L6: Mean-Field Methods and Density Functional Theory II

February 12, 2025

Practical Implementation of DFT

- The previous chapter introduced the theoretical framework of density-functional theory (DFT).
- Kohn and Sham (1965) provided a practical approach for applying DFT.
- Their method reduces the complexity by rewriting the energy functional as:

$$E[n] = T_0[n] + \int d^3r n(r) \left(V_{ext}(r) + \frac{1}{2}\Phi(r) \right) + E_{xc}[n], \tag{1}$$

where:

  - $T_0[n]$: Kinetic energy of a **non-interacting electron system** with density $n(r)$.
  - $\Phi(r)$: Hartree potential.
  - $E_{xc}[n]$: Exchange-correlation energy (key unknown component).

Kohn-Sham Equations and Orbital-Free DFT

- The original many-body problem is **transformed** into a mean-field-like system:

$$V(r) = V_{ext}(r) + \Phi(r) + \frac{\delta E_{xc}[n]}{\delta n(r)}. \tag{2}$$

- This allows solving for **non-interacting electrons** in an effective potential.
- A key area of research is finding **better approximations** for the universal functional F.
- A major challenge:
  - The kinetic energy functional $T[n]$ is hard to model from the density alone.
  - This difficulty stems from atomic **shell structures** and the role of antisymmetric wavefunctions.
- **Orbital-Free DFT** aims to remove orbitals entirely, but remains an active area of development.

Kohn-Sham Energy Functional

- Following Jones and Gunnarsson, we express the functional as:
$$E[n] = T_0[n] + \int d^3r n(r) \left(V_{ext}(r) + \frac{1}{2}\Phi(r) \right) + E_{xc}[n]. \tag{3}$$

- The variational principle applied to this functional gives:
$$\frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_0[n]}{\delta n(r)} + V_{ext}(r) + \Phi(r) + \frac{\delta E_{xc}[n]}{\delta n(r)} = \mu. \tag{4}$$

- μ is the Lagrange multiplier ensuring particle number conservation.

Effective Potential and Exchange-Correlation

- Comparing this result with a system under an effective potential $V(r)$:

$$\frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_0[n]}{\delta n(r)} + V(r) = \mu, \tag{5}$$

- This shows the mathematical equivalence of both problems, if:

$$V(r) = V_{ext}(r) + \Phi(r) + V_{xc}[n](r), \tag{6}$$

where we define the **exchange-correlation potential** as:

$$V_{xc}[n](r) = \frac{\delta E_{xc}[n]}{\delta n(r)}. \tag{7}$$

- This formulation forms the foundation of the **Kohn-Sham equations**.

Kohn-Sham Equations

- The independent particle problem under the potential $V(r)$ is solved using the Schrödinger equation:

$$\left(-\frac{1}{2}\nabla^2 + V(r)\right)\psi_i(r) = \epsilon_i \psi_i(r). \tag{8}$$

- The corresponding **electron density** is obtained as:

$$n(r) = \sum_i f_i |\psi_i(r)|^2. \tag{9}$$

- Here, f_i represents the occupation of the state, which can follow the **Fermi-Dirac distribution**.
- This framework enables the determination of electronic structure in a self-consistent manner.

Kinetic Energy Functional and Levy's Construction

- The kinetic energy for non-interacting electrons is computed as:

$$T_0[n(\mathbf{r})] = -\frac{1}{2}\sum_{i}^{N}\langle\psi_{ni}|\nabla^2|\psi_{ni}\rangle. \tag{10}$$

- This raises a paradox: How can T_0 be a **functional of the density** if it is computed from the orbitals?
- **Levy's construction** provides the resolution:
  - For an independent-electron system, the universal functional in Levy's approach is **precisely** $T_0[n]$.
  - This ensures that the kinetic energy derived from ψ_i is indeed a valid functional of $n(r)$.
- Given $n(r)$, we can compute the total energy functionals:
  - External potential, Hartree energy, and exchange-correlation energy.
  - With an exact E_{xc}, both $n(r)$ and E_{GS} would match the exact many-electron solution.
- The orbitals $\psi_{ni}(r)$ and their eigenvalues are auxiliary quantities without direct physical significance.

