

Lecture 7

Hartree-Fock Theory

Particle-number representation: General formalism

The simplest starting point for a **many-body state** is a **system of noninteracting particles**, i.e. the Hamiltonian of the total system H is the sum of the **single-particle Hamiltonians** $h(i)$ for each individual particle; there are no interaction terms depending on the coordinates of more than one particle:

$$\hat{H} = \sum_{i=1}^A \hat{h}(\mathbf{r}_i, \hat{p}_i)$$

A solution of the Schrödinger equation can be found in terms of a product of single-particle states: i.e. a set of **single-particle wave functions** $\psi_k(\mathbf{r})$ that fulfil

$$\hat{h}(\mathbf{r}, \hat{p}) \psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r})$$

A product state like

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_A) = \psi_{k_1}(\mathbf{r}_1) \cdots \psi_{k_A}(\mathbf{r}_A)$$

will be an **eigenstate** of H with $\hat{H}\Psi = E\Psi$, $E = \sum_{k=1}^A \varepsilon_k$

Additionally the wave function must still be **symmetrized for bosons** and **antisymmetrized for fermions** in order to fulfil the requirement that the wave function takes the same value (bosons) or changes its sign (fermions) under the exchange of two particles.

Second quantization: General formalism

□ **For fermions** suitable basis states are given by **Slater-determinants**:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_A) = \frac{1}{\sqrt{A!}} \sum_{\pi} (-1)^{\pi} \prod_{k=1}^A \psi_k(\mathbf{r}_{k_{\pi}})$$

where π is a **permutation** of the indices $i = 1, \dots, A$ ($\pi = 1, \dots, A!$) and $(-1)^{\pi}$ is its sign, i.e., $+1$ for even and -1 for odd permutations. The permutation changes the index i into i_{π} . For **bosons** this sign is left out.

□ **Quantum mechanics**: the information **which** particle occupies a particular state is **meaningless** because the particles are **indistinguishable**.

The only **meaningful** information is **how many particles populate each state** $\psi_i(\mathbf{r})$ = **the occupation numbers** n_i → one can define the many-particle state as an abstract (normalized) vector in the **occupation-number representation**:

$$|\Psi\rangle = |n_1, n_2, \dots, n_A\rangle$$

The space of these abstract vectors characterized by varying particle numbers is called **Fock space**. Each of the occupation numbers n_i can take values of **0 or 1** for **fermions**, and **0, ..., ∞** for **bosons**.

Second quantization for bosons

□ Introduce the **annihilation operator** a and the **creation operator** a^+ describing the annihilation and creation of excitations (**phonons**), respectively, in a **given single-particle state**. For **bosons** they are required to fulfil the **commutation relations**

$$[\hat{a}, \hat{a}] = 0 \quad , \quad [\hat{a}^\dagger, \hat{a}^\dagger] = 0 \quad , \quad [\hat{a}, \hat{a}^\dagger] = 1$$

□ The **particle-number operator** n : $\hat{n} = \hat{a}^\dagger \hat{a}$

a and a^+ lower and raise, respectively, the eigenvalues of n by 1:

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle \quad , \quad \hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$$

The **eigenvalue** n : $\hat{n}|n\rangle = n|n\rangle$

$$\implies n = \langle n|\hat{n}|n\rangle = \langle n|\hat{a}^\dagger \hat{a}|n\rangle$$

with $a|0\rangle = 0$

The **states** n may also be generated from the **vacuum** by repeated application of a^+ :

$$|n\rangle = \frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^n |0\rangle$$

Second quantization for bosons

□ For the case of **many single-particle states (for bosons)** the operators are indexed by i to denote **which** state they affect, and the commutation relations become

$$[\hat{a}_i, \hat{a}_j] = 0 \quad , \quad [\hat{a}_i^\dagger, \hat{a}_j^\dagger] = 0 \quad , \quad [\hat{a}_i, \hat{a}_j^\dagger] = \delta_{ij}$$

