

Week 40: Mean-field theories, stability of Hartree-Fock equations and the homogeneous electron gas

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Week 40, September 30-October 4

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Week 40, September 30-October 4, 2024

1. Topics to be covered

1.1 Thursday:

- 1.1.1 Efficient ways of implementing the Hartree-Fock algorithm,
- 1.1.2 Thouless' theorem and stability of Hartree-Fock equations
- 1.1.3 Video of lecture
- 1.1.4 Whiteboard notes

1.2 Friday:

- 1.2.1 Stability of Hartree-Fock equations and Thouless' theorem
- 1.2.2 The homogeneous electron gas in three dimensions
- 1.2.3 Video of lecture TBA
- 1.2.4 Whiteboard notes

2. Lecture Material: These slides and Szabo and Ostlund, sections 3.1-3.4

3. Seventh exercise set at

<https://github.com/ManyBodyPhysics/FYS4480/blob/master/doc/Exercises/2024/ExercisesWeek40.pdf>

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

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

$$\psi_p^{HF} = \sum_{\lambda} C_{p\lambda} \phi_{\lambda}. \quad (1)$$

In this case we vary the coefficients $C_{p\lambda}$. If the basis has infinitely many solutions, we need to truncate the above sum. We assume that the basis ϕ_{λ} is orthogonal.

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 deriving the Hartree-Fock equations, we will expand the single-particle functions in a known basis and vary the coefficients, that is, the new single-particle wave function is written as a linear expansion in terms of a fixed chosen orthogonal basis (for example the well-known harmonic oscillator functions or the hydrogen-like functions etc).

We stated that a unitary transformation keeps the orthogonality. To see this consider first a basis of vectors v_i ,

$$v_i = \begin{bmatrix} v_{i1} \\ \dots \\ v_{in} \end{bmatrix}$$

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

We assume that the basis is orthogonal, that is

$$\mathbf{v}_j^T \mathbf{v}_i = \delta_{ij}.$$

An orthogonal or unitary transformation

$$\mathbf{w}_i = \mathbf{U} \mathbf{v}_i,$$

preserves the dot product and orthogonality since

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

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

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

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

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

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

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

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. This applies also to our previous discussion on full configuration interaction theory. Consider the following determinant

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

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

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

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

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

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

We can generalize the previous results, now with all elements a_{ij} being given as functions of linear combinations of various coefficients c and elements b_{ij} ,

$$\begin{vmatrix} \sum_{k=1}^n b_{1k} c_{k1} & \sum_{k=1}^n b_{1k} c_{k2} & \cdots & \sum_{k=1}^n b_{1k} c_{kj} & \cdots & \sum_{k=1}^n b_{1k} c_{kn} \\ \sum_{k=1}^n b_{2k} c_{k1} & \sum_{k=1}^n b_{2k} c_{k2} & \cdots & \sum_{k=1}^n b_{2k} c_{kj} & \cdots & \sum_{k=1}^n b_{2k} c_{kn} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \sum_{k=1}^n b_{nk} c_{k1} & \sum_{k=1}^n b_{nk} c_{k2} & \cdots & \sum_{k=1}^n b_{nk} c_{kj} & \cdots & \sum_{k=1}^n b_{nk} c_{kn} \end{vmatrix} =$$

where $\det(C)$ and $\det(B)$ are the determinants of $n \times n$ matrices with elements c_{ij} and b_{ij} respectively. This is a property we will use in our Hartree-Fock discussions. Convince yourself about the correctness of the above expression by setting $n = 2$.

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

With our definition of the new basis in terms of an orthogonal basis we have

$$\psi_p(x) = \sum_{\lambda} C_{p\lambda} \phi_{\lambda}(x).$$

If the coefficients $C_{p\lambda}$ belong to an orthogonal or unitary matrix, the new basis is also orthogonal. Our Slater determinant in the new basis $\psi_p(x)$ is written as

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

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

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

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 $pqrs \dots$.

We have

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

we found the expression for the energy functional in terms of the basis function $\phi_\lambda(r)$. We then varied the above energy functional with respect to the basis functions $|\mu\rangle$.

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

Now we are interested in defining a new basis defined in terms of a chosen basis as defined in Eq. (1). We can then rewrite the energy functional as

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

where Φ^{HF} is the new Slater determinant defined by the new basis of Eq. (1).

