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Higher Roots of the Coupled-Cluster Equations

Abstract: *In this work, we report studies that have been done along the way to fix the breakdowns of single-reference coupled-cluster (CC) for strongly correlated systems. We start by giving the theoretical background needed to discuss these works. Then the methods designed to tackle the single-reference CC failures are classified in three parts. The first one deals with alternative subspaces to the usual one in terms of excitation degree. Secondly, we investigate the effect of the terms of the CC equations during the failures of single-reference CC in order to design modifications of the equations. Finally, methods which purpose is to include the variational principle within CC are presented. In a second phase, we give an historical overview of results on the CC solution structure. The internship aims at investigating the CC solution structure presented in the last part within the alternative CC formulations discussed before.*

Keywords: *coupled-cluster, static correlation, single reference, excited states, non-standard solutions*

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1 Introduction

Since the dawn of quantum chemistry, numerous methods have been designed to calculate ground-state energies, and properties deriving from these energies, of chemical systems [1]. However, for the moment none of them is a black-box method suitable for any systems, each of them has its own advantages and its own flaws. Thus, an efficient black-box method applicable to any systems is still highly coveted by chemists. Chemical systems can be classified according to the nature of the correlation energy, which is by definition the energy missed by a mean-field Hartree-Fock (HF) calculation [1]. Weakly correlated systems are well described by a single HF reference and the correlation energy is mainly due to instantaneous repulsion between electrons. Such correlation is called *dynamic correlation*. On the other hand, *static correlation* refers to systems with a strong multireference character, *e.g.*, bond breaking processes, transition metal compounds, actinides, etc. The HF determinant is no more a good starting approximation and more than one determinant is needed to accurately describe strongly correlated systems. Currently, the coupled-cluster (CC) with single, double and non-iterative triple excitations CCSD(T) [2], is considered as the *gold standard* method of quantum chemistry for ground state [3]. This method, and the other standard CC approximations, gives very accurate results for weakly correlated systems at a tractable polynomial computational cost [4–6].

The CC method [7–9] relies on the fact that the ground-state wave function of a many-electron system can be written as the exponential of a many-electron operator acting on a reference state [10]. Unfortunately, the single-reference CC, at least its computationally tractable standard approximations, is known to fail to describe strongly correlated systems, *e.g.*, the potential energy curve of the N_2 molecule [11]. One way to prevent this problem is to use multi-reference CC methods, see Ref. [12] for a review of this type of methods, which have been proved to be able to fix the breakdowns of CC in strongly correlated cases [11]. However, multi-reference CC is highly system dependent and its use requires being extremely cautious [12]. Hence, multi-reference CC cannot be used in a black-box manner, at least for the time being. It would be more convenient to be able to describe strong correlation efficiently using a single-reference wave function. For the sake of conciseness, CC will now refer to single-reference CC throughout the report.

Actually, if the cluster operator is not truncated, the CC method is equivalent to full configuration interaction (FCI) [6]. FCI gives the exact solution in the subspace of the Hilbert space spanned by the one-electron basis set, hence full CC (FCC) too. It proves that it is possible to exactly describe a strongly correlated system, in a given subspace of the complete Hilbert space, using a single-reference method. Although this is a proof of concept, it cannot be considered because the FCC equations cannot be solved except for few electrons. In practice, one needs to truncate the cluster operator to a given excitation number to be able to solve the CC equations [4–6]. Hence, new CC approximation schemes or alternative CC formulations capable of describing strong correlation at a tractable computational cost are highly desirable. Hereafter, we will refer to the usual CC methods relying on the truncation of the cluster operator as traditional CC (TCC) [13].

The truncation of the cluster operator is equivalent to restricting the complete Hilbert space to subspaces of given excitation numbers. A conceptually simple idea is to change the partitioning of the complete Hilbert space in order to obtain a faster convergence. In other words, finding other subspaces of the Hilbert space which are more efficient to describe strong correlation than the usual subspaces of k -fold excited determinant. An alternative way of partitioning the Hilbert space is to use the seniority number defined as the number of unpaired electrons [14]. The seniority zero subspace is the subspace of all closed-shell determinants. The doubly occupied CI method (DOCI), *i.e.*, a CI calculation restricted to the subspace of seniority zero has been proved to give accurate results for strongly correlated systems [14]. Unfortunately, this method has a factorial scaling rendering it unusable for real systems. However, one can obtain results nearly indistinguishable of the DOCI ones, in a majority of cases [15], at a tractable polynomial cost, by restricting CCD to the seniority zero subspace [16–21]. This method is called pair coupled-cluster doubles (pCCD).

As it is said by Bulik *et al.* [22], instead of working harder by adding higher excitation terms in the

cluster operator, one should work smarter and remove the terms causing the failures of CCD in cases where CC breaks down. A variety of methods based on this underlying idea have been designed during the last decades: the approximate coupled pair [23], the n CC methods [24], the parametrized CCSD [25], the distinguishable cluster (DC) [26], the ring coupled-cluster doubles (rCCD) [27] and its variants [28] ... All these methods have been proved to be able to describe strongly correlated systems but they also have all their own flaws [29].

A shared feature of all the methods previously mentioned that has not been emphasized is that their equations are solved by means of projective methods. Hence, the resulting energies are not upper bounds of the exact energy. It is desirable to incorporate this upper bound property within the CC paradigm. Various alternatives to TCC have been designed to try to fix this problem: the variational CC/expectation value CC (VCC/XCC) [30, 31], the unitary CC (UCC) [32–34] and the extended CC (ECC) [35]. If the CC equations are not usually solved variationally, this is because the variational energy functional is an infinite expansion. Whereas, the energy functional given by projective methods truncates naturally at the fourth order. Therefore, one needs to introduce an arbitrary truncation to numerically solve the VCC equations. UCC appears as another natural possibility to a CC theory based on the variational principle. The UCC exponential parametrization of the wave function uses an anti-hermitian operator, closely related to the cluster operator, to generate unitary transformation of the reference determinant. Until recently, it was unclear whether VCC and UCC are equivalent [36] or not [13], but Harsha *et al.* proved that VCC and UCC are not equivalent [37]. There has been a regain of interest for this alternative formulation of the exponential ansatz because quantum simulators can evolve unitary operators [38, 39]. Finally, the ECC parametrizes the expectation value of the energy in order to introduce a hierarchy of methods between TCC and VCC.

The previous discussion on alternative CC methods focused on the ground state of strongly correlated systems but excited states often have a strong multi-reference character too. The usual way to obtain excited states energies within the CC paradigm is to use the equation of motion CC (EOM-CC) method, see Ref. [40] for a review of this type of method. However, we will focus on another way, somewhat unusual, to get excited states energy. Because the CC equations are highly non-linear [6], other solutions than the usual *standard solution* exist, we will refer to these solutions as higher roots of the CC equations, or *non-standard solutions*. The standard solution is close to the reference wave function and the associated cluster amplitudes are often small. This solution is the most easily attainable by the usual iterative process used to solve the CC equations. One can wonder if these solutions represent physical states or not. And if they do, are they excited states, symmetry-broken states... The use of the standard solution of CC to target excited states is usually limited to states of lower energy of a given symmetry [41]. But it has been shown that non-standard solutions can give access to excited states of the same symmetry as the standard solution [42, 43]. Additionally, there is another implicit source of non-linearity in the CC paradigm, namely the reference determinants. In fact, the HF equations are also non-linear [44], thus, it is possible to cleverly use the higher roots of the HF equations as CC reference determinants to target excited states [45, 46]. However, there is a major difference between these two nonlinear equations, namely that the Hartree and exchange operators in the HF equations are Hermitian and bounded. Whereas the CC effective Hamiltonian is non-Hermitian. [47, 48]

This bibliographical report is organized as follows: in Sec. 2 we provide the theoretical background necessary to develop and discuss the alternative CC methods presented in Sec. 3. Section 3 is divided in three parts corresponding to the three ideas introduced above: Sec. 3.1 discusses the effect of alternative subspaces, Sec. 3.2 is about methods relying on modifications of the amplitude equations. Finally, Sec. 3.3 addresses the problem of variational principle applied to the CC paradigm. In Sec. 4, we provide an historical overview of results on the non-standard solutions of the CC methods and their link with excited states. Section 5 concludes this report and presents what will be done and investigated during the internship.

2 Theoretical Background

2.1 The Schrödinger Equation and the Hartree-Fock approximation

To have access to the energies of the ground and excited states of a molecule, one needs to solve the time-independent Schrödinger equation (1). Within the Born-Oppenheimer approximation, the exact non-relativistic molecular Hamiltonian for a system with N electrons and M nuclei is given by (2). $\Psi(\mathbf{R})$ is the exact many-body wave function associated to the energy $E(\mathbf{R})$ for the given clamped positions $\mathbf{R} = (\mathbf{R}_1, \dots, \mathbf{R}_M)$ of the nuclei. Each nucleus A carries a charge eZ_A and each electron is charged $-e$. The position of the i th electron is denoted by \mathbf{r}_i and its kinetic energy is represented by the summand of the first term of the Hamiltonian. The two other terms account for the nucleus-electron attraction and the electron-electron repulsion, respectively. Unless otherwise stated, atomic units will be used throughout ($\hbar = e = m_e = 1$).

$$\hat{H}(\mathbf{R}) \Psi(\mathbf{R}) = E(\mathbf{R}) \Psi(\mathbf{R}) \quad (1)$$

$$\hat{H}(\mathbf{R}) = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_A^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2)$$

From now on, the parametric dependence on the nuclei coordinates will be dropped. Unfortunately, exact solutions to the quantum many-body problem are available only in a few cases like the one-electron hydrogen atom or some well-behaved two-electron systems. Therefore a myriad of approximations have been developed in order to find approximate solutions of the Schrödinger equation [1]. The standard starting approximation is to treat the electrons as independent particles in a mean-field potential created by the other electrons. The usual mean-field approximation in quantum chemistry is known as the Hartree-Fock method. The HF method approximates the wave function $|\Psi\rangle$ as a Slater determinant, *i.e.*, a normalized antisymmetric combination of N spin-orbitals $\phi_p(\mathbf{x})$ [where $\mathbf{x} = (\sigma, \mathbf{r})$ is a composite vector gathering spin and spatial coordinates]. Throughout the report, the index p, q, r and s are used to denote general spin-orbitals, the index i, j, k and l refer to occupied spin-orbitals (hole states) and index a, b, c and d to unoccupied spin-orbitals (particle states). In practice, the spin-orbitals are expanding in a finite basis set of one-electron functions spanning a subspace of the complete Hilbert space. Then according to the variational principle the best approximation to the exact wave function is the Slater determinant $|\Psi_0\rangle$ minimizing the energy with respect to the spin-orbitals. In generic cases, the HF method is a very good approximation to the ground state, yielding approximately 99% of the exact energy and 95% of the wave function [1]. However, this approximation can break down flagrantly in some cases. A well-known such case is the inability of the HF wave function to describe multireference processes *e.g.* bond dissociation [44]. To ensure the proper spin symmetry of the system, the spatial part of a spin-orbital is restricted to be the same for electrons of spin up and down. This is called restricted HF (RHF). A way to improve the performance of HF for multi-reference systems is to discard this restriction, *i.e.* spatial orbital associated to electrons with different spins can differ. We will refer to it as unrestricted HF (UHF). UHF allows a better description of multireference systems by sacrificing the spin symmetry of the system, see for example the UHF description of the H_2 dissociation in Ref. [44]. However, quantum numbers like spin are hard to recover once they are sacrificed during a calculation so this method is not a panacea. Hence, other ways to recover the part of the exact energy missed by the HF method is required. The energy missed by the independent particles model, defined as the difference between the HF energy and the exact energy, is called the correlation energy. Numerous correlated methods have been developed in order to recover this correlation energy [44]. The conceptually, but not computationally, simplest one is the Configuration Interaction (CI) method [44]. Self-consistently solving the HF equation for a given basis set of K one-electron functions gives a set of K spatial orbitals. The HF ground state is the Slater determinant composed of the $N/2$ lowest spatial orbitals, each one doubly occupied. All the possible N -electron Slater determinants that can be formed by placing the N electron in the $2K$ spin-orbitals form a complete basis set of the Hilbert space spanned by the one-electron functions basis set. Then the solutions obtained by diagonalizing

the Hamiltonian in the N -electron basis set are the exact solutions in this Hilbert space[44]. However this method scales factorially with the number of one-electron functions. So it is almost always too computationally expensive to be used because of the size of the basis set needed to get an accurate description of real chemical systems. To lessen the computational cost it is possible to restrict the CI matrix to a given subspace of the N -electron determinants, which is often the subspace of the at most k -fold excited determinants.

