

Abstract

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1 Introduction

In this white paper we will discuss a Configurational Coupled Cluster approach to particular many-body systems. Typical examples of systems include chains (or slaps) of rotors, or chains of magnetic systems. The simplest systems are 1-dimensional chains or periodic rings. We will also be interested in 2d and 3d lattices in the near future. The key feature of the systems is that they consist of sites. Each site is associated with a set of basis functions or quantum states. Let us start by introducing notation to describe the systems. We will use the following labels:

x, y, z, w : site labels.

p, q, r, s : generic (many body) states associated with a site.

i, j, k, l : low lying state(s) associated with a site. The theory is simplest if there is only one-low-lying state.

a, b, c, d : high lying states associated with a site. Typically there are a small number of these (around 10-20).

We use an index convention that tries to associate p, a, i with site x , q, b, j with site y etc. The complete many body states can then be represented as linear combinations of product states:

$$|\Psi\rangle = \sum_{p,q,r,\dots,z} C^{pqr\dots s} |p, q, r, \dots, z\rangle = \sum_{p,q,r,\dots,z} C^{pqr\dots z} |p\rangle |q\rangle |r\rangle \dots |z\rangle$$

The Hamiltonian only contains operators that explicitly act on one-site or at most two-sites. We denote the elementary substitution operators on side x as

$$\hat{e}_{p'}^p(x) = |p\rangle \langle p'| (x)$$

The one-body hamiltonian can then be written as

$$\hat{h}_1 = \sum_x \hat{K}(x) = \sum_x \sum_{p,p'} h_{p'}^p(x) \hat{e}_{p'}^p(x) \equiv \sum_x \sum_{p,p'} \hat{h}_{p'}^p(x)$$

The two-body component is written as

$$\begin{aligned} \hat{V} &= \sum_{x<y} \hat{V}(x, y) = \sum_{x<y} \sum_{p,p',q,q'} v_{p',q'}^{p,q}(x, y) \hat{e}_{p'}^p(x) \hat{e}_{q'}^q(y) \\ &= \sum_{x<y} \sum_{p,p',q,q'} \hat{V}_{p',q'}^{p,q}(x, y) \end{aligned} \tag{1}$$

The conceptually simplest solution is to construct the full configurational Hamiltonian over the set of complete many-site basis states and diagonalize. This procedure can also be implemented using direct diagonalization. These provide useful benchmark results, but are computationally very expensive. In what follows we can assume that each one-site hamiltonian is the same, while each two-body operator is the same for any two sites x, y that have the same 'distance' $|x - y|$, e.g. nearest neighbours or next nearest neighbours. We can also assume periodic boundary conditions, connecting sites in a ring. These notions can be generalized to 2 and 3d lattices. It is possible that the site-operators in the Hamiltonian explicitly depends on the site label, but this is not the usual case. The theory we discuss is general. We may simplify the implementation. Let me first discuss truncated Configuration interaction. We may not actually implement this approach but it would introduce a number of useful concepts that helps understanding the ultimate Configurational Coupled Cluster approach.

2 Truncated Configuration Interaction

We assume that the single configuration in which on every site the system is in its lowest energy state is a reasonable qualitative description of the ground state. This is referred to as the reference state

$$|0\rangle = |i, j, k, l, \dots\rangle$$

We now express an improved ground state as the sum of the reference state plus additional configurations, in which some of the sites are excited to higher lying states a, b, c, \dots . These configurations are generically denoted as $|\lambda\rangle$.

$$|\Phi\rangle = |0\rangle + \sum_{\lambda \neq 0} |\lambda\rangle$$

Importantly this state is expressed in so-called intermediate normalization:

$$\langle 0|\Phi\rangle = \langle 0|0\rangle + \sum_{\lambda \neq 0} \langle 0|\lambda\rangle = \langle 0|0\rangle = 1$$

As a consequence the (approximate) ground state energy can be obtained as

$$E_0 = \langle 0|\hat{H}|\Phi\rangle$$

Since \hat{H} contains only one and two-site operators only so-called singly and doubly excited states enter this expression. In this context one might call them one-site and two-site excited states. In the context of what

follows it is convenient to introduce excitation operators:

$$\begin{aligned}\hat{C}_1 &= \sum_x \sum_{a,i} c_i^a(x) \hat{e}_i^a(x) \\ \hat{C}_2 &= \sum_{x < y} \sum_{a,i,b,j} c_{ij}^{ab}(x,y) \hat{e}_{ij}^{ab}(x,y)\end{aligned}\tag{2}$$

