Density Functional Theory Overview

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Electronic Structure

The many-body interacting-electron problem

A grand challenge of physics
One of the most deep, fundamental problems in physics.

With important consequences

Enormous variety of properties and phenomena
Applications in all areas of science and technology

Must be quantitatively accurate to describe real materials

For such a difficult problem, how can we possibly expect to calculate properties accurately enough?

Electronic Structure

Before 1964, how many calculations had been done to accurately determine the minimum energy structure of a complex solid or molecule?

One Metallic sodium by Wigner and Seitz in 1933

The many-body interacting-electron problem is <u>a hard problem</u>!

Today, how many papers per year report accurate calculations of the minimum energy structure of a complex solid or molecule?

Approximately 50,000 papers per year!

(Estimate based on current trends and a study of the literature 10 years ago, which found ~30,000 papers per year.)

What is the difference?

Density functional theory
Computational power – available software

Electronic Structure

Density functional theory
Computational power – available software

The stroke of genius was the invention of DFT

But we should also apreciate the role of computers that make it feasible to solve the equations

Quote from Wigner ands Seitz, 1934

The calculation of a wavefunction took about two afternoons, and five wavefunctions were calculated on the whole giving ten points on the figure.

Contents of a book on solid state physics or molecular theory

ALL are properties of the electrons
in the presence of the nuclei

- Structural properies
  - Structure of crystal or molecule
  - Vibrations (phonons)
  - Elastic constants
  - ……..

Modern DFT calculations determine properties like these
stable crystal structure
lattice constants – within ~ 1%
phonon frequencies ~ 5%
……..

- “Electronic Properties”
  - Band structure
  - Metals, insulators – conductivity
  - Optical properties
  - ……...

These properties are problematic in the theory and applications of DFT
Band gaps
Optical spectra
………

Other topics of lectures/projects in this school

Density Functional Theory

The Hohenberg-Kohn Theorem

- **The ground state density determines everything, energy, excitations, … of the interacting electron system**

The Kohn Sham construction

- **The solution of the Kohn-Sham equations determines only the ground state density – in principle exactly - and nothing else**

Is there a contradiction? How can we understand this?

The goal of this lecture is to provide background and basic ideas of the revolutionary way Kohn, Hohenberg and Sham approached the problem of treating the full interacting electron problem

A Bit of History

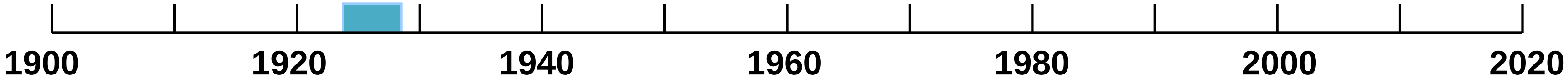
Background for DFT

Almost 100 years ago!

- L. de Broglie –
  Nature 112, 540 (1923).

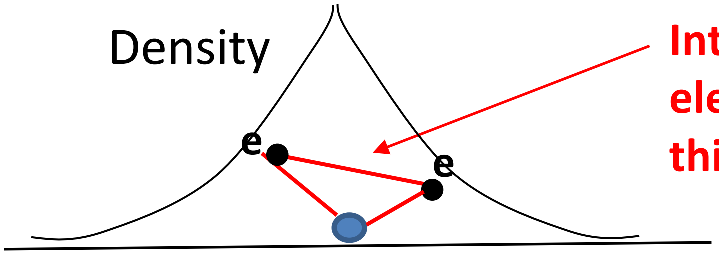
- E. Schrödinger –
  1925, ….

- Pauli exclusion Principle - 1925
- Fermi statistics - 1926
- Thomas-Fermi approximation – 1927
- First density functional – Dirac – 1928
- Dirac equation – relativistic quantum mechanics - 1928
- Bloch theorem - 1928



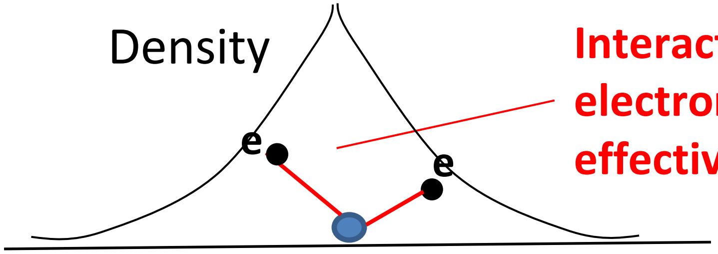
Already in the 1920’s

- E. Hylleraas - Numerically exact calculations of the two electron problems in He

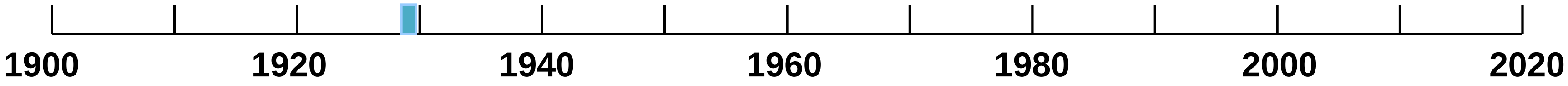


Interaction between electrons is what makes this problem hard!