There is now also a **particle-number operator for each single-particle state i :**

$$\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i$$

as well as one operator counting the **total number of particles** for all possible single-particle states i

$$\hat{n} = \sum_i \hat{n}_i = \sum_i \hat{a}_i^\dagger \hat{a}_i$$

The states of the system are characterized by all the **occupation numbers**:

$$\hat{n}_i |n_1, n_2, \dots, n_i, \dots\rangle = n_i |n_1, n_2, \dots, n_i, \dots\rangle$$

and may be written in terms of the **vacuum state** as

$$|n_1, n_2, \dots, n_i, \dots\rangle = \prod_i \frac{(\hat{a}_i^\dagger)^{n_i}}{\sqrt{n_i!}} |0\rangle$$

with

$$\begin{aligned} \hat{a}_i |n_1, n_2, \dots, n_i, \dots\rangle &= \sqrt{n_i} |n_1, n_2, \dots, n_i - 1, \dots\rangle \quad , \\ \hat{a}_i^\dagger |n_1, n_2, \dots, n_i, \dots\rangle &= \sqrt{n_i + 1} |n_1, n_2, \dots, n_i + 1, \dots\rangle \end{aligned}$$

Second quantization for fermions

□ In case of fermions the **annihilation operator** a and the **creation operator** a^\dagger follow **anticommutation relations**:

$$\{\hat{a}_i, \hat{a}_j\} = 0 \quad , \quad \{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} = 0 \quad , \quad \{\hat{a}_i, \hat{a}_j^\dagger\} = \delta_{ij}$$

For systems with **many single-particle levels**:

the states are characterized by the eigenvalues of the **particle-number operators**

$$\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i \quad , \quad \hat{n}_i |n_1, n_2, \dots, n_i, \dots\rangle = n_i |n_1, n_2, \dots, n_i, \dots\rangle$$

and may be written in terms of the **vacuum state**

$$\hat{a}_i \hat{a}_i^\dagger |0\rangle = |0\rangle$$

as

$$|n_1, n_2, \dots, n_i, \dots\rangle = (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \dots (\hat{a}_i^\dagger)^{n_i} \dots |0\rangle$$

$$\hat{a}_i |n_1, \dots, n_i, \dots\rangle = \sigma_i (1 - n_i) |n_1, \dots, n_i - 1, \dots\rangle$$

$$\hat{a}_i^\dagger |n_1, \dots, n_i, \dots\rangle = \sigma_i n_i |n_1, \dots, n_i + 1, \dots\rangle$$

$$\sigma_i = (-1)^{\sum_{j=1}^{i-1} n_j}$$

Representation of operators: one-body operators

□ Let's translate operators in **occupation-number representation** (i.e. second quantization) as it has been done for the wave functions.

Consider **one-body operators** that depend only on the coordinates of one particle, for example: the **kinetic energy or an external potential**; **two-body operators** involve coordinates of two particles, such as an interaction potential.

□ Let's consider **fermions**.

A **one-body operator** has the general form $f(r_k)$, where the coordinate r_k of the k^{th} particle also represents the momentum, spin, and any other needed degrees of freedom.

Note: quantum mechanics: in a system of **nondistinguishable particles** it makes no sense to ask for the properties of a certain particle; instead only quantities should be evaluated that are invariant under an **arbitrary permutation of the particles**.

The reasonable definition of a **one-body operator** is thus

$$\hat{f} = \sum_{k=1}^A \hat{f}(r_k)$$

Representation of operators: one-body operator

□ **Matrix elements** of such operators have to be evaluated between **Slater determinants** and then an operator in second quantization has to be constructed that yields the same matrix elements in the equivalent occupation-number states.

→ Consider the matrix element between the two **determinantal wave functions** :

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_A) = \frac{1}{\sqrt{A!}} \sum_{\pi} (-1)^{\pi} \prod_{i \in O} \psi_{i_{\pi}}(\mathbf{r}_i)$$

$$\Psi'(\mathbf{r}_1, \dots, \mathbf{r}_A) = \frac{1}{\sqrt{A!}} \sum_{\pi'} (-1)^{\pi'} \prod_{i' \in O'} \psi_{i'_{\pi'}}(\mathbf{r}_{i'})$$

$$\begin{aligned} \langle \Psi | \hat{f} | \Psi' \rangle &= \sum_{k=1}^A \frac{1}{A!} \int d^3 r_1 \cdots \int d^3 r_A \\ &\times \sum_{\pi \pi'} (-1)^{\pi + \pi'} \left(\prod_{i \in O} \psi_{i_{\pi}}^*(\mathbf{r}_i) \right) \hat{f}(\mathbf{r}_k) \left(\prod_{i' \in O'} \psi_{i'_{\pi'}}(\mathbf{r}_{i'}) \right) \end{aligned}$$

