A COUPLED CLUSTER TECHNIQUE WITH ITERATIVE BOGOLIUBOV TRANSFORMATIONS FOR COMPUTING EIGENVALUES OF PERTURBED QUANTUM HARMONIC OSCILLATORS

by

Carson Huey-You

Bachelor of Science, May 2017
Texas Christian University
Fort Worth, Texas

Submitted to the Graduate Faculty of the
College of Science and Engineering
Texas Christian University
in partial fulfillment of the requirements
for the degree of

Master of Science
December 2019

ACKNOWLEDGEMENTS

I would like to truly thank all of the people who have supported me on my journey to this point in my studies. First and foremost, Dr. Rittby has been an incredibly positive influence in my life - not only as my advisor, but also as a mentor. I'm so grateful to him for his part in advancing my scientific knowledge, life advice and even just for his encouragement in times when I needed it. He has really looked out for me from the very first day I came to TCU, and I can't express how appreciative I am for all of his help and guidance.

I'm beyond thankful to my family, who have shown me nothing but love and support as well. To my mom and my brother, thank you both *especially* for always being there for me. I really can't thank either of you enough for all that you've done, and I'll always be there for you in the same way. The same goes for any extended family, church family, and even for close friends - your support, prayers and encouragement have had an incredible effect on me as a person, and I cannot thank all of you enough for it.

Lastly, I would like to thank all of my fellow graduate students and all of the faculty here. You're all responsible for the amazing environment in the Physics & Astronomy department, and I can't thank you enough for that. Thanks to you, this place has become a second home for me in many ways, and I'm so so proud to be a part of it.

CONTENTS

LIST OF FIGURES

1. Introduction

1.1. Motivation

Molecules are complex many-body systems of electrons and nuclei, and being able to describe such systems accurately is an ongoing challenge. In this paper, we will be interested in improving the description of the relative motion of nuclei in a molecule, i.e. improving the description of molecular vibrations. The non-relativistic Hamiltonian governing the electron-electron, electron-nuclei and nuclei-nuclei interactions can be approximated using the so called Born-Oppenheimer approximation so as to separate the electronic and nuclear degrees of freedom. This allows for nuclear motion to be described as the motion on a multi-dimensional potential energy surface. Continuous advances in theoretical models for the solution of the systems of electronic many-body problem have led to the ability to calculate increasingly more accurate potential energy surfaces, thereby improving the accuracy of molecular structure and properties. Since potential energy surfaces are essential for the description of nuclear motion, improvements in their quality also open up the possibility for improving on the prediction of vibrational transition frequencies and probabilities. Due in part to the high dimensionality of the problem, vibrational frequencies have typically only been conducted using the harmonic approximation where the potential is approximated by the first non-zero term in a Taylor expansion about a minimum on the potential surface. While this may be adequate for low-level vibrational excitations, more accurate results can be obtained by including additional terms in the Taylor expansion of the potential, albeit with a dramatic increase in computational complexity.

Spectroscopy is defined as the study of the interaction between matter and electromagnetic radiation. The resulting spectra of a certain sample provides information about transition energies and transition probabilities between different quantum mechanical states of its constituent molecules, and can be used to infer

information about their environment, such as temperature and pressure. Information about geometric symmetries can also be revealed in spectral patterns, due to the effects of isotopic substitution. Vast data sets have over time been compiled listing atomic and molecular transition frequencies. Such data sets can in turn be used to identify the constituents of an unknown sample, by studying the observed spectral patterns. One particularly important application of spectroscopic knowledge is in astronomy, where observed transition energies can help determine which atomic and molecular species are in, for example, a gas cloud or a stellar atmosphere.

The current focus of the research is in the generation and analysis of general and isotopic spectral results, which for many experiments contain a mixture of isotopomers for multiple molecules (1). Therefore, assigning observed transition energies to their corresponding molecules requires an accurate study of vibrational frequency patterns and intensities. The evolution of better and better theoretical and computational methods has increased our ability to generate simulated spectra of new molecules for comparison with experiment and in doing so, simplifying the identification of new species.

In this paper, we investigate a new method of calculating vibrational state energies, taking advantage of coupled cluster (CC) techniques. This process can be thought of as solving two distinct problems. Firstly, one must develop a method in order to accurately generate so-called 'anharmonic parameters' from the potential energy surface, from higher-order cubic and quartic terms in the Taylor expansion of the potential energy. The second problem is finding a solution for eigenvalues of a coupled set of perturbed harmonic oscillators, discussed in detail in this paper. Although we are aware of a number of implementations of similar approaches, the aim of the project is to create our own independent computer codes which will allow us the ability to create our own extensions to the code and pursue the implementation of new methods as they are developed.

1.2. Anharmonic Molecular Vibrations

We first begin with a general mathematical description of molecular motion, from the Hamiltonian of a molecular system (in atomic units).

$$H = -\sum_{i}^{el} \frac{1}{2}\nabla_i^2 - \sum_{A}^{nuc} \frac{1}{2m_A}\nabla_A^2 - \sum_{i}^{el}\sum_{A}^{nuc} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{el} \frac{1}{r_{ij}} + \sum_{A>B}^{nuc} \frac{Z_A Z_B}{r_{AB}} \tag{1.1}$$

Here, we have included the kinetic energy of both the electron and nuclei, as well as the potential energy for electronuclear attraction, electronic repulsion, and internuclear repulsion. In the first step of the Born-Oppenheimer approximation, nuclear kinetic energy is assumed to be negligible. Then, the remaining terms are gathered into an 'electronic Hamiltonian' H_{el}, which has eigenvalues only dependent on nuclear coordinates. Using $\mathbf{r}_i$ and $\mathbf{r}_A$ to denote sets of all electronic and nuclear coordinates respectively, we find:

$$\sum_{A}^{nuc} \frac{1}{2m_A}\nabla_A^2 \approx 0 \quad \Rightarrow \quad H_{el}(\mathbf{r}_i, \mathbf{r}_A)\psi_{el}(\mathbf{r}_i, \mathbf{r}_A) = E_{el}(\mathbf{r}_A)\psi_{el}(\mathbf{r}_i, \mathbf{r}_A) \tag{1.2}$$

Varying nuclear coordinates will give rise to a multi-dimensional 'potential energy surface' (PES), given by $E_{el}(\mathbf{r}_A)$. In other words, each molecular geometry directly corresponds to a different potential energy. A number of methods with varying accuracy have been developed in quantum chemistry in order to handle this problem (2; 3; 4). In our case, we are concerned with molecular vibration, which is motion about a certain equilibrium geometry of the molecule. This would correspond to a local minimum on the potential surface. Modeling the potential surface around a given minimum for N nuclei can be done via a Taylor expansion where, for convenience, we have set the potential to zero at the minimum.

$$V(x_1, x_2, ...x_{3N}) = \frac{1}{2!}\sum_{pq}\left(\left.\frac{\partial^2 V}{\partial x_p \partial x_q}\right|_{eq}\right) x_p x_q + \frac{1}{3!}\sum_{pqr}\left(\left.\frac{\partial^3 V}{\partial x_p \partial x_q \partial x_r}\right|_{eq}\right) x_p x_q x_r + \\ + \frac{1}{4!}\sum_{pqrs}\left(\left.\frac{\partial^4 V}{\partial x_p \partial x_q \partial x_r \partial x_s}\right|_{eq}\right) x_p x_q x_r x_s + ... \tag{1.3}$$

Rather than using Cartesian coordinates, the surface is more conveniently expanded in normal-mode coordinates:

$$q_i = \sum_{j=1}^{N}\sum_{s=1}^{3} c(i)_{js}\sqrt{m_j}x_{js} \tag{1.4}$$

These coordinates are linear combinations of mass-weighted nuclear displacement coordinates, defined such that the harmonic term is diagonalized. In this representation, translational and rotational degrees of freedom can be separated, and the potential governing nuclear vibrations can be Taylor expanded about an equilibrium point:

$$V(q_1, q_2, ...q_M) = \frac{1}{2!}\sum_{p}\left(\left.\frac{\partial^2 V}{\partial q_p^2}\right|_{eq}\right) q_p^2 + \frac{1}{3!}\sum_{pqr}\left(\left.\frac{\partial^3 V}{\partial q_p \partial q_q \partial q_r}\right|_{eq}\right) q_p q_q q_r + \\ + \frac{1}{4!}\sum_{pqrs}\left(\left.\frac{\partial^4 V}{\partial q_p \partial q_q \partial q_r \partial q_s}\right|_{eq}\right) q_p q_q q_r q_s + ... \tag{1.5}$$

where $M = 3N - 5$ ($3N - 6$ if the molecule is linear) denotes the number of vibrational modes.

We next use the first term in this expansion and define a set of unperturbed harmonic oscillator Hamiltonians.

$$H_0 = \sum_i \left(-\frac{1}{2}\frac{\partial^2}{\partial q_i^2} + \frac{1}{2}\omega_i q_i^2\right) \tag{1.6}$$

Figure 1 shows a generic depiction of a potential molecular energy surface. Although any potential is harmonic around a local minimum for sufficiently small displacement, this figure illustrates that we generally have to view the surface as anharmonic in order to get an accurate description of nuclear motion.

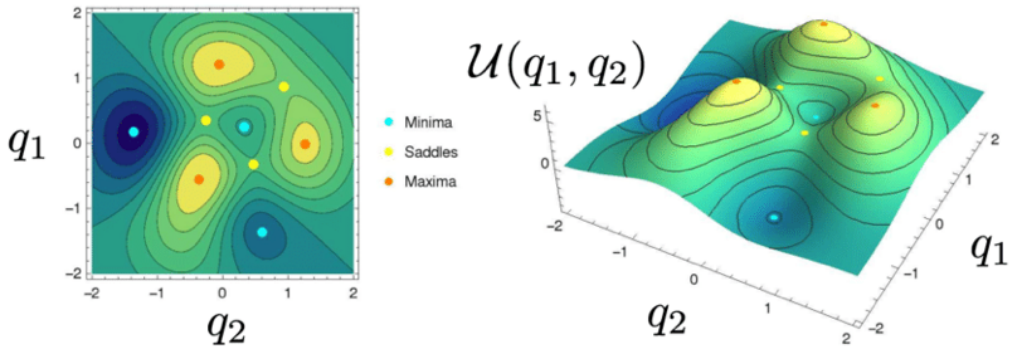


Fig. 1.— A generic depiction of a potential energy surface for a molecule with multiple vibrational degrees of freedom (q_1 and q_2 depict arbitrary coordinates).

While even higher order terms could be included in the Taylor expansion, it quickly becomes important to notice the dimensionality of the problem. Given the number of vibrational degrees of freedom, calculating higher-order derivatives of the potential energy surface is computationally costly even for relatively small molecules. With the advance of numerical techniques and computer speeds, such calculations will become increasingly feasible. To date however, most practical applications have made use of the harmonic approximation, with vibrational frequencies simply being obtained from a mass-weighted Hessian matrix (which has matrix elements consisting of second-order derivates of the PES).

Although harmonic frequencies can often be sufficiently accurate for many applications, in some cases even small changes in the second derivative of the potential can give rise to problems when attempting to identify a particular molecular spectrum.

Figure 2 shows simulations of the isotopic spectrum of the ν_6 (σ_u) mode of linear C_9 at the harmonic approximation using three different models for solving the electronic many-body problem. As is apparent from the figure, the isotopic pattern differs quite remarkably between the three calculations.

Even though this situation is quite unusual, it speaks to the need for highly accurate potential energy surfaces for certain applications and the desire to be able to include anharmonic effects. Note that all three full ^{12}C isotopomers have been scaled to coincide the experimental value of 1998.0 cm^{-1} (5).

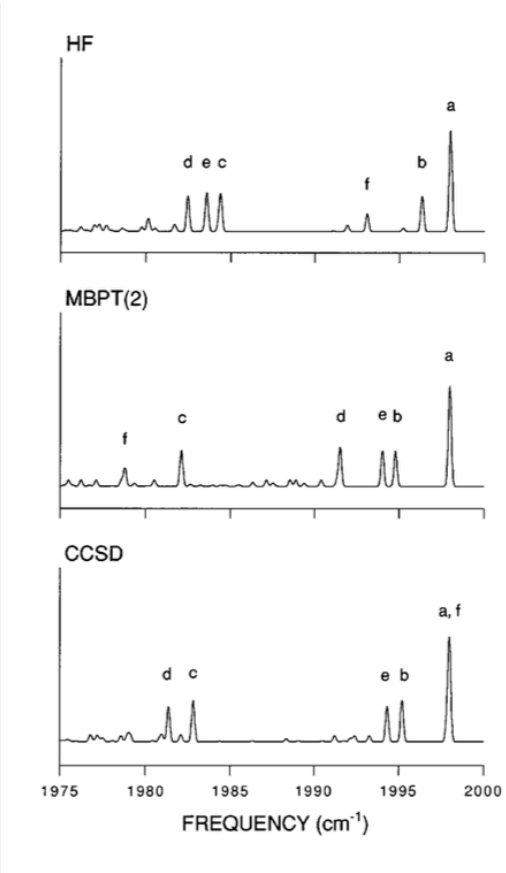


Fig. 2.— Comparison of harmonic isotopic spectra obtained via Hartree-Fock (Top, HF); Many-Body Perturbation Theory to Second-Order (Middle, MBPT2); and Coupled-Cluster Theory with Single & Double Excitations (Bottom, CCSD) methods.

As seen from the potential expressions in equation (1.5), this leads to the necessity of obtaining higher-order derivatives of the potential energy surface as well as solving the Schrödinger equation for a set of coupled perturbed harmonic oscillators, each presenting its own challenges. In this paper, we will focus on finding solutions to the second problem, calculating eigenvalues of a set of perturbed harmonic oscillators.

2. Methodology

2.1. Ladder Operators and the Unperturbed Hamiltonian

Rather than using the operators q_i and $p_i = -i\dfrac{\partial}{\partial q_i}$ to represent position and momentum for our harmonic oscillators in our normal coordinate space, we will recast the problem by making use of the canonical 'ladder operator' formalism, as follows. We first define the creation and annihilation operators for each mode, $a_i^\dagger$ and a_i respectively.

$$a_i^\dagger = \sqrt{\frac{\omega_i}{2}}\left(q_i - \frac{i}{\omega_i}p_i\right) \qquad ; \qquad a_i = \sqrt{\frac{\omega_i}{2}}\left(q_i + \frac{i}{\omega_i}p_i\right) \tag{2.1}$$

For reference, this relation can be inverted so that:

$$q_i = \sqrt{\frac{1}{2\omega_i}}\left(a_i^\dagger + a_i\right) \qquad ; \qquad p_i = i\sqrt{\frac{\omega_i}{2}}\left(a_i^\dagger - a_i\right) \tag{2.2}$$

These operators satisfy the following canonical bosonic commutation relations.

$$[a_i, a_j^\dagger] = \delta_{ij} \qquad ; \qquad [a_i, a_j] = 0 \qquad ; \qquad [a_i^\dagger, a_j^\dagger] = 0 \tag{2.3}$$

These operators have the following important properties. All annihilation operators kill the vacuum.

$$a_i \left|0\right\rangle = 0 \tag{2.4}$$

A creation operator increases the number of quanta for a particular oscillator when acting on the system ket.

$$a_i^\dagger \left|n_1, n_2, ..., n_N\right\rangle = \sqrt{n_i + 1}\left|n_1, n_2, ..., n_i + 1, n_N\right\rangle \tag{2.5}$$

An annihilation operator decreases the number of quanta for a particular oscillator when acting on the system ket.

$$a_i \left|n_1, n_2, ..., n_N\right\rangle = \sqrt{n_i}\left|n_1, n_2, ..., n_i - 1, n_N\right\rangle \tag{2.6}$$

The number operator returns the number of quanta when acting on the system ket.

$$N_i \left|n_1, n_2, ..., n_N\right\rangle = a_i^\dagger a_i \left|n_1, n_2, ..., n_N\right\rangle = n_i \left|n_1, n_2, ..., n_N\right\rangle \tag{2.7}$$

In terms of the ladder operators, the Schrödinger equation for the unperturbed system of N oscillators with individual frequencies ω_i can then be expressed as:

$$\begin{aligned} H_0 &= \sum_{i=1}^{N} \left(N_i + \frac{1}{2}\right) \omega_i = \sum_{i=1}^{N} \left(a_i^\dagger a_i + \frac{1}{2}\right) \omega_i \\ H_0 \left|n_1, n_2, ..., n_N\right\rangle &= E_{n_1,n_2,...,n_N} \left|n_1, n_2, ..., n_N\right\rangle \end{aligned} \tag{2.8}$$

with the eigenenergies for the system given by:

$$E_{n_1,n_2,...,n_N} = \sum_i \left(n_i + \frac{1}{2}\right) \omega_i \tag{2.9}$$

By making use of the ladder operator representation, we have in effect transformed the original set of differential equations to a set of algebraic equations. We note that this is a conceptually very satisfying picture of molecular vibrations, i.e each vibrational mode is described as a harmonic oscillator and excited vibrational states are simply described by providing the appropriate set of integers $(n_1, n_2, ..., n_N)$.

2.2. The Form of the Anharmonic Perturbation

Consider now the unperturbed Hamiltonian H_0, perturbed by some potential V. In our case, the perturbation is obtained from the Taylor expansion around the minimum of a potential surface encountered earlier. Consisting of powers of the normal mode coodinate, the perturbing potential can of course also be expressed in terms of ladder operators.

We will assume that this potential has been normal-ordered, i.e. the commutation relations between the ladder operators have been used in such a way that all strings of operators are of the form $(a_i^\dagger a_j^\dagger ...)(a_r a_s ...)$. (We will discuss this further in the section

on Wick's theorem). Upon normal ordering, we can write the potential in the terms of contributions V_m

$$V = V_0 + V_1 + V_2 + V_3 + V_4 + ... \tag{2.10}$$

such that each term V_m, consists of all possible combinations of m normal ordered creation and annihilation operators. For a potential containing up to quartic terms in the normal mode coordinate, the normal ordered potential takes on the following form.

$$\begin{aligned}
V_0 &= (constant) \quad ; \quad V_1 = \sum_a \left(A_a a_a^\dagger + A^a a_a \right) \\
V_2 &= \sum_{ab} \left(\frac{1}{2!} B_{ab} a_a^\dagger a_b^\dagger + J_a^b a_a^\dagger a_b + \frac{1}{2!} B^{ab} a_a a_b \right) \\
V_3 &= \sum_{abc} \left(\frac{1}{3!} C_{abc} a_a^\dagger a_b^\dagger a_c^\dagger + \frac{1}{2!} K_{ab}^c a_a^\dagger a_b^\dagger a_c + \frac{1}{2!} K_a^{bc} a_a^\dagger a_b a_c + \frac{1}{3!} C^{abc} a_a a_b a_c \right) \\
V_4 &= \sum_{abcd} \left(\frac{1}{4!} D_{abcd} a_a^\dagger a_b^\dagger a_c^\dagger a_d^\dagger + \frac{1}{3!} L_{abc}^d a_a^\dagger a_b^\dagger a_c^\dagger a_d + \frac{1}{2!}\frac{1}{2!} M_{ab}^{cd} a_a^\dagger a_b^\dagger a_c a_d + \right. \\
&\qquad \left. \frac{1}{3!} L_a^{bcd} a_a^\dagger a_b a_c a_d + \frac{1}{4!} D^{abcd} a_a a_b a_c a_d \right)
\end{aligned} \tag{2.11}$$

In what follows we will seek solutions to the Schrödinger equation where the perturbing potential is exactly of this form, thereby modeling a system of nuclei moving in an anharmonic potential.

