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**Challenges Posed by Electron Correlation
in Wave-Function Methods within
Non-Relativistic Molecular Electronic
Structure Theory**

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Abstract

Challenges of describing electron motion in multi-electron systems under the Born-Oppenheimer approximation within non-relativistic electronic structure theory are illustrated discussing select wave-function methods. Using few, but illustrative examples, namely Hartree-Fock, Coupled-Cluster and Multi-Configuration-Self-Consistent-Field theories, the relevance of electron correlation is discussed, with emphasis on the electronic ground-state. The need for a universal method is presented, and ways Hartree-Fock, Coupled-Cluster and Multi-Configuration-Self-Consistent-Field methods fail to satisfy requirements to such a method are reviewed. Finally, outlooks of combining Coupled-Cluster and Multi-Configuration-Self-Consistent-Field theories to produce a universal Multi-Reference-Coupled-Cluster method are examined.

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1 Introduction

In non-relativistic quantum chemistry, under the Born-Oppenheimer approximation, the solution of the electronic Schrödinger-equation, the electronic wave-function, is the foundation for all further descriptions of the system. It must be determined before the Schrödinger-equation of the nuclei, and subsequently for the complete system can be solved. The exact electronic wave-function is analytically derivable only for single-electron systems. Electronic structure theory, the study of and search for reliable, computationally cheap and accurate approximations of electronic wave-functions, thus is a fundamental field of quantum chemistry. Electron-electron interactions, though physically well understood, are challenging to describe mathematically. Because of this, developing a single method of sufficient accuracy and practicality for all types of systems has proven difficult. Instead, a multitude of methods, accurate for different types of systems, have been developed. Much research is done attempting to extend their applicability without increasing computational cost or causing theoretical issues. The combination of Coupled-Cluster theory with multi-reference methods, such as CASSCF, is an example of such research.

2 Theory

2.1 The Physical Cause of Electron Correlation

Electron correlation refers to codependency in electron motion in multi-electron systems. By physical cause electron correlation is divided into Coulomb-correlation and Fermi-correlation [1].

2.1.1 Coulomb-Correlation

Under the Born-Oppenheimer approximation, the non-relativistic Hamiltonian, \hat{H} , of a system of N electrons and M nuclei, onward simply Hamiltonian, is

$$\hat{H}(\mathbf{r}_i; \mathbf{R}_A) = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \right) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = \sum_{i=1}^N \hat{h}(\mathbf{r}_i; \mathbf{R}_A) + \sum_{i=1}^N \sum_{j>i}^N \hat{g}(\mathbf{r}_i, \mathbf{r}_j). \quad (1)$$

Electron coordinates, \mathbf{r}_i , are variables, whereas nuclear coordinates, \mathbf{R}_A , are para-

meters henceforth skipped in notation. ∇_i^2 is the Laplacian of \mathbf{r}_i , Z_A are nuclear charges, and r_{iA} and r_{ij} denote distances between electron i and nucleus A , and electrons i and j respectively.

Eigenfunctions of the core Hamiltonian, \hat{h} , are analytically derivable one-electron wave-functions termed orbitals. However, the two-electron part, \hat{g} , makes the Hamiltonian additive inseparable in one-electron operators, and its eigenvalues multiplicative inseparable in orbitals. \hat{g} represents Coulombic electron-electron interactions, with resulting correlation in electron motion termed Coulomb-correlation. Factors $1/r_{iA}$ and $1/r_{ij}$ in Equation 1 cause the Hamiltonian becoming singular as an electron approaches a nucleus or another electron, which may cause cusps within the exact wave-function, termed Coulomb-cusps [1].

2.1.2 Fermi-Correlation

As fermions, electrons have spin which is essential to their proper description. Defining the total spin-operator, \hat{S}^2 , and the projected spin-operator, \hat{S}_z , with orthonormal eigenfunctions spin-up, $\alpha(\omega)$, and spin-down, $\beta(\omega)$, where ω is a spin coordinate, the electrons' spin states can be represented [2].

$$\hat{S}^2\alpha(\omega) = \frac{3}{4}\hbar^2\alpha(\omega) \quad (2a) \quad \hat{S}^2\beta(\omega) = \frac{3}{4}\hbar^2\beta(\omega) \quad (2c)$$

$$\hat{S}_z\alpha(\omega) = \frac{1}{2}\hbar\alpha(\omega) \quad (2b) \quad \hat{S}_z\beta(\omega) = -\frac{1}{2}\hbar\beta(\omega) \quad (2d)$$

Accounting for spin, electrons are described by three spatial and one spin coordinate, denoted collectively as $\mathbf{x} = \{\mathbf{r}, \omega\}$. Similarly, combining spatial orbitals with spin-eigenfunctions yields spin-orbitals, describing both spatial and spin states. For each spatial orbital, ψ_i , two spin-orbitals, $\{\phi_i\}$, can be constructed

$$\phi_i = \begin{cases} \psi_i(\mathbf{x}) = \psi_i(\mathbf{r})\alpha(\omega) \\ \bar{\psi}_i(\mathbf{x}) = \psi_i(\mathbf{r})\beta(\omega) \end{cases} \quad (3)$$

As ω isn't a variable in the Hamiltonian, introducing spin-orbitals doesn't itself impose additional requirements to electronic wave-functions. However, it enables requiring them to fit the fermionic character of electrons. Fermi-correlation refers to effects such requirements have on electron motion.

Firstly, any exact electronic wave-function, Ψ , must be anti-symmetric with respect

to the exchange of any electron coordinates \mathbf{x}_k and \mathbf{x}_l

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_k, \dots, \mathbf{x}_l, \dots, \mathbf{x}_n) = -\Psi(\mathbf{x}_1, \dots, \mathbf{x}_l, \dots, \mathbf{x}_k, \dots, \mathbf{x}_n) \quad (4)$$

known as the anti-symmetry principle [2]. As direct consequence the Pauli exclusion principle states that two electrons cannot occupy the same spin-orbital, $\phi(\mathbf{x}_k) = \phi(\mathbf{x}_l)$, as Equation 4 then couldn't hold.

By the Born-interpretation the square of the electronic wave-function determines expected measurements of observables. Squaring Equation 4 gives

$$|\Psi(\mathbf{x}_1, \dots, \mathbf{x}_k, \dots, \mathbf{x}_l, \dots, \mathbf{x}_n)|^2 = |\Psi(\mathbf{x}_1, \dots, \mathbf{x}_l, \dots, \mathbf{x}_k, \dots, \mathbf{x}_n)|^2 \quad (5)$$

implying that, secondly, physical measurements should be independent of electron exchanges, meaning electronic wave-functions should treat electrons as indistinguishable.

2.2 Simple Approximate Wave-Functions

2.2.1 The Hartree-Product

The simplest multi-electron wave-function is the Hartree-product, which for N spin-orbitals $\{\phi_i\}$ is

$$|\text{HP}\rangle = \phi_1\phi_2 \dots \phi_n \quad (6)$$

As Hartree-products neither are anti-symmetric nor treat electrons as indistinguishable, they do not include Fermi-correlation [2]. Some Coulomb-correlation may be included, though as one-electron potentials, as Hartree-products are multiplicative separable in one-electron eigenfunctions and thus cannot be eigenstates of the two-electron term \hat{g} , representing instantaneous electron-electron interactions [2].

