Slides from FYS-KJM4480 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
- Wednesday: Exercises 1 and 2

Lectures and exercise sessions

and syllabus

- Lectures: Monday (8.15-10.00, room LilleFys) and Tuesday (8.15-10.00, room LilleFys)
- Detailed lecture notes, all exercises presented and projects can be found at the homepage of the course.
- Exercises: 14.15-16 Wednesday, room FV311
- 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

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 theory/Mean-field theory and Hartree-Fock theory
5. Monte-Carlo methods (FYS4411)
6. Green's function theories
7. Density functional theories

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

Plan for the semester

Projects, deadlines and oral exam

1. Midterm project, counts 30%: hand out October 11, handin October 14 (12pm)
2. Final written exam, to be decided.

Lectures and exercise sessions

and syllabus

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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

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

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 $u_i = u_{\mathrm{ext}}(x_i)$ 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 $\Psi_\lambda(x_1, x_2, \dots, x_N)$ is an eigenfunction of $\hat{P}$ as well, that is

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

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

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

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

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

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 (6.0.132) 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 $a_\alpha^\dagger$ and a_α which create and annihilate, respectively, a particle in the single-particle state φ_α. We define the fermion creation operator $a_\alpha^\dagger$

$$a_\alpha^\dagger|0\rangle \equiv |\alpha\rangle, \tag{2.0.17}$$

and

$$a_\alpha^\dagger|\alpha_1 \ldots \alpha_n\rangle_{\mathrm{AS}} \equiv |\alpha\alpha_1 \ldots \alpha_n\rangle_{\mathrm{AS}} \tag{2.0.18}$$

Second quantization

In Eq. (2.0.17) the operator $a^\dagger_\alpha$ 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) $a^\dagger_\alpha$ 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.

$$|\alpha_1 \dots \alpha_n\rangle_{\mathrm{AS}} = a^\dagger_{\alpha_1} a^\dagger_{\alpha_2} \dots a^\dagger_{\alpha_n} |0\rangle \qquad (2.0.19)$$

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)

$$|\alpha_1 \dots \alpha_i \dots \alpha_k \dots \alpha_n\rangle_{\mathrm{AS}} = -|\alpha_1 \dots \alpha_k \dots \alpha_i \dots \alpha_n\rangle_{\mathrm{AS}} \qquad (2.0.20)$$

we obtain

$$a_{\alpha_i}^\dagger a_{\alpha_k}^\dagger = -a_{\alpha_k}^\dagger a_{\alpha_i}^\dagger \qquad (2.0.21)$$

Second quantization

Using the Pauli principle

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

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 $|\alpha_1\alpha_2\dots\alpha_n\rangle_{\mathrm{AS}}$? Consider the following matrix element

$$\langle\alpha_1\alpha_2\dots\alpha_n|a_\alpha|\alpha'_1\alpha'_2\dots\alpha'_m\rangle \tag{2.0.27}$$

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

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

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

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

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

$$\langle \alpha_1 \alpha_2 \dots \alpha_n | a_\alpha | \alpha'_1 \alpha'_2 \dots \alpha'_m \rangle = \langle \alpha_1 \alpha_2 \dots \alpha_n | \, \alpha \alpha'_1 \alpha'_2 \dots \alpha'_m \qquad (2.0.30)$$

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

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

Second quantization

For the last case, the minus and plus signs apply when the sequence $\alpha, \alpha_1, \alpha_2, \ldots, \alpha_n$ and $\alpha'_1, \alpha'_2, \ldots, \alpha'_{n+1}$ 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)

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

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

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

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.

Second quantization

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

$$\begin{aligned} a_\alpha^\dagger a_\alpha \underbrace{|\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} &= 0 \\ a_\alpha a_\alpha^\dagger \underbrace{|\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} &= a_\alpha \underbrace{|\alpha\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} = \underbrace{|\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} \end{aligned} \tag{2.0.37}$$

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

Second quantization

If it is present we arrive at

$$\begin{aligned}
a_\alpha^\dagger a_\alpha|\alpha_1\alpha_2\dots\alpha_k\alpha\alpha_{k+1}\dots\alpha_{n-1}\rangle &= a_\alpha^\dagger a_\alpha(-1)^k|\alpha\alpha_1\alpha_2\dots\alpha_{n-1}\rangle \\
= (-1)^k|\alpha\alpha_1\alpha_2\dots\alpha_{n-1}\rangle &= |\alpha_1\alpha_2\dots\alpha_k\alpha\alpha_{k+1}\dots\alpha_{n-1}\rangle \\
a_\alpha a_\alpha^\dagger|\alpha_1\alpha_2\dots\alpha_k\alpha\alpha_{k+1}\dots\alpha_{n-1}\rangle &= 0
\end{aligned} \tag{2.0.38}$$

From Eqs. (2.0.37) and (2.0.38) we arrive at

$$\{a_\alpha^\dagger, a_\alpha\} = a_\alpha^\dagger a_\alpha + a_\alpha a_\alpha^\dagger = 1 \tag{2.0.39}$$

Second quantization

The action of $a_\alpha^\dagger, a_\beta$, 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

$$
\begin{aligned}
a^\dagger_\alpha a_\beta |\alpha\beta\alpha_1\alpha_2\dots\alpha_{n-2}\rangle &= 0 \\
a_\beta a^\dagger_\alpha |\alpha\beta\alpha_1\alpha_2\dots\alpha_{n-2}\rangle &= 0
\end{aligned}
\tag{2.0.40}
$$

while the second case gives

$$
\begin{aligned}
a^\dagger_\alpha a_\beta |\beta \underbrace{\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle &= |\alpha \underbrace{\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle \\
a_\beta a^\dagger_\alpha |\beta \underbrace{\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle &= a_\beta |\alpha\beta \underbrace{\beta\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle \\
&= -|\alpha \underbrace{\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle
\end{aligned}
\tag{2.0.41}
$$

Second quantization

Finally if the state vector does not contain α and β

$$\begin{aligned} a^\dagger_\alpha a_\beta | \underbrace{\alpha_1 \alpha_2 \dots \alpha_n}_{\neq \alpha,\beta} \rangle &= 0 \\ a_\beta a^\dagger_\alpha | \underbrace{\alpha_1 \alpha_2 \dots \alpha_n}_{\neq \alpha,\beta} \rangle &= a_\beta | \alpha \underbrace{\alpha_1 \alpha_2 \dots \alpha_n}_{\neq \alpha,\beta} \rangle = 0 \end{aligned} \tag{2.0.42}$$

For all three cases we have

$$\{a^\dagger_\alpha, a_\beta\} = a^\dagger_\alpha a_\beta + a_\beta a^\dagger_\alpha = 0, \quad \alpha \neq \beta \tag{2.0.43}$$

Second quantization

We can summarize our findings in Eqs. (2.0.39) and (2.0.43) as

$$\{a_\alpha^\dagger, a_\beta\} = \delta_{\alpha\beta} \tag{2.0.44}$$

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

$$a_\alpha^\dagger|0\rangle \equiv |\alpha\rangle,$$

and

$$a_\alpha^\dagger|\alpha_1 \dots \alpha_n\rangle_{\mathrm{AS}} \equiv |\alpha\alpha_1 \dots \alpha_n\rangle_{\mathrm{AS}}.$$

from which follows

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

Second quantization

The hermitian conjugate has the folowing properties

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

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

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

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

$$a^\dagger_\alpha a_\alpha |\alpha_1\alpha_2\ldots\alpha_n\rangle = \begin{cases} 0 & \alpha \notin \{\alpha_i\} \\ \\ |\alpha_1\alpha_2\ldots\alpha_n\rangle & \alpha \in \{\alpha_i\} \end{cases} \tag{2.0.45}$$

Summing over all possible one-particle states we arrive at

$$\left(\sum_\alpha a^\dagger_\alpha a_\alpha\right)|\alpha_1\alpha_2\ldots\alpha_n\rangle = n|\alpha_1\alpha_2\ldots\alpha_n\rangle \tag{2.0.46}$$

Operators in second quantization

The operator

$$\hat{N} = \sum_\alpha a_\alpha^\dagger a_\alpha \tag{2.0.47}$$

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

$$\hat{H}_0 = \sum_i \hat{h}_0(x_i) \tag{2.0.48}$$

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

$$\Phi(x_1, x_2, \dots, x_n, \alpha_1, \alpha_2, \dots, \alpha_n) = \frac{1}{\sqrt{n!}} \sum_p (-1)^p \psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2) \dots \psi_{\alpha_n}(x_n). \tag{2.0.49}$$

Operators in second quantization

Defining

$$\hat{h}_0(x_i)\psi_{\alpha_i}(x_i) = \sum_{\alpha'_k} \psi_{\alpha'_k}(x_i)\langle\alpha'_k|\hat{h}_0|\alpha_k\rangle \tag{2.0.50}$$

we can easily evaluate the action of $\hat{H}_0$ on each product of one-particle functions in Slater determinant. From Eqs. (2.0.49) (2.0.50) we obtain the following result without permuting any particle pair

$$\begin{aligned}
& \left(\sum_i \hat{h}_0(x_i)\right) \psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\dots\psi_{\alpha_n}(x_n) \\
= & \sum_{\alpha'_1}\langle\alpha'_1|\hat{h}_0|\alpha_1\rangle\psi_{\alpha'_1}(x_1)\psi_{\alpha_2}(x_2)\dots\psi_{\alpha_n}(x_n) \\
+ & \sum_{\alpha'_2}\langle\alpha'_2|\hat{h}_0|\alpha_2\rangle\psi_{\alpha_1}(x_1)\psi_{\alpha'_2}(x_2)\dots\psi_{\alpha_n}(x_n) \\
+ & \dots \\
+ & \sum_{\alpha'_n}\langle\alpha'_n|\hat{h}_0|\alpha_n\rangle\psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\dots\psi_{\alpha'_n}(x_n)
\end{aligned} \tag{2.0.51}$$

Operators in second quantization

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

$$\begin{aligned}
& \left(\sum_i \hat{h}_0(x_i)\right) \psi_{\alpha_1}(x_2)\psi_{\alpha_1}(x_2)\ldots\psi_{\alpha_n}(x_n) \\
= & \sum_{\alpha_2'} \langle\alpha_2'|\hat{h}_0|\alpha_2\rangle \psi_{\alpha_1}(x_2)\psi_{\alpha_2'}(x_1)\ldots\psi_{\alpha_n}(x_n) \\
+ & \sum_{\alpha_1'} \langle\alpha_1'|\hat{h}_0|\alpha_1\rangle \psi_{\alpha_1'}(x_2)\psi_{\alpha_2}(x_1)\ldots\psi_{\alpha_n}(x_n) \\
+ & \ldots \\
+ & \sum_{\alpha_n'} \langle\alpha_n'|\hat{h}_0|\alpha_n\rangle \psi_{\alpha_1}(x_2)\psi_{\alpha_1}(x_2)\ldots\psi_{\alpha_n'}(x_n)
\end{aligned} \tag{2.0.52}$$

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

$$
\begin{aligned}
\hat{H}_0|\alpha_1,\alpha_2,\dots,\alpha_n\rangle &= \sum_{\alpha_1'}\langle\alpha_1'|\hat{h}_0|\alpha_1\rangle|\alpha_1'\alpha_2\dots\alpha_n\rangle \\
&+ \sum_{\alpha_2'}\langle\alpha_2'|\hat{h}_0|\alpha_2\rangle|\alpha_1\alpha_2'\dots\alpha_n\rangle \\
&+ \dots \\
&+ \sum_{\alpha_n'}\langle\alpha_n'|\hat{h}_0|\alpha_n\rangle|\alpha_1\alpha_2\dots\alpha_n'\rangle \qquad (2.0.53)
\end{aligned}
$$

Operators in second quantization

In Eq. (2.0.53) we have expressed the action of the one-body operator of Eq. (2.0.48) on the n-body state of Eq. (2.0.49) 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

$$|\alpha_1\alpha_2\dots\alpha'_k\dots\alpha_n\rangle = a^\dagger_{\alpha'_k} a_{\alpha_k} |\alpha_1\alpha_2\dots\alpha_k\dots\alpha_n\rangle \tag{2.0.54}$$

Inserting this in the right-hand side of Eq. (2.0.53) results in

$$\begin{aligned}
\hat{H}_0|\alpha_1\alpha_2\dots\alpha_n\rangle &= \sum_{\alpha'_1}\langle\alpha'_1|\hat{h}_0|\alpha_1\rangle a^\dagger_{\alpha'_1} a_{\alpha_1}|\alpha_1\alpha_2\dots\alpha_n\rangle \\
&+ \sum_{\alpha'_2}\langle\alpha'_2|\hat{h}_0|\alpha_2\rangle a^\dagger_{\alpha'_2} a_{\alpha_2}|\alpha_1\alpha_2\dots\alpha_n\rangle \\
&+ \dots \\
&+ \sum_{\alpha'_n}\langle\alpha'_n|\hat{h}_0|\alpha_n\rangle a^\dagger_{\alpha'_n} a_{\alpha_n}|\alpha_1\alpha_2\dots\alpha_n\rangle \\
&= \sum_{\alpha,\beta}\langle\alpha|\hat{h}_0|\beta\rangle a^\dagger_{\alpha} a_{\beta}|\alpha_1\alpha_2\dots\alpha_n\rangle \qquad (2.0.55)
\end{aligned}$$

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

$$\hat{H}_0 = \sum_{\alpha\beta} \langle \alpha | \hat{h}_0 | \beta \rangle a_\alpha^\dagger a_\beta \tag{2.0.56}$$

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. (2.0.56) by computing the expectation value of $\hat{H}_0$ between two single-particle states

$$\langle\alpha_1|\hat{H}_0|\alpha_2\rangle = \sum_{\alpha\beta}\langle\alpha|\hat{h}_0|\beta\rangle\langle 0|a_{\alpha_1}a_{\alpha}^{\dagger}a_{\beta}a_{\alpha_2}^{\dagger}|0\rangle \tag{2.0.57}$$

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

$$a_{\alpha_1}a_{\alpha}^{\dagger}a_{\beta}a_{\alpha_2}^{\dagger} = (\delta_{\alpha\alpha_1} - a_{\alpha}^{\dagger}a_{\alpha_1})(\delta_{\beta\alpha_2} - a_{\alpha_2}^{\dagger}a_{\beta}), \tag{2.0.58}$$

which results in

$$\langle 0|a_{\alpha_1}a_{\alpha}^{\dagger}a_{\beta}a_{\alpha_2}^{\dagger}|0\rangle = \delta_{\alpha\alpha_1}\delta_{\beta\alpha_2} \tag{2.0.59}$$

and

$$\langle\alpha_1|\hat{H}_0|\alpha_2\rangle = \sum_{\alpha\beta}\langle\alpha|\hat{h}_0|\beta\rangle\delta_{\alpha\alpha_1}\delta_{\beta\alpha_2} = \langle\alpha_1|\hat{h}_0|\alpha_2\rangle \tag{2.0.60}$$

as expected.

Topics for Week 36

Second quantization

- Monday:
- Summary from last week
- Second quantization and operators, two-body operator
- Anti-commutation rules
- Wick's theorem
- Tuesday:
- Wick's theorem: proof and examples of use thereof
- Exercises 3, 4 and 5 on Wednesday

The material is taken from chapter 3.1-3.6 and 4.1-4.4 of Shavitt and Bartlett. There is a small typo in exercise 4. See updated version of exercises on the webpage of the course

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

$$\hat{H}_I = \sum_{i<j} V(x_i, x_j) \tag{3.0.61}$$

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

$$V(x_i, x_j)\psi_{\alpha_k}(x_i)\psi_{\alpha_l}(x_j) = \sum_{\alpha'_k \alpha'_l} \psi'_{\alpha_k}(x_i)\psi'_{\alpha_l}(x_j)\langle \alpha'_k \alpha'_l | V | \alpha_k \alpha_l \rangle \tag{3.0.62}$$

Operators in second quantization

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

$$
\begin{aligned}
& \left(\sum_{i<j} V(x_i,x_j)\right)\psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\ldots\psi_{\alpha_n}(x_n) \\
= & \sum_{\alpha_1'\alpha_2'}\langle\alpha_1'\alpha_2'|V|\alpha_1\alpha_2\rangle\psi_{\alpha_1}'(x_1)\psi_{\alpha_2}'(x_2)\ldots\psi_{\alpha_n}(x_n) \\
+ & \ldots \\
+ & \sum_{\alpha_1'\alpha_n'}\langle\alpha_1'\alpha_n'|V|\alpha_1\alpha_n\rangle\psi_{\alpha_1}'(x_1)\psi_{\alpha_2}(x_2)\ldots\psi_{\alpha_n}'(x_n) \\
+ & \ldots \\
+ & \sum_{\alpha_2'\alpha_n'}\langle\alpha_2'\alpha_n'|V|\alpha_2\alpha_n\rangle\psi_{\alpha_1}(x_1)\psi_{\alpha_2}'(x_2)\ldots\psi_{\alpha_n}'(x_n) \\
+ & \ldots
\end{aligned}
\tag{3.0.63}
$$

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

$$
\begin{aligned}
H_I|\alpha_1\alpha_2\ldots\alpha_n\rangle &= \sum_{\alpha_1',\alpha_2'}\langle\alpha_1'\alpha_2'|V|\alpha_1\alpha_2\rangle|\alpha_1'\alpha_2'\ldots\alpha_n\rangle \\
&+ \ldots \\
&+ \sum_{\alpha_1',\alpha_n'}\langle\alpha_1'\alpha_n'|V|\alpha_1\alpha_n\rangle|\alpha_1'\alpha_2\ldots\alpha_n'\rangle \\
&+ \ldots \\
&+ \sum_{\alpha_2',\alpha_n'}\langle\alpha_2'\alpha_n'|V|\alpha_2\alpha_n\rangle|\alpha_1\alpha_2'\ldots\alpha_n'\rangle \\
&+ \ldots \qquad (3.0.64)
\end{aligned}
$$

