Ground state energy of quantum dots using the coupled cluster method

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Something about coupled-cluster... Preferably doubles.

CONTENTS

I. INTRODUCTION

In this project we will study the ground state energy of quantum dots.

II. THEORY

In this project we will study a system of N interacting electrons. We will be looking at a Hamiltonian consisting of a one-body and a two-body part. The one-body part is given by

$$h(\mathbf{r}_i) = -\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2\mathbf{r}_i^2, \tag{1}$$

where we use natural units $\hbar = c = e = 1$ and set the mass to unity. The two-body part is the Coulomb interaction potential.

$$u(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{2}$$

We thus get the total Hamiltonian

$$H = h + u = \sum_{i=1}^{N} h(\mathbf{r}_i) + \sum_{i<j}^{N} u(\mathbf{r}_i, \mathbf{r}_j), \tag{3}$$

where h is the full one-body operator and u the full two-body operator, i.e., over the entire system. Working in a basis of L single particle functions, $\{|p\rangle\}_{p=1}^{L}$. We define the reference Slater determinant as

$$|\Phi_0\rangle \equiv |1, 2, \dots, N\rangle, \tag{4}$$

i.e., a tensorproduct of the N first single particle functions, $|i\rangle$, of the system. We call these single particle functions *occupied* as they are contained in the Slater determinant. We will denote the occupied indices with $i, j, k, l, \dots \in \{1, \dots, N\}$, the *virtual* states with $a, b, c, d, \dots \in \{N+1, \dots, L\}$ and general indices with $p, q, r, s, \dots \in \{1, \dots, L\}$. In terms of sets of basis functions we can write this as

$$\{|p\rangle\}_{p=1}^{L} = \{|i\rangle\}_{i=1}^{N} \cup \{|a\rangle\}_{a=N+1}^{L}, \tag{5}$$

i.e., the general indexed states consists of both occupied and virtual states. Note that the single particle functions are orthonormal, i.e.,

$$\langle p|q\rangle = \delta_{pq}. \tag{6}$$

We can construct other Slater determinants in this basis by exciting or relaxing the reference determinant. A general excitation is labeled $|\Phi_{ij\dots}^{ab\dots}\rangle$ which means that we have removed the single particle functions with indices $i, j, \dots$ from the reference and added $a, b, \dots$. Note that

$$\langle \Phi_{ij\dots}^{ab\dots}|\Phi_0\rangle = 0, \tag{7}$$

for any excitation.

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[*] Project code: https://github.com/Schoyen/FYS4411

A. Second quantization

Employing the creation operators, $a_p^\dagger$, and the destruction operators, a_p, we can write the Hamiltonian as

$$H = \sum_{pq} h_q^p a_p^\dagger a_q + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r, \tag{8}$$

where the sums are general indices over all L basis states and the matrix elements are defined as

$$h_q^p \equiv \langle p|h|q\rangle, \tag{9}$$

$$\langle pq||rs\rangle \equiv \langle pq|u|rs\rangle - \langle pq|u|sr\rangle. \tag{10}$$

Note that we use the chemists notation to label the antisymmetric matrix elements.

B. The coupled cluster approximation

We approximate the true wavefunction, $|\Psi\rangle$, of the system by the coupled cluster wavefunction, $|\Psi_{\mathrm{CC}}\rangle$, defined by

$$|\Psi_{\mathrm{CC}}\rangle \equiv e^T|\Phi_0\rangle = \left(\sum_{i=0}^{n}\frac{1}{n!}T^n\right)|\Phi_0\rangle, \tag{11}$$

where the *cluster operator*, T, is given by a sum of p-excitation operators labeled T_p. They consist of *cluster amplitudes*, $t_{i\dots}^{a\dots}$, and creation and annihilation operators.

$$T = T_1 + T_2 + \dots + T_p \tag{12}$$

$$= \sum_{ia} t_i^a a_a^\dagger a_i + \left(\frac{1}{2!}\right)^2 \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_i a_j + \dots. \tag{13}$$

In the doubles approximation we limit the cluster operator to

$$T \equiv T_2 = \frac{1}{4}\sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i. \tag{14}$$

The first part of the coupled cluster method consists of constructing the cluster amplitudes using the *amplitude equations*. After we have found the amplitudes we can compute the energy.

C. Energy of the coupled cluster approximation

When we're going to compute the energy of a system using the coupled cluster approximation we would ideally want to find the expectation value of the energy using the coupled cluster wavefunction.

$$E_{\mathrm{CC}} = \langle\Psi_{\mathrm{CC}}|H|\Psi_{\mathrm{CC}}\rangle. \tag{15}$$

As it turns out, this is an uncomfortable way of finding the energy as $T \neq T^\dagger$. Instead we will define what we call the *similarity transformed Hamiltonian*. We plug the coupled cluster wavefunction into the Schrödinger equation.

$$H|\Psi_{\mathrm{CC}}\rangle = E_{\mathrm{CC}}|\Psi_{\mathrm{CC}}\rangle. \tag{16}$$

Next, we left multiply with the inverse of the cluster expansion, i.e.,

$$e^{-T}H|\Psi_{\mathrm{CC}}\rangle = e^{-T}E_{\mathrm{CC}}|\Psi_{\mathrm{CC}}\rangle = E_{\mathrm{CC}}|\Phi_0\rangle. \tag{17}$$

Projecting this equation on the reference state we get

$$E_{\mathrm{CC}} = \langle\Phi_0|e^{-T}H|\Psi_{\mathrm{CC}}\rangle = \langle\Phi_0|e^{-T}He^T|\Phi_0\rangle, \tag{18}$$

where in the latter inner-product we have located the similarity transformed Hamiltonian defined by

$$\bar{H} \equiv e^{-T}He^T. \tag{19}$$

To simplify the energy equation and the amplitude equations we use the normal ordered Hamiltonian.

$$H = H_N + \langle\Phi_0|H|\Phi_0\rangle. \tag{20}$$

The energy equation thus becomes

$$E_{\mathrm{CC}} = \langle\Phi_0|\bar{H}|\Phi_0\rangle = E_0 + \langle\Phi_0|e^{-T}H_Ne^T|\Phi_0\rangle, \tag{21}$$

where the reference energy is given by

$$E_0 = \langle\Phi_0|H|\Phi_0\rangle. \tag{22}$$

We now define the normal ordered similiarity transformed Hamiltonian as

$$\bar{H}_N \equiv e^{-T}H_Ne^T. \tag{23}$$

By expanding the exponentials of this Hamiltonian and recognizing the commutators we get the Baker-Campbell-Hausdorff expansion.

$$\bar{H}_N = H_N + [H_N, T] + \frac{1}{2!}\big[[H_N, T], T\big] + \dots. \tag{24}$$

From the connected cluster theorem we know that the only nonzero terms in the Baker-Campbell-Hausdorff expansion will be the terms where the normal ordered Hamiltonian has at least one contraction[1] with every cluster operator on its right. This lets us write the expansion as

$$\bar{H}_N = H_N + (H_NT)_c + \frac{1}{2!}\left(H_NT^2\right)_c + \dots, \tag{25}$$

where the subscript c signifies that only contributions where at least one contraction between H_N and T has been performed will be included.

