The Potato and its dynamics

by

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Abstract

This is an abstract text.

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Chapter 1

Introduction

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

Part I

Theory

Chapter 2

Quantum Mechanics

YOLO

P. A. M. Dirac

2.1 Density matrices

When working with many-body quantum mechanics, computing expectation values can at times prove easier when done using density matrices. A general density matrix of a *pure state* is on the form

$$\hat{\rho} = |\psi\rangle\langle\psi|, \tag{2.1}$$

that is, a pure state is a quantum state $|\psi\rangle$ containing the maximum amount of information about a given system. For a *mixed state*, i.e., a linear combination of pure states $|\psi_k\rangle$ with a classical probability p_k associated with the state, we get a density matrix on the form

$$\hat{\rho} = \sum_k p_k |\psi_k\rangle\langle\psi_k|. \tag{2.2}$$

Any density operator must satisfy the following properties [8]:

1. Hermiticity, that is

$$p_k = p_k^* \implies \hat{\rho} = \hat{\rho}^\dagger. \tag{2.3}$$

   This translates to the probabilities being real, $p_k \in \mathbb{R}$.

2. Positivity,

$$p_k \geqslant 0 \implies \langle\chi|\hat{\rho}|\chi\rangle \geqslant 0. \tag{2.4}$$

   In other words, density matrices are *positive semidefinite*.

3. Normalization of the probabilities,

$$\sum_k p_k = 1 \implies \mathrm{Tr}(\hat{\rho}), \tag{2.5}$$

   that is, the probabilities must sum up to one.

Furthermore, by squaring the density matrix and taking the trace we can infer if the system we are perusing is in a mixed state or a pure state [8].

$$\mathrm{Tr}(\hat{\rho}^2) = \sum_k p_k^2 \leqslant 1, \tag{2.6}$$

with equality if, and only if, the system is in a pure state, viz.

$$\hat{\rho} = |\psi\rangle\langle\psi| \implies \hat{\rho}^2 = \hat{\rho} \implies \mathrm{Tr}(\hat{\rho}^2) = 1. \tag{2.7}$$

Using density matrices, we can compute the expectation value of any operator $\hat{O}$, by [8]

$$\left\langle \hat{O} \right\rangle = \mathrm{Tr}(\hat{O}\hat{\rho}). \tag{2.8}$$

2.1.1 Many-body density matrices

In a seminal paper by Löwdin [9], the concept of a many-body density matrix in terms of the orbitals of a Slater determinant is discussed. These are dubbed N-body density matrices, where N depends on the N-body interaction, that is, the number of particles included in the interaction. Of the most useful for our work, we have the one- and two-body density matrices. As we will work almost exclusively in second quantization, we will follow the derivation of the one- and two-body density matrices done by Helgaker, Jørgensen, and Olsen. Löwdin's paper [9] did not employ second quantization, and all matrices are expressed in the coordinate representation. We will list these as they arrive.

Chapter 3

Formalism

In this chapter we'll describe some of the formalism used when describing many-body quantum mechanics.

3.1 Basis sets

In this document we will rely heavily on basis transformations and creating linear combinations from a basis to another. When creating many-body wavefunctions we will use a finite basis of *orbitals* $\left\{|\chi_\alpha\rangle\right\}_{\alpha=1}^{L}$ as our *atomic orbitals*. These represent known basis states, e.g., the harmonic oscillator eigenstates, etc. We can construct many-body wavefunctions from a linear combination of tensor products of single-particle states,

$$|\Psi\rangle = \sum_{\sigma\in S} c_\sigma |\chi_{\sigma(1)}\rangle \otimes \cdots \otimes |\chi_{\sigma(L)}\rangle, \tag{3.1}$$

where we have assumed normalized single-particle functions $\langle\chi_\alpha|\chi_\alpha\rangle = 1$, but not necessarily orthonormal.

3.1.1 Fermi level

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

$$\left\{|p\rangle\right\}_{p=1}^{L} = \left\{|i\rangle\right\}_{i=1}^{N} \cup \left\{|a\rangle\right\}_{a=N+1}^{L}. \tag{3.2}$$

Here $i, j, k, \dots$ represents the N first occupied states of the reference Slater determinant whereas $a, b, c, \dots$ represent the remaining $M = L - N$ virtual states in the total basis $p, q, r, \dots$[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 4

Hartree-Fock theory

One can not tackle the subject of many-body theory without a discussion of the Hartree-Fock method. It serves as an excellent initial approximation, and in many cases the *only* approximation, to the many-body wavefunction for a given system. It is a rather cheap method, in terms of computational intensity, and explains much of the underlying physics of a given system of many particles.

4.1 Assumptions used in the Hartree-Fock method

In the Hartree-Fock method we make five assumptions in order to make the many-body problem tractable.

1. We assume that the *Born-Oppenheimer approximation* is a good approximation.
2. We assume that the motion of the electrons can be described non-relativistically.
3. We assume that the solution to the variational problem can be represented as a linear combination of a finite number of basis functions.
4. The energy eigenfunctions of the time-independent Schrödinger equation can be described by a single Slater determinant.
5. We assume that correlation between particles can be described in the *mean-field approximation*.

These assumptions provides the basis for the Hartree-Fock method. We shall see later that we quickly reach a limit where these assumptions break apart thus motivating the use of *post Hartree-Fock methods* such as the coupled cluster method.

4.2 Deriving the time-independent Hartree-Fock equations

Much of the theory shown in this section draws from the excellent lecture notes by Kvaal and Szabo and Ostlund. We start by making the ansatz that the full many-body wavefunction is a single Slater determinant. For a given system Hamiltonian

$$\hat{H} = \hat{h} + \hat{u}, \tag{4.1}$$

where $\hat{h}$ is the one-body part of the Hamiltonian and $\hat{u}$ the higher order correlations. In our case we will limit ourselves to Coulomb two-body interactions. We know that the ground state of $\hat{h}$ will be a single Slater determinant. If the two-body interactions are "small" we can assume that there will exist a Slater determinant which will capture most of the true ground state of the full Hamiltonian[1].

