Slides from FYS-KJM4480 Lectures

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Topics for Week 34, August 17-21

Introduction, systems of identical particles and physical systems

- Monday:
- Presentation of topics to be covered and introduction to Many-Body physics (Lecture notes, Raimes chapter 1 and Gross, Runge and Heinonen (GRH) chapter 1).
- Tuesday:
- Discussion of wave functions for fermions and bosons, Lecture notes and GRH chapters 2 and 3. Raimes chapter 1.
- No exercises this week.

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. Green's function methods
5. Density functional theory/Mean-field theory and Hartree-Fock theory
6. Monte-Carlo methods (FYS4410)
7. Renormalization group (RG) methods, in particular density matrix RG

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

17 August - 30 November

Projects, deadlines and oral exam

1. Deadline project 1: September 25 (12pm)
2. Deadline project 2: October 30 (12pm)
3. Deadline project 3: November 27 (12pm)

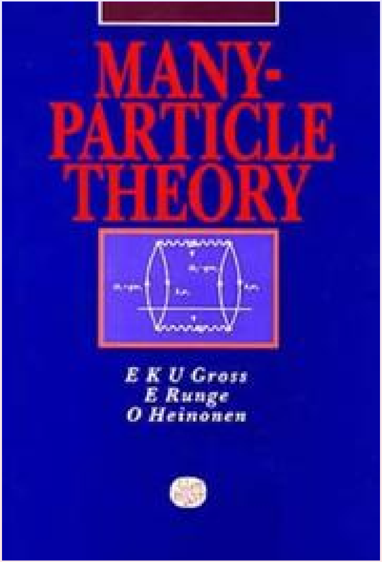
There is no exam. The projects are marked with points from 0 to 100 and the final mark is the average of all three projects.

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. Gross, Runge and Heinonen chapters 1-10 and 14-27. Raimes is also a good alternative, chapter 1-3, and 5-11 form large fractions of the syllabus.

Gross, Runge and Heinonen's text



Many-particle theory

- Chapters which cover large fraction of the syllabus:
- Chapters 1-10 and 14-27
- See also Raimes, chapters 1-3 and 5-11.

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 and notations

The Schrödinger equation reads

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)\Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_\lambda \Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (1)$$

where the vector $\mathbf{r}_i$ 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

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

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

$$\hat{V} = \sum_{i=1}^{N} u(\mathbf{r}_i) + \sum_{ji=1}^{N} v(\mathbf{r}_i, \mathbf{r}_j) + \sum_{ijk=1}^{N} v(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \quad (2)$$

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

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

with $k = 1.44$ eVnm

Definitions and notations

We can rewrite this as

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{n_e} \hat{h}_0(r_i) + \sum_{i<j=1}^{n_e} \frac{1}{r_{ij}}, \tag{3}$$

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

$$\hat{h}_0(r_i) = \hat{t}(\mathbf{r}_i) - \frac{Z}{r_i}. \tag{4}$$

The first term of eq. (3), H_0, is the sum of the N *one-body* Hamiltonians $\hat{h}_0$. Each individual Hamiltonian $\hat{h}_0$ contains the kinetic energy operator of an electron and its potential energy due to the attraction of the nucleus. The second term, H_I, is the sum of the $n_e(n_e - 1)/2$ two-body interactions between each pair of electrons. Note that the double sum carries a restriction $i < j$.

Definitions and notations

The potential energy term due to the attraction of the nucleus defines the onebody field $u_i = u_{\rm ext}(\mathbf{r}_i)$ of Eq. (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). 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

$$\hat{H} = \hat{H}_0 + \hat{H}_I = \sum_{i=1}^{N} \hat{h}_0(r_i) + \sum_{i<j=1}^{N} V(r_{ij}), \tag{5}$$

with

$$H_0 = \sum_{i=1}^{N} \hat{h}_0(r_i) = \sum_{i=1}^{N} \left(\hat{t}(\mathbf{r}_i) + \hat{u}_{\mathrm{ext}}(\mathbf{r}_i) \right). \tag{6}$$

The onebody part $u_{\mathrm{ext}}(\mathbf{r}_i)$ 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 $\Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is an eigenfunction of $\hat{P}$ as well, that is

$$\hat{P}_{ij}\Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = \beta\Psi_\lambda(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N),$$

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

$$\Phi(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N,\alpha,\beta,\dots,\sigma)=\frac{1}{\sqrt{N!}}\left|\begin{array}{ccccc} \psi_{\alpha}(\mathbf{r}_1) & \psi_{\alpha}(\mathbf{r}_2) & \dots & \dots & \psi_{\alpha}(\mathbf{r}_N)\\ \psi_{\beta}(\mathbf{r}_1) & \psi_{\beta}(\mathbf{r}_2) & \dots & \dots & \psi_{\beta}(\mathbf{r}_N)\\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_{\sigma}(\mathbf{r}_1) & \psi_{\sigma}(\mathbf{r}_2) & \dots & \dots & \psi_{\gamma}(\mathbf{r}_N)\end{array}\right|, \quad (7)$$

where $\mathbf{r}_i$ 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 $\psi_\alpha(\mathbf{r}_i)$ are eigenfunctions of the onebody Hamiltonian h_i, that is

$$\hat{h}_0(r_i) = \hat{t}(\mathbf{r}_i) + \hat{u}_{\mathrm{ext}}(\mathbf{r}_i),$$

with eigenvalues

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

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 $d\tau = d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$.

Definitions and notations

In the Hartree-Fock method the trial function is the Slater determinant of Eq. (7) which can be rewritten as

$$\Phi(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N,\alpha,\beta,\dots,\nu) = \frac{1}{\sqrt{N!}}\sum_{P}(-)^P\hat{P}\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2)\dots\psi_\nu(\mathbf{r}_N) = \sqrt{N!}\mathcal{A}\Phi_H, \tag{8}$$

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

Definitions and notations

It is defined as

$$\mathcal{A} = \frac{1}{N!}\sum_{p}(-)^p\hat{P}, \tag{9}$$

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

$$\Phi_H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \alpha, \beta, \dots, \nu) = \psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2)\dots\psi_\nu(\mathbf{r}_N).$$

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 $\mathcal{A}$

$$[H_0, \mathcal{A}] = [H_I, \mathcal{A}] = 0. \tag{10}$$

Furthermore, $\mathcal{A}$ satisfies

$$\mathcal{A}^2 = \mathcal{A}, \tag{11}$$

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. (10) and (11). The next step is to replace the antisymmetrization operator by its definition Eq. (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

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^{N} \int \psi_\mu^*(\mathbf{r}) \hat{h}_0 \psi_\mu(\mathbf{r}) d\mathbf{r}. \qquad (12)$$

Definitions and notations

We introduce the following shorthand for the above integral

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

and rewrite Eq. (12) as

$$\int \Phi^{*} \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^{N} \langle \mu | h | \mu \rangle. \tag{13}$$

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 nucleon i and nucleon j. Again we use the assumption that the single-particle wave functions are orthogonal.

