Slides from FYS-KJM4480/9480 Lectures

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Topics for Week 34

Introduction, systems of identical particles and physical systems

- Monday:
- Presentation of topics to be covered and introduction to Many-Body physics (Lecture notes, Shavitt and Bartlett chapter 1, Raimes chapter 1 and Gross, Runge and Heinonen (GRH) chapter 1).
- Tuesday:
- Discussion of wave functions for fermions and bosons.
- Calculations of expectation values and start defining second quantization
- No exercises this week.

Topics for Week 35

Introduction, systems of identical particles and physical systems

- Monday:
- Second quantization and representation of operators
- Tuesday:
- Second quantization and representation of operators
- Exercises 1 and 2

Lectures and exercise sessions

and syllabus

- Lectures: Monday (10.15-12.00, room 394) and Tuesday (10.15-12.00, room 394)
- Detailed lecture notes, all exercises presented and projects can be found at the homepage of the course.
- Exercises: No allocated time (but a given time can be determined)
- Weekly plans and all other information are on the official webpage.
- Syllabus: Lecture notes, exercises and projects. Shavitt and Bartlett as main text, chapter 1-7 and 9-10. Gross, Runge and Heinonen chapters 1-10 and 14-27or Raimes (chapter 1-3, and 5-11) are also good alternatives.

Quantum Many-particle Methods covered

1. Large-scale diagonalization (Iterative methods, Lanczo's method, dimensionalities 10^{10} states)
2. Coupled cluster theory, favoured method in quantum chemistry, molecular and atomic physics. Applications to ab initio calculations in nuclear physics as well for large nuclei.
3. Perturbative many-body methods
4. Density functional theories/Mean-field theory and Hartree-Fock theory (covered partly also in FYS-MENA4111)
5. Monte-Carlo methods (Only in FYS4411, Computational quantum mechanics)
6. Green's function theories (depending on interest)
7. and other .....

The physics of the system hints at which many-body methods to use.

Plan for the semester

Projects, deadlines (proposed) and oral exam (not determined)

Two projects

1. Weekly exercises count 10% of final mark (no exercises first week)
2. Project 1, counts 25%: hand out October 6, handin October 17 (12pm)
3. Project 2, counts 25%: hand out November 10, handin November 21 (12pm)
4. Final oral exam in December 15-19, counts 40% of final mark

Selected Texts and Many-body theory

- Blaizot and Ripka, *Quantum Theory of Finite systems*, MIT press 1986
- Negele and Orland, *Quantum Many-Particle Systems*, Addison-Wesley, 1987.
- Fetter and Walecka, *Quantum Theory of Many-Particle Systems*, McGraw-Hill, 1971.
- Helgaker, Jørgensen and Olsen, *Molecular Electronic Structure Theory*, Wiley, 2001.
- Mattuck, *Guide to Feynman Diagrams in the Many-Body Problem* , Dover, 1971.
- Dickhoff and Van Neck, *Many-Body Theory Exposed*, World Scientific, 2006.

Definitions

An operator is defined as $\hat{O}$ throughout. Unless otherwise specified the number of particles is always N and d is the dimension of the system. In nuclear physics we normally define the total number of particles to be $A = N + Z$, where N is total number of neutrons and Z the total number of protons. In case of other baryons such isobars Δ or various hyperons such as Λ or Σ, one needs to add their definitions. Hereafter, N is reserved for the total number of particles, unless otherwise specificied.

Definitions

The quantum numbers of a single-particle state in coordinate space are defined by the variable $x = (\mathbf{r}, \sigma)$, where $\mathbf{r} \in \mathbb{R}^d$with $d = 1, 2, 3$ represents the spatial coordinates and σ is the eigenspin of the particle. For fermions with eigenspin $1/2$ this means that

$$x \in \mathbb{R}^d \oplus (\frac{1}{2}),$$

and the integral

$$\int dx = \sum_{\sigma} \int d^d r = \sum_{\sigma} \int d\mathbf{r},$$

and

$$\int d^N x = \int dx_1 \int dx_2 \dots \int dx_N.$$

Definitions

The quantum mechanical wave function of a given state with quantum numbers λ (encompassing all quantum numbers needed to specify the system), ignoring time, is

$$\Psi_\lambda = \Psi_\lambda(x_1, x_2, \dots, x_N),$$

with $x_i = (\mathbf{r}_i, \sigma_i)$ and the projection of σ_i takes the values $\{-1/2, +1/2\}$ for particles with spin $1/2$. We will hereafter always refer to Ψ_λ as the exact wave function, and if the ground state is not degenerate we label it as

$$\Psi_0 = \Psi_0(x_1, x_2, \dots, x_N).$$

Definitions

Since the solution Ψ_λ seldomly can be found in closed form, approximations are sought. In this text we define an approximative wave function or an ansatz to the exact wave function as

$$\Phi_\lambda = \Phi_\lambda(x_1, x_2, \dots, x_N),$$

with

$$\Phi_0 = \Phi_0(x_1, x_2, \dots, x_N),$$

being the ansatz to the ground state.

Definitions

The wave function Ψ_λ is sought in the Hilbert space of either symmetric or anti-symmetric N-body functions, namely

$$\Psi_\lambda \in \mathcal{H}_N := \mathcal{H}_1 \oplus \mathcal{H}_1 \oplus \cdots \oplus \mathcal{H}_1,$$

where the single-particle Hilbert space $\mathcal{H}_1$ is the space of square integrable functions over $\in \mathbb{R}^d \oplus (\sigma)$ resulting in

$$\mathcal{H}_1 := L^2(\mathbb{R}^d \oplus (\sigma)).$$

Definitions

Our Hamiltonian is invariant under the permutation (interchange) of two particles. Since we deal with fermions however, the total wave function is antisymmetric. Let $\hat{P}$ be an operator which interchanges two particles. Due to the symmetries we have ascribed to our Hamiltonian, this operator commutes with the total Hamiltonian,

$$[\hat{H}, \hat{P}] = 0,$$

meaning that $\Psi_\lambda(x_1, x_2, \ldots, x_N)$ is an eigenfunction of $\hat{P}$ as well, that is

$$\hat{P}_{ij}\Psi_\lambda(x_1, x_2, \ldots, x_i, \ldots, x_j, \ldots, x_N) = \beta\Psi_\lambda(x_1, x_2, \ldots, x_j, \ldots, x_i, \ldots, x_N),$$

where β is the eigenvalue of $\hat{P}$. We have introduced the suffix *ij* in order to indicate that we permute particles *i* and *j*. The Pauli principle tells us that the total wave function for a system of fermions has to be antisymmetric, resulting in the eigenvalue $\beta = -1$.

Definitions and notations

The Schrödinger equation reads

$$\hat{H}(x_1, x_2, \ldots, x_N)\Psi_\lambda(x_1, x_2, \ldots, x_N) = E_\lambda \Psi_\lambda(x_1, x_2, \ldots, x_N), \tag{2.0.1}$$

where the vector x_i represents the coordinates (spatial and spin) of particle i, λ stands for all the quantum numbers needed to classify a given N-particle state and Ψ_λ is the pertaining eigenfunction. Throughout this course, Ψ refers to the exact eigenfunction, unless otherwise stated.

Definitions and notations

We write the Hamilton operator, or Hamiltonian, in a generic way

$$\hat{H} = \hat{T} + \hat{V}$$

where $\hat{T}$ represents the kinetic energy of the system

$$\hat{T} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m_i} \nabla_{\mathbf{i}}{}^2 \right) = \sum_{i=1}^{N} t(x_i)$$

while the operator $\hat{V}$ for the potential energy is given by

$$\hat{V} = \sum_{i=1}^{N} \hat{u}_{\mathrm{ext}}(x_i) + \sum_{ji=1}^{N} v(x_i, x_j) + \sum_{ijk=1}^{N} v(x_i, x_j, x_k) + \ldots \tag{2.0.2}$$

Hereafter we use natural units, viz. $\hbar = c = e = 1$, with e the elementary charge and c the speed of light. This means that momenta and masses have dimension energy.

Definitions and notations

If one does quantum chemistry, after having introduced the Born-Oppenheimer approximation which effectively freezes out the nucleonic degrees of freedom, the Hamiltonian for $N = n_e$ electrons takes the following form

$$\hat{H} = \sum_{i=1}^{n_e} t(x_i) - \sum_{i=1}^{n_e} k\frac{Z}{r_i} + \sum_{i<j}^{n_e} \frac{k}{r_{ij}},$$

with $k = 1.44$ eVnm

Definitions and notations

We can rewrite this as

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{n_e} \hat{h}_0(x_i) + \sum_{i<j=1}^{n_e} \frac{1}{r_{ij}}, \tag{2.0.3}$$

where we have defined $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and

$$\hat{h}_0(x_i) = \hat{t}(x_i) - \frac{Z}{x_i}. \tag{2.0.4}$$

The first term of eq. (2.0.3), H_0, is the sum of the N *one-body* Hamiltonians $\hat{h}_0$. Each individual Hamiltonian $\hat{h}_0$ contains the kinetic energy operator of an electron and its potential energy due to the attraction of the nucleus. The second term, H_I, is the sum of the $n_e(n_e-1)/2$ two-body interactions between each pair of electrons. Note that the double sum carries a restriction $i<j$.

Definitions and notations

The potential energy term due to the attraction of the nucleus defines the onebody field $u_i = u_{\rm ext}(x_i)$ of Eq. (2.0.2). We have moved this term into the $\hat{H}_0$ part of the Hamiltonian, instead of keeping it in $\hat{V}$ as in Eq. (2.0.2). The reason is that we will hereafter treat $\hat{H}_0$ as our non-interacting Hamiltonian. For a many-body wavefunction Φ_λ defined by an appropriate single-particle basis, we may solve exactly the non-interacting eigenvalue problem

$$\hat{H}_0\Phi_\lambda = w_\lambda\Phi_\lambda,$$

with w_λ being the non-interacting energy. This energy is defined by the sum over single-particle energies to be defined below. For atoms the single-particle energies could be the hydrogen-like single-particle energies corrected for the charge Z. For nuclei and quantum dots, these energies could be given by the harmonic oscillator in three and two dimensions, respectively.

Definitions and notations

We will assume that the interacting part of the Hamiltonian can be approximated by a two-body interaction. This means that our Hamiltonian is written as

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{N} \hat{h}_0(x_i) + \sum_{i<j=1}^{N} V(r_{ij}), \tag{2.0.5}$$

with

$$H_0 = \sum_{i=1}^{N} \hat{h}_0(x_i) = \sum_{i=1}^{N} \left(\hat{t}(x_i) + \hat{u}_{\mathrm{ext}}(x_i)\right). \tag{2.0.6}$$

The onebody part $u_{\mathrm{ext}}(x_i)$ is normally approximated by a harmonic oscillator potential or the Coulomb interaction an electron feels from the nucleus. However, other potentials are fully possible, such as one derived from the self-consistent solution of the Hartree-Fock equations.

Definitions and notations

Our Hamiltonian is invariant under the permutation (interchange) of two particles. Since we deal with fermions however, the total wave function is antisymmetric. Let $\hat{P}$ be an operator which interchanges two particles. Due to the symmetries we have ascribed to our Hamiltonian, this operator commutes with the total Hamiltonian,

$$[\hat{H}, \hat{P}] = 0,$$

meaning that $\Psi_\lambda(x_1, x_2, \ldots, x_N)$ is an eigenfunction of $\hat{P}$ as well, that is

$$\hat{P}_{ij}\Psi_\lambda(x_1, x_2, \ldots, x_i, \ldots, x_j, \ldots, x_N) = \beta\Psi_\lambda(x_1, x_2, \ldots, x_i, \ldots, x_j, \ldots, x_N),$$

where β is the eigenvalue of $\hat{P}$. We have introduced the suffix ij in order to indicate that we permute particles i and j. The Pauli principle tells us that the total wave function for a system of fermions has to be antisymmetric, resulting in the eigenvalue $\beta = -1$.

Definitions and notations

In our case we assume that we can approximate the exact eigenfunction with a Slater determinant

$$\Phi(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \sigma) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_\alpha(x_1) & \psi_\alpha(x_2) & \dots & \dots & \psi_\alpha(x_N) \\ \psi_\beta(x_1) & \psi_\beta(x_2) & \dots & \dots & \psi_\beta(x_N) \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\sigma(x_1) & \psi_\sigma(x_2) & \dots & \dots & \psi_\gamma(x_N) \end{vmatrix}, \tag{2.0.7}$$

where x_i stand for the coordinates and spin values of a particle *i* and $\alpha, \beta, \dots, \gamma$ are quantum numbers needed to describe remaining quantum numbers.

Definitions and notations

The single-particle function $\psi_\alpha(x_i)$ are eigenfunctions of the onebody Hamiltonian h_i, that is

$$\hat{h}_0(x_i) = \hat{t}(x_i) + \hat{u}_{\mathrm{ext}}(x_i),$$

with eigenvalues

$$\hat{h}_0(x_i)\psi_\alpha(x_i) = \left(\hat{t}(x_i) + \hat{u}_{\mathrm{ext}}(x_i)\right)\psi_\alpha(x_i) = \varepsilon_\alpha\psi_\alpha(x_i).$$

The energies ε_α are the so-called non-interacting single-particle energies, or unperturbed energies. The total energy is in this case the sum over all single-particle energies, if no two-body or more complicated many-body interactions are present.

Definitions and notations

Let us denote the ground state energy by E_0. According to the variational principle we have

$$E_0 \leq E[\Phi] = \int \Phi^* \hat{H} \Phi d\tau$$

where Φ is a trial function which we assume to be normalized

$$\int \Phi^* \Phi d\tau = 1,$$

where we have used the shorthand $d\tau = d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N$.

Definitions and notations

In the Hartree-Fock method the trial function is the Slater determinant of Eq. (2.0.7) which can be rewritten as

$$\Phi(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \nu) = \frac{1}{\sqrt{N!}} \sum_P (-)^P \hat{P} \psi_\alpha(x_1) \psi_\beta(x_2) \dots \psi_\nu(x_N) = \sqrt{N!} \mathcal{A} \Phi_H, \tag{2.0.8}$$

where we have introduced the antisymmetrization operator $\mathcal{A}$ defined by the summation over all possible permutations of two particles.

Definitions and notations

It is defined as

$$\mathcal{A} = \frac{1}{N!}\sum_{p}(-)^p\hat{P}, \tag{2.0.9}$$

with p standing for the number of permutations. We have introduced for later use the so-called Hartree-function, defined by the simple product of all possible single-particle functions

$$\Phi_H(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \nu) = \psi_\alpha(x_1)\psi_\beta(x_2)\dots\psi_\nu(x_N).$$

Definitions and notations

Both $\hat{H}_0$ and $\hat{\hat{H}_I}$ are invariant under all possible permutations of any two particles and hence commute with $\mathcal{A}$

$$[H_0, \mathcal{A}] = [H_I, \mathcal{A}] = 0. \tag{2.0.10}$$

Furthermore, $\mathcal{A}$ satisfies

$$\mathcal{A}^2 = \mathcal{A}, \tag{2.0.11}$$

since every permutation of the Slater determinant reproduces it.

Definitions and notations

The expectation value of $\hat{H}_0$

$$\int \Phi^* \hat{H}_0 \Phi d\tau = N! \int \Phi_H^* \mathcal{A} \hat{H}_0 \mathcal{A} \Phi_H d\tau$$

is readily reduced to

$$\int \Phi^* \hat{H}_0 \Phi d\tau = N! \int \Phi_H^* \hat{H}_0 \mathcal{A} \Phi_H d\tau,$$

where we have used eqs. (2.0.10) and (2.0.11). The next step is to replace the antisymmetrization operator by its definition Eq. (2.0.8) and to replace $\hat{H}_0$ with the sum of one-body operators

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{i=1}^{N} \sum_{p} (-)^p \int \Phi_H^* \hat{h}_0 \hat{P} \Phi_H d\tau.$$

Definitions and notations

The integral vanishes if two or more particles are permuted in only one of the Hartree-functions Φ_H because the individual single-particle wave functions are orthogonal. We obtain then

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{i=1}^{N} \int \Phi_H^* \hat{h}_0 \Phi_H d\tau.$$

Orthogonality of the single-particle functions allows us to further simplify the integral, and we arrive at the following expression for the expectation values of the sum of one-body Hamiltonians

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^{N} \int \psi_\mu^*(\mathbf{r}) \hat{h}_0 \psi_\mu(\mathbf{r}) d\mathbf{r}. \tag{2.0.12}$$

Definitions and notations

We introduce the following shorthand for the above integral

$$\langle\mu|\hat{h}_0|\mu\rangle = \int \psi_\mu^*(\mathbf{r})\hat{h}_0\psi_\mu(\mathbf{r}),$$

and rewrite Eq. (2.0.12) as

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^{N} \langle\mu|\hat{h}_0|\mu\rangle. \tag{2.0.13}$$

Definitions and notations

The expectation value of the two-body part of the Hamiltonian is obtained in a similar manner. We have

$$\int \Phi^* \hat{H}_I \Phi d\tau = N! \int \Phi_H^* \mathcal{A} \hat{H}_I \mathcal{A} \Phi_H d\tau,$$

which reduces to

$$\int \Phi^* \hat{H}_I \Phi d\tau = \sum_{i \le j=1}^{N} \sum_{p} (-)^p \int \Phi_H^* V(r_{ij}) \hat{P} \Phi_H d\tau,$$

by following the same arguments as for the one-body Hamiltonian.

Definitions and notations

Because of the dependence on the inter-particle distance r_{ij}, permutations of any two particles no longer vanish, and we get

$$\int \Phi^* \hat{H}_I \Phi d\tau = \sum_{i<j=1}^{N} \int \Phi_H^* V(r_{ij})(1 - P_{ij})\Phi_H d\tau.$$

where P_{ij} is the permutation operator that interchanges particle i and particle j. Again we use the assumption that the single-particle wave functions are orthogonal.

Definitions and notations

We obtain

$$
\begin{aligned}
\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N} \Big[& \int \psi_\mu^*(x_i)\psi_\nu^*(x_j)V(r_{ij})\psi_\mu(x_i)\psi_\nu(x_j)dx_ix_j \\
& - \int \psi_\mu^*(x_i)\psi_\nu^*(x_j)V(r_{ij})\psi_\nu(x_i)\psi_\mu(x_j)dx_ix_j \Big].
\end{aligned}
\tag{2.0.14}
$$

The first term is the so-called direct term. It is frequently also called the Hartree term, while the second is due to the Pauli principle and is called the exchange term or just the Fock term. The factor $1/2$ is introduced because we now run over all pairs twice.

Definitions and notations

The last equation allows us to introduce some further definitions. The single-particle wave functions $\psi_\mu(\mathbf{r})$, defined by the quantum numbers μ and $\mathbf{r}$ (recall that $\mathbf{r}$ also includes spin degree) are defined as the overlap

$$\psi_\alpha(x) = \langle x|\alpha\rangle.$$

Definitions and notations

We introduce the following shorthands for the above two integrals

$$\langle \mu\nu|V|\mu\nu\rangle = \int \psi_\mu^*(x_i)\psi_\nu^*(x_j)V(r_{ij})\psi_\mu(x_i)\psi_\nu(x_j)dx_ix_j,$$

and

$$\langle \mu\nu|V|\nu\mu\rangle = \int \psi_\mu^*(x_i)\psi_\nu^*(x_j)V(r_{ij})\psi_\nu(x_i)\psi_\mu(x_j)dx_ix_j.$$

Definitions and notations

The direct and exchange matrix elements can be brought together if we define the antisymmetrized matrix element

$$\langle \mu\nu|V|\mu\nu\rangle_{\mathrm{AS}} = \langle \mu\nu|V|\mu\nu\rangle - \langle \mu\nu|V|\nu\mu\rangle,$$

or for a general matrix element

$$\langle \mu\nu|V|\sigma\tau\rangle_{\mathrm{AS}} = \langle \mu\nu|V|\sigma\tau\rangle - \langle \mu\nu|V|\tau\sigma\rangle.$$

It has the symmetry property

$$\langle \mu\nu|V|\sigma\tau\rangle_{\mathrm{AS}} = -\langle \mu\nu|V|\tau\sigma\rangle_{\mathrm{AS}} = -\langle \nu\mu|V|\sigma\tau\rangle_{\mathrm{AS}}.$$

Definitions and notations

The antisymmetric matrix element is also hermitian, implying

$$\langle \mu\nu|V|\sigma\tau\rangle_{\mathrm{AS}} = \langle \sigma\tau|V|\mu\nu\rangle_{\mathrm{AS}}.$$

With these notations we rewrite Eq. (2.0.14) as

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\langle \mu\nu|V|\mu\nu\rangle_{\mathrm{AS}}. \tag{2.0.15}$$

Definitions and notations

Combining Eqs. (2.0.13) and (7.0.2) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^{N} \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \langle \mu\nu | V | \mu\nu \rangle_{\mathrm{AS}}. \tag{2.0.16}$$

which we will use as our starting point for the Hartree-Fock calculations later in this course.

Second quantization

We introduce the time-independent operators $a^\dagger_\alpha$ and a_α which create and annihilate, respectively, a particle in the single-particle state φ_α. We define the fermion creation operator $a^\dagger_\alpha$

$$a^\dagger_\alpha|0\rangle \equiv |\alpha\rangle, \tag{2.0.17}$$

and

$$a^\dagger_\alpha|\alpha_1 \dots \alpha_n\rangle_{\mathrm{AS}} \equiv |\alpha\alpha_1 \dots \alpha_n\rangle_{\mathrm{AS}} \tag{2.0.18}$$

Second quantization

In Eq. (2.0.17) the operator $a_\alpha^\dagger$ acts on the vacuum state $|0\rangle$, which does not contain any particles. Alternatively, we could define a closed-shell nucleus or atom as our new vacuum, but then we need to introduce the particle-hole formalism, see the discussion to come.
In Eq. (2.0.18) $a_\alpha^\dagger$ acts on an antisymmetric n-particle state and creates an antisymmetric $(n+1)$-particle state, where the one-body state φ_α is occupied, under the condition that $\alpha \neq \alpha_1, \alpha_2, \dots, \alpha_n$. It follows that we can express an antisymmetric state as the product of the creation operators acting on the vacuum state.

$$|\alpha_1 \dots \alpha_n\rangle_{\mathrm{AS}} = a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger \dots a_{\alpha_n}^\dagger |0\rangle \tag{2.0.19}$$

Second quantization

It is easy to derive the commutation and anticommutation rules for the fermionic creation operators $a_\alpha^\dagger$. Using the antisymmetry of the states (2.0.19)

$$|\alpha_1 \ldots \alpha_i \ldots \alpha_k \ldots \alpha_n\rangle_{\mathrm{AS}} = -|\alpha_1 \ldots \alpha_k \ldots \alpha_i \ldots \alpha_n\rangle_{\mathrm{AS}} \tag{2.0.20}$$

we obtain

$$a_{\alpha_i}^\dagger a_{\alpha_k}^\dagger = -a_{\alpha_k}^\dagger a_{\alpha_i}^\dagger \tag{2.0.21}$$

Second quantization

Using the Pauli principle

$$|\alpha_1 \ldots \alpha_i \ldots \alpha_i \ldots \alpha_n\rangle_{\mathrm{AS}} = 0 \tag{2.0.22}$$

it follows that

$$a^\dagger_{\alpha_i} a^\dagger_{\alpha_i} = 0. \tag{2.0.23}$$

If we combine Eqs. (2.0.21) and (2.0.23), we obtain the well-known anti-commutation rule

$$a^\dagger_\alpha a^\dagger_\beta + a^\dagger_\beta a^\dagger_\alpha \equiv \{a^\dagger_\alpha, a^\dagger_\beta\} = 0 \tag{2.0.24}$$

Second quantization

The hermitian conjugate of $a_\alpha^\dagger$ is

$$a_\alpha = (a_\alpha^\dagger)^\dagger \tag{2.0.25}$$

If we take the hermitian conjugate of Eq. (2.0.24), we arrive at

$$\{a_\alpha, a_\beta\} = 0 \tag{2.0.26}$$

Second quantization

What is the physical interpretation of the operator a_α and what is the effect of a_α on a given state $|\alpha_1\alpha_2\ldots\alpha_n\rangle_{\mathrm{AS}}$? Consider the following matrix element

$$\langle\alpha_1\alpha_2\ldots\alpha_n|a_\alpha|\alpha_1'\alpha_2'\ldots\alpha_m'\rangle \tag{2.0.27}$$

where both sides are antisymmetric. We distinguish between two cases

1. $\alpha\in\{\alpha_i\}$. Using the Pauli principle of Eq. (2.0.22) it follows

$$\langle\alpha_1\alpha_2\ldots\alpha_n|a_\alpha = 0 \tag{2.0.28}$$

2. $\alpha\notin\{\alpha_i\}$. It follows that an hermitian conjugation

$$\langle\alpha_1\alpha_2\ldots\alpha_n|a_\alpha = \langle\alpha\alpha_1\alpha_2\ldots\alpha_n| \tag{2.0.29}$$

Second quantization

Eq. (2.0.29) holds for case (1) since the lefthand side is zero due to the Pauli principle. We write Eq. (2.0.27) as

$$\langle \alpha_1 \alpha_2 \ldots \alpha_n | a_\alpha | \alpha'_1 \alpha'_2 \ldots \alpha'_m \rangle = \langle \alpha_1 \alpha_2 \ldots \alpha_n | \, \alpha \alpha'_1 \alpha'_2 \ldots \alpha'_m \tag{2.0.30}$$

Here we must have $m = n + 1$ if Eq. (2.0.30) has to be trivially different from zero. Using Eqs. (2.0.28) and (2.0.28) we arrive at

$$\langle \alpha_1 \alpha_2 \ldots \alpha_n | a_\alpha | \alpha'_1 \alpha'_2 \ldots \alpha'_{n+1} \rangle = \left\{ \begin{array}{cc} 0 & \alpha \in \{\alpha_i\} \vee \{\alpha\alpha_i\} \neq \{\alpha'_i\} \\ \pm 1 & \alpha \notin \{\alpha_i\} \cup \{\alpha\alpha_i\} = \{\alpha'_i\} \end{array} \right\} \tag{2.0.31}$$

Second quantization

For the last case, the minus and plus signs apply when the sequence $\alpha, \alpha_1, \alpha_2, \dots, \alpha_n$ and $\alpha'_1, \alpha'_2, \dots, \alpha'_{n+1}$ are related to each other via even and odd permutations. If we assume that $\alpha \notin \{\alpha_i\}$ we have from Eq. (2.0.31)

$$\langle \alpha_1 \alpha_2 \dots \alpha_n | a_\alpha | \alpha'_1 \alpha'_2 \dots \alpha'_{n+1} \rangle = 0 \tag{2.0.32}$$

when $\alpha \in \{\alpha'_i\}$. If $\alpha \notin \{\alpha'_i\}$, we obtain

$$a_\alpha \underbrace{|\alpha'_1 \alpha'_2 \dots \alpha'_{n+1}\rangle}_{\neq \alpha} = 0 \tag{2.0.33}$$

and in particular

$$a_\alpha |0\rangle = 0 \tag{2.0.34}$$

Second quantization

If $\{\alpha\alpha_i\} = \{\alpha'_i\}$, performing the right permutations, the sequence $\alpha, \alpha_1, \alpha_2, \ldots, \alpha_n$ is identical with the sequence $\alpha'_1, \alpha'_2, \ldots, \alpha'_{n+1}$. This results in

$$\langle\alpha_1\alpha_2\ldots\alpha_n|a_\alpha|\alpha\alpha_1\alpha_2\ldots\alpha_n\rangle = 1 \tag{2.0.35}$$

and thus

$$a_\alpha|\alpha\alpha_1\alpha_2\ldots\alpha_n\rangle = |\alpha_1\alpha_2\ldots\alpha_n\rangle \tag{2.0.36}$$

Second quantization

The action of the operator a_α from the left on a state vector is to to remove one particle in the state α. If the state vector does not contain the single-particle state α, the outcome of the operation is zero. The operator a_α is normally called for a destruction or annihilation operator.

The next step is to establish the commutator algebra of $a_\alpha^\dagger$ and a_β.

Topics for Week 36

Second quantization

- Monday:
- Summary from last week
- Second quantization and operators, two-body operator with examples
- Tuesday:
- No lecture Tuesday due to Gustav Baardsen's PhD defense
- Exercises 3 and 4

The material is taken from chapter 3.1-3.6 and 4.1-4.4 of Shavitt and Bartlett.

Second quantization

The action of the anti-commutator $\{a_\alpha^\dagger, a_\alpha\}$ on a given n-particle state is

$$\begin{aligned}
a_\alpha^\dagger a_\alpha \underbrace{|\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} &= 0 \\
a_\alpha a_\alpha^\dagger \underbrace{|\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} &= a_\alpha \underbrace{|\alpha\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} = \underbrace{|\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha}
\end{aligned} \tag{3.0.1}$$

if the single-particle state α is not contained in the state.

Second quantization

If it is present we arrive at

$$\begin{aligned} a^\dagger_\alpha a_\alpha|\alpha_1\alpha_2\dots\alpha_k\alpha\alpha_{k+1}\dots\alpha_{n-1}\rangle &= a^\dagger_\alpha a_\alpha(-1)^k|\alpha\alpha_1\alpha_2\dots\alpha_{n-1}\rangle \\ = (-1)^k|\alpha\alpha_1\alpha_2\dots\alpha_{n-1}\rangle &= |\alpha_1\alpha_2\dots\alpha_k\alpha\alpha_{k+1}\dots\alpha_{n-1}\rangle \\ a_\alpha a^\dagger_\alpha|\alpha_1\alpha_2\dots\alpha_k\alpha\alpha_{k+1}\dots\alpha_{n-1}\rangle &= 0 \end{aligned} \tag{3.0.2}$$

From Eqs. (3.0.1) and (3.0.2) we arrive at

$$\{a^\dagger_\alpha, a_\alpha\} = a^\dagger_\alpha a_\alpha + a_\alpha a^\dagger_\alpha = 1 \tag{3.0.3}$$

Second quantization

The action of $a^\dagger_\alpha, a_\beta$, with $\alpha \neq \beta$ on a given state yields three possibilities. The first case is a state vector which contains both α and β, then either α or β and finally none of them.

