ab initio Many-Electron Dynamics

by

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> Hierzu ist es notwendig, die Energy nicht als eine stetige unbeschränkt teilbare, sondern als eine discrete, ause einer ganzen Zahl von endlichen gleichen Teilen zusammengesetzte Grösse aufzufassen.
>
> — Max Planck

1.1 Classical Mechanics

The formalism used in quantum mechanics largely stems from William Rowan Hamilton's formulation of classical mechanics. Through the process of canonical quantisation any classical model of a physical system is turned into a quantum mechanical model.

In Hamilton's formulation of classical mechanics, a complete description of a system of N particles is described by a set of canonical coordinates $q = (\vec{q}_1, \ldots, \vec{p}_N)$ and corresponding conjugate momenta $p = (\vec{p}_1, \ldots \vec{p}_N)$. Together, each pair of coordinate and momentum form a point $\xi = (q, p)$ in phase space, which is a space of all possible states of the system. Moreover, pairs of generalised coordinates and conjugate momenta are canonical if they satisfy the Poisson brackets so that $\{q_i, p_k\} = \delta_{ij}$. The Poisson bracket of two functions is defined as

$$\{f, g\} = \frac{\partial f}{\partial q}\frac{\partial g}{\partial g} - \frac{\partial f}{\partial p}\frac{\partial g}{\partial q}. \tag{1.1}$$

The governing equations of motion in a classical system is Hamilton's equations,

$$\dot{q} = \frac{\partial}{\partial p}\mathscr{H}(q, p) \tag{1.2}$$

$$\dot{p} = -\frac{\partial}{\partial q}\mathscr{H}(q, p) \tag{1.3}$$

where $\mathscr{H}(q, p)$ is the Hamiltonian, a function for the total energy of the system. Hamilton's equations may also be stated in terms of the Poisson brackets,

$$\frac{dp_i}{dt} = \{p_i, \mathscr{H}\}, \ \frac{dq_i}{dt} = \{q_i, \mathscr{H}\}. \tag{1.4}$$

A system consisting of N of equal mass m, subject forces caused by an external potential, as well as acting on each other with forces stemming from a central potetntial $w(q_ij)$ has the following Hamiltonian,

$$\mathscr{H}(q,p) = \mathscr{T}(q) + \mathscr{V}(p) + \mathscr{W}(p) = \frac{1}{2m}\sum_i |\vec{p}_i|^2 + \sum_i v(\vec{r}_i) + \frac{1}{2}\sum_{i<j} w(\vec{r_{ij}}). \tag{1.5}$$

This Hamiltonian conveniently contains several parts - the kinetic energy, the external potential energy and the interaction energy; denoted by $\mathscr{T}$, $\mathscr{V}$ and $\mathscr{W}$ respectively.

1.2 Canonical Quantisation

In order to transition from a classical system to a quantum system, we move from the classucal phase space to the Hilbert space, through the procedure known as canonical, or first[1]-, quantisation. Whilst the state of a classical system is a point in phase space, a quantum state is a complex-valued state vector in discrete, infinite dimensional, Hilbert space, that is a complete vector space equipped with an inner product. This space is most commonly chosen to be the space of square-integrable functions Ψ, dependent on all coordinates

$$\Psi = \Psi(x_1, x_2, \ldots, x_N). \tag{1.6}$$

These functions are dubbed wavefunctions and are maps from a point $(x_1, \ldots, x_N)$ in configuration space to the complex vector space,

$$\Psi : X^N \to \mathbb{C}. \tag{1.7}$$

It has been widely discussed how such an object can represent the state of a particle. The answer is provided by Max Born's probabilistic interpretation, which says that $|\Psi(x_1, \ldots, x_N)|^2$, gives the probability of finding the particle at a certain position. For a situation with one particle in one dimension we have,

$$\int_a^b |\Psi(x)|^2 dx = \begin{Bmatrix} \text{probability of finding the} \\ \text{particle between } a \text{ and } b \end{Bmatrix} \tag{1.8}$$

while $|\Psi(x_1, x_2, \ldots, x_N)|^2$ is the probability density for locating all particles at the point $(x_1, \ldots x_N) \in X^N$. Since the total probability must be 1, we are provided with a normalisation condition for the wavefunction,

$$\int_{X^N} |\Psi(x_1, x_2, \ldots, x_N)|^2 dx_1 dx_2 \ldots dx_N = \mathbb{1}. \tag{1.9}$$

1.2.1 The Dirac-von Neumann Postulates

The following postulates, or axioms, provide a precise and concise description of quantum mechanics in terms of operators on the Hilbert space. There are many variations of these postulates, introduced both by their namesakes Paul Adriene Maurice Dirac[12] and John von Neumann[46].

Hilbert Space A quantum state of an isolated physical system is described by a vector with unit norm in a Hilbert space, a complex vector space quipped with a scalar product.

[1]Second quantisation comes later.

Observables Each physical observable of a system is accociated with a *hermitian* operator acting on the Hilbert space. The eigenstates of each such operator define a *complete*, *orthonormal* set of vectors.

With $\hat{O}$ an operator, hermiticity means,

$$\langle\phi|\,\hat{O}\psi\rangle = \langle\hat{O}\phi\,|\psi\rangle \equiv \langle\phi|\,\hat{O}\,|\psi\rangle\,. \tag{1.10}$$

Completeness means,

$$\sum_i |i\rangle\,\langle i| = \mathbb{1}. \tag{1.11}$$

Orthonormal means,

$$\langle i|j\rangle = \delta_{ij}. \tag{1.12}$$

Time Evolution The time evolution of the state vector, $|\psi\rangle = |\psi(t)\rangle$, is given by the Schrödinger equation[2].

$$i\hbar\frac{d}{dt}\,|\psi(t)\rangle = \hat{H}\,|\psi(t)\rangle\,. \tag{1.13}$$

Measurements Physically measurable values, associated with an obeservable $\hat{O}$ are defined by the eigenvalues o_n of the observable,

$$\hat{O}\,|n\rangle = o_n\,|n\rangle\,. \tag{1.14}$$

The probability for finding a particular eigenvalue in the measurement is

$$p_n = |\langle n|\psi\rangle|^2, \tag{1.15}$$

with the system in state $|\psi\rangle$ before the measurement, and $|n\rangle$ as the eigenstate corresponding to the eigenvalue o_n.

1.3 The Many-Body Quantum Hamiltonian

The full Hamiltionian for a quantum many-body system can be a large and unwieldy thing. In this study we will constrain ourselves to the study of electronic systems. Purely on a phenomenological basis, one would include nuclear terms in the Hamiltonian as well. In this study however, we will stay within the Born-Oppenheimer approximation and treat the nuclei as stationary particles, thereby refraining from introducing terms that involve the motion of nuclei. Here we introduce the molecular electronic Breit-Pauli Hamiltionian, throrougly described in Helgaker et al.[31],

$$\hat{H}^{\mathrm{BP}}_{\mathrm{mol}} = \begin{cases} \hat{H}_{\mathrm{kin}} & \leftarrow \text{kinetic energy} \\ +\hat{H}_{\mathrm{cou}} & \leftarrow \text{Coulomb interactions} \\ +\hat{H}_{\mathrm{ee}} & \leftarrow \text{external electric field interaction} \\ +\hat{H}_{Z} & \leftarrow \text{Zeeman intercations} \\ +\hat{H}_{\mathrm{so}} & \leftarrow \text{spin-orbit interactions} \\ +\hat{H}_{\mathrm{ss}} & \leftarrow \text{spin-spin interactions} \\ +\hat{H}_{\mathrm{oo}} & \leftarrow \text{spin-spin interactions} \\ +\hat{H}_{\mathrm{dia}} & \leftarrow \alpha^4\text{diamagnetic interactions} \end{cases} \tag{1.16}$$

[2] In the Schrödinger picture.

Kinetic energy The Breit-Pauli kinetic energy term in Equation 1.16 is

$$\hat{H}_{\text{kin}} = -\frac{1}{2}\sum_i \nabla_i^2 - \frac{\alpha^2}{8}\sum_i \nabla_i^4, \tag{1.17}$$

where the first term is the common classical kinetic energy operator and the second term is the relativistic mass-velocity term. This term arises because of the dependence of mass on velocity. This is one of the larger relativistic corrections for slow electrons. The mass-velocity term is unbounded from below and should not be included in variational calculations[38].

Coulomb interactions Coulomb interaction terms in the Breit-Pauli Hamiltonian (Equation 1.16) are the following,

$$\begin{aligned} \hat{H}_{\text{cou}} = &-\sum_{iK}\frac{Z_K}{r_{iK}} + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} + \frac{1}{2}\sum_{K\neq L}\frac{Z_k Z_L}{R_{KL}} \\ &+ \frac{\alpha^2\pi}{2}\sum_{iK} Z_K\delta(\mathbf{r}_{iK}) - \frac{\alpha^2\pi}{2}\sum_{i\neq j}\delta(\mathbf{r}_{ij}) \\ &+ \frac{2\pi}{3}\sum_{iK} Z_K R_K^2\delta(\mathbf{r}_{iK}) - \frac{1}{3}\sum_{iK}\frac{\operatorname{tr}\Theta_K(3\mathbf{r}_{iK}\mathbf{r}_{iK}^T - r_{iK}^2 I_3)}{r_{ik}^5}. \end{aligned} \tag{1.18}$$

The first three terms are the nonrelativistic Coulomb point-charge interactions between nucles and electron, electron and electron and nucleus and nucleus, respectively. The fourth and fifth terms are the Darwin corrections caused by the Zitterbewegung of the electrons. Because the nuclear point-charge model is not always adequate, the second-to-last and last term correct errors from this approximation. Here, R_K is the nuclear extent and Θ_K is the nuclear quadropole moment. These terms are important in nuclear resonance studies[38] and nucllear quadropole resonance studies[1].

External electric field interactions The Breit-Pauli Hamiltonian includes terms that model the effects of an externally applied scalar potential $\phi(\mathbf{r})$,

$$\hat{H}_{\text{ef}} = -\sum_i \phi_i + \sum_K Z_K\phi_K + \frac{\alpha^2}{\phi_K}\sum_i(\nabla_i \cdot \mathbf{E}_i). \tag{1.19}$$

It is often safe to assume that the applied field are quite uniform on the molecular scale, and one therefore often expands Equation 1.19 in multipoles,

$$\hat{H}_{\text{ef}} = Q_{\text{tot}}\phi_0 - \mu_{\text{tot}}\cdot\mathbf{E}_0 - \frac{1}{2}\operatorname{tr}\mathbf{Q}_{\text{tot}}\mathbf{V}_0 + \ldots, \tag{1.20}$$

where q_{tot} is the total charge of the molecule, μ_0 is the dipole moment, $\mathbf{Q}_{\text{tot}}$ is the second moment, and $\mathbf{V}_0$ is the electric field gradient. Higher-order terms are only necessary for fields that vary greatly in time.

Zeeman interactions Paramagnetic interactions of the molecule with an externally applied magnetic field $\mathbf{B}$ are described by the Zeeman term in the Breit-Pauli Hamiltonian (Equation 1.16),

$$\hat{H}_Z = -\mathbf{B}\cdot\sum_i\left(-\frac{1}{2}\mathbf{l}_{iO} - \mathbf{s}_i + \frac{1}{2}\alpha^2\mathbf{s}_i\nabla_i^2\right) - \mathbf{B}\cdot\sum_K \mathbf{M}_K. \tag{1.21}$$

The nuclear part, here represented by the last term in Equation 1.21, are on the order of 10^{-3} in atomic units. This is much smaller than the electronic part, given by the first sum in

Equation 1.21, but the nuclear part is very important in nuclear magnetic resonance (NMR) computations, where it determines the unshielded resonance lines in the spectra.

The first term inside the parenthesis in Equation 1.21 corresponds to Zeeman interaction with the magnetic moment generated by the orbital angular momentum of the electrons, $\mathbf{l}_{iO} = \mathbf{r}_{iO} \times \mathbf{p}_i$. The second and third terms in the paranthesis are electronic contributions to Zeeman effect from the spin of the electrons. The relativistic correction constituted in the third term is important in electron paramegnetic resonance (EPR) spectroscopy.

Spin-orbit interactions Up to second order in the fine-structure constant, the terms that couple motion of eletrons to particle spins in Equation 1.16 are

$$\begin{aligned}\hat{H}_{\text{so}} =& \frac{\alpha^2}{2}\sum_{iK}\frac{Z_K \mathbf{s}_i \cdot \mathbf{l}_{iK}}{r_{iK}^3} - \frac{\alpha^2}{2}\sum_{i\neq j}\frac{\mathbf{s}_i \mathbf{l}_{ij}}{r_{ij}^3} - \alpha^2 \sum_{i\neq j}\frac{\mathbf{s}_j \mathbf{l}_{ij}}{r_{ij}^3} \\ &+ \alpha^2 \sum_{iK}\frac{\mathbf{M}_K \cdot \mathbf{l}_{iK}}{r_{iK}^3} + \frac{\alpha^2}{4}\sum_i (\mathbf{E}_i \times \mathbf{p}_i - \mathbf{p}_i \times \mathbf{E}_i)\end{aligned} \tag{1.22}$$

When electron spin coupled to magnetic filed induced by other charges i motion we have spin-orbit interaction. The first term in Equation 1.22 models nuclear spin-orbit effect, the second term models interaction between the spin of a particle with its own orbit, the third is interaction with other orbits. The fourth term is known as the orbital hyperfin operator and couples magnetic moments to the orbital motion of electrons, while the fifth and last term is modles coupling of electric fields and orbits.

Spin-psin interaction All terms that arises in the Breit-Pauli Hamiltionian (Equation 1.16) due to coupling between magnetic momenta or spin of two particles are

$$\begin{aligned}\hat{H}_{\text{ss}} &= \frac{\alpha^2}{2}\sum_{i\neq j}\left[\frac{r_{ij}^2 \mathbf{s}_i \cdot \mathbf{s}_j - 3\mathbf{s}_i \cdot \mathbf{r}_{ij}\mathbf{r}_{ij} \cdot \mathbf{s}_j}{r_{ij}^5} - \frac{8\pi}{3}\delta(\mathbf{r}_{ij})\mathbf{s}_i \cdot \mathbf{s}_j\right] \\ &= \alpha^2 \sum_{iK}\left[\frac{r_{iK}^2 \mathbf{s}_i \cdot \mathbf{M}_K - 3\mathbf{s}_i \cdot \mathbf{r}_{iK}\mathbf{r}_{iK} \cdot \mathbf{M}_K}{r_{iK}^5} - \frac{8\pi}{3}\delta(\mathbf{r}_{iK})\mathbf{s}_i \cdot \mathbf{M}_k\right] \\ &= \frac{\alpha^2}{2}\sum_{K\neq L}\left[\frac{r_{KL}^2(\mathbf{M}_K \mathbf{M}_L - 3(\mathbf{M}_K \cdot \mathbf{R}_{KL})(\mathbf{R}_{KL} \cdot \mathbf{M}_L)}{R_{KL}^5}\right]\end{aligned} \tag{1.23}$$

Diamagnetic Interactions The magnitude of effects from diamagnetic interaction in the Breit-Pauli Hamiltonian (Equation 1.16) are terms of order α^4 or smaller. Most of these effects are only important in some cases where strong external magnetic fields are applied (NMR, EPR).

1.3.1 Atomic Units

In the Hamiltionian above (Equation 1.16), we have grown up and set $\hbar = m_e = e = \cdots = 1$. This is a result of using atomic units, a form of commonly used dimensionless units. To see how these units arise, consider the time-independent Schrödinger equation for a Hydrogen atom,

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right)\phi = E\phi, \tag{1.24}$$

where $\hbar$ is the reduced Planck constant, equal to Planck's constant divided by 2π; m_e is the mass of the electron, $-e$ is the charge of the electron and ϵ_0 is the permitivity of free space. We make this equation dimensionless by letting $r \to \lambda r'$,

Table 1.1: Conversion of atomic units to SI units.

Physical quantity	Conversion factor	Value
Length	a_0	$5.2918 \times 10^{-11} m$
Mass	m_e	$9.1095 \times 10^{-31} kg$
Time	$\hbar/E_a$	$2.4189 \times 10^{-17} s$
Charge	e	$1.6022 \times 10^{-19} C$
Energy	E_a	$4.3598 \times 10^{-18} J$
Velocity	$a_0 E_a/\hbar$	$2.1877 \times 10^{6} ms^{-1}$
Angular momentum	$\hbar$	$1.0546 \times 10^{-34} Js$
Electric dipole moment	ea_0	$8.4784 \times 10^{-30} Cm$
Electric polarizability	$e^2 a_0^2/E_a$	$1.6488 \times 10^{-41} C^2 m^2 J^{-1}$
Electric field	$E_a/(ea_0)$	$5.1423 \times 10^{11} Vm^{-1}$
Wave function	$a_0^{-3/2}$	$2.5978 \times 10^{15} m^{-3/2}$

$$\left(-\frac{\hbar^2}{2m_e\lambda^2}\nabla'^2 - \frac{e^2}{4\pi\epsilon_0\lambda r'}\right)\phi' = E\phi'. \tag{1.25}$$

We can factor out the constants in front of the operators, if we choose λ so that,

$$\frac{\hbar^2}{m_e\lambda^2} = \frac{e^2}{4\pi\epsilon_0\lambda} = E_a \rightarrow \lambda\frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0 \tag{1.26}$$

where E_a is the atomic unit of energy that chemists call Hartree. Incidently, we see that λ is just the Bohr radius, a_0. If we let $E' = E/E_a$, we obtain the dimensionless Schrödinger equation,

$$\left(-\frac{1}{2}\nabla'^2 - \frac{1}{r'}\right)\phi' = E'\phi'. \tag{1.27}$$

Some conversion factors between atomic units and SI units can be found in Table 1.1.

1.4 Indistinguishable Particles

In classical mechanics, although particles are indistinguishable, one typically regards particles as individuals because a permutation of particles is counted as a new arrangement and something different than the initial configuration. This was called "Transcedental Individuality" by Heinz Post[53]. In quantum mechanics, on the other hand, a permutation is not regarded as giving rise to a new arrangement. It follows that quantum objects are very different from anything else we know from everyday life, and must be considered "non-individual". By taken this idea to it's extreme one may postulate that all particles of a given type are one and the same. Here from a telephone call betwwen John Wheeler and Richard Feynman[13], "I received a telephone call one day at the graduate college at Princeton from Professor Wheeler, in which he said, 'Feynman, I know why all electrons have the same charge and the same mass' 'Why?' 'Because, they are all the same electron!' "

Following the brief discussion above one may conclude that, the probability density for the location of particles in a system must be permutation invariant,

$$|\Psi(x_1, x_2, \ldots, x_i, x_j, \ldots, x_N)|^2 = |\Psi(x_1, x_2, \ldots, x_j, x_i, \ldots, x_N)|^2. \tag{1.28}$$

For any arbitrary permutation, this is equivalent to

$$\Psi(x_1, \ldots x_N) = e^{i\alpha(\sigma)}\Psi(x_{\sigma(1)}, x_{\sigma(2)}, \ldots, x_{\sigma(N)}), \tag{1.29}$$

where $\sigma \in S_N$ is some permutation of N indices and α is some real number that may be dependent on σ. The same relation can be written by way of a linear permutation operator,

$$(\hat{P}_\sigma \Psi)(x_1, \ldots, x_N) = \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \ldots, x_{\sigma(N)}). \tag{1.30}$$

The 'indistinguishability postulate" states that if a permutation P is applied to a state representing an assembly of particles, there is no way of distinguishing between the permuted state and the original, by means of an observation at any time.

One can show (Difficult to show? exercise 2.2 in FYS-KJM4480) that

$$\hat{P}_\sigma \Psi = \begin{cases} \Psi \\ (-1)^{|\sigma|}\Psi \end{cases} \quad \forall \sigma \in S_N \tag{1.31}$$

where $|\sigma|$ is the number of transpositions in σ and the sign will be $(-1)^{|\sigma|} = \pm 1$. In the former case, when the sign is $+$, the wavefunction is "totally symmetric with respect to permutations"; while in the latter case, when the sign is $-$, the wavefunction is "totally anti-symmetric."

This leads us to another postulate in quantum theory that we have only two types of basic particles, *bosons* have totally symmetric wavefunctions only, while *fermions* have totally anti-symmetric wavefunctions only. "The physical consequences of this postulate seems to be in good agreement with experimental data" [41]. Moreover, all particles with integer spin are bosons, and all particles with half-integer spin are fermions [15, 49]. This can be proved in relativistic quantum mechanics, but must be accepted as an axiom in nonrelativistic theory[32]. Boson follow Bose-Einsten statistics and fermions follow Fermi-Dirac statistics.

To this day, particles with no other spin has been found, but norwegian physicists Jon Magne Leinaas and Jan Myrheim discovered that in one- and two dimensions, more general permutations symmetries are possible. The dubbed this third class of fundamental particles "anyons"[41].

1.5 Representation of the Wavefunction

We have already invested some time in what the wave-function is, but some more time is necessary in order to build a nomenclature for writing down wavefunctions that actually describe many-electron systems with which we are concerned. For some smaller systems it can be satisfactory or even provident to use a single, special function to describe the entire system. Here however, we introduce the Slater determinant as we will only consider many-electron wavefunctions that can be written as a single Slater determinant or as a linear combination of several Slater determinants.

We define an *orbital*[3] which is the wavefunction for a single particle, or more precicely a single electron. The wavefunction a larger group of electrons, for instance those electrons surround an atom or molecule, we call the *molecular orbital*. We also discriminate between spatial orbitals which are functions of spatial coordinates; and spinorbitals, which are functions of the space and spin coordinates (typically a product of a spatial orbital and a spin function). A very complete description and thorough discussion of all things concerning electronic sructure wavefunctions is given by Szabo and Ostlund[64].

[3]Sometimes also called a single-particle function, a single-particle orbital, a single-electron orbital or similar. There is a chance that these terms will be used interchangably throughout this text without warning.

1.5.1 Slater Determinants

The best description for a multiple-electron wavefunction, given by the independent-particle approximation is the Slater determinant,

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \dots & \psi_N(N) \end{vmatrix} = \mathscr{A}\psi_1\psi_2\dots\psi_N, \tag{1.32}$$

where $\psi_i(\mu)$ is a spinorbital and $\mathscr{A}$ is the antisymmetriser. The spinorbitals, are single-particle functions in $L^2(X)$, not necessarily orthonormal.

To illustrate why this is a good approximation of the electronic wave function, condiser first the two-electron case,

$$\Phi_{N=2} = \frac{1}{\sqrt{(2)}}(\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)). \tag{1.33}$$

We see from this relatively simple expression that if the electrons where to occupy the same state. This ensures that the Pauli exclusion principle for fermions[50]. Moreover, if we switch coordinates of any two single-particle functions (spinorbitals), corresponding to the interchange of rows in Equation 1.32, the result is a change of sign. This attribute accomodates the total anti-symmetry necessary for a fermionic wavefunction.

Chapter 2

Second Quantisation

Some Slater determinant is written,

$$|\Phi\rangle = |\phi_i \phi_j \phi_k \dots \phi_z\rangle = |ijk \dots z\rangle \,. \tag{2.1}$$

2.1 Creation and Annihilation Operators

The notation of creation and annihilation operators vary,

$$\text{creation operator for spinorbital } \phi_i, \; \hat{X}_i^\dagger, \hat{a}_i^\dagger, \hat{c}_i^\dagger, \hat{\imath}^\dagger;$$
$$\text{annihilation operator for spinorbital } \phi_i, \; \hat{X}_i, \hat{a}_i, \hat{c}_i, \hat{\imath}.$$

Herein, $\hat{a}_i^\dagger$, $\hat{a}_i$ is used and, if there is no change of confusion, $\hat{\imath}^\dagger$, $\hat{\imath}$.

The Creation Operator . For every single-particle index q, we define the creation operator $c_q^\dagger$ acting on the vacuum state by

$$\hat{a}_i^\dagger \, |0\rangle = |q\rangle \,. \tag{2.2}$$

For any slater determinant with $N > 0$, the action is defined by

$$\hat{a}_i^\dagger \, |jk \dots z\rangle = |ijk \dots z\rangle \,, \tag{2.3}$$
$$\hat{a}_i^\dagger \, |ijk \dots z\rangle = 0 \tag{2.4}$$

The Annihilation Operator . It i sufficient to state that the annihilation c_i operator is the hermitian adjoint of the creation operator $\hat{c}_i$, but to specify we have

$$\hat{a}_i \, |0\rangle = 0, \tag{2.5}$$

as there is no particle in the vacuum state to annihilate.

For any arbitrary Slater determinant, we have

$$\hat{a}_i \, |ijk \dots z\rangle = |ij \dots z\rangle \,, \tag{2.6}$$
$$\hat{a}_i \, |jk \dots z\rangle = 0 \tag{2.7}$$

SOMETHING MORE ABOUT THE DIFFERENT PERMUTATIONS.

We can now build a Slater determinant as the result of successive operation of several creation operators $\hat{a}_q^\dagger$ on the vacuum state,

$$\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k^\dagger \dots \hat{a}_z^\dagger \, |0\rangle = |ijk \dots z\rangle \,. \tag{2.8}$$

It is convenient to arrange the spinorbitals in a Slater determinant in alphabetical order, as in Equation 2.8. This makes it necessary to ascertain the effects a creation or annihilation operator will have on a Slater determinant when the affected orbital is not at the beginning of the string of orbitals in the Slater determinant. Generally we have,

$$\hat{P}\left|ijk\ldots z\right\rangle = (-1)^{\sigma(\hat{P})}\left|ijk\ldots z\right\rangle, \tag{2.9}$$

where $\hat{P}$ permutes the string of orbitals and $\sigma(\hat{P})$ is the parity of the permutation $\hat{P}$. we have

$$\hat{a}_p^\dagger\left|ijk\ldots z\right\rangle = (-1)^{\eta_p}\left|ijk\ldots p\ldots z\right\rangle, \tag{2.10}$$

$$\hat{a}_p\left|ijk\ldots p\ldots z\right\rangle = (-1)^{\eta_p}\left|ijk\ldots z\right\rangle, \tag{2.11}$$

where η_p is the number of orbitals preceeding the orbital ϕ_p, pertaining to the creation (annihilation) operator, in the Slater determinant.

2.2 Anticommutator Relations

Consider some creation operators acting on a Slater determinant,

$$\begin{aligned}\hat{a}_p^\dagger\hat{a}_q^\dagger\left|ijk\ldots\right\rangle &= \left|pqijk\ldots\right\rangle\\ \hat{a}_q^\dagger\hat{a}_p^\dagger\left|ijk\ldots\right\rangle &= \left|qpijk\ldots\right\rangle = -\left|pqijk\ldots\right\rangle.\end{aligned} \tag{2.12}$$

We demand that these two opartions be equivalent, or that

$$\begin{aligned}\hat{a}_p^\dagger\hat{a}_q^\dagger &= -\hat{a}_q^\dagger\hat{a}_p^\dagger\\ \{\hat{a}_p^\dagger,\hat{a}_q^\dagger\} &\equiv \hat{a}_p^\dagger\hat{a}_q^\dagger + \hat{a}_q^\dagger\hat{a}_p^\dagger = \hat{0}.\end{aligned} \tag{2.13}$$

This is one of several important anti-commutator relations for creation and annihilation operators.

Similarly, for annihilation operators we have

$$\begin{aligned}\hat{a}_p\hat{a}_q\left|qpijk\ldots\right\rangle &= \hat{a}_p\left|pijk\ldots\right\rangle = \left|ijk\ldots\right\rangle\\ \hat{a}_q\hat{a}_p\left|qpijk\ldots\right\rangle &= -\hat{a}_q\hat{a}_p\left|pqijk\ldots\right\rangle = -\hat{a}_q\left|qijk\ldots\right\rangle = -\left|ijk\ldots\right\rangle.\end{aligned} \tag{2.14}$$

These two operations must also be equivalent,

$$\begin{aligned}\hat{a}_p\hat{a}_q &= -\hat{a}_q\hat{a}_p\\ \{\hat{a}_p,\hat{a}_q\} &\equiv \hat{a}_p\hat{a}_q + \hat{a}_q\hat{a}_p = \hat{0}.\end{aligned} \tag{2.15}$$

One case remains, when a creation operator and an annihilation operator is applied together on a Slater determinant,

$$\hat{a}_p^\dagger\hat{a}_q\left|qijk\ldots\right\rangle = \hat{a}_p^\dagger\left|ijk\ldots\right\rangle = \left|pijk\ldots\right\rangle. \tag{2.16}$$

This operation will replace ϕ_q by ϕ_p even if ϕ_p would have been somewhere else in the interior of the Slater determinant. Any sign change as an effect of moving the orbital to the front of the string would be negated when the orbital is moved back to the original position. Exchanging the order of the operators however,

$$\hat{a}_q\hat{a}_p^\dagger\left|qijk\ldots\right\rangle = \hat{a}_q\left|pqijk\ldots\right\rangle = -\hat{a}_q\left|qpijk\ldots\right\rangle = -\left|pijk\ldots\right\rangle. \tag{2.17}$$

We again see a sign change and have,

$$\{\hat{a}_p^\dagger,\hat{a}_q\} = \hat{0} \quad (p \neq q). \tag{2.18}$$

If, on the other hand, $p = q$ we have

$$\begin{aligned}
\hat{a}_p^\dagger \hat{a}_p \left| pijk \ldots \right\rangle &= \left| pijk \ldots \right\rangle, \\
\hat{a}_p \hat{a}_p^\dagger \left| pijk \ldots \right\rangle &= 0,
\end{aligned} \tag{2.19}$$

and if the orbital ϕ_p in question does not appear in the Slater determinant,

$$\begin{aligned}
\hat{a}_p^\dagger \hat{a}_p \left| ijk \ldots \right\rangle &= 0, \\
\hat{a}_p \hat{a}_p^\dagger \left| ijk \ldots \right\rangle &= \hat{a}_p \left| pijk \ldots \right\rangle = \left| ijk \ldots \right\rangle.
\end{aligned} \tag{2.20}$$

For all cases we have that,

$$\left(\hat{a}_p^\dagger \hat{a}_p + \hat{a}_p \hat{a}_p^\dagger\right) \left| \ldots \right\rangle = \left| \ldots \right\rangle, \tag{2.21}$$

or

$$\{\hat{a}_p^\dagger, \hat{a}_p\} = \{\hat{a}_p, \hat{a}_p^\dagger\} = \hat{1}. \tag{2.22}$$

In conclusion, the anti-commutator relations of the creation and annihilation operators are,

$$\{\hat{a}_p, \hat{a}_q\} = \hat{0}, \tag{2.23}$$

$$\{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = \hat{0}, \tag{2.24}$$

$$\{\hat{a}_p^\dagger, \hat{a}_q\} = \{\hat{a}_p, \hat{a}_q^\dagger\} = \hat{\delta}_{pq}. \tag{2.25}$$

2.3 Representation of Operators

A second-qunatised one-body operator is written like

$$\hat{h} = \sum_{i=1}^{N} \hat{h}(i) = \sum_{ij} \left\langle i \right| \hat{h} \left| j \right\rangle \hat{a}_i^\dagger \hat{a}_j, \tag{2.26}$$

where in general, $\left\langle p \right| \hat{h} \left| q \right\rangle$ is the matrix element of the single-particle operator $\hat{h}$ in a given one-particle basis,

$$\left\langle p \right| \hat{h} \left| q \right\rangle = \int dx \phi_p(x)^* \hat{h} \phi_q(x). \tag{2.27}$$

More accurately, we see from Equation 2.26, that $\hat{h}$ weighs each occupied orbital of a Slater determinant with the appropriate matrix element.

A second-quantised two-body operator is written like

$$\hat{w} = \sum_{i,j}^{N} \hat{w}(i,j) = \frac{1}{2} \sum_{ijkl} \left\langle ij \right| \hat{w} \left| kl \right\rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k = \frac{1}{4} \sum_{ijkl} \left\langle ij|kl \right\rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k, \tag{2.28}$$

where

$$\left\langle ij \right| \hat{w} \left| kl \right\rangle \equiv \left\langle i(1) j(2) \right| \hat{w}_{12} \left| k(1) l(2) \right\rangle \tag{2.29}$$

and the antisymmetric two-eletron integral for $\hat{u}$ is abreviated,

$$\left\langle ij \right| \hat{w} \left| kl \right\rangle - \left\langle ij \right| \hat{w} \left| kl \right\rangle = \left\langle ij \right| \hat{w} \left| kl \right\rangle \equiv \left\langle ij|kl \right\rangle. \tag{2.30}$$

Similarly to the one-particle operator, the two-particle operator assigns the correct matrix element to pairs of single particle functions.

The second-quantised Hamiltonian can therefore be written,

$$\hat{H} = \hat{h} + \hat{w} = \sum_{ij} \hat{h}_{ij} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{4} \left\langle ij|kl \right\rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k. \tag{2.31}$$

2.4 Normal Order and Wick's Theorem

We have built the foundations necessary to describe wavefunctions in terms of creation- and annihilation operators as well as a simple way of writing a general electronic Hamiltionian in the second-quantised manner. The following is a necessety to be able to compute vacuum expectation values ($\langle -| \hat{A}\hat{B} \ldots |-\rangle$) of products of creation- and annihilation operators. Such expectation values are very important for several computational methods, see Harris, Monkhorst and Freeman (1992)[22].

2.4.1 Normal ordering and contractions

The normal-ordered product of a string of operators $\hat{A}_1$, $\hat{A}_2$, $\hat{A}_3$, ..., is defined as the rearranged product of operators such that all the creation operators are the left of all the annihilation operators, including a phase factor corresponding to the parity of the permutation producing the rearrangent

$$
\begin{aligned}
n[\hat{A}_1\hat{A}_2\ldots\hat{A}_n] &\equiv (-1)^{|\sigma|}\hat{A}_{\sigma(1)}\hat{A}_{\sigma(2)}\ldots\hat{A}_{\sigma(n)} \\
&= (-1)^{\sigma(\hat{P})}\hat{P}(\hat{A}_1\hat{A}_2\ldots\hat{A}_n) \\
&= (-1)^{|\sigma|}[\text{creation operators}]\cdot[\text{annihilation operators}] \\
&= (-1)^{|\sigma|}\hat{a}^\dagger\hat{b}^\dagger\ldots\hat{u}\hat{v},
\end{aligned}
\tag{2.32}
$$

where $\hat{P}$ is a permutation operator actiing on the product of operators, and σ is the parity of the permutation. One should bear in mind that this definition is by no means unique. Here are some examples,

$$
\begin{gathered}
n[\hat{a}^\dagger\hat{b}] = \hat{a}^\dagger\hat{b} \quad n[\hat{b}\hat{a}^\dagger] = -\hat{a}^\dagger\hat{b} \\
n[\hat{a}\hat{b}] = \hat{a}\hat{b} = -\hat{b}\hat{a} \\
n[\hat{a}^\dagger\hat{b}^\dagger] = \hat{a}^\dagger\hat{b}^\dagger = -\hat{b}^\dagger\hat{a}^\dagger \\
n[\hat{a}^\dagger\hat{b}\hat{c}^\dagger\hat{d}] = -\hat{a}^\dagger\hat{c}^\dagger\hat{b}\hat{d} = \hat{c}^\dagger\hat{a}^\dagger\hat{b}\hat{d} = \hat{a}^\dagger\hat{c}^\dagger\hat{d}\hat{b} = -\hat{c}^\dagger\hat{a}^\dagger\hat{d}\hat{b}.
\end{gathered}
$$

Note that the second quantised Hamiltonian in Equation 2.31 is already on normal-ordered form.

For two arbitrary creation and annihilation operators, we define their contraction as

$$\overbracket{\hat{A}\hat{B}} \equiv \langle -| \hat{A}\hat{B} |-\rangle, \tag{2.33}$$

equivalently,

$$\overbracket{\hat{A}\hat{B}} \equiv \hat{A}\hat{B} - n[\hat{A}\hat{B}]. \tag{2.34}$$

For a creation- and annihilation operator there are four possible contractions,

$$
\begin{aligned}
\overbracket{\hat{a}^\dagger\hat{b}^\dagger} &= \langle -| \hat{a}^\dagger\hat{b}^\dagger |-\rangle = \hat{a}^\dagger\hat{b}^\dagger - n[\hat{a}^\dagger\hat{b}^\dagger] = 0 \\
\overbracket{\hat{a}\hat{b}} &= \langle -| \hat{a}\hat{b} |-\rangle = \hat{a}\hat{b} - n[\hat{a}\hat{b}] = 0 \\
\overbracket{\hat{a}^\dagger\hat{b}} &= \langle -| \hat{a}^\dagger\hat{b} |-\rangle = \hat{a}^\dagger\hat{b} - n[\hat{a}^\dagger\hat{b}] = 0 \\
\overbracket{\hat{a}\hat{b}^\dagger} &= \langle -| \hat{a}\hat{b}^\dagger |-\rangle = \hat{a}\hat{b}^\dagger - n[\hat{a}\hat{b}^\dagger] = \hat{a}\hat{b}^\dagger - (-\hat{b}^\dagger\hat{a}) = \{\hat{a}, \hat{b}^\dagger\} = \delta_{ab}.
\end{aligned}
\tag{2.35}
$$

We see that all contractions between creation- and annihilation operators are a number, most of them are zero and only those with a annihilation operator to the left and a creation operator to the right can be one.

Contrations inside a normal ordered product is definded as follows,

$$n[\hat{A}\hat{B}\hat{C}\ldots\hat{R}\ldots\hat{S}\ldots\hat{T}\ldots\hat{U}\ldots] = (-1)^{\sigma}\hat{R}\hat{T}\hat{S}\hat{U}\ldots n[\hat{A}\hat{B}\hat{C}\ldots], \tag{2.36}$$

where all contracted operator pairs are moved to the front of the normal ordered product, and σ is the parity of the permutations required for this relocation. The result will be zero, or plus or minus the normal ordred product without the contracted operator pairs.

2.4.2 Wick's Theorem

Wick's theorem states that every string of creation and annihilation operators can be written as a sum of normal-ordered products with all possible contractions,

$$\begin{aligned}\hat{A}\hat{B}\hat{C}\hat{D}\cdots =& n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] \\ &+ \cdots + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + \cdots + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + \cdots + \\ &+ n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + n[\hat{A}\hat{B}\hat{C}\hat{D}\ldots] + \ldots,\end{aligned} \tag{2.37}$$

where eventually all possible contractions of one, two pairs etc, are included.

Especially when computing vacuum expectation values of normal-ordred products is Wick's theorem very important. The reason for this is that each contraction will not contribute to the result, unless it is a fully contracted operator string,

$$\langle|\,\hat{A}\ldots\hat{B}\ldots\hat{C}\ldots\hat{D}\ldots|\rangle = \sum_{\substack{\text{all possible}\\ \text{contractions}}} \langle|\,n[\hat{A}\ldots\hat{B}\ldots\hat{C}\ldots\hat{D}\ldots]\,|\rangle\,. \tag{2.38}$$

Most vacuum expectation values contain operators strings already have substrings that are already normal-ordered. This warrants a very useful generalisation of Wick's theorem for such strings,

$$\begin{aligned}n[\hat{A}_1\hat{A}_2\ldots]n[\hat{B}_1\hat{B}_2\ldots]\ldots n[\hat{Z}_1\hat{Z}_2\ldots] &= n[\hat{A}_1\hat{A}_2\cdots:\hat{B}_1\hat{B}_2\cdots:\cdots:\hat{Z}_1\hat{Z}_2\ldots] \\ + \sum_{(1)} n[\hat{A}_1\hat{A}_2\cdots:\hat{B}_1\hat{B}_2\cdots:\cdots:\hat{Z}_1\hat{Z}_2\ldots] &+ \cdots + \sum_{(n)} n[\hat{A}_1\ldots\ldots\ldots\hat{Z}_N],\end{aligned} \tag{2.39}$$

where we sum over all combinations of contractions that each involce operators from different substrings, starting with one contractions and up to when all opertors, or as many as possible, are contracted.

2.4.3 Particle-Hole Formalism

We see that a Slater determinant can be built recursively with creation operators,

$$\hat{I} = \widehat{i_1 i_2 \ldots i_N} = \hat{i}_1^{\dagger}\hat{i}_2^{\dagger}\ldots\hat{i}_N^{\dagger}\,|\rangle\,. \tag{2.40}$$

Instead of rewriting Slater determinants with operators applied to the vacuum state in this manner we will introduce the convenient reference state, or Fermi vacuum, Slater determinant,

$$|0\rangle = |\Phi_0\rangle = |ijk\ldots n\rangle\,. \tag{2.41}$$

We will define other Slater determinants relative to this reference state. For instance,

$$|\Phi_i^a\rangle \equiv \hat{a}^\dagger \hat{i} |\Phi_0\rangle = |ajk\dots n\rangle \tag{2.42}$$

$$\left|\Phi_{ij}^{ab}\right\rangle \equiv \hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i} |\Phi_0\rangle = |abk\dots n\rangle \tag{2.43}$$

$$|\Phi_i\rangle \equiv \hat{i} |\Phi_0\rangle = |jk\dots n\rangle \tag{2.44}$$

$$|\Phi^a\rangle \equiv \hat{a}^\dagger |\Phi_0\rangle = |aijk\dots n\rangle \tag{2.45}$$

where equations 2.42, 2.43 2.44 and 2.45 constitues a single excitation, a double excitation, an electorn removal and an electron attachment, respectively. Note that these reference relative Slater determinants have the following properties,

$$\left|\Phi_{ij}^{ab}\right\rangle = \left|\Phi_{ji}^{ba}\right\rangle = -\left|\Phi_{ij}^{ba}\right\rangle = -\left|\Phi_{ji}^{ab}\right\rangle. \tag{2.46}$$

Take note of the specific letters used for creating and annihilating electrons in the example above. $i, j, k, l, \dots$ are letters restricted to indices of *hole* states, $a, b, c, d, \dots$ are letters restriced to indices of *particle* states and the $p, q, r, \dots$ are for general use, indicating any state. Notice that

$$\begin{aligned} \hat{i}^\dagger |0\rangle = 0 \quad \hat{a} |0\rangle = 0, \\ \langle 0| \hat{i} = 0 \quad \langle 0| \hat{a}^\dagger = 0. \end{aligned} \tag{2.47}$$

Whenever we try to insert an electron where there already is one, or when we try to remove an electron that is not there, we get zero as result.

2.4.4 Wick's theorem relative to the Fermi vacuum

Now we will modify the concepts of normal-ordering, contractions and Wick's theoreom so that the work better in conjunction with the Fermi vacuum, instead of the physical vacuum.

First we introduce pseudo-operators,

$$\begin{aligned} \hat{b}_i = \hat{i}^\dagger, \quad \hat{b}_i^\dagger = \hat{i} \\ \hat{b}_a = \hat{a}^\dagger, \quad \hat{b}_i^\dagger = \hat{a}^\dagger, \end{aligned} \tag{2.48}$$

where $\hat{b}_i^\dagger$ is a hole creation operator and $\hat{b}_i$ is a particle creation operator, but only for vacant spaces below the fermi level. The reasoning for introducing such operators is to be able to work with the fermi vacuum in the same manner as regular operators work with the physical vacuum.