2.2.2 The Slater-Determinant

Slater-determinants are linear combinations of Hartree products, combined as to obtain anti-symmetry and indistinguishability of electrons. A Slater-determinant of N spin-orbitals $\{\phi_i\}$ is

$$\begin{aligned}
|\text{SD}\rangle = |\phi_1, \dots, \phi_n\rangle &= \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^i \mathcal{P}_i \{ \phi_1(\mathbf{x}_1) \phi_2(\mathbf{x}_2) \dots \phi_n(\mathbf{x}_N) \} \\
&= \frac{1}{\sqrt{N!}} \left| \begin{pmatrix} \phi_1(\mathbf{x}_1) & \dots & \phi_n(\mathbf{x}_1) \\ \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_n) & \dots & \phi_n(\mathbf{x}_n) \end{pmatrix} \right| \tag{7}
\end{aligned}$$

where the permutation operator, \mathcal{P}_n , produces all permutations of N electrons, \mathbf{x}_i , occupying $\{\phi_i\}$. The normalisation factor, $\frac{1}{\sqrt{N!}}$, guarantees that if $\{\phi_i\}$ are normalised, the Slater-determinant remains so.

From Equation 7 a Slater-determinant includes all Hartree products construable from the spin-orbitals in use, with each possible distribution of electrons included once. This way electrons are treated as indistinguishable. Further, the exchange of any two rows in Slater-determinants corresponds to exchanging two electrons, and the exchange of any two columns corresponds to the exchange of two spin-orbitals, which is equivalent. For determinants the exchange of any two rows or columns changes its sign, meaning Equation 4 holds for Slater-determinants.

Accounting for anti-symmetry and indistinguishability of electrons causes Fermi-correlation in Slater-determinants. However, only parallel-spin electrons experience such so called exchange correlation [2]. Further, Coulomb-correlation is described crudely, as electrostatic repulsion between electrons is treated in an average way rather than instantaneously, quite analogous to Hartree-products [2]. Because of this Slater-determinants are said to remain uncorrelated approximate wave-functions.

2.3 The Variation Theorem

The Hamiltonian has infinite eigenfunctions, $\{\Phi_i\}$, forming a complete orthogonal basis spanning the vector-space of possible wave-functions [2]. Consequently, any approximate wave-function of the ground state, Ψ , is expressible as a linear combination of $\{\Phi_i\}$.

$$\Psi = \sum_i c_i \Phi_i \tag{8}$$

Assuming $\{\Phi_i\}$ are normalised, the energy of Ψ , determined as the Hamiltonian's expectation value, is shown to be greater than the Hamiltonian's lowest eigenvalue, \mathcal{E}_0 , as

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_m \sum_n c_m^* c_n \langle \Phi_m | \hat{H} | \Phi_n \rangle}{\sum_m \sum_n c_m^* c_n \langle \Phi_m | \Phi_n \rangle} = \frac{\sum_n |c_n|^2 \mathcal{E}_n}{\sum_n |c_n|^2} \geq \frac{\sum_n |c_n|^2 \mathcal{E}_0}{\sum_n |c_n|^2} = \mathcal{E}_0$$

This inequality is the variation theorem, allowing comparing the quality of approximate wave-functions by their expectation value of the Hamiltonian. The lower this value, the more accurate is the approximate wave-function.

2.4 Hartree-Fock Theory

Hartree-Fock theory applies the variation theorem to determine the best single Slater-determinant wave-function. This makes Hartree-Fock theory the energy minimisation of a single Slater-determinant.

2.4.1 Minimising the Energy of a Slater-determinant

Given a Slater-determinant of N orthonormal spin-orbitals $\{\phi_i\}$, $|\text{SD}\rangle = |\phi_1, \phi_2, \dots, \phi_n\rangle$, its energy, $E[|\text{SD}\rangle]$, determined as the Hamiltonian's expectation value, is

$$\begin{aligned} E[|\text{SD}\rangle] &= \langle \Psi | \hat{H} | \Psi \rangle = \left\langle \Psi \left| \sum_i^N -\frac{1}{2} \nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} \right| \Psi \right\rangle + \left\langle \Psi \left| \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} \right| \Psi \right\rangle \\ &= \sum_i^N \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \langle \phi_i \phi_j | | \phi_i \phi_j \rangle \end{aligned} \quad (9)$$

where

$$\langle \phi_i \phi_j | | \phi_i \phi_j \rangle = \langle \phi_i \phi_j | r_{12}^{-1} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | r_{12}^{-1} | \phi_j \phi_i \rangle \quad (10)$$

Minimising the energy with respect to variation in the spin-orbitals under the constraint that they remain orthonormal, yields the canonical Hartree-Fock equations [2]

$$\left[\hat{h} + \sum_{j=1}^N \mathcal{J}_j - \mathcal{K}_j \right] \phi_i = \epsilon_i \phi_i \quad i = 1, 2, \dots, N \quad (11)$$

$$\Updownarrow$$

$$f|\phi_i\rangle = \epsilon_i|\phi_i\rangle \quad i = 1, 2, \dots, N$$

Here Coulomb-, exchange- and Fock-operators, \mathcal{J} , \mathcal{K} , and f are

$$\mathcal{J}_j(\mathbf{x}_1)\phi_i(\mathbf{x}_1) = \left[\int \mathbf{d}\mathbf{x}_2 |\phi_j(\mathbf{x}_2)|^2 r_{12}^{-1} \right] \phi_i(\mathbf{x}_1) \quad (12)$$

$$\mathcal{K}_j(\mathbf{x}_1)\phi_i(\mathbf{x}_1) = \left[\int \mathbf{d}\mathbf{x}_2 \phi_j^*(\mathbf{x}_2) r_{12}^{-1} \phi_i(\mathbf{x}_2) \right] \phi_j(\mathbf{x}_1) \quad (13)$$

$$f(\mathbf{x}_1)\phi_i(\mathbf{x}_1) = \left[\hat{h}(\mathbf{x}_1) + \sum_{j=1}^N (\mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)) \right] \phi_i(\mathbf{x}_1) \quad (14)$$

Minimising the Slater-determinant's energy thus is equivalent to determining the Fock-operator's eigenstates $|\phi_i\rangle$. These are called molecular orbitals (MOs), with values ϵ_i interpreted as their energies. Projecting Equation 11 onto $\langle\phi_i|$, MO-energies are shown to be

$$\epsilon_i = \langle\phi_i|\hat{h}|\phi_i\rangle + \sum_{j=1}^N \langle\phi_i\phi_j|\phi_i\phi_j\rangle \quad (15)$$

Finally, the minimised Slater-determinant is constructed from the N MOs with lowest energies.

