Density Functional Theory (蔡政達 2024 Fall)

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1 Introduction

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1.1 What is Density Functional Theory?

Wikipedia: *"Density functional theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (or nuclear structure) (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases."*

Density functional theory (DFT) was developed by Walter Kohn, (1998 Nobel Prize in Chemistry laureate), and Pierre Hohenberg to study the ground-state (GS) properties of large systems using first principle methods. DFT can be used to study electronic systems, including atoms, molecules, and solids...

In order to solve the system for the electronic wavefunction Ψ_e, we keep $(\mathbf{R}_k, Z_k)$ fixed and solve for the time-independent Schrödinger equation (TISE) of the system. Then we can find the energy of the system by computing

$$E = \left\langle \Psi_\mathrm{e} \middle| \hat{H} \middle| \Psi_\mathrm{e} \right\rangle . \tag{1}$$

The methodologies described in this lecture note will focus on using various computational methods to achieve this incredible goal.

1.2 Notation

For future reference, this note will adhere to the following notation conventions.

- The units in use are either **SI international units** or **atomic units** , which one of them is in use will be obvious from context and dimensionality. Note: it is usually for the sake of taking notes faster that I resort to atomic units, otherwise I think it is of great pedagogical value to keep the dimensional constants.
- An iterated integral or volume integral over a domain Ω is denoted

  $$\int_\Omega \mathrm{d}\mathbf{r}\ (\ \cdots\ ) \ \text{ or } \int_\Omega \mathrm{d}^3 r\ (\ \cdots\ ),$$

  but never with a power *and* boldface font at the same time:

  $$\int_\Omega \mathrm{d}^3\mathbf{r}\ (\ \cdots\ ).$$

- Operators may or may not be notated with a hat symbol, and may be written in calligraphic font, so H, $\hat{H}$, and $\mathcal{H}$ represent equally well the Hamiltonian operator.

2 Born-Oppenheimer Approximation

2.1 Formulation of Problem

Consider the following electronic system of M nuclei of atomic number Z_k and N electrons. The positions of the k-th nuclei is denoted $\mathbf{R}_k$. Our system is then described by the (position - atomic no.) tuples $(\mathbf{R}_k, Z_k)$, $k = 1, 2, \dots, M$.

2.2 The Approximation

The Born-Oppenheimer approximation allows the **separate treatment of nuclear and electronic parts of the time-independent Schrödinger equation**. Recall the fact that a proton is approximately 1836 times heavier than an electron, and the j-th nucleus is made of Z_j protons and neutrons in total, making it approximately

$$1840 Z_j \sim 10^5$$

times heavier than the electrons. This means the nucleus moves slowly compared to the electron, so we have the **Born-Oppenheimer approximation** :

1. The velocities of the particles (as seen quantum mechanically) satisfy
$$\text{velocity(nucleus)} \ll \text{velocity(electron)}, \tag{2}$$
where we can safely assume the electrons respond ”instantaneously” to nuclei movement.
2. The neclear positions $\{\mathbf{R}_k\}$, $k = 1, 2, \dots, M$ are fixed.

We can separete the total Hamiltonian $\hat{H}$ into its electronic and nuclear parts:

$$\hat{H} = \hat{H}_{\mathrm{e}} + \hat{V}_{\mathrm{nuc}},$$

where

$$\hat{H}_{\mathrm{e}} = \hat{T} + \hat{V} + \hat{U} = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) + \sum_{i=1}^{N} V(\mathbf{r}_i) + \left(\frac{e^2}{4\pi\epsilon_0} \right) \sum_{i=1}^{N} \sum_{j<i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{3}$$

is the electronic Hamiltonian, and

$$\hat{V}_{\mathrm{nuc}} = \left(\frac{e^2}{4\pi\epsilon} \right) \sum_{=1}^{N} \sum_{j<i}^{N} \frac{Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{4}$$

is the nuclear Hamiltonian.

2.3 Method Overview

Let the electronic wavefunction $\Psi_{\mathrm{e},n}$ be defined as $\Psi_n(x_1, \dots, x_N)$, where $x_k = (\mathbf{r}_k, \sigma_k)$ is the (spatial + spin) coordinate of each electron. Similarly we can define the nucleaer wavefunction $\Phi_n = \Phi_n(X_1, \dots, X_M)$, where $X_l = (\mathbf{R}_l, \Sigma_l)$. The TISE reads

$$\hat{H}_{\mathrm{e}} \Psi_n = E_n \Psi_n, \quad \hat{V}_{\mathrm{nuc}} \Phi_n = E_{\mathrm{nuc}} \Phi_n. \tag{5}$$

The total energy is simply their sum, by the B-O approximation:

$$E_{\mathrm{total}} = E_n + E_{\mathrm{nuc}} \equiv U_n, \tag{6}$$

with

$$E_0(\text{GS energy}) \leq E_1 \leq E_2 \leq E_3 \leq \cdots.$$

Remark. The goal of DFT is to find the ground state (GS) energy.

We solve the above TISE for a fixed initial $\{\mathbf{R}_1^{(1)}, \mathbf{R}_2^{(1)}, \dots, \mathbf{R}_M^{(1)}\}$, giving the total energy of the configuration $U_n^{(1)} = U_n^{(1)}\left(\mathbf{R}_1^{(1)}, \dots, \mathbf{R}_M^{(1)}\right)$. Here we postpone the detailed methodology for solving the equation to later sections. Following this computation, the next natural step to take is to vary $\{\mathbf{R}_k\}$ and repeat the computation, and for each iteration we get a potential $U_n^{(r)}$, giving us after many iterations a **potential energy surface (PES)**

$$U_n = U_n\left(\mathbf{R}_1, \dots, \mathbf{R}_M\right).$$

Remark. Shouldn't this be simply called the **energy surface** instead, since it includes the kinetic energy contribution?

3 Variational Methods

3.1 Functionals and Their Derivatives

In physics, we are often confronted with optimisation problems with complex functional dependencies. A famous example would be extremising the action with respect to position in the Lagrangian formalism of physics:

$$\frac{\delta S}{\delta \mathbf{r}(t)} = \frac{\delta}{\delta \mathbf{r}}\left[\int \mathrm{d}\mathbf{r}\, L(t, \mathbf{r}(t), \dot{\mathbf{r}}(t))\right] = 0.$$

But before going on any further, we shall put the concept of a "functional derivative" on a firm mathematical footing. To define rigorously what a functional derivative is, first we introduce the idea of a **functional differential**, or **first variation**.

Definition 3.1 (Functional differential)**.** *The* functional differential *can be defined in various ways. Here we introduce two of the most common definitions:*

1. *As a* Frechet derivative*: Let F be a functional defined on a Banach space B. The differential of F at a point $\rho \in B$ is the linear functional $\delta F[\rho; \cdot]$ on B satisfying the condition*

   $$F[\rho + \delta\rho] - F[\rho] = \delta F[\rho; \delta\rho] + \eta \left\|\delta\rho\right\|,$$

   where $\|\cdot\|$ is the norm associated with B, $\eta \in \mathbb{R}$, and $\eta \to 0$ as $\|\delta\rho\| \to 0$.

   Remark. A Banach space is a complete normed vector space.

2. *As a* Gateaux derivative*: Let F be a functional defined on a vector space. The functional differential of F at point ρ with respect to variation $\delta\rho$ is defined as*

   $$\delta F[\rho; \delta\rho] = \lim_{\eta \to 0} \frac{F[\rho + \eta\delta\rho] - F[\rho]}{\eta} = \left[\frac{\mathrm{d}}{\mathrm{d}\eta} F[\rho + \eta\delta\rho]\right]_{\eta = 0}.$$

Remark. The definition of functional differential as a Frechet derivative on a Banach space is so strong that sometimes it does not exist at all. This is a problem, because we need the functional differential in order to proceed with a sensible definition of functional derivatives, which is widely used in physics. The Gateaux derivative definition is a lot weaker, and used for practical applications.

Definition 3.2 (Functional derivative)**.** *For a functional F defined on a space of differentiable functions over some space Ω, a function $\rho \in \Omega$, and some scalar η, there exists some function*

$$\frac{\delta F}{\delta \rho}(\mathbf{r}) \equiv \frac{\delta F}{\delta \rho(\mathbf{r})} \equiv D(\mathbf{r}),$$

such that

$$\lim_{\eta \to 0} \frac{F[\rho + \eta \delta \rho] - F[\rho]}{\eta} = \int_{\Omega} \mathrm{d}^3 r \, D(\mathbf{r}) \delta \rho(\mathbf{r}).$$

We call $\delta F / \delta \rho(\mathbf{r})$ the functional derivative *or* first variation *of F at ρ.*

Now that we have a definition of a functional derivative, we can apply it to a common class of functionals that often appear in physics: ”action-like” functionals (I have not heard of similar terms for this integral, so I’ll go with what name I came up with).

Example 3.1 (Lagrangian formalism)**.** Recall that in the Lagrangian formalism, we can write the Lagrangian L of a system as a functional of position $\mathbf{r}(t)$, velocity $\dot{\mathbf{r}}(t)$, and the independent variable time t, i.e. $L = L(\mathbf{r}, \dot{\mathbf{r}}, t)$.

The action is defined as the following integral on some time interval $[t_1, t_2]$:

$$S = S[\mathbf{r}(t)] \equiv \int_{t_1}^{t_2} \mathrm{d}\mathbf{r} \, L(\mathbf{r}, \dot{\mathbf{r}}, t).$$

Hamilton’s principle tells us that the first variation of action vanishes on the true path of evolution of the system. So

$$\frac{\delta S}{\delta \mathbf{r}(t)} = 0.$$

In a moment we will see that solving this functional equation is equivalent to solving the well-known *Euler-Lagrange equation*:

$$\frac{\partial L}{\partial \mathbf{r}(t)} - \frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial L}{\partial \dot{\mathbf{r}}(t)} = 0.$$

Theorem 3.1 (Euler-Lagrange equation)**.** *Consider an ”action-like” functional F of some function ρ, given by*

$$F[\rho] = \int \mathrm{d}\mathbf{r} \, f\left(\mathbf{r}, \rho(\mathbf{r}), \nabla \rho(\mathbf{r})\right).$$

Then the first variation of F at ρ is

$$\frac{\delta F}{\delta \rho(\mathbf{r})} = \frac{\partial f}{\partial \rho(\mathbf{r})} - \nabla \cdot \left(\frac{\partial f}{\partial \nabla \rho(\mathbf{r})} \right).$$

Proof. Use the definition of $\frac{\delta F}{\delta \rho}$ as a Gateaux derivative:

$$\begin{aligned}
\int \mathrm{d}\mathbf{r}\, \frac{\delta F}{\delta \rho(\mathbf{r})}\delta\rho(\mathbf{r}) &= \frac{\mathrm{d}}{\mathrm{d}\eta}\left[\int \mathrm{d}\mathbf{r}\, f\left(\mathbf{r}, \rho + \eta\rho, \nabla\rho + \eta\nabla\delta\rho\right)\right]_{\eta=0} \\
&= \left[\int \mathrm{d}\mathbf{r}\, \left(\frac{\partial}{\partial\eta}\frac{\partial\rho}{\partial\eta} + \frac{\partial}{\partial\nabla\rho}\frac{\partial\nabla\rho}{\partial\eta}\right) f\left(\mathbf{r}, \rho + \eta\delta\rho, \nabla\rho + \eta\nabla(\delta\rho)\right)\right]_{\eta=0} \\
&= \int \mathrm{d}\mathbf{r}\, \left[\frac{\partial f}{\partial\rho}\delta\rho + \frac{\partial f}{\partial\nabla\rho}\nabla(\delta\rho)\right] \\
&= \int \mathrm{d}\mathbf{r}\, \left[\frac{\partial f}{\partial\rho}\delta\rho - \left(\nabla\cdot\frac{\partial f}{\partial\nabla\rho}\right)\delta\rho + \nabla\cdot\left(\frac{\partial f}{\partial\nabla\rho}\delta\rho\right)\right] \\
&= \int \mathrm{d}\mathbf{r}\, \left[\frac{\partial f}{\partial\rho} - \nabla\cdot\left(\frac{\partial f}{\partial\nabla\rho}\right)\right]\delta\rho(\mathbf{r}).
\end{aligned}$$

Then

$$\frac{\delta F}{\delta\rho} = \frac{\partial f}{\partial\rho} - \nabla\cdot\left(\frac{\partial f}{\partial\nabla\rho}\right)$$

by the **fundamental lemma of calculus of variation** . □

Remark. For an action-like functional of higher-order derivatives, the generalisation is the **Euler-Poisson equation** . Let

$$F[\rho] = \int_\Omega \mathrm{d}\mathbf{r}\, f\left(\mathbf{r}, \rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \ldots, \nabla^{(N)}\rho(\mathbf{r})\right),$$

where $\mathbf{r} \in \Omega \subseteq \mathbb{R}^n$, and

$$[\nabla^i]_{\alpha_1\alpha_2\cdots\alpha_N} = \frac{\partial^i}{\partial r_{\alpha_1}\partial r_{\alpha_2}\cdots\partial r_{\alpha_i}}$$

is a rank i tensor. Then

$$\frac{\delta F}{\delta\rho(\mathbf{r})} = \frac{\partial f}{\partial\rho} + \sum_{i=1}^{N}\nabla^{(i)}\left(\frac{\partial f}{\partial\nabla^{(i)}\rho(\mathbf{r})}\right).$$

3.2 Rayleigh-Ritz Variational Principle

Consider the trial function Φ, and define the corresponding energy $E[\Phi] = \left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle$. This trial function has to satisfy

1. Normalisation: $\langle \Phi \mid \Phi \rangle$.
2. Antisymmetrisation: $\Phi(\ldots x_i, \ldots, x_j, \ldots) = -\Phi\left(\ldots x_j, \ldots, x_i, \ldots\right)$.

The object $E[\Phi] : \Phi \mapsto \left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle$ is a **functional** from the Hilbert space $\mathcal{H}$ to $\mathbb{R}$.

3.3 Short Introduction to Quantum Monte Carlo Methods

From Wikipedia: "Quantum Monte Carlo encompasses a large family of computational methods whose common aim is the study of complex quantum systems. One of the major goals of these approaches is to provide a reliable solution (or an accurate approximation) of the quantum many-body problem."

4 Hartree-Fock Method

Remark. This method is one of many iterative schemes called **self-consistent field methods (SCF)** .

4.1 Single-Particle Wavefunction

Definition 4.1. *(Non-interacting Hamiltonian)*

1. *Single-particle wavefunctions* ϕ_i *are solutions to the TISE*

$$\hat{h}\phi_i = \epsilon_i \phi_i, \tag{7}$$

where $\hat{h}_i = \hat{T} + \hat{V}_i$ *is the i-th Hamiltonian without interaction. We call* ϕ_i *the* ***orbital wavefunctions****.*

2. *The non-interacting Hamiltonian* $\hat{H}^{NI}$ *is then simply*

$$\hat{H}^{NI} = \sum_{i=1}^{N} \hat{h}_i. \tag{8}$$

To clarify, the TISE becomes

$$\hat{h}(\mathbf{x})\phi_i(\mathbf{x}) = \varepsilon_i \phi_i(\mathbf{x}) \implies \left[\left(-\frac{\hbar^2}{2m}\right)\nabla^2 + \hat{V}(\mathbf{r})\right]\phi_i(\mathbf{x}) = \varepsilon_i \phi_i(\mathbf{x}),$$

we can drop the subscript for $\mathbf{x}$ and $\mathbf{r}$ because the Hamiltonian is the same when seen from different electrons when there are no interaction.

The non-interacting Hamiltonian is the result of letting $U \to 0$, so $\hat{H} \to \hat{H}_{\text{HF}}$.

Now the total TISE is

$$\hat{H}^{\text{NI}}\Phi_n^{\text{NI}}(\mathbf{x}_1, \dots, \mathbf{x}_N) = E^{\text{NI}}\Phi_n^{\text{NI}}(\mathbf{x}_1, \dots, \mathbf{x}_N),\ \mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i).$$

A natural choice to construct $\Phi_n^{\text{NI}}(\mathbf{x}_1, \dots, \mathbf{x}_N)$ from the orbitals is

$$\Phi_n^{\text{NI}}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\cdots\phi_N(\mathbf{x}_N), \tag{9}$$

but sadly this does not satisfy Pauli's well-known antisymmetrisation property for fermions. So we shall resort to the Slater determinant construction:

$$\begin{aligned}\Phi^{\text{NI}} &= \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}}\det\left(\phi_1, \phi_2, \dots, \phi_N\right).\end{aligned} \tag{10}$$

The energy is simply

$$E^{\text{NI}} = \left\langle \Phi^{\text{NI}} \middle| \hat{H}^{\text{NI}} \middle| \Phi^{\text{NI}} \right\rangle.$$

4.2 Hartree's Equation

Although we just debunked the ansatz equ. (9) as not physical, it still helps to use it as an initial value for simple calculations. This is where Hartree's equation comes from. We write the **Hartree product** of orbitals as

$$\Phi_n^{\mathrm{NI}}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2) \cdots \phi_N(\mathbf{x}_N),$$

and define the inner product as

$$\begin{aligned} \langle \phi_i \,|\, \phi_j \rangle &\equiv \int \mathrm{d}x_k \phi_i(\mathbf{x}_k)^* \phi_j(\mathbf{x}_k) \\ &= \sum_{\sigma_k} \int \mathrm{d}^3\mathbf{r}_k \phi_i(\mathbf{r}_k) * \phi_j(\mathbf{x}_k). \end{aligned}$$

Then

$$\langle \phi_i \,|\, \phi_j \rangle = \delta_{ij}.$$

By explicit calculation as detailed below, we have the first significant result of Hartree's theory:

$$E^{\mathrm{H}} = \left\langle \Phi^{\mathrm{H}} \,\middle|\, \hat{H} \,\middle|\, \Phi^{\mathrm{H}} \right\rangle = \sum_{i=1}^{N} \left\langle i \,\middle|\, \hat{H} \,\middle|\, i \right\rangle + \sum_{i=1}^{N} \sum_{j<1}^{N} [ii|jj], \tag{11}$$

where $\hat{h}_i$ is the i-th single particle Hamiltonian. In the above equation, we introduce the following abbreviations for some terms that shall show up frequently in our analysis:

Definition 4.2 (Orbital brakets). *Given the finite set of (approximate) orbitals $\{\phi_k\}$ for an N-electron system, we define*

1. *The braket with respect to orbitals:*

$$\left\langle i \,\middle|\, \hat{H} \,\middle|\, j \right\rangle \equiv \left\langle \phi_i \,\middle|\, \hat{H} \,\middle|\, \phi_j \right\rangle, \tag{12}$$

2. *The inner-product like four-component braket:*

$$\begin{aligned} [ij|kl] &\equiv \int \mathrm{d}x_1 \int \mathrm{d}x_2 \, \phi_i(\mathbf{x}_1)\phi_j(\mathbf{x}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_k(\mathbf{x}_2)\phi_l(\mathbf{x}_2) \\ &\equiv \sum_{\sigma_1} \sum_{\sigma_2} \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, \phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_k(\mathbf{r}_2)\phi_l(\mathbf{r}_2). \end{aligned} \tag{13}$$

Exercise 4.1 (Hartree energy functional)**.** Derive equation (11) by explictly computing the inner product.

By varying with respect to the orbitals $\phi_k^*(\mathbf{x}_k)$, under the constraint that orbitals be orthonormal, we can derive the **Hartree equation**

$$\left[\hat{h}(\mathbf{r}) + \sum_{j \neq k} \int \mathrm{d}^3 x' \, \phi_j^*(\mathbf{x}') \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \phi_j(\mathbf{x}') \right] \phi_k(\mathbf{x}) = \varepsilon_k \phi_k(\mathbf{x}). \tag{14}$$

The summation in the square brackets will be defined as the Coulomb operator in the next section, where we will talk about the Hartree-Fock method.

Exercise 4.2 (Hartree energy)**.** Derive equation (14) by variational methods. *Hint: notice that orbitals must be orthonormalised, then vary equation (11) with respect to some orbital.*

4.3 Slater-Condon Rules

Before dealing with the Hartree-Fock equation itself, we need to acquire a more thorough understanding of the Hartree-Fock wavefunction, and develop the necessary tools to analyse various operations on it. To do this, we need to first discuss the **Slater determinant** .

