Computational Chemistry Univ. of Iceland 2025

Coupled Cluster Approach

So far, we have considered two different post Hartree-Fock methods: Configuration Interaction (CI) based on a linear expansion of the HF and excited Slater determinants, $|\Psi_{CI}\rangle = \left(1 + \hat{C}\right)|\Psi_0\rangle$, where $\hat{C}$ is the excitation operator generating a sum of all excited determinants, and applying the variational principle to determine the expansion coefficients, and Møller-Plesset perturbation theory where the Hamiltonian is written as $\hat{H} = \hat{H}_0 + \hat{H}'$, with $\hat{H}_0$ being the effective HF Hamiltonian and $\hat{H}'$ being the correction in order to recover the exact Hamiltonian. Both methods address the issue of missing correlation in the single determinant approach. However, they both suffer from some shortcomings. The perturbation expansion does not in general converge and problems can arise with degenerate orbitals, while truncated CI leads to size-inconsistency which is problematic when calculating the binding energy of molecular fragments. The Q correction in QCISD introduces approximate size-consistency but only for a dimer. Here the third commonly used post HF method will be introduced, namely the coupled cluster (CC) approach. It has the advantage of being size-consistent and can include high excitation Slater determinants in a consistent way.

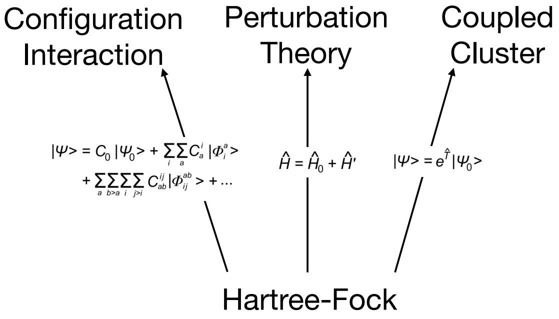

Figure 1: *The three most commonly used post Hartree-Fock methods are based on different approaches: Configuration interaction makes use of the variational principle to optimise a linear combination of Slater determinants, perturbation theory estimates the weight on excited Slater determinants at various levels of an expansion, and coupled cluster expands the wave function in terms of an exponential of the excitation operator.*

The cluster operator is defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... \tag{1}$$

where $\hat{T}_1$ is the operator that generates a sum over all single excitations, $\hat{T}_2$ double excitations, etc. Letting $|\Psi_0\rangle$ denote the HF ground state Slater determinants, the action of the first two operators can be written as

$$\hat{T}_1 |\Psi_0\rangle = \sum_i \sum_a t_a^i |\Phi_i^a\rangle \tag{2}$$

$$\hat{T}_2 |\Psi_0\rangle = \sum_{ij} \sum_{ab} t_{ab}^{ij} |\Phi_{ij}^{ab}\rangle . \tag{3}$$

The coefficients, t_a^i, t_{ab}^{ij}, etc., are referred to as amplitudes and will be determined in a special way without carrying out a variational calculation or a perturbation calculation.

In order to effectively include high order excitations in a systematic way, the exponential of the cluster operator is defined as $e^{\hat{T}}$ and applied to the HF ground state Slater determinant to give the CC wave function. The exponential is written out in a Taylor expansion

$$|\Psi_{CC}\rangle = e^{\hat{T}} |\Psi_0\rangle = \left(1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + ...\right) |\Psi_0\rangle . \tag{4}$$

The Taylor expansion truncates naturally due to the finite number of electrons and basis functions used in a practical calculation.

Tt follows that

$$e^{\hat{T}} = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{2}\hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2\hat{T}_1 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_1^3 + \ldots \tag{5}$$

$$= 1 + \color{red}{\hat{T}_1} + \color{green}{\frac{1}{2}\hat{T}_1^2 + \hat{T}_2} + \color{blue}{\frac{1}{6}\hat{T}_1^3 + \hat{T}_1\hat{T}_2 + \hat{T}_3} + ... \tag{6}$$

Note that single excitations are marked in red, double excitations in green and triple excitations in blue.