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

Using Eq. (1) we can rewrite Eq. (2) as

$$E[\Psi] = \sum_{i=1}^N \sum_{\alpha\beta} C_{i\alpha}^* C_{i\beta} \langle \alpha | h | \beta \rangle + \frac{1}{2} \sum_{ij=1}^N \sum_{\alpha\beta\gamma\delta} C_{i\alpha}^* C_{j\beta}^* C_{i\gamma} C_{j\delta} \langle \alpha\beta | \hat{v} | \gamma\delta \rangle_{AS}. \quad (3)$$

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

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

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

$$F[\Phi^{HF}] = E[\Phi^{HF}] - \sum_{i=1}^N \epsilon_i \sum_{\alpha} C_{i\alpha}^* C_{i\alpha}. \quad (4)$$

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

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

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

We can rewrite this equation as (changing dummy variables)

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

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

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

Defining

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

we can rewrite the new equations as

$$\sum_{\beta} h_{\alpha\beta}^{HF} C_{i\beta} = \epsilon_i^{HF} C_{i\alpha}. \quad (5)$$

The latter is nothing but a standard eigenvalue problem.

We see that we do not need to compute any integrals in an iterative procedure for solving the equations. It suffices to tabulate the matrix elements $\langle \alpha | h | \beta \rangle$ and $\langle \alpha\gamma | \hat{v} | \beta\delta \rangle_{AS}$ once and for all. Successive iterations require thus only a look-up in tables over one-body and two-body matrix elements. These details will be discussed below when we solve the Hartree-Fock equations numerically.

Hartree-Fock algorithm

Our Hartree-Fock matrix is thus

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

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

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

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

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

The Hartree-Fock eigenvalue problem

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

can be written out in a more compact form as

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

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

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)

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

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

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

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

The diagonalization with the new Hartree-Fock potential yields new eigenvectors and eigenvalues. This process is continued till for example

$$\frac{\sum_p |\epsilon_i^{(n)} - \epsilon_i^{(n-1)}|}{m} \leq \lambda,$$

where λ is a user prefixed quantity ($\lambda \sim 10^{-8}$ or smaller) and p runs over all calculated single-particle energies and m is the number of single-particle states.

Using the density matrix

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

$$\rho_{\gamma\delta} = \sum_{i=1}^N \langle \gamma | i \rangle \langle i | \delta \rangle = \sum_{i=1}^N C_{i\gamma} C_{i\delta}^*. \quad (6)$$

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

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

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

Code example

```
import numpy as np
class HartreeFock:
    def __init__(self, num_electrons, num_orbitals):
        self.num_electrons = num_electrons
        self.num_orbitals = num_orbitals
        # You would need to replace these by proper integrals
        self.h = np.random.rand(num_orbitals, num_orbitals) # One-ele
        self.coulomb = np.random.rand(num_orbitals, num_orbitals, num_
    def build_fock_matrix(self, density_matrix):
        fock_matrix = self.h.copy()
        for i in range(self.num_orbitals):
            for j in range(self.num_orbitals):
                fock_matrix[i, j] += np.sum(density_matrix * self.coul
        return fock_matrix
    def build_density_matrix(self, coefficients):
        density_matrix = np.zeros((self.num_orbitals, self.num_orbital
        for i in range(self.num_electrons):
            density_matrix += np.outer(coefficients[:, i], coefficient
        return density_matrix
    def diagonalize(self, fock_matrix):
        energy, coefficients = np.linalg.eigh(fock_matrix)
        return energy, coefficients
    def run(self, max_iter=100, tol=1e-6):
        coeffs = np.zeros((self.num_orbitals, self.num_electrons))
        density_matrix = np.zeros((self.num_orbitals, self.num_orbital
        for iteration in range(max_iter):
            fock_matrix = self.build_fock_matrix(density_matrix)
            energies, coeffs = self.diagonalize(fock_matrix)
```


Hartree-Fock in second quantization and stability of HF solution

We wish now to derive the Hartree-Fock equations using our second-quantized formalism and study the stability of the equations. Our ansatz for the ground state of the system is approximated as (this is our representation of a Slater determinant in second quantization)

$$|\Phi_0\rangle = |c\rangle = a_i^\dagger a_j^\dagger \dots a_l^\dagger |0\rangle.$$

We wish to determine \hat{u}^{HF} so that $E_0^{HF} = \langle c | \hat{H} | c \rangle$ becomes a local minimum.

