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Highly accurate simulations and benchmarking of molecule-surface reactions

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SBH17: Benchmark Database of Barrier Heights for Dissociative Chemisorption on Transition Metal Surfaces

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Abstract

Accurate barriers for rate controlling elementary reactions on metal surfaces are key to understanding, controlling, and predicting the rate of heterogeneously catalyzed processes. While barrier heights for gas phase reactions have been extensively benchmarked, dissociative chemisorption barriers for the reactions of molecules on metal surfaces have received much less attention. A first database called SBH10 and containing 10 entries was recently constructed based on the specific reaction parameter approach to density functional theory (SRP-DFT) and more appropriate semi-empirical approaches. We have now constructed a new and improved database (SBH17) containing 17 entries based on SRP-DFT and more appropriate semi-empirical approaches. For this new SBH17 benchmark study, we have tested three algorithms (high, medium, and light) for calculating barrier heights for dissociative chemisorption on metals, which we have named for the amount of computational effort involved in their use. We test the performance of 14 density functionals at the generalized gradient approximation (GGA), GGA+vdW-DF and meta-GGA rungs. Our results show that, in contrast with the previous SBH10 study where the BEEF-vdW-DF2 functional seemed to be most accurate, the work horse functional PBE and the MS2 density functional are the most accurate of the GGA and meta-GGA functionals tested. Of the GGA+vdW functionals tested, the SRP32-vdW-DF1 functional is the

most accurate. Additionally we found that the medium algorithm is accurate enough for assessing the performance of the density functionals tested, while it avoids geometry optimizations of minimum barrier geometries for each density functional tested. The medium algorithm does require metal lattice constants and interlayer distances that are optimized separately for each functional. While these are avoided in the light algorithm, this algorithm is found not to give a reliable description of functional performance. The combination of relative ease of use and demonstrated reliability of the medium algorithm will likely pave the way for incorporation of the SBH17 database in larger databases used for testing new density functionals and electronic structure methods.

3.1 Introduction

Heterogeneous catalyzed processes are of large importance to the chemical industry¹, well-known examples of such processes being ammonia synthesis² and steam reforming³. In heterogeneously catalyzed processes on metal surfaces, the steps with a high degree of rate control often involve the dissociative chemisorption (DC, the process whereby the interaction of a molecule with a surface leads to the breaking of a bond in the molecule and the formation of two new bonds of the molecular fragments to the surface) of a molecule on the surface^{4,5}. Understanding how heterogeneous catalysis works is of huge importance. Our ability to understand the different mechanisms underlying DC on metal surfaces could benefit significantly from the availability of an accurate database for barrier heights of elementary molecule-metal surface reactions. Just like chemisorption energies of (intermediate) reactants and products, accurate barriers for rate controlling elementary reactions are key to understanding, controlling, and predicting the rate of overall heterogeneously catalyzed processes⁶⁻⁹.

Ideally, accurate barrier heights could be extracted directly from detailed systematic experiments. However, it is not possible to measure barrier heights for DC directly. An observable that can be measured experimentally and that is strongly related to the barrier height for DC is the sticking probability (S_0)¹⁰. The best way to access barrier heights using theory is through a theoretical approach in which potential energy surfaces (PESs) are computed and used in dynamics calculations to evaluate S_0 as a function of average incidence energy¹⁰. Comparison with experimental S_0 ¹⁰⁻¹⁴ will then allow one to evaluate the accuracy of the electronic structure method used to compute the PES for the calculated barrier height¹⁰. Only when experimental data are reproduced within chemical accuracy (i.e., with errors smaller than 1 kcal/mol^{11,12}) to a sufficiently large extent, a claim can be made that the computed barrier height is of high accuracy.

For adsorption bond energies to transition metal surfaces, a database containing 39 entries for use with DFT benchmarking studies has recently been constructed¹⁵. This database, subsets of it^{16,17}, and a slightly extended version¹⁸ of it, have been used in several benchmark DFT studies^{15–21}, and a considerably extended database containing 81 entries also exists²². Barrier heights for gas phase reaction have been extensively benchmarked^{23–26}. However, barriers for DC on metal surfaces have been mapped out to a much smaller extent¹⁰, and have been little used for benchmark calculations. For many gas phase reactions, it has been possible to use the very accurate CCSD(T)²⁷ electronic structure method to compute reference values. On the other hand, for molecule-metal surface reactions, until very recently only semi-local density functional theory (DFT)²⁸ could be used, which is much less accurate. As result, it is not yet known how large the errors in barriers for molecule-metal surface reactions are when using standard exchange-correlation (XC) functionals. For reactions occurring in the gas phase, it is well known that the density functionals (DFs) at the second rung on Jacob's ladder^{28,29} (GGA level^{30,31}) underestimate barrier heights as a consequence of self-interaction errors^{24,32}. An idea of the performance of semi-local functionals on gas phase reaction barriers can be obtained from their performance on the BH206 database²⁴, tests showing that application of the best performing MN12-L³³ and N12³⁴ non-separable meta-GGA and GGA DFs resulted in root mean square deviations of 4.3 and 7.1 kcal/mol, respectively. To overcome this potential problem of the XC functional for molecule-metal surface reactions, the SRP-DFT method^{35,36} (which uses weighted averages of two XC functionals) has been adopted for such reactions¹¹. This semi-empirical (SE) method has allowed prediction of barrier heights to within chemical accuracy (1 kcal/mol) for specific systems¹⁰.

Some theoretical studies have been carried out recently in attempts to build databases of barrier heights for molecule-metal surface reactions. The first database (CatApp^{37,38}) was built based on DFT calculations using only one functional (RPBE³⁹). More recently, a first attempt was made to construct a database of molecule-metal surface reaction barriers for benchmarking purposes⁴⁰. This database, called SHB10, contained 6 entries based on SRP-DFT and 4 entries based on more ad-hoc SE procedures. The SBH10 database was used⁴⁰ to test the performance of one DF consisting of GGA exchange and non-local correlation (BEEF-vdW-DF2¹⁶), one meta-GGA (MS2⁴¹), and one screened hybrid DF (HSE06⁴²). A surprising conclusion was that BEEF-vdW-DF2 performed the best.

With more than 30 000 papers published annually⁴³, DFT arguably is the most important electronic structure method for dealing with complex systems. It is therefore important to develop a large enough database that allows testing

the method on barrier heights for molecule-metal surface reactions. As discussed below, accurate SRP-DFT barriers for DC are now available for 14 molecule-metal surface reactions, allowing the former database to be extended with 7 systems if additional results from three more ad-hoc procedures are included as before. In the present chapter, we therefore develop a new and larger database for benchmarking (SBH17), which contains benchmark results for 17 systems. We now also test a much larger number of DFs on this larger database, i.e., 3 GGA-type DFs, 4 meta-GGA DFs, and 7 DFs containing GGA exchange and non-local correlation. In performing these tests, we also take an improved approach over that taken in the previous paper⁴⁰, in which the metal surface was allowed to relax in response to the incoming molecule while computing the barrier height. This approach is flawed in that the metal surface atoms have too little time to respond to the motion of the incoming molecule in the hypersonic molecular beam experiments employed to perform sticking experiments, which are used in the SE procedure to construct SRP DFs¹⁰.

In performing the tests of the 14 DFs to be discussed below, three different algorithms will be used to compute barrier heights. These algorithms differ in the computational effort that may be required to compute metal lattice constants and metal slabs that have interlayer distances simulating metal surfaces interacting with the vacuum, and to locate the transition state geometry for a specific functional. These three algorithms will be compared among each other for their performance. A new database for molecule-metal surface reaction barriers is of course more likely to be used if it meets the following two demands, which may conflict with one another. When used in testing new functionals or electronic structure methods in general, the algorithm should be as easy and straightforward to use, and require as little computational effort, as possible. At the same time, the algorithm should also still yield reliable results regarding how functionals or new methods perform, because otherwise it would not be useful.

The outline of our chapter is as follows: In Section 3.2, the methods used are explained, beginning with the DFs tested in Section 3.2.1. The description of the SE procedures used to obtain reference values of barrier heights, and the motivation of the use of SRP-DFT are presented in Section 3.2.2, the choice of the reference values is clearly explained in Section 3.2.3, and the details of the algorithms used are described in Section 3.2.4. Computational details are presented in Section 3.2.5. The results are presented in Section 3.3, beginning with the structure of the metals in Section 3.3.1 while Section 3.3.2 presents the DC barriers. The discussion is provided in Section 3.4. The description of the metals with the DFs tested is discussed in Section 3.4.1. The description of the barrier heights to DC is discussed in Section 3.4.2. In this Section, the performance of the algorithms is discussed in Section 3.4.2.A. Subsequently, the

TABLE 3.1: XC functionals tested in this work, and how their exchange and correlation parts are chosen. The type 'GGA-vdW' means that GGA exchange is combined with vdW-DF1⁴⁴ or vdW-DF2⁴⁵ correlation..

	Name	Type	Exchange	Correlation
1	PBE	GGA	PBE ³⁰	PBE ³⁰
2	RPBE	GGA	RPBE ³⁹	PBE ³⁰
3	SRP50	GGA	0.50RPBE ³⁹ +0.50PBE ³⁰	PBE ³⁰
4	vdW-DF1	GGA+vdW	revPBE ⁴⁶	vdW-DF1 ⁴⁴
5	vdW-DF2	GGA+vdW	rPW86 ⁴⁷	vdW-DF2 ⁴⁵
6	PBE-vdW-DF2	GGA+vdW	PBE ³⁰	vdW-DF2 ⁴⁵
7	SRP32-vdW-DF1	GGA+vdW	0.32RPBE ³⁹ +0.68PBE ³⁰	vdW-DF1 ⁴⁴
8	PBE α 57-vdW-DF2	GGA+vdW	PBE α = 0.57 ⁴⁸	vdW-DF2 ⁴⁵
9	BEEF-vdW-DF2	GGA+vdW	BEEF ¹⁶	BvdW-DF2 ^{16,44}
10	optPBE-vdW-DF1	GGA-vdW	optPBE ⁴⁹	vdW-DF1 ⁴⁴
11	revTPSS	meta-GGA	revTPSS ⁵⁰	revTPSS ⁵⁰
12	SCAN	meta-GGA	SCAN ⁵¹	SCAN ⁵¹
13	MS-B86bl ⁵²	meta-GGA	MS-B86bl	revTPSS ⁵⁰
14	MS2	meta-GGA	MS2 ⁴¹	MS2 ⁴¹

performance of the DFs using the medium algorithm for SBH17 is discussed in Section 3.4.2.B. The dependence of the performance for the barrier heights on the type of system is discussed in 3.4.2.C. The comparison with results for the previous SBH10 database is provided in Section 3.4.2.D. Section 3.4.3 provides a comparison of how the DFs tested perform on the SBH17 database for DC barriers (kinetics) to how they perform for molecular chemisorption (thermochemistry), and to how they perform for gas phase kinetics and thermochemistry. A discussion on future improvements is given in Section 3.4.4. Finally, the conclusions and outlook are given in Section 3.5.

3.2 Methods

3.2.1 Density functionals tested

The DFs that we have tested on reaction barriers for DC on metal surfaces, as present in our new database discussed below, are listed in Table 3.1. Of these XC DFs, three fall in the GGA²⁸ category, seven consist of GGA exchange²⁸ and vdW-DF1⁴⁴ or vdW-DF2⁴⁵ Rutgers-Chalmers type non-local correlation, and four fall within the meta-GGA²⁸ category. Here, we will only briefly describe the DFs tested; for details we refer to the original papers.

In the GGA, which is at the second rung of "Jacob's ladder"^{28,29}, use is made of the density and its gradient. As discussed by Perdew²⁸, at the GGA level a constraint based DF can be made to satisfy a subset of constraints, but not all known constraints. For applications to surface reaction dynamics, to some extent the constraint based PBE and RPBE DFs selected here may be considered to be "at extremes", with PBE³⁰ often underpredicting and RPBE³⁹

often overpredicting reaction barrier heights according to conventional wisdom¹⁰. The PBE DF³⁰ is often considered to be a "workhorse" GGA DF, in a sense that it describes a range of properties of molecules and materials with a fair accuracy. The PBE DF was designed³⁰ to replace the PW91⁵³ DF, yielding similar results while employing a mathematical framework superior to that of PW91. The RPBE DF is mainly used for molecule-metal surface interactions, and was introduced to correct for the overbinding observed for adsorption of small atoms and molecules to metal surfaces³⁹ as obtained with the PBE DF. In addition to RPBE and PBE we also test a 50/50 % mixture of these DFs, which is called SRP50 here. The choice of this DF stems from the similar 48/52 % RPBE/PBE mixture providing a chemically accurate description of the well-studied H₂+Cu(111) system (see also below). We only test 3 GGA DFs here because they suffer from a fundamental drawback: optimizing GGA DFs for their performance of adsorption energies of molecules to metal surfaces goes at the cost of an accurate description of the metal surface itself^{54,55}. It has been argued that this problem can be solved with GGA DFs of which the XC DF is non-separable in an exchange and a correlation part³⁴, but we do not test such DFs here.

Like the meta-GGA DFs discussed below, GGA DFs are not capable of a reasonably accurate description of the van der Waals interaction. For this reason, and because we are dealing with metals, we have tested seven DFs consisting of GGA exchange and non-local correlation functionals, for which we use either one of two Rutgers-Chalmers correlation functionals, which we call vdW-DF1⁴⁴ and vdW-DF2⁴⁵, respectively. These van der Waals DFs were originally designed to be a part of a non-empirical XC DF where the exchange DF was somehow matched to the specific correlation DF^{44,45}, and these non-empirical XC DFs, which are both tested here, are simply called vdW-DF1 and vdW-DF2 here. The vdW-DF2 correlation DF has also been incorporated in the so-called BEEF-vdW DF (here called BEEF-vdW-DF2) also tested here, which was semi-empirically fitted to adsorption energies on transition metal surfaces, gas phase reaction barriers, and other properties¹⁶. The optPBE-vdW-DF1 functional is an example of a DF in which the vdW-DF1 correlation functional has been combined with a semi-empirically adjusted exchange DF, in this case to obtain good interactions of weakly interacting dimers⁴⁷. Finally, the PBE-vdW-DF2, SRP32-vdW-DF1, and PBE α 57-vdW-DF2 are combinations of GGA exchange DFs and vdW-DF1 or vdW-DF2 correlation DFs designed to describe particular DC systems with chemical accuracy, i.e., H₂ + Ru(0001)⁵⁶, CH₄ + Ni(111)¹³, and H₂ + Pt(111)⁵⁷, respectively. These DFs are more fully described in Table 3.1. We note that for all of the DFs incorporating vdW-DF1 or vdW-DF2 discussed here except BEEF-vdW-DF2, the full correlation functional can be written as the sum of correlation

from the local density approximation (LDA) and a non-local functional, which is the non-local part of the vdW-DF1⁴⁴ or vdW-DF2⁴⁵ DF. For BEEF-vdW-DF2, the full correlation functional is written as a weighted average of the LDA and the semi-local PBE correlation functional (with the sum of the weights equal to 1)¹⁶ plus the non-local part of vdW-DF2⁴⁵. To emphasize this difference, the correlation DF of BEEF-vdW-DF2 is represented by the acronym BvdW-DF2 in Table 3.1.

In the meta-GGA, which is at the third rung of "Jacob's ladder"^{28,29}, additional use is made of the kinetic energy density, which is equivalent to the Laplacian of the electron density. Of these, the revTPSS DF⁵⁰ was designed to be the workhorse counterpart of the GGA PBE DF. The SCAN DF was designed to enforce all known physical constraints on the DF⁵¹ (this can be done at the meta-GGA level but not at the GGA level⁵¹). The MS2 functional has two semi-empirically fitted parameters in it, and was designed with the specific aim of accurately describing both metals and molecules⁴¹. Finally, the MS-B86bl DF has been shown to accurately describe the earlier mentioned H₂ + Cu(111) system, and its design⁵² should ensure reasonable accuracy for any system in which H₂ interacts with a metal surface. Again, details on the composition of these XC DFs may be found in Table 3.1.

