

Exchange-Correlation Functionals: GGA vs. meta-GGA

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Abstract

Density Functional Theory (DFT) is a widely used electronic structure method due to its balance between computational efficiency and reasonable accuracy. One of the many important choices a user must make when utilizing DFT is that of an appropriate exchange-correlation functional for the system being studied. In this worksheet we will explore the theory underlying two groups of functionals: Generalized Gradient Approximation (GGA) and Meta-Generalized Gradient Approximation (meta-GGA). We will then utilize the Maple Quantum Chemistry Toolbox in two different examples to demonstrate how these functionals perform relative to each other.

Introduction to Density Functional Theory¹⁻⁵

Density Functional Approximation

The Hohenberg-Kohn theorem proved that a functional for the energy of a particle can be defined in terms of its 1-electron density and that minimizing the functional will lead to the exact ground state energy of the particle. This theory paved the way for Density Functional Theory (DFT), which is formally an exact description of a many-body quantum system based on density rather than the many-electron wave function. We must now note a confusing, but important, notion that while DFT is exact in principle, in practice it is implemented with approximations. As Becke wrote, we should thus keep in mind that "The failures we report at meetings and in papers are not failures of DFT, but failures of DFAs" (whereby DFAs stand for Density Functional Approximations).²

Exchange-Correlation Energy

Although the foundation of DFT was established by the Hohenberg-Kohn theorem, it was implemented computationally by Kohn and Sham using Kohn-Sham orbitals (note that there exists an orbital-free approach to DFT, but the KS approach is the norm). The KS approach converts a real interacting electronic system into an analogous non-interacting electronic system in a way that preserves the density of the former system.

A crucial component in constructing the KS non-interacting system is the exchange-correlation (XC) energy, E_{XC} , which is a functional of the electron density. While the exchange-correlation functional is universal, meaning that is applicable to all possible many-electron systems, the explicit form is unknown and therefore approximated in practice. Though the exchange-correlation energy contributes only a small fraction of a system's total energy, accurate E_{XC} values are still integral to obtaining an accurate description of chemical bonds.

Theory

Electronic Structure^{6,7}

The time-independent, non-relativistic Schrödinger equation, $\hat{H}\Psi = E\Psi$, is exactly solvable for a one-electron atom. Unfortunately, this is not the case for multi-electron systems, as our N-electron Hamiltonian is now inseparable and consists of the following terms:

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ee}$$

where \hat{T} is the kinetic energy operator, \hat{V} is the one-body operator, and \hat{V}_{ee} is the electron-electron repulsion operator, defined as follows:

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2$$
$$\hat{V} = \sum_{i=1}^N v(r_i)$$
$$\hat{V}_{ee} = \frac{1}{2} \sum_{i < j}^N \frac{1}{|r_i - r_j|}$$

r_i represent the coordinate and Laplacian of electron i , respectively.

Many methods, including coupled-cluster and Møller-Plesset perturbation theory, calculate the ground-state energy for a multi-electron system by invoking the variational principle and minimizing the wave function over all antisymmetric N-particle wavefunctions:

$$E[\Psi] = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

In many cases, however, the poor scaling and resulting high computational cost of these methods are impractical. We will now explore below how DFT takes a different approach to tackling this many-body problem!

DFT & XC Functionals^{6,7}

As mentioned in the introduction, in DFT, we make use of the Hohenberg-Kohn theorem and express the ground-state energy as a functional of the electron density $n(\mathbf{r})$, rather than the wavefunction Ψ . In doing so, we can apply the variational principle twice in order to obtain the ground-state energy for a system -- first minimizing over all wavefunctions that yield a certain density $n(\mathbf{r})$ and then minimizing over all densities:

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \{ \hat{T} + \hat{V}_{ee} \} | \Psi \rangle$$
$$E = \min_n \left\{ F[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r}) \right\}$$

where $F[n]$ is a universal functional of the density and is composed of the following terms in the Kohn-Sham approach:

$$F[n] = T[n] + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{XC}[n]$$

whereby $T[n]$ represents the kinetic energy of a system of interacting electrons with density $n(\mathbf{r})$, the second term represents the classical electrostatic energy, and E_{XC} represents the exchange-correlation

energy.