Another possible way of recovering correlation energy is to use Rayleigh-Schrödinger perturbation theory. The HF solution can be used as a zeroth order reference and the HF Hamiltonian, defined as the sum of the one-electron Fock operator, as the unperturbed part of the Hamiltonian. The use of Rayleigh-Schrödinger perturbation theory along with this partitioning of the Hamiltonian and this reference is commonly called the Møller-Plesset Perturbation Theory [49]. Because the perturbation series can be slowly convergent or even divergent [50–53], Møller-Plesset low-order perturbative corrections to the energy cannot be considered unimpeachable. The CC method mentioned earlier is another correlated method somewhat related to the two previous ones.

2.2 The Coupled-Cluster Method

The CC method is a wave function method, in which the wave function Ψ_{CC} is based on the exponential ansatz of the many-electron wave function [7–10]:

$$|\Psi_{CC}\rangle = e^{\hat{T}} |\Psi_0\rangle, \quad (3)$$

where Ψ_0 is the reference wave function, often taken from a mean-field calculation. Hereafter, we assume that the reference is taken to be a HF determinant. The cluster operator \hat{T} is defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N. \quad (4)$$

The k th excitation operator \hat{T}_k is defined, in the second quantized form, as

$$\hat{T}_k = \frac{1}{(k!)^2} \sum_{ij\ldots, ab\ldots} t_{ij\ldots}^{ab\ldots} a_a^\dagger a_b^\dagger \cdots a_j a_i. \quad (5)$$

a_i and a_a^\dagger are the second quantization annihilation and creation operators, respectively, which annihilates (creates) an electron in the spin-orbital i (a). The cluster amplitudes $t_{ij\ldots}^{ab\ldots}$ are the quantities to determine in order to know the CC wave function $|\Psi_{CC}\rangle$ and the CC correlation energy ΔE_{CC} defined by

$$\hat{H} |\Psi_{CC}\rangle = E_{CC} |\Psi_{CC}\rangle = (E_{HF} + \Delta E_{CC}) |\Psi_{CC}\rangle. \quad (6)$$

The cluster amplitudes of the operator \hat{T}_k are determined by projecting the equation (6) onto the manifold of k th excited Slater determinants. Rewriting the Hamiltonian in its normal ordered form, using Wick's theorem [54], gives

$$\hat{H}_N |\Psi_{CC}\rangle = \Delta E_{CC} |\Psi_{CC}\rangle, \quad (7)$$

where \hat{H}_N is the normal-ordered Hamiltonian operator. A normal-ordered string of second quantized is such that all the annihilation operators are placed to the right of the string, and the creation ones to the left. Then multiplying (7) by $e^{-\hat{T}}$ to the left and projecting onto the reference wave function $\langle\Psi_0|$ and the excited determinants $\langle\Psi_{ij\ldots}^{ab\ldots}|$ leads to the energy and amplitude equations,

$$\Delta E_{CC} = \langle\Psi_0| e^{-\hat{T}} \hat{H}_N e^{\hat{T}} |\Psi_0\rangle, \quad (8)$$

$$0 = \langle\Psi_{ij\ldots}^{ab\ldots}| e^{-\hat{T}} \hat{H}_N e^{\hat{T}} |\Psi_0\rangle, \quad (9)$$

respectively. The excited determinant $|\Psi_{ij\ldots}^{ab\ldots}\rangle$ corresponds to the reference determinant with the electrons in the orbitals i and j moved to the virtual orbitals a and b , respectively. The CC correlation

energy can be viewed as the energy of the reference wave function for the similarity-transformed non-Hermitian Hamiltonian $\hat{\hat{H}} = e^{-\hat{T}}\hat{H}_N e^{\hat{T}}$. The product of normal-ordered strings in these equations can be transformed, using the generalized Wick theorem, into a sum of normal-ordered strings with contraction between second quantized operators. It is possible to show that the only terms giving non-zero contributions to the Eqs. (8) and (9) are the term with all the second quantized operators [6]. Using the Baker-Campbell-Hausdorff formula [55–57], the similarity-transformed Hamiltonian can be expanded as a series of nested commutators. To give non-zero contribution to (??) and (9), the Hamiltonian must have at least one contraction with each cluster operator, because the Hamiltonian is a two-electron operator, this series expansion truncates after the fourth term [6],

$$e^{-\hat{T}}\hat{H}_N e^{\hat{T}} = \hat{H}_N + [\hat{H}_N, \hat{T}] + \frac{1}{2!} [[\hat{H}_N, \hat{T}], \hat{T}] + \frac{1}{3!} [[[\hat{H}_N, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!} [[[[\hat{H}_N, \hat{T}], \hat{T}], \hat{T}], \hat{T}]. \quad (10)$$

The fact that the Hamiltonian must be connected to each nested operator leads to the so-called connected form of the CC equations

$$\Delta E_{CC} = \langle \Psi_0 | [\hat{H}_N e^{\hat{T}}]_C | \Psi_0 \rangle, \quad (11)$$

$$0 = \langle \Psi_{ij\dots}^{ab\dots} | [\hat{H}_N e^{\hat{T}}]_C | \Psi_0 \rangle, \quad (12)$$

where the subscript C means that only connected terms are retained in the expansion. A connected term is such that the Hamiltonian have at least one second-quantized operator contracted with each cluster operator \hat{T}_k (see Ref. [6] for the detailed derivation of these equations and extensive discussion of their consequences).

Because the Hamiltonian is a two-electron operator, for a matrix element of the Hamiltonian to be non-zero the difference of excitation number between the projected determinant and the expansion of $e^{\hat{T}}$ must be at most two. Thus the series in (12) truncates after \hat{T}_2 , which gives

$$\Delta E_{CC} = \left\langle \Psi_0 \left| \left[\hat{H}_N (1 + \hat{T}_1 + \hat{T}_1^2 + \frac{1}{2!} \hat{T}_2) \right]_C \right| \Psi_0 \right\rangle, \quad (13)$$

or equivalently the algebraic form

$$\Delta E_{CC} = \sum_{ia} f_i^a t_i^a + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab} + \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b \quad (14)$$

after evaluation of the matrix elements, where $\langle ij || ab \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle$ are the anti-symmetrized two-electron integrals. The two-electron integrals are defined as

$$\langle pq | rs \rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2 \phi_p(\mathbf{x}_1) \phi_q(\mathbf{x}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_r(\mathbf{x}_1) \phi_s(\mathbf{x}_2) \quad (15)$$

in the spin-orbital basis. In the HF case, the matrix elements of the Fock operator between an occupied and unoccupied spin-orbitals are zero, *i.e.*, $f_i^a = 0$. Because the bra state in (9) is a k -tuply excited determinant, the truncation in the amplitude equation is at \hat{T}_{k+2} . As a consequence, solving the full set of energy and amplitude equations (8)-(9) up to $k = N$ is too computationally expensive in practice and one needs to truncate the cluster operator \hat{T} at a given excitation number. The simplest truncation that first comes in mind is to restrict the cluster operator \hat{T} to the single excitation cluster operator \hat{T}_1 . Because Brillouin's theorem states that [6, 44]

$$\langle \Psi_i^a | \hat{H} | \Psi_0 \rangle = 0, \quad (16)$$

a CC calculation restricted to single excitations would not improve the HF energy. Thus the simplest approximation is the coupled-cluster restricted to double excitations (CCD). The single excitation can improve the result through their interaction with the double excitations, this approximation is referred

to as CCSD for coupled-cluster restricted to single and double excitations. By adding successively the \hat{T}_k operators up to $k = N$, we recover the FCC equations which are equivalent to the FCI ones. However, there is an essential difference between the truncation scheme in CC and CI. Namely, truncated CC remains size-extensive whereas truncated CI loses the size-extensivity property of its FCI parent. The size-extensivity property of a method is linked to the scalability of this method with respect to the number of electrons. A method is said to be size-extensive if the correlation energy scales linearly with the number of electrons. Again we refer the reader to Ref. [6] for an extensive discussion of this property, which is beyond the scope of this report. We would just want to emphasize that size-extensivity is a highly desirable property to fulfill for a quantum chemistry method and that CC inherits its size-extensivity from the exponential form of the CC ansatz.

Usually the CC equations are solved iteratively [5], this process scales polynomially in the size of the basis set K . The degree of the polynomial cost depends on the truncation of the cluster operator. The simplest approximation, CCD, scales as $\mathcal{O}(K^6)$. More precisely, it scales as $\mathcal{O}(o^2v^4)$, with o and v the number of occupied and virtual orbitals, respectively. Adding the single excitation operator, CCSD, does not change the scaling order. Whereas adding triple excitations, CCSDT, increases the scaling of the iterative process to $\mathcal{O}(K^8)$. It is possible to add a non-iterative perturbation to a CCSD result in order to account approximately for the triple excitations with a lower computational cost of $\mathcal{O}(K^7)$. The most popular triple correction is the CCSD(T) one [2]. The CCSDTQ method, *i.e.*, CCSDT with iterative quadruple excitations, scales as $\mathcal{O}(K^{10})$.

