L5: Mean-Field Methods and Density Functional Theory I

February 10, 2025

Outline

Introduction

- **Mean-field methods** replace an interacting many-body problem with a set of independent-particle problems using an effective potential.
- The effective potential approximates interaction effects either on an average basis or as an auxiliary system reproducing selected properties.
- These methods provide practical starting points for calculations and help interpret interactions.
- **Focus:** Two key methods relevant to interacting electron systems:
  1. Hartree–Fock approximation
  2. Density Functional Theory (DFT)

Independent-Particle Approaches

There are two fundamental independent-particle approximations:

1. **Hartree–Fock Approximation (HFA):** The many-body wavefunction is approximated by a single Slater determinant while retaining the full N-body Hamiltonian.
2. **Non-interacting Electron Methods:** Use a local effective potential (often called "Hartree-like") to describe the system.

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Note: The challenge is defining the effective particles correctly.

Hartree–Fock Wavefunction

In the Hartree–Fock approximation the many-body wavefunction is assumed to be an antisymmetrized product of single-particle orbitals:

$$\Psi_{\mathrm{HF}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1, \sigma_1) & \psi_1(r_2, \sigma_2) & \dots \\ \psi_2(r_1, \sigma_1) & \psi_2(r_2, \sigma_2) & \dots \\ \vdots & \vdots & \ddots \end{vmatrix} . \tag{4.1}$$

(Here, $\psi_i(r, \sigma)$ is a product of a spatial orbital and a spin function. For more details on spatial and spin symmetries, see [**?**, **?**].)

Hartree–Fock Total Energy

The total energy in the HF approximation is expressed as:

$$\langle \Psi_{\mathrm{HF}} | \hat{H} | \Psi_{\mathrm{HF}} \rangle = - \sum_{i,\sigma} \int d^3r \, \psi_i^{\sigma *}(r) \frac{\nabla^2}{2} \psi_i^{\sigma}(r) + \int d^3r \, v_{ext}(r) \, n(r) + E_H + E_X \, . \quad (4.2)$$

- $v_{ext}(r)$ is the external potential.
- $n(r)$ is the electron density.

Hartree and Exchange Energies

Hartree Energy

$$E_H = \frac{1}{2} \int d^3r \, d^3r' \, \frac{n(r)n(r')}{|r - r'|} \, . \tag{4.3}$$

Exchange Energy

$$E_X = -\frac{1}{2} \sum_{\sigma} \sum_{\substack{i,j \\ \text{occ}}} \int d^3r \, d^3r' \, \psi^*_{j\sigma}(r') \, \psi_{i\sigma}(r') \, \frac{1}{|r - r'|} \, \psi_{j\sigma}(r) \, \psi^*_{i\sigma}(r) \, . \tag{4.4}$$

Hartree–Fock Equations

Minimizing the total energy with respect to the orthonormal orbitals $\psi_{i\sigma}(r)$ yields:

$$\begin{aligned}
&\left[-\frac{1}{2}\nabla^2 + v_{ext}(r) + \sum_{\substack{j,\sigma_j \\ \text{occ}}} \int d^3r'\, \psi_j^{\sigma_j *}(r')\, \psi_j^{\sigma_j}(r')\, \frac{1}{|r-r'|}\right] \psi_i^{\sigma}(r) \\
&\qquad - \sum_{\substack{j \\ \text{occ}}} \int d^3r'\, \psi_j^{\sigma *}(r')\, \psi_i^{\sigma}(r')\, \frac{1}{|r-r'|}\, \psi_j^{\sigma}(r) = \varepsilon_i^{\sigma}\, \psi_i^{\sigma}(r)\,.
\end{aligned} \tag{4.5}$$

Hartree and Fock Potentials

Hartree Potential

$$v_H(r) \equiv \sum_{\substack{j,\sigma_j \\ \mathrm{occ}}} \int d^3r' \, \psi_j^{\sigma_j *}(r') \, \psi_j^{\sigma_j}(r') \, \frac{1}{|r-r'|} = \int d^3r' \, \frac{n(r')}{|r-r'|} \, . \tag{4.6}$$

Non-local Fock Operator

$$\hat{x}_\sigma(r,r') = -\sum_{\substack{j \\ \mathrm{occ}}} \psi_j^{\sigma *}(r') \, \frac{1}{|r-r'|} \, \psi_j^{\sigma}(r) = -\frac{\rho(r,\sigma;r',\sigma)}{|r-r'|} \, . \tag{4.7}$$

Additional Remarks on Hartree–Fock

- **Excited States:** Excitations can be formed by substituting ground-state orbitals with higher-energy orbitals. Koopmans' theorem relates eigenvalues to electron addition/removal energies.
- **Self-Consistent Field (SCF) Calculations:** Allow orbital relaxation by performing separate SCF calculations for systems with N, $N+1$, or $N-1$ electrons.
- **Second Quantization:** The HF mean field emerges naturally from the factorization of the two-body interaction operator.