The Slater determinant is a natural way to construct fermionic wavefunctions that obey antisymmetry with respect to particle interchange. Not every wavefunction can be written as a Slater determinant, in fact, only a small subset of them can be written as a single Slater determinant, but those form an important and useful subset because of their simplicity.

4.4 Hartree-Fock Hamiltonian

Given a set of N initial orbital wavefunctions $(\phi_1, \phi_2, \dots, \phi_N)$, we can construct the initial total (electronic) wavefunction, which we call Φ^{HF}, using a **Slater determinant** :

$$\begin{aligned}\Phi^{\mathrm{HF}} &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}} \det\left(\phi_1, \phi_2, \dots, \phi_N\right). \end{aligned} \tag{15}$$

This formulation means that Φ^{HF} trivially satisfies Pauli's antisymmetry principle.

Remark (Slater determinant for a symmetric system)*.* Following the example above, a symmetric system (i.e. a **bosonic system**) should be described by a **permanent** , that is:

$$\Phi^{\mathrm{boson}} \overset{?}{=} \frac{1}{\sqrt{N!}} \operatorname{perm} \begin{pmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{pmatrix}.$$

However, this is not it, as the permanent wavefunction is not normalised. To normalise the function, consider the counting variable n_m that counts the number of particles in state ϕ_m, $1 \le m \le N$. Then we can write the normalised bosonic wavefunction

$$\Phi^{\mathrm{boson}} = \sqrt{\frac{\prod_{m=1}^{N} n_m!}{N!}} \operatorname{perm} \begin{pmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{pmatrix}. \tag{16}$$

Such an object can be more compactly represented as an **antysymmetriser** (for fermionic systems) or a **symmetriser** (for bosonic systems).

Continuing with the Hartree-Fock method, we note that the orbital wavefunctions should be orthonormal, i.e.

$$\langle \phi_i \,|\, \phi_j \rangle = \delta_{ij}.$$

By expanding the inner products with respect to the determinant, we derive the **Hartree-Fock energy**

$$\begin{aligned} E^{\mathrm{HF}} = E[\Phi^{\mathrm{HF}}] &= \left\langle \Phi^{\mathrm{HF}} \,\middle|\, \hat{H} \,\middle|\, \Phi^{\mathrm{HF}} \right\rangle \\ &= \sum_{i=1}^{N} \left\langle i \,\middle|\, \hat{h} \,\middle|\, j \right\rangle + \frac{1}{2} \sum_{i=1}^{N} \sum_{i \neq j}^{N} \left\{ [ii|jj] - [ij|ji] \right\}. \end{aligned} \tag{17}$$

Furthermore, by variational methods we have the **Hartree-Fock equation**

$$\hat{\mathscr{F}}(\mathbf{x})\phi_{\mathbf{x}} \equiv \left[\hat{h}(\mathbf{r}) + \hat{\mathscr{J}}(\mathbf{x}) + \hat{\mathscr{K}}(\mathbf{x}) \right] \phi_k(\mathbf{x}) = \varepsilon_k \phi_k(\mathbf{x}) \tag{18}$$

for single-electron orbitals. Here we have defined the **Coulomb** and **exchange operators** as follows:

$$\hat{\mathscr{J}}(\mathbf{x}) \equiv \sum_{j=1}^{N} \int \mathrm{d}x' \, \phi_j^*(\mathbf{x}') \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \phi_j(\mathbf{x}'), \tag{19}$$

$$\hat{\mathscr{K}}(\mathbf{x})\phi_k(\mathbf{x}) \equiv \sum_{j=1}^{N} \phi_j(\mathbf{x}) \int \mathrm{d}x' \, \phi_j^*(\mathbf{x}') \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \phi_k(\mathbf{x}'). \tag{20}$$

In the HF scheme, the following approximations are assumed:

- Born-Oppenheimer approximation.
- Non-relativistic momentum operator is used in the Hartree-Fock Hamiltonian, that is, all relativistic effects are ignored.
- Energy eigenfunction is assumed to be describable by a single Slater determinant constructed from the orbitals. This is in general not true.
- Mean-field approximation. The effects of any deviation from this is collectively defined to be the **electron correlation**, where

$$\text{electron correlation} = \text{Coulomb correlation} + \text{Fermi (exchange) correlation}.$$

The Hartree-Fock method only accounts for the exchange-correlation (XC) term.

Remark. Precisely because of the mean-field approximation, the Hartree-Fock method does not predict any nonlocal interaction such as the *London dispersion force.*

Now we will give a derivation of equations (17) and (18), and in the process flesh out details of the proof of two of the aforementioned *Slater-Condon Rules.* The following proof is taken from my solution to Problem 1 of Homework 1 of the course.

Proof. Assume the Hartree-Fock energy eigenfunction is of the form

$$\begin{aligned}\Phi^{\mathrm{HF}} &= \frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N)\\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N)\\ \vdots & \vdots & \ddots & \vdots\\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N)\end{vmatrix}\\ &= \frac{1}{\sqrt{N!}}\det\left(\phi_1,\phi_2,\dots,\phi_N\right).\end{aligned} \tag{21}$$

For simplicity we call it Φ from now on. We give another expression of the determinant, in terms of permutations:

$$\det A = \sum_{\sigma\in S_N}\operatorname{sgn}(\sigma)\prod_{i=1}^{N} a_{i,\sigma(i)}, \tag{22}$$

where A is an $N\times N$ matrix, with a_{ij} denoting the ij-th entry, and $\sigma:\{1,\dots,N\}\leftrightarrow\{1,\dots,N\}$ is a permutation, which is bijective.

(I) Energy expression: Recall that the Hartree-Fock Hamiltonian is

$$H = \sum_{i=1}^{N} h(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}, \tag{23}$$

The energy as a functional of Φ (and therefore of $\{\phi_k\}_{1\le k\le N}$) is, using equation (22):

$$\begin{aligned}E[\{\phi_k\}] &= \left\langle\Phi\,\middle|\,\hat{H}\,\middle|\,\Phi\right\rangle\\ &= \int \mathrm{d}x_1\cdots\int \mathrm{d}x_N\left(\frac{1}{\sqrt{N!}}\sum_{\sigma}\operatorname{sgn}(\sigma)\prod_{i=1}^{N}\phi_{\sigma(i)}(\mathbf{x}_i)\right)\\ &\quad\times\left(\sum_{i=1}^{N}\hat{h}_k+\sum_{k=1}^{N}\sum_{l\neq k}^{N}\frac{1}{|\mathbf{r}_k-\mathbf{r}_l|}\right)\left(\frac{1}{\sqrt{N!}}\sum_{\sigma'}\operatorname{sgn}(\sigma')\prod_{j=1}^{N}\phi_{\sigma'(j)}(\mathbf{x}_j)\right).\end{aligned} \tag{24}$$

We will discuss the braket of one- and two-electron operators separately. Notation: σ_i with subscripts denotes spin coordinate, while σ without subscripts denotes elements of the symmetric group S_N.

1. The expectation value of the one-electron operator $\hat{h}_k$ does not distinguish between elec-

trons, so we can pick a representative (say 1) to do the calculation:

$$\begin{aligned}
\left\langle \Phi \middle| \sum_{k=1}^{N} \hat{h}_k \middle| \Phi \right\rangle &= N \left\langle \Phi \middle| \hat{h}_1 \middle| \Phi \right\rangle \\
&= \frac{1}{N!} \cdot N \cdot \int \mathrm{d}x_1 \cdots \int \mathrm{d}x_N \left(\sum_{\sigma} \operatorname{sgn}(\sigma) \prod_{i=1}^{N} \phi^*_{\sigma(i)}(\mathbf{x}_1) \right) \hat{h}_1 \\
&\quad \times \left(\sum_{\sigma'} \operatorname{sgn}(\sigma) \prod_{j=1}^{N} \phi^*_{\sigma'(j)}(\mathbf{x}_1) \right) \\
&= \frac{1}{(N-1)!} \sum_{\sigma_1, \dots, \sigma_N} \int \mathrm{d}^3 r_1 \cdots \int \mathrm{d}^3 r_N \sum_{\sigma} \sum_{\sigma'} \operatorname{sgn}(\sigma) \operatorname{sgn}(\sigma') \\
&\quad \times \prod_{i=1}^{N} \prod_{j=1}^{N} \phi^*_{\sigma(i)} \hat{h}_1(\mathbf{x}_1) \phi_{\sigma'(j)}(\mathbf{x}_j) \qquad (25) \\
&\overset{\dagger}{=} \frac{1}{(N-1)!} \sum_{\sigma_1, \dots \sigma_N} \int \mathrm{d}^3 r_1 \cdots \int \mathrm{d}^3 r_N \sum_{\sigma} \prod_{i=1}^{N} \phi^*_{\sigma(i)}(\mathbf{x}_i) \hat{h}_1(\mathbf{r}_1) \phi_{\sigma(i)}(\mathbf{x}_i) \\
&\overset{\ddagger}{=} \frac{1}{(N-1)!} \cdot (N-1)! \sum_{\sigma_1} \int \mathrm{d}^3 r_1 \sum_{k=1}^{N} \phi^*_k(\mathbf{x}_1) \hat{h}(\mathbf{r}_1) \phi_k(\mathbf{x}_1) \\
&= \sum_{k=1}^{N} \sum_{\sigma_1} \int \mathrm{d}^3 r_1 \, \phi^*_k(\mathbf{x}_1) \hat{h}(\mathbf{r}_1) \phi_k(\mathbf{r}_1) = \sum_{i=1}^{N} \left\langle i \middle| \hat{h} \middle| i \right\rangle .
\end{aligned}$$

†: $\{\phi_k\}$ is orthonormal, so the integrals over r_2 to r_N multiply to zero unless the electrons occupy the same orbital in the two products, i.e. for each $\sigma(i)$ in the first product, we have $\sigma'(j) = \sigma(i)$ in the second. By the bijectivity of $\sigma : \{1, \dots, N\} \leftrightarrow \{1, \dots, N\}$, we know that $\sigma(1) = \sigma'(1)$. j is just a dummy variable, so we rename it to be $\phi_{\sigma'(j)}(\mathbf{x}_j) = \phi_{\sigma(i)}(\mathbf{x}_i)$.

‡: Electron 1 occupies each orbital exactly $(N-1)!$ times, since fixing 1, the remaining $N-1$ electrons can be permuted in $(N-1)!$ ways, the integral of each of which multiply to 1.

2. The determinant does not differentiate between different electrons, so we can use 1 and 2 as the representative. We use the shorthand $\hat{O}$ for the two-electron term to get

$$\begin{aligned}
\left\langle \Phi \middle| \hat{O} \middle| \Phi \right\rangle &= \left\langle \Phi \middle| \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left(\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \middle| \Phi \right\rangle \\
&= \frac{N(N-1)}{2} \left\langle \Phi \middle| \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \middle| \Phi \right\rangle .
\end{aligned} \qquad (26)$$

Then

$$
\begin{aligned}
\left\langle \Phi \middle| \hat{O} \middle| \Phi \right\rangle \equiv{}& \frac{N(N-1)}{2} \int \mathrm{d}x_1 \cdots \int \mathrm{d}x_N \left(\frac{1}{\sqrt{N!}} \sum_{\sigma} \operatorname{sgn}(\sigma) \prod_{i=1}^{N} \phi^*_{\sigma(i)}(\mathbf{x}_1) \right) \\
&\times \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \left(\frac{1}{\sqrt{N!}} \sum_{\sigma'} \operatorname{sgn}(\sigma) \prod_{j=1}^{N} \phi^*_{\sigma'(j)}(\mathbf{x}_1) \right) \\
\overset{\dagger}{=}{}& \left(\frac{N(N-1)}{2} \right) \frac{1}{N!} \sum_{\sigma_1,\ldots,\sigma_N} \int \mathrm{d}^3 r_1 \cdots \int \mathrm{d}^3 r_N \sum_{\sigma \in S_N} \left(\prod_{i=3}^{N} \phi^*_{\sigma(i)}(\mathbf{x}_i) \phi_{\sigma(i)}(\mathbf{x}_i) \right) \\
&\times \left(\phi^*_{\sigma(1)}(\mathbf{x}_1) \phi^*_{\sigma(2)}(\mathbf{x}_2) \right) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \\
&\times \left[\phi_{\sigma(1)}(\mathbf{x}_1) \phi_{\sigma(2)}(\mathbf{x}_2) + (-1) \phi_{\sigma(1)}(\mathbf{x}_2) \phi_{\sigma(2)}(\mathbf{x}_1) \right] \\
\overset{\ddagger}{=}{}& \frac{1}{2(N-2)!} \sum_{\sigma_1,\sigma_2} \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, (N-2)! \left\{ \sum_{k=1}^{N} \sum_{l=1}^{N} \phi^*_k(\mathbf{x}_1) \phi^*_l(\mathbf{x}_2) \right. \\
&\left. \times \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \left[\phi_k(\mathbf{x}_1) \phi_l(\mathbf{x}_2) - \phi_k(\mathbf{x}_2) \phi_l(\mathbf{x}_1) \right] \right\} .
\end{aligned} \tag{27}
$$

†: Again, electrons 3 to N must occupy the same orbital in the σ and σ' permutations for the integral to not vanish. So $\sigma(i) = \sigma'(j)$ for $3 \leq i, j \leq N$, $\operatorname{sgn}(\sigma) \operatorname{sgn}(\sigma') = 1$. Electrons 1 and 2 may be in the same orbital or related by an exchange of coordinates.

‡: Each orbital combination of electrons 1 and 2 (interchanged and not interchanged) occurs $(N-2)!$ times, because there are $(N-2)!$ ways to permute the remaining electrons, such that the product gives 1.

Continuing with the simplication, we get

$$
\begin{aligned}
\left\langle \Phi \middle| \hat{O} \middle| \Phi \right\rangle ={}& \frac{1}{2} \sum_{\sigma_1,\sigma_2} \sum_{k=1}^{N} \sum_{l=1}^{N} \left\{ \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, \phi^*_k(\mathbf{x}_1) \phi_k(\mathbf{x}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi^*_l(\mathbf{x}_2) \phi_l(\mathbf{x}_2) \right. \\
&\left. - \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, \phi^*_k(\mathbf{x}_1) \phi_l(\mathbf{x}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi^*_l(\mathbf{x}_2) \phi_k(\mathbf{x}_2) \right\} \\
\overset{\dagger}{=}{}& \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\{ [ii|jj] - [ij|ji] \right\} .
\end{aligned} \tag{28}
$$

†: The $i = j$ term cancels out in the sum, so for symmetry reasons we include this zero term.

Combining the result of equs. (25) and (28), we have the Hartree-Fock energy functional:

$$
E[\{\phi_k\}] = \sum_{i}^{N} \left\langle i \middle| \hat{h} \middle| i \right\rangle + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\{ [ii|jj] - [ij|ji] \right\} . \tag{29}
$$

(II) Variation: We have to minimise the energy function $E[\phi_k(\mathbf{x}_1)]$ (again using 1 as a representative) subject to the constraint that the orbitals are orthonormal:

$$
\delta E[\phi^*_k(\mathbf{x}_k)] = \delta \left\{ \left\langle \Phi^{\mathrm{HF}} \middle| \hat{H} \middle| \Phi^{\mathrm{HF}} \right\rangle - \left[\sum_{i=1}^{N} \sum_{j=1}^{N} \lambda_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right) \right] \right\} := 0, \tag{30}
$$

where

$$\left\langle \phi_i \,\middle|\, \phi_j \right\rangle \equiv \int \mathrm{d}x \phi_i^*(\mathbf{x})\phi_j(\mathbf{x}). \tag{31}$$

We can choose a basis in which the Lagrange multiplier λ_{ij} is diagonal, i.e. $\lambda_{ij} = \varepsilon_i \delta_{ij}$. Then the constraint term becomes

$$\sum_{i=1}^{N} \varepsilon_i \int \mathrm{d}x_1 \, |\phi_i(\mathbf{x}_1)|^2 . \tag{32}$$

Recall the fact that

$$\frac{\delta \phi_k(\mathbf{x}_i)}{\delta \phi_k(\mathbf{x}_i)} = \delta(\mathbf{x}_i - \mathbf{x}_j), \tag{33}$$

since

$$\phi_k(\mathbf{x}_i) = \int \mathrm{d}x_j \, \phi_k(\mathbf{x}_j)\delta(\mathbf{x}_i - \mathbf{x}_j). \tag{34}$$

Then

$$\begin{aligned}
\frac{\delta}{\delta \phi_k^*(\mathbf{x}_1)} E[\phi_k^*(\mathbf{x}_1)] &= \frac{\delta}{\delta \phi_k^*(\mathbf{x}_1)} \{ \left\langle \Psi \,\middle|\, \hat{H} \,\middle|\, \Psi \right\rangle - \sum_{i=1}^{N} \varepsilon_i \int \mathrm{d}x_1 \, |\phi_i(\mathbf{x}_1)|^2 \} \\
&= \frac{\delta}{\delta \phi_k^*(\mathbf{x}_1)} \left\{ \sum_{i=1}^{N} \int \mathrm{d}x_1 \phi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \phi_i(\mathbf{x}_1) \right. \\
&\quad + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \int \mathrm{d}x_1 \int \mathrm{d}x_2 \phi_i^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_j^*(\mathbf{x}_2)\phi_j(\mathbf{x}_2) \\
&\quad - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \int \mathrm{d}x_1 \int \mathrm{d}x_2 \phi_i^*(\mathbf{x}_1)\phi_j(\mathbf{x}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_j^*(\mathbf{x}_2)\phi_i(\mathbf{x}_2) \\
&\quad \left. - \sum_{i=1}^{N} \varepsilon_i \int \mathrm{d}x_1 \, \phi_i^*(\mathbf{x}_1)\phi_i(\mathbf{x}_1) \right\}.
\end{aligned} \tag{35}$$

So

$$\begin{aligned}
\frac{\delta}{\delta \phi_k^*(\mathbf{x}_1)} E[\phi_k^*(\mathbf{x}_1)] &= \sum_{i=1}^{N} \int \mathrm{d}x_1 h(\mathbf{r}_1) \phi_i(\mathbf{x}_1) \delta(\mathbf{x}_1 - \mathbf{x}_k) \delta_{1,k} \\
&\quad + \sum_{i=1}^{N} \sum_{j=1}^{N} \int \mathrm{d}x_1 \int \mathrm{d}x_2 \phi_i(\mathbf{x}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_j^*(\mathbf{x}_2)\phi_j(\mathbf{x}_2) \delta(\mathbf{x}_1 - \mathbf{x}_k) \delta_{1,k} \\
&\quad - \sum_{i=1}^{N} \sum_{j=1}^{N} \int \mathrm{d}x_1 \int \mathrm{d}x_2 \phi_j(\mathbf{x}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_j^*(\mathbf{x}_2)\phi_i(\mathbf{x}_2) \delta(\mathbf{x}_1 - \mathbf{x}_k) \delta_{1,k} \\
&\quad - \sum_{i=1}^{N} \varepsilon_i \int \mathrm{d}x_1 \, \phi_i(\mathbf{x}_1) \delta(\mathbf{x}_1 - \mathbf{x}_k) \delta_{1,k} \\
&= h(\mathbf{r}_1)\phi_k(\mathbf{x}_1) + \sum_{j=1}^{N} \int \mathrm{d}x_2 \phi_1(\mathbf{x}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_j^*(\mathbf{x}_2)\phi_j(\mathbf{x}_2) \\
&\quad - \sum_{j=1}^{N} \int \mathrm{d}x_2 \phi_j(\mathbf{x}_k) \left(\frac{k}{|\mathbf{r}_k - \mathbf{r}_2|} \right) \phi_j^*(\mathbf{x}_2)\phi_k(\mathbf{x}_2) - \varepsilon_k \phi_k(\mathbf{x}_k).
\end{aligned} \tag{36}$$

Observe that the first and second terms correspond to equations (19) and (20), as desired.

□

The Hartree-Fock method, despite its physically more accurate picture, was little used until the advent of electronic computers. Before then, Hartree's method and other empirical models were favoured for their small computational cost.

Note that technically Hartree-Fock is not a density functional theory (DFT), as the term specifically refers to *orbital-free (orbital-independent) methods*, such as the Thomas-Fermi model.

4.5 Iterative Scheme

The iterative scheme of the Hartree-Fock method is illustrated in the figure 1, taken from Wikipedia, Hartree-Fock Method.

