Inclusion of Dispersion Effects in Density Functional Theory
Development and Application

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Inclusion of Dispersion Effects in Density Functional Theory: Development and Application

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Abstract

In this thesis, applications and development will be presented within the field of van der Waals interactions in density functional theory. The thesis is based on the three projects: i) van der Waals interactions effect on the structure of liquid water at ambient conditions, ii) development and benchmarking of a new van der Waals density functional, and iii) the application of the newly developed functional to CO desorption from Ru(0001).

The effect of van der Waals interactions in water was studied by performing \emph{ab initio} molecular dynamics simulations using PBE and the two recent van der Waals density functionals optPBE-vdW and vdW-DF2 with identical computational setup. The two van der Waals functionals have been found to give excellent descriptions of the constituents of water (e.g., water dimers and hexamers). Including van der Waals interactions gives a softer water structure as seen from structural parameters and a distribution of water networks with fewer H-bonds for the van der Waals molecular dynamics simulations compared to the PBE results. The most significant change for the van der Waals molecular dynamics simulations is the oxygen-oxygen pair-correlation function, which has a much lower first peak consistent with recent experiments, while the outer structure is completely smeared out. The water structures obtained from the \emph{ab initio} van der Waals simulations clearly resemble high-density liquid water, whereas the PBE molecular dynamics simulation with equivalent computational setup resembles low-density liquid. Mixing the vdW-DF2 and the experimental low-density liquid in a 70/30\% ratio gives agreement with experimental results. This is consistent with the bimodal picture of water.

Also, in this thesis the BEEF-vdW exchange-correlation functional is presented based on fitting to high-level \emph{ab initio} and experimental results. The fitting scheme, based on Bayesian theory, focuses on the three aspects: a) model space, b) datasets, and c) model selection. The model space consists of a flexible expansion of the exchange enhancement factor in the generalized gradient approximation plus local density approximation, and the non-local Rutgers-Chalmers correlations. The datasets are chosen to represent gas phase chemistry, surface chemistry, solid state physics, and non-covalently bound systems in order to produce a generally applicable functional that is particularly useful for catalysis. The model selection is a two-step scheme. First the model is fitted to the individual datasets, and subsequently the combined solution are
found. To avoid overfitting, a regularization term is added to the cost function, which punishes non-smooth functions and effectively reduces the 31 parameters to close to 7. The ideal weights for the combined solution are found by minimizing the product of relative cost functions. Error estimation is naturally obtained from a distribution of functionals around the optimum solution. The produced exchange-correlation functional is benchmarked against various other exchange-correlation functionals, and is seen to indeed be generally applicable, contrary to other fitted van der Waals functionals.

Lastly, the newly developed BEEF-van der Waals functional is applied to the desorption of CO from Ru(0001). The results here support and help interpret the very first spectroscopic measurement of a precursor state performed as a pump-probe experiment at the Linac Coherent Light Source at Stanford Linear Accelerator Center. The support from the theoretical point of view is based on the potential of mean force, which is a free energy potential curve where all degrees of freedom except the reaction coordinate have been thermally averaged. The potential of mean force develops an adsorption/desorption barrier for increasing temperatures and a second minimum occurs at larger surface separations. A correct description of both the chemical interaction and the long-range van der Waals interactions is essential to describe the adsorption/desorption process and commonly used generalized gradient approximation functionals are seen to be incapable of this.
Resume

I denne afhandling præsenteres anvendelser og udvikling inden for van der Waals interaktioner i tæthedsfunktionalteori. Afhandlingen er baseret på tre projekter: i) van der Waals interaktioners’ indflydelse på strukturen af flydende vand ved standard betingelser, ii) udvikling og benchmarking af et nyt van der Waals funktional og iii) anvendelse af det nyudviklede funktional til CO desorption fra Ru(0001).