[1] In the Wick's theorem sense.

1. Coupled cluster doubles energy equation

Using the doubles approximation with the cluster operator T_2 defined in Equation 14 the energy equation becomes

$$E_{\text{CCD}} = E_0 + \langle \Phi_0 | e^{-T_2} H_N e^{T_2} | \Phi_0 \rangle. \tag{26}$$

As the doubles cluster operator doubly excites the reference and using the expansion in Equation 25 we see that we can write the energy equation as

$$E_{\text{CCD}} = E_0 + \langle \Phi_0 | H_N | \Phi_0 \rangle + \langle \Phi_0 | (H_N T_2)_c | \Phi_0 \rangle, \tag{27}$$

as the Hamiltonian is only able to relax one pair of single particle functions. By construction we have that

$$\langle \Phi_0 | H_N | \Phi_0 \rangle = 0. \tag{28}$$

In the second term only the normal ordered two-body operator can contribute as the cluster operator gives a total excitation of +2. As we are projecting onto the reference we have to relax to zero again. The normal ordered Fock operator is at most able to excite and relax by 1 and does therefore not contribute to the overall expression.

$$\langle \Phi_0 | (W_N T_2)_c | \Phi_0 \rangle = \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}. \tag{29}$$

In total the energy equation reduces to

$$E_{\text{CCD}} = \sum_i h_i^i + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}, \tag{30}$$

where the first two terms come from the reference energy as shown in Equation A10.

D. Coupled cluster amplitude equations

In order for us to solve the energy equation using the coupled cluster approximation we need to figure out what the cluster amplitudes, $t_{ij\dots}^{ab\dots}$, are. This is done by projecting Equation 17 onto an excited Slater determinant, i.e.,

$$\langle \Phi_{ij\dots}^{ab\dots} | e^{-T} H e^{T} | \Phi_0 \rangle = 0. \tag{31}$$

Note that in the amplitude equations we can use both the regular and the normal ordered Hamiltonian. They are equal as the reference energy term disappears due to Equation 7. The order of the excitation in the projection determines the order of the amplitudes you will find. In our case we are only interested in the second order ampltiudes found in the doubles approximation, hence we will solve the equation

$$\langle \Phi_{ij}^{ab} | e^{-T} H_N e^{T} | \Phi_0 \rangle = 0, \tag{32}$$

to find an expression that can be used to solve for t_{ij}^{ab}. By employing the Baker-Campbell-Haussdorf (BCH) expansion, while setting $T = T_2$, we find

$$\bar{H} = \left(H_N + H_N T_2 + \frac{1}{2} H_N T_2^2 \right)_C. \tag{33}$$

The subscript c indicates that only those terms in which the Hamiltonian is connected[2] to every cluster operator on its right should be included. Since the Hamiltonian contains at most four annihilation and creation operators, H_N can connect to at most four cluster operators at once. Therefor, the BCH expansion must truncate at the fourth-order terms.

Now comes the rather tedious task of evaluating all the terms that arises from inserting Equation 33 into Equation 32. This can be done by applying Wick's generalised theorem, but the task is a daunting and streneous one. A few example computations of how this can be done is included in section B. Instead of doing it in this manner, we employ the second quantisation library from SymPy instead[3]. The CCD amplitude equation, from SymPy computation, is

$$\begin{aligned} 0 = & u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\ & + \frac{1}{4} t_{ij}^{cd} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} t_{ij}^{cd} u_{cd}^{ab} \\ & + \frac{1}{2} t_{jm}^{cd} t_{in}^{ab} u_{cd}^{mn} P(ij) - \frac{1}{2} t_{nm}^{ac} t_{ij}^{bd} u_{cd}^{nm} P(ab) \\ & + t_{im}^{ac} t_{jn}^{bd} u_{cd}^{mn} P(ij) + t_{im}^{ac} u_{jc}^{bm} P(ab) P(ij) \\ & - \frac{1}{2} t_{im}^{ab} u_{jn}^{mn}. \end{aligned} \tag{34}$$

1. The Iterative Scheme

At first, we pick only diagonal elements of f to be part of the unperturbed Hamiltonian and consider the rest of the terms a perturbation. The second and third terms in Equation 34 can now be rewritten,

$$\begin{aligned} & f_c^b t_{ij}^{ab} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\ & \quad \to f_b^b t_{ij}^{ab} - f_a^a t_{ij}^{ba} - f_j^j t_{ij}^{ab} + f_i^i t_{ji}^{ab} \\ & \quad = (f_a^a + f_b^b - f_i^i - f_j^j) t_{ij}^{ab} \\ & \quad = (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) t_{ij}^{ab} \\ & \quad = -(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) t_{ij}^{ab} \\ & \quad = -D_{ij}^{ab} t_{ij}^{ab}. \end{aligned} \tag{35}$$

The we can define a new function consisting of all of

[2] In a Wick's theorem sense

[3] This is also more in the spirit of this project, as it is within the realm of *Computational* Physics.

Equation 34 except term number two and three,

$$\begin{aligned}g(u,\tau) =& u^{ab}_{ij} + f^{b}_{c}t^{ac}_{ij}P(ab) - f^{k}_{j}t^{ab}_{ik}P(ij)\\ &+\frac{1}{4}t^{cd}_{ij}t^{ab}_{mn}u^{mn}_{cd} + \frac{1}{2}t^{cd}_{ij}u^{ab}_{cd}\\ &+\frac{1}{2}t^{cd}_{jm}t^{ab}_{in}u^{mn}_{cd}P(ij) - \frac{1}{2}t^{ac}_{nm}t^{bd}_{ij}u^{nm}_{cd}P(ab)\\ &+t^{ac}_{im}t^{bd}_{jn}u^{mn}_{cd}P(ij) + t^{ac}_{im}u^{bm}_{jc}P(ab)P(ij)\\ &-\frac{1}{2}t^{ab}_{im}u^{mn}_{jn}.\end{aligned} \tag{36}$$

where $\tilde{f}$ are the non-diagonal parts of the Fock matrix.

