Introduction to DFT and Density Functionals

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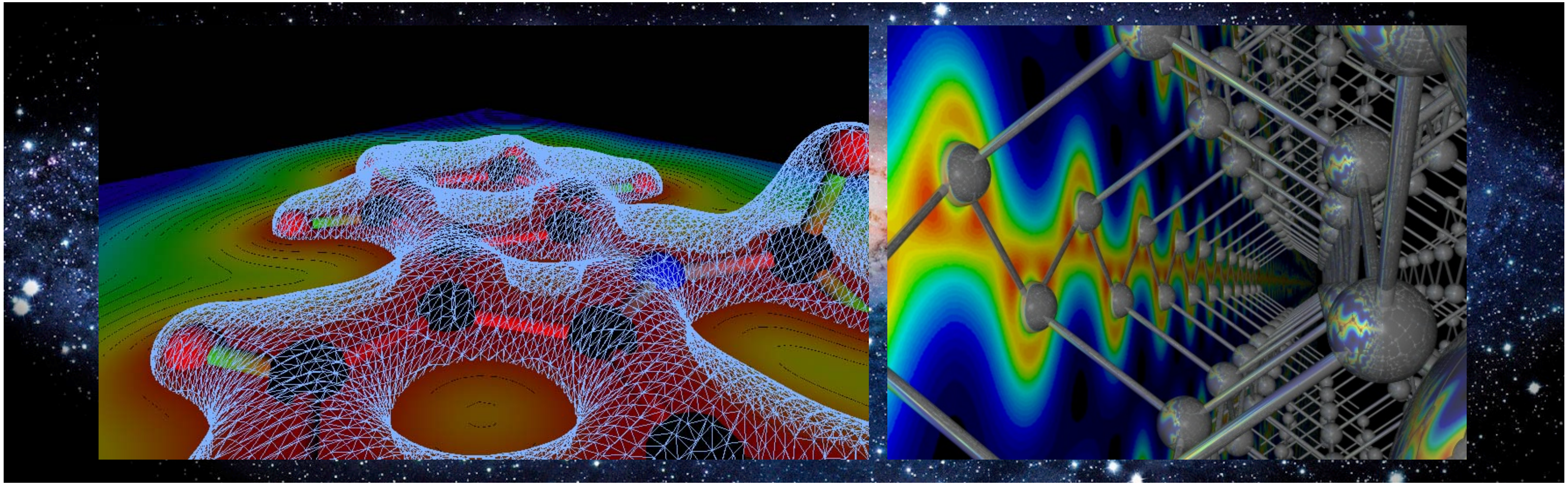
Introduction:



carbazole molecule   inside diamond

… a lot more than pretty pictures…

Hamiltonian in condensed matter

Here's the complete hamiltonian in condensed matter including electrons and ions :

$$H = \sum_{i}^{N_{\text{el}}} -\frac{\hbar^2 \nabla_{r_i}^2}{2m} + \sum_{l}^{N_{\text{ion}}} -\frac{\hbar^2 \nabla_{R_l}^2}{2M_l} + V_{\text{el}} + V_{\text{ion}} + V_{\text{ion-el}}$$

Interaction terms:

$$V_{\text{el}} = \sum_{i,j,j\neq i} \frac{e^2}{|r_i - r_j|} \qquad V_{\text{ion}} = \sum_{l,k,l\neq k} \frac{Z_l Z_k e^2}{|R_l - R_k|}$$

$$V_{\text{ion-el}} = \sum_{i}^{N_{\text{el}}} \sum_{l}^{N_{\text{ion}}} V_l(r_i - R_l)$$

We assign the interaction between electrons and ions to a potential V_l and not simply $Z_l e^2/|r_i - R_l|$ as the ion potential could be "pseudo potential" that accounts for the interaction of the atomic nucleus and the core electrons contributions. In that case, the Z_l are pseudo charges, meaning only the charge of the valence electrons of that atoms. We can always revert back to the coulomb form of the potential if need be.

After Born-Oppenheimer approximation:

The electronic hamiltonian

$$H = \sum_{i=1}^{N} \left[\frac{-\hbar^2}{2m} \nabla_i^2 + V_{\text{ext}}(r_i) \right] + \sum_{i<j}^{N} \frac{e^2}{|r_i - r_j|}$$

$V_{\text{ext}}(r_i)$ is the external potential, most often produced by the ions.
It will be represented by pseudopotentials in DFT.

We are looking for the solutions of the time-independent Schrödinger equation:

$$H\Psi_n = E_n \Psi_n$$

The wave function is a multi-variable function:

$$\Psi(r_1, r_2, \ldots, r_N)$$

An impractical problem:

$$\Psi(r_1, r_2, \ldots, r_N)$$

Storage required:

Let us assume that each coordinate is discretized on a 10x10x10 real space grid, which means that there are 1000 data per coordinate.

$$10 \text{ electrons} \rightarrow 1000^{10} \text{ data} \rightarrow 10^{30} \times 16 \text{ bytes}$$

$$= 16 \times 10^{21} \text{ Gb}$$

Impracticable!!!

Dirac’s quote of 1929

« The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. »

Réf: *Quantum mechanics of many-electron systems*, Proceedings of the Royal Society of London, pp.714. (1929)

Dirac’s quote of 1929 (suite)

« It, therefore, becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation. »

Réf: *Quantum mechanics of many-electron systems*, Proceedings of the Royal Society of London, pp.714. (1929)

This is the subject of this school!

