Original software publication

Recent developments in LIBXC — A comprehensive library of functionals for density functional theory

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ARTICLE INFO

ABSTRACT

LIBXC is a library of exchange–correlation functionals for density-functional theory. We are concerned with semi-local functionals (or the semi-local part of hybrid functionals), namely local-density approximations, generalized-gradient approximations, and meta-generalized-gradient approximations. Currently we include around 400 functionals for the exchange, correlation, and the kinetic energy, spanning more than 50 years of research. Moreover, LIBXC is by now used by more than 20 codes, not only from the atomic, molecular, and solid-state physics, but also from the quantum chemistry communities.

Code metadata

Current code version	4.0.2
Permanent link to code/repository used for this code version	https://github.com/ElsevierSoftwareX/SOFTX-D-17-00051
Legal Code License	LGPL v3
Code versioning system used	git
Software code languages, tools, and services used	C, Maple
Compilation requirements, operating environments & dependencies	Compilers: C compiler, OS: Unix, Linux, or MacOS.
If available Link to developer documentation/manual	https://gitlab.com/libxc/libxc/wikis/home
Support email for questions	libxc@tddft.org

1. Motivation and significance

Over the past 50 years density-functional theory [1–4] (DFT) has evolved into an almost ubiquitous approach, used in numerous fields of physics, chemistry, and even biology to describe the interaction of electrons in atoms, molecules, clusters, polymers, liquids, solids, etc. It relies on the deceivingly simple idea that the electronic density $n(\mathbf{r})$ is by itself capable of determining all ground-state properties. To calculate the electronic density, nearly all DFT calculations rely on the so-called Kohn–Sham scheme [5], where a non-interacting electronic system is used to obtain the density of the interacting system [6].

The Kohn–Sham equations read

$$\left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n](\mathbf{r}) + v_{\text{xc}}^{\sigma}[n_\alpha, n_\beta](\mathbf{r}) \right] \psi_i^{\sigma}(\mathbf{r}) = \varepsilon_i^{\sigma} \psi_i^{\sigma}(\mathbf{r}), \tag{1}$$

where we used Hartree atomic units ($e^2 = \hbar = m_e = 1$), that are also used throughout the paper and in LIBXC. In Eq. (1), the first term describes the kinetic energy of the electrons, $v_{\text{ext}}(\mathbf{r})$ is the external potential (usually generated by the nuclei), and $v_{\text{Hartree}}[n](\mathbf{r})$ accounts for the classical Coulomb interaction between the electrons. The quantity $v_{\text{xc}}^{\sigma}[n_\alpha, n_\beta](\mathbf{r})$ is the famous exchange–correlation (xc) potential, defined as the functional derivative of an xc energy functional

$$v_{\text{xc}}^{\sigma}[n_\alpha, n_\beta](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n_\alpha, n_\beta]}{\delta n_\sigma(\mathbf{r})}. \tag{2}$$

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Finally, α and β denote spin-up and spin-down, respectively, σ denoting either one of α and β.

The xc functional is, without doubt, the most important quantity of Kohn–Sham DFT. Its exact mathematical form as a functional of the density is unknown, and its explicit construction probably requires solving all possible systems of electrons interacting through the Coulomb potential. Approximations are therefore required at this point. We emphasize that this is the only approximation in DFT, and therefore the quality of the final results is a direct consequence of the quality of the approximated E_{xc}. In view of this, it is not surprising that hundreds of different approximations have been suggested over the past decades [7,8]. LIBXC [9] is a library whose sole purpose is to include xc functionals that have been proposed in the literature. Simply put, it is a huge collection of mathematical formulas (some of them quite intricate) that have been collected from the literature, implemented and tested, and that can easily be used from within the many DFT programs that are interfaced to LIBXC.

Traditionally, each DFT code implemented a selection of functionals independently. This was however rather tedious, error-prone, and time-consuming, with the consequence that most DFT programs only included 5–15 of the most popular functionals. A few other libraries (such as XCFun [10]) or repositories (such as the density-functional repository in Daresbury of H. J. J. van Dam [11]) also exist, but unfortunately for a rather limited number of functionals. LIBXC, on the other hand, contains nearly 400 functionals [12], including e.g. the recent functionals by the groups of Perdew [13,14], Truhlar [15–17], and Head-Gordon [18–20].

