Introduction to Density Functional Theory

a short PhD course
March 2024

by
Antimo Marrazzo
Maria Peressi

From foundations…

- ab-initio methods
- nuclei and electrons
- Born-Oppenheimer approximation
- limits of one-electron scheme
- density functional theory:
  - Hoenberg-Kohn theorem
  - functionals
  - one-electron (Kohn-Sham) equations and self-consistent cycle

… to practical implementation (towards Quantum Espresso suite of codes):

- pseudopotentials
- basis sets for wavefunctions (plane waves) and periodic systems
- k-point sampling for integrals in the Brillouin zone

with physical approximation and numerical issues

Ab-initio methods

PURPOSES: to describe and explain material properties at a quantum and atomic level

INGREDIENTS: Electrons / nuclei / interactions; NO external parameters

METHOD: solution of Schr. Eq. through:

– modeling (physical approximations)

– algorithms for a numerical solution

PECULIARITIES: reliable / predictive power / extensively used in materials of medium complexity and for a wide range of physical properties (mainly related to the ground state; extended with limitations also to excited states -e.g. optical spectra-)

Ab initio simulations

A many-body problem:

$$H_{tot} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_I \frac{\mathbf{P}_I^2}{2M_I} + \sum_i V_{nucl}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{r_{ij}} + \frac{1}{2}\sum_{I\neq J} \frac{Z_I Z_J e^2}{R_{IJ}}$$

$$V_{nucl}(\mathbf{r}) = -\sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|}$$

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$$

$$R_{IJ} = |\mathbf{R}_I - \mathbf{R}_J|$$

Indicating with V the total (e-e, e-nucl., nucl-nucl., ext.) the total potential...

Ab initio simulations

... the time-dependent Schr eq. reads:

$$i\hbar\frac{\partial\Phi(r,R;t)}{\partial t}=\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R_I^2}-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r_i^2}+V(r,R)\right)\Phi(r,R;t)$$

A <u>physical</u> approximation: Born-Oppenheimer (adiab.) (M>>m)

Classic eq. of motion for nuclei fixing electrons -> E (**R**):

$$M\ddot{R}_I=-\frac{\partial E(R)}{\partial R_I}$$

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r_i^2}+V(r,R)\right)\Psi(r|R)=E(R)\Psi(r|R)$$

Electr. Hamiltonian for nuclei fixed in {**R**}

Hartree-Fock method for electrons

- Also the electronic problem is a difficult one (many-body, interacting) -> yet another physical approx. is necessary

- One-electron approx.: interacting but independent electrons (NO correlations):

- the ground-state can be written as an individual Slater determinant (antisymmetrized product of one-electron spin- orbitals)

$$\Psi_0(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \ldots \mathbf{r}_{\mathrm{N}}\sigma_N) = \mathcal{A}\{\psi_1(\mathbf{r}_1\sigma_1)\psi_2(\mathbf{r}_2\sigma_2)\ldots\psi_N(\mathbf{r}_N\sigma_N)\}$$

$$\psi_i(\mathbf{r}\sigma) = \phi_i(\mathbf{r})\chi_i(\sigma)$$

How to overcome the limits of one-electron methods?

- Instead of looking for better approximations to the many-body wavefunction, let’s follow an alternative way:

- Focus on the one-particle electron density n(**r**) which is easier to treat (less degrees of freedom)

- HOENBERG-KOHN THEOREM: correspondence

ground state of a system characterized by n(**r**) <=> external potential

Great idea ! **Walter Kohn:**
Nobel prize in Chemistry, 1998

$$\boxed{H_e = H_{int} + V_{ext}}$$

$$H_{int} = T + V_{ee} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{r_{ij}}$$

$$V_{ext} = \sum_i v_{ext}(\mathbf{r}_i) = \sum_i \int v_{ext}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_i)d\mathbf{r}$$

$$v_{ext}(\mathbf{r}) \equiv V_{nucl}(\mathbf{r}) = -\sum_I \frac{Z_I e^2}{|\mathbf{r}-\mathbf{R}_I|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{R_{IJ}}$$

$\Psi_0(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N})$: Many-body wfc

$n(\mathbf{r}) = \langle\Psi_0|\sum_i \delta(\mathbf{r}-\mathbf{r}_i)|\Psi_0\rangle$: Single-particle density

$$\langle\Psi_0|V_{ext}|\Psi_0\rangle = \int n(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r}$$

(1 PART): V_{ext} => n (**r**) is trivial:

$v_{ext}(\mathbf{r}) \Longrightarrow \Psi_0[v_{ext}] \Longrightarrow n(\mathbf{r})$ i.e., $\boxed{n(\mathbf{r}) = F[v_{ext}]}$

(2 PART): V_{ext} <= n (**r**) is NOT trivial: (per absurdum)

$$\boxed{v_{ext} \neq \overline{v}_{ext} \Longrightarrow n(\mathbf{r}) \neq \overline{n}(\mathbf{r})}$$

(and not only for a rigid shift)

i.e.,

$$\boxed{n(\mathbf{r}) \Longrightarrow V_{ext}(\mathbf{r})}$$

Let be: $\begin{array}{l} H = H_{int} + V_{ext} \\ \overline{H} = H_{int} + \overline{V}_{ext} \end{array}$ with: $\begin{array}{l} \Psi_0,\ E_0 \\ \overline{\Psi}_0,\ \overline{E}_0; \end{array}$

$$\begin{aligned} \langle\overline{\Psi}_0|H|\overline{\Psi}_0\rangle &= \langle\overline{\Psi}_0|H_{int} + V_{ext} + \overline{V}_{ext} - \overline{V}_{ext}|\overline{\Psi}_0\rangle \\ &= \overline{E_0} + \langle\overline{\Psi}_0|V_{ext} - \overline{V}_{ext}|\overline{\Psi}_0\rangle \\ &= \overline{E_0} + \int \overline{n}(\mathbf{r})[v_{ext}(\mathbf{r}) - \overline{v}_{ext}(\mathbf{r})]d\mathbf{r} \end{aligned}$$

For the variational principle:

$$\langle\Psi_0|H|\Psi_0\rangle < \langle\overline{\Psi}_0|H|\overline{\Psi}_0\rangle$$

i.e.:

$$E_0 < \overline{E}_0 + \int \overline{n}(\mathbf{r})[v_{ext}(\mathbf{r}) - \overline{v}_{ext}(\mathbf{r})]d\mathbf{r}$$

Similarly:

$$\overline{E}_0 < E_0 + \int n(\mathbf{r})[\overline{v}_{ext}(\mathbf{r}) - v_{ext}(\mathbf{r})]d\mathbf{r}$$

Combining the two we must exclude that

$$n = \overline{n}$$

Ok, $n(\mathbf{r})$ is a fundamental quantity...

But what will we do in practice to solve the Schr. eq.?
How to reduce the number of variables from 3N to 3 ?

The path:

From HK theorem
to single electron (Kohn-Sham) eqs.

HK theorem and functionals

Consequence of the HK theorem:

E is a functional $E[n(\mathbf{r})]$ of $n(\mathbf{r})$

$$E[n(\mathbf{r})] = \langle\Psi|T+U+V|\Psi\rangle = \langle\Psi|T+U|\Psi\rangle + \langle\Psi|V|\Psi\rangle$$
$$= F[n(\mathbf{r})] + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r}$$

$F[n(\mathbf{r})]$ is a universal functional of $n(\mathbf{r})$ (and not of $V(\mathbf{r})$)

(unknown!)

Problem: determine $n(\mathbf{r})$ which minimizes $E[n(\mathbf{r})]$

Kohn-Sham equations (I)

The system of interacting electrons is mapped on to a non- interacting electrons having the same density $n(\mathbf{r})$

For non-interacting electrons:

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

<= link between *n(**r**)* and single-electron wavefunctions

with $\psi_i(\mathbf{r})$ one-electron orthonormal orbitals (Kohn-Sham orbitals) satisfying:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \underbrace{V_H(\mathbf{r}) + V(\mathbf{r}) + V_{xc}(\mathbf{r})}_{= V_{KS}(\mathbf{r})}\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

But what is that?

Kohn-Sham equations (II)

recover the expression for the energy:

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r}$$

From the mapping on to a non-interacting system:

$$F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})]$$

with:

$$T_s[n(\mathbf{r})] = -\frac{\hbar^2}{2m}\sum_i \int \Psi_i^*(\mathbf{r})\nabla^2\Psi_i(\mathbf{r})d\mathbf{r}$$

kinetic energy of non-interacting electrons

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

Hartree energy:
electrostatic energy of non-interacting electrons

$$E_{xc}[n(\mathbf{r})]$$

exchange-correlation energy:

contains all the remaining terms!!! (unknown) tricks…

Local density approximation for the exchange-correlation energy

Kohn-Sham approximate the functional with a function of the density:

$$E_{xc}[n(\mathbf{r})] = \int \epsilon(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

But $\epsilon(n)$ is unknown even in case of homog. electron gas!