The third term, E_{XC} , quantifies the difference between classical and quantum mechanical electron-electron repulsion and is the only term that is not known explicitly. We thus segue into our discussion of the various groups of exchange-correlation functionals -- the functionals that approximate this energy in DFT.

Jacob's Ladder of XC Functionals^{3,5}

John P. Perdew, renowned physicist for his work on DFT, described a "Jacob's ladder" metaphor in which the rungs of a ladder represent different density functional approximations that increase in complexity as you ascend it.³ Accordingly the lowest rung, the Local Density Approximation (LDA), is the simplest functional and calculates the exchange-correlation energy only as a function on the electron density. The next rung is the Generalized Gradient Approximation (GGA), which includes both the density and its gradient. Meta-GGA, the third rung, additionally considers the Kohn-Sham kinetic energy density. The fourth rung, hybrid functionals (also termed hyper-GGAs), include some percent of the non-local, exact exchange-energy density with a GGA. The highest rung, the fully nonlocal functionals, build upon hybrid functionals by including unoccupied Kohn-Sham orbitals and energies.

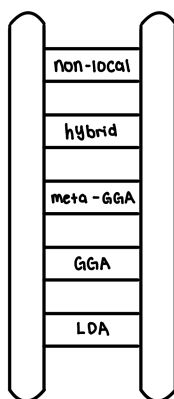


Figure 1. Jacob's ladder of exchange-correlation (XC) functionals

In this worksheet, we will take a closer look at the second and third rungs of our ladder: GGA and meta-GGA.

Generalized Gradient Approximation (GGA)^{3,8-10}

As stated above, LDAs only have a dependence on the local electron density and typically overestimates the strengths of all bonds near equilibrium. GGAs build upon LDAs by depending explicitly on both the density and its gradient (ie. how fast the density is changing locally). In this manner, GGAs account for the fact that a molecule's electron density is not spatially uniform, thereby typically resulting in more accurate bond descriptions.

$$E_{XC}^{GGA}[\rho] = \int d^3r f(\rho(r), \nabla\rho(r))$$

Popular GGA functionals include PBE, BLYP, OLYP, and BP86.

Meta-generalized Gradient Approximation (meta-GGA)^{3,5,10,11}

Meta-GGAs typically improve upon the accuracy of GGAs as they additionally take into account the local kinetic energy density. This allows meta-GGAs to more accurately treat different chemical bonds (eg. covalent, metallic, and weak) compared to LDAs and GGAs.

The meta-GGA can be written as:

$$E_{XC}^{mGGA}[\rho, \tau] = \int d^3r f(\rho(r), \nabla\rho(r), \tau(r)),$$

where the kinetic energy density is defined as the following summation over all occupied Kohn-Sham orbitals $\varphi_i(r)$:

$$\tau(r) = \frac{1}{2} \sum_i^{occ} (\nabla\varphi_i(r))^2$$

Popular meta-GGA functionals include TPSS, M06-L, revTPSS, and SCAN.

Application - Ionization Energy

Note: To improve readability, in the following sections colons (:) were included at the end of the majority of the Maple commands in order to suppress the commands' output. To see the full output for a command, simply delete the colon and re-run the worksheet.

To begin, we set the number of **Digits** to be used in our computations to 10 and load our [Quantum Chemistry](#) package:

- > `Digits := 10 :`
- > `with(QuantumChemistry) :`

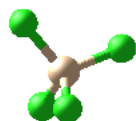
For our examples we will be comparing the GGA functional PBE and the meta-GGA functional TPSS.

Silicon Tetrachloride¹¹⁻¹³

Our first example is the ionization energy of SiCl_4 .

We will first retrieve the geometry of silicon tetrachloride using its PubChem CID (24816) and visualize the molecule's structure:

- > `siCl4 := MolecularGeometry(24816)`
- `siCl4 := [["Cl", 0.25630000, -1.35590000, 1.48720000], ["Cl", 1.45040000, 1.41420000, 0.11690000], ["Cl", -1.81920000, 0.87850000, 0.19150000], ["Cl", 0.11270000, -0.93720000, -1.79570000], ["Si", -0.00020000, 0.00040000, 0.00010000]]` **(1)**
- > `PlotMolecule(siCl4)`



We will now compute the ionization energies using PBE and TPSS.

