

# Bridging quantum chemistry and nuclear physics: Coupled-cluster calculations for closed- and open-shell nuclei

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**Abstract.** We review basic elements of the single-reference coupled-cluster theory and discuss large scale *ab initio* calculations of ground and excited states of  $^{15}\text{O}$ ,  $^{16}\text{O}$ , and  $^{17}\text{O}$  using coupled-cluster methods and algorithms developed in quantum chemistry. By using realistic two-body interactions and the renormalized form of the Hamiltonian obtained with a no-core G-matrix approach, we obtain the converged results for  $^{16}\text{O}$  and promising results for  $^{15}\text{O}$  and  $^{17}\text{O}$  at the level of two-body interactions. The calculated properties other than energies include matter density, charge radius, and charge form factor. The relatively low costs of coupled-cluster calculations, which are characterized by the low-order polynomial scaling with the system size, enable us to probe large model spaces with up to 7 or 8 major oscillator shells, for which non-truncated shell-model calculations for nuclei with  $A = 15 - 17$  active particles are presently not possible. We argue that the use of coupled-cluster methods and computer algorithms developed by quantum chemists to calculate properties of nuclei is an important step toward the development of accurate and affordable many-body theories that cross the boundaries of various physical sciences.

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## 1. INTRODUCTION

One of the most powerful microscopic approaches to quantum many-body systems, which provides a highly accurate and usually rigorously size extensive description of many-particle correlation effects at the relatively low computer cost, is coupled-cluster theory [1]. This can be best illustrated by spectacular successes of coupled-cluster methods in chemistry and molecular physics. After the introduction of the exponential wave function ansatz defining coupled-cluster approaches and diagrammatic methods of many-body theory into quantum chemistry by Čížek [2] and after the pioneering studies of various formal and practical aspects of coupled-cluster theory in the context of molecular applications by Čížek, Paldus, and their collaborators, which was followed by the development of general-purpose coupled-cluster computer codes, primarily by Bartlett's, Pople's, and Schaefer's groups (see, e.g., [3] for historical remarks), coupled-cluster methods have assumed the prominent position in quantum chemistry, enjoying tremendous success over a broad range of problems related to molecular structure, properties, and reactivity. A large variety of accurate and yet affordable coupled-cluster methods have been developed for closed-shell, open-shell, nondegenerate, and quasidegenerate ground and excited states of many-electron systems [4]. In consequence, coupled-cluster approaches are nowadays routinely applied to molecular systems containing dozens of light atoms, several transition metal atoms, hundreds of electrons, and thousands of single-particle basis functions (see, e.g., [5]). Coupled-cluster methods are often regarded as predictive approaches which can successfully guide experimental effort or be used to resolve significant controversies in important experimental studies (cf., e.g., citehnoo). Most remarkably, many coupled-cluster methods are nowadays available in the popular quantum chemistry software packages, such as, for example, ACES [6], GAMESS [7], GAUSSIAN [8], and MOLPRO [9], enabling predictive *ab initio* calculations of various molecular properties by experts as well as non-experts (the success and significance of these general-purpose electronic structure packages resulted in the 1998 Nobel Prize in Chemistry, awarded to Professors J.A. Pople and W. Kohn). As all many-body methods, coupled-cluster methods have their own grand challenges, particularly when ground and excited states of interest cannot be easily obtained by particle-hole ( $p-h$ ) excitations from a single Fermi vacuum (examples of these challenges in chemistry are bond breaking or ground and excited states of radical and

biradical species [1]), but remarkable progress has already been made toward the development of the so-called multi-reference coupled-cluster techniques [2], which use multi-dimensional model spaces or multiple Fermi vacua in the design of correlated many-particle states, enabling accurate studies of bond breaking, open-shell molecular species, and all kinds of ground and excited states involving significant quasi-degeneracy effects, increasing the applicability of coupled-cluster methods to a wide range of problems involving many-electron systems (cf., e.g., [3–5] for selected recent examples).

We strongly believe that other fields of many-body theory, including, among others, nuclear physics may significantly benefit from the vast experience in the development of accurate and computationally efficient coupled-cluster approximations and algorithms by quantum chemists. Indeed, one of the grand challenges of modern nuclear theory is to understand how various properties, such as masses, excitation spectra, and life-times of quasi-bound nuclei arise from the underlying nucleon-nucleon interactions. While significant progress has been made in the development of the Green's Function Monte Carlo [6] and no-core shell model [7] techniques, which have produced converged results for nuclei with up to  $A = 12$  active particles, the applicability of these methods is limited to light nuclei. Given that present nuclear structure research facilities and the proposed Rare Isotope Accelerator will continue to provide increasingly precise information about properties of medium-mass and heavier nuclei, it becomes absolutely critical to examine alternative approaches to the nuclear many-body problem that do not suffer from the exponential growth of computer costs with the system size characterizing the existing quantum Monte Carlo and shell model approaches. As in chemistry and molecular physics, nuclear science would tremendously benefit from having access to fully microscopic, general purpose *ab initio* many-body methods and highly efficient computer codes that could routinely be applied to medium size and heavier systems in the  $A = 20 - 100$  region. Clearly, it would be most remarkable if *ab initio* nuclear structure methods based on underlying nucleon-nucleon interactions became as predictive as various electronic structure methods used by thousands of chemists. Precise description of many-particle correlation effects would also enable us to considerably improve our understanding of nucleon-nucleon interactions, which is another grand challenge for the nuclear many-body theory. In our view, coupled-cluster methods pioneered by Coester and Kümmel in physics and Čížek and Paldus in chemistry, which we discuss in this paper, are among the most promising candidates for such endeavors due to their ability to provide precise description of many-particle correlation effects at the relatively low computer cost when compared to shell-model or configuration interaction techniques aimed at similar accuracies, as has been demonstrated over and over again in numerous chemistry applications (see, e.g., [8–10] for reviews).

Historically, coupled-cluster theory originated in nuclear physics [11], but its applications to the nuclear many-body problem have been relatively rare (see, e.g., [12]), particularly when we compare them to quantum chemistry. Part of the problem has been an inadequate understanding of nucleon-nucleon interactions and lack of adequate computer resources in the 70s and 80s. However, construction of realistic nucleon-nucleon potentials and spectacular improvements in computer technology in recent years have caused that there has been renewed interest in applying coupled-cluster methods in nuclear physics. Recent coupled-cluster calculations for light nuclei, using modern nucleon-nucleon interactions and approximations similar to those used by quantum chemists, have demonstrated that perhaps one may be able to overcome the computational bottlenecks posed by the prohibitive costs of the shell-model and Monte Carlo calculations. In particular, using bare interactions, Mihaila and Heisenberg performed coupled-cluster calculations for the binding energy and the electron scattering form factor of  $^{16}\text{O}$  [13–15]. We have taken an alternative route and combined a few basic coupled-cluster techniques developed in the context of electronic structure studies with the renormalized form of the Hamiltonian to determine ground and excited states of  $^4\text{He}$  and ground-state energies of  $^{16}\text{O}$  in a small model space consisting of 4 major oscillator shells, demonstrating highly promising results when compared with the results of the exact shell-model diagonalization in the same model space [16]. More recently, we have extended these studies to ground- and excited-state energies and selected properties of  $^{16}\text{O}$  using much larger single-particle basis sets including 7 or even 8 major oscillator shells [17] and started exploring ground and excited states of open-shell nuclei, such as  $^{15}\text{O}$  and  $^{17}\text{O}$  [18]. The fact that we could go from small-scale benchmark calculations involving 4 major oscillator shells (80 single-particle states only) to large-scale calculations involving 7 or 8 major oscillator shells consisting of 336 or 480 single-particle states has been greatly facilitated by the use of the elegant diagram factorization techniques developed by quantum chemists that lead to almost perfectly vectorized computer codes [19–21] and by the development of parallel coupled-cluster codes [22]. It should be emphasized that although we are still in the early stages of developing a library of efficient coupled-cluster programs for nuclear structure applications, there are already several differences between our approach to nuclear coupled-cluster calculations and the approach pursued by Mihaila and Heisenberg [13–15]. First of all, Mihaila and Heisenberg use bare interactions, making the convergence with the number of single-particle basis states very slow, whereas we use the renormalized form of the Hamiltonian exploiting a no-core G-matrix theory [23], which leads to a rapid convergence of binding and excitation energies and other

nuclear properties with the number of major oscillator shells in a basis. Second, we are able to calculate ground and excited states of open-shell nuclei. Finally, as already mentioned above, our coupled-cluster computer codes have been developed using diagram factorization techniques, which minimize the operation count, rather than the commutator expansions used by Mihaila and Heisenberg and the Bochum school. The coding style adopted by us is similar to that practiced by the developers of coupled-cluster methods in chemistry. In particular, we focus on the general-purpose character of our codes, meaning that the only essential input variables are the number of particles and matrix elements of the Hamiltonian in some single-particle basis set.

The purpose of the present paper is to highlight the results of our recent large-scale coupled-cluster calculations of ground- and excited-state energies and selected properties of  $^{16}\text{O}$  [?] and describe preliminary coupled-cluster calculations for two open-shell nuclei,  $^{15}\text{O}$  and  $^{17}\text{O}$ . We also discuss the basic elements of our coupled-cluster machinery, which we will continue to develop in months and perhaps years to come. Our ultimate goal is to develop a system of general-purpose computer codes that can perform all kinds of accurate coupled-cluster calculations for nuclei in the mass 20–100 region.

