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# Ab initio coupled cluster calculations for nuclei using methods of quantum chemistry

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**Abstract.** We report preliminary large scale *ab initio* calculations of ground and excited states of $^{16}$O using quantum chemistry inspired coupled cluster methods and realistic two-body interactions. By using the renormalized Hamiltonians obtained with a no-core $G$-matrix approach, we obtain the virtually converged results at the level of two-body interactions. Due to the polynomial scaling with the system size that characterizes coupled cluster methods, we can probe large model spaces with up to seven major oscillator shells, for which standard non-truncated shell-model calculations are not possible.

**PACS.** 31.15.Dv Coupled cluster theory – 21.60.-n Nuclear structure models and methods

## 1 Introduction

One of the biggest challenges in nuclear physics is to understand how various properties, such as masses and excitation spectra arise from the nucleon-nucleon interactions. In recent years, construction of realistic nucleon-nucleon potentials and progress in the development of Monte Carlo [1] and no-core shell-model [2] techniques, combined with improvements in computer technology, have enabled to obtain converged results for nuclei with up to $A = 12$ nucleons, but one has to explore alternative approaches that do not suffer from the exponential growth of the configuration space with the system size and that could eventually be applied to medium-size systems in the mass 50–100 region. Coupled cluster theory [3,4] discussed in this paper is a particularly promising candidate for such an endeavor due to its ability to provide precise description of particle correlations at the relatively low computer cost when compared to shell-model or configuration interaction techniques aimed at similar accuracies [5,6].

Historically, coupled cluster theory originated in nuclear physics [3], but its applications to the nuclear many-body problem have been relatively rare (see, *e.g.*, [7]). On the other hand, after the early introduction of the coupled cluster wave function ansatz and diagrammatic methods of many-body theory into quantum chemistry by Čížek [4], coupled cluster methods have enjoyed tremendous success over a broad range of problems related to molecular structure, properties, and reactivity. All kinds of coupled cluster methods have been developed for closed-shell, open-shell, nondegenerate, and quasidegenerate ground and excited states of many-electron systems [5,6]. As a result, coupled cluster methods of the type of approximations discussed in this article can nowadays be routinely applied to many-electron systems containing dozens of light atoms, several transition metal atoms, hundreds of electrons and thousands of basis functions (see, *e.g.*, [8]). Several coupled cluster methods are available in the popular quantum chemistry software packages, enabling highly accurate *ab initio* calculations of useful molecular properties by non-experts. Much of this impressive development in coupled cluster theory made in quantum chemistry in the last 30 years still awaits applications to the nuclear many-body problem. In our view, the field of nuclear physics may significantly advance by adapting coupled cluster algorithms, developed in the context of electronic structure calculations, to the nuclear many-body problem.

Recent coupled cluster calculations for light nuclei using modern nucleon-nucleon interactions and methods similar to those used by quantum chemists show that one may be able to overcome the difficulties posed by the enormous dimensionalities of the shell-model eigenvalue

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problem. In particular, using bare interactions, Mihaila and Heisenberg performed large scale coupled cluster calculations for the binding energy and the electron scattering form factor of $^{16}$O [9]. We used a few quantum chemistry inspired coupled cluster methods and the renormalized interactions to compute ground- and excited-state energies of $^{4}$He and ground-state energies of $^{16}$O in a small model space consisting of 4 major oscillator shells [10]. These calculations indicate that quantum chemical coupled cluster methods combined with realistic nucleon-nucleon interactions and renormalized Hamiltonians can provide very good accuracies at the relatively low computer cost when compared to the exact shell-model diagonalization.