To begin, we compute the energy of the neutral molecule using an arbitrary basis set 6-311+g:

> `neut_pbe := DensityFunctional(sic14, xc = "PBE", basis = "6-311+g")`

$$\text{neut_pbe} := \text{table} \left(\begin{array}{l} \left[\begin{array}{c} 0.16082420 \\ 0.16102194 \\ 0.16115909 \\ 0.16079550 \\ -0.64380073 \end{array} \right], \text{populations} = \left[\begin{array}{c} 0.77765604 \\ 1.18706965 \\ 0.89122195 \\ 1.09149234 \\ 1.01581448 \\ 1.07325983 \\ \vdots \\ \text{125 element Vector[column]} \end{array} \right], \text{rdm1} = [[\end{array} \right. \quad (2)$$

[0.37185487, 0.62657538, -0.12551115, -0.18515093, 0.03567984, 0.05514298, ...],

[0.62657538, 1.09253030, -0.35358343, -0.49769010, 0.10257459, 0.15768153, ...],

[-0.12551115, -0.35358343, 0.59486177, 0.79456707, -0.22421177, -0.31559700, ...],

[-0.18515093, -0.49769010, 0.79456707, 1.09478626, -0.45196383, -0.56392482, ...],

[0.03567984, 0.10257459, -0.22421177, -0.45196383, 0.80547725, 0.79396323, ...],

[0.05514298, 0.15768153, -0.31559700, -0.56392482, 0.79396323, 0.86092684, ...],

[; ; ; ; ; ;]],

$$\left[\begin{array}{c} \text{125} \times \text{125 Matrix} \end{array} \right], aolabels = \left[\begin{array}{c} \text{"0 Cl 1s"} \\ \text{"0 Cl 2s"} \\ \text{"0 Cl 3s"} \\ \text{"0 Cl 4s"} \\ \text{"0 Cl 5s"} \\ \text{"0 Cl 6s"} \\ \vdots \end{array} \right], mo_coeff = [[$$

125 element Vector[column]

$$\begin{aligned} & [0.00091429, 0.00156533, 0.41171472, -0.00820600, -2.44778081 \times 10^{-7}, \\ & -0.00929603, \dots], \\ & [0.00145028, 0.00248381, 0.65359782, -0.01302819, 2.14881344 \times 10^{-6}, -0.02492255, \\ & \dots], \\ & [0.00004031, 0.00006507, 0.01568679, -0.00030724, -0.00001241, 0.03793159, \dots], \\ & [-0.00002196, -0.00002926, -0.00468080, 0.00008185, 0.00002034, 0.04644375, \dots \\ &], \\ & [0.00003794, 0.00004046, 0.00178561, -1.97053879 \times 10^{-6}, -2.58387655 \times 10^{-6}, \\ & 0.00537162, \dots], \\ & [-0.00008614, -0.00008751, -0.00130902, -0.00005636, 0.00013720, \\ & -0.00374678, \dots], \\ & [\ddots \ddots \ddots \ddots \ddots \ddots]]], \end{aligned}$$

$$\left[\begin{array}{c} \text{125} \times \text{125 Matrix} \end{array} \right], mo_occ = \left[\begin{array}{c} 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ \vdots \end{array} \right], mo_symmetry = \left[\begin{array}{c} \text{"A"} \\ \text{"A"} \\ \text{"A"} \\ \text{"A"} \\ \text{"A"} \\ \text{"A"} \\ \text{"A"} \\ \vdots \end{array} \right], e_tot$$

125 element Vector[column]

125 element Vector[column]

$$= -2129.49626752, mo_energy = \begin{bmatrix} -100.73527465 \\ -100.73523972 \\ -100.73519171 \\ -100.73518257 \\ -65.58656598 \\ -9.23047787 \\ \vdots \end{bmatrix}, group = "C1", converged = 1,$$

125 element Vector[column]

$$dipole = \begin{bmatrix} -0.00167675 \\ 0.00316346 \\ 0.00074349 \end{bmatrix}$$

