Computational Physics: Hartree-Fock methods and introduction to Many-body Theory

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Spring 2017

Why Hartree-Fock?

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

- Define a single-particle basis $\{\psi_\alpha\}$ so that
$$\hat{h}^{\mathrm{HF}}\psi_\alpha = \varepsilon_\alpha \psi_\alpha$$

with the Hartree-Fock Hamiltonian defined as

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

- The term $\hat{u}^{\mathrm{HF}}$ is a single-particle potential to be determined by the HF algorithm.
- The HF algorithm means to choose $\hat{u}^{\mathrm{HF}}$ in order to have
$$\langle \hat{H} \rangle = E^{\mathrm{HF}} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$$

that is to find a local minimum with a Slater determinant Φ_0 being the ansatz for the ground state.

Why Hartree-Fock?

We will show that the Hartree-Fock Hamiltonian $\hat{h}^{\text{HF}}$ equals our definition of the operator $\hat{f}$ discussed in connection with the new definition of the normal-ordered Hamiltonian (see later lectures), that is we have, for a specific matrix element

$$\langle p|\hat{h}^{\text{HF}}|q\rangle = \langle p|\hat{f}|q\rangle = \langle p|\hat{t} + \hat{u}_{\text{ext}}|q\rangle + \sum_{i\leq F}\langle pi|\hat{V}|qi\rangle_{AS},$$

meaning that

$$\langle p|\hat{u}^{\text{HF}}|q\rangle = \sum_{i\leq F}\langle pi|\hat{V}|qi\rangle_{AS}.$$

The so-called Hartree-Fock potential $\hat{u}^{\text{HF}}$ brings an explicit medium dependence due to the summation over all single-particle states below the Fermi level F. It brings also in an explicit dependence on the two-body interaction (in nuclear physics we can also have complicated three- or higher-body forces). The two-body interaction, with its contribution from the other bystanding fermions, creates an effective mean field in which a given fermion

Quantum Many-particle Methods

- ▶ 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
- ▶ Monte-Carlo methods (Only in FYS4411, Computational quantum mechanics)
- ▶ Green's function theories
- ▶ and other. The physics of the system hints at which many-body methods to use.

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 isobars Δ or various hyperons such as Λ or Σ, one needs to add their definitions. Hereafter, N is reserved for the total number of particles, unless otherwise specificied.

Definitions

The quantum numbers of a single-particle state in coordinate space are defined by the variable

$$x = (\boldsymbol{r}, \sigma),$$

where

$$\boldsymbol{r} \in \mathbb{R}^d,$$

with $d = 1, 2, 3$ represents the spatial coordinates and σ is the eigenspin of the particle. For fermions with eigenspin $1/2$ this means that

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

and the integral $\int dx = \sum_\sigma \int d^d r = \sum_\sigma \int d\boldsymbol{r}$, and

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

Definitions

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

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

with $x_i = (\boldsymbol{r}_i, \sigma_i)$ 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

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

Definitions

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

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

with

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

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 $\in \mathbb{R}^d \oplus (\sigma)$ resulting in

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

Definitions

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

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

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

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

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

Definitions and notations

The Schrodinger equation reads

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

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

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

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

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

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 $k = 1.44$ eVnm

Definitions and notations

We can rewrite this as

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

where we have defined

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

and

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

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 $u_i = u_{\text{ext}}(x_i)$ 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

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

with

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

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

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

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

Definitions and notations

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

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

where x_i stand for the coordinates and spin values of a particle i and $\alpha, \beta, \ldots, \gamma$ 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

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

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

Definitions and notations

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

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

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

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

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

Brief reminder on some linear algebra properties

Before we proceed with a more compact representation of a Slater determinant, we would like to repeat some linear algebra properties which will be useful for our derivations of the energy as function of a Slater determinant, Hartree-Fock theory and later the nuclear shell model.