We introduce a new type of normal ordering for the pseudo-operators (and for the actual operators that the represent),

$$\{\hat{A}\hat{B}\hat{C}\} = (-1)\hat{b}_p^\dagger \hat{b}_q^\dagger \dots \hat{b}_u \hat{b}_v. \tag{2.49}$$

We write a contraction in the same manner,

$$\overline{\hat{A}\hat{B}} = \hat{A}\hat{B} - \{\hat{A}\hat{B}\}. \tag{2.50}$$

A normal-ordered product with contractions inside is also definede the same way.

For contractions we see that the only non-zero contractions are

$$\overline{\hat{b}_i \hat{b}_j^\dagger} = \overline{\hat{i}^\dagger \hat{j}} = \delta_{ij}, \quad \overline{\hat{b}_a \hat{b}_b^\dagger} = \overline{\hat{a}\hat{b}^\dagger} = \delta_{ab}. \tag{2.51}$$

Here we are also made aware the first benefit of pseudo-operators. More generally we have the anticommutator relations

$$\{\hat{b}_p, \hat{b}_q^\dagger\} = \delta_{pq}, \quad \{\hat{b}_p, b_q\} = 0 \tag{2.52}$$

Excited Slater determinants can be written using pseudo-operators,

$$|\Phi_i^a\rangle \equiv \hat{b}_a^\dagger \hat{b}_i^\dagger |\Phi_0\rangle \tag{2.53}$$

$$\left|\Phi_{ij}^{ab}\right\rangle \equiv \hat{b}_b^\dagger \hat{b}_j^\dagger \hat{b}_a^\dagger \hat{b}_i^\dagger |\Phi_0\rangle \tag{2.54}$$

Part II

Quantum Many-Body Approximations

Chapter 3

Hartree-Fock Theory

In 1927, soon after the discovery of the Schrödinger equation in 1926, Douglas R. Hartree introduced a procedure which he called the self-consistent field method[23]. Hartree sought to do without empirical parameters and to solve the many-body time-independent Schrödinger equation from fundamental principles, *ab initio*. A year later John C. Slater and John A. Gaunt provided a sounder theoretical basis for the Hartree method by applying the variational principle to a trial wave function as a product of single-particle functions[62][19]. Slater later pointed out, with support from Vladimir A. Fock, that the method merely applied the Pauli exclusion principle in its older, incorrect formulation; forbidding presence of two electrons in the same state, but neglecting quantum statistics[61][18]. It was shown that a Slater determinant satisfies the antisymmetric property of the exact solution and would be a suitable ansatz for applying the variational principle. Later, Hartree reformulated the method for calculation[24].

The Hartree-Fock methods makes the following simplications to the multi-electron atomic (molecular) problem,

- The full molecular wavefunction is contrained to a function of the coordinates of only the electrons in the molecule. In not so many words, the Born-Oppernheimer approximation is inerent in the method.

- Any relativistic effects are completely ignored, i.e. the momentum operator is assumed to be completely non-relativistic.

- A variational solution is assumed to be a linear combination of a basis set, which is assumed to be approximately complete. This set of basis functions is usually orthogonal, but may not be.

- Some electron correlation effects are ignored, as the methods implies a mean-field approximation. Coulomb correlation is fully incorporated in the Hartree-Fock method, but it ignores Fermi Correlation and is therefore inable to describe some effects, like London dispersion[1].

- Any energy eigenfunction is assumed to be describable by a single Slater determinant.

Relaxation of the last two simplifications give rise to the large group of many-body methods commonly referred to as post-Hartree-Fock methods.

[1]Named after Fritz London; London dispersion forces (LDF) are a type of force between atoms and molecules[26]

3.1 Deriving the Hartree-Fock Equations

Consider a Hamiltonian for some system

$$\hat{H} = \hat{H}_0 + \hat{W}, \quad \hat{H}_0 = \sum_{i}^{N} \hat{h}(i), \tag{3.1}$$

where the ground state of $\hat{H}_0$ is a Slater determinant consisting of N single-particle functions,

$$\Phi = \mathscr{A}\phi_1\phi_2\ldots\phi_N, \quad \langle\phi_i|\phi_j\rangle = \delta_{ij}. \tag{3.2}$$

If $\hat{W}$ is only a limited perturbation to the system, it is reasonable to assume that the actual ground state of the full system can also be represented by a Slater determinant. Because the Hartree-Fock theory includes a mean-field approximation, each particle moves independently of the others interacting with the remainding electrons only idirectly through an average potential $\hat{v}^{\mathrm{HF}}$.

The expectation value of the Hamiltonian in Equation 3.1 is

$$\langle\Phi|\,\hat{H}\,|\Phi\rangle = \sum_i \langle\phi_i|\,\hat{h}\,|\phi_i\rangle + \frac{1}{2}\sum_{ij}\langle\phi_i\phi_k|\,\hat{w}\,|\phi_i\phi_j - \phi_j\phi_i\rangle\,, \tag{3.3}$$

where

$$\langle\phi_i\phi_j|\,\hat{w}\,|\phi_k\phi_l\rangle = \int\int \bar{\phi}_i(1)\bar{\phi}_j(2)\hat{w}(1,2)\phi_k(1)\phi_l(2)d1d2$$

Now we want to minimise the energy (Equation 3.1) under the contraint of orthonormal single-particle functions, id est $\langle\phi_i|\phi_k\rangle = \delta_{ij}$. The minimum solution is called the Hatree-Fock state, $|\Phi_{\mathrm{HF}}\rangle$. An optimisation problem with a constraint begs the formualtion of a Lagrangian functional with a Lagrange multiplier for each constraint,

$$\begin{aligned}\mathscr{L}(\phi_1,\ldots,\phi_n,\lambda) &= \langle\Phi|\,\hat{H}\,|\Phi\rangle - \sum_{ij}\lambda_{ij}(\langle\phi_i|\phi_j\rangle - \delta_{ij}) \\ &= \sum_i\langle\phi_i|\,\hat{h}\,|\phi_i\rangle + \frac{1}{2}\sum_{ij}\langle\phi_i\phi_j|\,\hat{w}\,|\phi_i\phi_j - \phi_j\phi_i\rangle - \sum_{ij}\lambda_{ij}(\langle\phi_i|\phi_j - \delta_{ij}\rangle).\end{aligned} \tag{3.4}$$

The constraints can always be treated separately, $\partial\mathscr{L}/\partial\lambda_{ij}\,\langle\phi_i|\phi_j\rangle - \delta_{ij}$, as this demand will be fullfilled by finding that the solutions ϕ_i are orthonormal.

In order to find the optimum of the Lagrangian in (Equation 3.4), we choose a $k \in \{1,\ldots,N\}$ and compute the directional derivative of ϕ_k^*, by varying this single particle function and leaving all others fixed,

$$\delta\phi_k = \epsilon\eta, \quad \delta\phi_l = 0, k \neq l, \tag{3.5}$$

where ϵ is some small number, and η is a normalized single-particle function. We define a function representing this variation,

$$f(\epsilon) = \mathscr{L}(\phi_1,\ldots,\phi_k + \epsilon\eta,\ldots,\phi_N,\lambda), \tag{3.6}$$

expanded to first order in ϵ,

$$f(\epsilon) = f(0) + \epsilon f'(0) + \mathscr{O}(\epsilon^2). \tag{3.7}$$

For an optimum we must have

$$f'(0) = 0, \quad \forall\eta, \tag{3.8}$$

which means that the directional derivative of $\mathscr{L}$ at $\{\phi_i\}_{i=1}^N$, in the direction η vanishes.

We compute the Taylor expansion of the varied Lagrangian (Equation 3.6),

$$\begin{aligned} f(\epsilon) = \sum_i \langle \phi_i + \delta_{ki}\epsilon\eta | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_{ij} \langle (\phi_i + \delta_{ki}\epsilon\eta)(\phi_j + \delta_{kj}\epsilon\eta) | \hat{w} | \phi_i\phi_j - \phi_j\phi_i \rangle \\ - \sum_{ij} \lambda_{ij} (\langle \phi_i + \delta_{ik}\epsilon\eta | \phi_j \rangle - \delta_{ij}) + \mathscr{O}(\epsilon^2) \end{aligned} \tag{3.9}$$

$$\begin{aligned} = \sum_i \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_i j \langle \phi_i\phi_j | \hat{w} | \phi_i\phi_j - \phi_j\phi_i \rangle + \epsilon \langle \eta | \hat{h} | \phi_k \rangle \\ + \frac{1}{2} \sum_{ij} \langle \phi_i \delta_{kj} \epsilon\eta | \hat{w} | \phi_i\phi_j - \phi_j\phi_i \rangle \\ + \frac{1}{2} \sum_{ij} \langle \delta_{ki} \epsilon\eta\phi_j | \hat{w} | \phi_i\phi_j - \phi_j\phi_i \rangle \\ - \sum_{ij} \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) - \sum_{ij} \lambda_{ij} (\langle \delta_{ik}\epsilon\eta | \phi_j \rangle - \delta_{ij}) + \mathscr{O}(\epsilon^2) \end{aligned} \tag{3.10}$$

$$\begin{aligned} = \sum_i \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_i j \langle \phi_i\phi_j | \hat{w} | \phi_i\phi_j - \phi_j\phi_i \rangle + \epsilon \langle \eta | \hat{h} | \phi_k \rangle - \sum_{ij} \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \\ + \frac{1}{2}\epsilon \sum_i \langle \phi_i\eta | \hat{w} | \phi_i\phi_k \rangle - \frac{1}{2}\epsilon \sum_i \langle \phi_i\eta | \hat{w} | \phi_k\phi_i \rangle \\ + \frac{1}{2}\epsilon \sum_j \langle \eta\phi_j | \hat{w} | \phi_k\phi_j \rangle - \frac{1}{2}\epsilon \sum_j \langle \eta\phi_j | \hat{w} | \phi_j\phi_k \rangle \\ - \epsilon \sum_j \lambda_{jk} \langle \eta | \phi_j \rangle + \mathscr{O}(\epsilon^2) \end{aligned} \tag{3.11}$$

$$\begin{aligned} = \sum_i \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_i j \langle \phi_i\phi_j | \hat{w} | \phi_i\phi_j - \phi_j\phi_i \rangle - \sum_{ij} \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \\ + \epsilon \langle \eta | \hat{h} | \phi_k \rangle + \epsilon \sum_i \langle \eta\phi_i | \hat{w} | \phi_k\phi_i \rangle - \epsilon \sum_i \langle \eta\phi_i | \hat{w} | \phi_i\phi_k \rangle \\ - \epsilon \sum_j \lambda_{jk} \langle \eta | \phi_j \rangle + \mathscr{O}(\epsilon^2) \end{aligned} \tag{3.12}$$

Notice that the zeroth term, represented by the first line in Equation 3.12, is simply the original Lagrangian in Equation 3.4. We equate all the first-order terms to zero,

$$\langle \eta | \hat{h} | \phi_k \rangle + \sum_i \langle \eta\phi_i | \hat{w} | \phi_k\phi_i \rangle - \sum_i \langle \eta\phi_i | \hat{w} | \phi_i\phi_k \rangle - \sum_i \lambda_{ik} \langle \eta | \phi_i \rangle = 0. \tag{3.13}$$

This must be valid for any choice η, meaning

$$\hat{h} | \phi_k \rangle + \sum_i \langle \cdot\ \phi_i | \hat{w} | \phi_k\phi_i \rangle - \sum_i \langle \cdot\ \phi_i | \hat{w} | \phi_i\phi_k \rangle - \sum_i \lambda_{ik} | \phi_i \rangle = 0, \tag{3.14}$$

where $\langle \cdot\ \phi_1 | \hat{w} | \phi_2\phi_3 \rangle \in L_1^2$ is interpreted as an integral over only the second particle in the matrix element. We define,

$$\hat{v}_{\text{HF}} = \hat{v}_{\text{direct}} + \hat{v}_{\text{exchange}} = \sum_i \langle \cdot\ \phi_i | \hat{w} | \phi_k\phi_i \rangle - \sum_i \langle \cdot\ \phi_i | \hat{w} | \phi_i\phi_k \rangle \tag{3.15}$$

$$\hat{f} = \hat{h} + \hat{v}_{\text{HF}}, \tag{3.16}$$

and can then rewrite Equation 3.14 to

$$\hat{f}\,|\phi_i\rangle = \sum_j \lambda_{ij}\,|\phi_j\rangle\,, \tag{3.17}$$

which are the non-canonical Hartree-Fock equations.

It so happends that the Slater dertminant $|\Phi\rangle$ is invariant under unitary transformation of the single particle functions. Consider

$$\tilde{\phi}_k = \sum_j \phi_j U_{jk}, \tag{3.18}$$

where U is a unitary matrix. This implies that $\left|\tilde{\Phi}\right\rangle = \det(U)\,|\Phi\rangle$, is the same state and the energy must be the same as well. We choose a particular unitary transformation U, rotating the single particle functions in a certain manner so that $\lambda = UEU^H$, where $E_{jk} = \delta_{jk}\epsilon_k$ are the elemnets of a diagonal matrix (the eigenvalues of λ). This provides us with a new set of eigenvalue equations,

$$\hat{f}(\tilde{\phi}_1, \dots, \tilde{\phi}_N)\,|\tilde{\phi}_i\rangle = \epsilon_i\,|\tilde{\phi}_i\rangle\,, \tag{3.19}$$

which are the canonical Hartree-Fock equations. From now on we will stick with these equations and suppress the tilde notations.

3.2 The Roothan-Hall Equations

In order to solve the Hartree-Fock equations (Equation 3.19) we render the equations in a finite, fixed basis $\{\chi_p\}_{p=1}^{L}$ of a finite size L. It is not a necessity for this basis to be orthonormal, and we therefore define the overlap matrix,

$$S_{pq} \equiv \langle \chi_p | \chi_q \rangle\,. \tag{3.20}$$

The Hartree-Fock single-particle functions are expanded in this basis,

$$|\phi_p\rangle = \sum_q |\chi_q\rangle\, U_{qp}, \tag{3.21}$$

where U is not necessarily unitary, because the basis is not necessarily orthongonal. However, we do have $U^H S U = \hat{1}$.

We insert the expansion from Equation 3.21 into the expression for the canonical Hatree-Fock equations from Equation 3.19,

$$\hat{f}\sum_r |\chi_r\rangle\, U_{rp} = \epsilon_p \sum_r |\chi_r\rangle\, U_{rp}. \tag{3.22}$$

Then we left project with an arbitrary function from our new basis,

$$\begin{aligned} \langle \chi_q|\,\hat{f}\sum_r |\chi_r\rangle\, U_{rp} &= \epsilon_r\,\langle \chi_q|\chi_r\rangle \sum_r U_{rp}\ \forall q,p \\ \sum_r F_{qr}U_{rp} &= \epsilon_r \sum_r S_{qr}U_{rp}\ \forall q,p \\ F(D)U &= SU\epsilon. \end{aligned} \tag{3.23}$$

where the last line is the Roothan-Hall equations.

Elaborating on the computation of the Fock matrix element,

$$F_{qp} = \langle \chi_q | \hat{f} | \chi_p \rangle = \langle \chi_q | \hat{h} | \chi_p \rangle + \langle \chi_q | \hat{v}_{\text{direct}} | \chi_p \rangle - \langle \chi_q | \hat{v}_{\text{exchange}} | \chi_p \rangle , \tag{3.24}$$

where

$$\begin{aligned} \langle \chi_q | \hat{v}_{\text{direct}} | \chi_p \rangle &= \sum_j \langle \chi_q \phi_j | \hat{w} | \chi_p \phi_j \rangle = \sum_{p'q'j} U_{jq'} U^*_{jp'} \langle \chi_q \chi_{q'} | \hat{w} | \chi_p \chi_{p'} \rangle \\ &= \sum_{p'q'} D_{p'q'} \langle \chi_q \chi_{q'} | \hat{w} | \chi_p \chi_{p'} \rangle \end{aligned} \tag{3.25}$$

$$\begin{aligned} \langle \chi_q | \hat{v}_{\text{exchange}} | \chi_p \rangle &= \sum_j \langle \chi_q \phi_j | \hat{w} | \phi_j \chi_p \rangle = \sum_{p'q'j} U_{jq'} U^*_{jp'} \langle \chi_q \chi_{q'} | \hat{w} | \chi_{p'} \chi_p \rangle \\ &= \sum_{p'q'} D_{p'q'} \langle \chi_q \chi_q' | \hat{w} | \chi_p' \chi_p \rangle , \end{aligned} \tag{3.26}$$

giving us,

$$F_{qp} = \langle \chi_q | \hat{h} | \chi_p \rangle + \sum_{p'q'} D_{p'q'} (\langle \chi_q \chi_{q'} | \hat{w} | \chi_p \chi_{p'} \rangle - \langle \chi_q \chi_{q'} | \hat{w} | \chi_{p'} \chi_p \rangle), \tag{3.27}$$

where $D = UU^H$, is the density matrix.

The benefit of the Roothan-Hall equations (Equation 3.21), is that they are represented by matrices, and therefore easy to implement on a computer. The Roothan-Hall equations are solved iterably, starting from an initial guess for U. This guess can be used to compute the density matrix, $D^(k) = \sum_i u_i^{(k)} (u_i^{(k)})^*$, where k denotes the iteration. The density matrix is used to compute the Fock matrix. This provides us with a general eigenvalue problem, from which a new U and ϵ can be found. This formula is then repeated until the the iterations converge. At this point we say that we have self-consitency in the mean field, and this method is usually called the method of self-constistent field (SCF) iterations.

3.3 Restricted Hartree-Fock Theory

Consider some jolly band of N electrons confined in a potential. To begin with we will assumes that these are non-interacting, and can therefore be described only by the one-body part of the Hamiltionian,

$$\hat{h}(\mathbf{r}) = \hat{t}(\mathbf{r}) + \hat{v}(\mathbf{r}), \tag{3.28}$$

where $\hat{v}$ is potential set up by an atomic nucleus, or some other confining force. The one-body operators $\hat{h}$ does noe coupled to electron spin, so the spinorbitals or single-particle eigenfunctions of $\hat{h}$ separate,

$$\phi_P(\mathbf{r}, \sigma) = \varphi_p(\mathbf{r}) \chi_\alpha(\sigma), \tag{3.29}$$

where $P = (p, \sigma)$ si the combined spin- and spatial index, $\alpha = \pm 1/2$ is the value of the projection of the electron spin along the z-axis. The spin indcex/coordnitate can only take values $\sigma \pm 1$, and we have orthonormal spinorbitals, $\langle \chi_\alpha | \chi_\beta \rangle = \delta_{\alpha\beta}$.

We restrict the orbitals to have the same spatial wavefunction for spin up and spin down, and we consider only closed-shell configurations. This means that our molecular wavefunctions, in the form of a Slater determinant, can only have an even number of N electrons, with all electrons paired in such a manner that there are two spin values for each of the $n = N/2$ spatial orbitals. The N-electron ground state of $\hat{h}$ is given by the first N eigenfunctions $\phi_{(p,\sigma)}$ occupied,

$$|\Phi\rangle = \left| \phi_{1,+} \phi_{1,-} \dots \phi_{\frac{N}{2},+} \phi_{\frac{N}{2},-} \right\rangle , \tag{3.30}$$

commonly also written as

$$|\Phi\rangle_{\text{RHF}} = |\varphi_1\bar{\varphi}_1 \dots \varphi_{N/2}\bar{\varphi}_{N/2}\rangle\,. \tag{3.31}$$

The reasoning behind this restriction is that one would assume, for many systems, that the exact wavefunctions has the same kind of structure. This is true for almost all electronic systems in nature. We thererfore do not optimise all the N single-particle functions freely, but asume that they form sets fo doubly occupied spatial orbitals. Matrix elements can now be computed more easily on the restricted form,

$$\langle\phi_{(p,\alpha)}|\hat{h}|\phi_{(q,\beta)}\rangle = \langle\chi_\alpha|\chi_\beta\rangle \int d\mathbf{r}\varphi_p(\mathbf{r})^*\hat{h}\varphi_q(\mathbf{r}). \tag{3.32}$$

And similarly for two-body operators,

$$\langle\phi_{p\alpha}\phi_{q\beta}|\hat{w}|\phi_{r\gamma}\phi_{s\delta}\rangle = \langle\chi_\alpha|\chi_\gamma\rangle\,\langle\chi_\beta|\chi_\delta\rangle \int\int d\mathbf{r}_1 d\mathbf{r}_2\varphi_p(\mathbf{r}_1)\varphi_q(\mathbf{r}_2)\hat{w}(\mathbf{r}_1\mathbf{r}_2)\varphi_r(\mathbf{r}_1)\varphi_s(\mathbf{r}_2) \tag{3.33}$$

Now we will find the special form of the Fock operator in restricted Hartree-Fock theory. First we insert the wavefunction restriction into the Hartree-Fock equation

$$\begin{aligned} \hat{f}\phi_I(\mathbf{r},\sigma) &= \epsilon_i\phi_I(\mathbf{r},\sigma) \\ \hat{f}\varphi(\mathbf{r})\chi_\alpha(\sigma) &= \epsilon_i\varphi_i(\mathbf{r})\chi_\alpha(\sigma). \end{aligned} \tag{3.34}$$

Here we have joined the spatial- and spin index with a capital letter $I = (i, \alpha)$. We left multipy with χ_α^*, suppress indices for brevity and integrate over spin,

$$\langle\chi_\alpha|\hat{f}|\varphi_i\chi_\alpha\rangle = \left\langle\chi_\alpha\middle|\hat{f}\middle|\phi_{I=(i,\alpha)}\right\rangle = \epsilon_i\varphi_i. \tag{3.35}$$

Next we insert the Fock operator,

$$\hat{f} = \hat{h} + \sum_i \langle\cdot\varphi_i|(\hat{w} - \hat{P}_{12})|\cdot\varphi_i\rangle$$

This special notation is means that we integrate over the second orbital in the bra and ket only. After insertion we get

$$\begin{aligned} \langle\chi_\alpha|\hat{h}|\chi_\alpha\rangle\,\varphi_i + \sum_J \langle\chi_\alpha\phi_J|(\hat{w} - \hat{P}_{12})|\phi_I\phi_J\rangle &= \epsilon_i\varphi_i \\ \to \hat{h}\varphi_i + \sum_J \langle\chi_\alpha\phi_J|\hat{w}|\phi_I\phi_J\rangle - \sum_J \langle\chi_\alpha\phi_J|\hat{w}|\phi_J\phi_I\rangle &= \epsilon_i\varphi_i. \end{aligned} \tag{3.36}$$

Because if we have a closed-shell system, them over occupied spinorbitals include an equal sum over spin up and spin down functions so that

$$\sum_J^n = \sum_\beta \sum_j^{n/2}.$$

We next insert this into our eigenvalue equation and split the single-particle functions into separate spin- and spatial orbitals,

$$\begin{aligned} \hat{h}\varphi_i + \sum_\beta\sum_j^{n/2} \langle\chi_\alpha\varphi_j\chi_\beta|\hat{w}|\varphi_i\chi_\alpha\varphi_j\chi_\beta\rangle - \sum_\beta\sum_j^{n/2} \langle\chi_\alpha\varphi_j\chi_\beta|\hat{w}|\varphi_j\chi_\beta\varphi_i\chi_\alpha\rangle \\ = \hat{h}\varphi_i + 2\sum_j^{n/2} \langle\cdot\varphi_j|\hat{w}|\varphi_i\varphi_j\rangle + \sum_j^{n/2} \langle\cdot\varphi_j|\hat{w}|\varphi_j\varphi_i\rangle = \epsilon_i\varphi_i. \end{aligned} \tag{3.37}$$

We now have the from of the Fock operator within the restricted Hartree-Fock theory,

$$
\begin{aligned}
\hat{f} &= \hat{h} + \sum_{i}^{n/2} \langle \cdot\varphi_i | (2\hat{w} - \hat{P}_{12}) | \cdot\varphi_i \rangle \\
&= \hat{h} + 2\sum_{i}^{n/2} \int d\mathbf{r}_2 \varphi_i^*(\mathbf{r}_2) \hat{w} \varphi_i(\mathbf{r}_2) - \sum_{i}^{n/2} \int d\mathbf{r}_2 \varphi_i^*(\mathbf{r}_2) \hat{w} \varphi_j(\mathbf{r}_2)
\end{aligned}
\tag{3.38}
$$

The Hartee-Fock energy also has a special form in the restricted Hartree-Fock realm,

$$
\begin{aligned}
\langle \Phi | \hat{H} | \Phi \rangle =& \sum_P \langle \phi_P | \hat{h} | \phi_P \rangle + \frac{1}{2} \sum_P \sum_Q \langle \phi_P \phi_Q | (\hat{w} - \hat{P}_{12}) | \phi_P \phi_Q \rangle \\
=& \sum_\alpha \sum_p^{n/2} \left\langle \phi_{(p,\alpha)} \middle| \hat{h} \middle| \phi_{(p,\alpha)} \right\rangle \\
&+ \sum_\alpha \sum_p^{n/2} \sum_\beta \sum_q^{n/2} \left\langle \phi_{(p,\alpha)} \phi_{(q,\beta)} \right| \hat{w} \left(\left| \phi_{(p,\alpha)} \phi_{(q,\beta)} \right\rangle - \left| \phi_{(q,\beta)} \phi_{(p,\alpha)} \right\rangle \right) \\
=& 2\sum_p^{n/2} \langle \varphi_p | \hat{h} | \varphi_q \rangle + 2\sum_{pq}^{n/2} \langle \varphi_p \varphi_q | \hat{w} | \varphi_p \varphi_q \rangle - \sum_{pq}^{n/2} \langle \varphi_p \varphi_q | \hat{w} | \varphi_p \varphi_q \rangle
\end{aligned}
\tag{3.39}
$$

3.4 Unrestricted Hartree-Fock Theory

The restricted Hartree-Fock model i often a good enough approximation, but under some circumstances it will fail to provide a good result. The unrestricted Hartree-Fock model is an intermediate between the general Hartree-Fock model and the restricted Hatree-Fock model. Compared with the restricted Hartre-Fock single-particle wavefunction form, the unrestricted for is somewhat obviuous as we now allo the spins to be different,

$$
\phi_P(\mathbf{r}, \sigma) = \varphi_p^\alpha(\mathbf{r}) \chi_\alpha(\sigma), \tag{3.40}
$$

where we have given a the spatial orbitals a spin-index as well. As before, a capital index is the combined spatial- and spin index $P = (p, \alpha)$, where $P \in [1, L]$, $p \in [1, L/2]$ and $\alpha = \pm 1/2$. Like before, we require the states to be orthonormal

$$
\langle \phi_P | \phi_Q \rangle = \left\langle \varphi_p^\alpha \middle| \varphi_q^\beta \right\rangle \varphi \chi_\alpha \chi_\beta = \delta_{PQ}. \tag{3.41}
$$

we can write a general unrestricted Hartree-Fock state as

$$
|\Phi\rangle_{\mathrm{UHF}} = |\varphi_1^{1/2} \varphi_1^{-1/2} \varphi_2^{1/2} \varphi_2^{-1/2} \ldots \varphi_{L/2}^{1/2} \varphi_{L/2}^{-1/2}\rangle = |\phi_1 \phi_2 \phi_3 \phi_4 \ldots \phi_{L-1} \phi_L\rangle. \tag{3.42}
$$

In order to find an expression for the Fock operator we insert the wavefunction into the canonical Hartree-Fock equation,

$$
\hat{f} \phi_P = \epsilon_p \phi_P, \;\rightarrow\; \hat{f} \varphi_p^\alpha \chi_\alpha = \epsilon_p \varphi_p^\alpha \chi_\alpha. \tag{3.43}
$$

Now we left multiply by χ_α^* and itegrate over spin,

$$
\left\langle \chi_\alpha \middle| \hat{f} \middle| \varphi_p^\alpha \chi_\alpha \right\rangle = \left\langle \chi_\alpha \middle| \epsilon_p \middle| \varphi_p^\alpha \chi_\alpha \right\rangle \tag{3.44}
$$

$$
\hat{f}^\alpha \varphi_p^\alpha = \left[\int d\sigma_1 \chi_\alpha(\sigma_1)^* \hat{f}(\mathbf{r}, \sigma_1) \chi_\alpha(\sigma_1) \right] \varphi_p^\alpha = \epsilon_p \varphi_p^\alpha. \tag{3.45}
$$

We now have what is called the spatial unrestricted Hartree-Fock equations. Inserting for the canonical Fock operator yields the following left-hand side

$$
\begin{aligned}
\hat{f}^{\alpha}\varphi_p^{\alpha} =& \hat{h}\varphi_p^{\alpha} + \sum_{Q}^{L} \left\langle \chi_\alpha \phi_Q \middle| \hat{w} \middle| \varphi_p^{\alpha}\chi_\alpha\phi_Q \right\rangle q - \sum_{Q}^{L} \left\langle \chi_\alpha\phi_Q \middle| \hat{w} \middle| \phi_Q\varphi_p^{\alpha}\chi_\alpha \right\rangle \\
=& \hat{h}\varphi_p^{\alpha} + \sum_{\beta}\sum_{q}^{L/2} \left\langle \chi_\alpha\varphi_q^{\beta}\chi_\beta \middle| \hat{w} \middle| \varphi_p^{\alpha}\chi_\alpha\varphi_q^{\beta}\chi_\beta \right\rangle \\
& - \sum_{\beta}\sum_{q}^{L/2} \left\langle \chi_\alpha\varphi_q^{\beta}\chi_\beta \middle| \hat{w} \middle| \varphi_q^{\beta}\chi_\beta\varphi_p^{\alpha}\chi_\alpha \right\rangle \\
=& \hat{h}\varphi_p^{\alpha} + \sum_{\beta}\sum_{q}^{L/2} \left\langle \cdot\varphi_q^{\beta} \middle| \hat{w} \middle| \cdot\varphi_q^{\beta} \right\rangle \varphi_p^{\alpha} - \sum_{q}^{L/2} \left\langle \cdot\varphi_q^{\alpha} \middle| \hat{w} \middle| \cdot\varphi_p^{\alpha} \right\rangle \varphi_q^{\beta}
\end{aligned}
\tag{3.46}
$$

This means that we get the following form for the spatial Fock operators in unrestricted Hartree-Fock

$$
\hat{f}^{\uparrow} = \hat{h} + \sum_{p}^{L/2} [\hat{v}^{\uparrow}_{\text{Coulomb}} - \hat{v}^{\uparrow}_{\text{exchange}}] + \sum_{p}^{L/2} \hat{v}^{\downarrow}_{\text{Coulomb}} \tag{3.47}
$$

$$
\hat{f}^{\downarrow} = \hat{h} + \sum_{p}^{L/2} [\hat{v}^{\downarrow}_{\text{Coulomb}} - \hat{v}^{\downarrow}_{\text{exchange}}] + \sum_{p}^{L/2} \hat{v}^{\uparrow}_{\text{Coulomb}} \tag{3.48}
$$

From the definition of the two spatial Fock operators in Equation 3.47 and Equation 3.48, we see that the two integro-differential eigenvalue equations that arises from inserting $\hat{f}^{\uparrow}$ and $\hat{f}^{\downarrow}$ into the canonical Hartree-Fock equation,

$$
\hat{f}^{\uparrow}\varphi_p^{\uparrow} = \epsilon_p^{\uparrow}\varphi_p^{\uparrow} \tag{3.49}
$$

$$
\hat{f}^{\downarrow}\varphi_p^{\downarrow} = \epsilon_p^{\downarrow}\varphi_p^{\downarrow}, \tag{3.50}
$$

are coupled and cannot be solved independently. The spin-up orbitals depend on the occupied spin-down orbitals and vice versa. This means that the two equations must be solved by a simultaneous iterative process.

We can also derive an equation for the unrestricted Hartree-Fock energy,

$$
\begin{aligned}
E_{UHF} =& \langle \Phi_{\text{UHF}} | \hat{H} | \Phi_{\text{UHF}} \rangle \\
=& \sum_{\alpha}\sum_{p}^{L/2} \left\langle \varphi_p^{\alpha}\chi_\alpha \middle| \hat{h} \middle| \varphi_p^{\alpha}\chi_\alpha \right\rangle + \sum_{\alpha}\sum_{p}^{L/2}\sum_{\beta}\sum_{q}^{L/2} \left\langle \varphi_p^{\alpha}\chi_\alpha\varphi_q^{\beta}\chi_\beta \middle| (\hat{w} - \hat{P}_{12}) \middle| \varphi_p^{\alpha}\chi_\alpha\varphi_q^{\beta}\chi_\beta \right\rangle \\
=& \sum_{\alpha}\sum_{pq}^{L/2} \left\langle \varphi_p^{\alpha} \middle| \hat{h} \middle| \varphi_p^{\alpha} \right\rangle + \sum_{\alpha\beta}\sum_{q}^{L/2} \left\langle \varphi_p^{\alpha}\varphi_q^{\beta} \middle| \hat{w} \middle| \varphi_p^{\alpha}\varphi_q^{\beta} \right\rangle - \sum_{\alpha}\sum_{pq}^{L/2} \left\langle \varphi_p^{\alpha}\varphi_q^{\alpha} \middle| \hat{w} \middle| \varphi_q^{\alpha}\varphi_p^{\alpha} \right\rangle
\end{aligned}
\tag{3.51}
$$

3.4.1 Pople-Nesbet-Bethier...

... would be nice to have here.

3.5 Time-Dependent Hartree-Fock

This section follows closesly the narrative of the gentlemen Hochstuhl, Hinz and Bonitz[33]. Deriving the time-dependent Hartree-Fock equations start, of course, with the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\left|\Phi(t)\right\rangle = \hat{H}(t)\left|\Phi(t)\right\rangle, \tag{3.52}$$

where the Hamiltonian is

$$\hat{H}(t) = \hat{h}(t) + \hat{w}(t). \tag{3.53}$$

This is very similar to the one used the same, except for the introduction of a time-dependence. We start by multiplying from the left with the reference Slater determinant $\langle\Phi|$. The right-hand side of the Schrödinger equation becomes the familiar Hartree-Fock energy,

$$\langle\Phi|\hat{H}|\Phi\rangle = \sum_p \langle\phi_p|\hat{h}|\phi_p\rangle + \frac{1}{2}\sum_{pq}\langle\phi_p\phi_q|(\hat{w}+\hat{P}_{12})|\phi_p\phi_q\rangle. \tag{3.54}$$

The left-hand side, is more interesting,

$$\langle\Phi|\frac{\partial}{\partial t}|\Phi\rangle = \sum_p \langle\phi_p|\frac{\partial}{\partial t}|\phi_p\rangle, \tag{3.55}$$

which we will deal with in due time, but before doing so we need to introduce functional derivatives and the functional derivatives of various matrix elements. First, the one-body matrix elements,

$$\frac{\delta}{\delta\phi_r^*}\sum_p \langle\phi_p|\hat{h}|\phi_p\rangle = \sum_p \frac{\delta}{\delta\phi_r^*}\int dr\phi_p^*\hat{h}\phi_p = \sum_p \delta_{pr}\hat{\phi} = \hat{h}\left|\phi_r\right\rangle. \tag{3.56}$$

Second, the matrix elements of the time-derivate,

$$\frac{\delta}{\delta\phi_r^*}\sum_p \langle\phi_p|\frac{\partial}{\partial t}|\phi_p\rangle = \frac{\partial}{\partial t}\left|\phi_q\right\rangle, \tag{3.57}$$

which is so similar to the one-body computation that the result is simply written down, instead of computing the result explicitly. Lastly, we have the two-body matrix elements,

$$\begin{aligned}
&\frac{\delta}{\delta\phi_r^*}\sum_{pq}\langle\phi_p\phi_q|(\hat{w}-\hat{P}_{12})|\phi_p\phi_q\rangle \\
&\quad= \frac{\delta}{\delta\phi_r^*(r_1)}\sum_{pq}\int dr_1 dr_2\phi_p^*(r_1)\phi_q^*(r_2)(\hat{w}-\hat{P}_{12})\phi_p(r_1)\phi_q(r_2) \\
&\quad= \sum_{pq}\delta_{pq}\int dr_2\phi_q^*(r_2)(\hat{w}-\hat{P}_{12})\phi_p(r_1)\phi_q(r_2) = \sum_q \langle\cdot\phi_q|(\hat{w}-\hat{P}_{12})|\phi_r\phi_q\rangle.
\end{aligned} \tag{3.58}$$

Now we want to vary the reference state to find the optimal one, applying the so-called time-dependent variational principle,

$$\langle\delta\Phi|(\hat{H}-i\hbar\frac{\partial}{\partial t})|\Phi\rangle = 0, \tag{3.59}$$

which we want to minimise under the requirement of orthonormal single-particle functions in time,

$$\langle\phi_p(t)|\phi_q(t)\rangle = \delta_{pq}. \tag{3.60}$$

Such an optimization problem under a constraint begs for the formulation of a Lagrangian, which we will let manifest itself,

$$\mathscr{L}(\Phi, \lambda_{pq}) = \langle\Phi|(\hat{H} - i\hbar\frac{\partial}{\partial t})|\Phi\rangle - \sum_{pq} \lambda_{pq}(\langle\phi_p|\phi_q\rangle - \delta_{pq}). \tag{3.61}$$

We find a stationary point of this Lagrangian functional, by variation of the single-particle functions so that

$$\frac{\delta\mathscr{L}}{\delta\phi_r^*} = 0, \quad \forall r. \tag{3.62}$$

This is where we will make use of the functional derivatives we computed before,

$$\frac{\delta\mathscr{L}}{\delta\phi_r^*} = \hat{h}\,|\phi_r\rangle + \sum_q \langle\cdot\phi_q|(\hat{w} - \hat{P}_{12})|\phi_r\phi_q\rangle - i\hbar\frac{\partial}{\partial t}\,|\phi_r\rangle - \sum_q \lambda_{rq}\,|\phi_r\rangle = 0. \tag{3.63}$$

Now we want to solve for the Langrange mulitplier, we do this be left-projection of the functional derivative above with $\langle\phi_s|$ and move resulting multiplier λ_{sq} to the left, and all other terms to the right. We get the following expression for the Lagrange multiplier,

$$\lambda_{sq} = \langle\phi_s|\hat{h}|\phi_r\rangle + \langle\phi_s\phi_q|(\hat{w} - \hat{P}_{12})|\phi_r\phi_q\rangle - i\hbar\,\langle\phi_s|\frac{\partial}{\partial t}|\phi_r\rangle \tag{3.64}$$

We insert this expression for the Lagrange multiplier into Equation 3.63 which results in,

$$\hat{P}\left[\hat{h}\,|\phi_r\rangle + \sum_q \langle\cdot\phi_q|(\hat{w}, \hat{P}_{12})|\phi_r\phi_q\rangle - i\hbar\frac{\partial}{\partial t}\,|\phi_k\rangle\right] = 0, \tag{3.65}$$

where we have the confusing operator $\hat{P}$, which is not a permutation operator like $\hat{P}_{12}$, but a projection operator;

$$\hat{P} = \hat{1} - \sum_p |\phi_p\rangle\langle\phi_p|\,. \tag{3.66}$$

Rearranging Equation 3.65 yields

$$i\hbar\hat{P}\frac{\partial}{\partial t}\,|\phi_r\rangle = \hat{P}\left[\hat{h}\,|\phi_r\rangle + \langle\cdot\phi_q|(\hat{w} - \hat{P}_{12})|\cdot\phi_q\rangle\right]|\phi_r\rangle = \hat{P}\hat{f}\,|\phi_r\rangle\,, \tag{3.67}$$

where we see that Fock operator has appeared. This equation is an integro-differential equation, as the projection operator $\hat{P}$ appear on both sides of the equality sign, and a solution can be difficutl to find. Because the time-dependent Hartree-Fock wavefunction is invariant under unitary transformation, we can obtain equations that are numerically more apporiate, by applying a unitary transformation $\hat{Q}(t)$ which satisfies

$$i\hbar\,\langle\phi_p|\frac{\partial}{\partial t}|\phi_q\rangle \equiv \langle\phi_p|\hat{Q}(t)|\phi_q\rangle\,. \tag{3.68}$$

It turns out that a reasonable choice for $\hat{Q}(t)$ is $\hat{f}t$, in which case Equation 3.67 becomes

$$i\hbar\frac{\partial}{\partial t}\,|\phi_p(t)\rangle = \hat{f}(t)\,|\phi_p(t)\rangle\,, \tag{3.69}$$

where we have explicitly written out the time-dependence. This is the time-dependent Hartree-Fock equation.

Now we pick a specific, finite and static basis $\{\chi_p\}_{p=1}^{L}$ and expand the Hartree-Fock single-particle functions in this basis,

$$\left|\phi_p\right\rangle(t) = \sum_q \left|\chi_q\right\rangle U_{qp}(t). \tag{3.70}$$

Notice that the basis set is indeed static, with no time-dependence, only the coefficients of the expansions $U_{pq}(t)$ evolve in time. We insert the expansion into Equation 3.69,

$$i\hbar\frac{\partial}{\partial}\sum_q \left|\chi_q\right\rangle U_{pq}(t) = \hat{f}(t)\sum_q \left|\chi_q\right\rangle U_{pq}(t). \tag{3.71}$$

We left-project this equation with $\langle\chi_r|$,

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\sum_q U_{pq}(t)\left\langle\chi_r|\chi_q\right\rangle &= \sum_q U_{pq}(t)\left\langle\chi_r|\hat{f}(t)|\chi_q\right\rangle \\ \rightarrow i\hbar\sum_q \dot{U}_{pq}S_{rq} &= \sum_q U_{pq}\hat{f}_{rq}(t), \end{aligned} \tag{3.72}$$

which can be written as a matrix equation,

$$i\hbar\mathbf{S}\dot{\mathbf{U}}(t) = \mathbf{F}(t)\mathbf{U}(t). \tag{3.73}$$

Chapter 4

Perturbation Theory

Perturbation theory is a very powerful method and a generic method applicable to all matrix problems. Additionally, perturbation theory is relatively cheap in terms of computing time especially compared with coupled cluster theory. As the method provides a different route to the solution of the Schrödinger equation, by approaching the exact solution systematically, based on an order-by-order expansion of the energy and wave function. Therefore, perturbation theory is often used to improve the results from other computation schemes. What is more, the exponential form of the wave function in coupled cluster theory stems from the non-degenerate Rayleigh-Schrödinger perturbation theory (RSPT) expansion.