Exchange-Correlation Energy and Potential

- Both the exchange-correlation energy functional $E_{xc}[n]$ and its potential $V_{xc}[n](r)$ are unknown.
- In principle, there exists an **exact** functional for E_{xc}, but its form is unknown.
- The Kohn-Sham formalism conveniently packages everything unknown into a small term.
- From this point forward, all calculations will be based on **approximate** $E_{xc}[n]$ functionals.

Nature of $V_{xc}[n](r)$

- The exchange-correlation potential $V_{xc}[n](r)$ is:
  - A local potential in **real space**.
  - A functional of the electron density: **the potential at a point depends on the full density distribution**.
- To approximate V_{xc}, we rely on two main approaches:
  - **Local Density Approximation (LDA)**
  - **Generalized Gradient Approximation (GGA)**

Local Density Approximation (LDA)

- The simplest approximation: Assume that V_{xc} depends only on the local density at each point.
- The **homogeneous electron liquid** (jellium) serves as the reference system.
- The exchange-correlation energy is written as:

$$E_{xc}^{LDA}[n] = \int d^3 r n(r) \epsilon_{xc}^{HEG}(n(r)). \tag{11}$$

- Here, $\epsilon_{xc}^{HEG}(n)$ is the exchange-correlation energy per electron in jellium.

Exchange and Correlation in LDA

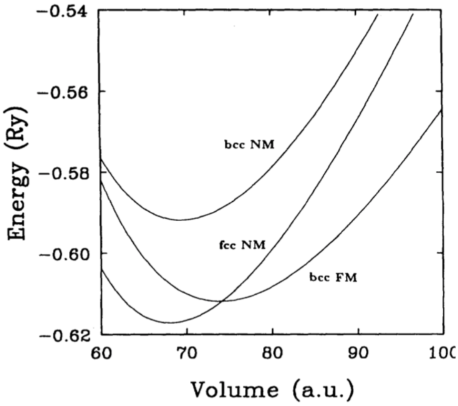
- The **exchange energy** (from Hartree-Fock for jellium) is:

$$E_x^{LDA}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d^3 r n(r)^{4/3}. \tag{12}$$

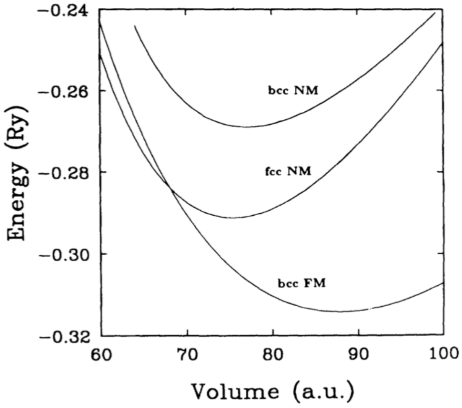
- This was originally introduced by Dirac and later used by Slater.
- The **correlation energy** was obtained via Quantum Monte Carlo (QMC) calculations (Ceperley Alder, 1980):

$$\varepsilon_c(r_s) = \begin{cases} A \log r_s + B + C r_s \log r_s + D r_s, & r_s \leq 1 \\ \frac{a}{1+b_1\sqrt{r_s}+b_2 r_s}, & r_s > 1 \end{cases} \tag{13}$$

Exchange and Correlation in LDA



LDA



GGA (PW91)

From: D. M. Ceperley and B. J. Alder (Phys. Rev. Lett. 1980)

Accuracy and Limitations of LDA

- With defined $\varepsilon_x(n)$ and $\varepsilon_c(n)$, LDA provides a **full DFT approximation**.
- Despite its simplicity, LDA predictions are often **surprisingly accurate**.
- However, LDA suffers from:
  - **Self-interaction error**: Exchange does not fully cancel Hartree term.
  - Overbinding in molecules and solids.
  - Poor treatment of van der Waals interactions.