- D . R. Hartree – Numerical solution for electrons in atoms using an approximate method – each electron moving independently in an effective potential



Interaction between electrons approximated by effective potential



Theory for independent particles well understood in 1920’s

Schrodinger Equation

Central Issue: What is the Effective Potential?

$$\hat{H}\psi(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}),$$

For N fermions the ground state has the lowest N states filled

Density

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

In a crystal, the potential and density are periodic and the eigenstates are labeled by momentum k and a band index (Bloch theorem)

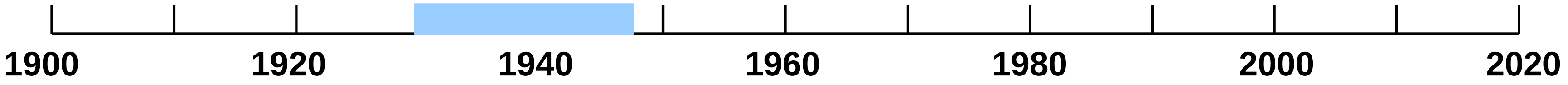
$$\psi_i(\mathbf{r}) \rightarrow \psi_{i,\mathbf{k}}(\mathbf{r}) \qquad n(\mathbf{r}) = \sum_{i,\mathbf{k}} |\psi_{i,\mathbf{k}}(\mathbf{r})|^2$$

1930's - 40's
Methods for independent particles developed

- Hartree-Fock - 1930
- Wilson - Implications of band theory - Insulators/metals –1931
- Wigner- Seitz – Quantitative calculation for Na - 1935
- Slater - Bands of Na - 1934 (proposal of APW in 1937)
- Psudopotentials - Fermi - 1934, Hellman - 1935
- . . . .
- First understanding of semiconductors – 1930's

All this was done using independent electron approximations

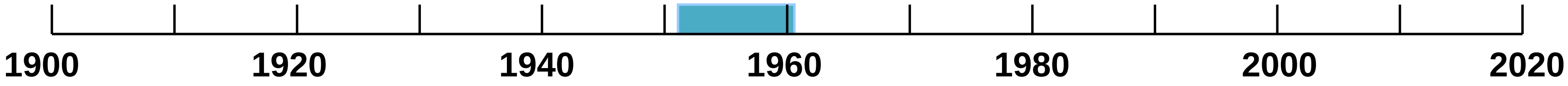
- Invention of the Transistor – 1940's
  - Bardeen – student of Wigner
    - thesis on the Fermi surface of a metal - 1935
  - Shockley – student of Slater
    - thesis on the electronic bands of NaCl - 1936



1950’s

- The first calculations of electrons in materials using computers (within an independent electron approximation)
  - Perhaps the first was the bands of Ge by Frank Herman

- A story from Herman
  - Before the computers were available at IBM, Herman’s mother did calculations on a calculator!
  - Later he did the computer calculations
  - He said he never found a mistake in his mother’s work!



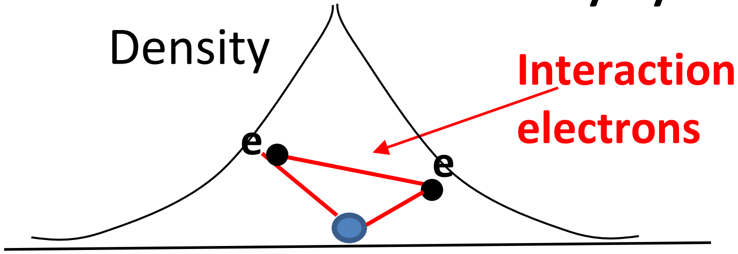
What about the original problem?

The grand challenge of interacting electrons

Why is this problem Hard

- With today’s (tomorrow’s) computers, why can’t we solve the problem directly
- Interactions between the electrons!
- For two electrons in He

problem in 6 dimensions solved by Hyleraas - 1929



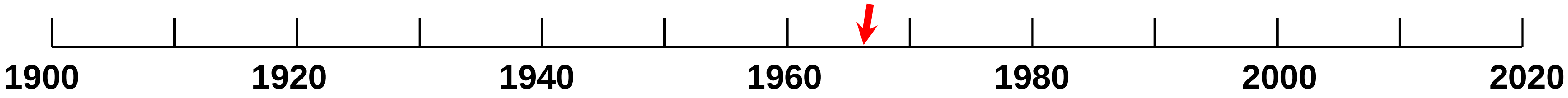
Interaction between electrons

- What if we have
  - 3 electrons (9 dimensions)
  - 100
  - 10^{23}
- The difficulty scales exponentially with the number!
  - Today – ~ exact calculations for ~11 electrons
  - Tomorrow (a few years?) ~ 12 electrons

Landmark years 1964-65

- **Density functional theory**
  - Hohenberg and Kohn, Kohn-Sham
  - Uses independent particle methods
  - But treats the interacting electron problem – see next slide

- **Also the other most widely used methods for solids**
- **The GW approximation**
  - Hedin 1964
  - Many-body methods
- **Quantum Monte Carlo**
  - McMillan – 1964
  - Uses random sampling to treat the many-body problem



The Electronic Structure Problem

Hamiltonian for interacting particles

Interacting electrons in an external potential

Kinetic energy of electrons

electron-nuclei interactions

electron-electron interactions

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

$$-\sum_I \cancel{\frac{\hbar^2}{2M_I}}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},$$

Only one small term kinetic energy of nuclei

Interaction between nuclei must be included but is just an additive term

Density Functional Theory
Recasting the problem in a different form

Hohenberg-Kohn formulation

Interacting electrons in an external potential

Kinetic energy of electrons

electron-nuclei interactions

electron-electron interactions

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

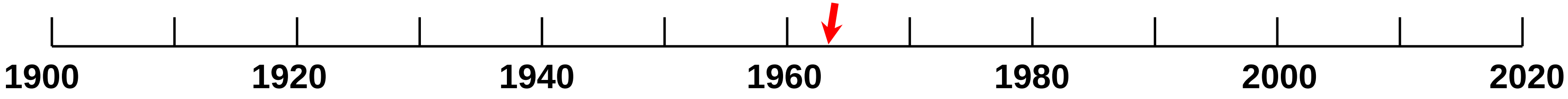
Hohenberg-Kohn Functional

$$E_{\mathrm{HK}}[n] = T[n] + E_{\mathrm{int}}[n] + \int \mathrm{d}^3r\, V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + E_{II}$$

$$\equiv F_{\mathrm{HK}}[n] + \int \mathrm{d}^3r\, V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})$$

All the difficult parts of the problem are in this universal term

Functional of only potential and density



Density Functional Theory II

Hohenberg-Kohn Functional

$$E_{\mathrm{HK}}[n] = T[n] + E_{\mathrm{int}}[n] + \int \mathrm{d}^3 r\, V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r})$$

$$\equiv F_{\mathrm{HK}}[n] + \int \mathrm{d}^3 r\, V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r})$$

All the difficult parts of the problem are in this universal term

Functional of only potential and density

How do we know the energy is a functional of thed density.