van der Waals vekselvirkningers effekt på vands struktur er undersøgt ved at udføre ab initio molekylære simuleringer med PBE funktionalalet samt to nye van der Waals funktionaler (optPBE-vdw og vdw-DF2) alle med identisk beregningsmæssige setup. De to van der Waals funktionaler gav fremragende beskrivelser af vands strukturelementer (f.eks vand dimerer og hexamere). I forhold til PBE resultaterne viste van der Waals simuleringerne en blødere vandstruktur, hvilket sås fra strukturelle parametre samt flere vandmolekyler med færre hydrogen bindinger. Den vigtigste ændring, beskrevet ved van der Waals simuleringerne, er oxygen-oxygen par-korrelationsfunktionen. Denne viste en betydeligt lavere første top, i overensstemmelse med nylige eksperimentelle forsøg, mens den ydre struktur er helt tværet ud. Vandstrukturerne, fundet ved ab initio van der Waals simuleringer, ligner høj-densitet flydende vand, hvorimod PBE simuleringer ligner lav-densitets vand. En kombination af 70% vdw-DF2 og 30% eksperimental lav-densitet væske giver overensstemmelse med eksperimentelle resultater ved standard betingelser for vand. Dette er konsistent med det bimodale billede af vand.


Preface and Acknowledgements

This dissertation is submitted in candidacy for a PhD degree in Physics from the Technical University of Denmark, DTU. The presented research was carried out from July 2009 to June 2012. The research was partitioned in two almost equal periods of time at the Center for Atomic-scale Materials Design (CAMD), at the department of Physics from July 2009 to 2010, and subsequently from November 2010 to 2012 at the SUNCAT Center for Interface Science and Catalysis at Stanford Linear Accelerator Center (SLAC).

I have had the pleasure both at CAMD and SLAC to be in groups containing more than 15 nationalities all sharing a passion for science. Both groups consisted of people with different scientific backgrounds and at different places in their scientific carriers, which gave a symbiotic effect and a great culture of helping each other. I cannot emphasize enough the benefits of having a flourishing scientific environment. One of the elements I particularly enjoyed was the close collaboration with experimentalists at SLAC. Even though theoreticians are from Mars and experimentalists are from Venus, when these two groups of people manage to communicate clearly with each other, the relevance and focus of their combined work more than doubles. I was privileged to be part of that.

The work presented here was performed under the competent supervision of Professors Jens K. Nørskov and Karsten W. Jacobsen. During the PhD process both were very ambitions when choosing projects and working within them. Unlike in the Garden of Eden, low hanging fruit was off-limits, which as a PhD student is fascinating, inspiring and slightly scary. In retrospect, I think it is commendable, and I wish that more scientists had this point of view. The approaches of my two supervisors complemented each other perfectly, one was goal-oriented, whereas the other was more stringent and focused on details. Both properties are required for a successful PhD project.

A dissertation is written by one person; however, the corresponding research is normally performed in collaboration with several people. I have to thank numerous people for supporting me, giving me feedback, and excellent scientific discussions:

• Dr. André Kelkkanen for passionate discussions on water and soccer
games, and professor Lars Pettersson for excellent suggestions for the water chapter and healthy fruitful debates on the structure of liquid water.


- Dr. Thomas Bligaard for taking the time to discuss the basics of fitting theory and density functional theory. Professor Karsten W. Jacobson for excellent supervising and challenging scientific discussions. Professor Jens K. Nørskov for excellent supervising and giving me the opportunity to work at the edge of the scientific research frontier at Stanford.

- The secretaries at CAMD and SUNCAT, Helle Wellejus and Marianne Ærsøe, for everyday logistic and practical help. The fact that your work often goes unnoticed only illustrates how well you do it. Your time and help has been essential and is highly appreciated.