These operators can be extended to higher excitation operators \hat{C}_3 etc. The overall excitation operator is then expressed as

$$\hat{C} = \hat{C}_1 + \hat{C}_2 + \dots$$

Generically one might also write

$$\hat{C} = \sum_{\lambda \neq 0} c_\lambda \hat{\Omega}_\lambda$$

Here λ is a shorthand for one particular excitation, and $\hat{\Omega}_\lambda |0\rangle = |\lambda\rangle$. The truncated CI equations then read

$$\hat{H}(1 + \hat{C}) |0\rangle = (1 + \hat{C}) |0\rangle E_0$$

and more explicit equations can be expressed as

$$\begin{aligned}\langle 0 | \hat{H}(1 + \hat{C}) |0\rangle &= \langle 0 | (1 + \hat{C}) |0\rangle E_0 \\ \langle \mu | \hat{H}(1 + \hat{C}) |0\rangle &= \langle 0 | (1 + \hat{C}) |0\rangle E_0\end{aligned}\tag{3}$$

This is just a matrix eigenvalue equation in disguise. We can write

$$\begin{pmatrix} H_{00} & H_{0\lambda} \\ H_{\mu 0} & H_{\mu\lambda} \end{pmatrix} \begin{pmatrix} 1 \\ c_\lambda \end{pmatrix} = \begin{pmatrix} 1 \\ c_\mu \end{pmatrix} E_0\tag{4}$$

This clearly shows the eigenvector is written in intermediate normalization. This analysis highlights the importance on single and double excitations, as in intermediate normalization they are the only expansion coefficients needed to calculate the exact energy. This procedure also introduces many of the building blocks we can use to discuss the next section.

3 Single reference Configurational Coupled Cluster

As in CI we assume a reference state $|0\rangle = |i, j, k, \dots, l\rangle$. Here we again explicitly assume there is only one low-lying state per site, such that the reference state is well-defined. In addition we define one-and two-site

cluster excitation operators

$$\begin{aligned}
\hat{T}_1 &= \sum_x \hat{t}(x) = \sum_x \sum_{a,i} t_i^a(x) \hat{e}_i^a(x) \equiv \sum_x \sum_{a,i} \hat{t}_i^a(x) \\
\hat{T}_2 &= \sum_{x < y} \hat{T}(x, y) = \sum_{x < y} \sum_{a,b,i,j} t_{i,j}^{a,b}(x, y) \hat{e}_i^a(x) \hat{e}_j^b(y) \\
&= \sum_{x < y} \sum_{a,i,b,j} \hat{T}_{ij}^{ab}(x, y)
\end{aligned} \tag{5}$$

Since the low-energy labels i, j refer to one state only, there is strictly no need for a summation. Including the summation makes the theory more closely related to the usual CC theory, and it may be useful for future extensions in the future. At the level of abstract theory it doesn't matter much. We can reconsider during implementation. It is straightforward to extend the cluster operator to higher rank operators. Let us remember the index convention we use. These operator forms are exactly the same as in truncated CI, only the operators have a different name (and will be used differently).

The ansatz for the Configurational Coupled Cluster wave function is

$$|\Psi\rangle = e^{\hat{T}} |0\rangle$$

If we substitute this ansatz in the Schrödinger equation we obtain

$$\hat{H} e^{\hat{T}} |0\rangle = e^{\hat{T}} |0\rangle E_0$$

We can multiply the equations on the right by $e^{-\hat{T}}$ (a non-singular operator) to obtain the equivalent equation

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |0\rangle = e^{-\hat{T}} e^{\hat{T}} |0\rangle E_0 = |0\rangle E_0$$

and the equations equations for the cluster amplitudes can be expressed as

$$\langle 0 | \hat{\Omega}_\lambda e^{-\hat{T}} \hat{H} e^{\hat{T}} |0\rangle = 0$$

Here $\langle 0 | \hat{\Omega}_\lambda$ represents an excited (bra) state, orthogonal to $|0\rangle$. These non-linear equations can be solved for the t -amplitudes, and the energy can then be obtained from

$$\begin{aligned}
E_0 &= \langle 0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} |0\rangle = \langle 0 | \hat{H} e^{\hat{T}} |0\rangle \\
&= \langle 0 | \hat{H} (1 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_1^2) |0\rangle
\end{aligned} \tag{6}$$

In the first line we use that $\langle 0 | \hat{T} = 0$, as \hat{T} excites. The second line expresses the fact that in intermediate normalization one only needs one and two-site operators for a hamiltonian of the type under consideration.

