# Libxc

## a library of xc functionals

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Exciting – August 2023

# Outline

1. Density-functional theory
   - ❖ A success story
2. Functionals
   - ❖ Functionals, and more functionals
3. LIBXC
   - ❖ A library of density functionals

# Introduction

Our starting point is the most popular theory in solid-state physics and theoretical chemistry since the 70s–80s:

## Density Functional Theory

# Density functional theory

Kohn-Sham equations:

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\boldsymbol{r}) + v_{\text{H}}(\boldsymbol{r}) + v_{\text{xc}}(\boldsymbol{r})\right] \varphi_i^{\text{KS}}(\boldsymbol{r}) = \varepsilon_i^{\text{KS}} \varphi_i^{\text{KS}}(\boldsymbol{r})$$


Walter Kohn (1923–2016)
Nobel Prize 1998

P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)
W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

# Density functional theory

Kohn-Sham equations:

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}\left(\boldsymbol{r}\right) + v_{\text{H}}\left(\boldsymbol{r}\right) + v_{\text{xc}}\left(\boldsymbol{r}\right)\right] \varphi_i^{\text{KS}}\left(\boldsymbol{r}\right)$$
$$= \varepsilon_i^{\text{KS}} \varphi_i^{\text{KS}}\left(\boldsymbol{r}\right)$$

Walter Kohn (1923–2016)
Nobel Prize 1998

“At a fundamental level, DFT can be used to describe all of chemistry, biochemistry, biology, nanosystems and materials. Everything in our terrestrial world depends on the motions of electrons, therefore DFT literally underlies everything.” (Axel Becke)

P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)
W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

# Most cited articles in science

In 2014, 13 of the 100 most cited papers in **all science** were about DFT:

**7**. Lee. C., Yang, W. & Parr, R. G., *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density.*
**8**. Becke, A. D., *Density-functional thermochemistry. III. The role of exact exchange.*
**16**. Perdew, J. P., Burke, K. & Ernzerhof, M., *Generalized gradient approximation made simple.*
**25**. Becke, A. D., *Density-functional exchange-energy approximation with correct asymptotic-behavior.*
**34**. Kohn, W. & Sham, L. J., *Self-consistent equations including exchange and correlation effects.*
**39**. Hohenberg, P. & Kohn, W., *Inhomogeneous electron gas.*
**43**. Kresse, G. & Furthmüller, J., *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set.*
**49**. Monkhorst, H. J. & Pack, J. D, *Special points for Brillouin-zone integrations.*

R. Van Noorden, B. Maher, and R. Nuzzo, Nature **514**, 550–553 (2014)
M. Dumaz, R. Boucher, M.A.L. Marques, A.H. Romero, Scientometrics **126**, 6681-6695 (2021)

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# The families — Jacob's ladder

Chemical Heaven

Many-body

All orbitals

Occ. orbitals

mGGA

GGA

LDA

Machine-learning

Semi-empirical

Marc Chagall – Jacob's dream

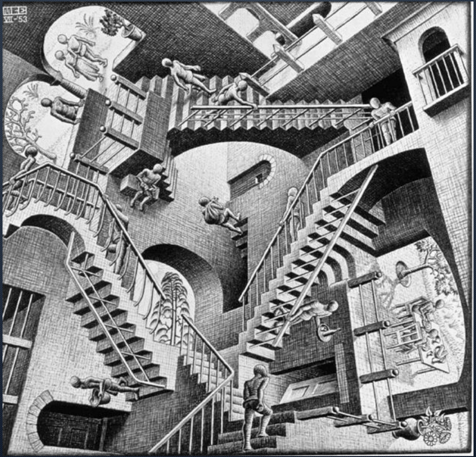
We want to approximate:

$$E_{\text{xc}}$$

or (not equivalently):

$$v_{\text{xc}}(\boldsymbol{r}) = \frac{\delta E_{\text{xc}}}{\delta n(\boldsymbol{r})}$$

# The true ladder!



M.C. Escher – Relativity

# Let's start from the bottom: the LDA

In the original LDA from Kohn and Sham, one writes the xc energy as

$$E_{\mathrm{xc}}^{\mathrm{LDA}} = \int \mathrm{d}^3 r \, n(\boldsymbol{r}) e_{\mathrm{xc}}^{\mathrm{HEG}}(n(\boldsymbol{r}))$$

The quantity $e_{\mathrm{xc}}^{\mathrm{HEG}}(n)$, the xc energy per unit particle, is a function of $n$.
The fits you should know about:

- 1980: Vosko, Wilk & Nusair
- 1981: Perdew & Zunger
- 1992: Perdew & Wang (do not mix with the GGA from '91)

These are all fits to the correlation energy of Ceperley-Alder. They differ in some details, but all give more or less the same results.