Now we have $D^{ab}_{ij}t^{ab}_{ij} = g(u,\tau)$. This allows us to define an iterative scheme,

$$\tau^{(k+1)} = \frac{g(u,\tau^{(k)})}{D^{ab}_{ij}}, \tag{37}$$

with the initial guess

$$\tau^{(0)} = \frac{u^{ab}_{ij}}{D^{ab}_{ij}}. \tag{38}$$

2. *Intermediate Computations*

Looking closely at the amplitude equation in (34) one might come to realize that it contains that this equation contains many of the same structures in several of the terms. This warrants the search for an algebraic transformation of the CCD amplitude equation that has the potential to reduce the amount of floating point operations needed to compute it. As it turns out, such terms exist and they will decrease the computing time necessary by an order of magnitude. We will define the following "intermediates",

$$\chi^{ab}_{cd} = \frac{1}{4}t^{ab}_{mn}u^{mn}_{cd} + \frac{1}{2}u^{ab}_{cd} \tag{39}$$

$$\chi^{n}_{j} = \frac{1}{2}t^{cd}_{jm}u^{mn}_{cd} \tag{40}$$

$$\chi^{a}_{d} = \frac{1}{2}t^{ac}_{nm}u^{nm}_{cd} \tag{41}$$

$$\chi^{bm}_{jc} = u^{bm}_{jc} + \frac{1}{2}t^{bd}_{jn}u^{mn}_{cd} \tag{42}$$

These intermediate structures will allow us to rewrite Equation 34 to,

$$\begin{aligned}0 =& u^{ab}_{ij} + f^{b}_{c}t^{ac}_{ij}P(ab) - f^{k}_{j}t^{ab}_{ik}P(ij)\\ &+ t^{cd}_{ij}\chi^{ab}_{cd} + t^{ab}_{in}\chi^{n}_{j}P(ij) - t^{bd}_{ij}\chi^{a}_{d}P(ab)\\ &+ t^{ac}_{im}\chi^{bm}_{jc}P(ab)P(ij) + \frac{1}{2}t^{ab}_{im}u^{mn}_{jn}.\end{aligned} \tag{43}$$

The importance of this "trick" will become apparent in due time.

E. Constructing the matrix elements

Having found the equations needed in order to find an estimate to the ground state energy using the coupled cluster doubles approximation is a well and dandy. But, we need basis functions to create the matrix elements needed to feed into the coupled cluster code. Often these basis functions are not known and we have to use an approximation or utilize Hartree-Fock to create more optimized basis functions.

1. *Harmonic oscillator basis*

We will be looking at a system of two-dimensional quantum dots with a Coulomb repulsion. If we assume, or make it so, that the repulsive two-body part is small we can use eigenfunctions of the one-body part our basis. In this case we have two-dimensional harmonic oscillator functions as eigenfunctions. We can then compute the matrix elements, h^{p}_{q} and u^{pq}_{rs}, before feeding these into the coupled cluster code.

In polar coordinates we can write the harmonic oscillator wavefunction for a single particle in two dimensions as[4].

$$\phi_{nm}(r,\theta) = N_{nm}(ar)^{|m|}L^{|m|}_{n}(a^2r^2)e^{-a^2r^2/2}e^{im\theta}, \tag{44}$$

where $a = \sqrt{m\omega/\hbar}$ is the Bohr radius, $L^{|m|}_{n}$ is the associated Laguerre polynomials, n and m are the principal and azimuthal quantum numbers respectively and N_{nm} is a normalization constant given by

$$N_{nm} = a\sqrt{\frac{n!}{\pi(n+|m|)!}}. \tag{45}$$

Included is also the spin, σ, of the wavefunction, which can be either up or down. This means each level, (n,m), is doubly occupied. We also have that the wavefunctions are orthonormal

$$\langle n_1m_1\sigma_1|n_2m_2\sigma_2\rangle = \delta_{n_1n_2}\delta_{m_1m_2}\delta_{\sigma_1\sigma_2}. \tag{46}$$

The eigenenergy of a single harmonic oscillator is given by

$$\epsilon_{nm} = \hbar\omega(2n+|m|+1). \tag{47}$$

Our next job is now to create a mapping from the three quantum numbers n, m and σ to a single quantum number α as the matrices h and u use single indices for each wavefunction. In Figure 1 we can see the energy levels that needs to be mapped.

[4] Note that this is without spin. As we are looking at fermions this means that each mode of the harmonic oscillator functions will be repeated twice.

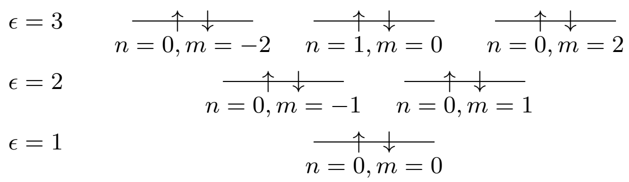

FIG. 1: In this plot we can see the energy degeneracy of the lowest three energy levels in the two-dimensional quantum dot. Each arrow representes a spin up or a spin down state with the quantum numbers n and m as listed below.

Starting from the bottom and working our way upwards from left to right we can label each line from 0 to n in increasing order. This enumeration will serve as our common quantum number α[5]. We will only work with full *shells*, i.e., we restrict our views to systems of N particles where N will be a magic number which we get by counting all spin states for each energy level and the energy levels below. In Figure 1 we can see the magic number $N \in [2, 6, 12]$.

The normalization condition now reads

$$\langle \alpha | \beta \rangle = \delta_{\alpha\beta}\delta_{\sigma_\alpha\sigma_\beta}, \tag{48}$$

The one-body matrix will be a diagonal matrix with the eigenenergies of the single particle harmonic oscillator functions as elements.

$$\langle \alpha | h | \beta \rangle = \epsilon_\beta \delta_{\alpha\beta}\delta_{\sigma_\alpha\sigma_\beta}. \tag{49}$$

The two-body matrix elements are a little harder to work out as the harmonic oscillator wavefunctions are not eigenfunctions to the correlation operator. Luckily, from E. Anisimovas and A. Matulis (Equation A2)[1] we can get an analytical expression for the two-body matrix elements. We can then construct the antisymmetric two-body matrix elements in the harmonic oscillator basis.

$$\langle \alpha\beta || \gamma\delta \rangle = \langle \alpha\beta | \gamma\delta \rangle - \langle \alpha\beta | \delta\gamma \rangle. \tag{50}$$

As we only need to compute these once it is a good idea to save all non-zero values of $\langle \alpha\beta || \gamma\delta \rangle$ to a file.

2. *Constructing the Hartree-Fock basis*

Having found the matrix elements of h and u we can now use the *self-consistent field iteration* method to construct h and u in a *restricted Hartree-Fock* basis. This will yield a better estimate to the actual, unknown basis functions of the system.

