The CCSD Energy Equations (And a gentle introduction to quantum chemistry)

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(Dated: Fall 2025)

I. INTRODUCTION

This write-up is meant to serve as a short, general introduction to coupled cluster methods for undergraduates in chemistry/physics.

In computational quantum chemistry, our primary concern is to describe the interactions of molecules using the tools of quantum physics. We write computer codes to solve the equations governing these systems, and can thereby simulate (usually by many approximations) what occurs in nature. Molecules consist of negatively charged electrons and positively charged nuclei. Opposite charges attract, and like charges repel each other. The forces these particles exert on each other depend on the magnitude of the charge, as well as the distance between the particles. Electrons are in constant motion surrounding the nuclei, occupying permissible volumes of space called orbitals. These orbitals can be thought of as places to put electrons.

The most basic property of our system that we typically care to solve for is the energy. The well-known Schrodinger equation allows us to solve for the energy of a quantum mechanical system. However, the exact solution is typically not possible to obtain, and approximations must be made. The most common starting point is called the Hartree Fock method. In this method, we use the approximation that each electron feels the repulsive forces of the other electrons based on the average of their positions to solve for the ground state energy and wavefunction (a function that describes our quantum system). This generally gives a very good approximation, but still misses out on the instantaneous, explicit electron-electron interactions (also called electron correlation). Because the electrons repel each other, there are nonzero probabilities that they will exist in higher energy orbitals (to "get away" from each other). The missing energy contribution due to these instantaneous interactions is denoted the correlation energy. One way to capture this correlation energy is to use coupled cluster theory, where we solve for the amplitudes (or "contributions") corresponding to all the possible permutations of our electrons occupying the various orbitals. In theory, this coupled cluster method gives us an exact solution to the Schrodinger equation given the approximations made in our reference wave function (the Hartree Fock result). However, due to the high computational cost of coupled cluster methods, a popular approximation is to only consider contributions where we permute one and two electrons at a time. This method is known as coupled cluster singles and doubles (CCSD). Section II below gives a

quick summary of the main equations involved in this procedure.

II.   THEORY

In order to start to understand coupled cluster methods, we must first begin with some rudimentary quantum mechanics (QM). In QM, our starting place begins with the Schrodinger equation (see Equation 1). If we want to solve for the energy of our system, we must apply the Hamiltonian operator $\hat{H}$ to our wavefunction $|\Psi\rangle$. The Hamiltonian "operates" on our wavefunction and gives us back our original wavefunction along with the energy E.

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{1}$$

The problem is we typically do not know what the true wavefunction of our system looks like beforehand. We need to solve for it. We know from the variational principle that any guess wavefunction will be of higher or equal energy to our true ground-state wavefunction. The most common starting point is then the Hartree-Fock (HF) procedure, where we start with a guess wavefunction and optimize some parameters until we arrive at an energy minimum for our guess wavefunction. This method performs very well in recovering most of the energy of our system. However, because it makes the approximation that each electron only feels the effects of the average position of other electrons in our system, it fails to capture the effect of electron correlation (the instantaneous electron-electron interactions). This is where coupled cluster (CC) methods come into play.

We begin by incorporating the CC wavefunction into the Schrodinger equation:

$$\hat{H}|\Psi_{\mathrm{CC}}\rangle = \hat{H}e^{\hat{T}}|\Phi_0\rangle = Ee^{\hat{T}}|\Phi_0\rangle \tag{2}$$

where we have defined our CC wavefunction as the application of the exponential of the cluster operator $e^{\hat{T}}$ on our reference HF wavefunction $|\Phi_0\rangle$. The cluster operator $\hat{T}$ is defined as:

$$\hat{T} = \sum_n \hat{T}_n \tag{3}$$

where n denotes the number of electrons excited at a time.