## 2. BASIC ELEMENTS OF COUPLED-CLUSTER THEORY AND THE MOST ESSENTIAL COMPUTATIONAL DETAILS

In general, all coupled-cluster methods classify as either the single-reference approaches or multi-reference methods (see, e.g., [? ? ? ?]). In our nuclear structure calculations to date, we have focused on single-reference coupled-cluster methods, in which the correlated wave functions of the  $A$ -body system are constructed via particle–hole ( $p-h$ ) excitations from a single determinant. Thus, we begin this section by discussing basic elements of single-reference coupled-cluster theory. Selected computational details, such as the form of the effective Hamiltonian used in our coupled-cluster calculations, are discussed in Section 2.2.

### 2.1. Single-reference coupled-cluster theory

The single-reference coupled-cluster theory is based on the exponential ansatz for the ground-state wave function,

$$|\Psi_0\rangle = |\Psi_0^{(\text{CC})}\rangle \equiv e^T |\Phi\rangle, \quad (1)$$

where  $T$  is the cluster operator (a  $p-h$  excitation operator) and  $|\Phi\rangle$  is the reference determinant obtained by performing some mean-field calculation or by simply filling the lowest-energy single-particle states (this is what we have done in the calculations discussed in this paper). In all standard coupled-cluster approximations, we truncate the many-body expansion for the cluster operator  $T$  at a given  $p-h$  excitation level  $M < A$ , where  $A$  is the number of correlated particles in a system (in our calculations for the isotopes of oxygen, all particles were correlated). An example of the standard coupled-cluster method is the CCSD approach [?]. In this case,  $M = 2$  and the cluster operator  $T$  is approximated by

$$T^{(\text{CCSD})} \equiv T^{(2)} = T_1 + T_2, \quad (2)$$

where

$$T_1 = t_a^i a^a a_i \quad (3)$$

and

$$T_2 = \frac{1}{4} t_{ab}^{ij} a^a a^b a_j a_i \quad (4)$$

are  $1p-1h$  or singly excited and  $2p-2h$  or doubly excited cluster components,  $t_a^i$  and  $t_{ab}^{ij}$  are the corresponding singly and doubly excited cluster amplitudes,  $i, j, \dots$  ( $a, b, \dots$ ) are the single-particle states (orbitals) occupied (unoccupied) in the reference determinant  $|\Phi\rangle$ , and  $a^p$  ( $a_p$ ) are the usual creation (annihilation) operators associated with the orthonormal orbitals  $|p\rangle$ . Here and elsewhere in the present paper, we use the Einstein summation convention over repeated upper and lower indices, so that the summation symbols corresponding to unrestricted summations over occupied (hole) and/or unoccupied (particle) are omitted. The general form of the truncated cluster operator defining a standard coupled-cluster approximation characterized by the excitation level  $M$ , is

$$T^{(M)} = \sum_{n=1}^M T_n, \quad (5)$$

where

$$T_n = \left( \frac{1}{n!} \right)^2 t_{a_1 \dots a_n}^{i_1 \dots i_n} a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} \quad (6)$$

( $n = 1, \dots, M$ ) are the many-body components of  $T^{(M)}$  and  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  are the corresponding cluster amplitudes.

The cluster amplitudes  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  are determined by solving a coupled system of nonlinear and energy-independent algebraic equations of the form:

$$\langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | \bar{H}^{(M)} | \Phi \rangle = 0, \quad i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \quad (7)$$

where  $n = 1, \dots, M$ ,

$$\bar{H}^{(M)} = e^{-T^{(M)}} H e^{T^{(M)}} = (H e^{T^{(M)}})_C \quad (8)$$

is the similarity-transformed Hamiltonian of the coupled-cluster theory, subscript  $C$  designates the connected part of the corresponding operator expression, and  $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle \equiv a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} |\Phi\rangle$  are the  $np - nh$  or  $n$ -tuply excited determinants relative to  $|\Phi\rangle$ . In particular, the standard CCSD equations for the singly and doubly excited cluster amplitudes  $t_a^i$  and  $t_{ab}^{ij}$ , defining  $T_1$  and  $T_2$ , respectively, can be written as

$$\langle \Phi_i^a | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0, \quad (9)$$

$$\langle \Phi_{ij}^{ab} | \bar{H}^{(\text{CCSD})} | \Phi \rangle = 0, \quad i < j, \quad a < b, \quad (10)$$

where

$$\bar{H}^{(\text{CCSD})} \equiv \bar{H}^{(2)} = e^{-T^{(\text{CCSD})}} H e^{T^{(\text{CCSD})}} = (H e^{T^{(\text{CCSD})}})_C \quad (11)$$

is the similarity-transformed Hamiltonian of the CCSD approach. As mentioned in the Introduction, we do not use the bare Hamiltonian in our nuclear structure calculations. Thus, the Hamiltonian  $H$  used to construct the similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$  for the nuclear structure calculations discussed in this paper is replaced by the renormalized form of Hamiltonian resulting from a no-core G-matrix theory (see Section 2.2 for more information).

The system of coupled-cluster equations, Eq. (7), is obtained in the following way: We first insert the coupled-cluster wave function  $|\Psi_0\rangle$ , Eq. (1), into the Schrödinger equation,

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle, \quad (12)$$

and premultiply both sides of Eq. (12) on the left by  $e^{-T}$  to obtain the connected cluster form of the Schrödinger equation [????],

$$\bar{H}|\Phi\rangle = E_0|\Phi\rangle, \quad (13)$$

where

$$\bar{H} = e^{-T} H e^T = (H e^T)_C \quad (14)$$

is the similarity-transformed Hamiltonian. Next, we project Eq. (13), in which  $T$  is replaced by its approximate form  $T^{(M)}$ , Eq. (5), onto the excited determinants  $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$ , with  $n = 1, \dots, M$ , corresponding to the  $p - h$  excitations included in  $T^{(M)}$ . The excited determinants  $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$  are orthogonal to the reference determinant  $|\Phi\rangle$ , so that we end up with the nonlinear and energy-independent algebraic equations of the form of Eq. (7). Once the system of equations, Eq. (7), is solved for  $T^{(M)}$  or  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  (or Eqs. (9) and (10) are solved for  $T_1$  and  $T_2$  or  $t_a^i$  and  $t_{ab}^{ij}$ ), the ground-state coupled-cluster energy is calculated using the equation

$$E_0^{(M)} = \langle \Phi | \bar{H}^{(M)} | \Phi \rangle \equiv \langle \Phi | \bar{H}_{\text{closed}}^{(M)} | \Phi \rangle, \quad (15)$$

where  $\bar{H}_{\text{closed}}^{(M)}$  is a “closed” part of  $\bar{H}^{(M)}$  which is represented by those diagrams contributing to  $\bar{H}^{(M)}$  that have no external (uncontracted) Fermion lines (as opposed to the “open” part of  $\bar{H}^{(M)}$  which is represented by the diagrams having external or uncontracted Fermion lines). It can easily be shown that if the Hamiltonian  $H$  (in our case, the renormalized Hamiltonian  $H$ ) does not contain higher-than-two-body interactions and  $M \leq 2$ ,

$$E_0^{(M)} = \langle \Phi | H | \Phi \rangle + \langle \Phi | [H_N(T_1 + T_2 + \frac{1}{2}T_1^2)]_C | \Phi \rangle, \quad (16)$$

where  $H_N = H - \langle \Phi | H | \Phi \rangle$  is the Hamiltonian in the normal-ordered form. In other words, we only need  $T_1$  and  $T_2$  cluster to calculate the energy  $E_0^{(M)}$ . Equation (15) can be obtained by projecting the connected cluster form of the Schrödinger equation, Eq. (13), on the reference configuration  $|\Phi\rangle$  and replacing  $T$  by  $T^{(M)}$ . In fact, the nonlinear character of the system of coupled-cluster equations of the form of Eq. (7) does not mean that the resulting equations contain very high powers of  $T^{(M)}$ . For example, if the Hamiltonian  $H$  (in our case, the renormalized Hamiltonian obtained using G-matrix theory) does not contain higher-than-pairwise interactions, the CCSD equations for the  $T_1$  and  $T_2$  clusters or for the amplitudes  $t_a^i$  and  $t_{ab}^{ij}$  that represent these clusters become

$$\langle \Phi_i^a | [H_N(1 + T_1 + T_2 + \frac{1}{2}T_1^2 + T_1T_2 + \frac{1}{6}T_1^3)]_C | \Phi \rangle = 0, \quad (17)$$

$$\langle \Phi_{ij}^{ab} | [H_N(1 + T_1 + T_2 + \frac{1}{2}T_1^2 + T_1T_2 + \frac{1}{6}T_1^3 + \frac{1}{2}T_2^2 + \frac{1}{2}T_1^2T_2 + \frac{1}{24}T_1^4)]_C | \Phi \rangle = 0. \quad (18)$$

In general, if the Hamiltonian  $H$  contains two-body interactions only, there are no terms in cluster components  $T_n$  that are higher than quartic terms in the coupled-cluster system, Eq. (7), independent of the truncation scheme  $M$  used to define  $T^{(M)}$ . This is a mathematical fact, not the result of some arbitrary truncation of the exponential coupled-cluster wave function.

In this work, we focus on the applications of coupled-cluster methods, such as CCSD, to Hamiltonians containing two-body interactions. The explicit and computationally efficient form of the corresponding equations used in actual calculations, in terms of one- and two-body matrix elements of the renormalized form of Hamiltonian and cluster amplitudes  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  or, in the CCSD ( $M = 2$ ) case,  $t_a^i$  and  $t_{ab}^{ij}$ , can be derived by applying diagrammatic techniques of many-body theory combined with diagram factorization methods which yield highly vectorized computer codes [? ? ?]. Once these equations are properly coded, we solve them using iterative procedures, such as DIIS [?]. The explicitly connected form of coupled-cluster equations, such as Eqs. (7) or (17) and (18), guarantees that the process of solving these equations leads to connected terms in cluster components  $T_n$  and connected terms in the energy  $E_0^{(M)}$ , independent of the truncation scheme  $M$  used to define  $T^{(M)}$ . The absence of disconnected terms in  $T^{(M)}$  and  $E_0^{(M)}$  is essential to obtain the rigorously size extensive results.

