

### Why Hartree-Fock?

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

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

with the Hartree-Fock Hamiltonian defined as

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

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

that is to find a local minimum with a Slater determinant  $\Phi_0$  being the ansatz for the ground state.

### Why Hartree-Fock?

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

$$\langle 
ho | \hat{h}^{
m HF} | q 
angle = \langle 
ho | \hat{f} | q 
angle = \langle 
ho | \hat{t} + \hat{u}_{
m ext} | q 
angle + \sum_{i < F} \langle 
ho i | \hat{V} | q i 
angle_{AS},$$

meaning that

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

The so-called Hartree-Fock potential  $\hat{u}^{\rm HF}$  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

#### 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

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

(2)

with

The onebody part  $u_{\mathrm{ext}}(x_i)$  is normally approximated by a harmonic oscillator or Woods-Saxon potential or for electronic systems 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.

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

#### Definitions and notations

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

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

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

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

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

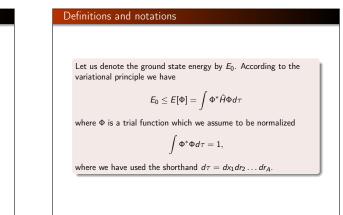
The single-particle function  $\psi_{\alpha}(\mathbf{x}_i)$  are eigenfunctions of the onebody Hamiltonian  $h_i$ , that is

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

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  $\varepsilon_{\alpha}$  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.



### 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

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

A unitary matrix  ${\boldsymbol{\mathsf{A}}}$  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

 $A = A^{\dagger}$ .

#### Basic Matrix Features Matrix Properties Reminder 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 $\sum_k a_{ik}a_{jk}^* = \sum_k a_{ki}^*a_{kj} = \delta_{ij}$

### **Basic Matrix Features**

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

For a given  $n \times n$  matrix **A** we can write its determinant

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

in a more compact form as

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

### Basic Matrix Features, simple $2 \times 2$ determinant

A simple  $2\times 2$  determinant illustrates this. We have

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

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

**Definitions and notations**  
With the above we can rewrite our Slater determinant in a more  
compact form. In the Hartree-Fock method the trial function is the  
Slater determinant of Eq. (3) which can be rewritten as  

$$\Phi(x_1, x_2, \dots, x_A, \alpha, \beta, \dots, \nu) = \frac{1}{\sqrt{A!}} \sum_p (-)^p \hat{P} \psi_\alpha(x_1) \psi_\beta(x_2) \dots \psi_\nu(x_A) =$$
where we have introduced the antisymmetrization operator  $\hat{A}$   
defined by the summation over all possible permutations of two  
particles.  
Definitions and notations  
Lt is defined as  
 $\hat{A} = \frac{1}{A!} \sum_p (-)^p \hat{P},$  (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  
 $\Phi_H(x_1, x_2, \dots, x_A, \alpha, \beta, \dots, \nu) = \psi_\alpha(x_1)\psi_\beta(x_2)\dots\psi_\nu(x_A).$ 

ny two particles and hence commute with $\hat{A}$ $[H_0, \hat{A}] = [H_I, \hat{A}] = 0.$ (5)	Furthermore, Â satisfies	finitions and notations	
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	$\hat{A}^2 = \hat{A},\tag{6}$	$[H_0, \hat{A}] = [H_I, \hat{A}] = 0.$	(5)
	$\hat{A}^2 = \hat{A},\tag{6}$	Furthermore  satisfies	
	since every permutation of the Slater determinant reproduces it.		(6)
ince every permutation of the Slater determinant reproduces it.		since every permutation of the Slater determinant reproduc	es it.

Definitions and notations The expectation value of  $\hat{H}_0$  $\int \Phi^* \hat{H}_0 \Phi d\tau = A! \int \Phi^*_H \hat{A} \hat{H}_0 \hat{A} \Phi_H d\tau$ used to  $\int \Phi^* \hat{H}_0 \Phi d\tau = A! \int \Phi^*_H \hat{H}_0 \hat{A} \Phi_H d\tau,$ is readily reduced to 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  $\int \Phi^* \hat{H}_0 \Phi d au = \sum_{i=1}^A \sum_p (-)^p \int \Phi_H^* \hat{h}_0 \hat{P} \Phi_H d au.$ 

### Definitions and notations

The integral vanishes if two or more particles are permuted in only one of the Hartree-functions  $\Phi_H$  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