To solve the canonical Hartree-Fock equations, MOs are expanded in a known basis, usually atomic orbitals, meaning nuclei centred orbitals, allowing reformulating Equation 11 as a matrix equation. Different requirements made to MOs and pairing of electrons yields HF-methods with varying simplification in calculations. Two main HF-methods are restricted closed-shell Hartree-Fock (RHF), and unrestricted open-shell Hartree-Fock (UHF).

2.4.2 Restricted Hartree-Fock

Restricted MOs are constructed in pairs of two MOs from each spatial orbital, as shown in Equation 3. A closed-shell system contains an even number of all paired electrons, meaning they occupy spatial orbitals pairwise. Then in a restricted closed-shell system spin-orbitals ψ and $\bar{\psi}$ obtained from a spatial orbital ψ , are either both occupied or unoccupied. The corresponding Slater-determinant takes the form

$$|\text{RHF}\rangle = |\phi_1\phi_2 \dots \phi_N\rangle = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2 \dots \psi_{N/2}\bar{\psi}_{N/2}\rangle \quad (16)$$

with half electrons in each spin state [2].

Integrating over spin variables and expanding the $N/2$ spatial MOs ψ_i in a basis of K known spatial orbitals, $\{\chi_\nu\}$,

$$\psi_i = \sum_{\nu=1}^K C_{\nu i} \chi_\nu \quad i = 1, \dots, K \quad (17)$$

Equation 11 are rewritten as the Roothaan-Hall equations

$$\mathbf{FC} = \mathbf{SC}\epsilon \quad (18)$$

Here the coefficient matrix \mathbf{C} and MO-energy matrix ϵ are $K \times K$ -matrices

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \dots & C_{1K} \\ C_{21} & C_{22} & \dots & C_{2K} \\ \vdots & \vdots & \ddots & \vdots \\ C_{K1} & C_{K2} & \dots & C_{KK} \end{pmatrix} \quad (19) \quad \epsilon = \begin{pmatrix} \epsilon_1 & 0 & \dots & 0 \\ 0 & \epsilon_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \epsilon_K \end{pmatrix} \quad (20)$$

and $K \times K$ Fock- and overlap matrices, \mathbf{F} and \mathbf{S} have elements

$$F_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^*(1) f(1) \phi_\nu(1) \quad (21)$$

$$S_{\mu\nu} = \int d\mathbf{r}_1 \chi_\mu^*(1) \chi_\nu(1) \quad (22)$$

Here in turn f is the closed-shell Fock-operator

$$f(1) = \hat{h}(1) + \sum_a^{N/2} 2J_a(1) - K_a(1) \quad (23)$$

with the closed-shell Coulomb- and exchange-operators, J_a and K_a , being

$$J_a(1) = \int d\mathbf{r}_2 \psi_a^*(2) r_{12}^{-1} \psi_a(2) \quad (24)$$

$$K_a(1)\psi_i(1) = \left[\int d\mathbf{r}_2 \psi_a^*(2) r_{12}^{-1} \psi_i(2) \right] \psi_a(1) \quad (25)$$

After orthogonalising the basis to remove linear dependencies, Equation 18 is solved for \mathbf{C} by diagonalizing \mathbf{F} [2]. Obtained coefficients $C_{\nu i}$ define molecular orbitals ψ_i and their energies ϵ_i . Using N MOs constructed from $N/2$ spatial MOs of lowest energy, the RHF wave-function, called Hartree-Fock determinant, is constructed. Its energy is [2]

$$E_{\text{HF}} = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\mu\nu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu}) \quad (26)$$

where

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* \quad (27)$$

2.4.3 Unrestricted Hartree-Fock

An open-shell system allows for unpaired electrons, meaning numbers of alpha- and beta-spin electrons, N^α and N^β , may differ. Unrestricted MOs, $\{\phi_i\}$, are of the form

$$\phi_i(\mathbf{x}) = \begin{cases} \psi_i^\alpha(\mathbf{r})\alpha(\omega) \\ \psi_i^\beta(\mathbf{r})\beta(\omega) \end{cases} \quad (28)$$

where orthogonality of sets $\{\psi_i^\alpha\}$ and $\{\psi_i^\beta\}$ of spatial orbitals is required only separately. The corresponding Slater-determinant is

$$|\text{UHF}\rangle = |(\psi_1^\alpha \alpha)(\psi_2^\alpha \alpha) \dots (\psi_{N_\alpha}^\alpha \alpha)(\psi_1^\beta \beta)(\psi_2^\beta \beta) \dots (\psi_{N_\beta}^\beta \beta)\rangle \quad (29)$$

Correspondingly as the Roothaan-Hall equations were derived for RHF, for UHF the Pople-Nesbet equations are obtained [2]. They are similarly solved for coefficient matrices [2], in turn defining MOs and their energies, from which finally the lowest energy Slater-determinant for the system, within the chosen basis, the UHF wavefunction, is constructed.

2.5 Electron Correlation in Wave-Function Methods

2.5.1 Interpretation of the Fock-Operator

The Fock-operator is understood as an effective Hamiltonian. Whereas the Hamiltonian contains two-electron terms, the one-electron Fock-operator replaces these with one-electron Coulomb- and exchange-operators. This transition introduces an approximation.

From a classical viewpoint, the Coulomb-operator \mathcal{J}_j acting on a spin-orbital ϕ_i represents the potential experienced by an electron occupying ϕ_i from an electron occupying ϕ_j [2]. In the Fock-operator, including Coulomb-operators acting on ϕ_i for all indices j , represents the total potential an electron occupying ϕ_i experiences from all electrons. However, electrons aren't charge distributions, but experience instantaneous repulsion between one another. Thus the Coulomb-operator only approximates actual electron-electron repulsion.

The exchange-operator, stemming from Slater-determinant anti-symmetry, has no classical analogue. Acting between opposite-spin spin-orbitals it is zero. However, acting between parallel-spin spin-orbitals it causes reduction in MO- and total energies, meaning only parallel-spin electrons experience exchange correlation, as expected in single Slater-determinant wave-functions.

Acting between a spin-orbital with itself, Coulomb- and exchange-operators cancel. Summation over all spin-orbitals in the Fock-operator then doesn't count interactions between an electron with itself, as it could seem.

2.5.2 Excited Determinants and Fock-Space

Given a system containing N electrons, with $K > N$ MOs obtained using Hartree-Fock theory, the N MOs included in the Hartree-Fock determinant, $\{\phi_i\}$, are termed occupied, with the remaining $N - K$ MOs, $\{\phi_a\}$, termed virtual. Exchanging any number of occupied MOs, $\{\phi_i, \dots\}$, with equally many virtual MOs, $\{\phi_a, \dots\}$, yields an excited determinant $\Psi_{a\dots}^{i\dots}$. The total number of constructible $N \times N$ Slater-determinants for the system is

$$N^{\text{SD}} = \binom{N}{K} \quad (30)$$

The space they span will within this text be called a Fock-space. More broadly, the term will describe any space spanned by a set of Slater-determinants. The mathematical definition of Fock-space is more general [3], but not relevant to this text.

