How Accurate is Density Functional Theory for Molecules in Electric Fields?

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Abstract

The use of oriented external electric fields (OEEFs) as a potential tool for catalyzing chemical reactions has gained traction in recent years. Electronic structure calculations using OEEFs are commonly done using methods based on density functional theory (DFT), but until now, the performance of DFT methods for calculating molecules in OEEFs had not been assessed in a more general scope. Looking at the accuracy of both molecular geometries and electronic energies, we have investigated a wide variety of density functionals using different basis sets to determine how well the individual functionals perform on various types of chemical bonds. We found that most functionals accurately calculate geometries in OEEFs, and that small basis sets are sufficient in many cases. Calculations of electronic energies show a significant error introduced by the OEEF, which the use of a larger basis set helps mitigate. Our findings show that DFT methods can be used for accurate calculations in OEEFs, allowing researchers to make full use of the advantages that they bring.

1 Introduction

Oriented external electric fields (OEEFs) have emerged as a promising way of catalyzing chemical reactions, and research into the field has gained traction in recent years.[1,2] With the ability to weaken or strengthen chemical bonds, OEEFs allow for precise control over both selectivity and reactivity.[1,3–5] By aligning the field along the reaction axis, reaction speed and outcome can be adjusted using the strength and direction of the field alone.[2,5] OEEFs can selectively stabilize ionic and polar transition states, catalyzing otherwise unfavourable reactions.[1,6] This possibility for precise reaction control has led to an increasing number of computational investigations into the effects of electric fields on chemical reactions.[3,5,7–9] The effect of OEEFs can be seen through the change in molecular properties such as bond lengths, vibrational frequencies, and polarizabilities.[10,11]
In one notable example, OEEFs were used to catalyze a Diels-Alder reaction on a surface.[3] Aragonès et al. successfully demonstrated the potential of OEEFs for catalyzing carbon-carbon bond formations. They performed theoretical calculations to determine reaction barriers at various electric field strenghts and found qualitative agreement with their experimental results.

Electronic structure calculations of chemical systems in OEEFs are commonly done using methods based on density functional theory (DFT).[12,13] Different density functionals are based on different approximations and parameterizations. Density functionals that are commonly used for determining molecular geometries or electronic energies suffer from inaccuracies to varying degrees, and there are well-known issues with describing charged systems and molecules in electric fields which are caused by the self-interaction or delocalization error.[14–18] As the interest in using DFT methods for calculating molecules in OEEFs increases, a need to assess their performance for molecules in OEEFs starts to emerge. This has been done for the hydrogen molecule by Schirmer and Grimme, who found all density functionals investigated by them to “provide acceptable accuracy” in that case.[19] However, to the best of our knowledge, there has not been a thorough assessment of the general performance of density functionals in OEEFs until now, particularly in the context of organic molecules.

In this work, we investigate the accuracy of different density functionals for a selection of 18 small molecules, both inorganic and organic, in OEEFs of various strengths. These molecules represent a variety of bonding situations encountered in larger structures. We calculated molecular geometries and electronic energies for 14 different density functionals at 11 different electric field strengths and compare the results to accurate coupled-cluster calculations. We do this using three different basis sets to estimate the effect of the basis set size on the accuracy of DFT results. Our goal is to quantify the error that can be expected when applying an OEEF in a DFT calculation, and to determine how well density functionals describe the effects that OEEFs have on molecules.

The rest of this work is structured as follows: In Section 2, we present the metholody of our benchmark, the molecules used for the benchmark and the investigated methods. Reference calculations and the way performance was quantified are described as well. In Section 3, we present the performance of the investigated functionals when calculating molecular geometries (Section 3.1) and electronic energies (Section 3.2).