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

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

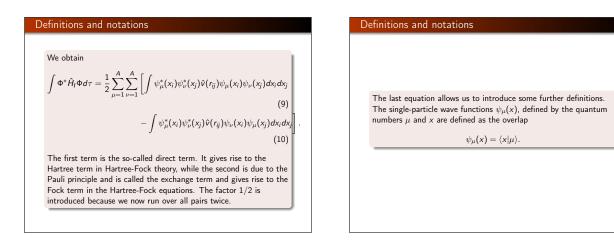
# Definitions and notations The expectation value of the two-body part of the Hamiltonian is obtained in a similar manner. We have $\int \Phi^* \hat{H}_I \Phi d\tau = A! \int \Phi_H^* \hat{A} \hat{H}_I \hat{A} \Phi_H d\tau,$ which reduces to $\int \Phi^* \hat{H}_I \Phi d\tau = \sum_{i \le j=1}^{A} \sum_{\rho} (-)^{\rho} \int \Phi_H^* \hat{v}(r_{ij}) \hat{P} \Phi_H d\tau,$ by following the same arguments as for the one-body Hamiltonian.

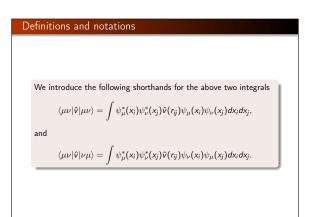
### Definitions and notations

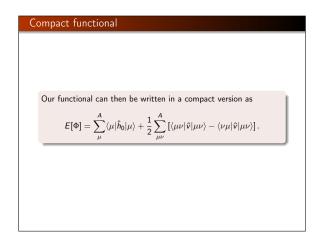
Because of the dependence on the inter-particle distance  $r_{ij}$ , permutations of any two particles no longer vanish, and we get

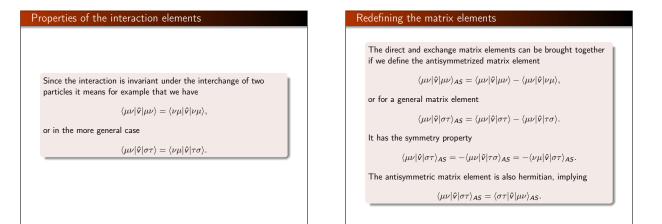
$$\int \Phi^* \hat{H}_I \Phi d au = \sum_{i < j=1}^A \int \Phi^*_H \hat{v}(r_{ij}) (1 - P_{ij}) \Phi_H d au$$

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.









### Rewriting the energy functional

With these notations we rewrite the energy functional as

$$\int \Phi^* \hat{H}_l \Phi d\tau = \frac{1}{2} \sum_{\mu=1}^A \sum_{\nu=1}^A \langle \mu \nu | \hat{\nu} | \mu \nu \rangle_{AS}. \tag{11}$$

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

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

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

### Reminder on Variational Calculus and Lagrangian Multipliers

The calculus of variations involves problems where the quantity to be minimized or maximized is an integral. In the general case we have an integral of the type

$$E[\Phi] = \int_a^b f(\Phi(x), \frac{\partial \Phi}{\partial x}, x) dx,$$

where *E* is the quantity which is sought minimized or maximized. The problem is that although *f* is a function of the variables  $\Phi$ ,  $\partial \Phi / \partial x$  and *x*, the exact dependence of  $\Phi$  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  $\delta E$  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, simple example

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

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

with the constraint

$$dxdydz\psi^*(x, y, z)\psi(x, y, z) = 1,$$

and a Hamiltonian

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

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

### Manipulating terms

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

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

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

### Adding the Lagrangian multiplier

The constraint appears in integral form as

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

and multiplying with a Lagrangian multiplier  $\lambda$  and taking the variational minimum we obtain the final variational equation

$$\delta\left\{\int d\mathsf{x}d\mathsf{y}d\mathsf{z}\left(\frac{1}{2}\nabla\psi^*\nabla\psi+V\psi^*\psi-\lambda\psi^*\psi\right)\right\}=0$$

We introduce the function  $\boldsymbol{f}$ 

$$f = \frac{1}{2} \nabla \psi^* \nabla \psi + V \psi^* \psi - \lambda \psi^* \psi = \frac{1}{2} (\psi_x^* \psi_x + \psi_y^* \psi_y + \psi_z^* \psi_z) + V \psi^* \psi - \lambda \psi^* \psi$$

where we have skipped the dependence on x, y, z and introduced the shorthand  $\psi_x, \psi_y$  and  $\psi_z$  for the various derivatives.