Operators in second quantization

We introduce second quantization via the relation

$$
\begin{aligned}
& a^\dagger_{\alpha'_k} a^\dagger_{\alpha'_l} a_{\alpha_l} a_{\alpha_k} |\alpha_1\alpha_2\dots\alpha_k\dots\alpha_l\dots\alpha_n\rangle \\
= \;& (-1)^{k-1}(-1)^{l-2} a^\dagger_{\alpha'_k} a^\dagger_{\alpha'_l} a_{\alpha_l} a_{\alpha_k} |\alpha_k\alpha_l \underbrace{\alpha_1\alpha_2\dots\alpha_n}_{\neq\alpha_k,\alpha_l}\rangle \\
= \;& (-1)^{k-1}(-1)^{l-2} |\alpha'_k\alpha'_l \underbrace{\alpha_1\alpha_2\dots\alpha_n}_{\neq\alpha'_k,\alpha'_l}\rangle \\
= \;& |\alpha_1\alpha_2\dots\alpha'_k\dots\alpha'_l\dots\alpha_n\rangle
\end{aligned}
\tag{3.0.65}
$$

Operators in second quantization

Inserting this in (3.0.64) gives

$$
\begin{aligned}
H_I|\alpha_1\alpha_2\ldots\alpha_n\rangle &= \sum_{\alpha_1',\alpha_2'} \langle\alpha_1'\alpha_2'|V|\alpha_1\alpha_2\rangle a^\dagger_{\alpha_1'} a^\dagger_{\alpha_2'} a_{\alpha_2} a_{\alpha_1} |\alpha_1\alpha_2\ldots\alpha_n\rangle \\
&+ \ldots \\
&= \sum_{\alpha_1',\alpha_n'} \langle\alpha_1'\alpha_n'|V|\alpha_1\alpha_n\rangle a^\dagger_{\alpha_1'} a^\dagger_{\alpha_n'} a_{\alpha_n} a_{\alpha_1} |\alpha_1\alpha_2\ldots\alpha_n\rangle \\
&+ \ldots \\
&= \sum_{\alpha_2',\alpha_n'} \langle\alpha_2'\alpha_n'|V|\alpha_2\alpha_n\rangle a^\dagger_{\alpha_2'} a^\dagger_{\alpha_n'} a_{\alpha_n} a_{\alpha_2} |\alpha_1\alpha_2\ldots\alpha_n\rangle \\
&+ \ldots \\
&= \sum_{\alpha,\beta,\gamma,\delta}{}' \langle\alpha\beta|V|\gamma\delta\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma |\alpha_1\alpha_2\ldots\alpha_n\rangle \qquad (3.0.66)
\end{aligned}
$$

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

$$\langle\alpha\beta|V|\gamma\delta\rangle = \langle\beta\alpha|V|\delta\gamma\rangle \tag{3.0.67}$$

we get

$$\begin{aligned}\sum_{\alpha,\beta}\langle\alpha\beta|V|\gamma\delta\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma &= \sum_{\alpha,\beta}\langle\beta\alpha|V|\delta\gamma\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \qquad (3.0.68)\\ &= \sum_{\alpha,\beta}\langle\beta\alpha|V|\delta\gamma\rangle a^\dagger_\beta a^\dagger_\alpha a_\gamma a_\delta \qquad (3.0.69)\end{aligned}$$

where we have used the anti-commutation rules.

Operators in second quantization

Changing the summation indices α and β in (3.0.69) we obtain

$$\sum_{\alpha,\beta} \langle \alpha\beta|V|\gamma\delta\rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma = \sum_{\alpha,\beta} \langle \alpha\beta|V|\delta\gamma\rangle a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta \tag{3.0.70}$$

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

$$\hat{H}_I = \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} \langle \alpha\beta|V|\gamma\delta\rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma \tag{3.0.71}$$

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. (3.0.71) results in the same matrix between two anti-symmetrized two-particle states as its corresponding coordinate space representation. We have

$$\langle\alpha_1\alpha_2|\hat{H}_I|\beta_1\beta_2\rangle = \frac{1}{2}\sum_{\alpha\beta\gamma,\delta}\langle\alpha\beta|V|\gamma\delta\rangle\langle 0|a_{\alpha_2}a_{\alpha_1}a^{\dagger}_{\alpha}a^{\dagger}_{\beta}a_{\delta}a_{\gamma}a^{\dagger}_{\beta_1}a^{\dagger}_{\beta_2}|0\rangle. \tag{3.0.72}$$

Operators in second quantization

Using the commutation relations we get

$$
\begin{aligned}
& a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma a^\dagger_{\beta_1} a^\dagger_{\beta_2} \\
= \; & a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta (a_\delta \delta_{\gamma\beta_1} a^\dagger_{\beta_2} - a_\delta a^\dagger_{\beta_1} a_\gamma a^\dagger_{\beta_2}) \\
= \; & a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta (\delta_{\gamma\beta_1} \delta_{\delta\beta_2} - \delta_{\gamma\beta_1} a^\dagger_{\beta_2} a_\delta - a_\delta a^\dagger_{\beta_1} \delta_{\gamma\beta_2} + a_\delta a^\dagger_{\beta_1} a^\dagger_{\beta_2} a_\gamma) \\
= \; & a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta (\delta_{\gamma\beta_1} \delta_{\delta\beta_2} - \delta_{\gamma\beta_1} a^\dagger_{\beta_2} a_\delta \\
& \quad - \delta_{\delta\beta_1} \delta_{\gamma\beta_2} + \delta_{\gamma\beta_2} a^\dagger_{\beta_1} a_\delta + a_\delta a^\dagger_{\beta_1} a^\dagger_{\beta_2} a_\gamma)
\end{aligned}
\tag{3.0.73}
$$

Operators in second quantization

The vacuum expectation value of this product of operators becomes

$$\begin{aligned} & \langle 0|a_{\alpha_2}a_{\alpha_1}a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma a^\dagger_{\beta_1}a^\dagger_{\beta_2}|0\rangle \\ = \; & (\delta_{\gamma\beta_1}\delta_{\delta\beta_2} - \delta_{\delta\beta_1}\delta_{\gamma\beta_2})\langle 0|a_{\alpha_2}a_{\alpha_1}a^\dagger_\alpha a^\dagger_\beta|0\rangle \\ = \; & (\delta_{\gamma\beta_1}\delta_{\delta\beta_2} - \delta_{\delta\beta_1}\delta_{\gamma\beta_2})(\delta_{\alpha\alpha_1}\delta_{\beta\alpha_2} - \delta_{\beta\alpha_1}\delta_{\alpha\alpha_2}) \end{aligned} \tag{3.0.74}$$

Operators in second quantization

Insertion of Eq. (3.0.74) in Eq. (3.0.72) results in

$$\begin{aligned}\langle\alpha_1\alpha_2|\hat{H}_I|\beta_1\beta_2\rangle &= \frac{1}{2}\big[\langle\alpha_1\alpha_2|V|\beta_1\beta_2\rangle - \langle\alpha_1\alpha_2|V|\beta_2\beta_1\rangle \\ &\quad -\langle\alpha_2\alpha_1|V|\beta_1\beta_2\rangle + \langle\alpha_2\alpha_1|V|\beta_2\beta_1\rangle\big] \\ &= \langle\alpha_1\alpha_2|V|\beta_1\beta_2\rangle - \langle\alpha_1\alpha_2|V|\beta_2\beta_1\rangle \\ &= \langle\alpha_1\alpha_2|V|\beta_1\beta_2\rangle_{\mathrm{AS}}. \end{aligned} \tag{3.0.75}$$

Operators in second quantization

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

$$
\begin{aligned}
\hat{H}_I &= \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \\
&= \frac{1}{4}\sum_{\alpha\beta\gamma\delta}\left[\langle\alpha\beta|V|\gamma\delta\rangle - \langle\alpha\beta|V|\delta\gamma\rangle\right] a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \\
&= \frac{1}{4}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{\mathrm{AS}} a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \qquad (3.0.76)
\end{aligned}
$$

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

$$H = \sum_{\alpha,\beta} \langle \alpha | t + u | \beta \rangle a_\alpha^\dagger a_\beta + \frac{1}{4} \sum_{\alpha,\beta,\gamma,\delta} \langle \alpha\beta | V | \gamma\delta \rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma. \tag{3.0.77}$$

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

$$\left\{\widehat{\mathbf{A}}\widehat{\mathbf{B}}..\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\right\} \equiv (-1)^p \,[\text{creation operators}] \cdot [\text{annihilation operators}]\,. \tag{3.0.78}$$

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

$$\overbracket{\widehat{\mathbf{X}}\widehat{\mathbf{Y}}} \equiv \langle 0|\widehat{\mathbf{X}}\widehat{\mathbf{Y}}|0\rangle. \tag{3.0.79}$$

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

$$\left\{ \overbracket{\hat{\mathbf{A}}\hat{\mathbf{B}}..\hat{\mathbf{X}}}\hat{\mathbf{Y}} \right\} = (-1)^p \left\{ \overbracket{\hat{\mathbf{A}}\hat{\mathbf{B}}}..\hat{\mathbf{X}}\hat{\mathbf{Y}} \right\} . \tag{3.0.80}$$

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

$$(-1)^{p_1+p_2+..+p_m} . \tag{3.0.81}$$

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,

$$\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z} = \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} \tag{3.0.82}$$

$$+ \sum_{(1)} \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} \tag{3.0.83}$$

$$+ \sum_{(2)} \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} \tag{3.0.84}$$

$$+ \dots \tag{3.0.85}$$

$$+ \sum_{\left[\frac{N}{2}\right]} \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\,\hat{R}\hat{X}\hat{Y}\hat{Z}\right\}. \tag{3.0.86}$$

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,

$$\left[\frac{N}{2}\right] = \frac{N}{2}, \tag{3.0.87}$$

and the last sum in Eq. (3.0.82) is over fully contracted terms. When N is odd,

$$\left[\frac{N}{2}\right] \neq \frac{N}{2}, \tag{3.0.88}$$

and non of the terms in Eq. (3.0.82) 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,

$$
\begin{aligned}
\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\right\}\left\{\hat{R}\hat{X}\hat{Y}\hat{Z}..\right\} &= \left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} && (3.0.89)\\
&+ \sum_{(1)}\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} && (3.0.90)\\
&+ \sum_{(2)}\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\} && (3.0.91)\\
&+ \ldots && (3.0.92)
\end{aligned}
$$

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. (3.0.82), as a sum over normal ordered products with all possible numbers and combinations of contractions,

$$\langle 0|\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}|0\rangle = \langle 0|\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\}|0\rangle \tag{3.0.93}$$

$$+\sum_{(1)}\langle 0|\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\}|0\rangle \tag{3.0.94}$$

$$+\sum_{(2)}\langle 0|\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\}|0\rangle \tag{3.0.95}$$

$$+\dots \tag{3.0.96}$$

$$+\sum_{\left[\frac{N}{2}\right]}\langle 0|\left\{\hat{A}\hat{B}\hat{C}\hat{D}..\hat{R}\hat{X}\hat{Y}\hat{Z}\right\}|0\rangle. \tag{3.0.97}$$

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,

$$\langle 0|\widehat{\mathbf{A}}\widehat{\mathbf{B}}\widehat{\mathbf{C}}\widehat{\mathbf{D}}..\widehat{\mathbf{R}}\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\widehat{\mathbf{Z}}|0\rangle = \sum_{(all)} \langle 0| \left\{ \widehat{\mathbf{A}}\widehat{\mathbf{B}}\widehat{\mathbf{C}}\widehat{\mathbf{D}}..\ \widehat{\mathbf{R}}\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\widehat{\mathbf{Z}} \right\} |0\rangle \tag{3.0.98}$$

$$= \sum_{(all)} \widehat{\mathbf{A}}\widehat{\mathbf{B}}\widehat{\mathbf{C}}\widehat{\mathbf{D}}..\ \widehat{\mathbf{R}}\widehat{\mathbf{X}}\widehat{\mathbf{Y}}\widehat{\mathbf{Z}}. \tag{3.0.99}$$

Wick's theorem

To obtain fully contracted terms, Eq. (3.0.87) 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

$$\contraction{}{a}{_\alpha}{a} a_\alpha a^\dagger_\beta = \delta_{\alpha\beta}, \tag{3.0.100}$$

the terms that contribute are reduced even more.

Wick's theorem provides us with an algebraic method for easy determine 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.

Topics for Week 37

Second quantization

- Monday:
- Summary from last week
- Wick's theorem and its proof
- Particle-hole formalism
- Tuesday:
- Particle-hole formalism
- Diagrammatic representation of operators.
- Exercises 6 and 7, recommended.

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

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

$$
\begin{aligned}
|\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\rangle &= a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\dots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}|0\rangle && (4.0.101)\\
|\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\alpha_{n+1}\rangle &= a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\dots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}a^\dagger_{\alpha_{n+1}}|0\rangle && (4.0.102)\\
|\alpha_1\alpha_2\dots\alpha_{n-1}\rangle &= a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\dots a^\dagger_{\alpha_{n-1}}|0\rangle && (4.0.103)
\end{aligned}
$$

Particle-hole formalism

If we use Eq. (4.0.101) as our new reference state, we can simplify considerably the representation of this state

$$|c\rangle \equiv |\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\rangle = a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\dots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}|0\rangle \tag{4.0.104}$$

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

$$|\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\alpha_{n+1}\rangle = (-1)^n a^\dagger_{\alpha_{n+1}}|c\rangle \equiv (-1)^n|\alpha_{n+1}\rangle_c \tag{4.0.105}$$

$$|\alpha_1\alpha_2\dots\alpha_{n-1}\rangle = (-1)^{n-1} a_{\alpha_n}|c\rangle \equiv (-1)^{n-1}|\alpha_{n-1}\rangle_c \tag{4.0.106}$$

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. (4.0.106)

$$a_\alpha|c\rangle \neq 0 \tag{4.0.107}$$

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

$$\begin{aligned} b_\alpha|c\rangle &= 0 \qquad (4.0.108) \\ \{b_\alpha^\dagger, b_\beta^\dagger\} = \{b_\alpha, b_\beta\} &= 0 \\ \{b_\alpha^\dagger, b_\beta\} &= \delta_{\alpha\beta} \qquad (4.0.109) \end{aligned}$$

We assume also that the new reference state is properly normalized

$$\langle c|c\rangle = 1 \qquad (4.0.110)$$

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

$$b_\alpha^\dagger|c\rangle = \left\{ \begin{array}{ll} a_\alpha^\dagger|c\rangle = |\alpha\rangle, & \alpha > F \\ \\ a_\alpha|c\rangle = |\alpha^{-1}\rangle, & \alpha \le F \end{array} \right. \tag{4.0.111}$$

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

$$b_\alpha^\dagger = \begin{cases} a_\alpha^\dagger & \alpha > F \\ \\ a_\alpha & \alpha \leq F \end{cases} \qquad b_\alpha = \begin{cases} a_\alpha & \alpha > F \\ \\ a_\alpha^\dagger & \alpha \leq F \end{cases} \tag{4.0.112}$$

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

$$|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle \equiv \underbrace{b_{\beta_1}^\dagger b_{\beta_2}^\dagger \dots b_{\beta_{n_p}}^\dagger}_{>F} \underbrace{b_{\gamma_1}^\dagger b_{\gamma_2}^\dagger \dots b_{\gamma_{n_h}}^\dagger}_{\leq F} |c\rangle \qquad (4.0.113)$$

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

$$\hat{N} = \sum_{\alpha} a_{\alpha}^{\dagger} a_{\alpha} = \sum_{\alpha > F} b_{\alpha}^{\dagger} b_{\alpha} + n_c - \sum_{\alpha \leq F} b_{\alpha}^{\dagger} b_{\alpha} \tag{4.0.114}$$

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

$$N|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle = (n_p + n_c - n_h)|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle \tag{4.0.115}$$

Particle-hole formalism

Here $n = n_p + n_c - n_h$ is the total number of particles in the quasi-particle state of Eq. (4.0.113). Note that $\hat{N}$ counts the total number of particles present

$$N_{qp} = \sum_{\alpha} b_{\alpha}^{\dagger} b_{\alpha}, \tag{4.0.116}$$

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

$$N_{qp} = |\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1}\rangle = (n_p + n_h)|\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1}\rangle \tag{4.0.117}$$

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

$$
\begin{aligned}
\hat{H}_0 &= \sum_{\alpha\beta>F} \langle\alpha|h|\beta\rangle b_\alpha^\dagger b_\beta + \sum_{\substack{\alpha>F\\ \beta\leq F}} \left[\langle\alpha|h|\beta\rangle b_\alpha^\dagger b_\beta^\dagger + \langle\beta|h|\alpha\rangle b_\beta b_\alpha\right] \\
&+ \sum_{\alpha\leq F} \langle\alpha|h|\alpha\rangle - \sum_{\alpha\beta\leq F} \langle\beta|h|\alpha\rangle b_\alpha^\dagger b_\beta \qquad (4.0.118)
\end{aligned}
$$

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

$$\begin{aligned}\hat{H}_0 &= \sum_{ab} \langle a|h|b\rangle b_a^\dagger b_b + \sum_{ai}\left[\langle a|h|i\rangle b_a^\dagger b_i^\dagger + \langle i|h|a\rangle b_i b_a\right] \\ &+ \sum_i \langle i|h|i\rangle - \sum_{ij} \langle j|h|i\rangle b_i^\dagger b_j \end{aligned} \tag{4.0.119}$$

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

$$\hat{H}_I = \hat{H}_I^{(a)} + \hat{H}_I^{(b)} + \hat{H}_I^{(c)} + \hat{H}_I^{(d)} + \hat{H}_I^{(e)} \tag{4.0.120}$$

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

$$\hat{H}_I^{(a)} = \frac{1}{4}\sum_{abcd}\langle ab|V|cd\rangle b_a^\dagger b_b^\dagger b_d b_c \tag{4.0.121}$$

Particle-hole formalism

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

$$\hat{H}_I^{(b)} = \frac{1}{4}\sum_{abci}\left(\langle ab|V|ci\rangle b_a^\dagger b_b^\dagger b_i^\dagger b_c + \langle ai|V|cb\rangle b_a^\dagger b_i b_b b_c\right) \qquad (4.0.122)$$

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

$$\begin{aligned}\hat{H}_I^{(c)} &= \frac{1}{4}\sum_{abij}\left(\langle ab|V|ij\rangle b_a^\dagger b_b^\dagger b_j^\dagger b_i^\dagger + \langle ij|V|ab\rangle b_a b_b b_j b_i\right) + \\ & \frac{1}{2}\sum_{abij}\langle ai|V|bj\rangle b_a^\dagger b_j^\dagger b_b b_i + \frac{1}{2}\sum_{abi}\langle ai|V|bi\rangle b_a^\dagger b_b. \qquad (4.0.123)\end{aligned}$$