2.5.3 Sources of Error in Wave-Function Methods and Correlation Energy

Neglecting errors stemming from a non-relativistic approach and the Born-Oppenheimer approximation, two main sources of error remain in Hartree-Fock and other Slater-determinant methods, henceforth referred to as wave-function methods. Firstly, the Fock-operator having infinite eigenstates [2], an infinite basis is required to find exact solutions to the Hartree-Fock equations. In practice a finite, and as such incomplete, basis is introduced, causing a basis set truncation error limiting accuracy of results. The lowest possible RHF-energy, obtained using a complete basis, is called the Hartree-Fock limit, and may be approximated, at least for small systems [2].

More relevant to discussing electron correlation is the error stemming from single Slater-determinants' inadequacy as approximate wave-functions. The energy difference between the RHF-energy, E_{HF} , and the actual lowest energy, within the basis, E_{exact} , will be the definition of correlation energy, E_{corr} , in this text. Another common definition is based on the Hartree-Fock limit and the exact energy in an infinite basis [4].

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \quad (31)$$

Generally a linear combination including all Slater-determinants of a systems Fock-space can describe its wave-function exactly, within the applied basis [4]. This Full-Configuration-Interaction (FCI) wave-function corresponds to describing electron-electron interactions instantaneously rather than as potentials [4]. However, it is calculable only for the smallest systems, with the FCI ground-state energy of benzene, still a small molecule, being successfully determined only recently [5].

2.5.4 Dynamic and Static Correlation

Within wave-function methods, electron-correlation commonly is split into static- and dynamic correlation.

Dynamic correlation denominates correlation associated with the need for small contributions from many Slater-determinants to describe Coulomb interactions between electrons instantaneously. As illustration, around Coulomb-cusps wave-function methods converge slowly toward the exact wave-function, with respect to the number of included Slater-determinants [1]. Dynamic correlation contributes strongly in systems where one Slater-determinant dominates the FCI wave-function.

Static correlation refers to requiring large contributions from multiple Slater-determinants to obtain a good approximate wave-function, and can be attributed to two causes [6]. The first is several Slater-determinants approaching degeneracy and gaining substantial importance in the FCI wave-function. The second is symmetry requirements, spin or spatial, to the exact wave-function, which within the given Fock-space are only satisfiable by large contributions from several Slater-determinants [6]. Static correlation usually dominates in energetically less favourable states such as bond breaking and formation processes, excited- and transition states. The specific case of several restricted Slater-determinants being required to describe homolytic bond-cleavage, is termed left-right correlation [6].

2.6 Correlated Wave-Function Methods

FCI rarely being practical, a number of correlated wave-function methods exist, using incomplete combinations of Slater-determinants, while aiming to maintain high accuracy in the approximate wave-function.

2.6.1 Coupled-Cluster Theory

Introducing excitation operators

$$\begin{aligned}\hat{X}_i^a|\Psi\rangle &= |\Psi_i^a\rangle \\ \hat{X}_{ij}^{ab}|\Psi\rangle &= |\Psi_{ij}^{ab}\rangle \\ &\vdots\end{aligned}\tag{32}$$

moving electrons from occupied MOs to virtual MOs, the cluster-operator of a system containing N electrons is

$$\hat{T} = \sum_{ia} t_i^a \hat{X}_i^a + \sum_{\substack{i<j \\ a<b}} t_{ij}^{ab} \hat{X}_{ij}^{ab} + \dots = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_N\tag{33}$$

where coefficients t are excitation amplitudes [7], and \hat{T}_i also termed cluster-operators. The corresponding Full-Coupled-Cluster (FCC) wave-function, in the exponential ansatz is

$$|\text{CC}\rangle = N e^{(\hat{T})} |\text{HF}\rangle\tag{34}$$

where N is a normalisation coefficient [4]. Equation 34 uses the Hartree-Fock determinant as reference determinant, $|\text{HF}\rangle$. However, any determinant with a non-zero contribution to the FCI solution may be used.

Using the Maclaurin expansion of the exponential function, the FCC wave-function is rewritten as

$$|\text{CC}\rangle = N \left\{ 1 + \hat{T}_1 + \left(\frac{1}{2} \hat{T}_1^2 + \hat{T}_2 \right) + \left(\frac{1}{6} \hat{T}_1^3 + \hat{T}_1 \hat{T}_2 + \hat{T}_3 \right) + \dots \right\} |\text{HF}\rangle\tag{35}$$

and shown to be equivalent to the FCI wave-function [4]. However, the FCC wave-function includes doubly or higher excited determinants in several terms, one for each series of excitations producing it from the reference determinant. Single-step excitation processes, termed connected, have single-factor excitation amplitudes, whereas multi-step excitations, termed disconnected, associate with products of lower order amplitudes. The FCI expansion coefficient of a Slater-determinant is then as sum over all its connected and disconnected amplitudes in the FCC wave-function.

Truncating the CC wave-function means not including all cluster operators in the

Coupled-cluster operator. Including \hat{T}_1 and \hat{T}_2 gives Coupled-Cluster-Singles-Doubles (CCSD), further including \hat{T}_3 yields Coupled-Cluster-Singles-Doubles-Triples (CCSDT), and so on. Several hybrid methods adding approximate further excitation operators to truncated CC-methods by the use of perturbation theory [4] exist, examples being CC2 [8] and CCSD(T) [9].

The Coupled-Cluster energy is determined inserting the CC wave-function into the electronic Schrödinger-equation and projecting onto the Hartree-Fock determinant. For any CC wave-function of order CCSD or higher it is [7]

$$E_{CC} = \langle \Psi_{HF} | \hat{H} | CC \rangle = E_{HF} + \sum_{\substack{a>b \\ i>j}} \left(\frac{1}{2} t_i^a t_j^b + t_{ij}^{ab} \right) \langle \phi_i \phi_j | | \phi_a \phi_b \rangle \quad (36)$$

Since energy isn't determined as the Hamiltonians' expectation value, the variation theorem doesn't apply.

Excitation amplitudes are determined similarly, though by projection onto the set of excited determinants with connected excitations in the applied truncation [4].

The CCSD wave-function is

$$|CCSD\rangle = N \left\{ 1 + \hat{T}_1 + \left(\frac{1}{2} \hat{T}_1^2 + \hat{T}_2 \right) + \left(\frac{1}{6} \hat{T}_1^3 + \hat{T}_1 \hat{T}_2 \right) + \dots \right\} |HF\rangle \quad (37)$$

with excitation amplitudes determined by [7]

$$\begin{aligned} \langle \Psi_i^a | e^{(-\hat{T})} \hat{H} | CCSD \rangle &= 0 \\ \langle \Psi_{ij}^{ab} | e^{(-\hat{T})} \hat{H} | CCSD \rangle &= 0 \end{aligned} \quad (38)$$

Equation 35 shows that any truncated CC wave-function still includes all excited determinants. However, the truncation lowers accuracy in their contributions, as disregarding excitation processes reduces the number of free variables, making the contributions dependent. Further, as a two-electron operator, the Hamiltonian only allows interactions of determinants differing in at most two MOs [2]. Then from Equation 38 follows that only up to quadruply excited determinants affect the CCSD amplitudes and energy. Generally any CC-method, though including all Slater-determinants of the given Fock-space in its wave-function, only regards excited determinants up to two excitation levels above truncation level when determining energy and excitation amplitudes.