Our many-body wavefunction will now be represented as a single Slater determinant

$$|\Phi\rangle = |\phi_1, \phi_2, \dots, \phi_N\rangle, \tag{4.2}$$

where the *molecular orbitals* $\{\phi_i\}_{i=1}^{N}$ are the primary unknowns subject to the constraint that they are orthonormal. That is,

$$\langle\phi_i|\phi_j\rangle = \delta_{ij} \implies \langle\Phi|\Phi\rangle = 1. \tag{4.3}$$

Defining the energy functional

$$\mathcal{E}[\Phi] = \langle\Phi|\hat{H}|\Phi\rangle, \tag{4.4}$$

the variational principle tells us that the true ground state energy, E_0, will be a lower bound to the energy found from Equation 4.4 for any normalized trial wavefunction $|\Phi\rangle$. That is,

$$E_0 \leqslant \mathcal{E}[\Phi] = \langle\Phi|\hat{H}|\Phi\rangle. \tag{4.5}$$

Our task is now to find the molecular orbitals $\{\phi_i\}_{i=1}^{N}$ that minimizes $\mathcal{E}[\Phi]$[2]. By performing a variation in the Slater determinant,

$$\Phi \to \Phi + \delta\Phi, \tag{4.6}$$

we find the that the energy functional is changed by

$$\begin{aligned}\mathcal{E}[\Phi + \delta\Phi] &= \langle\Phi + \delta\Phi|\hat{H}|\Phi + \delta\Phi\rangle && (4.7)\\ &= \mathcal{E}[\Phi] + \langle\delta\Phi|\hat{H}|\Phi\rangle + \langle\Phi|\hat{H}|\delta\Phi\rangle + \dots && (4.8)\\ &= \mathcal{E}[\Phi] + \delta\mathcal{E}[\Phi] + \dots, && (4.9)\end{aligned}$$

where the *first variation* in $\mathcal{E}[\Phi]$ is given by

$$\delta\mathcal{E}[\Phi] \equiv \langle\delta\Phi|\hat{H}|\Phi\rangle + \langle\Phi|\hat{H}|\delta\Phi\rangle. \tag{4.10}$$

Note that we treat δ as a linear differential operator. Higher order variations are ignored and we are thus only interested in finding the Slater $|\Phi\rangle$ for which

$$\delta\mathcal{E}[\Phi] = 0, \tag{4.11}$$

i.e., the stationary point of the energy functional in terms of Φ. Note however that $\mathcal{E}[\Phi]$ does not incorporate the constraint that the molecular orbitals should be orthonormal. To ensure this we use the method of Lagrange multipliers, with one multiplier for every constraint. We thus construct the Lagrangian functional

$$\begin{aligned}\mathcal{L}[\Phi, \lambda] &= \mathcal{E}[\Phi] - \lambda_{ji}\left(\langle\phi_i|\phi_j\rangle - \delta_{ij}\right) && (4.12)\\ &= \langle\phi_i|\hat{h}|\phi_i\rangle + \frac{1}{2}\langle\phi_i\phi_j|\hat{u}|\phi_i\phi_j\rangle_{AS} - \lambda_{ji}\left(\langle\phi_i|\phi_j\rangle - \delta_{ij}\right), && (4.13)\end{aligned}$$

where the Einstein summation convention is implied. As the Lagrangian functional, $\mathcal{L}[\Phi, \lambda]$, is real, and as the constraint is Hermitian, the Lagrange multipliers, λ_{ji}, can be taken to be Hermitian as well.

---

[1] We will see that it does not take much before the two-body interaction becomes a little more than just a small perturbation.

[2] This is done by finding a stationary state for $\mathcal{E}[\Phi]$, which does not guarantee that we have found a minimum, but often the stationary state will be a minimum.

Proof that the Lagrange multipliers can be chosen Hermitian. Following the derivation done by Mayer [10], we start by noticing that the constraint is Hermitian, i.e.,

$$\langle \phi_i | \phi_j \rangle - \delta_{ij} = \langle \phi_j | \phi_i \rangle^* - \delta_{ji}. \tag{4.14}$$

As of now we have two independent Lagrange multipliers for overlap $\langle \phi_i | \phi_j \rangle$ and the complex conjugate $\langle \phi_j | \phi_i \rangle$. We can formulate the constraint for the real and imaginary part separately. This yields

$$\mathfrak{R}\left\{\langle \phi_i | \phi_j \rangle\right\} = \frac{1}{2}\left\{\langle \phi_i | \phi_j \rangle + \langle \phi_j | \phi_i \rangle\right\} = 0, \tag{4.15}$$

$$\mathfrak{I}\left\{\langle \phi_i | \phi_j \rangle\right\} = \frac{1}{2i}\left\{\langle \phi_i | \phi_j \rangle - \langle \phi_j | \phi_i \rangle\right\} = 0. \tag{4.16}$$

Introducing two separate Lagrange multipliers μ_{ij} and ν_{ij} for the two latter conditions, we get

$$\mu_{ij}\mathfrak{R}\left\{\langle \phi_i | \phi_j \rangle\right\} + \nu_{ij}\mathfrak{I}\left\{\langle \phi_i | \phi_j \rangle\right\} = \frac{1}{2}\left[\mu_{ij} - i\nu_{ij}\right]\langle \phi_i | \phi_j \rangle + \frac{1}{2}\left[\mu_{ij} + i\nu_{ij}\right]\langle \phi_j | \phi_i \rangle. \tag{4.17}$$

We now choose our combined Lagrange multipliers to be

$$\lambda_{ji} = -\frac{1}{2}\left[\mu_{ij} - i\nu_{ij}\right], \tag{4.18}$$

$$\lambda_{ij} = -\frac{1}{2}\left[\mu_{ij} + i\nu_{ij}\right], \tag{4.19}$$

which implies that $\lambda_{ji} = \lambda_{ij}^*$, as was to be shown. □

Chapter 5

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.

$$|\Psi_{CI}\rangle = A_0|\Phi\rangle + \sum_{ai} A_i^a|\Phi_i^a\rangle + \frac{1}{4}\sum_{abij} A_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \dots, \tag{5.1}$$

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 $\binom{L}{N}$. [7]

5.1 Time-independent configuration interaction theory

We start with the time-independent Schrödinger equation

$$\hat{H}|\Psi_J\rangle = E_J|\Psi_J\rangle, \tag{5.2}$$

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

$$|\Psi_J\rangle = \sum_K A_{KJ}|\Phi_K\rangle, \tag{5.3}$$

where A_{KJ} are the amplitudes for a certain excitation K for a specific energy level J. Inserting Equation 5.3 into Equation 5.2 and left projecting on a state $|\Phi_I\rangle$ we get

$$\sum_K \langle\Phi_I|\hat{H}|\Phi_K\rangle A_{KJ} = E_J \sum_K \langle\Phi_I|\Phi_K\rangle A_{KJ}. \tag{5.4}$$

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

$$\sum_K H_{IK}A_{KJ} = E_J \sum_K S_{IK}A_{KJ} \tag{5.5}$$

$$\implies HA = ESA, \tag{5.6}$$

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

$$HA = EA, \tag{5.7}$$

which means our job is to construct H_{IJ} and diagonalize the matrix[5]. The elements H_{IJ} are computed by

$$\langle\Phi_I|\hat{H}|\Phi_J\rangle = \sum_{pq}\langle p|\hat{h}|q\rangle\langle\Phi_I|\hat{p}^\dagger\hat{q}|\Phi_J\rangle + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\langle\Phi_I|\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}|\Phi_J\rangle. \tag{5.8}$$

Chapter 6

Coupled cluster theory

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

$$|\Psi_{\mathrm{CC}}\rangle \equiv e^{\hat{T}}|\Phi\rangle = \sum_{n=0}^{\infty} \frac{1}{n!}\hat{T}^{n}|\Phi\rangle, \tag{6.1}$$

where the *cluster operator* $\hat{T}$ is given by a sum of excitation operators $\hat{T}_p$.

$$\hat{T} = \sum_{p=1}^{n} \hat{T}_p = \tau_i^a \hat{a}^\dagger \hat{i} + \left(\frac{1}{2!}\right)^2 \tau_{ij}^{ab} \hat{a}^\dagger \hat{b}^\dagger \hat{i}\hat{j} + \left(\frac{1}{3!}\right)^2 \tau_{ijk}^{abc} \hat{a}^\dagger \hat{b}^\dagger \hat{c}^\dagger \hat{i}\hat{j}\hat{k} + \ldots. \tag{6.2}$$

Here the *coupled cluster amplitudes* $\tau_{ij\ldots}^{ab\cdots}$ are the unknowns. As the method only uses a single reference Slater determinant in Equation 6.1 the approximation is called single-reference coupled cluster theory.

