

Fundamentals: the quantum-mechanical many-electron problem and the Density Functional Theory approach

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

Javier Junquera

UC

UNIVERSIDAD DE CANTABRIA

Most important reference followed in the tutorial:

INSTITUTE OF PHYSICS PUBLISHING

JOURNAL OF PHYSICS: CONDENSED MATTER

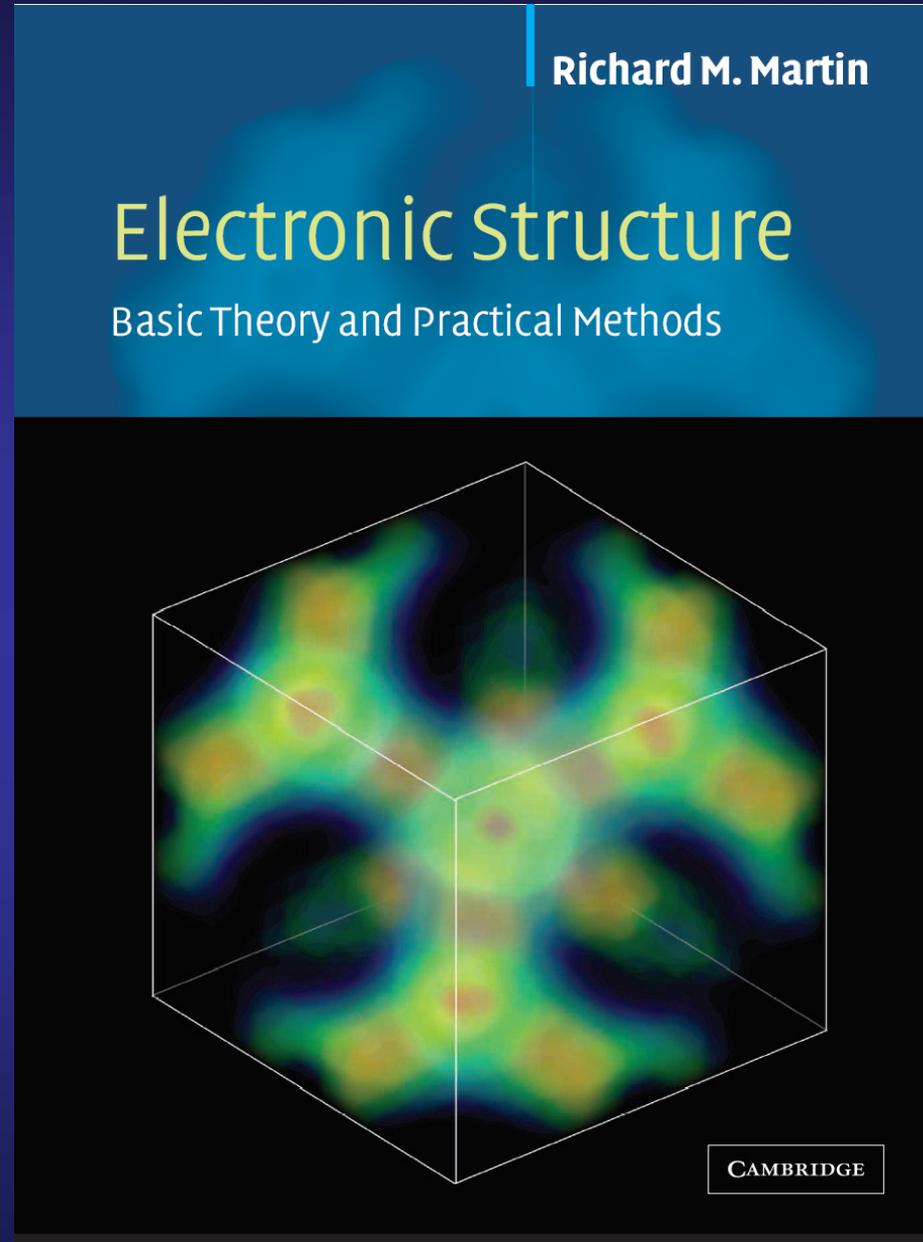
J. Phys.: Condens. Matter **14** (2002) 2745–2779

PII: S0953-8984(02)30737-9

The SIESTA method for *ab initio* order- N materials simulation

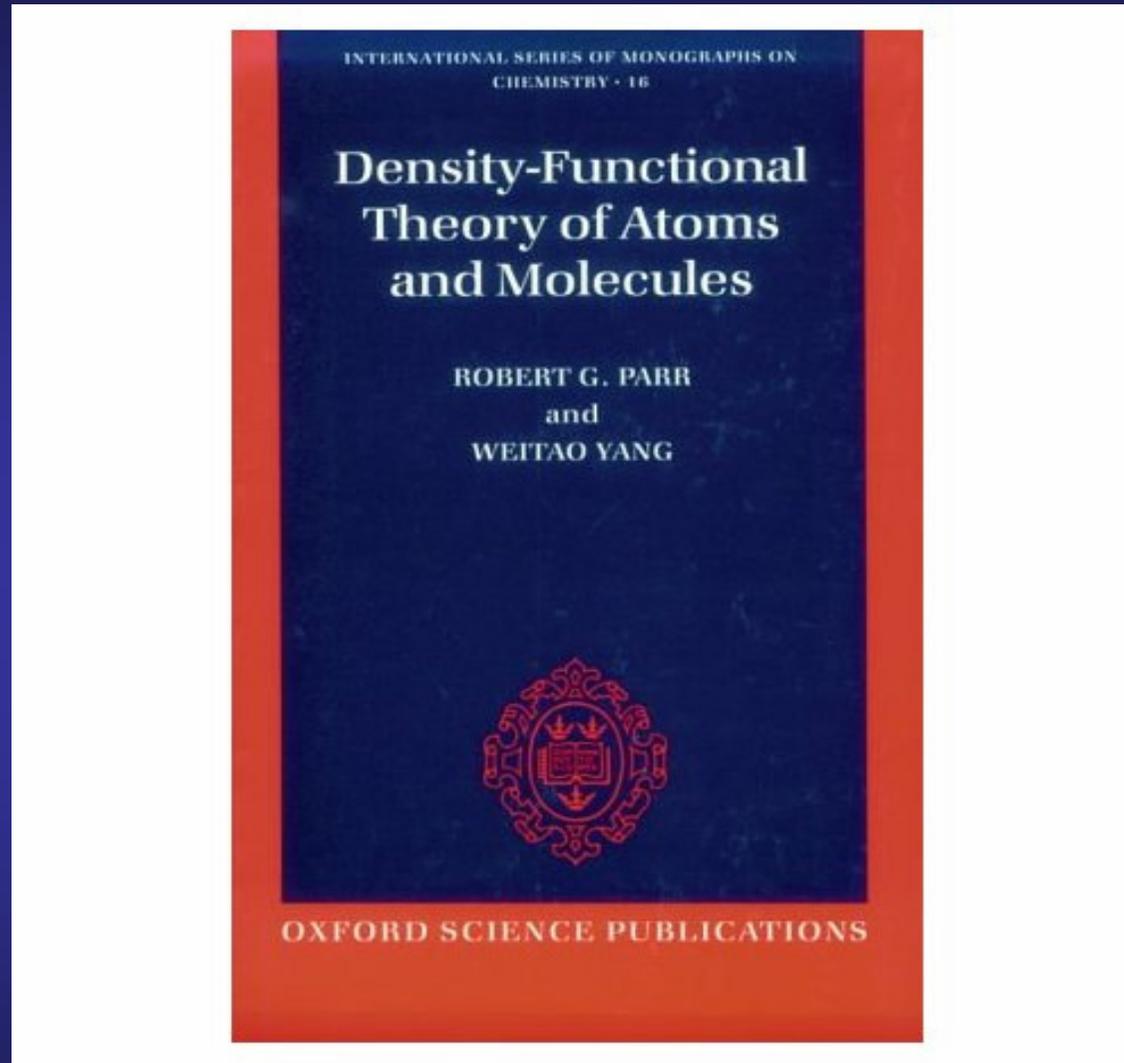
**José M Soler¹, Emilio Artacho², Julian D Gale³, Alberto García⁴,
Javier Junquera^{1,5}, Pablo Ordejón⁶ and Daniel Sánchez-Portal⁷**

Most important reference followed in the tutorial:



**comprehensive review of DFT,
including most relevant references and exercises**

Other reference books



Rigorous and unified account of the *fundamental principles* of DFT

More intended for researchers and advanced students

Other references: original milestones reviews and papers

Iterative minimization techniques for *ab initio* total-energy calculations: molecular dynamics and conjugate gradients

M. C. Payne

Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, United Kingdom

M. P. Teter and D. C. Allan

Applied Process Research, Corning Incorporated, Corning, New York 14831

T. A. Arias and J. D. Joannopoulos

Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Other interesting references: Nobel lectures by W. Kohn and J. A. Pople

