From Quantum Mechanics to Materials Design
The Basics of Density Functional Theory

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Outline

1. Formalism
   - Definitions and Theorems
   - Approximations

2. Applications
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   - Definitions and Theorems
   - Approximations

2. Applications
Calculated Electronic Properties

Moruzzi, Janak, Williams (IBM, 1978)

Cohesive Energies \( \Rightarrow \) Stability
Wigner-Seitz-Rad. \( \Rightarrow \) Volume
Compressibility \( \Rightarrow \) Hardness
Energy band structures from screened HF exchange

**Si, AlP, AlAs, GaP, and GaAs**

Experimental and theoretical bandgap properties

Shimazaki, Asai, JCP 132, 224105 (2010)
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1. Formalism
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Hamiltonian (within Born-Oppenheimer approximation)

\[ H = H_{el,\text{kin}} + H_{el-el} + H_{\text{ext}} \]

\[ = \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 \right] + \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_i v_{ext}(r_i) \]

where

\[ \sum_i v_{ext}(r_i) = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \sum_{\mu\nu} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|} - \frac{e^2}{4\pi\varepsilon_0} \sum_\mu \sum_i \frac{Z_\mu}{|R_\mu - r_i|} \]

\( \mu \): ions with charge \( Z_\mu \), \( i \): electrons
Electron Density Operator

\[ \hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) = \sum_{\alpha\beta} \chi_\alpha^*(\mathbf{r}) \chi_\beta(\mathbf{r}) a_\alpha^* a_\beta \]

\(\chi_\alpha\): single particle state
Electron Density Operator

\[ \hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) = \sum_{\alpha \beta} \chi_\alpha^*(\mathbf{r}) \chi_\beta(\mathbf{r}) a_\alpha^+ a_\beta \]

\[ \chi_\alpha: \text{ single particle state} \]

Electron Density

\[ \rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle = \sum_{\alpha} |\chi_\alpha(\mathbf{r})|^2 n_\alpha \]

\[ |\Psi\rangle: \text{ many-body wave function, } n_\alpha: \text{ occupation number} \]

Normalization:

\[ N = \int d^3\mathbf{r} \rho(\mathbf{r}) \]
### Functionals

#### Universal Functional (independent of ionic positions!)

\[ F = \langle \psi | H_{el, \text{kin}} + H_{el - el} | \psi \rangle \]

#### Functional due to External Potential:

\[
\langle \psi | H_{\text{ext}} | \psi \rangle = \langle \psi | \sum_i v_{\text{ext}}(r) \delta(r - r_i) | \psi \rangle = \int d^3r \, v_{\text{ext}}(r) \rho(r)
\]
Authors

Pierre C. Hohenberg

Walter Kohn

Lu Jeu Sham

From Quantum Mechanics to Materials Design
Hohenberg and Kohn, 1964: Theorems

1st Theorem
The external potential $v_{\text{ext}}(r)$ is determined, apart from a trivial constant, by the electronic ground state density $\rho(r)$.

2nd Theorem
The total energy functional $E[\rho]$ has a minimum equal to the ground state energy at the ground state density.
Hohenberg and Kohn, 1964: Theorems

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Nota bene
Both theorems are formulated for the ground state!
- Zero temperature!
- No excitations!
Hohenberg and Kohn, 1964: Theorems

Maps

Ground state $|\psi_0\rangle$ (from minimizing $\langle \psi_0 | H | \psi_0 \rangle$):

$$v_{\text{ext}}(r) \xrightarrow{(1)} |\psi_0\rangle \xrightarrow{(2)} \rho_0(r)$$
Hohenberg and Kohn, 1964: Theorems

Maps

Ground state $|\psi_0\rangle$ (from minimizing $\langle \psi_0 | H | \psi_0 \rangle$):

$$v_{\text{ext}}(r) \stackrel{(1)}{\longrightarrow} |\psi_0\rangle \stackrel{(2)}{\longrightarrow} \rho_0(r)$$

