

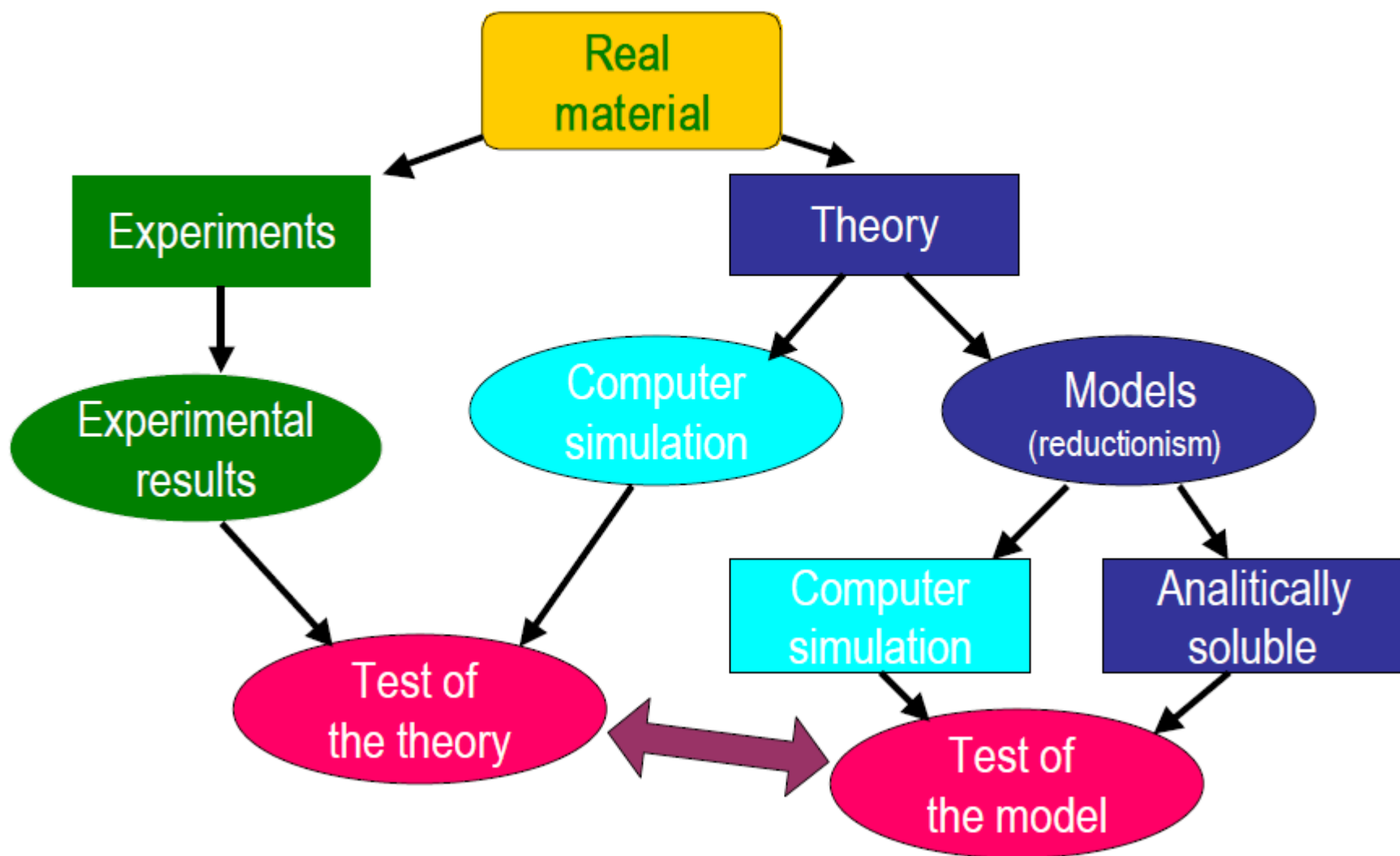


Cálculos ab initio de propiedades estructurales, electrónicas, magnéticas e hiperfinas de sólidos.