Chapter 7

Quantum systems

In this chapter we'll discuss different quantum systems which will be explored. We'll be discussing the one-body part of the systems and explore how we can construct basis sets from the different systms. Furthermore, we'll be discussing how we can construct expectation values of different operators such as the dipole moment and the two-body Coulomb interaction.

Much of the limitation of good basis sets to be used in our methods comes from the calculation of the two-body matrix elements.

7.1 Quantum dots

Artificial atoms, or the so-called quantum dots, constitute a hot topic in condensed matter physics and material sciences. We will be exploring several types of quantum dots in both one and two dimensions in this thesis. The difference between the types of quantum dots is found in the one-body potential. All of the dots share the characteristic of being in an infinite well which makes the systems *bound*. In our study of systems subject to intense laser fields, this will prove to be a bad approximation as the particles have no way of being excited, i.e., escape the potential well. Even so, for weak laser fields and for ground state calculations, they serve as excellent candidates for our methods.

7.1.1 One-dimensional harmonic oscillator

One of the simplest theoretical models studied. The one-dimensional harmonic oscillator is usually one of the first models studied in undergraduate quantum mechanics courses. The one-body Hamiltonian of the one-dimensional harmonic oscillator is given by

$$\hat{h} = -\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2, \tag{7.1}$$

where the latter term, i.e., the one-body potential, gives rise to the name of the system. Plugging this operator into the time-independent Schrödinger equation

$$\hat{h}|n\rangle = \epsilon_n|n\rangle, \tag{7.2}$$

which results in an energy eigenvalue equation we wish to solve in order to find an expression for $|n\rangle$.

7.1.2 One-dimensional double well quantum dot

A slightly more complicated model is the *double well* quantum dot. Succintly named due to its "bump" in the bottom of the parabolic potential from the harmonic oscillator. The one-body hamiltonian is given by

$$\hat{h} = -\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\left(\hat{x}^2 + \frac{1}{4}l^2 - l|\hat{x}|\right), \tag{7.3}$$

where l is the "width" of the potential barrier in the bottom of the parabola.

7.1.3 Two-dimensional harmonic oscillator

The one-body Hamiltonian of the two-dimensional harmonic oscillator is virtually identical to the one-body Hamiltonian of the one-dimensional harmonic oscillator, i.e., Equation 7.1, but with the position and momentum operators being represented in two-dimensions. We will be looking at a circular, symmetric potential. We will thus be working in a polar coordinate basis. The main reason we choose the polar coordinate representation is due to the evaluation of the two-body Coulomb integral elements. This is the most costly part of the construction of the matrix elements and in a polar basis we have *analytical* expressions for these elements [1]. The Hamiltonian can thus be represented by

$$\hat{h} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \frac{1}{2}m\omega^2\left(\hat{x}^2 + \hat{y}^2\right) = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right] + \frac{1}{2}m\omega^2\hat{r}^2, \tag{7.4}$$

where $\hat{r}^2 = \hat{x}^2 + \hat{y}^2$. Next we insert the Hamiltonian into the time-independent Schrödinger equation

$$\hat{h}|nm\rangle = \epsilon_{nm}|nm\rangle, \tag{7.5}$$

and diagonalize in order to find the eigenstates, $|nm\rangle$. Representing the eigenstates in polar coordinates

$$\phi_{nm}(\mathbf{r}) = \phi_{nm}(r,\theta) \equiv \langle r\theta|nm\rangle, \tag{7.6}$$

we solve the eigenvalue problem by separating the radial and the angular part of the eigenstate and solve each term individually. That is,

$$\phi_{nm}(r,\theta) = N_{nm}R_{nm}(r)\Theta_m(\theta). \tag{7.7}$$

Solving the two coupled ordinary differential equations and finding the normalization constant, we find the terms

$$N_{nm} = a\sqrt{\frac{n!}{\pi(n+|m|)!}}, \tag{7.8}$$

as the normalization factor with

$$a = \sqrt{\frac{m\omega}{\hbar}}, \tag{7.9}$$

the Bohr radius. The radial contribution is given by

$$R_{nm}(r) = (ar)^{|m|}L_n^{|m|}(a^2r^2)\exp\left\{-\frac{a^2r^2}{2}\right\}, \tag{7.10}$$

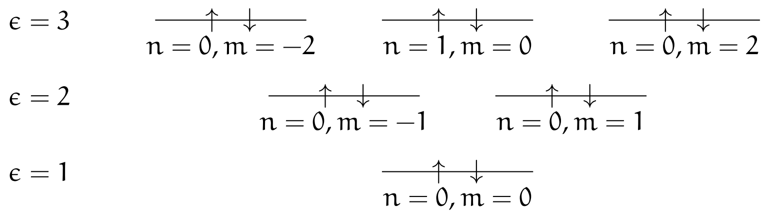

Figure 7.1: In this plot we can see the energy degeneracy of the lowest three energy levels in the two-dimensional quantum dot. Each arrow representes a spin up or a spin down state with the quantum numbers n and m as listed below. This pattern goes on indefinitly with the addition of one bar (two oscillators) per level.

where $L_n^m(r)$ is the *associated Laguerre polynomials*. The angular part is given by

$$\Theta_m(\theta) = \exp\{im\theta\}. \tag{7.11}$$

The eigenenergy, ϵ_{nm}, of the two-dimensional eigenstates is given by

$$\epsilon_{nm} = \hbar\omega\left[2n + |m| + 1\right]. \tag{7.12}$$

Staring at the eigenenergy equation we notice quite fast that the states are degenerate in the energy. A drawing of the first three energy levels with their corresponding quantum numbers is shown in Figure 7.1. The basis functions are orthonormal. By including spin as a quantum number σ, we can represent this by

$$\langle n_1 m_1 \sigma_1 | n_2 m_2 \sigma_2 \rangle = \delta_{n_1 n_2} \delta_{m_1 m_2} \delta_{\sigma_1 \sigma_2}. \tag{7.13}$$

Mapping the quantum numbers to a single value

When working with second quantized operators, we distinguish single particle functions in a Slater determinant by a single index. Including spin in the two-dimensional harmonic oscillator eigenstates we have to deal with three quantum numbers n, m and σ per state. We are thus interested in finding a mapping $(n, m) \mapsto p$ and the inverse mapping $p \mapsto (n, m)$[1]. Due to the degeneracy of the eigenenergies such a mapping will not be unique. We thus have to decide in advance how we should count the basis states. In this thesis we choose the convention that we start from the lowest energy level and move up by counting from left to right. Tabulating Figure 7.1 we get the table shown in Table 7.1.