Since the high lying states a, b are orthonormal to the low-lying states i, j the cluster operators commute. For each site the excitation operator can only act once. Even if the Hamiltonian contains nearest neighbours only, the \hat{T} operators extend over multiple sites. In practice they might be non-zero over a range $|x - y| < R$.

The theory can be developed as usual for CC. As a first step we use the Baker-Campbell-Hausdorf expansion

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!} [[\hat{H}, \hat{T}], \hat{T}] + \dots$$

The commutators play an essential role. We first note that operators with different side labels commute. If we have operator (components) with the same side label we can evaluate, e.g.

$$\begin{aligned} \sum_{p,p',q,q'} [\hat{A}_{p'}^p(x), \hat{B}_{q'}^q(x)] &= \sum_{p,p',q,q'} (\hat{A}_{p'}^p(x) \hat{B}_{q'}^q(x) - \hat{B}_{q'}^q(x) \hat{A}_{p'}^p(x)) \\ &= \sum_{p,p',q'} A_{p'}^p B_{q'}^{p'} \hat{e}_{q'}^p - \sum_{q,q',p'} B_{q'}^q A_{p'}^{q'} \hat{e}_{p'}^q \end{aligned} \quad (7)$$

We see that "contractions" arise from the $\langle p' | q \rangle = \delta_{p'q}$ multiplication, involving a lower label on the left (bra) and an upper label on the right (ket). The commutator means there have to be contractions (i.e. common labels) between the operators in the commutator. Since \hat{T} operators cannot be contracted (they commute), it follows every \hat{T} operator is contracted to the Hamiltonian. Either having a T on the right, or a T on the left. If \hat{T} occurs on the left there is a minus sign (from the minus part of the commutator). It would be convenient to represent terms graphically. I made a second document in one-note where I discuss this diagrammatic representation. It forms a compendium pdf file to this white paper.

As discussed in the one-note file, for this theory the single excitation operators are easy to include using a simple protocol. I will include singles in effective ways using the following intermediates.

$$\begin{aligned} A_p^a &= \delta_p^a - \sum_i t_i^a \delta_p^i \\ B_i^{p'} &= \delta_i^{p'} + \sum_a \delta_a^{p'} t_i^a \end{aligned}$$

Then we can focus on the detailed contributions from $e^{\hat{T}_2}$ contributions and dress up the lines coming from the hamiltonian with A-operators (on top), or B-operators at the bottom. The diagrams are represented top to bottom and this corresponds to operator expressions on paper that go from left (bottom) to right (top). This is pretty common in CC. Here we could have easily drawn everything like it is written on paper, but I forgot to do this, and stuck to what is familiar to me.

The (labeled) diagrams immediately allow us to write down the detailed equations. To simplify the formulas we use some conventions. Repeated (upper/lower) state labels are summed. Site labels are summed explicitly. We arrive at the following equations:

Energy equation

$$E = \sum_x h_p^i(x) B_i^p(x) + \sum_{x < y} (v_{ab}^{ij}(x, y) t_{ij}^{ab}(x, y) + v_{pq}^{ij}(x, y) B_i^p(x) B_j^q(y))$$

Singles equation.

$$R_i^a(x) = A_p^a(x) h_q^p(x) B_i^q(x) + \sum_{z \neq x} A_p^a V_{cd}^{pl}(x, z) t_{il}^{cd}((x, z) + \sum_{z \neq x} A_p^a(x) V_{qs}^{pl}(x, z) B_i^q(x) B_l^s(z) \quad (8)$$

Doubles equation A: symmetric contributions (under $ai \rightarrow jb$) permutation

$$\begin{aligned} Rs_{ij}^{ab}(x < y) &+ = A_p^a(x) A_q^b(y) V_{rs}^{pq}(x, y) B_i^r(x) B_j^s(y) \\ &+ A_p^a(x) A_q^b(y) V_{cd}^{pq}(x, y) t_{ij}^{cd}(x, y) - t_{kl}^{ab}(x, y) V_{p,q}^{kl}(x, y) B_i^p(x) B_j^q(y) \\ &- t_{kl}^{ab}(x, y) V_{cd}^{kl}(x, y) t_{ij}^{cd}(x, y) + \sum_{z, w \neq x, y} v_{cd}^{kl}(z, w) t_{ik}^{ac}(x, z) t_{jl}^{bd}(y, w) \end{aligned}$$