This paper highlights the results of our preliminary large-scale calculations of ground- and excited-state energies and properties of the $^{16}$O nucleus using a new system of efficient general-purpose coupled cluster computer programs for nuclear structure that we developed in recent months using the elegant diagram factorization techniques developed by quantum chemists [11,12]. While the earlier large-scale coupled cluster calculations of Mihaila and Heisenberg [9] used bare interactions, making the convergence with the number of single-particle basis states very slow, our calculations use the renormalized form of the Hamiltonian exploiting a no-core $G$-matrix approach [13], which allows us to obtain a rapid convergence with the number of major oscillator shells in a basis. The ground- and excited-state energies of $^{16}$O reported in this work were calculated in basis sets consisting of up to 7 major oscillator shells (336 single-particle states), whereas the properties other than energy, such as charge radius, were obtained in basis sets consisting of up to 6 major oscillator shells. This is a significant progress compared to our earlier calculations [10], in which we had to limit ourselves to 80 single-particle states and energy calculations only. The complete set of converged results will be reported elsewhere once we complete the calculations.

## 2 Theory and computational details

We begin our discussion with the construction of the suitable form of the effective Hamiltonian (see fig. 1 for the key components of our coupled cluster "machinery").

### 2.1 Effective Hamiltonian

In this work, we use the Idaho-A nucleon-nucleon potential [14] which was produced using techniques of chiral effective field theory [15]. The modern nucleon-nucleon interactions, such as Idaho-A, include short-range repulsive cores that require calculations in extremely large model spaces to reach converged results [9]. In order to remove the hard-core part of the interaction from the problem and allow for realistic calculations in manageable model spaces, we renormalize the interactions through a no-core $G$-matrix procedure [13], which introduces a starting-energy dependence $\tilde{\omega}$ in the effective two-body matrix elements $G(\tilde{\omega})$. We use the Bethe-Brandow-Petschek [16] theorem to alleviate much of the starting-energy dependence. As a result, the dependence of our results on $\tilde{\omega}$ is weak (see ref. [13] for details). After renormalization, our Hamiltonian is given by $H' = t + G(\tilde{\omega})$, where $t$ is the kinetic energy. We correct $H'$ for center-of-mass contaminations using the formula $H = H' + \beta_{\rm c.m.} H_{\rm c.m.}$, where $\beta_{\rm c.m.}$ is chosen such that the expectation value of the center-of-mass Hamiltonian $H_{\rm c.m.}$ is 0.0 MeV. This simple method of correcting $H'$ for center-of-mass contaminations has several advantages. One of them is the ease of separation of intrinsic and center-of-mass contaminated states by analyzing the dependence of the calculated coupled cluster energies on $\beta_{\rm c.m.}$. The physical eigenstates of the Hamiltonian are essentially independent of $\beta_{\rm c.m.}$ (see table 1 for the example). The center-of-mass contaminated states show a strong, nearly linear dependence of excitation energies on $\beta_{\rm c.m.}$. We are currently working on the alternative approach, in which instead of the $G$-matrix method, we will construct the renormalized Hamiltonian with the help of the Lee-Suzuki approach [17], exploited in no core shell-model calculations [2], which will eliminate the starting-energy dependence from our calculations.

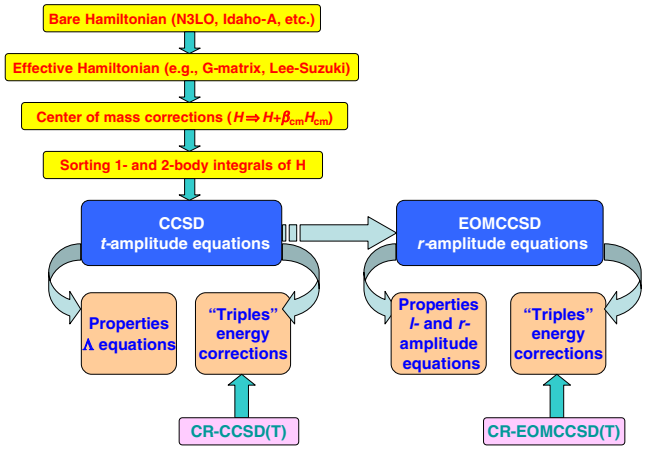


**Fig. 1.** The key components of the system of nuclear-structure coupled cluster programs used in this work.

**Table 1.** The excitation energies for the lowest $3^-$ state of $^{16}$O obtained with the EOMCCSD approach and a basis set of 5 major oscillator shells for a few values of $\beta_{\rm c.m.}$ (in MeV).

| $\beta_{\rm c.m.} = 0.5$ | $\beta_{\rm c.m.} = 1.0$ | $\beta_{\rm c.m.} = 1.5^{\rm (a)}$ |
|---|---|---|
| 13.413 | 13.497 | 13.574 |

(a) The optimum value of $\beta_{\rm c.m.}$ giving the expectation value of $H_{\rm c.m.}$ of 0.0 MeV.