Nobel prize in Chemistry 1998



Walter Kohn

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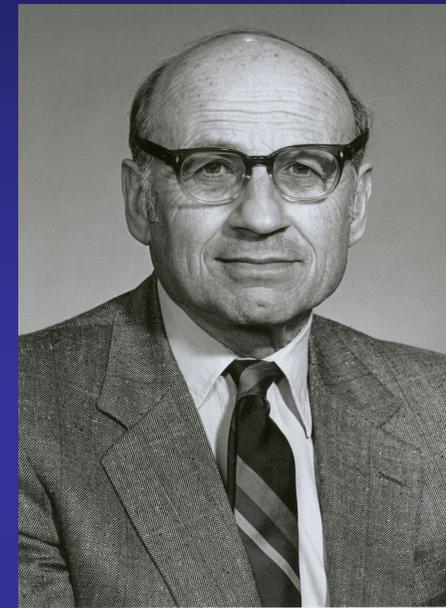
ELECTRONIC STRUCTURE OF MATTER – WAVE FUNCTIONS AND DENSITY FUNCTIONALS

Nobel Lecture, January 28, 1999

by

WALTER KOHN

Department of Physics, University of California, Santa Barbara, CA 93106-
9530, USA



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QUANTUM CHEMICAL MODELS

Nobel Lecture, December 8, 1998

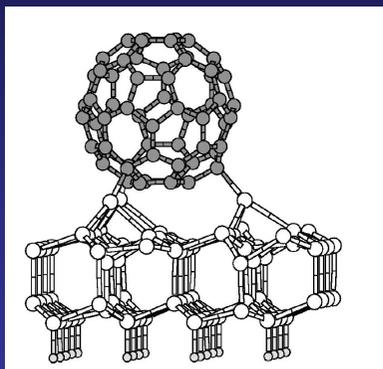
by

JOHN A. POPLE

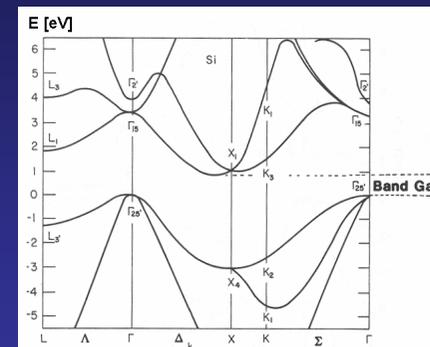
Department of Chemistry, Northwestern University, 2145 Sheridan Road,
Evanston, Illinois 60208, USA



Goal: Describe properties of matter from theoretical methods firmly rooted in fundamental equations



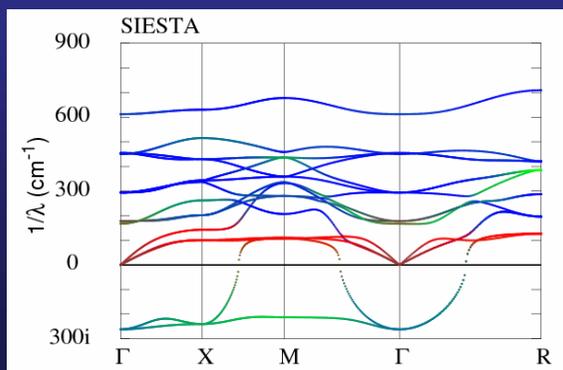
structural



electronic

PROPERTIES

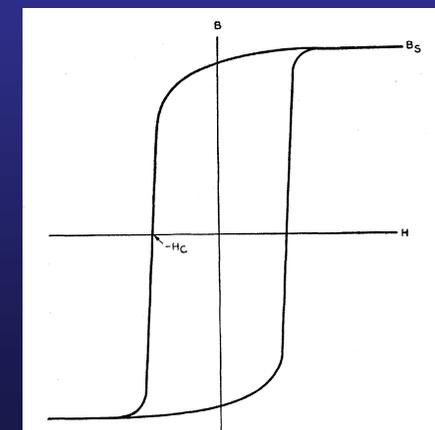
vibrational



optical



magnetic



Goal: Describe properties of matter from theoretical methods firmly rooted in fundamental equations

Quantum Mechanics: Schrödinger equation (assuming no relativistic)

$$i\hbar \frac{\partial \Psi \left(\{\vec{x}_i\}, \{\vec{R}_\alpha\}; t \right)}{\partial t} = \hat{H} \Psi \left(\{\vec{x}_i\}, \{\vec{R}_\alpha\}; t \right)$$

Coordinates of electron i \vec{x}_i comprise

$$\left\{ \begin{array}{ll} \text{Space coordinates} & \vec{r}_i \\ \text{Spin coordinates} & \sigma_i \end{array} \right.$$

Electromagnetism: Coulomb's law

$$\hat{H} = \hat{T} + \hat{V}_{Coulomb}$$

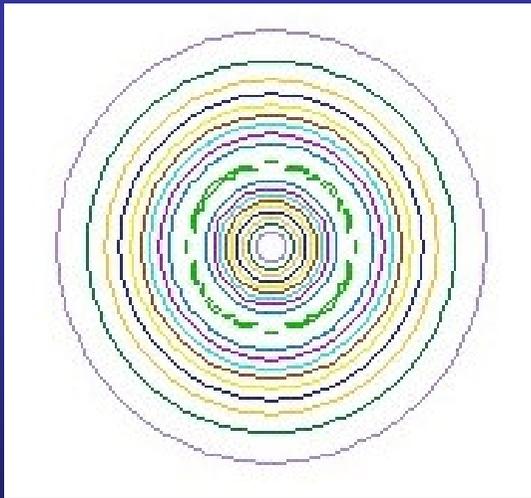
For a pair of charged particles

$$\hat{V}_{Coulomb} = \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|}$$

The Schrödinger equation (differential) must be solved subject to appropriate boundary conditions

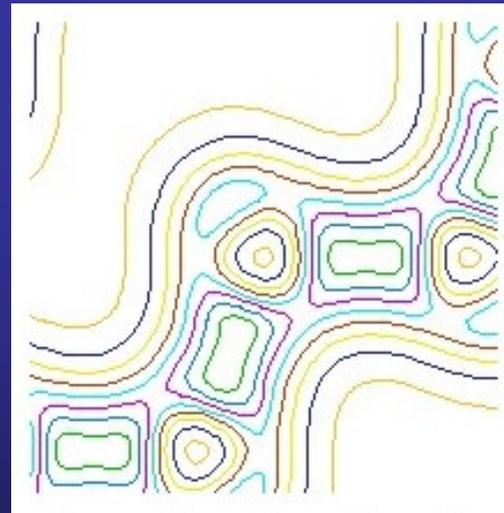
Ψ must be well behaved everywhere

Atoms and molecules



→ 0 at infinity

Regular infinite solid



Appropriate periodic boundary conditions

The electrons are fermions, the solution must satisfy the Pauli exclusion principle

A many electron wave function must be **antisymmetric with respect to the interchange** of the coordinate (both space and spin) of any two electrons

$$\Psi(\vec{x}_1, \dots, \vec{x}_i, \dots, \vec{x}_j, \dots, \vec{x}_N) = -\Psi(\vec{x}_1, \dots, \vec{x}_j, \dots, \vec{x}_i, \dots, \vec{x}_N)$$

Once the many-body wave function is known,
we compute the expectation values of observables

$$\langle \hat{A} \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int \Psi^* \hat{A} \Psi d\vec{x}}{\int \Psi^* \Psi d\vec{x}}$$

Integration over all spatial coordinates

Summation over spin coordinates

A particular measurement give particular eigenvalue of \hat{A}

Many measurements average to $\langle \hat{A} \rangle$

The total energy is the expectation value of the hamiltonian

$$E[\Psi] = \langle \hat{H} \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Ground state energy

$$E_0 = \min_{\Psi} E[\Psi]$$

Minimization of the energy functional, totally equivalent to diagonalize the eigenvalue problem

Since the eigenstates of the many-body hamiltonian are stationary points (saddle points or the minimum)

$$\delta E [\Psi] = 0$$

The normalization condition can be imposed using Lagrange multipliers

$$\delta \left[\langle \Psi | \hat{H} | \Psi \rangle - E (\langle \Psi | \Psi \rangle - 1) \right] = 0$$

Variation of the bra from $\langle \Psi | \longrightarrow \langle \Psi + \delta \Psi |$

$$\langle \delta \Psi | \hat{H} - E | \Psi \rangle = 0$$

This must holds for any variation in the bra, so this can be satisfied if the ket satisfies

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

A closer look to the hamiltonian: A difficult interacting many-body system.

$$\hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|}$$

Kinetic energy operator for the electrons

Potential acting on the electrons due to the nuclei

$$+ \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Electron-electron interaction

$$+ \sum_\alpha -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2$$

Kinetic energy operator for the nuclei

$$+ \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

Nucleus-nucleus interaction

This hamiltonian can not be solved exactly: practical and fundamental problems

Fundamental problem:

Schrödinger's equation is exactly solvable for

- Harmonic oscillator (analytically)
- Two particles (analytically)
- Very few particles (numerically)

Practical problem:

The number of electrons and nuclei in a pebble is of the order of 10^{23}

If the problem can not be solved exactly,
how can we work it out from first-principles?

Use a set of “accepted” approximations
to solve the corresponding equations on a computer

NO EMPIRICAL INPUT

Chemical composition

Number of atoms

Type

Position



Properties

Equilibrium structure

Band structure

Vibrational spectrum

Magnetic properties

Transport properties

...