Unlike the CI expansion, CC naturally includes both coupled and decoupled excitations with certain weights, as is evident from the relationship between the excitation operators in the two representations. Letting $\hat{C}$ denote the CI excitation operator of a certain order and $\hat{T}$ the CC excitation operator

$$\hat{C}_1 = \hat{T}_1 \tag{7}$$

$$\hat{C}_2 = \frac{1}{2}\hat{T}_1^2 + \hat{T}_2 \tag{8}$$

$$\hat{C}_3 = \frac{1}{6}\hat{T}_1^3 + \hat{T}_1\hat{T}_2 + \hat{T}_3 \tag{9}$$

Higher excitations are present in $e^{\hat{T}}$, even if only $\hat{T}_1$ and $\hat{T}_2$ are explicitly included.

The challenge now is to determine the amplitudes, t. They could be evaluated variationally as in the CI calculations, but instead the common practice is to make use of the Schrödinger equation in a non-variational calculation. There, one equation is obtained for every type of Slater determinant projected onto the Schrödinger equation. As all excited states are orthogonal to the ground state, matrix elements between excited Slater determinants and the ground state determinant are 0. This condition can directly be applied to the Hamiltonian matrix elements because $e^{\hat{T}}|\Psi_0\rangle$ is an eigenfunction of $\hat{H}$, meaning that the Hamiltonian can be applied to $e^{\hat{T}}|\Psi_0\rangle$, yielding a scalar. Starting with the basic CC equation where the energy E_{CC} is obtained when the Hamiltonian is applied to the CC ket

$$\hat{H}|\Psi_{CC}\rangle = E_{CC}|\Psi_{CC}\rangle \tag{10}$$

which can be rewritten using $|\Psi_{CC}\rangle = e^{\hat{T}}|\Psi_0\rangle$ as

$$\hat{H}e^{\hat{T}}|\Psi_0\rangle = E_{CC}e^{\hat{T}}|\Psi_0\rangle\,. \tag{11}$$

Now, left multiplying with the CC ket

$$\langle\Psi_0|\,e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle = E_{CC}\langle\Psi_0|\Psi_0\rangle = E_{CC} \tag{12}$$

gives the E_{CC} energy again, but left multiplying with any of the excited Slater determinants, $|\Phi\rangle$, gives zero because of orthogonality

$$\langle\Phi|\,e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Psi_0\rangle = E_{CC}\langle\Phi|\Psi_0\rangle \overset{!}{=} 0. \tag{13}$$

This non-linear set of equations is solved to determine the amplitudes, t.

The most common form of CC is to truncate at double excitations, the CCSD approximation, i.e. $\hat{T} = \hat{T}_1 + \hat{T}_2$ in which case the equations become

$$\langle\Psi_0| e^{-(\hat{T}_1+\hat{T}_2)}\hat{H}e^{(\hat{T}_1+\hat{T}_2)} |\Psi_0\rangle = E_{CCSD} \tag{14}$$

$$\langle\Phi_i^a| e^{-(\hat{T}_1+\hat{T}_2)}\hat{H}e^{(\hat{T}_1+\hat{T}_2)} |\Psi_0\rangle = 0 \tag{15}$$

$$\left\langle\Phi_{ij}^{ab}\right| e^{-(\hat{T}_1+\hat{T}_2)}\hat{H}e^{(\hat{T}_1+\hat{T}_2)} |\Psi_0\rangle = 0. \tag{16}$$

There are many different ways of solving this coupled set of non-linear equations.

The corresponding CCSD energy is

$$\begin{aligned} E_{CCSD} = \langle\Psi_0| e^{-T}He^{T} |\Psi_0\rangle = E_{HF} + E_C = E_{HF} + 2\sum_{ia} F_{ia}t_a^i \\ + \sum_{ijab}[2(ia|jb) - (ib|ja)](t_{ab}^{ij} + t_a^i t_b^j) \ . \end{aligned} \tag{17}$$

where $F_{rs} = h_{rs} + \sum_r(2(rr|st) - (rs|rt))$ are elements of the Fock matrix obtained in the HF calculation preceding the CC calculation and E_C is the correlation energy. The integrals h_{rs}, $(rr|st)$ and $(rs|rt)$ are the one-electron parts of the Fock matrix, the Coulomb and the exchange integrals in the chemist's notation.