1. We know F_{HK} is a functional of the external potential $V_{ext}(r)$ because everything follows from the solution of the Schrodinger Equation

2. The proof that $F_{HK}[n]$ is a functional of the density n is just a change of variable --- a Legendre transformation!

Exactly the same as the familiar idea that the energy of a crystal is a function of the volume (density) or pressure (analogous to external potential)

Density Functional Theory III

Hohenberg-Kohn theorem

The proof of Hohenberg and Kohn is that for a given density n(r) there is only one unique potential V_{ext}(r) (except for an arbitrary constant) for which the ground state density n_0(r) is equal to n(r).

Thus the ground state density n_0(r) determines the potential V_{ext}(r) and therefore the density determines everything!

BUT
The theorems do not provide a way to calculate anything!
(except by solving the Schrodinger Equation!)

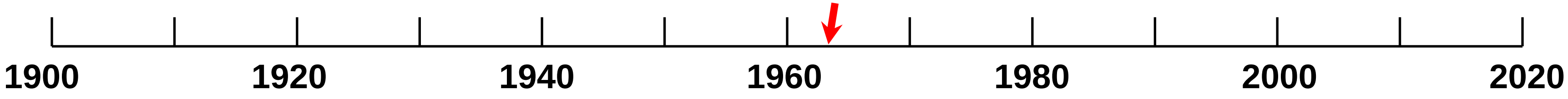
A Nobel Prize for that???

The Kohn-Sham auxiliary system

This was the ingenious idea that deserved a Nobel Prize!

- Kohn-Sham method provides a practical way to use DFT
  - Construct auxiliary system of non-interacting “electrons”
  - Include an exchange-correlation energy that takes into account the effects of the interaction in the actual system
  - The result is the density and total energy of the interacting system!
    - Strictly nothing else is supposed to be correct

- In principle it is exact
- In practice it makes possible useful approximations



The Kohn-Sham auxiliary system II

- Kohn-Sham functional - rewriting the Hohenberg-Kohn functional
- Auxiliary system of independent particles

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$

kinetic energy

$$T_{\mathrm{ip}}[n] = -\frac{\hbar^2}{2m_e} \sum_i \int \mathrm{d}^3 r \psi(\mathbf{r})^* \nabla^2 \psi(\mathbf{r})$$

Hartree energy

$$E_{\mathrm{Hartree}} = \frac{1}{2} \int \mathrm{d}^3 r \mathrm{d}^3 r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

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

Equations for independent particles - **soluble**

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

The Kohn-Sham auxiliary system III

The problem has been divided into two parts!

Finding a good approximation 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!

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

Equations for independent particles - **soluble**

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

The new paradigm – find useful, approximate E_{xc} functionals

The Kohn-Sham Equations

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

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

Constraint for functions to be Orthonormal

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

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

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

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

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

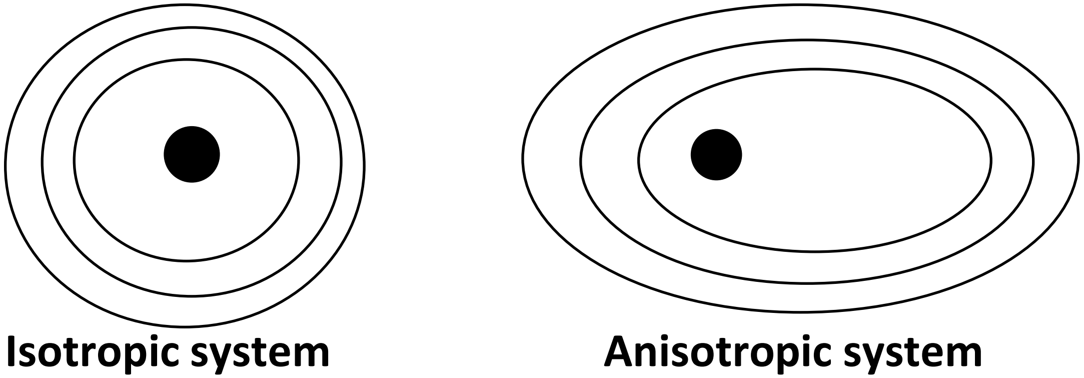
Eigenvalues are auxiliary quantities - not meant to be a identified as energie to add or subtract electrons (electron bands)
More later on this

Exchange-correlation energy, potential

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
- Near each electron, there is a reduced probability for finding other electrons
  - The “exchange correlation hole”
  - Exchange: exclusion principle
  - Correlation: repulsive Coulomb pushes away other electrons