In hybrid DFs, which are at the fourth rung of Jacob's ladder^{28,29}, a fraction of the semi-local exchange in the exchange part of the XC functional is replaced by exact exchange. Screened exact exchange DFs (in which the exact exchange component is switched off at large electron-electron distances) have been used in a few instances in studies of a specific DC system (see e.g. Ref.⁵⁸). However, their use is computationally expensive, and a screened hybrid DF was only used to study 4 of the 10 systems addressed in the SBH10 paper⁴⁰. For this reason, and because their use will be more appropriate once systems are addressed for which electron transfer from the surface to the molecule is likely⁵⁸, we will not test such functionals here.

In rung 5 functionals^{28,29} virtual orbitals are added in addition to exact exchange. The random phase approximation (RPA)⁵⁹⁻⁶² is a well known example of such functionals. The RPA has been used in one specific study of reaction barriers in a DC molecule-metal surface system that we know of⁶³, and in a limited number of benchmark studies of molecular adsorption on metal surfaces^{17,64}. However, its use is even more computationally expensive than that of hybrid functionals. For this reason, we have not tested the RPA, nor have we tested any other rung 5 DFs.

3.2.2 Semi-empirical approaches to obtaining reference values of barrier heights

In determining reference values for barrier heights of gas phase reactions for use in databases, theorists have often benefited from the availability of electronic structure methods and associated algorithms delivering reaction barrier heights with chemical accuracy. For instance, barriers for the NHBTH38 database (a database for 38 non-hydrogen atom transfer reactions) were obtained with an algorithm in which results obtained with the highly accurate CCSD(T)²⁷ method were extrapolated to the basis set limit⁶⁵. In the construction of the HBTH38 database theorists likewise relied on barrier heights obtained from high level *ab initio* electronic structure methods, although in this case the *ab initio* results were also compared to experiment to extract best guesses (i.e., reference values) of barrier heights^{66,67}.

As already noted in the introduction, the situation is quite different in the field of reaction dynamics on metal surfaces. In this field semi-local density functionals are routinely applied to DC reactions occurring on metal surfaces. However, the results are semi-quantitative at best, as one might expect from the performance of these functionals on gas phase reactions^{10,56,68,69}. In attempts to do better, the first principles diffusion Monte-Carlo (DMC) method has been used to compute barrier heights for e.g. $\text{N}_2 + \text{Cu}(111)$ ⁷⁰ and for $\text{H}_2 + \text{Mg}(0001)$ ⁷¹, $\text{Cu}(111)$ ⁷², and $\text{Al}(110)$ ⁷³. The results for $\text{H}_2 + \text{Cu}(111)$ ⁷² suggested that DMC can deliver near chemical accuracy for barrier heights for DC on transition metal surfaces (accuracy better than 2 kcal/mol), in line with results for the HBTH38 and NHBTH38 gas phase reaction barrier databases^{10,74,75}. However, chemical accuracy was not yet achieved for this benchmark reaction, and DMC calculations are computationally expensive. Embedded correlated wave function (ECW) calculations based on multi-reference perturbation theory embedded in DFT provided near chemical accuracy for a DC reaction on a simple metal surface ($\text{O}_2 + \text{Al}(111)$ ⁷⁶). However, the computational expense of such calculations is presently too high for molecules interacting with transition metals (TMs), as calculations⁷⁷ on $\text{H}_2 + \text{Cu}(111)$ suggest. Zhao et al. made a positive assessment of their ECW method on the basis of the comparison of the emb-CASPT2 barrier height for DC of H_2 on $\text{Cu}(111)$ (0.15 eV)⁷⁷ with an "experimental" value⁷⁸ from the literature (0.05 eV). However, this value was extracted through an invalid extrapolation procedure (over temperature, to 0 K, see fig.15 of Ref.⁷⁸) in an analysis that was at best approximate for higher temperatures, and was originally meant to make contact with kinetics experiments⁷⁸. The best value of the $\text{H}_2 + \text{Cu}(111)$ barrier height is however 0.63 eV¹¹, and not 0.05 eV.

As argued in most detail in Ref.¹⁰ (to which we refer for these details) accurate

reaction barriers heights for DC reactions on metals are therefore best determined through a SE approach. This approach is best based on supersonic molecular beam experiments that probe the reactivity on the ideal surface, whereas rate measurements usually probe the reaction at (often unknown) defects^{79,80}, making the latter experiments less useful for benchmarking purposes^{10,81}. The basic idea of the SE SRP-DFT approach used to extract reference barrier heights is to adjust a DF until appropriate dynamics calculations on the basis of that DF yield agreement with measured DC probabilities. The correctness of this procedure can be argued¹⁰ on the basis of the so-called hole model⁸², which essentially states that computed reaction probabilities will be correct if the potential energy surface (and the minimum barrier height extracted from it) is correct. We deem the approach to deliver chemical accuracy because numerous instances have now shown that with appropriate dynamics methods and models measured DC probability curves can be reproduced to within energy shifts less than 1 kcal/mol on the basis of appropriately constructed functionals. Essentially the spirit of the method is not so different from the approach taken to originally construct the HTBH38 gas phase reaction barrier database, which also combined theoretical and experimental information^{66,67}. We also recall that in any case a reaction barrier height is not an observable. The procedure to validate a computed barrier height through comparison with an experiment must necessarily take recourse to the use of a measured observable that is as closely related to the barrier height as possible.

The SE SRP-DFT approach discussed above is used for most reactions in the SBH17 database (i.e., for 14 out of 17 cases). With this approach, an appropriate dynamical method and model was used to model supersonic molecular beam experiments in all but one case ($\text{CH}_4 + \text{Ni}(211)$, see below)¹⁰. This means, for instance, that all (or all relevant) molecular degrees of freedom were usually modeled in dynamics calculations. We will discuss the SRP-DFT electronic structure method used for these cases in Section 3.2.2.A below. In the earlier SBH10 database⁴⁰, four systems were introduced for which reference values were derived using experiments and their analysis by a more primitive SE approach. These analyses were carried out before 2009, when SRP-DFT became available¹¹. Reference values for three of these systems in our present SBH17 database were inherited from the earlier SBH10 database, which we will briefly discuss in Section 3.2.2.B below. (For one of the four systems ($\text{CH}_4 + \text{Ni}(211)$, called 'CH₄/Ni(111) step' in Ref.⁴⁰, accurate results are now available and we have moved this system to the SRP-DFT part of the database.) As will also be discussed below, it would be good if the reference values for these three systems be replaced in future by more accurate values from for instance SRP-DFT. For each system in the SBH17 database Section 3.2.3 describes what the specific

reference value used for the system is, and how it was derived.

3.2.2.A The specific reaction parameter approach to density functional theory (SRP-DFT)

The SRP-DFT method as introduced is a SE method, and was originally applied to reactions in the gas and condensed phases by Truhlar and co-workers^{35,36}. SRP-DFT was first applied to DC on a metal surface by Díaz et al¹¹. They used an implementation in which the SRP-DF is a weighted average of two GGA DFs according to a mixing parameter \mathbf{x} . Changing the mixing parameter "tunes" the functional to reproduce S_0 , which is strongly correlated with the minimum barrier height. In the most straightforward approach, a GGA XC DF that underestimates and one that overestimates the barrier height is used:

$$E_{xc}^{SRP-DFT} = \mathbf{x}E_{xc}^{GGA-DF1} + (1 - \mathbf{x})E_{xc}^{GGA-DF2}. \quad (3.1)$$

Standard GGA DFs often used for mixing in applications to molecule-metal surface reactions are the RPBE³⁹ and PBE³⁰ functionals discussed in Section 3.2.1. For weakly activated H₂-metal and for CH₄-metal systems, the correlation part of the SRP-DF is best substituted by the van der Waals non-local correlation functional of Dion et al⁴⁴ (vdW-DF1) or of Lee et al⁴⁵ (vdW-DF2), changing equation 3.1 to become:

$$E_{xc}^{SRP-DFT} = \mathbf{x}E_x^{GGA-DF1} + (1 - \mathbf{x})E_x^{GGA-DF2} + E_c^{non-local}. \quad (3.2)$$

In equation 3.2, the mixing parameter only tunes the exchange part of the XC DF in the SRP-DF. Instead of a weighted average of two XC or exchange DFs, one can also use an inherently tunable DF, such as the PBE α exchange DF, in which α can be adjusted. Using non-local correlation, the equation for the SRP-DF then becomes:

$$E_{xc}^{SRP-DFT} = E_x^{PBE\alpha} + E_c^{non-local}. \quad (3.3)$$

As originally defined, a DF is only considered to be a SRP-DF if after fitting \mathbf{x} it not only reproduces a particular sticking experiment with chemical accuracy, but also reproduces another experiment on the same system with comparable accuracy¹¹. In contrast, if a parameterized DF only reproduces the sticking experiment it was fitted to, it was originally called a candidate SRP-DF¹⁰. Here we drop this distinction and refer to both categories of DFs as SRP-DFs. Additionally, the SRP-DF can be considered to be transferable if it can reproduce experimental results for a system it was not fitted to⁸³. For example, in some cases, the SRP-DF fitted to reproduce molecular beam dissociation

chemisorption experiments for H_2 and D_2 were shown to be transferable among systems in which H_2 interacts with different crystal faces of the same metal^{84–86}. One downside of the SE SRP-DFT approach to DC of the molecules on the metal surfaces used so far, in which semi-local exchange DFs are used, is that successful applications of this approach have only been demonstrated to systems for which the difference of the metal work function (WF) and the molecule's electron affinity (EA) is larger than 7 eV. The SRP-DF approach has allowed the construction of chemically accurate barriers for 14 systems^{10,85} with (WF-EA) > 7 eV, as shown in Table 3.2 and now discussed further below.

The supersonic molecular beam experiments referred to above need to be modeled with an appropriate dynamical method (e.g., quasi-classical or quantum dynamics) and dynamical model. Here, the latter refers to whether or not all molecular degrees of freedom, the motion of the surface atoms, and electron-hole pair (ehp) excitation are considered¹⁰. Because dynamics rather than transition state theory is used, and because the surface atoms usually do not have time to respond to the incoming molecule, it makes most sense to tabulate "classical reaction barrier heights". By this we mean barrier heights arising directly from electronic structure calculations without corrections for zero-point energies (zpes) and entropy effects, for the molecule interacting with the "ideal" surface, i.e., with the surface atoms sitting in their equilibrium lattice positions for a classical 0 K surface. The SRP-DFT barriers reported below all are classical barrier heights computed with a SRP-DF or with a PES based on SRP-DFT calculations.

3.2.2.B Ad hoc semi-empirical approaches

As noted above, for three systems ($\text{CH}_4 + \text{Ni}(100)$, $\text{CH}_4 + \text{Ru}(0001)$, and $\text{N}_2 + \text{Ru}(10\bar{1}0)$) reference values were taken from the paper on the SBH10 database, and these were extracted using a more primitive SE approach than used in SRP-DFT. As will be detailed below in Section 3.2.3, reduced dimensionality modeling of supersonic molecular beam sticking experiments was used to derive a minimum barrier height for $\text{CH}_4 + \text{Ni}(100)$. Thermal S_0 measured for N_2 dissociating on $\text{Ru}(0001)$ were fitted to an Arrhenius type equation to derive an activation energy for DC at defects, which were considered to be the steps occurring in $\text{Ru}(10\bar{1}0)$. Finally, an activation energy for CH_4 dissociation on $\text{Ru}(0001)$ was derived from associative desorption experiments as described below, invoking detailed balance. Even though activation energies were derived for N_2 and CH_4 dissociation on $\text{Ru}(10\bar{1}0)$ and $\text{Ru}(0001)$, respectively, we felt that the approaches used were too crude to attempt extracting classical minimum barrier heights for these systems by subtracting zpe corrections using known approximate values⁴⁰. Instead we simply use the semi-empirically extracted

TABLE 3.2: Summary of the SBH17 database. Barrier heights (in eV) and the most important co-ordinates defining the barrier geometry are presented. The "site" defines the projection of the molecule's center-of-mass position on the surface, r_b (in Å) the length of the dissociating bond, and Z_b (in Å) the distance of the molecule's center-of-mass to the surface. The molecule's orientation is defined by the polar angles of orientation (θ) of the diatomic molecule, or partly defined by the (θ, φ) pair of angles giving the polar angle of the breaking CH-bond and the umbrella axis the remaining methyl fragment makes with the surface normal, respectively. Barrier heights obtained from PESs used in the dynamics are marked with an asterisk (*). For some CH₄+metal systems the barrier height is also given without residual correction (in brackets, see the text).

N_s	System	functional	site	r_b	Z_b	θ	φ/β	E_b
1	H ₂ +Cu(111) ¹¹	SRP43	brg	1.03	1.16	90	90	0.628
2	H ₂ +Cu(100) ⁸⁶	SRP43	brg	1.23	1.0054	90	90	0.740
3	H ₂ +Cu(110) ⁸⁷	optPBE-vdW-DF1	short-brg	1.20	0.89	64	90	0.789
4	H ₂ +Pt(111) ⁵⁷	PBE α 57-vdW-DF2	top(early)	0.769	2.202	90	0	-0.008*
5	H ₂ +Pt(211) ⁸⁴	PBE α 57-vdW-DF2	top	0.75	2.79	90	90	-0.083*
6	H ₂ +Ru(0001) ⁵⁶	PBE-vdW-DF2	top(early)	0.751	2.605	90	0	0.004*
7	H ₂ +Ni(111) ⁸⁸	PBE-vdW-DF2	top(early)	0.763	2.083	90	0	0.024*
8	H ₂ +Ag(111) ⁸⁵	MS-PBEL-rVV10	brg	1.224	1.157	90	0	1.082*
9	N ₂ +Ru(0001) ⁸⁹	RPBE	brg	1.741	1.318	84	30	1.840
10	N ₂ +Ru(1010) ^{79,90}	experiment						0.40
11	CH ₄ +Ni(111) ¹³	SRP32-vdW-DF1	top	1.606	2.176	135.7	164.7	1.015 (1.055)
12	CH ₄ +Ni(100) ⁹¹	experiment						0.76
13	CH ₄ +Ni(211) ⁹²	SRP32-vdW-DF1	top	1.632	2.033	126.0		0.699
14	CH ₄ +Pt(111) ⁸³	SRP32-vdW-DF1	top	1.56	2.28	133.4	168.3	0.815 (0.856)
15	CH ₄ +Pt(211) ¹⁴	SRP32-vdW-DF1	top	1.53	2.27	133	168	0.559 (0.581)
16	CH ₄ +Ir(111) ⁹³	SRP32-vdW-DF1	top					0.836
17	CH ₄ +Ru(0001) ⁹⁴	experiment						0.80

activation energies as reference values for the minimum barrier heights for these two systems.

3.2.3 The SBH17 database

The systems that constitute our SBH17 benchmark database of barrier heights for DC on transition metal surfaces are listed in Table 3.2. This table contains reference barrier heights and data concerning the barrier geometries for 17 systems. The bulk of the data come from SRP-DFT, such that 14 entries in Table 3.2 may also be viewed as constituting a database that can be named SBH14/SRP. Three entries in Table 3.2 come from more ad-hoc SE approaches, as also discussed in the original SBH10 paper⁴⁰. In this Section we justify our choice of the reference values of the barrier height and our reference geometries, which is important to do especially in cases where conflicting data exists. Note that barrier heights obtained from SRP-DFT are given in eV using 3 significant digits behind the decimal place (i.e., expressed in meV), even though the accuracy

claimed for these numbers is only one kcal/mol \approx 43 meV. This claim is based on the energy shift between the sticking probabilities that were measured and computed on the basis of the SRP DF yielding the minimum barrier height being smaller than 1 kcal/mol^{10,11}, as more fully discussed in Section 3.2.2. In expressing barrier heights like this, we follow a rather common practice in computational chemistry, as this will allow other researchers to check whether they can reproduce our numbers. The barrier heights extracted using more ad-hoc approaches (Section 3.2.2.B) have been stated with the amount of significant digits used originally by the scientists providing these benchmark results, and the errors in these reference values may well be larger than 1 kcal/mol. Finally, we note that the average value of the absolute barrier heights of SBH17 is 14.8 kcal/mol.

