# The Potato and its dynamics

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# Abstract

This is an abstract text.

# Acknowledgements

I acknowledge my acknowledgements.

# Contents

# List of Figures

# List of Tables

# Chapter 1

# Introduction

Start your chapter by writing something smart. Then go get coffee.

# Part I

# Theory

# Chapter 2

# Formalism

Given a basis of $L$ single particle functions $|p\rangle$ where

$$\{|p\rangle\}_{p=1}^{L} = \{|i\rangle\}_{i=1}^{N} \cup \{|a\rangle\}_{a=N+1}^{L} . \tag{2.1}$$

Here $i, j, k, \ldots$ represents the $N$ first occupied states of the reference Slater determinant whereas $a, b, c, \ldots$ represent the remaining $M = L - N$ virtual states in the total basis $p, q, r, \ldots$ [1].

[1] Occupied and virtual states are also known as hole and particle states if we treat the reference Slater determinant as the *Fermi level*

# Chapter 3

# Hartree-Fock theory

Because its all about that energy, ’bout that energy, ’bout that energy!

# Chapter 4

# Configuration interaction

A popular post Hartree-Fock method is *configuration interaction*. It consists of expressing the wavefunction as a linear combination of excited Slater determinants in a truncated single-particle and Slater determinant basis.

$$|\Psi_{\mathrm{CI}}\rangle = A_0|\Phi_0\rangle + \sum_{ai} A_i^a|\Phi_i^a\rangle + \frac{1}{4}\sum_{abij} A_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \ldots, \tag{4.1}$$

where we have divided by a factor 4 in the double sum to avoid over counting as both the coefficients and the excited determinants are antisymmetric. By generating all the possible Slater determinants from the $L$ single-particle functions we employ the *full configuration interaction* method. This will give the most accurate value of the energy for the system, but quickly becomes computationally impossible as the FCI space grows in dimensions as $\binom{L}{N}$. [4]

## 4.1 Time-independent configuration interaction theory

We start with the time-independent Schrödinger equation

$$\hat{H}|\Psi_J\rangle = E_J|\Psi_J\rangle, \tag{4.2}$$

where $(E_J, |\Psi_J\rangle)$ is an eigenpair for $\hat{H}$. Expanding the CI wavefunction in a Slater determinant basis.

$$|\Psi_J\rangle = \sum_K A_{KJ}|\Phi_K\rangle, \tag{4.3}$$

where $A_{KJ}$ are the amplitudes for a certain excitation $K$ for a specific energy level $J$. Inserting Equation 4.3 into Equation 4.2 and left projecting on a state

$|\Phi_I\rangle$ we get

$$\sum_K \langle \Phi_I|\hat{H}|\Phi_K\rangle A_{KJ} = E_J \sum_K \langle \Phi_I|\Phi_K\rangle A_{KJ}. \tag{4.4}$$

We now define the Hamiltonian matrix $H_{IK} = \langle \Phi_I|\hat{H}|\Phi_K\rangle$ and the overlap matrix $S_{IK} = \langle \Phi_I|\Phi_K\rangle$. We can thus formulate the generalized eigenvalue equation

$$\sum_K H_{IK} A_{KJ} = E_J \sum_K S_{IK} A_{KJ} \tag{4.5}$$

$$\implies HA = ESA, \tag{4.6}$$

where $S_{IK} = 1 \iff \langle \Phi_I|\Phi_K\rangle = \delta_{IK}$. We will in this text only care about systems where the Slater determinants are orthonormal. Thus the eigenvalue equation we will solve will be

$$HA = EA, \tag{4.7}$$

which means our job is to construct $H_{IJ}$ and diagonalize the matrix[2]. The elements $H_{IJ}$ are computed by

$$\langle \Phi_I|\hat{H}|\Phi_J\rangle = \sum_{pq} \langle p|\hat{h}|q\rangle \langle \Phi_I|\hat{p}^\dagger \hat{q}|\Phi_J\rangle + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \langle \Phi_I|\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}|\Phi_J\rangle. \tag{4.8}$$