The energy depends only on the spherical average

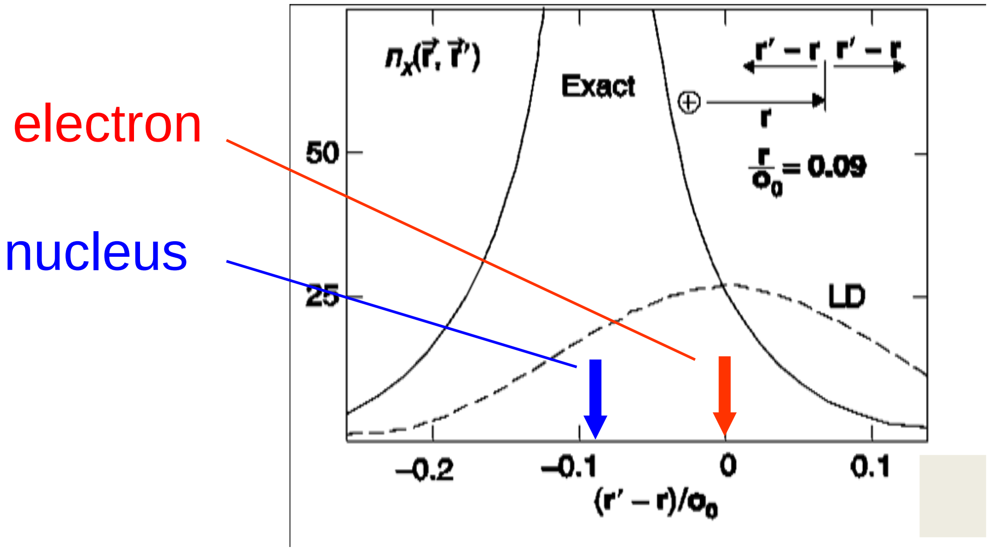
Approximate Functionals $E_{xc}[n]$

- **How to find a [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

- 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

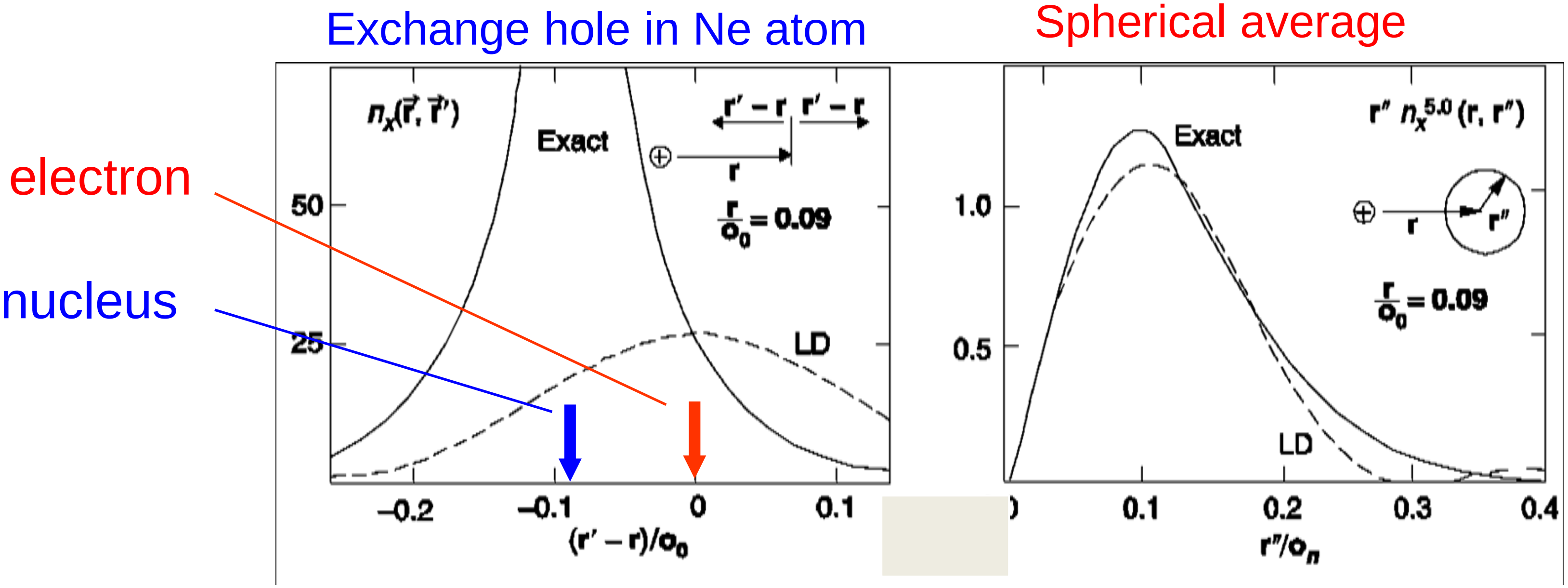


(From Gunnarsson, et al. PRB 20, 3136 (1979)

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

- 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 a spherical average!