Here we note that the coefficients in the equation above must satisfy certain symmetry requirements. We know that since the operators fulfill the commutation relations in equation (2.3), purely changing the order of subscripts or superscripts can cause no change in the corresponding coefficient (e.g. $M_{ab}^{cd} = M_{ab}^{dc} = M_{ba}^{cd} = M_{ba}^{dc} \neq M_{ac}^{bd}$). Additionally, we can make use of the fact that in our application V is assumed to be Hermitian. Therefore, swapping subscripts and superscipts of a coefficient is equivalent to taking the complex conjugate (e.g. $L_{abc}^{d*} = L_d^{abc}$).

The mathematical solutions for single quartic oscillators have been studied extensively in the literature through a variety of techniques (see for examples (6-13)),

and can serve as a reference for evaluating the method we have developed. However, explicit details for the treatment of a system of coupled quartic oscillators in the literature is lacking.

2.3. Perturbation Theory

One commonly encountered approach for finding eigenvalues for systems where we can divide the Hamiltonian into an unperturbed Hamiltonian, for which solutions are known, and a perturbation, is by the use of perturbation theory. In perturbation theory, the energies as well as the eigenvectors are expressed in an order-by-order expansion in terms of powers of the perturbation strength. For reference, here we give a compact presentation of the expansion of the energy eigenvalues by use of the Bracketing Theorem.

Let us define a bracketing $\langle X\rangle = \langle\alpha|X|\alpha\rangle$, where $|\alpha\rangle$ is the unperturbed ket for the state for which the perturbed energy is sought. For the general case of multiple oscillators, $|\alpha\rangle$ could represent any combination of excitations in the system. We can then define the resolvent, R, as follows.

$$R = \sum_{\beta\neq\alpha} \frac{|\beta\rangle\langle\beta|}{E_\alpha - E_\beta} \tag{2.12}$$

The order-by-order energy corrections due to a perturbation V are now given by:

$$\begin{aligned}
E^{(1)} =& \langle V\rangle \qquad ; \qquad E^{(2)} = \langle VRV\rangle \\
E^{(3)} =& \left\langle V\left(RV\right)^2\right\rangle - \langle V\rangle\left\langle VR^2V\right\rangle \\
E^{(4)} =& \left\langle V\left(RV\right)^3\right\rangle - \langle V\rangle\left[\left\langle VR\left(RV\right)^2\right\rangle + \left\langle\left(VR\right)^2RV\right\rangle\right] + \\
& \langle V\rangle^2\left\langle VR^3V\right\rangle - \langle VRV\rangle\left\langle VR^2V\right\rangle \\
& ...etc.
\end{aligned} \tag{2.13}$$

The nth order contribution consists of a 'principal' leading term $\langle V(RV)^{n-1}\rangle$. In addition, there are contributions from terms where bracketing has been inserted around $V,\ VRV, ...$ in all possible ways in the principal term. Bracketings which include the left and rightmost V vanish. Each bracketing term is multiplied by a sign given by $(-1)^{n_B}$, where n_B is the number of bracketings in the term. Bracketings within bracketings are also allowed.

Given the bracketing rules there can be no additional bracketing terms in first and second order since they would have to involve the left and/or rightmost V. In third order, however, we have the possibility to form the bracketing term $\langle VR\langle V\rangle RV\rangle = \langle V\rangle \langle VR^2V\rangle$. No more bracketings are possible. In fourth order there are four possible bracketings. In general the total number of term for each order n, including the principal term, equals $\dfrac{(2n-2)!}{n!(n-1)!}$.

As an example of the resolvent raised to a power, we can write out:

$$R^2 = \sum_{\beta\neq\alpha}\sum_{\gamma\neq\alpha} \frac{|\beta\rangle\langle\beta|\gamma\rangle\langle\gamma|}{(E_\alpha - E_\beta)(E_\alpha - E_\gamma)} = \sum_{\beta\neq\alpha}\sum_{\gamma\neq\alpha} \frac{|\beta\rangle\delta_{\beta\gamma}\langle\gamma|}{(E_\alpha - E_\beta)(E_\alpha - E_\gamma)} = \sum_{\beta\neq\alpha} \frac{|\beta\rangle\langle\beta|}{(E_\alpha - E_\beta)^2} \tag{2.14}$$

Interpreting the order-by-order expressions using the definitions above, we can recoup the more familiar expressions for the energy contributions, e.g.

$$\begin{aligned} E^{(1)} &= \langle\alpha|V|\alpha\rangle \qquad ; \qquad E^{(2)} = \sum_{\beta\neq\alpha} \frac{\langle\alpha|V|\beta\rangle\langle\beta|V|\alpha\rangle}{(E_\alpha - E_\beta)} \\ E^{(3)} &= \sum_{\beta\neq\alpha}\sum_{\gamma\neq\alpha} \frac{\langle\alpha|V|\beta\rangle\langle\beta|V|\gamma\rangle\langle\gamma|V|\alpha\rangle}{(E_\alpha - E_\beta)(E_\alpha - E_\gamma)} - \langle\alpha|V|\alpha\rangle \sum_{\beta\neq\alpha} \frac{\langle\alpha|V|\beta\rangle\langle\beta|V|\alpha\rangle}{(E_\alpha - E_\beta)^2} \end{aligned} \tag{2.15}$$

...etc.

2.4. The Coupled Cluster Approach

In the current paper, we will be making use of a different perturbative approach termed coupled cluster theory, to find solutions for perturbed harmonic oscillators.

This approach differs from perturbation theory by including contributions from singly, doubly, etc. excited states to infinite order. In other words - perturbation theory truncates the order by which we accumulate energy corrections, but includes all possible excitations at a given order, while coupled cluster theory collects energy contributions by considering up to infinite order contributions from specific levels of excitation.

In the present paper we will make use of the so-called Equation of Motion Coupled Cluster (EoM-CC) approach to calculate the ground state and excited state energies for a perturbed system. In the process of developing this model, we will first present the basic approach which coupled cluster methods take to find the perturbed ground state, using an exponential operator to generate all possible excitations from the unperturbed ground state. Before being able to derive the operating equations for specific perturbations, we will present a set of tools which will enable us to efficiently generate the necessary terms in our equations. This approach compares closely to the first implementation of the EoM-CC approach for the many-electron problem (14), although here the quasi-particles abide by the commutation rules for bosonic operators (vibrational quanta) as opposed to the anti-commutation rules for fermions (electronic quanta). Variants of this method have been applied to a general study of the vibrational structure of molecules (15) and have been proven to be relatively accurate compared to other methods (16). One of the goals of the current paper is to develop the details of this approach independently and explore novel ways in which the method can be expanded to provide more accurate results.

We begin by considering the Schrödinger equation for the ground state of our perturbed system. We will denote the perturbed ground state by $|\tilde{0}\rangle$.

$$(H_0 + V)|\tilde{0}\rangle = H|\tilde{0}\rangle = \tilde{E}_0|\tilde{0}\rangle \tag{2.16}$$

It is fair to assume that the perturbed ground state has a non-zero overlap with the unperturbed ground state, such that $\langle 0|\tilde{0}\rangle \neq 0$. In this case, since the unperturbed

solutions form a complete set, we may write the perturbed ground state as a linear combination of all possible unperturbed excitations. In the EoM-CC method, this is done using the cluster operator T.

$$\begin{aligned} |\tilde{0}\rangle &= e^T|0\rangle = \left(1 + T + \frac{1}{2!}T^2 + \frac{1}{3!}T^3 + ...\right)|0\rangle \\ T &= T_1 + T_2 + T_3 + ... = \sum_k t_k a_k^\dagger + \frac{1}{2!}\sum_{kl} t_{kl} a_k^\dagger a_l^\dagger + \frac{1}{3!}\sum_{klm} t_{klm} a_k^\dagger a_l^\dagger a_m^\dagger + ... \end{aligned} \tag{2.17}$$

The lowercase t coefficients for each cluster operator are referred to as 'cluster amplitudes'. We can use this relation to rewrite the perturbed Schrödinger equation, in order to directly solve for $\tilde{E}_0$.

$$H|\tilde{0}\rangle = He^T|0\rangle = \tilde{E}_0 e^T|0\rangle \quad ; \quad e^{-T}He^T|0\rangle = \tilde{E}_0|0\rangle \quad ; \quad \tilde{E}_0 = \langle 0|e^{-T}He^T|0\rangle \tag{2.18}$$

The perturbed ground state and its energy can thus be obtained if we can determine the cluster amplitudes defined in equation (2.17). In order to do so we project the above Schrödinger equation with all possible unperturbed excited states.

$$\begin{aligned} \langle 0|a_i e^{-T}He^T|0\rangle = 0 \quad &\rightarrow \quad t_i \\ \langle 0|a_i a_j e^{-T}He^T|0\rangle = 0 \quad &\rightarrow \quad t_{ij} \\ \langle 0|a_i a_j a_k ... e^{-T}He^T|0\rangle = 0 \quad &\rightarrow \quad t_{ijk...} \end{aligned} \tag{2.19}$$

Since the cluster expansion is an infinite series, the process will generally result in an infinite number of coupled non-linear equations, providing the necessary cluster amplitudes when solved. This introduces the need to truncate the cluster expansion at some level. Of course, including higher order excitations in the cluster operator T gives rise to better approximations of the ground state, but it is also important to note here that the expressions for the ground state energy in equation (2.18) as well as for the cluster amplitudes in equation (2.19) are self-truncating for a given perturbation as a result of the Baker-Campbell-Hausdorff (BCH) expansion of the operator $e^{-T}He^T$.

$$e^{-T}He^T = H + [H,T] + \frac{1}{2!}[[H,T],T] + \frac{1}{3!}[[[H,T],T],T] + ... \tag{2.20}$$

2.5. Wick's Theorem

The brute force way to evaluate the commutators in the BCH expansion from (2.20) is by directly applying the commutation relations for our ladder operators. A more effective approach is making use of Wick's theorem. In a future section, we use these results to create a diagrammatic scheme, which is significantly faster and more visually intuitive. Using the commutator relationship between our operators, we begin by writing:

$$\left[a_i, a_j^\dagger\right] = \delta_{ij} \qquad ; \qquad a_i a_j^\dagger = a_j^\dagger a_i + \delta_{ij} \tag{2.21}$$

While this seems straightforward, longer strings of operators will require multiple steps of using this relation, which is an arduous task at best. In order to simplify this process, we will formally define the following notation:

$$\left\{a_i a_j^\dagger\right\} = a_j^\dagger a_i \qquad ; \qquad a_i^\bullet a_j^{\dagger\bullet} = \delta_{ij} \tag{2.22}$$

so that we can write:

$$a_i a_j^\dagger = \left\{a_i a_j^\dagger\right\} + a_i^\bullet a_j^{\dagger\bullet} \tag{2.23}$$

The curly bracket here denotes the 'normal order' of the operators within. Normal-ordering a string of operators quite simply brings any $a_j^\dagger$ operators to the left-hand side of the string, leaving all a_i operators to the right. The bullet symbols ($^\bullet$) indicate that a 'contraction' has been made between the two operators in question, resulting in a Kronecker delta. The contraction between two operators occurs between some a_i and an $a_j^\dagger$ operator somewhere to the right of it in a given string of operators.

We will use different numbers of bullet symbols to denote different contractions, so as not to confuse them. Single contractions include terms with only one contraction, double contractions contain two sets of contracted operators, and so on. Wick's Theorem states that for any string of operators A, we may express it using a sum

over normal-ordered single contractions, double contractions, and all other possible combinations.

$$A = \{A\} + \sum_{single} \{A^{\bullet}\} + \sum_{double} \{A^{\bullet\bullet}\} + ... \tag{2.24}$$

In order see this in practice, let us apply this example to a string of multiple operators. Consider the operator $a_i a_j a_k^\dagger a_l^\dagger$.

$$a_i a_j a_k^\dagger a_l^\dagger = \left\{a_i a_j a_k^\dagger a_l^\dagger\right\} + \sum_{single} \left\{\left(a_i a_j a_k^\dagger a_l^\dagger\right)^{\bullet}\right\} + \sum_{double} \left\{\left(a_i a_j a_k^\dagger a_l^\dagger\right)^{\bullet\bullet}\right\} + ... \tag{2.25}$$

Each sum can then be expanded into multiple terms, as follows.

$$\begin{aligned}
\sum_{single} \left\{\left(a_i a_j a_k^\dagger a_l^\dagger\right)^{\bullet}\right\} &= \left\{a_i^{\bullet} a_j a_k^{\dagger\bullet} a_l^\dagger\right\} + \left\{a_i^{\bullet} a_j a_k^\dagger a_l^{\dagger\bullet}\right\} + \left\{a_i a_j^{\bullet} a_k^{\dagger\bullet} a_l^\dagger\right\} + \left\{a_i a_j^{\bullet} a_k^\dagger a_l^{\dagger\bullet}\right\} \\
&= \left\{a_j a_l^\dagger \delta_{ik}\right\} + \left\{a_j a_k^\dagger \delta_{il}\right\} + \left\{a_i a_l^\dagger \delta_{jk}\right\} + \left\{a_i a_k^\dagger \delta_{jl}\right\} \\
&= a_l^\dagger a_j \delta_{ik} + a_k^\dagger a_j \delta_{il} + a_l^\dagger a_i \delta_{jk} + a_k^\dagger a_i \delta_{jl}
\end{aligned}$$

$$\begin{aligned}
\sum_{double} \left\{\left(a_i a_j a_k^\dagger a_l^\dagger\right)^{\bullet\bullet}\right\} &= \left\{a_i^{\bullet} a_j^{\bullet\bullet} a_k^{\dagger\bullet} a_l^{\dagger\bullet\bullet}\right\} + \left\{a_i^{\bullet} a_j^{\bullet\bullet} a_k^{\dagger\bullet\bullet} a_l^{\dagger\bullet}\right\} \\
&= \{\delta_{ik}\delta_{jl}\} + \{\delta_{il}\delta_{jk}\} = \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}
\end{aligned} \tag{2.26}$$

As there are no possible triple contractions here, adding each of the above terms as well as the normal-ordered term in the beginning will be equivalent to using the original operator string.

$$\begin{aligned}
a_i a_j a_k^\dagger a_l^\dagger &= \left\{a_i a_j a_k^\dagger a_l^\dagger\right\} + \sum_{single} \left\{\left(a_i a_j a_k^\dagger a_l^\dagger\right)^{\bullet}\right\} + \sum_{double} \left\{\left(a_i a_j a_k^\dagger a_l^\dagger\right)^{\bullet\bullet}\right\} + ... \\
&= a_k^\dagger a_l^\dagger a_i a_j + \left(a_l^\dagger a_j \delta_{ik} + a_k^\dagger a_j \delta_{il} + a_l^\dagger a_i \delta_{jk} + a_k^\dagger a_i \delta_{jl}\right) + (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})
\end{aligned} \tag{2.27}$$

While this is true, the result can be greatly simplified when a given string of operators is summed over their indices. Recall that in our potential (and most other terms we will encounter in this problem), each operator string is summed over all

existing oscillators. Then, each individual operator index can be permuted or rearranged so that they match, as shown below. For the contracted terms specifically, we have:

$$\begin{aligned}
\sum_{ijkl}\sum_{single}\left\{\left(a_i a_j a_k^\dagger a_l^\dagger\right)^{\bullet}\right\} &= \sum_{ijkl}\left(a_l^\dagger a_j\delta_{ik} + a_k^\dagger a_j\delta_{il} + a_l^\dagger a_i\delta_{jk} + a_k^\dagger a_i\delta_{jl}\right) \\
&= \sum_{ijkl} a_l^\dagger a_j\delta_{ik} + \sum_{ijkl} a_k^\dagger a_j\delta_{il} + \sum_{ijkl} a_l^\dagger a_i\delta_{jk} + \sum_{ijkl} a_k^\dagger a_i\delta_{jl} \\
&= \sum_{ijkl} a_l^\dagger a_j\delta_{ik} + \sum_{ijlk} a_l^\dagger a_j\delta_{ik} + \sum_{jikl} a_l^\dagger a_j\delta_{ik} + \sum_{jilk} a_l^\dagger a_j\delta_{ik} \\
&= 4\sum_{ijkl} a_l^\dagger a_j\delta_{ik} = 4\sum_{ijl} a_l^\dagger a_j
\end{aligned} \tag{2.28}$$

$$\begin{aligned}
\sum_{ijkl}\sum_{double}\left\{\left(a_i a_j a_k^\dagger a_l^\dagger\right)^{\bullet\bullet}\right\} &= \sum_{ijkl}\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right) = \sum_{ijkl}\delta_{ik}\delta_{jl} + \sum_{ijkl}\delta_{il}\delta_{jk} \\
&= \sum_{ijkl}\delta_{ik}\delta_{jl} + \sum_{ijlk}\delta_{ik}\delta_{jl} = 2\sum_{ijkl}\delta_{ik}\delta_{jl} = 2N^2
\end{aligned}$$

where N indicates the summation limit for the operators. Therefore, expressing the sum of all operators of the form $a_i a_j a_k^\dagger a_l^\dagger$ becomes far more convenient (and useful) than expressing each individual term.

$$\sum_{ijkl} a_i a_j a_k^\dagger a_l^\dagger = a_k^\dagger a_l^\dagger a_i a_j + 4\sum_{ijl} a_l^\dagger a_j + 2N^2 \tag{2.29}$$

The same method can be applied to any string of operators, although it is necessary to include triple or higher-order contractions if they are possible. Note that we obtain a similar result for the single oscillator case, where the only values in the sum are $i, j, k, l = 1$. This would be equivalent to getting rid of the sums over i, j, k, and l, giving us:

$$aaa^\dagger a^\dagger = a^\dagger a^\dagger aa + 4a^\dagger a + 2 \tag{2.30}$$

Having introduced Wick's Theorem, we can apply it to the BCH expansion which we enountered earlier in equation (2.20). Take the first commutator in the expansion,

$[H,T] = HT - TH$. Keeping in mind that the cluster operator T consists of only $a_i^\dagger$ operators, the term TH is already normal-ordered. Therefore, the only remaining terms from the commutator are the contractions that we would find using Wick's Theorem (as the first normal-ordered term in HT is simply TH). The sum of all possible contractions between two terms such as H and T will be called 'connections', denoted by a subscript C.

Caution should especially be used when connecting large blocks of terms, instead of strings of individual operators. In this case, a connection must occur between each term. For example, consider a connection occurring between the operators $A = a_i a_j^\dagger$ and $B = a_k^\dagger a_l^\dagger$:

$$\begin{aligned}(AB)_C &= \left(a_i a_j^\dagger \cdot a_k^\dagger a_l^\dagger\right)_C = \sum_{single} \left\{\left(a_i a_j^\dagger \cdot a_k^\dagger a_l^\dagger\right)^\bullet\right\} \\ &= \left\{\left(a_i^\bullet a_j^\dagger\right)\left(a_k^{\dagger\bullet} a_l^\dagger\right)\right\} + \left\{\left(a_i^\bullet a_j^\dagger\right)\left(a_k^\dagger a_l^{\dagger\bullet}\right)\right\} = a_j^\dagger a_l^\dagger \delta_{ik} + a_j^\dagger a_k^\dagger \delta_{il}\end{aligned} \tag{2.31}$$

The hypothetical term $\left\{\left(a_i^\bullet a_j^{\dagger\bullet}\right)\left(a_k^\dagger a_l^\dagger\right)\right\}$ does not appear, as the second term is not included in any connection. Note also that a single term cannot be connected with itself.

