Plan of the lecture

- Born-Oppenheimer approximation
- Hartree approximation
- Hartree-Fock method
- Density functional theory
- Orbital momentum and spin
- Spin-orbit coupling

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Current problems

1. The Schrödinger equation cannot be solved exactly for systems with a large number of electrons

$$\hat{H}\psi = \varepsilon\psi \qquad -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + U(\vec{r})\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

2. It is necessary to consider the multi-electron wave function $\psi = \psi(r_1, r_2, \dots, R_1, R_2 \dots; t)$

3. The Hamiltonian takes a very complex form

$$\hat{H} = \underbrace{-\sum_n \frac{\hbar^2}{2M}\nabla_n^2 - \sum_i \frac{\hbar^2}{2m}\nabla_i^2}_{\hat{T}_R \qquad \hat{T}_r} \underbrace{+ \frac{1}{4\pi}\frac{1}{2}\sum_{n\neq m}\frac{Z_n Z_m e^2}{|R_n - R_m|}}_{\hat{V}_R} \underbrace{+ \frac{1}{4\pi}\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|}}_{\hat{V}_r} \underbrace{+ \frac{1}{4\pi}\sum_{i,n}\frac{Z_n e^2}{|r_i - R_n|}}_{\hat{V}_{r,R}}$$

Kinetic energy   **Potential energy**

R nuclei contributions

r electron contribution

r, R mixed contribution

General Hamiltonian
$$\hat{H} = \hat{T}_R + \hat{T}_r + \hat{V}_R + \hat{V}_r + \hat{V}_{r,R}$$
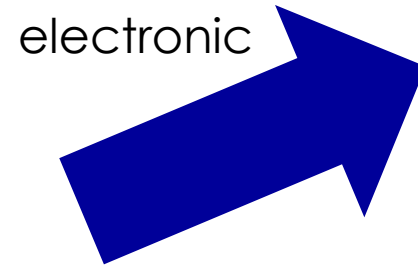
Born-Oppenheimer approximation

- Nuclei are much heavier than electrons
- Nuclei move much slower than electrons
- We can decouple electronic and nuclear motions

electronic

decoupling

nuclear

Max Born

Robert Oppenheimer

Born-Oppenheimer approximation

- Nuclei are much heavier than electrons
- Nuclei move much slower than electrons
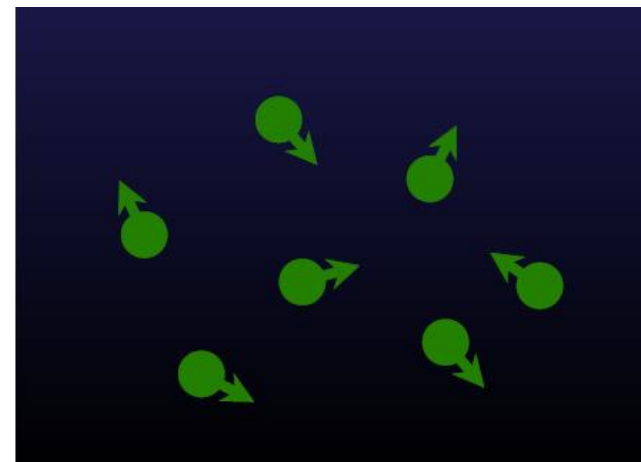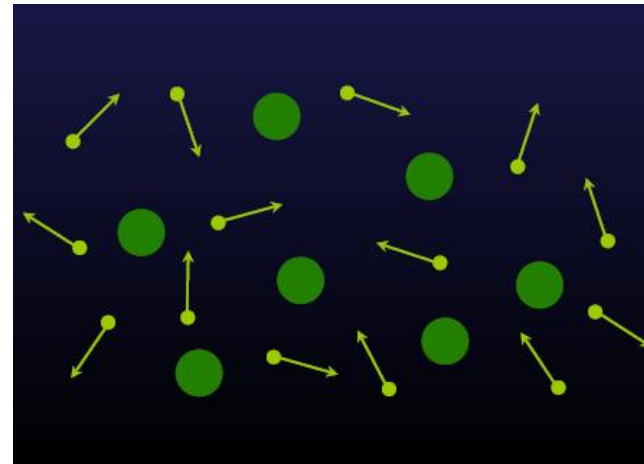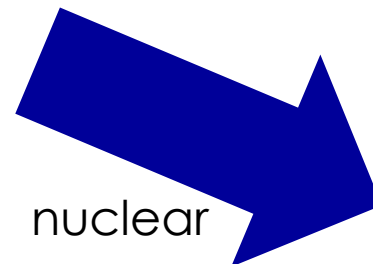- We can decouple electronic and nuclear motions

Max Born   Robert Oppenheimer

$$\widehat{H} = \widehat{T}_R + \widehat{T}_r + \widehat{V}_R + \widehat{V}_r + \widehat{V}_{r,R} \quad\longrightarrow\quad \widehat{H} = \widehat{T}_r + \widehat{V}_r + \widehat{V}_{r,R}$$

$$\widehat{H}_e = -\sum_i \frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{4\pi}\frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|} + \frac{1}{4\pi}\sum_{i,n}\frac{Z_n e^2}{|r_i - R_n|}$$

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Hartree approximation

- We need to simplify a complex multi-electron interaction
- Electrons are independent and on average interact with each other equally
- For an **n**-electron system, each electron does not sense the other electrons individually, but as an average field
- The **n**-electron system becomes a set of non-interacting one-electron systems, where each electron moves in the average density of the other electrons

Douglas Rayner Hartree

In the one-electron approximation, the potential must include the potentials of all ions

$$U^{ion}(\vec{r}) = -\frac{1}{4\pi} \sum_{\vec{R}} \frac{Ze^2}{|\vec{r} - \vec{R}|}$$

The potential should reflect the fact that the electron senses the electric field of other electrons. The other electrons are a continuous distribution of negative charge with a density **ρ**

$$U^{el}(\vec{r}) = -e \int d\vec{r}' \rho(\vec{r}') \cdot \frac{1}{|\vec{r} - \vec{r}'|}$$

Hartree approximation

If we switch to the representation of independent electrons, then each electron on the level with a wave function ψ_i will contribute to the electron density as

$$\rho_i(\vec{r}) = -e|\psi_i(\vec{r})|^2$$

Then the total electron charge density will be

$$\rho(\vec{r}) = -e \sum_i |\psi_i(\vec{r})|^2$$

Substituting these expressions into the Schrödinger equation we obtain

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r}) + U^{ion}(\vec{r})\psi_i(\vec{r}) + \left[e^2 \sum_j \int d\vec{r}' \left|\psi_j(\vec{r}')\right|^2 \frac{1}{|\vec{r} - \vec{r}'|} \right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

The one-electron equation (system of equations) is solved separately for each occupied one-electron level $\psi_i(\vec{r})$

The resulting system of equations are **Hartree Equations**

Hartree approximation

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r}) + U^{ion}(\vec{r})\psi_i(\vec{r}) + \left[e^2\sum_j\int d\vec{r}'\left|\psi_j(\vec{r}')\right|^2\frac{1}{|\vec{r}-\vec{r}'|}\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

Practically, the system of non-linear Hartree equations can only be solved iteratively

1. First, we make assumption about the form of the potential U^{ion}
2. Solve the resulting equation
3. Obtain the wave functions
4. Using the resulting wave functions, we find the new form of U^{ion}

The procedure is repeated until the following iterations do not significantly change the type of potential

The Hartree approximation is called the **self-consistent field approximation**

Hartree approximation. Notes

1. The Hartree equations **fail** to take into account **how a particular** (not averaged) arrangement of **N-1 electrons affects** on particular electron (the equation only takes into account the interaction with the field from the other electrons)
2. The Hartree approximation **does not take into account the Pauli-exclusion principle** (no separation into electrons by spin)
3. The exchange interaction between electrons has not taken into account the contribution from the correlation energy, which is presented in the n-electron system.

Such a crude assumptions in the Hartree approximation are associated with incredibly difficult numerical calculations.
The use of more accurate approximations will lead to even greater difficulties in solving the Schrödinger equation, requiring the development of more sophisticated techniques for solving it

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Hartree-Fock

One of the important drawbacks of the Hartree approximation is that the resulting wave function in the form of

$$\Psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \dots, \vec{r}_N s_N) = \psi_1(\vec{r}_1 s_1)\psi_2(\vec{r}_2 s_2)\cdots\psi_N(\vec{r}_N s_N)$$

would not be compatible with the Pauli-exclusion principle, which requires that the function **ψ** changes sign when any two arguments of the function are rearranged, i.e.

$$\Psi = \psi_i(\vec{r}_1 s_1, \dots, \vec{r}_i s_i, \dots, \vec{r}_j s_j, \dots, \vec{r}_N s_N) = -\psi_i(\vec{r}_1 s_1, \dots, \vec{r}_j s_j, \dots, \vec{r}_i s_i, \dots, \vec{r}_N s_N)$$

This relation cannot be fulfilled for a function of the form

The simplest generalization in the Hartree approximation that would account for the **Pauli-exclusion principle** is

Using the **Slater Determinant**

Vladimir Alexandrovich Fock

John Clark Slater

Slater Determinant

This is an antisymmetric with respect to permutation of particles wave function of a multiparticle quantum-mechanical system, constructed from single-particle functions

Slater determinant specifies a simple way to construct an antisymmetric wave function necessary to describe systems consisting of many electrons.

