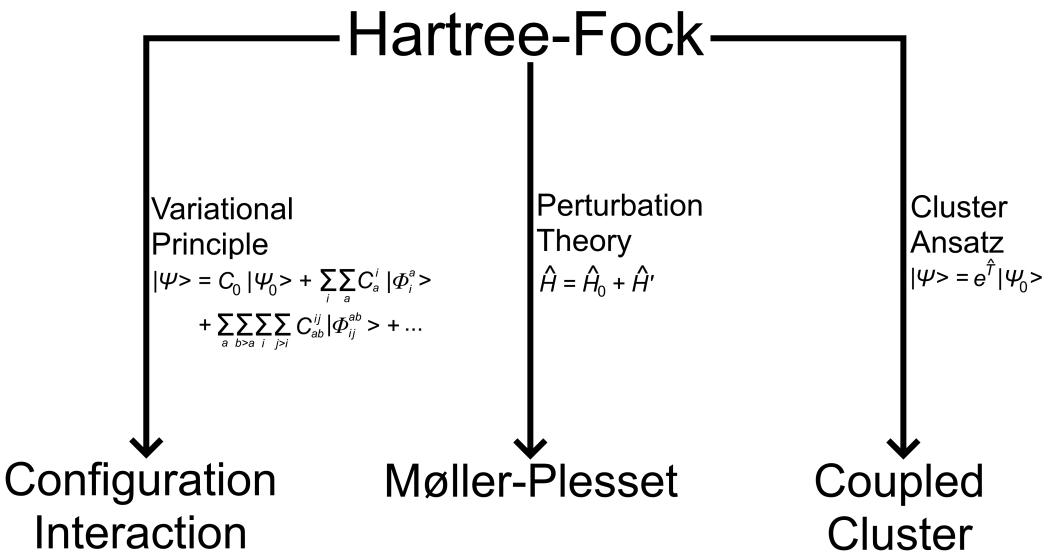

Figure 1: The three post Hartree-Fock methods are based on different ansatzes: Configuration interaction makes use of the variational principle by applying it to a linear expansion in Slater determinant space and Møller-Plesset perturbates the Hartree-Fock solution, while Coupled Cluster expands the wave function in terms of an exponential of an excitation operator.

Introduction

We have considered two different post Hartree-Fock (HF) methods: (Linear) Configuration Interaction (CI) based on the linear inclusion of excited Slater determinants ($|\Psi_{CI}\rangle = \left(1 + \hat{C}\right) |\Psi_0\rangle$, $\hat{C}$ being the excitation operator generating a sum of all excited determinants) and applying the variational principle to the extended determinant space, and Møller-Plesset perturbation theory ($\hat{H} = \hat{H}_0 + \hat{H}'$, $\hat{H}_0$ and $\hat{H}'$ being the HF and perturbation Hamiltonians, respectively). Both methods address the issue of missing dynamical correlation in the single determinant approach. However, they suffer from systematic shortcomings. While perturbation theory struggles with degenerate orbitals, truncated LCI leads to size-inconsistency due to the exclusion of simultaneous excitations in case of non-interacting (sub-)systems. Møller-Plesset perturbation theory succeeds to circumvent this problem by avoiding the linear expansion in determinant space entirely and is therefore much more useful for calculations of physicochemical properties, such as reaction enthalpies.

Another approach improves upon the LCI expansion by adding in the missing excitations by hand and moving to higher order polynomials. As these additional determinants are part of a quadratic expansion for the simplest case of two non-interacting (sub-)systems, this approach is referred to as QCI for this case.

$$E_{QCISD} = E_{HF} + \frac{1}{4}\sum_{ijab} \langle ij||ab\rangle \, C_{ab}^{ij} \tag{1}$$

$$E_C C_a^i = \langle \Phi_i^a | \, \hat{H} \left(1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_1\hat{C}_2\right) |\Psi_0\rangle \tag{2}$$

$$E_C C_{ab}^{ij} = \left\langle \Phi_{ij}^{ab} \right| \hat{H} \left(1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_2\hat{C}_2\right) |\Psi_0\rangle \tag{3}$$

In these equations, E_{QCISD} is the QCISD energy, E_{HF} is the HF energy, E_C is the correlation energy, $\hat{H}$ is the Hamiltonian, $\langle rs||tu\rangle$ is an antisymmetrized two-electron integral in the physicist's notation, C are the expansion coefficients of the total wave function $|\Psi\rangle$, $|\Psi_0\rangle$ is the ground state HF wave function and Φ is any kind of excited slater determinant, obtained from the HF ground state determinant $|\Psi_0\rangle$ by switching occupied and virtual orbitals. Note that occupied orbitals are denoted by $i, j, k, l...$, virtual orbitals by $a, b, c, d...$ and general orbitals by $r, s, t, u...$, respectively. The red operator products are the manually added terms. These are decoupled products of excitations. In the case of more than two non-interacting (sub-)systems, it becomes necessary to add higher-order terms than quadratic, such as cubic for three non-interacting systems, quarternary for four non-interacting systems and infinite-order for infinite non-interacting systems. A more rigorous and systematic way of forming such an infinite-order polynomial of the excitation operator in order to recover size consistency for all systems originates in nuclear physics and is called the coupled cluster (CC) ansatz. This approach is the third wave function based quantum chemical ansatz.

