

Review

A Critical Look at Density Functional Theory in Chemistry: Untangling Its Strengths and Weaknesses

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Abstract: Density functional theory (DFT) is a commonly used methodology favored by experts and non-experts alike. It is a useful tool for the investigation of atomic, molecular and surface systems, offering an efficient and often reliable approach to calculate ground state properties such as electron density, total energy and molecular structure. However, fundamental issues are not rare. Of course, no one can really question the bold impact of DFT on modern chemical science. It is not only the way research is conducted that has been influenced by DFT, but also textbooks, datasets and our chemical intuition as well. In this review, issues pertaining to DFT are discussed, and it is pointed out that without a clear understanding of why we use calculations, an effective combination of experiment and theory will never be accomplished. Using low-level theoretical frameworks surely does not shed light on profound problems. To excel in our scientific field and make good use of our tools, we must very carefully decide which methodologies we are to employ.

Keywords: density functional theory; computational chemistry; physical chemistry; electronic structure theory



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1. Introduction

No one can really question the bold impact of density functional theory (DFT) on modern chemical science. It is not only the way research is conducted that has been influenced by DFT, but also textbooks, datasets and our chemical intuition as well. But what is more profound is the incomparable rate at which it is being used in research articles. The literature has been growing exponentially between 1990 and 2000. Since then, there has been a linear growth, where publications more than double in a time interval of 5 years [1].

Figure 1 highlights this growing trend since 1999, accessed from the Web of Science. The platform indicates that more than 200,000 papers have the keyword “Density Functional Theory” in their abstract, while the number exceeds 500,000 if we include more relaxed keywords (such as DFT and TD-DFT). The current situation does not show any signs of why this should change, conversely, in the years to come.

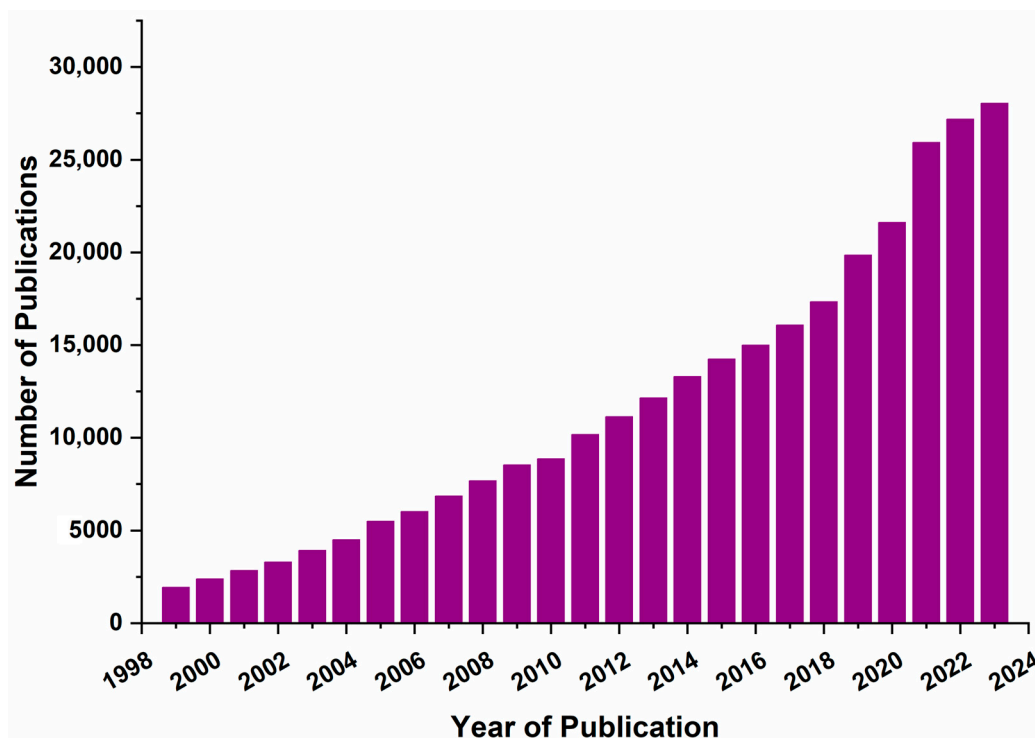


Figure 1. A bar chart accessed from Web of Science, indicating the growing interest in density functional methodologies between 1999 and 2023. The chart was constructed based on the occurrence of the keyword “Density Functional Theory” or “DFT” that are included in an article’s abstract.