2.3 The algebraic CCD equations

To clarify the following discussions about the different ways of fixing the failures of CC in strongly correlated systems, we will take time to explicitly write the CCD algebraic equations. In the CCD approximation, the cluster operator is $\hat{T} = \hat{T}_2$, thus the equations (13) and (14) are reduced to

$$\Delta E_{\text{CCD}} = \left\langle \Psi_0 \left| \left[\hat{H}_N \hat{T}_2 \right]_C \right| \Psi_0 \right\rangle, \quad (17)$$

$$\Delta E_{\text{CCD}} = \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}. \quad (18)$$

The amplitude equation is given below

$$0 = \left\langle \Psi_{ij}^{ab} \left| \hat{H}_N (1 + \hat{T}_2 + \frac{1}{2!} \hat{T}_2^2) \right| \Psi_0 \right\rangle, \quad (19)$$

$$0 = E_I + E_L + E_Q. \quad (20)$$

This equation can be separated in three parts: one which is independent of the cluster operator E_I , and the two others which are linear and quadratic in the cluster amplitudes, E_L and E_Q , respectively. The algebraic interpretation of these equations yields the following expressions for the three parts of the equation (20):

$$E_I = \langle ij || ab \rangle \quad (21a)$$

$$E_L = \hat{P}_{ab} f_c^a t_{ij}^{cb} - \hat{P}_{ij} f_i^k t_{kj}^{ab} + \frac{1}{2} \langle ab || cd \rangle t_{ij}^{cd} + \frac{1}{2} \langle ij || kl \rangle t_{kl}^{ab} + \hat{P}_{ij,ab} t_{ik}^{ac} \langle cj || kb \rangle \quad (21b)$$

$$E_Q = \underbrace{\frac{1}{4} \langle cd || kl \rangle t_{kl}^{ab} t_{ij}^{cd}}_A - \underbrace{\frac{1}{2} \hat{P}_{ij} \langle cd || kl \rangle t_{lj}^{ab} t_{ik}^{dc}}_B - \underbrace{\frac{1}{2} \hat{P}_{ab} \langle cd || kl \rangle t_{lk}^{ac} t_{ij}^{db}}_C + \underbrace{\frac{1}{2} \hat{P}_{ij,ab} \langle cd || kl \rangle t_{ik}^{ac} t_{lj}^{db}}_D \quad (21c)$$

In the above equations, and from now on, the Einstein summation convention is used so a repeated index implies a summation over all possible values of this index. The operators \hat{P}_{ij} and $\hat{P}_{ij,ab}$ are permutation operators,

$$\hat{P}_{pq} f(p, q) = f(p, q) - f(q, p), \quad \hat{P}_{pq,rs} g(p, q, r, s) = \hat{P}_{pq} \hat{P}_{rs} g(p, q, r, s). \quad (22)$$

Expanding the permutation operators and summing the three equations (21a), (21b) and (21c) gives the following CCD amplitude equation

$$0 = \langle ab||ij \rangle + f_c^a t_{ij}^{cb} + f_c^b t_{ij}^{ac} - f_i^k t_{kj}^{ab} - f_j^k t_{ik}^{ab} \quad (23a)$$

$$+ \frac{1}{2} \langle ab||cd \rangle t_{ij}^{cd} + \frac{1}{2} \langle kl||ij \rangle t_{kl}^{ab} + \frac{1}{4} \langle kl||cd \rangle t_{kl}^{ab} t_{ij}^{cd} \quad (23b)$$

$$+ \langle kb||cj \rangle t_{ik}^{ac} + \langle ka||ci \rangle t_{kj}^{cb} + \langle kl||cd \rangle t_{ik}^{ac} t_{lj}^{db} \quad (23c)$$

$$- \langle ka||cj \rangle t_{ik}^{bc} - \langle kb||ci \rangle t_{kj}^{ca} - \langle kl||cd \rangle t_{lj}^{ad} t_{ik}^{cb} \quad (23d)$$

$$- \frac{1}{2} \langle kl||cd \rangle t_{il}^{cd} t_{kj}^{ab} + \frac{1}{2} \langle kl||cd \rangle t_{jl}^{cd} t_{ki}^{ab} + \frac{1}{2} \langle kl||cd \rangle t_{il}^{cd} t_{kj}^{ba} - \frac{1}{2} \langle kl||cd \rangle t_{jl}^{cd} t_{ki}^{ba} \quad (23e)$$

In the above equation the terms have been sorted according to the types of contraction, *i.e.*, the position of the summation index. From top to bottom, the class of terms are referred to as the driver terms (23a), the ladder terms (23b), the ring terms (23c), the crossed-ring terms (23d) and the mosaic terms (23e).

2.4 Orbital relaxation

Thouless' theorem [58] states that any two Slater determinants that are non-orthogonal can be related by the operator $e^{\hat{T}_1}$. Hence, adding the single excitation cluster operator \hat{T}_1 to the cluster operator \hat{T} permits the relaxation of the one-electron orbitals [6]. The CCSD method can be seen as a CCD calculation with the orbitals allowed to relax. Sometimes, it can also be convenient to use Brueckner orbitals [59, 60] to account for orbital relaxation. The Brueckner orbitals are the set of orbitals such that the single excitations do not contribute to the FCI energy, *i.e.*, the CI expansion does not contain singly excited determinants. Within CC, one can define approximate Brueckner orbitals as the orbitals such that the cluster operator \hat{T}_1 is equal to zero. They can be obtained iteratively in a CCSD calculation by rotating the orbitals at each iteration such that the cluster amplitudes t_i^a are equal to zero [61]. Alternatively, one can see the Brueckner CCD (BCCD) as an effective Hamiltonian method [62, 63]. It is possible to modify the CCD equations to ensure that $\hat{T}_1 = 0$ throughout the iterative process. To do this, we need to use the ordinary form of the Hamiltonian of Eq. (6). For $\hat{T} = \hat{T}_2$, this equation becomes

$$\begin{aligned} \hat{H} |\Psi_{\text{CCD}}\rangle &= E_{\text{CCD}} |\Psi_{\text{CCD}}\rangle = (E_{\text{HF}} + \Delta E_{\text{CCD}}) |\Psi_{\text{CCD}}\rangle \\ &= \left(\frac{1}{2} (h_i^i + f_i^i) + \frac{1}{4} \langle ij||ab \rangle t_{ij}^{ab} \right) |\Psi_{\text{CCD}}\rangle, \end{aligned} \quad (24)$$

where h_i^i are the matrix elements of the one-electron part, the kinetic energy plus the nuclei attraction, of the Hamiltonian. One can define a Brueckner effective one-electron Hamiltonian as

$$E_{\text{CCD}} = \frac{1}{2} (h_i^i + F_i^i), \quad (25)$$

$$F_i^k = f_i^k + \frac{1}{2} \langle kj||ab \rangle t_{ij}^{ab}, \quad (26)$$

$$F_c^a = f_c^a - \frac{1}{2} \langle ij||cb \rangle t_{ij}^{ab}. \quad (27)$$

The last equation is imposed to preserve particle-hole symmetry. Finally, the particle-hole block of F is chosen as the amplitude equations for singles in CCSD within the Brueckner doubles approximation, *i.e.*, with the cluster amplitudes $t_i^a = 0$.

$$F_i^a = f_i^a + f_b^j t_{ij}^{ab} + \frac{1}{2} \langle aj||bc \rangle t_{ij}^{bc} - \frac{1}{2} \langle jk||ib \rangle t_{jk}^{ab} \quad (28)$$

By doing this, the convergence of the BCCD equations ensures that $F_i^a = 0$. The matrix elements of the generalized Fock matrix appear naturally in the CCD amplitude equation (23) by including the

mosaic terms (23e) in the driver terms (23a). Finally, another way to account for the orbital relaxation is to variationally optimize the orbitals during the CCD calculation [64–66]. This is possible to obtain the usual amplitude equations (9) mentioned above by introducing a de-excitation operator $\hat{\Lambda}$ in the energy equation. Minimizing this energy functional with respect to the de-excitation amplitudes yields the amplitude equations.

$$\Delta E_{CC} = \left\langle \Psi_0 \left| (1 + \hat{\Lambda}) e^{-\hat{T}} e^{-\hat{K}} \hat{H}_N e^{\hat{K}} e^{\hat{T}} \right| \Psi_0 \right\rangle \quad (29)$$

In the above energy functional, the operator \hat{K} is anti-Hermitian thus $e^{\hat{K}}$ defines a unitary transformation accounting for the orbital variations. Then, it is possible to minimize this energy functional with respect to the de-excitations amplitudes and also to the orbital variation parameters [67]. This procedure leads to an orbital-optimized CC. Even if the equations are solved by a variational minimization, the resulting energy is not an upper bound of the exact energy because the energy functional is not a symmetric expectation value.

3 Alternative Coupled-Cluster Methods

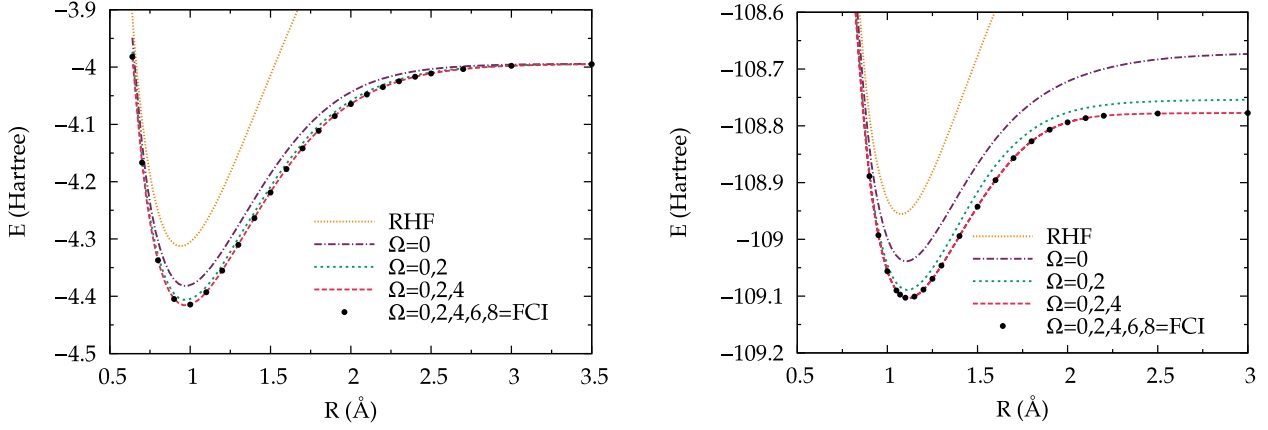
As mentioned previously, CC is the current method of choice for weakly correlated systems but breaks down for strongly correlated ones. Numerous methods have been designed to attempt to describe strong correlation within the CC paradigm. We will present some of these methods in this section. It has been organized such that the methods are sorted in three subsections according to the underlying idea used to tackle this problem. (4) [Byt]

3.1 Projective methods: Alternative subspace

3.1.1 Pair Coupled-Cluster

Surprisingly, it is possible to obtain an accurate description of a strongly correlated system with a CI calculation using only a small part of the vast complete Hilbert space of determinants [14]. To do this we need to introduce a different partitioning of the Hilbert space than the usual one in terms of excitation numbers. The seniority number Ω is defined as the number of unpaired electrons in a determinant [68]. Whereas the excitation number partitioning has been proved to be slowly convergent for strongly correlated systems, *i.e.*, highly excited determinants are needed to get a correct modelization, the seniority zero subspace seems to be efficient to describe such systems. Restricting a CI calculation to the seniority zero subspace, DOCI, can be seen as the best possible closed-shell wave function for a given basis of one-electron functions [69]. Because the subspace of seniority number zero is not invariant under rotations of the orbitals, the orbitals need to be optimized during a DOCI calculation to enhance the correlation energy recovered by this method [14, 17, 21]. The following results have all been obtained with variationally optimized orbitals. Bytautas *et al.* [14] have shown that the excitation number partitioning was more efficient for the neon atom which is a model weakly correlated system. On the other hand, for the beryllium atom, which has a strong multireference character, the excitation number hierarchy has been proved to be more efficient. In other words, the seniority number scheme is more efficient to describe strong correlation whereas the excitation number performs better for dynamic correlation. Figure 1a shows the success of DOCI, and of the excitation number scheme, for the symmetric stretching of the H_8 linear chain. For the N_2 potential energy curve (PEC), the $\Omega = 0$ curve in Fig. 1b is qualitatively good for all bond length but less accurate than Fig. 1a's ones. This is due to the dynamic correlation being more important in the N_2 dissociation and inherently missed by DOCI. Nonetheless, adding higher seniority number determinants recover this part of the correlation energy.