To do this we use the property of the determinant to change the sign when the columns are rearranged.

A simple case: two electrons

We write the two-electron wave function in one-electron form

???

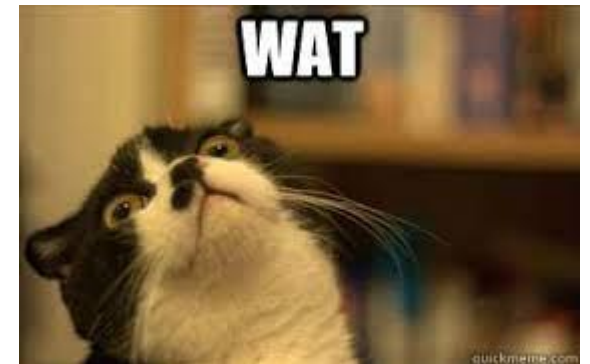$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \quad \textbf{Hartree product}$$

It is not a satisfactory description for electrons because such a wave function is not antisymmetric, i.e., the equality is not satisfied

$$\Psi(\vec{r}_1, \vec{r}_2) = -\Psi(\vec{r}_2, \vec{r}_1)$$

Does not satisfy the principle of indistinguishability of particles (!)

This problem can be solved

Slater Determinant

This problem can be solved

if one takes a linear combination of both Hartree products

Normalization factor

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \{\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) - \psi_1(\vec{r}_2)\psi_2(\vec{r}_1)\} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) \end{vmatrix}$$

Such a wave function is antisymmetric and becomes zero if any two wave functions are the same

The Pauli-exclusion principle is fulfilled (!)

In the more general form of a system of N electrons we have

$$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_i, \ldots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \cdots & \psi_i(\vec{r}_1) & \cdots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \cdots & \psi_i(\vec{r}_2) & \cdots & \psi_N(\vec{r}_2) \\ & & & \vdots & & \\ \psi_1(\vec{r}_i) & \psi_2(\vec{r}_i) & \ldots & \psi_i(\vec{r}_i) & \cdots & \psi_N(\vec{r}_i) \\ & & & \vdots & & \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \ldots & \psi_i(\vec{r}_N) & \cdots & \psi_N(\vec{r}_N) \end{vmatrix}$$

Hartree-Fock

Simple(??) but cumbersome calculations show that the Schrödinger equation for this kind of wave function will be as follows

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r}) + U^{ion}(\vec{r})\psi_i(\vec{r}) + U^{el}(\vec{r})\psi_i(\vec{r}) -$$

$$-\sum_j \int d\vec{r}' \frac{e^2}{|\vec{r}-\vec{r}'|}\psi_j^*(\vec{r}')\psi_i(\vec{r}')\psi_j(\vec{r})\delta_{s_i s_j} = \varepsilon_i\psi_i(\vec{r})$$

Where the potential **U^{el}** is defined by the expressions

$$U^{el}(\vec{r}) = -e\int d\vec{r}'\rho(\vec{r}')\cdot\frac{1}{|\vec{r}-\vec{r}'|}$$

$$\rho(\vec{r}) = -e\sum_i |\psi_i(\vec{r})|^2$$

Hartree-Fock

Exchange contribution

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r}) + U^{ion}(\vec{r})\psi_i(\vec{r}) + U^{el}(\vec{r})\psi_i(\vec{r}) -$$

$$\boxed{-\sum_j \int d\vec{r}' \frac{e^2}{|\vec{r}-\vec{r}'|}\psi_j^*(\vec{r}')\psi_i(\vec{r}')\psi_j(\vec{r})\delta_{s_i s_j}} = \varepsilon_i\psi_i(\vec{r})$$

This expression differs from the Hartree equations

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r}) + U^{ion}(\vec{r})\psi_i(\vec{r}) + \left[e^2\sum_j \int d\vec{r}' \left|\psi_j(\vec{r}')\right|^2 \frac{1}{|\vec{r}-\vec{r}'|}\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

by the presence of an additional summand
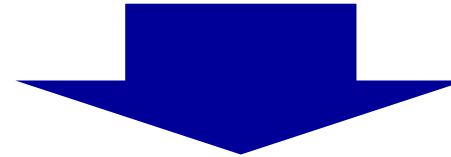
$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r}) + U^{ion}(\vec{r})\psi_i(\vec{r}) + U^{el}\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

Hartree-Fock

The emergence of the exchange contribution **SIGNIFICANTLY** complicates the situation

Like the self-consistent contribution (U^{el}), the exchange contribution is nonlinearly dependent on ψ, but it has no form of $V(\vec{r})\psi(\vec{r})$

Instead, the exchange contribution is written as - integral operator
$\int V(\vec{r}, \vec{r}')\,\psi(\vec{r}')d\vec{r}'$

As a result, in the most general form, the Hartree-Fock equations are unusually difficult to solve, which, nevertheless, can be solved exactly for the case of a free electron when the external potential is zero.

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Density Functional Theory

Key Points

DFT is based on the fact that the most important properties of a system of interacting particles can be expressed using the electron density functional $n(\vec{r})$

$n(\vec{r})$ is a scalar function of three variables that determines, in principle, all information about the ground state and the excitation spectrum

The existence of such a functional for a multi-electronic system at zero temperature was first proved by Kohn and Hohenberg

Density Functional Theory

Inhomogeneous Electron Gas*

P. HOHENBERG†

*École Normale Superieure, Paris, France*

AND

W. KOHN‡

École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France

and

University of California at San Diego, La Jolla, California

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 \ll 1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \to \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.
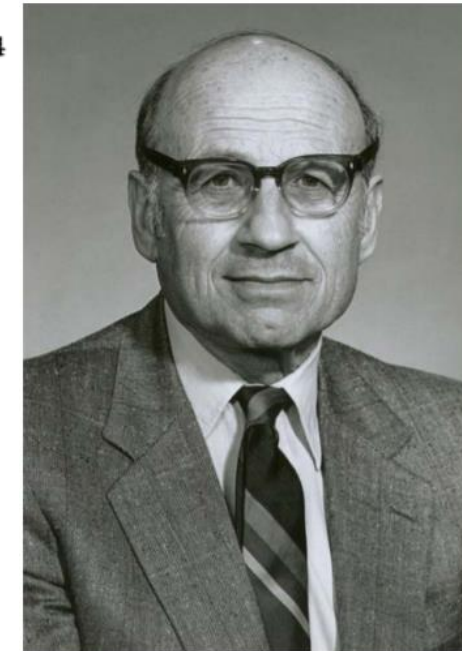
Walter Kohn

In this paper it was proposed to use a density functional, but there was no specific way to build it

Density Functional Theory

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM
University of California, San Diego, La Jolla, California
(Received 21 June 1965)

Cited more than 60 000 times

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

Walter Kohn

1998

A practical way of constructing the density functional is shown

After that, a huge number of publications appeared, in which the density functional was constructed and on its basis the calculations of **specific physical systems** were performed.

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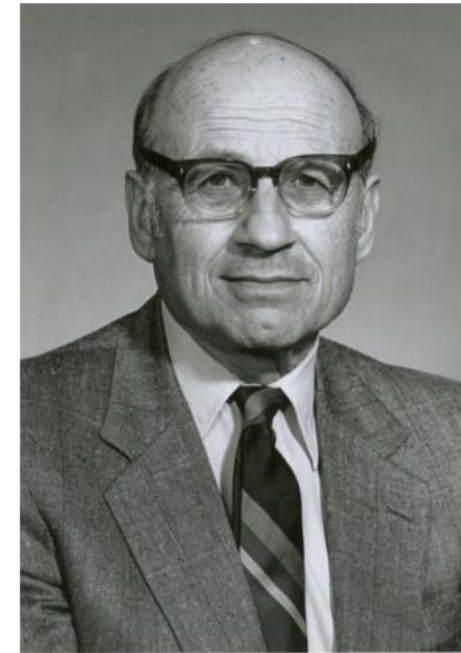
Kohn-Hohenberg theorems

According to Thomas-Fermi theory **the average energy is determined only by the density** $\boldsymbol{n(\vec{r})}$.