Exchange hole in Ne atom

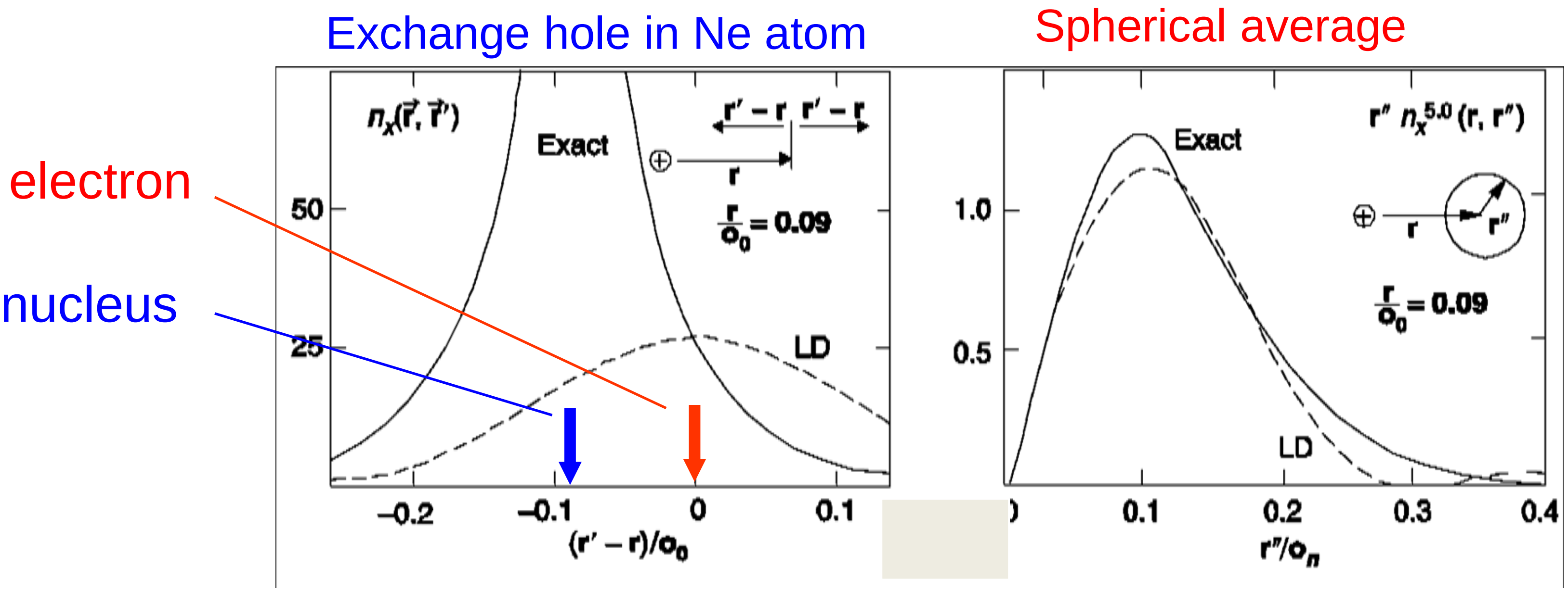
Spherical average

Supports the local density approximation for the total energy!

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

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

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

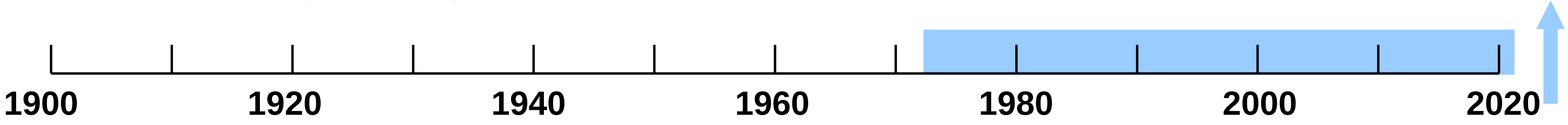

Exchange hole in Ne atom

Spherical average

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

Examples of DFT Calculations

- Properties of crystals – many calculations are now routine
  - Definitive tests of the theory – comparisons with experiments
- Calculations for complex systems
  - Theory provides key role along with experiments
  - Understanding
  - Predictions
  - Direct simulation of atomic scale quantum phenomena
- Examples
  - Surfaces, interfaces, defects, ….
  - Thermodynamic phase transitions, Liquids, Melting, …
  - Nanostructures – in real environments, …
  - Large complex molecules – in solution, ….



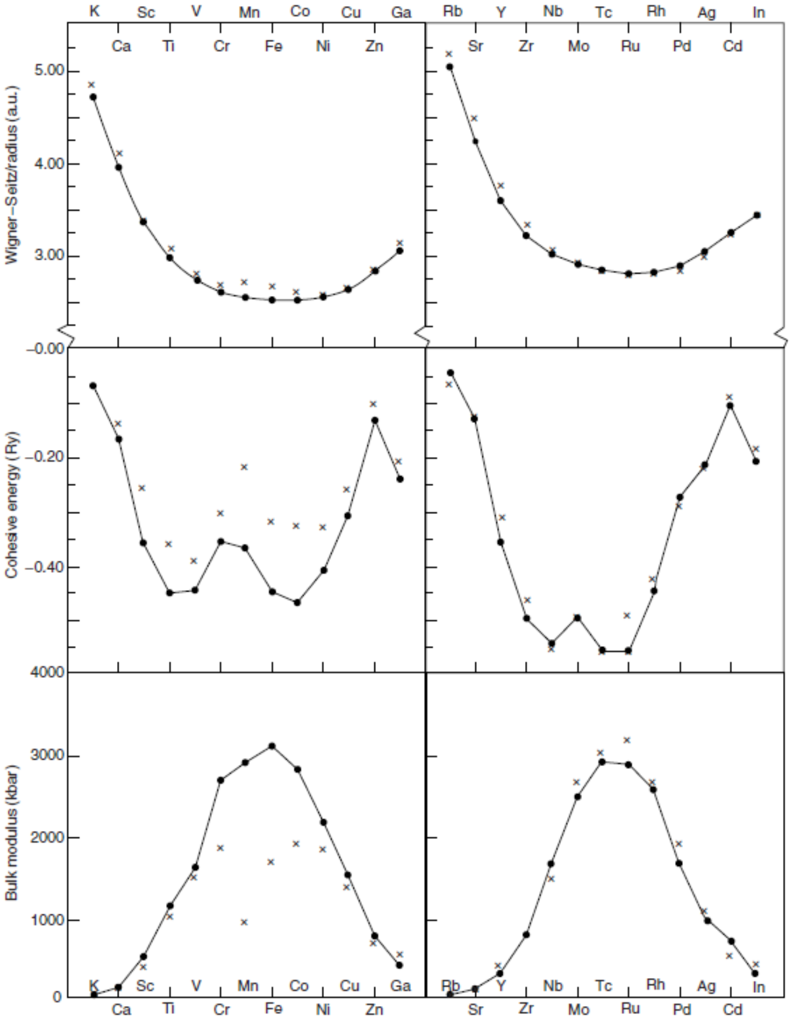
An early DFT calculation (1977)

Transition Metal
Series

Cohesive energy
Lattice constant
Bulk Modulus

Moruzzi and Williams
PRB 15, 2854 (1977)

(IBM computers!)