The ground-state coupled-cluster theory, as described above, has a natural extension to excited states  $|\Psi_\mu\rangle$  via the equation of motion [?] or linear response coupled-cluster [?] method, in which we write

$$|\Psi_\mu\rangle = |\Psi_\mu^{(\text{CC})}\rangle \equiv R_\mu e^T |\Phi\rangle, \quad (19)$$

where  $T$  is obtained in the ground-state coupled-cluster calculations and  $R_\mu$  is a linear particle-hole excitation operator similar to  $T$  obtained by diagonalizing the similarity-transformed Hamiltonian  $\bar{H} = e^{-T} H e^T$ . As in the ground-state case, the standard equation of motion coupled-cluster approximations are obtained by truncating the many-body expansion for the excitation operator  $R_\mu$  at a given excitation level  $M < A$ , which is the same as the excitation level used to define the truncated form of  $T$ . Thus, in the equation of motion CCSD (EOMCCSD) theory, which is a basic equation of motion coupled-cluster approximation where  $M$  is set at 2, we write

$$R_\mu^{(\text{CCSD})} \equiv R_\mu^{(2)} = R_{\mu,0} + R_{\mu,1} + R_{\mu,2}, \quad (20)$$

where

$$R_{0,\mu} = r_0(\mu) \mathbf{1}, \quad (21)$$

$$R_{\mu,1} = r_a^i(\mu) a^a a_i, \quad (22)$$

and

$$R_{\mu,2} = \frac{1}{4} r_{ab}^{ij}(\mu) a^a a^b a_j a_i \quad (23)$$

are the reference,  $1p-1h$ , and  $2p-2h$  components of  $R_\mu^{(\text{CCSD})}$ , and  $r_0(\mu)$ ,  $r_a^i(\mu)$ , and  $r_{ab}^{ij}(\mu)$  are the corresponding excitation amplitudes ( $\mathbf{1}$  in Eq. (21) is a unit operator). In general, when  $T$  is approximated by  $T^{(M)}$ , Eq. (5), the corresponding excitation operator  $R_\mu$  is approximated by

$$R_\mu^{(M)} = R_{\mu,0}^{(M)} + R_{\mu,\text{open}}^{(M)}, \quad (24)$$

where the “open” part of  $R_\mu^{(M)}$  is defined as

$$R_{\mu,\text{open}}^{(M)} = \sum_{n=1}^M R_{\mu,n}, \quad (25)$$

with

$$R_{\mu,n} = \left(\frac{1}{n!}\right)^2 r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu) a^{a_1} \dots a^{a_n} a_{i_n} \dots a_{i_1} \quad (26)$$

representing the  $np - nh$  components of  $R_\mu^{(A)}$ . The excitation amplitudes  $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu)$  defining  $R_{\mu,\text{open}}^{(M)}$  are obtained by solving the eigenvalue problem involving the similarity-transformed Hamiltonian  $\bar{H}^{(M)}$  in the space spanned by the excited determinants  $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$  with  $n = 1, \dots, M$ , i.e.

$$\begin{aligned} \langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | (\bar{H}_{\text{open}}^{(M)} R_{\mu,\text{open}}^{(M)})_C | \Phi \rangle &= \omega_\mu^{(M)} r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu), \\ i_1 < \dots < i_n, \quad a_1 < \dots < a_n, \end{aligned} \quad (27)$$

where

$$\bar{H}_{\text{open}}^{(M)} = \bar{H}^{(M)} - \bar{H}_{\text{closed}}^{(M)} = \bar{H}^{(M)} - E_0^{(M)} \mathbf{1} \quad (28)$$

is the “open” part of  $\bar{H}^{(M)}$ , represented by the diagrams of  $\bar{H}^{(M)}$  that have external Fermion lines, and

$$\omega_\mu^{(M)} = E_\mu^{(M)} - E_0^{(M)} \quad (29)$$

is the vertical excitation energy. In particular, the  $r_a^i(\mu)$ , and  $r_{ab}^{ij}(\mu)$  amplitudes of the EOMCCSD theory and the corresponding excitation energies  $\omega_\mu^{(\text{CCSD})}$  are obtained by diagonalizing the similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$ , Eq. (11), in the relatively small space of singly and doubly excited determinants  $|\Phi_i^a\rangle$  and  $|\Phi_{ij}^{ab}\rangle$ . Equation (27) alone does not provide information about the coefficient  $r_0(\mu)$  at the reference determinant  $|\Phi\rangle$  in the corresponding equation of motion coupled-cluster wave function  $R_\mu^{(M)} e^{T^{(M)}} |\Phi\rangle$ . This coefficient can be determined *a posteriori* using the equation

$$r_0(\mu) = \langle \Phi | (\bar{H}_{\text{open}}^{(M)} R_{\mu,\text{open}}^{(M)})_C | \Phi \rangle / \omega_\mu^{(M)}, \quad (30)$$

once the excitation amplitudes  $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu)$  defining  $R_{\mu,\text{open}}^{(M)}$  are known. For consistency of our presentation, we use the notation in which  $\mu > 0$  means that we are dealing with excited states, whereas  $\mu = 0$  corresponds to the ground-state problem. In particular, the excitation operator  $R_\mu^{(M)}$  is formally defined as a unit operator when  $\mu = 0$ , i.e.  $r_0(\mu = 0) = 1$  and  $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu = 0) = 0$  for  $n \geq 1$ , so that the equation of motion coupled-cluster ansatz, Eq. (19), reduces to the ground-state coupled-cluster ansatz, Eq. (1), in the ground-state,  $\mu = 0$ , case. With this definition of  $R_{\mu=0}^{(M)}$ , the system of equations, Eq. (27), defining the equation of motion coupled-cluster calculations formally reduces to the standard system of the ground-state coupled-cluster equations, Eq. (7), although we must, of course, remember that in the equation of motion coupled-cluster calculations for excited states employing Eq. (27) we only solve for the linear excitation operator  $R_\mu^{(M)}$  (or, for the corresponding excitation amplitudes  $r_{a_1 \dots a_n}^{i_1 \dots i_n}(\mu)$ ) using the given values of cluster amplitudes  $t_{a_1 \dots a_n}^{i_1 \dots i_n}$  defining the cluster operator  $T^{(M)}$ , obtained in the corresponding ground-state coupled-cluster calculations that precede the excited-state calculations.

The similarity-transformed Hamiltonians  $\bar{H}^{(M)}$  or  $\bar{H}^{(\text{CCSD})}$  are not hermitian, so that in addition to the right eigenstates  $R_\mu^{(M)} |\Phi\rangle$  or  $R_\mu^{(\text{CCSD})} |\Phi\rangle$ , which define the “ket” coupled-cluster or equation of motion coupled-cluster wave functions, we can also determine the left eigenstates of  $\bar{H}^{(M)}$  or  $\bar{H}^{(\text{CCSD})}$ ,  $\langle \Phi | L_\mu^{(M)}$  or  $\langle \Phi | L_\mu^{(\text{CCSD})}$ , respectively, which define the corresponding “bra” coupled-cluster or equation of motion coupled-cluster wave functions

$$\langle \tilde{\Psi}_\mu^{(\text{CC})} | = \langle \Phi | L_\mu e^{-T} \quad (31)$$

that match the “ket” states given by Eq. (19). Here,  $L_\mu$  (in approximate methods,  $L_\mu^{(A)}$  or  $L_\mu^{(\text{CCSD})}$ ) is a hole-particle ( $h - p$ ) deexcitation operator, so that, for example,

$$L_\mu^{(\text{CCSD})} \equiv L_\mu^{(2)} = L_{\mu,0} + L_{\mu,1} + L_{\mu,2}, \quad (32)$$

where

$$L_{0,\mu} = l_0(\mu) \mathbf{1}, \quad (33)$$

$$L_{\mu,1} = l_i^a(\mu) a^i a_a, \quad (34)$$

and

$$L_{\mu,2} = \frac{1}{4} l_{ij}^{ab}(\mu) a^i a^j a_b a_a \quad (35)$$

are the reference, one-body, and two-body components of  $L_\mu^{(\text{CCSD})}$ , and  $l_0(\mu)$ ,  $l_i^a(\mu)$ , and  $l_{ij}^{ab}(\mu)$  are the corresponding deexcitation amplitudes. The right and left eigenstates of  $\tilde{H}^{(\text{CCSD})}$  form a biorthonormal set,

$$\langle \Phi | L_\mu^{(\text{CCSD})} R_\nu^{(\text{CCSD})} | \Phi \rangle = \delta_{\mu,\nu}, \quad (36)$$

where  $\delta_{\mu,\nu}$  is the usual Kronecker delta, so that the coefficient  $l_0(\mu)$  at  $\langle \Phi |$  in the left CCSD/EOMCCSD eigenstate  $\langle \Phi | L_\mu^{(\text{CCSD})}$  satisfies

$$l_0(\mu) = \delta_{\mu,0}, \quad (37)$$

meaning that  $l_0(\mu) = 0$  in the excited-state ( $\mu > 0$ ) case. In general, the deexcitation operators  $L_\mu^{(M)}$  generating the left eigenstates of the similarity-transformed Hamiltonian  $\tilde{H}^{(M)}$ ,  $\langle \Phi | L_\mu^{(M)}$ , can be written as