4.1 Formal perturbation theory

We split the Hamiltonian into a known part and a perubed part,

$$\hat{H} = \hat{H}_0 + \hat{V}. \tag{4.1}$$

Sometimes it is convenient to write

$$\hat{H} = \hat{H}_0 + \lambda\hat{V}, \tag{4.2}$$

where we have included an "order parameter" λ. This parameter is used to categorise the contributions of different order. The exact solution is given by

$$\begin{aligned} \hat{H}\Psi_n &= E_n\Psi_n \\ (\hat{H}_0 + \hat{V})\Psi_n &= E_n\Psi_n, \quad \Psi_n = \Phi_n + \chi_n \end{aligned} \tag{4.3}$$

while the solvable and simple zero order problem is given by

$$\hat{H}_0\Phi_n = E_n^{(0)}\Phi_n \tag{4.4}$$

By projecting Equation 4.3 with $\langle\Phi_0|$ we get

$$\begin{aligned} \langle\Phi_n|\,\hat{H}_0\,|\Psi_n\rangle + \langle\Phi_n|\,\hat{V}\,|\Psi_n\rangle &= E_n\,\langle\Phi_n|\Psi_n\rangle \\ \rightarrow E_n &= \langle\Phi_n|\,\hat{H}\,|\Psi_n\rangle \\ \rightarrow \Delta E_n = E_n - E_n^0 &= \langle\Phi_n|\,\hat{V}\,|\Psi_n\rangle \end{aligned} \tag{4.5}$$

where we have used that

$$\langle\Phi_m|\Phi_n\rangle = \delta_{mn} \tag{4.6}$$

$$\langle \Psi_n | \Phi_n \rangle = \langle \Phi_n + \chi_n | \Phi_n \rangle = 1 \tag{4.7}$$
$$\langle \Psi_n | \Psi_n \rangle = 1 + \langle \chi_n | \chi_n \rangle \,. \tag{4.8}$$

This is called the intermediate normalisation assumption.

4.1.1 Energy- and Wavefunction Expansion

We now have need for the order parameter from λ Equation 4.2 as we expand the wavefunction and energy,

$$\begin{aligned} \Psi_n &= \Phi_n + \chi_n = \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots \quad (\Psi_n^{(0)} \equiv \Phi_n) \\ E_n &= E_n^{(0)} + \Delta E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned} \tag{4.9}$$

We insert these expansions into the Schrödinger equation,

$$\begin{aligned} (\hat{H} - E_n)\Psi_n &= 0 \\ (\hat{H}_0 + \lambda \hat{V})\Psi_n &= 0, \end{aligned} \tag{4.10}$$

resulting in

$$(\hat{H}_0 + \lambda \hat{V} - E_n^{(0)} - \lambda E_n^{(1)} - \lambda^2 E_n^{(2)} - \dots)(\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda \Psi_n^{(2)} + \dots) = 0. \tag{4.11}$$

Now we gather the coefficients of different powers of λ,

$$(\hat{H}_0 - E_n^{(0)})\Psi_n^{(0)} = 0 \tag{4.12}$$
$$(\hat{H}_0 - E_n^{(0)})\Psi_n^{(1)} = (E_n^{(1)} - \hat{V})\Psi_n^{(0)} \tag{4.13}$$
$$(\hat{H}_0 - E_n^{(0)})\Psi_n^{(2)} = (E_n^{(1)} - \hat{V})\Psi_n^{(1)} + E_n^{(2)}\Psi_n^{(0)} \tag{4.14}$$
$$\dots$$
$$(\hat{H}_0 - E_n^{(0)})\Psi_n^{(m)} = (E_n^{(1)} - \hat{V})\Psi_n^{(m-1)} + \sum_{l=0}^{m-2} E_n^{(m-l)}\Psi_n^{(l)}. \tag{4.15}$$

Where the last line gives a general mth-order equation. This equation can be simplified somewhat,

$$(E_n^{(0)} - \hat{H}_0)\Psi_n^{(m)} = \hat{V}\Psi_n^{(m-1)} - \sum_{l=0}^{m-1} E_n^{(m-l)}\Psi_n^{(l)}. \tag{4.16}$$

By applying $\langle \Phi_n |$ to each of the equations, we get expressions for $E_n^{(m)}$. For λ^1 (Equation 4.13) we get,

$$\begin{aligned} \langle \Phi_n | \hat{H}_0 - E_n^{(0)} \left| \Psi_n^{(1)} \right\rangle &= \langle \Phi_n | E_n^{(1)} - \hat{V} | \Phi_n \rangle \\ \left\langle (\hat{H}_0 - E_n^{(0)})\Phi_n \middle| \Psi_n^{(1)} \right\rangle &= \langle \Phi_n | E_n^{(1)} - \hat{V} | \Phi_n \rangle \\ \rightarrow E_n^{(1)} &= \langle \Phi_n | \hat{V} | \Phi_n \rangle = \hat{V}_{nn} \end{aligned} \tag{4.17}$$

Since we have an expression for $E_n^{(1)}$, we can solve the inhomogeneous differential equation for $\Psi_n^{(1)}$, by also requiring the intermediate normalisation condition $\left\langle \Phi_n \middle| \Psi_n^{(1)} \right\rangle = \delta_{l0}$. For the general mth-order expression (Equation 4.15),

$$\begin{aligned} \langle \Phi_n | E_n^0 - \hat{H}_0 \left| \Psi_n^{(m)} \right\rangle &= \langle \Phi_n | \hat{V} \left| \Psi_n^{(m-1)} \right\rangle - \sum_{l=0}^{m-1} E_n^{(m-l)} \left\langle \Phi_n \middle| \Psi_n^{(l)} \right\rangle \\ E_n^{(m)} = \left\langle \Phi_n^{(m)} \right| &= \langle \Phi_n | \hat{V} \left| \Psi_n^{(m-1)} \right\rangle . \end{aligned} \tag{4.18}$$

In principle, we can obtain every next-order energy contribution $E_n^{(m)}$ from the previous-order wavefunctions $\Psi_n^{(m-1)}$ and then solve for $\Psi_n^{(m)}$.

4.1.2 The 2n+1 Wigner Rule

4.1.3 Projection Operators

We define the projection operators in terms of the zero-order wave functions,

$$\begin{aligned}\hat{P} &= \left|\Phi_0\right\rangle\left\langle\Phi_0\right| \\ \hat{Q} &= \hat{1} - \hat{P} = \sum_{i=1}^{N}\left|\Phi_i\right\rangle\left\langle\Phi_i\right|.\end{aligned} \tag{4.19}$$

The projecton operators have the following conventient properties,

$$\begin{gathered}\hat{P}^2 = \left|\Phi_0\right\rangle\left\langle\Phi_0|\Phi_0\right\rangle\left\langle\Phi_0\right| = \left|\Phi_0\right\rangle\left\langle\Phi_0\right| = \hat{P} \\ \hat{Q}^2 = (1-\hat{P})^2 = \hat{1} - \hat{P} - \hat{P} + \hat{P} = \hat{1} - \hat{P} = \hat{Q} \\ \hat{P}\hat{Q} = \hat{Q}\hat{P} = 0 \\ [\hat{P}, \hat{H}_0] = [\hat{Q}, \hat{H}_0] = 0\end{gathered} \tag{4.20}$$

If we write the wavefunction as a linear expansion in terms of Φ_i,

$$\Phi = \sum_i a_i \Phi_i, \tag{4.21}$$

acting on it with the projection operators will yield

$$\hat{P}\Psi = \sum_i a_i \left|\Phi_0\right\rangle\left\langle\Phi_0|\Phi_i\right\rangle = \sum_i a_i \left|\Phi_0\right\rangle \delta_{0i} = a_0\Phi_0. \tag{4.22}$$

In not so many greek letters, the operator $\hat{P}$ will extract Φ_0 from Ψ, while $\hat{Q}$ annihilates $\hat{Q}$,

$$\hat{Q}\Psi = (\hat{1} - \hat{P}) = \Psi - a_0\Phi_0 = \sum_{i=1}^{N} a_i\Phi_i, \tag{4.23}$$

meaning we can write

$$\Psi = \hat{P}\Psi + \hat{Q}\Psi. \tag{4.24}$$

4.1.4 The Resolvent

Now follows what some considers a more elegant derivation of the perturbation equations, including the introduction of the *resolvent* of the unperturbed part of the Hamiltonian $\hat{H}_0$.

Starting from a rearrangment of the Schrödinger equation,

$$\begin{gathered}(\hat{H}_0 + \hat{V})\Psi = E\Psi, \\ \to -\hat{H}_0\Phi = (\hat{V} - E)\Psi,\end{gathered} \tag{4.25}$$

we introduce a seemingline arbirary parameter ζ by adding $\zeta\Phi$ to both sides,

$$(\xi - \hat{H}_0)\Phi = (\hat{V} - E + \xi)\Phi. \tag{4.26}$$

Next, we apply $\hat{Q}$ to both sides,

$$\hat{Q}(\zeta - \hat{H}_0)\Psi = \hat{Q}(\hat{V} - E + \zeta)\Psi. \tag{4.27}$$

The right-hand side of this expression can be rewritten as,

$$\begin{aligned}\hat{Q}(\zeta-\hat{H}_0)\Psi &= \hat{Q}^2(\zeta-\hat{H}_0) = \hat{Q}(\zeta-\hat{H}_0)\hat{Q}\Psi \\ &= \sum_{i\neq 0}\sum_{j\neq 0} |\Phi_i\rangle \langle\Phi_i| \, \zeta-\hat{H}_0 \, |\Phi_j\rangle \langle\Phi_j| \,,\end{aligned} \tag{4.28}$$

Equation 4.27 is now

$$\hat{Q}(\zeta-\hat{H}_0)\hat{Q}\Psi = \hat{Q}(\hat{V}-E+\zeta)\Psi. \tag{4.29}$$

By restricting to choice of ζ, so they do not coincide with the eigenvalues of $\hat{H}_0$ in $\hat{Q}$-space, we ensure that the inverse of $\hat{Q}(\zeta-\hat{H}_0)\hat{Q}$ exists. This inverse is the *resolvent* of $\hat{H}_0$,

$$\hat{R}_0(\zeta) = \frac{\hat{Q}}{\zeta-\hat{H}_0} \equiv \sum_{i\neq 0}\sum_{j\neq 0} |\phi_i\rangle \langle\Phi_i| \, (\zeta-\hat{H}_0)^{-1} \, |\Phi_j\rangle \langle\Phi_j| \,. \tag{4.30}$$

The resolvent simplifies in the diagonal case to

$$\hat{R}_0(\zeta) = \sum_{i\neq 0} |\Phi_i\rangle \langle\Phi_i| \, (\zeta-E_j^{(0)})^{-1} \, |\Phi_j\rangle \langle\Phi_j| = \sum_{i\neq 0} \frac{|\Phi_i\rangle \langle\Phi_i|}{(\zeta-E_i^{(0)})}. \tag{4.31}$$

It is somewhat straightforward to prove that $\hat{R}_0(\zeta)$ is the inverse of $\hat{Q}(\zeta-\hat{H}_0)\hat{Q}$ in $\hat{Q}$-space,

$$\begin{aligned}&\frac{\hat{Q}}{\zeta-\hat{H}_0}\hat{Q}(\zeta-\hat{H}_0)\hat{Q} \\ &= \left(\sum_{i,j\neq 0} |\Phi_i\rangle \langle\Phi_i| \, (\zeta-\hat{H}_0)^{-1} \, |\Phi_j\rangle \langle\Phi_j|\right)\left(\sum_{k,l\neq 0} |\Phi_k\rangle \langle\Phi_k| \, (\zeta-\hat{H}_0) \, |\Phi_l\rangle \langle\Phi_l|\right) \\ &= \sum_{i,l\neq 0} |\Phi_i\rangle \langle\Phi_i| \, (\zeta-\hat{H}_0)^{-1}\left(\sum_{j\neq 0} |\Phi_j\rangle \langle\Phi_j|\right)(\zeta-\hat{H}_0) \, |\Phi_l\rangle \langle\Phi_l| \\ &= \sum_{i,l\neq 0} |\Phi_i\rangle \langle\Phi_i| \, (\zeta-\hat{H}_0)^{-1}(1-|\Phi_0\rangle \langle\Phi_0|)(\zeta-\hat{H}_0) \, |\Phi_l\rangle \langle\Phi_l| \\ &= \sum_{i\neq 0} |\Phi_i\rangle \langle\Phi_i| = \hat{Q}.\end{aligned} \tag{4.32}$$

Applying the resolvent to both sides of Equation 4.29,

$$\begin{aligned}\hat{Q}\Psi &= \hat{R}_0(\zeta)(\hat{V}-E++\zeta)\Psi \\ \to \Psi &= \Phi_0 + \hat{R}_0(\zeta)(\hat{V}-E+\zeta)\Psi,\end{aligned} \tag{4.33}$$

which can be interpreted as a recursive relation for Ψ. Substituting the right-hand side into Ψ on the right-hand side repeatedly yields,

$$\Psi = \sum_{m=0}^{\infty}\{\hat{R}_0(\zeta)(\hat{V})-E+\zeta\}^m\Phi_0. \tag{4.34}$$

The problem with this equation is that E, which is unknown, appears on the right-hand side. A question also arises regarding what to do with ζ. There are two common choices for ζ that give rise to two important theories,

$$\zeta = E \leftarrow \text{Brillouin-Wigner Perturbation}$$

$$\zeta = E_0^{(0)} \to -E+\zeta = -\Delta E \leftarrow \text{Rayleigh-Schrödinger Perturbation}$$

4.2 [UNFINISHED] Brillouin-Wigner Perturbation Theory

Set $\zeta = E$ and get BWPT[6, 66].

4.3 [UNFINISHED] Rayleigh-Schrödinger Perturbation Theory

set $\zeta = E_n^{(0)}$ and get RSPT[56, 58].

Chapter 5

Coupled Cluster

In the late 1950s Fritz Coester constructed a rigorous formal solution of the bound state Schrödinger equation as a set of single particle wave functions[9]. He wanted to find an expression for the wave operator ω, which transforms a zero-order wavefunction to the exact wave function,

$$\Psi = \Omega\Phi_0. \tag{5.1}$$

From Coester's solutions it would become apparent that the Rayleigh-Schrödinger perturbation expansions of the energy does not contain matrix elements representing the products of so-called unlinked diagram. In other words, one form of Ω is given a "linked-diagram expansion",

$$\Omega\left|\Phi_0\right\rangle = \left|\Phi_0\right\rangle = \sum_{k=1}^{\infty}\left((\hat{R}_0\hat{W})^k\left|\Phi_0\right\rangle\right)_L. \tag{5.2}$$

a This is further underlined in discussions by John Hubbard[34] and Nicolaas Marinus Hugenholtz[35].

Conveniently, Ω may be written quite generally as

$$\Omega = e^{\hat{T}}, \quad \Psi = e^{\hat{T}}\Phi_0. \tag{5.3}$$

This exponential form has been come to be known as the Coupled Cluster ansatz, even though it is much more than a simple guess for the form of the exact wavefunction. To underline this point we quote Herman Kümmel: "Strange as it may be, in spite of the many successes of the coupled cluster method there is still a widespread belief that the underlying exponential structure is something artificial, accidental or an approximation only. This is why I want to make it clear that this feature is extremely natural - even necessary - on a very fundamental level, not necessarily connected with many-body theory"[37].

Throughout the 1950s and early 1960s, Coester and Kümmel developed the coupled cluster method together and proposed using the exponential-form wave operator as coupling between the shell-model state and the correct state vector for nuclear matter[10]. At the time, the method proved too computationally intensive. Specifically, the hard core potenatials of nuclear physics leaves no freedom in truncating the set of coupled cluster equations. However, the method was picked up by Jiří Čížek who in 1966 reformulated the method for modelling of electron correlation in atoms and molecules[8]. Further development with Josef Paldus made the coupled cluster method one of the most succesfull[1] methods in quantum chemistry. Together with Isaiah Shavitt, Čížek and Paldus did the first *ab initio* comutations with the method, which they called the coupled-pair many-electron-theory (MET)[47], as it can be intepreted as the perturbative variant of the many-electron-theory of Oktay Sinanoğlu[60].

[1]At least one of the most prevalent

5.1 The Cluster Operator

Having established the form of the coupled cluster wavefunction as

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle , \tag{5.4}$$

we now take a closer look at the cluster operator, which is divided into sub-operators

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_2 + \hat{T}_3 + \dots , \tag{5.5}$$

where the one-, two- and three-body operators are defined thusly,

$$\hat{T}_1 = \sum_{ai} t_i^a \{\hat{a}^\dagger \hat{i}\} \tag{5.6}$$

$$\hat{T}_2 = \frac{1}{(2!)^2} \sum_{ijab} t_{ij}^{ab} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j}\} \tag{5.7}$$

$$\hat{T}_3 = \frac{1}{(3!)^2} \sum_{ijkabc} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j} \hat{c}^\dagger \hat{k}\}, \tag{5.8}$$

where the coefficients $t_{ijk\dots}^{abc\dots}$ are commonly referred to as the coupled cluster *amplitudes*, and are coefficients to be determined. The strings of operators are automatically normal-ordered. The general m-body cluster operator is given by

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ij\dots \\ ab\dots}} t_{ij\dots}^{ab\dots} \{\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j} \dots\}, \tag{5.9}$$

which produces an m-fold excitation. It is not necessary to include cluster-operators up to a infinite-fold excitation. Logically, the maximum excitation order is dictated by the number of electrons in the system n, such that $n \geq m$. Any higher-order excitation operator would eventually annihilate an unoccupied orbital, resulting in a zero-contribution. The prefactor $1/(m!)^2$ accounts for the redundancy created by unrestricted summations, as a permutation of any of the m hole or m particle indices will not produce a distinct contributions. Indeed, we have for example that

$$\hat{a}^\dagger \hat{i} \hat{b}^\dagger \hat{j} = -\hat{a}^\dagger \hat{j} \hat{b}^\dagger \hat{i} = -\hat{b}^\dagger \hat{i} \hat{a}^\dagger \hat{j} = \hat{b}^\dagger \hat{j} \hat{a}^\dagger \hat{j}, \tag{5.10}$$

and therefore we must also have that

$$t_{ij}^{ab} = -t_{ji}^{ab} = -t_{ij}^{ba} = t_{ji}^{ba}. \tag{5.11}$$

Hence, the $(2!)^2 = 4$ contributions of two hole indices, ab, and two particle indices, ij, will produce four equal terms, which is offset by the prefactor $1/4$.

The exponential wave operator $e^{\hat{T}}$ may be expanded as a Taylor series,

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots . \tag{5.12}$$

By including only single- and double excitations, $\hat{T}_{\text{CCSD}} = \hat{T}_1 + \hat{T}_2$, this expressions becomes

$$e^{\hat{T}_{\text{CCSD}}} = 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{2}\hat{T}_1\hat{T}_2^2 + \frac{1}{3!}\hat{T}_2^3 + \dots \tag{5.13}$$

Contributions to the wave function containing only a single cluster operator, $\hat{T}_m$, are called connected cluster contributions, while those containing products of cluster operators, $\hat{T}_{m_1}^{\alpha}\hat{T}_{m_2}^{\beta}$, are called disconnected cluster contributions.

This inclusion of only sigle- and double excitations is called "Coupled Cluster Singles Doubles", elucidating the subscript CCSD[55]. The most common approximation in coupled cluster theory is the CCSD model. Here, the operator $\hat{T}_2$ describes the important electron-pair interaction and the $\hat{T}_1$ operator carries out the orbital relaxations induced by the field set up by electron-pair interactions.

Importance of different parts of the cluster operator

The most important contribution to the wave-function in quantum chemistry is undoubtedlty $\hat{T}_2$, because of the two-electron nature of the Hamiltonian. It describes the most important interaction of quantum chemistry, the electron-pair interaction. The inclusion of $\hat{T}_1$ and its products are relatively insensitive to the choice of basis set, as the operators $e^{\hat{T}_1}$ has the effect of transforming thereference state $|\Phi_0\rangle$ to another Slater determinant. This is known as Thouless theorem[65]. With very high electron-density, the three-particle operator $\hat{T}_3$ becomes important. Higher-order terms are usually of less and decreasing importance, but they can be of concern in special situations. For instance, the four-particle operator $\hat{T}_4$ is very important in nuclear physics. See for instance Helgaker et ali[30] or Shavitt & Bartlett[59] for further discussion on this topic.

5.2 Coupled-Cluster Doubles (CCD)

As a good starting point for understanding the coupled cluster scheme and especially where the coupled-cluster equations come from, we now constrain the cluster operator to

$$\hat{T}_{\text{CCD}} = \hat{T}_2, \tag{5.14}$$

and completely derive the coupled cluster equations for this case. The CCD wave function includes all connected and disconnected clusters involving $\hat{T}_2$ only,

$$\Psi_{\text{CCD}} = e^{\hat{T}_2} = \Phi_0 + \hat{T}_2\Phi_0 + \frac{1}{2}\hat{T}_2^2\Phi_0 + \frac{1}{3!}\hat{T}_2^3\Phi_0 + \dots \tag{5.15}$$

There are several methods with which to arrive at the coupled-cluster equations and here we employ two of them for the coupled cluster doubles truncation. First, we use configuration-interaction techniques and the Slater-Condon rules (Appendix A) and second, we use the "algebraic method", employing second quantisation and Wick's theorem. A third way is with the aid of diagrams. A brief note on such diagrams can be found in Appendix B.

5.2.1 Configuration space derivation

We start from the CCD-constrained time-independent Schrödinger equation,

$$\hat{H}\Psi_{\text{CCD}} = E_{\text{CCD}}\Psi_{\text{CCD}}, \tag{5.16}$$

which we left project with the reference state,

$$\begin{aligned}\langle\Phi_0|\,\hat{H}\,|\Psi_{\text{CCD}}\rangle &= \langle\Phi_0|\,E_{\text{CCD}}\,|\Psi_{\text{CCD}}\rangle\\ \rightarrow E_{\text{CCD}} &= \langle\Phi_0|\,\hat{H}\,|\Psi_{\text{CCD}}\rangle\,,\end{aligned}$$

where we have taken advandage of the intermediate normalisation, $\langle \Phi_0 | \Psi_{\mathrm{CCD}} \rangle = 1$. We then insert the exponential expansion from the coupled cluster ansatz,

$$\begin{aligned} E_{\mathrm{CCD}} &= \langle \Phi_0 | \hat{H}(1+\hat{T}_2) | \Phi_0 \rangle \\ &= E_{\mathrm{ref}} + \sum_{\substack{i>j \\ a>b}} \langle \Phi_0 | \hat{H} \left| \Phi_{ij}^{ab} \right\rangle t_{ij}^{ab} \\ &= E_{\mathrm{ref}} + \sum_{\substack{i>j \\ a>b}} \langle ij|ab \rangle \, t_{ij}^{ab}. \end{aligned} \tag{5.17}$$

The energy expression will truncate here because no higher order terms will contribute. It is common to substract E_{ref} to get,

$$\hat{H}_N \Psi_{\mathrm{CCD}} = \Delta E_{\mathrm{CCD}} \Psi_{\mathrm{CCD}}, \tag{5.18}$$

where $\hat{H}_N = \hat{H} - E_{\mathrm{ref}}$. Now follows a bunch of expressions intended to show the correspondence between coupled cluster- and perturbation theory,

$$\hat{H}_N = \hat{F} - \hat{U} + \hat{H}_2 - E_{\mathrm{ref}} = \hat{H}_0 + \hat{F}^0 - \hat{U} + \hat{H}_2 - E_{\mathrm{ref}}, \tag{5.19}$$

where,

$$\hat{H}_0 = \hat{F}^d = \sum_{\mu} \hat{f}_{\mu}^d, \quad \langle p | \hat{f}_{\mu}^d | q \rangle = \epsilon_p \delta_{pq} \tag{5.20}$$

$$\hat{F}^0 = \sum_{\mu} \hat{f}_{\mu}^0, \quad \langle p | \hat{f}^0 | q \rangle = (1 - \delta_{pq}) \langle p | \hat{f} | q \rangle \tag{5.21}$$

$$\hat{U} = \sum_{\mu} \hat{u}_{\mu}, \quad \langle p | \hat{u}_{\mu} | q \rangle = \sum_i \langle pi | qi \rangle \tag{5.22}$$

$$\hat{H}_2 = \sum_{\mu>\nu} \frac{1}{r_{\mu\nu}}, \quad E_{\mathrm{ref}} = E_0 + E^{(1)}, \tag{5.23}$$

$$E_0 = \sum_i \epsilon_i, \quad E^{(1)} = -\frac{1}{2} \sum_{ij} \langle ij | ij \rangle . \tag{5.24}$$

In the canonical HF case we have $\hat{F}^0 = 0$ and $\hat{F}^d = \hat{F}$.

In order to compute the energy of the system we need the amplitudes t_{ij}^{ab}. Starting from the modified Schrödinger equation,

$$\hat{H}_N \Psi_{\mathrm{CCD}} = \Delta E_{\mathrm{CCD}} \Psi_{\mathrm{CCD}}. \tag{5.25}$$

We left project with a doubly-excited Slater determinant, and insert for the CC ansatz,

$$\left\langle \Phi_{ij}^{ab} \right| \hat{H}_N e^{\hat{T}_2} | \Phi_0 \rangle = \Delta E_{\mathrm{CCD}} \left\langle \Phi_{ij}^{ab} \right| e^{\hat{T}_2} | \Phi_0 \rangle \tag{5.26}$$

$$\left\langle \Phi_{ij}^{ab} \right| \hat{H}_N \left(1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 \right) | \Phi_0 \rangle = \Delta E_{\mathrm{CCD}} t_{ij}^{ab}. \tag{5.27}$$

Here we have only expanded the exponential function up to the quadratic term. The next term in the series will triple-excite the bra Slater determinant, which will give a zero-contribution according to the Slater-Condon rules, because of two noncoincidences. Next we apply the Slater-Condon rules to the rest of the terms on the right-hand side, starting with just the normal-ordered Hamiltonian,

$$\left\langle \phi_{ij}^{ab} \right| \hat{H}_N | \Phi_0 \rangle = \langle ab | ij \rangle , \tag{5.28}$$

where only $\hat{H}_2$ contributes.

Next we look at the linear term,

$$
\begin{aligned}
\langle \Phi_{ij}^{ab} | \hat{H}_N \hat{T}_2 | \Phi_0 \rangle &= \sum_{klcd} \langle \phi_{ij}^{ab} | \hat{H}_N | \phi_{kl}^{cd} \rangle \\
&= \langle \Phi_{ij}^{ab} | \hat{H}_0 - E_{\text{ref}} | \Phi_{ij}^{ab} \rangle t_{ij}^{ab} + \sum_{\substack{k>l \\ c>d}} \langle \Phi_{ij}^{ab} | \hat{F}^0 - \hat{U} | \Phi_{kl}^{cd} \rangle t_{kl}^{cd} \\
&+ \sum_{\substack{k>l \\ c>l}} \langle \Phi_{ij}^{ab} | \hat{H}_2 | \Phi_{kl}^{cd} \rangle t_{kl}^{cd} = L_0 + L_1 + L_2.
\end{aligned} \tag{5.29}
$$

We are going to evaluate these terms one-by-one, starting with L_0,

$$
\begin{aligned}
L_0 = \langle \Phi_{ij}^{ab} | \hat{H}_0 - E_{\text{ref}} | \Phi_{ij}^{ab} \rangle &= \langle \Phi_{ij}^{ab} | \hat{H}_0 - E_0 - E^{(1)} | \Phi_{ij}^{ab} \rangle \\
&= \left(-\varepsilon_{ij}^{ab} + \frac{1}{2} \sum_{kl} \langle kl | kl \rangle \right) t_{ij}^{ab}.,
\end{aligned} \tag{5.30}
$$

where $\varepsilon_{ij}^{ab} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$.

The next term,

$$
L_1 = \sum_{\substack{k>l \\ c>d}} \langle \Phi_{ij}^{ab} | \hat{F}^0 - \hat{U} | \Phi_{kl}^{cd} \rangle t_{kl}^{cd}, \tag{5.31}
$$

yields contributions if at least three of the indices k, l, c, d are equal to the indices i, j, a, b (we want one or zero noncoincidences). All the possible terms are,

$$
L_1 = \begin{cases}
-\sum_k u_{kk} t_{ij}^{ab} & \text{all indices equal} \\
-\sum_k (f_{jk}^0 - u_{jk}) t_{ik}^{ab} & \text{one hole index unequal} \\
+\sum_k (f_{ik}^0 - u_{ik}) t_{jk}^{ab} & \text{the other hole index unequal} \\
-\sum_c (f_{ac}^0 - u_{ac}) t_{ij}^{bc} & \text{one particle index unequal} \\
+\sum_c (f_{bc}^0 - u_{bc}) t_{ij}^{zc} & \text{the other particle index unequal.}
\end{cases} \tag{5.32}
$$

For the last linear term,

$$
L_2 = \sum_{\substack{k>l \\ c>d}} \langle \Phi_{ij}^{ab} | \hat{H}_2 | \Phi_{kl}^{cd} \rangle t_{kl}^{cd}, \tag{5.33}
$$

we require that at least two of the indices k, l, c, d are equal to the indices i, j, a, b, as we can do with at most two noncoincidences in the bra and the ket. For equality in both the hole indices or both the particle indices we have

$$
cd = ab \quad \rightarrow \quad \sum_{k>l} \langle ij | kl \rangle t_{kl}^{ab} \tag{5.34}
$$

$$
kl = ij \quad \rightarrow \quad \sum_{c>d} \langle ab | cd \rangle t_{ij}^{cd}. \tag{5.35}
$$

For one equality in both hole and particle index we have

$$
-\sum_{kl} \left(\langle bk | cj \rangle t_{ik}^{ac} - \langle bk | ci \rangle t_{jk}^{ac} - \langle ak | cj \rangle t_{ik}^{bc} - \langle bk | ci \rangle t_{jk}^{ac} \right), \tag{5.36}
$$

where the sign stems from the maximum coincidence permutations as dictated by the Slater-Condon rules. Most of the three- and four euqal index terms are accounted for by the expression above, the remaining three-index equality terms are

$$-\sum_{kl}\big(\langle jl|kl\rangle\, t_{ik}^{ab} - \langle il|kl\rangle\, t_{jk}^{ab}\big) \tag{5.37}$$

$$+\sum_{cl}\big(\langle bl|cl\rangle\, t_{ij}^{ac} - \langle al|cl\rangle\, t_{ij}^{bc}\big), \tag{5.38}$$

and there is one term for the case where all indices are equal,

$$\sum_{k>l}\langle kl|kl\rangle\, t_{ij}^{ab} = \frac{1}{2}\sum_{kl}\langle kl|kl\rangle\, t_{ij}^{ab}. \tag{5.39}$$

Difference between Coupled Cluster and Configuration Interaction

THIS BOX MAY BELONG SOMEWHERE ELSE (or may not be in a box)
Monkhorst[44] gives a general formuala for transferring back and forth between CC operators $\hat{T}_m$ and CI operators $\hat{C}_m$,

$$\hat{C}_m = \sum_{k}^{m}\frac{1}{k!}\sum_{|m_\mu|}\delta(m_1+m_2+\cdots+m_k, m)\prod_{\mu=1}^{k}\hat{T}_{m_\mu}, \tag{5.40}$$

where the second sum is over all sets of k m_μ-values that sum up to m. The first four of the terms are,

$$\hat{C}_1 = \hat{T}_1 \tag{5.41}$$

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 \tag{5.42}$$

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{3!}T_1^3 \tag{5.43}$$

$$\hat{C}_4 = \hat{T}_4 + \frac{1}{2}\hat{T}_2 + \frac{1}{2}\hat{T}_2\hat{T}_1^2 + \frac{1}{4!}\hat{T}_1^4. \tag{5.44}$$

For the CCSD and CISDTQ wavfunctions we have,

$$|\Psi_{\text{CCSD}}\rangle = \left(1+\hat{T}_1+\frac{1}{2}\hat{T}_1^2+\frac{1}{3!}\hat{T}_1^3+\hat{T}_2+\frac{1}{2}\hat{T}_2^2+\frac{1}{4!}\hat{T}_1^4+\hat{T}_1\hat{T}_2\right)|\Phi_0\rangle \tag{5.45}$$

$$|\Psi_{\text{CISDTQ}}\rangle = \left(1+\hat{C}_1+\hat{C}_2+\hat{C}_3+\hat{C}_4\right)|\Phi_0\rangle \tag{5.46}$$

which provides us with a relation between the two,

$$|\Psi_{\text{CCSD}}\rangle = |\Psi_{\text{CCSDTQ}}\rangle - (\hat{T}_3+\hat{T}_4)\,|\Phi_0\rangle\,. \tag{5.47}$$

Moreover, we see that for a system of $n = 2$ particles, that

$$|\Psi_{\text{CCSD}}\rangle = |\Psi_{\text{CCSDTQ}}\rangle\,. \tag{5.48}$$

FILL IN MORE...

These last three- and four-index equality terms are expressible in terms of $\hat{u}$, and will cancel the first term in L_1 together with the $\hat{u}$ term from L_0. All terms so far are the same as in a configuration interaction with doubles excitations (CID) computation. The difference between coupled cluster with doubles (CCD) and CID is the following extra quadratic terms,

$$Q = \frac{1}{2} \langle \Phi_{ij}^{ab} | \hat{H}_N \hat{T}_2^2 | \Phi_0 \rangle = \frac{1}{2} \sum_{\substack{k>l \\ c>d}} \sum_{\substack{m>n \\ e>f}} \langle \phi_{ij}^{ab} | \hat{H}_N \left| \Phi_{klmn}^{cdef} \right\rangle t_{kl}^{cd} t_{mn}^{ef}. \tag{5.49}$$

From this expression we will have a contrition only when four of the indices k, l, m, n, c, d, e, f are equal to i, j, a, b, and only $\hat{H}_2$ can contribute. After some algebraic acrobatics we'll find that this becomes

$$\begin{aligned} Q = \sum_{\substack{k>l \\ c>d}} \langle kl|cd \rangle \big[&(t_{ij}^{ab} t_{kl}^{cd} + t_{ij}^{cd} t_{kl}^{ab}) - 2(t_{ik}^{ac} t_{jl}^{cd} + t_{ij}^{bd} t_{ij}^{bd}) \\ &-2(t_{ik}^{ab} t_{jl}^{cd} + t_{ik}^{cd} t_{jl}^{ab}) + 4(t_{ik}^{ac} t_{jl}^{bd} + t_{ik}^{bd} t_{jl}^{ac}) \big]. \end{aligned} \tag{5.50}$$

From Equation 5.17 we see that

$$\Delta E_{\mathrm{CCD}} = \sum_{\substack{i>j \\ a>b}} \langle ij|ab \rangle \, t_{ij}^{ab}, \tag{5.51}$$

and because the indices in Equation 5.50 are dummy variables we see that the first term here cancels with the right-hand side of Equation 5.27. Some algebraic massage after the initial acrobatic exercises leads to,

$$\begin{aligned} \varepsilon_{ij}^{ab} t_{ij}^{ab} = \langle ab|ij \rangle &+ \frac{1}{2} \sum_{cd} \langle ab|cd \rangle \, t_{ij}^{cd} + \frac{1}{2} \sum_{kl} \langle ij|kl \rangle \, t_{kl}^{ab} \\ &- \sum_{kl} \big(\langle bk|cj \rangle \, t_{ik}^{ac} - \langle bk|ci \rangle \, t_{jk}^{ac} - \langle ak|cj \rangle \, t_{ik}^{bc} + \langle ak|ci \rangle \, t_{jk}^{bc} \big) \\ &- \sum_{k} \hat{f}_{jk}^0 t_{ik}^{ab} + \sum_{k} \hat{f}_{ik}^0 t_{jk}^{ab} + \sum_{c} \hat{f}_{bc}^0 t_{ij}^{ac} - \sum_{c} \hat{f}_{ac}^0 t_{ij}^{bc} \\ &+ \sum_{klcd} \langle kl|cd \rangle \Big[\frac{1}{4} t_{ij}^{cd} t_{kl}^{ab} - \frac{1}{2} (t_{ij}^{ac} t_{kl}^{bd} + t_{ij}^{bd} t_{kl}^{ac}) \\ &\qquad - \frac{1}{2} (t_{ik}^{ab} t_{jl}^{cd} + t_{ik}^{cd} t_{jl}^{ab}) + (t_{ik}^{ac} t_{jl}^{bd} + t_{ik}^{bd} t_{jl}^{ac}) \Big], \end{aligned} \tag{5.52}$$

which is the CCD amplitude equations. This equation contains simultaneous algebraic expressions, contrary to CI. The equations must be solved iteratively, substituting t_{ij}^{ab} obtained in each iteration, into the quadratic terms for the next iteration.

5.2.2 Algebraic Derivation

In this derivation we make great use of second quantisation formalism and Wick's theorem. We start with the normal-ordered Hamiltonian,

$$\begin{aligned} \hat{H}_N &= (\hat{H}_0)_N + \hat{F}_N^0 + \hat{W} \\ &= \sum_p \varepsilon_p \{\hat{p}^\dagger \hat{p}\} + \sum_{p \neq q} f_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{pqrs} \langle pq|rs \rangle \, \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\}. \end{aligned} \tag{5.53}$$

The one-particle terms $(\hat{H}_0)_N$ and $\hat{F}_N^0$ can be combined by setting $\varepsilon_p = f_{pp}$, reducing the normal-ordered Hamilionian to

$$\begin{aligned} \hat{H}_N &= \hat{F}_N + \hat{W} \\ &= \sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4} \sum_{pqrs} \langle pq|rs \rangle \, \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\}. \end{aligned} \tag{5.54}$$

First we want to find an expression for the energy,

$$\Delta E_{\mathrm{CCD}} = \langle 0| \hat{H}_N (1+\hat{T}^2) |0\rangle = \langle 0| \hat{H}_N \hat{T}_2 |0\rangle , \tag{5.55}$$

where only the vacuum expectation value of the product of the Hamiltonian and the doubles cluster operators gives a contributions, because the vacuum expectation value of just the Hamiltonian is zero. Inserting for the operators,

$$\Delta E_{\mathrm{CCD}} = \sum_{\substack{i>j\\a>b}} \langle 0| \left[\sum_{pq} f_{pq} \{\hat{p}^\dagger \hat{q}\} + \frac{1}{4}\sum_{pqrs} \langle pq|rs\rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} \right] \{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} |0\rangle t_{ij}^{ab}. \tag{5.56}$$

Here the one-particle part will vanish as there is no manner one can contract all the operators in this term without using an internal contraction in the normal-ordered product. It is also useful to convert the first sum to an unrestricted sum,

$$\Delta E_{\mathrm{CCD}} = \frac{1}{16}\sum_{ijab}\sum_{pqrs} \langle pq|rs\rangle \langle 0| \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} |0\rangle t_{ij}^{ab}. \tag{5.57}$$

We contract the operators in the normal-ordered products,

$$\begin{aligned}&\langle 0|\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\}\\ &+\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} |0\rangle\end{aligned} \tag{5.58}$$

$$\begin{aligned}&=\delta_{pi}\delta_{qj}\delta_{sb}\delta_{ra} - \delta_{pi}\delta_{qj}\delta_{sa}\delta_{rb}\\ &-\delta_{pj}\delta_{qi}\delta_{sb}\delta_{ra} + \delta_{pj}\delta_{qi}\delta_{sa}\delta_{rn}.\end{aligned} \tag{5.59}$$

All these products of delta functions give us a reduction in the sums and the CCD energy becomes,

$$\Delta E_{\mathrm{CCD}} = \frac{1}{4}\sum_{ijab} \langle ij|ab\rangle t_{ij}^{ab}. \tag{5.60}$$

The natural next step is to find the amplitude equations,

$$\left\langle \Phi_{ij}^{ab}\right| \hat{H}_N \left(1 + \hat{T}_2 + \frac{1}{2}\hat{T}^2\right) |0\rangle = \Delta E_{\mathrm{CCD}} t_{ij}^{ab}. \tag{5.61}$$

We compute this expression in steps, starting with the lone normal-ordred Hamiltonian,

$$\left\langle \Phi_{ij}^{ab}\right| \hat{H}_N |0\rangle = \frac{1}{4}\sum_{pqrs} \langle 0| \{\hat{a}\hat{b}\hat{j}^\dagger \hat{i}^\dagger\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} |0\rangle \langle pq|rs\rangle , \tag{5.62}$$

here we also have to compute a few contractions,

$$\begin{aligned}&\langle 0|\{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} + \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\\ &+\{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} + \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} |0\rangle\end{aligned} \tag{5.63}$$

$$\begin{aligned}&=\delta_{ir}\delta_{js}\delta_{bq}\delta_{ap} - \delta_{ir}\delta_{js}\delta_{bp}\delta_{aq}\\ &-\delta_{is}\delta_{jr}\delta_{bq}\delta_{ap} + \delta_{is}\delta_{jr}\delta_{bp}\delta_{aq}.\end{aligned} \tag{5.64}$$

This will leave us with a similar expression as the one in the energy equation,

$$\left\langle \Phi_{ij}^{ab}\right| \hat{H}_N \left|0\right\rangle = \left\langle ab|ij\right\rangle . \tag{5.65}$$

Now for the linear terms,

$$\begin{aligned}\left\langle \phi_{ij}^{ab}\right| \hat{H}_N\hat{T}_2 \left|0\right\rangle &= \sum_{\substack{k>l\\c>d}} \left\langle \phi_{ij}^{an}\right| \hat{H}_n\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\} \left|0\right\rangle t_{kl}^{cd}\\ &= \frac{1}{4}\sum_{klcd} \left\langle \Phi_{ij}^{ab}\right| \hat{F}_N + \hat{W} \left|\Phi_{kl}^{cd}\right\rangle t_{kl}^{cd}\end{aligned} \tag{5.66}$$

Starting with the first term,

$$\begin{aligned}L_1 &= \frac{1}{4}\sum_{klcd} \left\langle \phi_{ij}^{ab}\right| \hat{F}_N \left|\phi_{kl}^{cd}\right\rangle t_{kl}^{cd}\\ &= \frac{1}{4}\sum_{klcd}\sum pq f_{pq} \left\langle \phi_{ij}^{ab}\right| \{\hat{p}^\dagger\hat{q}\} \left|\phi_{kl}^{cd}\right\rangle t_{kl}^{cd}\\ &= \frac{1}{4}\sum_{klcd}\sum_{pq} f_{pq} \left\langle 0\right| \{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\} \left|0\right\rangle t_{kl}^{cd}\end{aligned} \tag{5.67}$$

The product of normal-ordered operators must be contracted in such a way that tree and three operators in the first and last operators string are contracted with one another, and the two operators in the middle string is contracted with one operator in the last and first one. This provides us with $3 \times 3 \times 2 = 16$ possible contractions. Here are the first four contractions,

$$\begin{aligned}&\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\} + \{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\\ &+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\} + \{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\end{aligned} \tag{5.68}$$

$$\begin{aligned}&=\delta_{ik}\delta_{jl}\delta_{bd}\delta_{ap}\delta_{cq} + \delta_{ik}\delta_{jl}\delta_{ac}\delta_{bp}\delta_{dq}\\ &-\delta_{ik}\delta_{jq}\delta_{bd}\delta_{ac}\delta_{pl} - \delta_{iq}\delta_{pk}\delta_{jl}\delta_{bd}\delta_{ac}.\end{aligned} \tag{5.69}$$

The last 12 contractions will be equivalent to these four, and thus we rid ourselves of the $\frac{1}{4}$-prefactor, yielding

$$L_1 = \sum_c (f_{bc}t_{ij}^{ac} - f_{ac}t_{ij}^{bc}) + \sum_k (f_{ik}t_{jk}^{ab} - f_{jk}t_{ik}^{ab}). \tag{5.70}$$

Proceeding to the second linear term,

$$\begin{aligned}L_2 &= \frac{1}{4}\sum_{klcd} \left\langle \Phi_{ij}^{ab}\right| \hat{W} \left|\Phi_{kl}^{cd}\right\rangle t_{kl}^{cd}\\ &= \frac{1}{16}\sum_{pqrs}\sum_{klcd} \left\langle pq|rs\right\rangle \left\langle 0\right| \{\hat{j}^\dagger\hat{b}\hat{i}^\dagger\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{k}\hat{l}\} \left|0\right\rangle t_{kl}^{cd}\end{aligned} \tag{5.71}$$

Here there are many possible ways to contract the operators string, so it is convenient to label the different kinds of contractions. Subscript a-term consist of two hole-hole contractions, subscript b-terms consist of two particle-particle contractions and subscript c-terms consist of one particle-hole and one hole-particle contractions,

$$
\begin{aligned}
L_{2a} &= \frac{1}{8}\sum_{pqrs}\sum_{klcd} \langle pq|rs\rangle \langle 0|\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{k}\hat{l}\}|0\rangle t_{kl}^{cd} \\
&= \frac{1}{8}\sum_{pqrs}\sum_{cd} \langle pq|rs\rangle \langle 0|\{\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\}|0\rangle t_{kl}^{cd}
\end{aligned}
\tag{5.72}
$$

$$
\begin{aligned}
L_{2b} &= \frac{1}{8}\sum_{pqrs}\sum_{klcd} \langle pq|rs\rangle \langle 0|\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}|0\rangle t_{kl}^{cd} \\
&= \frac{1}{8}\sum_{pqrs}\sum_{kl} \langle pq|rs\rangle \langle 0|\{\hat{i}^\dagger\hat{j}^\dagger\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{l}\hat{k}\}|0\rangle t_{kl}^{cd}
\end{aligned}
\tag{5.73}
$$

$$
\begin{aligned}
L_{2c} = \frac{1}{4}\sum_{pqrs}\sum_{klcd} \langle pq|rs\rangle \langle 0|&\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\} \\
&+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\} \\
&+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\} \\
&+\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}|0\rangle t_{kl}^{cd} \\
= \frac{1}{4}\sum_{pqrs}\sum_{kc} \langle pq|rs\rangle \langle 0|&\{\hat{i}^\dagger\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{k}\} \\
&-\{\hat{j}^\dagger\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{k}\} \\
&-\{\hat{i}^\dagger\hat{b}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{k}\} \\
&+\{\hat{j}^\dagger\hat{b}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{k}\}|0\rangle .
\end{aligned}
\tag{5.74}
$$

The vacuum expectation value in L_{2a} can be evaluated as,

$$
\begin{aligned}
\langle 0|&\{\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\} + \{\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\} \\
&+\{\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\} + \{\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\}|0\rangle
\end{aligned}
\tag{5.75}
$$

$$
\begin{aligned}
&=\delta_{bq}\delta_{ap}\delta_{sd}\delta_{rc} - \delta_{bq}\delta_{ap}\delta_{sc}\delta_{rd} \\
&-\delta_{aq}\delta_{bp}\delta_{sd}\delta_{rc} + \delta_{aq}\delta_{bp}\delta_{sc}\delta_{rd}
\end{aligned}
\tag{5.76}
$$

Inserting this result into the original expression and substituting to similar indicies will yield,

$$
L_{2a} = \frac{1}{2}\sum_{cd} \langle ab|cd\rangle t_{ij}^{cd}. \tag{5.77}
$$

A very similar computation will yield the following result for the next linear term,

$$
L_{2b} = \frac{1}{2}\sum_{kl} \langle kl|ij\rangle t_{kl}^{ab}. \tag{5.78}
$$

The last linear term is very different, however. INSERT SOMETHING HERE!