# Chapter 5

# Coupled cluster theory

In coupled cluster theory one seeks to approximate the "true" many-body wave-function using an *exponential ansatz*.

$$|\Psi_{\mathrm{CC}}\rangle \equiv e^{T}|\Phi\rangle = \sum_{n=0}^{\infty} \frac{1}{n!} T^{n} |\Phi\rangle, \tag{5.1}$$

where the *cluster operator* $T$ is given by a sum of excitation operators $T_p$.

$$T = \sum_{p=1}^{n} T_p = t_i^a \hat{a}^\dagger \hat{i} + \left(\frac{1}{2!}\right)^2 t_{ij}^{ab} \hat{a}^\dagger \hat{b}^\dagger \hat{i} \hat{j} + \left(\frac{1}{3!}\right)^2 t_{ijk}^{abc} \hat{a}^\dagger \hat{b}^\dagger \hat{c}^\dagger \hat{i} \hat{j} \hat{k} + \dots. \tag{5.2}$$

Here the *coupled cluster amplitudes* $t_{ij\dots}^{ab\dots}$ are the unknowns. As the method only uses a single reference Slater determinant in Equation 5.1 the approximation is called single-reference coupled cluster theory.

# Part II

# Appendices

# Appendix A

# Hartree-Fock

Hartree-Fock appendix.

# Appendix B

# Reformulating the amplitude equations as matrix products

We will in this appendix show how to formulate the tensor contractions occuring in the coupled cluster equations as matrix products. The reason we wish to do this is to be able to perform these contractions as dot products (or matrix products) as there exists highly optimized code performing these operations, e.g., BLAS[1].

To be able to treat tensors of rank $> 2$ as matrices we have to create *compound indices* by stacking the dimensions after one another. For instance, by looking at the tensor $g \in \mathbb{C}^{I\times J\times K\times L}$, where we denote a single element by $g_{ijkl}$. Here $g$ is a tensor of rank 4. By creating compound indices $\tilde{I} = IJ$ and $\tilde{K} = KL$ we can create a new tensor $\tilde{g} = \mathbb{C}^{\tilde{I}\times\tilde{K}}$ of rank 2 (represented as a matrix). Using the indices $\tilde{i} = iJ + j$ and $\tilde{k} = kL + l$ we now construct $\tilde{g}$ in such a way that $\tilde{g}_{\tilde{i}\tilde{k}} = g_{ijkl}$.

It is also possible to create compound indices of more than two indices. For instance, choosing $\tilde{J} = JKL$ and setting $\tilde{j} = jKL + kL + l$ we can construct $\bar{g} = \mathbb{C}^{I\times\tilde{J}}$ where $\bar{g}_{i\tilde{j}} = g_{ijkl}$.

For the sake of brevity and clarity we will in the following avoid renaming the compound indices and their sizes, but we will instead indicate with a comma where we construct new indices.

## B.1 Reformulating the CCD equations

## B.2 Reformulating the CCSD equations

We use the expressions for the CCSD equations derived by Gauss et al.[1]. We start with the *effective double excitation amplitudes* found at the bottom of table

[1]BLAS can be found here: http://www.netlib.org/blas/

3 in their article. Note that we rename $\tilde{\tau} \to \xi$ thus reserving the twiddle for intermediate calculations.

$$\tau_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2}P(ij)P(ab)t_i^a t_j^b \tag{B.1}$$

$$\implies \tau_{ab,ij} = t_{ab,ij} + \frac{1}{2}P(ij)P(ab)\left(t_{a,i}t_{b,j}\right)_{ab,ij}, \tag{B.2}$$

$$\xi_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{4}P(ij)P(ab)t_i^a t_j^b \tag{B.3}$$

$$\implies \xi_{ab,ij} = t_{ab,ij} + \frac{1}{4}P(ij)P(ab)\left(t_{a,i}t_{b,j}\right)_{ab,ij}. \tag{B.4}$$

Next we look at the one-body intermediates found at the top of table 3 in the article by Gauss et al.[1]. We use the notation

$$u_{ef}^{am} \equiv \langle am||ef\rangle, \tag{B.5}$$

that is, we treat the matrix elements $u$ as the antisymmetric matrix elements of the two-body operator.

