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Introducing LibXC into GAMESS (US)

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The interface between LibXC and GAMESS (US), which enables the latter to perform calculations with > 200 popular density functional approximations, including recently proposed r^{2}SCAN, M06-SX and CAM-QTP00, is presented. The LibXC-GAMESS interface allows users to specify custom functionals as linear combinations of the present ones, exact exchange (producing hybrids) and MP2-correlation (producing double-hybrids).

Keywords: density functional theory, exchange–correlation functionals, quantum chemistry, GAMESS, LibXC, DFT.

Dedicated to Nikolay S. Zefirov, one of the pioneers of molecular modeling in Russia

Although Density Functional Theory (DFT) was proposed[1–3] more than 65 years ago, it is now one of the most popular theories for evaluating chemical and physical properties of atoms, molecules, and solid materials.[4–6] The high popularity of DFT compared to *ab initio* wavefunction theory methods (WFT, *e.g.*, HF,[7] MPn,[8] CC,[9] *etc.*) arises from its use of the 3-dimensional electron density function instead of the 3N-dimensional wavefunction used in WFT (N is the total number of electrons). This reduction in dimensionality, in principle, leads to a significant simplification of the modeled physical system of nuclei and electrons and can result in an improvement in computational efficiency.

Nearly four decades of practice have shown that this efficiency comes with only a small loss in accuracy for many chemical tasks, which made DFT an attractive method in quantum chemistry relative to sophisticated wavefunction methods.[6,10,11] DFT is now widely used in chemistry to establish mechanisms of complex chemical reactions,[12–17] dissect their driving forces,[18–20] optimize catalysts,[21,22] predict spectral properties of organic compounds[23,24] and even determine molecular structures of natural products.[25,26]

According to the Hohenberg–Kohn theorem[1] and Levy's constrained search,[3] which underly DFT, all ground-state electronic properties of a system of electrons in an external potential (*e.g.*, nuclei charges) can be evaluated solely from the ground-state electron density of this system. In standard WFT, the energy is the eigenvalue of the system's Hamiltonian, while, in DFT, it is the functional of the electron density (ρ): $E[\rho]$.

Proposed in 1965,[2] the Kohn–Sham formalism of DFT separates the functional $E[\rho]$ into several exactly defined terms and one unknown – $E_{xc}[\rho]$:

$$E[\rho] = T_s[\rho] + V_{ext}[\rho] + U[\rho] + E_{xc}[\rho]. \qquad (1)$$

Here, $T_s[\rho]$ is the kinetic energy of non-interacting electrons; $V_{ext}[\rho]$ is the interaction energy between ρ and external electric and magnetic fields; $U[\rho]$ is the energy of electrostatic interactions of the electron density with itself; finally, $E_{xc}[\rho]$ is the exchange–correlation energy, which, by definition, is the difference between the exact energy and all known terms described earlier.

$E_{xc}[\rho]$ consists of exchange and correlation energies, including[6,27] the difference between the exact and the non-interacting kinetic energies:

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]. \qquad (2)$$

The first term is known as the exchange energy, which can be determined exactly from the Hartree–Fock equation. The *exact* expression for the correlation term is currently unknown; moreover, it is known that if it were found, the computational cost of this functional would be comparable to the full-CI method.[28] On the other hand, even the simplest *approximate* DFT functional (local density approximation, LDA) outperforms Hartree–Fock in some tasks while being computationally less elaborate.[29] This has driven researchers to develop new density functional approximations (DFAs), the number of which has grown up to several hundred by now.

Present day density functionals differ in mathematical forms (most of which require multiple empirically fitted parameters that cannot be determined from first principles[6]) and 'ingredients' – information about the electron density (or wavefunction) the functional utilizes to compute the energy density, which provides the system's electronic energy upon integration over the whole space. Popular ingredients are local electron density, its gradient norm, kinetic energy density, exact exchange energy, and non-local correlation energy. DFAs based on these ingredients form LDA, GGA, meta-GGA, hyper-(m)GGA, and the 'fifth' rung of Jacob's ladder,[30] respectively. A detailed discussion of various density functionals can be found in the following reviews.[6,10]

One of the main shortcoming of DFT is that DFAs are generally not systematically improvable and choosing an appropriate DFA for a given chemical problem requires extensive benchmarking of many suitable DFAs.[6,10,31,32] However, most DFAs are implemented only in few quantum chemical packages, which precludes their benchmarking and use. For example, the AM05[33] functional, quite popular in the solid-state community, is absent in most packages used for chemical reactions modeling (*e.g.*, Gaussian,[34] Orca,[35] NWChem[36]). The same situation holds for the recently proposed functional SCAN,[11,37] which incorporates all 17 known exact constraints that a meta-GGA can satisfy, and its numerically stabilized version – r^{2}SCAN.[38]

To simplify and disambiguate the process of DFT functionals implementation, Susi Lehtola *et al.*[39] have developed a library – LibXC – containing almost all published density functionals and providing interfaces in C, FORTRAN, and Python. The authors of the library are following the current progress in DFT functionals development. As a result, new functionals are added quickly to the development branch of LibXC, accelerating their incorporation into quantum chemical packages which support it.

