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REGULAR ARTICLE

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Coupled cluster theory with emphasis on selected new developments

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Abstract Coupled cluster (CC) methods for the description of the correlated motion of electrons and nuclei are reviewed with emphasis on selected new initiatives. The basic aspects of standard electronic CC theory are described including the rationale behind the most widely used methods like coupled cluster singles and doubles (CCSD) and the CCSD(T) approach. The hierarchy of coupled cluster models consisting of coupled cluster singles (CCS), CC2, CCSD and CC3 is also described. A brief account of the theory behind the calculation of molecular properties using CC methods, and the description of response properties and excited states using CC response theory is followed by a discussion of the use of CC theory in the context of effective models for describing molecules in solution. In another part of the review we consider recent initiatives aimed at the development of coupled cluster methods for describing the correlated motion of the atomic nuclei. A recently developed second quantization formulation of many-mode dynamics for distinguishable degrees of freedom forms the basis for developing new quantum dynamical methods in particular vibrational coupled cluster (VCC) methods. The VCC theory is reviewed and discussed in comparison with vibrational configuration interaction (VCI), and vibrational Møller–Plesset (VMP) perturbation theory. The review concludes with a discussion of some important future research topics.

1 Introduction

Central to the success of applying quantum mechanics to the study of the molecular electronic structure has been the development of methods that have high enough *accuracy* and low enough computational *cost* to be of general interest. To have sufficient accuracy in quantum chemical calculations it is often necessary to use so-called many-body methods. Many-body methods seek to describe the correlated motion of the electrons in the molecule following from their instantaneous interactions. In this review we discuss a number of aspects related to the development of accurate many-body methods for both electrons and nuclear motion. The main focus is on the use of coupled cluster (CC) theory for approximating the quantum mechanical description of the many-body system in certain applications. The development of CC methods have been pursued for close to 50 years now. CC methods were originally developed within the framework of nuclear physics in the late 1950s [1–3]. The CC ansatz was introduced into quantum chemistry for the description of electron correlation by Cizek and Paldus in papers from 1966 and onward [4,5]. During the 1980s CC methods made its way to a wider audience as the advantages of CC theory in comparison to other approaches became known and efficient computer implementations began to appear. Examples of papers that turned out to be seminal are the first coupled cluster singles and doubles (CCSD) implementation by Purvis and Bartlett [6] in 1982 and the introduction of the CCSD(T) method by Raghavachari et al. [7] in 1989. From the 1980s and onward the development of CC methods became a very active research area and the CC approach was applied in many different contexts by many different groups.

The present review is not intended to be a complete survey of the development of CC methods, as it does not assert to cover in any detail all the many contexts in which CC methods are currently applied and all the many new developments constantly taking place. Besides giving an account of some basic aspects defining the CC approach we shall focus in this review only on a limited number of selected new developments which relate to the authors own interest and recent work. Furthermore, among the issues discussed, completeness with respect to describing all past and present developments would lead to a very long and very different review and this was abandoned from the outset. For more complete descriptions and references related to the development of electronic CC methods and many related methods that historically were important steps on the way, the reader may consult other reviews [8–23] and monographs[24–29]

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describing CC methods in quantum chemistry at various levels. Concerning the use of the coupled cluster theory in physics we refer to [30] and [31] for reviews and note that recently the description of nuclear matter by CC methods has received renewed interest [32,33].

For systems that have an electronic ground state that is dominated by a single Slater determinant, the primary CC models in use have been CCSD and CCSD(T) for many years. Together with the second order Møller-Plesset [34] perturbation theory (MP2), these methods have in recent years been the most widely used ab initio methods for going beyond mean field Hartree–Fock (HF) calculations. Coupled cluster singles doubles and triples (CCSDT) [35–37] has received significant attention, but is often too expensive to be useful for molecules with more than a few atoms. Over the years there have been many suggestions for various other CC based electronic structure methods of varied complexity and designed for various purposes. Among the first approximate triple excitations methods are the non-iterative triples corrections and the CCSDT-*n* models of Bartlett and coworkers from the mid 1980s [38–40], which were important in establishing the potential of approximate triples methods prior to the introduction of the CCSD(T) method. About 10 years ago we introduced the CC2 and CC3 models [41–43]. The CC2 and CC3 methods were designed with a particular emphasis on predicting certain molecular properties where the use of MP2 and CCSD(T) turned out to be problematic. These issues were primarily related to the calculation of molecular response properties, including electronic excitation energies and frequency-dependent (hyper-) polarizabilities. The introduction of CC2 and CC3 gave rise to a hierarchy of methods comprising of CCS, CC2, CCSD, CC3, ... The models of this hierarchy have been implemented for the calculation of many different properties in different contexts and by different researchers. For the calculation of electronic excitation energies, black box methods including electron correlation at different levels like CC2 and CC3 were in great need. It was soon also established that CC3 provides high accuracy for many other challenging response properties. Over the years many other approximate CC models have been developed including other approximate triples methods to which we shall return later in this introduction.

If for a moment we assume that the electronic structure problem is solved, it becomes clear that not only is the motion of the electrons important for accurate calculation of quantities of experimental interest but also the motion of the atomic nuclei. Molecular vibrations are of course a primary issue in relation to high-resolution vibrational spectroscopy, UV spectroscopy, photo-electron spectroscopy etc. Furthermore, consideration of molecular vibrations is important for molecular properties due to the averaging of electronic properties over the vibrational motion. In addition, some molecular properties have important pure-vibrational contributions as has been amply demonstrated for non-linear optical properties [44]. Most obviously, the correlated motion of the atomic nuclei is important in chemical reactions including photo-induced dissociation etc. Describing the dynamics of the atomic nuclei involves a number of different problems and the field of quantum molecular dynamics has traditionally been an issue separate from electronic structure research. Nevertheless, one of the basic problems is to describe the correlated motion of some pseudo particles. Thus, for molecular vibrations and nuclear dynamics also we may speak more generally of a many-body problem. Consider, for example, the description of molecular vibrations. The basic harmonic oscillator treatment defines a set of distinguishable molecular vibrations that are uncoupled. This treatment is not exact with anharmonicities causing sometimes large deviations from the harmonic oscillator description. Calculation of the bound states by various methods has been developed in many different flavors, see for example the reviews in [45]. One branch of the methods are based upon the vibrational self-consistent field (VSCF) approach [46–52]. In the VSCF approach each degree of freedom vibrates in the average field of the other modes thereby providing an approximate treatment of anharmonicities. For vibrational wave functions the neglect of direct correlations leads also to critical limitations in the final accuracy that can be achieved, and a number of different methods have been suggested to overcome this. The approaches used have primarily been vibrational configuration interaction (VCI) [53–58] and Vibrational Møller–Plesset perturbation theoretical methods [50,59–61]. In a recent publication [51] a new second quantization (SQ) formulation of many-mode dynamics was outlined. Building on this new formulation a vibrational coupled cluster (VCC) approach could be defined and implemented [51,52]. The initial results have been highly encouraging while at the same time a number of new issues are raised.

In this review we shall consider selected issues in electronic CC theory, solvent modeling in conjunction with the use of CC methods, and vibrational many-body methods including VCC. We shall discuss the most widely used electronic CC methods, the CCSD and CCSD(T) methods, as well as some of our own CC models. We shall discuss very briefly the theory behind the calculation of molecular properties. This very broad issue will not be discussed in great detail as it is well described in other reviews [9,14,62]. However, widely used and very important concepts such as variational *Lagrangian's* and the auxiliary $\langle\Lambda|$ state [31,62–64] will be introduced and used in subsequent sections. In addition, a brief account of response theoretical methods will be given as a necessary introduction to the study of excited states by response theoretical methods. The relation to the equation of motion CC (EOM-CC) [65] and symmetry-adapted-cluster CI (SAC-CI) approaches [66–68] will be discussed briefly. Coupled cluster response theory methods by themselves have a long history with many important contributions following the Monkhorst linear response paper of 1977 [69]. For the description of many other contributions to this field we refer to [9,14,62,70,71] and the references therein. A review covering specifically the CC response theory in the context of non-linear optical properties will appear else-where [72]. In a later section the construction of effective solvent models using CC methods is considered focusing on the most basic problems in defining such approaches in the CC context. Another forthcoming review [73] will detail certain aspects of the theory in a CC context. Reviews and a few defining papers on solvent models, hybrid methods and related aspects can be found in [24,25,74–83]. Finally, we shall describe vibrational CC theory and discuss characteristics of this theory in comparison with the VCI and VMP theories as well as the principal and practical differences between CC theory as applied to electrons and to nuclear motion. We shall conclude with a summary including remarks on future research directions that are expected to be important.

Many other important issues and developments in CC theory are not treated in detail in this review. A few of these issues will be mentioned in the remaining part of this introduction to give a flavor of the activity in the field and some references to the literature. However, it should again be emphasized that completeness has not been striven for. Among the many other areas of research which are not treated in this review are such important topics as relativistic quantum mechanics [84–86], exchange perturbation theoretical calculation of intermolecular interactions [88,87], extended systems [89], the many issues special to open-shell systems [23], etc.

Besides the approximate single reference models previously mentioned above, many other approximate single reference models have been developed through the years. Full CCSDT models have been explicitly implemented for calculation of ground state energies [35–37,90], excitation energies [91], energies of ionization [92] and electron attachment [93] as well as for analytical calculation of properties [94, 95]. There are many papers discussing explicit inclusion of quadruple and higher excitations, see [89,91,96,97] and references therein. It should also be mentioned that alternative hierarchies of CC methods have been suggested including the quadratic coupled cluster model methods of Gwaltney and Head-Gordon [98], Gwaltney et al [99] and van Voorhis and Head-Gordon [100].