In spite of the fact that the expression

Thomas-Fermi theory

$$E_{TF}[n] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \left(n(\vec{r})\right)^{\frac{5}{3}} d\vec{r} + \int n(\vec{r})v_{ext} d\vec{r} + \frac{1}{2}\int d\vec{r}d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

is an approximation, but it is hoped that the same property will hold in the more general case.

The Kohn-Hohenberg theorems establish an **exact correspondence between the electron density, the external potential, and the wave function**

Theorem 1

For any system of interacting electrons in an external potential $v_{ext}(\vec{r})$, the potential is uniquely determined (with an accuracy to an insignificant constant) by the electron density of the ground state $n(\vec{r})$

In the terms of the theorem, we are talking about a system of interacting electrons:

$$\widehat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_i v_{ext}(\vec{r}_i) + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Kinetic energy of electrons

Energy of electrons in external potential

Interaction of electrons

OR

$$\widehat{H} = T + V_{ext} + U$$

Theorem 1

$$\hat{H} = T + V_{ext} + U$$

Let us write each of the contributions through wave functions

$$T = \frac{1}{2}\int d\vec{r}\,\nabla\widehat{\Psi}^+(\vec{r})\nabla\widehat{\Psi}(\vec{r}) \qquad \text{where} \qquad \widehat{\Psi}(\vec{r}) = \sum_{i\sigma}\hat{c}_{i\sigma}\Psi_{i\sigma}(\vec{r})$$

$$V_{ext} = \int d\vec{r}\,v_{\text{ext}}\widehat{\Psi}^+(\vec{r})\widehat{\Psi}(\vec{r})$$

$$\widehat{\Psi}^+(\vec{r}) = \sum_{i\sigma}\hat{c}_{i\sigma}^+\Psi_{i\sigma}^*(\vec{r})$$

$$U = \frac{1}{2}\int d\vec{r}d\vec{r}'\,\widehat{\Psi}^+(\vec{r}')\widehat{\Psi}^+(\vec{r})\frac{1}{|\vec{r}-\vec{r}'|}\widehat{\Psi}(\vec{r}')\widehat{\Psi}(\vec{r})$$

The electron density is determined by averaging the density operator $\widehat{\Psi}^+(\vec{r})\widehat{\Psi}(\vec{r})$

$$n(\vec{r}) = \langle\Psi|\widehat{\Psi}^+(\vec{r})\widehat{\Psi}(\vec{r})|\Psi\rangle$$

Then the energy of the system can be calculated from the expression

$$E = \langle\Psi|H|\Psi\rangle = \langle\Psi|V + T + U|\Psi\rangle = \int d\vec{r}\,v_{ext}(\vec{r})n(\vec{r}) + \langle\Psi|T + U|\Psi\rangle$$

Theorem 1. Proof

Proof is made from the contrary

Let the density $n(\vec{r})$ of **N** electrons in the potential $v_{ext}^1(\vec{r})$, with the corresponding function Ψ^1 and average energy E^1

Then
$$E^1 = \langle \Psi^1 | H^1 | \Psi^1 \rangle = \int d\vec{r} \, v_{ext}^1(\vec{r}) n(\vec{r}) + \langle \Psi^1 | T + U | \Psi^1 \rangle$$

Hamiltonian of the system in potential $v_{ext}^1(\vec{r})$

Let there be a second potential that is not equal to the first, with a corresponding wave function that gives the same density, then

$$E^2 = \langle \Psi^2 | H^2 | \Psi^2 \rangle = \int d\vec{r} \, v_{ext}^2(\vec{r}) n(\vec{r}) + \langle \Psi^2 | T + U | \Psi^2 \rangle$$

Since Ψ^1 assumed to be nondegenerate, the variational principle gives an estimate for Ψ^1

$$E^1 < \langle \Psi^2 | H^1 | \Psi^2 \rangle = \int d\vec{r} \, v_{ext}^1(\vec{r}) n(\vec{r}) + \langle \Psi^2 | T + U | \Psi^2 \rangle = E^2 + \int d\vec{r} \, [v_{ext}^1(\vec{r}) - v_{ext}^2(\vec{r})] n(\vec{r})$$

Theorem 1. Proof

The same for Ψ^1

$$E^2 < \langle \Psi^1 | H^2 | \Psi^1 \rangle = E^1 + \int d\vec{r}\,[v_{ext}^2(\vec{r}) - v_{ext}^1(\vec{r})]n(\vec{r})$$

By adding these expressions, we get $\boldsymbol{E^1 + E^2 < E^1 + E^2}$

We conclude that the initial assumption about the existence of a second potential $v_{ext}^2(\vec{r})$, different from $v_{ext}^1(\vec{r}) + const$, corresponding to the same density $n(\vec{r})$ is incorrect.

There is a **universal** electron density functional $E[n]$ that is **valid for any external potential $v_{ext}(\vec{r})$**

For some well-defined external potential $v_{ext}(\vec{r})$, the extremum of $E[n]$ is reached for the electron density of the ground state $n(\vec{r})$

According to the first Kohn-Hohenberg theorem, there is a one-to-one correspondence between the external potential and the electron density.

Let us call such systems "**v-representative**". This property defines a class of electron densities, which uniquely determines any density functional, e.g. the mean energy $E[n]$

Since all properties are uniquely defined by the density, there exists a functional

$$E_{HK}[n] = T[n] + E_{int}[n] + \int d\vec{r} \, v_{ext}(\vec{r})n(\vec{r})$$

OR

$$E_{HK}[n] = F_{HK}[n] + \int d\vec{r} \, v_{ext}(\vec{r})n(\vec{r})$$

$$F_{HK}[n] = T[n] + E_{int}[n]$$

is determined by all internal properties of the system: the kinetic energy and the interaction of electrons.

Kohn-Sham Ansatz

The theorems are important, but they do not provide practical methods for calculating the observed quantities. We can establish the form of the Kohn-Hohenberg functional only for a non-interacting gas or for a system of particles described in the Thomas-Fermi approximation

The method gained practical importance only after Kohn and Sham proposed an approach to calculate the density functional. The idea was to replace the true functional by the functional of an auxiliary system of free particles.
This ansatz served as a basis for successful calculations of the electronic structure of condensed systems

denotes some kind of guess about what form the solution to
an equation or system of equations should have

Auxiliary system

The idea of Kohn and Sham is to replace the Hamiltonian of a complex system by a system for which the density functional can be calculated explicitly.
This point is the weakest point in the theory, since it is not always possible to perform such calculations.

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_i v_{ext}(\vec{r}_i) + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

The Kohn-Sham approach is based on two assumption

1. the exact electron density of the ground state can be replaced by the density of free particles of the auxiliary system

2. the auxiliary Hamiltonian is chosen so that it has the usual kinetic energy and the effective local potential, which is responsible for the Coulomb interaction, correlation and exchange.

Simple example. Hartree appr.

Each electron moves in an effective single-particle potential

$$v_H(\vec{r}) = -\frac{Z}{\vec{r}} + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

the potential
of a nucleus
with charge Z

potential due to the
remaining electrons with
density *n(r)*

Then the wave function of each electron obeys the equation

$$\left(-\frac{1}{2}\nabla^2 + v_H(\vec{r})\right)\Psi_j = \varepsilon_j \Psi_j$$

denotes spatial
indices and spin

The average electron density is defined as

$$n(\vec{r}) = \sum_j |\Psi_j(\vec{r})|^2$$

runs through all states that are occupied
by electrons according to the Pauli
principle

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Equation

$$\left(-\frac{1}{2}\nabla^2 + v_H(\vec{r})\right)\Psi_j = \varepsilon_j\Psi_j$$

has the form of a single-particle Schrödinger equation for non-interacting electrons moving in an external field $v_H(\vec{r})$

Let us now apply the Kohn-Hohenberg idea to such a system. Let us write the Kohn-Hohenberg functional in the form:

$$E_{HK}[n] = T_s[n] + \frac{1}{2}\int d\vec{r}d\vec{r}' \frac{n(\vec{r}')n(\vec{r})}{|\vec{r}-\vec{r}'|} + \int d\vec{r}\, v_{ext}(\vec{r})n(\vec{r})$$

kinetic energy of free electrons with density *n(r)*
corresponding to the ground state energy

the Lagrange multiplier related to the conservation of the number of particles

Varying this expression by density, we obtain

Effective potential

$$\frac{\delta T_s[n]}{\delta n(\vec{r})} + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{ext}(\vec{r}) - \varepsilon = 0$$

Simple example. Hartree appr.

Equation

$$\left(-\frac{1}{2}\nabla^2 + v_H(\vec{r})\right)\Psi_j = \varepsilon_j \Psi_j$$

Thus, the extremum of the Kohn-Hohenberg functional with the appropriate choice of kinetic energy leads to the same result as the Hartree theory.

