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

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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

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

with the Hartree-Fock Hamiltonian defined as

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

- The term $\hat{u}^{\text{HF}}$ is a single-particle potential to be determined by the HF algorithm.

- The HF algorithm means to choose $\hat{u}^{\text{HF}}$ in order to have

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

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

- The variational principle ensures that $E^{\text{HF}} \geq E_0$, with E_0 the exact ground state energy.

Why Hartree-Fock?

We will show that the Hartree-Fock Hamiltonian $\hat{h}^{\mathrm{HF}}$ 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

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

meaning that

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

The so-called Hartree-Fock potential $\hat{u}^{\mathrm{HF}}$ 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 moves, in addition to the external potential $\hat{u}_{\mathrm{ext}}$ which confines the motion of the fermion. For systems like nuclei, there is no external confining potential. Nuclei are examples of self-bound systems, where the binding arises due to the intrinsic nature of the strong force. For nuclear systems thus, there would be no external one-body potential in the Hartree-Fock Hamiltonian.

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

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

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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

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

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

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

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

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

where we have defined

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

and

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

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 $u_i = u_{\text{ext}}(x_i)$ 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 indices $1, 2, 3, \dots, n$ and the sum runs over all $n!$ permutations. The quantity p_i represents the number of transpositions of column indices that are needed in order to bring a given permutation back to its initial ordering, in our case given by $a_{11} a_{22} \dots a_{nn}$ here.

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

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

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 $\hat{A}$

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

Furthermore, $\hat{A}$ satisfies

$$\hat{A}^2 = \hat{A},$$
(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 anti-symmetrization 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

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

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

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

$$\left. - \int \psi_\mu^*(x_i)\psi_\nu^*(x_j)V(r_{ij})\psi_\nu(x_i)\psi_\mu(x_j)dx_i dx_j \right]. \tag{14}$$

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 $\psi_\mu(x)$, 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

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

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

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

Definitions and notations

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

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

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

Our system, quantum dots

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

$$\hat{V} = \sum_{i<j}^{N_e} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}.$$

The unperturbed part of the Hamiltonian yields the single-particle energies

$$\epsilon_i = \omega \left(2n + |m| + 1\right),$$

where $n = 0, 1, 2, 3, ..$ and $m = 0, \pm 1, \pm 2, ...$ The index i runs from $0, 1, 2, ...$.

First tasks

Set up the harmonic oscillator wave function in cartesian coordinates for an electron with $n_x = n_y = 0$ and find the oscillator energy. Use this result to find the unperturbed energy

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

for two electrons with the same quantum numbers.

- Repeat for six electrons (find the relevant harmonic oscillator quantum numbers)

- Repeat for 12 and 20 electrons

- Write now a program which sets up all relevant quantum numbers for the single-particle basis

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 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

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 $\mathbf{v}_i$,

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

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

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

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

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

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

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},

$$\begin{vmatrix} \sum_{k=1}^n b_{1k} c_{k1} & \sum_{k=1}^n b_{1k} c_{k2} & \dots & \sum_{k=1}^n b_{1k} c_{kj} & \dots & \sum_{k=1}^n b_{1k} c_{kn} \\ \sum_{k=1}^n b_{2k} c_{k1} & \sum_{k=1}^n b_{2k} c_{k2} & \dots & \sum_{k=1}^n b_{2k} c_{kj} & \dots & \sum_{k=1}^n b_{2k} c_{kn} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \sum_{k=1}^n b_{nk} c_{k1} & \sum_{k=1}^n b_{nk} c_{k2} & \dots & \sum_{k=1}^n b_{nk} c_{kj} & \dots & \sum_{k=1}^n b_{nk} c_{kn} \end{vmatrix} = det(\mathbf{C}) det(\mathbf{B}),$$

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

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

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 $pqrs\dots$.

