ASESMA 2025

Introduction to Density Functional Theory

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Welcome to ASESMA

Electronic Structure

Methods

Applications

The Electronic Structure Problem

The problem of many interacting electrons
One of the grand challenges of physics

Recognized since the start of quantum mechanics
but
too difficult to solve in anything but very special models

Would you like to be the person who:

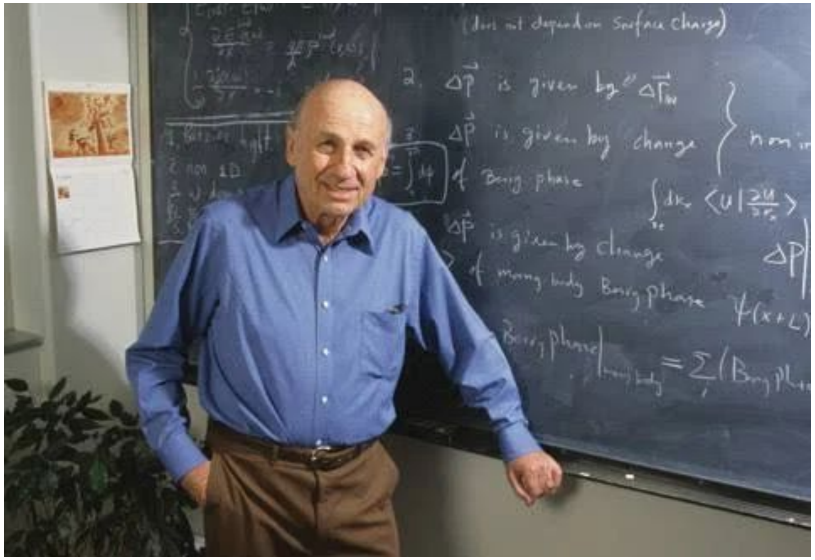
Figured out the right question to ask - that no one else has asked - with an answer that can be written down in half a page with no complicated mathematics

Wins a Nobel Prize

Has led to the most cited papers in physics (all of science?) with > 50,000 citations per year!

Densitry Functional Theory

Walter Kohn



One of the nicest, most generous people you could meet

Was an active member of the International Advisory Panel for ASESMA

Electronic Structure

The first step

Quantum Mechanics(1920’s)

The fundamental quantum theory is the Schrodinger Equation

For one particle

wave function

$$-\frac{\hbar^2}{2m_e}\cdot\frac{d^2}{dx^2}\psi(x)+V(x)\psi(x)=\epsilon\psi(x)$$

Kinetic energy

Potential

energy eigenvalue

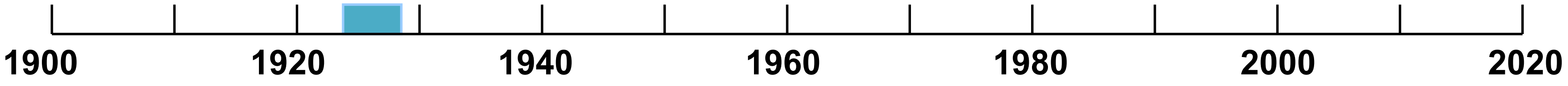
which can be written

$$H\psi(x)=\epsilon\psi(x)$$

Soluble

Analytically for one electron, e.g., the hydrogen atom

With numerical methods can solve any problem



Electronic Structure

The next step

The problem of electrons in molecules, solids, liquids, ….

The fundamental quantum theory is the Schrodinger Equation

For many particles

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

many-body wave function

$$\Psi(\{x_1, x_2, \ldots\})$$

Kinetic energy of electrons

Electron-nuclei interactions -- or other potential V(r)

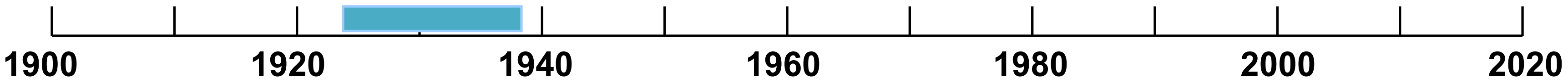
$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}$$

If there were no electron interactions, the electrons would be independent - except they must obey the exclusion principle

Soluble -- scales as N^2, N^3, N^4

Methods well known since the 1920's and 30's

With computers can solve problems with many electrons (thousands)



The Grand Challenge

The Many-Body Problem of interacting electrons in molecules, solids, liquids, ….