2. Discussion

The reason behind this unprecedented exploitation of a theoretical framework is multifaceted. Firstly, the advance of computer technology, in terms of both software and hardware, has made DFT essentially a very easy computational task. Nowadays, even macro- and biomolecules can be treated with such methodologies to yield results in a reasonable time. Secondly, DFT is innately a more computationally efficient theory, compared to the other wavefunction-based theories (termed as *ab initio*), thus making it possible to study larger, and of course more realistic, systems. The above leads to the point where DFT is applicable to a plethora of scientific fields, ranging from chemistry, condensed matter physics and biology, further contributing to its popularization. Another thing, which is also the most concerning and most criticized, is the straightforwardness with which density functional calculations are performed these days. The user-friendly character of modern quantum chemical packages, along with their computing efficiency, has made DFT a “black-box” technique [2], where the nonchalant user yields dubious results.

But, beyond the aforementioned problem of a “black-box technique” and the question it generates: “Is it for everybody?”, we should also focus our attention on another, less mentioned question: “Is it really useful?”. To put it another way, is it really that important to include DFT calculations in almost every paper, for example, where a new compound has been synthesized?

It is clear that some areas of chemistry (such as catalysis and synthesis) have been heavily influenced by the use of density functional calculations. They reportedly “shed light” on the molecules described in the experimental part of the work. While this may occasionally be true, it acts more like an obstruction to the original experimental query, just accompanying it rather than offering something. Usually, such calculations are performed with doubtful levels of theory and without any real need to be carried out in the first place; therefore, they do not offer any insightful comments on the results already obtained. Current methodology involves searching for a functional/basis set combination that yields

results similar to the experiment, and further extrapolating this with false reliability. The way the theory is used currently is like sweeping things under the carpet: we add DFT calculations to a research paper to compensate for any ambiguous or disappointing experimental results we obtained. And it is not the use of DFT that is to blame, rather it is the haphazard way it is used.

In most cases, using our logic and intuition as chemists could yield important and meaningful results, just by the addition of simple experiments. The resort to questionable theoretical frameworks can be easily replaced by a thoughtful and logical set of questions that will ultimately prove/disprove a concept just through experimentation. Such recourses would render a simple DFT calculation unneeded and the research article more mature and trustworthy, since it is founded on sound experimental data.

For example, a computed reaction path could be the first step towards a more elaborate mechanism elucidation based on reaction kinetics and spectroscopy, which are far more important than a mechanism that was calculated so as to satisfy our chemical disposition. Moreover, *ab initio* methods are far more authoritative than low-level DFT methods in systems where density functionals are by nature unsuitable, e.g., in situations where charge transfer dominates. By low-level we mean a functional not well-suited to the particular case and/or a small and incompetent basis set. Of course, using a time- and resource-demanding *ab initio* calculation may be prohibitive and may even provide the same results the DFT calculation; but still, adding it would yield a much more reliable and reproducible result. Compressing theory into a few sentences does not enable the theoretician to study the problem from its root, and thus yields a story not fully completed!

Many deficiencies of the DFT method have been pointed out throughout its long history and a lot of ground-breaking work has been realized during this time and still continues to push forth boundaries, in order to overcome them [3–10]. Nevertheless, many such illnesses still remain unresolved, either due to fundamental issues concerning the implementation of the theory or due to the profound difficulties of the matter at hand [11]. Some characteristic areas where the DFT method fails are presented below, along with indicative examples from the literature. Any justification for the resulting failure will be indicated and potential remedies will be proposed.

An archetypal problem for DFT is the correct description of weak, long-range interactions, and many excellent reviews exist [12–15]. The need to describe such interactions correctly is obvious, due to their ubiquitous involvement in nature [16–18], and the years before the 21st century were full of such cases, even for atomic/diatomic systems [19–24]. Although the conventionally used semilocal and hybrid functionals offer a great accuracy/cost ratio, they fail to describe correctly: first, situations with strong electron delocalization, due to fractional charges (delocalization error [25,26]), and second, attractive dispersion interactions at large distances, which decay with $1/R^6$. It has been found that such issues are strongly functional-dependent [12,24] and, despite the different schemes developed to overcome these, our solutions include various empirical components and still no universally sound functional exists [12]. Therefore, in order to obtain meaningful results, many combinations of functionals and dispersion corrections have to be used, before settling on a preferred method. Still, it is essential to understand how and why the chosen functionals were developed and for what types of systems. However, to date, dispersion-corrected density functional theory (DFT-D) methods represent the most effective methods for conducting precise quantum mechanical calculations on molecular systems, spanning from small clusters to microscopic and even mesoscopic samples, containing hundreds or thousands of molecules [27–29].