2.6. Diagrammatics

The above results of Wick's theorem can be condensed into diagrammatic techniques in order to efficiently derive non-zero contributions to our equations. Keep in mind that we are assuming that our Hamiltonian has been normal-ordered. Let us first define the concept of an open part of an operator as any parts which contain strings of annihilation and/or creation operators, and a closed part of an operator as any possible scalar. As a simple example, for our unperturbed Hamiltonian, we have:

$$H_0 = \sum_{i=1}^{N} \left(a_i^\dagger a_i + \frac{1}{2}\right)\omega_i \quad ; \quad H_{0,open} = \sum_{i=1}^{N} a_i^\dagger a_i \omega_i \quad ; \quad H_{0,closed} = \frac{1}{2}\sum_{i=1}^{N} \omega_i \tag{2.32}$$

Any normal-ordered operator can be written as the sum of its (normal-ordered) open and closed parts, such that $A = A_{open} + A_{closed}$. We can now take advantage of this fact, as the term $e^{-T}He^{T}$ becomes slightly simplified:

$$e^{-T}He^{T} = e^{-T}\left(H_{open} + H_{closed}\right)e^{T} = e^{-T}H_{open}e^{T} + H_{closed} \tag{2.33}$$

Applying this to the BCH expansion in (2.20), we can rewrite the term with H_{open} using the formalism of connections defined in Wick's Theorem. Note that a connection involving a constant is not defined, so each of the connected terms below only involve the open part of H.

$$e^{-T}H_{open}e^{T} = (He^{T})_{C} = H_{open} + (HT)_{C} + \frac{1}{2}(HT^{2})_{C} + ... \tag{2.34}$$

Each of these connections will result in both open and closed parts, and can be separated as such. While this seems trivial, we can write out the three terms needed to compute $e^{-T}He^{T}$ explicitly.

$$\begin{aligned} e^{-T}He^{T} &= e^{-T}H_{open}e^{T} + H_{closed} = (He^{T})_{C} + H_{closed} \\ &= (He^{T})_{C,open} + (He^{T})_{C,closed} + H_{closed} \end{aligned} \tag{2.35}$$

From here, we can take similar steps following the ground state energy equation in (2.18). As the perturbed ground state energy is calculated between two $|0\rangle$ states, the contribution from all open operators is zero.

$$\tilde{E}_{0} = \langle 0|e^{-T}He^{T}|0\rangle = (He^{T})_{C,closed} + H_{closed} \tag{2.36}$$

Alternatively, we can consider cluster amplitude equations in (2.19). As the equations are now being calculated between $|0\rangle$ and some excited state, the contributions from closed terms become zero. Therefore:

$$
\begin{aligned}
&\langle 0|a_i(He^T)_{C,open}|0\rangle = 0 \quad &\rightarrow \quad t_i \\
&\langle 0|a_i a_j(He^T)_{C,open}|0\rangle = 0 \quad &\rightarrow \quad t_{ij} \\
&\langle 0|a_i a_j a_k ...(He^T)_{C,open}|0\rangle = 0 \quad &\rightarrow \quad t_{ijk...} \\
&...etc.
\end{aligned}
\tag{2.37}
$$

Conveniently, we now see that the only surviving terms from $(He^T)_{C,open}$ which directly contribute to cluster amplitudes are purely combinations of $a_i^\dagger$ operators. Terms ending in any number of a_i operators immediately have zero contribution, as they operate on the $|0\rangle$ state.

In order to readily express the resulting operator terms above, we now introduce the diagrammatic representation of each operator. Various diagrammatic schemes have been defined in the past (17), although in our case we will define a slightly different scheme for our specific use. Let us define a diagram for each string of normal ordered operators and its associated coefficient. A horizontal line or 'vertex' will denote the amplitude for the term, and the operators a_i and $a_i^\dagger$ will be denoted by vertical lines, leading down or up from the horizontal vertex. For example, terms from a perturbed Hamiltonian H or cluster operator T can be rewritten in the form of diagrams as

$$
\frac{1}{2!}\sum_{ij} B^{ij} a_i a_j \quad : \quad \begin{array}{c} \frac{1}{2!}\sum_{ij} B^{ij} \\ a_i \left[\text{- - - - - - -}\right] a_j \end{array} \quad ; \quad \frac{1}{2!}\sum_{kl} t_{kl} a_k^\dagger a_l^\dagger \quad : \quad \begin{array}{c} a_k^\dagger \left[\text{\quad\quad\quad}\right] a_l^\dagger \\ \frac{1}{2!}\sum_{kl} t_{kl} \end{array}
\tag{2.38}
$$

An important distinction to make is that we use a dotted horizontal line for coefficients in the Hamiltonian, and a solid line for amplitudes in the cluster operator. Generally, it is not necessary to label these horizontal lines any further, as each constant already corresponds to a certain number of creation and annihilation operators. The constants can therefore be inferred.

In preparation for future calculation, the ω energy term will be written slightly differently, such that it mirrors the notation of other existing terms.

$$\sum_i \omega_i a_i^\dagger a_i \quad \rightarrow \quad \sum_{ij} \omega_i^j \delta_{ij} a_i^\dagger a_j \tag{2.39}$$

The normal ordered open part of the Hamiltonian under a quadratic perturbation can as an example be expressed using simple diagrams as follows.

$$H_{open} = \sum_{ab} \omega_a^b \delta_{ab} a_a^\dagger a_b + \frac{1}{2!} \sum_{ab} B_{ab} a_a^\dagger a_b^\dagger + \sum_{ab} J_a^b a_a^\dagger a_b + \frac{1}{2!} \sum_{ab} B^{ab} a_a a_b$$

$$= \times \overset{a}{\underset{b}{|}} + a \sqcup b + \blacksquare \overset{a}{\underset{b}{|}} + a \sqcap b \tag{2.40}$$

The cross symbol and square symbol above are used to differentiate the ω energy term and the J term, as both have the same diagrammatic shape. The cluster operator T will be expressed in diagrams, as:

$$T = T_1 + T_2 + T_3 + ... = \sum_k t_k a_k^\dagger + \frac{1}{2!} \sum_{kl} t_{kl} a_k^\dagger a_l^\dagger + \frac{1}{3!} \sum_{klm} t_{klm} a_k^\dagger a_l^\dagger a_m^\dagger + ...$$

$$= k\bullet + k \sqcup l + k \sqcap\!\!\sqcup m + ... \tag{2.41}$$

A key process in developing the operating equations for the coupled cluster method is the evaluation of products of normal ordered operators. Below we will derive the general expression for such operator products, but here we will hint at the usefulness of diagrams through an example of the product between two operators in diagrammatic form.

A connection between two diagrams occurs between an a_i operator in H and any of the $a_i^\dagger$ operators in T. Diagrammatically, this connects a 'down-facing line' in H with any 'up-facing line' in T. One specific example could be:

$$\left(\hat{B}^{ab} \cdot T_4\right)_C = a \sqcap b \sqcup i \sqcup j \sqcup k + a \sqcap b \sqcup i \sqcup j \tag{2.42}$$

Notice that each connected line only requires one index. Here we have condensed the operators and factorials into one symbol, based on the coefficient.

$$\hat{B}^{ab} = \frac{1}{2!}\sum_{ab} B^{ab} a_a a_b \qquad ; \qquad T_4 = \frac{1}{4!}\sum_{ijkl} t_{ijkl} a_i^\dagger a_j^\dagger a_k^\dagger a_l^\dagger \tag{2.43}$$

The above diagrams will represent a sum over all possible connections between $\hat{B}^{ab}$ and T_4, with single and double connections represented by different diagrams.

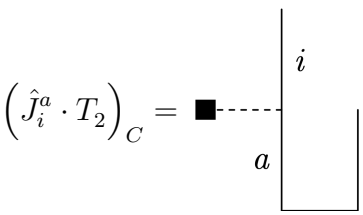
2.7. Symmetry

Before being able to fully interpret factors corresponding to each diagram, we should briefly discuss the topic of symmetry.

Firstly, recall that the order of any $a_i^\dagger$ operators in a term are interchangeable, as $[a_i^\dagger, a_j^\dagger] = 0$. The indices over any sum are interchangeable as well, therefore we can write:

$$\frac{1}{2!}\sum_{ij} t_{ij} a_i^\dagger a_j^\dagger = \frac{1}{2!}\sum_{ji} t_{ji} a_j^\dagger a_i^\dagger = \frac{1}{2!}\sum_{ji} t_{ji} a_i^\dagger a_j^\dagger = \frac{1}{2!}\sum_{ij} t_{ji} a_i^\dagger a_j^\dagger \tag{2.44}$$

By swapping indices, we can quickly show that $t_{ij} = t_{ji}$ and is symmetric. This identity was briefly discussed earlier, although now the same issue can be applied to diagrammatics. Consider the only connection occuring between $\hat{J}_i^a$ and T_2. The diagram and result found via Wick's Theorem are written below.

$\left(\hat{J}_i^a \cdot T_2\right)_C =$ 

$= \sum_{ij}\sum_{a} \left(J_i^a t_{aj}\right) a_i^\dagger a_j^\dagger$ (2.45)

As we have two $a^\dagger$ operators in the sum, we would expect the indices i and j to be interchangeable. We can quickly see, however, that written as above this is in general not the case, in that

$$\sum_{ij}\sum_{a}\left(J_i^a t_{aj}\right)a_i^\dagger a_j^\dagger \neq \sum_{ji}\sum_{a}\left(J_j^a t_{ai}\right)a_j^\dagger a_i^\dagger \tag{2.46}$$

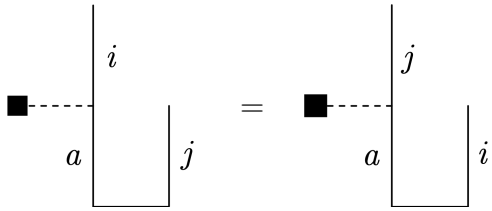
In order to fix this problem, we symmetrize the coefficient by separating it and interchanging indices, as shown below.

$$\begin{aligned}\sum_{ij}\sum_{a}\left(J_i^a t_{aj}\right)a_i^\dagger a_j^\dagger &= \frac{1}{2}\left(\sum_{ij}\sum_{a}\left(J_i^a t_{aj}\right)a_i^\dagger a_j^\dagger + \sum_{ij}\sum_{a}\left(J_i^a t_{aj}\right)a_i^\dagger a_j^\dagger\right)\\ &= \frac{1}{2}\left(\sum_{ij}\sum_{a}\left(J_i^a t_{aj}\right)a_i^\dagger a_j^\dagger + \sum_{ji}\sum_{a}\left(J_j^a t_{ai}\right)a_j^\dagger a_i^\dagger\right)\\ &= \frac{1}{2}\sum_{ij}\sum_{a}\left(J_i^a t_{aj} + J_j^a t_{ai}\right)a_i^\dagger a_j^\dagger\end{aligned} \tag{2.47}$$

Now, the coefficient in parentheses is symmetric with respect to interchanging i and j, and matches the result we find using Wick's theorem.

$$\frac{1}{2}\sum_{ij}\sum_{a}\left(J_i^a t_{aj} + J_j^a t_{ai}\right)a_i^\dagger a_j^\dagger = \frac{1}{2}\sum_{ji}\sum_{a}\left(J_j^a t_{ai} + J_i^a t_{aj}\right)a_j^\dagger a_i^\dagger \tag{2.48}$$

We would like to directly interpret diagrams in such a way that they are already symmetrized, as the labels for lines are entirely arbitrary. Any indices for free 'up-facing lines' (not participating in a connection) should commute the same way, so we could write the above equation as:



(2.49)

For the case of a single oscillator, the symmetrized coefficients would collapse, as all indices act on the same oscillator.

$$\frac{1}{2}\sum_{ij}\sum_{a}\left(J_i^a t_{aj} + J_j^a t_{ai}\right)a_i^\dagger a_j^\dagger \quad \rightarrow \quad \frac{1}{2}\left(2Jt_2\right)a^\dagger a^\dagger \tag{2.50}$$

While writing Jt_2 would be more simple, we may wish to keep the information on factors and how many terms are needed to properly symmetrize the coefficient. Therefore, we will keep the single oscillator term in the form shown in the above equation. In the future, some diagrams will take numerous terms in order to completely symmetrize, so let us define some operator S which turns a single term into all of its properly symmetrized counterparts. If a subscript S_V is included, it will tell how many terms are required to symmetrize (and therefore, the factor needed for a single oscillator), as shown below.

$$S(J_i^a t_{aj}) = S_2(J_i^a t_{aj}) = J_i^a t_{aj} + J_j^a t_{ai} \tag{2.51}$$

2.8. Symmetrized Operator Products

In the general case, we want to be able to find the product of two normal ordered operators with symmetrized coefficients after n contractions using diagrams. For the sake of generality, let us investigate this as a connection between two (already symmetrized) operators $\hat{A}^{ab...}_{rs...}$ and $\hat{B}^{cd...}_{tu...}$.

$$\begin{aligned}
\hat{A}^{ab...}_{rs...} &= \frac{1}{K!}\frac{1}{L!}\sum_{ab...rs...} A^{ab...(L\ indices)}_{rs...(K\ indices)} \left(a_r^\dagger a_s^\dagger ...\right)_{K\ operators} \left(a_a a_b ...\right)_{L\ operators} \\
\hat{B}^{cd...}_{tu...} &= \frac{1}{M!}\frac{1}{N!}\sum_{cd...tu...} B^{cd...(N\ indices)}_{tu...(M\ indices)} \left(a_t^\dagger a_u^\dagger ...\right)_{M\ operators} \left(a_c a_d ...\right)_{N\ operators}
\end{aligned} \tag{2.52}$$

Note that in our case, $\hat{B}^{cd...}_{tu...}$ will actually represent one of our cluster operators T_M, which have no attached a operators at all. Therefore, $N = 0$ for diagrams we will use in practice. It would be most convenient to interpret any connected diagram immediately into the following form:

$$\hat{\Pi}^{ab...}_{rs...} = \frac{1}{R!}\frac{1}{S!}\sum_{ab...rs...} \Pi^{ab...(S\ indices)}_{rs...(R\ indices)} \left(a_r^\dagger a_s^\dagger ...\right)_{R\ operators} \left(a_a a_b ...\right)_{S\ terms} \tag{2.53}$$

where the $\Pi^{ab...}_{rs...}$ coefficient is interpreted such that it is already symmetrized.

The number of possible unique nth contractions all represented by the same diagram when using symmetrized coefficients is shown below.

$$\begin{aligned} U_n(L,M) &= \frac{L(L-1)(L-2)...(L-(n-1)) \times M(M-1)(M-2)...(M-(n-1))}{n!} \\ &= \frac{L!M!}{(L-n)!(M-n)!}\frac{1}{n!} \end{aligned} \tag{2.54}$$

For a single contraction ($n = 1$), the expression simplifies to $L \times M$ unique possibilities.

We can now figure out how many terms we need to symmetrize the new coefficient. There are $(K + M - n)!$ ways of labeling the indices for creation operators. K of these are given by the $\hat{A}^{ab...}_{rs...}$ coefficient, and $M - n$ of these are given by the remaining operators on the $\hat{B}^{cd...}_{tu...}$ coefficient after connections. There are therefore $K!$ ways in which permuting the $(K + M - n)!$ labels give rise to the same labeling on the $\hat{A}^{ab...}_{rs...}$ coefficient since it is symmetrized. Similarly, there are $(M-n)!$ ways in which permuting the $(K + M - n)!$ labels give rise to the same labeling on the $\hat{B}^{cd...}_{tu...}$ coefficient.

The unique number of labels for the creation operators is therefore:

$$\frac{(K+M-n)!}{K!(M-n)!} = \binom{K+M-n}{K} \tag{2.55}$$

A similar argument for the annihilation operators gives that the number of unique labels is:

$$\frac{(N+L-n)!}{N!(L-n)!} = \binom{N+L-n}{N} \tag{2.56}$$

So, the total number of unique labels is given by multiplying equations (2.55) and (2.56):

$$V_n(K,L,M,N) = \frac{(K+M-n)!}{K!(M-n)!}\frac{(N+L-n)!}{N!(L-n)!} = \binom{K+M-n}{K}\binom{N+L-n}{N} \tag{2.57}$$

This is the number of terms needed to properly symmetrize the coefficient, shown in the subscript of the S_V operator. When connecting a diagram with a cluster operator

$(N = 0)$, the expression in equation (2.56) becomes 1. Then, equations (2.55) and (2.57) are equivalent.

The resulting factor we need to use in front of the resulting sum of coefficient and operators is therefore given by multiplying the factorials in the definition of operators $\hat{A}^{ab\ldots}_{rs\ldots}$ and $\hat{B}^{cd\ldots}_{tu\ldots}$ and number of possible ways to form n contractions $U_n(L, M)$, then dividing by the total number of necessary symmetrizing products $V_n(K, L, M, N)$. Let us call this total term in front some $\Lambda_n(K, L, M, N)$.

$$\begin{aligned}
\Lambda_n(K,L,M,N) &= \frac{1}{K!}\frac{1}{L!}\frac{1}{M!}\frac{1}{N!} \times \frac{U_n(L,M)}{V_n(K,L,M,N)} \\
&= \frac{1}{K!}\frac{1}{L!}\frac{1}{M!}\frac{1}{N!} \times \frac{L!M!}{(L-n)!(M-n)!}\frac{1}{n!} \times \frac{1}{\frac{(K+M-n)!}{K!(M-n)!}\frac{(N+L-n)!}{N!(L-n)!}} \\
&= \frac{1}{K!}\frac{1}{L!}\frac{1}{M!}\frac{1}{N!} \times \frac{L!M!}{(L-n)!(M-n)!}\frac{1}{n!} \times \frac{K!(M-n)!}{(K+M-n)!}\frac{N!(L-n)!}{(N+L-n)!} \\
&= \frac{1}{(K+M-n)!(N+L-n)!}\frac{1}{n!}
\end{aligned} \tag{2.58}$$

In terms of the remaining number of creation and annihilation operators in the final diagram after connection, we can write the factor simply as:

$$\Lambda_n(K,L,M,N) = \frac{1}{(\#\text{ remaining creation})!}\frac{1}{(\#\text{ remaining annihilation})!}\frac{1}{n!} \tag{2.59}$$

Therefore, the general diagrammatic form we defined in equation (2.53) has coefficients related as:

$$R = K + M - n \quad ; \quad S = N + L - n \quad ; \quad \Pi^{ab\ldots}_{rs\ldots} = \frac{1}{n!}\left\{A^{ab\ldots}_{rs\ldots}B^{cd\ldots}_{tu\ldots}\right\} \tag{2.60}$$

R is simply the number of remaining creation operators and S the number of remaining annihilation operators. $\left\{A^{ab\ldots}_{rs\ldots}B^{cd\ldots}_{tu\ldots}\right\}$ denotes the symmetrized coefficient product where indices which represent contractions have been set equal.

