

DETERMINISTIC AND SEMI-STOCHASTIC CC($P;Q$) APPROACHES: NEW
DEVELOPMENTS AND APPLICATIONS TO SPECTROSCOPY AND
PHOTOCHEMISTRY

By

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ABSTRACT

DETERMINISTIC AND SEMI-STOCHASTIC CC(P ; Q) APPROACHES: NEW DEVELOPMENTS AND APPLICATIONS TO SPECTROSCOPY AND PHOTOCHEMISTRY

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The development of electronic structure methods that can accurately describe ground and excited states of molecular systems with manageable computational costs and in a systematically improvable manner continues to be the central theme of quantum chemistry. This dissertation focuses on some of the recent developments in the coupled-cluster (CC) theory and its equation-of-motion (EOM) extension to excited electronic states. One of the key challenges in the development of the CC and EOMCC methodologies is the incorporation of many-electron correlation effects due to higher-rank components of the cluster and EOM excitation operators without incurring significant increase in the computational costs, while avoiding failures of perturbative methods of the CCSD(T) type in multireference situations, such as bond breaking and excited states dominated by two-electron transitions, and in certain weakly bound systems. Among the best ways to address these issues is the CC(P ; Q) framework, which provides robust and computationally affordable noniterative energy corrections to lower-order CC/EOMCC calculations. In this dissertation, we discuss the different CC(P ; Q) variants relying on both the conventional and unconventional truncations in the cluster and EOM excitation operators. The advantages of the CC(P ; Q) hierarchy are illustrated using a few examples ranging from small molecule spectroscopy to photochemistry of large organic species in solution. In particular, we discuss the computational investigations of the novel super photobase **FR0-SB**, which exhibits a drastic increase in basicity upon photoexcitation, including the energetics and properties of its excited states, the steric effects governing the excited-state proton transfer involving **FR0-SB** and alcohols, and the enhanced photoreactivity of **FR0-SB** resulting from two-photon excitations,

where the δ -CR-EOMCC(2,3) approach that belongs to the $CC(P;Q)$ hierarchy played a key role. Furthermore, we demonstrate that the relatively inexpensive $CC(t;3)$ and $CC(q;4)$ approaches derived from the $CC(P;Q)$ framework are as accurate in describing the challenging weakly bound magnesium dimer, including its ground-state potential and vibrational levels supported by it, as the much more demanding CCSDT and CCSDTQ parent theories. We also show how the highly accurate ground- and excited-state *ab initio* potentials obtained in the state-of-the-art CCSDT, CR-EOMCCSD(T), and full configuration interaction (CI) computations allowed us to resolve the existing laser-induced fluorescence and photoabsorption spectra of the magnesium dimer and find the missing high-lying vibrational states of Mg_2 that have eluded scientists for half a century. Last, but not least, we discuss our recent extension of the semi-stochastic $CC(P;Q)$ framework, which combines the deterministic $CC(P;Q)$ theory with stochastic CI quantum Monte Carlo (QMC), to excited electronic states, providing rapid convergence to the parent high-level EOMCC methods, such as EOMCCSDT, out of the early stages of QMC propagations. The advantages of the semi-stochastic $CC(P;Q)$ approach targeting EOMCCSDT are illustrated by examining vertical excitations in CH^+ and adiabatic excitations in the CH and CNC species.

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To Christy and Alethia.

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CHAPTER 1

INTRODUCTION

The goal of quantum chemistry is to solve the electronic Schrödinger equation for molecular systems. Although the analytical solution of this equation can only be obtained for nothing more than one-electron systems, such as the hydrogen atom or the H_2^+ molecule, numerically exact solutions can still be obtained by designing suitable basis sets and computer algorithms. Indeed, since the time the Schrödinger equation was proposed, decades of advancement in computer technologies have allowed for the calculations of increasingly complex and large molecular systems, ranging from the spectroscopically accurate *ab initio* description of weakly bound diatomics in the gas phase [1, 2] to the computations of excitation energies and one-electron properties of solvated organic chromophores [3–8], to name a few examples from my own work. Nevertheless, current quantum chemical calculations are still wrought with problems, especially when the target chemical systems suffer from a significant multireference (MR) character, which is a main issue in situations such as potential energy surfaces along bond breaking coordinates, electronic spectra of radicals and biradicals, and excited states dominated by two- and other many-electron transitions.

The brute-force solution to this problem exists in the form of full configuration interaction (FCI), where the electronic wave function is expressed as a linear combination of all possible Slater determinants that can be obtained from a given basis set of one-particle functions. By inserting this expansion into the electronic Schrödinger equation, one obtains an eigenvalue problem which is equivalent to diagonalizing the Hamiltonian matrix in the many-electron Hilbert space spanned by Slater determinants. In doing so, the FCI method provides the numerically exact solution of the many-electron Schrödinger equation in a given basis and all that remains to be done is to perform FCI computations in larger basis sets and extrapolate the complete basis set (CBS) limit to obtain the numerically exact solution of the Schrödinger equation. While this entire procedure seems straightforward, it is

almost of no practical use because the dimensionality of the FCI eigenvalue problem scales factorially with respect to the system size (*i.e.*, the number of electrons and the size of the basis set) [9, 10]. Indeed, this scaling is so steep that it can hardly be overcome by relying on the growth of computer processing speed alone, making the routine application of FCI in quantum chemistry impractical for systems with more than a few electrons. This issue motivates one of the core efforts of quantum chemistry research, namely, the development of alternative approaches that are computationally much more efficient than FCI without compromising accuracy too much.

Since using all Slater determinants that a given basis set provides is generally impractical, one might consider the simplest possible alternative, namely, employing only a single Slater determinant to describe the many-electron wave function. This is exactly what is done in the well-known Hartree–Fock (HF) procedure [11–15], where one applies the variational principle to a single Slater determinant via the procedure which is usually called the self-consistent field (SCF) approach. While the HF method is much more affordable than FCI, it treats inter-electronic repulsion in an averaged manner and, thus, fails to capture the many-electron correlation effects that are fundamental in describing most of chemical problems of interest. For example, when we consider the potential energy curve (PEC) of the F_2 molecule, the restricted HF (RHF) approach, in which each molecular orbital can be occupied by a pair of electrons with opposite spins, significantly overestimate the binding energy due to RHF overemphasizing the ionic character at the dissociation limit (*i.e.*, RHF predicts $F_2 \rightarrow F^+ + F^-$) [16]. On the other hand, the unrestricted HF (UHF) method, in which the alpha and beta spin orbitals are allowed to have different spatial components, does not bind the molecule at all [16], in addition to introducing various symmetry-broken solutions (see, *e.g.*, Refs. [17, 18] for the classification of the various symmetry-broken UHF solutions). Furthermore, the HF approximation also fails to describe the binding interaction in systems such as the dimers of alkaline earth metal and noble gas atoms, because the underlying dispersion interactions require explicit treatment of the many-electron correlation

effects, which are neglected in HF computations, as already mentioned above. Nevertheless, despite all its shortcomings, the HF approach provides a convenient starting point for various correlated electronic structure methods.

Among the numerous quantum chemistry approaches that have been developed so far to capture the many-electron correlation effects, methods based on the exponential wave function ansatz of coupled-cluster (CC) [19–24] theory offer the best balance between accuracy and computational costs, thus providing an excellent alternative to FCI. Historically, the CC theory emerged as an infinite-order generalization of the finite-order many-body perturbation theory (MBPT), which is achieved by summing the linked wave function and connected energy diagrams to infinite order with the help of the linked [25–28] and connected [27, 28] cluster theorems, respectively. As a result of this construction, CC methods satisfy several important conditions characterizing the exact theory. First of all, CC approaches are size extensive, *i.e.*, the energy is expressed in terms of connected diagrams only. In practice, size extensivity means that the results of CC calculations do not lose accuracy as the size of the system is increased. Furthermore, the exponential form of the CC wave function allows for separability or size consistency of the wave function in the noninteracting limit, provided the reference function is also separable, enabling CC methods to properly describe fragmentation phenomena. These properties, among others that will be discussed further in this dissertation, establish the CC theory as the *de facto* standard in high-accuracy *ab initio* quantum chemistry calculations, even those involving larger molecular systems.

Within the CC framework, the seemingly natural way of dealing with MR situations is by using a genuine MRCC formalism. In the MRCC theory, one constructs a multi-dimensional model space consisting of multiple reference determinants such that a proper zeroth-order description of the problem of interest is attained when a single Slater determinant, obtained, for example, from a HF calculation, is a poor reference state. Then, the remaining, mostly dynamical, correlation effects are captured through particle–hole excitations from each reference determinant included in the model space. There are various ways to achieve this,

leading to a number of MRCC formulations (see, *e.g.*, Refs. [29–33] for selected reviews), which, unfortunately, also means that there is no unambiguous way of writing the exponential ansatz of the CC wave function within this framework. The situation is further complicated by the fact that the genuine MRCC methodologies cannot compete with the ease of use and implementation of their single-reference (SR) counterparts, which are capable of recovering the relevant dynamical and nondynamical correlation effects in a dynamical manner, namely, through conventional particle–hole excitations from a single reference determinant, as long as the underlying cluster operator contains the many-body components of the sufficiently high rank. Thus, this dissertation will focus on the more straightforward SRCC formalism and for the remainder of this document the term SRCC and CC will be used interchangeably, unless the explicit distinction is required for clarity.

In the SRCC framework, the exact ground-state N -electron wave function $|\Psi_0\rangle$ is expressed using the exponential ansatz, $|\Psi_0\rangle = e^T |\Phi\rangle$, where T is the cluster operator, which is expressed in terms of its many-body components as $T = \sum_{n=1}^N T_n$, and $|\Phi\rangle$ is the Fermi vacuum, usually a HF determinant. When T_n acts on $|\Phi\rangle$, it creates all possible connected n -tuply excited components of the exact ground-state wave function $|\Psi_0\rangle$, while powers of T_n in e^T produce the remaining, disconnected but linked, contributions to $|\Psi_0\rangle$. One can extend the CC formalism to excited states in a relatively straightforward manner through the use of, for example, the equation-of-motion (EOM) [31, 34–36] and linear response (LR) [37–40] formalisms, as well as their symmetry-adapted-cluster (SAC) CI counterpart [41], where one applies a linear excitation operator R_μ to the ground-state CC wave function $|\Psi_0\rangle$, thus producing the μ -th excited-state wave function $|\Psi_\mu\rangle = R_\mu e^T |\Phi\rangle$. The R_μ operator, in analogy to T , is expressed in terms of a many-body expansion, namely, $R_\mu = r_{\mu,0} \mathbf{1} + \sum_{n=1}^N R_{\mu,n}$, with $\mathbf{1}$ representing the unit operator and $r_{\mu,0}$ and $R_{\mu,n}$ being the zero- and n -body components of R_μ , respectively. It is worth mentioning that the CC and EOMCC formalisms described above, where the T and R_μ operators contain up to N -tuple excitations, are equivalent to FCI and, thus, they are numerically exact, albeit computationally intractable. Therefore, in

practice, one truncates T and R_μ at a particular excitation rank $m_A < N$ (usually $m_A \ll N$). For example, by truncating the many-body expansions of T and R_μ at $m_A = 2$, *i.e.*, by setting $T \approx T_1 + T_2$ and $R_\mu \approx r_{\mu,0}\mathbf{1} + R_{\mu,1} + R_{\mu,2}$, one obtains the basic CC approach with singles and doubles (CCSD) [42, 43] and its excited-state EOMCCSD [34, 35, 44] counterpart. One could, of course, incorporate the higher-order components of T and R_μ to define higher-level CC and EOMCC schemes, such as the CC approach with singles, doubles, and triples (CCSDT) [45, 46] and its EOMCCSDT [47–51] extension, where $m_A = 3$, the CC approach with singles, doubles, triples, and quadruples (CCSDTQ) [52–55] and EOMCCSDTQ [49, 50, 56, 57], where $m_A = 4$, and so on. One of the main appeals of the SRCC theory, as described above, is that the CCSD/EOMCCSD, CCSDT/EOMCCSDT, CCSDTQ/EOMCCSDTQ, *etc.* hierarchy rapidly converges to the exact, FCI limit (see, *e.g.*, Ref. [31] and references therein). As long as the number of strongly correlated electrons is not too large, this remains true even when the system of interest suffers from substantial MR character.

As already alluded to above, the flexibility and ease of implementation of the CC and EOMCC theories make them attractive choices for handling quantum chemical problems with significant MR character, since one can account for MR correlation effects by the explicit inclusion of higher-than-doubly excited components of T and R_μ . Unfortunately, the computational cost of CC/EOMCC methods quickly becomes prohibitively expensive as one goes from CCSD/EOMCCSD to CCSDT/EOMCCSDT, CCSDTQ/EOMCCSDTQ, and so on. For example, the CPU time scalings of CCSDT/EOMCCSDT and CCSDTQ/EOMCCSDTQ are $n_o^3 n_u^5 (\mathcal{N}^8)$ and $n_o^4 n_u^6 (\mathcal{N}^{10})$, respectively, where n_o (n_u) is the number of correlated occupied (unoccupied) orbitals and $\mathcal{N}$ is a measure of the system size. These scalings are much higher than the $n_o^2 n_u^4$, or $\mathcal{N}^6$, CPU time scaling characterizing the basic CCSD/EOMCCSD approach. Therefore, the key challenge in the development of CC/EOMCC approaches is the incorporation of many-electron correlation effects brought by the T_n and $R_{\mu,n}$ components with $n > 2$ without incurring the computational costs of the parent CCSDT/EOMCCSDT, CCSDTQ/EOMCCSDTQ, *etc.* methods.

Traditionally, one can include the correlation effects due to the higher-than-two-body components of T and R_μ through MBPT arguments, either iteratively, as in the CCSDT- n [58–61] and CCSDTQ- n [62] approaches, or through the use of noniterative corrections, resulting in ground-state methods such as CCSD[T] [63], CCSD(T) [64], and CCSD(TQ_f) [65], and their various excited-state extensions based on EOMCC or LRCC [66–72] (see Ref. [31] for a review). Although these methods reduce the prohibitive costs of the full CCSDT/EOM-CCSDT and CCSDTQ/EOMCCSDTQ approaches, while offering high accuracies near the equilibrium geometries of molecules or for excited states dominated by one-electron transitions, they fail at properly describing bond breaking and doubly excited states due to the perturbative nature of the employed approximations. Furthermore, while it is well-known that perturbative corrections of the CCSD(T) type fail to properly describe the dissociation of a closed-shell system into its constituent open-shell fragments, it is worth pointing out that such methods are also far from being accurate in describing certain classes of weakly bound dimers that dissociate into closed-shell atoms, such as Be₂ [73] and Mg₂ [1, 2], and we will further discuss the latter example in this dissertation.

Among the most successful remedies to failures of perturbative CC/EOMCC approximations, such as CCSD(T) and its EOM extensions, in MR situations, within the SRCC framework is the CC(P ; Q) [73–77] formalism developed by the Piecuch group, which will be the main focus of this dissertation. The key idea behind the CC(P ; Q) theory is to first solve the CC/EOMCC problem in a subspace of the N -electron Hilbert space designated as the P space and correct the resulting CC/EOMCC energies using the suitably generalized form of the method of moments of CC equations (MMCC) [74, 78–93], with the help of determinants residing on another subspace of the N -electron Hilbert space called the Q space. The CC(P ; Q) formalism is very versatile owing to the flexibility in defining the P and Q spaces. For example, if the P and Q spaces are defined following the conventional truncation of the cluster and EOM excitation operators, the resulting CC(P ; Q) approaches become equivalent to the left-eigenstate completely renormalized (CR) CC/EOMCC approaches and

related schemes [74, 89–95]. Examples of methods in those categories include the ground-state CR-CC(2,3) [89–92] and CR-CC(2,4) [89, 90, 94, 96] approaches, which correct the CCSD energy for the correlation effects due to connected triples or triples and quadruples, respectively, and their excited-state extensions, including CR-EOMCC(2,3) [91, 93] and its rigorously size-intensive modification designated as δ -CR-EOMCC(2,3) [95], to name a few examples. The CR-CC/EOMCC methods have shown considerable successes in recovering the correlation effects due to the higher-than-two-body components of T and R_μ at a reasonable cost, while avoiding the failures of CCSD(T)-type approaches. However, the CR-CC/EOMCC computations may fail in situations where higher-than-two-body components of T and R_μ become large and strongly coupled to their low-rank T_1 , T_2 , $R_{\mu,1}$, and $R_{\mu,2}$ counterparts. In the CR-CC(2,3)/CR-EOMCC(2,3) approach, for example, one uses the T_1 and T_2 as well as $R_{\mu,1}$ and $R_{\mu,2}$ components obtained in CCSD/EOMCCSD calculations to determine the noniterative triples corrections, even though one should relax the T_1 , T_2 , $R_{\mu,1}$, and $R_{\mu,2}$ amplitudes in the presence of their T_3 and $R_{\mu,3}$ counterparts, which become prominent in MR situations, affecting the one- and two-body components of T and R_μ .

One can address the issue of coupling the lower- and higher-rank T_n and $R_{\mu,n}$ components by turning to the active-space CC/EOMCC ideas [47, 48, 55, 81, 97–101], where the cluster and excitation amplitudes defining the T_n and $R_{\mu,n}$ components with $n > 2$ are downselected by introducing a set of active orbitals relevant to the MR problem of interest, which in most cases are much fewer than the total number of orbitals, allowing the active-space CC/EOMCC schemes to capture most of the relevant nondynamical and dynamical correlation effects with relatively low computational costs. The resulting unconventional truncations include methods such as CCSDt (the CC approach with all singles, all doubles, and a subset of triples defined through active orbitals), CCSDtq (the CC method with all singles and doubles, and active-space triples and quadruples), and CCSDTq (the CC scheme with all singles, doubles, and triples and active-space quadruples), as well as their EOMCC extensions. Combined with the CC(P ; Q) moment corrections, they yield the CC(t;3), CC(t,q;3), CC(t,q;3,4),

CC(q;4), *etc.* hierarchy, in which the energies obtained in the active-space CC/EOMCC calculations, such as CCSDt/EOMCCSDt, CCSDtq/EOMCCSDtq, or CCSDTq/EOMCCSDTq, are corrected for the missing, mostly dynamical, correlations due to the remaining triples [CC(t;3), CC(t,q;3)], triples and quadruples [CC(t,q;3,4)], or quadruples [CC(q;4)] that cannot be captured with active orbitals, and the relevant lower-rank components of T and R_μ are relaxed in the presence of their higher-rank counterparts. As shown in Refs. [1, 73–77]), this leads to substantial improvements to their corresponding CR-CC results, especially when the higher-than-two-body cluster components become large, and the CC(t;3), CC(t,q;3), CC(t,q;3,4), and CC(q;4) approaches accurately reproduce the parent CCSDT and CCSDTQ energetics, but performing CC(P ; Q) computations in this way requires chemical intuition regarding the choice of the appropriate set of active orbitals, needed to select the dominant triply, triply and quadruply, or quadruply excited determinants in the wave function for the inclusion in the P space defining the CC(P ; Q) expansions. Therefore, the natural next step in the development of novel CC(P ; Q) approaches is to search for possible avenues for automating the selection of higher-than-doubly excited determinants entering the P space in a CC(P ; Q) computation. If such an automated protocol exists, it needs to be designed in such a way that the resulting CC(P ; Q) energies rapidly converge to their CCSDT/EOMCCSDT, CCSDTQ/EOMCCSDTQ, *etc.* parents, even when the higher-than-two-body T and $R_{\mu,n}$ components become substantial, at the fraction of the computational costs.

To that end, the Piecuch group has recently proposed a new class of hybrid CC(P ; Q) methods that can be loosely categorized into two different approaches. The first one arose from the merger of the deterministic CC(P ; Q) theory with the stochastic quantum Monte Carlo (QMC) wave function propagations in the many-electron Hilbert space defining the CIQMC [102–106] and CC Monte Carlo (CCMC) [107–110] methods, culminating in the “semi-stochastic” or “QMC-driven” CC(P ; Q) schemes [111–114]. The second strategy resulted from combining CC(P ; Q) with deterministic or largely deterministic ways of sampling

many-electron wave functions carried out with the help of selected CI [115–131] diagonalizations, which led to the selected-CI-driven $CC(P;Q)$ framework [132]. These hybrid $CC(P;Q)$ approaches combine the strengths of CIQMC, CCMC, and selected CI, especially their effectiveness in identifying the leading determinants in the many-electron wave function, with the robustness of the $CC(P;Q)$ moment corrections. One of the main topics of this dissertation is the extension of the semi-stochastic $CC(P;Q)$ methodology of Refs. [111, 114] to excited electronic states, but before discussing the key concepts behind it, let us take a moment to review some background information pertaining to QMC.

The idea behind QMC methods dates back to the 1949 work of Metropolis and Ulam [133], which resulted in stochastic sampling procedures to numerically integrate various forms of differential equations [133–135]. This, in turn, inspired the simplest form of QMC methodology, namely, the variational MC (VMC) method [136, 137], where one optimizes a trial wave function, while applying stochastic sampling to compute the required expectation values of the Hamiltonian operator. Although VMC calculations are computationally efficient, their results depend heavily on the quality of the trial wave function. An improvement to VMC was found in the diffusion MC (DMC) approach [138–140], which works by treating the Schrödinger equation in the imaginary time as a diffusion equation and letting a trial wave function evolve to the exact wave function by adopting a projection technique (see, *e.g.*, Refs. [141–143] for further details). Thus, as long as the trial wave function is not orthogonal to the exact wave function, the DMC propagation is guaranteed to project out the exact solution of the Schrödinger equation in the infinite imaginary time limit. In addition, DMC (and its VMC predecessor) is appealing due to its capability to circumvent the need for finite one-particle basis sets, because one can perform the propagation in the real space of $3N$ electronic coordinates instead. The DMC and VMC algorithms are also easily parallelizable across many multi-core nodes, further increasing their popularity in the quantum chemistry community. Nevertheless, despite the advantages that DMC propagation offers, it is plagued by the fact that if the wave function propagation is run without any constraint,

it will produce the bosonic solution to the many-electron Schrödinger equation, which is the true ground state of the spin-free Hamiltonian violating the Pauli exclusion principle, resulting in the so-called “boson catastrophe” or “fermion sign problem”. The most common way to circumvent this issue has been to employ the so-called fixed-node approximation [144–147], where one imposes the nodal structure of the wave function obtained in an inexpensive quantum chemistry calculation, such as HF or multiconfigurational SCF, but in doing so the DMC propagation can no longer produce the exact solution of the Schrödinger equation.

A novel way to tackle the fermion sign problem plaguing the DMC methodology is given by the full CIQMC (FCIQMC) approach and its truncated CIQMC analogs [102, 103], where one replaces the wave function propagation in the real space of $3N$ electronic coordinates by the propagations of CI expansions in the N -electron Hilbert space spanned by Slater determinants. Because Slater determinants are antisymmetric with respect to the exchange of any pair of electronic coordinates by construction, the many-electron wave functions produced by the FCIQMC and other CIQMC propagations are guaranteed to be antisymmetric as well. FCIQMC and its truncated CIQMC analogs use stochastic walker population dynamics in the wave function propagations, where the more important Slater determinants are populated by larger walker numbers. If all possible Slater determinants are allowed to be populated throughout the CIQMC simulation, as in FCIQMC, then at the infinite imaginary time limit one is guaranteed to converge the FCI solution within the employed basis set. Similar to the fully deterministic CI computations, one could also converge the truncated CISD, CISDT, CISDTQ, *etc.* results by limiting the space in which the propagation is being performed to be spanned by determinants of up to a certain excitation rank (*e.g.*, including up to triply excited Slater determinants in the sampled subspace means that the CIQMC propagation will converge to CISDT). While the rate of convergence of CIQMC can be slow, there exist modifications, such as the initiator approximation [103] or its newer adaptive shift modification [105, 106], that serve to accelerate the convergence of the CIQMC propagations. One can also develop the CC analogs of the CIQMC methods, resulting in the

CCMC approaches of Refs. [107–110], by replacing the CI expansions, when propagating the wave functions in the many-electron Hilber space, by the CC ansatz.

Although the FCIQMC algorithm is guaranteed to provide the exact solution to the Schrödinger equation within a given basis set and truncated CIQMC methods converge the corresponding truncated CI results, one has to deal with the stochastic noise inherent to these methodologies. To reduce the numerical noise to acceptable levels, one usually needs to run the propagation for a very long time, namely, tens or hundreds of thousands of MC imaginary time steps called “MC cycles” or “MC iterations”. Furthermore, if excited states of the same symmetry as the ground state are of interest, one has to resort to highly complex protocols by adopting, for example, a Gram–Schmidt procedure to orthogonalize higher-energy states against the lower-energy ones, so that the collapse of the dynamically propagated excited states on the lower-energy states within the same irreducible representation is avoided [148, 149]. Nevertheless, FCIQMC and its truncated counterparts are able to identify the leading determinants in the many-electron wave functions in the early stages of the QMC propagation. This observation is the basis of the semi-stochastic $CC(P;Q)$ approach, where one uses the information about the leading determinants populated in the early stages of CIQMC (or CCMC) simulations to build a P space for the $CC(P;Q)$ considerations, while accounting for the remaining determinants using the $CC(P;Q)$ noniterative corrections. In this way, one can do what is done using the aforementioned $CC(t;3)$, $CC(t,q;3)$, $CC(t,q;3,4)$, *etc.* hierarchy, but without relying on system- and user-dependent active orbitals or any other *a priori* knowledge of the wave function to capture the dominant higher-than-two-body components of the cluster and excitation operators of CC/EOMCC. In other words, by combining the stochastic CIQMC and CCMC ideas with the deterministic $CC(P;Q)$ framework, one can achieve an objective construction of the P and Q spaces for the $CC(P;Q)$ considerations because the identification of the leading triply excited, quadruply excited, *etc.* determinants does not depend on any input from the user. Recent studies in the Piecuch group have demonstrated that this new paradigm shows a lot of promise in the

ground-state considerations [111, 114]. In this dissertation, we will discuss our efforts in extending the semi-stochastic $CC(P;Q)$ algorithm to excited electronic states [112, 113], where we do not have to rely on the complicated excited-state CIQMC propagations described in Refs. [148, 149].

The overall goal of this dissertation is to survey different variants of the $CC(P;Q)$ theory defined using conventional and unconventional truncations in the cluster and EOM excitation operators. This includes several molecular applications of the CR-CC/EOMCC methodologies and active-space $CC(P;Q)$ approaches and our work on extending the semi-stochastic $CC(P;Q)$ formalism to excited electronic states. The molecular examples illustrating the accuracies of the various $CC(P;Q)$ methods include chemical problems relevant to spectroscopy and photochemistry. We will begin with the discussion of the salient features of the CC and EOMCC theories. This will be followed by the sophisticated quantum chemistry and spectroscopic computations for the weakly bound magnesium dimer, where we utilized high-level CC and EOMCC approaches including up to triple excitations and FCI to describe the PECs of Mg_2 in its ground and excited states relevant to experimental measurements, demonstrating that we can achieve spectroscopic accuracy when comparing the theoretical results with the experimentally observed spectral lines. This allowed us to provide information about the unresolved high-lying vibrational states of the magnesium dimer in the ground-state potential. We will then discuss the key concepts behind the $CC(P;Q)$ formalism and examine the conventional ways of using it via the CR-CC/EOMCC formalism and the unconventional active-space $CC(P;Q)$ approaches. The efficacy of the CR-CC/EOMCC methods will be illustrated by examining the super photobase **FR0-SB**, which is a molecule exhibiting a drastic increase in pK_a , of about 14 units, upon photoexcitation [3–8, 150]. We will also return to the discussion of the magnesium dimer, focusing on its ground electronic state, to demonstrate how the active-space-based $CC(P;Q)$ approaches can improve the results obtained using their CR-CC predecessors. Last, but not least, we will discuss the semi-stochastic $CC(P;Q)$ theory, especially its extension to excited electronic states that

resulted from this dissertation research [112, 113]. The usefulness of the semi-stochastic $\text{CC}(P;Q)$ methodology in excited-state applications will be illustrated by examining vertical excitations in the CH^+ ion and adiabatic excitations in the CH and CNC radicals.

CHAPTER 2

SINGLE-REFERENCE COUPLED-CLUSTER THEORY AND ITS EQUATION-OF-MOTION EXTENSION TO EXCITED ELECTRONIC STATES

2.1 Theory

In the SRCC formalism, the exact ground-state wave function of an N -electron system is expressed as

$$|\Psi_0\rangle = e^T |\Phi\rangle, \quad T = \sum_{n=1}^N T_n, \quad (2.1)$$

where $|\Phi\rangle$ is an independent-particle-model (*e.g.*, HF) reference determinant defining the Fermi vacuum and T is the cluster operator. In Eq. (2.1), T_n is the n -body component of T and is defined as

$$T_n = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} t_{a_1 \dots a_n}^{i_1 \dots i_n} E_{i_1 \dots i_n}^{a_1 \dots a_n}, \quad (2.2)$$

where $t_{a_1 \dots a_n}^{i_1 \dots i_n}$ are the cluster amplitudes and $E_{i_1 \dots i_n}^{a_1 \dots a_n} = a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1}$ are the particle-hole excitation operators, with a^p (a_p) representing the usual creation (annihilation) operators associated with the spin-orbital basis set $\{|p\rangle\}$, which excite electrons from the occupied spin-orbitals, indicated by $i_1, i_2, \dots$ (or $i, j, \dots$), to the unoccupied ones, designated by $a_1, a_2, \dots$ (or $a, b, \dots$). In practice, one usually truncates the cluster operator at a low excitation rank $m_A < N$, thus replacing T with its approximation $T^{(A)} = \sum_{n=1}^{m_A} T_n$. In this way, we obtain a hierarchy of CC methods, which includes approaches such as CCSD ($m_A = 2$), CCSDT ($m_A = 3$), CCSDTQ ($m_A = 4$), and so on.

As mentioned in the Introduction, one can extend the CC formalism as described above to excited electronic states using, for example, the EOM framework, where the EOMCC ansatz is defined as

$$|\Psi_\mu\rangle = R_\mu |\Psi_0\rangle = R_\mu e^T |\Phi\rangle, \quad (2.3)$$

in which $|\Psi_\mu\rangle$ is the μ -th excited-state wave function and R_μ is a CI-like linear excitation operator, defined as

$$R_\mu = r_{\mu,0}\mathbf{1} + \sum_{n=1}^N R_{\mu,n}, \quad (2.4)$$

with

$$R_{\mu,n} = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} r_{\mu,a_1\dots a_n}^{i_1\dots i_n} E_{i_1\dots i_n}^{a_1\dots a_n} \quad (2.5)$$

being the n -body component of R_μ and $\mathbf{1}$ denoting the unit operator. As in the case of the ground-state CC formalism, one truncates the R_μ operator at a particular rank m_A corresponding to the truncation of T , resulting in approaches such as EOMCCSD ($m_A = 2$), where $T^{(\text{CCSD})} = T_1 + T_2$ and $R_\mu^{(\text{EOMCCSD})} = r_{\mu,0}\mathbf{1} + R_{\mu,1} + R_{\mu,2}$, EOMCCSDT ($m_A = 3$), in which $T^{(\text{CCSDT})} = T_1 + T_2 + T_3$ and $R_\mu^{(\text{EOMCCSDT})} = r_{\mu,0}\mathbf{1} + R_{\mu,1} + R_{\mu,2} + R_{\mu,3}$, *etc.*

Once the ground-state CC and excited-state EOMCC wave functions are defined, we proceed to the derivation of equations for the unknown cluster and excitation amplitudes, $t_{a_1\dots a_n}^{i_1\dots i_n}$ and $r_{\mu,a_1\dots a_n}^{i_1\dots i_n}$, respectively. In the case of the ground state, we start by inserting the exponential ansatz, Eq. (2.1), into the Schrödinger equation, $H|\Psi_0\rangle = E_0|\Psi_0\rangle$, approximating T by $T^{(A)}$, and multiplying from the left by $e^{-T^{(A)}}$, to obtain the connected cluster form of the Schrödinger equation

$$\overline{H}^{(A)}|\Phi\rangle = E_0^{(A)}|\Phi\rangle, \quad (2.6)$$

where $\overline{H}^{(A)} = e^{-T^{(A)}} H e^{T^{(A)}} = (H e^{T^{(A)}})_C$ is the similarity-transformed Hamiltonian of the truncated CC method A , in which subscript C indicates the connected operator product and $E_0^{(A)}$ is the corresponding ground-state energy. Subsequently, we project Eq. (2.6) on the excited determinants $|\Phi_{i_1\dots i_n}^{a_1\dots a_n}\rangle = E_{i_1\dots i_n}^{a_1\dots a_n}|\Phi\rangle$ with $n \leq m_A$, which leads to a system of nonlinear equations

$$\langle \Phi_{i_1\dots i_n}^{a_1\dots a_n} | \overline{H}^{(A)} | \Phi \rangle = 0, \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \quad n = 1, \dots, m_A, \quad (2.7)$$

for the cluster amplitudes $t_{a_1 \dots a_n}^{i_1 \dots i_n}$ defining $T^{(A)}$. Once the cluster amplitudes defining $T^{(A)}$ are known, we calculate the ground-state CC energy $E_0^{(A)}$ by taking the expectation value of $\bar{H}^{(A)}$ with respect to the reference determinant $|\Phi\rangle$,

$$E_0^{(A)} = \langle \Phi | \bar{H}^{(A)} | \Phi \rangle. \quad (2.8)$$

After the ground-state cluster amplitudes $t_{a_1 \dots a_n}^{i_1 \dots i_n}$ and energy $E_0^{(A)}$ are obtained, we proceed to the determination of the excited-state energies, $E_\mu^{(A)}$, and wave functions, $|\Psi_\mu^{(A)}\rangle$, using the EOMCC ansatz given by Eq. (2.3) in which we have also approximated R_μ by $R_\mu^{(A)}$. By inserting this ansatz into the electronic Schrödinger equation, $H |\Psi_\mu\rangle = E_\mu |\Psi_\mu\rangle$, multiplying the resulting eigenvalue problem from the left by $e^{-T^{(A)}}$, and projecting on the excited determinants $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$ with $n \leq m_A$, we obtain the eigenvalue problem

$$\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | (\bar{H}_{\text{open}}^{(A)} R_{\mu, \text{open}}^{(A)})_C | \Phi \rangle = \omega_\mu^{(A)} r_{\mu, a_1 \dots a_n}^{i_1 \dots i_n}, \quad (2.9)$$

where $\bar{H}_{\text{open}}^{(A)} = \bar{H}^{(A)} - \bar{H}_{\text{closed}}^{(A)} = \bar{H}^{(A)} - E_0^{(A)} \mathbf{1}$ and $R_{\mu, \text{open}}^{(A)} = R_\mu^{(A)} - r_{\mu, 0} \mathbf{1}$ are the open parts of $\bar{H}^{(A)}$ and $R_\mu^{(A)}$, respectively, which are represented by diagrams possessing external Fermion lines, and $\omega_\mu^{(A)} = E_\mu^{(A)} - E_0^{(A)}$ is the corresponding vertical excitation energy. The zero-body component of the EOM excitation operator is calculated *a posteriori* as

$$r_{\mu, 0} = \langle \Phi | (\bar{H}_{\text{open}}^{(A)} R_{\mu, \text{open}}^{(A)})_C | \Phi \rangle / \omega_\mu^{(A)}. \quad (2.10)$$

If one is only interested in the electronic energies of the system, then one does not need to go further in the CC/EOMCC computations. However, if properties other than energy, such as dipole moment, transition dipole moment, or polarizability are desired, then an extra step has to be taken. This is because the similarity-transformed Hamiltonian $\bar{H}^{(A)}$ is not Hermitian, which means that the left (“bra”) CC/EOMCC states are not the same as the right (“ket”) CC/EOMCC states given by Eqs. (2.1) and (2.3). In the CC/EOMCC framework, one obtains the left CC/EOMCC states in a straightforward manner using the ansatz

$$\langle \tilde{\Psi}_\mu | = \langle \Phi | L_\mu e^{-T}, \quad (2.11)$$

where the hole-particle de-excitation operator L_μ satisfies the biorthonormality condition

$$\langle \tilde{\Psi}_\mu | \Psi_\nu \rangle = \langle \Phi | L_\mu R_\nu | \Phi \rangle = \delta_{\mu\nu}, \quad (2.12)$$

with $\delta_{\mu\nu}$ representing the Kronecker delta. The de-excitation operator L_μ is defined as

$$L_\mu = \delta_{\mu 0} \mathbf{1} + \sum_{n=1}^N L_{\mu,n}, \quad (2.13)$$

where

$$L_{\mu,n} = \sum_{\substack{i_1 < \dots < i_n \\ a_1 < \dots < a_n}} l_{\mu,i_1\dots i_n}^{a_1\dots a_n} (E_{i_1\dots i_n}^{a_1\dots a_n})^\dagger \quad (2.14)$$

is the n -body component of L_μ . As in the case of T and R_μ , in practice, we approximate L_μ by $L_\mu^{(A)}$, in which the summation in Eq. (2.13) is truncated at an excitation rank m_A corresponding to the previously discussed CC/EOMCC calculations for $T^{(A)}$ and $R_\mu^{(A)}$. The de-excitation amplitudes defining the left CC/EOMCC states, $l_{\mu,i_1\dots i_n}^{a_1\dots a_n}$, are obtained by solving the left eigenvalue problem

$$\delta_{\mu 0} \langle \Phi | \overline{H}_{\text{open}}^{(A)} | \Phi_{i_1\dots i_n}^{a_1\dots a_n} \rangle + \langle \Phi | L_{\mu,\text{open}}^{(A)} \overline{H}_{\text{open}}^{(A)} | \Phi_{i_1\dots i_n}^{a_1\dots a_n} \rangle = \omega_\mu^{(A)} l_{\mu,i_1\dots i_n}^{a_1\dots a_n}, \quad (2.15)$$

where, in analogy to the $R_\mu^{(A)}$ operator, $L_{\mu,\text{open}}^{(A)} = L_\mu^{(A)} - \delta_{\mu 0} \mathbf{1}$ is the open part of $L_\mu^{(A)}$.

One can then use the bra and ket CC/EOMCC states to calculate expectation values and transition matrix elements of quantum-mechanical operators (observables) involving the CC and EOMCC ground and excited states as

$$\langle \tilde{\Psi}_\mu^{(A)} | \Theta | \Psi_\nu^{(A)} \rangle = \langle \Phi | L_\mu^{(A)} \overline{\Theta}^{(A)} R_\nu^{(A)} | \Phi \rangle, \quad (2.16)$$

where $\overline{\Theta}^{(A)} = e^{-T^{(A)}} \Theta e^{T^{(A)}} = (\Theta e^{T^{(A)}})_C$ represents a similarity-transformed form of the observable of interest, Θ , which could be, for example, the dipole moment operator if we are interested in determining the dipole moments in various electronic states or transition dipole moments between different states. In writing Eq. (2.16), we combine the ground- and excited-state formalisms into a compact notation by defining $R_{\nu=0}^{(A)}$ to be the unit operator $\mathbf{1}$. While Eq. (2.16) seems straightforward to evaluate, determining properties in this way

requires forming $\bar{\Theta}^{(A)}$ for each desired property, which may become impractical. One could instead consider an alternative route by precomputing the CC and EOMCC reduced density matrix (RDM). If one-electron properties, which are of interest in this dissertation, are to be computed, one constructs the CC/EOMCC one-body RDM (1-RDM), $\gamma_q^{p(A)}(\mu, \nu)$, as

$$\gamma_q^{p(A)}(\mu, \nu) = \langle \Phi | L_\mu^{(A)} e^{-T^{(A)}} \Gamma_q^p e^{T^{(A)}} R_\nu^{(A)} | \Phi \rangle = \langle \Phi | L_\mu^{(A)} \bar{\Gamma}_q^{p(A)} R_\nu^{(A)} | \Phi \rangle, \quad (2.17)$$

where $\Gamma_q^p = a^p a_q$ and $\bar{\Gamma}_q^{p(A)} = e^{-T^{(A)}} \Gamma_q^p e^{T^{(A)}} = (\Gamma_q^p e^{T^{(A)}})_C$ (one can generalize the above expression to obtain the CC and EOMCC n -body reduced density matrices by replacing Γ_q^p by the corresponding string of n creation and n annihilation operators, namely, $\Gamma_{q_1 \dots q_n}^{p_1 \dots p_n} = a^{q_1} \dots a^{q_n} a_{p_n} \dots a_{p_1}$). Note that the 1-RDM computed for a particular state μ , $\gamma_q^{p(A)}(\mu, \mu) \equiv \gamma_q^{p(A)}(\mu)$, can be used to compute the one-electron properties for that state, while the corresponding 1-body transition matrix $\gamma_q^{p(A)}(\mu, \nu)$, $\mu \neq \nu$ gives us access to transition properties coupling two different electronic states. By calculating the 1-RDM of ground and excited states and the corresponding transition density matrices, $\gamma_q^{p(A)}(\mu, \nu)$, we can determine all one-electron properties and the corresponding transition matrix elements involving one-electron properties using a single mathematical expression

$$\langle \tilde{\Psi}_\mu^{(A)} | \Theta | \Psi_\nu^{(A)} \rangle = \sum_{p,q} \theta_p^q \gamma_q^{p(A)}(\mu, \nu), \quad (2.18)$$

where θ_p^q are matrix elements of the one-body operator Θ in a basis set of molecular spin-orbitals $|p\rangle$ used in the calculations. Indeed, the calculation of 1-RDMs provides the most convenient way of calculating CC and EOMCC properties of ground and excited states, since by having these matrices around we can calculate all kinds of one-electron properties in a single calculation. In addition, 1-RDMs allow one to compute the CC and EOMCC electron densities,

$$\rho_\mu^{(A)}(\mathbf{x}) = \sum_{p,q} \gamma_q^{p(A)}(\mu) \phi_q^*(\mathbf{x}) \phi_p(\mathbf{x}), \quad (2.19)$$

where $\phi_p(\mathbf{x})$ and $\phi_q(\mathbf{x})$ are molecular spin-orbitals and $\mathbf{x}$ represents the electronic (spatial and spin) coordinates. By diagonalizing $\gamma_q^{p(A)}(\mu)$, one can determine the natural occupation numbers and natural orbitals for the CC or EOMCC state $|\Psi_\mu^{(A)}\rangle$.

Because of the non-Hermitian nature of the CC and EOMCC theories, there is one caveat that we have to keep in mind, which is that the RDMs originating from CC and EOMCC calculations are not symmetric. Thus, if we, for example, want to calculate the x component of the dipole strength between states μ and ν , namely, $\left| \left\langle \Psi_{\mu}^{(A)} \right| \mu_x \left| \Psi_{\nu}^{(A)} \right\rangle \right|^2$, we must write

$$\left| \left\langle \Psi_{\mu}^{(A)} \right| \mu_x \left| \Psi_{\nu}^{(A)} \right\rangle \right|^2 = \left\langle \tilde{\Psi}_{\mu}^{(A)} \right| \mu_x \left| \Psi_{\nu}^{(A)} \right\rangle \left\langle \tilde{\Psi}_{\nu}^{(A)} \right| \mu_x \left| \Psi_{\mu}^{(A)} \right\rangle, \quad (2.20)$$

where each matrix element in the above expression is evaluated using the expression for $\left\langle \tilde{\Psi}_{\mu}^{(A)} \right| \Theta \left| \Psi_{\nu}^{(A)} \right\rangle$ shown in Eq. (2.18). In other words, both matrix elements $\left\langle \tilde{\Psi}_{\mu}^{(A)} \right| \mu_x \left| \Psi_{\nu}^{(A)} \right\rangle$ and $\left\langle \tilde{\Psi}_{\nu}^{(A)} \right| \mu_x \left| \Psi_{\mu}^{(A)} \right\rangle$ have to be evaluated, since they are not identical.

2.2 Application: Resolving a Half-Century-Old Enigma: The Elusive $v'' = 14$ – 18 Vibrational Levels of Mg_2

In order to demonstrate the effectiveness of high-level CC and EOMCC calculations, let us consider the intriguing example of the magnesium dimer. Specifically, in this section, we summarize the *ab initio* investigation of Mg_2 reported in Ref. [2]. Mg_2 is one of the weakly bound alkaline-earth dimers (AE_2), which have emerged as probes of fundamental physics relevant to ultracold collisions [151], doped helium nanodroplets [152], coherent control of binary reactions [153], and even fields rarely associated with molecular science, such as optical lattice clocks [154] and quantum gravity [155]. The magnesium dimer is especially important, since it has several desirable characteristics that can be useful in the above applications, such as the absence of hyperfine structure in the most abundant ^{24}Mg isotope that facilitates the analysis of binary collisions involving laser-cooled and trapped atoms, it helps us understand heavier AE_2 diatomics, and, unlike its lighter Be_2 analog, it is nontoxic [156]. Unfortunately, the status of Mg_2 as a prototype heavier AE_2 species is complicated by the fact that its high-lying vibrational levels and, consequently, the long-range part of its ground-state PEC have eluded experimental characterization for half a century. In this regard, the magnesium dimer is even more challenging than its celebrated beryllium counterpart, whose elusive 12th vibrational level near the dissociation threshold [157, 158], which was also found by

the Piecuch group in Ref. [73], was confirmed in 2014 [159] after reanalyzing the spectra obtained in stimulated emission pumping experiments [160].

Experimentally, probing vibrational manifold of the magnesium dimer in its ground, $X^1\Sigma_g^+$, electronic state has to involve excited electronic states, since Mg_2 , being a homonuclear diatomic, is infrared inactive. The first high-resolution photoabsorption spectra of Mg_2 , corresponding to a transition from the ground state to the electronically excited $A^1\Sigma_u^+$ state, were reported in 1970 by Balfour and Douglas [161]. Their spectroscopic analysis resulted in 285 $G(v'', J'')$ and 656 $G(v', J')$ rovibrational term values of $^{24}Mg_2$ involving 13 ($v'' = 0$ to 12) $X^1\Sigma_g^+$ and 24 ($v' = 1$ to 24) $A^1\Sigma_u^+$ vibrational levels, respectively. In this section, we are using the notation in which the vibrational, v , and rotational, J , quantum numbers in the ground electronic state are designated by a double prime, whereas those corresponding to the excited $A^1\Sigma_u^+$ state are marked with a prime. In their pioneering work, Balfour and Douglas constructed a Rydberg–Klein–Rees (RKR) [162–165] $X^1\Sigma_g^+$ PEC in the 3.25 to 7.16 Å range and located the last experimentally resolved $v'' = 12$ level about 25 cm^{-1} below the dissociation threshold, pointing to the existence of extra vibrational states with $v'' > 12$. It did not take long to detect one of such states. In 1973, Li and Stwalley [166] identified $X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$ transitions involving the $v'' = 13$ level in the spectra reported in Ref. [161]. They accomplished this by extending the original RKR PEC of Balfour and Douglas to the asymptotic region beyond 7.16 Å using theoretical values of C_6 and C_8 van der Waals coefficients [167, 168]. The resulting PEC supported 19 vibrational levels, *i.e.*, five levels more than what was observed experimentally [166]. Four decades later, in an effort to characterize states with $v'' > 13$, Knöckel *et al.* [169, 170] examined the $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition using laser-induced fluorescence (LIF), repeating and refining the earlier LIF experiment by Scheingraber and Vidal [171]. They improved and expanded the original $^{24}Mg_2$ dataset of Balfour and Douglas by reporting a total of 333 $G(v'', J'')$ and 1,351 $G(v', J')$ rovibrational term values involving $v'' = 0$ –13 and $v' = 1$ –46, respectively, and constructed a few experimentally derived analytical forms of the $X^1\Sigma_g^+$ PEC, extrapolated to the asymptotic region

using the theoretical C_6 [172], C_8 [173], and C_{10} [173] coefficients, which support the discrete spectral data in the 3.27 to 8.33 Å range [169]. Although these refined PECs supported 19 $^{24}\text{Mg}_2$ vibrational levels, reinforcing the initial prediction of Li and Stwalley [166], Knöckel *et al.* [169] were unable to identify $\text{A } ^1\Sigma_u^+(v', J') \rightarrow \text{X } ^1\Sigma_g^+(v'', J'')$ transitions involving the elusive high-lying vibrational levels with $v'' > 13$ in their LIF spectra.

Typically, high-lying vibrational states near dissociation constitute a small fraction of the entire vibrational manifold, but this is not the case for the weakly bound magnesium dimer, which has a shallow minimum on the ground-state PEC at $r_e = 3.89039$ Å [169] and a tiny dissociation energy D_e of 430.472(500) cm^{-1} [169, 170]. If the five extra levels, which have been speculated about, truly existed, they would represent more than a quarter of the entire vibrational manifold in the ground electronic state. Furthermore, without precise knowledge of the ground-state PEC of Mg_2 , especially its long-range part that determines the positions of the high-lying vibrational states near the dissociation threshold, one cannot accurately interpret the aforementioned ultracold and collisional phenomena involving interacting magnesium atoms. It is intriguing why a seemingly docile main group diatomic continues to challenge state-of-the-art spectroscopic techniques. The experimental difficulties in detecting the elusive $v'' > 13$ states of the magnesium dimer originate from several factors, including small energy gaps between high-lying vibrations that are comparable to rotational spacings [161, 174], resulting in overlapping spectral lines, and unfavorable signal-to-noise ratio in the existing LIF spectra [169]. Rotational effects complicate the situation even more, since, in addition to affecting line intensities [169, 171, 174], they may render the high-lying vibrational states of Mg_2 unbound. All of these and similar difficulties prompted Knöckel *et al.* [169, 170] to conclude that experimental work alone is insufficient and that accurate theoretical calculations are needed to guide further analysis of the ground-state PEC and rovibrational states of Mg_2 , especially the elusive $v'' > 13$ levels near the dissociation threshold.

Unfortunately, there have only been a handful of theoretical investigations attempting

to determine the entire vibrational manifold of the magnesium dimer. This is, at least in part, related to the intrinsic complexity of the underlying electronic structure and difficulties with obtaining an accurate representation of the ground-state PEC using purely *ab initio* quantum-chemical means. As already mentioned above, at the HF theory level, which neglects electron correlation and dispersion interactions, Mg_2 remains unbound. As demonstrated below, one needs to go to much higher theory levels, incorporate high-order many-electron correlation effects, including valence as well as inner-shell electrons, and use large, carefully calibrated, one-electron basis sets to accurately capture the relevant physics and obtain a reliable description of the $X^1\Sigma_g^+$ potential and of the corresponding rovibrational manifold (see Ref. [1] for a detailed discussion and historical account, including references to the earlier quantum chemistry computations for the magnesium dimer). *Ab initio* quantum mechanical calculations for the $A^1\Sigma_u^+$ PEC, the rovibrational states supported by it, and the $X^1\Sigma_g^+ - A^1\Sigma_u^+$ electronic transition dipole moment function, needed to interpret and aid the photoabsorption and LIF experiments using purely theoretical means, are similarly challenging, and this investigation shows this too [2].

The initial theoretical estimates of the number of vibrational states supported by the $X^1\Sigma_g^+$ potential ranged from 18 to 20 [175], while the more recent *ab initio* quantum chemistry computations based on the various levels CC theory, reported in Refs. [1, 176], suggested that the highest vibrational level of $^{24}\text{Mg}_2$ is $v'' = 18$. Among the previous theoretical studies, only Amaran *et al.* [176] considered the $A^1\Sigma_u^+$ state involved in the photoabsorption and LIF experiments and included rotational effects, but they have not provided any information about the calculated rovibrational term values other than the root mean square deviations (RMSDs) relative to the experimental data of Balfour and Douglas [161]. Furthermore, as demonstrated in our earlier benchmark study [1], which will be summarized in a later chapter in this dissertation as well, where a large number of CC methods were tested using the $X^1\Sigma_g^+$ PEC of the magnesium dimer and the rotationless term values of $^{24}\text{Mg}_2$ as examples, and consistent with the earlier calculations [177, 178], the popular CCSD(T) approximation

exploited in Ref. [176] could not possibly produce the small RMSD value reported in Ref. [176], of 1.3 cm^{-1} , for the rovibrational manifold of Mg_2 in its ground electronic state; the value on the order of a dozen cm^{-1} would be more appropriate [1]. Similar remarks apply to the $\text{A } ^1\Sigma_u^+$ state, which was treated in Ref. [176] using the LRCCSD approach, resulting in noticeable deviations from the experimentally derived $\text{A } ^1\Sigma_u^+$ potential shown in Fig. 4 of Ref. [170]. To simulate and properly interpret the $\text{A } ^1\Sigma_u^+ \rightarrow \text{X } ^1\Sigma_g^+$ LIF spectra obtained in Ref. [169] using purely theoretical means, one needs much higher accuracy levels in the computations of line positions and robust information about line intensities, which has not been obtained in the previous quantum chemistry studies.