3.2.3.A Dissociative chemisorption of H₂ on transition metals

H₂ on Cu(111), Cu(100) and Cu(110)

The DC of H₂ on copper surfaces perhaps represents the most widely studied class of DC systems by both theory^{11,85,87,95–97} and experiment^{78,97–101}. Being activated systems, in the absence of strong effects of ehp excitation and energy transfer involving phonons¹⁰² on reactive scattering they represent perfect systems for benchmarking electronic structure methods for their capability to accurately predict barriers.

H₂ + Cu(111)

The first system for which a SRP-DF was derived for DC on a metal surface was H₂ on Cu(111)¹¹, and the first SRP-DF for this system (SRP43) was a weighted average of the PW91⁵³ (57%) and the RPBE³⁹ (43%) DF. With the PES developed with this SRP-DF and using the BOSS model quasi-classical trajectory and time-dependent wave packet calculations reproduced measured molecular beam S₀ for H₂ and D₂, initial-state selected reaction probabilities for H₂^{78,99}, and data for rotationally inelastic scattering¹⁰³ to within chemical accuracy. Density functional molecular dynamics (DFMD) calculations with the subsequently developed SRP48-DF¹⁰⁴ (48% RPBE³⁹ and 52% PBE³⁰) also accurately reproduced measured¹⁰⁵ rotational quadrupole alignment parameters A₀⁽²⁾(J), and enabled a chemically accurate description of initial-state selected reaction probabilities of D₂ on Cu(111), after an appropriate re-analysis of the experimental data⁹⁵. Recent studies^{87,106} using optPBE-vdW-DF1 exchange combined with non-local vdW-DF1 correlation (re-parameterized PBE for vdW-DF1)⁴⁹ also provided a chemically accurate description of S₀ for H₂ and D₂

on Cu(111). Additionally, three different combinations of GGA exchange DFs with non-local vdW-DF2 correlation¹⁰⁶ allowed chemically accurate descriptions of the reaction of H₂ and D₂ on Cu(111), and the same was true for three newly developed meta-GGA DFs⁵². The barriers reported for the vdW-DF1 and vdW-DF2 combinations and the new meta-GGA DFs were somewhat different from the one obtained with the original SRP43 DF (the SRP48 DF was designed to reproduce the SRP43 energy at the SRP43 barrier geometry¹⁰⁴). As reference for our benchmark database, the SRP43 barrier height (0.628 eV)¹¹ will be used. While calculations with some of the other mentioned DFs in cases described the sticking experiments more accurately than SRP48¹⁰⁴ or SRP43¹¹, only calculations with the latter 2 DFs reproduced initial-state selected reaction probabilities extracted from associative desorption experiments with chemical accuracy, suggesting that these two DFs should be the DFs best describing H₂+Cu(111)¹⁰⁶.

H₂ + Cu(100)

H₂ on Cu(100) is the second system for which an SRP-DF was demonstrated⁸⁶. The SRP-DF(SRP43¹¹) originally developed for H₂ on Cu(111) could also be used to reproduce the measured S₀⁹⁸ for H₂ on Cu(100) within the BOSS model⁸⁶. This also represents an example of the transferability that SRP-DFs may exhibit for chemically closely related systems¹⁰, in this case systems in which the same molecule interacts with different low index faces of the same metal. As reference value for our database we use the value of the barrier height reported for SRP43⁸⁶ (0.74 eV).

H₂ + Cu(110)

In a recent study, effectively a new SRP-DF was demonstrated for H₂ + Cu(110)⁸⁷. The optPBE-vdW-DF1 was used to develop PESs based on embedded atom neural network (EANN) fits for H₂ on Cu(111), Cu(100) and Cu(110) by Jiang and coworkers⁸⁷. Dynamics calculations employing the resulting PES for H₂ + Cu(110) yield a chemically accurate description of molecular beam sticking experiments on H₂ + Cu(110)¹⁰⁷. The optPBE-vdW-DF1 functional had previously¹⁰⁸ been shown to yield a chemically accurate description of molecular beam sticking experiments on D₂ on Cu(111)¹⁰⁹. Jiang and co-workers also demonstrated chemically accurate descriptions of sticking experiments on H₂ + Cu(111) and Cu(100). This therefore represents another example of transferability of SRP-DFs among chemically related systems¹⁰, where one DF (optPBE-vdW-DF1) can be used to model sticking of one and the same molecule on several low index faces

of the same metal. The barrier height reported by Jiang and coworkers for their PES (0.789 eV)⁸⁷ will be used as the reference value for our database.

H₂ on Pt(111) and Pt(211)

H₂ + Pt(111)

H₂ on Pt(111) is considered as a weakly activated system because of its low minimum barrier height. Three DFs have been found that describe the sticking of D₂ on Pt(111) with chemical accuracy^{57,106}. The SRP-DF first developed for D₂ + Pt(111) was the PBE α 57-vdW-DF2 functional (see Section 3.2.2 and Tables 3.1 and 3.2). With this DF measured¹¹⁰ S₀ for both normal and off-normal incidence of D₂ were reproduced with chemical accuracy⁵⁷. The SRP48¹⁰⁴ and a DF consisting of 68% B86r exchange¹¹¹ and 32% RPBE exchange³⁹ combined with vdW-DF2 correlation⁴⁵ (SRPB86r68-vdW-DF2) also both reproduced the measured¹¹⁰ S₀ for normal incidence with overall chemical accuracy¹⁰⁶. However, the PBE α 57-vdW-DF2 resulted in the most accurate results near the reaction threshold⁵⁷, suggesting that this DF yields the barrier height with the highest accuracy¹⁰⁶. Furthermore, recent work has shown that this DF can reproduce experiments of D₂ on chemically related curved Pt crystals with (111) terraces and (100) steps with chemical accuracy¹¹². The barrier height reported for PBE α 57-vdW-DF2 was -0.008 eV. We retain this value as the reference value (see Table 3.2), even though it was set to 0.0 eV in the previous SBH10 database⁴⁰.

H₂ + Pt(211)

The PBE α 57-vdW-DF2 functional developed for H₂ on Pt(111) was also employed to test transferability to H₂ on Pt(211)⁸⁴. This SRP-DF also yields⁸⁴ a chemically accurate description of experiments on DC of H₂ and D₂ on the stepped Pt(211) surface¹¹³. The lowest barrier height found in reduced dimensionality (by finding saddle points in the reduced 2D spaces formed by the elbow plots in figure 4 of Ref.⁸⁴) was -0.083 eV, and this is the value that we use, along with the "top1 ($\varphi = 90^\circ$)" geometry defined in Ref.⁸⁴.

H₂ + Ru(0001)

Like H₂ + Pt(111), H₂ on Ru is a weakly activated system. For this system, two DFs were found⁵⁶ to reproduce measured¹¹⁴ S₀ for H₂ + Ru(0001) with chemical accuracy. These DFs were the PBE-vdW-DF2 functional (see Tables 3.1 and 3.2) and the functional containing 50% PBE³⁰ and 50% RPBE³⁹ exchange combined with vdW-DF1 correlation⁴⁴ (SRP50-vdW-DF1). The barrier height reported

for both DFs was 0.004 eV. This is the value we use in our database, even though it was set to 0.0 in the previous SBH10 database⁴⁰.

H₂ + Ni(111)

The DC of H₂ on Ni(111) is also weakly activated. Similar to the case of H₂ on Ru(0001), agreement with existing sticking experiments^{115,116} was achieved⁸⁸ to within chemical accuracy with dynamics calculations based on the PBE-vdW-DF2 functional (see Tables 3.1 and 3.2 and also **Chapter 2**). The PBE-vdW-DF2 calculations for H₂ + Ni(111) were done with the spin-corrected vdW-DF2 functional¹¹⁷ (spin-vdW-DF2) to take into account the magnetic character of the Ni(111) surface, whereas for all other considered systems the original non-spin corrected vdW-DF1 and vdW-DF2 functionals were used. The barrier height reported is that of the early top site barrier (as also used for H₂ + Pt(111) and Ru(0001)), which is 0.024 eV⁸⁸. In all VASP calculations we perform here, we employ the non-spin corrected vdW-DF1 and vdW-DF2 functionals; however, we note that earlier calculations suggested little influence of the spin-correction on the barrier height computed for CH₄ + Ni(111) with a functional featuring vdW-DF1 correlation¹³. The barrier height we use as the reference value (obtained with PBE-spin-vdW-DF2) in our database is 0.024 eV.

H₂ + Ag(111)

H₂ + Ag(111) is a highly activated system, for which molecular beam sticking experiments were performed by Hodgson and co-workers¹¹⁸. Recently it was shown⁸⁵ that the measurements^{118,119} can be reproduced with chemical accuracy using recently developed made-simple meta-GGA exchange DFs⁵² combined with rVV10 non-local correlation¹²⁰. Here we use the barrier height obtained with the functional yielding the best agreement with experiment (MS-PBE1-rVV10)⁸⁵ as the reference value for our database (1.082 eV).

3.2.3.B N₂ dissociation on Ru surfaces

N₂ + Ru(0001)

Ru is well-known as a catalyst for the Haber-Bosch process used to make ammonia, which is a raw material for artificial fertilizer¹²¹. As noted in the original SBH10 paper⁴⁰, for N₂ + Ru(0001) barrier heights are available from both SRP-DFT^{89,122} and from a direct estimate based on experimental results¹²³. The directly estimated barrier height based on a laser-assisted associative desorption experiment¹²³ was 1.8 eV, whereas the calculations based on the RPBE DF

that were found to give a chemically accurate description^{89,122} of the best experimentally measured S_0 ¹²⁴ gave a barrier height of 1.84 eV. Specifically, computed S_0 on the basis of the RPBE DF and a dynamical model in which energy transfer was allowed to surface atom vibrations and ehp excitation gave good agreement¹²² with the best estimates of measured S_0 ¹²⁴. Table S1 in the supporting information (SI) of Ref.¹²⁵ presents data concerning the dependence of the computed barrier height on the pseudo-potentials used for this system. In the calculations presented here we used for both N- and Ru- atoms a hard pseudo-potential, i.e. Ru_{pv} and N_h . As the reference value for our database, we will use 1.84 eV, which value was obtained using a hard pseudo-potential for Ru (Ru_{pv}) but an ordinary pseudo-potential for N(N)⁸⁹ in the DFT calculations performed to produce the PES underlying the good agreement with experiment.

$N_2 + Ru(10\bar{1}0)$

Because of the absence of SRP-DFT data for $N_2 + Ru(10\bar{1}0)$, as was done in the original SBH10 paper⁴⁰, we use a reference value of 0.4 eV for the barrier height. Note that this value actually represents an activation energy obtained from thermal rate measurements on DC of N_2 on $Ru(0001)$ ^{79,90}, suggesting that the barrier height contains zpe corrections. Another presumption implicitly used in Refs.^{79,90}, and therefore in Ref.⁴⁰, is that the activation energy derived from measurements^{79,90} on (necessarily defected) $Ru(0001)$ should be the same as the activation energy that would be obtained for $Ru(10\bar{1}0)$, i.e., that the steps occurring on the latter surface have the same promoting effect on the reaction on $Ru(0001)$ as do the unspecified defects on $Ru(0001)$.

3.2.3.C CH_4 dissociation on transition metals

The DC of CH_4 on metal surfaces is important to industry as it constitutes the first step in the steam reforming of natural gas, producing CO, which can be used for alcohol synthesis and for the Fischer-Tropsch process, and hydrogen, which can be used as a fuel and for ammonia production. The dissociation of CH_4 on metal surfaces has been the subject of many theoretical^{13,14,91–93,126} and experimental studies^{13,14,94,127–136}.

$CH_4 + Ni(111)$

$CH_4 + Ni(111)$ is the first CH_4 on metal system for which a SRP-DF was derived¹³. The generic expression given by Eq. 3.2 was employed, using a weighted average of the RPBE (32%) and the PBE exchange DFs (68%) combined with non-local vdW-DF1⁴⁴. This SRP-DF (SRP32-vdW-DF1¹³) was fitted to laser-off

experiments performed on $\text{CHD}_3 + \text{Ni}(111)$ for $T_N = 600$ and 650 K using DFMD calculations. Subsequent DFMD calculations also reproduced measured S_0 for CH-stretch excited CHD_3 on $\text{Ni}(111)$ with chemical accuracy. The barrier height that was computed with an appropriate residual energy correction for the vacuum distance was 1.015 eV¹³ (Table 3.2, see also table S6 of Ref¹⁴). This is the reference value that should be used for calculations in which CH_4 is placed far enough from the surface to obtain a value of the asymptotic energy that is converged with respect to the vacuum length¹³ (i.e, the value of E_b^c in table S6 of Ref¹⁴, see also the discussion in Section 3.1 of the SI to Ref¹⁴). This is the reference value we use to compare results to that were computed with the GGA and meta-GGA calculations, as with these DFs the asymptotic energy is converged with respect to the vacuum length used in our calculations. For the calculations with vdW-DF1 and vdW-DF2 correlation DFs, we take into account that a correction has to be applied for the fact that in the present calculations the vacuum distance was too short (at 13 Å), and the molecule too close to the surface (at 6 Å) for these DFs. Instead, for these DFs we use the value of E_b^{13} quoted in table S6 of Ref¹⁴ (i.e, 1.055 eV, see Table 3.2).

$\text{CH}_4 + \text{Ni}(100)$

Sticking of CH_4 on $\text{Ni}(100)$ has been simulated with quantum dynamics calculations explicitly modeling motion in eight molecular degrees of freedom⁶⁸, with QCT calculations¹³⁷ and with reaction path Hamiltonian (RPH) calculations^{137–141}. In none of these calculations agreement with existing molecular beam experiments was achieved to within chemical accuracy. Therefore, for this system we instead use the same reference value of the barrier height as the value quoted in the previous SBH10 database⁴⁰. However, we note that the earlier paper⁴⁰ gave an incomplete explanation of how this value (0.76 eV) of the barrier height was obtained in the paper referenced⁹¹. The value used refers to the barrier height employed in calculations⁹¹ with a three-dimensional dynamical model augmented with the so-called hole model⁸², which approximately reproduced previously measured S_0 ¹²⁷. The value quoted for the minimum barrier height (0.76 eV) is in fact not a minimum barrier height in the model employed in Ref.⁹¹, but rather the barrier height averaged over the impact points on the surface and the orientations of the dissociating molecule. We will analyze the consequences of this misinterpretation below, and make a recommendation as to whether and how this value should be replaced in a future version of the database.

CH₄ on Ni(211)

The SRP32-vdW-DF1 developed for CH₄ on Ni(111) has also been used in RPH calculations on sticking of CH₄ + Ni(211)⁹². However, molecular beam sticking experiments are not yet available for this system. A recent study of Guo and Jackson¹²⁶ also reported computed thermal S₀ for step and terrace sites calculated for CH₄ on Ni(211) with harmonic and anharmonic transition state theory. It was possible to compare these results to analogous results extracted from experiments on CH₄+Ni(14 13 13)¹⁴², which surface also consists of (100) steps and (111) terraces, albeit that the terraces are much wider than on Ni(211). Excellent agreement was obtained for the sticking at the step sites, suggesting that the SRP-DF for CH₄ + Ni(111) should also describe sticking of methane on Ni surfaces consisting of (111) terraces and (100) steps (like Ni(211)) with chemical accuracy. For our benchmark study, we will use therefore as the reference value the minimum barrier height reported by Jackson and coworkers for DC at the steps of Ni(211), which is 0.699 eV.