We obtain

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \psi_\mu^*(\mathbf{r}_i)\psi_\nu^*(\mathbf{r}_j)V(r_{ij})\psi_\mu(\mathbf{r}_i)\psi_\nu(\mathbf{r}_j)d\mathbf{r}_i\mathbf{r}_j \right. \\ \left. - \int \psi_\mu^*(\mathbf{r}_i)\psi_\nu^*(\mathbf{r}_j)V(r_{ij})\psi_\nu(\mathbf{r}_i)\psi_\mu(\mathbf{r}_j)d\mathbf{r}_i\mathbf{r}_j\right]. \tag{14}$$

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

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

Definitions and notations

We introduce the following shorthands for the above two integrals

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

and

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

Definitions and notations

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

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

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

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

Definitions and notations

The antisymmetric matrix element is also hermitian, implying

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

With these notations we rewrite Eq. (14) as

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\langle \mu\nu|V|\mu\nu\rangle_{AS}. \quad (15)$$

Definitions and notations

Combining Eqs. (13) and (96) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^{N} \langle \mu | h | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \langle \mu\nu | V | \mu\nu \rangle_{AS}. \tag{16}$$

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

Topics for Week 35, August 24-28

Second quantization

- Monday:
- Summary from last week
- Expectation values of a given Hamiltonian for a Slater determinant
- Introduction of second quantization
- Tuesday:
- Operators and wave functions in second quantization
- Exercise 1 and 2 on Wednesday

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 $a_\alpha^\dagger$

$$a_\alpha^\dagger|0\rangle \equiv |\alpha\rangle, \quad (17)$$

and

$$a_\alpha^\dagger|\alpha_1\dots\alpha_n\rangle_{a}s \equiv |\alpha\alpha_1\dots\alpha_n\rangle_{as} \quad (18)$$

In Eq. (17) the operator $a_\alpha^\dagger$ acts on the vacuum state $|0\rangle$, which does not contain any particles. Alternatively, we could define a closed-shell nucleus as our new vacuum,but then we need to introduce the particle-hole formalism, see next section.
In Eq. (18) $a_\alpha^\dagger$ acts on an antisymmetric *n*-particle state and creates an antisymmetric $(n+1)$-particle state, where the one-body state φ_α is occupied, under the condition that $\alpha \neq \alpha_1, \alpha_2, \dots, \alpha_n$. From Eq. (**??**) it follows that we can express an antisymmetric state as the product of the creation operators acting on the vacuum state.

$$|\alpha_1 \dots \alpha_n\rangle_{AS} = a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger \dots a_{\alpha_n}^\dagger |0\rangle \tag{19}$$

It is easy to derive the commutation and anticommutation rules for the fermionic creation operators $a_\alpha^\dagger$. Using the antisymmetry of the states (19)

$$|\alpha_1 \dots \alpha_i \dots \alpha_k \dots \alpha_n\rangle_{as} = -|\alpha_1 \dots \alpha_k \dots \alpha_i \dots \alpha_n\rangle_{as} \tag{20}$$

we obtain

$$a_{\alpha_i}^\dagger a_{\alpha_k}^\dagger = -a_{\alpha_k}^\dagger a_{\alpha_i}^\dagger \tag{21}$$

Using the Pauli principle

$$|\alpha_1 \dots \alpha_i \dots \alpha_i \dots \alpha_n\rangle_{as} = 0 \tag{22}$$

it follows that

$$a^\dagger_{\alpha_i} a^\dagger_{\alpha_i} = 0. \tag{23}$$

If we combine Eqs. (21) and (23), we obtain the well-known anti-commutation rule

$$a^\dagger_\alpha a^\dagger_\beta + a^\dagger_\beta a^\dagger_\alpha \equiv \{a^\dagger_\alpha, a^\dagger_\beta\} = 0 \tag{24}$$

Second quantization

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

$$a_\alpha = (a_\alpha^\dagger)^\dagger \tag{25}$$

If we take the hermitian conjugate of Eq. (24), we arrive at

$$\{a_\alpha, a_\beta\} = 0 \tag{26}$$

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

$$\langle\alpha_1\alpha_2\dots\alpha_n|a_\alpha|\alpha'_1\alpha'_2\dots\alpha'_m\rangle \tag{27}$$

where both sides are antisymmetric. We distinguish between two cases

1. $\alpha \in \{\alpha_i\}$. Using the Pauli principle of Eq. (22) it follows

$$\langle\alpha_1\alpha_2\dots\alpha_n|a_\alpha = 0 \tag{28}$$

2. $\alpha \notin \{\alpha_i\}$. From Eq. (**??**) it follows ia hermitian conjugation

$$\langle\alpha_1\alpha_2\dots\alpha_n|a_\alpha = \langle\alpha\alpha_1\alpha_2\dots\alpha_n| \tag{29}$$

Second quantization

Eq. (29) holds for case (1) since the lefthand side is zero due to the Pauli principle. We write Eq. (27) as

$$\langle \alpha_1\alpha_2 \dots \alpha_n | a_\alpha | \alpha'_1\alpha'_2 \dots \alpha'_m \rangle = \langle \alpha_1\alpha_2 \dots \alpha_n | \alpha\alpha'_1\alpha'_2 \dots \alpha'_m \rangle \tag{30}$$

Here we must have $m = n + 1$ if Eq. (30) has to be trivially different from zero. Using Eqs. (28) and (28) we arrive at

$$\langle \alpha_1\alpha_2 \dots \alpha_n | a_\alpha | \alpha'_1\alpha'_2 \dots \alpha'_{n+1} \rangle = \left\{ \begin{array}{ll} 0 & \alpha \in \{\alpha_i\} \vee \{\alpha\alpha_i\} \neq \{\alpha'_i\} \\ \pm 1 & \alpha \notin \{\alpha_i\} \cup \{\alpha\alpha_i\} = \{\alpha'_i\} \end{array} \right\} \tag{31}$$

Second quantization

For the last case, the minus and plus signs apply when the sequence $\alpha, \alpha_1, \alpha_2, \dots, \alpha_n$ and $\alpha'_1, \alpha'_2, \dots, \alpha'_{n+1}$ are related to each other via even and odd permutations. If we assume that $\alpha \notin \{\alpha_i\}$ we have from Eq. (31)

$$\langle \alpha_1 \alpha_2 \dots \alpha_n | a_\alpha | \alpha'_1 \alpha'_2 \dots \alpha'_{n+1} \rangle = 0 \tag{32}$$

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

$$a_\alpha \underbrace{|\alpha'_1 \alpha'_2 \dots \alpha'_{n+1}\rangle}_{\neq \alpha} = 0 \tag{33}$$

and in particular

$$a_\alpha |0\rangle = 0 \tag{34}$$

Second quantization

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

$$\langle \alpha_1 \alpha_2 \dots \alpha_n | a_\alpha | \alpha \alpha_1 \alpha_2 \dots \alpha_n \rangle = 1 \tag{35}$$

and thus

$$a_\alpha | \alpha \alpha_1 \alpha_2 \dots \alpha_n \rangle = | \alpha_1 \alpha_2 \dots \alpha_n \rangle \tag{36}$$

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

$$
\begin{aligned}
a_\alpha^\dagger a_\alpha \underbrace{|\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} &= 0 \\
a_\alpha a_\alpha^\dagger \underbrace{|\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} &= a_\alpha \underbrace{|\alpha\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha} = \underbrace{|\alpha_1\alpha_2\dots\alpha_n\rangle}_{\neq\alpha}
\end{aligned}
\tag{37}
$$

