

Approximating the Many Body Problem Through Refining Couple Cluster Theory

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Abstract

Here, we present a proof of principle through prototype calculations. CC calculations scale as n^7 , and are therefore become expensive very quickly. The only computationally affordable systems have about 30 particles. This is unhelpful for quantum chemists, nuclear physicists, and condensed matter physicists who are interested in large systems that contain a large number of atoms. In general, quantum chemists use CC in the frequency or energy space. We hope that our approximate real-time method will improve upon the efficiency of the standard CC methods, while retaining accuracy. We have confirmed that the new method of calculations produces that exact same result as the analytic solution for the 3-state/2-electron model. Through working with the 4-state/2-electron model, we have confirmed that the equations are correct, but we must be careful with which v_{pq}^{rs} we keep because of issues that arise when the valence-valence interactions are zeroed out. An ancillary goal is to expand the ability of the cumulant expansion which works very well in larger systems but produces inaccurate results in smaller systems. By observing the regimes where the cumulant expansion and CC are both accurate, we may be able to better approximate the cumulant expansion in smaller systems.

1 Introduction

Particle models with over 3 interacting electrons have non-analytically solvable Schrödinger's equations and must be solved numerically. The goal of this research project is to approximate the electronic many body effects on the one electron Green's function through strengthening the cumulant by observing its relationship to the coupled cluster theory. While there are some approximations that can nearly describe theoretical systems, many are unsatisfying when compared to the experimental results. The approximations break down easily when there are many particles and do not describe a real time dependence whatsoever. The Coupled Clusters (CC) method works well on smaller systems, but quickly becomes computationally expensive as its calculation times typically scale as N^7 where N is the amount of particles. The cumulant method only works well in large regimes and gives inaccurate results in smaller systems.

The Coupled Cluster term is defined as

$$C^R(t) = i \int_0^t \left(- \sum_{ia} v_{ci}^{ca} t_i^a + \frac{1}{2} \sum_{ijab} v_{ij}^{ab} t_i^a t_j^b \right) dt' \quad (1)$$

where the amplitudes, t_i^a , are obtained from the following differential equation:

$$\begin{aligned} -it_i^a &= -v_{ac}^{ic} + (\epsilon_a - \epsilon_i)t_i^a \\ &+ \sum_j v_{jc}^{ic} t_j^a - \sum_b v_{ac}^{bc} t_i^b + \sum_{jb} v_{ja}^{bi} t_j^b \\ &+ \sum_{jb} v_{jc}^{bc} t_i^b t_j^a + \sum_{jbd} v_{aj}^{bd} t_i^b t_j^d - \sum_{jkb} v_{jk}^{ib} t_j^a t_k^b \\ &\quad - \sum_{jkb d} v_{jk}^{bd} t_i^b t_j^a t_k^d \end{aligned} \quad (2)$$

The Green's function and the Fourier transform to frequency space can be done in one step where γ is the broadening term.

$$G(\omega) = \int_0^t \left(e^{C(t)} e^{i\omega t - (\gamma t)^2} \right) dt' \quad (3)$$

The 3 state/2 electron system where the exact solutions are available, to see how the approximation works. The model has a core and two valence levels and starts in the ground state. It has a core electron in the lowermost energy level and one electron in one of the valence shells. More information is referred to in Sec. 2.4. Through varying the coupling energy – which is a measure of the Coulomb interaction between the core electron and the valence electron – and the band gap energy – which is the difference in energy between the two valence states, we can examine how the model acts in different limits. In order to examine the coupling potential, v_{pq}^{rs} (See Sec 2.3), and coupled cluster terms, bloop, more closely, more complicated systems, specifically the 4 state/ 2 electron and N_2 , are used. The overall goal is to be able to generalize the many body problem with a real time dependence.

Given their apparent similarity (i.e. they are both formed using an exponential ansatz), many physicists are interested in the relationship between the

cumulant and the CC approximation. Using CC, physicists can understand the cumulant better and try to get it to lead to better solutions in smaller electronic systems. Conversely, by finding a relationship between CC and the cumulant, we can develop CC approximations that are computationally affordable and capable of describing larger systems with a real time dependence. This is an ancillary goal to the project.