5 Post Hartree-Fock Methods

In the last section we have devised a way to formulate the problem of solving our TISE using a recursive scheme. Now we build on the previous method and make corrections to approximate the true value even better, using the Hartree-Fock wavefunction as our new initial value. We call these methods **Post Hartree-Fock methods**.

To remove any ambiguity, from now on we shall call write the Hartree-Fock wavefunction as Φ^{HF}, and recall that it should satisfy

$$\Phi^{\mathrm{HF}} = \frac{1}{\sqrt{N!}} \det\left(\phi_1, \phi_2, \dots, \phi_N\right),$$

$$\left\langle \Phi_i^{\mathrm{HF}} \,\middle|\, \Phi_j^{\mathrm{HF}} \right\rangle.$$

The orbital wavefunctions $(\phi_1, \phi_2, \dots, \phi_N)$ can be separated into their spatial and spin components (why?), so that

$$\phi_{i,\alpha_j}(\mathbf{x}) = \overline{\phi}_{i,\alpha_j}(\mathbf{r})\alpha_j(\sigma). \tag{37}$$

Example 5.1 (Two-spin systems)**.** In a two spin system, the spin function only takes on two values, namely $\alpha_j = \{\alpha, \beta\}$, representing spin-up and spin-down respectively. Then we can write

$$\phi_{i,\alpha}(\mathbf{x}) = \overline{\phi}_{i,\alpha}(\mathbf{r})\alpha(\sigma), \quad \phi_{i,\beta}(\mathbf{x}) = \overline{\phi}_{i,\beta}(\mathbf{r})\beta(\sigma).$$

Example 5.2 (Spin channel)**.** Calculate spin channel?

Using a known complete basis $\{\chi_\mu(\mathbf{r})\}$, $\mu = 1, 2, \dots, \mu_M$ we can expand $\overline{\phi}_{i,\sigma}$ as

$$\overline{\phi}_{i,\sigma}(\mathbf{r}) = \sum_{\mu=1}^{M} C_{i,\sigma}^{\mu} \chi_\mu(\mathbf{r}).$$

By definition of the ground state energy E_0, we have

$$E_0 \leq E^{\mathrm{HF}} \equiv E^{\mathrm{GHF}} \leq E^{\mathrm{UHF}} \leq E^{\mathrm{RHF}}, \tag{38}$$

where the superscripts refer to the following specific SCF methods:

- GHF: Generalised Hartree-Fock method.

- UHF: Unrestricted Hartree-Fock method.
- RHF: Restricted Hartree-Fock method.

We set $E_0 = E^{\mathrm{HF}} + E^{\mathrm{C}}$, where E^{C} is the correlation energy such that $E^{\mathrm{C}} = E_{0-E^{\mathrm{HF}}} \leq 0$.

Remark. E^{C} can be obtained systematically in post Hartree-Fock methods with a cost that also increases <u>systematically</u> (what does this mean?).

5.1 Perturbation theory

When defining the non-interacting particles Hamiltonian, we let

$$\hat{H}^{\mathrm{NI}} = \sum_{i=1}^{N} \hat{f}(x_i).$$

In a similar light, we define a many particle Fock operator by

$$\hat{F} \equiv \sum_{i=1}^{N} \hat{f}(x_i) = \sum_{i=1}^{N} \left\{ \hat{h}(\mathbf{r}_i) + \sum_{j=1}^{N} \left[\mathcal{J}_j(\mathbf{x}_i) - \mathcal{K}_j(\times,_i) \right] \right\}.$$

Remark. $\hat{F}$ is Hermitian.

Exercise 5.1. Check the above remark.

This is the Hartree-Fock Hamiltonian for the whole system. Note that the HF wavefunction is in general not a eigenfunction of the electronic Hamiltonian $\hat{H}_{\mathrm{e}}$, but it *is* an eigenfunction of $\hat{F}$ i.e.

$$\hat{F}\Psi^{\mathrm{HF}} = \alpha \Psi^{\mathrm{HF}}.$$

Then we have

$$\hat{F}\Psi^{\mathrm{HF}} = \left(\sum_{i=1}^{N} \hat{f} \right) \Psi^{\mathrm{HF}} = \sum_{i=1}^{N} \varepsilon_i \Psi^{\mathrm{HF}}.$$

Following the time-independent perturbation method of quantum mechanics, we define the unperturbed Hamiltonian $\hat{H}_0$ to be $\hat{F}$, and treat the external potential as our perturbation:

$$\begin{aligned} \hat{V} &= \hat{H} - \hat{T} - \hat{U} \\ &= \hat{H} - \hat{H}_0 = \hat{H} - \hat{F}, \end{aligned}$$

$$\hat{H} = \hat{H}^{\mathrm{NI}} + \left(\frac{e^2}{4\pi\epsilon_0} \right) \sum_{i=1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Set up the following perturbation problem:

$$\begin{aligned} &(1) \quad \hat{H} = \hat{H}_0 + \lambda \hat{V} + \cdots, \\ &(2) \quad \Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \cdots, \\ &(3) \quad E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots. \end{aligned} \tag{39}$$

Christian Møller and Milton S. Plesset (1934) developed a systematic way to treat quantum chemical systems using the perturbation method. This is called the Møller-Plesset perturbation theory (MP). Matching coefficients, we get:

- Level 0 (λ^0):
$$\hat{H}_0\Psi^{(0)} = E^{(0)}\Psi^{(0)}$$
$$\implies \Psi^{(0)} = \Psi^{\mathrm{HF}},\ E^{\mathrm{MP}\ 0} \equiv E^{(0)} = \sum_{i=1}^{N} \varepsilon_i.$$

  Remark. This can be used for systems of up to $N \sim 500$ electrons.

- Level 1 (λ^1):
$$E^{\mathrm{MP}\ 1} \equiv E^{(1)} = \left\langle \Psi^{\mathrm{HF}} \middle| \hat{V} \middle| \Psi^{\mathrm{HF}} \right\rangle = E^{\mathrm{HF}} - \left(\sum_{i=1}^{N} \varepsilon_i \right).$$

  Then
$$E^{(0)} + E^{(1)} = E^{\mathrm{MP}\ 0} + E^{\mathrm{MP1}} = E^{\mathrm{HF}}.$$

- Higher levels:
$$\text{MP2, MP3, MP4, ...}$$

  The computational cpomplexity for solving for 2nd-order (MP2), 3rd-order(MP3), etc. are, respectively, $\Theta(N^5)$, $\Theta(N^6)$ (??), $\Theta(N^7)$. Carrying up to n-th order gives the exact solution.

5.2 Full Configuration Interaction

In the full configuration interacting (FCI) method, we use HF orbitals to generate all possible (or, as many as computationally effective) Ψ^{HF}. This produces configuration state functions (CSFs) $\{\Psi_n^{\mathrm{HF}}\}$.

From perturbative methods:
$$\hat{F}\Psi_n^{\mathrm{HF}} = E_n^{(0)}\Psi_n^{\mathrm{HF}} = \left(\sum_{i=1}^{N} \varepsilon_i \right) \Psi_n^{\mathrm{HF}}.$$

Example 5.3 (Transition wavefunctions)**.** We can actually construct wavefunctions that describe the transition of electrons between different orbitals.

- Single excitation ($i \to a$):
$$\Psi_i^a = \frac{1}{\sqrt{N!}} \det\left(\phi_1, \dots, \phi_{i-1}, \phi_a, \phi_{i+1}, \dots, \phi_N\right).$$

- Double excitation ($i \to a, j \to b$):
$$\Psi_{ij}^{ab} = \frac{1}{\sqrt{N!}} \det\left(\phi_1, \dots, \phi_{i-1}, \phi_a, \phi_{i+1}, \dots, \phi_{j-1}, \phi_b, \phi_{j+1}, \dots, \phi_N\right).$$

And so on and so forth. The states $(i, j, k, \dots)$ describe occupied states: $1, 2, \dots, N$, while the states $(a, b, c, \dots)$ describe unoccupied or virtual states: $N+1, N+2, \dots$.

Finding the exact solution of FCI determinants is an *NP-complete problem* , i.e. solutions can be verified quickly (in polynomial time) but not found quickly.

Definition 5.1 (NP-complete).

Remark. NP-complete problems also include

Since $\hat{F}$ is Hermitian, $\{\Psi^{\text{HF}}\}_n$ is a complete basis. This means we can calculate the **exact** electronic wavefunction using the expansion

$$\Psi = \sum_n C_n \Psi_n^{\text{HF}},$$

so in principle we can obtain exact solutions to Ψ_0 and E_0 using FCI. However, the cost goes like $\Theta(e^{\alpha N})$, and the limit is around $N \sim 20$.

Example 5.4 (FCI in practice). We consider the singlet state of the water molecule $\mathsf{H_2O}$:

1. Using the $6-31G(d)$ basis ($M = 19$) requires $\sim 30 \times 10^6$ CSFs.
2. Using the $6-311G(2d, 2p)$ basis ($M = 41$) requires $\sim 106 \times 10^9$ CSFs. This is already over limit for classical computers and even quantum computers!
3. Take the limit $M \to \infty$ gives the exact result and the lowest E^{HF} prediction.

Remark. The Hartree-Fock energy is an upperbound of the true GS energy, i.e. $E_0 \leq E^{\text{HF}}$.

In the above example, we found that it is unfeasible to use FCI to solve even a small system. In order to make computation easier, we introduce the *truncation* of FCI, at the cost of accuracy:

$$CISD,\ CISDT,\ CISDTQ,\ CISDTQ5,\ \dots, CI(SDTQ56\cdots N).$$

The truncated configuration interaction (TCI) method has size-onconsistency issues. When solving for the helium dimer. This problem is solved by introducing the **coupled-cluster (CC) theory** .

6 Electron Density

Problem of storing wavefunction information: a system of N particles has $3N$ degrees of freedom, so it lives in a $3D$-dimensional configuration space. There are

$$\left(10^3\right)^N = 10^{3N}$$

states, so for a small system of $N \sim 10$ there are $\sim 10^{30}$ states to consider. This is beyond any modern computation capacity.

To solve the problem, we look for another quantity that also uniquely encodes the information we need, i.e. ground state energy, and minimise with respect to that quantity. The quantity is electron (number) density.

The electron density is given by $\rho = \rho(\mathbf{r})$, which is 3 dimensional. Question: can we minimise E_0 as a function of ρ, namely,

$$E_0 = \min_\rho E[\rho]$$

subject to $\int \mathrm{d}^3 r\, \rho(\mathbf{r}) = N$?

6.1 Two Theorems

Theorem 6.1. *Given the wavefunction* Ψ*, electron density* $\rho(\mathbf{r})$ *is determined as a functional of* Ψ*.*

Theorem 6.2. *Given the electron density* $\rho(\mathbf{r})$*, energy* E *is determined as a functional of* ρ*.*

6.2 Deriving the Electron Density Relation

Definition 6.1 (density operator)**.** *The electron density is, according to quantum mechanics, the expectation value of some corresponding operator, which we call the electron density operator* $\hat{\rho}$*. Then*

$$\rho(\mathbf{r}) = \langle \Psi \,|\, \hat{\rho} \,|\, \Psi \rangle \,,$$

where

$$\hat{\rho} = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i).$$

Example 6.1 (One-electron system)**.** For a one-electron system,

$$\rho(\mathbf{r}_1) = \sum_{\sigma} \left|\Psi(\mathbf{x}_1)\right|^2 .$$

By definition, it is easy to check that

$$\int \mathrm{d}^3 r_1 \, \rho(\mathbf{r}) = \int \mathrm{d}^3 r \sum_{\sigma} \left|\Psi(\mathbf{x}_1)\right|^2 = 1.$$

Example 6.2 (N-electron system)**.** For an N-electron system,

$$\rho(\mathbf{x}_1) = N \sum_{\sigma_1, \sigma_2, \dots, \sigma_N} \int \mathbf{d}^3 r_2 \int \mathbf{d}^3 r_3 \cdots \int \mathbf{d}^3 r_N \, \left|\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\right|^2 .$$

Then the normalisation is

$$\int \mathrm{d}^3 r_1 \, \rho(\mathbf{r}_1) = N \cdot 1 = N,$$

as expected. This equation can be used to compute $\rho(\mathbf{r})$ given some wavefunction $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$.

Recall the definition of the energy functional from Hartree's method:

$$\begin{aligned} E[\Phi] &\equiv \left\langle \Phi \,\middle|\, \hat{H} \,\middle|\, \Phi \right\rangle \\ &= \left\langle \Phi \,\middle|\, \hat{T} \,\middle|\, \Phi \right\rangle + \left\langle \Phi \,\middle|\, \hat{V} \,\middle|\, \Phi \right\rangle + \left\langle \Phi \,\middle|\, \hat{U} \,\middle|\, \Phi \right\rangle \\ &\equiv T + V_{\mathrm{ex}} + V_{\mathrm{int}}. \end{aligned} \tag{40}$$

We will show that the external potential term in $\hat{H}$ can be written as a functional of $\rho(\mathbf{r})$.

$$\begin{aligned}
V_{\text{ex}} &= V[\Psi] = \left\langle \Psi \middle| \hat{V} \middle| \Psi \right\rangle \\
&= \sum_{\sigma_1,\sigma_2,\dots,\sigma_N} \int \mathbf{d}^3 r_1 \int \mathbf{d}^3 r_2 \cdots \int \mathbf{d}^3 r_N \, \Psi(\mathbf{x}_1,\dots,\mathbf{x}_N)^* \left(\sum_{i=1}^N V(\mathbf{r}_i) \right) \Psi(\mathbf{x}_1,\dots,\mathbf{x}_N) \\
&= \sum_{i=1}^N \int \mathrm{d}^3 r_i V(\mathbf{r}_i) \left\{ \sum_{\sigma_1,\sigma_2,\dots,\sigma_N} \int \mathbf{d}^3 r_1 \cdots \int \mathbf{d}^3 r_{i-1} \int \mathrm{d}^3 r_{i+1} \cdots \int \mathbf{d}^3 r_N \, \left| \Psi(\mathbf{x}_1,\dots,\mathbf{x}_N) \right|^2 \right\} \\
&= \sum_{i=1}^N \int \mathrm{d}^3 r_i V(\mathbf{r}_i) \left\{ \frac{1}{N} \rho(\mathbf{x}_i) \right\} = N \int \mathbf{d}^3 \mathbf{r} \, V(\mathbf{r}) \left\{ \frac{1}{N} \rho(\mathbf{x}) \right\} \\
&= \int \mathrm{d}^3 \mathbf{r} \, \rho(\mathbf{r}) V(\mathbf{r}) \equiv V[\rho].
\end{aligned}$$

This way, the external potential V_{ex} is also a functional of $\rho(\mathbf{r})$. This is the reason DFT succeeds.

Example 6.3 (Electron density for an N-electron system with SD wavefunction)**.** Given a set of wavefunctions $\phi_1, \phi_2, \dots, \phi_N$, suppose the wavefunction can be represented as a single Slater determinant. We obtain

$$\rho(\mathbf{r}_1) = \sum_{i=1}^N \sum_{\sigma_i} \left| \phi_i(\mathbf{x}_i) \right|^2 .$$

Showing that this (kind of intuitive) relation holds is actually not trivial, and requires exmploying the Slater-Condon rules. The below derivation is my solution to Problem 2 of Homework 1.

Proof. Again assume the N-electron wave function is of the form

$$\begin{aligned}
\Psi^{\text{SL}}(\mathbf{x}_1,\dots,\mathbf{x}_N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{vmatrix} \\
&= \frac{1}{\sqrt{N!}} \det\left(\phi_1, \phi_2, \dots, \phi_N\right) .
\end{aligned} \tag{41}$$

For simplicity we denote Φ^{SL} with Ψ from now on.

Again using equ. (22), we can express the determinant more compactly in its expansion form, which has $N!$ terms and is organised as follows:

$$\Psi(\mathbf{x}_1,\dots,\mathbf{x}_N) = \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \operatorname{sgn}(\sigma) \prod_{i=1}^N \phi_{\sigma(i)}(\mathbf{x}_i), \tag{42}$$

where $\sigma \in S_N$ is a permutation of the indices (belonging to the permutation group S_N), and sgn accounts for antisymmetry.

By definition we have

$$\begin{aligned}\rho(\mathbf{r}) &= \left\langle \Psi \,\middle|\, \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_k) \,\middle|\, \Psi \right\rangle \\ &= \int \mathrm{d}x_2 \cdots \int \mathrm{d}x_N \, \Psi^*(\mathbf{x}, \mathbf{x}_2 \dots, \mathbf{x}_N) \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_k) \Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N),\end{aligned} \tag{43}$$

Since non-interacting operators do not distinguish between electrons, we take 1 as a representative to get

$$\begin{aligned}\rho(\mathbf{r}) &= N \left\langle \Psi \,\middle|\, \delta(\mathbf{r}-\mathbf{r}_1) \,\middle|\, \Psi \right\rangle \\ &= N \int \mathrm{d}x_1 \cdots \int \mathrm{d}x_N \left(\frac{1}{\sqrt{N!}} \sum_{\sigma} \operatorname{sgn}(\sigma) \prod_{i=1}^{N} \phi^*_{\sigma(i)}(\mathbf{x}_i) \right) (\delta(\mathbf{r}-\mathbf{r}_1)) \left(\frac{1}{\sqrt{N!}} \sum_{\sigma'} \operatorname{sgn}(\sigma') \prod_{j=1}^{N} \phi^*_{\sigma'(j)}(\mathbf{x}_j) \right) \\ &= \frac{1}{(N-1)!} \sum_{\sigma_1, \dots, \sigma_N} \int \mathrm{d}^3 r_1 \delta(\mathbf{r}-\mathbf{r}_1) \int \mathrm{d}^3 r_2 \cdots \int \mathrm{d}^3 r_N \sum_{\sigma} \sum_{\sigma'} \operatorname{sgn}(\sigma) \operatorname{sgn}(\sigma') \prod_{i=1}^{N} \prod_{j=1}^{N} \phi^*_{\sigma(i)}(\mathbf{x}_i) \phi_{\sigma'(j)}(\mathbf{x}_j \\ &\overset{\dagger}{=} \frac{1}{(N-1)!} \sum_{\sigma_1, \dots, \sigma_N} \int \mathrm{d}^3 r_1 \delta(\mathbf{r}-\mathbf{r}_1) \int \mathrm{d}^3 r_2 \cdots \int \mathrm{d}^3 r_N \sum_{\sigma} \prod_{i=1}^{N} \left| \phi_{\sigma(i)}(\mathbf{x}_i) \right|^2 \\ &\overset{\ddagger}{=} \frac{1}{(N-1)!} \sum_{\sigma_1} (N-1)! \int \mathrm{d}^3 r_1 \, \delta(\mathbf{r}-\mathbf{r}_1) \sum_{k=1}^{N} \left| \phi_k(\mathbf{r}_1) \right|^2 \\ &= \sum_{k=1}^{N} \sum_{\sigma_1} \int \mathrm{d}^3 r_1 \, \delta(\mathbf{x}-\mathbf{x}_1) \left| \phi_k(\mathbf{x}_1) \right|^2 = \sum_{i=1}^{N} \sum_{\sigma} \left| \phi_k(\mathbf{x}) \right|^2 .\end{aligned} \tag{44}$$

†: As in problem 1, since $\{\phi_k\}$ is orthonormal, the integrals over r_2 to r_N multiply to zero unless the electrons occupy the same orbital in the two products, i.e. for each $\sigma(i)$ in the first product, we have $\sigma'(j) = \sigma(i)$ in the second. By the bijectivity of $\sigma : \{1, \dots, N\} \leftrightarrow \{1, \dots, N\}$, we know that $\sigma(1) = \sigma'(1)$. j is just a dummy variable, so we rename it to be $\phi_{\sigma'(j)}(\mathbf{x}_j) = \phi_{\sigma(i)}(\mathbf{x}_i)$.