The inverse of a matrix is defined by

$$\mathbf{A}^{-1} \cdot \mathbf{A} = I$$

A unitary matrix $\mathbf{A}$ is one whose inverse is its adjoint

$$\mathbf{A}^{-1} = \mathbf{A}^{\dagger}$$

A real unitary matrix is called orthogonal and its inverse is equal to its transpose. A hermitian matrix is its own self-adjoint, that is

$$\mathbf{A} = \mathbf{A}^{\dagger}.$$

Basic Matrix Features

Matrix Properties Reminder

Relations	Name	matrix elements
$A = A^T$	symmetric	$a_{ij} = a_{ji}$
$A = \left(A^T\right)^{-1}$	real orthogonal	$\sum_k a_{ik} a_{jk} = \sum_k a_{ki} a_{kj} = \delta_{ij}$
$A = A^*$	real matrix	$a_{ij} = a_{ij}^*$
$A = A^\dagger$	hermitian	$a_{ij} = a_{ji}^*$
$A = \left(A^\dagger\right)^{-1}$	unitary	$\sum_k a_{ik} a_{jk}^* = \sum_k a_{ki}^* a_{kj} = \delta_{ij}$

Basic Matrix Features

Since we will deal with Fermions (identical and indistinguishable particles) we will form an ansatz for a given state in terms of so-called Slater determinants determined by a chosen basis of single-particle functions.

For a given $n \times n$ matrix $\mathbf{A}$ we can write its determinant

$$det(\mathbf{A}) = |\mathbf{A}| = \begin{vmatrix} a_{11} & a_{12} & \dots & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & \dots & a_{2n} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & \dots & \dots & a_{nn} \end{vmatrix},$$

in a more compact form as

$$|\mathbf{A}| = \sum_{i=1}^{n!} (-1)^{p_i} \hat{P}_i a_{11} a_{22} \dots a_{nn},$$

where $\hat{P}_i$ is a permutation operator which permutes the column

Basic Matrix Features, simple 2 × 2 determinant

A simple 2×2 determinant illustrates this. We have

$$det(\mathbf{A}) = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = (-1)^0 a_{11} a_{22} + (-1)^1 a_{12} a_{21},$$

where in the last term we have interchanged the column indices 1 and 2. The natural ordering we have chosen is $a_{11} a_{22}$.

Definitions and notations

With the above we can rewrite our Slater determinant in a more compact form. In the Hartree-Fock method the trial function is the Slater determinant of Eq. (7) which can be rewritten as

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

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

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

(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

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

Definitions and notations

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

$$[H_0, \hat{A}] = [H_I, \hat{A}] = 0. \tag{9}$$

Furthermore, $\hat{A}$ satisfies

$$\hat{A}^2 = \hat{A}, \tag{10}$$

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. (9) and (10). 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

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

Definitions and notations

We introduce the following shorthand for the above integral

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

and rewrite Eq. (11) as

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

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

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

(13)

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

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

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

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

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

or for a general matrix element

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

It has the symmetry property

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

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. (14) as

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \langle \mu\nu | \hat{v} | \mu\nu \rangle_{\text{AS}}. \tag{15}$$

Combining Eqs. (12) and (15) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^{N} \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \langle \mu\nu | \hat{v} | \mu\nu \rangle_{\mathrm{AS}}. \qquad (16)$$

which we will use as our starting point for the Hartree-Fock calculations.

Our system, quantum dots

We will deal only with systems where all possible single-particle states below a certain level are filled up. Such systems are called closed shell systems, a naming inspired from atomic and nuclear physics. These closed shell systems define what is frequently named **magic numbers**. Quantum dots exhibit also magic numbers, meaning that the addition or removal of one eletron requires more energy than systems where the lowest-lying shells are not filled. Using the harmonic oscillator in two dimensions as basis functions (with degenerate single-particle energies) the magic numbers are $N = 2$, $N = 6$, $N = 12$, $N = 20$ etc, where N is the number of electrons. See the table below for more details.

We write our Hamiltonian as a one-body part

$$\hat{H}_0 = \sum_{i=1}^{N_e} \left(-\frac{1}{2}\nabla_i^2 + \frac{\omega^2}{2}r_i^2 \right),$$

and an interacting part

First tasks

The first project deals with setting up a Hartree-Fock program that is flexible enough to handle different magic numbers. Hartree-Fock is the simplest possible many-body method. We will use the harmonic oscillator functions as basis functions and via the Hartree-Fock method modify the potential which confines the motion of the electrons by accounting for the Coulomb repulsion between electrons. The Hartree-Fock method leads to a set of coupled single-particle equations. If properly written, the system can easily be extended to three-dimensional electronic systems or other fermionic many-body systems.