One interesting activity is the development of more general and open ended CC implementations including the work of Kallay et al. [101–105], Olsen and coworkers [106,107] and the work of Hirata et al. [108] and Hirata and Barlett [109]. While most standard CCSD and CCSD(T) implementations proceed by implementing a large number of terms derived in full detail, these newer implementations aim at using more general and flexible schemes. These general developments allow calculations with high excitation levels, implicitly covering also CCSDT and CCSDTQ and so on. However, in some variants, it also allows introducing only selected types of higher excitations, for example only those which fulfill certain limitations on the orbitals involved in the excitations joining earlier related work, see [21,110,111] and references therein. In this manner one may employ the concept of distinct active spaces in the CC theory also. This can be used to construct wave functions of a certain restricted multi-reference character. A related approach that is general in another way is the automatic generation of codes with the tensor contraction engine of Hirata, as a recent and impressive example [112,113]. The tensor contraction engine automates the time-consuming, error-prone processes of deriving the working equations of a well-defined model of second-quantized many-electron theory, and translates these into a potentially parallel program. There have been other reports on automated implementation of CC methods [114–117] following the work of Janssen and Schaefer [118]. These various types of more general approaches for working with CC methods can lead to competitive implementations while at the same time allowing much more general and flexible wave functions than in previous standards. This is certainly an important message for those developing new CC methods and although more general multi-reference CC methods have been proposed, such developments may have high impact in the coming years.

Multi-reference CC theory in all its flavors is an important topic not covered in detail in this review. The interested reader is referred to the previously mentioned general references as entries to broader parts of the literature on these subjects. A similar comment applies to various alternative ansatzes such as unitary and expectation value based CC methods, see [119, 120] for further references and interesting formal analysis. Still today the description of the breaking of chemical bonds is a challenge to theoretical chemistry in general and to CC methods in particular in spite of its obvious importance in chemistry [121]. However, many researchers have over the years advanced new ideas and tested various methods with respect to this issue including the work of Paldus reviewed in [12] and others, only a few of which will be mentioned here. Krylov et al. [122,123] have suggested a valence active space optimized orbital coupled-cluster doubles model and, more recently, a spin-flip method. The spin-flip methods of Krylov and coworkers [124–127] relies on the fact that open shell triplet states are often easier to describe than open shell singlet states. In this formalism a high-spin triplet state is thus used as a single-reference wave function for studying the more difficult singlet state. The method of moments and renormalized CC methods reviewed in [15] are other frameworks within which a number of new CC models have been developed including also new approximate triple excitation methods [128]. A generalization of the renormalized approaches has recently been reported [129] addressing the important issue of size-extensivity. Interesting developments and test comparisons of selected single and multi reference methods are presented in recent papers by Sherrill and coworkers [130, 131] and others [132,107].

Over the years quantum chemical calculations have been applied to systems of increasing size. While one reason has been the steady increase in computer power, the other important reason is the development of more efficient implementations of methods with significantly reduced computational cost. These developments may be due to the invention of new models with lower cost, as for example the CC2 method which was developed as an approximation to CCSD. This reduced the computational scaling of the method in terms of CPU time from N^6 for CCSD to N^5 for CC2, where N is the number of orbitals. However, developments providing access to larger molecules may also be due to reformulation and/or approximations in other aspects than the CC model itself. For example, the CC2 model has been implemented in combination with the so-called resolution of identity approach by Hättig [133]. The RI-CC2 implementation gave significant additional reductions in computational scaling in terms of both CPU time and storage requirements compared to the previous CC2 implementations with the introduction of an additional, very small error. Further developments of RI-CC2 has established this approach as a competitive candidate for calculation of excitation energies and excited state structures for large molecules [134]. Another interesting approach aimed at excited states of larger molecules is the similarity transformed EOM-CC (STEOM-CC) approach of Nooijen and coworkers [115, 135, 136]. It should also be noted that the SAC-CI approach has been used for rather large molecular systems for a number of years [137].

The quest for formulations and implementations of CC applicable to still larger systems has more generally lead to a number of different suggestions for new approximations and implementations. Initial promising works on creating linear-scaling AO-based CC strategies and related issues have only been little used [138, 139]. There has been significant activity in the area of local correlation CC methods [140–144] and related approaches [145] and rather large systems can indeed be handled using such localized CC methods. It is important to stress that these local methods do not give equivalent results to standard CC methods and the results depend on the definition of local domains which in practice seems most often to be based on the original ideas of Saebø and Pulay [146] developed within the MP2 framework. One important issue that has been investigated is the discontinuity of the potential energy surface obtained using such local methods [143]. It is certainly possible and likely that CC methods better suited for large molecular systems will involve other or additional approximations compared to those used today for small molecules, but exactly which is still difficult to guess at this stage. This research area will be very important for the future of electronic CC theory and the success of the developed methods is encouraging.

One acute practical problem in many CC calculations is the need for rather large one-electron basis set to obtain accurate results. This is due to the convergence of the description of electron correlation with respect to the size of the one-electron basis. One promising area of research that relates to this issue are the explicitly correlated methods including the so-called r_{12} [147–150] and Gaussian Geminal methods [87, 151–155] that includes explicitly inter-electronic distances in the wave function. It has been established that close to basis set limit can be achieved using such methods and in conjunction with the CC method this has been used to obtain very accurate results.

Finally, there has recently been significant discussion of the potential of using coupled-cluster with generalized single and double excitations (CCGSD) based on a recent work by Nakatsuji [156] and Nooijen [157]. Whether approaches of this type are useful and can describe the exact wave function with a minimal number of parameters is still being debated [158–163].

2 Electronic structure theory

In non-relativistic electronic structure theory the aim is to solve the many-electron molecular electronic Schrödinger equation approximately but accurately. The approximations commonly used in modern quantum chemistry have a two-step approach: (a) A finite one-electron basis set is used. Ideally a complete basis set (CBS) should be used but in practice one is forced to employ finite and thereby incomplete basis sets. (b) The use of an approximate N-electron model. For a given one-electron basis the best electronic wave function that can be obtained is the full configuration interaction (FCI) wave function having contributions from all Slater determinants (SD) that can be constructed from the given one-electron basis set. Conventional FCI calculations can only be carried out for small systems and small basis sets and most often a less flexible approximate wave function must be used. Such an approximation can be seen as a particular *model* for the description of the correlated motion of the N electrons. To obtain the exact solution to the Schrödinger equation we must simultaneously extend our calculation toward the CBS and FCI limits. In this review we focus solely on the N-electron models and refer to text books and references therein for discussions on the equally important basis set issue [24, 28]. For simplicity we discuss only the single reference closed shell theory here.

2.1 Second quantization and excitation operators

Second quantization [28, 29, 164–166] (SQ) for electrons is formulated in terms of creation and annihilation operators built upon a basis of spin-orbitals. SQ should be well known to the reader, but a very short account is included here to illustrate the extent to which the introduction of SQ is similar in electronic and vibrational theories. The spin-orbitals are typically products of a spatial orbital being a function of the coordinates of the electrons ($\vec{r}$) times a spin-function reflecting the spin projection ($M_s = \pm\frac{1}{2}$). The *creation* operator $a_p^\dagger$ creates an electron in spin–orbital p while the *annihilation* operator a_p annihilates an electron in spin–orbital p. The second quantization algebra is defined by the usual fermion anti-commutator relations

$$[a_p^\dagger, a_q]_+ = a_p^\dagger a_q + a_q a_p^\dagger = \delta_{pq}, \tag{1}$$

$$[a_p^\dagger, a_q^\dagger]_+ = [a_p, a_q]_+ = 0, \tag{2}$$

and

$$a_p|vac\rangle = 0. \tag{3}$$

Here the vacuum state denoted $|vac\rangle$ is a state with no electrons. Both the relevant quantum mechanical states and the operators are expressed in terms of creation and annihilation operators. This includes the electronic Hamilton operator,

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q + h_{\text{nuc}}, \tag{4}$$

that in SQ is given in terms of one-electron integrals accounting for the kinetic energy and the electron–nuclear attraction, $h_{pq} = \int \phi_p^*(\vec{x}) \left(-\frac{1}{2}\nabla^2 - \sum_{m=1}^{M} \frac{Z_m}{|\vec{r}-\vec{R}_m|} \right) \phi_q(\vec{x}) d\vec{x}$, and the two-electron integrals accounting for the electron–electron repulsion, $g_{pqrs} = \int\int \frac{\phi_p^*(\vec{x}_1)\phi_r^*(\vec{x}_2)\phi_q(\vec{x}_1)\phi_s(\vec{x}_2)}{|\vec{r}_1-\vec{r}_2|} d\vec{x}_1 d\vec{x}_2$. The $\vec{x}$-vectors denote a combined set of spatial ($\vec{r}$) and spin coordinates ($M_s = \pm\frac{1}{2}$). The last term in Eq.(4) is the nuclear repulsion energy.