General CC

Within the general CC ansatz, the cluster operator $e^{\hat{T}}$ is applied to the HF ground state wave function. The exponential $e^{\hat{T}}$ of the CC excitation operator $\hat{T}$ consists of a sum of different n-tuple excitations of the ground state determinant, i. e. $\hat{T}_1$ is a single excitation, $\hat{T}_2$ is double excitation etc. Since it is impossible to diagonalize the cluster operator matrix due to the lack of an analytical representation, the common way to treat the exponential is to form a complete Taylor expansion which truncates naturally due to the finite number of electrons and basis functions used in the calculation.

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

where

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... \tag{5}$$

and it follows that

$$e^{\hat{T}} = \hat{T}_1 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_2 + \frac{1}{6}\hat{T}_1^3 + \hat{T}_1\hat{T}_2 + \hat{T}_3 + ... \tag{6}$$

As opposed to CI, CC naturally differentiates between coupled and decoupled excitations, as is evident from the relationship between the excitation operators in the two representations.

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

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

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

$\hat{C}$ is the CI excitation operator and $\hat{T}$ is the CC excitation operator. Note that single excitations are marked in red, double excitations in green and triple excitations in blue. Higher excitations are present, but not explicitely shown.

The wave function within the CC formalism is defined as

$$|\Psi_{CC}\rangle = |\Psi_0\rangle + \sum_{ia} t_a^i |\Phi_i^a\rangle + \sum_{ijab} t_{ab}^{ij} |\Phi_{ij}^{ab}\rangle + \sum_{ijkabc} t_{abc}^{ijk} |\Phi_{ijk}^{abc}\rangle + ... \tag{10}$$

The expansion coefficients t are called amplitudes and our primary goal is to determine them, similarly to the calculation of the coefficients C in the CI scheme. In principle, the CC amplitudes could be evaluated variationally.

$$E_{CC} = \frac{\langle\Psi_{CC}|\,\hat{H}\,|\Psi_{CC}\rangle}{\langle\Psi_{CC}|\Psi_{CC}\rangle} = \frac{\langle\Psi_0|\,e^{-\hat{T}}\hat{H}e^{\hat{T}}\,|\Psi_0\rangle}{\langle\Psi_0|\,e^{-\hat{T}}e^{\hat{T}}\,|\Psi_0\rangle} \tag{11}$$

$$= \frac{\left\langle\left(1+\hat{T}+\frac{1}{2}\hat{T}^2+\frac{1}{6}\hat{T}^3+...\right)\Psi_0\middle|\,\hat{H}\,\middle|\left(1+\hat{T}+\frac{1}{2}\hat{T}^2+\frac{1}{6}\hat{T}^3+...\right)\Psi_0\right\rangle}{\left\langle\left(1+\hat{T}+\frac{1}{2}\hat{T}^2+\frac{1}{6}\hat{T}^3+...\right)\Psi_0\middle|\left(1+\hat{T}+\frac{1}{2}\hat{T}^2+\frac{1}{6}\hat{T}^3+...\right)\Psi_0\right\rangle}$$

It is evident that this approach is computationally demanding and infeasible since none of the four Taylor expansions of the total CC wave function can be truncated in this general description (complete basis set, arbitrary number of electrons). Therefore, it is much more convenient to obtain the amplitudes non-variationally by projecting the entire Slater determinant space onto the Schrödinger equation. In following this scheme, one obtains one equation 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.

$$\hat{H}\,|\Psi_{CC}\rangle = E_{CC}\,|\Psi_{CC}\rangle \tag{12}$$

$$\hat{H}e^{\hat{T}}\,|\Psi_0\rangle = E_{CC}e^{\hat{T}}\,|\Psi_0\rangle \tag{13}$$

$$\langle\Psi_0|\,e^{-\hat{T}}\hat{H}e^{\hat{T}}\,|\Psi_0\rangle = E_{CC}\,\langle\Psi_0|\Psi_0\rangle = E_{CC} \tag{14}$$

$$R = \langle\Phi|\,e^{-\hat{T}}\hat{H}e^{\hat{T}}\,|\Psi_0\rangle = E_{CC}\,\langle\Phi|\Psi_0\rangle \overset{!}{=} 0 \tag{15}$$

The residuals R in the latter equation are enforced to vanish due to the orthogonality of the excited states to the ground state based on first principles of quantum mechanics in order to be able to calculate the CC amplitudes. The amplitudes are obtained by solving this non-linear set of equations.

Note that, in principle, the CI coefficients can be obtained from the CC amplitudes, but the reverse is not true. Therefore, CC always yields better results.