7.1.4 Two-dimensional double well quantum dot

7.2 Finite basis sets

In this section we'll explore some systems which allow for excitation of the particles. That is, the their one-body potential wells are *finite* which lets us excite particles so much that they'll escape the potential well.

---

[1] The spin quantum number is easiest to deal with in the end as we can double each dimension in every tensor and label all odd or even indices by a spin direction.

Table 7.1: In this table we show an example of how our mapping convention will index the states shown in Figure 7.1.

ϵ_{nm}	(n, m)	p
1	$(0, 0)$	0
2	$(0, -1)$	1
2	$(0, 1)$	2
3	$(0, -2)$	3
3	$(1, 0)$	4
3	$(0, 2)$	5

Part II

Appendices

Appendix A

Hartree-Fock

Hartree-Fock appendix.

Appendix B

Coupled cluster equations

In this appendix we will show the explicit equations used for ground state calculations in coupled cluster for different truncation levels.

B.1 Coupled cluster doubles

The energy for the doubles truncation is given by

$$E_{CCD} = E_0 + \langle \Phi | e^{-\hat{T}_2} H_N e^{\hat{T}_2} | \Phi \rangle = E_0 + \frac{1}{4} \tau^{cd}_{kl} u^{kl}_{cd}. \tag{B.1}$$

The doubles amplitude equations is given by[12]

$$\begin{aligned}
0 = g(f, u, \tau) &\equiv \langle \Phi^{ab}_{ij} | e^{-\hat{T}_2} H_N e^{\hat{T}_2} | \Phi \rangle \qquad \text{(B.2)} \\
&= u^{ab}_{ij} + f^{b}_{c} \tau^{ac}_{ij} P(ab) - f^{k}_{j} \tau^{ab}_{ik} P(ij) + \frac{1}{2} \tau^{cd}_{ij} u^{ab}_{cd} + \frac{1}{2} \tau^{ab}_{kl} u^{kl}_{ij} \\
&\quad + \tau^{ac}_{ik} u^{bk}_{jc} P(ab) P(ij) + \frac{1}{4} \tau^{cd}_{ij} \tau^{ab}_{kl} u^{kl}_{cd} + \tau^{ac}_{ik} \tau^{bd}_{jl} u^{kl}_{cd} P(ij) \\
&\quad - \frac{1}{2} \tau^{ab}_{lj} \tau^{dc}_{ik} u^{kl}_{cd} P(ij) - \frac{1}{2} \tau^{ac}_{lk} \tau^{db}_{ij} u^{kl}_{cd} P(ab). \qquad \text{(B.3)}
\end{aligned}$$

In order to reduce the number of FLOPS when contracting the tensors, we introduce so-called *intermediates*[4]. In practice, this consists of precomputing some of the terms by choosing which tensors to contract first. In the doubles approximation there are four sensible intermediates we can define[1].

$$g(f, u, \tau) \leftarrow \frac{1}{4} \tau^{cd}_{ij} \tau^{ab}_{kl} u^{kl}_{cd} + \frac{1}{2} \tau^{cd}_{ij} u^{ab}_{cd} = \tau^{cd}_{ij} \left(\frac{1}{4} \tau^{ab}_{kl} u^{kl}_{cd} + \frac{1}{2} u^{ab}_{cd} \right) = \tau^{cd}_{ij} W^{ab}_{cd}, \tag{B.4}$$

$$g(f, u, \tau) \leftarrow \frac{1}{2} \tau^{cd}_{jk} \tau^{ab}_{il} u^{kl}_{cd} P(ij) = \tau^{ab}_{il} \left(\frac{1}{2} \tau^{cd}_{jk} u^{kl}_{cd} \right) P(ij) = \tau^{ab}_{il} W^{l}_{j} P(ij), \tag{B.5}$$

$$g(f, u, \tau) \leftarrow \frac{1}{2} \tau^{ac}_{ij} \tau^{bd}_{kl} u^{kl}_{cd} P(ab) = \tau^{ac}_{ij} \left(\frac{1}{2} \tau^{bd}_{kl} u^{kl}_{cd} \right) P(ab) = \tau^{ac}_{ij} W^{b}_{c} P(ab). \tag{B.6}$$

---

[1] Note that we use the notation "←" to signify part of the expression, i.e., some of the terms contained in the function.

Table B.1: In this table we summarize the intermediates used in the τ-amplitudes of the coupled cluster doubles approximation. We also list the computational complexity in FLOPS needed to construct the intermediate. Recall that n is the number of holes and m the number of particles.

Intermediate	Complexity [FLOPS]
$W^{ab}_{cd} = \frac{1}{4}\tau^{ab}_{kl}u^{kl}_{cd} + \frac{1}{2}u^{ab}_{cd}$	$\mathcal{O}(m^4n^2)$
$W^{l}_{j} = \frac{1}{2}\tau^{cd}_{jk}u^{kl}_{cd}$	$\mathcal{O}(m^2n^3)$
$W^{b}_{c} = \frac{1}{2}\tau^{bd}_{kl}u^{kl}_{cd}$	$\mathcal{O}(m^3n^2)$
$W^{bk}_{jc} = \frac{1}{2}\tau^{bd}_{jl}u^{kl}_{cd} + u^{bk}_{jc}$	$\mathcal{O}(m^3n^3)$

The last intermediate requires a little work, as we have to insert an extra exchange operator, $P(ij)$, in one of the terms in order to group two terms into a single intermediate.

$$g(f, u, \tau) \leftarrow \tau^{ac}_{ik}\tau^{bd}_{jl}u^{kl}_{cd}P(ab) + \tau^{ac}_{ik}u^{bk}_{jc}P(ab)P(ij) \tag{B.7}$$

$$= \tau^{ac}_{ik}\left(\frac{1}{2}\tau^{bd}_{jl}u^{kl}_{cd} + u^{bk}_{jc}\right)P(ab)P(ij) \tag{B.8}$$

$$= \tau^{ac}_{ik}W^{bk}_{jc}P(ab)P(ij). \tag{B.9}$$

We summarize the expression for the intermediates in Table B.1, along with their computational complexity. The total right-hand side of the τ-amplitudes in the doubles approximation using the intermediate calculations is thus

$$\begin{aligned} g(f, u, \tau) = {} & f^{b}_{c}\tau^{ac}_{ij}P(ab) - f^{k}_{j}\tau^{ab}_{ik}P(ij) + \tau^{cd}_{ij}W^{ab}_{cd} + \tau^{ab}_{il}W^{l}_{j}P(ij) \\ & + \tau^{ac}_{ik}W^{bk}_{jc}P(ab)P(ij) - \tau^{ac}_{ij}W^{b}_{c}P(ab) + \frac{1}{2}\tau^{ab}_{kl}u^{kl}_{ij} + u^{ab}_{ij}. \end{aligned} \tag{B.10}$$

The most time-consuming contraction is now the term $\tau^{cd}_{ij}W^{ab}_{cd}$. This term uses $\mathcal{O}(m^4n^2)$ FLOPS, which is a reduction from $\mathcal{O}(m^4n^4)$ when computing $\tau^{cd}_{ij}\tau^{ab}_{kl}u^{kl}_{cd}$ directly.