1st Theorem

$$v_{\text{ext}}(r) \stackrel{(1)}{\longleftarrow} |\psi_0\rangle \stackrel{(2)}{\longleftarrow} \rho_0(r)$$
Levy, Lieb, 1979-1983: Constrained Search

Percus-Levy partition
Formalism

Applications

Definitions and Theorems

Approximations

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Levy, Lieb, 1979-1983: Constrained Search

Variational principle

\[
E_0 = \inf \langle \psi | H | \psi \rangle \bigg|_{\psi} \\
= \inf \langle \psi | H_{el,kin} + H_{el-el} + H_{ext} | \psi \rangle \bigg|_{\psi} \\
= \inf_{\rho(r)} \left[ \inf_{\psi \in S(\rho)} \langle \psi | H_{el,kin} + H_{el-el} | \psi \rangle + \int d^3r \ v_{ext}(r) \rho(r) \right] \\
= \inf_{\rho(r)} \left[ F_{LL}[\rho] + \int d^3r \ v_{ext}(r) \rho(r) \right] = \inf_{\rho(r)} E[\rho]
\]

\( S(\rho) \): set of all wave functions leading to density \( \rho \)

\( F_{LL}[\rho] \): Levy-Lieb functional, universal (independent of \( H_{ext} \))
Levy-Lieb functional

\[ F_{LL}[\rho] = \inf_{|\psi\rangle \in S(\rho)} \langle \psi | H_{el,\text{kin}} + H_{el-el} | \psi \rangle \]

\[ = T[\rho] + W_{xc}[\rho] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r' \frac{\rho(r)\rho(r')}{|r - r'|} \]

\[ = G[\rho] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r' \frac{\rho(r)\rho(r')}{|r - r'|} \]

Functionals

- Kinetic energy funct.: \( T[\rho] \) not known!
- Exchange-correlation energy funct.: \( W_{xc}[\rho] \) not known!
- Hartree energy funct.: \( \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r' \frac{\rho(r)\rho(r')}{|r - r'|} \) known!
Thomas, Fermi, 1927: Early Theory

Approximations

- Ignore exchange-correlation energy functional:

  \[ W_{xc}[\rho] = 0 \]

- Approximate kinetic energy functional:

  \[ T[\rho] = C_F \int d^3r \rho(r)^{\frac{5}{3}}, \quad C_F = \frac{3}{5} \frac{\hbar^2}{2m} \left(3\pi^2\right)^{\frac{2}{3}} \]

Failures

1. Atomic shell structure missing
   \[ \rightarrow \text{periodic table can not be described} \]
2. No-binding theorem (Teller, 1962)
Kohn and Sham, 1965: Single-Particle Equations

**Ansatz**

1. use different splitting of the functional $G[\rho]$

   $$T[\rho] + W_{xc}[\rho] = G[\rho] = T_0[\rho] + E_{xc}[\rho]$$

2. reintroduce single-particle wave functions

**Imagine: non-interacting electrons with same density**

- **Density:** $\rho(r) = \sum_{\alpha}^{occ} |\chi_{\alpha}(r)|^2$ known!
- **Kinetic energy funct.:**
  $$T_0[\rho] = \sum_{\alpha}^{occ} \int d^3r \chi^*_{\alpha}(r) \left[ -\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha}(r)$$ known!
- **Exchange-correlation energy funct.:** $E_{xc}[\rho]$ not known!
Euler-Lagrange Equations (Kohn-Sham Equations)

\[
\frac{\delta E[\rho]}{\delta \chi^*_\alpha(r)} - \varepsilon_\alpha \chi_\alpha(r) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(r) - \varepsilon_\alpha \right] \chi_\alpha(r) = 0
\]

- Effective potential: \( v_{\text{eff}}(r) := v_{\text{ext}}(r) + v_H(r) + v_{\text{xc}}(r) \)
- Exchange-correlation potential: not known!

\[
v_{\text{xc}}(r) := \delta E_{\text{xc}}[\rho] \frac{\delta}{\delta \rho}
\]

- „Single-particle energies“:
  \( \varepsilon_\alpha \) (Lagrange-parameters, orthonormalization)
Kohn and Sham, 1965: Local Density Approximation

Be Specific!