2 Methods

2.1 Green's and Spectral Functions

Green's Functions are used to solve difficult ordinary and partial differential equations which may be unsolvable by other methods. A prime example of a great time to use a Green's function is when solving a Schrodinger's equation. This is the Greens function we use in our calculations.

$$G(x, x_0) = G(rt, r_0t_0) = -i\Theta(t - t_0) \left\langle 0 \left| \left\{ \psi(rt), \psi^\dagger(r_0t_0) \right\} \right| 0 \right\rangle \quad (4)$$

The $\theta(t)$ represents a step Function, $\psi^\dagger(rt)$ is the creation operator at rt and ψ is the annihilation operator at rt and $|0\rangle$ is the ground state. The curly bracket is an anti-commutator. We can approximate the Green's functions of excited states using the Coupled cluster operator.

The CC method is particularly useful in approximating the Green's Function of excited states. From the Greens Function, it is easy to obtain the spectral function

$$A(\omega) = -\frac{1}{\pi} \text{Im} |G(\omega)| \quad (5)$$

The spectral function is useful for verifying theoretical approximations against experimental results, such as X-Ray Photoemission Spectroscopy (XPS).

2.2 CC Theory Background and Relation to Cumulant Expansion

CC Theory is a numerical technique used to describe many-body systems that provides the exact solution to the ground state Schrödinger's Equation

$$H|\Psi\rangle = E|\Psi\rangle \quad (6)$$

It takes Hartee-Fock (See Sec 2.3) molecular Orbital method and constructs a multi-electron wave function using the exponential cluster operator to account for electron correlation. Ab initio quantum chemistry methods attempt to solve the electronic Schrödinger's Equation using the given positions of nuclei and number electrons. From know the exact ground state solution provided by CC theory, we can use an ansatz to solve for excited states.

$$|\Psi\rangle = e^{\hat{T}} |\Psi_0\rangle \quad (7)$$

CC Theory was initially developed in the late 60's by Josef Paldus and Jiří Čížek²⁻⁴, both of whom were quantum chemists. It became a very accurate way

to approximate the solution to the electronic Schrödinger’s equation and to predict molecular properties. Ten years later, Hurley rederived the Couple Cluster Doubles (CCD) equations⁵ to be more accessible to the majority of quantum chemists. Munkhurst strengthened the ability of CC theory by developing general CC response theory, which could calculate molecular properties⁶. By the end of the 70’s, Pople⁷ and Bartlett⁸ created spin orbital CCD programs. A few years later, Purvis and Bartlett derived CC single and double (CCSD) equations and implemented them in a computer program⁹. This caused an explosion in the creation of CC methods.

CC theory provides very accurate energies and wavefunctions in most systems and ensure size extensivity, unlike other approximations, such as configuration interaction (CI). However, the CC equations can be very expensive computationally since it scales as N^7 and thus is difficult to apply for systems with more than 20-30 electrons. In addition, the theory has been mostly formulated statically only, and does not account for real time dependence.

Another popular method to solve the many body electronic Green’s Function is the cumulant expansion.

$$g_{cc}(t) = e^{i\epsilon_c t} e^{c(t)} \quad (8)$$

Here, $c(t)$ is the cumulant polynomial term. The cumulant describes the interaction between n electrons. Mathematically, it is a complex function that, when it is placed in the exponent, acts as a scalar on the Green’s function. works well in systems that can be mapped onto a polaron Hamiltonian that describes electrons interacting with bosonic excitations, such as plasmons. This translates to systems that are about 20-30 particles. It provides very bad approximations for smaller systems. Since both the cumulant expansion and CC method use a similar exponential ansatz, there is interest in comparing their behaviors in the regimes were both work well in order to increase understanding of both approximations.

2.3 The Coupling Potential v_{pq}^{rs}

The coupling potential describes the Coulombic interaction between electrons. Its approximate value comes from the Hartree-Fock method. We start with a Time Independent Schrödinger’s Equations (TISE), $h_{HF}^N |\Phi_{HF}^N\rangle = (h_{nuc} + f^N) |\Phi_{HF}^N\rangle = E_{HF}^N |\Phi_{HF}^N\rangle$, where N represents the number of electrons in the system, $|\Phi_{HF}^N\rangle$ is the ground state, h_{HF}^N is the N -electron Hartree-Fock Hamiltonian, h_{nuc} is the nuclear Hamiltonian, f^N is the N -electron Fock operator, and E_{HF}^N is the associated energy. $|\Phi_{HF}^N\rangle$ is an eigenstate of h_{HF}^N , making E_{HF}^N an eigenvalue. In order to figure out the time-dependence part of how the system acts when we remove an electron, we can use what we already know of the time-independent annihilation operator, a_c , $|\Phi^{N-1}\rangle = a_c |\Phi_{HF}^N\rangle$. The associated Hamiltonian, H , for the reference state, $|\Phi^{N-1}\rangle$, is comprised of the nuclear Hamiltonian and the Coulombic interactions, \hat{V} . We can rewrite it in terms of the Hartee Fock Hamiltonian as follows:

$$H |\Phi^{N-1}\rangle = (\hat{h}_{nuc} + \hat{V}) |\Phi^{N-1}\rangle = (\hat{h}_{nuc} + f^N - f^N) |\Phi^{N-1}\rangle = (h_{HF}^N - f^N + f^{N-1} + \hat{V}) |\Phi^{N-1}\rangle \quad (9)$$

The Coulombic potential is defined as

$$\hat{V} = \sum_{ijkl} v_{ij}^{kl} a_k^\dagger a_l^* a_i a_j \quad (10)$$

where a_k^\dagger is the creation operator. v_{pq}^{rs} has four indices (p,q,r,s) where each index represent a single-particle state. In the N state model, p,q,r,s can take any value that is determined by the atomic orbital basis set

$$\langle pq|rs \rangle = \int_{-\infty}^{\infty} dr_1 dr_2 \frac{\phi_p^*(r_1) \phi_q^*(r_2) \phi_r(r_1) \phi_s(r_2)}{|r_2 - r_1|} \quad (11)$$

Eq.[11] describes the basic bra-ket notation that we use to obtain the potential. Coupled Clusters theory is a post-Hartree Fock ab initio method, so the $\phi_p(r_1)$ functions come from the Hartree-Fock method. In this specific case, all of the $\phi_p(r_1)$ functions are real, so we can consider that $\phi_p^*(r_1) = \phi_p(r_1)$

$$v_{pq}^{rs} = \langle pq||rs \rangle \quad (12)$$

We define the energy of the coupling potential by Eq.[12]. We can further expand Eq.[12] by

$$v_{pq}^{rs} = \langle pq||rs \rangle = \langle pq|rs - pq|sr \rangle \quad (13)$$

From these equations, the following symmetry relationships can be derived:

$$v_{pq}^{rs} = -v_{pq}^{sr} = v_{qp}^{sr} = -v_{qp}^{rs} \quad (14)$$

Further, by the properties of Eq. [14]

$$v_{pp}^{rs} = v_{pq}^{rr} = 0 \quad (15)$$

2.4 3-State/2-Electron Model

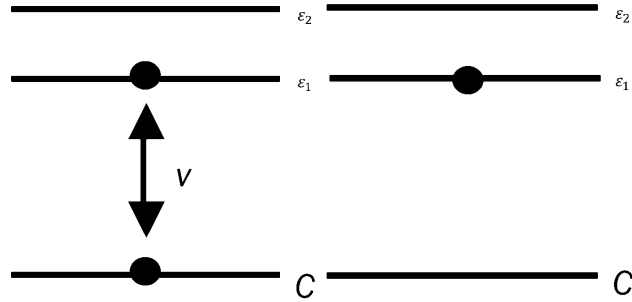


Figure 1: The left image represents the initial state of the 3-State/2-Electron system. The right image depicts the moment after a photon kicks the core electron out of the model and ionizes the overall system

The 3-State/2-Electron can be equated corresponding classical system. Consider a spring with the top attached to an infinite ceiling and the bottom attached to an infinite board of wood. Exactly on the other side of where the

spring attaches to the board, there is a pendulum. The pendulum has a mass and is in its ground state – it does not oscillate. Now, we removed the pendulum and want to see how the spring responds to this perturbation of the system. The spring to continuously stretch out and contract. If the pendulum was very light, we expect that the spring would barely be affected. However, if the pendulum was very heavy, the spring would be greatly affected by the pendulum’s removal.

We can loosely make some comparisons between the classical and quantum model. The ceiling and the board act as the excited state. The distance between the ceiling and the board is the band gap energy between the two states. Removing the pendulum is related to creating a core hole. The weight of the pendulum acts as the coupling potential between the core electron and the valence electron. How the spring contracts is correlated to the state we find the valence electron after the system is let go.

The electron model acts very similarly with one stark difference. Consider a core electron occupying a deep core level and another electron occupying two valence energy levels. There is a coupling potential, v , between the two electrons and ω_{21} , between the two valence energy levels. Then, a photon knocks the core electron out of the system, creating a core hole. The system ionizes and the valence electron begins oscillating. The resulting spectral function $A(w)$ gives the probability that the core hole has a specific energy. Either, the valence electron remains in the ground state (quasi particle peak) or it gets excited (satellite peak). Since this model operates on a quantum level, the electron will be located at a quantized level, whereas in the classical system, the spring could move continuously.