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

Second quantization

If it is present we arrive at

$$\begin{aligned} a_\alpha^\dagger a_\alpha|\alpha_1\alpha_2\dots\alpha_k\alpha\alpha_{k+1}\dots\alpha_{n-1}\rangle &= a_\alpha^\dagger a_\alpha(-1)^k|\alpha\alpha_1\alpha_2\dots\alpha_{n-1}\rangle \\ =(-1)^k|\alpha\alpha_1\alpha_2\dots\alpha_{n-1}\rangle &= |\alpha_1\alpha_2\dots\alpha_k\alpha\alpha_{k+1}\dots\alpha_{n-1}\rangle \\ a_\alpha a_\alpha^\dagger|\alpha_1\alpha_2\dots\alpha_k\alpha\alpha_{k+1}\dots\alpha_{n-1}\rangle &= 0 \end{aligned} \quad (38)$$

From Eqs. (37) and (38) we arrive at

$$\{a_\alpha^\dagger, a_\alpha\} = a_\alpha^\dagger a_\alpha + a_\alpha a_\alpha^\dagger = 1 \quad (39)$$

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

$$
\begin{aligned}
a_\alpha^\dagger a_\beta |\alpha\beta\alpha_1\alpha_2\dots\alpha_{n-2}\rangle &= 0 \\
a_\beta a_\alpha^\dagger |\alpha\beta\alpha_1\alpha_2\dots\alpha_{n-2}\rangle &= 0
\end{aligned} \tag{40}
$$

while the second case gives

$$
\begin{aligned}
a_\alpha^\dagger a_\beta |\beta \underbrace{\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle &= |\alpha \underbrace{\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle \\
a_\beta a_\alpha^\dagger |\beta \underbrace{\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle &= a_\beta |\alpha\beta \underbrace{\beta\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle \\
&= -|\alpha \underbrace{\alpha_1\alpha_2\dots\alpha_{n-1}}_{\neq\alpha}\rangle
\end{aligned} \tag{41}
$$

Finally if the state vector does not contain α and β

$$\begin{aligned} a_\alpha^\dagger a_\beta|\underbrace{\alpha_1\alpha_2\dots\alpha_n}_{\neq\alpha,\beta}\rangle &= 0 \\ a_\beta a_\alpha^\dagger|\underbrace{\alpha_1\alpha_2\dots\alpha_n}_{\neq\alpha,\beta}\rangle &= a_\beta|\alpha\underbrace{\alpha_1\alpha_2\dots\alpha_n}_{\neq\alpha,\beta}\rangle = 0 \end{aligned} \quad (42)$$

For all three cases we have

$$\{a_\alpha^\dagger, a_\beta\} = a_\alpha^\dagger a_\beta + a_\beta a_\alpha^\dagger = 0, \quad \alpha \neq \beta \quad (43)$$

Second quantization

We can summarize our findings in Eqs. (39) and (43) as

$$\{a_\alpha^\dagger, a_\beta\} = \delta_{\alpha\beta} \tag{44}$$

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

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

from which follows

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

Second quantization

The hermitian conjugate has the folowing properties

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

Finally we found

$$a_\alpha \underbrace{|\alpha_1'\alpha_2' \dots \alpha_{n+1}'\rangle}_{\neq\alpha} = 0, \quad \text{spesielt } a_\alpha|0\rangle = 0,$$

and

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

and the corresponding commutator algebra

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

Topics for Week 36, August 31- September 4

Second quantization

- Monday:
- Summary from last week
- Second quantization and operators
- Anti-commutation rules
- Tuesday:
- Operators and wave functions in second quantization
- Exercise 3, 4 and 5 on Wednesday

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. (add about DFT here and reactions with connections to onebody densities and spectroscopic factors.) In eaction such (d, p) or (p, d) reactions it is important to be able to describe quantum mechanical states where particles get added or removed from. A creation operator $a_\alpha^\dagger$ adds one particle to the single-particle state α of a give many-body state vector, while an annihilation operator a_α removes a particle from a single-particle state α.

Operators in second quantization

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

$$a^\dagger_\alpha a_\alpha |\alpha_1\alpha_2\dots\alpha_n\rangle = \begin{cases} 0 & \alpha \notin \{\alpha_i\} \\ \\ |\alpha_1\alpha_2\dots\alpha_n\rangle & \alpha \in \{\alpha_i\} \end{cases} \qquad \text{(2-16)}$$

Summing over all possible one-particle states we arrive at

$$\left(\sum_\alpha a^\dagger_\alpha a_\alpha\right)|\alpha_1\alpha_2\dots\alpha_n\rangle = n|\alpha_1\alpha_2\dots\alpha_n\rangle \qquad (45)$$

Operators in second quantization

The operator

$$N = \sum_{\alpha} a_{\alpha}^{\dagger} a_{\alpha} \quad (46)$$

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

$$\hat{H}_0 = \sum_i h(\mathbf{r}_i) \tag{47}$$

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

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \alpha_1, \alpha_2, \dots, \alpha_n) = \frac{1}{\sqrt{n!}} \sum_p (-1)^p \psi_{\alpha_1}(\mathbf{r}_1)\psi_{\alpha_2}(\mathbf{r}_2) \dots \psi_{\alpha_n}(\mathbf{r}_n). \tag{48}$$

Operators in second quantization

Defining

$$h(\mathbf{r}_i)\psi_{\alpha_i}(\mathbf{r}_i) = \sum_{\alpha'_k} \psi_{\alpha'_k}(\mathbf{r}_i)\langle\alpha'_k|\hat{h}|\alpha_k\rangle \tag{49}$$

we can easily evaluate the action of $\hat{H}_0$ on each product of one-particle functions in Slater determinant. From Eqs. (48) (49) we obtain the following result without permuting any particle pair

$$\begin{aligned} & \left(\sum_i h(\mathbf{r}_i)\right) \psi_{\alpha_1}(\mathbf{r}_1)\psi_{\alpha_2}(\mathbf{r}_2)\dots\psi_{\alpha_n}(\mathbf{r}_n) \\ = & \sum_{\alpha'_1}\langle\alpha'_1|h|\alpha_1\rangle\psi_{\alpha'_1}(\mathbf{r}_1)\psi_{\alpha_2}(\mathbf{r}_2)\dots\psi_{\alpha_n}(\mathbf{r}_n) \\ + & \sum_{\alpha'_2}\langle\alpha'_2|h|\alpha_2\rangle\psi_{\alpha_1}(\mathbf{r}_1)\psi_{\alpha'_2}(\mathbf{r}_2)\dots\psi_{\alpha_n}(\mathbf{r}_n) \\ + & \dots \\ + & \sum_{\alpha'_n}\langle\alpha'_n|h|\alpha_n\rangle\psi_{\alpha_1}(\mathbf{r}_1)\psi_{\alpha_2}(\mathbf{r}_2)\dots\psi_{\alpha'_n}(\mathbf{r}_n) \end{aligned} \tag{50}$$