Density Functional Theory (DFT)

- **Density Functional Theory (DFT)** is a theory of the interacting many-electron system.
- It was originally developed in the context of quantum mechanics and later applied to classical liquids (e.g., van der Waals, Cahn & Hilliard).
- In this course, we focus on aspects of DFT that relate conceptually to methods such as Green's functions and quantum Monte Carlo, and on its role as a practical starting point for many-body calculations.
- DFT inherently reflects the many-body nature of the problem and is pursued even in the strong-interaction limit (e.g., where electrons form a Wigner crystal).
- The **Kohn–Sham (KS) construction** introduces an auxiliary system of non-interacting electrons that reproduces the correct ground-state density.

Total Energy in DFT

The total energy of an interacting many-electron system can be written as

$$E = \langle \hat{H} \rangle = \langle \hat{T} + \hat{V}_{ee} \rangle + \int d\mathbf{r}\; v_{\text{ext}}(\mathbf{r})\, n(\mathbf{r})\,.$$

- Here, $n(\mathbf{r})$ is the electron density.
- Minimizing over all normalized, antisymmetric many-body wavefunctions yields the ground state with density n_0 and energy E_0.
- Since E_0 is determined by the external potential $v_{\text{ext}}(\mathbf{r})$, each term is, in effect, a functional of v_{ext}.

General Definition of the Ground-State Energy

- The formalism of Density Functional Theory (DFT) allows us to define a ground-state energy functional
$$E[v_{\text{ext}}]$$
for **any** admissible external potential $v_{\text{ext}}(\mathbf{r})$.
- **What does this mean?**
  - For each external potential $v_{\text{ext}}(\mathbf{r})$, the corresponding many-electron Hamiltonian
$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i)$$
has a well-defined ground state and ground-state energy E.
  - The energy functional $E[v_{\text{ext}}]$ is a mapping from the *entire* function $v_{\text{ext}}(\mathbf{r})$ to a number, i.e., the ground-state energy.

Hohenberg–Kohn Energy Functional

Hohenberg and Kohn showed that the ground-state energy can be expressed as a functional of the density:

$$E_{\mathrm{HK}}[n] = F_{\mathrm{HK}}[n] + \int d\mathbf{r}\; v_{\mathrm{ext}}(\mathbf{r})\, n(\mathbf{r})\,, \tag{4.15}$$

where

$$F_{\mathrm{HK}}[n] = \langle \hat{T} \rangle + \langle \hat{V}_{ee} \rangle$$

is universal (i.e., independent of v_{ext}).

- This result is an example of a Legendre transformation.
- It implies a one-to-one correspondence between $n(\mathbf{r})$ and $v_{\mathrm{ext}}(\mathbf{r})$ for densities that are *v-representable*.

Legendre Transformation in DFT

- **Starting Point:** The ground-state energy is originally expressed as a functional of the external potential:
$$E[v_{\text{ext}}] = \langle \Psi[v_{\text{ext}}] | \hat{H}[v_{\text{ext}}] | \Psi[v_{\text{ext}}] \rangle \, .$$
- **Conjugate Variables:** The ground-state density is given by
$$n(\mathbf{r}) = \frac{\delta E[v_{\text{ext}}]}{\delta v_{\text{ext}}(\mathbf{r})} \, ,$$
showing that $n(\mathbf{r})$ is conjugate to $v_{\text{ext}}(\mathbf{r})$.
- **Legendre Transform:** By performing a Legendre transformation, we define the energy as a functional of the density:
$$E_{\text{HK}}[n] = F_{\text{HK}}[n] + \int d\mathbf{r} \; v_{\text{ext}}(\mathbf{r}) \, n(\mathbf{r}) \, ,$$
where
$$F_{\text{HK}}[n] = \langle \hat{T} \rangle + \langle \hat{V}_{ee} \rangle$$
is universal.
- **Implication:** The transformation is invertible (by the one-to-one relation between n and v_{ext}), meaning the formalism applies to any external potential, with each v_{ext} yielding its own ground-state energy.

v-Representability

v-Representability:

- A density $n(\mathbf{r})$ is *v-representable* if there exists a local external potential $v_{\text{ext}}(\mathbf{r})$ such that $n(\mathbf{r})$ is the ground-state density of the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i) \,.$$

- In the original HK proofs, only v-representable densities were considered.
- This condition is crucial to establish the one-to-one mapping between $n(\mathbf{r})$ and $v_{\text{ext}}(\mathbf{r})$.

N-Representability

- A density $n(\mathbf{r})$ is *N-representable* if there exists an antisymmetric N-electron wavefunction Ψ such that

$$n(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N \, .$$

- The density must integrate to the correct number of electrons:

$$\int n(\mathbf{r}) \, d\mathbf{r} = N \, .$$

- N-representability ensures that the density corresponds to a physically realizable many-electron state.
- This condition is more general than *v-representability*, which requires the density to arise as the ground-state density for some local external potential.
- In DFT, the universal energy functional is defined only on the set of N-representable densities.