### And with the Euler-Lagrange equations we get

For  $\psi^*$  the Euler-Lagrange equations yield

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\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,
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which results in

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

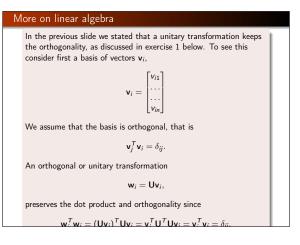
We can then identify the Lagrangian multiplier as the energy of the system. The last equation is nothing but the standard Schroedinger equation and the variational approach discussed here provides a powerful method for obtaining approximate solutions of the wave function.

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

In deriving the Hartree-Fock equations, we will expand the single-particle functions in a known basis and vary the coefficients, that is, the new single-particle wave function is written as a linear expansion in terms of a fixed chosen orthogonal basis (for example the well-known harmonic oscillator functions or the hydrogen-like functions etc). We define our new Hartree-Fock single-particle basis by performing a unitary transformation on our previous basis (labelled with greek indices) as

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

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  $\phi_{\lambda}$  is orthogonal. A unitary transformation keeps the orthogonality, as discussed in exercise 1 below.



### Coefficients of a wave function expansion

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

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

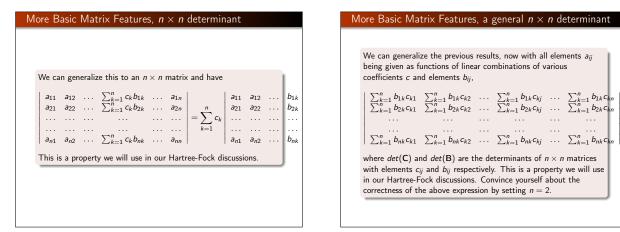
orthogonality is preserved, that is  $\langle \alpha | \beta \rangle = \delta_{\alpha\beta}$  and  $\langle p | q \rangle = \delta_{\rho q}$ . This propertry is extremely useful when we build up a basis of many-body Stater determinant based states.

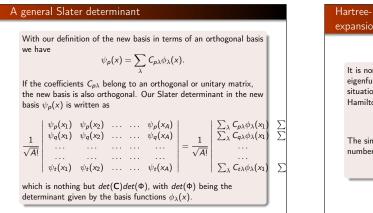
Note also that although a basis  $|\alpha\rangle$  contains an infinity of states, for practical calculations we have always to make some truncations.

### More Basic Matrix Features, simple $2 \times 2$ determinant, useful property of determinants

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

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







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  $\lambda$  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  $ijkl \cdots \ge F$  for so-called single-hole states and  $abcd \cdots > F$  for so-called particle states. For general single-particle states we employ the labels  $pars \ldots$ 

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

In Eq. (12), restated here

$$E[\Phi] = \sum_{\mu=1}^{A} \langle \mu | h | \mu 
angle + rac{1}{2} \sum_{\mu=1}^{A} \sum_{
u=1}^{A} \langle \mu 
u | \hat{
u} | \mu 
u 
angle_{\mathcal{AS}},$$

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

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

where  $\Phi^{\textit{HF}}$  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  

$$E[\Psi] = \sum_{i=1}^{A} \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | h | \beta \rangle + \frac{1}{2} \sum_{ij=1}^{A} \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha \beta | \hat{\nu} | \gamma \delta \rangle_{AS}.$$
(15)  
(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  
 $\langle i|j \rangle = \delta_{i,j} = \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | \beta \rangle = \sum_{\alpha} C_{i\alpha}^* C_{i\alpha},$   
which allows us to define a functional to be minimized that reads  
 $F[\Phi^{HF}] = E[\Phi^{HF}] - \sum_{i=1}^{A} \epsilon_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha}.$  (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  $\alpha$  (recalling  
that the coefficients  $C_{i\alpha}$  are matrix elements of a unitary (or  
orthogonal for a real symmetric matrix) matrix) the following  
Hartree-Fock equations  
 $\sum_\beta C_{i\beta} \langle \alpha | h | \beta \rangle + \sum_{j=1}^A \sum_{\beta \gamma \delta} C_{j\beta}^* C_{j\delta} C_{i\gamma} \langle \alpha \beta | \hat{v} | \gamma \delta \rangle_{AS} = \epsilon_i^{HF} C_{i\alpha}.$ 

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

We can rewrite this equation as (changing dummy variables)