The neatest, yet arguably the most abstract, way to write the Hartree-Fock equations for electron i[6] is

$$f_i \varphi_i = \varepsilon_i \varphi_i, \tag{51}$$

where f_i is the Fock operator, φ_i are eigenstates of the Fock operator consiting of a set of one-electron wave funcitons, called the Hartree-Fock molecular orbitals, and ε_i are the eigenenergies of the Fock operator. The fock operator, in matrix notation, is given by

$$F_{pa} = H_{pq} + J(D)_{pq} - \frac{1}{2}K(D)_{pq}, \tag{52}$$

where h_i is the one-body operatore, while the two-body operator is divided into what we call a direct part,

$$J(D)_{pq} = \langle pq | rs \rangle D_{sr}, \tag{53}$$

and an exchange part,

$$K(D)_{pq} = \langle ps | rq \rangle D_{sr}. \tag{54}$$

The direct part of the two-body operator is comparable to classical Coloumb repulsion, while the exchange does not have a classical analog as it arises from the antisymmetry requirement of the wavefunction. D_{sr} is the density matrix of the system.

Introducing a basis set transforms the Hartree-Fock equations into the Rothaan equations

$$FC = SC\varepsilon. \tag{55}$$

This is a generalised eigenvalue problem where S serves as an overlap matrix that must be there in case of non-orthogonal basis. Since the Fock matrix F depends on it's own solution through the orbitals, the eigenvalue problem must be solved iteratively[7].

III. IMPLEMENTATION

We have costructed a flexible framework for making performing CCD computations, consisting of package for python that is easy to install globally on any computer.

A. Installation

The software is easy to install by first cloning the GitHub reopsitory,

```
git clone git@github.com:Schoyen/FYS4411.git
```

[5] Note that we use greek letters $\alpha, \beta, \ldots$ for the harmonic oscillator wavefunctions as opposed to latin letters for the general indices.

[6] This is weird, as electron should be indistinguishable and therefor impossible to label.

[7] This is also the reason why the Hartree-Fock-Roothaan equations are often called the self-consistent-field procedure.

Then all you need to do is change directory to the project code folder where a MakeFile is included so you only need to build and install,

```
cd FYS4411/project_2/coupled-cluster
make build
make install
```

Now everything should be able to run from anywhere on your computer. To ensure that all requirements of the program are satified you can install with make installr instead.

B. Program Structure

There are three main subsetions within our program structure, given in the directory tree below.

```
coupled_cluster
├── matrix_elements
│   ├── generate_matrices
│   └── index_map
├── hartree_fock
│   ├── scf_rhf
│   └── basis_transformation
└── schemes
    ├── ccd
    ├── ccd_sparse
    └── ccd_optimized
```

The first subsection, `matrix_elemtents`, contains methods for computing matrix elements in harmonic oscillator basis from an analytical expression[1]. Computing the matrix elements is a very intensive task, and the central functions are therefore implemented in C++ with a Cython interface to enable use in Python.

The `hartree_fock` subsection contains methods for changing from harmonic oscillator basis to Hartree-Fock basis as well as an implementation of the self-consistent-field algorithm to make this transaction possible.

The `schemes` subsection is arguably the most important part of this project. The subsection has three different classes that perform the exact same computations, but in different and increasingly intelligent ways. First, `CoupledClusterDoubles` is the most straightforward and naïve way to solve the CCD amplitude equations. Second, because an overbearing amount of the elements in the operator matrices in this problem are zero, we have implemented a sparse matrix CDD solver in `CoupledClusterDoublesSparse`. Third, `CoupledClusterDoublesOptimized` takes advantage of sparse matrices as well, but is also parallellized and optimized with memory use and number of floating point operations in mind.

C. Mixing

A way to try "massage" convergence out of the CCD-method is to use *mixing*. A popular solution is Pulay mixing[8]. We did not implement Pulay mixing but used a more naïve and simpler solution.

$$\tilde{t}^{k+1} = \theta t^{k+1} + (1-\theta)t^k, \qquad (56)$$

where t^{k+1} is the current value computed using Equation 37 and t^k is the previous value for the amplitude. Choosing $\theta \in [0, 1]$ we can tune how much of the previous amplitude we wish to include in the new state. This allows for a more gradual transition between the iterations. We now use $\tilde{t}^{k+1}$ as our estimate of the new amplitude.

IV. RESULTS

V. DISCUSSION

A. Validity of results

All of our results have been compared with the master thesis of M. P. Lohne[2] for up to 10 shells. Lohne gets two sets of energies, one set from RHF and one set from CCSD code with harmonic oscillator basis functions. Our CCD code with Hartree-Fock basis will for some configurations[9] beat CCSD with plain harmonic oscillator basis. For 12 shells we can compare with the results from M. P. Lohne et al.[3], but in this article an *effective interaction* for the Hamiltonian with a CCSD code has been used. These results are therefore significanlty better than ours, but we can get a "ball-park" idea to benchmark against.

B. Convergence trouble

For a large number of particles and a low frequency the CCD-method get trouble with convergence. This happens as the confining potential $v \propto \omega^2$ will not be able to confine the particles when the interaction gets too strong. The CCD-method will in particular get a hard time keep the particles together as the excitation operator t only excites pairs of particles leading too strong increase in the interaction when the particles increase their energy level. This effect can potentially be somewhat alleviated by including the singles excitation, e.g., using the CCSD-method.

C. Sparse implementation

Appendix A: The normal ordered Hamiltonian

When constructing the normal ordered Hamiltonian we use Wick's theorem to write the one-body, h, and

[8] Commonly known as DIIS (direct inversion in the iterative subspace).

[9] By configurations we mean frequency ω and number of particles N.

TABLE I: N = 2

ω	R	RHF	CCD(HO)	CCD(HF)
0.1	1	0.596333	0.596333	0.596333
	2	0.596333	0.512520	0.512520
	3	0.526903	0.505972	0.442235
	4	0.526903	0.499216	0.442011
	5	0.525666	0.497172	0.443293
	6	0.525666	0.494232	0.443145
	7	0.525635	0.493142	0.443056
	8	0.525635	0.491895	0.442981
	9	0.525635	0.491262	0.491262
	10	0.525635	0.490649	0.442886
	11			
	12			
0.5	1	1.886227	1.886227	1.886227
	2	1.886227	1.786914	1.786914
	3	1.799856	1.778903	1.681979
	4	1.799856	1.760117	1.673881
	5	1.799748	1.754385	1.670053
	6	1.799748	1.748232	1.667804
	7	1.799745	1.745231	1.666474
	8	1.799745	1.742548	1.665494
	9	1.799743	1.740860	1.664805
	10	1.799743	1.739444	1.664270
	11			
	12			
1.0	1	3.253314	3.253314	3.253314
	2	3.253314	3.152328	3.152328
	3	3.162691	3.141827	3.039048
	4	3.162691	3.118679	3.025273
	5	3.161921	3.110967	3.017944
	6	3.161921	3.103338	3.013923
	7	3.161909	3.099324	3.011405
	8	3.161909	3.095916	3.009621
	9	3.161909	3.093662	3.008343
	10	3.161909	3.091818	3.007357
	11			
	12			
2.0	1	5.772454	5.772454	5.772454
	2	5.772454	5.671234	5.671234
	3	5.679048	5.658272	5.553528
	4	5.679048	5.631669	5.534333
	5	5.677282	5.622092	5.523490
	6	5.677282	5.613118	5.517552
	7	5.677206	5.608130	5.513709
	8	5.677206	5.604026	5.511012
	9	5.677204	5.601216	5.509050
	10	5.677204	5.598946	5.507540
	11			
	12			