A Slater determinant with n electrons in the spin-orbitals 1,2,... n is represented in SQ as a state where electrons are filled in by multiple applications of SQ creation operators, $|SD\rangle = \prod_i^n a_i^\dagger |vac\rangle = a_1^\dagger a_2^\dagger, ..., a_n^\dagger |vac\rangle$. The operator $a_q^\dagger a_p$ is an *excitation operator*. It excites an electron from orbital p (if occupied) to orbital q when working on a given Slater determinant. Making products of such one-electron operators, multiple-electron excitation operators can be constructed. The excitation operators are used extensively in the following. In particular we shall use a formulation where we promote electrons from occupied orbitals $i, j, k, ..$ to unoccupied orbitals a,b,c,... in a reference state, which typically will be a Hartree–Fock state. The excitation operators for doing this are of type $a_a^\dagger a_i$ for single excitations, $a_a^\dagger a_b^\dagger a_i a_j$ for double excitations, etc. We shall denote these operators by τ_{μ_i} for i-tuple excitations. Thus the i-index denotes the excitation level (i=1 corresponds to single excitations, i=2 to double excitations, etc.) and μ denotes a particular index set (ai, $aibj$,.. etc). We note a few properties of the excitation operators which follows directly from commutator algebra and the basic relations in Eqs.(1–3). The excitation operators commute

$$[\tau_{\mu_i}, \tau_{\nu_j}] = 0, \tag{5}$$

while in general τ_{μ_i} and $\tau_{\nu_j}^\dagger$ do not commute. We have the "killer" conditions (from Eq.(3))

$$\tau_{\nu_j}^\dagger |HF\rangle = 0. \tag{6}$$

Finally, we have the orthogonality conditions

$$\langle \mu_i | \nu_j \rangle = \langle HF | \tau_{\mu_i}^\dagger \tau_{\nu_j} | HF \rangle = \delta_{\mu,\nu} \delta_{i,j}, \tag{7}$$

where the states $|\mu_i\rangle = \tau_{\mu_i}|HF\rangle$ denote the manifold of excitations out of the HF reference. The whole space of N-electron wave functions with the given orbital basis set is given in terms of the reference state and the manifold of excitations out of the reference state, e.g., $\{|HF\rangle, \tau_{\mu_i}|HF\rangle\}$.

2.2 The coupled cluster ansatz

The coupled cluster ansatz is given by

$$|CC\rangle = \exp(T)|HF\rangle, \tag{8}$$

where $|HF\rangle$ is the Hartree–Fock reference wave function and T is the so-called cluster operator

$$T = T_1 + T_2 + T_3 + \cdots + T_n = \sum_{i=1}^{n} \sum_{\mu_i} t_{\mu_i} \tau_{\mu_i}. \tag{9}$$

The t_{μ_i} parameters denote the cluster amplitudes. The number of electrons in the system is n. The exponential of the cluster operator is defined through its Taylor expansion. Reference states other than the HF state can also easily be used.

The CC wave function ansatz is introduced into the time-independent Schrödinger equation and pre-multiplying with $\exp(-T)$ we obtain

$$\exp(-T) H \exp(T)|HF\rangle = E_{CC}|HF\rangle. \tag{10}$$

Projection onto the HF reference state gives an expression for the CC energy

$$E_{CC} = \langle HF | H \exp(T) | HF \rangle. \tag{11}$$

(where the killer condition of Eq.(6) ensures the $\exp(-T)$ operator drops out). The CC amplitudes are determined by projection onto the excitations out of the reference state

$$e_{\mu_i} = \langle \mu_i | \exp(-T) H \exp(T) | HF \rangle = 0. \tag{12}$$

These are the basic working equations for CC theory. We first solve the non-linear set of equation in Eq.(12) and subsequently use the calculated cluster amplitudes to calculate the energy according to Eq.(11).

One important advantage of the CC equations above resulting from projection is that they give a set of algebraic equations for the amplitudes that are at most quartic in the cluster amplitudes. The drawback is that the CC method is not variational. Thus the CC total ground state energy is unbound and may be, and sometimes is lower than the exact energy. This does not by itself necessarily give rise to problems, but does make the results unbound which may be problematic if, for example, the reference state is a poor approximation. The non-variational nature of the CC ansatz does require additional attention for analytical calculation of molecular properties and the construction of effective solvent models as we shall see to later.

When the cluster expansion includes all possible excitations, the CC parameterization has the necessary flexibility to represent the FCI solution. However, the exponential form of the parameterization has some crucial advantages in approximate theories. Truncating the cluster expansion in Eq. (9) and the corresponding projection manifold at a certain excitation level, yields approximate CC models. The CCS [41], CCSD [6], CCSDT [35,37], etc. models are obtained with $T = T_1, T = T_1 + T_2, T = T_1 + T_2 + T_3$, ... and so on. Since the exponential ansatz includes the higher excitations that are the product of lower ones also in the truncated case, only the so-called *connected* higher excitations are left out. For example the connected quadruple excitations given by T_4 are neglected in CCSD while the *disconnected* quadrupole excitations due to $\frac{1}{2}T_2^2$ are included. Impressive improvements in accuracy are obtained at each step in the hierarchy defined above. A major problem is, however, that the complexity also increases very fast. The CCS model gives the same ground state energies as HF and has similar complexity as HF (thus the HF abbreviation is used and should be used except in the context of molecular response properties where CCS means something different than HF). CCSD is significantly more expensive having an N^6 computational scaling. CCSDT is a computationally very expensive approach for two reasons: (a) The operation count increases steeply as N^8. (b) The number of triples excitation amplitudes are in many cases prohibitive. Thus in reality there seems to be only little of a CC hierarchy. However, methods in between CCS and CCSD and in between CCSD and CCSDT can be constructed based on additional approximations as will be discussed in the following subsections.

2.3 Møller–Plesset perturbation theory and the mixed hierarchy of methods

Møller–Plesset perturbation theory [34] is the perturbation theoretical approach to the many-body problem. A partitioning of the Hamiltonian into 'unperturbed' and a perturbation is introduced on the basis of the Fock potential – the mean field – found in an HF calculation

$$H = h + g = h + V^F + (g - V^F) = F + U. \tag{13}$$

U denotes the fluctuation potential and measures the difference between the true two-electron repulsion operator, g, and the Fock mean field representation, V^F. The HF state is an eigenfunction for the Fock operator, e.g., $F|HF\rangle = \sum_i \epsilon_i |HF\rangle$ where $F = \sum_i \epsilon_i a_i^\dagger a_i$ in a canonical basis. We may thus perform a perturbation expansion in orders of U with the HF state as the zeroth order state. The HF energy contains the first order energy correction in U and proceeding to higher order in U we obtain MP2, MP3, MP4, ... etc. Though MP2 in many cases includes a major part of the correlation effects, it is now well understood that the MP series should not be expected to be convergent [167, 168] and typically divergent and oscillating behavior is obtained in the MP series [167–170]. Thus, if MP2 is not sufficiently accurate one should look into other theories to proceed, and not into a higher order MP. However, though CC does not rest on the same assumptions as the MP theory, perturbational arguments may in some cases still provide inspiration with respect to introducing approximate CC methods as will be discussed in the following.

The CCSD energy is correct through third order in the perturbation theory but includes infinitely many higher order terms of a restricted type. Correctness through fourth order requires inclusion of triples excitations. This has inspired various approximate triples excitation models in-between CCSD and CCSDT in accuracy and cost as mentioned in the introduction. The CCSD(T) method has been the most widely adopted and successful of these triples excitation methods and is defined by the following approximation for the ground state energy [7]

$$\begin{aligned} E_{\mathrm{CCSD(T)}} = E_{\mathrm{CCSD}} &+ \sum_{\mu_1} t_{\mu_1} \langle \mu_1 | [H, T_3] | HF \rangle \\ &+ \sum_{\mu_2} t_{\mu_2} \langle \mu_2 | [H, T_3] | HF \rangle \end{aligned} \tag{14}$$

Here the triples amplitudes are estimated from the triples excitation equations as they occur in lowest non-vanishing order for MP theory ($t_{\mu_3} = -(\omega_{\mu_3})^{-1} \langle \mu_3 | [U, T_2] | HF \rangle$ where ω_{μ_3} denotes a simple sum of orbital energies of the type $\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k$) but using CCSD amplitudes in their calculation. The triples correction ensures the energy is fully correct *through* the fourth order but contains simultaneously infinitely many higher order terms. Though CCSD(T) is related to perturbation theory in some aspects, it is certainly not a perturbation method and not defined by any order expansion. Thus the convergence problems of MP does not affect the CC models. Of course, the quality of a particular approximation must always be considered in practice. CCSD(T) has been one of the most successful approximations in quantum chemistry. For systems where a single reference ansatz is appropriate, it gives very accurate results. CCSD(T) requires an iterative solution of the CCSD equations with N^6 operation count followed by a non-iterative N^7 step to obtain the triples correction. This is a significant reduction compared to the iterative N^8 steps for CCSDT. Furthermore, even though CCSD(T) includes connected triples excitations they do not need to be stored explicitly as for CCSDT. When a particular triples excitation is required for the energy it can simply be evaluated "on the fly" from the doubles excitation CCSD amplitudes and the U operator.

The sequence HF, MP2, CCSD and CCSD(T) is an often used hierarchy of methods for calculating the ground state frequency-independent properties, including equilibrium structures, vibrational frequencies, NMR shielding constants and chemical shifts [9, 22]. A practical note is that for some applications, for example the calculation of equilibrium structure of molecules consisting of very light elements, MP2 is surprisingly good and perhaps even competes with CCSD.

2.4 A coupled cluster hierarchy of models for molecular response properties

A drawback of non-iterative methods like MP2 and CCSD(T) is that they cannot be used for calculating the excitation energies and frequency-dependent molecular properties. It is therefore desirable to introduce an alternative hierarchy for the calculation of molecular properties, that is, for describing the interaction of molecules with light. We now describe how additional CC models can be constructed by approximating the amplitude equations for the standard CC models CCS, CCSD, CCSDT, ...

We invoke again a Møller–Plesset type of partitioning of the Hamiltonian, but in addition to the Fock operator, F, and the fluctuation operator, U, an external one-electron perturbation, V, is also included

$$H = F + V + U. \tag{15}$$

We do not include V into the Fock operator F. This indicates that the HF reference state and therefore also the Fock operator are kept fixed in the presence of the external perturbation V. This is what corresponds to an orbital unrelaxed approach. An orbital-relaxed approach would include V in F.