‡: Electron 1 can occupy each orbital exactly $(N-1)!$ times, since with 1 fixed, the remaining can be permuted in $(N-1)!$ ways, giving

$$\sum_{\overline{\sigma}_2, \dots, \overline{\sigma}_N} \prod_{i=1}^{N} \int \mathrm{d}^3 r_2 \cdots \int \mathrm{d}^3 r_N \left| \phi_{\overline{\sigma}(i)}(\mathbf{x}_i) \right|^2 = 1, \tag{45}$$

where $\overline{\sigma} \in S_{N-1}$ is a permutation of $N-1$ elements. □

Example 6.4 (Spin-unrestricted system)**.** The system is described by an α-channel and a β-channel, which don't necessarily share the same spatial wavefunction.

$$\phi_i(\mathbf{x}_1) = \overline{\phi}_{i,\alpha}(\mathbf{r}_i) \alpha(\sigma_1), \; i = 1, \dots, N_\alpha,$$

or

$$\phi_i(\mathbf{x}_1) = \overline{\phi}_{i,\beta}(\mathbf{r}_i), \; i = 1, \dots, N_\beta.$$

Using the formula in example 6.2, we get

$$\begin{aligned}
\rho(\mathbf{r}_1) &= \sum_{i=1}^{N_\alpha}\sum_{\sigma_1}\left|\overline{\phi}_{i,\alpha}(\mathbf{r}_i)\alpha(\sigma_1)\right|^2 + \sum_{i=1}^{N_\beta}\sum_{\sigma_1}\left|\overline{\phi}_{i,\beta}(\mathbf{r}_i)\beta(\sigma_1)\right|^2,\ \sigma_1 = \left\{\pm\frac{1}{2}\right\} \\
&= \sum_{i=1}^{N_\alpha}\left|\overline{\phi}_{i,\alpha}(\mathbf{r}_1)\right|^2 + \sum_{i=1}^{N_\beta}\left|\overline{\phi}_{i,\beta}(\mathbf{r}_1)\right|^2 \equiv \rho_\alpha(\mathbf{r}_1) + \rho_\beta(\mathbf{r}_1) \\
&= \sum_{\sigma=\{\alpha,\beta\}}\sum_{i=1}^{N_\sigma}\left|\overline{\phi}_{i,\sigma}(\mathbf{r}_1)\right|^2 \equiv \sum_{\sigma=\{\alpha,\beta\}}\rho_\sigma(\mathbf{r}_1).
\end{aligned}$$

Recall that

$$\sum_{\sigma_1=\{\pm 1/2\}}\left|\alpha(\sigma_1)\right|^2 = 1+0 = 1,\quad \sum_{\sigma_1=\{\pm 1/2\}}\left|\beta(\sigma_1)\right|^2 = 0+1 = 1.$$

Question: Can we do the same for $\hat{T}$ and $\hat{U}$?

1. Kinetic energy: In atomic units,

$$T = \left\langle\Psi\middle|\hat{T}\middle|\Psi\right\rangle = \sum_{i=1}^{N}\left\langle\phi_i\middle|\hat{T}_i\middle|\phi_i\right\rangle = \left\langle\phi_i\middle|-\frac{\nabla^2}{2}\middle|\phi_i\right\rangle = T\left[\{\phi_i\}\right],$$

as appears in Hartree-Fock theory. Then

$$\begin{aligned}
T &= \sum_{i=1}^{N}\left\langle\phi_i\middle|-\frac{\nabla^2}{2}\middle|\phi_i\right\rangle \\
&= \sum_{i=1}^{N}\int \mathrm{d}^3x\,\phi_i(\mathbf{x})^*\left(-\frac{\nabla^2}{2}\right)\phi_i(\mathbf{x}) \\
&= \sum_{\sigma=\{\alpha,\beta\}}\sum_{i=1}^{N}\left\langle\overline{\phi}_{i,\sigma}\middle|-\frac{\nabla^2}{2}\middle|\overline{\phi}_{i,\sigma}\right\rangle,
\end{aligned}$$

where the last equality holds if it is a spin-unrestricted system.

Kinetic energy is functional of Ψ, and if $\Psi = \Psi_{\text{SD}}$, $\langle\phi_i|\phi_j\rangle = \delta_{ij}$, it is a funtional of the orbitals. But in general it is **not** a functional of $\rho(\mathbf{r})$.

2. Interaction potential energy: Again, in atomic units,

$$U = U[\Phi] = \left\langle\Psi\middle|\hat{U}\middle|\Psi\right\rangle,$$

where

$$\hat{U} = \sum_{i<j}^{N}\frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}.$$

If $\Psi = \Psi_{\text{SD}}$ (single-Slater determinant) and $\langle\phi_i|\phi_j\rangle = \delta_{ij}$, then

$$U = \frac{1}{2}\sum_{i,j}^{N}\left\{[ii|jj] - [ij|ji]\right\} \equiv E^{\text{H}} + E^{\text{X}}.$$

Here we define the Hartree energy E^{H} and the exchange energy E^{X} , and we shall show that they are determined by ρ and $\{\phi_i\}$, respectively:

$$E^{\text{H}} = E^{\text{H}}[\rho],\ E^{\text{X}} = E^{\text{X}}\left[\{\phi_i\}\right].$$

The square braket defines a certain inner product-like integral between the states in position 1 and position 2:

$$[ij|kl] \equiv \int \mathrm{d}x_1 \int \mathrm{d}^3x_2\, \phi_1(\mathbf{x}_1)^* \phi_j(\mathbf{x}_1) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_k(\mathbf{x}_2)^* \phi_l(\mathbf{x}_2).$$

Then

$$\begin{aligned} E^{\mathrm{H}} &= \frac{1}{2} \sum_{i,j}^{N} \int \mathrm{d}x_1 \int \mathrm{d}x_2\, \frac{\phi_i(\mathbf{x}_1)^* \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_2)^* \phi_j(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &= \frac{1}{2} \int \mathrm{d}x_1 \int \mathrm{d}x_2\, \frac{\sum_{i=1}^{N} |\phi_i(\mathbf{x}_1)|^2 \sum_{j=1}^{N} |\phi_j(\mathbf{x}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &= \frac{1}{2} \int \mathrm{d}^3r_1 \int \mathrm{d}^3r_2\, \frac{\left(\sum_{i=1}^{N} \sum_{\sigma_2} |\phi_i(\mathbf{x}_1)|^2 \right) \left(\sum_{j=1}^{N} \sum_{\sigma_2} |\phi_j(\mathbf{x}_2)|^2 \right)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &= \frac{1}{2} \int \mathrm{d}^3r_1 \int \mathrm{d}^3r_2\, \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \equiv E^{\mathrm{H}}[\rho]. \end{aligned}$$

Remark. This is analogous to the classical picture of electrostatic charge density $\rho(\mathbf{r})$.

Remark. Hartree energy includes an unphysical self-interaction term. For $i = j$, we have

$$\begin{aligned} \frac{1}{2} \sum_{i=1}^{N} [ii|ii] &= \sum_{i=1}^{N} \left\{ \frac{1}{2} \int \mathrm{d}^3r_1 \int \mathrm{d}^3r_2\, \frac{\rho_i(\mathbf{r}_1)\rho_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\} \\ &= \sum_{i=1}^{N} E^{\mathrm{H}}[\rho_i] = \text{self-interaction energy}. \end{aligned}$$

This will be cancelled by a corresponding term in exchange energy (again, the $i = j$ term).

Now we work on the exchange term, E^{X}:

$$\begin{aligned} E_{\mathrm{X}} &= -\frac{1}{2} \sum_{i,j}^{N} [ij|ji] = -\frac{1}{2} \sum_{,j}^{N} \int \mathrm{d}x_1 \int \mathrm{d}x_2\, \frac{\phi_i(\mathbf{x}_1)^* \phi_j(\mathbf{x}_1) \phi_j(\mathbf{x}_2)^* \phi_i(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &= -\frac{1}{2} \int \mathrm{d}x_1 \int \mathrm{d}x_2\, \frac{\left\{ \sum_{i}^{N} \phi_i(\mathbf{x}_1)^* \phi_i(\mathbf{x}_2) \right\} \left\{ \sum_{j=1}^{N} \phi_j(\mathbf{x}_1)^* \phi_j(\mathbf{x}_2) \right\}}{|\mathbf{r}_1 - \mathbf{r}_2|}. \end{aligned}$$

For the spin-unrestricted (spin-polarised) case, we let $\phi_i(\mathbf{x}) = \phi_i(\mathbf{r}, \sigma)$, and $\phi_i(\mathbf{r}, \sigma) = \phi_{i,\alpha}(\mathbf{r})\alpha(\sigma)$ or $\phi(\mathbf{r}, \sigma) = \phi_{i,\beta}(\mathbf{r})\beta(\sigma)$. Here σ is the electron spin. Then

$$\begin{aligned} E_{\mathrm{X}} &= -\frac{1}{2} \sum_{\sigma \in \{\alpha,\beta\}} \int \mathrm{d}^3r_1 \int \mathrm{d}^3r_2\, \frac{\left| \sum_{i=1}^{N} \phi_{i,\sigma}(\mathbf{r}_1)^* \phi_{i,\sigma}(\mathbf{r}_2) \right|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &= -\frac{1}{2} \sum_{\sigma \in \{\alpha,\beta\}} \int \mathrm{d}^3r_1 \int \mathrm{d}^3r_2\, \frac{|\gamma_\sigma(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \end{aligned}$$

where

$$\gamma_\sigma(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^{N_\sigma} \phi_{i,\sigma}(\mathbf{r}_1)^* \phi_{i,\sigma}(\mathbf{r}_2)$$

is the σ-spin one-electron reduced density matrix (1-RDM).

Remark.

Definition 6.2 (RDM in terms of wavefunctions)**.**

(a) One-electron spin-orbital RDM:

$$\gamma(\mathbf{x}_1,\mathbf{x}_1') \equiv N\int \mathrm{d}x_2 \cdots \int \mathrm{d}x_N\, \Psi(x_1',\mathbf{x}_2,\dots,\mathbf{x}_N)^*\Psi(\mathbf{x}_1,\mathbf{x}_2,\dots,\mathbf{x}_N). \tag{46}$$

(b) One-electron RDM (1-RDM):

$$\gamma(\mathbf{x}_1,\mathbf{x}_1') \equiv N\sum_{\sigma_1}\int \mathrm{d}x_2 \cdots \int \mathrm{d}x_N\, \Psi(\mathbf{r}_1',\sigma_1,\mathbf{x}_2,\dots,\mathbf{x}_N)^*\Psi(\mathbf{r}_1,\sigma_1,\mathbf{x}_2,\dots,\mathbf{x}_N). \tag{47}$$

(c) Two-electron RMD (2-RDM): Might need extra constraints. Otherwise the model may not be variational, since E^{2-RDM} may be lower than E_0.

(d) Pair-density functional theory.

What is the physical interpretation of these functions?

Similarly, we can define the N-electron spin-orbital density matrix:

$$\begin{aligned}\gamma_N(\mathbf{x}_1,\dots,\mathbf{x}_N,\mathbf{x}_1',\dots,\mathbf{x}_N') &= \Psi(\mathbf{x}_1,\dots,\mathbf{x}_N)\Psi^*(\mathbf{x}_1',\dots,\mathbf{x}_N') \\ &= \langle \mathbf{x}_1,\dots,\mathbf{x}_N \mid \Psi\rangle \langle \Psi \mid \mathbf{x}_1',\dots,\mathbf{x}_N'\rangle \\ &= \langle \mathbf{x}_1,\dots,\mathbf{x}_N |\, \hat{\rho}_N \,| \mathbf{x}_1',\dots,\mathbf{x}_N'\rangle .\end{aligned} \tag{48}$$

Conclusion: The interaction potential energy can be separated into two parts: Hartree energy and exchange energy. We have shown that Hartree energy **is** a functional of ρ.

7 Thomas-Fermi Model

The Thomas-Fermi model was separately developed by Thomas and Fermi around 1927. It is the first density functional theory. In this section we also employ atomic units.

$$\begin{aligned}E = E[\Psi] &= \left\langle \Psi \,\middle|\, \hat{H} \,\middle|\, \Psi \right\rangle \\ &= T[\Psi] + V[\Psi] + U[\Psi].\end{aligned}$$

When is it possible to write

$$E = E[\rho] = T[\rho] + V[\rho] + U[\rho], \tag{49}$$

as a sole functional of ρ?

In a moment, we will se that while no analytic solution exists for T and U, we can achieve this approximately in the Thomas-Fermi model.

For the interaction energy, use the classical picture:

$$U[\rho] \approx E^{\mathrm{H}}[\rho] = \frac{1}{2}\int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2\, \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

Note that in the Thomas-Fermi model they ignored the exchange energy. Fock only introduced the idea of exchange energy when he formulated the Hartree-Fock theory in 1928. Until then, Hartree's equation was the main theory for multi-electron systems.

For the kinetic energy term, consider a large amount of **non-interacting** electrons in the presence of **no external fields** ($V(\mathbf{r}) = 0$) at absolute zero. This is the **ideal Fermi gas** approximation.

Consider a box of free electrons in a square box of length L, so $V = L^3$. Then we write the density of uniform electron gas as $\rho_0 = \frac{N}{V}$. For the spin unpolarised case, we have

$$\frac{E_0}{N} = \frac{T}{N} = \frac{3}{5}\epsilon_{\mathrm{F}} = \frac{3}{5}\left(\frac{1}{2}\right)\left(3\pi^2\rho_0\right)^{2/3}.$$

But also

$$\frac{T}{N} = \left(\frac{T}{V}\right)\left(\frac{V}{N}\right) = \frac{t}{\rho_0},$$

where

$$t = \frac{T}{V} = \frac{3}{10}\left(3\pi^2\right)^{2/3}\rho_0^{5/3} = C_F\rho_0^{5/3}$$

is the kinetic energy density.

Then we assume that $t(\mathbf{r})$ depends only on the local density $\rho(\mathbf{r})$. This is the **local density (LD) approximation**, i.e.

$$t^{\mathrm{TF}}(\mathbf{r}) \equiv t^{\mathrm{UEG}}(\rho(\mathbf{r})) = C_F\rho(\mathbf{r})^{5/3}.$$

Then

$$T^{\mathrm{TF}}[\rho] = \int \mathrm{d}^3r\, t^{\mathrm{TF}}(\mathbf{r}) = C_F\int \mathrm{d}^3r\, \rho(\mathbf{r})^{5/3}.$$

Remark. The TF model is also the first LDA model.

For the spin-unrestricted case, we can make the following alterations, called the spin-scaling relation:

$$T^{\mathrm{TF}}[\rho_\alpha, \rho_\beta] = \frac{1}{2}\left(T^{\mathrm{TF}}[2\rho_\alpha] + T^{\mathrm{TF}}[2\rho_\beta]\right).$$

Collecting the result of the above approximations, we have the full funtional $E[\rho]$ written as

$$\begin{aligned} E[\rho] &= T^{\mathrm{TF}}[\rho] + \int \mathrm{d}^3r\, \rho(\mathbf{r})V(\mathbf{r}) + E^{\mathrm{H}}[\rho] \\ &= C_F\int \mathrm{d}^3r\, \rho(\mathbf{r})^{5/3} + \int \mathrm{d}^3r\, \rho(\mathbf{r})V(\mathbf{r}) + \frac{1}{2}\int \mathrm{d}^3r_1\int \mathrm{d}^3r_2\, \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \end{aligned} \tag{50}$$

7.1 Solving the variational problem

We have the following variation problem to solve:

$$\frac{\delta}{\delta\rho(\mathbf{r})}\left\{E[\rho] - \mu\left[\int \mathrm{d}^3r\, \rho(\mathbf{r}) - N\right]\right\} = 0.$$

Here we give an example calculation for the kinetic energy functional.

Example 7.1 (Kinetic energy functional)**.** Let $F[\rho] = T^{\mathrm{TF}}[\rho] = C_F\int \mathrm{d}^3r\, \rho(\mathbf{r})^{5/3}$.

Solving the above variational equation (use the Euler-Lagrange equation), we get

$$\mu = \frac{\delta E[\rho]}{\delta\rho(\mathbf{r})},$$

which is exactly the chemical potential, as shown here: Recall the definition of the chemical potential:

$$\begin{aligned}
\text{(chemical potential)} &= \left(\frac{\partial E}{\partial N}\right) = \left(\frac{\partial E[\rho(\mathbf{r})]}{\partial N}\right) \\
&= \int \mathrm{d}^3 r \, \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial N} \\
&= \mu \int \mathrm{d}^3 r \, \frac{\partial \rho(\mathbf{r})}{\partial N} \\
&= \mu \frac{\partial}{\partial N} \left(\int \mathrm{d}^3 r \rho(\mathbf{r}) \right) = \mu,
\end{aligned}$$

where the second equality follows from the first Hohenberg-Kohn theorem, which states that GS energy is uniquely determined by electron number density.

This is an **orbital-free density functional theory**, which is the original DFT (notice that the derivation does not refer to orbitals).

Remark. The complexity of this method is said to be $O(N)$.

The interaction integral appears at first sight to be of order $O(M^2)$, where M is the number of grid points. However, we can approximately lower it to $O(M)$ using the following methods:

1. Fourier transform: The integral is in the form of a convolution integral, so we can do the following procedure:

   $$\text{Fourier transform} \to \text{scalar multiplication} \to \text{Inverse Fourier transform}$$

   Using fast Fourier transform we can reduce the cost to $\sim O(M \log M) \approx O(M)$.

2. Poisson equation:

Thus TF theory has very low computational complexity $O(N)$, but it is not accurate enough for most applications in condensed state physics. For example, the TF model predicts no binding between electrons, and the inter-atomic force is repulsive regardless of distance (Teller's theorem, Rev. Mod. Phys. 34, 627 (1962)).

Example 7.2 (Coulomb potential)**.** Consider the potential as a functional of electron density:

$$V[\rho] = \int \mathrm{d}^3 r' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r}'|}.$$

Example 7.3 (Electron-electron interaction energy)**.** Consider the functional

$$J[\rho] = \frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

Example 7.4 (One-electron system)**.** The kinetic energy of a single-electron system can be written in its von Weizsacker form:

$$T = T^{\mathrm{W}} = \frac{1}{8} \int \mathrm{d}^3 r \, \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})}. \tag{51}$$

This may be regarded as the energy of a bosonic ground state, since all particles are condensed into the same orbital. Define the kinetic energy density t^{W} to be

$$t^{\mathrm{W}} \equiv \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \implies T^{\mathrm{W}} = \int \mathrm{d}^3 r\, t^{\mathrm{W}}.$$

After some calculation, it can be shown that

$$\frac{\delta T^{\mathrm{W}}}{\delta\rho(\mathbf{r})} = \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} - \frac{1}{4}\frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})}.$$

However, the von Weizsäcker kinetic energy is not accurate. To make more accurate predictions, we can make the following modification to the kinetic energy density term, called the **TFW model**.

Example 7.5 (TFW model)**.** Define the kinetic energy as

$$T^{\mathrm{TFW}} \equiv T^{\mathrm{TF}} + T^{\mathrm{W}}.$$

Here T^{W} is the von Weizsäcker kinetic energy functional. This form binds atoms. Disappointly, the kinetic energy predicted by this approach is not much better than the original TF model, e.g. the results for Ar dimers are 29% below the experimental value.

Example 7.6 (TF$\frac{1}{9}$W model)**.** Another similar kinetic energy functional that has been shown to bind atoms is given by

$$T^{\mathrm{TF}\frac{1}{9}\mathrm{W}} \equiv T^{\mathrm{TF}} + \frac{1}{9}T^{\mathrm{W}}.$$

This model is *exact* for long-wavelength perturbations, and gives the correct second-order gradient expansion correction to the TF functional. However, energy predictions are again inaccurate.

Similarly, the more general combination

$$T^{\mathrm{TF}\lambda\mathrm{W}} \equiv T^{\mathrm{TF}} + \lambda T^{\mathrm{W}}$$

has been investigated. All TFλW models predict a finite ρ at the nucleus, and exponential decay far away. However, only at $\lambda = 1$ is the correct exponential decay constant predicted (Cf. Jeng-Da Chai; Weeks, John D. (2004). Modified statistical treatment of kinetic energy in the Thomas-Fermi model.)

8 Hohenberg-Kohn Theorem

Recall the various assumptions used in the Thomas-Fermi model of section 7:

1. We assumed E is a sole functional of ρ.
2. We assumed the desired ground state energy is $E_0 = \min_\rho E[\rho]$ subject to $\int \mathrm{d}^3 r\, \rho(\mathbf{r}) = N$.
3. The expression for energy

$$E[\rho] = \int \mathrm{d}^3 r\, \rho(\mathbf{r}) V(\mathbf{r}) + T^{\mathrm{TF}}[\rho] + E^{\mathrm{H}}[\rho]$$

is approximate.