Wavefunction approaches: Hartree method

$$\Psi(x_1, x_2, \ldots, x_N) = \phi_1(x_1)\phi_2(x_2)\cdots\phi_N(x_N) = \prod_{l=1}^{N}\phi_l(x_l)$$

$$n(x) = \sum_{l=1}^{N}\phi_l^*(x)\phi_l(x)$$

$$E = \langle\Psi|H|\Psi\rangle - \sum_{l=1}^{N}\lambda_l\langle\phi_l|\phi_l\rangle$$

Lagrange multipliers to assure that the ϕ_l remain orthogonal.

$$\frac{\partial E}{\partial\phi_l^*(x)} = \left[\frac{-\hbar^2}{2m}\nabla^2 + U_{\text{ion}}(x) + e^2\int dx'\frac{n(x')}{|x-x'|}\right]\phi_l(x) - \lambda_l\phi_l(x) = 0$$

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + U_{\text{ion}}(x) + V_H(x)\right]\phi_l(x) = \lambda_l\phi_l(x)$$

Same equation for all ϕ_l.

Hartree-Fock method

$$\Psi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \prod_{l=1}^{N} \phi_{Pl}(x_l) = \Phi_0(x_1, x_2, \ldots, x_N)$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{vmatrix}$$

Slater determinant

Particles are not independent, change the position of one and all the others are affected.

Pauli's exclusion principle is respected.

"Correlation" is purely statistics, and not due to interaction.

Hartree-Fock method

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + U_{\text{ion}}(x) + V_H(x)\right]\phi_l(x) - \underbrace{\sum_{j=1}^{N}\delta_{ss'}\phi_j(x)\int dx' \frac{\phi_j^*(x')\phi_l(x')}{|x-x'|}}_{\text{Exchange potential}} = \lambda_l\phi_l(x)$$

Because of the exchange term, the problem is much harder to resolve.

Results are better than those of the Hartree method but still not very satisfying.

Configuration Interaction method

$$\Psi(x_1, x_2, \ldots, x_N) = \sum_i C_i \Phi_i (x_1, x_2, \ldots, x_N)$$

Sum of Slater determinants (configurations)

Must find the coefficients C_i

CI = configuration interaction

CIS = CI with single excitations only

CISD = CI with single and double excitations only

Correlation energy (chemistry): contribution over that of Hartree-Fock

Wavefunction methods

Advantages:

- Control approximations
- Systematic approach (H, HF, CIS, …)
- Upper bound (variational principle)

Disadvantages:

- Very costly numerically

  (up to 20-30 electrons, forget solids!)

Progress in theoretical methods

Nobel Prize 1998 in Chemistry

John A. Pople

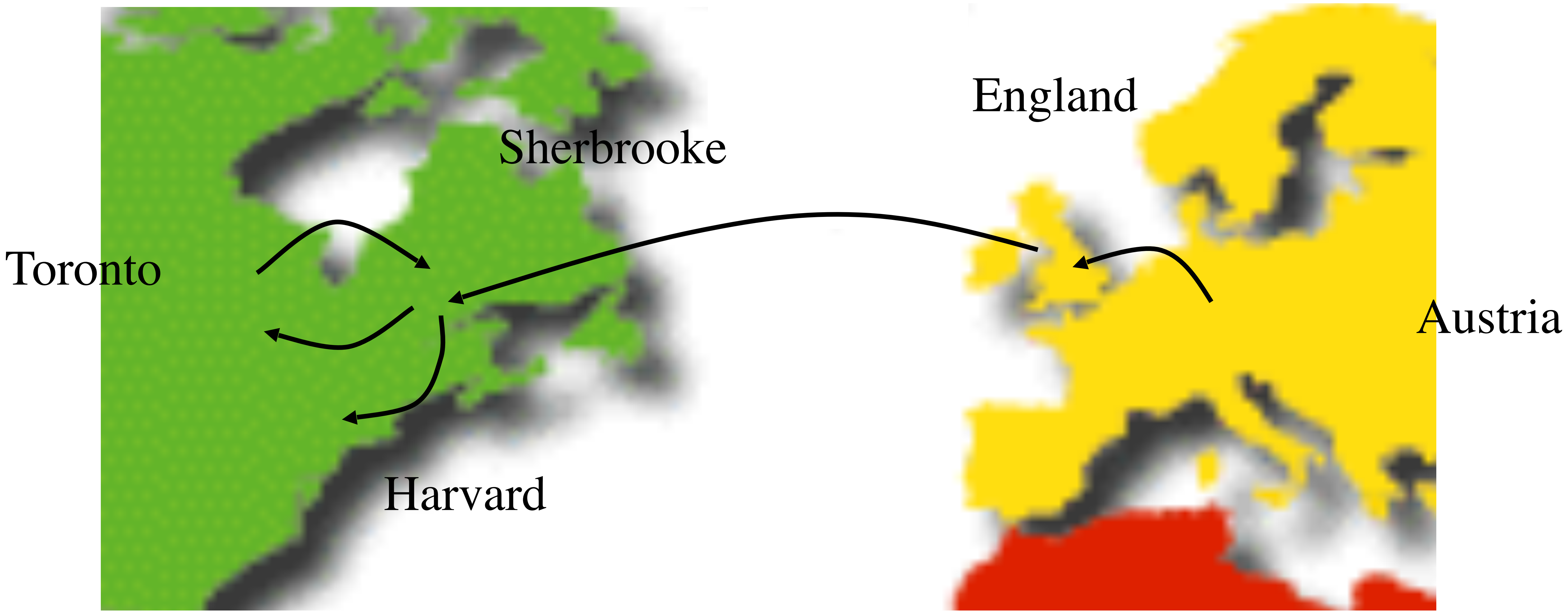
"for his development of computational methods in quantum chemistry”