### 2.2 Coupled cluster 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 theory. In order to construct coupled cluster equations in the most efficient way, we first 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.

Figure 1 provides information about the types of computations our system of nuclear-structure coupled cluster programs can perform at this time. We always begin with the basic CCSD ("coupled cluster singles and doubles") calculations, which provide information about the correlated ground state $|\Psi_0\rangle$. The CCSD method [18] is obtained by truncating the many-body expansion for the cluster operator $T$ in the exponential wave function ansatz exploited in coupled cluster theory, $|\Psi_0\rangle = \exp(T)|\Phi\rangle$, where $|\Phi\rangle$ is the reference determinant obtained by filling the lowest-energy oscillator states, at the 2-particle-2-hole ($2p$-$2h$) component $T_2$. Thus, the truncated cluster operator $T$ used in the CCSD calculations is $T = T_1 + T_2$, where $T_1 = \sum_{i,a} t_a^i a^a a_i$ and $T_2 = \frac{1}{4}\sum_{ij,ab} t_{ab}^{ij} a^a a^b a_j a_i$ are the singly and doubly excited clusters, $i, j, \ldots$ $(a, b, \ldots)$ are the single-particle states occupied (unoccupied) in the reference determinant $|\Phi\rangle$, and $a^p$ $(a_p)$ are the usual creation (annihilation) operators associated with the orthonormal single-particle states $|p\rangle$. We determine the singly and doubly excited cluster amplitudes $t_a^i$ and $t_{ab}^{ij}$, defining $T_1$ and $T_2$, respectively, by solving the nonlinear system of coupled, energy-independent, algebraic equations, $\langle\Phi_i^a|\bar{H}|\Phi\rangle = 0$, $\langle\Phi_{ij}^{ab}|\bar{H}|\Phi\rangle = 0$, where $\bar{H} = \exp(-T)\, H \exp(T)$, and $|\Phi_i^a\rangle = a^a a_i|\Phi\rangle$ and $|\Phi_{ij}^{ab}\rangle = a^a a^b a_j a_i|\Phi\rangle$ are the singly and doubly excited determinants, respectively, relative to the Fermi vacuum $|\Phi\rangle$. The explicit form of these and other equations used in coupled cluster calculations, in terms of matrix elements of the Hamiltonian and cluster amplitudes $t_a^i$ and $t_{ab}^{ij}$, can be derived by applying diagram factorization methods which yield vectorized computer codes [11,12]. Once $t_a^i$ and $t_{ab}^{ij}$ are determined, the ground-state CCSD energy $E_0^{\mathrm{CCSD}}$ is calculated as $E_0 = \langle\Phi|\bar{H}|\Phi\rangle$.