IDEAL AB-INITIO CALCULATION

What are the main approximations?

Born-Oppenheimer

Decouple the movement of the electrons and the nuclei.

Density Functional Theory

Treatment of the electron – electron interactions.

Pseudopotentials

Treatment of the (nuclei + core) – valence.

Basis set

To expand the eigenstates of the hamiltonian.

Numerical evaluation of matrix elements

Efficient and self-consistent computations of H and S .

Supercells

To deal with periodic systems

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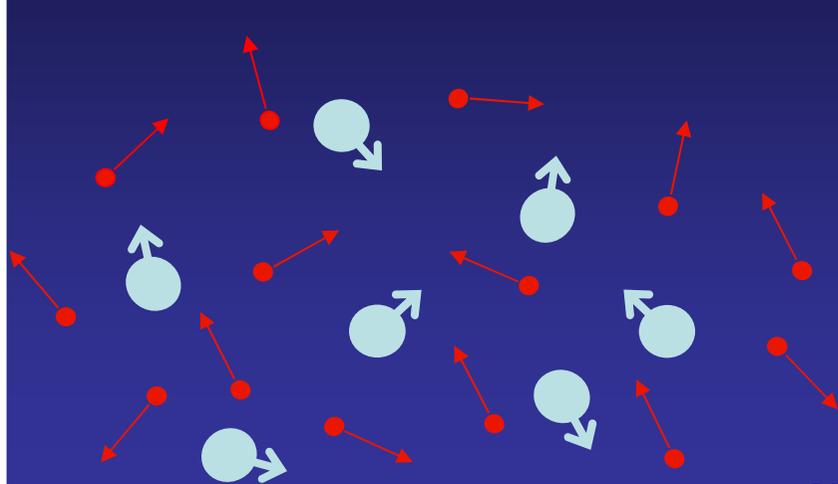
Numerical evaluation of matrix elements

Efficient and self-consistent computations of H and S .

Supercells

To deal with periodic systems

Adiabatic or Born-Oppenheimer approximation decouple the electronic and nuclear degrees of freedom



$$\frac{M_{\alpha}}{m_e} \gg \gg 1$$

\Rightarrow Nuclei much slower than the electrons $\frac{v_{electron}}{v_{nucleus}} \gg \gg 1$

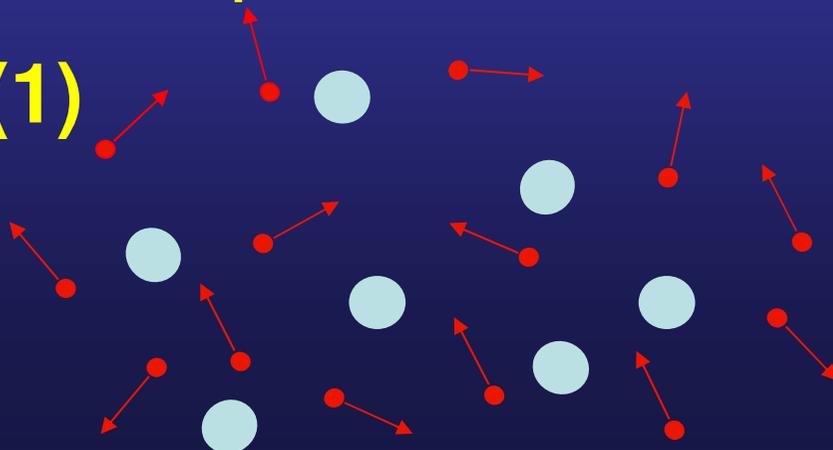
$$v_{electron} \approx v_F \approx 10^8 \text{ cm/s}$$

$$v_{nucleus} \approx 10^5 \text{ cm/s}$$

At any moment the electrons will be in their ground state for that particular instantaneous ionic configuration.

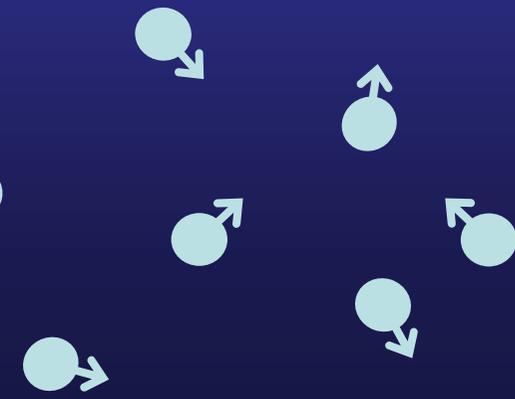
Solve electronic equations assuming fixed positions for nuclei

(1)



Move the nuclei as classical particles in the potential generated by the e^-

(2)



If the nuclear positions are fixed (ignore nuclear velocities), the wave function can be decoupled

$$\hat{H} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \cancel{\sum_\alpha -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i, \alpha} \frac{Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

Fixed potential
"external" to e⁻

Constant
(scalar)

Electrons

$$\left\{ \begin{aligned} \hat{H}_{\{\vec{R}_\alpha\}}^{el} &= \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V_{\{\vec{R}_\alpha\}}^{ext}(\{\vec{r}_i\}) \\ \hat{H}_{\{\vec{R}_\alpha\}}^{el} \Psi_{n, \{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\}) &= E_n^{el} \Psi_{n, \{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\}) \end{aligned} \right.$$

Nuclei

$$\left\{ \begin{aligned} \hat{H} &= \sum_\alpha -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + E_n^{el}(\{\vec{R}_\alpha\}) \\ \text{Classical displacement} \quad \vec{F}_\alpha &= -\frac{\partial E_0^{el}(\{\vec{R}_\mu\})}{\partial \vec{R}_\alpha} \end{aligned} \right.$$

The next problem...

how to solve the electronic equation

$$\left\{ \begin{array}{l} \hat{H}_{\{\vec{R}_\alpha\}}^{el} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V_{\{\vec{R}_\alpha\}}^{ext}(\{\vec{r}_i\}) \\ \hat{H}_{\{\vec{R}_\alpha\}}^{el} \Psi_{n, \{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\}) = E_n^{el} \Psi_{n, \{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\}) \end{array} \right.$$

Exact solution only for one electron systems \Rightarrow H, hydrogenoid atoms, H_2^+

Main difficulty: very complicate electron-electron interactions.

What are the main approximations?

Born-Oppenheimer

Decouple the movement of the electrons and the nuclei.

Density Functional Theory

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Supercells

To deal with periodic systems

The many-electron problem in interaction: An old and extremely hard problem.

Different approaches

- Quantum Chemistry (Hartree-Fock, CI...)
- Quantum Monte Carlo
- Perturbation theory (propagators)
- Density Functional Theory (DFT)
 - Very efficient and general
 - BUT implementations are approximate and hard to improve (no systematic improvement)
 - (... actually running out of ideas ...)

DFT: primary tool for calculation of electronic structure in condensed matter

Many electron wave function

$$\bar{\Psi} (\vec{x}_1, \dots, \vec{x}_N)$$

Undoubted merit: satisfies the many-electron Schrödinger equation

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

Contains a huge amount of information

3N degrees of freedom for N electrons

One electron density

$$n(\vec{r})$$

All properties of the system can be considered as unique functionals of the ground state density

Integrates out this information

One equation for the density is remarkably simpler than the full many-body Schrödinger equation

A special role can be assigned to the density of particles in the ground-state of a quantum many-body system

First theorem of Hohenberg-Kohn

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

We shall now show that conversely $v(\mathbf{r})$ is a unique functional of $n(\mathbf{r})$, apart from a trivial additive constant. The proof proceeds by *reductio ad absurdum*. As-

For any system of interacting particles in an external potential $V_{ext}(\vec{r})$, the potential $V_{ext}(\vec{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\vec{r})$

Corollary of first theorem of Hohenberg-Kohn

$$n_0(\vec{r})$$

↓ First theorem of Hohenberg-Kohn

$$V_{ext}(\vec{r})$$

↓ Definition of the Hamiltonian of interacting electrons in an external potential

$$\hat{H}_{\{\vec{R}_\alpha\}}^{el} = \sum_i -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V_{\{\vec{R}_\alpha\}}^{ext}(\{\vec{r}_i\})$$

↓ Solving the Schrödinger equation: ground and excited many body wave functions

$$\hat{H}_{\{\vec{R}_\alpha\}}^{el} \Psi_{n, \{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\}) = E_n^{el} \Psi_{n, \{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\})$$

No prescription to solve this problem.

At this level we have gained nothing

**All the properties of the system are completely determined
given only the ground state density $n_0(\vec{r})$**

Second theorem of Hohenberg-Kohn

PHYSICAL REVIEW

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where $F[n]$ is a universal functional, valid for any number of particles¹¹ and *any* external potential. This functional plays a central role in the present paper.

With its aid we define, for a given potential $v(\mathbf{r})$, the energy functional

$$E_v[n] \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n]. \quad (10)$$

Clearly, for the correct $n(\mathbf{r})$, $E_v[n]$ equals the ground-state energy E .