Second quantization

The first case results in

$$
\begin{aligned}
a_\alpha^\dagger a_\beta |\alpha\beta\alpha_1\alpha_2 \ldots \alpha_{n-2}\rangle &= 0 \\
a_\beta a_\alpha^\dagger |\alpha\beta\alpha_1\alpha_2 \ldots \alpha_{n-2}\rangle &= 0
\end{aligned} \tag{3.0.4}
$$

while the second case gives

$$
\begin{aligned}
a_\alpha^\dagger a_\beta |\beta \underbrace{\alpha_1\alpha_2 \ldots \alpha_{n-1}}_{\neq\alpha}\rangle &= |\alpha \underbrace{\alpha_1\alpha_2 \ldots \alpha_{n-1}}_{\neq\alpha}\rangle \\
a_\beta a_\alpha^\dagger |\beta \underbrace{\alpha_1\alpha_2 \ldots \alpha_{n-1}}_{\neq\alpha}\rangle &= a_\beta |\alpha\beta \underbrace{\beta\alpha_1\alpha_2 \ldots \alpha_{n-1}}_{\neq\alpha}\rangle \\
&= -|\alpha \underbrace{\alpha_1\alpha_2 \ldots \alpha_{n-1}}_{\neq\alpha}\rangle
\end{aligned} \tag{3.0.5}
$$

Second quantization

Finally if the state vector does not contain α and β

$$
\begin{aligned}
a_\alpha^\dagger a_\beta |\underbrace{\alpha_1\alpha_2\dots\alpha_n}_{\neq\alpha,\beta}\rangle &= 0 \\
a_\beta a_\alpha^\dagger |\underbrace{\alpha_1\alpha_2\dots\alpha_n}_{\neq\alpha,\beta}\rangle &= a_\beta|\alpha\underbrace{\alpha_1\alpha_2\dots\alpha_n}_{\neq\alpha,\beta}\rangle = 0
\end{aligned}
\tag{3.0.6}
$$

For all three cases we have

$$
\{a_\alpha^\dagger, a_\beta\} = a_\alpha^\dagger a_\beta + a_\beta a_\alpha^\dagger = 0, \quad \alpha \neq \beta \tag{3.0.7}
$$

Second quantization

We can summarize our findings in Eqs. (3.0.3) and (3.0.7) as

$$\{a^\dagger_\alpha, a_\beta\} = \delta_{\alpha\beta} \tag{3.0.8}$$

with $\delta_{\alpha\beta}$ is the Kroenecker δ-symbol.
The properties of the creation and annihilation operators can be summarized as (for fermions)

$$a^\dagger_\alpha|0\rangle \equiv |\alpha\rangle,$$

and

$$a^\dagger_\alpha|\alpha_1 \dots \alpha_n\rangle_{\mathrm{AS}} \equiv |\alpha\alpha_1 \dots \alpha_n\rangle_{\mathrm{AS}}.$$

from which follows

$$|\alpha_1 \dots \alpha_n\rangle_{\mathrm{AS}} = a^\dagger_{\alpha_1} a^\dagger_{\alpha_2} \dots a^\dagger_{\alpha_n}|0\rangle.$$

Second quantization

The hermitian conjugate has the folowing properties

$$a_\alpha = (a_\alpha^\dagger)^\dagger.$$

Finally we found

$$a_\alpha \underbrace{|\alpha'_1\alpha'_2\dots\alpha'_{n+1}\rangle}_{\neq\alpha} = 0, \quad \text{spesielt } a_\alpha|0\rangle = 0,$$

and

$$a_\alpha|\alpha\alpha_1\alpha_2\dots\alpha_n\rangle = |\alpha_1\alpha_2\dots\alpha_n\rangle,$$

and the corresponding commutator algebra

$$\{a_\alpha^\dagger, a_\beta^\dagger\} = \{a_\alpha, a_\beta\} = 0 \qquad \{a_\alpha^\dagger, a_\beta\} = \delta_{\alpha\beta}.$$

Operators in second quantization

A very useful operator is the so-called number-operator. Most physics cases we will study in this text conserve the total number of particles. The number operator is therefore a useful quantity which allows us to test that our many-body formalism conserves the number of particles. In for example (d, p) or (p, d) reactions it is important to be able to describe quantum mechanical states where particles get added or removed. A creation operator $a_\alpha^\dagger$ adds one particle to the single-particle state α of a give many-body state vector, while an annihilation operator a_α removes a particle from a single-particle state α.

Operators in second quantization

Let us consider an operator proportional with $a^\dagger_\alpha a_\beta$ and $\alpha = \beta$. It acts on an n-particle state resulting in

$$a^\dagger_\alpha a_\alpha |\alpha_1 \alpha_2 \dots \alpha_n\rangle = \begin{cases} 0 & \alpha \notin \{\alpha_i\} \\ \\ |\alpha_1 \alpha_2 \dots \alpha_n\rangle & \alpha \in \{\alpha_i\} \end{cases} \tag{3.0.9}$$

Summing over all possible one-particle states we arrive at

$$\left(\sum_\alpha a^\dagger_\alpha a_\alpha \right) |\alpha_1 \alpha_2 \dots \alpha_n\rangle = n |\alpha_1 \alpha_2 \dots \alpha_n\rangle \tag{3.0.10}$$

Operators in second quantization

The operator

$$\hat{N} = \sum_{\alpha} a_{\alpha}^{\dagger} a_{\alpha} \tag{3.0.11}$$

is called the number operator since it counts the number of particles in a give state vector when it acts on the different single-particle states. It acts on one single-particle state at the time and falls therefore under category one-body operators. Next we look at another important one-body operator, namely $\hat{H}_0$ and study its operator form in the occupation number representation.

Operators in second quantization

We want to obtain an expression for a one-body operator which conserves the number of particles. Here we study the one-body operator for the kinetic energy plus an eventual external one-body potential. The action of this operator on a particular n-body state with its pertinent expectation value has already been studied in coordinate space. In coordinate space the operator reads

$$\hat{H}_0 = \sum_i \hat{h}_0(x_i) \tag{3.0.12}$$

and the anti-symmetric n-particle Slater determinant is defined as

$$\Phi(x_1, x_2, \dots, x_n, \alpha_1, \alpha_2, \dots, \alpha_n) = \frac{1}{\sqrt{n!}} \sum_p (-1)^p \psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\dots\psi_{\alpha_n}(x_n). \tag{3.0.13}$$

Operators in second quantization

Defining

$$\hat{h}_0(x_i)\psi_{\alpha_i}(x_i) = \sum_{\alpha'_k} \psi_{\alpha'_k}(x_i)\langle\alpha'_k|\hat{h}_0|\alpha_k\rangle \tag{3.0.14}$$

we can easily evaluate the action of $\hat{H}_0$ on each product of one-particle functions in Slater determinant. From Eqs. (3.0.13) (3.0.14) we obtain the following result without permuting any particle pair

$$\begin{aligned}
& \left(\sum_i \hat{h}_0(x_i)\right)\psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\dots\psi_{\alpha_n}(x_n) \\
= & \sum_{\alpha'_1}\langle\alpha'_1|\hat{h}_0|\alpha_1\rangle\psi_{\alpha'_1}(x_1)\psi_{\alpha_2}(x_2)\dots\psi_{\alpha_n}(x_n) \\
+ & \sum_{\alpha'_2}\langle\alpha'_2|\hat{h}_0|\alpha_2\rangle\psi_{\alpha_1}(x_1)\psi_{\alpha'_2}(x_2)\dots\psi_{\alpha_n}(x_n) \\
+ & \dots \\
+ & \sum_{\alpha'_n}\langle\alpha'_n|\hat{h}_0|\alpha_n\rangle\psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\dots\psi_{\alpha'_n}(x_n)
\end{aligned} \tag{3.0.15}$$

Operators in second quantization

If we interchange the positions of particle 1 and 2 we obtain

$$
\begin{aligned}
& \left(\sum_i \hat{h}_0(x_i)\right) \psi_{\alpha_1}(x_2)\psi_{\alpha_1}(x_2)\dots\psi_{\alpha_n}(x_n) \\
= & \sum_{\alpha_2'} \langle\alpha_2'|\hat{h}_0|\alpha_2\rangle \psi_{\alpha_1}(x_2)\psi_{\alpha_2'}(x_1)\dots\psi_{\alpha_n}(x_n) \\
+ & \sum_{\alpha_1'} \langle\alpha_1'|\hat{h}_0|\alpha_1\rangle \psi_{\alpha_1'}(x_2)\psi_{\alpha_2}(x_1)\dots\psi_{\alpha_n}(x_n) \\
+ & \dots \\
+ & \sum_{\alpha_n'} \langle\alpha_n'|\hat{h}_0|\alpha_n\rangle \psi_{\alpha_1}(x_2)\psi_{\alpha_1}(x_2)\dots\psi_{\alpha_n'}(x_n)
\end{aligned}
\tag{3.0.16}
$$

Operators in second quantization

We can continue by computing all possible permutations. We rewrite also our Slater determinant in its second quantized form and skip the dependence on the quantum numbers x_i. Summing up all contributions and taking care of all phases $(-1)^p$ we arrive at

$$
\begin{aligned}
\hat{H}_0|\alpha_1,\alpha_2,\dots,\alpha_n\rangle &= \sum_{\alpha_1'}\langle\alpha_1'|\hat{h}_0|\alpha_1\rangle|\alpha_1'\alpha_2\dots\alpha_n\rangle \\
&+ \sum_{\alpha_2'}\langle\alpha_2'|\hat{h}_0|\alpha_2\rangle|\alpha_1\alpha_2'\dots\alpha_n\rangle \\
&+ \dots \\
&+ \sum_{\alpha_n'}\langle\alpha_n'|\hat{h}_0|\alpha_n\rangle|\alpha_1\alpha_2\dots\alpha_n'\rangle \qquad (3.0.17)
\end{aligned}
$$

Operators in second quantization

In Eq. (3.0.17) we have expressed the action of the one-body operator of Eq. (3.0.12) on the *n*-body state of Eq. (3.0.13) in its second quantized form. This equation can be further manipulated if we use the properties of the creation and annihilation operator on each primed quantum number, that is

$$|\alpha_1\alpha_2\dots\alpha_k'\dots\alpha_n\rangle = a^\dagger_{\alpha_k'}a_{\alpha_k}|\alpha_1\alpha_2\dots\alpha_k\dots\alpha_n\rangle \tag{3.0.18}$$

Inserting this in the right-hand side of Eq. (3.0.17) results in

$$\begin{aligned}
\hat{H}_0|\alpha_1\alpha_2\dots\alpha_n\rangle &= \sum_{\alpha_1'}\langle\alpha_1'|\hat{h}_0|\alpha_1\rangle a^\dagger_{\alpha_1'}a_{\alpha_1}|\alpha_1\alpha_2\dots\alpha_n\rangle \\
&+ \sum_{\alpha_2'}\langle\alpha_2'|\hat{h}_0|\alpha_2\rangle a^\dagger_{\alpha_2'}a_{\alpha_2}|\alpha_1\alpha_2\dots\alpha_n\rangle \\
&+ \dots \\
&+ \sum_{\alpha_n'}\langle\alpha_n'|\hat{h}_0|\alpha_n\rangle a^\dagger_{\alpha_n'}a_{\alpha_n}|\alpha_1\alpha_2\dots\alpha_n\rangle \\
&= \sum_{\alpha,\beta}\langle\alpha|\hat{h}_0|\beta\rangle a^\dagger_\alpha a_\beta|\alpha_1\alpha_2\dots\alpha_n\rangle
\end{aligned} \tag{3.0.19}$$

Operators in second quantization

In the number occupation representation or second quantization we get the following expression for a one-body operator which conserves the number of particles

$$\hat{H}_0 = \sum_{\alpha\beta} \langle\alpha|\hat{h}_0|\beta\rangle a_\alpha^\dagger a_\beta \tag{3.0.20}$$

Obviously, $\hat{H}_0$ can be replaced by any other one-body operator which preserved the number of particles. The stucture of the operator is therefore not limited to say the kinetic or single-particle energy only.

The opearator $\hat{H}_0$ takes a particle from the single-particle state β to the single-particle state α with a probability for the transition given by the expectation value $\langle\alpha|h|\beta\rangle$.

Operators in second quantization

It is instructive to verify Eq. (3.0.20) by computing the expectation value of $\hat{H}_0$ between two single-particle states

$$\langle\alpha_1|\hat{H}_0|\alpha_2\rangle = \sum_{\alpha\beta}\langle\alpha|\hat{h}_0|\beta\rangle\langle 0|a_{\alpha_1}a^{\dagger}_{\alpha}a_{\beta}a^{\dagger}_{\alpha_2}|0\rangle \tag{3.0.21}$$

Using the commutation relations for the creation and annihilation operators we have

$$a_{\alpha_1}a^{\dagger}_{\alpha}a_{\beta}a^{\dagger}_{\alpha_2} = (\delta_{\alpha\alpha_1} - a^{\dagger}_{\alpha}a_{\alpha_1})(\delta_{\beta\alpha_2} - a^{\dagger}_{\alpha_2}a_{\beta}), \tag{3.0.22}$$

which results in

$$\langle 0|a_{\alpha_1}a^{\dagger}_{\alpha}a_{\beta}a^{\dagger}_{\alpha_2}|0\rangle = \delta_{\alpha\alpha_1}\delta_{\beta\alpha_2} \tag{3.0.23}$$

and

$$\langle\alpha_1|\hat{H}_0|\alpha_2\rangle = \sum_{\alpha\beta}\langle\alpha|\hat{h}_0|\beta\rangle\delta_{\alpha\alpha_1}\delta_{\beta\alpha_2} = \langle\alpha_1|\hat{h}_0|\alpha_2\rangle \tag{3.0.24}$$

as expected.

Topics for Week 37

Second quantization

- Monday:
- Summary from last week
- Operators in second quantization and Wick's theorem
- Tuesday:
- Wick's theorem continues
- Begin Particle-hole formalism

Exercises 5 and 6. The material is taken from chapter 3.1-3.6 and 4.1-4.4 of Shavitt and Bartlett.

Operators in second quantization

Let us now derive the expression for our two-body interaction part, which also conserves the number of particles. We can proceed in exactly the same way as for the one-body operator. In the coordinate representation our two-body interaction part takes the following expression

$$\hat{H}_I = \sum_{i<j} V(x_i, x_j) \tag{4.0.1}$$

where the summation runs over distinct pairs. The term V can be an interaction model for the nucleon-nucleon interaction or the interaction between two electrons. It can also include additional two-body interaction terms.

Operators in second quantization

The action of this operator on a product of two single-particle functions is defined as

$$V(x_i, x_j)\psi_{\alpha_k}(x_i)\psi_{\alpha_l}(x_j) = \sum_{\alpha_k'\alpha_l'} \psi'_{\alpha_k}(x_i)\psi'_{\alpha_l}(x_j)\langle\alpha_k'\alpha_l'|V|\alpha_k\alpha_l\rangle \qquad (4.0.2)$$

Operators in second quantization

We can now let $\hat{H}_I$ act on all terms in the linear combination for $|\alpha_1\alpha_2\dots\alpha_n\rangle$. Without any permutations we have

$$\begin{aligned}
& \left(\sum_{i<j} V(x_i,x_j)\right)\psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\dots\psi_{\alpha_n}(x_n) \\
= & \sum_{\alpha_1'\alpha_2'} \langle\alpha_1'\alpha_2'|V|\alpha_1\alpha_2\rangle\psi_{\alpha_1}'(x_1)\psi_{\alpha_2}'(x_2)\dots\psi_{\alpha_n}(x_n) \\
+ & \dots \\
+ & \sum_{\alpha_1'\alpha_n'} \langle\alpha_1'\alpha_n'|V|\alpha_1\alpha_n\rangle\psi_{\alpha_1}'(x_1)\psi_{\alpha_2}(x_2)\dots\psi_{\alpha_n}'(x_n) \\
+ & \dots \\
+ & \sum_{\alpha_2'\alpha_n'} \langle\alpha_2'\alpha_n'|V|\alpha_2\alpha_n\rangle\psi_{\alpha_1}(x_1)\psi_{\alpha_2}'(x_2)\dots\psi_{\alpha_n}'(x_n) \\
+ & \dots
\end{aligned} \tag{4.0.3}$$

where on the rhs we have a term for each distinct pairs.

Operators in second quantization

For the other terms on the rhs we obtain similar expressions and summing over all terms we obtain

$$
\begin{aligned}
H_I|\alpha_1\alpha_2\dots\alpha_n\rangle &= \sum_{\alpha_1',\alpha_2'}\langle\alpha_1'\alpha_2'|V|\alpha_1\alpha_2\rangle|\alpha_1'\alpha_2'\dots\alpha_n\rangle \\
&+ \dots \\
&+ \sum_{\alpha_1',\alpha_n'}\langle\alpha_1'\alpha_n'|V|\alpha_1\alpha_n\rangle|\alpha_1'\alpha_2\dots\alpha_n'\rangle \\
&+ \dots \\
&+ \sum_{\alpha_2',\alpha_n'}\langle\alpha_2'\alpha_n'|V|\alpha_2\alpha_n\rangle|\alpha_1\alpha_2'\dots\alpha_n'\rangle \\
&+ \dots \qquad (4.0.4)
\end{aligned}
$$

Operators in second quantization

We introduce second quantization via the relation

$$
\begin{aligned}
& a^\dagger_{\alpha'_k} a^\dagger_{\alpha'_l} a_{\alpha_l} a_{\alpha_k} |\alpha_1\alpha_2 \dots \alpha_k \dots \alpha_l \dots \alpha_n\rangle \\
= \quad & (-1)^{k-1}(-1)^{l-2} a^\dagger_{\alpha'_k} a^\dagger_{\alpha'_l} a_{\alpha_l} a_{\alpha_k} |\alpha_k\alpha_l \underbrace{\alpha_1\alpha_2 \dots \alpha_n}_{\neq \alpha_k, \alpha_l}\rangle \\
= \quad & (-1)^{k-1}(-1)^{l-2} |\alpha'_k\alpha'_l \underbrace{\alpha_1\alpha_2 \dots \alpha_n}_{\neq \alpha'_k, \alpha'_l}\rangle \\
= \quad & |\alpha_1\alpha_2 \dots \alpha'_k \dots \alpha'_l \dots \alpha_n\rangle
\end{aligned}
\qquad (4.0.5)
$$

Operators in second quantization

Inserting this in (4.0.4) gives

$$
\begin{aligned}
H_I|\alpha_1\alpha_2\ldots\alpha_n\rangle &= \sum_{\alpha_1',\alpha_2'} \langle\alpha_1'\alpha_2'|V|\alpha_1\alpha_2\rangle a^\dagger_{\alpha_1'} a^\dagger_{\alpha_2'} a_{\alpha_2} a_{\alpha_1} |\alpha_1\alpha_2\ldots\alpha_n\rangle \\
&+ \ldots \\
&= \sum_{\alpha_1',\alpha_n'} \langle\alpha_1'\alpha_n'|V|\alpha_1\alpha_n\rangle a^\dagger_{\alpha_1'} a^\dagger_{\alpha_n'} a_{\alpha_n} a_{\alpha_1} |\alpha_1\alpha_2\ldots\alpha_n\rangle \\
&+ \ldots \\
&= \sum_{\alpha_2',\alpha_n'} \langle\alpha_2'\alpha_n'|V|\alpha_2\alpha_n\rangle a^\dagger_{\alpha_2'} a^\dagger_{\alpha_n'} a_{\alpha_n} a_{\alpha_2} |\alpha_1\alpha_2\ldots\alpha_n\rangle \\
&+ \ldots \\
&= \sum_{\alpha,\beta,\gamma,\delta}{}' \langle\alpha\beta|V|\gamma\delta\rangle a^\dagger_{\alpha} a^\dagger_{\beta} a_{\delta} a_{\gamma} |\alpha_1\alpha_2\ldots\alpha_n\rangle \qquad (4.0.6)
\end{aligned}
$$

Operators in second quantization

Here we let $\sum'$ indicate that the sums running over α and β run over all single-particle states, while the summations γ and δ run over all pairs of single-particle states. We wish to remove this restriction and since

$$\langle \alpha\beta|V|\gamma\delta\rangle = \langle \beta\alpha|V|\delta\gamma\rangle \tag{4.0.7}$$

we get

$$\begin{aligned} \sum_{\alpha,\beta} \langle \alpha\beta|V|\gamma\delta\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma &= \sum_{\alpha,\beta} \langle \beta\alpha|V|\delta\gamma\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma & (4.0.8) \\ &= \sum_{\alpha,\beta} \langle \beta\alpha|V|\delta\gamma\rangle a^\dagger_\beta a^\dagger_\alpha a_\gamma a_\delta & (4.0.9) \end{aligned}$$

where we have used the anti-commutation rules.

Operators in second quantization

Changing the summation indices α and β in (4.0.9) we obtain

$$\sum_{\alpha,\beta}\langle\alpha\beta|V|\gamma\delta\rangle a^{\dagger}_{\alpha}a^{\dagger}_{\beta}a_{\delta}a_{\gamma} = \sum_{\alpha,\beta}\langle\alpha\beta|V|\delta\gamma\rangle a^{\dagger}_{\alpha}a^{\dagger}_{\beta}a_{\gamma}a_{\delta} \tag{4.0.10}$$

From this it follows that the restriction on the summation over γ and δ can be removed if we multiply with a factor $\frac{1}{2}$, resulting in

$$\hat{H}_I = \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\langle\alpha\beta|V|\gamma\delta\rangle a^{\dagger}_{\alpha}a^{\dagger}_{\beta}a_{\delta}a_{\gamma} \tag{4.0.11}$$

where we sum freely over all single-particle states α, β, γ og δ.

Operators in second quantization

With this expression we can now verify that the second quantization form of $\hat{H}_I$ in Eq. (4.0.11) results in the same matrix between two anti-symmetrized two-particle states as its corresponding coordinate space representation. We have

$$\langle\alpha_1\alpha_2|\hat{H}_I|\beta_1\beta_2\rangle = \frac{1}{2}\sum_{\alpha\beta\gamma,\delta}\langle\alpha\beta|V|\gamma\delta\rangle\langle 0|a_{\alpha_2}a_{\alpha_1}a^{\dagger}_{\alpha}a^{\dagger}_{\beta}a_{\delta}a_{\gamma}a^{\dagger}_{\beta_1}a^{\dagger}_{\beta_2}|0\rangle. \qquad (4.0.12)$$

Operators in second quantization

Using the commutation relations we get

$$
\begin{aligned}
& a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma a^\dagger_{\beta_1} a^\dagger_{\beta_2} \\
= \quad & a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta (a_\delta \delta_{\gamma\beta_1} a^\dagger_{\beta_2} - a_\delta a^\dagger_{\beta_1} a_\gamma a^\dagger_{\beta_2}) \\
= \quad & a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta (\delta_{\gamma\beta_1} \delta_{\delta\beta_2} - \delta_{\gamma\beta_1} a^\dagger_{\beta_2} a_\delta - a_\delta a^\dagger_{\beta_1} \delta_{\gamma\beta_2} + a_\delta a^\dagger_{\beta_1} a^\dagger_{\beta_2} a_\gamma) \\
= \quad & a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta (\delta_{\gamma\beta_1} \delta_{\delta\beta_2} - \delta_{\gamma\beta_1} a^\dagger_{\beta_2} a_\delta \\
& \quad -\delta_{\delta\beta_1} \delta_{\gamma\beta_2} + \delta_{\gamma\beta_2} a^\dagger_{\beta_1} a_\delta + a_\delta a^\dagger_{\beta_1} a^\dagger_{\beta_2} a_\gamma) \qquad (4.0.13)
\end{aligned}
$$

Operators in second quantization

The vacuum expectation value of this product of operators becomes

$$
\begin{aligned}
& \langle 0|a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma a^\dagger_{\beta_1} a^\dagger_{\beta_2}|0\rangle \\
= \quad & (\delta_{\gamma\beta_1}\delta_{\delta\beta_2} - \delta_{\delta\beta_1}\delta_{\gamma\beta_2})\langle 0|a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta|0\rangle \\
= \quad & (\delta_{\gamma\beta_1}\delta_{\delta\beta_2} - \delta_{\delta\beta_1}\delta_{\gamma\beta_2})(\delta_{\alpha\alpha_1}\delta_{\beta\alpha_2} - \delta_{\beta\alpha_1}\delta_{\alpha\alpha_2})
\end{aligned}
\tag{4.0.14}
$$

Operators in second quantization

Insertion of Eq. (4.0.14) in Eq. (4.0.12) results in

$$
\begin{aligned}
\langle \alpha_1 \alpha_2 | \hat{H}_I | \beta_1 \beta_2 \rangle &= \frac{1}{2}\big[\langle \alpha_1 \alpha_2 | V | \beta_1 \beta_2 \rangle - \langle \alpha_1 \alpha_2 | V | \beta_2 \beta_1 \rangle \\
&\quad - \langle \alpha_2 \alpha_1 | V | \beta_1 \beta_2 \rangle + \langle \alpha_2 \alpha_1 | V | \beta_2 \beta_1 \rangle\big] \\
&= \langle \alpha_1 \alpha_2 | V | \beta_1 \beta_2 \rangle - \langle \alpha_1 \alpha_2 | V | \beta_2 \beta_1 \rangle \\
&= \langle \alpha_1 \alpha_2 | V | \beta_1 \beta_2 \rangle_{\mathrm{AS}}. \qquad (4.0.15)
\end{aligned}
$$

Operators in second quantization

The two-body operator can also be expressed in terms of the anti-symmetrized matrix elements we discussed previously as

$$
\begin{aligned}
\hat{H}_I &= \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma \\
&= \frac{1}{4}\sum_{\alpha\beta\gamma\delta}\left[\langle\alpha\beta|V|\gamma\delta\rangle - \langle\alpha\beta|V|\delta\gamma\rangle\right] a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma \\
&= \frac{1}{4}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{\mathrm{AS}} a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma \qquad (4.0.16)
\end{aligned}
$$

Operators in second quantization

The factors in front of the operator, either $\frac{1}{4}$ or $\frac{1}{2}$ tells whether we use antisymmetrized matrix elements or not.
We can now express the Hamiltonian operator for a many-fermion system in the occupation basis representation as

$$H = \sum_{\alpha,\beta} \langle \alpha | t + u | \beta \rangle a_\alpha^\dagger a_\beta + \frac{1}{4} \sum_{\alpha,\beta,\gamma,\delta} \langle \alpha\beta | V | \gamma\delta \rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma. \tag{4.0.17}$$

This is form we will use in the rest of these lectures, assuming that we work with anti-symmetrized two-body matrix elements.

Wick's theorem

Wick's theorem is based on two fundamental concepts, namely *normal ordering* and *contraction*. The normal-ordered form of $\widehat{\mathbf{A}}\widehat{\mathbf{B}}..\widehat{\mathbf{X}}\widehat{\mathbf{Y}}$, where the individual terms are either a creation or annihilation operator, is defined as

$$\left\{\widehat{\mathbf{A}}\widehat{\mathbf{B}}..\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\right\} \equiv (-1)^p \,[\text{creation operators}] \cdot [\text{annihilation operators}]\,. \tag{4.0.18}$$

The p subscript denotes the number of permutations that is needed to transform the original string into the normal-ordered form. A contraction between to arbitrary operators $\widehat{\mathbf{X}}$ and $\widehat{\mathbf{Y}}$ is defined as

$$\overbracket{\widehat{\mathbf{X}}\widehat{\mathbf{Y}}} \equiv \langle 0|\widehat{\mathbf{X}}\widehat{\mathbf{Y}}|0\rangle. \tag{4.0.19}$$

Wick's theorem

It is also possible to contract operators inside a normal ordered products. We define the original relative position between two operators in a normal ordered product as p, the so-called permutation number. This is the number of permutations needed to bring one of the two operators next to the other one. A contraction between two operators with $p \neq 0$ inside a normal ordered is defined as

$$\left\{\contraction{}{\widehat{\mathbf{A}}}{\widehat{\mathbf{B}}..}{\widehat{\mathbf{X}}}\widehat{\mathbf{A}}\widehat{\mathbf{B}}..\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\right\} = (-1)^p \left\{\contraction{}{\widehat{\mathbf{A}}}{}{\widehat{\mathbf{B}}}\widehat{\mathbf{A}}\widehat{\mathbf{B}}..\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\right\}. \tag{4.0.20}$$

In the general case with m contractions, the procedure is similar, and the prefactor changes to

$$(-1)^{p_1+p_2+..+p_m}. \tag{4.0.21}$$

Wick's theorem

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

$$
\begin{aligned}
\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z} &= \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} && (4.0.22)\\
&+ \sum_{(1)} \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} && (4.0.23)\\
&+ \sum_{(2)} \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} && (4.0.24)\\
&+ \ldots && (4.0.25)\\
&+ \sum_{\left[\frac{N}{2}\right]} \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\,\hat{R}\hat{X}\hat{Y}\hat{Z}\right\}. && (4.0.26)
\end{aligned}
$$

Wick's theorem

The $\sum_{(m)}$ means the sum over all terms with m contractions, while $\left[\frac{N}{2}\right]$ means the largest integer that not do not exceeds $\frac{N}{2}$ where N is the number of creation and annihilation operators. When N is even,

$$\left[\frac{N}{2}\right] = \frac{N}{2}, \tag{4.0.27}$$

and the last sum in Eq. (4.0.22) is over fully contracted terms. When N is odd,

$$\left[\frac{N}{2}\right] \neq \frac{N}{2}, \tag{4.0.28}$$

and non of the terms in Eq. (4.0.22) are fully contracted. See later for a proof.

Wick's theorem

An important extension of Wick's theorem allow us to define contractions between normal-ordered strings of operators. This is the so-called generalized Wick's theorem,

$$\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\right\}\left\{\hat{R}\hat{X}\hat{Y}\hat{Z}..\right\} = \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} \tag{4.0.29}$$

$$+ \sum_{(1)} \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} \tag{4.0.30}$$

$$+ \sum_{(2)} \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} \tag{4.0.31}$$

$$+ \dots \tag{4.0.32}$$

Wick's theorem

Turning back to the many-body problem, the vacuum expectation value of products of creation and annihilation operators can be written, according to Wick's theoren in Eq. (4.0.22), as a sum over normal ordered products with all possible numbers and combinations of contractions,

$$\langle 0|\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}|0\rangle = \langle 0|\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\}|0\rangle \tag{4.0.33}$$

$$+\sum_{(1)}\langle 0|\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\}|0\rangle \tag{4.0.34}$$

$$+\sum_{(2)}\langle 0|\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\}|0\rangle \tag{4.0.35}$$

$$+\ldots \tag{4.0.36}$$

$$+\sum_{\left[\frac{N}{2}\right]}\langle 0|\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\ \hat{R}\hat{X}\hat{Y}\hat{Z}\right\}|0\rangle. \tag{4.0.37}$$

Wick's theorem

All vacuum expectation values of normal ordered products without fully contracted terms are zero. Hence, the only contributions to the expectation value are those terms that *is* fully contracted,

$$\langle 0|\widehat{\mathbf{A}}\widehat{\mathbf{B}}\widehat{\mathbf{C}}\widehat{\mathbf{D}}..\widehat{\mathbf{R}}\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\widehat{\mathbf{Z}}|0\rangle = \sum_{(all)} \langle 0| \left\{ \widehat{\mathbf{A}}\widehat{\mathbf{B}}\widehat{\mathbf{C}}\widehat{\mathbf{D}}..\ \widehat{\mathbf{R}}\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\widehat{\mathbf{Z}} \right\} |0\rangle \tag{4.0.38}$$

$$= \sum_{(all)} \widehat{\mathbf{A}}\widehat{\mathbf{B}}\widehat{\mathbf{C}}\widehat{\mathbf{D}}..\ \widehat{\mathbf{R}}\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\widehat{\mathbf{Z}}. \tag{4.0.39}$$

Wick's theorem

To obtain fully contracted terms, Eq. (4.0.27) must hold. When the number of creation and annihilation operators is odd, the vacuum expectation value can be set to zero at once. When the number is even, the expectation value is simply the sum of terms with all possible combinations of fully contracted terms. Observing that the only contractions that give nonzero contributions are

$$\contraction{}{a}{_\alpha}{a} a_\alpha a_\beta^\dagger = \delta_{\alpha\beta}, \tag{4.0.40}$$

the terms that contribute are reduced even more.

Wick's theorem provides us with an algebraic method for easy determination of the terms that contribute to the matrix element. Our next step is the particle-hole formalism, which is a very useful formalism in many-body systems. But that is the topic for next week!

Second quantization and configuration interaction (CI) theory

Essentially most CI theory manipulations involve one and two-body operators with either one creation and one annihilation operators or two creation and two annihilations operators. Our Hamiltonian reads

$$\hat{H} = \sum_{\alpha\beta} \langle\alpha|t+u|\beta\rangle a_\alpha^\dagger a_\beta + \frac{1}{4}\sum_{\alpha\beta\gamma\delta} \langle\alpha\beta|V|\gamma\delta\rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma .$$

This is form we have used in CI codes, assuming that we work with anti-symmetrized two-body matrix elements. The two-body operator can be rewritten as

$$\hat{V} = \sum_{\alpha\leq\beta;\gamma\leq\delta} \langle\alpha\beta|V|\gamma\delta\rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma .$$

Normally we have a diagonal one-body operator.