$$L_\mu^{(M)} = L_{\mu,0}^{(M)} + L_{\mu,\text{open}}^{(M)}, \quad (38)$$

where the “open” part of  $L_\mu^{(M)}$  is defined as

$$L_{\mu,\text{open}}^{(M)} = \sum_{n=1}^M L_{\mu,n}^{(M)}, \quad (39)$$

with

$$L_{\mu,n}^{(M)} = \left( \frac{1}{n!} \right)^2 l_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu) a^{i_1} \dots a^{i_n} a_{a_n} \dots a_{a_1}, \quad (40)$$

representing the  $n$ -body components of  $L_\mu^{(M)}$ . As in the CCSD case, the left and right eigenstates of  $\tilde{H}^{(M)}$ ,  $\langle \Phi | L_\mu^{(M)}$  and  $R_\mu^{(M)} | \Phi \rangle$ , respectively, form a biorthonormal set,

$$\langle \Phi | L_\mu^{(M)} R_\nu^{(M)} | \Phi \rangle = \delta_{\mu,\nu}, \quad (41)$$

and the zero-body part of  $L_\mu^{(M)}$  satisfies

$$L_{\mu,0}^{(M)} = \delta_{\mu,0} \mathbf{1}, \quad (42)$$

i.e.  $L_{\mu,0}^{(M)}$  vanishes for excited states ( $\mu > 0$ ), while being equal to the unit operator in the ground-state ( $\mu = 0$ ) case. The deexcitation amplitudes  $l_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu)$  defining  $L_{\mu,\text{open}}^{(M)}$  are obtained by solving the left eigenvalue problem involving the similarity-transformed Hamiltonian  $\tilde{H}^{(M)}$  in the space spanned by the excited determinants  $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$  with  $n = 1, \dots, M$ ,

$$\delta_{\mu,0} \langle \Phi | \tilde{H}_{\text{open}}^{(M)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle + \langle \Phi | L_{\mu,\text{open}}^{(M)} \tilde{H}_{\text{open}}^{(M)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle = \omega_\mu^{(M)} l_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu), \quad (43)$$

$$i_1 < \dots < i_n, \quad a_1 < \dots < a_n,$$

where  $\omega_\mu^{(M)}$  is the vertical excitation energy, Eq. (29), and where we already used Eq. (42). In particular,

$$\langle \Phi | L_{\mu,\text{open}}^{(M)} \tilde{H}_{\text{open}}^{(M)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle = \omega_\mu^{(M)} l_{i_1 \dots i_n}^{a_1 \dots a_n}(\mu), \quad (44)$$

$$i_1 < \dots < i_n, \quad a_1 < \dots < a_n,$$

in the excited-state ( $\mu > 0$ ) case. When the ground-state ( $\mu = 0$ ) case is considered, we usually write

$$L_0^{(M)} = \mathbf{1} + \Lambda^{(M)}, \quad (45)$$

where

$$\Lambda^{(M)} = \sum_{n=1}^M \Lambda_n \equiv L_{0,\text{open}}^{(M)}, \quad (46)$$

with

$$\Lambda_n = \left( \frac{1}{n!} \right)^2 \lambda_{i_1 \dots i_n}^{a_1 \dots a_n} a^{i_1} \dots a^{i_n} a_{a_n} \dots a_{a_1}, \quad (47)$$

represents the well-known “lambda” operator of the analytic gradient CC theory [? ]. The ground-state deexcitation amplitudes  $\lambda_{i_1 \dots i_n}^{a_1 \dots a_n} \equiv l_{i_1 \dots i_n}^{a_1 \dots a_n}(0)$  that define the  $\Lambda^{(M)}$  operator are obtained by solving the following system of linear equations (cf. Eq. (43)):

$$\begin{aligned} \langle \Phi | \bar{H}_{\text{open}}^{(M)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle + \langle \Phi | \Lambda^{(M)} \bar{H}_{\text{open}}^{(M)} | \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} \rangle &= 0, \\ i_1 < \dots < i_n, \quad a_1 < \dots < a_n. \end{aligned} \quad (48)$$

The CCSD/EOMCCSD equations for the deexcitation amplitudes  $l_i^a(\mu)$ ,  $l_{ij}^{ab}(\mu)$ ,  $\lambda_i^a \equiv l_i^a(0)$ , and  $\lambda_{ij}^{ab} \equiv l_{ij}^{ab}(0)$  are obtained by setting  $M = 2$  in Eqs. (44) and (48).

If the only purpose of the calculation is to obtain energies  $E_\mu^{(M)}$  or vertical excitation energies  $\omega_\mu^{(M)}$  (in the  $M = 2$  case, the CCSD/EOMCCSD energies  $E_\mu^{(\text{CCSD})}$  and vertical excitation energies  $\omega_\mu^{(\text{CCSD})} = E_\mu^{(\text{CCSD})} - E_0^{(\text{CCSD})}$ ), the left eigenstates of  $\bar{H}^{(M)}$  or  $\bar{H}^{(\text{CCSD})}$ ,  $\langle \Phi | L_\mu^{(M)}$  or  $\langle \Phi | L_\mu^{(\text{CCSD})}$ , respectively, are not needed and it is sufficient to solve the right eigenvalue problem involving  $\bar{H}^{(M)}$  or  $\bar{H}^{(\text{CCSD})}$ , Eq. (27). However, if one has to calculate properties other than energy, such as the expectation values and transition matrix elements involving the coupled-cluster or equation of motion coupled-cluster states  $\langle \tilde{\Psi}_\mu |$  and  $|\Psi_\nu\rangle$ , both right and left eigenstates of  $\bar{H}^{(M)}$  (or  $\bar{H}^{(\text{CCSD})}$ ) are important. Indeed, if  $\theta$  is a property operator, we obtain

$$\langle \tilde{\Psi}_\mu^{(\text{CC})} | \theta | \Psi_\nu^{(\text{CC})} \rangle = \langle \Phi | L_\mu \bar{\theta} R_\nu | \Phi \rangle, \quad (49)$$

where

$$\bar{\theta} = e^{-T} \theta e^T = (\theta e^T)_C \quad (50)$$

is the similarity-transformed form of  $\theta$  analogous to the similarity-transformed Hamiltonians  $\bar{H}^{(M)}$  and  $\bar{H}^{(\text{CCSD})}$ . In particular, when  $\theta = a^p a_q$  in Eq. (49), we can determine the CCSD or EOMCCSD one-body reduced density matrices in the coupled-cluster or equation of motion coupled-cluster states  $|\Psi_\mu\rangle$ , designated by  $\gamma_q^p(\mu) \equiv \gamma_q^p(\mu, \mu)$ , or the corresponding transition one-body reduced density matrices  $\gamma_q^p(\mu, \nu)$ . We obtain,

$$\gamma_q^p(\mu, \nu) = \langle \Phi | L_\mu \overline{a^p a_q} R_\nu | \Phi \rangle. \quad (51)$$

We can use the above expressions to calculate matter and charge densities and various (transition) one-body properties,

$$\langle \tilde{\Psi}_\mu^{(\text{CC})} | \theta | \Psi_\nu^{(\text{CC})} \rangle = \theta_p^q \gamma_q^p(\mu, \nu), \quad (52)$$

where  $\theta_p^q \equiv \langle p | \theta | q \rangle$  are matrix elements of the one-electron property operator  $\theta$  and  $\gamma_q^p(\mu, \nu)$  is defined by Eq. (51). In approximate CC/EOMCC calculations, the cluster operator  $T$  and the excitation and deexcitation operators  $R_\mu$  and  $L_\mu$  are, of course, replaced by their truncated forms ( $T^{(M)}$ ,  $R_\mu^{(M)}$ , and  $L_\mu^{(M)}$ , respectively).

An interesting feature of the equation of motion coupled-cluster methods, such as EOMCCSD, is the possibility to study ground and excited states of open-shell nuclei that are obtained by adding or removing one particle in a closed-shell system. This can be done by exploiting the particle attached (PA) (in chemistry electron attached or EA) and particle removed (PR) (in chemistry ionized or IP) equation of motion coupled-cluster methods, such as PA-EOMCCSD and PR-EOMCCSD, in which we define the wave functions of the  $(A + 1)$  and  $(A - 1)$  systems as

$$|\Psi_\mu^{(A+1)}\rangle = (r_a(\mu) a^a + \frac{1}{2} r_{ab}^{ij}(\mu) a^a a^b a_j) e^{T^{(\text{CCSD})}} |\Phi\rangle \quad (53)$$

and

$$|\Psi_\mu^{(A-1)}\rangle = (r^i(\mu) a_i + \frac{1}{2} r_{ab}^{ij}(\mu) a^b a_j a_i) e^{T^{(\text{CCSD})}} |\Phi\rangle, \quad (54)$$



respectively (see, e.g., [? ? ?]). The  $1p$  and  $2p - 1h$  amplitudes  $r_a(\mu)$  and  $r_{ab}^j(\mu)$ , respectively, are determined by diagonalizing the similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$  obtained in the CCSD calculations for the closed-shell  $A$ -particle system in the  $(A + 1)$  particle sector of the Fock-space spanned by the  $|\Phi^a\rangle = a^a|\Phi\rangle$  and  $|\Phi_j^{ab}\rangle = a^a a^b a_j|\Phi\rangle$  determinants. Similarly, the  $1h$  and  $2h - 1p$  amplitudes  $r^i(\mu)$  and  $r_{ij}^a(\mu)$ , respectively, are obtained by diagonalizing  $\bar{H}^{(\text{CCSD})}$  in the  $(A - 1)$ -particle subspace spanned by  $|\Phi_i\rangle = a_i|\Phi\rangle$  and  $|\Phi_{ij}^b\rangle = a^b a_i a_j|\Phi\rangle$  determinants. The PA-EOMCCSD and PR-EOMCCSD methods can be generalized to higher-order truncation schemes in the cluster operator  $T$  (see [?] for details). These methods and the underlying EOMCCSD and other equation of motion coupled-cluster approaches are closely related to the Fock-space or valence-universal multi-reference coupled-cluster methods [].