Ceperley-Alder QMC results

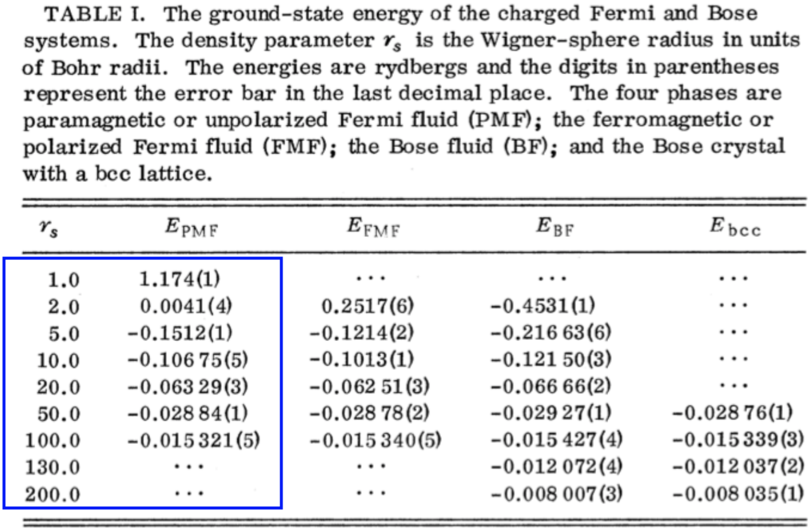


TABLE I. The ground-state energy of the charged Fermi and Bose systems. The density parameter r_s is the Wigner-sphere radius in units of Bohr radii. The energies are rydbergs and the digits in parentheses represent the error bar in the last decimal place. The four phases are paramagnetic or unpolarized Fermi fluid (PMF); the ferromagnetic or polarized Fermi fluid (FMF); the Bose fluid (BF); and the Bose crystal with a bcc lattice.

r_s	E_{PMF}	E_{FMF}	E_{BF}	E_{bcc}
1.0	1.174(1)	...	...	...
2.0	0.0041(4)	0.2517(6)	-0.4531(1)	...
5.0	-0.1512(1)	-0.1214(2)	-0.216 63(6)	...
10.0	-0.106 75(5)	-0.1013(1)	-0.121 50(3)	...
20.0	-0.063 29(3)	-0.062 51(3)	-0.066 66(2)	...
50.0	-0.028 84(1)	-0.028 78(2)	-0.029 27(1)	-0.028 76(1)
100.0	-0.015 321(5)	-0.015 340(5)	-0.015 427(4)	-0.015 339(3)
130.0	...	...	-0.012 072(4)	-0.012 037(2)
200.0	...	...	-0.008 007(3)	-0.008 035(1)

LDA results

Results for bond lengths in selected dimers. In many ways and systems, they are better than Hartree-Fock's, in spite of its also being a mean-field-like solution of the correlated problem.

Bond length (Å)	Experiment	LDA	Error
H_2	0.74	0.77	0.03
B_2	1.59	1.60	0.02
N_2	1.10	1.10	0.00
F_2	1.42	1.38	0.04
Na_2	3.08	3.00	0.08
Al_2	2.47	2.46	0.01
P_2	1.89	1.89	0.01
S_2	1.89	1.89	0.00
Cl_2	1.99	1.98	0.01
Average			0.02

R G Parr & W Yang, *Density-Functional Theory of Atoms and Molecules*
Oxford University Press (1994)

Generalized Gradient Approximation (GGA)

- GGA improves upon LDA by incorporating **density gradients**.
- The functional form is:

$$E_{xc}^{GGA}[n] = \int d^3 r n(r) \epsilon_{xc}(n, \nabla n). \tag{14}$$

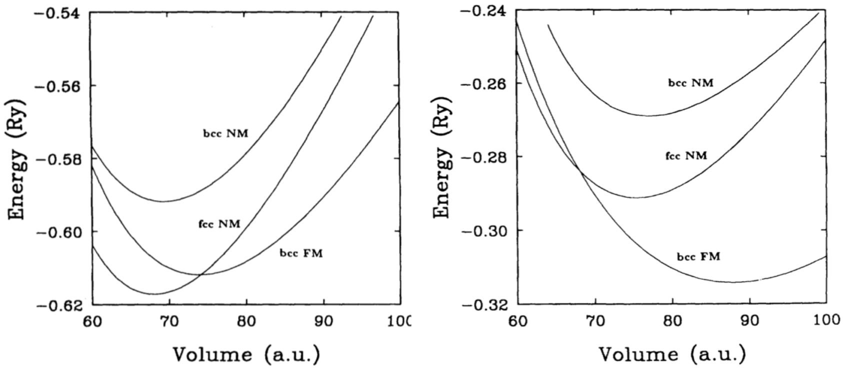
- GGA corrects some of LDA's systematic errors:
  - Improves bond lengths and reaction barriers.
  - Better treatment of electron localization.