Representation of operators: one-body operator

The products can be **split up** into A single-particle matrix elements. One of these involves the operator $f(\mathbf{r}_k)$

$$\int d^3 r_k \psi_{k_\pi}^*(\mathbf{r}_k) \hat{f}(\mathbf{r}_k) \psi_{k_{\pi'}}(\mathbf{r}_k) = f_{k_\pi k_{\pi'}}$$

whereas the others can be reduced because of **orthonormality** of the wave functions

$$\int d^3 r_k \psi_{i_\pi}^*(\mathbf{r}_i) \psi_{i'_{\pi'}}(\mathbf{r}_i) = \delta_{i_\pi i'_{\pi'}}$$

and the **total matrix element** may now be written as

$$\langle \Psi | \hat{f} | \Psi' \rangle = \sum_k \frac{1}{A!} \sum_{\pi \pi'} (-1)^{\pi + \pi'} f_{k_\pi k_{\pi'}} \prod_{\substack{i \in O, i' \in O' \\ i \neq k, i' \neq k}}^A \delta_{i_\pi i'_{\pi'}}$$



The matrix element is totally independent of the permutation. It only contains the factor σ and the matrix element $f_{k_\pi k_{\pi'}}$, always obtains the same indices: those of the two single-particle states which differ between Ψ and Ψ' (let us simply call them j and j').

$$\langle \Psi | \hat{f} | \Psi' \rangle = \sum_{k=1}^A \frac{1}{A!} \sigma f_{jj'} \sum_{\pi, j \text{ fixed}} 1 = \frac{1}{A!} \sigma A f_{jj'} (A-1)! = \sigma f_{jj'}$$

Representation of operators: one-body operator

□ **One-body operator in second quantization:** $\hat{f} = \sum_{jj'} f_{jj'} \hat{a}_j^\dagger \hat{a}_{j'}$

It must remove one particle from state j' and put it into the state j while not doing anything to the other states; the resulting matrix element is $f_{jj'}$

$$\begin{aligned} |\Psi\rangle &= \hat{a}_{i_1}^\dagger \cdots \hat{a}_{i_A}^\dagger |0\rangle, & |\Psi'\rangle &= \hat{a}_{i'_1}^\dagger \cdots \hat{a}_{i'_A}^\dagger |0\rangle \\ \langle \Psi | \hat{f} | \Psi' \rangle &= \sum_{jj'} f_{jj'} \langle 0 | \hat{a}_{i_A} \cdots \hat{a}_{i_1} \hat{a}_j^\dagger \hat{a}_{j'} \hat{a}_{i'_1}^\dagger \cdots \hat{a}_{i'_A}^\dagger | 0 \rangle \\ &= \sum_{jj'} f_{jj'} \langle 0 | \hat{a}_{i_A} \cdots \hat{a}_{i_1} \hat{a}_{i_1}^\dagger \cdots \hat{a}_j^\dagger \hat{a}_{j'} \hat{a}_{j'}^\dagger \cdots \hat{a}_{i_A}^\dagger | 0 \rangle = \sigma f_{jj'} \end{aligned}$$

and this agrees with the previous result.

The rule for transcribing a single-particle operator in second-quantized form is thus

$$\hat{f} = \sum_{k=1}^A \hat{f}(\mathbf{r}_k) \quad \rightarrow \quad \hat{f} = \sum_{jj'} f_{jj'} \hat{a}_j^\dagger \hat{a}_{j'}$$

with the **single-particle matrix elements** $f_{jj'}$ given by

$$\int d^3 r_k \psi_{k_\pi}^*(\mathbf{r}_k) \hat{f}(\mathbf{r}_k) \psi_{k_{\pi'}}(\mathbf{r}_k) = f_{k_\pi k_{\pi'}}$$

Representation of operators: two-body operators

- Consider **two-body operators** such as the **potential energy**:

$$\hat{V} = \frac{1}{2} \sum_{k \neq k'} \hat{v}(\mathbf{r}_k, \mathbf{r}_{k'})$$

The second quantized operator is

$$\hat{V} = \frac{1}{2} \sum_{ijkl} v_{ijkl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k$$

with the **two-particle matrix element** defined by

$$v_{ijkl} = \int d^3 r \int d^3 r' \psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \psi_k(\mathbf{r}) \psi_l(\mathbf{r}')$$

• Note that the operator can change two single-particle states simultaneously and that the index order in the operator products has the last two indices interchanged relative to the ordering in the matrix element.