At present, the basic methods for our nuclear structure studies are the CCSD method for the ground state calculations, the EOMCCSD approach for calculations of excited states and properties other than energy, and the PA-EOMCCSD and PR-EOMCCSD methods for open-shell nuclei that are obtained by adding or removing one particle in a closed-shell system. In this work, the CCSD and EOMCCSD methods were used to determine the ground- and excited-state energies and properties of  $^{16}\text{O}$ , whereas the PA-EOMCCSD and PR-EOMCCSD approaches were used to determine the binding and selected excitation energies of the  $^{17}\text{O}$  and  $^{15}\text{O}$  nuclei, using the similarity-transformed Hamiltonian  $\bar{H}^{(\text{CCSD})}$  obtained in the CCSD/EOMCCSD calculations for the closed-shell  $^{16}\text{O}$  nucleus.

The CCSD and EOMCCSD methods capture the bulk of correlation effects with the inexpensive computational steps that scale as  $n_o^2 n_u^4$ , where  $n_o$  ( $n_u$ ) is the number of occupied (unoccupied) single-particle states, but there may be cases where  $3p - 3h$  (triply excited) clusters  $T_3$  and three-body components  $R_{\mu,3}$  and  $L_{\mu,3}$  or, even,  $4p - 4h$  (quadruply excited)  $T_4$ ,  $R_{\mu,4}$  and  $L_{\mu,4}$  components become important. While the full inclusion of triply and quadruply excited clusters,  $T_3$  and  $T_4$ , respectively, in the cluster operator  $T$  and three- and four-body components  $R_{\mu,3}$  and  $R_{\mu,4}$  in the excitation operator  $R_\mu$  (using the language of quantum chemistry, “triples” and “quadruples”) is possible, the resulting CCSDT (“T” stands for “triples”) [? ?] and EOMCCSDT [?] or CCSDTQ (“Q” stands for quadruples”) [? ? ?] and EOMCCSDTQ [?] methods scale as  $n_o^3 n_u^5$  or  $n_o^4 n_u^6$ , respectively, and are, therefore, rather expensive. Large costs of the CCSDT/EOMCCSDT and CCSDTQ/EOMCCSDTQ calculations can be alleviated by switching, for example, to the active-space variants of these methods, such as CCSDt, CCSDtq, [], or EOMCCSDt [], in which the dominant triply or triply and quadruply excited cluster amplitudes  $t_{abc}^{ijk}$  and  $t_{abcd}^{ijkl}$  and the corresponding excitation amplitudes  $r_{abc}^{ijk}(\mu)$  and  $r_{abcd}^{ijkl}(\mu)$  are carefully selected with the help of active orbitals (usually, the single particle functions in the highest occupied and lowest unoccupied major shells), but we have not implemented these methods yet within the context of nuclear structure studies (they have been implemented in quantum chemistry []). For this reason, in our calculations for  $^{16}\text{O}$  we estimate the effects of the  $T_3$  and  $R_{\mu,3}$  operators on ground- and excited-state energies by adding the *a posteriori* corrections due to triples to CCSD/EOMCCSD energies, which only require the  $n_o^3 n_u^4$  noniterative steps. These corrections, which can be derived using the method of moments of coupled cluster equations [? ? ? ?] and the perturbative analysis of the full CCSDT/EOMCCSDT problem, are similar, in spirit, to the popular CCSD(T) approach of the electronic structure theory [], which enables one to improve the ground-state CCSD energies through noniterative corrections describing the leading  $T_3$  effects. The ground- and excited-state corrections to CCSD/EOMCCSD energies due to the  $T_3$  and  $R_{\mu,3}$  components, which we use in our work and which we designate here as  $\delta_0$  and  $\delta_\mu$  ( $\mu > 0$ ), respectively, are calculated with the CR-CCSD(T) and CR-EOMCCSD(T) approaches (“CR” stands for completely renormalized and “(T)” indicates an approximate treatment of triples) [? ? ? ?], where

$$\delta_\mu = \frac{1}{36} \langle \tilde{\Psi}_\mu | \Phi_{ijk}^{abc} \rangle \mathcal{M}_{abc}^{ijk}(\mu) / \Delta_\mu \quad (\mu \geq 0). \quad (55)$$

Here  $|\Phi_{ijk}^{abc}\rangle$  are the triply excited determinants relative to  $|\Phi\rangle$  and  $\mathcal{M}_{abc}^{ijk}(\mu)$  are the generalized moments of the CCSD ( $\mu = 0$ ) or EOMCCSD ( $\mu > 0$ ) equations [? ? ?] obtained by projecting these equations on triples,

$$\mathcal{M}_{abc}^{ijk}(\mu) = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} R_\mu^{(\text{CCSD})} | \Phi \rangle \quad (56)$$

(recall that we formally define the  $\mu = 0$  operator  $R_\mu^{(\text{CCSD})}$  as a unit operator). They can be calculated using the CCSD and EOMCCSD cluster and excitation operators  $T^{(\text{CCSD})}$  and  $R_\mu^{(\text{CCSD})}$ , respectively, in a straightforward fashion []. For the two-body effective Hamiltonians  $H$  used in our work,

$$\begin{aligned} \mathcal{M}_{abc}^{ijk}(\mu) &= \langle \Phi_{ijk}^{abc} | (\bar{H}_2^{(\text{CCSD})} R_{\mu,2})_C | \Phi \rangle + \langle \Phi_{ijk}^{abc} | [\bar{H}_3^{(\text{CCSD})} (R_{\mu,1} + R_{\mu,2})]_C | \Phi \rangle + \langle \Phi_{ijk}^{abc} | (\bar{H}_4^{(\text{CCSD})} R_{\mu,1})_C | \Phi \rangle \\ &\quad + r_0(\mu) \mathcal{M}_{abc}^{ijk}(0), \end{aligned} \quad (57)$$

where  $\mathcal{M}_{abc}^{ijk}(0)$  represents the triply excited moments of the CCSD equations,

$$\mathcal{M}_{abc}^{ijk}(0) = \langle \Phi_{ijk}^{abc} | [H_N(T_2 + T_1 T_2 + \frac{1}{2} T_2^2 + \frac{1}{2} T_1^2 T_2 + \frac{1}{2} T_1 T_2^2 + \frac{1}{6} T_1^3 T_2)]_C | \Phi \rangle, \quad (58)$$

and where  $\bar{H}_n^{(\text{CCSD})}$  is an  $n$ -body component of the similarity-transformed Hamiltonian of the CCSD theory,  $\bar{H}^{(\text{CCSD})}$ . The  $\Delta_\mu$  denominators entering Eq. (55) are defined as

$$\Delta_\mu = \langle \tilde{\Psi}_\mu | R_\mu^{(\text{CCSD})} e^{T^{(\text{CCSD})}} | \Phi \rangle. \quad (59)$$

The approximate states  $|\tilde{\Psi}_\mu\rangle$  in Eqs. (55) and (59) represent relatively simple perturbative estimates of the CCSDT and EOMCCSDT wave functions,

$$|\tilde{\Psi}_0\rangle = \bar{P} e^{T^{(\text{CCSD})} + \tilde{T}_3} | \Phi \rangle \quad (60)$$

for the ground-state, and

$$|\tilde{\Psi}_\mu\rangle = \bar{P} (R_\mu^{(\text{CCSD})} + \tilde{R}_3) e^{T^{(\text{CCSD})}} | \Phi \rangle \quad (61)$$

for excited ( $\mu > 0$ ) states, where  $\bar{P}$  is a projection operator on the subspace spanned by the reference determinant  $|\Phi\rangle$  and singly, doubly, and triply excited determinants,  $|\Phi_i^a\rangle$ ,  $|\Phi_{ij}^{ab}\rangle$ , and  $|\Phi_{ijk}^{abc}\rangle$ , respectively. The approximate  $T_3$  and  $R_3$  operators,  $\tilde{T}_3$  and  $\tilde{R}_3$ , respectively, are defined as [? ? ]

$$\tilde{T}_3 = \frac{1}{36} (\mathcal{M}_{abc}^{ijk}(0) / D_{ijk}^{abc}(0)) a^a a^b a^c a_k a_j a_i, \quad (62)$$

$$\tilde{R}_3 = \frac{1}{36} (\mathcal{M}_{abc}^{ijk}(\mu) / D_{ijk}^{abc}(\mu)) a^a a^b a^c a_k a_j a_i, \quad (63)$$

where

$$\begin{aligned} D_{ijk}^{abc}(\mu) &= E_\mu^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \\ &= \omega_\mu^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}_1^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle - \langle \Phi_{ijk}^{abc} | \bar{H}_2^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle - \langle \Phi_{ijk}^{abc} | \bar{H}_3^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle, \end{aligned} \quad (64)$$

where  $\bar{H}_1^{(\text{CCSD})}$ ,  $\bar{H}_2^{(\text{CCSD})}$ , and  $\bar{H}_3^{(\text{CCSD})}$  are one-, two-, and three-body components of  $\bar{H}^{(\text{CCSD})}$ . In the ground-state ( $\mu = 0$ ) case, we replace the EOMCCSD excitation energy  $\omega_\mu^{(\text{CCSD})}$  in Eq. (64) by 0. The  $D_{ijk}^{abc}(\mu)$  denominators can be viewed as the “dressed” forms of the more usual perturbative denominators  $\omega_\mu^{(\text{CCSD})} - (\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k)$ , where  $\epsilon_i$  and  $\epsilon_a$  are the diagonal elements of the Fock matrix. The use of the more accurate form of these denominators, represented by Eq. (64), improves the accuracies of the calculated ground- and excited-state energies. We refer the reader to the original work [ ] for further details about the approximate triples CR-CCSD(T) and CR-EOMCCSD(T) approaches.

