

Libxc

a library of xc functionals

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exciting NEWS 2021 – June 2021



1. Density-functional theory

- ❖ A success story

2. Functionals

- ❖ Functionals, and more functionals

3. Libxc



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

Density Functional Theory



Kohn-Sham equations:

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



Walter Kohn (1923–2016)
Nobel Prize 1998

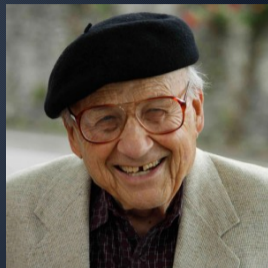
P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)
W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

M.A.L. Marques // DFT // exciting 2021



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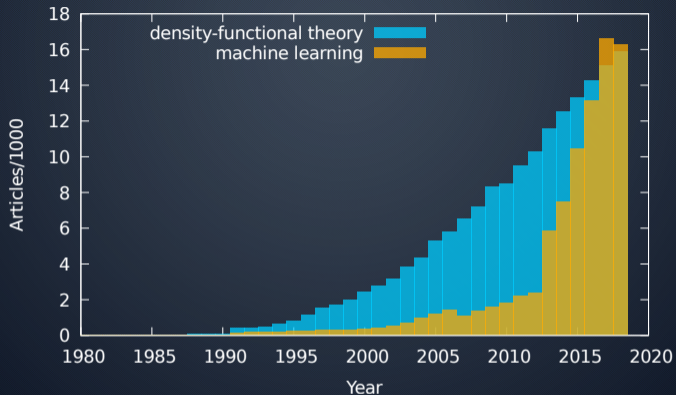
“At a fundamental level, DFT can be used to describe all of chemistry, biochemistry, biology, nanosystems and materials. Everything in our terrestrial world depends on the motions of electrons, therefore DFT literally underlies everything.” (Axel Becke)

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

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The second computer revolution



- In 2014, 13 of the 100 most cited papers were about DFT
- Now, the top 100 list includes several works on machine learning

Source: Web of Science; Nature **514**, 550-553 (2014)

M. Dumaz, R. Boucher, M.A.L. Marques, and A.H. Romero, *Scientometrics* (2021)

M.A.L. Marques // DFT // exciting 2021

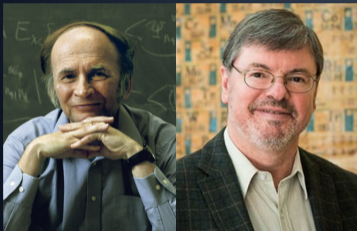


50 most cited articles in science

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)





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The families — Jacob's ladder



Marc Chagall – Jacob's dream

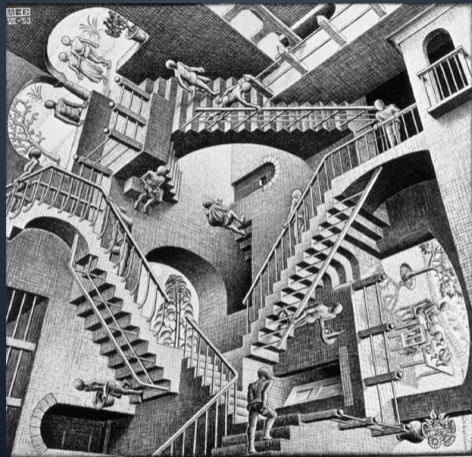
We want to approximate:

$$E_{xc}$$

or (not equivalently):

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

The true ladder!



(M. Escher – Relativity)

Let's start from the bottom: the LDA

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

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

The quantity $e_{xc}^{HEG}(n)$, 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.



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

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

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 generalized-gradient approximations read:

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

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



Example: LYP correlation

- The starting point is the **Colle-Salvetti** correlation functional
 - From an ansatz to the many-body wave-function.
 - Approximate the one- and two-particle density matrices.
 - Approximate the Coulomb hole.
 - Fudge the resulting formula and perform a dubious fit to the He atom.
 - The results is a meta-GGA (i.e., it depends on τ).
- **Lee-Yang-Parr** transformed the meta-GGA of Colle-Salvetti by using the gradient expansion of the kinetic energy density leading to a functional depending on $\nabla^2 n$.
- Later it was found that the $\nabla^2 n$ term could be rewritten by integrating by parts, leading to the current LYP GGA functional.



- 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 τ .
- Note that there are several other possibilities to define τ 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

The experimental values of some quantities lie often between they Hartree-Fock and DFT (LDA or GGA) values. So, we can try to mix, or to “hybridize” both theories.