Use approximate forms !

Local density approximation: successes and failures

- simpler than other approaches (e.g. Hartree-Fock)
- several results of good quality (e.g. structural properties)
- good even in highly inhomogeneous systems such as atoms and molecules

- self-interaction not exactly cancelled
- overbinding (overestimate of cohesive energies ~20% and more; VdW interactions: absent by construction (due to charge fluctuations, not to overla but part of the attractive effect recovered by wrong overestimate of the overla
- underestimate of band gap in insulators (up to 50%!)

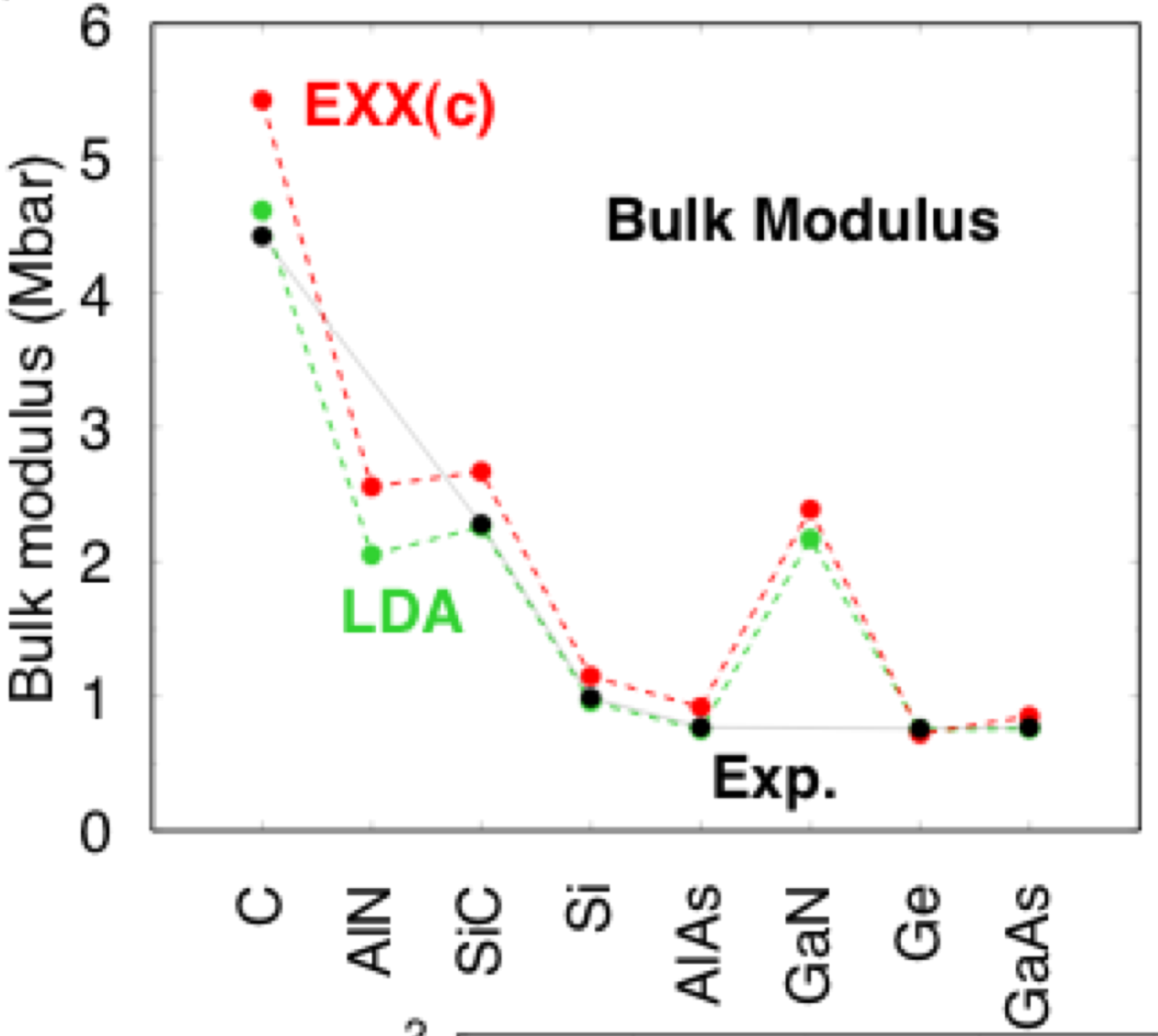
• several results of good quality (e.g. structural properties)

- Bulk moduli B to within ±10%.