2. Software description

From a theoretical point of view, we can divide the functionals that are present in LIBXC into separate rungs, following Perdew's idea of Jacob's ladder [21]. The first rung is given by the local spin density approximation (LDA), where we write

$$E_{xc}^{LDA} = \int d^3r\, n(\mathbf{r})\, \epsilon_{xc}^{LDA}\left(\{n_\sigma(\mathbf{r})\}\right), \tag{3}$$

where $\epsilon_{xc}^{LDA}(\{n_\sigma\})$ is the xc energy density per electron. Successive rungs complicate the functional form by adding a dependency on further ingredients. The next rung is the generalized-gradient approximation (GGA)

$$E_{xc}^{GGA} = \int d^3r\, n(\mathbf{r})\, \epsilon_{xc}^{GGA}\left(\{n_\sigma(\mathbf{r})\}, \{\nabla n_\sigma(\mathbf{r})\}\right), \tag{4}$$

where the functional now depends explicitly both on the density and its gradient. In the physics community, GGAs are often called "semi-local" functionals, as the functional depends on an infinitesimal region around $\mathbf{r}$ through the gradient.

For the next rung, we include a local dependence on the Laplacian of the density $\nabla^2 n_\sigma(\mathbf{r})$ and/or the kinetic energy density

$$\tau_\sigma(\mathbf{r}) = \frac{1}{2} \sum_i^{occ} \left|\nabla \psi_i^\sigma(\mathbf{r})\right|^2. \tag{5}$$

(Note the introduction of the factor $1/2$ in the definition of $\tau(\mathbf{r})$ since version 1.0 of LIBXC.) The so-called meta-GGA (mGGA) approximation is thus defined as

$$E_{xc}^{mGGA} = \int d^3r\, n(\mathbf{r})\, \epsilon_{xc}^{mGGA}$$
$$\left(\{n_\sigma(\mathbf{r})\}, \{\nabla n_\sigma(\mathbf{r})\}, \{\tau_\sigma(\mathbf{r})\}, \{\nabla^2 n_\sigma(\mathbf{r})\}\right). \tag{6}$$

The non-interacting kinetic energy τ can be used to some extent as a measure of single-orbital structure (basically lost in the charge density and its derivatives). Note that the Laplacian of the density is much more sensitive than τ to the integration grid, and that many published mGGAs only depend on the latter.

The next rung includes the so-called hybrid functionals, where the functional is written as a mixture of a fraction a_x of exact (Hartree–Fock, HF) exchange and a "normal" DFT functional (such as a GGA or a mGGA)

$$E_{xc}^{hyb} = -\frac{a_x}{2} \int d^3r \int d^3r' \frac{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r}')\psi_j^*(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$
$$+ E_{xc}^{DFT}[n_\alpha, n_\beta]. \tag{7}$$

In contrast to the "semi-local" pure GGA functionals, exact exchange makes hybrid functionals truly non-local.

Many modern functionals further refine the hybrid approach by e.g. using semi-local DFT for the short range and switching to exact exchange in the long range [22]. In contrast, within the solid state community the opposite approach of using exact exchange only in the short range has proven very popular due to the slow convergence of lattice summations of long-range exact exchange [23]. These so-called range-separated functionals are also included within LIBXC, however at present only one range separation parameter is supported. Note also that LIBXC only handles the semi-local DFT part of the hybrid functional, while the exact exchange component of the hybrid has to be computed by the upstream program.

Several so-called double-hybrid functionals [24], which include a post-HF correlation component, have also been suggested in the literature. They are not supported by LIBXC at present, but they will be added in a future version.

Dispersion (van der Waals) interactions are ill-described by conventional xc functionals. However, they can be treated efficiently with *ab initio* type approaches [25] or with semi-empirical atomic pair-wise potentials [26,27]. At present, LIBXC only provides the semi-local part of the functional for these cases, while the remaining of the functional must be treated separately in the main program. However, LIBXC does provide the parameters for VV10-type [28] dispersion corrections used in several recently published functionals [18–20], and we plan to support Grimme-type empirical dispersion corrections [26,27] in a near future. We note that the LIBVDWXC library [29] has been recently published for the implementation of van der Waals functionals in solid state programs.

2.1. Software architecture

Each functional in LIBXC is assigned an unique (integer) identifier, which is guaranteed to be backward- and forward-compatible. Functionals can also be accessed through human-readable string identifiers, such as gga_x_pbe for the Perdew, Burke, and Ernzerhof GGA exchange functional [30]. The library also includes generic information for every functional, such as its full name, to which rung it belongs to, references to the articles where it was defined etc., as well as possible information related to its specific implementation in LIBXC.