Doubles equations B: non-symmetrix contributions. We need to add $ai \rightarrow jb$) permutation eventually. This is easiest to do on residual

$$\begin{aligned} Rn_{ij}^{ab}(x, y) &+ = A_p^a(x) h_c^p(x) t_{ij}^{cb}(x, y) - t_{kj}^{ab}(x, y) h_b^k(x) B_i^p(x) + \sum_{z \neq x, y} t_{ik}^{ac}(x, z) V_{cs}^{kr}(z, y) A_r^b(y) B_j^s(y) \\ &+ \sum_{z \neq x, y} A_q^b(y) v_{ds}^{ql}(y, z) t_{ij}^{ad}(x, y) B_l^s(z) - \sum_{z \neq x, y} t_{kj}^{ab} v_{rp}^{lk}(z, x) B_i^p(x) B_l^r(z) \end{aligned} \quad (9)$$

Total doubles residual

$$Rt_{ij}^{ab}(x < y) = Rs_{ij}^{ab}(x < y) + Rn_{ij}^{ab}(x, y) + Rn_{ji}^{ba}(y, x)$$

4 Sparse Matrix representation of Single reference Coupled Cluster Equations

The above equations can be implemented straightforwardly using the Einsum summation procedure, in which site labels are included through explicit loops. In the above native representation most quantities are 4-dimensional tensors, and for such quantities Einsum assumes dense quantities. In reality the t -amplitudes and hamiltonian matrix elements are very sparse. Einsum can use sparse matrix techniques provided the elementary quantities are vectors and matrices, i.e. up to 2d tensors. In the CC equations the indices i, j, k, l refer to a single low-lying state. Therefore this index can be removed as it is immaterial. The site indices can be used to identify which low-lying state is used. In the equations below the CC equations are repeated, but the low-lying indices are replaced by dots. This allows us to identify which terms in the equations automatically reduce to products of

matrices and vectors. This can include outer products. The dots serve a purpose as they might define different 2-index quantities that need to be distinguished. No information is lost.

Energy equation

$$E = \sum_x h_p(x) B^p(x) + \sum_{x < y} (v_{ab}(x, y) t^{ab}(x, y) + v_{pq}(x, y) B^p(x) B^q(y))$$

Singles equation.

$$R^a(x) = A_p^a(x) h_q^p(x) B^q(x) + \sum_{z \neq x} A_p^a V_{cd}^p(x, z) t^{cd}(x, z) + \sum_{z \neq x} A_p^a V_{qs}^p(x, z) B^q(x) B^s(z) \quad (10)$$

Doubles equation A: symmetric contributions (under $ai \rightarrow jb$ permutation)

$$\begin{aligned} R s^{ab}(x < y) &+ = A_p^a(x) A_q^b(y) V_{rs}^{pq}(x, y) B^r(x) B^s(y) \\ &+ A_p^a(x) A_q^b(y) V_{cd}^{pq}(x, y) t^{cd}(x, y) - t^{ab}(x, y) V_{p,q}(x, y) B^p(x) B^q(y) \\ &- t^{ab}(x, y) V_{cd}(x, y) t^{cd}(x, y) + \sum_{z, w \neq x, y} v_{cd}(z, w) t^{ac}(x, z) t^{bd}(y, w) \end{aligned}$$

Doubles equations B: non-symmetrix contributions. We need to add $ai \rightarrow jb$ permutation eventually. This is easiest to do on residual

$$\begin{aligned} R n_{ij}^{ab}(x, y) &+ = A_p^a(x) h_c^p(x) t^{cb}(x, y) - t^{ab}(x, y) h_p(x) B^p(x) + \sum_{z \neq x, y} t^{ac}(x, z) V_{cs}^r(z, y) A_r^b(y) B^s(y) \\ &+ \sum_{z \neq x, y} A_q^b(y) v_{ds}^q(y, z) t^{ad}(x, y) B^s(z) - \sum_{z \neq x, y} t^{ab}(z, x) v_{rp}^p(z, x) B^p(x) B^r(z) \end{aligned} \quad (11)$$