We note that in the case of a single oscillator, symmetrization of the coefficient is unnecessary since there is only a single index. Our operators can then be written:

$$\hat{A} = \frac{1}{K!}\frac{1}{L!}A_K^L \left(a^\dagger\right)^K (a)^L \qquad ; \qquad \hat{B} = \frac{1}{M!}\frac{1}{N!}B_M^N \left(a^\dagger\right)^M (a)^N \tag{2.61}$$

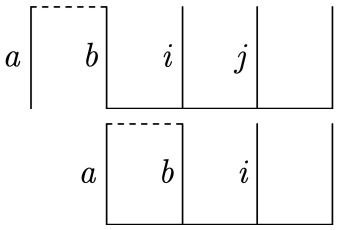
The diagrammatic product after n contractions would be similarly simplified:

$$\hat{\Pi} = \frac{1}{M!}\frac{1}{N!}\Pi_R^S \left(a^\dagger\right)^R (a)^S \quad ; \quad \Pi_R^S = \binom{K+M-n}{K}\binom{N+L-n}{N}\frac{1}{n!}A_K^L B_M^N \tag{2.62}$$

This form is particularly emanable to implementation in computer code which would automate the generation of operator product coefficients and ultimately the coupled cluster equations themselves, a path which we will explore in the future.

2.8.1. Diagrammatic Examples

Let's take the example of diagrams encountered in equation (2.42), as a result of connecting $\hat{B}^{ab}$ and T_4. The two diagrams would be interpreted as:

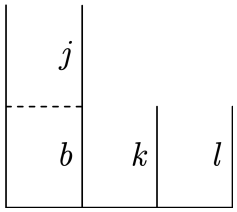


$$= \frac{1}{3!}\frac{1}{1!}\frac{1}{1!}\sum_{a,ijk}\sum_{b} B^{ab} t_{bijk} a_i^\dagger a_j^\dagger a_k^\dagger a_a$$

$$= \frac{1}{2!}\frac{1}{0!}\frac{1}{2!}\sum_{ij}\sum_{ab} B^{ab} t_{abij} a_i^\dagger a_j^\dagger \tag{2.63}$$

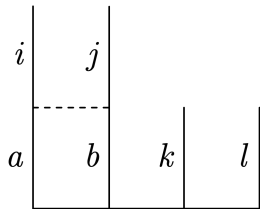
No symmetrizing is needed in either case, as all of the creation operators are attached to the same vertex. An example of a situation where symmetrizing is needed is shown below, for the double connection between $\hat{M}_{ij}^{ab}$ and T_4.

$$\left(\hat{M}_{ij}^{ab} \cdot T_4\right)_C \quad \rightarrow$$



$$= \frac{1}{4!}\frac{1}{0!}\frac{1}{2!}\sum_{ijkl}\sum_{ab} S\left(M_{ij}^{ab} t_{abkl}\right) a_i^\dagger a_j^\dagger a_k^\dagger a_l^\dagger \tag{2.64}$$

There are now 4 total creation operators. As there are 2 pairs of operators connected to the same vertex (i and j, as well as k and l), the number of terms needed to properly symmetrize is $\frac{4!}{2!2!} = 6$. Therefore:



$$\begin{aligned}
&= \frac{1}{4!}\frac{1}{2!}\sum_{ijkl}\sum_{ab} S\left(M_{ij}^{ab}t_{abkl}\right) a_i^\dagger a_j^\dagger a_k^\dagger a_l^\dagger \\
&= \frac{1}{4!}\frac{1}{2!}\sum_{ijkl}\sum_{ab} S_6\left(M_{ij}^{ab}t_{abkl}\right) a_i^\dagger a_j^\dagger a_k^\dagger a_l^\dagger \\
&= \frac{1}{4!}\frac{1}{2!}\sum_{ijkl}\sum_{ab} \left(M_{ij}^{ab}t_{abkl} + M_{kj}^{ab}t_{abil} + M_{lj}^{ab}t_{abki} + \right. \\
&\qquad \left. M_{ik}^{ab}t_{abjl} + M_{il}^{ab}t_{abkj} + M_{kl}^{ab}t_{abij}\right) a_i^\dagger a_j^\dagger a_k^\dagger a_l^\dagger
\end{aligned} \tag{2.65}$$

Again, for a single oscillator, we would find that all 6 terms collapse into one.

$$\frac{1}{4!}\frac{1}{2!}\left(6Mt_4\right) a^\dagger a^\dagger a^\dagger a^\dagger \tag{2.66}$$

For a final example, we will consider terms connected by multiple cluster operators, occuring in the higher order connections in equation (2.34) resulting from rewriting the BCH expansion, or the expansion of e^T in equation (2.17).

$$\begin{aligned}
\left(\hat{D}^{abcd}\cdot\frac{1}{3!}T_2^3\right)_C \quad &\rightarrow \quad \left(\frac{1}{3!}\right) i \left\lfloor\, a \,\right\rceil \left\lfloor\, b \,\right\rceil \left\lfloor\, c \,\right\rceil \left\lfloor\, d \,\right\rceil \left\lfloor\, j \,\right\rceil \\
&= \quad \left(\frac{1}{3!}\right)\frac{1}{2!}\frac{1}{0!}\frac{1}{2!}\sum_{ij}\sum_{abcd} S\left(D^{abcd}t_{ia}t_{bc}t_{dj}\right) a_i^\dagger a_j^\dagger
\end{aligned} \tag{2.67}$$

There are now 2 total creation operators. As there are no operators connected to the same vertex, the number of terms needed to properly symmetrize is $\frac{2!}{0!} = 2$. Dropping any factorials or operators, the symmetrized coefficient becomes:

$$\begin{aligned}
\sum_{ij}\sum_{abcd} S\left(D^{abcd}t_{ia}t_{bc}t_{dj}\right) &= \sum_{ij}\sum_{abcd} S_2\left(D^{abcd}t_{ia}t_{bc}t_{dj}\right) \\
&= \sum_{ij}\sum_{abcd}\left(D^{abcd}t_{ia}t_{bc}t_{dj} + D^{abcd}t_{ja}t_{bc}t_{di}\right)
\end{aligned} \tag{2.68}$$

In this case, we have two T_2 operators which are being treated equivalently (singly connected to $\hat{D}^{abcd}$). For this reason, a slight simplification can be made when symmetrizing. As indices in each individual sum can be permuted, we will be able to swap a and d. Doing this and exchanging indices on the (already symmetric) t coefficients will show that:

$$\begin{aligned} ... &= \sum_{ij}\sum_{abcd}\left(D^{abcd}t_{ia}t_{bc}t_{dj} + D^{abcd}t_{ja}t_{bc}t_{di}\right) \\ &= \sum_{ij}\sum_{abcd}\left(D^{abcd}t_{ia}t_{bc}t_{dj} + D^{abcd}t_{jd}t_{bc}t_{ai}\right) \\ &= \sum_{ij}\sum_{abcd}2\left(D^{abcd}t_{ia}t_{bc}t_{dj}\right) \end{aligned} \tag{2.69}$$

And therefore, the symmetrization collapses - similarly to what we would see for a single oscillator. Again, this simplification only occurs when we have two T operators which are being treated equivalently, and will not generally collapse the entire symmetrized expression.

2.9. Excited States

For this section we will limit the discussion to a single oscillator, although the generalization to multiple oscillators is relatively straightforward. To calculate excited states, we again use the fact that the unperturbed states form a complete set to define an excitation operator which generates the $\tilde{n}$'th excited state from the unperturbed ground state, as follows.

$$\begin{aligned} |\tilde{n}\rangle &= \hat{1}|\tilde{n}\rangle = \sum_{n}^{\infty}|n\rangle\langle n|\tilde{n}\rangle = \sum_{n}^{\infty}c_n(\tilde{n})|n\rangle = \sum_{n}^{\infty}c_n(\tilde{n})\frac{1}{\sqrt{n!}}\left(a^\dagger\right)^n|0\rangle = \Omega(\tilde{n})|0\rangle \\ \Omega(\tilde{n}) &= \sum_{n}^{\infty}c_n(\tilde{n})\frac{1}{\sqrt{n!}}\left(a^\dagger\right)^n \end{aligned} \tag{2.70}$$

Due to the fact that both $\Omega(\tilde{n})$ and e^T consist exclusively of $a^\dagger$ operators, we know that they commute as $\left[\Omega(\tilde{n}), e^T\right] = 0$. It also becomes convenient to introduce an operator $\tilde{\Omega}(\tilde{n})$, defined below for shorthand notation.

$$\begin{aligned}\tilde{\Omega}(\tilde{n}) = e^{-T}\Omega(\tilde{n}) \quad ; \quad |\tilde{n}\rangle = \Omega(\tilde{n})|0\rangle = e^{-T}e^{T}\Omega(\tilde{n})|0\rangle = e^{-T}\Omega(\tilde{n})e^{T}|0\rangle = \tilde{\Omega}(\tilde{n})|\tilde{0}\rangle \\ \text{or alternatively,} \ = e^{T}e^{-T}\Omega(\tilde{n})|0\rangle = e^{T}\tilde{\Omega}(\tilde{n})|0\rangle\end{aligned} \tag{2.71}$$

We can use these expressions for $|\tilde{n}\rangle$ to rewrite the Schrödinger equation for the $\tilde{n}$'th excited state in two different ways, which are shown below.

$$\begin{aligned}H|\tilde{n}\rangle = \tilde{E}_n|\tilde{n}\rangle \quad ; \qquad H\tilde{\Omega}(\tilde{n})|\tilde{0}\rangle = \tilde{E}_n\tilde{\Omega}(\tilde{n})|\tilde{0}\rangle \\ e^{-T}He^{T}\tilde{\Omega}(\tilde{n})|0\rangle = \tilde{E}_n\tilde{\Omega}(\tilde{n})|0\rangle\end{aligned} \tag{2.72}$$

Noting the above equation and results from equation (2.18), we can write:

$$\begin{aligned}\left[e^{-T}He^{T}, \tilde{\Omega}(\tilde{n})\right]|0\rangle &= \left(e^{-T}He^{T}\tilde{\Omega}(\tilde{n}) - \tilde{\Omega}(\tilde{n})e^{-T}He^{T}\right)|0\rangle \\ &= \left(\tilde{E}_n\tilde{\Omega}(\tilde{n}) - \tilde{\Omega}(\tilde{n})\tilde{E}_0\right)|0\rangle \\ &= \left(\tilde{E}_n - \tilde{E}_0\right)\tilde{\Omega}(\tilde{n})|0\rangle = \Delta\tilde{E}_n\tilde{\Omega}(\tilde{n})|0\rangle\end{aligned} \tag{2.73}$$

Normal-ordering and separating the $e^{-T}He^{T}$ as shown in equation (2.35) would show that the commutator becomes:

$$\begin{aligned}\left[e^{-T}He^{T}, \tilde{\Omega}(\tilde{n})\right]|0\rangle &= \left[(He^{T})_{C,open} + (He^{T})_{C,closed} + H_{closed}, \tilde{\Omega}(\tilde{n})\right]|0\rangle \\ &= \left[(He^{T})_{C,open}, \tilde{\Omega}(\tilde{n})\right]|0\rangle = \Delta\tilde{E}_n\tilde{\Omega}(\tilde{n})|0\rangle\end{aligned} \tag{2.74}$$

Where we have used the fact that the commutator between any constant and any operator is zero. Similarly to what we did with e^T earlier, due to the form of $\tilde{\Omega}(\tilde{n})$ we can write:

$$\left[(He^{T})_{C,open}, \tilde{\Omega}(\tilde{n})\right]|0\rangle = \left((He^{T})_{C,open}\tilde{\Omega}(\tilde{n})\right)_C|0\rangle = \Delta\tilde{E}_n\tilde{\Omega}(\tilde{n})|0\rangle \tag{2.75}$$

This equation can be rewritten in matrix form, where we now change notation in order to define some $\widehat{\mathbf{H}} = (He^T)_{C,open}$ with eigenvalues $\Delta\tilde{E}_n$ and eigenkets given by $\tilde{\Omega}(\tilde{n})|0\rangle$.

$$\begin{pmatrix} \langle 0|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 0|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 0|\,\widehat{\mathbf{H}}\,|2\rangle & \cdots \\ \langle 1|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 1|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 1|\,\widehat{\mathbf{H}}\,|2\rangle & \cdots \\ \langle 2|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 2|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 2|\,\widehat{\mathbf{H}}\,|2\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{0n} \\ c_{1n} \\ c_{2n} \\ \vdots \end{pmatrix} = \Delta\tilde{E}_n \begin{pmatrix} c_{0n} \\ c_{1n} \\ c_{2n} \\ \vdots \end{pmatrix} \tag{2.76}$$

We can continue the above derivation in order to find the matrix elements of $\widehat{\mathbf{H}}$. Let us write a general term in the connected Hamiltonian as $\hat{W}$, such that:

$$\hat{W} = \frac{1}{k!}\frac{1}{l!}W(a^\dagger)^k(a)^l \tag{2.77}$$

Any general matrix element from this perturbation can now be written as follows.

$$\begin{aligned} \langle m|\hat{W}|n\rangle &= \frac{1}{k!}\frac{1}{l!}W\langle m|(a^\dagger)^k(a)^l|n\rangle \\ &= \frac{1}{k!}\frac{1}{l!}W\langle 0|\frac{1}{\sqrt{m!}}(a)^m(a^\dagger)^k(a)^l\frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle \\ &= \frac{1}{k!}\frac{1}{l!}W\frac{1}{\sqrt{m!}}\frac{1}{\sqrt{n!}}\langle 0|(a)^m(a^\dagger)^k(a)^l(a^\dagger)^n|0\rangle \end{aligned} \tag{2.78}$$

We can then show that the matrix element is greatly simplified. In fact, the only case for which the matrix element is non-zero occurs for:

$$\langle 0|(a)^m(a^\dagger)^k(a)^l(a^\dagger)^n|0\rangle = \frac{m!n!}{(n-l)!} \quad \textit{iff} \quad m-k=n-l \tag{2.79}$$

And therefore, the matrix elements can be written:

$$\langle m|\hat{W}|n\rangle = W\frac{\sqrt{m!n!}}{(n-l)!k!l!} \quad \textit{iff} \quad m=n+k-l \tag{2.80}$$

3. Applications

After having derived the general framework of our coupled cluster approach as well as the necessary tool with which to generate our operating equations, we next

present some explicit applications in order to evaluate the approach. We note that the method is still under development and the presented examples do not constitute an exhaustive testing of the method, but point to some basic properties. In addition, the application process lead to a somewhat unexpected development by which to improve on the numerical results, i.e. the use of an operator transformation scheme by which an improved unperturbed Hamiltonian can be obtained.

In this section, we will derive and illustrate the results for two different cases with different levels of complexity. The case of a quadratic perturbation allows for a relatively simple application of our diagrammatic techniques to derive operating equations. An example of a quadratic perturbation would be a simple modification of the original harmonic oscillator potentials by changing the mass of the oscillators. A change in mass could be directly incorporated into the mass-weighted normal coordinates which would immediately give rise to a new set of harmonic oscillators with new frequencies. One would therefore expect that any successful model would mirror this situation. Here we will show the details of the development of the EoM-CC model for a set of oscillators under a quadratic perturbation. In a second application we investigate a single oscillator subjected to a perturbation including a quartic term. Before we venture into solving the general case of coupled equations at the quartic level, we used this example to gain some additional experience regarding the behavior of our model.

3.1. Quadratic Perturbation

In order to keep things general, we will write the Hamiltonian with a quadratic perturbation as follows, noting that a quadratic perturbation will create some zeroth order perturbative constants when normal ordered (e.g. $aa^\dagger = a^\dagger a + 1$).

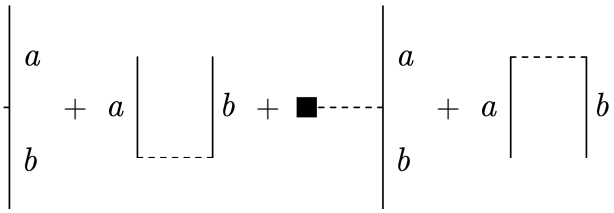
$$
\begin{aligned}
H_0 &= \sum_a \left(a_a^\dagger a_a + \frac{1}{2} \right) \omega_a = \sum_{ab} \omega_a^b \delta_{ab} a_a^\dagger a_b + \sum_a \frac{1}{2} \omega_a \\
V &= \frac{1}{2!} \sum_{ab} B_{ab} a_a^\dagger a_b^\dagger + \sum_{ab} J_a^b a_a^\dagger a_b + \frac{1}{2!} \sum_{ab} B^{ab} a_a a_b + c
\end{aligned}
\tag{3.1}
$$

The perturbation consists of the V_2 terms introduced earlier, as well as a constant V_0 term with no operators. For a simple comparison, a quadratic perturbation for a single oscillator would look something like $V = \beta q^2$. In the formalism of creation and annihilation operators, this reads:

$$
\beta q^2 = \frac{\beta}{2} (a^\dagger a^\dagger + 2 a^\dagger a + a a + 1) \tag{3.2}
$$

Now for the general case we have expressed $H = H_0 + V$ in diagrammatic form below. We have already encountered this in a previous example, although here the extra closed part of the Hamiltonian is added on.

$$
H_{open} = \sum_{ab} \omega_a^b \delta_{ab} a_a^\dagger a_b + \frac{1}{2!} \sum_{ab} B_{ab} a_a^\dagger a_b^\dagger + \sum_{ab} J_a^b a_a^\dagger a_b + \frac{1}{2!} \sum_{ab} B^{ab} a_a a_b
$$



(3.3)

$$
H_{closed} = c + \sum_a \frac{1}{2} \omega_a
$$

The next step is to choose the appropriate cluster operators, so that we can solve for the desired amplitudes. Consideration of parity is especially useful here, due to relations between the parity operator and operators in the Hamiltonian.

$$
\{P, a_i^\dagger\} = \{P, a_i\} = 0 \quad \forall i \tag{3.4}
$$

By definition of the parity operator, we already know that the unperturbed ground state is of even parity. In the case of the quadratic perturbation we can quickly show

that $[V_2, P] = 0$, since each term consists of two creation/annihilation operators. For this reason, we can assume that the new perturbed ground state is also of even parity. This limits the cluster operators needed in the expansion to only even operators $T_2, T_4, ..., T_{2n}$. While this seems like an easy simplification, one should note that when, for example, cubic potential terms are included in the anharmonic perturbation, the parity operator no longer commutes with the full Hamiltonian.

We can also use the shape of the diagrams to infer where the BCH expansion 'self-truncates'. The term with the most amount of a_i operators (or 'down-facing lines') is $\hat{B}^{ab}$, which is able to participate in two connections at most. This way, the BCH expansion only requires us to use terms up to T^2.

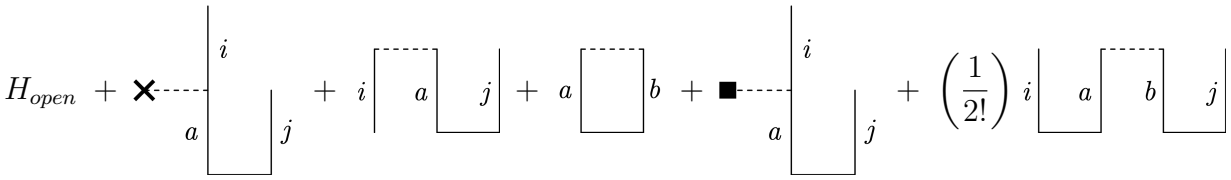
For the specific case of a quadratic perturbation, analysis of the Hamiltonian diagrams can be used to further infer the highest T_n operator which needs to be considered. We can see that, if left unconnected, the $\hat{B}_{ab}$ term in the Hamiltonian is the only term which will directly contribute to the cluster amplitudes in T_2. Furthermore, no terms in the Hamiltonian will contribute to T_4 or higher excitations when connected with T_2. Therefore, any terms past T_2 are not needed. By this, we now know that T_2 is the only required operator in the expansion for this case.