A universal functional for the energy $E[n]$ in terms of the density $n(\vec{r})$ can be defined, valid for any external potential $V_{ext}(\vec{r})$. For any particular $V_{ext}(\vec{r})$, the exact ground state of the system is the global minimum value of this functional, and the density $n(\vec{r})$ that minimizes the functional is the exact ground state density $n_0(\vec{r})$

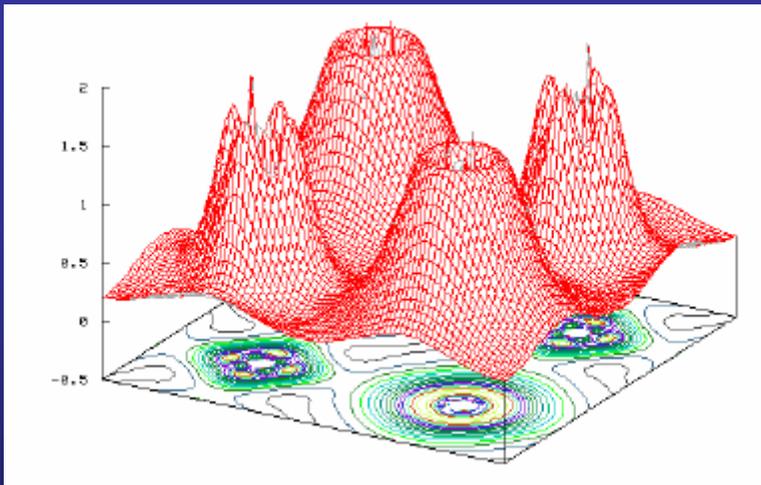
Some definitions

Function: rule for going from a **variable** x to a **number** $f(x)$

Functional: rule for going from a **function** to a **number**

A function of which the variable is a function

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



→ -300 eV (a value for the energy)

Universal means the same for all electron systems, **independent of** the external potential $V_{ext} (\vec{r})$

The kinetic energy and the interaction energy of the particles are functionals only of the density

$$\begin{aligned} E_{HK} [n] &= T [n] + E_{int} [n] + \int d\vec{r} V_{ext} (\vec{r}) n (\vec{r}) + E_{II} \\ &\equiv F_{HK} [n] + \int d\vec{r} V_{ext} (\vec{r}) n (\vec{r}) + E_{II} \end{aligned}$$

If known, minimization of $E_{HK} [n]$ with respect variations of the density would determine the exact **ground state** density and energy.

Excited states for the electrons must be determined by other means.

PROBLEM: Functional is unknown

The Kohn-Sham ansatz replaces the many-body problem with an independent-particle problem

All the **properties** of the system are completely **determined** given only the **ground state density** $n_0(\vec{r})$

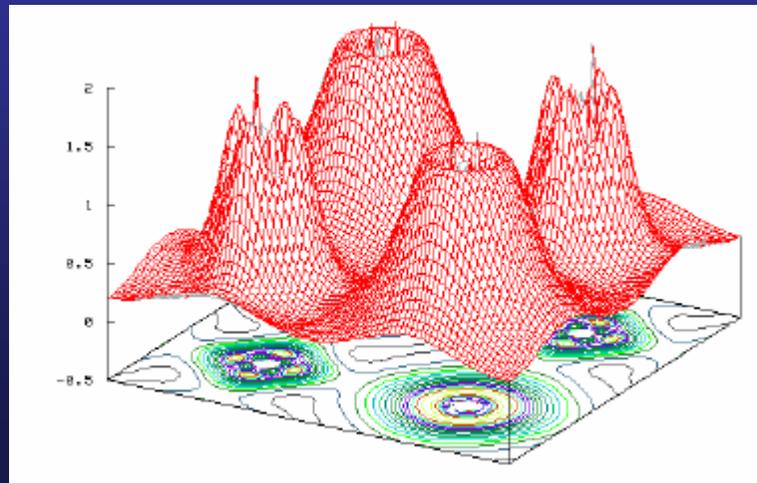
But no prescription to **solve** the difficult interacting **many-body hamiltonian**

$$\hat{H}_{\{\vec{R}_\alpha\}}^{el} \Psi_{n, \{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\}) = E_n^{el} \Psi_{n, \{\vec{R}_\alpha\}}^{el}(\{\vec{r}_i\})$$

Ground state density of the many-body interacting system

=

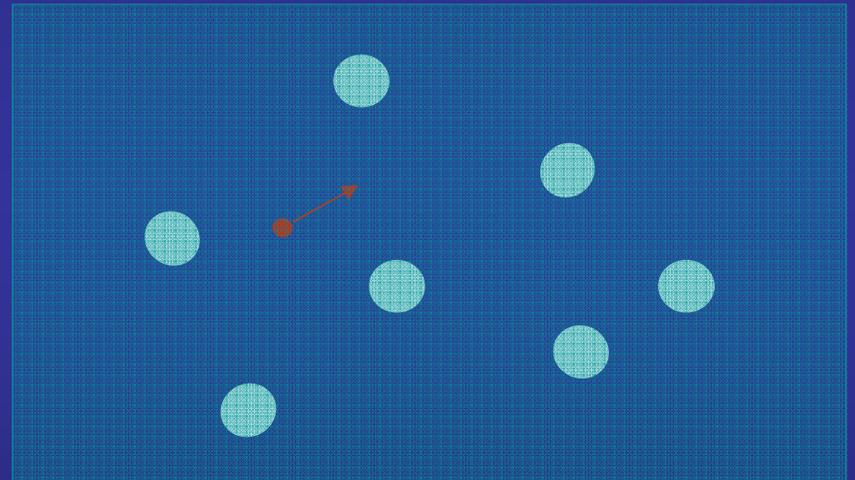
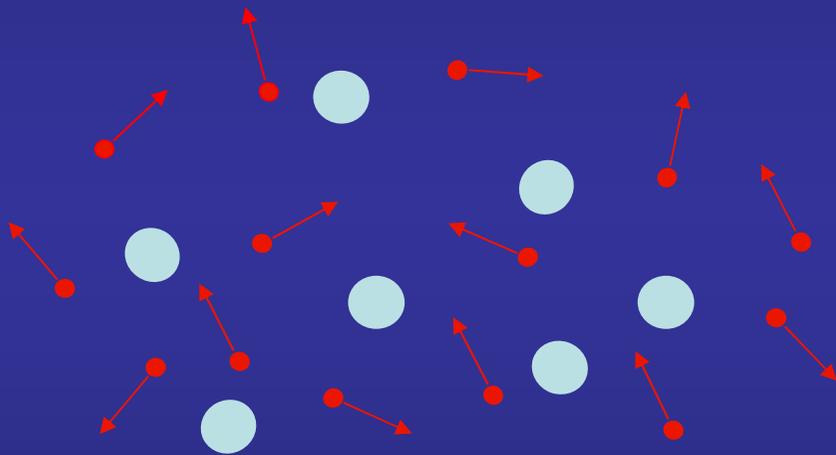
Density of an auxiliary non-interacting independent particle system



Kohn-Sham ansatz
(never proven in general)

One electron or independent particle model

We assume that each electron moves independently in a potential created by the nuclei and the rest of the electrons.



Actual calculations performed on the auxiliary independent-particle system

$$\hat{H}_{\text{aux}}^{\sigma} = -\frac{1}{2}\nabla^2 + V_{\text{eff}}^{\sigma}(\vec{r})$$

The independent-particle kinetic energy is given explicitly as a functional of the orbitals

$$T_s = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \langle \psi_i^{\sigma} | \nabla^2 | \psi_i^{\sigma} \rangle = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\nabla \psi_i^{\sigma}|^2$$

They rewrote the functional as

$$E_{KS}[n] = T_s[n] + \int d\vec{r} V_{ext}(\vec{r}) n(\vec{r}) + E_{Hartree}[n] + E_{xc}[n]$$