- Most of all my wife Dr. Kiki L. Larsen for correcting my English grammar and supporting me through adversity.
List of Included Publications

Paper 1

vdW interactions in simulations of water Ab initio van der Waals interactions in simulations of water alter structure from mainly tetrahedral to high-density-like


Paper 2

Density functionals for surface science: Exchange–correlation model development with Bayesian error estimation


submitted *Phys. Rev. B*

Paper 3

Real-Time Observation of Surface Bond Breaking with an X-ray Laser


submitted *Science*
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Part I

Intro
Chapter 1

Introduction

As the available computer power for scientific computing has increased over the last couple of decades, so has the focus on understanding fundamental science on the atomic level from a theoretical point of view. The challenge in describing quantum mechanical systems lies in solving the electronic Schrödinger equation [1]. The fact that the equation was derived in 1933 and almost a hundred years later, scientist still struggle with getting accurate approximative solutions in solid state physics, surface science, quantum chemistry and molecular biology emphasizes the complexity of the task.

The difficult part of solving the electronic Schrödinger equation is the correct description of the electron-electron interaction, i.e., correlation and exchange. An early simple approach to solve electronic structure problems was density functional theory (DFT) [2, 3], where the energy is a functional of the density instead of the wave function. This is an immense simplification since the density is only a function of the three spatial directions, whereas the wave function depends on the coordinates of each electron. Initially the approach was too crude [2]. Nevertheless, in 1965 Kohn and Sham partitioned the challenge of solving the Schrödinger equation in a very clever way within the framework of DFT [4]. In the Kohn-Sham (KS) method, as much as possible is solved simply and exactly and a small residual term, the exchange-correlation (XC) functional, has to be approximated. The XC functional corrects for the fact that electrons interact with each other. The approach is cost-efficient considering the accuracy obtained [5].

Several levels of approximations for the XC functional exist and they can be classified using "Jacob’s ladder" [6], where each step up the stairways includes an additional model term in the approximation leading towards the "chemical accuracy heaven". In ascending order of complexity the functionals on the rungs depend on the: I) local density, II) gradient of the density, III) Laplacian of the density, IV) exact exchange, and V) unoccupied orbitals. One of the major drawbacks of DFT is that there is no systematic approach for developing XC functionals nor a way to a priori know how accurate a method is. This means that an XC functional on a lower rung can be better than an XC functional on
a higher rung for a particular system and property. Secondly, before testing, the accuracy of an XC functional remains unknown. Therefore, benchmarking of DFT methods and development of error estimation are essential.

In general, XC functionals are either developed using empiricism [7, 8, 9, 10, 11] or reductionism [12, 13, 14, 15]. The latter is based on mathematical modeling of an approximative XC functional fulfilling as many constraints as possible which are known to be valid for the exact solution. The empirical approach, on the other hand, is based on fitting a functional model to experimental or high accuracy \textit{ab initio} results. When fitting very complex XC models, overfitting to the training data becomes a central issue [6, 16, 17]. If care is not taken, a very flexible model can be fitted extremely well to the training data; however, it might have zero transferability to other systems and properties. By introducing a regularization in the cost function, part of the model space can be made inaccessible and a very flexible model can be controlled [18].

Becke introduced the concept of molecular training or fitting XC functionals, and thereby obtained significantly improved accuracy than previously observed in DFT [5]. This work later lead to the development of the most popular XC functional in quantum chemistry, B3LYP [9]. Other functionals such as revPBE [19] and RPBE [7] show that atomic total energies can be reproduced 10 times more accurately than their non-empirical predecessor PBE [13]. Early on Becke stated that using least squares fit and a polynomial expansions of orders above four of GGA exchange and correlation gave increasingly oscillatory and unphysical XC functionals [16]. Nonetheless, several XC functionals have been optimized with little attention to overfitting [20, 8, 21]. Among the most pragmatic approaches for empirical development of XC functionals using many parameters and large amounts of data are the HTCH series [22, 23, 8] of XC functionals and the extensive functional development by Truhlar et al. [24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34].

The exact XC functional obviously contains all the physical interactions not included in the non-interacting Kohn-Sham (KS) system, \textit{e.g.}, the self-interaction error, exchange, local correlation, and van der Waals (vdW) interactions. vdW interactions stems from quantum mechanical spontaneous fluctuating charge in one part of space, which induces an opposite dipole moment in another part of space. The attractive long-range interactions of these dipole moments lower the total energy. The interaction is especially important for sparse matter systems, \textit{e.g.}, liquids, polymers, DNA, protein folding, and graphene [35].