We introduce T_1 similarity transformed operators [171] denoted by a hat

$$\hat{O} = \exp(-T_1) O \exp(T_1). \tag{16}$$

The CCSD amplitude equations can be written (using the T_1 similarity transformed operators and the Baker–Campbell–Hausdorff expansion)

$$\langle \mu_1 | [F, T_1] + \hat{V} + \hat{U} + [\hat{V} + \hat{U}, T_2] | HF \rangle = 0, \tag{17}$$

$$\langle \mu_2 | [F + \hat{V}, T_2] + \hat{U} + [\hat{U}, T_2] + \frac{1}{2}[[\hat{U}, T_2], T_2] | HF \rangle = 0. \tag{18}$$

All other terms in the expansion vanish identically.

In CC2, the doubles equation is simplified by including only terms entering in lowest non-vanishing order with the proviso that T_1 is treated as zeroth order [41]. This extra criteria comes in since the response of the singles excitations to an *external* one-electron perturbation is zeroth order in U. Denoting order by n, m referring to order in V and U, respectively, in a double perturbation expansion the situation is readily analyzed as follows. To first-order in V and zeroth order in U we have for example, $\omega_{\mu_1} t_{\mu_1}^{(10)} = \langle \mu_1 | V | HF \rangle \neq 0$ when V is non-vanishing. Consider now the case where we wish to study the system both with V present and absent. Without V, singles excitations are second order in U meaning they are zero in zeroth and first order, while when V is present, singles excitations are non-zero already in zeroth order in U. To have a balanced description of the system with and without an external perturbation we must give special attention to the singles excitations. We do this by enforcing that they should be considered as being zeroth order in U all the time. This is most conveniently achieved in practice simply by taking $\hat{U}$ as a first-order effective Hamiltonian. T_2 and T_3 enter, respectively, in first and second order in U. We now introduce the CC2 model with the above slightly modified order counting by inspecting the CCSD equations. The singles equation of CC2 is kept as that of CCSD, but the doubles equations are approximated to lowest non-vanishing order, e.g.

$$\langle \mu_2 | [F + \hat{V}, T_2] + \hat{U} | HF \rangle = 0. \tag{19}$$

The "hats are kept on" to give the specialized treatment of singles. Since T_2 is first order in U the $[\hat{U}, T_2]$ and $\frac{1}{2}[[\hat{U}, T_2], T_2]$ terms are, respectively, second and third order in U and neglected in the CC2 doubles equations. This defines the CC2 model. Without the special treatment of singles due to the external perturbation a second-order approximation to CCSD gives MP2, but accounting for a possible external perturbation (in an orbital un-relaxed fashion) we arrive at CC2 as the second-order CC approximation.

This philosophy can also be applied in higher order, most important is the introduction of CC3 as an approximated CCSDT model. In CC3, the singles and doubles equations are identical to those of CCSDT, while in the triples equations only terms in lowest non-vanishing order of U are retained. In approximating the triples equations, the singles excitation amplitudes are treated as zero-order parameters using similar arguments as for CC2. Thus the CCSDT triples equations

$$\langle \mu_3 | [F + \hat{V}, T_3] + [\hat{U}, T_2] + \frac{1}{2}[[\hat{V} + \hat{U}, T_2], T_2] + [\hat{U}, T_3] + [[\hat{V} + \hat{U}, T_2], T_3] | HF \rangle = 0. \tag{20}$$

are approximated to give the CC3 triples amplitude equations [42]

$$\langle \mu_3 | [F + \hat{V}, T_3] + [\hat{U}, T_2] + \frac{1}{2}[[\hat{V}, T_2], T_2] | HF \rangle = 0. \tag{21}$$

Since T_2 is first order in U and T_3 is second order in U the remaining terms in the CCSDT triples equations are of third and higher order in U. The CC3 ground state energy includes the same fourth- and fifth-order energy as CCSD(T). The CC3 method is also closely related to some of the earlier suggested CCSDT-*n* models for the ground state energy [38–40]. Relaxing for example the special treatment of singles excitations, one obtained the CCSDT-1b model. On the other hand if also the $\frac{1}{2}[[\hat{U}, T_2], T_2]$ term is included, one obtains the CCSDT-3 model, which thus includes the terms included in CC3 as a subset. In this respect it should be clear that the new concept in the construction of CC3 is that it is designed especially for calculation of response properties giving additional guidance as to which terms are important for that purpose and which are not. For the ground state energy alone, neither of the above approximate triples excitation methods seems to hold significant general advantages compared to the computationally cheaper CCSD(T) method. Other recent triples and higher excitation models were mentioned in the introduction but shall not be detailed here.

The formal operational cost in the CCS, CC2, CCSD, CC3.... sequence of models increases as N^4, N^5, N^6, N^7,... We have thus obtained a practical hierarchy of CC models with a guaranteed convergence to the FCI limit. The primary area of application of CC2 and CC3 is for the response theory where we exactly describe the response of a system to an external perturbation as was discussed in connection with the defining equations for CC2 and CC3. In the response theory we first calculate the unperturbed state and thereafter investigate the response. It turns out that also for CC3 we can avoid the explicit storage of the triples excitations in a similar way as for CCSD(T), both for the unperturbed ground state and in the solution to the response equations [42].

2.5 Molecular properties from CC methods

2.5.1 Energy derivatives

The CC energy and parameters are determined by projection and the CC method is thereby non-variational. However, a variational *Lagrangian* can be introduced [31,62,63] to aid us in the derivation of expressions for calculations of derivatives of the energy (and other issues as we shall see later). Accordingly, we consider the Lagrangian

$$L(t,\bar{t}) = E_{CC}(t) + \bar{t}e(t). \tag{22}$$

The vector $\bar{t}$ multiplied onto the vector of cluster amplitude equations $e(t)$ consists of the so-called Lagrangian multipliers. Requiring that L be simultaneously stationary with respect to both the t and $\bar{t}$ parameters we obtain

$$\begin{aligned} 0 &= \frac{\partial L(t,\bar{t})}{\partial \bar{t}_{\mu_i}} \\ &= e_{\mu_i}(t) = \langle \mu_i | \exp(-T) H \exp(T) | HF \rangle, \end{aligned} \tag{23}$$

$$\begin{aligned} 0 &= \frac{\partial L(t,\bar{t})}{\partial t_{\nu_j}} \\ &= \frac{\partial E_{CC}(t)}{\partial t_{\nu_j}} + \sum_{i,\mu_i} \bar{t}_{\mu_i} \frac{de_{\mu_i}(t)}{dt_{\nu_j}} = \langle \Lambda | [H, \tau_{\nu_j}] | CC \rangle. \end{aligned} \tag{24}$$

In Eq.(24) we have introduced the auxiliary state

$$\langle \Lambda | = (\langle HF | + \sum_{i,\mu_i} \bar{t}_{\mu_i} \langle \mu_i |) \exp(-T). \tag{25}$$

The first equation (Eq.(23)) is the cluster amplitude equation (Eq.(12)) and it ensures that the Lagrangian is variational with respect to $\bar{t}$. The second equation (Eq.(24)) determines $\bar{t}$ such that the Lagrangian is variational with respect to t. When these equations are fulfilled the Lagrangian gives the CC energy, $L(t,\bar{t}) = E_{CC}(t)$. The $\bar{t}$ parameters are not needed in the actual calculation of the ordinary CC energy where it is simpler just to solve the cluster amplitude equations (Eq.(12)) and then calculate the energy according to Eq.(11). On the other hand the $\bar{t}$ parameters are important for efficient analytical calculation of molecular properties and, as we shall see later, in CC effective solvent models.

Next, we consider the calculation of a first-order property - an expectation value. We consider the Hamiltonian, $H = H_o + F_x X$, where F_x is the perturbing field and X is the operator for the molecular property. For an exact state, $|\Psi\rangle$, we have the Hellman–Feynman theorem

$$\langle X \rangle = \frac{dE}{dF_x}|_{F_x=0} = \langle \Psi | X | \Psi \rangle. \tag{26}$$

In CC theory we determine equivalently an expression for the expectation value through the energy derivative expression which can be calculated as the derivative of the Lagrangian

$$\begin{aligned} &\frac{dL_{CC}}{dF_x}|_{F_x=0} \\ &= \frac{\partial L}{\partial F_x}|_{F_x=0} + \frac{\partial L}{\partial t}|_{F_x=0} \frac{\partial t}{\partial F_x}|_{F_x=0} + \frac{\partial L}{\partial \bar{t}}|_{F_x=0} \frac{\partial \bar{t}}{\partial F_x}|_{F_x=0} \\ &= \frac{\partial L}{\partial F_x}|_{F_x=0}, \end{aligned} \tag{27}$$

where the stationary criteria on the Lagrangian simplifies the expression since the two terms involving $\frac{\partial L}{\partial t}|_{F_x=0}$ and $\frac{\partial L}{\partial \bar{t}}|_{F_x=0}$, are zero. Thus we have that in CC the first order energy derivative, the expectation value, is obtained from

$$\langle X \rangle = \langle \Lambda | X | CC \rangle. \tag{28}$$

We note that the different "left" and "right" states are a consequence of the non-variational projection nature of the CC methodology. When complex wave-functions or imaginary perturbation operators X are considered, only the real parts of the expression should be considered ($\langle X \rangle = \frac{1}{2}\langle \Lambda | X | CC \rangle + \frac{1}{2}\langle \Lambda | X | CC \rangle^*$).

The first-order derivative of the energy allows for the determination of the molecular gradient (X correspond to geometrical distortions – note that in this case the geometry dependence through the basis set and the orbitals must be considered in addition), dipole moments, electric field gradients and so on. The advantage of the Lagrangian approach is that it gives expressions for calculation of energy derivatives which requires only a limited number of additional equations to be solved. For example, first order properties can be calculated without knowledge of the derivatives of the cluster amplitudes requiring only the solution of one set of linear set of equations (for $\bar{t}$) to determine all first-order properties. Similar advantages are obtained for higher order properties. The Lagrangian approach thereby automatically includes the results obtained by applying the inter-change technique of Handy and Schaefer [172] used in many works. The Lagrangian approach is already very helpful as an auxiliary tool and we shall see in a later section how it can take an even more crucial role.