First tasks, single-particle basis

If only the harmonic oscillator part of the Hamiltonian, the so-called unperturbed part is given by

$$\hat{H}_0 = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\omega^2 r_i^2 \right).$$

The wave function for one electron in an oscillator potential in two dimensions is

$$\phi_{n_x,n_y}(x,y) = AH_{n_x}(\sqrt{\omega}x)H_{n_y}(\sqrt{\omega}y)\exp\left(-\omega(x^2+y^2)/2\right).$$

The functions $H_{n_x}(\sqrt{\omega}x)$ are so-called Hermite polynomials, discussed in the appendix while A is a normalization constant. For the lowest-lying state we have $n_x = n_y = 0$ and an energy $\epsilon_{n_x,n_y} = \omega(n_x + n_y + 1) = \omega$.

Project 1 a): getting started

Make a program that sets up all the quantum numbers for the single-particle basis using a harmonic oscillator in two dimensions. The list should contain the quantum numbers n_x and n_y, spin and its projection and the single particle energies in atomic units. Define a cutoff in the list according to the harmonic oscillator excitation energy. The table here lists the first four harmonic oscillator shells, with its pertinent degeneracies, and the total number of electrons which can be accomodated up to a given energy. These numbers are the so-called *magic numbers* for a two-dimensional quantum dot. The degeneracies take into account the two spin values an electron can take. Convince yourself about the correctness of this table and use it to check that your code is running correctly.

Shell number	(n_x, n_y)	Energy	Degeneracy	N
1	$(0, 0)$	$\hbar\omega$	2	2
2	$(1, 0), (0, 1)$	$2\hbar\omega$	4	6
3	$(2, 0), (0, 2), (1, 1)$	$3\hbar\omega$	6	12
3	$(3, 0), (0, 3), (2, 1), (1, 2)$	$4\hbar\omega$	8	20

Project 1 b): Setting up the single-particle basis

With the single-particle basis from the previous step, you should now write a class which encodes the information about the harmonic oscillator single-particle basis. This should include the single-particle energies, spin and its projections as well as the harmonic oscillator functions that depend on n_x and n_y. This class can then used for both the Monte Carlo and the Hartree-Fock calculations.

Project 1 c): Computing the two-body matrix elements

In the Hartree-Fock project we need to be able to compute the two-electron matrix elements of the two-body Coulomb interaction. In order to set up the two-body matrix elements, we need to define the so-called direct and exchange matrix elements. This leads to what we call an anti-symmetrized matrix element.
We introduce the following shorthands for the integrals

$$\langle pq|\hat{v}|rs\rangle = \int \psi_p^*(x_i)\psi_q^*(x_j)V(r_{ij})\psi_r(x_i)\psi_s(x_j)dx_i dx_j,$$

which defines the so-called direct matrix element and

$$\langle pq|\hat{v}|sr\rangle = \int \psi_p^*(x_i)\psi_q^*(x_j)V(r_{ij})\psi_s(x_i)\psi_r(x_j)dx_i dx_j,$$

which defines the exchange element. The variables $pqrs$ define all the single-particle quantum numbers. In our case these are n_x, n_y and spin and its projections.

Two-body matrix elements

These matrix elements are defined in terms of two-body quantum numbers. Which quantum numbers are conserved? Which are the possible values the total spin of a two-body state can have?

The direct and exchange matrix elements can be brought together if we define the anti-symmetrized matrix element

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

It has the symmetry property

$$\langle pq|\hat{v}|rs\rangle_{\mathrm{AS}} = -\langle pq|\hat{v}|sr\rangle_{\mathrm{AS}} = -\langle qp|\hat{v}|rs\rangle_{\mathrm{AS}},$$

and

$$\langle pq|\hat{v}|rs\rangle_{\mathrm{AS}} = \langle qp|\hat{v}|sr\rangle_{\mathrm{AS}}.$$

Your task is to write a function which calculates the integral

$$\langle pq|\hat{v}|rs\rangle = \int \psi_p^*(x_i)\psi_q^*(x_j)V(r_{ij})\psi_r(x_i)\psi_s(x_j)dx_i dx_j,$$

Program example for numerical integration

The following program shows the integration of a first-order Hermite polynomial for the four-dimensional case. The Hermite polynomials have the following norm

$$\int_{-\infty}^{\infty} e^{-x^2} H_n(x)^2 dx = 2^n n! \sqrt{\pi}.$$

```cpp
// OpenMP code for numerical integration with Gauss-Hermite quadrature
#include <cstdlib>
#include <iostream>
#include <cmath>
#include <iomanip>
#include  <omp.h>
using namespace std;

// The integrand in Cartesian coordinates
double Integrand(double, double,double, double);
// The Gauss Hermite integration function
double  GaussHermiteIntegration(int);
// Getting the Gaussian quadrature weights and integration points
void GaussHermiteQuadrature(double *, double *, int);
// Start main program
int main (int argc, char* argv[])
{
  // read from terminal the number of integration points
  int n = atoi(argv[1]);
  int thread_num;
```