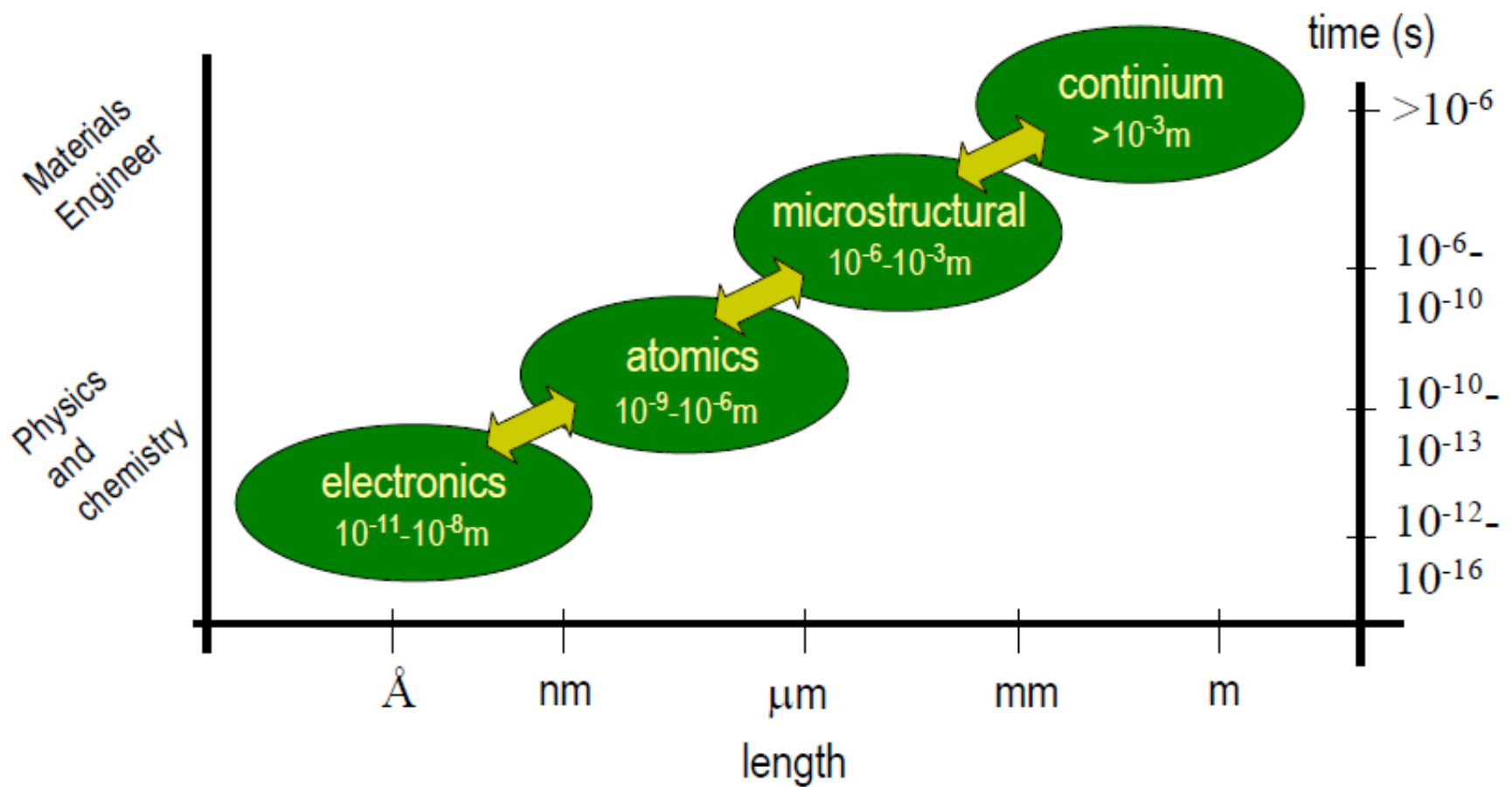
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Computer simulation



Space and time in materials



Una posibilidad para estudiar sistemas que contienen muchos átomos (“sistemas complejos”) es emplear simulaciones computacionales.