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

$$
\begin{aligned}
\hat{H}_I^{(d)} &= \frac{1}{4}\sum_{aijk}\left(\langle ai|V|jk\rangle b_a^\dagger b_k^\dagger b_j^\dagger b_i + \langle ji|V|ak\rangle b_k^\dagger b_j b_i b_a\right) + \\
& \frac{1}{4}\sum_{aij}\left(\langle ai|V|ji\rangle b_a^\dagger b_j^\dagger + \langle ji|V|ai\rangle - \langle ji|V|ia\rangle b_j b_a\right). \qquad (4.0.124)
\end{aligned}
$$

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

$$\hat{H}_I^{(e)} = \frac{1}{4}\sum_{ijkl}\langle kl|V|ij\rangle b_i^\dagger b_j^\dagger b_l b_k + \frac{1}{2}\sum_{ijk}\langle ij|V|kj\rangle b_k^\dagger b_i + \frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle \tag{4.0.125}$$

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

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

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

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

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

Notation

Second quantization, quasiparticles

Reference state

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

Creation and annihilation operators

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

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

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

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

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

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

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

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

$$\begin{aligned} a^\dagger_p a_q &= \left\{a^\dagger_p a_q\right\} + \left\{ a^\dagger_p a_q \right\} \\ &= \left\{a^\dagger_p a_q\right\} + \delta_{pq\in i} \end{aligned}$$

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

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

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

Definitions

The basics, Normal ordered Hamiltonian

Derivation, twobody part

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

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

Definitions

The basics, Normal ordered Hamiltonian

Derivation, twobody part

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

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

Definitions

The basics, Normal ordered Hamiltonian

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

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

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

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

where

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

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 38

Second quantization

- Monday:
- Summary from last week
- Summary of Wick's theorem and diagrammatic representation of operators and expectation values
- Tuesday:
- Diagrammatic representation of of operators and expectation values
- Begin of Hartree-Fock theory
- Exercises 9-12 on Wednesday

Diagram elements - Directed lines

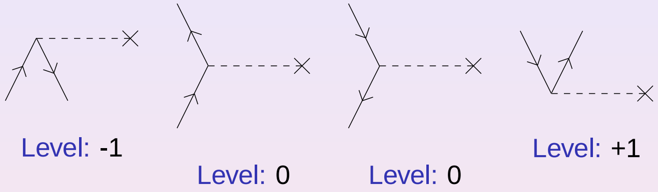
Figure: Particle line

Figure: Hole line

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

Diagram elements - Onebody Hamiltonian

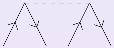
$$\hat{F}_N = \sum_{pq} f_q^p \left\{ a_p^\dagger a_q \right\}$$



- 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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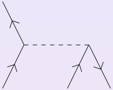

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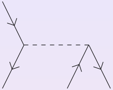

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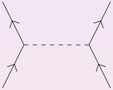

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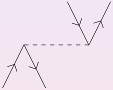
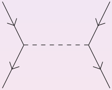
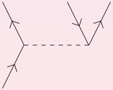


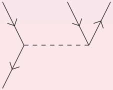
Level: 0



Level: 0



Level: +1



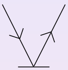
Level: +1

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.

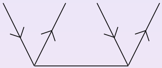
Diagram elements - Onebody cluster operator



Level: +1

- We have here assumed that a one-body operator has acted on a 1p1h Slater determinant $|\Phi_i^a\rangle$.
- Horisontal line segment with one vertex.
- Excitation level of +1.

Diagram elements - Twobody cluster operator



Level: +2

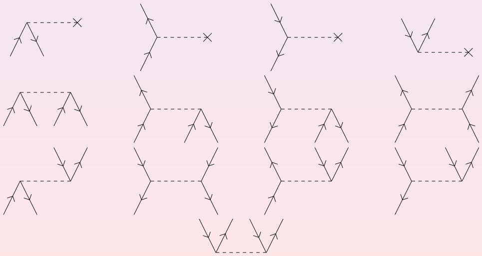
- We have here assumed that a one-body operator has acted on a 2p2h Slater determinant $|\Phi_{ij}^{ab}\rangle$.
- Horisontal line segment with two vertices.
- Excitation level of +2.

The expectation value of the energy

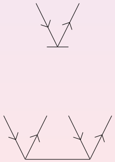
$$\mathrm{E} = \langle \Phi_0 | \overline{H}_N | \Phi_0 \rangle$$

- No external lines.
- Final excitation level: 0

Elements: $\widehat{H}_N$



Elements:
Cluster operator



Topics for Week 39

Hartree-Fock theory

- Monday:
- Summary from last week
- Basic ingredients
- Reminder on variational calculus
- Hartree-Fock theory (coordinate space, traditional approach) and Thouless' theorem
- Tuesday:
- Hartree-Fock theory, stability and diagrammatic interpretation
- Exercise 13 a, b and c.

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: what we argued last week

Last week we computed 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 found 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: what we argued last week

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

Euler-Lagrange equations

We assume the existence of an optimum path, that is a path for which $E[\Phi]$ is stationary. There are infinitely many such paths. The difference between two paths $\delta\Phi$ is called the variation of Φ.
We call the variation $\eta(x)$ and it is scaled by a factor α. The function $\eta(x)$ is arbitrary except for

$$\eta(a) = \eta(b) = 0,$$

and we assume that we can model the change in Φ as

$$\Phi(x, \alpha) = \Phi(x, 0) + \alpha\eta(x),$$

and

$$\delta\Phi = \Phi(x, \alpha) - \Phi(x, 0) = \alpha\eta(x).$$

Euler-Lagrange equations

We choose $\Phi(x, \alpha = 0)$ as the unkonwn path that will minimize E. The value $\Phi(x, \alpha \neq 0)$ describes a neighbouring path.
We have

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

In the slides I will use the shorthand

$$\Phi_x(x, \alpha) = \frac{\partial \Phi(x, \alpha)}{\partial x}.$$

In our case $a = 0$ and $b = \infty$ and we know the value of the wave function.

Euler-Lagrange equations

The condition for an extreme of

$$E[\Phi(\alpha)] = \int_a^b f(\Phi(x,\alpha), \Phi_x(x,\alpha), x)dx,$$

is

$$\left[\frac{\partial E[\Phi(\alpha)]}{\partial x}\right]_{\alpha=0} = 0.$$

The α dependence is contained in $\Phi(x,\alpha)$ and $\Phi_x(x,\alpha)$ meaning that

$$\left[\frac{\partial E[\Phi(\alpha)]}{\partial \alpha}\right] = \int_a^b \left(\frac{\partial f}{\partial \Phi}\frac{\partial \Phi}{\partial \alpha} + \frac{\partial f}{\partial \Phi_x}\frac{\partial \Phi_x}{\partial \alpha}\right) dx.$$

We have defined

$$\frac{\partial \Phi(x,\alpha)}{\partial \alpha} = \eta(x)$$

and thereby

$$\frac{\partial \Phi_x(x,\alpha)}{\partial \alpha} = \frac{d(\eta(x))}{dx}.$$

Euler-Lagrange equations

Using

$$\frac{\partial \Phi(x,\alpha)}{\partial \alpha} = \eta(x),$$

and

$$\frac{\partial \Phi_x(x,\alpha)}{\partial \alpha} = \frac{d(\eta(x))}{dx},$$

in the integral gives

$$\left[\frac{\partial E[\Phi(\alpha)]}{\partial \alpha}\right] = \int_a^b \left(\frac{\partial f}{\partial \Phi}\eta(x) + \frac{\partial f}{\partial \Phi_x}\frac{d(\eta(x))}{dx}\right) dx.$$

Integrate the second term by parts

$$\int_a^b \frac{\partial f}{\partial \Phi_x}\frac{d(\eta(x))}{dx} dx = \eta(x)\frac{\partial f}{\partial \Phi_x}\Big|_a^b - \int_a^b \eta(x)\frac{d}{dx}\frac{\partial f}{\partial \Phi_x} dx,$$

and since the first term dissappears due to $\eta(a) = \eta(b) = 0$, we obtain

$$\left[\frac{\partial E[\Phi(\alpha)]}{\partial \alpha}\right] = \int_a^b \left(\frac{\partial f}{\partial \Phi} - \frac{d}{dx}\frac{\partial f}{\partial \Phi_x}\right)\eta(x) dx = 0.$$

Euler-Lagrange equations

$$\left[\frac{\partial E[\Phi(\alpha)]}{\partial \alpha}\right] = \int_a^b \left(\frac{\partial f}{\partial \Phi} - \frac{d}{dx}\frac{\partial f}{\partial \Phi_x}\right)\eta(x)dx = 0,$$

can also be written as

$$\alpha\left[\frac{\partial E[\Phi(\alpha)]}{\partial \alpha}\right]_{\alpha=0} = \int_a^b \left(\frac{\partial f}{\partial \Phi} - \frac{d}{dx}\frac{\partial f}{\partial \Phi_x}\right)\delta\Phi(x)dx = \delta E = 0.$$

The condition for a stationary value is thus a partial differential equation

$$\frac{\partial f}{\partial \Phi} - \frac{d}{dx}\frac{\partial f}{\partial \Phi_x} = 0,$$

known as Euler's equation. Can easily be generalized to more variables.

Lagrangian Multipliers

Consider a function of three independent variables $f(x, y, z)$. For the function f to be an extreme we have

$$df = 0.$$

A necessary and sufficient condition is

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = \frac{\partial f}{\partial z} = 0,$$

due to

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \frac{\partial f}{\partial z} dz.$$

In physical problems the variables x, y, z are often subject to constraints (in our case Φ and the orthogonality constraint) so that they are no longer all independent. It is possible at least in principle to use each constraint to eliminate one variable and to proceed with a new and smaller set of independent varables.

Lagrangian Multipliers

The use of so-called Lagrangian multipliers is an alternative technique when the elimination of of variables is incovenient or undesirable. Assume that we have an equation of constraint on the variables x, y, z

$$\phi(x, y, z) = 0,$$

resulting in

$$d\phi = \frac{\partial \phi}{\partial x}dx + \frac{\partial \phi}{\partial y}dy + \frac{\partial \phi}{\partial z}dz = 0.$$

Now we cannot set anymore

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = \frac{\partial f}{\partial z} = 0,$$

if $df = 0$ is wanted because there are now only two independent variables! Assume x and y are the independent variables. Then dz is no longer arbitrary.

Lagrangian Multipliers

However, we can add to

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz,$$

a multiplum of $d\phi$, viz. $\lambda d\phi$, resulting in

$$df + \lambda d\phi = (\frac{\partial f}{\partial z} + \lambda\frac{\partial \phi}{\partial x})dx + (\frac{\partial f}{\partial y} + \lambda\frac{\partial \phi}{\partial y})dy + (\frac{\partial f}{\partial z} + \lambda\frac{\partial \phi}{\partial z})dz = 0.$$

Our multiplier is chosen so that

$$\frac{\partial f}{\partial z} + \lambda\frac{\partial \phi}{\partial z} = 0.$$

Lagrangian Multipliers

However, we took dx and dy as to be arbitrary and thus we must have

$$\frac{\partial f}{\partial x} + \lambda \frac{\partial \phi}{\partial x} = 0,$$

and

$$\frac{\partial f}{\partial y} + \lambda \frac{\partial \phi}{\partial y} = 0.$$

When all these equations are satisfied, $df = 0$. We have four unknowns, x, y, z and λ. Actually we want only x, y, z, λ need not to be determined, it is therefore often called Lagrange's undetermined multiplier. If we have a set of constraints ϕ_k we have the equations

$$\frac{\partial f}{\partial x_i} + \sum_k \lambda_k \frac{\partial \phi_k}{\partial x_i} = 0.$$

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

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

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

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

as

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

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

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 $d\tau = dx_1 dx_2 \ldots dx_N$.

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

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

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

where we have introduced the anti-symmetrization operator $\mathcal{A}$ defined by the summation over all possible permutations of two eletrons. 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 (two for helium, four for beryllium and ten for neon)

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

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

Both $\hat{H}_1$ and $\hat{H}_2$ are invariant under electron permutations, 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 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

$$
\begin{aligned}
&\sum_{\mu=1}^{N}\int \delta\psi_\mu^* \hat{h}_i \psi_\mu dx_i + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \delta\psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\psi_\mu\psi_\nu dx_i dx_j - \int \delta\psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\psi_\nu\psi_\mu dx_i dx_j\right] \\
&+\sum_{\mu=1}^{N}\int \psi_\mu^* \hat{h}_i \delta\psi_\mu dx_i + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\delta\psi_\mu\psi_\nu dx_i dx_j - \int \psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\psi_\nu\delta\psi_\mu dx_i dx_j\right] \\
&\qquad -\sum_{\mu=1}^{N}E_\mu\int \delta\psi_\mu^*\psi_\mu dx_i - \sum_{\mu=1}^{N}E_\mu\int \psi_\mu^*\delta\psi_\mu dx_i = 0.
\end{aligned}
$$

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

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

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 electron 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

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

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)

$$\psi_a = \sum_{\lambda} C_{a\lambda}\psi_{\lambda}. \tag{6.0.131}$$

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

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

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

$$\int \Phi^* \hat{H}_1 \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^{A} \sum_{\nu=1}^{A} \langle \mu\nu | V | \mu\nu \rangle_{AS}. \tag{6.0.132}$$

Combining Eqs. (2.0.13) and (6.0.132) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^{N} \langle \mu | h | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \langle \mu\nu | V | \mu\nu \rangle_{AS}. \tag{6.0.133}$$

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. (6.0.131). We can then rewrite the energy functional as

$$E[\Psi] = \sum_{a=1}^{N} \langle a|h|a\rangle + \frac{1}{2}\sum_{ab=1}^{N} \langle ab|V|ab\rangle_{AS}, \tag{6.0.134}$$

where Ψ is the new Slater determinant defined by the new basis of Eq. (6.0.131).

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

Using Eq. (6.0.131) we can rewrite Eq. (6.0.134) as

$$E[\Psi]=\sum_{a=1}^{N}\sum_{\alpha\beta}C^*_{a\alpha}C_{a\beta}\langle\alpha|h|\beta\rangle+\frac{1}{2}\sum_{ab=1}^{N}\sum_{\alpha\beta\gamma\delta}C^*_{a\alpha}C^*_{b\beta}C_{a\gamma}C_{b\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}. \quad (6.0.135)$$

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

$$E[\Psi] - \sum_{a=1}^{N} \epsilon_a \sum_{\alpha} C^*_{a\alpha} C_{a\alpha}. \tag{6.0.136}$$

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

$$\frac{d}{dC^*_{k\alpha}}\left[E[\Psi]-\sum_a \epsilon_a \sum_\alpha C^*_{a\alpha}C_{a\alpha}\right]=0, \tag{6.0.137}$$

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

$$\sum_\gamma C_{k\gamma}\langle\alpha|h|\gamma\rangle+\sum_{a=1}^{N}\sum_{\beta\gamma\delta} C^*_{a\beta}C_{a\delta}C_{k\gamma}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}=\epsilon_k C_{k\alpha}. \tag{6.0.138}$$

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

We can rewrite this equation as

$$\sum_{\gamma}\left\{\langle\alpha|h|\gamma\rangle+\sum_{a}^{N}\sum_{\beta\delta}C_{a\beta}^{*}C_{a\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}\right\}C_{k\gamma}=\epsilon_{k}C_{k\alpha}. \tag{6.0.139}$$

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

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

we can rewrite the new equations as

$$\sum_{\gamma} h^{HF}_{\alpha\gamma}C_{k\gamma} = \epsilon_k C_{k\alpha}. \tag{6.0.140}$$

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

Hartree-Fock formalism in second quantization, Thouless' theorem

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

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

Topics for Week 40

Hartree-Fock

- Monday:
- Summary from last week
- Thouless' theorem
- Stability of Hartree-Fock theory
- Koopman's theorem
- Electron gas
- Tuesday:
- Electron gas
- Configuration interaction theory
- Exercises 14, 16 and 17

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.

Topics for Week 41

Electron gas, Configuration interaction theory and Density functional theory

- Monday:
- Summary from last week on the electron gas
- Calculating the total energy for the electron gas (slides only, and first hour)
- Configuration interaction theory
- Tuesday:
- Configuration interaction theory

The midterm exam will be available on Tuesday morning from 7am on the webpage. It will also be discussed during the Tuesday lecture.

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 $L \to \infty$ is to be taken after we have computed various expectation values)

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

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

Last week we demonstrated 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 introduced a convergence factor $e^{-\mu|\boldsymbol{r}-\boldsymbol{r'}|}$ and used $\sum_{\boldsymbol{k}} \to \frac{\Omega}{(2\pi)^3}\int d\boldsymbol{k}$. The results were also 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 $a_0 = \hbar^2/e^2m$, 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 proportional 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

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

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

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

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 $\phi_i(\mathbf{x}_i)$

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

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.