Reminder on Variational Calculus and Lagrangian Multipliers

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

Variational Calculus and Lagrangian Multipliers, simple example

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

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

with the constraint

$$\int dx\,dy\,dz\, \psi^*(x, y, z) \psi(x, y, z) = 1,$$

and a Hamiltonian

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

We will, for the sake of notational convenience, skip the variables x, y, z below, and write for example $V(x, y, z) = V$.

Manipulating terms

The integral involving the kinetic energy can be written as, with the function ψ vanishing strongly for large values of x, y, z (given here by the limits a and b),

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

We will drop the limits a and b in the remaining discussion. Inserting this expression into the expectation value for the energy and taking the variational minimum we obtain

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

Adding the Lagrangian multiplier

The constraint appears in integral form as

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

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

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

We introduce 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.

And with the Euler-Lagrange equations we get

For ψ^* the Euler-Lagrange equations yield

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

which results in

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

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

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

In deriving the Hartree-Fock equations, we will 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 the well-known harmonic oscillator functions or the hydrogen-like functions etc). We define our new Hartree-Fock single-particle basis by performing a unitary transformation on our previous basis (labelled with greek indices) as

$$\psi_p^{HF} = \sum_\lambda C_{p\lambda}\phi_\lambda. \tag{17}$$

In this case we vary the coefficients $C_{p\lambda}$. If the basis has infinitely many solutions, we need to truncate the above sum. We assume that the basis ϕ_λ is orthogonal. A unitary transformation keeps the orthogonality, as discussed in exercise 1 below.

More on linear algebra

In the previous slide we stated that a unitary transformation keeps the orthogonality, as discussed in exercise 1 below. To see this consider first a basis of vectors $\mathbf{v}_i$,

$$\mathbf{v}_i = \begin{bmatrix} v_{i1} \\ \cdots \\ \cdots \\ v_{in} \end{bmatrix}$$

We assume that the basis is orthogonal, that is

$$\mathbf{v}_j^T \mathbf{v}_i = \delta_{ij}.$$

An orthogonal or unitary transformation

$$\mathbf{w}_i = \mathbf{U} \mathbf{v}_i,$$

preserves the dot product and orthogonality since

$$\mathbf{w}_j^T \mathbf{w}_i = (\mathbf{U} \mathbf{v}_j)^T \mathbf{U} \mathbf{v}_i = \mathbf{v}_j^T \mathbf{U}^T \mathbf{U} \mathbf{v}_i = \mathbf{v}_j^T \mathbf{v}_i = \delta_{ij}$$

Coefficients of a wave function expansion

This means that if the coefficients $C_{p\lambda}$ belong to a unitary or orthogonal trasformation (using the Dirac bra-ket notation)

$$|p\rangle = \sum_{\lambda} C_{p\lambda} |\lambda\rangle,$$

orthogonality is preserved, that is $\langle\alpha|\beta\rangle = \delta_{\alpha\beta}$ and $\langle p|q\rangle = \delta_{pq}$. This propertry is extremely useful when we build up a basis of many-body Stater determinant based states.

Note also that although a basis $|\alpha\rangle$ contains an infinity of states, for practical calculations we have always to make some truncations.

More Basic Matrix Features, simple 2×2 determinant, useful property of determinants

Before we develop the Hartree-Fock equations, there is another very useful property of determinants that we will use both in connection with Hartree-Fock calculations and later shell-model calculations. Consider the following determinant

$$\begin{vmatrix} \alpha_1 b_{11} + \alpha_2 s b_{12} & a_{12} \\ \alpha_1 b_{21} + \alpha_2 b_{22} & a_{22} \end{vmatrix} = \alpha_1 \begin{vmatrix} b_{11} & a_{12} \\ b_{21} & a_{22} \end{vmatrix} + \alpha_2 \begin{vmatrix} b_{12} & a_{12} \\ b_{22} & a_{22} \end{vmatrix}$$