TABLE II: N = 6

«««< HEAD ω	R	RHF	CCD(HO)	C
0.1	1	😱	😱	
	2	4.864244	4.864244	
	3	4.435740	😱	
	4	4.019787	😱	
	5	3.963149	😱	
	6	3.870617	😱	
	7	3.863135	😱	
	8	3.852880	😱	
	9	3.852591	😱	
	10	3.852393	😱	
	11			
	12			
0.5	1	😱	😱	
	2	13.640713	13.640713	1
	3	13.051620	13.385987	1
	4	12.357471	13.261097	1
	5	12.325128	13.138572	1
	6	12.271499	13.084158	1
	7	12.271375	13.068399	1
	8	12.271361	13.055561	1
	9	12.271337	13.045386	1
	10	12.271326	13.037878	1
	11			
	12			
1.0	1	😱	😱	
	2	22.219813	22.219813	2
	3	21.593198	21.974675	2
	4	20.766919	21.854191	2
	5	20.748402	21.793624	2
	6	20.720257	21.750091	2
	7	20.720132	21.718843	2
	8	20.719248	21.695224	2
	9	20.719248	21.675931	2
	10	20.719217	21.661830	20
	11			
	12			
2.0	1	😱	😱	
	2	37.281425	37.281425	3
	3	36.637217	37.042127	3
	4	35.689555	36.925664	3
	5	35.681729	36.864367	3
	6	35.672333	36.812895	3
	7	35.671851	36.775986	3
	8	35.670358	36.747864	3
	9	35.670333	36.725261	3
	10	35.670144	36.708362	3
	11			
	12			
======= ω	R	RHF	CCD(HO)	CCD(HF) »»»> 777eb698a

the two-body, u, operators onto a normal ordered form. Specifically we define the normal ordered form in terms of the *Fermi vacuum*[10]. That is, an operator on normal ordered form destroys the reference Slater determinant.

We start by writing the one-body operator, h, to its

[10] Fermi vacuum defines the reference state, i.e., $|\Phi_0\rangle$, as the vacuum.

TABLE III: Here we look at $N = 12$ particles ($R = 3$ shells). We did not achieve convergence using the harmonic oscillator basis for the lower frequency values and large number of shells.

ω	R	RHF	CCD(HO)	CCD(HF)
0.5	3	46.361130	46.361130	46.361130
	4	43.663266	45.837079	43.309845
	5	41.108850	45.456882	40.654709
	6	40.750512	☹	40.068340
	7	40.302718	☹	39.508500
	8	40.263751	☹	39.399128
	9	40.216688	☹	39.329310
	10	40.216251	☹	39.309409
	11	40.216194	☹	39.296007
	12	40.216165	☹	39.285968
1.0	3	73.765549	73.765549	73.765549
	4	70.673849	73.314476	70.324250
	5	67.569930	72.990679	67.031096
	6	67.296869	☹	66.526677
	7	66.934744	☹	66.049564
	8	66.923094	☹	65.972157
	9	66.912244	☹	65.921204
	10	66.912035	☹	65.889281
	11	66.911364	☹	65.866715
	12	66.911364	☹	65.849775
2.0	3	120.722260	120.722260	120.722260
	4	117.339641	120.299999	116.995036
	5	113.660396	120.012284	113.048934
	6	113.484866	119.872007	112.658821
	7	113.247601	119.662201	112.309482
	8	113.246578	119.584733	112.235521
	9	113.246302	119.524417	112.181828
	10	113.245854	119.472283	112.140661
	11	113.245255	119.430435	112.109972
	12	113.245183	119.394712	112.085683
5.0	3	242.334878	242.334878	242.334878
	4	238.739590	241.927593	238.394598
	5	234.352741	241.663950	233.680649
	6	234.282331	241.507595	233.425243
	7	234.194820	241.390524	233.226529
	8	234.194058	241.293416	233.137932
	9	234.190796	241.221056	233.070206
	10	234.190714	241.158896	233.020009
	11	234.190665	241.109926	232.980634
	12	234.190552	241.068091	232.948528

TABLE IV: In this table we look at $N = 20$ particles ($R = 4$ shells). We did not achieve convergence using the harmonic oscillator basis for the lower frequency values and large number of shells.

ω	R	RHF	CCD(HO)	CCD(HF)
1.0	4	177.963297	177.963297	177.963297
	5	168.792442	177.206535	168.459124
	6	161.339720	☹	160.594507
	7	159.958722	☹	158.841119
	8	158.400172	☹	157.038330
	9	158.226030	☹	156.676039
	10	158.017666	☹	156.367930
	11	158.010276	☹	156.292422
	12	158.004951	☹	156.238258
2.0	4	286.825295	286.825295	286.825295
	5	276.898195	286.159165	276.381708
	6	267.269712	266.413122	285.614965
	7	266.213200	☹	264.969415
	8	264.933621	☹	263.434546
	9	264.874009	☹	263.215451
	10	264.809953	☹	263.046184
	11	264.809900	☹	262.963702
	12	264.809306	☹	262.899697
5.0	4	563.773951	563.773951	563.773951
	5	552.630093	563.160136	552.118708
	6	540.804719	562.692231	539.824400
	7	540.227792	562.306124	538.886073
	8	539.499326	562.114280	537.925127
	9	539.495940	☹	537.769045
	10	539.494611	☹	537.646667
	11	539.493512	☹	537.548827
	12	539.491764	☹	537.470616
10.0	4	973.032700	973.032700	973.032700
	5	961.371081	972.439477	960.862053
	6	948.057077	972.002302	947.019789
	7	947.765473	971.716015	946.399546
	8	947.410304	971.508583	945.827806
	9	947.409439	971.332132	945.663819
	10	947.404929	971.193592	945.528489
	11	947.404360	971.076617	945.424174
	12	947.403875	970.978571	945.339079

normal-ordered form.