Creation and annihilation operators and CI

In the build-up of a CI code that is meant to tackle large dimensionalities is the action of the Hamiltonian $\hat{H}$ on a Slater determinant represented in second quantization as

$$|\alpha_1 \dots \alpha_n\rangle = a^\dagger_{\alpha_1} a^\dagger_{\alpha_2} \dots a^\dagger_{\alpha_n} |0\rangle.$$

The time consuming part stems from the action of the Hamiltonian on the above determinant,

$$\left(\sum_{\alpha\beta} \langle\alpha|t+u|\beta\rangle a^\dagger_\alpha a_\beta + \frac{1}{4}\sum_{\alpha\beta\gamma\delta} \langle\alpha\beta|V|\gamma\delta\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma\right) a^\dagger_{\alpha_1} a^\dagger_{\alpha_2} \dots a_{\alpha_n}^{gger|0\rangle.}$$

A practically useful way to implement this action is to encode a Slater determinant as a bit pattern.

Creation and annihilation operators

Assume that we have at our disposal n different single-particle orbits $\alpha_0, \alpha_2, \dots, \alpha_{n-1}$ and that we can distribute among these orbits $N \leq n$ particles.
A Slater determinant can then be coded as an integer of n bits. As an example, if we have $n = 16$ single-particle states $\alpha_0, \alpha_1, \dots, \alpha_{15}$ and $N = 4$ fermions occupying the states α_3, α_6, α_{10} and α_{13} we could write this Slater determinant as

$$\Phi_\Lambda = a^\dagger_{\alpha_3} a^\dagger_{\alpha_6} a^\dagger_{\alpha_{10}} a^\dagger_{\alpha_{13}} |0\rangle.$$

The unoccupied single-particle states have bit value 0 while the occupied ones are represented by bit state 1. In the binary notation we would write this 16 bits long integer as

α_0	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8	α_9	α_{10}	α_{11}	α_{12}	α_{13}	α_{14}	α_{15}
0	0	0	1	0	0	1	0	0	0	1	0	0	1	0	0

which translates into the decimal number

$$2^3 + 2^6 + 2^{10} + 2^{13} = 9288.$$

We can thus encode a Slater determinant as a bit pattern.

Hilbert space dimensionality in CI calculations

With N particles that can be distributed over n single-particle states, the total number of Slater determinats (and defining thereby the dimensionality of the system) is

$$\dim(\mathcal{H}) = \left(\begin{array}{c} n \\ N \end{array} \right).$$

The total number of bit patterns is 2^n.

Compact representation of Slater determinants

We assume again that we have at our disposal n different single-particle orbits $\alpha_0, \alpha_2, \dots, \alpha_{n-1}$ and that we can distribute among these orbits $N \leq n$ particles. The ordering among these states is important as it defines the order of the creation operators. We will write the determinant

$$\Phi_\Lambda = a^\dagger_{\alpha_3} a^\dagger_{\alpha_6} a^\dagger_{\alpha_{10}} a^\dagger_{\alpha_{13}} |0\rangle,$$

in a more compact way as

$$\Phi_{3,6,10,13} = |0001001000100100\rangle.$$

The action of a creation operator is thus

$$a^\dagger_{\alpha_4}\Phi_{3,6,10,13} = a^\dagger_{\alpha_4}|0001001000100100\rangle = a^\dagger_{\alpha_4} a^\dagger_{\alpha_3} a^\dagger_{\alpha_6} a^\dagger_{\alpha_{10}} a^\dagger_{\alpha_{13}} |0\rangle,$$

which becomes

$$-a^\dagger_{\alpha_3} a^\dagger_{\alpha_4} a^\dagger_{\alpha_6} a^\dagger_{\alpha_{10}} a^\dagger_{\alpha_{13}} |0\rangle = -|0001101000100100\rangle.$$

Compact representation of Slater determinants

Similarly

$$a^\dagger_{\alpha_6}\Phi_{3,6,10,13} = a^\dagger_{\alpha_6}|0001001000100100\rangle = a^\dagger_{\alpha_6}a^\dagger_{\alpha_3}a^\dagger_{\alpha_6}a^\dagger_{\alpha_{10}}a^\dagger_{\alpha_{13}}|0\rangle,$$

which becomes

$$-a^\dagger_{\alpha_4}(a^\dagger_{\alpha_6})^2a^\dagger_{\alpha_{10}}a^\dagger_{\alpha_{13}}|0\rangle = 0!$$

This gives a simple recipe:

- If one of the bits b_j is 1 and we act with a creation operator on this bit, we return a null vector
- If $b_j = 0$, we set it to 1 and return a sign factor $(-1)^l$, where l is the number of bits set before bit j.

We see now the basic recipe for acting on a Slater determinant

Consider the action of $a^{\dagger}_{\alpha_2}$ on various slater determinants:

$$
\begin{array}{lll}
a^{\dagger}_{\alpha_2}\Phi_{00111} & = a^{\dagger}_{\alpha_2}|00111\rangle & = 0\times|00111\rangle \\
a^{\dagger}_{\alpha_2}\Phi_{01011} & = a^{\dagger}_{\alpha_2}|01011\rangle & = (-1)\times|01111\rangle \\
a^{\dagger}_{\alpha_2}\Phi_{01101} & = a^{\dagger}_{\alpha_2}|01101\rangle & = 0\times|01101\rangle \\
a^{\dagger}_{\alpha_2}\Phi_{01110} & = a^{\dagger}_{\alpha_2}|01110\rangle & = 0\times|01110\rangle \\
a^{\dagger}_{\alpha_2}\Phi_{10011} & = a^{\dagger}_{\alpha_2}|10011\rangle & = (-1)\times|10111\rangle \\
a^{\dagger}_{\alpha_2}\Phi_{10101} & = a^{\dagger}_{\alpha_2}|10101\rangle & = 0\times|10101\rangle \\
a^{\dagger}_{\alpha_2}\Phi_{10110} & = a^{\dagger}_{\alpha_2}|10110\rangle & = 0\times|10110\rangle \\
a^{\dagger}_{\alpha_2}\Phi_{11001} & = a^{\dagger}_{\alpha_2}|11001\rangle & = (+1)\times|11101\rangle \\
a^{\dagger}_{\alpha_2}\Phi_{11010} & = a^{\dagger}_{\alpha_2}|11010\rangle & = (+1)\times|11110\rangle
\end{array}
$$

What is the simplest way to obtain the phase when we act with one annihilation(creation) operator on the given Slater determinant representation?

Manipulating Slater determinants

We have an SD representation

$$\Phi_\Lambda = a^\dagger_{\alpha_0} a^\dagger_{\alpha_3} a^\dagger_{\alpha_6} a^\dagger_{\alpha_{10}} a^\dagger_{\alpha_{13}} |0\rangle,$$

in a more compact way as

$$\Phi_{0,3,6,10,13} = |1001001000100100\rangle.$$

The action of

$$a^\dagger_{\alpha_4} a_{\alpha_0} \Phi_{0,3,6,10,13} = a^\dagger_{\alpha_4} |0001001000100100\rangle = a^\dagger_{\alpha_4} a^\dagger_{\alpha_3} a^\dagger_{\alpha_6} a^\dagger_{\alpha_{10}} a^\dagger_{\alpha_{13}} |0\rangle,$$

which becomes

$$-a^\dagger_{\alpha_3} a^\dagger_{\alpha_4} a^\dagger_{\alpha_6} a^\dagger_{\alpha_{10}} a^\dagger_{\alpha_{13}} |0\rangle = -|0001101000100100\rangle.$$

Manipulating Slater determinants

The action

$$a_{\alpha_0}\Phi_{0,3,6,10,13} = |0001001000100100\rangle,$$

can be obtained by subtracting the logical sum (AND operation) of $\Phi_{0,3,6,10,13}$ and a word which represents only α_0, that is

$$|1000000000000000\rangle,$$

from $\Phi_{0,3,6,10,13} = |1001001000100100\rangle$.
This operation gives $|0001001000100100\rangle$.

Similarly, we can form $a^\dagger_{\alpha_4}a_{\alpha_0}\Phi_{0,3,6,10,13}$, say, by adding $|0000100000000000\rangle$ to $a_{\alpha_0}\Phi_{0,3,6,10,13}$, first checking that their logical sum is zero in order to make sure that orbital α_4 is not already occupied.

Manipulating Slater determinants, getting the phase

It is trickier however to get the phase $(-1)^l$. One possibility is as follows

- Let S_1 be a word that represents the $1-$bit to be removed and all others set to zero. In the previous example $S_1 = |1000000000000000\rangle$
- Define S_2 as the similar word that represents the bit to be added, that is in our case $S_2 = |0000100000000000\rangle$.
- Compute then $S = S_1 - S_2$, which here becomes

$$S = |0111000000000000\rangle$$

- Perform then the logical AND operation of S with the word containing

$$\Phi_{0,3,6,10,13} = |1001001000100100\rangle,$$

which results in $|0001000000000000\rangle$. Counting the number of $1-$bits gives the phase. Here you need however an algorithm for bitcounting. Several efficient ones available.

Topics for Week 38

Second quantization

- Monday:
- Summary from last week
- Particle-hole formalism
- Tuesday:
- Particle-hole formalism
- Diagrammatic representation of operators and expectation values
- Begin of Hartree-Fock theory
- Exercises 7-8

Particle-hole formalism

Second quantization is a useful and elegant formalism for constructing many-body states and quantum mechanical operators. As we will see later, one can express and translate many physical processes into simple pictures such as Feynman diagrams. Expecation values of many-body states are also easily calculated. However, although the equations are seemingly easy to set up, from a practical point of view, that is the solution of Schrödinger's equation, there is no particular gain. The many-body equation is equally hard to solve, irrespective of representation. The cliche that there is no free lunch brings us down to earth again. Note however that a transformation to a particular basis, for cases where the interaction obeys specific symmetries, can ease the solution of Schrödinger's equation.

Particle-hole formalism

But there is at least one important case where second quantization comes to our rescue. It is namely easy to introduce another reference state than the pure vacuum $|0\rangle$, where all single-particle are active. With many particles present it is often useful to introduce another reference state than the vacuum state $|0\rangle$. We will label this state $|c\rangle$ (c for core) and as we will see it can reduce considerably the complexity and thereby the dimensionality of the many-body problem. It allows us to sum up to infinite order specific many-body correlations. (add more stuff in the description below)

The particle-hole representation is one of these handy representations.

Particle-hole formalism

In the original particle representation these states are products of the creation operators $a^\dagger_{\alpha_i}$ acting on the true vacuum $|0\rangle$. Following (2.0.19) we have

$$
\begin{aligned}
|\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\rangle &= a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\dots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}|0\rangle && (5.0.1)\\
|\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\alpha_{n+1}\rangle &= a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\dots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}a^\dagger_{\alpha_{n+1}}|0\rangle && (5.0.2)\\
|\alpha_1\alpha_2\dots\alpha_{n-1}\rangle &= a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\dots a^\dagger_{\alpha_{n-1}}|0\rangle && (5.0.3)
\end{aligned}
$$

Particle-hole formalism

If we use Eq. (5.0.1) as our new reference state, we can simplify considerably the representation of this state

$$|c\rangle \equiv |\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\rangle = a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\dots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}|0\rangle \tag{5.0.4}$$

The new reference states for the $n+1$ and $n-1$ states can then be written as

$$|\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\alpha_{n+1}\rangle = (-1)^n a^\dagger_{\alpha_{n+1}}|c\rangle \equiv (-1)^n|\alpha_{n+1}\rangle_c \tag{5.0.5}$$

$$|\alpha_1\alpha_2\dots\alpha_{n-1}\rangle = (-1)^{n-1} a_{\alpha_n}|c\rangle \equiv (-1)^{n-1}|\alpha_{n-1}\rangle_c \tag{5.0.6}$$

Particle-hole formalism

The first state has one additional particle with respect to the new vacuum state $|c\rangle$ and is normally referred to as a one-particle state or one particle added to the many-body reference state. The second state has one particle less than the reference vacuum state $|c\rangle$ and is referred to as a one-hole state.

Particle-hole formalism

When dealing with a new reference state it is often convenient to introduce new creation and annihilation operators since we have from Eq. (5.0.6)

$$a_\alpha|c\rangle \neq 0 \tag{5.0.7}$$

since α is contained in $|c\rangle$, while for the true vacuum we have $a_\alpha|0\rangle = 0$ for all α.

Particle-hole formalism

The new reference state leads to the definition of new creation and annihilation operators which satisfy the following relations

$$
\begin{aligned}
b_\alpha|c\rangle &= 0 && (5.0.8)\\
\{b_\alpha^\dagger, b_\beta^\dagger\} = \{b_\alpha, b_\beta\} &= 0 \\
\{b_\alpha^\dagger, b_\beta\} &= \delta_{\alpha\beta} && (5.0.9)
\end{aligned}
$$

We assume also that the new reference state is properly normalized

$$
\langle c|c\rangle = 1 \qquad (5.0.10)
$$

Particle-hole formalism

The physical interpretation of these new operators is that of so-called quasiparticle states. This means that a state defined by the addition of one extra particle to a reference state $|c\rangle$ may not necesseraly be interpreted as one particle coupled to a core.

Particle-hole formalism

We define now new creation operators that act on a state α creating a new quasiparticle state

$$b_\alpha^\dagger|c\rangle = \left\{ \begin{array}{ll} a_\alpha^\dagger|c\rangle = |\alpha\rangle, & \alpha > F \\ \\ a_\alpha|c\rangle = |\alpha^{-1}\rangle, & \alpha \leq F \end{array} \right. \tag{5.0.11}$$

where F is the Fermi level representing the last occupied single-particle orbit of the new reference state $|c\rangle$.

Particle-hole formalism

The annihilation is the hermitian conjugate of the creation operator

$$b_\alpha = (b_\alpha^\dagger)^\dagger,$$

resulting in

$$b_\alpha^\dagger = \begin{cases} a_\alpha^\dagger & \alpha > F \\ a_\alpha & \alpha \leq F \end{cases} \qquad b_\alpha = \begin{cases} a_\alpha & \alpha > F \\ a_\alpha^\dagger & \alpha \leq F \end{cases} \tag{5.0.12}$$

Particle-hole formalism

With the new creation and annihilation operator we can now construct many-body quasiparticle states, with one-particle-one-hole states, two-particle-two-hole states etc in the same fashion as we previously constructed many-particle states. We can write a general particle-hole state as

$$|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle \equiv \underbrace{b^\dagger_{\beta_1}b^\dagger_{\beta_2}\dots b^\dagger_{\beta_{n_p}}}_{>F}\underbrace{b^\dagger_{\gamma_1}b^\dagger_{\gamma_2}\dots b^\dagger_{\gamma_{n_h}}}_{\leq F}|c\rangle \tag{5.0.13}$$

Particle-hole formalism

We can now rewrite our one-body and two-body operators in terms of the new creation and annihilation operators. The number operator becomes

$$\hat{N} = \sum_{\alpha} a^{\dagger}_{\alpha} a_{\alpha} = \sum_{\alpha > F} b^{\dagger}_{\alpha} b_{\alpha} + n_c - \sum_{\alpha \leq F} b^{\dagger}_{\alpha} b_{\alpha} \tag{5.0.14}$$

where n_c is the number of particle in the new vacuum state $|c\rangle$. The action of $\hat{N}$ on a many-body state results in

$$N|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle = (n_p + n_c - n_h)|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle \tag{5.0.15}$$

Particle-hole formalism

Here $n = n_p + n_c - n_h$ is the total number of particles in the quasi-particle state of Eq. (5.0.13). Note that $\hat{N}$ counts the total number of particles present

$$N_{qp} = \sum_{\alpha} b_{\alpha}^{\dagger} b_{\alpha}, \tag{5.0.16}$$

gives us the number of quasi-particles as can be seen by computing

$$N_{qp} = |\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1}\rangle = (n_p + n_h)|\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1}\rangle \tag{5.0.17}$$

where $n_{qp} = n_p + n_h$ is the total number of quasi-particles.

Particle-hole formalism

We express the one-body operator $\hat{H}_0$ in terms of the quasi-particle creation and annihilation operators, resulting in

$$\begin{aligned} \hat{H}_0 &= \sum_{\alpha\beta>F} \langle\alpha|h|\beta\rangle b_\alpha^\dagger b_\beta + \sum_{\substack{\alpha > F \\ \beta \leq F}} \left[\langle\alpha|h|\beta\rangle b_\alpha^\dagger b_\beta^\dagger + \langle\beta|h|\alpha\rangle b_\beta b_\alpha\right] \\ &+ \sum_{\alpha\leq F} \langle\alpha|h|\alpha\rangle - \sum_{\alpha\beta\leq F} \langle\beta|h|\alpha\rangle b_\alpha^\dagger b_\beta \end{aligned} \tag{5.0.18}$$

Particle-hole formalism

The first term gives contribution only for particle states, while the last one contributes only for holestates. The second term can create or destroy a set of quasi-particles and the third term is the contribution from the vacuum state $|c\rangle$. The physical meaning of these terms will be discussed in the next section, where we attempt at a diagrammatic representation.

Particle-hole formalism

Before we continue with the expressions for the two-body operator, we introduce a nomenclature we will use for the rest of this text. It is inspired by the notation used in coupled cluster theories. We reserve the labels $i, j, k, \dots$ for hole states and $a, b, c, \dots$ for states above F, viz. particle states. This means also that we will skip the constraint $\leq F$ or $> F$ in the summation symbols. Our operator $\hat{H}_0$ reads now

$$\begin{aligned} \hat{H}_0 &= \sum_{ab} \langle a|h|b\rangle b_a^\dagger b_b + \sum_{ai} \left[\langle a|h|i\rangle b_a^\dagger b_i^\dagger + \langle i|h|a\rangle b_i b_a \right] \\ &+ \sum_i \langle i|h|i\rangle - \sum_{ij} \langle j|h|i\rangle b_i^\dagger b_j \end{aligned} \tag{5.0.19}$$

Particle-hole formalism

The two-particle operator in the particle-hole formalism is more complicated since we have to translate four indices $\alpha\beta\gamma\delta$ to the possible combinations of particle and hole states. When performing the commutator algebra we can regroup the operator in five different terms

$$\hat{H}_I = \hat{H}_I^{(a)} + \hat{H}_I^{(b)} + \hat{H}_I^{(c)} + \hat{H}_I^{(d)} + \hat{H}_I^{(e)} \tag{5.0.20}$$

Using anti-symmetrized matrix elements, the term $\hat{H}_I^{(a)}$ is

$$\hat{H}_I^{(a)} = \frac{1}{4}\sum_{abcd}\langle ab|V|cd\rangle b_a^\dagger b_b^\dagger b_d b_c \tag{5.0.21}$$

Particle-hole formalism

The next term $\hat{H}_I^{(b)}$ reads

$$\hat{H}_I^{(b)} = \frac{1}{4}\sum_{abci}\left(\langle ab|V|ci\rangle b_a^\dagger b_b^\dagger b_i^\dagger b_c + \langle ai|V|cb\rangle b_a^\dagger b_i b_b b_c\right) \tag{5.0.22}$$

This term conserves the number of quasiparticles but creates or removes a three-particle-one-hole state. For $\hat{H}_I^{(c)}$ we have

$$\begin{aligned}\hat{H}_I^{(c)} &= \frac{1}{4}\sum_{abij}\left(\langle ab|V|ij\rangle b_a^\dagger b_b^\dagger b_j^\dagger b_i^\dagger + \langle ij|V|ab\rangle b_a b_b b_j b_i\right) + \\ &\quad \frac{1}{2}\sum_{abij}\langle ai|V|bj\rangle b_a^\dagger b_j^\dagger b_b b_i + \frac{1}{2}\sum_{abi}\langle ai|V|bi\rangle b_a^\dagger b_b.\end{aligned} \tag{5.0.23}$$

Particle-hole formalism

The first line stands for the creation of a two-particle-two-hole state, while the second line represents the creation to two one-particle-one-hole pairs while the last term represents a contribution to the particle single-particle energy from the hole states, that is an interaction between the particle states and the hole states within the new vacuum state. The fourth term reads

$$\begin{aligned} \hat{H}_I^{(d)} &= \frac{1}{4}\sum_{aijk}\left(\langle ai|V|jk\rangle b_a^\dagger b_k^\dagger b_j^\dagger b_i + \langle ji|V|ak\rangle b_k^\dagger b_j b_i b_a\right) + \\ & \frac{1}{4}\sum_{aij}\left(\langle ai|V|ji\rangle b_a^\dagger b_j^\dagger + \langle ji|V|ai\rangle - \langle ji|V|ia\rangle b_j b_a\right). \end{aligned} \tag{5.0.24}$$

Particle-hole formalism

The terms in the first line stand for the creation of a particle-hole state interacting with hole states, we will label this as a two-hole-one-particle contribution. The remaining terms are a particle-hole state interacting with the holes in the vacuum state. Finally we have

$$\hat{H}_I^{(e)} = \frac{1}{4}\sum_{ijkl}\langle kl|V|ij\rangle b_i^\dagger b_j^\dagger b_l b_k + \frac{1}{2}\sum_{ijk}\langle ij|V|kj\rangle b_k^\dagger b_i + \frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle \tag{5.0.25}$$

The first terms represents the interaction between two holes while the second stands for the interaction between a hole and the remaining holes in the vacuum state. It represents a contribution to single-hole energy to first order. The last term collects all contributions to the energy of the ground state of a closed-shell system arising from hole-hole correlations.

Notation

Second quantization

Antisymmetrized wavefunction

$$\Phi_{AS}(\alpha_1, \ldots, \alpha_A; \mathbf{x}_1, \ldots \mathbf{x}_A) = \frac{1}{\sqrt{A}} \sum_{\hat{P}} (-1)^P \hat{P} \prod_{i=1}^{A} \psi_{\alpha_i}(\mathbf{x}_i)$$
$$\equiv |\alpha_1 \ldots \alpha_A\rangle$$
$$= a^\dagger_{\alpha_1} \ldots a^\dagger_{\alpha_A} |0\rangle$$

$$a^\dagger_p|0\rangle = |p\rangle, \quad a_p|q\rangle = \delta_{pq}|0\rangle$$

$$\delta_{pq} = \left\{a_p, a^\dagger_q\right\}$$
$$0 = \left\{a^\dagger_p, a_q\right\} = \{a_p, a_q\} = \left\{a^\dagger_p, a^\dagger_q\right\}$$

Notation

Second quantization, quasiparticles

Reference state

$$|\Phi_0\rangle = |\alpha_1 \dots \alpha_A\rangle, \quad \alpha_1, \dots, \alpha_A \leq \alpha_F$$

Creation and annihilation operators

$$\left\{a_p^\dagger, a_q\right\} = \delta_{pq}, p, q \leq \alpha_F \qquad \left\{a_p, a_q^\dagger\right\} = \delta_{pq}, p, q > \alpha_F$$

$$i, j, \dots \leq \alpha_F, \quad a, b, \dots > \alpha_F, \quad p, q, \dots - \text{any}$$

$$a_i|\Phi_0\rangle = |\Phi_i\rangle \qquad a_a^\dagger|\Phi_0\rangle = |\Phi^a\rangle$$

$$a_i^\dagger|\Phi_0\rangle = 0 \qquad a_a|\Phi_0\rangle = 0$$

Notation

Second quantization, operators

Onebody operator

$$\hat{F} = \sum_{pq} \langle p|\hat{f}|q\rangle a_p^\dagger a_q$$

Notation

Second quantization, operators

Twobody operator

$$\hat{V} = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle_{AS} a_p^\dagger a_q^\dagger a_s a_r \equiv \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

where we have defined the antisymmetric matrix elements

$$\langle pq|\hat{v}|rs\rangle_{AS} = \langle pq|\hat{v}|rs\rangle - \langle pq|\hat{v}|sr\rangle.$$

Notation

Second quantization, operators

Threebody operator

$$\hat{V}_3 = \frac{1}{36}\sum_{pqrstu}\langle pqr|\hat{v}_3|stu\rangle_{AS} a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s \equiv \frac{1}{36}\sum_{pqrstu}\langle pqr|\hat{v}_3|stu\rangle a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s$$

where we have defined the antisymmetric matrix elements

$$\begin{aligned}\langle pqr|\hat{v}_3|stu\rangle_{AS} = &\langle pqr|\hat{v}_3|stu\rangle + \langle pqr|\hat{v}_3|tus\rangle + \langle pqr|\hat{v}_3|ust\rangle \\ &- \langle pqr|\hat{v}_3|sut\rangle - \langle pqr|\hat{v}_3|tsu\rangle - \langle pqr|\hat{v}_3|uts\rangle.\end{aligned}$$

Notation

Second quantization, operators

Normal ordered operators

$$\left\{a_a a_b \ldots a_c^\dagger a_d^\dagger\right\} = (-1)^P a_c^\dagger a_d^\dagger \ldots a_a a_b$$

All creation operators to the left and all annihilation operators to the right times a factor determined by how many operators have been switched.

Definitions

The basics, Normal ordered Hamiltonian

Definition

The normal ordered Hamiltonian is given by

$$\begin{aligned}\hat{H}_N &= \frac{1}{36}\sum_{\substack{pqr\\stu}}\langle pqr|\hat{v}_3|stu\rangle\left\{a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s\right\}\\ &+\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}+\sum_{pq} f_q^p\left\{a_p^\dagger a_q\right\}\\ &= \hat{H}_3^N+\hat{V}_N+\hat{F}_N\end{aligned}$$

where

$$\hat{F}_N = \sum_{pq} f_q^p\left\{a_p^\dagger a_q\right\} \qquad \hat{V}_N = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}$$

$$\hat{H}_3^N = \frac{1}{36}\sum_{\substack{pqr\\stu}}\langle pqr|\hat{v}_3|stu\rangle\left\{a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s\right\}$$

Definitions

The basics, Normal ordered Hamiltonian

Definition

The amplitudes are given by

$$f_q^p = \langle p|\hat{h}_0|q\rangle + \sum_i \langle pi|\hat{v}|qi\rangle + \frac{1}{2}\sum_{ij}\langle pij|\hat{v}_3|qij\rangle$$

$$\langle pq||rs\rangle = \langle pq|\hat{v}|rs\rangle + \sum_i \langle pqi|\hat{v}_3|rsi\rangle,$$

In relation to the Hamiltonian, $\hat{H}_N$ is given by

$$\hat{H}_N = \hat{H} - E_0$$

$$E_0 = \langle \Phi_0|\hat{H}|\Phi_0\rangle$$

$$= \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle + \frac{1}{6}\sum_{ijk}\langle ijk|\hat{v}_3|ijk\rangle,$$

where E_0 is the energy expectation value between reference states.

Definitions

The basics, Normal ordered Hamiltonian

Derivation

We start with the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_I$$

where

$$\hat{H}_0 = \sum_{pq} \langle p|\hat{h}_0|q\rangle a_p^\dagger a_q$$

$$\hat{H}_I = \frac{1}{4} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

$$\hat{H}_3 = \frac{1}{36} \sum_{\substack{pqr \\ stu}} \langle pqr|\hat{v}_3|stu\rangle a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s$$

Definitions

The basics, Normal ordered Hamiltonian

Derivation, onebody part

$$\hat{H}_0 = \sum_{pq} \langle p|\hat{h}_0|q\rangle a_p^\dagger a_q$$

$$\begin{aligned} a_p^\dagger a_q &= \left\{a_p^\dagger a_q\right\} + \left\{\overbrace{a_p^\dagger a_q}\right\} \\ &= \left\{a_p^\dagger a_q\right\} + \delta_{pq\in i} \end{aligned}$$

$$\begin{aligned} \hat{H}_0 &= \sum_{pq} \langle p|\hat{h}_0|q\rangle a_p^\dagger a_q \\ &= \sum_{pq} \langle p|\hat{h}_0|q\rangle \left\{a_p^\dagger a_q\right\} + \delta_{pq\in i} \sum_{pq} \langle p|\hat{h}_0|q\rangle \\ &= \sum_{pq} \langle p|\hat{h}_0|q\rangle \left\{a_p^\dagger a_q\right\} + \sum_{i} \langle i|\hat{h}_0|i\rangle \end{aligned}$$

Definitions

The basics, Normal ordered Hamiltonian

Derivation, onebody part

A onebody part

$$\hat{F}_N \Leftarrow \sum_{pq} \langle p|\hat{h}_0|q\rangle \left\{ a_p^\dagger a_q \right\}$$

and a scalar part

$$E_0 \Leftarrow \sum_i \langle i|\hat{h}_0|i\rangle$$

Derivation, twobody part

$$\hat{H}_I = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

$$\begin{aligned}
a_p^\dagger a_q^\dagger a_s a_r = & \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \\
& + \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \\
& + \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \\
= & \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \\
& + \delta_{qs\in i} \left\{ a_p^\dagger a_r \right\} - \delta_{qr\in i} \left\{ a_p^\dagger a_s \right\} - \delta_{ps\in i} \left\{ a_q^\dagger a_r \right\} \\
& + \delta_{pr\in i} \left\{ a_q^\dagger a_s \right\} + \delta_{pr\in i}\delta_{qs\in i} - \delta_{ps\in i}\delta_{qr\in i}
\end{aligned}$$

Definitions

The basics, Normal ordered Hamiltonian

Derivation, twobody part

$$\hat{H}_I = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

$$\begin{aligned}
a_p^\dagger a_q^\dagger a_s a_r = & \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} \\
& + \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} \\
& + \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} \\
= & \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} \\
& + \delta_{qs\in i}\left\{a_p^\dagger a_r\right\} - \delta_{qr\in i}\left\{a_p^\dagger a_s\right\} - \delta_{ps\in i}\left\{a_q^\dagger a_r\right\} \\
& + \delta_{pr\in i}\left\{a_q^\dagger a_s\right\} + \delta_{pr\in i}\delta_{qs\in i} - \delta_{ps\in i}\delta_{qr\in i}
\end{aligned}$$

Derivation, twobody part

$$
\begin{aligned}
\hat{H}_I &= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r \\
&= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} + \quad \frac{1}{4}\sum_{pqrs}\Big(\delta_{qs\in i}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_r\right\} \\
&\quad - \delta_{qr\in i}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_s\right\} - \delta_{ps\in i}\langle pq|\hat{v}|rs\rangle \left\{a_q^\dagger a_r\right\} \\
&\quad + \delta_{pr\in i}\langle pq|\hat{v}|rs\rangle \left\{a_q^\dagger a_s\right\} + \delta_{pr\in i}\delta_{qs\in i} - \delta_{ps\in i}\delta_{qr\in i}\Big)
\end{aligned}
$$

Definitions

The basics, Normal ordered Hamiltonian

Derivation, twobody part

$$
\begin{aligned}
&= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} \\
&\quad + \frac{1}{4}\sum_{pqi}\Big(\langle pi|\hat{v}|qi\rangle - \langle pi|\hat{v}|iq\rangle - \langle ip|\hat{v}|qi\rangle + \langle ip|\hat{v}|iq\rangle\Big)\left\{a_p^\dagger a_q\right\} \\
&\quad + \frac{1}{4}\sum_{ij}\Big(\langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle\Big) \\
&= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} + \sum_{pqi}\langle pi|\hat{v}|qi\rangle \left\{a_p^\dagger a_q\right\} + \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle
\end{aligned}
$$

Definitions

The basics, Normal ordered Hamiltonian

Derivation, twobody part

A twobody part

$$\hat{V}_N \Leftarrow \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\}$$

A onebody part

$$\hat{F}_N \Leftarrow \sum_{pqi}\langle pi|\hat{v}|qi\rangle \left\{a_p^\dagger a_q\right\}$$

and a scalar part

$$E_0 \Leftarrow \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle$$

Definitions

The basics, Normal ordered Hamiltonian

Twobody Hamiltonian

$$
\begin{aligned}
\hat{H}_N &= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} + \sum_{pq} f_q^p \left\{a_p^\dagger a_q\right\} \\
&= \hat{V}_N + \hat{F}_N
\end{aligned}
$$

where

$$
\begin{aligned}
\hat{F}_N &= \sum_{pq} f_q^p \left\{a_p^\dagger a_q\right\} \\
\hat{V}_N &= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\}
\end{aligned}
$$

Twobody Hamiltonian

The amplitudes are given by

$$f_q^p = \langle p|\hat{h}_0|q\rangle + \sum_i \langle pi|\hat{v}|qi\rangle$$

$$\langle pq||rs\rangle = \langle pq|\hat{v}|rs\rangle$$

In relation to the Hamiltonian, $\hat{H}_N$ is given by

$$\begin{aligned}\hat{H}_N &= \hat{H} - E_0 \\ E_0 &= \langle \Phi_0|\hat{H}|\Phi_0\rangle \\ &= \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle\end{aligned}$$

where E_0 is the energy expectation value between reference states.