Preliminaries: Electron Density

It can be proven (trivially) that for a set of indistinguishable independent particles the electron density is given by:

$$n(\mathbf{r}) = \sum_{\text{occ } i} \left|\psi_i(\mathbf{r})\right|^2 .$$

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For electrons with spin:

$$n(\mathbf{r}) = \sum_{\text{occ } i,\sigma} \left|\psi_{i\sigma}(\mathbf{r})\right|^2 = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}),$$

$$n_\sigma(\mathbf{r}) = \sum_{\text{occ } i} \left|\psi_{i\sigma}(\mathbf{r})\right|^2,$$

$$n_s(\mathbf{r}) = n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r}).$$

Preliminaries: Local Potential Operator

Consider a general many-particle wavefunction $\Psi(\{s_i\})$ and a local potential energy operator:

$$\hat{V} = \sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i)\,.$$

One can prove that:

$$\langle\Psi|\hat{V}|\Psi\rangle = \int d^3r\; n(\mathbf{r})\; V_{\text{ext}}(\mathbf{r})\,.$$

- This relies on the fact that a local potential acts multiplicatively in the coordinate representation.

Constrained Search: The Levy–Lieb Approach

To bypass the limitations of v-representability, Levy and Lieb introduced a two-step constrained search:

$$E_{\mathrm{LL}}[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d\mathbf{r}\; v_{\mathrm{ext}}(\mathbf{r})\, n(\mathbf{r})\,.$$

- The minimization is performed over all N-particle wavefunctions Ψ that yield the density $n(\mathbf{r})$.
- This formulation does not require that the density be v-representable.
- Although this expression is concise, its practical evaluation is more complex than solving the full quantum problem.

Hohenberg–Kohn Theorems: Statement

For a non-degenerate ground state, the following hold:

- One can define an energy functional of the electron density:

  $$E[n] = F[n] + \int d^3r\, n(\mathbf{r})\, V_{\text{ext}}(\mathbf{r})\,,$$

  where $F[n]$ is universal.
- The variational principle states that

  $$E[n] \geq E_{\text{GS}},$$

  with equality if and only if $n(\mathbf{r}) = n_{\text{GS}}(\mathbf{r})$.

First Hohenberg–Kohn Theorem

Rewriting Levy's expression:

$$F[n] = \langle \Psi_n^{\text{min}} | \hat{T} + \hat{V}_{ee} | \Psi_n^{\text{min}} \rangle \, .$$

Then, by adding the external potential contribution:

$$F[n] + \int d^3r \, n(\mathbf{r}) \, V_{\text{ext}}(\mathbf{r}) = \langle \Psi_n^{\text{min}} | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi_n^{\text{min}} \rangle \geq E_{\text{GS}} \, .$$

- This inequality follows from the variational principle.

Second Hohenberg–Kohn Theorem

For the ground-state density $n_{\mathrm{GS}}(\mathbf{r})$, we have:

$$E_{\mathrm{GS}} = \langle \Psi_{\mathrm{GS}} | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi_{\mathrm{GS}} \rangle \leq \langle \Psi^{\mathrm{min}}_{n_{\mathrm{GS}}} | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi^{\mathrm{min}}_{n_{\mathrm{GS}}} \rangle \, .$$

Since the external potential contribution is the same for both wavefunctions,

$$\langle \Psi_{\mathrm{GS}} | \hat{T} + \hat{V}_{ee} | \Psi_{\mathrm{GS}} \rangle = \langle \Psi^{\mathrm{min}}_{n_{\mathrm{GS}}} | \hat{T} + \hat{V}_{ee} | \Psi^{\mathrm{min}}_{n_{\mathrm{GS}}} \rangle \, .$$

Hence,

$$E[n_{\mathrm{GS}}] = F[n_{\mathrm{GS}}] + \int d^3r \; n_{\mathrm{GS}}(\mathbf{r}) \, V_{\mathrm{ext}}(\mathbf{r}) = E_{\mathrm{GS}} \, .$$

Summary

- **DFT** replaces the many-body wavefunction Ψ with the electron density $n(\mathbf{r})$, reducing the complexity from a $3N$-dimensional function to a 3-dimensional function.
- The **Hohenberg–Kohn Theorems** establish:
  - A one-to-one mapping between $n(\mathbf{r})$ and $v_{\text{ext}}(\mathbf{r})$ (for v-representable densities).
  - A variational principle: $E[n] \geq E_{\text{GS}}$ with equality for $n(\mathbf{r}) = n_{\text{GS}}(\mathbf{r})$.
- The **Levy–Lieb constrained search** overcomes the v-representability restriction by considering all N-representable densities.
- The **Kohn–Sham construction** introduces an auxiliary non-interacting system that reproduces the true ground-state density.

Questions?

Any Questions?