Modelos clásicos: basados en esquemas semiempíricos.

Interacción entre los átomos se modela de forma tal de reproducir ciertos datos experimentales.

Alto grado de sofisticación

Muy útiles a nivel de ingeniería y cuando diferentes parámetros experimentales son conocidos con mucha precisión *en un conjunto de materiales estructural y electrónicamente similares.*

Si estos parámetros no son conocidos o el material en estudio presenta comportamientos anómalos o no bien comprendidos, este tipo de métodos no son adecuados, y es preferible una aproximación de

primeros principios.

Desventaja: demandante desde el punto de vista de requerimientos y tiempos computacionales.

Ventaja: no requieren ningún tipo de parámetro externo o conocimiento experimental del sistema en estudio.

Dos tipos de aproximaciones dentro del tratamiento cuántico :

Hartree Fock (HF)

Teorema de la Funcional Densidad (DFT).

HF: esquema tradicional, descripción de funciones de onda. En esta aproximación el intercambio exacto, correlación no es tenida en cuenta.

DFT: densidad electrónica, correlación e intercambio ambos en forma aproximada.

Aproximación universal al problema cuántico de un sistema de partículas cargadas (electrones) interactuantes en un potencial externo (el generado por los núcleos).


- Equation of the system

$$H|\Psi\rangle = E|\Psi\rangle$$

- Solid state physics hamiltonian:

$$(T_{ion} + T_e + V_{e-e} + V_{e-ion} + V_{ion-ion})\Psi(r_1, \dots, r_N; R_1, \dots, R_M) = E\Psi(r_1, \dots, r_N; R_1, \dots, R_M)$$

- Adiabatic approximation: splitting of the ionics and electronics degree of freedom



$$(T_e + V_{e-e} + V_{e-ion} + V_{ion-ion})\Phi(r_1, \dots, r_N; \{R\}) = \varepsilon(\{R\})\Phi(r_1, \dots, r_N; \{R\})$$

Electrons $(T_e + V_{e-e} + V_{e-ion} + V_{ion-ion})\Phi(r_1, \dots, r_N; \{R\}) = \mathcal{E}(\{R\})\Phi(r_1, \dots, r_N; \{R\})$

• **knowing $\mathcal{E}(R)$ we can have:**

- Ground state (T=0)
- Crystalline structure and PV diagram
- Elastic, optics, magnetics, etc, properties
- Potential energy surface
- Interatomic potential
 \Rightarrow **interatomic forces**

Electrons : solution of the Schrödinger Eq.

- Hamiltonian of a many electrons system:

$$\left(\sum_{j=1}^N -\frac{\hbar^2}{2m} \nabla_j^2 + V_{e-e} + V_{ext} \right) \Phi(\vec{r}_1, \dots, \vec{r}_N) = E \Phi(\vec{r}_1, \dots, \vec{r}_N)$$

- To look for the GS by means of a variational method:

$$E_0[\Phi_0] = \text{Min}_{\tilde{\Phi}} \langle \tilde{\Phi} | H | \tilde{\Phi} \rangle$$

$$\tilde{\Phi}(\vec{r}_1, \dots, \vec{r}_N) \quad 3N \text{ dimensions trial function}$$

- **Approximate Methods** : one electron selfconsistent equations

Hartree: $\Phi(\vec{r}_1, \dots, \vec{r}_N) = \phi_1 \dots \phi_N$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{Z}{r} + \int \frac{n(r')}{|r-r'|} dr' \right) \phi_i = \varepsilon_i \phi_i, \quad \text{con } n(r) = \sum_i |\phi_i|^2$$

Hartree-Fock: $\Phi(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \det[\phi_1 \dots \phi_{N_i}]$

Density Functional Theorem

1927: Thomas and Fermi: Semiclassical model for isolated heavy atoms in terms of the electronic density $\rho(r)$ of the ground state of the atoms.