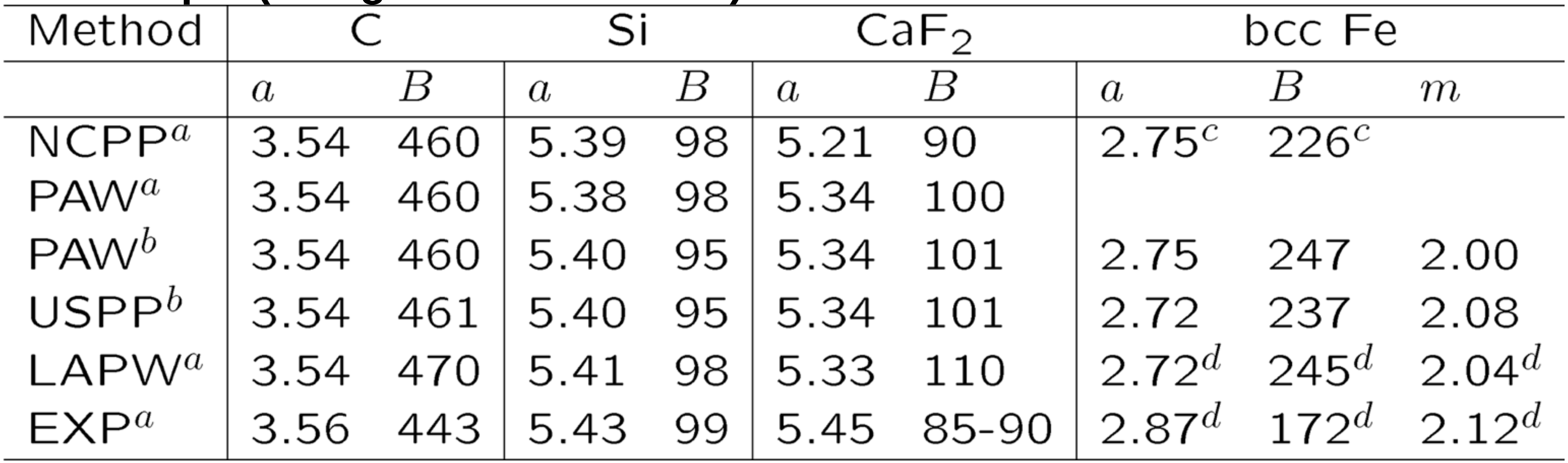


There are many different methods

Each has advantages - but they should all agree if done carefully!

It is satisfying that in many cases results agree with experiment!

Example (using data from ~2000):



Method	C		Si		CaF_2		bcc Fe		
	a	B	a	B	a	B	a	B	m
NCPP[a]	3.54	460	5.39	98	5.21	90	2.75[c]	226[c]	
PAW[a]	3.54	460	5.38	98	5.34	100			
PAW[b]	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPP[b]	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW[a]	3.54	470	5.41	98	5.33	110	2.72[d]	245[d]	2.04[d]
EXP[a]	3.56	443	5.43	99	5.45	85-90	2.87[d]	172[d]	2.12[d]

- **a – lattice constant, B – bulk modulus, m – magnetization**
- [a]Holzwarth , *et al.*; [b]Kresse & Joubert; [c]Cho & Scheffler; [d]Stizrude, *et al.*

(From R. M. Martin, Electronic Structure, Cambridge U, Press, 2004, 2020)

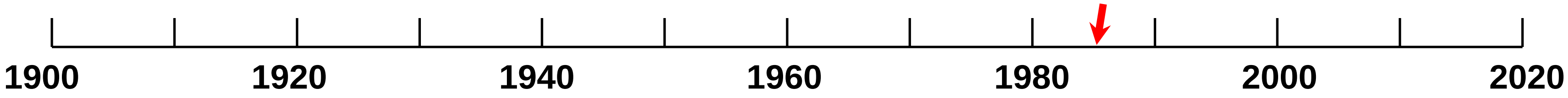
The Car-Parrinello Advance

- **Car-Parrinello Method – 1985**
  - Simultaneous solution of Kohn-Sham equations for electrons and Newton's equations for nuclei
- **A revolution in the power of the methods**
  - Relaxation of positions of nuclei to find structures
  - "First principles" molecular dynamics simulations of solids and liquids with nuclei moving thermally
  - Chemical reactions, . . .

A new relation of theory/computation and experiment!

- Stimulated further developments . . . .
- The power of computers – uses computational methods

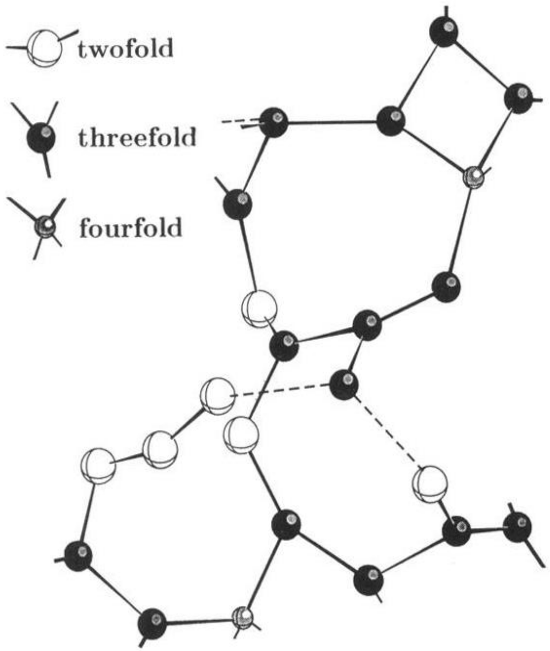
  FFTs, iterative methods, ….