After long last, we have only the quadratic term to deal with,

$$
Q = \frac{1}{8}\sum_{pqrs}\sum_{\substack{k>l\\c>d}}\sum_{\substack{m>n\\e>f}} \langle pq|rs\rangle \langle 0|\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\{\hat{e}^\dagger\hat{f}^\dagger\hat{n}\hat{m}\}|0\rangle t_{kl}^{dc}t_{mn}^{ef}. \tag{5.79}
$$

In this expression there are no non-zero contractions between the third and fourth normal ordered operator string. We therefore need to contract operators in the first normal-ordered string with operators either in the third or four string, and the operator in the second string with the rest.

We start by contracting all operators in the first normal-ordered string with all the operators in the fourth normal-ordered string,

$$\begin{aligned}
&\frac{1}{8}\sum_{pqrs}\sum_{\substack{k>l\\c>d}}\sum_{\substack{m>n\\e>f}} \langle pq|rs\rangle \langle 0|\,\{\hat{i}^\dagger\hat{j}^\dagger\hat{b}\hat{a}\}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\{\hat{e}^\dagger\hat{f}^\dagger\hat{n}\hat{m}\}\,|0\rangle\, t_{kl}^{cd}t_{mn}^{ef} \\
&\qquad = \frac{1}{8}\sum_{pqrs}\sum_{\substack{k>l\\c>d}} \langle pq|rs\rangle \langle 0|\,\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\,|0\rangle\, t_{kl}^{cd}t_{ij}^{ab}.
\end{aligned} \tag{5.80}$$

There are four possible ways to contract this last term, resulting in

$$\frac{1}{2}\sum_{\substack{k>l\\c>d}} \langle kl|cd\rangle\, t_{kl}^{cd}t_{ij}^{ab}. \tag{5.81}$$

We get the same result by contracting the four operators in the first string with the four operators in the third string, cancelling the factor $\frac{1}{2}$, eventually yielding a result equal to $\Delta E_{\text{CCD}}t_{ij}^{ab}$, which we see by comparing this result to Equation 5.51.

There are four remaining reasonable classes in which to sort the permutations of contractions that remain;

a the two hole operators in the first string are contracted with the third or fourth operator string, yielding equal results;

b one hole and one particle operators in the first string are contracted with operators in the third string, the rest of the operators in the first string are contracted with operators in the fourth string;

c two particle operators and one hole operator from the first string are contracted with operators in the third string, the last hole operator is contracted with an operator in the fourth string;

d one particle operator and two hole operators are contracted with operators in the third string and the last particle operator with an operator in the fourth string.

The results for class a and class b are somewhat straight-forward to compute, giving the following,

$$\begin{aligned}
Q_a &= \frac{1}{16}\sum_{pqrs}\sum_{klcd} \langle pq|rs\rangle \langle 0|\,\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{l}\hat{k}\}\{\hat{c}^\dagger\hat{d}^\dagger\}\,|0\rangle\, t_{ij}^{cd}t_{kl}^{ab} \\
&\qquad\qquad = \frac{1}{4}\sum_{klcd} \langle kl|rs\rangle\, t_{ij}^{cd}t_{kl}^{ab}
\end{aligned} \tag{5.82}$$

$$\begin{aligned}
Q_b &= \frac{1}{4}\sum_{pqrs}\sum_{klcd} \langle pq|rs\rangle \langle 0|\,\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{k}\}\{\hat{d}^\dagger\hat{l}\}\,|0\rangle\, (t_{ik}^{ac}t_{jl}^{bd} - t_{ik}^{bc}t_{jl}^{ad}) \\
&= \sum_{klcd} \langle kl|cd\rangle\, (t_{ik}^{ac}t_{jl}^{bd} - t_{ik}^{bc}t_{jl}^{ad}) = \sum_{klcd} \langle kl|cd\rangle\, (t_{ik}^{ac}t_{jl}^{bd} - t_{ik}^{bd}t_{jl}^{ac})
\end{aligned} \tag{5.83}$$

The sets of terms for class c and d can each be generated in two distinct ways, dependent on the choice of the tree operators from the first operator string ($\hat{i}^\dagger\hat{a}\hat{b}$ or $\hat{j}^\dagger\hat{a}\hat{b}$ for c and $\hat{i}^\dagger\hat{j}^\dagger\hat{a}$ or $\hat{i}^\dagger\hat{j}^\dagger\hat{b}$

for d). In each case there are 16 possibilities; the three operators from the first string can be contracted with operators in both the third or fourth string in four ways and the remaining operators can be then be contracted in two ways. All these possibilities lead to equivalent results. For example, here is the first Q_c term,

$$\begin{aligned}
&\frac{1}{8}\sum_{pqrs}\sum_{klcd}\sum_{mnef} \langle pq|rs\rangle \langle 0| \{\hat{i}^\dagger \hat{j}^\dagger \hat{b}\hat{a}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{l}\hat{k}\}\{\hat{e}^\dagger\hat{f}^\dagger\hat{n}\hat{m}\} |0\rangle\, t_{kl}^{cd} t_{mn}^{ef} \\
&\quad = -\frac{1}{8}\sum_{pqrs}\sum_{klcd} \langle pq|rs\rangle \langle 0| \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{k}\}\{\hat{l}\} |0\rangle\, t_{kj}^{cd} t_{li}^{ab} |0\rangle
\end{aligned} \tag{5.84}$$

The remaining operators in this expression can be contracted in four ways,

$$\begin{aligned}
&\langle 0|\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{k}\}\{\hat{l}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{k}\}\{\hat{l}\} \\
&\quad + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{k}\}\{\hat{l}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{c}^\dagger\hat{d}^\dagger\hat{k}\}\{\hat{l}\} |0\rangle
\end{aligned} \tag{5.85}$$

$$= \delta_{pl}\delta_{qk}\delta_{rd}\delta_{sc} - \delta_{pk}\delta_{ql}\delta_{rd}\delta_{sc} - \delta_{pl}\delta_{qk}\delta_{rc}\delta_{sd} + \delta_{pk}\delta_{ql}\delta_{rc}\delta_{sd} \tag{5.86}$$

Algbra eventually leads to,

$$-\frac{1}{2}\sum_{klcd} \langle kl|cd\rangle\, t_{ik}^{ab} t_{jl}^{cd}. \tag{5.87}$$

A similar computations provides the second Q_c term,

$$-\frac{1}{2}\sum_{klcd} \langle kl|cd\rangle\, t_{ik}^{cd} t_{jl}^{ab} \tag{5.88}$$

These two terms give us,

$$Q_c = -\frac{1}{2}\sum_{klcd} \langle kl|cd\rangle\, (t_{ik}^{ab} t_{jl}^{cd} - t_{ik}^{cd} t_{jl}^{ab}) \tag{5.89}$$

Treating the class d terms gives,

$$Q_d - \frac{1}{2}\sum_{klcd} \langle kl|cd\rangle\, (t_{ij}^{ac} t_{kl}^{bd} - t_{ij}^{bd} t_{kl}^{ac}). \tag{5.90}$$

Combining all the quadratic terms will now yield the same as in Equation 5.50, and we can conclude that an algebraic derivation of the coupled cluster method is equivalent to the configuration space derivation.

5.3 The Coupled Cluster Equations

In general there is a more useful and compact approach that can be used to derive the coupled cluster equations, compared to the lengthy derivation of the CCD equations above. We start by inserting the coupled cluster wavefunctions into the time-independent Schrödinger equation,

$$\hat{H}_N e^{\hat{T}} |\Phi_0\rangle = \Delta E e^{\hat{T}} |\Phi_0\rangle . \tag{5.91}$$

In order to find an expression for the energy and amplitude equations one could try to left-project with $\langle \Phi_0|$. This would propel us in the same direction as in the previous section, i.e. Equation 5.17 and onwards. Instead, we multipy from the left with $e^{-\hat{T}}$ first, and then left-project with $\langle\Phi_0|$,

$$\begin{aligned}\langle\Phi_0| e^{-\hat{T}}\hat{H}_N e^{\hat{T}} |\Phi_0\rangle &= \langle\Phi_0| e^{-\hat{T}}\Delta E e^{\hat{T}} |\Phi_0\rangle \\ \rightarrow \langle\Phi_0| e^{-\hat{T}}\hat{H}_N e^{\hat{T}} |\Phi_0\rangle &= \Delta E.\end{aligned} \tag{5.92}$$

Left-projecting with an excited state, $\langle\Phi_{ij\dots}^{ab\dots}|$ will give us expression for the corresponding amplitude $t_{ij\dots}^{ab\dots}$,

$$\langle\Phi_{ij\dots}^{ab\dots}| e^{-\hat{T}}\hat{H}_N e^{\hat{T}} |\Phi_0\rangle = 0. \tag{5.93}$$

Now we have obtained a *non-Hermitian*[2], similarity-transformed Hamiltonian,

$$\mathscr{H} = e^{-\hat{T}}\hat{H}_N e^{\hat{T}}, \tag{5.94}$$

which has $|\Phi_0\rangle$ as right eigenfunction and E as the corresponding eigenvalue. Importantly, a similarity-transformation will not change the eigenvalue spectrum of the operator.

A benefit of the similarity-transformed Hamiltonians is that we can write the operators more expicitly by applying the Baker-Campbell-Haussdorff expansion[7, 4, 25],

$$\begin{aligned}e^{-\hat{B}}\hat{A}e^{\hat{B}} =&(1-\hat{B}+\frac{1}{2}\hat{B}^2-\frac{1}{3!}+\dots)\hat{A}(1+\hat{B}+\frac{1}{2}+\frac{1}{3!}\hat{B}^3+\dots) \\ =&\hat{A}+(\hat{A}\hat{B}-\hat{B}\hat{A})+\frac{1}{2}(\hat{A}\hat{B}^2+2\hat{B}\hat{A}\hat{B}+\hat{B}^2\hat{A}) \\ &+\frac{1}{3!}(\hat{A}\hat{B}^3-3\hat{B}\hat{A}\hat{B}^2+3\hat{B}^2\hat{A}\hat{B}-\hat{B}^3\hat{A})+\dots \\ =&\hat{A}+[\hat{A},\hat{B}]+\frac{1}{2}\{(\hat{A}\hat{B}-\hat{B}\hat{A})\hat{B}-\hat{B}(\hat{A}\hat{B}-\hat{B}\hat{A})\} \\ &+\frac{1}{3!}\{[(\hat{A}\hat{B}-\hat{B}\hat{A})\hat{B}-\hat{B}(\hat{A}\hat{B}-\hat{B}\hat{A})]\hat{B} \\ &-\hat{B}[(\hat{A}\hat{B}-\hat{B}\hat{A})\hat{B}-\hat{B}(\hat{A}\hat{B}-\hat{B}\hat{A})]\}+\dots \\ =&\hat{A}+[\hat{A},\hat{B}]+\frac{1}{2}[[\hat{A},\hat{B}],\hat{B}]+\frac{1}{3!}[[[\hat{A},\hat{B}],\hat{B}],\hat{B}]+\dots.\end{aligned} \tag{5.95}$$

Applying the Baker-Campbell-Haussdorff expansion to the similarity-transformed Hamiltonians yields

$$\begin{aligned}\mathscr{H} = e^{-\hat{T}}\hat{H}_N e^{\hat{T}} = \hat{H}_N &+ [\hat{H}_N,\hat{T}] + \frac{1}{2}[[\hat{H}_N,\hat{T}],\hat{T}] + \frac{1}{3!}[[[\hat{H}_N,\hat{T}],\hat{T}],\hat{T}] \\ &+\frac{1}{4!}[[[[\hat{H}_N,\hat{T}],\hat{T}],\hat{T}],\hat{T}].\end{aligned} \tag{5.96}$$

Notice the absence of an “and so on”-operator ($\dots$) in this expression. The Baker-Campbell-Hausdorff expansion for the electronic Hamiltonian, containing at most two-particle interactions, will terminate with the four-fold commutator.

By applying the generalised Wick’s theorem to the Baker-Campbell-Hausdorff expansion of the Hamiltonian in Equation 5.96, we will be confronted with a vast simplification. Applying the generalised Wick’s theorm to a commutator gives the following

$$[\hat{A},\hat{B}] = \hat{A}\hat{B}-\hat{B}\hat{A} = \{\hat{A}\hat{B}\} + \{\overbracket{\hat{A}\hat{B}}\} - \{\hat{B}\hat{A}\} - \{\overbracket{\hat{B}\hat{A}}\}, \tag{5.97}$$

where $\hat{A}$ and $\hat{B}$ are normal-ordered operators, each with an even number of creation- and annihilation operators[3]. In this expression $\{\}$ denotes a normal-ordering of the operators inside

[2]We will show later that this non-Hermiticity is somewhat problematic.

[3]It is not a coincidence that both the normal-ordred Hamiltonian $\hat{H}_N$ and the cluster operator $\hat{T}$ satisfy these condtions

the braces and $\{\overbracket{\hat{A}\hat{B}}\}$ represents a sum of all normal-ordered products of operators in which there are one or more contractions between creation or annihilation operators in $\hat{A}$ and those in $\hat{B}$. We must also have that

$$\{\hat{A}\hat{B}\} = \{\hat{B}\ \hat{A}\}, \tag{5.98}$$

since the two operators both contain an even number of creation- and annihilation operators. This means that what remains of Equation 5.97 is simply

$$[\hat{A}, \hat{B}] = \{\overbracket{\hat{A}\hat{B}}\} - \{\overbracket{\hat{B}\hat{A}}\}. \tag{5.99}$$

The general m-fold cluster operator T_m contains some number of creation operators $\hat{a}^\dagger, \hat{b}^\dagger \ldots$ and hole operators $\hat{\imath}, \hat{\jmath}, \ldots$, and the only possible non-zero contractions are $\overbracket{\hat{a}\hat{b}^\dagger} = \delta_{ab}$ and $\overbracket{\hat{\imath}^\dagger\hat{\jmath}} = \delta_{ij}$. Moreover, since the different cluster operators commute, no nonzero conatractions exist between different $\hat{T}_m$ operators. Ergo, in the neste commutators from Equation 5.96, we only see surviving terms between the Hamiltonian $\hat{H}_N$ and one or more of the cluster operators $\hat{T}_m$. This accounts for the natural truncation at the four-fold commutator. In fact, we can rewrite the Baker-Campbell-Haussdorff-expanded similarity-transformed Hamiltonian as

$$\mathscr{H} = e^{-\hat{T}}\hat{H}_N e^{\hat{T}} = \hat{H}_N + \overbracket{\hat{H}_N\hat{T}} + \frac{1}{2}\overbracket{\hat{H}_N\overline{\hat{T}\hat{T}}} + \frac{1}{3!}\overbracket{\hat{H}_N\overline{\hat{T}\hat{T}\hat{T}}} + \frac{1}{4!}\overbracket{\hat{H}_N\overline{\hat{T}\hat{T}\hat{T}\hat{T}}}, \tag{5.100}$$

where the very interesting notation combining a contraction line and an horizontal bar indicates a sum over all terms in which the Hamiltonian $\hat{H}_N$ is connected by at least one contraction with each of the following cluster operators $\hat{T}$.

Disconnected clusters that on the form $\hat{T}_m\hat{T}_n$, which can be found in the coupled cluster wavefunction are not present in the Baker-Campbell-Hausdorff expansion of the similarity-transformed Hamiltonian. This is true also for the coupled cluster amplitude equations, which may be written

$$\langle\Phi_0| e^{-\hat{T}}\hat{H}_N e^{\hat{T}} |\Phi_0\rangle = \langle\Phi_0| \hat{H}_N e^{\hat{T}} |\Phi_0\rangle_C = \Delta E \tag{5.101}$$

$$\left\langle\Phi_{ij\ldots}^{ab\ldots}\right| e^{-\hat{T}}\hat{H}_N e^{\hat{T}} |\Phi_0\rangle = \left\langle\Phi_{ij\ldots}^{ab\ldots}\right| \hat{H}_N e^{\hat{T}} |\Phi_0\rangle_C = 0, \tag{5.102}$$

where the inclusion of only connected terms is underlined.

The CCSD equations take the form

$$\langle\Phi_0| \hat{H}_N \Big(\hat{T}_1 + \frac{1}{2}\hat{T}_1^2 + \hat{T}_2\Big) |\Phi_0\rangle_C = \Delta E \tag{5.103}$$

$$\langle\Phi_i^a| \hat{H}_N \Big(1 + \hat{T}_1 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_1\hat{T}_2 + \hat{T}_2\Big) |\Phi_0\rangle_C = 0 \tag{5.104}$$

$$\left\langle\Phi_{ij}^{ab}\right| \hat{H}_N \Big(1 + \hat{T}_1 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{4!}\hat{T}_1^4 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2\Big) |\Phi_0\rangle_C = 0. \tag{5.105}$$

For CCSDT, the energy expression is the same, whil the amplitude equations take the form

$$\langle\Phi_i^a| \hat{H}_N \Big(1 + \hat{T}_1 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_1\hat{T}_2 + \hat{T}_2 + \hat{T}_3\Big) |\Phi_0\rangle_C = 0 \tag{5.106}$$

$$\begin{aligned}\left\langle\Phi_{ij}^{ab}\right| \hat{H}_N \Big(1 &+ \hat{T}_1 + \frac{1}{2}\hat{T}_1^2 + \frac{1}{3!}\hat{T}_1^3 + \frac{1}{4!}\hat{T}_1^4 + \hat{T}_2 \\ &+ \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \hat{T}_3 + \hat{T}_1\hat{T}_3\Big) |\Phi_0\rangle_C = 0\end{aligned} \tag{5.107}$$

$$\begin{aligned}\left\langle\Phi_{ij}^{ab}\right| \hat{H}_N \Big(\hat{T}_2 &+ \hat{T}_3 + \frac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_2 + \hat{T}_2\hat{T}_3 + \hat{T}_1\hat{T}_3 \\ &+ \frac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{2}\hat{T}_1\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_3 + \frac{1}{3!}\hat{T}_1^3\hat{T}_2) |\Phi_0\rangle_C = 0\end{aligned} \tag{5.108}$$

the final result of the computation of these equations are provided in the appendices INSERT INTO THE APPENDICES!

5.4 A Variational Formulation of Coupled Cluster

See Kvaal[40]

The Coupled Cluster method is very successful in computing energies, but computing other expectations values has been a problem. For instance we see that the way we compute the coupled cluster energy,

$$E_{\mathrm{CC}} = \langle \Phi | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi \rangle \,, \tag{5.109}$$

is not the same as one would compute the energy of the system variationally,

$$\langle \hat{H} \rangle_{\mathrm{var}} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Phi | e^{\hat{T}^\dagger} \hat{H} e^{\hat{T}} | \Phi \rangle}{\langle \Phi | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi \rangle} \tag{5.110}$$

Moreover, the similarity transformed operators are not Hermitian. This can be showed by inference

$$\hat{T}_1^\dagger = \left(\sum_{ia} t_i^a \hat{a}^\dagger \hat{i} \right)^\dagger \sum_{ia} (t_i^a)^* \hat{i}^\dagger \hat{a} \neq \hat{T}_1, \tag{5.111}$$

from which it follows that

$$\left(e^{-\hat{T}} \hat{H} e^{\hat{T}} \right)^\dagger = (e^{\hat{T}})^\dagger \hat{H} (e^{-\hat{T}})^\dagger = e^{\hat{T}^\dagger} \hat{H} e^{-\hat{T}^\dagger} \neq e^{-\hat{T}} \hat{H} e^{\hat{T}}. \tag{5.112}$$

Variational computations as in Equation 5.110 has been attempted by Cizek[8] and Fink[16]. Regrettably, the coupled cluster exponential wavefunction is not a variationally optimal wavefunction, as it give rise to series expansions in the numerator and denominator in the expression for the variational expectation value. For a general operator $\hat{O}$, we have

$$\begin{aligned}
\langle \hat{O} \rangle_{\mathrm{var}} &= \frac{\langle \Psi | \hat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Phi | e^{\hat{T}^\dagger} \hat{O} e^{\hat{T}} | \Phi \rangle}{\langle \Phi | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi \rangle} \\
&= \frac{\langle \Phi | [1 + \hat{T}^\dagger + \frac{1}{2!} (\hat{T}^\dagger)^2 + \frac{1}{3!} (\hat{T}^\dagger)^3 + \ldots] \hat{O} [1 + \hat{T} + \frac{1}{2!} \hat{T} 2 + \frac{1}{3!} \hat{T}^3 + \ldots] | \Phi \rangle}{\langle \Phi | [1 + \hat{T}^\dagger + \frac{1}{2!} (\hat{T}^\dagger)^2 + \frac{1}{3!} (\hat{T}^\dagger)^3 + \ldots][1 + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \ldots] | \Phi \rangle}.
\end{aligned} \tag{5.113}$$

In contrast with the expansions if the coupled cluster amplitude equations, which truncates naturally after products of four $\hat{T}$ operators, the expansions for $e^{\hat{T}^\dagger}$ and $e^{\hat{T}}$ terminates only if the total excitation level represented by a product of $\hat{T}$ operators exceed the number of electrons in the wavefunctions. This means that the number of terms and the computational effort required to compute expectation values in this way is usually very high.

An idea is to simply use a similar expression to the coupled cluster energy expression

$$\langle O \rangle_{\mathrm{Goldstone}} = \langle \Phi | e^{-\hat{T}} \hat{O} e^{\hat{T}} | \Phi \rangle \,. \tag{5.114}$$

The problem with this expression, as well as with Equation 5.113, is that none of them conform with the Hellmann-Feynman theorem and the problem remains, the coupled cluster energy is arrived at non-variationally, and is therefore non-stationary.

5.4.1 The Hellmann-Feynman Theorem

The Hellmann-Feynmann[14] theorem relates the first order change of total energy with respect to a parameter to the first order change of the Hamiltonian with respect to the same parameters,

$$\left.\frac{dE}{d\alpha}\right|_{\alpha=0} = \frac{\partial}{\partial t} \langle \Psi_\alpha | \hat{H} | \Psi_\alpha \rangle \,, \tag{5.115}$$

where Ψ is the exact state, variationally determined from the Hamiltonian of the system, and $\Psi_\alpha = N(\Psi + \alpha\delta\Psi)$ is varitation of this state, implicitly dependent on the parameter α.

Proof of the Hellmann-Feynman theorem

Using the following conditions,

$$\hat{H}_\lambda \left|\psi_\lambda\right\rangle = E_\lambda \left|\psi_\lambda\right\rangle \tag{5.116}$$

$$\langle \psi_\lambda | \psi_\lambda \rangle = 1, \tag{5.117}$$

we prove

$$\frac{\partial E_\lambda}{\partial \lambda} = \left\langle\psi_\lambda\right| \frac{\partial \hat{H}}{\partial \lambda} \left|\psi_\lambda\right\rangle . \tag{5.118}$$

Now,

$$E_\lambda = \left\langle\psi_\lambda\right| \hat{H} \left|\psi_\lambda\right\rangle = \int \psi_\lambda \hat{H} \psi_\lambda^* dr \tag{5.119}$$

whence,

$$\begin{aligned} \frac{\partial E_\lambda}{\partial \lambda} &= \int \psi_\lambda \frac{\hat{H}}{\partial \lambda} \psi_\lambda^* dr + \int \frac{\psi_\lambda}{\partial \lambda} \hat{H} \psi_\lambda^* dr + \int \psi_\lambda \hat{H} \frac{\psi_\lambda^*}{\partial \lambda} dr \\ &= \int \psi_\lambda \frac{\hat{H}}{\partial \lambda} \psi_\lambda^* dr + E_\lambda \int \frac{\psi_\lambda}{\partial \lambda} \psi_\lambda^* dr + E_\lambda \int \psi_\lambda \frac{\psi_\lambda^*}{\partial \lambda} dr \\ &= \int \psi_\lambda \frac{\hat{H}}{\partial \lambda} \psi_\lambda^* dr + E_\lambda \frac{\partial}{\partial \lambda} \langle \psi_\lambda | \psi_\lambda \rangle = \left\langle\psi_\lambda\right| \frac{\partial \hat{H}}{\partial \lambda} \left|\psi_\lambda\right\rangle . \end{aligned} \tag{5.120}$$

By treating an observable of the system as a perturbation of the Hamiltonian,

$$\hat{H}'(\alpha) = \hat{H} + \alpha \hat{V},$$

the Hellman-Feynman theorem provides us with a way to evaluate the expected value of this observable if we have the exact wavefunction and energy,

$$\left.\frac{dE}{d\alpha}\right|_{\alpha=0} = \frac{\partial}{\partial \alpha} \langle \Psi_\alpha | \hat{H} + \alpha \hat{O} | \Psi_\alpha \rangle = \langle \hat{O} \rangle \,. \tag{5.121}$$

The problem with some computational techniques, like the coupled cluster method, is that the final energy is not variationally determined (non-stationary), and we cannot invoke the Hellmann-Feynman theorem to simplify computation of molecular properties. At first, it would appear that one would have to resort to a more cumbersome computation, like the expansionn of clustes operators above (Equation 5.113). But fortunately, there exists a way to reformulate the energy function of a non-variational wavefunction in such a way that the energy is stationary with respect to the variables of the new formulation.

Consider an energy that depends on two sets of parameters. The parameter α which describes a perturbation and the parameters α which describe the wavefunction. The optimal energy $E(\alpha)$ is obtained by an optimised set of parameters λ^*, which are innserted into the energy function $E(\alpha, \alpha)$;

$$E(\alpha) = E(\alpha, \lambda^*), \tag{5.122}$$

the values for α and λ^* are obtained as the solution to some set of equations

$$\mathbf{f}(\alpha, \lambda^*) = 0 \quad \forall \alpha, \tag{5.123}$$

For *variational* wavefunctions, this condition corresponds to the stationarity requirement,

$$\frac{\partial E_{\text{var}}(\alpha, \lambda)}{\partial \lambda}\Big|_{(\lambda=\lambda^*)} = 0 \quad \forall \alpha, \tag{5.124}$$

but not for *non-variational* wavefunctions. Writing out this derivative yields,

$$\frac{dE(\alpha)}{d\alpha} = \frac{dE(\alpha, \lambda)}{d\alpha}\Big|_{(\lambda=\lambda^*)} = \frac{\partial E(\alpha, \lambda)}{\partial \alpha}\Big|_{(\lambda=\lambda^*)} + \frac{\partial E(\alpha, \lambda)}{\partial \lambda}\Big|_{(\lambda=\lambda^*)} \cdot \frac{\partial \lambda}{\partial}\alpha\Big|_{(\lambda=\lambda^*)}. \tag{5.125}$$

For a variational wavefunction, the last term will vanish due to the stationarity condition in Equation 5.124. This would leave us with

$$\frac{dE_{\text{var}}(\alpha)}{d\alpha} = \frac{\partial E(\alpha, \lambda)}{\partial \alpha}\Big|_{(\lambda=\lambda^*)}, \tag{5.126}$$

i.e. that the total derivative corresponds to the partial derivative. This means that if the variational eneryg corresponds to an expectation value $E_{\text{var}}(\alpha, \lambda) = \langle \lambda | \hat{H}(\alpha) | \lambda \rangle$, and the perturbed system is described by the Hamiltonian $\hat{H}(\alpha) = \hat{H} + \alpha \hat{V}$, we recover the presumed expression

$$\frac{dE(\alpha, \lambda)}{d\alpha}\Big|_{(\alpha=0)}, \tag{5.127}$$

in accordance with first-order perturbation theory and the Hellmann-Feynmann theorem.

But if we look at nonvariational energies, Equation 5.125, will not simplify to just the partial derivative, since the stationarity condition does not hold. What we do is replace the now nonvariational function $E(\alpha, \lambda)$ by a new function $L(\alpha, \lambda, \bar{\lambda})$ with a stationary point $(\lambda^*, \bar{\lambda}^*)$ that satisfies the nonvariational condition Equation 5.123 , and whose values at this point correspond to the optimals energy. Inded, we apply Langrange's method of undetermined multipliers, by regarding the energy $E(\alpha, \lambda)$ a an *unconstrained* optimisation problem, but subject to the constraints of the variational parameters λ, which satisfy Equation 3.17;

$$L(\alpha, \lambda, \bar{\lambda}) = E(\alpha, \lambda) + \bar{\lambda} \cdot \mathbf{f}(\alpha, \lambda). \tag{5.128}$$

A necessary condition for the optimum Lagrange multipliers $\bar{\lambda}^*$ to be unique is that the the Jacobian of $\mathbf{f}$, $\mathscr{J} \equiv \partial \mathbf{f}(\alpha, \lambda)/\partial \lambda$ is non-singular and invertible.

5.4.2 The Lagrangian Formulation of Coupled Cluster

As we outlined in the previous section, the solution to making the coupled cluster theory into a variational theory is to find a set of equations which are zero for a set of parameters (Equation 5.123). These parameters should in turn provide the optimal energy by insertion into the expression for energy. Luckily, Helgaker and Jørgensen[28, 29] had the insight to realise that we are already given such a set of parameters and equations in the formulation of coupled cluster, namely the amplitudes and the amplitude equations respectively. The Hellmann-Feynman theorem will be baked into the very definition of such a expectation value functional,

$$\langle \hat{O} \rangle_{\text{H-F}} = \mathscr{L}_{\text{O}}(\alpha^*, \lambda^*, \bar{\lambda}^*) = E(\alpha^*, \lambda^*, \bar{\lambda}^*) + \bar{\lambda}^* \cdot \mathbf{f}(\alpha^*, \lambda^*). \tag{5.129}$$

This equation is essentially a restatement of Equation 5.128, with the optimal parameters.

More specifically, we simplify the notation in some measure and state the coupled cluster energy Lagrangian,

$$\mathscr{L}_{\hat{H}}(t,\lambda) = \langle\Phi|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi\rangle + \sum_{\mu}\lambda_\mu \langle\Phi|X_\mu^\dagger e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi\rangle = \langle\Phi|(1+\Lambda)e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi\rangle\,, \tag{5.130}$$

where we have introduced $\Lambda = \sum_\mu X_\mu^\dagger$. Here, $X_\mu^\dagger$ is a general relaxation operator, for instance $\hat{X}_1^\dagger = \{\hat{i}\hat{a}^\dagger\}$. So Λ written out is

$$\Lambda = \sum_{ia}\lambda_a^i\hat{i}^\dagger + \frac{1}{2!^2}\sum_{ijab}\lambda_{ab}^{ij}\hat{i}^\dagger\hat{a}\hat{j}^\dagger\hat{a} + \dots \tag{5.131}$$

The coupled cluster Lagrangian in Equation 5.130 can be rewritten with the use of density operators,

$$\mathscr{L}_{\hat{H}}(t,\lambda) = \mathrm{tr}\{\hat{H}\hat{\rho}\}, \quad \hat{\rho} = e^{\hat{T}}|\Phi\rangle\langle\Phi|(1+\Lambda)e^{-\hat{T}}, \tag{5.132}$$

in a pure state description. We check to see if the attributes of the density operator endures,

$$\begin{aligned}\hat{\rho}^2 &= e^{\hat{T}}|\Phi\rangle\langle\Phi|(1+\Lambda)e^{-\hat{T}}e^{\hat{T}}|\Phi\rangle\langle\Phi|(1+\Lambda)e^{-\hat{T}} \\ &= e^{\hat{T}}|\Phi\rangle\langle\Phi|(1+\Lambda)e^{-\hat{T}} + e^{\hat{T}}|\Phi\rangle\cancelto{0}{\langle\Phi|\Lambda|\Phi\rangle}\langle\Phi|e^{-\hat{T}} = \hat{\rho} \\ \mathrm{Tr}\{\hat{\rho}\} &= \sum_{pq}\langle\phi_p|e^{\hat{T}}|\phi_q\rangle\langle\phi_q|(1+\Lambda)e^{-\hat{T}}|\phi_p\rangle = \sum_{pq}\delta_{pq} = 1\end{aligned}$$

NOT ENTIRELY SURE THAT THE LAST ONE IS GOOD. We see however, that another problem has presented itself, as the density operator is non-Hermitian. This leads us to the *bivariational*, Hellmann-Feynman conforming framework developed by Arponen[3].

5.4.3 The Bivariational Principle

Arponen approached the coupled cluster problem by employing a very general form of the variational principle callsed the bivariational principle. Letting $\hat{H}$, be a (possibly non-Hermitian) operator over Hilbert space $\mathcal{H}$, the bivariational expectation functional is defined by

$$\mathscr{E}_{\hat{H}} : \mathcal{H}'\times\mathcal{H}\to\mathbb{C}, \quad \mathscr{E}_{\hat{H}}(\tilde{\Psi},\Psi) = \frac{\left\langle\tilde{\Psi}\middle|\hat{H}\middle|\Psi\right\rangle}{\left\langle\tilde{\Psi}\middle|\Psi\right\rangle} = \frac{\mathrm{tr}\left\{\hat{H}\hat{\rho}\right\}}{\mathrm{tr}\{\rho\}}. \tag{5.133}$$

The main difference from the traditional and usual variational principle is that $\langle\tilde{\Psi}|$ and $|\Psi\rangle$ are treated as independent elements of the Hilbert space, and $\hat{\rho} = |\Psi\rangle\langle\tilde{\Psi}|$. In the usual variational principle, we have $\langle\tilde{\Psi}| \equiv |\Psi\rangle$, which are *not* independent. Nevertheless, since the Hamiltonian $\hat{H}$ is Hermitian, $\langle\tilde{\Psi}|$ and $|\Psi\rangle$ can be treated independent in the derivations of stationary conditions, which are that the left- and right eigenvalues of $\langle\tilde{\Psi}|$ and $|\Psi\rangle$, repectably, must be the same, id est

$$\hat{H}|\Psi\rangle = E|\Psi\rangle\,, \quad \langle\tilde{\Psi}|\hat{H} = \langle\tilde{\Psi}|E. \tag{5.134}$$

Here $E = \mathcal{E}_{\hat{H}}(\tilde{\Psi},\Psi)$ is the value at the stationary point.

We transition to coupled cluster theory by inserting the coupled cluster exponential wave functions, $|\Psi\rangle = e^{\hat{T}}|\Phi\rangle$ and $\left\langle\tilde{\Psi}\right| = \langle\Phi|e^{\tilde{T}}$, where $\tilde{T} = \tilde{t}X^\dagger$ are some general relaxation operator. The bivariational functional becomes

$$\mathscr{E}_{\hat{H}} = \frac{\langle\Phi|e^{\tilde{T}}\hat{H}e^{\hat{T}}|\Phi\rangle}{\langle\Phi|e^{\tilde{T}}e^{\hat{T}}|\Phi\rangle} \tag{5.135}$$

Varying this functional over all untruncated excitation and relaxation operators, $\hat{T}$ and $\tilde{T}$, is the foundation of variational coupled cluster theory[5], which is equivalent to full configuration interaction within the given single-particle basis set.

Now we wish to show that Arponen's framework corresponds to that of Helgakger and Jørgensen. We simplfy the expression by performing a variable change $(\hat{T}, \tilde{T}) \rightarrow (\hat{T}, \hat{S})$, where S is a new relaxation operator. We start by introducing

$$\langle \omega | = \frac{\langle \tilde{\Psi} | e^{\hat{T}}}{\langle \tilde{\Psi} | \Psi \rangle}, \tag{5.136}$$

which satisfies $\langle \omega | \Phi \rangle = 1$, implying that there must exist an operator $\hat{S} = sX^{\dagger}$, such that $\langle \omega | = \langle \Phi | e^{\hat{S}}$. Then we can write,

$$\frac{\langle \tilde{\Psi} | e^{\hat{T}}}{\langle \tilde{\Psi} | \Psi \rangle} = \langle \Psi | e^{\hat{S}}, \rightarrow \langle \tilde{\Psi} | = \langle \tilde{\Psi} | \Psi \rangle \langle \Phi | e^{\hat{S}} e^{-\hat{T}}. \tag{5.137}$$

This enables us to rewrite the bivariational principle (Equation 5.135) to

$$\mathscr{E}_{\hat{H}} = \langle \Phi | e^{\hat{S}} e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi \rangle, \tag{5.138}$$

which is an exact functional if $\hat{T}$ and $\hat{S}$ are not truncated. Comparing this expression to the coupled cluster Lagrangian in Equation 5.130, we can only conlude that our seemingly serendipitous algebra acrobatics has revealed that $e^{\hat{S}} = 1 + \Lambda$. Truthfully, we have strong indication the coupled cluster bivariational functional (Equation 5.135) is the same as the the coupled cluster Lagrangian (Equation 5.130). As a sidenote, pruning the expression in Equation 5.138 to only include single and double excitations will yield Arponen's *extended coupled cluster* (ECC) method.

First order conditions of the coupled cluster energy Lagrangian in Equation 5.130 gives us a new set of amplitude equations,

$$\frac{\partial}{\partial \lambda_{\mu}} \mathscr{L}(t, \lambda) = \left\langle \Phi_{X_{\mu}} \middle| e^{-\hat{T}} \hat{H} e^{\hat{T}} \middle| \Phi \right\rangle = 0 \tag{5.139}$$

$$\frac{\partial}{\partial t_{\mu}} \mathscr{L}(t, \lambda) = \langle \Phi | (1 + \Lambda) e^{-\hat{T}} [\hat{H}, X_{\mu}] e^{\hat{T}} | \Phi \rangle = 0. \tag{5.140}$$

Under constrained optimisation all partial derivatives vanish at the same point,

$$\frac{\partial \mathscr{L}}{\partial \lambda_{\mu}}\Big|_{t=t^*} = 0, \quad \frac{\partial \mathscr{L}}{\partial t_{\mu}}\Big|_{(t,\lambda)=(t^*,\lambda^*)} = 0, \quad \forall X_{\mu}. \tag{5.141}$$

What we have arrived at are amplitude equations both for the "bra part" and the "ket part" of the problem, which we refer to as the λ amplitude equations (Equation 5.140) and the τ amplitude equations (Equation 5.140), respectively. Notice that the τ amplitude equations only depend on τ, whilst the λ equations depend both on τ and λ. This means that the τ amplitude equations are solved iteratively first, and then the λ amplitudes are solved similarly. The full equations are given in appendix (LINK TO APPENDIX).

5.5 Generealisation in Time

Here, we will outline a derivation of the orbital-adaptive time-dependent coupled cluster method, a generalisation in time for the coupled cluster method put forth by Kvaal[39]. The method inherits both size-extensivity and size-consistency from the coupled cluster method and is a hierarchy of approximations to the multi-configurational time-dependent Hartree method for fermions.

We now define a time-dependent generalisation of the bivariational principle (Equation 5.133). This is similar to the usual time-dependent action functional and the time-dependent Schrödinger equation can be recovered from it, (IT MAY BE proper to use ' instead of † here.)

$$\mathcal{S}[\Psi^\dagger(\cdot),\Psi(\cdot)] = \int_0^T dt \frac{\langle \Psi^\dagger(t)\big|\Big(i\hbar\frac{\partial}{\partial t} - \hat{H}\Big)\big|\Psi(t)\rangle}{\langle \Psi'(t)|\Psi(t)\rangle}. \tag{5.142}$$

Functionals like these are quite common throughout the historical literature on quantum mechanics, appearing as early as in Dirac[12]. The integral of the functional depends on all history for the system in question. Under normal rariation of the functional. By applying the principle of least action, requiring that the functional is stationary, $\delta\mathcal{S} = 0$, under all variations of $\langle\Psi'|$ and $|\Psi\rangle$ and vanishing in the endpoints $t = 0$ and $t = T$, gives us the following conditions

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle \qquad -i\hbar\frac{\partial}{\partial t}\langle\Psi'| = \langle\Psi'|\hat{H}.$$

By a specific parametrisation of $\langle\Psi'|$, such that $\langle\Psi'|\Psi\rangle = 1$ we have indeed recovered the familiar time-dependent Schrödinger euqation.

