

Hartree-Fock methods

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Why Hartree-Fock? Derivation of Hartree-Fock equations in coordinate space

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

We will show that the Hartree-Fock Hamiltonian \hat{h}^{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}^{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}_{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.

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

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 $V(x, y, z) = V$.

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),

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

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

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

The constraint appears in integral form as

$$\int dx dy dz \psi^* \psi = \text{constant},$$

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

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

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.

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.

Definitions and notations

Before we proceed we need some definitions. 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 the sum of some onebody part and a twobody part

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

with

$$H_0 = \sum_{i=1}^A \hat{h}_0(x_i). \quad (2)$$

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 to be discussed here.

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

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

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

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

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 $\beta = -1$.

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

$$\Phi(x_1, x_2, \dots, x_A, \alpha, \beta, \dots, \sigma) = \frac{1}{\sqrt{A!}} \begin{vmatrix} \psi_\alpha(x_1) & \psi_\alpha(x_2) & \dots & \dots & \psi_\alpha(x_A) \\ \psi_\beta(x_1) & \psi_\beta(x_2) & \dots & \dots & \psi_\beta(x_A) \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\sigma(x_1) & \psi_\sigma(x_2) & \dots & \dots & \psi_\sigma(x_A) \end{vmatrix}, \quad (3)$$

where x_i stand for the coordinates and spin values of a particle i and $\alpha, \beta, \dots, \gamma$ are quantum numbers needed to describe remaining quantum numbers.

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

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

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

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.

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 $a_{11} a_{22}$.

Back to the derivation of the energy. The single-particle function $\psi_\alpha(x_i)$ are eigenfunctions of the onebody Hamiltonian h_i , that is

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

with eigenvalues

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

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

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

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

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

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

where we have used the shorthand $d\tau = dx_1 dr_2 \dots dr_A$.

In the Hartree-Fock method the trial function is the Slater determinant of Eq. (3) which can be rewritten as

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

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

It is defined as

$$\hat{A} = \frac{1}{A!} \sum_p (-)^p \hat{P}, \quad (4)$$

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

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

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

$$[H_0, \hat{A}] = [H_I, \hat{A}] = 0. \quad (5)$$

Furthermore, \hat{A} satisfies

$$\hat{A}^2 = \hat{A}, \quad (6)$$

since every permutation of the Slater determinant reproduces it.

The expectation value of \hat{H}_0

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

is readily reduced to

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

where we have used Eqs. (5) and (6). 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

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{i=1}^A \sum_p (-)^p \int \Phi_H^* \hat{h}_0 \hat{P} \Phi_H d\tau.$$

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

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{i=1}^A \int \Phi_H^* \hat{h}_0 \Phi_H d\tau.$$

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

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^A \int \psi_\mu^*(x) \hat{h}_0 \psi_\mu(x) dx d\mathbf{r}. \quad (7)$$

We introduce the following shorthand for the above integral

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

and rewrite Eq. (7) as

$$\int \Phi^* \hat{H}_0 \Phi d\tau = \sum_{\mu=1}^A \langle \mu | \hat{h}_0 | \mu \rangle. \quad (8)$$

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

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

which reduces to

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

by following the same arguments as for the one-body Hamiltonian.

Because of the dependence on the inter-particle distance r_{ij} , permutations of any two particles no longer vanish, and we get

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

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.

We obtain

$$\begin{aligned} \int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^A \sum_{\nu=1}^A \left[\int \psi_\mu^*(x_i) \psi_\nu^*(x_j) \hat{v}(r_{ij}) \psi_\mu(x_i) \psi_\nu(x_j) dx_i dx_j \right. \\ \left. - \int \psi_\mu^*(x_i) \psi_\nu^*(x_j) \hat{v}(r_{ij}) \psi_\nu(x_i) \psi_\mu(x_j) dx_i dx_j \right]. \end{aligned} \quad (9)$$

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.

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

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

and

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

Derivation of Hartree-Fock equations in coordinate space

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

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

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

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

where we have used the shorthand $d\tau = dx_1 dx_2 \dots dx_A$.