CCSD Equations

For example, for $n = 1$ we have:

$$\hat{T}_1 = \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i \tag{4}$$

In order to get an understanding of the meaning of this equation, we will analyze it piece by piece. Starting from the right and working to the left, we will first consider $\hat{a}_i$. This is an annihilation operator which performs the action of "deleting" an electron in orbital i ($i, j, k, ...$ are our lower energy, occupied orbitals). After deleting the electron in orbital i, we then apply the creation operator $\hat{a}_a^\dagger$, which "creates" an electron in orbital a ($a, b, c, ...$ are our higher energy, unoccupied orbitals). The t_i^a is the amplitude corresponding to the electrons configured in this way (where orbital i is empty and a is occupied) and is proportional to the probability of this configuration. The summation runs over all i and a, meaning that we are successively deleting electrons in lower energy orbitals, creating them in higher energy orbitals, and then solving for the corresponding amplitude. For clarity, the equation for $n = 2$ is shown below.

$$\hat{T}_2 = \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \tag{5}$$

Here we are considering contributions from the simultaneous excitations of $i \rightarrow a$ and $b \rightarrow j$.

The advantage in the use of the exponential formulation is due to the power series expansion:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + ... \tag{6}$$

and so we see that this implicitly includes higher order excitations through the higher order terms.

In CCSD, we truncate $\hat{T}$ at $n = 2$, meaning our Schrodinger equation takes the form:

$$\hat{H} e^{\hat{T}_1 + \hat{T}_2} |\Phi_0\rangle = E e^{\hat{T}_1 + \hat{T}_2} |\Phi_0\rangle \tag{7}$$

The full derivation of the equations implemented in the code is lengthy and the details go beyond the intended scope of this introduction. Essentially what we do from this point is a lot of algebraic manipulation and many applications of Wick's theorem to obtain sets of equations which allow us to iteratively solve for the sets of amplitudes (t_i^a and t_{ij}^{ab}) and the

energy, which depends on these amplitudes. I will, however, include the final equations as outlined in the paper from Gauss et al.[1] to allow the user to match them to those in the code. In Section IV, the equations defining the necessary intermediates and other miscellaneous terms are included. Section V includes the equations for both t1 and t2, and Section VI shows the energy equation. Details regarding the DIIS extrapolation can be found in the referenced paper by Scuseria et al.[2]

III. IMPLEMENTATION DETAILS

The program has four different scripts. The main driver is `runccsd.py`. This contains the loop that is responsible for iterating through the equations and checking for convergence at each step.

The information from the Hartree-Fock calculation is read-in in `readInp.py`. This reads in information such as number of occupied and unoccupied orbitals (`O` and `V`), the Hartree-Fock energy (`scfE`), the Fock matrix (`Fock`), the molecular orbital (MO) coefficients, (`Coeff`), and the two electron integrals in atomic orbital (AO) basis (`AOInt`). The CCSD equations are cast in terms of molecular spin-orbitals, and thus the change of basis from AO to MO is carried out here. The equation for the change of basis is shown below:

$$\langle pq||rs\rangle = \sum_{pqrs}\sum_{\mu\nu\lambda\sigma} C_\mu^p C_\nu^q C_\lambda^r C_\sigma^s \langle\mu\nu||\lambda\sigma\rangle \tag{8}$$

where p, q, r, s denote MO basis indices, and $\mu, \nu, \lambda, \sigma$ denote AO basis indices. The MO basis integrals are then sorted into arrays, whose dimensionality depends on the number of occupied and unoccupied orbitals (for example, `IJAB` corresponds to an array of dimensionality O^2V^2). These arrays are the sets of double bar integral terms which appear later in the equations in Sections IV-VI, represented in the form $\langle ij||ab\rangle$.

The file `ccsdEqs.py` contains the equations listed out in Sections IV-VI, and `diis.py` contains the DIIS extrapolation.

