

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

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

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

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

meaning that

$$\langle p | \hat{u}^{\text{HF}} | q \rangle = \sum_{i \leq F} \langle p | \hat{V} | q i \rangle \langle i | A S.$$

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

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

Variational Calculus and Lagrangian Multipliers

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

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

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

Variational Calculus and Lagrangian Multipliers

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

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

Variational Calculus and Lagrangian Multipliers

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.

Variational Calculus and Lagrangian Multipliers

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 Schrodinger 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

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

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.

Definitions and notations

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

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

meaning that $\Psi_\lambda(x_1, x_2, \dots, x_A)$ 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 $\beta = -1$.

Definitions and notations

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

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

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.

Definitions and notations

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

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

with eigenvalues

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

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

Definitions and notations

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

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

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

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

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

Definitions and notations

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

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

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

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

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

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

Definitions and notations

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

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

Furthermore, \hat{A} satisfies

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

since every permutation of the Slater determinant reproduces it.

Definitions and notations

The expectation value of \hat{H}_0

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

is readily reduced to

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

where we have used Eqs. (5) and (6). The next step is to replace the antisymmetrization operator by its definition and to replace \hat{H}_0 with the sum of one-body operators

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

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

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

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

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

Definitions and notations

We introduce the following shorthand for the above integral

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

and rewrite Eq. (7) as

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

Definitions and notations

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

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

which reduces to

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

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

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

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

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

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.

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

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

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 $d\tau = dx_1 dx_2 \dots dx_A$.

Derivation of Hartree-Fock equations in coordinate space

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

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

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

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

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

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

Derivation of Hartree-Fock equations in coordinate space

Our functional is written as

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

The more compact version reads

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

Derivation of Hartree-Fock equations in coordinate space

Recalling our discussions earlier, we introduced the following shorthands for the integrals, replacing here the two-body Coulomb interaction with a more general two-body interaction V ,

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

and

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

Derivation of Hartree-Fock equations in coordinate space

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

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

or in the more general case

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

Derivation of Hartree-Fock equations in coordinate space

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

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

or for a general matrix element

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

It has the symmetry property

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

The antisymmetric matrix element is also hermitian, implying

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

Derivation of Hartree-Fock equations in coordinate space

With these notations we rewrite the Hartree-Fock functional as

$$\int \Phi^* \hat{H}_I \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^A \sum_{\nu=1}^A \langle \mu\nu | V | \mu\nu \rangle_{AS}. \quad (10)$$

Adding the contribution from the one-body operator \hat{H}_0 to (10) we obtain the energy functional

$$E[\Phi] = \sum_{\mu=1}^A \langle \mu | h | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^A \sum_{\nu=1}^A \langle \mu\nu | V | \mu\nu \rangle_{AS}. \quad (11)$$

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

Derivation of Hartree-Fock equations in coordinate space

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

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

Derivation of Hartree-Fock equations in coordinate space

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

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

Derivation of Hartree-Fock equations in coordinate space

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

$$\left[-\frac{1}{2} \nabla_i^2 + \sum_{\nu=1}^A \int \psi_\nu^*(x_j) \hat{v}(r_{ij}) \psi_\nu(x_j) dx_j \right] \psi_\mu(x_i) - \left[\sum_{\nu=1}^A \int \psi_\nu^*(x_j) \hat{v}(r_{ij}) \psi_\mu(x_j) dx_j \right] \psi_\mu(x_i) = \epsilon_\mu \psi_\mu(x_i) \quad (12)$$

Notice that the integration $\int dx_j$ implies an integration over the spatial coordinates 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.

Derivation of Hartree-Fock equations in coordinate space

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 (12), 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 bystander 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

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

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

respectively.

Analysis of Hartree-Fock equations in coordinate space

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

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

We may then rewrite the Hartree-Fock equations as

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

with

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

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

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

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

$$\psi_\rho^{\text{HF}} = \sum_\lambda C_{\rho\lambda} \phi_\lambda. \quad (13)$$

In this case we vary the coefficients $C_{\rho\lambda}$. 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.

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

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

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 $ijkl \dots \leq F$ for so-called single-hole states and $abcd \dots > F$ 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. (11), restated here

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

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

$$E[\Phi^{\text{HF}}] = \sum_{i=1}^A \langle i | h | i \rangle + \frac{1}{2} \sum_{ij=1}^A \langle ij | V | ij \rangle_{AS}, \quad (14)$$

where Φ^{HF} is the new Slater determinant defined by the new basis of Eq. (13).

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

Using Eq. (13) we can rewrite Eq. (14) as

$$E[\Psi] = \sum_{i=1}^A \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | h | \beta \rangle + \frac{1}{2} \sum_{ij=1}^A \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS}. \quad (15)$$

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

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

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

$$F[\Phi^{HF}] = E[\Phi^{HF}] - \sum_{i=1}^A \epsilon_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha}. \quad (16)$$

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

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

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

We can rewrite this equation as (changing dummy variables)

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

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

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

we can rewrite the new equations as

$$\sum_{\gamma} h_{\alpha\beta}^{HF} C_{i\beta} = \epsilon_i^{HF} C_{i\alpha}. \quad (17)$$

The latter is nothing but a standard eigenvalue problem. Compared with Eq. (12), 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 $\langle \alpha\gamma|V|\beta\delta\rangle_{AS}$ 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

Hartree-Fock algorithm

Our Hartree-Fock matrix is thus

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

The Hartree-Fock equations are solved in an iterative way 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

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

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

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

Hartree-Fock algorithm

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

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

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

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

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

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

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

which results in

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

Our single-particle states $ijk \dots$ 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

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

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

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

where $\Phi^{HF}(N)$ is the new Slater determinant defined by the new basis of Eq. (13) 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

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

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

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

we obtain

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

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

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

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 $abcd > F$)

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

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.

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

Analysis of Hartree-Fock equations, Koopman's theorem

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

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

where $\Phi^{\text{HF}}(A)$ is the new Slater determinant defined by the new basis of Eq. (13) 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

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

Analysis of Hartree-Fock equations and Koopman's theorem

Calculating the difference

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

which becomes

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

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

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

Analysis of Hartree-Fock equations and Koopman's theorem

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.

Analysis of Hartree-Fock equations and Koopman's theorem

We have thus the following interpretations (if the single-particle field 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 oxygen-16 as our closed-shell nucleus, we could then interpret the separation energy

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

and

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

Analysis of Hartree-Fock equations and Koopman's theorem

Similarly, 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 ^4He , ^{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.

Analysis of Hartree-Fock equations and Koopman's theorem

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

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

and

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