Topics for Week 39

Hartree-Fock theory

- Monday:
- Summary from last week
- Diagrammatic representation of operators and matrix elements
- Brief reminder on variational calculus
- Hartree-Fock theory (coordinate space, traditional approach) and mention of Thouless' theorem (no proof this week)
- Tuesday:
- Hartree-Fock theory, continues with diagrammatic interpretation
- Koopman's theorem
- Exercises 9 and 10

Diagram elements - Directed lines

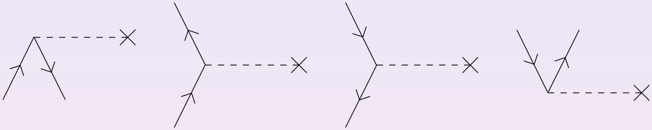
Figure: Particle line

Figure: Hole line

- A line represents a contraction between second quantized operators of the type $a_i^\dagger a_j = \delta_{ij}$ and $a_a a_b^\dagger = \delta_{ab}$.
- Hole (vacant) states are represented as downgoing lines
- Particle (virtual) states are represented as upgoing lines

Diagram elements - Onebody Hamiltonian

$$\hat{F}_N = \sum_{pq} f_q^p \left\{ a_p^\dagger a_q \right\}$$

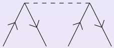


Level: -1 Level: 0 Level: 0 Level: +1

- Horisontal dashed line segment with one vertex. Assume time axis pointing upward, with the state $\langle p|$ being above the vertex and the state $|q\rangle$ being below.
- Excitation level identify the number of particle/hole pairs created by the operator.

Diagram elements - Twobody Hamiltonian

$$\hat{V}_N = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\}$$



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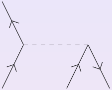

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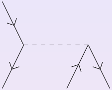

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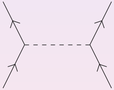

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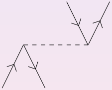

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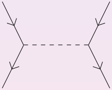

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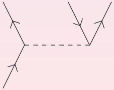
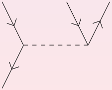
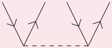


Level: +1



Level: +1



Level: +2

Diagram rules for operators

- Label all lines.
- Sum over all indices.
- For two-body operators draw dotted lines for the operator from endpoint to endpoint. Keep only topologically distinct diagrams and draw incoming and outgoing lines at every endpoint.
- Mark the lines as either holes or particles.
- Extract matrix elements from diagrams as follows: $f_{\mathrm{in}}^{\mathrm{out}}$ or $\langle \mathrm{out}|f|\mathrm{in}\rangle$, $\langle \mathrm{leftout}, \mathrm{rightout}|\hat{v}|\mathrm{leftin}, \mathrm{rightin}\rangle)$
- For the two-body operators, crossing lines (below or above the interaction line) give rise to a minus sign.
- For hole states, a hole line which goes through the whole diagram, add a minus sign.

Summary Particle-hole formalism

We defined the normal-ordered Hamiltonian wrt to the new vacuum as:

Twobody Hamiltonian

$$
\begin{aligned}
\hat{H}_N &= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} + \sum_{pq} f_q^p \left\{a_p^\dagger a_q\right\} \\
&= \hat{V}_N + \hat{F}_N
\end{aligned}
$$

where

$$
\begin{aligned}
\hat{F}_N &= \sum_{pq} f_q^p \left\{a_p^\dagger a_q\right\} \\
\hat{V}_N &= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\}
\end{aligned}
$$

How do we translate this to the standard particle-hole operators?

Summary: Particle-hole formalism

We can define

$$b_\alpha^\dagger = \begin{cases} a_\alpha^\dagger & \alpha > F \\ a_\alpha & \alpha \leq F \end{cases} \qquad b_\alpha = \begin{cases} a_\alpha & \alpha > F \\ a_\alpha^\dagger & \alpha \leq F \end{cases}$$

Summary: Particle-hole formalism

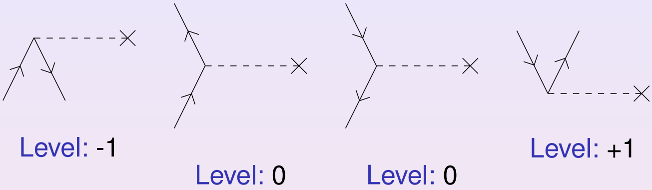
The compact notation is

$$\hat{H}_0 = \sum_{pq} \langle p|h_0|q\rangle \left\{ a_p^\dagger a_q \right\} + \sum_i \langle i|h_0|i\rangle .$$

Spelling it out we can write H_0 as

$$\begin{aligned} \hat{H}_0 &= \sum_{ab} \langle a|h_0|b\rangle b_a^\dagger b_b + \sum_{ai} \left[\langle a|h_0|i\rangle b_a^\dagger b_i^\dagger + \langle i|h_0|a\rangle b_i b_a \right] \\ &+ \sum_i \langle i|h_0|i\rangle - \sum_{ij} \langle j|h_0|i\rangle b_i^\dagger b_j \end{aligned}$$

This translates into the following diagram elements



- Horisontal dashed line segment with one vertex. Assume time axis pointing upward, with the state $\langle p|$ being above the vertex and the state $|q\rangle$ being below.
- Excitation level identify the number of particle/hole pairs created by the operator.

Summary: Particle-hole formalism

Similarly, the compact notation for the two-body operator A twobody part

$$\hat{V}_N \Leftarrow \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a^\dagger_p a^\dagger_q a_s a_r\right\}$$

A onebody part

$$\hat{F}_N \Leftarrow \sum_{pqi}\langle pi|\hat{v}|qi\rangle \left\{a^\dagger_p a_q\right\}$$

and a scalar part

$$E_0 \Leftarrow \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle$$

has its root in the particle-hole operators as:

Summary: Particle-hole formalism

$$\hat{H}_I = \hat{H}_I^{(a)} + \hat{H}_I^{(b)} + \hat{H}_I^{(c)} + \hat{H}_I^{(d)} + \hat{H}_I^{(e)}$$

Using anti-symmetrized matrix elements, the term $\hat{H}_I^{(a)}$ is

$$\hat{H}_I^{(a)} = \frac{1}{4}\sum_{abcd}\langle ab|V|cd\rangle b_a^\dagger b_b^\dagger b_d b_c$$

Particle-hole formalism

The next term $\hat{H}_I^{(b)}$ reads

$$\hat{H}_I^{(b)} = \frac{1}{2}\sum_{abci}\left(\langle ab|V|ci\rangle b_a^\dagger b_b^\dagger b_i^\dagger b_c + \langle ai|V|cb\rangle b_a^\dagger b_i b_b b_c\right)$$

This term conserves the number of quasiparticles but creates or removes a three-particle-one-hole state. For $\hat{H}_I^{(c)}$ we have

$$\begin{aligned}\hat{H}_I^{(c)} &= \frac{1}{4}\sum_{abij}\left(\langle ab|V|ij\rangle b_a^\dagger b_b^\dagger b_j^\dagger b_i^\dagger + \langle ij|V|ab\rangle b_a b_b b_j b_i\right) + \\ &\quad \sum_{abij}\langle ai|V|bj\rangle b_a^\dagger b_j^\dagger b_b b_i + \sum_{abi}\langle ai|V|bi\rangle b_a^\dagger b_b.\end{aligned}$$

Particle-hole formalism

The first line stands for the creation of a two-particle-two-hole state, while the second line represents the creation to two one-particle-one-hole pairs while the last term represents a contribution to the particle single-particle energy from the hole states, that is an interaction between the particle states and the hole states within the new vacuum state. The fourth term reads

$$
\begin{aligned}
\hat{H}_I^{(d)} \quad = \quad & \frac{1}{2}\sum_{aijk}\left(\langle ai|V|jk\rangle b_a^\dagger b_k^\dagger b_j^\dagger b_i + \langle ji|V|ak\rangle b_k^\dagger b_j b_i b_a\right) + \\
& \sum_{aij}\left(\langle ai|V|ji\rangle b_a^\dagger b_j^\dagger + \langle ji|V|ai\rangle b_j b_a\right).
\end{aligned}
$$

Particle-hole formalism

The terms in the first line stand for the creation of a particle-hole state interacting with hole states, we will label this as a two-hole-one-particle contribution. The remaining terms are a particle-hole state interacting with the holes in the vacuum state. Finally we have

$$\hat{H}_I^{(e)} = \frac{1}{4}\sum_{ijkl}\langle kl|V|ij\rangle b_i^\dagger b_j^\dagger b_l b_k - \sum_{ijk}\langle ij|V|kj\rangle b_k^\dagger b_i + \frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle$$

The first terms represents the interaction between two holes while the second stands for the interaction between a hole and the remaining holes in the vacuum state. It represents a contribution to single-hole energy to first order. The last term collects all contributions to the energy of the ground state of a closed-shell system arising from hole-hole correlations.

Topics for Week 40

Hartree-Fock theory

- Monday:
- Summary from last week
- Derivation of Hartree-Fock equations
- Koopman's theorem
- Tuesday:
- Thouless' theorem
- Stability of Hartree-Fock theory

Hartree-Fock: our first many-body approach

HF theory is an algorithm for a finding an approximative expression for the ground state of a given Hamiltonian. The basic ingredients are

- Define a single-particle basis $\{\psi_\alpha\}$ so that

$$\hat{h}^{\mathrm{HF}}\psi_\alpha = \varepsilon_\alpha\psi_\alpha$$

  with

$$\hat{h}^{\mathrm{HF}} = \hat{t} + \hat{u}_{ext} + \hat{u}^{\mathrm{HF}}$$

- where $\hat{u}^{\mathrm{HF}}$ is a single-particle potential to be determined by the HF algorithm.
- The HF algorithm means to choose $\hat{u}^{\mathrm{HF}}$ in order to have

$$\langle\hat{H}\rangle = E^{\mathrm{HF}} = \langle\Phi_0|\hat{H}|\Phi_0\rangle$$

  a local minimum with Φ_0 being the SD ansatz for the ground state.
- The variational principle ensures that $E^{\mathrm{HF}} \geq \tilde{E}_0$, $\tilde{E}_0$ the exact ground state energy.

Hartree-Fock:

Let us now compute the Hamiltonian matrix for a system consisting of a Slater determinant for the ground state $|\Phi_0\rangle$ and two 1p1h SDs $|\Phi_i^a\rangle$ and $|\Phi_j^b\rangle$. This can obviously be generalized to many more 1p1h SDs. Using diagrammatic as well as algebraic representations we obtain the following expectation values

$$\langle\Phi_0|\hat{H}|\Phi_0\rangle = E_0,$$

$$\langle\Phi_i^a|\hat{H}|\Phi_0\rangle = \langle a|\hat{f}|i\rangle,$$

$$\langle\Phi_j^b|\hat{H}|\Phi_0\rangle = \langle b|\hat{f}|j\rangle,$$

$$\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle = \langle aj|\hat{v}|ib\rangle,$$

and the diagonal elements

$$\langle\Phi_i^a|\hat{H}|\Phi_i^a\rangle = E_0 + \varepsilon_a - \varepsilon_i + \langle ai|\hat{v}|ia\rangle,$$

and

$$\langle\Phi_j^b|\hat{H}|\Phi_j^b\rangle = E_0 + \varepsilon_b - \varepsilon_j + \langle bj|\hat{v}|jb\rangle.$$

Hartree-Fock

We can then set up a Hamiltonian matrix to be diagonalized

$$\left(\begin{array}{ccc} E_0 & \langle i|\hat{f}|a\rangle & \langle j|\hat{f}|b\rangle \\ \langle a|\hat{f}|i\rangle & E_0+\varepsilon_a-\varepsilon_i+\langle ai|\hat{v}|ia\rangle & \langle aj|\hat{v}|ib\rangle \\ \langle b|\hat{f}|j\rangle & \langle bi|\hat{v}|ja\rangle & E_0+\varepsilon_b-\varepsilon_j+\langle bj|\hat{v}|jb\rangle \end{array}\right).$$

The HF method corresponds to finding a similarity transformation where the non-diagonal matrix elements

$$\langle i|\hat{f}|a\rangle = 0$$

. We will link this expectation value with the HF method, meaning that we want to find

$$\langle i|\hat{h}^{\mathrm{HF}}|a\rangle = 0$$

Variational Calculus and Lagrangian Multiplier

The calculus of variations involves problems where the quantity to be minimized or maximized is an integral.
In the general case we have an integral of the type

$$E[\Phi] = \int_a^b f(\Phi(x), \frac{\partial \Phi}{\partial x}, x) dx,$$

where E is the quantity which is sought minimized or maximized. The problem is that although f is a function of the variables Φ, $\partial\Phi/\partial x$ and x, the exact dependence of Φ on x is not known. This means again that even though the integral has fixed limits a and b, the path of integration is not known. In our case the unknown quantities are the single-particle wave functions and we wish to choose an integration path which makes the functional $E[\Phi]$ stationary. This means that we want to find minima, or maxima or saddle points. In physics we search normally for minima. Our task is therefore to find the minimum of $E[\Phi]$ so that its variation δE is zero subject to specific constraints. In our case the constraints appear as the integral which expresses the orthogonality of the single-particle wave functions. The constraints can be treated via the technique of Lagrangian multipliers

Reminder on Variational Calculus and Lagrangian Multipliers

Let us specialize to the expectation value of the energy for one particle in three-dimensions. This expectation value reads

$$E = \int dxdydz\psi^*(x,y,z)\hat{H}\psi(x,y,z),$$

with the constraint

$$\int dxdydz\psi^*(x,y,z)\psi(x,y,z) = 1,$$

and a Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla^2 + V(x,y,z).$$

I will skip the variables x, y, z below, and write for example $V(x,y,z) = V$.

Variational Calculus and Lagrangian Multiplier

The integral involving the kinetic energy can be written as, if we assume periodic boundary conditions or that the function ψ vanishes strongly for large values of x, y, z,

$$\int dxdydz\psi^* \left(-\frac{1}{2}\nabla^2\right)\psi dxdydz = \psi^*\nabla\psi| + \int dxdydz\frac{1}{2}\nabla\psi^*\nabla\psi.$$

Inserting this expression into the expectation value for the energy and taking the variational minimum we obtain

$$\delta E = \delta\left\{\int dxdydz\left(\frac{1}{2}\nabla\psi^*\nabla\psi + V\psi^*\psi\right)\right\} = 0.$$

Variational Calculus and Lagrangian Multiplier

The constraint appears in integral form as

$$\int dxdydz\psi^*\psi = \text{constant},$$

and multiplying with a Lagrangian multiplier λ and taking the variational minimum we obtain the final variational equation

$$\delta\left\{\int dxdydz\left(\frac{1}{2}\nabla\psi^*\nabla\psi + V\psi^*\psi - \lambda\psi^*\psi\right)\right\} = 0.$$

Introducing the function f

$$f = \frac{1}{2}\nabla\psi^*\nabla\psi + V\psi^*\psi - \lambda\psi^*\psi = \frac{1}{2}(\psi_x^*\psi_x + \psi_y^*\psi_y + \psi_z^*\psi_z) + V\psi^*\psi - \lambda\psi^*\psi,$$

where we have skipped the dependence on x, y, z and introduced the shorthand ψ_x, ψ_y and ψ_z for the various derivatives.

Variational Calculus and Lagrangian Multiplier

For ψ^* the Euler equation results in

$$\frac{\partial f}{\partial \psi^*} - \frac{\partial}{\partial x}\frac{\partial f}{\partial \psi_x^*} - \frac{\partial}{\partial y}\frac{\partial f}{\partial \psi_y^*} - \frac{\partial}{\partial z}\frac{\partial f}{\partial \psi_z^*} = 0,$$

which yields

$$-\frac{1}{2}(\psi_{xx} + \psi_{yy} + \psi_{zz}) + V\psi = \lambda\psi.$$

We can then identify the Lagrangian multiplier as the energy of the system. Then the last equation is nothing but the standard Schrödinger equation and the variational approach discussed here provides a powerful method for obtaining approximate solutions of the wave function.

Finding the Hartree-Fock functional $E[\Phi]$

We rewrite our Hamiltonian (we specialize to atomic physics, but the interactions can easily be changed with other one and two-body ones)

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N} \frac{Z}{r_i} + \sum_{i<j}^{N} \frac{1}{r_{ij}},$$

as

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{N} \hat{h}_o(x_i) + \sum_{i<j=1}^{N} \frac{1}{r_{ij}},$$

$$\hat{h}_0(x_i) = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}.$$

Finding the Hartree-Fock functional $E[\Phi]$

Let us denote the ground state energy by E_0. According to the variational principle we have

$$E_0 \leq E[\Phi] = \int \Phi^* \hat{H} \Phi d\tau$$

where Φ is a trial function which we assume to be normalized

$$\int \Phi^* \Phi d\tau = 1,$$

where we have used the shorthand $d\tau = dx_1 dx_2 \dots dx_N$.

Finding the Hartree-Fock functional $E[\Phi]$

In the Hartree-Fock method the trial function is the Slater determinant which can be rewritten as

$$\Psi(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \nu) = \frac{1}{\sqrt{N!}} \sum_P (-)^P P\psi_\alpha(x_1)\psi_\beta(x_2)\dots\psi_\nu(x_N) = \sqrt{N!}\mathcal{A}\Phi_H,$$

where we have introduced the anti-symmetrization operator $\mathcal{A}$ defined by the summation over all possible permutations of two fermions. It is defined as

$$\mathcal{A} = \frac{1}{N!} \sum_P (-)^P P,$$

with the the Hartree-function given by the simple product of all possible single-particle function (in case of atomic systems: two electrons for helium, four electrons for beryllium and ten for neon)

$$\Phi_H(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \nu) = \psi_\alpha(x_1)\psi_\beta(x_2)\dots\psi_\nu(x_N).$$

Finding the Hartree-Fock functional $E[\Phi]$

Both $\hat{H}_0$ and $\hat{H}_I$ are invariant under permutations of fermions, and hence commute with $\mathcal{A}$

$$[H_0, \mathcal{A}] = [H_I, \mathcal{A}] = 0.$$

Furthermore, $\mathcal{A}$ satisfies

$$\mathcal{A}^2 = \mathcal{A},$$

since every permutation of the Slater determinant reproduces it.

Variational Calculus and Lagrangian Multiplier, back to Hartree-Fock

Our functional is written (recall that we have specialized to the case of atoms) as

$$E[\Phi] = \sum_{\mu=1}^{N} \int \psi_{\mu}^{*}(x_i)\hat{h}_0(x_i)\psi_{\mu}(x_i)dx_i + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \psi_{\mu}^{*}(x_i)\psi_{\nu}^{*}(x_j)\frac{1}{r_{ij}}\psi_{\mu}(x_i)\psi_{\nu}(x_j)dx_i dx_j \right.$$

$$\left. - \int \psi_{\mu}^{*}(x_i)\psi_{\nu}^{*}(x_j)\frac{1}{r_{ij}}\psi_{\nu}(x_i)\psi_{\mu}(x_j)dx_i dx_j\right]$$

The more compact version is

$$E[\Phi] = \sum_{\mu=1}^{N}\langle\mu|\hat{h}_0|\mu\rangle + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\langle\mu\nu|\frac{1}{r_{ij}}|\mu\nu\rangle - \langle\mu\nu|\frac{1}{r_{ij}}|\nu\mu\rangle\right].$$

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

If we generalize the Euler-Lagrange equations to more variables and introduce N^2 Lagrange multipliers which we denote by $\epsilon_{\mu\nu}$, we can write the variational equation for the functional of E

$$\delta E - \sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\epsilon_{\mu\nu}\delta\int\psi_\mu^*\psi_\nu = 0.$$

For the orthogonal wave functions ψ_μ this reduces to

$$\delta E - \sum_{\mu=1}^{N}\epsilon_{\mu}\delta\int\psi_\mu^*\psi_\mu = 0.$$

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

Variation with respect to the single-particle wave functions ψ_μ yields then

$$\sum_{\mu=1}^{N}\int \delta\psi_\mu^*\hat{h}_0(x_i)\psi_\mu dx_i + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \delta\psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\psi_\mu\psi_\nu dx_i dx_j - \int \delta\psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\psi_\nu\psi_\mu dx_i dx_j\right]$$

$$+\sum_{\mu=1}^{N}\int \psi_\mu^*\hat{h}_0(x_i)\delta\psi_\mu dx_i + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\delta\psi_\mu\psi_\nu dx_i dx_j - \int \psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\psi_\nu\delta\psi_\mu dx_i dx_j\right]$$

$$-\sum_{\mu=1}^{N}E_\mu\int \delta\psi_\mu^*\psi_\mu dx_i - \sum_{\mu=1}^{N}E_\mu\int \psi_\mu^*\delta\psi_\mu dx_i =$$

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

Although the variations $\delta\psi$ and $\delta\psi^*$ are not independent, they may in fact be treated as such, so that the terms dependent on either $\delta\psi$ and $\delta\psi^*$ individually may be set equal to zero. To see this, simply replace the arbitrary variation $\delta\psi$ by $i\delta\psi$, so that $\delta\psi^*$ is replaced by $-i\delta\psi^*$, and combine the two equations. We thus arrive at the Hartree-Fock equations

$$\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \sum_{\nu=1}^{N}\int \psi_\nu^*(x_j)\frac{1}{r_{ij}}\psi_\nu(x_j)dx_j\right]\psi_\mu(x_i)$$

$$-\left[\sum_{\nu=1}^{N}\int \psi_\nu^*(x_j)\frac{1}{r_{ij}}\psi_\mu(x_j)dx_j\right]\psi_\nu(x_i) = \epsilon_\mu\psi_\mu(x_i).$$

Notice that the integration $\int dx_j$ implies an integration over the spatial coordinates $\mathbf{r_j}$ and a summation over the spin-coordinate of fermion j.

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

The two first terms are the one-body kinetic energy and the electron-nucleus potential. The third or *direct* term is the averaged electronic repulsion of the other electrons. This term is identical to the Coulomb integral introduced in the simple perturbative approach to the helium atom. As written, the term includes the 'self-interaction' of electrons when $i = j$. The self-interaction is cancelled in the fourth term, or the *exchange* term. The exchange term results from our inclusion of the Pauli principle and the assumed determinantal form of the wave-function. The effect of exchange is for electrons of like-spin to avoid each other.

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

A theoretically convenient form of the Hartree-Fock equation is to regard the direct and exchange operator defined through

$$V_{\mu}^{d}(x_i) = \int \psi_{\mu}^{*}(x_j)\frac{1}{r_{ij}}\psi_{\mu}(x_j)dx_j$$

and

$$V_{\mu}^{ex}(x_i)g(x_i) = \left(\int \psi_{\mu}^{*}(x_j)\frac{1}{r_{ij}}g(x_j)dx_j\right)\psi_{\mu}(x_i),$$

respectively.

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

The function $g(x_i)$ is an arbitrary function, and by the substitution $g(x_i) = \psi_\nu(x_i)$ we get

$$V_\mu^{ex}(x_i)\psi_\nu(x_i) = \left(\int \psi_\mu^*(x_j)\frac{1}{r_{ij}}\psi_\nu(x_j)dx_j\right)\psi_\mu(x_i).$$

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

We may then rewrite the Hartree-Fock equations as

$$\hat{h}^{HF}(x_i)\psi_\nu(x_i) = \epsilon_\nu\psi_\nu(x_i),$$

with

$$\hat{h}^{HF}(x_i) = \hat{h}_0(x_i) + \sum_{\mu=1}^{N} V_\mu^d(x_i) - \sum_{\mu=1}^{N} V_\mu^{ex}(x_i),$$

and where $\hat{h}_0(i)$ is the one-body part. The latter is normally chosen as a part which yields solutions in closed form. The harmonic oscilltor is a classical problem thereof. We normally rewrite the last equation as

$$\hat{h}^{HF}(x_i) = \hat{h}_0(x_i) + \hat{u}^{HF}(x_i).$$

Rewriting the energy functional

The last equation

$$\hat{h}^{HF}(x_i) = \hat{h}_0(x_i) + \hat{u}^{HF}(x_i),$$

allows us to rewrite the ground state energy (adding and subtracting $\hat{u}^{HF}(x_i)$)

$$E_0^{HF} = \langle \Phi_0|\hat{H}|\Phi_0\rangle = \sum_{i\le F}^{N}\langle i|\hat{h}_0 + \hat{u}^{HF}|j\rangle + \frac{1}{2}\sum_{i\le F}^{N}\sum_{j\le F}^{N}\left[\langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle\right] - \sum_{i\le F}^{N}\langle i|\hat{u}^{HF}|i\rangle,$$

as

$$E_0^{HF} = \sum_{i\le F}^{N}\varepsilon_i + \frac{1}{2}\sum_{i\le F}^{N}\sum_{j\le F}^{N}\left[\langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle\right] - \sum_{i\le F}^{N}\langle i|\hat{u}^{HF}|i\rangle,$$

which is nothing but

$$E_0^{HF} = \sum_{i\le F}^{N}\varepsilon_i - \frac{1}{2}\sum_{i\le F}^{N}\sum_{j\le F}^{N}\left[\langle ij|\hat{v}|ij\rangle - \langle ij|\hat{v}|ji\rangle\right].$$

This form will be used in our discussion of Koopman's theorem.

Hartree-Fock by varying the coefficients of a wave function expansion

Another possibility is to expand the single-particle functions in a known basis and vary the coefficients, that is, the new single-particle wave function is written as a linear expansion in terms of a fixed chosen orthogonal basis (for example harmonic oscillator, Laguerre polynomials etc)

$$\psi_a = \sum_{\lambda} C_{a\lambda}\psi_{\lambda}. \tag{7.0.1}$$

In this case we vary the coefficients $C_{a\lambda}$. If the basis has infinitely many solutions, we need to truncate the above sum. In all our equations we assume a truncation has been made.

The single-particle wave functions $\psi_{\lambda}(\mathbf{r})$, defined by the quantum numbers λ and $\mathbf{r}$ are defined as the overlap

$$\psi_{\lambda}(\mathbf{r}) = \langle \mathbf{r}|\lambda\rangle.$$

Hartree-Fock by varying the coefficients of a wave function expansion

We will omit the radial dependence of the wave functions and introduce first the following shorthands for the Hartree and Fock integrals

$$\langle \mu\nu|V|\mu\nu\rangle = \int \psi_\mu^*(\mathbf{r}_i)\psi_\nu^*(\mathbf{r}_j)V(r_{ij})\psi_\mu(\mathbf{r}_i)\psi_\nu(\mathbf{r}_j)d\mathbf{r}_i\mathbf{r}_j,$$

and

$$\langle \mu\nu|V|\nu\mu\rangle = \int \psi_\mu^*(\mathbf{r}_i)\psi_\nu^*(\mathbf{r}_j)V(r_{ij})\psi_\nu(\mathbf{r}_i)\psi_\mu(\mathbf{r}_i)d\mathbf{r}_i\mathbf{r}_j.$$

Hartree-Fock by varying the coefficients of a wave function expansion

Since the interaction is invariant under the interchange of two particles it means for example that we have

$$\langle \mu\nu|V|\mu\nu\rangle = \langle \nu\mu|V|\nu\mu\rangle,$$

or in the more general case

$$\langle \mu\nu|V|\sigma\tau\rangle = \langle \nu\mu|V|\tau\sigma\rangle.$$

Hartree-Fock by varying the coefficients of a wave function expansion

The direct and exchange matrix elements can be brought together if we define the antisymmetrized matrix element

$$\langle \mu\nu|V|\mu\nu\rangle_{AS} = \langle \mu\nu|V|\mu\nu\rangle - \langle \mu\nu|V|\nu\mu\rangle,$$

or for a general matrix element

$$\langle \mu\nu|V|\sigma\tau\rangle_{AS} = \langle \mu\nu|V|\sigma\tau\rangle - \langle \mu\nu|V|\tau\sigma\rangle.$$

It has the symmetry property

$$\langle \mu\nu|V|\sigma\tau\rangle_{AS} = -\langle \mu\nu|V|\tau\sigma\rangle_{AS} = -\langle \nu\mu|V|\sigma\tau\rangle_{AS}.$$

The antisymmetric matrix element is also hermitian, implying

$$\langle \mu\nu|V|\sigma\tau\rangle_{AS} = \langle \sigma\tau|V|\mu\nu\rangle_{AS}.$$

Hartree-Fock by varying the coefficients of a wave function expansion

With these notations we rewrite the Hartree-Fock functional as

$$\int \Phi^* \hat{H}_1 \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^{A} \sum_{\nu=1}^{A} \langle \mu\nu | V | \mu\nu \rangle_{AS}. \tag{7.0.2}$$

Combining Eqs. (2.0.13) and (7.0.2) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^{N} \langle \mu | h | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \langle \mu\nu | V | \mu\nu \rangle_{AS}. \tag{7.0.3}$$

Hartree-Fock by varying the coefficients of a wave function expansion

If we vary the above energy functional with respect to the basis functions $|\mu\rangle$, this corresponds to what was done in the previous case. We are however interested in defining a new basis defined in terms of a chosen basis as defined in Eq. (7.0.1). We can then rewrite the energy functional as

$$E[\Psi] = \sum_{a=1}^{N} \langle a|h|a\rangle + \frac{1}{2}\sum_{ab=1}^{N} \langle ab|V|ab\rangle_{AS}, \tag{7.0.4}$$

where Ψ is the new Slater determinant defined by the new basis of Eq. (7.0.1).

Hartree-Fock by varying the coefficients of a wave function expansion

Using Eq. (7.0.1) we can rewrite Eq. (7.0.4) as

$$E[\Psi] = \sum_{a=1}^{N} \sum_{\alpha\beta} C^*_{a\alpha} C_{a\beta} \langle \alpha | h | \beta \rangle + \frac{1}{2} \sum_{ab=1}^{N} \sum_{\alpha\beta\gamma\delta} C^*_{a\alpha} C^*_{b\beta} C_{a\gamma} C_{b\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \quad (7.0.5)$$

Hartree-Fock by varying the coefficients of a wave function expansion

We wish now to minimize the above functional. We introduce again a set of Lagrange multipliers, noting that since $\langle a|b\rangle = \delta_{a,b}$ and $\langle\alpha|\beta\rangle = \delta_{\alpha,\beta}$, the coefficients $C_{a\gamma}$ obey the relation

$$\langle a|b\rangle = \delta_{a,b} = \sum_{\alpha\beta} C^*_{a\alpha} C_{a\beta} \langle\alpha|\beta\rangle = \sum_{\alpha} C^*_{a\alpha} C_{a\alpha},$$

which allows us to define a functional to be minimized that reads

$$E[\Psi] - \sum_{a=1}^{N} \epsilon_a \sum_{\alpha} C^*_{a\alpha} C_{a\alpha}. \qquad (7.0.6)$$

Hartree-Fock by varying the coefficients of a wave function expansion

Minimizing with respect to $C^*_{k\alpha}$, remembering that $C^*_{k\alpha}$ and $C_{k\alpha}$ are independent, we obtain

$$\frac{d}{dC^*_{k\alpha}}\left[E[\Psi]-\sum_a \epsilon_a \sum_\alpha C^*_{a\alpha}C_{a\alpha}\right]=0, \qquad (7.0.7)$$

which yields for every single-particle state k the following Hartree-Fock equations

$$\sum_\gamma C_{k\gamma}\langle\alpha|h|\gamma\rangle+\sum_{a=1}^{N}\sum_{\beta\gamma\delta} C^*_{a\beta}C_{a\delta}C_{k\gamma}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}=\epsilon_k C_{k\alpha}. \qquad (7.0.8)$$

Hartree-Fock by varying the coefficients of a wave function expansion

We can rewrite this equation as

$$\sum_{\gamma}\left\{\langle\alpha|h|\gamma\rangle+\sum_{a}^{N}\sum_{\beta\delta}C^{*}_{a\beta}C_{a\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}\right\}C_{k\gamma}=\epsilon_{k}C_{k\alpha}. \tag{7.0.9}$$

Note that the sums over greek indices run over the number of basis set functions (in principle an infinite number).