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

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

where we have introduced the anti-symmetrization operator \hat{A} defined by the summation over all possible permutations p of two fermions. It is defined as

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

with the the Hartree-function given by the simple product of all possible single-particle function

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

Our functional is written as

$$E[\Phi] = \sum_{\mu=1}^A \int \psi_\mu^*(x_i) \hat{h}_0(x_i) \psi_\mu(x_i) dx_i + \frac{1}{2} \sum_{\mu=1}^A \sum_{\nu=1}^A \left[\int \psi_\mu^*(x_i) \psi_\nu^*(x_j) \hat{v}(r_{ij}) \psi_\mu(x_i) \psi_\nu(x_j) dx_i dx_j - \int \psi_\mu^*(x_i) \psi_\nu^*(x_j) \right]$$

The more compact version reads

$$E[\Phi] = \sum_{\mu}^A \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu\nu}^A [\langle \mu\nu | \hat{v} | \mu\nu \rangle - \langle \nu\mu | \hat{v} | \mu\nu \rangle].$$

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

$$\langle \mu\nu | \hat{v} | \mu\nu \rangle = \langle \nu\mu | \hat{v} | \nu\mu \rangle,$$

or in the more general case

$$\langle \mu\nu | \hat{v} | \sigma\tau \rangle = \langle \nu\mu | \hat{v} | \tau\sigma \rangle.$$

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

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

or for a general matrix element

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

It has the symmetry property

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

The antisymmetric matrix element is also hermitian, implying

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

With these notations we rewrite the Hartree-Fock functional as

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^A \sum_{\nu=1}^A \langle \mu\nu | \hat{v} | \mu\nu \rangle_{AS}. \quad (11)$$

Adding the contribution from the one-body operator \hat{H}_0 to (11) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^A \langle \mu | h | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^A \sum_{\nu=1}^A \langle \mu\nu | \hat{v} | \mu\nu \rangle_{AS}. \quad (12)$$

In our coordinate space derivations below we will spell out the Hartree-Fock equations in terms of their integrals.

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

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

For the orthogonal wave functions ψ_i this reduces to

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

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

$$\begin{aligned} & \sum_{\mu=1}^A \int \delta \psi_\mu^* \hat{h}_0(x_i) \psi_\mu dx_i + \frac{1}{2} \sum_{\mu=1}^A \sum_{\nu=1}^A \left[\int \delta \psi_\mu^* \psi_\nu^* \hat{v}(r_{ij}) \psi_\mu \psi_\nu dx_i dx_j - \int \delta \psi_\mu^* \psi_\nu^* \hat{v}(r_{ij}) \psi_\nu \psi_\mu dx_i dx_j \right] + \\ & \sum_{\mu=1}^A \int \psi_\mu^* \hat{h}_0(x_i) \delta \psi_\mu dx_i + \frac{1}{2} \sum_{\mu=1}^A \sum_{\nu=1}^A \left[\int \psi_\mu^* \psi_\nu^* \hat{v}(r_{ij}) \delta \psi_\mu \psi_\nu dx_i dx_j - \int \psi_\mu^* \psi_\nu^* \hat{v}(r_{ij}) \psi_\nu \delta \psi_\mu dx_i dx_j \right] - \sum_{\mu=1}^A E_\mu \int \delta \psi_\mu^* \psi_\mu \end{aligned}$$

Although the variations $\delta\psi$ and $\delta\psi^*$ are not independent, they may in fact be treated as such, so that the terms dependent on either $\delta\psi$ and $\delta\psi^*$ individually may be set equal to zero. To see this, simply replace the arbitrary variation $\delta\psi$

by $i\delta\psi$, so that $\delta\psi^*$ is replaced by $-i\delta\psi^*$, and combine the two equations. We thus arrive at the Hartree-Fock equations

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_{\nu=1}^A \int \psi_\nu^*(x_j) \hat{v}(r_{ij}) \psi_\nu(x_j) dx_j \right] \psi_\mu(x_i) - \left[\sum_{\nu=1}^A \int \psi_\nu^*(x_j) \hat{v}(r_{ij}) \psi_\mu(x_j) dx_j \right] \psi_\nu(x_i) = \epsilon_\mu \psi_\mu(x_i). \quad (13)$$

Notice that the integration $\int dx_j$ implies an integration over the spatial coordinates \mathbf{r}_j and a summation over the spin-coordinate of fermion j . We note that the factor of $1/2$ in front of the sum involving the two-body interaction, has been removed. This is due to the fact that we need to vary both $\delta\psi_\mu^*$ and $\delta\psi_\nu$. Using the symmetry properties of the two-body interaction and interchanging μ and ν as summation indices, we obtain two identical terms.