The most simplistic approach of including the interaction is the $R^{12} - R^{-6}$ Lennard-Jones potential [36]. This is still being applied for large scale calculations; however, the mathematic model is insufficient especially when bond breaking and formation occur.

Until recently, DFT has been largely unsuccessful in describing systems where vdW interactions are essential because the description of the interaction has been absent in the XC functionals. In the last decade, however, the development within the field has flourished. Based on the adiabatic-connection
fluctuation-dissipation (ACFD) theorem [37] several approximative ways of including vdW interactions in DFT have been proposed. One of the most accurate methods currently available in DFT is the fully non-local random phase approximation (RPA) [38, 39, 40]. Since RPA depends on unoccupied orbitals, it is only computationally feasible to perform calculations non-selfconsistently, making both structural relaxations and large scale calculations unavailable. Nevertheless, the approach is excellent to benchmark less accurate methods.

The primary approach considered in this thesis is the vdW-DF method by Langreth et al. [14, 41] and derivatives thereof [10, 15, 42, 43, 44, 45]. These methods are also based on the ACFD; however, several more approximations have been enforced compared to RPA [40]. In the vdW-DF XC functionals, a GGA exchange functional is combined with the local density approximation for correlation and an additional non-local correlation term. The non-local term is calculated as a six dimensional integral over densities in two parts of space and an interaction kernel that depends on the density and its gradient.

In the last couple of years a number of XC flavors have been suggested based on the vdW-DF, where either the correlation and/or exchange have been altered [10, 15, 42, 43, 44, 45], improving the description of dispersion dominated, hydrogen-bonded (H-bonded), and vdW bonded systems [46, 15, 10]. The vdW-DF method is relatively inexpensive, considering that it opens the door to study systems previously inaccessible with DFT. Since the approach is fairly new several questions still remain unanswered. It is still unclear what the effect are of the several approximations used in the derivation of the non-local term in the vdW-DF functional [40, 47]. As mentioned, gauging the accuracy and usability of new XC functionals is empirical in nature, and since the vdW-DF flavors have only been developed recently, one open question is: "are the vdW-DF functionals generally applicable, or does the inclusion of vdW interactions deteriorate the description of systems that common DFT functionals predict accurately?". This question will be addressed in this thesis.

A simplistic approach in DFT to include vdW interactions is adding an empirical $C_6 R^{-6}$-correction term to the normal DFT calculation in what is known as DFT-D (dispersion) [48, 49, 50, 51, 52, 53, 54, 55]. To avoid the singularity at zero separation a damping function is used. Because of the empirical nature of the approach, transferability could be an issue. Furthermore, the correction is not density dependent, so if the density changes significantly from the non-local interaction, this will not be included in the model. Nonetheless, the DFT-D method has shown promising results for dispersion dominated systems [48, 49], and since it utilizes a correction term the approach will also describe systems with negligible vdW interactions well, as long as the underlying XC functional (to which the correction is added) performs well for the system. A great advantage of the approach is that it comes at no additional computational cost compared to the basic DFT calculation. To remedy the empirical nature of the approach, Tkatchenko and Scheffler have developed a non-empirical method for determining the $C_6$ coefficients and vdW radii from a mean-field ground-state electron density for molecules and solids [52, 53, 54, 55]. Nevertheless, the damping function parameter remains empirical.
An important example where a correct description of vdW interactions may be essential is liquid water. During the last decade there has been a great dispute concerning the structure of liquid water at ambient conditions [56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82]. The textbook picture of the structure of liquid water is a continuous network of broken tetrahedral structured water molecules. This view was challenged by Wernet et al. in an x-ray absorption measurement [56], where the structure of liquid water was found to look more like surface ice than bulk ice. This lead to an alternative model of water where the liquid fluctuates between two different structures: one which is symmetrical and tetrahedral, and one which is less coordinated and asymmetrical. It has been speculated that the two structures each have a minimum from either the potential energy or the entropy in the free energy [67, 70, 74, 83]. Other experimental approaches such as emission spectroscopy combined with x-ray Raman scattering and small angle x-ray scattering support the bimodal model for ambient water [70]. Nevertheless, other interpretations of the experimental data also exists [73, 72, 66, 57, 63, 75, 76, 77, 78, 84].