CC-methods have flexibility regarding MOs of the reference determinant, due to single excitations from \hat{T}_1 . Exponentials of single excitation operators closely resemble MO mixing [10] [7], meaning single excitation amplitudes induce MO optimisation if the reference determinant doesn't use the MO-space most energetically favourable for the CC wave-function.

2.6.2 Multi-Configuration-Self-Consistent-Field Theory

Multi-configuration-self-consistent-field (MCSCF) theory generalises Hartree-Fock theory to systems with multiple Slater-determinants contributing strongly to the FCI wave-function. The MCSCF wave-function is

$$|\text{MCSCF}\rangle = D_1|\text{SD}_1\rangle + D_2|\text{SD}_2\rangle + \dots + D_N|\text{SD}_N\rangle \quad (39)$$

where Slater-determinants $|\text{SD}_i\rangle$ are constructed each using N of K total MOs with basis expansion coefficients $\{C_{\nu\mu}\}$. Its energy is optimised varying both expansion coefficients $\{D_i\}$ and basis expansion coefficients $\{C_{\mu\nu}\}$ [4].

To obtain a MCSCF wave-function, Slater-determinants to include must be selected. An established selection strategy is the Complete-Active-Space-Self-Consistent-Field (CASSCF) method [11], subdividing MO-space into inactive, active and virtual orbitals. Inactive orbitals are doubly occupied in all Slater-determinants, virtual orbitals staying empty. Remaining electrons are distributed in all possible ways between active orbitals. Resulting Slater-determinants of correct spin and spatial symmetry are included in the CASSCF wave-function [11], which can be understood as a FCI wave-function constructed from a subspace of the systems complete Fock-space.

2.6.3 Multi-Reference Coupled-Cluster Theory

Multi-reference CC (MRCC) methods extend upon single reference CC (SRCC) methods to allow large contributions from several Slater-determinants. Multiple Slater-determinants are used as reference state, Lyakh et al. [6] terming them model determinants spanning the model space. The MRCC Coupled-cluster operator includes excitations from all model determinants to further excited determinants. Using terminology of Lyakh et al. [6], methods determining such MRCC wave functions by a multi-reference computational framework are called genuine-MRCC (gen-MRCC) methods, whereas approaches using computational methods

resembling SRCC-methods are called alternative-MRCC (alt-MRCC) methods.

2.7 Properties of Interest of Wave-Function Methods

2.7.1 Computational Cost

The fundamental challenge of electronic structure theory isn't incomplete theory, but computational cost. The conceptually simple FCI wave-function is an exact solution to the electronic Schrödinger-equation within a given basis, with mathematical procedures for its determination well understood. The issue is the required number of calculations, which approximate methods aim to reduce.

Computational cost can be examined by scaling, describing how the number of required calculations increases with some relative measure of system size, M , usually related to basis size. For polynomial scaling this number scales with M^N , N being a number specific to the method. In exponential scaling it scales as X^M , where X also is a number. Table 1 summarises scaling of relevant wave-function methods.

Method	FCI	HF	CC2	CCSD	CCSD(T)	CCSDT	CASSCF
Scaling	X^M	M^4	M^5	M^6	M^7	M^8	X^M

Table 1: The scaling of select methods of electronic structure theory [2, 4, 8].

2.7.2 Spin-Contamination

The exact wave-function is an eigenstate of both total- and projected spin-operators. Whereas the total spin-operator doesn't relate to an observable, the projected spin-operator represents a measurable quantity. Thus, although approximate wave-functions ideally should be eigenfunctions of both spin-operators, the projected spin-operator is most important [2]. A wave-function being no such eigenstate, may predict non-physical spins, and is said to be spin-contaminated.

2.7.3 Size-Extensivity

Size-extensivity refers to energy scaling correctly with system size. For a size-extensive method the energy of a system of non-interacting subsystems A and B equals the sum of energies of the subsystems individually

$$E(A + B) = E(A) + E(B) \tag{40}$$

3 Discussion

3.1 HF-Methods

RHF by definition includes no electron correlation. However, in equilibrium geometry, correlation energy is often down to 1% of total energy [12]. Still, 1% errors generally being orders of magnitude above chemical accuracy of 0.0016 hartree, needed for quantitative calculations, RHF is at best considered a qualitative method. Even so, RHF usually predicts equilibrium geometries with good accuracy, bond length errors typically being 2-3 pm [4]. Observables more sensitive to crude descriptions of electron motion see larger errors [12]. Hickey and Rowley [13] found RHF systematically overestimating dipole moments, while underestimating polarizabilities, both on average by 7%. Such systematic errors speak to the inaccurate description of electron motion in RHF-theory.

Near equilibrium geometry RHF and UHF usually converge to the same solution [4]. However, with increasing bond lengths, approaching homolytic bond cleavage, solutions diverge. RHF-theory requires electrons occupying spatial orbitals in pairs in a singlet spin-state. Electrons of a broken bond must then remain in the same spatial orbital. As homolytic cleavages instead result in unpaired electrons, occupying different spatial orbitals centred on separate nuclei, the RHF description is qualitatively wrong. In fact, for the water molecule in Figure 1, the RHF energy continues increasing for increasing bond lengths, surpassing the expected limit of two independent systems [4]. This error corresponds to complete disregard of left-right correlation in RHF, which commonly breaks down similarly for other systems where restricted singlet-state descriptions are not applicable, such as open-shell systems and excited states [2].

In contrast, UHF allows bonding electrons occupying separate spatial orbitals and becoming unpaired, meaning they mustn't remain having spin. Thus UHF enables a qualitative description of homolytic bond cleavage with ground-state energies approaching the limit of independent HF calculations on the fragments, meaning left-right correlation is included. This difference between RHF and UHF, shown for the water molecule in Figure 1, can be understood as unrestricted Slater-determinants being capable of combining multiple restricted determinants [2].

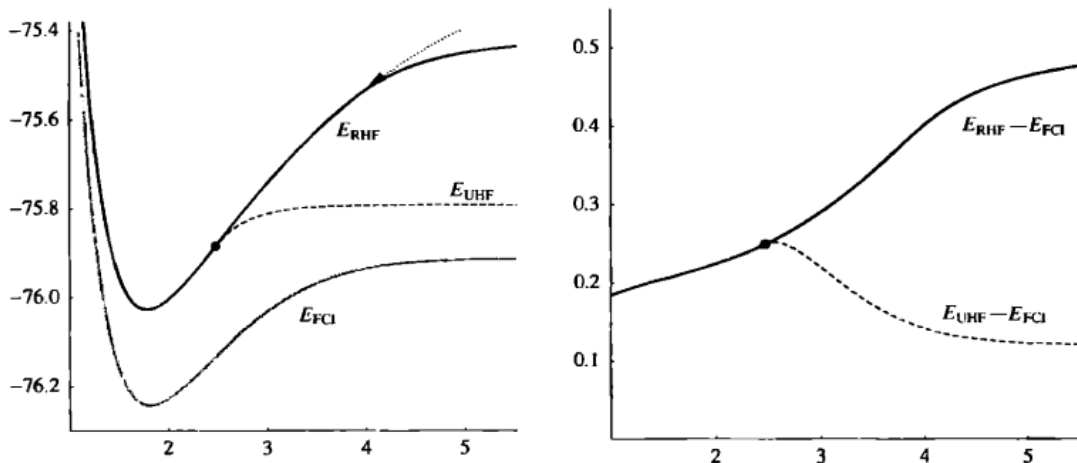


Figure 1: RHF, UHF and FCI potential energy surfaces for the water molecule within the cc-pVDZ basis set for a fixed HOH bond angle of 110.565° are shown on the left. On the right the corresponding errors relative to the FCI wave-function are plotted. Energies are given in E_h , whereas bond lengths are given in \AA . Reprinted from [4] with permission from Wiley Books.