The fundamental quantum theory is the Schrodinger Equation

For many interacting particles

many-body wave function

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \qquad \Psi(\{x_1, x_2, \ldots\})$$

Kinetic energy of electrons

Electron-nuclei interactions -- or other potential V(r)

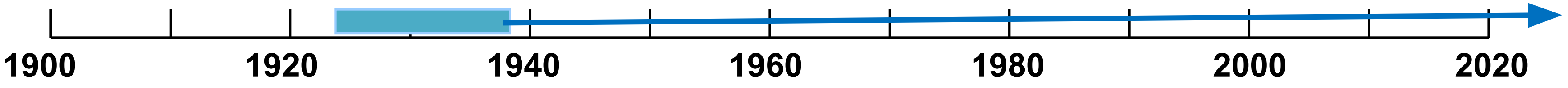
electron-electron interactions

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

The problem is many interacting electrons!

Soluble only for a few electrons -- scales as N ~ exponentual

Even with the largest computers today only ~10 electrons



The Grand Challenge

The Many-Body Problem of interacting electrons in molecules, solids, liquids, ….

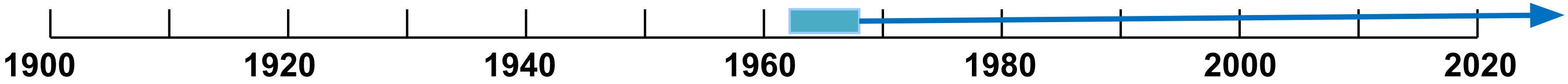
The many-body problem is one of the grand challenges of physics

For materials, chemistry, physics, … there are real technological consequences
(solar energy, batteries, catalysis, magnets, nanosystems, . . .)

But to be useful, these difficult grand challenge problems must be solved accurately

Until the 1960’s there was no way to make quantitatively accurate calculations for real materials

In 1964-5 was the advance that has made possible accurate calculations for many properties of real materials!



Same idea as P-V relation in a material

Density Functional Theory (DFT)

Hohenberg-Kohn Theorem (1964)

All properties of the system are determined by the ground state density $n_0(r)$

Function of r
3 dimensions

Sounds like magic! How can this possibly be true?

Answer

1. **All properties of the system are determined by the potential acting on the electrons (due to the nuclei) $V_{ext}(r)$**

   Function of r
   3 dimensions

   But only by solving the Schrodinger Equation!

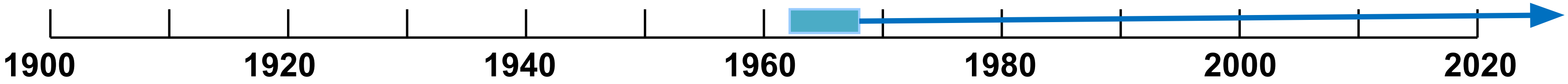
2. **HK showed there is a one-to-one correspondence $V_{ext}(r) \rightleftarrows n_0(r)$**

3. **Therefore all properties of the system are determined by $n_0(r)$**

   Each property is a functional $F_{HK}[n_0(r)]$ of $n_0(r)$

But

The "theorem" gives no way to calculate any property except to solve the original problem - the Schrodinger Equation!



A Nobel Prize for that?

The Grand Challenge

The Many-Body Problem of <u>interacting</u> electrons

The fundamental quantum theory is the Schrodinger Equation

For many <u>interacting</u> particles

many-body wave function

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \qquad \Psi(\{x_1, x_2, \ldots\})$$

Kinetic energy of electrons

Electron-nuclei interactions -- or other potential V(r)

electron-electron interactions

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

The same for all electron problems

In general, this can be any potential V(r)

The same for all electron problems

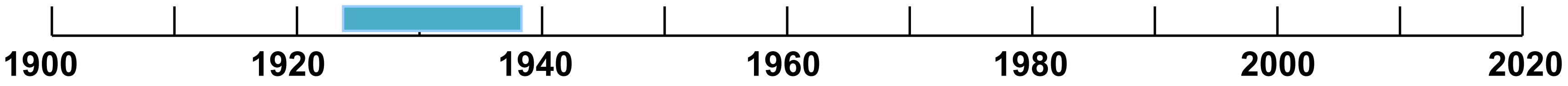
<u>All</u> properties of the system are determined by the potential V(r)