We can generalize this to an $n \times n$ matrix and have

$$
\begin{vmatrix}
a_{11} & a_{12} & \ldots & \sum_{k=1}^{n} c_k b_{1k} & \ldots & a_{1n} \\
a_{21} & a_{22} & \ldots & \sum_{k=1}^{n} c_k b_{2k} & \ldots & a_{2n} \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
a_{n1} & a_{n2} & \ldots & \sum_{k=1}^{n} c_k b_{nk} & \ldots & a_{nn}
\end{vmatrix}
= \sum_{k=1}^{n} c_k
\begin{vmatrix}
a_{11} & a_{12} & \ldots & b_{1k} \\
a_{21} & a_{22} & \ldots & b_{2k} \\
\ldots & \ldots & \ldots & \ldots \\
\ldots & \ldots & \ldots & \ldots \\
a_{n1} & a_{n2} & \ldots & b_{nk}
\end{vmatrix}
$$

This is a property we will use in our Hartree-Fock discussions.

More Basic Matrix Features, a general $n \times n$ determinant

We can generalize the previous results, now with all elements a_{ij} being given as functions of linear combinations of various coefficients c and elements b_{ij},

$$
\begin{vmatrix}
\sum_{k=1}^{n} b_{1k} c_{k1} & \sum_{k=1}^{n} b_{1k} c_{k2} & \cdots & \sum_{k=1}^{n} b_{1k} c_{kj} & \cdots & \sum_{k=1}^{n} b_{1k} c_{kn} \\
\sum_{k=1}^{n} b_{2k} c_{k1} & \sum_{k=1}^{n} b_{2k} c_{k2} & \cdots & \sum_{k=1}^{n} b_{2k} c_{kj} & \cdots & \sum_{k=1}^{n} b_{2k} c_{kn} \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\sum_{k=1}^{n} b_{nk} c_{k1} & \sum_{k=1}^{n} b_{nk} c_{k2} & \cdots & \sum_{k=1}^{n} b_{nk} c_{kj} & \cdots & \sum_{k=1}^{n} b_{nk} c_{kn}
\end{vmatrix} =
$$

where $det(\mathbf{C})$ and $det(\mathbf{B})$ are the determinants of $n \times n$ matrices with elements c_{ij} and b_{ij} respectively. This is a property we will use in our Hartree-Fock discussions. Convince yourself about the correctness of the above expression by setting $n = 2$.

A general Slater determinant

With our definition of the new basis in terms of an orthogonal basis we have

$$\psi_p(x) = \sum_\lambda C_{p\lambda} \phi_\lambda(x).$$

If the coefficients $C_{p\lambda}$ belong to an orthogonal or unitary matrix, the new basis is also orthogonal. Our Slater determinant in the new basis $\psi_p(x)$ is written as

$$\frac{1}{\sqrt{A!}} \begin{vmatrix} \psi_p(x_1) & \psi_p(x_2) & \dots & \dots & \psi_p(x_A) \\ \psi_q(x_1) & \psi_q(x_2) & \dots & \dots & \psi_q(x_A) \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_t(x_1) & \psi_t(x_2) & \dots & \dots & \psi_t(x_A) \end{vmatrix} = \frac{1}{\sqrt{A!}} \begin{vmatrix} \sum_\lambda C_{p\lambda}\phi_\lambda(x_1) & \sum \\ \sum_\lambda C_{q\lambda}\phi_\lambda(x_1) & \sum \\ \dots & \\ \dots & \\ \sum_\lambda C_{t\lambda}\phi_\lambda(x_1) & \sum \end{vmatrix}$$

which is nothing but $det(\mathbf{C})det(\Phi)$, with $det(\Phi)$ being the determinant given by the basis functions $\phi_\lambda(x)$.

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

It is normal to choose a single-particle basis defined as the eigenfunctions of parts of the full Hamiltonian. The typical situation consists of the solutions of the one-body part of the Hamiltonian, that is we have

$$\hat{h}_0 \phi_\lambda = \epsilon_\lambda \phi_\lambda.$$

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

$$\phi_\lambda(\boldsymbol{r}) = \langle \boldsymbol{r} | \lambda \rangle.$$

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

In our discussions hereafter we will use our definitions of single-particle states above and below the Fermi (F) level given by the labels $ijkl \cdots \leq F$ for so-called single-hole states and $abcd \cdots > F$ for so-called particle states. For general single-particle states we employ the labels $pqrs \ldots$.