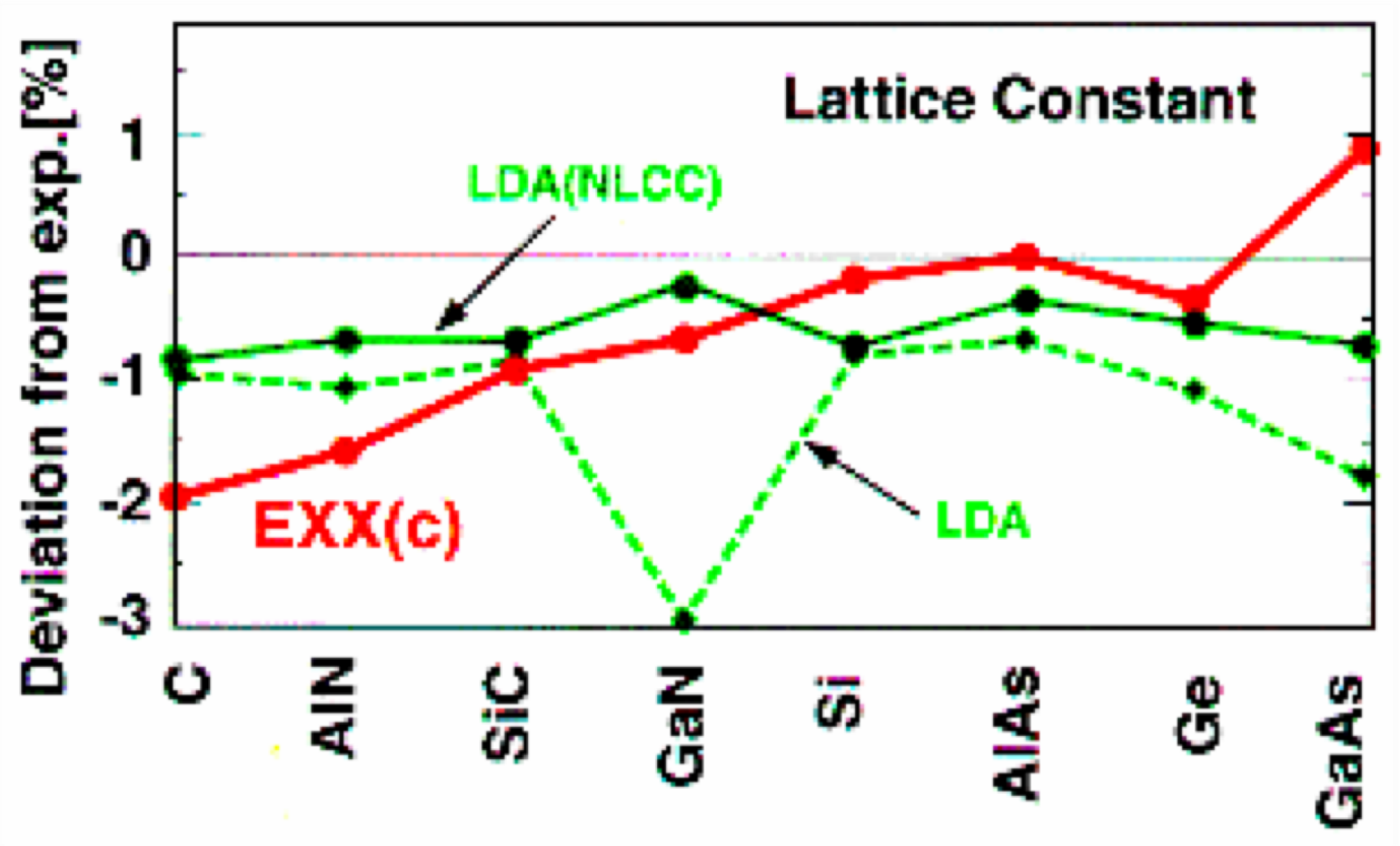
$$B = -V \left.\frac{\partial P}{\partial V}\right|_{V_0} = -V \left.\frac{\partial^2 E}{\partial V^2}\right|_{V_0}$$

V = crystal volume,

$P = \partial E/\partial V$ = pressure.



- Lattice constants to within −1%.



LDA(NLCC) = approximate treatment of core electrons.

LDA = core electrons not treated.