We can now write the cluster operator e^T as:

$$e^T = e^{T_2} = 1 + T_2 + \frac{1}{2!}T_2^2 + ... = 1 \; + \; k \left\lfloor \quad \right\rfloor l \; + \; \frac{1}{2!}\, k \left\lfloor \quad \right\rfloor l \; m \left\lfloor \quad \right\rfloor n + ... \quad (3.5)$$

where we will only include terms up to and including T_2^2 since no additional higher power terms can completely connect with the Hamiltonian in the BCH expansion. The connections between the Hamiltonian and the exponential operator will be represented in diagrammatic form below.

$(He^{T_2})_C =$



(3.6)

Our diagrammatic rules can then be used to interpret each term as follows.

$$(He^{T_2})_C = H_{open} + \frac{1}{2!}\sum_{ij}\sum_{a} S_2\left(\omega_i^a \delta_{ai} t_{aj}\right) a_i^\dagger a_j^\dagger + \sum_{i,j}\sum_{a} B^{ia} t_{aj} a_j^\dagger a_i + \frac{1}{2!}\sum_{ab} B^{ab} t_{ab}$$
$$+ \frac{1}{2!}\sum_{ij}\sum_{a} S_2\left(J_i^a t_{aj}\right) a_i^\dagger a_j^\dagger \; + \; \left(\frac{1}{2!}\right)\frac{1}{2!}\sum_{ij}\sum_{ab} S_2'\left(B^{ab} t_{ia} t_{bj}\right) a_i^\dagger a_j^\dagger \tag{3.7}$$

We have used S' here to denote a term that should be symmetrized, but may partially or completely collapse due to having two or more T operators being treated equivalently. After symmetrization, the above terms read:

$$(He^{T_2})_C = H_{open} + \frac{1}{2!}\sum_{ij}\sum_{a}\left(\omega_i^a \delta_{ai} t_{aj} + \omega_j^a \delta_{aj} t_{ai}\right) a_i^\dagger a_j^\dagger + \sum_{i,j}\sum_{a} B^{ia} t_{aj} a_j^\dagger a_i$$
$$+ \frac{1}{2!}\sum_{ab} B^{ab} t_{ab} + \frac{1}{2!}\sum_{ij}\sum_{a}\left(J_i^a t_{aj} + J_j^a t_{ai}\right) a_i^\dagger a_j^\dagger + \left(\frac{1}{2!}\right)\frac{1}{2!}\sum_{ij}\sum_{ab} 2B^{ab} t_{ia} t_{bj} a_i^\dagger a_j^\dagger \tag{3.8}$$

Now that we have derived all of the terms in $(He^{T_2})_C$, we may wish to group them together based on their operators for convenience. Let us define the following.

$$(He^{T_2})_{C,open} = \sum_{ij} \omega_i^j \delta_{ij} a_i^\dagger a_j + \frac{1}{2!}\sum_{ij} \mathcal{K}_{ij} a_i^\dagger a_j^\dagger + \sum_{ij} \mathcal{L}_i^j a_i^\dagger a_j + \frac{1}{2!}\sum_{ij} \mathcal{M}^{ij} a_i a_j \tag{3.9}$$

The script $\mathcal{K}_{ij}$, $\mathcal{L}_i^j$, and $\mathcal{M}^{ij}$ represent the groups of terms found after connections.

$$\begin{aligned}
\frac{1}{2!}\mathcal{K}_{ij} =& \frac{1}{2!}B_{ij} + \frac{1}{2!}\sum_a \left(\omega_i^a \delta_{ai} t_{aj} + \omega_j^a \delta_{aj} t_{ai}\right) \\
&+ \frac{1}{2!}\sum_a \left(J_i^a t_{aj} + J_j^a t_{ai}\right) + \left(\frac{1}{2!}\right)\frac{1}{2!}\sum_{ab} 2B^{ab} t_{ia} t_{bj} \\
\mathcal{L}_i^j =& J_i^j + \sum_a B^{ja} t_{ai} \\
\frac{1}{2!}\mathcal{M}^{ij} =& \frac{1}{2!}B^{ij}
\end{aligned} \tag{3.10}$$

We have dropped the operators and their sum for convenience. Note that, in this (unique) case, each term can be written directly as a matrix product. Permuting indices and cancelling the factorials would allow us to write an equation for the cluster amplitude directly. Let us define some matrix $\mathbf{T}_2$, which has matrix elements t_{ij}. The matrix form of $\mathcal{K}_{ij}$, $\mathcal{L}_i^j$, and $\mathcal{M}^{ij}$ are as follows.

$$\begin{aligned}
\mathcal{K}_{ij} &= \mathbf{B}^*_{ij} + \left(\omega_i t_{ij} + \omega_j t_{ji}\right) + \left(\mathbf{J}\mathbf{T}_2\right)_{ij} + \left(\mathbf{T}_2\mathbf{J}\right)_{ij} + \left(\mathbf{T}_2\mathbf{B}\mathbf{T}_2\right)_{ij} \\
\mathcal{L}_i^j &= \mathbf{J}_{ij} + \left(\mathbf{T}_2\mathbf{B}\right)_{ij} \\
\mathcal{M}^{ij} &= \mathbf{B}_{ij}
\end{aligned} \tag{3.11}$$

As the some of the coefficients here are symmetric (e.g. $B_{ij} = B_{ji}$; $t_{ij} = t_{ji}$), their corresponding matrices will be symmetric as well ($\mathbf{B}^T = \mathbf{B}$; $\mathbf{T}_2^T = \mathbf{T}_2$). The operating equations for cluster amplitudes which were derived earlier show that:

$$\langle 0|a_r a_s (He^T)_C|0\rangle = \langle 0|a_r a_s \frac{1}{2!}\sum_{ij}\mathcal{K}_{ij} a_i^\dagger a_j^\dagger|0\rangle = \frac{1}{2!}\sum_{ij}\mathcal{K}_{ij}\langle 0|a_r a_s a_i^\dagger a_j^\dagger|0\rangle = 0 \tag{3.12}$$

As every term $\langle 0|a_r a_s a_i^\dagger a_j^\dagger|0\rangle$ is greater than zero, the only solution is that for which all $\mathcal{K}_{ij} = 0$. Therefore, we have:

$$\mathbf{B}^*_{ij} + \left(\omega_i + \omega_j\right) t_{ij} + \left(\mathbf{J}\mathbf{T}_2\right)_{ij} + \left(\mathbf{T}_2\mathbf{J}\right)_{ij} + \left(\mathbf{T}_2\mathbf{B}\mathbf{T}_2\right)_{ij} = 0 \tag{3.13}$$

An iterative procedure is used to solve the above equation, beginning by setting all cluster amplitudes to some $\mathbf{T}_2^{(0)} = 0$, and iterating according to:

$$t_{ij}^{(n+1)} = -\frac{\left[\mathbf{B}^* + \mathbf{J}\mathbf{T}_2^{(n)} + \mathbf{T}_2^{(n)}\mathbf{J} + \mathbf{T}_2^{(n)}\mathbf{B}\mathbf{T}_2^{(n)}\right]_{ij}}{\left(\omega_i + \omega_j\right)} \tag{3.14}$$

Although it may seem trivial, it is important to relate the fact that once $t_{ij}^{(n)}$ is converged, $\mathcal{K}_{ij} = 0$. The perturbed ground state energy is subsequently given by:

$$\begin{aligned} \tilde{E}_0 &= (He^T)_{C,closed} + H_{closed} \\ &= \frac{1}{2!}\sum_{ab} B^{ab}t_{ab} + c + \sum_a \frac{1}{2}\omega_a = \frac{1}{2!}Tr(\mathbf{B}\mathbf{T}_2) + c + E_0 \end{aligned} \tag{3.15}$$

Where we have again permuted the indices to write the expression in matrix form. We have also used the fact that the unperturbed ground state energy is $E_0 = \sum_a \frac{1}{2}\omega_a$.

3.1.1. Excited States

Transitioning to the excited states of a single oscillator, the matrix equation for $\widehat{\mathbf{H}} = (He^T)_{C,open}$ is simplified as well. As all open terms in $(He^T)_C$ contain an even amount of operators, any matrix elements between states differing by an odd number become zero.

$$\widehat{\mathbf{H}} = \begin{pmatrix} \langle 0|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 0|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 0|\,\widehat{\mathbf{H}}\,|2\rangle & \cdots \\ \langle 1|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 1|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 1|\,\widehat{\mathbf{H}}\,|2\rangle & \cdots \\ \langle 2|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 2|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 2|\,\widehat{\mathbf{H}}\,|2\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} \langle 0|\,\widehat{\mathbf{H}}\,|0\rangle & 0 & \langle 0|\,\widehat{\mathbf{H}}\,|2\rangle & \cdots \\ 0 & \langle 1|\,\widehat{\mathbf{H}}\,|1\rangle & 0 & \cdots \\ \langle 2|\,\widehat{\mathbf{H}}\,|0\rangle & 0 & \langle 2|\,\widehat{\mathbf{H}}\,|2\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{3.16}$$

The matrix then decouples, separating states with even and odd parity.

$$\begin{pmatrix} \langle 0|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 0|\,\widehat{\mathbf{H}}\,|2\rangle & \langle 0|\,\widehat{\mathbf{H}}\,|4\rangle & \cdots \\ \langle 2|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 2|\,\widehat{\mathbf{H}}\,|2\rangle & \langle 2|\,\widehat{\mathbf{H}}\,|4\rangle & \cdots \\ \langle 4|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 4|\,\widehat{\mathbf{H}}\,|2\rangle & \langle 4|\,\widehat{\mathbf{H}}\,|4\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{0n} \\ c_{2n} \\ c_{4n} \\ \vdots \end{pmatrix} = \Delta\tilde{E}_n \begin{pmatrix} c_{0n} \\ c_{2n} \\ c_{4n} \\ \vdots \end{pmatrix} \tag{3.17}$$

$$\begin{pmatrix} \langle 1|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 1|\,\widehat{\mathbf{H}}\,|3\rangle & \langle 1|\,\widehat{\mathbf{H}}\,|5\rangle & \cdots \\ \langle 3|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 3|\,\widehat{\mathbf{H}}\,|3\rangle & \langle 3|\,\widehat{\mathbf{H}}\,|5\rangle & \cdots \\ \langle 5|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 5|\,\widehat{\mathbf{H}}\,|3\rangle & \langle 5|\,\widehat{\mathbf{H}}\,|5\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{1n} \\ c_{3n} \\ c_{5n} \\ \vdots \end{pmatrix} = \Delta\tilde{E}_n \begin{pmatrix} c_{1n} \\ c_{3n} \\ c_{5n} \\ \vdots \end{pmatrix} \tag{3.18}$$

Looking at individual terms in $(He^T)_{C,open}$, we see that the number of operators in any term is either 2 or 0, which causes another massive simplification in the form of our matrices. The only non-zero matrix elements therefore lie along or immediately adjacent to the diagonal.

$$\begin{pmatrix} \langle 0|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 0|\,\widehat{\mathbf{H}}\,|2\rangle & 0 & \cdots \\ \langle 2|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 2|\,\widehat{\mathbf{H}}\,|2\rangle & \langle 2|\,\widehat{\mathbf{H}}\,|4\rangle & \cdots \\ 0 & \langle 4|\,\widehat{\mathbf{H}}\,|2\rangle & \langle 4|\,\widehat{\mathbf{H}}\,|4\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{0n} \\ c_{2n} \\ c_{4n} \\ \vdots \end{pmatrix} = \Delta\tilde{E}_n \begin{pmatrix} c_{0n} \\ c_{2n} \\ c_{4n} \\ \vdots \end{pmatrix} \tag{3.19}$$

$$\begin{pmatrix} \langle 1|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 1|\,\widehat{\mathbf{H}}\,|3\rangle & 0 & \cdots \\ \langle 3|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 3|\,\widehat{\mathbf{H}}\,|3\rangle & \langle 3|\,\widehat{\mathbf{H}}\,|5\rangle & \cdots \\ 0 & \langle 5|\,\widehat{\mathbf{H}}\,|3\rangle & \langle 5|\,\widehat{\mathbf{H}}\,|5\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{1n} \\ c_{3n} \\ c_{5n} \\ \vdots \end{pmatrix} = \Delta\tilde{E}_n \begin{pmatrix} c_{1n} \\ c_{3n} \\ c_{5n} \\ \vdots \end{pmatrix} \tag{3.20}$$

In the special case when $\mathbf{T}_2$ has converged, we know that we will have reached a solution where $\frac{1}{2!}\mathcal{K}a^\dagger a^\dagger = 0$. Therefore, any elements of the form $\langle m+2|\,\widehat{\mathbf{H}}\,|m\rangle$ will become zero as well.

$$\begin{pmatrix} \langle 0|\,\widehat{\mathbf{H}}\,|0\rangle & \langle 0|\,\widehat{\mathbf{H}}\,|2\rangle & 0 & \cdots \\ 0 & \langle 2|\,\widehat{\mathbf{H}}\,|2\rangle & \langle 2|\,\widehat{\mathbf{H}}\,|4\rangle & \cdots \\ 0 & 0 & \langle 4|\,\widehat{\mathbf{H}}\,|4\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{0n} \\ c_{2n} \\ c_{4n} \\ \vdots \end{pmatrix} = \Delta\tilde{E}_n \begin{pmatrix} c_{0n} \\ c_{2n} \\ c_{4n} \\ \vdots \end{pmatrix} \tag{3.21}$$

$$\begin{pmatrix} \langle 1|\,\widehat{\mathbf{H}}\,|1\rangle & \langle 1|\,\widehat{\mathbf{H}}\,|3\rangle & 0 & \cdots \\ 0 & \langle 3|\,\widehat{\mathbf{H}}\,|3\rangle & \langle 3|\,\widehat{\mathbf{H}}\,|5\rangle & \cdots \\ 0 & 0 & \langle 5|\,\widehat{\mathbf{H}}\,|5\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_{1n} \\ c_{3n} \\ c_{5n} \\ \vdots \end{pmatrix} = \Delta\tilde{E}_n \begin{pmatrix} c_{1n} \\ c_{3n} \\ c_{5n} \\ \vdots \end{pmatrix} \tag{3.22}$$

For such upper triangular matrices there is no need for diagonalization to find the eigenvalues, since they can be obtained directly from the diagonal elements of the matrices given by $\widehat{\mathbf{H}}_{mm}$.

$$\begin{aligned} \widehat{\mathbf{H}}_{mm} &= \langle m|\,\widehat{\mathbf{H}}\,|m\rangle = \langle m|\left(\omega a^\dagger a + \mathcal{L}a^\dagger a\right)|m\rangle = \tilde{E}_m - \tilde{E}_0 \\ \tilde{E}_m &= m\left(\omega + \mathcal{L}\right) + \tilde{E}_0 = m\left(\omega + J + Bt_2\right) + \tilde{E}_0 \end{aligned} \tag{3.23}$$

This result is better illustrated if we write the new ground state out to mirror this equation.

$$\tilde{E}_0 = \frac{1}{2!}Bt_2 + c + \frac{1}{2}\omega = \frac{1}{2}\left(\omega + J + Bt_2\right) + \left(c - \frac{1}{2}J\right) \tag{3.24}$$

We have therefore showed that the quadratic problem simplifies into a new harmonic oscillator where the ground state energy has been shifted up by $\left(c - \frac{1}{2}J\right)$. The new transition energy of this oscillator is given by $\tilde{\omega} = \omega + J + Bt_2$.

3.1.2. Bogoliubov Transformations

The fact that the coupled cluster solution for a quadratic perturbation leads to a new set of harmonic oscillators can also be obtained through the application of a

Bogoliubov transformation, with an example for a single oscillator shown in (18). We note that a number of other possible transformations exist (19), but this becomes the most convenient to use in our case. The following derivation illustrates the result of such a transformation for a single oscillator, though the generalization to multiple oscillators is straightforward. Our perturbed Hamiltonian reads:

$$H = a^\dagger a\omega + \frac{1}{2!}Ba^\dagger a^\dagger + \frac{1}{2!}Baa + Ja^\dagger a + c + \frac{1}{2}\omega \tag{3.25}$$

For the case of a quadratic perturbation, we make use of the following Bogoliubov transformation.

$$b^\dagger = Fa^\dagger + Ga \qquad ; \qquad b = F^*a + G^*a^\dagger \tag{3.26}$$

We seek a transformation for which the transformed operators satisfy the bosonic commutation relation.

$$[b, b^\dagger] = 1 \tag{3.27}$$

This commutator relates the transformation coefficients as:

$$\begin{aligned}
&[b, b^\dagger] = bb^\dagger - b^\dagger b \\
&= (F^*a + G^*a^\dagger)(Fa^\dagger + Ga) - (Fa^\dagger + Ga)(F^*a + G^*a^\dagger) \\
&= (F^*G - GF^*)aa + (G^*G - FF^*)a^\dagger a + (F^*F - GG^*)aa^\dagger + (G^*F - FG^*)a^\dagger a^\dagger \\
&= (G^*G - FF^*)a^\dagger a + (F^*F - GG^*)aa^\dagger = (F^*F - GG^*)(aa^\dagger - a^\dagger a) \\
&= (F^*F - GG^*)[a, a^\dagger] = |F|^2 - |G|^2 = 1
\end{aligned} \tag{3.28}$$

These transformed operators will act on a new set of states denoted by $|n\rangle_b$, i.e.

$$\begin{aligned}
b|n\rangle_b = \sqrt{n}|n-1\rangle_b \qquad ; \qquad b^\dagger|n\rangle_b = \sqrt{n+1}|n+1\rangle_b \\
b|0\rangle_b = 0 \qquad ; \qquad b^\dagger b|n\rangle_b = n|n\rangle_b
\end{aligned} \tag{3.29}$$

Let's consider the condition for $b|0\rangle_b = 0$. As we can write any state as a linear combination of all states in the unperturbed basis, this equation can be expanded as

follows for a quadratic perturbation. We again note that the discussion of parity for this problem allows us to exclude any odd excitations.

$$b|0\rangle_b = be^S|0\rangle = 0 \quad ; \quad S = S_2 + S_4 + ... \quad ; \quad S_n = \frac{1}{n!}s_n(a^\dagger a^\dagger ... a^\dagger)_{n\ terms} \tag{3.30}$$

Where S is a cluster operator mirroring the T cluster operator for the original $|0\rangle$ vacuum state. Note however, that we cannot assume $s_n = t_n$ at this point. Applying e^{-S} to both sides, we find:

$$e^{-S}be^S|0\rangle = (be^S)_C|0\rangle = \left((F^*a + G^*a^\dagger)e^S\right)_C|0\rangle = 0 \tag{3.31}$$

The resulting terms of this connection can be obtained algebraically or by use of diagrammatics.

$$\begin{aligned}\left((F^*a + G^*a^\dagger)e^S\right)_C|0\rangle &= \left(F^*a + G^*a^\dagger + F^*s_2a^\dagger + \frac{1}{3!}F^*s_4a^\dagger a^\dagger a^\dagger + ...\right)|0\rangle \\ &= \left(\left(G^* + F^*s_2\right)a^\dagger + \frac{1}{3!}F^*s_4a^\dagger a^\dagger a^\dagger + ...\right)|0\rangle\end{aligned} \tag{3.32}$$

For the above relation to hold, we must have that

$$s_2 = -\frac{G^*}{F^*} \quad ; \quad s_4 = s_6 = ... = 0 \tag{3.33}$$

Using the result of the commutator in equation (3.28), we can rearrange the above expression for s_2.

$$G^* = -F^*s_2 \quad ; \quad F^*F - GG^* = F^*F - F^*s_2^*s_2F = 1 \tag{3.34}$$

We can now directly solve for the F and G needed in a Bogoliubov Transformation, in terms of s_2.

$$F = F^* = \left(1 - s_2^*s_2\right)^{-1/2} \quad ; \quad G = -Fs_2^* = -\left(1 - s_2^*s_2\right)^{-1/2}s_2^* \tag{3.35}$$

So far, we have only shown that any S_2 cluster operator generates a specific Bogoliubov transformation where the transformed operators have $e^{S_2}|0\rangle$ as the vacuum state.