For the excited states $|\Psi_\mu\rangle$, we use the equation of motion (EOM) CCSD method [19] (equivalent to the linear response CCSD approach [20]), in which we write $|\Psi_\mu\rangle = R^{(\mu)}\exp(T)|\Phi\rangle$, where $T = T_1 + T_2$ and $R^{(\mu)} = R_0 + R_1 + R_2$ is a linear excitation operator, with $R_0$, $R_1$, and $R_2$ representing the relevant reference, one-body, and two-body components of $R^{(\mu)}$. Each $n$-body component of $R^{(\mu)}$ with $n > 0$ is a particle-hole excitation operator similar to $T_n$, *i.e.* $R_1 = \sum_{i,a} r_a^i a^a a_i$ and $R_2 = \frac{1}{4}\sum_{ij,ab} r_{ab}^{ij} a^a a^b a_j a_i$, where $r_a^i$ and $r_{ab}^{ij}$ are the corresponding excitation amplitudes. These amplitudes and the corresponding excitation energies $E_\mu - E_0$ are obtained by diagonalizing the similarity transformed Hamiltonian $\bar{H}$ in the relatively small space of singly and doubly excited determinants $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$. The similarity transformed Hamiltonian $\bar{H}$ is not hermitian, so that in addition to the right eigenstates $R^{(\mu)}|\Phi\rangle$, we can also determine the left eigenstates of $\bar{H}$, $\langle\Phi|L^{(\mu)}$, which define the "bra" coupled cluster wave functions $\langle\tilde{\Psi}_\mu| = \langle\Phi|L^{(\mu)}\exp(-T)$. Here, $L^{(\mu)}$ is a hole-particle de-excitation operator, so that $L_1 = \sum_{i,a} l_i^a a^i a_a$ and $L_2 = \frac{1}{4}\sum_{ij,ab} l_{ij}^{ab} a^i a^j a_b a_a$. The right and left eigenstates of $\bar{H}$ form a biorthonormal set, $\langle\Phi|L^{(\mu)}\, R^{(\nu)}|\Phi\rangle = \delta_{\mu\nu}$. The left eigenstates $\langle\Phi|L^{(\mu)}$ become important if we are to calculate properties other than energy, such as expectation values and transition matrix elements involving coupled cluster states $\langle\tilde{\Psi}_\mu|$ and $|\Psi_\nu\rangle$ [19]; $\langle\tilde{\Psi}_\mu|\theta|\Psi_\nu\rangle = \langle\Phi|L^{(\mu)}\,\overline{\theta}\,R^{(\nu)}|\Phi\rangle$, where $\overline{\theta} = \exp(-T)\theta\exp(T)$ is a similarity transformed property operator $\theta$. In particular, when $\theta = a^p a_q$ and $\mu = \nu$, we can determine the CCSD or EOMCCSD one-body reduced density matrices in quantum states $|\Psi_\mu\rangle$, which can in turn be used to calculate one-body properties, including charge and matter densities (in the CCSD ground-state case, where $T = T_1 + T_2$, we have $R^{(0)} = 1$ and $L^{(0)} = 1 + \Lambda_1 + \Lambda_2$, where $\Lambda_1$ and $\Lambda_2$ are obtained by solving the CCSD left eigenvalue problem, often referred to as the "lambda equations"; cf. fig. 1).

The CCSD and EOMCCSD methods capture the bulk of the correlation effects with the relatively 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 the effects of three-body clusters $T_3$ and three-body components $R_3$ and $L_3$ on the calculated ground- and excited-state energies and properties become important. We can estimate the effects of $T_3$ and $R_3$ on ground- and excited-state energies by adding the *a posteriori* corrections to the CCSD and EOMCCSD energies $E_\mu$, defining the CR-CCSD(T) and CR-EOMCCSD(T) approaches [6,12,21], which require the relatively inexpensive $n_o^3 n_u^4$ noniterative steps. These corrections can be calculated using the $T$ and $R^{(\mu)}$ operators obtained in the CCSD and EOMCCSD calculations. Here, we use variant "c" (or ID) of the ground-state CR-CCSD(T) approach [10] (see [21] for the original work).

**Table 2.** The energies of the ground state and the lowest $3^-$ state obtained with CCSD, CR-CCSD(T), and EOMCCSD, and $N = 5$, 6, and 7 major oscillator shells (in MeV) using the Idaho-A potential without Coulomb. The starting-energy value used in the calculations was $\tilde{\omega} = -80$ MeV.

| | Ground state | | The lowest $3^-$ state |
|---|---|---|---|
| $N$ | CCSD | CR-CCSD(T) | EOMCCSD |
| 5 | −125.92 | −126.26 | −112.35 |
| 6 | −121.53 | −121.76 | −108.55 |
| 7 | −120.16 | −120.76 | −108.20 |

## 3 Results and discussion

We discuss the preliminary large-scale coupled cluster calculations for $^{16}$O using methods described in sect. 2. Shown in table 2 are the energies of the ground state and the lowest $3^-$ state obtained with CCSD (ground state), EOMCCSD (the $3^-$ state) and CR-CCSD(T) (ground state), and 5, 6, and 7 major oscillator shells. The triples corrections to the EOMCCSD energies of the $3^-$ state will be calculated in the near future along with other excited

states and larger numbers of single-particle states to verify the rapid convergence observed here.