• Note also the symmetry of the matrix element under the interchange of two pairs of single-particle wave functions: $v_{ijkl} = v_{klij}$

The particle-hole picture

- The lowest state – **ground state** - of the A -fermion system is

with an energy

$$E_0 = \sum_{i=1}^A \varepsilon_i$$
$$|\Psi_0\rangle = \prod_{i=1}^A \hat{a}_i^\dagger |0\rangle$$
$$\varepsilon_1 < \varepsilon_2 < \cdots < \varepsilon_A < \varepsilon_{A+1} < \cdots$$

- The **highest occupied state** with energy ε_A is the **Fermi level**.

- The **expectation value of an operator \hat{O}** in the ground state may then be written as

$$\langle \Psi_0 | \hat{O} | \Psi_0 \rangle = \langle 0 | \hat{a}_A \cdots \hat{a}_1 \hat{O} \hat{a}_1^\dagger \cdots \hat{a}_A^\dagger | 0 \rangle$$

For the **vacuum state**: $\hat{a}_i |0\rangle = 0$ for all i

The **ground state** fulfills

$$\hat{a}_i |\Psi_0\rangle = 0, \quad i > A \quad (\text{above Fermi level})$$

$$\hat{a}_i^\dagger |\Psi_0\rangle = 0, \quad i \leq A \quad (\text{below Fermi level})$$

The particle-hole picture

■ The simplest **excited states** will have one particle lifted from an occupied state into an unoccupied one:

$$|\Psi_{mi}\rangle = \hat{a}_m^\dagger \hat{a}_i |\Psi_0\rangle \quad , \quad m > A \quad , \quad i \leq A$$

and the associated **excitation energy** is

$$E_{mi} - E_0 = \varepsilon_m - \varepsilon_i$$

The state $|\Psi_{mi}\rangle$ has an unoccupied level i , a **hole** below the Fermi energy, and a **particle** in the state m above the Fermi energy.

For that reason it is called a **one-particle / one-hole state** or ***1p1h* state**.

■ The next excitation is a **two-particle/two-hole (2p2h)** state:

$$|\Psi_{mnij}\rangle = \hat{a}_m^\dagger \hat{a}_n^\dagger \hat{a}_i \hat{a}_j |\Psi_0\rangle$$

with **excitation energy**

$$E_{mnij} = \varepsilon_m + \varepsilon_n - \varepsilon_i - \varepsilon_j$$

Hamiltonian with two-body interactions

The aim: develop a **microscopic model** that describes the structure of the nucleus in terms of the degrees of freedom of its microscopic constituents - the nucleons.

□ Consider a **nonrelativistic Hamiltonian** containing only **two-body interactions**; a general form is provided in **particle-number representation** (‘second quantization’) by

$$\hat{H} = \sum_{ij} t_{ij} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{2} \sum_{ijkl} v_{ijkl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k$$

where the indices i, j, k , and l label the **single-particle states** in some complete orthonormal basis and run over all available states. The complex numbers v_{ijkl} are the **matrix elements of the nucleon-nucleon interaction**.

□ An **eigenstate** of this Hamiltonian can be expanded as a **sum over states** which all have the same total number of nucleons, but with the nucleons occupying the available single-particle states in **all possible combinations**:

$$|\Psi\rangle = \sum_{i_1, i_2, \dots, i_A} c_{i_1, i_2, \dots, i_A} \hat{a}_{i_1}^\dagger \hat{a}_{i_2}^\dagger \cdots \hat{a}_{i_A}^\dagger |0\rangle$$

where i_n ($n=1, \dots, A$) select a **subset of A single-particle states occupied** from the infinite number of available states.

Variational method

□ Consider the nonrelativistic Schrödinger equation $\hat{H} \Psi_k = E_k \Psi_k$ (1)

How to find an exact solution:

E_k – eigenvalues and Ψ_k - eigenfunctions in Hilbert space

Let's assume a solution in the form of a **trial wave function Φ** which is restricted in its functional form, so that all possible Φ span a subspace of the Hilbert space available with Ψ_k . Any function Φ can be expanded in terms of Ψ_k :

$$\Phi = \sum_k c_k \Psi_k, \quad \text{with } \sum_k |c_k|^2 = 1 \quad (2)$$

where $k=0$ corresponds to the **ground-state of the Hamiltonian**.