Operators in second quantization

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

$$
\begin{aligned}
& \left(\sum_i h(\mathbf{r}_i)\right)\psi_{\alpha_1}(\mathbf{r}_2)\psi_{\alpha_1}(\mathbf{r}_2)\dots\psi_{\alpha_n}(\mathbf{r}_n) \\
= & \sum_{\alpha_2'}\langle\alpha_2'|h|\alpha_2\rangle\psi_{\alpha_1}(\mathbf{r}_2)\psi_{\alpha_2'}(\mathbf{r}_1)\dots\psi_{\alpha_n}(\mathbf{r}_n) \\
+ & \sum_{\alpha_1'}\langle\alpha_1'|h|\alpha_1\rangle\psi_{\alpha_1'}(\mathbf{r}_2)\psi_{\alpha_2}(\mathbf{r}_1)\dots\psi_{\alpha_n}(\mathbf{r}_n) \\
+ & \dots \\
+ & \sum_{\alpha_n'}\langle\alpha_n'|h|\alpha_n\rangle\psi_{\alpha_1}(\mathbf{r}_2)\psi_{\alpha_1}(\mathbf{r}_2)\dots\psi_{\alpha_n'}(\mathbf{r}_n)
\end{aligned}
\tag{51}
$$

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 $\mathbf{r}_i$. Summing up all contributions and taking care of all phases $(-1)^p$ we arrive at

$$
\begin{aligned}
\hat{H}_0|\alpha_1,\alpha_2,\dots,\alpha_n\rangle &= \sum_{\alpha_1'}\langle\alpha_1'|h|\alpha_1\rangle|\alpha_1'\alpha_2\dots\alpha_n\rangle \\
&+ \sum_{\alpha_2'}\langle\alpha_2'|h|\alpha_2\rangle|\alpha_1\alpha_2'\dots\alpha_n\rangle \\
&+ \dots \\
&+ \sum_{\alpha_n'}\langle\alpha_n'|h|\alpha_n\rangle|\alpha_1\alpha_2\dots\alpha_n'\rangle
\end{aligned} \tag{52}
$$

Operators in second quantization

In Eq. (52) we have expressed the action of the one-body operator of Eq. (47) on the n-body state of Eq. (48) 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

$$|\alpha_1\alpha_2\dots\alpha_k'\dots\alpha_n\rangle = a_{\alpha_k'}^\dagger a_{\alpha_k}|\alpha_1\alpha_2\dots\alpha_k\dots\alpha_n\rangle \tag{53}$$

Inserting this in the right-hand side of Eq. (52) results in

$$\begin{aligned}\hat{H}_0|\alpha_1\alpha_2\dots\alpha_n\rangle &= \sum_{\alpha_1'}\langle\alpha_1'|h|\alpha_1\rangle a_{\alpha_1'}^\dagger a_{\alpha_1}|\alpha_1\alpha_2\dots\alpha_n\rangle \\ &+ \sum_{\alpha_2'}\langle\alpha_2'|h|\alpha_2\rangle a_{\alpha_2'}^\dagger a_{\alpha_2}|\alpha_1\alpha_2\dots\alpha_n\rangle \\ &+ \dots \\ &+ \sum_{\alpha_n'}\langle\alpha_n'|h|\alpha_n\rangle a_{\alpha_n'}^\dagger a_{\alpha_n}|\alpha_1\alpha_2\dots\alpha_n\rangle \\ &= \sum_{\alpha,\beta}\langle\alpha|h|\beta\rangle a_\alpha^\dagger a_\beta|\alpha_1\alpha_2\dots\alpha_n\rangle \end{aligned} \tag{54}$$

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

$$\hat{H}_0 = \sum_{\alpha\beta} \langle \alpha | h | \beta \rangle a^\dagger_\alpha a_\beta \tag{55}$$

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

$$\langle\alpha_1|\hat{H}_0|\alpha_2\rangle = \sum_{\alpha\beta}\langle\alpha|h|\beta\rangle\langle 0|a_{\alpha_1}a_{\alpha}^{\dagger}a_{\beta}a_{\alpha_2}^{\dagger}|0\rangle \tag{56}$$

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

$$a_{\alpha_1}a_{\alpha}^{\dagger}a_{\beta}a_{\alpha_2}^{\dagger} = (\delta_{\alpha\alpha_1} - a_{\alpha}^{\dagger}a_{\alpha_1})(\delta_{\beta\alpha_2} - a_{\alpha_2}^{\dagger}a_{\beta}), \tag{57}$$

which results in

$$\langle 0|a_{\alpha_1}a_{\alpha}^{\dagger}a_{\beta}a_{\alpha_2}^{\dagger}|0\rangle = \delta_{\alpha\alpha_1}\delta_{\beta\alpha_2} \tag{58}$$

and

$$\langle\alpha_1|\hat{H}_0|\alpha_2\rangle = \sum_{\alpha\beta}\langle\alpha|h|\beta\rangle\delta_{\alpha\alpha_1}\delta_{\beta\alpha_2} = \langle\alpha_1|h|\alpha_2\rangle \tag{59}$$

as expected.

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

$$\hat{H}_I = \sum_{i<j} V(\mathbf{r}_i, \mathbf{r}_j) \tag{60}$$

where the summation runs over distinct pairs. The term V can be an interaction model for the nucleon-nucleon interaction. 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

$$V(\mathbf{r}_i, \mathbf{r}_j)\psi_{\alpha_k}(\mathbf{r}_i)\psi_{\alpha_l}(\mathbf{r}_j) = \sum_{\alpha_k'\alpha_l'} \psi'_{\alpha_k}(\mathbf{r}_i)\psi'_{\alpha_l}(\mathbf{r}_j)\langle\alpha_k'\alpha_l'|V|\alpha_k\alpha_l\rangle \tag{61}$$

Operators in second quantization

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

$$
\begin{aligned}
& \left(\sum_{i<j} V(\mathbf{r}_i,\mathbf{r}_j)\right)\psi_{\alpha_1}(\mathbf{r}_1)\psi_{\alpha_2}(\mathbf{r}_2)\dots\psi_{\alpha_n}(\mathbf{r}_n) \\
= & \sum_{\alpha_1'\alpha_2'}\langle\alpha_1'\alpha_2'|V|\alpha_1\alpha_2\rangle\psi'_{\alpha_1}(\mathbf{r}_1)\psi'_{\alpha_2}(\mathbf{r}_2)\dots\psi_{\alpha_n}(\mathbf{r}_n) \\
+ & \dots \\
+ & \sum_{\alpha_1'\alpha_n'}\langle\alpha_1'\alpha_n'|V|\alpha_1\alpha_n\rangle\psi'_{\alpha_1}(\mathbf{r}_1)\psi_{\alpha_2}(\mathbf{r}_2)\dots\psi'_{\alpha_n}(\mathbf{r}_n) \\
+ & \dots \\
+ & \sum_{\alpha_2'\alpha_n'}\langle\alpha_2'\alpha_n'|V|\alpha_2\alpha_n\rangle\psi_{\alpha_1}(\mathbf{r}_1)\psi'_{\alpha_2}(\mathbf{r}_2)\dots\psi'_{\alpha_n}(\mathbf{r}_n) \\
+ & \dots
\end{aligned}
\tag{62}
$$

Operators in second quantization

Summing all possible terms we arrive at

$$\hat{H}_I = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta|V|\gamma\delta\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \quad (63)$$

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

$$\langle\alpha_1\alpha_2|\hat{H}_I|\beta_1\beta_2\rangle = \frac{1}{2}\sum_{\alpha\beta\gamma,\delta}\langle\alpha\beta|V|\gamma\delta\rangle\langle 0|a_{\alpha_2}a_{\alpha_1}a^{\dagger}_{\alpha}a^{\dagger}_{\beta}a_{\delta}a_{\gamma}a^{\dagger}_{\beta_1}a^{\dagger}_{\beta_2}|0\rangle. \quad (64)$$