Next we seek to express our perturbed Hamiltonian in our new operator basis. After substitution of our new operators into our perturbed Hamiltonian, we find that in order for the transformed Hamiltonian to be diagonal in the new basis we must have:

$$F^2 \left[(\omega + J)s^2 + \frac{1}{2}B^* + \frac{1}{2}B^* s^2 \right] = 0 \tag{3.36}$$

The expression in the parenthesis is nothing but the equation for the t_2 amplitudes found previously, so to make the Hamiltonian diagonal we must have that $s_2 = t_2$.

Normal ordering the remaining terms of the transformed Hamiltonian, we find that we can write:

$$H = \left(b^\dagger b + \frac{1}{2} \right) \tilde{\omega} + \left(c - \frac{1}{2} J \right) \quad ; \quad \tilde{\omega} = \omega + J + Bt_2 \tag{3.37}$$

We have found that if we select the cluster amplitude obtained from solving the coupled cluster equation, the corresponding Bogoliubov transformation results in our perturbed Hamiltonian being transformed into a new harmonic oscillator Hamiltonian. The Bogoliubov transformation also provides explicit expressions for the shift in the zero-point energy, as well as the frequency for the new oscillator identical to the ones we found using the EoM-CC approach. This result can be straightforwardly generalized to a set of harmonic oscillators subjected to a quadratic perturbation.

3.1.3. Illustrative Results

The equations derived were incorporated into a Python code which iteratively solved the coupled cluster amplitude equations and generated the ground state energy. Throughout the iterative process, we constructed matrices for the calculation of excited stated energies.

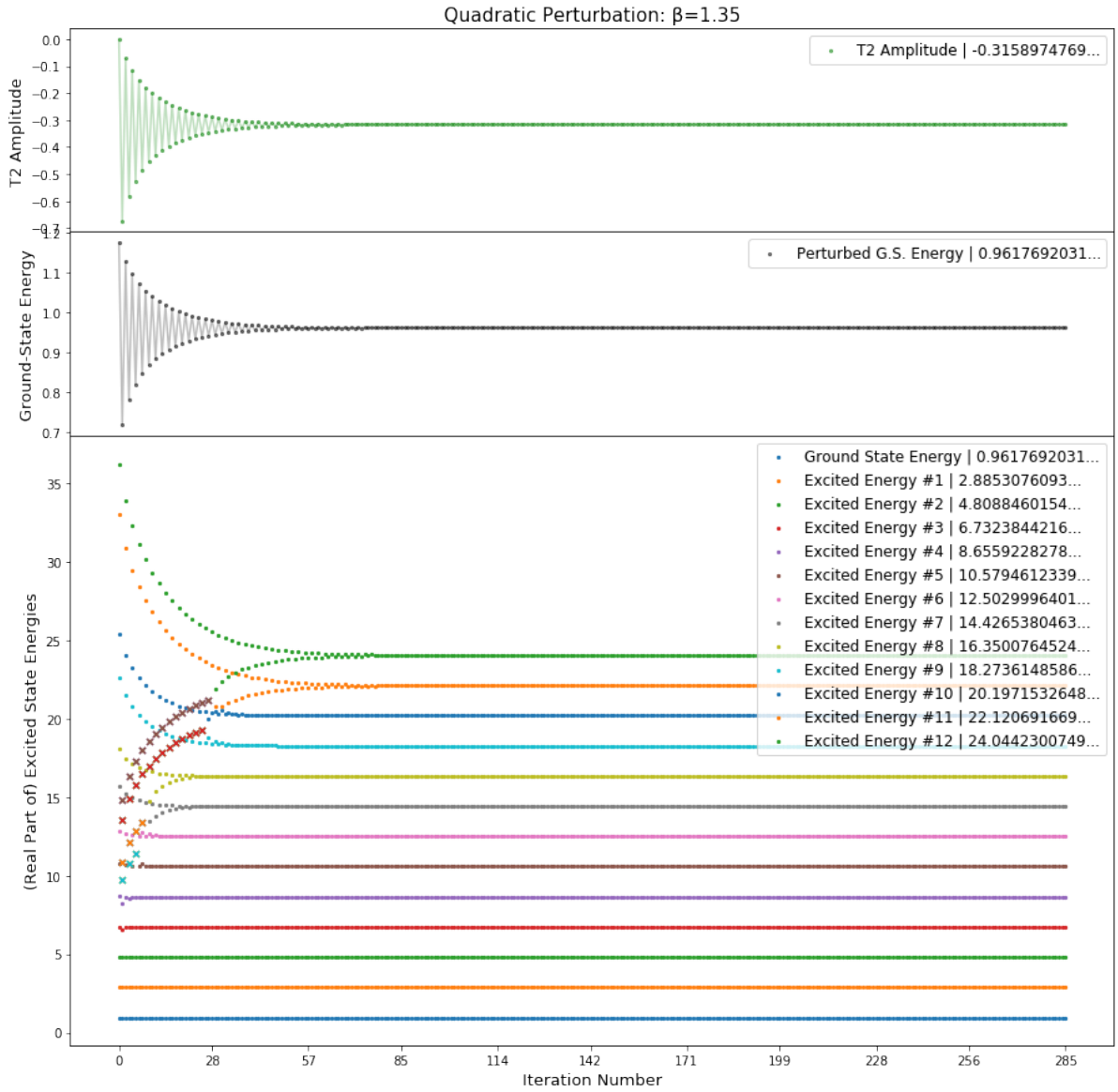


Fig. 3.— An illustration of the iterative scheme derived earlier, depicting how the T_2 amplitude, new ground state and excited state energies vary for each iteration. See text for further details.

Here we illustrate the behavior of the numerical results as we iterate our coupled cluster amplitude equations. The harmonic frequency in all of these examples will be set to $\omega = 1$ for simplicity. Figure 3 shows the numerical results for each iteration with potential coefficients given by $B = J = 1.35,\ c = 0.675$. The top graph in the figure

shows the oscillatory behavior towards convergence of the iterative values of the t_2 amplitude, and the middle graph depicts the corresponding oscillating perturbed ground state energy. Finally, the bottom part of the figure shows the behavior of the real part of the iterative excited state energies as obtained from the diagonalization of the matrix.

The effects of the fact that the matrix is non-hermitian are seen in the first (roughly) 30 iterations of the bottom graph, where certain eigenvalues of the Hamiltonian are complex (marked by x-points) until t_2 is closer to convergence. The graph also shows that the perturbed system exhibits a harmonic oscillator spectrum with equidistant energy levels as was expected from the analysis above.

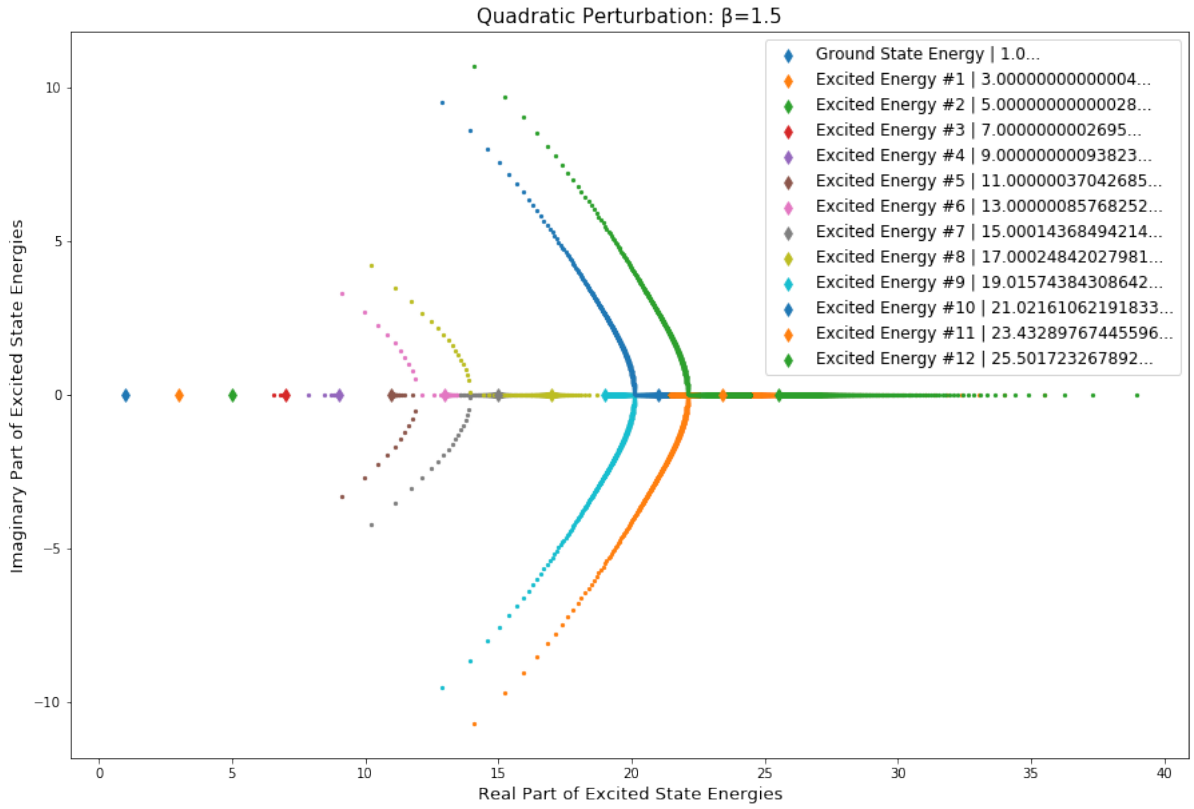


Fig. 4.— An illustration of the iterative scheme derived earlier, depicting how the energy of each state changes over each iteration in the complex plane. See text for further details.

Since we can expect the appearance of complex eigenvalues in our method, we also studied their behavior in more detail by plotting their paths in the complex plane as a function of iteration number. Here we used a slightly larger set of potential parameters, $B = J = 1.5,\ c = 0.75$. From Figure 4, we see how conjugate pairs of eigenvalues with large imaginary parts appear at the beginning of the iterative solution of the t_2 amplitude, only to end up on the real axis once the amplitude has converged. This behavior is to be expected, as we know that our method provides the exact solution in the quadratic case (i.e. all final eigenvalues will be real). For a more general perturbation, this may not be the case.

The perturbation parameters used in both cases correspond to a perturbation for which we can easily obtain the exact result, in the form of some $V = \beta q^2$. For the perturbation shown immediately above ($B = J = 1.5,\ c = 0.75$), the exact excited state energies turn out to simply be the odd integers 1, 3, 5, 7, and so on. This result is well reproduced by our calculated excited state energies. Discrepancies seen in higher excited states are able to be eliminated by using either a tighter convergence criterion for the cluster amplitude, or considering higher excited states when diagonalizing the $\widehat{\mathbf{H}}$ matrix.

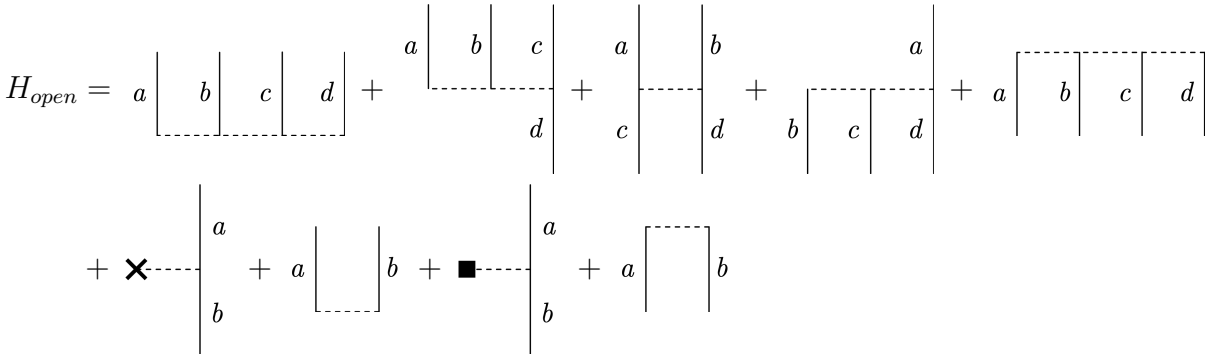
3.2. Quadratic + Quartic Perturbation

Following the earlier derivation, we can find the solution of a perturbation including both quadratic and quartic terms. A perturbation quadratic in q gives rise to normal ordered contributions to V_0 and V_2, and a perturbation quartic in q gives rise to normal ordered contributions to V_0, V_2, and V_4, (e.g. $aaa^\dagger a^\dagger = a^\dagger a^\dagger aa + 4a^\dagger a + 2$). Therefore, the formalism for handling a quartic perturbation automatically handles also the quadratic + quartic case and the Hamiltonian takes on the form:

$$
\begin{aligned}
H_0 &= \sum_a \left(a_a^\dagger a_a + \frac{1}{2} \right) \omega_a = \sum_{ab} \omega_a^b \delta_{ab} a_a^\dagger a_b + \sum_a \frac{1}{2} \omega_a \\
V &= \frac{1}{4!} \sum_{abcd} D_{abcd} a_a^\dagger a_b^\dagger a_c^\dagger a_d^\dagger + \frac{1}{3!} \sum_{abcd} L_{abc}^d a_a^\dagger a_b^\dagger a_c^\dagger a_d + \frac{1}{2!} \frac{1}{2!} \sum_{abcd} M_{ab}^{cd} a_a^\dagger a_b^\dagger a_c a_d \\
&+ \frac{1}{3!} \sum_{abcd} L_a^{bcd} a_a^\dagger a_b a_c a_d + \frac{1}{4!} \sum_{abcd} D^{abcd} a_a a_b a_c a_d \\
&+ \frac{1}{2!} \sum_{ab} B_{ab} a_a^\dagger a_b^\dagger + \sum_{ab} J_a^b a_a^\dagger a_b + \frac{1}{2!} \sum_{ab} B^{ab} a_a a_b + c
\end{aligned}
\tag{3.38}
$$

In diagrammatic form, we have $H = H_0 + V$ expressed in the equation below.

$H_{open} =$



$$
H_{closed} = c + \sum_a \frac{1}{2} \omega_a
\tag{3.39}
$$

Similar arguments can be made as before in order to simplify the cluster operator. Once again, all terms in the Hamiltonian have even parity, and therefore only $T_2, T_4, ..., T_{2n}$ terms are required. The term with the most amount of a_i operators (or 'down-facing lines') is $\hat{D}^{abcd}$, which is able to participate in four connections at most. This way, the BCH expansion again 'self-truncates' and only requires us to use terms up to T^4. The individual T operator is still an infinite sum, and requires us to manually truncate at some point.

In the present development we will include contributions from T_2 and T_4, but note that future work will also investigate the effects of higher levels of excitation. Additionally, in what follows we will only present results for a single oscillator although

the generalization of the equations to the case of multiple oscillators is straightforward. In this case, the perturbation can be written as $V = \beta q^2 + \delta q^4$. In terms of normal ordered annihilation and creation operators we find:

$$\begin{aligned}\beta q^2 &= \frac{\beta}{2}(a^\dagger a^\dagger + 2a^\dagger a + aa + 1) \\ \delta q^4 &= \frac{\delta}{4}(a^\dagger a^\dagger a^\dagger a^\dagger + 4a^\dagger a^\dagger a^\dagger a + 6a^\dagger a^\dagger aa + 4a^\dagger aaa + aaaa + 6a^\dagger a^\dagger + 12a^\dagger a + 6aa + 3)\end{aligned} \tag{3.40}$$

Applying our previously derived diagrammatic rules, we can now write down the equations for determining the cluster amplitudes, where we have deliberately retained the expressions on a form conducive for the application to multiple oscillators.

$$\begin{aligned}-\frac{1}{2!}2\omega t_2 = &\frac{1}{2!}B + \frac{1}{2!}2Jt_2 + \frac{1}{2!}B\left(\frac{1}{2!}2t_2t_2 + \frac{1}{2!}t_4\right) + \frac{1}{2!}\frac{1}{2!}Mt_2 \\ &+ \frac{1}{2!}L\left(\frac{1}{2!}\frac{1}{2!}2t_2t_2 + \frac{1}{3!}2t_4\right) \\ &+ \frac{1}{2!}D\left(\frac{1}{3!}\frac{1}{2!}2t_2t_2t_2 + \frac{1}{3!}2t_2t_4 + \frac{1}{2!}\frac{1}{2!}t_2t_4\right)\end{aligned} \tag{3.41}$$

$$\begin{aligned}-\frac{1}{4!}4\omega t_4 = &\frac{1}{4!}4Jt_4 + \frac{1}{4!}4Bt_2t_4 + \frac{1}{4!}D + \frac{1}{4!}4Lt_2 \\ &+ \frac{1}{4!}M\left(\frac{1}{2!}12t_2t_2 + \frac{1}{2!}6t_4\right) \\ &+ \frac{1}{4!}L\left(\frac{1}{3!}24t_2t_2t_2 + \frac{1}{2!}12t_2t_4 + \frac{1}{2!}4t_2t_4\right) \\ &+ \frac{1}{4!}D\left(\frac{1}{4!}24t_2t_2t_2t_2 + \frac{1}{2!}\frac{1}{2!}4t_2t_2t_4 + \frac{1}{2!}\frac{1}{2!}12t_2t_2t_4\right. \\ &\left.+ \frac{1}{2!}\frac{1}{2!}\frac{1}{2!}6t_4t_4 + \frac{1}{2!}\frac{1}{3!}4t_4t_4\right)\end{aligned} \tag{3.42}$$

as well as the ground state energy:

$$\tilde{E}_0 = \frac{1}{2!}Bt_2 + \frac{1}{4!}Dt_4 + \frac{1}{2!}\frac{1}{2!}\frac{1}{2!}Dt_2^2 + c + \frac{1}{2}\omega \tag{3.43}$$

The coefficients in the above expressions are given by

$$\begin{aligned} c &= \frac{\beta}{2} + \frac{3\delta}{4} \quad ; \quad B = 2! \left(\frac{\beta}{2} + \frac{6\delta}{4} \right) \quad ; \quad J = \frac{2\beta}{2} + \frac{12\delta}{4} \\ D &= 4! \frac{\delta}{4} \quad ; \quad L = 3! \frac{4\delta}{4} \quad ; \quad M = 2!2! \frac{6\delta}{4} \end{aligned} \tag{3.44}$$

3.2.1. Generalized Bogoliubov Transformations

As shown in the case of a quadratic perturbation, a Bogoliubov transformation based on converged T_2 amplitudes generates a new basis in which the Hamiltonian is diagonal (and the quadratic perturbation is transformed away). This leaves any further attempts to refine the energy using a CC calculation useless, since the amplitudes would be identically zero. The effect of the quadratic perturbation is shifted to a set of new harmonic frequencies and a constant energy contribution, as shown in equation (3.37).