Total doubles residual

$$R t^{ab}(x < y) = R s^{ab}(x < y) + R n^{ab}(x, y) + R n^{ba}(y, x)$$

By inspection it can be seen that many terms directly reduce to include 2-body tensors only. The position of the dots indicate the quantity this represents. All of these quantities can be represented as sparse matrices, and terms can be directly evaluated using a sparse Einsum. There are some additional terms in which 3 or more indices on V occur. Such indices have to be concatenated. Let us use capital letters to indicate concatenation. The basic V integrals can be expressed as

$$V_{rs}^{pq} \rightarrow V_R^P; P \rightarrow (pq), R \rightarrow (rs)$$

$$V_{cd}^{ab} \rightarrow V_C^A; A \rightarrow (ab), C \rightarrow (cd)$$

$$V_{rs}^{a\cdot} \rightarrow V_R^{A\cdot}; A \rightarrow (a, i), R \rightarrow rs$$

Likewise the t operator needs to be simplified at times

$$t^{cd}(x, y) \rightarrow t^C(x, y)$$

Finally, we may have to predefine some sparse matrix quantities, e.g.

$$A_p^a(x)A_q^b(y) \rightarrow AA_Q^B, B \rightarrow (ab), Q \rightarrow (pq)$$

Using these definitions we can define quantities on the fly as needed and express in sparse matrix format. Then the equations can be recast as

Energy equation

$$E = \sum_x h_p(x)B^p(x) + \sum_{x < y} (v_{ab}(x, y)t^{ab}(x, y) + v_{pq}(x, y)B^p(x)B^q(y))$$

Singles equation.

$$R^a(x) = A_p^a(x)h_q^p(x)B^q(x) + \sum_{z \neq x} A_p^a V_C^p(x, z)t^C(x, z) + \sum_{z \neq x} A_p^a(x)V_Q^p(x, z)BB^{Q=qs}(x, z) \quad (12)$$

Doubles equation A: symmetric contributions (under $ai \rightarrow jb$ permutation)

$$\begin{aligned} Rs^{ab}(x < y) &= AA_{Q=pq}^{B=ab}(x, y)V_R^Q(x, y)BB^{R=rs}(x, y) \\ &+ AA_{Q=pq}^{B=ab}(x, y)V_C^Q(x, y)t^C(x, y) - t^{ab}(x, y)V_{p,q}(x, y)B^p(x)B^q(y) \\ &- t^{ab}(x, y)V_{cd}(x, y)t^{cd}(x, y) + \sum_{z, w \neq x, y} v_{cd}(z, w)t^{ac}(x, z)t^{bd}(y, w) \end{aligned}$$

Doubles equations B: non-symmetrix contributions. We need to add $ai \rightarrow jb$ permutation eventually. This is easiest to do on residual

$$\begin{aligned} Rn_{ij}^{ab}(x, y) &= A_p^a(x)h_c^p(x)t^{cb}(x, y) - t^{ab}(x, y)h_p(x)B^p(x) + \sum_{z \neq x, y} t^{ac}(x, z)V_{cs}^r(z, y)A_r^b(y)B^s(y) \\ &+ \sum_{z \neq x, y} A_q^b(y)v_{ds}^q(y, z)t^{ad}(x, y)B^s(z) - \sum_{z \neq x, y} t^{ab}(z, x)v_{rp}(z, x)B^p(x)B^r(z) \end{aligned} \quad (13)$$

Total doubles residual

$$Rt^{ab}(x < y) = Rs^{ab}(x < y) + Rn^{ab}(x, y) + Rn^{ba}(y, x)$$

Most terms have been cast in a suitable format. Two terms need further scrutiny:

$$\begin{aligned} &\sum_{z \neq x, y} t^{ac}(x, z)V_{cs}^r(z, y)A_r^b(y)B^s(y) \\ &+ \sum_{z \neq x, y} t^{ac}(x, z)V_{cs}^r(z, y)A_r^b(y)B^s(y) \end{aligned}$$

Suitable intermediates can be defined, and the contribution can then be cast in terms of sparse matrices.

5 Iterative procedure to solve for t -amplitudes.

Let us assume we can define a diagonal one-site hamiltonian that provides a zeroth order approximation to the full hamiltonian. The details on how to obtain this hamiltonian can be discussed later. It may be best to do a preliminary mean field calculation and use this as a zeroth-order approximation. Let us assume the diagonal elements are given by ϵ_a, ϵ_b respectively. Then we can define diagonal elements associated with the t -amplitudes. The iterative procedure can also be adjusted.

$$\begin{aligned}\Delta_a(x) &= \epsilon_a(x) - \epsilon(x) \\ \Delta_{ab}(x, y) &= \epsilon_a(x) + \epsilon_b(y) - \epsilon(x) - \epsilon(y)\end{aligned}\tag{14}$$

Then we can approximate the new residual if amplitudes t_λ would be replaced by $t_\lambda + \Delta t_\lambda$

$$R_\lambda(\mathbf{t} + \Delta \mathbf{t}) \approx \Delta_\lambda \Delta t_\lambda + R_\lambda(\mathbf{t})$$

and we can find the correction Δt_λ from a simple "denominator update"

$$\Delta t_\lambda = -(\Delta_\lambda)^{-1} R_\lambda(\mathbf{t})$$

This iterative procedure can be accelerated by standard DIIS procedure used routinely when solving CC equations.