GAMESS (US)[40,41] – General Atomic and Molecular Electronic Structure System – is one of the oldest and most reliable quantum chemical packages distributed as source code, which is still often used for implementing experimental and proof-of-concept developments in computational chemistry, such as CAMY-DFT[42] and mixed-reference spin-flip time-dependent DFT (MR-SF-TD-DFT[43]). Thus, GAMESS affords excellent capabilities for density functionals development,[42] testing,[31,44–46] and application,[47–49] but supports a limited number of density functionals. To address this limitation, the LibXC density functional theory library was interfaced with the GAMESS quantum chemistry code.

GAMESS has a modular structure that allows users to control the installation of various methods and capabilities during the build process. For example, the LibCChem C++ accelerated library and OpenMP-threaded version of GAMESS can be enabled or disabled at the configuration stage. The LibXC interface introduced in this work can be enabled in the same manner. The interface supports all exchange–correlation functionals based on the ingredients described in the introduction (kinetic and Laplacian-dependent functionals are currently excluded).

The LibXC interface is written according to the modern ISO Fortran 2003 standard. It consists of four files: *libxc_empty.src*, *mod_nameio.src*, *libxc.src*, and *functionals.src*. If the LibXC interface is disabled, only *libxc_empty.src* is compiled as a dummy module. Other files are compiled and linked only when the LibXC interface is enabled. *mod_nameio.src* and *libxc.src* constitute the interface, while *functionals.src* expands the capabilities of LibXC.

GAMESS has its own platform-independent namelists parser, implemented in *nameio.src*, which supports key names of no more than 6 symbols and key groups of no more than 70 keys in a group. To address this limitation, we have developed *mod_nameio.src* to avoid these restrictions. *mod_nameio.src* contains two Fortran modules: (1) *class_Pair* module with *Pair* class, which organizes key–value pairs of a group into a linked list, and (2) *mod_nameio* module with *input_group* class, which takes values from the linked lists created by the *class_Pair* module in required types (supported are logical, integer, double, and string types, as well as their arrays) simultaneously checking correctness of the keywords.

libxc.src contains routines for density functional selection and arrays interconversion between GAMESS and LibXC. *libxc.src* takes care of (1) efficient utilization of the vectorized LibXC routines for DFT energy evaluation, (2) reordering of the energy derivatives, and (3) passing 0's in place of Laplacian values required by LibXC when a meta-GGA is called (even if the meta-GGA does not explicitly depend on the Laplacian, as most of the popular ones depend only on the electron density, its gradient, and the kinetic energy density).

Functionals to be used are read from the GAMESS input file, parsed using the *input_group* class. They can be selected not only from the predefined set, but also constructed by mixing any number of the available functionals in any ratios. The routine required for the latter feature can be generated automatically using *${GMS_PATH}/tools/libxc/gen_all.py* script to incorporate all functionals available in the latest version of LibXC.

functionals.src provides the *functional* module that enables calling custom (mixed) DFT functionals *via* the *functional* class containing data of the requested DFT functional: LibXC IDs of the required functionals and mixing coefficients. Generally, the idea of custom functionals is that we can combine energy densities computed with several DFAs (e_{DFT_i}) with coefficients a_i to obtain the overall exchange–correlation energy density:

$$e_{xc}(\boldsymbol{r}) = \sum_i a_i e_{DFT_i}(\boldsymbol{r}). \tag{3}$$

Thus, to compute energy using a custom functional, the interface sequentially evaluates energy densities for several DFT functionals with LibXC.

A ground-state DFT calculation in GAMESS starts with the INPGDFT subroutine, where GAMESS sets-up parameters of DFT functionals and where the *libxc* module takes over control to read its own sections and initialize variables in *functionals.src*, as well as internal LibXC parameters. After initialization, the control returns to GAMESS. Then, when GAMESS needs DFT energies, the routine, similar to CALCEXC, is called, producing the energy and its first derivatives at each point.

In the case of a TD-DFT calculation, the LibXC interface is called from the DFTXCSET routine as it is done for pure DFT functionals.

The calculation flow is schematically represented in Figure 1.

In order to use the LibXC interface, the build option must first be enabled during the configuration of GAMESS (*e.g.*, running *${GMS_PATH}/config*).

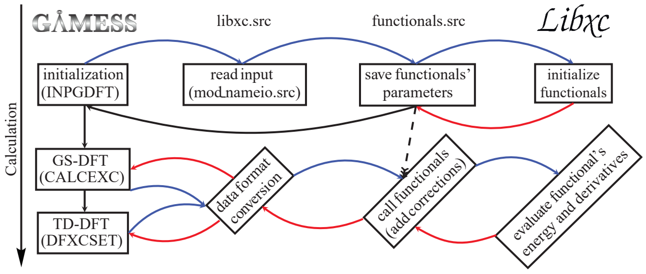

Figure 1 Schematic representation of the computation flow at the LibXC-GAMESS interface. Blue lines show the data passed from GAMESS, and red lines show the data returned from LibXC. Solid black lines designate call sequence where data is not passed. The dashed black line shows passing data from the initialization process to DFAs evaluation in the *functional* module. The names of routines are given in the round brackets (see the text for description).