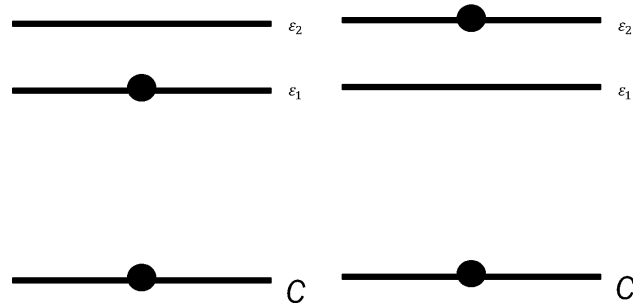


Figure 2: These images represent the possible final states the system could take. The left image is associated with the quasiparticle peak. The right image is associated with the satellite peak.

3 Results

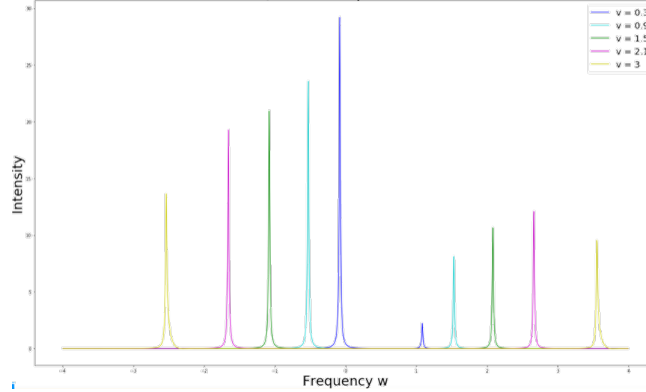


Figure 3: This figure depicts the spectral functions as a function of frequency. $\omega_{21} = -1$ for each spectral function. The dark blue line is where $\nu=0.3$. The light blue line is where $\nu=0.9$. The green line is where $\nu=1.5$. The pink line is where $\nu=2.1$. The yellow line is where $\nu=3$.

As the coupling energy increases, the quasi-particle (QP) peak – which represents the probability that the valence electron maintains its energy level– decreases in amplitude and displaces in the negative x direction. As this happens, the satellite peak – which represents the probability that the remaining valence electron will become excited – increases and displaces in the positive x direction. Since this spectral function includes a nonlinear term – which is the coupled clusters term, there are only two peaks, as the remaining possible satellite peaks are suppressed using magic. The fact that the peaks are clearly sharp and very narrow is a product of a small broadening term. This system is very

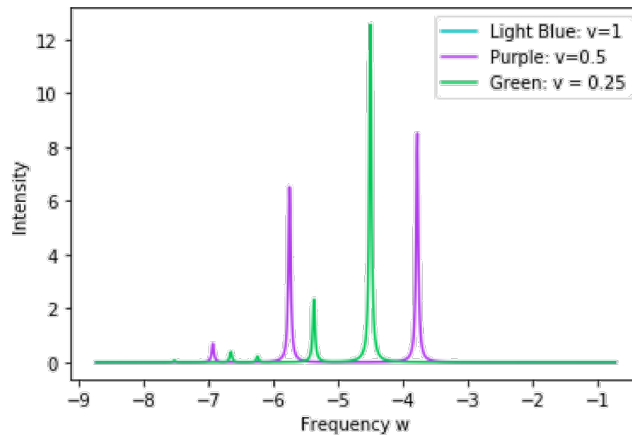


Figure 4: This figure depicts the spectral function of a 4-State/2-Electron system. The green line is when $\nu=0.25$. The purple line is when $\nu=0.5$. The light blue line is when $\nu=1$

similar the 3-State/2 Electron system in that there are still only core-valence

electron interactions. The main difference is that there are more associated satellite peaks because there are more available states for the valence electron to end up in. In order to present a proof of principle, we want to demonstrate