$$F_e^a = f_e^a - \frac{1}{2}f_e^m t_m^a + t_m^f u_{ef}^{am} - \frac{1}{2}\xi_{mn}^{af}u_{ef}^{mn} \tag{B.6}$$

$$\implies F_{a,e} = f_{a,e} - \frac{1}{2}t_{a,m}f_{m,e} + \left(t_{fm}\tilde{u}_{fm,ae}\right)_{a,e} - \frac{1}{2}\xi_{a,fmn}\tilde{u}_{fmn,e}, \tag{B.7}$$

$$F_i^m = f_i^m + \frac{1}{2}f_e^m t_i^e + t_n^e u_{ie}^{mn} + \frac{1}{2}\xi_{in}^{ef}u_{ef}^{mn} \tag{B.8}$$

$$\implies F_{m,i} = f_{m,i} + \frac{1}{2}f_{m,e}t_{e,i} + \left(t_{en}\tilde{u}_{en,mi}\right)_{m,i} + \frac{1}{2}\tilde{u}_{m,nef}\tilde{\xi}_{nef,i}, \tag{B.9}$$

$$F_e^m = f_e^m + t_n^f u_{ef}^{mn} \tag{B.10}$$

$$\implies F_{m,e} = f_{m,e} + \left(t_{fn}\tilde{u}_{fn,me}\right)_{m,e}. \tag{B.11}$$

We now move on to the two-body intermediates found just below the one-body intermediates in table 3 in the article by Gauss et al.[1]. To avoid storing two matrices with $M^4$ elements we will not create the intermediate $W_{ef}^{ab}$ but rather compute the products in place in the amplitude equations by splitting up the products and do them one-by-one (this will shown in due time). We will therefore still preserve the asymptotical scaling $\mathcal{O}(M^4N^2)$ but add a constant term at the price of saving memory.

# Appendix C

# Computing the one-body density matrices

From Kvaal[3] we have an expression for the one-body density matrices $\rho^q_p$[1] as a function of the coupled cluster amplitudes $t$ and $\lambda$.

$$\rho^q_p = \langle\tilde{\Psi}|\hat{p}^\dagger\hat{q}|\Psi\rangle = \langle\tilde{\Phi}|(1+\Lambda)e^{-T}\hat{p}^\dagger\hat{q}e^{T}|\Phi\rangle. \tag{C.1}$$

We wish to find an expression for $\rho^q_p$ in terms of the amplitudes $t$ and $\lambda$ which we can contract. We start by splitting up the expression to

$$\rho^q_p = \langle\tilde{\Phi}|e^{-T}\hat{p}^\dagger\hat{q}e^{T}|\Phi\rangle + \langle\tilde{\Phi}|\Lambda e^{-T}\hat{p}^\dagger\hat{q}e^{T}|\Phi\rangle. \tag{C.2}$$

Next we expand the exponentials and use the Baker-Campbell-Hausdorff formula. This lets us write

$$e^{-T}\hat{p}^\dagger\hat{q}e^{T} = \hat{p}^\dagger\hat{q} + \left[\hat{p}^\dagger\hat{q}, T\right] + \frac{1}{2!}\left[\left[\hat{p}^\dagger\hat{q}, T\right], T\right] + \dots. \tag{C.3}$$

To determine how many terms to include we have to look at the number of excitations that will be performed by the excitation operators $T$ and relaxation operators $\Lambda$. We know that $T$ will *at least* excite the reference by 1. The combined operator $\hat{p}^\dagger\hat{q}$ is able to excite and relax the reference with at most 1 or leave it unchanged. The relaxation operator $\Lambda$ will *at least* relax the reference by 1. As $\langle\tilde{\Phi}_X|\Phi_Y\rangle = \delta_{XY}$, where $X$ and $Y$ are arbitrary excitations, the only non-zero contributions to $\rho^q_p$ will be the operator combinations that leave the reference unchanged after applying the total operator chain. For the term without $\Lambda$ in $\rho^q_p$ this leaves us with

$$\langle\tilde{\Phi}|e^{-T}\hat{p}^\dagger\hat{q}e^{T}|\Phi\rangle = \langle\tilde{\Phi}|\hat{p}^\dagger\hat{q}|\Phi\rangle + \langle\tilde{\Phi}|\left[\hat{p}^\dagger\hat{q}, T\right]|\Phi\rangle, \tag{C.4}$$