In the Thomas-Fermi model, we used the uniform Fermi gas approximation (a delocalised picture) to treat the kinetic energy, but assumed LDA on $\rho(\mathbf{r})$ to carry out the calculation. This is inherently contradictory.

The Hohenberg-Kohn theorems put DFT on firm theoretical footing. We state the Hohenberg-Kohn theorems as follows:

Theorem 8.1 (First Hohenberg-Kohn theorem)**.** *Suppose the ground state wavefunction* Ψ *is* nondegenerate *for a system of* N *electrons in the presence of an external potential* $V(\mathbf{r})$*. Then there is a one-to-one correspondence between the ground state density* $\rho(\mathbf{r})$ *and the external potential* $V(\mathbf{r})$*, up to a constant. That is,*

$$\rho(\mathbf{r}) \xleftrightarrow{\text{one−to−one}} V(\mathbf{r}) \text{ up to a constant.}$$

Proof. We show the two directions of the mapping:

($\Longleftarrow$) Given $V(\mathbf{r})$, the Hamiltonian is determined, so we have a Schrödinger equation to solve. Solving

$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U}\right]\Psi$$

gives the wavefunction Ψ uniquely up to a phase factor, so

$$\rho(\mathbf{r}) = N \int \mathrm{d}^3 r_2 \cdots \int \mathrm{d}^3 r_N \, \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N)\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

is uniquely determined up to an integration constant. Here we used the fact that the ground state is non-degenerate.

($\Longrightarrow$) Assume by way of contradition that there are two potentials $V_a(\mathbf{r})$, $V_b(\mathbf{r})$ differing by more than a constant that produce the same $\rho(\mathbf{r})$.

Let $\hat{H}_a \equiv \hat{T} + \hat{V}_a + \hat{U}$, $\hat{H}_b = \hat{T} + \hat{V}_b + \hat{U}$. Then assume their ground state energy is E_a, E_b, given by

$$\hat{H}_a \left|\Psi_a\right\rangle = E_a \left|\Psi_a\right\rangle, \; \hat{H}_b \left|\Psi_b\right\rangle = E_b \left|\Psi_b\right\rangle.$$

Assume again by way of contradiction that $\left|\Psi_a\right\rangle$ is an eigenstate of $\hat{H}_b$, and $\hat{H}_b \left|\Psi_a\right\rangle = \tilde{E}_a \left|\Psi_a\right\rangle$. Subtracting gives

$$(\hat{H}_a - \hat{H}_b)\left|\Psi_a\right\rangle = (\hat{V}_a - \hat{V}_b)\left|\Psi_a\right\rangle = (E_a - \tilde{E}_a)\left|\Psi_a\right\rangle.$$

So

$$\left[\sum_{i=1}^{N} V_a(\mathbf{r}_i) - \sum_{i=1}^{N} V_b(\mathbf{r}_i)\right]\Psi_a(\mathbf{x}_1, \dots, \mathbf{x}_N) = (E_a - \tilde{E}_a)\Psi_a(\mathbf{x}_1, \dots, \mathbf{x}_N),$$

which is a contradiction since the left hand side is a function of $\mathbf{r}$ while the right hand side isn't. Thus $\left|\Psi_a\right\rangle$ is not an eigenstate of $\hat{H}_b$. By the same reasoning, $\left|\Psi_b\right\rangle$ is not an eigenstate of $\hat{H}_a$.

By the Rayleigh-Ritz variational principle,

$$\begin{aligned}
E_a &= \left\langle \Psi_a \middle| \hat{H}_a \middle| \Psi_a \right\rangle < \left\langle \Psi_b \middle| \hat{H}_a \middle| \Psi_b \right\rangle \\
&= \left\langle \Psi_b \middle| \hat{H}_b + \hat{V}_b - \hat{V}_a \middle| \Psi_b \right\rangle \\
&= E_b + \int \mathrm{d}^3 r \, \rho(\mathbf{r}) V_b(\mathbf{r}) - \int \mathrm{d}^3 r \, \rho(\mathbf{r}) V_a(\mathbf{r}) \\
&= E_b + \int \mathrm{d}^3 r \, \rho(\mathbf{r}) \left[V_b(\mathbf{r}) - V_a(\mathbf{r})\right].
\end{aligned}$$

Exchanging the role of a and b:

$$E_b < E_a + \int \mathrm{d}^3 r \, \rho(\mathbf{r}) \left[V_a(\mathbf{r}) - V_b(\mathbf{r}) \right].$$

Add the two inequalities to get

$$E_a + E_b < E_b + E_a,$$

thus the contradiction. □

Remark. The proof seems very general. Can we extend the result to any functional of the wavefunction Ψ, as $\rho(\mathbf{r}) = \rho[\Psi(\mathbf{r})]$ itself is?

By the first Hohenberg-Kohn theorem, we get the following result: the external potential $V(\mathbf{r})$, the wavefunction Ψ, and the density $\rho(\mathbf{r})$ are equally capable of representing a physical system. That $\rho(\mathbf{r})$ can fully characterise a system is the foundation of density functional theory.

The first Hohenberg-Kohn theorem isn't enough to determine the ground state density in practice, since it only applies if we could guess at the correct $\rho(\mathbf{r})$. The second Hohenberg-Kohn theorem gives a way to find the correct ground state energy.

Theorem 8.2 (Second Hohenberg-Kohn theorem)**.** *The electron density that minimises the energy of the overall functional $E[\rho]$ is the true ground state electron density corresponding to the full solutions of the Schrödinger equation. That is,*

$$E[\rho] \geq \min_{\rho} E[\rho] = E_0.$$

where the minimisation is subject to $\int \mathrm{d}^3 r \, \rho(\mathbf{r}) = 1$.

Proof. Suppose $\rho_{\mathrm{T}}(\mathbf{r})$ is a trial density, and $\rho(\mathbf{r})$ is the true ground state density. By theorem 8.1, if $\rho_{\mathrm{T}}(\mathbf{r}) \neq \rho(\mathbf{r})$, their corresponding potentials $V_{\mathrm{T}}(\mathbf{r})$ and $V(\mathbf{r})$ differ by more than a constant, and their corresponding states $|\Psi_{\mathrm{T}}\rangle$ and $|\Psi\rangle$ differ by more than a phase factor.

Then

$$\begin{aligned} E[\rho_{\mathrm{T}}] = E[\Psi_{\mathrm{T}}] &= \left\langle \Psi_{\mathrm{T}} \middle| \hat{H} \middle| \Psi_{\mathrm{T}} \right\rangle \\ &\leq \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = E = E[\rho] \\ &= T[\rho] + \int \mathrm{d}^3 r \, \rho(\mathbf{r}) V(\mathbf{r}) + U[\rho]. \end{aligned}$$

So, for all possible $\rho(\mathbf{r})$, we have

$$E[\rho] \geq \min_{\rho'} E[\rho'] = E[\rho] = E_0.$$

□

In theorem 8.1 and theorem 8.2, $\rho(\mathbf{r})$ must be the *ground state* density of some external potential $V(\mathbf{r})$.

Remark. Noticce that the second Hohenberg-Kohn theorem is very much like the Rayleigh-Ritz variational method, but now we are confining the search to only a subset of the space of all possible $\rho(\mathbf{r})$. In particular, we are searching under the condition that $\rho(\mathbf{r})$ is normalised.

Definition 8.1 (v-representability)**.** *In the above discussion, ρ must be the* non-degenerate ground state density *of some external potential. Such a density $\rho(\mathbf{r})$ is called v-*representable*. However, not all ρ has to be v-representable.*

8.1 Levy Constrained-Search Formulation

This method is based on the Rayleigh-Ritz variational method, and was developed in 1982. Consider the following optimisation problem:

$$E_0 = \min_{\Phi} E[\Phi] = \min_{\Phi} \left\langle \Phi \middle| \hat{T} + \hat{V} + \hat{U} \middle| \Phi \right\rangle .$$

This can be written as a minimisation problem with respect to ρ:

$$E_0 = \min_{\rho} \left\{ \min_{\Phi\to\rho} \left[\left\langle \Phi \middle| \hat{V} \middle| \Phi \right\rangle + \left\langle \Phi \middle| \hat{T} + \hat{U} \middle| \Phi \right\rangle \right] \right\} . \tag{52}$$

Here we search for all possible trial N-electron wavefunction Φ that yield a given N-representable ρ, and minimise $\{\cdots\}$. Then we search for all possible N-representable density ρ that minimises $[\cdots]$. The inner minimisation is possible because given ρ, $\Phi = \Phi[\rho]$ is a functional of ρ. Then

$$\begin{aligned} E_0 &= \min_{\rho} \left\{ \min_{\Phi\to\rho} \left[\int \mathrm{d}^3 r\, \rho(\mathbf{r}) V(\mathbf{r}) + \left\langle \Phi \middle| \hat{T} + \hat{U} \middle| \Phi \right\rangle \right] \right\} \\ &= \min_{\rho} \left\{ \int \mathrm{d}^3 r\, \rho(\mathbf{r}) V(\mathbf{r}) + \min_{\Phi\to\rho} \left[\left\langle \Phi \middle| \hat{T} + \hat{U} \middle| \Phi \right\rangle \right] \right\} \\ &\equiv \min_{\rho} \left\{ \int \mathrm{d}^3 r\, \rho(\mathbf{r}) V(\mathbf{r}) + F[\rho] \right\} \\ &= E[\rho]. \end{aligned}$$

The ρ does not have to be the non-degenerate ground state of some external potential. That is, ρ does not have to be v-representable, but only N-representable. Practicality of this method is limited.

If the exact universal functional $F[\rho]$ can be found, we can minimise $E[\rho]$ subject to the constraint $\int \mathrm{d}^3 r\, \rho(\mathbf{r}) V(\mathbf{r}) = N$:

$$\frac{\delta}{\delta \rho(\mathbf{r})} \left[E\rho - \mu \left(\int \mathrm{d}^3 r\, \rho(\mathbf{r}) V(\mathbf{r}) - N \right) \right] = 0,$$

$$\implies \mu = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = V(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})}.$$

The physical significance of μ is simply

$$\implies \rho_0(\mathbf{r}),\ E_0 = E[\rho_0].$$

The main problem of determining the $F[\rho]$ lies in the difficulty of finding the correct kinetic energy functional. Now we can restate the two HK theorems as follows: If the ground state wavefunction is nondegenerate, then

1. $E = E[\rho] = \int \mathrm{d}^3 r\, \rho(\mathbf{r}) V(\mathbf{r}) + F[\rho]$.
2. The ground state energy is given by $E_0 = \min_\rho E[\rho]$, and the Lagrange multiplier is

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = V(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})}.$$

9 Kohn-Sham Method

The Kohn-Sham method was developed in 1965 in a paper by Walter Kohn and Lu Jeu Sham. *"Kohn received a Nobel Prize in Chemistry in 1998 for the Kohn-Sham equations and other work related to density functional theory (DFT)."*

In my opinion, it is unfortunate that Sham and Hohenberg were not awarded that year's Nobel prize alongside Kohn. Instead, the other half of that year's prize was awarded to John Pople, for the development of ab initio calculations in quantum chemistry. I think this is a good start of a conversation on the scientific culture shaped by the Nobel Prize Committee, which almost too often exemplifies the image of individual genius and undermines the importance of the collective scientific machinery.

9.1 Exchange-Correlation Energy

The principle goes as follows: for a physical system with external potential $V(\mathbf{r})$, we find a **Kohn-Sham reference system**, which is an N-particle non-interacting system. We suppose that we can find an effective potential V_{eff} for the reference system such that the ground state density $\rho_{\text{S}}(\mathbf{r})$ is the same as that of the physical system $\rho(\mathbf{r})$.

A natural question to ask now is: what is V_{eff}? This question may be answered as follows: Since the Hohenberg-Kohn theorems are applicable to both systems, for the reference system we have

$$E_{\text{S}}[\rho_{\text{S}}] = \int \mathrm{d}^3 r\, \rho_{\text{S}}(\mathbf{r}) V(\mathbf{r}) + F_{\text{S}}[\rho_{\text{S}}].$$

Here $F_{\text{S}}[\rho_{\text{S}}] = \left\langle \Phi \middle| \hat{T} \middle| \Phi \right\rangle \equiv T_{\text{S}}[\rho_{\text{S}}]$ is the non-interacting kinetic energy functional. Then by the Euler equation we have

$$\mu_{\text{S}} = \frac{\delta E_{\text{S}}[\rho_{\text{S}}]}{\delta \rho_{\text{S}}(\mathbf{r})} = V_{\text{eff}}(\mathbf{r}) + \frac{\delta T_{\text{S}}[\rho_{\text{S}}]}{\delta \rho_{\text{S}}(\mathbf{r})}.$$

For the physical system, we have

$$E = E[\rho] = \int \mathrm{d}^3 r\, \rho(\mathbf{r}) V(\mathbf{r}) + F[\rho],$$

where $F[\rho] = \left\langle \Psi \middle| \hat{T} + \hat{U} \middle| \Psi \right\rangle = T^{\text{S}}[\rho] + E^{\text{H}}[\rho] + (F[\rho] - T^{\text{S}}[\rho] - E^{\text{H}}[\rho])$, and we define the term in parenthesis as the **exchange-correlation energy functional** $E^{\text{XC}}[\rho]$. By the Euler equation, we get

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = V(\mathbf{r}) + \frac{\delta T^{\text{S}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E^{\text{H}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E^{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})}.$$

By our assumption, $\rho(\mathbf{r}) = \rho^{\text{S}}(\mathbf{r})$, so subtracting gives

$$\mu^{\text{S}} - \mu = V_{\text{eff}}(\mathbf{r}) - \left[V(\mathbf{r}) + \frac{\delta E^{\text{H}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E^{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})} \right]$$

$$\implies V_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + \frac{\delta E^{\text{H}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E^{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})} + \text{const.}$$

Here we can without loss of generality (really!) set that constant equal to 0, since there is a degree of freedom induced by (*). Note that without the assumption that $\rho = \rho^{\text{S}}$, it is not even guaranteed that $E^{\text{XC}}[\rho]$ is defined.

There are three assumptions used in the identification of the physical system with the chosen Kohn-Sham reference system:

- The Hohenberg-Kohn theorems hold for the physical system
- The Hohenberg-Kohn theorems hold for the reference system
- The ground state density of the reference system $\rho_{\mathrm{S}}(\mathbf{r})$ is equal to that of the physical system $\rho(\mathbf{r})$.

Remark. The Kohn-Sham scheme relies on the construction of reliable exchange-correlation (XC) functionals for accuracy.

Definition 9.1 (Exchange-correlation energy functional)**.** *The exchange-correlation energy functional $E^{XC}[\rho]$ of a system under the Kohn-Sham scheme quantifies the deviation of the system from the Hartree energy functional. It is given by*

$$\begin{aligned} E^{XC}[\rho] &\equiv F[\rho] - T^S[\rho] - E^H[\rho] \\ &= \left\langle \Psi \middle| \hat{T} + \hat{U} \middle| \Psi \right\rangle - \left\langle \Phi \middle| \hat{T} \middle| \Phi \right\rangle - E^H. \end{aligned} \tag{53}$$

9.2 Solving the Kohn-Sham Equations

The upside of using a . So now we instead solve the Schrödinger equation for the Kohn-Sham reference system, which is composed of single-electron wavefunctions. Consider the Hamiltonian

$$\hat{H}^{\mathrm{S}} = \hat{T} + \hat{V}_{\mathrm{eff}} = \sum_{j=1}^{N} \left(-\frac{\nabla_j^2}{2} \right) + \sum_{j=1}^{N} V_{\mathrm{eff}}(\mathbf{r}_j). \tag{54}$$

We introduce the single-particle Hamiltonian, as in section (), and write

$$\hat{H}^{\mathrm{S}} = \sum_{j=1}^{N} \hat{h}(\mathbf{r}_j), \tag{55}$$

where

$$\hat{h}(\mathbf{r}) \equiv -\frac{\nabla^2}{2} + V_{\mathrm{eff}}(\mathbf{r}), \tag{56}$$

and $\hat{h}$ satisfies the Schrödinger-like equation (this is not actually a Schrödinger equation in the usual sense, since the wavefunctions are Kohn-Sham orbitals, and do not correspond to anything physical)

$$\hat{h}(\mathbf{r}) \phi_i(\mathbf{x}) = \epsilon_i \phi_i(\mathbf{x}). \tag{57}$$

Here $\mathbf{x} = (\mathbf{r}, \sigma)$, and the orbital energy ϵ_i is ordered as $\epsilon_1 \leq \epsilon_2 \leq \epsilon_3 \leq \cdots$.

To sum up, the three steps to carry out the calculations are:

(A) Effective potential:

$$V_{\mathrm{eff}}(\mathbf{r}) = V(\mathbf{r}) + \frac{\delta E^{\mathrm{H}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E^{\mathrm{XC}}[\rho]}{\delta \rho(\mathbf{r})}.$$

(B) Solve the Kohn-Sham equations with the given Hamiltonian:

$$\left\{ -\frac{\nabla^2}{2} + V_{\mathrm{eff}}(\mathbf{r}) \right\} \phi_i(\mathbf{x}) = \epsilon_i \phi_i(\mathbf{x}),$$

where $\epsilon_1 \leq \epsilon_2 \leq \cdots$.

(C) Calculate density as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \sum_{\sigma} |\phi_i|^2 .$$

The goal is to avoid solving Schrödinger's equation for the physical system, which may include interactions, but it is alright to solve the Schrödinger equation for the Kohn-Sham system.

Search for all possible effective potential, we get the non-interacting Hamiltonian. Then we can diagonalise the Hamiltonian for the n orbitals with smallest eigenvalues. Then we can calculate the Kohn-Sham ground state density ρ with the corresponding orbitals.

Chai: "ρ must come from some v-representable, non-inetracting orbitals."

Chai: "the need for nondegeneracy is manifest here: because of the nondegeneracy of ground state wavefunction, we can write Φ as one single Slater determinant."

9.3 Hellmann-Feynman Theorem

Proposed independently in 1937 by Hellman and R. P. Feynman (*Phys Rev 56, 340 (1939) Force in Molecules*). For a Hamiltonian dependent on some continuous variable λ, the theorem gives the expectation value of the derivative of the Hamiltonian with respect to λ.

Theorem 9.1 (Hellmann-Feynman theorem)**.** *Let $\hat{H}_\lambda$ be a Hamiltonian operator depending upon a continuous parameter λ, satisfying*

$$\hat{H}_\lambda \left|\Psi_\lambda\right\rangle = E_\lambda \left|\Psi_\lambda\right\rangle.$$

Then

$$\frac{dE_\lambda}{d\lambda} = \left\langle \Psi_\lambda \middle| \frac{d\hat{H}_\lambda}{d\lambda} \middle| \Psi_\lambda \right\rangle. \tag{58}$$

Proof. First notice that $\langle \Psi_\lambda \mid \Psi_\lambda \rangle$ is normalised at all times, so

$$\langle \Psi_\lambda \mid \Psi_\lambda \rangle = 1 \implies \frac{\mathrm{d}}{\mathrm{d}\lambda} \langle \Psi_\lambda \mid \Psi_\lambda \rangle = 0.$$

For simplicity of notation, from now on λ-dependence of the Hamiltonian $\hat{H}_\lambda$ and wavefunction Ψ_λ is implied, so all λ subscripts are neglected. Differentiate the energy expectation value with respect to λ:

$$\begin{aligned}
\frac{\mathrm{d}E_\lambda}{\mathrm{d}\lambda} &= \frac{\mathrm{d}}{\mathrm{d}\lambda} \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle \\
&= \left\langle \frac{\mathrm{d}\Psi}{\mathrm{d}\lambda} \middle| \hat{H} \middle| \Psi \right\rangle + \left\langle \Psi \middle| \frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda} \middle| \Psi \right\rangle + \left\langle \Psi \middle| \hat{H} \middle| \frac{\mathrm{d}\Psi}{\mathrm{d}\lambda} \right\rangle \\
&= E\left(\left\langle \frac{\mathrm{d}\Psi}{\mathrm{d}\lambda} \middle| \Psi \right\rangle + \left\langle \Psi \middle| \frac{\mathrm{d}\Psi}{\mathrm{d}\lambda} \right\rangle \right) + \left\langle \Psi \middle| \frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda} \middle| \Psi \right\rangle \\
&= \left\langle \Psi \middle| \frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda} \middle| \Psi \right\rangle.
\end{aligned}$$

□

Example 9.1 (Appliaction of the Hellmann-Feynman theorem)**.** Consider a system whose energy changes as a function of some continuous variable λ. Then we have

$$E_{\lambda=1} - E_{\lambda=0} = \int_0^1 \mathrm{d}\lambda \, \frac{\mathrm{d}E_\lambda}{\mathrm{d}\lambda} = \int_0^1 \mathrm{d}\lambda \, \left\langle \Psi_\lambda \middle| \hat{H}_\lambda \middle| \Psi_\lambda \right\rangle.$$

By the Hellmann-Feynman theorem, we then deduce that

$$E_{\lambda=1} - E_{\lambda=0} = \left\langle \Psi_\lambda \middle| \hat{H}_\lambda \middle| \Psi_\lambda \right\rangle_{\lambda=1} - \left\langle \Psi_\lambda \middle| \hat{H}_\lambda \middle| \Psi_\lambda \right\rangle_{\lambda=0}.$$

It is useful to introduce the following correlation function.