Effective potential

$$\frac{}{\delta n(\vec{r})} + \int d\vec{r}' \frac{}{|\vec{r} - \vec{r}'|} + v_{ext}(\vec{r}) - \varepsilon = 0$$

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Kohn-Hohenberg variational principle

Returning now to the system of interacting electrons, we first slightly reformulate the variational principle. We know that the Schrödinger equation can be derived from the variational principle

$$E[\Psi] = \langle \Psi | H | \Psi \rangle$$

Remind that $\langle \Psi | \Psi \rangle = 1$

According to Kohn-Hohenberg, the ground state function is uniquely related to the electron density, since we have mappings

or

$$\int \Psi(\vec{r}) \Psi^*(\vec{r}) dV = 1$$

ground state wave function

$$E[n] = \min_{\Psi} \langle \Psi[n] | H | \Psi[n] \rangle$$

$v_{ext} \leftarrow n(\vec{r})$

$\Psi \rightarrow \Psi_{gs}$

Thus, it is convenient to divide the variation procedure into two steps

Since the sample wave function is related to the density, we will vary the functional with respect to the wave function

In the second step, we vary $E[n]$ with respect to n.

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Kohn-Hohenberg variational principle

Returning now to the system of interacting electrons, we first slightly reformulate the variational principle. We know that the Schrödinger equation can be derived from the variational principle

Thus, we obtain the Kohn-Sham functional expressed in terms of the density corresponding to the ground state.

the functional with respect to the wave function

In the second step, we vary $E[n]$ with respect to n.

Kohn-Sham equations

For this purpose, considering the theorems formulated above, let us rewrite the functional for the average energy in the form

$$E[n] = \langle \Psi[n] | (\hat{T} + \hat{U} + \hat{V}_{ext}) | \Psi[n] \rangle = T + U + V_{ext} = T_s + V_H + V_{ext} + (T - T_s + U - V_H)$$

$$V_{XC} = (T - T_s) + (U - V_H)$$

Exchange-correlation energy (exchange-correlation)

the difference in kinetic energy of interacting and free particles

the difference of the exact energy of the Coulomb interaction and the Hartree energy

Let us rewrite the Kohn-Sham functional, emphasizing the functional dependence of the individual terms

$$E_{KS}[n] = T_s[n] + V_H[n] + V_{ext}[n] + V_{XC}[n]$$

Kohn-Sham equations

Let's write down a chain of ratios that will help us perform variation

$$\frac{\delta E_{KS}}{\delta \Psi_{i\sigma}(\vec{r})} = \frac{\delta T_s}{\delta \Psi_{i\sigma}(\vec{r})} + \left[\frac{\delta V_H}{\delta n(\vec{r})} + \frac{\delta V_{ext}}{\delta n(\vec{r})} + \frac{\delta V_{XC}}{\delta n(\vec{r})} \right] \frac{\delta n(\vec{r})}{\delta \Psi_{i\sigma}(\vec{r})} = 0$$

$$\frac{\delta T_s}{\delta \Psi_{i\sigma}(\vec{r})} = -\frac{1}{2} \nabla^2 \Psi_{i\sigma}(\vec{r}) \qquad \frac{\delta n(\vec{r})}{\delta \Psi_{i\sigma}(\vec{r})} = \Psi_{i\sigma}(\vec{r})$$

The normalization condition can be considered by introducing the Lagrange multiplier ($\varepsilon_{i\sigma}$).
Putting all expressions together, we proceed to the Kohn-Sham equation:

System of equations (!)

$$-\frac{1}{2} \nabla^2 \Psi_{i\sigma}(\vec{r}) + v_{KS}(\vec{r}) \Psi_{i\sigma}(\vec{r}) = \varepsilon_{i\sigma} \Psi_{i\sigma}(\vec{r})$$

Kohn-Sham equations

where the Kohn-Sham potential is defined by the expression: $v_{KS}(\vec{r}) = v_{ext}(\vec{r}) + v_H(\vec{r}) + v_{XC}(\vec{r})$

$$v_{XC}(\vec{r}) = \frac{\delta V_{XC}}{\delta n(\vec{r})} \qquad n(\vec{r}) = \sum_{i\sigma} |\Psi_{i\sigma}(\vec{r})|^2$$

Kohn-Sham equations

$$-\frac{1}{2}\nabla^2\Psi_{i\sigma}(\vec{r}) + v_{KS}(\vec{r})\Psi_{i\sigma}(\vec{r}) = \varepsilon_{i\sigma}\Psi_{i\sigma}(\vec{r})$$

It has the form of a one-particle Schrödinger equation for a particle moving in a self-consistent potential, the structure of which can be seen from the expression

$$v_{KS}(\vec{r}) = v_{ext}(\vec{r}) + v_H(\vec{r}) + v_{XC}(\vec{r})$$

All the difference from the Hartree equation is contained in the exchange-correlation potential, as well as in the interpretation of the eigenvalue $\varepsilon_{i\sigma}$

The Kohn-Sham equation can be seen as a formal generalization of Hartree theory.
If we knew the exact expression for the exchange-correlation energy, we would have a way to accurately describe the multielectron effects.

It is possible to find a good approximation for the exchange-correlation energy, which accounts for the success of the Kohn-Sham theory in practical applications

Exchange-Correlation energy

The simplest approximation is the local-density approximation (LDA)

$$V_{XC}^{LDA} = \int d\vec{r}\, v_{xc}\big(n(\vec{r})\big)\, n(\vec{r})$$

exchange-correlation energy per particle of homogeneous electron gas

Skipping the details, the expression for the exchange-correlation energy, valid at any density is as follows

$$v_{XC}(n) = -\frac{1.222}{r_s(n)} - 0.66 \ln\left(1 + \frac{11.4}{r_s(n)}\right)$$

$$r_s(n) = \left(\frac{3}{4\pi n}\right)^{1/3}$$

This expression was verified by direct calculation.
It is correct to within ±1%

Exchange-Correlation energy

In addition to LDA, a theory was also constructed that takes into account the inhomogeneous electron density distribution or the so-called generalized gradient approximation (GGA).

In this approach the expression for exchange-correlation energy is decomposed into degrees of density gradient.

The expression for the decomposition has the form:

$$V_{XC}^{GGA} = V_{XC}^{LDA} + \int d\vec{r} \, f(n(\vec{r}), |\nabla n(\vec{r})|) n(\vec{r})$$

is some function for which an approximate expression is obtained

Examples

Examples

Calculation of the ionization potential of various atoms

Calculation of spin susceptibility of some metals

TABLE III. Ionization potentials in eV of some light atoms calculated in the LSD, LD (Ref. 76), and HF-ΔSCF (Ref. 79) approximations and compared with experimental results (Ref. 80).

Atom	LSD	LD	HF-ΔSCF	Expt.
H	13.4	12.0	...	13.6
He	24.5	26.4	...	24.6
Li	5.7	5.4	5.3	5.4
Be	9.1	...	8.0	9.3
B	8.8	...	7.9	8.3
C	12.1	...	10.8	11.3
N	15.3	...	14.0	14.5
O	14.2	16.5	11.9	13.6
F	18.4	...	16.2	17.4
Ne	22.6	22.5	19.8	21.6
Na	5.6	5.3	4.9	5.1
Ar	16.2	16.1	14.8	15.8
K	4.7	4.5	4.0	4.3

TABLE I. Spin susceptibility of the alkali metals.

Metal	χ/χ_0[a]	
	Variational theory	Experiment
Li	2.66	2.57
Na	1.62	1.65
K	1.79	1.70
Rb	1.78	1.72
Cs	2.20	2.24

[a]χ_0 is the Pauli susceptibility of a free-electron gas.