The goal of the *ab initio* electronic structure calculations performed in Ref. [2] and summarized here is to obtain highly accurate $\text{X } ^1\Sigma_g^+$ and $\text{A } ^1\Sigma_u^+$ PECs of the magnesium dimer and the corresponding $\text{X } ^1\Sigma_g^+ - \text{A } ^1\Sigma_u^+$ transition dipole moment function $\mu_z^{\text{X-A}}(r)$ involved in the photoabsorption and LIF experiments reported in Refs. [161, 169–171]. In the case of the ground-state PEC, we combined the numerically exact description of the valence electron correlation effects provided by FCI with the high-level description of subvalence correlations involving all electrons but the 1s shells of Mg atoms obtained using CCSDT. Thus, the $\text{X } ^1\Sigma_g^+$ PEC of Mg_2 reported in this work was obtained by adopting the composite scheme

$$E_{\text{X } ^1\Sigma_g^+} = E_{\text{X } ^1\Sigma_g^+}^{\text{CCSDT/AwCQZ}} + \left(E_{\text{X } ^1\Sigma_g^+}^{\text{FCI/A(Q+d)Z}} - E_{\text{X } ^1\Sigma_g^+}^{\text{CCSDT/A(Q+d)Z}} \right). \quad (2.21)$$

The first term on the right-hand side of Eq. (2.21) denotes the total electronic energy obtained in the full CCSDT calculations correlating all electrons other than the 1s shells of the Mg monomers and using the aug-cc-pwCVQZ basis set developed in Ref. [179], abbreviated as AwCQZ. The second and third terms on the right-hand side of Eq. (2.21), which represent the difference between the frozen-core FCI and CCSDT energies obtained using the aug-cc-pV(Q+d)Z basis of [179], abbreviated as A(Q+d)Z, correct the nearly all-electron CCSDT/AwCQZ energy for the valence correlation effects beyond CCSDT. The A(Q+d)Z and AwCQZ basis sets were taken from the Peterson group’s website [180]. We used these bases rather than their standard aug-cc-pVnZ and aug-cc-pCVnZ counterparts, since it has

been demonstrated that the aug-cc-pV($n+d$)Z and aug-cc-pwCV n Z basis set families, including A(Q+d)Z and AwCQZ, accelerate the convergence of bond lengths, dissociation energies, and spectroscopic properties of magnesium compounds [1, 179]. We will comment on the convergence of our computational scheme in Eq. (2.21) with respect to the size of the basis set and the level of theory employed later.

In principle, one could extend the above composite scheme, given by Eq. (2.21), to the electronically excited A $^1\Sigma_u^+$ state by replacing CCSDT in Eq. (2.21) with its EOMCCSDT counterpart, but the nearly all-electron full EOMCCSDT calculations using the large AwCQZ basis set turned out to be prohibitively expensive for us. To address this problem, we resorted to one of the CR-EOMCCSD(T) approximations to EOMCCSDT, namely, CR-EOMCCSD(T),IA [85], which is capable of providing highly accurate excited-state PECs of near-EOMCCSDT quality at the small fraction of the cost. Thus, our composite scheme for the calculations of the A $^1\Sigma_u^+$ PEC was defined as

$$E_{A^1\Sigma_u^+} = E_{A^1\Sigma_u^+}^{\text{CR-EOMCCSD(T),IA/AwCQZ}} + \left(E_{A^1\Sigma_u^+}^{\text{FCI/A(Q+d)Z}} - E_{A^1\Sigma_u^+}^{\text{CR-EOMCCSD(T),IA/A(Q+d)Z}} \right), \quad (2.22)$$

where the first term on the right-hand side of Eq. (2.22) is the total electronic energy of the A $^1\Sigma_u^+$ state obtained in the CR-EOMCCSD(T),IA/AwCQZ calculations correlating all electrons other than the 1s shells of the Mg monomers and the next two terms correct the nearly all-electron CR-EOMCCSD(T),IA/AwCQZ calculations for the valence correlation effects beyond the CR-EOMCCSD(T),IA level using the difference of the FCI and CR-EOMCCSD(T),IA energies obtained with the A(Q+d)Z basis. Before deciding on the use of CR-EOMCCSD(T),IA, we tested other CR-EOMCC schemes by comparing the resulting A $^1\Sigma_u^+$ potentials obtained using Eq. (2.22) and the corresponding rovibrational term $G(v', J')$ values with the available experimentally derived data reported in Refs. [169, 181]. Although all of these schemes worked well, the computational protocol defined by Eq. (2.22), with the CR-EOMCCSD(T),IA approach serving as a baseline method, turned out to produce the smallest maximum unsigned errors and RMSD values relative to experiment.

All electronic structure calculations for Mg_2 performed in this study were based on the tightly converged RHF reference functions (the convergence criterion for the RHF density matrix was set up at 10^{-9}). The valence FCI calculations for the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ states were performed using the GAMESS package [182–184], whereas the valence and subvalence CCSDT computations for the $X^1\Sigma_g^+$ state were carried out with NWChem [185]. The valence and subvalence CR-EOMCCSD(T),IA calculations for the $A^1\Sigma_u^+$ state were executed using the RHF-based CR-EOMCCSD(T) routines developed in [85], which take advantage of the underlying ground-state CC codes described in [186] and which are part of GAMESS as well. The GAMESS RHF-based CC routines [186] were also used to perform the CCSD(T) calculations needed to explore the basis set convergence and the viability (or the lack thereof) of the alternative to the CCSDT-based composite scheme given by Eq. (2.21) (*vide infra*). The convergence thresholds used in the post-RHF steps of the CC and EOMCC computations reported in this work were set up at 10^{-7} for the relevant excitation amplitudes and 10^{-7} hartree (0.02 cm^{-1}) for the corresponding electronic energies. The default GAMESS input options that were used to define our FCI calculations guaranteed energy convergence to 10^{-10} hartree.

The grid of Mg–Mg separations r , at which the electronic energies of the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ states determined were determined, was as follows: 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.6, 3.7, 3.8, 3.9, 4.0, 4.1, 4.2, 4.4, 4.6, 4.8, 5.0, 5.2, 5.4, 5.6, 5.8, 6.0, 6.4, 6.8, 7.2, 7.6, 8.0, 8.4, 8.8, 9.2, 9.6, 10.0, 11.0, 12.0, 13.0, 15.0, 20.0, 25.0, 30.0, and 100.0 Å [2]. We adopted the same set of r values to determine the electronic transition dipole moment function $\mu_z^{\text{X-A}}(r)$ between the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ electronic states, needed to calculate LIF line intensities using the Einstein coefficients. The $\mu_z^{\text{X-A}}(r)$ calculations reported in this work were performed using the valence FCI approach, as implemented in GAMESS, adopting the A(Q+d)Z basis set of Ref. [179].

The rovibrational term values, including bound and quasi-bound states supported by our *ab initio* $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ PECs defined by Eqs. (2.21) and (2.22), were computed

by numerically integrating the radial Schrödinger equation from 2.2 to 100.0 Å using the Numerov–Cooley algorithm [187] available in the LEVEL16 code [188] (LEVEL16 uses the Airy function approach described in Ref. [189] to locate quasi-bound states). The widths and the tunneling lifetimes for predissociation by rotation characterizing the quasi-bound rovibrational states supported by the $X^1\Sigma_g^+$ potential were calculated using LEVEL16 as well. In this case, we followed the semiclassical procedure described in Ref. [188] and implemented in LEVEL16, which requires numerical integrations between turning points in the classically allowed and classically forbidden regions of the relevant effective potentials including centrifugal barriers (see Ref. [188] for further details).

We also used LEVEL16 to determine the rovibrational term values characterizing the experimentally derived analytical X-representation potential developed in [169], which we used to assess the accuracy of our *ab initio*–determined $X^1\Sigma_g^+$ PEC. To be consistent with our LEVEL16 calculations for the ground-state PEC resulting from the *ab initio* protocol based on Eq. (2.21), we first determined the energies corresponding to the X-representation potential on the grid of 47 internuclear distances r adopted in our *ab initio* work. We then followed the same numerical procedure as described above for the $X^1\Sigma_g^+$ PEC resulting from the *ab initio* quantum chemistry calculations.

Last, but not least, we used LEVEL16 to compute the line positions of all allowed $A^1\Sigma_u^+(v', J') \rightarrow X^1\Sigma_g^+(v'', J'')$ rovibronic transitions and, with the help of our *ab initio* transition dipole moment function $\mu_z^{X-A}(r)$, the corresponding line intensities, as defined by the Einstein coefficients. The only adjustment that we had to make to be able to compare our calculated line positions and intensities for the allowed $A^1\Sigma_u^+(v', J') \rightarrow X^1\Sigma_g^+(v'', J'')$ transitions with the LIF data reported in Refs. [169, 170] was a uniform downward shift of the entire $A^1\Sigma_u^+$ PEC resulting from our *ab initio* computations by $1,543.2\text{ cm}^{-1}$, needed to match the experimentally determined adiabatic electronic gap T_e of $26,068.9\text{ cm}^{-1}$ [170]. Other than that, all of the calculated spectroscopic properties, including the D_e , r_e , and rovibrational term values corresponding to the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ states and the line positions

and intensities characterizing the $A\ ^1\Sigma_u^+(v', J') \rightarrow X\ ^1\Sigma_g^+(v'', J'')$ transitions reported in this study, rely on the raw *ab initio* data combined with the LEVEL16 processing, as described above.

The most essential numerical information, generated using the computational protocol described above, is summarized in Tables 2.1–2.3 and Figs. 2.1–2.5. In describing and discussing our results, we begin with the PECs and rovibrational term values characterizing the $X\ ^1\Sigma_g^+$ and $A\ ^1\Sigma_u^+$ states of the magnesium dimer, focusing on a comparison of our *ab initio* calculations with the available experimental and experimentally derived data reported in Refs. [161, 169, 170]. Next, we compare the experimental LIF spectra reported in Refs. [169, 170] with those resulting from our computations and suggest potential avenues for detection of the elusive $v'' > 13$ levels of the magnesium dimer. Lastly, we also discuss further observation on the convergence of the computational protocol described in Eqs. (2.21) and (2.22). Additional information that complements the discussion in this section, including further comments on the accuracy and convergence characteristics of the computational protocol used in the present study, the effect of isotopic substitution on the calculated rovibrational term values, the discussion of the validity of the Franck–Condon analysis adopted in Ref. [169] to examine the LIF spectra reported in Refs. [169, 170], and the lifetimes for predissociation by rotation characterizing quasi-bound rovibrational states supported by the $X\ ^1\Sigma_g^+$ potential, can be found in Ref. [2] and the accompanying Supplementary Materials.

As shown in Table 2.1, our *ab initio* $X\ ^1\Sigma_g^+$ PEC reproduces the experimentally derived dissociation energy D_e and equilibrium bond length r_e of Mg_2 [169, 170] to within 0.9 cm^{-1} (0.2%) and $0.003\text{ \AA}$ (0.07%), respectively. These high accuracies in describing D_e and r_e are reflected in our calculated rovibrational term values of $^{24}\text{Mg}_2$ and its isotopologs, which are in very good agreement with the available experimental information [161, 169, 170]. Indeed, the RMSDs characterizing our *ab initio* $G(v'', J'')$ values for $^{24}\text{Mg}_2$ relative to their experimentally determined counterparts, reported in Ref. [161] for $v'' < 13$ and Refs. [169, 170] for $v'' < 14$, are 1.1 cm^{-1} , when the spectroscopic data from Ref. [161] are used, and 1.5

cm^{-1} , when we rely on Refs. [169, 170] instead [2]. At the same time, the maximum unsigned errors in our calculated $G(v'', J'')$ values relative to the experiment do not exceed $\sim 2 \text{ cm}^{-1}$, even when the quasi-bound states above the potential asymptote arising from centrifugal barriers are considered. Although the experimental information about the $G(v'', J'')$ values characterizing other Mg_2 isotopologs is limited to $^{24}\text{Mg}^{25}\text{Mg}$, $^{24}\text{Mg}^{26}\text{Mg}$, and $^{26}\text{Mg}_2$ and includes very few v'' values [169, 170], the RMSDs relative to the experiment resulting from our calculations are similarly small (see the Supplementary Materials to Ref. [2] for more details).

Further insights into the quality of our *ab initio* calculations for the ground-state PEC can be obtained by comparing the resulting rovibrational term values with their counterparts determined using the most accurate, experimentally derived, analytical forms of the $X^1\Sigma_g^+$ potential to date constructed in Ref. [169]. In the discussion below, we focus on the so-called X-representation of the ground-state PEC developed in Ref. [169], which the authors of Ref. [169] regard as a reference potential in their analyses (see Table 2.2). We recall that the X-representation of the ground-state PEC of the magnesium dimer was obtained by simultaneously fitting the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ PECs to a large number of the experimentally determined $A^1\Sigma_u^+(v', J') \rightarrow X^1\Sigma_g^+(v'', J'')$ rovibronic transition frequencies and extrapolating the resulting $X^1\Sigma_g^+$ PEC to the asymptotic region using the theoretical C_6 [172], C_8 [173], and C_{10} [173] coefficients. As shown in Table 2.2, our *ab initio* $G(v'', J'')$ energies characterizing the most abundant $^{24}\text{Mg}_2$ isotopolog are in very good agreement with those generated using the X-representation of the ground-state PEC developed in Ref. [169]. When all of the rovibrational bound states supported by both potentials are considered, the RMSD and the maximum unsigned error characterizing our *ab initio* $G(v'', J'')$ values for $^{24}\text{Mg}_2$ relative to their counterparts arising from the X-representation are 1.3 and 2.0 cm^{-1} , respectively [2]. What is especially important in the context of the present study is that our *ab initio* ground-state PEC and the state-of-the-art analytical fit to the experimental data defining the X-representation, constructed in Ref. [169], bind the $v'' = 18$ level if the rotational quantum

number J'' is not too high (see the discussion below).

The high quality of our calculated $G(v'', J'')$ values and spacings between them, which can also be seen in Tables 2.1 and 2.2 and Fig. 2.1, allows us to comment on the existence of the $v'' > 13$ levels that have escaped experimental detection for decades. As already alluded to above and as shown in Table 2.2 and Fig. 2.1, our *ab initio* $X^1\Sigma_g^+$ PEC supports the same number of rotationless vibrational levels as the latest experimentally derived PEC defining the X-representation [169], which for the most abundant $^{24}\text{Mg}_2$ isotopolog is 19. Table 2.1, which compares the rovibrational term values of $^{24}\text{Mg}_2$ resulting from our *ab initio* calculations for the representative rotational quantum numbers ranging from 0 to 80 with the available experimental data, shows that the elusive high-lying states with $v'' > 13$ quickly become unbound as J'' increases, so by the time $J'' = 20$, the $v'' = 15$ to 18 levels are no longer bound. This is demonstrated in Fig. 2.2, where we show a graphical representation of the $J'' = 20, 40, 60$, and 80 effective potentials including centrifugal barriers characterizing the rotating $^{24}\text{Mg}_2$ molecule, along with the corresponding vibrational wave functions and information about the lifetimes for predissociation by rotation associated with tunneling through centrifugal barriers characterizing quasi-bound states. In fact, according to our *ab initio* data [2], the maximum rotational quantum number that allows for at least one bound rovibrational state decreases with v'' , from $J'' = 68$ for $v'' = 0$ to $J'' = 4$ for $v'' = 18$, with all states becoming quasi-bound or unbound when $J'' \geq 70$, when the most abundant $^{24}\text{Mg}_2$ isotopolog is considered. In general, as exemplified in Fig. 2.2 (*cf.*, also, the lifetime data compiled in the Supplementary Materials to Ref. [2]), the mean lifetimes for predissociation by rotation characterizing quasi-bound states with a given J'' rapidly decrease as v'' becomes larger. They decrease equally fast when J'' increases and v'' is fixed. These observations imply that the spectroscopic detection of the high-lying vibrational states of Mg_2 can only be achieved if the molecule does not rotate too fast (*cf.* Table 2.1 and Fig. 2.2).

As shown in Fig. 2.1, where we plot the wave functions of the high-lying, purely vibrational, states of $^{24}\text{Mg}_2$, starting with the last experimentally observed $v'' = 13$ level, along

with the $X^1\Sigma_g^+$ PEC obtained in our *ab initio* calculations, the $v'' = 18$ state, located only 0.2 cm^{-1} below the potential asymptote, is barely bound (see also Table 2.1). This makes the existence of an additional, $v'' = 19$, level for the most abundant isotopolog of the magnesium dimer unlikely. Further insights into the number of purely vibrational bound states of $^{24}\text{Mg}_2$ supported by the $X^1\Sigma_g^+$ PEC are provided by the inset in Fig. 2.1, where we plot the rotationless $G(v'' + 1) - G(v'')$ energy differences, resulting from the *ab initio* calculations reported in this work and the experiment, as a function of $v'' + 1/2$ (the Birge–Sponer plot). Fitting the experimental data to a line, *i.e.*, assuming a Morse potential, results in $v'' = 16$ being the last bound vibrational level of $^{24}\text{Mg}_2$. Although the deviation from the Morse potential, as predicted by our *ab initio* calculations, is not as severe as in the case of Be_2 [73], it is large enough to result in the $v'' = 17$ and 18 states becoming bound, emphasizing the importance of properly describing the long-range part of the PEC.

As shown in Table 2.1 and Fig. 2.1, the $G(v'' + 1) - G(v'')$ vibrational spacings rapidly decrease with increasing v'' , from 47.7 cm^{-1} or 68.6 K for $v'' = 0$ to 11.7 cm^{-1} or 16.8 K for $v'' = 12$, and to 0.8 cm^{-1} or 1.2 K for $v'' = 17$, when $^{24}\text{Mg}_2$ is considered. This means that at regular temperatures all vibrational levels of the magnesium dimer, which is a very weakly bound system, are substantially populated, making selective probing of the closely spaced higher-energy states, including those with $v'' > 13$, virtually impossible, since practically every molecular collision (*e.g.*, with another dimer) may result in a superposition of many rovibrational states, with some breaking the dimer apart. At room temperature, for example, the cumulative population of the $v'' > 13$ states of $^{24}\text{Mg}_2$, determined using the normalized Boltzmann distribution involving all rotationless levels bound by the $X^1\Sigma_g^+$ potential, of about 12%, is comparable to the populations of the corresponding low-lying states (16% for $v'' = 0$, 13% for $v'' = 1$, and 10% for $v'' = 2$). The situation changes in the cold/ultracold regime, where the available thermal energies, which are on the order of millikelvin or even microkelvin, are much smaller than the vibrational spacings, even when the high-lying states with $v'' > 13$ near the dissociation threshold are considered, suppressing collisional effects

and allowing one to probe the long-range part of the ground-state PEC, where the $v'' > 13$ states largely localize (*cf.* Fig. 2.1). This makes the accurate characterization of the $v'' > 13$ bound and quasi-bound states provided by the high-level *ab initio* calculations reported in this work relevant to the applications involving cold/ultracold Mg atoms separated by larger distances in magneto-optical traps (see, *e.g.*, Ref. [156]).

The accuracy of our *ab initio* description of the more strongly bound $A^1\Sigma_u^+$ electronic state ($D_e = 9414\text{ cm}^{-1}$ and $r_e = 3.0825\text{ Å}$ [170]; *cf.* Fig. 2.3 for the corresponding PEC), which we need to consider to simulate the LIF spectra, is consistent with that obtained for the weakly bound ground state. For example, the errors relative to the experiment [170] resulting from our calculations of the dissociation energy D_e and equilibrium bond length r_e are 0.91% (86 cm^{-1}) and 0.2% (0.006 Å), respectively [2]. This high accuracy of our *ab initio* $A^1\Sigma_u^+$ PEC, obtained using Eq. (2.22), is reflected in the excellent agreement between the $^{24}\text{Mg}_2\ G(v', J')$ values obtained in Ref. [2] and their experimentally derived counterparts reported in Refs. [161, 170]. In particular, the RMSDs characterizing our rovibrational term values in the $A^1\Sigma_u^+$ state relative to the data of Balfour and Douglas [161] and Knöckel *et al.* [170] are only 3.2 and 4.5 cm^{-1} , respectively, which is a major improvement over the RMSD of 30 cm^{-1} reported in Ref. [176]. According to our *ab initio* calculations using the computational protocol described above, the total number of vibrational states supported by the $A^1\Sigma_u^+$ potential well for the most abundant $^{24}\text{Mg}_2$ species is 169 [2].

The most compelling evidence for the predictive power of our *ab initio* electronic structure and rovibrational calculations is the nearly perfect reproduction of the experimental $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ LIF spectrum reported in Refs. [169, 170], shown in Fig. 2.4 and Table 2.3 (The theoretical line intensities shown in Fig.2.4 were normalized such that the tallest peaks in the calculated and experimental LIF spectra corresponding to the $v'' = 5$ P12 line representing the $A^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X^1\Sigma_g^+(v'' = 5, J'' = 12)$ transition match). Figure 2.3 uses our calculated $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ PECs and the corresponding rovibrational wave functions to illustrate the photoexcitation and fluorescence processes that resulted in the experimental

LIF spectrum shown in Fig. 3 of Ref. [169], which is reproduced in Fig. 2.4(a). This particular spectrum represents the fluorescence progression from the $A^1\Sigma_u^+(v' = 3, J' = 11)$ state of $^{24}\text{Mg}_2$, populated by laser excitation from the $X^1\Sigma_g^+(v'' = 5, J'' = 10)$ state, to all accessible $X^1\Sigma_g^+(v'', J'')$ rovibrational levels, resulting in the P12/R10 doublets that correspond to $J'' = 12$ for the P branch and $J'' = 10$ for the R branch. Figure 2.4 and Table 2.3 compare the experimentally observed $A^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X^1\Sigma_g^+(v'', J'' = 10, 12)$ transitions with the corresponding line positions (Fig. 2.4 and Table 2.3) and intensities (Fig. 2.4) resulting from our *ab initio* calculations. As already mentioned earlier, the only adjustment that we made to produce the theoretical LIF spectrum shown in Fig. 2.4 and Table 2.3 was a uniform shift of the entire $A^1\Sigma_u^+$ PEC obtained in our *ab initio* computations to match the experimentally determined adiabatic electronic excitation energy T_e of $26,068.9 \text{ cm}^{-1}$ [170]. Other than that, the theoretical LIF spectrum in Fig. 2.4 and Table 2.3 relies on the raw *ab initio* electronic structure and rovibrational data. Note that in order to produce Fig. 2.4, we superimposed our theoretical $A^1\Sigma_u^+(v', J') \rightarrow X^1\Sigma_g^+(v'', J'' = 10, 12)$ LIF spectrum on top of the experimental one reported in Fig. 3 of Ref. [169]. The theoretical line intensities shown in Fig. 3 were normalized such that the tallest peaks in the calculated and experimental LIF spectra corresponding to the $v'' = 5$ P12 line representing the $A^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X^1\Sigma_g^+(v'' = 5, J'' = 12)$ transition match.

The notable agreement between the theoretical and experimental LIF spectra shown in Fig. 2.4(a) and Table 2.3, with differences in line positions not exceeding 1 to 1.5 cm^{-1} and with virtually identical intensity patterns, suggests that our predicted transition frequencies involving the elusive $v'' > 13$ states are very accurate, allowing us to provide guidance for their potential experimental detection in the future. Before discussing our suggestions in this regard, we note that owing to our *ab initio* calculations, we can now locate the previously unidentified P12/R10 doublets involving the $v'' > 13$ states within the experimental LIF spectrum reported in Fig. 3 of Ref. [169]. Indeed, as shown in Fig. 2.4 and Table 2.3, the LIF spectrum corresponding to the $A^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X^1\Sigma_g^+(v'', J'' = 10, 12)$

transitions contains the P12/R10 doublets involving the $v'' = 0$ to 16 states and the R10 line involving the $v'' = 17$ state. It is worth mentioning that the $A\ ^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X\ ^1\Sigma_g^+(v'' = 17, J'' = 12)$ and $A\ ^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X\ ^1\Sigma_g^+(v'' = 18, J'' = 10, 12)$ transitions are absent, since the $v'' = 17, J'' = 12$ and $v'' = 18, J'' = 10$ and 12 states are unbound, but they could potentially be observed if one used different initial $A\ ^1\Sigma_u^+(v', J')$ states (see the discussion below).

As one can see by inspecting Fig. 2.4, and consistent with the remarks made by Knöckel *et al.* in Ref. [169], the experimental detection of the P12/R10 doublets involving $v'' > 13$, when transitioning from the $A\ ^1\Sigma_u^+(v' = 3, J' = 11)$ state, was hindered by the unfavorable signal-to-noise ratio (transitions to the $v'' = 16$ and 17 states exhibit low Einstein coefficients) and the presence of overlapping lines outside the P12/R10 progression, originating from collisional relaxation effects [169] and having similar ($v'' = 15$) or higher ($v'' = 14$) intensities. To fully appreciate this, in Fig. 2.4(b), we magnified the region of the LIF spectrum recorded in Ref. [169] that contains the calculated $A\ ^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X\ ^1\Sigma_g^+(v'' = 13 \text{ to } 16, J'' = 10, 12)$ and $A\ ^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X\ ^1\Sigma_g^+(v'' = 17, J'' = 10)$ transitions. As shown in Fig. 2.4 and Table 2.3, the identification of the P12/R10 doublets corresponding to the $A\ ^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X\ ^1\Sigma_g^+(v'' = 0 \text{ to } 13, J'' = 10, 12)$ transitions is unambiguous. The observed and calculated line positions and intensities and line intensity ratios within every doublet match each other very closely. Figure 2.4(b) demonstrates that the identification of the remaining doublets in the P12/R10 progression is much harder. On the basis of our *ab initio* work and taking into account the fact that our calculated line positions may be off by about 1 cm^{-1} (*cf.* Table 2.3), the $v'' = 14$ P12/R10 doublet, marked in Fig. 2.4(b) by the blue arrows originating from the $v'' = 14$ label, is largely hidden behind the higher-intensity feature that does not belong to the P12/R10 progression and that most likely originates from collisional relaxation [169]. Because of our calculations, we can also point to the most likely location of the $v'' = 15$ P12/R10 doublet in the LIF spectrum recorded in Ref. [169] [see the blue arrows originating from the $v'' = 15$ label in Fig. 2.4(b)]. Doing this

without backing from the theory is virtually impossible due to the presence of other lines near the $A^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X^1\Sigma_g^+(v'' = 15, J'' = 10, 12)$ transitions having similar intensities. As shown in Fig. 2.4(b), the situation with the remaining $A^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X^1\Sigma_g^+(v'' = 16, J'' = 10, 12)$ and $A^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X^1\Sigma_g^+(v'' = 17, J'' = 10)$ transitions is even worse, since they have very low Einstein coefficients that hide them in the noise.

In general, our *ab initio* calculations carried out in this work indicate that under the constraints of the LIF experiments reported in Refs. [169, 170], where the authors populated the $A^1\Sigma_u^+(v', J')$ states with $v' = 1$ to 46, the $X^1\Sigma_g^+(v'', J'')$ states with $v'' = 14$ to 18 cannot be realistically detected because of very small Franck–Condon factors and Einstein coefficients characterizing the corresponding $A^1\Sigma_u^+(v', J') \rightarrow X^1\Sigma_g^+(v'', J'')$ transitions [2]. As shown in Fig. 2.1, the $v'' = 14$ to 18 states are predominantly localized in the long-range $r = 8$ to 16 Å region. At the same time, as illustrated in Fig. 2.3, the potential well characterizing the electronically excited $A^1\Sigma_u^+$ state is much deeper and shifted toward shorter internuclear separations compared to its $X^1\Sigma_g^+$ counterpart. Thus, the only way to access the $X^1\Sigma_g^+(v'', J'')$ states with $v'' = 14$ to 18 via fluorescence from $A^1\Sigma_u^+$ is by populating the high-lying $A^1\Sigma_u^+(v', J')$ levels with $v' \gg 46$.

In an effort to assist the experimental community in detecting the elusive $v'' = 14$ to 18 vibrational levels, we searched for the $A^1\Sigma_u^+(v', J') \rightarrow X^1\Sigma_g^+(v'' = 14 \text{ to } 18, J'' = J' \pm 1)$ transitions in the most abundant isotopolog of the magnesium dimer, $^{24}\text{Mg}_2$, that would result in spectral lines of maximum intensity based on the computed Einstein coefficients. To ensure the occurrence of allowed transitions involving the last, $v'' = 18$, level, which for $^{24}\text{Mg}_2$ becomes unbound when $J'' > 4$, we focused on the J'' values not exceeding 4, *i.e.*, the fluorescence from the $A^1\Sigma_u^+(v', J')$ states with $J' = 1, 3$, and 5. According to our calculations, the optimum v' values for observing the $v'' = 14$ to 18, $J'' \leq 4$ states via the LIF spectroscopy are in the neighborhood of $v' = 60, 66$ to 69, and 74 to 84 for $v'' = 14$; 72 to 75 and 80 to 91 for $v'' = 15$; 79 to 82 and 88 to 100 for $v'' = 16$; 88, 89,

and 97 to 111 for $v'' = 17$; and 109 to 129 for $v'' = 18$ [see Ref. [2] for the details of all allowed rovibronic transitions in $^{24}\text{Mg}_2$ involving the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ states, including, in particular, the relevant $X^1\Sigma_g^+(v'', J'' \leq 4) \rightarrow A^1\Sigma_u^+(v', J')$ pump and $A^1\Sigma_u^+(v', J' = 1, 3, 5) \rightarrow X^1\Sigma_g^+(v'' = 14 \text{ to } 18, J'' \leq 4)$ fluorescence processes]. In determining these optimum v' values, we chose the cutoff value of 1.0×10^7 Hz in the Einstein coefficients, which is similar to the Einstein coefficients calculated for the most intense $v'' = 5$ P12/R10 doublet in the experimental LIF spectrum shown in Fig. 3 of Ref. [169], reproduced in Fig. 2.4(a). Our predicted $A^1\Sigma_u^+(v', J' = 1, 3, 5) \rightarrow X^1\Sigma_g^+(v'' = 14 \text{ to } 18, J'' \leq 4)$ fluorescence frequencies resulting from the aforementioned optimum v' ranges, which might allow one to detect the $v'' = 14$ to 18 states of $^{24}\text{Mg}_2$ via a suitably designed LIF experiment, are estimated at about 33,360, 33,740 to 33,910, and 34,150 to 34,530 cm^{-1} for $v'' = 14$; 34,050 to 34,190 and 34,390 to 34,710 cm^{-1} for $v'' = 15$; 34,350 to 34,460 and 34,640 to 34,880 cm^{-1} for $v'' = 16$; 34,630 to 34,660 and 34,830 to 35,000 cm^{-1} for $v'' = 17$; and 34,990 to 35,100 cm^{-1} for $v'' = 18$ [given the 86 cm^{-1} error in the calculated D_e characterizing the $A^1\Sigma_u^+$ state and the RMSD of ~ 3 to 5 cm^{-1} in our $^{24}\text{Mg}_2$ $G(v', J')$ values relative to the spectroscopic data of Refs. [169, 170], the above frequency ranges may have to be shifted by a dozen or so cm^{-1}].

As shown by the results reported in Ref. [2] and summarized above, the results of our high-level CC/EOMCC and FCI computations show an unprecedented level of accuracy relative to the available experimental data of the magnesium dimer. Thus, we are now well positioned to comment on the convergence of our computational protocol employed in Ref. [2]. In particular, let us focus on the ground $X^1\Sigma_g^+$ PEC of Mg_2 , where the D_e and vibrational term values characterizing the $^{24}\text{Mg}_2$ isotopolog are accurate to within ~ 1 cm^{-1} relative to experimentally available data. In our discussion, we rely on the results of the auxiliary calculations reported in Ref. [2] employing the aug-cc-pV(T+d)Z, aug-cc-pwCVTZ, and aug-cc-pwCV5Z bases of Ref. [179], taken from the Peterson group's website [180], which we abbreviate as A(T+d)Z, AwCTZ, and AwC5Z, respectively.

To begin with, as shown in Ref. [2], the valence FCI correction on top of CCSDT in

Eq. (2.21), *i.e.*, the $E_{X^1\Sigma_g^+}^{\text{FCI/A(Q+d)Z}} - E_{X^1\Sigma_g^+}^{\text{CCSDT/A(Q+d)Z}}$ contribution to the $X^1\Sigma_g^+$ energetics, are well converged with respect to the size of the basis set. Indeed, if we compare the valence FCI correction in Eq. (2.21) with its less saturated counterpart, in which we replace the A(Q+d)Z basis set used in Ref. [2] by its smaller A(T+d)Z counterpart, *i.e.*, $E_{X^1\Sigma_g^+}^{\text{FCI/A(T+d)Z}} - E_{X^1\Sigma_g^+}^{\text{CCSDT/A(T+d)Z}}$, the changes in the valence FCI correction are $\sim 1 \text{ cm}^{-1}$ or less throughout the entire 3.2–1.00 Å range of Mg–Mg separations considered in our computations. One could instead consider improving Eq. (2.21) by extrapolating, for example, the nearly all-electron CCSDT energetics to the CBS limit. Unfortunately, a widely used two-point CBS extrapolation [190, 191] based on the subvalence CCSDT/AwCTZ and CCSDT/AwCQZ data, which are the only CCSDT data of this type available to us, to determine the CBS counterpart of the first term on the right-hand side of Eq. (2.21) would not be reliable enough. As demonstrated in Ref. [1] and as elaborated on in the Supplementary Materials to Ref. [2], a CBS extrapolation using the AwCTZ and AwCQZ basis sets worsens, instead of improving, the D_e , r_e , and vibrational term values of the magnesium dimer compared to the unextrapolated results using the AwCQZ basis. The CBS extrapolation using the AwCQZ and AwC5Z basis sets would be accurate enough, but the CCSDT/AwC5Z calculations for the magnesium dimer correlating all electrons but the 1s shells of Mg atoms turned out to be prohibitively expensive for us.

One could try to address the above concern by replacing CCSDT in Eq. (2.21) by the more affordable CCSD(T) approach, resulting in

$$\tilde{E}_{X^1\Sigma_g^+} = E_{X^1\Sigma_g^+}^{\text{CCSD(T)/AwCQZ}} + \left(E_{X^1\Sigma_g^+}^{\text{FCI/A(Q+d)Z}} - E_{X^1\Sigma_g^+}^{\text{CCSD(T)/A(Q+d)Z}} \right), \quad (2.23)$$

but the computational protocol defined by Eq. (2.23) is not sufficiently accurate for the spectroscopic considerations reported in this work due to the inadequate treatment of triples by the baseline CCSD(T) approximation. Indeed, this is demonstrated in Fig. 2.5, where we compare the rotationless vibrational term values for the $X^1\Sigma_g^+$ state obtained from our *ab initio* computations employing Eqs. (2.21) and (2.23) against their experimental counterparts [161, 166] (see the Supplementary Materials to Ref. [2] for further details on

how the experimental $G(v'' = 0 \text{ to } 13, J'' = 0)$ data were obtained). As shown in Fig. 2.5, our computational protocol based on the nearly all-electron CCSDT/AwCQZ and valence CCSDT/A(Q+d)Z and FCI/A(Q+d)Z calculations, as in Eq. (2.21), produces the $G(v'', J'' = 0)$ values that can hardly be distinguished from their experimentally derived counterparts, with errors not exceeding 1.4 cm^{-1} or 0.5%, when all experimentally observed $v'' = 0\text{--}13$ states are considered. What is especially important, errors in the $G(v'', J'' = 0)$ values resulting from the computational protocol based on Eq. (2.21) relative to experiment remain small for all v'' values. They slightly increase in the $v'' = 0\text{--}9$ region, from 0.0 cm^{-1} for $v'' = 0$ to 1.4 cm^{-1} for $v'' = 8$ and 9 , but then they decrease again, to 0.7 cm^{-1} when the last experimentally observed $v'' = 13$ level is considered. These observations should be contrasted with the results obtained using Eq. (2.23), where full CCSDT is replaced by CCSD(T). As demonstrated in Fig. 2.5, errors in the $G(v'', J'' = 0)$ energies obtained for the $X^1\Sigma_g^+$ potential resulting from Eq. (2.23) steadily grow with v'' , from 0.7 cm^{-1} for $v'' = 0$ to 14.7 cm^{-1} for $v'' = 13$, representing 3–4% of the corresponding experimentally derived $G(v'', J'' = 0)$ values. This clearly implies that it is not sufficient to run the CCSD(T) calculations for the purpose of capturing the bulk of many-electron correlation effects, assuming that one can incorporate the missing correlations with the help of valence FCI. If one is interested in attaining the nearly spectroscopic (1 cm^{-1} -type) accuracy, the bulk of the correlation effects must be captured by the more complete treatment of the connected triply excited clusters, beyond CCSD(T), which in the case of the $X^1\Sigma_g^+$ PEC is represented in this study by full CCSDT, prior to applying the FCI-based correction. Otherwise, there is a significant risk of introducing substantial errors in the calculated vibrational term values. Given the nearly linear error growth characterizing the $G(v'', J'' = 0)$ values corresponding to the $X^1\Sigma_g^+$ potential obtained using Eq. (2.23), seen in Fig. 2.5, one should not use CCSD(T) as a substitute for CCSDT in Eq. (2.21) in calculations involving higher-energy vibrational levels. In particular, the CCSD(T)-based composite approach defined by Eq. (2.23) is unsuitable for locating the elusive $v'' = 14\text{--}18$ states of the magnesium dimer. One

can see this by comparing, for example, the nearly 15 cm^{-1} error in the $G(v'' = 13, J'' = 0)$ energy obtained using the $X^1\Sigma_g^+$ PEC resulting from Eq. (2.23), which, according to Fig. 2.5, is expected to become even larger for $v'' > 13$ (*cf.*, also, Ref. [1]), with the small spacings between the consecutive vibrational levels in the $v'' = 14$ – 18 region. Indeed, based on our best *ab initio* calculations summarized in Table 2.1, these spacings decrease from about 6 cm^{-1} for the $G(v'' = 15, J'' = 0) - G(v'' = 14, J'' = 0)$ difference to $\sim 1\text{ cm}^{-1}$ when the gap between the rotationless $v'' = 17$ and $v'' = 18$ states is considered. For all these reasons, we have to rely on Eq. (2.21) in our calculations for the magnesium dimer, in which we use CCSDT, not CCSD(T), and finite (albeit large and carefully optimized) AwCQZ and A(Q+d)Z basis sets rather than the poor-quality CBS extrapolation from the CCSDT/AwCTZ and CCSDT/AwCQZ information. This analysis also highlights the need for robust approximations to high-level CC methods, such as CCSDT and CCSDTQ, which is exactly the main focus of the following chapters.

Table 2.1: Comparison of the *ab initio* (Calc.) and experimentally derived (Expt) rovibrational $G(v'', J'')$ energies for selected values of J'' characterizing $^{24}\text{Mg}_2$ in the ground electronic state (in cm^{-1}), along with the corresponding dissociation energies D_e (in cm^{-1}) and equilibrium bond lengths r_e (in Å). The $G(v'', J'')$ energies calculated using the *ab initio* X $^1\Sigma_g^+$ PEC defined by Eq. (2.21) are reported as errors relative to experiment, whereas D_e and r_e are the actual values of these quantities. If the experimental $G(v'', J'')$ energies are not available, we provide their calculated values in square brackets. Quasi-bound rovibrational levels are given in italics. Horizontal bars indicate term values not supported by the X $^1\Sigma_g^+$ PEC. Adapted from Ref. [2].

v''	$G(v'', J'' = 0)$		$G(v'', J'' = 20)$		$G(v'', J'' = 40)$		$G(v'', J'' = 60)$		$G(v'', J'' = 80)$	
	Calc.	Expt ^a	Calc.	Expt ^b	Calc.	Expt ^b	Calc.	Expt ^b	Calc.	Expt ^b
0	0.0	25.2	−0.2	63.3	−0.4	171.2	−0.9	340.4	−1.8	<i>552.8</i>
1	−0.2	73.0	−0.4	109.7	−0.7	213.1	−1.2	374.6	−2.2	<i>573.2</i>
2	−0.5	117.8	−0.7	153.0	−1.0	252.0	−1.6	405.4	[<i>585.0</i>]	
3	−0.7	159.4	−1.0	193.2	−1.3	287.7	−1.9	<i>432.9</i>	—	
4	−0.9	198.0	−1.3	230.3	−1.6	320.3	−2.1	<i>456.7</i>	—	
5	−1.1	233.6	−1.5	264.4	−1.8	349.7	−2.1	<i>476.5</i>	—	
6	−1.2	266.2	−1.7	295.5	−1.9	375.9	−1.7	<i>491.7</i>	—	
7	−1.3	295.8	−1.8	323.6	−1.9	398.8		—	—	
8	−1.4	322.5	−1.7	348.5	−1.7	418.1		—	—	
9	−1.4	346.2	−1.6	370.3	−1.4	<i>433.9</i>		—	—	
10	−1.3	366.8	−1.4	389.0	[<i>444.5</i>]			—	—	
11	−1.2	384.4	−1.2	404.4	[<i>451.6</i>]			—	—	
12	−0.9	398.8	−0.9	416.6	—			—	—	
13	−0.7	410.3	−0.5	425.5	—			—	—	
14	[418.4]		[431.1]		—			—	—	
15	[424.6]		—		—			—	—	
16	[428.4]		—		—			—	—	
17	[430.4]		—		—			—	—	
18	[431.2]		—		—			—	—	
D_e	431.4	430.472 ^c								
r_e	3.893	3.89039 ^c								

^aExperimentally derived values for $v'' = 0$ to 12 taken from Ref. [161]. The $v'' = 13$ value is calculated as $G(v'' = 13, J'' = 14) - 210B(v'' = 13, J'' = 14)$ with the information about $G(v'' = 13, J'' = 14)$ and $B(v'' = 13, J'' = 14)$ taken from Ref. [166].

^bExperimentally derived values taken from the supplementary material of Ref. [169].

^cExperimentally derived values taken from Ref. [169, 170] assuming the X-representation of the X $^1\Sigma_g^+$ potential developed in Ref. [169].

Table 2.2: Comparison of the rovibrational $G(v'', J'')$ energies obtained using the *ab initio* X $^1\Sigma_g^+$ PEC (Calc.) and its X-representation counterpart constructed in Ref. [169] (X-rep.) for selected values of J'' characterizing $^{24}\text{Mg}_2$ in the ground electronic state (in cm^{-1}), along with the corresponding dissociation energies D_e (in cm^{-1}) and equilibrium bond lengths r_e (in Å). The $G(v'', J'')$ energies calculated using the *ab initio* X $^1\Sigma_g^+$ PEC defined by Eq. (2.21) are reported as errors relative to experiment, whereas D_e and r_e are the actual values of these quantities. If the experimental $G(v'', J'')$ energies are not available, we provide their calculated values in square brackets. Quasi-bound rovibrational levels are given in italics. Horizontal bars indicate term values not supported by the X $^1\Sigma_g^+$ PEC. Adapted from Ref. [2].

v''	$G(v'', J'' = 0)$		$G(v'', J'' = 20)$		$G(v'', J'' = 40)$		$G(v'', J'' = 60)$		$G(v'', J'' = 80)$		
	Calc.	X-rep.	Calc.	X-rep.	Calc.	X-rep.	Calc.	X-rep.	Calc.	X-rep.	
0	-0.1	25.2	-0.2	63.3	-0.4	171.2	-0.9	340.4	-1.8	<i>552.8</i>	
1	-0.3	73.1	-0.4	109.7	-0.7	213.1	-1.2	374.6	-2.2	<i>573.2</i>	
2	-0.6	117.9	-0.7	153.0	-1.0	252.0	-1.6	405.4	[<i>585.0</i>]		
3	-0.9	159.6	-1.0	193.2	-1.3	287.7	-1.9	<i>432.9</i>	—		
4	-1.1	198.2	-1.2	230.3	-1.6	320.3	-2.1	<i>456.7</i>	—		
5	-1.4	233.9	-1.5	264.4	-1.8	349.7	-2.1	<i>476.5</i>	—		
6	-1.5	266.5	-1.6	295.5	-1.9	375.9	-1.7	<i>491.7</i>	—		
7	-1.7	296.2	-1.7	323.5	-1.9	398.8		—	—		
8	-1.7	322.8	-1.7	348.5	-1.7	418.1		—	—		
9	-1.6	346.4	-1.6	370.3	-1.4	<i>433.8</i>		—	—		
10	-1.5	367.0	-1.4	389.0	-1.0	[<i>445.5</i>]		—	—		
11	-1.3	384.5	-1.2	404.4		[<i>451.6</i>]		—	—		
12	-1.0	399.0	-0.9	416.6		—		—	—		
13	-0.7	410.4	-0.5	425.5		—		—	—		
14	-0.5	418.9	-0.2	<i>431.2</i>		—		—	—		
15	-0.2	424.7		—		—		—	—		
16	0.2	428.3		—		—		—	—		
17	0.5	429.9		—		—		—	—		
18	0.8	430.4		—		—		—	—		
D_e	431.4	430.472									
r_e	3.893	3.89039									

Table 2.3: Comparison of the theoretical line positions of the $A\ ^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X\ ^1\Sigma_g^+(v'', J'' = 10, 12)$ fluorescence progression in the LIF spectrum of $^{24}\text{Mg}_2$ calculated in this work with experiment. All line positions are in cm^{-1} . The available experimental values are the actual line positions, whereas our calculated results are errors relative to experiment. If the experimentally determined line positions are not available, we provide their calculated values in square brackets. Horizontal bars indicate term values not supported by the $X\ ^1\Sigma_g^+$ PEC. Adapted from Ref. [2].

v''	P12		R10	
	Calc.	Expt. ^a	Calc.	Expt. ^a
0	-1.5	26,701.9	-1.5	26,706.0
1	-1.2	26,654.5	-1.3	26,658.5
2	-1.0	26,610.3	-1.0	26,614.1
3	-0.7	26,569.2	-0.7	26,572.8
4	-0.4	26,531.1	-0.5	26,534.6
5	-0.2	26,496.0	-0.2	26,499.3 ^b
6	0.0	26,463.9	[26,467.1]	
7	0.1	26,434.9	0.1	26,437.9
8	0.1	26,408.8	0.1	26,411.7
9	0.0	26,385.9	0.0	26,388.5
10	-0.2	26,366.0	-0.2	26,368.4
11	-0.4	26,349.2	-0.4	26,351.4
12	-0.7	26,335.6	-0.6	26,337.5
13	-1.0	26,325.0	-0.9	26,326.7
14	[26,316.2]		[26,317.7]	
15	[26,311.1]		[26,312.2]	
16	[26,308.4]		[26,309.1]	
17	—		[26,308.0]	
18	—		—	

^aDifferences between the experimental $X\ ^1\Sigma_g^+(v'', J'' = 10, 12)$ and $A\ ^1\Sigma_u^+(v' = 3, J' = 11)$ term values reported in the supplementary material of Ref. [170] (see the Supplementary Materials of Ref. [2] for further details), unless stated otherwise.

^bThe $X\ ^1\Sigma_g^+(v'' = 5, J'' = 10) \rightarrow A\ ^1\Sigma_u^+(v' = 3, J' = 11)$ pump frequency reported in Fig. 3 of Ref. [169].

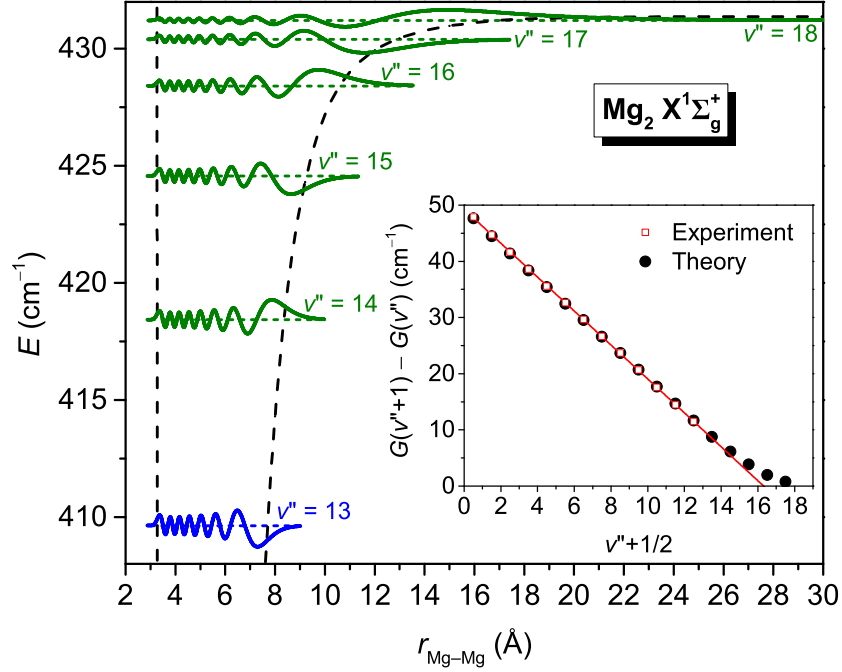


Figure 2.1: The wave functions of the high-lying, purely vibrational, states of $^{24}\text{Mg}_2$ and the underlying $X^1\Sigma_g^+$ potential. The last experimentally observed $v'' = 13$ level is marked in blue, the predicted $v'' = 14$ to 18 levels are marked in green, and the *ab initio* $X^1\Sigma_g^+$ PEC obtained in this study is marked by a long-dashed black line. The inset is a Birge–Spencer plot comparing the rotationless $G(v'' + 1) - G(v'')$ energy differences as functions of $v'' + 1/2$ obtained in this work (black circles) with their experimentally derived counterparts (red open squares) based on the data reported in Refs. [161] ($v'' = 0$ to 12) and [166] ($v'' = 13$; *cf.* also Table 2.1). The red solid line is a linear fit of the experimental points. Adapted from Ref. [2].