Walter Kohn

"for his development of the density-functional theory”

- efficient
- flexible
- precise
- parameter free

Walter Kohn and Canada/Sherbrooke



Walter Kohn

INSTITUT QUANTIQUE
UNIVERSITÉ DE SHERBROOKE

EVENTS

CALENDAR

SERIES OF SEMINARS

Walter Kohn

André-Marie initiated the Walter Kohn public lecture at UdeS.

Walter Kohn himself was the first speaker.

Walter Kohn died April 16, 2016.

Milestones in DFT

Precursor: Thomas-Fermi approximation (1927)

Inhomogeneous electron gas
P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)
Self-consistent equations including exchange and correlation effects
W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965)

Ceperley, Alder (1980); Perdew, Zunger (1981) : computation and parametrization of the exchange and correlation energy needed in the local density approximation

Most cited papers

Papers published in APS journals (PRL, PRA, PRB, .. RMP), most cited by papers published in APS journals

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

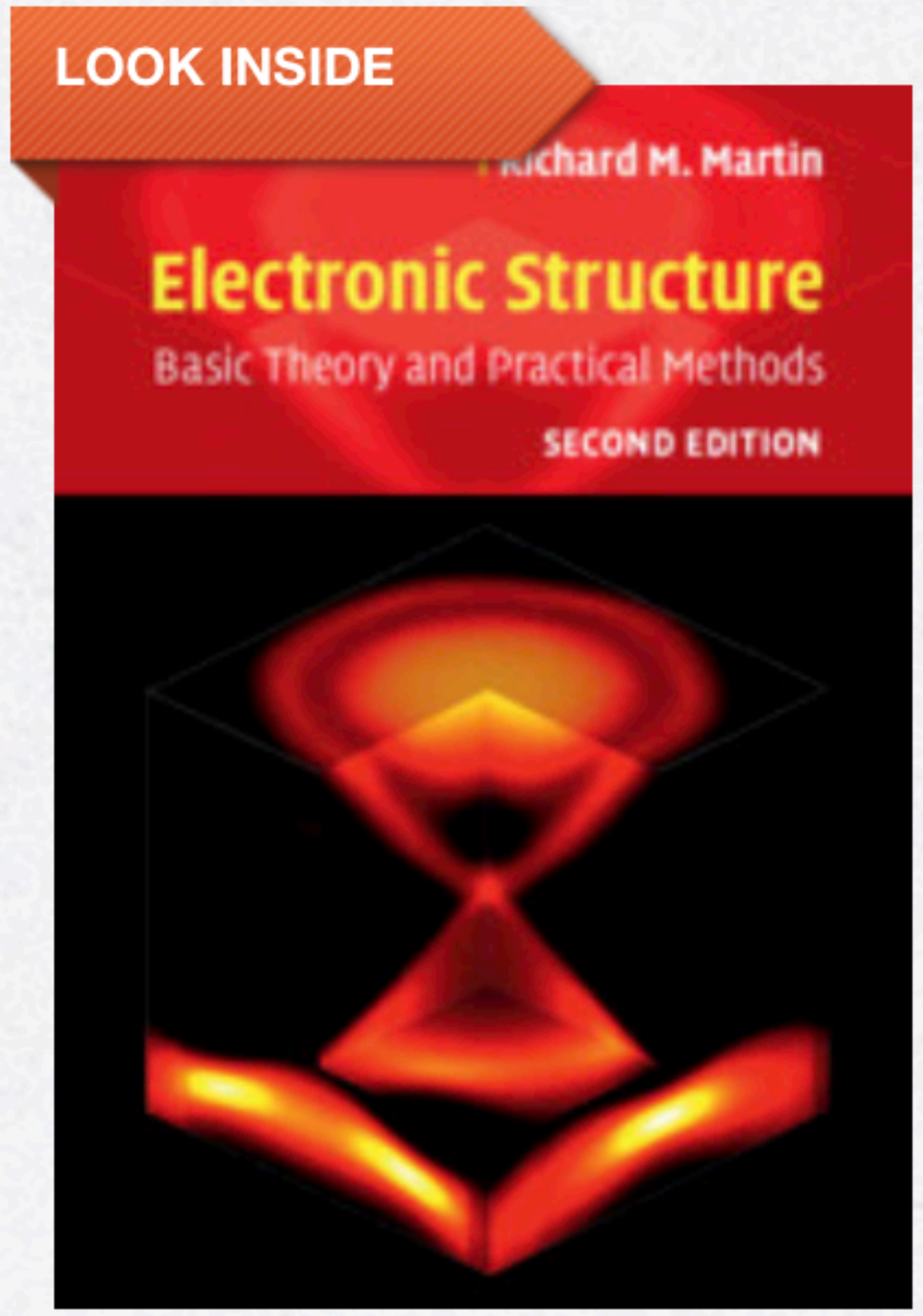
Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction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

S. Redner, *Citation Statistics from 110 Years of Physical Review*, Physics Today, June 2005.

Today, according to Google Scholar: K&S, 66k; H&K, 58k; PBE functional, 150k !

