

Quantum Mechanics of Many-Particle Systems

FYS-KJM4480/9480

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Overview of week 34

- ▶ 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.

Overview of week 35

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

Lectures, exercise sessions and syllabus

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

Quantum Many-particle Methods covered

- ▶ Large-scale diagonalization (Iterative methods, Lanczo's method, dimensionalities 10^{10} states)
- ▶ 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.
- ▶ Perturbative many-body methods
- ▶ Density functional theories/Mean-field theory and Hartree-Fock theory (covered partly also in FYS-MENA4111)
- ▶ Monte-Carlo methods (Only in FYS4411, Computational quantum mechanics)
- ▶ Green's function theories (depending on interest)
- ▶ and other. The physics of the system hints at which many-body methods to use.

Plan for the semester

Projects, deadlines (proposed) and oral exam

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

Selected Texts and Many-body theory

- ▶ Blaizot and Ripka, *Quantum Theory of Finite systems*, MIT press 1986
- ▶ Negele and Orland, *Quantum Many-Particle Systems*, Addison-Wesley, 1987.
- ▶ Fetter and Walecka, *Quantum Theory of Many-Particle Systems*, McGraw-Hill, 1971.
- ▶ Helgaker, Jorgensen 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 as 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 specified.

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

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

and the integral

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

and

$$\int \dots \int \dots \int \dots \int$$

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 \hat{H}_1 is the space of square integrable functions over $\mathbb{R}^d \oplus (\sigma)$ 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 $\Psi_{\lambda}(x_1, x_2, \dots, x_N)$ is an eigenfunction of \hat{P} as well, that is

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

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

The Schrodinger equation reads

$$\hat{H}(x_1, x_2, \dots, x_N) \Psi_{\lambda}(x_1, x_2, \dots, x_N) = E_{\lambda} \Psi_{\lambda}(x_1, x_2, \dots, x_N), \quad (1)$$

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

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

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

$$\hat{V} = \sum_{i=1}^N \hat{u}_{\text{ext}}(x_i) + \sum_{ji=1}^N v(x_i, x_j) + \sum_{ijk=1}^N v(x_i, x_j, x_k) + \dots \quad (2)$$

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

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

with $k = 1.44 \text{ eVnm}$

Definitions and notations

We can rewrite this as

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

where we have defined

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|,$$

and

$$\hat{h}_0(x_i) = \hat{t}(x_i) - \frac{Z}{x_i}. \quad (4)$$

The first term of Eq. (??), 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 $u_i = u_{\text{ext}}(x_i)$ of Eq. (??). We have moved this term into the \hat{H}_0 part of the Hamiltonian, instead of keeping it in \hat{V} as in Eq. (??). 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

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

with

$$H_0 = \sum_{i=1}^N \hat{h}_0(x_i) = \sum_{i=1}^N (\hat{t}(x_i) + \hat{u}_{\text{ext}}(x_i)). \quad (6)$$

The onebody part $u_{\text{ext}}(x_i)$ 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

$$\Phi(x_1, x_2, \dots, x_N, \alpha, \beta, \dots, \sigma) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_\alpha(x_1) & \psi_\alpha(x_2) & \dots & \dots & \psi_\alpha(x_N) \\ \psi_\beta(x_1) & \psi_\beta(x_2) & \dots & \dots & \psi_\beta(x_N) \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\sigma(x_1) & \psi_\sigma(x_2) & \dots & \dots & \psi_\sigma(x_N) \end{vmatrix} \quad (7)$$

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

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

with eigenvalues

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

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

Definitions and notations

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

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

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

Definitions and notations

It is defined as

$$\hat{A} = \frac{1}{N!} \sum_p (-)^p \hat{P}, \quad (8)$$

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

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

Definitions and notations

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

$$[H_0, \hat{A}] = [H_I, \hat{A}] = 0. \quad (9)$$

Furthermore, \hat{A} satisfies

$$\hat{A}^2 = \hat{A}, \quad (10)$$

since every permutation of the Slater determinant reproduces it.