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

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

Hartree-Fock by varying the coefficients of a wave function  
expansion  
  
Defining  
$$h_{\alpha\beta}^{HF} = \langle \alpha | h | \beta \rangle + \sum_{j=1}^{A} \sum_{\gamma \delta} C_{j\gamma}^* C_{j\delta} \langle \alpha \gamma | \hat{v} | \beta \delta \rangle_{AS},$$
we can rewrite the new equations as  
$$\sum_{\gamma} h_{\alpha\beta}^{HF} C_{i\beta} = \epsilon_i^{HF} C_{i\alpha}.$$
(17)  
The latter is nothing but a standard eigenvalue problem.  
It suffices to tabulate the matrix elements  $\langle \alpha | h | \beta \rangle$  and

It suffices to tabulate the matrix elements  $\langle \alpha | h | \beta \rangle$  and  $\langle \alpha \gamma | \hat{\nu} | \beta \delta \rangle_{AS}$  once and for all. Successive iterations require thus only a look-up in tables over one-body and two-body matrix elements. These details will be discussed below when we solve the Hartree-Fock equations numerically.

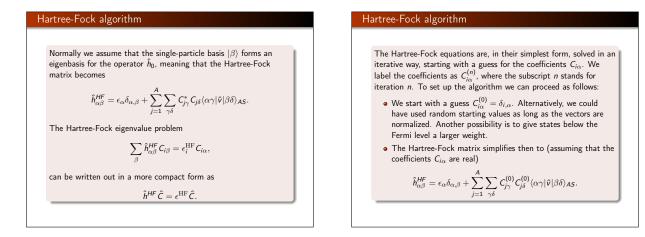
### Hartree-Fock algorithm

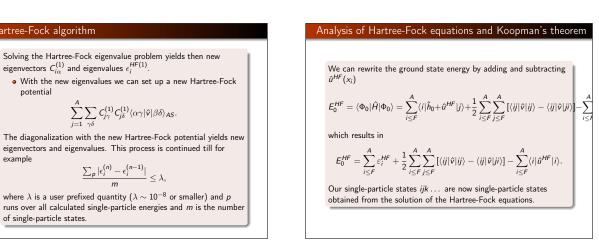
Our Hartree-Fock matrix is thus

ĥ

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

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





Analysis of Hartree-Fock equations and Koopman's theorem  
Using our definition of the Hartree-Fock single-particle energies we  
obtain then the following expression for the total ground-state  
energy  

$$E_0^{HF} = \sum_{i \leq F}^{A} \varepsilon_i - \frac{1}{2} \sum_{i \leq F}^{A} \sum_{j \leq F}^{A} [\langle ij | \hat{v} | j \rangle - \langle ij | \hat{v} | j \rangle].$$
This form will be used in our discussion of Koopman's theorem.

Hartree-Fock algorithm

potential

of single-particle states.

example

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Atomic physics case

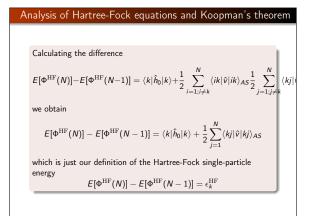
We have

$$E[\Phi^{\mathrm{HF}}(N)] = \sum_{i=1}^{H} \langle i|\hat{h}_{0}|i\rangle + rac{1}{2} \sum_{ij=1}^{N} \langle ij|\hat{v}|ij
angle_{AS},$$

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

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

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



#### Analysis of Hartree-Fock equations and Koopman's theorem

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

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

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

### Analysis of Hartree-Fock equations and Koopman's theorem

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

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

where  $\Phi^{\mathrm{HF}}(A)$  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 th enumber 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

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

nalysis of Hartree-Fock equations and Koopman's theorer
Calculating the difference
$E[\Phi^{\rm HF}(A)] - E[\Phi^{\rm HF}(A-1)] = \langle k \hat{h}_0 k\rangle + \frac{1}{2} \sum_{i=1;i\neq k}^{A} \langle ik \hat{v} ik\rangle_{AS} \frac{1}{2} \sum_{j=1;j\neq k}^{A} \langle ik \hat{v} ik\rangle_{AS} \frac{1}{2} \sum_{j=1}^{A} \langle ik \hat{v} ik\rangle_{AS} \frac{1}{2} \sum_{j=1$
which becomes
$E[\Phi^{\mathrm{HF}}(\mathcal{A})] - E[\Phi^{\mathrm{HF}}(\mathcal{A}-1)] = \langle k \hat{h}_0 k angle + rac{1}{2}\sum_{j=1}^A \langle kj \hat{v} kj angle_{\mathcal{AS}}$
which is just our definition of the Hartree-Fock single-particle
energy $E[\Phi^{\mathrm{HF}}(A)] - E[\Phi^{\mathrm{HF}}(A-1)] = \epsilon^{\mathrm{HF}}_k$