Molecular dynamics (MD) can sample the motion and structure of liquid water. Both classical potentials and ab initio (AI) MD simulations of water, evaluated using standard DFT XC functionals, are consistent with the original picture of water. Nevertheless, both simulation types tend to give overstructured results compared to recent x-ray experiments [85, 65, 69, 86, 87, 88]. Including isotropic vdW interactions may counter the directional H-bonds and produce softer potentials. AIMD water simulations using the vdW-DF and BLYP-D XC functionals both show this; however, the structure of the second solvation shell is completely smeared out. New flavors of vdW-DFs show great potential in describing weakly interacting systems including the correct energetic trend of the water hexamers [10, 15]. This has previously been a limitation in DFT. More studies of water with accurate vdW type methods may help to elucidate the complex nature of water and help settle the current dispute.

The usages of DFT are numerous; one example that illustrates the power of a cost-effective computational approach is screening studies of different catalysts [89]. Instead of having experimental investigations of the catalytic effect of metals or compounds by time consuming trial and error, simple DFT calculations can narrow down thousands of possible candidates to close to ten. This saves time and money on lab research. The approach hinges on reliable theoretical results, i.e., the XC functional. In catalysis, sometimes vdW interactions are as important as other chemical interactions. Therefore, to accurately describe the catalytic processes a generally applicable XC functional is required. Furthermore, an estimate of the accuracy of the method is highly desirable. In short, DFT is a powerful tool for basic understanding, screening, and, in general, acquiring knowledge about systems at the atomic level; however, the crux of the method is having an accurate XC functional that describes the relevant interactions which has been validated by thorough testing.
1.1 Scope

This thesis is based on three main research projects pertaining to vdW interactions in DFT: a) the influence of vdW interactions on the structure of ambient water, b) the development and testing of a new vdW XC functional, and c) an application of the newly developed XC functional to CO desorption from Ru(0001). Before the results are presented two method chapters are given. Below the scope of each chapter is outlined.

- Chapter 2 is a method chapter, which explains DFT, including the introduction of the electronic density as a basic variable, the general idea behind Kohn-Sham theory, and the various levels of approximations in DFT.

- Chapter 3 outlines various methods for including vdW interactions in DFT. The main focus of the chapter is the vdW-DF XC functional and derivatives thereof; however the semi-empirical C$_6$-correction method and RPA are also succinctly discussed.

- Chapter 4 focuses on the structure of water at ambient conditions. The background of the current dispute in the community is given, followed by an explanation of molecular dynamics simulations. Lastly, the results of \textit{ab initio} simulations using the vdW-DF2 and optPBE-vdW XC functionals are presented, which are consistent with the bimodal model of liquid water.

- Chapter 5 presents a new XC functional, BEEF-vdW, which is based on fitting a model space consisting of a flexible expansion of the exchange enhancement factor in the generalized gradient approximation, and the vdW-DF2 non-local, LDA and PBE correlations. The complex model space is controlled using regularization that punishes non-smoothness, and as a consequence several properties can be fitted simultaneously producing a generally applicable and transferable XC functional.

- Chapter 6 presents benchmarking results using various popular approximative XC methods, including the newly developed BEEF-vdW functional. The benchmarking results include a number of properties and systems representing gas phase chemistry, vdW interactions, surface chemistry and solid state physics.