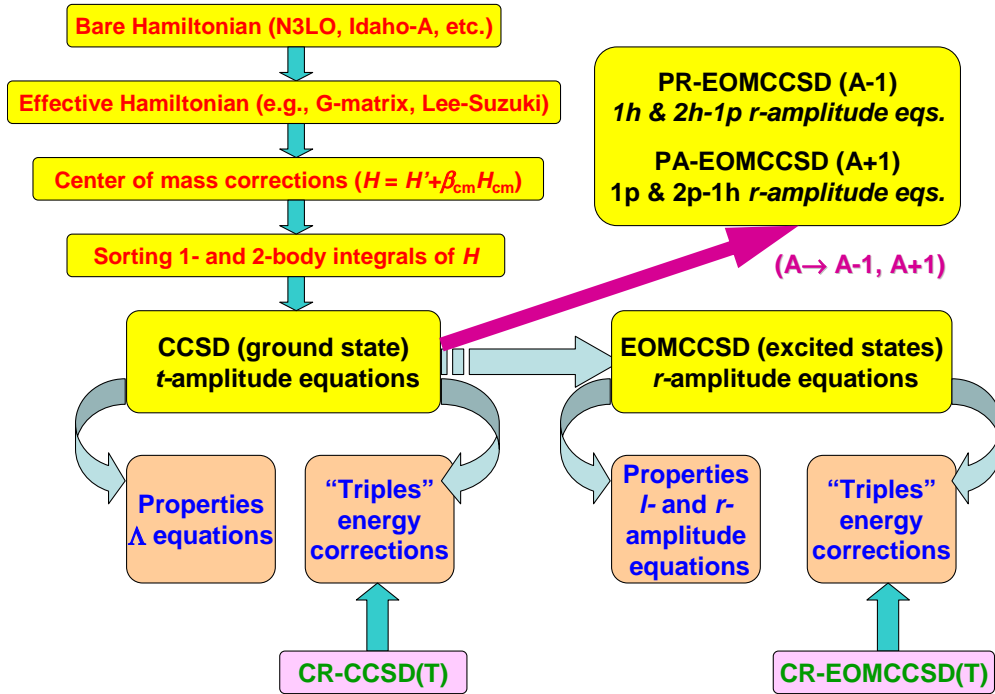
The key components of our present coupled cluster “machinery” for nuclear structure applications are shown in Fig. 1. As one can see, the coupled-cluster and equation of motion coupled-cluster calculations are preceded by the construction of the renormalized or effective Hamiltonian from the bare interactions. Basic information about the renormalized form of the Hamiltonian used in the calculations for  $^{15}\text{O}$ ,  $^{16}\text{O}$ , and  $^{17}\text{O}$  described in Section 3 is discussed next.

## 2.2. Effective Hamiltonian

In calculations for  $^{16}\text{O}$ , we used two potentials derived from the effective field theory [? ? ], namely, Idaho-A [? ] and N3LO [? ]. The Idaho-A potential is derived with up to chiral-order three diagrams, while N3LO includes chiral-order four diagrams and charge-symmetry and charge-independence breaking terms. We also include the Coulomb interaction in N3LO, which is not included in Idaho-A. In calculations for  $^{15}\text{O}$  and  $^{17}\text{O}$ , we used the N3LO potential only (to distinguish between  $^{15}\text{O}/^{17}\text{O}$  and  $^{15}\text{N}/^{17}\text{F}$ ). In order to remove the hard-core part of the interaction that would require calculations in extremely large model spaces to reach converged results [? ? ? ? ] and enable realistic calculations in manageable single-particle spaces, we renormalize the Hamiltonian through a

no-core  $G$ -matrix procedure [? ]. The no-core  $G$ -matrix approach introduces a starting-energy ( $\tilde{\omega}$ ) dependence in the effective two-body matrix elements  $G(\tilde{\omega})$  defining the renormalized two-body interactions, but much of the  $\tilde{\omega}$  dependence can be eliminated through the use of the Bethe-Brandow-Petschek theorem [? ] (see Ref. [? ] for details). After renormalizing bare interactions, our Hamiltonian is given by the formula  $H' = t + G(\tilde{\omega})$ , where  $t$  is the kinetic energy. We correct the renormalized Hamiltonian  $H'$  for center-of-mass contaminations using the expression  $H = H' + \beta_{\text{c.m.}} H_{\text{c.m.}}$ , where  $\beta_{\text{c.m.}}$  is chosen such that the expectation value of the center-of-mass Hamiltonian  $H_{\text{c.m.}}$  is 0.0 MeV. One of the advantages of this procedure is the ease of separation of intrinsic and center-of-mass contaminated states by analyzing the dependence of coupled-cluster energies on  $\beta_{\text{c.m.}}$ . As shown in Table 1, the physical states obtained in coupled-cluster calculations are virtually independent of  $\beta_{\text{c.m.}}$ . The center-of-mass contaminated states show a strong, nearly linear dependence of excitation energies on  $\beta_{\text{c.m.}}$ . We have started working on the alternative approach to construct the renormalized Hamiltonian  $H$  for coupled-cluster calculations, in which instead of the  $G$ -matrix method, we construct  $H$  with the help of the Lee-Suzuki approach [? ], exploited in no core shell-model calculations [? ], which will eliminate the starting-energy dependence from our calculations.

Once the one- and two-body matrix elements of the center-of-mass-corrected renormalized Hamiltonian  $H$  are determined, we solve the nuclear many-body problem using coupled cluster and equations of motion coupled-cluster methods, such as CCSD, EOMCCSD, CR-CCSD(T), CR-EOMCCSD(T) (for  $^{16}\text{O}$ ), PA-EOMCCSD (for  $^{17}\text{O}$ ), and PR-EOMCCSD (for  $^{15}\text{O}$ ). In order to construct the relevant cluster and excitation amplitude equations in the most efficient way, we sort the one- and two-body matrix elements of  $H$  according to the particle-hole character of single-particle indices that label them (cf. Fig. 1). This is a common practice in coding coupled-cluster methods in quantum chemistry and this is what we do in our nuclear CCSD, EOMCCSD, CR-CCSD(T), CR-EOMCCSD(T), PA-EOMCCSD, and PR-EOMCCSD calculations. The results of these calculations for the three isotopes of oxygen are discussed in the next section.



**FIGURE 1.** The key ingredients of the system of nuclear-structure coupled cluster programs discussed in this paper

**TABLE 1.** The  $\beta_{\text{c.m.}}$  dependence of the excitation energies for the lowest-energy  $3^-$  state of  $^{16}\text{O}$  obtained in the EOMCCSD calculations employing the Idaho-A interaction and a basis set of 5 major oscillator shells (excitation energies and  $\beta_{\text{c.m.}}$  values in MeV).

$\beta_{\text{c.m.}} = 0.5$	$\beta_{\text{c.m.}} = 1.0$	$\beta_{\text{c.m.}} = 1.5^*$
13.413	13.497	13.574

\* The optimum value of  $\beta_{\text{c.m.}}$  giving the expectation value of  $H_{\text{c.m.}}$  of 0.0 MeV.

### 3. RESULTS FOR $^{15}\text{O}$ , $^{16}\text{O}$ , AND $^{17}\text{O}$ AND THEIR DISCUSSION

In this section, we review the results of our recent coupled-cluster and equation of motion coupled-cluster calculations for  $^{15}\text{O}$ ,  $^{16}\text{O}$ , and  $^{17}\text{O}$ . We begin with the discussion of binding energies in  $^{16}\text{O}$ . Calculations of  $^{16}\text{O}$  properties other than energy, such as matter density, charge radius and charge form factor, excited states of  $^{16}\text{O}$ , and ground and excited states of  $^{15}\text{O}$  and  $^{17}\text{O}$  are discussed afterwards.

#### 3.1. Ground-state energy of $^{16}\text{O}$

The results of the CCSD and CR-CCSD(T) results for the ground-state energy of  $^{16}\text{O}$  with up to 7 (CR-CCSD(T)) or 8 (CCSD) major oscillator shells and two interactions, Idaho-A and N3LO, are shown in Table 2. As one can see, we obtain a rapid convergence of the CCSD and CR-CCSD(T) ground-state energies of  $^{16}\text{O}$  with the number of major oscillator shells ( $N$ ), so that the results obtained with 7 major oscillator shells are essentially converged. For example, the difference between the  $N = 8$  and  $N = 7$  CCSD/Idaho-A energies is only 0.5 MeV. We can also see that the corrections to the ground-state CCSD energies due to  $T_3$  clusters, resulting from the CR-CCSD(T) calculations, are small, contributing less than 1% of the total binding energy. This agrees with our earlier findings for  $^{16}\text{O}$  obtained in the calculations employing 4 major oscillator shells [? ].