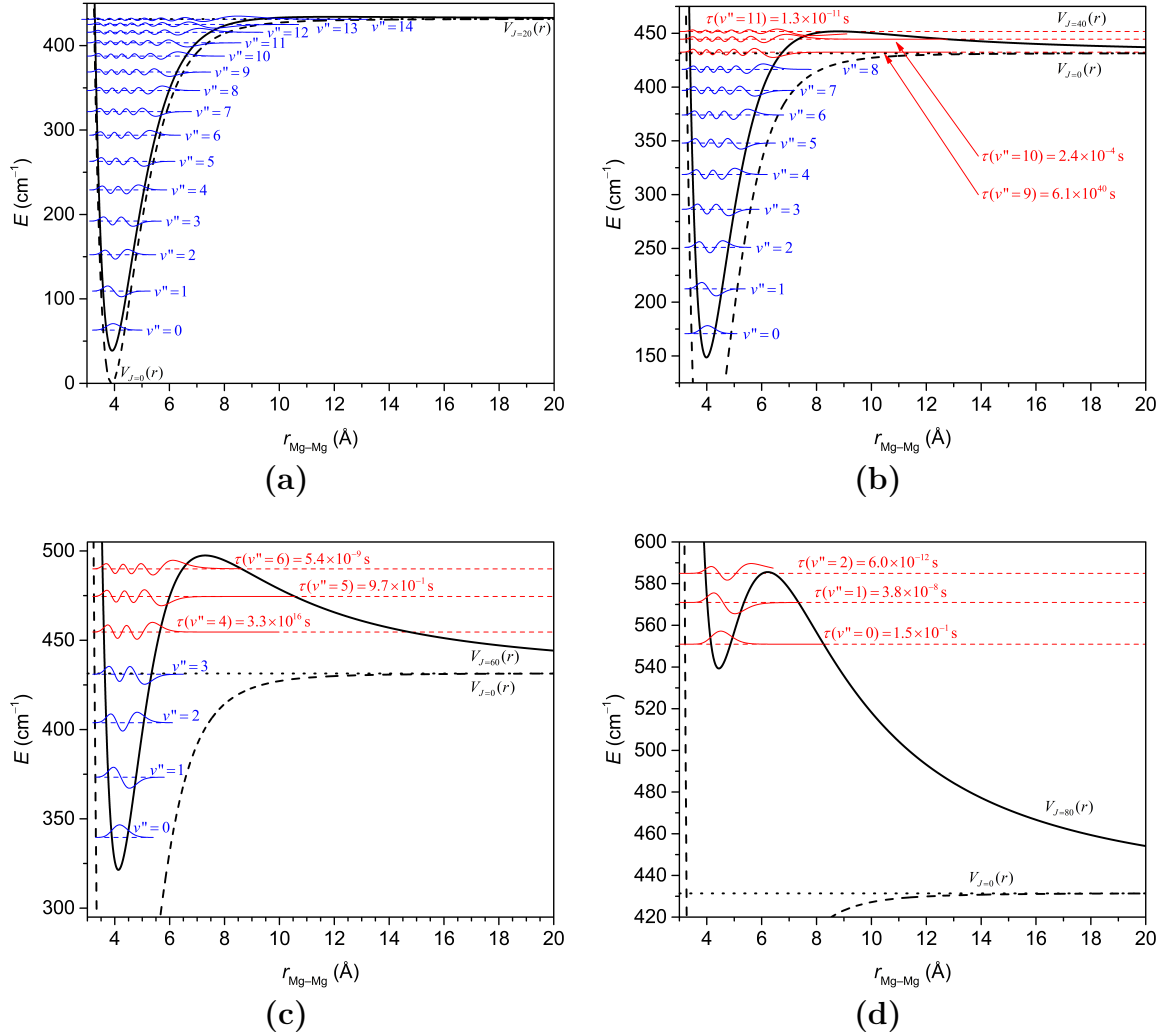


Figure 2.2: The $V_{J''}(r)$ effective potentials including centrifugal barriers characterizing the rotating $^{24}\text{Mg}_2$ molecule at selected values of J'' , along with the corresponding vibrational wave functions and information about the lifetimes for predissociation by rotation, $\tau(v'')$, characterizing quasi-bound states. The selected values of J'' used to construct the effective potentials $V_{J''}(r)$ (black curves) and determine the corresponding bound (blue lines) and quasi-bound (red lines) vibrational wave functions are (a) 20, (b) 40, (c) 60, and (d) 80. The black dashed line represents the rotationless, purely electronic, $X^1\Sigma_g^+$ potential $V(r) = V_{J''=0}(r)$ calculated using the *ab initio* composite scheme defined by Eq. (2.21). The horizontal black dotted line at 431.4 cm^{-1} marks the dissociation threshold of the *ab initio* $X^1\Sigma_g^+$ potential. Adapted from Ref. [2].

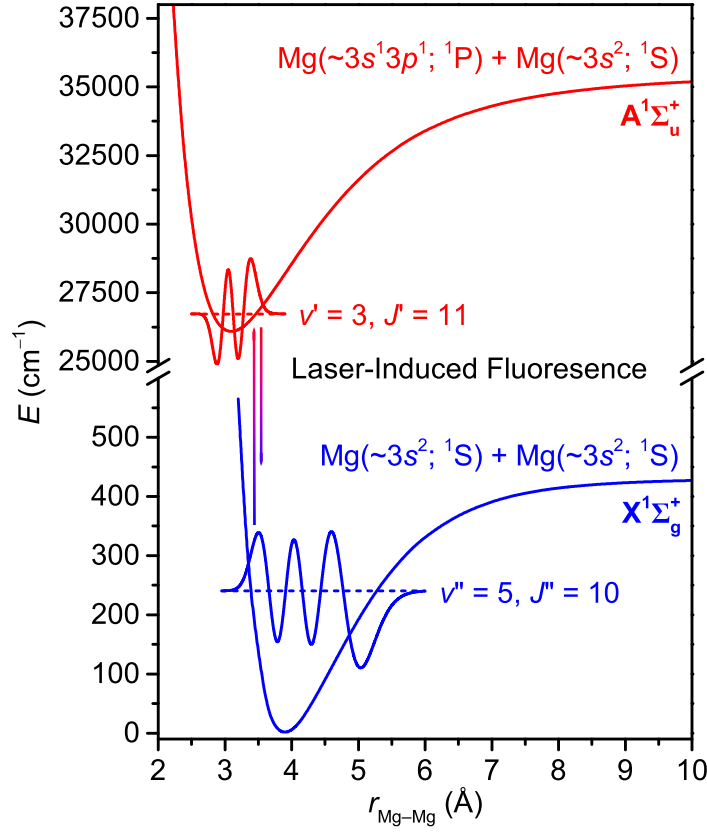


Figure 2.3: Schematics of the pump, $X^1\Sigma_g^+(v'' = 5, J'' = 10) \rightarrow A^1\Sigma_u^+(v' = 3, J' = 11)$, and fluorescence, $A^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X^1\Sigma_g^+(v'', J'' = 10, 12)$, processes resulting in the LIF spectrum for $^{24}\text{Mg}_2$ shown in Fig. 3 of Ref. [169]. The $A^1\Sigma_u^+$ and $A^1\Sigma_u^+$ PECs and the corresponding $X^1\Sigma_g^+(v'' = 5, J'' = 10)$ and $A^1\Sigma_u^+(v' = 3, J' = 11)$ rovibrational wave functions were calculated in this work. The $A^1\Sigma_u^+$ PEC was shifted to match the experimentally determined adiabatic electronic excitation energy T_e of $26,068.9 \text{ cm}^{-1}$ [170]. Adapted from Ref. [2].

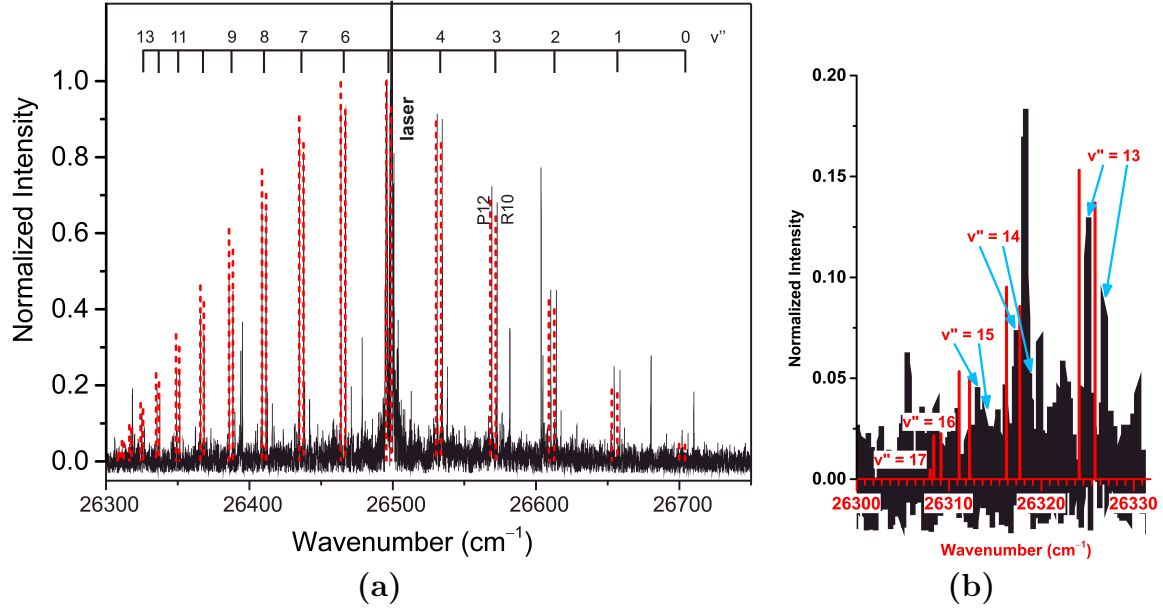


Figure 2.4: The $A\ ^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X\ ^1\Sigma_g^+(v'', J'' = 10, 12)$ LIF spectrum of $^{24}\text{Mg}_2$. (a) Comparison of the experimental $A\ ^1\Sigma_u^+(v' = 3, J' = 11) \rightarrow X\ ^1\Sigma_g^+(v'', J'' = 10, 12)$ fluorescence progression (black solid lines; adapted from Fig. 3 of Ref. [169] with the permission of AIP Publishing) with its *ab initio* counterpart obtained in this work (red dashed lines). The theoretical line intensities were normalized such that the tallest peaks in the calculated and experimental spectra corresponding to the $v'' = 5$ P12 line match. (b) Magnification of the low-energy region of the LIF spectrum shown in (a), with red solid lines representing the calculated transitions. The blue arrows originating from the $v'' = 13$ label indicate the location of the experimentally observed $v'' = 13$ P12/R10 doublet. The blue arrows originating from the $v'' = 14$ and 15 labels point to the most probable locations of the corresponding P12/R10 doublets. Spectral lines involving $v'' = 16$ and 17 are buried in the noise (see also Table 2.3). Adapted from Ref. [2].

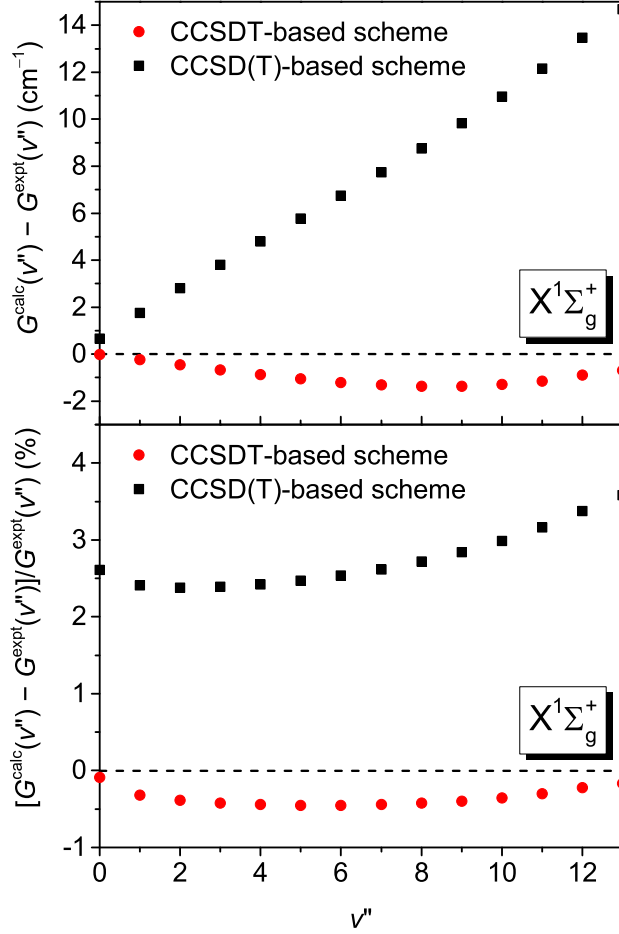


Figure 2.5: Comparison of the vibrational term values characterizing $^{24}\text{Mg}_2$ supported by the *ab initio* $X^1\Sigma_g^+$ potential calculated in Ref. [2] with their experimentally derived counterparts. The top and bottom panels show the errors and relative errors, respectively, in the $G(v'', J'' = 0)$ vibrational energies corresponding to the $X^1\Sigma_g^+$ PECs obtained using the CCSDT-based composite scheme defined by Eq. (2.21) and its CCSD(T)-based analog defined by Eq. (2.23) relative to the experimentally derived data [161, 166]. Adapted from Ref. [2].

CHAPTER 3

THE $CC(P;Q)$ FORMALISM

3.1 Introduction to the $CC(P;Q)$ Methodology

As mentioned in the Introduction, the $CC(P;Q)$ approach provides a robust way of systematically approaching the energetics obtained using high-level CCSDT/EOMCCSDT, CCSDTQ/EOMCCSDTQ, *etc.* parent methods, while avoiding failures of perturbative approaches, without resorting to the full computational costs. The idea behind the $CC(P;Q)$ formalism dates back to the original MMCC expansions of Refs. [78–80] (see Refs. [83] and [84] for reviews), where one applies a nonperturbative, noniterative correction to the energy obtained in a lower-order CC/EOMCC computation. While the MMCC ideas can be used in a plethora of ways, we will focus on the form of $CC(P;Q)$ energy correction which resulted from generalization of the biorthogonal formulation of MMCC [74, 89–91]. In this section, we will summarize the key concepts and equations behind the $CC(P;Q)$ theory relevant to the works described in this dissertation.

The key component of the $CC(P;Q)$ theory is the identification of two disjoint subspaces of the N -electron Hilbert space, $\mathcal{H}$, which are designated as the P and Q spaces or $\mathcal{H}^{(P)}$ and $\mathcal{H}^{(Q)}$, respectively. The P space is spanned by excited Slater determinants $|\Phi_K\rangle$, which together with the reference determinant $|\Phi\rangle$ dominates the many-electron wave function. On the other hand, the Q space is spanned by the excited determinants that are utilized to construct the noniterative correction to the electronic energy obtained by solving the CC/EOMCC equations in the P space.

Once the P and Q spaces are appropriately defined, we then proceed as follows. In the first, iterative, part of a $CC(P;Q)$ computation, designated as $CC(P)/EOMCC(P)$, we begin

by approximating the T , R_μ , and L_μ operators, used in Eqs. (2.1), (2.3), and (2.11), as

$$T \approx T^{(P)} = \sum_{|\Phi_K\rangle \in \mathcal{H}^{(P)}} t_K E_K, \quad (3.1)$$

$$R_\mu \approx R_\mu^{(P)} = r_{\mu,0} \mathbf{1} + \sum_{|\Phi_K\rangle \in \mathcal{H}^{(P)}} r_{\mu,K} E_K, \quad (3.2)$$

and

$$L_\mu \approx L_\mu^{(P)} = \delta_{\mu 0} \mathbf{1} + \sum_{|\Phi_K\rangle \in \mathcal{H}^{(P)}} l_{\mu,K} (E_K)^\dagger, \quad (3.3)$$

respectively, where E_K is the usual particle-hole excitation operator that generates the excited Slater determinants $|\Phi_K\rangle = E_K |\Phi\rangle$. Note that in Eqs. (3.1)–(3.3), we explicitly restrict the many-body expansion of T , R_μ , and L_μ to the P space.

We then proceed to solving the CC/EOMCC equations in the P space. In the case of the ground state, we insert the CC(P) wave function $|\Psi_0^{(P)}\rangle = e^{T^{(P)}} |\Phi\rangle$ into the Schrödinger equation to form the connected cluster form of the Schrödinger equation in the P space, $\bar{H}^{(P)} |\Phi\rangle = E_0^{(P)} |\Phi\rangle$, and projecting it onto excited determinants in the P space to obtain the system of nonlinear equations

$$\langle \Phi_K | \bar{H}^{(P)} | \Phi \rangle = 0 \quad \forall |\Phi_K\rangle \in \mathcal{H}^{(P)}, \quad (3.4)$$

where $\bar{H}^{(P)} = e^{-T^{(P)}} H e^{T^{(P)}} = (H e^{T^{(P)}})_C$ is the similarity-transformed Hamiltonian in the P space and $E_0^{(P)}$ is the ground-state CC(P) energy. After solving Eq. (3.4) for the cluster amplitudes t_K in the usual way, the CC(P) energy is computed as

$$E_0^{(P)} = \langle \Phi | \bar{H}^{(P)} | \Phi \rangle. \quad (3.5)$$

Subsequently, the excitation amplitudes $r_{\mu,K}$ and excitation energies $\omega_\mu^{(P)} = E_\mu^{(P)} - E_0^{(P)}$ associated with the EOMCC(P) wave function $|\Psi_\mu^{(P)}\rangle = R_\mu^{(P)} e^{T^{(P)}} |\Phi\rangle$ are determined by diagonalizing the similarity-transformed Hamiltonian $\bar{H}^{(P)}$ in the P space (for simplicity, we assume that the excited state of interest has the same symmetry as the ground state; we

will discuss the necessary adjustment for excited states having different symmetries from the ground state later), which correspond to solving the eigenvalue problem

$$\langle \Phi_K | (\overline{H}_{\text{open}}^{(P)} R_{\mu, \text{open}}^{(P)})_C | \Phi \rangle = \omega_{\mu}^{(P)} r_{\mu, K} \quad \forall |\Phi_K\rangle \in \mathcal{H}^{(P)}, \quad (3.6)$$

where $\overline{H}_{\text{open}}^{(P)} = \overline{H}^{(P)} - E_0^{(P)} \mathbf{1}$ and $R_{\mu, \text{open}}^{(P)} = R_{\mu}^{(P)} - r_{\mu, 0} \mathbf{1}$. The zeroth-body component of $R_{\mu}^{(P)}$ is computed *a posteriori* in the usual way as

$$r_{\mu, 0} = \langle \Phi | (\overline{H}_{\text{open}}^{(P)} R_{\mu, \text{open}}^{(P)})_C | \Phi \rangle / \omega_{\mu}^{(P)}. \quad (3.7)$$

In addition to the above CC(P)/EOMCC(P) steps, we also solve the corresponding left CC/EOMCC system of equations in the P space,

$$\delta_{\mu 0} \langle \Phi | \overline{H}_{\text{open}}^{(P)} | \Phi_K \rangle + \langle \Phi | L_{\mu, \text{open}}^{(P)} \overline{H}_{\text{open}}^{(P)} | \Phi_K \rangle = \omega_{\mu}^{(P)} l_{\mu, K} \quad \forall |\Phi_K\rangle \in \mathcal{H}^{(P)}, \quad (3.8)$$

for the $l_{\mu, K}$ amplitudes defining the EOMCC(P) bra state $\langle \tilde{\Psi}_{\mu}^{(P)} | = \langle \Phi | L_{\mu}^{(P)} e^{-T^{(P)}}$, which are necessary to construct the CC($P; Q$) energy correction (*vide infra*), while enforcing the biorthonormality condition $\langle \Phi | L_{\mu}^{(P)} R_{\nu}^{(P)} | \Phi \rangle = \delta_{\mu\nu}$ as described earlier.

Once the iterative CC(P)/EOMCC(P) procedure is completed, we proceed to the second key step in the CC($P; Q$) calculation, namely, the noniterative determination of energy correction for the many-electron correlation effects of interest with the help of the Q -space determinants. The CC($P; Q$) energy correction used in this dissertation has the form [74, 75]

$$\delta_{\mu}(P; Q) = \sum_{|\Phi_K\rangle \in \mathcal{H}^{(Q)}} \ell_{\mu, K}(P) \mathfrak{M}_{\mu, K}(P), \quad (3.9)$$

where

$$\mathfrak{M}_{\mu, K}(P) = \langle \Phi_K | \overline{H}^{(P)} R_{\mu}^{(P)} | \Phi \rangle \quad (3.10)$$

is the generalized moments of CC/EOMCC equations corresponding to projection of the connected cluster form of Schrödinger equation containing the CC/EOMCC wave function in the P space onto excited Slater determinants residing in the Q space. Note that in writing Eq. (3.10) we combined the ground- and excited-state cases, denoted with $\mu = 0$ and $\mu > 0$,

respectively, into a single formalism by setting $R_{\mu=0}^{(P)} = \mathbf{1}$. In defining the $\ell_{\mu,K}(P)$ amplitudes that multiply the $\mathfrak{M}_{\mu,K}(P)$ quantities in Eq. (3.9), we adopt the quasi-perturbative formula

$$\ell_{\mu,K}(P) = \frac{\langle \Phi | L_{\mu}^{(P)} \overline{H}^{(P)} | \Phi_K \rangle}{D_{\mu,K}(P)}, \quad (3.11)$$

where the denominator $D_{\mu,K}(P)$ is defined via the Epstein–Nesbet partitioning,

$$D_{\mu,K}(P) = E_{\mu}^{(P)} - \langle \Phi_K | \overline{H}^{(P)} | \Phi_K \rangle. \quad (3.12)$$

Note that one has the option to use the approximate Møller–Plesset form of $D_{\mu,K}(P)$ (see below for details), but, as shown in Refs. [1, 73, 76, 77, 114], among others, and as illustrated by example calculations shown in this dissertation, the Epstein–Nesbet form is generally more accurate. The final CC($P;Q$) energy is given by

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P;Q). \quad (3.13)$$

At this point, the only thing that remains to be decided is how to define the P and Q spaces underlying the CC($P;Q$) calculation. As already mentioned in the Introduction, the CC($P;Q$) formalism is very versatile due to the flexibility it grants the user in defining the P and Q spaces. For example, the simplest manner of defining the P and Q spaces is by following the traditional truncation scheme in the many-body expansion of T , R_{μ} , and L_{μ} , *i.e.*, partitioning the two subspaces based on the excitation ranks of determinants. In doing so, the resulting CC($P;Q$) schemes become equivalent to their CR-CC/EOMCC precursors. One could also turn to defining the P and Q spaces based on active-space ideas, or turn to hybrid schemes relying on CIQMC wave function sampling or selected CI runs. For the remainder of this chapter, we will focus on the CR-CC/EOMCC methodology and active-space CC($P;Q$) approaches.

3.2 The Completely Renormalized CC/EOMCC Framework

3.2.1 Theory

Let us begin our survey of the many forms of $\text{CC}(P;Q)$ -based approaches by discussing the most straightforward way of defining the P and Q spaces, namely, by relying on the traditional truncation level defining the CC/EOMCC hierarchy as done in the left-eigenstate CR-CC/EOMCC methods [82–84, 89–91, 93, 95]. Within the CR-CC/EOMCC methodology, we define the P space to be spanned by n -tuply excited Slater determinants with $n = 1, \dots, m_A$, while the complementary Q space is spanned by m -tuply excited determinants with $m = m_A + 1, \dots, m_B$. In other words, we are correcting the conventional CC/EOMCC calculations where T and R_μ are truncated at m_A , as described in Section 2.1, with the many-electron correlation effects described by the remaining T_n and $R_{\mu,n}$ components with $n = m_A + 1, \dots, m_B$.

To illustrate how the CR-CC/EOMCC methodologies work, let us focus on the triples correction to CCSD/EOMCCSD, defining the CR-CC(2,3) and CR-EOMCC(2,3) approaches that are of interest in this dissertation. In these cases, we set $m_A = 2$ and $m_B = 3$, which means that the P space is spanned by all singly and doubly excited determinants and the Q space is populated by all triply excited determinants in the language of the $\text{CC}(P;Q)$ theory. Thus, the initial $\text{CC}(P)/\text{EOMCC}(P)$ step in a CR-CC/EOMCC(2,3) calculation is none other than performing CCSD/EOMCCSD iterations as usual, in addition to solving for left CCSD/EOMCCSD amplitudes needed to construct the noniterative moment corrections. After the CCSD/EOMCCSD energy $E_\mu^{[(\text{EOM})\text{CCSD}]}$ and the cluster and EOM excitation and de-excitation amplitudes are obtained, the noniterative triples correction is determined as

$$\delta_\mu(2, 3) = \sum_{\substack{i < j < k \\ a < b < c}} \ell_{\mu,ijk}^{abc}(2) \mathfrak{M}_{\mu,ijk}^{abc}(2), \quad (3.14)$$

where

$$\mathfrak{M}_{\mu,ijk}^{abc}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} R_\mu^{(\text{EOMCCSD})} | \Phi \rangle \quad (3.15)$$

is the projection of the connected cluster form of the Schrödinger equation containing the CCSD/EOMCCSD wave function onto the triply excited determinants $|\Phi_{ijk}^{abc}\rangle$, assuming $R_{\mu=0}^{(\text{EOMCCSD})} = \mathbf{1}$, and

$$\ell_{\mu,ijk}^{abc}(2) = \frac{\langle \Phi | L_{\mu}^{(\text{EOMCCSD})} \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle}{D_{\mu,ijk}^{abc}(2)}. \quad (3.16)$$

In Eqs. (3.15) and (3.16), $\bar{H}^{(\text{CCSD})}$ is the CCSD similarity-transformed Hamiltonian. The denominator in Eq. (3.16) is defined as

$$D_{\mu,ijk}^{abc}(2) = E_{\mu}^{[(\text{EOM})\text{CCSD}]} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \quad (3.17)$$

for the full Epstein–Nesbet variant of CR-CC/EOMCC(2,3), which is commonly designated as CR-CC/EOMCC(2,3),D or simply CR-CC/EOMCC(2,3). As mentioned above, one can evoke the Møller–Plesset approximation, where the denominator becomes

$$D_{\mu,ijk}^{abc}(2) = \omega_{\mu}^{(\text{EOMCCSD})} - [\epsilon_a + \epsilon_b + \epsilon_c - (\epsilon_i + \epsilon_j + \epsilon_k)], \quad (3.18)$$

in which ϵ_p is the orbital energy of the spin orbital $|p\rangle$. In this case, one obtains the CR-CC(2,3),A and CR-EOMCC(2,3),A approaches, which are equivalent to CCSD(2)_T [192] and EOMCC(2)PT(2) [193, 194], respectively. Once the $\delta_{\mu}(2,3)$ correction is determined, the final CR-CC/EOMCC(2,3) energy is given by

$$E_{\mu}^{[\text{CR-CC/EOMCC}(2,3)]} = E_{\mu}^{[(\text{EOM})\text{CCSD}]} + \delta_{\mu}(2,3). \quad (3.19)$$

It is worth mentioning that there is one caveat when excited-state computations are considered within the $\text{CC}(P;Q)$ methodology, namely, the violation of strict size intensivity in the CR-EOMCC(2,3) and similar methods. In the context of excitation energy calculations, one can view size intensivity as the correct description of a given many-electron system that is separated into noninteracting fragments, in which only a single fragments is excited while the remaining ones continue to be in their respective ground state. The consequences of violating strict size intensivity, while being typically small compared to other sources of

error (*e.g.*, the neglect of higher-than-two-body cluster and excitation components) when small- to medium-sized molecules are considered, may become substantial for larger systems, such as the **FR0**-SB photobase that is of interest in this dissertation work. As shown in Refs. [93, 95], one can identify the cause of this issue by analyzing the various contributions to the CR-EOMCC(2,3) vertical excitation energy,

$$\omega_{\mu}^{[\text{CR-EOMCC}(2,3)]} = E_{\mu}^{[\text{CR-EOMCC}(2,3)]} - E_0^{[\text{CR-CC}(2,3)]} = \omega_{\mu}^{(\text{EOMCCSD})} + \alpha_{\mu}(2, 3) + \beta_{\mu}(2, 3), \quad (3.20)$$

where $\omega_{\mu}^{(\text{EOMCCSD})}$ is the underlying EOMCCSD vertical excitation energy,

$$\alpha_{\mu}(2, 3) = \sum_{\substack{i < j < k \\ a < b < c}} \ell_{\mu,ijk}^{abc}(2) \tilde{\mathfrak{M}}_{\mu,ijk}^{abc}(2) \quad (3.21)$$

is the contribution of the triply excited moment of EOMCCSD due to $R_{\mu,1}$ and $R_{\mu,2}$, namely, $\tilde{\mathfrak{M}}_{\mu,ijk}^{abc}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2}) | \Phi \rangle$, and

$$\beta_{\mu}(2, 3) = \sum_{\substack{i < j < k \\ a < b < c}} \left[r_{\mu,0} \ell_{\mu,ijk}^{abc}(2) - \ell_{0,ijk}^{abc}(2) \right] \mathfrak{M}_{0,ijk}^{abc}(2), \quad (3.22)$$

is a size-extensive or approximately size-extensive term due to the presence of the ground-state moment $\mathfrak{M}_{0,ijk}^{abc}(2)$ in it. Note that the complete moment $\mathfrak{M}_{\mu,ijk}^{abc}(2)$ is a sum of $\tilde{\mathfrak{M}}_{\mu,ijk}^{abc}(2)$ in Eq. (3.21) and $r_{\mu,0} \mathfrak{M}_{0,ijk}^{abc}(2)$. Because the EOMCCSD vertical excitation energy and the $\alpha_{\mu}(2, 3)$ contribution, which does not contain any size-extensive term, are size intensive, one could then define a rigorously size-intensive modification to CR-EOMCC(2,3) by eliminating the $\beta_{\mu}(2, 3)$ term, which grows with the system size [93, 194], from Eq. (3.20). In doing so, one obtains a method designated as δ -CR-EOMCC(2,3).

As already mentioned above, the CR-CC/EOMCC family of methods are very powerful. For example, focusing on excited-state computations relevant to photochemistry and spectroscopy that are of interest in this dissertation work, in a report [195] where about 200 excited states of 28 organic molecules were examined by using a variety of EOMCC methods, it was shown that one needs triples corrections, such as those of the δ -CR-EOMCC(2,3)

approach, on top of EOMCCSD to obtain a quantitative description (errors reduced to ~ 0.1 – 0.2 eV; EOMCCSD produces errors on the order of 0.5 eV or higher). Furthermore, these results are achievable with considerable savings in the computational costs. Indeed, the computational time of performing a CR-CC(2,3) or CR-EOMCC(2,3) scales as $n_o^2 n_u^4$ in the iterative CCSD/EOMCCSD steps and $n_o^3 n_u^4$ for the determination of the noniterative $\delta_\mu(2,3)$ correction. This means that CR-CC(2,3) and CR-EOMCC(2,3) have reduced computational costs compared to the parent CCSDT/EOMCCSDT calculations, which have iterative steps that scale as $n_o^3 n_u^5$.

3.2.2 Application: Photochemistry of the Novel Super Photobase **FR0-SB**

To illustrate the effectiveness of the CR-CC/EOMCC approaches belonging to the $CC(P;Q)$ methodology, we proceed to the description of our work in the investigation of the super photobase **FR0-SB**. This work has been part of an ongoing collaboration at Michigan State University involving synthesis, theory, and experiments, and so far has resulted in several publications [3–8] (see, also, Ref. [150]). In this section, we will discuss the computational and theoretical portions of Refs. [3–5], where we rely on the CR-CC(2,3) and δ -CR-EOMCC(2,3) energetics, along with one-electron properties obtained using EOMCCSD, to shed light on the origin of the photobasicity of **FR0-SB**, the enhancement in excited-state proton transfer (ESPT) reaction using two-photon excitation (TPE), and the steric effect that govern the extent of the ESPT reaction in alcohol solvents.

The **FR0-SB** molecule is benign in its ground electronic state, having a pK_a of about 7, *i.e.*, neutral [3, 150], but upon photoexcitation to its excited state **FR0-SB*** it becomes a very strong base with pK_a of about 21 units. Such behavior is useful in precision chemistry, where the ability to activate chemical reagents to perform spatially and temporally localized reactions is desirable. Among the best method to achieve such precision is through the use of photoactivated chemical reagents, with the most common type being super photoacids [196, 197]. Such species exhibit a very large negative shift in pK_a upon photoexcitation,

typically to the first excited electronic state. While there have been a large number of photoacids investigated to date (see, *e.g.*, Refs. [198–211]), only a handful of their photobase counterparts have been studied. While there are other compounds, primarily quinoline derivatives, which are able to undergo ESPT in methanol, with 5-methoxyquinoline being able to attain a pK_a of about 16 in its excited state [212–219], here we focus on the fluorene-based **FR0**-SB, which is the much stronger photobase.

The structure of **FR0**-SB is shown in Fig. 3.1. Upon photoexcitation from its ground S_0 state to the first excited singlet S_1 state, **FR0**-SB is able to abstract proton from the surrounding alcohol solvent molecules. This behavior is shown in Fig. 3.1, adapted from Figure 2 of Ref. [150] where the results of absorption and fluorescence spectroscopy measurements of **FR0**-SB in protic and aprotic solvents were reported. To be precise, when **FR0**-SB is dissolved in acetonitrile, which is an aprotic solvent, the absorption and fluorescence maxima of the chromophore in the visible region are located at 369 and 479 nm, respectively [150]. These two bands corresponds to the excitation of **FR0**-SB to the excited **FR0**-SB* species and the subsequent emission from the relaxed **FR0**-SB* back to the ground electronic state. However, when **FR0**-SB is dissolved in ethanol, which is a protic solvent, two overlapping emission bands were observed with maxima at 463 and 628 nm [150], while the absorption spectrum practically stays unchanged. To verify the identity of the extra peak at 628 nm that is not observed in acetonitrile, the authors of Ref. [150] performed an additional set of measurements for **FR0**-SB in ethanol, but now acidified using HClO_4 . In doing so, one could then observe the absorption spectrum corresponding to the excitation of **FR0**-HSB⁺, which is the protonated form of **FR0**-SB, and the subsequent emission of the relaxed **FR0**-HSB⁺* back to the ground state in the fluorescence spectrum. Indeed, as seen in Fig. 3.1, the emission peak at 630 nm observed for the acidified species matches perfectly the secondary emission peak observed for **FR0**-SB in ethanol, which is missing in acetonitrile. Thus, the authors of Ref. [150] were able to conclude that there is indeed proton transfer from the alcohol solvent environment to the **FR0**-SB chromophore, and this reaction has to happen

in the excited state, not in the ground state. Furthermore, by using the 0–0 transition frequencies of **FR0**-SB and **FR0**-HSB⁺, which can be approximated from the crossings of the respective absorption and emission curves, one can construct a thermodynamic cycle involving **FR0**-SB, **FR0**-SB*, **FR0**-HSB⁺, and **FR0**-HSB⁺⁺ and use the Förster equation [220, 221] to estimate the change in the p*K*_a of **FR0**-SB upon photoexcitation. Using the measured p*K*_a in the ground state, of ~ 7 , and the predicted increase of 14 units determined using the Förster equation, the authors of Ref. [150] noted that the excited-state p*K*_a of **FR0**-SB is on the order of 21, which makes **FR0**-SB the strongest known photobase to date [3, 150].

Our initial task in this collaborative project was to investigate the driving force behind the photobasicity of **FR0**-SB [3]. To that end, we performed electronic structure calculations to determine some of the key properties of the ground (*S*₀) and low-lying excited singlet electronic (*S*_{*n*}, *n* > 0) states of the isolated **FR0**-SB molecule, including the ground-state geometry, the excitation energies and oscillator strengths characterizing the vertical *S*₀ → *S*_{*n*} transitions, and the electronic dipole moments of the calculated states. With the exception of the molecular geometry, which was optimized using the Kohn–Sham formulation [222] of the density functional theory (DFT) [223], all of the characteristics of the calculated electronic states were obtained by using high-level *ab initio* methods of quantum chemistry based on the CC theory and its EOM extension to excited states. Given the relatively large size of the **FR0**-SB molecule, which consists of 58 atoms and 190 electrons, to use the CC and EOMCC methods as fully as possible and to make sure that the higher-order many-electron correlation effects beyond the basic EOMCCSD level are properly accounted for we used the following composite approach to determine the vertical excitation energies corresponding to the *S*₀ → *S*_{*n*} transitions:

$$\omega_n^{(\text{EOMCC})} = \omega_n^{(\text{EOMCCSD}/6-31+\text{G}^*)} + \left[\omega_n^{(\delta\text{-CR-EOMCC}(2,3)/6-31\text{G})} - \omega_n^{(\text{EOMCCSD}/6-31\text{G})} \right]. \quad (3.23)$$

The first term on the right-hand side of Eq. (3.23) denotes the vertical excitation energy obtained in the EOMCCSD calculations using the 6-31+G* basis set [224–226], which was

the largest basis set we could afford in such computations. The next two terms on the right-hand side of Eq. (3.23), which represent the difference between the δ -CR-EOMCC(2,3) and EOMCCSD vertical excitation energies obtained by using a smaller 6-31G basis [224], correct the EOMCCSD/6-31+G* results for the higher-order many-electron correlation effects due to triple excitations. The size intensivity of the EOMCCSD and δ -CR-EOMCC(2,3) excitation energies entering our composite computational protocol defined by Eq. (3.23), combined with the size extensivity of the underlying CCSD and CR-CC(2,3) approaches, is important, too, since without reinforcing these formal theory features one risks losing accuracy with growing molecular size.

The CCSD/6-31+G* and EOMCCSD/6-31+G* calculations were also used to determine the dipole moments in the ground and excited states and the oscillator strengths characterizing the vertical $S_0 \rightarrow S_n$ (in general, $S_m \rightarrow S_n$) transitions. As usual, this was done by solving both the right and left EOMCCSD eigenvalue problems and constructing the relevant one-electron reduced density and transition density matrices. While triples corrections, such as those of CR-CC(2,3) and δ -CR-EOMCC(2,3), are important to improve the energetics, the description of one-electron properties, such as dipole moments and oscillator strengths characterizing one-electron transitions examined in this study, by the CCSD and EOMCCSD approaches is generally quite accurate.

All single-point CC and EOMCC calculations reported in our initial investigation [3] and summarized here relied on the ground-state geometry of **FR0**-SB, which we optimized using the analytic gradients of the CAM-B3LYP [227] DFT approach employing the 6-31+G* basis set. We chose the CAM-B3LYP functional because the extension of this functional to excited states using the time-dependent (TD) DFT formalism [228] provided vertical excitation energies closest to those obtained with EOMCC. Furthermore, the ground-state geometry of the **FR0**-SB molecule resulting from the CAMB3LYP/6-31+G* calculations turned out to be virtually identical (to within 0.004 Å on average and not exceeding 0.02 Å for the bond lengths) to that obtained with the second-order Møller–Plesset perturbation

theory (MP2) approach using the same basis. All of the electronic structure calculations for the **FR0**-SB molecule reported in Ref. [3] and summarized here, including the CAM-B3LYP and MP2 geometry optimizations and the CC/EOMCC single-point calculations, were performed by using the GAMESS package [182–184]. The relevant CCSD, EOMCCSD, and δ -CR-EOMCC(2,3) computations using the RHF determinant as a reference and the corresponding left-eigenstate CCSD and EOMCCSD calculations, which were needed to determine the triples corrections of δ -CR-EOMCC(2,3) and the one-electron properties of interest, including the dipole moments and oscillator strengths, were performed by using the CC/EOMCC routines developed by the Piecuch group [183], which form part of the GAMESS code. In all of the post-RHF calculations, the core orbitals associated with the 1s shells of C and N atoms were kept frozen; *i.e.*, we correlated 138 electrons. In the calculations employing the 6-31+G* basis set, we used spherical d-type polarization functions. The visualization of the optimized structure of **FR0**-SB in its ground and excited electronic states shown in Fig. 3.2 was accomplished by using VMD software [229].

We show in Table 3.1 some of the key properties of the low-lying singlet electronic states of the **FR0**-SB molecule obtained in the *ab initio* EOMCC calculations described above. They include the excitation energies and oscillator strengths characterizing the vertical $S_0 \rightarrow S_n$ ($n = 1-4$) transitions and the electronic dipole moments of the calculated ground and excited states. To verify the reliability of our EOMCC-based computational protocol defined by Eq. (3.23), we compared our theoretical gas-phase value of the $S_0 \rightarrow S_1$ vertical excitation energy of **FR0**-SB with the corresponding experimental photoabsorption energy characterizing **FR0**-SB dissolved in hexane, which is the least polar solvent considered in our experiments that will be reported in a future publication. Our best *ab initio* EOMCC value based on Eq. (3.23), of 3.70 eV, matches closely the experimentally derived $S_0 \rightarrow S_1$ transition energy corresponding to the maximum of the photoabsorption band characterizing **FR0**-SB dissolved in hexane, which is 3.52 eV. If we did not correct the EOMCCSD/6-31+G* excitation energy for the triples using Eq. (3.23), we would obtain 4.10 eV, which shows that high-order

many-electron correlation effects beyond the EOMCCSD level, estimated in this study with the help of the δ -CR-EOMCC(2,3) approach, are significant. We should also mention that our best TD-DFT result for the $S_0 \rightarrow S_1$ vertical excitation energy of **FR0**-SB, obtained using the CAM-B3LYP functional, of 3.92 eV, is not as good as the EOMCC value shown in Table 3.1. Moving to our main theoretical findings summarized in Table Eq. (3.23), we can see that of the four lowest-energy singlet excited states of **FR0**-SB calculated in this study, two, namely, S_1 and S_2 , can be accessed by photoabsorption. The remaining two states, S_3 and S_4 , are characterized by negligible oscillator strengths. What is most important for this study are the observations that both S_1 and S_2 have similar peak positions and intensities on the same order, resulting in broadening of the **FR0**-SB $\rightarrow$ **FR0**-SB* photoabsorption band, and that the electronic dipole moment of **FR0**-SB increases significantly upon photoexcitation, from 2.6 D in the ground electronic state to 8.6 D for S_1 and to 6.7 D for S_2 . This more-or-less 3-fold increase in the dipole moment as a result of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ optical transitions in **FR0**-SB, observed in our EOMCC calculations and shown in Fig. 3.2 for S_1 , demonstrates that the deprotonation of protic solvent molecules by the photoactivated **FR0**-SB species is indeed possible, since there is an accumulation of the net negative charge on the imine nitrogen that is accompanied by a decrease of electron density on the amine nitrogen. This very small charge transfer, of about $0.1e$, occurs over a very large distance of >10 Å, which is made possible by the central fluorene linker, and this is exactly what is causing the very large increase in the dipole moment of **FR0**-SB upon $S_0 \rightarrow S_1$ photoexcitation.

Table 3.1: Orbital character, vertical excitation energies $\omega_n^{(\text{EOMCC})}$ (in eV and nm), oscillator strengths, and electronic dipole moment values μ_n (in D) of the four lowest-energy excited singlet electronic states S_n of **FR0**-SB as obtained in the EOMCC calculations described in the text. Adapted from Ref. [3].

State	Orbital character	$\omega_n^{(\text{EOMCC})}$		Oscillator strength	μ_n^{a}
		(eV)	(nm)		
S_1	$\pi \rightarrow \pi^*$	3.70	335	0.74	8.6
S_2	$\pi \rightarrow \pi^*$	3.96	313	0.35	6.7
S_3	$\pi \rightarrow \pi^*$	4.23	293	0.02	5.4
S_4	$\pi \rightarrow \pi^*$	4.45	279	0.03	4.3

^aThe CCSD value of the dipole moment in the ground electronic state S_0 is 2.6 D.

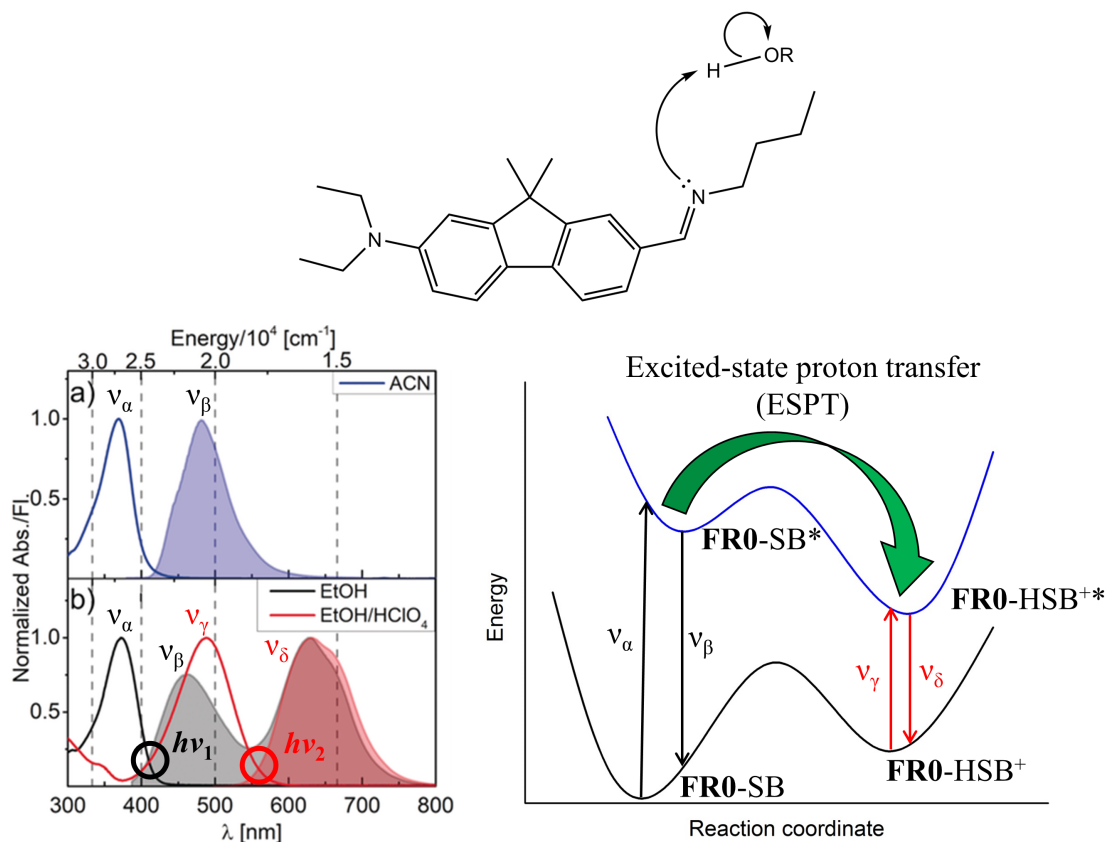


Figure 3.1: The molecular structure of **FR0-SB** with a representation of the excited-state proton transfer (ESPT) process. The bottom left panel, adapted from Ref. [150], shows the absorption (unshaded) and fluorescence (shaded) spectra of **FR0-SB** dissolved in acetonitrile (ACN, blue), ethanol (EtOH, black), and ethanol acidified with HClO₄ (EtOH/HClO₄, red). The $h\nu_1$ and $h\nu_2$ labels correspond to the approximate 0-0 transition wavelengths of **FR0-SB** and **FR0-HSB⁺**, respectively. The bottom right panel provides a simplified illustration of the excitation and emission processes involving the unprotonated and protonated forms of **FR0-SB**, with labels corresponding to the maxima observed in the absorption and emission spectra.

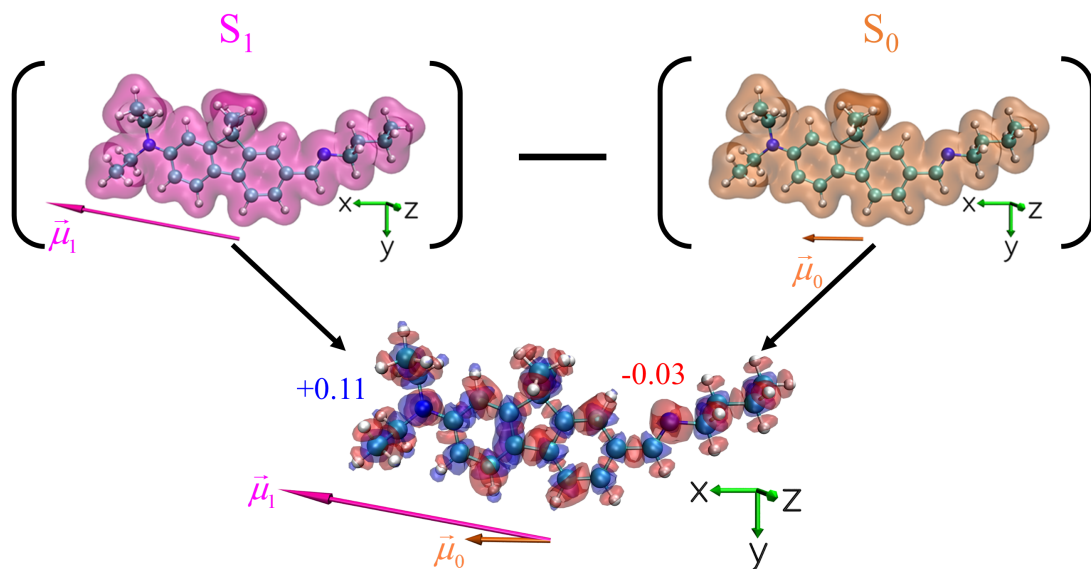


Figure 3.2: The minimum-energy geometry of the ground electronic state of **FRO-SB** along with the EOMCCSD/6-31+G* electronic densities and dipole moment vectors characterizing the S₀ (orange) and S₁ (magenta) states. The S₁-S₀ electronic density difference, adapted from Ref. [4], is shown in the bottom, in which areas shaded with red (blue) indicate an increase (decrease) in the electronic density upon S₁ → S₀ photoexcitation. The change in Mulliken charges of the amine and imine nitrogens of the **FRO-SB** chromophore upon photoexcitation are also indicated.

Once we understood the origin of photobasicity of **FR0**-SB, our experimental collaborators performed experiments where chromophore is excited via TPE instead of the conventional one-photon excitation (OPE) process and observed an interesting phenomenon. This is demonstrated in Fig. 3.3, adapted from Fig. 2 of Ref. [5], where we show the steady-state fluorescence spectra following OPE and TPE of **FR0**-SB dissolved in methanol, ethanol, *n*-propanol, and i-propanol. Focusing on the spectra in methanol shown in Fig. 3.3(a), it is clear that the emission peak area corresponding to the protonated **FR0**-SB species is larger for the TPE-induced fluorescence than in the OPE-induced fluorescence after normalizing for the unprotonated emission peak area. In fact, ESPT between **FR0**-SB and methanol is enhanced by a factor of $\sim 62\%$. Interestingly, we also observe a solvent-dependent behavior in this TPE enhancement of ESPT of **FR0**-SB, where the enhancement decreases from methanol to ethanol to *n*-propanol and there is no observed enhancement at all in i-propanol.

To investigate this phenomenon, we begin by looking at the OPE and TPE absorption cross sections arising from the first- and second-order time-dependent perturbation theory, respectively (see, *e.g.*, Ref. [230]). The $0 \rightarrow f$ OPE absorption cross section, with 0 and f denoting the initial and final electronic states, respectively, is [230]

$$\sigma_{f0}^{(1)}(\omega) = A |\mu_{f0}|^2 g_{M1}(\omega), \quad (3.24)$$

where ω is the frequency of the exciting photon (in our case, the frequency of a 400 nm laser), A is a constant, μ_{f0} denotes the magnitude of the transition dipole moment between the ground and excited electronic states, and $g_{M1}(\omega)$ is the OPE distribution function or linewidth associated with the molecular system of interest. In presenting Eq. (3.24), we have assumed an isotropic averaging over the directions of the transition dipole moment vector $\boldsymbol{\mu}_{f0}$. To arrive at an expression for the absorption cross section associated with the isoenergetic one-color TPE, where the laser frequency is half of its OPE counterpart, we take advantage of the fact that no resonance at 800 nm is observed in our experiments, in agreement with our electronic structure calculations. Under these conditions, the absorption

cross section for TPE becomes [231]

$$\sigma_{f0}^{(2)}(\omega) = B \left| \sum_{\nu} \frac{\mu_{f\nu}\mu_{\nu 0}}{\omega_{\nu 0} - \omega/2 + i\Gamma_{\nu}(\omega/2)} \right|^2 g_{M2}(\omega), \quad (3.25)$$

where B is a constant, $\omega_{\nu 0}$ is the frequency needed to reach the intermediate state ν from the ground state 0, $i\Gamma_{\nu}(\omega/2)$ is a damping factor that is inversely proportional to the lifetime of a given intermediate state ν , and $g_{M2}(\omega)$ is the TPE line shape function. In analogy to the OPE absorption cross section, we have performed an isotropic averaging over the directions of the transition dipole moment vectors $\boldsymbol{\mu}_{f\nu}$ and $\boldsymbol{\mu}_{\nu 0}$.