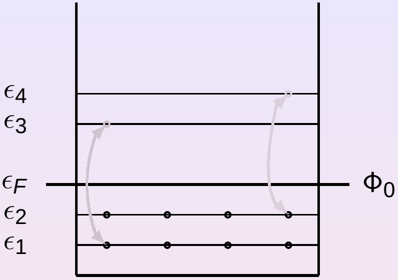
Configuration interaction theory

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



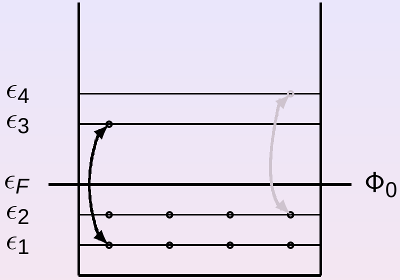
From T_1 to T_1^2

$T_1 \propto a_a^+ a_i$

From T_2 to T_2^2

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

Excitations in Pictures



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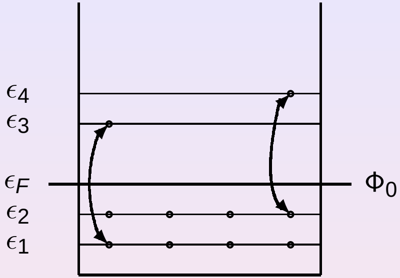

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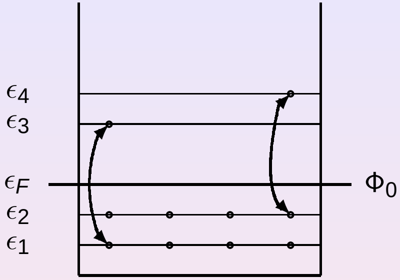

From T_1 to T_1^2

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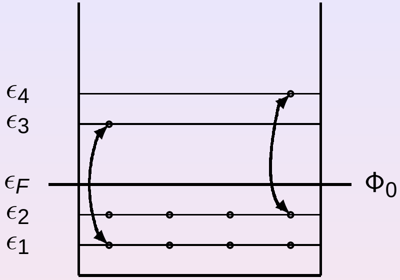

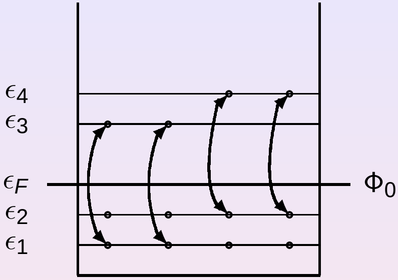

From T_1 to T_1^2

$T_1 \propto a_a^+ a_i$

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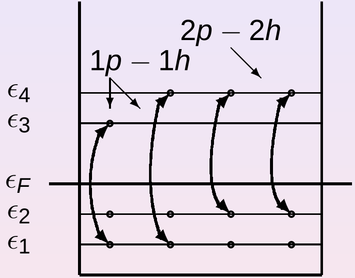
Excitations



Truncations

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

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

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

Topics for Week 42

Configuration Interaction theory and Perturbation theory

- Monday:
- No lecture Monday
- Tuesday:
- Configuration interaction theory
- Start many-body perturbation theory, Rayleigh-Schrödinger and Brillouin-Wigner perturbation theory (chapter 2 of Shavitt and Bartlett)
- Rayleigh-Schrödinger and Brillouin-Wigner perturbation theory

Exercises this week: 18b, 18c, 18d, 19e and 19f.

Configuration interaction theory

We defined the projection operators

$$P = \sum_{i=1}^{D} |\psi_i\rangle\langle\psi_i|,$$

and

$$Q = \sum_{i=D+1}^{\infty} |\psi_i\rangle\langle\psi_i|,$$

with D being the dimension of the model space, and $PQ = 0$, $P^2 = P$, $Q^2 = Q$ and $P + Q = I$. The wave functions $|\psi_i\rangle$ are eigenfunctions of the unperturbed hamiltonian $H_0 = T + U$ (with eigenvalues ε_i), where T is the kinetic energy and U an external one-body potential.

The full hamiltonian is then rewritten as $H = H_0 + H_I$ with $H_I = V - U$.

Simple Toy Model to illustrate basic principles

Choose a hamiltonian that depends linearly on a strength parameter z

$$H = H_0 + zH_1,$$

with $0 \leq z \leq 1$, where the limits $z = 0$ and $z = 1$ represent the non-interacting (unperturbed) and fully interacting system, respectively. The model is an eigenvalue problem with only two available states, which we label P and Q. Below we will let state P represent the model-space eigenvalue whereas state Q represents the eigenvalue of the excluded space. The unperturbed solutions to this problem are

$$H_0 \Phi_P = \epsilon_P \Phi_P$$

and

$$H_0 \Phi_Q = \epsilon_Q \Phi_Q,$$

with $\epsilon_P < \epsilon_Q$. We label the off-diagonal matrix elements X, while $X_P = \langle \Phi_P | H_1 | \Phi_P \rangle$ and $X_Q = \langle \Phi_Q | H_1 | \Phi_Q \rangle$.

Simple Two-Level Model

The exact eigenvalue problem

$$\begin{pmatrix} \epsilon_P + zX_P & zX \\ zX & \epsilon_Q + zX_Q \end{pmatrix}$$

yields

$$E(z) = \frac{1}{2}\{\epsilon_P + \epsilon_Q + zX_P + zX_Q \pm (\epsilon_Q - \epsilon_P + zX_Q - zX_P)$$

$$\times \sqrt{1 + \frac{4z^2X^2}{(\epsilon_Q - \epsilon_P + zX_Q - zX_P)^2}}\right\}.$$

Another look at the problem: Similarity Transformations

We have defined a transformation

$$\Omega^{-1}H\Omega\Omega^{-1}|\Psi_\alpha\rangle = E_\alpha\Omega^{-1}|\Psi_\alpha\rangle.$$

We rewrite this for later use, introducing $\Omega = e^T$, as

$$H' = e^{-T}He^T,$$

and T is constructed so that $QH'P = PH'Q = 0$. The P-space effective Hamiltonian is given by

$$H^{\text{eff}} = PH'P,$$

and has d exact eigenvalues of H.

Another look at the simple 2×2 Case, Jacobi Rotation

We have the simple model

$$\begin{pmatrix} \epsilon_P + zX_P & zX \\ zX & \epsilon_Q + zX_Q \end{pmatrix}$$

Rewrite for simplicity as a symmetric matrix $H \in \mathbb{R}^{2\times 2}$

$$H = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}.$$

The standard Jacobi rotation allows to find the eigenvalues via the orthogonal matrix Ω

$$\Omega = e^{T} = \begin{bmatrix} c & s \\ -s & c \end{bmatrix},$$

with $c = \cos\gamma$ and $s = \sin\gamma$. We have then that $H' = e^{-T} H e^{T}$ is diagonal.

Simple 2×2 Case, Jacobi Rotation first

To have non-zero nondiagonal matrix H' we need to solve

$$(H_{22} - H_{11})cs + H_{12}(c^2 - s^2) = 0,$$

and using $c^2 - s^2 = \cos(2\gamma)$ and $cs = \rho(2\gamma)/2$ this is equivalent with

$$\tan(2\gamma) = \frac{2H_{12}}{H_{11} - H_{22}}.$$

Solving the equation we have

$$\gamma = \frac{1}{2}\tan^{-1}\left(\frac{2H_{12}}{H_{11} - H_{22}}\right) + \frac{k\pi}{2}, \quad k = \ldots, -1, 0, 1, \ldots, \qquad (9.0.141)$$

where $k\pi/2$ is added due to the periodicity of the tan function.

Simple 2×2 Case, Jacobi Rotation first

Note that $k = 0$ gives a diagonal matrix on the form

$$H'_{k=0} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}, \tag{9.0.142}$$

while $k = 1$ changes the diagonal elements

$$H'_{k=1} = \begin{bmatrix} \lambda_2 & 0 \\ 0 & \lambda_1 \end{bmatrix}. \tag{9.0.143}$$

Perturbation theory (time-independent)

The projection operators defining the model and excluded spaces are defined by

$$P = \sum_{i=1}^{D} |\psi_i\rangle\langle\psi_i|, \qquad (9.0.144)$$

and

$$Q = \sum_{i=D+1}^{\infty} |\psi_i\rangle\langle\psi_i|, \qquad (9.0.145)$$

with D being the dimension of the model space, and $PQ = 0$, $P^2 = P$, $Q^2 = Q$ and $P + Q = I$. The wave functions $|\psi_i\rangle$ are eigenfunctions of the unperturbed hamiltonian $H_0 = T + U$ (with eigenvalues ε_i), where T is the kinetic energy and U an appropriately chosen one-body potential, normally that of the harmonic oscillator (h.o.).

Perturbation theory (time-independent)

We define the projection of the exact wave function $|\Psi_\alpha\rangle$ of a state α, i.e. the solution to the full Schrödinger equation

$$H|\Psi_\alpha\rangle = E_\alpha|\Psi_\alpha\rangle, \tag{9.0.146}$$

as $P|\Psi_\alpha\rangle = |\Psi_\alpha^M\rangle$ and a wave operator Ω which transforms all the model states back into the corresponding exact states as $|\Psi_\alpha\rangle = \Omega|\Psi_\alpha^M\rangle$. The latter statement is however not trivial, it actually means that there is a one-to-one correspondence between the d exact states and the model functions.

Perturbation theory (time-independent)

We will now assume that the wave operator Ω has an inverse and consider a similarity transformation of the Hamiltonian H such that Eq. (250) can be rewritten as

$$\Omega^{-1} H \Omega \Omega^{-1} |\Psi_\alpha\rangle = E_\alpha \Omega^{-1} |\Psi_\alpha\rangle. \tag{9.0.147}$$

Recall also that $|\Psi_\alpha\rangle = \Omega|\Psi_\alpha^M\rangle$, which means that $\Omega^{-1}|\Psi_\alpha\rangle = |\Psi_\alpha^M\rangle$ insofar as the inverse of Ω exists.

Perturbation theory (time-independent)

Let us define the transformed hamiltonian $\mathcal{H} = \Omega^{-1} H \Omega$, which can be rewritten in terms of the operators P and Q ($P + Q = I$) as

$$\mathcal{H} = P\mathcal{H}P + P\mathcal{H}Q + Q\mathcal{H}P + Q\mathcal{H}Q. \tag{9.0.148}$$

The eigenvalues of $\mathcal{H}$ are the same as those of H, since a similarity transformation does not affect the eigenvalues.

Perturbation theory (time-independent)

If we now operate on Eq. (250), which in terms of the model space wave function reads

$$\mathcal{H}|\Psi_\alpha^M\rangle = E_\alpha|\Psi_\alpha^M\rangle, \tag{9.0.149}$$

with the operator Q, we readily see that

$$Q\mathcal{H}P = 0. \tag{9.0.150}$$

Perturbation theory (time-independent)

Eq. (251) is an important relation which states that the eigenfunction $P|\Psi_\alpha\rangle$ is a *pure model space eigenfunction*. This implies that we can define an *effective model space hamiltonian*

$$H_{\mathrm{eff}} = P\mathcal{H}P = P\Omega^{-1}H\Omega P, \tag{9.0.151}$$

or equivalently

$$H\Omega P = \Omega P H_{\mathrm{eff}} P, \tag{9.0.152}$$

which is the Bloch equation. This equation can be used to determine the wave operator Ω.

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

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle,$$

and multiplying the latter from the left with $\langle\Phi_0|$ gives

$$\langle\Phi_0|\hat{H}|\Psi_0\rangle = E_0\langle\Phi_0|\Psi_0\rangle = E_0,$$

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

$$\Delta E_0 = E_0 - W_0 = \langle\Phi_0|\hat{H}_I|\Psi_0\rangle,$$

which is an exact result.

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 subtractiing a term $\omega|\Psi_0\rangle$ as

$$\left(\omega - \hat{H}_0\right)|\Psi_0\rangle = \left(\omega - E_0 - \hat{H}_I\right)|\Psi_0\rangle,$$

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

$$|\Psi_0\rangle = \frac{1}{\omega - \hat{H}_0}\left(\omega - E_0 - \hat{H}_I\right)|\Psi_0\rangle,$$

and multiplying from the left with $\hat{Q}$ results in

$$\hat{Q}|\Psi_0\rangle = \frac{\hat{Q}}{\omega - \hat{H}_0}\left(\omega - E_0 - \hat{H}_I\right)|\Psi_0\rangle,$$

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

$$|\Psi_0\rangle=|\Phi_0\rangle+\frac{\hat{Q}}{\omega-\hat{H}_0}\left(\omega-E_0-\hat{H}_I\right)|\Psi_0\rangle.$$

Perturbation theory (time-independent)

$$|\Psi_0\rangle = |\Phi_0\rangle + \frac{\hat{Q}}{\omega - \hat{H}_0}\left(\omega - E_0 - \hat{H}_I\right)|\Psi_0\rangle.$$

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_0 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

$$|\Psi_0\rangle = \sum_{i=0}^{\infty}\left\{\frac{\hat{Q}}{\omega - \hat{H}_0}\left(\omega - E_0 - \hat{H}_I\right)\right\}^i |\Phi_0\rangle,$$

for the wave function and

$$\Delta E_0 = \sum_{i=0}^{\infty}\langle\Phi_0|\hat{H}_I\left\{\frac{\hat{Q}}{\omega - \hat{H}_0}\left(\omega - E_0 - \hat{H}_I\right)\right\}^i |\Phi_0\rangle,$$

which is now a perturbative expansion of the exact energy in terms of the interaction $\hat{H}_I$ and the unperturbed wave function $|\Psi_0\rangle$.

Topics for Week 43

Time-independent Perturbation theory

- Monday:
- Derivation of Brillouin-Wigner and Rayleigh-Schrödinger perturbation theory
- Wave operator in perturbation theory
- Tuesday:
- Discussion of diagrams and derivation of diagram rules

The material can be found in chapters 4 and 5 of Shavitt and Bartlett. Exercises 24 and 26.

Brillouin-Wigner theory

In our equations for $|\Psi_0\rangle$ and ΔE_0 in terms of the unperturbed solutions $|\Phi_i\rangle$ we have still an undetermined parameter ω and a dependecy on the exact energy E_0. Not much has been gained thus from a practical computational point of view.
In Brilluoin-Wigner perturbation theory it is customary to set $\omega = E_0$. This results in the following perturbative expansion for the energy ΔE_0

$$\Delta E_0 = \sum_{i=0}^{\infty} \langle \Phi_0 | \hat{H}_I \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} \left(\omega - E_0 - \hat{H}_I \right) \right\}^i |\Phi_0\rangle =$$

$$\langle \Phi_0 | \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E_0 - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{E_0 - \hat{H}_0} \hat{H}_I + \dots \right) |\Phi_0\rangle.$$

Brillouin-Wigner theory

$$\Delta E_0 = \sum_{i=0}^{\infty} \langle \Phi_0 | \hat{H}_I \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} \left(\omega - E_0 - \hat{H}_I \right) \right\}^i |\Phi_0\rangle =$$

$$\langle \Phi_0 | \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E_0 - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{E_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{E_0 - \hat{H}_0} \hat{H}_I + \dots \right) |\Phi_0\rangle.$$

This expression depends however on the exact energy E_0 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_0 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

$$\Delta E_0 = \sum_{i=0}^{\infty} \langle \Phi_0 | \hat{H}_I \left\{ \frac{\hat{Q}}{W_0 - \hat{H}_0} \left(\hat{H}_I - \Delta E_0 \right) \right\}^i | \Phi_0 \rangle =$$

$$\langle \Phi_0 | \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E_0) + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E_0) \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E_0) + \dots \right) | \Phi_0$$

Rayleigh-Schrödinger perturbation theory

Recalling that $\hat{Q}$ commutes with $\hat{H}_0$ and since ΔE_0 is a constant we obtain that

$$\hat{Q}\Delta E_0|\Phi_0\rangle = \hat{Q}\Delta E_0|\hat{Q}\Phi_0\rangle = 0.$$

Inserting this results in the expression for the energy results in

$$\Delta E_0 = \langle\Phi_0|\left(\hat{H}_I + \hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I + \hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}(\hat{H}_I-\Delta E_0)\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I + \dots\right)|\Phi_0\rangle.$$

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_0

$$\Delta E_0 = \sum_{i=1}^{\infty} \Delta E_0^{(i)}.$$

We get the following expression for $\Delta E_0^{(i)}$

$$\Delta E_0^{(1)} = \langle \Phi_0 | \hat{H}_I | \Phi_0 \rangle,$$

which is just the contribution to first order in perturbation theory,

$$\Delta E_0^{(2)} = \langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I | \Phi_0 \rangle,$$

which is the contribution to second order.

Rayleigh-Schrödinger perturbation theory

$$\Delta E_0^{(3)} = \langle\Phi_0|\hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \Phi_0\rangle - \langle\Phi_0|\hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle\Phi_0|\hat{H}_I|\Phi_0\rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I|\Phi_0\rangle,$$

being the third-order contribution. The last term is a so-called unlinked diagram!

Rayleigh-Schrödinger perturbation theory

The fourth order term is

$$\Delta E_0^{(4)} = \langle\Phi_0|\hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \Phi_0\rangle -$$

$$\langle\Phi_0|\hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle\Phi_0|\hat{H}_I|\Phi_0\rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \Phi_0\rangle$$

$$-\langle\Phi_0|\hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle\Phi_0|\hat{H}_I|\Phi_0\rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \Phi_0\rangle$$

$$+\langle\Phi_0|\hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \langle\Phi_0|\hat{H}_I|\Phi_0\rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle\Phi_0|\hat{H}_I|\Phi_0\rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \Phi_0\rangle -$$

$$\langle\Phi_0|\hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle\Phi_0|\hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I|\Phi_0\rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I|\Phi_0\rangle,$$

Wave Operator I

We define the projection of the exact wave function $|\Psi_\alpha\rangle$ of a state α, i.e. the solution to the full Schrödinger equation

$$H|\Psi_\alpha\rangle = E_\alpha|\Psi_\alpha\rangle,$$

as $P|\Psi_\alpha\rangle = |\Psi_\alpha^M\rangle$ and a wave operator Ω which transforms all the model states back into the corresponding exact states as $|\Psi_\alpha\rangle = \Omega|\Psi_\alpha^M\rangle$. The latter statement is however not trivial, it actually means that there is a one-to-one correspondence between the d exact states and the model functions. We will now assume that the wave operator Ω has an inverse. Use a similarity transformation of the hamiltonian

$$\Omega^{-1}H\Omega\Omega^{-1}|\Psi_\alpha\rangle = E_\alpha\Omega^{-1}|\Psi_\alpha\rangle.$$

Wave Operator II

Recall also that $|\Psi_\alpha\rangle = \Omega|\Psi_\alpha^M\rangle$, which means that $\Omega^{-1}|\Psi_\alpha\rangle = |\Psi_\alpha^M\rangle$ insofar as the inverse of Ω exists. Let us define the transformed hamiltonian $\mathcal{H} = \Omega^{-1}H\Omega$, which can be rewritten in terms of the operators P and Q ($P + Q = I$) as

$$\mathcal{H} = P\mathcal{H}P + P\mathcal{H}Q + Q\mathcal{H}P + Q\mathcal{H}Q.$$

The eigenvalues of $\mathcal{H}$ are the same as those of H, since a similarity transformation does not affect the eigenvalues.

$$\mathcal{H}|\Psi_\alpha^M\rangle = E_\alpha|\Psi_\alpha^M\rangle,$$

with the operator Q, one can show the so-called decoupling condition

$$Q\mathcal{H}P = 0.$$

Wave Operator III

The last equation is an important relation which states that the eigenfunction $P|\Psi_\alpha\rangle$ is a *pure model space eigenfunction*. This implies that we can define an *effective model space hamiltonian*

$$H_{\mathrm{eff}} = P\mathcal{H}P = P\Omega^{-1}H\Omega P,$$

or equivalently

$$H\Omega P = \Omega P H_{\mathrm{eff}} P,$$

which is the Bloch equation. This equation can be used to determine the wave operator Ω.
The wave operator is often expressed as

$$\Omega = 1 + \chi,$$

where χ is known as the correlation operator.