6 Periodic Boundary conditions and translational symmetry (in 1d)

It is not my intention to immediately implement periodic boundary conditions and to exploit translational symmetry. The concepts will be useful to simplify aspects of finite cluster calculations. Let us assume we have an odd number of site indices that are labelled $x = -L \cdots L$, and which include the central site 0. In the Hamiltonian we assume translational symmetry and the only matrix elements to be provided are

$$h_q^p(x=0), V_{rs}^{pq}(0, y)$$

that are centred on the central site. We can refer to this as invariant Hamiltonian matrix elements. We assume moreover that these matrices are hermitean, and they are symmetric under an interchange of sites: $V_{rs}^{pq}(y, x) = V_{rs}^{pq}(x, y)$. Other matrix elements are then determined by translational symmetry

$$h_q^p(x) = h_q^p(0) V_{rs}^{pq}(x, [x + y/L]) = V_{rs}^{pq}(0, y)\tag{15}$$

This includes the periodic boundary conditions, so the sites $L, -L$ are nearest neighbours. The function $[x/L]$ keeps track of the proper indexing (needs discussion). The key observation is that the t_1 and t_2 amplitudes have exactly the same symmetry, and the ground state is a $k = 0$ state, which is totally symmetric (in a Bloch sense). This has the important consequence that one only has to solve the equations that determine

$$t_i^a(0) = t_{ij}^{ab}(0, y) \quad (16)$$

The equations require amplitudes with different side labels, but they can all be constructed from the t -amplitudes containing the central cell 0. This discussion is too brief to do full justice to calculations for periodic systems. It does help to discuss a next topic.

7 Optimization of orbitals, preserving invariance of Hamiltonian matrix elements

The solution to the CCC equations do depend on the definition of the low-lying state i for each site. Moreover, the choice of virtual states a and corresponding site-energies ϵ_a can affect convergence of the solution of the non-linear equations through the definition of the denominators. I think it is important to preserve the invariance of the Hamiltonian matrix elements as this reduces storage aspects, and simplicity of the code. For this reason the approaches I want to consider define a scheme to define states at the central site 0. We will design an equation for the occupied state. The virtual states are defined to be orthonormal and in particular orthogonal to the low-lying state. For the rest these states are in principle arbitrary (would not affect the final result). The only consideration is to improve convergence, and we can define a Fock-like operator to define semi-canonical states that diagonalize this one-body operator over the space of virtual states. I can think of two scenarios.

7.1 Mean Field Solution for central site

7.2 Brueckner states for central site

8 Facilitating the solution for large g

The calculations for large g pose some problems. There are two states that are closely degenerate. One state has all the dipoles aligned to the right, the other state has all the dipoles aligned to the left. In practice, for finite g ,

the true eigenstates may/will be the symmetric and antisymmetric combination of the two. Such states can not be represented using the single reference CCC approach. We can modify the problem by adding a finite field on each side of the form $\lambda \cos(\phi)$. In the plane wave $e^{im\phi}$ basis this yields matrix elements $\frac{1}{2}\lambda(\delta_{m,m-1} + \delta_{m,m+1})$. We can add this field to the one-electron Hamiltonian for each side. If we choose $\lambda \approx -0.1$ this would create a bias, such that all dipoles point to the right (if $\lambda < 0$). Using this new hamiltonian we can attempt to solve HF mean field equations and also the CCC equations. It may also be possible to use the new hamiltonian only for the mean field calculation, and to restore the hamiltonian to $\lambda = 0$ form, but use the states as obtained from the mean field calculation. It is likely that a larger basis is needed for large g .