CCSD

So far we have considered the general CC formalism. Similarly to CI, the excitation operator, $\hat{T}$, in the CC method also has to be truncated in order to make the calculations feasible. The expansion is commonly truncated at the double excitations. Applying the Taylor expansion, we obtain

$$e^{\hat{T}_1+\hat{T}_2} = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + ... \tag{16}$$

and the corresponding CCSD energies are

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

Remember that $F_{rs} = h_{rs} + \sum_r (2(rr|st) - (rs|rt))$ 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, respectively. The residuals

$$R_a^i = \langle\Phi_i^a| e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Psi_0\rangle \overset{!}{=} 0 \tag{18}$$

and

$$R_{ab}^{ij} = \left\langle\Phi_{ij}^{ab}\right| e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Psi_0\rangle \overset{!}{=} 0 \tag{19}$$

are necessary to obtain the CCSD amplitudes t. There are many different ways of solving this coupled set of non-linear equations.

The basic CCSD method scales as $O(N^6)$.

Triples Correction

As CCSDT calculations are computationally too demanding (scaling: $O(N^8)$), the usual way of improving upon the CCSD method is to apply a perturbative ansatz to include triple excitations approximately. This ansatz, denoted by CCSD(T), leads to the following triples corrections:

$$\Delta E^{(T)} = -\frac{1}{36} \sum_{ijkabc} t_{abc}^{ijk} \left(t_{abc}^{ijk} + \tilde{t}_{abc}^{ijk} \right) (\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k) \tag{20}$$

$$t_{abc}^{ijk} = -\hat{P}(ijk)\hat{P}(abc) \frac{\sum_d t_{ad}^{ij} \langle bc||dk\rangle - \sum_l t_{ab}^{il} \langle lc||jk\rangle}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k} \tag{21}$$

$$\tilde{t}_{abc}^{ijk} = -\hat{P}(ijk)\hat{P}(abc) \frac{t_a^i \langle bc||jk\rangle}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k} \tag{22}$$

The orbital energies are denoted by ϵ_r. The operators $\hat{P}(rst)$ create a sum of all six possible permutations of the indices r, s and t.

The perturbative triples correction decreases the scaling from $O(N^8)$ to $O(N^7)$ since the perturbative correction scales linearly. CCSD(T) is considered the gold standard in quantum chemistry due to its high accuracy and reliability when applied to single-reference systems.

Further Improvements and Applications

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 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 CC2 and 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

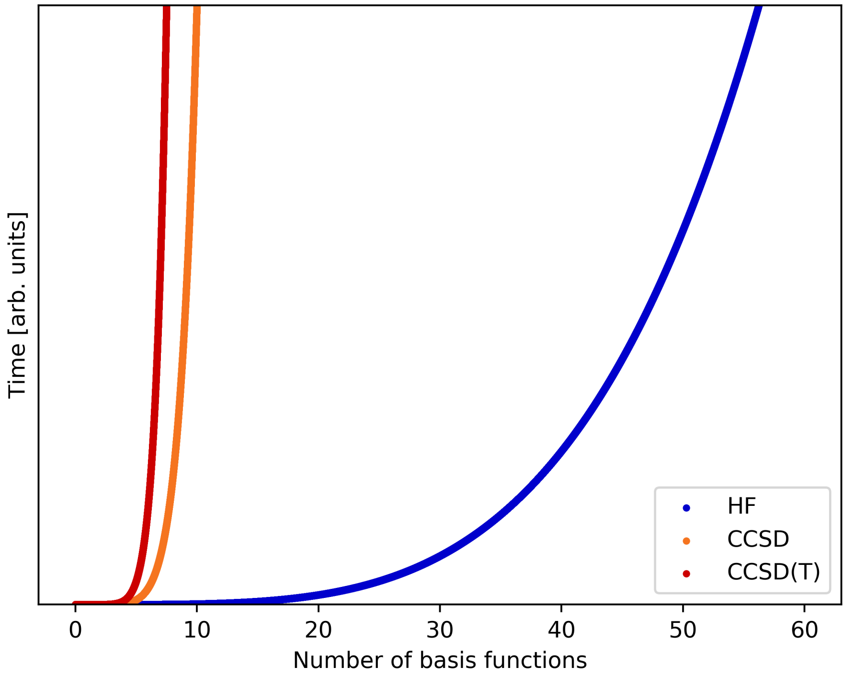

Figure 2: The three methods HF, CCSD and CCSD(T) scale as $O(N^4)$, $O(N^7)$ and $O(N^8)$ with respect to the highest order terms. Note that the plot only shows the leading terms without any prefactors in order to illustrate the general scaling difference. The HF scaling is depicted in blue, CCSD scaling in orange and CCSD(T) scaling in red.

method is obtained, which conserves 99.8% of the correlation energy compared to standard CC approaches. Neglecting the contributions of electron pairs can be dangerous though since it is as of now unclear whether important contributions, such as van-der-Waals interactions, are lost.

Though methods beyond CCSD(T) are infrequent in use, higher-order CC truncations, such as CCSDT or CCSDTQ etc., have been implemented in specialized code packages as e. g. MRCC. Such high truncations are rather academic as CCSDTQ already scales as $O(N^{10})$ and the scaling only becomes even faster for the even higher truncations (the exponent increases by 2 for

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every higher excitation included in $\hat{T}$).