Instead of venturing down this path, we will presuppose that it is possible that $\langle\Psi'|\Psi\rangle \neq 1$. Indeed, that $\langle\Psi'|$ and $|\Psi\rangle$ are independent. This means we must enact Arponen's[3] Hellmann-Feynman conforming bivariational principle, where the energy expectation functial is given by

$$\mathscr{E}_{\hat{H}}(\tau^\dagger,\tau,\Phi^\dagger,\Phi) = \frac{\langle\Phi^\dagger|e^{\hat{T}\dagger}\hat{H}e^{\hat{H}}|\Phi\rangle}{\langle\Phi^\dagger|e^{\hat{T}^\dagger}e^{\hat{T}}|\Phi\rangle}. \tag{5.143}$$

We perform a variable change $(T',T) \to (\lambda,T)$, similarly to the section above, and introduce

$$\langle\tilde{\Psi}| = \frac{\langle\Psi^\dagger|}{\langle\Psi^\dagger|\Psi\rangle} = \langle\tilde{\Phi}|(1+\Lambda)e^{\hat{T}}, \tag{5.144}$$

Where Λ is the same as in Equation 5.131. The bivariational energy expectation functional in Equation 5.143 now becomes

$$\mathscr{E}_{\hat{H}}(\lambda,\tau,\tilde{\Phi},\Phi) = \langle\tilde{\Phi}|(\hat{1}+\lambda)e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi\rangle. \tag{5.145}$$

Disregarding the differene in $\tilde{\Phi}$ and Φ, this expression is the same as the coupled cluster expectation functional in Equation 5.138, where the interpretation is that the λs are Lagrange multipliers for a constrained energy minimisation problem. This is not the interprestation here, as the λ-part of the problem is seen as equatlly important.

We are now assuming biorthogonality in orbitals, $\langle\tilde{\phi}_p|\phi_q\rangle = \delta_{pq}$, but independence of bra en ket states otherwise. For a full Slater determinant state consisting of these orbitals, we have

$$\langle\tilde{\phi}_{p_1}\dots\tilde{\phi}_{p_n}|\phi_{q_1}\dots\phi_{q_n}\rangle = \delta_{p_q q_1}\dots\delta_{p_N q_N}. \tag{5.146}$$

The second quantised operators ascociated with these Slater determinants are defined through

$$|\phi_{q_1}\dots\phi_{q_n}\rangle \equiv c^\dagger_{p_1}\dots c^\dagger_{p_N}|\rangle \qquad \langle\tilde{\phi}_{p_1}\dots\tilde{\phi}_{p_n}| = \langle|\tilde{c}_{q_N}\dots\tilde{c}_{q_1}. \tag{5.147}$$

These creation- and annihilation operators can furtermore be defined by,

$$c^\dagger_p = \int \phi_p(\mathbf{x})\Psi^\dagger(\mathbf{x})d\mathbf{x} \quad \tilde{c}_p = \int \tilde{\phi}_p(\mathbf{x})\Psi(\mathbf{x})d\mathbf{x}, \tag{5.148}$$

where $\Psi^\dagger$ and Ψ are field creation- and annihilation operators. This particular definition may seem like an unecessary and stringent tangent, but its purpose is to underline the dependence of the cluster operator $\hat{T}$ not only on the amplitudes τ, but also on the orbitals. This is an important point to emphasise, in "ordinary" coupled cluster theory, one thinks of the amplitudes as the only unknowns while keeping the orbitals fixed and the dependence on τ are 1-1. This becomes very important when one computes derivatives with respect to time of the cluster operators $\hat{T}$. Furthermore, the second quantised operators are subject to the anticommutator relation,

$$\{\tilde{c}_p, c_q^\dagger\} \equiv \tilde{c}_p c_q^\dagger + c_q^\dagger \tilde{c}_p \overset{!}{\equiv} \langle \tilde{\phi}_p | \phi_q \rangle = \delta_{pq}. \tag{5.149}$$

The time-dependent action(-like) functional (Equation 5.142) defining the Schrödinger dynamics becomes,

$$\begin{aligned} \mathcal{S}[\lambda, \tau, \tilde{\Phi}, \Phi] &= \int_0^T \left\langle \tilde{\phi} \middle| (1+\Lambda) e^{-\hat{T}} \left(\frac{\partial}{\partial t} - \hat{H} \right) e^{\hat{T}} \middle| \phi \right\rangle dt \\ &= \int_0^T i\hbar \left\langle \tilde{\phi} \middle| (1+\Lambda) e^{-\hat{T}} \frac{\partial}{\partial t} e^{\hat{T}} \middle| \phi \right\rangle dt - \mathscr{E}_{\hat{H}}(\lambda, \tau, \tilde{\Phi}, \Phi). \end{aligned} \tag{5.150}$$

Herein, it is necessary to compute $\frac{\partial}{\partial t} |\Psi\rangle = \frac{\partial}{\partial t} e^{\hat{T}} |\phi\rangle$. In order to accomplish this we indroduce the expansion,

$$|\Psi\rangle = \Pi |\Psi\rangle = |\phi\rangle + \sum_\mu A^\mu |\phi_\mu\rangle, \quad A^\mu = A^\mu(\tau) = \langle \tilde{\phi}^\mu | e^{\hat{T}} | \phi \rangle \tag{5.151}$$

Here we write ϕ as the reference Slater determinant and ϕ_μ are all the other excited Slater determinant. The coefficients A^μ do not depend explicitly on the orbitals, only on the the amplitudes τ. It is important to note that this summation is not truncated, regardless of the truncation of the cluster amplitudes at some excitation level τ^μ. To further the matter, we have introduced a projection operator,

$$\Pi \equiv |\phi\rangle\langle\tilde{\phi}| + \sum_\mu |\phi_\mu\rangle\langle\tilde{\phi}^\mu|. \tag{5.152}$$

The projection operator has the following properties,

$$\begin{gathered} \Pi |\Psi\rangle = |\Psi\rangle, \quad \langle \Psi' | \Phi = \langle \Psi' |, \\ \langle \Psi' | \hat{H} | \Psi \rangle = \langle \Psi' | \Pi \hat{H} \Pi | \Psi \rangle, \quad \Pi^\dagger \neq \Pi \end{gathered} \tag{5.153}$$

and unless orbitals are complete we have $\Pi \hat{H} \Pi \neq \hat{H}$.

Now we compute the time derivative of a Slater determinant,

$$\begin{aligned} \frac{\partial}{\partial t} c_{p_1}^\dagger c_{p_2}^\dagger \dots c_{p_N}^\dagger |\rangle &= \dot{c}_{p_1}^\dagger c_{p_2}^\dagger \dots c_{p_N}^\dagger |\rangle + c_{p_1}^\dagger \dot{c}_{p_2}^\dagger \dots c_{p_N}^\dagger |\rangle + \dots \\ &= \left(\sum_q \dot{c}_q^\dagger \tilde{c}_q \right) c_{p_1}^\dagger c_{p_2}^\dagger \dots c_{p_N}^\dagger |\rangle = \hat{D} c_{p_1}^\dagger c_{p_2}^\dagger \dots c_{p_N}^\dagger |\rangle, \end{aligned}$$

where we have defined the operator $\hat{D}$ by

$$\hat{D} = \sum_q \dot{c}_q^\dagger \tilde{c}_q, \tag{5.154}$$

which depends explicitly on orbitals, unlike $\hat{H}$. The derivative of the exact wavefunction becomes,

$$\begin{aligned}\frac{\partial}{\partial t}\left|\Psi\right\rangle &= \sum_\mu \left(\frac{\partial}{\partial t}A^\mu(\tau)\right)\left|\phi_\mu\right\rangle + \hat{D}\left|\phi\right\rangle + \sum_\mu A^\mu(\tau)\hat{D}\left|\phi_\mu\right\rangle \\ &= \left(\sum_\nu \dot{\tau}^\nu \frac{\partial}{\partial \tau^\nu} + \hat{D}\right)\left|\Psi\right\rangle = \left(\sum_\nu \dot{\tau}^\nu X_\nu + \hat{D}\right)\left|\Psi\right\rangle .\end{aligned} \tag{5.155}$$

The time-derivative part of the functional (Equation 5.150) integrand becomes,

$$\begin{aligned}&i\hbar\left\langle \tilde{\phi}\middle|(1+\Lambda)e^{-\hat{T}}\frac{\partial}{\partial t}e^{\hat{T}}\middle|\phi\right\rangle \\ &= i\hbar\left\langle \tilde{\phi}\middle|\left(1+\sum_\mu \lambda_\mu \tilde{X}^\mu\right)e^{-\hat{T}}\left(\sum_\nu \dot{\tau}^\nu X_\nu + \hat{D}\right)e^{\hat{T}}\middle|\phi\right\rangle \\ &= i\hbar\sum_\mu \lambda_\mu \dot{\tau}^\mu + i\hbar\left\langle \tilde{\phi}\middle|(1+\Lambda)e^{-\hat{T}}\Pi\hat{D}\Pi e^{\hat{T}}\middle|\phi\right\rangle ,\end{aligned} \tag{5.156}$$

where the projected operator $\Pi\hat{D}\Pi$ is given by

$$\Pi\hat{D}\Pi = \hat{D}_0 \equiv \sum_{pq} \langle\tilde{\phi}_p|\dot{\phi}_q\rangle\, c_p^\dagger \tilde{c}_q. \tag{5.157}$$

Finally we obtain a new expression for the functional in Equation 5.150

$$\mathcal{S}[\lambda,\tau,\tilde{\Phi},\Phi] = \sum_0^T i\hbar\sum_\mu \lambda_\mu\dot{\tau}^\mu - \mathcal{E}_{\hat{H}-i\hbar\hat{D}_0}[\lambda,\tau,\tilde{\Phi},\Phi]dt \tag{5.158}$$

$$= \int_0^T i\hbar\lambda_\mu\dot{\tau}^\mu + \rho_p^q(h_q^p - i\hbar\eta_q^p) + \frac{1}{4}\rho_{pr}^{qs}u_{qs}^{pr}dt, \tag{5.159}$$

(HERE THE u IS TWO-BODY OPERATOR. CHANGE OTHER PLACES? YES I THINK SO..) where

$$\rho_p^q = \rho_p^q(\lambda,\tau) \equiv \langle\tilde{\rho}|(1+\Lambda)e^{-\hat{T}}c_p^\dagger\tilde{c}_q e^{\hat{T}}|\phi\rangle , \tag{5.160}$$

$$\rho_{pr}^{qs} = \rho_{pr}^{qs}(\lambda,\tau) \equiv \langle\tilde{\rho}|(1+\Lambda)e^{-\hat{T}}c_p^\dagger c_r^\dagger\tilde{c}_s\tilde{c}_q e^{\hat{T}}|\phi\rangle , \tag{5.161}$$

$$h_q^p = h_q^p(\tilde{\Phi},\Phi) \equiv \langle\tilde{\varphi}_p|\hat{h}|\varphi_q\rangle , \tag{5.162}$$

$$\eta_q^p = \eta_q^p(\tilde{\Phi},\Phi) \equiv \langle\tilde{\varphi}_p|\dot{\varphi}_q\rangle , \tag{5.163}$$

$$u_{qs}^{pr} = u_{qs}^{pr}(\tilde{\Phi},\Phi) \equiv \langle\tilde{\varphi}_p\tilde{\varphi}_r|(\hat{u}-\hat{P}_{12})|\varphi_q\varphi_s\rangle . \tag{5.164}$$

We introduced Einsten summation convention over repeated indices of opposite vertical placement in Equation 5.159.

5.5.1 Equations of Motion

The time has now come to apply the principle of least action to the orbital-adaptive coupled cluster functional from Equation 5.158 in order to find the equations of motion. First we keep τ^ν constant and vary λ_μ,

$$\delta\mathcal{S}[\lambda,\tau] = \int_0^T i\hbar\delta\lambda_\mu\dot{\tau}^\nu - \frac{\partial\mathscr{E}_{\hat{H}-i\hbar\hat{D}_0}}{\partial\lambda_\mu}\delta\lambda_\mu dt = 0. \tag{5.165}$$

We see that the stationary condition is

$$\boxed{i\hbar\dot{\tau}^{\mu} = \frac{\partial}{\partial\lambda_{\mu}}\mathscr{E}_{\hat{H}-i\hbar\hat{D}_0}[\lambda,\tau,\tilde{\Phi},\Phi] = \langle\tilde{\phi}_{\mu}|e^{-\hat{T}}(\hat{H}-i\hbar\hat{D}_0)e^{\hat{T}}|\phi\rangle\,,} \tag{5.166}$$

which is also the eqution of motion, dictating the time-development of τ. Next, we hold λ_μ fixed and vary τ^ν,

$$\delta\mathcal{S}[\lambda,\tau] = \int_0^T i\hbar\lambda_\nu\delta\dot{\tau}^\nu - \frac{\partial\mathscr{E}_{\hat{H}-i\hbar\hat{D}_0}}{\partial\lambda^\nu}dt. \tag{5.167}$$

through integration by parts we see that the first term becomes,

$$i\hbar\int_0^T \lambda_\nu\delta\dot{\tau}^\nu = i\hbar\cancelto{0}{\lambda_\nu\delta\tau^\nu} - i\hbar\int_0^T \dot{\lambda}_\nu\delta\tau^\nu dt,$$

yielding

$$\delta\mathcal{S}[\lambda,\tau] = \int_0^T \delta\tau^\nu\left(-i\hbar\dot{\lambda}_\nu - \frac{\partial\mathscr{E}_{\hat{H}-i\hbar\hat{D}_0}}{\partial\tau^\nu}\right). \tag{5.168}$$

Here the stationary condition is

$$\boxed{-i\hbar\dot{\lambda}_\nu = \frac{\partial}{\partial\tau^\nu}\mathscr{E}_{\hat{H}-i\hbar\hat{D}_0}[\lambda,\tau,\tilde{\Phi},\Phi] = \langle\tilde{\phi}|(1+\Lambda)e^{-\hat{T}}[\hat{H}-i\hbar\hat{D}_0,X_\mu]e^{\hat{T}}|\phi\rangle\,.} \tag{5.169}$$

Equation 5.166 and Equation 5.169 together make up the orbital-adaptive coupled cluster (OACC) amplitude equations of motion.

We will return to the OACC equations of motion shortly, but first we consider a special situation where the operator $\hat{D}_0 \equiv \sum_{pq}\langle\tilde{\phi}_p|\dot{\phi}_q\rangle\, c_p^\dagger\tilde{c}_q$, equates to zero. This is the same as keeping the orbitals static over time. The resulting equations of motions are

$$i\hbar\dot{\tau}^{\mu} = \frac{\partial}{\partial\lambda_{\mu}}\mathscr{E}_{\hat{H}}[\lambda,\tau,\tilde{\Phi},\Phi] = \langle\tilde{\phi}_{\mu}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\phi\rangle \tag{5.170}$$

$$-i\hbar\dot{\lambda}_\nu = \frac{\partial}{\partial\tau^\nu}\mathscr{E}_{\hat{H}}[\lambda,\tau,\tilde{\Phi},\Phi] = \langle\tilde{\phi}|(1+\Lambda)e^{-\hat{T}}[\hat{H},X_\mu]e^{\hat{T}}|\phi\rangle\,. \tag{5.171}$$

We call these equations the time-developted coupled cluster (TDCC) amplitude equations. Setting the left-hand side of Equation 5.170 and Equation 5.171 to zero will give a set of non-linar equations that can be solved in order to find initial amplitudes ($\lambda^{(0)}$, $\tau^{(0)}$). These equations are the same as Equation 5.139 and Equation 5.140.

Returning to the orbital-adaptive scheme, the OATDCC equations (Equation 5.166 and Equation 5.169) have parametric redundancies that we need to address briefly[4]. The parametric redundancies exist in the sense that when one derives equations of motion for $(\tau,\lambda,\tilde{\Phi},\Phi) = (\tau^\mu,\lambda_\mu,\tilde{\phi}_p,\phi_q)$, under the stationary condition $\delta\mathcal{S} = 0$, for a given pair of coupled cluster wavefunctions $(\langle\tilde{\Psi}|\,,|\Psi\rangle) \in \mathcal{M}$, there are many choices for the amplitudes and orbitals that would give this same wavefunction pair. It is therefore necessary to define a transformation as a many-to-one mapping from this collection of points $(\lambda,\tau,\tilde{\Phi},\Phi) \in \mathcal{N}$ to the wavefunction pair on $(\langle\tilde{\Psi}|\,,|\Psi\rangle) \in \mathcal{M}$,

$$f : \mathcal{N} \to \mathcal{M}. \tag{5.172}$$

As circumstances would have it, the simplest of such transformations corresponds to a rotation that elminates the singles amplitudes τ_i^a. This is the same ansatz employed in orbital-optimised- or Bruecker coupled cluster theory (see box). Additionally, including λ_a^i after this rotation

[4] A thorough decription of this matter can be found in the supplementary to Kvaal's articl on OATDCC[39]

would leave the equations of motions overdetermined. The presence of $\hat{T}_1$ is compensated by the freely varying orbitals, but this does not hold for Λ_1, which gives more parameters in the $\left\langle\tilde{\Psi}\right|$ than in $|\Psi\rangle$. As such, we set all single amplitudes, τ_i^a and λ_a^i equal to zero.

Orbital-optimised and Bruecker coupled cluster theories [36, 51]

In standard coupled cluster theory including single excitations,

$$e^{\hat{T}_1} = \exp\left\{\sum_{ai} \tau_i^a c_a^\dagger c_i\right\}, \tag{5.173}$$

we determine a set of non-zero single-excitation amplitudes τ_i^a together with any higher-excitation amplitudes. An alternative parametrisation of the singles manifold in Equation 5.173 is the orthogonal orbital-rotation operator

$$e^{-\kappa} = \exp\left\{-\sum_{ai} \kappa_a i (c_a^\dagger c_i - c_i^\dagger c_a)\right\} \tag{5.174}$$

This is a rephrasing of Thouless theorem[65]. We may therefore use

$$|\Psi_{\mathrm{OCC}}\rangle = e^{-\kappa} e^{\hat{T}_{\mathrm{O}}} |\Phi\rangle \tag{5.175}$$

as a wavefunction ansatz instead. Here,

$$\hat{T}_{\mathrm{O}} = \hat{T}_2 + \hat{T}_3 + \dots \tag{5.176}$$

In OATDCC theory such a gauge condition corresponds to considering orbital time derivatives of the form

$$|\dot{\varphi}_q\rangle = (P+Q)|\dot{\varphi}_q\rangle = \sum_p |\varphi_p\rangle\langle\tilde{\varphi}_p|\dot{\varphi}_q\rangle + Q|\dot{\varphi}_q\rangle = \sum_p \eta_q^p + Q|\dot{\varphi}_q\rangle \tag{5.177}$$

$$\langle\dot{\tilde{\varphi}}_p| = \langle\dot{\tilde{\varphi}}_p|(P+Q) = \sum_q \langle\dot{\tilde{\varphi}}_p|\varphi_q\rangle\langle\tilde{\varphi}_q| + \langle\dot{\tilde{\varphi}}_p|Q = -\sum_q \eta_q^p\langle\tilde{\varphi}_q| + \langle\dot{\tilde{\varphi}}_p|Q, \tag{5.178}$$

with $\eta_j^i = \eta_b^a = 0$, $\eta_q^p = \langle\tilde{\varphi}_p|\dot{\varphi}_q\rangle = -\langle\dot{\tilde{\varphi}}_p|\varphi_1\rangle$. Here we have defined the projection operators P and Q, where $P = \Phi\tilde{\Phi} = \sum_p |\varphi_p\rangle\langle\varphi_p|$ projects onto the single-particle space defined by the orbitals, and $Q = 1 - P$ projects onto everything else.

We can write down equations of motions just for the nonzero P-components η_i^a and η_a^i of the orbital derivatives,

$$i\hbar\sum_{bj} A_{aj}^{ib}\eta_b^j = \sum_p \rho_p^i h_a^p - \sum_q \rho_a^q h_q^i + \frac{1}{2}\left[\sum_{qrs}\rho_{pr}^{is}u_{as}^{pr} - \sum_{rqs}\rho_{ar}^{qs}u_{qs}^{ir}\right] \tag{5.179}$$

$$-i\hbar\sum_{bj} A_{bi}^{ja}\eta_j^b = \sum_p \rho_p^a h_i^p - \sum_q \rho_i^q h_q^a + \frac{1}{2}\left[\sum_{prs}\rho_{ps}^{as}u_{is}^{pr} - \sum_{rqs}\rho_{ir}^{qs}u_{qs}^{ar}\right] + i\hbar\dot{\rho}_i^a, \tag{5.180}$$

where the matrix elements A_{aj}^{ib} are defined by,

$$A_{aj}^{ib} \equiv \left\langle\tilde{\Psi}\middle|[c_j^\dagger\tilde{c}_b, c_a^\dagger\tilde{c}_i]\middle|\Psi\right\rangle = \delta_a^b\rho_j^i - \delta_j^i\rho_a^b. \tag{5.181}$$

The Q-part of the orbital derivatives are,

$$i\hbar\sum_q \rho_p^q Q\frac{\partial}{\partial t}|\varphi_q\rangle = \sum_q \rho_p^q Qh|\varphi_q\rangle + \sum_{qrs}\rho_{pr}^{qs}QW_s^r|\varphi_q\rangle\,,\ \forall p \tag{5.182}$$

$$-i\hbar\sum_p \rho_p^q\left(\frac{\partial}{\partial t}\langle\tilde{\varphi}_p|\right)Q = \sum_p \rho_p^q\langle\tilde{\varphi}_p|hQ + \sum_{prs}\rho_{pr}^{qs}\langle\tilde{\varphi}_p|W_s^rQ,\ \forall q, \tag{5.183}$$

where mean-field operators W_s^r are defined by

$$W_s^r|\psi\rangle \equiv \langle\cdot\tilde{\varphi}_r|u|\psi\varphi_s\rangle\,. \tag{5.184}$$

The logical next step is to write down the equations of motion for the lowest truncated from of OATDCC available too us, namely OATDCCD. In addition to the orbitals Φ and $\tilde{\Phi}$, the only parameters of the exact wavefunction are the amplitudes $\tau = \tau_{ij}^{ab}$ and $\lambda = \lambda_{ab}^{ij}$. The OATDCCD amplitude equations read

$$i\hbar\dot{\tau}_{ij}^{ab} = \frac{\partial}{\partial\lambda_{ab}^{ij}}\mathscr{E}_{\mathrm{H}}[\lambda,\tau,\tilde{\Phi},\Phi] = \left\langle\tilde{\phi}_{ij}^{ab}\middle|e^{-\hat{T}}\hat{H}e^{\hat{T}}\middle|\phi\right\rangle \tag{5.185}$$

$$-i\hbar\dot{\lambda}_{ab}^{ij} = \frac{\partial}{\partial\tau_{ij}^{ab}}\mathscr{E}[\lambda,\tau,\tilde{\Phi},\Phi] = \left\langle\tilde{\phi}\middle|(1+\Lambda)e^{-\hat{T}}[\hat{H},X_{ab}^{ij}]e^{\hat{T}}\middle|\phi\right\rangle. \tag{5.186}$$

The P-space orbitals read

$$i\hbar\sum_{bj}A_{aj}^{ib}\eta_b^j = \sum_j \rho_j^i h_a^j - \sum_b \rho_a^b h_b^i + \frac{1}{2}\left[\sum_{prs}\rho_{pr}^{is}u_{as}^{pr} - \sum_{rqs}\rho_{ar}^{qs}U_{qs}^{ir}\right], \tag{5.187}$$

$$-i\hbar\sum_{bj}A_{bi}^{ja}\eta_j^b = \sum_b \rho_b^a h_i^b - \sum_j \rho_i^j h_j^a + \frac{1}{2}\left[\sum_{prs}\rho_{pr}^{as}u_{is}^{pr} - \sum_{rqs}\rho_{ir}^{qs}U_{qs}^{ar}\right] \tag{5.188}$$

and the Q-space orbitales read

$$i\hbar\sum_q \rho_p^q Q\frac{\partial}{\partial t}|\varphi_q\rangle = \sum_q \rho_q^p Qh|\varphi_q\rangle + \sum_{qrs}\rho_{pr}^{qs}QW_s^r|\varphi_q\rangle\,, \tag{5.189}$$

$$-i\hbar\sum_p \rho_p^q\left(\frac{\partial}{\partial t}\langle\tilde{\varphi}_q|\right)Q = \sum_p \rho_p^q|\varphi_q\rangle Qh + \sum_{prs}\rho_{pr}^{qs}\langle\varphi_q|W_s^rQ. \tag{5.190}$$

Notice that the τ and λ OATDCCD equations (Equation 5.185 and Equation 5.186) are the same equations as the ones used in standard TDCCD (Equation 5.170 and Equation 5.171), because the operator $\hat{D}_0$ is eliminated due to $\rho_i^a = \rho_a^i = 0$. Because the operators $\hat{D}_0$ disappears from Equation 5.185 and Equation 5.186, the right-hand sides can be evaluated independently of equations 5.187, 5.188, 5.189, 5.190. In order to compute $\dot{\tilde{\Phi}}$ and $\dot{\Phi}$, η must be solved for in addition to $Q|\dot{\varphi}_q\rangle$ and $\langle\dot{\tilde{\varphi}}_p|Q$, according to Equation 5.177 and Equation 5.178.

Part III

Implementatin and Results

Chapter 6

Implementation: Quantum Systems

For a quantum system to be studied on the computer it is necessary to make a distinction for what defines the system. One must therefore undergo the mathematical procedure of defining a finite basis sets that defines the quantum system under scrutiny when dealing with the electronic problem.

Here we present the `quantum_systems` python module, designed to provide basis sets for one- and two-dimensional quantum dots. The two-dimensional quantum dot can also be modelled with a constant, homogeneous magnetic field; and as a double quantum dot. Moreover, the module includes an option for constructing a custom system which can be interfaced with popular quantum chemistry packages `PySCF`[63] and `Psi4`[48]. This allows one to construct basis sets representing all kinds of systems of interest in quantum chemistry, like atoms and molecules.

The `quantum_systems` module also contains an implementation of a plane wave or homogenous electron gas basis set, sometimes called the jellium model. However, this implementation exists mainly as a curiosity at this point. In the future it can be developed into something more useful, as the electron gas can serve as a first approximation to a metal or a semi-conductor.

The `quantum_system` module can installed from github with `pip` by the following command,

```
pip install git+https://github.com/Schoyen/quantum-systems.git
```

The same task can of course be accomplished by more commands,

```
git clone https://github.com/Schoyen/quantum-systems.git
cd quantum-systems
pip install .
```

It can be useful to install the module to a separate environment. We have made this possible through `conda`,

```
conda environment create -f environment.yml
conda activate quantum-systems
```

6.1 Quantum Dots

In reality, quantum dots are nanometre-sized structures made of semiconductor materials. Theoretically, quantum dots are easy to model by harmonic oscillator potential and in practice they are relativelty easy to manufacture in a laboratory. This doubly theoretical-experimental benefit has made quantum dots a popular area of study. Moreover so because of their wide area of apllications.

The possible applications of quantum dots are many. Coupled single-electron quantum dots could potentially be used as harware elements in quantum computers, i.e. qubits[42]; quantum dots also promise to increase the efficiency of photvoltaic solar cells; and they have already found use in cellular imaging in biology. Reimann and Manninen[57] has written an outstandingly thorough review on quantum dots, covering their varied types of fabrication, theoretical methods common in their study and vast ocean of applications.

The usefulness and relative theoretical ease of modelling warrants the study of quantum dots. Herein, several classes have been implemented in order to construct basis sets modelling quantum dots in both one and two dimensions. These basis sets models *bound* systems as the common harmonic oscillator-type potentials that are used have the characteristics of infinite quantum wells.

6.1.1 One Dimension

This is perhaps one of the simplest of all quantum mechanical models, being studied ad nauseum in everyones introductory quantum mechanics course. The one-body part of the Hamiltonian for the one-dimensional quantum harmonic oscillator is,

$$\hat{h} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2. \tag{6.1}$$

The potential, $\hat{v} = \frac{1}{2} m\omega^2 \hat{x}^2$, forms the well known parabolig curve. In a general one-dimensional system, this potenation could readily be exchanged for something else. For instance that of the *double well*,

$$\hat{v} = \frac{1}{2} m\omega^2 \left(\hat{x}^2 + \frac{1}{4} l^2 - l|\hat{x}| \right), \tag{6.2}$$

where l is the width of a barrier in the middle of the parabolic potential.

In atomic units we can set $\hbar = m = 1$. Substituting for the momentum operator, $\hat{p} = -i\hbar(\hat{\partial}/\partial x)$, gives us

$$\hat{h} = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + \hat{v}. \tag{6.3}$$

The second-order derivate can be approximated by the central difference formula for some function $f(x)$, yielding

$$f''(x) = \frac{f(x+dx) - 2f(x) + f(x-dx)}{dx^2}, \tag{6.4}$$

for some small dx. This means that we approximate the Hamilton operator of the system (Equation 6.3) by a matrix,

$$h^p_q = \begin{pmatrix} 1/dx^2 + v_1 & -1/2dx^2 & \ddots & & & \\ -1/2dx^2 & 1/dx^2 + v_2 & -1/2dx^2 & \ddots & & \\ \ddots & -1/2dx^2 & 1/dx^2 + v_3 & -1/2dx^2 & \ddots & \\ & \ddots & \ddots & \ddots & \ddots & \ddots \\ & & \ddots & -1/2dx^2 & 1/dx^2 + v_{n-1} & -1/2dx^2 \\ & & & \ddots & -1/2dx^2 & 1/dx^2 + v_n \end{pmatrix}, \tag{6.5}$$

and we have thus transformed the time-independent Schrödinger equation

$$\hat{h}\,|n\rangle = \epsilon\,|n\rangle\,, \tag{6.6}$$

into a matrix equation which is easily representable and solvable on a computer, where n is the number of points used to numerically represent the wavefunciton and Hamiltonian mateix representation. This is done with some generic eigenvalue solver, for instance `numpy.linalg.eigh`. The eigen functions provide the foundations for the single-particle functions.

Since we would like to model interaction between particles we need something more, than just a numerical representation of the one-body operator. We therefore need to compute coulomb interaction, in the form of an integral. This is done in several steps, starting with an "inner intergral" over all all space and two and two single-particle functions,

$$u_s^q = \int \phi_q(x_1)\frac{\alpha}{(x_1 - x_2)^2 + 2a^2}\phi_s(x_2)dx, \tag{6.7}$$

where a and α are parameters that are necessary to include for this integral to be calculable. Numerically, this part is divided into two functions in our python implementation,

```python
def _shielded_coulomb(x_1, x_2, alpha, a):
    return alpha / np.sqrt((x_1 - x_2) ** + a ** 2)

def _compute_inner_integral(spf, l, num_grid_points, grid, alpha, a):
    inner_integral = np.zeros((l, l, num_grid_points), dtype=np.complex128)

    for q in range(l):
        for s in range(l):
            for i in range(num_grid_points):
                inner_integral[q, s, i] = _trapz(
                    spf[q]
                    * _shielded_coulomb(grid[i], grid, alpha, a)
                    * spf[s],
                    grid,
                )

    return inner_integral
```

The inner orbital is then used in the computation in the orbial integral,

$$w_{rs}^{pq} = \int \phi_p u_s^q \phi_r dx, \tag{6.8}$$

which numerically is implemented as follows,

```python
def _compute_orbital_integrals(spf, l, inner_integral, grid):
    u = np.zeros((l, l, l, l), dtype=np.complex128)

    for p in range(l):
        for q in range(l):
            for r in range(l):
                for s in range(l):
                    u[p, q, r, s] = _trapz(
                        spf[p] * inner_integral[q, s] * spf[r], grid
                    )

    return u
```

Each integral is solved by the trapezoidal scheme,

```python
def _trapz(f, x):
    n = len(x)
    delta_x = x[1] - x[0]
    val = 0

    for i in range(1, n):
        val += f[i - 1] + f[i]

    return 0.5 * val * delta_
```

Needless to say, computing the coulomb integrals is one of the more compute-heave tasks, and we therefore make great use of just-in-time compulation from the `numba` module for python.

A full representation of the one-dimensional quantum dot (oscillator) class is provided below,

class quantum_systems.**OneDimensionalHarmonicOscillator**
(*n*, *l*, *grid_length*, *num_grid_points*, *omega*=0.25, *mass*=*1*, *a*=0.25, *alpha*=1.0)

Create One-Dimensional Quantum Dot basis set.

Parameters

- **n**(*int*) Number of electrons
- **l**(*int*) Number of spinorbitals
- **grid_length**(*int or float*) Space over which to construct wavefunction.
- **num_grid_points**(*int of float*) Number of points for construction of wavefunction.
- **omega**(*float, default* 0.25) Angular frequency of harmonic oscillator potential.
- **mass**(*int or float, default* 1.0) Mass of electrons. Atomic units is used as default.
- **a**(*float, default* 0.25) Necessary in Coulomb integral computation.
- **alpha**(*float, default* 1.0) Necessary in Coulomb integral computation.

Attributes

- **h** One-body matrix **Type** np.array
- **f** Fock matrix **Type** np.array
- **u** Two-body matrix **Type** np.array

Methods

setup_system(*Potential=None*)
: Must be called in order to compute basis functions. The method will revert to regular harmonic oscillator potential if no potential has been provided. Optional potentials include one-dimensional double well potentials.

contruct_dipole_moment()
: Constructs dipole moment. This method is called by **setup_system**(). Necessary when constructing custom systems with time development.

6.1.2 Two Dimensions

The one-body part of the Hamiltonian for a two-dimensional quantum dots is almost identical to the one-body part for a one-dimensional quantum dot. In cartesian coordinates we simple include a y in the potential as well as an x, but mostly because we have analytical expressions for the Coulomb integrals in polar coordinates[2], we write the one-body operators in polar coordinates as well with $\hat{r}^2 = \hat{x}^2 + \hat{y}^2$,

$$\hat{h} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{r}^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}\right) + \frac{1}{2}m\omega^2\hat{r}^2. \tag{6.9}$$

The wavefunctions for a two-dimensional harmonic oscillator can be written

$$\phi(r,\theta) = N_{nm}R_{nm}(r)Y_m(\theta) = N_{nm}(ar)^{|m|}L_n^{|m|}(a^2r^2)e^{-a^2r^2/2}e^{im\theta}, \tag{6.10}$$

where $a = \sqrt{m\omega/\hbar}$ si the Bohr radius, $L_n^{|m|}$ is the associated Laguerre polynomials, n and m are the principal and the azimutal quantum numbers respectively[1], and N_{nm} is a normalisation factor given by,

$$N_{nm} = a\sqrt{\frac{n!}{\pi(n+|m|)!}}. \tag{6.11}$$

The energy eigenvalues of a two-dimensional harmonic oscillator is given by

$$\epsilon_{nm} = \hbar\omega(2n + |m| + 1). \tag{6.12}$$

It is very beneficial that such a nice expression exists, because the one-body matrix elements of a harmonic oscillator is simply,

$$\langle\phi_p|\,\hat{h}\,|\phi_q\rangle = \hat{h}^p_q = \epsilon_p\delta^p_q. \tag{6.13}$$

These matrix elements encompass both the kinetic energy operator matrix element and potential energy matrix element. If we were dealing with completely none-interacting particles not much more would be nedded. We see, however, that this form of one-body matrix elements necessitates a mapping from the general coordinates p, q, as used above, and the quantum numbers n, m.

This functionality $(n, m) \mapsto p$ is achieved by the following python function

```python
def get_index_p(n, m):
    num_shells = 2 * n + abs(m) + 1

    previous_shell = 0
    for i in range(1, num_shells):
        previous_shell += i

    current_shell = previous_shell + num_shells

    if m == 0:
        if n == 0:
            return 0

        p = previous_shell + (current_shell - previous_shell) // 2

        return p

    elif m < 0:
        return previous_shell + n
```

[1]There is usually another quantum number called the magnetic quantum number. Because of our restriction to two dimensions, this quantum number does not appear. In three dimensions we would usually denote the azimuthal quantum number by l and the magnetic quantum number by m or m_l. A fourth quantum number is the spin projection quantum number commonly written m_s.

```
    else:
        return current_shell - (n + 1)
```

It will also be necessary to map back $p \mapsto (n, m)$,

```
def get_indices_nm(p):
    n, m = 0, 0
    previous_shell = 0
    current_shell = 1
    shell_counter = 1

    while current_shell <= p:
        shell_counter += 1
        previous_shell = current_shell
        current_shell = previous_shell + shell_counter

    middle = (current_shell - previous_shell) / 2 + previous_shell

    if (current_shell - previous_shell) & 0x1 == 1 and abs(
        p - math.floor(middle)
    ) < 1e-8:
        n = shell_counter // 2
        m = 0

        return n, m

    if p < middle:
        n = p - previous_shell
        m = -((shell_counter - 1) - 2 * n)

    else:
        n = (current_shell - 1) - p
        m = (shell_counter - 1) - 2 * n

    return n, m
```

An important difference between the one-dimensional quantum dot and a two-dimensional quantum dot is that in the latter we have energy degeneracies of the eigenstates. This is illustrated in Figure 6.1. In this figure we have included a spin-up and a spin-down state for each n, m-state. This spin feature is not in any way included in Equation 6.10, but we may represent the spin condition by including it in the orthonormality conditions of the wavefunctions,

$$\langle n_1 m_1 \sigma_1 | n_2 m_2 \sigma_2 \rangle = \delta_{n_1 n_2} \delta_{m_1 m_2} \delta_{\sigma_1 \sigma_2}, \tag{6.14}$$

where σ is the spin.

Because the electrons we will be studying are interacting, we need two-body matrix elements as well. The analytical formula for the Coulomb interaction integrals, provided by Anisimovas

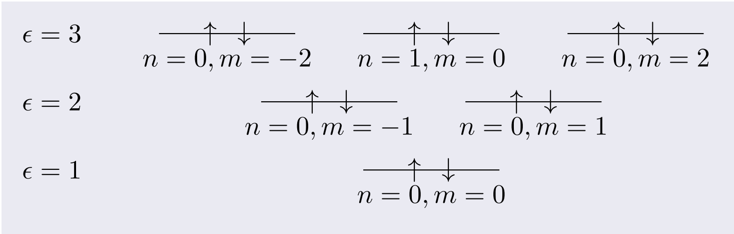


Figure 6.1: The lowest three energy levels in the two-dimensional quantum dot. Each arrow representes a spin up or a spin down state with the quantum numbers n and m as listed below. This pattern goes on indefinitly with the addition of one bar (two oscillators) per level.

and Matulis[2] is

$$\begin{aligned}\langle \phi_1\phi_2|\hat{W}|\phi_3\phi_4\rangle =&\delta_{s_1,s_4}\delta_{s_2,s_3}\delta_{m_1+m_2,m_3+m_4}\left[\prod_{i=1}^{4}\frac{n_i!}{(|m_i|+n_i)}\right]^{1/2}\sum_{(4)j=0}^{n}\frac{(-1)^{j_1+j_2+j_3+j_4}}{j_1!j_2!j_3!j_4!}\\ &\times\left[\prod_{i=1}^{n}\binom{n_i+|m_i|}{n_i+j_i}\right]\frac{1}{2^{(G+1)/2}}\sum_{(4)l=0}^{\gamma}(-1)^{\gamma_2+\gamma_3-l_2-l_3}\\ &\times\delta_{l_1+l_2,l_3+l_4}\left[\prod_{i=1}^{4}\binom{\gamma_i}{l_i}\right]\Gamma\left(1+\frac{L}{2}\right)\Gamma\left(\frac{G-L+1}{2}\right).\end{aligned} \tag{6.15}$$

The symbols j_i are integer summation indices (regular indices) running from 0 to n_i. The symbols γ_i stand for numbers,

$$\gamma_1 = j_1 + j_4 + (|m_1| + m_1)/2 + (|m_4| - m_4)/2$$
$$\gamma_4 = j_1 + j_4 + (|m_1| - m_1)/2 + (|m_4| + m_4)/2$$

γ_2 and γ_3 can be obtained by replacing indices $1 \to 2$ and $4 \to 3$. Moreover,

$$\sum_{(4)j=0}^{n} = \sum_{j_1=0}^{n_1}\sum_{j_2=0}^{n_2}\sum_{j_3=0}^{n_3}\sum_{j_4=0}^{n_4}, \quad G=\sum_i \gamma_i, \quad L=\sum_i l_i$$

For the implementation of this expression for the purpose of computing the two-dimensional quantum dot basis sets, we refer the reader to the appendices (Appendix C).

Dipole Moments For our implementation of time dependent Hamiltonians, outlined below, we make use of a dipole approximation of an electric field. For this reason it is necessary to compute dipole moments. Moreover, the "transitions rules " of quantum mechanics stems from evalueting matrix elements of this kind,

$$\mathbf{d}_{pq} = \langle\phi_p|\,\hat{\mathbf{r}}\,|\phi_q\rangle = \hat{i}\,\langle\phi_p|\,\hat{x}\,|j\rangle + \hat{j}\,\langle\phi_p|\,\hat{y}\,|\phi_q\rangle\,, \tag{6.16}$$

where ϕ_p, ϕ_q are some typical state vectors, on the form in Equation 6.10. As we will be representing the two-dimensional quantum dots in polar coordinates, we can rewrite this to,

$$\mathbf{d}_{pq} = \hat{i}\,\langle\phi_p|\,\hat{r}\cos\hat{\theta}\,|\phi_q\rangle = \hat{j}\,\langle\phi_p|\,\hat{r}\cos\hat{\theta}\,|\phi_q\rangle\,. \tag{6.17}$$

The integrals we need to compute are

$$\langle\phi_p|\,r\cos\theta\,|\phi_q\rangle = N^*_{nm}N_{nm}\int_0^\infty r^2 R^*_{nm}(r)R_{nm}(r)dr\int_0^{2\pi}\cos\theta Y^*_m(\theta)Y_m(\theta)d\theta \tag{6.18}$$

$$\langle \phi_p | \, r \sin\theta \, | \phi_q \rangle = N^*_{nm} N_{nm} \int_0^\infty r^2 R^*_{nm}(r) R_{nm}(r) dr \int_0^{2\pi} \sin\theta Y^*_m(\theta) Y_m(\theta) d\theta. \tag{6.19}$$

The radially dependent integrals are the most difficult to compute, and we compute this symbolically with `sympy`. For the angular integrals, we can find analytical expressions that can be evaluated quickly,

$$\int_0^{2\pi} \cos\theta e^{i\bar{m}\theta} = \frac{e^{i\bar{m}\theta}}{1-\bar{m}^2} (\sin\theta - i\bar{m}\cos\theta)\Big|_0^{2\pi}, \tag{6.20}$$

where $\bar{m} = (m_q - m_p) \in \mathbb{Z}$. We see that the integral evalues to 0 for all possible values of $\bar{m}$ except for ± 1. This special case warrants further investigation,

$$\int_0^{2\pi} \cos\theta e^{i\theta} d\theta = \int_0^{2\pi} \cos^2\theta + i\cos\theta\sin\theta d\theta = \frac{1}{2}\sin\theta\cos\theta + \frac{\theta}{2} + \frac{i}{2}\sin^2\theta\Big|_0^{2\pi} = \pi. \tag{6.21}$$

Similarly,

$$\begin{aligned} \int_0^{2\pi} \sin\theta\theta e^{i\bar{m}\theta} d\theta = \frac{e^{i\bar{m}\theta}}{1-\bar{m}^2}(i\bar{m}\sin\theta - \cos\theta)\Big|_0^{2\pi} = 0 \quad \forall \bar{m} \in \mathbb{Z} \neq 1 \\ \int_0^{2\pi} \sin\theta e^{i\theta} d\theta = \int_0^{2\pi} \cos\theta\sin\theta + i\sin^2\theta d\theta = \frac{1}{2}\sin\theta - \frac{i}{2}\sin\theta\cos\theta + i\frac{\theta}{2}\Big|_0^{2\pi} = i\pi \end{aligned} \tag{6.22}$$

This is a very nice result, as it conforms with the selection rule related to the azimutal quantum number m.