Moving on to the $\hat{\Lambda}$-equations we have for the doubles approximation

$$0 = \tag{B.11}$$

B.2 Coupled cluster singles doubles

The energy for the singles-doubles truncation is given by

$$E_{\text{CCSD}} = E_0 + \langle\Phi|e^{-\hat{T}_1-\hat{T}_2}H_N e^{\hat{T}_1+\hat{T}_2}|\Phi\rangle \tag{B.12}$$

$$= E_0 + f^{k}_{c}\tau^{c}_{k} - \frac{1}{2}\tau^{c}_{l}\tau^{d}_{k}u^{kl}_{cd} + \frac{1}{4}\tau^{cd}_{kl}u^{kl}_{cd}. \tag{B.13}$$

The singles amplitude equations becomes

$$0 = \langle\Phi^{a}_{i}|e^{-\hat{T}_1-\hat{T}_2}H_N e^{\hat{T}_1+\hat{T}_2}|\Phi\rangle \tag{B.14}$$

$$\begin{aligned} = {} & f^{a}_{i} - f^{k}_{c}\tau^{c}_{i}\tau^{a}_{k} + f^{k}_{c}\tau^{ac}_{ik} - f^{k}_{i}\tau^{a}_{k} + f^{a}_{c}\tau^{c}_{i} - \tau^{c}_{k}\tau^{d}_{i}\tau^{a}_{l}u^{kl}_{cd} - \tau^{c}_{k}\tau^{d}_{i}u^{ak}_{cd} \\ & + \tau^{c}_{k}\tau^{a}_{l}u^{kl}_{ic} + \tau^{c}_{k}\tau^{ad}_{il}u^{kl}_{cd} + \tau^{c}_{k}u^{ak}_{ic} - \frac{1}{2}\tau^{c}_{i}\tau^{ad}_{kl}u^{kl}_{cd} \\ & + \frac{1}{2}\tau^{a}_{l}\tau^{cd}_{ik}u^{kl}_{cd} + \frac{1}{2}\tau^{cd}_{ik}u^{ak}_{cd} - \frac{1}{2}\tau^{ac}_{kl}u^{kl}_{ic}. \end{aligned} \tag{B.15}$$

The doubles amplitude equations are

$$\begin{aligned}
0 &= \langle \Phi_{ij}^{ab} | e^{-\hat{T}_1 - \hat{T}_2} H_N e^{\hat{T}_1 + \hat{T}_2} | \Phi \rangle && \text{(B.16)} \\
&= f_c^k \tau_i^c \tau_{jk}^{ab} P(ij) + f_c^k \tau_k^a \tau_{ij}^{bc} P(ab) + f_i^k \tau_{jk}^{ab} P(ij) - f_c^a \tau_{ij}^{bc} P(ab) \\
&\quad + \tau_k^c \tau_i^d \tau_{jl}^{ab} u_{cd}^{kl} P(ij) + \tau_k^c \tau_l^a \tau_{ij}^{bd} u_{cd}^{kl} P(ab) - \tau_k^c \tau_{ij}^{ad} u_{cd}^{bk} P(ab) \\
&\quad + \tau_k^c \tau_{il}^{ab} u_{jc}^{kl} P(ij) + \tau_i^c \tau_j^d \tau_k^a \tau_l^b u_{cd}^{kl} + \tau_i^c \tau_j^d \tau_k^a u_{cd}^{bk} P(ab) + \frac{1}{2} \tau_i^c \tau_j^d \tau_{kl}^{ab} u_{cd}^{kl} 1 \\
&\quad + \tau_i^c \tau_j^d u_{cd}^{ab} - \tau_i^c \tau_k^a \tau_l^b u_{jc}^{kl} P(ij) - \tau_i^c \tau_k^a \tau_{jl}^{bd} u_{cd}^{kl} P(ab) P(ij) \\
&\quad - \tau_i^c \tau_k^a u_{jc}^{bk} P(ab) P(ij) - \tau_i^c \tau_{jk}^{ad} u_{cd}^{bk} P(ab) P(ij) - \frac{1}{2} \tau_i^c \tau_{kl}^{ab} u_{jc}^{kl} P(ij) \\
&\quad - \tau_i^c u_{jc}^{ab} P(ij) + \frac{1}{2} \tau_k^a \tau_l^b \tau_{ij}^{cd} u_{cd}^{kl} + \tau_k^a \tau_l^b u_{ij}^{kl} + \frac{1}{2} \tau_k^a \tau_{ij}^{cd} u_{cd}^{bk} 1 P(ab) \\
&\quad + \tau_k^a \tau_{il}^{bc} u_{jc}^{kl} P(ab) P(ij) + \tau_k^a u_{ij}^{bk} P(ab) + \frac{1}{4} \tau_{ij}^{cd} \tau_{kl}^{ab} u_{cd}^{kl} 1 + \frac{1}{2} \tau_{ij}^{cd} u_{cd}^{ab} \\
&\quad + \frac{1}{2} \tau_{jk}^{cd} \tau_{il}^{ab} u_{cd}^{kl} P(ij) + \tau_{ik}^{ac} \tau_{jl}^{bd} u_{cd}^{kl} P(ab) + \tau_{ik}^{ac} u_{jc}^{bk} P(ab) P(ij) \\
&\quad - \frac{1}{2} \tau_{ij}^{ac} \tau_{kl}^{bd} u_{cd}^{kl} P(ab) + \frac{1}{2} \tau_{kl}^{ab} u_{ij}^{kl} 1 + u_{ij}^{ab}. && \text{(B.17)}
\end{aligned}$$

B.3 Coupled cluster doubles triples

The energy of the doubles-triples truncation is given by

$$\begin{aligned}
E_{CCDT} &= E_0 + \langle \Phi | e^{-\hat{T}_2 - \hat{T}_3} H_N e^{\hat{T}_2 + \hat{T}_3} | \Phi \rangle && \text{(B.18)} \\
&= E_0 + \frac{1}{4} \tau_{lm}^{de} u_{de}^{lm}. && \text{(B.19)}
\end{aligned}$$