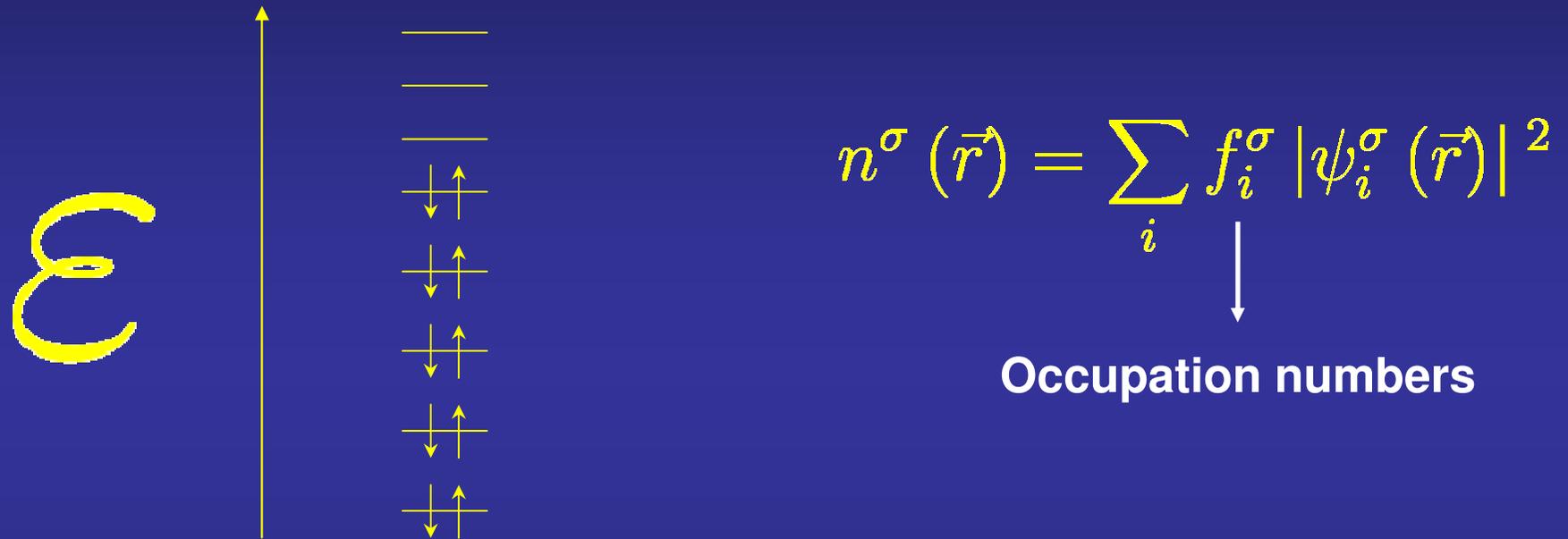
Coulomb

The rest:
Exchange-correlation

Equivalent to independent particles under the potential

$$V_{KS}^{\sigma}(\vec{r}) = V_{ext}(\vec{r}) + V_{Hartree}(\vec{r}) + V_{xc}^{\sigma}(\vec{r})$$

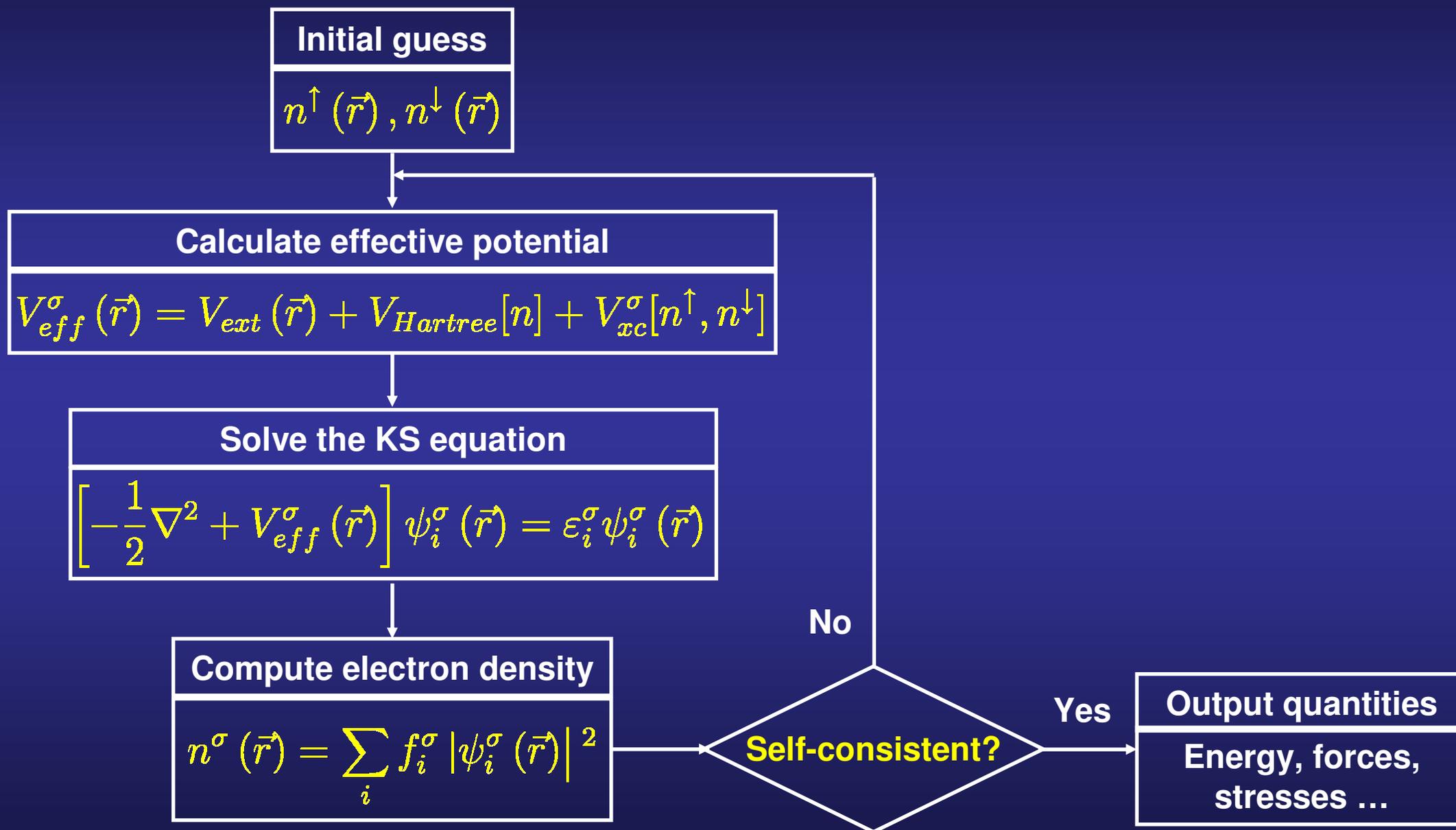
The one-particle eigenstates are filled following the “Aufbau” principle: from lower to higher energies



The ground state has one (or two if spin independent) in each of the orbitals with the lowest eigenvalues

The Kohn-Sham equations must be solved self-consistently

The potential (input) depends on the density (output)



The paper by Kohn-Sham contains an error...

PHYSICAL REVIEW

VOLUME 140, NUMBER 4A

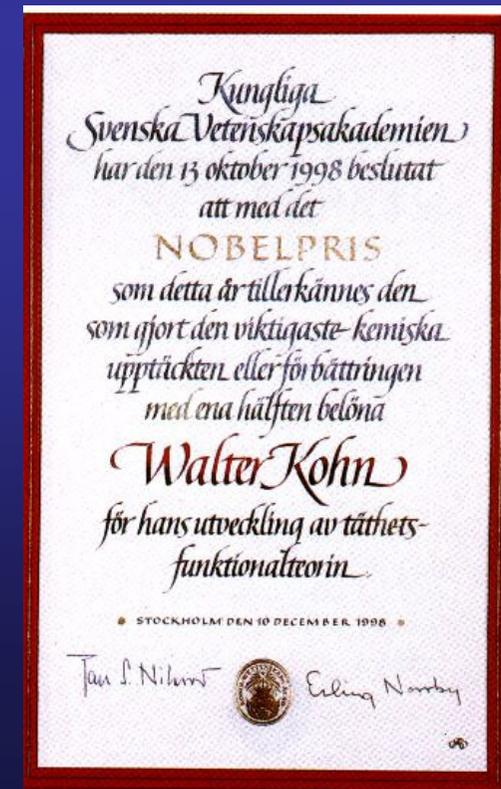
15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM

main source of error. We do not expect an accurate description of chemical binding. In large atoms, of course,

Density functional theory is the **most widely used method** today for electronic structure calculations **because** of the approach proposed by **Kohn and Sham**



All the unknown terms below a carpet: the exchange-correlation functional

$$V_{xc}^{\sigma}(\vec{r}) \equiv \frac{\delta E_{xc}}{\delta n(\vec{r}, \sigma)}$$

Local Density Approximation (LDA)

Solids can be often considered as close to the limit of the homogeneous electron gas
In this limit, effects of exchange and correlation are local in character

$$V_{xc}[n] \approx V_{xc}[n(\vec{r})]$$

Exchange-correlation energy of the homogeneous electron gas a function of density

Exchange:
analytic form

Correlation:
calculated to great accuracy
with Monte Carlo methods

GGA follows LDA



DFT thanks to Claudia Ambrosch (Graz)

All the unknown terms below a carpet: the exchange-correlation functional

$$V_{xc}^{\sigma}(\vec{r}) \equiv \frac{\delta E_{xc}}{\delta n(\vec{r}, \sigma)}$$