However, the UHF wave-function can be spin-contaminated [2], a sometimes serious problem for describing spin-dependent quantities, as magnetic properties, and even spin-independent quantities, as energies [12]. Theory to remove spin-contamination by imposing spin-requirements onto the UHF wave-function was presented by Lowdin already in 1955 [14]. However, methods applying such projections are computationally challenging, as spin requirements cause loss of orthogonality between unrestricted states [12], complicating calculations. Still, there are developments arguing for the feasibility of UHF both on its own, and in combination with further methods [15], though this hasn't yet become a standard approach.

Further, though able to include left-right correlation, UHF does not generally include all static correlation [4]. As example, not being a spin eigenstate, the UHF wave-function cannot properly include static correlation caused by spin-symmetry requirements. Such lack of static correlation, in addition to complete lack of dynamic correlation, explains the substantial difference between UHF and FCI energies in the dissociation limit in Figure 1.

3.2 CC-Methods

Truncated CC wave-functions include all FCI Slater-determinants, though not all actually influence energies. Still, the inclusion of large numbers of excited determinants enables good descriptions of instantaneous electron-electron interactions. For

systems dominated by dynamic correlation, CCSD and CCSDT commonly recover over 90% and 99% of correlation energy respectively [16]. The disadvantage of CC-methods being non-variational is usually overlooked, due to their high accuracy in such systems [4].

Also other properties depending on precise description of electron movement see substantial improvements. Equilibrium geometries, though generally well described by RHF, in an extensive study of small molecules by Oliphant and Bartlett [17], using CCSD(T) saw an average reduction in bond length and -angle errors to around 60% and 20% of RHF-errors respectively. In the same study CCSD(T) yielded average errors in dipole moment only 17% of RHF-errors, whereas using CCSD, Hickey and Rowley [13] saw such errors halving. Generally, CCSD reduces RHF-errors to around one third or fourth, with similar improvements for each further included excitation order [1].

In states where multiple Slater determinants contribute strongly to the FCI wavefunction, CC-methods using a restricted reference determinant break down. Truncated CC wave-functions have reduced numbers of free variables, making contributions from separate determinants dependent through disconnected excitation amplitudes. This prohibits independent contributions from all but the Hartree-Fock determinant. Consequently, in truncated CC-methods severely lacking descriptions of static correlation are expected, relieved only slowly by including higher order excitations. Only severely truncated CC-methods having acceptable cost, restricted CC-methods are ill suited to describe static correlation. Figure 2 shows errors in energy rapidly increasing for restricted CC-methods as bond-cleavage introduces left-right correlation in the water molecule from bond lengths of around 4 Å. Similar errors are common for other homolytic bond cleavages, as well as other systems with substantial static correlation [6].

Problems posed by static correlation in restricted CC-methods may be addressed by introducing unrestricted MOs. Generally, unrestricted CC-methods include left-right correlation in systems where homolytic bond cleavages are complete, approaching the energy of independent fragments, shown for the water molecule in Figure 2. However, quite analogous to UHF, unrestricted CC wave-functions may be spin-contaminated, thus susceptible to the corresponding problems [4]. In an article exploring spin contamination in unrestricted CCSD, Stanton [18] argues the problem may be sufficiently remedied by the intrinsic MO optimisation of CC-theory. Even so, for only partially broken bonds, unrestricted CC-methods may deviate substantially from allowed spin states [4]. In Figure 2 this shows as characteristic bulks in energy errors at intermediate bond lengths. Further, unrestricted CC-methods

have cost several times those of restricted ones [4]. As for UHF, theory for spin projecting the unrestricted CC wave-function is known [19], though developing implementations without increasing cost beyond practical limits has proven challenging [6].