CH₄ + Pt(111) and Pt(211)

For the DC of CH₄ on metals, several cases of transferability were observed. DFMD calculations with the SRP32-vdW-DF1 functional developed for CHD₃ on Ni(111) also reproduced molecular beam sticking experiments on CHD₃ + Pt(111) and Pt(211) with chemical accuracy¹⁴. The barrier heights reported for these two systems, again including a residual energy correction for the short vacuum distance and the short distance of the methane to the surface in the initial state used in the DFMD calculations, are E_b^e = 0.815 eV¹⁴ and 0.559 eV, and these are the reference values we use when testing GGA and meta-GGA DFs^{13,143}. As for CH₄ + Ni(111), for our benchmark purposes, when testing DFs with vdW-DF1 and vdW-DF2 correlation, we will use the values with residual energy correction (0.856 eV and 0.581 eV respectively) as reported by Migliorini et al¹⁴ (table S6 of Ref¹⁴ and table 3 of Ref¹⁴³).

CH₄ + Ir(111)

As was the case for CH₄ + Ni(211), the SRP32-vdW-DF1 developed for CH₄ + Ni(111) has also been used in RPH dynamics calculations on CH₄ + Ir(111)⁹³. The S₀ computed with this method for sticking of CH₄ in its vibrational ground state have been compared with values measured in molecular beam experiments^{128,130,136}. An analysis of how these data compare (see fig.67 of Ref¹⁰) shows that the RPH dynamics calculations reproduce the measured S₀

with chemical accuracy. For this system we therefore used the barrier height reported by Ref.⁹³, which is 0.836 eV, as the reference value.

CH₄ + Ru(0001)

As already noted in the SBH10 paper⁴⁰, this reference value was extracted from experiments on laser assisted associative desorption (LAAD)⁹⁴. Specifically, the "adiabatic minimum barrier height $V^*(0)$ " was extracted from the experiments by taking temperature dependent values of the highest CH₄ translational energy observed as a function of the surface temperature (T_s), and extrapolating the maximum translational energy observed to $T_s = 0$ K. While this gave values not too different from the $V^*(0)$ values extracted in an approximate fashion⁹⁴ from earlier molecular beam sticking experiments¹²⁹ and from earlier DFT calculations^{94,144}, the method used was approximate. Moreover it is clear from the paper⁹⁴ that the $V^*(0)$ value should be interpreted as an activation energy, i.e., in DFT it would be the minimum barrier height with zpe corrections added.

3.2.4 Algorithms for computing minimum barrier heights

The minimum barrier height to DC may be computed with DFT as

$$E_b = E_{TS} - E_{asym} \quad . \quad (3.4)$$

Here, E_{TS} is the energy of the system with the molecule at the transition state (TS) or minimum barrier geometry, and E_{asym} the energy of the system with the molecule in its equilibrium gas phase geometry, and far enough from the surface that molecule and surface no longer interact with each other. This coincides with an approach that is usually taken to extract barrier heights from PESs used in dynamics calculations. We also suggest that this approach might benefit from cancellation of errors, which might not result if the energies of the reactants (the bare surface and the incoming molecule) are calculated separately, in calculations that might differ in the size of the supercell and k-points used. In any case the asymptotic state will somehow have to be represented in the PES used for the dynamics calculations, so that it makes sense to compute it in the same manner as the minimum barrier height.

Ideally, these geometries would be known to high accuracy from theory or experiment. While this is true for the equilibrium geometry of the small molecules investigated here, and usually also for the structure of the metal surfaces investigated here, it is not true for the transition state geometries. In this sense, the field of molecule-metal surface chemistry differs from that of gas phase chemistry^{23–26}, where transition state geometries of at least small

systems are often well known from accurate *ab initio* (CCSD(T)²⁷) calculations. When benchmarking electronic structure methods on gas phase systems, the availability of CCSD(T) geometries carries the advantage with it that only single point calculations have to be performed, and that geometry optimizations can be omitted.

This is not the case for calculations on DC on metals. Choices have to be made regarding several issues. These issues are: (i) how to choose the equilibrium gas phase geometry of the molecule, (ii) how to choose the geometry of the molecule in the transition state, and (iii) how to choose the geometry of the metal surface in the TS and asymptotic geometries. In this work we have tested how the results depend on different choices regarding these issues. We have tested this using three algorithms, which we call high, medium, and light according to the computational effort associated with the algorithms.

3.2.4.A Light Algorithm

Calculations with the light algorithm are least expensive as only single point calculations are involved. The following choices are made: (i) the experimental equilibrium geometry of the molecule is used for the asymptotic state, (ii) the TS geometry of the molecule relative to that of the surface is taken as the SRP-DFT geometry of the molecule relative to the metal surface (see Table 3.2), and (iii) the metal surface is built up by simply using the experimental lattice constant at 0 K, without relaxation of the interlayer distances in the slab.

3.2.4.B Medium Algorithm

In the case of medium algorithm, for (ii) the same choice is made for the geometry of the molecule relative to the surface in the system's TS geometry as in the light algorithm. However, for (i) and (iii) different choices are made: the molecule's equilibrium geometry is now computed on the basis of the DF tested, and the lattice constant of the metal surface as well as the relaxed interlayer distances of the metal surface at the interface with the vacuum are now also optimized separately for each functional tested. This takes into account that the lattice constant and the relaxed interlayer distances may depend strongly on the DF tested¹⁴⁵, while in turn the minimum barrier height may depend rather strongly on the parameters determining the geometry of the metal surface. The dependence of the minimum barrier height on the geometry of the metal surface is relevant to DFMD calculations^{146,147}, as incorrect initial geometries of the metal may lead to surface strain, which can in turn affect the barrier height to DC¹⁴⁸. In the medium as well as in the high algorithm below, the geometry of the metal surface in the TS is taken the same as that in the asymptotic state,

as the metal surface atoms will usually not have time to respond to the fast incoming motion of the molecule in the hypersonic molecular beam experiments to which comparison is made for assessing the accuracy of SRP DFs¹⁰. We note that for CH₄ the molecule's geometry has only been optimized once, with the RPBE functional, and the RPBE geometry was used with all other DFs. Table S2 of the SI of Ref.¹²⁵ shows that this leads to errors no greater than 5 meV.

3.2.4.C High Algorithm

The high algorithm differs from the medium algorithm only in that now the TS geometry of the molecule relative to the surface is determined by geometry optimization using the dimer method as implemented in the VASP Transition State Tools (VTST) package^{149–152}. As stated above, in the TS search process, the metal surface was kept frozen in its relaxed 0 K geometry. The optimization of the TS geometry of the molecule was stopped when the maximum force on any degree of freedom was smaller than 5 meV/Å. All the TS geometries reported here have been confirmed to be the first-order saddle points in the molecular coordinate space by frequency analysis (by checking that one and only one imaginary frequency was found).

3.2.5 Computational details

All the new calculations presented here are performed using the Vienna *ab initio* simulation package^{153–156} (Vasp5.4.4). The calculations with DFs incorporating vdW-DF1⁴⁴ or vdW-DF2⁴⁵ correlation have therefore been performed with the Vasp implementation of these DFs⁴⁷, except the calculations with the BEEF-vdW-DF2 DF¹⁶, for which the libbeef library¹⁵⁷ was used. Through the way these DFs were implemented, they all inherit the LDA correlation from the PBE DF³⁰, which means that the PW92 variant of the LDA correlation¹⁵⁸ is used. All calculations with vdW-DF1 or vdW-DF2 were performed with the algorithm due to Román-Pérez and Soler¹⁵⁹, which speeds up the evaluation of these DFs. Because of the amount of the calculations that had to be done, the Atomic Simulation Environment (ASE) was used as a convenient interface package^{160,161}. Typically, the default projected augmented wave (PAW) pseudo-potentials were used; however, for N₂+Ru(0001) and N₂-Ru(1010) we used hard core pseudo-potential: **Ru**_{pv} (a **Z**_n core pseudo-potential leaving 14 of the electrons of **Ru** in its 4p⁶5s¹4d⁷ configuration to be modeled) and **N**_h (a **H**_e core pseudo-potential leaving 5 electrons of **N** in its 2s²2p³ configuration to be modeled). For all systems containing a **Ni** surface, spin polarization has been taken into account. A complete description of the input parameters (e.g., number of metal layers in the metal slab, size of the surface unit cell, the plane wave cut-off energy, the

number of k-points, the vacuum distance, etc.) used in this work can be seen in Table S3 of the SI of Ref.¹²⁵. In the optimization of the metal slab, for all systems, we used a 1×1 surface unit cell, kept the bottom layer frozen and the upper $n-1$ layers of the metal surface were allowed to relax. For the 3 systems for which only ad-hoc SE results are available ($\text{CH}_4 + \text{Ru}(0001)$, $\text{CH}_4 + \text{Ni}(100)$, and $\text{N}_2 + \text{Ru}(10\bar{1}0)$), the geometries we used for the medium and light algorithms were obtained from the calculations where we used the high algorithm based on the SRP32-vdW-DF1 for CH_4 on metal systems, and on the RPBE DF for $\text{N}_2 - \text{Ru}(10\bar{1}0)$.

3.3 Results

3.3.1 Structure of the metals

Table 3.3 presents, for all metals in the database, the calculated lattice constants as computed with all DFs tested, comparing with zpe corrected experimental values^{162,163}, and also showing the MAE and MSE with respect to the experiment for each DF. The lowest MAEs are found for the meta-GGA DFs, and the highest MAEs for the DFs consisting of GGA exchange but vdW-DF1 or vdW-DF2 correlation, with the vdW-DF2 functional exhibiting the poorest performance. For this property the GGA-DFs are found to be of intermediate accuracy.

Table 3.4 shows, for each DF tested, the computed percentage change of the distance between the top two layers of the relaxed (111) metal surface relative to the ideal bulk interlayer distance, for the (111) surfaces relevant to SBH17, also comparing to the corresponding experimental results. Again, the best results are found with the meta-GGA DFs. For instance, with the revTPSS DF, the correct sign was found for all four metal surfaces for which experimental results are available. The GGA DFs get the sign wrong for Pt(111), while the functionals with vdW-DF1 and vdW-DF2 correlation all get the sign wrong for Ag(111). With the functionals and input parameters used, neither experiment nor other DFT calculations presented in Table 3.4 are quantitatively reproduced.

3.3.2 Dissociative chemisorption barriers

To give an idea of the size of the error that may arise from the DF and algorithm used for a particular system, Table 3.5 and Figure 3.1 present the barrier heights computed for $\text{H}_2 + \text{Cu}(111)$ (the barrier heights for the other systems in the database and geometries can be found in Tables S4 to S19 and Figures S1 to S16 of the SI of Ref.¹²⁵). With the medium algorithm, three DFs (SRP50, revTPSS, and MS-B86bl) yield barrier heights close to the SRP reference value of 0.636

TABLE 3.3: Comparison of metal lattice constants computed in this work with experiment and with other computational results. Lattice constants computed in this work are marked with "†" and listed for each tested DF, also providing other computational results for the DFs tested where available. The experimental values (Exp) have been corrected for zpe effects. The MAE and MSE represent the means of the absolute and signed deviations of the lattice constants computed in this work from the experimental values, for each DF tested. All results are in Å.

	Ag	Ir	Cu	Pt	Ni	Ru		
Exp	4.062 ¹⁶²	3.831 ¹⁶²	3.597 ¹⁶²	3.912 ¹⁶²	3.499 ¹⁶²	2.703 ¹⁶³	4.274 ¹⁶³	
Functional								
PBE	4.146 [†]	3.889 [†]	3.624 [†]	3.985 [†]	3.519 [†]	2.722 [†]	4.293 [†]	MAE
	4.152 ¹⁶²	3.887 ¹⁶²	3.632 ¹⁶²	3.985 ¹⁶²	3.518 ¹⁶²	2.735 ⁵⁶	4.304 ⁵⁶	0.0506
		3.916 ⁴						
		3.873 ¹⁶⁵						
		3.877 ¹⁶⁶						
RPBE	4.201 [†]	3.903 [†]	3.673 [†]	4.010 [†]	3.553 [†]	2.734 [†]	4.315 [†]	0.0824
		3.908 ¹⁶⁴				2.744 ⁵⁶	4.325 ⁵⁶	
		3.891 ¹⁶⁶						
SRP60	4.173 [†]	3.896 [†]	3.648 [†]	3.997 [†]	3.535 [†]	2.727 [†]	4.304 [†]	0.0678
vdW-DF1	4.226 [†]	3.934 [†]	3.703 [†]	4.052 [†]	3.573 [†]	2.753 [†]	4.338 [†]	0.115
						2.761 ⁵⁶	4.351 ⁵⁶	
vdW-DF2	4.288 [†]	3.988 [†]	3.775 [†]	4.126 [†]	3.615 [†]	2.791 [†]	4.398 [†]	0.176
		3.987 ¹⁶⁶						
SRP32-vdW-DF1	4.203 [†]	3.928 [†]	3.680 [†]	4.042 [†]	3.558 [†]	2.747 [†]	4.330 [†]	0.100
		3.923 ⁶⁶						
PBE-vdW-DF2	4.204 [†]	3.927 [†]	3.681 [†]	4.040 [†]	3.518 [†]	2.747 [†]	4.330 [†]	0.092
						2.754 ⁵⁶	4.341 ⁵⁶	0.092

Table 3.3 Continued.

	Ag	Ir	Cu	Pt	Ni	Ru		
Exp	4.062 ¹⁶²	3.831 ¹⁶²	3.597 ¹⁶²	3.912 ¹⁶²	3.499 ¹⁶²	2.703 ¹⁶³	4.274 ¹⁶³	
Functional								MSE
PBEa67-vdW-DF2	4.173 [†] 4.176 ¹⁶⁷	3.918 [†]	3.653 [†]	4.025 [†] 4.015 ⁵⁷	3.537 [†]	2.739 [†]	4.319 [†]	0.0792
BEEF-vdW-DF2	4.196 [†]	3.899 [†]	3.656 [†]	4.014 [†]	3.536 [†]	2.730 [†]	4.306 [†]	0.0782
optPBE-vdW-DF1	4.160 [†]	3.907 [†]	3.641 [†]	4.007 [†]	3.526 [†]	2.730 [†]	4.306 [†]	0.066
revTPSS	4.064 [†]	3.851 [†]	3.561 [†]	3.927 [†]	3.457 [†]	2.700 [†] 2.69 ⁵⁶	4.268 [†] 4.246 ⁵⁶	0.0244 -0.010
SCAN	4.091 [†]	3.808 [†]	3.580 [†]	3.906 [†]	3.460 [†]	2.696 [†]	4.249 [†]	0.0246 -0.013
MS-B86b1	4.101 [†] 4.092 ⁵²	3.841 [†]	3.583 [†] 3.583 ⁵²	3.907 [†] 3.906 ⁵²	3.472 [†]	2.700 [†]	4.260 [†]	0.0208 -0.001
MS2	4.0745 [†]	3.8407 [†]	3.5543 [†]	3.9115 [†]	3.4498 [†]	2.7002 [†]	4.2631 [†]	0.0248 -0.016

TABLE 3.4: Comparison of computed and measured results characterizing surface relaxation. The relaxation of the interlayer lattice spacing between the upper two layers of the surface relative to the bulk value is given in % for all (111) surfaces relevant to the SBH17 database and for all DFs tested in this work, also comparing to experimental results (Exp) and other DFT results where available. Values computed in this work are marked with a "†".