$$h = \sum_{pq} h^p_q a^\dagger_p a_q = \sum_{pq} h^p_q \left(\{a^\dagger_p a_q\} + \{\wick{\c{a}^\dagger_p \c{a}_q}\} \right) \tag{A1}$$

$$= \sum_{pq} h^p_q \{a^\dagger_p a_q\} + \sum_{pq} h^p_q \delta_{p\in i} \delta_{pq} \tag{A2}$$

$$= h_N + \sum_i h^i_i, \tag{A3}$$

where we have used $\delta_{p\in i}$ to mean that p must be an occupied index. Doing the same for the two-body operator is a slightly more tedious endeavor. For brevity we will only write out the operator strings and only keep the non-zero contributions.

$$\begin{aligned} a^\dagger_p a^\dagger_q a_s a_r &= \{a^\dagger_p a^\dagger_q a_s a_r\} + \{\wick{\c{a}^\dagger_p a^\dagger_q \c{a}_s a_r}\} + \{\wick{\c{a}^\dagger_p a^\dagger_q a_s \c{a}_r}\} \\ &+ \{\wick{a^\dagger_p \c{a}^\dagger_q \c{a}_s a_r}\} + \{\wick{a^\dagger_p \c{a}^\dagger_q a_s \c{a}_r}\} \\ &+ \{\wick{\c1{a}^\dagger_p \c2{a}^\dagger_q \c1{a}_s \c2{a}_r}\} + \{\wick{\c1{a}^\dagger_p \c2{a}^\dagger_q \c2{a}_s \c1{a}_r}\} \end{aligned} \tag{A4}$$

$$\begin{aligned} &= \{a^\dagger_p a^\dagger_q a_s a_r\} - \delta_{p\in i}\delta_{ps}\{a^\dagger_q a_r\} + \delta_{p\in i}\delta_{pr}\{a^\dagger_q a_s\} \\ &+ \delta_{q\in i}\delta_{qs}\{a^\dagger_p a_r\} - \delta_{q\in i}\delta_{qr}\{a^\dagger_p a_s\} \\ &- \delta_{p\in i}\delta_{ps}\delta_{q\in j}\delta_{qr} + \delta_{p\in i}\delta_{pr}\delta_{q\in j}\delta_{qs}. \end{aligned} \tag{A5}$$

Inserted into the full two-body operator and sorting out the sums we get

$$
\begin{aligned}
u = &\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} - \frac{1}{4}\sum_{iqr}\langle iq||ri\rangle\{a_q^\dagger a_r\} \\
&+ \frac{1}{4}\sum_{iqs}\langle iq||is\rangle\{a_q^\dagger a_s\} + \frac{1}{4}\sum_{pir}\langle pi||ri\rangle\{a_p^\dagger a_r\} \\
&- \frac{1}{4}\sum_{pis}\langle pi||is\rangle\{a_p^\dagger a_s\} - \frac{1}{4}\sum_{ij}\langle ij||ji\rangle \\
&+ \frac{1}{4}\sum_{ij}\langle ij||ij\rangle. \qquad \text{(A6)}
\end{aligned}
$$

Using the antisymmetric properties of the two-body matrix elements,

$$\langle pq||rs\rangle = -\langle pq||sr\rangle = -\langle qp||rs\rangle = \langle qp||sr\rangle, \qquad \text{(A7)}$$

and relabeling of the indices we can rearrange and collect some terms.

$$u = W_N + \sum_{pir}\langle pi||ri\rangle\{a_p^\dagger a_r\} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle, \qquad \text{(A8)}$$

where the normal ordered two-body operator is

$$W_N = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\}. \qquad \text{(A9)}$$

When we now construct the full Hamiltonian we can collect some terms. The constants in both the one-body and the two-body operator in total constitues the reference energy.

$$E_0 \equiv \langle\Phi_0|H|\Phi_0\rangle = \sum_i h_i^i + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle. \qquad \text{(A10)}$$

Combining the normal ordered one-body operator and the second term in the two-body operator, i.e., the term with a single creation and annihilation operator pair, we get the normal ordered Fock-operator.

$$
\begin{aligned}
F_N &= \sum_{pq} h_q^p\{a_p^\dagger a_q\} + \sum_{pqi}\langle pi||qi\rangle\{a_p^\dagger a_q\} \qquad \text{(A11)} \\
&= \sum_{pq} f_q^p\{a_p^\dagger a_q\}, \qquad \text{(A12)}
\end{aligned}
$$

where we have defined the Fock matrix elements as

$$f_q^p = h_q^p + \sum_i\langle pi||qi\rangle. \qquad \text{(A13)}$$

In total we get the full Hamiltonian

$$
\begin{aligned}
H &= F_N + W_N + \langle\Phi_0|H|\Phi_0\rangle \qquad \text{(A14)} \\
&= H_N + \langle\Phi_0|H|\Phi_0\rangle, \qquad \text{(A15)}
\end{aligned}
$$

which is what we wanted to show.[4]

Appendix B: Amplitude Equations

In this section we have provided a few sample computations of how one would evaluate the amplitude equations using wicks theorem. Starting with the simplest term including only the normal-ordered Hamiltonian,

$$
\begin{aligned}
&\langle\Phi_{ij}^{ab}|(F_N + V_N)|\Phi_0\rangle \\
&\quad= \sum_{pq} f_{pq}\langle\Phi_0|\{a_i^\dagger a_j^\dagger a_b a_a\}\{a_p^\dagger a_q\}|\Phi_0\rangle \\
&\qquad+ \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_0|\{a_i^\dagger a_j^\dagger a_b a_a\}\{a_p^\dagger a_q^\dagger a_s a_r\}|\Phi_0\rangle.
\end{aligned}
\qquad \text{(B1)}
$$

The one-electron component does not have any full contractions, while the two-electron component produces one contributing integral,

$$
\begin{aligned}
&\langle\Phi_{ij}^{ab}|(V_N)|\Phi_0\rangle \\
&= \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_0|\{a_i^\dagger a_j^\dagger a_b a_a\}\{a_p^\dagger a_q^\dagger a_s a_r\}|\Phi_0\rangle \\
&= \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle \\
&\quad\times\Big(\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} \\
&\qquad+ \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q^\dagger a_s a_r\}\Big) \\
&= \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle(\delta_{ap}\delta_{bq}\delta_{js}\delta_{ir} - \delta_{aq}\delta_{bp}\delta_{js}\delta_{ir} \\
&\qquad- \delta_{ap}\delta_{bq}\delta_{jr}\delta_{is} + \delta_{aq}\delta_{bp}\delta_{jr}\delta_{is}) \\
&= \langle ab||ij\rangle = u_{ij}^{ab}.
\end{aligned}
\qquad \text{(B2)}
$$

Next we would like to evaluate $\langle\Phi_{ij}^{ab}|(F_N + V_N)T_2|\Phi_0\rangle$.