Then the **expectation value of the Hamiltonian in Φ** will be:

$$\langle \Phi | \hat{H} | \Phi \rangle = \sum_k |c_k|^2 E_k = E_0 + \sum_{k>0} |c_k|^2 (E_k - E_0) \quad (3)$$

and $\langle \Phi | \hat{H} | \Phi \rangle$ will always be larger than or equal to E_0 with the **minimum** realized if $c_0 = 1$ and $c_k = 0$ for $k > 0$ = **ground-state** (exact solution). Any admixture of states $k > 0$ to Φ will increase its energy.

Variational method

□ Variational principle:

The optimal approximation to the ground state for the Hamiltonian H is obtained for the wave function Φ whose energy expectation value is **minimal**:

$$\delta\langle\Phi|\hat{H}|\Phi\rangle = 0 \quad (4)$$

for normalized Φ : $\langle\Phi|\Phi\rangle=1$

For a **nonnormalized** wave function Φ :

$$\delta(\langle\Phi|\hat{H}|\Phi\rangle - E\langle\Phi|\Phi\rangle) = 0 \quad (5)$$

where E is a **variational parameter**.

The variation in (5) can be carried out either with respect to $\langle\Phi|$ or $|\Phi\rangle$, since they correspond to two different degrees of freedom, like a number and its complex conjugate. Since the resulting equations are hermitian conjugates of each other, it suffices to examine one of these cases. Varying $\langle\Phi|$ yields

$$\langle\delta\Phi|\hat{H}|\Phi\rangle - E\langle\delta\Phi|\Phi\rangle = 0 \quad (6)$$

Hartree-Fock approximation

- The **variational method** allows to find an optimal approximation to the groundstate within a restricted space of wave functions.
- We need to select the set of allowed single-particle wave functions →
- **The lowest order choice:** single Slater determinant → **Hartree-Fock approximation**

I. **Hartree approximation:** a single Slater determinant, i.e., a wave function of the form

$$|\Psi\rangle = \hat{a}_1^\dagger \hat{a}_2^\dagger \cdots \hat{a}_A^\dagger |0\rangle \quad \text{or} \quad \Leftrightarrow \quad |\Psi\rangle = \prod_{i=1}^A \hat{a}_i^\dagger |0\rangle \quad (6)$$

Here the index of the creation operators refers to a set of single particle states with the corresponding wave functions $\phi_i(r)$, $i = 1, \dots, A$ to be determined from the variational principle.

- Consider a system of two particles (1,2): $\psi_{12}(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1) \psi(\vec{r}_2)$

The joint probability reads: $|\psi_{12}(\vec{r}_1, \vec{r}_2)|^2 = |\psi(\vec{r}_1)|^2 |\psi(\vec{r}_2)|^2 \quad (7)$

→ two particles are independent of each other = **no correlations** included

Hartree-Fock approximation

II. Hartree-Fock approximation: account additionally for the **Fermi antisymmetrization**. For a system of two particles:

$$\psi_{12}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)] \quad (8)$$

Now the joint probability is:

$$\begin{aligned} |\psi_{12}(\mathbf{r}_1, \mathbf{r}_2)|^2 &= \frac{1}{2} (|\psi_1(\mathbf{r}_1)|^2 |\psi_2(\mathbf{r}_2)|^2 + |\psi_2(\mathbf{r}_1)|^2 |\psi_1(\mathbf{r}_2)|^2 \\ &\quad - \psi_1^*(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) \\ &\quad - \psi_1^*(\mathbf{r}_2)\psi_2^*(\mathbf{r}_1)\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)) \quad . \end{aligned} \quad (9)$$

(9) is no longer the same as the product of the single probabilities!

If $r_1=r_2=r_3=r$, the joint probability is zero: the probability for finding two fermions at the same location vanishes, so that there is always a **strong correlation** between the particles, i.e. **deviations from the joint probability (7)**.

This effect is always present for fermions and even does not need any interaction between the particles!

The Hartree-Fock Equations

□ How can the wave function be varied?