	Ag	Ir	Cu	Pt	Ni
Exp	-2.5% ¹⁶⁸ -0.5% ¹⁷¹		-1.0% ¹⁶⁹ -0.7% ¹⁷²	1.1% ¹⁷⁰	-0.07% ¹⁶⁹
			GGA		
PBE	-0.34† -0.20 ¹⁴⁵ -0.30 ¹⁷³	-2.66†	-0.26† -0.30 ¹⁴⁵	-0.07† 0.90 ¹⁴⁵ 0.90 ¹⁷³	-1.38†
RPBE	0.38†	-2.58†	-0.47†	-0.05†	-0.80†
SRP50	-0.04†	-2.62†	-0.33†	-0.06†	-1.32†
			GGA+vdW		
vdW-DF1	1.19† 0.10 ¹⁶⁷	-2.37†	-0.38† -0.20 ¹⁶⁷	0.00† 1.30 ¹⁶⁷	-1.26† -1.10 ¹⁶⁷
vdW-DF2	2.24† 0.50 ¹⁶⁷	-1.99†	-1.63† 0.00 ¹⁶⁷	0.31† 1.50 ¹⁶⁷	-1.46† -1.10 ¹⁶⁷
SRP32-vdW-DF1	0.73†	-2.44†	-0.20†	-0.06†	-1.21†
PBE-vdW-DF2	0.77†	-2.42†	-0.13†	-0.07†	0.66†
PBE α 57-vdW-DF2	0.51† 0.00 ¹⁶⁷	-2.14†	-0.02† -0.40 ¹⁶⁷	-0.10† -0.80 ¹⁶⁷	-1.16† -0.80 ¹⁶⁷
BEEF-vdW-DF2	0.54†	-2.51†	-0.09†	0.03†	-1.17†
			meta-GGA		
revTPSS	-0.86†	-2.81†	-0.31†	0.35†	-0.92†
SCAN	-0.95† -0.40 ¹⁴⁵	-2.70†	-0.99† -0.40 ¹⁴⁵	2.39† 2.50 ¹⁴⁵	-1.57†
MS-B86bl	-0.73† -0.50 ⁵²	-2.76†	-0.85† -1.00 ⁵²	1.16† 1.00 ⁵²	-1.00†
MS2	-0.54†	-2.77†	-0.94†	0.4†	-0.96†

eV¹¹. However, other DFs yield barriers that are far off the mark, with the largest overestimate (by 0.48 eV) coming from the vdW-DF2 and the largest underestimate (by 0.28 eV) coming from the SCAN functional.

Table 3.6 shows MAEs and MSEs for all algorithms and DFs. To compare the results obtained with different algorithms, the average is always taken over the number of systems for which reliable saddle point geometries could be obtained with the high algorithm for a given DF. As Table 3.6 shows, with the high algorithm reliable saddle point geometries were obtained for 16 systems using the PBE, SRP50, and the MS-B86bl DFs, for 15 systems using the SCAN DF, and for all 17 systems for all remaining DFs. Table 3.6 shows that in general the errors obtained with the medium algorithm are close to those obtained with the high algorithm, which is much more cpu intensive. Interestingly, this was not true for the majority of the meta-GGA DFs: for these DFs the medium and high algorithms only give similar results for the revTPSS DF.

Table 3.7 shows the MAEs and MSEs for all DFs tested with averaging over all 17 systems, using the medium algorithm. With the MSE as accuracy criterion,

TABLE 3.5: Barrier heights for $\text{H}_2+\text{Cu}(111)$ (in eV) for all the DFs and algorithms tested. Values marked with "CRP" come from an accurate fit of the $\text{H}_2 + \text{Cu}(111)$ PES to DFT data computed with the DF listed¹⁷⁴.

Functional	High Algo	Light Algo	Medium Algo	Literature values
		GGA		
PBE	0.478	0.488	0.467	0.484(CRP) ¹⁰⁸
RPBE	0.762	0.819	0.762	0.797(CRP) ¹⁷⁴
SRP50	0.618	0.654	0.616	0.636(SRP48) ¹⁷⁴
		GGA+vdW		
vdW-DF1	1.026	1.102	1.019	1.004(CRP) ¹⁷⁴
vdW-DF2	1.144	1.260	1.117	
PBE-vdW-DF2	0.889	0.952	0.885	0.863(CRP) ¹⁷⁴
SRP32-vdW-DF1	0.863	0.926	0.860	
PBEa57-vdW-DF2	0.736	0.781	0.735	0.72(CRP) ¹⁷⁴
BEEF-vdW-DF2	0.928	0.966	0.925	
optPBE-vdW-DF1	-	-	0.736	
		meta-GGA		
revTPSS	0.667	0.648	0.674	0.605(CRP) ¹⁷⁴
SCAN	0.382	0.334	0.354	0.398(CRP) ¹⁷⁴
MS-B86b1	0.647	0.619	0.634	0.683(CRP) ⁵²
MS2	0.378	0.340	0.382	

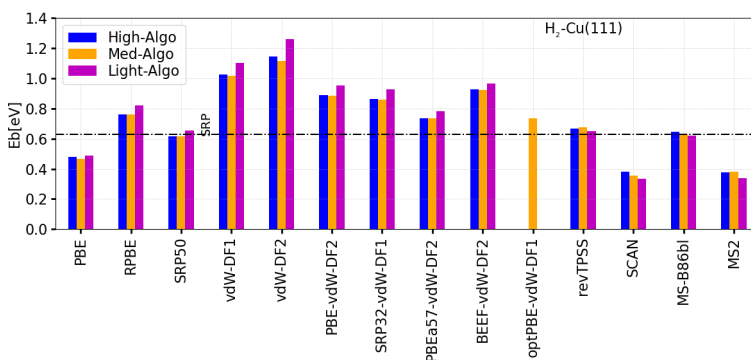


FIGURE 3.1: Performance of the DFs and algorithms tested on the DC of H_2 on $\text{Cu}(111)$. Computed barrier heights are compared with the reference value for this system, which is indicated by the horizontal dot-dashed line (see Table 3.2).

the revTPSS meta-GGA comes out as the best for DC barrier heights. The next three highest-ranked DFs all combine GGA exchange with vdW-DF1 or vdW-DF2 correlation, with the optPBE-DF1 showing the best performance. The PBE DF ranks fifth and is the best performing GGA DF. If the DFs are ranked according to their performance for the MAE the PBE DF actually performs best, with SRP32-vdW-DF2 coming out second, and the MS2 meta-GGA DF ranking third, and thereby outperforming the revTPSS meta-GGA, which now ranks ninth.

Table 3.8 shows the performance of the DFs for the smaller and older SBH10

TABLE 3.6: Performance of the DFs and algorithms tested on the SBH17 database. Mean absolute errors (MAE) and mean signed errors (MSE, both in eV) measure average deviations of the barrier heights computed with each DF and algorithm from the reference values listed in Table 3.2. N_{ex} represents the number of systems that had to be excluded for specific DFs, and N_s their numbers (see Table 3.2 and the text).

N_{ex}	Functional	Type	High		Med		Light		N_s System missing
			MAE Algo	MSE	MAE Algo	MSE	MAE Algo	MSE	
1	PBE	GGA	0.116	-0.075	0.106	-0.065	0.148	-0.067	
0	RPBE	GGA	0.230	0.230	0.228	0.228	0.263	0.263	5
1	SRP80	GGA	0.126	0.081	0.127	0.085	0.161	0.102	5
0	vdW-DF1	GGA+vdW	0.230	0.230	0.220	0.220	0.297	0.297	
0	vdW-DF2	GGA+vdW	0.329	0.329	0.311	0.311	0.461	0.461	
0	optPBE-vdW-DF1	GGA+vdW	-	-	0.131	-0.033	-	-	
0	PBEa57-vdW-DF2	GGA+vdW	0.139	-0.053	0.124	-0.040	0.135	-0.002	
0	SRP32-vdW-DF1	GGA+vdW	0.127	0.060	0.115	0.057	0.170	0.119	
0	PBE-vdW-DF2	GGA+vdW	0.144	0.109	0.141	0.112	0.191	0.166	
0	BEEF-vdW-DF2	GGA+vdW	0.190	0.190	0.191	0.191	0.228	0.222	
2	SCAN	meta-GGA	0.185	-0.172	0.154	-0.120	0.249	-0.242	5,7
0	revTPSS	meta-GGA	0.147	-0.060	0.146	-0.025	0.165	-0.105	
0	MS2	meta-GGA	0.196	-0.176	0.117	-0.074	0.173	-0.149	
1	MS-B86b1	meta-GGA	0.173	0.157	0.214	0.199	0.191	0.133	5
Average			0.179	0.065	0.166	0.075	0.218	0.092	

TABLE 3.7: Performance of the DFs tested on the SBH17 database using the medium algorithm. The MAE and MSE (in eV) are computed with averaging over all 17 systems. The values of r_{MAE} and $r_{|MSE|}$ rank the DFs according to best performance for the MAE and $|MSE|$ error criteria, respectively.

Functional	Med Algo			
	MAE	r_{MAE}	MSE	$r_{ MSE }$
PBE	0.103	1	-0.058	5
RPBE	0.228	13	0.228	13
SRP50	0.125	5	0.085	7
vdW-DF1	0.219	12	0.219	12
vdW-DF2	0.312	14	0.312	14
PBE-vdW-DF2	0.141	8	0.112	9
SRP32-vdW-DF1	0.115	2	0.057	4
PBE α 57-vdW-DF2	0.124	4	-0.040	3
BEEF-vdW-DF2	0.191	10	0.191	10
optPBE-vdW-DF1	0.131	6	-0.033	2
revTPSS	0.146	9	-0.025	1
SCAN	0.140	7	-0.105	8
MS-B86bl	0.210	11	0.195	11
MS2	0.117	3	-0.074	6
Average	0.164		0.076	

database. The three DFs featuring GGA exchange and vdW-DF1 or vdW-DF2 correlation that performed well for the SBH17 database with the absolute value of the MSE as the accuracy criterion again do well, with SRP32-vdW-DF now ranking first. The PBE performance is also consistent, with PBE ranking fifth, but as a GGA DF PBE is now outperformed by SRP50, which takes third place. The DFs performing well in terms of their absolute value of the MSE also do well on the MAE for SBH10.

The top panels of Figure 3.2 presents the correlation of the minimum barrier height of the whole system with the computed lattice constant of the metal for the DFs tested, also comparing to the SE and the experimental values of these parameters, respectively, for $H_2 + Cu(111)$ and $CH_4 + Pt(111)$. The bottom panels show the correlation of the computed minimum barrier height with the distance of the molecule to the surface in the optimized minimum barrier geometry for these two systems. An interesting feature of the revTPSS DF is that it predicts both the lattice constant of the metal and the minimum barrier height with reasonably high accuracy, while the computed distance of the molecule to the metal surface also agrees well with that obtained using the SRP-DFT approach.

Table 3.9 presents the errors made with the medium algorithm for the 8 H_2 -metal systems in the database (see also Figs.S17 and S18 of the SI of Ref.¹²⁵). For these systems and with the absolute value of the MSE as accuracy criterion, the PBE GGA DF does best, with the SRP50 DF as the runner up. The three DFs in which GGA exchange was combined with non-local correlation and which did well for SBH17 also do reasonably well for the H_2 -metal reactions. The

TABLE 3.8: Performance of the DFs and algorithms tested on the SBH10 database. Both MAE and MSE (in eV) are calculated by including, and averaging over, the ten systems present in the previous SBH10⁴⁰ database. The DFs have been ranked according to the best performance of the high algorithm according to the $|\text{MSE}|$ criterion. For the BEEF-vdW-DF2 and MS2 DFs we also present the values computed earlier while allowing surface relaxation in the TS⁴⁰.

Functional	Type	High Algo			Med Algo			Light Algo			SBH10 ⁴⁰ MAE/MSE
		MAE	MSE	MSE	MAE	MSE	MSE	MAE	MSE	MSE	
SRP32-vdW-DF1	GGA+vdW	0.134	0.041	0.041	-0.126	0.034	0.151	0.066			
SRP50	GGA	0.132	0.063	0.063	-0.133	0.067	0.155	0.061			
optPBE-vdW-DF1	GGA+vdW	-	-	0.074	-0.141	-0.074	-	-			
PBEd57-vdW-DF2	GGA+vdW	0.135	-0.076	0.076	-0.132	-0.073	0.143	-0.060			
PBE-vdW-DF2	GGA+vdW	0.142	0.093	0.093	-0.148	0.098	0.163	0.120			
PBE	GGA	0.149	-0.098	0.098	-0.143	-0.091	0.170	-0.112			
revTPSS	meta-GGA	0.198	-0.124	0.124	-0.177	-0.117	0.237	-0.185			
MS-B96bl	meta-GGA	0.196	0.165	0.165	-0.154	-0.123	0.173	0.064			
SCAN	meta-GGA	0.198	-0.178	0.178	-0.179	-0.156	0.253	-0.245			
BEEF-vdW-DF2	GGA+vdW	0.182	0.182	0.182	-0.179	-0.179	0.193	0.183	0.12/0.03		
MS2	meta-GGA	0.220	-0.188	0.188	-0.171	-0.117	0.223	-0.198	0.36/-0.34		
vdW-DF1	GGA+vdW	0.214	0.214	0.214	-0.211	-0.211	0.256	0.256			
RPBE	GGA	0.223	0.223	0.223	-0.224	-0.224	0.235	0.235			
vdW-DF2	GGA+vdW	0.331	0.331	0.331	-0.324	-0.324	0.435	0.435			
Average		0.189	0.050		-0.174	0.045	0.214	0.047			

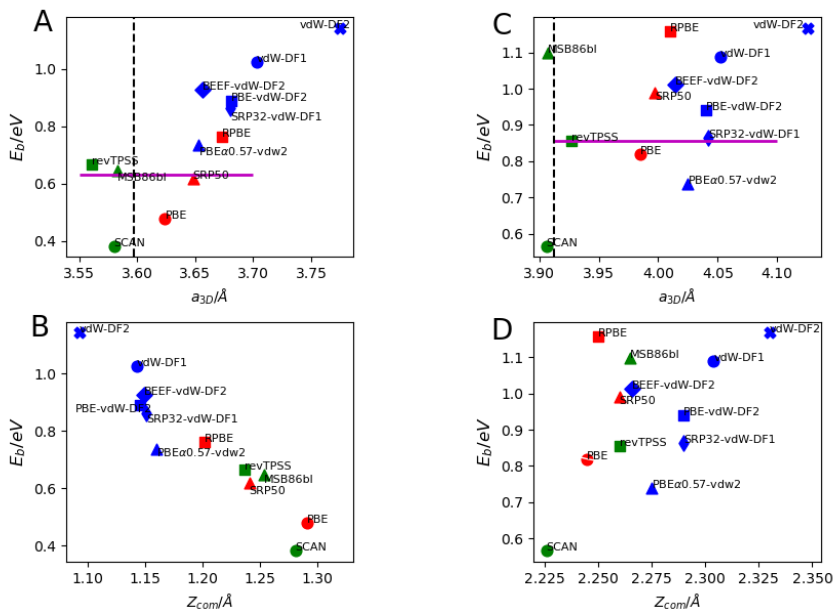


FIGURE 3.2: Correlation of the barrier height for DC with the optimized lattice constant (a_{3D}) of the metal (upper panels), and of the barrier height with the distance of the molecule to the surface at the transition state (Z_{com}), as computed with all DFs tested in this work. The high algorithm was used. The left panels present results for $H_2 + Cu(111)$ and the right panels for $CH_4 + Pt(111)$. The vertical black dashed lines in the upper panels represent the experimental lattice constants, and the horizontal magenta solid lines the reference values of the barrier heights.

same is true for revTPSS which came out as best for SBH17, but is not best for the H_2 -metal systems. Table 3.10 presents the errors made with the medium algorithm for the 2 N_2 -metal systems in the database (see also Figs.S19 and S20 of the SI of Ref. 125). For these systems, DFs that did well for SBH17 generally are not very good. MS-B86bl, BEEF-vdW-DF2 and RPBE perform best for the N_2 -metal systems. Table 3.11 presents the errors made with the medium algorithm for the 7 CH_4 -metal systems in the database (see also Figs.S21 and S22 of the SI of Ref. 125). The DFs that did well for SBH17 also do reasonably well for the $CH_4 +$ metal systems. However, for the latter category SCAN is now the best performing DF using the MSE as accuracy criterion. Using the MAE as accuracy criterion, the best CH_4 -metal results are obtained with the SRP32-vdW-DF1, PBE, and revTPSS DFs, respectively.