Hartree-Fock by varying the coefficients of a wave function expansion

Defining

$$h_{\alpha\gamma}^{HF} = \langle\alpha|h|\gamma\rangle + \sum_{a=1}^{N}\sum_{\beta\delta} C_{a\beta}^{*}C_{a\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS},$$

we can rewrite the new equations as

$$\sum_{\gamma} h_{\alpha\gamma}^{HF}C_{k\gamma} = \epsilon_k C_{k\alpha}. \tag{7.0.10}$$

Note again that the sums over greek indices run over the number of basis set functions (in principle an infinite number).

We wish now to derive the Hartree-Fock equations using our second-quantized formalism and study the stability of the equations. Our SD ansatz for the ground state of the system is approximated as

$$|\Phi_0\rangle = |c\rangle = a_i^\dagger a_j^\dagger \dots a_l^\dagger |0\rangle.$$

We wish to determine $\hat{u}^{HF}$ so that $E_0^{HF} = \langle c|\hat{H}|c\rangle$ becomes a local minimum. An arbitrary Slater determinant $|c'\rangle$ which is not orthogonal to a determinant $|c\rangle = \prod_{i=1}^{n} a_i^\dagger |0\rangle$, can be written as

$$|c'\rangle = exp\left\{\sum_{a>F}^{\infty}\sum_{i\le F} C_{ai} a_a^\dagger a_i\right\}|c\rangle$$

Thouless' theorem

An arbitrary Slater determinant $|c'\rangle$ which is not orthogonal to a determinant $|c\rangle = \prod_{i=1}^{n} a^\dagger_{\alpha_i}|0\rangle$, can be written as

$$|c'\rangle = exp\left\{\sum_{a>F}\sum_{i\le F} C_{ai} a^\dagger_a a_i\right\}|c\rangle$$

Proof: see blackboard.

Stability of the Hartree-Fock equations

The variational condition for deriving the Hartree-Fock equations guarantees only that the expectation value $\langle c|\hat{H}|c\rangle$ has an extreme value, not necessarily a minimum. To figure out whether the extreme value we have found is a minimum, we can use second quantization to analyze our results and find a criterion for the above expectation value to a local minimum. We will use Thouless' theorem and show that

$$\frac{\langle c'|\hat{H}|c'\rangle}{\langle c'|c'\rangle} \geq \langle c|\hat{H}|c\rangle = E_0,$$

with

$$|c'\rangle = |c\rangle + |\delta c\rangle.$$

Using Thouless' theorem we can write out $|c'\rangle$ as

$$|c'\rangle = exp\left\{\sum_{a>F}\sum_{i\leq F}\delta C_{ai}a_a^{\dagger}a_i\right\}|c\rangle =$$

$$\left\{1 + \sum_{a>F}\sum_{i\leq F}\delta C_{ai}a_a^{\dagger}a_i + \frac{1}{2!}\sum_{ab>F}\sum_{ij\leq F}\delta C_{ai}\delta C_{bj}a_a^{\dagger}a_i a_b^{\dagger}a_j + \dots\right\}$$

where the amplitudes δC are small.

Stability of the Hartree-Fock equations

The norm of $|c'\rangle$ is given by (using the intermediate normalization condition $\langle c'|c\rangle = 1$)

$$\langle c'|c'\rangle = 1 + \sum_{a>F}\sum_{i\le F}|\delta C_{ai}|^2 + O(\delta C_{ai}^3).$$

The expectation value for the energy is now given by (using the Hartree-Fock condition)

$$\langle c'|\hat{H}|c'\rangle = \langle c|\hat{H}|c\rangle + \sum_{ab>F}\sum_{ij\le F}\delta C_{ai}^*\delta C_{bj}\langle c|a_i^\dagger a_a\hat{H}a_b^\dagger a_j|c\rangle +$$

$$\frac{1}{2!}\sum_{ab>F}\sum_{ij\le F}\delta C_{ai}\delta C_{bj}\langle c|\hat{H}a_a^\dagger a_i a_b^\dagger a_j|c\rangle + \frac{1}{2!}\sum_{ab>F}\sum_{ij\le F}\delta C_{ai}^*\delta C_{bj}^*\langle c|a_j^\dagger a_b a_i^\dagger a_a\hat{H}|c\rangle + \dots$$

We will skip higher-order terms later.

Stability of the Hartree-Fock equations

We have already calculated the second term on the rhs of the previous equation

$$\langle c| \left(\left\{ a_i^\dagger a_a \right\} \widehat{H} \left\{ a_b^\dagger a_j \right\} \right) |c\rangle =$$

$$\sum_{pq} \sum_{ijab} \delta C_{ai}^* \delta C_{bj} \langle p|\hat{h}_0|q\rangle \langle c| \left(\left\{ a_i^\dagger a_a \right\} \left\{ a_p^\dagger a_q \right\} \left\{ a_b^\dagger a_j \right\} \right) |c\rangle +$$

$$\frac{1}{4} \sum_{pqrs} \sum_{ijab} \delta C_{ai}^* \delta C_{bj} \langle pq|\hat{v}|rs\rangle \langle c| \left(\left\{ a_i^\dagger a_a \right\} \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \left\{ a_b^\dagger a_j \right\} \right) |c\rangle,$$

resulting in

$$E_0 \sum_{ai} |\delta C_{ai}|^2 + \sum_{ai} |\delta C_{ai}|^2 (\varepsilon_a - \varepsilon_i) - \sum_{ijab} \langle aj|\hat{v}|bi\rangle \delta C_{ai}^* \delta C_{bj}.$$

Stability of the Hartree-Fock equations

The third term in the rhs of the last equation can then be written out (where is the reference energy and why do we only consider the two-particle interaction $\hat{V}_N$?)

$$
\begin{aligned}
&\frac{1}{2!}\langle c|\left(\widehat{V}_N\left\{a_a^\dagger a_i\right\}\left\{a_b^\dagger a_j\right\}\right)|c\rangle = \\
&\quad \frac{1}{8}\sum_{pqrs}\sum_{ijab}\delta C_{ai}\delta C_{bj}\langle pq|\hat{v}|rs\rangle\langle c|\left(\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}\left\{a_a^\dagger a_i\right\}\left\{a_b^\dagger a_j\right\}\right)|c\rangle \\
&= \frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq|\hat{v}|rs\rangle\delta C_{ai}\delta C_{bj}\langle c| \\
&\quad \left(\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\}\right. \\
&\quad \left. + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\}\right)|c\rangle \\
&= \frac{1}{2}\sum_{ijab}\langle ij|\hat{v}|ab\rangle\delta C_{ai}\delta C_{bj}
\end{aligned}
$$

Stability of the Hartree-Fock equations

The final term in the rhs of the last equation can then be written out as

$$\frac{1}{2!}\langle c|\left(\left\{a_j^\dagger a_b\right\}\left\{a_i^\dagger a_a\right\}\widehat{V}_N\right)|c\rangle = \frac{1}{2!}\langle c|\left(\widehat{V}_N\left\{a_a^\dagger a_i\right\}\left\{a_b^\dagger a_j\right\}\right)^\dagger|c\rangle$$

which is nothing but

$$\frac{1}{2!}\langle c|\left(\widehat{V}_N\left\{a_a^\dagger a_i\right\}\left\{a_b^\dagger a_j\right\}\right)|c\rangle^* = \frac{1}{2}\sum_{ijab}(\langle ij|\hat{v}|ab\rangle)^*\delta C_{ai}^*\delta C_{bj}^*$$

or

$$\frac{1}{2}\sum_{ijab}(\langle ab|\hat{v}|ij\rangle)\delta C_{ai}^*\delta C_{bj}^*$$

where we have used the relation

$$\langle a|\hat{A}|b\rangle = (\langle b|\hat{A}^\dagger|a\rangle)^*$$

due to the hermiticity of $\hat{H}$ and $\hat{V}$.

Stability of the Hartree-Fock equations

We define two matrix elements

$$A_{ai,bj} = -\langle aj|\hat{v}|bi\rangle$$

$$B_{ai,bj} = \langle ab|\hat{v}|ij\rangle$$

both being anti-symmetrized.

Stability of the Hartree-Fock equations

We can then write out the energy

$$\langle c'|H|c'\rangle = \left(1 + \sum_{ai}|\delta C_{ai}|^2\right)\langle c|H|c\rangle +$$

$$\sum_{ai}|\delta C_{ai}|^2(\varepsilon_a^{HF} - \varepsilon_i^{HF}) + \sum_{ijab} A_{ai,bj}\delta C_{ai}^*\delta C_{bj} +$$

$$\frac{1}{2}\sum_{ijab} B_{ai,bj}^*\delta C_{ai}\delta C_{bj} + \frac{1}{2}\sum_{ijab} B_{ai,bj}\delta C_{ai}^*\delta C_{bj}^* + O(\delta C_{ai}^3),$$

which allows us to rewrite it as

$$\langle c'|H|c'\rangle = \left(1 + \sum_{ai}|\delta C_{ai}|^2\right)\langle c|H|c\rangle + \Delta E + O(\delta C_{ai}^3),$$

and skipping higher-order terms we have

$$\frac{\langle c'|\hat{H}|c'\rangle}{\langle c'|c'\rangle} = E_0 + \frac{\Delta E}{\left(1 + \sum_{ai}|\delta C_{ai}|^2\right)}.$$

Stability of the Hartree-Fock equations

We have defined

$$\Delta E = \frac{1}{2}\langle\chi|\hat{M}|\chi\rangle$$

with the vectors

$$\chi = [\delta C \quad \delta C^*]^T$$

and the matrix

$$\hat{M} = \begin{pmatrix} \Delta + A & B \\ B^* & \Delta + A^* \end{pmatrix},$$

with $\Delta_{ai,bj} = (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ij}$.

Stability of the Hartree-Fock equations

The condition

$$\Delta E = \frac{1}{2}\langle\chi|\hat{M}|\chi\rangle \geq 0$$

for an arbitrary vector

$$\chi = [\delta C \quad \delta C^*]^T$$

means that all eigenvalues of the matrix have to be larger than or equal zero. A necessary (but no sufficient) condition is that the matrix elements (for all *ai*)

$$(\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ij} + A_{ai,bj} \geq 0.$$

This equation can be used as a first test of the stability of the Hartree-Fock equation.

Koopman's theorem and interpretation of the Hartree-Fock energies, nuclear physics example

We have defined

$$E[\Phi^{\mathrm{HF}}(A)] = \sum_{i=1}^{A}\langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij=1}^{A}\langle ij|V|ij\rangle_{AS},$$

where $\Phi^{\mathrm{HF}}(A)$ is the new Slater determinant defined by the new basis of Eq. (7.0.1) for A nucleons. If we assume that the single-particle wave functions in the new basis do not change from a nucleus with A nucleons to a nucleus with $A-1$ nucleons, we can then define the corresponding energy for the $A-1$ systems as

$$E[\Phi^{\mathrm{HF}}(A-1)] = \sum_{i=1;i\neq k}^{A}\langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij=1;i,j\neq k}^{A}\langle ij|V|ij\rangle_{AS},$$

where we have removed a single-particle state $k \le F$, that is a state below the Fermi level.

Koopman's theorem and interpretation of the Hartree-Fock energies

Calculating the difference

$$E[\Phi^{\mathrm{HF}}(A)] - E[\Phi^{\mathrm{HF}}(A-1)] = \langle k|\hat{h}_0|k\rangle + \frac{1}{2}\sum_{i=1;i\neq k}^{A}\langle ik|V|ik\rangle_{AS}\frac{1}{2}\sum_{j=1;j\neq k}^{A}\langle kj|V|kj\rangle_{AS},$$

which becomes

$$E[\Phi^{\mathrm{HF}}(A)] - E[\Phi^{\mathrm{HF}}(A-1)] = \langle k|\hat{h}_0|k\rangle + \frac{1}{2}\sum_{j=1}^{A}\langle kj|V|kj\rangle_{AS}$$

which is just our definition of the Hartree-Fock single-particle energy

$$E[\Phi^{\mathrm{HF}}(A)] - E[\Phi^{\mathrm{HF}}(A-1)] = \epsilon_k^{\mathrm{HF}}$$

Koopman's theorem and interpretation of the Hartree-Fock energies

Similarly, we can now compute the difference (recall that the single-particle states $abcd > F$)

$$E[\Phi^{\mathrm{HF}}(A+1)] - E[\Phi^{\mathrm{HF}}(A)] = \epsilon_a^{\mathrm{HF}}.$$

This equation and the one on the previous slide, are linked to Koopman's theorem. In atomic physics it is used to define the electron ionization or affinity energies. Koopman's theorem states that the ionization energy of closed-shell systems is given by the energy of the highest occupied single-particle state. In nuclear physics, the binding energy differences

$$BE(A) - BE(A-1) \quad \text{and} \quad BE(A+1) - BE(A),$$

define the so-called separation energies. We see that the Hartree-Fock single-particle energies can be used to define separation energies. We have thus our first link between nuclear forces (included in the potential energy term) and possible observables.

Koopman's theorem and interpretation of the Hartree-Fock energies

We have thus the following interpretations (if the single-particle field do not change)

$$BE(A) - BE(A-1) \approx E[\Phi^{\mathrm{HF}}(A)] - E[\Phi^{\mathrm{HF}}(A-1)] = \epsilon_k^{\mathrm{HF}},$$

and

$$BE(A+1) - BE(A) \approx E[\Phi^{\mathrm{HF}}(A+1)] - E[\Phi^{\mathrm{HF}}(A)] = \epsilon_a^{\mathrm{HF}}.$$

If we use the ^{16}O as our closed-shell nucleus, we could then interpret the separation energy

$$BE(^{16}\mathrm{O}) - BE(^{15}\mathrm{O}) \approx \epsilon_{0p^{\nu}_{1/2}}^{\mathrm{HF}},$$

and

$$BE(^{16}\mathrm{O}) - BE(^{15}\mathrm{N}) \approx \epsilon_{0p^{\pi}_{1/2}}^{\mathrm{HF}}.$$

Koopman's theorem and interpretation of the Hartree-Fock energies

Similalry, we could interpret

$$BE(^{17}\mathrm{O}) - BE(^{16}\mathrm{O}) \approx \epsilon^{\mathrm{HF}}_{0d^{\nu}_{5/2}},$$

and

$$BE(^{17}\mathrm{F}) - BE(^{16}\mathrm{O}) \approx \epsilon^{\mathrm{HF}}_{0d^{\pi}_{5/2}}.$$

We can continue like this for all $A \pm 1$ nuclei where A is a good closed-shell (or subshell closure) nucleus. Examples are ^{4}He, ^{22}O, ^{24}O, ^{40}Ca, ^{48}Ca, ^{52}Ca, ^{54}Ca, ^{56}Ni, ^{68}Ni, ^{78}Ni, ^{90}Zr, ^{88}Sr, ^{100}Sn, ^{132}Sn and ^{208}Pb, to mention some possile cases.

We see thus that we can make our first interpretation of the separation energies in terms of the simplest possible many-body theory.

Koopman's theorem and interpretation of the Hartree-Fock energies

If we also recall the so-called energy gap for neutrons (or protons) defined as

$$\Delta S_n = 2BE(N,Z) - BE(N-1,Z) - BE(N+1,Z),$$

for neutrons and the corresponding gap for protons

$$\Delta S_p = 2BE(N,Z) - BE(N,Z-1) - BE(N,Z+1),$$

we can define the neutron and proton energy gaps for ^{16}O as

$$\Delta S_{\nu} = \epsilon^{\mathrm{HF}}_{0d^{\nu}_{5/2}} - \epsilon^{\mathrm{HF}}_{0p^{\nu}_{1/2}},$$

and

$$\Delta S_{\pi} = \epsilon^{\mathrm{HF}}_{0d^{\pi}_{5/2}} - \epsilon^{\mathrm{HF}}_{0p^{\pi}_{1/2}}.$$

Topics for Week 41

The electron gas in three dimensions and begin configuration interaction theory

- Monday:
- Summary from last week and discussion of the first midterm project
- Discussion of the electron gas, computing the Hartree-Fock energy
- Calculating the total energy for the electron gas
- Tuesday:
- Calculating the total energy for the electron gas

Topics for Week 42

Configuration Interaction theory and Perturbation theory

- Monday:
- Computing the energy of the electron gas and discussion of the midterm project
- Tuesday:
- Finalizing the electron gas and discussion of the midterm project

The electron gas

The electron gas is perhaps the only realistic model of a system of many interacting particles that allows for a solution of the Hartree-Fock equations on a closed form. Furthermore, to first order in the interaction, one can also compute on a closed form the total energy and several other properties of a many-particle systems. The model gives a very good approximation to the properties of valence electrons in metals. The assumptions are

- System of electrons that is not influenced by external forces except by an attraction provided by a uniform background of ions. These ions give rise to a uniform background charge. The ions are stationary.
- The system as a whole is neutral.
- We assume we have N_e electrons in a cubic box of length L and volume $\Omega = L^3$. This volume contains also a uniform distribution of positive charge with density $N_e e/\Omega$.

The electron gas

This is a homogeneous system and the one-particle wave functions are given by plane wave functions normalized to a volume Ω for a box with length L (the limit $L \rightarrow \infty$ is to be taken after we have computed various expectation values)

$$\psi_{\mathbf{k}\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp\left(i\mathbf{k}\mathbf{r}\right)\xi_\sigma$$

where $\mathbf{k}$ is the wave number and ξ_σ is a spin function for either spin up or down

$$\xi_{\sigma=+1/2} = \left(\begin{array}{c} 1 \\ 0 \end{array}\right) \qquad \xi_{\sigma=-1/2} = \left(\begin{array}{c} 0 \\ 1 \end{array}\right).$$

We assume that we have periodic boundary conditions which limit the allowed wave numbers to

$$k_i = \frac{2\pi n_i}{L} \qquad i = x, y, z \qquad n_i = 0, \pm 1, \pm 2, \dots$$

We assume first that the electrons interact via a central, symmetric and translationally invariant interaction $V(r_{12})$ with $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The interaction is spin independent.
The total Hamiltonian consists then of kinetic and potential energy

$$\hat{H} = \hat{T} + \hat{V}.$$

The operator for the kinetic energy can be written as

$$\hat{T} = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma}.$$

The electron gas

The Hamilton operator is given by

$$\hat{H} = \hat{H}_{el} + \hat{H}_b + \hat{H}_{el-b},$$

with the electronic part

$$\hat{H}_{el} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu|\mathbf{r}_i - \mathbf{r}_j|}}{|\mathbf{r}_i - \mathbf{r}_j|},$$

where we have introduced an explicit convergence factor (the limit $\mu \to 0$ is performed after having calculated the various integrals). Correspondingly, we have

$$\hat{H}_b = \frac{e^2}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}') e^{-\mu|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|},$$

which is the energy contribution from the positive background charge with density $n(\mathbf{r}) = N/\Omega$. Finally,

$$\hat{H}_{el-b} = -\frac{e^2}{2} \sum_{i=1}^{N} \int d\mathbf{r} \frac{n(\mathbf{r}) e^{-\mu|\mathbf{r} - \mathbf{x}_i|}}{|\mathbf{r} - \mathbf{x}_i|},$$

is the interaction between the electrons and the positive background.

The electron gas

In exercise 18 we show that the Hartree-Fock energy can be written as

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2}{\Omega^2} \sum_{k' \leq k_F} \int d\mathbf{r} e^{i(\mathbf{k'}-\mathbf{k})\mathbf{r}} \int d\mathbf{r'} \frac{e^{i(\mathbf{k}-\mathbf{k'})\mathbf{r'}}}{|\mathbf{r}-\mathbf{r'}|}$$

resulting in

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2 k_F}{2\pi} \left[2 + \frac{k_F^2 - k^2}{k k_F} ln \left| \frac{k + k_F}{k - k_F} \right| \right]$$

The electron gas

We introduce a convergence factor $e^{-\mu|\boldsymbol{r}-\boldsymbol{r'}|}$ and use $\sum_{\boldsymbol{k}} \rightarrow \frac{\Omega}{(2\pi)^3}\int d\boldsymbol{k}$. The results can be rewritten in terms of the density

$$n = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3},$$

where $n = N_e/\Omega$, N_e being the number of electrons, and r_s is the radius of a sphere which represents the volum per conducting electron. It can be convenient to use the Bohr radius $a_0 = \hbar^2/e^2 m_e$. For most metals we have a relation $r_s/a_0 \sim 2-6$.

The electron gas, total energy (Exercise 19)

We wish to show first that

$$\hat{H}_b = \frac{e^2}{2}\frac{N_e^2}{\Omega}\frac{4\pi}{\mu^2},$$

and

$$\hat{H}_{el-b} = -e^2\frac{N_e^2}{\Omega}\frac{4\pi}{\mu^2}.$$

And then that the final Hamiltonian can be written as

$$H = H_0 + H_I,$$

with

$$H_0 = \sum_{\mathbf{k}\sigma}\frac{\hbar^2 k^2}{2m_e}a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma},$$

and

$$H_I = \frac{e^2}{2\Omega}\sum_{\sigma_1\sigma_2}\sum_{\mathbf{q}\neq 0,\mathbf{k},\mathbf{p}}\frac{4\pi}{q^2}a^\dagger_{\mathbf{k}+\mathbf{q},\sigma_1}a^\dagger_{\mathbf{p}-\mathbf{q},\sigma_2}a_{\mathbf{p}\sigma_2}a_{\mathbf{k}\sigma_1}.$$

The electron gas, total energy

Finally, we want to calculate $E_0/N_e = \langle\Phi_0|H|\Phi_0\rangle/N_e$ for for this system to first order in the interaction. Using

$$\rho = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_0^3},$$

with $\rho = N_e/\Omega$, r_0 being the radius of a sphere representing the volume an electron occupies and the Bohr radius $a_0 = \hbar^2/e^2 m$, that the energy per electron can be written as

$$E_0/N_e = \frac{e^2}{2a_0}\left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s}\right].$$

Here we have defined $r_s = r_0/a_0$ to be a dimensionless quantity.

The electron gas, total energy

Let us now calculate the following part of the Hamiltonian

$$\hat{H}_b = \frac{e^2}{2} \iint \frac{n(\boldsymbol{r})n(\boldsymbol{r}')e^{-\mu|\boldsymbol{r}-\boldsymbol{r}'|}}{|\boldsymbol{r}-\boldsymbol{r}'|} \,\mathrm{d}^3\boldsymbol{r}\,\mathrm{d}^3\boldsymbol{r}',$$

where $n(\boldsymbol{r}) = N_e/\Omega$, the density of the positive backgroun charge. We define $\boldsymbol{r}_{12} = \boldsymbol{r} - \boldsymbol{r}'$, reulting in $\mathrm{d}^3\boldsymbol{r}_{12} = \mathrm{d}^3 r$, and allowing us to rewrite the integral as

$$\hat{H}_b = \frac{e^2 N_e^2}{2\Omega^2} \iint \frac{e^{-\mu|\boldsymbol{r}_{12}|}}{|\boldsymbol{r}_{12}|} \,\mathrm{d}^3\boldsymbol{r}_{12}\,\mathrm{d}^3\boldsymbol{r}' = \frac{e^2 N_e^2}{2\Omega} \int \frac{e^{-\mu|\boldsymbol{r}_{12}|}}{|\boldsymbol{r}_{12}|} \,\mathrm{d}^3\boldsymbol{r}_{12}.$$

Here we have used that $\int \mathrm{d}^3\boldsymbol{r} = \Omega$. We change to spherical coordinates and the lack of angle dependencies yields a factor 4π, resulting in

$$\hat{H}_b = \frac{4\pi e^2 N_e^2}{2\Omega} \int_0^\infty r e^{-\mu r} \,\mathrm{d}r.$$

The electron gas, total energy

Solving by partial integration

$$\int_0^\infty re^{-\mu r}\,\mathrm{d}r = \left[-\frac{r}{\mu}e^{-\mu r}\right]_0^\infty + \frac{1}{\mu}\int_0^\infty e^{-\mu r}\,\mathrm{d}r = \frac{1}{\mu}\left[-\frac{1}{\mu}e^{-\mu r}\right]_0^\infty = \frac{1}{\mu^2},$$

gives

$$\hat{H}_b = \frac{e^2}{2}\frac{N_e^2}{\Omega}\frac{4\pi}{\mu^2}.$$

The next term is

$$\hat{H}_{el-b} = -e^2\sum_{i=1}^{N}\int \frac{n(\boldsymbol{r})e^{-\mu|\boldsymbol{r}-\boldsymbol{x}_i|}}{|\boldsymbol{r}-\boldsymbol{x}_i|}\,\mathrm{d}^3\boldsymbol{r}.$$

Inserting $n(\boldsymbol{r})$ and changing variables in the same way as in the previous integral $\boldsymbol{y} = \boldsymbol{r} - \boldsymbol{x}_i$, we get $\mathrm{d}^3\boldsymbol{y} = \mathrm{d}^3\boldsymbol{r}$. This gives

$$\hat{H}_{el-b} = -\frac{e^2 N_e}{\Omega}\sum_{i=1^N}\int \frac{e^{-\mu|\boldsymbol{y}|}}{|\boldsymbol{y}|}\,\mathrm{d}^3\boldsymbol{y} = -\frac{4\pi e^2 N_e}{\Omega}\sum_{i=1}^{N}\int_0^\infty ye^{-\mu y}\mathrm{d}y.$$

We have already seen this type of integral. The answer is

$$\hat{H}_{el-b} = -\frac{4\pi e^2 N_e}{\Omega}\sum_{i=1}^{N}\frac{1}{\mu^2},$$

which gives

$$\hat{H}_{el-b} = -e^2\frac{N_e^2}{\Omega}\frac{4\pi}{\mu^2}.$$

The electron gas, total energy

Finally, we need to evaluate $\hat{H}_{el}$. This term reads

$$\hat{H}_{el} = \sum_{i=1}^{N_e} \frac{\hat{\boldsymbol{p}}_i^2}{2m_e} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu|\boldsymbol{r}_i - \boldsymbol{r}_j|}}{\boldsymbol{r}_i - \boldsymbol{r}_j}.$$

The last term represents the repulsion between two electrons. It is a central symmetric interaction and is translationally invariant. The potential is given by the expression

$$v(|\boldsymbol{r}|) = e^2 \frac{e^{\mu|\boldsymbol{r}|}}{|\boldsymbol{r}|},$$

which we derived last week in connection with the Hartree-Fock derivation.

The electron gas, total energy

The results becomes

$$\int v(|\boldsymbol{r}|)e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\,\mathrm{d}^3\boldsymbol{r} = e^2\int \frac{e^{\mu|\boldsymbol{r}|}}{|\boldsymbol{r}|}e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\,\mathrm{d}^3\boldsymbol{r} = e^2\frac{4\pi}{\mu^2+q^2},$$

which gives us

$$\begin{aligned}\hat{H}_{el} &= \sum_{\boldsymbol{k}\sigma}\frac{\hbar^2k^2}{2m}\hat{a}^\dagger_{\boldsymbol{k}\sigma}\hat{a}_{\boldsymbol{k}\sigma} + \frac{e^2}{2\Omega}\sum_{\sigma\sigma'}\sum_{\boldsymbol{kpq}}\frac{4\pi}{\mu^2+q^2}\hat{a}^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma}\hat{a}^\dagger_{\boldsymbol{p}-\boldsymbol{q},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma}\\ &= \sum_{\boldsymbol{k}\sigma}\frac{\hbar^2k^2}{2m_e}\hat{a}^\dagger_{\boldsymbol{k}\sigma}\hat{a}_{\boldsymbol{k}\sigma} + \frac{e^2}{2\Omega}\sum_{\sigma\sigma'}\sum_{\substack{\boldsymbol{kpq}\\ q\neq 0}}\frac{4\pi}{q^2}\hat{a}^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma}\hat{a}^\dagger_{\boldsymbol{p}-\boldsymbol{q},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma}+\\ &\quad\frac{e^2}{2\Omega}\sum_{\sigma\sigma'}\sum_{\boldsymbol{kp}}\frac{4\pi}{\mu^2}\hat{a}^\dagger_{\boldsymbol{k},\sigma}\hat{a}^\dagger_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma},\end{aligned}$$

where in the last sum we have split the sum over $\boldsymbol{q}$ in two parts, one with $\boldsymbol{q}\neq 0$ and one with $\boldsymbol{q}=0$. In the first term we also let $\mu\to 0$.

The electron gas, total energy

The last term has the following set of creation and annihilation operatord

$$\hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}^{\dagger}_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma} = -\hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}^{\dagger}_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{k}\sigma}\hat{a}_{\boldsymbol{p}\sigma'} = -\hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}_{\boldsymbol{p}\sigma'}\delta_{\boldsymbol{pk}}\delta_{\sigma\sigma'} + \hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}_{\boldsymbol{k}\sigma}\hat{a}^{\dagger}_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'},$$

which gives

$$\sum_{\sigma\sigma'}\sum_{\boldsymbol{kp}}\hat{a}^{\dagger}_{\boldsymbol{k},\sigma}\hat{a}^{\dagger}_{\boldsymbol{p},\sigma'}\hat{a}_{\boldsymbol{p}\sigma'}\hat{a}_{\boldsymbol{k}\sigma} = \hat{N}^2 - \hat{N},$$

where we have used the expression for the number operator. The term to the first power in $\hat{N}$ goes to zero in the thermodynamic limit since we are interested in the energy per electron E_0/N_e. This term will then be pr¡oportional with $1/(\Omega\mu^2)$. In the thermodynamical limit $\Omega \to \infty$ we can set this term equal to zero.