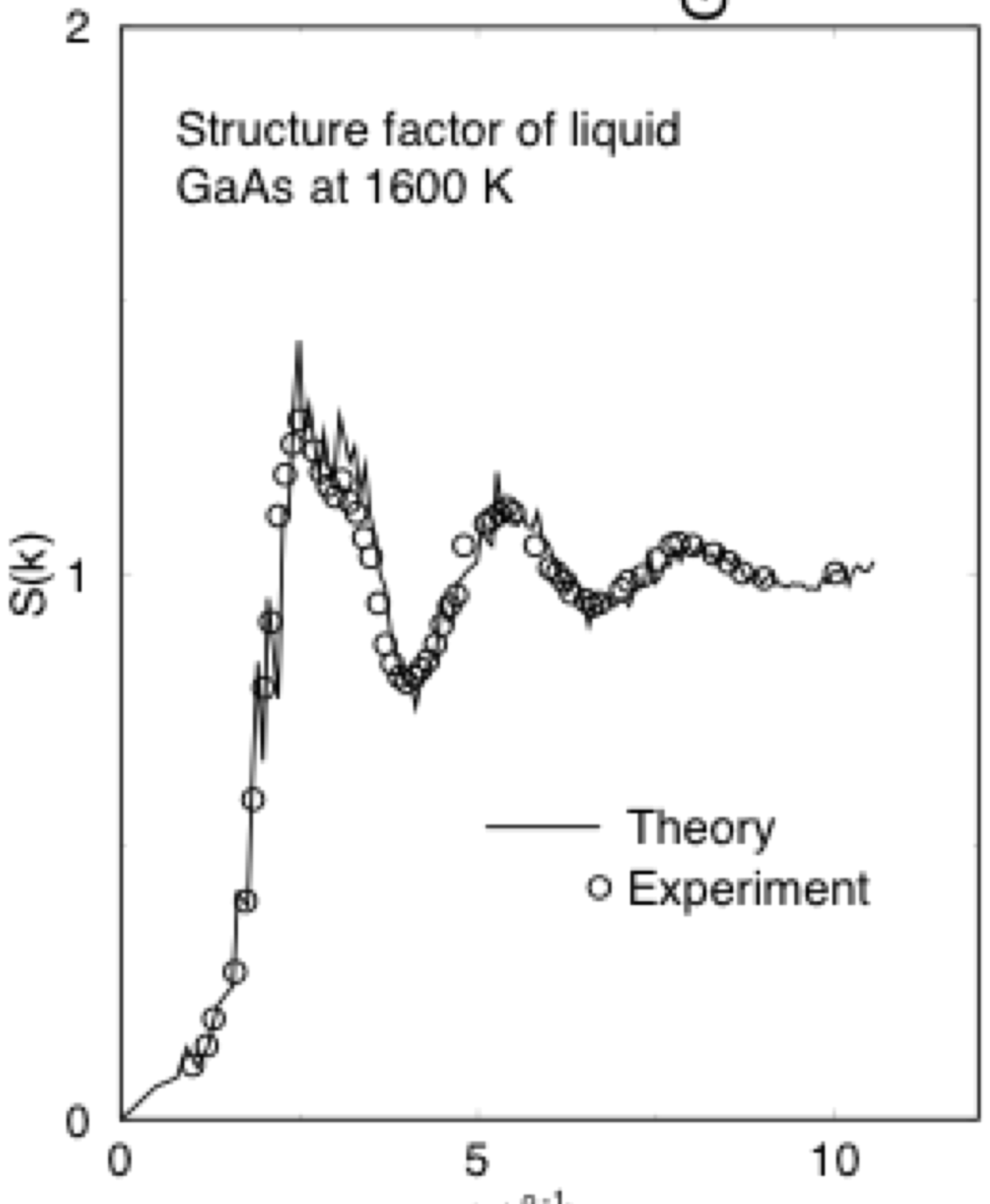
- Structure factor (⇒ pair correlation function) to within a few percent:

$$S(\mathrm{k}) = \frac{1}{N}\langle\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle - N\delta_{\mathbf{k},0}$$