THE reference in DFT for solids



Electronic Structure

Basic Theory and Practical Methods

2nd Edition

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What is a functional?

A **function** takes a *number* as argument and returns a *number*.

A **functional** takes a *function* as argument and returns a *number*.

Example of a function: $f(x) = Ax^2$

Example of a functional: $f[n(x)] = \int v(x)n(x)dx$

Function derivative: $$\frac{df}{dx} = \lim_{\alpha \to 0} \frac{f(x+\alpha) - f(x)}{\alpha}$$

Functional derivative: $$\frac{\partial f}{\partial n(x')} = \lim_{\alpha \to 0} \frac{f[n(x) + \alpha\delta(x - x')] - f[n(x')]}{\alpha}$$

A functional is like a multi-variable function but with continuous argument instead of being discrete.

DFT: first theorem

Hohenberg et Kohn, Physical Review, vol 136, B864, (1964)

Proof by contradiction

Different potentials
$$v(r) \to \Psi_o(r_1, \ldots, r_n) \to n_o(r)$$
$$v'(r) \to \Psi'_o(r_1, \ldots, r_n) \to n_o(r)$$
same density

Using variational principle:

$$E_o = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle = < \langle \Psi' | H' - v'(r) + v(r) | \Psi' \rangle = E'_o + \int n(r)(-v'(r) + v(r))$$

But also:

$$E'_o = \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle = < \langle \Psi | H - v(r) + v'(r) | \Psi \rangle = E_o + \int n(r)(-v(r) + v'(r))$$

Adding the last two expressions, we get:

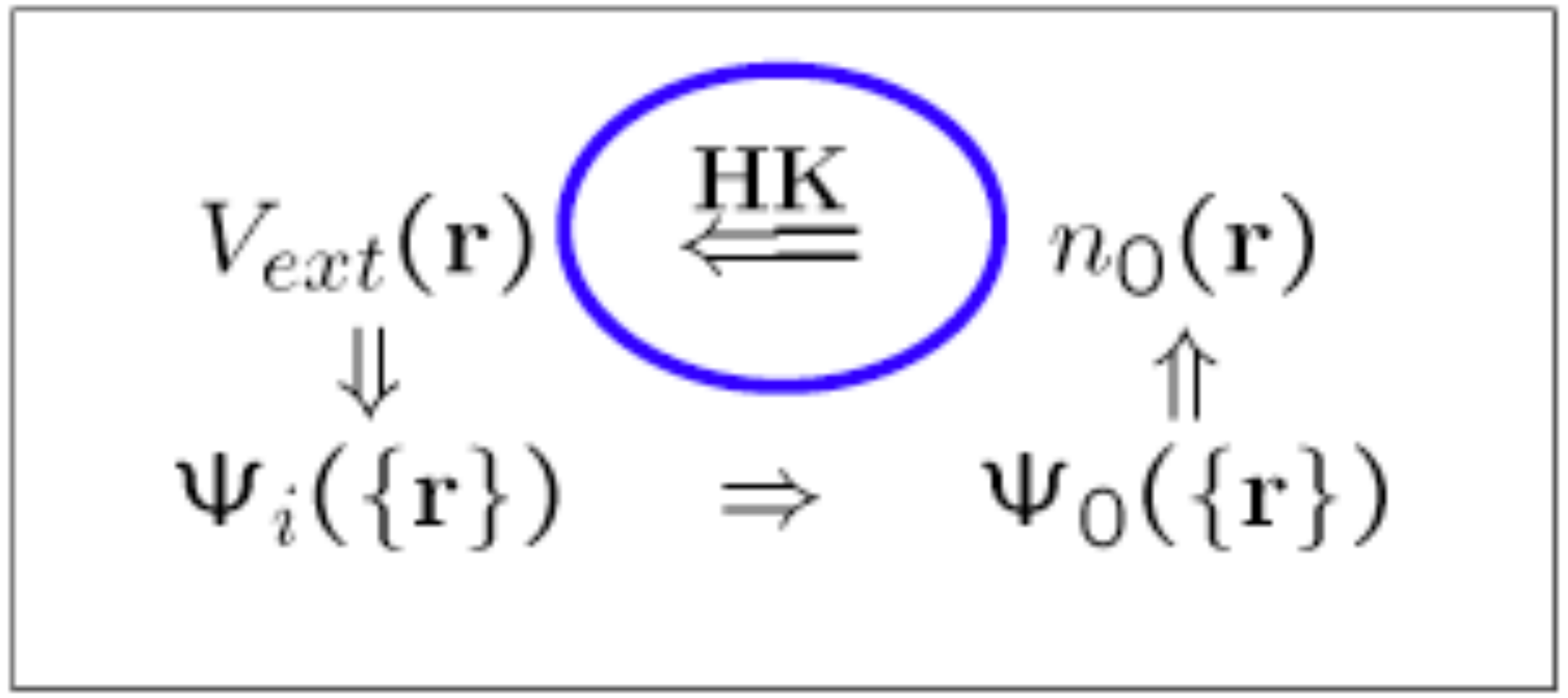
$$E_o + E'_o < E'_o + E_o$$

an obvious contradiction.