TABLE 3.9: Performance of the DFs tested on the 8 H₂-metal systems present in the SBH17 database using the medium algorithm. The MAE and MSE (in eV) are computed with averaging over all 8 systems. The values of r_{MAE} and $r_{|MSE|}$ rank the DFs according to best performance for the MAE and $|MSE|$ error criteria, respectively.

Functional	Med Algo			
	MAE	r_{MAE}	MSE	$r_{ MSE }$
PBE	0.080	2	-0.049	1
RPBE	0.167	10	0.167	10
SRP50	0.070	1	0.063	2
vdW-DF1	0.264	13	0.264	13
vdW-DF2	0.290	14	0.290	14
PBE-vdW-DF2	0.174	11	0.174	11
SRP32-vdW-DF1	0.152	9	0.147	9
PBE α 67-vdW-DF2	0.090	5	0.071	3
BEEF-vdW-DF2	0.227	12	0.227	12
optPBE-vdW-DF1	0.096	6	0.091	6
revTPSS	0.086	4	0.086	5
SCAN	0.121	7	-0.117	7
MS-B86bl	0.128	8	0.128	8
MS2	0.084	3	-0.084	4
Average	0.145		0.104	

TABLE 3.10: Performance of the DFs tested on the 2 N₂-metal systems present in the SBH17 database using the medium algorithm. The MAE and MSE (in eV) are computed with averaging over all 2 systems. The values of r_{MAE} and $r_{|MSE|}$ rank the DFs according to best performance for the MAE and $|MSE|$ error criteria, respectively.

Functional	Med Algo			
	MAE	r_{MAE}	MSE	$r_{ MSE }$
PBE	0.409	10	-0.409	10
RPBE	0.088	3	0.088	4
SRP50	0.157	6	-0.157	6
vdW-DF1	0.048	2	0.048	3
vdW-DF2	0.372	8	0.372	8
PBE-vdW-DF2	0.123	5	-0.123	5
SRP32-vdW-DF1	0.217	7	-0.217	7
PBE α 67-vdW-DF2	0.378	9	-0.378	9
BEEF-vdW-DF2	0.026	1	0.026	2
optPBE-vdW-DF1	0.434	11	-0.434	11
revTPSS	0.723	14	-0.723	14
SCAN	0.525	13	-0.525	13
MS-B86bl	0.102	4	-0.024	1
MS2	0.454	12	-0.454	12
Average	0.290		-0.208	

TABLE 3.11: Performance of the DFs tested on the 7 CH₄-metal systems present in the SBH17 database using the medium algorithm. The MAE and MSE (in eV) are computed with averaging over all 7 systems. The values of r_{MAE} and $r_{|MSE|}$ rank the DFs according to best performance for the MAE and $|MSE|$ error criteria, respectively.

Functional	Med Algo			
	MAE	r_{MAE}	MSE	$r_{ MSE }$
PBE	0.045	2	-0.016	2
RPBE	0.336	14	0.336	14
SRP50	0.177	9	0.177	9
vdW-DF1	0.218	11	0.218	11
vdW-DF2	0.319	12	0.319	12
PBE-vdW-DF2	0.108	8	0.108	8
SRP32-vdW-DF1	0.040	1	0.032	3
PBE α 57-vdW-DF2	0.090	7	-0.071	7
BEEF-vdW-DF2	0.196	10	0.196	10
optPBE-vdW-DF1	0.086	6	-0.060	6
revTPSS	0.05	3	0.047	5
SCAN	0.077	5	-0.007	1
MS-B86bl	0.333	13	0.333	13
MS2	0.059	4	0.046	4
Average	0.153		0.121	

Table 3.12 shows the MAEs and the MSEs for the 17 systems investigated here, where now the averaging is done over the DFs. For both the medium and the high algorithms, the largest MAEs are found for the H₂ + Ag(111), N₂ + Ru(10 $\bar{1}$ 0), and CH₄ + Ni(100) systems. If results for these 3 systems are left out (leading to the database SBH14-3SBER, i.e., SBH17 with the 3 systems with the biggest errors removed), the MAEs and MSEs obtained with averaging over the systems now come out as shown in Table 3.13. As can be seen, omitting the systems for which the largest errors are made does not lead to large changes in the conclusions: according to the MSE criterion, revTPSS comes still out as best, followed by the same three DFs made up of GGA-exchange and non-local correlation (although now with a slightly different order), and PBE (see Tables 3.7 and 3.13). Omitting the three systems for which reference barrier heights came from an ad-hoc SE analysis rather than from SRP-DFT (resulting in the SBH14-SRP database) also does not yield large differences: the revTPSS and optPBE-vdW1 DFs still come out as the two best ranking DFs according to the $|MSE|$ accuracy criterion (see Tables 3.7 and 3.13). Finally, the correlation of the signed error with (WF-EA) is shown in Figures 3.3, 3.4, and 3.5 for the GGA-DFs, the DFs consisting of GGA exchange and vdW-DF1 or vdW-DF2 correlation, and the meta-GGAs tested here, respectively. A weak correlation seems to be present, with the GGA and meta-GGA DFs producing lower (higher) signed errors for systems with lower (higher) (WF-EA).

3.4 Discussion

With the large amount of data here considered, a full analysis is beyond the scope of this chapter. Instead, in the discussion below we will focus on (i) the description of the metal, and (ii) how well the different algorithms do for describing the barriers for DC for the new database. Having determined an optimal algorithm, we then discuss (iii) how the different DFs perform overall for the new SBH17 database, and (iv) how this depends on the three different types of systems in our database. Then, we (v) compare to new and old results for the earlier SBH10 database. We also (vi) compare to the performance of DFs with earlier results for molecular chemisorption, and for gas phase reaction kinetics and thermochemistry. Finally, we also discuss future improvements and extensions of our database.

3.4.1 Description of the metal

The trends in how accurately the tested DFs describe the lattice constants of the metals investigated here (Ag, Ir, Cu, Pt, Ni, and Ru), as revealed through Table 3.3, agree well with earlier work done on different sets of bulk solids. For instance, the RPBE DF is known to overestimate lattice constants more than the PBE DF^{16,175}, and it makes sense that the lattice constant computed with their 50/50 weighted average (SRP50) falls in between. It is also known that the vdW-DF1 and vdW-DF2 DFs substantially overestimate lattice constants, and much more so than PBE, but that the performance of optPBE-vdW-DF1 is similar to that of PBE, in agreement with Table 3.3^{16,47}. Our finding that BEEF-vdW-DF2 performs somewhat worse than optPBE-vdW-DF1 is likewise in agreement with earlier findings¹⁶, and the same is true for the earlier finding that PBE α 57-vdW-DF2 and optPBE-vdDF1 perform similarly for lattice constants¹⁰⁶. The SRP32-vdW-DF1 and PBE-vdW-DF2 DFs, which to our knowledge have not been widely tested on solids yet, show a performance that is just a little better than that of vdW-DF1 and vdW-DF2.

Our finding that the four meta-GGA DFs tested here are better for lattice constants than PBE is likewise in agreement with earlier work. This has been confirmed in Refs.^{16,175} for revTPSS and in Refs.^{175,176} for SCAN. Tran et al.¹⁷⁵ found a similarly good performance for MS2 as for revTPSS and SCAN, in agreement with Table 3.3. Finally, like MS2⁴¹ the MS-B86b1⁵² was developed to perform like the PBEsol⁵⁴ GGA for metals, and its resulting good performance for metals is in agreement with earlier findings¹⁰⁶.

Interlayer distances computed with the tested DFs (Table 3.4) are not always in good agreement with experimental values and with literature values obtained

with the same DFs. This is not any reason for concern: converging the values of interlayer distances requires thicker slabs (a larger number of layers, of the order of eight or more^{145,173}) than needed for converging reaction barrier heights (typically 4 or 5). As the focus in this work is on reaction barrier heights, no attempts were made to compute interlayer distances that were converged with slab thickness.

3.4.2 Description of barrier heights to DC

3.4.2.A Preferred algorithm

Table 3.6 can be used to select the optimal algorithm for testing DFs on reaction barrier heights for DC. In selecting this algorithm we also take into account that, for a typical system, the high algorithm requires more "human time", and roughly an order of magnitude more cpu time than the medium algorithm, due to the need to find the saddle point geometry corresponding to the DF tested and the system described. The light algorithm requires even less "human time" than the medium algorithm, as the lattice constant(s) of the metal and the geometry of the metal slab representing the surface also do not need to be optimized for each metal and metal surface, respectively. However, the light algorithm is not much less cpu-intensive than the medium algorithm.

Table 3.6 suggests the use of the medium algorithm for the following two reasons. The first reason is that for all GGA DFs, for all DFs combining GGA exchange with non-local correlation, and for revTPSS the medium algorithm leads to results that hardly differ from the results of the much more expensive high algorithm. In contrast, the light algorithm leads to results that differ considerably from those of the medium algorithm, i.e., higher MAEs and MSEs. This result suggests that, at least for now and while DFs are developed that yield a simultaneously good description of interaction energies and metal structure, the medium algorithm should be used. Figure 3.2 suggests an explanation: for GGA DFs, and apparently also for the DFs combining GGA exchange with non-local correlation, the predicted barrier height and metal lattice constant are correlated, with higher barriers corresponding to larger lattice constants, which has been known for some time^{54,55}. Apparently reaction barrier heights are then best computed with the metal surface appropriately relaxed with the DF tested (as done in the high and medium algorithms), which may be related to the observation that reaction barrier heights may be strongly affected by lattice strain¹⁴⁸. We note that the problem that with GGA DFs barrier heights are usually correctly predicted at the cost of overestimated lattice constants may in principle be solved by resorting to a meta-GGA DF, as the use of the kinetic energy density allows the DF to distinguish between metallic and covalent

TABLE 3.12: Overall accuracy achieved for each system in the SBH17 database with the algorithms tested. For a given system, mean absolute errors (MAE) and mean signed errors (MSE, both in eV) measure average deviations of the barrier heights computed using the DFs tested in this work from the reference values listed in Table 3.2. The averaging is done over the DFs, so that large deviations are likely to be indicative of inaccurate reference values.

System	High Algo		Med Algo		Light Algo	
	MAE	MSE	MAE	MSE	MAE	MSE
H ₂ /Cu111	0.205	0.104	0.197	0.098	0.245	0.133
H ₂ /Cu100	0.218	0.115	0.209	0.118	0.240	0.101
H ₂ /Cu110	0.205	0.104	0.165	0.120	0.286	0.171
H ₂ /Ag111	0.339	0.334	0.335	0.330	0.380	0.375
H ₂ /Pt211	0.126	-0.048	0.054	0.048	0.056	0.056
H ₂ /Pt111	0.125	0.124	0.084	0.082	0.135	0.132
H ₂ /Ru0001	0.074	-0.008	0.039	0.016	0.046	0.028
H ₂ /Ni111	0.075	0.028	0.063	0.049	0.078	0.059
N ₂ /Ru0001	0.230	-0.138	0.231	-0.141	0.318	-0.203
N ₂ /Ru1010	0.340	-0.259	0.349	-0.275	0.400	-0.293
CH ₄ /Ni100	0.264	0.264	0.266	0.266	0.270	0.270
CH ₄ /Ni111	0.144	0.091	0.132	0.100	0.182	0.132
CH ₄ /Ni211	0.126	0.058	0.120	0.090	0.134	0.045
CH ₄ /Pt111	0.155	0.098	0.146	0.084	0.280	0.246
CH ₄ /Pt211	0.118	0.024	0.117	0.068	0.164	-0.032
CH ₄ /Ru0001	0.152	0.142	0.157	0.144	0.187	0.176
CH ₄ /Ir111	0.124	0.084	0.131	0.094	0.239	0.221
Average	0.177	0.065	0.164	0.076	0.214	0.095

bonding¹⁷⁷. This should also explain why the correlation observed in the upper two panels of Figure 3.2 between lattice constant and barrier height is not observed for the meta-GGA DFs.

The second reason to use the medium algorithm is simply that it produces the lowest averaged MAE when the MAEs of the barrier heights are averaged over all DFs tested (Table 3.6). The simplest explanation being that the medium algorithm allows the best description of the reaction barrier height, Occam’s razor then suggests the use of the medium algorithm. From now on, our discussion will therefore focus on results obtained with the medium algorithm.

3.4.2.B Performance of DFs for SBH17 with medium algorithm

If we take the absolute value of the MSE as the accuracy criterion, of the DFs tested the revTPSS meta-GGA comes out as best with a |MSE| of 25 meV, which corresponds to 0.58 kcal/mol (see also Table 3.7). Of the five best performing DFs, three are made of GGA exchange and non-local correlation, and the DF ranked fifth is the PBE GGA DF. Both the revTPSS and PBE DFs may be described as non-empirical, constraint-based DFs, and interestingly both have been cast as general purpose, workhorse functionals.

TABLE 3.13: Density functional performance on two smaller databases with 14 barrier heights in them. SBH14-3SBER was obtained from SBH17 by removing the 3 systems yielding the largest MAE when averaging over all DFs tested (see Table 12). SBH14-SRP only contains the 14 systems for which reference values of barrier heights were obtained from SRP-DFT. For each database, r_{MAE} and $r_{|MSE|}$ rank the DFs according to best performance for the MAE and $|MSE|$ criterion, respectively. All errors are in eV.

Database	SBH14-3SBER			SBH14-SRP		
	MAE	r_{MAE}	$ MSE $	MAE	r_{MAE}	$ MSE $
Density functional						
PBE	0.074	1-2	-0.050	0.074	1	-0.050
SRP50	0.098	7	0.080	0.098	3	0.081
RPBE	0.208	13	0.208	0.210	12	0.210
vdW-DF1	0.191	11	0.191	0.219	13	0.219
vdW-DF2	0.267	14	0.267	0.294	14	0.294
PBE-vdW-DF2	0.107	8	0.093	0.128	9	0.115
SRP32-vdW-DF1	0.074	1-2	0.041	0.103	4-5	0.070
PBEc57-vdW-DF2	0.091	5	-0.045	0.112	7	-0.020
BEF-vdW-DF2	0.163	10	0.163	0.189	11	0.189
optPBE-vdW-DF1	0.093	6	-0.033	0.114	8	-0.007
revTPSS	0.089	4	0.004	0.103	4-5	0.017
SCAN	0.108	9	-0.084	0.107	6	-0.082
MS-B86b1	0.196	12	0.196	0.186	10	0.186
MS2	0.086	3	-0.058	0.085	2	-0.064

The MAE is probably the best accuracy criterion, as this quantity tells us by how much the barrier height we compute with a given DF will typically be off from the real value. According to this criterion, the PBE DF comes out best, with a MAE of 0.103 eV (2.4 kcal/mol). With this criterion revTPSS comes out as ninth, with a MAE of 0.146 eV (3.4 kcal/mol). The MS2 DF now comes out as the best meta-GGA DF (MAE = 0.117 eV = 2.7 kcal/mol). The highest ranked GGA+vdW DF now is SRP32-vdW-DF1, which has a second overall ranking (MAE = 0.115 eV = 2.7 kcal/mol).

The major conclusions regarding the accuracy of DFs for the type of DC reactions on SBH17 are robust in the sense that if we remove the three systems from the database that lead to the largest errors (leading to the SBH14-3SBER database) the order of the best performing DFs remains more or less the same. As Table 3.13 shows, revTPSS is still the best in terms of MSEs, and PBE still ranks first in terms of MAEs (although now together with SRP32-vdW-DF2). The best five performing DFs in terms of MSEs and the best three in terms of MAEs remain the same (compare Tables 3.7 and 3.13).