We demonstrated earlier [10] that the corrections due to $T_3$ clusters resulting from CR-CCSD(T) calculations are small in a basis including 4 major oscillator shells. The same is true when larger basis sets are employed (see table 2). Our results indicate that triples corrections to the ground-state energy in $^{16}$O are less than 1% of the total energy. For example, for the $N = 7$ calculation, the difference between the CCSD and CR-CCSD(T) results is 0.6 MeV. A simple extrapolation based on fitting the data in table 2 to $E(N) = E_\infty + a\exp(-b \cdot N)$, where $E_\infty$ is the extrapolated energy and $a$ and $b$ are coefficients for the fit shows that the extrapolated CR-CCSD(T) energy is $-120.5$ MeV. Coulomb adds to the binding approximately 11.2 MeV, so that our estimated Idaho-A ground state energy is $-109.3$ MeV, compared to an experimental value of $-128$ MeV. Thus, the two-body interactions underbind $^{16}$O by approximately 1 MeV per particle, leaving room for extra binding to be produced by three-nucleon interactions. Our preliminary conclusions are that connected three-body clusters are small and that the basic CCSD approximation produces a highly accurate estimate of the binding energy in $^{16}$O due to two-nucleon interactions. We plan to verify this statement by running calculations with 8 major oscillator shells and other interactions.

The first-excited $3^-$ state in $^{16}$O, located experimentally at 6.12 MeV above the ground state, is thought to be a $1p$-$1h$ state [22]. The vast experience of quantum chemistry with the EOMCCSD calculations for $1p$-$1h$ electronic states is telling us that the EOMCCSD method should describe the $3^-$ state of $^{16}$O well, if indeed this is a $1p$-$1h$ state and provided that the three-body interactions in the Hamiltonian can be neglected (there are no three-electron interactions in molecular systems). According to our EOMCCSD calculations, the largest excitation amplitudes for the $3^-$ state of $^{16}$O are for the $1p$-$1h$ excitations from the $0p_{1/2}$ orbital to the $0d_{5/2}$ orbital. The $2p$-$2h$ excitations in the EOMCCSD wave function are very small, confirming the $1p$-$1h$ nature of the lowest $3^-$ state. If we again extrapolate the CCSD and EOMCCSD energies for the ground and $3^-$ state, we obtain that the $3^-$ state is located at $-108.2$ MeV, *i.e.* 11.3 MeV above the CCSD ground state. The $\sim$ 5 MeV difference between the extrapolated EOMCCSD and experimental results suggests that we may have to incorporate higher–than–two-body clusters and/or three-nucleon interactions in the future to explain the observed discrepancy between theory and experiment. If the $3^-$ state is predominantly a $1p$-$1h$ state, triples effects should be small. This would mean that the observed discrepancy between theory and experiment may reside in the Hamiltonian. We plan to explore this issue by performing the CR-EOMCCSD(T) calculations for the first-excited $3^-$ state and other interactions.

We also performed the preliminary CCSD calculations of the ground-state density, using the recipe described in sect. 2. The resulting densities for the 5 and 6 major oscillator shells were used to determine the root-mean-square (r.m.s.) charge radii. After correcting for the finite sizes of the nucleons and the center-of-mass motion, we obtained 2.45 fm and 2.50 fm, respectively, in good agreement with experimental charge radius of $2.73 \pm 0.025$ fm.

In summary, we have developed a system of coupled cluster programs for nuclear structure calculations, using methods and algorithms developed in the context of electronic structure studies. We discussed our preliminary large scale calculations for the $^{16}$O nucleus. These calculations are among the first to probe, from an *ab initio* point of view, the structure of both the ground and excited states of $^{16}$O in enormous model spaces, for which non-truncated shell-model calculations are not possible.

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