Operators in second quantization

Using the commutation relations we get

$$
\begin{aligned}
& a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma a^\dagger_{\beta_1} a^\dagger_{\beta_2} \\
= \; & a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta (a_\delta \delta_{\gamma\beta_1} a^\dagger_{\beta_2} - a_\delta a^\dagger_{\beta_1} a_\gamma a^\dagger_{\beta_2}) \\
= \; & a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta (\delta_{\gamma\beta_1} \delta_{\delta\beta_2} - \delta_{\gamma\beta_1} a^\dagger_{\beta_2} a_\delta - a_\delta a^\dagger_{\beta_1} \delta_{\gamma\beta_2} + a_\delta a^\dagger_{\beta_1} a^\dagger_{\beta_2} a_\gamma) \\
= \; & a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta (\delta_{\gamma\beta_1} \delta_{\delta\beta_2} - \delta_{\gamma\beta_1} a^\dagger_{\beta_2} a_\delta \\
& \quad - \delta_{\delta\beta_1} \delta_{\gamma\beta_2} + \delta_{\gamma\beta_2} a^\dagger_{\beta_1} a_\delta + a_\delta a^\dagger_{\beta_1} a^\dagger_{\beta_2} a_\gamma)
\end{aligned}
\tag{65}
$$

Operators in second quantization

The vacuum expectation value of this product of operators becomes

$$\begin{aligned}
& \langle 0|a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma a^\dagger_{\beta_1} a^\dagger_{\beta_2}|0\rangle \\
= \quad & (\delta_{\gamma\beta_1}\delta_{\delta\beta_2} - \delta_{\delta\beta_1}\delta_{\gamma\beta_2})\langle 0|a_{\alpha_2} a_{\alpha_1} a^\dagger_\alpha a^\dagger_\beta|0\rangle \\
= \quad & (\delta_{\gamma\beta_1}\delta_{\delta\beta_2} - \delta_{\delta\beta_1}\delta_{\gamma\beta_2})(\delta_{\alpha\alpha_1}\delta_{\beta\alpha_2} - \delta_{\beta\alpha_1}\delta_{\alpha\alpha_2}) \qquad (66)
\end{aligned}$$

Insertion of Eq. (66) in Eq. (64) results in

$$\begin{aligned}
\langle \alpha_1 \alpha_2 | \hat{H}_I | \beta_1 \beta_2 \rangle &= \frac{1}{2} \left[\langle \alpha_1 \alpha_2 | V | \beta_1 \beta_2 \rangle - \langle \alpha_1 \alpha_2 | V | \beta_2 \beta_1 \rangle \right. \\
&\quad \left. - \langle \alpha_2 \alpha_1 | V | \beta_1 \beta_2 \rangle + \langle \alpha_2 \alpha_1 | V | \beta_2 \beta_1 \rangle \right] \\
&= \langle \alpha_1 \alpha_2 | V | \beta_1 \beta_2 \rangle - \langle \alpha_1 \alpha_2 | V | \beta_2 \beta_1 \rangle \\
&= \langle \alpha_1 \alpha_2 | V | \beta_1 \beta_2 \rangle_{\mathrm{AS}}. \qquad (67)
\end{aligned}$$

Operators in second quantization

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

$$
\begin{aligned}
\hat{H}_I &= \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \\
&= \frac{1}{4}\sum_{\alpha\beta\gamma\delta}\left[\langle\alpha\beta|V|\gamma\delta\rangle - \langle\alpha\beta|V|\delta\gamma\rangle\right] a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \\
&= \frac{1}{4}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS} a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \qquad (68)
\end{aligned}
$$

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 of Eq. (**??**) as

$$H = \sum_{\alpha,\beta} \langle \alpha | t + u | \beta \rangle a_\alpha^\dagger a_\beta + \frac{1}{4} \sum_{\alpha,\beta,\gamma,\delta} \langle \alpha\beta | V | \gamma\delta \rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma. \quad (69)$$

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

Topics for Week 37, September 7-11

Second quantization

- Monday:
- Summary from last week
- Particle-hole representation
- Tuesday:
- Wick's theorem and diagrammatic representation of expressions
- Exercise 6-8 on Wednesday

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. An example you will encounter here is the solution of the two-particle Schrödinger equantion in relative and center-of-mass coordinates. Or the solution of the three-body problem in so-called Jacobi coordinates.

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 $a_{\alpha_i}^\dagger$ acting on the true vacuum $|0\rangle$. Following (19) we have

$$
\begin{aligned}
|\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\rangle &= a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger \dots a_{\alpha_{n-1}}^\dagger a_{\alpha_n}^\dagger|0\rangle \qquad (70)\\
|\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\alpha_{n+1}\rangle &= a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger \dots a_{\alpha_{n-1}}^\dagger a_{\alpha_n}^\dagger a_{\alpha_{n+1}}^\dagger|0\rangle \qquad (71)\\
|\alpha_1\alpha_2\dots\alpha_{n-1}\rangle &= a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger \dots a_{\alpha_{n-1}}^\dagger|0\rangle \qquad (72)
\end{aligned}
$$

Particle-hole formalism

If we use Eq. (70) as our new reference state, we can simplify considerably the representation of this state

$$|c\rangle \equiv |\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\rangle = a^\dagger_{\alpha_1}a^\dagger_{\alpha_2}\dots a^\dagger_{\alpha_{n-1}}a^\dagger_{\alpha_n}|0\rangle \tag{73}$$

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

$$|\alpha_1\alpha_2\dots\alpha_{n-1}\alpha_n\alpha_{n+1}\rangle = (-1)^n a^\dagger_{\alpha_{n+1}}|c\rangle \equiv (-1)^n|\alpha_{n+1}\rangle_c \tag{74}$$

$$|\alpha_1\alpha_2\dots\alpha_{n-1}\rangle = (-1)^{n-1} a_{\alpha_n}|c\rangle \equiv (-1)^{n-1}|\alpha_{n-1}\rangle_c \tag{75}$$

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. (75)

$$a_\alpha |c\rangle \neq 0 \tag{76}$$

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

$$b_\alpha|c\rangle = 0 \quad (77)$$

$$\{b_\alpha^\dagger, b_\beta^\dagger\} = \{b_\alpha, b_\beta\} = 0$$

$$\{b_\alpha^\dagger, b_\beta\} = \delta_{\alpha\beta} \quad (78)$$

We assume also that the new reference state is properly normalized

$$\langle c|c\rangle = 1 \quad (79)$$

Particle-hole formalism

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

Particle-hole formalism

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

$$b_\alpha^\dagger|c\rangle = \left\{ \begin{array}{ll} a_\alpha^\dagger|c\rangle = |\alpha\rangle, & \alpha > F \\ \\ a_\alpha|c\rangle = |\alpha^{-1}\rangle, & \alpha \leq F \end{array} \right. \tag{80}$$

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

$$b_\alpha^\dagger = \left\{ \begin{array}{ll} a_\alpha^\dagger & \alpha > F \\ \\ a_\alpha & \alpha \leq F \end{array} \right. \qquad b_\alpha = \left\{ \begin{array}{ll} a_\alpha & \alpha > F \\ \\ a_\alpha^\dagger & \alpha \leq F \end{array} \right. \tag{81}$$