We now wish to employ a similar tactic with respect to the quartic oscillator, in an attempt to create a basis in which the effects of the quartic perturbation would be lessened. Let's first consider a Hamiltonian for a single oscillator of the general form below, where a superscript has been introduced for the appearing constants for reasons which will shortly become apparent.

$$H_a = \Delta^{(0)} a^\dagger a + \frac{\omega}{2} + \Lambda^{(0)} a^\dagger a^\dagger + \Lambda^{(0)} a a + \Gamma^{(0)} + \delta^{(0)} \left[\frac{1}{\sqrt{2}} \left(a^\dagger + a \right) \right]^4 \tag{3.45}$$

Now, consider the effects on the above Hamiltonian due to a real Bogoliubov transformation of the same form presented in (3.26).

$$b^\dagger = F^{(0)} a^\dagger + G^{(0)} a \qquad ; \qquad b = G^{(0)} a^\dagger + F^{(0)} a \tag{3.46}$$

Note that we have again introduced superscripts, and $F^{(0)}$ and $G^{(0)}$ are both now defined to be real coefficients. Inverting these relations would lead to the expressions:

$$a^\dagger = F^{(0)} b^\dagger - G^{(0)} b \qquad ; \qquad a = -G^{(0)} b^\dagger + F^{(0)} b \tag{3.47}$$

Now, we can use these expressions to rewrite each individual term in equation (3.45), in terms of the operators arising from the Bogoliubov transformation.

$$\begin{aligned}
\Delta^{(0)}a^\dagger a &= \left((F^{(0)})^2 + (G^{(0)})^2\right)\Delta^{(0)}b^\dagger b - F^{(0)}G^{(0)}\Delta^{(0)}b^\dagger b^\dagger - F^{(0)}G^{(0)}\Delta^{(0)}bb + (G^{(0)})^2\Delta^{(0)} \\
\Lambda^{(0)}\left(a^\dagger a^\dagger + aa\right) &= \left((F^{(0)})^2 + (G^{(0)})^2\right)\Lambda^{(0)}\left(b^\dagger b^\dagger + bb\right) - 4F^{(0)}G^{(0)}\Lambda^{(0)}b^\dagger b - 2F^{(0)}G^{(0)}\Lambda^{(0)} \\
\delta^{(0)}\left[\frac{1}{\sqrt{2}}\left(a^\dagger + a\right)\right]^4 &= \left(F^{(0)} - G^{(0)}\right)^4\delta^{(0)}\left[\frac{1}{\sqrt{2}}\left(b^\dagger + b\right)\right]^4
\end{aligned} \tag{3.48}$$

Collecting terms, we find that we can write the transformed operator on the same form as equation (3.45).

$$H_b = \Delta^{(1)}b^\dagger b + \frac{\omega}{2} + \Lambda^{(1)}b^\dagger b^\dagger + \Lambda^{(1)}bb + \Gamma^{(1)} + \delta^{(1)}\left[\frac{1}{\sqrt{2}}\left(b^\dagger + b\right)\right]^4 \tag{3.49}$$

This new Hamiltonian and the one in equation (3.45) are identical, where we have now defined:

$$\begin{aligned}
\Delta^{(1)} &= \left((F^{(0)})^2 + (G^{(0)})^2\right)\Delta^{(0)} - 4F^{(0)}G^{(0)}\Lambda^{(0)} \\
\Lambda^{(1)} &= \left((F^{(0)})^2 + (G^{(0)})^2\right)\Lambda^{(0)} - F^{(0)}G^{(0)}\Delta^{(0)} \\
\Gamma^{(1)} &= \Gamma^{(0)} + (G^{(0)})^2\Delta^{(0)} - 2F^{(0)}G^{(0)}\Lambda^{(0)} \\
\delta^{(1)} &= \left(F^{(0)} - G^{(0)}\right)^4\delta^{(0)}
\end{aligned} \tag{3.50}$$

Both sets of operators sets, by construction, also satisfy the bosonic commutation relations (i.e. $[a, a^\dagger] = 1$ and $[b, b^\dagger] = 1$). The Bogoliubov transformation does, however, change our zeroth order harmonic oscillator Hamiltonians. For the two sets of operators, we find:

$$H_a^{(0)} = \Delta^{(0)}a^\dagger a + \frac{\omega}{2} + \Gamma^{(0)} \qquad \rightarrow \qquad H_b^{(0)} = \Delta^{(1)}b^\dagger b + \frac{\omega}{2} + \Gamma^{(1)} \tag{3.51}$$

We note that two sets of operators refer to different vacuum states, and consequently also have different ground state energies. One would therefore also expect different results for any approximate calculation of the eigenvalues to the Hamiltonian $H_a(= H_b)$.

Here we propose the following scheme, using iterative Bogoliubov transformations, to improve the accuracy of the energy derived in our coupled cluster method for any particular truncation of the cluster operator. Below, we will specifically illustrate the method with $T = T_2 + T_4$.

First we note that our quartic oscillator Hamiltonian can be written in the form given in equation (3.45).

$$\Delta^{(0)} = \omega \quad ; \quad \Lambda^{(0)} = 0 \quad ; \quad \Gamma^{(0)} = 0 \quad ; \quad \delta^{(0)} = \delta \tag{3.52}$$

Solving the EoM-CC equations for this Hamiltonian provides us with cluster amplitudes $t_2^{(0)}$ and $t_4^{(0)}$, via equations (2.19). Next, we perform the Bogoliubov transformation using the $t_2^{(0)}$ cluster amplitude, such that the commutation relation for the new operator is guaranteed ($[b, b^\dagger] = 1$).

$$F^{(0)} = \left(1 - \left(t_2^{(0)}\right)^2\right)^{-1/2} \quad ; \quad G^{(0)} = -\left(1 - \left(t_2^{(0)}\right)^2\right)^{-1/2} t_2^{(0)} \tag{3.53}$$

This then generates the new Hamiltonian, H_b. In the case of the quadratic perturbation, the effect of this transformation was to bring the Hamiltonian to a diagonal form where $t_2 = 0$. Although this does not immediately occur for a quartic perturbation, we still expect the t_2 amplitude to be reduced in magnitude over a number of iterations. Once new amplitudes $t_2^{(1)}$ and $t_4^{(1)}$ are obtained, we can create a second Bogoliubov transformation using new transformation parameters:

$$F^{(1)} = \left(1 - \left(t_2^{(1)}\right)^2\right)^{-1/2} \quad ; \quad G^{(1)} = -\left(1 - \left(t_2^{(1)}\right)^2\right)^{-1/2} t_2^{(1)} \tag{3.54}$$

The process above is the basis for a calculation scheme using iterative Bogoliuov transformations with constants obtained from the following sets of equations

$$F^{(i)} = \left(1 - \left(t_2^{(i)}\right)^2\right)^{-1/2} \quad ; \quad G^{(i)} = -\left(1 - \left(t_2^{(i)}\right)^2\right)^{-1/2} t_2^{(i)} \tag{3.55}$$

$$
\begin{aligned}
\Delta^{(i+1)} &= \left((F^{(i)})^2 + (G^{(i)})^2\right)\Delta^{(i)} - 4F^{(i)}G^{(i)}\Lambda^{(i)} \\
\Lambda^{(i+1)} &= \left((F^{(i)})^2 + (G^{(i)})^2\right)\Lambda^{(i)} - F^{(i)}G^{(i)}\Delta^{(i)} \\
\Gamma^{(i+1)} &= \Gamma^{(i)} + (G^{(i)})^2\Delta^{(i)} - 2F^{(i)}G^{(i)}\Lambda^{(i)} \\
\delta^{(i+1)} &= \left(F^{(i)} - G^{(i)}\right)^4 \delta^{(i)}
\end{aligned}
\tag{3.56}
$$

In each step of the iterations we would expect the $t_2^{(i)}$ amplitude to diminish in magnitude, leading to the coefficients $F \to 1$ and $G \to 0$. The eigenvalues would then converge as when $F = 1$ and $G = 0$, the Bogoliubov transformation has no effect.

3.2.2. Illustrative Results

Below we illustrate the results for a perturbations of the form $V = \beta q^2 + \delta q^4$. The harmonic frequency in these examples was again set to $\omega = 1$.

Figure 5 shows the numerical results for each iteration with potential coefficients given by $B = J = 0.525,\ D = L = M = 0.75,\ C = 0.16875$. The top graph in the figure shows the oscillatory behavior towards convergence of the iterative values of the cluster amplitudes and the bottom graph depicts the corresponding oscillating perturbed ground state energy.

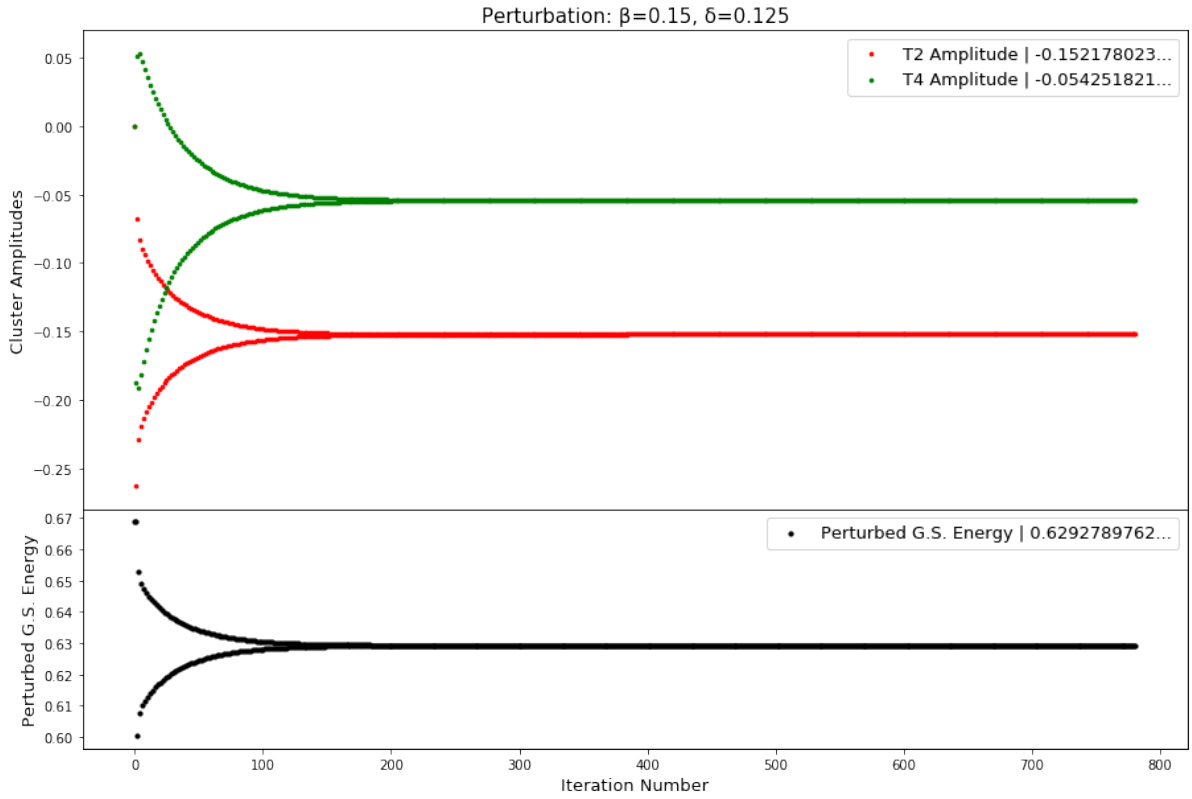


Fig. 5.— An illustration of the iterative scheme derived earlier, depicting how the cluster amplitudes and new ground state vary for each iteration. See text for further details.

As we showed earlier, in the pure quadratic case (when $\delta = 0$) we expect the T_2 operator to give the only nonzero cluster amplitude. On the other hand, this simplification cannot be made for a pure quartic perturbation (when $\beta = 0$). This is shown in the following two figures.

We note that the rate of convergence can be greatly improved by a very simple modification in our iterations. The oscillatory behavior of our iterated cluster amplitude can be damped to a large extent using the following scheme.

$$\frac{t_m^{(n-1)} + t_m^{(n-2)}}{2} \quad \Rightarrow \quad t_m^{(n)} \tag{3.57}$$

In the future we will experiment with other schemes by which to improve the rate of convergence of our coupled cluster iterations.

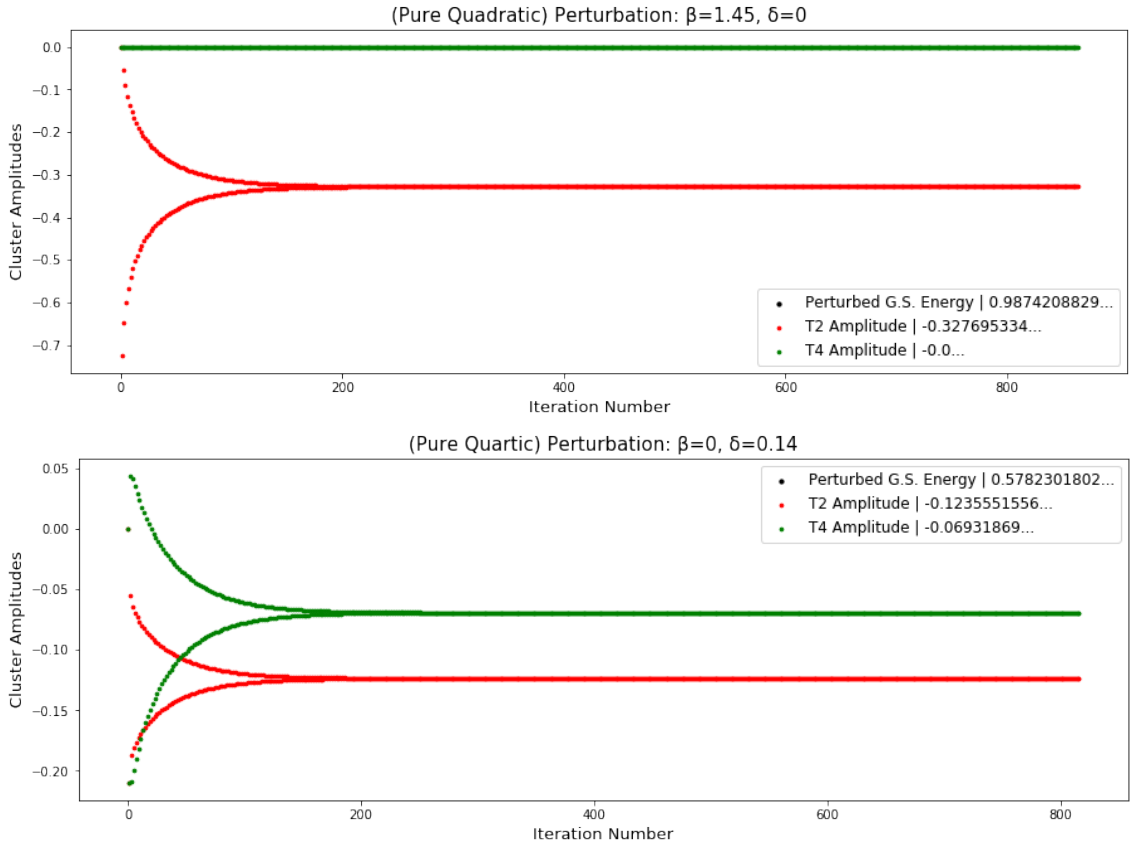


Fig. 6.— The iterative scheme applied to purely quadratic and purely quartic perturbations. In the quadratic example, we see T_2 leads to the only nonzero cluster amplitude as expected. For comparison, none of the amplitudes become zero in the quartic example.

Next, we discuss the accuracy of the coupled cluster results when compared to other methods. In Figure 7, we compare our numerical coupled clusters results for the ground state energy calculation for a single oscillator with other methods for a quartic perturbation of varying strength. For the single oscillator case we can calculate the (virtually) exact energies by numerical integration of the Schrödinger equation. We have previously developed a Python code for this purpose where the Schrödinger equation is recast into a Riccati equation and the eigenvalues are found by matching the logarithmic derivatives of the wave function. The exact result is shown in red in Figure 7.

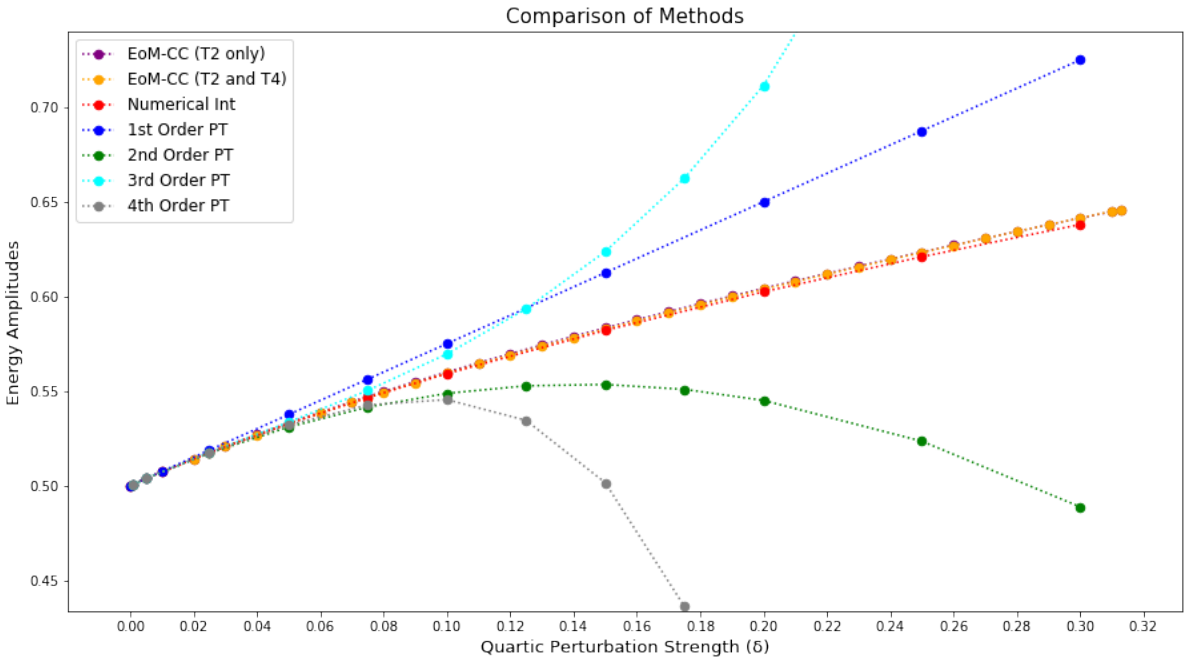


Fig. 7.— Comparison of results obtained by different orders of perturbation theory, coupled cluster methods, and numerical integration.