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

In Eq. (16), restated here

$$E[\Phi] = \sum_{\mu=1}^{A} \langle \mu|h|\mu \rangle + \frac{1}{2} \sum_{\mu=1}^{A} \sum_{\nu=1}^{A} \langle \mu\nu|\hat{v}|\mu\nu \rangle_{AS},$$

we found the expression for the energy functional in terms of the basis function $\phi_\lambda(\boldsymbol{r})$. We then varied the above energy functional with respect to the basis functions $|\mu\rangle$. Now we are interested in defining a new basis defined in terms of a chosen basis as defined in Eq. (17). We can then rewrite the energy functional as

$$E[\Phi^{HF}] = \sum_{i=1}^{A} \langle i|h|i \rangle + \frac{1}{2} \sum_{ij=1}^{A} \langle ij|\hat{v}|ij \rangle_{AS}, \qquad (18)$$

where Φ^{HF} is the new Slater determinant defined by the new basis of Eq. (17).

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

Using Eq. (17) we can rewrite Eq. (18) as

$$E[\Psi] = \sum_{i=1}^{A} \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha|h|\beta \rangle + \frac{1}{2} \sum_{ij=1}^{A} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta|\hat{v}|\gamma\delta \rangle_{AS}.$$

(19)

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 $\langle i|j \rangle = \delta_{i,j}$ and $\langle \alpha|\beta \rangle = \delta_{\alpha,\beta}$, the coefficients $C_{i\gamma}$ obey the relation

$$\langle i|j \rangle = \delta_{i,j} = \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha|\beta \rangle = \sum_{\alpha} C_{i\alpha}^* C_{i\alpha},$$

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

$$F[\Phi^{HF}] = E[\Phi^{HF}] - \sum_{i=1}^{A} \epsilon_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha}. \qquad (20)$$

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

Minimizing with respect to $C_{i\alpha}^*$, remembering that the equations for $C_{i\alpha}^*$ and $C_{i\alpha}$ can be written as two independent equations, we obtain

$$\frac{d}{dC_{i\alpha}^*} \left[E[\Phi^{HF}] - \sum_j \epsilon_j \sum_\alpha C_{j\alpha}^* C_{j\alpha} \right] = 0,$$

which yields for every single-particle state i and index α (recalling that the coefficients $C_{i\alpha}$ are matrix elements of a unitary (or orthogonal for a real symmetric matrix) matrix) the following Hartree-Fock equations

$$\sum_\beta C_{i\beta} \langle \alpha | h | \beta \rangle + \sum_{j=1}^{A} \sum_{\beta\gamma\delta} C_{j\beta}^* C_{j\delta} C_{i\gamma} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS} = \epsilon_i^{HF} C_{i\alpha}.$$

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

We can rewrite this equation as (changing dummy variables)

$$\sum_{\beta} \left\{ \langle \alpha | h | \beta \rangle + \sum_{j}^{A} \sum_{\gamma\delta} C_{j\gamma}^{*} C_{j\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS} \right\} C_{i\beta} = \epsilon_{i}^{HF} C_{i\alpha}.$$

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

$$h_{\alpha\beta}^{HF} = \langle\alpha|h|\beta\rangle + \sum_{j=1}^{A} \sum_{\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle\alpha\gamma|\hat{v}|\beta\delta\rangle_{AS},$$

we can rewrite the new equations as

$$\sum_{\gamma} h_{\alpha\beta}^{HF} C_{i\beta} = \epsilon_i^{HF} C_{i\alpha}. \qquad (21)$$

The latter is nothing but a standard eigenvalue problem. It suffices to tabulate the matrix elements $\langle\alpha|h|\beta\rangle$ and $\langle\alpha\gamma|\hat{v}|\beta\delta\rangle_{AS}$ once and for all. Successive iterations require thus only a look-up in tables over one-body and two-body matrix elements. These details will be discussed below when we solve the Hartree-Fock equations numerically.

Hartree-Fock algorithm

Our Hartree-Fock matrix is thus

$$\hat{h}^{HF}_{\alpha\beta} = \langle\alpha|\hat{h}_0|\beta\rangle + \sum_{j=1}^{A}\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\langle\alpha\gamma|\hat{v}|\beta\delta\rangle_{AS}.$$

The Hartree-Fock equations are solved in an iterative waym starting with a guess for the coefficients $C_{j\gamma} = \delta_{j,\gamma}$ and solving the equations by diagonalization till the new single-particle energies ϵ_i^{HF} do not change anymore by a prefixed quantity.