Wave Operator IV

The wave operator Ω can be ordered in terms of the number of interactions with the perturbation H_I

$$\Omega = 1 + \Omega^{(1)} + \Omega^{(2)} + \dots,$$

where $\Omega^{(n)}$ means that we have n H_I terms. Explicitly, the above equation reads

$$\begin{aligned}\Omega|\psi_\alpha\rangle = \quad & |\psi_\alpha\rangle + \sum_i \frac{|i\rangle\langle i|H_I|\psi_\alpha\rangle}{\varepsilon_\alpha - \varepsilon_i} + \sum_{ij} \frac{|i\rangle\langle i|H_I|j\rangle\langle j|H_I|\psi_\alpha\rangle}{(\varepsilon_\alpha - \varepsilon_i)(\varepsilon_\alpha - \varepsilon_j)} \\ & - \sum_{\beta i} \frac{|i\rangle\langle i|H_I|\psi_\beta\rangle\langle\psi_\beta|H_I|\psi_\alpha\rangle}{(\varepsilon_\alpha - \varepsilon_i)(\varepsilon_\alpha - \varepsilon_\beta)} + \dots,\end{aligned}$$

where ε are the unperturbed energies of the P-space

Topics for Week 44

Perturbation theory

- Monday:
- Summary from last week
- Diagram examples, rules and unlinked diagrams
- Introduction to time-dependent perturbation theory
- Schrödinger, Heisenberg and interaction pictures
- Tuesday:
- Schrödinger, Heisenberg and interaction pictures
- Linked diagram theorem
- Diagram rules and examples

Exercise 31.

Schrödinger picture

The time-dependent Schrödinger equation (or equation of motion) reads

$$\imath\hbar\frac{\partial}{\partial t}|\Psi_S(t)\rangle = \hat{H}\Psi_S(t)\rangle,$$

where the subscript S stands for Schrödinger here. A formal solution is given by

$$|\Psi_S(t)\rangle = \exp\left(-\imath\hat{H}(t-t_0)/\hbar\right)|\Psi_S(t_0)\rangle.$$

The Hamiltonian $\hat{H}$ is hermitian and the exponent represents a unitary operator with an operation carried ut on the wave function at a time t_0.

Interaction picture

Our Hamiltonian is normally written out as the sum of an unperturbed part $\hat{H}_0$ and an interaction part $\hat{H}_I$, that is

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

In general we have $[\hat{H}_0, \hat{H}_I] \neq 0$ since $[\hat{T}, \hat{V}] \neq 0$. We wish now to define a unitary transformation in terms of $\hat{H}_0$ by defining

$$|\Psi_I(t)\rangle = \exp\left(\imath \hat{H}_0 t/\hbar\right)|\Psi_S(t)\rangle,$$

which is again a unitary transformation carried out now at the time t on the wave function in the Schrödinger picture.

Interaction picture

We can easily find the equation of motion by taking the time derivative

$$\imath\hbar\frac{\partial}{\partial t}|\Psi_I(t)\rangle = -\hat{H}_0\exp(\imath\hat{H}_0 t/\hbar)\Psi_S(t)\rangle + \exp(\imath\hat{H}_0 t/\hbar)\imath\hbar\frac{\partial}{\partial t}\Psi_S(t)\rangle.$$

Interaction picture

Using the definition of the Schrödinger equation, we can rewrite the last equation as

$$\imath\hbar\frac{\partial}{\partial t}|\Psi_I(t)\rangle = \exp\left(\imath\hat{H}_0 t/\hbar\right)\left[-\hat{H}_0 + \hat{H}_0 + \hat{H}_I\right]\exp\left(-\imath\hat{H}_0 t/\hbar\right)\Psi_I(t)\rangle,$$

which gives us

$$\imath\hbar\frac{\partial}{\partial t}|\Psi_I(t)\rangle = \hat{H}_I(t)\Psi_I(t)\rangle,$$

with

$$\hat{H}_I(t) = \exp\left(\imath\hat{H}_0 t/\hbar\right)\hat{H}_I\exp\left(-\imath\hat{H}_0 t/\hbar\right).$$

Interaction picture

The order of the operators is important since $\hat{H}_0$ and $\hat{H}_I$ do generally not commute. The expectation value of an arbitrary operator in the interaction picture can now be written as

$$\langle \Psi'_S(t)|\hat{O}_S|\Psi_S(t)\rangle = \langle \Psi'_I(t)| \exp(\imath \hat{H}_0 t/\hbar)\hat{O}_I \exp(-\imath \hat{H}_0 t/\hbar)|\Psi_I(t)\rangle,$$

and using the definition

$$\hat{O}_I(t) = \exp(\imath \hat{H}_0 t/\hbar)\hat{O}_I \exp(-\imath \hat{H}_0 t/\hbar),$$

we obtain

$$\langle \Psi'_S(t)|\hat{O}_S|\Psi_S(t)\rangle = \langle \Psi'_I(t)|\hat{O}_I(t)|\Psi_I(t)\rangle,$$

stating that a unitary transformation does not change expectation values!

Interaction picture

If the take the time derivative of the operator in the interaction picture we arrive at the following equation of motion

$$\imath\hbar\frac{\partial}{\partial t}\hat{O}_I(t) = \exp\left(\imath\hat{H}_0 t/\hbar\right)\left[\hat{O}_S\hat{H}_0 - \hat{H}_0\hat{O}_S\right]\exp\left(-\imath\hat{H}_0 t/\hbar\right) = \left[\hat{O}_I(t), \hat{H}_0\right].$$

Here we have used the time-independence of the Schrödinger equation together with the observation that any function of an operator commutes with the operator itself.

Interaction picture

In order to solve the equation of motion equation in the interaction picture, we define a unitary operator time-development operator $\hat{U}(t, t')$. Later we will derive its connection with the linked-diagram theorem, which yields a linked expression for the actual operator. The action of the operator on the wave function is

$$|\Psi_I(t)\rangle = \hat{U}(t, t_0)|\Psi_I(t_0)\rangle,$$

with the obvious value $\hat{U}(t_0, t_0) = 1$.

Interaction picture

The time-development operator U has the properties that

$$\hat{U}^\dagger(t,t')\hat{U}(t,t') = \hat{U}(t,t')\hat{U}^\dagger(t,t') = 1,$$

which implies that U is unitary

$$\hat{U}^\dagger(t,t') = \hat{U}^{-1}(t,t').$$

Further,

$$\hat{U}(t,t')\hat{U}(t't'') = \hat{U}(t,t'')$$

and

$$\hat{U}(t,t')\hat{U}(t',t) = 1,$$

which leads to

$$\hat{U}(t,t') = \hat{U}^\dagger(t',t).$$

Topics for Week 45

Time-dependent Perturbation theory

- Monday:
- Summary from last week
- Pictures and adiabatic hypothesis
- Goldstone's Linked diagram theorem and Gell-Mann's and Low's theorem
- Linked and unlinked diagrams, examples
- Tuesday:
- Gell-Mann's and Low's theorem
- Wick's theorem for time-dependent products
- Diagram rules with examples

Exercises 29, 30 and second 23!

Interaction picture

Using our definition of Schrödinger's equation in the interaction picture, we can then construct the operator $\hat{U}$. We have defined

$$|\Psi_I(t)\rangle = \exp\left(\imath\hat{H}_0 t/\hbar\right)|\Psi_S(t)\rangle,$$

which can be rewritten as

$$|\Psi_I(t)\rangle = \exp\left(\imath\hat{H}_0 t/\hbar\right)\exp\left(-\imath\hat{H}(t-t_0)/\hbar\right)|\Psi_S(t_0)\rangle,$$

or

$$|\Psi_I(t)\rangle = \exp\left(\imath\hat{H}_0 t/\hbar\right)\exp\left(-\imath\hat{H}(t-t_0)/\hbar\right)\exp\left(-\imath\hat{H}_0 t_0/\hbar\right)|\Psi_I(t_0)\rangle.$$

Interaction picture

From the last expression we can define

$$\hat{U}(t, t_0) = \exp\left(\imath \hat{H}_0 t/\hbar\right) \exp\left(-\imath \hat{H}(t - t_0)/\hbar\right) \exp\left(-\imath \hat{H}_0 t_0/\hbar\right).$$

It is then easy to convince oneself that the properties defined above are satisfied by the definition of $\hat{U}$.

Interaction picture

We derive the equation of motion for $\hat{U}$ using the above definition. This results in

$$\imath\hbar\frac{\partial}{\partial t}\hat{U}(t,t_0)=\hat{H}_I(t)\hat{U}(t,t_0),$$

which we integrate from t_0 to a time t resulting in

$$\hat{U}(t,t_0)-\hat{U}(t_0,t_0)=\hat{U}(t,t_0)-1=-\frac{\imath}{\hbar}\int_{t_0}^{t}dt'\hat{H}_I(t')\hat{U}(t',t_0),$$

which can be rewritten as

$$\hat{U}(t,t_0)=1-\frac{\imath}{\hbar}\int_{t_0}^{t}dt'\hat{H}_I(t')\hat{U}(t',t_0).$$

Interaction picture

We can solve this equation iteratively keeping in mind the time-ordering of the of the operators

$$\hat{U}(t,t_0) = 1 - \frac{\imath}{\hbar}\int_{t_0}^{t} dt' \hat{H}_I(t') + \left(\frac{-\imath}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{H}_I(t')\hat{H}_I(t'') + \dots$$

The third term can be written as

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{H}_I(t')\hat{H}_I(t'') = \frac{1}{2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{H}_I(t')\hat{H}_I(t'') + \frac{1}{2}\int_{t_0}^{t} dt'' \int_{t''}^{t} dt' \hat{H}_I(t')\hat{H}_I(t'').$$

Interaction picture

We obtain this expression by changing the integration order in the second term via a change of the integration variables t' and t'' in

$$\frac{1}{2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{H}_I(t')\hat{H}_I(t'').$$

We can rewrite the terms which contain the double integral as

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{H}_I(t')\hat{H}_I(t'') =$$

$$\frac{1}{2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \left[\hat{H}_I(t')\hat{H}_I(t'')\Theta(t'-t'') + \hat{H}_I(t')\hat{H}_I(t'')\Theta(t''-t')\right],$$

with $\Theta(t''-t')$ being the standard Heavyside or step function. The step function allows us to give a specific time-ordering to the above expression.

Interaction picture

With the Θ-function we can rewrite the last expression as

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{H}_I(t')\hat{H}_I(t'') = \frac{1}{2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{T}\left[\hat{H}_I(t')\hat{H}_I(t'')\right],$$

where $\hat{T}$ is the so-called time-ordering operator.

Interaction picture

With this definition, we can rewrite the expression for $\hat{U}$ as

$$\hat{U}(t, t_0) = \sum_{n=0}^{\infty} \left(\frac{-\imath}{\hbar}\right)^n \frac{1}{n1} \int_{t_0}^{t} dt_1 \ldots \int_{t_0}^{t} dt_N \hat{T} \left[\hat{H}_I(t_1) \ldots \hat{H}_I(t_n)\right] = \hat{T} \exp\left[\frac{-\imath}{\hbar} \int_{t_0}^{t} dt' \hat{H}_I(t')\right].$$

The above time-evolution operator in the interaction picture will be used to derive various contributions to many-body perturbation theory.

Heisenberg picture

We wish now to define a unitary transformation in terms of $\hat{H}$ by defining

$$|\Psi_H(t)\rangle = \exp\left(\imath \hat{H} t/\hbar\right)|\Psi_S(t)\rangle,$$

which is again a unitary transformation carried out now at the time t on the wave function in the Schrödinger picture. If we combine this equation with Schrödinger's equation we obtain the following equation of motion

$$\imath\hbar\frac{\partial}{\partial t}|\Psi_H(t)\rangle = 0,$$

meaning that $|\Psi_H(t)\rangle$ is time independent. An operator in this picture is defined as

$$\hat{O}_H(t) = \exp\left(\imath \hat{H} t/\hbar\right)\hat{O}_S \exp\left(-\imath \hat{H} t/\hbar\right).$$

Heisenberg picture

The time dependence is then in the operator itself, and this yields in turn the following equation of motion

$$\imath\hbar\frac{\partial}{\partial t}\hat{O}_H(t) = \exp\left(\imath\hat{H}t/\hbar\right)\left[\hat{O}_H\hat{H} - \hat{H}\hat{O}_H\right]\exp\left(-\imath\hat{H}t/\hbar\right) = \left[\hat{O}_H(t), \hat{H}\right].$$

We note that an operator in the Heisenberg picture can be related to the corresponding operator in the interaction picture as

$$\hat{O}_H(t) = \exp\left(\imath\hat{H}t/\hbar\right)\hat{O}_S\exp\left(-\imath\hat{H}t/\hbar\right) =$$

$$\exp\left(\imath\hat{H}_It/\hbar\right)\exp\left(-\imath\hat{H}_0t/\hbar\right)\hat{O}_I\exp\left(\imath\hat{H}_0t/\hbar\right)\exp\left(-\imath\hat{H}_It/\hbar\right).$$

Heisenberg picture

With our definition of the time evolution operator we see that

$$\hat{O}_H(t) = \hat{U}(0,t)\hat{O}_I\hat{U}(t,0),$$

which in turn implies that $\hat{O}_S = \hat{O}_I(0) = \hat{O}_H(0)$, all operators are equal at $t = 0$. The wave function in the Heisenberg formalism is related to the other pictures as

$$|\Psi_H\rangle = |\Psi_S(0)\rangle = |\Psi_I(0)\rangle,$$

since the wave function in the Heisenberg picture is time independent. We can relate this wave function to that a given time t via the time evolution operator as

$$|\Psi_H\rangle = \hat{U}(0,t)|\Psi_I(t)\rangle.$$

Adiabatic hypothesis

We assume that the interaction term is switched on gradually. Our wave function at time $t = -\infty$ and $t = \infty$ is supposed to represent a non-interacting system given by the solution to the unperturbed part of our Hamiltonian $\hat{H}_0$. We assume the ground state is given by $|\Phi_0\rangle$, which could be a Slater determinant.
We define our Hamiltonian as

$$\hat{H} = \hat{H}_0 + \exp\left(-\varepsilon t/\hbar\right)\hat{H}_I,$$

where ε is a small number. The way we write the Hamiltonian and its interaction term is meant to simulate the switching of the interaction.

Adiabatic hypothesis

The time evolution of the wave function in the interaction picture is then

$$|\Psi_I(t)\rangle = \hat{U}_\varepsilon(t, t_0)|\Psi_I(t_0)\rangle,$$

with

$$\hat{U}_\varepsilon(t, t_0) = \sum_{n=0}^{\infty} \left(\frac{-\imath}{\hbar}\right)^n \frac{1}{n!} \int_{t_0}^{t} dt_1 \ldots \int_{t_0}^{t} dt_N \exp\left(-\varepsilon(t_1 + \cdots + t_n)/\hbar\right) \hat{T} \left[\hat{H}_I(t_1) \ldots \hat{H}_I(t_n)\right]$$

Adiabatic hypothesis

In the limit $t_0 \to -\infty$, the solution ot Schrödinger's equation is $|\Phi_0\rangle$, and the eigenenergies are given by

$$\hat{H}_0|\Phi_0\rangle = W_0|\Phi_0\rangle,$$

meaning that

$$|\Psi_S(t_0)\rangle = \exp\left(-\imath W_0 t_0/\hbar\right)|\Phi_0\rangle,$$

with the corresponding interaction picture wave function given by

$$|\Psi_I(t_0)\rangle = \exp\left(\imath \hat{H}_0 t_0/\hbar\right)|\Psi_S(t_0)\rangle = |\Phi_0\rangle.$$

Adiabatic hypothesis

The solution becomes time independent in the limit $t_0 \to -\infty$. The same conclusion can be reached by looking at

$$\imath\hbar \frac{\partial}{\partial t}|\Psi_I(t)\rangle = \exp\left(-\varepsilon|t|/\hbar\right)\hat{H}_I|\Psi_I(t)\rangle$$

and taking the limit $t \to \pm\infty$. We can rewrite the equation for the wave function at a time $t = 0$ as

$$|\Psi_I(0)\rangle = \hat{U}_\varepsilon(0, -\infty)|\Phi_0\rangle.$$

Topics for Week 46

Perturbation theory and Coupled cluster theory

- Monday:
- Repetion from last week
- Gell-Mann and Low's theorem on the ground state
- Time-dependent Perturbation theory, computation of diagrams
- Tuesday:
- Coupled cluster theory, chapter 9 of Shavitt and Bartlett
- Wednesday:
- Exercises: 27, 32d and e

Goldstone's theorem and Gell-Mann and Low theorem on the ground state

Our wave function for ground state is then

$$\frac{|\Psi_0\rangle}{\langle\Phi_0|\Psi_0\rangle} = \lim_{\epsilon\to 0}\lim_{t'\to-\infty(1-i\epsilon)} \frac{U(0,-\infty)|\Phi_0\rangle}{\langle\Phi_0|U(0,-\infty)|\Phi_0\rangle},$$

and we ask whether this quantity exists to all orders in perturbation theory. Goldstone's theorem states that only linked diagrams enter the expression for the final binding energy. It means that energy difference reads now

$$\Delta E_0 = \sum_{i=0}^{\infty}\langle\Phi_0|\hat{H}_I\left\{\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I\right\}^i|\Phi_0\rangle_L,$$

where the subscript L indicates that only linked diagrams are included. In our Rayleigh-Schrödinger expansion, the energy difference included also unlinked diagrams.

Goldstone's theorem and Gell-Mann and Low theorem on the ground state

If it does, Gell-Mann and Low showed that it is an eigenstate of $\hat{H}$ with eigenvalue

$$\hat{H}\frac{|\Psi_0\rangle}{\langle\Phi_0|\Psi_0\rangle} = E_0\frac{|\Psi_0\rangle}{\langle\Phi_0|\Psi_0\rangle}$$

and multiplying from the left with $\langle\Phi_0|$ we can rewrite the last equation as

$$E_0 - W_0 = \frac{\langle\Phi_0|\hat{H}_I|\Psi_0\rangle}{\langle\Phi_0|\Psi_0\rangle},$$

since $\hat{H}_0|\Phi_0\rangle = W_0|\Phi_0\rangle$. The numerator and the denominators of the last equation do not exist separately. The theorem of Gell-Mann and Low asserts that this ratio exists.