Equation (3.25) is useful, but in this work we are interested in relating the TPE absorption cross section with the change in the dipole moment upon $0 \rightarrow f$ photoexcitation. One can derive such a relationship if we perform the following mathematical manipulations [232]. First, we separate the $\nu = 0$ and $\nu = f$ terms from the sum over states in Eq. (3.25). Next, we take advantage that, in our case, 0 and f correspond to the electronically bound S_0 and S_1 states of **FR0**-SB, respectively. This allows us to eliminate the $i\Gamma_{\nu}(\omega/2)$ term in the $\nu = 0$ and $\nu = f$ denominators in Eq. (3.25). In the final step, we replace ω_{f0} in the $\nu = f$ denominator by ω and combine the $\nu = 0$ and $\nu = f$ contributions to obtain [232]

$$\sigma_{f0}^{(2)}(\omega) = B \left| \sum_{\nu \neq 0, f} \frac{\mu_{f\nu}\mu_{\nu 0}}{\omega_{\nu 0} - \omega/2 + i\Gamma_{\nu}(\omega/2)} + \frac{\mu_{f0}\Delta\mu_{f0}}{\omega/2} \right|^2 g_{M2}(\omega). \quad (3.26)$$

It is customary to refer to the first term in Eq. (3.26) as the “virtual” pathway and to the second one, which relies on the transition dipole moment μ_{f0} and the difference between the permanent ground- and excited-state dipoles $\Delta\mu_{f0} \equiv \mu_{ff} - \mu_{00}$, as the “dipole” pathway [233]. Equation (3.26) shows that for centrosymmetric molecules, for which $\Delta\mu_{f0}$ vanishes identically, the virtual pathway is the only contributing term to the TPE absorption cross section. However, **FR0**-SB is not centrosymmetric and, thus, it is interesting to examine the extent to which each pathway contributes to the $S_0 \rightarrow S_1$ one-color TPE considered here. For the first term in Eq. (3.26) to be large, the following three conditions would have to be satisfied: (i) the $\omega_{\nu 0}$ frequency characterizing the $0 \rightarrow \nu$ transition would have to be close to the frequency $\omega/2$ of each of the two photons associated with TPE, (ii)

the $i\Gamma_\nu(\omega/2)$ damping factor would have to be very small, *i.e.*, the intermediate state ν would have to be sufficiently long-lived, and (iii) the $0 \rightarrow \nu$ and $\nu \rightarrow f$ transitions would have to be allowed, giving rise to larger $\mu_{\nu 0}$ and $\mu_{f\nu}$ transition dipole moments. In the case of the TPE experiments performed in Ref. [5], it is unlikely that conditions (i)–(iii) can be simultaneously satisfied. Indeed, since there are no dipole-allowed electronic states between S_0 and S_1 , the intermediate state ν satisfying condition (i) would have to be a rovibrational resonance supported by the ground-state electronic potential. It is unlikely that such resonances are long-lived and characterized by large $0 \rightarrow \nu$ and $\nu \rightarrow f$ transition dipole moments. It is possible that the intermediate states ν characterized by larger $\mu_{\nu 0}$ and $\mu_{f\nu}$ values exist, but those would have to be electronic states higher in energy than S_1 , which cannot satisfy the resonant condition (i). Furthermore, as demonstrated in Ref. [3] and summarized above, the low-lying electronically excited states above S_1 are characterized by small or even negligible transition dipole moments from the ground state. In other words, while the virtual pathway contributes to the TPE cross section, the probability that it dominates it seems low, especially when we realize that there are reasons for the dipole pathway to play a substantial role in the case of the molecular systems considered in this work. Indeed, as shown in Refs. [3, 4] and as further elaborated on below, the $S_0 \rightarrow S_1$ excitations in the isolated and solvated **FR0**-SB are characterized by large transition dipole moments and significant changes in the permanent dipoles. This suggests that the second term in Eq. (3.26) plays a major role, which is consistent with the well-established fact that the dipole pathway becomes critical when TPE involves charge transfer associated with substantial change in the permanent dipole upon photoexcitation [234–240]. Although the $S_0 \rightarrow S_1$ transition in **FR0**-SB is accompanied by a migration of a small amount of charge [3, 4], this migration happens over a very large distance, giving rise to more than a threefold increase in dipole moment and a substantial enhancement of the second term in Eq. (3.26). Given the above analysis, from this point on, we focus on the dipole pathway and assume that we can approximate the TPE absorption cross section by the second term in Eq. (3.26),

i.e. [238],

$$\sigma_{f0}^{(2)}(\omega) \approx B' |\mu_{f0}|^2 |\Delta\mu_{f0}|^2 g_{M2}(\omega), \quad (3.27)$$

where $B' = 4B/\omega^2$. Furthermore, by forming the ratio of Eqs. (3.24) and (3.27), we can obtain a new expression that summarizes the difference between OPE and TPE, in which the change in permanent dipole moment acts as an amplification factor,

$$\frac{\sigma_{f0}^{(2)}(\omega/2)}{\sigma_{f0}^{(1)}(\omega)} = \frac{B'}{A} \frac{|\mu_{f0}|^2 |\Delta\mu_{f0}|^2 g_{M2}(\omega)}{|\mu_{f0}|^2 g_{M1}(\omega)} = C \frac{|\Delta\mu_{f0}|^2 g_{M2}(\omega)}{g_{M1}(\omega)}, \quad (3.28)$$

where $C = B'/A$.

As illustrated in the mathematical derivation above, the absorption cross sections for both one- and two-photon excitation processes depend on the square of the absolute value of the transition dipole moment μ_{f0} characterizing the $0 \rightarrow f$ vertical electronic excitation, which, in our case, is the transition dipole μ_{10} corresponding to the $S_0 \rightarrow S_1$ photoabsorption for the **FR0**-SB system in various solvents. However, in the case of TPE, the absorption cross section also depends on the difference between the electronic dipole moments of the f and 0 states, $\Delta\mu_{f0}$, which, in our case, is the difference $\Delta\mu_{10} \equiv \mu_1 - \mu_0$ between the dipole moment μ_1 characterizing the first excited singlet S_1 state of **FR0**-SB and its S_0 counterpart μ_0 . Consequently, $\Delta\mu_{10}$ and its dependence on the solvent environment hold the key to understanding the enhancement of the ESPT reactions between the **FR0**-SB photobase and alcohol solvents observed in the case of TPE. To provide insights into the effect of solvation on $\Delta\mu_{10}$ and other properties characterizing the S_0 and S_1 states of the solvated FR0-SB chromophore and transitions between them, we performed electronic structure calculations using the following CC/EOMCC-based composite approach.

In the computations reported in Ref. [5] and summarized here, we focus on analyzing the role of solvation effects on the S_0 - S_1 vertical and adiabatic transition energies and vertical transition dipole moments, along with the electronic dipoles characterizing the individual S_0 and S_1 states of **FR0**-SB, which are key quantities in comparing the one- and two-photon $S_0 \rightarrow S_1$ absorption cross sections. The solvent dependence of the enhancement necessitates

the incorporation of solvation effects in the CC/EOMCC computations, which our protocol described in Ref. [3] and summarized above does not take into account. As explained in Ref. [5], in modeling the solvated **FR0**-SB chromophore, we considered the complex of **FR0**-SB hydrogen-bonded to a cluster of three alcohol solvent molecules, designated as [**FR0**-SB $\cdots$ HOR], which, according to our earlier investigation of the steric effects on the ESPT process involving **FR0**-SB and *n*- and *i*-propanol, is the minimum number of explicit solvent molecules required for the proton transfer to occur [4]. Following Ref. [4], we used the “branched” arrangement of the three alcohol solvent molecules treated in our modeling explicitly, with one of them hydrogen-bonded to **FR0**-SB and the other two solvating it, since such an arrangement leads to the lowest energy barriers for the ESPT reactions involving **FR0**-SB (see Ref. [4] and the discussion below for further details). The remaining, bulk, solvation effects were described using the continuum solvation model based on the solute electron density (SMD) approach [241]. The alcohol solvents considered in our computations were methanol, ethanol, *n*-propanol, and *i*-propanol.

For each of the alcohol solvents considered in our calculations, the geometry optimization of the [**FR0**-SB $\cdots$ HOR] complex in its S_0 state, used in the subsequent CC/EOMCC calculations, was performed employing the Kohn–Sham formulation of DFT. To obtain the corresponding minimum-energy structures of the [**FR0**-SB $\cdots$ HOR] species in the S_1 state, we used the TD-DFT extension to excited electronic states. Following Refs. [3, 4], in carrying out these geometry optimizations we used the CAM-B3LYP functional. All geometry optimizations of the [**FR0**-SB $\cdots$ HOR] complex employed the 6-31+G* basis and accounted for the bulk solvation effects using the aforementioned SMD model.

To provide accurate information about the transition energies and transition dipole moments characterizing the absorption ($S_0 \rightarrow S_1$) and emission ($S_1 \rightarrow S_0$) processes involving the solvated **FR0**-SB species and the corresponding dipoles in the S_0 and S_1 states, which are all needed to model the one- and two-photon cross sections for each of the alcohol solvents considered in our calculations, we performed the following series of single-point CC

and EOMCC computations at the aforementioned CAM-B3LYP/6-31+G*/SMD optimized geometries. First, we determined the S_0 – S_1 electronic transition energies,

$$\omega_{10}^{(\text{EOMCC})} = E_{S_1}^{(\text{EOMCC})} - E_{S_0}^{(\text{CC})}, \quad (3.29)$$

corresponding to the [**FR0**-SB $\cdots$ HOR] complex in the absence of the SMD continuum solvation, where the total electronic energies of the S_0 and S_1 states entering Eq. (3.29) were computed as

$$E_{S_0}^{(\text{CC})} = E_{S_0}^{(\text{CCSD}/6-31+G^*)} + \left[E_{S_0}^{(\text{CR-CC}(2,3)/6-31G)} - E_{S_0}^{(\text{CCSD}/6-31G)} \right] \quad (3.30)$$

for the ground state and

$$E_{S_1}^{(\text{EOMCC})} = E_{S_1}^{(\text{EOMCCSD}/6-31+G^*)} + \left[E_{S_1}^{(\delta\text{-CR-EOMCC}(2,3)/6-31G)} - E_{S_1}^{(\text{EOMCCSD}/6-31G)} \right] \quad (3.31)$$

for the first excited singlet state. The first term on the right-hand side of Eq. (3.31) denotes the total electronic energy of the S_0 state computed at the CCSD level utilizing the largest basis set considered in this study, namely, 6-31+G*. The term in the square brackets on the right-hand side of Eq. (3.31) corrects the CCSD/6-31+G* energy for the many-electron correlation effects due to triply excited clusters obtained in the CR-CC(2,3) calculations employing the smaller and more affordable 6-31G basis. Similarly, the first term on the right-hand side of Eq. (3.31) designates the EOMCCSD/6-31+G* energy of the S_1 state and the expression in the square brackets represents the triples correction to EOMCCSD obtained in the δ -CR-EOMCC(2,3)/6-31G calculations. Ideally, one would like to use basis sets larger than 6-31+G* and, in particular, incorporate polarization and diffuse functions on hydrogen atoms, but such calculations at the CC/EOMCC levels used in this work turned out to be prohibitively expensive. Nevertheless, we tested the significance of the polarization and diffuse functions on hydrogen atoms by performing the CAM-B3LYP/6-31++G**/SMD calculations for the [**FR0**-SB $\cdots$ HOR] complexes that show that neither the excitation energies nor the dipole and transition dipole moment values change by more than 1% compared to the CAM-B3LYP/6-31+G*/SMD results.

Before describing the remaining elements of our computational protocol, it is important to emphasize that the composite approach defined by Eqs. (3.29)–(3.31) is more general than the analogous expressions shown in Eq. (3.23) [3], where we focused on the vertical excitation processes only. Equations (3.29)–(3.31) encompass both the vertical and adiabatic transition energies. Indeed, if $E_{S_0}^{(CC)}$ and $E_{S_1}^{(EOMCC)}$ are calculated at the minimum on the S_0 potential energy surface, $\omega_{10}^{(EOMCC)}$ given by Eqs. (3.29)–(3.31) becomes the vertical excitation energy $\omega_{10}^{(EOMCC)}(\text{abs.})$ characterizing the $S_0 \rightarrow S_1$ absorption defined by Eq. (3.23). If $E_{S_0}^{(CC)}$ and $E_{S_1}^{(EOMCC)}$ are determined at the minimum characterizing the [**FR0**-SB $\cdots$ HOR] complex in the S_1 state, we obtain the vertical transition energy $\omega_{10}^{(EOMCC)}(\text{em.})$ corresponding to the $S_0 \rightarrow S_1$ emission. The $\omega_{10}^{(EOMCC)}$ energy defined by Eq. (3.29) becomes the adiabatic transition energy, abbreviated as $\omega_{10}^{(EOMCC)}(\text{ad.})$, when $E_{S_0}^{(CC)}$ and $E_{S_1}^{(EOMCC)}$ are computed at their respective minima. As far as the transition dipole moments characterizing the vertical absorption and emission processes involving the solvated **FR0**-SB species are concerned, they were calculated from the one-electron transition density matrices obtained at the EOMCCSD level of theory employing the 6-31+G* basis set. Similarly, we used the CCSD/6-31+G* and EOMCCSD/6-31+G* one-electron reduced density matrices to determine the dipole moments of the S_0 and S_1 states at each of the two potential minima.

Given the large computational costs associated with the EOMCCSD and δ -CR-EOMCC(2,3) calculations for the [**FR0**-SB $\cdots$ HOR] system, which consists of three alcohol molecules bound to the **FR0**-SB chromophore and requires correlating as many as 216 electrons and 758 molecular orbitals in the case of the *n*- or *i*-propanol solvents when the 6-31+G* basis set is employed, we replaced the three explicit alcohol molecules with the corresponding effective fragment potentials (EFPs) [242]. We were able to do this because, based on our CAM-B3LYP/6-31+G*/SMD calculations for the [**FR0**-SB $\cdots$ HOR] complexes, the S_0 – S_1 electronic transition does not involve charge transfer between the photobase and its solvent environment. Indeed, the S_0 – S_1 transition in the bare and solvated **FR0**-SB species has a predominantly π – π^* character with the π and π^* orbitals localized on the **FR0**-SB

chromophore, *i.e.*, the alcohol solvent molecules are mere spectators to this excitation process (see the supplementary material of Ref. [5] for further details). The use of EFPs to represent the cluster of three alcohol molecules bonded to **FR0**-SB in our CC/EOMCC computations allowed us to reduce the system size to that of the bare **FR0**-SB species embedded in the external potential providing a highly accurate description of the intermolecular interactions between **FR0**-SB and solvent molecules in the [**FR0**-SB $\cdots$ HOR] complex, including electrostatic, polarization, dispersion, and exchange repulsion effects [242].

Once the electronic transition energies and the corresponding one-electron properties of the [**FR0**-SB $\cdots$ HOR] complex were determined, we proceeded to the second stage of our modeling protocol, which was the incorporation of the remaining bulk solvation effects that turned out to be nonnegligible as well. As in the case of the aforementioned geometry optimizations, the bulk solvation effects were calculated with the help of the implicit solvation SMD approach. Due to the limitations of the computer codes available to us, we could not perform the CC/EOMCC computations in conjunction with the SMD model, so we estimated the SMD effects using the *a posteriori* corrections $\delta_X^{(\text{SMD})}$ to the various CC/EOMCC properties X of the [**FR0**-SB $\cdots$ HOR] complex, such as transition energies and dipole moments, using DFT and TD-DFT. These corrections were constructed in the following way. First, for each of the four alcohol solvents considered in our calculations, we performed single-point DFT/TD-DFT calculations for the [**FR0**-SB $\cdots$ HOR] complex at the previously optimized S_0 and S_1 geometries accounting for the bulk solvation effects using SMD. As in the case of the geometry optimizations, we used the CAM-B3LYP functionals and the 6-31+G* basis set and, in analogy to the CC/EOMCC computations, replaced the cluster of three explicit alcohol solvent molecules bound to **FR0**-SB by the corresponding EFPs. We then repeated the analogous calculations without SMD. This allowed us to determine the desired $\delta_X^{(\text{SMD})}$ corrections using the formula

$$\delta_X^{(\text{SMD})} = X^{(\text{CAM-B3LYP/6-31+G}^*/\text{SMD})} - X^{(\text{CAM-B3LYP/6-31+G}^*)}, \quad (3.32)$$

where the first and second terms on the right-hand side of Eq. (3.32) designate property X

obtained in the CAM-B3LYP/6-31+G* calculations with and without SMD, respectively. The final SMD-corrected EOMCC electronic transition energies were computed as

$$\omega_{10} = \omega_{10}^{(\text{EOMCC})} + \delta_{\omega_{10}}^{(\text{SMD})}, \quad (3.33)$$

where $\omega_{10}^{(\text{EOMCC})}$ is the transition energy for the [**FR0**-SB $\cdots$ HOR] complex defined by Eqs. (3.29)–(3.31), whereas the SMD-corrected one-electron properties were determined using the formula

$$X = X^{[(\text{EOM})\text{CCSD}/6-31+\text{G}^*]} + \delta_X^{(\text{SMD})}, \quad (3.34)$$

with $X^{[(\text{EOM})\text{CCSD}/6-31+\text{G}^*]}$ denoting the value of property X calculated at the (EOM)CCSD/6-31+G* level. If the property of interest was a vector, such as dipole or transition dipole moment, we used Eq. (3.34) for each of the Cartesian components of the vector.

Finally, to gauge the effects of solvation on the various calculated properties, including transition energies and dipole and transition dipole moments, we also performed single-point CC/EOMCC calculations for the bare super photobase, *i.e.*, **FR0**-SB without the presence of explicit solvent molecules or equivalent EFPs and SMD implicit solvation, at the gas-phase geometry of the S_1 state optimized using CAM-B3LYP/6-31+G*. In the case of the S_0 minimum-energy structure, we relied on our previous gas-phase CC/EOMCC results reported in Ref. [3] and summarized earlier.

All of the electronic structure calculations reported in Ref. [5] and summarized here, including the CAM-B3LYP geometry optimizations with and without the SMD continuum solvation, the CC and EOMCC single-point calculations without implicit SMD solvation, and the CAM-B3LYP single-point calculations with and without SMD, needed to estimate the SMD corrections to CC/EOMCC properties, were performed using the GAMESS package (specifically, we used the 2019 R2 version of GAMESS for our works in Ref. [5] and discussed here). In the case of the $S_0 \rightarrow S_1$ absorption process, whenever the SMD implicit solvation model was utilized, we incorporated the nonequilibrium solvation effects associated with the solvent relaxation delay, as implemented in GAMESS [243]. In all of our CC/EOMCC

calculations, the core orbitals associated with the 1s shells of C and N atoms of **FR0**-SB were kept frozen. The EFPs that were used to replace the cluster of three explicit alcohol solvent molecules bound to **FR0**-SB in the CC/EOMCC single-point calculations and the CAM-B3LYP computations aimed at determining the SMD solvation effects were generated using the RHF approach and the 6-31+G* basis set. Thanks to the use of EFPs, our frozen-core CC/EOMCC calculations for the [**FR0**-SB $\cdots$ HOR] complex correlated only 138 electrons of the **FR0**-SB system. In all of the calculations employing the 6-31+G* basis set, we used spherical components of d orbitals.

In Table 3.2, we report the vertical transition energies $\omega_{10}(\text{abs.})$ and transition dipole moments μ_{10} characterizing the $S_0 \rightarrow S_1$ photoabsorption process, along with the dipoles corresponding to the S_0 and S_1 states, μ_0 and μ_1 , respectively, and their ratios resulting from our calculations for **FR0**-SB in the gas phase and in the aforementioned four solvents determined at the minima on the respective S_0 potential energy surfaces. The analogous information for the $S_1 \rightarrow S_0$ emission and the dipole moment values of the S_0 and S_1 states determined at the S_1 minima characterizing the isolated and solvated **FR0**-SB is presented in Table 3.3. We begin our discussion of computational results by comparing the vertical absorption and emission energies characterizing the solvated **FR0**-SB species obtained with the CC/EOMCC-based protocol adopted in this work against their experimental counterparts. The vertical excitation energies for the [**FR0**-SB $\cdots$ HOR] complexes calculated at the respective S_0 minima, shown in Table 3.2, are essentially identical to the locations of the peak maxima in the corresponding experimental photoabsorption spectra reported in Ref. [4], which are 3.32 eV, 3.33 eV, 3.32 eV, and 3.34 eV for methanol, ethanol, *n*-propanol, and *i*-propanol, respectively. The same accuracies are also seen in the case of the vertical emission energies calculated at the S_1 minima of the [**FR0**-SB $\cdots$ HOR] species reported in Table 3.3, which can hardly be distinguished from the maxima in the experimental emission peaks for **FR0**-SB in methanol, ethanol, *n*-propanol, and *i*-propanol of 2.57 eV, 2.61 eV, 2.62 eV, and 2.65 eV, respectively [4]. These observations corroborate the accuracy of the com-

putational protocol used in this study to model the interactions of the **FR0**-SB photobase with the various alcohol solvents. The observed good agreement between the theoretical vertical transition energies reported in Tables 3.2 and 3.3 and the corresponding experimental data can largely be attributed to the use of high-level *ab initio* CC/EOMCC approaches in describing the [**FR0**-SB $\cdots$ HOR] complexes. This becomes apparent when one considers the errors relative to the experiment characterizing the vertical transition energies obtained in the single-point CAM-B3LYP/6-31+G*/SMD computations, which are about 0.2 eV–0.3 eV (9%–11%).

Having established the accuracy of our quantum chemistry protocol, we proceed to the discussion of our computational findings regarding the dipole moments of the S_0 and S_1 states and the transition dipoles between them, which are the key quantities for the one- and two-photon absorption cross sections given by Eqs. (3.24) and (3.27), respectively. In the absence of direct experimental information, our computations provide insights into the effects of solvation on these quantities. To begin with, as reported in our earlier work for the bare **FR0**-SB species [3], and as shown in Table 3.2, there is a large, by a factor of more than 3, increase in the electronic dipole moment following $S_0 \rightarrow S_1$ photoabsorption, giving rise to the superbase character of **FR0**-SB*. Upon solvation, both S_0 and S_1 dipole moments of the **FR0**-SB chromophore are significantly enhanced, becoming approximately twice as large as their gas-phase counterparts. This can be attributed to the polarization of the electron cloud of the **FR0**-SB photobase by the alcohol molecules surrounding it. Furthermore, the fact that the electronic dipole moment characterizing the S_1 state is much larger than its S_0 counterpart translates into a stronger stabilization of the S_1 state relative to S_0 , leading to lower $S_0 \rightarrow S_1$ vertical excitation energies in the case of **FR0**-SB in alcohol solvents when compared to the bare **FR0**-SB system. The transition dipole moment characterizing the $S_0 \rightarrow S_1$ photoabsorption process is amplified by solvation as well (by about 40%), which results in larger OPE and TPE absorption cross sections for the solvated **FR0**-SB species relative to their gas-phase values. Similar trends are observed when we examine the dipoles

and transition dipoles shown in Table 3.3. It is also interesting to note that the dipole moments characterizing the S_0 and S_1 states and the corresponding transition dipoles increase upon geometrical relaxation from the S_0 to S_1 minima, with a concomitant red shift in the vertical transition energies. This bathochromic shift is more pronounced in the case of the solvated **FR0**-SB species as a consequence of μ_1 being much larger than μ_0 , implying a stronger stabilization of the S_1 state due to the polar solvent environment compared to the S_0 state.

As already alluded to above, the transition dipole moments characterizing the S_0 - S_1 absorption and emission processes and the S_0 and S_1 dipoles at the respective potential minima could not be determined from our experiments. However, by analyzing the solvatochromic shift of the absorption and fluorescence bands in 16 different solvents as a function of solvent dielectric constant and index of refraction, we could estimate the magnitude of the transition dipole moment μ_{10} and the change in the dipole moment, $\Delta\mu_{10}$, associated with the $S_0 \rightarrow S_1$ adiabatic excitation [244, 245]. Based on our analysis, we found $\Delta\mu_{10}$ of **FR0**-SB in the alcohol solvents considered in our experiments to be ~ 15 D, a magnitude usually associated with substantial charge transfer, and μ_{10} to be about 10 D. The procedure outlining how the experimental values of μ_{10} and $\Delta\mu_{10}$ were derived is given in the supplementary material of Ref. [5]. Having access to the dipole moments characterizing the S_0 and S_1 states at their respective minimum-energy structures and the vertical transition dipole moments associated with the S_0 - S_1 transitions resulting from our quantum chemistry computations (see Tables 3.2 and 3.3) allowed us to assess the quality of our experimentally derived values of μ_{10} and $\Delta\mu_{10}$. As shown in Tables 3.2 and 3.3, the vertical transition dipole moments μ_{10} characterizing the **FR0**-SB chromophore in the alcohol solvents included in our calculations range from 9.4 D to 11.8 D, in very good agreement with the experimentally derived value of about 10 D. According to the data collected in Table 3.4, the calculated and experimentally derived changes in the dipole moment associated with the $S_0 \rightarrow S_1$ adiabatic transition, which are about 15 D in both cases, are virtually identical. Given that both theory and experiment

point to the large values of μ_{10} and $\Delta\mu_{10}$ as a result of solvation and that the dipole pathway defined by the second term in Eq. (3.26) is anticipated to be the dominant TPE pathway, as discussed above, we can conclude that using Eq. (3.27) in approximating the TPE absorption cross section of **FR0**-SB in alcohol solvents is justified.

We are now well-situated to rely on our computational data to help interpret the experimental findings of Ref. [5]. Indeed, as shown in Tables 3.2–3.4, there is a massive increase in permanent dipole moment as **FR0**-SB undergoes $S_0 \rightarrow S_1$ excitation, which is further enhanced by the presence of polar solvent environment enveloping the **FR0**-SB chromophore. We also know from Eq. (3.28) that the TPE absorption cross section is enhanced by a significant $\Delta\mu_{10}$ value, while OPE absorption cross section does not take such contribution into account. Therefore, in Ref. [5], we hypothesized that by using TPE, one can selectively excite [**FR0**-SB $\cdots$ H-OR] configurations which would result in considerable increase in permanent dipole moment. Such configurations may then be characterized by energetically favorable ESPT reaction pathways toward the formation of protonated **FR0**-SB in the excited state, especially considering the magnitude of the dipole moment in the excited state. This could be confirmed by performing, for example, molecular dynamics simulations of **FR0**-SB in various alcohol solvent environment, taking snapshots of different solvent configurations around the **FR0**-SB chromophore, and performing the same solvation-corrected EOMCC calculations described above, which we will consider in our future works.

Table 3.2: The vertical transition energies $\omega_{10}(\text{abs.})$ (in eV) and transition dipole moments μ_{10} (in D) corresponding to the $S_0 \rightarrow S_1$ absorption, along with the μ_0 and μ_1 dipoles characterizing the S_0 and S_1 states (in D) and their ratios for **FR0**-SB in the gas phase and in selected alcohol solvents calculated at the respective S_0 minima following the CC/EOMCC-based protocol described in the text. Adapted from Ref. [5].

Solvent ^a	$\omega_{10}(\text{abs.})$	μ_{10}	μ_0	μ_1	μ_1/μ_0
None (gas phase) ^b	3.70	6.9	2.6	8.6	3.3
MeOH	3.30	9.6	4.4	16.4	3.8
EtOH	3.32	9.5	4.3	15.9	3.7
<i>n</i> -PrOH	3.32	9.5	4.2	15.9	3.7
i-PrOH	3.33	9.4	4.2	15.7	3.7

^aAbbreviations: MeOH = methanol, EtOH = ethanol, *n*-PrOH = *n*-propanol, and i-PrOH = i-propanol.

^bTaken from our previous gas-phase CC/EOMCC calculations reported in Ref. [3].

Table 3.3: The vertical transition energies $\omega_{10}(\text{em.})$ (in eV) and transition dipole moments μ_{10} (in D) corresponding to the $S_1 \rightarrow S_0$ emission, along with the μ_0 and μ_1 dipoles characterizing the S_0 and S_1 states (in D) and their ratios for **FR0**-SB in the gas phase and in selected alcohol solvents calculated at the respective S_1 minima following the CC/EOMCC-based protocol described in the text. Adapted from Ref. [5].

Solvent ^a	$\omega_{10}(\text{em.})$	μ_{10}	μ_0	μ_1	μ_1/μ_0
None (gas phase)	3.26	8.9	3.4	10.9	3.2
MeOH	2.68	11.8	6.6	20.0	3.0
EtOH	2.69	11.8	6.5	19.7	3.0
<i>n</i> -PrOH	2.70	11.8	6.5	19.6	3.0
i-PrOH	2.72	11.7	6.4	19.1	3.0

^aAbbreviations: MeOH = methanol, EtOH = ethanol, *n*-PrOH = *n*-propanol, and i-PrOH = i-propanol.

Table 3.4: A comparison of the calculated S_0 – S_1 adiabatic transition energies without $[\omega_{10}(\text{ad.})]$ and with $[\omega_{10}(0-0)]$ zero-point energy (ZPE) vibrational corrections (in eV), along with the differences and ratios of the μ_0 and μ_1 dipoles characterizing the S_0 and S_1 states at the respective minima (in D) for **FR0**-SB in the gas phase and in selected alcohol solvents obtained following the CC/EOMCC-based protocol described in the text with the corresponding experimentally derived data. Adapted from Ref. [5].

Theory					Experiment			
Solvent ^a	$\omega_{10}(\text{ad.})$	$\omega_{10}(0-0)^b$	$\Delta\mu_{10}^c$	μ_1/μ_0^c	Solvent ^a	$\omega_{10}(0-0)$	$\Delta\mu_{10}^d$	μ_1/μ_0^d
None (gas phase)	3.42	3.33	8.3	4.2	<i>c</i> -Hexane	3.4	—	—
MeOH	2.88	2.80	15.6	4.6	MeOH	2.9	15.2 ± 0.2	4.4 ± 0.1
EtOH	2.89	2.80	15.4	4.6	EtOH	3.0	15.3 ± 0.3	4.6 ± 0.1
<i>n</i> -PrOH	2.89	2.81	15.3	4.6	<i>n</i> -PrOH	3.0	15.3 ± 0.3	4.6 ± 0.1
i-PrOH	2.88	2.80	14.9	4.5	i-PrOH	3.0	15.5 ± 0.5	4.7 ± 0.1

^aAbbreviations: MeOH = methanol, EtOH = ethanol, *n*-PrOH = *n*-propanol, i-PrOH = i-propanol, and *c*-Hexane = cyclohexane.

^bCalculated as $\omega_{10}(\text{ad.}) + \Delta\text{ZPE}$, where ΔZPE is the difference between the zero-point vibrational energies characterizing the S_1 and S_0 electronic states of the bare **FR0**-SB molecule in the gas phase computed at the CAM-B3LYP/6-31+G* level of theory. Our calculations with and without solvent indicate that the effect of solvation on ΔZPE is negligible (less than 0.01 eV).

^cCalculated using the μ_0 values reported in Table 3.2 and the μ_1 values reported in Table 3.3.

^dCalculated using the theoretical values of μ_0 reported in Table 3.2 and the procedure based on the analysis of the experimental solvatochromic shifts described in the supplementary material of Ref. [5].

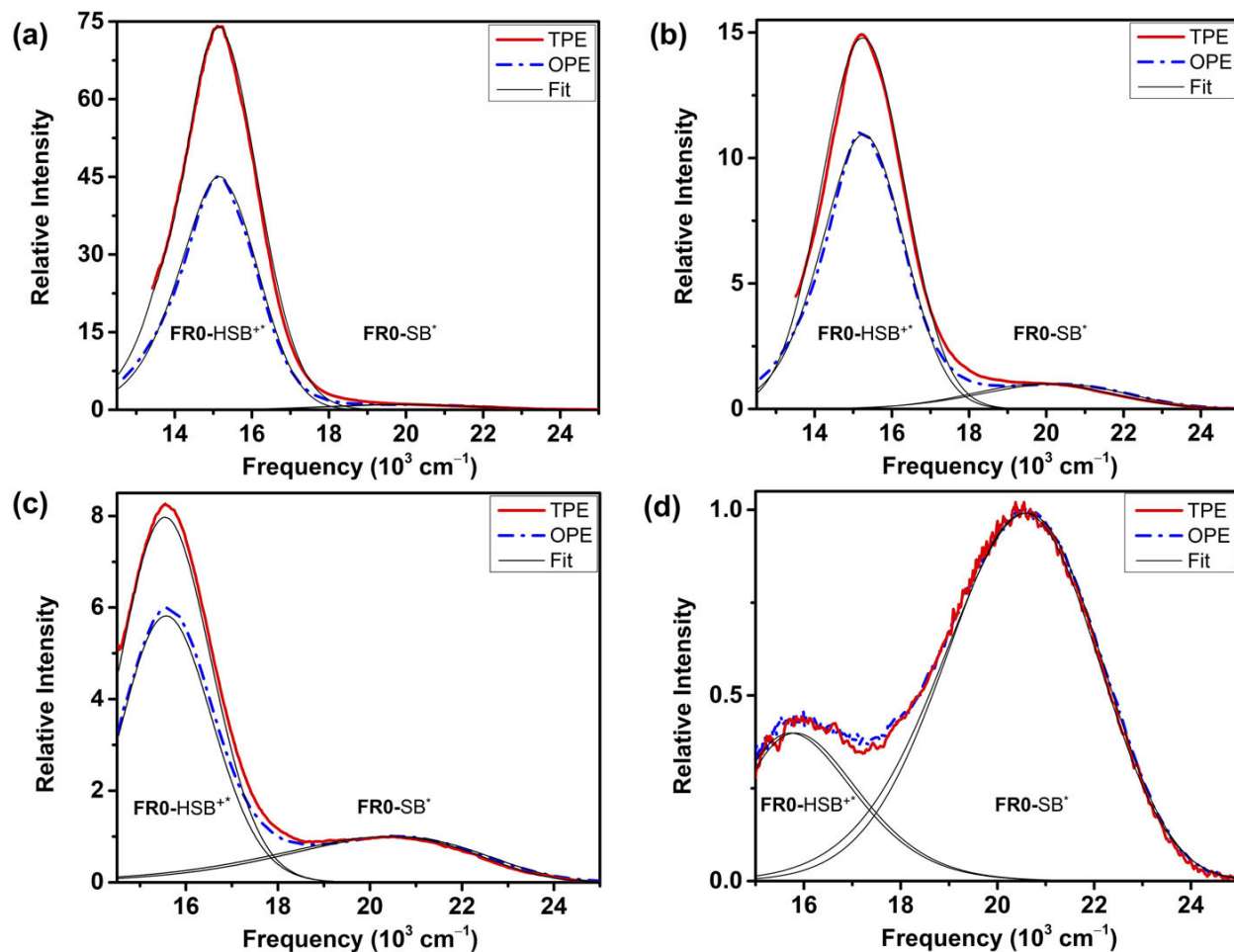


Figure 3.3: OPE and TPE steady-state fluorescence spectra obtained for **FR0-SB** in (a) methanol, (b) ethanol, (c) *n*-propanol, and (d) *i*-propanol. In each of the panels, OPE (blue line) is compared with TPE (red line). The fluorescence spectra are normalized to the nonprotonated emission intensity. The ratio between the areas for **FR0-HSB⁺*** ($\sim 15,000 \text{ cm}^{-1}$) and **FR0-SB^{*}** ($\sim 21,000 \text{ cm}^{-1}$) emission following OPE and TPE is determined by fits to log-normal functions (thin black lines). Adapted from Ref. [5].

As already alluded to above and as shown in the experimental data reported in Refs. [3–5], there are various effects that govern the extent of ESPT between the alcohol solvent environment and the **FR0**-SB chromophore. Among these effects, one that could significantly affect the ESPT reaction is steric effects due to the structure of the alcohol solvent molecules. We have seen this behavior in the OPE- and TPE-induced fluorescence spectra of **FR0**-SB in *i*-propanol, which do not differ from each other. Furthermore, when steady-state OPE-induced fluorescence measurements were performed on **FR0**-SB dissolved in various alcohol solvents, including primary, secondary, and tertiary alcohols, one observe varying degrees of proton transfer occurring. As shown in Fig. 3.4, adapted from Fig. 2 of Ref. [4], where each fluorescence spectrum is normalized with respect to the tallest peak in the spectrum, the extent of ESPT reaction, represented by the ratio between the emission peak areas of the protonated and unprotonated **FR0**-SB*, is considerably lower in secondary alcohols (represented by *i*-propanol and cyclopentanol in the figure) than in primary alcohol (represented by *n*-propanol in the figure). In fact, the ESPT reaction is not observed at all in tertiary alcohols, such as *t*-amyl alcohol, which exhibits very similar spectrum to the aprotic acetonitrile solvent. Thus, we set out to provide insights into the effect of solvent steric factors on the ESPT process. Specifically, we report the details of the ESPT reaction pathways between **FR0**-SB and representative primary and secondary alcohols predicted by quantum chemistry calculations.

To address this issue and to provide deeper insights into the role of steric effects in the proton transfer reactions between the excited **FR0**-SB* chromophore and alcohol solvent molecules, we augmented the experimental effort by performing electronic structure calculations focusing on the ground, S_0 , and first-excited singlet, S_1 , electronic states of the solvated **FR0**-SB system. In the calculations reported in this work, we focused on the reactions of **FR0**-SB* with *n*- and *i*-propanol. The *n*- and *i*-propanol molecules are the smallest alcohol species in the primary and secondary categories considered in our experiments that permit structural isomerism.

In modeling the ESPT process, we considered the interaction between **FR0**-SB* and a cluster of three alcohol molecules, which, according to our computations, is the minimum number of explicit solvent molecules necessary for the proton transfer to occur. In trying to use complexes consisting of **FR0**-SB* bound to fewer alcohol molecules, our calculations could not detect the presence of the second minimum corresponding to ESPT. The remaining, *i.e.*, bulk, solvation effects were incorporated using the SMD continuum solvation model.

In constructing the reaction pathways characterizing the proton transfer between **FR0**-SB* and *n*- and *i*-propanol, the following protocol was adopted. For each of the two alcohols, the geometries of the electronically excited reactant and product complexes were optimized. The reactant complex is the **FR0**-SB* chromophore hydrogen-bonded to the cluster of three solvent molecules, *i.e.*, the [**FR0**-SB*...HOR] species with two ROH molecules attached to the alcohol bonded to **FR0**-SB*. The product of the proton transfer reaction is the [**FR0**-HSB⁺*...⁻OR] complex with two ROH molecules attached to it. Having established the internuclear distances between the proton being transferred and the imine nitrogen of **FR0**-SB* in the reactant and the product complexes, designated in Fig. 3.5 as r_1 and r_2 , respectively, we probed the [**FR0**-SB*...HOR]→[**FR0**-HSB⁺*...⁻OR] reaction pathway by introducing an equidistant grid of N–H separations using the step size defined as $(r_1 - r_2)/10$. The molecular structure at each point along the above ESPT reaction pathway was obtained by freezing the N–H distance at the respective grid value and reoptimizing the remaining geometrical parameters. We also optimized the geometry of **FR0**-SB hydrogen-bonded to the cluster of three alcohol molecules in the ground electronic state, needed to calculate the $S_0 \rightarrow S_1$ vertical excitation energy.

All of the geometry optimizations relied on the Kohn–Sham formulation of DFT using, in the case of the structures along the ESPT reaction pathway, the TD-DFT extension to excited states combined with the SMD continuum solvation model to account for the bulk solvation effects (the analogous protocol employing SMD was used in the DFT ground-state optimizations). All of the calculations reported for this work [4] employed the 6-

31+G* basis set using spherical components of d functions and the CAM-B3LYP functional. All of the electronic structure calculations reported in this study were performed using the GAMESS package. As in the case of the OPE vs TPE study discussed above, when considering the optimized ground-state geometries, the $S_0 \rightarrow S_1$ vertical excitation energies, which, from the fundamental physics perspective, correspond to a very fast process resulting in an abrupt change in the solute electron density, were computed by taking advantage of the nonequilibrium solvation effects associated with the solvent relaxation delay, incorporating a fast component of the solvent dielectric constant in addition to its bulk value, as implemented in GAMESS.

The results of our quantum chemistry computations, shown in Figs. 3.6–3.8, reveal the intricacies of the excited-state proton abstraction process initiated by the formation of the [FR0-SB*...HOR] complex. In Fig. 3.6, we present the calculated minimum-energy pathways characterizing the ESPT reactions involving FR0-SB in its first-excited singlet S_1 state and the *n*- and *i*-propanol molecules along the internuclear distance between the imine nitrogen of FR0-SB and the proton being transferred. For completeness, the energetics characterizing the corresponding S_0 ground states as well as the S_0 and S_1 energies obtained at the optimized ground-state structures of the relevant [FR0-SB*...HOR] complexes are also provided (the leftmost points in Fig. 3.6). As shown in Fig. 3.6, the ground-state energy monotonically increases as the alcohol proton approaches the imine nitrogen of FR0-SB, indicating that the proton abstraction occurs in the excited state of FR0-SB, not in the ground state, in agreement with the experimental observations. As elaborated on above, in the experiments reported in this work, the excited state of FR0-SB is populated by photoabsorption from the ground electronic state. Our calculated $S_0 \rightarrow S_1$ excitation energies of FR0-SB in *n*- and *i*-propanol of ~ 3.6 eV agree quite well with their corresponding experimental values of ~ 3.3 eV (see Fig. 3.4 and 3.6–3.8). Upon relaxing the excited-state geometries (see the dashed lines in Fig. 3.6), the difference in the behavior of the bulkier *i*-propanol species in the [FR0-SB*...HOR] complex relative to its *n*-propanol counterpart

becomes apparent already in the early stages of the deprotonation process. In particular, the internuclear distance between the imine nitrogen of **FR0**-SB and the alcohol proton that is hydrogen-bonded to it is ~ 0.1 Å larger in i-propanol than in *n*-propanol (*cf.* Fig. 3.6–3.8). Furthermore, Fig. 3.6 reveals that even though the ESPT process takes place in both *n*- and i-propanol, the barrier height characterizing the reaction involving the secondary alcohol i-propanol species is $\sim 50\%$ higher than the analogous barrier associated with its primary alcohol *n*-propanol counterpart, consistent with the larger distance between the proton being transferred and the oxygen of the alcohol in i-propanol relative to that in *n*-propanol in the corresponding transition states (see Figs. 3.7 and 3.8). At the same time, the barrier for the reverse process, *i.e.*, deprotonation of **FR0**-HSB⁺*, in i-propanol is about 35% lower than that characterizing the analogous process in *n*-propanol.

Our calculations summarized in Figs. 3.7 and 3.8 imply that there is a need for a complex with two hydrogen bonds to the –OH group of the alcohol that transfers the proton. This “branched” arrangement is unusual; X-ray diffraction structures of the *n*-alkanols ethanol and butanol, congeners of *n*-propanol, show only linear structures of –OH moieties, in which each oxygen accepts only one hydrogen bond [246, 247]. However, the “structure” of *n*-propanol in the liquid phase has been studied and consists of chains of various lengths with modest amounts (a few percent) of branching [248–250]. For i-propanol, which has a stronger preference for cyclic clusters, such configurations are unlikely and again, are not observed in the crystal structure of the pure solvent [251].

Indeed, for both *n*- and i-propanol, our computations predict the linear alcohol clusters to be about 8–12 kJ mol^{−1} lower in energy compared to the branched arrangements, not only for the ground-state [**FR0**-SB...HOR] species, but also in the case of the [**FR0**-SB*...HOR] ESPT reactant. Nevertheless, the situation changes dramatically, in favor of the branched alcohol conformations, when one considers the [**FR0**-HSB⁺*...[−]OR] product of the ESPT reaction. In the case of *n*-propanol, for example, the branched [**FR0**-HSB⁺*...[−]OR] structure is lower in energy than the linear one by about 2 kJ mol^{−1}. This is related to the fact that

the branched alcohol arrangement solvates the RO^- species more effectively. Consequently, the $E_{\text{product}} - E_{\text{reactant}}$ energy difference in the case of the linear n -propanol configuration, of 14.3 kJ mol^{-1} , is higher than the 13.1 kJ mol^{-1} activation barrier characterizing the branched conformation (see Fig. 3.7), implying that the activation energy characterizing the linear arrangement is even larger. The difference between the branched and linear conformations is pronounced even more when one considers i-propanol. In this case, the $E_{\text{product}} - E_{\text{reactant}}$ energy difference in the linear cluster is about 8 kJ mol^{-1} higher than the activation barrier characterizing the branched arrangement (*cf.* Fig. 3.8). Based on our calculations we can conclude that the branched structures adopted in modeling of the ESPT reactions, while unusual in the case of the pure solvents, are a more realistic representation of the $[\mathbf{FR0}\text{-SB}^*\cdots\text{HOR}]\rightarrow[\mathbf{FR0}\text{-HSB}^{+*}\cdots\text{-OR}]$ process, since they lead to smaller activation energies compared to the linear arrangements of alcohol molecules bound to $\mathbf{FR0}\text{-SB}^*$. Last, but not least, the difficulty in achieving the configurations shown in Fig. 3.8 is consistent with the greatly diminished protonation yield observed for i-propanol and the lack of protonation observed for tertiary alcohols.

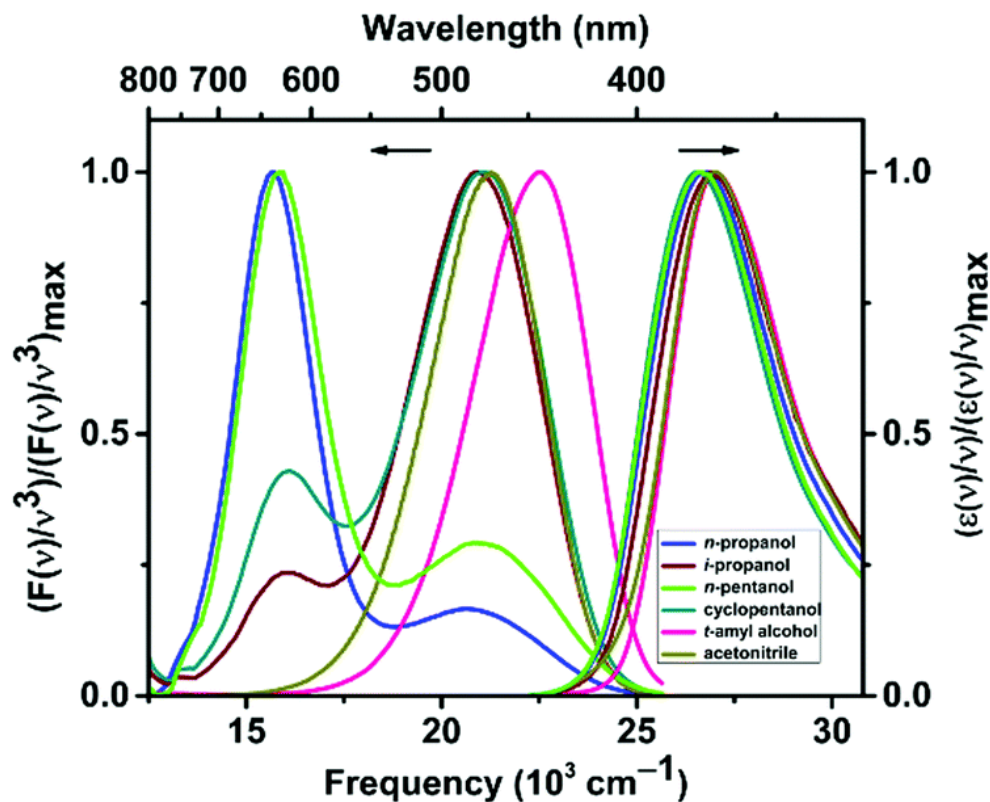


Figure 3.4: The absorption and emission spectra of **FR0-SB** in various solvents to compare steric hindrance. The long wavelength emission near 630 nm ($\sim 15,870 \text{ cm}^{-1}$) corresponds to **FR0-HSB⁺***, while the short wavelength emission near 460 nm ($\sim 21,740 \text{ cm}^{-1}$) corresponds to **FR0-SB***. Adapted from Ref. [4].

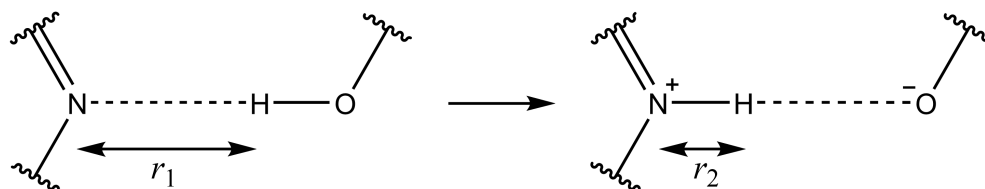


Figure 3.5: Schematic representation of the r_1 and r_2 N-H internuclear distances needed to create the grid defining the ESPT reaction pathway.

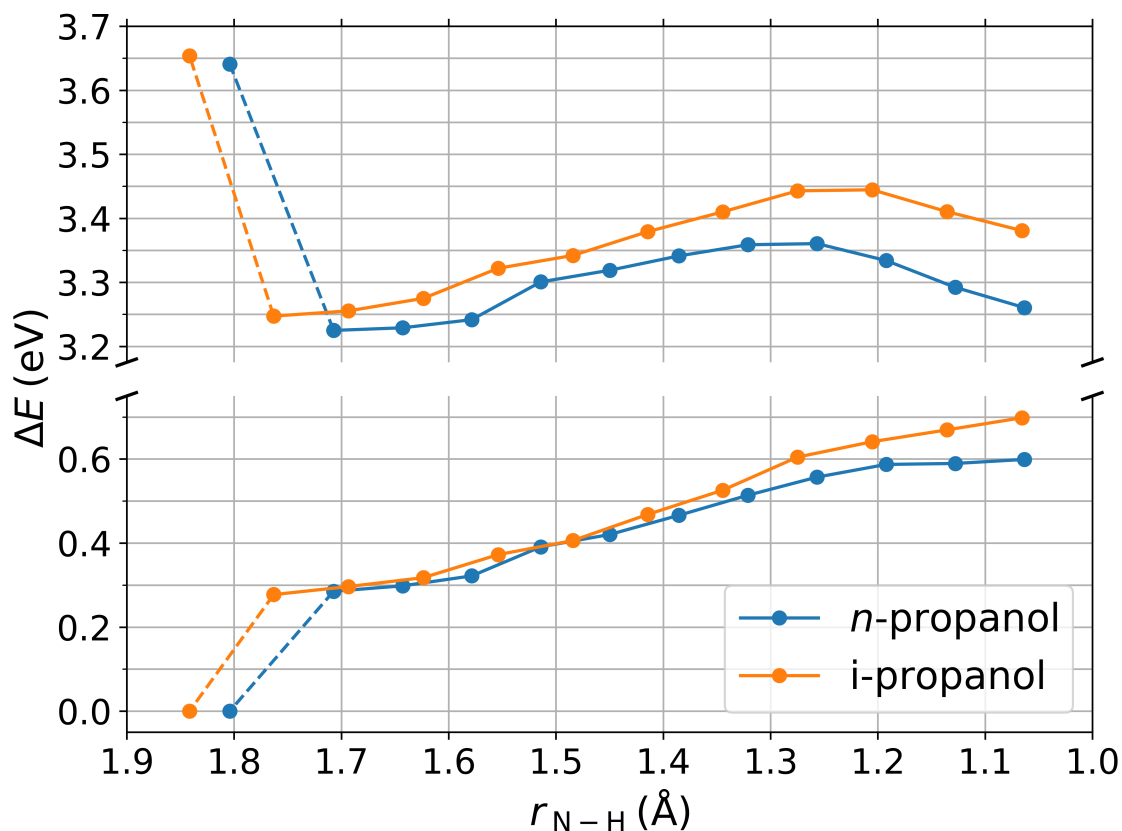


Figure 3.6: Results from the reaction pathway calculations showing ground- and excited-state energy differences as a function of proton abstraction. The CAM-B3LYP/6-31+G*/SMD ground-state (S_0) and excited-state (S_1) reaction pathways corresponding to the proton abstraction from *n*-propanol (blue) and *i*-propanol (orange) by **FR0-SB** along the internuclear distance between the imine nitrogen and the alcohol proton being transferred. The energies ΔE are shown relative to the ground-state minimum of the respective pathways. The dashed line in each pathway indicates the excited-state geometry relaxation following the S_0 - S_1 excitation of **FR0-SB**. Adapted from Ref. [4].

