_I \hat{R}_I |\Phi_0\rangle} \quad (60)$$

Excited states: EOM-CC

- **CISD** (configuration interaction singles and doubles):

$$\mathbf{H}_{\text{CISD}} = \begin{bmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & 0 & \langle \Phi_0 | \hat{H} | \Phi_{mn}^{de} \rangle \\ 0 & \langle \Phi_i^a | \hat{H} | \Phi_m^d \rangle & \langle \Phi_i^a | \hat{H} | \Phi_{mn}^{de} \rangle \\ \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_m^d \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{mn}^{de} \rangle \end{bmatrix} \quad (61)$$

- **EOM-CCSD** (equation-of-motion singles and doubles):

$$\hat{R}_I = r_0 + \sum_{ai} r_i^a a_i^a + \frac{1}{4} \sum_{abij} r_{ij}^{ab} a_{ij}^{ab} \quad (62)$$

$$\begin{aligned} \bar{\mathbf{H}}_{\text{EOM-CCSD}} &= \begin{bmatrix} \langle \Phi_0 | \bar{H} | \Phi_0 \rangle & \langle \Phi_i^a | \bar{H} | \Phi_{mn}^{de} \rangle & \langle \Phi_0 | \bar{H} | \Phi_{mn}^{de} \rangle \\ \langle \Phi_i^a | \bar{H} | \Phi_0 \rangle & \langle \Phi_i^a | \bar{H} | \Phi_m^d \rangle & \langle \Phi_i^a | \bar{H} | \Phi_{mn}^{de} \rangle \\ \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_0 \rangle & \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_m^d \rangle & \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_{mn}^{de} \rangle \end{bmatrix} \\ &= \begin{bmatrix} \textcolor{red}{E_{\text{CC}}} & \langle \Phi_i^a | \bar{H} | \Phi_{mn}^{de} \rangle & \langle \Phi_0 | \bar{H} | \Phi_{mn}^{de} \rangle \\ \mathbf{0} & \langle \Phi_i^a | \bar{H} | \Phi_m^d \rangle & \langle \Phi_i^a | \bar{H} | \Phi_{mn}^{de} \rangle \\ \mathbf{0} & \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_m^d \rangle & \langle \Phi_{ij}^{ab} | \bar{H} | \Phi_{mn}^{de} \rangle \end{bmatrix} \end{aligned} \quad (63)$$

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MRPT2

There are different flavors of MRPT2 as generalizations of MP2 to a CASSCF reference. Some widely used variants include

- **CASPT2**: complete active space second-order perturbation theory[2, 1]
- **NEVPT2**: N -electron valence state perturbation theory[4, 3]

Other MRPT2 include: MRPT2 (Hirao), configuration-based PT2, MCPT2 (Surjan), SS-MRPT2, GVVPT2, SDS-PT2, MRDSRG-PT2, etc.

Why there are many different variants in MR case?

- **Underlying theory**: some derived from PT approximation to MRCC
- **Less uniquely defined \hat{H}_0** : Fock, Dyall's, Fink's \hat{H}_0 ⁸
- **Perturbed configuration**: uncontracted/internally contracted

⁸Yuri Alexandre Aoto et al. "Perturbation Expansion of Internally Contracted Coupled-Cluster Theory up to Third Order". In: *Journal of chemical theory and computation* 15.4 (2019), pp. 2291–2305.

MRCC

Multi-reference generalization of CC: **too many of them!**

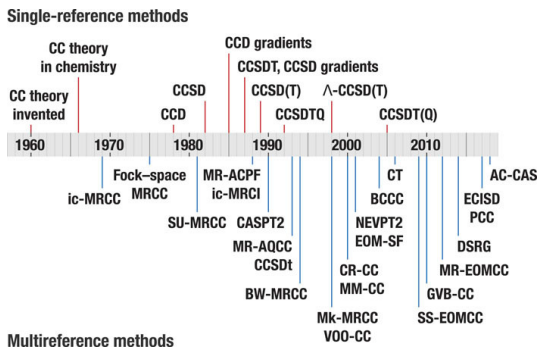


Figure 1: Timeline of the development of SR and MR electronic structure theories.⁹

⁹Francesco A Evangelista. "Perspective: Multireference coupled cluster theories of dynamical electron correlation". In: *The Journal of chemical physics* 149.3 (2018), p. 030901.

MRCC

MRCC methods and their deficiencies (**may not be precise!**):

- 1 SU-MRCC: intruder state
- 2 SS-MRCC: BW-MRCC (extensivity), Mk-MRCC (sufficiency condition, proper residue), Malrieu's MRCC (extensivity?)
- 3 MRexpT: core-extensive
- 4 ic-MRCC: linear dependent excitation operators - numerical issues
- 5 CT: linear dependence
- 6 SS-EOMCC/pIC-MRCC: core-extensive
- 7 BCCC: linear parameterization for excitations involving active orbitals
- 8 SR-MRCC: higher-rank excitations, reference dependent
- 9 QS-MRCC: reference dependent
- 10 MRDSRG: parameter-dependent intruder state
- 11 FS-MRCC: too complicated?

Desiderata for a good MRCC theory¹⁰¹¹:

- preserve symmetry of wavefunction, unbiased with respect to reference,
- high accuracy, proper residual,
- size extensivity, naturally reduce to SRCC,
- numerically stable,
- orbital invariance,
- multi-state extension, ...

Unfortunately, no MRCC satisfies all criteria after decades of extensive developments! Perhaps, these requirements are too restrictive for an approximate method.

¹⁰[Dmitry I Lyakh et al.](#) "Multireference nature of chemistry: The coupled-cluster view". In: *Chemical reviews* 112.1 (2012), pp. 182–243.

¹¹[Andreas Koehn et al.](#) "State-specific multireference coupled-cluster theory". In: *Wiley Interdisciplinary Reviews: Computational Molecular Science* 3.2 (2013), pp. 176–197.

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