LIBXC provides implementations of the energy functional (if one exists) and its derivatives. Only the functional and its first derivatives are necessary for a standard DFT energy calculation or geometry optimization. However, more elaborate calculations, such as the determination of molecular vibrational frequencies, require higher-order derivatives. At the moment we provide up to third-order derivatives of most functionals, which is enough to access physical response properties in second-order.

The input variables of LIBXC are $\{n_\sigma\}$, $\{\gamma_{\sigma\sigma'}\}$, $\{\tau_\sigma\}$, and $\{\nabla^2 n_\sigma\}$, where $\gamma_{\sigma\sigma'} = \nabla n_\sigma \cdot \nabla n_{\sigma'}$, while the output is the exchange–correlation energy density per unit particle ϵ_{xc} and its derivatives with respect to the input quantities. However, the input variables are often not the natural quantities that appear in the functionals.

For this reason, we divide the functionals into five categories (different from the rungs above), with each handled by a different, specialized driver routine. This routine is responsible for translating the input variables into (mostly dimensionless) quantities, calling the evaluation of the functional in these quantities, and finally back-transforming the derivatives using the chain rule. The first driver routine is `work_lda` and handles all LDA functionals that are of the form

$$\epsilon_{\text{xc}} = \epsilon_{\text{xc}}^{\text{LDA}}(r_s, \zeta), \tag{8}$$

where $r_s = \sqrt[3]{3/(4\pi n)}$ is the Wigner–Seitz radius, $n = n_\alpha + n_\beta$ is the total density, and $\zeta = (n_\alpha - n_\beta)/n$ is the spin polarization density.

The second driver routine is `work_gga_x` that handles all exchange GGA and hybrid-GGA functionals of the form

$$\epsilon_{\text{xc}} = \sum_\sigma \epsilon_{\text{x}}^{\text{LDA}}(n_\sigma) F(x_\sigma), \tag{9}$$

where $\epsilon_{\text{x}}^{\text{LDA}}(n_\sigma) = -3/4 \cdot (6/\pi)^{1/3} \cdot n_\sigma^{4/3}/n$ and $x_\sigma = n_\sigma^{-4/3}\sqrt{\gamma_{\sigma\sigma}} = n_\sigma^{-4/3}|\nabla n_\sigma|$ is a dimensionless (reduced) gradient. This form includes most GGA exchange functionals.

The third driver routine is `work_gga_c` that takes care of GGA and hybrid-GGA functionals in their most general form, i.e.

$$\epsilon_{\text{xc}} = \epsilon_{\text{x}}^{\text{GGA}}(r_s, \zeta, x_t, x_\alpha, x_\beta), \tag{10}$$

with $x_t = n^{-4/3}\sqrt{\gamma} = n^{-4/3}|\nabla n_\alpha + \nabla n_\beta|$. The choice of the three independent reduced gradients (x_α, x_β, x_t) is arbitrary and is a compromise in view of the diversity of existing GGA functionals. Non-separable exchange GGAs such as the N12 functional [31] are also written using this form.

The fourth driver routine `work_mgga_x` handles all exchange mGGAs and hybrid mGGAs of the form

$$\epsilon_{\text{xc}} = \sum_\sigma \epsilon_{\text{x}}^{\text{LDA}}(n_\sigma) F^{\text{mGGA}}(x_\sigma, t_\sigma, u_\sigma), \tag{11}$$

with the dimensionless variables $t_\sigma = n_\sigma^{-5/3}\tau_\sigma$ and $u_\sigma = n_\sigma^{-5/3}\nabla^2 n_\sigma$. As for the GGAs, most mGGA exchange functionals are written in this separable form.

The fifth and final driver `work_gga_c` takes care of the most general form of a mGGA functional

$$\epsilon_{\text{xc}} = \epsilon_{\text{x}}^{\text{mGGA}}(r_s, \zeta, x_t, x_\alpha, x_\beta, t_\alpha, t_\beta, u_\alpha, u_\beta). \tag{12}$$

From the developer's perspective, the most convenient way to implement a new functional is to use a high-level computer algebra program to generate all the necessary partial derivatives and to output the resulting code in C or Fortran [32–34]. However, automatically generated code is often extremely verbose, inefficient, and unreadable. In some cases we found that code generated using MATHEMATICA or MAPLE was around 10 times slower than optimized hand-written C code, adding a considerable overhead for DFT calculations. It is also possible to use automatic differentiation through truncated Taylor expansions to evaluate the derivatives exactly at the wanted point. This path, used e.g. by XCFUN [10], leads to very elegant code. Unfortunately, our tests using the cTAYLOR [35] package led to code that was more than 1000 times slower than the hand-written C code. Depending on the used variables, Taylor series approaches can also lead to catastrophic error cancellation and unreliable derivatives [36]. For these reasons, all functionals in the previous versions of LIBXC [9] were implemented by hand in C.