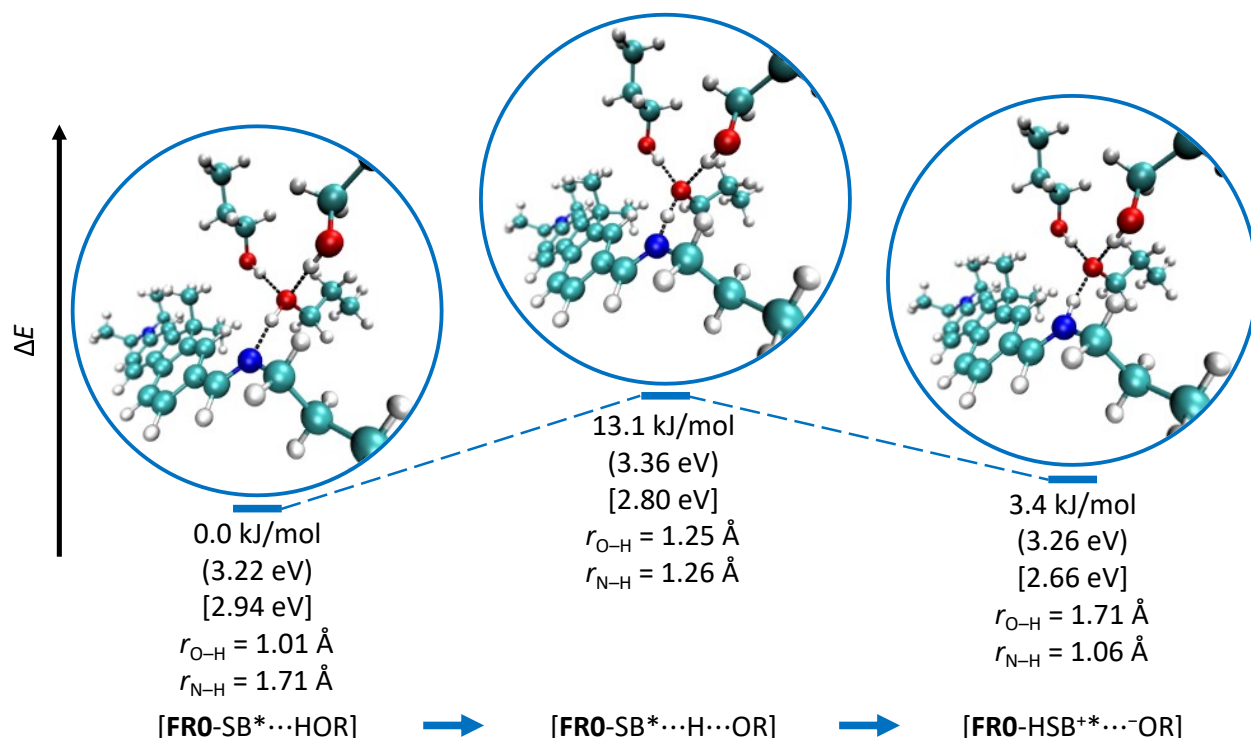


Figure 3.7: Snapshots of the proton abstraction process from *n*-propanol. The CAM-B3LYP/6-31+G*/SMD optimized geometries of the reactant ([**FR0**-SB*...HOR]), transition state ([**FR0**-SB*...H...OR]), and product ([**FR0**-HSB⁺*...⁻OR]) of the ESPT process between **FR0**-SB in its S_1 electronic state and three *n*-propanol molecules. The ΔE values in kJ mol^{-1} are given relative to the reactant energy. The energies inside parentheses, in eV, are given relative to the [**FR0**-SB*...HOR] minimum in the ground electronic state S_0 , while those inside square brackets correspond to the S_0 - S_1 vertical transitions at each respective geometry. The r_{O-H} and r_{N-H} distances at each geometry represent the internuclear separations between the proton being transferred and the oxygen of *n*-propanol and the imine nitrogen of **FR0**-SB, respectively. Adapted from Ref. [4].

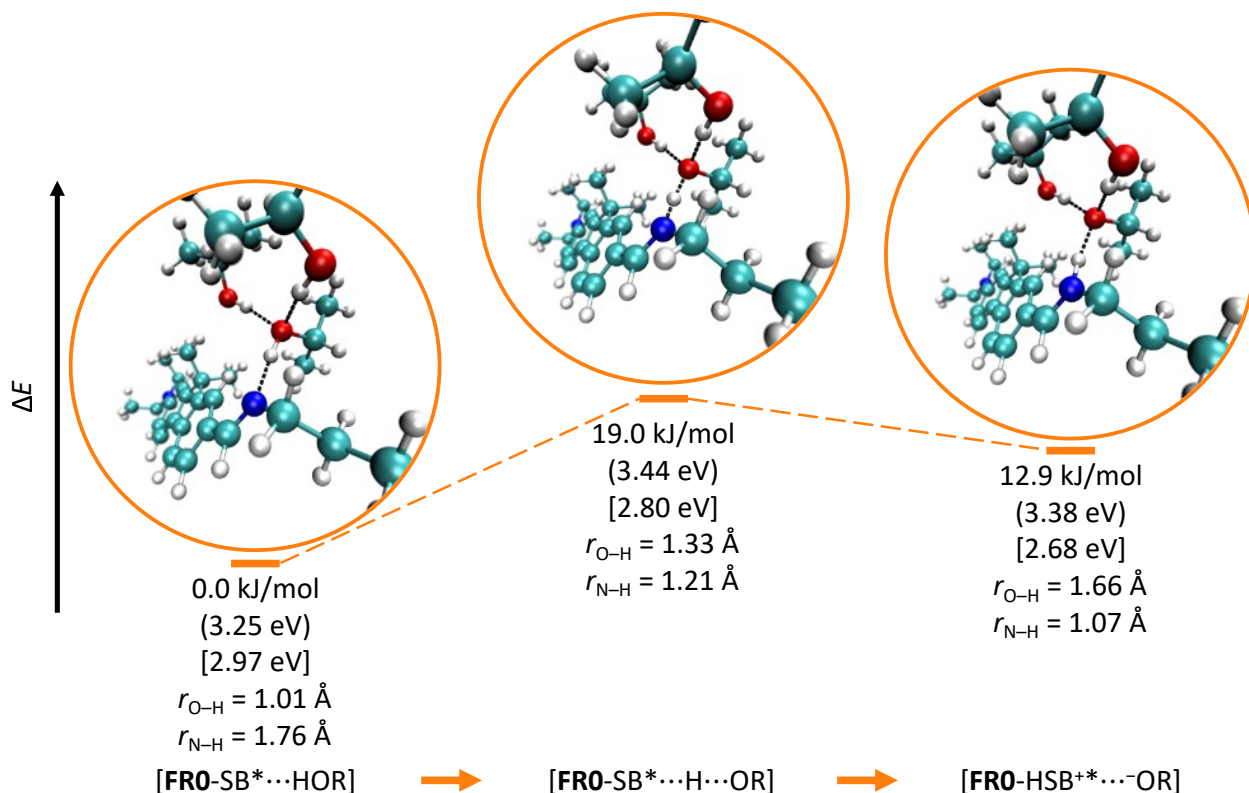


Figure 3.8: Snapshots of the proton abstraction process from i-propanol. The CAM-B3LYP/6-31+G*/SMD optimized geometries of the reactant ([**FR0-SB***...HOR]), transition state ([**FR0-SB***...H...OR]), and product ([**FR0-HSB**⁺*...-OR]) of the ESPT process between **FR0-SB** in its S_1 electronic state and three i-propanol molecules. The ΔE values in kJ mol^{-1} are given relative to the reactant energy. The energies inside parentheses, in eV, are given relative to the [**FR0-SB***...HOR] minimum in the ground electronic state S_0 , while those inside square brackets correspond to the S_0 - S_1 vertical transitions at each respective geometry. The r_{O-H} and r_{N-H} distances at each geometry represent the internuclear separations between the proton being transferred and the oxygen of i-propanol and the imine nitrogen of **FR0-SB**, respectively. Adapted from Ref. [4].

3.3 Active-Space CC/EOMCC Approaches and Their CC(P ; Q) Extensions

3.3.1 Theory

In the previous section, we discussed the simplest forms of CC(P ; Q) formalism, namely, the CR-CC and CR-EOMCC schemes. As shown by applying the CR-CC(2,3) and δ -CR-EOMCC(2,3) methods to the **FR0**-SB photobase, the CR-CC/EOMCC approaches can be very accurate. However, as mentioned in the Introduction, there are certain problems where CR-CC/EOMCC methods fail. In such situation, there usually exists a large coupling between the lower-order components of the cluster and EOM excitation operators, such as T_1 and T_2 in the former case and $R_{\mu,1}$ and $R_{\mu,2}$ in the latter case, and their higher-order counterparts, *e.g.*, T_3 ($R_{\mu,3}$), T_4 ($R_{\mu,4}$), *etc.* Within the CR-CC/EOMCC way of performing CC(P ; Q) calculations, the P space is defined by relying on traditional truncations of the cluster and EOM excitation operators and, thus, the aforementioned coupling is neglected. This becomes an issue when the higher-order T_n and $R_{\mu,n}$ components with $n > 2$ become large. However, one can rely on “unconventional” partitioning of the P and Q spaces to allow for the relaxation of T_1 and T_2 , as well as $R_{\mu,1}$ and $R_{\mu,2}$ if EOMCC computations are concerned, in the presence of their dominant higher-order counterparts. One way to do this is via the use of active-space CC and EOMCC methodology, where one downselects T_3 , T_4 , *etc.* and their $R_{\mu,n}$ counterparts using a set of predefined active orbitals. Here, we focus on the ground-state approaches relevant to this dissertation work, namely, active-space CC methods with up to quadruply excited clusters and their CC(P ; Q) extension.

In the active-space CC/EOMCC approaches, we divide the spin-orbitals used in the CC/EOMCC calculations into four separate categories, namely core, active occupied, active unoccupied, and virtual spin-orbitals, and approximate the higher-order cluster and excitation operators with the help of active orbitals, while treating the lower-order ones fully. This provides us with a mechanism to relax the T_1 , T_2 , $R_{\mu,1}$, and $R_{\mu,2}$ amplitudes in the

presence of the dominant, higher-order cluster and excitation amplitudes, which is absent in the CR-CC/EOMCC framework, while avoiding the steep computational costs of the full CCSDT/EOMCCSDT and CCSDTQ/EOMCCSDTQ approaches.

The active-space methods employed in this dissertation are CCSDt and CCSDTq, where we follow a general recipe how to design the active-space CC methods at any level of truncation in the cluster operator laid down in Refs. [99, 101]. Thus, in CCSDt, we approximate the cluster operator T as

$$T \approx T^{(\text{CCSDt})} = T_1 + T_2 + t_3, \quad (3.35)$$

where T_1 and T_2 are the standard one- and two-body components of T , treated fully, and

$$t_3 = \sum_{\substack{i < j < \mathbf{K} \\ \mathbf{A} < b < c}} t_{\mathbf{A}bc}^{ij\mathbf{K}} E_{ij\mathbf{K}}^{\mathbf{A}bc} \quad (3.36)$$

is an approximate form of T_3 defined using active orbitals. We use a convention where upper-case bold letters $\mathbf{I}, \mathbf{J}, \mathbf{K}, \mathbf{L}, \dots$ are the active occupied spin-orbitals, whereas $\mathbf{A}, \mathbf{B}, \mathbf{C}, \mathbf{D}, \dots$ designate the active unoccupied spin-orbitals. We continue using the lower-case italic indices, $i, j, \dots$ for the occupied and $a, b, \dots$ for the unoccupied spin-orbitals, if the active/inactive character is not specified. Adopting the same convention, in the CCSDTq approach we approximate the cluster operator T using

$$T \approx T^{(\text{CCSDTq})} = T_1 + T_2 + T_3 + t_4, \quad (3.37)$$

where T_3 is the normal three-body component of T , treated fully, and

$$t_4 = \sum_{\substack{i < j < k < \mathbf{L} \\ \mathbf{A} < b < c < d}} t_{\mathbf{A}bcd}^{ijk\mathbf{L}} E_{ijk\mathbf{L}}^{\mathbf{A}bcd}. \quad (3.38)$$

The corresponding cluster amplitudes, t_a^i , t_{ab}^{ij} , and $t_{\mathbf{A}bc}^{ij\mathbf{K}}$ in the CCSDt case and t_a^i , t_{ab}^{ij} , t_{abc}^{ijk} , and $t_{\mathbf{A}bcd}^{ijk\mathbf{L}}$ in the case of CCSDTq, are obtained by solving the CC amplitude equations, Eq. (2.7), projected on the excited determinants corresponding to the definitions of $T^{(\text{CCSDt})}$ and $T^{(\text{CCSDTq})}$. For example, in CCSDt we project Eq. (2.6), in which T is replaced by $T^{(\text{CCSDt})}$ as defined in Eq. (3.35), on the excited determinants $|\Phi_i^a\rangle$, $|\Phi_{ij}^{ab}\rangle$, and

$|\Phi_{ij\mathbf{K}}^{\mathbf{A}bc}\rangle$, *i.e.*, on all singly and doubly excited determinants, and on a subset of triply excited determinants defined using active orbitals. This and other similar simplifications in the CC amplitude equations result in significant CPU time savings. The computational costs associated with the CCSDt and CCSDTq methods equal to those of CCSD and CCSDT, respectively, multiplied by small prefactors that depend on the numbers of active occupied (N_o) and active unoccupied (N_u) orbitals. To be precise, the most expensive CPU steps of the CCSDt and CCSDTq calculations scale as $N_o N_u n_o^2 n_u^4$ and $N_o N_u n_o^3 n_u^5$, respectively. Once the corresponding cluster amplitudes are determined, the CCSDt and CCSDTq energies are obtained, in direct analogy with the conventional SRCC methods, by projecting Eq. (2.6) on the reference determinant, *i.e.*, we continue using Eq. (2.8), where T is approximated by $T^{(\text{CCSDt})}$ and $T^{(\text{CCSDTq})}$, respectively.

After the cluster amplitudes and ground-state energy are determined, we can then employ the $\text{CC}(P;Q)$ formalism to correct the active-space CC energy for the remaining correlation effects of interest. To do so, we simply have to design the suitable Q space, which should not contain the higher-than-doubly excited determinants already incorporated in the P space. This is shown in Table 3.5, which displays the key elements of the various ground-state $\text{CC}(P;Q)$ methodologies that we have discussed so far, *i.e.*, the CR-CC approaches and the active-space-based $\text{CC}(P;Q)$ schemes, summarized using the language of the $\text{CC}(P;Q)$ along with the corresponding CPU time scalings. As shown in Table 3.5, we obtain the $\text{CC}(\text{t};3)$ energy by solving the CCSDt equations in the P space $\mathcal{H}^{(P)} = \mathcal{G}^{(\text{SD})} \oplus \mathcal{G}^{(\text{t})}$ and correcting the resulting CCSDt energy for the triples outside the active set using the $\delta_0(P;Q)$ correction defined in the Q space $\mathcal{H}^{(Q)} = \mathcal{G}^{(\text{T})} \ominus \mathcal{G}^{(\text{t})}$, where $\mathcal{G}^{(\text{SD})} = \text{span}\{|\Phi_i^a\rangle, |\Phi_{ij}^{ab}\rangle \mid i < j, a < b\}$, $\mathcal{G}^{(\text{t})} = \text{span}\{|\Phi_{ij\mathbf{K}}^{\mathbf{A}bc}\rangle \mid i < j < \mathbf{K}, \mathbf{A} < b < c\}$, and $\mathcal{G}^{(\text{T})} = \text{span}\{|\Phi_{ijk}^{abc}\rangle \mid i < j < k, a < b < c\}$. Similarly, we obtain the $\text{CC}(\text{q};4)$ energy by solving the CCSDTq equations in the P space $\mathcal{H}^{(P)} = \mathcal{G}^{(\text{SD})} \oplus \mathcal{G}^{(\text{T})} \oplus \mathcal{G}^{(\text{q})}$ and correcting the resulting CCSDTq energy for the subsets of quadruply excited determinants in $\mathcal{H}^{(Q)} = \mathcal{G}^{(\text{Q})} \ominus \mathcal{G}^{(\text{q})}$, where $\mathcal{G}^{(\text{q})} = \text{span}\{|\Phi_{ijk\mathbf{L}}^{\mathbf{A}bcd}\rangle \mid i < j < k < \mathbf{L}, \mathbf{A} < b < c < d\}$ and $\mathcal{G}^{(\text{Q})} = \text{span}\{|\Phi_{ijkl}^{abcd}\rangle \mid i < j < k < l, a < b < c < d\}$.

Table 3.5: The key elements of the various deterministic CC methodologies employed in this work summarized using the language of the $\text{CC}(P;Q)$ formalism, including the P spaces $\mathcal{H}^{(P)}$ adopted in the iterative CC calculations and the Q spaces $\mathcal{H}^{(Q)}$ and $D_{0,K}(P)$ denominators defining the appropriate noniterative $\delta_0(P;Q)$ corrections (if any), along with the corresponding CPU time scalings.^a Adapted from Ref. [1].

Method	$\mathcal{H}^{(P)}$ space ^b	$\mathcal{H}^{(Q)}$ space ^b	$D_{0,K}(P)$ type ^c	CPU time scaling	
				Iterative	Noniterative
CCSD	$\mathcal{G}^{(\text{SD})}$	$\{\emptyset\}$	—	$n_o^2 n_u^4$	—
CCSD(2) _T	$\mathcal{G}^{(\text{SD})}$	$\mathcal{G}^{(\text{T})}$	MP	$n_o^2 n_u^4$	$n_o^3 n_u^4$
CR-CC(2,3)	$\mathcal{G}^{(\text{SD})}$	$\mathcal{G}^{(\text{T})}$	EN	$n_o^2 n_u^4$	$n_o^3 n_u^4$
CCSDt	$\mathcal{G}^{(\text{SD})} \oplus \mathcal{G}^{(\text{t})}$	$\{\emptyset\}$	—	$N_o N_u n_o^2 n_u^4$	—
CC(t;3)	$\mathcal{G}^{(\text{SD})} \oplus \mathcal{G}^{(\text{t})}$	$\mathcal{G}^{(\text{T})} \ominus \mathcal{G}^{(\text{t})}$	EN	$N_o N_u n_o^2 n_u^4$	$n_o^3 n_u^4$
CCSDT	$\mathcal{G}^{(\text{SD})} \oplus \mathcal{G}^{(\text{T})}$	$\{\emptyset\}$	—	$n_o^3 n_u^5$	—
CCSDT _q	$\mathcal{G}^{(\text{SD})} \oplus \mathcal{G}^{(\text{T})} \oplus \mathcal{G}^{(\text{q})}$	$\{\emptyset\}$	—	$N_o N_u n_o^3 n_u^5$	—
CC(q;4)	$\mathcal{G}^{(\text{SD})} \oplus \mathcal{G}^{(\text{T})} \oplus \mathcal{G}^{(\text{q})}$	$\mathcal{G}^{(\text{Q})} \ominus \mathcal{G}^{(\text{q})}$	MP	$N_o N_u n_o^3 n_u^5$	$n_o^2 n_u^5$
CCSDTQ	$\mathcal{G}^{(\text{SD})} \oplus \mathcal{G}^{(\text{T})} \oplus \mathcal{G}^{(\text{Q})}$	$\{\emptyset\}$	—	$n_o^4 n_u^6$	—

^aThe conventional CCSD(T) approach is not included, since CCSD(T) is an approximation to CCSD(2)_T and CR-CC(2,3). The relationships between the CCSD(T) approach and the CCSD(2)_T and CR-CC(2,3) methods have been discussed in Refs. [89, 90, 92].

^bThe P and Q spaces are defined in terms of subsets of Slater determinants in the many-electron Hilbert space referred to as $\mathcal{G}^{(\text{SD})}$, $\mathcal{G}^{(\text{t})}$, $\mathcal{G}^{(\text{T})}$, $\mathcal{G}^{(\text{q})}$, and $\mathcal{G}^{(\text{Q})}$. The corresponding definitions can be found in the text.

^cEN stands for the Epstein–Nesbet-like form of the $D_{0,K}(P)$ denominator, Eq. (3.12). MP stands for the Møller–Plesset-type approximation to Eq. (3.12), obtained by replacing $\overline{H}^{(P)}$ by the Fock operator, assuming a canonical RHF basis.

3.3.2 Application: Ground-State Potential Curve and Vibrational Term Values of Mg₂

To demonstrate the power of the active-space-based $\text{CC}(P;Q)$ schemes, we now return to the example of the challenging weakly bound Mg₂ dimer. As explained in Section 2.2, one needs to go to at least CCSDT correlating nearly all electrons and correcting for valence FCI correlation effects to achieve spectroscopic, *i.e.*, $\sim 1 \text{ cm}^{-1}$, accuracy relative to experiment. We have also discussed the failure of CCSD(T) to capture the entire vibrational manifold supported by the $X^1\Sigma_g^+$ state of Mg₂. Therefore, in this section we will summarize the results reported in Ref. [1], where we benchmarked various CC methods including up to triples and quadruples against the parent CCSDT and CCSDTQ schemes, respectively.

All of the CCSD, CCSD(T), CCSD(2)_T, and CR-CC(2,3) computations reported here were performed using the CC routines developed by the Piecuch group and described in Refs. [89, 90, 186], which are available in the GAMESS package as standard options. The remaining CCSDt, CC(t;3), CCSDT, CCSDT_q, CC(q;4), and CCSDTQ calculations were carried out using our group’s codes as well, although in this case we relied on the routines developed in Refs. [73–77], which, with the exception of CCSDt and CC(t;3), are still outside GAMESS (they are interfaced with the GAMESS HF and integral transformation routines though). To facilitate our CCSDTQ calculations, in which we froze the core electrons, we took advantage of the GAMESS determinantal FCI code, since CCSDTQ and FCI become equivalent when only four electrons are correlated and FCI in GAMESS can take advantage of the spatial symmetry, which our CCSDTQ routines cannot do. As in the case of the earlier study of the beryllium dimer [73], all of the CC calculations for Mg₂ reported in this work used the restricted HF (RHF) references. The active-space CCSDt and CCSDT_q computations and the CC(t;3) and CC(q;4) corrections to CCSDt and CCSDT_q used two active occupied and six active unoccupied orbitals corresponding to the 3s and 3p valence shells of the magnesium atoms.

To enrich our analysis of the performance of the various methods and to enable appropriate basis set extrapolations, we used four different atomic orbital basis sets. In the case of the frozen-core CC calculations correlating the 3s valence shells of the magnesium atoms, we used the A(T+d)Z (all methods) and A(Q+d)Z (all methods up to full CCSDT) bases developed in Ref. [179] and taken from the Peterson group’s website [180]. The A(n+d)Z family of basis sets incorporates an additional tight d function in comparison to its more commonly used aug-cc-pVnZ counterpart, which has been shown to help accelerate the convergence of bond lengths and dissociation energies [179]. For methods with up to triply excited clusters, we estimated the subvalence correlation effects by correlating all electrons other than the 1s shells of the Mg monomers. In these calculations, we used the augmented weighted core-valence AwCTZ and AwCQZ basis sets, which were constructed by augmenting the cc-pwCVTZ and

cc-pwCVQZ bases with the diffuse functions of the corresponding aug-cc-pVTZ and aug-cc-pVQZ basis sets, respectively [179]. Prascher *et al.* [179] have demonstrated that the use of the aug-cc-pwCVnZ basis sets over their standard aug-cc-pCVnZ counterparts is generally beneficial in determining dissociation energies and spectroscopic properties of magnesium compounds. We took these basis sets from the Peterson group’s website [180] as well.

In analogy to the earlier Be₂ work [73], the $J = 0$ vibrational term values of ²⁴Mg₂ (the most abundant isotopolog of the magnesium dimer) corresponding to the various CC PECs obtained in this study were determined by numerically integrating the radial Schrödinger equation from 3.2 to 15.0 Å. To do this, we used the Numerov–Cooley algorithm [187] available in the LEVEL16 code [188]. The list of internuclear separations r , at which the electronic energies were calculated, is as follows: 3.2, 3.3, 3.4, 3.6, 3.7, 3.8, 3.9, 4.0, 4.1, 4.2, 4.4, 4.6, 4.8, 5.0, 5.2, 5.4, 5.6, 5.8, 6.0, 6.4, 6.8, 7.2, 7.6, 8.0, 8.4, 8.8, 9.2, 9.6, 10.0, 11.0, 12.0, 13.0, and 15.0 Å. The D_e and r_e values corresponding to the various PECs obtained in this work were determined using LEVEL16 as well. There was only one situation where we had to extend the radius for integrating the radial Schrödinger equation beyond 15.0 Å, namely, the determination of the barely bound $v = 18$ state found in our extrapolated highest-level CC(q;4)- and CCSDTQ-type computations, and we will return to this issue later when we compare our best results with experiment.

Our calculations for Mg₂ are summarized in Tables 3.6–3.17 and Figs. 3.9 and 3.10. We split our discussion into the following three parts: (i) the valence and nearly all-electron calculations using CCSD(T), CCSD(2)_T, CR-CC(2,3), CCSDt, CC(t;3), and CCSDT, *i.e.*, the CC methods with connected triples and (ii) the valence calculations using CCSDT_q, CC(q;4), and CCSDTQ, *i.e.*, the CC methods with connected triples and quadruples, and (iii) comparisons of two kinds of composite calculations, in which the valence CC(q;4) and CCSDTQ computations are combined with the nearly all-electron CCSDT energetics, both with each other and with experiment.

In this section, we compare the CCSD(T), CCSD(2)_T, CR-CC(2,3), CCSDt, and CC(t;3)

results for the magnesium dimer, using the A(T+d)Z and A(Q+d)Z basis sets in the frozen-core calculations and the AwCTZ and AwCQZ bases in the subvalence computations correlating all electrons but the 1s shells of the Mg atoms, with the parent full CCSDT data. The ground-state electronic energies at selected values of r are shown in Tables 3.6–3.9 and Fig. 3.9. The D_e , r_e , and vibrational term values can be found in Tables 3.10–3.13.

As shown in Tables 3.6–3.13 and Fig. 3.9, the relative accuracy patterns observed in the calculations for the previously studied beryllium dimer [73] apply to its larger Mg_2 counterpart as well. In particular, in analogy to Be_2 , the CR-CC(2,3) method works better than the other employed triples corrections to CCSD. This can be seen by inspecting the mean unsigned error (MUE) and, especially, the nonparallelity error (NPE) values relative to CCSDT characterizing the CCSD(T), CCSD(2)_T, and CR-CC(2,3) PECs. For example, when the A(T+d)Z basis set is employed and the core electrons of Mg_2 are frozen in post-RHF calculations, the MUE and NPE values relative to CCSDT characterizing the CCSD(T), CCSD(2)_T, and CR-CC(2,3) PECs of Mg_2 are 0.185 and 0.559 millihartree, respectively, in the case of CCSD(T), 0.268 and 0.805 millihartree, respectively, in the case of CCSD(2)_T, and 0.085 and 0.237 millihartree, respectively, in the CR-CC(2,3) case (see Table 3.6). When the larger A(Q+d)Z basis set is employed or when all but the 1s electrons of the Mg atoms are correlated, the CR-CC(2,3) approach offers similar improvements. For example, when the valence A(T+d)Z basis set is replaced by its core-valence AwCTZ counterpart and all but the 1s electrons of the magnesium monomers are correlated, the CR-CC(2,3) method reduces the NPE values relative to CCSDT characterizing the CCSD(T) and CCSD(2)_T potentials from 0.415 and 0.687 millihartree, respectively, to 0.185 millihartree (see Table 3.7). The MUE value resulting from the CR-CC(2,3)/AwCTZ calculations, of 0.331 millihartree, is somewhat larger than the 0.190 millihartree obtained with CCSD(T)/AwCTZ, and a similar pattern is observed when the AwCQZ basis set is considered, but the overall shapes of the CR-CC(2,3) PECs are always closer to those obtained in the CCSDT calculations than the shapes of the corresponding CCSD(T) and CCSD(2)_T PECs, independent of the basis set

and independent of the number of correlated electrons (*cf.* Fig. 3.9). The more accurate description of the $X\ ^1\Sigma_g^+$ potential of Mg_2 by the CR-CC(2,3) method, when compared to its CCSD(T) and CCSD(2)_T counterparts, can also be seen by comparing the corresponding dissociation energies D_e . For the four basis sets used in this study, the CR-CC(2,3) calculations recover 92–97% of the parent CCSDT D_e values, which is considerably better than the 84–89% obtained with CCSD(T) and 77–82% obtained with CCSD(2)_T.

Similarly to the smaller beryllium dimer [73], the improvements in the CCSD(T) and CCSD(2)_T PECs of Mg_2 offered by CR-CC(2,3) result in the improved vibrational term values $G(v)$ (see Tables 3.10–3.13). In the frozen-core calculations correlating valence electrons only, summarized in Tables 3.10 and 3.12, the CR-CC(2,3) approach reduces the deviations from CCSDT characterizing the CCSD(T) and CCSD(2)_T $G(v)$ values by factors of 1.8–2.4 and 2.7–3.4, respectively. When all but the 1s electrons of the magnesium atoms are correlated, each CR-CC(2,3) PEC supports one extra vibrational level compared to the corresponding CCSDT potential, but other than that the CR-CC(2,3) method is considerably more accurate than its CCSD(T) and CCSD(2)_T counterparts, reducing errors in the $G(v)$ values relative to CCSDT by factors of 1.6–2.8 and 2.7–4.3, respectively.

We can conclude this part of our discussion by stating that the CR-CC(2,3) approach improves the results obtained with the other noniterative triples corrections to the CCSD energies examined in this work, overcoming major deficiencies in the underlying CCSD potentials, which display unphysically shallow minima, but when compared to the full treatment of triples by CCSDT, the CR-CC(2,3) calculations for Mg_2 are still not as accurate as desired. For example, the CR-CC(2,3) PECs, although better than those obtained with the CCSD(T) and CCSD(2)_T methods, remain too shallow compared to their parent CCSDT counterparts (by 15–36 cm^{-1} or 3–8%, when the dissociation energies D_e are examined). As a result, as shown in Table 3.13, when the last, $v = 17$, vibrational level supported by the CCSDT/AwCQZ potential is examined, the difference between the corresponding CR-CC(2,3)/AwCQZ and CCSDT/AwCQZ $G(v)$ values, which is 19.7 cm^{-1} or 5%, is still

quite large. The CR-CC(2,3)/AwCQZ calculations improve the corresponding CCSD(T) and CCSD(2)_T potentials, which do not even support the $v = 17$ bound state in this case, but it would be useful to improve the CR-CC(2,3) description of Mg₂, while retaining the simplicity of the idea of noniterative triples corrections. The opportunity to do this is provided by the CC(t;3) approach, in which instead of correcting the CCSD energies for all triples, as in CCSD(T), CCSD(2)_T, and CR-CC(2,3), one corrects the CCSDt energies for the subset of triples outside the $\mathcal{G}^{(t)}$ subspace defined above, missing in CCSDt. Although, as shown in Tables 3.6–3.13 and Fig. 3.9, the CCSDt method using small numbers of active orbitals to select the leading triply excited (T_3) clusters is incapable of producing an accurate PEC for the magnesium dimer, it does improve the CCSD results and, as emphasized in the earlier works reporting CC(P ; Q) calculations [73–77], it also improves the quality of the singly and doubly excited clusters, T_1 and T_2 , respectively, compared to their CCSD values, since in CCSDt they are iterated in the presence of the dominant T_3 contributions captured using active orbitals. As a result, we can anticipate further improvements in the description of the ground-state PEC of the magnesium dimer, when the triples corrections to CCSD are replaced by the CC(t;3) correction to CCSDt.

Direct inspection of the CC(t;3) results in Tables 3.6–3.13 and Fig. 3.9 confirms our expectations. Indeed, we see a significant improvement in the description of the Mg₂ X $^1\Sigma_g^+$ potential by the CCSD-based CR-CC(2,3) and underlying CCSDt approaches. As shown in Fig. 3.9, the CC(t;3) method always deepens the minimum and brings the resulting PECs to an excellent agreement with their CCSDT counterparts. As a result, the MUE and NPE values relative to CCSDT characterizing the CC(t;3) potentials are tiny, ranging from 0.038 to 0.369 millihartree in the case of MUEs and 0.039 to 0.131 millihartree for NPEs (see Tables 3.6–3.9). To appreciate the degree of improvement offered by the CC(t;3) approach, we should compare the MUE and NPE values relative to CCSDT characterizing the CC(t;3) calculations with the MUEs and NPEs obtained with CR-CC(2,3), which are 0.085–0.448 and 0.185–0.282 millihartree, respectively, not to mention the much worse MUE and NPE values

obtained with CCSDt, which can be as large as 9.159 millihartree for the MUEs and 2.057 millihartree for the NPEs. The above improvements in the description of the ground-state PEC of Mg_2 offered by the CC(t;3) correction to CCSDt result in the excellent agreements between the CC(t;3) and full CCSDT data for the binding energies D_e , the equilibrium bond lengths r_e , and the vibrational term values $G(v)$, which parallel those observed for the beryllium dimer [73]. As shown in Tables 3.10–3.13, the CC(t;3) calculations replace the 15–36 cm^{-1} and 0.025–0.035 Å errors relative to CCSDT in the D_e and r_e values obtained with CR-CC(2,3) by the substantially smaller 1–19 cm^{-1} and 0.006–0.013 Å errors, and we observe similarly impressive improvements when the vibrational term values are examined. For example, when the subvalence electrons are included in the post-RHF calculations and the largest basis set employed in this study, namely, AwCQZ, is considered, the CC(t;3) approach reduces the 1–21 cm^{-1} or 4–5% errors relative to CCSDT obtained in the CR-CC(2,3) calculations for the $v = 0$ –17 vibrational states supported by the CCSDT potential to 0.5–7 cm^{-1} or 1–2% (see Table 3.13). Even though the CC(t;3)/AwCQZ potential, just like its CR-CC(2,3)/AwCQZ counterpart, captures an additional, $v = 18$, vibrational level, which is not supported by the corresponding CCSDT PEC, the $v = 17$ vibrational state obtained with the CC(t;3)/AwCQZ approach, which the full CCSDT/AwCQZ calculation places at 411.3 cm^{-1} , is only 4.2 cm^{-1} away from the parent CCSDT/AwCQZ value, in contrast to the much larger 19.7 cm^{-1} deviation from CCSDT/AwCQZ obtained using CR-CC(2,3)/AwCQZ.

Based on the above analysis, and consistent with our earlier findings for the beryllium dimer [73], we can conclude this subsection by stating that the CC(t;3) correction to the CCSDt energy produces the results of the nearly CCSDT quality when the larger and similarly challenging Mg_2 species is examined. By replacing the nonrelaxed T_1 and T_2 cluster components obtained with CCSD in defining the triples energy correction by the T_1 and T_2 clusters iterated in the presence of the leading T_3 contributions captured by CCSDt and by using the CC(P ; Q)-based CC(t;3) correction $\delta_0(P; Q)$ to describe the remaining rather than

all T_3 correlations, we generate PECs that are much closer to their CCSDT parents than the analogous PECs obtained using the CCSD(T), CCSD(2)_T, and CR-CC(2,3) corrections to CCSD. We now proceed to the examination of the effectiveness of the CC(q;4) correction to the CCSDTq energy in reproducing the results of the full CCSDTQ calculations for Mg₂.

Table 3.6: Electronic energies of the magnesium dimer at selected internuclear separations r (in Å) obtained in the various valence CC calculations with up to triply excited clusters using the A(T+d)Z basis set.^a Adapted from Ref. [1].

r	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3)	CCSDt	CC(t;3)	CCSDT
3.2	2.796	0.559	0.805	0.237	1.870	0.092	−0.293121
3.4	2.395	0.490	0.702	0.208	1.626	0.085	−0.294880
3.6	2.023	0.421	0.603	0.185	1.389	0.079	−0.295699
3.8	1.689	0.356	0.511	0.162	1.168	0.072	−0.296013
3.9	1.537	0.325	0.469	0.151	1.066	0.068	−0.296061
4.0	1.396	0.296	0.429	0.140	0.969	0.064	−0.296062
4.2	1.145	0.244	0.357	0.120	0.796	0.056	−0.295976
4.8	0.610	0.130	0.197	0.072	0.419	0.036	−0.295464
5.4	0.317	0.068	0.106	0.043	0.212	0.022	−0.294986
6.0	0.166	0.036	0.057	0.025	0.107	0.013	−0.294664
6.8	0.073	0.016	0.026	0.012	0.045	0.007	−0.294429
7.6	0.035	0.008	0.013	0.006	0.021	0.003	−0.294318
8.8	0.013	0.003	0.005	0.003	0.008	0.001	−0.294251
10.0	0.006	0.001	0.002	0.001	0.003	0.001	−0.294228
11.0	0.003	0.001	0.001	0.001	0.002	0.000	−0.294219
15.0	0.000	0.000	0.000	0.000	0.000	0.000	−0.294209
MUE ^b	0.888	0.185	0.268	0.085	0.606	0.038	—
NPE ^c	2.795	0.559	0.805	0.237	1.870	0.092	—

^a The CCSDT energies $E_0^{(\text{CCSDT})}$ are reported as $E_0^{(\text{CCSDT})} + 399.0$ hartree, whereas all of the remaining energies are errors relative to CCSDT in millihartree.

^b Mean unsigned error relative to CCSDT.

^c Non-parallelity error relative to CCSDT.

Table 3.7: Electronic energies of the magnesium dimer at selected internuclear separations r (in Å) obtained in the various subvalence CC calculations with up to triply excited clusters correlating all electrons other than the 1s shells of the Mg atoms and using the AwCTZ basis set.^a Adapted from Ref. [1].

r	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3)	CCSDt	CC(t;3)	CCSDT
3.2	9.244	0.468	1.189	0.460	7.760	0.272	−0.774474
3.4	8.840	0.417	1.094	0.424	7.544	0.263	−0.776080
3.6	8.481	0.365	1.005	0.401	7.341	0.261	−0.776824
3.8	8.168	0.317	0.926	0.380	7.157	0.257	−0.777101
3.9	8.028	0.294	0.890	0.369	7.072	0.255	−0.777137
4.0	7.899	0.272	0.856	0.359	6.993	0.252	−0.777128
4.2	7.671	0.234	0.795	0.342	6.851	0.248	−0.777023
4.8	7.193	0.150	0.662	0.306	6.540	0.238	−0.776469
5.4	6.934	0.104	0.588	0.288	6.366	0.235	−0.775962
6.0	6.801	0.080	0.548	0.279	6.274	0.233	−0.775620
6.8	6.719	0.065	0.523	0.275	6.219	0.234	−0.775358
7.6	6.684	0.059	0.513	0.275	6.200	0.235	−0.775223
8.8	6.664	0.056	0.506	0.278	6.197	0.241	−0.775141
10.0	6.657	0.054	0.504	0.283	6.205	0.246	−0.775113
11.0	6.655	0.054	0.503	0.286	6.212	0.250	−0.775101
15.0	6.651	0.053	0.503	0.296	6.217	0.259	−0.775080
MUE ^b	7.456	0.190	0.725	0.331	6.697	0.249	—
NPE ^c	2.592	0.415	0.687	0.185	1.563	0.039	—

^a The CCSDT energies $E_0^{(\text{CCSDT})}$ are reported as $E_0^{(\text{CCSDT})} + 399.0$ hartree, whereas all of the remaining energies are errors relative to CCSDT in millihartree.

^b Mean unsigned error relative to CCSDT.

^c Non-parallelity error relative to CCSDT.

Table 3.8: Electronic energies of the magnesium dimer at selected internuclear separations r (in Å) obtained in the various valence CC calculations with up to triply excited clusters using the A(Q+d)Z basis set.^a Adapted from Ref. [1].

r	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3)	CCSDt	CC(t;3)	CCSDT
3.2	2.870	0.509	0.766	0.282	2.058	0.131	−0.295534
3.4	2.464	0.447	0.668	0.243	1.799	0.118	−0.297255
3.6	2.085	0.385	0.575	0.209	1.543	0.105	−0.298027
3.8	1.742	0.326	0.489	0.179	1.303	0.093	−0.298294
3.9	1.586	0.298	0.448	0.166	1.191	0.087	−0.298321
4.0	1.441	0.271	0.411	0.154	1.086	0.082	−0.298303
4.2	1.182	0.224	0.342	0.131	0.895	0.071	−0.298185
4.8	0.630	0.121	0.190	0.078	0.477	0.045	−0.297618
5.4	0.327	0.064	0.103	0.045	0.245	0.027	−0.297119
6.0	0.171	0.034	0.056	0.027	0.124	0.017	−0.296787
6.8	0.075	0.015	0.025	0.013	0.052	0.008	−0.296545
7.6	0.035	0.008	0.012	0.007	0.024	0.004	−0.296434
8.8	0.013	0.003	0.005	0.003	0.009	0.002	−0.296367
10.0	0.006	0.001	0.002	0.001	0.004	0.001	−0.296344
11.0	0.003	0.001	0.001	0.001	0.002	0.000	−0.296336
15.0	0.000	0.000	0.000	0.000	0.000	0.000	−0.296327
MUE ^b	0.914	0.169	0.256	0.096	0.676	0.050	—
NPE ^c	2.870	0.509	0.765	0.282	2.057	0.131	—

^a The CCSDT energies $E_0^{(\text{CCSDT})}$ are reported as $E_0^{(\text{CCSDT})} + 399.0$ hartree, whereas all of the remaining energies are errors relative to CCSDT in millihartree.

^b Mean unsigned error relative to CCSDT.

^c Non-parallelity error relative to CCSDT.

Table 3.9: Electronic energies of the magnesium dimer at selected internuclear separations r (in Å) obtained in the various subvalence CC calculations with up to triply excited clusters correlating all electrons other than the 1s shells of the Mg atoms and using the AwCQZ basis set.^a Adapted from Ref. [1].

r	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3)	CCSDt	CC(t;3)	CCSDT
3.2	11.615	0.381	1.248	0.621	10.284	0.426	−0.882431
3.4	11.208	0.335	1.157	0.574	10.061	0.411	−0.884063
3.6	10.843	0.289	1.073	0.533	9.848	0.395	−0.884805
3.8	10.525	0.245	0.998	0.503	9.653	0.385	−0.885071
3.9	10.382	0.225	0.963	0.489	9.563	0.380	−0.885102
4.0	10.251	0.206	0.931	0.476	9.479	0.375	−0.885090
4.2	10.020	0.171	0.874	0.454	9.327	0.366	−0.884986
4.8	9.538	0.097	0.751	0.417	8.998	0.355	−0.884460
5.4	9.278	0.057	0.681	0.396	8.812	0.348	−0.883988
6.0	9.144	0.036	0.644	0.384	8.714	0.343	−0.883670
6.8	9.063	0.024	0.620	0.379	8.651	0.341	−0.883438
7.6	9.030	0.018	0.610	0.379	8.627	0.343	−0.883332
8.8	9.012	0.015	0.604	0.383	8.621	0.349	−0.883268
10.0	9.005	0.014	0.602	0.388	8.628	0.355	−0.883245
11.0	9.003	0.013	0.601	0.391	8.636	0.359	−0.883237
15.0	9.001	0.013	0.600	0.403	8.648	0.371	−0.883228
MUE ^b	9.807	0.134	0.810	0.448	9.159	0.369	—
NPE ^c	2.615	0.368	0.648	0.242	1.663	0.085	—

^a The CCSDT energies $E_0^{(\text{CCSDT})}$ are reported as $E_0^{(\text{CCSDT})} + 399.0$ hartree, whereas all of the remaining energies are errors relative to CCSDT in millihartree.

^b Mean unsigned error relative to CCSDT.

^c Non-parallelity error relative to CCSDT.

Table 3.10: Vibrational energies $G(v)$ (in cm^{-1}), dissociation energies D_e (in cm^{-1}), and equilibrium bond lengths r_e (in $\text{\AA}$) for the magnesium dimer obtained in the various valence CC calculations with up to triply excited clusters using the A(T+d)Z basis set.^a Adapted from Ref. [1].

v^b	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3)	CCSDt	CC(t;3)	CCSDT
0	-10.8	-2.5	-3.5	-1.0	-8.0	-0.5	24.1
1	-31.8	-7.4	-10.3	-3.1	-23.5	-1.3	69.8
2	-52.0	-12.0	-16.8	-5.0	-38.4	-2.2	112.5
3	-71.7	-16.5	-23.2	-7.0	-52.7	-3.0	152.3
4	-90.9	-20.8	-29.4	-8.9	-66.6	-3.9	189.2
5	-109.9	-25.0	-35.4	-10.8	-80.2	-4.7	223.2
6	-128.6	-29.1	-41.4	-12.7	-93.5	-5.5	254.3
7	-147.0	-33.2	-47.3	-14.6	-106.5	-6.4	282.5
8	-165.2	-37.2	-53.2	-16.5	-119.3	-7.3	307.8
9	-182.9	-41.2	-59.0	-18.4	-131.7	-8.2	330.1
10	-199.6	-45.0	-64.7	-20.3	-143.8	-9.0	349.5
11	— ^c	-48.8	-70.3	-22.2	-155.4	-9.9	365.9
12	— ^c	-52.5	-75.7	-24.1	-166.1	-10.8	379.3
13	— ^c	-56.0	-80.8	-25.9	-175.2	-11.7	389.8
14	— ^c	-59.2	-85.3	-27.7	— ^c	-12.5	397.6
15	— ^c	-61.8	-88.2	-29.1	— ^c	-13.2	402.8
16	— ^c	— ^c	— ^c	-30.3	— ^c	-13.8	405.8
17	— ^c	— ^c	— ^c	— ^c	— ^c	— ^c	407.4
D_e	151.1	342.2	314.3	376.2	214.7	393.2	407.7
r_e	4.492	4.034	4.069	3.982	4.286	3.963	3.952

^a The CCSDT vibrational energies are total $G(v)$ values, whereas all of the remaining vibrational term values are errors relative to CCSDT.

^b Vibrational quantum number.

^c PEC is too shallow to support this vibrational level.

Table 3.11: Vibrational energies $G(v)$ (in cm^{-1}), dissociation energies D_e (in cm^{-1}), and equilibrium bond lengths r_e (in $\text{\AA}$) for the magnesium dimer obtained in the various subvalence CC calculations with up to triply excited clusters using the AwCTZ basis set.^a Adapted from Ref. [1].

v^b	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3)	CCSDt	CC(t;3)	CCSDT
0	-9.4	-1.8	-2.8	-0.8	-6.5	-0.3	24.7
1	-27.8	-5.3	-8.2	-2.3	-19.1	-0.8	71.8
2	-45.5	-8.6	-13.4	-3.8	-31.3	-1.2	115.9
3	-62.9	-11.9	-18.5	-5.2	-43.2	-1.6	157.2
4	-79.8	-15.1	-23.5	-6.5	-54.8	-1.9	195.7
5	-96.3	-18.2	-28.5	-7.8	-66.1	-2.2	231.4
6	-112.4	-21.2	-33.3	-9.1	-77.3	-2.5	264.3
7	-128.0	-24.2	-38.1	-10.3	-88.1	-2.8	294.3
8	-143.0	-27.1	-42.8	-11.5	-98.5	-3.0	321.6
9	-157.5	-29.9	-47.3	-12.7	-108.4	-3.3	346.0
10	-171.6	-32.6	-51.7	-13.7	-117.7	-3.5	367.7
11	-185.5	-35.2	-55.8	-14.7	-126.5	-3.6	386.6
12	-198.8	-37.6	-59.8	-15.6	-134.8	-3.7	403.0
13	-210.5	-39.9	-63.7	-16.4	-142.5	-3.8	416.8
14	— ^c	-42.3	-67.6	-17.1	-149.1	-3.7	428.0
15	— ^c	-44.7	-71.5	-17.6	-154.1	-3.5	436.7
16	— ^c	-46.7	-74.4	-17.9	-157.2	-3.0	442.7
17	— ^c	-47.9	-76.1	-17.7	-159.2	-2.4	446.5
18	— ^c	-48.6	— ^c	-17.3	— ^c	-1.6	449.1
19	— ^c	— ^c	— ^c	-16.8	— ^c	-0.9	450.9
20	— ^c	— ^c	— ^c	[435.9] ^d	— ^c	[451.9] ^d	— ^c
D_e	207.9	401.3	371.9	436.3	287.5	452.7	451.6
r_e	4.362	3.982	4.018	3.951	4.171	3.932	3.926

^a The CCSDT vibrational energies are total $G(v)$ values, whereas all of the remaining vibrational term values are errors relative to CCSDT.

^b Vibrational quantum number.

^c PEC is too shallow to support this vibrational level.

^d The actual term value, as this PEC supports an extra vibrational level which is not bound by the CCSDT potential.

Table 3.12: Vibrational energies $G(v)$ (in cm^{-1}), dissociation energies D_e (in cm^{-1}), and equilibrium bond lengths r_e (in $\text{\AA}$) for the magnesium dimer obtained in the various valence CC calculations with up to triply excited clusters using the A(Q+d)Z basis set.^a Adapted from Ref. [1].

v^b	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3)	CCSDt	CC(t;3)	CCSDT
0	-11.9	-2.4	-3.5	-1.1	-9.5	-0.5	25.5
1	-34.7	-7.0	-10.2	-3.4	-27.6	-1.6	73.8
2	-56.6	-11.4	-16.7	-5.6	-44.9	-2.7	118.9
3	-77.8	-15.7	-22.9	-7.8	-61.6	-3.8	160.9
4	-98.4	-19.7	-29.0	-10.0	-77.6	-4.9	199.8
5	-118.5	-23.7	-35.0	-12.1	-93.3	-6.0	235.8
6	-138.3	-27.6	-40.8	-14.2	-108.6	-7.1	268.8
7	-157.9	-31.4	-46.6	-16.3	-123.5	-8.2	298.8
8	-177.1	-35.2	-52.3	-18.4	-138.3	-9.3	325.9
9	-196.0	-38.9	-58.0	-20.5	-152.7	-10.4	349.9
10	-214.2	-42.5	-63.5	-22.7	-166.8	-11.5	371.0
11	— ^c	-46.1	-69.1	-24.8	-180.3	-12.7	389.0
12	— ^c	-49.6	-74.4	-27.0	-192.8	-13.9	404.0
13	— ^c	-53.0	-79.6	-29.1	— ^c	-15.0	415.9
14	— ^c	-56.1	-84.4	-31.1	— ^c	-16.1	424.9
15	— ^c	-58.8	-88.4	-32.8	— ^c	-17.1	431.2
16	— ^c	-61.0	— ^c	-34.3	— ^c	-18.0	435.0
17	— ^c	— ^c	— ^c	— ^c	— ^c	— ^c	437.0
D_e	158.1	374.3	343.5	401.6	212.1	418.5	437.5
r_e	4.439	3.972	4.005	3.935	4.260	3.917	3.904

^a The CCSDT vibrational energies are total $G(v)$ values, whereas all of the remaining vibrational term values are errors relative to CCSDT.

^b Vibrational quantum number.

^c PEC is too shallow to support this vibrational level.