Changes in the input files are minor: foremost, instead of setting a specific functional in the $CONTRL group, the user will instead specify DFTTYP=USELIBXC, which will trigger the call to the LibXC driver. The LibXC driver will then read in the $LIBXC group in the input file.

The $LIBXC group contains the FUNCTIONAL keyword, which can be used to specify the use of a density functional from a collection of more than 200 popular DFAs. Alternatively, the user can specify a custom functional with FUNCTIONAL=MIXED and providing additional input groups:

1. Contributions of local exchange (X), correlation (C), and exchange–correlation (XC) functionals can be set up using $LDA_X, $LDA_C, and $LDA_XC groups.
2. Contributions of GGA functionals can be set up using $GGA_X, $GGA_C, and $GGA_XC groups.
3. Contributions of meta-GGA functionals can be set up using $MGGA_X, $MGGA_C, and $MGGA_XC groups.
4. Contributions of hyper-GGA functionals can be set up using $HLDA_XC, $HGGA_X, $HGGA_XC, $HMGGA_X, and $HMGGA_XC. Note that in this case, the HFEX key in $LIBXC should mirror the expected ratio of exact exchange in the custom functional (see an example for PBE0[50] below).
5. Hybrid functionals can be invoked by setting the contribution of exact exchange with the HFEX key in $LIBXC.
6. Double-hybrid functionals can be initialized by setting the contribution of the MP2-correlation with the MP2 key in $LIBXC. Same-spin and opposite-spin scaling factors can be set with MP2SS and MP2OS keys in $LIBXC, respectively. Note that in our implementation, the self-consistent orbitals of the pure/hybrid functional underlying the double hybrid are used as a reference for computing the MP2 correlation energy.

Some examples of input files utilizing the LibXC interface:

r^{2}SCAN[38] as a preset functional:

```
$CONTRL DFTTYP=USELIBXC $END
$LIBXC FUNCTIONAL=R2SCAN $END
```

r^{2}SCAN[38] as custom functional:

```
$CONTRL DFTTYP=USELIBXC $END
$LIBXC FUNCTIONAL=MIXED $END
$MGGA_X R2SCAN=1.0 $END
$MGGA_C R2SCAN=1.0 $END
```

Custom hybrid DFT functional (PBE0[50]):

```
$CONTRL DFTTYP=USELIBXC $END
$LIBXC FUNCTIONAL=MIXED HFEX=0.25 $END
$HGGA_XC PBEH=1.0 $END
```

Custom double-hybrid DFT functional (PBE0-2[51]):

```
$CONTRL DFTTYP=USELIBXC $END
$LIBXC FUNCTIONAL=MIXED HFEX=0.793701 MP2=0.5 $END
$GGA_X PBE=0.206299 $END
$GGA_C PBE=0.5 $END
```

More complex hybrid DFT functional (APF,[52] note that one group can contain several values):

```
$CONTRL DFTTYP=USELIBXC $END
$LIBXC HFEX=0.22945 $END
$GGA_X B88=0.29592 PBE=0.44175 $END
$LDA_C PW=0.07809 $END
$GGA_C PW91=0.33291 PBE=0.58900 $END
```

In conclusion, this article introduces and details the LibXC interface for the GAMESS quantum chemistry code, which enables the latter to perform calculations with more than 200 popular density functionals, including the recently proposed r^{2}SCAN, M06-SX, and CAM-QTP00. The LibXC interface also allows users to specify custom functionals as linear combinations of the present ones, including exact exchange (producing hybrids) and MP2-correlation (producing double-hybrids). The LibXC interface is available since the June 30, 2020 R1 public release of GAMESS. Routines for double hybrid functionals will be corrected in the June 30, 2021 R1 public release.

Inclusion of the LibXC library significantly broadens GAMESS applicability to chemical problems by introducing many density functionals of physics-based and task-optimized families. Among the first family, SCAN and r^{2}SCAN offer outstanding accuracy for many chemical and physical properties.[11,38] Among the second one, there are various Minnesota density functionals, which offer exceptional accuracy for systems and properties close to those they were designed for;[10,53] B3LYP*, fitted for low-spin/high-spin splitting in Fe^{2+} complexes;[54] KT1,[55] KT2,[55] KT3,[56] WC04[57] and WP04,[57] designed for calculating NMR chemical shifts; EDF2, designed to provide accurate vibrational frequencies (infrared spectra) of organic molecules.[58] We expect that the developed interface would be of great benefit both for organic chemists and for density functional developers and benchmarkers.

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