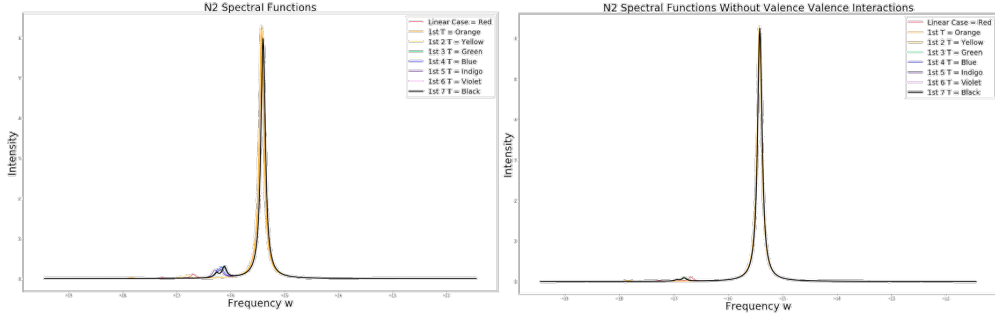


Figure 5: These figures represent the spectral function of an N_2 system. The left figure includes all coupling potentials and the right figure represents the spectral functions where the valence-valence interactions are zeroed out. It was computationally derived with a basis set of 20. The red line is the completely linear case from Eq.[2]. The orange line includes the first sum from Eq.[2]. The yellow line includes the first two sums from Eq.[2]. The green line includes the first three sums from Eq.[2]. The blue line includes the first four sums from Eq.[2]. The indigo line includes the first five sums from Eq.[2]. The violet line includes the first 6 sums from Eq.[2]. The black line includes all of the sums from Eq.[2].

that the Coupled Clusters method can produce affordable, good approximations of realistic systems. We also wanted to find out exactly how removing valence-valence interactions affects the approximation. Even before we completed the calculation, we expected for there to be inherent differences between our approximation and experimental results. We were working in a basis set of 20 for a 14 electron system while a realistic N_2 model has an infinite basis set. We expect that removing valence-valence interactions will affect the approximation; however, we do not know by how much. Removing valence-valence interactions allows for the calculations to be completed much quicker, which is significant in a system that scales by N^7 .

4 Discussion

4.1 3-State/2-Electron

The merit of analyzing the 3-State/2-Electron system is to verify the accuracy of the approximation since the 3-State/2-Electron system has an analytically solvable Green's function. By comparing the the numerical calculations to the

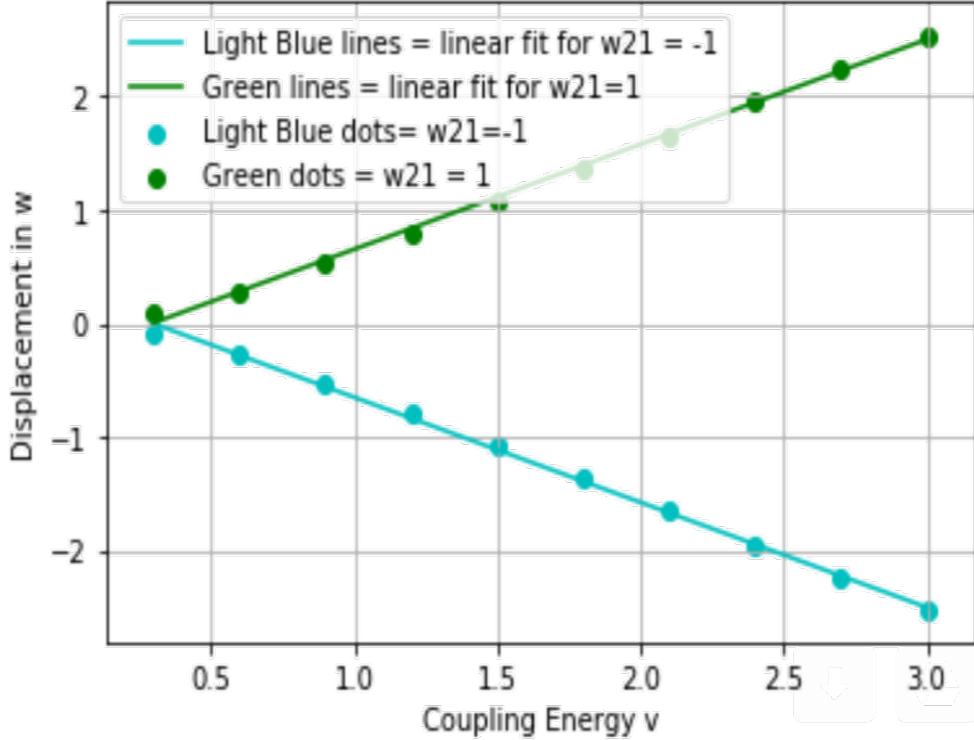


Figure 6: This figure shows the comparison between the numerical approximation and analytic solution for a 3-State/2-Electron system. It depicts the Quasiparticle peak as a function of the coupling potential. The green dots is the numerical approximation when the band gap $\omega_{21}=1$ and the green line is the associated analytical solution. The light blue dots is the numerical approximation when the band gap $\omega_{21}=-1$ and the light blue line is the associated analytical solution