The two first terms in the last equation are the one-body kinetic energy and the electron-nucleus potential. The third or *direct* term is the averaged electronic repulsion of the other electrons. As written, the term includes the *self-interaction* of electrons when $\mu = \nu$. The self-interaction is cancelled in the fourth term, or the *exchange* term. The exchange term results from our inclusion of the Pauli principle and the assumed determinantal form of the wave-function. Equation (13), in addition to the kinetic energy and the attraction from the atomic nucleus that confines the motion of a single electron, represents now the motion of a single-particle modified by the two-body interaction. The additional contribution to the Schrodinger equation due to the two-body interaction, represents a mean field set up by all the other bystanding electrons, the latter given by the sum over all single-particle states occupied by N electrons.

The Hartree-Fock equation is an example of an integro-differential equation. These equations involve repeated calculations of integrals, in addition to the solution of a set of coupled differential equations. The Hartree-Fock equations can also be rewritten in terms of an eigenvalue problem. The solution of an eigenvalue problem represents often a more practical algorithm and the solution of coupled integro-differential equations. This alternative derivation of the Hartree-Fock equations is given below.

Analysis of Hartree-Fock equations in coordinate space

A theoretically convenient form of the Hartree-Fock equation is to regard the direct and exchange operator defined through

$$V_\mu^d(x_i) = \int \psi_\mu^*(x_j) \hat{v}(r_{ij}) \psi_\mu(x_j) dx_j$$

and

$$V_\mu^{ex}(x_i)g(x_i) = \left(\int \psi_\mu^*(x_j) \hat{v}(r_{ij}) g(x_j) dx_j \right) \psi_\mu(x_i),$$

respectively.

The function $g(x_i)$ is an arbitrary function, and by the substitution $g(x_i) = \psi_\nu(x_i)$ we get

$$V_\mu^{ex}(x_i)\psi_\nu(x_i) = \left(\int \psi_\mu^*(x_j)\hat{v}(r_{ij})\psi_\nu(x_j)dx_j \right) \psi_\mu(x_i).$$

We may then rewrite the Hartree-Fock equations as

$$\hat{h}^{HF}(x_i)\psi_\nu(x_i) = \epsilon_\nu\psi_\nu(x_i),$$

with

$$\hat{h}^{HF}(x_i) = \hat{h}_0(x_i) + \sum_{\mu=1}^A V_\mu^d(x_i) - \sum_{\mu=1}^A V_\mu^{ex}(x_i),$$

and where $\hat{h}_0(i)$ is the one-body part. The latter is normally chosen as a part which yields solutions in closed form. The harmonic oscillator is a classical problem thereof. We normally rewrite the last equation as

$$\hat{h}^{HF}(x_i) = \hat{h}_0(x_i) + \hat{u}^{HF}(x_i).$$

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

Another possibility is to expand the single-particle functions in a known basis and vary the coefficients, that is, the new single-particle wave function is written as a linear expansion in terms of a fixed chosen orthogonal basis (for example 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

$$\psi_p^{HF} = \sum_{\lambda} C_{p\lambda}\phi_{\lambda}. \quad (14)$$

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.

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 $\phi_{\lambda}(\mathbf{r})$, defined by the quantum numbers λ and \mathbf{r} are defined as the overlap

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

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 stated that a unitary transformation keeps the orthogonality. To see this consider first a basis of vectors \mathbf{v}_i ,

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

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

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

This means that if the coefficients $C_{p\lambda}$ belong to a unitary or orthogonal transformation (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 property is extremely useful when we build up a basis of many-body Slater 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.

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

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

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

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

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

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} ,

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

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 $n = 2$.

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

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

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

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 $pqrs \dots$.