Bender and Wu (20) calculated the perturbation theory corrections for a quartic oscillator and found that the energy expression to fourth order is given by (note that $E = \omega$ in our units

$$E = E_0 + \frac{3}{4}\delta - \frac{21}{8}\delta^2 + \frac{333}{16}\delta^3 - \frac{30885}{128}\delta^4 \tag{3.58}$$

In the figure we have clearly gone beyond this limit as we see no hint of convergence. The figure provides the separate results obtained from perturbation theory for first, second, third, and fourth order. The quartic perturbation is interesting in that the perturbation series is divergent beyond a certain value of the perturbation strength. For small strengths of the perturbation parameter ($\delta < 0.1$), subsequent orders give an improvement to the energy but the results diverge for larger values. This is not to say that perturbation theory is not generally useful, but can be of limited range of applicability.

Our coupled cluster results, on the other hand, show good agreement with the exact results, even when only the T_2 cluster operator is included. We have to remind ourselves, however, that the T_2 operator also generates higher levels of excitations due to the exponential character of the theory.

To illustrate the effect on the calculated energy due to this iterative Bogoliubov transformation approach, Figure 8 shows results for a quartic perturbation with $\delta = 0.1$. For reference, the exact perturbed energy value obtained by numerical integration for this perturbation is $E = 0.55914633$.

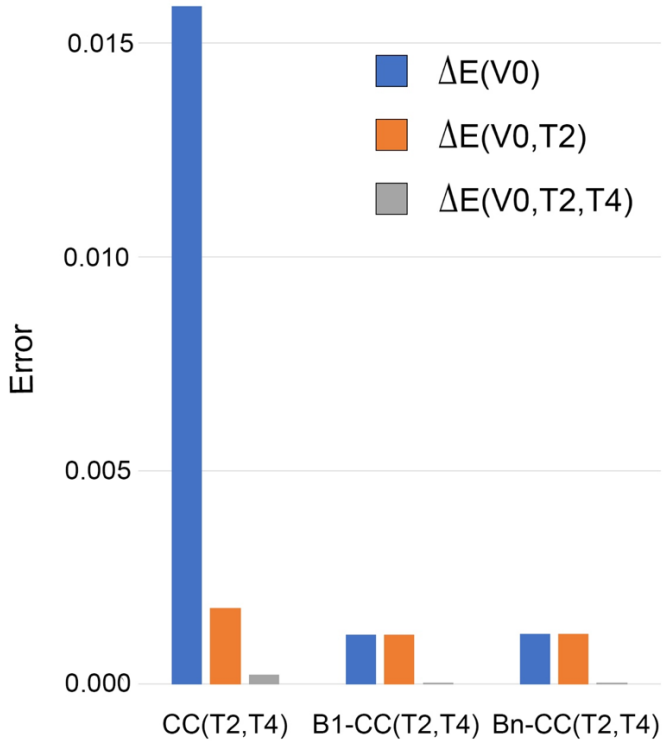


Fig. 8.— Error in the energy (calculated vs. exact) using three methods of calculation of the ground state energy for the quartic oscillator. See text for further details.

The blue bars show the deviation from the exact result when only first order contributions are considered (e.g. the constant terms in the normal ordered

Hamiltonian). Orange bars show the effect of only adding in the contribution due to T_2. Finally, the grey bar shows the full coupled cluster result including contributions from both T_2 and T_4.

The pre-Bogoliubov transformation results using T_2 and T_4 are labeled CC(T2,T4). We note that the energy to first order deviates considerably from the exact answer. Including contributions from T_2 reduces the error and finally, including contributions from both T_2 and T_4 improves the results even further.

The results labeled B1-CC(T2,T4) were obtained after solving the coupled cluster equations after a single Bogoliubov transformation using amplitudes from an initial set of calculated cluster amplitudes. Note the dramatic reduction in error in the first order result. This is due to the fact that a new zeroth order Hamiltonian is being used, which deviates less from the perturbed Hamiltonian than the original zeroth order Hamiltonian. Including contributions from T_2 does not seem to improve the situation, this being a result of the t_2 amplitude having been dramatically reduced after only one Bogoliubov transformation. Most importantly, the error obtained with including both T_2 and T_4 contributions has also diminished dramatically. Even a single Bogoliubov transformation gave us a much smaller error for our ground state eigenvalue. Finally, Bn-CC(T2,T4) labels the results after several consecutive Bogoliubov transformations, which only produces minor changes as the t_2 amplitude converges to zero rapidly after a few Bogoliubov iterations.

3.3. Full Quartic Perturbation

Although a code has not yet been written for the full quartic case, we have derived the iterative equations needed for a solution. As before, quartic perturbations in q give rise to normal ordered contributions to V_0, V_2 and V_4. A cubic perturbation q would similarly give rise to normal ordered contributions to V_1 and V_3. Therefore, a cubic

and quartic perturbation in q together would result in a full quartic perturbation as expressed in (2.11). Here we give the equations where the cluster operators T_2 and T_4 have been included.

The ground state energy is given by:

$$\begin{aligned} E_0 = V_0 + At_1 + B\left(\frac{1}{2!}t_2 + \frac{1}{2!}t_1t_1\right) + C\left(\frac{1}{3!}t_3 + \frac{1}{2!}t_1t_2 + \frac{1}{3!}t_1t_1t_1\right) + \\ D\left(\frac{1}{4!}t_4 + \frac{1}{2!}\frac{1}{2!}\frac{1}{2!}t_2t_2 + \frac{1}{3!}t_1t_3 + \frac{1}{2!}\frac{1}{2!}t_1t_1t_2 + \frac{1}{4!}t_1t_1t_1t_1\right) + \frac{1}{2}\omega \end{aligned} \tag{3.59}$$

And the coupled-cluster amplitude equations are given by:

$$\begin{aligned} -\omega t_1 = A + At_2 + Jt_1 + B\left(\frac{1}{2!}t_3 + t_1t_2\right) + K\left(\frac{1}{2!}t_2 + \frac{1}{2!}t_1t_1\right) + \\ C\left(\frac{1}{3!}t_4 + \frac{1}{2!}\frac{1}{2!}t_2t_2 + \frac{1}{2!}t_1t_3 + \frac{1}{2!}t_1t_1t_2\right) + L\left(\frac{1}{3!}t_3 + \frac{1}{2!}t_1t_2 + \frac{1}{3!}t_1t_1t_1\right) + \\ D\left(\frac{1}{3!}t_1t_4 + \left\{\frac{1}{2!}\frac{1}{2!}t_2t_3 + \frac{1}{3!}t_2t_3\right\} + \frac{1}{2!}\frac{1}{2!}t_1t_2t_2 + \frac{1}{2!}\frac{1}{2!}t_1t_1t_3 + \frac{1}{3!}t_1t_1t_1t_2\right) \end{aligned} \tag{3.60}$$

$$\begin{aligned} -\frac{1}{2!}2\omega t_2 = \frac{1}{2!}At_3 + \frac{1}{2!}B + \frac{1}{2!}2Jt_2 + \frac{1}{2!}B\left(\frac{1}{2!}t_4 + \frac{1}{2!}2t_2t_2 + t_1t_3\right) + \\ \frac{1}{2!}Kt_1 + \frac{1}{2!}K\left(\frac{1}{2!}2t_3 + 2t_1t_2\right) + \\ \frac{1}{2!}C\left(\frac{1}{2!}t_1t_4 + \left\{\frac{1}{2!}t_2t_3 + \frac{1}{2!}2t_2t_3\right\} + \frac{1}{2!}2t_1t_2t_2 + \frac{1}{2!}t_1t_1t_3\right) + \\ \frac{1}{2!}M\left(\frac{1}{2!}t_2 + \frac{1}{2!}t_1t_1\right) + \frac{1}{2!}L\left(\frac{1}{3!}2t_4 + \frac{1}{2!}\frac{1}{2!}2t_2t_2 + \frac{1}{2!}2t_1t_3 + \frac{1}{2!}2t_1t_1t_2\right) + \\ \frac{1}{2!}D\left(\left\{\frac{1}{2!}\frac{1}{2!}t_2t_4 + \frac{1}{3!}2t_2t_4\right\} + \left\{\frac{1}{2!}\frac{1}{2!}\frac{1}{2!}2t_3t_3 + \frac{1}{2!}\frac{1}{3!}t_3t_3\right\} + \right. \\ \left\{\frac{1}{2!}t_1t_2t_3 + \frac{1}{2!}2t_1t_2t_3\right\} + \frac{1}{2!}\frac{1}{2!}t_1t_1t_4 + \frac{1}{3!}\frac{1}{2!}2t_2t_2t_2 + \frac{1}{2!}\frac{1}{2!}2t_1t_1t_2t_2 + \\ \left.\frac{1}{3!}t_1t_1t_1t_3\right) \end{aligned} \tag{3.61}$$

$$
\begin{aligned}
-\frac{1}{3!}3\omega t_3 = {} & \frac{1}{3!}At_4 + \frac{1}{3!}3Jt_3 + \frac{1}{3!}B\left(t_1t_4 + 3t_2t_3\right) + \frac{1}{3!}C + \\
& \frac{1}{3!}3Kt_2 + \frac{1}{3!}K\left(\frac{1}{2!}3t_4 + \frac{1}{2!}6t_2t_2 + 3t_1t_3\right) + \\
& \frac{1}{3!}C\left(\left\{\frac{1}{2!}t_2t_4 + \frac{1}{2!}3t_2t_4\right\} + \frac{1}{2!}\frac{1}{2!}3t_3t_3 + t_1t_2t_3 + \frac{1}{2!}3t_1t_1t_4 + \frac{1}{3!}6t_2t_2t_2\right) + \\
& \frac{1}{3!}Lt_1 + \frac{1}{3!}M\left(\frac{1}{2!}3t_3 + 3t_1t_2\right) + \\
& \frac{1}{3!}L\left(\frac{1}{2!}3t_1t_4 + \left\{\frac{1}{2!}6t_2t_3 + \frac{1}{2!}3t_2t_3\right\} + \frac{1}{2!}6t_1t_2t_2 + \frac{1}{2!}3t_1t_1t_3\right) + \\
& \frac{1}{3!}D\left(\left\{\frac{1}{3!}t_3t_4 + \frac{1}{2!}\frac{1}{2!}3t_3t_4 + \frac{1}{3!}3t_3t_4\right\} + \left\{\frac{1}{2!}t_1t_2t_4 + \frac{1}{2!}3t_1t_2t_4\right\} + \right. \\
& \frac{1}{2!}\frac{1}{2!}3t_1t_3t_3 + \left\{\frac{1}{2!}\frac{1}{2!}6t_2t_2t_3 + \frac{1}{2!}\frac{1}{2!}3t_2t_2t_3\right\} + \frac{1}{3!}6t_1t_2t_2t_2 + \\
& \left.\frac{1}{2!}3t_1t_1t_2t_3 + \frac{1}{3!}t_1t_1t_1t_4\right)
\end{aligned}
\tag{3.62}
$$

$$
\begin{aligned}
-\frac{1}{4!}4\omega t_4 = {} & \frac{1}{4!}4Jt_4 + \frac{1}{4!}B\left(4t_2t_4 + \frac{1}{2!}6t_3t_3\right) + \frac{1}{4!}6Kt_3 + \frac{1}{4!}K(4t_1t_4 + 12t_2t_3) + \\
& \frac{1}{4!}C\left(\left\{\frac{1}{2!}6t_3t_4 + \frac{1}{2!}4t_3t_4\right\} + 4t_1t_2t_4 + \frac{1}{2!}6t_1t_3t_3 + \frac{1}{2!}12t_2t_2t_3\right) + \\
& \frac{1}{4!}D + \frac{1}{4!}Lt_2 + \frac{1}{4!}M\left(\frac{1}{2!}6t_4 + \frac{1}{2!}12t_2t_2 + 6t_1t_3\right) + \\
& \frac{1}{4!}L\left(\left\{\frac{1}{2!}12t_2t_4 + \frac{1}{2!}4t_2t_4\right\} + \frac{1}{2!}\frac{1}{2!}12t_3t_3 + 12t_1t_2t_3 + \right. \\
& \left.\frac{1}{2!}4t_1t_1t_4 + \frac{1}{3!}24t_2t_2t_2\right) + \frac{1}{4!}D\left(\left\{\frac{1}{2!}\frac{1}{3!}4t_4t_4 + \frac{1}{2!}\frac{1}{2!}\frac{1}{2!}6t_4t_4\right\} + \right. \\
& \left\{\frac{1}{2!}4t_1t_3t_4 + \frac{1}{2!}6t_1t_3t_4\right\} + \left\{\frac{1}{2!}\frac{1}{2!}12t_2t_3t_3 + \frac{1}{2!}\frac{1}{2!}6t_2t_3t_3\right\} + \\
& \left\{\frac{1}{2!}\frac{1}{2!}12t_2t_2t_4 + \frac{1}{2!}\frac{1}{2!}4t_2t_2t_4\right\} + \frac{1}{2!}12t_1t_2t_2t_3 + \frac{1}{2!}6t_1t_1t_2t_4 + \\
& \left.\frac{1}{2!}\frac{1}{2!}t_1t_1t_3t_3 + \frac{1}{4!}24t_2t_2t_2t_2\right)
\end{aligned}
\tag{3.63}
$$

As before, these equations can be written into an iterative code to find the cluster amplitudes t_1, t_2, t_3 and t_4, leading to the ground state energy E_0.

4. Conclusion

We have derived a method combining coupled cluster theory and iterative Bogoliubov transformations for the solution of a set of perturbed harmonic oscillators. Using our general operator product, matrix element and diagrammatic rules we found explicit expressions for calculating coupled cluster amplitudes and ground state energies for perturbations of quadratic and quartic form.

To illustrate the accuracy of the method, we presented the results for a few test cases. For a set of coupled oscillators with a quadratic perturbation, we showed that following the calculation of the ground state energy, the full excitation spectrum could be easily obtained by considering the diagonalization of an effective Hamiltonian in the space of unperturbed harmonic oscillator states. We also showed that this eigenvalue spectrum is equivalent to the spectrum obtained through a suitable Bogoliubov transformation of our ladder operators.

We presented a series of test cases for a quartic perturbation of variable strength, and compared the accuracy with results obtained from numerical integration of the Schrödinger equation. Although the CC results agreed well with the exact results, we showed that they could be dramatically improved through the inclusion of an iterative Bogoliubov transformation scheme which in effect generates an improved zeroth order Hamiltonian through a series of transformations of the operator basis.

4.1. Future Work

To fully investigate the feasibility and accuracy of our proposed new method using coupled cluster techniques and iterative Bogoliubov transformations, we need to perform a sequence of additional steps:

Implementation and testing of the inclusion of linear and cubic terms in the perturbation potential. This will necessitate the inclusion of additional cluster operators in our coupled cluster scheme, as well as a modification of our Bogoliubov transformation.

Implementation and testing of excitation energy calculations using the EoM-CC scheme, using an effective Hamiltonian derived from the operators obtained at the end of the iterative Bogoliubov process.

Implementation and testing of higher excitation in the coupled cluster operator to assess convergence for stronger perturbations. Here we propose to make use of a computer driven code generation scheme which we are currently developing.

Ultimately, our goal is to apply our numerical code to calculate anharmonic transition frequencies for molecular systems. Initially we will make use of existing anharmonic potential parameters and evaluate our method against other approaches, but we will in addition perform our own calculations and develop new parameters for small molecules.

REFERENCES

[1] Graham, W. and Rittby, M. (2008). Unpublished.

[2] Szabo, A. and Ostlund, N. (1996). Modern Quantum Chemistry. Dover.

[3] Crawford, T. D. and Schaefer, H. F. (2000). Reviews of Computational Chemistry.

[4] Shavitt, I. and Bartlett R. J. (2009) Cambridge University Press.

[5] Kranze, R., Withey, P., Rittby, M., and Graham, W. (1995). J. Chem. Phys., **103**, 6841.

[6] Drummond, J. E. (1981) J. Phys. A: Math. Gen. 14, 1651.

[7] Kaulfuss, U. B. and Altenbokum, M. (1986) The American Physical Society, Physical Review D, Vol. **33**, No. 12.

[8] Bay, K. and Lay, W. (1997) J. Math. Phys. **38**, 2127.

[9] Banik, Subrata; Pal, Sourav and Prasad, M. Durga (2017) J. Chem. Phys. **129**, 134111.

[10] Killingbeck, J. P. and Lakhlifi, A. (2017) J. Math. Chem. **55**

[11] Znojil, M. (2016) Phys. Lett. A 380

[12] Liverts, E. Z., Mandelzweig, V. B., Tabakin, F. (2006) J. Math. Phys. **47**

[13] Eremenko, A. and Gabrielov, A. (2009) Comm. Math. Phys. 287

[14] Geertsen, J., Rittby, M., and Bartlett, R. (1989). Chem. Phys. Letters, 164, 57.

[15] Christiansen, O. (2004). "Vibrational Coupled Cluster Theory" J. Chem. Phys., **120**, 5.

[16] Bartlett, R. J. and Musial, M. (2007) American Institute of Physics, Reviews of Modern Physics, 79.

[17] Faucheaux, Jacob A. and Hirata, So (2015) J. Chem. Phys. **143**, 134105.

[18] Jauregui, R. and Recamier, J. (1992) The American Physical Society, Physical Review A, Vol. **46**, No. 5.

[19] Masmaliev, G. M. and Khanmamedov, A. Kh. (2019) Mat. Zametki 105

[20] Bender, C. M. and Wu, T. T. (1969) The Physical Review, Second Series, Vol. **184**, No. 5.

VITA

Curriculum Vitae: Carson Huey-You

Address	Texas Christian University	**Phone**	817-257-6963
	Dept. of Physics & Astronomy	**Email**	c.huey10@tcu.edu
	2800 S. University Ave.		
	Fort Worth, TX 76129		

Education

Texas Christian University - Fort Worth, TX, USA

Graduate (Physics): *2017 - Present*

Undergraduate: *2013 - 2017*

Physics Major; Mathematics & Chinese Language Double-Minor

Research Experience

- **Determining the Eigenvalues and Associated Isotopic Spectra of Systems using Coupled Cluster Techniques** with Dr. Magnus Rittby : *2017 - Present*
  Texas Christian University (Quantum Mechanics)
- **Quantum Mechanics in the Complex Plane** with Dr. Magnus Rittby : *2015 - 2017*
  Texas Christian University (Quantum Mechanics)
- **Mathematics of Signal Processing** with Dr. Ken Richardson : *2016*
  Texas Christian University (Mathematics)
- **Tumor Growth Modeling** with Dr. Hana Dobrovolny : *2015*
  Texas Christian University (Biophysics)

ABSTRACT

A COUPLED CLUSTER TECHNIQUE WITH ITERATIVE BOGOLIUBOV TRANSFORMATIONS FOR COMPUTING EIGENVALUES OF PERTURBED QUANTUM HARMONIC OSCILLATORS

by Carson Huey-You, M.S., 2019

Department of Physics & Astronomy

Texas Christian University

Research Advisor: C. Magnus L. Rittby, Senior Associate Dean & Professor of Physics

The details of a coupled cluster technique making use of iterative Bogoliubov transformations for the calculation of the ground and excited states of a coupled set of perturbed harmonic oscillators are developed. A diagrammatic approach is presented and implemented for the efficient development of cluster amplitude and energy equations. The method is applied to a quadratic and quartic perturbations to illustrate the power of Bogoliubov transformations in providing an improved zeroth order Hamiltonian for perturbative methods. Some initial numerical results for a single quartic oscillator are also presented showing good agreement with exact results obtained from numerical integration of the Schrdinger equation. A new iterative Bogoliubov transformation scheme is applied and shown to improve the agreement with exact results considerably. Finally, explicit coupled cluster and energy equations are presented for a set of coupled oscillators subjected to cubic and quartic perturbations.