In our analysis here we will need Thouless' theorem, which states that an arbitrary Slater determinant $|c'\rangle$ which is not orthogonal to

a determinant $|c\rangle = \prod_{i=1}^n a_{\alpha_i}^\dagger |0\rangle$, can be written as

$$|c'\rangle = \exp \left\{ \sum_{a>F} \sum_{i\leq F} C_{ai} a_a^\dagger a_i \right\} |c\rangle$$

Thouless' theorem

Let us give a simple proof of Thouless' theorem. The theorem states that we can make a linear combination of particle-hole excitations with respect to a given reference state $|c\rangle$. With this linear combination, we can make a new Slater determinant $|c'\rangle$ which is not orthogonal to $|c\rangle$, that is

$$\langle c|c'\rangle \neq 0.$$

To show this we need some intermediate steps. The exponential product of two operators $\exp \hat{A} \times \exp \hat{B}$ is equal to $\exp(\hat{A} + \hat{B})$ only if the two operators commute, that is

$$[\hat{A}, \hat{B}] = 0.$$

Thouless' theorem

If the operators do not commute, we need to resort to the Baker-Campbell-Hauersdorf. This relation states that

$$\exp \hat{C} = \exp \hat{A} \exp \hat{B},$$

with

$$\hat{C} = \hat{A} + \hat{B} + \frac{1}{2}[\hat{A}, \hat{B}] + \frac{1}{12}[[\hat{A}, \hat{B}], \hat{B}] - \frac{1}{12}[[\hat{A}, \hat{B}], \hat{A}] + \dots$$

Thouless' theorem

From these relations, we note that in our expression for $|c'\rangle$ we have commutators of the type

$$[a_a^\dagger a_i, a_b^\dagger a_j],$$

and it is easy to convince oneself that these commutators, or higher powers thereof, are all zero. This means that we can write out our new representation of a Slater determinant as

$$|c'\rangle = \exp \left\{ \sum_{a>F} \sum_{i\leq F} C_{ai} a_a^\dagger a_i \right\} |c\rangle = \prod_i \left\{ 1 + \sum_{a>F} C_{ai} a_a^\dagger a_i + \left(\sum_{a>F} C_{ai} a_a^\dagger a_i \right) \right.$$

Thouless' theorem

We note that

$$\prod_i \sum_{a>F} C_{ai} a_a^\dagger a_i \sum_{b>F} C_{bi} a_b^\dagger a_i |c\rangle = 0,$$

and all higher-order powers of these combinations of creation and annihilation operators disappear due to the fact that $(a_i)^n |c\rangle = 0$ when $n > 1$. This allows us to rewrite the expression for $|c'\rangle$ as

$$|c'\rangle = \prod_i \left\{ 1 + \sum_{a>F} C_{ai} a_a^\dagger a_i \right\} |c\rangle,$$

which we can rewrite as

$$|c'\rangle = \prod_i \left\{ 1 + \sum_{a>F} C_{ai} a_a^\dagger a_i \right\} |a_{i_1}^\dagger a_{i_2}^\dagger \dots a_{i_n}^\dagger |0\rangle.$$

Thouless' theorem

The last equation can be written as

$$|c'\rangle = \prod_i \left\{ 1 + \sum_{a>F} C_{ai} a_a^\dagger a_i \right\} |a_{i_1}^\dagger a_{i_2}^\dagger \dots a_{i_n}^\dagger |0\rangle = \left(1 + \sum_{a>F} C_{ai_1} a_a^\dagger a_{i_1} \right) a_{i_1}^\dagger \quad (7)$$

$$\times \left(1 + \sum_{a>F} C_{ai_2} a_a^\dagger a_{i_2} \right) a_{i_2}^\dagger \dots |0\rangle = \prod_i \left(a_i^\dagger + \sum_{a>F} C_{ai} a_a^\dagger \right) |0\rangle. \quad (8)$$

New operators

If we define a new creation operator

$$b_i^\dagger = a_i^\dagger + \sum_{a>F} C_{ai} a_a^\dagger, \quad (9)$$

we have

$$|c'\rangle = \prod_i b_i^\dagger |0\rangle = \prod_i \left(a_i^\dagger + \sum_{a>F} C_{ai} a_a^\dagger \right) |0\rangle,$$

meaning that the new representation of the Slater determinant in second quantization, $|c'\rangle$, looks like our previous ones. However, this representation is not general enough since we have a restriction on the sum over single-particle states in Eq. (9). The single-particle states have all to be above the Fermi level.