Particle-hole formalism

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

$$|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle \equiv \underbrace{b^\dagger_{\beta_1}b^\dagger_{\beta_2}\dots b^\dagger_{\beta_{n_p}}}_{>F}\underbrace{b^\dagger_{\gamma_1}b^\dagger_{\gamma_2}\dots b^\dagger_{\gamma_{n_h}}}_{\leq F}|c\rangle \qquad (82)$$

Particle-hole formalism

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

$$\hat{N} = \sum_{\alpha} a^{\dagger}_{\alpha} a_{\alpha} = \sum_{\alpha > F} b^{\dagger}_{\alpha} b_{\alpha} + n_c - \sum_{\alpha \leq F} b^{\dagger}_{\alpha} b_{\alpha} \tag{83}$$

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

$$N|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle = (n_p + n_c - n_h)|\beta_1\beta_2\dots\beta_{n_p}\gamma_1^{-1}\gamma_2^{-1}\dots\gamma_{n_h}^{-1}\rangle \tag{84}$$

Particle-hole formalism

Here $n = n_p + n_c - n_h$ is the total number of particles in the quasi-particle state of Eq. (82). Note that $\hat{N}$ counts the total number of particles present

$$N_{qp} = \sum_{\alpha} b_{\alpha}^{\dagger} b_{\alpha}, \tag{85}$$

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

$$N_{qp} = |\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1}\rangle = (n_p + n_h)|\beta_1 \beta_2 \dots \beta_{n_p} \gamma_1^{-1} \gamma_2^{-1} \dots \gamma_{n_h}^{-1}\rangle \tag{86}$$

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

$$
\begin{aligned}
\hat{H}_0 &= \sum_{\alpha\beta>F} \langle\alpha|h|\beta\rangle b^\dagger_\alpha b_\beta + \sum_{\substack{\alpha > F \\ \beta \leq F}} \left[\langle\alpha|h|\beta\rangle b^\dagger_\alpha b^\dagger_\beta + \langle\beta|h|\alpha\rangle b_\beta b_\alpha\right] \\
&+ \sum_{\alpha\leq F} \langle\alpha|h|\alpha\rangle - \sum_{\alpha\beta\leq F} \langle\beta|h|\alpha\rangle b^\dagger_\alpha b_\beta \qquad (87)
\end{aligned}
$$

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 $i, j, k, \ldots$ for hole states and $a, b, c, \ldots$ 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

$$\begin{aligned}\hat{H}_0 &= \sum_{ab}\langle a|h|b\rangle b_a^\dagger b_b + \sum_{ai}\left[\langle a|h|i\rangle b_a^\dagger b_i^\dagger + \langle i|h|a\rangle b_i b_a\right] \\ &+ \sum_{i}\langle i|h|i\rangle - \sum_{ij}\langle j|h|i\rangle b_i^\dagger b_j \end{aligned} \tag{88}$$

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

$$\hat{H}_I = \hat{H}_I^{(a)} + \hat{H}_I^{(b)} + \hat{H}_I^{(c)} + \hat{H}_I^{(d)} + \hat{H}_I^{(e)} \tag{89}$$

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

$$\hat{H}_I^{(a)} = \frac{1}{4}\sum_{abcd} \langle ab|V|cd\rangle b_a^\dagger b_b^\dagger b_d b_c \tag{90}$$

Particle-hole formalism

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

$$\hat{H}_I^{(b)} = \frac{1}{4}\sum_{abci}\left(\langle ab|V|ci\rangle b_a^\dagger b_b^\dagger b_i^\dagger b_c + \langle ai|V|cb\rangle b_a^\dagger b_i b_b b_c\right) \tag{91}$$

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

$$\begin{aligned}\hat{H}_I^{(c)} &= \frac{1}{4}\sum_{abij}\left(\langle ab|V|ij\rangle b_a^\dagger b_b^\dagger b_j^\dagger b_i^\dagger + \langle ij|V|ab\rangle b_a b_b b_j b_i\right) + \\ &\frac{1}{2}\sum_{abij}\langle ai|V|bj\rangle b_a^\dagger b_j^\dagger b_b b_i + \frac{1}{2}\sum_{abi}\langle ai|V|bi\rangle b_a^\dagger b_b.\end{aligned} \tag{92}$$

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

$$
\begin{aligned}
\hat{H}_I^{(d)} &= \frac{1}{4}\sum_{aijk}\left(\langle ai|V|jk\rangle b_a^\dagger b_k^\dagger b_j^\dagger b_i + \langle ji|V|ak\rangle b_k^\dagger b_j b_i b_a\right) + \\
& \frac{1}{4}\sum_{aij}\left(\langle ai|V|ji\rangle b_a^\dagger b_j^\dagger + \langle ji|V|ai\rangle - \langle ji|V|ia\rangle b_j b_a\right). \qquad (93)
\end{aligned}
$$

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

$$\hat{H}_I^{(e)} = \frac{1}{4}\sum_{ijkl}\langle kl|V|ij\rangle b_i^\dagger b_j^\dagger b_l b_k + \frac{1}{2}\sum_{ijk}\langle ij|V|kj\rangle b_k^\dagger b_i + \frac{1}{2}\sum_{ij}\langle ij|V|ij\rangle \tag{94}$$

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

Topics for Week 38, September 14-18

Second quantization

- Monday:
- Summary from last week
- Summary of Wick's theorem and diagrammatic representation of diagrams
- Tuesday:
- Hartree-Fock theory
- Exercise 9-12 on Wednesday

Topics for Week 39, September 21-25

Second quantization

- Tuesday:
- Hartree-Fock theory and project 1
- Wednesday:
- Hartree-Fock theory and project 1

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

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

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

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

The constraint appears in integral form as

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

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

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

Introducing the function f

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

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

Variational Calculus and Lagrangian Multiplier

For ψ^* the Euler equation results in

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

which yields

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

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

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

We rewrite our Hamiltonian

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

as

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{i=1}^{N} \hat{h}_i + \sum_{i<j=1}^{N} \frac{1}{r_{ij}},$$

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}.$$

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 $d\tau = d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$.

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

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

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \alpha, \beta, \ldots, \nu) = \frac{1}{\sqrt{N!}} \sum_P (-)^P P \psi_\alpha(\mathbf{r}_1) \psi_\beta(\mathbf{r}_2) \ldots \psi_\nu(\mathbf{r}_N) = \sqrt{N!} \mathcal{A} \Phi_H,$$

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)

$$\Phi_H(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, \alpha, \beta, \ldots, \nu) = \psi_\alpha(\mathbf{r}_1) \psi_\beta(\mathbf{r}_2) \ldots \psi_\nu(\mathbf{r}_N).$$

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

Both $\hat{H}_1$ and $\hat{H}_2$ are invariant under electron permutations, and hence commute with $\mathcal{A}$

$$[H_1, \mathcal{A}] = [H_2, \mathcal{A}] = 0.$$

Furthermore, $\mathcal{A}$ satisfies

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

since every permutation of the Slater determinant reproduces it.