The doubles amplitude equations are

$$\begin{aligned}
0 &= \langle \Phi_{ij}^{ab} | e^{-\hat{T}_2 - \hat{T}_3} H_N e^{\hat{T}_2 + \hat{T}_3} | \Phi \rangle && \text{(B.20)} \\
&= f_d^l \tau_{ijl}^{abd} + f_i^l \tau_{jl}^{ab} P(ij) - f_d^a \tau_{ij}^{bd} P(ab) + \frac{1}{4} \tau_{ij}^{de} \tau_{lm}^{ab} u_{de}^{lm} \\
&\quad + \frac{1}{2} \tau_{ij}^{de} u_{de}^{ab} + \frac{1}{2} \tau_{jl}^{de} \tau_{im}^{ab} u_{de}^{lm} P(ij) + \tau_{il}^{ad} \tau_{jm}^{be} u_{de}^{lm} P(ab) \\
&\quad + \tau_{il}^{ad} u_{jd}^{bl} P(ab) P(ij) - \frac{1}{2} \tau_{ij}^{ad} \tau_{lm}^{be} u_{de}^{lm} P(ab) + \frac{1}{2} \tau_{lm}^{ab} u_{ij}^{lm} \\
&\quad + \frac{1}{2} \tau_{ijl}^{ade} u_{de}^{bl} P(ab) - \frac{1}{2} \tau_{ilm}^{abd} u_{jd}^{lm} P(ij) + u_{ij}^{ab}. && \text{(B.21)}
\end{aligned}$$

Now to the beast...

The triples amplitude equations are

$$
\begin{align}
0 &= \langle \Phi_{ijk}^{abc} | e^{-\hat{T}_2 - \hat{T}_3} H_N e^{\hat{T}_2 + \hat{T}_3} | \Phi \rangle \tag{B.22}\\
&= f_d^l \tau_{ij}^{ad} \tau_{kl}^{bc} P(ab)P(ik) + f_d^l \tau_{il}^{ab} \tau_{jk}^{cd} P(ij) + f_d^l \tau_{kl}^{ab} \tau_{ij}^{cd} + f_d^l \tau_{jl}^{ac} \tau_{ik}^{bd} P(ab) \nonumber\\
&\quad - f_i^l \tau_{jkl}^{abc} P(ij) - f_k^l \tau_{ijl}^{abc} + f_d^a \tau_{ijk}^{bcd} P(ab) + f_d^c \tau_{ijk}^{abd} \nonumber\\
&\quad + \frac{1}{2} \tau_{il}^{de} \tau_{jkm}^{abc} u_{de}^{lm} P(ij) + \frac{1}{2} \tau_{ij}^{de} \tau_{kl}^{ab} u_{de}^{cl} - \frac{1}{2} \tau_{ij}^{de} \tau_{kl}^{ac} u_{de}^{bl} P(ab) \nonumber\\
&\quad + \frac{1}{4} \tau_{ij}^{de} \tau_{klm}^{abc} u_{de}^{lm} - \frac{1}{4} \tau_{ik}^{de} \tau_{jlm}^{abc} u_{de}^{lm} P(ij) + \frac{1}{2} \tau_{jk}^{de} \tau_{il}^{ab} u_{de}^{cl} P(ij) \nonumber\\
&\quad - \frac{1}{2} \tau_{jk}^{de} \tau_{il}^{ac} u_{de}^{bl} P(ab)P(ij) + \frac{1}{2} \tau_{kl}^{de} \tau_{ijm}^{abc} u_{de}^{lm} + \frac{1}{2} \tau_{lm}^{ad} \tau_{ijk}^{bce} u_{de}^{lm} P(ab) \nonumber\\
&\quad + \tau_{il}^{ad} \tau_{jm}^{bc} u_{kd}^{lm} P(ab) + \tau_{il}^{ad} \tau_{jk}^{ce} u_{de}^{bl} P(ab)P(ij) + \tau_{il}^{ad} \tau_{jkm}^{bce} u_{de}^{lm} P(ab)P(ij) \nonumber\\
&\quad - \tau_{ij}^{ad} \tau_{kl}^{be} u_{de}^{cl} P(ab) + \tau_{ij}^{ad} \tau_{kl}^{ce} u_{de}^{bl} P(ab) + \frac{1}{2} \tau_{ij}^{ad} \tau_{klm}^{bce} u_{de}^{lm} P(ab) \nonumber\\
&\quad - \tau_{ij}^{ad} u_{kd}^{bc} P(ab) + \tau_{ik}^{ad} \tau_{jl}^{be} u_{de}^{cl} P(ab)P(ij) + \frac{1}{2} \tau_{ik}^{ad} \tau_{lm}^{bc} u_{jd}^{lm} P(ab)P(ij) \nonumber\\
&\quad - \tau_{ik}^{ad} \tau_{jl}^{ce} u_{de}^{bl} P(ab)P(ij) - \frac{1}{2} \tau_{ik}^{ad} \tau_{jlm}^{bce} u_{de}^{lm} P(ab)P(ij) + \tau_{ik}^{ad} u_{jd}^{bc} P(ab)P(ij) \nonumber\\
&\quad + \tau_{kl}^{ad} \tau_{ij}^{ce} u_{de}^{bl} P(ab) + \tau_{kl}^{ad} \tau_{ijm}^{bce} u_{de}^{lm} P(ab) - \frac{1}{2} \tau_{lm}^{ab} \tau_{ij}^{cd} u_{kd}^{lm} \nonumber\\
&\quad + \frac{1}{2} \tau_{lm}^{ab} \tau_{ik}^{cd} u_{jd}^{lm} P(ij) + \frac{1}{4} \tau_{lm}^{ab} \tau_{ijk}^{cde} u_{de}^{lm} + \tau_{il}^{ab} \tau_{jm}^{cd} u_{kd}^{lm} P(ij) \nonumber\\
&\quad - \tau_{il}^{ab} \tau_{km}^{cd} u_{jd}^{lm} P(ij) + \frac{1}{2} \tau_{il}^{ab} \tau_{jkm}^{cde} u_{de}^{lm} P(ij) + \tau_{il}^{ab} u_{jk}^{cl} P(ij) \nonumber\\
&\quad + \tau_{kl}^{ab} \tau_{im}^{cd} u_{jd}^{lm} P(ij) + \frac{1}{2} \tau_{kl}^{ab} \tau_{ijm}^{cde} u_{de}^{lm} + \tau_{kl}^{ab} u_{ij}^{cl} \nonumber\\
&\quad + \frac{1}{2} \tau_{lm}^{ac} \tau_{ij}^{bd} u_{kd}^{lm} P(ab) - \frac{1}{4} \tau_{lm}^{ac} \tau_{ijk}^{bde} u_{de}^{lm} P(ab) - \tau_{il}^{ac} \tau_{jm}^{bd} u_{kd}^{lm} P(ab) \nonumber\\
&\quad + \tau_{il}^{ac} \tau_{km}^{bd} u_{jd}^{lm} P(ab)P(ij) - \frac{1}{2} \tau_{il}^{ac} \tau_{jkm}^{bde} u_{de}^{lm} P(ab)P(ij) - \tau_{il}^{ac} u_{jk}^{bl} P(ab)P(ij) \nonumber\\
&\quad - \tau_{kl}^{ac} \tau_{im}^{bd} u_{jd}^{lm} P(ab)P(ij) - \frac{1}{2} \tau_{kl}^{ac} \tau_{ijm}^{bde} u_{de}^{lm} P(ab) - \tau_{kl}^{ac} u_{ij}^{bl} P(ab) \nonumber\\
&\quad - \tau_{ij}^{cd} u_{kd}^{ab} + \tau_{ik}^{cd} u_{jd}^{ab} P(ij) - \frac{1}{2} \tau_{lm}^{ce} \tau_{ijk}^{abd} u_{de}^{lm} \nonumber\\
&\quad + \tau_{im}^{ce} \tau_{jkl}^{abd} u_{de}^{lm} P(ij) - \frac{1}{2} \tau_{ij}^{ce} \tau_{klm}^{abd} u_{de}^{lm} + \frac{1}{2} \tau_{ik}^{ce} \tau_{jlm}^{abd} u_{de}^{lm} P(ij) \nonumber\\
&\quad + \tau_{km}^{ce} \tau_{ijl}^{abd} u_{de}^{lm} + \frac{1}{2} \tau_{ijk}^{ade} u_{de}^{bc} P(ab) + \tau_{ijl}^{abd} u_{kd}^{cl} \nonumber\\
&\quad - \tau_{ikl}^{abd} u_{jd}^{cl} P(ij) + \frac{1}{2} \tau_{ilm}^{abc} u_{jk}^{lm} P(ij) + \frac{1}{2} \tau_{klm}^{abc} u_{ij}^{lm} \nonumber\\
&\quad - \tau_{ijl}^{acd} u_{kd}^{bl} P(ab) + \tau_{ikl}^{acd} u_{jd}^{bl} P(ab)P(ij) + \frac{1}{2} \tau_{ijk}^{cde} u_{de}^{ab}. \tag{B.23}
\end{align}
$$