Schrodinger

<u>Each</u> property is a functional $F^n_{\text{Schr}}[V(r)]$ of the potential V(r)

A function of a function

Function of r - 3 dimensions



The Grand Challenge

The Many-Body Problem of interacting electrons

The fundamental quantum theory is the Schrodinger Equation

For many interacting particles

many-body wave function

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \qquad \Psi(\{x_1, x_2, \ldots\})$$

Kinetic energy of electrons

Electron-nuclei interactions -- or other potential V(r)

electron-electron interactions

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

The same for all electron problems

The same for all electron problems

In general, this can be any potential V(r)

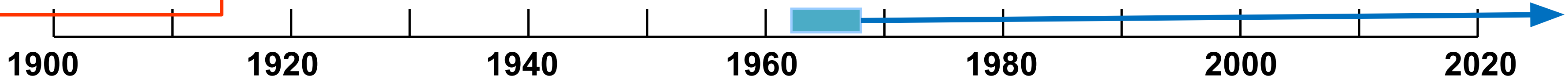
All properties of the system are determined by the density $n_0(r)$

Hohenberg Kohn

Each property is a universal functional $F^n_{HK}[n_0(r)]$ of the potential $n_0(r)$

A function of a function

Function of r -- 3 dimensions



The Kohn-Sham Auxiliary System

This is the idea worth a Nobel Prize!

Construct a soluble independent-particle problem with density equal to the density $n_0(r)$ of the full interacting electron problem

$$\text{Energy} = E_{\text{Ind. part.}} + E_{xc}[n_0]$$

Soluble on a computer!
Many very efficient codes

This is what is done in this school in lectures and hands-on tutorials
QE, SIESTA, FHI, ….

All the hard parts of the problem!
A universal functional!

There are now many good approximate forms escribed in the lectures
LDA, PBE, ……

The Nobel Prize is because of the genius idea of a way to deal with THE GRAND CHALLENGE with a new way to make approximations which has revolutionized how science is done in many fields

The Kohn-Sham auxiliary system

The problem has been divided into two parts!

Finding a good <u>approximation</u> for $E_{xc}[n]$ requires information about the interacting many-body problem

Once one has an explicit expression for $E_{xc}[n]$, the rest is a soluble problem!

$$\underbrace{E_{\mathrm{KS}} = T_{\mathrm{ip}}[n] + \int \mathrm{d}\mathbf{r} V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\mathrm{Hartree}}[n] + E_{II}} + \underbrace{E_{\mathrm{xc}}[n]}$$

Equations for independent particles - **soluble**

Exchange-Correlation Functional – Exact formulation but **approximate** functional!

The Kohn-Sham Equations

- **Assuming a form for $E_{xc}[n]$**
- **Minimizing energy (with constraints) → Kohn-Sham Eqs.**

$$E_{\mathrm{KS}} = T_{\mathrm{ip}}[n] + \int d\mathbf{r} V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\mathrm{Hartree}}[n] + E_{II} + E_{\mathrm{xc}}[n]$$

$$\frac{\delta E_{KS}}{\delta \psi_i^{\sigma *}(\mathbf{r})} = 0, \qquad (1)$$

Constraint for functions to be Orthonormal

$$\langle \psi_i^{\sigma} | \psi_j^{\sigma'} \rangle = \delta_{i,j}\delta_{\sigma,\sigma'}. \qquad (2)$$

$$(-\frac{1}{2}\nabla^2 + V_{KS}^{\sigma}(\mathbf{r}) - \varepsilon_i^{\sigma})\psi_i^{\sigma}(\mathbf{r}) = 0 \qquad (3)$$

Eigenvalues are auxiliary quantities - not meant to be a identified as energies to add or subtract electrons (electron bands)