DFT: first theorem

The ground state density $n_o(r)$ of a many-electron system determines uniquely the external potential $v(r)$, modulo one global constant.

Consequence : **formally**, the density can be considered as the fundamental variable of the formalism, instead of the potential.



No need for wavefunctions or Schrödinger equation !

The second theorem is actually simply the demonstration that the variation principle still holds.

The constrained-search approach to DFT

M. Levy, Proc. Nat. Acad. Sci. USA, 76, 6062 (1979)

Use the extremal principle of QM.

$$E_o = \min_{\Psi} \langle \Psi | H | \Psi \rangle = \min_{n(r)} \left\{ \min_{\Psi \to n(r)} \langle \Psi | H | \Psi \rangle \right\},$$

$$E_o = \min_{n(r)} \left\{ \min_{\Psi \to n(r)} \langle \Psi | T + v_{\mathrm{int}} + v_{\mathrm{ext}} | \Psi \rangle \right\},$$

$$E_o = \min_{n(r)} \left\{ \min_{\Psi \to n(r)} \langle \Psi | T + v_{\mathrm{int}} | \Psi \rangle + \int n(r) v_{\mathrm{ext}}(r) dr \right\},$$

$$E_o = \min_{n(r)} \left\{ F[n] + E_{\mathrm{ext}}[n(r)] \right\}$$

$F[n]$ is a universal functional of the density.
The problem is that we do not know it explicitly.

Thomas-Fermi method

A pure density approach

Although introduced before DFT, it can be considered as a pure DFT approach that relies only on the density.

In DFT, the $F[n]$ needs to be approximated. In the TF method, it is approximated as the kinetic energy of the non-interacting homogeneous electron gas at each point in space.

For a non-interacting homogeneous electron gas of density n, we can define its density kinetic energy by the *function*: $E_{\text{kin}}(n)$. In the TF method, the kinetic energy contribution to the total energy is computed be:

$$F[n] = E_{\text{kin}}^{TF}[n] = \int E_{\text{kin}}(n(r))dr$$

We then proceed with a minimization that involves only the density.

The Kohn-Sham approach

A way to get a better value for the kinetic energy

$F[n]$: large part of the total energy, hard to approximate

Kohn & Sham (Phys. Rev. 140, A1133 (1965)) :

A mapping of the interacting system on a non-interacting system in order to get a better approximation for the kinetic energy.

For a non-interacting system, the ground state is a single Slater determinant which kinetic energy is easy to evaluate.

$$\Psi(r_1, \ldots, r_N) = \text{Slater determinant of } \phi_{\mathrm{i}}(\mathrm{r})$$

$$T_S[n] = \sum_i^N \int \phi_i^*(r) \left(\frac{-\hbar^2}{2m} \nabla^2 \right) \phi_i(r) dr$$

Definition of exchange-correlation energy *à la* DFT

not quite the same as for the wave function methods

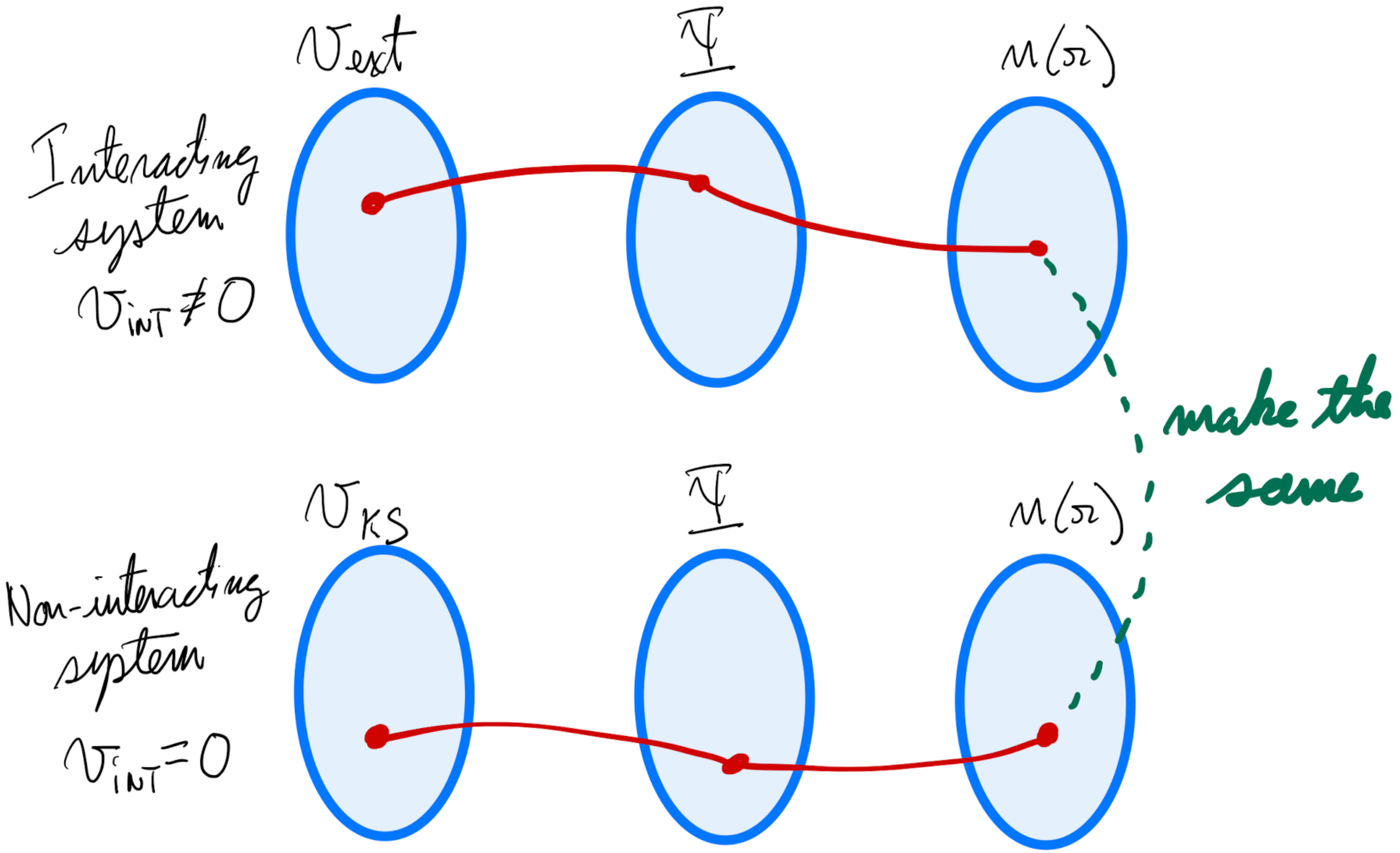
K&S assumed that there exists a non-interacting system with the same density as the studied interacting system which they can use to approximate the kinetic energy contribution.