Plan of the lecture

- **Born-Oppenheimer approximation**
- **Hartree approximation**
- **Hartree-Fock method**
- **Density functional theory**
- **Orbital momentum and spin**
- **Spin-orbit coupling (SOC)**

Orbital momentum

Usual orbital momentum is a vector property $\quad \vec{l} = \vec{r} \times \vec{p}$

Using the correspondence principle, one find a vector operator $\quad \hat{\vec{l}} = -i\hbar \left(\hat{\vec{r}} \times \widehat{\vec{\nabla}} \right)$

It has three components and for example $\quad \hat{l}_z = -i\hbar \left(\hat{x} \dfrac{\partial}{\partial y} - \hat{y} \dfrac{\partial}{\partial x} \right)$

Determination of quantum eigenfunctions and eigenvalues can be evaluated by solving

$$\hat{l}_z \varphi = l_z \varphi \qquad\qquad -i\hbar \left(x \frac{\partial \varphi}{\partial y} - y \frac{\partial \varphi}{\partial x} \right) = l_z \varphi$$

This can be rewritten in spherical coordinates as $\quad \varphi(r, \theta, \Phi) = f(r, \theta) e^{i l_z \Phi / \hbar}$

eigenfunction

Rotation angle
w.r.t. z-axis

where

$$l_z = m \cdot \hbar, \quad m = 0, \pm 1, \pm 2, \ldots$$

Discrete spectrum of $\hat{l}_z$

Representation of spin

Representation based on vectors (wavefunctions) and matrices (operators), because intrinsic angular momentum cannot be represented using spatially-dependent wavefunction only

Thus, we need to deal with **Spinorial wavefunction: 2-component vector called as "spinor"**

$$\Psi(\vec{r}) = \begin{pmatrix} \Psi_\uparrow(\vec{r}) \\ \Psi_\downarrow(\vec{r}) \end{pmatrix} \quad \text{or} \quad \Psi(\vec{r}, \sigma)$$

can take two "values": ↓ and ↑

There are several notations possible to deal with the spin

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

With the value of $\alpha(\uparrow) = 1 \qquad \alpha(\downarrow) = 0$

$$\beta(\uparrow) = 0 \qquad \beta(\downarrow) = 1$$

We can write the spinor with spatial part and two-component vectors of spin

$$\Psi(\vec{r}, \sigma) = \Psi_\uparrow(\vec{r})\alpha(\sigma) + \Psi_\downarrow(\vec{r})\beta(\sigma)$$

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Representation of spin

How to calculate the usual properties with the concept of quantum mechanics generalized in spinor wavefunctions

The norm $\mathrm{N}^2 = \langle\Psi|\Psi\rangle = \int (\Psi_\uparrow(\vec{r}) \quad \Psi_\downarrow(\vec{r}))^* \begin{pmatrix} \Psi_\uparrow(\vec{r}) \\ \Psi_\downarrow(\vec{r}) \end{pmatrix} d\vec{r} = \int |\Psi_\uparrow(\vec{r})|^2 + |\Psi_\downarrow(\vec{r})|^2 d\vec{r}$

One electron can have **both spin-up and spin-down** probability and for norm **both spins should be considered**

The Scalar product can be defined the same way

$$\langle\Phi|\Psi\rangle = \int (\varphi_\uparrow(\vec{r}) \quad \varphi_\downarrow(\vec{r}))^* \begin{pmatrix} \Psi_\uparrow(\vec{r}) \\ \Psi_\downarrow(\vec{r}) \end{pmatrix} d\vec{r} = \int \varphi_\uparrow^*(\vec{r})\Psi_\uparrow(\vec{r}) + \varphi_\downarrow^*(\vec{r})\Psi_\downarrow(\vec{r}) \, d\vec{r}$$

In most of the first principles calculations the only spin-up or spin-down wavefunctions are used

Explicitly $\qquad\qquad \Psi(\vec{r}) = \begin{pmatrix} \Psi_\uparrow(\vec{r}) \\ 0 \end{pmatrix}$ or $\Psi(\vec{r}) = \begin{pmatrix} 0 \\ \Psi_\downarrow(\vec{r}) \end{pmatrix}$

Such pure spin-up or spin-down wavefunctions are orthogonal to each others. **Correspond to different quantum states**.

Not pure spin-up or –down WF

Need to clarify what is electronic density in this case, or what is spin density

The expectation value of the electronic density is $n(\vec{r}) = |\Psi_\uparrow(\vec{r})|^2 + |\Psi_\downarrow(\vec{r})|^2$

The expectation value of the spin along z direction (spin polarization) $s_z(\vec{r}) = (|\Psi_\uparrow(\vec{r})|^2 - |\Psi_\downarrow(\vec{r})|^2)\dfrac{\hbar}{2}$

What about the x- or y- spin-polarization?
Or expectation along any other direction?

We introduce so called Pauli matrices $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Not pure spin-up or –down WF

Spin-polarization vector (expectation value):

$$s_x(\vec{r}) = \left(\Psi_\downarrow^*(\vec{r})\Psi_\uparrow(\vec{r}) + \Psi_\uparrow^*(\vec{r})\Psi_\downarrow(\vec{r})\right)\frac{\hbar}{2} = \Psi^+(\vec{r})\sigma_x\Psi(\vec{r})\frac{\hbar}{2}$$

$$s_y(\vec{r}) = \left(i\Psi_\downarrow^*(\vec{r})\Psi_\uparrow(\vec{r}) - i\Psi_\uparrow^*(\vec{r})\Psi_\downarrow(\vec{r})\right)\frac{\hbar}{2} = \Psi^+(\vec{r})\sigma_y\Psi(\vec{r})\frac{\hbar}{2}$$

$$s_z(\vec{r}) = \left(|\Psi_\uparrow(\vec{r})|^2 - |\Psi_\downarrow(\vec{r})|^2\right)\frac{\hbar}{2} = \Psi^+(\vec{r})\sigma_z\Psi(\vec{r})\frac{\hbar}{2}$$

Spin-density matrix $\quad n_{\alpha\beta}(\vec{r}) = \Psi_\alpha^*(\vec{r})\Psi_\beta(\vec{r})$ $\qquad \alpha = \uparrow, \downarrow$ 4 different components of $n_{\alpha\beta}(\vec{r})$ in
$\beta = \uparrow, \downarrow$ total

The total density is $\quad n(\vec{r}) = n_{\uparrow\uparrow}(\vec{r}) + n_{\downarrow\downarrow}(\vec{r})$

The projection along z-direction of spin $s_z(\vec{r}) = \left(n_{\uparrow\uparrow}(\vec{r})^2 - n_{\downarrow\downarrow}(\vec{r})^2\right)\frac{\hbar}{2}$
polarization is

Operators acting on spinors

Operators acting on spinors are 2×2 matrices

non-diagonal components
refer to spin-flip operators

$$\widehat{\mathbb{R}} = \begin{pmatrix} \hat{R}_{\uparrow\uparrow} & \hat{R}_{\uparrow\downarrow} \\ \hat{R}_{\downarrow\uparrow} & \hat{R}_{\downarrow\downarrow} \end{pmatrix}$$

where $\hat{R}_{\alpha\beta}$ are operators acting in usual Hilbert space (=spatial part)

Apply spinor operator to spinor wavefunction

$$\widehat{\mathbb{R}}|\Psi\rangle = \begin{pmatrix} \hat{R}_{\uparrow\uparrow}|\Psi_\uparrow\rangle & \hat{R}_{\uparrow\downarrow}|\Psi_\downarrow\rangle \\ \hat{R}_{\downarrow\uparrow}|\Psi_\uparrow\rangle & \hat{R}_{\downarrow\downarrow}|\Psi_\downarrow\rangle \end{pmatrix}$$

Classical treatment of magnetic field

How does spin relates to magnetic dipole?

Classical mechanics: for a particle rotating around origin, with mass M and charge q:

Angular momentum $\qquad \vec{L} = M\vec{r} \times \vec{v}$

Magnetic momentum $\qquad \vec{\mu} = \dfrac{q}{2}\vec{r} \times \vec{v}$

There is a direct relationship in the classical case between angular momentum and magnetic momentum

$$\vec{\mu} = \frac{q}{2M}\vec{L}$$

Placed inside a magnetic field $\vec{B}$

a magnetic dipole acquire an energy $\qquad E_{int} = -\vec{\mu} \cdot \vec{B}$

Quantum treatment of magnetic field

$$\vec{\mu} = \frac{q}{2M}\vec{L} \quad + \text{Correspondence principle} \quad \Longrightarrow \quad \hat{\mu} = \frac{q}{2M}\hat{L}$$

Suppose a magnetic field along z.