Thouless' theorem

The question then is whether we can construct a general representation of a Slater determinant with a creation operator

$$\tilde{b}_i^\dagger = \sum_p f_{ip} a_p^\dagger,$$

where f_{ip} is a matrix element of a unitary matrix which transforms our creation and annihilation operators a^\dagger and a to \tilde{b}^\dagger and \tilde{b} . These new operators define a new representation of a Slater determinant as

$$|\tilde{c}\rangle = \prod_i \tilde{b}_i^\dagger |0\rangle.$$

Showing that $|\tilde{c}\rangle = |c'\rangle$

We need to show that $|\tilde{c}\rangle = |c'\rangle$. We need also to assume that the new state is not orthogonal to $|c\rangle$, that is $\langle c|\tilde{c}\rangle \neq 0$. From this it follows that

$$\langle c|\tilde{c}\rangle = \langle 0|a_{i_n} \dots a_{i_1} \left(\sum_{p=i_1}^{i_n} f_{i_1 p} a_p^\dagger \right) \left(\sum_{q=i_1}^{i_n} f_{i_2 q} a_q^\dagger \right) \dots \left(\sum_{t=i_1}^{i_n} f_{i_n t} a_t^\dagger \right) |0\rangle,$$

which is nothing but the determinant $\det(f_{ip})$ which we can, using the intermediate normalization condition, normalize to one, that is

$$\det(f_{ip}) = 1,$$

meaning that f has an inverse defined as (since we are dealing with orthogonal, and in our case unitary as well, transformations)

$$\sum_k f_{ik} f_{kj}^{-1} = \delta_{ij},$$

and

$$\sum_j f_{ij}^{-1} f_{jk} = \delta_{ik}.$$

Thouless' theorem

Using these relations we can then define the linear combination of creation (and annihilation as well) operators as

$$\sum_i f_{ki}^{-1} \tilde{b}_i^\dagger = \sum_i f_{ki}^{-1} \sum_{p=i_1}^{\infty} f_{ip} a_p^\dagger = a_k^\dagger + \sum_i \sum_{p=i_{n+1}}^{\infty} f_{ki}^{-1} f_{ip} a_p^\dagger.$$

Defining

$$c_{kp} = \sum_{i \leq F} f_{ki}^{-1} f_{ip},$$

we can redefine

$$a_k^\dagger + \sum_i \sum_{p=i_{n+1}}^{\infty} f_{ki}^{-1} f_{ip} a_p^\dagger = a_k^\dagger + \sum_{p=i_{n+1}}^{\infty} c_{kp} a_p^\dagger = b_k^\dagger,$$

our starting point.

Thouless' theorem

We have shown that our general representation of a Slater determinant

$$|\tilde{c}\rangle = \prod_i \tilde{b}_i^\dagger |0\rangle = |c'\rangle = \prod_i b_i^\dagger |0\rangle,$$

with

$$b_k^\dagger = a_k^\dagger + \sum_{p=i_{n+1}}^{\infty} c_{kp} a_p^\dagger.$$

Thouless' theorem

This means that we can actually write an ansatz for the ground state of the system as a linear combination of terms which contain the ansatz itself $|c\rangle$ with an admixture from an infinity of one-particle-one-hole states. The latter has important consequences when we wish to interpret the Hartree-Fock equations and their stability. We can rewrite the new representation as

$$|c'\rangle = |c\rangle + |\delta c\rangle,$$

where $|\delta c\rangle$ can now be interpreted as a small variation. If we approximate this term with contributions from one-particle-one-hole ($1p$ - $1h$) states only, we arrive at

$$|c'\rangle = \left(1 + \sum_{ai} \delta C_{ai} a_a^\dagger a_i \right) |c\rangle.$$

Thouless' theorem

In our derivation of the Hartree-Fock equations we have shown that

$$\langle \delta c | \hat{H} | c \rangle = 0,$$

which means that we have to satisfy

$$\langle c | \sum_{ai} \delta C_{ai} \{ a_a^\dagger a_i \} \hat{H} | c \rangle = 0.$$

With this as a background, we are now ready to study the stability of the Hartree-Fock equations. This is the topic for week 40.