2 Computational Details

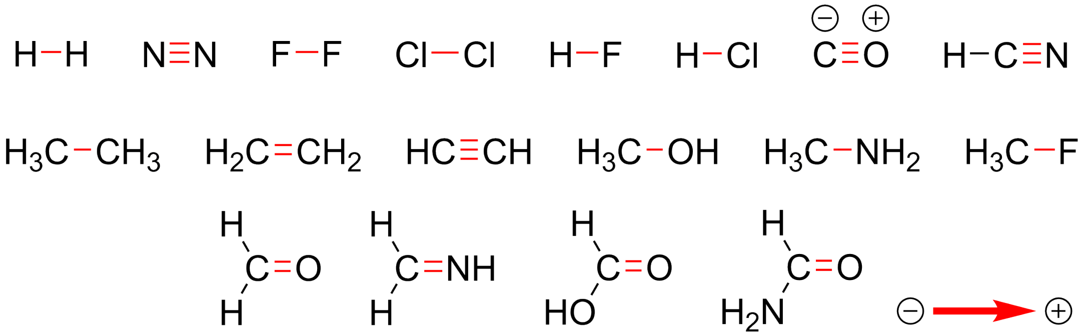

Figure 1: *Molecules used for the benchmark of density functionals in OEEFs. The bond that the electric field was applied along is shown in red. The red arrow indicates the orientation of the applied field.*

For the benchmark, a set of 18 small organic and inorganic molecules was chosen to cover a wide variety of possible bonding situations (Figure 1). The inorganic molecules used for evaluation are H_2, N_2, F_2, Cl_2, HF, HCl, CO, and HCN. The organic molecules used are ethane, ethylene, acetylene, methanol, methylamine, fluoromethane, formaldehyde, methylene imine, formic acid, and formamide.

All electronic structure calculations were performed using Q-Chem 5.3.2.[20] OEEFs were applied to molecules during the calculations as implemented therein. Electric fields were always applied along the axis of the bond of interest (shown in red in Figure 1). In Q-Chem, a positive electric field along an axis places the negative pole towards positive infinity and the positive pole towards negative infinity.

In this work, electric field strength is given in atomic units (1 a.u. $\approx$ 51.4 V Å^{-1}). For the benchmark, electric field strengths between -0.05 a.u. and 0.05 a.u. in steps of 0.01 a.u. were tested. This range represents the largest possible range at which all investigated molecules remained stable. At higher field strenghts, many started breaking apart in our calculations. Therefore, the range chosen represents the electric field strengths that can be used to catalyze chemical reactions without decomposing the reagents. Typical calculations found in literature were performed with electric field strengths around and below 0.03 a.u., with experimental conditions being an order of magnitude lower yet.[3,5,21]

One goal of this benchmark is to cover a wide range of functional types and include both non-hybrid and hybrid functionals. The functionals evaluated are B2PLYP,[22] B3LYP,[23] B97,[24] BHHLYP,[25] BLYP,[26,27] M06,[28] M06-L,[29] PBE,[30] PBE0,[31] PTPSS-D3,[32] TPSS,[33] ωB97M-V,[34] ωB97X-D3,[35] and ωB97X-V.[36] All calculations were performed using the Dunning basis sets cc-PVXZ ($X = D, T, Q$).[37]

For the reference calculations, the singles and doubles coupled-cluster with perturbative triples method CCSD(T)[38] was used. Atomic distances from geometry optimizations using DFT were compared to the distances in geometries optimized at the CCSD(T)/cc-pVQZ level of theory. Each electronic energy calculated via DFT was compared to the energy of the optimized structure extrapolated to the complete basis set (CBS) limit based on energies from calculations at CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ using parameters found by Neese and Valeev.[39]

For any given density functional, molecule, and field strength, we performed a geometry optimization of the molecule in the electric field. We calculated the difference in atomic distance along the bond marked in Figure 1 between the optimized geometry and the reference geometry. We calculated the increase in electronic energy between the geometry optimized in an electric field and the geometry optimized without an electric field. We then compared this difference with the difference of corresponding energies at the CBS limit of CCSD(T). The root-mean-square deviation (RMSD) across the relevant distances and energy increases of all molecules yields the average performance for a given density functional when doing calculations with a variety of molecular geometries at a given electric field strength. While a low RMSD indicates better agreement with the reference calculations and therefore higher overall accuracy, the influence of the OEEF on the accuracy is also indicated by the variance in the RMSD across changes in the electric field strength. If a method has an RMSD that is the same for any field strength, it has field-independent accuracy. A low dependence on the field strength is desirable because it reduces the error in interpreting differences between calculations performed at different field strengths, making such comparisons possible.

All geometry optimizations converged as expected, except for optimizations of H_2 using PTPSS-D3. We were not able to calculate the optimized geometry of this molecule using any of the tested basis sets. This particular case is therefore not included in the RMSD calculations.