> *neut_tpss* := DensityFunctional(sic14, xc = "TPSS", basis = "6-311+g") :

Now we compute the absolute energy of the ionized molecule SiCl_4^+ :

> *ion_pbe* := DensityFunctional(sic14, xc = "PBE", basis = "6-311+g", charge = 1) :

> *ion_tpss* := DensityFunctional(sic14, xc = "TPSS", basis = "6-311+g", charge = 1) :

We may now compute the ionization energy and compare the values we obtain with the experimental value:

> *ie_exp* := 0.4263 :

> *ie_pbe* := *ion_pbe*[*e_tot*] - *neut_pbe*[*e_tot*]
ie_pbe := 0.43333000 (3)

> *ie_tpss* := *ion_tpss*[*e_tot*] - *neut_tpss*[*e_tot*]
ie_tpss := 0.42039900 (4)

> *err_pbe* := $\frac{\text{abs}(ie_pbe - ie_exp)}{ie_exp} \cdot 100$
err_pbe := 1.64907342 (5)

> *err_tpss* := $\frac{\text{abs}(ie_tpss - ie_exp)}{ie_exp} \cdot 100$
err_tpss := 1.38423645 (6)

We see that as expected our meta-GGA functional comes closer to the experimental ionization energy

for silicon tetrachloride!

Methane¹⁴

Our next example is the ionization energy of CH₄.

We will first retrieve the geometry of methane:

- > *methane* := *MolecularGeometry*(*methane*) :
- > *PlotMolecule*(*methane*)



Now we repeat the same process as followed in the previous example in order to compare the ionization energy of methane as calculated using PBE and TPSS:

- > *neut_pbe* := *DensityFunctional*(*methane*, *xc* = "PBE", *basis* = "6-311+g") :

- > *neut_tpss* := *DensityFunctional*(*methane*, *xc* = "TPSS", *basis* = "6-311+g") :

- > *ion_pbe* := *DensityFunctional*(*methane*, *xc* = "PBE", *basis* = "6-311+g", *charge* = 1) :

- > *ion_tpss* := *DensityFunctional*(*methane*, *xc* = "TPSS", *basis* = "6-311+g", *charge* = 1) :

- > *ie_exp* := 0.46340899 :

- > *ie_pbe* := *ion_pbe*[*e_tot*] - *neut_pbe*[*e_tot*]

$$ie_pbe := 0.52906251 \quad (7)$$

- > *ie_tpss* := *ion_tpss*[*e_tot*] - *neut_tpss*[*e_tot*]

$$ie_tpss := 0.53340363 \quad (8)$$

- > *err_pbe* := $\frac{\text{abs}(ie_pbe - ie_exp)}{ie_exp} \cdot 100$

$$err_pbe := 14.16751108 \quad (9)$$

- > *err_tpss* := $\frac{\text{abs}(ie_tpss - ie_exp)}{ie_exp} \cdot 100$

$$err_tpss := 15.10429049 \quad (10)$$

Surprisingly, TPSS calculates an ionization energy that is further away from the experimental value than the value calculated with PBE! This is surprising as the TPSS functional is from the more sophisticated family of functionals!

Discussion & Conclusion

As semilocal approximations, GGAs and meta-GGAs employ only local and semilocal information. While this means that they remain computationally efficient for large systems, they typically will only be reasonably accurate for systems that are not strongly correlated or do not have important long range van der Waals interactions.

A second key takeaway from this worksheet is that it is **not** valid to simply assume that a higher-rung functional is the ideal tool for the job. In some cases, a lower-rung functional will not only be less computationally demanding, but overall more suitable. As Perdew wrote, "When we climb to a higher rung, we do not kick away the lower rungs, which retain their value and importance. The accuracy and sophistication of the higher rungs is complemented by the simplicity and transparency of the lower ones."³

Unfortunately, in the case of DFT functionals, there is no one-size-fits-all option. In fact, still today, new density functionals are being developed -- some aim to develop functionals best suited for certain systems, while others are developing functionals that are meant to be widely-applicable. Luckily, these newly developed functionals are often benchmarked and heavily studied to validate their reliability; these studies should be carefully considered when choosing the right functional for a given system.

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