Hartree-Fock in second quantization and stability of HF solution

The variational condition for deriving the Hartree-Fock equations guarantees only that the expectation value $\langle c | \hat{H} | c \rangle$ has an extreme value, not necessarily a minimum. To figure out whether the extreme value we have found is a minimum, we can use second quantization to analyze our results and find a criterion for the above expectation value to a local minimum. We will use Thouless' theorem and show that

$$\frac{\langle c' | \hat{H} | c' \rangle}{\langle c' | c' \rangle} \geq \langle c | \hat{H} | c \rangle = E_0,$$

with

$$|c'\rangle = |c\rangle + |\delta c\rangle.$$

Using Thouless' theorem we can write out $|c'\rangle$ as

$$|c'\rangle = \exp \left\{ \sum_{a>F} \sum_{i\leq F} \delta C_{ai} a_a^\dagger a_i \right\} |c\rangle \quad (10)$$

The infinite electron gas

The electron gas is perhaps the only realistic model of a system of many interacting particles that allows for an analytical solution of the Hartree-Fock equations. Furthermore, to first order in the interaction, one can also obtain an analytical expression for the total energy and several other properties of a many-particle systems. The model gives a very good approximation to the properties of valence electrons in metals. The assumptions are

- ▶ System of electrons that is not influenced by external forces except by an attraction provided by a uniform background of ions. These ions give rise to a uniform background charge. The ions are stationary.
- ▶ The system as a whole is neutral.
- ▶ We assume we have N_e electrons in a cubic box of length L and volume $\Omega = L^3$. This volume contains also a uniform distribution of positive charge with density $N_e e / \Omega$.

The infinite electron gas and environment

The homogeneous electron gas is a system of electrons that is not influenced by external forces except by an attraction provided by a uniform background of ions. These ions give rise to a uniform background charge. The ions are stationary and the system as a whole is neutral. Irrespective of this simplicity, this system, in both two and three-dimensions, has eluded a proper description of correlations in terms of various first principle methods, except perhaps for quantum Monte Carlo methods. In particular, the diffusion Monte Carlo calculations of [Ceperley](#) and [Ceperley and Tanatar](#) are presently still considered as the best possible benchmarks for the two- and three-dimensional electron gas.

The infinite electron gas, test-bed for many-body theories

The electron gas, in two or three dimensions is thus interesting as a test-bed for electron-electron correlations. The three-dimensional electron gas is particularly important as a cornerstone of the local-density approximation in density-functional theory. In the physical world, systems similar to the three-dimensional electron gas can be found in, for example, alkali metals and doped semiconductors. Two-dimensional electron fluids are observed on metal and liquid-helium surfaces, as well as at metal-oxide-semiconductor interfaces. However, the Coulomb interaction has an infinite range, and therefore long-range correlations play an essential role in the electron gas.

The infinite electron gas at low densities

At low densities, the electrons become localized and form a lattice. This so-called Wigner crystallization is a direct consequence of the long-ranged repulsive interaction. At higher densities, the electron gas is better described as a liquid. When using, for example, Monte Carlo methods the electron gas must be approximated by a finite system. The long-range Coulomb interaction in the electron gas causes additional finite-size effects that are not present in other infinite systems like nuclear matter or neutron star matter. This poses additional challenges to many-body methods when applied to the electron gas.

The infinite electron gas as a homogenous system

This is a homogeneous system and the one-particle wave functions are given by plane wave functions normalized to a volume Ω for a box with length L (the limit $L \rightarrow \infty$ is to be taken after we have computed various expectation values)

$$\psi_{\mathbf{k}\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{k}\mathbf{r})\xi_{\sigma}$$

where \mathbf{k} is the wave number and ξ_{σ} is a spin function for either spin up or down

$$\xi_{\sigma=+1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \xi_{\sigma=-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Periodic boundary conditions

We assume that we have periodic boundary conditions which limit the allowed wave numbers to

$$k_i = \frac{2\pi n_i}{L} \quad i = x, y, z \quad n_i = 0, \pm 1, \pm 2, \dots$$

We assume first that the electrons interact via a central, symmetric and translationally invariant interaction $V(r_{12})$ with $r_{12} = |r_1 - r_2|$. The interaction is spin independent.