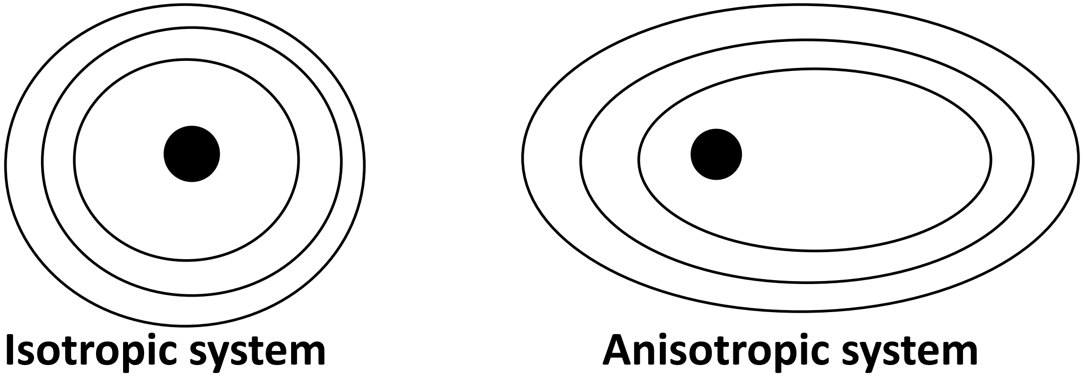
$$\begin{aligned} V_{KS}^{\sigma}(\mathbf{r}) &= V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r},\sigma)} \\ &= V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}^{\sigma}(\mathbf{r}) \qquad (4) \end{aligned}$$

Exchange-correlation energy, potential

Self-consistent Kohn-Sham Equations for independent "electrons"

Exchange Correlation Energy E_{xc}

- If the electrons were independent, the problem would be easy !
  - Just add the individual energies
- The difficult part of the problem: many-body effects
- Fortunately, for the ground state there is a very useful approach
- Near each electron, there is a reduced probability for finding other electrons
  - The "exchange correlation hole"
  - Exchange: exclusion principle
  - Correlation: repulsive Coulomb interaction pushes away other electrons



The energy depends only on the spherical average

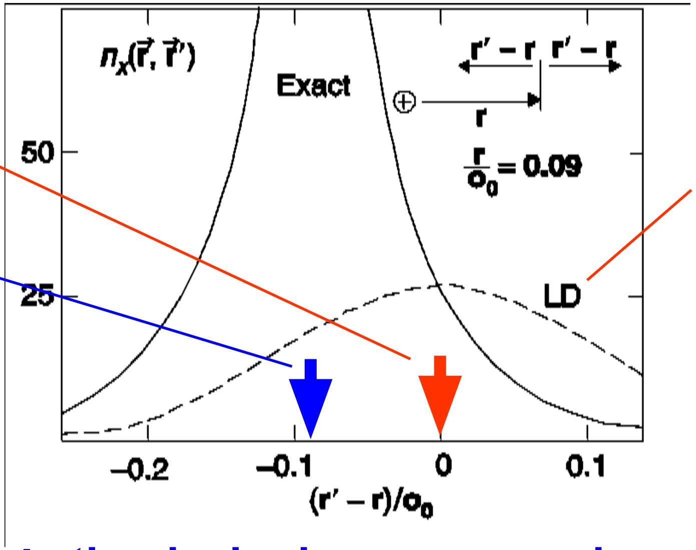
Approximate Functionals $E_{xc}[n]$

- **How to find an approximate functional $E_{xc}[n]$?**
- **One Approach: Use a model system where the exchange correlation energy can be calculated**
  - **Local Density Approximation - LDA**
    - Assume the functional is the same as a model problem – the homogeneous electron gas
    - E_{xc} has been calculated as a function of density using quantum Monte Carlo methods (Ceperley & Alder)
  - **Gradient approximations - GGA**
    - Various theoretical improvements for electron density that varies in space
  - **More recently increased use of theory of interacting systems**
    - **Hybrid functionals**
    - **van der Waals functionals**
    - **. . . .**

Understanding $E_{xc}[n]$ - an example - LDA

- Exchange and correlation ⟶ around each electron, other electrons tend to be excluded – "x-c hole"
- E_{xc} is the interaction of the electron with the "hole"

Exchange hole in Ne atom



electron

nucleus

Local density approximation

Is the dashed curve a good approximation for the solid curve?