The major conclusions regarding DF accuracy also remain unchanged if we use the SBH14-SRP instead of the SBH17 database (compare Tables 3.7 and 3.13). For instance, the PBE DF remains the best performing DF according to the MAE criterion. SRP32-vdW-DF1 ranks second according to this criterion for SBH17, and still fourth (together with revTPSS) for SBH14-SRP; MS2 ranks third for SBH17, and second for SBH14-SRP. Removing the three systems for which reference barrier heights were obtained using an ad-hoc SE approach does lead to considerably smaller absolute values of the MAE, e.g. 74 meV (1.7 kcal/mol) for PBE under SBH14-SRP vs. 103 meV (2.4 kcal/mol) under SBH17. This suggests that the conclusions regarding DF performance on DC barrier heights in SBH17 would be even more favorable than now obtained if the reference values for the three systems discussed were to be replaced with more accurate SRP-DFT values. The following two observations provide additional evidence that the reference values for at least two of the three systems left out in SBH14-SRP are inaccurate: (i) the SRP32-vdW-DF1 functional, which performs so well for CH₄ + metal surface systems, shows a comparatively poor performance on CH₄ + Ni(100) (Table 3.11 and Fig. 3.4), and (ii) the PBE DF, which shows the lowest MAE for SBH17, shows a larger error on the N₂ + Ru(10 $\bar{1}$ 0) system than on any other system (Fig. 3.3).

If we compare trends found for barriers for DC on metals to trends found for gas phase reaction barriers, a number of important differences stand out. First of all, the MAEs tend to be smaller for DC barriers than for gas phase reaction barriers. To give an example: the MAE of the PBE DF for the BH76 database for hydrogen atom transfer and non-hydrogen atom transfer reactions

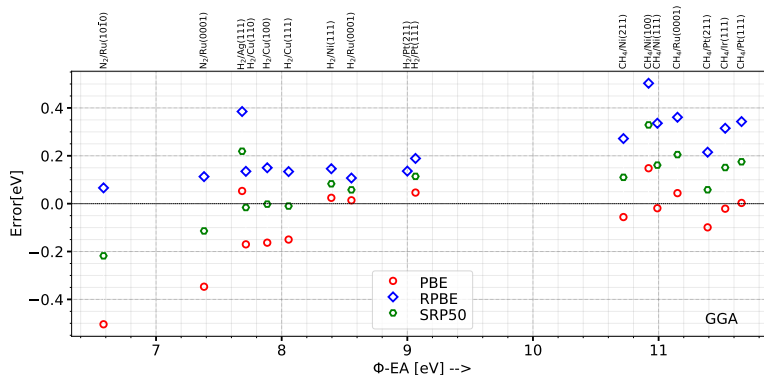


FIGURE 3.3: Correlation between the signed error and the difference of the work function of the metal surface Φ and the electron affinity EA of the molecule for all the systems investigated. The results are for the high algorithm, for the GGA DFs tested.

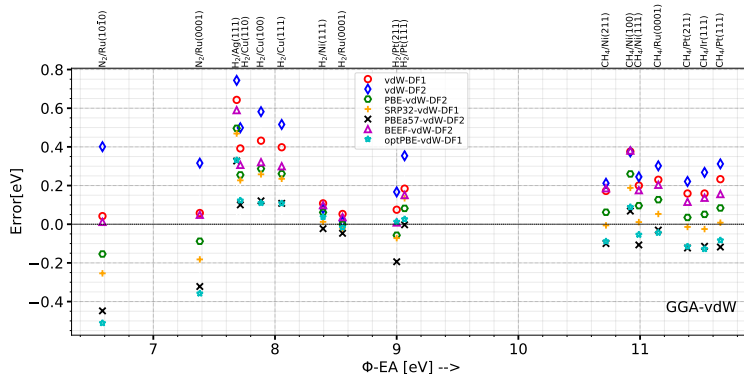


FIGURE 3.4: Correlation between the signed error and the difference of the work function of the metal surface Φ and the electron affinity EA of the molecule for all the systems investigated. The results are for the high algorithm, for the GGA-vdW-DF1,2 DFs tested.

is 8.9 kcal/mol²⁶, while the MAE found here is 2.4 kcal/mol. It is important to note that this difference does not arise from the barrier heights being much larger for the BH76 database: the average over the absolute values of the barrier heights is 18.6 kcal/mol for BH76²³, which is not much larger than for SBH17 (14.8 kcal/mol). Second, while RPBE clearly outperforms PBE for gas phase reactions^{24,26,178}, the opposite is the case for the DC barriers we consider here. Thirdly, and most importantly: while the PBE and RPBE DFs both systematically underestimate gas phase reaction barrier heights¹⁷⁸, here we find that the RPBE DF systematically overestimates reaction barrier heights,

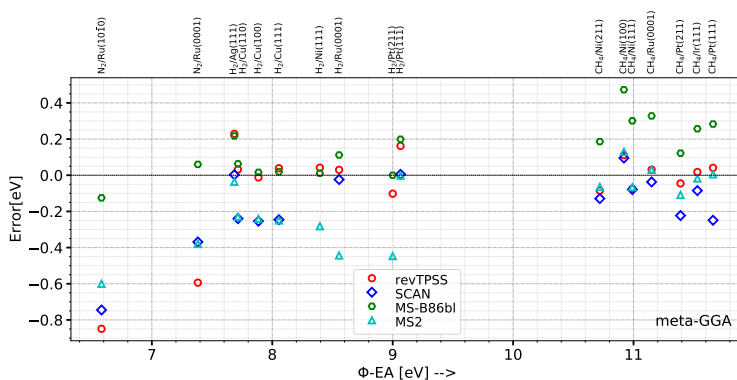


FIGURE 3.5: Correlation between the signed error and the difference of the work function of the metal surface Φ and the electron affinity EA of the molecule for all the systems investigated. The results are for the high algorithm, for the meta-GGA DFs tested.

while the PBE DF neither systematically underestimates nor systematically overestimates DC barriers for the systems we consider. We consider this last point a key point, which should be a telltale concerning semi-local DFT and fundamental differences between gas phase reactions and DC on metals. For this we note that the deficiency of semi-local DFT for gas phase reactions has often been rationalized in terms of the delocalization error of Yang and co-workers^{179–181}. The following hand waving explanation has been put forward for explaining the comparatively good performance of semi-local DFT for DC barriers in the systems in the database¹³: of the electrons responsible for the formation of bonds between the molecular fragments and the surface, the ones coming from the molecule become more delocalized in the transition state, but the opposite is true for the electrons coming from the metal, which are quite delocalized to start with. This leads to error cancellation. A weakness of this explanation is that it is hard to see how it can be tested or falsified, and more research is needed to clarify the origin of the differences between the performance of semi-local DFT for reaction kinetics in the gas phase and on metal surfaces.

Considering specific DFs, we note that, as found in other studies of molecules interacting with metal surfaces^{52,182}, the maximally constrained meta-GGA DF SCAN does not outperform the PBE GGA DF for DC barriers, showing a similar performance to the revTPSS DF for the MAE. The somewhat weak performance of SCAN for adsorption of molecules on metal surfaces has been attributed to density driven errors¹⁸². The MS2 meta-GGA DF performs reasonably well for DC barriers, ranking third according to the MAE criterion, with a MAE of 0.117 eV (2.7 kcal/mol). The MS86bl DF, which has been constructed in such a way

that its performance should be biased in favor of systems containing hydrogen⁵², is the meta-GGA DF performing least well for DC barriers here.

Of the DFs built from GGA exchange and non-local correlation, the optPBE-vdW-DF1, the SRP32-vdW-DF1, and the PBE α 57-vdW-DF2 DFs perform quite well here, ranking among the best 4 according to the MSE and among the best 6 according to the MAE criterion. For the SRP32-vdW-DF1 and the PBE α 57-vdW-DF2 DFs this is not so surprising as they are known to be SRP-DFs for some of the systems in our database (see Table 3.2). However, the optPBE-vdW-DF1 DF was first developed to obtain an improved description of weak interactions⁴⁹, and only later was this DF shown to accurately model systems in which H₂ interacts with copper surfaces^{87,108}. The original vdW-DF1 and vdW-DF2 DFs do not exhibit a very good performance for DC, ranking 12th and 14th on both accuracy criteria. PBE-vdW-DF2 exhibits a reasonable performance. The performance of BEEF-vdW-DF2 would seem to be disappointing as well, as it seemed to perform much better in the earlier tests on the SBH10 database⁴⁰. This issue will be further considered below.

3.4.2.C Dependence on the type of system

The performance of the tested DFs on H₂-metal systems (Table 3.9) does not contain great surprises. The SRP50 DF performs better on this sub-database than on SBH17, but this is no great surprise as this DF is close to the SRP48 DF, which is an SRP-DF for H₂ + Cu(111)¹⁰⁴. The SRP32-vdW-DF is also less good for the H₂-metal sub-database than for SBH17, which may be explained from this DF being an SRP-DF for several CH₄ + metal systems, while it performs poorly for DC of H₂ on Cu and Ag surfaces (see Table 3.2 and Fig. 3.4).

The performance of the tested DFs on N₂-metal systems (Table 3.10) is rather different from that on the SBH17 database. Specifically, the best four performing DFs for N₂-metal systems (MS-B86bl, BEEF-vdW-DF2, vdW-DF1, and RPBE according to both the MSE and MAE criteria) show a rather poor overall performance on SBH17. The origin of this discrepancy is not entirely clear. However, there appears to be a weak correlation between the MSE of a given functional and (WF-EA) (see Figures 3.3-3.5). A trend that may be discerned is that the MSE increases with the (WF-EA). The N₂-metal systems have a low (WF-EA), and lie on one of the outer edges of the range of (WF-EA) spanned by the systems investigated here (see Figures 3.3-3.5). These two observations together perhaps explain why the DFs that come out best for N₂-metal systems do not do well for SBH17 as a whole: for many of the systems in the database with higher (WF-EA), these DFs will produce much higher unsigned errors.

Finally coming to the CH₄-metal systems (Table 3.11) the only real surprise is that SCAN performs quite well for these systems. The good performance of SCAN for systems with high (WF-EA) (see Figures 3.3-3.5) is consistent with the explanation that for this DF errors in molecule-metal surface interactions are density driven: for the methane-metal systems, little if no electron transfer will occur from the metal surface to the molecule. This would suggest that errors associated with electron delocalization and self-interaction should be small⁵⁸, which would in turn suggest that density driven errors should be small.

3.4.2.D Comparison to present and previous results for SBH10

To allow a better comparison between the results for the present SBH17 and the older SBH10 database, in Table 3.14 we compare the MAEs obtained for both databases for the 9 DFs that performed best for SBH17 according to the MAE accuracy criterion. In Table 3.14 we also show how these DFs ranked according to both the MAE and the MSE accuracy criterion in both databases.

The comparison shows that, on the whole, not much changes when comparing our new results for SBH10 to our new results for SBH17. Only in one case is the MSE changed by more than 1 kcal/mol (~ 43 meV), i.e., for the meta-GGA MS2 functional (by 54 meV). The second largest change occurred for the GGA PBE DF (40 meV), and the third largest change for the meta-GGA revTPSS DF (by 31 meV). In all three cases the MAE is increased going from SBH17 to SBH10. Inspection of Figs 3.3 and 3.5 suggests that for these 3 DFs the discrepancy could to a large extent be due to the larger weight of the N₂-metal systems in the SBH10 database (20 %) compared to that in the SBH17 database (12 %), as the three DFs mentioned all perform rather poorly for the systems containing N₂.

Finally, there is the matter of how the old results for SBH10⁴⁰ compare to the new results for SBH10, and for SBH17. The old study compared results for three DFs where each is a representative of a specific class of DFs, i.e., rung 2 (GGA) exchange with vdW-DF2 correlation (BEEF-vdW-DF2), rung 3 exchange and rung 3 correlation (MS2), and a rung 4, screened hybrid DF (HSE06)⁴². With the latter DF, only results were obtained for the H₂ metal systems. For this reason, and because we did not test any rung 4 DFs here, we will not discuss the old HSE06 results here.

First comparing the old SBH10 to the new SBH10 results here (see Table 3.8), fairly large differences are noted for the two DFs tested. The old results showed a somewhat better performance for the BEEF-vdW-DF2 DF (MAE, MSE = 0.12, 0.03 eV) than here obtained (MAE, MSE = 0.18, 0.18 eV for the medium algorithm, see also Table 3.8). On the other hand the old results showed a

TABLE 3.14: Comparison of DF performance on the SBH17 and SBH10 databases. For the nine DFs that performed best for SBH17 according to the MAE (eV) criterion, a comparison is made with their performance for the SBH10 database. For this, the rank r_{MAE} of the DF is presented according to the MAE (eV) criterion for both SBH17 and SBH10, as well as the MAE (eV) for the DF for each database. The last column lists the ranks $r_{|MSE|}$ according to the MSE (eV) as accuracy criterion, for both SBH17 and SBH10 (with $r_{|MSE|}$ for the latter given in brackets). All results are for the medium algorithm.

DF	r_{MAE} SBH17	MAE SBH17	MAE SBH17	r_{MAE} SBH10	MAE SBH10	$r_{ MSE }$
PBE	1	0.103	0.103	5	0.143	5 (5)
SRP32-vdW-DF1	2	0.115	0.115	1	0.126	4 (1)
MS2	3	0.117	0.117	8	0.171	6 (7)
PBE α 57-vdW-DF2	4	0.124	0.124	2	0.132	3 (3)
SRP50	5	0.125	0.125	3	0.133	7 (2)
optPBE-vdW-DF1	6	0.131	0.131	4	0.141	2 (4)
SCAN	7	0.140	0.140	7	0.179	8 (10)
PBE-vdW-DF2	8	0.141	0.141	6	0.148	9 (6)
revTPSS	9	0.146	0.146	9	0.177	1 (7)

considerably worse performance for the MS2 DF (MAE, MSE = 0.36, -0.34 eV) than here obtained (MAE, MSE = 0.17, -0.12 eV for the medium algorithm, see also Table 3.6). The explanation for this difference is as follows. A shortcoming of the method to compute barrier heights in the older work was that the metal surface was allowed to relax in the presence of the molecule for 9 of the 10 systems in the database in the calculation of the transition state energy. From a physical point of view, this is incorrect when interpreting the outcome of supersonic molecular beam experiments, where the molecule comes in fast and the surface atoms do not have time to respond to its presence¹⁰. Using this incorrect procedure should lead to an underestimate of the classical barrier height relative to SRP-DFT or experimentally estimated values obtained from supersonic molecular beam sticking experiments, which should reflect the situation where the surface atoms have not relaxed in response to the incoming molecule. How this affects the results for a given DF depends on its MSE. The BEEF-vdW-DF2 DF has a small positive MSE for SBH10 with the old algorithm, which should then go up with the new algorithm, as should the MAE. This explains the worse performance of BEEF-vdW-DF2 for SBH10 with the newer and better algorithm (as Figure 3.6 shows, barrier heights increase with the new algorithm, the reason being that the TS energy comes out higher because the surface is not allowed to relax). The MS2 DF has a large negative MSE for SBH10 with the old algorithm, which should then become smaller but still negative with the new algorithm, and this should lead to a smaller MAE, as indeed observed.