In Eq. (12), 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 $\phi_{\lambda}(\mathbf{r})$. 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. (14). We can then rewrite the energy functional as

$$E[\Phi^{HF}] = \sum_{i=1}^A \langle i | h | i \rangle + \frac{1}{2} \sum_{ij=1}^A \langle ij | \hat{v} | ij \rangle_{AS}, \quad (15)$$

where Φ^{HF} is the new Slater determinant defined by the new basis of Eq. (14).

Using Eq. (14) we can rewrite Eq. (15) as

$$E[\Psi] = \sum_{i=1}^A \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha|h|\beta \rangle + \frac{1}{2} \sum_{ij=1}^A \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta|\hat{v}|\gamma\delta \rangle_{AS}. \quad (16)$$

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

$$F[\Phi^{HF}] = E[\Phi^{HF}] - \sum_{i=1}^A \epsilon_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha}. \quad (17)$$

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

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

We can rewrite this equation as (changing dummy variables)

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

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

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

$$\sum_{\gamma} h_{\alpha\beta}^{HF} C_{i\beta} = \epsilon_i^{HF} C_{i\alpha}. \quad (18)$$

The latter is nothing but a standard eigenvalue problem. Compared with Eq. (13), we see that we do not need to compute any integrals in an iterative procedure for solving the equations. 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 numerical.

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.

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

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

can be written out in a more compact form as

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

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)

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

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.

- TODO: add code with Hartree-Fock for nuclear system

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

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

Our single-particle states $ijk \dots$ 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

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

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

In the atomic physics case we have

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

where $\Phi^{HF}(N)$ is the new Slater determinant defined by the new basis of Eq. (14) 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

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

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

Calculating the difference

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

we obtain

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

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

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

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

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

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.

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 $\epsilon_{3s}^{\text{HF}}$.

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.

With similar arguments as in atomic physics, we can now use Hartree-Fock theory to make a link between nuclear forces and separation energies. Changing to nuclear system, we define

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

where $\Phi^{\text{HF}}(A)$ is the new Slater determinant defined by the new basis of Eq. (14) for A nucleons, where $A = N + Z$, with N now being the number of neutrons and Z the number of protons. If we assume again that the single-particle wave functions in the new basis do not change from a nucleus with A nucleons to a nucleus with $A - 1$ nucleons, we can then define the corresponding energy for the $A - 1$ systems as

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

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

Calculating the difference

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

which becomes

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

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

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

Similarly, we can now compute the difference (recall that the single-particle states $abcd > F$)

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

If we then recall that the binding energy differences

$$BE(A) - BE(A - 1) \quad \text{and} \quad BE(A + 1) - BE(A),$$

define the separation energies, we see that the Hartree-Fock single-particle energies can be used to define separation energies. We have thus our first link between nuclear forces (included in the potential energy term) and an observable quantity defined by differences in binding energies.

We have thus the following interpretations (if the single-particle fields do not change)

$$BE(A) - BE(A - 1) \approx E[\Phi^{\text{HF}}(A)] - E[\Phi^{\text{HF}}(A - 1)] = \epsilon_k^{\text{HF}},$$

and

$$BE(A + 1) - BE(A) \approx E[\Phi^{\text{HF}}(A + 1)] - E[\Phi^{\text{HF}}(A)] = \epsilon_a^{\text{HF}}.$$

If we use ^{16}O as our closed-shell nucleus, we could then interpret the separation energy

$$BE(^{16}\text{O}) - BE(^{15}\text{O}) \approx \epsilon_{0p_{1/2}^{\nu}}^{\text{HF}},$$

and

$$BE(^{16}\text{O}) - BE(^{15}\text{N}) \approx \epsilon_{0p_{1/2}^{\pi}}^{\text{HF}}.$$

Similalry, we could interpret

$$BE(^{17}\text{O}) - BE(^{16}\text{O}) \approx \epsilon_{0d_{5/2}^{\nu}}^{\text{HF}},$$

and

$$BE(^{17}\text{F}) - BE(^{16}\text{O}) \approx \epsilon_{0d_{5/2}^{\pi}}^{\text{HF}}.$$

We can continue like this for all $A \pm 1$ nuclei where A is a good closed-shell (or subshell closure) nucleus. Examples are ^{22}O , ^{24}O , ^{40}Ca , ^{48}Ca , ^{52}Ca , ^{54}Ca , ^{56}Ni , ^{68}Ni , ^{78}Ni , ^{90}Zr , ^{88}Sr , ^{100}Sn , ^{132}Sn and ^{208}Pb , to mention some possible cases.