3 Results and Discussion

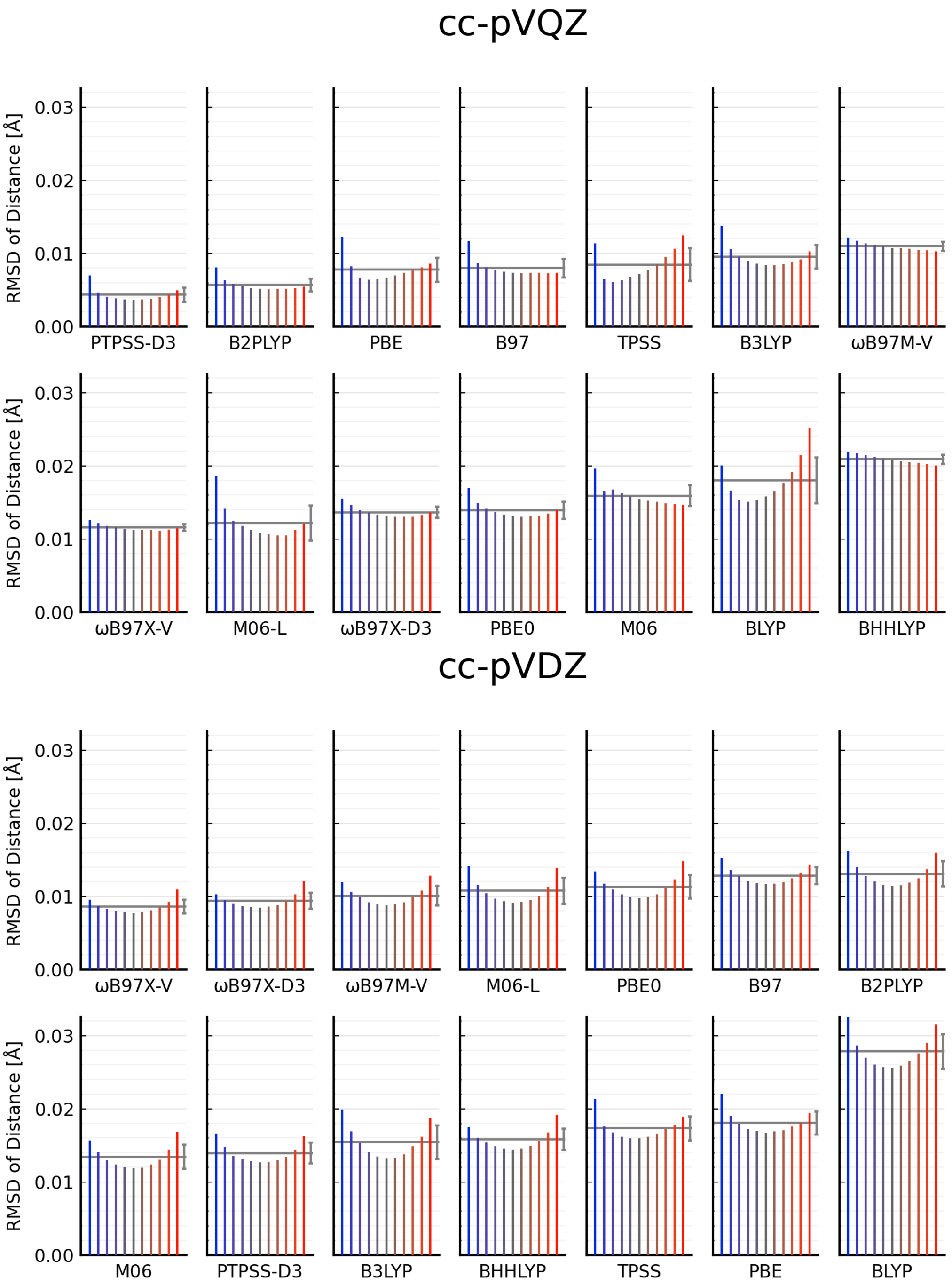

Figure 2: *Average performance of density functionals when calculating molecular geometries in different electric fields. Shown is the root-mean-square deviation of the investigated atomic distances in Å at different field strengths. Each plot for a density functional shows the deviation from reference data at fields from -0.05 a.u. (blue) to 0.05 a.u. (red) in steps of 0.01 a.u. Shown in grey are the mean (horizontal line) and standard deviation (vertical error bar) across all electric fields. Reference values were calculated at the CCSD(T)/cc-pVQZ level of theory. Basis sets used for the DFT calculations are cc-pVQZ (top) and cc-pVDZ (bottom).*