- Approximate exchange-correlation energy functional

\[ E_{xc}[\rho] = \int \rho(r) \varepsilon_{xc}(\rho(r)) d^3r \]

- Exchange-correlation energy density \( \varepsilon_{xc}(\rho(r)) \)
  - depends on **local** density only!
  - is calculated from **homogeneous, interacting** electron gas

- Exchange-correlation potential

\[ v_{xc}(\rho(r)) = \left[ \frac{\partial}{\partial \rho} \{ \rho \varepsilon_{xc}(\rho) \} \right]_{\rho=\rho(r)} \]
Kohn and Sham, 1965: Local Density Approximation

### Homogeneous, Interacting Electron Gas

- **Split**

  \[ \varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho) \]

- **Exchange energy density** \( \varepsilon_x(\rho) \)
  (exact for homogeneous electron gas)

  \[ \varepsilon_x(\rho) = \frac{-3}{4\pi} \frac{e^2}{4\pi\varepsilon_0} \left(3\pi^2\rho\right)^{\frac{1}{3}} \]

  \[ \nu_x(\rho) = \frac{-1}{\pi} \frac{e^2}{4\pi\varepsilon_0} \left(3\pi^2\rho\right)^{\frac{1}{3}} \]

- **Correlation energy density** \( \varepsilon_c(\rho) \)

  **Calculate and parametrize**
  - RPA (Hedin, Lundqvist; von Barth, Hedin)
  - QMC (Ceperley, Alder; Vosko, Wilk, Nusair; Perdew, Wang)
Kohn and Sham, 1965: Local Density Approximation

Limitations and Beyond

- LDA exact for homogeneous electron gas (within QMC)
- Spatial variation of \( \rho \) ignored
  - \( \nabla \rho(\mathbf{r}), \ldots \)
  - Generalized Gradient Approximation (GGA)
- Cancellation of self-interaction in \( v_{\text{Hartree}}(\rho(\mathbf{r})) \) and \( v_x(\rho(\mathbf{r})) \)
  - violated for \( \rho = \rho(\mathbf{r}) \)
  - Self-Interaction Correction (SIC)
  - Exact Exchange (EXX),
    Optimized Effective Potential (OEP)
  - Screened Exchange (SX)
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Iron Pyrite: FeS$_2$

Pyrite

- $Pa\bar{3}$ ($T^6_h$)
- $a = 5.4160$ Å
- “NaCl structure”
  - sublattices occupied by
    - iron atoms
    - sulfur pairs
  - sulfur pairs $\parallel \langle 111 \rangle$ axes
- $x_S = 0.38484$
- rotated FeS$_6$ octahedra
FeS$_2$: Equilibrium Volume and Bulk Modulus

$V_0 = 1056.15 \ a_B^3$
$E_0 = -16532.904060 \ \text{Ryd}$
$B_0 = 170.94 \ \text{GPa}$
FeS$_2$: From Atoms to the Solid
FeS$_2$: Structure Optimization

The graph shows the energy (E) in Rydberg as a function of $x_S$. The energy values range from $-16532.910$ to $-16532.850$ Rydberg, with corresponding values of $x_S$ from 0.374 to 0.394.
Phase Stability in Silicon

diamond structure most stable
pressure induced phase transition to $\beta$-tin structure
LTO(Γ)-Phonon in Silicon

- phonon frequency: $f_{calc} = 15.34 \text{ THz}$ ($f_{exp} = 15.53 \text{ THz}$)
Formalism
Applications

Dielectric Function of Al₂O₃
Imaginary Part

FLAPW, Hosseini et al., 2005
FPLMTO, Ahuja et al., 2004

FPASW
Dielectric Function of Al₂O₃

Real Part

FLAPW, Hosseini et al., 2005
FPLMTO, Ahuja et al., 2004

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Hydrogen site energetics in LaNi$_5$H$_n$ and LaCo$_5$H$_n$