Issues with GGA

- GGA is an **empirical improvement** over LDA but not a systematic expansion.
- Problems include:
    - No unique reference system, unlike LDA.
    - Many different GGA functionals exist, leading to inconsistency.

GGA Vs LDA: A Clear improvement

LDA vs. GGA for Fe



LDA

GGA (PW91)

Spin Polarization in DFT

- In ferromagnetic materials like iron, a **spontaneous magnetic moment** per unit cell exists.
- This magnetization results from an **imbalance in electron spins**.
- Up to now, we have assumed electrons pair up in single-particle orbitals.
- However, certain materials, like ferromagnetic iron, require **spin-polarized** solutions.

Spin-Polarized Density Functional Theory

- DFT can be extended to include **spin-polarized** solutions.
- Instead of a single electron density $n(r)$, we introduce separate spin densities:

$$E[n^{\uparrow}, n^{\downarrow}] \tag{15}$$

- The total electron density remains:

$$n(r) = n^{\uparrow}(r) + n^{\downarrow}(r). \tag{16}$$

- Each spin density is computed separately using the corresponding wave functions:

$$n^{\sigma}(r) = \sum_{i} |\psi_i^{\sigma}(r)|^2. \tag{17}$$

Spin Density and Magnetic Moments

- The **spin density** is defined as:

$$n_s(r) = n^{\uparrow}(r) - n^{\downarrow}(r). \tag{18}$$

- This quantity determines the degree of spin polarization in a system.
- Spin-polarized DFT allows:
  - Accurate modeling of **magnetic materials**.
  - Computation of **local magnetic moments**.
  - Study of **spin-dependent electronic properties**.

Total Energy in DFT

- Once the Kohn-Sham (KS) equations are solved, the total ground-state energy is given by:

$$E = -\frac{1}{2} \sum_{\text{occ } i} \langle \psi_i | \nabla^2 | \psi_i \rangle + \int d^3 r n(r) \left[V_{\text{ext}}(r) + \frac{1}{2} v_H(r) + \epsilon_{xc}(n(r), \nabla n(r)) \right] . \quad (19)$$

- This equation contains:
  - **Kinetic energy** of occupied KS orbitals.
  - **External potential** contribution.
  - **Hartree energy** ($v_H(r)$).
  - **Exchange-correlation energy** (ϵ_{xc}).

Double Counting Correction in DFT

- An alternative form of the total energy expression:

$$E = \sum_{\text{occ } i} \epsilon_i + \int d^3 r n(r) \left[\epsilon_{xc}(n(r), \nabla n(r)) - V_{xc}(n(r), \nabla n(r)) - \frac{1}{2} v_H(r) \right] . \qquad (20)$$

- The second equation explicitly corrects for **double counting errors**.
- **Why is this correction needed?**
  - The total energy includes an **integral over the energy density**.
  - The KS Hamiltonian already contains V_{xc}, which must be subtracted.
  - The Hartree term is included twice and must be corrected.

Band Energy in Solid-State Physics

- The sum of KS eigenvalues is known as the **band energy**:

$$\sum_i \epsilon_i \tag{21}$$

- In solid-state physics, this term represents the integration over occupied bands.
- However, it is **not the true total energy** due to missing exchange-correlation and Hartree corrections.
- This distinction is crucial for:
  - Computing accurate **total energies**.
  - Understanding **energy differences** in materials.
  - Avoiding misinterpretations of KS eigenvalues as physical energies.

The Bandgap Problem in DFT

- Kohn-Sham (KS) density functional theory is **exact** for ground-state density and total energy.
- However, approximations for other observables, such as band structures, remain uncertain.
- KS eigenvalues are commonly used for:
  - Band structures.
  - Response functions.
- These interpretations introduce errors, particularly in bandgap predictions.