A simple extrapolation based on fitting the data in Table 2 to  $E(N) = E_\infty + a \exp(-bN)$ , where the extrapolated energy  $E_\infty \equiv E(N = \infty)$  and  $a$  and  $b$  are parameters for the fit, shows that the extrapolated CCSD and CR-CCSD(T) energies obtained with the Idaho-A potential without Coulomb are  $-119.4$  and  $-120.5$  MeV, respectively. The Coulomb interaction reduces the unsigned binding energy by approximately 11.2 MeV, so that we estimate the  $N = \infty$  CR-CCSD(T)/Idaho-A ground-state energy at  $-109.3$  MeV. Our  $N = 7$  CCSD and CR-CCSD(T) energies obtained with N3LO, which include the Coulomb interactions, are  $-112.4$  and  $-112.8$  MeV, respectively, in excellent agreement with the Coulomb-corrected energies obtained with Idaho-A. Again, there is almost no difference between the  $N = 7$  and  $N = 8$  CCSD energies, when the N3LO potential is employed. The ground-state energy of  $\approx -110$  MeV resulting from the CCSD and CR-CCSD(T) calculations with Idaho-A and N3LO should be compared with the experimental binding energy of  $-128$  MeV. Since  $^{16}\text{O}$  is a closed-shell nucleus and since the effect of  $T_3$  clusters on the binding energy is very small, we believe that our calculations are converged at the two-body level. We conclude that the two-body Idaho-A and N3LO interactions underbind  $^{16}\text{O}$  by approximately 1 MeV per particle, leaving room for the additional binding to be produced by three-body forces.

#### 3.2. Calculations of the lowest-energy $3^-$ state and other negative parity states of $^{16}\text{O}$

The first excited  $3^-$  state of  $^{16}\text{O}$ , located experimentally at 6.12 MeV above the ground state, is thought to be a  $1p - 1h$  state [? ]. The experience of quantum chemistry tells us that the EOMCCSD method describes  $1p - 1h$  excited states very well and that the effects of triples ( $T_3$  and  $R_{\mu,3}$ ) on excitation energies of such states are very small. This is, of course, based on the assumption that three-body interactions in the Hamiltonian (obviously not present in quantum chemical calculations) can be neglected. The largest  $R_{\mu,1}$  amplitudes obtained in the EOMCCSD calculations for the  $3^-$  state of  $^{16}\text{O}$  show that the dominant  $1p - 1h$  excitations are from the  $0p_{1/2}$  orbital to the  $0d_{5/2}$  orbital and that the

**TABLE 2.** The energies of the ground state and the lowest  $3^-$  state of  $^{16}\text{O}$  obtained with the CCSD/EOMCCSD and CR-CCSD(T)/CR-EOMCCSD(T) approaches and  $N = 5 - 8$  major oscillator shells (in MeV), using the Idaho-A potential without Coulomb (ground state and the  $3^-$  state) and the N3LO potential (ground-state only). The starting-energy value was  $\bar{\omega} = -80$  MeV.

$N$	Ground state (Idaho-A)		Ground state (N3LO)		The lowest $3^-$ state (Idaho-A)	
	CCSD	CR-CCSD(T)	CCSD	CR-CCSD(T)	EOMCCSD	CR-EOMCCSD(T)
5	-125.92	-126.26	-108.94	-109.22	-112.35	-112.48
6	-121.53	-121.76	-113.34	-113.51	-108.55	-108.72
7	-120.16	-120.76	-112.45	-112.81	-108.20	-108.46
8	-119.62		-111.22			

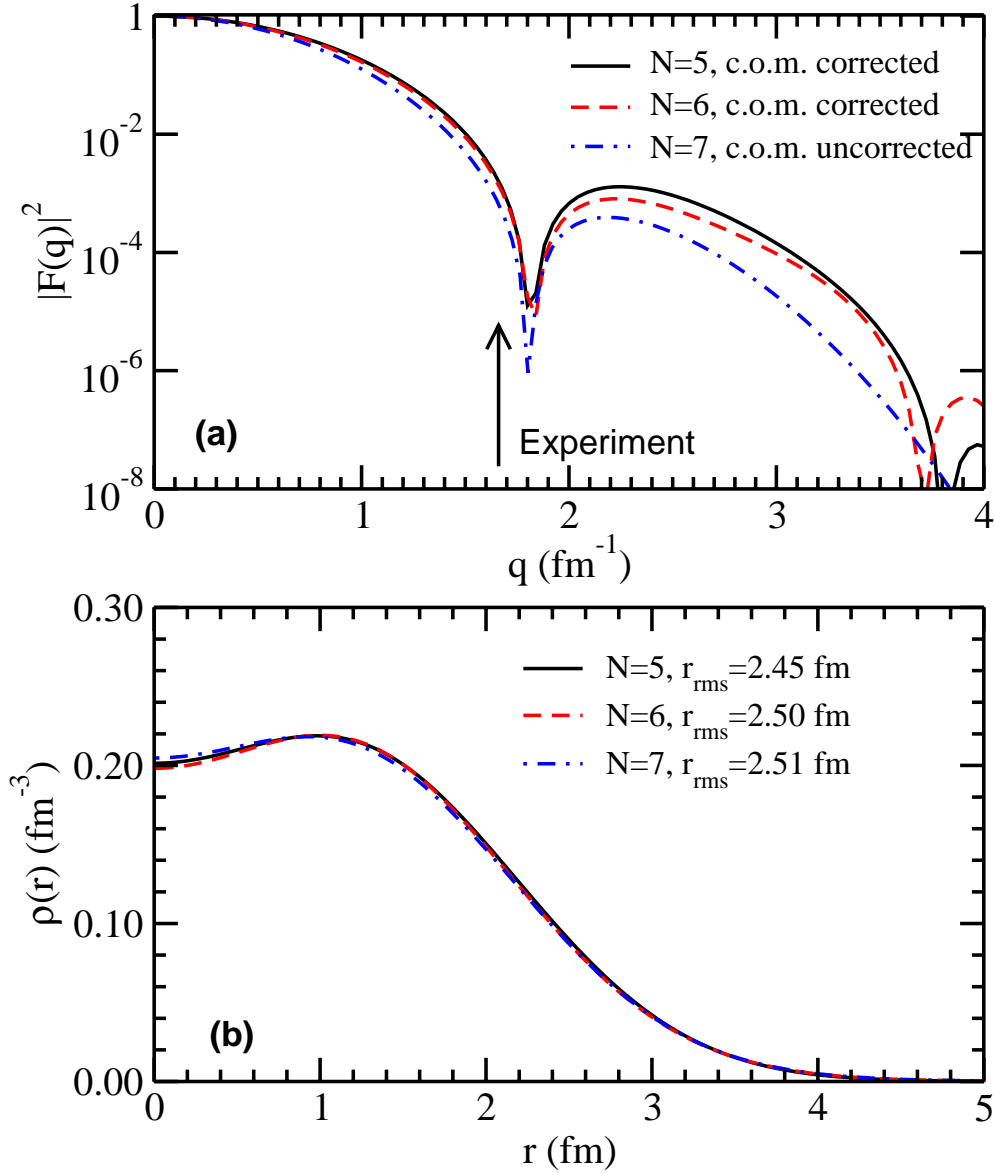
$2p - 2h$  excitations in the EOMCCSD wave function, defined as  $R_{\mu,2} + R_{\mu,1}T_1 + R_{\mu,0}(T_2 + \frac{1}{2}T_1^2)$  ( $R_{\mu,0} = 0$  in this case due to symmetry reasons), are much smaller than the  $R_{\mu,1}$  amplitudes, confirming the  $1p - 1h$  nature of the  $3^-$  state. As one might expect, the CR-EOMCCSD(T) calculations, in which we are trying to correct the EOMCCSD results for the  $T_3$  and  $R_{\mu,3}$  effects hardly changes the total energy of the state. Indeed, our extrapolated Idaho-A results, employing the  $3^-$  energies shown in Table 2 and the same  $E(N) = E_\infty + a \exp(-bN)$  fit as used in the ground-state case, indicate that the lowest  $3^-$  state of  $^{16}\text{O}$  lies at  $-108.2$  and  $-108.4$  MeV in the EOMCCSD and CR-EOMCCSD(T) calculations, respectively. Thus, the CR-EOMCCSD(T) method employing Idaho-A gives an excitation energy of 12.0 MeV for this state. The N3LO calculations (not shown in Table 2) yield a very similar result. The  $\sim 6$  MeV difference between the extrapolated CR-EOMCCSD(T) and experimental results suggests that the Idaho-A and N3LO potentials cannot yield an excitation energy for the  $3^-$  state which would agree with experiment. We believe that our results are converged at the coupled-cluster level employing the Idaho-A and N3LO two-body interactions, so that it is quite possible that the discrepancy between theory and experiment resides in the Hamiltonian. One cannot exclude the possibility that we have to include three-body forces to reduce the  $\sim 6$  MeV difference between coupled-cluster and experimental excitation energies for the lowest  $3^-$  state of  $^{16}\text{O}$ .

We have also performed preliminary calculations for other negative parity states. The quartet of negative parity states starting with the  $3^-$  state, and including the  $1^-$ ,  $2^-$ , and  $0^-$  states, are all believed to have a similar  $1p-1h$  character [?]. The EOMCCSD calculation with 5 major oscillator shells and Idaho-A confirms the existence of this quartet, giving excitation energies of 13.57, 15.37, 17.07, and 17.15 MeV for the  $3^-$ ,  $1^-$ ,  $2^-$ , and  $0^-$  states, respectively. While these states are all a few MeV above the experimental values, their ordering predicted by the EOMCCSD approach is correct. We will have to examine if this finding does not change when the number of major oscillator shells in a basis set increases to 6 or 7.