The **single-particle wave functions** $\phi_l(\mathbf{r})$ are the **objects to be determined**. They can be **varied via an infinitesimal admixture** of other wave functions from the complete set:

$$\delta\phi_j(\mathbf{r}) = \sum_{k \neq j} \delta c_{jk} \phi_k(\mathbf{r}) \quad (10)$$

Equivalently the **creation operators** can be varied as: $\delta\hat{a}_j^\dagger = \sum_{k \neq j} \delta c_{jk} \hat{a}_k^\dagger$

Insert the new operator into the wave function of (6). The **result of varying only the single-particle wave function** $\delta\Psi_j$ gives:

$$|\Psi + \delta\Psi_j\rangle = |\Psi\rangle + \sum_{k \neq j} \delta c_{jk} \hat{a}_1^\dagger \hat{a}_2^\dagger \cdots \hat{a}_{j-1}^\dagger \hat{a}_k^\dagger \hat{a}_{j+1}^\dagger \cdots \hat{a}_A^\dagger |0\rangle \quad (11)$$

Eq. (11) may also be expressed more compact by using an annihilation operator to depopulate the wave function j :

$$|\Psi + \delta\Psi_j\rangle = |\Psi\rangle + \sum_k \sigma c_{jk} \hat{a}_k^\dagger \hat{a}_j |\Psi\rangle \quad , \quad k > A \quad , \quad j \leq A \quad (12)$$

with $\sigma = \pm 1$ keeping track of the sign changes caused by permuting the operators to put them in front of all the other operators in $|\Psi\rangle$.

The Hartree-Fock Equations

For the variation it is not necessary to keep the sign or the sum over j and κ , as all of these variations are independent; it suffices to demand that the expectation value of H is stationary with respect to variations of the form

$$|\delta\Psi\rangle = \varepsilon \hat{a}_k^\dagger \hat{a}_j |\Psi\rangle \quad (13)$$

as a function of the parameter ε for arbitrary values of the indices fulfilling $\kappa > A$ and $j < A$.

Notation: it will be necessary to distinguish **three types of indices:** those referring to **occupied or unoccupied states** only, and others that are **unrestricted**.

- The **indices i, j** and their subscripted forms i_1, j_1 , etc., refer to **occupied states only**, i.e., they take values from 1 through A exclusively, where A is the number of occupied states: $i, j = 1, \dots, A$
- The **indices m, n** and their subscripted forms refer to **unoccupied single-particle states only**: $m, n = A + 1, \dots, \infty$
- The letters **κ and l** are reserved for **unrestricted** indices: $k, l = 1, \dots, \infty$

The Hartree-Fock Equations

□ One can now reformulate the variational problem in this notation.

The **Hamiltonian** becomes

$$\hat{H} = \sum_{k_1 k_2} t_{k_1 k_2} \hat{a}_{k_1}^\dagger \hat{a}_{k_2} + \frac{1}{2} \sum_{k_1 k_2 k_3 k_4} v_{k_1 k_2 k_3 k_4} \hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger \hat{a}_{k_4} \hat{a}_{k_3} \quad (14)$$

and the **fundamental variations** take the form

$$|\delta\Psi\rangle = \varepsilon \hat{a}_m^\dagger \hat{a}_i |\Psi\rangle \quad (15)$$

Since $\delta\langle\Phi|\Phi\rangle \approx \langle\delta\Phi|\Phi\rangle + \langle\Phi|\delta\Phi\rangle = 0$ (16)

the variation does not change the normalization of the wave function to first order.

Conventionally the ,bra'- vector is varied, so we have to take the Hermitian conjugate of $|\delta\Phi\rangle$,

$$\langle\delta\Psi| = \langle\Psi|\varepsilon^* \hat{a}_i^\dagger \hat{a}_m \quad (17)$$

The Hartree-Fock Equations

The **variational equation** now becomes

$$0 = \langle \delta\Psi | \hat{H} | \Psi \rangle = \varepsilon^* \langle \Psi | \hat{a}_i^\dagger \hat{a}_m \hat{H} | \Psi \rangle \quad (18)$$

Insert (14) into (18) \rightarrow

$$t_{mi} + \frac{1}{2} \sum_j (v_{mjij} - v_{mjji} - v_{jmij} + v_{jmji}) = 0 \quad (19)$$