From Gunnarsson, et al.
PRB 20, 3136 (1979)

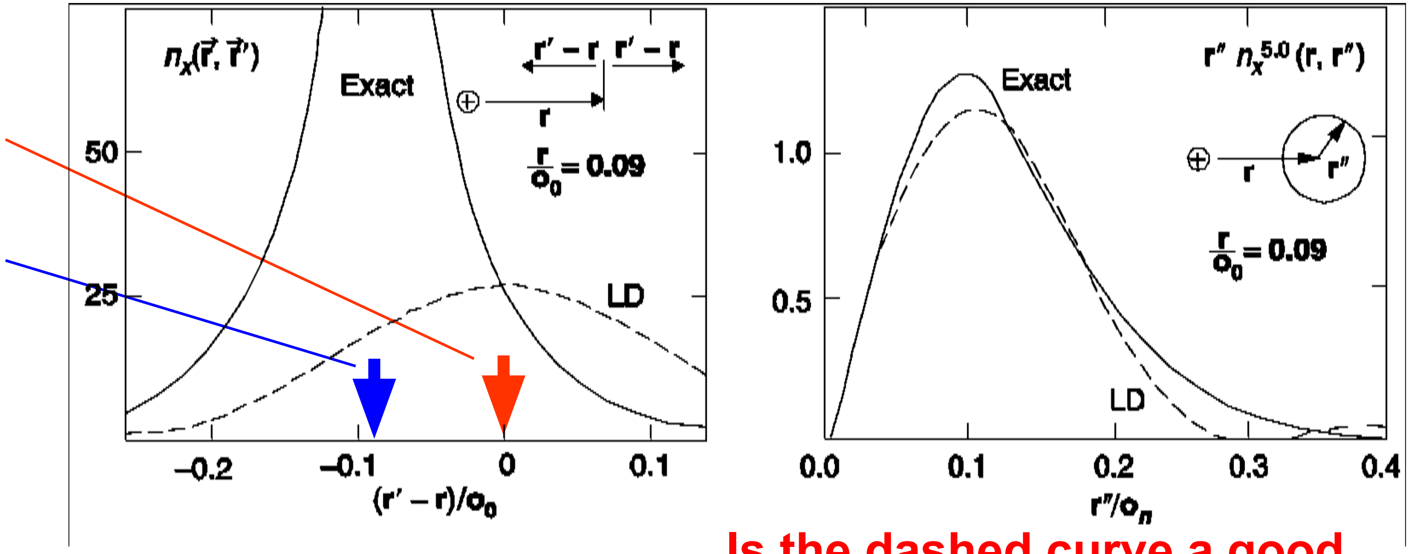
Understanding $E_{xc}[n]$ - an example - LDA

- Exchange and correlation ⟶ around each electron, other electrons tend to be excluded – “x-c hole”
- E_{xc} is the interaction of the electron with the “hole” –

The energy involves only the spherical average!

Exchange hole in Ne atom

Spherical average



electron

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Understanding $E_{xc}[n]$ - an example - LDA

- **Supports the local density approximation for the total energy!**
- **Improved approximations are better!**

- **This also shows what is NOT given by the Kohn-Sham solution**
  - **It does NOT describe actual correlation**
  - **It only contains the information embedded in the functional and does NOT describe correlation in the actual system**

How useful is it?

My own survey of Science Magazine

The main journal in the United States that covers all of science - biology, chemistry, ecology, medicine, neuroscience, physics, …

I have given general talks like this many times and each time I have checked how much DFT is used in the most recent issues at the time

In every survey I have done in recent years
DFT was an integral part of at least ½ the experimental papers
on atomic scale physics, chemistry and materials science

Now an essential part of research!

Latest issue of Science Magazine

Resiliency, morphology, and entropic transformations in high-entropy oxide nanoribbons

Science 29 May 2025 Vol 388, pp. 950-956

Abstract

We present the successful synthesis and characterization of a one-dimensional high-entropy oxide (1D-HEO) exhibiting nanoribbon morphology. … This finding offers a way to create low-dimensional, resilient, and high-entropy materials.

In the text

…. This experimental result was in good agreement with the findings from the DFT calculations. …

Next paper

Vapor-assisted surface reconstruction enables outdoor-stable perovskite solar modules

Science 29 May 2025 Vol 388, pp. 957-963

Abstract

….. Our perovskite modules maintained stable power output during 45 days of outdoor operation under severe summer conditions, exhibiting stability comparable with that of the reference silicon cell.

In the text

…. We also performed bond length, charge density distribution ….. using density functional theory (DFT). These calculations suggest that the high mechanical hardness of the HEO stems from …

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