Bytautas *et al.* also demonstrated that the flexibility offered by spatial symmetry-broken orbitals is needed to obtain smooth PECs. However, by doing this nothing ensures that the resulting wave function will have the correct symmetry [14]. The fact that doubly occupied determinants offer a good description of strong correlation is not a new one [70–73]. But this idea has been dropped because of



(a) Potential energy curves (1A -ground state) for the symmetric dissociation of the H_8 molecule using CAS [8/8] active space and cc-pVDZ basis sets with symmetry-broken molecular orbitals.

(b) Potential energy curves (1A -ground state) for the N_2 molecule using CAS [10/8] active space and cc-pVDZ basis sets with symmetry-broken molecular orbitals.

Figure 1: Taken from Ref. [15], which use data from [14].

the factorial scaling of DOCI. In fact, even if the seniority zero is a small subspace of the complete Hilbert space, DOCI still inherits the factorial scaling of its FCI parent.

However, restricting the excitation in CCD to pair excitation leads to a method which yields almost indistinguishable results from DOCI but at a polynomial cost [15, 17–19, 21, 74]. Fig. 2a exemplifies this using the example of the symmetric stretching of a water molecule. Pair CCD (pCCD) and DOCI predicts a qualitatively good shape of the PEC in comparison with unrestricted CC. The main difference is that pCCD maintains the proper spin-symmetry of the system contrary to the quantitatively correct unrestricted CCSD and unrestricted CCSD(T) curves. The cost of the pCCD algorithm is $\mathcal{O}(N^3)$ but the genuine computational cost in practice is $\mathcal{O}(N^5)$ because of the one-electron functions to spin-orbitals double-electron integrals transformation. The pCCD energy and amplitude equations can be easily obtained by restricting CCD to pair excitations, *i.e.*, setting $j = i$ and $b = a$ in the CCD equations (18)-(19):

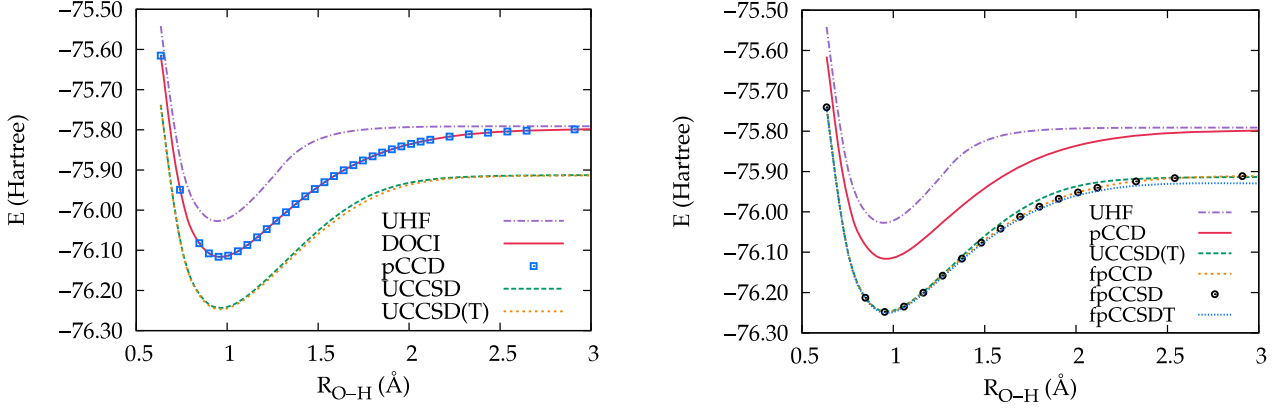
$$\Delta E_{\text{CCD}} = \frac{1}{2} \sum_{ia} \langle ii || aa \rangle t_{ii}^{aa} \quad (30)$$

$$0 = \langle aa || ii \rangle + 2(f_c^a t_{ii}^{ca} - f_i^k t_{ki}^{aa}) + \frac{1}{2} (\langle aa || cd \rangle t_{ii}^{cd} + \langle kl || ii \rangle t_{kl}^{aa}) + \langle kl || cd \rangle \left(\frac{1}{4} t_{kl}^{aa} t_{ii}^{cd} + t_{ik}^{ac} t_{li}^{da} - t_{li}^{ad} t_{ik}^{ca} \right) \quad (31)$$

Henderson *et al.* proved that the numerical equivalence between DOCI and pCCD holds for larger systems [74]. Unfortunately, the factorial scaling of DOCI prohibits its use for large systems. Hence, they used a stochastic algorithm to estimate the DOCI energy for various sizes of the 2D Hubbard model. The DOCI results were in agreement with pCCD for these large systems too. However, the equivalence between pCCD and DOCI is not formal. Using the pairing Hamiltonian,

$$H = \sum_i \epsilon_i (a_{i\uparrow}^\dagger a_{i\uparrow} + a_{i\downarrow}^\dagger a_{i\downarrow}) - G \sum_{ij} a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger a_{j\uparrow} a_{j\downarrow}, \quad (32)$$

where ϵ_i is the single-particle energy and G is the interaction strength, Henderson and his co-workers proved that the two methods are not equivalent [20]. Because pCCD misses the dynamic correlation, enhancements of this method to recover this part of the energy are needed. One way to do this is to use the frozen-pair CC (fpCC) method which consists of a TCC calculation with the pair amplitudes frozen to the values obtained with pCCD [20]. Figure 2b shows that fpCC recover the dynamic correlation and gives results in agreement with unrestricted CCSD(T) while maintaining the spin symmetry. Scuseria and co-workers also developed a singlet-paired CCD (CCD0), a generalization of



(a) Symmetric double dissociation of H_2O in the cc-pVDZ basis set.

(b) Frozen pair symmetric double dissociation of H_2O in the cc-pVDZ basis set.

Figure 2: Taken from Ref. [15]

pCCD, where the cluster operator \hat{T}_2 is restricted to excitations creating singlet determinants [22, 75]. Thus the alternative subspace used in CCD0 is a little larger than the one of pCCD. This method has also been shown to be able to describe strongly correlated systems such as the PEC of N_2 [22].

3.1.2 The geminal point of view

pCCD was originally introduced as a functional of geminals [16] before being recognized as equivalent to the CC functional discussed above [17]. A geminal is a two-electron wave function, it can also be called a pairing function. Instead of using N spin-orbitals, one can define an N -electron wave function as an antisymmetric product of $N/2$ geminals (APG), the general expression of this type of wave function is given by

$$|\Psi_{\text{APG}}\rangle = \prod_{n=1}^{N/2} \left(\sum_{p,q} c_{n;pq} a_p^\dagger a_q^\dagger \right) |0\rangle \quad (33)$$

in second-quantized form, where $|0\rangle$ denotes the vacuum state. Unfortunately, this type of wave function has been proved to be computationally intractable [16]. One can restrict the orbital pairing scheme to be the same for all geminals which leads to the antisymmetric product of interacting geminals (APIG)

$$|\Psi_{\text{APIG}}\rangle = \prod_{n=1}^{N/2} \left(\sum_p c_{n;p} a_{p\uparrow}^\dagger a_{p\downarrow}^\dagger \right) |0\rangle. \quad (34)$$

Even with this approximation, the computational cost of this geminal based wave function is still not affordable. Ayers and co-workers developed an approximation to this type of wave function named antisymmetric product of 1-reference-orbital geminals (AP1roG),

$$\begin{aligned} \Psi_{\text{AP1roG}} &= \prod_i (a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger + \sum_a t_i^a a_{a\uparrow}^\dagger a_{a\downarrow}^\dagger) |0\rangle \\ &= \prod_i \prod_a (1 + t_i^a a_{a\uparrow}^\dagger a_{a\downarrow}^\dagger a_{i\uparrow} a_{i\downarrow}) |\Psi_0\rangle \\ &= \exp \left(\sum_i \sum_a t_i^a a_{a\uparrow}^\dagger a_{a\downarrow}^\dagger a_{i\uparrow} a_{i\downarrow} \right) |\Psi_0\rangle. \end{aligned} \quad (35)$$

In this approximation, each pair of orbitals of the reference determinant $|\Psi_0\rangle$ can contribute to only one geminal. As can be readily seen from the expression above, the AP1roG wave function is equivalent to the pCCD one. Logically because it is equivalent to pCCD, AP1roG have also provided qualitatively

good results for numerous strongly correlated systems such as PEC [18, 69, 76, 77] or actinide chemistry [78, 79]. AP1roG has also been used to determine pair orbital energies analogue to one-electron Fock energy [80]. Similarly to the interpretation of the Fock operators eigenvalues as one-electron ionization potentials and electron affinities thanks to Koopmans’ theorem [44], these pair orbital energies can be interpreted as double ionization potentials and double electron affinities [80].

3.2 Projective methods: Corrections to the amplitude equations

The previous method was taking advantage of the fact that seniority zero determinants gives a qualitatively good description of a strongly correlated wave function. One obtains pCCD from CCD by restricting the subspace of the Hilbert space used in the calculation. In the following approximations, the subspaces of the Hilbert space will remain the same as in TCC and we will be interested in modifying the amplitude equations. Identifying the terms that cause the problems in cases where standard CC breaks down leads to correction of the amplitude equations aiming at solving these problems.

3.2.1 Connected and disconnected quadruple excitations

As stated by Paldus, the correlation due to the connected \hat{T}_4 operator, inherently missed by CCD, can be accounted “implicitly by considering only a subset of diagrams that are associated with the disconnected $\frac{1}{2}\hat{T}_2^2$ clusters” [29]. Different ways to change the quadratic terms of (21c) have been proposed, see Ref. [29] for a review of this type of methods, the first was the approximate coupled pair ACP-D45 method [81]. Because the inclusion of \hat{T}_4 discards the terms C and D, ACP-45 uses only the two first terms A and B in order to model the inclusion of \hat{T}_4 . Here we will focus on the distinguishable cluster (DC) method introduced by Kats and Manby [26, 82]. Exchange processes arise from the indistinguishability of particles, thus they argue that exchange processes between different cluster operators are physically irrelevant. Yet, CCSD is bound to approximately describe these processes at dissociation hence that could be a source of the breakdown of CC away from equilibrium geometry. Therefore, they discard the quadratic terms accounting for these physically irrelevant processes, *i.e.*, A and the exchange part of D of (21c). To do this they consider two-electron systems for which the terms in (21c) are linked by the relations below:

$$0 = A + \frac{B}{2}, \quad 0 = C + D, \quad 0 = \frac{C}{2} + D_{\text{ex}}, \quad (36)$$

where D_{ex} is the exchange part of D (the direct part is denoted by D_c). Using these relations, the quadratic part of the amplitude equation can be rewritten as

$$E_{\text{Q;DCD}} = \frac{B}{2} + \frac{C}{2} + D_c, \quad (37)$$

$$E_{\text{Q;DCD}} = -\frac{1}{4}\hat{P}_{ij}\langle cd||kl\rangle t_{ik}^{dc}t_{lj}^{ab} - \frac{1}{4}\hat{P}_{ab}\langle cd||kl\rangle t_{lk}^{ac}t_{ij}^{db} + \frac{1}{2}\hat{P}_{ij,ab}\langle cd||kl\rangle t_{ik}^{ac}t_{lj}^{db}. \quad (38)$$

This equation is exact for a two-electron system and the particle-hole symmetry is preserved. Using this equation, in place of the amplitude equation 19, for a CCD calculation yields the distinguishable cluster doubles (DCD) approximation [26]. As can be seen in Fig. 3a, the DCD approximation gives a qualitatively well-behaved N_2 PEC in comparison with the multireference benchmark.