Hartree-Fock algorithm

Normally we assume that the single-particle basis $|\beta\rangle$ forms an eigenbasis for the operator $\hat{h}_0$, meaning that the Hartree-Fock matrix becomes

$$\hat{h}_{\alpha\beta}^{HF} = \epsilon_\alpha \delta_{\alpha,\beta} + \sum_{j=1}^{A} \sum_{\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS}.$$

The Hartree-Fock eigenvalue problem

$$\sum_\beta \hat{h}_{\alpha\beta}^{HF} C_{i\beta} = \epsilon_i^{\mathrm{HF}} C_{i\alpha},$$

can be written out in a more compact form as

$$\hat{h}^{HF} \hat{C} = \epsilon^{\mathrm{HF}} \hat{C}.$$

Hartree-Fock algorithm

The Hartree-Fock equations are, in their simplest form, solved in an iterative way, starting with a guess for the coefficients $C_{i\alpha}$. We label the coefficients as $C_{i\alpha}^{(n)}$, where the subscript n stands for iteration n. To set up the algorithm we can proceed as follows:

- We start with a guess $C_{i\alpha}^{(0)} = \delta_{i,\alpha}$. Alternatively, we could have used random starting values as long as the vectors are normalized. Another possibility is to give states below the Fermi level a larger weight.

- The Hartree-Fock matrix simplifies then to (assuming that the coefficients $C_{i\alpha}$ are real)

$$\hat{h}_{\alpha\beta}^{HF} = \epsilon_\alpha \delta_{\alpha,\beta} + \sum_{j=1}^{A} \sum_{\gamma\delta} C_{j\gamma}^{(0)} C_{j\delta}^{(0)} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS}.$$

Hartree-Fock algorithm

Solving the Hartree-Fock eigenvalue problem yields then new eigenvectors $C_{i\alpha}^{(1)}$ and eigenvalues $\epsilon_i^{HF(1)}$.

- With the new eigenvalues we can set up a new Hartree-Fock potential

$$\sum_{j=1}^{A} \sum_{\gamma\delta} C_{j\gamma}^{(1)} C_{j\delta}^{(1)} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS}.$$

The diagonalization with the new Hartree-Fock potential yields new eigenvectors and eigenvalues. This process is continued till for example

$$\frac{\sum_{p} |\epsilon_i^{(n)} - \epsilon_i^{(n-1)}|}{m} \leq \lambda,$$

where λ is a user prefixed quantity ($\lambda \sim 10^{-8}$ or smaller) and p runs over all calculated single-particle energies and m is the number of single-particle states.

Analysis of Hartree-Fock equations and Koopman's theorem

We can rewrite the ground state energy by adding and subtracting $\hat{u}^{HF}(x_i)$

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

which results in

$$E_0^{HF} = \sum_{i \leq F}^A \varepsilon_i^{HF} + \frac{1}{2} \sum_{i \leq F}^A \sum_{j \leq F}^A [\langle ij | \hat{v} | ij \rangle - \langle ij | \hat{v} | ji \rangle] - \sum_{i \leq F}^A \langle i | \hat{u}^{HF} | i \rangle.$$

Our single-particle states $ijk \ldots$ are now single-particle states obtained from the solution of the Hartree-Fock equations.

Using our definition of the Hartree-Fock single-particle energies we obtain then the following expression for the total ground-state energy

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

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

Analysis of Hartree-Fock equations and Koopman's theorem

Atomic physics case

We have

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

where $\Phi^{\mathrm{HF}}(N)$ is the new Slater determinant defined by the new basis of Eq. (17) for N electrons (same Z). If we assume that the single-particle wave functions in the new basis do not change when we remove one electron or add one electron, we can then define the corresponding energy for the $N-1$ systems as

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

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

Analysis of Hartree-Fock equations and Koopman's theorem

Calculating the difference

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

we obtain

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

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

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

Similarly, we can now compute the difference (we label the single-particle states above the Fermi level as $abcd > F$)

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

These two equations can thus be used to the electron affinity or ionization energies, respectively. Koopman's theorem states that for example the ionization energy of a closed-shell system is given by the energy of the highest occupied single-particle state. If we assume that changing the number of electrons from N to $N+1$ does not change the Hartree-Fock single-particle energies and eigenfunctions, then Koopman's theorem simply states that the ionization energy of an atom is given by the single-particle energy of the last bound state. In a similar way, we can also define the electron affinities.