[1]Note the ordering of the indices. We use the same convention as Kvaal in his article.

where the last term of the commutator will not contribute as leaving a $T$ on the left hand side of $\hat{p}^\dagger \hat{q}$ will leave the reference excited.

$$\langle \tilde{\Phi} | \Lambda e^{-T} \hat{p}^\dagger \hat{q} e^T | \Phi \rangle = \langle \tilde{\Phi} | \Lambda \hat{p}^\dagger \hat{q} | \Phi \rangle + \langle \tilde{\Phi} | \Lambda \left[ \hat{p}^\dagger \hat{q}, T \right] | \Phi \rangle + \frac{1}{2!} \langle \tilde{\Phi} | \Lambda \left[ \left[ \hat{p}^\dagger \hat{q}, T \right], T \right] | \Phi \rangle + \dots . \tag{C.5}$$

Depending on the truncation level of the coupled cluster equations, e.g., singles, doubles etc, this will provide a natural truncation for Equation C.5.

## C.1 One-body density matrices for CCSD

Truncating at CCSD Equation C.5 will truncate at the double commutator as written. Employing SymPy[5] we can compute an expression for the one-body density matrices.

$$\rho^q_p = \langle \tilde{\Phi} | \hat{p}^\dagger \hat{q} | \Phi \rangle + \langle \tilde{\Phi} | \left[ \hat{p}^\dagger \hat{q}, T \right] | \Phi \rangle + \langle \tilde{\Phi} | \Lambda \hat{p}^\dagger \hat{q} | \Phi \rangle + \langle \tilde{\Phi} | \Lambda \left[ \hat{p}^\dagger \hat{q}, T \right] | \Phi \rangle + \frac{1}{2!} \langle \tilde{\Phi} | \Lambda \left[ \left[ \hat{p}^\dagger \hat{q}, T \right], T \right] | \Phi \rangle \tag{C.6}$$

$$= \delta^a_p \delta^q_b \left( l^i_a t^b_i + \frac{1}{2} l^{ij}_{ac} t^{bc}_{ij} \right) + \delta^a_p \delta^q_i l^i_a + \delta^q_j \delta^i_p \left( \delta^j_i - l^j_a t^a_i + \frac{1}{2} l^{jk}_{ab} t^{ab}_{ki} \right) + \delta^q_a \delta^i_p \left( t^a_i + l^j_b \left[ t^{ab}_{ij} - t^b_i t^a_j \right] + \frac{1}{2} t^b_i l^{kj}_{cb} t^{ac}_{kj} - \frac{1}{2} t^a_j l^{kj}_{cb} t^{cb}_{ki} \right) . \tag{C.7}$$

In this expression we have only kept the fully contracted terms. SymPy sets the indices arbitrarily so the expression shown in Equation C.7 has been factorized and had a relabeling of the indices for improved readability.

# Appendix D

# Time evolution of the coupled cluster wavefunction

We compute the time evolution of any wavefunction from an initial state at time $t_0$ to a later time $t$ by

$$P(t_0 \to t) \equiv |\langle \psi(t)|\psi(t_0)\rangle|^2. \tag{D.1}$$

That is, we compute the squared overlap between the initial state $|\psi(t_0)\rangle$ and the final state $|\psi(t)\rangle$. In the case of coupled cluster and the use of the bivariational principle some care must be taken as to how the squared overlap should be computed. We get

$$P(t_0 \to t) \equiv |\langle \tilde{\Psi}(t)|\Psi(t_0)\rangle|^2 = \langle \tilde{\Psi}(t)|\Psi(t_0)\rangle\langle \tilde{\Psi}(t_0)|\Psi(t)\rangle. \tag{D.2}$$