Many implementations of analytical derivatives have been reported since the first CCSD molecular gradient code in 1987 [173]. For more concrete aspects about implementations as well as many more examples and references, consult the reviews in [9] and [22].

2.5.2 Response theory

Consider a molecular system in vacuum described by a time-dependent Hamiltonian, H,

$$H = H + V^t \ , \tag{29}$$

where H is the unperturbed Hamiltonian and V^t is a time-dependent perturbation. The term, V^t, may be written as a Fourier expansion

$$\begin{aligned} V^t &= \sum_{k=-N}^{N} \exp(-i\omega_k t) V^{\omega_k} \\ &= \sum_{k=-N}^{N} \exp(-i\omega_k t) \sum_y \epsilon_y(\omega_k) Y \ . \end{aligned} \tag{30}$$

It is required that $\epsilon_y(\omega_k) = \epsilon_k(-\omega_k)^*$ and that the operators Y are Hermitian. The expansion of the expectation value of an observable, X, in orders of the perturbation

$$\begin{aligned}\langle\bar{\Psi}_o(t)|X|\bar{\Psi}_o(t)\rangle &= \langle\Psi_o|X|\Psi_o\rangle \\ &\quad + \sum_y \epsilon_y(\omega_y)\langle\langle X, Y\rangle\rangle_{\omega_y}\exp(-i\omega_y t) \\ &\quad + \cdots \qquad (31)\end{aligned}$$

defines the linear response function $\langle\langle X, Y\rangle\rangle_{\omega_y}$ as well as the higher order response function.

The derivation of the explicit expression for response functions is easily described, though the theory behind this machinery can be somewhat involved, see Refs. [62,174–176]. The ansatz for the time evolution of the coupled cluster wave function may be expressed as

$$\begin{aligned}|\bar{C}C(t)\rangle &= \exp(-iP(t))|\widetilde{CC}(t)\rangle \\ &= \exp(-iP(t))\exp(T(t))|HF\rangle \qquad (32)\end{aligned}$$

where $P(t)$ is a function of time. We assume that the reference state $|HF\rangle$ is fixed and thus time-independent. From the time-dependent Schrödinger equation and projecting onto $\langle HF|$ and the manifold of excitations we derive the following equations for the so called time-dependent coupled cluster quasi-energy

$$Q(t) = \dot{P}(t) = \langle HF|H(t)\exp(T(t))|HF\rangle, \qquad (33)$$

and the coupled cluster amplitudes

$$\begin{aligned}e_{\mu_i}(t) - i\dot{t}_{\mu_i}(t) &= \langle\mu_i|\exp(-T(t))H(t)\exp(T(t))|HF\rangle \\ &\quad - i\dot{t}_{\mu_i}(t) = 0. \qquad (34)\end{aligned}$$

In the time-independent limit, Eqs. (33) and (34) reduce to the usual coupled cluster energy and amplitude equations. We may in the time-dependent case construct a quasi-energy coupled cluster Lagrangian [42,62]

$$L_{CC}(t) = Q(t) + \sum_{i,\mu_i}\bar{t}_{\mu_i}(t)(e_{\mu_i}(t) - i\partial t_{\mu_i}(t)/\partial t) \qquad (35)$$

The response functions can now be obtained as derivatives of the time-average of this Lagrangian.

$$\langle\langle X; Y\rangle\rangle_{\omega_y} = \frac{d^2\{L(t)\}_T}{d\epsilon_x(\omega_x)d\epsilon_y(\omega_y)}, \qquad (36)$$

where $\omega_x + \omega_y = 0$. Similar derivative expressions exist for the higher order response functions. Here it is assumed that a common period T exists for the perturbations in Eq. (30) ($V(t + T) = V(t)$) and the time-average over a period T is denoted as $\{f(t)\}_T = \frac{1}{T}\int_{-\frac{T}{2}}^{\frac{T}{2}} f(t)dt$ While the quasi-energy is real for normalized variational wave-functions, the above Lagrangian is not assured to be real but extracting the relevant part from the general derivative expressions is trivial [62]. In practice the response function and the necessary response equations to be solved are thus obtained by expanding the t and $\bar{t}$ parameters in orders of the perturbation and carrying out the differentiations implied by the above equations. This leads to expressions for response functions requiring the solution of some linear equations. These response equations are essentially just derivative versions of Eqs. (23) and (24). The message is that though significant work is required, the solution of the CC response equations and the final calculation of the response function can be worked out using strategies rather similar to those for the calculation of the ground state energy and molecular gradient.

Overall, the calculation of molecular properties using CC response theory have become more and more widespread, being implemented in several computer programs in various flavors, see for example Refs. [177–186]. We do not wish to detail further the rather involved CC response theory here. The development of the theory over the years is discussed for example in Refs.[9,62,72]. A recent review discussing more extensively the use of CC response theory in the context of non-linear optical properties will appear elsewhere [72]. This review includes also some discussions on the consequences of neglect/inclusion of orbital relaxation. One important issue in CC response theory namely the study of excited states, will be given some further attention here.

2.5.3 *Excited electronic states*

In the response theory, the equations for determining excitations energies and transition properties are determined by inspecting the frequency dependence of the response functions. For exact states, the linear response function can be written in terms of the unperturbed eigenstates $\{|\Psi_o\rangle, |\Psi_k\rangle\}$ of H_o as

$$\langle\langle X, Y\rangle\rangle_{\omega_y} = P^{XY}\sum_k \frac{\langle\Psi_o|X|\Psi_k\rangle\langle\Psi_k|Y|\Psi_o\rangle}{\omega_y - \omega_k} \qquad (37)$$

where $P^{XY}f_{xy} = f_{xy} + f_{yx}$. The excitation energies of the system are $\omega_k = E_k - E_o$, where E_0 is the ground state energy and E_k is the energy of the excited state Ψ_k. Thus, the linear response function has poles when the external frequency is equal to an excitation energy of the system, $\omega = \omega_k$, and the corresponding residue $\langle\Psi_o|X|\Psi_k\rangle\langle\Psi_k|Y|\Psi_o\rangle$ is related to the transition strength. An analogous pole-search is carried out for the response function describing the response of the approximate wave function, and equations for the determination of excitation and transition properties are identified. A unique feature of response theory is that, in addition to one-photon absorption that can be described using residues of the linear response function, a two-photon (and n-photon) absorption can be described using residues of the non-linear response function. In addition, residues of higher order response functions for the ground state can be used to determine various excited state properties. In essence, from the response expansion for one particular state, one can obtain adiabatic energies, properties and transition properties for *all* states of the system [62,176,187].

Excitation energies in coupled cluster response theory are found as the eigenvalues of the asymmetric coupled cluster Jacobian A[62,69,188]

$$A_{\mu_i\nu_j} = \langle\mu_i|\exp(-T)[H, \tau_{\nu_j}]\exp(T)|HF\rangle. \qquad (38)$$

The EOM-CC approach provides a closely related alternative framework for the calculation of excitation energies [65]. For the pure models CCSD, CCSDT, etc. EOM-CC and and coupled cluster response theory excitation energies are exactly equivalent. EOM-CC can be seen as a consistent bi-orthogonal approach for diagonalizing the similarity transformed Hamiltonian $\exp(-T)H\exp(T)$. While other properties in EOM-CC differ from the CC response predictions including transition properties, the EOM framework on the other hand provides a simple and neat generalization of this direct approach to the calculation of the energies of ionization and electron attachment [65,92,93,189–192]. Developments similar to EOM-CC for excited states were derived and implemented by Nakatsuji in the late 1970s as CI (SAC-CI) [66–68]. This approach is still used today. Though in practice various additional approximations are introduced in SAC-CI, there are a number of formal similarities to EOM-CC. Another possibility for a "direct" CC approach to excitation energies, ionization potentials, and electron attachment is Fock-space CC theory, see for example [193,194].

A CC response theory calculation of excitation energies starts off with the calculation of the ground state amplitude equations followed by the solution of the CC response eigenvalue equations providing directly the excitation energy. Thus, the CC response theory is a direct approach providing equations for the excitation energy directly. This should be seen in contrast to state specific methods, where the ground and excited states are independently optimized. This distinction is important. While the CC approach for the ground state requires solution of non-linear equations, the equations for the excitation energy is a simpler linear eigenvalue problem. For the single reference CC method to be accurate, the ground state is required to be dominated by a single configuration, but the excited state does not have to be dominated by a single configuration. In fact, it is one of the principal and unique advantages of the CC response theory for excitation energies that states are allowed to mix freely at the correlated level. However, there is a strong bias toward low-electron excitations. Thus CC response theory is more accurate for states dominated by single electron excitation compared to two-electron excitation, and so on.

Several implementations of CC methods for excited states have been presented at various levels, see for example Refs. [42,65,183,184,195], following the first CCSD implementation of Koch et al [188]. A triples correction to CCSD response excitation energies, CCSDR(3), has been presented with the purpose of mirroring the quality of CC3 excitation energy in a computationally cheaper non-iterative manner [196,197]. Formally this approach has some similarity to the previously suggested CIS(D) [183] doubles correction to CIS excitation energies. Other approximate triples methods for calculations of excitation energies have been suggested by Watts and Bartlett before and after the CCSDR(3) approach [198,199]. Also other approximate triples excitation methods have been promoted by other workers [128].