Kats and Manby investigated three ways to introduce orbital relaxation in the DCD approximation [82]: inclusion of the singles excitations (DCSD), use of Brueckner orbitals (BDCD) and variational optimization of the orbitals (ODCD). DCD is less sensitive to the orbitals choice than pCCD which needs optimized orbitals whereas DCD yields qualitatively good PECs even without orbital relaxation. Still, there are systems where a proper orbital optimization is needed, for example the dissociation of the CO molecule. We can see in Fig. 3b that DCD and DCSD could not be converged for all bond lengths. BDCD gives acceptable results along almost all the PEC but there is an unphysical hump around 4 bohr. On the other hand, ODCD appears as the most robust method for this case. Although DCSD seems less robust it has an advantage over BDCD and ODCD which is that its extension to explicitly

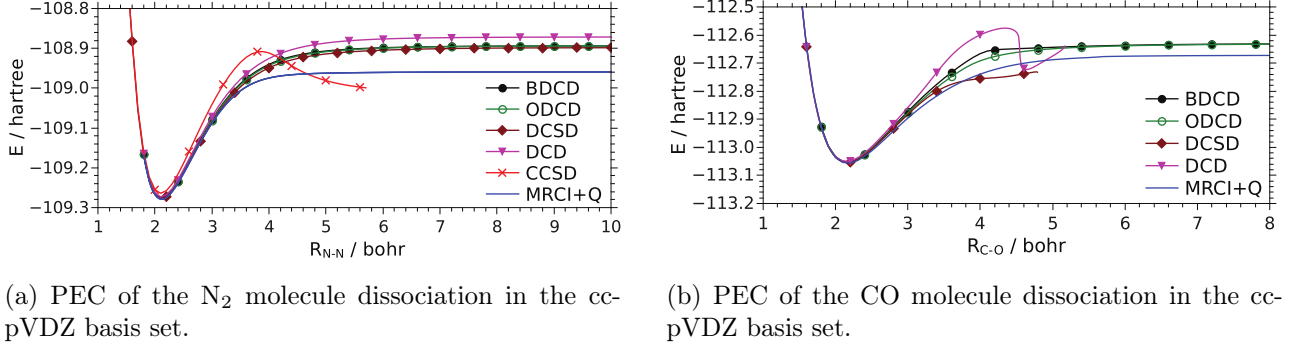


Figure 3: Taken from Ref. [82]

correlated methods is straightforward [83, 84]. Rishi *et al.* showed that the approximate description of the exchange description between separated cluster operators is caused by the delocalized nature of the orbitals [85]. As the N_2 bond is stretched, a symmetry-broken HF solution appears. Two spatial symmetry-broken RHF solutions referred to as $RHF(\sigma_u^-)$ and $RHF(\pi)$ according to their symmetry, C_{2h} and C_2 , respectively. Additionally, there is a spin-spatial symmetry-broken UHF solution. As can be seen in Fig. 4a, using a symmetry-broken RHF wave function as the reference determinant $|\Psi_0\rangle$ for the CCSD calculation can remove the unphysical hump of RHF CCSD. Moreover, Fig. 4b shows that CCD and DCD using UHF reference gives almost the same results. The two previous results shows that the localization of the orbitals offered by symmetry breaking removes the indistinguishability of the cluster operators. This is consistent with the idea of removing the exchange terms in DCD when using delocalized orbitals [85]. We briefly mention that work along the way to include triple excitations in DC methods are currently done [86–88].

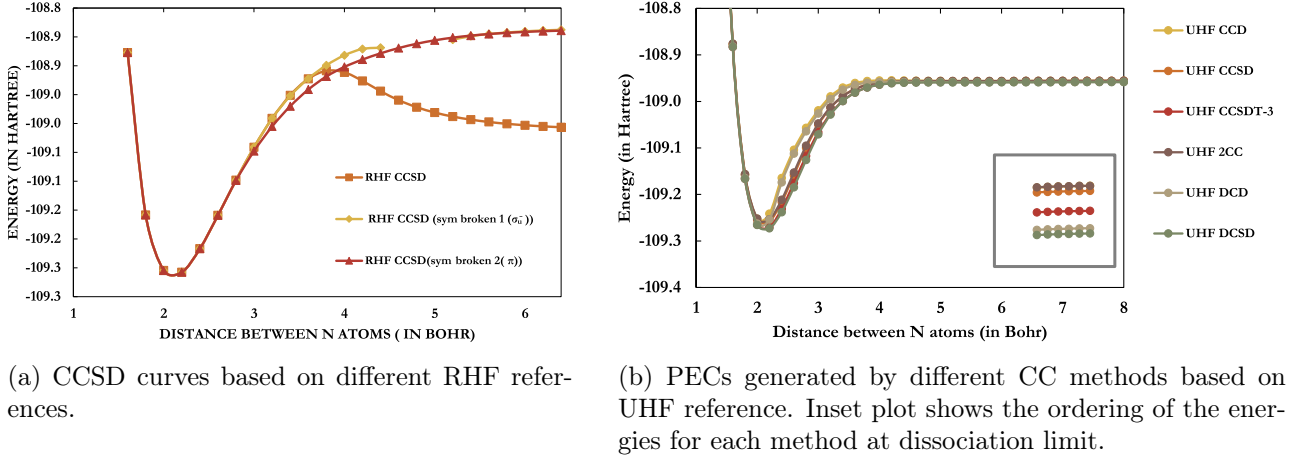


Figure 4: Taken from Ref. [85]

The parameterized CCSD (pCCSD) [25] is closely related to the quadratic terms equation (37) of DCD. This method uses the relations holding for two-electron systems (36) to introduce the following parametrization of the quadratic terms:

$$E_{Q;pCCSD}(\alpha, \beta) = \frac{B}{2} + \alpha(A + \frac{B}{2}) + \beta(C + D). \quad (39)$$

The numerical study of Huntington and Nooijen showed that there is no optimized value of the parameters α and β consistent with all systems. Nevertheless, they found that the optimized parameters are almost ways in the interval $\alpha \in [-\frac{3}{2}, -1]$ and $\beta \in [1, \frac{3}{2}]$. And that pCCSD(-1,1) seems to be a robust method all along PECs [25]. Taking $\alpha = 1$ and $\beta = 0$ recovers the 2CC method of Bartlett and

Musial [24]. The n CC hierarchy of methods is defined as exact methods for n electrons systems using the minimal number of diagrams regardless of the orbitals choice.

3.2.2 Connections between CCD and RPA

In this subsection, we will be interested in the whole amplitude equations (23) and not just in the quadratic terms as before. Scuseria and co-workers highlighted connections [27, 28] between the class of terms of the amplitude equations (23) and the random phase approximation (RPA) [89]. These new connections shed light on some of the breakdowns of CC [22, 90]. First, we will briefly recall what is RPA and the different variants thereof. It has been widely used in range-separated functional because of its ability to accurately describe long-range correlation [89]. Usually in RPA, thanks to the adiabatic-connection formalism and the fluctuation-dissipation theorem, the energy correlation can be expressed as below [89].

$$E_c = \frac{1}{2} \sum_n (\omega_n^{\text{RPA}} - \omega_n^{\text{TDA}}) \quad (40)$$

This equation is known as the plasmon formula [91]. ω_n^{TDA} are the single particle-hole excitation energies in the Tamm-Dancoff approximation (TDA), *i.e.*, without interaction. The Tamm-Dancoff approximation is equivalent to the CIS approximation in quantum chemistry which is a CI calculation restricted to single excited determinants [27]. Similarly, ω_n^{RPA} are the excitation energies of the real interacting system. Alternatively, RPA can be seen as an attempt to treat fermionic particle-hole excitation as bosons $a_a^\dagger a_i \rightarrow b_\beta$ [28], thus we refer to this method as particle-hole RPA (ph-RPA). The resulting bosonic operators obey the usual bosonic commutation relations:

$$[b_\beta, b_{\beta'}^\dagger] = \delta_{\beta\beta'} \quad [b_\beta, b_{\beta'}] = 0 \quad [b_\beta^\dagger, b_{\beta'}^\dagger] = 0 \quad (41)$$

The above relations are an approximation because the real commutation relations of particle-hole excitations operators satisfy a more complex Lie algebra [28]. In this approximation, the fermionic Hamiltonian (42) can be bozonised as below:

$$\hat{H} = h_{pq} a_p^\dagger a_q + \frac{1}{4} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r, \quad (42)$$

$$\hat{H} = E_{\text{HF}} + A_{\beta\beta'} b_\beta^\dagger b_{\beta'} + \frac{1}{2} (B_{\beta\beta'} b_\beta^\dagger b_{\beta'}^\dagger + B_{\beta\beta'}^* b_\beta b_{\beta'}), \quad (43)$$

with

$$A_{\beta\beta'} \rightarrow A_{jb,ia} = f_{ab} \delta_{ij} - f_{ij} \delta_{ab} + \langle ij || ab \rangle, \quad B_{\beta\beta'} \rightarrow B_{ia,jb} = \langle ij || ab \rangle. \quad (44)$$

This bosonized Hamiltonian can be expressed in a matrix form and then diagonalized using a Bogoliubov transformation [28]. The correlation energy resulting from this diagonalization is the same as the one in Eq. (40). In 2008, using this formulation of RPA Scuseria *et al.* proved that the RPA correlation energy obtained this way is equivalent to the CC correlation energy obtained when using the amplitude equations below [27]. This equation is obtained by discarding all the terms of the CCD amplitude equations except the driver (23a) and ring terms (23c),