Enthalpy of hydride formation in LaNi$_5$H$_n$

\[ \Delta H_{min} = -40 \text{kJ/molH}_2 \]

for H at $2b6c_16c_2$

agrees with

- neutron data
- calorimetry:
  \[ \Delta H_{min} = -(32/37) \text{kJ/molH}_2 \]

Herbst, Hector, APL 85, 3465 (2004)
Hydrogen site energetics in $\text{LaNi}_5\text{H}_n$ and $\text{LaCo}_5\text{H}_n$

Enthalpy of hydride formation in $\text{LaCo}_5\text{H}_n$

$$\Delta H_{\text{min}} = -45.6\text{kJ/molH}_2$$

for H at $4e4h$

agrees with

- neutron data
- calorimetry:
  $$\Delta H_{\text{min}} = -45.2\text{kJ/molH}_2$$

Herbst, Hector,
APL 85, 3465 (2004)
Problems of the Past

Si bandgap
- exp: 1.11 eV
- GGA: 0.57 eV

Ge bandgap
- exp: 0.67 eV
- GGA: 0.09 eV
Critical review of the Local Density Approximation

Limitations and Beyond

- **Self-interaction cancellation** in $\nu_{\text{Hartree}} + \nu_x$ violated
- **Repair** using exact Hartree-Fock exchange functional → class of hybrid functionals
  - **PBE0**
    \[
    E_{xc}^{\text{PBE0}} = \frac{1}{4} E_{x}^{\text{HF}} + \frac{3}{4} E_{x}^{\text{PBE}} + E_{c}^{\text{PBE}}
    \]
  - **HSE03, HSE06**
    \[
    E_{xc}^{\text{HSE}} = \frac{1}{4} E_{x}^{\text{HF},sr,\mu} + \frac{3}{4} E_{x}^{\text{PBE},sr,\mu} + E_{x}^{\text{PBE},lr,\mu} + E_{c}^{\text{PBE}}
    \]

Based on decomposition of Coulomb kernel

\[
\frac{1}{r} = S_\mu(r) + L_\mu(r) = \frac{\text{erfc}(\mu r)}{r} + \frac{\text{erf}(\mu r)}{r}
\]
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Critical review of the Local Density Approximation

SrTiO$_3$ Bandgap

GGA: $\approx 1.6$ eV, exp.: 3.2 eV
Critical review of the Local Density Approximation

SrTiO$_3$ Bandgap
GGA: $\approx 1.6$ eV, HSE: $\approx 3.1$ eV, exp.: 3.2 eV
LaAlO$_3$

**GGA**

LaAlO$_3$ Bandgap

GGA: ≈ 3.5 eV, \hspace{1cm} \text{exp.: 5.6 eV}
LaAlO$_3$

**LaAlO$_3$ Bandgap**

**GGA:** $\approx 3.5$ eV,  
**HSE:** $\approx 5.0$ eV,  
**exp.:** $5.6$ eV
Critical review of the Local Density Approximation

Calculated vs. experimental bandgaps

The graph compares the calculated and experimental bandgaps for various materials using different functionals: PBE, HSE03, and PBE0. The x-axis represents the experimental bandgap, while the y-axis shows the calculated bandgap. Different materials are represented by distinct symbols, illustrating the agreement and discrepancies between theory and experiment.
Industrial Applications

Computational Materials Engineering

- Automotive
- Energy & Power Generation
- Aerospace
- Steel & Metal Alloys
- Glass & Ceramics
- Electronics
- Display & Lighting
- Chemical & Petrochemical
- Drilling & Mining

Optimization of Materials Properties Design of Materials

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### Summary

**Density Functional Theory**
- exact (!) mapping of full many-body problem to an effective single-particle problem

**Local Density Approximation**
- approximative treatment of exchange (!) and correlation
- considerable improvement: exact treatment of exchange

**Applications**
- very good agreement DFT/Exp. in numerous cases
- theory meets industry

**Further Reading**
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Further Reading
Augsburg/München

Thank You for Your Attention!