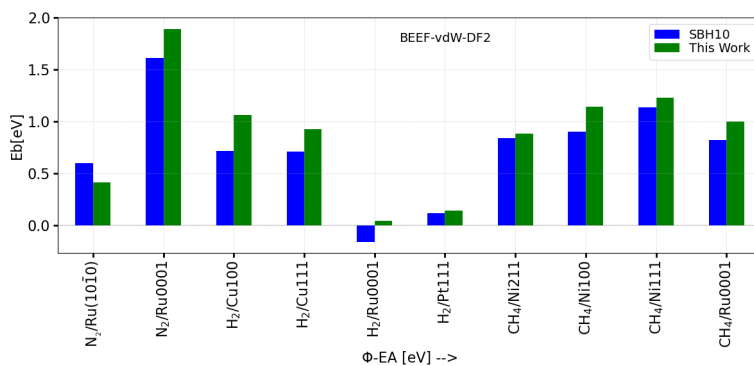


FIGURE 3.6: Comparison of barrier heights computed with the BEEF-vdW-DF2 DF for the systems in the SBH10 database, allowing the surface to relax in the TS (SBH10, results from Ref.⁴⁰) and using the medium algorithm, in which the surface is held fixed at the metal-vacuum interface geometry (This work).

We now compare the old SBH10 to the new SBH17 results. The old results showed a somewhat better performance for the BEEF-vdW-DF2 DF (MAE,

MSE = 0.12, 0.03 eV) than here obtained for SBH17 (MAE, MSE = 0.19, 0.19 eV, medium algorithm, see also Table 3.7). On the other hand the old SBH10 results showed a considerably worse performance for the MS2 DF (MAE, MSE = 0.36, -0.34 eV) than here obtained for SBH17 (MAE, MSE = 0.12, -0.07 eV, medium algorithm, see also Table 3.7). In contrast to the older SBH10 work, we thus find a better performance of the MS2 DF than of the BEEF-vdW-DF2 DF. However, this better performance could in principle reflect the smaller proportion of N₂-metal systems in SBH17 than in SBH10. If it turns out that, as discussed above in Section 3.4.2.B, MS2 also systematically underestimates barrier heights for N₂-metal systems, then the performance of this DF for a more balanced database (which should contain more N₂-metal systems relative to H₂- and CH₄-metal systems than now is the case) could be somewhat worse than now found. However, our results do not support the conclusion that might be drawn from the older SBH10 work that meta-GGA functionals systematically underestimate reaction barrier heights for DC on metals: this is not true for revTPSS (MSE = -25 meV), for MS2, and even for SCAN (MAE = 140 meV, MSE = -105 meV, see Table 3.7), and it is certainly not true for MS-B86bl (MSE = 195 meV). Our new study also does not support the idea that meta-GGA DFs should be worse for DC on metals than GGA DFs.

3.4.3 Comparison to results for adsorption and to gas phase results

In Table 3.15 our new results for SBH17 are compared to results for adsorption of molecules to metal surfaces, focusing on strong molecule-metal surface interactions, i.e., on chemisorption. The data we compare to come from calculations on the CE26 database¹⁸ and from calculations on the CE21b database¹⁸³, where the latter may be viewed as a sub-database of the former. We use the MAE (or, if not available, the RMSE) as the accuracy criterion, and the DFs are listed in order of increasingly RMSE for the CE26 database. The most important observation that can be made is that the DFs that perform best for DC barrier heights (a kinetic property) usually are not best for chemisorption energies (a thermochemical property), and vice versa. To give a few examples: PBE performs best for DC barriers in SBH17, but ranks sixth of the DFs listed in Table 3.15 for chemisorption energies. Similarly, the three best DFs for chemisorption (BEEF-vdW-DF2, vdW-DF1, and RPBE) did not perform particularly well for dissociation barriers, ranking 10th, 12th, and 13th among the 14 DFs tested on SBH17. A DF performing reasonably well on both chemisorption and DC is MS2, which ranks 4th for chemisorption and 3rd for DC barriers in Table 3.15, and may be said to yield the best overall performance on molecule-metal surface

interactions. On the basis of the results in Table 3.15 we do not agree with the statement that "a functional that predicts chemisorption energies accurately can also predict barrier heights with comparable accuracy"¹⁸. In Ref.¹⁸ this conclusion referred to the BEEF-vdW-DF2, which performs well for chemisorption and performed well in the earlier tests on DC of Ref.⁴⁰. However, as shown here its performance for barrier heights is not particularly good if the metal surface is treated appropriately (see Section 3.4.2.B), which was not the case in Ref.⁴⁰.

In Table 3.16 kinetic data coming from barrier height databases (the present SBH17 results for surface reactions, and BH76 and BH206 for gas phase reactions) and thermochemical data (the CE26 results for chemisorption at metal surfaces, and AE6 for atomization energies and TCE for "easy" thermochemical gas phase interactions) are compared for a selection of the GGA and meta-GGA DFs tested here. We see that some of the observations for surface reactions also hold for gas phase interactions. For example, the functional that of PBE and RPBE is best for gas phase reaction barriers (RPBE in BH76 and BH206) is not necessarily best for gas phase thermochemistry (with RPBE outperformed by PBE for the large TCE database, although not for the small AE6 database). For the databases listed in Table 3.16, MS2 has the best overall performance. A striking observation is that RPBE is good for chemisorption (for which it was optimized³⁹) while PBE is good for DC barrier heights (for which it was not optimized), as already noted above. In Section 3.4.2 the point that RPBE is better than PBE for gas phase reactions but not for metal surface reactions was already discussed. The revTPSS DF exhibits a fairly robust performance for all the databases in Table 3.16. SCAN is robust for the gas phase databases, poor for chemisorption, but rather good for DC barriers.

3.4.4 Future improvements

On the basis of the above, we see the following possible improvements of the present database for DC barriers on metals, and for testing DFs on the database.

First, we suggest that in future the entries in the database are as much as possible based on SRP-DFT, and not on more ad-hoc SE procedures. This would require dynamics calculations with trial DFs on $\text{CH}_4 + \text{Ru}(0001)$ and $\text{CH}_4 + \text{Ni}(100)$, for which molecular beam experiments are already available^{91,129}, and new experiments and dynamics calculations on $\text{N}_2 + \text{Ru}(10\bar{1}0)$, for which molecular beam sticking experiments are, to our knowledge, not yet available. As noted above our comparison between MAEs computed with PBE for SBH17 and SBH14-SRP suggests that replacing the reference values with SRP-DFT values for the three systems mentioned is likely to lead to smaller MAEs for a thus improved version of the SBH17 database. Second, we suggest that the database

TABLE 3.15: DF performance for kinetics and thermochemistry of molecules reacting with metal surfaces. Errors for adsorption energies as present in the CE21b¹⁸³, and CE26¹⁸ databases are compared to MAEs computed for DC barriers for the new SBH17 database, for the DFs for which results were provided in the chemisorption databases. All errors are in eV.

DF	Database	CE21b		CE26		SBH17	
	Type DF	MAE	MSE	RMSE	MSE	MAE	Rank
BEEF-vdW-DF2	GGA+vdW	-	-	0.21	0.0	0.19	10
vdW-DF1	GGA+vdW	-	-	0.21	0.09	0.22	12
RPBE	GGA	0.15	0.07	0.23	0.09	0.23	13
MS2	meta-GGA	-	-	0.27	-0.15	0.12	3
vdW-DF2	GGA+vdW	-	-	0.29	0.15	0.31	14
PBE	GGA	0.30	-0.28	0.31	-0.19	0.10	1
revTPSS	meta-GGA	0.30	-0.28	0.31 ^a	-	0.15	9
SCAN	meta-GGA	0.47	-0.46	0.45	-0.39	0.14	7
optPBE-vdW-DF1	GGA+vdW	-	-	0.54	-0.42	0.13	6

^a Inferred from PBE value for CE26 and similar performance of PBE and revTPSS on the MAE in CE21b.

TABLE 3.16: DF performance for kinetics and thermochemistry of molecules reacting with metal surfaces, and for gas phase chemistry. Comparison of performance of a selection of GGA and meta-GGA DFs for gas phase and metal-surface interactions. Unless indicated otherwise with explicit references the data come from the present results for the SBH17 database (this work), and works presenting data for the BH76 database²⁶, the BH206 database²⁴, the CE26 database¹⁸, the AE6 database¹⁸³, and the TCE database²⁴. All errors in eV.

DF	Database Type DF	SBH17 MAE	BH76 MAE	BH206 RMSE	CE26 RSME	AE6 MAE	TCE RMSE
PBE	GGA	0.10	0.43	0.40	0.31	1.02	0.40
MS2	meta-GGA	0.12	0.27 ¹⁸⁴	0.27	0.27	0.19 ¹⁸⁵	0.29
SCAN	meta-GGA	0.14	0.34 ⁵¹	0.33	0.45	0.15	0.23
revTPSS	meta-GGA	0.15	0.35	0.32	0.31	0.28	0.27
RPBE	GGA	0.23	0.34	0.33	0.23	0.42	0.42

be extended with additional N₂-metal systems. It may be possible to do this by semi-empirically fitting SRP-DFs to supersonic molecular beam sticking data on N₂ + Fe(111)^{186,187}, W(110)^{188,189}, and W(100)^{189–192}. Adding these data is desirable to make the database more balanced, as it is now dominated by data for DC of H₂ and CH₄ on metal surfaces. Also, it would show whether our results for the MS2 DF are robust to addition of more N₂-metal systems to the database, for which this DF did not perform so well, and the same holds for the optPBE-vdW-DF1 and PBE DFs.

On the longer term, it should be necessary to extend the database with systems for which the charge transfer energy, which equals (WF-EA), is less than 7 eV. As noted in Ref.⁵⁸, DFs with semi-local exchange would appear to systematically overestimate the reactivity of such systems, suggesting that DFs with screened exact exchange are required for a good description. Examples of systems for which molecular beam sticking data are available include e.g. H₂O + Ni(111)¹⁹³, HCl + Au(111)¹⁹⁴, and O₂ + Al(111)^{195,196}, Ag(110)^{197,198}, Cu(100)¹⁹⁹, and Cu(111)²⁰⁰. Inclusion of such systems in the database would certainly alter the view of the performance of DFs for DC on metal surfaces, where the view offered in the present work is specific to systems with (WF-EA) > 7 eV, the only exception being N₂ + Ru(1010).

Finally, of course a far larger number of DFs exists than here tested. While we could mention specific DFs here that would be nice to test, this might not do justice to others, as several DFs exist (see e.g. the DFs tested in Refs.^{23,24,26}). However, a particular DF we would like to mention is the new machine learned DF DM21²⁰¹. Even though this DF has not been trained on interactions involving transition metals, it would be good to see how it performs on SBH17. It would also be good to test recently developed functionals combining screened exact exchange with vdW-DF1 and vdW-DF2 correlation^{202,203}, which may work especially well for the representative database we envisage. We advocate that such future benchmark tests would also incorporate calculations employing the CE26 database for chemisorption on metals¹⁸.

Last but not least, it would also be good to mention something we would like to keep the same for now. A nice conclusion from the present work is that benchmarking of DFs on the SBH17 database can be done with the "medium algorithm". While this requires some additional work to what is needed for benchmarking DFs on kinetic and thermochemical data on chemical reactions, the overall extra effort required (of determining the lattice constant of the 6 metals present in the database for each DF, and the interlayer relaxation of the metal slabs of the 12 different metal surfaces used here) is manageable. For this reason, we also hope that others will start using the SBH17 database, and that it will be incorporated in the larger databases that are now used for extensive

benchmarks of gas phase reactions^{23,24,26}, which unfortunately do not yet include data for reactions on metal surfaces.

3.5 Conclusions and outlook

We have presented a new database with barrier heights for DC on metal surfaces that can be used for benchmarking electronic structure methods. The new database is called SBH17 and contains barriers for 17 systems, including 8 H₂ metal systems, 2 N₂ metal systems, and 7 CH₄ metal systems. For 16 systems (WF-EA) exceeds 7 eV. The barrier heights come from SRP-DFT (14 systems) and from more ad-hoc SE procedures (3 systems). The new database is meant to replace an older database (SBH10) that contained barriers for 10 of the 17 systems now treated.

We have tested 14 DFs on the new database, of which three were GGA DFs, 4 meta-GGA DFs, and 7 DFs containing GGA exchange and vdW-DF1 or vdW-DF2 non-local correlation. We first tested how the performance of these DFs depend on the algorithm or procedure used. Three different algorithms were tested, which were labeled “high”, “medium” and “light” according to the investment of computer time that was required for the calculation. In the algorithm that is the best compromise between accuracy and invested computer time (the medium algorithm), for each DF tested one computes the lattice constant of the metals in the database. Next, for each DF tested, for each metal surface in the database one performs a relaxation of the interlayer distances between the top layers. Then, for each system in the database and for each DF the barrier height is computed on the basis of two single point calculations. One of these calculations is for a geometry where the molecule is in the gas phase, and one for a geometry where the molecule is in the saddle-point geometry with respect to the surface obtained from the previous calculations. This saddle point geometry is either the one previously obtained from an SRP-DFT calculation (if the barrier height comes from SRP-DFT) or from a calculation with a functional that is expected to perform best (if the barrier height is a guess based on more approximate SE procedure).

Of the DFs tested, the meta-GGA DFs perform best at describing the metal, followed by PBE and optPBE-DF1. When the MAE is taken as the accuracy criterion, the workhorse PBE GGA DF performs best on the SBH17 database, with a MAE of 2.4 kcal/mol. Other top performers are the MS2 meta-GGA functional and two functionals consisting of GGA exchange and non-local correlation (SRP32-vdW-DF1 and PBE α 57-vdW-DF2). Surprisingly, none of the DFs tested systematically underestimates reaction barriers for DC on metals, in contrast to findings for gas phase reactions. This finding should

be a telltale on the origin of flaws of semi-local DFs for gas phase reaction barriers, and differences between gas phase reactions and DC reactions on metals, suggesting further research on these topics.

Our results for the accuracy of the DFs for DC barriers are robust to the extent that their ranking according to MAE is rather insensitive to removing the three systems yielding the biggest errors in the database, to removing the three systems for which reference barrier heights were obtained with an ad-hoc SE analysis, and to applying the functionals to the older SBH10 database. Improving SBH17 by ensuring that all reference barrier heights come from SRP-DFT is likely to reduce the MAEs of the best performing functionals considerably, e.g. to an error less than 2 kcal/mol for PBE. We obtain different results regarding the relative accuracy of the MS2 and BEEF-vdW-DF2 functionals than obtained in an earlier study of the SBH10 database, which we attribute to an incorrect treatment of the surface atoms in the transition states in the earlier study.

For the sub-databases with H₂-metal systems, N₂-metal systems, and CH₄-metal systems, rankings are obtained that differ from the overall ranking for the complete database. The SRP50-DF (the 50/50 mixture of the PBE and RPBE GGA DFs) performs best for H₂-metal systems. BEEF-vdW-DF2 performs best for N₂-metal systems, and SRP32-vdW-DF1 for CH₄-metal systems.

The DFs performing best for DC barriers (i.e., kinetics) are not the ones that perform best for databases (CE26, CE21b) of chemisorption energies on metals (i.e., thermochemistry). This trend is paralleled in the performance of DFs on databases for kinetics (BH76, BH206) and thermochemistry (AE6, TCE) in the gas phase. The meta-GGA MS2 DF is the functional with the best overall performance for DC barriers and chemisorption energies on metals. Of the five GGA and meta-GGA DFs considered for their performance on 6 databases for kinetics and thermochemistry on metal surfaces and in the gas phase (PBE, RPBE, revTPSS, MS2, and SCAN) again MS2 showed the best overall performance.

Future improvements of the present database include replacing estimates of barrier heights from ad-hoc SE procedures with SRP-DFT values, adding data for the underrepresented N₂-metal systems, and extending the databases with systems for which (WF-EA) is less than 7 eV. Chemically accurate barriers for the latter category of systems do not yet exist, and obtaining them may require a fundamentally different approach than the SE SRP-DFT approach forming the basis of the present database. Adding such systems should be important because they include systems relevant to sustainable chemistry (e.g., oxygen containing molecules like water and methanol), and because conclusions regarding the performance of DFs for the more general database also including such systems might be different from the present conclusions. In spite of the

present limitations of the database we hope that the new database finds its way into benchmark tests of new and already existing DFs, as it is rather odd that such tests do not yet include the type of reactions that arguably is most important for producing chemicals.

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