3.1 Molecular Geometries

Figure 2 shows the accuracy of molecular geometries calculated with the investigated density functionals. A lower deviation indicates better agreement with the reference calculation (CCSD(T)/ cc-pVQZ), but it is also important to scrutinize the variance in deviation across changes in the applied electric field: A flatter curve indicates a low dependence of the performance of the density functional on the electric field strength.
With the larger basis set cc-pVQZ, the two computationally most expensive functionals, PTPSS-D3 and B2PLYP, display both the lowest overall deviation from reference geometries as well as low variance across field strengths. All other density functionals show an average deviation of over 0.005 Å, but all remain below 0.02 Å. BLYP and BHHLYP perform the worst. Both show deviations over 0.015 Å, and BLYP shows strong variance in deviation across field strengths. Between the two extremes, performance is difficult to order, as some density functionals show lower deviation while others show lower dependence on field strength. Overall, there is no consistent pattern across all density functionals, and some functionals perform nearly as well in strong fields as they do in no field; ωB97M-V and ωB97X-V stand out with their particularly low field strength dependence.

In the case of asymmetric molecules, the investigated bond was aligned such that the more electronegative atom pointed towards the positive pole, meaning that a positive field would increase polarity and a negative field would reduce or invert the polarity. It is clear that different density functionals react differently to changes in polarity, as some show stronger deviations at negative fields and others show stronger deviations at positive fields. Most show stronger deviation at negative fields, indicating decreased accuracy of such density functionals in molecules with weakened or inverted polarity. However, the differences between negative and positive fields are very small, around and usually below 0.002 Å, calling the meaningfulness of this observation into question. In significantly larger molecules with extended delocalized electronic systems, this effect may be more pronounced and could become significant.

Use of the smaller basis set cc-pVDZ yields different results. Here, B2PLYP and PTPSS-D3 are not the best-performing density functionals. Overall, accuracy of the molecular geometries tends to

drop compared to calculations done with cc-pVQZ, although the degree to which the accuracy drops varies. ωB97M-V, ωB97X-D3 and ωB97M-V have the lowest mean deviations, around or below 0.01 Å, and also the lowest variance in deviation; their accuracy hardly changes when using the smaller basis set.
Similarly to the case of cc-pVQZ, all density functionals remain below a deviation of 0.02 Å, with a few exceptions in strong negative fields. BLYP stands out as the worst-performing functional with deviations approaching or reaching 0.03 Å and a difference in variation of 0.005 Å between zero field and a strong electric field. BHHLYP shows similar accuracy compared to the case of cc-pVQZ, although the variance across field strengths increases. The use of a smaller basis set introduces greater variance across different field strengths for all investigated density functionals, with varying intensity. The density functionals perform best with no electric field applied and become less accurate as the electric field gets more intense in either direction. Given that this effect is more pronounced with cc-pVDZ than in the case of cc-pVQZ, a lower dependence on field strength appears to be an additional benefit of using a larger basis set.

The accuracy of geometries calculated using the basis set cc-pVTZ may be found in the supporting information (Figure S1). Generally, all functionals show similar accuracy compared to calculations done with cc-pVQZ, displaying only minor variations. No notable performance improvement for geometries in electric fields can be observed between the two basis sets.

For molecular geometries, most of the investigated density functionals perform sufficiently well for most use cases in both weak and strong electric fields. While the use of a larger basis set reduces the dependence of the geometric accuracy on the field strength, it is not required for achieving differences below the threshold of chemical accuracy in electric fields, particularly when using density functionals that describe non-local interactions. The ability of the density functionals to describe the effect of electric fields on various types of chemical bonds appears to be sufficient. However, care must be taken in situations where small differences in bond lengths become relevant, especially when using computationally less expensive density functionals such as BLYP.