The electron gas, total energy

We then get

$$\hat{H}_{el} = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} \hat{a}^\dagger_{\mathbf{k}\sigma} \hat{a}_{\mathbf{k}\sigma} + \frac{e^2}{2\Omega} \sum_{\sigma\sigma'} \sum_{\substack{\mathbf{kpq} \\ q \neq 0}} \frac{4\pi}{q^2} \hat{a}^\dagger_{\mathbf{k}+\mathbf{q},\sigma} \hat{a}^\dagger_{\mathbf{p}-\mathbf{q},\sigma'} \hat{a}_{\mathbf{p}\sigma'} \hat{a}_{\mathbf{k}\sigma} + \frac{e^2}{2} \frac{N_e^2}{\Omega} \frac{4\pi}{\mu^2}.$$

The total Hamiltonian is $\hat{H} = \hat{H}_{el} + \hat{H}_b + \hat{H}_{el-b}$. Collecting all our terms we end up with

$$\hat{H}_0 = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m_e} \hat{a}^\dagger_{\mathbf{k}\sigma} \hat{a}_{\mathbf{k}\sigma},$$

and

$$\hat{H}_I = \frac{e^2}{2\Omega} \sum_{\sigma\sigma'} \sum_{\substack{\mathbf{kpq} \\ q \neq 0}} \frac{4\pi}{q^2} \hat{a}^\dagger_{\mathbf{k}+\mathbf{q},\sigma} \hat{a}^\dagger_{\mathbf{p}-\mathbf{q},\sigma'} \hat{a}_{\mathbf{p}\sigma'} \hat{a}_{\mathbf{k}\sigma},$$

The electron gas, total energy

Now we need $E_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$. The kinetic energy gives simply

$$\langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle = \frac{\hbar^2 \Omega}{10\pi^2 m_e} k_F^5.$$

The electron gas, total energy

The expectation value for $\hat{H}_I$ is

$$\langle\Phi_0|\hat{H}_I|0\rangle = \langle\Phi_0| \left(\frac{e^2}{2\Omega} \sum_{\sigma\sigma'} \sum_{\substack{\boldsymbol{kpq} \\ q\neq 0}} \frac{4\pi}{q^2} \hat{a}^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma} \hat{a}^\dagger_{\boldsymbol{p}-\boldsymbol{q},\sigma'} \hat{a}_{\boldsymbol{p}\sigma'} \hat{a}_{\boldsymbol{k}\sigma} \right) |\Phi_0\rangle$$

$$= \frac{e^2}{2\Omega} \sum_{\sigma\sigma'} \sum_{\substack{\boldsymbol{kpq} \\ q\neq 0}} \frac{4\pi}{q^2} \langle\Phi_0| \hat{a}^\dagger_{\boldsymbol{k}+\boldsymbol{q},\sigma} \hat{a}^\dagger_{\boldsymbol{p}-\boldsymbol{q},\sigma'} \hat{a}_{\boldsymbol{p}\sigma'} \hat{a}_{\boldsymbol{k}\sigma} |\Phi_0\rangle.$$

The electron gas, total energy

For the matrix element to be different from zero 0, we must have $\boldsymbol{k}+\boldsymbol{q}=\boldsymbol{p}$ and $\sigma=\sigma'$. We must also have $p \leq k_F$ and $k \leq k_F$. We get

$$\langle\Phi_0|\hat{H}_I|0\rangle = -\frac{4\pi e^2}{2\Omega}\sum_{\sigma}\sum_{\substack{\boldsymbol{k},\boldsymbol{p}\neq\boldsymbol{k}\\ k,p\leq k_F}}\frac{1}{|\boldsymbol{p}-\boldsymbol{k}|^2} = -\frac{4\pi e^2}{\Omega}\sum_{\substack{\boldsymbol{k},\boldsymbol{p}\neq\boldsymbol{k}\\ k,p\leq k_F}}\frac{1}{|\boldsymbol{p}-\boldsymbol{k}|^2}.$$

Changing to an integral we get

$$\langle\Phi_0|\hat{H}_I|\Phi_0\rangle = -\frac{4\pi e^2}{\Omega}\left(\frac{\Omega}{(2\pi)^3}\right)^2\int_0^{k_F}\int_0^{k_F}\frac{1}{|\boldsymbol{p}-\boldsymbol{k}|^2}\,\mathrm{d}^3\boldsymbol{k}\,\mathrm{d}^3\boldsymbol{p}.$$

The electron gas, total energy

Using spherical coordinates

$$\int_0^{k_F}\int_0^{k_F} \frac{1}{|\boldsymbol{p}-\boldsymbol{k}|^2}\,\mathrm{d}^3\boldsymbol{k}\,\mathrm{d}^3\boldsymbol{p} = 2\pi \int_0^{k_F}\int_0^{\pi}\int_0^{k_F} \frac{k^2\sin\theta}{p^2+k^2-2kp\cos\theta}\,\mathrm{d}k\mathrm{d}\theta\,\mathrm{d}^3\boldsymbol{p},$$

since p is a constant in the integral over k. First we integrate over θ, resulting in

$$\begin{aligned}
\int_0^{k_F}\int_0^{k_F} \frac{1}{|\boldsymbol{p}-\boldsymbol{k}|^2}\,\mathrm{d}^3\boldsymbol{k}\,\mathrm{d}^3\boldsymbol{p} &= 2\pi \int_0^{k_F}\int_0^{k_F} \left[\frac{k^2\ln\left(k^2+p^2-2kp\cos\theta\right)}{2kp}\right]_{\theta=0}^{\theta=\pi}\mathrm{d}k\,\mathrm{d}^3\boldsymbol{p} \\
&= \pi \int_0^{k_F}\int_0^{k_F} \frac{k}{p}\ln\left(\frac{(p+k)^2}{(p-k)^2}\right)\mathrm{d}k\,\mathrm{d}^3\boldsymbol{p} \\
&= 2\pi \int_0^{k_F}\int_0^{k_F} \frac{k}{p}\ln\left|\frac{p+k}{p-k}\right|\mathrm{d}k\,\mathrm{d}^3\boldsymbol{p} \\
&= 2\pi \int_0^{k_F}\int_0^{k_F} \frac{k}{p}\ln|p+k| - \frac{k}{p}\ln|k-p|\,\mathrm{d}k\,\mathrm{d}^3\boldsymbol{p}.
\end{aligned}$$

The electron gas, total energy

We use the following relations

$$\int k \ln|k+p| = \frac{1}{2}k^2 \ln|k+p| - \frac{k^2}{4} - \frac{1}{2}p^2 \ln|k+p| + \frac{kp}{2} + C,$$

which give

$$\int_0^{k_F} k \ln|k+p| = \frac{1}{2}k_F^2 \ln|k_F+p| - \frac{k_F^2}{4} - \frac{1}{2}p^2 \ln|k_F+p| + \frac{k_F p}{2} + \frac{1}{2}p^2 \ln p,$$

and

$$\int_0^{k_F} k \ln|k-p| = \frac{1}{2}k_F^2 \ln|k_F-p| - \frac{k_F^2}{4} - \frac{1}{2}p^2 \ln|k_F-p| - \frac{k_F p}{2} + \frac{1}{2}p^2 \ln p.$$

The electron gas, total energy

Summing up we get

$$\int_0^{k_F}\int_0^{k_F} \frac{1}{|\boldsymbol{p}-\boldsymbol{k}|^2}\,\mathrm{d}^3\boldsymbol{k}\,\mathrm{d}^3\boldsymbol{p} = 2\pi\int_0^{k_F}\frac{1}{p}\left(\frac{1}{2}k_F^2\ln\left|\frac{k_F+p}{k_F-p}\right| - \frac{1}{2}p^2\ln\left|\frac{k_F+p}{k_F-p}\right| + k_F p\right)\,\mathrm{d}^3\boldsymbol{p}$$

$$= 2\pi k_F\frac{4}{3}\pi k_F^3 + \pi\int_0^{k_F}\left(\frac{k_F^2}{p}-p\right)\ln\left|\frac{k_F+p}{k_F-p}\right|\,\mathrm{d}^3\boldsymbol{p}$$

$$= \frac{8\pi^2}{3}k_F^4 + 4\pi^2\int_0^{k_F}\left(k_F^2 p - p^3\right)\ln\left|\frac{k_F+p}{k_F-p}\right|\,\mathrm{d}p.$$

The electron gas, total energy

Utilizing

$$\int_0^{k_F} p \ln|p+k_F| \, \mathrm{d}p = \frac{1}{4} k_F^2 \left(2 \ln k_F + 1\right),$$

$$\int_0^{k_F} p^3 \ln|p+k_F| \, \mathrm{d}p = \frac{1}{48} k_F^4 \left(12 \ln k_F + 7\right),$$

$$\int_0^{k_F} p \ln|p-k_F| \, \mathrm{d}p = \frac{1}{4} k_F^2 \left(2 \ln k_F - 3\right),$$

and

$$\int_0^{k_F} p^3 \ln|p-k_F| \, \mathrm{d}p = \frac{1}{48} k_F^4 \left(12 \ln k_F - 25\right).$$

The electron gas, total energy

This gives

$$\int_0^{k_F}\int_0^{k_F} \frac{1}{|\boldsymbol{p}-\boldsymbol{k}|^2}\,\mathrm{d}^3\boldsymbol{k}\,\mathrm{d}^3\boldsymbol{p} =$$

$$\frac{8\pi^2}{3}\pi k_F^4 + 4\pi^2\left(k_F^2\frac{1}{4}k_F^2\left(2\ln k_F+1\right) - k_F^2\frac{1}{4}k_F^2\left(2\ln k_F-3\right) - \frac{1}{48}k_F^4\left(12\ln k_F+7\right) + \frac{1}{48}k_F^4\left(12\ln k_F-25\right)\right),$$

which we can bring together to

$$\int_0^{k_F}\int_0^{k_F} \frac{1}{|\boldsymbol{p}-\boldsymbol{k}|^2}\,\mathrm{d}^3\boldsymbol{k}\,\mathrm{d}^3\boldsymbol{p} = \frac{8}{3}\pi^2 k_F^4 + 4\pi^2\left(k_F^4 - \frac{2}{3}k_F^4\right) = 4\pi^2 k_F^4.$$

Inserting this in the expression for $\langle\Phi_0|\hat{H}_I|\Phi_0\rangle$ we obtain

$$\langle\Phi_0|\hat{H}_I|\Phi_0\rangle = -\frac{4\pi e^2}{\Omega}\left(\frac{\Omega}{(2\pi)^3}\right)^2 4\pi^2 k_F^4.$$

We get

$$\frac{E_0}{N} = \frac{1}{N}\left(\frac{\hbar^2\Omega}{10\pi^2 m}k_F^5 - \frac{4\pi e^2}{\Omega}\left(\frac{\Omega}{(2\pi)^3}\right)^2 4\pi^2 k_F^4\right).$$

The electron gas, total energy

Inserting k_F we get

$$\begin{aligned}
\frac{E_0}{N} &= \frac{\hbar^2\Omega}{10\pi^2 mN}k_F^5 - \frac{4\pi e^2}{\Omega N}\left(\frac{\Omega}{(2\pi)^3}\right)^2 4\pi^2 k_F^4 \\
&= \frac{\hbar^2\Omega}{10\pi^2 mN}k_F^5 - \frac{e^2\Omega}{4\pi^3 N}k_F^4 \\
&= \frac{\hbar^2\Omega}{10\pi^2 mN}\left(\frac{3\pi^2 N}{\Omega}\right)^{5/3} - \frac{e^2\Omega}{4\pi^3 N}\left(\frac{3\pi^2 N}{\Omega}\right)^{4/3} \\
&= \frac{\hbar^2 N^{2/3}}{\Omega^{2/3}}\frac{(3\pi^2)^{5/3}}{10\pi^2 m} - \frac{e^2\Omega^{1/3}}{N^{1/3}}\frac{(3\pi^2)^{4/3}}{4\pi^3}.
\end{aligned}$$

The electron gas, total energy

Finally, we introduce

$$r_0 = \left(\frac{3\Omega}{4\pi N}\right)^{1/3}, \quad \text{og} \quad a_0 = \frac{\hbar^2}{e^2 m},$$

which gives

$$\begin{aligned}\frac{E_0}{N} &= \hbar^2 \frac{(3\pi^2)^{5/3}}{10\pi^2 m}\left(\frac{3}{4\pi}\right)^{2/3}\frac{1}{r_0^2} - e^2 \frac{(3\pi^2)^{4/3}}{4\pi^3}\left(\frac{3}{4\pi}\right)^{1/3}\frac{1}{r_0} \\ &= \frac{1}{2}\left(\frac{\hbar^2}{m}\frac{2.21}{r_0^2} - e^2\frac{0.916}{r_0}\right)\end{aligned}$$

The electron gas, total energy

Finally we define $r_s = r_0/a_0$, and get

$$\frac{E_0}{N} = \frac{e^2}{2a_0}\left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s}\right).$$

To find the minimum we take the partial derivative

$$\frac{\partial}{\partial r_s}\left(\frac{E_0}{N}\right) = 0 \quad \Rightarrow \quad \frac{2\times 2.21}{r_s^3} - \frac{0.916}{r_s^2} = 0,$$

which results in

$$r_s = \frac{2\times 2.21}{0.916} \approx 4.83.$$

Topics for Week 43

Configuration interaction theory and time-independent Perturbation theory

- Monday:
- Configuration interaction theory
- Diagrammatic interpretation
- Tuesday:
- Configuration interaction theory continues
- Derivation of Brillouin-Wigner and Rayleigh-Schrödinger perturbation theory
- Wave operator in perturbation theory

The material can be found in chapters 4 and 5 of Shavitt and Bartlett.

Configuration interaction theory, understanding excitations

We always start with a 'vacuum' reference state, the Slater determinant for the believed dominating configuration of the ground state. Here a simple case of eight particles with single-particle wave functions $\phi_i(\mathbf{x}_i)$

$$
\Phi_0 = \frac{1}{\sqrt{8!}} \left(\begin{array}{cccc}
\phi_1(\mathbf{x}_1) & \phi_1(\mathbf{x}_2) & \dots & \phi_1(\mathbf{x}_8) \\
\phi_2(\mathbf{x}_1) & \phi_2(\mathbf{x}_2) & \dots & \phi_2(\mathbf{x}_8) \\
\phi_3(\mathbf{x}_1) & \phi_3(\mathbf{x}_2) & \dots & \phi_3(\mathbf{x}_8) \\
\dots & \dots & \dots & \dots \\
\dots & \dots & \dots & \dots \\
\phi_8(\mathbf{x}_1) & \phi_8(\mathbf{x}_2) & \dots & \phi_8(\mathbf{x}_8)
\end{array} \right)
$$

We can allow for a linear combination of excitations beyond the ground state, viz., we could assume that we include 1p-1h and 2p-2h excitations

$$
\Psi_{2p-2h} = (1 + T_1 + T_2)\Phi_0
$$

T_1 is a 1p-1h excitation while T_2 is a 2p-2h excitation.

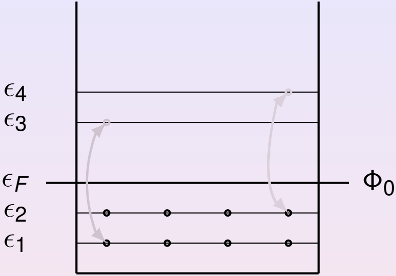
Configuration interaction theory

The single-particle wave functions of

$$
\Phi_0 = \frac{1}{\sqrt{8!}} \left(\begin{array}{cccc} \phi_1(\mathbf{x}_1) & \phi_1(\mathbf{x}_2) & \dots & \phi_1(\mathbf{x}_8) \\ \phi_2(\mathbf{x}_1) & \phi_2(\mathbf{x}_2) & \dots & \phi_2(\mathbf{x}_8) \\ \phi_3(\mathbf{x}_1) & \phi_3(\mathbf{x}_2) & \dots & \phi_3(\mathbf{x}_8) \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \phi_8(\mathbf{x}_1) & \phi_8(\mathbf{x}_2) & \dots & \phi_8(\mathbf{x}_8) \end{array} \right)
$$

are normally chosen as the solutions of the so-called non-interacting part of the Hamiltonian, H_0. A typical basis is provided by the harmonic oscillator problem or hydrogen-like wave functions.

Excitations in Pictures



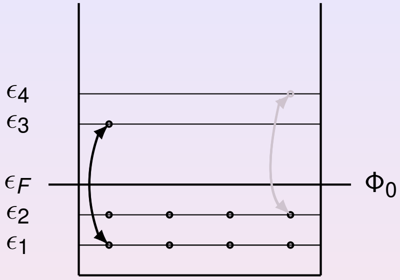
From T_1 to T_1^2

$T_1 \propto a_a^+ a_i$

From T_2 to T_2^2

$T_2 \propto a_a^+ a_b^+ a_j a_i$

Excitations in Pictures



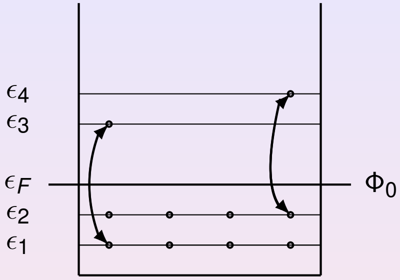
From T_1 to T_1^2

$T_1 \propto a_a^+ a_i$

From T_2 to T_2^2

$T_2 \propto a_a^+ a_b^+ a_j a_i$

Excitations in Pictures



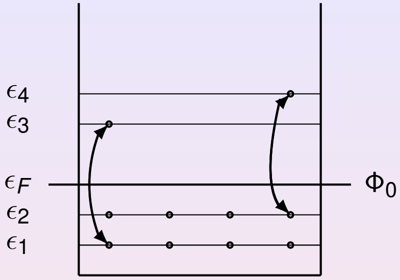
From T_1 to T_1^2

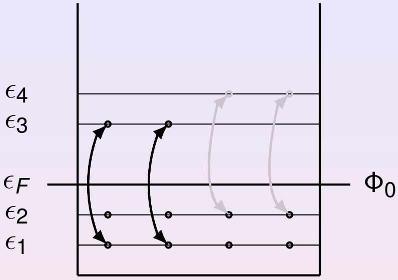
$T_1 \propto a_a^+ a_i$

From T_2 to T_2^2

$T_2 \propto a_a^+ a_b^+ a_j a_i$

Excitations in Pictures





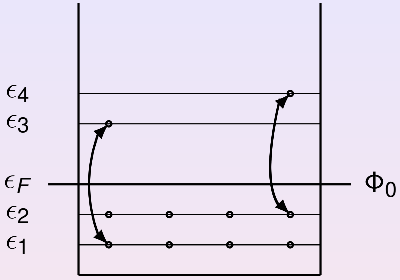
From T_1 to T_1^2

$T_1 \propto a_a^+ a_i$

From T_2 to T_2^2

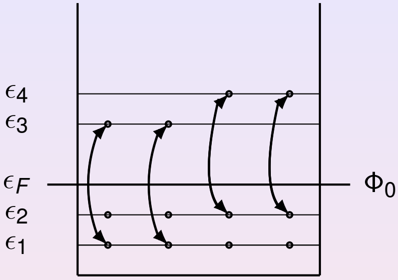
$T_2 \propto a_a^+ a_b^+ a_j a_i$

Excitations in Pictures



From T_1 to T_1^2

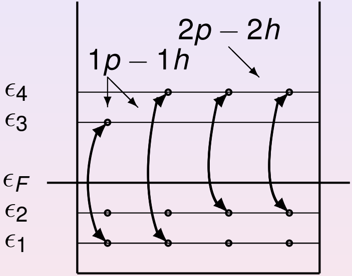
$T_1 \propto a_a^+ a_i$



From T_2 to T_2^2

$T_2 \propto a_a^+ a_b^+ a_j a_i$

Excitations



Truncations

- Truncated basis of Slater determinants with $2p-2h$ has $\Psi_{2p-2h} = (1 + T_1 + T_2)\Phi_0$
- Energy contains then

$$E_{2p-2h} =$$

$$\langle \Phi_0 (1 + T_1^\dagger + T_2^\dagger) | H | (1 + T_1 + T_2) \Phi_0 \rangle$$

Configuration interaction (CI) theory

We have defined the ansatz for the ground state as

$$|\Phi_0\rangle = \left(\prod_{i=1}^{n} \hat{a}_i^\dagger\right)|0\rangle,$$

where the i define different single-particle states up to the Fermi level. We have assumed that we have n fermions. A given one-particle-one-hole ($1p1h$) state can be written as

$$|\Phi_i^a\rangle = \hat{a}_a^\dagger \hat{a}_i|\Phi_0\rangle,$$

while a $2p2h$ state can be written as

$$|\Phi_{ij}^{ab}\rangle = \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i|\Phi_0\rangle,$$

and a general $npnh$ state as

$$|\Phi_{ijk\dots}^{abc\dots}\rangle = \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \dots \hat{a}_k \hat{a}_j \hat{a}_i|\Phi_0\rangle.$$

Configuration interaction (CI) theory

We can then expand our exact state function for the ground state as

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{ai} C_i^a|\Phi_i^a\rangle + \sum_{abij} C_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \cdots = (C_0 + \hat{C})|\Phi_0\rangle,$$

where we have introduced the so-called correlation operator

$$\hat{C} = \sum_{ai} C_i^a \hat{a}_a^\dagger \hat{a}_i + \sum_{abij} C_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i + \dots$$

Since the normalization of Ψ_0 is at our disposal and since C_0 is by hypothesis non-zero, we may arbitrarily set $C_0 = 1$ with corresponding proportional changes in all other coefficients. Using this so-called intermediate normalization we have

$$\langle \Psi_0 | \Phi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle = 1,$$

resulting in

$$|\Psi_0\rangle = (1 + \hat{C})|\Phi_0\rangle.$$

Configuration interaction (CI) theory

We rewrite

$$|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{ai} C_i^a|\Phi_i^a\rangle + \sum_{abij} C_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \dots,$$

in a more compact form as

$$|\Psi_0\rangle = \sum_{PH} C_H^P \Phi_H^P = \left(\sum_{PH} C_H^P \hat{A}_H^P\right)|\Phi_0\rangle,$$

where H stands for $0, 1, \dots, n$ hole states and P for $0, 1, \dots, n$ particle states. Our requirement of unit normalization gives

$$\langle\Psi_0|\Phi_0\rangle = \sum_{PH} |C_H^P|^2 = 1,$$

and the energy can be written as

$$E = \langle\Psi_0|\hat{H}|\Phi_0\rangle = \sum_{PP'HH'} C_H^{*P}\langle\Phi_H^P|\hat{H}|\Phi_{H'}^{P'}\rangle C_{H'}^{P'}.$$

Configuration interaction (CI) theory

Normally

$$E = \langle\Psi_0|\hat{H}|\Phi_0\rangle = \sum_{PP'HH'} C_H^{*P}\langle\Phi_H^P|\hat{H}|\Phi_{H'}^{P'}\rangle C_{H'}^{P'},$$

is solved by diagonalization setting up the Hamiltonian matrix defined by the basis of all possible Slater determinants. A diagonalization is equivalent to finding the variational minimum of

$$\langle\Psi_0|\hat{H}|\Phi_0\rangle - \lambda\langle\Psi_0|\Phi_0\rangle,$$

where λ is a variational multiplier to be identified with the energy of the system. The minimization process results in

$$\delta\left[\langle\Psi_0|\hat{H}|\Phi_0\rangle - \lambda\langle\Psi_0|\Phi_0\rangle\right] = \sum_{P'H'}\left\{\delta[C_H^{*P}]\langle\Phi_H^P|\hat{H}|\Phi_{H'}^{P'}\rangle C_{H'}^{P'} + C_H^{*P}\langle\Phi_H^P|\hat{H}|\Phi_{H'}^{P'}\rangle\delta[C_{H'}^{P'}].\right.$$

$$.\left. -\lambda(\delta[C_H^{*P}]C_{H'}^{P'} + C_H^{*P}\delta[C_{H'}^{P'}]\right\} = 0.$$

Since the coefficients $\delta[C_H^{*P}]$ and $\delta[C_{H'}^{P'}]$ are complex conjugates it is necessary and sufficient to require the quantities that multiply with $\delta[C_H^{*P}]$ to vanish.

Configuration interaction (CI) theory

This leads to

$$\sum_{P'H'} \langle \Phi_H^P | \hat{H} | \Phi_{H'}^{P'} \rangle C_{H'}^{P'} - \lambda C_H^P = 0,$$

for all sets of P and H.
If we then multiply by the corresponding C_H^{*P} and sum over PH we obtain

$$\sum_{PP'HH'} C_H^{*P} \langle \Phi_H^P | \hat{H} | \Phi_{H'}^{P'} \rangle C_{H'}^{P'} - \lambda \sum_{PH} |C_H^P|^2 = 0,$$

leading to the identification $\lambda = E$. This means that we have for all PH sets

$$\sum_{P'H'} \langle \Phi_H^P | \hat{H} - E | \Phi_{H'}^{P'} \rangle = 0. \tag{10.0.1}$$

Configuration interaction (CI) theory

An alternative way to derive the last equation is to start from

$$(\hat{H}-E)|\Psi_0\rangle = (\hat{H}-E)\sum_{P'H'} C_{H'}^{P'}|\Phi_{H'}^{P'}\rangle = 0,$$

and if this equation is successively projected against all Φ_H^P in the expansion of Ψ, then the last equation on the previous slide results. As stated previously, one solves this equation normally by diagonalization. If we are able to solve this equation exactly (that is numerically exactly) in a large Hilbert space (it will be truncated in terms of the number of single-particle states included in the definition of Slater determinants), it can then serve as a benchmark for other many-body methods which approximate the correlation operator $\hat{C}$.

For reasons to come (link with Coupled-Cluster theory and Many-Body perturbation theory), we will rewrite Eq. (10.0.1) as a set of coupled non-linear equations in terms of the unknown coefficients C_H^P.

Configuration interaction (CI) theory

To see this, we look at $\langle\Phi_H^P| = \langle\Phi_0|$ in Eq. (10.0.1), that is we multiply with $\langle\Phi_0|$ from the left in

$$(\hat{H}-E)\sum_{P'H'} C_{H'}^{P'}|\Phi_{H'}^{P'}\rangle = 0,$$

and we assume that we have a two-body operator at most. Using Slater's rule gives then and equation for the correlation energy in terms of C_i^a and C_{ij}^{ab}. We get then

$$\langle\Phi_0|\hat{H}-E|\Phi_0\rangle + \sum_{ai}\langle\Phi_0|\hat{H}-E|\Phi_i^a\rangle C_i^a + \sum_{abij}\langle\Phi_0|\hat{H}-E|\Phi_{ij}^{ab}\rangle C_{ij}^{ab} = 0,$$

or

$$E-E_0 = \Delta E = \sum_{ai}\langle\Phi_0|\hat{H}|\Phi_i^a\rangle C_i^a + \sum_{abij}\langle\Phi_0|\hat{H}|\Phi_{ij}^{ab}\rangle C_{ij}^{ab},$$

where the E_0 is the reference energy and ΔE becomes the correlation energy. We have already computed the expectation values $\langle\Phi_0|\hat{H}|\Phi_i^a$ and $\langle\Phi_0|\hat{H}|\Phi_{ij}^{ab}\rangle$.

Configuration interaction (CI) theory

We can rewrite

$$E - E_0 = \Delta E = \sum_{ai} \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle C_i^a + \sum_{abij} \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle C_{ij}^{ab},$$

as

$$\Delta E = \sum_{ai} \langle i | \hat{f} | a \rangle C_i^a + \sum_{abij} \langle ij | \hat{v} | ab \rangle C_{ij}^{ab}.$$

This equation determines the correlation energy but not the coefficients C. We need more equations. Our next step is to set up

$$\langle \Phi_i^a | \hat{H} - E | \Phi_0 \rangle + \sum_{bj} \langle \Phi_i^a | \hat{H} - E | \Phi_j^b \rangle C_j^b + \sum_{bcjk} \langle \Phi_i^a | \hat{H} - E | \Phi_{jk}^{bc} \rangle C_{jk}^{bc} + \sum_{bcdjkl} \langle \Phi_i^a | \hat{H} - E | \Phi_{jkl}^{bcd} \rangle C_{jkl}^{bcd} = 0,$$

as this equation will allow us to find an expression for the coefficents C_i^a since we can rewrite this equation as

$$\langle i | \hat{f} | a \rangle + \langle \Phi_i^a | \hat{H} - E | \Phi_i^a \rangle C_i^a + \sum_{bj \neq ai} \langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle C_j^b + \sum_{bcjk} \langle \Phi_i^a | \hat{H} | \Phi_{jk}^{bc} \rangle C_{jk}^{bc} + \sum_{bcdjkl} \langle \Phi_i^a | \hat{H} | \Phi_{jkl}^{bcd} \rangle C_{jkl}^{bcd} = 0.$$

Configuration interaction (CI) theory

We rewrite this equation as

$$C_i^a = -(\langle\Phi_i^a|\hat{H}-E|\Phi_i^a\rangle)^{-1}\left(\langle i|\hat{f}|a\rangle + \sum_{bj\neq ai}\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle C_j^b + .\right.$$

$$\left. . \sum_{bcjk}\langle\Phi_i^a|\hat{H}|\Phi_{jk}^{bc}\rangle C_{jk}^{bc} + \sum_{bcdjkl}\langle\Phi_i^a|\hat{H}|\Phi_{jkl}^{bcd}\rangle C_{jkl}^{bcd}\right).$$

Since these equations are solved iteratively (that is we can start with a guess for the coefficients C_i^a), it is common to start the iteration by setting

$$C_i^a = -\frac{\langle i|\hat{f}|a\rangle}{\langle\Phi_i^a|\hat{H}-E|\Phi_i^a\rangle},$$

and the denominator can be written as

$$C_i^a = \frac{\langle i|\hat{f}|a\rangle}{\langle i|\hat{f}|i\rangle - \langle a|\hat{f}|a\rangle + \langle ai|\hat{v}|ai\rangle - E}.$$

The observant reader will however see that we need an equation for C_{jk}^{bc} and C_{jkl}^{bcd} as well. To find equations for these coefficients we need then to continue our multiplications from the left with the various Φ_H^P terms.

Configuration interaction (CI) theory

For C_{jk}^{bc} we need then

$$\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_0\rangle+\sum_{kc}\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_k^c\rangle C_k^c+\sum_{cdkl}\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_{kl}^{cd}\rangle C_{kl}^{cd}+$$

$$\sum_{cdeklm}\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_{klm}^{cde}\rangle C_{klm}^{cde}+\sum_{cdefklmn}\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_{klmn}^{cdef}\rangle C_{klmn}^{cdef}=0,$$

and we can isolate the coefficients C_{kl}^{cd} in a similar way as we did for the coefficients C_i^a. At the end we can rewrite our solution of the Schrödinger equation in terms of n coupled equations for the coefficients C_H^P. This is a very cumbersome way of solving the equation. However, by using this iterative scheme we can illustrate how we can compute the various terms in the wave operator or correlation operator $\hat{C}$. We will later identify the calculation of the various terms C_H^P as parts of different many-body approximations to full CI. In particular, we will relate this non-linear scheme with Coupled Cluster theory and many-body perturbation theory.

Configuration interaction (CI) theory

If we use a Hartree-Fock basis, how can one simplify the equation

$$\Delta E = \sum_{ai} \langle i|\hat{f}|a\rangle C_i^a + \sum_{abij} \langle ij|\hat{v}|ab\rangle C_{ij}^{ab}?$$

And what about

$$\langle\Phi_i^a|\hat{H}-E|\Phi_0\rangle + \sum_{bj}\langle\Phi_i^a|\hat{H}-E|\Phi_j^b\rangle C_j^b + \sum_{bcjk}\langle\Phi_i^a|\hat{H}-E|\Phi_{jk}^{bc}\rangle C_{jk}^{bc} + \sum_{bcdjkl}\langle\Phi_i^a|\hat{H}-E|\Phi_{jkl}^{bcd}\rangle C_{jkl}^{bcd} = 0,$$

and

$$\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_0\rangle + \sum_{kc}\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_k^c\rangle C_k^c + \sum_{cdkl}\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_{kl}^{cd}\rangle C_{kl}^{cd} +$$

$$\sum_{cdeklm}\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_{klm}^{cde}\rangle C_{klm}^{cde} + \sum_{cdefklmn}\langle\Phi_{ij}^{ab}|\hat{H}-E|\Phi_{klmn}^{cdef}\rangle C_{klmn}^{cdef} = 0?$$

Perturbation theory (time-independent)

We assume here that we are only interested in the ground state of the system and expand the exact wave function in term of a series of Slater determinants

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{m=1}^{\infty} C_m|\Phi_m\rangle,$$

where we have assumed that the true ground state is dominated by the solution of the unperturbed problem, that is

$$\hat{H}_0|\Phi_0\rangle = W_0|\Phi_0\rangle.$$

The state $|\Psi_0\rangle$ is not normalized, rather we have used an intermediate normalization $\langle\Phi_0|\Psi_0\rangle = 1$ since we have $\langle\Phi_0|\Phi_0\rangle = 1$.

Perturbation theory (time-independent)

The Schrödinger equation is

$$\hat{H}|\Psi_0\rangle = E|\Psi_0\rangle,$$

and multiplying the latter from the left with $\langle\Phi_0|$ gives

$$\langle\Phi_0|\hat{H}|\Psi_0\rangle = E\langle\Phi_0|\Psi_0\rangle = E,$$

and subtracting from this equation

$$\langle\Psi_0|\hat{H}_0|\Phi_0\rangle = W_0\langle\Psi_0|\Phi_0\rangle = W_0,$$

and using the fact that the both operators $\hat{H}$ and $\hat{H}_0$ are hermitian results in

$$\Delta E = E - W_0 = \langle\Phi_0|\hat{H}_I|\Psi_0\rangle,$$

which is an exact result. We call this quantity the correlation energy.