Appendix C

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.

C.1 Reformulating the CCD equations

C.2 Reformulating the CCSD equations

We use the expressions for the CCSD equations derived by Gauss et al.[2]. We start with the *effective double excitation amplitudes* found at the bottom of table 3 in their article. Note that we rename $\tilde{\tau} \to \xi$, thus reserving the twiddle for intermediate calculations.

---

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

$$\tau^{ab}_{ij} = t^{ab}_{ij} + \frac{1}{2}P(ij)P(ab)t^a_i t^b_j \tag{C.1}$$

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

$$\xi^{ab}_{ij} = t^{ab}_{ij} + \frac{1}{4}P(ij)P(ab)t^a_i t^b_j \tag{C.3}$$

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

Next we look at the one-body intermediates found at the top of table 3 in the article by Gauss et al.[2]. We use the notation

$$u^{am}_{ef} \equiv \langle am||ef\rangle, \tag{C.5}$$

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

$$F^a_e = f^a_e - \frac{1}{2}f^m_e t^a_m + t^f_m u^{am}_{ef} - \frac{1}{2}\xi^{af}_{mn}u^{mn}_{ef} \tag{C.6}$$

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

$$F^m_i = f^m_i + \frac{1}{2}f^m_e t^e_i + t^e_n u^{mn}_{ie} + \frac{1}{2}\xi^{ef}_{in}u^{mn}_{ef} \tag{C.8}$$

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

$$F^m_e = f^m_e + t^f_n u^{mn}_{ef} \tag{C.10}$$

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

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.[2]. To avoid storing two matrices with M^4 elements we will not create the intermediate W^{ab}_{ef} 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 D

Computing one-body density matrices

From Kvaal[6] we have an expression for the one-body density matrices ρ^q_p[1] as a function of the coupled cluster amplitudes t and λ.

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

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

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

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

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

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 Λ. 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 Λ 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 ρ^q_p will be the operator combinations that leave the reference unchanged after applying the total operator chain. For the term without Λ in ρ^q_p this leaves us with

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

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.

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

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

---

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

D.1 The one-body density matrix for doubles excitation

In the doubles truncation, the only contribution to Equation D.5 will be

$$\langle\tilde{\Phi}|\Lambda e^{-T}\hat{p}^{\dagger}\hat{q}e^{T}|\Phi\rangle = \langle\tilde{\Phi}|\Lambda\left[\hat{p}^{\dagger}\hat{q}, T\right]|\Phi\rangle. \tag{D.6}$$

This happens as the first term in Equation D.5 will at best leave the reference relaxed by 1 as $\hat{p}^{\dagger}\hat{q}$ can only excite a single particle. The next commutator will suffer the same effect, but in reverse. Two T operators will leave the reference in a $+4$ state, $\hat{p}^{\dagger}\hat{q}$ will at best relax this to a $+3$ state. Then, Λ, will only be able to relax the total down to a $+1$, thus annihilating the overlap. The one-body density matrix for coupled cluster doubles is then

$$\begin{aligned}\rho^{q}_{p} &= \langle\tilde{\Phi}|\hat{p}^{\dagger}\hat{q}|\Phi\rangle + \langle\tilde{\Phi}|\left[\hat{p}^{\dagger}\hat{q}, T\right]|\Phi\rangle + \langle\tilde{\Phi}|\Lambda\left[\hat{p}^{\dagger}\hat{q}, T\right]|\Phi\rangle && \text{(D.7)}\\ &= \delta^{q}_{j}\delta^{i}_{p}\left(\delta^{j}_{i} + \frac{1}{2}l^{ik}_{ab}t^{ab}_{kj}\right) - \frac{1}{2}\delta^{q}_{b}\delta^{a}_{p}l^{ij}_{ac}t^{cb}_{ij}. && \text{(D.8)}\end{aligned}$$

We note that there are no contribution to the terms with an occupied and a virtual index, that is, $\rho^{i}_{a} = \rho^{a}_{i} = 0$. This is a direct consequence of the lack of single excitations. The density operators $\hat{a}^{\dagger}\hat{\imath}$ and $\hat{\imath}^{\dagger}\hat{a}$ will excite and relax a single particle respectively. But, Λ and T only works on pairs therefore leaving the reference oddly excited or relaxed thus annihilating the overlap.