# the meta-LDAs

Meta-local density approximation (meta-LDA) functionals depend on $n_\sigma(\mathbf{r})$ and the local kinetic energy density $\tau_\sigma$, and are still (almost) fully derivable from the homogeneous electron gas

$$E_{\text{xc}} = \int n(\mathbf{r})\epsilon_{\text{xc}}(n(\mathbf{r}), \tau(\mathbf{r}))\mathrm{d}^3r$$

with the kinetic-energy density:

$$\tau = \frac{1}{2}\sum_i^{\text{occupied}} [\nabla\psi_i(\mathbf{r})]^2$$

S. Lehtola, and M.A.L. Marques, J. Chem. Theory Comput. **17**, 943 (2021)

# the GGAs

The generalized-gradient approximations read:

$$E_{\text{xc}}^{\text{GGA}} = \int \mathrm{d}^3r \, n(\boldsymbol{r}) e_{\text{xc}}^{\text{GGA}}(n(\boldsymbol{r}), \nabla n)$$

Probably the first modern GGA for the xc was by Langreth & Mehl in 1981.

Famous functionals

- Becke's '88 exchange functional
- Lee-Yang-Parr
- Perdew-Burke-Ernzerhof

D. C. Langreth and M. J. Mehl., Phys. Rev. Lett. **47**, 446 (1981)

# The metaGGAs

- To go beyond the GGAs, one can try the same trick and increase the number of arguments of the functional. In this case, we use both the Laplacian of the density $\nabla^2 n$ and the kinetic energy density $\tau$.
- Note that there are several other possibilities to define $\tau$ that lead to the same (integrated) kinetic energy, but to different local values.
- Often, the variables appear in the combination $\tau - \tau_W$, where $\tau_W = \frac{|\nabla n|^2}{8n}$ is the von Weizsäcker kinetic energy. This is also the main quantity entering the electron localization function (ELF).

Some famous functionals

- SCAN: Strongly-Constrained and Appropriately-Normed
- M06L: from Don Truhlar's group

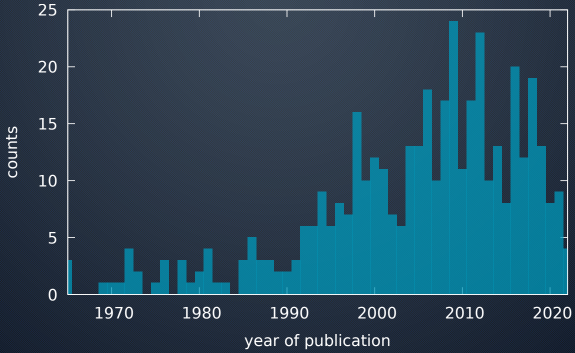
# Hybrid functionals

These functionals belong to the two higher rungs of Jacob's ladder:

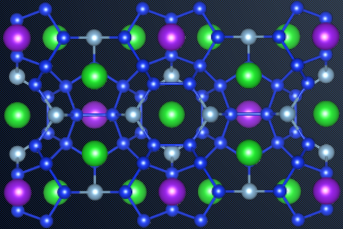
- ➜ Global hybrids: include constant fraction of Hartree-Fock exchange
- ➜ Range-separated hybrids: include fraction of short-range or long-range exact exchange (various kernels are possible)
- ➜ Local hybrids: local exchange energy becomes a variable of the functional. They are also know as hyper-GGAs
- ➜ Double hybrids: include post-Hartree-Fock correlation, e.g. Møller-Plesset, RPA, etc.

In any case, all these functionals still contain a density functional part.

# Number of functionals per year



Development of functionals is still going strong!



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# What is Libxc?

LIBXC is a library that:

1. evaluates the density functional contributions
2. provides the parameters to be used for non-local contributions (such as exact exchange, VV10 non-local correlation, MP2 correlation energy, etc.) **that need to be evaluated by the calling program**

LIBXC currently implements **600+** density functionals!