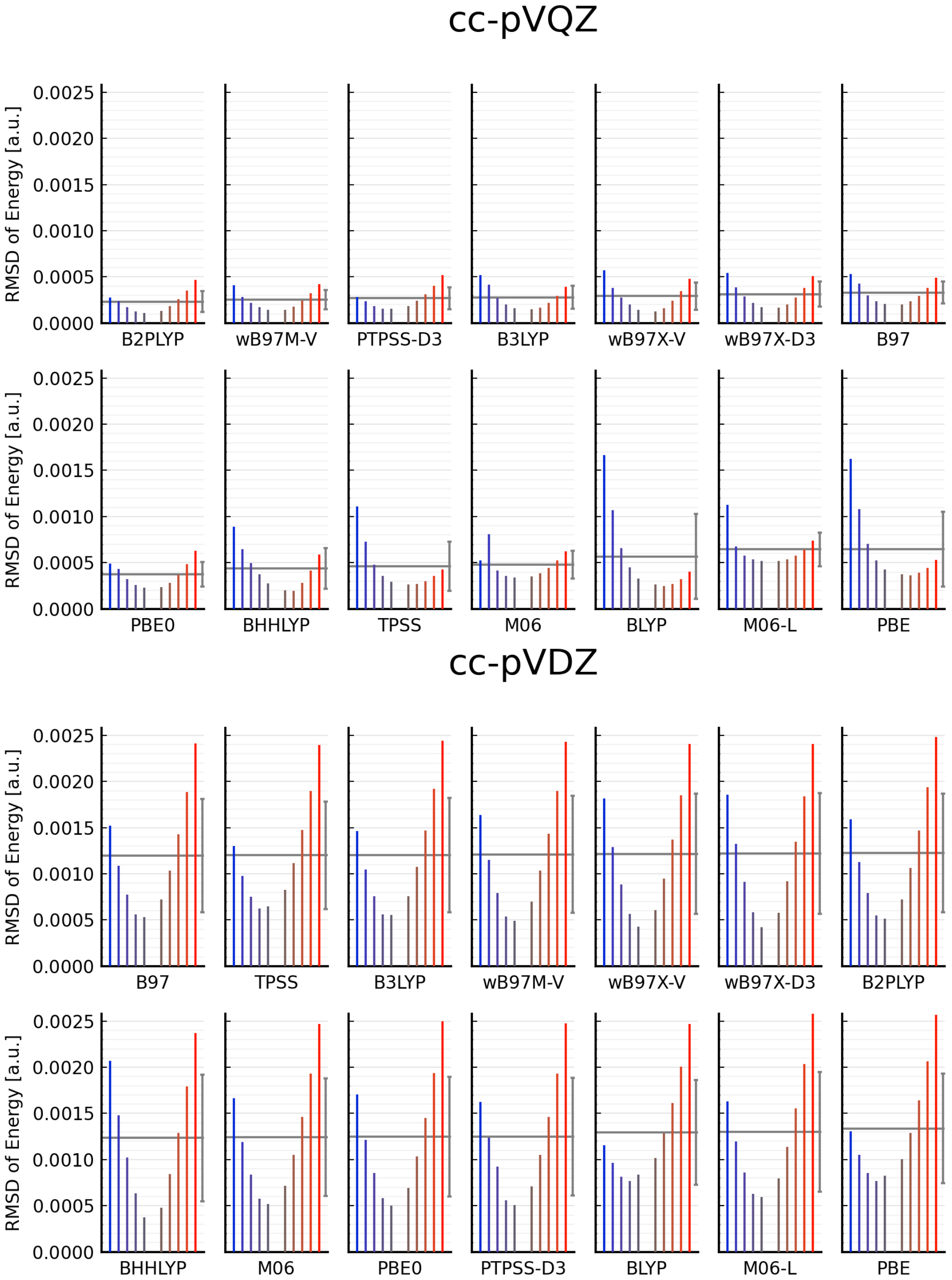

Figure 3: *Average performance of density functionals when calculating electronic energies in different electric fields. The increase in electronic energy due to the application of an electric field was calculated; shown is the root-mean-square deviation of these differences across the investigated molecules. Each plot for a density functional shows the deviation from reference data at fields from -0.05 a.u. (blue) to 0.05 a.u. (red) in steps of 0.01 a.u. Shown in grey are the mean (horizontal line) and standard deviation (vertical error bar) across all electric fields. Reference values were calculated with CCSD(T) extrapolated to the CBS limit from cc-pVTZ and cc-pVQZ calculations. Basis sets used for the DFT calculations are cc-pVQZ (top) and cc-pVDZ (bottom).*