Another case where DFT struggles a lot is spin. As spin is an invaluable property for the development of electronic and magnetic devices, a method to properly describe such systems is imperative. Due to the size, and often multimetallic nature, of such common systems, DFT presents the only obvious choice. Still, it suffers from the inability to make correct predictions of spin-state energetics [30]. The major limitation is the unsystematic nature of the errors of the relative energies for different spin states [30–37].

Exchange–correlation functionals depend on both the spin state and the spin density. The latter is also a factor that undermines the DFT method, as it gives incorrect qualitative results [38–40]. It has been found [30–32] that, in order to obtain at least qualitative results concerning the correct ground state multiplicity, a very judicious choice of functional and basis set must be made. Furthermore, the reparametrization of the commonly used functionals might be imperative, which contradicts the black-box character of DFT and its implantation by the chemical community. Again, safe predictions are only to be made by using high-level (and also highly resource-hungry) *ab initio* methods, while at the same time DFT goes hand in hand with experimental results in order to be referenced. However, some of the DFT issues regarding symmetry and spin can be successfully handled via the broken symmetry DFT (BS-DFT) technique. BS-DFT is an extension of DFT that accounts for situations where the symmetry of the calculated system is “broken” or lower than the symmetry of the underlying Hamiltonian symmetry, i.e., the calculated system does not retain the Hamiltonian symmetry due to charge distribution, spin polarization and geometrical distortion. The symmetry constraints, such as spin or spatial symmetry, are relaxed to allow for lower-symmetry solutions. For instance, the electronic structure of transition-metal complexes may show lower symmetry due to the presence of different ligand environments or in cases where spin symmetry is broken, and spin-polarized DFT calculations can be carried out. A system with two possible spin states (up and down) would also be problematic and might undergo a “spin-flip” in the calculation to find a more accurate ground state and, in general, the spin arrangement can then be handled. In general, BS-DFT is widely used in the study of magnetic materials, where spin symmetry is often spontaneously broken [41–43]. Furthermore, in the case of metallic complexes, with significant dynamical correlation, BS-DFT can predict the experimental geometries of low-spin multiplicity, which the *ab initio* complete active space SCF (CASSCF) cannot, while at the same time standard DFT fails. However, BS-DFT significantly overestimates the difference between the low- and high-spin electronic states for a given oxidation state. For this type of system, the *ab initio* N-electron valence state perturbation theory (NEVPT2) can lead to an accurate calculation of the energetics [44].

Another seemingly innocent thing to calculate via DFT is torsional barriers. Although hybrid and semilocal functionals give accurate descriptions for common torsional barriers [45–47], some cases remain problematic [48]. For example, conjugated systems represent a difficult case, as the delocalization error [49] of DFT yields extremely density-sensitive results. It has been shown [48] that many of the commonly used functionals are unable to describe the torsional barriers of simple molecules, both qualitatively and quantitatively. Increasing the percentage of HF exchange may improve the results, but with significant errors always lurking, as it may, for example, interrupt the cancelation of errors [50]. Another informative study [51] showed that, among a plethora of routinely used functionals, only M05-2X managed to provide good results for the specific system and was the only approach that featured the correct geometry for styrene. It has to be noted here that such functionals are developed [52] for specific tasks and generality, again, is not a feature of DFT.

Presumably, the most precarious path to walk in the DFT-realm is the chemistry of transition metals (TMs [53]), along with its applications ranging across chemical reactions [54–56], investigation of excited states [57–59], charge-transfer processes [60–62], etc. As before, schemes have been developed to overcome such issues, with task-specific functionals, but the situation is still slippery. The modeling of mechanistic pathways entails many pitfalls, and an excellent recent tutorial review exists on this topic [63]. In the case of excited states, the use of TDDFT [64] has been an irreplaceable tool for the computational chemist. Nevertheless, it should still represent the starting step for more profound methods, as the errors are unpredictable and of the order of 0.5 eV [65] and are susceptible to even larger errors concerning, for example, charge transfer states [66]. In general, many are the pitfalls [67] awaiting the careless. Singlet–triplet gaps may be difficult and, apart from quantitative errors [68], may lead to inverted [59] singlet–triplet gaps or may not even be

able to predict them. The study of potential energy surfaces may lead to subtle situations where incorrect qualitative results may also be obtained [69,70].

Regarding atoms and common molecules, DFT is particularly effective in calculating the ground state electron density. DFT directly solves electron density, which is a natural representation for atoms and molecules. It provides a good approximation for many atomic and molecular properties, i.e., geometry, ionization energies, electron affinities and electron density distributions with a reasonable balance between computational cost and accuracy. Regarding the electron correlation, while DFT does not account explicitly for electron–electron correlation, as do sophisticated ab initio methods such as coupled-cluster (CC) methods, multireference configuration interactions (MRCIs), perturbation theory (PT), etc., it still captures a part of both dynamic and static electron correlation.