Table 3.13: Vibrational energies $G(v)$ (in cm^{-1}), dissociation energies D_e (in cm^{-1}), and equilibrium bond lengths r_e (in $\text{\AA}$) for the magnesium dimer obtained in the various subvalence CC calculations with up to triply excited clusters using the AwCQZ basis set.^a Adapted from Ref. [1].

v^b	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3)	CCSDt	CC(t;3)	CCSDT
0	-10.3	-1.7	-2.8	-1.1	-7.5	-0.5	24.4
1	-30.1	-5.1	-8.3	-2.8	-21.9	-1.2	70.7
2	-49.1	-8.2	-13.6	-4.4	-35.8	-1.6	113.9
3	-67.5	-11.3	-18.7	-5.9	-49.2	-2.1	154.1
4	-85.4	-14.2	-23.7	-7.5	-62.2	-2.6	191.3
5	-102.8	-17.1	-28.5	-9.0	-74.9	-3.1	225.6
6	-120.0	-19.9	-33.3	-10.6	-87.3	-3.7	257.0
7	-137.0	-22.6	-37.9	-12.1	-99.6	-4.3	285.4
8	-153.9	-25.3	-42.6	-13.6	-111.9	-4.8	311.0
9	-170.5	-27.9	-47.2	-15.1	-123.9	-5.3	333.6
10	-186.4	-30.5	-51.7	-16.5	-135.5	-5.8	353.3
11	-201.2	-33.1	-56.3	-17.8	-146.1	-6.3	369.9
12	— ^c	-35.6	-60.7	-19.1	-155.0	-6.7	383.4
13	— ^c	-38.0	-64.8	-20.1	-162.0	-6.9	394.0
14	— ^c	-40.2	-68.5	-20.7	-166.9	-6.8	401.7
15	— ^c	-42.0	-71.5	-20.8	-170.2	-6.3	406.8
16	— ^c	-43.4	— ^c	-20.5	— ^c	-5.4	409.8
17	— ^c	— ^c	— ^c	-19.7	— ^c	-4.2	411.3
18	— ^c	— ^c	— ^c	[393.1] ^d	— ^c	[408.8] ^d	— ^c
D_e	169.1	366.7	336.0	393.4	236.8	409.6	411.4
r_e	4.397	3.969	4.007	3.952	4.200	3.930	3.917

^a The CCSDT vibrational energies are total $G(v)$ values, whereas all of the remaining vibrational term values are errors relative to CCSDT.

^b Vibrational quantum number.

^c PEC is too shallow to support this vibrational level.

^d The actual term value, as this PEC supports an extra vibrational level which is not bound by the CCSDT potential.

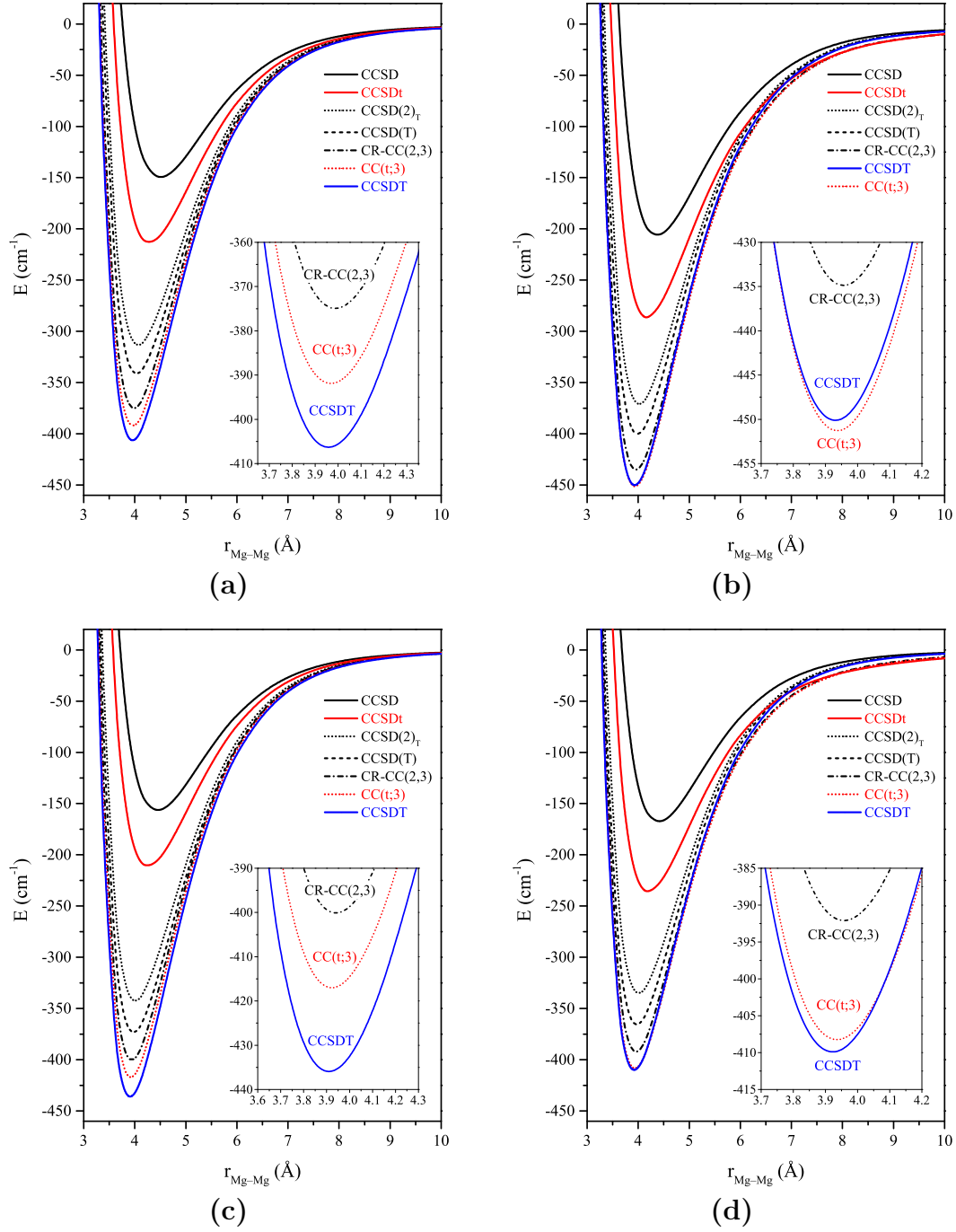


Figure 3.9: The ground-state PECs of Mg_2 resulting from the CCSD and various CC calculations with up to triply excited clusters using the (a) A(T+d)Z, (b) AwCTZ, (c) A(Q+d)Z, and (d) AwCQZ basis sets. All PECs have been aligned such that the corresponding electronic energies at the internuclear separation $r = 15 \text{ \AA}$ are identical and set at 0 hartree. Adapted from Ref. [1].

The ground-state PECs of the magnesium dimer resulting from the CC calculations with up to connected quadruply excited clusters, represented in this work by the active-space CCSDTq approach, the CC(q;4) correction to CCSDTq, and their CCSDTQ parent, can be found in Table 3.14 and Fig. 3.10. The corresponding D_e , r_e , and vibrational term values are shown in Table 3.15. To appreciate the effect of connected quadruples on the ground-state PEC and vibrational spectrum of Mg_2 , Tables 3.14 and 3.15 and Fig. 3.10 also contain the CCSDT data. Due to enormous costs of the CCSDTQ computations, we used the A(T+d)Z basis set and correlated valence electrons only. As a consequence, the CCSDTQ results shown in Tables 3.14 and 3.15 and Fig. 3.10 are equivalent to the FCI/A(T+d)Z data.

Let us first consider the performance of the CCSDTq approximation to full CCSDTQ, where, in contrast to CCSDT, which completely neglects T_4 clusters, the dominant connected quadruples are incorporated through the use of active orbitals. As shown in Table 3.14, the CCSDTq approach alone is already very accurate. Indeed, the MUE and NPE values characterizing the CCSDTq calculations relative to CCSDTQ, of 0.032 and 0.091 millihartree, respectively, are not only very small, but they also reduce the corresponding CCSDT values by a factor of about 2. The high quality of the CCSDTq PEC is further exemplified by its vibrational term values (see Table 3.15). Although the CCSDT and CCSDTq zero-point energies, $G(v = 0)$, do not differ too much and are both excellent, the situation changes, in favor of CCSDTq, when the higher-energy vibrational states, especially those with $v \geq 10$, are considered. For example, as shown in Table 3.15, the 11.8 cm^{-1} difference in the $G(v = 17)$ vibrational energy between CCSDTq and CCSDTQ is smaller than the corresponding CCSDT–CCSDTQ difference by a factor of 1.5.

In analogy to the previously studied beryllium dimer [73], the CC(q;4) correction to CCSDTq improves the highly accurate CCSDTq energies even further. This can be seen in Table 3.14, which shows that the already very small MUE and NPE values relative to CCSDTQ characterizing the CCSDTq calculations for Mg_2 , of 0.032 and 0.091 millihartree, respectively, reduce to the even smaller 0.022 millihartree for MUE and 0.061 millihartree

for NPE, when the CC(q;4) approach is employed, making the CC(q;4) and CCSDTQ potentials virtually indistinguishable. As a result, the CC(q;4) calculations capture 98% of the CCSDTQ binding energy, reproduce the CCSDTQ equilibrium bond length to within 0.007 Å, and yield excellent vibrational term values that are very close to their full CCSDTQ counterparts. Indeed, as shown in Table 3.15, the CC(q;4) and CCSDTQ values of the zero-point vibrational energies differ by a tiny 0.3 cm⁻¹. For the last, $v = 17$, vibrational level supported by the CC(q;4)/A(T+d)Z and CCSDTQ/A(T+d)Z potentials, the difference between the CC(q;4) and CCSDTQ data is only 8.1 cm⁻¹ or 2%. This is a noticeable improvement over the 11.8 cm⁻¹ obtained in the corresponding CCSDTq calculations, and the even more impressive improvement when compared to the 17.8 cm⁻¹ difference between the CCSDT/A(T+d)Z $G(v = 17)$ value, ignoring T_4 clusters, and its CCSDTQ/A(T+d)Z counterpart. It is clear from Tables 3.14 and 3.15 and Fig. 3.10 that one cannot obtain a fully quantitative description of the magnesium dimer without a highly accurate treatment of the connected triply and quadruply excited clusters.

In summary, in analogy to the previously reported calculations for Be₂ [73], the CC(q;4) method provides an accurate representation of the ground-state PEC of the magnesium dimer obtained in the considerably more expensive CCSDTQ calculations. This finding is further examined below, where we combine the valence CC(q;4)/A(T+d)Z and CCSDTQ/A(T+d)Z computations with the reasonably converged, nearly all-electron, CCSDT energetics to extrapolate our best D_e , r_e , and $G(v)$ values that can subsequently be compared with the available experimental or experimentally derived information.

Table 3.14: Electronic energies of the magnesium dimer at selected internuclear separations r (in Å) obtained in the various valence CC calculations with up to quadruply excited clusters using the A(T+d)Z basis set.^a Adapted from Ref. [1].

r	CCSDT	CCSDTq	CC(q;4)	CCSDTQ
3.2	0.182	0.091	0.061	−0.293303
3.4	0.149	0.081	0.055	−0.295029
3.6	0.120	0.071	0.049	−0.295819
3.8	0.097	0.061	0.042	−0.296110
3.9	0.087	0.057	0.039	−0.296148
4.0	0.078	0.052	0.036	−0.296140
4.2	0.063	0.044	0.030	−0.296039
4.8	0.033	0.026	0.017	−0.295497
5.4	0.018	0.014	0.009	−0.295004
6.0	0.010	0.008	0.005	−0.294674
6.8	0.005	0.004	0.002	−0.294433
7.6	0.002	0.002	0.001	−0.294320
8.8	0.001	0.001	0.000	−0.294252
10.0	0.000	0.000	0.000	−0.294228
11.0	0.000	0.000	0.000	−0.294219
15.0	0.000	0.000	0.000	−0.294209
MUE ^b	0.053	0.032	0.022	—
NPE ^c	0.182	0.091	0.061	—

^a The CCSDTQ energies $E_0^{(\text{CCSDTQ})}$, which are equivalent in this case to the energies obtained in the FCI calculations, are reported as $E_0^{(\text{CCSDTQ})} + 399.0$ hartree, whereas all of the remaining energies are errors relative to CCSDTQ in millihartree.

^b Mean unsigned error relative to CCSDTQ.

^c Non-parallelity error relative to CCSDTQ.

Table 3.15: Vibrational energies $G(v)$ (in cm^{-1}), dissociation energies D_e (in cm^{-1}), and equilibrium bond lengths r_e (in $\text{\AA}$) for the magnesium dimer obtained in the various valence CC calculations with up to quadruply excited clusters using the A(T+d)Z basis set.^a Adapted from Ref. [1].

v^b	CCSDT	CCSDTq	CC(q;4)	CCSDTQ
0	-0.6	-0.4	-0.3	24.7
1	-1.9	-1.2	-0.8	71.7
2	-3.1	-2.0	-1.4	115.6
3	-4.2	-2.7	-1.9	156.5
4	-5.3	-3.5	-2.4	194.5
5	-6.4	-4.2	-3.0	229.6
6	-7.5	-4.9	-3.5	261.8
7	-8.6	-5.6	-3.9	291.1
8	-9.7	-6.4	-4.4	317.5
9	-10.8	-7.1	-4.9	340.9
10	-11.8	-7.8	-5.4	361.3
11	-12.9	-8.5	-5.9	378.7
12	-13.9	-9.2	-6.3	393.2
13	-14.9	-9.8	-6.8	404.7
14	-15.8	-10.5	-7.2	413.4
15	-16.7	-11.0	-7.6	419.4
16	-17.3	-11.5	-7.9	423.2
17	-17.8	-11.8	-8.1	425.2
D_e	407.7	413.8	417.7	425.9
r_e	3.952	3.941	3.937	3.930

^a The CCSDTQ vibrational energies, which are equivalent in this case to the energies obtained in the FCI calculations, are total $G(v)$ values, whereas all of the remaining vibrational term values are errors relative to CCSDTQ.

^b Vibrational quantum number.

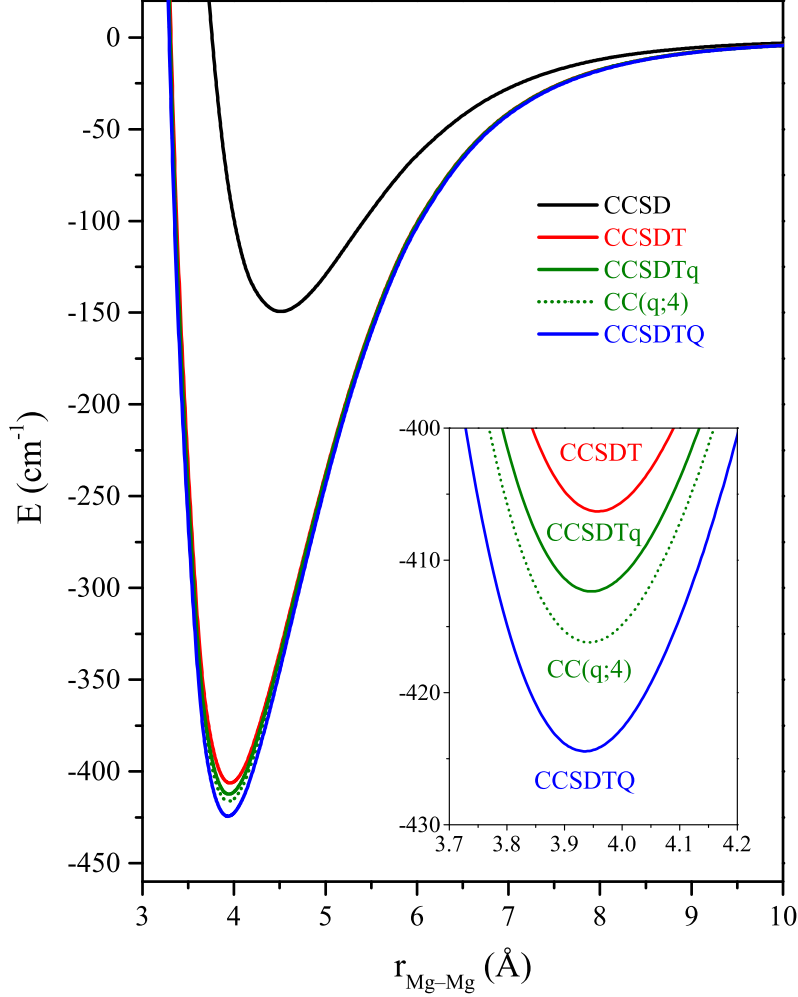


Figure 3.10: The ground-state PECs of Mg_2 resulting from the CCSD, CCSDT, and various CC calculations with up to quadruply excited clusters using the A(T+d)Z basis set. All PECs have been aligned such that the corresponding electronic energies at the internuclear separation $r = 15 \text{ \AA}$ are identical and set at 0 hartree. Adapted from Ref. [1].

In this, final, part of our discussion of Mg_2 , we compare our best CC calculations with the experimentally derived spectroscopic data for Mg_2 , reported in Refs. [161, 166, 169], and provide additional comments on the performance of the highest-level CC(P ; Q) methodology considered in this work, which is the CC(q;4) correction to CCSDTq. We do this by examining the performance of two composite schemes, referred to, throughout the rest of this section, as schemes A and B, in which the ground-state electronic energies are calculated as follows:

$$E_0^{(\text{A})} = E_0^{(\text{CCSDT}/\text{AwCQZ})} + \left(\Delta E_0^{(\text{CC}(\text{q};4)/\text{A}(\text{T}+d)\text{Z})} - \Delta E_0^{(\text{CCSDT}/\text{A}(\text{T}+d)\text{Z})} \right), \quad (3.39)$$

for scheme A, and

$$E_0^{(B)} = E_0^{(\text{CCSDT}/\text{AwCQZ})} + \left(\Delta E_0^{(\text{CCSDTQ}/\text{A}(\text{T}+d)\text{Z})} - \Delta E_0^{(\text{CCSDT}/\text{A}(\text{T}+d)\text{Z})} \right), \quad (3.40)$$

for scheme B. The first term on the right-hand side of each of the above two equations represents the total CCSDT energy obtained using the largest basis set employed in this work, *i.e.*, AwCQZ, and correlating all electrons other than the 1s shells of the Mg monomers. The difference between schemes A and B is in the treatment of the many-electron correlation effects associated with the connected quadruply excited clusters. In scheme A, they are estimated by forming the difference between the CC(q;4)/A(T+d)Z and CCSDT/A(T+d)Z valence correlation energies [see Eq. (3.39)]. In scheme B, they are calculated more accurately by forming the difference between the valence correlation energies resulting from the CCSDTQ/A(T+d)Z and CCSDT/A(T+d)Z calculations [see Eq. (3.40)]. Given the fact that the CC(q;4) approach is an approximation to CCSDTQ, we can treat scheme B as a parent method for judging the performance of scheme A.

Before going any further, we need to comment on the usage of the CCSDT/AwCQZ energy in Eqs. (3.39) and (3.40). In principle, following the previous investigation of Be₂ [73], one could think of extrapolating the subvalence CCSDT correlation energies to the CBS limit and use the resulting CCSDT/CBS estimates instead of the CCSDT/AwCQZ energies in Eqs. (3.39) and (3.40). Unfortunately, as demonstrated below, unlike in the beryllium dimer, an extrapolation based on basis sets of triple- and quadruple- ζ quality does not determine the CBS limit for the magnesium dimer in a correct manner and one is better off by using the unextrapolated results obtained with the AwCQZ basis. This is, most likely, related to the fact that Mg is a much larger atom than Be, having subvalence 2s and 2p shells, which the Be atom does not have, that are correlated in our nearly all-electron CCSDT calculations. As explained below, the AwCQZ–AwC5Z extrapolation would work well, but we could not afford the full CCSDT calculations for Mg₂ correlating valence and subvalence electrons and using basis sets larger than AwCQZ, whereas, as already demonstrated above, the use of the more affordable CCSD(T), CCSD(2)_T, and CR-CC(2,3) approximations to

CCSDT would result in additional accuracy losses due to the inadequate treatment of triples. This forced us to use the unextrapolated CCSDT/AwCQZ energies in Eqs. (3.39) and (3.40) instead of the CCSDT/CBS estimates resulting from the AwCTZ–AwCQZ extrapolation, which would not be reliable enough for making comparisons with the experimentally derived spectroscopic data reported in Refs. [161, 166, 169].

The problem with using the AwCTZ and AwCQZ basis sets to extrapolate the CBS limit for Mg_2 is explained in Table 3.16. We provide in this table the D_e , r_e , and vibrational term values obtained in the subvalence CCSD(T) calculations using the AwCTZ, AwCQZ, and AwC5Z basis sets, along with the two CBS extrapolation schemes, denoted as CBS-1 and CBS-2, employing the two-point formula [190, 191]

$$\Delta E_0^{(\text{CCSD(T)/CBS})} = \frac{n^3 \Delta E_0^{(\text{CCSD(T)/AwC}n\text{Z})} - (n-1)^3 \Delta E_0^{(\text{CCSD(T)/AwC}(n-1)\text{Z})}}{n^3 - (n-1)^3}, \quad (3.41)$$

where n and $(n-1)$ are the cardinal numbers of the AwC n Z and AwC $(n-1)$ Z basis sets, respectively (the CCSD(T) approach is a lot less expensive than full CCSDT, so the nearly all-electron CCSD(T)/AwC5Z calculations, correlating all electrons but the 1s shells of the magnesium atoms, are affordable). The CBS-1 scheme is based on an AwCTZ–AwCQZ extrapolation [$n = 4$ in Eq. (3.41)]. CBS-2 uses a much better extrapolation scheme based on the AwCQZ and AwC5Z results [$n = 5$ in Eq. (3.41)]. In both cases, the extrapolated CCSD(T) correlation energy is added to the RHF/AwC5Z result, which we treat as equivalent to the RHF/CBS value due to the very fast (exponential) convergence of HF energies with respect to the basis set (so fast that the RHF/AwCQZ and RHF/AwC5Z PECs are virtually identical). As shown in Table 3.16, the CCSD(T)/AwCQZ D_e , r_e , and $G(v)$ values faithfully reproduce those obtained with the CBS-2 scheme, to within $\sim 5 \text{ cm}^{-1}$ for D_e and $G(v)$ and $0.001 \text{ \AA}$ in the case of r_e . In contrast, the CBS-1 scheme not only has a large, $\sim 20 \text{ cm}^{-1}$, error relative to CBS-2 when the corresponding D_e values are examined, but it also fails to capture the last two vibrational levels resulting from the CBS-2 calculations. This indicates that one is much better off by using the AwCQZ basis set alone, which gives results similar to those obtained with AwC5Z and CBS-2, and not performing an AwCTZ–AwCQZ

CBS extrapolation. Therefore, in the above schemes A and B, defined by Eqs. (3.39) and (3.40), respectively, we use the CCSDT/AwCQZ results as replacements for the CBS-limit CCSDT energetics, which we could not properly determine due to the prohibitive costs of the CCSDT/AwC5Z calculations correlating all electrons but the 1s shells of the Mg monomers.

The results obtained with schemes A and B, as defined above, are compared with one another and with the experimentally derived data reported in Refs. [161, 166, 169] in Table 3.17. To make sure that the entire vibrational manifold of Mg_2 is captured and no vibrational states near the dissociation threshold are lost as a result of the potential defects of the numerical integration of the radial Schrödinger equation, we integrate the latter equation from 3.2 to 100.0 Å by including four additional internuclear separations r , namely, 20.0, 25.0, 30.0, and 100.0 Å, in the grid described above, and determining the corresponding energies at the nearly all-electron CCSDT/AwCQZ and valence CCSDT/A(T+d)Z, CC(q;4)/A(T+d)Z, and CCSDTQ/A(T+d)Z (*i.e.*, FCI/A(T+d)Z) levels required by Eqs. (3.39) and (3.40).

As demonstrated in Table 3.17, the results obtained with scheme A, which uses the difference between the CC(q;4)/A(T+d)Z and CCSDT/A(T+d)Z correlation energies to estimate the effect of the connected quadruply excited clusters, are very similar to those determined with scheme B, in which CC(q;4) is replaced by CCSDTQ. This is particularly true when the energy spacings between the successive vibrational levels, $\Delta G_{v+1/2} \equiv G(v+1) - G(v)$, are examined. The differences between the $\Delta G_{v+1/2}$ values resulting from the calculations using schemes A and B do not exceed 0.6 cm^{-1} , when all of the vibrational levels, including those near the dissociation threshold, are considered, being 0.5 cm^{-1} on average. This is an improvement compared to the previously studied beryllium dimer case [73], where the replacement of CCSDTQ by CC(q;4) in composite calculations similar to schemes A and B used here had a larger effect on the resulting $\Delta G_{v+1/2}$ values. In analogy to Be_2 , the differences between the $G(v)$ values obtained for the magnesium dimer using the CC(q;4)-based scheme A and its CCSDTQ-based counterpart defining scheme B, which range from 0.3 cm^{-1} for $v = 0$ to $\sim 8 \text{ cm}^{-1}$ when the higher-energy vibrational states near the

dissociation threshold are considered, are larger than the analogous differences characterizing the corresponding $\Delta G_{v+1/2}$ spacings, but once again they are smaller when compared to the similar calculations for the beryllium dimer reported in Ref. [73]. This might be related to the fact that the T_4 effects in Be_2 , which change its dissociation energy D_e by about 17%, when the analog of scheme B used here is compared to the all-electron CCSDT/CBS computations, are larger than those characterizing the magnesium dimer. Indeed, the effect of T_4 clusters on the D_e value characterizing Mg_2 , estimated by comparing the results of the scheme B and nearly all-electron CCSDT/AwCQZ calculations, is only about 4%. As shown in Table 3.17, both composite schemes examined in the present study give very similar equilibrium bond lengths and binding energies that agree to within 0.008 Å and less than 9 cm^{-1} (2%), respectively. Thus, in analogy to the earlier Be_2 work in our group [73], we can conclude that the CC(q;4)-based scheme A is a reliable substitute for the more expensive scheme B based on CCSDTQ. This is promising for the future applications of the CC(q;4) approach, especially if we take into consideration savings in the computational effort offered by CC(q;4) compared to CCSDTQ (*cf.* Table 3.5).

Now, after establishing the accuracy of the CC(q;4)-based scheme A relative to scheme B, in which CC(q;4) is replaced by CCSDTQ, we move to a comparison of the D_e , r_e , $G(v)$, and $\Delta G_{v+1/2}$ values determined using schemes A and B with the experimentally derived data obtained in Refs. [161, 166, 169]. As shown in Table 3.17, the D_e and r_e values calculated with scheme A agree with their experimentally derived counterparts reported in Ref. [169] to within 8.1 cm^{-1} and 0.012 Å, respectively. Unsurprisingly, scheme B, being a parent approach to scheme A, is more accurate in this regard, giving an almost exact binding energy relative to experiment and a 0.004 Å error relative to the experimentally derived equilibrium bond length, but scheme A performs very well too, especially if we keep in mind that the calculations carried out in this benchmark study neglect relativistic and post-Born–Oppenheimer effects (see the remarks below). The vibrational term values $G(v)$ determined using scheme A reproduce their experimental counterparts to within 7.7 cm^{-1} , when the

experimentally resolved, $v = 0\text{--}13$, part of the vibrational spectrum is examined, and $0.3\text{--}3.5\text{ cm}^{-1}$ for the $v = 0\text{--}4$ states having energies below 200 cm^{-1} . Again, similarly to D_e and r_e , scheme B performs better, with errors relative to the available experimental $G(v)$ values not exceeding 1.3 cm^{-1} , but scheme A is quite accurate too. As one might expect, the agreement with experiment is even more impressive when the vibrational energy spacings $\Delta G_{v+1/2}$ are examined. As shown in Table 3.17, the $\Delta G_{v+1/2}$ values obtained with schemes A and B agree with the available experimental data for these spacings to within 1 cm^{-1} . The excellent agreement between the $G(v)$ and $\Delta G_{v+1/2}$ values obtained for the magnesium dimer with the composite schemes defined by Eqs. (3.39) and (3.40) and the corresponding experimentally derived data, which is as good as that observed in the analogous calculations for the smaller Be_2 system [73], demonstrates that by developing the $\text{CC}(P;Q)$ framework and the resulting approximations, such as $\text{CC}(q;4)$, we have come up with a new generation of affordable *ab initio* methods that can accurately capture the physics necessary to describe complex spectroscopic problems. Table 3.17 also reveals that both schemes A and B are capable of predicting the existence of the additional $v = 14\text{--}18$ states initially postulated by Li and Stwalley in Ref. [166], which shows that novel methods developed in our group, such as $\text{CC}(q;4)$, remain reliable even when the experimental data are unavailable or uncertain.

In analogy to the previously studied beryllium dimer [73], in commenting on the results included in Table 3.17 and making comparisons with experiment, we should not ignore the fact that in this methodological study focusing on testing the $\text{CC}(P;Q)$ approaches, we neglected the post-Born–Oppenheimer and relativistic effects. The post-Born–Oppenheimer effects in the magnesium dimer are negligible [169], but special relativity changes the dissociation energy D_e in Mg_2 by $\sim 4\text{--}5\text{ cm}^{-1}$ [177] and this will affect our calculated vibrational term values, especially the $G(v)$ values characterizing higher-energy states near the dissociation threshold. The effect of relativity on the $\Delta G_{v+1/2}$ spacings resulting from our nonrelativistic calculations will likely be much smaller due to error cancellation, but we plan to reexamine the D_e , r_e , $G(v)$, and $\Delta G_{v+1/2}$ values characterizing the magnesium dimer using the higher-

level $CC(P;Q)$ and CC methods, such as $CC(q;4)$ and $CCSDTQ$, correcting the resulting potentials and spectroscopic properties for the post-Born–Oppenheimer and relativistic effects, in the future work. The ability of the $CC(t;3)$ and $CC(q;4)$ methods to accurately reproduce the parent full $CCSDT$ and $CCSDTQ$ data encourages us to do so.

Table 3.16: Vibrational energies $G(v)$ (in cm^{-1}), dissociation energies D_e (in cm^{-1}), and equilibrium bond lengths r_e (in $\text{\AA}$) for the magnesium dimer obtained in the subvalence $CCSD(T)$ calculations using the $AwCnZ$ basis sets with $n = T, Q$, and 5 and two CBS extrapolation schemes, designated as CBS-1 and CBS-2, described in the text.^a Adapted from Ref. [1].

v^b	AwCTZ ^c	AwCQZ ^d	AwC5Z	CBS-1 ^e	CBS-2 ^f
0	0.1	-0.1	0.0	-0.2	22.8
1	0.6	-0.2	-0.1	-0.7	65.9
2	1.2	-0.4	-0.2	-1.4	106.1
3	1.9	-0.6	-0.3	-2.3	143.5
4	2.7	-0.8	-0.5	-3.3	177.9
5	3.7	-1.0	-0.6	-4.3	209.5
6	4.9	-1.1	-0.6	-5.3	238.2
7	6.3	-1.0	-0.6	-6.3	263.8
8	8.1	-0.6	-0.4	-7.1	286.4
9	10.2	-0.1	-0.1	-8.0	305.8
10	12.8	0.5	0.2	-9.1	322.2
11	15.9	1.2	0.5	-10.8	335.6
12	19.4	1.8	0.8	-13.0	346.0
13	23.3	2.4	1.1	-15.1	353.6
14	27.4	3.2	1.5	— ^g	358.4
15	31.1	4.0	1.9	— ^g	360.9
D_e	401.3	366.7	364.1	341.5	361.7
r_e	3.982	3.969	3.968	3.960	3.968

^aThe CBS-2 vibrational energies are total $G(v)$ values, whereas all of the remaining vibrational term values are errors relative to CBS-2.

^bVibrational quantum number.

^cPEC supports three extra levels, $v = 16$ –18, which are not supported by the CBS-2 potential.

^dPEC supports one extra level, $v = 16$, which is not supported by the CBS-2 potential.

^eObtained by using Eq. (3.41) and the AwCTZ and AwCQZ bases.

^fObtained by using Eq. (3.41) and the AwCQZ and AwC5Z bases.

^gPEC is too shallow to support this vibrational level.

Table 3.17: Vibrational energies $G(v)$ and spacings $\Delta G_{v+1/2} \equiv G(v+1) - G(v)$ (in cm^{-1}), dissociation energies D_e (in cm^{-1}), and equilibrium bond lengths r_e (in $\text{\AA}$) for the magnesium dimer, as obtained with the two composite schemes discussed in the text and integrating the radial Schrödinger equation from 3.2 to 100.0 $\text{\AA}$ to capture the barely bound $v = 18$ state. Adapted from Ref. [1].

v^a	Scheme A ^b				Scheme B ^c		Expt ^d	
	$G(v)^e$		$\Delta G_{v+1/2}^e$		$G(v)^f$	$\Delta G_{v+1/2}^f$	$G(v)$	$\Delta G_{v+1/2}$
0	-0.3	(-0.3)	-0.8	(-0.6)	0.0	-0.3	25.2	47.9
1	-1.2	(-0.9)	-0.8	(-0.6)	-0.3	-0.3	73.0	44.7
2	-2.0	(-1.5)	-0.8	(-0.5)	-0.6	-0.2	117.8	41.6
3	-2.8	(-2.0)	-0.7	(-0.5)	-0.8	-0.2	159.4	38.6
4	-3.5	(-2.5)	-0.7	(-0.5)	-1.0	-0.1	198.0	35.6
5	-4.2	(-3.1)	-0.6	(-0.5)	-1.1	-0.1	233.6	32.6
6	-4.8	(-3.6)	-0.6	(-0.5)	-1.2	-0.1	266.2	29.6
7	-5.4	(-4.1)	-0.5	(-0.5)	-1.3	0.0	295.8	26.7
8	-5.9	(-4.6)	-0.4	(-0.5)	-1.3	0.0	322.5	23.7
9	-6.3	(-5.1)	-0.4	(-0.5)	-1.2	0.1	346.2	20.6
10	-6.7	(-5.6)	-0.4	(-0.5)	-1.1	0.1	366.8	17.6
11	-7.1	(-6.1)	-0.3	(-0.5)	-1.0	0.2	384.4	14.4
12	-7.4	(-6.5)	-0.4	(-0.5)	-0.8	0.1	398.8	11.5
13	-7.7	(-7.0)	— ^g	(-0.4)	-0.8	[8.7] ^h	410.3 ⁱ	NR ^j
14	— ^g	(-7.4)	— ^g	(-0.4)	[418.2] ^h	[6.0] ^h	NR ^j	NR ^j
15	— ^g	(-7.8)	— ^g	(-0.3)	[424.2] ^h	[3.7] ^h	NR ^j	NR ^j
16	— ^g	(-8.1)	— ^g	(-0.2)	[427.9] ^h	[1.9] ^h	NR ^j	NR ^j
17	— ^g	(-8.3)	— ^g	(-0.1)	[429.8] ^h	[0.7] ^h	NR ^j	NR ^j
18	— ^g	(-8.5)	—	—	[430.6] ^h	—	NR ^j	—
D_e		422.2			430.7		430.3	
r_e		3.902			3.894		3.890	

^aVibrational quantum number.

^bComposite scheme A defined by Eq. (3.39).

^cComposite scheme B defined by Eq. (3.40).

^dExperimentally derived values taken from Refs. [161] ($G(v)$ and $\Delta G_{v+1/2}$) and [169] (D_e and r_e), unless otherwise noted (see footnote i).

^eErrors relative to experiment and, in parentheses, relative to scheme B.

^fErrors relative to experiment.

^gErrors relative to experiment cannot be determined, since the experimental data for the $G(v)$ values with $v = 14$ –18 are not available.

^hPredicted value; no experimental data for comparison.

ⁱValue obtained as $G(v = 13) \equiv G(v = 13, J = 0) = G(v = 13, J = 14) - 210B(v = 13, J = 14)$ with the information about $G(v = 13, J = 14)$ and $B(v = 13, J = 14)$ taken from Ref. [166].

^jNot resolved experimentally.

CHAPTER 4

THE SEMI-STOCHASTIC $CC(P;Q)$ METHODOLOGY FOR EXCITED ELECTRONIC STATES

In the previous chapter, we have discussed the $CC(P;Q)$ theory and how it can be used in the form of the CR-CC/EOMCC and active-space-based $CC(P;Q)$ computations. We have also seen how the inclusion of dominant higher-than-two-body cluster and EOM excitation components through active orbitals can result in significant improvements over the CR-CC and EOMCC calculations, where the lower-order T_n and $R_{\mu,n}$ components are decoupled from their higher-order counterparts. However, as mentioned in the Introduction, such schemes rely on the user- and system-dependent active orbitals, rendering these methods not computational black boxes anymore. In this chapter, we discuss a novel way of addressing this issue, which is produced by combining the deterministic $CC(P;Q)$ formalism as described earlier with the stochastic CIQMC wave function samplings. In particular, we focus on my work on extending the semi-stochastic $CC(P;Q)$ methodology to excited electronic states.

4.1 Theory

As mentioned in the Introduction, the main idea of the CIQMC methodology, including FCIQMC and truncated CIQMC schemes, originally introduced in Ref. [102], is that of a stochastic population dynamics of a set of walkers, which simulates the underlying imaginary-time Schrödinger equation in the many-fermion Hilbert space spanned by Slater determinants. In other words, instead of propagating the wavefunction $|\Psi(\tau)\rangle = e^{-(H-S)\tau} |\Phi\rangle$, where τ is the imaginary time and S is a suitable energy shift, in the coordinate space, as in the conventional DMC approaches, knowing that

$$\lim_{\tau \rightarrow \infty} |\Psi(\tau)\rangle = \begin{cases} c_0 |\Psi_0\rangle & \text{for } S = E_0 \\ \infty & \text{for } S > E_0 \\ 0 & \text{for } S < E_0 \end{cases}, \quad (4.1)$$

i.e., knowing that the long time limit of such a propagation accompanied by S approaching E_0 projects out the desired ground state $|\Psi_0\rangle$, one propagates the CI (*e.g.*, FCI) state $|\Psi(\tau)\rangle = c_0(\tau)|\Phi_0\rangle + \sum_K c_K(\tau)|\Phi_K\rangle$ in the Slater determinant space, where the τ -dependent CI coefficients satisfy the system of equations [102]

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL}c_L(\tau), \quad (4.2)$$

which in the $\tau \rightarrow \infty$ limit and for $S \rightarrow E_0$ becomes equivalent to the conventional CI eigenvalue problem

$$\sum_L H_{KL}c_L(\infty) = E_0 c_K(\infty). \quad (4.3)$$

A direct numerical integration of the system given by Eq. (4.2) would require the determination of the full set of $c_K(\tau)$ coefficients at each time step, which is prohibitive. Instead, in the spirit of DMC, in the FCIQMC and truncated CIQMC schemes introduced in Ref. [102], one considers a population of walkers, denoted by α , which can carry positive or negative signs, $s_\alpha = \pm 1$, and defines the $c_K(\tau)$ amplitudes associated with determinants $|\Phi_K\rangle$ to be proportional to the signed sums of walkers, *i.e.*,

$$c_K(\tau) \sim N_K = \sum_\alpha s_\alpha \delta_{K,K_\alpha}, \quad (4.4)$$

where K_α designates the determinant on which walker α is located. In other words, the walkers inhabit the Slater determinant space, arriving at various determinants with positive or negative signs and evolving according to simple rules that include, in every time step, spawning and diagonal birth or death processes, which reflect on the content of Eq. (4.2), and annihilation. Spawning walkers at different (“child”) determinants is associated with the second term on the right-hand side of Eq. (4.2), which translates into

$$c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL}c_L(\tau), \quad (4.5)$$

in which $\Delta\tau$ is a propagation time step. The diagonal birth or death, which is a creation or a destruction of a walker at a given determinant, is driven by the first term on the right

hand side of Eq. (4.2), which represent the amplitude change

$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau). \quad (4.6)$$

The annihilation step eliminates pairs of oppositely signed walkers at a given determinant. The pattern of walker growth displays a characteristic plateau once a critical or sufficiently large number of walkers is reached, at which point one begins to stabilize the correlation energy and walker population using suitable energy shifts S [which in the long time limit approach the ground-state energy E_0 ; *cf.* Eq. (4.1)]. Upon convergence, the FCIQMC propagation, where walkers are allowed to explore the entire Hilbert space, produces a FCI-level state and the corresponding energy without any *a priori* knowledge of the nodal structure of the wavefunction needed in traditional DMC considerations [140, 144, 145, 147, 252, 253], since the population of walkers evolves in the space of Slater determinants, which have the proper fermionic symmetry. Similarly, the truncated CIQMC approximations, such as CISDT-MC, CISDTQ-MC, *etc.*, where spawning walkers at determinants beyond the specified truncation (*i.e.*, determinants with higher than triples in the CISDT-MC case, determinants higher than quadruples in the case of CISDTQ-MC, *etc.*) is not allowed, converge to the corresponding truncated CI (CISDT, CISDTQ, *etc.*) states.

Several ideas have been explored to improve the original CIQMC methodology and accelerate its convergence [103, 254–257], including the initiator CIQMC (*i*-CIQMC) approach, where only those determinants that acquire walker population exceeding a preset value (n_a) are allowed to spawn new walkers onto empty determinants [103]. These determinants, called the initiator determinants, are dynamically adjusted, *i.e.*, they remain initiators as long as their walker population exceeds n_a . One can begin the *i*-FCIQMC or truncated *i*-CIQMC simulations using a fixed set of initiator determinants, following, for example, MR ideas, or start from a single determinant, *e.g.*, a RHF state, placing a certain, sufficiently large, number of walkers on it, allowing the corresponding *i*-CIQMC algorithm to grow the walker population capturing other determinants. The CIQMC ideas can be extended to other many-body schemes [107, 258], including high-level CC (CCSDT, CCSDTQ, *etc.*) theories,

resulting in the corresponding CCMC (CCSDT-MC, CCSDTQ-MC, *etc.*) methodologies, in which instead of sampling determinants, one samples the space of excitation amplitudes (amplitudes of “excitators”) by “excips,” whose population dynamics converges to the desired CC solution [107–109]. As in the case of CIQMC, one can use the initiator CCMC (*i*-CCMC) algorithm, adopted in Ref. [111], to accelerate convergence [109]. Last, but not least, as with other stochastic approaches, it is rather straightforward to parallelize the CIQMC and CCMC techniques through partitioning of the relevant many-fermion Hilbert space across multiple processors [255] and, to reduce the amount of communication among processors, by running independent simulations on different processors and combining statistics gathered in each calculation [257].

Although one may need longer propagation times τ to stabilize walker (CIQMC) or excip (CCMC) populations to achieve the desired wavefunction and energy convergence using purely stochastic means, the most important determinants or cluster amplitude types, which significantly contribute to the wavefunction in the end, are captured already in the early propagation stages, which require small computational effort relative to the target CC calculation. In other words, it may take longer propagation times τ to come up with the reasonably stable numbers of walkers/excips at the individual determinants/excitators, but the leading determinants and cluster amplitude types are identified much sooner. The usefulness of this idea has been demonstrated in Ref. [111], where one could use the information about the leading determinants or excitations captured during the early stages of *i*-CIQMC or *i*-CCMC propagations to create lists of determinants defining P spaces for $CC(P)$ calculations and then use the $CC(P;Q)$ correction $\delta_0(P;Q)$ to capture the remaining correlation effects missing in the P -space CC calculations. In essence, the T operator in the P space is defined as $T^{(P)} = T_1 + T_2 + T_3^{(\text{MC})} + T_4^{(\text{MC})} + \dots$, where $T_3^{(\text{MC})}$, $T_4^{(\text{MC})}$, *etc.*, are the cluster operator components defined using the lists of selected triples, quadruples, *etc.*, identified via full or truncated *i*-CIQMC or *i*-CCMC runs at a given imaginary time.

In the initial study of the semi-stochastic $CC(P;Q)$ methodology [111], we demonstrated

that the CIQMC methodology of Refs. [102, 103] is very good in identifying the leading determinants and generating meaningful P spaces for the deterministic $\text{CC}(P)/\text{EOMCC}(P)$ calculations already in the early stages of QMC propagations without any *a priori* knowledge of the states being calculated. We show in this work that the excited-state $\text{CC}(P;Q)$ corrections $\delta_\mu(P;Q)$, defined by Eq. (3.9), similarly to their $\mu = 0$ ground-state counterparts examined in Ref. [111], are highly effective in accounting for the many-electron correlation effects outside the stochastically determined P spaces. While the specific computations reported in this work, which aim at recovering the EOMCCSDT energetics, rely on the FCIQMC propagations to identify the dominant triply excited determinants for defining the relevant P spaces, the algorithm summarized below is quite general, permitting the use of truncated CIQMC and CCMC approaches and extensions to higher EOMCC levels than EOMCCSDT, such as EOMCCSDTQ (not implemented yet). In the stochastic part of the excited-state $\text{CC}(P;Q)$ algorithm proposed in this work, we rely on the initiator CIQMC (*i*-CIQMC) approach developed in Ref. [103], but we could certainly take advantage of improvements in the original *i*-CIQMC and *i*-CCMC algorithms, such as those recently reported in Refs. [104, 105, 259]. It is also worth pointing out that by combining the stochastic CIQMC and deterministic EOMCC ideas via the $\text{CC}(P;Q)$ methodology, we can extract highly accurate excited-state information on the basis of relatively short CIQMC propagations for the ground state or the lowest-energy state of a given symmetry, without having to resort to the more complex excited-state CIQMC framework proposed in Refs. [148, 149], although exploring the utility of the latter framework would be an interesting direction to pursue.

The key steps of the semi-stochastic $\text{CC}(P;Q)$ algorithm proposed in Ref. [113], which builds upon the semi-stochastic $\text{CC}(P)/\text{EOMCC}(P)$ framework suggested in Ref. [112] (steps 1–3 below) and which extends the previously developed merger of the ground-state $\text{CC}(P;Q)$ methodology with CIQMC or CCMC to excited states, are as follows:

1. Initiate a CIQMC (or CCMC) run for the ground state and, if the system of interest has spin, spatial, or other symmetries, the analogous QMC propagation for the lowest

state of each irreducible representation (irrep) to be considered in the $CC(P;Q)$ calculations by placing a certain number of walkers (in CCMC, “excips” [108, 109]) on the appropriate reference function(s) $|\Phi\rangle$ [*e.g.* the RHF or restricted open-shell HF (ROHF) determinants].

2. At some propagation time $\tau > 0$, *i.e.* after a certain number of CIQMC (or CCMC) time steps, called MC iterations, extract a list or, if states belonging to multiple irreps are targeted, lists of determinants relevant to the desired $CC(P;Q)$ computations from the QMC propagation(s) initiated in step 1 to determine the P space or spaces needed to set up the ground-state $CC(P)$ and excited-state $EOMCC(P)$ calculations. If the goal is to converge the CCSDT/EOMCCSDT-level energetics, the P space for the $CC(P)$ calculations and the $EOMCC(P)$ calculations for excited states belonging to the same irrep as the ground state is defined as all singly and doubly excited determinants and a subset of triply excited determinants, where each triply excited determinant in the subset is populated by a minimum of n_P positive or negative walkers/excips (in this work, $n_P = 1$). For the excited states belonging to other irreps, the P space defining the $CC(P)$ problem is the same as that used in the case of the ground state, but the lists of triply excited determinants defining the $EOMCC(P)$ diagonalizations are provided by the CIQMC (or CCMC) propagations for the lowest-energy states of these irreps. One proceeds in a similar way when the goal is to converge other types of high-level CC/EOMCC energetics. For example, if we want to obtain the results of the CCSDTQ/EOMCCSDTQ quality, we also have to extract the lists of quadruples, in addition to the triples, from the CIQMC (or CCMC) runs to define the corresponding P spaces.
3. Solve the $CC(P)$ and $EOMCC(P)$ equations in the P space or spaces obtained in the previous step. If we are targeting the CCSDT/EOMCCSDT-level energetics and the excited states of interest belong to the same irrep as the ground state, we define $T^{(P)} =$

$T_1+T_2+T_3^{(\text{MC})}$, $R_\mu^{(P)} = r_{\mu,0}\mathbf{1}+R_{\mu,1}+R_{\mu,2}+R_{\mu,3}^{(\text{MC})}$, and $L_\mu^{(P)} = \delta_{\mu 0}\mathbf{1}+L_{\mu,1}+L_{\mu,2}+L_{\mu,3}^{(\text{MC})}$, where the list of triples in $T_3^{(\text{MC})}$, $R_{\mu,3}^{(\text{MC})}$, and $L_{\mu,3}^{(\text{MC})}$ is extracted from the ground-state CIQMC (or CCMC) propagation at time τ . For the excited states belonging to other irreps, we construct the similarity-transformed Hamiltonian $\overline{H}^{(P)}$, to be diagonalized in the EOMCC steps, in the same way as in the ground-state computations, but then use the CIQMC (or CCMC) propagations for the lowest states of these irreps to define the lists of triples in $R_{\mu,3}^{(\text{MC})}$ and $L_{\mu,3}^{(\text{MC})}$. We follow a similar procedure when targeting the CCSDTQ/EOMCCSDTQ-level energetics, in which case $T^{(P)} = T_1+T_2+T_3^{(\text{MC})}+T_4^{(\text{MC})}$, $R_\mu^{(P)} = r_{\mu,0}\mathbf{1}+R_{\mu,1}+R_{\mu,2}+R_{\mu,3}^{(\text{MC})}+R_{\mu,4}^{(\text{MC})}$, and $L_\mu^{(P)} = \delta_{\mu 0}\mathbf{1}+L_{\mu,1}+L_{\mu,2}+L_{\mu,3}^{(\text{MC})}+L_{\mu,4}^{(\text{MC})}$.

4. Correct the $\text{CC}(P)$ and $\text{EOMCC}(P)$ energies for the missing correlations of interest that were not captured by the CIQMC (or CCMC) propagations at the time τ the lists of the P -space excitations were created (the remaining triples if the goal is to recover the CCSDT/EOMCCSDT energetics, the remaining triples and quadruples if one targets CCSDTQ/EOMCCSDTQ, *etc.*) using the $\text{CC}(P;Q)$ corrections $\delta_\mu(P;Q)$ defined by Eq. (3.9).
5. Check the convergence of the resulting $E_\mu^{(P+Q)}$ energies calculated using Eq. 3.13 by repeating steps 2–4 at some later CIQMC (or CCMC) propagation time $\tau' > \tau$. If the $E_\mu^{(P+Q)}$ energies do not change within a given convergence threshold, we can stop the calculations. One can also stop them if τ in steps 2–4 is chosen such that the stochastically determined P space(s) contain sufficiently large fraction(s) of higher–than–doubly excited determinants relevant to the target CC/EOMCC level. Our unpublished tests using the $\text{CC}(t;3)$ corrections to the EOMCCSDt energies, the ground-state semi-stochastic $\text{CC}(P;Q)$ calculations reported in Ref. [113], and the excited-state $\text{CC}(P;Q)$ calculations using *i*-FCIQMC to generate the underlying P spaces performed in this work indicate that one should be able to reach millihartree or sub-millihartree accuracies relative to the parent CC/EOMCC computations, when the stochastically

determined P spaces contain as little as $\sim 5\text{--}10\%$ and no more than $\sim 30\text{--}40\%$ of higher-than-double excitations of interest, although this may need further study.