$$F[n] = T[n] + E_{\text{int}}[n] + E_{\text{ext}}[n],$$
$$F[n] = T_S[n] + E_H[n] + E_{\text{ext}}[n] + (E_{\text{int}}[n] - E_H[n] + T[n] - T_S[n]),$$
$$F[n] = T_S[n] + E_H[n] + E_{\text{xc}}[n]$$

$$E_{\text{xc}}[n] = F[n] - E_H[n] - T_S[n]$$

This definition of E_{xc} differs from the definition of the usual definition as it also includes the difference between the true kinetic energy and the real system and the one obtained from the non-interacting system.

The K-S non-interacting system



The question is now: How to obtain $v_{KS}(r)$?

The K-S potential

We have to minimize (under the constraint of the number of particles):

$$E_{KS}[n] = T_S[n] + E_H[n] + E_{\text{ext}}[n] + E_{xc}[n],$$

$$E_{KS}[n] = T_S[n] + \frac{1}{2}\int \frac{n(r)n(r')}{|r - r'|}drdr' + \int v_{\text{ext}}(r)n(r)dr + E_{xc}[n]$$

Introducing Lagrange multipliers for the constraint:

$$0 = \delta\left(E_{KS}[n] - \lambda\left\{\int n(r)dr - N\right\}\right) = \int\left\{\frac{\partial T_S}{\partial n(r)} + \int \frac{n(r')}{|r - r'|}dr' + v_{\text{ext}}(r) + \frac{\partial E_{xc}}{\partial n(r)} - \lambda\right\}\delta n(r)dr$$

If one considers the minimization for non-interacting electrons in potential $v_{KS}(r)$, with the same density $n(r)$, one gets:

$$0 = \int\left\{\frac{\partial T_S}{\partial n(r)} + v_{KS}(r) - \lambda\right\}\delta n(r)dr$$

Hence: $$v_{KS}(r) = v_{\text{ext}}(r) + \int \frac{n(r')}{|r - r'|}dr' + \frac{\partial E_{xc}}{\partial n(r)}$$

K-S orbitals and eigenvalues

Non-interacting electrons in the Kohn-Sham potential :

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + v_{KS}(r)\right)\phi_i(r) = \epsilon_i \phi_i(r)$$

Density $n(r) = \sum_i^N \phi_i^*(r)\phi_i(r)$

$$v_{KS}(r) = v_{\text{ext}}(r) + \boxed{\int \frac{n(r')}{|r-r'|}dr'} + \boxed{\frac{\partial E_{xc}}{\partial n(r)}}$$

Hartree potential

Exchange-correlation potential

To be solved self-consistently !

Note : by construction, at self-consistency, and assuming the exchange-correlation functional to be exact, the density will be the exact density, the total energy will be the exact one, but Kohn-Sham wavefunctions and eigenenergies correspond to a fictitious set of independent electrons, so they do not correspond to any exact physical quantities.

Constructing Functionals

Doing clever approximations

The hope is that it is easier to find good approximations for $E_{xc}[n]$ than for $F[n]$.