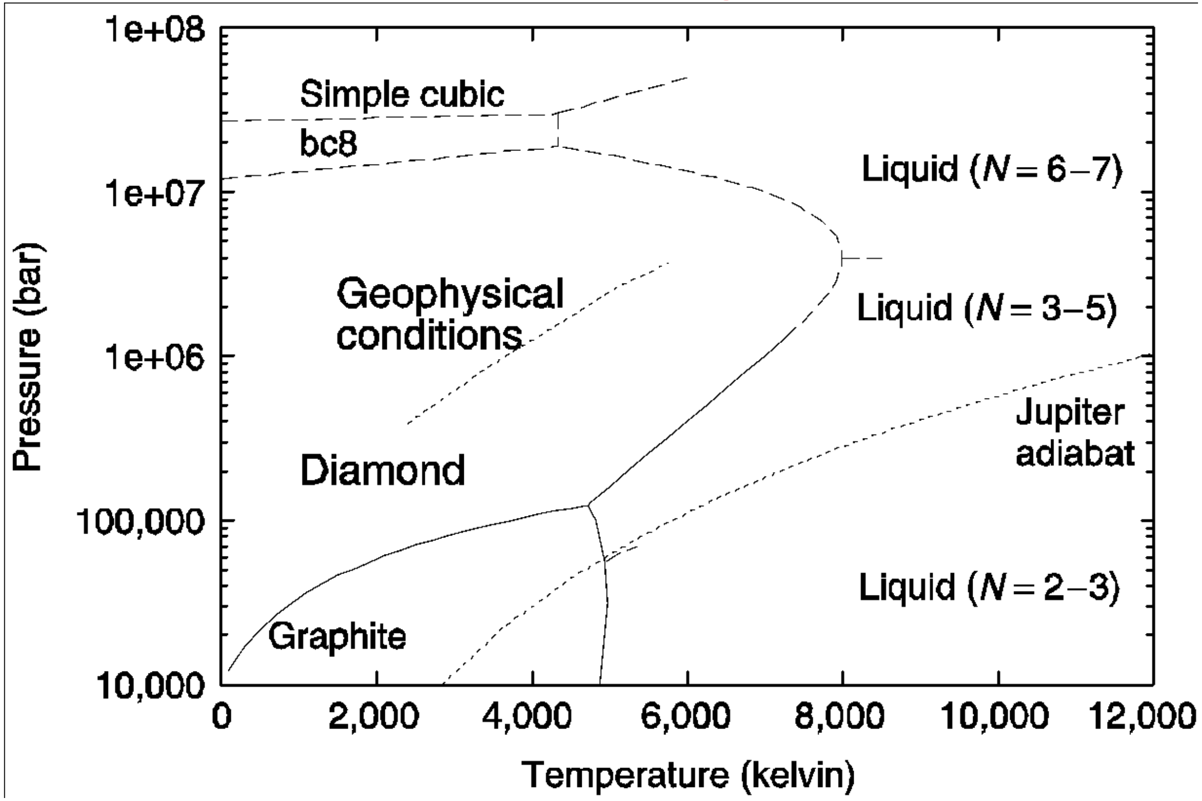
Car-Parrinello molecular dynamics (CPMD) Example of Carbon

Melting of diamond at high pressure – other phases - geophysical, planetary physics

Phase diagram



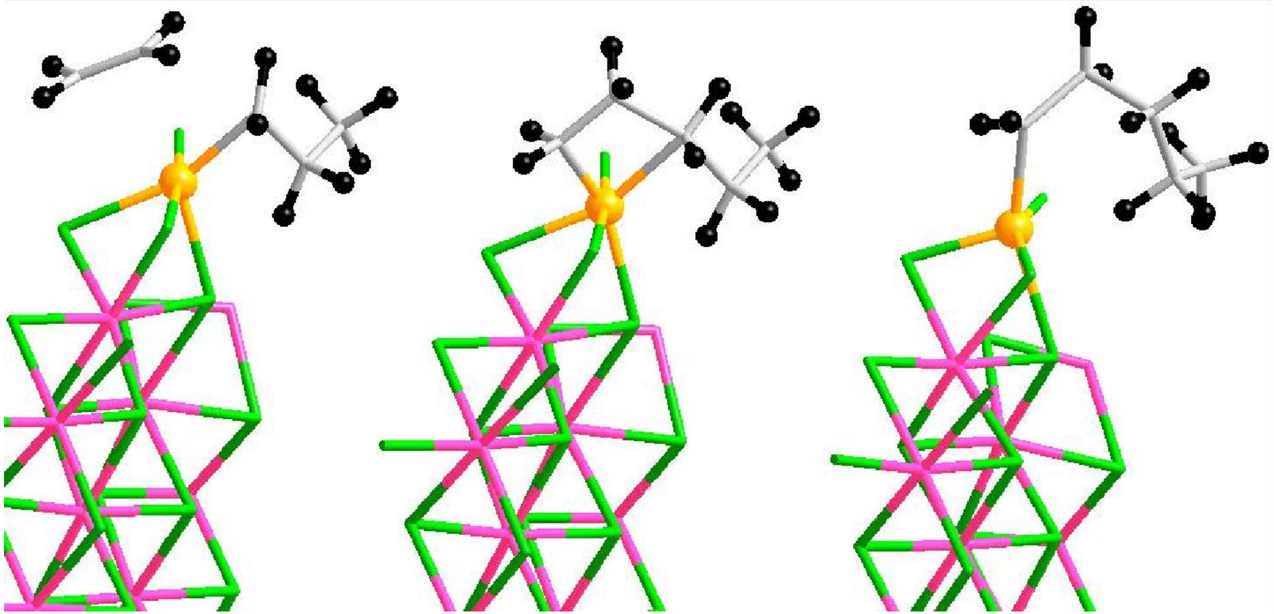
“Snapshot” of liquid



Grumbach, Galli, Martin, Car 1989-1994

Examples of Modern Calculations

- **Unraveling the steps in the Ziegler-Nata reaction**
  - **Industrial process for production of polyethylene**
  - Simulations with Car-Parrinello molecular dynamics – M. Boero, et al.