1. Write an energy functional:

$$E_{xc} = aE^{\text{Fock}}[\varphi_i] + (1 - a)E^{\text{DFT}}[n]$$

2. Minimize energy functional w.r.t. to **the orbitals**:

$$v_{xc}(\mathbf{r}, \mathbf{r}') = av^{\text{Fock}}(\mathbf{r}, \mathbf{r}') + (1 - a)v^{\text{DFT}}(\mathbf{r})$$

Note: for pure density functionals, minimizing w.r.t. the orbitals or w.r.t. the density gives the same, as:

$$\frac{\delta F[n]}{\delta \varphi^*} = \int \frac{\delta F[n]}{\delta n} \frac{\delta n}{\delta \varphi^*} = \frac{\delta F[n]}{\delta n} \varphi$$



A short history of hybrid functionals

- 1993: The first hybrid functional was proposed by Becke, the B3PW91. It was a mixture of Hartree-Fock with LDA and GGAs (Becke 88 and PW91). The mixing parameter is $1/5$.
- 1994: The famous B3LYP appears, replacing PW91 with LYP in the Becke functional.
- 1999: PBE0 proposed. The mixing was now $1/4$.
- 2003: The **screened** hybrid HSE06 was proposed. It gave much better results for the band-gaps of semiconductors and allowed the calculation of metals.



Problems with traditional hybrids

Hybrids certainly improve some properties of both molecules and solids, but a number of important problems do remain. For example:

- For **metals**, the long-range part of the Coulomb interaction leads to a vanishing density of states at the Fermi level due to a logarithmic singularity (as Hartree-Fock).
- For **semiconductors**, the quality of the gaps varies very much with the material and the mixing.
- For **molecules**, the asymptotics of the potential are still wrong, which leads to problems, e.g. for charge transfer states.



Splitting of the Coulomb interaction

The solution is to split the Coulomb interaction in a **short-range** and a **long-range** part:

$$\frac{1}{r_{12}} = \underbrace{\frac{1 - \operatorname{erf}(\mu r_{12})}{r_{12}}}_{\text{short range}} + \underbrace{\frac{\operatorname{erf}(\mu r_{12})}{r_{12}}}_{\text{long range}}$$

We now treat the one of the terms by a standard DFT functional and make a hybrid out of the other. There are two possibilities

1. DFT: long-range; Hybrid: short-range. Such as HSE, good for metals.
2. DFT: short-range; Hybrid: long-range. The LC functionals for molecules.



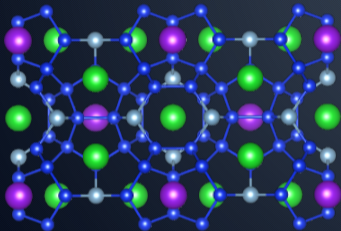
For LC functionals to have the right asymptotics they need $\alpha = 1$. This value is however too large in order to obtain good results for several molecular properties. To improve this behavior one needs more flexibility

$$\frac{1}{r_{12}} = \underbrace{\frac{1 - [\alpha + \beta \operatorname{erf}(\mu r_{12})]}{r_{12}}}_{\text{short range}} + \underbrace{\frac{\alpha + \beta \operatorname{erf}(\mu r_{12})}{r_{12}}}_{\text{long range}}$$

The asymptotics are now determined by $\alpha + \beta$. Note that this form leads to a normal hybrid for $\beta = 0$ and to a screened hybrid for $\alpha = 0$.

The most used CAM functional is probably CAM-B3LYP.





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Libxc is a library that evaluates the density functional contributions.

- Libxc currently implements 600+ density functionals ϵ_{xc} .
- From a presentation in 2012: “There are many approximations for the xc (probably of the order of 250–300)”

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, etc)
- up to 4th derivatives for (almost) all functionals
- double hybrids in the upcoming major release
- and uses a permissible Mozilla Public License that allows its inclusion also in non-free/non-open-source programs.

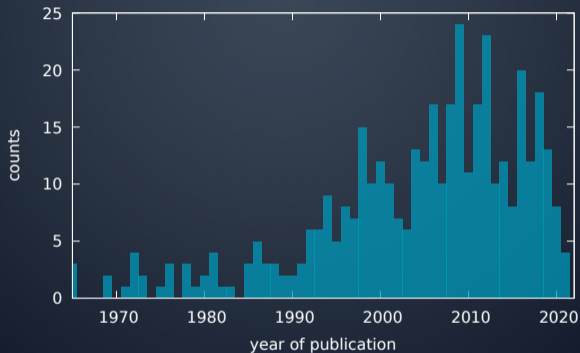


Libxc is currently used in over 30 electronic structure programs differing in numerical approaches, size of developer community, as well as development model (free software vs open source vs proprietary/closed-source/commercial).

- 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
- WIEN2k
- Yambo



Number of functionals per year



Development of functionals is still going strong!



Libxc was originally based on **hand-written C code**

- Functional itself i.e. energy: pretty simple
- First derivatives: compute derivatives wrt 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 version 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 **r²SCAN** on top of **SCAN**, **rSCAN** and **PW92** is about 100 lines of Maple code; the original published equations are 4 pages long.



Thank you for your attention

Please visit us in

<https://gitlab.com/libxc/libxc>



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