Perturbation theory (time-independent)

This equation forms the starting point for all perturbative derivations. However, as it stands it represents nothing but a mere formal rewriting of Schrödinger's equation and is not of much practical use. The exact wave function $|\Psi_0\rangle$ is unknown. In order to obtain a perturbative expansion, we need to expand the exact wave function in terms of the interaction $\hat{H}_I$.
Here we have assumed that our model space defined by the operator $\hat{P}$ is one-dimensional, meaning that

$$\hat{P} = |\Phi_0\rangle\langle\Phi_0|,$$

and

$$\hat{Q} = \sum_{m=1}^{\infty} |\Phi_m\rangle\langle\Phi_m|.$$

Perturbation theory (time-independent)

We can thus rewrite the exact wave function as

$$|\Psi_0\rangle = (\hat{P} + \hat{Q})|\Psi_0\rangle = |\Phi_0\rangle + \hat{Q}|\Psi_0\rangle.$$

Going back to the Schrödinger equation, we can rewrite it as, adding and a subtracting a term $\omega|\Psi_0\rangle$ as

$$\left(\omega - \hat{H}_0\right)|\Psi_0\rangle = \left(\omega - E + \hat{H}_I\right)|\Psi_0\rangle,$$

where ω is an energy variable to be specified later.

Perturbation theory (time-independent)

We assume also that the resolvent of $\left(\omega - \hat{H}_0\right)$ exits, that is it has an inverse which defined the unperturbed Green's function as

$$\left(\omega - \hat{H}_0\right)^{-1} = \frac{1}{\left(\omega - \hat{H}_0\right)}.$$

Perturbation theory (time-independent)

We can rewrite Schrödinger's equation as

$$|\Psi_0\rangle = \frac{1}{\omega - \hat{H}_0}\left(\omega - E + \hat{H}_I\right)|\Psi_0\rangle,$$

and multiplying from the left with $\hat{Q}$ results in

$$\hat{Q}|\Psi_0\rangle = \frac{\hat{Q}}{\omega - \hat{H}_0}\left(\omega - E + \hat{H}_I\right)|\Psi_0\rangle,$$

which is possible since we have defined the operator $\hat{Q}$ in terms of the eigenfunctions of $\hat{H}$.

Perturbation theory (time-independent)

These operators commute meaning that

$$\hat{Q}\frac{1}{\left(\omega-\hat{H}_0\right)}\hat{Q}=\hat{Q}\frac{1}{\left(\omega-\hat{H}_0\right)}=\frac{\hat{Q}}{\left(\omega-\hat{H}_0\right)}.$$

With these definitions we can in turn define the wave function as

$$|\Psi_0\rangle=|\Phi_0\rangle+\frac{\hat{Q}}{\omega-\hat{H}_0}\left(\omega-E+\hat{H}_I\right)|\Psi_0\rangle.$$

Perturbation theory (time-independent)

$$|\Psi_0\rangle = |\Phi_0\rangle + \frac{\hat{Q}}{\omega - \hat{H}_0}\left(\omega - E + \hat{H}_I\right)|\Psi_0\rangle.$$

This equation is again nothing but a formal rewrite of Schrödinger's equation and does not represent a practical calculational scheme. It is a non-linear equation in two unknown quantities, the energy E and the exact wave function $|\Psi_0\rangle$. We can however start with a guess for $|\Psi_0\rangle$ on the right hand side of the last equation.

Perturbation theory (time-independent)

The most common choice is to start with the function which is expected to exhibit the largest overlap with the wave function we are searching after, namely $|\Phi_0\rangle$. This can again be inserted in the solution for $|\Psi_0\rangle$ in an iterative fashion and if we continue along these lines we end up with

$$|\Psi_0\rangle = \sum_{i=0}^{\infty}\left\{\frac{\hat{Q}}{\omega-\hat{H}_0}\left(\omega-E+\hat{H}_I\right)\right\}^i|\Phi_0\rangle,$$

for the wave function and

$$\Delta E = \sum_{i=0}^{\infty}\langle\Phi_0|\hat{H}_I\left\{\frac{\hat{Q}}{\omega-\hat{H}_0}\left(\omega-E+\hat{H}_I\right)\right\}^i|\Phi_0\rangle,$$

which is now a perturbative expansion of the exact energy in terms of the interaction $\hat{H}_I$ and the unperturbed wave function $|\Psi_0\rangle$.

Brillouin-Wigner theory

In our equations for $|\Psi_0\rangle$ and ΔE in terms of the unperturbed solutions $|\Phi_i\rangle$ we have still an undetermined parameter ω and a dependecy on the exact energy E. Not much has been gained thus from a practical computational point of view.
In Brilluoin-Wigner perturbation theory it is customary to set $\omega = E$. This results in the following perturbative expansion for the energy ΔE

$$\Delta E = \sum_{i=0}^{\infty} \langle\Phi_0|\hat{H}_I \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} \left(\omega - E + \hat{H}_I\right) \right\}^i |\Phi_0\rangle =$$

$$\langle\Phi_0| \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \dots \right) |\Phi_0\rangle.$$

Brillouin-Wigner theory

$$\Delta E = \sum_{i=0}^{\infty} \langle \Phi_0 | \hat{H}_I \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} \left(\omega - E + \hat{H}_I \right) \right\}^i | \Phi_0 \rangle =$$

$$\langle \Phi_0 | \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{E - \hat{H}_0} \hat{H}_I + \dots \right) | \Phi_0 \rangle .$$

This expression depends however on the exact energy E and is again not very convenient from a practical point of view. It can obviously be solved iteratively, by starting with a guess for E and then solve till some kind of self-consistency criterion has been reached.

Actually, the above expression is nothing but a rewrite again of the full Schrödinger equation.

Rayleigh-Schrödinger (RS) perturbation theory

In RS perturbation theory we set $\omega = W_0$ and obtain the following expression for the energy difference

$$\Delta E = \sum_{i=0}^{\infty} \langle \Phi_0 | \hat{H}_I \left\{ \frac{\hat{Q}}{W_0 - \hat{H}_0} \left(\hat{H}_I - \Delta E \right) \right\}^i | \Phi_0 \rangle =$$

$$\langle \Phi_0 | \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E) + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E) \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E) + \ldots \right) | \Phi_0 \rangle .$$

Rayleigh-Schrödinger perturbation theory

Recalling that $\hat{Q}$ commutes with $\hat{H}_0$ and since ΔE is a constant we obtain that

$$\hat{Q}\Delta E|\Phi_0\rangle = \hat{Q}\Delta E|\hat{Q}\Phi_0\rangle = 0.$$

Inserting this results in the expression for the energy results in

$$\Delta E = \langle\Phi_0|\left(\hat{H}_I + \hat{H}_I\frac{\hat{Q}}{W_0 - \hat{H}_0}\hat{H}_I + \hat{H}_I\frac{\hat{Q}}{W_0 - \hat{H}_0}(\hat{H}_I - \Delta E)\frac{\hat{Q}}{W_0 - \hat{H}_0}\hat{H}_I + \dots\right)|\Phi_0\rangle.$$

Rayleigh-Schrödinger perturbation theory

We can now this expression in terms of a perturbative expression in terms of $\hat{H}_I$ where we iterate the last expression in terms of ΔE

$$\Delta E = \sum_{i=1}^{\infty} \Delta E^{(i)}.$$

We get the following expression for $\Delta E^{(i)}$

$$\Delta E^{(1)} = \langle \Phi_0 | \hat{H}_I | \Phi_0 \rangle,$$

which is just the contribution to first order in perturbation theory,

$$\Delta E^{(2)} = \langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I | \Phi_0 \rangle,$$

which is the contribution to second order.

Rayleigh-Schrödinger perturbation theory

$$\Delta E^{(3)} = \langle\Phi_0|\hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I\Phi_0\rangle - \langle\Phi_0|\hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}\langle\Phi_0|\hat{H}_I|\Phi_0\rangle\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I|\Phi_0\rangle,$$

being the third-order contribution. The last term is a so-called unlinked diagram!

Rayleigh-Schrödinger perturbation theory

The fourth order term is

$$\Delta E^{(4)} = \langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \Phi_0 \rangle -$$

$$\langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle \Phi_0 | \hat{H}_I | \Phi_0 \rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \Phi_0 \rangle$$

$$- \langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle \Phi_0 | \hat{H}_I | \Phi_0 \rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \langle \Phi_0 | \hat{H}_I | \Phi_0 \rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle \Phi_0 | \hat{H}_I | \Phi_0 \rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \Phi_0 \rangle -$$

$$\langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I | \Phi_0 \rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I | \Phi_0 \rangle,$$

Topics for Week 44

Perturbation theory

- Monday:
- Summary from last week
- Derivation and discussion of Rayleigh-Schrödinger perturbation theory
- Tuesday:
- Derivation and discussion of Rayleigh-Schrödinger perturbation theory
- Diagram rules and examples

No exercises this week.

Topics for Week 45

Many-body Perturbation theory

- Monday:
- Summary from last week
- Diagram rules and unlinked diagrams
- Tuesday:
- More on diagram rules and examples

Diagram rules

- Draw all topologically distinct diagrams by linking up particle and hole lines with various interaction vertices. Two diagrams can be made topologically equivalent by deformation of fermion lines under the restriction that the ordering of the vertices is not changed and particle lines and hole lines remain particle and hole lines.
- For the explicit evaluation of a diagram: Sum freely over all internal indices and label all lines.
- Extract matrix elements for the one-body operators (if present) as $\langle \mathrm{out}|\hat{f}|\mathrm{in}\rangle$ and for the two-body operator (if present) as $\langle \mathrm{left\ out}, \mathrm{right\ out}||\hat{v}||\mathrm{left\ in}, \mathrm{right\ in}\rangle$.

Diagram rules

- Calculate the phase factor: $(-1)^{\text{holelines}+\text{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent pair of lines (particle lines or hole lines) that begin at the same interaction vertex and end at the same (yet different from the first) interaction vertex.
- For each interval between successive interaction vertices with minimum one single-particle state above the Fermi level with n hole states and m particle states there is a factor

$$\frac{1}{\sum_i^n \epsilon_i - \sum_a^m \epsilon_a}.$$

CCSD with twobody Hamiltonian

Truncating the cluster operator $\widehat{T}$ at the $n = 2$ level, defines CCSD approximation to the Coupled Cluster wavefunction. The coupled cluster wavefunction is now given by

$$|\Psi_{CC}\rangle = e^{\widehat{T}_1 + \widehat{T}_2}|\Phi_0\rangle$$

where

$$\hat{T}_1 = \sum_{ia} t_i^a a_a^\dagger a_i$$

$$\hat{T}_2 = \frac{1}{4}\sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i.$$

CCSD with twobody Hamiltonian cont.

Normal ordered Hamiltonian

$$
\begin{aligned}
\widehat{H} &= \sum_{pq} f^p_q \left\{a^\dagger_p a_q\right\} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle \left\{a^\dagger_p a^\dagger_q a_s a_r\right\} \\
&+ \mathrm{E}_0 \\
&= \widehat{F}_N + \widehat{V}_N + \mathrm{E}_0 = \widehat{H}_N + \mathrm{E}_0
\end{aligned}
$$

where

$$
\begin{aligned}
f^p_q &= \langle p|\widehat{t}|q\rangle + \sum_i \langle pi|\widehat{v}|qi\rangle \\
\langle pq||rs\rangle &= \langle pq|\widehat{v}|rs\rangle \\
\mathrm{E}_0 &= \sum_i \langle i|\widehat{t}|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|\widehat{v}|ij\rangle
\end{aligned}
$$

Diagram equations - Derivation

Contract $\widehat{H}_N$ with $\widehat{T}$ in all possible unique combinations that satisfy a given form. The diagram equation is the sum of all these diagrams.

- Contract one $\widehat{H}_N$ element with $0, 1$ or multiple $\widehat{T}$ elements.
- All $\widehat{T}$ elements must have atleast one contraction with $\widehat{H}_N$.
- No contractions between $\widehat{T}$ elements are allowed.
- A single $\widehat{T}$ element can contract with a single element of $\widehat{H}_N$ in different ways.

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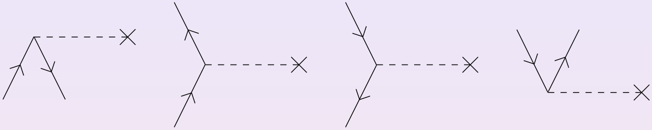
Diagram elements - Directed lines

Figure: Particle line

Figure: Hole line

- Represents a contraction between second quantized operators.
- External lines are connected to one operator vertex and infinity.
- Internal lines are connected to operator vertices in both ends.

Diagram elements - Onebody Hamiltonian



Level: -1

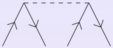
Level: 0

Level: 0

Level: +1

- Horisontal dashed line segment with one vertex.
- Excitation level identify the number of particle/hole pairs created by the operator.

Diagram elements - Twobody Hamiltonian



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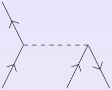

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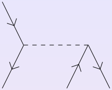

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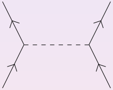

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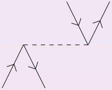

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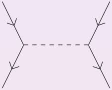

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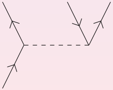
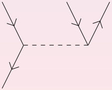


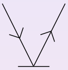
Level: +1



Level: +1

Level: +2

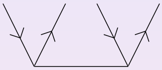
Diagram elements - Onebody cluster operator



Level: +1

- Horisontal line segment with one vertex.
- Excitation level of +1.

Diagram elements - Twobody cluster operator



Level: +2

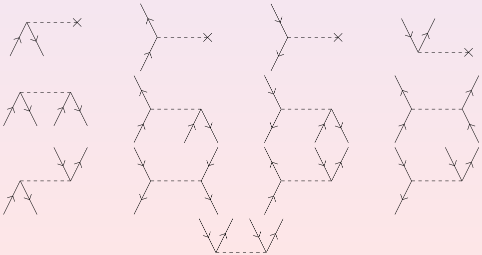
- Horisontal line segment with two vertices.
- Excitation level of +2.

CCSD energy equation - Derivation

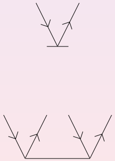
$$E_{\text{CCSD}} = \langle \Phi_0 | | \Phi_0 \rangle$$

- No external lines.
- Final excitation level: 0

Elements: $\widehat{H}_N$



Elements: $\widehat{T}$



CCSD energy equation

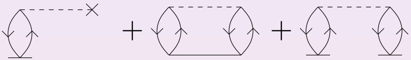
$E_{CCSD} =$ 

Diagram rules

- Label all lines.
- Sum over all internal indices.
- Extract matrix elements. ($f_{\mathrm{in}}^{\mathrm{out}}$, $\langle \mathrm{lout}, \mathrm{rout} || \mathrm{lin}, \mathrm{rin} \rangle$)
- Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{\mathrm{in}}^{\mathrm{out}}$, $t_{\mathrm{lin,rin}}^{\mathrm{lout,rout}}$)
- Calculate the phase: $(-1)^{\mathrm{holelines}+\mathrm{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.

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- Sum over all internal indices.
- Extract matrix elements. ($f_{\text{in}}^{\text{out}}$, $\langle \text{lout}, \text{rout} || \text{lin}, \text{rin} \rangle$)
- Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{\text{in}}^{\text{out}}$, $t_{\text{lin},\text{rin}}^{\text{lout},\text{rout}}$)
- Calculate the phase: $(-1)^{\text{holelines}+\text{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.

Diagram rules

- Label all lines.
- Sum over all internal indices.
- Extract matrix elements. ($f_{\mathrm{in}}^{\mathrm{out}}$, $\langle \mathrm{lout}, \mathrm{rout} || \mathrm{lin}, \mathrm{rin} \rangle$)
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- Calculate the phase: $(-1)^{\text{holelines}+\text{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.

CCSD energy equation

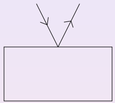
$$E_{CCSD} = f_a^i t_i^a + \frac{1}{4}\langle ij||ab\rangle t_{ij}^{ab} + \frac{1}{2}\langle ij||ab\rangle t_i^a t_j^b$$

Note the implicit sum over repeated indices.

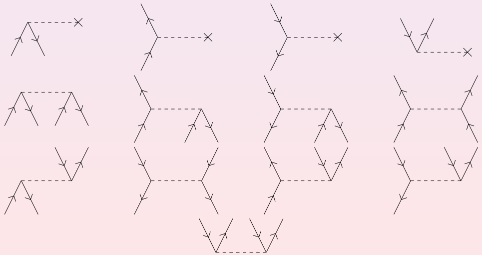
CCSD $\widehat{T}_1$ amplitude equation - Derivation

$$0 = \langle \Phi_i^a | | \Phi_0 \rangle$$

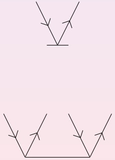
- One pair of particle/hole external lines.
- Final excitation level: +1



Elements: $\widehat{H}_N$



Elements: $\widehat{T}$



CCSD $\widehat{T}_1$ amplitude equation

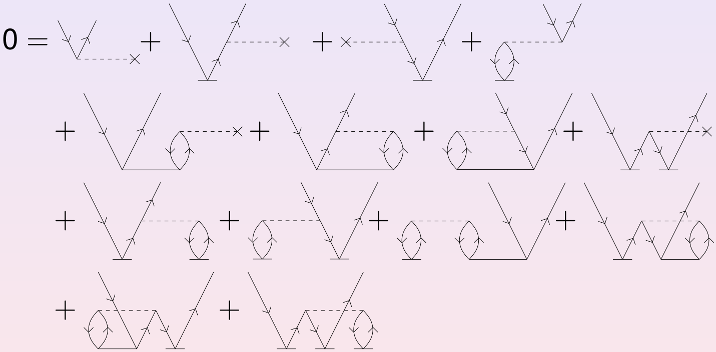


Diagram rules

- Label all lines.
- Sum over all internal indices.
- Extract matrix elements. ($f_{\text{in}}^{\text{out}}$, $\langle \text{lout}, \text{rout} || \text{lin}, \text{rin} \rangle$)
- Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{\text{in}}^{\text{out}}$, $t_{\text{lin},\text{rin}}^{\text{lout},\text{rout}}$)
- Calculate the phase: $(-1)^{\text{holelines}+\text{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.

Diagram rules

- Label all lines.
- Sum over all internal indices.
- Extract matrix elements. ($f_{\text{in}}^{\text{out}}$, $\langle \text{lout}, \text{rout} || \text{lin}, \text{rin} \rangle$)
- Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{\text{in}}^{\text{out}}$, $t_{\text{lin,rin}}^{\text{lout,rout}}$)
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- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.

Diagram rules

- Label all lines.
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- Calculate the phase: $(-1)^{\text{holelines}+\text{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.

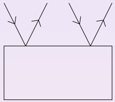
CCSD $\widehat{T}_1$ amplitude equation

$$
\begin{aligned}
0 = {} & f_i^a + f_e^a t_i^e - f_i^m t_m^a + \langle ma||ei\rangle t_m^e + f_e^m t_{im}^{ae} + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\
& - \frac{1}{2}\langle mn||ei\rangle t_{mn}^{ea} - f_e^m t_i^e t_m^a + \langle am||ef\rangle t_i^e t_m^f - \langle mn||ei\rangle t_m^e t_n^a \\
& + \langle mn||ef\rangle t_m^e t_{ni}^{fa} - \frac{1}{2}\langle mn||ef\rangle t_i^e t_{mn}^{af} - \frac{1}{2}\langle mn||ef\rangle t_n^a t_{mi}^{ef} \\
& - \langle mn||ef\rangle t_i^e t_m^a t_n^f
\end{aligned}
$$

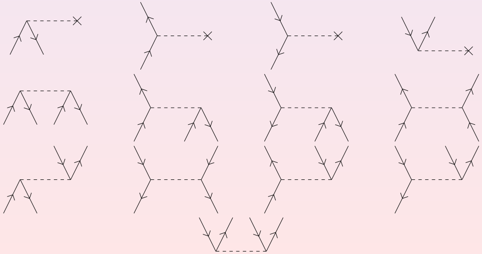
CCSD $\widehat{T}_2$ amplitude equation - Derivation

$$0 = \langle \Phi_{ij}^{ab} || \Phi_0 \rangle$$

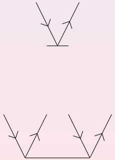
- Two pairs of particle/hole external lines.
- Final excitation level: +2



Elements: $\widehat{H}_N$



Elements: $\widehat{T}$



CCSD $\widehat{T}_2$ amplitude equation

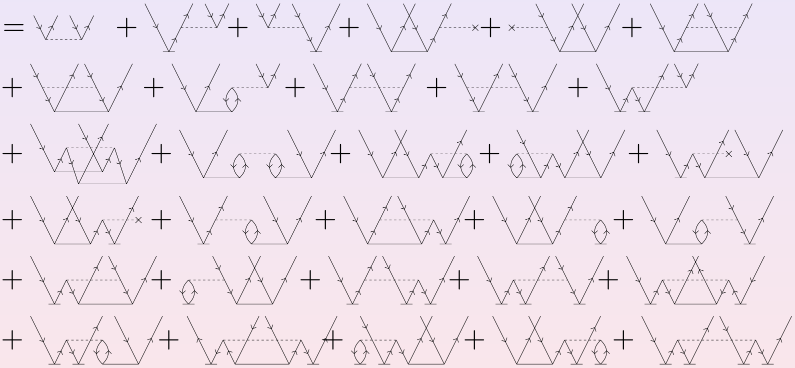
$0 =$ 

Diagram rules

- Label all lines.
- Sum over all internal indices.
- Extract matrix elements. ($f_{\rm in}^{\rm out}$, $\langle {\rm lout}, {\rm rout} || {\rm lin}, {\rm rin} \rangle$)
- Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{\rm in}^{\rm out}$, $t_{\rm lin,rin}^{\rm lout,rout}$)
- Calculate the phase: $(-1)^{\rm holelines+loops}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.
- Antisymmetrize a pair of external particle/hole line that does not connect to the same operator.

Diagram rules

- Label all lines.
- Sum over all internal indices.
- Extract matrix elements. ($f_{\text{in}}^{\text{out}}$, $\langle \text{lout}, \text{rout} || \text{lin}, \text{rin} \rangle$)
- Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{\text{in}}^{\text{out}}$, $t_{\text{lin,rin}}^{\text{lout,rout}}$)
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- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.
- Antisymmetrize a pair of external particle/hole line that does not connect to the same operator.

CCSD $\widehat{T}_2$ amplitude equation

$$
\begin{aligned}
0 = {} & \langle ab||ij\rangle + P(ij)\langle ab||ej\rangle t_i^e - P(ab)\langle am||ij\rangle t_m^b + P(ab) f_e^b t_{ij}^{ae} - P(ij) f_i^m t_{mj}^{ab} \\
& + \frac{1}{2}\langle ab||ef\rangle t_{ij}^{ef} + \frac{1}{2}\langle mn||ij\rangle t_{mn}^{ab} + P(ij)P(ab)\langle mb||ej\rangle t_{im}^{ae} \\
& + \frac{1}{2}P(ij)\langle ab||ef\rangle t_i^e t_j^f + \frac{1}{2}P(ab)\langle mn||ij\rangle t_m^a t_n^b - P(ij)P(ab)\langle mb||ej\rangle t_i^e t_m^a \\
& + \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab} + \frac{1}{2}P(ij)P(ab)\langle mn||ef\rangle t_{im}^{ae} t_{nj}^{fb} - \frac{1}{2}P(ab)\langle mn||ef\rangle t_{ij}^{ae} t_{mn}^{bf} \\
& - \frac{1}{2}P(ij)\langle mn||ef\rangle t_{mi}^{ef} t_{nj}^{ab} - P(ij) f_e^m t_i^e t_{mj}^{ab} - P(ab) f_e^m t_{ij}^{ae} t_m^b \\
& + P(ij)P(ab)\langle am||ef\rangle t_i^e t_{mj}^{fb} - \frac{1}{2}P(ab)\langle am||ef\rangle t_{ij}^{ef} t_m^b + P(ab)\langle bm||ef\rangle t_{ij}^{ae} t_m^f \\
& - P(ij)P(ab)\langle mn||ej\rangle t_{im}^{ae} t_n^b + \frac{1}{2}P(ij)\langle mn||ej\rangle t_i^e t_{mn}^{ab} - P(ij)\langle mn||ei\rangle t_m^e t_{nj}^{ab} \\
& - \frac{1}{2}P(ij)P(ab)\langle am||ef\rangle t_i^e t_j^f t_m^b + \frac{1}{2}P(ij)P(ab)\langle mn||ej\rangle t_i^e t_m^a t_n^b \\
& + \frac{1}{4}P(ij)\langle mn||ef\rangle t_i^e t_{mn}^{ab} t_j^f - P(ij)P(ab)\langle mn||ef\rangle t_i^e t_m^a t_{nj}^{fb} \\
& + \frac{1}{4}P(ab)\langle mn||ef\rangle t_m^a t_{ij}^{ef} t_n^b - P(ij)\langle mn||ef\rangle t_m^e t_i^f t_{nj}^{ab} - P(ab)\langle mn||ef\rangle t_{ij}^{ae} t_m^b t_n^f \\
& + \frac{1}{4}P(ij)P(ab)\langle mn||ef\rangle t_i^e t_m^a t_j^f t_n^b
\end{aligned}
$$

The expansion

$$E_{CC} = \langle\Psi_0|\Big(\hat{H}_N + \left[\hat{H}_N, \hat{T}\right] + \frac{1}{2}\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right] + \frac{1}{3!}\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right], \hat{T}\right] + +\Big)|\Psi_0\rangle$$

$$0 = \langle\Psi_{ij\ldots}^{ab\ldots}|\Big(\hat{H}_N + \left[\hat{H}_N, \hat{T}\right] + \frac{1}{2}\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right] + \frac{1}{3!}\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right], \hat{T}\right] + +\Big)|\Psi_0\rangle$$

The CCSD energy equation revisited

The expanded CC energy equation involves an infinite sum over nested commutators

$$E_{CC} = \langle\Psi_0|\Big(\hat{H}_N + \left[\hat{H}_N, \hat{T}\right] + \frac{1}{2}\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right]$$
$$+ \frac{1}{3!}\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right]$$
$$+ \frac{1}{4!}\left[\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right], \hat{T}\right] + +\Big)|\Psi_0\rangle,$$

but fortunately we can show that it truncates naturally, depending on the Hamiltonian.

The first term is zero by construction.

$$\langle\Psi_0|\widehat{H}_N|\Psi_0\rangle = 0$$

The CCSD energy equation revisited.

The second term can be split up into different pieces

$$\langle\Psi_0|\left[\hat{H}_N,\hat{T}\right]|\Psi_0\rangle = \langle\Psi_0|\Big(\left[\hat{F}_N,\hat{T}_1\right]+\left[\hat{F}_N,\hat{T}_2\right]+\left[\hat{V}_N,\hat{T}_1\right]+\left[\hat{V}_N,\hat{T}_2\right]\Big)|\Psi_0\rangle$$

Since we need the explicit expressions for the commutators both in the next term and in the amplitude equations, we calculate them separately.

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$
\begin{aligned}
\left[\hat{F}_N, \hat{T}_1\right] &= \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right) \\
&= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)
\end{aligned}
$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$
\begin{aligned}
\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} &= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&\quad + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&\quad + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa} \delta_{pi}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p \left\{a_p^\dagger a_q\right\} t_i^a \left\{a_a^\dagger a_i\right\} - t_i^a \left\{a_a^\dagger a_i\right\} f_q^p \left\{a_p^\dagger a_q\right\} \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(\left\{a_p^\dagger a_q\right\} \left\{a_a^\dagger a_i\right\} - \left\{a_a^\dagger a_i\right\} \left\{a_p^\dagger a_q\right\} \right)$$

$$\left\{a_a^\dagger a_i\right\} \left\{a_p^\dagger a_q\right\} = \left\{a_a^\dagger a_i a_p^\dagger a_q\right\} = \left\{a_p^\dagger a_q a_a^\dagger a_i\right\}$$

$$\left\{a_p^\dagger a_q\right\} \left\{a_a^\dagger a_i\right\} = \left\{a_p^\dagger a_q a_a^\dagger a_i\right\}$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_i\right\}$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_i\right\}$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_i\right\} + \delta_{qa} \left\{a_p^\dagger a_i\right\} + \delta_{pi} \left\{a_q a_a^\dagger\right\} + \delta_{qa}\delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$
\begin{aligned}
\left[\hat{F}_N, \hat{T}_1\right] &= \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right) \\
&= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)
\end{aligned}
$$

$$
\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}
$$

$$
\begin{aligned}
\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} &= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&\quad + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&\quad + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa} \delta_{pi}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right)$$
$$= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$
$$\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$
$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$
$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$
$$= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa}\delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f^p_q \left\{a^\dagger_p a_q\right\} t^a_i \left\{a^\dagger_a a_i\right\} - t^a_i \left\{a^\dagger_a a_i\right\} f^p_q \left\{a^\dagger_p a_q\right\}\right)$$
$$= \sum_{pqia} f^p_q t^a_i \left(\left\{a^\dagger_p a_q\right\} \left\{a^\dagger_a a_i\right\} - \left\{a^\dagger_a a_i\right\} \left\{a^\dagger_p a_q\right\}\right)$$

$$\left\{a^\dagger_a a_i\right\}\left\{a^\dagger_p a_q\right\} = \left\{a^\dagger_a a_i a^\dagger_p a_q\right\} = \left\{a^\dagger_p a_q a^\dagger_a a_i\right\}$$
$$\left\{a^\dagger_p a_q\right\}\left\{a^\dagger_a a_i\right\} = \left\{a^\dagger_p a_q a^\dagger_a a_i\right\}$$
$$+ \left\{a^\dagger_p a_q a^\dagger_a a_i\right\} + \left\{a^\dagger_p a_q a^\dagger_a a_i\right\}$$
$$+ \left\{a^\dagger_p a_q a^\dagger_a a_i\right\}$$
$$= \left\{a^\dagger_p a_q a^\dagger_a a_i\right\} + \delta_{qa}\left\{a^\dagger_p a_i\right\} + \delta_{pi}\left\{a_q a^\dagger_a\right\} + \delta_{qa}\delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$
\begin{aligned}
\left[\hat{F}_N, \hat{T}_1\right] &= \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right) \\
&= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)
\end{aligned}
$$

$$
\begin{aligned}
\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} &= \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} &= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&\quad + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&\quad + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa} \delta_{pi}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa}\delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

Wicks theorem gives us

$$\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_i\right\} - \left\{a_a^\dagger a_i\right\}\left\{a_p^\dagger a_q\right\} = \delta_{qa}\left\{a_p^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger\right\} + \delta_{qa}\delta_{pi}.$$

Inserted into the original expression, we arrive at the explicit value of the commutator

$$\begin{aligned}\left[\hat{F}_N, \hat{T}_1\right] &= \sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a \\ &= \left(\widehat{F}_N \widehat{T}_1\right)_c.\end{aligned}$$

The subscript means that the product only includes terms where the operators are connected by atleast one shared index.