The final specification of the two-dimensional harmonic oscillator basis set class, which is everything the user sees is the following,

class quantum_systems.**TwoDimensionalHarmonicOscillator**
(*n*, *l*, *radius_length*, *num_grid_points*, *omega*=0.25, *mass=1*)

Create Two-Dimensional Quantum Dot basis set.

Parameters

- **n**(*int*) Number of electrons
- **l**(*int*) Number of spinorbitals
- **grid_length**(*int or float*) Space over which to construct wavefunction.
- **num_grid_points**(*int of float*) Number of points for construction of wavefunction.
- **omega**(*float*, *default* 0.25) Angular frequency of harmonic oscillator potential.
- **mass**(*int or float*, *default* 1.0) Mass of electrons. Atomic units is used as default.

Attributes

- **h** One-body matrix **Type** np.array
- **f** Fock matrix **Type** np.array
- **u** Two-body matrix **Type** np.array

Methods

- **setup_system**()
  Must be called in order to compute basis functions.
- **contruct_dipole_moment**()
  Constructs dipole moment. This method is called by **setup_system**().

Double well

The extension from a single two-dimensional quantum dot to a double quantum dot is a relatively straigth-forward proecedure, as it is a mere perturbation of the regular single dot. What is more, the double dot system has more possible energy tranistions and it has more enery degeneracies, makin it a more interestin system to study. There are several ways to define the double quantum dot. We have devised two diffrent potentials that accomplish the task. The first is with a sharp edge and the other with a smoother bulge dividing the two potential wells.

Startin with the sharp-edge implementation the one-body operators is as follows,

$$\hat{h} = \frac{\hat{p}}{2m} + \frac{1}{2}m\omega^2\hat{r}^2 + \frac{1}{2}\left(\frac{1}{4}l^2 - l|\hat{x}|\right), \tag{6.23}$$

where l is the "strength" of the barrier between the wells. We can readily see what makes the barrier so acute, namely the absolute value of the position operator, $|\hat{x}|^2$.

In Equation 6.23, we immediately reconise the first two terms as the normal quantum dot. This is beneficial, as we can reuse single-particle functions from Equation 6.10. This means that the one-body matrix elements are simply,

$$\begin{aligned} h^p_q &= \epsilon_p\delta^p_q + \frac{1}{2}m\omega^2\left\langle\phi_p\right|\frac{1}{4}l^2 - l|\hat{x}|\left|\phi_q\right\rangle \\ &= \epsilon_p\delta^p_q + \frac{1}{8}m\omega^2 l^2\delta^p_q - \frac{1}{2}m\omega^2 l\left\langle\phi_p\right||\hat{x}|\left|\phi_q\right\rangle. \end{aligned} \tag{6.24}$$

We see from the first two terms a perturbation in the diagonal matrix elements, i.e.

$$\epsilon^{\mathrm{DW}}_p = \epsilon_p + \frac{1}{8}m\omega^2 l^2, \tag{6.25}$$

and that we need only compute the matrix elements of the position operator. Because we are still working with polar coordinates, we make the necessary transformation, and the interal becomes

$$\left\langle\phi_p\right||\hat{x}|\left|\phi_q\right\rangle = \int_0^\infty\int_0^{2\pi}\phi^*_{n_p m_p}(r,\theta)r^2|\cos\theta|\phi_{n_q m_q}(r,\theta)drd\theta \tag{6.26}$$

We see that the wavefunctions $\phi_n m$ are the same as for the unperturbed two-dimensional quantum dot, and this directs us to the same kind of interals as for the dipole calculations above. The radial interal is cumbersome, and therefore left for a symbolic solver, but for angular integral we can at least give the computer some help,

$$\int_0^{2\pi}|\cos\theta|e^{i\bar{m}\theta}d\theta = \frac{i(1+e^{i\pi n})(\bar{m} + 2ie^{(i\pi\bar{m}/2)} - \bar{m}e^{i\pi n})}{\bar{m}^2 - 1}, \tag{6.27}$$

where $\bar{m} = (m_q - m_p) \in \mathbb{Z}$. We see that this expression is not defined for $\bar{m} = 1$, but inserting for this value in the interegal will yield zero as a resut. In fact, the integral will evaluate to zero for each odd value of $\bar{m}$. If the barrier was aligned in the other direction, alon the y-axis, a similar computation can be performed for sin instead of cos.

Since the particles are interacting in the same way as before, there is no need to compute a special version of the Coulomb integral matrix elements for the double well. We do, however, need to transform the single-particle functions and two-body elements from the regular harmonic oscillator basis to an approximate basis for the double-well problem. This can be done via diaonalisation of the one-body Hamiltonian in order to find a matrix of coefficients $\mathbf{C}$, that perform this basis change,

$$\left|\phi_q\right\rangle_{\mathrm{DW}} = \sum_p C_p\left|\phi_p\right\rangle_{\mathrm{HO}}, \tag{6.28}$$

[2] Here we might as well have used the position operator $\hat{y}$, which would have resulted in an equivalent potential, rotated ninety degrees.

which can be inserted into an eigenvalue equation for the one-body operator,

$$\begin{aligned} \hat{h} |\psi_q\rangle_{\text{DW}} &= \epsilon_q |\psi_q\rangle_{\text{DW}} \\ \sum_p \hat{h} C_p |\phi_p\rangle &= \sum_p \epsilon_p C_{pq} |\phi_p\rangle . \end{aligned} \tag{6.29}$$

Assuming that the eigenvalues ϵ_q are eigenvalues for the double well single-particle functions, we project onto the regular harmonic oscillator basis,

$$\begin{aligned} \sum_p \langle\phi_r|\hat{h}|\phi_p\rangle &= \sum_p C_{pr}\epsilon_p \langle\phi_r|\phi_p\rangle \\ \sum_p h_{pr} C_{pr} &= C_{pr}\epsilon_p \\ \mathbf{hC} &= \mathbf{C}\epsilon \end{aligned} \tag{6.30}$$

This is an eigenvalue equation we can solve in order to obtain the coefficient matrix which transforms from the one basis to the other. This transformation can subsequently be applied to the two-body operator,

$$\langle\psi_\alpha\psi_\beta|\hat{w}|\psi_\gamma\psi_\delta\rangle = C_\alpha^{p*} C_\beta^{p*} \langle\phi_p\phi_q|\hat{w}|\phi_r\phi_s\rangle C_\gamma^r C_\delta^s, \tag{6.31}$$

where summation over same indices is assumed.

class quantum_systems.**TwoDimensionalDoubleWell**
(*n*, *l*, *radius_length*, *num_grid_points*, *barrier_strength*=1.0, *l_ho_factor*=1.0, *omega*=0.25, *mass*=1)

Create Two-Dimensional Quantum Dot with double well potential, i.e. the Double Dot. This class inherits from **TwoDimensionalHarmonicOscillator**.

Parameters
- **n**(*int*) Number of electrons
- **l**(*int*) Number of spinorbitals
- **grid_length**(*int or float*) Space over which to construct wavefunction.
- **num_grid_points**(*int of float*) Number of points for construction of wavefunction.
- **barrier_strength**(*float*, *default* 1.0) Barrier strength in double well potential.
- **l_ho_factor**(*float*, *default* 1.0) Normal HO vs double well basis function multiple.
- **omega**(*float*, *default* 0.25) Angular frequency of harmonic oscillator potential.
- **mass**(*int or float*, *default* 1.0) Mass of electrons. Atomic units is used as default.

Attributes
- **h** One-body matrix **Type** np.array
- **f** Fock matrix **Type** np.array
- **u** Two-body matrix **Type** np.array

Methods
- **setup_system**(*axis*=0)
  Must be called in order to compute basis functions. Parameter *axis* decices to which axis the well barrier is aligned. $(0, 1) = (x, y)$.

HERE COMES THE SMOOTH *potentiâl doublé*.

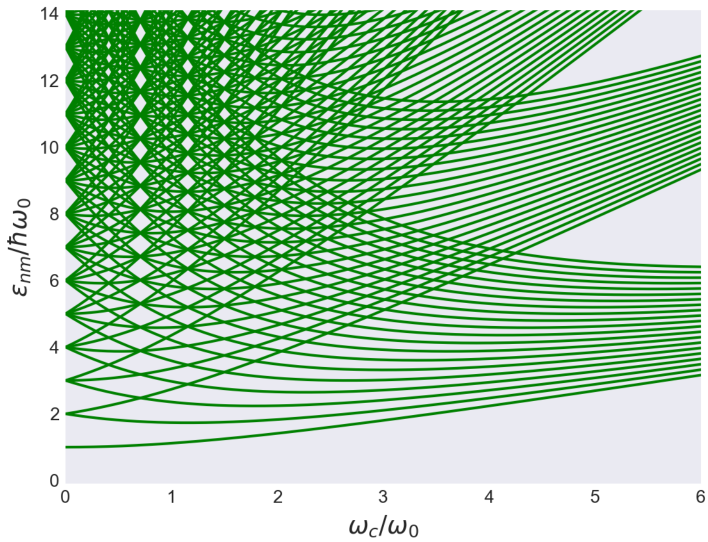


Figure 6.2: A few of the lowest eigenvalues ϵ_{nm} for a two-dimensional quantum dot for transverse magnetic field of increasing strength. This plot of the single-particle energies form the Fock-Darwin spectrum. Some states for very high values of m are omitted to make the formation of Landau bands in strong fields more visible.

Magnetic field

Extending the two-dimensional quantum dot to be under the influence of a static, transverse magnetic field is relatively effortless. We are considering a system with the following one-body hamiltonian,

$$\hat{h} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\Omega^2\hat{r}^2 + \frac{\omega_c}{2}\hat{L}_z, \tag{6.32}$$

where $\Omega = \sqrt{\omega_0^2 + \frac{\omega_c^2}{4}}$ and ω_c is the parameter dictating the strength of the magnetic field. We see that this Hamiltonian is the same as the normal two-dimensional quantum dot one-body Hamiltonian (Equation 6.9) for $\omega_c = 0$ as $\Omega \to \omega_0$, which is the well potential frequency. Conversely, if the magnetic field is infitinely strong we see that $\Omega \to \omega_c/2$ and Equation 6.32 becomes the one-body hamiltonian of a free electron in a transverse magnetic field. The single-particle functions (Equation 6.10) with the adjusted Bohr radius $a = \sqrt{m\Omega/\hbar}$, are also eigenfunctions of the angular momentum L_z and the energy eigenvalues are simply

$$\epsilon_{nm} = \hbar\Omega(2n + |m| + 1) - \frac{\hbar\omega_c}{2}m. \tag{6.33}$$

We see immediately that the energy undergoes a general shift due to the new Ω which is dependent on ω_c, but also that the energy shift of a particular shift is dependent on the sign of the azimuthal quantum number m for the given state. These factors will give different degeneracies, as illustrated in Figure 6.2. Such a plot of single-particle particle energies are sometimes referred to as the Fock-Darwin spectrum[17, 11]. With this comes the challenge of sorting the one-body matrix elements correctly, and ensuring that the closed-shell structure.

Notice in Figure 6.2, that there are lengthy intervals of b-field strength were there is no degeneracy in the eigenenergies. Conversely, there for certain specific field strengths there

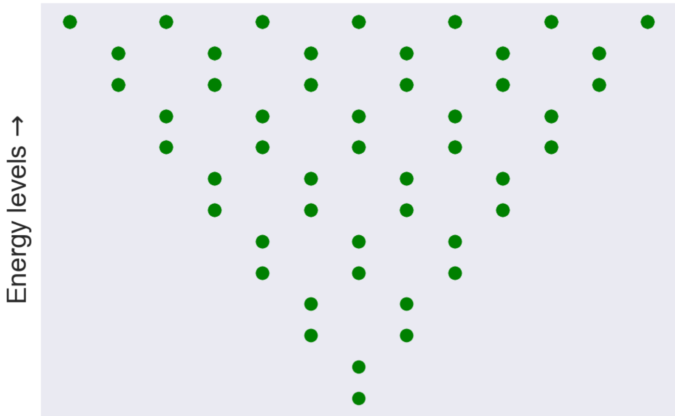


Figure 6.3: Illustration of eigenenergy degeneracies for two-dimensional quantum dot for transverse magnetic field of strength $\omega_c = 1/\sqrt{2}$. Each dot

are very interesting shell structures with diverse energies. For $\omega_c/\omega = 1/\sqrt{2}$ we get the interesting shell structure depicted in Figure 6.3. Such accidental bunching also occurs for $\omega_c/\omega = 2/\sqrt{3}, 3/2, 4/\sqrt{5}\ldots.$ We also see from figure Figure 6.2 that for an infinitely strong magnetic field as $\omega_c/\omega \to \infty$, in the free particle limit, that the energy levels form a sequence of so-called Landau bands.

As for the computation of the basis set, not much needs to be added in the computation than the extra energy to the diagonal part of the one-body matrix elements h^p_q, as everything else is the same, including the two-body Coulomb integrals. But, as we have already mentioned and displayed in Figure 6.2, for increasing strength of the magnetic field, the eigenenergies as function of ω_c eventually cross over one another. The magnetic field has the effect of decreasing the energy of a state with $m > 0$ and increasing the energy of a state with $m < 0$. This means that it is necessary to sort the eigenvalues after they have been computed.

The class specification of the two-dimensional quantum dot subjected to a transverse, homogeneous, static magnetic field is below.

class quantum_systems.**TwoDimHarmonicOscB**
(*n*, *l*, *radius_length*, *num_grid_points*, *omega_0*=1.0, *mass*=1, *omega_c*=0)

Create Two-Dimensional Quantum Dot with constant homogenous magnetic field. This class inherits from **TwoDimensionalHarmonicOscillator**.

Parameters
- **n**(*int*) Number of electrons
- **l**(*int*) Number of spinorbitals
- **grid_length**(*int or float*) Space over which to construct wavefunction.
- **num_grid_points**(*int of float*) Number of points for construction of wavefunction.
- **omega_0**(*float*, *default* 1.0) Part of harmonic osc. not dep. on magnetic field.
- **mass**(*int or float*, *default* 1.0) Mass of electrons. Atomic units is used as default.
- **omega_c**(*float*, *default* 0) Frequency corresponding to strenght of magnetic field.

Attributes
- **h** One-body matrix **Type** np.array
- **f** Fock matrix **Type** np.array
- **u** Two-body matrix **Type** np.array

Methods
- **setup_system**()
  Must be called in order to compute basis functions.
- **construct_dipole_moment**()
  Constucts dipole moment. This method is called by setup_system().

6.2 [UNFINISHED] Constructing a Custom System

6.3 [UNFINISHED] Time Evolution

Chapter 7

Implementation: Coupled Cluster

The main product of this study is manifested in the `coupled_cluster` module for Python. This module is designed to fit together with the `quantum_systems` module described in the previous chapter. We have tried to make this module easy to extend, resulting in a framework where every solver scheme inherits from an abstract parent class that specifies what must be implemented in order to make a supplemental solver or class operational in conjunction with the rest of the framework.

As a beginning to this project, which we hope will continue to grow and be used, we have implemented several different ground state solver classes, and several time-dependent solver classes. In order of increasing sophistication and elegance, we have a ground state- and a time-dependent solver for both the coupled cluster method with double excitations (CCD), the coupled cluster method with singles- and double excitations (CCSD), and for the orbital-adaptive coupled cluster method with double excitations (OACCD). The time-dependent solvers within a particular categor are dependent on its ground state counterpart, but the ground state solvers can be used independently.

The `coupled_cluster` module can be install from github via `pip` by the following command,

```
pip install git+https://github.com/Schoyen/coupled-cluster.git
```

If one prefers, the same task can be accomplished by the following commands,

```
git clone https://github.com/Schoyen/coupled-cluster.git
cd coupled-cluster
pip install .
```

We have supplied environment specifications for `conda`, with requirement specifications for the convenience of the user. Assuming the git repository is cloned properly,

```
conda environment create -f environment.yml
```

Activate the environment with,

```
conda activate cc
```

Full documentation, which we hope will be kept up to date with any future revisions can be found at `www.coupled-cluster.com`.

7.1 Ground State Computations

All ground state solver within the `coupled_cluster` module are built as sub-classes of the abstract base class `CoupledCluter`. The most important method of this class is the `compute_ground_state()`

method. This method in turn calls the `iterate_t_amplitudes()` and `iterate_l_amplitudes()` successively.

class coupled_cluster.cc.**CoupledCluster**
(*system*, *mixer=<class'coupled_cluster.mix.DIIS'>*, *verbose=False*, *np=None*)

Abstract base class defining the basic structure of a coupled cluster ground state solver class.

Parameters

system(*QuantumSystem*) A system class from the *quantum_systems* module.
mixer(*AlphaMixer, default AlphaMixer*) Mixer - Subclass of *AlphaMixer* class.
verbose(*bool, default False*) Will print results for each iteration if *True*.

Methods

compute_ground_state (*t_args=[], t_kwargs={}, l_argys=[], l_kwargs={}*)
Computes ground state of system given as parameter. Allows for parameters relating the the τ- and λ amplitudes, for use in inheriting classes.

compute_particle_density()
Computes the one-body density of the system.
Returns: Particle density
Return type: *np.array*

compute_reference_energy()
Computes reference energy
Returns: Reference energy
Return type: *np.array*

get_amplitudes(*get_t_0=False*)
Getter for amplitudes.
Parameters:
get_t_0 (*bool, default False*) Returns amplitude at $t = 0$ if `True`.
Returns: Amplitudes
Return type: *AmplitudeContainer*

iterate_l_amplitudes (*max_iterations*=100, *tol*=$1e^{-4}$, ***mixer_kwargs*)
Finds solution to λ amplitudes iteratively.
Parameters:
max_iterations (*int*) The limit of iterations allowed.
tol (*float, default* $1e^{-4}$) The tolerance for convergence.

iterate_t_amplitudes (*max_iterations*=100, *tol*=$1e^{-4}$, ***mixer_kwargs*)
Finds solution to τ amplitudes iteratively.
Parameters:
max_iterations (*int*) The limit of iterations allowed.
tol (*float, default* $1e^{-4}$) The tolerance for convergence.

_get_t_copy Abstract method
_get_l_copy Abstract method
compute_energy Abstract method
compute_one_body_density_matrix Abstract method
compute_t_amplitudes Abstract method
compute_l_amplitudes Abstract method
setup_t_mixer Abstract method
setup_l_mixer Abstract method
compute_t_residuals Abstract method
compute_l_residuals Abstract method

As we have outlined in chapter 5, the τ amplitudes are only dependent on τ, while the λ amplitudes are dependent on both τ and λ. Therefore, the τ amplitude equation iterative solver `iterate_t_amplitudes()` is called first, and the λ amplitude equation solver is called second. The most important section of the `compute_l_amplitudes()` method is the following

```
for i in range(max_iterations):
self.compute_l_amplitudes()
residuals = self.compute_l_residuals()

if self.verbose:
    print(f"Iteration: {i}\tResiduals (l): {residuals}")

if all(res < tol for res in residuals):
    break

assert i < (
    max_iterations - 1
), f"The l amplitudes did not converge. Last residual: {residuals}"
```

The equivalent section in the `compute_t_amplitudes()` method is nearly identical. The `CoupledCluster` class is supposed to provide a framework for which to implement various coupled cluster ground state solver classes. It therefore has several abstract classes that such subclasses need to implement and overwrite. The most important of these are the methods `compute_t_amplitudes` and `compute_l_amplitudes`, which are supposed to contain the evaluation of amplitude equations for a given coupled cluster truncation and scheme.

With the hope that the functunality of the rest of the methods can be inferred from name, and with the goal of brevity we proceed to a study of the simplest ground state coupled cluster solver, namely CCD, implemented in the `CoupledClusterDoubles` class.

7.1.1 Coupled Cluster Doubles

Starting from construction, the `CoupledClusterDoubles` class passes the system, defined through a `QuantumSystem` object to the parent class constructor, along with any keyword arguments, such as turning on verbosity, mixer type to us and what matrix library to apply. The `QuantumSystem` class will contain all the information necessary to set up the system, i.e. construct a one-body matrix, fock matrix and two-body matrix. These will be used to set up empty arrays for the τ and λ amplitudes. The `comput_initial_guess` is called lastly in the constructor, computing the inital guess of the double-excited amplitudes as

$$\tau^{(0)} = \frac{u_{ij}^{ab}}{D_{ij}^{ab}}, \tag{7.1}$$

where u is the two-body operator and $D_{ij}^{ab} = f_a^a + f_b^b - f_i^i - f_j^j$, where f is the Fock operator.

In the `CoupledClusterDobles` class specification one would notice that it has implementations of all the abstract methods from the `CoupledCluster` abstract class. The reason for the existence of the class, the `compute_ground_state()` method, is inherited from the parent class, and does the same thing as described above - calling `iterate_t_amplitudes()` and `iterate_l_amplitudes()`. These methods alos excist as members of `CoupledClusterDoubles`, but are excluded from the class specification for sake of brevity. It is possible to pass arguments to the the two iterator methods; one list for each iteration method, or as keywords. One can also pass arguments to the mixer through the `compute_ground_state_method()`. An overview of mixing applied to iterative solvers is given in the next section.

The important part of the specific coupled cluster scheme solver is contained in the two methods `compute_t_amplitudes()` and `compute_l_amplitudes()`. These functions evaluate the entire coupled cluster doubles amplitude equations. The computation of each term (diagram) in the amplitude equation is done in separate functions, as calls to `numpy.tensordot()`, for a total of ten terms for the τ amplitude equation in the coupled cluster doubles method including permutation operators:

$$\begin{aligned} 0 = &u^{ab}_{ij} + f^b_c \tau^{ac}_{ij} P(ab) - f^k_j \tau^{ab}_{ik} P(ij) + \frac{1}{4}\tau^{ac}_{ij}\tau^{ab}_{mn}u^{mn}_{cd} + \frac{1}{2}\tau^{cd}_{ij}u^{ab}_{cd} + \frac{1}{2}\tau^{cd}_{jm}\tau^{ab}_{in}u^{mn}_{cd}P(ij) \\ &- \frac{1}{2}\tau^{ac}_{nm}\tau^{bd}_{ij}u^{nm}_{cd}P(ab) + \tau^{ac}_{im}\tau^{bd}_{jn}u^{mn}_{cd}P(ij) + \tau^{ac}_{im}u^{bm}_{jc}P(ab)P(ij) + \frac{1}{2}\tau^{ab}_{mn}u^{mn}_{ij}. \end{aligned} \tag{7.2}$$

class coupled_cluster.cc.**CoupledClusterDoubles** (*system*, ***kwargs*)

Implementation of coupled cluster with double excitations ground state solver. Inherits from the **CoupledCluster** abstract base class.

Parameters

system(*QuantumSystem*) A system class from the *quantum_systems* module.

Methods

compute_ground_state (*t_args=[]*, *t_kwargs={}*, *l_args=[]*, *l_kwargs={}*)
Computes CCD ground state of given system.
compute_initial_guess() Computes initial guess for amplitudes.
_get_t_copy()
Returns: Copy of τ^{ab}_{ij} amplitudes
Return type: *AmplitudeContainer*
_get_l_copy()
Returns: Copy of λ^{ij}_{ab} amplitudes
Return type: *AmplitudeContainer*
compute_t_residuals()
Returns: Norm of τ^{ab}_{ij} amplitudes
Return type: *float*
compute_l_residuals()
Returns: Norm of λ^{ij}_{ab} amplitudes
Return type: *float*
setup_t_mixer(***kwargs*) Sets up mixer for τ amplitudes
setup_l_mixer(***kwargs*) Sets up mixer for λ amplitudes
compute_energy()
Returns: CCD ground state energy
Return type: *float*
compute_t_amplitudes() Computes τ amplitudes
compute_l_amplitudes() Computes λ amplitudes
compute_one_body_density()
Returns: One-body density matrix
Return type: *np.array*
compute_two_body_density()
Returns: Two-body density matrix
Return type: *np.array*

THIS IS NOT CORRECT WHEN INCLUDING LAMBDA.. The initial guess in equation Equation 7.1 is terms 2 and 3 from Equation 7.2. These terms also form the basis of the iterative scheme, if we move them to the left of the equal sign in Equation 7.2,

$$D_{ij}^{ab}\tau_{ij}^{ab} = g(u,\tau), \tag{7.3}$$

where $g(u,\tau)$ now consists of the rest of the doubles amplitude equation, our recursion relation can be written

$$t^{(k+1)} = \frac{g(u,\tau^{(k)})}{D_{ij}^{ab}}. \tag{7.4}$$

An example of a computation of one term from Equation 7.2 is,

```
def add_d2e_t(u, t, o, v, out, np):
    term = np.tensordot(t, u[o, v, v, o], axes=((1, 3), (2, 0))).transpose(
        0, 2, 1, 3
    )
    term -= term.swapaxes(0, 1)
    term -= term.swapaxes(2, 3)
    out += term
```

This function particular computes the D_{2e} diagram[1].

7.1.2 Coupled Cluster Singles Doubles

Most of the rest of the methods in the `CoupledClusterDoubles` class are there for the use of other methods, or for extracting observables. Moving to the next logical coupled cluster solver scheme; the coupled cluster method with single- and double excitations is now a matter of taking into account the extra computations needed in this scheme, for each method in the abstract base clase `CoupledCluster`. There are indeed many more computations, but the code will structurally be the same. The class specification for `CoupledClusterSinglesDoubles` is therefore given here without specification of the methods as they are excactly the same. For testing purposes, the `CoupledClusterSingelsDoubles` class have the possibility to only include double excitation at construction.

class coupled_cluster.cc.**CoupledClusterSinglesDoubles**
(*system*, *include_singles=True*, ***kwargs*)

Implementation of coupled cluster with single- and double excitations ground state solver. Inherits from the **CoupledCluster** abstract base class.

Parameters
- **system**(*QuantumSystem*) A system class from the *quantum_systems* module.
- **include_singles**(*bool, default True*) Includes single excitations if `True`.

7.1.3 Orbital-Adaptive Coupled Cluster Doubles

The algorithm applied when computing the ground state in the orbital-adaptive sphere is the nonorthogonal orbital-optimised coupled cluster (NOCC) method, developed by Myhre[45]. The NOCC scheme is shown to converge towards full configuration interaction. Since the `OACCD` class is acutally applying NOCC it can be perceived as a misnomer, but as of yet there exist no ground state equivalent of the time-dependent orbital-adaptive coupled cluster (OACC) method. Such a method is in development, and there is strong indication that NOCC would

[1] After the labelling from chapter 5 and Shavitt & Bartlett[59]

be equivalent to a OACC ground state solver. What is more, NOCC does vary the orbitals as well as iterate over amplitude, and we have therefore opted to call it OACC.

class coupled_cluster.cc.**OACCD** (*system*, ***kwargs*)

Implementation of the orbital-adaptive coupled cluster method with double excitation (OACCD), also called the nonorthogonal orbital-optimized coupled cluster model with double excitations (NOCCD). This algorithm require orthonormal basis functions. Based on work by Rolf H. Myhre[45].
Inherits from the **CoupledClusterDoubles** class.

Parameters
- **system**(*QuantumSystem*) A system class from the *quantum_systems* module.

Methods
- **compute_ground_state** (*max_iterations*=100, *tol*=$1e^{-4}$, *termination_tol*=$1e^{-4}$, *tol_factor*=0.1, *change_system_basis*=*False*, ***mixer_kwargs*)
  Computes ground state of system by iterating over κ equations.
  Parameters:
  - **max_iterations** (*int*, *default* 100) Maximum number of iterations.
  - **tol** (*float*, *default* $1e^{-4}$) Tolerance of convergence.
  - **termination_tol** (*float*, *default* $1e^{-4}$) Give up if tolerance is below this.
  - **tol_factor** (*float*, *default* 0.1) Stricter for each κ-iteration.
  - **change_system_basis** (*bool*, *default False*) Changes basis after calculation.
- **setup_kappa_mixer** (**kwargs) Set up mixer for κ vector iterations.
- **compute_kappa_down_rhs** (*f*, *u*, *t_2*, *l_2*, *o*, *v*, *np*)
  Parameters:
  - **f** (*np.array*) Fock matrix.
  - **u** (*np.array*) Two-body operator, Coulomb integrals.
  - **t_2** (*np.array*) τ^{ab}_{ij} amplitudes.
  - **l_2** (*np.array*) λ^{ij}_{ab} amplitudes.
  - **o** (*Slice*) Occupied arbitals.
  - **v** (*Slice*) Virtual orbitals.
  - **np** (*Module*) Linear algebra library.
- **compute_kappa_up_rhs** (*f*, *u*, *t_2*, *l_2*, *o*, *v*, *np*)
  Parameters:
  - **f** (*np.array*) Fock matrix.
  - **u** (*np.array*) Two-body operator, Coulomb integrals.
  - **t_2** (*np.array*) τ^{ab}_{ij} amplitudes.
  - **l_2** (*np.array*) λ^{ij}_{ab} amplitudes.
  - **o** (*Slice*) Occupied arbitals.
  - **v** (*Slice*) Virtual orbitals.
  - **np** (*Module*) Linear algebra library.

Our implementation of the NOCC ground state solver is inderited from code written by Rolf Myhre and adapted to our framework. We supply a brief overview of the algorithm here. The starting point for the NOCC model is the bivariational Lagrangian

$$\mathscr{L} = \langle\tilde{\Psi}|\hat{H}|\Psi\rangle = \langle\tilde{\phi}|(1+\Lambda)e^{-\hat{T}}e^{-\kappa}\hat{H}e^{\kappa}e^{\hat{T}}|\phi\rangle \tag{7.5}$$

which is very similar to the coupled cluster Lagrangian (Equation 5.130), except for a biorthogonal basis and a transformation of the Hamiltonian, defined as follows

$$
\begin{aligned}
\tilde{c}_p^\dagger &= e^{-\kappa}\hat{c}_p^\dagger e^{\kappa} \\
c_p &= e^{-\kappa}\hat{c}_p^\dagger e^{\kappa} \\
|\phi\rangle &= e^{-\kappa}\,|\hat{\phi}\rangle
\end{aligned} \tag{7.6}
$$

where the orthogonal reference creation- and annihilation operators marked with a hat (̂), as is the reference state function. We require that κ is antihermitian,

$$
\kappa = \sum_{pq} \kappa_{pq} c_p^\dagger c_q, \quad \kappa^\dagger = -\kappa. \tag{7.7}
$$

Moreover, we split κ into excitations and relaxations (up and down),

$$
\kappa = \sum_{ai} \kappa_{ai}^u c_a^\dagger \tilde{a}_i + \kappa_{ia}^d c_i^\dagger \tilde{c}_a = \sum_{ai} \kappa_{ai}^u X_a i + \kappa_{ia}^d \tilde{X}_{ia}^\dagger. \tag{7.8}
$$

As in any many-body formulation that includes a Lagrangian, we would like to compute the first-order conditions of the Lagrangian, in order to derive what would be the NOCC equation. The problem with this is that the result would be some extremely lengthy expressions, because κ does not commute with $\hat{T}$ or Λ. Therefore, we express the NOCC equations with an optimized basis where $\kappa = 0$, where a solution would correspond to a stationary point of the Schrödinger equation. This is the same as expanding the exponentials in κ and keeping only zero-order terms. This trick leads to an algorithm which iterates between orbital transformations and amplitudes until self-consistency.

At a particular stationary point the differential of the Lagrangian (Equation 7.5) must be zero with respect to the four sets of parameters $\{\tau\}$, $\{\lambda\}$, $\{\kappa^u\}$ and $\{\kappa^d\}$, giving us four sets of equations,

$$
\frac{\partial \mathscr{L}}{\partial \lambda_{\mu_n}} = \langle\tilde{\phi}|\tilde{X}_{\mu_n} e^{-\hat{T}}\hat{H}e^{\hat{T}}|\phi\rangle\,, \tag{7.9}
$$

$$
\frac{\partial \mathscr{L}}{\partial \tau_{\mu_n}} = \langle\tilde{\phi}|(1+\Lambda)e^{-\hat{T}}[\hat{H}, X_{\mu_n}]e^{\hat{T}}|\phi\rangle\,, \tag{7.10}
$$

$$
\frac{\partial \mathscr{L}}{\partial \kappa_{\mu_1}^u} = \langle\tilde{\phi}|(1+\Lambda)e^{-\hat{T}}[\hat{H}, X_{\mu_1}]e^{\hat{T}}|\phi\rangle\,, \tag{7.11}
$$

$$
\frac{\partial \mathscr{L}}{\partial \kappa_{\mu_1}^d} = \langle\tilde{\phi}|(1+\Lambda)e^{-\hat{T}}[\hat{H}, \tilde{X}_{\mu_1}]e^{\hat{T}}|\phi\rangle\,. \tag{7.12}
$$

We are now ready to outline the full algorithm of the `compute\_ground\_state()` in what we have called the `OACCD`. The method is iterating over the the norm of κ^u and κ^d, called the residuals of κ, until consistency compared to a tolerance value us achieved. For each such iteration, iteration over the τ and λ double excitation amplitudes is performed, but at a much less strict tolarance value than under the `CoupledClusterDoubles` scheme. After the iteration over τ and λ is achieved, the values for κ^u and κ^d are recalculated, in order to compute the aggragate κ (Equation 7.8), which in turn can be used to transform the orbitals,

$$
\begin{aligned}
h^{(k+1)} &= e^{-\kappa}h^{(k)}e^{\kappa}, \\
(u_{rs}^{pq})^{(k+1)} &= (e^{-\kappa})_a^p(e^{-\kappa})_b^q(u_{cd}^{ab})^{(k)}(e^{\kappa})_s^d(e^{\kappa})_r^c,
\end{aligned}
$$

which (in addition to being written with incomprehensible notation) is used to compute a new Fock operator. The resulting rotation of the orbitals will aid in better convergence towards the ground state.

7.1.4 Mixing

Iterative many-body methods are prone to convergence problems for certain configurations. This would be doubly important since we have moved to a variational description of coupled cluster theory, where generalisations of the variational theory dictate inifitesimal variations, which is not always feasible to implement. Moreover, an iterative optimisation scheme may not always converge properly at all. Luckily, there exists numerous techniques both for controlling and acceleration convergence.

Alpha mixer

The simplest way to "massage" convergence out of the coupled cluster ground state methods to use a dampening, where one would include a part of the result from the previous iteration, here applied to the τ amplitudes,

$$\bar{\tau}^{(k+1)} = (1-\theta)\tau^{(k+1)} + \theta\tau^{(k)}, \tag{7.13}$$

where $\tau^{(k+1)}$ is the current result from evaluating the amplitude equations, and $\tau^{(k)}$ is the previous value. Choosing $\theta \in [0, 1]$ will tune how much of the previous amplitude to include in the new state. The idea is to allow for a more gentle transition between the iterations. We have implemented this very simple mixing scheme in the `AlphaMixer` class, which also serves as a base class for further mixer implementations.

class coupled_cluster.mix.**AlphaMixer** (*theta=0.1*, *np=None*)

Class defining the α mixer. Computes a superposition of current and new amplitude vector. Also defines base class and methods the new mixer classes must implement.

Parameters

theta(*float, default 0.1*) Mixing parameter. $\theta \in [0, 1]$
np(*Module*) Matrix library to be used, e.g. numpy, cupy.

Methods

compute_new_vector (*trial_vector*, *direction_vector error_vector*)

Computes new trial vector for mixing with full right hand side of amplitude equation.

Parameters:

trial_vector (*np.array*) Initial vector for mixing
direction_vector (*np.array*) Vector to be added to *trial_vector*.
error_vector (*np.array*) Not used in α mixer. Needed in subclasses.

Returns: New mixed vector
Return type: *np.array*

The Quasi-Newton method with DIIS acceleration

A more sophisticated method to aid in convergence, and perhaps the most popular, is by performing a direct inversion of iterative subspace (DIIS). The DIIS method is built to accelerate the quasi-Newton method, an we will necesarily outline the quasi-Newton before we examine DIIS, which is explained in Helgaker et al.[30].

The commutator of Fock operator with the cluster operator is generally

$$[\hat{f}, \hat{T}] = \sum_{\mu} D_\mu \tau_\mu X_\mu, \tag{7.14}$$

where ϵ_μ is the sum of unoccupied energies minus sum of all occupied energies, i.e. $D_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$, τ_μ is the amplitude of a particular excitation, and X_μ is an excitation operator. For CCD Equation 7.14 becomes,

$$[\hat{f}, \hat{T}_2] = D_{ij}^{ab} \tau_{ij}^{ab} c_a^\dagger c_b^\dagger c_i c_j. \tag{7.15}$$

This allows us to write the coupled cluster vector function $\Omega_\mu^{(0)}$, and its Jacobian $\Omega_{\mu\nu}^{(1)}$ of the nth iteration in the form

$$\Omega_\mu^{(0)} = D_\mu \tau_\mu^{(n)} + \langle \Phi_\mu | e^{-\hat{T}^{(n)}} \hat{U} e^{\hat{T}^{(n)}} | \Phi_0 \rangle \tag{7.16}$$

$$\Omega_{\mu\nu}^{(1)} = D_\mu \delta_{\mu\nu} + \langle \Phi_\mu | e^{-\hat{T}^{(n)}} [\hat{U}, X^\nu] e^{\hat{T}^{(n)}} | \Phi_0 \rangle \tag{7.17}$$

which are very similar to the coupled cluster energy and amplitude equations, but the matrix element contains just $\hat{U}$, the fluctuation potential, instead of the entire Hamiltonian $\hat{H} = \hat{F} + \hat{U}$. HERE I AM BEING INCONSISTENT WITH MY NOTATION AGAIN.

The Jacobian constists only of a diagonal part, involving differences of the orbital energies, and a nondiagonal part, containing the fluctuation potential. The trick from *Newton's* method is to expand the vector functions around the set of amplitudes of the current iteration $\tau^{(n)}$,

$$\Omega(\tau^{(n)} + \Delta\tau) = \Omega^{(0)}(\tau^{(n)}) + \Omega^{(1)}(\tau^{(n)})\Delta\tau + \ldots, \tag{7.18}$$

which leads to a recursion relation be neglecting terms that are nonlinear in $\Delta\tau$,

$$\Omega^{(1)}(\tau^{(n)})\Delta\tau^{(n)} = -\Omega^{(0)}(\tau^{(n)}). \tag{7.19}$$

By inserting Equation 7.16 and Equation 7.17 we get the *quasi-Newton* equations for the optimisation of the coupled-cluster wavefunction,

$$\Delta\tau_\mu^{(n)} = -\frac{\Omega_\mu^{(0)}(\tau^{(n)})}{D_\mu} \tag{7.20}$$

The quasi-Newton method is fairly robust, but the convergence may be improved significantly by introducing DIIS.

In the DIIS framework[54], the new amplitudes $\tau^{(n+1)}$ are obtained by a linear interpolation among the previous estimates of the amplitudes,

$$\tau^{(n+1)} = \sum_{k+1}^{n} w_k (\tau^{(k)} + \Delta\tau^{(k)}), \tag{7.21}$$

where $\Delta\tau^{(k)}$ are obtained from Equation 7.20, and the interpolations weights sum to unity,

$$\sum_{k=1}^{n} w_k = 1.$$

To determine the DIIS weights, we associate each set of amplitudes $\tau^{(k)}$ with an error vector. We use the scaled vector function $\Delta\tau^{(k)}$ as error vector and determine the interpolation coefficients by minimising the norm of the averaged vector

$$\Delta\tau^{\text{ave}} = \sum_{k=1}^{n} w_k \Delta\tau^{(k)} \tag{7.22}$$

subject to Equation 7.1.4.

We have implemented the DIIS acceleration of the quasi-Newton method in the class `DIIS`. This class inherits from the `AlphaMixer` class and would function in its place. The `DIIS` class allows one to pick how many vectors to store and compute a linear interpolation of, with a default value of 10 vectors.

class coupled_cluster.mix.**DIIS** (*num_vecs*=10, *np=None*)

General vector mixing class to accelerate quasi-Newton method using the direct inversion of iterative space (DIIS) scheme. Inherits from *AlphaMixer*.

Parameters

- **num_vecs**(*float, default 10*) Number of vectors to keep in memory.
- **np**(*Module*) Matrix library to be used, e.g. numpy, cupy.

Methods

compute_new_vector (*trial_vector*, *direction_vector error_vector*)

Computes new trial vector for mixing with full right hand side of amplitude equation.

Parameters:

- **trial_vector** (*np.array*) Initial vector for mixing
- **direction_vector** (*np.array*) Vector to be added to *trial_vector*.
- **error_vector** (*np.array*) Error vector associated with QN DIIS.

Returns: New mixed vector

Return type: *np.array*

clear_vectors()

Delete all stored vectors.

7.2 [UNFINISHED] Time Development

Simlarly to the rest of the `coupled_cluster` module, the portion relating to time development begins with an abstract base class, `TimeDependentCoupledCluster` functioning as an interface for the rest of the classes. At construction, the `TimeDependentCoupledCluster` class is passed an affiliated ground state solver in the form of a `CoupledCluster` object, a `QuantumSystems` object and an `Integrator` object. All these are necessary in order to compute a time-development. The starting point of a time development is a system at it's ground state, necessitating the specification of a system and a ground state solver. The system is developed in time by solving the equations of motion with a numerical integrator. We will consider integrators separately in the next section.

Inclusion of a `CoupledCluster` object in the `TimeDependentCoupledCluster` class allows one to call the `compute_ground_state()` from this object, and it is included as a wrapper. Severak other methods are included from the ground state realm, like the methods for particle density computations.