3.2 Electronic Energies

Figure 3 shows the accuracy of electronic energies calculated with the investigated density functionals. The figure shows the deviation of the energy increase from the reference compared to the calculation without a field. The cc-pVQZ calculations show clear inaccuracies in electric fields; most density functionals deviate by up to an additional 0.0005 a.u. compared to the reference calculation. The deviation steadily increases as the field strength increases in either direction. Some density functionals, such as BLYP and PBE, perform worse at negative electric fields than at positive electric fields. This observation matches the findings for geometric accuracy, although no direct correlation can be found. As an example, BLYP produces less accurate geometries at positive fields but has less accurate energies at negative fields. Overall, the density functionals PTPSS-D3 and B2PLYP along with ωB97M-V show the lowest overall inaccuracy and the smallest dependence on field strength, but differences across most density functionals are small. BLYP and PBE show the highest deviation in strong negative electric fields. This suggests that these functionals have issues with describing molecules with weakened or inverted polarities in electric fields. M06-L stands out for having the highest deviation in weaker electric fields. Even these errors are below the threshold of chemical accuracy.

Use of the basis set cc-pVDZ results in significantly worse performance. All functionals display deviations over 0.002 a.u. in strong electric fields, above the threshold of chemical accuracy. All density functionals display similar deviations in strong electric fields. While BLYP and PBE show the highest deviations in weaker electric fields, all investigated density functionals show deviations below chemical accuracy in fields up to 0.02 a.u.

All functionals display the same behaviour with increasing field strengths, becoming significantly less accurate in strong fields; deviation tends to be higher at positive fields. This suggests that effects that density functionals do not describe well have a significant impact on the electronic energy in stronger electric fields. It should be noted that Hartree-Fock, second-order Møller-Plesset (MP2) and CCSD calculations display the same behaviour and show comparable performance. The reader is kindly referred to the supporting information for details (Figure S4).

The accuracy of electronic energies calculated using the basis set cc-pVTZ may be found in the supporting information (Figure S2). All functionals show performance between that of cc-pVDZ and of cc-pVQZ, going as high as 0.0013 a.u. in strong electric fields.

It is evident that a small basis set is not sufficient for describing electronic energies with high precision. Should small energetic differences be significant, the use of a large basis set is recommended. Using large basis sets, all investigated density functionals other than BLYP and PBE show dependence on the field strength that is below chemical accuracy, and they may be safely be used in strong fields for situations where very small differences in electronic energy are not relevant. However, the effect of the field strength on the accuracy of the calculation is always to be kept in mind.

4 Conclusions and Outlook

In conclusion, we were surprised by the overall performance of common density functionals in OEEFs despite the problems with separated charges that they have in theory. While the investigated density functionals show errors introduced into the molecular geometry caused by an OEEF, these errors are usually around or below the threshold of chemical accuracy and the functionals perform sufficiently well for use in both weak and strong fields, even using smaller basis sets. For electronic energies, the application of an OEEF introduces a significant error that increases with electric field strength. The error can be mitigated by using a larger basis set, but not eliminated. For weaker electric fields or large basis sets, the error is usually below the threshold of chemical accuracy, but should always be kept in mind when comparing calculations performed at different electric field strengths.

Density functionals are evidently a viable choice for investigating molecules in OEEFs. While this work only investigated the DFT behaviour of molecular geometries and electronic energies in OEEFs, other molecular properties such as polarizabilities or optical activity could be investigated in the future. One may also observe different results when investigating larger chemical systems such as aromatic or conjugated structures; those systems are beyond the scope of the present benchmark. We are excited to see what kinds of electric-field calculations DFT methods will be used for, and how the use of OEEFs for catalyzing chemical reactions will progress in the coming years.

5 Acknowledgements

Funding by the Deutsche Forschungsgemeinschaft is gratefully acknowledged (grant no. STA 1526/3-1, project no. 441071849). Calculation time was provided by the North-German Supercomputing Alliance (HLRN) (project ID hbc00045).

6 Conflicts of Interest

The authors declare no conflicts of interest.

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