Definition 9.2 (Pair correlation function)**.** *The electron pait correlation function (PCF) is given by*

$$\Pi(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_1,\sigma_2} \int \mathrm{d}x_3 \int \mathrm{d}x_4 \cdots \int \mathrm{d}x_N \, \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N). \quad (59)$$

The $\Pi(\mathbf{r}_1, \mathbf{r}_2)$ *thus defined is proportional to the probability density of finding one electrom at* $\mathbf{r}_1$ *and another at* $\mathbf{r}_2$.

Remark. We will introduce the following fun notation convention for dealing with these integrals of many variables, where we leave out integration with respect to certain indices in the sequences.

For an integral with respect to all subscripts *except* the i- and j-th indices, we shall write

$$\int \mathrm{d}x_1 \cdots \int \mathrm{d}x_{i-1} \int \mathrm{d}x_{i+1} \cdots \int \mathrm{d}x_{j-1} \int \mathrm{d}x_{j+1} \cdots \int \mathrm{d}x_N \equiv \int \cdots \int \left(\frac{\mathrm{d}x_1 \mathrm{d}x_2 \cdots \mathrm{d}x_N}{\mathrm{d}x_i \mathrm{d}x_j} \right). \quad (60)$$

For example, in the above definition of the pair correlation function (equ. (59)), we can instead write

$$\begin{aligned}\Pi(\mathbf{r}_1, \mathbf{r}_2) &= N(N-1) \sum_{\sigma_1,\sigma_2} \int \cdots \int \left(\frac{\mathrm{d}x_1 \mathrm{d}x_2 \cdots \mathrm{d}x_N}{\mathrm{d}x_1 \mathrm{d}x_2} \right) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &= N(N-1) \sum_{\sigma_1,\sigma_2} \int \cdots \int (\mathrm{d}x_3 \mathrm{d}x_4 \cdots \mathrm{d}x_N) \, \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N).\end{aligned}$$

Now, we will work on the interaction potential term using the pair correlation function. The interaction potential is given by

$$U = U[\Psi] = \left\langle \Psi \middle| \hat{U} \middle| \Psi \right\rangle,$$

where

$$\hat{U} = \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \equiv \sum_{i<j}^{N} \frac{1}{r_{ij}} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j\neq i}^{N} \frac{1}{r_{ij}}.$$

We will do the following manipulation to express the interaction energy in terms of the pair correlation function:

$$\begin{aligned}U = \left\langle \Psi \middle| \hat{U} \middle| \Psi \right\rangle &= \frac{1}{2} \sum_{i=1}^{N} \sum_{j\neq i}^{N} \left\langle \Psi \middle| \frac{1}{r_{ij}} \middle| \Psi \right\rangle \\ &= \frac{1}{2} \sum_{i=1}^{N} \sum_{j\neq i}^{N}\end{aligned}$$

Remark. A note on the notation: it is difficult to type out big-sigma summation (Σ) with a prime, i.e. Σ', in math mode, so the abbreviation

$$\Sigma' \equiv \sum_{i=1}^{N} \sum_{j \neq i}^{N}$$

will be written out in its full form.

If we know 2-RDN, then we can derive everything (?). But the problem is how to get the 2-RDN in the first place -> search for all 2-RDN that come from N-electron wave fcuntions. So: Exact functional of PCF.

Remark. Does a Kohn-Sham model system exist for all physical electron systems? This (open) question is equivalent to asking whether electron densities of real physical systems are always noninteracting v-representable.

9.4 Revisiting Correlation Energy

We can rephrase the problem of solving the Schrödinger equation in the language of perturbation theory. That is, *we introduce the interaction energy as a perturbation to the noninteracting Hamiltonian.*

$$\hat{H}_\lambda = \hat{T} + \hat{V}_\lambda + \lambda \hat{U}, \tag{61}$$

where

$$\hat{H}_\lambda \left|\Psi_\lambda\right\rangle = E_\lambda \left|\Psi_\lambda\right\rangle, \; 0 \leq \lambda \leq 1.$$

Recall that we define the exchange-correlation energy functional $E^{\mathrm{XC}}[\rho]$ as the deviation of the interaction energy from the Hartree energy, i.e.

$$E^{\mathrm{XC}}[\rho] = \int_0^1 \mathrm{d}\lambda \, \left\langle \Psi_\lambda \middle| \hat{U} \middle| \Psi_\lambda \right\rangle - E^{\mathrm{H}}[\rho].$$

Define the quantity

$$\int_0^1 \mathrm{d}\lambda \, \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)$$

to be the average pair correlation function,

$$\int_0^1 \mathrm{d}\lambda \, \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) \equiv \Pi_{ave}(\mathbf{r}_1, \mathbf{r}_2). \tag{62}$$

Using the notation from last section, we have

$$\begin{aligned} E^{\mathrm{XC}}[\rho] &= \frac{1}{2} \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, \frac{1}{r_{12}} \left\{ \int_0^1 \mathrm{d}\lambda \, \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{x}_1)\rho(\mathbf{x}_2) \right\} \\ &= \frac{1}{2} \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, \frac{1}{r_{12}} \left\{ \Pi_{\mathrm{ave}}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \right\} \\ &= \frac{1}{2} \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, \frac{\rho(\mathbf{r}_1) h^{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}, \end{aligned}$$

where we further define

$$h^{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\Pi_{\mathrm{ave}}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2).$$

This quantity has many interesting properties, so we give it a name.

Definition 9.3 (Exchange hole)**.** *Given the electron density* $\rho(\mathbf{r})$ *and the electron pair correlation function* $\Pi(\mathbf{r}_1, \mathbf{r}_2)$*, we first define the average pair correlation function*

$$\int_0^1 \mathrm{d}\lambda \, \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2). \tag{63}$$

Then we can define the ***exchange-correlation hole****, written as*

$$h^{XC}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\Pi_{ave}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2). \tag{64}$$

The exchange-correlation (XC) hole describes the reduction in the probability of finding two electrons at the same position in space due to exchange and correlation effects. I.e. since the electron is a **fermion**, the probability of finding an electron is affected by the presence of another electron.

In the spin-polarised case, we consider the decomposition of $\rho(\mathbf{r})$ into its spatial part and its spin part, where unlike previous notation we leave out the overline of ρ_σ:

$$\rho(\mathbf{r}) = \sum_{\sigma \in \{\alpha, \beta\}} \rho_\sigma(\mathbf{r}).$$

Then

$$\begin{aligned} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) &= \left(\sum_{\sigma \in \{\alpha,\beta\}} \rho_\sigma(\mathbf{r}_1) \right) \left(\sum_{\sigma' \in \{\alpha,\beta\}} \rho_{\sigma'}(\mathbf{r}_2) \right) \\ &= \sum_{\sigma, \sigma' \in \{\alpha,\beta\}} \rho_\sigma(\mathbf{r}_1)\rho_{\sigma'}(\mathbf{r}_2). \end{aligned}$$

Also,

$$\begin{aligned} \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{\sigma_1, \sigma_2 \in \{\pm\frac{1}{2}\}} \left[N(N-1) \int \mathrm{d}^3 r_3 \cdots \int \mathrm{d}^3 r_N \left| \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \right|^2 \right] \\ &= \sum_{\sigma_1, \sigma_2} \Pi_\lambda(\mathbf{x}_1, \mathbf{x}_2) \\ &= \sum_{\sigma_1, \sigma_2} \Pi_\lambda((\mathbf{r}_1, \sigma_1), (\mathbf{r}_2, \sigma_2)) \\ &= \sum_{\sigma, \sigma' \in \{\alpha, \beta\}} \Pi_\lambda^{\sigma, \sigma'}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned}$$

In our derivation above, we find that it makes things easier if we define a more general form of the exchange-correlation hole in equation (64), so we introduce the following definition:

$$\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\sigma, \sigma'} \Pi_\lambda^{\sigma, \sigma'}(\mathbf{r}_1, \mathbf{r}_2).$$

The average pair correlation function can in turn be given a more general form in terms of its spin-polarised components:

$$\begin{aligned}\Pi_{\text{ave}}(\mathbf{r}_1,\mathbf{r}_2) &= \int_0^1 \mathrm{d}\lambda\, \Pi_\lambda(\mathbf{r}_1,\mathbf{r}_2)\\ &= \int_0^1 \mathrm{d}\lambda \sum_{\sigma,\sigma'} \Pi_\lambda^{\sigma,\sigma'}(\mathbf{r}_1,\mathbf{r}_2)\\ &\equiv \sum_{\sigma,\sigma'} \Pi_{\text{ave}}^{\sigma,\sigma'}(\mathbf{r}_1,\mathbf{r}_2).\end{aligned}$$

Finally, we are ready to give a spin-polarised version of the exchange-correlation hole:

$$\begin{aligned}E^{\text{XC}} &= \frac{1}{2}\sum_{\sigma,\sigma'}\int \mathrm{d}^3r_1 \int \mathrm{d}^3r_2 \frac{\Pi_{\text{ave}}^{\sigma,\sigma'}(\mathbf{r}_1,\mathbf{r}_2) - \rho_\sigma(\mathbf{r}_1)\rho_{\sigma'}(\mathbf{r}_2)}{r_{12}}\\ &= \frac{1}{2}\sum_{\sigma,\sigma'}\int \mathrm{d}^3r_1 \int \mathrm{d}^3r_2 \frac{\rho_\sigma(\mathbf{r}_1) h_{\text{XC}}^{\sigma,\sigma'}(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}},\end{aligned}$$

where we define the spin-polarised hole (since Chai doesn't mention an already-established name for this quantity, this is my own terminology) as

$$h_{\text{XC}}^{\sigma,\sigma'} = \frac{\Pi_{\text{ave}}^{\sigma,\sigma'}(\mathbf{r}_1,\mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_1)} - \rho_{\sigma'}(\mathbf{r}_2). \tag{65}$$

Remark. This is an unfortunate instance of bypassing cumbersome notation at the sacrifice of notational consistency: $h^{\text{XC},\sigma,\sigma'}$ does not look good, while $h_{\text{XC}}^{\sigma,\sigma'}$ does, so we temporarily forget our subscript-superscript convention for text descriptions.

Here we list some computation rules for the above-defined exchange-correlation hole function.

Sum rules:

$$\int \mathrm{d}^3r_2\, h_{\text{XC}}^{\alpha,\alpha}(\mathbf{r}_1,\mathbf{r}_2) = \int \mathrm{d}^3r_2\, h_{\text{XC}}^{\beta,\beta}(\mathbf{r}_1,\mathbf{r}_2) = -1,$$

$$\int \mathrm{d}^3r_2\, h_{\text{XC}}^{\alpha,\beta}(\mathbf{r}_1,\mathbf{r}_2) = \int \mathrm{d}^3r_2\, h_{\text{XC}}^{\beta,\alpha}(\mathbf{r}_1,\mathbf{r}_2) = 0,$$

Therefore

$$\int \mathrm{d}^3r_2\, h_{\text{XC}}^{\sigma,\sigma'}(\mathbf{r}_1,\mathbf{r}_2) = -\delta_{\sigma,\sigma'}. \tag{66}$$

Furthermore, from Pauli's exclusion principle we get

$$\Pi_\lambda^{\alpha,\alpha}(\mathbf{r},\mathbf{r}) = \Pi_\lambda^{\beta,\beta}(\mathbf{r},\mathbf{r}) = 0.$$

This is because the pair correlation function gives the probablity of finding another electron at place 2 given that an electron already exists at position 1. By Pauli's exclusion principle, two electrons cannot occupy the same quantum state (position).

Therefore

$$h_{\text{XC}}^{\sigma,\sigma}(\mathbf{r},\mathbf{r}) = -\rho_\sigma(\mathbf{r}). \tag{67}$$

The exchange-correlation energy is then

$$E^{\mathrm{X}} = \frac{1}{2}\sum_{\sigma,\sigma'}\int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2\, \frac{\rho_\sigma(\mathbf{r}_1) h_{XC}^{\sigma\sigma'}(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}},$$

and

$$h_{\mathrm{X}}^{\sigma,\sigma'}(\mathbf{r}_1,\mathbf{r}_2) = \delta_{\sigma,\sigma'}\left\{-\frac{|\gamma_\sigma(\mathbf{r}_1,\mathbf{r}_2)|^2}{\rho_\sigma(\mathbf{r}_1)}\right\}.$$

A rough translation of Chai's quote from the 4/11/2024 lecture: ”DFT is popular definitely not because it finds an exact expression for the Hamiltonian of electron systems. It is popular because it strikes a balance between being efficient and being approximately exact.”

9.5 Levy approach

The Levy approach gives us a way to bypass v-representibility requirements. This in turn gives us a λ-generalised universal functional:

$$F_\lambda[\rho] \equiv \min_{\Psi\to\rho}\left\langle \Psi[\rho]\,\middle|\,\hat{T}+\lambda\hat{U}\,\middle|\,\Psi[\rho]\right\rangle = \left\langle \Psi_\lambda[\rho]\,\middle|\,\hat{T}+\lambda\hat{U}\,\middle|\,\Psi_\lambda[\rho]\right\rangle.$$

Here $\Psi_\lambda[\rho]$ is the N-electron wavefunction that yields a given N-representible density ρ and minimises

$$\left\langle \Psi\,\middle|\,\hat{T}+\lambda\hat{U}\,\middle|\,\Psi\right\rangle,$$

while satisfying the normalisation condition

$$\langle \Psi_\lambda[\rho]\,|\,\Psi_\lambda[\rho]\rangle = 1.$$

Now we can (partial) differentiate with respect to λ:

$$\begin{aligned}\frac{\partial F_\lambda[\rho]}{\partial\lambda} &= \frac{\partial}{\partial\lambda}\left(\left\langle \Psi\,\middle|\,\hat{T}+\lambda\hat{U}\,\middle|\,\Psi\right\rangle\right)\\ &= \left\langle \Psi_\lambda\,\middle|\,\hat{U}\,\middle|\,\Psi_\lambda\right\rangle + \frac{\partial}{\partial\lambda'}\left(\left\langle \Psi_{\lambda'}\,\middle|\,\hat{T}+\lambda\hat{U}\,\middle|\,\Psi_{\lambda'}\right\rangle\right)\Big|_{\lambda'=\lambda}\\ &= \left\langle \Psi_\lambda\,\middle|\,\hat{U}\,\middle|\,\Psi_\lambda\right\rangle.\end{aligned}$$

In the last equality, the second term vanishes because

$$\left\langle \Psi_{\lambda'}\,\middle|\,\hat{T}+\lambda\hat{U}\,\middle|\,\Psi_{\lambda'}\right\rangle$$

attains its minimum at $\lambda' = \lambda$, so the derivative becomes zero.

Then by integrating we have

$$\begin{aligned}\int_0^1 \mathrm{d}\lambda\,\frac{\partial F_\lambda[\rho]}{\partial\lambda} &= F_{\lambda=1}[\rho] - F_{\lambda=0}[\rho]\\ &= F[\rho] - T^{\mathrm{s}}[\rho]\\ &= E^{\mathrm{H}}[\rho] + E^{\mathrm{XC}}[\rho]\\ &= \int_0^1 \mathrm{d}\lambda\,\left\langle \Psi_\lambda[\rho]\,\middle|\,\hat{U}\,\middle|\,\Psi_\lambda[\rho]\right\rangle.\end{aligned}$$

To proceed with our discussion, we define a density for the energy functional in question, along the lines of previous methods (refer: Thomas-Fermi enegry).

Definition 9.4 (Exchange correlation energy density)**.** *Given an exchange correlation energy functional $E^{XC}[\rho]$, the corresponding XC energy density is the functional*

$$\varepsilon^{XC}(\mathbf{r}) = \varepsilon^{XC}[\rho(\mathbf{r})]$$

such that

$$E^{XC}[\rho] = \int \mathrm{d}^3 r \, \varepsilon^{XC}(\mathbf{r}). \tag{68}$$

Then we can express the density in terms of the exchange-correlation hole we previously defined.

$$\begin{aligned} \epsilon^{\mathrm{XC}}(\mathbf{r}_1) &= \frac{1}{2} \int \mathrm{d}^3 r_2 \, \frac{\rho(\mathbf{r}_1) h^{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} \\ &= \frac{\rho(\mathbf{r}_1)}{2} \int \mathrm{d}^3 r_{21} \, \frac{h^{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_{21})}{r_{21}} \end{aligned}$$

where in the second equality we defined $\mathbf{r}_{21} \equiv \mathbf{r}_2 - \mathbf{r}_1$ and $r_{21} \equiv |\mathbf{r}_{21}|$. Then

$$\begin{aligned} \varepsilon^{\mathrm{XC}}(\mathbf{r}_1) &= \frac{\rho(\mathbf{r}_1)}{2} \int_0^\infty \mathrm{d}^3 r_{21} \, r_{21}^2 \frac{\int \mathrm{d}\Omega_{21} \, h^{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_{21})}{r_{21}} \\ &= \frac{\rho(\mathbf{r}_1)}{2} \int_0^\infty \mathrm{d}^3 r_{21} \, r_{21} h^{\mathrm{AA}}_{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_{21}). \end{aligned}$$

Note that the quantity $h^{\mathrm{AA}}_{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_{21})$ in the final expression is the angular averaged exchange-correlation hole, so

$$h^{\mathrm{AA}}_{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_{21}) \equiv \int \mathrm{d}\Omega_{21} \, h^{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_{21}). \tag{69}$$

10 Discussion of DFT functional approximations

In this section, we list a few approximations to exchange-correlation functionals, and discuss various aspects of their usefulness and application.

10.1 Jacob's Ladder

The various approximation methods for the exchange-correlation energy density functoinal can be summarised in a table which we call ”Jacob's ladder”.

In Jacob's Ladder (table 1), the higher up the ladder the higher the accuracy, but lower the efficiency. The following is a list of comments on and notes for content of the table:

- Density functional approximations on rung 1 and 2 are explicit (pure) density functionals.
- Density functional approximations on rung 1 to 3 are called semilocal functionals. We will give the precise mathematical definition of local and semilocal functionals in the paragraph immediately following this section.
- For the MGGA (meta generalised gradient approximation) energy density functional, we introduce the term $\tau(\mathbf{r})$, which stands for the Kohn-Sham kinetic energy density functional.
- In the fully nonlocal energy density functional, the term $\{\phi_p\}$ refers to all the Kohn-Sham orbitals of the system.

Heaven		
Rung 5	Fully Nonlocal	$\varepsilon_{\text{XC}}^{\text{FNL}}\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau(\mathbf{r}), \varepsilon_{\text{X}}^{\text{exact}}(\mathbf{r}), \{\phi_p(\mathbf{r})\}\right)$
Rung 4	Hybrid	$\varepsilon_{\text{XC}}^{\text{hybrid}}\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau(\mathbf{r}), \varepsilon_{\text{X}}^{\text{exact}}(\mathbf{r})\right)$
Rung 3	MGGA	$\varepsilon_{\text{XC}}^{\text{MGGA}}\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau(\mathbf{r})\right)$
Rung 2	GGA	$\varepsilon_{\text{XC}}^{\text{GGA}}\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right)$
Rung 1	LDA	$\varepsilon_{\text{XC}}^{\text{LDA}}\left(\rho(\mathbf{r})\right)$
Earth	Hartree Theory	$\varepsilon_{\text{XC}}\left(\mathbf{r}\right) = 0$

Table 1: Jacob's Ladder

- Some functionals do not fit into any of the rungs. The Hartree functional is the most simple example, but a more sophisticated example will be given later in this section.