The bare minimum that a time-dependent coupled cluster scheme needs to implement in order to function is the methods `rhs_t_amplitudes()` and `rhs_l_amplitudes()`, which should return the right-hand side of the amplitude equations. These methods should be integrated as generators, to make it possible to iterate over them, and should yield the amplitudes in order of increasing excitation level.

class coupled_cluster.cc.**TimeDependentCoupledCluster**
(*cc*, *np=None*, *system*, *integrator=None* ***cc_kwargs*)

Abstract base class defining the basic structure for a time-dependent coupled cluster solver.

Parameters

cc(*CoupledCluster*) Class instance defining the ground state solver.
system(*QuantumSystem*) Class instance defining the system to be solved.
np(*module*) Matrix/linear algebra library to be used, e.g. Numpy, Cupy
integrator(*Integrator*) Integrator class instance, e.g. RK4, GaussIntegrator

Methods

compute_ground_state (*t_args=[]*, t_kwargs={}, l_args=[], l_kwargs)
Call on method from *CoupledCLuster* class to compute ground state of system.

compute_particle_density()
Computes one-body density at time t.
Returns: Particle density
Return type: *np.array*

rhs_l_amplitudes()
Abstract function that needs to be implemented as a generator. The generator should return the λ-amplitudes right-hand sides, in order of increasing excitation.

rhs_t_amplitudes()
Abstract function that needs to be implemented as a generator. The generator should return the τ-amplitudes right-hand sides, in order of increasing excitation.

set_initial_conditions(*amplitudes=None*)
Set initial condition of system. It is necessary to make a call to this system before computing time-development. Can be called without argument. Will in that case revert to amplitudes of ground state solver.
Parameters:
amplitudes(*AmplitudeContainer*) Amplitudes for initial system configuration.

solve (*time_points*, *timestep_tol*=$1e^{-8}$)
Develop given system in time, specified by an array of *time_points*. Integrates equations of motion repeatedly, over all time points.
Parameters:
time_points (*list*, *np.array*) Time points over which to integrate EOM.
timestep_tol (*float, default* $1e^{-8}$) Tolerance in size of steps `dt`.
Returns: Amplitudes **Return type:** *Generator(AmplitudeContainer)*

compute_energy() Abstract function.
compute_one_body_density_matrix() Abstract function.
compute_two_body_density_matrix() Abstract function.
compute_time_dependent_overlap() Abstract function.
compute_particle_density() Calls *compute_one_body_density_matrix*.
update_hamiltonian(*current_time*, *amplitudes*)
Updates Hamiltonian of system in time, constructs new Fock operator.

Arguably the most important method in the `TimeDependentCoupledCluster` abstract base class is the `solve(time_steps)` method. For the array of time steps supplied, this method propagates with the integrator member of the class for all amplitudes. This method remains the same for all time-propagation schemes, and is therefore implemented in the base class for inheritance in sub-classes. This method in full is

```
def solve(self, time_points, timestep_tol=1e-8):
    n = len(time_points)

    for i in range(n - 1):
        dt = time_points[i + 1] - time_points[i]
        amp_vec = self.integrator.step(
            self._amplitudes.asarray(), time_points[i], dt
        )

        self._amplitudes = type(self._amplitudes).from_array(
            self._amplitudes, amp_vec
        )

        if abs(self.last_timestep - (time_points[i] + dt)) > timestep_tol:
            self.update_hamiltonian(time_points[i] + dt, self._amplitudes)
            self.last_timestep = time_points[i] + dt

        yield self._amplitudes
```

We see that after the integrator is advanced one step in time, returning an amplitude vector. This amplitude object is stored as a member of the class by use of the `from_array()` method from the `AmplitudeContainer` class, after which the Hamiltonian of the system is updated if enough time has passed.

SECTION ON IMPLEMENTATION OF `__call__` HERE?

7.2.1 Time-Dependent Coupled Cluster Singles Doubles

We have implemented both a time-dependent CCD (TDCCD) solver and a time-dependent CCSD (TDCCSD) solver. For the sake of brevity, we present only the TDCCSD here. The `TDCCSD` class, a sub-class of `TimeDependentCoupledCluster`, inheriting all methods from this super-class. It accepts the same parameter as the super-class, except the parameter that defines the ground state solver to be used - the `CoupledCluster` class implementation. The ground state solver is already decided by the level of excitation for the computation at hand. All parameters are passed to the constructor in the parent class.

The `solve()` method will have the exact same functionality as in the parent class, but since the `TDCCSD` contains amplitudes and everything else needed to solve the equations of motions in a singles and doubles trunctation, it will now yield a `Generator` object containing amplitudes that are developed in time. Any observable can be extracted during an iteration over this `Generator` object. We have implemeted several methods that can be useful in extracting information about the state of the time-developed system, for instance `compute_time_dependent_overlap` which computes the probability of the system being in the ground state, and `compute_energy` which computes the energy of the system in the current time-dependent state. The ground state probability, i.e. `compute_time_dependent_overlap`, is given by a general time-dependent auto-correlation function,

$$A(t', t) \equiv \langle S(t') | S(t) \rangle \,. \tag{7.23}$$

Because coupled cluster theory is not variational in the usual sense it is necessary to define a general state vector as combination of both $|\Psi\rangle$ and $\langle\tilde{\Psi}|$,

$$|S\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} |\Psi\rangle \\ |\tilde{\Psi}\rangle \end{pmatrix} \tag{7.24}$$

which makes the time-dependent auto-correlation function (Equation 7.23),

$$A(t', t) = \frac{1}{2} \Big(\langle\tilde{\Psi}(t')|\Psi(t)\rangle + \langle\Psi(t')|\tilde{\Psi}(t)\rangle \Big) \tag{7.25}$$

according to the definitions of the *indefinite* innerproduct by Pedersen and Kvaal[52]. Here we would set $t' = 0$, because we are interested in the ground state overlap, translating to the state before developement in time.

class coupled_cluster.cc.**TDCCSD** (**args*, ***kwargs*)

Sub-class of **TimeDependentCoupledCluster**. Computes time-development of provided system, employing time-dependent coupled cluster method with single- and double excitations. The orbitals are kept static. This class inherits all methods from the parent class, but includes a few extra.

Parameters

- **system**(*QuantumSystem*) Class instance defining the system to be solved.
- **np**(*module*) Matrix/linear algebra library to be used, e.g. Numpy, Cupy
- **integrator**(*Integrator*) Integrator class instance, e.g. RK4, GaussIntegrator

Methods

rhs_t_0_amplitude (**args*, ***kwargs*)
Evaluates CC energy expression
Returns: CCSD ground state energy.
Return type: *np.array*

rhs_t_amplitudes()
Evaluates τ_i^a and τ_{ij}^{ab} amplitude equations
Returns: τ_i^a, τ_{ij}^{ab}
Return type: *Generator*

rhs_l_amplitudes()
Evaluates λ_a^i and λ_{ab}^{ij} amplitude equations
Returns: λ_a^i, λ_{ab}^{ij}
Return type: *Generator*

compute_energy ()
Computes energy at current time step.
Returns: energy
Return type: *float*

compute_particle_density()
Computes one-body density matrix
Returns: One-body density
Return type: *np.array*

compute_time_dependent_overlap ()
Computes overlap of current time-developed state with the ground state.
Returns: Probability of grond state **Return type:** *np.array*

solve (*time_points*, *timestep_tol*=$1e^{-8}$)
Develop given system in time, specified by an array of *time_points*. Integrates equations of motion repeatedly, over all time points.
Parameters:
- **time_points** (*list, np.array*) Time points over which to integrate EOM.
- **timestep_tol** (*float, default* $1e^{-8}$) Tolerance in size of steps `dt`.

Returns: Amplitudes **Return type:** *AmplitudeContainer*

Within our truncation to includ only single- and double escitations, an inner product of two state vectors, in the normal coupled cluster scheme with static orbitals, can be computed in the following manner

$$
\begin{aligned}
\langle\Psi'|\Psi\rangle &= \langle\Phi|(1+\Lambda)e^{-\hat{T}'}e^{\hat{T}}|\Phi\rangle \\
&= \langle\Phi|(1+\Lambda_1+\Lambda_2)(1-\hat{T}_1'-\hat{T}_2'+\frac{1}{2}\hat{T}_1'^2)(1+\hat{T}_1+\hat{T}_2+\frac{1}{2}\hat{T}_1^2)|\Phi\rangle \\
&= \langle\Phi|\Phi\rangle - \langle\Phi|\Lambda_1\hat{T}_1'|\Phi\rangle + \langle\Phi|\Lambda_1\hat{T}_1'|\Phi\rangle - \langle\Phi|\Lambda_2\hat{T}_1'\hat{T}_1|\Phi\rangle - \langle\Phi|\Lambda_2\hat{T}_2'|\Phi\rangle \\
&\quad + \langle\Phi|\Lambda_2\hat{T}_2|\Phi\rangle + \frac{1}{2}\langle\Phi|\Lambda_2\hat{T}_1'\hat{T}_1'|\Phi\rangle + \frac{1}{2}\langle\Phi|\Lambda_2\hat{T}_1\hat{T}_1|\Phi\rangle\,,
\end{aligned}
\tag{7.26}
$$

where we have ignored terms that would give a zero-contribution. Evaluating the remaining terms can be done with your favourite method. Here is an example using Wick's theorem,

$$
\begin{aligned}
\langle\Phi|\Lambda_2\hat{T}_2|\Phi\rangle &= \langle\Phi|\sum_{abij}\frac{1}{4}\lambda^{ij}_{ab}\{\hat{i}^\dagger\hat{a}\hat{j}^\dagger\hat{b}\}\sum_{cdkl}\frac{1}{4}\tau^{cd}_{kl}\{\hat{c}^\dagger\hat{k}\hat{d}^\dagger\hat{l}\}|\Phi\rangle \\
&= \langle\Phi|\sum_{\substack{abcd\\ijkl}}\frac{1}{16}\lambda^{ij}_{ab}\tau^{cd}_{kl}\{\hat{i}^\dagger\hat{a}\hat{j}^\dagger\hat{b}\}\{\hat{c}^\dagger\hat{k}\hat{d}^\dagger\hat{l}\}|\Phi\rangle + \text{three more equivalent contractions} \\
&= \frac{1}{4}\langle\Phi|\sum_{\substack{abcd\\ijkl}}\lambda^{ij}_{ab}\tau^{cd}_{kl}\delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl}|\Phi\rangle = \frac{1}{4}\sum_{abij}\lambda^{ij}_{ab}\tau^{ab}_{ij}.
\end{aligned}
\tag{7.27}
$$

The entirity of the `compute_time_dependent_overlap_method()` consists of similar computations,

```python
def compute_time_dependent_overlap():
    np = self.np
    t_0, t_1, t_2, l_1, l_2 = self._amplitudes.unpack()
    t_1_0, t_2_0 = self.cc.t_1, self.cc.t_2
    l_1_0, l_2_0 = self.cc.l_1, self.cc.l_2

    psi_t_0 = 1
    psi_t_0 += np.einsum("ia, ai ->", l_1, t_1_0)
    psi_t_0 -= np.einsum("ia, ai ->", l_1, t_1)
    psi_t_0 += 0.25 * np.einsum("ijab, abij ->", l_2, t_2_0)
    psi_t_0 -= 0.5 * np.einsum("ijab, aj, bi ->", l_2, t_1_0, t_1_0)
    psi_t_0 -= np.einsum("ijab, ai, bj ->", l_2, t_1, t_1_0)
    psi_t_0 -= 0.5 * np.einsum("ijab, aj, bi ->", l_2, t_1, t_1)
    psi_t_0 -= 0.25 * np.einsum("ijab, abij ->", l_2, t_2)

    psi_0_t = 1
    psi_0_t += np.einsum("ia, ai ->", l_1_0, t_1)
    psi_0_t -= np.einsum("ia, ai ->", l_1_0, t_1_0)
    psi_0_t += 0.25 * np.einsum("ijab, abij ->", l_2_0, t_2)
    psi_0_t -= 0.5 * np.einsum("ijab, aj, bi ->", l_2_0, t_1_0, t_1_0)
    psi_0_t -= np.einsum("ijab, ai, bj ->", l_2_0, t_1, t_1_0)
    psi_0_t -= 0.5 * np.einsum("ijab, aj, bi ->", l_2_0, t_1, t_1)
    psi_0_t -= 0.25 * np.einsum("ijab, abij ->", l_2_0, t_2_0)

    auto_corr = 0.5 * (psi_t_0 * np.exp(-t_0) + (psi_0_t * np.exp(t_0)).conj())

    return np.abs(auto_corr) ** 2
```

7.2.2 Orbital-Adaptive Time-Dependent Coupled Cluster Doubles

Disappearing RHS of Q-space equations. A necessary additon to an orbital-adaptive time-dependent coupled cluster framework is the computation of P- and Q-space equations. The Q-space equations can be simplified substatially, because they equate to zero for an infinite basis. We will show this now, starting with Equation 5.189,

$$i\hbar \sum_q \rho_p^q Q \frac{\partial}{\partial t} |\varphi_q\rangle = \sum_q \rho_p^q Q h |\varphi_q\rangle + \sum_{qrs} \rho_{pr}^{qs} Q W_s^r |\varphi_q\rangle . \tag{7.28}$$

Inserting for Q in the second term on the right-hand side gives

$$\sum_{qrs} \rho_{pr}^{qs} Q W_s^r |\varphi_q\rangle = \sum_{qrs} \rho_{pr}^{qs} W_s^r |\varphi_q\rangle - \sum_{qrs} \rho_{pr}^{qs} W_s^r \sum_t |\varphi_t\rangle \langle\tilde{\varphi}_t|\varphi_q\rangle . \tag{7.29}$$

If we assume an infinite orthogonal basis, we have

$$\sum_t |\varphi_t\rangle\langle\tilde{\varphi}_t| \, |\varphi_q\rangle = \hat{1},$$

and the term will disappear. Inserting for Q in the first term on the right hand side of the first Q-space equations also yields zero. This means that the first Q-space equations reduce to

$$\begin{aligned}
i\hbar \sum_q \rho_p^q Q \frac{\partial}{\partial t} &= 0 \\
i\hbar \sum_q \rho_p^q \frac{\partial}{\partial t} |\varphi_p\rangle &= i\hbar \sum_q \rho_p^q \sum_s |\varphi_s\rangle\langle\tilde{\varphi}_s| \frac{\partial}{\partial t} |\varphi_p\rangle \\
\frac{\partial}{\partial t} |\varphi_p(t)\rangle &= \sum_s |\varphi_s(t)\rangle \, \langle\tilde{\varphi}_s(t)| \frac{\partial}{\partial t} |\varphi_p(t)\rangle \\
\frac{\partial}{\partial t} C_p^\alpha(t) |\chi_\alpha\rangle &= \sum_s C_s^\alpha(t) |\chi_\alpha\rangle \, \eta_p^s \\
\dot{C}_p^\alpha &= \sum_s C_s^\alpha \eta_p^s,
\end{aligned} \tag{7.30}$$

which we rewrite more nicely on einsten summation form,

$$\dot{\mathbf{C}} = \mathbf{C} \eta_q^p . \tag{7.31}$$

Similarly for the second Q-space equations (Equation 5.190),

$$\dot{\tilde{\mathbf{C}}} = -\eta_q^p \tilde{\mathbf{C}} . \tag{7.32}$$

We see that the Q space equation has provided us with equations that describe the time propagation of the orbitals through the coefficient matrices $\mathbf{C}$ and $\tilde{\mathbf{C}}$. These equations are valid for all excitations levels of orbital-adaptive time-dependent coupled cluster (OATDCC), and have been implemented in the new abstract class `OATDCC`.

class coupled_cluster.cc.**OATDCCD** (**args*, ***kwargs*)

Class for computing time-development of provided system, employing orbital-adaptive time-dependent coupled cluster with double excitations. Subclass of abstract class **OATDCC**, which redefines the essential computations for the orbital-adaptive framework. **OATDCC** inherits all methods from **TimeDependentCoupledCluster**, overwriting those that are necessary to overwrite.

Parameters

- **cc**(*CoupledCluster*) Class instance defining the ground state solver.
- **system**(*QuantumSystem*) Class instance defining the system to be solved.
- **np**(*module*) Matrix/linear algebra library to be used, e.g. Numpy, Cupy
- **integrator**(*Integrator*) Integrator class instance, e.g. RK4, GaussIntegrator

Methods

compute_energy()

Computes energy at current time step.
Returns: energy
Return type: *float*

7.2.3 Integrators and ODE Solvers

Most, if not all, physical systems that evolve in time will can be described by as set of equations that we call the equations of motion. These can be usually be formulated as a single- or a set of ordinary differential equations written on the abstract form

$$u'(t) = f(u(t), t). \tag{7.33}$$

To this particular equation there is an infinite number of solutions, so in order to make the solution unique, we must also specify an initial condition

$$u(0) = U_0. \tag{7.34}$$

Given the right hand side of Equation 7.33, $f(u, t)$ and the initial condition U_0, our task would be to compute $u(t)$. The simplest equation of motion in physics is Newton's second law,

$$a(t) = \frac{F(t)}{m}, \tag{7.35}$$

which we have reformulated to be on the standard form as Equation 7.33.

In any numerical scheme, the ODE defining our problem will be discretised, such that the inital value problem Equation 7.33 becomes the following

$$u_{n+1} = u_n + hf(u_n, t_n), \quad u(t_0) = u_0, \tag{7.36}$$

where h is some small time step, $t_{n+1} = t_n + h$. We see that the equation(s) at hand is solve in steps and the most important method of an implementation of any integrator scheme will be the method defining how one would step from one point to the next.

We have already derived the equations of motions for several coupled cluster frameworks[2]. Solving these equations in time is done in the same manner as any other equations of motion. The right hand side of these equations is put into practice by implementing `__call__()` for

[2] TDCC:Equation 5.170 and Equation 5.171. OATDCC:Equation 5.166, Equation 5.169

all the time-dependent classes, and the initial condition of the problem is some configuration defined by the amplitudes of the problem. By formulating the time-dependent many-body problem in this way, we can find solutions to the equations of motion by any numerical integrator scheme. For convenience, we have included two integrator implementations in the `coupled_cluster` module - the common fourth order Runge-Kutta method and the symplectic Gauss-Legendre method. Moreover, we have defined an abstract base class `Integrator`, which defines a general integrator for eventual future additons.

class coupled_cluster.integrators.**Integrator** (*np*)

Abtract integrator parent class. Subclass must implement *step* method **Parameters**

> **np**(*Module*) Matrix library to be used, e.g. numpy, cupy.

Methods

- **set_rhs** (*rhs*)
  Setter for right-hand side of problem.
  Parameters:
  rhs (*callable, int, float*) Right hand side of ODE.
- **step** (*u, t, dt*)
  Shell method. Must be implemented by subclass.

The Runge-Kutta Method

The Runge-Kutta methods are a large family of implicit and iterative methods or increasing order. The first-order Runge-Kutta method is the same as the forward Euler method, where a step is defined as follows,

$$u_{n+1} = u_n + hf(u_n, t_n). \tag{7.37}$$

The general step of an explicit n-th order Runge-Kutta method is defined by

$$u_{n+1} = u_n = h\sum_{i=1}^{s} b_i k_i, \tag{7.38}$$

where

$$\begin{aligned}
k_1 =& f(u_n, t_n), \\
k_2 =& f(u_n + h(a_{21}k_1), t_n + c_2 h), \\
k_3 =& f(u_n + h(a_{31}k_1 + a_{32}k_2), t_n + c_3 h), \\
&\vdots \\
k_s =& f(u_n + h(a_{s1}k_1 + a_{s2}k_2 + \cdots + a_{s,s-1}k_{s-1}), t_n + c_s),
\end{aligned} \tag{7.39}$$

where s is the number of stages, and the coefficients a_{ij} (for $j \in [1, i\rangle$ and $i \in \langle j, s]$), b_i (for $b \in [1, s]$) and c_i (for $i \in [2, s]$) defines the particular method. The matrix a_{ij} is called the Runge-Kutta matrix and b_i and c_i are known as the *weights* and *nodes*, respectively. We call the Runge-Kutta method consistent if

$$\sum_{j=1}^{i-1} a_{ij} = c_i, \quad i \in [2, s].$$

We have implemented the fourth-order Runge-Kutta method in the class `RungeKutta4`. This is the most common of the Runge-Kutta method, and is often sometimes referred to as simply “the Runge-Kutta method”.

class coupled_cluster.integrators.**RungeKutte4** (*np*)

Classical fourth-order Runge-Kutta numerical integrator.

Parameters
np(*Module*) Matrix library to be used, e.g. numpy, cupy.

Methods
set_rhs (*rhs*)
Setter for right-hand side of problem.
Parameters:
rhs (*callable, int, float*) Right hand side of ODE.
step(*u, t, dt*)
One itegration step
Parameters:
u (np.array) Array of equations to be integrated.
f (float) Current time step.
dt (float) Time step size.
Returns: RHS advanced one step, u_{n+1}.
Return type: *np.array*

A step of size h in the fourth order Runge-Kutta method is defined by

$$\begin{aligned} u_{n+1} =& u_n + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4), \\ t_{n+1} =& t_n + h, \end{aligned} \tag{7.40}$$

where

$$\begin{aligned} k_1 =& hf(u_n, t_n), \\ k_2 =& hf(u_n + \frac{k_1}{2}, t_n + \frac{h}{2}), \\ k_3 =& hf(u_n + \frac{k_2}{2}, t_n + \frac{h}{2}), \\ k_4 =& hf(u_n + k_3, t_n + h), \end{aligned}$$

This is implemented in the `step(u, t, dt)` method as

```
f = self.rhs
K1 = dt * f(u, t)
K2 = dt * f(u + 0.5 * K1, t + 0.5 * dt)
K3 = dt * f(u + 0.5 * K2, t + 0.5 * dt)
K4 = dt * f(u + K3, t + dt)
u_new = u + (1 / 6.0) * (K1 + 2 * K2 + 2 * K3 + K4
```

Symplectic Gauss Integrator

The Runge-Kutta method, as described above, will be unstable for most systems becuase of its inability to preserve structure and energy of the system. It is necessary to apply an integrator which is both structure-preserving and symplectic. We have inherited code used by Pedersen and Kvaal[52] and have adapted it to our framework. Nevertheless, we give a brief overview of its inner mechanics here.

A quadrature rule is an approximation of the definite integral of a function over an interval $[a, b]$.

The most common family of quadrature rules are derived by defining an equidistant grid of N points on the interval $[a, b]$, where the grid points x_n are given by

$$x_n = a + nh \tag{7.41}$$

where $h = (b - a)/N$, with index $n \in [0, N]$. A quadrature rule is commonly stated as a weighted sum of function values at specified points.

$$\int_a^b f(x)dx \approx \sum_{i=1}^{(N-1)} hf(x_i).$$

The simplest of such schemes of equidistant points is the *trapezoidal* rule given by

$$\int_a^b f(x)dx = h\left(\frac{1}{2}g(x_0) + f(x_1) + f(x_2) + \dots f(x_{N-1}) + \frac{1}{2}f(x_N)\right) + \mathscr{O}(h^2). \tag{7.42}$$

A very efficient method consists of repeating the trapezoidal rule and performing it for successive values of h, each having half the size of the previous one. This yields a sequence of approximations to the integral for various values of h can be fitted to a polynomial, and the value for this polynomial for $h = 0$ will yield a very accurate approximation to the exact value. This is called the *Romberg* method.

The n-point Gaussian quadrature rule functions similarly to the family of methods described above, but instead of equidistant points we use the zeros of orthogonal polynomials for the gripd points x_n. The first pick of orthogonal polynomials are Legendre polynomials, which are orthogonal on the interval $[-1, 1]$, i.e.,

$$\int_{-1}^1 P_l(x)P_{l'}(x)dx = \delta_{ll'}. \tag{7.43}$$

We also approximate the function f with Legendre polynomials.

The Gauss-Legendre quadrature rule is constructed to yield an exact result for polynomials of degree $2n - 1$ or less. An advantage of the Gauss-Legendre method is that its accuracy is much better than that of other methods using the same number of integration points. In fact, the accuracy of an N-point Gauss-Legendre method is equivalent to that of an equidistiant point method using $2N$ points. The resulting Gauss-Legendre quadrature rule can be stated as

$$\int_{-1}^1 f(x)dx = \sum_{n=1}^N w_n f(x_n) + \mathscr{O}(h^{2N}), \tag{7.44}$$

where x_n are the zeroes of the Legendre polynomial P_n, h is $2/N$ and w_n are appropriately chosen weights for the method.

Orthogonal polynomials p_r of degree r and leading coefficient one, satisfy the following recurrence realtion,

$$P_{r+1}(x) = (x - a_{r,r})p_r(x) - a_{r,r-1}p_{r-1}(x) \cdots - a_{r,0}p_0(x). \tag{7.45}$$

The trhee-term recurrence relation can be written as a matrix equation

$$J\tilde{P} = x\tilde{P} - p_n(x) \times \mathbf{e}_n, \tag{7.46}$$

where $\tilde{P} = [p_0(x), p_1(x), \ldots, p_{n-1}(x)]^T$, $\mathbf{e}_n$ is the nth standard basis vector and J is the Jacobian matrix,

$$J = \begin{pmatrix} a_0 & 1 & 0 & \ldots & & \\ b_1 & a_1 & 1 & 0 & \ldots & \\ 0 & b_2 & a_2 & 1 & 0 & \ldots \\ 0 & \ldots & & & \ldots & 0 \\ & \ldots & 0 & b_{N-2} & a_{N-2} & 1 \\ & & \ldots & 0 & n_{N-1} & a_{N-1} \end{pmatrix} \tag{7.47}$$

The eigenvalues of this matrix will be the nodes x_n, i.e. the zeros of the polynomials up to degree N. If $\phi^{(n)}$ is an eigenvector corresponding to an eigenvalue such an eigenvalue x_n, the corresponding weight can be found from the first component of this vector

$$w_n = \mu_0 \left(\phi_1^{(n)}\right)^2, \tag{7.48}$$

where

$$\mu_0 = \int_a^b \omega(x)dx$$

and $\omega(x)$ is the weight function. $\omega(x) = 1$ when Legendre polynomials are used in the Gauss quadrature. This efficient way of arriving at weights and nodes is called the Golub-Welsh algorithm[20].

Generally, a quadrature method is not used to compute the solution to ODEs, but we adapt it to a Runge-Kutta solver in the way explained in Pedersen and Kvaal[52]. A general implicit s-stage Runge-Kutta method is defined by

$$u_{n+1} = u_n + h\sum_{i=1}^{s} x_i f(u_n + Z_{ij}, t_n + w_i h), \tag{7.49}$$

$$Z_{in} h\sum_{j=1}^{s} a_{ij} f(u_n + Z_{jn}, t_n + w_j h). \tag{7.50}$$

This allows us to make an interpolation between each time step t_n and t_n+h by a polynomial of order s and requiring the ODE to be satisfied at the s Gauss-Legendre quadrature points gives a symplectic and reversible integrator of order $2s$. The matrix a_{ij} is computed analytically,

$$a_{ij} = \int_0^{w_j} \ell_j(x)dx, \tag{7.51}$$

where

$$\ell_j(x) = \prod_{k=1,k\neq j}^{s} \frac{x - w_k}{w_j - w_k}, \tag{7.52}$$

is the jth Lagrange interpolation polynomial. The nonlinear equation Equation 7.50 is solved iteratively for each time step, making the method implicit. These fixed-point iterations are defined by

$$Z_{in}^{(k+1)} = h\sum_{j=1}^{s} a_{ij} f(u_n + Z_{jn}^{(k)}, t_n + w_j h). \tag{7.53}$$

The initial guess is crucial to the convergence speed of the method. We have employed guess (A) scheme described in section VIII.6.1 of Ref.[21].

For the user of the Gauss integrator, the experience will be much more pleasant than dealing with the derivations of the method, because its opeartion are the same, as evidenced by the `GaussIntegrator` class specification.

class coupled_cluster.integrators.**GaussIntegrator** (*np*, *s*=2, *maxit*=20, *eps*=$1e^{-14}$)

Simple implementation of symplectic Gauss-Legendre integrator of order 4 and 6 ($s = 2$ and $2 = 3$).

Parameters

- **np** (*Module*) Matrix library to be used, e.g. numpy, cupy.
- **s** (*int*, *default* 2) Order $= 2s$. Scheme only implemented for $s \in \{2, 3\}$.
- **maxit** (*int*) Maximum number of iterations.
- **eps** (*float*, *default* $1e^{-4}$) Convergence tolerance.

Methods

step (*u*, *t*, *dt*)

One itegration step

Parameters:

- **u** (*np.array*) Array of equations to be integrated.
- **f** (*float*) Current time step.
- **dt** (*float*) Time step size.

Returns: RHS advanced one step, u_{n+1}.

Return type: *np.array*

Chapter 8

Quantum Dots

8.1 One Dimension

We blast the guy with

$$E(t) = E_0 \sin^2\left(\frac{t\pi}{T}\right)\cos(\omega t), \tag{8.1}$$

which defines a laser pulse, consisting of several parts. Blah blah blah.

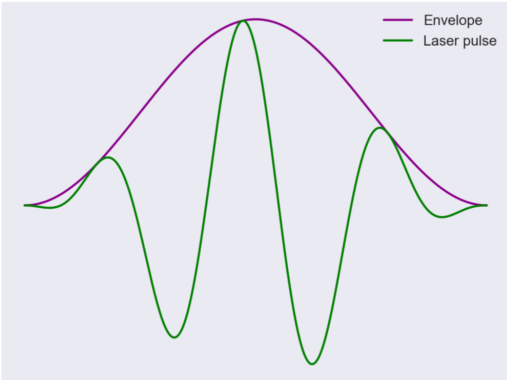


Figure 8.1:

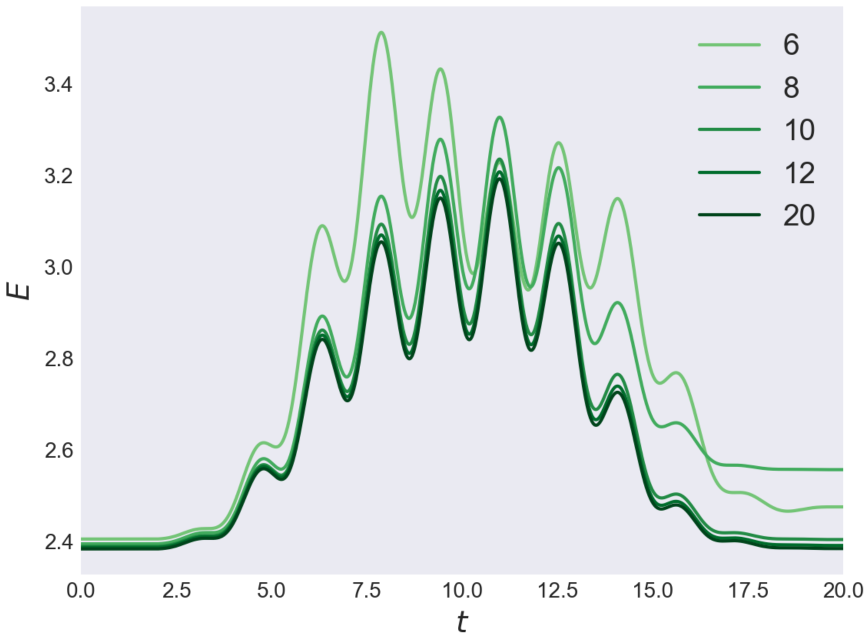


Figure 8.2: Energy $n = 2$.

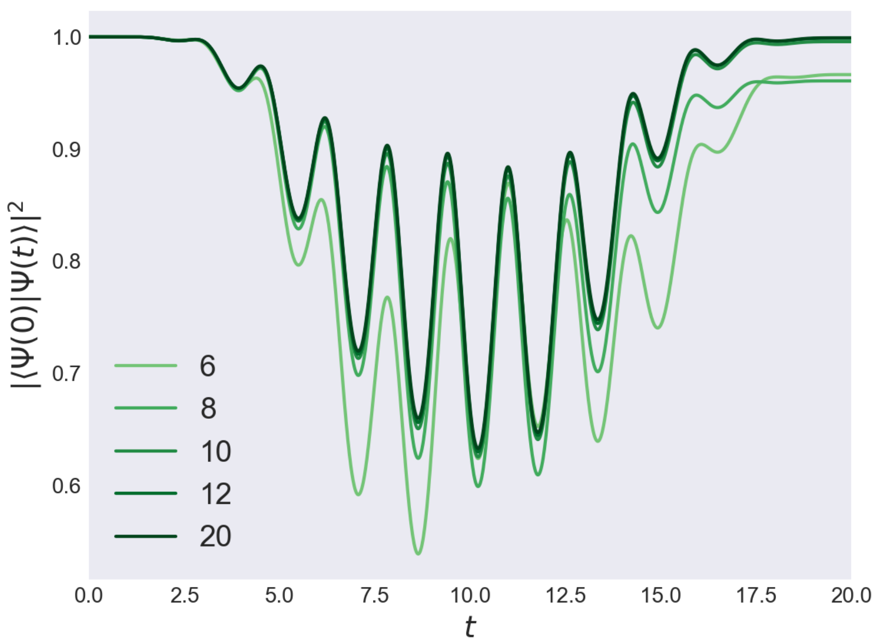

1.0
0.9
0.8
0.7
0.6
$|\langle\Psi(0)|\Psi(t)\rangle|^2$
6
8
10
12
20
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
t

Figure 8.3:

Chapter 9

Benchmarks

9.1 Zanghellini

Zanghellini et al.[67] calculate the time development of a one-dimensional quantum dot with two electrons using the multi-configurational time-dependent Hartree-Fock method (MCTDHF). This method yields excact results for a very large number of configurations, $\eta \to \infty$. This study would provide a proper benchmark for our implementation because the coupled cluster method with singles and doubles excitations (CCSD) is excact for $n = 2$ particles. The harmonic oscillator potential applied in their study had a frequency of $\omega = 0.25$, used a strong laser-like field with maximum intensity of $E = 1$ and a laser frequency of $\Omega = 8\omega = 2$. Their MCTDHF scheme convergences with $\eta = 15$ configurations up to the resulotion of their figures. We are able to reproduce their results precisely by employing the time-dependent coupled cluster method with singles and double excitations (TDCCSD) with static orbitals, using $l = 20$ spin-orbitals in the basis set.

In Figure 9.1 we see the ground state electron density for the ground state wavefunction computed with CCSD. Zanghellini et al. computed the electron density for an increasing number of configurations η using multi-configurational Hartree-Fock (MCHF). This figure matches the convergent electron density found by Zanghellini et al. as $\eta \to \infty$, in figure 1 from their article.

Figure 9.2 depicts the probability fo the system being in the ground state as a function of time. Here we have included both a time-dependent Hartree-Fock computation, corresponding to a MCTDHF computation with $\eta = 1$ configurations, and a TDCCSD computation, corresponding to MCTDHF when $\eta \to \infty$. We find that our plots matches Zanghellin et ali's plots in their figure 2 precicely.

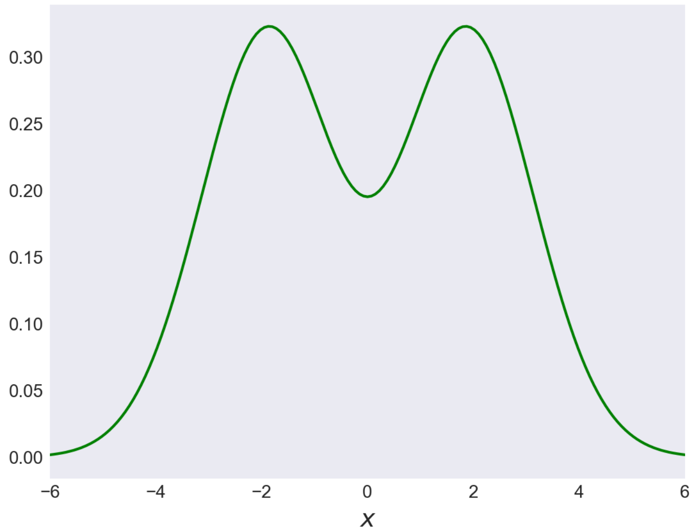


Figure 9.1: Electron density for the ground state wavefunction of a quantum dot with $n = 2$ eletrons and $l = 20$ spin-orbitals in the basis set computed with CCSD. This plot corresponds precisely with figure 1 in Zanghellini et al.[67].

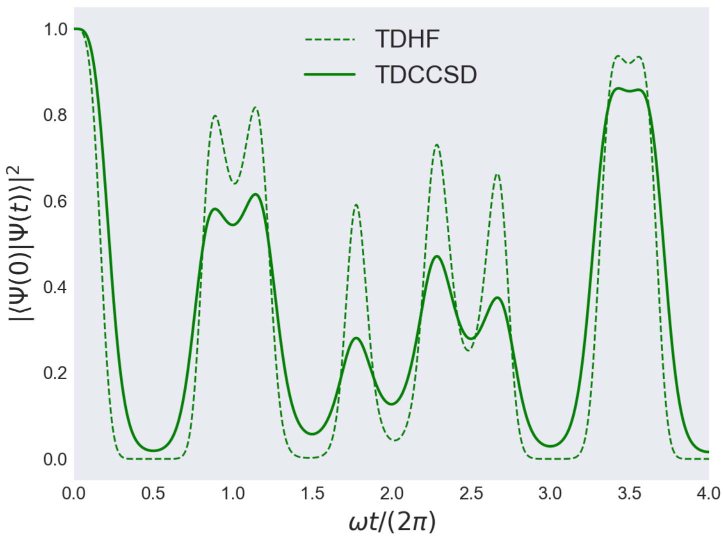


Figure 9.2: Probability of being in the ground state $|\langle\Phi(0)|\Phi(t)\rangle|$ using both TDHF and TDCCSD, for a one-dimensional quantum dot with $n = 2$ particles and $l = 20$ spin-orbitals. This plot corresponds precisely with figure 2 in Zanghellini el al.[67].

Chapter 10

Magnetic Fields

We start the study of two-dimensional quantum dots under the influence of a magnetic field by defining a system of only one particle and solving the time-dependent Schrödinger equation directly. This is a accomplished by using the `TwoDimHarmonicOscB` class to produce a basis set, single-particle functions and transition/intearction matrix (dipole elements), which is everything we need. All of these items are properties of the class and can be easily extracted. A simple periodic function simulates an electric field is constructed, as the product of such a time-dependent operator and the interaction matrix defines the time propagation. We then use a simple integration scheme, in this case the fourth-order Runge-Kutta method, to propagate the ground state single particle function of the system. Taking care to extract the dipole for every time step, we can compute the discrete Fourier transform of the dipole and compute the frequency spectrum of our system. This procedure is applied to a system comletely absent of a magnetic field, and a system under direct influence of a magnetic field.

Before going straight to the results, we study the shell structure and allowed transitions of our two systems. The left part of Figure 10.1 presents the shell structure of a the regular two-dimensional quantum dot. The states have all been assigned a number for easier examination. This shell structure is identical to the one presented in Figure 6.1. Additionally, here we have added coloured double arrows to illustrate the allowed transitions in the quantum dot. These transitions are can be encountered in the transition matrix for the system, which is reproduced in the artistic way in Figure 10.2. Notice that the coloured arrows representing allowed transitions match in colour with the elements of the transition matrix.

When we apply apply a magnetic field of strength $\omega_c/\omega = \sqrt{2}/2$ we obtain the shell struc-

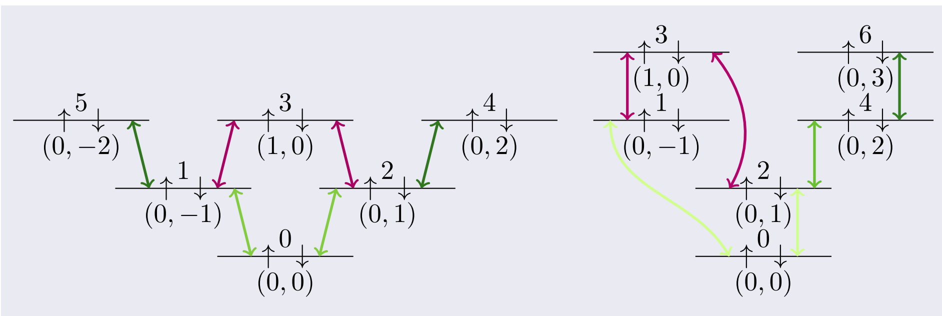


Figure 10.1: Shell structure of six lowest orbitals before (left), and after (right) a magnetic field is applied to a 2D quantum dot.

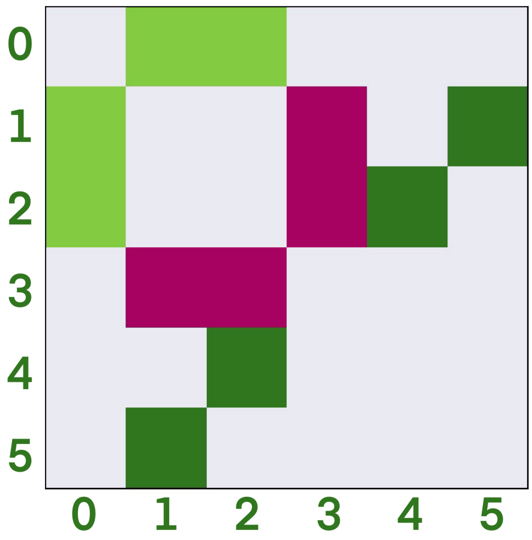


Figure 10.2: Transition matrix dictating the allowed transitions for a 2D quantum dot.

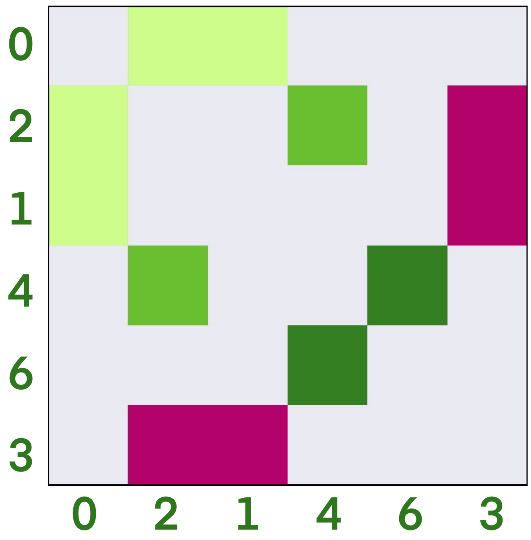


Figure 10.3: transition matrix for a 2D quantum dot when a magnetic field is applied.

ture represented to the right in Figure 10.1, where the allowed transitions correpsond to the transition matrix in Figure 10.3. The chosen magnetic field strength was not chosen arbitrarily, as these accidental degenracies occur only rarely as a function of magnetic field strength[1]. For succinctness we repeat the function for energy eigenvalues for two-dimensional quantum dot influenced by a magnetic field (Equation 6.33),

$$\epsilon_{nm} = \hbar\Omega(2n + |m| + 1) - \frac{\hbar\omega_c}{2}m, \tag{10.1}$$

where $\Omega = \sqrt{\omega_0^2 + \frac{\omega_c^2}{4}}$. Apart from a general shift up in energy by adding a magnetic field, the states with negative azimuthal quantum number m will experience an increase in energy eigenvalue, and vice versa. We see this effect clearly in the new shell structure in Figure 10.1. The states with negative m have indeed undergone a relative shift upwards, whilst the states with positive m have been shifted downwards, relative to the other states. The ground state, labelled 0, remains relatively stationary, the states labelled 2 ($m = 1$) and 4 ($m = 2$) have been shifted downwards and the states labelled 1 ($m = -1$) and 5 ($m = -2$) have been shifted upwards. State number 5 so much that it has disappeared from the shell structure, with a new state 6 ($= 3$) appearing. This is due to our restriction to include only the six lowest-energy orbitals. We see that the possible remaining allowed transitions remain the same, with the exception of transitioning between state 1 and 5, because state 5 is no more, and the addition of a possible transition between state 4 and 6.