The CCS, CC2, CCSD and CC3 hierarchy of CC methods has been thoroughly tested in many benchmark and production calculations. For example, in studies comparing CC and FCI excitation energies for the lowest *single-electron* excited states of BH, CH_2, Ne, H_2O, N_2, C_2 (that is, states where in a qualitative picture, only one electron is excited) [197,200] a significant reduction of the scatter of errors at a given level was obtained proceeding to high levels in the CCS, CC2, CCSD, and CC3 hierarchy. Both the mean and maximum errors are reduced by about a factor of three in each step. At the CC3 level, the mean (max) errors are around 0.04 (0.1) eV. The CCSDR(3) approach provides results rather similar to CC3 in quality [196,197]. For two-electron excitations the errors are significantly larger. Thus, CCSD (CC3) is for a close to 100% two-electron excitation no better than CCS (CC2) for a single electron excitation.

Excited state properties relating to derivatives of the total excited state energy as for example excited state molecular gradients can also be obtained from the CC theory, being first formulated and implemented at the CCSD level in the EOM-CC theory context [201,202] and later formulated using Lagrangian techniques [62,120]. Excited state gradients have been developed for many excited state CC methods including RI-CC2 [134], spin-flip EOM-CCSD [203], and other methods [204]. For electronic spectra the combination of (a) CC with accurate triples models as in CC3 and CCSDR(3), (b) the use of large basis sets, and (c) the use of excited state gradients to investigate the importance of changes in structure and vibrations upon excitation, have provided theoretical results of unforeseen accuracy and detail for a number of fundamental organic compounds including, for example, benzene [195,205], s-tetrazine [206–208], furan [209], pyrrole [210], cyclopentadiene [211], pyrimidine [212], amino acids and related compounds [213]. One noteworthy perspective is that it is only accounting for all the three aspects above that one in general can obtain results within 0.1 eV for single excited states. Thus the high accuracy does not come for free. For example, it is our experience that the very widespread approach of calculating theoretical vertical excitation energies and comparing them with the experimental energy of maximum absorption can involve additional errors of the same magnitude (one or a few tenth of an eV) as the error in modern theoretical methods. Geometrical relaxation in many coordinates and small changes in many vibrational frequencies may add up to a significant value aside from experimental limitations. Obviously, this makes it problematic to estimate the accuracy of ab initio methods from such comparisons, and careful benchmark calculations are necessary for this purpose.

2.6 Coupled cluster theory and effective solvent models

It is not the topic of this review to discuss the basis assumptions behind the different solvent models which are discussed in other sources [73,80,81,214]. We shall only briefly describe a general strategy of how such models can be employed in combination with CC models. Solvent models include additional terms in the construction of the wave function and energy of the solute to account for the interactions between solute and solvent. The wave function is typically allowed to relax to this coupling by determining the wave function parameters using the variational principle. The problem to be addressed now is that CC is not variational.

We begin from the energy expression of the general form

$$E = \langle\Psi|H_{QM}|\Psi\rangle + \sum_p \lambda_p \langle\Psi|X_p|\Psi\rangle + \sum_q \gamma_q \langle\Psi|Y_q|\Psi\rangle\langle\Psi|Z_q|\Psi\rangle + U \quad (39)$$

where H_{QM} is the usual quantum mechanical electronic Hamiltonian operator for the solute system. The constants (from the solute electrons point of view) λ_p, γ_q and U as well as the operators X_p, Y_q and Z_q depends on the solvent model. The simplest model is the dielectric continuum (DC) model. In the DC model the solute resides in a cavity of some size and the charge distribution of the solute is assumed to introduce polarizations in a dielectric continuum described by dielectric constants characteristic for the solvent. The DC model can be represented by $\lambda_p = U = 0$, and the sum over q corresponds to a multi-pole expansion where $Y_q = Z_q$ are related to the multi-pole operators for the charge distribution of the solute. A more realistic and atomistic model is the QM/MM approach. In the QM/MM approach [80,81,214,215] to solvation the "solute" molecule is described by QM electronic methods while the surroundings are described by a molecular mechanics (MM) force field. The interactions with the QM solute wave function is typically restricted to electrostatic interactions by some partial charges and in more advanced cases, also by polarizabilities. The partial charges in the MM system give a number of contributions to U and the sum over p in the above equation. We have found explicit polarization effects to be important. Inclusion of explicit polarization effects gives rise to contributions to the sum over q.

Effective CC solvent models can be defined employing an extended Lagrangian approach using the equation for the expectation value derived in Eq. (28). We thus replace Eq. (39) by the following equation, where in all expectation values we replace $\langle\Psi|$ by $\langle\Lambda|$ and all $|\Psi\rangle$ by $|CC\rangle$ and we replace the energy by the vacuum CC Lagrangian function

$$L(t,\bar{t}) = \langle\Lambda|H_{QM}|CC\rangle + \sum_p \lambda_p \langle\Lambda|X_p|CC\rangle + \sum_q \gamma_q \langle\Lambda|Y_q|CC\rangle\langle\Lambda|Z_q|CC\rangle + U. \quad (40)$$

The trick is now that requiring this Lagrangian to be stationary with respect to both t and $\bar{t}$ results in coupled equations determining these parameters

$$0 = \langle\mu_i|\exp(-T)(H_{QM} + G)\exp(T)|HF\rangle, \quad (41)$$

$$0 = \langle\Lambda|[(H_{QM} + G), \tau_{\nu_j}]|CC\rangle. \quad (42)$$

In Eq.(42) we have introduced the effective operator

$$G = \sum_p \lambda_p X_p + \sum_q \gamma_q (Y_q \langle\Lambda|Z_q|CC\rangle + \langle\Lambda|Y_q|CC\rangle Z_q) \quad (43)$$

Since the G operator depends on both t and $\bar{t}$ Eqs. (41) and (42) are coupled but can be solved for both CC/DC [216] and CC/MM [217] models. For both CC/DC and CC/MM models one can introduce time-dependent solvent quasi-energy Lagrangian's from which CC/DC and CC/MM response theory can be derived and implemented [215,218–222]. Both equilibrium and non-equilibrium CC/DC models have been developed [216,218].

A few formal comments concerning this formalism is required. First of all one should recall again that CC is non-variational and the energy is therefore not bound but this has not been seen to cause problems. It is important to note that the Lagrangian now takes a more central and direct role. In the usual "vacuum" CC theory, the Lagrangian is a theoretical *tool* to derive equations that are tractable for computer implementation. The Lagrangian is not actually used or even necessary to calculate the energy. For the effective solvent models the non-linear terms in the energy function (the sum over q) cause the QM part of the energy calculated from the Lagrangian in Eq. (40) to differ from that calculated from the standard CC energy expression in Eq. (11). It is the Lagrangian that gives the correct energy, and it is the Lagrangian that converges to the FCI energy when the wave function approaches the exact limit. In fact, this issue could also be relevant to other non-variational methods for solvent effects. Inserting simply an effective operator in the vacuum equations to obtain working equations in the solvent case does not necessarily give results that converge to the exact result when the exact wave function is employed in a non-variational parameterization for a particular solvent model.

One of the advantages of the CC/DC and CC/MM methods is that with the use of CC for the solute, the accuracy is so high that one can begin to reliably debate the intrinsic error of the solvent models. This is important also since the relative importance of the correlation effects and solvent effects obviously vary with solute, solvent and property. The CC/DC approach is of course primarily attractive due to its simplicity. The definition of the size and shape of the cavity adds to the more empirical nature of this approach and the DC/CC approach with only a cavity reaction field for a spherical cavity cannot be expected to have predictive power.

The QM/MM approach is more complicated in use, but is more promising in a number of ways, accounting for more specific interactions between solvent and solute molecules. Since the QM/MM approach is atomistic, one can test the performance of the interaction models in comparison between CC/MM and CC cluster calculations using the later as reference (which is safe since CC is size extensive). Furthermore, in combination with molecular dynamics simulation, the QM/MM approach can be used to calculate a true statistical distribution of the particular property in the solvent. An example of such a calculation, on the $n \rightarrow \pi^*$ transition of formaldehyde in aqueous solution, will illustrate this. This excitation is an often used benchmark case, see Refs. [223–225] for other recent calculations. In a first study, the CC/MM was tested to give reasonable result in micro-solvation by comparing results obtained for small clusters of formaldehyde with a few water molecules in CC/MM and full CC calculations with counter poise corrections [226]. In a second part of the study [227], a classical molecular dynamics (MD) simulation of formaldehyde in water was carried out dumping every 1 ps a configuration of the system. Using up to 1,200 such configurations in CC/MM calculations, the electronic excitation energy was investigated providing a statistical distribution of the vertical excitation energy. Such studies are unique in the sense of accounting for the effects of both the solvent dynamics/statistics and electron correlation. The final predictions of the shift in the vertical excitation energy was found to be 2,803 cm^{-1} including polarization effects at the CCSD/aug-cc-pVTZ level (excluding the effects of relaxing the geometry in the solvent which is also important for accurate comparison with experiment). Excluding polarization effects gave 2,139 cm^{-1}. The results for the largest studied formaldehyde-water cluster gave 1,911 cm^{-1} while the CC/DC approach gave less than 700 cm^{-1}. Clearly the CC/DC method fails to reproduce the results obtained by the more elaborate CC/MM calculations. Also polarization effects are seen to be significant.

3 Vibrational structure theory

In this section attention is shifted from the electrons to the nuclei. We discuss methods for calculating accurately the bound states of molecules relating to the motion of the atomic nuclei relative to each other based upon the vibrational self consistent field (VSCF) method.

3.1 Second quantization for vibrational structure theory

The second quantization formulation for vibrational structure theory developed in Ref.[51] is a very convenient framework for deriving and analyzing the theory for wave functions for nuclear motion. In the definition of VCC methods, the construction and effective handling of this algebra was one of the crucial challenges. Once the appropriate (not just any) SQ was defined, the basic formulation of VCC is rather straightforward and the next challenge is the actual implementation and testing of various approximations.