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analytic form

Correlation:
calculated to great accuracy
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Generalized Gradient Approximation (GGA)

$$V_{xc}[n] \approx V_{xc}[n(\vec{r}), \nabla n(\vec{r})]$$

Provide required accuracy for DFT to be adopted by the Chemistry Community

Problem: does not lead to consistent improvement over the LSDA

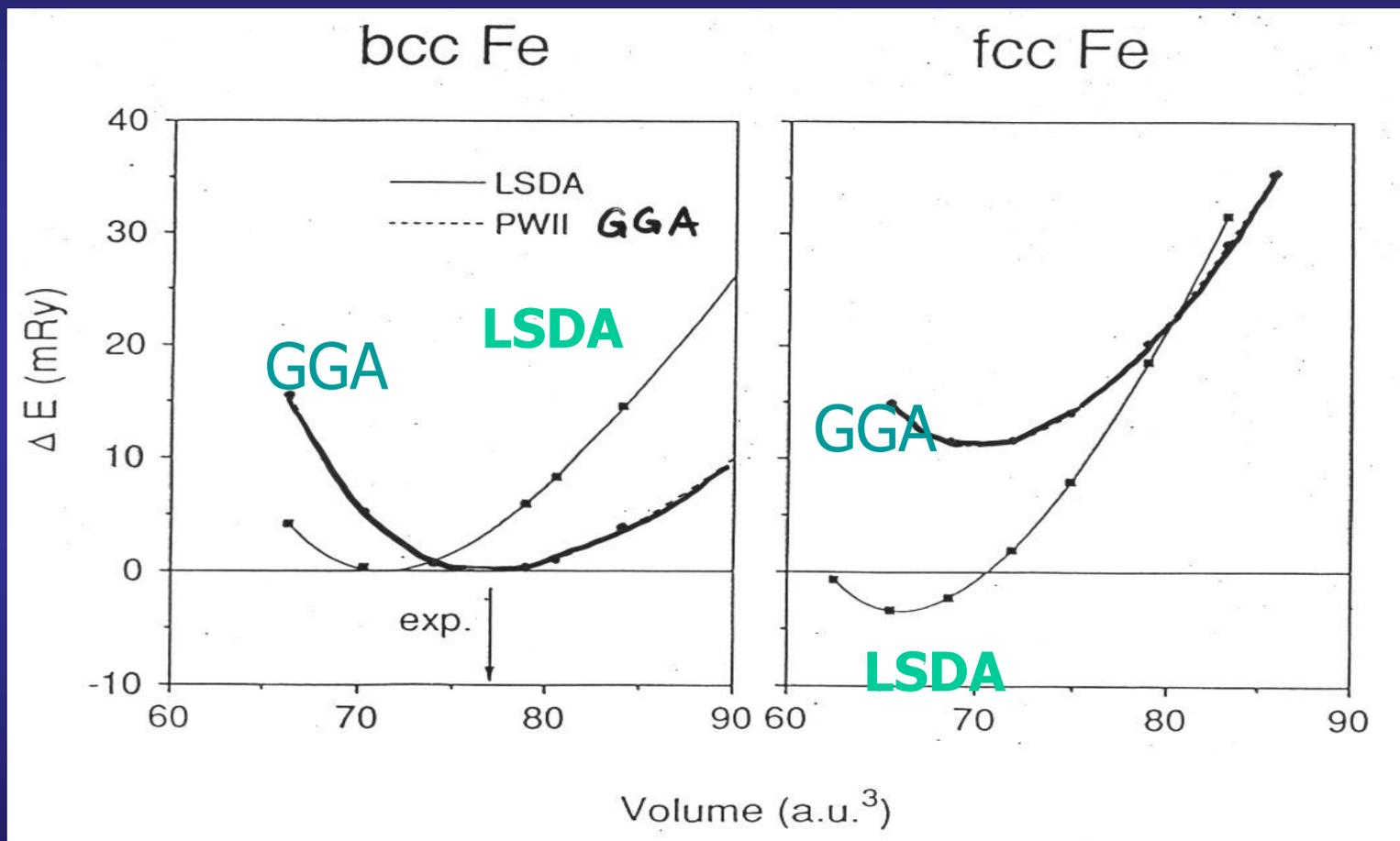
Accuracy of the xc functionals in the structural and electronic properties

	LDA	GGA
a	-1% , -3%	+1%
B	+10, +40%	-20%, +10%
E_c	+15%	-5%
E_{gap}	-50%	-50%

LDA: crude approximation but sometimes is accurate enough (structural properties, ...).

GGA: usually tends to overcompensate LDA results, not always better than LDA.

In some cases, GGA is a must: DFT ground state of iron



LSDA

- NM
- fcc
- in contrast to experiment

GGA

- FM
- bcc
- Correct lattice constant

Experiment

- FM
- bcc

Results obtained with Wien2k.

Courtesy of Karl H. Schwartz

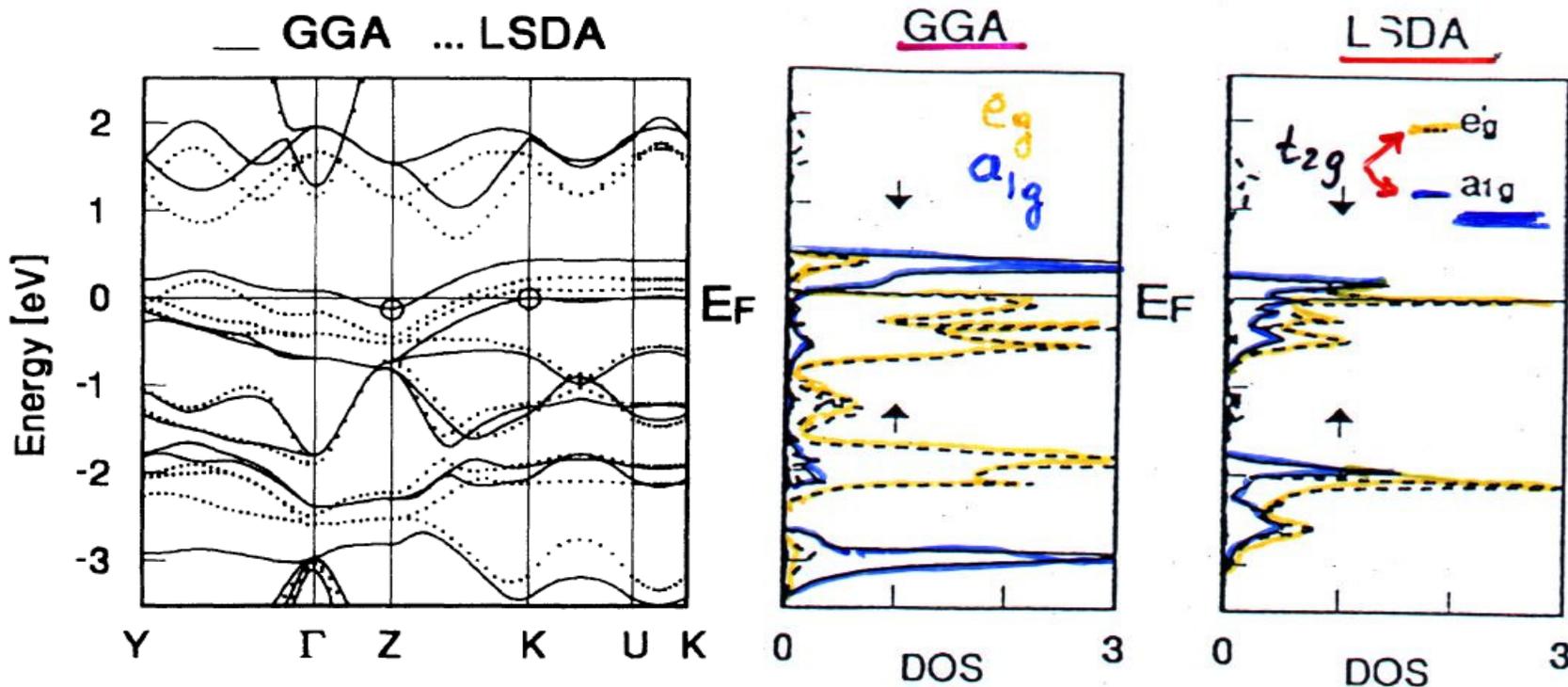
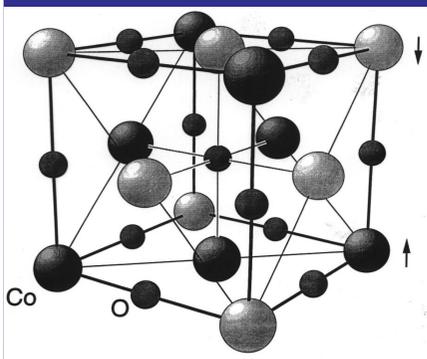
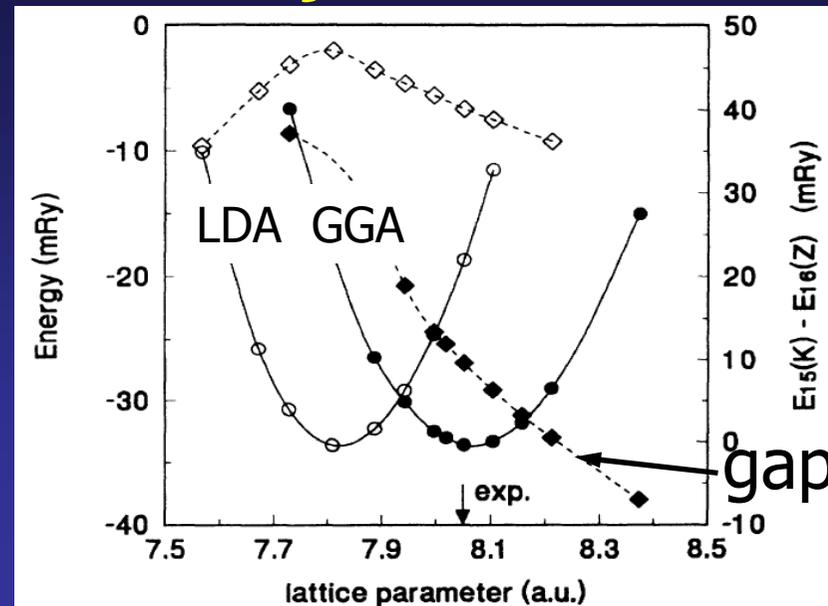
Kohn-Sham fails in strongly correlated systems

CoO

- in NaCl structure
- **antiferromagnetic: AF II**
- **insulator**
- t_{2g} splits into a_{1g} and e_g
- Both LDA and GGA find them to be metals (although GGA almost splits the bands)

Results obtained with Wien2k.