If we compute the frequency spectrum of the two systems (Figure 10.4) we get a single line for the normal quantum dot. This is expected, as the quantum harmonic oscillator has the same energy difference between each level. However, when we apply a magnetic field and shift the energies of the orbitals in the quantum dot, we see that we get two different energy transitions. This is revealed as two lines in the frequency spectrum in Figure 10.4. This is equivalent to a splitting in transmisstion spectra of quantum dot arrays under the effect of a magnetic field in experiments[27, 43].

[1] Hence the term “accidental”.

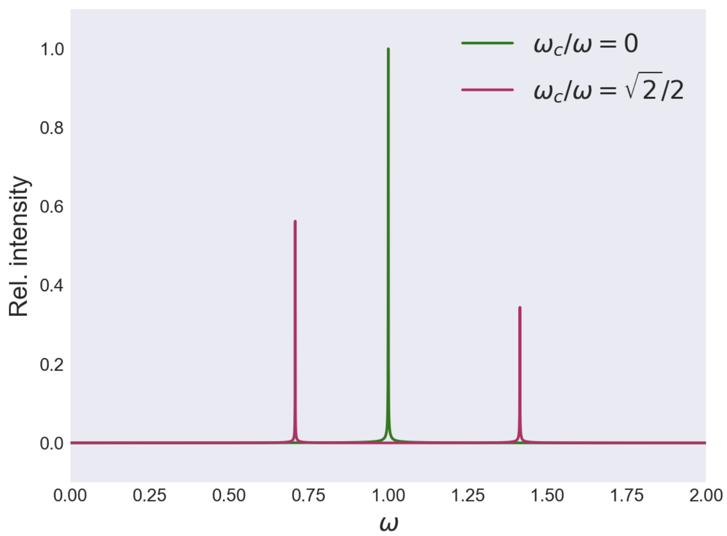


Figure 10.4: Spectrum of a 2D quantum dot both with and without a magnetic field.

Part IV

Appendices

Appendix A

Slater-Condon Rules

The Slater-Condon rules are ways to express integrals over operators in terms of single-particle orbitals. Here is an outline of a proof for these rules.

Consider first some Slater determinants,

$$|I\rangle = |i_1 i_2 \dots i_N\rangle = \hat{i}_1^\dagger \hat{i}_2^\dagger \dots \hat{i}_N^\dagger \,|\rangle \tag{A.1}$$

$$|J\rangle = |j_1 j_2 \dots j_N\rangle = \hat{j}_1^\dagger \hat{j}_2^\dagger \dots \hat{j}_N^\dagger \,|\rangle \,. \tag{A.2}$$

To get started, we want to compute the inner product $\langle I|J\rangle$ of these two Slater determinants,

$$\langle I|J\rangle = \langle|\, \hat{i}_N \dots \hat{i}_2 \hat{i}_1 \hat{j}_1^\dagger \hat{j}_2^\dagger \dots \hat{j}_N^\dagger \,|\rangle \,. \tag{A.3}$$

In order to evaluate this expression, we move every annihilation operater $\hat{i}_p$ to the right. Starting with $\hat{i}_1$, for instance, we have two possible outcomes. If there is no $\hat{j}_q$ that is the same as $\hat{i}_1$ we get

$$\langle I|J\rangle = \langle|\, \hat{i}_N \dots \hat{i}_2 \hat{j}_1^\dagger \hat{j}_2^\dagger \dots \hat{j}_N^\dagger \hat{i}_1 \,|\rangle\, (-1)^N = 0, \tag{A.4}$$

because $\hat{i}_1 \,|\rangle = 0$. The other possibility that may arise is that $\hat{i}_1 = \hat{j}_q$, so that

$$\hat{i}_1 \hat{j}_q^\dagger = \{\hat{i}_1, \hat{j}_q^\dagger\} - \hat{j}_q^\dagger \hat{i}_1 = \hat{\delta}_{i_1 k_q} - \hat{j}_p^\dagger \hat{i}_1 = \hat{1} - \hat{j}_q^\dagger \hat{i}_1, \tag{A.5}$$

and

$$\langle I|J\rangle = \langle|\, \hat{i}_N \dots \hat{i}_2 \hat{j}_1^\dagger \hat{j}_2^\dagger \dots \hat{j}_{p-1}^\dagger \hat{j}_{p+1}^\dagger \dots \hat{j}_N^\dagger \hat{i}_1 \,|\rangle\, (-1)^{p-1} - 0. \tag{A.6}$$

We continue in this manner, moving all $\hat{i}$ to the right and the final result will be zero if there are any $\hat{i}_p$ without a matching $\hat{j}_q$ or $(-1)^\tau$ if the two operator strings are identical to a permutation τ.

Next, consider a symmetric one-body operator

$$\hat{F} = \sum_{\mu=1}^{N} \hat{f}_\mu, \tag{A.7}$$

where μ is the identity of the electron on which the identical $\hat{f}_\mu$ operate. Computing a matrix element of this one-body operator between two Slater determinants will yield three possible results,

$$\begin{aligned}
\langle I|\,\hat{F}\,|J\rangle &= \langle i_1 i_2 \dots i_N|\,\hat{F}\,|j_1 j_2 \dots j_N\rangle \\
&= \sum_\mu \langle i_1 i_2 \dots i_N|\,\hat{f}_\mu\,|j_1 j_2 \dots j_N\rangle \\
&= \sum_\mu \langle \phi_{i_1}\phi_{i_2}\dots\phi_{i_N}|\,\hat{f}_\mu \sum_{\hat{P}} (-1)^{\sigma(\hat{P})} \left|\hat{P}\phi_{j_1}\phi_{j_2}\dots\phi_{j_N}\right\rangle = \begin{cases} \sum_k \langle i_k|\,\hat{f}\,|i_k\rangle\,(-1)^{\sigma(\hat{P})} & \text{I} \\ \langle i_k|\,\hat{f}\,|i'_k\rangle\,(-1)^{\sigma(\hat{P})} & \text{II} \\ 0 & \text{III} \end{cases}
\end{aligned} \tag{A.8}$$

In the last line, the integral is written with spinorbitals instead of Slater determinants. The result will be the first case (I), if the operators needed to construct the Slater determinants are the same, up to a permutation with permutation parity σ associated with the permutation operator $\hat{P}$ needed to permute the product of spinorbitals. If there exists excactly one noncoincidence in the string of operators so that $\hat{P}j_1 j_2 \dots j_N = i_1 i_2 \dots i'_k \dots i_N$ where $i_k \neq i'_k$, we get the result in the second case (II). If there are two or more noncoincidences, the result is zero (III).

With second quantisation we might write a one-electron operators differently,

$$\sum_{kl} \langle k|\,\hat{f}\,|l\rangle\,\hat{a}_k^\dagger \hat{a}_l = \sum_{kl} f_{kl}\hat{a}_k^\dagger \hat{a}_l. \tag{A.9}$$

It is possible to show that the results are the same in this representation. First, consider the case where the two Slater determinants are equal,

$$\begin{aligned}
\langle I|\sum_{kl} f_{kl}\hat{a}_k^\dagger \hat{a}_l\,|I\rangle &= \sum_{kl} f_{kl}\,\langle I|\,\hat{a}_k^\dagger \hat{a}_l\,|I\rangle \\
&= \sum_{kl} f_{kl}\delta_{kl} n_l(I) = \sum_{k\in I} f_{kk} = \sum_{k=1}^{N} \langle i_k|\,\hat{f}\,|i_k\rangle\,.
\end{aligned} \tag{A.10}$$

Second, we look at the case where we have one noncoincidence, $i_p \neq j_p$,

$$\begin{aligned}
\langle I|\sum_{kl} f_{kl}\,\langle I|\,\hat{a}_k^\dagger \hat{a}_l\,|J\rangle &= \sum_{kl} f_{kl}\,\langle I|\,\hat{a}_k^\dagger \hat{a}_l\,|J\rangle \\
&= \sum_{kl\neq p} f_{kl}\,\langle I|\,\hat{a}_k^\dagger \hat{a}_l\,|J\rangle + f_{i_p j_p}\,\langle I|\,\hat{i}_p^\dagger \hat{j}_p\,|J\rangle \\
&= 0 + f_{i_p j_p}\,\langle I'|I'\rangle = \left\langle \hat{i}_p\right|\,\hat{f}\,\left|\hat{i}_p\right\rangle.
\end{aligned} \tag{A.11}$$

Lastly, there is no pair of operators $\hat{a}_k^\dagger \hat{a}_l$ that will give a non-zero result. Consequently, we see that the second-quantised form of the one-body operator gives the same result.

Similarly, consider a symmetric two-body operator,

$$\hat{G} = \sum_{\mu<\nu}^{N} \hat{g}_{\mu\nu} = \frac{1}{2}\sum_{\mu\neq\nu}^{N} \hat{g}_{\mu\nu} = \frac{1}{2}\sum_{ijkl} \langle ij|\,\hat{g}\,|kl\rangle\,\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k. \tag{A.12}$$

We would like to show that the second-quantized form is correct, and therefore firstly consider the case where the two Slater determinants are equal, i.e. zero noncoincidences;

$$\langle I|\,\hat{G}\,|I\rangle = \frac{1}{2}\sum_{ijkl} \langle ij|\,\hat{G}\,|kl\rangle\,\langle I|\,\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k\,|I\rangle\,. \tag{A.13}$$

We must have $k = i_p$ and $l = i_q$ appear in $|I\rangle$, so that

$$\begin{aligned}\langle I|\,\hat{G}\,|I\rangle =& \frac{1}{2}\sum_{ij}\langle ij|\,\hat{g}\,|i_p i_q\rangle\,\langle I|\,\hat{a}^\dagger\hat{a}^\dagger\hat{a}_{i_p}\hat{a}_{i_q}\,|i_1 i_2\ldots i_p\ldots i_q\ldots\rangle\\ =& \frac{1}{2}\sum_{ij}\langle ij|\,\hat{g}\,|i_p i_q\rangle\,\langle I|\,\hat{a}_i^\dagger\hat{a}_j^\dagger\,|i_1 i_2\ldots\rangle\,(-1)^{(p-1)+(q-2)}.\end{aligned} \tag{A.14}$$

From this point we have two possibilities for the values of i and j, because the creation operators must put the same values back into the ket,

$$\begin{aligned}&\langle i_p i_q|\,\hat{g}\,|i_p i_q\rangle\,\langle I|i_1 i_2\ldots i_p\ldots i_q\ldots\rangle\,(-1)^{(p-1)+(q-2)}(-1)^{(p-1)+(q-2)}\\ &\quad= \langle i_p i_q|\,\hat{g}\,|i_p i_q\rangle\end{aligned} \qquad (i = i_p,\ j = i_q); \tag{A.15}$$

$$\begin{aligned}&\langle i_q i_p|\,\hat{g}\,|i_p i_q\rangle\,\langle I|i_1 i_2\ldots i_p\ldots i_q\ldots\rangle\,(-1)^{(p-1)+(q-2)}(-1)^{(p-1)+(q-1)}\\ &\quad= -\langle i_q i_p|\,\hat{g}\,|i_p i_q\rangle = -\langle i_p i_q|\,\hat{g}\,|i_q i_p\rangle\end{aligned} \qquad (i = i_q,\ j = i_p). \tag{A.16}$$

By starting in the reverse order, we obtain the same contributions. The total matrix element is therefore,

$$\langle I|\,\hat{G}\,|I\rangle = \frac{1}{2}\sum_{i\in I}\sum_{j\in J}(\langle ij|\,\hat{g}\,|ij\rangle - \langle ij|\,\hat{g}\,|ji\rangle) = \sum_{\substack{i<j\\ i,j\in I}}\langle ij|\,\hat{g}\,|ij\rangle_{\mathrm{AS}}\,. \tag{A.17}$$

Next, we consider a single noncoincidence in $|I\rangle$, $i_p \neq i'_p$,

$$|I\rangle = |i_1 i_2\ldots i_p\ldots\rangle\,, \tag{A.18}$$

$$|I'\rangle = \left|i_1 i_2\ldots i'_p\ldots\right\rangle. \tag{A.19}$$

We get contributions to $\langle I|\,\hat{G}\,|I'\rangle$ from the operator string $\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\hat{a}_k$ in the following cases,

$$i = i'_p,\ k = i_p,\ j = l = i_q \to \left\langle i'_p i_q\middle|i_p i_q\right\rangle \tag{A.20}$$

$$i = i'_p,\ l = i_p,\ j = k = i_q \to -\left\langle i'_p i_q\middle|i_q i_p\right\rangle \tag{A.21}$$

$$j = i'_p,\ l = i_p,\ i = k = i_q \to \left\langle i_q i'_p\middle|i_q i_q\right\rangle \tag{A.22}$$

$$j = i'_p,\ k = i_p,\ i = l = i_q \to -\left\langle i_q i'_p\middle|i_p i_q\right\rangle, \tag{A.23}$$

where the two first terms are egual to the last terms, respectively. This leaves us with,

$$\langle I'|\,\hat{G}\,|I\rangle = 2\times\frac{1}{2}(\left\langle i'_p j\right|\,\hat{g}\,|i_p j\rangle - \left\langle i'_p j\right|\,\hat{g}\,|j i_p\rangle) = \sum_{j\in I}\left\langle i'_p j\right|\,\hat{g}\,|i_p j\rangle_{\mathrm{AS}}\,. \tag{A.24}$$

After a while we see a pattern emerges. For two noncoincidences ($i_p \neq i'_p$, $i_q \neq i'_q$) we have,

$$\langle I'|\,\hat{G}\,|I\rangle = \left\langle i'_p i'_q\right|\,\hat{g}\,|i_p i_q\rangle\,, \tag{A.25}$$

while for three or more noncoincidences,

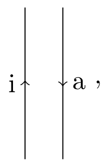
$$\langle I'|\,\hat{G}\,|I\rangle = 0. \tag{A.26}$$

Appendix B

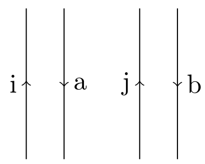
Diagrammatic Notation

B.1 Slater determinants

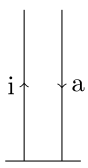
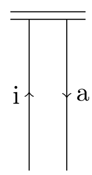
Drawing the reference state will result in a drawing of nothing. A single-excited reference state is two vertical arrows

$$\Phi_i^a = $$  , (B.1)

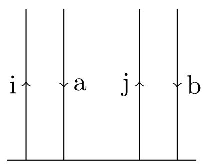
while the double-excited Slater determinant consists of four vertical arrows,

$$\Phi_{ij}^{ab} = $$  . (B.2)

The horizontal positions of the lines have no significance. If we want to indicate a bra or ket form we draw a couple of horizontal lines,

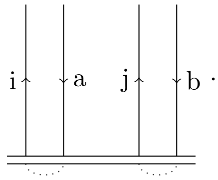
$$|\Phi_i^a\rangle = \{\hat{a}^\dagger \hat{i}\}\,|0\rangle = $$  , $$\langle \Phi_i^a| = \langle 0|\,\{\hat{i}^\dagger \hat{a}\} = $$  , (B.3)

where $\{ABC\ldots\}$ is a normal ordered product relative to the Fermi vacuum. A double-excited ket state could be drawn like

$$\left|\phi_{ij}^{ab}\right\rangle = \{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\}\,|0\rangle = \{(\hat{a}^\dagger \hat{i})(\hat{b}^\dagger \hat{j})\}\,|0\rangle = $$  (B.4)

This drawing could, however, also mean $\left|\phi_{ij}^{ba}\right\rangle$. The use of diagrams will be independent of this ambiguity, as long as one remains consistent. To be precise one can introduce dotted/dashed lines,

$$\left|\phi_{ij}^{ab}\right\rangle = \{\hat{a}^\dagger\hat{b}^\dagger\hat{j}\hat{i}\}\,|0\rangle = \{(\hat{a}^\dagger\hat{i})(\hat{b}^\dagger\hat{j})\}\,|0\rangle = \tag{B.5}$$



These indicate what index letters should be above and below one another.

B.2 One-Body Operator

The one-electron operator on normal-ordered from is given by

$$\hat{U}_N = \sum_{pq} \langle p|\,\hat{u}\,|q\rangle\,\{\hat{p}^\dagger\hat{q}\}, \tag{B.6}$$

acting on a singly excited Slater determinant

$$|\Phi_i^a\rangle = \{\hat{a}^\dagger\hat{i}\}\,|0\rangle\,, \tag{B.7}$$

id est

$$\sum_{pq} \langle p|\,\hat{u}\,|q\rangle\,\{\hat{p}^\dagger\hat{q}\}\{\hat{a}^\dagger\hat{i}\}\,|0\rangle\,. \tag{B.8}$$

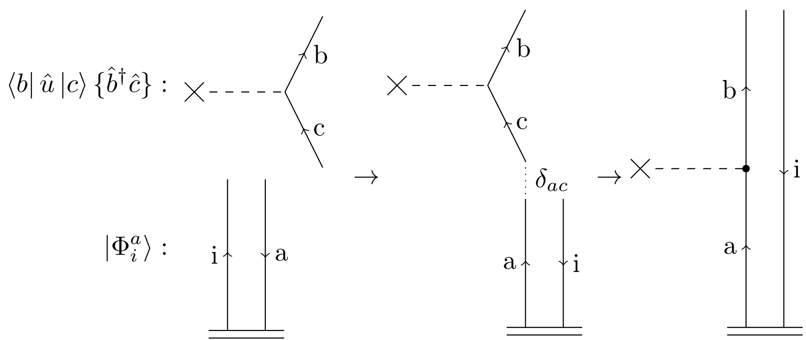
There are four different terms arising from this expression, depending on whether p and q represents particles or holes. Beginning with a *particle-particle* term,

$$\begin{aligned}\langle b|\,\hat{u}\,|c\rangle\,\{\hat{b}^\dagger\hat{c}\}\{\hat{a}^\dagger\hat{i}\}\,|0\rangle &= \langle b|\,\hat{u}\,|c\rangle\,\{\hat{b}^\dagger\hat{c}\hat{a}^\dagger\hat{i}\}\,|0\rangle + \langle b|\,\hat{u}\,|c\rangle\,\{\hat{b}^\dagger\hat{c}\hat{a}^\dagger\hat{i}\}\,|0\rangle \\ &= \langle b|\,\hat{u}\,|c\rangle\,\hat{b}^\dagger\hat{a}^\dagger\hat{i}\hat{c}\,|0\rangle + \langle b|\,\hat{u}\,|c\rangle\,\delta_{ac}\{\hat{b}^\dagger\hat{i}\} \\ &= 0 + \langle b|\,\hat{u}\,|c\rangle\,\delta_{ac}\,|\Phi_i^a\rangle\,,\end{aligned} \tag{B.9}$$

giving non-zero contributions of the type

$$\langle b|\,\hat{u}\,|a\rangle\,\{\hat{b}^\dagger\hat{a}\}\,|\Phi_i^a\rangle = \langle b|\,\hat{u}\,|a\rangle\,|\Phi_i^b\rangle. \tag{B.10}$$

We can draw a graphical representation of this contraction process,



(B.11)

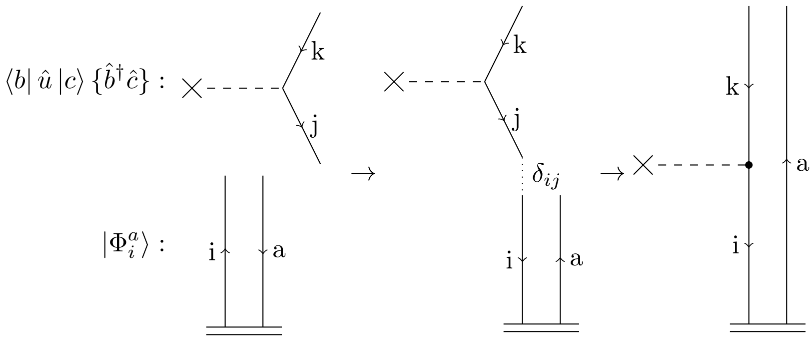
Now, let's consider a *hole-hole* term acting on the same single-excited Slater determinant,

$$\begin{aligned}\langle j|\,\hat{u}\,|k\rangle\,\{\hat{j}^\dagger\hat{k}\}\{\hat{a}^\dagger\hat{i}\}\,|0\rangle &= \langle j|\,\hat{u}\,|k\rangle\,\{\hat{j}^\dagger\hat{k}\hat{a}^\dagger\hat{i}\}\,|0\rangle + \langle j|\,\hat{u}\,|k\rangle\,\{\hat{j}^\dagger\hat{k}\hat{a}^\dagger\hat{i}\}\,|0\rangle \\ &= -\langle j|\,\hat{u}\,|k\rangle\,\{\hat{k}\hat{a}^\dagger\hat{i}\hat{j}^\dagger\}\,|0\rangle + \delta_{ij}\,\langle i|\,\hat{u}\,|k\rangle\,\{\hat{k}\hat{a}^\dagger\}\,|0\rangle \\ &= 0 - \delta_{ij}\,\langle i|\,\hat{u}\,|j\rangle\,\{\hat{a}^\dagger\hat{k}\}\,|0\rangle \\ &= -\delta_{ij}\,\langle i|\,\hat{u}\,|j\rangle\,|\Phi_k^a\rangle\,,\end{aligned} \tag{B.12}$$

meaning we are only left with non-zero contributions of the type,

$$\langle i|\,\hat{u}\,|j\rangle\,\{\hat{i}^\dagger\hat{k}\}\,|\Phi_i^a\rangle = -\,\langle i|\,\hat{u}\,|k\rangle\,|\Phi_k^a\rangle\,. \tag{B.13}$$

One can make a diagrammatic representation of this contraction as well,

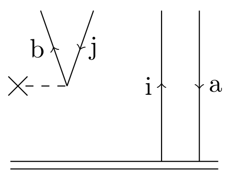


(B.14)

Next, we look at the *particle-hole* term,

$$\begin{aligned}\langle b|\,\hat{u}\,|j\rangle\,\{\hat{b}^\dagger\hat{j}\}\{\hat{a}^\dagger\hat{i}\}\,|0\rangle &= \langle b|\,\hat{u}\,|j\rangle\,\{\hat{b}^\dagger\hat{j}\hat{a}^\dagger\hat{i}\}\,|0\rangle\\ &= \langle b|\,\hat{u}\,|j\rangle\,\hat{a}^\dagger\hat{b}^\dagger\hat{j}\hat{i}\,|0\rangle\\ &= \langle b|\,\hat{u}\,|j\rangle\,\left|\Phi_{ij}^{ab}\right\rangle,\end{aligned} \tag{B.15}$$

with no contraction in this case. This expression is represented by



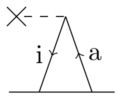
(B.16)

showing the resulting determinant is $\left|\Phi_{ij}^{ab}\right\rangle$. Holes and particles joined at the same vertex, on the same path, are in the same vertical position in the excited Slater determinant. This representation may appear to leave out the cases where $i = j$ and/or $a = b$, but these diagrams will give a vanishing Slater determinant.

The *hole-particle* term is

$$\hat{U}_N = \begin{aligned}\langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\}\{\hat{a}^\dagger\hat{i}\}\,|0\rangle &= \langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\hat{a}^\dagger\hat{i}\}\,|0\rangle + \langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\hat{a}^\dagger\hat{i}\}\,|0\rangle\\ &+ \langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\hat{a}^\dagger\hat{i}\}\,|0\rangle + \langle j|\,\hat{u}\,|b\rangle\,\{\hat{j}^\dagger\hat{b}\hat{a}^\dagger\hat{i}\}\,|0\rangle\\ &= \delta_{ij}\delta_{ab}\,\langle j|\,\hat{u}\,|b\rangle\,|0\rangle = \langle i|\,\hat{u}\,|a\rangle\,|0\rangle\,,\end{aligned} \tag{B.17}$$

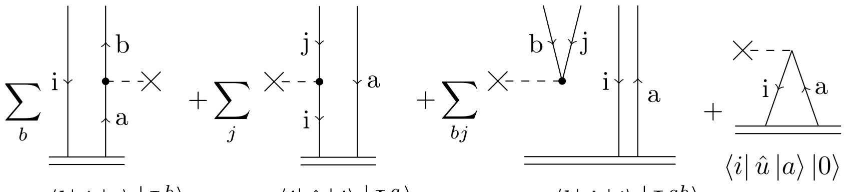
which is represented by



(B.18)

which shows that the result of the operation involved the vacuum state.

The full one-body operator becomes,



$$\sum_b \langle b|\,\hat{u}\,|a\rangle \left|\Phi_i^b\right\rangle + \sum_j - \langle i|\,\hat{u}\,|j\rangle \left|\Phi_j^a\right\rangle + \sum_{bj} \langle b|\,\hat{u}\,|j\rangle \left|\Phi_{ij}^{ab}\right\rangle + \langle i|\,\hat{u}\,|a\rangle \left|0\right\rangle \tag{B.19}$$

Appendix C

2D Coulomb elements

Implementation of two-body matrix elements for the two-dimensional quantum dots[2]. Note that Anisimovas and Matulis uses the chemist's convention $\langle ij| \hat{u} |lk\rangle$ which is $\langle ij| \hat{u} |kl\rangle$ in the physcist's notation. That is, the last two indices are interchanged.

```python
def coulomb_ho(n_i, m_i, n_j, m_j, n_l, m_l, n_k, m_k):
    element = 0

    if m_i + m_j != m_k + m_l:
        return 0

    M_i = 0.5 * (abs(m_i) + m_i)
    dm_i = 0.5 * (abs(m_i) - m_i)

    M_j = 0.5 * (abs(m_j) + m_j)
    dm_j = 0.5 * (abs(m_j) - m_j)

    M_k = 0.5 * (abs(m_k) + m_k)
    dm_k = 0.5 * (abs(m_k) - m_k)

    M_l = 0.5 * (abs(m_l) + m_l)
    dm_l = 0.5 * (abs(m_l) - m_l)

    n = np.array([n_i, n_j, n_k, n_l], dtype=np.int64)
    m = np.array([m_i, m_j, m_k, m_l], dtype=np.int64)
    j = np.array([0, 0, 0, 0], dtype=np.int64)
    l = np.array([0, 0, 0, 0], dtype=np.int64)
    g = np.array([0, 0, 0, 0], dtype=np.int64)

    for j_1 in range(n_i + 1):
        j[0] = j_1
        for j_2 in range(n_j + 1):
            j[1] = j_2
            for j_3 in range(n_k + 1):
                j[2] = j_3
                for j_4 in range(n_l + 1):
                    j[3] = j_4
```

```
                g[0] = j_1 + j_4 + M_i + dm_l
                g[1] = j_2 + j_3 + M_j + dm_k
                g[2] = j_3 + j_2 + M_k + dm_j
                g[3] = j_4 + j_1 + M_l + dm_i

                G = np.sum(g)
                ratio_1 = log_ratio_1(j)
                prod_2 = log_product_2(n, m, j)
                ratio_2 = log_ratio_2(G)

                temp = 0
                for l_1 in range(g[0] + 1):
                    l[0] = l_1
                    for l_2 in range(g[1] + 1):
                        l[1] = l_2
                        for l_3 in range(g[2] + 1):
                            l[2] = l_3
                            for l_4 in range(g[3] + 1):
                                l[3] = l_4

                                if l_1 + l_2 != l_3 + l_4:
                                    continue

                                L = np.sum(l)

                                temp += (
                                    -2
                                    * (int(g[1] + g[2] - l[1] - l[2]) & 0x1)
                                    + 1
                                ) * np.exp(
                                    log_product_3(l, g)
                                    + math.lgamma(1.0 + 0.5 * L)
                                    + math.lgamma(0.5 * (G - L + 1.0))
                                )

                element += (
                    (-2 * (int(np.sum(j)) & 0x1) + 1)
                    * np.exp(ratio_1 + prod_2 + ratio_2)
                    * temp
                )

    element *= log_product_1(n, m)

    return element
```

Appendix D

CCSD Equations

Singly excited τ-amplitude equation

$$
\begin{gathered}
f^a_c {t_1}^c_i + f^k_c {t_2}^{ac}_{ik} + {t_1}^c_k u^{ak}_{ic} + \frac{1}{2}{t_2}^{cb}_{ik} u^{ak}_{cb} - f^k_i {t_1}^a_k - \frac{1}{2}{t_2}^{ac}_{kl} u^{kl}_{ic} + {t_1}^c_k {t_1}^a_l u^{kl}_{ic} + {t_1}^c_k {t_2}^{ab}_{il} u^{kl}_{cb} \\
-f^k_c {t_1}^c_i {t_1}^a_k - {t_1}^c_k {t_1}^b_i u^{ak}_{cb} - \frac{1}{2}{t_1}^a_k {t_2}^{cb}_{il} u^{kl}_{cb} - \frac{1}{2}{t_1}^c_i {t_2}^{ab}_{kl} u^{kl}_{cb} - {t_1}^c_k {t_1}^b_i {t_1}^a_l u^{kl}_{cb} + f^a_i = 0
\end{gathered}
$$

Doubly excited τ-amplitude equation

$$
\begin{gathered}
\frac{1}{2}{t_2}^{AB}_{ij} u^{ij}_{IJ} + \frac{1}{2}{t_2}^{ab}_{IJ} u^{AB}_{ab} + f^i_I {t_2}^{AB}_{Ji} P(IJ) + {t_1}^A_i {t_1}^B_j u^{ij}_{IJ} + {t_1}^A_i u^{Bi}_{IJ} P(AB) + {t_1}^a_I {t_1}^b_J u^{AB}_{ab} \\
-f^A_a {t_2}^{Ba}_{IJ} P(AB) - {t_1}^a_I u^{AB}_{Ja} P(IJ) + \frac{1}{4}{t_2}^{ab}_{IJ} {t_2}^{AB}_{ij} u^{ij}_{ab} + f^i_a {t_1}^A_i {t_2}^{Ba}_{IJ} P(AB) + f^i_a {t_1}^a_I {t_2}^{AB}_{Ji} P(IJ) \\
+{t_1}^a_i {t_2}^{AB}_{Ij} u^{ij}_{Ja} P(IJ) + {t_2}^{Aa}_{Ii} {t_2}^{Bb}_{Jj} u^{ij}_{ab} P(AB) + {t_2}^{Aa}_{Ii} u^{Bi}_{Ja} P(AB)P(IJ) + \frac{1}{2}{t_1}^A_i {t_1}^B_j {t_2}^{ab}_{IJ} u^{ij}_{ab} \\
+\frac{1}{2}{t_1}^A_i {t_2}^{ab}_{IJ} u^{Bi}_{ab} P(AB) + \frac{1}{2}{t_1}^a_I {t_1}^b_J {t_2}^{AB}_{ij} u^{ij}_{ab} + \frac{1}{2}{t_2}^{ab}_{Ji} {t_2}^{AB}_{Ij} u^{ij}_{ab} P(IJ) - {t_1}^a_i {t_2}^{Ab}_{IJ} u^{Bi}_{ab} P(AB) \\
-\frac{1}{2}{t_1}^a_I {t_2}^{AB}_{ij} u^{ij}_{Ja} P(IJ) - \frac{1}{2}{t_2}^{Aa}_{IJ} {t_2}^{Bb}_{ij} u^{ij}_{ab} P(AB) + {t_1}^a_I {t_1}^b_J {t_1}^A_i {t_1}^B_j u^{ij}_{ab} \\
+{t_1}^a_I {t_1}^b_J {t_1}^A_i u^{Bi}_{ab} P(AB) + {t_1}^A_i {t_2}^{Ba}_{Ij} u^{ij}_{Ja} P(AB)P(IJ) + {t_1}^a_i {t_1}^A_j {t_2}^{Bb}_{IJ} u^{ij}_{ab} P(AB) \\
+{t_1}^a_i {t_1}^b_I {t_2}^{AB}_{Jj} u^{ij}_{ab} P(IJ) - {t_1}^a_I {t_1}^A_i {t_1}^B_j u^{ij}_{Ja} P(IJ) - {t_1}^a_I {t_1}^A_i u^{Bi}_{Ja} P(AB)P(IJ) \\
-{t_1}^a_I {t_2}^{Ab}_{Ji} u^{Bi}_{ab} P(AB)P(IJ) - {t_1}^a_I {t_1}^A_i {t_2}^{Bb}_{Jj} u^{ij}_{ab} P(AB)P(IJ) + u^{AB}_{IJ} = 0
\end{gathered}
$$

Single-excited λ-amplitude equation

$$
\begin{gathered}
f^a_A {\lambda_1}^I_a + {\lambda_1}^i_a u^{Ia}_{Ai} + {t_1}^a_i u^{Ii}_{Aa} + \frac{1}{2}{\lambda_2}^{Ii}_{ab} u^{ab}_{Ai} - f^I_i {\lambda_1}^i_A - \frac{1}{2}{\lambda_2}^{ij}_{Aa} u^{Ia}_{ij} \\
+{\lambda_1}^I_a {t_1}^b_i u^{ai}_{Ab} + {\lambda_1}^i_A {t_1}^a_j u^{Ij}_{ai} + {\lambda_1}^i_a {t_1}^b_i u^{Ia}_{Ab} + {\lambda_1}^i_a {t_2}^{ab}_{ij} u^{Ij}_{Ab} + {\lambda_2}^{Ii}_{ab} {t_1}^a_j u^{bj}_{Ai} \\
+\frac{1}{2}{\lambda_2}^{Ii}_{ab} {t_1}^c_i u^{ab}_{Ac} + \frac{1}{2}{\lambda_2}^{ij}_{Aa} {t_1}^a_k u^{Ik}_{ij} + \frac{1}{2}{\lambda_2}^{ij}_{ab} {t_2}^{ac}_{ij} u^{Ib}_{Ac} - f^I_a {\lambda_1}^i_A {t_1}^a_i \\
-f^i_A {\lambda_1}^I_a {t_1}^a_i - {\lambda_1}^i_a {t_1}^a_j u^{Ij}_{Ai} - {\lambda_2}^{Ii}_{ab} {t_2}^{ac}_{ij} u^{bj}_{Ac} - {\lambda_2}^{ij}_{Aa} {t_1}^b_i u^{Ia}_{bj} \\
-{\lambda_2}^{ij}_{Aa} {t_2}^{ab}_{ik} u^{Ik}_{bj} - \frac{1}{2}f^I_a {\lambda_2}^{ij}_{Ab} {t_2}^{ab}_{ij} - \frac{1}{2}f^i_A {\lambda_2}^{Ij}_{ab} {t_2}^{ab}_{ij} - \frac{1}{2}{\lambda_1}^I_a {t_2}^{ab}_{ij} u^{ij}_{Ab} \\
-\frac{1}{2}{\lambda_1}^i_A {t_2}^{ab}_{ij} u^{Ij}_{ab} - \frac{1}{2}{\lambda_2}^{ij}_{ab} {t_2}^{ab}_{ik} u^{Ik}_{Aj} - \frac{1}{4}{\lambda_2}^{ij}_{Aa} {t_2}^{bc}_{ij} u^{Ia}_{bc} + \frac{1}{4}{\lambda_2}^{Ii}_{ab} {t_2}^{ab}_{jk} u^{jk}_{Ai} \\
+{\lambda_2}^{Ii}_{ab} {t_1}^a_j {t_1}^c_i u^{bj}_{Ac} + {\lambda_2}^{ij}_{Aa} {t_1}^a_k {t_1}^b_i u^{Ik}_{bj} + \frac{1}{2}{\lambda_2}^{ij}_{Aa} {t_1}^b_j {t_1}^c_i u^{Ia}_{bc}
\end{gathered}
$$

$$
\begin{aligned}
&+\frac{1}{2}{\lambda_2}^{ij}_{ab}{t_1}^{a}_{k}{t_2}^{bc}_{ij}u^{Ik}_{Ac}+\frac{1}{2}{\lambda_2}^{ij}_{ab}{t_1}^{c}_{i}{t_2}^{ab}_{jk}u^{Ik}_{Ac}-{\lambda_1}^{I}_{a}{t_1}^{a}_{i}{t_1}^{b}_{j}u^{ij}_{Ab}\\
&-{\lambda_1}^{i}_{A}{t_1}^{a}_{i}{t_1}^{b}_{j}u^{Ij}_{ab}-{\lambda_1}^{i}_{a}{t_1}^{a}_{j}{t_1}^{b}_{i}u^{Ij}_{Ab}-{\lambda_2}^{Ii}_{ab}{t_1}^{a}_{j}{t_2}^{bc}_{ik}u^{jk}_{Ac}\\
&-{\lambda_2}^{ij}_{Aa}{t_1}^{b}_{i}{t_2}^{ac}_{jk}u^{Ik}_{bc}-\frac{1}{2}{\lambda_2}^{Ii}_{ab}{t_1}^{a}_{k}{t_1}^{b}_{j}u^{jk}_{Ai}-\frac{1}{2}{\lambda_2}^{Ii}_{ab}{t_1}^{c}_{j}{t_2}^{ab}_{ik}u^{jk}_{Ac}\\
&-\frac{1}{2}{\lambda_2}^{ij}_{Aa}{t_1}^{b}_{k}{t_2}^{ac}_{ij}u^{Ik}_{bc}+\frac{1}{4}{\lambda_2}^{Ii}_{ab}{t_1}^{c}_{i}{t_2}^{ab}_{jk}u^{jk}_{Ac}+\frac{1}{4}{\lambda_2}^{ij}_{Aa}{t_1}^{a}_{k}{t_2}^{bc}_{ij}u^{Ik}_{bc}\\
&-\frac{1}{2}{\lambda_2}^{Ii}_{ab}{t_1}^{a}_{k}{t_1}^{b}_{j}{t_1}^{c}_{i}u^{jk}_{Ac}-\frac{1}{2}{\lambda_2}^{ij}_{Aa}{t_1}^{a}_{k}{t_1}^{b}_{j}{t_1}^{c}_{i}u^{Ik}_{bc}+f^{I}_{A}=0
\end{aligned}
$$

Doubly excited λ-amplitude equation

$$
\begin{aligned}
&+\frac{1}{2}{\lambda_2}^{IJ}_{ab}u^{ab}_{AB}+\frac{1}{2}{\lambda_2}^{ij}_{AB}u^{IJ}_{ij}+f^{I}_{i}{\lambda_2}^{Ji}_{AB}P(IJ)+{\lambda_1}^{i}_{A}u^{IJ}_{Bi}P(AB)+{\lambda_2}^{IJ}_{ab}{t_1}^{a}_{i}u^{bi}_{AB}+{\lambda_2}^{ij}_{AB}{t_1}^{a}_{i}u^{IJ}_{aj}\\
&-f^{a}_{A}{\lambda_2}^{IJ}_{Ba}P(AB)-{\lambda_1}^{I}_{a}u^{Ja}_{AB}P(IJ)+\frac{1}{4}{\lambda_2}^{IJ}_{ab}{t_2}^{ab}_{ij}u^{ij}_{AB}+\frac{1}{4}{\lambda_2}^{ij}_{AB}{t_2}^{ab}_{ij}u^{IJ}_{ab}+f^{I}_{A}{\lambda_1}^{J}_{B}P(AB)P(IJ)\\
&+f^{I}_{a}{\lambda_2}^{Ji}_{AB}{t_1}^{a}_{i}P(IJ)+f^{i}_{A}{\lambda_2}^{IJ}_{Ba}{t_1}^{a}_{i}P(AB)+{\lambda_1}^{I}_{a}{t_1}^{a}_{i}u^{Ji}_{AB}P(IJ)+{\lambda_1}^{i}_{A}{t_1}^{a}_{i}u^{IJ}_{Ba}P(AB)\\
&+{\lambda_2}^{IJ}_{Aa}{t_1}^{b}_{i}u^{ai}_{Bb}P(AB)+{\lambda_2}^{Ii}_{AB}{t_1}^{a}_{j}u^{Jj}_{ai}P(IJ)+{\lambda_2}^{Ii}_{Aa}u^{Ja}_{Bi}P(AB)P(IJ)-\frac{1}{2}{\lambda_2}^{IJ}_{Aa}{t_2}^{ab}_{ij}u^{ij}_{Bb}P(AB)\\
&-\frac{1}{2}{\lambda_2}^{IJ}_{ab}{t_1}^{a}_{j}{t_1}^{b}_{i}u^{ij}_{AB}-\frac{1}{2}{\lambda_2}^{Ii}_{AB}{t_2}^{ab}_{ij}u^{Jj}_{ab}P(IJ)-\frac{1}{2}{\lambda_2}^{Ii}_{ab}{t_2}^{ab}_{ij}u^{Jj}_{AB}P(IJ)\\
&-\frac{1}{2}{\lambda_2}^{ij}_{AB}{t_1}^{a}_{j}{t_1}^{b}_{i}u^{IJ}_{ab}-\frac{1}{2}{\lambda_2}^{ij}_{Aa}{t_2}^{ab}_{ij}u^{IJ}_{Bb}P(AB)+{\lambda_1}^{I}_{A}{t_1}^{a}_{i}u^{Ji}_{Ba}P(AB)P(IJ)\\
&+{\lambda_2}^{Ii}_{Aa}{t_1}^{b}_{i}u^{Ja}_{Bb}P(AB)P(IJ)+{\lambda_2}^{Ii}_{Aa}{t_2}^{ab}_{ij}u^{Jj}_{Bb}P(AB)P(IJ)-{\lambda_2}^{IJ}_{Aa}{t_1}^{a}_{i}{t_1}^{b}_{j}u^{ij}_{Bb}P(AB)\\
&-{\lambda_2}^{Ii}_{AB}{t_1}^{a}_{i}{t_1}^{b}_{j}u^{Jj}_{ab}P(IJ)-{\lambda_2}^{Ii}_{Aa}{t_1}^{a}_{j}u^{Jj}_{Bi}P(AB)P(IJ)\\
&-{\lambda_2}^{Ii}_{Aa}{t_1}^{a}_{j}{t_1}^{b}_{i}u^{Jj}_{Bb}P(AB)P(IJ)+u^{IJ}_{AB}=0
\end{aligned}
$$

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