From the definition of the matrix elements follows that they do not change their value if the first index is exchanged with the second and simultaneously the third with the fourth ($v_{ijkl} = v_{klij}$), so the equation can be simplified to the matrix equation:

$$t_{mi} + \sum_j (v_{mjij} - v_{mjji}) = 0 \quad (20)$$

The **notation** is further simplified by abbreviating the **antisymmetrized matrix element** as

$$\bar{v}_{k_1 k_2 k_3 k_4} = v_{k_1 k_2 k_3 k_4} - v_{k_1 k_2 \overleftrightarrow{k_4 k_3}} \quad (21)$$

The Hartree-Fock Equations

We obtain

$$t_{mi} + \sum_{j=1}^A \bar{v}_{mji} = 0 \quad (22)$$

Here i denotes an **occupied** state ($i < A$), m an **unoccupied** one ($m > A$), and j sums over **all occupied states**.

The equation (22) requires that the single-particle states should be chosen such that the matrix elements

$$h_{kl} = t_{kl} + \sum_{j=1}^A \bar{v}_{kjl} \quad (23)$$

vanish between occupied and unoccupied states.

If we allow (k,l) to refer to arbitrary combinations of states, this defines a **single-particle operator** h in the Hilbert space, which is called the **single-particle or Hartree-Fock Hamiltonian**.

The condition (22) characterizes the **set of occupied states** and not those states individually.

The Hartree-Fock Equations

Let's **split** the operator h into **four parts** corresponding to different index ranges:

- h_{pp} (**particle-particle**) denotes those matrix elements with both indices referring to unoccupied single-particle states,
- h_{hh} (**hole-hole**) has both states occupied,
- h_{ph} and h_{hp} denote the appropriate **mixed cases**:

$$\hat{h} = \begin{pmatrix} \hat{h}_{hh} & \hat{h}_{hp} \\ \hat{h}_{ph} & \hat{h}_{pp} \end{pmatrix} \quad (24)$$

with the condition (22): $\hat{h}_{ph} = 0$ and $\hat{h}_{hp} = 0$

To fulfill these conditions: the states may be chosen such as to make h itself **diagonal**:

$$h_{kl} = t_{kl} + \sum_{j=1}^A \bar{v}_{kjlj} = \varepsilon_k \delta_{kl} \quad (25)$$

(25) - **Hartree-Fock equations** with **single-particle energies** ε_k

The Hartree-Fock Equation

Writing the Hartree-Fock equations (25) in **configuration space** we get:

$$\begin{aligned} \varepsilon_k \phi_k(\mathbf{r}) = & -\frac{\hbar^2}{2m} \nabla^2 \phi_k(\mathbf{r}) + \left(\int d^3 r' v(\mathbf{r}' - \mathbf{r}) \sum_{j=1}^A |\phi_j(\mathbf{r}')|^2 \right) \phi_k(\mathbf{r}) \\ & \text{average potential} \\ & - \sum_{j=1}^A \phi_j(\mathbf{r}) \int d^3 r' v(\mathbf{r}' - \mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}') \quad . \\ & \text{exchange term} \end{aligned} \quad (26)$$

□ The equations are quite similar in form to Schrödinger equations for each of the single-particle states. The second term on the right-hand side is the

average potential

$$U(\mathbf{r}) = \int d^3 r' v(\mathbf{r}' - \mathbf{r}) \sum_{j=1}^A |\phi_j(\mathbf{r}')|^2 \quad (27)$$

which has the simple interpretation of the **mean-field potential** generated by folding the interaction with the density distribution of nucleons.

□ The last term is the **exchange term**; together with the average potential it defines the **mean field**.

□ The **Hartree-Fock approximation** is often called the **mean-field approximation**.