Goldstone's theorem and Gell-Mann and Low theorem on the ground state

We note that also that the term D is nothing but the denominator of the equation for the energy. We obtain then the following expression for the energy

$$E_0 - W_0 = \Delta E_0 = N_L = \langle \Phi_0(0) | \hat{H}_I U_\epsilon(0, -\infty) | \Phi_0(-\infty) \rangle_L ,$$

and Goldstone's theorem is then proved. The corresponding expression from Rayleigh-Schrödinger perturbation theory is given by

$$\Delta E_0 = \langle \Phi_0 | \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I + \dots \right) | \Phi_0 \rangle_C .$$

Goldstone's theorem and Gell-Mann and Low theorem on the ground state

An important point in the derivation of the Gell-Mann and Low theorem

$$E_0 - W_0 = \frac{\langle \Phi_0 | \hat{H}_I | \Psi_0 \rangle}{\langle \Phi_0 | \Psi_0 \rangle},$$

is that the numerator and the denominators of the last equation do not exist separately. The theorem of Gell-Mann and Low asserts that this ratio exists. To prove it we proceed as follows. Consider the expression

$$(\hat{H}_0 - E_0) U_\epsilon(0, -\infty) | \Phi_0 \rangle = \left[\hat{H}_0, U_\epsilon(0, -\infty) \right] | \Phi_0 \rangle.$$

Goldstone's theorem and Gell-Mann and Low theorem on the ground state

To evaluate the commutator

$$(\hat{H}_0 - E_0)U_\epsilon(0,-\infty)|\Phi_0\rangle = \left[\hat{H}_0, U_\epsilon(0,-\infty)\right]|\Phi_0\rangle.$$

we write the associate commutator as

$$\left[\hat{H}_0, \hat{H}_I(t_1)\hat{H}_I(t_2)\ldots\hat{H}_I(t_n)\right] = \left[\hat{H}_0, \hat{H}_I(t_1)\right]\hat{H}_I(t_2)\ldots\hat{H}_I(t_n) +$$

$$\cdots + \hat{H}_I(t_1)\left[\hat{H}_0, \hat{H}_I(t_2)\right]\hat{H}_I(t_3)\ldots\hat{H}_I(t_n) + \ldots$$

Using the equation of motion for an operator in the interaction picture we have

$$\imath\hbar\frac{\partial}{\partial t}\hat{H}_I(t) = \left[\hat{H}_I(t), \hat{H}_0\right].$$

Each of the above commutators yield then a time derivative!

Goldstone's theorem and Gell-Mann and Low theorem on the ground state

We have then

$$\left[\hat{H}_0, \hat{H}_I(t_1)\hat{H}_I(t_2)\ldots\hat{H}_I(t_n)\right] = \imath\hbar\left(\frac{\partial}{\partial t_n} + \frac{\partial}{\partial t_1} + \cdots + \frac{\partial}{\partial t_n}\right)\hat{H}_I(t_1)\hat{H}_I(t_2)\ldots\hat{H}_I(t_n),$$

meaning that we can rewrite

$$(\hat{H}_0 - E_0)U_\epsilon(0,-\infty)|\Phi_0\rangle = \left[\hat{H}_0, U_\epsilon(0,-\infty)\right]|\Phi_0\rangle,$$

as

$$(\hat{H}_0 - E_0)U_\epsilon(0,-\infty)|\Phi_0\rangle = -\sum_{n=1}^{\infty}\left(\frac{-\imath}{\hbar}\right)^{n-1}\frac{1}{n!}\int_{t_0}^{t} dt_1 \ldots \int_{t_0}^{t} dt_N \exp\left(-\varepsilon(t_1 + \cdots + t_n)/\hbar\right)$$

$$\times\sum_{i=1}^{n}\left(\frac{\partial}{\partial t_i}\right)\hat{T}\left[\hat{H}_I(t_1)\ldots\hat{H}_I(t_n)\right].$$

Goldstone's theorem and Gell-Mann and Low theorem on the ground state

All the time derivatives in this equation

$$(\hat{H}_0 - E_0) U_\epsilon(0, -\infty)|\Phi_0\rangle = -\sum_{n=1}^{\infty} \left(\frac{-\imath}{\hbar}\right)^{n-1} \frac{1}{n!} \int_{t_0}^{t} dt_1 \ldots \int_{t_0}^{t} dt_N \exp\left(-\varepsilon(t_1 + \cdots + t_n)/\hbar\right)$$

$$\times \sum_{i=1}^{n} (\frac{\partial}{\partial t_i}) \hat{T}\left[\hat{H}_I(t_1) \ldots \hat{H}_I(t_n)\right],$$

make the same contribution, as can be seen by changing dummy variables. We can therefore retain just one time derivative $\partial/partialt$ and multiply with n. Integrating by parts wrt t_1 we obtain two terms, see rest on blackboard!!

Topics for Week 47

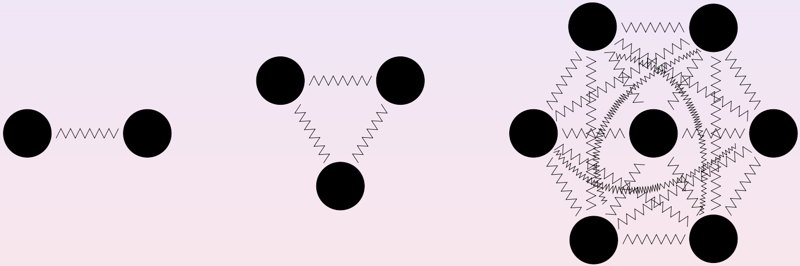
Coupled cluster theory

- Monday:
- Repetion from last week
- Coupled cluster theory with doubles only, chapter 9 of Shavitt and Bartlett
- Tuesday:
- Coupled cluster theory, chapter 10 of Shavitt and Bartlett
- Wednesday:
- Exercise: Set up the Coupled-cluster equations (doubles only) for solving the pairing problem of exercise 32. Find the result for the energy after one iteration. Can you find the final energy?

Problem statement

Many-body systems

- We study a bound system of A interacting particles ...



and it quickly becomes unmanageable . . .

Problem statement

We are looking at non-relativistic particles, so the solutions of the A-body system, is given by the A-body Schrödinger equation.

$$\widehat{H}_A|\Psi_A\rangle = E_A|\Psi_A\rangle$$

Manybody wavefunction

The wavefunction of the manybody system can be decomposed into a suitable manybody basis

$$|\Psi_A\rangle = \sum_i c_i |\Phi_i\rangle.$$

For fermions, these are Slater-determinants

$$\begin{aligned} |\Phi_i\rangle &= |\alpha_{i_1}\alpha_{i_2}\dots\alpha_{i_A}\rangle \\ &= \left(\prod_{j=1}^{A} a_{i_j}^\dagger\right)|0\rangle, \end{aligned}$$

Where $a^\dagger$ is a second quantized operator satisfying

$$\begin{aligned} a_p^\dagger|0\rangle &= |\alpha_p\rangle & \qquad a_p|\alpha_q\rangle &= \left(a_p^\dagger\right)^\dagger|\alpha_q\rangle = \delta_{pq}|0\rangle \\ \left\{a_p, a_q^\dagger\right\} &= \delta_{pq} & \qquad \{a_p, a_q\} &= \left\{a_p^\dagger, a_q^\dagger\right\} = 0 \end{aligned}$$

Manybody wavefunction

In the $\mathbf{x}$-representation the Slater-determinant is written

$$\langle \mathbf{x} | \Phi_i = \frac{1}{\sqrt{A}} \sum_{n=1}^{A!} (-1)^{P_n} \prod_{j=1}^{A} \phi_{i,n_j}(\mathbf{x}_j),$$

where

$$\phi_{i,k}(\mathbf{x}_j) = \left\langle \mathbf{x}_j \middle| \alpha_{i_k}\right.$$

are the solutions to a selected single particle problem

$$\widehat{h}\phi_k(\mathbf{x}) = \epsilon_k \phi_k(\mathbf{x}).$$

Manybody wavefunction

In the particle-hole formalism all quantities are expressed in relation to the reference state

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

The indices are partitioned according to their relation to the Fermi level

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

and the second quantized operators now satisfy

$$\left\{a_i, a_j^\dagger\right\} = \delta_{ij} \qquad \left\{a_a, a_b^\dagger\right\} = \delta_{ab}$$

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

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

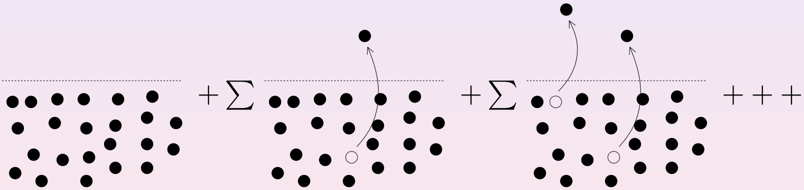
Manybody wavefunction

For use with Wicks theorem, we define the contractions between operators in the particle-hole formalism

$$\overbrace{a_p^\dagger a_q} = \langle \Phi_0 | a_p^\dagger a_q | \Phi_0 \rangle = \delta_{pq \in i}$$
$$\overbrace{a_q a_p^\dagger} = \langle \Phi_0 | a_q a_p^\dagger | \Phi_0 \rangle = \delta_{pq \in a}$$

Manybody wavefunction

The particle-hole expansion of a manybody wavefunction is a linear combination of all possible excitations of the reference wavefuncton.



Manybody wavefunction

The manybody wavefunction can be expanded in a linear combination of particle-hole excitations, which is complete in agiven basis set

$$
\begin{aligned}
|\Psi\rangle &= \sum_{ia} |\Phi_i^a\rangle + \frac{1}{4}\sum_{ijab} |\Phi_{ij}^{ab}\rangle + \ldots + \frac{1}{(A!)^2} \sum_{\substack{i_1\ldots i_A \\ a_1\ldots a_A}} |\Phi_{i_1\ldots i_A}^{a_1\ldots a_A}\rangle \\
&= \sum_{ia} c_i^a a_a^\dagger a_i |\Phi_0\rangle + \frac{1}{4}\sum_{ijab} c_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle + \ldots + \\
&\quad \frac{1}{(A!)^2} \sum_{\substack{i_1\ldots i_A \\ a_1\ldots a_A}} c_{i_1\ldots i_A}^{a_1\ldots a_A} a_{a_1}^\dagger \ldots a_{a_A}^\dagger a_{i_A} \ldots a_{i_1} |\Phi_0\rangle
\end{aligned}
$$

Manybody Hamiltonian

A general Hamiltonian contains up to A-body interactions

$$\widehat{H}_A = \sum_{i=1}^{A}\left(\widehat{t}_i + \widehat{u}_i\right) + \sum_{i<j=1}^{A} \widehat{v}_{ij} + + + \sum_{i_1<\cdots<i_A=1}^{A} \widehat{v}_{i_1,\dots,i_A}$$

$$= \widehat{T}_{\mathrm{kin}} + \widehat{U} + \sum_{n=2}^{A} \widehat{V}_n,$$

where $\widehat{T}_{\mathrm{kin}}$ is the kinetic energy operator, $\widehat{U}$ is a generic onebody potential and $\widehat{V}_n$ is an n-body potential.

Manybody Hamiltonian

In second quantized form, a general n-body operator is written

$$\widehat{V}_n = \frac{1}{(n!)^2} \sum_{\substack{\alpha_1\ldots\alpha_n \\ \gamma_1\ldots\gamma_n}} \langle \alpha_1 \ldots \alpha_n | \widehat{v}_n | \gamma_1 \ldots \gamma_n \rangle a^\dagger_{\alpha_1} \ldots a^\dagger_{\alpha_n} a_{\gamma_n} \ldots a_{\gamma_1},$$

where the matrix elements $\langle \alpha_1 \ldots \alpha_n | \widehat{V}_n | \gamma_1 \ldots \gamma_n \rangle$ are fully anti-symmetric with respect to the interchange of indices and the sum over α_i and γ_i runs over all possible single particle states.

Manybody Hamiltonian

We will truncate the Hamiltonian at the $n = 3$ level at the most and skip the onebody potential, so the Hamiltonian will be written

$$\widehat{H} = \sum_{pq} \langle p|\widehat{t}|q\rangle a_p^\dagger a_q + \frac{1}{4}\sum_{pqrs} \langle pq|\widehat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$
$$\frac{1}{36}\sum_{pqrstu} \langle pqr|\widehat{v}_3|stu\rangle a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s$$

Manybody Hamiltonian

We define the normal ordered operator

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

All creation operators to the left and all annihilation operators to the right times a factor determined by how many operators have been switched.
This object has the highly desired property that the expectation value is always zero

$$\langle\Phi_0| \left\{a_a a_b \dots a_c^\dagger a_d^\dagger\right\} |\Phi_0\rangle = 0$$

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

$$\widehat{T}_{\mathrm{kin}} = \sum_{pq} \langle p|\widehat{t}|q\rangle a_p^\dagger a_q$$

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

$$\begin{aligned} \widehat{T}_{\mathrm{kin}} &= \sum_{pq} \langle p|\widehat{t}|q\rangle a_p^\dagger a_q \\ &= \sum_{pq} \langle p|\widehat{t}|q\rangle \left\{ a_p^\dagger a_q \right\} + \delta_{pq\in i} \sum_{pq} \langle p|\widehat{t}|q\rangle \\ &= \sum_{pq} \langle p|\widehat{t}|q\rangle \left\{ a_p^\dagger a_q \right\} + \sum_{i} \langle i|\widehat{t}|i\rangle \end{aligned}$$

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

$$\hat{H}_2 = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

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

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

$$\hat{H}_2 = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

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

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

$$\hat{H}_2 = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

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

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

$$\hat{H}_2 = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

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

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

$$\hat{H}_2 = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

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

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

$$\hat{H}_2 = \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r$$

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

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

$$
\begin{aligned}
\hat{H}_2 &= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle a_p^\dagger a_q^\dagger a_s a_r \\
&= \frac{1}{4}\sum_{pqrs}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} + \quad \frac{1}{4}\sum_{pqrs}\Big(\delta_{qs\in i}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_r\right\} \\
&\quad - \delta_{qr\in i}\langle pq|\hat{v}|rs\rangle \left\{a_p^\dagger a_s\right\} - \delta_{ps\in i}\langle pq|\hat{v}|rs\rangle \left\{a_q^\dagger a_r\right\} \\
&\quad + \delta_{pr\in i}\langle pq|\hat{v}|rs\rangle \left\{a_q^\dagger a_s\right\} + \delta_{pr\in i}\delta_{qs\in i} - \delta_{ps\in i}\delta_{qr\in i}\Big)
\end{aligned}
$$

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

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

Manybody Hamiltonian

Derivation of the normal ordered Hamiltonian

$$
\begin{aligned}
\widehat{G}_N &= \frac{1}{36} \sum_{\substack{pqr\\stu}} \langle pqr|\widehat{v}_3|stu\rangle \left\{ a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s \right\} \\
\widehat{V}_N &= \frac{1}{4} \sum_{pqrs} \left(\langle pq|\widehat{v}|rs\rangle + \sum_i \langle ipq|\widehat{v}_3|irs\rangle \right) \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \\
\widehat{F}_N &= \sum_{pq} \left(\langle p|\widehat{t}|q\rangle + \sum_i \langle pi|\widehat{v}|qi\rangle + \frac{1}{2} \sum_{ij} \langle ijp|\widehat{v}_3|ijq\rangle \right) \left\{ a_p^\dagger a_q \right\} \\
E_0 &= \sum_i \langle i|\widehat{t}|i\rangle + \frac{1}{2} \sum_{ij} \langle ij|\widehat{v}|ij\rangle + \frac{1}{6} \sum_{ijk} \langle ijk|\widehat{v}_3|ijk\rangle \\
\widehat{H} &= \widehat{G}_N + \widehat{V}_N + \widehat{F}_N + E_0 \qquad (14.0.153)
\end{aligned}
$$

Coupled Cluster summary

The wavefunction is given by

$$|\Psi\rangle \approx |\Psi_{CC}\rangle = e^{\hat{T}}|\Phi_0\rangle = \left(\sum_{n=1}^{\infty} \frac{1}{n!}\hat{T}^n\right)|\Phi_0\rangle,$$

where $\widehat{T}$ is the cluster operator defined as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots + \hat{T}_A$$

$$\hat{T}_n = \left(\frac{1}{n!}\right)^2 \sum_{\substack{i_1,i_2,\ldots i_n \\ a_1,a_2,\ldots a_n}} t_{i_1 i_2 \ldots i_n}^{a_1 a_2 \ldots a_n} a_{a_1}^\dagger a_{a_2}^\dagger \ldots a_{a_n}^\dagger a_{i_n} \ldots a_{i_2} a_{i_1}.$$

Coupled Cluster summary cont.

The energy is given by

$$E_{\mathrm{CC}} = \langle \Phi_0 | | \Phi_0 \rangle,$$

where is a similarity transformed Hamiltonian

$$= e^{-\widehat{T}} \widehat{H}_N e^{\widehat{T}}$$

$$\widehat{H}_N = \widehat{H} - \langle \Phi_0 | \widehat{H} | \Phi_0 \rangle.$$

Coupled Cluster summary cont.