➜ From a presentation in 2012: "There are many approximations for the xc (probably of the order of 250–300)"

S. Lehtola, C. Steigemann, M.J.T. Oliveira, M.A.L. Marques, Software X **7**, 1-5 (2018)
M.A.L. Marques, M.J.T. Oliveira, T. Burnus, Comput. Phys. Commun. **183**, 2272-2281 (2012)

# Libxc features?

LIBXC supports:

- ➜ exchange, correlation, exchange-correlation, and kinetic energy functionals (for orbital-free DFT)
- ➜ pure functionals, global hybrids, range-separated hybrids (various kernels: error function, Yukawa, Gaussian)
- ➜ up to 4th derivatives for (almost) all functionals
- ➜ spin-unpolarized and polarized (non-collinear soon)
- ➜ double hybrids and hyper-GGAs in the upcoming major release
- ➜ LIBXC has native interfaces to C, Fortran 2003, and Python
- ➜ uses a permissible Mozilla Public License that allows its inclusion also in non-free/non-open-source programs.

# Programs using Libxc

LIBXC is currently used in over 30 electronic structure programs differing in numerical approaches, size of developer community, as well as development model.

- Abinit
- ACE-Molecule
- ADF
- APE
- AtomPAW
- BAGEL
- BigDFT
- CP2K
- DFT-FE
- DP
- Chronus Quantum
- Elk
- entos
- ERKALE
- exciting
- FHI-AIMS
- GAMESS (US)
- GPAW
- HelFEM
- Horton
- JDFTx
- MADNESS
- MOLGW
- Molpro
- MRCC
- Octopus
- ORCA
- PROFESS
- Psi4
- PySCF
- QuantumATK
- Quantum Espresso
- Turbomole
- Vasp
- WIEN2k
- Yambo

# Libxc before

LIBXC was originally based on hand-written C code

- ➜ Functional itself i.e. energy: pretty simple
- ➜ First derivatives: compute derivatives with respect to all parameters by hand, figure out optimal evaluation, implement
- ➜ Second derivatives: already hairy for many functionals

But, higher-order derivatives are sometimes needed for e.g. response properties

- ➜ DFT self-consistent field: 1st derivative (employing variational algorithm)
- ➜ DFT nuclear gradients: 2nd derivatives
- ➜ . . .
- ➜ TD-DFT vibrational frequencies: 4th derivatives needed!

# Current Libxc: Maple

LIBXC started switching over to Maple some years ago in the 4.x.x series; currently *all* functionals are implemented via Maple.

Using a computer algebra system greatly facilitates bug-free and fast implementation of functionals. For instance, this is what PBE exchange looks like

```
(* The enhancement factor in terms of s *)
pbe_f0 := s -> 1 + params_a_kappa*
              (1 - params_a_kappa/(params_a_kappa + params_a_mu*s^2)):

(* Transform from libxc's x variable into the s variable *)
pbe_f  := x -> pbe_f0(X2S*x):

(* Multiplies the enhancement with LDA exchange *)
f := (rs, z, xt, xs0, xs1) -> gga_exchange(pbe_f, rs, z, xs0, xs1):
```

Maple is especially useful for complicated functionals; e.g. the implementation of $\mathrm{r}^2$SCAN on top of SCAN, rSCAN and PW92 is about 100 lines of Maple code; the original published equations are 4 pages long.

# Common issues: Definition

Functionals are not defined identically across different programs!

- ➜ Often due to ambiguities (or errors) in the original articles
- ➜ In most cases we do not have reference implementations or reference data
- ➜ Some reference implementations contain bugs
- ➜ Most striking example is perhaps HSE06 as probably no two codes implement the same functional!

In LIBXC we try to follow the intent of the original authors. This sometimes requires a lot of detective work, and is not always possible.

- ➜ For HSE06 it took more than one month of work!

# Common issues: Numerical stability

We have been tying to minimize several issues with numerical stability in recent releases

- ➜ several floating point errors, e.g. FE_DIVBYZERO, FE_INEXACT, FE_OVERFLOW were eliminated
- ➜ in regions where double precision arithmetic is not accurate we switch over to automatically computed asymptotic polynomial expansions
- ➜ expansions always occur for range-separated functionals: evaluating short-range exchange at large $r$ tends to be numerically challenging (CAM-B3LYP, HSE06, etc)

However, some (many) functionals are intrinsically unstable!

S. Lehtola, M.A.L. Marques, arXiv:2206.14062 (2022)

# Thank you for your attention

Found a bug? Want / want us to implement a new functional? Contact us at

https://gitlab.com/libxc/libxc

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Miguel Marques