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

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

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

$$E[\Psi] = \sum_{i=1}^{A} \sum_{\alpha\beta} C_{i\alpha}^{*} C_{i\beta} \langle \alpha|h|\beta \rangle + \frac{1}{2} \sum_{ij=1}^{A} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^{*} C_{j\beta}^{*} C_{i\gamma} C_{j\delta} \langle \alpha\beta|\hat{v}|\gamma\delta \rangle_{AS}. \tag{19}$$

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

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

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

$$\sum_{\gamma} h_{\alpha\beta}^{HF} C_{i\beta} = \epsilon_{i}^{HF} C_{i\alpha}. \tag{21}$$

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

$$\hat{h}_{\alpha\beta}^{HF} = \langle \alpha | \hat{h}_{0} | \beta \rangle + \sum_{j=1}^{A} \sum_{\gamma\delta} C_{j\gamma}^{*} C_{j\delta} \langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS}.$$

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

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

can be written out in a more compact form as

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

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)

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

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 $\hat{u}^{HF}(x_i)$

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

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.

Analysis of Hartree-Fock equations and Koopman's theorem

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

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

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

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

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

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

Analysis of Hartree-Fock equations and Koopman's theorem

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 philosophy.

*

Exercise 1: Hartree-Fock Slater determinant

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 $a = 1, 2, \ldots, A$.
paragraphparagraph>paragraph>-0.5em

a) Show that the new basis is orthogonal.
paragraphparagraph>paragraph>-0.5em

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.
paragraphparagraph>paragraph>-0.5em

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.

*

Exercise 2: Matrix elements for the Hartree-Fock method and the nuclear shell model

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.

paragraphparagraph>paragraph>-0.5em

a) Calculate
$$\langle \Phi_0 | \hat{F} | \Phi_0 \rangle,$$
and
$$\langle \Phi_0 | \hat{G} | \Phi_0 \rangle.$$

paragraphparagraph>paragraph>-0.5em

b) Find thereafter
$$\langle \Phi_0 | \hat{F} | \Phi_i^a \rangle,$$
and
$$\langle \Phi_0 | \hat{G} | \Phi_i^a \rangle,$$

paragraphparagraph>paragraph>-0.5em

c) Finally, find
$$\langle \Phi_0 | \hat{F} | \Phi_{ij}^{ab} \rangle,$$
and
$$\langle \Phi_0 | \hat{G} | \Phi_{ij}^{ab} \rangle.$$

What happens with the two-body operator if we have a transition probability of the type
$$\langle \Phi_0 | \hat{G} | \Phi_{ijk}^{abc} \rangle,$$
where the Slater determinant to the right of the operator differs by more than two single-particle states?

paragraphparagraph>paragraph>-0.5em

d) With an orthogonal basis of Slater determinants Φ_λ, we can now construct an exact many-body state as a linear expansion of Slater determinants, that is, a given exact state
$$\Psi_i = \sum_{\lambda=0}^{\infty} C_{i\lambda} \Phi_\lambda.$$

In all practical calculations the infinity is replaced by a given truncation in the sum.

If you are to compute the expectation value of (at most) a two-body Hamiltonian for the above exact state
$$\langle \Psi_i | \hat{H} | \Psi_i \rangle,$$

based on the calculations above, which are the only elements which will contribute? (there is no need to perform any calculation here, use your results from exercises a), b), and c)).

These results simplify to a large extent shell-model calculations.

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

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

The Hartree-Fock eigenvalue problem

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

can be written out in a more compact form as

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

The equations are often rewritten in terms of a so-called density matrix, which is defined as

$$\rho_{\gamma\delta} = \sum_{i=1}^{N} \langle \gamma|i\rangle\langle i|\delta\rangle = \sum_{i=1}^{N} C_{i\gamma} C_{i\delta}^*. \tag{22}$$

It means that we can rewrite the Hartree-Fock Hamiltonian as

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

It is convenient to use the density matrix since we can precalculate in every iteration the product of two eigenvector components C.