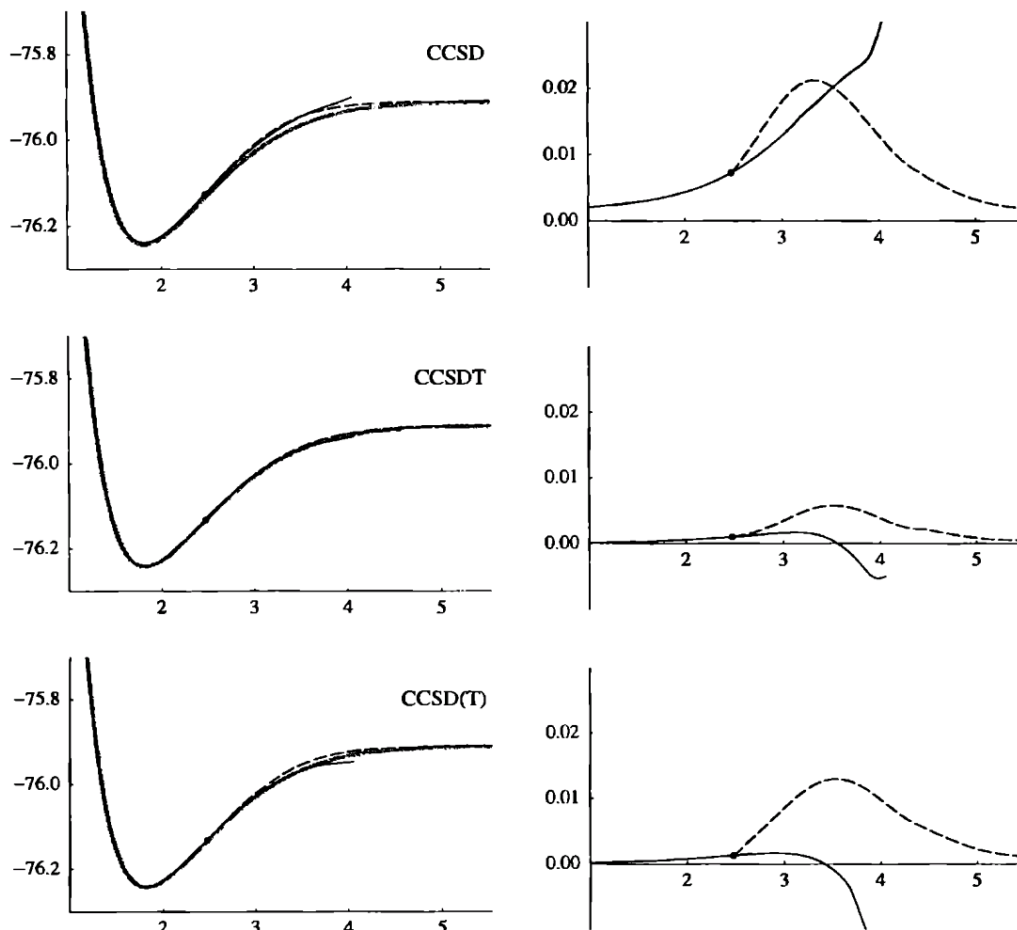


Figure 2: Restricted (full line) and unrestricted (dotted line) CC-methods, and FCI (grey line) potential energy surfaces for the water molecule within the cc-pVDZ basis set for a fixed HOH bond angle of 110.565° are shown on the left. On the right the corresponding errors relative to the FCI wave-function are plotted. Energies are given in E_h , whereas bond lengths are given in \AA . Reprinted from [4] with permission from Wiley Books.

3.3 CASSCF-methods

CASSCF wave-functions having full flexibility in both contribution of all reference Slater-determinants, and the MOs they're constructed from, a close to complete description of static correlation is possible. Indeed, in a study of small molecules

by Mok et al. [20], CASSCF results approached chemical accuracy already from intermediate bond lengths, as static correlation became the main contribution to correlation energy.

However, exponential scaling severely limits size of active space, and thus the amount of Slater determinants possible to include the wave-function. This in turn restrains inclusion of dynamic correlation, as few Slater-determinants cannot adequately describe instantaneous electron-electron interactions. An excellent description by CASSCF of the dissociating hydrogen molecule in Mok et al. [20] is thus only possible as hydrogen atoms, containing a single electron, have no dynamic correlation. For bonded hydrogen atoms with dynamic correlation results were far from excellent, with only around 50% of correlation energy recovered in equilibrium geometry.

Results are expected to be worse for systems including larger atoms, always containing dynamic correlation. Indeed, for dissociation of the nitrogen-molecule, shown in Figure 3, Roos [11] obtained good results only for the lowest energy state close to full dissociation. From near equilibrium geometries to intermediate bond-lengths CASSCF severely overestimated energies for all three calculated excitation levels. Roos himself suggests a lacking description of dynamic correlation being the main explanation [11].

A substantial drawback to CASSCF-methods is lack of “black-box” character, meaning prior chemical knowledge is needed before applying the method. The chosen active space strongly influences CASSCF performance, but isn’t optimised as it is selected before conducting CASSCF calculations. Even though strategies for active space selection exist, finding a “black-box” procedure has remained challenging [21]. The general procedure includes first by chemical intuition selecting a larger number of active orbitals, being orbitals generally important for atoms partaking in examined changes in the system, and remaining orbitals directly partaking in these changes. Subsequently calculations on relevant geometries using other methods are used to determine active orbitals that can be omitted and others that unexpectedly are relevant. Though conceptually simple, in practise this can become a tedious guess-and-test procedure [22].

As the active space required to satisfyingly describe static correlation increases with system size [4], even disregarding lacking inclusion of dynamic correlation, exponential scaling limits CASSCF to small systems. A major reason is the necessity to always simultaneously include relevant active MOs for all geometries considered in an application, if discontinuities in observables shall be omitted. Consequently at-

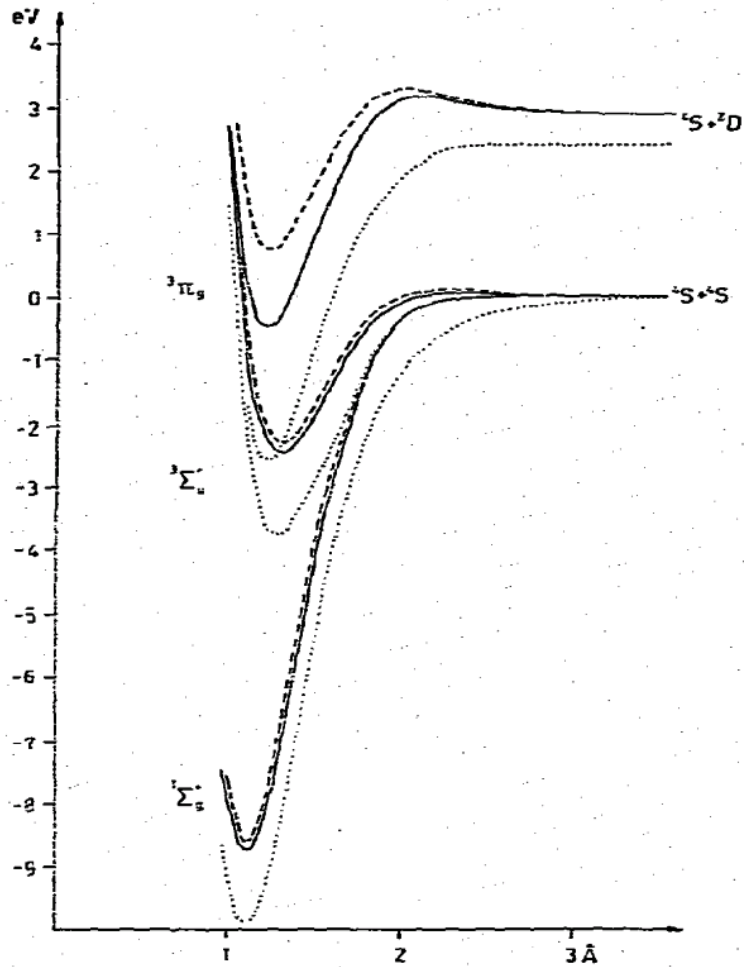


Figure 3: Calculated and experimental potential energy surfaces for the three lowest states of the N_2 molecule: (—) give the CASSCF-6 (6-dimensional active space) results, (---) the CASSCF-7 (7-dimensional active space) results, and (...) the experimental curves. Reprinted from [11] with permission from Elsevier.

tempts to better handle its scaling have been central to increasing the applicability of CASSCF [23].

Continuing improvements in traditional FCI algorithms have made CASSCF calculations using an active space of 20 electrons and 20 orbitals routine [24]. However, such an active space remains suitable only for systems with single-digits of atoms partaking in processes to be studied for the system [21]. Density-Matrix-Renormalization-Group (DMRG) approaches escape exponential scaling using a non-linear expansion of the wave-function [25]. Using such methods, MCSCF calculations on active spaces of around 30 electrons and 30 orbitals have been conducted, with little loss of accuracy [26]. This is, however, still in the range of simple systems. Another approach to reducing cost are CASCI-methods [22], optimising only CI coefficients, whereas MO coefficients are previously determined by another method. Although prior choice of

MOs constitutes a new “non-black-box” element, the issues severity is lessened by the development of several effective selection schemes [22]. CASCI-methods have produced results equalling or even surpassing traditional CASSCF in model calculations [22], but more research is needed to fully establish this variation of CASSCF.