The Hartree-Fock Equations

$$\varepsilon_k \phi_k(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 \phi_k(\mathbf{r}) + \underbrace{U(\mathbf{r}) \phi_k(\mathbf{r})}_{\text{direct term}} - \sum_{j=1}^A \phi_j(\mathbf{r}) \int d^3 r' v(\mathbf{r}' - \mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}') \quad (28)$$

exchange term

- ❑ The Hartree-Fock equations show a mechanism by which the nucleons themselves can produce a **strong central field in a nucleus**.
- ❑ The **assumption** of the Hartree-Fock approximation was the **neglect of correlations**, arising from direct particle-particle scattering not mediated by the mean field. This is reasonable if the scattering is prohibited by the **Pauli principle**, so that an inordinately large amount of energy is needed for the process. The **correlations are, however, important for the excited states**.
- ❑ The full two-body interaction - to the extent that it is not included in the mean field - is called the **residual interaction**. One important part of it is taken into account by the **pairing force**; other contributions lead to correlated excitations.
- ❑ The Hartree-Fock equations form a **self-consistent problem** in the sense that the wave functions determine the mean field, while the mean field in turn determines the wave functions. In practice this leads to **iterative solutions** in which one starts from an **initial guess for the wave functions**, such as harmonic-oscillator states and determines the mean field from them. Solving the Schrödinger equations then yields a new set of wave functions, and this process is repeated until, hopefully, convergence is achieved.

Properties of the states of the many-body system

Let's investigate the **properties of the states of the many-body system** in the Hartree-Fock approximation.

- The **ground state** is given by (index m refers to occupied states only):

$$|\text{HF}\rangle = \prod_m \hat{a}_m^\dagger |0\rangle$$

Its energy can be evaluated by using the methods developed above:

$$E_{\text{HF}} = \langle \text{HF} | \hat{H} | \text{HF} \rangle = \sum_m t_{mm} + \frac{1}{2} \sum_{mn} \bar{v}_{mnmn} \stackrel{\text{using (25)}}{=} \sum_m \varepsilon_m - \frac{1}{2} \sum_{mn} \bar{v}_{mnmn}$$

→ the energy of the Hartree-Fock ground state is not simply the sum of the individual single-particle energies, but has an **additional contribution** from the **potential interactions**.

The mathematical reason is that the Hamiltonian of the many-particle system is not the sum of the single-particle Hamiltonians, but contains the interactions weighted differently.

Properties of the states of the many-body system

■ Let's now construct **excited states** based on the Hartree-Fock ground state: these should simply be given by the particle-hole excitations of various orders.


Construct excited states as **one-particle/one-hole (1p1h) excitations** :

$$|mi\rangle = \hat{a}_m^\dagger \hat{a}_i |HF\rangle$$

or **two-particle/two-hole (2p2h) excitations** :

$$|mnij\rangle = \hat{a}_m^\dagger \hat{a}_n^\dagger \hat{a}_i \hat{a}_j |HF\rangle$$

The expectation value of the energy of (1p1h) states:

$$E_{mi} = \langle mi | \hat{H} | mi \rangle = E_{\text{HF}} + t_{mm} - t_{ii} + \sum_{\substack{k=1 \\ k \neq i}}^A (\bar{v}_{mnmn} - \bar{v}_{inin}) = E_{\text{HF}} + \epsilon_m - \epsilon_i - \bar{v}_{mimi}$$


Thus in addition to the expected contribution from the single-particle energies of the two particles involved, there is also one arising from the change in the mean field.

Properties of the states of the many-body system

A similar analysis also sheds light on the physical meaning of the single-particle energies ε_k . **Compare the energy** of the nucleus with **A nucleons** to that of the nucleus with **A - 1 nucleons**, for example, with one particle removed from the occupied state j . The latter is described by the wave function

$$|j\rangle = \hat{a}_j |\text{HF}\rangle$$

Its energy is given by

$$E_j = \sum_{i \neq j} t_{ii} + \frac{1}{2} \sum_{i_1, i_2 \neq j} \bar{v}_{i_1 i_2 i_1 i_2}$$

and the difference from the ground-state energy becomes

$$E_j - E_{\text{HF}} = -t_{jj} - \frac{1}{2} \sum_i \bar{v}_{ijij} - \frac{1}{2} \sum_i \bar{v}_{jiji} = -t_{jj} - \sum_i \bar{v}_{ijij} = -\varepsilon_j$$

Here the symmetry of the matrix elements $\bar{v}_{ijij} = \bar{v}_{jiji}$ was used.

Thus the **single-particle energy** indicates the energy required to remove a particle from the nucleus. This is the contents of **Koopman's theorem**.

➔ The results of Hartree-Fock calculations can be used not only to predict the **bulk properties** of the nuclear ground state, such as the binding energy, mean square radius, surface thickness, and so on, but also for the **description of excited states**.