9 Reduced density matrix from ED approach

When constructing the full Hamiltonian in the basis of product states, we can extract eigenstates with coefficients $C^{pqrs\dots z}$. one can extract the one-body density matrix to a particular site y , by mapping these coefficients to the form $C(\lambda_<, r(y), \mu_>)$, where all the states before site y are represented by $\lambda_<$ indices, while the states from sites $i > y$ are collected as $\mu_>$. The reduced density matrix for site y is then defined as

$$D_{r2}^{r1} = \sum_{\lambda_<, \mu_>} C(\lambda_<, r1(y), \mu_>) C(\lambda_<, r2(y), \mu_>)$$

For periodic systems I think the one-body density matrices are the same for each site. This is worth checking. If we assume the density matrices are the same (or taking the density from the central site), we can diagonalize the density matrix to obtain natural occupation numbers (eigenvalues between 0 and 1), with eigenvalues summing to 1, and natural 'orbitals', the corresponding eigenvectors. If one of the eigenvalues dominates, the state can be approximated by the single configuration made up from occupying only this dominant state on each site. This will be true for small g . For large g , we face the degeneracy problem. I think there are two orbitals with large occupations. We can obtain the $\cos(\phi)$, $\cos^2(\phi)$ expectation values and they should correspond to state pointing to the left and right for large g . Now we can add in the $\cos(\phi)$ perturbation to lift the near degeneracy. The corresponding states should have only one large occupation number. We can transform the one- and two-body elements to the natural orbital basis, and rediagonalize the full Hamiltonian (including the field). Now the eigenvector for the ground state should be more sparse, and the calculated reduced density matrix would be diagonal, (with hopefully one large eigenvalue).

9.1 Extracting starting values for CCC from ED for a few (e.g. 3) sites

We can proceed as above and obtain natural orbitals, and also calculate the ground state after transforming to the natural orbital basis. The largest coefficient in the ground state would be $C_{000\dots 0}$. We can redefine the coefficients to intermediate normalization by dividing by this largest coefficient. Let us just use the same symbol $C^{pqr\dots z}$ for the state in this new intermediate normalization. It is then easy to extract cluster amplitudes, where we assume the central site 0 is just the first site.

$$t_i^a(0) = C_{a000\dots 0}$$

$$C_{ij}^{ab}(0, y) = C_{a000b(y)\dots 0}; \quad t_{ij}^{ab}(0, y) = C_{ij}^{ab}(0, y) - t_i^a(0)t_j^b(y) \quad (17)$$

For 3 sites we can extract only nearest neighbours. It is possible to do larger calculations in a somewhat economical fashion. First we do a 3 site calculation with a large number of orbitals. Then we calculate natural orbitals and truncate this set to just a few orbitals with large occupations. We can transform the one-and two site Hamiltonian to this reduced natural orbital basis. Then we can do a periodic ED calculation with 5 sites. This allows the extraction of t-amplitudes from nearest and next nearest neighbours. These could be the starting values for t-amplitudes in the small basis. Then the full CCC in the larger basis could be started with just a few non-zero t1 and t2-values as an initial guess. It would be expected that the t_1 amplitudes are small, because the corresponding orbitals are natural orbitals for a 3-site Hamiltonian.

It is of interest to calculate the above quantities for 3,5,7 ... site periodic hamiltonians, for a range of g -values. These calculations can be done for any value of g , including critical values. It is interesting to analyse these results. They are exact but may not generalize to large systems. We can compare CCC results for the smaller systems to compare accuracy.

The most interesting part is if we extract Cluster amplitudes for small systems (presumably 5). Then we can get starting values for the t-amplitudes for nearest neighbour and next-nearest neighbour. They can be used as initial guesses for the solution. We would work in the corresponding natural orbital basis, as an additional aid.

10 Time-dependent CCC approaches

We would like to use time-dependent Quantum mechanics to extract eigenvalues and other useful properties.

$$i \frac{d}{d\tau} |\Psi(\tau)\rangle = \hat{H} |\Psi(\tau)\rangle \quad (18)$$

The formal solution to the TDSE is easy if we know the full set of eigenstates

$$\hat{H} |\psi_\lambda\rangle = E_\lambda |\psi_\lambda\rangle$$

Given some initial state $|\Phi_0\rangle$ the time-dependent wavefunction can be written,

$$|\Psi(\tau)\rangle = \sum_{\lambda} e^{-iE_\lambda\tau} |\psi_\lambda\rangle \langle\psi_\lambda|\Phi_0\rangle \quad (19)$$

We project the time-dependent wave function against the initial state to obtain the so-called autocorrelation function $A(\tau)$,

$$A(\tau) = \langle\Phi_0|\Psi(\tau)\rangle = \sum_{\lambda} e^{-iE_\lambda\tau} |\langle\Phi_0|\psi_\lambda\rangle|^2 \quad (20)$$

By taking the Fourier transform of $A(\tau)$ we obtain a spectrum and we can obtain (approximate) eigenvalues E_λ from the peak positions in the spectra. We in principle see any eigenvalue λ with $\langle\phi_0|\psi(\tau)\rangle \neq 0$ is in the wavefunction $|\psi(\tau)\rangle$. The intensity of peaks can change by choosing different initial states, and in this way we can find some reasonable eigenvalues.