1930: Dirac: Generalization of the theory: “Thomas-Fermi-Dirac Theory”.

1964: Hohenberg and Kohn

Hohenberg and Kohn Theorem: The total energy of a system of N electrons in an external potential can be written as a functional of $\rho(r)$

$$E = E[\rho(r)]$$

$$E = E[\rho(r)_{\uparrow}, \rho(r)_{\downarrow}]$$

The “good” $\rho(r)$ is those that minimize $E[\rho(r)]$

But:

Explicit form of $E[\rho(\mathbf{r})]$?



Approximations!!

$$E = E^{\text{hartree}} + E^{\text{exchange and correlation}}$$

$$E[\rho(r)] = T[\rho(r)] + E_H[\rho(r)] + E_{nn}[\rho(r)] + E_{xc}[\rho(r)]$$

$$E_H[\rho(r)] = \frac{e^2}{2} \int d^3r d^3r' \frac{\rho(r)\rho(r')}{|r-r'|}$$


- Remember, DFT is a great theory
- Highly accurate structures
- Sufficient accuracy for a huge range of problems
- Efficient!

- But it is not perfect


- DFT is an exact theory
- KS is an exact way of doing DFT
- The problem comes from our choice of $E_{xc}[\rho]$

Exchange and correlation

Different approximations

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

$\varepsilon_{xc}[\rho(r)]$ must reproduce the energy of
the electron gas.

GGA  $\varepsilon_{xc} = \varepsilon_{xc}[\rho(r), |\nabla\rho(r)|]$

- In Hartree-Fock (and KS) theory the Coulomb energy is

$$J[\rho] = \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}$$

- Includes interaction of each electron with *all* — including itself!
- In HF theory the self-interaction is exactly cancelled by exchange

$$J[\rho] = +\frac{1}{2} \sum_{ij} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\psi_i^*(\vec{r}_1)\psi_i(\vec{r}_1)\psi_j^*(\vec{r}_2)\psi_j(\vec{r}_2)}{r_{12}}$$

$$E_x^{\text{HF}} = -\frac{1}{2} \sum_{ij} \int d\vec{r}_1 \int d\vec{r}_2 \frac{\psi_i^*(\vec{r}_1)\psi_j(\vec{r}_1)\psi_j^*(\vec{r}_2)\psi_i(\vec{r}_2)}{r_{12}}$$

- Functionals in the form

$$E_{xc}[\rho] = \int d\vec{r} f(\rho(\vec{r}))$$

can never treat this correctly

- Local information not enough
- Even semi-local functionals fail

$$E_{xc}[\rho] = \int d\vec{r} f(\rho(\vec{r}), |\vec{\nabla}\rho|(\vec{r}), \dots)$$

- Exact exchange doesn't help — this is a correlation problem

Kohn and Sham (1965): “Kohn and Sham equations”

$$(T + V_{en}(r) + V_H(r) + V_{xc}(r))\mathcal{G}_i(r) = \varepsilon_i \mathcal{G}_i(r)$$

And $\rho(r)$ given by:

$$\rho(r) = \sum_{oc} \mathcal{G}_i^*(r) \mathcal{G}_i(r)$$

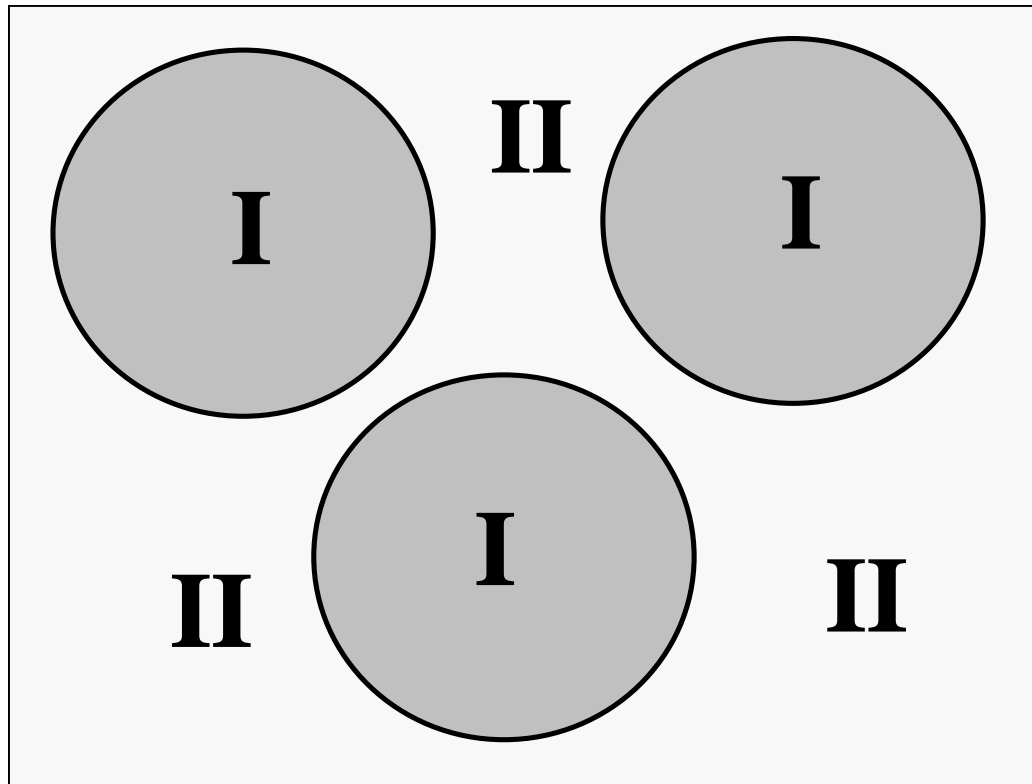
Methods of calculation

$$\mathcal{G}_i(\bar{r}) = \sum_{\alpha} C_{i,\alpha} \Phi_{\alpha}(\bar{r})$$

The basis is “defined” by the problem under study.

The APW Method

J. C. Slater, *Phys. Rev.* **51**, 846 (1937).



Two different basis:

Atomic spheres

$$\mathcal{G}(\bar{r}) = \sum_{l,m} A_{l,m} u_l(r) Y_{l,m}(\bar{r})$$

$$\left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right\} r u_l(r) = 0$$

Interstitial region

$$\mathcal{G}(\bar{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\bar{G}} C_{\bar{G}} e^{i(\bar{G}+\bar{k})\bar{r}}$$

$$A_{l,m} = \frac{4\pi i^l}{\sqrt{\Omega} u_l(E_l, R_i)} \sum_{\bar{G}} C_{\bar{G}} J_l(|\bar{G} + \bar{k}| R_i) Y_{l,m}^*(\bar{k} + \bar{G})$$

Problem: $u_l(r)$ are solution of the Radial Schrodinger equation only at E_l .