Although they can be made optimal in terms of performance, hand-written derivatives are tedious to derive and implement, and rather prone to bugs. Fortunately, computer algebra systems have improved considerably in the past couple of years, and with the introduction of optimized C output in MAPLE 2015 it became possible to eliminate much of the overhead in using these approaches. Therefore, the new version of LIBXC has been almost entirely rewritten with functionals expressed in MAPLE source code. A driver script is used to generate C code from the MAPLE sources [37]. In accordance with open source ideology, both the original MAPLE sources and the resulting autogenerated C routines (which are used to compile the LIBXC library) are included in the LIBXC distribution. Needless to say, the autogeneration approach speeds up considerably the introduction of new functionals in LIBXC and increases its reliability. Unfortunately, there remain a few functionals that could not be reimplemented using MAPLE due to technical reasons, one example being the Becke–Roussel exchange functional [38] which does not have an closed analytic form due to its reliance on a transcendental equation.

2.2. Software functionalities

By now, a large majority of the LDA, GGA, and mGGA functionals ever proposed in the literature are already included in the library. In fact, LIBXC is capable of evaluating the exchange–correlation functional and its derivatives for 48 LDAs, 261 GGAs, and 92 mGGAs. For curiosity, this is more than double the number of functionals present in version 1.0 of the library released in 2010. To our knowledge, LIBXC has by far the widest variety of functionals offered by any program package.

3. Impact

The popularity of LIBXC can be easily understood by looking at the large amount of codes (more than 20) that use it. The list includes, but is not limited to, (in alphabetic order) ABINIT [39–42], ADF [43–45], APE [46,47], BIGDFT [48,49], CP2K [50,51], ELK [52], ERKALE [53,54], EXCITING [55,56], FHI-AIMS [57,58], GPAW [59–62], OCTOPUS [63–66], PSI4 [67–69], QUANTUM ESPRESSO [70,71], WIEN2K [72], etc. We stress that this list includes not only several large, well-established codes that are the result of long, collaborative efforts, but also smaller one-person endeavors that usually tackle more specialized research questions. In our opinion, there are several outcomes of LIBXC that are worth mentioning:

- By interfacing with LIBXC a DFT code gains automatic access to an enormous amount of functionals. This enables researchers to be able to choose the functional that is the best suited for their research, and to easily compare the results obtained with different functionals — a method often used to validate DFT calculations.
- For the community of researchers that works on the study and development of exchange–correlation functionals, the use of LIBXC allows them to quickly compare the results obtained with their functional to others, and to benchmark their functional for a variety of different physical systems using different DFT codes.
- By now, LIBXC is used by a variety of codes not only from the solid-state physics community, but also from the atomic and molecular physics and quantum chemistry communities. These codes are able to tackle different systems – from atoms to molecules to clusters to solids – and rely on a diversity of numerical techniques: basis set approaches (Gaussian, numerical orbital, wavelet, plane-wave), as well as real-space grids employing finite difference approaches. As such, one can now use the same functional with exactly the same numerical implementation in a variety of codes. This not only facilitates studying the reproducibility of results obtained with different codes as in Ref. [73], but also allows one to use the best computational approach for the problem at hand.

- While the majority of the programs that rely on LIBXC follow the open source paradigm, the flexible licensing of LIBXC under the Lesser General Public License also allows its use within non-open source programs as witnessed by its inclusion in e.g. the ADF [43–45] and FHI-AIMS [57,58] programs.
- As new functionals are usually implemented in LIBXC within months from their publication, a simple recompilation will give the user of any code interfaced with LIBXC immediate access to new developments in the field.
- Similarly, if a bug is found in the implementation of a functional, it only needs to be fixed in LIBXC, after which the rectified implementation is available to all client programs.

In a certain way, the existence of LIBXC and other libraries has the continuous effect of stimulating the appearance of new and better software, by providing researchers with reliable black-box solutions that eliminate the need to "re-invent the wheel" for every code.

4. Conclusions

LIBXC is nowadays a mature library that includes the vast majority of the approximations to the exchange–correlation functional proposed in the literature of the last 50 years. However, the work in LIBXC is continuing. Besides the implementation of older functionals that are still absent from the library, every year we witness the development of new approximations that are quickly included in the library. From this perspective, LIBXC is not only a living museum of exchange–correlation functionals but also a state-of-the-art research tool pushing even further the reach of density-functional theory.

Acknowledgments

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