Courtesy of Karl H. Schwartz



The number of citations allow us to gauge the importance of the works on DFT

11 papers published in APS journals since 1893 with >1000 citations in APS journals (~5 times as many references in all science journals)

Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

Publication	# cites	Av. age	Title	Author(s)
<i>PR</i> 140, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
<i>PR</i> 136, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
<i>PRB</i> 23, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
<i>PRL</i> 45, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
<i>PR</i> 108, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
<i>PRL</i> 19, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
<i>PRB</i> 12, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
<i>PR</i> 124, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
<i>RMP</i> 57, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
<i>RMP</i> 54, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
<i>PRB</i> 13, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

PR, *Physical Review*; *PRB*, *Physical Review B*; *PRL*, *Physical Review Letters*; *RMP*, *Reviews of Modern Physics*.

From *Physics Today*, June, 2005

What are the main approximations?

Born-Oppenheimer

Decouple the movement of the electrons and the nuclei.

Density Functional Theory

Treatment of the electron – electron interactions.

Pseudopotentials

Treatment of the (nuclei + core) – valence.

Basis set

To expand the eigenstates of the hamiltonian.

Numerical evaluation of matrix elements

Efficient and self-consistent computations of H and S .

Supercells

To deal with periodic systems

Treatment of the boundary conditions

Isolated objects (atoms, molecules, clusters)

open boundary conditions
(defined at infinity)

3D periodic objects (crystals)

periodic boundary conditions
(might be considered as the repetition of a
building block, the unit cell)

Mixed boundary conditions

1D periodic (chains)

2D periodic (slabs and interfaces)

Periodic systems are idealizations of real systems

Conceptual problems

NO exactly periodic systems in Nature

(periodicity broken at the boundary)

BUT

The great majority of the **physical quantities**
are **unaffected by** the existence of a **border**

Periodic systems are idealizations of real systems

Computational problems

1. In a periodic solid:

∞ Number of atoms

∞ Number and electrons

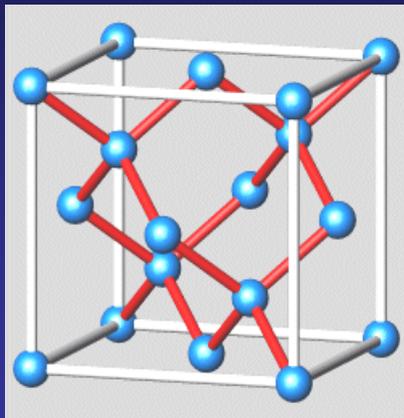


∞ Number of wave functions ??

2. Wave function will be extended over the entire solid (∞)

Bloch theorem will rescue us!!

A periodic potential commensurate with the lattice. The Bloch theorem



$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

Bloch Theorem: The eigenstates of the one-electron Hamiltonian in a periodic potential can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice.

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r}) \quad u_{n,\vec{k}}(\vec{r} + \vec{R}) = u_{n,\vec{k}}(\vec{r})$$

$$\text{Periodicity in reciprocal space} \left\{ \begin{array}{l} \psi_{n, \vec{k} + \vec{K}'}(\vec{r}) = \psi_{n\vec{k}}(\vec{r}) \\ \varepsilon_{n, \vec{k} + \vec{K}'} = \varepsilon_{n, \vec{k}} \end{array} \right.$$

The wave vector k and the band index n allow us to label each electron (good quantum numbers)

The Bloch theorem changes the problem

Instead of computing an **infinite** number of electronic **wave functions**

Finite number of **wave functions** at an infinite number of k-points.

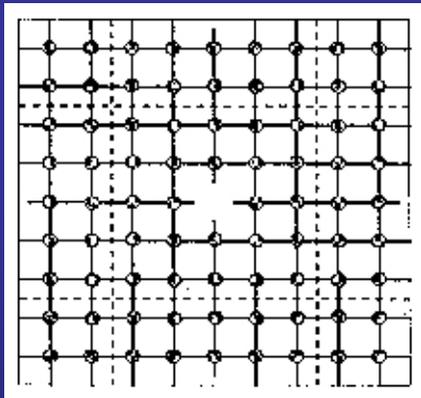
In practice: electronic wave functions at k-points that are very close together will be almost identical \Rightarrow

It is possible to represent electronic wave functions over a region of k-space by the wave function at a single k-point.

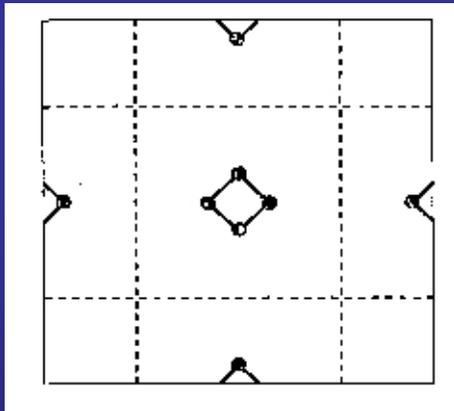
$$\int d\vec{k} \longrightarrow \sum_{\vec{k}} \Delta\vec{k}$$

Systems with open and mixed periodic boundary conditions are made artificially periodic: supercells

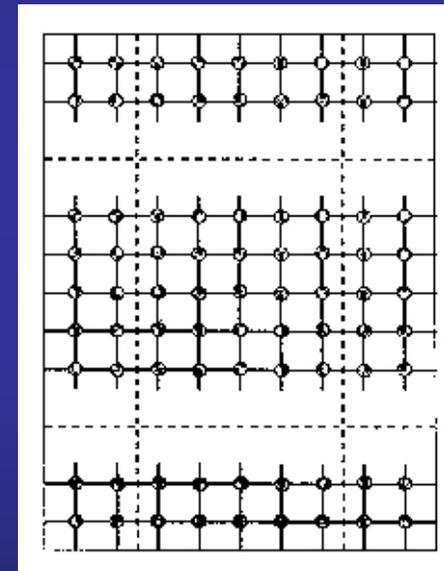
Defects



Molecules



Surfaces



M. C. Payne *et al.*, Rev. Mod. Phys., 64, 1045 (1992)

Recap

Born-Oppenheimer approximation

Electron nuclear decoupling

Many electron problem treated within DFT (LDA, GGA)

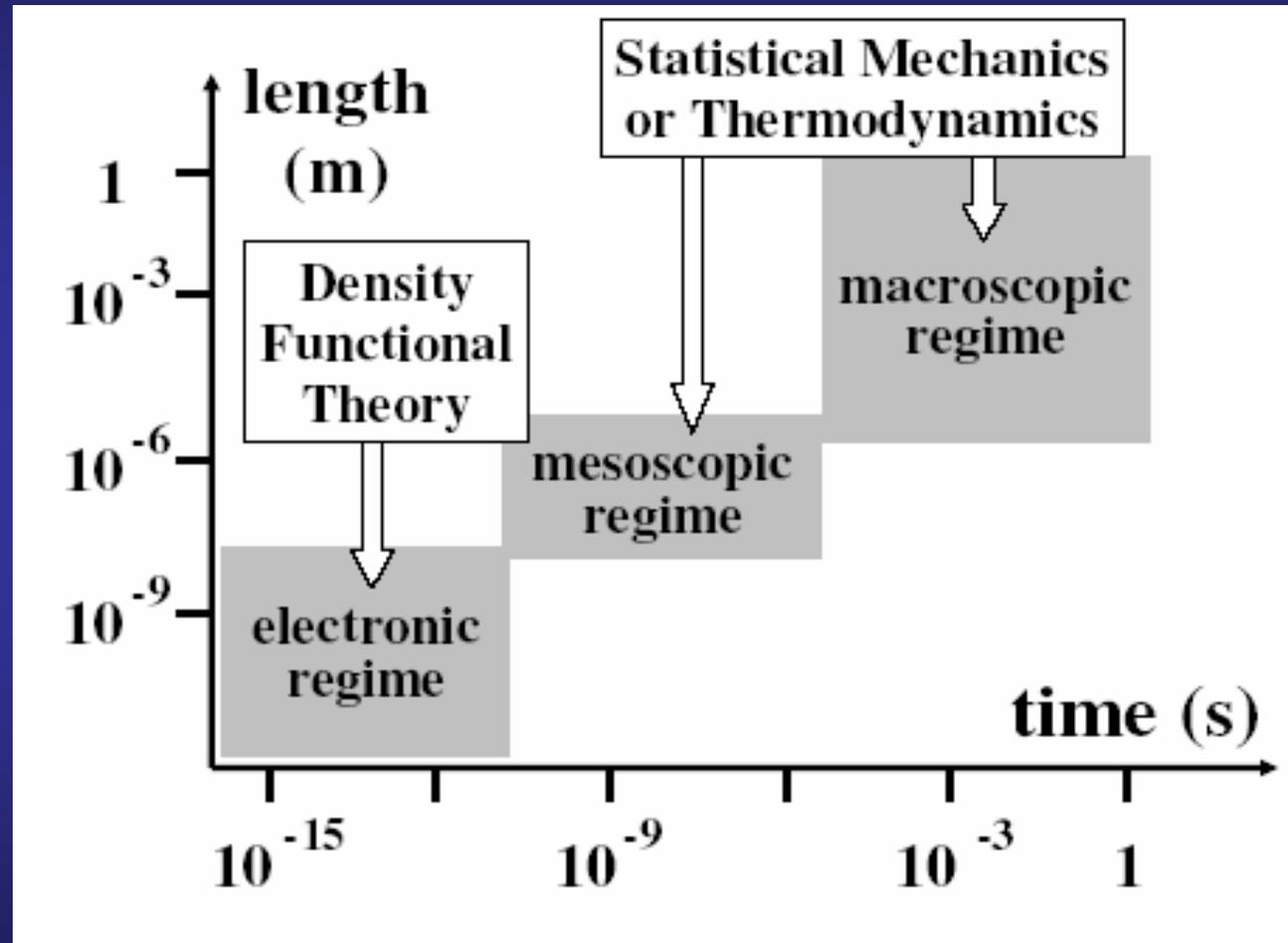
One electron problem in effective self-consistent potential
(iterate)