As for the electronic case the essence of SQ is that both the relevant quantum mechanical states and the operators can be expressed in terms of creation and annihilation operators. Consider a system with M modes, where a “mode” denotes a vibrational degree of freedom. For each mode m we have an orthonormal one-mode basis, $\{\phi^m_{s^m}(q_m), s^m = 1, N^m\}$.

The creation operator $a^{m,\dagger}_{s^m}$ creates mode m in the vibrational level with index s^m. The corresponding annihilation operator $a^m_{s^m}$ removes this vibrational level again. The second-quantization algebra is defined by the relations (to be compared to Eqs.(1–3)),

$$[a^m_{r^m}, a^{m'\dagger}_{s^{m'}}] = \delta_{mm'}\delta_{r^m s^m}, \tag{44}$$

$$[a^m_{r^m}, a^{m'}_{s^{m'}}] = [a^{m\dagger}_{r^m}, a^{m'\dagger}_{s^{m'}}] = 0, \tag{45}$$

and

$$a_p|vac\rangle = 0. \tag{46}$$

where |vac⟩ is the state vector where all modes are unoccupied in all levels.

Any Hartree-product M-mode basis state can be represented in terms of the creation operators as

$$|\mathbf{r}\rangle = \prod_{m=1}^{M} a^{m\dagger}_{r^m}|\mathrm{vac}\rangle. \tag{47}$$

As for the electronic case we may define excitation operators denoted τ_μ relative to a particular reference ket $|\Phi_{\boldsymbol{i}}\rangle$. In this context certain modes are excited out of their occupied levels into their virtual levels by the excitation operators τ_μ. The μ index is a compound index giving all necessary information to specify the excitation including which modes are excited and to which levels. The excitations can be written as products of one mode excitations of the type $a^{m\dagger}_{a^m}a^m_{i^m}$ for excitation from the occupied level i^m to the unoccupied level a^m. The excitation operators τ_μ satisfy similar relations as for the electronic case. Thus we have commutator relations ($[\tau_\mu, \tau_\nu] = 0,$), killer conditions ($\tau^\dagger_\nu|\Phi_{\boldsymbol{i}}\rangle = 0$) and orthogonality conditions ($\langle\mu|\nu\rangle = \langle\Phi_{\boldsymbol{i}}|\tau^\dagger_\mu\tau_\nu|\Phi_{\boldsymbol{i}}\rangle = \delta_{\mu,\nu}$). Accordingly the full configuration space may be written as $\{|\Phi_{\boldsymbol{i}}\rangle, \tau_\mu|\Phi_{\boldsymbol{i}}\rangle\}$.

Various forms and approximations for the vibrational Hamiltonian are in use. Any first quantization Hamiltonian can be represented in terms of a second quantization Hamiltonian, but the details will of course be different. One class of Hamiltonians is the sum over product form, which in both first and second quantization can be written as

$$H = \sum_{t=1}^{N_t} c_t \prod_{m=1}^{M} h^{m,t} \tag{48}$$

The one-mode operators in SQ notation are

$${}^{SQ}h^{m,t} = \sum_{r^m,s^m} h^{m,t}_{r^m s^m} a^{m\dagger}_{r^m} a^m_{s^m} \tag{49}$$

which is related to the first quantization representation through $h^{m,t}_{r^m s^m} = \langle\phi^m_{r^m}(q_m)|h^{m,t}|\phi^m_{s^m}(q_m)\rangle$. Here h^m_t is the first quantization one-mode operator. Taylor expanded force fields of the potential (including for example quartic force fields) is a special case where the one-mode operators are all of the form q^i_m.

3.2 Vibrational SCF, MP, and CI

Vibrational self-consistent field (VSCF) is based on the application of the Hartree approximation to the problem of coupled distinguishable anharmonic oscillators. The SQ form for the VSCF reference state can be written as

$$|\Phi_{\mathbf{i}}\rangle = \prod_{m=1}^{M} a^{m,\dagger}_{i^m}|vac\rangle \tag{50}$$

Applying variational criteria to the energy

$$E_{\mathbf{i}} = \langle\Phi_{\mathbf{i}}|H|\Phi_{\mathbf{i}}\rangle, \tag{51}$$

the one-mode functions for each mode, $\phi^m_{i^m}(q_m)$ are found to be constraints with the normalization conditions, $\langle\phi^m_{i^m}(q_m)|\phi^m_{j^m}(q_m)\rangle = \delta_{i^m j^m}$. The index vector, **i**, indicates the nature of the VSCF reference state. The variational criteria determine the VSCF one-mode functions as eigenfunctions of the effective one-mode operator

$$F^{m,\mathbf{i}}\phi^m_{i^m}(q_m) = \epsilon^m_{i^m}\phi^m_{i^m}(q_m), \tag{52}$$

$$F^{m,\mathbf{i}} = \langle\Phi_{\mathbf{i}}^{-m}|H|\Phi_{\mathbf{i}}^{-m}\rangle, \tag{53}$$

where $|\Phi_{\mathbf{i}}^{-m}\rangle$ is a state in the $(M-1)$ mode space excluding the mode m function factor.

The $\phi^m_{s^m}(q_m)$ functions can be represented in several ways, including expansion in a set of primitive basis functions, for example harmonic oscillator (HO) functions. The one-mode functions can be denoted modals in analogy to the orbitals of the electronic structure theory. The VSCF modals, both the occupied and the unoccupied (virtual) one-mode functions, can be used in the subsequent calculations with a more accurate wave function. Thus, we make a distinction between a one-mode and M-mode problem similar to the one-electron and N-electron problem in electronic structure theory. We now again focus on the correlation problem: the definition of more accurate M-mode wave functions. VSCF only includes interaction between the modes in a average sense. Excitations from occupied modals into "virtual" modals – the unoccupied levels in the VSCF – can be included using similar principles for proceeding beyond the mean-field description in the electronic case.

Applying the principles of the Møller–Plesset [34] perturbation theory to the vibrational correlation problem gives rise to vibrational Møller-Plesset (VMP) perturbation theory. In VMP theory the zeroth order Hamiltonian, H_0, and the corresponding zeroth order wave function are defined from the VSCF mean-field description providing the following partitioning of the Hamiltonian, $H = H_0 + U = F^{\mathbf{i}} + U^{\mathbf{i}}$, $F^{\mathbf{i}} = \sum_m F^{m,\mathbf{i}}$. The fluctuation operator $U^{\mathbf{i}}$ describes the difference between the true many-mode interaction and the VSCF mean field representation. This separation is unique to each state motivating the **i** index vector. Equations for the perturbed wave function and energies are obtained by introducing the perturbation expansion into the time-independent Schrödinger equation and collecting terms according to order. VMP approaches were first pursued by Gerber and collaborators [59–61] considering the second order variant under the name of correlation-corrected VSCF. Proceeding at a fairly general level, an open ended VMP approach can be implemented, [50].

The vibrational configuration interaction (VCI) [47,48, 51–55] parameterization of the wave-function is a linear expansion in the space of all Hartree products for the M-mode system

$$|\mathrm{VCI}\rangle = \mathrm{C}_{\mathbf{i}}|\Phi_{\mathbf{i}}\rangle + \sum_{\mu}\mathrm{C}_{\mu}\tau_{\mu}|\Phi_{\mathbf{i}}\rangle. \tag{54}$$

The parameters are determined from variational criteria giving standard CI eigenvalue equations. The Full VCI (FVCI) wave function is obtained by including the full sum over all excitations μ. Truncated VCI treatments include only some correlations between the modes, but potentially in a much less computationally demanding manner. One way of truncating the VCI wave function is by excitation level: only a limited number of modes are allowed to be excited at the same time.

3.3 Vibrational coupled cluster theory

Once the SQ algebra and the excitation operators are defined, the definition of vibrational CC (VCC) follows at a high level of abstraction, that of the previously discussed electronic case. The vibrational coupled cluster ansatz is the exponential wave function ansatz in the M-mode space of Hartree products

$$|\mathrm{VCC}\rangle = \exp(T)|\Phi_{\mathbf{i}}\rangle. \tag{55}$$

Here $|\Phi_{\mathbf{i}}\rangle$ is the VSCF wave function or any other single Hartree product reference state. T is the cluster operator that is a sum over allowed excitations $T = \sum_{\mu} t_{\mu}\tau_{\mu}$. The t_{μ} parameters are the VCC cluster amplitudes while τ_{μ} are the corresponding excitation operators.

The VCC wave function ansatz is now introduced into the time-independent vibrational Schrödinger equation, transformed with $\exp(-T)$, and equations for the cluster amplitudes are obtained by projection onto the manifold of excitations out of the reference state $\langle\mu| = \langle\Phi_{\mathbf{i}}|\tau_{\mu}^{\dagger}$

$$0 = e_{\mu} = \langle\mu|\exp(-T)H\exp(T)|\Phi_{\mathbf{i}}\rangle. \tag{56}$$

Once the non-linear cluster equations have been solved for the cluster amplitudes, the VCC energy can be calculated from the following equation obtained by a projection onto the VSCF reference state

$$E_{VCC} = \langle\Phi_{\mathbf{i}}|H\exp(T)|\Phi_{\mathbf{i}}\rangle \tag{57}$$

This was the easy part. The more challenging parts are the actual implementations in connection with various Hamiltonians. We will not here enter into any lengthy detail though the possibility of making an efficient implementation is of course decisive for the success of a theoretical method. Instead we will focus on explaining some of the differences of VCC relative to VMP and VCI, as well as the basic differences between CC for electrons and CC for the vibrational motion of the nuclei.