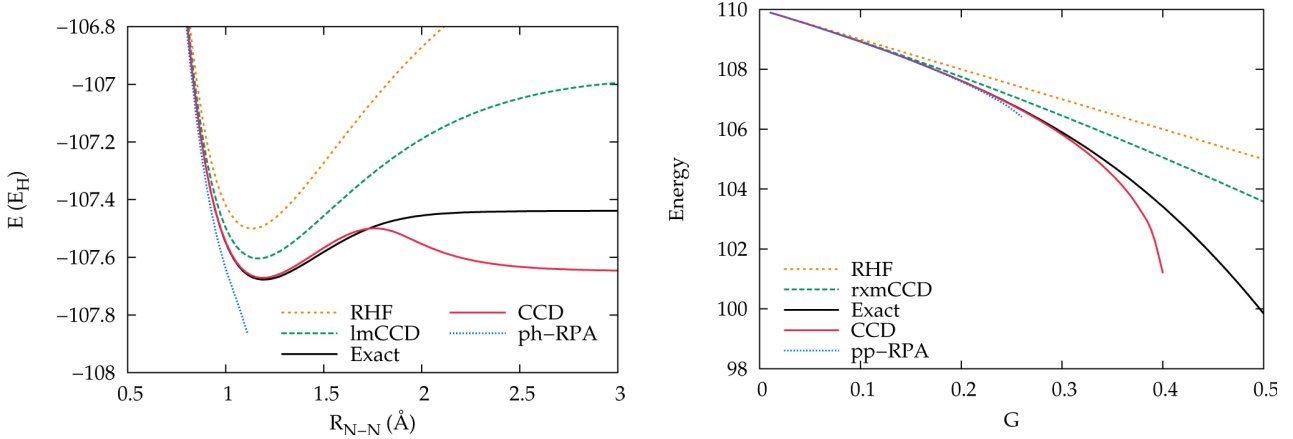
$$0 = \langle ij || ab \rangle + f_c^a t_{ij}^{cb} + f_c^b t_{ij}^{ac} - f_i^k t_{kj}^{ab} - f_j^k t_{ik}^{ab} + \langle cj || kb \rangle t_{ik}^{ac} + \langle ci || ka \rangle t_{kj}^{cb} + \langle cd || kl \rangle t_{ik}^{ac} t_{lj}^{db}. \quad (45)$$

This method is called ring CCD (rCCD). Removing the exchange integrals in (44) and (45), *i.e.*, replacing $\langle pq || rs \rangle$ by $\langle pq | rs \rangle$, yields the direct RPA approximation and direct rCCD which are also equivalent. The bosonization of the fermionic Hamiltonian can also be done in terms of particle-particle excitations approximated as bosons [28]. This leads to the particle-particle variant of RPA (pp-RPA), and hole-hole RPA (hh-RPA), involving non-number-conserving excitations. This has been proved simultaneously by Scuseria *et al.* [28] and Peng *et al.* [92] that pp-RPA is equivalent to ladder

CCD (lCCD). Similarly to rCCD, the lCCD amplitude equations include only the driver (23a) and the ladder terms (23b).

$$0 = \langle ij||ab \rangle + f_c^a t_{ij}^{cb} + f_c^b t_{ij}^{ac} - f_i^k t_{kj}^{ab} - f_j^k t_{ik}^{ab} + \frac{1}{2} \langle ab||cd \rangle t_{ij}^{cd} + \frac{1}{2} \langle ij||kl \rangle t_{kl}^{ab} + \frac{1}{4} t_{kl}^{ab} \langle cd||kl \rangle t_{ij}^{cd} \quad (46)$$

Because we know that failures of RPA can come from an instability of the reference determinant, using the connection with CCD could bring lights on the failures of CCD. An instability towards another HF determinant (*e.g.*, a symmetry-broken one) causes the failure of the ph-RPA method using a symmetry-adapted reference. While pp-RPA and hh-RPA are sensitive to instability towards an Hartree-Fock-Bose determinant, *i.e.*, a determinant breaking the particles number symmetry. Identifying the failures of RPA and consequently removing the associated terms in the amplitude equations can solve the failures of CCD. As we have seen before, symmetry-broken solutions appear during the stretching of the N_2 molecule [85]. Thus the RPA method is unstable in this case. It has been shown, see Fig. 5a, that removing the ring terms in the CCD amplitude equations remedy the failure of CCD [22]. They also remove the crossed-ring terms in order to preserve the anti-symmetry of the wave function. Similarly, the pairing Hamiltonian (32) is unstable towards non-number-conserving determinants, thus removing the ladder terms improves the CCD results in this case as can be seen in Fig. 5b.



(a) Total energies of the N_2 molecule in the STO-3G basis set as a function of bond length. lrmCCD corresponds to CCD with only the driver, the ladder and the mosaic terms.

(b) Total energies in the attractive pairing Hamiltonian as a function of interaction strength G . rxmCCD corresponds to CCD with only the ladder, the ring, the crossed-ring and the mosaic terms.

Figure 5: Taken from Ref. [22]

Shepherd *et al.* investigated the role of each class of terms in the homogeneous electron gas model [90, 93]. In the thermodynamic limit, the second order Møller-Plesset perturbative correction (MP2), rCCD and lCCD diverge at the same rate. This can be rationalized by the fact that in the thermodynamic limit the band gap of the homogeneous electron gas becomes smaller and smaller. Adding mosaic terms to these three methods renders them convergent. The effect of the mosaic terms can be seen as renormalizing the one-electron energy, see Eqs. (26)-(27). The mosaic terms open the band gap in the thermodynamic limit thus removing the divergence. Adding mosaic terms to the MP2 correction can be seen as the MP2 correction with Brueckner orbitals or alternatively as a CCD calculation with only driver (23a) and mosaic (23e) terms. ph-RPA and pp-RPA are known to be efficient for long range correlation and short correlation, respectively. Relying on this fact, Shepherd *et al.* designed a range-separated CCD method. They use a Yukawa potential to make the ring terms account for long-range correlation and ladder terms for short-range correlation [93]. This range separation enhances the result for the homogeneous electron gas in comparison with lCCD and rCCD.

3.3 Variational methods

The equations of all the methods that have been presented so far are solved using projection of the Schrödinger equation onto reference and excited determinants. On the other hand, correlated methods relying on the variational principle share the property that their energy is an upper bound to the exact FCI energy. Moreover, the derivatives of a variational energy are easily obtained thanks to the Hellmann-Feynman theorem [30]. Unfortunately, applying the variational principle to the CC ansatz (3) is computationally intractable. In this subsection, we will review methods attempting to include the desirable properties of variational methods into the CC paradigm.

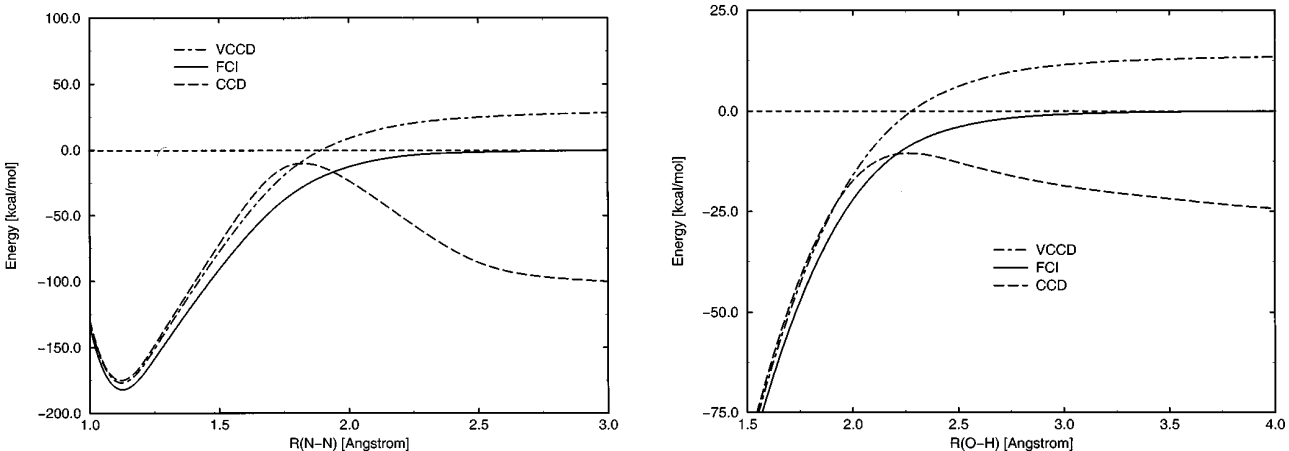
3.3.1 The Variational Coupled-Cluster

The VCC energy is given by

$$E_{\text{VCC}} = \frac{\langle \Psi_{\text{CC}} | H | \Psi_{\text{CC}} \rangle}{\langle \Psi_{\text{CC}} | \Psi_{\text{CC}} \rangle} = \frac{\langle \Psi_0 | e^{\hat{T}^\dagger} H e^{\hat{T}} | \Psi_0 \rangle}{\langle \Psi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Psi_0 \rangle}, \quad (47)$$

where \hat{T}^\dagger is a de-excitation operator. The above expression does not have a truncation such as in (8). Hence, the exponential series terminates at the N th order, the number of electrons, and even for truncated \hat{T} this method has a factorial scaling. Because of this scaling, exact VCC results are available only for small molecules in small basis sets. Van Voorhis and Head-Gordon used a brute-force FCI like algorithm to produce a benchmark of VCC results [31]. This shows that the upper bound property of VCCD prevents the variational collapse of CCD below the FCI energy. Figures 6a and 6b exemplifies this with the dissociation of N_2 and the symmetric stretching of H_2O .

In these two calculations they used Brueckner orbitals to account for the orbital relaxation. In the smaller STO-3G basis set the VCC results are closer to the FCI ones for these two systems. This shows that VCC improves the description of static correlation in comparison with CCD, but it cannot simultaneously describe dynamic correlation, because the correlation energy recovered when increasing the completeness of the basis is dynamic in nature. For larger molecules and larger basis sets, one needs to arbitrarily truncate the energy functional (47). Bartlett *et al.* introduced the expectation value CC hierarchy [XCC(n)] in which the truncation is done such as to include every term up to a given perturbation order n [30]. This method does not give an upper bound to the exact energy but it satisfies the Hellmann-Feynman theorem. In a recent series of paper, Robinson and Knowles introduced a method called quasi-variational CCD (QVCCD) [94–97]. They claim that a resummation

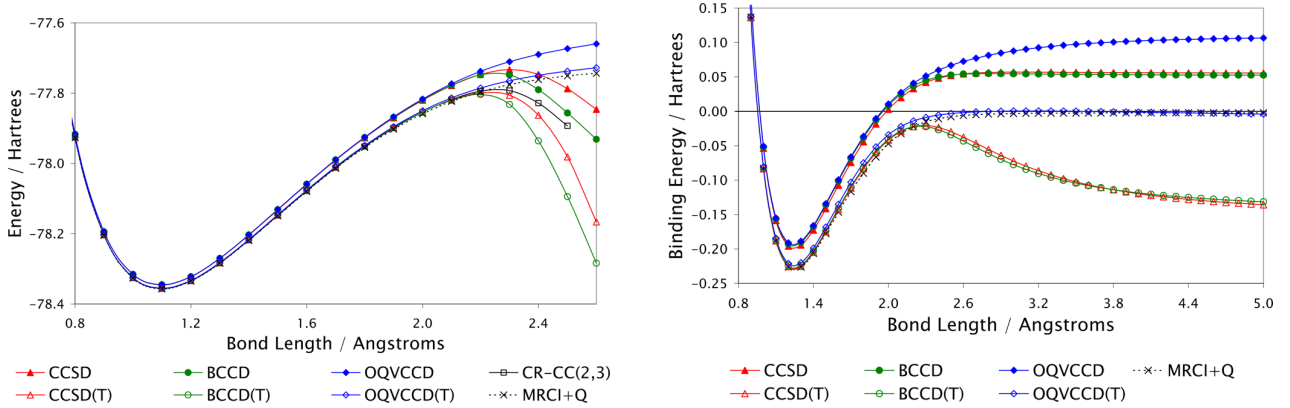


(a) N_2 dissociation. Calculations were run in the VDZ basis with all valence electrons correlated.

(b) Double dissociation of water. Calculations were run in the DZ basis with all valence electrons correlated.