The total Hamiltonian consists then of kinetic and potential energy

$$\hat{H} = \hat{T} + \hat{V}.$$

The operator for the kinetic energy can be written as

$$\hat{T} = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma}.$$

Defining the Hamiltonian operator

The Hamiltonian operator is given by

$$\hat{H} = \hat{H}_{el} + \hat{H}_b + \hat{H}_{el-b},$$

with the electronic part

$$\hat{H}_{el} = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{e^2}{2} \sum_{i \neq j} \frac{e^{-\mu|r_i-r_j|}}{|r_i-r_j|},$$

where we have introduced an explicit convergence factor (the limit $\mu \rightarrow 0$ is performed after having calculated the various integrals).

Correspondingly, we have

$$\hat{H}_b = \frac{e^2}{2} \int \int dr dr' \frac{n(r)n(r')e^{-\mu|r-r'|}}{|r-r'|},$$

which is the energy contribution from the positive background charge with density $n(r) = N/\Omega$. Finally,

$$\hat{H}_{el-b} = -\frac{e^2}{2} \sum_{i=1}^N \int dr \frac{n(r)e^{-\mu|r-x_i|}}{|r-x_i|},$$

is the interaction between the electrons and the positive

Single-particle Hartree-Fock energy

In the first exercise below we show that the Hartree-Fock energy can be written as

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2}{\Omega^2} \sum_{k' \leq k_F} \int dr e^{i(k'-k)r} \int dr' \frac{e^{i(k-k')r'}}{|r-r'|}$$

resulting in

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2 k_F}{2\pi} \left[2 + \frac{k_F^2 - k^2}{kk_F} \ln \left| \frac{k + k_F}{k - k_F} \right| \right]$$

The previous result can be rewritten in terms of the density

$$n = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3},$$

where $n = N_e/\Omega$, N_e being the number of electrons, and r_s is the radius of a sphere which represents the volume per conducting electron. It can be convenient to use the Bohr radius $a_0 = \hbar^2/e^2 m_e$. For most metals we have a relation $r_s/a_0 \sim 2 - 6$. The quantity r_s is dimensionless.

In the second exercise below we find that the total energy

$E = \langle N | \hat{H} | \Phi \rangle = \langle N | \hat{H} | \Phi \rangle = \langle N | \hat{H} | \Phi \rangle$ can be written as

The electron gas model allows closed form solutions for quantities like the single-particle Hartree-Fock energy. The latter quantity is given by the following expression

$$\epsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{V^2} \sum_{k' \leq k_F} \int dr e^{i(k'-k)r} \int dr' \frac{e^{i(k-k')r'}}{|r-r'|}$$

a) Show first that

$$\epsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{2\pi} \left[2 + \frac{k_F^2 - k^2}{kk_F} \ln \left| \frac{k + k_F}{k - k_F} \right| \right]$$

Hint. Hint: Introduce the convergence factor $e^{-\mu|r-r'|}$ in the potential and use $\sum_k \rightarrow \frac{V}{(2\pi)^3} \int dk$

Solution. We want to show that, given the Hartree-Fock equation for the electron gas

$$\epsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{V^2} \sum_{p \leq k_F} \int dr \exp(i(p-k)r) \int dr' \frac{\exp(i(k-p)r')}{|r-r'|}$$

the single-particle energy can be written as

$$\epsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{2\pi} \left[2 + \frac{k_F^2 - k^2}{kk_F} \ln \left| \frac{k + k_F}{k - k_F} \right| \right].$$

We consider a system of electrons in infinite matter, the so-called electron gas. This is a homogeneous system and the one-particle states are given by plane wave function normalized to a volume Ω for a box with length L (the limit $L \rightarrow \infty$ is to be taken after we have computed various expectation values)

$$\psi_{k\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{k}\mathbf{r})\xi_{\sigma}$$

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The total Hamiltonian consists then of kinetic and potential energy