Similarly to the semi-stochastic form of the ground-state $\text{CC}(P;Q)$ methodology introduced in Ref. [111], the above algorithm offers significant savings in the computational effort compared to the fully deterministic, high-level, EOMCC approaches it targets. These savings originate from three factors. First, the computational times associated with the early stages of the i -CIQMC or i -CCMC walker/excip propagations are very short compared to the corresponding converged runs. Second, the $\text{CC}(P)$ calculations and the subsequent $\text{EOMCC}(P)$ diagonalizations offer significant speedups compared to their CC/EOMCC parents, when the corresponding excitation manifolds contain small fractions of higher-than-doubly excited determinants. For example, as pointed out in Refs. [111, 112], when the most expensive $\langle \Phi_{ijk}^{abc} | [H, T_3] | \Phi \rangle$ (or $\langle \Phi_{ijk}^{abc} | [\bar{H}^{(2)}, T_3] | \Phi \rangle$, where $\bar{H}^{(2)} = e^{-T_1 - T_2} H e^{T_1 + T_2}$) and $\langle \Phi_{ijk}^{abc} | [\bar{H}^{(P)}, R_{\mu,3}] | \Phi \rangle$ terms in the CCSDT and EOMCCSDT equations are isolated and reprogrammed using techniques similar to implementing selected CI approaches, combined with sparse matrix multiplication and index rearrangement routines (rather than conventional many-body diagrams that assume continuous excitation manifolds labelled by occupied and unoccupied orbitals from the respective ranges of indices; generally, the stochastically determined lists of excitations do not form continuous manifolds that could be *a priori* identified), one can speed up their determination by a factor of up to $(D/d)^2$, where D and d denote the number of all triples and stochastically determined triples in the P space, respectively. Other terms, such as $\langle \Phi_{ijk}^{abc} | [H, T_2] | \Phi \rangle$ and $\langle \Phi_{ijk}^{abc} | [\bar{H}^{(P)}, R_{\mu,2}] | \Phi \rangle$ or $\langle \Phi_{ij}^{ab} | [H, T_3] | \Phi \rangle$ and $\langle \Phi_{ij}^{ab} | [\bar{H}^{(P)}, R_{\mu,3}] | \Phi \rangle$, when treated in a similar manner, may offer additional speedups, on the order of $(D/d)^2$, too. Our current $\text{CC}(P)$ and $\text{EOMCC}(P)$ routines are not as efficient yet, but the speedups that scale linearly with (D/d) in the most expensive $\langle \Phi_{ijk}^{abc} | [H, T_3] | \Phi \rangle$ and $\langle \Phi_{ijk}^{abc} | [\bar{H}^{(P)}, R_{\mu,3}] | \Phi \rangle$ contributions are attainable. The third factor contributing to major savings in the computational effort offered by the semi-stochastic $\text{CC}(P;Q)$ approach is the observation that the determination of the noniterative correction $\delta_\mu(P;Q)$ for a given

electronic state μ is much less expensive than the time required to complete a single iteration of the target CC/EOMCC calculation (in the case of the calculations aimed at the CCSDT/EOMCCSDT energetics, the computational time associated with each $\delta_\mu(P;Q)$ scales no worse than $\sim 2n_o^3n_u^4$, as opposed to the $n_o^3n_u^5$ scaling of every CCSDT and EOMCCSDT iteration).

There exists another interesting aspect of the semi-stochastic CC($P;Q$) algorithm as outlined above if we examine how the CC(P)/EOMCC(P) and CC($P;Q$) runs behave as τ is varied. For example, if we focus on the CCSDT and EOMCCSDT schemes that are of the main interest in this chapter, at $\tau = 0$, where the P space contains only singly and doubly excited determinants, the CC(P)/EOMCC(P) run becomes equivalent to CCSD/EOMCCSD, whereas the $\tau = 0$ CC($P;Q$) step corresponds to CR-CC(2,3) and CR-EOMCC(2,3). The target CCSDT/EOMCCSDT method is equivalent to CC(P)/EOMCC(P) at $\tau = \infty$, where all triply excited determinants have been captured by the QMC propagation and included in the P space. Consequently, CCSDT/EOMCCSDT are also equivalent to the $\tau = \infty$ CC($P;Q$) runs, because at this point the Q space is empty and the $\delta_\mu(P;Q)$ correction becomes zero by definition. Thus, the variable τ serves to connect the $\tau = 0$ and $\tau = \infty$ limits of our CC(P)/EOMCC(P) and CC($P;Q$) computations, which is useful for checking the correctness of our calculations.

4.2 Application: Electronic Excitation Spectra of CH⁺, CH, and CNC

In order to assess the performance of the semi-stochastic CC($P;Q$) approach to excited described above and examine, in particular, the ability of the noniterative $\delta_\mu(P;Q)$ corrections to accelerate the convergence of the CIQMC-driven EOMCC(P) calculations toward the desired EOMCC energetics, represented here by EOMCCSDT, we carried out benchmark calculations for the frequently studied vertical excitations in the CH⁺ molecule at the equilibrium [Table 4.1 and Fig. 4.1(a) and (b)] and stretched [Table 4.2 and Fig. 4.1(c)]

and (d)] geometries and the adiabatic excitations in the challenging open-shell CH (Table 4.3) and CNC (Table 4.4) systems, which have low-lying excited states dominated by two-electron transitions that require the EOMCCSDT theory level to obtain a reliable description [56, 86, 93, 101, 260–263]. The CH^+ ion was described by the [5s3p1d/3s1p] basis set of Ref. [264] and we used the aug-cc-pVDZ [265, 266] and DZP[4s2p1d] [267, 268] bases for the CH and CNC species, respectively. Following Refs. [111, 113] (*cf.*, also, Ref. [269]), we used the HANDE software package [270, 271] to execute the stochastic *i*-FCIQMC runs, needed to generate the lists of triply excited determinants included in the $\text{CC}(P)$ and $\text{EOMCC}(P)$ calculations. Our standalone CC/EOMCC codes, interfaced with the RHF, ROHF, and integral routines in the GAMESS package, were used to carry out the required $\text{CC}(P)$, $\text{EOMCC}(P)$, $\text{CC}(P;Q)$, and fully deterministic (CCSD/EOMCCSD and CCSDT/EOMCCSDT) computations [the Q spaces used to construct the $\text{CC}(P;Q)$ corrections to the $\text{CC}(P)$ and $\text{EOMCC}(P)$ energies consisted of the triples not captured by the *i*-FCIQMC runs at the corresponding propagation times τ]. It should be noted that the $\text{CC}(P)$ and $\text{EOMCC}(P)$ energies at $\tau = 0$ $\text{CC}(P;Q)$ corrections are equivalent to those of CR-CC(2,3) (the ground state) and CR-EOMCC(2,3) (excited states). It should also be noted that the $\text{CC}(P)$ and $\text{EOMCC}(P)$ energies at $\tau = \infty$ are identical to the energies obtained in the full CCSDT and EOMCCSDT calculations. The semi-stochastic $\text{CC}(P;Q)$ calculations recover the CCSDT and EOMCCSDT energetics in this limit, too, although the $\tau = \infty$ values of the $\delta_\mu(P;Q)$ corrections are zero in this case, since the $\tau = \infty$ P spaces contain all the triples, *i.e.*, the corresponding Q -space triples lists are empty. These relationships between the semi-stochastic $\text{CC}(P)$, $\text{EOMCC}(P)$, and $\text{CC}(P;Q)$ approaches and the fully deterministic CCSD/EOMCCSD, CR-CC(2,3)/CR-EOMCC(2,3), and CCSDT/EOMCCSDT methodologies were helpful in examining the correctness of our codes. They also point to the ability of the $\text{CC}(P)$, $\text{EOMCC}(P)$, and $\text{CC}(P;Q)$ calculations driven by the information extracted from CIQMC to offer a systematically improvable description as τ approaches ∞ . Each *i*-FCIQMC run was initiated by placing 1500 walkers on the relevant reference function (see

Tables 4.1–4.4 for the details) and we set the initiator parameter n_a at 3. All of the *i*-FCIQMC propagations used the time step τ of 0.0001 a.u. In the post-ROHF computations for the CH and CNC species, the core electrons corresponding to the 1s shells of the carbon and nitrogen atoms were kept frozen. In the case of CH^+ , we correlated all electrons.

We begin our discussion of the numerical results with the CH^+ ion, where we investigated the three lowest excited states of the $^1\Sigma^+$ symmetry (labeled as $2\ ^1\Sigma^+$, $3\ ^1\Sigma^+$, and $4\ ^1\Sigma^+$; the ground state is designated as $1\ ^1\Sigma^+$), two lowest states of the $^1\Pi^+$ symmetry ($1\ ^1\Pi^+$ and $2\ ^1\Pi^+$), and two lowest $^1\Delta^+$ states ($1\ ^1\Delta^+$ and $1\ ^1\Delta^+$). Two C–H internuclear separations were considered, the equilibrium distance $R = R_e = 2.13713$ bohr [Table 4.1 and Fig. 4.1(a) and (b)] and the stretched $R = 2R_e$ geometry [Table 4.2 and Fig. 4.1(c) and (d)]. Following the semi-stochastic $\text{CC}(P;Q)$ algorithm, as described above, and our interest in converging the CCSDT/EOMCCSDT energetics, the cluster and right and left EOM operators used in the calculations for the states were approximated by $T^{(P)} = T_1 + T_2 + T_3^{(\text{MC})}$, $R_\mu^{(P)} = r_{\mu,0}\mathbf{1} + R_{\mu,1} + R_{\mu,2} + R_{\mu,3}^{(\text{MC})}$, and $L_\mu^{(P)} = \delta_{\mu 0}\mathbf{1} + L_{\mu,1} + L_{\mu,2} + L_{\mu,3}^{(\text{MC})}$, respectively, where the list of triples defining the three-body components $T_3^{(\text{MC})}$, $R_{\mu,3}^{(\text{MC})}$, and $L_{\mu,3}^{(\text{MC})}$ at a given time τ was obtained from the ground-state *i*-FCIQMC propagation at the same value of τ . The $T_3^{(\text{MC})}$ component of $T^{(P)}$ used in the $\text{CC}(P;Q)$ computations of the $^1\Pi$ and $^1\Delta$ states, needed to determine the similarity-transformed Hamiltonian $\bar{H}^{(P)}$ to be diagonalized in the subsequent EOMCC steps, was defined in the same way as in the case of the states, but the lists of triples entering the $R_{\mu,3}^{(\text{MC})}$ and component of $R_\mu^{(P)}$ and the $L_{\mu,3}^{(\text{MC})}$ component of $L_\mu^{(P)}$ were obtained differently. They were extracted from the *i*-FCIQMC runs for the lowest states within the irreps of C_{2v} relevant to the symmetries of interest, meaning the $^1B_1(C_{2v})$ component of $1\ ^1\Pi$ for the $^1\Pi$ states and the $^1A_2(C_{2v})$ component of $1\ ^1\Delta$ for the $^1\Delta$ states (C_{2v} is the largest Abelian subgroup of the true point group of CH^+ , $C_{\infty v}$; our codes cannot handle non-Abelian symmetries). As implied by Eq. (3.9), the corrections to the $\text{CC}(P)$ and $\text{EOMCC}(P)$ energies at a given time τ were computed using the $\mathfrak{M}_{\mu,K}(P)$ and $\ell_{\mu,K}(P)$ amplitudes corresponding to the triply excited determinants $|\Phi_K\rangle$ not captured

by *i*-FCIQMC at the same τ .

As pointed out in Refs. [47, 48, 112], the $2^1\Sigma^+$, $2^1\Pi$, $1^1\Delta$, and $2^1\Delta$ states of CH^+ at $R = R_e$ and all of the excited states of the stretched $\text{CH}^+/R = 2R_e$ system, which we calculated in this work, are characterized by substantial MR correlations that originate from large two-electron excitation contributions (the $2^1\Delta$ state at $R = 2R_e$ also has significant triple excitations [47, 48, 112]). It is, therefore, not surprising that the basic EOMCCSD level, equivalent to the EOMCC(P) calculations at $\tau = 0$, performs poorly for all of these states, producing very large errors relative to EOMCCSDT that are about 12, 20, and 34–35 millihartree for the $2^1\Sigma^+$, $2^1\Pi$, and both $1^1\Delta$ states, respectively, at $R = R_e$ and ~ 14 – 144 millihartree when the excited states at $R = 2R_e$ are considered (see Tables 4.1 and 4.2). The EOMCCSD energies for the $3^1\Sigma^+$, $4^1\Sigma^+$, and $1^1\Pi$, states at the equilibrium geometry, which are dominated by one-electron transitions, are more accurate, but errors on the order of 3–6 millihartree still remain. As shown in Tables 4.1 and 4.2, the CR-EOMCC(2,3) triples correction to EOMCCSD, equivalent to the CC($P;Q$) calculations at $\tau = 0$, offers substantial improvements, as exemplified by the small errors, on the order of 1–3 millihartree, for the majority of excited states of CH^+ considered in this article, but there are cases, especially the and states at $R = 2R_e$, where the differences between the CR-EOMCC(2,3) and parent EOMCCSDT energies, which are about 13 millihartree in the former case and more than 63 millihartree in the case of the latter state, remain very large. This is related to the substantial coupling of the one- and two-body components of the cluster and EOM excitation and de-excitation operators with their three-body counterparts, which the CR-EOMCC(2,3) corrections to EOMCCSD neglect. Our older active-space EOMCCSDt calculations for CH^+ reported in Refs. [47, 48] and the more recent semi-stochastic EOMCC(P) calculations for the same system described in Ref. [112] are telling us that the incorporation of the leading triples in the relevant P spaces, which allows the one- and two-body components of T , R_μ , and L_μ to relax in the presence of their three-body counterparts, is the key to improve the results of the CR-EOMCC(2,3) calculations.

This is exactly what we observe in Tables 4.1 and 4.2 and Fig. 4.1. In agreement with Ref. [112], by enriching the P spaces used in the $\text{CC}(P)$ and $\text{EOMCC}(P)$ computations with the subsets of triples captured during i -FCIQMC propagations, the results greatly improve, allowing us to reach the millihartree or sub-millihartree accuracy levels for all the calculated excited states of CH^+ at both nuclear geometries considered in this work when the stochastically determined P spaces contain about 20–30% of all triples. The $\text{CC}(P;Q)$ corrections to the $\text{EOMCC}(P)$ energies based on Eq. (3.9) accelerate the convergence toward EOMCCSDT even further. As shown in Tables 4.1 and 4.2 and Fig. 4.1, these corrections are so effective that we reach the millihartree or sub-millihartree accuracy levels relative to the parent EOMCCSDT energetics almost instantaneously, *i.e.*, out of the early stages of the i -FCIQMC propagations, when no more than 5–10% of all triples are included in the relevant P spaces. This is true even when the highly complex $4^1\Sigma^+$ and $2^1\Delta$ states at $R = 2R_e$, for which the EOMCCSD calculations produce the massive, ~ 33 and ~ 144 millihartree, errors, which remain large (about 13 and 63 millihartree, respectively) at the $\text{CR-EOMCC}(2,3)$ level. As shown in Table 4.2, the $\text{CC}(P;Q)$ corrections to the $\text{EOMCC}(P)$ energies, which account for the missing triples that the i -FCIQMC propagations at a given time τ did not capture, allow us to reach the sub-millihartree accuracy levels with less than 5% (the $2^1\Delta$ state) or $\sim 10\%$ (the $4^1\Sigma^+$ state) of triples in the relevant P spaces. The uncorrected $\text{EOMCC}(P)$ calculations display the relatively fast convergence toward EOMCCSDT as well, but they reach similar accuracies at later propagation times τ , when about 15% (the $2^1\Delta$ state) or 25% (the $4^1\Sigma^+$ state) of triples are captured by i -FCIQMC. Obviously, the details of the rate of convergence of the semi-stochastic $\text{CC}(P;Q)$ calculations toward EOMCCSDT , especially when one wants to tighten it, depend on the specific excited state being calculated, but, as shown in Tables 4.1 and 4.2, once about 20% of triples are captured by the i -FCIQMC propagations, we recover the EOMCCSDT energetics for all the calculated excited states of CH^+ at both geometries examined in this study to within 0.1 millihartree or better.

Interestingly, there is a great deal of consistency between the behaviour of the uncorrected

semi-stochastic EOMCC(P) approach, in which the lists of triples defining the relevant P spaces are extracted from i -FCIQMC propagations, and the fully deterministic EOMCCSDt calculations for CH^+ reported in Refs. [47, 48], in which the leading triples were identified using active orbitals. Indeed, once the stochastically determined P spaces extracted from i -FCIQMC capture about 20–30% of all triples, which in the case of the CH^+ system examined here is achieved after 50,000 or fewer $\Delta\tau = 0.0001$ a.u. MC iterations, the energies resulting from the EOMCC(P) computations become very similar to those obtained with the EOM-CCSDt method using the active space that consists of the highest-energy occupied (3σ) and three lowest-energy unoccupied ($1\pi_x$, $1\pi_y$, and 4σ) orbitals. Following the definitions of the ‘little t’ T_3 and $R_{\mu,3}$ operators adopted in EOMCCSDt, for the state symmetries considered in this work, the active space consisting of the 3σ , $1\pi_x$, $1\pi_y$, and 4σ valence orbitals amounts to about 26–29% of all triples included in the respective EOMCC diagonalization spaces [47, 48]. This suggests that the types and values of the triply excited amplitudes defining the components of the EOM operators, which characterize the EOMCCSDt computations reported in Refs. [47, 48], and those that define the components obtained in the i -FCIQMC-driven EOMCC(P) calculations performed after 50,000 MC iterations using $\Delta\tau = 0.0001$ a.u. should be similar too. This is illustrated in Fig. 4.2, where we compare the distributions of the differences between the $R_{\mu,3}^{(\text{MC})}$ amplitudes and their full EOMCCSDT counterparts resulting from the EOMCC(P) computations at 4000 [Fig. 4.2(a)], 10,000 [Fig. 4.2(b)], and 50,000 [Fig. 4.2(c)] MC iterations for the $2^1\Sigma^+$ state of CH^+ at $R = 2R_e$ with the analogous distribution characterizing the amplitudes obtained with the EOMCCSDt approach using the 3σ , $1\pi_x$, $1\pi_y$, and 4σ active orbitals to define the corresponding triples space [Fig. 4.2(d); all EOM vectors R_μ needed to construct Fig. 4.2, corresponding to the EOMCC(P), EOMCCSDt, and EOMCCSDT calculations, were normalized to unity]. As shown in Fig. 4.2 [*cf.* Fig. 4.2(c) and Fig. 4.2(d)], the small differences between the $R_{\mu,3}^{(P)}$ amplitudes resulting from the EOMCC(P) calculations performed after 50,000 MC iterations and the $R_{\mu,3}$ amplitudes obtained with EOMCCSDT, including their numerical values and distribution,

closely resemble those characterizing the active-space EOMCCSDt computations reported in Refs. [47, 48]. This is in perfect agreement with the small errors relative to EOMCCSDT characterizing the two calculations, which are 0.302 millihartree in the former case (*cf.* Table 4.2) and 0.576 millihartree in the case of EOMCCSDt [47, 48]. When we start using considerably smaller fractions of triples and, as a consequence, significantly smaller P spaces in the EOMCC(P) calculations, which is what happens when the underlying i -FCIQMC propagation is terminated too soon, the differences between the amplitudes resulting from the EOMCC(P) calculations and their EOMCCSDT counterparts, including their values and distribution, and the errors in the EOMCC(P) energies relative to EOMCCSDT increase. This can be seen in Fig. 4.2, especially when one compares panel (a), which corresponds to the EOMCC(P) calculations performed after 4000 MC iterations that use only 7% of triples, with panel (d) representing EOMCCSDt, which uses a much larger fraction of triple excitations ($\sim 30\%$), and in Table 4.2, where the error in the EOMCC(P) energy of the state of CH^+ at $R = 2R_e$ relative to EOMCCSDT obtained after 4000 MC iterations, of 4.263 millihartree, is ~ 14 times larger than the analogous error obtained after 50,000 MC steps.

The above analysis, which could be repeated for the remaining states of CH^+ , reaching similar conclusions, has several interesting implications for the semi-stochastic $\text{CC}(P;Q)$ methodology pursued in this study, which will be examined by us in the future. It suggests, for example, that the $\text{CC}(P)/\text{EOMCC}(P)$ and $\text{CC}(P;Q)$ approaches using CIQMC propagations to determine the lists of higher-than-double excitations in the corresponding P spaces can be regarded as natural alternatives to the fully deterministic active-space EOMCC methods, such as EOMCCSDt, and their $\text{CC}(P;Q)$ -corrected counterparts, such as $\text{CC}(t;3)$, whose performance in excited-state calculations will be reported by us in a separate study. It also suggests that the fractions of higher-than-double excitations used to define the stochastically determined P spaces, needed to achieve high accuracies observed in the semi-stochastic $\text{CC}(P;Q)$ calculations discussed in this work, should decrease with the basis set. We have already observed this in the previous ground-state work [111], and we anticipate

that the same will remain true in the CIQMC-driven excited-state $CC(P;Q)$ calculations. While this remark requires a separate thorough study, beyond the scope of this initial work on the excited-state $CC(P;Q)$, we can rationalize it by referring to the analogies between the semi-stochastic $CC(P)/EOMCC(P)$ and $CC(P;Q)$ approaches and their deterministic CCSDt/EOMCCSDt and $CC(t;3)$ counterparts. Indeed, the aforementioned (D/d) ratio that controls the speedups offered by the $CC(P)/EOMCC(P)$ and $CC(P;Q)$ calculations becomes $(n_o/N_o)(n_u/N_u)$ when the active-space CCSDt/EOMCCSDt and $CC(t;3)$ calculations, based on the ideas laid down in Refs. [47, 48, 74, 75, 81, 101], are considered, where N_o and N_u are the numbers of active occupied and active unoccupied orbitals, respectively, which either do not grow with the basis set or grow with it very slowly compared to n_o and n_u .

Finally, before moving to the next molecular example, we would like to point out that, in analogy to the $CC(P;Q)$ -based $CC(t;3)$, $CC(t,q;3)$, and $CC(t,q;3,4)$ calculations using active orbitals to define the underlying P spaces (see, *e.g.*, Ref. [77]), one is better off by using smaller P spaces in the semi-stochastic $CC(P)/EOMCC(P)$ considerations, which can be extracted out of the early stages of CIQMC propagations, and capturing the remaining correlations using noniterative $CC(P;Q)$ corrections, than by running long-time CIQMC simulations to generate larger P spaces for the uncorrected $CC(P)/EOMCC(P)$ calculations. This can be seen in Tables 4.1 and 4.2 for CH^+ and in the remaining Tables 4.3 and 4.4 discussed in the next two subsections. We illustrate this remark by inspecting the $EOMCC(P)$ and $CC(P;Q)$ calculations for the state of CH^+ . As shown in Table 4.1, one needs to capture about 50% of triples in the P space to reach a 0.1 millihartree accuracy relative to $EOMCCSDT$ at $R = R_e$ using the uncorrected $EOMCC(P)$ approach. When the $CC(P;Q)$ correction is employed, only 15% of triples are needed to reach the same accuracy level. At the more challenging $R = 2R_e$ geometry (Table 4.2), one reaches a ~ 0.1 millihartree accuracy level with about 40% of triples in the P space when using the uncorrected $EOMCC(P)$ approach. This fraction reduces to about 20%, without any accuracy loss, when

the $\text{CC}(P;Q)$ correction is added to the $\text{EOMCC}(P)$ energy. Based on the information provided in above, running the $\text{EOMCC}(P)$ calculations with a smaller fraction of triples in the P space offers much larger savings in the computational effort than the additional time spent on determining the $\text{CC}(P;Q)$ correction, which is, as pointed out above, considerably less expensive than a single EOMCCSDT iteration. For example, in the pilot implementation of the excited-state $\text{EOMCC}(P)$ and $\text{CC}(P;Q)$ approaches aimed at recovering EOMCCSDT energetics, employed in this work, the uncorrected $\text{EOMCC}(P)$ run using 50% of triples in the P space, needed to reach a ~ 0.1 millihartree accuracy relative to EOMCCSDT for the state of CH^+ at $R = R_e$, is about twice as fast as the corresponding EOMCCSDT calculation. The $\text{EOMCC}(P)$ diagonalization that forms part of the analogous $\text{CC}(P;Q)$ run, which needs only 15% of triples in the P space to reach the same accuracy level, is about 6 times faster than EOMCCSDT . The noniterative $\text{CC}(P;Q)$ correction is so inexpensive here that one can largely ignore the computational costs associated with its determination in this context [*cf.* Ref. [73] for the analogous comments made in the context of comparing costs of the CCSDt computations with those of $\text{CC}(t;3)$].

Similar convergence patterns in the semi-stochastic $\text{EOMCC}(P)$ and $\text{CC}(P;Q)$ calculations are observed for the CH radical (see Table 4.3). In this case, following the earlier deterministic EOMCC work, including the CR-EOMCC [86, 93] and electron-attachment (EA) EOMCC [93, 260, 261] approaches, and a wide range of EOMCC computations, including the high EOMCCSDT and EOMCCSDTQ levels, published by Hirata [56], along with the $\text{X } ^2\Pi$ ground state, we examined the three low-lying doublet excited states, designated as $\text{A } ^2\Delta$, $\text{B } ^2\Sigma^-$, and $\text{C } ^2\Sigma^+$, which belong to different irreducible representations than that of the ground state. In analogy to the aforementioned EOMCC studies of CH [56, 86, 93, 260, 261], the relevant $\text{CC}(P)$ (the $\text{X } ^2\Pi$ state) and $\text{EOMCC}(P)$ (excited states) electronic energies and their $\text{CC}(P;Q)$ counterparts were determined at the corresponding experimentally derived equilibrium C–H distances, which are 1.1197868 Å for the $\text{X } ^2\Pi$ state [272], 1.1031 Å for the $\text{A } ^2\Delta$ state [272], 1.1640 Å for the $\text{B } ^2\Sigma^-$ state [273], and 1.1143 Å

for the $C^2\Sigma^+$ state [274] (*cf.* Table 4.3). Since all of our $CC(P)/EOMCC(P)$ and $CC(P;Q)$ calculations, starting from the $\tau = 0$ CCSD/EOMCCSD and CR-EOMCC(2,3) levels and ending up with the larger values of τ needed to examine the convergence toward the parent CCSDT/EOMCCSDT energetics, were performed using the ROHF reference determinant, we also computed the ROHF-based CCSDT and EOMCCSDT energies, which formally correspond to the $\tau = \infty$ $CC(P)/EOMCC(P)$ and $CC(P;Q)$ results. We had to do it, since the previously published CCSDT/EOMCCSDT results [56] relied on the UHF rather than the ROHF reference. In analogy to CH^+ , the lists of triples defining the $T_3^{(MC)}$ component of the cluster operator $T^{(P)}$ and the $R_{\mu,3}^{(MC)}$ and $L_{\mu,3}^{(MC)}$ components of the EOM excitation and de-excitation operators, $R_\mu^{(P)}$ and $L_\mu^{(P)}$, respectively, used in the $CC(P)$, $EOMCC(P)$, and $CC(P;Q)$ calculations for the CH radical, were extracted from the *i*-FCIQMC propagations for the lowest-energy states of the relevant irreps of C_{2v} , namely, the ${}^2B_2(C_{2v})$ component of the $X^2\Pi$ state, the lowest state of the ${}^2A_1(C_{2v})$ symmetry in the case of the $A^2\Delta$ and $C^2\Sigma^+$ states, and the lowest ${}^2A_2(C_{2v})$ state when considering the $B^2\Sigma^-$ state (again, we used C_{2v} , which is the largest Abelian subgroup of the true point group of CH, $C_{\infty v}$).

As explained in Refs. [86, 93, 260, 261] and as shown in Ref. [56], all three excited states of the CH radical considered here, especially $B^2\Sigma^-$ and $C^2\Sigma^+$, which are dominated by two-electron excitations (*cf.* the reduced excitation level (REL) diagnostic values in Tables II and III of Ref. [93] or Table II of Ref. [86]), constitute a significant challenge, requiring the full EOMCCSDT treatment to obtain a reliable adiabatic excitation spectrum. This can be seen by inspecting the $\tau = 0$ $EOMCC(P)$, *i.e.*, EOMCCSD, energies for the $A^2\Delta$, $B^2\Sigma^-$, and $C^2\Sigma^+$ states of CH shown in Table 4.3, which are characterized by the ~ 13 , ~ 39 , and ~ 44 millihartree errors relative to EOMCCSDT, respectively. The CR-EOMCC(2,3) triples corrections to EOMCCSD, represented in Table 4.3 by the $\tau = 0$ $CC(P;Q)$ values, help, especially in the case of the $C^2\Sigma^+$ state, but the situation is far from ideal, since errors on the order of 8 and 5 millihartree for the $A^2\Delta$ and $B^2\Sigma^-$ states, respectively, remain. The situation considerably improves when we turn to the semi-stochastic $CC(P;Q)$

calculations, which incorporate the leading triples in the relevant P spaces by extracting them from the corresponding i -FCIQMC propagations and correct the resulting energies for the remaining triple excitations that were not captured by i -FCIQMC at a given time τ . As shown in Table 4.3, in the case of the $A^2\Delta$ and $B^2\Sigma^-$ states, which are not only challenging to EOMCCSD, but also to CR-EOMCC(2,3), we can reach comfortable 1–2 millihartree errors relative to EOMCCSDT using the semi-stochastic $CC(P;Q)$ corrections developed in this work once the relevant P spaces contain about 20–40% of all triples. With $\sim 50\%$ triples in the same P spaces, the $CC(P;Q)$ energies of the $A^2\Delta$ and $B^2\Sigma^-$ states are within fractions of a millihartree from EOMCCSDT. These are considerable improvements relative to the purely deterministic EOMCCSD and CR-EOMCC(2,3) computations, which give ~ 13 – 39 and ~ 5 – 8 millihartree errors, respectively, for the same two states, and the semi-stochastic EOMCC(P) calculations that reach 1–2 millihartree accuracy levels with about 70–80% triples in the respective P spaces. In the case of the $C^2\Sigma^+$ state, which is a major challenge to EOMCCSD, but not to CR-EOMCC(2,3), the behaviour of the EOMCC(P) and $CC(P;Q)$ approaches is different, since the $CC(P;Q)$ corrections obtained with the help of some triples in the P space captured by i -FCIQMC are no longer needed to obtain the well-converged energetics, *i.e.*, the $\tau = 0$ $CC(P;Q)$ result, where the P space is spanned by singles and doubles only, is sufficiently accurate, but it is still interesting to observe that one can tighten the convergence further, reaching stable <0.1 millihartree errors relative to EOMCCSDT with about 50% of all triples in the P space. In analogy to the $A^2\Delta$ and $B^2\Sigma^-$ states, it is also interesting to observe a reasonably smooth convergence of the uncorrected EOMCC(P) energies toward EOMCCSDT. It is clear from the results presented in Table 4.3 that the $CC(P;Q)$ corrections to the semi-stochastic $CC(P)$ and EOMCC(P) energies offer considerable speedups compared to the uncorrected $CC(P)$ /EOMCC(P) calculations, not only for the closed-shell molecules, such as CH^+ , but also when examining open-shell species.

Our last example, which is also the largest many-electron system considered in the present

study, is the linear, $D_{\infty h}$ symmetric, CNC molecule. Following the earlier CR-CC(2,3)/CR-EOMCC(2,3) and electron-attached (EA) EOMCC calculations for this challenging open-shell molecular species [93, 262, 263], we considered the $X^2\Pi_g$ ground state and two low-lying doublet excited states, $A^2\Delta_u$ and $B^2\Sigma_u^+$. The *i*-FCIQMC-driven $CC(P)$ ground-state and EOMCC(P) excited-state energies and the corresponding $CC(P;Q)$ corrections, along with their deterministic EOMCCSD, CR-EOMCC(2,3), and EOMCCSDT counterparts, were calculated using the equilibrium C–N distances optimized in Ref. [262] with EA-SAC-CI. They are 1.253 Å for the $X^2\Pi_g$ state, 1.256 Å for the $A^2\Delta_u$ state, and 1.259 Å for the $B^2\Sigma_u^+$ state. As in the case of the CH radical, we used the ROHF reference determinant. Following the computational protocol adopted in this study, and in analogy to the CH^+ and CH species, the lists of triples defining the $T_3^{(MC)}$, $R_{\mu,3}^{(MC)}$, and $L_{\mu,3}^{(MC)}$ components used in the semi-stochastic $CC(P)$, EOMCC(P), and $CC(P;Q)$ calculations for CNC were obtained using the *i*-FCIQMC propagations for the lowest-energy states of the relevant irreps of the largest Abelian subgroup of $D_{\infty h}$, *i.e.*, D_{2h} , meaning the $^2B_{2g}(D_{2h})$ component of the $X^2\Pi_g$ state and the lowest state of the $^2B_{1u}(D_{2h})$ symmetry in the case of the $A^2\Delta_u$ and $B^2\Sigma_u^+$ states.

As shown in Table 4.4 and in agreement with one of our previous studies [93], all three states of CNC considered in this work, especially $A^2\Delta_u$ and $B^2\Sigma_u^+$, are poorly described by CCSD and EOMCCSD, which produce more than 18, 31, and 111 millihartree errors, respectively, relative to the target EOMCCSDT energetics [see the $\tau = 0$ $CC(P)$ and EOMCC(P) energies in Table 4.4]. The excessively large, >111 millihartree, error in the EOMCCSD energy of the $B^2\Sigma_u^+$ state is related to its strongly MR character dominated by two-electron excitations (*cf.* the REL values characterizing the excited states of CNC in Table IV of Ref. [93]). In the case of the ground state and the $B^2\Sigma_u^+$ excited state, the CR-CC(2,3) and CR-EOMCC(2,3) corrections to CCSD and EOMCCSD seem to be quite effective, reducing the large errors relative to CCSDT/EOMCCSDT observed in the CCSD and EOMCCSD calculations to a sub-millihartree level, but the ~ 16 millihartree error

resulting from the CR-EOMCC(2,3) calculations for the $A^2\Delta_u$ state, while considerably lower than the >31 millihartree error obtained with EOMCCSD, is still rather large (see the $\tau = 0$ CC($P;Q$) energies in Table 4.4). By incorporating the dominant triply excited determinants captured by the *i*-FCIQMC propagations in the respective P spaces, the semi-stochastic CC(P) and EOMCC(P) approaches help, allowing us to reach stable ~ 1 – 2 millihartree accuracy levels for the and states relative to the target CCSDT/EOMCCSDT energetics with about 50–60% triples, but the CC($P;Q$) corrections that account for the remaining triples, missing in the *i*-FCIQMC wave functions, are considerably more effective. In the case of the state, which poses problems to both EOMCCSD and CR-EOMCC(2,3), which give about 31 and 16 millihartree errors relative to EOMCCSDT, respectively, we reach a stable ~ 1 – 2 millihartree accuracy level with about 30–40% triples in the corresponding P space, as opposed to the aforementioned 50–60% needed in the uncorrected EOMCC(P) run. The benefits of using the semi-stochastic CC($P;Q$) versus deterministic CR-EOMCC(2,3) corrections for the $X^2\Pi_g$ and $A^2\Delta_u$ states are less obvious, but it is encouraging to observe the rapid convergence toward the target CCSDT and EOMCCSDT energetics in the former calculations. In particular, they allow us to lower the 0.4–0.5 millihartree errors obtained with CR-EOMCC(2,3) to a 0.1 millihartree level with about 10% of all triples, identified by *i*-FCIQMC, in the case of the state and with ~ 30 – 40 % triples in the P space when the state is considered. Once again, the CC($P;Q$) corrections to the energies resulting from the semi-stochastic CC(P) and EOMCC(P) calculations speed up the uncorrected CC(P)/EOMCC(P) computations, while allowing us to improve the CR-CC(2,3) and CR-EOMCC(2,3) energetics by bringing them very close to the CCSDT and EOMCCSDT levels at the fraction of the cost.

Table 4.1: Convergence of the $CC(P)/EOMCC(P)$ and $CC(P;Q)$ energies toward CCSDT/EOMCCSDT for CH^+ , calculated using the [5s3p1d/3s1p] basis set of Ref. [264], at the C–H internuclear distance $R = R_e = 2.13713$ bohr. The P spaces used in the $CC(P)$ and $EOMCC(P)$ calculations were defined as all singles, all doubles, and subsets of triples extracted from i -FCIQMC propagations for the lowest states of the relevant symmetries. Each i -FCIQMC run was initiated by placing 1500 walkers on the appropriate reference function [the RHF determinant for the $1^1\Sigma_g^+$ states, the $3\sigma \rightarrow 1\pi$ state of the $1B_1(C_{2v})$ symmetry for the 1Π states, and the $3\sigma^2 \rightarrow 1\pi^2$ state of the $1A_2(C_{2v})$ symmetry for the 1Δ states], setting the initiator parameter n_a at 3, and the time step $\Delta\tau$ at 0.0001 a.u. The Q spaces used in constructing the $CC(P;Q)$ corrections consisted of the triples not captured by i -FCIQMC. Adapted from Ref. [113].

MC iter. (10^3)	$1^1\Sigma_g^+$			$2^1\Sigma_g^+$			$3^1\Sigma_g^+$			$4^1\Sigma_g^+$			$1^1\Pi$			$2^1\Pi$			$1^1\Delta$			$2^1\Delta$	
	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$
0 ^d	1.845	0.063	0	19.694	1.373	3.856	0.787	5.537	0.954	3.080	0.792	0	11.656	2.805	34.304	−0.499	0	34.685	0.350				
2	1.071	0.024	7	11.004	0.909	3.248	0.587	4.826	−4.469	0.772	0.179	13	3.746	0.530	1.492	0.151	10	5.951	0.432				
4	0.423	0.009	15	5.474	0.090	1.893	0.047	1.980	0.100	0.513	0.102	20	1.852	0.128	0.525	0.051	16	2.542	0.128				
6	0.249	0.003	20	4.712	0.111	1.268	0.046	1.077	0.068	0.213	0.054	25	0.957	0.073	0.471	0.028	18	1.892	0.094				
8	0.181	0.003	23	1.371	0.112	0.643	0.067	0.702	0.075	0.170	0.058	27	0.743	0.060	0.240	0.021	22	0.940	0.057				
10	0.172	0.004	24	1.572	0.061	0.295	0.044	0.385	0.026	0.118	0.046	29	0.411	0.047	0.198	0.017	24	0.877	0.041				
50	0.077	0.001	37	0.755	0.026	0.139	0.037	0.208	0.032	0.053	0.027	43	0.157	0.027	0.039	0.008	42	0.133	0.011				
100	0.044	0.000	48	0.277	0.009	0.007	0.013	0.155	0.017	0.021	0.013	57	0.063	0.012	0.014	0.005	56	0.043	0.005				
150	0.015	0.000	59	0.085	0.005	0.058	0.006	0.041	0.007	0.008	0.005	71	0.020	0.004	0.004	0.002	71	0.008	0.003				
200	0.006	0.000	69	0.024	0.002	0.014	0.002	0.002	0.003	0.004	0.003	82	0.008	−0.001	0.003	0.002	82	0.003	0.002				
∞^e	−38.019516			−37.702621			−37.522457			−37.386872			−37.900921			−37.498143			−37.762113			−37.402308	

^aErrors in the $CC(P)$ (the $1^1\Sigma_g^+$ ground state) and $EOMCC(P)$ (excited states) energies relative to the corresponding CCSDT and EOMCCSDT data, in millihartree.

^bErrors in the $CC(P;Q)$ energies relative to the corresponding CCSDT and EOMCCSDT data, in millihartree.

^cThe %T values are the percentages of triples captured during the i -FCIQMC propagations for the lowest state of a given symmetry [the $1^1\Sigma_g^+ = 1^1A_1(C_{2v})$ ground state for the $1^1\Sigma_g^+$ states, the $1B_1(C_{2v})$ component of the $1^1\Pi$ state for the $1^1\Pi$ states, and the $1A_2(C_{2v})$ component of the $1^1\Delta$ state for the $1^1\Delta$ states].

^dThe $CC(P)$ and $EOMCC(P)$ energies at $\tau = 0.0$ a.u. are identical to the energies obtained in the CCSD and EOMCCSD calculations. The $\tau = 0.0$ a.u. $CC(P;Q)$ energies are equivalent to the CR- $CC(2,3)$ (the ground state) and the CR- $EOMCC(2,3)$ (excited states) energies.

^eThe $CC(P)$ and $EOMCC(P)$ energies at $\tau = \infty$ a.u. are identical to the energies obtained in the CCSDT and EOMCCSDT calculations.

Table 4.2: Same as Table 4.1 for the stretched C–H internuclear distance $R = 2R_e = 4.27426$ bohr. Adapted from Ref. [113].

MC iter. (10^3)	$1^1\Sigma_g^+$			$2^1\Sigma_g^+$			$3^1\Sigma_g^+$			$4^1\Sigma_g^+$			$1^1\Pi$			$2^1\Pi$			$1^1\Delta$			$2^1\Delta$		
	P	$(P;Q)$	%T	P	$(P;Q)$	%T	P	$(P;Q)$	%T	P	$(P;Q)$	%T	P	$(P;Q)$	%T	P	$(P;Q)$	%T	P	$(P;Q)$	%T	P	$(P;Q)$	%T
0	5.002	0.012	0	17.140	1.646	19.929	−2.871	32.639	12.657	13.552	2.303	0	21.200	−1.429	44.495	−4.526	0	144.414	−63.405					
2	1.588	0.031	3	5.209	0.478	12.524	−2.079	33.400	14.297	1.398	0.306	7	1.644	−0.060	1.372	0.046	6	13.363	0.368					
4	0.504	0.015	7	4.263	−1.741	6.383	−0.760	12.671	2.178	0.712	0.058	12	0.724	0.050	0.451	0.014	9	3.338	0.130					
6	0.275	0.002	11	1.405	0.047	1.352	0.051	5.870	0.593	0.409	0.033	14	0.612	0.031	0.422	0.022	12	2.340	0.063					
8	0.263	0.004	12	1.543	0.065	1.173	0.020	4.406	0.699	0.436	0.050	16	0.457	−0.002	0.253	0.007	13	2.088	0.021					
10	0.148	0.003	14	0.792	0.094	0.613	0.047	2.331	0.342	0.227	0.039	17	0.220	0.014	0.122	−0.001	14	0.862	0.038					
50	0.030	0.000	26	0.302	0.002	0.339	0.007	0.457	0.013	0.061	0.007	30	0.079	0.060	0.047	0.005	26	0.288	0.005					
100	0.009	0.000	39	0.103	0.003	0.119	0.006	0.110	0.011	0.013	0.002	41	0.016	0.004	0.013	0.004	36	0.038	0.000					
150	0.004	0.000	52	0.031	0.000	0.035	0.003	0.076	0.006	0.005	0.002	52	0.007	0.002	0.005	0.001	47	0.014	0.000					
200	0.001	0.000	63	0.024	0.000	0.019	0.000	−0.006	0.001	0.002	0.001	65	0.001	0.000	0.001	0.000	57	0.003	0.000					
∞	−37.900394			−37.704834			−37.650242			−37.495275			−37.879532			−37.702345			−37.714180			−37.494031		

Table 4.3: Convergence of the $CC(P)/EOMCC(P)$ and $CC(P;Q)$ energies toward CCSDT/EOMCCSDT for CH, calculated using the aug-cc-pVDZ basis set. The P spaces used in the $CC(P)$ and $EOMCC(P)$ calculations were defined as all singles, all doubles, and subsets of triples extracted from i -FCIQMC propagations for the lowest states of the relevant symmetries. Each i -FCIQMC run was initiated by placing 1500 walkers on the appropriate reference function [the ROHF $^2B_2(C_{2v})$ determinant for the X $^2\Pi$ state, the $1\pi \rightarrow 4\sigma$ state of the $^2A_1(C_{2v})$ symmetry for the A $^2\Delta$ and C $^2\Sigma^+$ states, and the $3\sigma \rightarrow 1\pi$ state of the $^2A_2(C_{2v})$ symmetry for the B $^2\Sigma^-$ state], setting the initiator parameter n_a at 3, and the time step $\Delta\tau$ at 0.0001 a.u. The Q spaces used in constructing the $CC(P;Q)$ corrections consisted of the triples not captured by i -FCIQMC. Adapted from Ref. [113].

MC iter. (10^3)	X $^2\Pi$			A $^2\Delta$			B $^2\Sigma^-$			C $^2\Sigma^+$		
	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c
0	2.987	0.231	0.0	13.474	7.727	0.0	38.620	-4.954	0.0	43.992	0.087	0.0
2	2.405	0.170	13.8	13.009	7.395	9.8	10.602	-1.848	18.5	40.700	-0.689	9.8
4	1.413	0.086	41.7	10.907	5.288	19.3	7.066	-1.259	38.9	31.017	-0.319	19.7
6	0.883	0.035	58.9	10.119	4.577	27.2	3.452	-0.371	53.2	26.364	-0.508	28.8
8	0.603	0.022	66.8	7.764	2.436	34.6	2.309	-0.149	61.4	20.545	-0.412	34.3
10	0.495	0.019	72.6	6.987	2.170	38.1	1.965	-0.024	64.8	17.180	0.435	38.3
12	0.445	0.015	76.5	6.640	1.981	42.3	1.832	-0.081	69.5	16.929	0.029	42.5
14	0.389	0.013	77.5	7.040	1.887	45.7	1.180	0.030	72.2	13.114	0.253	45.1
16	0.309	0.008	79.2	6.047	1.667	48.3	1.303	0.012	75.6	7.646	-0.041	48.7
18	0.292	0.008	80.3	4.646	0.875	49.8	1.349	-0.062	77.5	5.312	0.011	50.1
20	0.243	0.006	82.2	3.809	0.754	52.6	0.796	0.038	79.5	4.691	0.108	52.2
50	0.150	0.002	89.1	1.367	0.112	74.1	0.298	0.038	91.6	1.436	0.070	74.0
100	0.055	0.002	95.3	0.177	0.017	91.7	0.144	0.014	98.3	0.204	0.013	91.3
150	0.025	0.000	98.1	0.042	-0.003	98.0	0.010	0.007	99.6	0.063	0.010	98.2
200	0.010	0.000	99.2	0.007	0.001	99.7	-0.001	-0.001	99.9	0.010	0.001	99.7
∞^e	-38.387749			-38.276770			-38.267544			-38.238205		

^aErrors in the $CC(P)$ (the X $^2\Pi$ ground state) and $EOMCC(P)$ (excited states) energies relative to the corresponding CCSDT and EOMCCSDT data, in millihartree, calculated at the experimentally obtained equilibrium C–H distances used in Refs. [56, 86, 93], which are 1.1197868 Å for the X $^2\Pi$ state [272], 1.1031 Å for the A $^2\Delta$ state [272], 1.1640 Å for the B $^2\Sigma^-$ state [273], and 1.1143 Å for the C $^2\Sigma^+$ state [274]. The lowest-energy core orbital was frozen in all correlated calculations.

^bErrors in the $CC(P;Q)$ energies relative to the corresponding CCSDT and EOMCCSDT data, in millihartree, calculated at the experimentally determined equilibrium C–H distances as used in Refs. [56, 86, 93] (see footnote a for the C–H distances).

^cThe %T values are the percentages of triples captured during the i -FCIQMC propagations for the lowest state of a given symmetry [the $^2B_2(C_{2v})$ component of the X $^2\Pi$ ground state, the lowest $^2A_1(C_{2v})$ state for the A $^2\Delta$ and C $^2\Sigma^+$ states, and the lowest $^2A_2(C_{2v})$ state for the B $^2\Sigma^-$ state].

^dThe $CC(P)$ and $EOMCC(P)$ energies at $\tau = 0.0$ a.u. are identical to the energies obtained in the CCSD and EOMCCSD calculations. The $\tau = 0.0$ a.u. $CC(P;Q)$ energies are equivalent to the CR-CC(2,3) (the ground state) and the CR-EOMCC(2,3) (excited states) energies.

^eThe $CC(P)$ and $EOMCC(P)$ energies at $\tau = \infty$ a.u. are identical to the energies obtained in the ROHF-based CCSDT and EOMCCSDT calculations.

Table 4.4: Convergence of the $CC(P)/EOMCC(P)$ and $CC(P;Q)$ energies toward CCSDT/EOMCCSDT for CNC, calculated using DZP[4s2p1d] basis set. The P spaces used in the $CC(P)$ and $EOMCC(P)$ calculations were defined as all singles, all doubles, and subsets of triples extracted from i -FCIQMC propagations for the lowest states of the relevant symmetries. Each i -FCIQMC run was initiated by placing 1500 walkers on the appropriate reference function [the ROHF ${}^2B_{2g}(D_{2h})$ determinant for the $X {}^2\Pi_g$ state and the $3\sigma_u \rightarrow 1\pi_g$ state of the ${}^2B_{1u}(D_{2h})$ symmetry for the $A {}^2\Delta_u$ and $B {}^2\Sigma_u^+$ states], setting the initiator parameter n_a at 3, and the time step $\Delta\tau$ at 0.0001 a.u. The Q spaces used in constructing the $CC(P;Q)$ corrections consisted of the triples not captured by i -FCIQMC. Adapted from Ref. [113].

MC iter. (10^3)	$X {}^2\Pi_g$			$A {}^2\Delta_u$			$B {}^2\Sigma_u^+$		
	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c	P^a	$(P;Q)^b$	%T ^c
0	18.458	-0.495	0.0	31.157	16.017	0.0	111.307	-0.433	0.0
2	10.331	-0.043	13.2	18.835	9.114	6.5	81.493	-2.496	6.5
4	4.424	-0.029	33.2	10.637	5.717	16.1	53.677	-2.526	16.0
6	2.824	-0.011	44.1	7.555	4.199	22.7	35.539	-1.254	22.8
8	1.818	-0.013	49.9	6.181	3.090	27.5	26.767	-0.864	27.9
10	1.306	-0.006	53.3	5.187	2.441	30.8	21.337	-0.284	31.5
12	1.092	-0.003	56.5	4.162	1.778	34.0	17.056	0.196	34.3
14	0.911	-0.005	58.7	3.529	1.418	37.0	12.843	0.046	37.5
16	0.820	-0.003	60.6	3.106	1.149	39.5	9.197	0.134	39.9
18	0.651	-0.003	62.5	2.510	0.811	41.7	8.879	-0.034	42.4
20	0.610	-0.001	63.9	2.395	0.785	44.4	7.548	0.151	44.7
50	0.077	0.000	79.7	0.172	0.058	70.9	0.732	0.055	70.7
100	0.002	0.000	94.5	0.002	0.001	92.3	0.005	0.003	91.9
150	0.000	0.000	99.3	0.000	0.000	99.1	0.000	0.000	99.1
∞^e	-130.421932			-130.276946			-130.252999		

^aErrors in the $CC(P)$ ($X {}^2\Pi_g$ state) and $EOMCC(P)$ (the remaining states) energies relative to the corresponding CCSDT and EOMCCSDT data, in millihartree, calculated at the experimentally obtained equilibrium C–N distances optimized in Ref. [262], which are 1.253 Å for the $X {}^2\Pi_g$ state, 1.256 Å for the $A {}^2\Delta_u$ state, and 1.259 Å for the $B {}^2\Sigma_u^+$ state. The three lowest-energy core orbital was frozen in all correlated calculations.

^bErrors in the $CC(P;Q)$ energies relative to the corresponding CCSDT and EOMCCSDT data, in millihartree, calculated at the equilibrium C–N distances optimized in Ref. [262] (see footnote a for these C–N distances).

^cThe %T values are the percentages of triples captured during the i -FCIQMC propagations for the lowest state of a given symmetry [the ${}^2B_{2g}(D_{2h})$ component of the $X {}^2\Pi_g$ ground state and the lowest ${}^2B_{1u}(D_{2h})$ state for the $A {}^2\Delta$ and $B {}^2\Sigma_u^+$ states].

^dThe $CC(P)$ and $EOMCC(P)$ energies at $\tau = 0.0$ a.u. are identical to the energies obtained in the CCSD and EOMCCSD calculations. The $\tau = 0.0$ a.u. $CC(P;Q)$ energies are equivalent to the CR-CC(2,3) (the ground state) and the CR-EOMCC(2,3) (excited states) energies.

^eThe $CC(P)$ and $EOMCC(P)$ energies at $\tau = \infty$ a.u. are identical to the energies obtained in the ROHF-based CCSDT and EOMCCSDT calculations.