Figure 6: Taken from Ref. [31]

of a subset of terms of (47) should be more efficient than an arbitrary truncation because the series can converge slowly in strongly correlated systems. Doing this they lose the upper bound property of VCC but they preserve the Hellmann-Feynman theorem [95]. Additionally, they construct the QVCCD functional such as it is an agreement with the VCCD energy functional up to order $\mathcal{O}(\hat{T}^3)$ and the terms of order $\mathcal{O}(\hat{T}^4)$ computable in $\mathcal{O}(o^2v^4)$ [96]. Moreover, their functional preserves the size-extensivity, the exactness for two electron systems and the invariance under rotations of occupied and virtual orbitals. They used orbital optimization to account for orbital relaxation and the (T) correction [2] to account for triple excitations leading to the OQVCCD(T) methods. For weakly correlated systems, OQVCCD(T) is comparable with BCCD(T) but when the correlation becomes strong, OQVCCD(T) is more robust. This method gives an accurate PEC, in comparison with a multireference benchmark, for the symmetric stretching of the C–H bonds in ethene, Fig. 7a. Even for the difficult case of the dissociation of C_2 , Fig. 7b, OQVCCD(T) predicts the correct dissociation limit.



(a) Calculated potential energy curves for the symmetric stretching of the C–H bonds in ethene with the cc-pVDZ basis set.

(b) Calculated energies for C_2 relative to the atomic dissociation limits with the aug-cc-pVQZ basis set.

Figure 7: Taken from Ref. [96]

3.3.2 The Unitary Coupled-Cluster

The exact wave function can be expressed as a unitary transformation in the whole Hilbert space acting on a reference determinant [98]. Additionally, every unitary operator can be expressed as the exponential of an anti-hermitian operator [98]. Based on this two results, one can propose an ansatz wave function closely related to the CC one as

$$|\Psi_{UCC}\rangle = e^{\hat{\sigma}} |\Psi_0\rangle = e^{\hat{T} - \hat{T}^\dagger} |\Psi_0\rangle. \quad (48)$$

As can be readily seen, the operator $\hat{\sigma}$ is anti-hermitian. Hence, its exponential is a unitary transformation. Hence, this ansatz is normalized by construction. We will refer to this wave function as the UCC ansatz. The energy expectation value associated with this wave function is

$$E_{UCC} = \langle \Psi_0 | e^{-\hat{\sigma}} \hat{H} e^{\hat{\sigma}} | \Psi_0 \rangle. \quad (49)$$

This alternative ansatz has been proposed only a few years after the CC one [13, 32–34, 99]. But, such as VCC, the expression (49) has no natural truncation, so this alternative formulation has been seldom studied. As for VCC, there are different ways to truncate this expansion. Similarly to the XCC(n) hierarchy, Bartlett *et al.* introduced a UCC(n) hierarchy where the truncation is done according to the perturbation series order [99]. Differently, Kutzelnigg proposed to use the Baker-Campbell-Hausdorff formula in (49) and to truncate at a given order of this expansion of nested commutators [13]. Additionally, to these truncation hierarchies, one needs to couple them with the truncation hierarchy of the

alternative ansätze within the usual EOM-CC method already brought some answers to this problem [104–106]. In this report, we will focus on an alternative to the EOM-CC method to target excited states within CC. The CC equations (8)-(9) form a set of polynomial equations in the cluster amplitudes thus they are highly non-linear by definition. Therefore the usual CC solution resulting from the solving iterative process is not the only solution to this set of equations. It is still unclear whether these solutions represent physical states or not. And if so, can we use these solutions to get access to excited states energies? Unfortunately, these higher roots are hardly attainable in practice and one needs to be very cautious when targeting these solutions. The iterative algorithm used in practice strongly influences the solution that is attained by the computational process. Additionally, to start the iterative process one has to make a guess at the cluster amplitudes. This guess also greatly influences the results obtained and wisely choosing the starting point can help to target given other solutions. Finally, the orbitals set used to construct the reference also need to be carefully chosen because the attainability of each solution is strongly dependent on this choice. In this subsection, we present an historical overview of works on higher roots of the CC equations. Particularly, we will be interested in the question: could the non-standard CC solutions provide a reliable description of excited states?

The seminal works of Zivkovic and Monkhorst were the first to shed some light on the existence conditions of the higher roots of the CC equations [47, 48]. We know that the FCC solutions are the same as the FCI ones, thus it is natural to compare the CC solutions at a given excitation order to the FCI ones which have a relatively simple structure, at least in comparison with the CC ones. To investigate their relationship, they designed an analytic continuation between CI and CC. Their characteristic equation depends on a parameter λ which is such that at $\lambda = 0$ the characteristic equation is the CI equation and at $\lambda = 1$ it is equal to the CC one. Hence, solving the characteristic equation for $\lambda \in [0, 1]$ gives insight on the relationship between CI and CC solutions. Because the characteristic equation is very difficult to solve, they used two very simple models to rationalize their results on the structure of the solutions. Their investigation led to a classification of the type of singularities possibly encountered when studying this analytic continuation, among which some of them were very preoccupying. However, these two examples turned out to be too simple to describe real cases and the pathological singularities were due to these simplistic examples [107]. Several attempts have been made to use CC to target excited states that are not of the lowest energy for a given symmetry. These excited states are very hard to attain, because one needs to avoid the variational collapse on a same-symmetry state but lower in energy. Adamowicz and Bartlett studied the attainability of some excited states of the LiH molecule with CC [108]. They perform a CI calculation with up to 4-fold excited states. In the twenty states obtained, only four excited states had a clear single-reference character. The second column of Table 1 gives the coefficient in the CI expansion of the dominant determinants for these four solutions. Then they used the dominant determinants of these CI expansions as a reference state for a CCSD calculation. For three of them, they succeed to converge the iterative process towards an accurate excitation energy with respect to FCI. For the fourth one, the one with the least pronounced single-reference character, they were unable to converge towards the desired state.

Table 1: Comparison of the full CI and CCSD results for the ground and few excited states of the LiH molecule. (All energies in a.u.). Taken from Ref. [108].

Root no.	Largest CI coefficient	CCSD	FCI
1	0.99195	−7.615842	−7.615845
4	0.75565	DNC ^a	−6.913847
6	0.88303	−6.494522	−6.494561
15	0.96355	−2.686597	−2.686592

^aDNC = does not converge

This exemplifies that solutions corresponding to excited states can be hard to attain in practice because even with a relatively good reference state the excited state was unattainable. Later, Jankowski *et al.* investigated the CCD solutions of 1A_1 symmetry in the H4 model [41–43]. In this model, the

parameter α allows to continuously deform a linear H_4 into a square one, see Fig. 9a. This model has been widely used to study strong correlation because for ϕ close to zero, the system exhibits strong quasi degeneracies [23]. In Fig. 9b, we also report the P4 model which will be discussed later and which is also a useful model for study of strongly correlated systems.

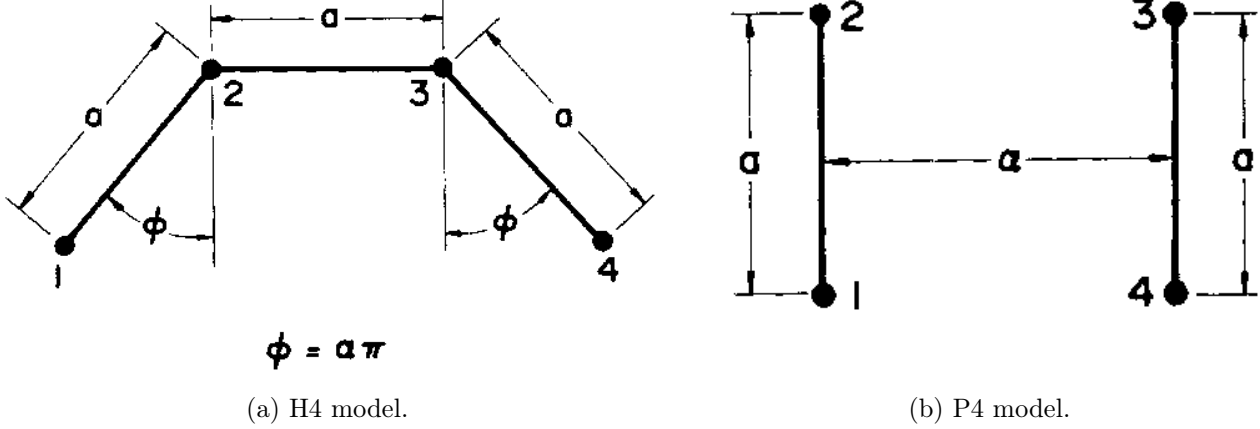


Figure 9: Taken from Ref. [23]

To construct the reference state they used the HF orbitals for the closed-shell ground state of the H_4 model [43]. Their numerical studies led them to the following classification: CC solutions can be classified as the standard or a non-standard solutions. Furthermore, non-standard solutions can be sorted as physical solutions, *i.e.*, corresponding to FCI solutions or non-physical. Using the usual HF determinant as reference they have been able to converge toward three CCD solutions: the standard 1^1A_1 and the non-standard 2^1A_1 and 5^1A_1 [42, 43]. But surprisingly, they did not attain the 3^1A_1 and the 4^1A_1 ones. In their complementary study [41], they found two other physical non-standard solutions while using the same reference, namely the 6^1A_1 and 12^1A_1 ones. Moreover, they showed that the number of attainable solutions depends on the choice of the reference determinants [41]. Using non-Aufbau determinants, *i.e.*, determinants in which the filled orbitals are not the lowest in energy, they attained also physical non-standard solutions corresponding to 3^1A_1 , 7^1A_1 , 10^1A_1 and 11^1A_1 . In the meantime, Meissner *et al.* emphasized that the linked-cluster theorem, with its current proof, is not verified for non-standard solution [109]. Hence, size-extensivity is not ensured for these solutions.