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

The expectation value of $\hat{H}_1$

$$\int \Phi^* \hat{H}_1 \Phi d\tau = N! \int \Phi_H^* \mathcal{A} \hat{H}_1 \mathcal{A} \Phi_H d\tau$$

is readily reduced to

$$\int \Phi^* \hat{H}_1 \Phi d\tau = N! \int \Phi_H^* \hat{H}_1 \mathcal{A} \Phi_H d\tau,$$

which can be rewritten as

$$\int \Phi^* \hat{H}_1 \Phi d\tau = \sum_{i=1}^{N} \sum_{P} (-)^P \int \Phi_H^* \hat{h}_i P \Phi_H d\tau.$$

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

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

$$\int \Phi^* \hat{H}_1 \Phi d\tau = \sum_{i=1}^{N} \int \Phi_H^* \hat{h}_i \Phi_H d\tau.$$

Orthogonality 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

$$\int \Phi^* \hat{H}_1 \Phi d\tau = \sum_{\mu=1}^{N} \int \psi_\mu^*(\mathbf{r}_i) \hat{h}_i \psi_\mu(\mathbf{r}_i) d\mathbf{r}_i,$$

or just as

$$\int \Phi^* \hat{H}_1 \Phi d\tau = \sum_{\mu=1}^{N} \langle \mu | h | \mu \rangle.$$

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

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

$$\int \Phi^* \hat{H}_2 \Phi d\tau = N! \int \Phi_H^* \mathcal{A} \hat{H}_2 \mathcal{A} \Phi_H d\tau,$$

which reduces to

$$\int \Phi^* \hat{H}_2 \Phi d\tau = \sum_{i \le j=1}^{N} \sum_P (-)^P \int \Phi_H^* \frac{1}{r_{ij}} P \Phi_H d\tau,$$

by following the same arguments as for the one-body Hamiltonian. Because of the dependence on the inter-electronic distance $1/r_{ij}$, permutations of two electrons no longer vanish, and we get

$$\int \Phi^* \hat{H}_2 \Phi d\tau = \sum_{i<j=1}^{N} \int \Phi_H^* \frac{1}{r_{ij}} (1 - P_{ij}) \Phi_H d\tau.$$

where P_{ij} is the permutation operator that interchanges electrons i and j.

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

We use the assumption that the orbitals are orthogonal, and obtain

$$\int \Phi^* \hat{H}_2 \Phi d\tau = \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \psi_\mu^*(\mathbf{r}_i)\psi_\nu^*(\mathbf{r}_j)\frac{1}{r_{ij}}\psi_\mu(\mathbf{r}_i)\psi_\nu(\mathbf{r}_j)d\mathbf{r}_i\mathbf{r}_j\right.$$

$$\left.-\int \psi_\mu^*(\mathbf{r}_i)\psi_\nu^*(\mathbf{r}_j)\frac{1}{r_{ij}}\psi_\nu(\mathbf{r}_i)\psi_\mu(\mathbf{r}_i)d\mathbf{x_i}\mathbf{x_j}\right].$$

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

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

Variational Calculus and Lagrangian Multiplier, back to Hartree-Fock

Our functional is written as

$$E[\Phi] = \sum_{\mu=1}^{N} \int \psi_{\mu}^{*}(\mathbf{r}_i)\hat{h}_i\psi_{\mu}(\mathbf{r}_i)d\mathbf{r}_i + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \psi_{\mu}^{*}(\mathbf{r}_i)\psi_{\nu}^{*}(\mathbf{r}_j)\frac{1}{r_{ij}}\psi_{\mu}(\mathbf{r}_i)\psi_{\nu}(\mathbf{r}_j)d\mathbf{r}_i\mathbf{r}_j\right.$$

$$\left. - \int \psi_{\mu}^{*}(\mathbf{r}_i)\psi_{\nu}^{*}(\mathbf{r}_j)\frac{1}{r_{ij}}\psi_{\nu}(\mathbf{r}_i)\psi_{\mu}(\mathbf{r}_i)d\mathbf{r}_i\mathbf{r}_j\right]$$

The more compact version is

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

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

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

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

For the orthogonal wave functions ψ_{μ} this reduces to

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

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

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

$$\sum_{\mu=1}^{N}\int \delta\psi_\mu^* \hat{h}_i \psi_\mu d\mathbf{r}_i + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \delta\psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\psi_\mu\psi_\nu d\mathbf{r}_i d\mathbf{r}_j - \int \delta\psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\psi_\nu\psi_\mu d\mathbf{r}_i d\mathbf{r}_j\right]$$
$$+\sum_{\mu=1}^{N}\int \psi_\mu^* \hat{h}_i \delta\psi_\mu d\mathbf{r}_i + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left[\int \psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\delta\psi_\mu\psi_\nu d\mathbf{r}_i d\mathbf{r}_j - \int \psi_\mu^*\psi_\nu^*\frac{1}{r_{ij}}\psi_\nu\delta\psi_\mu d\mathbf{r}_i d\mathbf{r}_j\right]$$
$$-\sum_{\mu=1}^{N} E_\mu \int \delta\psi_\mu^*\psi_\mu d\mathbf{r}_i - \sum_{\mu=1}^{N} E_\mu \int \psi_\mu^*\delta\psi_\mu d\mathbf{r}_i = 0.$$

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

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

$$\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \sum_{\nu=1}^{N}\int \psi_\nu^*(\mathbf{r}_j)\frac{1}{r_{ij}}\psi_\nu(\mathbf{r}_j)d\mathbf{r}_j\right]\psi_\mu(\mathbf{r}_i)$$
$$-\left[\sum_{\nu=1}^{N}\int \psi_\nu^*(\mathbf{r}_j)\frac{1}{r_{ij}}\psi_\mu(\mathbf{r}_j)d\mathbf{r}_j\right]\psi_\nu(\mathbf{r}_i) = \epsilon_\mu\psi_\mu(\mathbf{r}_i).$$

Notice that the integration $\int d\mathbf{r}_j$ 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

$$V_{\mu}^{d}(\mathbf{r}_i) = \int \psi_{\mu}^{*}(\mathbf{r}_j)\frac{1}{r_{ij}}\psi_{\mu}(\mathbf{r}_j)d\mathbf{r}_j$$

and

$$V_{\mu}^{ex}(\mathbf{r}_i)g(\mathbf{r}_i) = \left(\int \psi_{\mu}^{*}(\mathbf{r}_j)\frac{1}{r_{ij}}g(\mathbf{r}_j)d\mathbf{r}_j\right)\psi_{\mu}(\mathbf{r}_i),$$

respectively.

