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":"https://github.com/ManyBodyPhysics/FYS4480/blob/maste
   - 1.2 Friday:
     - 1.2.1 Stability of Hartree-Fock equations and Thouless' theorem
     - 1.2.2 The homogeneous electron gas in three dimensions
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

$$\psi_p^{HF} = \sum_\lambda C_{p\lambda}\phi_\lambda. \tag{1}$$

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

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

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,

$$\mathrm{v}_i = \begin{bmatrix} v_{i1} \\ \dots \\ \dots \\ v_{in} \end{bmatrix}$$

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

We assume that the basis is orthogonal, that is

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

An orthogonal or unitary transformation

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

preserves the dot product and orthogonality since

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

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 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 $\langle p|q\rangle = \delta_{pq}$. 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.

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},

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

where $det(\mathrm{C})$ and $det(\mathrm{B})$ 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

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

which is nothing but $det(\mathrm{C})det(\Phi)$, 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 $ijkl\cdots \leq F$ for so-called single-hole states and $abcd\cdots > F$ for so-called particle states. For general single-particle states we employ the labels $pqrs\ldots$.
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 $\phi_\lambda(\mathrm{r})$. 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

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

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

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

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

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

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

$$F[\Phi^{HF}] = E[\Phi^{HF}] - \sum_{i=1}^{N} \epsilon_i \sum_{\alpha} C^*_{i\alpha} C_{i\alpha}. \tag{4}$$

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

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

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 numerical.

Hartree-Fock algorithm

Our Hartree-Fock matrix is thus

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

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

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

The Hartree-Fock eigenvalue problem

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

can be written out in a more compact form as

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

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

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

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 av 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

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

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

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

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

New operators

If we define a new creation operator

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

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

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

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

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

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 homogeneus 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 $L \to \infty$ is to be taken after we have computed various expectation values)

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

where 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

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

We assume first that the electrons interact via a central, symmetric and translationally invariant interaction $V(r_{12})$ with $r_{12} = |\mathrm{r}_1 - \mathrm{r}_2|$.
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

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

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

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

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

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

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

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

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

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

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 volum 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

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

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

a) Show first that

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

Hint. Hint: Introduce the convergence factor $e^{-\mu|\mathrm{r}-\mathrm{r}'|}$ in the potential and use $\sum_{\mathrm{k}} \to \frac{V}{(2\pi)^3} \int d\mathrm{k}$

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

$$\varepsilon_k^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{V^2} \sum_{p \leq k_F} \int d\mathrm{r} \exp\left(i(\mathrm{p}-\mathrm{k})\mathrm{r}\right) \int d\mathrm{r}' \frac{\exp\left(i(\mathrm{k}-\mathrm{p})\mathrm{r}'\right)}{|\mathrm{r}-\mathrm{r}'|}$$

the single-particle energy can be written as

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

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 $L \to \infty$ is to be taken after we have computed various expectation values)

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

where k is the wave number and ξ_σ is a spin function for either spin up or down

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The total Hamiltonian consists then of kinetic and potential energy