Interpretation of Kohn-Sham Eigenvalues

- KS eigenvalues are sometimes interpreted as **total energy differences**.
- This interpretation is valid **only for the highest occupied state**, which gives the ionization energy:
$$I = -\epsilon_N. \tag{22}$$
- Important observations:
  - KS band structures do **not** correspond to electron addition/removal energies.
  - Approximate functionals introduce **self-interaction errors**.
  - Functionals like DFT+U, SIC, and hybrid functionals improve bandgap predictions.

Janak's Theorem and Ionization Energy

- Janak's theorem relates KS eigenvalues to energy derivatives:

$$\frac{\partial E}{\partial f_i} = \epsilon_i. \tag{23}$$

- The ionization energy is given by:

$$I = E_{N-1} - E_N = -\epsilon_N. \tag{24}$$

- Similarly, the electron affinity is:

$$A = E_{N+1} - E_N = \epsilon_{N+1}. \tag{25}$$

- However, this does **not** generalize to all eigenvalues.

The Bandgap Problem and Derivative Discontinuity

- The **fundamental bandgap** is defined in terms of total energy differences:

$$E_g = E_{N+1} - E_N - (E_N - E_{N-1}). \tag{26}$$

- The KS bandgap is commonly computed as:

$$E_g^{KS} = \epsilon_{N+1}(N) - \epsilon_N(N). \tag{27}$$

- The true bandgap includes an additional **derivative discontinuity** Δ:

$$E_g = E_g^{KS} + \Delta. \tag{28}$$

Origin and Consequences of the Derivative Discontinuity

- The discontinuity arises because the total energy function $E(N)$ is not smooth:

$$\left.\frac{\partial E}{\partial N}\right|_{N^-} \neq \left.\frac{\partial E}{\partial N}\right|_{N^+} . \tag{29}$$

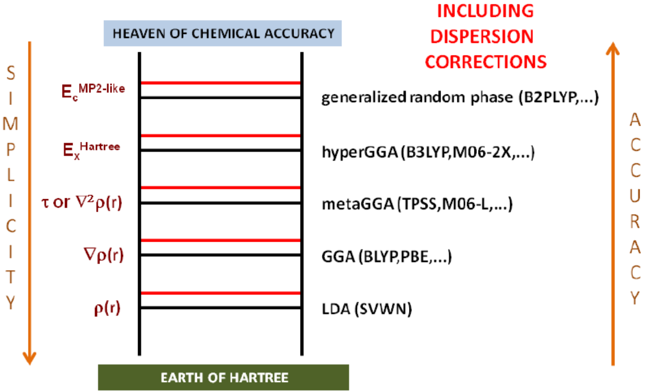
- In solids, this manifests as a **rigid shift in the KS potential**.
- Consequences:
  - The exact functional should have a nonzero Δ.
  - Standard functionals (LDA, GGA) lack this, leading to **underestimated bandgaps**.
  - Hybrid functionals and EXX capture part of the effect, improving predictions.

Implications and Beyond KS-DFT

- **Failure of Conventional Functionals:**
  - LDA and GGA fail to capture the derivative discontinuity.
  - Bandgaps predicted by these functionals are systematically too small.
- **Orbital-Dependent Functionals:**
  - Hybrid functionals and EXX recover part of the discontinuity.
- **Beyond KS-DFT:**
  - Many-body approaches like **GW corrections** explicitly account for Δ, leading to better bandgap predictions.

Beyond GGA: Jacob's Ladder

- Unlike some quantum-chemistry approaches, DFT does not have a systematic path toward exact solutions.
- However, functionals are classified in an accuracy hierarchy known as **Jacob's Ladder**, inspired by the biblical concept of a staircase to Heaven.



The Hierarchy of Functionals: Jacob's Ladder

- Functionals are classified based on their complexity and accuracy:
  1. **LDA**: Uses only the local density.
  2. **GGA**: Includes density gradients.
  3. **Meta-GGA**: Incorporates second derivatives or kinetic energy density.
  4. **Hybrids**: Mix DFT exchange with exact Hartree-Fock exchange.
  5. **RPA and Beyond**: Uses response functions.

Local Density Approximation (LDA)

- The simplest approximation: assumes that the exchange-correlation energy depends only on the local density.
- The Perdew-Zunger (PZ) parametrization is the most widely used LDA functional.
- LDA is derived from Quantum Monte Carlo (QMC) results for the homogeneous electron liquid.