For an electron (charge $q=-e$, mass m_e), observable values for the projection of magnetic moment along z are

$$\mu_z = -\frac{e}{2m_e}L_z = -\frac{e}{2m_e}m\hbar$$

definition of "Bohr magneton"

where m = magnetic quantum number (integer)

$$\mu_B = \frac{e\hbar}{2m_e}$$

A fundamental unit of magnetic momentum

Energy change (first approximation) for weak magnetic field

$$E_{int} = -\mu_z \cdot B_z = \frac{e}{2m_e}m\hbar B_z = \mu_B m B_z$$

The energy of classical magnetic dipole placed in the field B

Zeeman effect: lifting the degeneracy

Zeeman effect lifts the degeneracy of atomic levels

Atomic levels of same *n* and *l*, but different *m*, are not degenerate anymore in a magnetic field
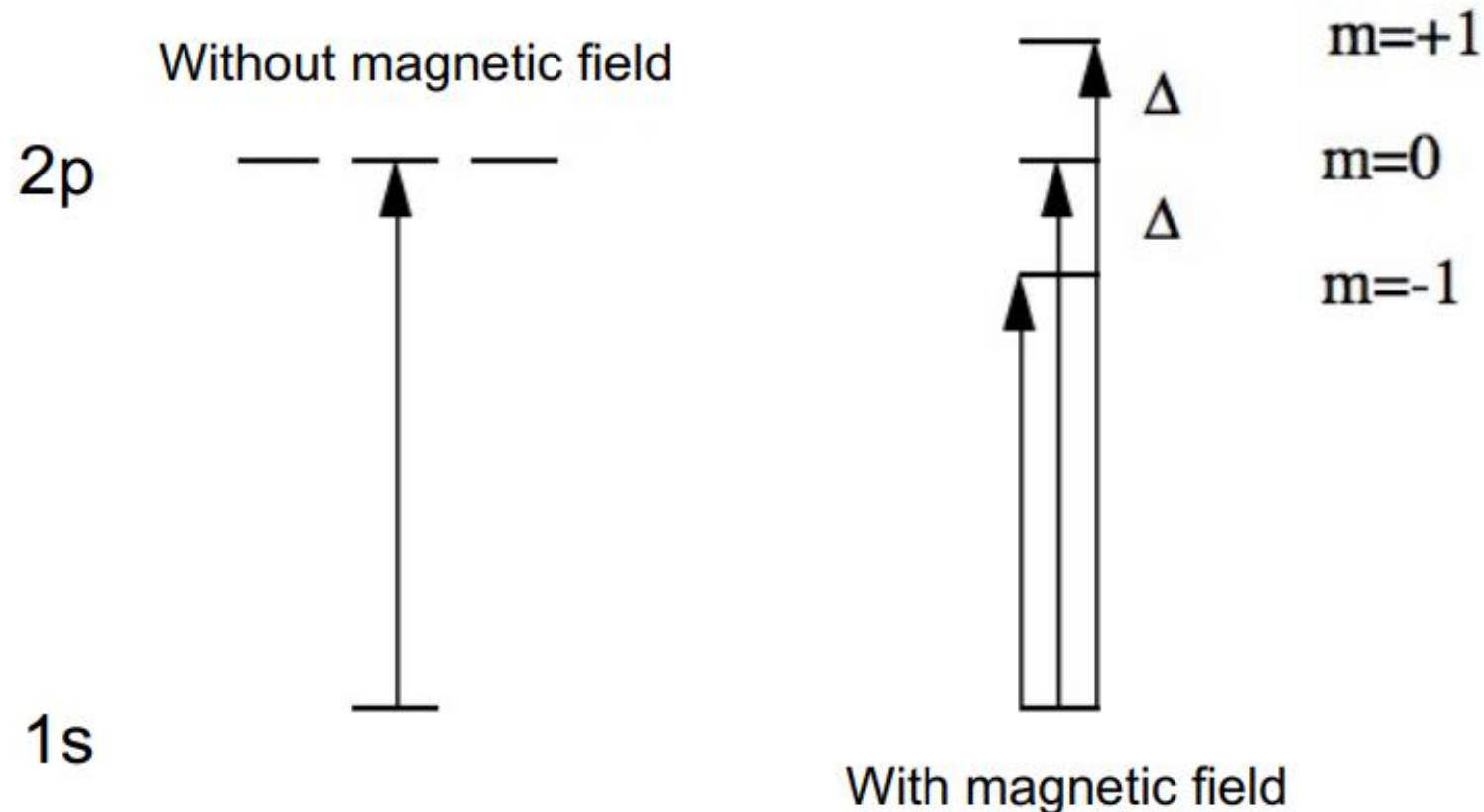
Intrinsic magnetic moment

Classical relation between orbital moment and magnetic moment

$$\hat{\mu} = \frac{q}{2M}\hat{L}$$

There exists also a spin magnetic moment, but the proportionality coefficient is not the same as in the classical relation:

$$\hat{\mu}_s = g_e \frac{(-e)}{2m_e}\hat{S}$$

g-factor

$$g_e \cong 2$$

$$E_{int} = -\mu_z \cdot B_z = \frac{g_e e}{2m_e} g_e m \hbar B_z = \mu_B g_e m B_z$$

If gradient of B exists a force appears
=> Stern-Gerlach exp !

Spin-orbit (SOC) coupling

Classically, magnetic dipoles interact with each others

(magnetic dipole induces a magnetic field, felt by the other dipole)

Magnetic dipole from orbital movement interacts with spin magnetic dipole

$$E_{SOC} \sim \vec{L} \cdot \vec{S}$$

In the atomic case the degeneracies are lifted

The examples of p-levels $m_l = -1, 0, +1 \quad m_s = -\frac{1}{2}, +\frac{1}{2}$

All together we have 6-fold degeneracy

$$\{|p_{m=-1}, \uparrow\rangle, |p_{m=-1}, \downarrow\rangle, |p_{m=0}, \uparrow\rangle, |p_{m=0}, \downarrow\rangle, |p_{m=+1}, \uparrow\rangle, |p_{m=+1}, \downarrow\rangle\}$$

Due to SOC, 6-fold degeneracy becomes doublet+quadruplet

One can compute the projection of the total orbital+spin angular momentum $m_j \hbar = m_l \hbar + m_s \hbar$

Six levels can be grouped in two sets of levels

$$j = \frac{1}{2} \text{ with } m_s = -\frac{1}{2}, +\frac{1}{2} \qquad\qquad j = \frac{3}{2} \text{ with } m_s = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$$

One talks about $p_{1/2} - p_{3/2}$ splitting, which is not very large

Spin-orbit interaction

Theory shows that SOC originates from relativistic corrections (Schrödinger to Dirac Eq.)
Mass-velocity + Darwin term

= modification of kinetic energy and potential (use pseudopotentials without any modifications)

Spin-orbit interaction

= new type of term $E_{SOC} = -\left(\dfrac{e\hbar}{2m_e c}\right) \vec{\sigma} \cdot \left[\nabla V \times \left(\dfrac{\vec{p}}{m_e c}\right)\right]$

= vector of Pauli matrices

Creates the effective magnetic field locally

Close to a nucleus $E_{SOC} \sim \vec{L} \cdot \vec{S}$ gives an energy modification proportional to Z^4 (it is very small for light elements and can be very large for heavy elements)

SOC vanishes for s electronic states where $l = 0$

Often NOT taken into account in first-principles calculations, except for electronic properties. Needs spinorial wavefunctions, increase of CPU time > 4.

Z=78 ... 83 ➡

$6p_{1/2}$-$6p_{3/2}$ splitting in Bi is about 1.5 eV

Incomplete p-shell

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Exchange-correlation functionals

In principle, exact functional is still a functional of density only $E_{XC}^{DFT}[n] = \int n(\vec{r}) \varepsilon_{XC}^{DFT}(\vec{r}; n) d\vec{r}$

However, information on **density + spin** gives better approximate functionals.
"Spin-density functional theory" (SDFT).

O. Gunnarsson and B.I. Lunqvist, Phys. Rev. B 13, 4274 (1976)

Spin-density functional theory is the right theory to deal with spins and SOC.

If spin-orbit coupling is ignored, then most materials have either no spin-polarization (nowhere in space), or their spin-polarization is aligned with only one direction (chosen as z), everywhere in space.

This is called a collinear case

$$E_{XC}^{DFT,coll}[n_{\uparrow}, n_{\downarrow}] = \int n(\vec{r}) \varepsilon_{XC}^{DFT,coll}(\vec{r}; n_{\uparrow}, n_{\downarrow}) d\vec{r}$$

If spin-orbit coupling is taken into account, either there is no spin-polarization (nowhere in space), or spin-polarization is not constrained to be aligned.