Extended crystals: periodic boundary conditions + k-sampling

Supplementary information

Length and time scales:

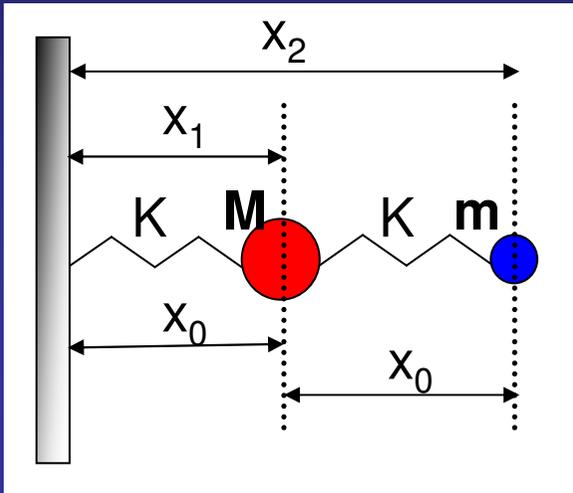
More suitable methods for a particular problem



K. Reuter, C. Stampfl, and M. Scheffler, cond-mat/0404510

A classical view of the Born-Oppenheimer approximation

In equilibrium



Atomic positions

$$x_1 = x_0$$

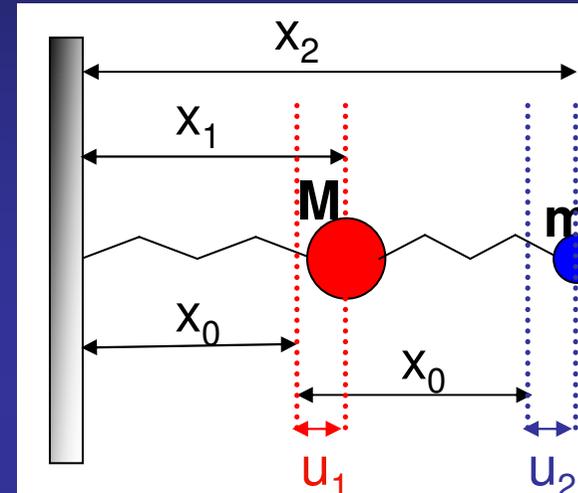
$$x_2 = 2x_0$$

Length of the springs

$$l_1 = x_0$$

$$l_2 = x_0$$

Out of equilibrium



Atomic displacements

$$u_1 = x_1 - x_0$$

$$u_2 = x_2 - 2x_0$$

Spring's elongation

$$\Delta l_1 = x_1 - x_0$$

$$\Delta l_2 = x_2 - x_1 - x_0$$

The potential energy of the system equals:

$$V = \frac{1}{2}K (x_1 - x_0)^2 + \frac{1}{2}K (x_2 - x_1 - x_0)^2 \quad ; K > 0$$

And the equation of motion of the two particles:

$$\begin{array}{l|l} M\ddot{x}_1 = -K(x_1 - x_0) + K(x_2 - x_1 - x_0) & \ddot{u}_1 = -\omega_N^2 u_1 + \omega_N^2 (u_2 - u_1) \quad \omega_N = \sqrt{\frac{K}{M}} \\ m\ddot{x}_2 = -K(x_2 - x_1 - x_0) & \ddot{u}_2 = -\omega_e^2 (u_2 - u_1) \quad \omega_e = \sqrt{\frac{K}{m}} \end{array}$$

A classical view of the Born-Oppenheimer approximation

$$\begin{aligned}\ddot{u}_1 &= -\omega_N^2 u_1 + \omega_N^2 (u_2 - u_1) & \omega_N &= \sqrt{\frac{K}{M}} \\ \ddot{u}_2 &= -\omega_e^2 (u_2 - u_1) & \omega_e &= \sqrt{\frac{K}{m}}\end{aligned}$$

Making the change of variables $u \equiv u_2 - u_1$

$$\ddot{u}_1 = -\omega_N^2 u_1 + \omega_N^2 u$$

$$\ddot{u} = \omega_N^2 u_1 - (\omega_N^2 + \omega_e^2) u$$

Seek stationary solutions of the kind: $u_1 = \Re(\alpha e^{i\omega t})$ $u = \Re(\beta e^{i\omega t})$

$$\begin{pmatrix} \omega_N^2 - \omega^2 & -\omega_N^2 \\ -\omega_N^2 & \omega_e^2 + \omega_N^2 - \omega^2 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Solving this equation, we find two solutions for ω , ω_1 and ω_2 , each with the corresponding eigenvector (normal between them)

$$\omega_1^2 \rightarrow \{\alpha_1, \beta_1\} \quad \omega_2^2 \rightarrow \{\alpha_2, \beta_2\} \quad \alpha_1 \alpha_2 + \beta_1 \beta_2 = 0$$

A classical view of the Born-Oppenheimer approximation

The equation

$$\begin{pmatrix} \omega_N^2 - \omega^2 & -\omega_N^2 \\ -\omega_N^2 & \omega_e^2 + \omega_N^2 - \omega^2 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

has non trivial solutions if and only if

$$\det [\mathbf{H} - \omega^2 \mathbf{I}] = 0, \quad \mathbf{H} = \begin{pmatrix} \omega_N^2 & -\omega_N^2 \\ -\omega_N^2 & \omega_e^2 + \omega_N^2 \end{pmatrix}, \quad \mathbf{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Assuming that $M \gg m \Rightarrow \omega_N^2 \ll \omega_e^2$, so we can decompose

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}', \quad \mathbf{H}_0 = \begin{pmatrix} 0 & 0 \\ 0 & \omega_e^2 \end{pmatrix}, \quad \mathbf{H}' = \begin{pmatrix} \omega_N^2 & -\omega_N^2 \\ -\omega_N^2 & \omega_N^2 \end{pmatrix}$$

Then, \mathbf{H}' is just a perturbation of \mathbf{H}_0

Then, at first order, the only thing we have to do is find the eigenvalue of \mathbf{H}_0

A classical view of the Born-Oppenheimer approximation

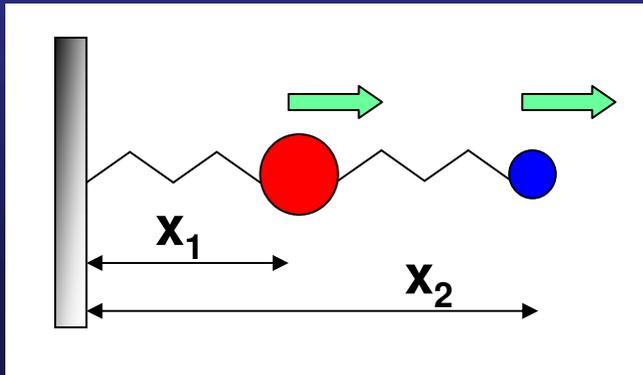
Solution at first-order:

$$\det [\mathbf{H}_0 - \omega^2 \mathbf{I}] = \begin{vmatrix} -\omega^2 & 0 \\ 0 & \omega_e^2 - \omega^2 \end{vmatrix} = 0$$

Mode 1

$$\omega_1^2 = 0 \rightarrow |N\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$u(t) = u_2(t) - u_1(t) = 0 \Rightarrow u_1(t) = u_2(t)$$



Mode 2

$$\omega_2^2 = \omega_e^2 \rightarrow |e\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$u_1(t) = 0$$

$$u(t) = u_2(t) - u_1(t) = u_2(t) = \Re(e^{i\omega_e t})$$