At this point, it might be useful to showcase more vividly some examples from the literature, where DFT (or its congener methods such as TD-DFT and BS-DFT) has been unable to correctly describe the system under study, or at least to do so in a consistent way. This may happen even with seemingly simple and small systems and the following table (Table 1) highlights exactly this.

Table 1. Examples of calculated systems where the DFT method fails. Green-hued are the cases where DFT gives the correct description, while red-hued are those where it fails.

Chemical System	Electronic Structure Method		Ref.
	DFT and Issues	Appropriate Methodology	
H ₂ ⁺ , H ₂	Geometry Potential Energy Curves Delocalisation error exists Static Correlation error exists	MR methods	[49]
RuC [−]	Assignment of the ground state (Λ value)	MRCISD	[71]
RuB, NbB, LaB, OsB	Assignment of the ground state (Λ value)	MRCISD	[72]
S=CH ₂	Geometry and Vertical Energies Potential Energy Surfaces Population Dynamics	MRCISD and MS-CASPT2	[73]
Heptazine, Cyclazine and Related Compounds	S-T gap (an inverted S-T gap is predicted)	MRPT2, MCSSCF, STEOM-CCSD, CIS(D) (MC-PDFT with a proper choice of double hydride functional)	[59]
[Fe ₂ S ₂ (SMe) ₄] ^{2−,3−,4−}	LS State Geometry: DFT, BS-DFT HS State Geometry: DFT, BS-DFT Energetics: DFT, BS-DFT	MRCISD, NEVPT2, AC0	[44]

Overall, the limitations of DFT are: **(1) The approximate exchange–correlation functional**—the accuracy of DFT depends heavily on the choice of this functional. Even for atoms, functionals like LDA or GGA can give reasonable results, but they are not always very good. In some cases, more advanced functionals, such as hybrid functionals like B3LYP or meta-GGA functionals are needed to improve accuracy. **(2) The Self-Interaction Error**—a well-known issue of DFT, and considered as one of the major sources of error in most approximate exchange–correlation functionals. Usually, it is large with all local exchange–correlation functionals and with some hybrid functionals. It occurs when an electron incorrectly “interacts” with itself due to approximations in the exchange–correlation functional. This error may affect some properties, mainly in systems with highly

localized electrons (e.g., anions or transition metal atoms with unfilled d-orbitals) [74]. **(3) Electron Localization**—for some systems, even atoms, having strong electron localization (e.g., highly charged ions), DFT may present issues with the accurate calculation of the electron density, leading to deviations from experimental values of atomic properties. In some diatomic molecules, DFT correctly predicts the spin multiplicity, but occasionally $^1\Lambda$ (e.g., for transition metal–boron diatomics such as YB, ZrB, RhB, etc.) has issues with the assignment of the Λ value of the ground state configuration $^{2S+1}\Lambda$ [72]. **(4) Relativistic Effects**—for heavy atoms, or molecules including heavy atoms, the relativistic effects (such as spin–orbit coupling) are important. Common DFT does not account for these effects. However, relativistic corrections can address this issue or the use of relativistic DFT methods using for instance the four-component Dirac equation or scalar relativistic approximations [75]. **(5) Excited States**—initially, DFT was developed for ground state properties, so it may not provide accurate results for excited states. However, for the calculation of the excited states, the time-dependent DFT (TD-DFT) may provide good results. In general, complexes of transition metal atoms can be calculated by DFT, but issues with electron correlation (especially for transition metals with partially filled d-orbitals) might require more advanced treatments than DFT.

Here, we should point out that several of the above-mentioned issues stem from the very fact that DFT is a single-reference method (SR), i.e., only one Slater determinant is used to describe the (approximate) wavefunction of the system. This leads to fundamental problems with electronic structure description. For example, even for the H_2 molecule, when one tries to stretch it, huge mistakes are made using such SR methods. This is also true for transition metal complexes where multiple electron configurations are at play, even in the ground state. Moreover, even the coupled cluster singles, doubles and perturbative triples CCSD(T) method is SR and can safely serve as “golden standard” only for the ground state of molecules. Multireference (MR) methods arise from the summation of multiple Slater determinants, representing the contribution of different electronic configurations, and are more than useful for a plethora of problems. Therefore, multiconfigurational and/or MR methods such as, multireference configuration interaction + singles + doubles (MRCISD), complete active space self-consistent field second-order perturbation theory (CASPT2), second-order N-electron valence state perturbation theory (NEVPT2), MR second-order perturbation theory (MRPT2), linearized integrand approximation of adiabatic connection (AC0) and others as outlined above, are not only recommended but imperative. Theoretically, this should leave DFT out of the discussion of excited-state chemistry, but the balance of advantages and disadvantages of the method (*vide infra*) changes that. Closing this comment, the emergence of the multideterminantal versions of DFT i.e., multiconfigurational DFT [76,77] (MCDFT) and multistate DFT [78,79] (MSDFT) along with their potential ground-breaking applications should not be disregarded.