This is called a non-collinear case

$$E_{XC}^{DFT,non-coll}[n, \vec{s}] = \int n(\vec{r}) \varepsilon_{XC}^{DFT,coll}(\vec{r}; n, \vec{s}) d\vec{r}$$

spin magnetization vector

Exchange-correlation potentials

Next, we need to generalize the Kohn-Sham equations, where the **Kohn-Sham potential will be different for spin-up electrons and spin-down**

Collinear case: pure spin-up or spin-down wavefunctions $|\Psi_i^\alpha\rangle$ *i* and a label the states a=↑ or ↓

$$\left(-\frac{1}{2}\nabla^2 + V_{KS,\alpha}(\vec{r})\right)\Psi_i^\alpha(\vec{r}) = \varepsilon_i^\alpha \Psi_i^\alpha(\vec{r}) \qquad V_{KS,\alpha}(\vec{r}) = V_{ext}(\vec{r}) + \int \frac{n(\vec{r}_1)}{|\vec{r}_1 - \vec{r}|}d\vec{r}_1 + \frac{\delta E_{XC}^{SDFT,coll}[n_\uparrow, n_\downarrow]}{\delta n_\alpha(\vec{r})}$$

Spin dependence of KS potential comes from the XC energy due to the derivative w.r.t. spin-up or spin-down density to find V$_{KS}$

Non-collinear case: spinorial wavefunctions $|\Psi_i\rangle$ $\left(-\frac{1}{2}\nabla^2 + V_{KS}(\vec{r}) + \frac{\hbar}{2}\vec{B}_{XC}(\vec{r})\cdot\vec{\sigma}\right)\Psi_i(\vec{r}) = \varepsilon_i \Psi_i(\vec{r})$

XC magnetic field   Pauli matrices

$$V_{KS,\alpha}(\vec{r}) = V_{ext}(\vec{r}) + \int \frac{n(\vec{r}_1)}{|\vec{r}_1 - \vec{r}|}d\vec{r}_1 + \frac{\delta E_{XC}^{SDFT,non-coll}[n,\vec{s}]}{\delta n(\vec{r})}$$ KS   potential   will   not depend on the spin

but $\vec{B}_{XC,j}(\vec{r}) = \dfrac{\delta E_{XC}^{SDFT,non-coll}[n,\vec{s}]}{\delta s_j(\vec{r})}$ *j*=x,y,z   Crucially depends on the spin

Approximate XC functionals

Approximate XC functionals can be also generated

E.g. Local spin-density approximation for the **collinear case**

$$E_{XC}^{LSDA}[n_\uparrow, n_\downarrow] = \int n(\vec{r})\varepsilon_{XC}^{LSDA}\left(n_\uparrow(\vec{r}), n_\downarrow(\vec{r})\right)d\vec{r} \qquad \varepsilon_{XC}^{LSDA}\left(n_\uparrow(\vec{r}), n_\downarrow(\vec{r})\right)$$

parameterized from homogeneous electron gas

Moreover, exchange energy in **collinear case** has simple general relationship with unpolarized exchange energy

G.L. Oliver and J.P. Perdew, Phys. Rev. A 20, 397 (1979)

$$E_X^{SDFT,coll}[n_\uparrow, n_\downarrow] = \frac{1}{2}\left(E_X^{DFT}[2n_\uparrow] + E_X^{DFT}[2n_\downarrow]\right)$$

This comes from the separate contribution of spins to exchange energy

$$E_X = -\frac{1}{2}\sum_\sigma \sum_{i,j}^{occ}\int d\vec{r}d\vec{r}' \frac{\Psi_{j\sigma}^*(\vec{r}')\Psi_{i\sigma}^*(\vec{r}')\Psi_{j\sigma}(\vec{r})\Psi_{i\sigma}(\vec{r})}{|\vec{r}' - \vec{r}|}$$
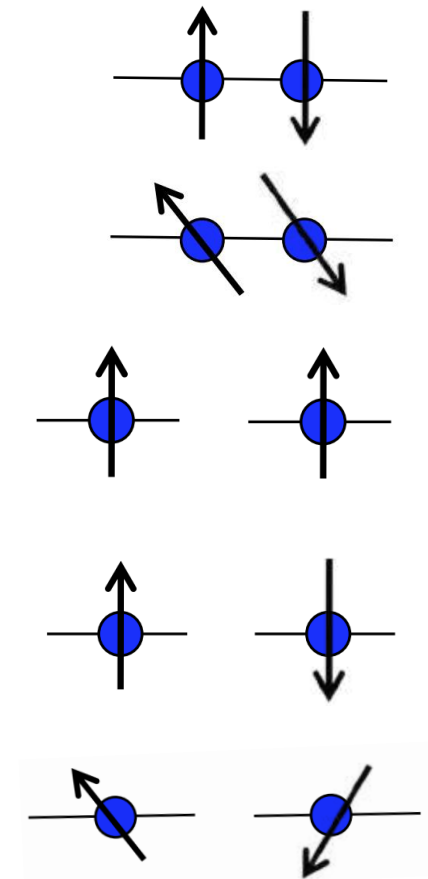
σ denoting spin-up or spin-down

Simple sum over spin-up and separately over spin-down contribution

For **non-collinear case**, neglect directional dependence of local spin-polarization => falls back to collinear case.
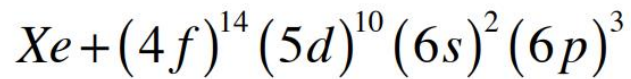
Methodologies. Spin+symmetry

In practice the user will have to choose one of the following procedures for first principles calculations to be done.
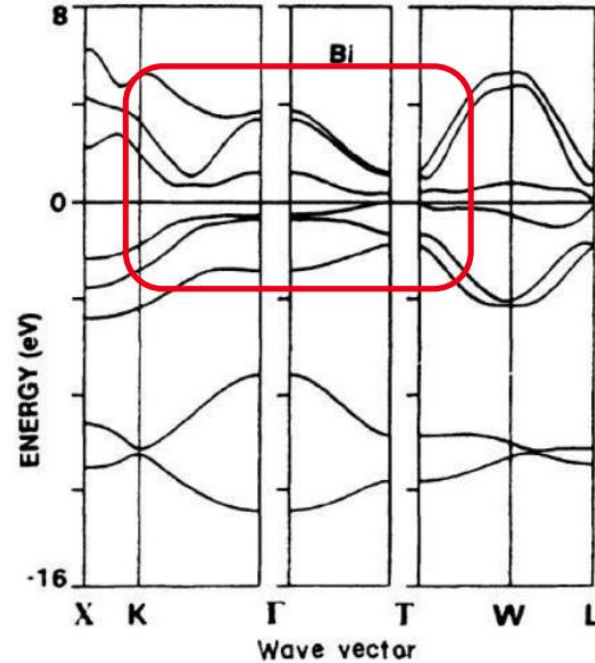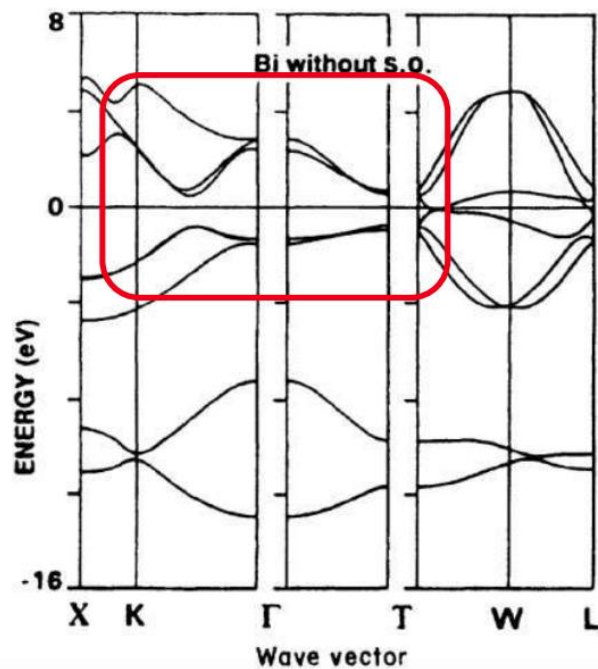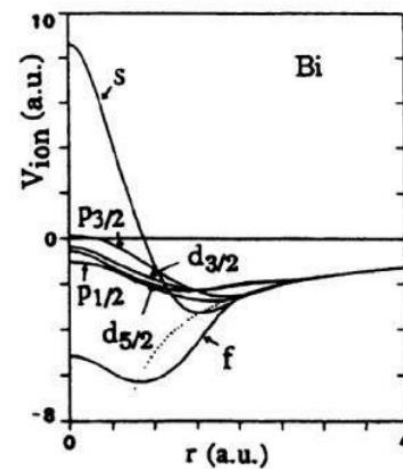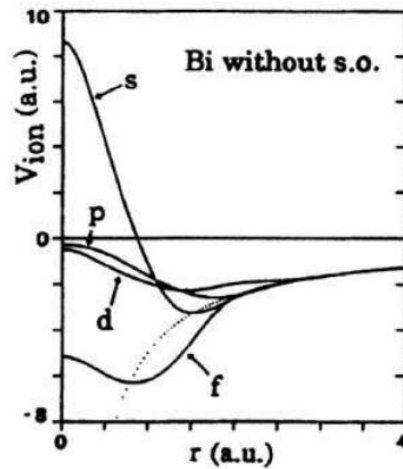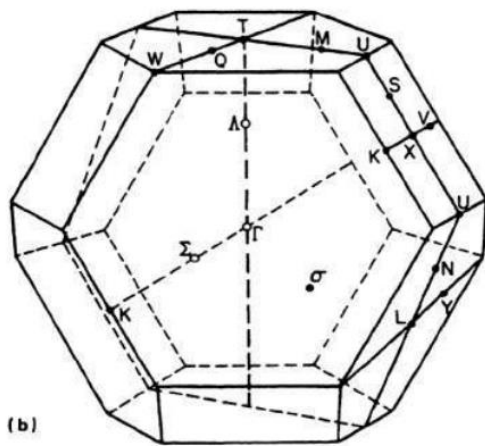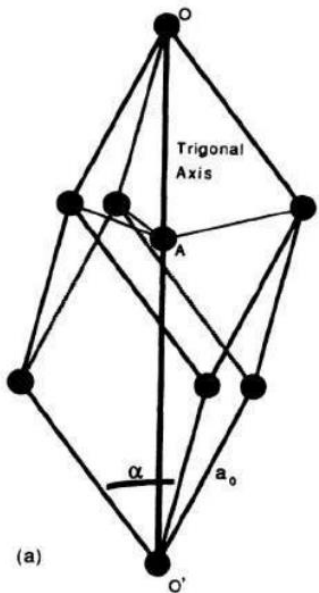
(1) No spin-polarization, scalar wavefunctions
   (Many metals/covalent/ionic solids with light nuclei)