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

The function $g(\mathbf{r}_i)$ is an arbitrary function, and by the substitution $g(\mathbf{r}_i) = \psi_\nu(\mathbf{r}_i)$ we get

$$V_\mu^{ex}(\mathbf{r}_i)\psi_\nu(\mathbf{r}_i) = \left(\int \psi_\mu^*(\mathbf{r}_j) \frac{1}{r_{ij}} \psi_\nu(\mathbf{r}_j) d\mathbf{r}_j \right) \psi_\mu(\mathbf{r}_i).$$

Hartree-Fock: Variational Calculus and Lagrangian Multiplier

We may then rewrite the Hartree-Fock equations as

$$H_i^{HF}\psi_\nu(\mathbf{r}_i) = \epsilon_\nu\psi_\nu(\mathbf{r}_i),$$

with

$$H_i^{HF} = h_i + \sum_{\mu=1}^{N} V_\mu^d(\mathbf{r}_i) - \sum_{\mu=1}^{N} V_\mu^{ex}(\mathbf{r}_i),$$

and where h_i is the one-body part

Topics for Week 40, September 28- October 2

Hartree-Fock theory

- Monday:
- Hartree-Fock theory
- Tuesday:
- Hartree-Fock theory

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)

$$\psi_a = \sum_\lambda C_{a\lambda}\psi_\lambda. \tag{95}$$

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

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

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

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

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

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

and

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

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

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

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

or in the more general case

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

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

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

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

or for a general matrix element

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

It has the symmetry property

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

The antisymmetric matrix element is also hermitian, implying

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

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

With these notations we rewrite the Hartree-Fock functional as

$$\int \Phi^* \hat{H}_1 \Phi d\tau = \frac{1}{2}\sum_{\mu=1}^{A}\sum_{\nu=1}^{A}\langle \mu\nu|V|\mu\nu\rangle_{AS}. \tag{96}$$

Combining Eqs. (13) and (96) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^{N}\langle \mu|h|\mu\rangle + \frac{1}{2}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\langle \mu\nu|V|\mu\nu\rangle_{AS}. \tag{97}$$

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

$$E[\Psi] = \sum_{a=1}^{N} \langle a|h|a\rangle + \frac{1}{2}\sum_{ab=1}^{N} \langle ab|V|ab\rangle_{AS}, \tag{98}$$

where Ψ is the new Slater determinant defined by the new basis of Eq. (95).

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

Using Eq. (95) we can rewrite Eq. (98) as

$$E[\Psi] = \sum_{a=1}^{N} \sum_{\alpha\beta} C^*_{a\alpha} C_{a\beta} \langle \alpha | h | \beta \rangle + \frac{1}{2} \sum_{ab=1}^{N} \sum_{\alpha\beta\gamma\delta} C^*_{a\alpha} C^*_{b\beta} C_{a\gamma} C_{b\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \quad (99)$$

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

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

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

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

$$E[\Psi] - \sum_{a=1}^{N} \epsilon_a \sum_{\alpha} C^*_{a\alpha} C_{a\alpha}. \qquad (100)$$

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

$$\frac{d}{dC^*_{k\alpha}}\left[E[\Psi]-\sum_a \epsilon_a \sum_\alpha C^*_{a\alpha}C_{a\alpha}\right]=0, \tag{101}$$

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

$$\sum_\gamma C_{k\gamma}\langle\alpha|h|\gamma\rangle+\sum_{a=1}^{N}\sum_{\beta\gamma\delta} C^*_{a\beta}C_{a\delta}C_{k\gamma}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}=\epsilon_k C_{k\alpha}. \tag{102}$$

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

We can rewrite this equation as

$$\sum_{\gamma}\left\{\langle\alpha|h|\gamma\rangle+\sum_{a}^{N}\sum_{\beta\delta}C_{a\beta}^{*}C_{a\delta}\langle\alpha\beta|V|\gamma\delta\rangle_{AS}\right\}C_{k\gamma}=\epsilon_{k}C_{k\alpha}. \tag{103}$$

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

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

Defining

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

we can rewrite the new equations as

$$\sum_{\gamma} h_{\alpha\gamma}^{HF}C_{k\gamma} = \epsilon_k C_{k\alpha}. \tag{104}$$

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

Topics for Week 41, October 5-9

Hartree-Fock theory

- Monday:
- Hartree-Fock theory, Thouless' theorem and stability of Hartree-Fock equations
- Tuesday:
- End Hartree-Fock theory, examples

Topics for Week 42, October 12-16

Hartree-Fock theory and many-body perturbation theory

- Monday:
- End Hartree-Fock theory and the electron gas
- Tuesday:
- Many-body perturbation theory

Topics for Week 43, October 19-23

Many-body perturbation theory

- Monday:
- Summary from previous week
- Time-independent perturbation theory
- Brillouin-Wigner and Rayleigh-Schrödinger perturbation theory
- Tuesday:
- Time-dependent perturbation theory
- Schrödinger, Heisenberg and interaction pictures

Time-independent perturbation 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

$$\left(\begin{array}{cc} \epsilon_P + zX_P & zX \\ zX & \epsilon_Q + zX_Q \end{array}\right)$$

yields

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

A Rayleigh-Schrödinger like expansion for the lowest eigenstate

$$E = \epsilon_P + zX_P + \frac{z^2X^2}{\epsilon_P - \epsilon_Q} + \frac{z^3X^2(X_Q - X_P)}{(\epsilon_P - \epsilon_Q)^2} + \frac{z^4X^2(X_Q - X_P)^2}{(\epsilon_P - \epsilon_Q)^3} - \frac{z^4X^4}{(\epsilon_P - \epsilon_Q)^3} + \dots,$$

which can be viewed as an effective interaction for state P in which state Q is taken into account to successive orders of the perturbation.

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

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

and has d exact eigenvalues of H.

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

We have the simple model

$$\left(\begin{array}{cc} \epsilon_P + zX_P & zX \\ zX & \epsilon_Q + zX_Q \end{array} \right)$$

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 $H' = e^{-T}He^{T}$ 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 $cs = \sin(2\gamma)/2$ this is equivalent with

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

Solving the equation we have

$$\gamma = \frac{1}{2}\tan^{-1}\left(\frac{2H_{12}}{H_{11} - H_{22}}\right) + \frac{k\pi}{2}, \quad k = \dots, -1, 0, 1, \dots, \tag{105}$$

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

Simple 2 $\times$ 2 Case, Jacobi Rotation first

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

$$H'_{k=0} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}, \tag{106}$$

while $k = 1$ changes the diagonal elements

$$H'_{k=1} = \begin{bmatrix} \lambda_2 & 0 \\ 0 & \lambda_1 \end{bmatrix}. \tag{107}$$

Understanding excitations, model spaces and excluded spaces

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

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

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

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

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

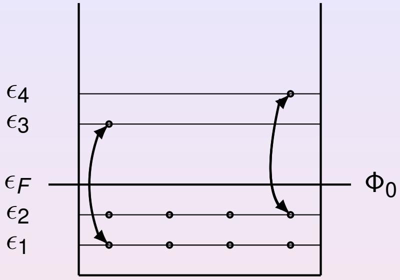
Understanding excitations, model spaces and excluded spaces

The single-particle wave functions of

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

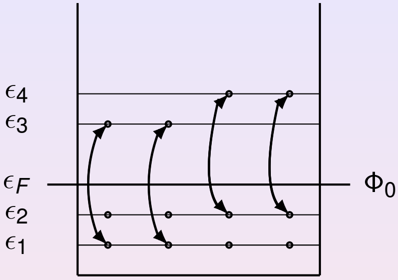
are normally chosen as the solutions of the so-called non-interacting part of the Hamiltonian, H_0. A typical basis is provided by the harmonic oscillator problem or hydrogen-like wave functions.

Excitations in Pictures



From T_1 to T_1^2

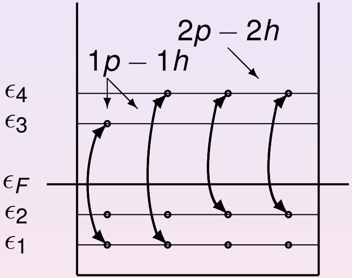
$T_1 \propto a_a^+ a_i$



From T_2 to T_2^2

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

Excitations



Truncations

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

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

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