Remark. We adopt the following conventoin for naming variables:

Following the comments on the table, it seems now the right time to define preciesly what we mean by "local" and "semilocal" functionals in DFT.

Definition 10.1 (Local and semilocal functionals)**.** *Consider a functional* Φ*, and functions* $f : A \to A \in \operatorname{dom}\Phi$*, then*

1. *The functional* Φ *is called* ***local*** *if it can be written as an explicit function of the independent variable and* f*, i.e.*
$$\Phi[f(x)] = \Phi\left(x, f(x)\right). \tag{70}$$
2. *The functional* Π *is called* ***semilocal*** *if it can be written as an explicit function of the independent variable and finitely many derivatives of* f*, i.e.*
$$\Phi[f(x)] = \Phi\left(x, f(x), f'(x), \dots, f^{(N)}(x)\right). \tag{71}$$

10.2 Local Density Approximation

The local density approximation (LDA) for spin-unpolarised systems was first derived by Dirac (1930). Refer to Jacob's Ladder (table (1)), this is rung 1 on the ladder. Consider a uniform electron gas (from now on denoted by the abbreviation UEG in superscripts) of density N inside a volume V. The density of UEG is then

$$\rho_0 = \frac{N}{V}, \tag{72}$$

and similarly we define the exchange energy density as

$$\varepsilon_{\text{X}}^{\text{UEG}} = \frac{E_{\text{X}}}{V}. \tag{73}$$

Remark. As the name itself suggests, in the LDA scheme, we define energy density functionals as local functionals, whose definition was given in equation (70).

In the spin-unpolarised case, we have

$$\varepsilon_{\mathrm{X}}^{\mathrm{UEG}}(\rho_0) = C_{\mathrm{X}}\rho_0^{4/3},\ C_{\mathrm{X}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}.$$

Then we define the *LDA exchange density* as

$$\varepsilon_{\mathrm{X}}^{\mathrm{LDA}}(\mathbf{r}) \equiv \varepsilon_{\mathrm{X}}^{\mathrm{UEG}}(\rho(\mathbf{r})) = C_{\mathrm{X}}\rho^{4/3}(\mathbf{r}), \tag{74}$$

and

$$E_{\mathrm{X}}^{\mathrm{LDA}}[\rho] = \int \mathrm{d}^3r\, \varepsilon_{\mathrm{X}}^{\mathrm{LDA}}(\mathbf{r}) = C_{\mathrm{X}} \int \mathrm{d}^3r\, \rho^{4/3}(\mathbf{r}).$$

The spin-unpolarised case corresponds to

$$\rho_\alpha = \rho_\beta = \frac{\rho}{2},$$

where ρ_α and ρ_β are the densities of spins $\sigma = \alpha$ and $\sigma = \beta$. In the case of general spins, i.e. spin-polarised systems, we can use the following spin-scaling relations

$$\begin{cases} E_{\mathrm{X}}[\rho_\alpha, \rho_\beta] = \frac{1}{2}\left(E_{\mathrm{X}}[2\rho_\alpha] + E_{\mathrm{X}}[2\rho_\beta]\right), & \text{(exchange energy)} \\ T_{\mathrm{S}}[\rho_\alpha, \rho_\beta] = \frac{1}{2}\left(T_{\mathrm{S}}[2\rho_\alpha] + T_{\mathrm{S}}[2\rho_\beta]\right). & \text{(kinetic energy)} \end{cases} \tag{75}$$

Now we consider the correlation energy E_{C}, and note that the exchange-correlation energy is just the sum of E_{X} and E_{C}. Chai: For $\varepsilon_{\mathrm{C}}^{\mathrm{LDA}}$, use *quantum Monte Carlo (QMC)* for UEG.

Remark. This remark needs some clarification, and as of now I am not sure what it means. Also, for more details on the quantum Monte Carlo method, refer to section (**).

Now we introduce a model for the external potential in the setting of LDA, using the **Jellium model**. The jellium model, also known as the uniform electron gas (UEG) model, is a quantum mechanical model of interacting electrons in a solid, where we approximate the positive nuclei as being uniformly distributed in space (i.e. by ”smearing out” the positive charges) and assume the electrons behave like a uniform electron gas. Per the latter approximation, we have

$$\rho(\mathbf{r}) = \text{const.} \tag{76}$$

throughout all of space. Let $\mathbf{R}$ denote the position of the (smeared out) nuclei, then the external potential operator is

$$\hat{V}_{\mathrm{ext}} = -\frac{N}{V}\sum_{i=1}^{N}\int_{\mathcal{V}} \mathrm{d}^3R\, \frac{1}{|\mathbf{r}_i - \mathbf{R}|}. \tag{77}$$

Then the potential is

$$\begin{aligned} V &= \int_{\mathcal{V}} \mathrm{d}^3r \int \mathrm{d}^3r_2 \cdots \int \mathrm{d}^3r_N\, \Psi^*(\mathbf{r}, \mathbf{r}_1, \dots, \mathbf{r}_N)\hat{V}\Psi(\mathbf{r}, \mathbf{r}_1, \dots, \mathbf{r}_N) \\ &= \int_{\mathcal{V}} \mathrm{d}^3r\, \rho(\mathbf{r})V_{\mathrm{ext}}(\mathbf{r}) = -\left(\frac{N}{V}\right)^2 \int_{\mathcal{V}} \mathrm{d}^3r \int_{\mathcal{V}} \mathrm{d}^3R\, \frac{1}{|\mathbf{r} - \mathbf{R}|}. \end{aligned}$$

We write the background potential $V_{\mathrm{background}}$ as V_{NN}, and

$$V_{\mathrm{NN}} = \frac{1}{2}\left(\frac{N}{V}\right)^2 \int_{\mathcal{V}} \mathrm{d}^3R \int_{\mathcal{V}} \mathrm{d}^3R'\, \frac{1}{|\mathbf{R} - \mathbf{R}'|},$$

$$E_{\mathrm{H}} = \frac{1}{2}\left(\frac{N}{V}\right)^2 \int_{\mathcal{V}} \mathrm{d}^3 r \int_{\mathcal{V}} \mathrm{d}^3 r' \, \frac{1}{|\mathbf{r}-\mathbf{r}'|}.$$

The external potential V, background potential V_{NN}, and the Hartree energy E_{H}, are related via the following equation:

$$V + V_{\mathrm{NN}} + E_{\mathrm{H}} = 0.$$

Finally, in the LDA approximation, the ground state energy E_0 is

$$\begin{aligned} E_0 &= T_{\mathrm{s}} + V + E_{\mathrm{H}} + E_{\mathrm{X}} + E_{\mathrm{C}} + V_{\mathrm{NN}} \\ &= T_{\mathrm{s}} + E_{\mathrm{X}} + E_{\mathrm{C}} \\ &\equiv T_{\mathrm{TF}} + E_{\mathrm{X}}^{\mathrm{LDA}} + E_{\mathrm{C}}. \end{aligned}$$

Note that in the above formula, we set $T_{\mathrm{s}} = T_{\mathrm{TF}}$ and E_{X} to $E_{\mathrm{X}}^{\mathrm{LDA}}$. Notice that E_0 can be obtained by the QMC method.

Due to the simplicity of this model, there are various caveats to using the LDA. Things that do not work in LDA:

- Van der Waals interactions: nonlocal interactions due to mutual dynamical charge polarisation of the atoms not properly included in any existing approximations to E_{XC}. This is further detailed in the final section.
- Excited states: DFT is a ground state theory. To extend the theory to include excited states, we may use time-dependent DFT or GW.
- Non Born-Oppenheimer processes. This includes non-radiative transitions between electronic states.
- Self-interaction problem: each electron lives in the field created by all electrons including itself, and the self-interaction problem is the spurious interaction of the electron with its own field. Recall that self-interaction exactly cancels out in Hartree-Fock, but in LDA it does not. Solutions include SIC and hybrid DFT.

10.3 Generalised Gradient Approximation

Again refer to table (1), this is rung 2 on the ladder. Consider the following generalisation of the LDA method:

$$\text{LDA} \longrightarrow \text{GEA (Gradient Expansion Approximation).} \tag{78}$$

This gives

$$E_{\mathrm{XC}} = E_{\mathrm{XC}}^{\mathrm{LDA}} + E_{\mathrm{XC}}^{\text{2nd-GEA}}, \tag{79}$$

where $E_{\mathrm{XC}}^{\text{2nd-GEA}}$ includes the terms $\rho(\mathbf{r})$ and $\nabla\rho(\mathbf{r})$.

Example 10.1 (Thomas-Fermi model with von Weizsacker correction)**.** The von Weizsacker kinetic energy functional is exact in the single-electron limit. The functional is given by equation (51):

$$T^{\mathrm{W}}[\rho] = \frac{1}{8}\int \mathrm{d}^3 r \, \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}.$$

This is an example of an energy functional which not only depends on $\rho(\mathbf{r})$, but also on its first derivative. The complete Thomas-Fermi-von Weizsacker kinetic energy functional is the approximation given by

$$\begin{aligned} T^{\mathrm{TF}\frac{1}{9}\mathrm{W}} &= T^{\mathrm{TF}} + T^{\text{2nd-GEA}} \\ &= T^{\mathrm{TF}} + \frac{1}{9}T^{\mathrm{W}} \\ &= C_F \int \mathrm{d}^3 r\, \rho(\mathbf{r})^{(5/3)} + \frac{1}{72}\int \mathrm{d}^3 r\, \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}. \end{aligned} \tag{80}$$

The GGA method works well for nearly uniform systems, i.e. systems with slowly varying density. To quantify this idea, we need something that would quantitatively describe how ”fast” the density is changing. The desired quantity is the **reduced density gradient**:

$$S(\mathbf{r}) \equiv \frac{|\rho(\mathbf{r})|}{\rho(\mathbf{r})^{4/3}}. \tag{81}$$

Notice that the reduced density gradient $S(\mathbf{r})$ is a dimensionless quantity. Using the reduce density gradient, we can rephrase the statement ”slowly varying density” mathematically as

$$S(\mathbf{r}) \approx 0. \tag{82}$$

GEA improves upon LDA for nearly uniform systems in which equation ((82)) is satisfied. However, GEA can be less accurate than LDA for *atoms and molecules*, where $S(\mathbf{r})$ can be very large (why?).

A careful analysis gives the following limits for the GGA method:

1. For small s, GGA approaches GEA. Representative: PBE (PRL 77, 3865 (1996)).
2. For large s, GGA can be very different. Representative: BLYP (B88 (PR A38, 3078 (1988)) × LYPC (PR B37, 785 (1988))).

10.4 Meta Generalised Gradient Approximation

Refer to table (1), this is rung 3 of the ladder. Consider the kinetic energy functional with spin:

$$T^{\mathrm{s}} = \sum_{\sigma\in\{\alpha,\beta\}} \int \mathrm{d}^3 d\, \tau_\sigma(\mathbf{r}), \tag{83}$$

where $\tau_\sigma(\mathbf{r})$ is the σ-spin kinetic energy density (KED), and we can write it as

$$\tau_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} \phi^*_{i,\sigma}(\mathbf{r})\left(-\frac{\nabla^2}{2}\phi_{i,\sigma}(\mathbf{r})\right).$$

Sometimes τ_σ is called the **type-one kinetic energy density**, and denoted

$$\tau_\sigma(\mathbf{r}) = \tau^{\mathrm{L}}_\sigma(\mathbf{r}) = \tau^{\mathrm{I}}_\sigma(\mathbf{r}).$$

This is the ”canonical” formulation of the kinetic enegry density, and is natural (as Chai said) in its derivation. Although the kinetic energy is well-defined and unique for any given system, the corresponding kinetic energy density is not, for it is acceptable as long as its integral over all space gives the correct kinetic energy functional.

We can give a second formulation for the energy density, called the **type-two kinetic energy density**:

$$\begin{aligned}\tau_\sigma^{\mathrm{II}}(\mathbf{r}) &= \frac{1}{2}\sum_{i=1}^{N_\sigma} \left|\nabla\phi_\sigma(\mathbf{r})\right|^2 \\ &= \tau_\sigma^{\mathrm{I}}(\mathbf{r}) + \frac{1}{4}\nabla^2\rho(\mathbf{r}).\end{aligned} \tag{84}$$

Notice that by a version of the divergence theorem†, giving us

$$\begin{aligned}\int_\Omega \mathrm{d}^3r\,\nabla^2\rho(\mathbf{r}) &= \int_\Omega \mathrm{d}^3r\,\nabla\cdot(\nabla\rho(\mathbf{r})) \\ &= \oint_{\partial\Omega} \mathrm{d}Sbv\hat{ecn}\cdot\nabla\rho(\mathbf{r}) \\ &= 0\end{aligned}$$

both for isolated boundary conditions and periodic boundary conditions.

†: The version of the divergence theorem we are using states that

$$\int_\Omega \mathrm{d}^3r\,\nabla\cdot\mathbf{u}(\mathbf{r}) = \int_{\partial\Omega} \mathrm{d}A\,\mathbf{n}\cdot\mathbf{u}. \tag{85}$$

Then

$$\int_\Omega \mathrm{d}^3r\,\nabla\cdot(\Psi^*\nabla\Psi) = \int_{\partial\Omega} \mathrm{d}A\,\mathbf{n}\cdot(\Psi^*\nabla\Psi), \tag{86}$$

which goes to zero as we let $\Omega\to\mathbb{R}^3$ if we assume $\Psi\to 0$ faster than $1/\sqrt{r}$ as $r\to\infty$.

Remark. Why do we need two formulations for the kinetic energy density functional? Because even though both types integrate to the kinetic energy, which is nonnegative, only the type-two KED is nonnegatvie locally at every point (as seen by its expression as a sum of squares). On the other hand, type-one KED is more natural, even though it does not guarantee nonnegaivity locally.

Remark. For a discussion of different kinetic energy densities, refer to the International Journal of Quantum Chemistry IJQC 75, 889 (1999).

For N-electron systems, we have

$$\tau_\sigma^{\mathrm{II}}(\mathbf{r}) \geq \tau_\sigma^{\mathrm{W}}(\mathbf{r}) \tag{87}$$

(e.g. see PR A38, 625 (1988). and IJQC 75, 889 (1999).) Call the ratio of the two densities $\omega_\sigma(\mathbf{r})$, then

$$\tau^{\mathrm{UEG}}(\mathbf{r}) = 0 \leq \omega_\sigma(\mathbf{r}) \equiv \frac{\tau_\sigma^{\mathrm{W}}(\mathbf{r})}{\tau^{\mathrm{II}}_{\sigma(\mathbf{r})}} \leq 1.$$

Since for a one-electron system we know von Weizsacker formulation gives the exact solution, $\omega_\sigma(\mathbf{r})\to 1$ in the one-electron region (e.g. in the asymptotic region (what?)).

Notable examples of the MGGA method are

1. TPSS (PRL 91, 146401 (2003).)
2. SCAN (PRL 115, 036402 (2015).)

Remark. Taking functional derivatives of the MGGA energy density can be difficult, because it include the Kohn-Sham kinetic energy term $\tau(\mathbf{r})$. For examples of dealing with functional derivatives like

$$\frac{\delta E_{\mathrm{XC}}^{\mathrm{MGGA}}}{\delta \rho(\mathbf{r})}, \frac{\delta E_{\mathrm{XC}}^{\mathrm{MGGA}}}{\delta \phi_i^*(\mathbf{r})},$$

refer to e.g. JCP 138, 244108 (2013).

From a result due to Becke, IJQC 23, 1915 (1983), the exact exchange functional E^{X} involves

$$|\gamma_\sigma(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\gamma_\sigma(\mathbf{r}_1, \mathbf{r}_1)|^2 + \Theta(r_{21})^2 \cdot f\left(\rho_\sigma(\mathbf{r}_1), \tau_\sigma(\mathbf{r}_1), \nabla^2 \rho_\sigma(\mathbf{r}_1)\right), \tag{88}$$

where $\gamma_\sigma(\mathbf{r}_1, \mathbf{r}_1) = \rho_\sigma(\mathbf{r}_1)$, f is some function, and the result holds for small r_{12}.

As mentioned in the comments after table (1), the above methods consisting rungs 1 to 3 are semilocal functionals, in the sense of equation (71). These functionals model the exchange-correlation density functional semilocally, and they are computationally efficient, even comparable to Hartree theory! Semilocal functionals capture the short-range (i.e. small r_{12}) part of the exchange-correlation hole (on average) reasonably well. However, it does not account for the long-range part as accurately. Examples of long-range, nonlocal interactions include the van der Waals interaction, which is discussed in section ** in detail.

Three qualitative errors of semilocal functionals are:

1. Self-Interaction Error (SIE)
2. Non-Covalent Interaction Error (NCE)
3. Static-Correlation Error (SCE)

Below we will discuss each of these in detail:

1. SIE (due to the lack of nonlocal exchange)

Example 10.2 (One-electron system)**.** In this example, we shall consider the case for a one-electron system. In one-electron systems the equation

$$E^{\mathrm{X}} = -E^{\mathrm{H}} = -\frac{1}{2} \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \, \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} \tag{89}$$

cannot be satisfied by *any* semilocal functional.

Notice that in this case

$$\begin{aligned} F &= T + U = T \\ &= T^{\mathrm{s}} = T^{\mathrm{W}} = \frac{1}{8} \int \mathrm{d}^3 r \, \frac{|\nabla; r(\mathbf{r})|^2}{\rho(\mathbf{r})}. \end{aligned}$$

Then the exchange-correlation is

$$\begin{aligned} E^{\mathrm{XC}} &= E^{\mathrm{X}} + E^{\mathrm{C}} = -E^{\mathrm{H}} + E^{\mathrm{C}} \\ &= F - T^{\mathrm{s}} - E^{\mathrm{H}} \\ &= T^{\mathrm{s}} - T^{\mathrm{s}} - E^{\mathrm{H}} = -E^{\mathrm{H}} \end{aligned}$$

So $E^{\mathrm{C}} = 0$. Furthermore, we remakr that the Hartree energy functional is a fully nonlocal functional, becauseit is given by

$$E^{\mathrm{H}} = \int \mathrm{d}^3 r_1 \, \varepsilon^{\mathrm{H}}(\mathbf{r}_1),$$

where we see from equation (89) that

$$\varepsilon^{\mathrm{H}}(\mathbf{r}_1) = \frac{\rho(\mathbf{r}_1)}{2}\int \mathrm{d}^3 r_2\, \frac{\rho(\mathbf{r}_2)}{r_{12}}. \tag{90}$$

Then since $\varepsilon^{\mathrm{X}}(\mathbf{r}_1) = -\varepsilon^{\mathrm{H}}(\mathbf{r}_1)$, we have

$$\varepsilon^{\mathrm{X}} = -\frac{\rho(\mathbf{r}_1)}{2}\int \mathrm{d}^3 r_2\, \frac{\rho(\mathbf{r}_2)}{r_{12}},$$

and

$$h^{\mathrm{X}}(\mathbf{r}_1, \mathbf{r}_2) = -\rho(\mathbf{r}_2). \tag{91}$$

In Hartree-Fock theory, the problem of self-energy blowing up is accounted for by a symmetry in the expression of the HF energy. The $i = j$ terms in U correspond to self energy, so in the Hartree-Fock energy expression (equation (17)) we get

$$E_{\text{self}} = \sum_{i=1}^{N}\left\{\frac{1}{2}[ii|ii] - \frac{1}{2}[ii|ii]\right\} = 0. \tag{92}$$

PZ81 SIC (PRB 23, 5048 (1981)) gives the self-interaction energy as

$$E_{\text{self}} \equiv \sum_{i=1}^{N}\left\{E^{\mathrm{H}}[\rho_i] + E^{\mathrm{XC}}[\rho_i, \sigma]\right\}. \tag{93}$$

For the spin-polarised case this is

$$E_{\text{self}} = \sum_{\sigma}\sum_{i=1}^{N_\sigma}\left\{E^{\mathrm{H}}[\rho_{i,\sigma}] + E^{\mathrm{XC}}[\rho_{i,\sigma}, \sigma]\right\}. \tag{94}$$

The one-electron density if given by $\rho_{i,\sigma}(\mathbf{r}) = \left|\phi_{i,\sigma}(\mathbf{r})\right|^2$, subject to the condition

$$\int \mathrm{d}^3 r\, \rho_{i,\sigma}(\mathbf{r}),$$

therefore

$$\begin{aligned} E^{\mathrm{X}}[\rho_{i,\sigma}, \sigma] &= -E^{\mathrm{H}}[\rho_{i,\sigma}], \\ E^{\mathrm{C}}[\rho_{i,\sigma}, \sigma] &= 0. \end{aligned} \tag{95}$$

For exact exchange-correlation energy E^{XC}, we have

$$E^{\mathrm{XC}}_{\text{self}} = 0.$$

For semilocal functionals, however, we in general have $E^{\mathrm{XC}}_{self} \neq 0$. In this case, in order to compensate for the self-interaction error, we define the self-interaction-free exchange-correlation functional

$$\tilde{E}^{\mathrm{XC}} \equiv E^{\mathrm{XC}} - E^{\mathrm{XC}}_{\text{self}}. \tag{96}$$

The pro of this definiton is that this is by construction self-interaction-free for a one-electron system. The con is that it is difficult to find the corresponding potential using equation (*), since it is in general difficult to evaluate

$$\tilde{V}^{\mathrm{XC}}(\mathbf{r}) = \frac{\delta \tilde{E}^{\mathrm{XC}}}{\delta \rho(\mathbf{r})}.$$

This is the end of the one-electron system example.