We can thus make our first interpretation of the separation energies in terms of the simplest possible many-body theory. If we also recall that the so-called energy gap for neutrons (or protons) is defined as

$$\Delta S_n = 2BE(N, Z) - BE(N - 1, Z) - BE(N + 1, Z),$$

for neutrons and the corresponding gap for protons

$$\Delta S_p = 2BE(N, Z) - BE(N, Z - 1) - BE(N, Z + 1),$$

we can define the neutron and proton energy gaps for ^{16}O as

$$\Delta S_{\nu} = \epsilon_{0d_{5/2}^{\nu}}^{\text{HF}} - \epsilon_{0p_{1/2}^{\nu}}^{\text{HF}},$$

and

$$\Delta S_{\pi} = \epsilon_{0d_{5/2}^{\pi}}^{\text{HF}} - \epsilon_{0p_{1/2}^{\pi}}^{\text{HF}}.$$

*

Exercise 1: Derivation of Hartree-Fock equations

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

The unitary transformation

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

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

aragraph!paragraph>paragraph>-0.5em

a) Show that the new basis is orthonormal.

aragraph!paragraph>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 .

aragraph!paragraph>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. Use the fact that C is a unitary matrix.

*

Exercise 2: Derivation of Hartree-Fock equations

Consider the Slater determinant

$$\Phi_0 = \frac{1}{\sqrt{n!}} \sum_p (-)^p P \prod_{i=1}^n \psi_{\alpha_i}(x_i).$$

A small variation in this function is given by

$$\delta\Phi_0 = \frac{1}{\sqrt{n!}} \sum_p (-)^p P \psi_{\alpha_1}(x_1) \psi_{\alpha_2}(x_2) \dots \psi_{\alpha_{i-1}}(x_{i-1}) (\delta\psi_{\alpha_i}(x_i)) \psi_{\alpha_{i+1}}(x_{i+1}) \dots \psi_{\alpha_n}(x_n).$$

aragraph!paragraph>paragraph>-0.5em

a) Show that

$$\langle \delta\Phi_0 | \sum_{i=1}^n \{t(x_i) + u(x_i)\} + \frac{1}{2} \sum_{i \neq j=1}^n v(x_i, x_j) | \Phi_0 \rangle = \sum_{i=1}^n \langle \delta\psi_{\alpha_i} | \hat{t} + \hat{u} | \phi_{\alpha_i} \rangle + \sum_{i \neq j=1}^n \{ \langle \delta\psi_{\alpha_i} \psi_{\alpha_j} | \hat{v} | \psi_{\alpha_i} \psi_{\alpha_j} \rangle - \langle \delta\psi_{\alpha_i} \psi_{\alpha_j} | \hat{v} \rangle \}$$

*

Exercise 3: Developing a Hartree-Fock program

Neutron drops are a powerful theoretical laboratory for testing, validating and improving nuclear structure models. Indeed, all approaches to nuclear structure, from ab initio theory to shell model to density functional theory are applicable in such systems. We will, therefore, use neutron drops as a test system for setting up a Hartree-Fock code. This program can later be extended to studies of the binding energy of nuclei like ^{16}O or ^{40}Ca . The single-particle energies obtained by solving the Hartree-Fock equations can then be directly related to experimental separation energies. Since Hartree-Fock theory is the starting point for several many-body techniques (density functional theory, random-phase approximation, shell-model etc), the aim here is to develop a computer program to solve the Hartree-Fock equations in a given single-particle basis, here the harmonic oscillator.

The Hamiltonian for a system of N neutron drops 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 $\hbar^2/2m = 20.73 \text{ fm}^2$, $mc^2 = 938.90590 \text{ MeV}$, and \hat{V}_{ij} is the two-body interaction potential whose matrix elements are precalculated and to be read in by you.