### 3.3. One-body density and charge form factor of $^{16}\text{O}$

In addition to binding and excitation energies, we calculated the CCSD reduced density matrices and the corresponding ground-state densities of  $^{16}\text{O}$ , using the recipe described in Section 2.1 (cf. Eq. (51)). The resulting radial densities  $\rho(r)$  for  $N = 5 - 7$ , shown in Fig. 2, were used to determine the root-mean-square (rms) charge radius. After correcting for the finite sizes of the nucleons and the center-of-mass motion, we obtained the rms charge radii of 2.45, 2.50, and 2.51 fm for 5, 6, and 7 major oscillator shells, respectively, when the Idaho-A interaction was employed, in good agreement with the experimental charge radius of  $^{16}\text{O}$ , which equals  $2.73 \pm 0.025$  fm. The CCSD calculations employing the N3LO potential gave similar values. We also calculated the nuclear charge form factor of  $^{16}\text{O}$ , following the general prescription described in [? ?]. The calculation of the charge form factor is somewhat more involving, since we have to include contributions due to the two-body reduced density matrix, resulting from the center-of-mass (c.o.m.) corrections, in addition to the contributions from the one-body density matrix. We computed the one-body density matrix contributions (for 5, 6, and 7 major oscillator shells) within the framework of CCSD theory precisely, using Eq. (51). The two-body density matrix, needed to correct the charge form factor for the c.o.m terms (for 5 and 6 major oscillator shells) was calculated as  $\rho_{pqrs} = \langle \Psi_0 | a^p a^q a_s a_r | \Psi_0 \rangle / \langle \Psi_0 | \Psi_0 \rangle$ , where the CCSD ground-state wave function  $|\Psi_0\rangle$  was approximated by the truncated shell-model-like expansion  $(1 + C_1 + C_2) |\Phi\rangle$ , with  $C_1 = T_1$  and  $C_2 = T_2 + \frac{1}{2}T_1^2$  representing the  $1p - 1h$  and  $2p - 2h$  components of the CCSD wave function  $\exp(T_1 + T_2)|\Phi\rangle$ . The results of these calculations are shown in Figure 1. As one can see, the c.o.m.-corrected charge form factors obtained

with 5 and 6 major oscillator shells are quite reasonable. This is promising, since the CCSD calculations of density matrices are rather inexpensive and we have not included three-body forces yet. Compared to experiment (the arrow in Figure 1), the location of the first zero of the CCSD form factor is slightly shifted toward larger  $q$  values. This is consistent with the fact that the CCSD approach underestimates the value of the rms charge radius.



**FIGURE 2.** Top panel (a): The charge form factor obtained from the CCSD density matrix. Bottom panel (b): the matter density in  $^{16}\text{O}$ . The results obtained with the Idaho-A potential

**TABLE 3.** Ground-state energies per particle for the  $^{15}\text{O}$ ,  $^{16}\text{O}$ , and  $^{17}\text{O}$  nuclei obtained with the PR-EOMCCSD, CCSD, and PA-EOMCCSD methods, respectively,  $N = 5$  and 6 major oscillator shells, and the N3LO interaction, and the corresponding experimental values (in MeV).

$N$	$^{15}\text{O}$	$^{16}\text{O}$	$^{17}\text{O}$
5	-6.07	-6.81	-6.43
6	-6.25	-7.08	-6.80
Experiment	-7.46	-7.98	-7.75

### 3.4. Preliminary results for the binding and excitation energies of $^{15}\text{O}$ and $^{17}\text{O}$

The results of the PR-EOMCCSD calculations for the ground-state of  $^{15}\text{O}$ , CCSD calculations for the ground-state  $^{16}\text{O}$ , and PA-EOMCCSD calculations for the ground-state of  $^{17}\text{O}$  for 5 and 6 major oscillator shells and the N3LO potential are shown in Table 3. The calculations for  $^{15}\text{O}$  and  $^{17}\text{O}$  are still preliminary in nature, since we have not yet examined the convergence of our results with  $N$ , but it is already quite encouraging to see that the binding energies per particle resulting from inexpensive CCSD-like calculations with 6 major oscillator shells are in reasonable agreement with experiment. As one can see, The PR-EOMCCSD/CCSD/PA-EOMCCSD approaches underbind the three nuclei by about 1 MeV per particle, pointing again to the need for the incorporation of three-body forces. On the other hand, the relative binding energies of  $^{15}\text{O}$ ,  $^{16}\text{O}$ , and  $^{17}\text{O}$  obtained in coupled-cluster calculations are in reasonable good agreement with experiment. For example, the difference between experimental binding energies of  $^{17}\text{O}$  and  $^{16}\text{O}$  is 0.23 MeV per particle. The PA-EOMCCSD and CCSD ground-state energies of  $^{17}\text{O}$  and  $^{16}\text{O}$  resulting from the calculations with 6 major oscillator shells differ by 0.28 MeV per particle. As in experiment, the unsigned binding energies per particle resulting from the PR-EOMCCSD/CCSD/PA-EOMCCSD calculations satisfy  $^{15}\text{O} < ^{17}\text{O} < ^{16}\text{O}$ .

We plan to extend these calculations to excited states of  $^{15}\text{O}$  and  $^{17}\text{O}$ , which may reveal useful information about the nature of three-nucleon interactions. Our preliminary PA-EOMCCSD calculations for the  $1/2^+$  and  $3/2^+$  states of  $^{17}\text{O}$ , employing 6 major oscillator shells, locate these states at 0.13 and 6.03 MeV above the  $5/2^+$  ground state, respectively. Experimentally, these states are located at 0.87 and 5.08 MeV above the ground state, respectively. The analogous PR-EOMCCSD calculations for the  $3/2^-$  state of  $^{15}\text{O}$  locate this state at 6.60 MeV above the  $1/2^-$  ground state. This result should be compared to 6.18 MeV observed experimentally. Clearly, we need to study the dependence of our PA-EOMCCSD and PR-EOMCCSD results with the number of major oscillator shells in a single-particle basis. Since the ground and low-lying states of  $^{15}\text{O}$  and  $^{17}\text{O}$  are dominated by the  $1h$  and  $1p$  terms, which are represented in the PR-EOMCCSD and PA-EOMCCSD calculations by the  $r_i(\mu)$  and  $r_a(\mu)$  amplitudes, respectively (for example, the  $5/2^+$ ,  $1/2^+$  and  $3/2^+$  states of  $^{17}\text{O}$  are obtained by adding a neutron to  $0d_{5/2}$ ,  $1s_{1/2}$ , and  $0d_{3/2}$  orbitals of  $^{16}\text{O}$ , respectively), and since the  $2h - 1p$  and  $2p - 1h$  terms resulting from our PR-EOMCCSD and PA-EOMCCSD calculations for  $^{15}\text{O}$  and  $^{17}\text{O}$  are relatively small, we expect that we may be able to obtain converged energies of the low-lying states of  $^{15}\text{O}$  and  $^{17}\text{O}$  at the level of two-body interactions with 8 major oscillator shells. The discrepancies with experimental positions of these states (if any) will, most likely, be due to the missing three-nucleon interactions, so that we may be able to come closer to a better understanding of these interactions and determine their effect on excitations in all isotopes of oxygen, including  $^{16}\text{O}$ , where we already see a  $\sim 6$  MeV difference between the converged equation of motion coupled-cluster and experimental excitation energies for the lowest-energy  $3^-$  state.

## 4. SUMMARY AND CONCLUDING REMARKS

We reviewed basic elements of the single-reference coupled-cluster theory, as developed by quantum chemists, and the results of our recent coupled-cluster and equation of motion coupled-cluster calculations for  $^{15}\text{O}$ ,  $^{16}\text{O}$ , and  $^{17}\text{O}$ . We demonstrated that the ground state of  $^{16}\text{O}$  is accurately described by the basic and relatively inexpensive CCSD method. The  $T_3$  clusters contribute less than 1% of the total binding energy and we attribute the 1 MeV per particle difference between the converged coupled-cluster and experimental binding energies of  $^{16}\text{O}$  to three-body forces. We believe that the  $\sim 6$  MeV difference between the converged equation of motion coupled-cluster results for the lowest-energy  $3^-$  state of  $^{16}\text{O}$  and the corresponding experimental excitation energy is due to an inadequate description of

the relevant nuclear forces by the two-body Idaho-A and N3LO Hamiltonians. This finding may point to the need for three-body interactions in such calculations. The CCSD method provides a reasonable description of nuclear matter density, charge radius, and charge form factor of  $^{16}\text{O}$ . Last, but not least, the PR-EOMCCSD and PR-EOMCCSD approximations provide encouraging results for the binding and excitation energies of  $^{15}\text{O}$  and  $^{17}\text{O}$ , although we need to examine the convergence of the PR-EOMCCSD and PR-EOMCCSD results with basis set. We demonstrated that the use of the renormalized rather than bare Hamiltonian guarantees fast convergence of the results with the number of major oscillator shells. All of this makes the low-cost coupled-cluster and equation of motion coupled-cluster methods developed in the context of electronic structure calculations a promising alternative to traditional shell-model diagonalization techniques used in nuclear physics. We hope that by developing *ab initio* many-body methods, such as coupled-cluster theory, which enable us to calculate important properties of many-body systems from the underlying particle-particle interactions, we may be able to unify various areas of quantum many-body theory into a single formalism. The use of coupled-cluster methods and computer algorithms developed by quantum chemists to address important questions in nuclear physics may be the first step toward the development of many-body theories that cross the boundaries of various physical sciences.

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