Now we can consider the general case. Asymmetric region:

Refer to PRB 31, 3231 (1985) and JCP 115, 4438 (2001). Recall the form of the Hartree potential energy, where we use an approximation:

$$\begin{aligned} V^{\mathrm{H}}(\mathbf{r}) &= \int \mathrm{d}^3r' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &\approx \frac{\int \mathrm{d}^3r' \, \rho(\mathbf{r}')}{|\mathbf{r}|} = \frac{N}{r}. \end{aligned}$$

Thus we have $V_{\mathrm{XC}} \sim -\frac{1}{r}$. For a neutral atom with $Z = N$, we have in the case $r \gg 1$

$$V_{\mathrm{eff}}(\mathbf{r}) \approx -\frac{Z}{r} + \frac{N}{r} - \frac{1}{r} = -\frac{1}{r}.$$

For general atoms in the region $r \gg 1$, PRA 16, 1782 (1977) tells us

$$\rho(\mathbf{r}) \approx e^{-\lambda r}. \tag{97}$$

Finally, for LDA and most GGAs, we have

$$V^{\mathrm{XC}} \approx -ae^{-br}$$

in the $r \gg 1$ region. For example, the exchange energy in LDA is given by

$$V_{\mathrm{X}}^{\mathrm{LDA}}(\mathbf{r}) = \frac{4}{3} C_{\mathrm{X}} \rho^{1/3}(\mathbf{r}). \tag{98}$$

Example 10.3 (Comparison between LDA and exact predictions)**.** $V_{\mathrm{eff}}^{\mathrm{LDA}}$ is less attractive than the exact V_{eff}. Thus,

$$\varepsilon_{\mathrm{HOMO}}^{\mathrm{LDA}} > \varepsilon_{\mathrm{HOMO}}^{\mathrm{exact}}.$$

For the hydrogen atom,

$$\varepsilon_{\mathrm{HOMO}}^{\mathrm{LDA}} \approx -0.26, \; \varepsilon_{\mathrm{HOMO}}^{\mathrm{exact}} \approx -0.5,$$

in accordance with the claim above. As another example, in exact KS-DFT, the ionisation energy I is given by

$$I \equiv E_{N-1} - E_N = -\varepsilon_{\mathrm{HOMO}}^{\mathrm{exact}}, \tag{99}$$

where the last equality is due to PRB 18, 7165 (1978) and PRL 49, 1691 (1982).

2. NCE (due to the lack of long-range dynamical correlation):

   It is helpful to note that here *long-range dynamical correlation* is the van der Waals force. A few methods have been developed to acconut for this qualitative error:

   (a) Van der Waals functional (PRL 92, 24640 (2004)): this is a *fully nonlocal* functional. (Question: what does fully nonlocal mean precisely?)

   (b) Dispersion correction (J Comput. Chem. 27, 1787 (2006)).

   (c) Double0hybrid (DH) (e.g. MP2 correction).

   (d) Random phase approximation (RPA) (PRA 88, 030501 (2013)).

   In the above list, the first two methods are the most widely adopted. Chai: The same result may come from different physical considerations.

3. SCE (due to the near degeneracy of KS orbitals at the Fermi level) Occurs in rungs 1 to 4. The problem may only be lifted on rung 5.

Remark. Optimised potential method.

10.5 Hybrid Exchange-Correlation Functional

A hybrid functional is obtained by mixing a fraction of Hartree-Fock exchange energy into a semilocal functional. It was mentioned in JCP 98, 1372 (1993). For the last time, refer back to table (1), this is rung 4 of the ladder.

The Hartree-Fock exact exchange functional is given by

$$\begin{aligned} E_{\mathrm{X}}^{\mathrm{HF}} &= -\frac{1}{2}\sum_{i,j}\int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2\, \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\left(\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2) \\ &= -\frac{1}{2}\sum_{i,j}[ij|ji]. \end{aligned} \tag{100}$$

Using the **adiabatic connection formula**, we have

$$E^{\mathrm{XC}}[\rho] = \int_0^1 \mathrm{d}\lambda\, U_\lambda^{\mathrm{XC}}, \tag{101}$$

where

$$U_\lambda^{\mathrm{XC}} \equiv \left\langle \Psi_\lambda \middle| \hat{V} \middle| \Psi_\lambda \right\rangle - E^{\mathrm{H}} = E_{\mathrm{X}}^{\mathrm{exact}} \approx E_{\mathrm{X}}^{\mathrm{HF}}. \tag{102}$$

Using the density functional approximation (DFA), we have

$$E_{\mathrm{XC}}^{\mathrm{LDA}}[\rho] = \int_0^1 \mathrm{d}\lambda\, U_{\mathrm{XC},\lambda}^{\mathrm{LDA}}, \tag{103}$$

due to PRA 32, 2010 (1985) and JCP 83, 2334 (1985).

$$\left\langle \Psi_{\lambda=1} \middle| \hat{V} \middle| \Psi_{\lambda=1} \right\rangle - E^{\mathrm{H}} = U_{\lambda=1}^{\mathrm{XC}} \approx U_{\mathrm{XC},\lambda=1}^{\mathrm{LDA}}.$$

The approximation is because of the fact that the XC hole is deeper and thus more localised at the reference electron at $\lambda = 1$ than at $\lambda = 0$. This remark is due to JCP 105, 9982 (1996) and CPL 265, 115 (1997). The exchange-correlation functional is then

$$\begin{aligned} E_{\mathrm{XC}}[\rho] &\approx \frac{1}{2}\left\{U_{\lambda=0}^{\mathrm{XC}} + U_{\lambda=1}^{\mathrm{XC}}\right\} \\ &\approx \frac{1}{2}\left\{E_{\mathrm{X}}^{\mathrm{HF}} + E_{\mathrm{X}}^{\mathrm{DFA}}[\rho] + 2E_{\mathrm{C}}^{\mathrm{DFA}}[\rho]\right\} \\ &= \frac{1}{2}E_{\mathrm{X}}^{\mathrm{HF}} + \frac{1}{2}E_{\mathrm{X}}^{\mathrm{DFA}}[\rho] + E_{\mathrm{C}}^{\mathrm{DFA}}[\rho], \end{aligned} \tag{104}$$

which fits the description of a hybrid functional.

In general, we have

$$E_{\mathrm{XC}} = a_0 E_{\mathrm{X}}^{\mathrm{HF}} + (1-a_0)E_{\mathrm{X}}^{\mathrm{DFA}} + E_{\mathrm{C}}^{\mathrm{DFA}}, \tag{105}$$

where $0 \le a_0 \le 1$. Then we can write

$$\left\{-\frac{\nabla^2}{2} + V_{\mathrm{eff}}^{\mathrm{loc}}(\mathbf{r}) - a_0\sum_{j=1}^{N} K_j(\mathbf{x})\right\}\phi_i(\mathbf{x}) = \varepsilon_i\phi_i(\mathbf{x}), \tag{106}$$

where

$$V_{\mathrm{eff}}^{\mathrm{loc}}(\mathbf{r}) = V(\mathbf{r}) + \frac{\delta E^{\mathrm{H}}[\rho]}{\delta\rho(\mathbf{r})} + (1-a_0)\frac{\delta E_{\mathrm{X}}^{\mathrm{DFA}}[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{\mathrm{C}}^{\mathrm{DFA}}[\rho]}{\delta\rho(\mathbf{r})}, \tag{107}$$

and we say equation (106) is the **generalised Kohn-Sham equation**.

Here, again,

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \sum_{\sigma} |\phi_i(\mathbf{x})|^2 .$$

If a_0 can reach 1, then asymptotics will be correct. Here we review a few related computation models.

- B3PV91 (JCP 98, 5648 (1993)): The exchange-correlation is given by

  $$E_{\mathrm{XC}} = E_{\mathrm{XC}}^{\mathrm{LDA}} + a_0 \left(E_{\mathrm{X}}^{\mathrm{HF}} - E_{\mathrm{X}}^{\mathrm{LDA}} \right) + a_{\mathrm{X}} \Delta E_{\mathrm{X}}^{\mathrm{B88}} + a_{\mathrm{C}} \Delta E_{\mathrm{C}}^{\mathrm{PW91}},$$

  where

  $$\Delta E_{\mathrm{X}}^{\mathrm{B88}} \equiv E_{\mathrm{X}}^{\mathrm{B88}} - E_{\mathrm{X}}^{\mathrm{LDA}},\ \Delta E_{\mathrm{C}}^{\mathrm{PW91}} \equiv E_{\mathrm{C}}^{\mathrm{PW91}} - E_{\mathrm{C}}^{\mathrm{LDA}},$$

  and the parameters are $a_0 = 0.2, a_{\mathrm{X}} = 0.72, a_{\mathrm{C}} = 0.81$.
- B3LYP (JPC 98, 11623 (1994)): The XC functional is the same as that of B3PV91, but with $E_{\mathrm{C}}^{\mathrm{PW91}}$ replaced with $E_{\mathrm{C}}^{\mathrm{LYP}}$.
- PBE0 (JCP 110, 6158 (1999)): Note the relation

  $$\text{PBE} \mid \text{PBE} \longrightarrow \text{PBE1} \longrightarrow \text{PBE0}.$$

  The XC functional is given by

  $$E_{\mathrm{XC}} = a_0 E_{\mathrm{X}}^{\mathrm{HF}} + (1 - a_0) E_{\mathrm{X}}^{\mathrm{PBE}} + E_{\mathrm{C}}^{\mathrm{PBE}}.$$

  In the paper JCP 105, 9982 (1996), the value $a_0 = \frac{1}{4}$ was derived using a perturbation theory argument (by whom? Probably Purdue).

Remark. From Chai: ”so the conclusion is that B3LYP does not have B as an author, while PBE0 does not have Purdue as an author. (repeats) (repeats)”

Next we will discuss Double-hybrid (DH) functionals. These are functionals obtained by mixing a fraction of Hartree-Fock exchange functional *and* a fraction of MP2 correlation into a semilocal functional. In the context of Görling-Levy (GL) perturbation theory (), we have

$$E_{\mathrm{XC}}^{\lambda} \approx E_{\mathrm{X}}^{\mathrm{exact}} + 2E_{\mathrm{C}}^{\mathrm{GL2}} \lambda \tag{108}$$

in the $\lambda \to 0$ limit, and

$$\begin{aligned} E_{\mathrm{C}}^{\mathrm{GL2}} &= E_{\mathrm{C}}^{\mathrm{MP2}} + \Delta E_{\mathrm{C}}^{\mathrm{HF}} \\ &\approx E_{\mathrm{C}}^{\mathrm{MP2}} \end{aligned}$$

for *most* cases. The MP2 correlation energy in the above formula is given by

$$E_{\mathrm{C}}^{\mathrm{MP2}} = \sum_{i<j} \sum_{a<b} \frac{|\langle ij \mid\mid ab \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \tag{109}$$

where

$$\langle ij \mid\mid ab \rangle \equiv [ia|jb] - [ja|ib].$$

In general, a Double-Hybrid functional is given by

$$E_{\mathrm{XC}}^{\mathrm{DH}} = a_{\mathrm{X}} E_{\mathrm{X}}^{\mathrm{HF}} + (1 - a_{\mathrm{X}}) E_{\mathrm{X}}^{\mathrm{DFA}} + (1 - a_{\mathrm{C}}) E_{\mathrm{C}}^{\mathrm{DFA}} + a_{\mathrm{C}} E_{\mathrm{C}}^{\mathrm{MD2}}. \tag{110}$$

In the above equation, the term $E_{\mathrm{C}}^{\mathrm{MP2}}$ is evaluated by the generalised Kohn-Sham (GKS) orbitals ** by the first three terms and added to toal energy. Notice that if $a_{\mathrm{X}} = a_{\mathrm{C}} = 1$, then

$$E_{\mathrm{XC}}^{\mathrm{DH}} = E_{\mathrm{X}}^{\mathrm{HF}} + E_{\mathrm{C}}^{\mathrm{MD2}}.$$

The corresponding Kohn-Sham equation to be solved in order to obtain orbitals is

$$\left\{-\frac{\nabla^2}{2} + V_{\mathrm{eff}}^{\mathrm{loc}}(\mathbf{r}) - a_{\mathrm{X}} \sum_{j=1}^{N} K_j(\mathbf{x})\right\} \phi_i(\mathbf{x}) = \varepsilon_i \phi_i(\mathbf{x}),$$

where $\varepsilon_1 \leq \varepsilon_2 \leq \cdots$, and the local effective potential is

$$V_{\mathrm{eff}}^{\mathrm{loc}}(\mathbf{r}) \equiv V(\mathbf{r}) + V^{\mathrm{H}}(\mathbf{r}) + (1 - a_{\mathrm{X}}) \frac{\delta E_{\mathrm{X}}^{\mathrm{DFA}}}{\delta\rho(\mathbf{r})} + (1 - a_{\mathrm{C}}) \frac{\delta E_{\mathrm{C}}^{\mathrm{DFA}}}{\delta\rho(\mathbf{r})}.$$

Chai: The computation cost of hybrid XC methods is about the same as that of the Hartree-Fock method.

11 Van der Waals Interaction

This section is a detour into the van der Waals interaction, which is the main topic of my final report. In the paper by Dion et al., they have demonstrated that it is possible to deal with van der Waals interaction for arbitrary geometries in the framework of DFT.

Example 11.1 (Basic theory of van der Waals interaction)**.** In 1930, London derived a general formula for the van der Waals interaction, which we now call the **London dispersion force**. Given two particles with first ionisation energies I_A and I_B, polarisability volumes α'_A and α'_B, and intermolecular distance R, the dispersion energy is

$$E_{AB}^{\mathrm{disp}} \approx -\frac{3}{2}\left(\frac{I_A I_B}{I_A + I_B}\right)\frac{\alpha'_A \alpha'_B}{R^6}. \tag{111}$$

The main goal of the paper is to construct an explicit nonlocal correlation functional of the form

$$E_{\mathrm{c}}^{\mathrm{nl}}[\rho] = \int \mathrm{d}^3 r' \int \mathrm{d}^3 r\, \rho(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}'), \tag{112}$$

where $\phi(\mathbf{r}, \mathbf{r}') = \phi(|\mathbf{r} - \mathbf{r}'|)$. It will be shown that their functional is applicable to *general geometries*. This construction is important because

By a choice of suitable variables with respect of which the energy functional is expanded, we arrive at the result

$$\phi(\mathbf{r}, \mathbf{r}') = \frac{2me^4}{\pi^2} \int_0^\infty \mathrm{d}a\, a^2 \int_0^\infty \mathrm{d}b\, b^2 W(a, b) T\left(\nu(a), \nu(b), \nu'(a), \nu'(b)\right), \tag{113}$$

where

$$T(w, x, y, z) = \frac{1}{2}\left[\frac{1}{w + x} + \frac{1}{y + z}\right]\left[\frac{1}{(w + y)(x + z)} + \frac{1}{(w + z)(y + x)}\right],$$

and

$$\begin{aligned} W(a, b) = 2 \big[&(3 - a^2) b \cos b \sin a + (3 - b^2) a \cos a \sin b \\ &+ (a^2 + b^2 - 3) \sin a \sin b - 3ab \cos a \cos b\big] / a^3 b^3. \end{aligned}$$

Here the quantites ν and ν' are given respectively by

$$\nu(y) = \frac{y^2}{2h(y/d)},\ \nu'(y) = \frac{y^2}{2h(y/d')},$$

where $d = |\mathbf{r} - \mathbf{r}'|q_0(\mathbf{r})$, $d' = |\mathbf{r} - \mathbf{r}'|q_0(\mathbf{r}')$, and q_0 is given by

$$q_0(\mathbf{r}) = \frac{\varepsilon^0_{\text{XC}}(\mathbf{r})}{\varepsilon^{\text{LDA}}_{\text{x}}(\mathbf{r})} k_{\text{F}}(\mathbf{r}) \approx \left[\frac{\varepsilon^{\text{LDA}}_{\text{XC}}(\mathbf{r})}{\varepsilon^{\text{LDA}}_{\text{X}}(\mathbf{r})} - \frac{Z_{ab}}{9}\left(\frac{\nabla n}{2k_{\text{F}}n}\right)^2\right] k_{\text{F}}(\mathbf{r}).$$

Notice that the kernel $\phi(\mathbf{r}, \mathbf{r}')$ depends on r and r' only through d and d', so ϕ can be tabulated in advance. For large separation d and d', we have the familiar (?) asymptotic form

$$\phi \sim -\frac{C}{d^2 d'^2 (d^2 + d'^2)}.$$

12 Papers

List of interesting papers from professor Chai and part of a list of possible choices for the final report:

- Perdew, J. P.; Burke, Kieron; Ernzerhof, Matthias (1996). Generalised gradient approximation made simple
- Reining, Lucia et al. (2002). Excitonic effects in solids described by time-dependent density-functional theory
- Dion, M. et al. (2004). Van der Waals density functional for general geometries
- Tsuneda, Takao et al. (2010). On Koopmans' theorem in density functional theory
- Cohen, Aron J.; Mori-Sanchez, Paula; Yang, Weitao (2008). Insights into current limitations of density functional theory
- Chai, Jeng-Da (2012). Density functional theory with fractional orbital occupations
- Brockherde, Felix et al. (2017). Bypassing the Kohn-Sham equations with machine learning
- Bosko, Ivan P.; Staroverov, Viktor N. (2023). Exchange energies and density functionals for systems of fermions of arbitrary spin
- Wang, Lin-Wang (1992). Kinetic-energy functional of the electron density
- Witt, William C. (2017). Orbital-free density functional theory for materials research
- Yeh, Chia-Nan; Lee, Pei-Yin; Chai, Jeng-Da (2016). Electronic and optical properties of the narrowest armchair graphene nanoribbons studied by density functional methods

Final report subject and related papers:

- Dion, M. et al. (2004). Van der Waals density functional for general geometries
- Rydberg, H. et al. (2003). Van der Waals density functional for layered structures
- Langreth, D. C. et al. (2004). Van der Waals density functional theory with application

13 Other References

- Szabo, Attila; Ostlund, N. S. (1996). *Modern Quantum Chemistry Introduction to Advanced Electronic Structure Theory*
- Pathria, R. K.; Beale, Paul D. (2011). *Statistical Mechanics 3e*
- Baer, Roi *Density functional theory*

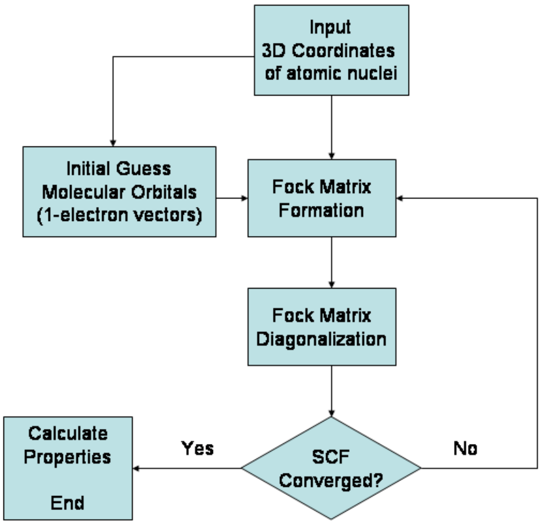

Figure 1: Iterative scheme of the Hartree-Fock method.