π-complex – Transition – insertion

Adds one ethelyne unit to polymer

Papers in Science Magazine in April and May

Science is the major journal in the United States that covers all fields of Science

I checked all the papers in the last two months.

There were 12 papers reporting atomic scale research

9 were experimental studies where DFT calculations had an essential role
  - 7 with PBE functional (4 VASP, 1 PWmat, 1 Gaussian, 1 CP2K)
  - 1 used the SCAN functional
  - 1 with Qchem methods including part with BLYP

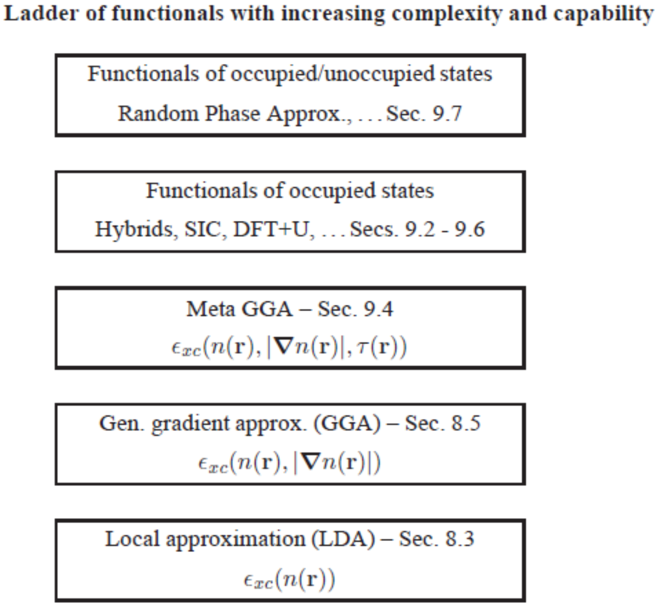
Only 3 had no Elec. Struct calculations - 1 with spin models – 1 with bose models of correlated excitons

DFT is an essential part of research today!

Improved Functionals

There has been much work to find better functionals that incorporate other effects and treat excitations more accurately.

Called "Jacob's Ladder" by John Perdew who is probably the best-known person in the development of functionals



Ladder of functionals with increasing complexity and capability

Functionals of occupied/unoccupied states
Random Phase Approx., . . . Sec. 9.7

Functionals of occupied states
Hybrids, SIC, DFT+U, . . . Secs. 9.2 - 9.6

Meta GGA – Sec. 9.4
$\epsilon_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \tau(\mathbf{r}))$

Gen. gradient approx. (GGA) – Sec. 8.5
$\epsilon_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$

Local approximation (LDA) – Sec. 8.3
$\epsilon_{xc}(n(\mathbf{r}))$

Figure 9.1. From bottom to top: Classes of functionals with increasing complexity, with the goal of increased capability and accuracy that offset the increased computational requirements. They are arranged as rungs on a ladder that has been termed a "Jacob's ladder" after the biblical story of a ladder reaching to heaven, i.e., extending toward the exact formulation. The van der Waals functionals in Sec. 9.8 can be placed at various levels. They are derived using many of the features in the more advanced functionals, but they have been formulated as functionals only of the density.

See lectures by Andrea Marini and Iurii Timrov

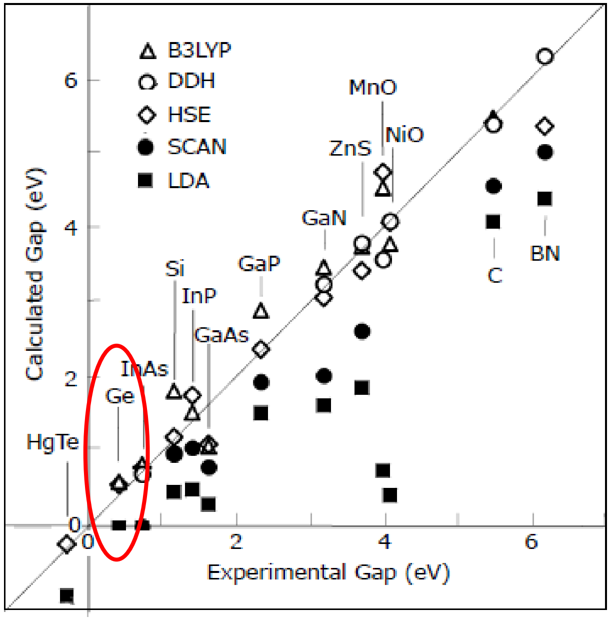
(From R. M. Martin, Electronic Structure, Cambridge U, Press, 2004, 2020)

Bands and Band Gaps

In the original derivation of Kohn and Sham, the eigenvalues and vectors do not have a rigorous physical meaning. In some cases they are famously wrong! But there has been much work to find a theoretical framework and functionals.

Example:
In LDA Ge is a metal!
Hybrid functionals are much closer to experiment

The “band gap problem”



(From R. M. Martin, Electronic Structure, Cambridge U, Press, 2020)

Conclusions

- **Kohn-Sham Density Functional theory has revolutionized the theory of condensed matter**.
  - A formulation that in principle provides the exact ground state density and energy
  - In practice it provides a way to make approximate Exc[n] functionals that have proven to be very useful

- **The problem is divided into two parts**
  - Finding Exc[n] functionals
  - Using the functionals
- **Because it is so useful, codes have been developed that are very useful! Like quantum Espresso!**
- **The challenge is to use them well to solve interesting problems!**