The FP-LAPW Method

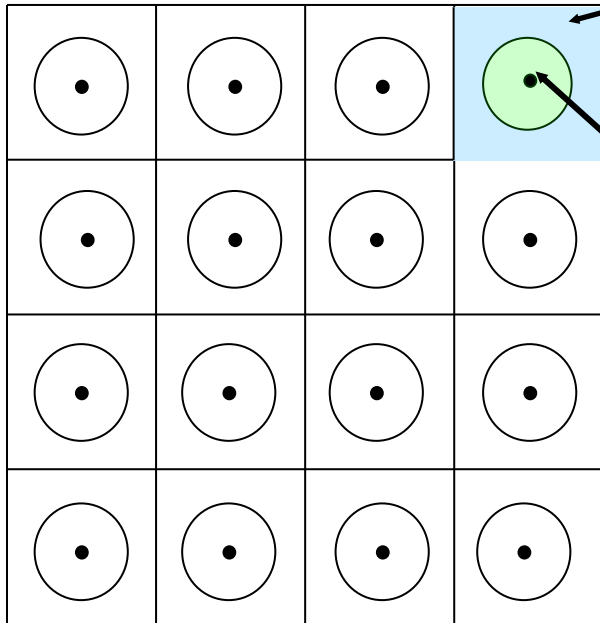
Interstitial region

$$\mathcal{G}(\bar{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\bar{G}} C_{\bar{G}} e^{i(\bar{G}+\bar{k})\bar{r}}$$

Atomic spheres

$$\mathcal{G}(\bar{r}) = \sum_{l,m} [A_{l,m} u_l(r, E_l) + B_{l,m} \dot{u}_l(r, E_l)] Y_{l,m}(\bar{r})$$

$$\left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E_l \right\} r \dot{u}_l(r) = r u_l(r)$$



$$\varphi(r) = \frac{1}{\Omega^{1/2}} \sum_G C_G e^{i(G+K)r}$$

$$\varphi(r) = \sum_{m,l} [A_{l,m} u(r) + B_{l,m} \dot{u}_l(r)] Y_{l,m}(r)$$

non-relativistic
relativistic

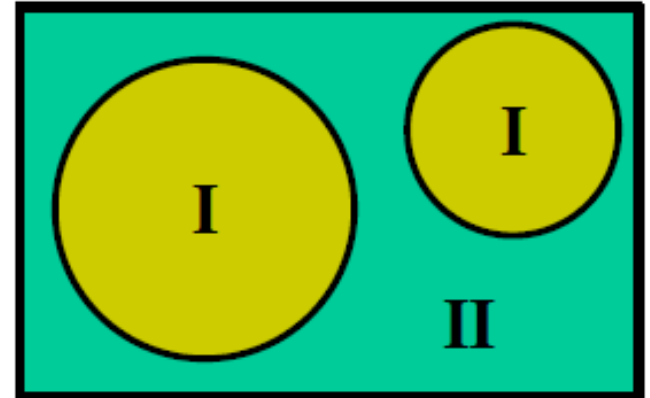
all-electron full-potential
all-electron muffin-tin
pseudopotenciales
jellium

LDA
GGA

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + v_{xc}(\vec{r}) \right] \varphi_i^k = \varepsilon_i^k \varphi_i^k$$