The coupled cluster energy is a function of the unknown cluster amplitudes $t_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n}$, given by the solutions to the amplitude equations

$$0 = \langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | | \Phi_0 \rangle.$$

Coupled Cluster summary cont.

is expanded using the .

$$
\begin{aligned}
&= \widehat{H}_N + \left[\widehat{H}_N, \widehat{T}\right] + \frac{1}{2}\left[\left[\widehat{H}_N, \widehat{T}\right], \widehat{T}\right] + \dots \\
&\frac{1}{n!}\left[\dots\left[\widehat{H}_N, \widehat{T}\right], \dots \widehat{T}\right] + ++
\end{aligned}
$$

and simplified using the connected cluster theorem

$$
= \widehat{H}_N + \left(\widehat{H}_N \widehat{T}\right)_c + \frac{1}{2}\left(\widehat{H}_N \widehat{T}^2\right)_c + \dots + \frac{1}{n!}\left(\widehat{H}_N \widehat{T}^n\right)_c + ++
$$

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

$$
\begin{aligned}
\widehat{H} &= \sum_{pq} f_q^p \left\{a_p^\dagger a_q\right\} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle \left\{a_p^\dagger a_q^\dagger a_s a_r\right\} \\
&\quad + \mathrm{E}_0 \\
&= \widehat{F}_N + \widehat{V}_N + \mathrm{E}_0 = \widehat{H}_N + \mathrm{E}_0
\end{aligned}
$$

where

$$
\begin{aligned}
f_q^p &= \langle p|\widehat{t}|q\rangle + \sum_i \langle pi|\widehat{v}|qi\rangle \\
\langle pq||rs\rangle &= \langle pq|\widehat{v}|rs\rangle \\
\mathrm{E}_0 &= \sum_i \langle i|\widehat{t}|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|\widehat{v}|ij\rangle
\end{aligned}
$$

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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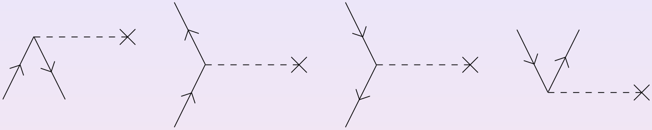
Diagram elements - Directed lines

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.

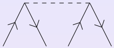
Diagram elements - Onebody Hamiltonian



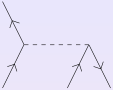
Level: -1 Level: 0 Level: 0 Level: +1

- Horisontal dashed line segment with one vertex.
- Excitation level identify the number of particle/hole pairs created by the operator.

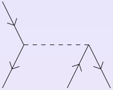
Diagram elements - Twobody Hamiltonian



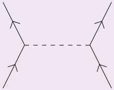
Level: -2



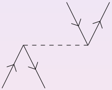
Level: -1



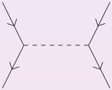
Level: -1



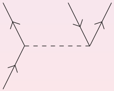
Level: 0



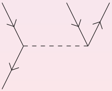
Level: 0



Level: 0



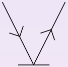
Level: +1



Level: +1

Level: +2

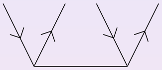
Diagram elements - Onebody cluster operator



Level: +1

- Horisontal line segment with one vertex.
- Excitation level of +1.

Diagram elements - Twobody cluster operator



Level: +2

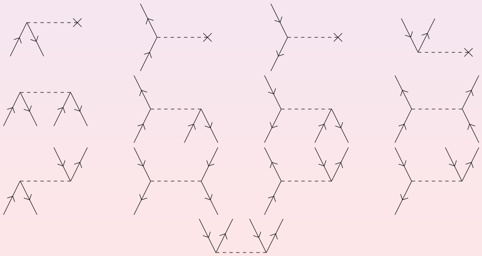
- Horisontal line segment with two vertices.
- Excitation level of +2.

CCSD energy equation - Derivation

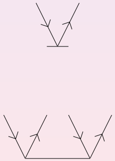
$$\mathrm{E}_{\mathrm{CCSD}} = \langle \Phi_0 | | \Phi_0 \rangle$$

- No external lines.
- Final excitation level: 0

Elements: $\widehat{H}_N$



Elements: $\widehat{T}$



CCSD energy equation

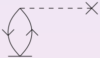
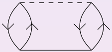
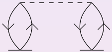
$E_{CCSD} =$  $+$  $+$ 

Diagram rules

- Label all lines.
- Sum over all internal indices.
- Extract matrix elements. ($f_{\text{in}}^{\text{out}}$, $\langle \text{lout}, \text{rout}||\text{lin}, \text{rin}\rangle$)
- 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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- Calculate the phase: $(-1)^{\mathrm{holelines}+\mathrm{loops}}$
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Diagram rules

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- 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: $(-1)^{\mathrm{holelines+loops}}$
- 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. ($f_{\mathrm{in}}^{\mathrm{out}}$, $\langle \mathrm{lout}, \mathrm{rout} || \mathrm{lin}, \mathrm{rin} \rangle$)
- 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.

CCSD energy equation

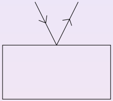
$$E_{CCSD} = f_a^i t_i^a + \frac{1}{4}\langle ij||ab\rangle t_{ij}^{ab} + \frac{1}{2}\langle ij||ab\rangle t_i^a t_j^b$$

Note the implicit sum over repeated indices.

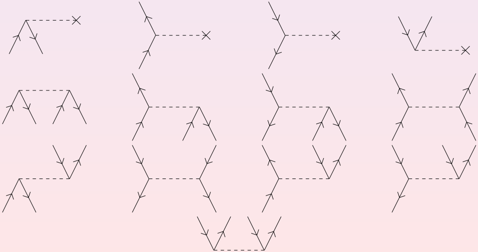
CCSD $\widehat{T}_1$ amplitude equation - Derivation

$$0 = \langle \Phi_i^a | | \Phi_0 \rangle$$

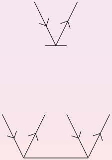
- One pair of particle/hole external lines.
- Final excitation level: +1



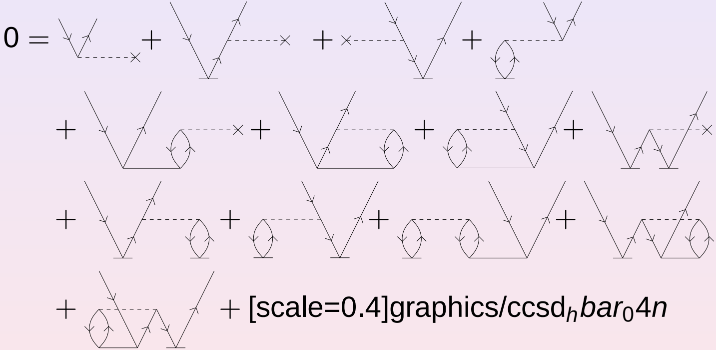
Elements: $\widehat{H}_N$



Elements: $\widehat{T}$



CCSD $\widehat{T}_1$ amplitude equation



$+$ [scale=0.4]graphics/ccsd$_h bar_0 4n$

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. ($f_{\mathrm{in}}^{\mathrm{out}}$, $\langle \mathrm{lout}, \mathrm{rout} || \mathrm{lin}, \mathrm{rin} \rangle$)
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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.

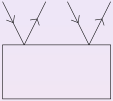
CCSD $\widehat{T}_1$ amplitude equation

$$
\begin{aligned}
0 = {} & f_i^a + f_e^a t_i^e - f_i^m t_m^a + \langle ma||ei\rangle t_m^e + f_e^m t_{im}^{ae} + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\
& - \frac{1}{2}\langle mn||ei\rangle t_{mn}^{ea} - f_e^m t_i^e t_m^a + \langle am||ef\rangle t_i^e t_m^f - \langle mn||ei\rangle t_m^e t_n^a \\
& + \langle mn||ef\rangle t_m^e t_{ni}^{fa} - \frac{1}{2}\langle mn||ef\rangle t_i^e t_{mn}^{af} - \frac{1}{2}\langle mn||ef\rangle t_n^a t_{mi}^{ef} \\
& - \langle mn||ef\rangle t_i^e t_m^a t_n^f
\end{aligned}
$$

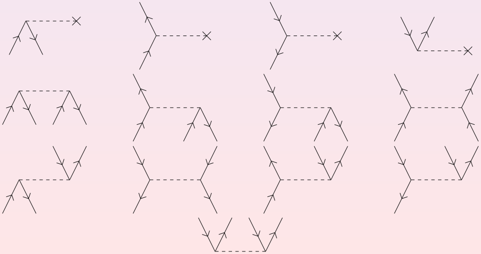
CCSD $\widehat{T}_2$ amplitude equation - Derivation

$$0 = \langle \Phi_{ij}^{ab} || \Phi_0 \rangle$$

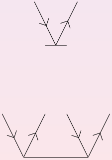
- Two pairs of particle/hole external lines.
- Final excitation level: +2



Elements: $\widehat{H}_N$



Elements: $\widehat{T}$



CCSD $\widehat{T}_2$ amplitude equation

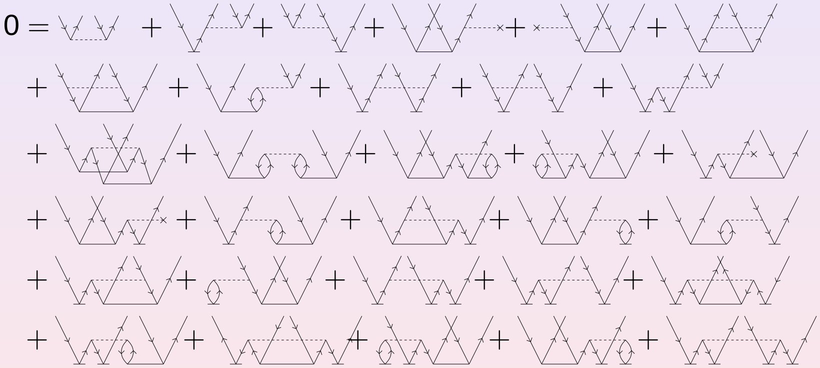


Diagram rules

- 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. ($t_{\mathrm{in}}^{\mathrm{out}}$, $t_{\mathrm{lin},\mathrm{rin}}^{\mathrm{lout},\mathrm{rout}}$)
- Calculate the phase: $(-1)^{\mathrm{holelines}+\mathrm{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.
- 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. ($f_{\mathrm{in}}^{\mathrm{out}}$, $\langle \mathrm{lout}, \mathrm{rout} || \mathrm{lin}, \mathrm{rin} \rangle$)
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- Calculate the phase: $(-1)^{\mathrm{holelines}+\mathrm{loops}}$
- 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.

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

$$E_{CC} = \langle\Psi_0|\Big(\hat{H}_N + \left[\hat{H}_N, \hat{T}\right] + \frac{1}{2}\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right] + \frac{1}{3!}\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right], \hat{T}\right] + + \Big)|\Psi_0\rangle$$

$$0 = \langle\Psi_{ij\dots}^{ab\dots}|\Big(\hat{H}_N + \left[\hat{H}_N, \hat{T}\right] + \frac{1}{2}\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right] + \frac{1}{3!}\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{H}_N, \hat{T}\right], \hat{T}\right], \hat{T}\right], \hat{T}\right] + + \Big)|\Psi_0\rangle$$

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

$$\langle \Psi_0 | \left[\hat{H}_N, \hat{T} \right] | \Psi_0 \rangle = \langle \Psi_0 | \left(\left[\hat{F}_N, \hat{T}_1 \right] + \left[\hat{F}_N, \hat{T}_2 \right] + \left[\hat{V}_N, \hat{T}_1 \right] + \left[\hat{V}_N, \hat{T}_2 \right] \right) | \Psi_0 \rangle$$

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 - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa} \delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa} \delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa} \delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa}\delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$
\begin{aligned}
\left[\hat{F}_N, \hat{T}_1\right] &= \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right) \\
&= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)
\end{aligned}
$$

$$
\begin{aligned}
\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} &= \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} &= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} \\
&\quad + \left\{ \overbracket{a_p^\dagger a_q a_a^\dagger a_i} \right\} + \left\{ a_p^\dagger \overbracket{a_q a_a^\dagger} a_i \right\} \\
&\quad + \left\{ \overbracket{a_p^\dagger \overbracket{a_q a_a^\dagger} a_i} \right\} \\
&= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa} \delta_{pi}
\end{aligned}
$$

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 - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p \left\{ a_p^\dagger a_q \right\} t_i^a \left\{ a_a^\dagger a_i \right\} - t_i^a \left\{ a_a^\dagger a_i \right\} f_q^p \left\{ a_p^\dagger a_q \right\} \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \left\{ a_a^\dagger a_i a_p^\dagger a_q \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} = \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\}$$

$$= \left\{ a_p^\dagger a_q a_a^\dagger a_i \right\} + \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa}\delta_{pi}$$

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 - $\left[\hat{F}_N, \hat{T}_2\right]$

$$
\begin{aligned}
\left[\hat{F}_N, \hat{T}_2\right] &= \left[\sum_{pq} f_q^p \left\{a_p^\dagger a_q\right\}, \frac{1}{4}\sum_{ijab} t_{ij}^{ab} \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right] \\
&= \frac{1}{4}\sum_{\substack{pq\\ijab}} \left[\left\{a_p^\dagger a_q\right\}, \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right] \\
&= \frac{1}{4}\sum_{\substack{pq\\ijab}} f_q^p t_{ij}^{ab} \left(\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} - \left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\}\right)
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$
\begin{aligned}
\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} &= \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\} \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}
\end{aligned}
$$

$$
\begin{aligned}
\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} &= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right. \\
&+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right. \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} \\
&+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} \\
&+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$
\begin{aligned}
\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} &= \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\} \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}
\end{aligned}
$$

$$
\begin{aligned}
\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} &= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} \\
&+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} \\
&+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$
\begin{aligned}
\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} &= \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\} \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}
\end{aligned}
$$

$$
\begin{aligned}
\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} &= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right. \\
&+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right. \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} \\
&+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} \\
&+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$
\begin{aligned}
\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} &= \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\} \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}
\end{aligned}
$$

$$
\begin{aligned}
\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} &= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} \\
&+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\} \\
&+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} = \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\}$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} = \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right.$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right.$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j\right.$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$

$$+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\}$$

$$+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\left\{a_p^\dagger a_q\right\} = \left\{a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\right\}$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$\left\{a_p^\dagger a_q\right\}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\} = \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right.$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j \right.$$

$$+ \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} + \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j \right.$$

$$= \left\{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i\right\} - \delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$

$$+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\}$$

$$+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

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 - $\left[\hat{F}_N, \hat{T}_2\right]$

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

$$\left[\widehat{F}_N, \widehat{T}_2\right] = \frac{1}{4}\sum_{\substack{pq\\abij}} f_q^p t_{ij}^{ab}\Big(-\delta_{pj}\left\{a_q a_a^\dagger a_b^\dagger a_i\right\} + \delta_{pi}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$

$$+ \delta_{qa}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\} - \delta_{qb}\left\{a_p^\dagger a_a^\dagger a_j a_i\right\} - \delta_{pj}\delta_{qa}\left\{a_b^\dagger a_i\right\}$$

$$+ \delta_{pi}\delta_{qa}\left\{a_b^\dagger a_j\right\} + \delta_{pj}\delta_{qb}\left\{a_a^\dagger a_i\right\} - \delta_{pi}\delta_{qb}\left\{a_a^\dagger a_j\right\}\Big).$$

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

$$\begin{aligned}\left[\widehat{F}_N, \widehat{T}_2\right] &= \frac{1}{2}\sum_{qijab} f_q^i t_{ij}^{ab}\left\{a_q a_a^\dagger a_b^\dagger a_j\right\} + \frac{1}{2}\sum_{pijab} f_a^p t_{ij}^{ab}\left\{a_p^\dagger a_b^\dagger a_j a_i\right\}\\ &\quad + \sum_{ijab} f_a^i t_{ij}^{ab}\left\{a_b^\dagger a_j\right\}\\ &= \left(\widehat{F}_N \widehat{T}_2\right)_c .\end{aligned}$$

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 - $\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a$$

$$\begin{aligned}
\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] &= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\} + \sum_{ai} f_a^i t_i^a, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right] \\
&= \left[\sum_{pai} f_a^p t_i^a \left\{a_p^\dagger a_i\right\} + \sum_{qai} f_q^i t_i^a \left\{a_q a_a^\dagger\right\}, \sum_{jb} t_j^b \left\{a_b^\dagger a_j\right\}\right] \\
&= \sum_{pabij} f_a^p t_i^a t_j^b \left[\left\{a_p^\dagger a_i\right\}, \left\{a_b^\dagger a_j\right\}\right] + \sum_{qabij} f_q^i t_i^a t_j^b \left[\left\{a_q a_a^\dagger\right\}, \left\{a_b^\dagger a_j\right\}\right]
\end{aligned}$$

$$\left\{a_b^\dagger a_j\right\}\left\{a_p^\dagger a_i\right\} = \left\{a_b^\dagger a_j a_p^\dagger a_i\right\} = \left\{a_p^\dagger a_i a_b^\dagger a_j\right\}$$

$$\left\{a_b^\dagger a_j\right\}\left\{a_q a_a^\dagger\right\} = \left\{a_b^\dagger a_j a_q a_a^\dagger\right\} = \left\{a_q a_a^\dagger a_b^\dagger a_j\right\}$$

The expansion - $\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$
\begin{aligned}
\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] &= \frac{1}{2}\left(\sum_{pabij} f_a^p t_i^a t_j^b \delta_{pj}\left\{a_i a_b^\dagger\right\} - \sum_{qabij} f_q^i t_i^a t_j^b \delta_{qb}\left\{a_a^\dagger a_j\right\}\right) \\
&= -\frac{1}{2} 2 \sum_{abij} f_b^j t_j^a t_i^b \left\{a_a^\dagger a_i\right\} \\
&= -\sum_{abij} f_b^j t_j^a t_i^b \left\{a_a^\dagger a_i\right\} \\
&= \frac{1}{2}\left(\widehat{F}_N \widehat{T}_1^2\right)_c
\end{aligned}
$$

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

$$\langle\Phi_0|\left[\hat{V}_N,\hat{T}_1\right]|\Phi_0\rangle = \langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\sum_{ia}t_i^a\left\{a_a^\dagger a_i\right\}\right]|\Phi_0\rangle$$

$$= \frac{1}{4}\sum_{\substack{pqr\\sia}}\langle pq||rs\rangle t_i^a\langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\left\{a_a^\dagger a_i\right\}\right]|\Phi_0\rangle$$

$$= 0$$

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

$$\langle\Phi_0|\left[\hat{V}_N,\hat{T}_2\right]|\Phi_0\rangle =$$

$$\langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\frac{1}{4}\sum_{ijab}t_{ij}^{ab}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$=\frac{1}{16}\sum_{\substack{pqr\\ sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$=\frac{1}{16}\sum_{\substack{pqr\\ sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\Big(\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}+\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}+\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}\Big)|\Phi_0\rangle$$

$$=\frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}$$

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

$$\langle\Phi_0|\left[\hat{V}_N,\hat{T}_2\right]|\Phi_0\rangle =$$

$$\langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\frac{1}{4}\sum_{ijab}t_{ij}^{ab}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$=\frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle$$

$$=\frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\Bigg(\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}+\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}$$

$$\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}+\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}\Bigg)|\Phi_0\rangle$$

$$=\frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}$$

The CCSD energy equation revisited

$$
\begin{aligned}
&\langle\Phi_0|\left[\hat{V}_N,\hat{T}_2\right]|\Phi_0\rangle = \\
&\quad\langle\Phi_0|\left[\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\frac{1}{4}\sum_{ijab}t_{ij}^{ab}\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle \\
&= \frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\left[\left\{a_p^\dagger a_q^\dagger a_s a_r\right\},\left\{a_a^\dagger a_b^\dagger a_j a_i\right\}\right]|\Phi_0\rangle \\
&= \frac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\Big(\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}+\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\} \\
&\quad\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}+\left\{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i\right\}\Big)|\Phi_0\rangle \\
&= \frac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}
\end{aligned}
$$

The CCSD energy equation revisited

The CCSD energy get two contributions from $\left(\widehat{H}_N \widehat{T}\right)_c$

$$E_{CC} \Leftarrow \langle\Phi_0| \left[\hat{H}_N, \hat{T}\right] |\Phi_0\rangle$$
$$= \sum_{ia} f_a^i t_i^a + \frac{1}{4} \sum_{ijab} \langle ij||ab\rangle t_{ij}^{ab}$$

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

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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.