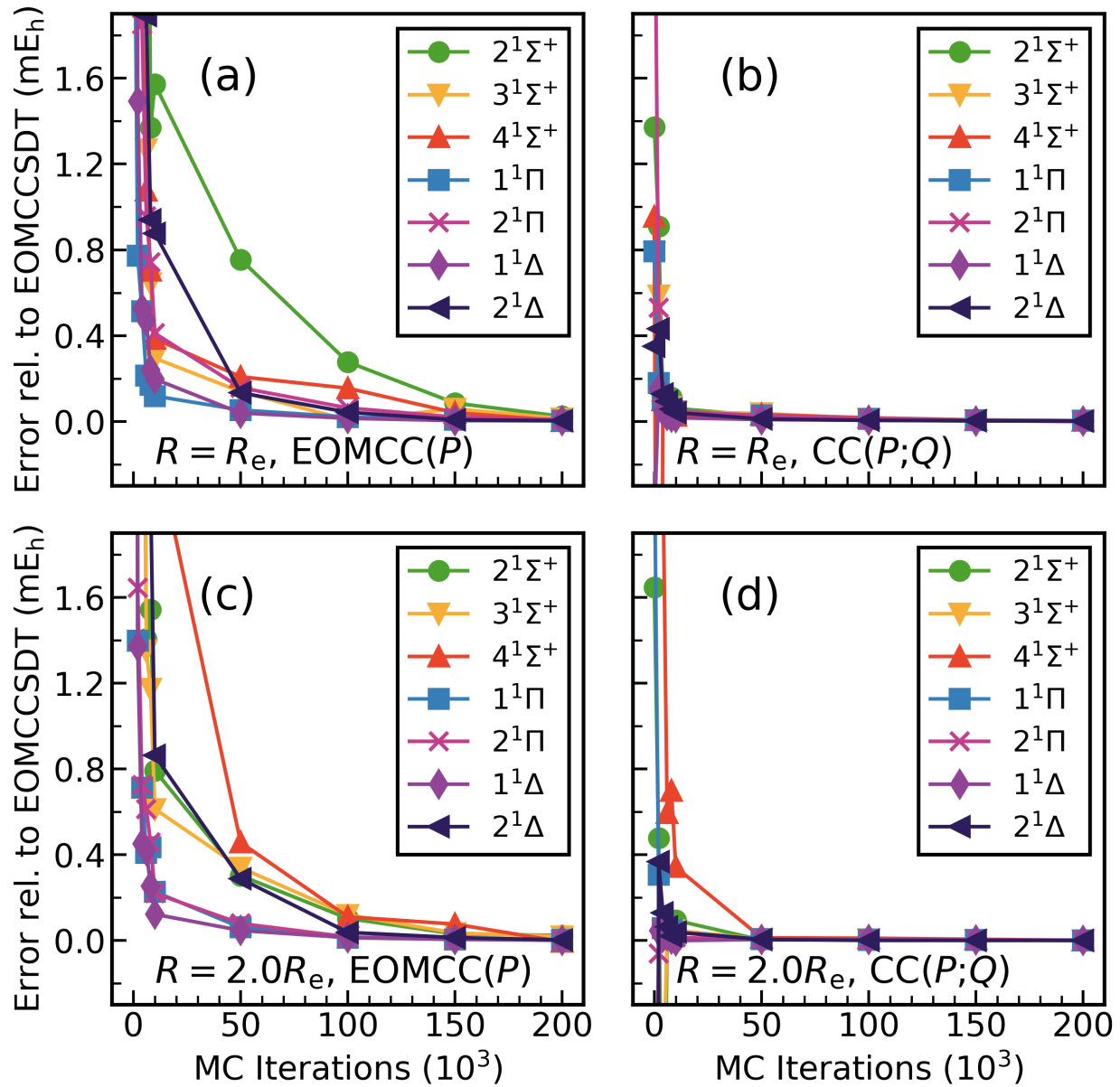


Figure 4.1: Convergence of the EOMCC(P) [panels (a) and (c)] and CC($P;Q$) [panels (b) and (d)] energies toward EOMCCSDT for the three lowest-energy excited states of the $1^1\Sigma^+$ symmetry, two lowest states of the $1^1\Pi$ symmetry, and two lowest $1^1\Delta$ states of the CH^+ ion, as described by the $[5s3p1d/3s1p]$ basis set of Ref. [264], at the C–H internuclear distance R set at $R_e = 2.13713$ bohr [panels (a) and (b)] and $2R_e = 4.27426$ bohr [panels (c) and (d)]. Adapted from Ref. [113].

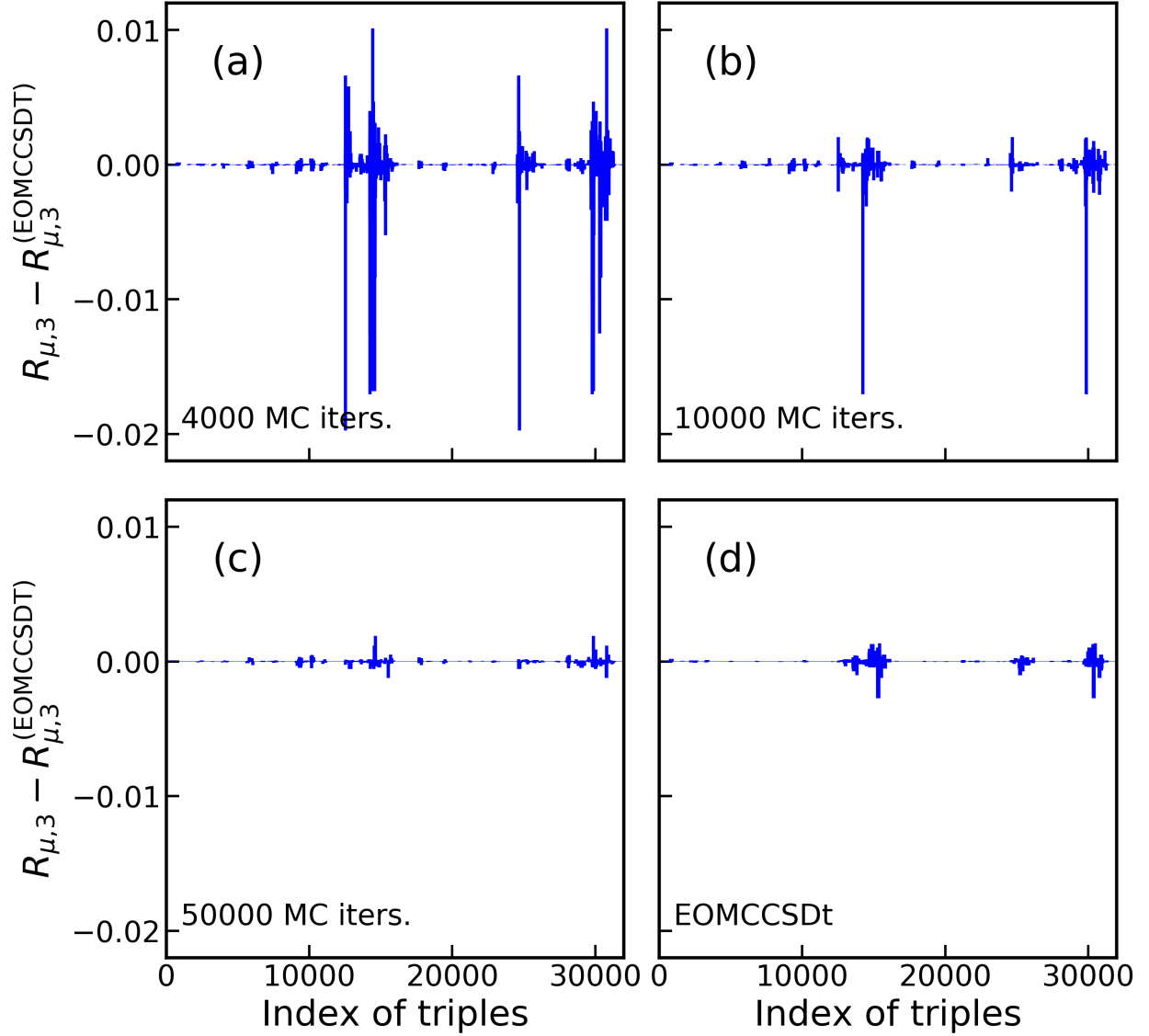


Figure 4.2: The distributions of the differences between the $R_{\mu,3}^{(\text{MC})}$ amplitudes and their EOMCCSDT counterparts resulting from the EOMCC(P) computations at (a) 4000, (b) 10,000, and (c) 50,000 MC iterations using $\tau = 0.0001$ a.u. for the $2^1\Sigma^+$ state of CH^+ at $R = 2R_e$ with the analogous distribution characterizing the $R_{\mu,3}$ amplitudes obtained with the EOMCCSDt approach employing the 3σ , $1\pi_x$, $1\pi_y$, and 4σ active orbitals to define the corresponding triples space [panel (d)]. All vectors R_μ needed to construct panels (a)–(d) were normalized to unity. Adapted from Ref. [113].

CHAPTER 5

CONCLUDING REMARKS AND FUTURE OUTLOOK

This dissertation surveys the recent developments in the realms of CC and EOMCC methodologies. In particular, we have discussed the various CC and EOMCC approaches belonging to the $CC(P;Q)$ framework, in which one have the flexibility of defining the underlying P and Q spaces to achieve the desired level of accuracy suitable to the system of interest.

In the first part of the dissertation, we have discussed the goal of quantum chemistry and the issue of computational cost scaling that plagues the brute-force FCI approach to it. We highlighted the CC theory as one of the best approximation to FCI, especially the $CC(P;Q)$ methodology when we contain the discussion to the realm of SRCC methodology. We have also provided a brief summary of SRCC theory and its EOM extension to excited electronic states and shown examples of high-level CC/EOMCC computations for Mg_2 dimer, where one has to include nearly all-electron correlation effects at the triples level and correct the results for valence FCI correlation effects to obtain spectroscopic ($\sim 1\text{ cm}^{-1}$) accuracy relative to experiment. Furthermore, the case study of Mg_2 also gives us the opportunity to see how the CCSD(T) approximation to CCSDT fail to be quantitative when weakly bound diatomic that dissociates into closed-shell fragments are examined. This gives us the motivation to look into more robust alternatives to high-level CC and EOMCC schemes, which brings us to the next part of this dissertation.

In the second part of this work, we have discussed the $CC(P;Q)$ formalism, beginning with a short summary of the key concepts and equations behind the $CC(P;Q)$ methodology. We proceeded by looking at the CR-CC and CR-EOMCC approaches, which is equivalent to $CC(P;Q)$ where the underlying P and Q spaces are defined by following the traditional truncation schemes defining the cluster and EOM excitation operators. The usefulness of the CR-CC/EOMCC method has been demonstrated by examining the performance of the δ -CR-EOMCC(2,3) triples correction to EOMCCSD in the investigation of the super photo-

base **FR0**-SB. In particular, we have shown that δ -CR-EOMCC(2,3) significantly improves the results obtained from EOMCCSD. Our calculations for **FR0**-SB have also demonstrated that δ -CR-EOMCC(2,3) has been applied to systems with >50 atoms and hundreds of electrons, including solvation effects, resulting in quantitative accuracy relative to experimental data (~ 0.1 – 0.2 eV in terms of excitation energies). We have also examined the $CC(P;Q)$ approaches that rely on active orbitals for defining the P and Q spaces. We also demonstrated the improvement that the resulting $CC(t;3)$ and $CC(q;4)$ schemes, where one corrects CCSDt and CCSDTq energetics for the missing T_3 [$CC(t;3)$] and T_4 [$CC(q;4)$] correlation effects not captured by active orbitals, respectively, offer compared to conventional CR-CC schemes, by returning to the example of Mg_2 , where the results obtained in $CC(t;3)$ and $CC(q;4)$ calculations are shown to faithfully reproduce the parent CCSDT and CCSDTQ data, respectively.

In the third and last part of this dissertation, we discussed the novel way of performing $CC(P;Q)$ computations that results from the merger of the deterministic $CC(P;Q)$ framework with the stochastic CIQMC wave function samplings developed in the Piecuch group. In particular, we have discussed my contribution to the extension of the semi-stochastic $CC(P;Q)$ methodology to excited electronic states, where we targeted EOMCCSDT energetics. The benefit of the semi-stochastic $CC(P;Q)$ scheme for excited state applications were demonstrated using several test cases, including the closed-shell CH^+ ion and the open-shell CH and CNC radicals. In the future, it will be interesting to see how the EOMCC(P) methodology underlying the semi-stochastic $CC(P;Q)$ approaches can be used to compute properties other than energy by constructing the appropriate RDM in the P space. For example, one could also investigate how one-electron properties evolve when the EOMCCSD P space is enriched with subsets of triply excited determinants captured in QMC propagations. To that end, I have derived the equations for the EOMCCSDT 1-RDM and implemented a pilot code for it, which is flexible enough to accept stochastically constructed $T_3^{(MC)}$, $R_{\mu,3}^{(MC)}$, and $L_{\mu,3}^{(MC)}$ amplitudes or their active-space counterparts. The derivation of the EOMCCSDT

1-RDM equations using diagrammatic method, the resulting algebraic expressions, and the spin-integrated equations can be found in the Appendix.

While this dissertation has explored a plethora of $CC(P;Q)$ schemes relying on different ways of defining the P and Q spaces, there exist more avenues that are still being explored. Recent works employing the active-space [77] and QMC-driven [114] $CC(P;Q)$ approaches including up to quadruples excitation have shown promising results in the ground-state case, so it would be interesting to extend them to excited states to converge EOMCCSDTQ energetics. Furthermore, as already mentioned in the Introduction, one could turn to methods belonging to the selected CI category, where one performs a sequence (or sequences) of Hamiltonian diagonalizations in a growing space of Slater determinants, to construct the P space in an automated manner but without the risk of introducing stochasticity into the $CC(P;Q)$ computations. As shown in Ref. [132], the resulting selected-CI-driven $CC(P;Q)$ computations produces energetics with comparable accuracy when compared to the QMC-driven $CC(P;Q)$ analogs in recovering the parent high-level CC energetics. Another appealing aspect of the Hamiltonian diagonalizations in selected CI procedure is their capability of naturally producing state-specific P spaces for use in excited-state $CC(P;Q)$ calculations, and, thus, it will be interesting to see how the results obtained in such computations would compare with those of our current semi-stochastic $CC(P;Q)$ methodology for excited states, which relies on P spaces constructed for the lowest state of a given symmetry. Last, but not least, it would also be interesting to extend the hybrid $CC(P;Q)$ ideas to particle non-conserving approaches, such as the electron-attachment (EA) and ionization-potential (IP) EOMCC formalisms, or their double EA (DEA) and double IP (DIP) counterparts. In these types of approaches, one uses EOM operators that formally add (EA and DEA) or remove (IP and DIP) electron(s) from a closed-shell reference function. These methodologies are well-suited for studying open-shell systems, such as radicals and biradicals, because they produce properly spin- and symmetry-adapted wave functions, unlike the conventional CC/EOMCC calculations performed using open-shell reference functions. Earlier works in

our group have utilized active-space ideas to downselect the higher-rank components of the many-body expansions underlying the EA/IP- and DEA/DIP-EOMCC approaches, obtaining computationally efficient approximations that are capable of faithfully reproducing the results obtained with their parent methods [260, 261, 275–279]. Therefore, it would be interesting to see if one could achieve the same by relying on CIQMC, CCMC, or selected CI to construct the appropriate P space within the particle nonconserving methodologies.

APPENDIX

APPENDIX

DIAGRAMMATIC DERIVATION OF EOMCCSDT 1-BODY REDUCED DENSITY MATRIX

This appendix provides the derivation of the 1-RDM at the CCSDT/EOMCCSDT level of theory. The general formulation for $\gamma_q^{p(\text{CCSDT})}(\mu, \nu)$ is given and specific cases subsequently examined. For simplicity, we refer to both $\gamma_q^{p(\text{CCSDT})}(\mu)$, which describes the density of a state μ , and $\gamma_q^{p(\text{CCSDT})}(\mu, \nu)$, which corresponds to the transition between to states μ and ν , as 1-RDM regardless of the states μ and ν describing the CC bra and ket states, respectively.

We begin the derivation by defining the CCSDT/EOMCCSDT wavefunction, namely,

$$|\Psi_\mu^{(\text{CCSDT})}\rangle = R_\mu^{(\text{CCSDT})} e^{T^{(\text{CCSDT})}} |\Phi\rangle, \quad (\text{A.1})$$

where $T^{(\text{CCSDT})} = T_1 + T_2 + T_3$ and $R_\mu^{(\text{CCSDT})} = r_{\mu,0}\mathbf{1} + R_{\mu,1} + R_{\mu,2} + R_{\mu,3}$ ($R_\mu^{(\text{CCSDT})} = \mathbf{1}$ for the $\mu = 0$ ground-state case). The corresponding left CCSDT/EOMCCSDT wavefunction is defined as

$$\langle \tilde{\Psi}_\mu^{(\text{CCSDT})} | = \langle \Phi | L_\mu^{(\text{CCSDT})} e^{-T^{(\text{CCSDT})}}, \quad (\text{A.2})$$

where $L_\mu^{(\text{CCSDT})} = \delta_{\mu,0}\mathbf{1} + L_{\mu,1} + L_{\mu,2} + L_{\mu,3}$.

We proceed to the definition of the CCSDT/EOMCCSDT 1-RDM. By inserting Eqs. (A.1) and (A.2) into Eq. (2.17), we obtain the following expression:

$$\gamma_q^{p(\text{CCSDT})}(\mu, \nu) = \langle \Phi | L_\mu^{(\text{CCSDT})} \bar{\Gamma}_q^{p(\text{CCSDT})} R_\nu^{(\text{CCSDT})} | \Phi \rangle, \quad (\text{A.3})$$

where $\bar{\Gamma}_q^{p(\text{CCSDT})} = (a^p a_q e^{T^{(\text{CCSDT})}})_C$. Let us begin our derivation by analyzing terms that will contribute to Eq. (A.3). We first focus on expanding the $\bar{\Gamma}_q^{p(\text{CCSDT})}$ in terms of the allowed nonoriented skeletons, which are presented in Fig. A.1. In constructing these diagrams, we consider several factors that simplify the derivation. First, only up to two T vertices may connect to $a^p a_q$. Second, because $\bar{\Gamma}_q^{p(\text{CCSDT})}$ can only contract with $L_\mu^{(\text{CCSDT})}$ from the left-hand side, the $\bar{\Gamma}_q^{p(\text{CCSDT})}$ diagrams can have a maximum of 6 external lines going to the left.

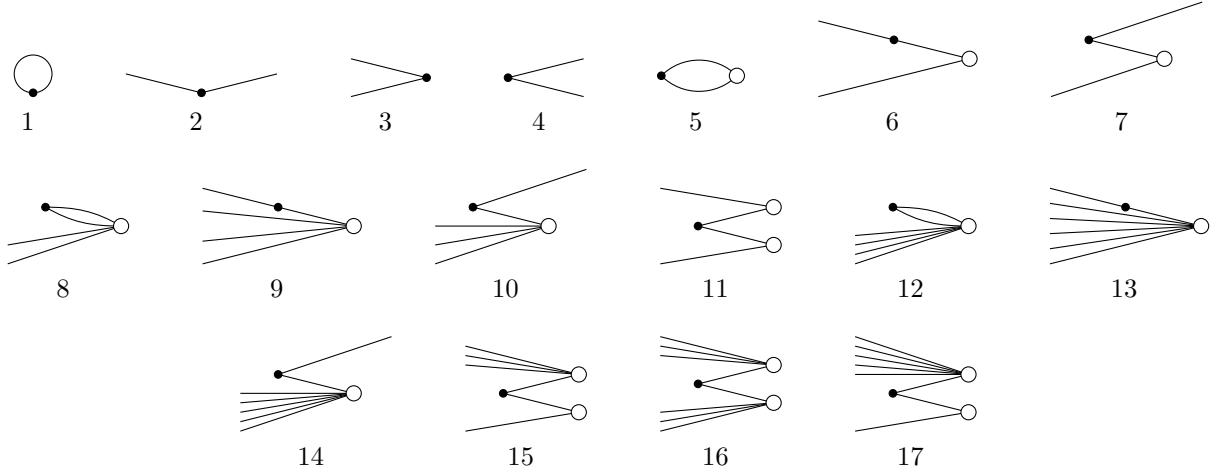


Figure A.1: The 17 nonoriented skeletons of $\bar{\Gamma}_q^{p(\text{CCSDT})}$

At this point, it is useful to start generating oriented skeletons and categorizing them based on the spin orbital type associated with the indices p and q of $\bar{\Gamma}_q^{p(\text{CCSDT})}$. We know *a priori* that the resulting CCSDT 1-RDM is a $(n_o + n_u)$ by $(n_o + n_u)$ matrix and, thus, we can recognize 4 distinct blocks within the matrix, namely, the occupied-occupied (oo), occupied-unoccupied (ou), unoccupied-occupied (uo), and unoccupied-unoccupied (uu) blocks. Based on the orientation of the fermion lines of $a^p a_q$, we can easily construct the oriented versions of the 17 skeletons in Fig. A.1 and categorize them based on the occupancy character of the indices, which are shown in Figs. A.2–A.5.

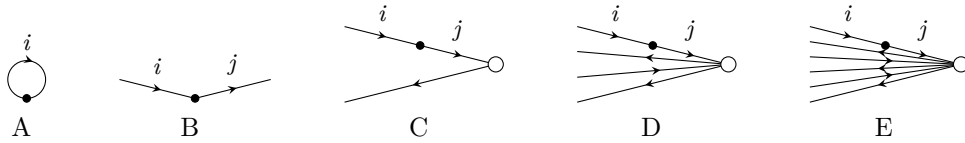


Figure A.2: Oriented skeletons of $\bar{\Gamma}_q^{p(\text{CCSDT})}$ corresponding to the oo block (γ_i^j) , ordered according to increasing many-body rank.

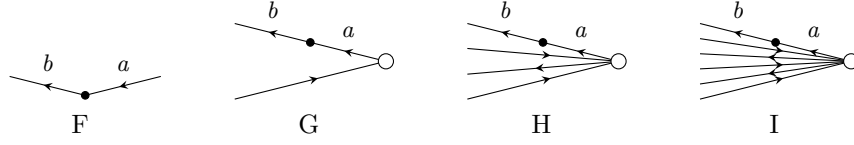


Figure A.3: Oriented skeletons of $\bar{\Gamma}_q^{p(\text{CCSDT})}$ corresponding to the uu block (γ_a^b) , ordered according to increasing many-body rank.

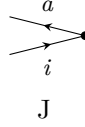


Figure A.4: Oriented skeleton of $\bar{\Gamma}_q^{p(\text{CCSDT})}$ corresponding to the ou block (γ_i^a) .

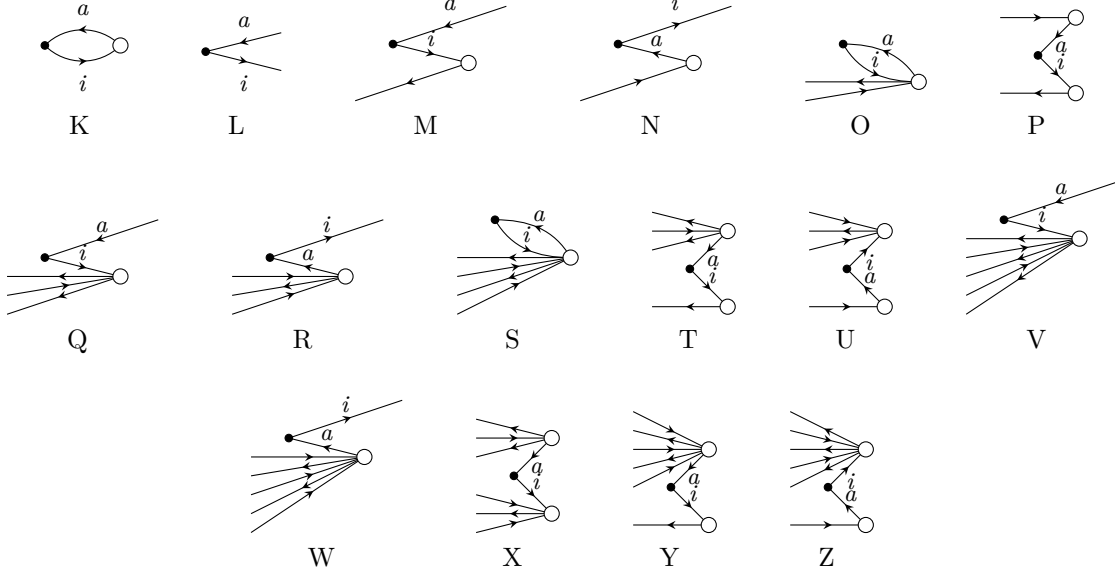


Figure A.5: Oriented skeletons of $\bar{\Gamma}_q^{p(\text{CCSDT})}$ corresponding to the uo block (γ_a^i) , ordered according to increasing many-body rank.

Using the oriented skeletons of $\bar{\Gamma}_q^{p(\text{CCSDT})}$ shown in Figs. A.2–A.5 and relying on the fact that Eq. (A.3) corresponds to fully contracted diagrams, we can now proceed to analyze the ranks of L_μ and R_ν that may form contraction with $\bar{\Gamma}_q^{p(\text{CCSDT})}$. This information is summarized in Table A.1. It is interesting to note that the skeletons labeled as A and K in the oo and uo blocks, respectively, are closed diagrams, *i.e.*, they do not have external fermion lines. Thus, if we examine Eq. (A.3) for these closed diagrams, we end up with terms of the form $\bar{\Gamma}_{q,\text{closed}}^{p(\text{CCSDT})} \langle \Phi | L_\mu^{(\text{CCSDT})} R_\nu^{(\text{CCSDT})} | \Phi \rangle = \bar{\Gamma}_{q,\text{closed}}^{p(\text{CCSDT})} \delta_{\mu\nu}$ in the oo and uo blocks of $\gamma_q^{p(\text{CCSDT})}(\mu, \nu)$.

Table A.1: Blocks of the CCSDT 1-RDM with the corresponding labels from Figs. A.2–A.5, contraction types, and possible ranks of L_μ and R_ν components.

Block	Label	Contraction type	n
oo	A ^a	$L_{\mu,n} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0, 1, 2, 3
	B	$L_{\mu,n} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	1, 2, 3
	C	$L_{\mu,n+1} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0, 1, 2
	D	$L_{\mu,n+2} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0, 1
	E	$L_{\mu,n+3} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0
uu	F	$L_{\mu,n} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	1, 2, 3
	G	$L_{\mu,n+1} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0, 1, 2
	H	$L_{\mu,n+2} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0, 1
	I	$L_{\mu,n+3} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0
ou	J	$L_{\mu,n+1} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0, 1, 2
uo	K ^a	$L_{\mu,n} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0, 1, 2, 3
	L	$L_{\mu,n} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n+1}$	0, 1, 2
	M, N	$L_{\mu,n} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	1, 2, 3
	O, P	$L_{\mu,n+1} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0, 1, 2
	Q, R	$L_{\mu,n+1} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	1, 2
	S, T, U	$L_{\mu,n+2} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0, 1
	V, W	$L_{\mu,n+2} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	1
	X, Y, Z	$L_{\mu,n+3} \bar{\Gamma}_q^{p(\text{CCSDT})} R_{\nu,n}$	0

^aCorresponds to a closed diagram; contraction with L_μ and R_ν will produce $\delta_{\mu\nu}$ (see text).

We have now reached the stage where we can derive $\gamma_q^{p(\text{CCSDT})}(\mu, \nu)$ in the spin orbital

basis. We do so by performing the contractions listed in Table A.1, obtaining

$$\begin{aligned}\gamma_i^{j(\text{CCSDT})}(\mu, \nu) = & \delta_{\mu\nu} \delta_{ij} - (l_{\mu,i}^e t_e^j + \frac{1}{2} l_{\mu,in}^{ef} t_{ef}^{jn} + \frac{1}{12} l_{\mu,ino}^{efg} t_{efg}^{jno}) r_{\nu,0} \\ & - l_{\mu,i}^e r_{\nu,e}^j - \frac{1}{2} l_{\mu,in}^{ef} r_{\nu,ef}^{jn} - \frac{1}{12} l_{\mu,ino}^{efg} r_{\nu,efg}^{jno} \\ & - l_{\mu,in}^{ef} t_e^j r_{\nu,f}^n - \frac{1}{4} l_{\mu,ino}^{efg} t_e^j r_{\nu,fg}^{no} - \frac{1}{2} l_{\mu,ino}^{efg} t_{ef}^{jn} r_{\nu,g}^o,\end{aligned}\tag{A.4}$$

$$\begin{aligned}\gamma_a^{b(\text{CCSDT})}(\mu, \nu) = & (l_{\mu,m}^b t_a^m + \frac{1}{2} l_{\mu,mn}^{bf} t_{af}^{mn} + \frac{1}{12} l_{\mu,mno}^{bfg} t_{afg}^{mno}) r_{\nu,0} \\ & + l_{\mu,m}^b r_{\nu,a}^m + \frac{1}{2} l_{\mu,mn}^{bf} r_{\nu,af}^{mn} + \frac{1}{12} l_{\mu,mno}^{bfg} r_{\nu,afg}^{mno} \\ & + l_{\mu,mn}^{bf} t_a^m r_{\nu,f}^n + \frac{1}{4} l_{\mu,mno}^{bfg} t_a^m r_{\nu,fg}^{no} + \frac{1}{2} l_{\mu,mno}^{bfg} t_{af}^{mn} r_{\nu,g}^o,\end{aligned}\tag{A.5}$$

$$\gamma_i^{a(\text{CCSDT})}(\mu, \nu) = l_{\mu,i}^a r_{\nu,0} + l_{\mu,in}^{ef} r_{\nu,f}^n + \frac{1}{4} l_{\mu,ino}^{efg} r_{\nu,fg}^{no},\tag{A.6}$$

and

$$\begin{aligned}\gamma_a^{i(\text{CCSDT})}(\mu, \nu) = & \delta_{\mu\nu} t_a^i + (l_{\mu,m}^e t_{ae}^{im} - l_{\mu,m}^e t_e^i t_a^m + \frac{1}{4} l_{\mu,mn}^{ef} t_{aef}^{imn} \\ & - \frac{1}{2} l_{\mu,mn}^{ef} t_{af}^{mn} t_e^i - \frac{1}{2} l_{\mu,mn}^{ef} t_{ef}^{in} t_a^m - \frac{1}{4} l_{\mu,mno}^{efg} t_{ag}^{mo} t_{ef}^{in} \\ & - \frac{1}{12} l_{\mu,mno}^{efg} t_{afg}^{mno} t_e^i - \frac{1}{12} l_{\mu,mno}^{efg} t_{efg}^{ino} t_a^m) r_{\nu,0} \\ & + \delta_{\mu 0} r_{\nu,a}^i + l_{\mu,n}^f r_{\nu,af}^{in} + \frac{1}{4} l_{\mu,no}^{fg} r_{\nu,afg}^{ino} - l_{\mu,m}^e t_e^i r_{\nu,a}^m \\ & - l_{\mu,m}^e t_a^m r_{\nu,e}^i - \frac{1}{2} l_{\mu,mn}^{ef} t_e^i r_{\nu,af}^{mn} - \frac{1}{2} l_{\mu,mn}^{ef} t_a^m r_{\nu,ef}^{in} \\ & - \frac{1}{12} l_{\mu,mno}^{efg} t_e^i r_{\nu,afg}^{mno} - \frac{1}{12} l_{\mu,mno}^{efg} t_a^m r_{\nu,efg}^{ino} + l_{\mu,mn}^{ef} t_{ae}^{im} r_{\nu,f}^n \\ & + \frac{1}{4} l_{\mu,mno}^{efg} t_{ae}^{im} r_{\nu,fg}^{no} - l_{\mu,mn}^{ef} t_e^i t_a^m r_{\nu,f}^n - \frac{1}{4} l_{\mu,mno}^{efg} t_e^i t_a^m r_{\nu,fg}^{no} \\ & - \frac{1}{2} l_{\mu,mn}^{ef} t_{ef}^{in} r_{\nu,a}^m - \frac{1}{2} l_{\mu,mn}^{ef} t_{af}^{mn} r_{\nu,e}^i - \frac{1}{4} l_{\mu,mno}^{efg} t_{ef}^{in} r_{\nu,ag}^{mo} \\ & - \frac{1}{4} l_{\mu,mno}^{efg} t_{af}^{mn} r_{\nu,eg}^{io} + \frac{1}{4} l_{\mu,mno}^{efg} t_{aef}^{imn} r_{\nu,g}^o - \frac{1}{2} l_{\mu,mno}^{efg} t_{af}^{mn} t_e^i r_{\nu,g}^o \\ & - \frac{1}{2} l_{\mu,mno}^{efg} t_{ef}^{in} t_a^m r_{\nu,g}^o - \frac{1}{12} l_{\mu,mno}^{efg} t_{efg}^{ino} r_{\nu,a}^m - \frac{1}{12} l_{\mu,mno}^{efg} t_{afg}^{mno} r_{\nu,e}^i.\end{aligned}\tag{A.7}$$

In writing the above expressions for $\gamma_q^{p(\text{CCSDT})}(\mu, \nu)$, we follow the convention for spin orbitals explained in Section 2.1 when dealing with fixed labels. In the case of free labels, we use $m, n, o, \dots$ and $e, f, g, \dots$ to indicate occupied and unoccupied spin orbitals, respectively.

One can do an extra step by performing spin integration to obtain the 1-RDM in the molecular orbital basis, $\gamma_Q^{P(\text{CCSDT})}(\mu, \nu)$, where we use capital letters to label spin orbitals following the convention described above, and molecular orbitals that correspond to the β electron spin are labeled with a tilde. Thus, we obtain, for the α spin case,

$$\begin{aligned}
\gamma_I^{J(\text{CCSDT})}(\mu, \nu) = & \delta_{\mu\nu} \delta_{IJ} - (l_{\mu,I}^E t_E^J + \frac{1}{2} l_{\mu,IN}^{EF} t_{EF}^{JN} + l_{\mu,IN}^{E\tilde{F}} t_{E\tilde{F}}^{J\tilde{N}} \\
& + \frac{1}{12} l_{\mu,INO}^{EFG} t_{EFG}^{JNO} + \frac{1}{2} l_{\mu,IN\tilde{O}}^{EFG\tilde{G}} t_{EFG\tilde{G}}^{JN\tilde{O}} + \frac{1}{4} l_{\mu,IN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{E\tilde{F}\tilde{G}}^{J\tilde{N}\tilde{O}}) r_{\nu,0} \\
& - l_{\mu,I}^E r_{\nu,E}^J - \frac{1}{2} l_{\mu,IN}^{EF} r_{\nu,EF}^{JN} - l_{\mu,IN}^{E\tilde{F}} r_{\nu,E\tilde{F}}^{J\tilde{N}} \\
& - \frac{1}{12} l_{\mu,INO}^{EFG} r_{\nu,EFG}^{JNO} - \frac{1}{2} l_{\mu,IN\tilde{O}}^{EFG\tilde{G}} r_{\nu,EFG\tilde{G}}^{JN\tilde{O}} - \frac{1}{4} l_{\mu,IN\tilde{O}}^{E\tilde{F}\tilde{G}} r_{\nu,E\tilde{F}\tilde{G}}^{J\tilde{N}\tilde{O}} \\
& - l_{\mu,IN}^{EF} t_E^J r_{\nu,F}^N - l_{\mu,IN}^{E\tilde{F}} t_E^J r_{\nu,\tilde{F}}^{\tilde{N}} - \frac{1}{4} l_{\mu,INO}^{EFG} t_E^J r_{\nu,FG}^{NO} \\
& - l_{\mu,IN\tilde{O}}^{EFG\tilde{G}} t_E^J r_{\nu,F\tilde{G}}^{N\tilde{O}} - \frac{1}{4} l_{\mu,IN\tilde{O}}^{E\tilde{F}\tilde{G}} t_E^J r_{\nu,\tilde{F}\tilde{G}}^{\tilde{N}\tilde{O}} - \frac{1}{2} l_{\mu,INO}^{EFG} t_{EF}^{JN} r_{\nu,G}^O \\
& - \frac{1}{2} l_{\mu,IN\tilde{O}}^{EFG\tilde{G}} t_{EF}^{JN} r_{\nu,\tilde{G}}^{\tilde{O}} - l_{\mu,IN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{E\tilde{F}}^{J\tilde{N}} r_{\nu,G}^O - l_{\mu,IN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{E\tilde{F}}^{J\tilde{N}} r_{\nu,\tilde{G}}^{\tilde{O}},
\end{aligned} \tag{A.8}$$

$$\begin{aligned}
\gamma_A^{B(\text{CCSDT})}(\mu, \nu) = & (l_{\mu,M}^B t_A^M + \frac{1}{2} l_{\mu,MN}^{BF} t_{AF}^{MN} + l_{\mu,M\tilde{N}}^{B\tilde{F}} t_{A\tilde{F}}^{M\tilde{N}} \\
& + \frac{1}{12} l_{\mu,MNO}^{BFG} t_{AFG}^{MNO} + \frac{1}{2} l_{\mu,MN\tilde{O}}^{BFG\tilde{G}} t_{AF\tilde{G}}^{MN\tilde{O}} + \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{B\tilde{F}\tilde{G}} t_{A\tilde{F}\tilde{G}}^{M\tilde{N}\tilde{O}}) r_{\nu,0} \\
& + l_{\mu,M}^B r_{\nu,A}^M + \frac{1}{2} l_{\mu,MN}^{BF} r_{\nu,AF}^{MN} + l_{\mu,M\tilde{N}}^{B\tilde{F}} r_{\nu,A\tilde{F}}^{M\tilde{N}} \\
& + \frac{1}{12} l_{\mu,MNO}^{BFG} r_{\nu,AFG}^{MNO} + \frac{1}{2} l_{\mu,MN\tilde{O}}^{BFG\tilde{G}} r_{\nu,AF\tilde{G}}^{MN\tilde{O}} + \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{B\tilde{F}\tilde{G}} r_{\nu,A\tilde{F}\tilde{G}}^{M\tilde{N}\tilde{O}} \\
& + l_{\mu,MN}^{BF} t_A^M r_{\nu,F}^N + l_{\mu,M\tilde{N}}^{B\tilde{F}} t_A^M r_{\nu,\tilde{F}}^{\tilde{N}} + \frac{1}{4} l_{\mu,MNO}^{BFG} t_A^M r_{\nu,FG}^{NO} \\
& + l_{\mu,MN\tilde{O}}^{BFG\tilde{G}} t_A^M r_{\nu,F\tilde{G}}^{N\tilde{O}} + \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{B\tilde{F}\tilde{G}} t_A^M r_{\nu,\tilde{F}\tilde{G}}^{\tilde{N}\tilde{O}} + \frac{1}{2} l_{\mu,MNO}^{BFG} t_{AF}^{MN} r_{\nu,G}^O \\
& + \frac{1}{2} l_{\mu,MN\tilde{O}}^{BFG\tilde{G}} t_{AF}^{MN} r_{\nu,\tilde{G}}^{\tilde{O}} + l_{\mu,M\tilde{N}\tilde{O}}^{B\tilde{F}\tilde{G}} t_{A\tilde{F}}^{M\tilde{N}} r_{\nu,G}^O + l_{\mu,M\tilde{N}\tilde{O}}^{B\tilde{F}\tilde{G}} t_{A\tilde{F}}^{M\tilde{N}} r_{\nu,\tilde{G}}^{\tilde{O}},
\end{aligned} \tag{A.9}$$

$$\begin{aligned}
\gamma_I^{A(\text{CCSDT})}(\mu, \nu) = & l_{\mu,I}^A r_{\nu,0} + l_{\mu,IN}^{AF} r_{\nu,F}^N + l_{\mu,IN}^{A\tilde{F}} r_{\nu,\tilde{F}}^{\tilde{N}} \\
& + \frac{1}{4} l_{\mu,INO}^{AFG} r_{\nu,FG}^{NO} + l_{\mu,IN\tilde{O}}^{AF\tilde{G}} r_{\nu,F\tilde{G}}^{N\tilde{O}} + \frac{1}{4} l_{\mu,IN\tilde{O}}^{A\tilde{F}\tilde{G}} r_{\nu,\tilde{F}\tilde{G}}^{\tilde{N}\tilde{O}},
\end{aligned} \tag{A.10}$$

and

$$\begin{aligned}
\gamma_A^{I(\text{CCSDT})}(\mu, \nu) = & \delta_{\mu\nu} t_A^I + (l_{\mu,M}^E t_{AE}^{IM} + l_{\mu,\tilde{M}}^{\tilde{E}} t_{A\tilde{E}}^{I\tilde{M}} - l_{\mu,M}^E t_{EA}^I t_A^M \\
& + \frac{1}{4} l_{\mu,MN}^{EF} t_{AEF}^{IMN} + l_{\mu,M\tilde{N}}^{E\tilde{F}} t_{A\tilde{E}\tilde{F}}^{I\tilde{M}\tilde{N}} + \frac{1}{4} l_{\mu,\tilde{M}\tilde{N}}^{\tilde{E}\tilde{F}} t_{A\tilde{E}\tilde{F}}^{I\tilde{M}\tilde{N}} \\
& - \frac{1}{2} l_{\mu,MN}^{EF} t_{AF}^{MN} t_E^I - l_{\mu,M\tilde{N}}^{E\tilde{F}} t_{A\tilde{F}}^{M\tilde{N}} t_E^I - \frac{1}{2} l_{\mu,MN}^{EF} t_{EF}^{IN} t_A^M \\
& - l_{\mu,M\tilde{N}}^{E\tilde{F}} t_{E\tilde{F}}^{I\tilde{N}} t_A^M - \frac{1}{4} l_{\mu,MNO}^{EFG} t_{AG}^{MO} t_{EF}^{IN} - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{A\tilde{G}}^{M\tilde{O}} t_{EF}^{IN} \\
& - \frac{1}{2} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{AG}^{MO} t_{E\tilde{F}}^{I\tilde{N}} - l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{A\tilde{G}}^{M\tilde{O}} t_{E\tilde{F}}^{I\tilde{N}} - \frac{1}{12} l_{\mu,MNO}^{EFG} t_{AFG}^{MNO} t_E^I \\
& - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{AF\tilde{G}}^{MN\tilde{O}} t_E^I - \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{A\tilde{F}\tilde{G}}^{M\tilde{N}\tilde{O}} t_E^I - \frac{1}{12} l_{\mu,MNO}^{EFG} t_{EFG}^{INO} t_A^M \\
& - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{E\tilde{F}\tilde{G}}^{IN\tilde{O}} t_A^M - \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{E\tilde{F}\tilde{G}}^{I\tilde{N}\tilde{O}} t_A^M) r_{\nu,0} \\
& + \delta_{\mu 0} r_{\nu,A}^I + l_{\mu,N}^F r_{\nu,AF}^{IN} + l_{\mu,\tilde{N}}^{\tilde{F}} r_{\nu,A\tilde{F}}^{I\tilde{N}} + \frac{1}{4} l_{\mu,NO}^{FG} r_{\nu,AFG}^{INO} + l_{\mu,N\tilde{O}}^{F\tilde{G}} r_{\nu,AF\tilde{G}}^{IN\tilde{O}} + \frac{1}{4} l_{\mu,\tilde{N}\tilde{O}}^{\tilde{F}\tilde{G}} r_{\nu,A\tilde{F}\tilde{G}}^{I\tilde{N}\tilde{O}} \\
& - l_{\mu,M}^E t_{EA}^I r_{\nu,A}^M - l_{\mu,M}^E t_A^M r_{\nu,E}^I - \frac{1}{2} l_{\mu,MN}^{EF} t_{EA}^I r_{\nu,AF}^{MN} \\
& - l_{\mu,M\tilde{N}}^{E\tilde{F}} t_{EA}^I r_{\nu,A\tilde{F}}^{M\tilde{N}} - \frac{1}{2} l_{\mu,MN}^{EF} t_A^M r_{\nu,EF}^{IN} - l_{\mu,M\tilde{N}}^{E\tilde{F}} t_A^M r_{\nu,E\tilde{F}}^{I\tilde{N}} \\
& - \frac{1}{12} l_{\mu,MNO}^{EFG} t_{EA}^I r_{\nu,AFG}^{MNO} - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{EA}^I r_{\nu,AF\tilde{G}}^{MN\tilde{O}} - \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{EA}^I r_{\nu,A\tilde{F}\tilde{G}}^{M\tilde{N}\tilde{O}} \\
& - \frac{1}{12} l_{\mu,MNO}^{EFG} t_A^M r_{\nu,EFG}^{INO} - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_A^M r_{\nu,E\tilde{F}\tilde{G}}^{IN\tilde{O}} - \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_A^M r_{\nu,E\tilde{F}\tilde{G}}^{I\tilde{N}\tilde{O}} \\
& + l_{\mu,MN}^{EF} t_{AE}^{IM} r_{\nu,F}^N + l_{\mu,M\tilde{N}}^{E\tilde{F}} t_{AE}^{IM} r_{\nu,\tilde{F}}^{\tilde{N}} + l_{\mu,\tilde{M}\tilde{N}}^{\tilde{E}\tilde{F}} t_{A\tilde{E}}^{I\tilde{M}} r_{\nu,F}^N + l_{\mu,\tilde{M}\tilde{N}}^{\tilde{E}\tilde{F}} t_{A\tilde{E}}^{I\tilde{M}} r_{\nu,\tilde{F}}^{\tilde{N}} \\
& + \frac{1}{4} l_{\mu,MNO}^{EFG} t_{AE}^{IM} r_{\nu,FG}^{NO} + \frac{1}{4} l_{\mu,\tilde{M}\tilde{N}\tilde{O}}^{\tilde{E}\tilde{F}\tilde{G}} t_{A\tilde{E}}^{I\tilde{M}} r_{\nu,FG}^{N\tilde{O}} + l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{AE}^{IM} r_{\nu,\tilde{F}\tilde{G}}^{N\tilde{O}} \\
& + \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{AE}^{IM} r_{\nu,\tilde{F}\tilde{G}}^{\tilde{N}\tilde{O}} + l_{\mu,\tilde{M}\tilde{N}\tilde{O}}^{\tilde{E}\tilde{F}\tilde{G}} t_{A\tilde{E}}^{I\tilde{M}} r_{\nu,\tilde{F}\tilde{G}}^{\tilde{N}\tilde{O}} + \frac{1}{4} l_{\mu,\tilde{M}\tilde{N}\tilde{O}}^{\tilde{E}\tilde{F}\tilde{G}} t_{A\tilde{E}}^{I\tilde{M}} r_{\nu,\tilde{F}\tilde{G}}^{\tilde{N}\tilde{O}} \\
& - l_{\mu,MN}^{EF} t_{EA}^I t_A^M r_{\nu,F}^N - l_{\mu,M\tilde{N}}^{E\tilde{F}} t_{EA}^I t_A^M r_{\nu,\tilde{F}}^{\tilde{N}} \\
& - \frac{1}{4} l_{\mu,MNO}^{EFG} t_{EA}^I t_A^M r_{\nu,FG}^{NO} - l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{EA}^I t_A^M r_{\nu,\tilde{F}\tilde{G}}^{N\tilde{O}} - \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{EA}^I t_A^M r_{\nu,\tilde{F}\tilde{G}}^{\tilde{N}\tilde{O}} \\
& - \frac{1}{2} l_{\mu,MN}^{EF} t_{EF}^{IN} r_{\nu,A}^M - l_{\mu,M\tilde{N}}^{E\tilde{F}} t_{E\tilde{F}}^{I\tilde{N}} r_{\nu,A}^M - \frac{1}{2} l_{\mu,MN}^{EF} t_{AF}^{MN} r_{\nu,E}^I - l_{\mu,M\tilde{N}}^{E\tilde{F}} t_{A\tilde{F}}^{M\tilde{N}} r_{\nu,E}^I \\
& - \frac{1}{4} l_{\mu,MNO}^{EFG} t_{EF}^{IN} r_{\nu,AG}^{MO} - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{EF}^{IN} r_{\nu,AG}^{M\tilde{O}} - \frac{1}{2} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{E\tilde{F}}^{I\tilde{N}} r_{\nu,AG}^{M\tilde{O}} - l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{E\tilde{F}}^{I\tilde{N}} r_{\nu,AG}^{M\tilde{O}} \\
& - \frac{1}{4} l_{\mu,MNO}^{EFG} t_{AF}^{MN} r_{\nu,EG}^{IO} - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{AF}^{MN} r_{\nu,E\tilde{G}}^{I\tilde{O}} - \frac{1}{2} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{A\tilde{F}}^{M\tilde{N}} r_{\nu,EG}^{IO} - l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{A\tilde{F}}^{M\tilde{N}} r_{\nu,E\tilde{G}}^{I\tilde{O}} \\
& + \frac{1}{4} l_{\mu,MNO}^{EFG} t_{AEF}^{IMN} r_{\nu,G}^O + \frac{1}{4} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{AEF}^{IMN} r_{\nu,\tilde{G}}^{\tilde{O}} + l_{\mu,\tilde{M}\tilde{N}\tilde{O}}^{\tilde{E}\tilde{F}\tilde{G}} t_{A\tilde{E}\tilde{F}}^{I\tilde{M}\tilde{N}} r_{\nu,G}^O \\
& + l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{A\tilde{E}\tilde{F}}^{I\tilde{M}\tilde{N}} r_{\nu,\tilde{G}}^{\tilde{O}} + \frac{1}{4} l_{\mu,\tilde{M}\tilde{N}\tilde{O}}^{\tilde{E}\tilde{F}\tilde{G}} t_{A\tilde{E}\tilde{F}}^{I\tilde{M}\tilde{N}} r_{\nu,G}^O + \frac{1}{4} l_{\mu,\tilde{M}\tilde{N}\tilde{O}}^{\tilde{E}\tilde{F}\tilde{G}} t_{A\tilde{E}\tilde{F}}^{I\tilde{M}\tilde{N}} r_{\nu,\tilde{G}}^{\tilde{O}} \\
& - \frac{1}{2} l_{\mu,MNO}^{EFG} t_{AF}^{MN} t_{EA}^I r_{\nu,G}^O - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{AF}^{MN} t_{EA}^I r_{\nu,\tilde{G}}^{\tilde{O}} - l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{A\tilde{F}}^{M\tilde{N}} t_{EA}^I r_{\nu,G}^O - l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{A\tilde{F}}^{M\tilde{N}} t_{EA}^I r_{\nu,\tilde{G}}^{\tilde{O}} \\
& - \frac{1}{2} l_{\mu,MNO}^{EFG} t_{EF}^{IN} t_A^M r_{\nu,G}^O - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{EF}^{IN} t_A^M r_{\nu,\tilde{G}}^{\tilde{O}} - l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{E\tilde{F}}^{I\tilde{N}} t_A^M r_{\nu,G}^O - l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{E\tilde{F}}^{I\tilde{N}} t_A^M r_{\nu,\tilde{G}}^{\tilde{O}} \\
& - \frac{1}{12} l_{\mu,MNO}^{EFG} t_{EFG}^{INO} r_{\nu,A}^M - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{EFG}^{IN\tilde{O}} r_{\nu,A}^M - \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{EFG}^{I\tilde{N}\tilde{O}} r_{\nu,A}^M \\
& - \frac{1}{12} l_{\mu,MNO}^{EFG} t_{AFG}^{MNO} r_{\nu,E}^I - \frac{1}{2} l_{\mu,MN\tilde{O}}^{E\tilde{F}\tilde{G}} t_{AF\tilde{G}}^{MN\tilde{O}} r_{\nu,E}^I - \frac{1}{4} l_{\mu,M\tilde{N}\tilde{O}}^{E\tilde{F}\tilde{G}} t_{A\tilde{F}\tilde{G}}^{M\tilde{N}\tilde{O}} r_{\nu,E}^I.
\end{aligned}$$

(A.11)

The β counterparts of Eqs. (A.8)–(A.11), namely, $\gamma_{\tilde{Q}}^{\tilde{P}(\text{CCSDT})}(\mu, \nu)$, can be obtained by simply flipping the spins in each orbital in Eqs. (A.8)–(A.11). The CCSDT 1-RDM in the molecular orbital basis has been implemented in a pilot code, written in Python. The correctness of the code was checked numerically by performing CCSDT calculations for three-electron systems and comparing the resulting 1-RDMs, natural orbitals, and computed one-electron properties with those obtained in FCI computations.

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