Generalized Gradient Approximation (GGA)

- GGA incorporates density gradients to improve upon LDA.
- Two major families of GGA functionals:
    - **Chemistry-based** (e.g., BLYP): Fit to molecular data.
    - **Physics-based** (e.g., PBE, revPBE, PBEsol): Built on universal constraints.
- Provides better structural and energetic predictions than LDA.

Meta-GGA Functionals

- Meta-GGA introduces the **kinetic-energy density** as an additional variable.
- SCAN (Strongly Constrained and Appropriately Normed) is a widely used Meta-GGA functional.
- Offers better accuracy for strongly correlated systems.

Hybrid Functionals

- Hybrid functionals combine:
  - Exact Hartree-Fock (HF) exchange.
  - Conventional DFT exchange-correlation functionals.
- The exchange-correlation energy in hybrid functionals is given by:

$$E_{xc}^{\text{hybrid}} = \alpha E_x^{\text{HF}} + (1 - \alpha) E_x^{\text{DFT}} + E_c^{\text{DFT}}. \tag{30}$$

- The mixing parameter α typically ranges from 0.2 to 0.3.

Exchange Potential in Hybrid Functionals

- The HF exchange potential explicitly depends on KS orbitals:

$$V_x^{\mathrm{HF}}(r, r') = -\sum_{i}^{\mathrm{occ}} \psi_i^*(r')\psi_i(r)\frac{1}{|r - r'|}. \tag{31}$$

- This non-local expression contrasts with standard DFT exchange, which is a simple function of density.
- The presence of $\psi_i(r)$ means that hybrid functionals are **not purely density functionals**.

Kohn-Sham Equations with Hybrid Functionals

- The Kohn-Sham equation in hybrid DFT becomes:

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}(r) + V_H(r) + V_{xc}^{\text{hybrid}}(r)\right)\psi_i(r) = \epsilon_i \psi_i(r). \tag{32}$$

- The exchange-correlation potential is:

$$V_{xc}^{\text{hybrid}}(r) = \alpha V_x^{\text{HF}}(r) + (1-\alpha) V_x^{\text{DFT}}(r) + V_c^{\text{DFT}}(r). \tag{33}$$

- The additional HF exchange term increases computational cost but improves accuracy.

Generalized Kohn-Sham (GKS) Theory and OEP

- Hybrid functionals require an extended framework beyond standard KS-DFT.
- The **Generalized Kohn-Sham (GKS) Theory** allows functionals of the density matrix:

$$\gamma(r, r') = \sum_i^{\text{occ}} \psi_i^*(r')\psi_i(r). \tag{34}$$

- The **Optimized Effective Potential (OEP)** method:
  - Finds a local potential that mimics the non-local HF exchange term.
  - Used to make hybrid functionals computationally more efficient.

Advantages and Limitations of Hybrid Functionals

- **Advantages**:
  - **Improved Band Gaps**: Reduces the bandgap underestimation problem.
  - **Better Treatment of Localized Electrons**: Useful for transition metals and rare-earth elements.
  - **More Accurate Molecular Energies**: Better predictions for reaction barriers and binding energies.
- **Limitations**:
  - **Computationally Expensive**: Non-local exchange evaluation increases cost.
  - **Empirical Mixing Parameter** α: No universal rule for choosing α.
  - **Not Always Suitable for Metals**: Hybrid functionals may fail in metallic systems.

Van der Waals Interactions in DFT

- Standard functionals (LDA, GGA) fail to capture dispersion interactions.
- The first ab initio Van der Waals (vdW) functional was developed in 2004.
- Non-local correlation energy is modeled as:

$$E_{\mathrm{xc}}^{\mathrm{nl}} = \frac{1}{2} \iint d^3 r_1 d^3 r_2 \, n(r_1) n(r_2) \Phi(q_1, q_2, r_{12}). \tag{35}$$

- Computational cost is 20-30% higher than GGA.

Extensions Beyond KS-DFT

- Non-local effective potentials introduce wavefunction dependence:
  - **Optimized Effective Potential (OEP)**: Constructs a local potential for non-local interactions.
  - **Quasiparticle Self-Consistent GW (QSGW)**: Corrects bandgaps and excitations.
- Despite these extensions, the **Hohenberg-Kohn theorems remain valid**.

Questions?

Any Questions?