Definitions and notations

The expectation value of \hat{H}_0

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

is readily reduced to

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

where we have used Eqs. (??) and (??). The next step is to replace the antisymmetrization operator by its definition 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

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^N \int \psi_{\mu}^*(\mathbf{r}) \hat{h}_0 \psi_{\mu}(\mathbf{r}) d\mathbf{r}. \quad (11)$$

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. (??) as

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^N \langle \mu | \hat{h}_0 | \mu \rangle. \quad (12)$$

Definitions and notations

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

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

which reduces to

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

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

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N \left[\int \psi_{\mu}^*(x_i) \psi_{\nu}^*(x_j) V(r_{ij}) \psi_{\mu}(x_i) \psi_{\nu}(x_j) dx_i dx_j \right. \\ \left. - \int \psi_{\mu}^*(x_i) \psi_{\nu}^*(x_j) V(r_{ij}) \psi_{\nu}(x_i) \psi_{\mu}(x_j) dx_i dx_j \right]. \quad (13)$$

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 $\psi_\mu(x)$, defined by the quantum numbers μ and x 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

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

and

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

Definitions and notations

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

$$\langle \mu\nu | \hat{v} | \mu\nu \rangle_{\text{AS}} = \langle \mu\nu | \hat{v} | \mu\nu \rangle - \langle \mu\nu | \hat{v} | \nu\mu \rangle,$$

or for a general matrix element

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

It has the symmetry property

$$\langle \mu\nu | \hat{v} | \sigma\tau \rangle_{\text{AS}} = -\langle \mu\nu | \hat{v} | \tau\sigma \rangle_{\text{AS}} = -\langle \nu\mu | \hat{v} | \sigma\tau \rangle_{\text{AS}}.$$

Definitions and notations

The antisymmetric matrix element is also hermitian, implying

$$\langle \mu\nu | \hat{v} | \sigma\tau \rangle_{\text{AS}} = \langle \sigma\tau | \hat{v} | \mu\nu \rangle_{\text{AS}}.$$

With these notations we rewrite Eq. (??) as

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N \langle \mu\nu | \hat{v} | \mu\nu \rangle_{\text{AS}}. \quad (14)$$

Definitions and notations

Combining Eqs. (??) and (??) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^N \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N \langle \mu\nu | \hat{v} | \mu\nu \rangle_{AS}. \quad (15)$$

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

Exercises week 35

Exercise 1

Consider the Slater determinant

$$\Phi_{\lambda}^{AS}(x_1 x_2 \dots x_N; \alpha_1 \alpha_2 \dots \alpha_N) = \frac{1}{\sqrt{N!}} \sum_p (-)^p P \prod_{i=1}^N \psi_{\alpha_i}(x_i).$$

where P is an operator which permutes the coordinates of two particles. We have assumed here that the number of particles is the same as the number of available single-particle states, represented by the greek letters $\alpha_1 \alpha_2 \dots \alpha_N$.

► Write out Φ^{AS} for $N = 3$.

► Show that

$$\int dx_1 dx_2 \dots dx_N \left| \Phi_{\lambda}^{AS}(x_1 x_2 \dots x_N; \alpha_1 \alpha_2 \dots \alpha_N) \right|^2 = 1.$$

► Define a general onebody operator $\hat{F} = \sum_i^N \hat{f}(x_i)$ and a general

twobody operator $\hat{G} = \sum_i^N \hat{g}(x_i, x_j)$ with α being invariant under

Exercises week 35

Exercise 2

We will now consider a simple three-level problem, depicted in the figure below. The single-particle states are labelled by the quantum number p and can accommodate up to two single particles, viz., every single-particle state is doubly degenerate (you could think of this as one state having spin up and the other spin down). We let the spacing between the doubly degenerate single-particle states be constant, with value d . The first state has energy d . There are only three available single-particle states, $p = 1$, $p = 2$ and $p = 3$, as illustrated in the figure.

- ▶ How many two-particle Slater determinants can we construct in this space?
- ▶ We limit ourselves to a system with only the two lowest single-particle orbits and two particles, $p = 1$ and $p = 2$.

We assume that we can write the Hamiltonian as

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

Python code for solving exercise 2

```
from numpy import *
from numpy.linalg import eig
from pylab import *
from matplotlib import rc, rcParams
import matplotlib.units as units
import matplotlib.ticker as ticker
import sys
import os
# set tickers etc
rc('text',usetex=True)
rc('font',**{'family':'serif','serif':['Energies']})
title(r'\bf Energies', fontsize=20)
```

```
def exercise2(g):
    z = ones((3,3), dtype = float)*-.5*g
    z[0,0] = 2-g
    z[1,1] = 4-g
    z[2,2] = 6-g
    n1 = range(3)
    n2 = range(3)
    n2.reverse()
    z[n2, n1] = 0
    return z
print exercise2(1)
```

```
N = 1000
```