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

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

can be written out in a more compact form as

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

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

$$\rho_{\gamma\delta} = \sum_{i=1}^N \langle \gamma | i \rangle \langle i | \delta \rangle = \sum_{i=1}^N C_{i\gamma} C_{i\delta}^*. \quad (19)$$

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 .

Note that $\langle \alpha | \hat{h}_0 | \beta \rangle$ denotes the matrix elements of the one-body part of the starting hamiltonian. For self-bound nuclei $\langle \alpha | \hat{h}_0 | \beta \rangle$ is the kinetic energy, whereas for neutron drops, $\langle \alpha | \hat{h}_0 | \beta \rangle$ represents the harmonic oscillator hamiltonian since the system is confined in a harmonic trap. If we are working in a harmonic oscillator basis with the same ω as the trapping potential, then $\langle \alpha | \hat{h}_0 | \beta \rangle$ is diagonal.

The python [program](#) shows how one can, in a brute force way read in matrix elements in m -scheme and compute the Hartree-Fock single-particle energies for four major shells. The interaction which has been used is the so-called N3LO interaction of [Machleidt and Entem](#) using the [Similarity Renormalization Group](#) approach method to renormalize the interaction, using an oscillator energy $\hbar\omega = 10$ MeV.

The nucleon-nucleon two-body matrix elements are in m -scheme and are fully anti-symmetrized. The Hartree-Fock programs uses the density matrix discussed above in order to compute the Hartree-Fock matrix. Here we display the Hartree-Fock part only, assuming that single-particle data and two-body matrix elements have already been read in.

```
import numpy as np
from decimal import Decimal
# expectation value for the one body part, Harmonic oscillator in three dimensions
def onebody(i, n, l):
    homega = 10.0
    return homega*(2*n[i] + l[i] + 1.5)

if __name__ == '__main__':

    Nparticles = 16
    """ Read quantum numbers from file """
    index = []
    n = []
    l = []
    j = []
    mj = []
    tz = []
    spOrbitals = 0
    with open("nucleispnumbers.dat", "r") as qnumfile:
        for line in qnumfile:
            nums = line.split()
            if len(nums) != 0:
                index.append(int(nums[0]))
                n.append(int(nums[1]))
                l.append(int(nums[2]))
                j.append(int(nums[3]))
                mj.append(int(nums[4]))
                tz.append(int(nums[5]))
                spOrbitals += 1
```

```

""" Read two-nucleon interaction elements (integrals) from file, brute force 4-dim array """
nninteraction = np.zeros([spOrbitals, spOrbitals, spOrbitals, spOrbitals])
with open("nucleitwobody.dat", "r") as infile:
    for line in infile:
        number = line.split()
        a = int(number[0]) - 1
        b = int(number[1]) - 1
        c = int(number[2]) - 1
        d = int(number[3]) - 1
        nninteraction[a][b][c][d] = Decimal(number[4])
""" Set up single-particle integral """
singleparticleH = np.zeros(spOrbitals)
for i in range(spOrbitals):
    singleparticleH[i] = Decimal(onebody(i, n, 1))

""" Star HF-iterations, preparing variables and density matrix """

""" Coefficients for setting up density matrix, assuming only one along the diagonals """
C = np.eye(spOrbitals) # HF coefficients
DensityMatrix = np.zeros([spOrbitals, spOrbitals])
for gamma in range(spOrbitals):
    for delta in range(spOrbitals):
        sum = 0.0
        for i in range(Nparticles):
            sum += C[gamma][i]*C[delta][i]
        DensityMatrix[gamma][delta] = Decimal(sum)
maxHFiter = 100
epsilon = 1.0e-5
difference = 1.0
hf_count = 0
oldenergies = np.zeros(spOrbitals)
newenergies = np.zeros(spOrbitals)
while hf_count < maxHFiter and difference > epsilon:
    print("##### Iteration %i ##### % hf_count)
    HFmatrix = np.zeros([spOrbitals, spOrbitals])
    for alpha in range(spOrbitals):
        for beta in range(spOrbitals):
            """ If tests for three-dimensional systems, including isospin conservation """
            if l[alpha] != l[beta] and j[alpha] != j[beta] and mj[alpha] != mj[beta]:
                continue
            """ Setting up the Fock matrix using the density matrix and antisymmetrization """
            sumFockTerm = 0.0
            for gamma in range(spOrbitals):
                for delta in range(spOrbitals):
                    if (mj[alpha]+mj[gamma]) != (mj[beta]+mj[delta]) and (tz[alpha] != tz[beta]):
                        continue
                    sumFockTerm += DensityMatrix[gamma][delta]*nninteraction[alpha][beta][gamma][delta]
            HFmatrix[alpha][beta] = Decimal(sumFockTerm)
            """ Adding the one-body term, here plain harmonic oscillator """
            if beta == alpha: HFmatrix[alpha][alpha] += singleparticleH[alpha]
spenergies, C = np.linalg.eigh(HFmatrix)
""" Setting up new density matrix in m-scheme """
DensityMatrix = np.zeros([spOrbitals, spOrbitals])
for gamma in range(spOrbitals):
    for delta in range(spOrbitals):
        sum = 0.0
        for i in range(Nparticles):
            sum += C[gamma][i]*C[delta][i]
        DensityMatrix[gamma][delta] = Decimal(sum)
newenergies = spenergies
""" Brute force computation of difference between previous and new sp HF energies """