Choosing $t_0 = 0$ as the ground state we can compute the overlap of the ground state to all later states $t$. For time-independent spin-orbitals we only evolve the amplitudes in time. We thus have to find an expression for the two inner-products below.

$$\langle \tilde{\Psi}(t)|\Psi(0)\rangle = \langle \tilde{\Phi}|\,[1 + \Lambda(t)]\, e^{-T(t)} e^{T} |\Phi\rangle, \tag{D.3}$$
$$\langle \tilde{\Psi}(0)|\Psi(t)\rangle = \langle \tilde{\Phi}|\,[1 + \Lambda]\, e^{-T} e^{T(t)} |\Phi\rangle. \tag{D.4}$$

Note that $T(t) \neq T$ and $\Lambda(t) \neq \Lambda$. We split up the equations on $\Lambda$ and expand the exponentials. As $T$ provides a net excitation of at least 1 and $\Lambda$ a net relaxation of at least 1[1], only terms with a combination of $\Lambda$ and $T$ will survive. This yields

$$\begin{aligned}\langle \tilde{\Psi}(t)|\Psi(0)\rangle &= \langle \tilde{\Phi}|e^{-T(t)} e^{T}|\Phi\rangle + \langle \tilde{\Phi}|\Lambda(t) e^{-T(t)} e^{T}|\Phi\rangle &\text{(D.5)}\\ &= 1 + \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \frac{1}{n!m!}\langle \tilde{\Phi}|\Lambda(t)[-T(t)]^n T^m|\Phi\rangle. &\text{(D.6)}\end{aligned}$$

[1]Note that this applies to the time-dependent versions of these operators as well as it is only the amplitudes that are time-dependent and not the creation nor the annihilation operators.

The conjugate of this equation is then

$$\langle\tilde{\Psi}(0)|\Psi(t)\rangle = 1 + \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\frac{1}{n!m!}\langle\tilde{\Phi}|\Lambda\left[-T^n\right]T(t)^m|\Phi\rangle. \tag{D.7}$$

# D.1 Time evolution of the CCSD wavefunction

Restricting ourselves to the singles and doubles approximation we will get that the $T$ operator can yield a net excitation of 1 and 2, whereas $\Lambda$ yields a net relaxation of 1 and 2. This truncates the infinite sums to $n, m \in \{0, 1, 2\}$. We get

$$\langle\tilde{\Psi}(t)|\Psi(0)\rangle = 1 + \langle\tilde{\Phi}|\Lambda(t)\left[1 - T(t) + T - T(t)T + \frac{1}{2}T(t)^2 + \frac{1}{2}T^2\right]|\Phi\rangle, \tag{D.8}$$

$$\langle\tilde{\Psi}(0)|\Psi(t)\rangle = 1 + \langle\tilde{\Phi}|\Lambda\left[1 - T + T(t) - TT(t) + \frac{1}{2}T^2 + \frac{1}{2}T(t)^2\right]|\Phi\rangle. \tag{D.9}$$

We again utilize SymPy[5] to get explicit tensor contractions. This yields

$$\begin{aligned}\langle\tilde{\Psi}(t)|\Psi(0)\rangle = 1 &+ l(t)^i_a\left[t^a_i - t(t)^a_i\right] \\ &+ l(t)^{ij}_{ab}\left[\frac{1}{4}t^{ab}_{ij} - \frac{1}{2}t^a_j t^b_i - t(t)^a_i t^b_j - \frac{1}{2}t(t)^a_j t(t)^b_i - \frac{1}{4}t(t)^{ab}_{ij}\right],\end{aligned} \tag{D.10}$$

$$\begin{aligned}\langle\tilde{\Psi}(0)|\Psi(t)\rangle = 1 &+ l^i_a\left[t(t)^a_i - t^a_i\right] \\ &+ l^{ij}_{ab}\left[\frac{1}{4}t(t)^{ab}_{ij} - \frac{1}{2}t^a_j t^b_i - t(t)^a_i t^b_j - \frac{1}{2}t(t)^a_j t(t)^b_i - \frac{1}{4}t^{ab}_{ij}\right].\end{aligned} \tag{D.11}$$

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