A serious issue of both CASSCF and its variations is prediction of unphysical discontinuities in observables, due to the large flexibility that is also their main strength. A large amount of variables leads to a multitude of local minima existing for the minimisation calculation, meaning the global minimum may not always be reached [22]. Starting from different geometries, convergence to different minima can lead to jumps in observables.

3.4 Finding a Universal Method

The term universal method describes a method able to satisfyingly describe electron movement of even large systems at acceptable cost. It should work for any system ideally having “black-box” character. The need for such a method stems from applications of electronic structure theory predominantly treating systems undergoing changes, such as chemical reactions or excitation- and relaxation processes. A system in one state may contain mostly dynamic correlation, while static correlation dominates another. When studying transitions between such states, a method able to adequately describe both is needed.

RHF-theory fails to satisfyingly describe electron motion in any state, even sometimes breaking down as for homolytic bond cleavages. Even UHF, though able to include left-right correlation, neither includes other static nor dynamic correlation, and produces spin-contaminated wave-functions. SRCC-methods, building upon HF-methods, successfully add dynamic correlation to the system, but fail to solve the remaining issues of HF-theory. In contrast, CASSCF-methods are well suited to describe static correlation, but consistently overestimate energies due to a lack of dynamic correlation, and sometimes predict discontinuities in observables. Thus none of the methods previously discussed fulfil the requirements made to a universal method.

As methods able to describe either dynamic or static correlation already exist, CC-methods and CASSCF-methods being examples, an intuitive approach to a universal method is using one method when dynamic correlation dominates and another where static correlation is most essential. Even disregarding that systems may contain both types of correlation simultaneously, there are multiple issues with such an approach.

Firstly, determining which method to use in which situation would likely require chemical intuition, thus compromising “black-box” character. Secondly, a transition between methods would generally cause unphysical discontinuities in observables. Consequently the universal method could break down in certain applications. For example, discontinuities in potential energy surfaces would likely cause molecular dynamics calculations to fail, if the geometry transitioned from one side of a jump to another. Lastly, calculating changes in observables, if different methods are used to calculate the separate values, errors in their difference become less predictable. Due to such issues, this approach to a universal method has been mostly disregarded.

Another possibility is combining methods well suited to describe either dynamic or static correlation in theory, rather than implementation, usually by adding dynamic correlation to a static method. Not causing problems related to discontinuities or loss of “black-box” character, this approach encounters other hurdles, as combining theories leads to increased complexity and cost. Even so, such approaches are constantly researched, with CASPT2 arguably the most established method [27] [28]. To be examined in this text are, however, developments in MRCC-methods.

3.5 MRCC-methods

MRCC-methods aim to combine efficient description of dynamic correlation in CC-theory with inclusion of static correlation, usually based on MCSCF-methods. Including required model determinants in the reference wave-function, MRCC methods should have sufficient flexibility to effectively include static correlation, while excitation operators for the complete model space secure a good description of dynamic correlation. However, challenges encountered in CASSCF and CC, such as lack of black-box character and large computational cost, extend to MRCC-theory [6]. Further, combining the theories without introducing additional issues has proven a challenge [6].

A promising example of gen-MRCC-methods is the MRexpT-method developed by Hanrath [29]. This method, when including single and double excitations, maintains M^6 scaling of CCSD, though with a far larger value of M [6]. It has produced results close to chemical accuracy for small model systems, such as H_4 and H_8 molecules [30]. Even so, though the scaling is low, memory-requirements limit the MRexpT-method to small active spaces, severely reducing its applicability. Further, theoretical problems include results not being independent with respect to MO-mixing within the orbital space [31]. Thus, two equivalent sets of active MOs generally yield different results in the MRexpT-method, which is not the case for the exact wave-function.

In addition, MRexpT wave-functions are susceptible to spin-contamination [29].

An alternative to gen-MRCC computational schemes is including static correlation within the existing SRCC computational framework. Such alt-MRCC-methods usually don't treat all model-space determinants equivalently, selecting one fundamental reference state, subsequently used to construct the model space [6]. One such method is the CASCCSD-method developed by Ivanov and Adamowicz [32]. Its cost scales as M^6 , and it produces good results for the dissociation of N_2 [33]. However, results are dependant on choice of reference determinant within the model space. Further, the method can break down in systems with degeneracies of strongly contributing determinants [34]. Attempts to correct such deficiencies resulted in new theoretical issues, namely loss of size-extensivity [6].

Many MRCC-methods beyond those mentioned have been developed. Still, thus far none manage to altogether avoid theoretical and computational problems. Unsolved issues include limitations to the size of active space, finding general procedures for selecting the active space, and large values of M in scaling due to algebraic complexity [31]. Clearly further developments are needed to achieve a MRCC-method of broad practical use, coming close to a universal method.

4 Conclusion

RHF, including no electron correlation, cannot describe electronic motion in molecular systems with quantitative accuracy, sometimes even failing to produce qualitative results, as for homolytic bond cleavage. Though UHF enables describing unrestricted and open-shell systems, susceptibility to spin-contamination is a severe theoretical issue. Further, correlation remains ill described, causing errors orders of magnitude above chemical accuracy for all but uncorrelated systems. Clearly, precisely representing electron-electron interactions is essential to describing electron motion.

Established methods approaching chemical accuracy in certain types of systems exist, but all have limitations regarding theoretical requirements, cost, or generality. CC-methods, able to quantitatively describe dynamic correlation, break down when static correlation is significant. Further, the comparatively cheap CC2-method is still only applicable to systems of up to about 60 second row atoms, CCSD already limited to half as many. CASSCF-methods, able to fully include static correlation, lack dynamic correlation and remain limited to even smaller systems.

As chemistry studies not only fixed systems, but also changes, the aim of electronic structure theory is a universal method able to describe electron motion in a system before, during and after some change. Processes in systems only ever containing either static or dynamic correlation, may well be described quantitatively by established methods such as CC or CASSCF. However, a universal method should do so even if the dominating type of correlation changes, or both static and dynamic correlation are significant simultaneously. HF-methods being qualitative at best, and CC- and CASSCF-methods only including sufficient dynamic or static correlation respectively, neither methods qualify as universal. This illustrates the reason no universal method yet exists, that approaches suitable for describing dynamic and static correlation are quite different.

Several attempts combining CASSCF- and CC-theory to obtain a universal MRCC-method have been made. Some are based on the established SRCC mathematical framework, as the CASCCSD-method. Though promising results have been produced in model calculations, Lyakh et al. [6] conclude that using a single-reference framework to describe a multi-reference system has intrinsic theoretical limitations. For CASCCSD degeneracies in model determinants cause failure. Instead using a multi-reference computational framework, as in MRexpT, causes steep computational costs and its own theoretical problems, MRexpT being susceptible to spin-contamination and inconsistent with respect to mixing of active orbitals. Lyakh et al. [6] and Evangelista [31] agree that though MRCC-methods seem a promising approach to a universal method, still much progress is needed addressing both theoretical issues and computational cost.

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