Analysis of Hartree-Fock equations and Koopman's theorem

As an example, consider a simple model for atomic sodium, Na. Neutral sodium has eleven electrons, with the weakest bound one being confined the 3s single-particle quantum numbers. The energy needed to remove an electron from neutral sodium is rather small, 5.1391 eV, a feature which pertains to all alkali metals. Having performed a Hartree-Fock calculation for neutral sodium would then allows us to compute the ionization energy by using the single-particle energy for the 3s states, namely $\epsilon_{3s}^{\mathrm{HF}}$.

From these considerations, we see that Hartree-Fock theory allows us to make a connection between experimental observables (here ionization and affinity energies) and the underlying interactions between particles. In this sense, we are now linking the dynamics and structure of a many-body system with the laws of motion which govern the system. Our approach is a reductionistic one, meaning that we want to understand the laws of motion in terms of the particles or degrees of freedom which we believe are the fundamental ones. Our Slater determinant, being constructed as the product of various single-particle functions, follows this

Consider a Slater determinant built up of orthogonal single-particle orbitals ψ_λ, with $\lambda = 1, 2, \ldots, A$.

The unitary transformation

$$\psi_a = \sum_\lambda C_{a\lambda} \phi_\lambda,$$

brings us into the new basis. The new basis has quantum numbers $a = 1, 2, \ldots, A$.

a) Show that the new basis is orthogonal.

b) Show that the new Slater determinant constructed from the new single-particle wave functions can be written as the determinant based on the previous basis and the determinant of the matrix C.

c) Show that the old and the new Slater determinants are equal up to a complex constant with absolute value unity.

Hint. Hint: C is a unitary matrix.

We will assume that we can build various Slater determinants using an orthogonal single-particle basis ψ_λ, with $\lambda = 1, 2, \ldots, A$. The aim of this exercise is to set up specific matrix elements that will turn useful when we start our discussions of the nuclear shell model. In particular you will notice, depending on the character of the operator, that many matrix elements will actually be zero. Consider three A-particle Slater determinants $|\Phi_0\rangle$, $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$, where the notation means that Slater determinant $|\Phi_i^a\rangle$ differs from $|\Phi_0\rangle$ by one single-particle state, that is a single-particle state ψ_i is replaced by a single-particle state ψ_a. It will later be interpreted as a so-called one-particle-one-hole excitation. Similarly, the Slater determinant $|\Phi_{ij}^{ab}\rangle$ differs by two single-particle states from $|\Phi_0\rangle$ and is normally thought of as a two-particle-two-hole excitation. Define a general onebody operator $\hat{F} = \sum_i^A \hat{f}(x_i)$ and a general twobody operator $\hat{G} = \sum_{i>j}^A \hat{g}(x_i, x_j)$ with g being invariant under the interchange of the coordinates of particles i and j. You can use here the results from the second exercise set, exercise 3.

a) Calculate

$$\langle \Phi_0 | \hat{F} | \Phi_0 \rangle,$$

and

Developing a Hartree-Fock program

The Hamiltonian for a system of N electrons confined in a harmonic potential reads

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} + \sum_{i=1}^{N} \frac{1}{2} m\omega r_i^2 + \sum_{i<j} \hat{V}_{ij},$$

with $\hat{V}_{ij}$ is the two-body potential whose matrix elements are calculated on fly in your program. See expression below.
The Hartree-Fock algorithm can be broken down as follows. We recall that our Hartree-Fock matrix is

$$\hat{h}_{\alpha\beta}^{HF} = \langle\alpha|\hat{h}_0|\beta\rangle + \sum_{j=1}^{N} \sum_{\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle\alpha\gamma|V|\beta\delta\rangle_{AS}.$$

Normally we assume that the single-particle basis $|\beta\rangle$ forms an eigenbasis for the operator $\hat{h}_0$ (this is our case), meaning that the Hartree-Fock matrix becomes

$$\hat{h}_{\alpha\beta}^{HF} = \epsilon_\alpha \delta_{\alpha,\beta} + \sum_{j=1}^{N} \sum_{\gamma\delta} C_{j\gamma}^* C_{j\delta} \langle\alpha\gamma|V|\beta\delta\rangle_{AS}.$$