#### Analysis of Hartree-Fock equations and Koopman's theorem

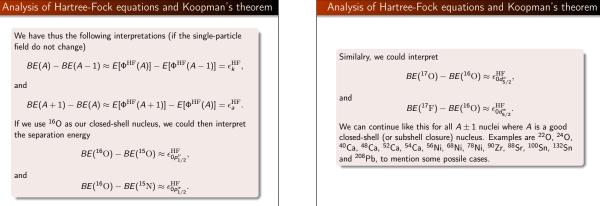
Similarly, we can now compute the difference (recall that the single-particle states abcd > F)

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

If we then recall that the binding energy differences

$$BE(A) - BE(A-1)$$
 and  $BE(A+1) - BE(A)$ ,

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.



### $BE(^{17}O) - BE(^{16}O) \approx \epsilon_{0d_{\nu',n}}^{HF}$ $BE(^{17}F) - BE(^{16}O) \approx \epsilon_{0d^{\pi}}^{HF}$ We can continue like this for all $A \pm 1$ nuclei where A is a good closed-shell (or subshell closure) nucleus. Examples are <sup>22</sup>O, <sup>24</sup>O, 40Ca, 48Ca, 52Ca, 54Ca, 56Ni, 68Ni, 78Ni, 90Zr, 88Sr, 100Sn, 132Sn and <sup>208</sup>Pb, to mention some possile 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 $\Delta S_n = 2BE(N, Z) - BE(N, Z-1) - BE(N, Z+1),$ we can define the neutron and proton energy gaps for <sup>16</sup>O as $\Delta S_{\nu} = \epsilon_{0d_{\nu}\nu}^{\rm HF} - \epsilon_{0p_{\nu}\nu}^{\rm HF},$ and $\Delta S_{\pi} = \epsilon_{0d_{\pi/2}}^{\rm HF} - \epsilon_{0p_{\pi/2}}^{\rm HF}.$

Consider a Slater determinant built up of orthogonal single-particle orbitals  $\psi_{\lambda}$ , with  $\lambda = 1, 2, \dots, A$ . The unitary transformation

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

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

a) Show that the new basis is orthogonal. b) Show that the new Slater determinant constructed from the new single-particle wave functions can be written as the determinant based on the previous basis and the determinant of the matrix C. c) Show that the old and the new Slater determinants are equal up to a complex constant with absolute value unity. **Hint.** Hint: *C* is a unitary matrix.

We will assume that we can build various Slater determinants using an orthogonal single-particle basis  $\psi_{\lambda}$ , with  $\lambda = 1, 2, \dots, A$ .

The aim of this exercise is to set up specific matrix elements that will turn useful when we start our discussions of the nuclear shell model. In particular you will notice, depending on the character of the operator, that many matrix elements will actually be zero.

Consider three *A*-particle Slater determinants  $|\Phi_0, |\Phi_i^a\rangle$  and  $|\Phi_{ii}^{ab}\rangle$ , where the notation means that Slater determinant  $|\Phi^a\rangle$  differs from  $|\Phi_0\rangle$  by one single-particle state, that is a single-particle state  $\psi_i$  is replaced by a single-particle state  $\psi_a$ . It will later be interpreted as a so-called one-particle-one-hole excitation. Similarly, the Slater determinant  $|\Phi_{ab}^{ab}\rangle$  differs by two single-particle states from  $|\Phi_{0}\rangle$ and is normally thought of as a two-particle-two-hole excitation.

Define a general onebody operator  $\hat{F} = \sum_{i}^{A} \hat{f}(x_i)$  and a general twobody operator  $\hat{G} = \sum_{i>j}^{A} \hat{g}(x_i, x_j)$  with g being invariant under the interchange of the coordinates of particles i and j. You can use here the results from the second exercise set, exercise 3.

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 <sup>16</sup>O or <sup>40</sup>Ca. The single-particle energies obtained by solving the Hartree-Fock equations can then be directly related to experimental separation energies. For those of you interested in such studies, the program you will end up developing here can be used in later projects, with simple extensions. 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  $\hat{\mu} = \sum_{i=1}^{N} \hat{\rho}_{i}^{2} + \sum_{i=1}^{N} \frac{1}{m_{i}m^{2}} + \sum_{i=1}^{N} \hat{V}_{i}$ 

a) Calculate