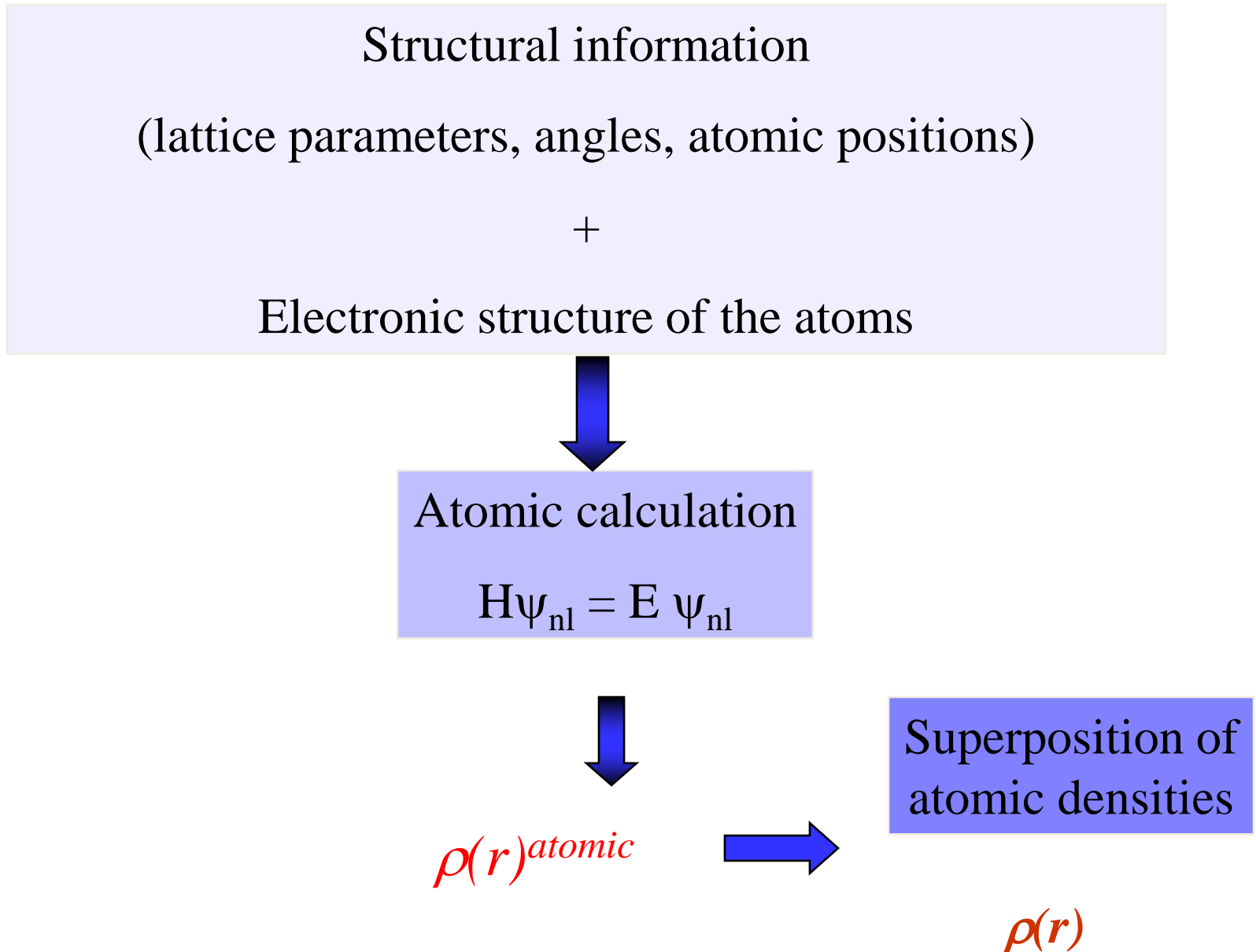
periodic
no-periodic

spin-polarized
non spin-polarized



linearized augmented
plane wave: LAPW
scattering functions
(ex.: Hankel): LMTO
plane wave
LCAO

General scheme of the calculation



$$\rho(r) \longrightarrow \nabla^2 V_C = -8\pi \rho(r)$$

$$V = V_C + V_{EXC}$$

$$[-\nabla^2 + V]\psi_k = E_k \psi_k$$

$$E_k, \psi_k$$

$$\rho(r)_{val} = \sum_{E_k < E_F} \psi_k^* \psi_k \quad \rho(r)_{core}$$

$$\rho(r)_{new} = \rho_{old} \otimes (\rho_{val} + \rho_{core})$$

We finish our calculation. What is the result of this calculation?

Of course, $\rho(r)$.

From $\rho(r)$ we can obtain the electrostatic potential and the energy of the ground state of the system under study.

$$V(\mathbf{r}) = \begin{cases} \sum_{l,m} V_{l,m}(\mathbf{r}) Y_{l,m}(\bar{\mathbf{r}}) & (I) \\ \sum_K V(K) \exp(iK\bar{\mathbf{r}}) & (II) \end{cases}$$

No shape approximations for the potential (“Full potential”)

20 years ago:
 only $l = 0, m = 0$
 and $k = 0$
 (“muffin tin approximation”)