(without demonstration)

The exchange-correlation energy, functional of the density is the integral over the whole space of the density times the local exchange-correlation energy per particle

$$E_{\mathrm{xc}}\left[n\right] = \int n(\mathbf{r}_1)\varepsilon_{xc}(\mathbf{r}_1; n)\,\mathrm{d}\mathbf{r}_1$$

while the local exchange-correlation energy per particle is the electrostatic interaction energy of a particle with its DFT exchange-correlation hole.

$$\varepsilon_{xc}(\mathbf{r}_1; n) = \int \frac{1}{2} \frac{\overline{n^{xc}}(\mathbf{r}_2 | \mathbf{r}_1; n)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,\mathrm{d}\mathbf{r}_2$$

Sum rule : $\int \overline{n^{xc}}(\mathbf{r}_2 | \mathbf{r}_1; n)\,\mathrm{d}\mathbf{r}_2 = -1$

Local-density approximation (I)

Hypothesis :
- the local XC energy per particle only depend on the local density
- and is equal to the local XC energy per particle of an
  homogeneous electron gas of same density
  (in a neutralizing background - « jellium »)

$$\varepsilon_{xc}^{LDA}(\mathbf{r}_1; n) = \varepsilon_{xc}^{hom}(\, n(\mathbf{r}_1)\,)$$

Gives excellent numerical results ! Why ?

1) Sum rule is fulfilled

2) Characteristic screening length indeed depend on local density

Local-density approximation (II)

Actual function : exchange part (x) + correlation part (c)

$$\varepsilon_x^{\text{hom}}(n) = Cn^{1/3} \qquad \text{with} \qquad C = -\frac{3}{4\pi}\left(3\pi^2\right)^{1/3}$$

for the correlation part, one resorts to accurate numerical simulations beyond DFT (e.g. Quantum Monte Carlo)

Corresponding exchange-correlation potential $V_{\text{xc}}(\mathbf{r}) = \dfrac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}$

$$V_{\text{xc}}^{\text{approx}}(\mathbf{r}) = \mu_{\text{xc}}\left(n(\mathbf{r})\right) \qquad \mu_{xc}(n) = \frac{\mathrm{d}\left(n\varepsilon_{xc}^{approx}(n)\right)}{\mathrm{d}n}$$

$$\mu_x(n) = C\frac{4}{3}n^{1/3} = \frac{4}{3}\varepsilon_x^{\text{hom}}(n)$$

Local-density approximation (III)

To summarize :

$$E^{LDA}\left[n\right] = T_s\left[n\right] + \int V_{ext}(\mathbf{r})n(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + E_{xc}^{LDA}\left[n\right]$$

or

$$E^{LDA}\left[\left\{\psi_i\right\}\right] = \sum_i \left\langle\psi_i\right| -\frac{1}{2}\nabla^2 \left|\psi_i\right\rangle + \int V_{ext}(\mathbf{r})n(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

$$+ \int n(\mathbf{r}_1)\varepsilon_{xc}^{LDA}(n(\mathbf{r}_1))\,\mathrm{d}\mathbf{r}_1$$

and

$$V_{\mathrm{KS}}^{LDA}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{\left|\mathbf{r}_1 - \mathbf{r}\right|}\mathrm{d}\mathbf{r}_1 + \mu_{xc}^{\mathrm{hom}}(n(\mathbf{r}))$$

Beyond the local-density approximation

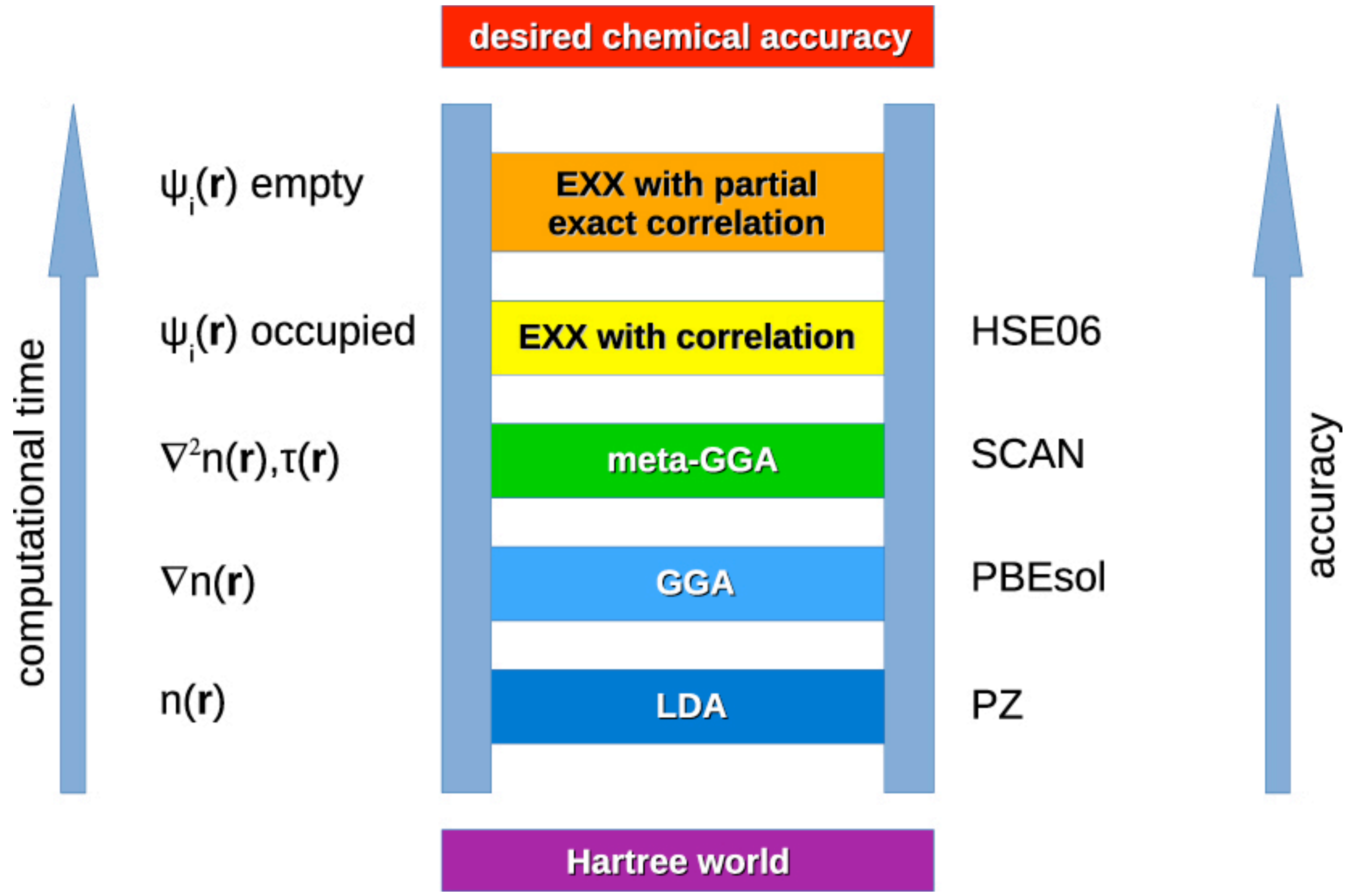
Generalized gradient approximations (GGA)