The computational effort of the CCSD method scales as O(N^6). By extending this to include triple excitations, CCSDT, the calculations become significantly more demanding, scaling as O(N^8). The usual way of improving upon the CCSD method is to apply an approximate perturbation correction due to triple excitations. This method is referred to as CCSD(T). With the perturbative triples correction the computational effort scales as O(N^7) since the perturbative correction scales linearly. CCSD(T) is considered the 'gold standard' of quantum chemistry due to its high accuracy and reliability, but is still a single-reference method in that it builds on the HF ground state Slater determinant.

The high accuracy and reliability of standard CCSD(T) are accompanied by a high computational cost, as shown in figure 2. However, the advantages of the CC approach have motivated scientists around the world to improve particularly its scaling while conserving as much of the recovered correlation energy as possible. Many different methods have been derived from basic

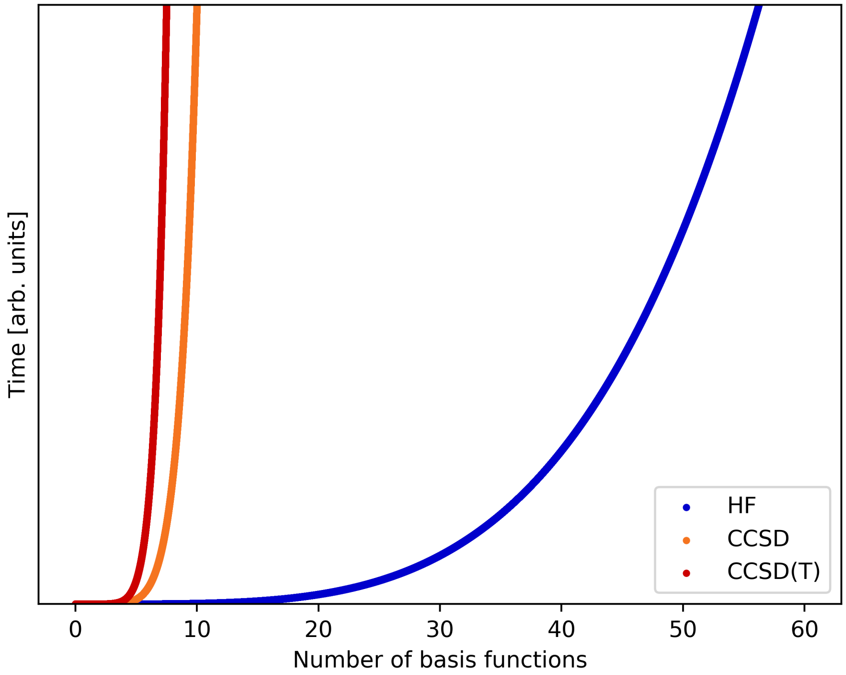

Figure 2: The computational effort of the three methods HF, CCSD and CCSD(T) scales as O(N^4), O(N^7) and O(N^8). Note that the graph only shows the leading terms without any prefactors in order to illustrate the general scaling difference. The HF scaling is depicted in blue, CCSD scaling in orange and CCSD(T) scaling in red.

CC theory, such as *local* CCSD(T) and *orbital specific virtual* CCSD. There are also CC-based methods which can evaluate excited state energies, such as equations-of-motion CC. Recently, an improved version of CC has been implemented in ORCA, which is called domain based local pair natural orbital CC (DLPNO-CC). In this approach, a truncated virtual orbital space is selected for each pair of electrons in order to describe their correlation more efficiently. Additionally, the contribution of each electron pair to the correlation energy is prescreened by evaluating a dipole approximation to the Coulomb integral of the pair. Weakly contributing pairs are neglected, intermediately interacting pairs are treated perturbatively and strongly interacting ones are included exactly. In this way, a nearly linearly scaling CC method is obtained, which captures most of the correlation energy compared to standard CC approaches. The neglect of some of these contributions can reduce the accuracy, however, and lead to an underestimate of, for example, the long range attractive dispersion interaction.

Methods beyond CCSD(T) are infrequently used, such as CCSDT, CCSDTQ, etc. They have been implemented in specialised software packages a e. g. MRCC. Such high truncations are computationally highly demanding, as CCSDTQ scales as $\mathrm{O}(\mathrm{N}^{10})$ and the scaling only becomes even faster for the higher truncations (the exponent increases by 2 for every higher excitation included in $\hat{T}$).