A crucial step in the study of non-standard CC solutions has been the introduction of the homotopy method by Kowalski *et al.* [110, 111]. This method allows one to find all the solutions of a set of polynomial equations [112]. The gist of this method is to create an analytic continuation between a set of equations for which the solutions are known and the set of equations to be solved.

$$\mathbf{H}(x, \lambda) = (1 - \lambda)\mathbf{G}(x) + \lambda\mathbf{F}(x) = 0 \quad (50)$$

$\mathbf{G}(x) = 0$ is the easily solvable set of equations. They applied this method to the CCD equation for the H_4 model, thus $\mathbf{F}(x)$ are the CCD equations and the unknowns x are the cluster amplitudes. The key difficulty of the homotopy method is to be able to follow distinctly the solutions from $\lambda = 0$ to $\lambda = 1$. In practice, this “path-tracking” is very difficult and computationally expensive. Within the H_4 model, the spin-orbital basis that they used implied that the corresponding CCD equations have ten unknown cluster amplitudes. Bezout’s number gives an upper bound to the number of solutions of a set of polynomial equations and in this case it is equal to 1024. Fortunately, their numerical study by means of the homotopy method showed that the complete set of solutions of the CCD equations in this case is composed of only 20 solutions. The question of the meaning of these solutions has been addressed in a follow-up study. The homotopy method is too computationally demanding to be

Table 2: Numbers of spin symmetry-adapted solutions of systems of equations representing various approximate CC methods for the H4 model. Taken from Ref. [115]

	CCD	CCSD	CCSDT	CCSDTQ
Number of solutions	12	60	34	12

used in practice, *e.g.*, finding the 20 solutions required 10 hours whereas there were only 10 cluster amplitudes [110]. Still, these two papers are a proof of concept that the homotopy method can be useful in understanding the structure of the CC solutions for small systems. //

In a subsequent series of papers, Jankowski and Kowalski explored in more details the CC solutions structure using this new homotopy method [45, 107, 113, 114]. In the meantime, Piecuch and Kowalski published an extensive review along the same way [115]. The first step in their study has been to study the characteristic equation of Zivkovic and Monkhorst under the lens of the homotopy method [107]. They have been able to solve the unabridged characteristic equation between CID and CCD for the H4 model for λ ranging from 0.0001 to 1. Among the 20 solutions, 7 are regular *i.e.*, continuously connecting a CCD solution to a CID one. The others CCD solutions have poles at $\lambda = 0$ so they do not correspond to CID solutions. Among the non-regular solutions, 8 of them are spin symmetry-broken CCD solutions (2 quintet and 6 triplet). The remaining ones are singlet and some of them form complex conjugate pairs with regular CCD solutions at $\lambda = 1$. They do not find pathological irregularities as the one predicted by Zivkovic and Monkhorst [47, 48]. They conclude that these irregularities were due to the too simplistic form of the approximate models considered. Using the spin-symmetry adapted version of the CCD equations [116] in this case lowers the number of solutions to 12. They investigated in more details the removal of spin symmetry-broken non-regular solutions by symmetry adaptation of the CC equations [113], but this is beyond the scope of this report. // Their next step has been to investigate the influence of the reference states on the CC solutions structure during the dissociation of the P4 model [45]. They used three reference states: A, B and Q respectively corresponding to the HF lowest, intermediate and highest energies. As for the H4 model, they found 20 CCD solutions, among which 12 were spin symmetry-adapted ones and 7 were regular ones. The main difference with H4 is that in this case the solutions were strongly dependent on the α parameter. For small α , the 7 regular solutions provide accurate approximation of a FCI energy and verify the size-consistency condition, whereas in the dissociation limit, $\alpha \rightarrow \infty$, there are only 2 regular solutions. This observation stands for the A and Q reference, using B as reference gives 7 regular solutions for any α but none of them are size-consistent. Finally, they investigated the CC structure solution dependence on the truncation of the cluster operator [114, 115]. We can see in Table 2 that the number of CC solutions is highly dependent on the level of truncation of the cluster operators. They performed these calculations with spin symmetry-adapted CC equations to lessen the number of solutions in order to lessen the computational cost. Moreover, they observed that the number of solutions associated with a complex energy increases when α goes from 0 to 0.5. Among the 34 CCSDT solutions, 18 are complex for the square geometry and 28 for the linear arrangement. According to the authors [115], this pattern could be related to the better performance of CC in non-degenerate regime than in the quasi-degenerate one. In the latter, several unphysical real solutions lie close to the physical targeted ones, increasing the probability that the numerical iterative process finds a non-physical solution. They also designed an analytic continuation procedure to connect two approximation levels of CC. This method is based on the β -nested set of equations [114, 115]. Figure 10 shows the continuation of solutions between CCD ($\beta = 0$) and FCC ($\beta = 1$). The twenty-first solution which diverges for β approaching 0 *i.e.*, does not correspond to a CCD solution. We can see that the additional CCD solutions, with respect to the FCC ones, diverge when β approaches 1. Such solutions are called solutions at infinity of the FCC set of equations [114]. The other continuation possible thanks to the β formalism (*e.g.*, CCSD to CCSDT) have been investigated in more detail and rationalized by Piecuch and Kowalski [115].

Few years later, the homotopy method was used to study the Pariser-Parr-Pople model of benzene and [10]-annulene [117, 118]. Recently, Mayhall *et al.* pointed out that the problem of the CC solutions

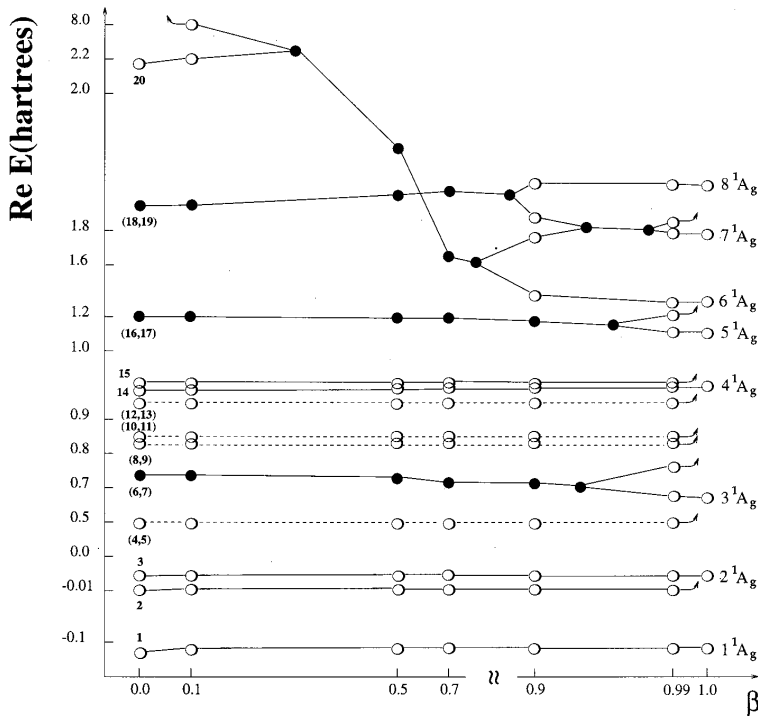


Figure 10: Dependence on the parameter β of the real parts of the energies (in hartrees, relative to the ground state RHF energy of -1.859099 hartrees) of the complete set of solutions to the β -NEs calculated for the P4 model at $\alpha=2.002$. Open and solid circles represent real and complex energies, respectively. Dotted lines indicate continuations of broken-symmetry solutions to the CCD ($\beta=0.0$) equations. Taken from Ref. [114]

structure still needs to be addressed for real systems. Thus, they investigated the appearance of multiple CCSD solutions for a real system, namely the NiH molecule and answered some questions along this way [119]. Finally, Lee *et al.* targeted doubly excited states and double core hole states of small molecules (CO, CO₂, NO, N₂O and NH₃) using CC with orbital optimized non-Aufbau determinants [46].

5 Conclusion and outlook

The quest for a black-box method capable of computing the quantized energies of any chemical system is still topical. CC arose as the method of choice for weakly correlated systems. However, a method dealing with strongly correlated systems is still coveted by quantum chemists. Because CC works so well for weak correlation, it is natural to look for an alternative method closely related to CC enhancing its performance for strongly correlated systems without deteriorating the results for the weakly ones. The exact wave function of the former systems can be very well approximated within the seniority zero subspace. This is highlighted by the accurate results yielded by DOCI in such cases. This wave function is the most flexible closed-shell wave function in a given one-electron basis set, yet, it is not computationally tractable. The pCCD method has been a huge step forward as it gives results nearly indistinguishable from DOCI, at least for repulsive interactions, whereas its computational cost is polynomial. Unfortunately, while gaining the ability to recover static correlation, pCCD loses the ability of CC to describe dynamic correlation. Still, it is possible to perform a fpCC calculation on top of pCCD to recover a part of the dynamic correlation. It can also be very instructive to investigate the breakdowns of CC by looking at each term of the amplitude equations in these situations. For example, the DCD method discards terms representing physically irrelevant processes in the dissociation limit but approximately described by CCD. The removal of these terms gives a method capable

of producing well-behaved PEC for strongly correlated systems. However, the inclusion of triple and higher excitations within DC is not straightforward and this is still an open question. Additionally, some terms of the CC equations are linked to other well-known quantum chemistry methods such as the RPA and its different flavors. It is thus possible to look at the failures of CC under the lens of the failures of RPA and to consequently design corrections to the CC amplitude equations. Finally, it would be convenient to prevent the variational collapse of CC below FCI by means of the variational principle. The VCC energy functional is an infinite expansion and, therefore, it is not usable in practice without an arbitrary truncation. Studies on truncation of this functional and resummation of subsets of its terms have already been proved to be able to give accurate results for some strongly correlated systems. The theoretical ability of quantum computers to compute the UCC wave function is also a promising way towards the inclusion of the variational principle within the CC paradigm.

These methods focus on recovering the static correlation of ground-state energies. Excited states often have a strong multi-reference character too and therefore have a non-negligible part of their energy which is static. In a second phase, this report presented results on the physical meaning of the non-standard CC solutions. These solutions can be symmetry-broken states, excited states or even more preoccupying non-physical solutions. A clear understanding of the solution structure of the CC equations is highly desirable. The homotopy method, which gives access to all the solutions of a set of polynomial equations, already shed lights on this open question. In particular, the investigation of the analytic continuation between CI and CC and the other ones between different standard TCC approximations has been really useful to tackle this problem. In addition, a wisely chosen reference state, and a fortiori an adapted orbitals set, can also allow one to target an excited state using CC. However, a good reference state is not sufficient and targeting excited states within CC requires to be extremely cautious in the guess of the cluster amplitudes and in the choice of the iterative algorithm. The aim of this internship is to investigate furthermore the CC solution structure and particularly the structure solution of the different alternative CC methods discussed in Sec. 3. It will be interesting to see if these non-standard solutions can give accurate excited state energies of strongly correlated systems. We also hope that investigating the link in the complex plane between these solutions could clarify some of the remaining grey area of the CC structure solution.

6 Glossary and References

Glossary

- BCCD** Brueckner Coupled-Cluster with Double excitations. 7
- CC** Coupled-Cluster. 1
- CCD** Coupled-Cluster with Double excitations. 1
- CCSD** Coupled-Cluster with Single and Double excitations. 6
- CCSD(T)** Coupled-Cluster with Single, Double and non-iterative Triple excitations. 1
- CCSDT** Coupled-Cluster with Single, Double and Triple excitations. 6
- CCSDTQ** Coupled-Cluster with Single, Double, Triple and Quadruple excitations. 6
- CI** Configuration Interaction. 1
- DC** Distinguishable Cluster. 2
- DOCI** Doubly Occupied Configuration Interaction. 1
- ECC** Extended Coupled-Cluster. 2
- EOM-CC** Equation Of Motion Coupled-Cluster. 2
- FCC** Full Coupled-Cluster. 1
- FCI** Full Configuration Interaction. 1
- HF** Hartree-Fock. 1
- hh-RPA** hole-hole Random Phase Approximation. 13
- ICCD** Coupled-Cluster with Double excitations. 14
- pCCD** pair Coupled-Cluster with Double excitations. 1
- PEC** Potential Energy Curve. 8
- ph-RPA** particle-hole Random Phase Approximation. 13
- pp-RPA** particle-particle Random Phase Approximation. 13
- QVCCD** Quasi Variational Coupled-Cluster with Double excitations. 15
- rCCD** ring Coupled-Cluster with Double excitations. 2
- RHF** Restricted Hartree-Fock. 3
- RPA** Random Phase Approximation. 13
- TCC** Traditional Coupled-Cluster. 1
- UCC** Unitary Coupled-Cluster. 2
- UHF** Unrestricted Hartree-Fock. 3
- VCC** Variational Coupled-Cluster. 2

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