analytical calculations, we see high agreement between the approximation and the analytic solutions. This demonstrates that the approximation is one the right track and works for the simplest systems. Further, from comparing the analytical and numerical solutions, an interesting observation arose from noticing the displacement of the Quasiparticle peak. The displacement of the Quasiparticle peak is linear with respect to the increasing of the coupling potential. Also, the slope of the line is directly correlated to the magnitude of the band gap.

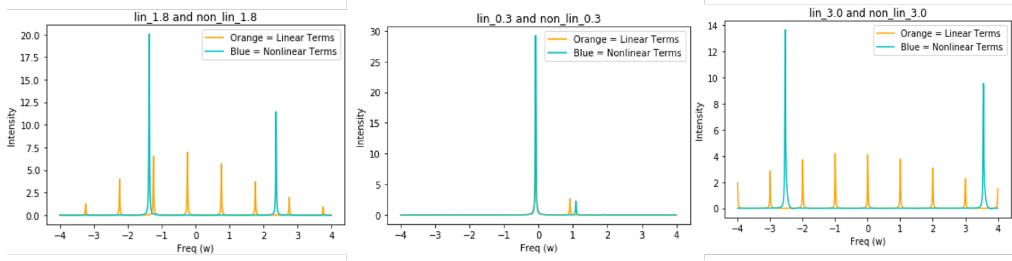


Figure 7: This figure shows the spectral function of 3-State/2-Electron at three different coupling potentials. The Orange line represents the spectral function that only keeps the linear amplitude terms from Eq.[2]. The blue line represents the spectral function that includes the non-linear coupled cluster term in Eq.[2]

Another important characteristic that required more investigation was that of how the nonlinear amplitude terms from Eq.[2] suppresses the extraneous satellite peaks. Before any calculation is made, it is expected that the 3-State/2-Electron system has a main Quasiparticle peak and a smaller satellite peak. There was interest seeing the difference between including or excluding the non-linear coupled cluster term. Due to some quality associated with the nonlinear coupled cluster term, all extraneous satellite peaks are suppressed.

The exclusion of valence-valence terms was investigated in N_2 model in order to find out whether they could be neglected and a good approximation could still be achieved.

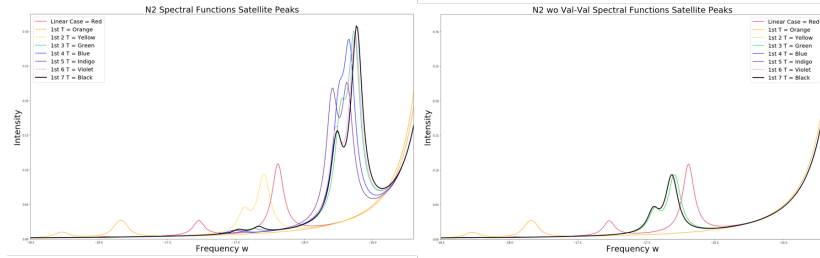


Figure 8: This figure zooms into the satellite peaks from Fig.[5].

While the Quasiparticle peaks align very well, zeroing out the valence-valence interaction terms fails in producing numerically accurate results for the satellite peaks. However, if the interest is mainly in located that Quasiparticle peaks, zeroing out the valence-valence terms can make calculating faster.

5 Conclusion

The purpose of this report is to provide background on what Coupled-Cluster theory currently is and what it is capable of. CCT came out of a need to find solutions to the many body Schrödinger's Equation ground states. However, there is a whole world of extending Coupled-Cluster method to approximate excited state solutions of the many body Schrödinger's Equation.

Many fascinating conclusions arose from initial complications. For instance, while producing spectral functions for the 4-State/2-Electron system, more was learned about how the coupling potential v_{pq}^{rs} works and how it affects the electronic Hamiltonian, as shown in Eq.[9]. By keeping in the valence-valence interaction terms in the coupling potential term, it will be canceled out by terms produced by the fock operator. However, from learning not to immediately zero out the valence-valence interaction terms, it was ascertained the approximation has viability.

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