D.2 The one-body density matrix for singles and doubles excitations

For coupled cluster singles-and-doubles Equation D.5 will truncate at the double commutator as written. Employing SymPy[11] we can compute an expression for the one-body density matrices.

$$\begin{aligned}\rho^{q}_{p} &= \langle\tilde{\Phi}|\hat{p}^{\dagger}\hat{q}|\Phi\rangle + \langle\tilde{\Phi}|\left[\hat{p}^{\dagger}\hat{q}, T\right]|\Phi\rangle + \langle\tilde{\Phi}|\Lambda\hat{p}^{\dagger}\hat{q}|\Phi\rangle\\ &\quad + \langle\tilde{\Phi}|\Lambda\left[\hat{p}^{\dagger}\hat{q}, T\right]|\Phi\rangle + \frac{1}{2!}\langle\tilde{\Phi}|\Lambda\left[\left[\hat{p}^{\dagger}\hat{q}, T\right], T\right]|\Phi\rangle && \text{(D.9)}\\ &= \delta^{a}_{p}\delta^{q}_{b}\left(l^{i}_{a}t^{b}_{i} + \frac{1}{2}l^{ij}_{ac}t^{bc}_{ij}\right) + \delta^{a}_{p}\delta^{q}_{i}l^{i}_{a} + \delta^{q}_{j}\delta^{i}_{p}\left(\delta^{j}_{i} - l^{j}_{a}t^{a}_{i} + \frac{1}{2}l^{jk}_{ab}t^{ab}_{ki}\right)\\ &\quad + \delta^{q}_{a}\delta^{i}_{p}\left(t^{a}_{i} + l^{j}_{b}\left[t^{ab}_{ij} - t^{b}_{i}t^{a}_{j}\right] + \frac{1}{2}t^{b}_{i}l^{kj}_{cb}t^{ac}_{kj} - \frac{1}{2}t^{a}_{j}l^{kj}_{cb}t^{cb}_{ki}\right). && \text{(D.10)}\end{aligned}$$

In this expression we have only kept the fully contracted terms. SymPy sets the indices arbitrarily so the expression shown in Equation D.10 has been factorized and had a relabeling of the indices for improved readability.

Appendix E

Overlap between time-evolved coupled cluster wavefunctions

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

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

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

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

This is a consequence of treating the two different Hilbert spaces indepedently. 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.

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

$$\langle \tilde{\Psi}(0) | \Psi(t) \rangle = \langle \tilde{\Phi} | \left[1 + \hat{\Lambda} \right] e^{-\hat{T}} e^{\hat{T}(t)} | \Phi \rangle. \tag{E.4}$$

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

$$\langle \tilde{\Psi}(t) | \Psi(0) \rangle = \langle \tilde{\Phi} | e^{-\hat{T}(t)} e^{\hat{T}} | \Phi \rangle + \langle \tilde{\Phi} | \hat{\Lambda}(t) e^{-\hat{T}(t)} e^{\hat{T}} | \Phi \rangle \tag{E.5}$$

$$= 1 + \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{1}{n!m!} \langle \tilde{\Phi} | \hat{\Lambda}(t) [-\hat{T}(t)]^n \hat{T}^m | \Phi \rangle. \tag{E.6}$$

The conjugate of this equation is then

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

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

E.1 Time-dependent overlap for the coupled cluster doubles wavefunction

In the doubles approximation $\hat{T}$ and $\hat{\Lambda}$ yield a net excitation and relaxation of 2, respectively. This means that $n, m \in \{0, 1\}$ as any higher exponentials will leave the reference excited. Furthermore, for $n = m = 0$ $\hat{\Lambda}$ will annihilate the reference. We also have for $n = m = 1$ that the reference will be left doubly excited thus annihilating the overlap. We then get

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

$$\langle\tilde{\Psi}(0)|\Psi(t)\rangle = 1 + \langle\tilde{\Phi}|\hat{\Lambda}\left[-\hat{T} + \hat{T}(t)\right]|\Phi\rangle. \tag{E.9}$$

Using SymPy [11] to construct the tensor contractions we are left with

$$\langle\tilde{\Psi}(t)|\Psi(0)\rangle = 1 + \frac{1}{4}\tau^{ab}_{ij}\lambda(t)^{ij}_{ab} - \frac{1}{4}\lambda(t)^{ij}_{ab}\tau(t)^{ab}_{ij}, \tag{E.10}$$

$$\langle\tilde{\Psi}(0)|\Psi(t)\rangle = 1 - \frac{1}{4}\lambda^{ij}_{ab}\tau^{ab}_{ij} + \frac{1}{4}\lambda^{ij}_{ab}\tau(t)^{ab}_{ij}. \tag{E.11}$$

E.2 Time-dependent overlap for the coupled cluster singles-and-doubles wavefuntion

Restricting ourselves to the singles and doubles approximation we will get that the $\hat{T}$ operator can yield a net excitation of 1 and 2, whereas $\hat{\Lambda}$ yields a net relaxation of 1 and 2. This truncates the infinite sums to $n, m \in \{0, 1, 2\}$. Note however that for $n = m = 0$, $\hat{\Lambda}$ will annihilate the vacuum. We are then left with

$$\langle\tilde{\Psi}(t)|\Psi(0)\rangle = 1 + \langle\tilde{\Phi}|\hat{\Lambda}(t)\left[-\hat{T}(t) + \hat{T} - \hat{T}(t)\hat{T} + \frac{1}{2}\hat{T}(t)^2 + \frac{1}{2}\hat{T}^2\right]|\Phi\rangle, \tag{E.12}$$

$$\langle\tilde{\Psi}(0)|\Psi(t)\rangle = 1 + \langle\tilde{\Phi}|\hat{\Lambda}\left[-\hat{T} + \hat{T}(t) - \hat{T}\hat{T}(t) + \frac{1}{2}\hat{T}^2 + \frac{1}{2}\hat{T}(t)^2\right]|\Phi\rangle. \tag{E.13}$$

We again utilize SymPy [11] to get explicit tensor contractions. This yields

$$\begin{aligned}\langle\tilde{\Psi}(t)|\Psi(0)\rangle = 1 &+ \lambda(t)^{i}_{a}\left[\tau^{a}_{i} - \tau(t)^{a}_{i}\right] \\ &+ \lambda(t)^{ij}_{ab}\left[\frac{1}{4}\tau^{ab}_{ij} - \frac{1}{2}\tau^{a}_{j}\tau^{b}_{i} - \tau(t)^{a}_{i}\tau^{b}_{j} - \frac{1}{2}\tau(t)^{a}_{j}\tau(t)^{b}_{i} - \frac{1}{4}\tau(t)^{ab}_{ij}\right],\end{aligned} \tag{E.14}$$

$$\begin{aligned}\langle\tilde{\Psi}(0)|\Psi(t)\rangle = 1 &+ \lambda^{i}_{a}\left[\tau(t)^{a}_{i} - \tau^{a}_{i}\right] \\ &+ \lambda^{ij}_{ab}\left[\frac{1}{4}\tau(t)^{ab}_{ij} - \frac{1}{2}\tau^{a}_{j}\tau^{b}_{i} - \tau(t)^{a}_{i}\tau^{b}_{j} - \frac{1}{2}\tau(t)^{a}_{j}\tau(t)^{b}_{i} - \frac{1}{4}\tau^{ab}_{ij}\right].\end{aligned} \tag{E.15}$$

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