$$E_{xc}^{approx}\left[n\right] = \int n(\mathbf{r}_1)\varepsilon_{xc}^{approx}(n(\mathbf{r}_1),\left|\nabla n(\mathbf{r}_1)\right|,\nabla^2 n(\mathbf{r}_1))\,\mathrm{d}\mathbf{r}_1$$

No model system like the homogeneous electron gas !
Many different proposals, including one from Perdew, Burke and Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996), often abbreviated « PBE ».
Others : PW86, PW91, LYP ...

Also : « hybrid » functionals (B3LYP),
« exact exchange » functional,
« self-interaction corrected » functionals ...

Jacob's ladder of functional



SCAN, r2SCAN

an accurate meta-GGA functional

- SCAN satisfies all 17 known constraints of meta-GGA.
- r2SCAN let go of a few constraints, but it is smoother and therefore more suitable for plane-wave basis.

COMMUNICATIONS PHYSICS

ARTICLE

DOI: 10.1038/s42005-018-0009-4 OPEN

An accurate first-principles treatment of doping-dependent electronic structure of high-temperature cuprate superconductors

La_2CuO_4

Table 1 Various theoretically predicted properties for LTO, LTT, and HTT structures of LCO using SCAN, PBE and LSDA functionals are compared with the corresponding experimental results

		Exp.			SCAN			PBE			LSDA		
		LTO[55]	LTT[56]	HTT[54]	LTO	LTT	HTT	LTO	LTT	HTT	LTO	LTT	HTT
ΔE	(meV FU^{-1})	10 K	15 K[a]	528 K	0.0	1.2	51.9	0.0	6.9	96.3	0.0	−0.1	22.1
Cu magnetic moment	(μ_B)	0.495	-	-	0.491	0.492	0.479	0.273	0.107	0.262	0.109	0.073	0.100
Indirect band gap	(eV)	1.0[b27]	-	-	0.979	1.006	0.918	0.026	0.000	0.000	0.000	0.000	0.000
Lattice constants	*a* (Å)	5.335	5.360	5.391	5.323	5.391	5.348	5.352	5.471	5.401	5.220	5.285	5.258
	b (Å)	5.421	5.360	5.391	5.459	5.391	5.348	5.576	5.471	5.401	5.353	5.285	5.256
	c (Å)	13.107	13.236	13.219	13.088	13.071	13.125	13.101	13.075	13.163	12.956	12.956	12.989
	V ($Å^3$)	379.1	380.3	384.2	380.3	379.8	375.4[c]	391.0	391.4	384.0[c]	362.0	361.8	358.9
Octahedral Tilt	axial (deg)	5.5	3.8	0.0	7.2	6.9	0.0	8.7	8.5	0.0	5.8	5.5	0.0
ΔE_d[a]	(meV FU^{-1})	-	15 K[56]	-	0.0	−0.5	18.3	0.0	−4.4	46.0	0.0	−0.4	2.7

FU denotes formula unit
[a]Only stabilized under special conditions, see text
[b]Leading edge in optical spectrum. ΔE and ΔE_d are energies relative to the LTO phase in the pristine and doped cases, respectively
[c]See "Comment on Calculated Lattice Volumes" in Methods section for discussion

[1]

J. W. Furness, Y. Zhang, C. Lane, I. G. Buda, B. Barbiellini, R. S. Markiewicz, A. Bansil, and J. Sun, *An Accurate First-Principles Treatment of Doping-Dependent Electronic Structure of High-Temperature Cuprate Superconductors*, Communications Physics **1**, 1 (2018).

What to remember

- DFT is excellent to predict ground state properties (bond length, etc.), at a reasonable computation cost.
- Using Kohn-Sham eigenvalues as band structure is certainly abusing the method, but it is a good first approximation.
- Treatment of Kohn-Sham eigenvalues can give them physical meaning.
- The accuracy of DFT functionals relies on exact physical constraints.