```



```

sum =0.0
for i in range(spOrbitals):
    sum += (abs(newenergies[i]-oldenergies[i]))/spOrbitals
difference = sum
oldenergies = newenergies
print ("Single-particle energies, ordering may have changed ")
for i in range(spOrbitals):
    print('{0:4d}  {1:.4f}'.format(i, Decimal(oldenergies[i])))
hf_count += 1

```

Running the program, one finds that the lowest-lying states for a nucleus like ^{16}O , we see that the nucleon-nucleon force brings a natural spin-orbit splitting for the $0p$ states (or other states except the s -states). Since we are using the m -scheme for our calculations, we observe that there are several states with the same eigenvalues. The number of eigenvalues corresponds to the degeneracy $2j + 1$ and is well respected in our calculations, as see from the table here.

The values of the lowest-lying states are (π for protons and ν for neutrons)

Quantum numbers	Energy [MeV]
$0s_{1/2}^{\pi}$	-40.4602
$0s_{1/2}^{\pi}$	-40.4602
$0s_{1/2}^{\nu}$	-40.6426
$0s_{1/2}^{\nu}$	-40.6426
$0p_{1/2}^{\pi}$	-6.7133
$0p_{1/2}^{\pi}$	-6.7133
$0p_{1/2}^{\nu}$	-6.8403
$0p_{1/2}^{\nu}$	-6.8403
$0p_{3/2}^{\pi}$	-11.5886
$0p_{3/2}^{\pi}$	-11.5886
$0p_{3/2}^{\pi}$	-11.5886
$0p_{3/2}^{\pi}$	-11.5886
$0p_{3/2}^{\nu}$	-11.7201
$0p_{3/2}^{\nu}$	-11.7201
$0p_{3/2}^{\nu}$	-11.7201
$0p_{3/2}^{\nu}$	-11.7201
$0d_{5/2}^{\pi}$	18.7589
$0d_{5/2}^{\nu}$	18.8082

We can use these results to attempt our first link with experimental data, namely to compute the shell gap or the separation energies. The shell gap for neutrons is given by

$$\Delta S_n = 2BE(N, Z) - BE(N - 1, Z) - BE(N + 1, Z).$$

For ^{16}O we have an experimental value for the shell gap of 11.51 MeV for neutrons, while our Hartree-Fock calculations result in 25.65 MeV. This means that correlations beyond a simple Hartree-Fock calculation with a two-body force

play an important role in nuclear physics. The splitting between the $0p'_{3/2}$ and the $0p'_{1/2}$ state is 4.88 MeV, while the experimental value for the gap between the ground state $1/2^-$ and the first excited $3/2^-$ states is 6.08 MeV. The two-nucleon spin-orbit force plays a central role here. In our discussion of nuclear forces we will see how the spin-orbit force comes into play here.