We then can extract some eigenstate for the eigenvalue E_μ through the following,

$$\int_{-\infty}^{\infty} d\tau e^{iE_\mu t} |\psi(t)\rangle = \int_{-\infty}^{\infty} d\tau \sum_{\lambda} e^{i(E_\mu - E_\lambda)t} |\psi_\lambda\rangle \langle\psi_\lambda|\phi_0\rangle \quad (21)$$

$$= \sum_{\lambda} \delta_{E_\mu, E_\lambda} |\psi_\lambda\rangle \langle\psi_\lambda|\phi_0\rangle \quad (22)$$

$$= |\psi_\mu\rangle \langle\psi_\mu|\phi_0\rangle \quad (23)$$

In practice we would integrate over a finite time interval and obtain an approximate eigenstate.

The ansatz for the time-dependent wave function in Configurational Coupled Cluster wave function is

$$|\Psi(\tau)\rangle = e^{T(\tau)} |0\rangle$$

If we substitute this ansatz in the Time-dependent Schrödinger equation we obtain

$$i \frac{d}{d\tau} e^{T(\tau)} |0\rangle = \hat{H} e^{T(\tau)} |0\rangle$$

We can multiply the equations on the right by $e^{-\hat{T}}$ (a non-singular operator) to obtain the equivalent equation

$$i e^{-\hat{T}} \frac{d\hat{T}}{d\tau} e^{\hat{T}} |0\rangle = e^{-\hat{T}} \hat{H} e^{\hat{T}} |0\rangle$$

and the equations equations for the cluster amplitudes can be simplified as

$$i \langle 0 | \hat{\Omega}_\lambda \frac{d\hat{T}}{d\tau} | 0 \rangle = \langle 0 | \hat{\Omega}_\lambda e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle$$

Here $\langle 0 | \hat{\Omega}_\lambda$ represents an excited (bra) state, orthogonal to $|0\rangle$. These non-linear equations can be solved for the t -amplitudes. It can be seen that the right hand side of the equations is exactly the same as the equations we use to solve for the ground state of the CCC equations, and which was referred to as the residual.

$$i \frac{dt_\lambda}{d\tau} = R_\lambda$$

Besides the singles and doubles operators, we will have a constant t_0 amplitude, that satisfies the differential equation that is the analogue of the energy in GS CCC equations.

$$i \langle 0 | \frac{dt_0}{d\tau} | 0 \rangle = i \frac{dt_0}{d\tau} = \langle 0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle$$

The time auto-correlation function is given by $A(\tau) = e^{t_0(\tau)}$. By taking the Fourier transform and analysing the peak positions one can extract the (approximate) energy eigenvalues E_λ . If know the energies we can also extract the corresponding eigenstates, and even better, we can extract the cluster amplitudes that describe a particular eigenstate. If we define

$$C_\mu = \int_{-\infty}^{\infty} \langle 0 | \hat{\Omega}_\mu | \Psi(t) \rangle e^{iE_\lambda \tau} d\tau = \int_{-\infty}^{\infty} e^{t_0(\tau)} \langle 0 | \hat{\Omega}_\mu e^{\hat{T}} | 0 \rangle e^{iE_\lambda \tau} d\tau$$

The coefficient C_0 equals $\langle 0 | \Psi_\lambda \rangle$.

We can obtain the wave function in intermediate normalization by dividing the coefficients by C_0 . From the C amplitudes we can extract the cluster amplitudes

$$t_i^a(x) = C_i^a(x)/C_0 t_{ij}^{ab}(x, y) = C_{ij}^{ab}(x, y)/C_0 - t_i^a(x) t_j^b(y) \quad (24)$$

We can use the t -amplitudes as a (very good?) initial guess of the cluster amplitudes that describe the state Ψ_λ , in intermediate normalization. We can simply solve the time-independent CCC equations $R_\mu = 0$, starting from the initial guess. The amazing aspect is that the residual equations R_λ is the same throughout. We just use them in different ways.