IV. INTERMEDIATES

$$D_i^a = f_{ii} - f_{aa} \tag{9}$$

CCSD Equations

$$D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb} \tag{10}$$

$$P_{\pm}(pq) = 1 \pm \mathcal{P}(pq) \tag{11}$$

$$\tilde{\tau}_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2}(t_i^a t_j^b - t_i^b t_j^a) \tag{12}$$

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a \tag{13}$$

$$\mathcal{F}_{ae} = (1 - \delta_{ae}) - \frac{1}{2}\sum_m f_{me} t_m^a + \sum_{mf} t_m^f \langle ma||fe \rangle - \frac{1}{2}\sum_{mnf} \tilde{\tau}_{mn}^{af} \langle mn||ef \rangle \tag{14}$$

$$\mathcal{F}_{mi} = (1 - \delta_{mi}) f_{mi} + \frac{1}{2}\sum_e t_i^e f_{me} + \sum_{en} t_n^e \langle mn||ie \rangle + \frac{1}{2}\sum_{nef} \tilde{\tau}_{in}^{ef} \langle mn||ef \rangle \tag{15}$$

$$\mathcal{F}_{me} = f_{me} + \sum_{nf} t_n^f \langle mn||ef \rangle \tag{16}$$

$$\mathcal{W}_{mnij} = \langle mn||ij \rangle + P_-(ij) \sum_e t_j^e \langle mn||ie \rangle + \frac{1}{4}\sum_{ef} \tau_{ij}^{ef} \langle mn||ef \rangle \tag{17}$$

$$\mathcal{W}_{abef} = \langle ab||ef \rangle - P_-(ab) \sum_m t_m^b \langle am||ef \rangle + \frac{1}{4}\sum_{mn} \tau_{mn}^{ab} \langle mn||ef \rangle \tag{18}$$

V. AMPLITUDES

$$t_i^a D_i^a = f_{ia} + \sum_e t_i^e \mathcal{F}_{ae} - \sum_m t_m^a \mathcal{F}_{mi} + \sum_{me} t_{im}^{ae} \mathcal{F}_{me} - \sum_{nf} t_n^f \langle na||if \rangle$$
$$- \frac{1}{2}\sum_{mef} t_{im}^{ef} \langle ma||ef \rangle - \frac{1}{2}\sum_{men} t_{mn}^{ae} \langle nm||ei \rangle \tag{19}$$

$$t_{ij}^{ab} D_{ij}^{ab} = \langle ij||ab \rangle + P_-(ab) \sum_e t_{ij}^{ae} \left(\mathcal{F}_{be} - \frac{1}{2} \sum_m t_m^b \mathcal{F}_{me} \right)$$

$$- P_-(ij) \sum_m t_{im}^{ab} \left(\mathcal{F}_{mj} + \frac{1}{2} \sum_e t_j^e \mathcal{F}_{me} \right) + \frac{1}{2} \sum_{mn} \tau_{mn}^{ab} \mathcal{W}_{mnij} + \frac{1}{2} \sum_{ef} \tau_{ij}^{ef} \mathcal{W}_{abef}$$

$$+ P_-(ij) P_-(ab) \sum_{me} \left(t_{im}^{ae} \mathcal{W}_{mbej} - t_i^e t_m^a \langle mb||ej \rangle \right)$$

$$+ P_-(ij) \sum_e t_i^e \langle ab||ej \rangle - P_-(ab) \sum_m t_m^a \langle mb||ij \rangle \quad (20)$$

VI.   ENERGY

$$E_{\mathrm{CCSD}} = \sum_{ai} t_i^a f_{ia} + \frac{1}{4} \sum_{abij} \tau_{ij}^{ab} \langle ij||ab \rangle \qquad (21)$$

REFERENCES

[1] J. Gauss, J. F. Stanton, and R. J. Bartlett, "Coupled-cluster open-shell analytic gradients - implementation of the direct-product decomposition approach in energy gradient calculations," J. Chem. Phys. **95**, 2623–2638 (1991).

[2] G. E. Scuseria, T. J. Lee, and H. F. Schaefer, "Accelerating the convergence of the coupled-cluster approach: The use of the diis method," Chem. Phys. Lett. **130**, 236–239 (1986).