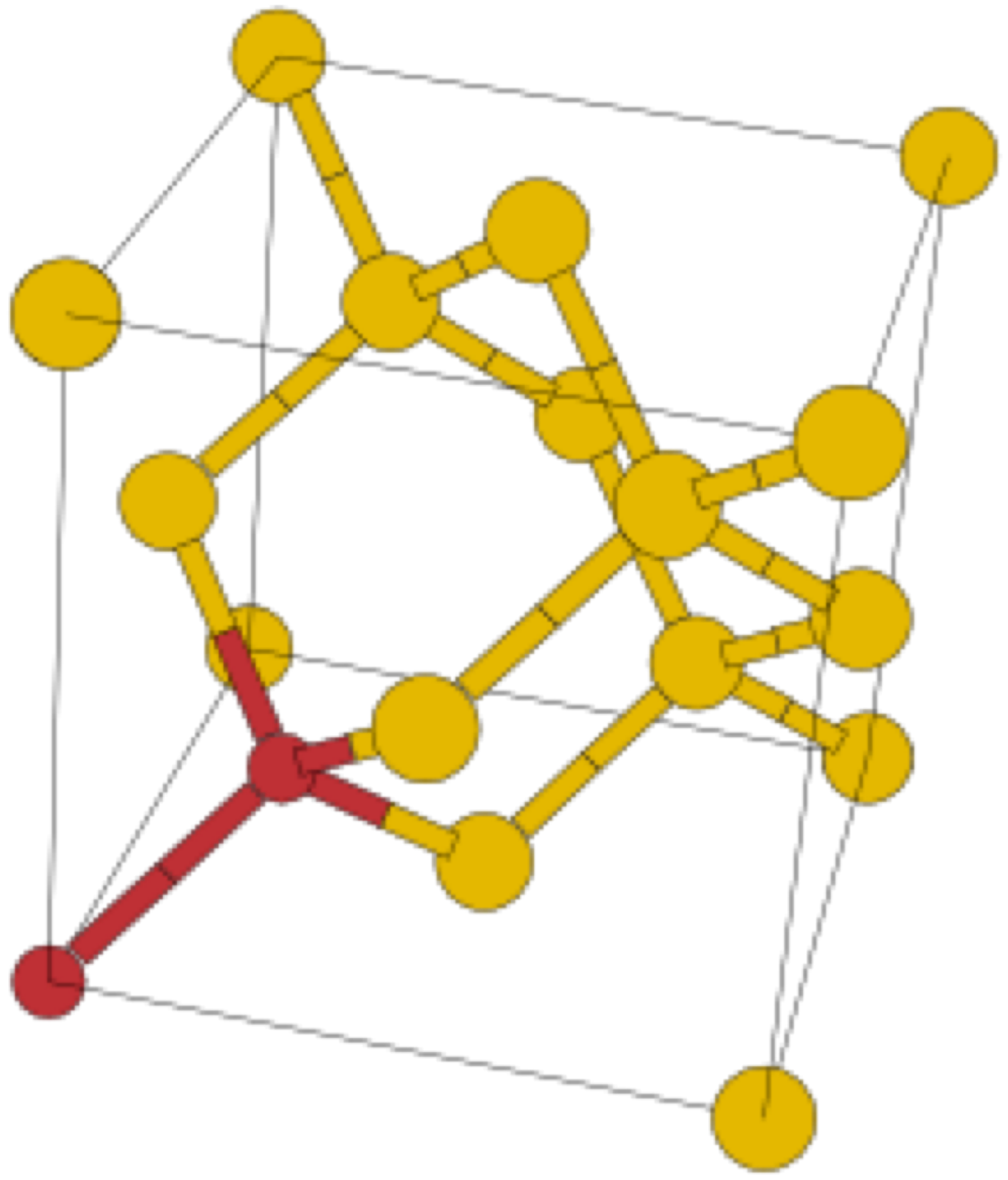
$$\rho(\mathbf{k}) = \sum_{\alpha} e^{-i\mathbf{k}\cdot\mathbf{R}_\alpha}$$