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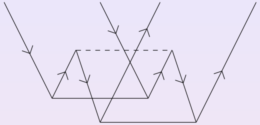
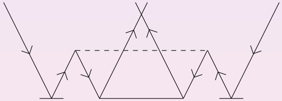
Factoring, motivation

Diagram (2.12)



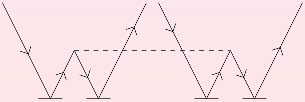
$$= \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

Diagram (2.26)



$$= \frac{1}{4}P(ij)\langle mn||ef\rangle t_{i}^{e} t_{mn}^{ab} t_{j}^{f}$$

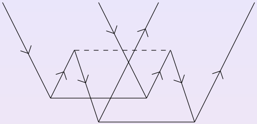
Diagram (2.31)



$$= \frac{1}{4}P(ij)P(ab)\langle mn||ef\rangle t_{i}^{e} t_{m}^{a} t_{j}^{f} t_{n}^{b}$$

Factoring, motivation

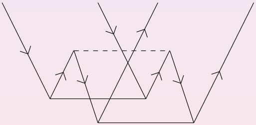
Diagram (2.12)



$$= \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

Diagram cost: $n_p^4 n_h^4$

Diagram (2.13) - Factored



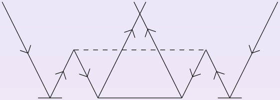
$$= \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

$$= \frac{1}{4}\left(\langle mn||ef\rangle t_{ij}^{ef}\right) t_{mn}^{ab}$$

$$= \frac{1}{4}X_{ij}^{mn} t_{mn}^{ab}$$

Factoring, motivation

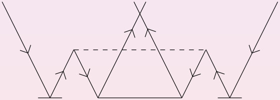
Diagram (2.26)



$$= \frac{1}{4} P(ij) \langle mn || ef \rangle t_i^e t_{mn}^{ab} t_j^f$$

Diagram cost: $n_p^4 n_h^4$

Diagram (2.26) - Factored



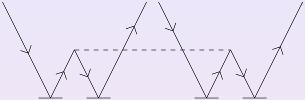
$$= \frac{1}{4} P(ij) \langle mn || ef \rangle t_i^e t_{mn}^{ab} t_j^f$$

$$= \frac{1}{4} P(ij) t_{mn}^{ab} t_i^e X_{ej}^{mn}$$

$$= \frac{1}{4} P(ij) t_{mn}^{ab} Y_{ij}^{mn}$$

Factoring, motivation

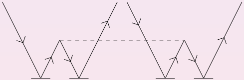
Diagram (2.31)



$$= \frac{1}{4} P(ij)P(ab)\langle mn||ef\rangle t_i^e t_m^a t_j^f t_n^b$$

Diagram cost: $n_p^4 n_h^4$

Diagram (2.31) - Factored



$$= \frac{1}{4} P(ij)P(ab)\langle mn||ef\rangle t_i^e t_m^a t_j^f t_n^b$$

$$= \frac{1}{4} P(ij)P(ab) t_m^a t_n^b t_i^e X_{ej}^{mn}$$

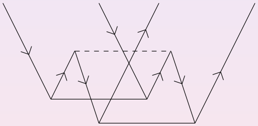
$$= \frac{1}{4} P(ij)P(ab) t_m^a t_n^b Y_{ij}^{mn}$$

$$= \frac{1}{4} P(ij)P(ab) t_m^a Z_{ij}^{mb}$$

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

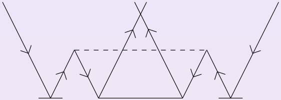


$$= \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

This diagram is classified as $T_2(p^2) \times T_2(h^2)$

Factoring, Classification

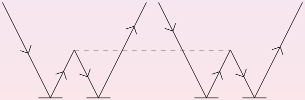
Diagram (2.26)



$$= \frac{1}{4}P(ij)\langle mn||ef\rangle t_i^e t_{mn}^{ab} t_j^f$$

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 $T_2(h)$

$$
\begin{aligned}
T_2(h) \Leftarrow & -P(ij) f_i^m t_{mj}^{ab} - \frac{1}{2} P(ij) \langle mn||ef\rangle t_{mi}^{ef} t_{nj}^{ab} - P(ij) f_e^m t_i^e t_{mj}^{ab} \\
& - P(ij) \langle mn||ei\rangle t_m^e t_{nj}^{ab} - P(ij) \langle mn||ef\rangle t_m^e t_i^f t_{nj}^{ab} \\
= & -P(ij) t_{im}^{ab} \left[f_j^m + \langle mn||je\rangle t_n^e + \frac{1}{2} \langle mn||ef\rangle t_{jn}^{ef} \right. \\
& \left. + t_j^e \left(f_e^m + \langle mn||ef\rangle t_n^f \right) \right] \\
= & -P(ij) t_{im}^{ab} (\overline{\mathrm{H}}3)_j^m
\end{aligned}
$$

Factoring, $T_2(h^2)$

Contribution to the $\hat{T}_2$ amplitude equation from $T_2(h^2)$

$$
\begin{aligned}
T_2(h^2) \Leftarrow\ & \frac{1}{2}\langle mn||ij\rangle t_{mn}^{ab} + \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab} + \frac{1}{2}P(ij)\langle mn||ej\rangle t_i^e t_{mn}^{ab} \\
& + \frac{1}{4}P(ij)\langle mn||ef\rangle t_i^e t_{mn}^{ab} t_j^f \\
=\ & \frac{1}{2} t_{mn}^{ab}\Big[\langle mn||ij\rangle + \frac{1}{2}\langle mn||ef\rangle t_{ij}^{ef} \\
& + P(ij) t_j^e \Big(\langle mn||ie\rangle + \frac{1}{2}\langle mn||fe\rangle t_i^f\Big)\Big] \\
=\ & \frac{1}{2} t_{mn}^{ab} (\overline{\mathrm{H}}9)_{ij}^{mn}
\end{aligned}
$$

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

$$0 = f_i^a + \langle ma||ei\rangle t_m^e + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + t_i^e(\mathrm{I2a})_e^a - t_m^a(\bar{\mathrm{H}}3)_i^m$$
$$+ \frac{1}{2}t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m$$
$$= f_i^a + \langle ma||ei\rangle t_m^e + t_i^a(\mathrm{I2a})_a^a + (1-\delta_{ea})t_i^e(\mathrm{I2a})_e^a$$
$$- t_i^a(\bar{\mathrm{H}}3)_i^i - (1-\delta_{mi})t_m^a(\bar{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + \frac{1}{2}t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn}$$
$$+ t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m$$
$$= f_i^a + t_i^a\left((\mathrm{I2a})_a^a - (\bar{\mathrm{H}}3)_i^i\right) + \langle ma||ei\rangle t_m^e$$
$$+ (1-\delta_{ea})t_i^e(\mathrm{I2a})_e^a - (1-\delta_{mi})t_m^a(\bar{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef}$$
$$+ \frac{1}{2}t_{mn}^{ea}(\bar{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae}(\bar{\mathrm{H}}1)_e^m$$

Factored T_1 amplitude equations

$$
\begin{aligned}
0 &= f_i^a + \langle ma||ei\rangle t_m^e + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + t_i^e (\mathrm{I2a})_e^a - t_m^a (\overline{\mathrm{H}}3)_i^m \\
&\quad + \frac{1}{2} t_{mn}^{ea} (\overline{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae} (\overline{\mathrm{H}}1)_e^m \\
&= f_i^a + \langle ma||ei\rangle t_m^e + t_i^a (\mathrm{I2a})_a^a + (1-\delta_{ea}) t_i^e (\mathrm{I2a})_e^a \\
&\quad - t_i^a (\overline{\mathrm{H}}3)_i^i - (1-\delta_{mi}) t_m^a (\overline{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + \frac{1}{2} t_{mn}^{ea} (\overline{\mathrm{H}}7)_{ie}^{mn} \\
&\quad + t_{im}^{ae} (\overline{\mathrm{H}}1)_e^m \\
&= f_i^a + t_i^a \left((\mathrm{I2a})_a^a - (\overline{\mathrm{H}}3)_i^i \right) + \langle ma||ei\rangle t_m^e \\
&\quad + (1-\delta_{ea}) t_i^e (\mathrm{I2a})_e^a - (1-\delta_{mi}) t_m^a (\overline{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\
&\quad + \frac{1}{2} t_{mn}^{ea} (\overline{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae} (\overline{\mathrm{H}}1)_e^m
\end{aligned}
$$

Factored T_1 amplitude equations

$$
\begin{aligned}
0 &= f_i^a + \langle ma||ei\rangle t_m^e + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + t_i^e (\mathrm{I2a})_e^a - t_m^a (\overline{\mathrm{H}}3)_i^m \\
&\quad + \frac{1}{2} t_{mn}^{ea} (\overline{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae} (\overline{\mathrm{H}}1)_e^m \\
&= f_i^a + \langle ma||ei\rangle t_m^e + t_i^a (\mathrm{I2a})_a^a + (1-\delta_{ea}) t_i^e (\mathrm{I2a})_e^a \\
&\quad - t_i^a (\overline{\mathrm{H}}3)_i^i - (1-\delta_{mi}) t_m^a (\overline{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} + \frac{1}{2} t_{mn}^{ea} (\overline{\mathrm{H}}7)_{ie}^{mn} \\
&\quad + t_{im}^{ae} (\overline{\mathrm{H}}1)_e^m \\
&= f_i^a + t_i^a \left((\mathrm{I2a})_a^a - (\overline{\mathrm{H}}3)_i^i \right) + \langle ma||ei\rangle t_m^e \\
&\quad + (1-\delta_{ea}) t_i^e (\mathrm{I2a})_e^a - (1-\delta_{mi}) t_m^a (\overline{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\
&\quad + \frac{1}{2} t_{mn}^{ea} (\overline{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae} (\overline{\mathrm{H}}1)_e^m
\end{aligned}
$$

Factored T_1 amplitude equations

Define

$$D_i^a = (\overline{\mathrm{H}}3)_i^i - (\mathrm{I2a})_a^a,$$

and we get the T_1 amplitude equations

$$\begin{aligned} D_i^a t_i^a = f_i^a + \langle ma||ei\rangle t_m^e + (1-\delta_{ea}) t_i^e (\mathrm{I2a})_e^a \\ - (1-\delta_{mi}) t_m^a (\overline{\mathrm{H}}3)_i^m + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\ + \frac{1}{2} t_{mn}^{ea} (\overline{\mathrm{H}}7)_{ie}^{mn} + t_{im}^{ae} (\overline{\mathrm{H}}1)_e^m . \end{aligned}$$

Factored T_2 amplitude equations

$$
\begin{aligned}
0 = \langle ab||ij\rangle &+ \frac{1}{2}\langle ab||ef\rangle t_{ij}^{ef} - P(ij)t_{im}^{ab}(\overline{\mathrm{H}}3)_j^m + \frac{1}{2}t_{mn}^{ab}(\overline{\mathrm{H}}9)_{ij}^{mn} \\
&+ P(ab)t_{ij}^{ae}(\overline{\mathrm{H}}2)_e^b + P(ij)P(ab)t_{im}^{ae}(\mathrm{I10c})_{ej}^{mb} - P(ab)t_m^a(\mathrm{I12a})_{ij}^{mb} \\
&+ P(ij)t_i^e(\mathrm{I11}a)_{ej}^{ab}
\end{aligned}
$$

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

$$D_{ij}^{ab} = (\overline{\mathrm{H}}3)_i^i + (\overline{\mathrm{H}}3)_j^j - (\overline{\mathrm{H}}2)_a^a - (\overline{\mathrm{H}}2)_b^b$$

and get the T_2 amplitude equations

$$\begin{aligned} D_{ij}^{ab} t_{ij}^{ab} = \langle ab||ij\rangle &+ \frac{1}{2}\langle ab||ef\rangle t_{ij}^{ef} - P(ij)(1-\delta_{jm}) t_{im}^{ab} (\overline{\mathrm{H}}3)_j^m \\ &+ \frac{1}{2} t_{mn}^{ab} (\overline{\mathrm{H}}9)_{ij}^{mn} + P(ab)(1-\delta_{be}) t_{ij}^{ae} (\overline{\mathrm{H}}2)_e^b \\ &+ P(ij)P(ab) t_{im}^{ae} (\mathrm{I10c})_{ej}^{mb} - P(ab) t_m^a (\mathrm{I12a})_{ij}^{mb} \\ &+ P(ij) t_i^e (\mathrm{I11}a)_{ej}^{ab} \end{aligned}$$

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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Coupled Cluster algorithm

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$t_i^a \leftarrow 0;\ t_{ij}^{ab} \leftarrow 0$
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while not converged ($E - E_{old} > \epsilon$)
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  $t_{ij}^{ab} \leftarrow$ calculated value
  $E_{old} \leftarrow E$
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Coupled Cluster algorithm

Setup modelspace
Calculate f and v amplitudes
$t_i^a \leftarrow 0$; $t_{ij}^{ab} \leftarrow 0$
$E \leftarrow 1$; $E_{old} \leftarrow 0$
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Coupled Cluster algorithm

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end while
$E_{GS} \leftarrow E_{ref} + E$

Coupled Cluster algorithm

Typical convergence of the T_2 amplitudes

Topics for Week 48

Density Functional Theory

- Monday:
- Repetion from last week
- Basics of Density functional theory
- Tuesday:
- Density functional theory
- Wednesday:
- Summary of course, syllabus and discussion of exam.

DFT: Selected literature

- R. van Leeuwen: *Density functional approach to the many-body problem: key concepts and exact functionals*, Adv. Quant. Chem. **43**, 25 (2003). (Mathematical foundations of DFT)
- R. M. Dreizler and E. K. U. Gross: *Density functional theory: An approach to the quantum many-body problem*. (Introductory book)
- W. Koch and M. C. Holthausen: *A chemist's guide to density functional theory*. (Introductory book, less formal than Dreizler/Gross)
- E. H. Lieb: Density functionals for Coulomb systems, Int. J. Quant. Chem. **24**, 243-277 (1983). (Mathematical analysis of DFT)

Density Functional Theory (DFT)

Hohenberg and Kohn proved that the total energy of a system including that of the many-body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum defines the ground state energy.

In Hartree-Fock theory one works with large basis sets. This poses a problem for large systems. An alternative to the HF methods is DFT. DFT takes into account electron correlations but is less demanding computationally than full scale diagonalization or Monte Carlo methods.

Density Functional Theory

The electronic energy E is said to be a *functional* of the electronic density, $E[\rho]$, in the sense that for a given function $\rho(r)$, there is a single corresponding energy. The *Hohenberg-Kohn theorem* confirms that such a functional exists, but does not tell us the form of the functional. As shown by Kohn and Sham, the exact ground-state energy E of an N-electron system can be written as

$$E[\rho] = -\frac{1}{2}\sum_{i=1}^{N}\int \Psi_i^*(\mathbf{r_1})\nabla_1^2\Psi_i(\mathbf{r_1})d\mathbf{r_1} - \int \frac{Z}{r_1}\rho(\mathbf{r_1})d\mathbf{r_1} + \frac{1}{2}\int \frac{\rho(\mathbf{r_1})\rho(\mathbf{r_2})}{r_{12}}d\mathbf{r_1}d\mathbf{r_2} + E_{EXC}[\rho]$$

with Ψ_i the *Kohn-Sham* (KS) *orbitals*.

Density Functional Theory

The ground-state charge density is given by

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\Psi_i(\mathbf{r})|^2,$$

where the sum is over the occupied Kohn-Sham orbitals. The last term, $E_{EXC}[\rho]$, is the *exchange-correlation energy* which in theory takes into account all non-classical electron-electron interaction. However, we do not know how to obtain this term exactly, and are forced to approximate it. The KS orbitals are found by solving the *Kohn-Sham equations*, which can be found by applying a variational principle to the electronic energy $E[\rho]$. This approach is similar to the one used for obtaining the HF equation.

Density Functional Theory

The KS equations reads

$$\left\{-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + \int \frac{\rho(\mathbf{r_2})}{r_{12}} d\mathbf{r_2} + V_{EXC}(\mathbf{r_1})\right\} \Psi_i(\mathbf{r_1}) = \epsilon_i \Psi_i(\mathbf{r_1})$$

where ϵ_i are the KS orbital energies, and where the *exchange-correlation potential* is given by

$$V_{EXC}[\rho] = \frac{\delta E_{EXC}[\rho]}{\delta \rho}.$$

Density Functional Theory

The KS equations are solved in a self-consistent fashion. A variety of basis set functions can be used, and the experience gained in HF calculations are often useful. The computational time needed for a DFT calculation formally scales as the third power of the number of basis functions.

The main source of error in DFT usually arises from the approximate nature of E_{EXC}. In the *local density approximation* (LDA) it is approximated as

$$E_{EXC} = \int \rho(\mathbf{r})\epsilon_{EXC}[\rho(\mathbf{r})]d\mathbf{r},$$

where $\epsilon_{EXC}[\rho(\mathbf{r})]$ is the exchange-correlation energy per electron in a homogeneous electron gas of constant density. The LDA approach is clearly an approximation as the charge is not continuously distributed.