To sum up, despite the already-known problematic cases of DFT, the theory is without doubt one of the most important (computational) tools of the modern chemist’s arsenal. Maintaining relatively low computational cost, DFT can provide highly accurate ground state geometries for a plethora of molecules, enabling the structural and electronic elucidation of thought-provoking molecules [80–83]. This can also serve as a sound starting point for even *ab initio* calculations, which can by no means treat the optimization calculations of big molecules. In combination with the high-level MRCI method (DFT/MRCI [84]), robust information can be nowadays obtained for the excited states [85,86] of (relatively big) molecules and the photodynamics of processes can even be reconsidered [87]. Nevertheless, in the hands of the trained computational chemist, DFT as a standalone theory can also produce meaningful results [88–93]. Transition-metal chemistry is a field where DFT is well appreciated [94,95], yielding fast and generally decent results that can provide answers and guidance. DFT also represents our best option for generating large databases for the training of machine learning [8,96–101] algorithms, and is thus an indispensable tool for the future [3] of (computational) chemistry.

All in all, some key advantages and disadvantages of DFT, as it is implemented, are shown in Figure 2 below.

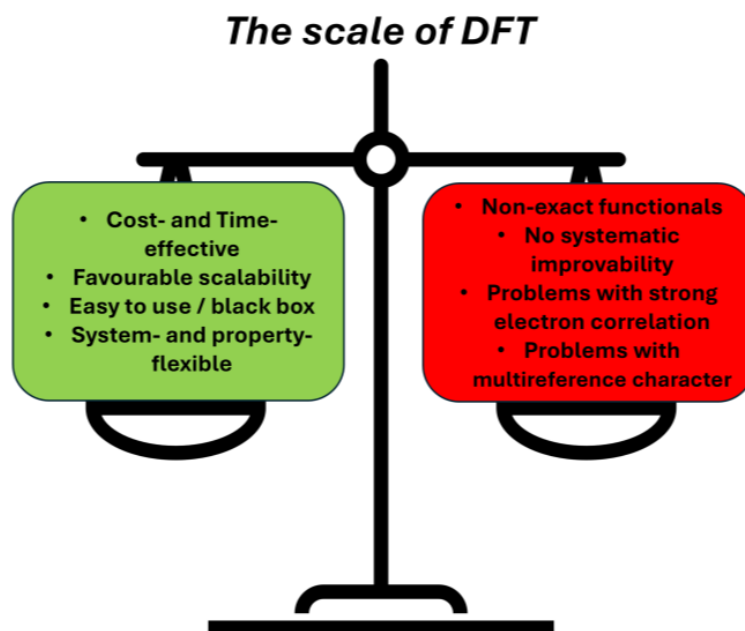


Figure 2. A collection of some important advantages and disadvantages of density functional theory as it is implemented nowadays, shown in the green and red box, respectively. One should always consider this “Scale of DFT” before attempting to tackle a chemical or physical problem.

3. Conclusions

To conclude, DFT is a useful tool for the investigation of chemically important systems, generally offering an efficient and reliable approach to calculate ground state properties such as electron density, total energy and molecular structure. However, its accuracy depends on the choice of the exchange–correlation function and special care may be required for elements exhibiting significant relativistic effects or strong electron correlation. For most molecular systems, DFT achieves a good balance between computational efficiency and accuracy.

In this article the problems of DFT have been highlighted, mainly because in recent years there has been an increasing tendency in articles to include both experimental and computational data. Since there are commercial or academic computational chemistry packages that are user-friendly, and that are becoming more and more user-friendly, everyone can run some calculations without the appropriate background and without the necessary knowledge. Thus, many experimental articles just include some calculations. What really needs to be emphasized is the fact that without a clear understanding of why we use calculations, an effective combination [102] of experiment and theory will never be accomplished. Just using low-level theoretical frameworks surely does not shed light on the problem we are dealing with. In order to excel in our scientific field and make good use of our tools, we must very carefully decide which methodologies we are to follow; both experimental and theoretical. Modern advances in quantum chemistry are bound to provide our community with exciting results; should we use them carefully. . .

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