Starting with the term involving the Fock operator F_N,

$$
\begin{aligned}
&\langle \Phi_{ij}^{ab} | F_N T_2 | \Phi_0 \rangle \\
&\quad = \frac{1}{4} \sum_{pq} \sum_{klcd} f_{pq} t_{kl}^{cd} \langle \Phi_0 | \{a_i^\dagger a_j^\dagger a_b a_a\} (\{a_p^\dagger a_q\} \{a_c^\dagger a_d^\dagger a_l a_k\})_c | \Phi_0 \rangle \\
&\quad = \frac{1}{4} \sum_{pq} \sum_{klcd} f_{pq} t_{kl}^{cd} \\
&\quad \times \Big(\{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} \\
&\quad + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} \\
&\quad + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} \\
&\quad + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} \\
&\quad + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} \\
&\quad + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} \\
&\quad + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} \\
&\quad + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} + \{a_i^\dagger a_j^\dagger a_b a_a a_p^\dagger a_q a_c^\dagger a_d^\dagger a_l a_k\} \Big) \\
&\quad = \sum_{pq} \sum_{klcd} f_{pq} t_{kl}^{cd} \\
&\quad \times (-\delta_{ac}\delta_{bd}\delta_{ik}\delta_{jq}\delta_{lp} + \delta_{ac}\delta_{bd}\delta_{il}\delta_{jq}\delta_{kp} \\
&\qquad + \delta_{ac}\delta_{bd}\delta_{iq}\delta_{jk}\delta_{lp} - \delta_{ac}\delta_{bd}\delta_{iq}\delta_{jl}\delta_{kp} \\
&\qquad + \delta_{ac}\delta_{bp}\delta_{dq}\delta_{ik}\delta_{jl} - \delta_{ac}\delta_{bp}\delta_{dq}\delta_{il}\delta_{jk} \\
&\qquad + \delta_{ad}\delta_{bc}\delta_{ik}\delta_{jq}\delta_{lp} - \delta_{ad}\delta_{bc}\delta_{il}\delta_{jq}\delta_{kp} \\
&\qquad - \delta_{ad}\delta_{bc}\delta_{iq}\delta_{jk}\delta_{lp} + \delta_{ad}\delta_{bc}\delta_{iq}\delta_{jl}\delta_{kp} \\
&\qquad - \delta_{ad}\delta_{bp}\delta_{cq}\delta_{ik}\delta_{jl} + \delta_{ad}\delta_{bp}\delta_{cq}\delta_{il}\delta_{jk} \\
&\qquad - \delta_{ap}\delta_{bc}\delta_{dq}\delta_{ik}\delta_{jl} + \delta_{ap}\delta_{bc}\delta_{dq}\delta_{il}\delta_{jk} \\
&\qquad + \delta_{ap}\delta_{bd}\delta_{cq}\delta_{ik}\delta_{jl} - \delta_{ap}\delta_{bd}\delta_{cq}\delta_{il}\delta_{jk}) \\
&\quad = (f_{bc} t_{ij}^{ac} - f_{ac} t_{ij}^{bc}) - (f_{jk} t_{ik}^{ab} - f_{ik} t_{jk}^{ab}) \\
&\quad = f_{bc} t_{ij}^{ac} P(ab) - f_{kj} t_{ik}^{ab} P(ij)
\end{aligned}
\tag{B3}
$$

Where in the last steps we have consigned the sums by Einstein summation notation.

Appendix C: Finding Amplitude Equation Intermediates

Starting from the CCD amplitude equation we factor out terms that will have the same indices if we contract them,

$$
\begin{aligned}
0 =& u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\
&+ \frac{1}{4} t_{ij}^{cd} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} t_{ij}^{cd} u_{cd}^{ab} \\
&+ \frac{1}{2} t_{jm}^{cd} t_{in}^{ab} u_{cd}^{mn} P(ij) - \frac{1}{2} t_{nm}^{ac} t_{ij}^{bd} u_{cd}^{nm} P(ab) \\
&+ t_{im}^{ac} t_{jn}^{bd} u_{cd}^{mn} P(ij) + t_{im}^{ac} u_{jc}^{bm} P(ab) P(ij) \\
&+ \frac{1}{2} t_{im}^{ab} u_{jn}^{mn},
\end{aligned}
\tag{C1}
$$

$$
\begin{aligned}
0 =& u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\
&+ t_{ij}^{cd} \left(\frac{1}{4} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} u_{cd}^{ab} \right) \\
&+ t_{in}^{ab} \left(\frac{1}{2} t_{jm}^{cd} u_{cd}^{mn} \right) P(ij) \\
&- t_{ij}^{bd} \left(\frac{1}{2} t_{nm}^{ac} u_{cd}^{nm} \right) P(ab) \\
&+ \frac{1}{2} t_{im}^{ac} t_{jn}^{bd} u_{cd}^{mn} P(ij) - \frac{1}{2} t_{im}^{bc} t_{jn}^{ad} u_{cd}^{mn} P(ij) \\
&+ t_{im}^{ac} u_{jc}^{bm} P(ab) P(ij) \\
&+ \frac{1}{2} t_{im}^{ab} u_{jn}^{mn}
\end{aligned}
\tag{C2}
$$

$$
\begin{aligned}
0 =& u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\
&+ t_{ij}^{cd} \left(\frac{1}{4} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} u_{cd}^{ab} \right) \\
&+ t_{in}^{ab} \left(\frac{1}{2} t_{jm}^{cd} u_{cd}^{mn} \right) P(ij) \\
&- t_{ij}^{bd} \left(\frac{1}{2} t_{nm}^{ac} u_{cd}^{nm} \right) P(ab) \\
&+ \frac{1}{2} t_{im}^{ac} t_{jn}^{bd} u_{cd}^{mn} P(ab) P(ij) \\
&+ t_{im}^{ac} u_{jc}^{bm} P(ab) P(ij) \\
&+ \frac{1}{2} t_{im}^{ab} u_{jn}^{mn}
\end{aligned}
\tag{C3}
$$

$$
\begin{aligned}
0 =& u_{ij}^{ab} + f_c^b t_{ij}^{ac} P(ab) - f_j^k t_{ik}^{ab} P(ij) \\
&+ t_{ij}^{cd} \left(\frac{1}{4} t_{mn}^{ab} u_{cd}^{mn} + \frac{1}{2} u_{cd}^{ab} \right) \\
&+ t_{in}^{ab} \left(\frac{1}{2} t_{jm}^{cd} u_{cd}^{mn} \right) P(ij) \\
&- t_{ij}^{bd} \left(\frac{1}{2} t_{nm}^{ac} u_{cd}^{nm} \right) P(ab) \\
&+ t_{im}^{ac} \left(\frac{1}{2} t_{jn}^{bd} u_{cd}^{mn} + u_{jc}^{bm} \right) P(ab) P(ij) \\
&+ \frac{1}{2} t_{im}^{ab} u_{jn}^{mn}.
\end{aligned}
\tag{C4}
$$