(2) No spin-polarization, spinorial wavefunctions (spin-orbit coupling)
   (Many metals/covalent/ionic solids with heavier nuclei)

(3) Collinear spin, different spin-up and spin-down wavefunctions
   (Ferromagnetic materials with light nuclei, finite systems with net spin, in particular open shell atoms, and paramagnetic molecules, if light nuclei)

(4) Collinear spin, antiferromagnetic case
   (Specific materials, often oxides – the spin-down density is space-symmetric to the spin-up density – spin-polarization does not vanish)

(5) Non-collinear spin-polarization
   (Heavy nuclei with magnetization, also important for some properties like the magnetocrystalline field, or spin diffusion)
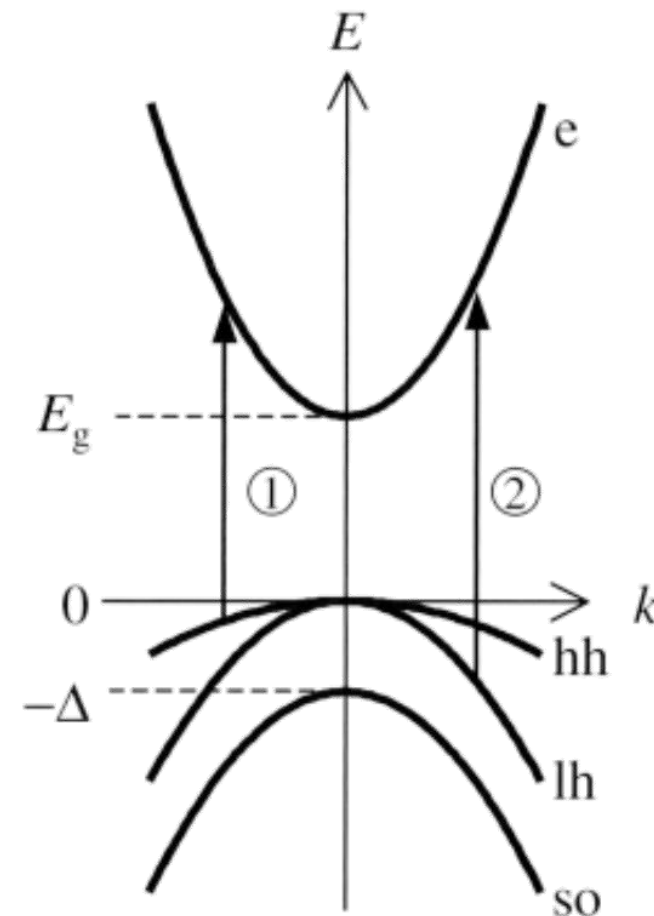
8 times heavier in terms of CPU time

$$Xe + (4f)^{14}(5d)^{10}(6s)^2(6p)^3$$

$6p_{1/2}$-$6p_{3/2}$ splitting is about 1.5 eV

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Electronic structure of III-V & II-VI compounds

III-V and II-VI compounds : important for opto-electronic applications (light-emitting diodes, IR and visible photodetectors, solid state lasers)

Crystalline structure : tetrahedrally coordinated
(zinc-blende -AlP, AlAs, AlSb, BN, BP, CdTe, GaAs, HgSe, HgTe, InAs, InP, InSb, ZnS;
or wurtzite - AlN, GaN, InN, CdS, CdSe, CdTe, ZnO, ZnS)

Band structure of several III-V and II-VI compounds near k=0.
E=0 : top of the valence band
E = Eg : bottom of the conduction band.
4 bands (should be 3-fold degenerated w/o SO)
heavy hole (hh) band, light hole (lh) band, spin-orbit hole (so) band, and electron (e) band.
Two optical transitions are indicated.
Transitions can also take place between spin-orbit hole band and conduction band but are not shown for the sake of clarity.
Δ ranges from <0.1 eV to 0.33 eV for GaAs and 0.8 eV for InSb
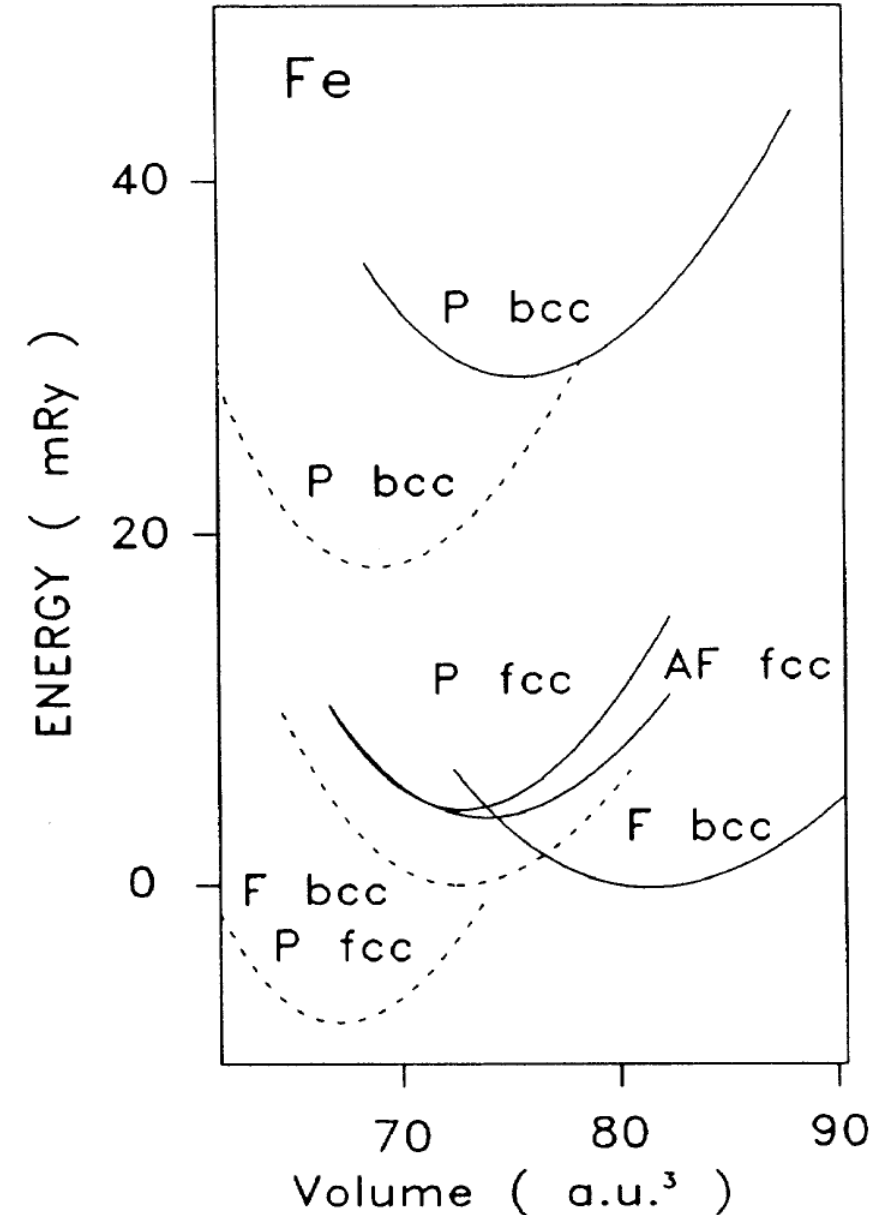
Role of XC functional. Iron

Total energy as a function of volume per atom for Irc

Dashed lines : Spin-LDA
Full lines : Spin-GGA

P = paramagnetic (no spin-polarization)
F = ferromagnetic
AF = antiferromagnetic

FCC= face-centered cubic
BCC= body-centered cubic

The GGA gets **the correct phase** :
Experimentally Fe is ferromagnetic BCC

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Thx!