How do we introduce approximate VCC methods? One approach is to truncate the cluster operator by the number of modes/pseudo-particles that are allowed to be excited simultaneously and solve the cluster amplitude equations in this excitation space. Thus, each calculation begins with the calculation of a VSCF state, and thereafter an excitation space is defined based on excitations out of the VSCF reference state. Doing this for each state corresponds to a state-specific approach.

Both VCI and VCC have the flexibility to represent the exact state employing a complete excitation space. This is an advantage over VMP where convergence of the VMP perturbation series cannot be guaranteed and in fact it is often unlikely [50,228]. A major advantage of VCC and its associated exponential parameterization compared to VCI is that VCC ensures size-extensivity [51,52]. In addition to long experience from the electronic structure calculations on the importance of this issue, the VCC calculations that have been carried out [51,52] show that typically the accuracy for the truncated VCC results is better than the one for their VCI counterparts with the same excitation space [52,228]. At a certain excitation level n VCC[n] and a corresponding VCI[n] have the same number of free parameters and they have formal operation counts of the same order of magnitude but with a larger pre-factor for VCC. VCC[n] is significantly more complicated to implement than VCI[n], and indeed the reported implementation of VCC is not fully optimal [52]. However, an improved implementation is on the way to resolve outstanding problems. Both VSCF, VMP, VCI and VCC methods have been implemented in the MidasCpp (Molecular Interactions, dynamics and simulation in C++/Chemistry program package) program using the sum over product Hamiltonian in Eq.(48) [50–52]. Other implementations of VSCF, second order VMP [59–61] and VCI [53–55] have been reported previously.

The VCC approach has many formal similarities with the CC approach for electrons. However, it is also appropriate to emphasize the differences. First of all, SQ techniques and formulations for electrons are well-developed, while the same cannot be said in vibrational theory (note that we do not use an ordinary boson SQ). The electrons are indistinguishable, share a common basis, have spin one half, and are assigned a position in the usual 3D coordinate space. For vibrational structure theory each of the distinguishable spin-free modes have a basis set of their own. In fact, the definition of the modes is one of the central issues. Normal coordinates is one option but generally different coordinates will give different results. In direct continuation, the electronic molecular Hamiltonian has a priori well-known one- and two-electron operators. In vibrational structure theory the Hamiltonian has a much more complicated form and is not known a priori. The kinetic energy operator is already a complicated issue even using normal coordinates. In normal coordinates the frequently used harmonic oscillator kinetic energy operator is simple but not exact. On the other hand, the exact Watson operator [229] formally couples all M modes through the inverse inertia tensor even under the assumption of J=0. Similar conclusions may be drawn for the potential. Within the Born-Oppenheimer approximation the exact potential energy surface (PES) is defined as the exact eigenenergy of the electronic molecular Hamiltonian and the PES depends on all coordinates. Though points of the PES can be calculated approximately using electronic structure methods, it is presently unrealistic to achieve accurate analytical representations of the PES for systems with many atoms. The PES can be defined by some model Hamiltonian, polynomial expansion, interpolation, etc. How to represent the Hamiltonian for the vibrational wave function is in short a research issue in itself which shall not be discussed here.

The recent calculations on formaldehyde [50,52] and ethylene [228] provides some illustrative test calculations for VCC and related methods. Let us consider the eight vibrations in ethylene that are not CH stretch vibrations. To investigate the behavior of the VCC method the error with respect to FVCI for VMP2, VCI[gs,3] (excitations are counted with respect to the ground state with ground state VSCF modals and excited states are obtained as roots of the same VCI matrix), VCI[ss,3] (state-specific: each state has its own VSCF modals and excitations are counted with respect to this) and VCC[3] (also state specific) can be considered. The triple excitation level is a reasonable level to consider as up to three mode direct couplings are included in the semi-quartic force field used. The first order wave function used to calculated the VMP2 energy includes therefore triples excitations. The four different approaches therefore include a similar number of free parameters but are constructed in different ways. The mean errors of the eight states are respectively 2.14, 33.55, 1.40 and 0.93 cm^{-1} for the four approaches. The most complicated method to implement, VCC, also comes out best. The fact that VCC gives the highest accuracy in comparison with other approaches with the same number of parameters has also been observed in other cases and is obviously the attractive feature of the methodology together with the correct scaling of the results with size of the system [51,52]. An example of the problems for VCC (as well as for the other methods) can be found among the CH vibrations of ethylene. One of the CH vibrations causes significant problems in simply converging the VCC equations since the VSCF reference is a very poor reference. The FVCI wave function for this state contains several large components and the VSCF approach cannot describe appropriately these mixings. This shows that multi-reference problems can also be present for vibrational wave functions. Possible solutions to this problem are discussed in the outlook.

4 Summary and outlook

We have reviewed selected research developments employing CC theory in the description of the electronic structure of molecules and the dynamics of atomic nuclei.

Today much is known about implementing and applying the standard methods of CC theory for molecules with a ground state dominated by a single Slater determinant. This includes the HF, MP2, CCSD, and CCSD(T), hierarchy of methods for calculation of ground state structures and static properties. A number of other single reference CC methods are interesting in different contexts. For example the CCS, CC2, CCSD and CC3 (or alternatively CCSDR(3) for excitation energies) hierarchy is now well established for describing response properties and electronic excitations. Due to their importance in applications to chemical systems, the further development of these methods is obviously important. At this moment there seems to be no real competition to high end CC methods with respect to accuracy for single reference systems. Unless major breakthroughs occur in other areas, the

CC methods will continue to be the methods of choice for high accuracy calculations whenever feasible.

On the other hand there are also some major obstacles to overcome if CC methods should develop their range of applicability considerably beyond the present status. In principle, the discussed CC methods should be perfectly applicable to many issues relating to large molecules. However, the use of CC methods is in many cases unrealistic due to the rapid increase in computational effort with the size of the system. Some low-scaling CC methods applicable to large systems have been developed as discussed in the introduction. Such lower-scaling could make CC calculations feasible for much larger systems where presently less accurate methods have to be used. However, it is certainly too early to consider this a closed issue. Therefore, CC methods for large molecules is an area where major breakthroughs are still to come and much work is needed if the CC approach for electrons is to have as central a role for theoretical chemistry in the coming 25 years as it has had the last 25 years.

Another major challenge is the construction of robust CC methods for multi-reference cases allowing all regions of the full potential energy surface to be investigated in a fairly accurate and user-friendly manner. This challenge is not new and there have been many attempts in the past. However, we are still optimistic in the sense that there has been recent progress and when new formulations of CC methods are found (for example in relation to the line of research mentioned above), they may inspire new approaches to this problem also.

As long as such low-scaling CC methods are not around the corner or still rather expensive in use, effective modeling of solvents etc. through, for example, QM/MM approaches will have a market. It is clear that accounting at the same time for solvent effects and electron correlation effects in an accurate way is certainly an important goal for quantum chemistry. Much of the history of quantum chemistry has been related to studies of molecules in the gas phase even though major parts of chemistry take place in condensed phases. CC/MM calculations accounting for both the statistics due to the dynamics in the solution as well as a CC description of the solute have been reported with MM force fields including polarization interactions. A topic calling for future research is the improvement of the interface between the part of the system described by QM and the part described by MM. For example, inclusion of exchange-repulsion and dispersion effects on the solute electronic wave function will be important for providing more accurate results. It is of course necessary that the great simplicity compared to full QM treatments is retained for the method to fulfill its role allowing, for example, inclusion of many hundred solvent water molecules without problem in conjunction with statistical averaging over many configurations.

Finally, I personally have great interest and hopes for the use of CC theory for describing the motion of the atomic nuclei. This is a research area still in its infancy. The initial results are encouraging, but a lot of research is still required to investigate the pros and cons of different schemes for constructing and calculating the wave functions as well as a full blown computer software that can be of general use. We are already addressing some outstanding issues but many more are pending. The practical solution of the VCC equations for excited states is sometimes challenging in the state-specific approach used so far, requiring the development of more robust algorithms. Another approach we are considering to develop in the near future is VCC response theoretical methods. This approach would use response theory for calculating vibrational excited states thereby circumventing some of the practical problems encountered in solving the non-linear equations for the excited states. This development also relates to another important issue in modern computational chemistry. With the accuracy obtainable in CC electronic structure calculations, the remaining errors in the predictions of a given property often lies in appropriately accounting for vibrational energies, vibrational averaging and/or pure vibrational contributions. Vibrational response theory provides a new approach for dealing with this issue [230] but has not been implemented at the VCC level yet. Further work is also required on the use of VCC together with flexible interfaces to general potentials. For example, developing algorithm for on the fly direct electronic structure calculation of the necessary points on the PES.

The transfer of the CC ansatz from the nuclear wave function to the electronic wave function has posed research challenges to theoretical chemists for close to 40 years now. It is our hope that this recent introduction of CC methods for describing the dynamics of the atomic nuclei will similarly have decisive impact on a fraction of theoretical research for many years. An area of application for the future that is very exciting is the use of approaches similar to VCC in the context of time-dependent dynamics for propagation of wave packets. Today's most flexible methods for propagating wave packets are based on linear expansion in the space of Hartree products. A very successful example is the multi-configurational time-dependent Hartree (MCTDH) approach [231]. VCC is interesting in this regard since (a) the stationary states are known to be accurately predicted and (b) the size-extensivity makes it a method where high accuracy can be maintained also for many degrees of freedom. However, it remains to be seen whether the standard approach of using projection in CC theory as opposed to variational criteria has consequences for the stability of the time-evolution. In addition the practical interface between the choice of coordinates, basis set, operator and the build of the VCC wave function is absolutely nontrivial.

The very short conclusion of this paper is that significant progress in CC theory has lead to a large impact of CC methods in chemistry, but there are still major research problems to address that, if successfully handled, can make the CC method even more central in future molecular sciences.

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