Now we can introduce the intermediate χ-terms,

$$\chi^{ab}_{cd} = \frac{1}{4} t^{ab}_{mn} u^{mn}_{cd} + \frac{1}{2} u^{ab}_{cd} \tag{C5}$$

$$\chi^{n}_{j} = \frac{1}{2} t^{cd}_{jm} u^{mn}_{cd} \tag{C6}$$

$$\chi^{a}_{d} = \frac{1}{2} t^{ac}_{nm} u^{nm}_{cd} \tag{C7}$$

$$\chi^{bm}_{jc} = \frac{1}{2} t^{bd}_{jn} u^{mn}_{cd} + u^{bm}_{jc}, \tag{C8}$$

this gives us,

$$\begin{aligned} 0 =& u^{ab}_{ij} + \tilde{f}^{b}_{c} t^{ac}_{ij} P(ab) - \tilde{f}^{k}_{j} t^{ab}_{ik} P(ij) \\ &+ t^{cd}_{ij} \chi^{ab}_{cd} + t^{ab}_{in} \chi^{n}_{j} P(ij) - t^{bd}_{ij} \chi^{a}_{d} P(ab) \\ &+ t^{ac}_{im} \chi^{bm}_{jc} P(ab) P(ij) + \frac{1}{2} t^{ab}_{im} u^{mn}_{jn}. \end{aligned} \tag{C9}$$

Appendix D: Coupled cluster doubles diagrams

In order to get an expression for the energy equation and the amplitude equations we use a diagrammatic approach.

Appendix E: Example Script

```
from coupled_cluster.schemes.ccd_sparse import CoupledClusterDoublesSparse
from coupled_cluster.schemes.ccd_optimized import CoupledClusterDoublesOptimized
from coupled_cluster.hartree_fock.scf_rhf import scf_rhf
from coupled_cluster.matrix_elements.generate_matrices import (
    get_one_body_elements, get_coulomb_elements,
    get_antisymmetrized_elements, add_spin_to_one_body_elements,
    get_one_body_elements_spin
)
from coupled_cluster.matrix_elements.index_map import (
    generate_index_map, IndexMap
)
from coupled_cluster.hartree_fock.basis_transformation import (
    transform_one_body_elements, transform_two_body_elements
)

import numpy as np
import time
import os

file_path = os.path.join("..", "dat")
filename = os.path.join(file_path, "coulomb_{0}.pkl")

num_shells = 1
generate_index_map(num_shells)

omega = 2.0
l = IndexMap.shell_arr[-1]
n = 6
theta = 0.3

filename = filename.format(l)

print ("""
w = {0},
num_shells = {1},
l = {2},
n = {3},
```

```
theta = {4},
filename = {5}
""".format(omega, num_shells, l, n, theta, filename))

h = omega * get_one_body_elements(l)
t0 = time.time()
u = np.sqrt(omega) * get_coulomb_elements(l, filename=filename, tol=1e-12)
t1 = time.time()
print ("Time spent creating Coulomb elements: {0} sec".format(t1 - t0))

t0 = time.time()
c, energy = scf_rhf(h.todense(), u, np.eye(l//2), n//2, tol=1e-6)
t1 = time.time()
print ("Time spent in SCF RHF: {0} sec".format(t1 - t0))

print ("\tRHF Energy: {0}".format(energy))

hi = transform_one_body_elements(h, c)
t0 = time.time()
oi = transform_two_body_elements(u, c)
t1 = time.time()
print ("Time spent transforming two body elements: {0} sec".format(t1 - t0))

_h = add_spin_to_one_body_elements(hi, l)
t0 = time.time()
_u = get_antisymmetrized_elements(l, oi=oi, tol=1e-12)
t1 = time.time()
print ("Time spent antisymmetrizing two body elements: {0} sec".format(t1 - t0))

#t0 = time.time()
#ccd_hf_sparse = CoupledClusterDoublesSparse(_h, _u, n)
#t1 = time.time()
#print ("Time spent setting up CCD code with HF basis: {0} sec".format(t1 - t0))
#
#t0 = time.time()
#energy, iterations = ccd_hf_sparse.compute_energy(tol=1e-4, theta=theta)
#t1 = time.time()
#print ("Time spent computing CCD energy with HF basis: {0} sec".format(t1 - t0))
#print ("\tCCD (HF) Energy: {0}\n\tIterations: {1}\n\tSecond/iteration: {2}".format(energy, iterations,

t0 = time.time()
ccd_hf = CoupledClusterDoublesOptimized(
        _h.todense(), _u.todense(), n, parallel=False)
t1 = time.time()
print ("Time spent setting up CCD (opt, parallel) code with HF basis: {0} sec"
    .format(t1 - t0))

t0 = time.time()
energy, iterations = ccd_hf.compute_energy(tol=1e-6, theta=theta)
t1 = time.time()
print ("Time spent computing CCD (opt, parallel) energy with HF basis: {0} sec"
   .format(t1 - t0))
print ("\tCCD (HF) Energy: {0}\n\tIterations: {1}\n\tSecond/iteration: {2}"
    .format(energy, iterations, (t1 - t0)/iterations))

#__import__("sys").exit()

__h = omega * get_one_body_elements_spin(l)
```

```
t0 = time.time()
__u = np.sqrt(omega) * get_antisymmetrized_elements(l, filename=filename)
t1 = time.time()
print ("Time spent getting antisymmetric two body elements: {0} sec".format(t1 - t0))

t0 = time.time()
ccd = CoupledClusterDoublesOptimized(__h.todense(), __u.todense(), n)
t1 = time.time()
print ("Time spent setting up CCD code with HO basis: {0} sec".format(t1 - t0))
t0 = time.time()
energy, iterations = ccd.compute_energy(theta=theta, tol=1e-6)
t1 = time.time()
print ("Time spent computing CCD energy with HO basis: {0} sec".format(t1 - t0))
print ("\tCCD Energy: {0}\n\tIterations: {1}\n\tSecond/iteration: {2}"
    .format(energy, iterations, (t1 - t0)/iterations))

print (h.density)
print (u.density)
print (_u.density)
print (_h.density)
print (__u.density)
print (__h.density)
```


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