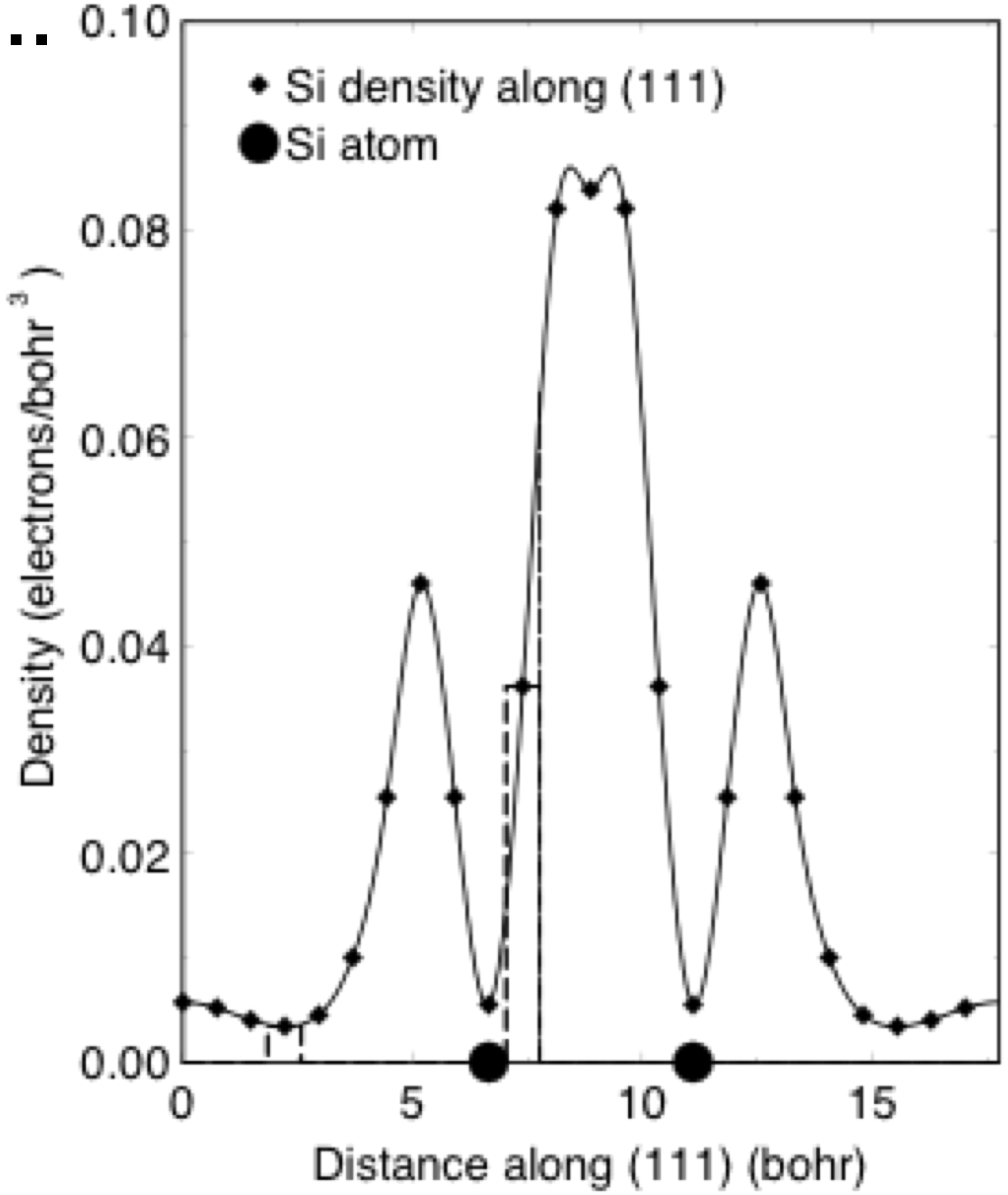
$\mathbf{R}_\alpha$ = atomic position.

- Phonon frequencies, surface reconstructions, catalysis, ...