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$\left[\hat{F}_N, \hat{T}_2\right] = \left[\sum_{pq} f_q^p \left\{a_p^\dagger a_q\right\}, \frac{1}{4}\sum_{ijab} t_{ij}^{ab} \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]$$

$$= \frac{1}{4}\sum_{\substack{pq\\ijab}} \left[\left\{a_p^\dagger a_q\right\}, \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]$$

$$= \frac{1}{4}\sum_{\substack{pq\\ijab}} f_q^p t_{ij}^{ab} \left(\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} - \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\}\right)$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} = \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\}$$
$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} = \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}$$
$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right.$$
$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right.$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$
$$+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\}$$
$$+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$
\begin{aligned}
\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} &= \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\} \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}
\end{aligned}
$$

$$
\begin{aligned}
\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} &= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right. \\
&+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right. \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} \\
&+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} \\
&+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} = \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\}$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} = \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \cdots\right.$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j \cdots\right.$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j \cdots\right.$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$

$$+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\}$$

$$+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$
\begin{aligned}
\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} &= \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\} \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} &= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&\quad + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right. \\
&\quad + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right. \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} \\
&\quad + \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} \\
&\quad + \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$
\begin{aligned}
\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} &= \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\} \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} &= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&\quad + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&\quad + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} \\
&\quad + \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} \\
&\quad + \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} = \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\}$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} = \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$

$$+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\}$$

$$+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

Wicks theorem gives us

$$\left(\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} - \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\}\right) =$$

$$- \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} + \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\}$$

$$- \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} + \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\}$$

$$- \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}$$

Inserted into the original expression, we arrive at

$$\left[\widehat{F}_N, \widehat{T}_2\right] = \frac{1}{4}\sum_{\substack{pq\\abij}} f_q^p t_{ij}^{ab}\left(-\delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\}\right.$$

$$+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\}$$

$$\left. + \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}\right).$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

Wicks theorem gives us

$$
\begin{aligned}
\left(\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} - \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\}\right) = \\
& - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} + \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} \\
& - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} + \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} \\
& - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}
\end{aligned}
$$

Inserted into the original expression, we arrive at

$$
\begin{aligned}
\left[\widehat{F}_N, \widehat{T}_2\right] = \frac{1}{4}\sum_{\substack{pq\\abij}} f_q^p t_{ij}^{ab}\Big(& -\delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} \\
& + \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} \\
& + \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}\Big).
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

After renaming indices and changing the order of operators, we arrive at the explicit expression

$$\begin{aligned}\left[\widehat{F}_N, \widehat{T}_2\right] &= \frac{1}{2}\sum_{qijab} f^i_q t^{ab}_{ij}\left\{a_q a^\dagger_a a^\dagger_b a_j\right\} + \frac{1}{2}\sum_{pijab} f^p_a t^{ab}_{ij}\left\{a^\dagger_p a^\dagger_b a_j a_i\right\} \\ &\quad + \sum_{ijab} f^i_a t^{ab}_{ij}\left\{a^\dagger_b a_j\right\} \\ &= \left(\widehat{F}_N \widehat{T}_2\right)_c .\end{aligned}$$

The subscript implies that only the connected terms from the product contribute.

The expansion $-\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a$$

$$\begin{aligned}
\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] &= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right] \\
&= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\}, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right] \\
&= \sum_{pabij} f_a^p t_i^a t_j^b \left[\left\{a_p^\dagger a_i\right\}, \left\{a_b^\dagger a_j\right\}\right] + \sum_{qabij} f_q^i t_i^a t_j^b \left[\left\{a_q a_a^\dagger\right\}, \left\{a_b^\dagger a_j\right\}\right]
\end{aligned}$$

$$\left\{a_b^\dagger a_j\right\}\left\{a_p^\dagger a_i\right\} = \left\{a_b^\dagger a_j a_p^\dagger a_i\right\} = \left\{a_p^\dagger a_i a_b^\dagger a_j\right\}$$

$$\left\{a_b^\dagger a_j\right\}\left\{a_q a_a^\dagger\right\} = \left\{a_b^\dagger a_j a_q a_a^\dagger\right\} = \left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$

The expansion - $\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a$$

$$\begin{aligned}
\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] &= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right] \\
&= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\}, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right] \\
&= \sum_{pabij} f_a^p t_i^a t_j^b \left[\left\{a_p^\dagger a_i\right\}, \left\{a_b^\dagger a_j\right\}\right] + \sum_{qabij} f_q^i t_i^a t_j^b \left[\left\{a_q a_a^\dagger\right\}, \left\{a_b^\dagger a_j\right\}\right]
\end{aligned}$$

$$\left\{a_b^\dagger a_j\right\}\left\{a_p^\dagger a_i\right\} = \left\{a_b^\dagger a_j a_p^\dagger a_i\right\} = \left\{a_p^\dagger a_i a_b^\dagger a_j\right\}$$

$$\left\{a_b^\dagger a_j\right\}\left\{a_q a_a^\dagger\right\} = \left\{a_b^\dagger a_j a_q a_a^\dagger\right\} = \left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$

The expansion - $\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a$$

$$\begin{aligned}
\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] &= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right. \\
&= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\}, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right. \\
&= \sum_{pabij} f_a^p t_i^a t_j^b \left[\left\{a_p^\dagger a_i\right\}, \left\{a_b^\dagger a_j\right\}\right] + \sum_{qabij} f_q^i t_i^a t_j^b \left[\left\{a_q a_a^\dagger\right\}, \left\{a_b^\dagger a_j\right\}\right]
\end{aligned}$$

$$\left\{a_b^\dagger a_j\right\}\left\{a_p^\dagger a_i\right\} = \left\{a_b^\dagger a_j a_p^\dagger a_i\right\} = \left\{a_p^\dagger a_i a_b^\dagger a_j\right\}$$

$$\left\{a_b^\dagger a_j\right\}\left\{a_q a_a^\dagger\right\} = \left\{a_b^\dagger a_j a_q a_a^\dagger\right\} = \left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$

The expansion - $\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a$$

$$\begin{aligned}
\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] &= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right] \\
&= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\}, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right] \\
&= \sum_{pabij} f_a^p t_i^a t_j^b \left[\left\{a_p^\dagger a_i\right\}, \left\{a_b^\dagger a_j\right\}\right] + \sum_{qabij} f_q^i t_i^a t_j^b \left[\left\{a_q a_a^\dagger\right\}, \left\{a_b^\dagger a_j\right\}\right]
\end{aligned}$$

$$\begin{aligned}
\left\{a_b^\dagger a_j\right\}\left\{a_p^\dagger a_i\right\} &= \left\{a_b^\dagger a_j a_p^\dagger a_i\right\} = \left\{a_p^\dagger a_i a_b^\dagger a_j\right\} \\
\left\{a_b^\dagger a_j\right\}\left\{a_q a_a^\dagger\right\} &= \left\{a_b^\dagger a_j a_q a_a^\dagger\right\} = \left\{a_q a_a^\dagger a_b^\dagger a_j\right\}
\end{aligned}$$

The expansion - $\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$
\begin{aligned}
\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] &= \frac{1}{2}\left(\sum_{pabij} f_a^p t_i^a t_j^b \delta_{pj}\left\{a_i a_b^\dagger\right\} - \sum_{qabij} f_q^i t_i^a t_j^b \delta_{qb}\left\{a_a^\dagger a_j\right\}\right) \\
&= -\frac{1}{2}2\sum_{abij} f_b^j t_j^a t_i^b \left\{a_a^\dagger a_i\right\} \\
&= -\sum_{abij} f_b^j t_j^a t_i^b \left\{a_a^\dagger a_i\right\} \\
&= \frac{1}{2}\left(\widehat{F}_N \widehat{T}_1^2\right)_c
\end{aligned}
$$

The CCSD energy equation revisited

$$\langle\Phi_0|\left[\hat{V}_N,\hat{T}_1\right]|\Phi_0\rangle = \langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\sum_{ia}t_i^a\left\{a_a^\dagger a_i\right\}\right]|\Phi_0\rangle$$

$$= \frac{1}{4}\sum_{\substack{pqr\\sia}}\langle pq||rs\rangle t_i^a\langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\left\{a_a^\dagger a_i\right\}\right]|\Phi_0\rangle$$

$$= 0$$

The CCSD energy equation revisited

$$
\begin{aligned}
\langle\Phi_0|\left[\hat{V}_N, \hat{T}_1\right]|\Phi_0\rangle &= \langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}, \sum_{ia} t_i^a\left\{a_a^\dagger a_i\right\}\right]|\Phi_0\rangle \\
&= \frac{1}{4}\sum_{\substack{pqr\\sia}}\langle pq||rs\rangle t_i^a \langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}, \left\{a_a^\dagger a_i\right\}\right]|\Phi_0\rangle \\
&= 0
\end{aligned}
$$

The CCSD energy equation revisited

$$\begin{aligned}
\langle\Phi_0|\left[\hat{V}_N, \hat{T}_1\right]|\Phi_0\rangle &= \langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}, \sum_{ia} t_i^a\left\{a_a^\dagger a_i\right\}\right]|\Phi_0\rangle \\
&= \frac{1}{4}\sum_{\substack{pqr\\sia}}\langle pq||rs\rangle t_i^a\langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}, \left\{a_a^\dagger a_i\right\}\right]|\Phi_0\rangle \\
&= 0
\end{aligned}$$

The CCSD energy equation revisited

$$\langle \Phi_0 | \left[\hat{V}_N, \hat{T}_2 \right] | \Phi_0 \rangle =$$

$$\langle \Phi_0 | \left[\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\}, \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \left\{ a_a^\dagger a_b^\dagger a_j a_i \right\} \right] | \Phi_0 \rangle$$

$$= \frac{1}{16} \sum_{\substack{pqr \\ sijab}} \langle pq || rs \rangle t_{ij}^{ab} \langle \Phi_0 | \left[\left\{ a_p^\dagger a_q^\dagger a_s a_r \right\}, \left\{ a_a^\dagger a_b^\dagger a_j a_i \right\} \right] | \Phi_0 \rangle$$

$$= \frac{1}{16} \sum_{\substack{pqr \\ sijab}} \langle pq || rs \rangle t_{ij}^{ab} \langle \Phi_0 | \Big(\left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} +$$

$$\left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} \Big) | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}$$

The CCSD energy equation revisited

$$\langle\Phi_0|\left[\hat{V}_N, \hat{T}_2\right]|\Phi_0\rangle =$$

$$\langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}, \frac{1}{4}\sum_{ijab} t_{ij}^{ab}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$= \frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}, \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$= \frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\left(\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}\right.$$

$$\left.\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}\right)|\Phi_0\rangle$$

$$= \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}$$

The CCSD energy equation revisited

$$\langle\Phi_0|\left[\hat{V}_N, \hat{T}_2\right]|\Phi_0\rangle =$$

$$\langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}, \frac{1}{4}\sum_{ijab} t_{ij}^{ab}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$= \frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}, \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$= \frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\Big(\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}\Big)|\Phi_0\rangle$$

$$= \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}$$

The CCSD energy equation revisited

$$\langle\Phi_0|\left[\hat{V}_N,\hat{T}_2\right]|\Phi_0\rangle =$$

$$\langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\frac{1}{4}\sum_{ijab}t_{ij}^{ab}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$=\frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$=\frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\Big(\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}+\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}+\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}\Big)|\Phi_0\rangle$$

$$=\frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}$$

The CCSD energy equation revisited

The CCSD energy get two contributions from $\left(\widehat{H}_N \widehat{T}\right)_c$

$$
\begin{aligned}
E_{CC} &\Leftarrow \langle \Phi_0 | \left[\hat{H}_N, \hat{T} \right] | \Phi_0 \rangle \\
&= \sum_{ia} f_a^i t_i^a + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}
\end{aligned}
$$

The CCSD energy equation revisited

$$E_{CC} \Leftarrow \langle\Phi_0|\frac{1}{2}\left(\widehat{H}_N\widehat{T}^2\right)_c|\Phi_0\rangle$$

$$\langle\Phi_0|\frac{1}{2}\left(\widehat{V}_N\widehat{T}_1^2\right)_c|\Phi_0\rangle =$$

$$\frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b \langle\Phi_0|\left(\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}\left\{a_a^\dagger a_i\right\}\left\{a_b^\dagger a_j\right\}\right)_c|\Phi_0\rangle$$

$$= \frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b \langle\Phi_0|$$

$$\left(\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\}\right.$$

$$\left. + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\}\right)|\Phi_0\rangle$$

$$= \frac{1}{2}\sum_{ijab}\langle ij||ab\rangle t_i^a t_j^b$$

The CCSD energy equation revisited

$$E_{CC} \Leftarrow \langle\Phi_0|\frac{1}{2}\left(\widehat{H}_N\widehat{T}^2\right)_c|\Phi_0\rangle$$

$$\langle\Phi_0|\frac{1}{2}\left(\widehat{V}_N\widehat{T}_1^2\right)_c|\Phi_0\rangle =$$

$$\frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b\langle\Phi_0|\left(\left\{a_p^\dagger a_q^\dagger a_s a_r\right\}\left\{a_a^\dagger a_i\right\}\left\{a_b^\dagger a_j\right\}\right)_c|\Phi_0\rangle$$

$$= \frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b\langle\Phi_0|$$

$$\left(\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\} + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\}\right.$$

$$\left. + \left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right\}\right)|\Phi_0\rangle$$

$$= \frac{1}{2}\sum_{ijab}\langle ij||ab\rangle t_i^a t_j^b$$

The CCSD energy equation revisited

$$E_{CC} \Leftarrow \langle \Phi_0 | \frac{1}{2} \left(\widehat{H}_N \widehat{T}^2 \right)_c | \Phi_0 \rangle$$

$$\langle \Phi_0 | \frac{1}{2} \left(\widehat{V}_N \widehat{T}_1^2 \right)_c | \Phi_0 \rangle =$$

$$\frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq||rs \rangle t_i^a t_j^b \langle \Phi_0 | \left(\left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \left\{ a_a^\dagger a_i \right\} \left\{ a_b^\dagger a_j \right\} \right)_c | \Phi_0 \rangle$$

$$= \frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq||rs \rangle t_i^a t_j^b \langle \Phi_0 |$$

$$\left(\left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right.$$

$$\left. + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right) | \Phi_0 \rangle$$

$$= \frac{1}{2} \sum_{ijab} \langle ij||ab \rangle t_i^a t_j^b$$

The CCSD energy equation revisited

$$E_{CC} \Leftarrow \langle \Phi_0 | \frac{1}{2} \left(\widehat{H}_N \widehat{T}^2 \right)_c | \Phi_0 \rangle$$

$$\langle \Phi_0 | \frac{1}{2} \left(\widehat{V}_N \widehat{T}_1^2 \right)_c | \Phi_0 \rangle =$$

$$\frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq||rs \rangle t_i^a t_j^b \langle \Phi_0 | \left(\left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \left\{ a_a^\dagger a_i \right\} \left\{ a_b^\dagger a_j \right\} \right)_c | \Phi_0 \rangle$$

$$= \frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq||rs \rangle t_i^a t_j^b \langle \Phi_0 |$$

$$\left(\left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right.$$

$$\left. + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right) | \Phi_0 \rangle$$

$$= \frac{1}{2} \sum_{ijab} \langle ij||ab \rangle t_i^a t_j^b$$

The CCSD energy equation revisited

- No contractions possible between cluster operators.
- Cluster operators need to contract with free indices to the left.
- Disconnected parts automatically cancel in the commutator.
- Onebody operators can connect to maximum two cluster operators.
- Twobody operators can connect to maximum four cluster operators.
- Different terms in the expansion contributes to different equations.

The CCSD energy equation revisited

- No contractions possible between cluster operators.
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The CCSD energy equation revisited

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The CCSD energy equation revisited

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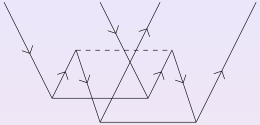
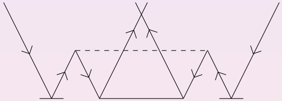
Factoring, motivation

Diagram (2.12)



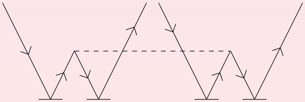
$$= \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

Diagram (2.26)



$$= \frac{1}{4}P(ij)\langle mn||ef\rangle t_i^{e} t_{mn}^{ab} t_j^{f}$$

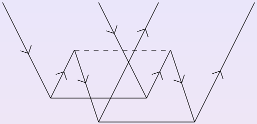
Diagram (2.31)



$$= \frac{1}{4}P(ij)P(ab)\langle mn||ef\rangle t_i^{e} t_m^{a} t_j^{f} t_n^{b}$$

Factoring, motivation

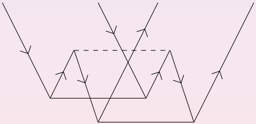
Diagram (2.12)



$$= \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

Diagram cost: $n_p^4 n_h^4$

Diagram (2.13) - Factored

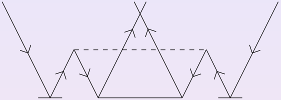


$$= \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

$$= \frac{1}{4}\left(\langle mn||ef\rangle t_{ij}^{ef}\right) t_{mn}^{ab}$$
$$= \frac{1}{4} X_{ij}^{mn} t_{mn}^{ab}$$

Factoring, motivation

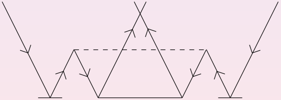
Diagram (2.26)



$$= \frac{1}{4} P(ij) \langle mn||ef \rangle t_i^e t_{mn}^{ab} t_j^f$$

Diagram cost: $n_p^4 n_h^4$

Diagram (2.26) - Factored



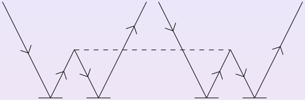
$$= \frac{1}{4} P(ij) \langle mn||ef \rangle t_i^e t_{mn}^{ab} t_j^f$$

$$= \frac{1}{4} P(ij) t_{mn}^{ab} t_i^e X_{ej}^{mn}$$

$$= \frac{1}{4} P(ij) t_{mn}^{ab} Y_{ij}^{mn}$$

Factoring, motivation

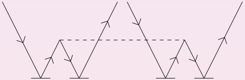
Diagram (2.31)



$$= \frac{1}{4}P(ij)P(ab)\langle mn||ef\rangle t_i^e t_m^a t_j^f t_n^b$$

Diagram cost: $n_p^4 n_h^4$

Diagram (2.31) - Factored



$$= \frac{1}{4}P(ij)P(ab)\langle mn||ef\rangle t_i^e t_m^a t_j^f t_n^b$$

$$= \frac{1}{4}P(ij)P(ab)t_m^a t_n^b t_i^e X_{ej}^{mn}$$

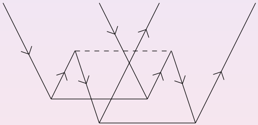
$$= \frac{1}{4}P(ij)P(ab)t_m^a t_n^b Y_{ij}^{mn}$$

$$= \frac{1}{4}P(ij)P(ab)t_m^a Z_{ij}^{mb}$$

Factoring, Classification

A diagram is classified by how many hole and particle lines between a $\hat{T}_i$ operator and the interaction ($T_i(p^{np}h^{nh})$).

Diagram (2.12) Classification

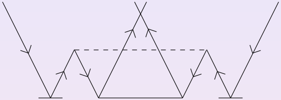


$$= \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

This diagram is classified as $T_2(p^2) \times T_2(h^2)$

Factoring, Classification

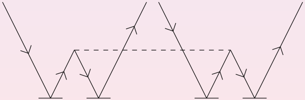
Diagram (2.26)



$$= \frac{1}{4} P(ij) \langle mn||ef \rangle t_i^e t_{mn}^{ab} t_j^f$$

This diagram is classified as $T_2(h^2) \times T_1(p) \times T_1(p)$

Diagram (2.31)



$$= \frac{1}{4} P(ij) P(ab) \langle mn||ef \rangle t_i^e t_m^a t_j^f t_n^b$$

This diagram is classified as $T_1(p) \times T_1(p) \times T_1(h) \times T_1(h)$

Factoring, Classification

Cost of making intermediates

Object	CPU cost	Memory cost
$T_2(h)$	$n_p^2 n_h$	n_p^2
$T_2(h^2)$	n_p^2	$n_h^{-2} n_p^2$
$T_2(p)$	$n_p n_h^2$	n_h^2
$T_2(ph)$	$n_p n_h$	1
$T_1(h)$	n_p	$n_h^{-1} n_p$
$T_2(ph^2)$	n_p	n_h^{-2}
$T_2(p^2)$	n_h^2	$n_p^{-2} n_h^2$
$T_1(p)$	n_h	$n_p^{-1} n_h$
$T_2(p^2 h)$	n_h	n_p^{-2}
$T_1(ph)$	1	$n_p^{-1} n_h^{-1}$

Factoring, Classification

Classification of $\hat{T}_1$ diagrams

Object	Expression id
$T_2(ph)$	5, 11
$T_1(h)$	3, 8, 10, 13, 14
$T_2(ph^2)$	7, 12
$T_1(p)$	2, 8, 9, 12, 14
$T_2(p^2h)$	6, 13
$T_1(ph)$	4, 9, 10, 11, 14

Factoring, Classification

Classification of $\hat{T}_2$ diagrams

Object	Expression id
$T_2(h)$	5, 15, 16, 23, 29
$T_2(h^2)$	7, 12, 22, 26
$T_2(p)$	4, 14, 17, 20, 30
$T_2(ph)$	8, 13, 13, 18, 21, 27
$T_1(h)$	3, 10, 10, 11, 17, 19, 21, 24, 25, 25, 27, 28, 28, 30, 31, 31
$T_2(ph^2)$	14
$T_2(p^2)$	6, 12, 19, 28
$T_1(p)$	2, 9, 9, 11, 16, 18, 22, 24, 24, 25, 26, 26, 27, 29, 31, 31
$T_2(p^2h)$	15
$T_1(ph)$	20, 23, 29, 30

Factoring, $T_2(h)$

Contribution to the $\hat{T}_2$ amplitude equation from $T_2(h)$

$$
\begin{aligned}
T_2(h) \Leftarrow & -P(ij) f_i^m t_{mj}^{ab} - \frac{1}{2} P(ij) \langle mn||ef\rangle t_{mi}^{ef} t_{nj}^{ab} - P(ij) f_e^m t_i^e t_{mj}^{ab} \\
& - P(ij)\langle mn||ei\rangle t_m^e t_{nj}^{ab} - P(ij)\langle mn||ef\rangle t_m^e t_i^f t_{nj}^{ab} \\
= & -P(ij) t_{im}^{ab} \Big[f_j^m + \langle mn||je\rangle t_n^e + \frac{1}{2}\langle mn||ef\rangle t_{jn}^{ef} \\
& + t_j^e \Big(f_e^m + \langle mn||ef\rangle t_n^f \Big) \Big] \\
= & -P(ij) t_{im}^{ab} (\bar{\mathrm{H}}3)_j^m
\end{aligned}
$$

Factoring, $T_2(h^2)$

Contribution to the $\hat{T}_2$ amplitude equation from $T_2(h^2)$

$$
\begin{aligned}
T_2(h^2) \Leftarrow & \frac{1}{2}\langle mn||ij\rangle t_{mn}^{ab} + \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab} + \frac{1}{2}P(ij)\langle mn||ej\rangle t_i^e t_{mn}^{ab} \\
& + \frac{1}{4}P(ij)\langle mn||ef\rangle t_i^e t_{mn}^{ab} t_j^f \\
= & \frac{1}{2} t_{mn}^{ab}\Big[\langle mn||ij\rangle + \frac{1}{2}\langle mn||ef\rangle t_{ij}^{ef} \\
& + P(ij) t_j^e \Big(\langle mn||ie\rangle + \frac{1}{2}\langle mn||fe\rangle t_i^f\Big)\Big] \\
= & \frac{1}{2} t_{mn}^{ab} (\bar{\mathrm{H}}9)_{ij}^{mn}
\end{aligned}
$$

Factored T_1 amplitude equations

$$0 = f_i^a + \langle ma||ei\rangle t_m^e + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + t_i^e (\mathrm{I2a})_e^a - t_m^a (\bar{\mathrm{H}}3)_i^m + \frac{1}{2} t_{mn}^{ea} (\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae} (\bar{\mathrm{H}}1)_e^m$$

Can be solved by

1. Matrix inversion for each iteration ($n_p^3 n_h^3$)
2. Extracting diagonal elements ($n_p^3 n_h^2$)

Factored T_1 amplitude equations

$$
\begin{aligned}
0 &= f_i^a + \langle ma||ei\rangle t_m^e + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + t_i^e(\mathrm{I2a})_e^a - t_m^a(\bar{\mathrm{H}}3)_i^m \\
&\quad + \frac{1}{2} t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m \\
&= f_i^a + \langle ma||ei\rangle t_m^e + t_i^a(\mathrm{I2a})_a^a + (1-\delta_{ea}) t_i^e(\mathrm{I2a})_e^a \\
&\quad - t_i^a(\bar{\mathrm{H}}3)_i^i - (1-\delta_{mi}) t_m^a(\bar{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + \frac{1}{2} t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} \\
&\quad + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m \\
&= f_i^a + t_i^a\Big((\mathrm{I2a})_a^a - (\bar{\mathrm{H}}3)_i^i\Big) + \langle ma||ei\rangle t_m^e \\
&\quad + (1-\delta_{ea}) t_i^e(\mathrm{I2a})_e^a - (1-\delta_{mi}) t_m^a(\bar{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\
&\quad + \frac{1}{2} t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m
\end{aligned}
$$

Factored T_1 amplitude equations

$$
\begin{aligned}
0 &= f_i^a + \langle ma||ei\rangle t_m^e + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + t_i^e(\mathrm{I2a})_e^a - t_m^a(\bar{\mathrm{H}}3)_i^m \\
&\quad + \frac{1}{2} t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m \\
&= f_i^a + \langle ma||ei\rangle t_m^e + t_i^a(\mathrm{I2a})_a^a + (1-\delta_{ea}) t_i^e(\mathrm{I2a})_e^a \\
&\quad - t_i^a(\bar{\mathrm{H}}3)_i^i - (1-\delta_{mi}) t_m^a(\bar{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + \frac{1}{2} t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} \\
&\quad + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m \\
&= f_i^a + t_i^a\Big((\mathrm{I2a})_a^a - (\bar{\mathrm{H}}3)_i^i\Big) + \langle ma||ei\rangle t_m^e \\
&\quad + (1-\delta_{ea}) t_i^e(\mathrm{I2a})_e^a - (1-\delta_{mi}) t_m^a(\bar{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\
&\quad + \frac{1}{2} t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m
\end{aligned}
$$

Factored T_1 amplitude equations

$$
\begin{aligned}
0 &= f_i^a + \langle ma||ei\rangle t_m^e + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + t_i^e(\mathrm{I2a})_e^a - t_m^a(\bar{\mathrm{H}}3)_i^m \\
&\quad + \frac{1}{2} t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m \\
&= f_i^a + \langle ma||ei\rangle t_m^e + t_i^a(\mathrm{I2a})_a^a + (1-\delta_{ea}) t_i^e(\mathrm{I2a})_e^a \\
&\quad - t_i^a(\bar{\mathrm{H}}3)_i^i - (1-\delta_{mi}) t_m^a(\bar{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + \frac{1}{2} t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} \\
&\quad + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m \\
&= f_i^a + t_i^a\Big((\mathrm{I2a})_a^a - (\bar{\mathrm{H}}3)_i^i\Big) + \langle ma||ei\rangle t_m^e \\
&\quad + (1-\delta_{ea}) t_i^e(\mathrm{I2a})_e^a - (1-\delta_{mi}) t_m^a(\bar{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\
&\quad + \frac{1}{2} t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m
\end{aligned}
$$

Factored T_1 amplitude equations

Define

$$D_i^a = (\bar{\mathrm{H}}3)_i^i - (\mathrm{I2a})_a^a,$$

and we get the T_1 amplitude equations

$$\begin{aligned} D_i^a t_i^a = f_i^a + \langle ma||ei\rangle t_m^e + (1-\delta_{ea}) t_i^e (\mathrm{I2a})_e^a \\ - (1-\delta_{mi}) t_m^a (\bar{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\ + \frac{1}{2} t_{mn}^{ea} (\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae} (\bar{\mathrm{H}}1)_e^m. \end{aligned}$$

Factored T_2 amplitude equations

$$
\begin{aligned}
0 = \langle ab||ij\rangle &+ \frac{1}{2}\langle ab||ef\rangle t_{ij}^{ef} - P(ij)t_{im}^{ab}(\bar{\mathrm{H}}3)_j^m + \frac{1}{2}t_{mn}^{ab}(\bar{\mathrm{H}}9)_{ij}^{mn} \\
&+ P(ab)t_{ij}^{ae}(\bar{\mathrm{H}}2)_e^b + P(ij)P(ab)t_{im}^{ae}(\mathrm{I10c})_{ej}^{mb} - P(ab)t_m^a(\mathrm{I12a})_{ij}^{mb} \\
&+ P(ij)t_i^e(\mathrm{I11}a)_{ej}^{ab}
\end{aligned}
$$

Can be solved by

1. Matrix inversion for each iteration ($n_p^6 n_h^6$)
2. Extracting diagonal elements ($n_p^4 n_h^2$)

Factored T_2 amplitude equations

Similarily we define

$$D_{ij}^{ab} = (\bar{\mathrm{H}}3)_i^i + (\bar{\mathrm{H}}3)_j^j - (\bar{\mathrm{H}}2)_a^a - (\bar{\mathrm{H}}2)_b^b$$

and get the T_2 amplitude equations

$$\begin{aligned}
D_{ij}^{ab} t_{ij}^{ab} = \langle ab||ij\rangle + \frac{1}{2}\langle ab||ef\rangle t_{ij}^{ef} - P(ij)(1-\delta_{jm}) t_{im}^{ab}(\bar{\mathrm{H}}3)_j^m \\
+ \frac{1}{2} t_{mn}^{ab}(\bar{\mathrm{H}}9)_{ij}^{mn} + P(ab)(1-\delta_{be}) t_{ij}^{ae}(\bar{\mathrm{H}}2)_e^b \\
+ P(ij)P(ab) t_{im}^{ae}(\mathrm{I10c})_{ej}^{mb} - P(ab) t_m^a(\mathrm{I12a})_{ij}^{mb} \\
+ P(ij) t_i^e(\mathrm{I11}a)_{ej}^{ab}
\end{aligned}$$

Coupled Cluster algorithm

Setup modelspace
Calculate f and v amplitudes
$t_i^a \leftarrow 0$; $t_{ij}^{ab} \leftarrow 0$
$E \leftarrow 1$; $E_{old} \leftarrow 0$
$E_{ref} \leftarrow \sum_i \langle i|\widehat{t}|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|\widehat{v}|ij\rangle$
while not converged ($E - E_{old} > \epsilon$)
    Calculate intermediates
    $t_i^a \leftarrow$ calculated value
    $t_{ij}^{ab} \leftarrow$ calculated value
    $E_{old} \leftarrow E$
    $E \leftarrow f_a^i t_i^a + \frac{1}{4}\langle ij||ab\rangle t_{ij}^{ab} + \frac{1}{2}\langle ij||ab\rangle t_i^a t_j^b$
end while
$E_{GS} \leftarrow E_{ref} + E$

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    $t_{ij}^{ab} \leftarrow$ calculated value
    $E_{old} \leftarrow E$
    $E \leftarrow f_a^i t_i^a + \frac{1}{4}\langle ij||ab\rangle t_{ij}^{ab} + \frac{1}{2}\langle ij||ab\rangle t_i^a t_j^b$
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Coupled Cluster algorithm

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while not converged ($E - E_{old} > \epsilon$)
 Calculate intermediates
 $t_i^a \leftarrow$ calculated value
 $t_{ij}^{ab} \leftarrow$ calculated value
 $E_{old} \leftarrow E$
 $E \leftarrow f_a^i t_i^a + \frac{1}{4}\langle ij||ab\rangle t_{ij}^{ab} + \frac{1}{2}\langle ij||ab\rangle t_i^a t_j^b$
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Coupled Cluster algorithm

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$t_i^a \leftarrow 0$; $t_{ij}^{ab} \leftarrow 0$
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    $t_i^a \leftarrow$ calculated value
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    $E_{old} \leftarrow E$
    $E \leftarrow f_a^i t_i^a + \frac{1}{4}\langle ij||ab\rangle t_{ij}^{ab} + \frac{1}{2}\langle ij||ab\rangle t_i^a t_j^b$
end while
$E_{GS} \leftarrow E_{ref} + E$

Coupled Cluster algorithm

Typical convergence of the T_2 amplitudes