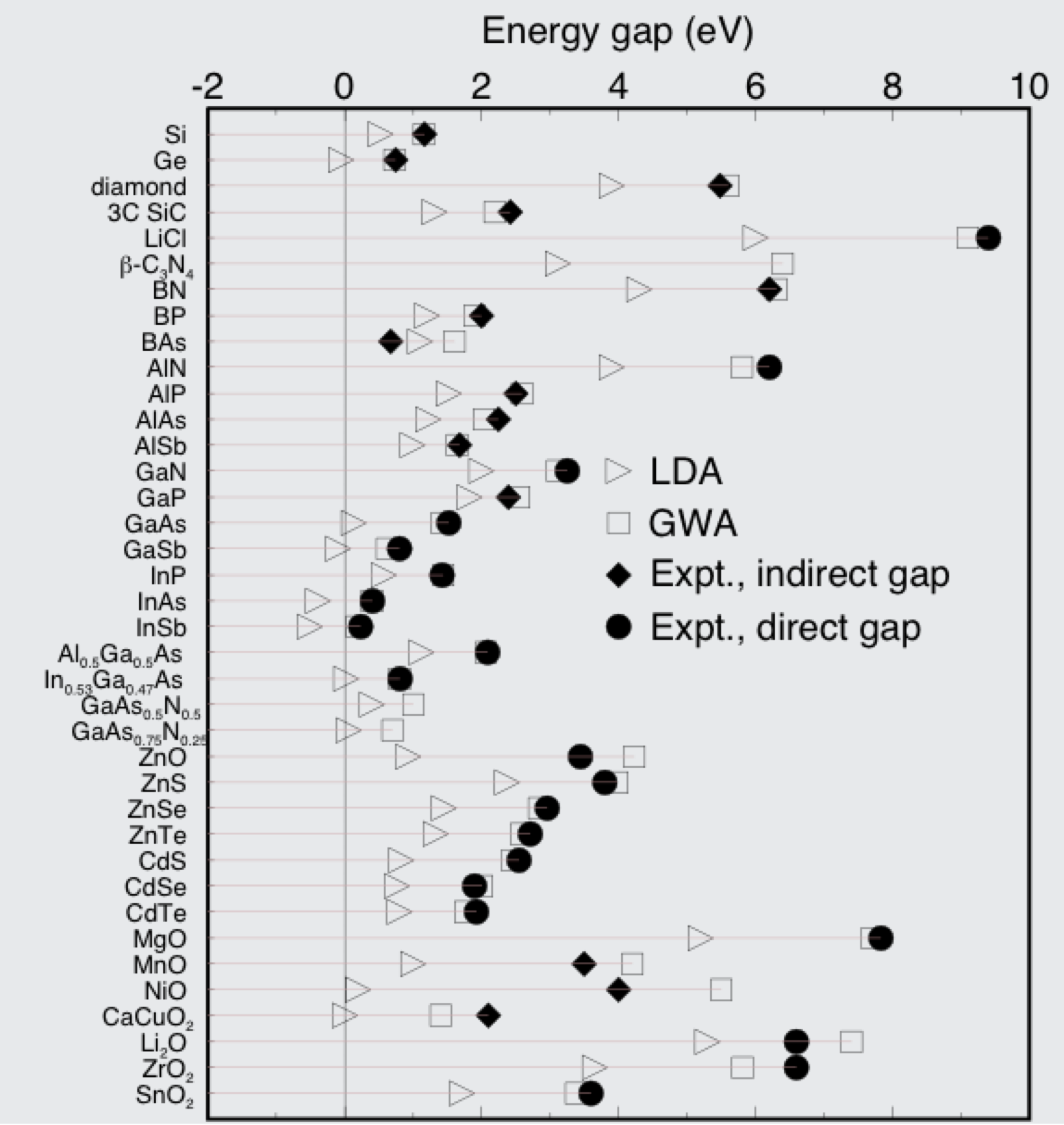
- good even in highly inhomogeneous systems such as atoms, molecules, non metallic solids...





correct description of not-so-slowly varying density along the chemical bonds

- **underestimate of band gap in insulators** (up to 50%!)



extension:
spin density functional theory

Two independent variables: Density $n(\mathbf{r})$ and magnetization

$$m(\mathbf{r}) = -\mu_0(n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})).$$

$m(\mathbf{r})$ couples to the magnetic field ($\alpha = \uparrow, \downarrow$):

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_H(n;\mathbf{r}) + V_{ext}(n;\mathbf{r}) - \alpha\mu_0 B(\mathbf{r}) + V_{xc}^\alpha(n_\uparrow, n_\downarrow;\mathbf{r})\right]\Phi_i^\alpha(\mathbf{r}) = \varepsilon_i^\alpha \Phi_i^\alpha(\mathbf{r}).$$

Practical implementation - I

- Use pseudopotentials: ignore chemically inert core states, focus on chemically active valence states (another physical approximation!)
- Choice of the xc functional
- Supercells used to treat finite systems (another physical approximation!)

Practical implementation - II

Expand KS orbitals into a suitable **basis set**: transform the problem into a **multivariate minimization** problem, and KS equations into a **non-linear matrix eigenvalue** problem

- **Plane wave basis set** is convenient (possible with pseudopotentials, since (pseudo)orbitals are rather smooth)

– to calculate matrix elements and matrix-vector products (they are orthonormal)
– to solve Poisson equation in reciprocal space using Fast Fourier Transforms (FFT)
– **How many? check completeness! (finiteness is a source of numerical inaccuracy)**

Practical implementation - III

- Solution on a discretized mesh (a numerical issue)
  - Self-consistent solution => Iterative diagonalization for minimizing E (a finite **tolerance** or **convergence threshold** is also a source of **numerical** inaccuracy)
-
  - **Special-point** technique to sum over occupied states for integration in reciprocal space (this is also a source of **numerical** inaccuracy)