- Chapter 7 applies the BEEF-vdW functional to the desorption of CO from Ru(0001). The free energy is estimated by sampling phase space with the functional, and the potential of mean force is calculated. This supports and helps to interpret the very first spectroscopic measurement of a precursor state in surface science.

- Chapter 8 suggests what future challenges could be investigated as direct consequence of the discoveries presented in the thesis.
• Chapter 9 gives a succinct summary of the results and conclusions from the thesis.
The challenge in atomic material design, quantum chemistry, molecular biology and many other scientific disciplines at the atomic level comes down to solving the electronic Schrödinger equation. DFT is a method for finding ground state solution for the equation. The theory has a long historical background [2], as it was already introduced in 1927 by Thomas and Fermi [3]. It was not until 1964 DFT evolved from model to theory, when Hohenberg and Kohn legitimized the electronic density as a basic variable [90]. Hohenberg and Kohn’s first theorem showed that the density completely determines all ground state properties. Their second theorem is a density analogous to the variational principle for wave functions.

Modern KS DFT is based on splitting up the problem in a clever way, solving as much as possible exactly, leaving a small residual term, called the XC functional, containing the challenging contributions. Although an exact solution in principle exists, the XC functional in practice has to be approximated. Theory development in DFT has, since the introduction of KS theory, primarily focused on the search for better and better approximations for the XC functional.

The possible usages of DFT are too numerous to all be mentioned here. The list includes condensed matter physics, molecular biology and calculations of spectra aiding experimentalists interpret their results. The increasing popularity of the method during the past two decades is illustrated in Fig. 2.1.

In this chapter, the Hohenberg-Kohn theorems will be proven and their implications explained, Kohn-Sham theory will be outlined, the local density and the generalized gradient approximations will be discussed, as will XC functionals in general with the introduction of "Jacob’s ladder". Lastly, plane wave implementation of DFT is described. The basic DFT theory in this chapter follows the book "Density-Functional Theory of Atoms and Molecules" by Parr and Yang [3], and the GPAW [91, 92, 93] description follows the notes by Rostgaard [94].
Figure 2.1: The number of search results, when using the keyword "DFT" on "Web of Science" as a function of year, illustrates the increase in popularity of the method.

2.1 The Density Functional Theory Framework

The energy of an $N$-electron molecular system within the non-relativistic Born-Oppenheimer approximation [95] can be obtained by solving the time-independent Schrödinger equation [1]

$$\left( -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} v(r_i) + \sum_{i<j}^{N} \frac{1}{|r_i - r_j|} \right) \Psi = E \Psi,$$

(2.1)

where $v(r_i)$ is the external potential due to the nuclear charges acting on electron $i$, $r_i$ denotes the position of electron $i$, $\Psi$ is the many-body electron wave function, and $E$ is the total electronic energy. The terms in Eq. (2.1) are from the left the: kinetic energy, electron-nuclear attraction and electron-electron repulsion. Exact analytical solutions for the electronic wave function obtained from the Schrödinger equation can only be obtained for one-electronic molecular systems like the $\text{H}_2^+$-ion. The exact solution for a general many-body system can, however, be represented from an infinite series of one-particle basis functions, from which all possible $N$-electron determinants can be generated. The wave function, which includes all possible $N$-determinants is referred to as the Full-Configuration-Interaction (FCI) wave function. Nevertheless, due to the large computational burden this is in practice only done for very small molecules. It is imperative to progress in the development of methods suitable for describing larger systems, such as semi-empirical approaches [96], linear scaling methods [96] and DFT [3], even with the exponential growth in the development of computers during the last decades.

For ground state properties DFT is a very cost-effective approach. The basic
variable in DFT is the number of electrons per unit volume in a state, known as the electron density, \( n(r) \). Expressed in terms of the wave function the density is given as

\[
n(r) = N \int \cdots \int |\Psi(r, r_2, \ldots, r_N)|^2 \, dr_2 \cdots dr_N.
\]  

(2.2)

Thus, \( n(r) \) is a non-negative simple function of three variables \( x, y \) and \( z \), normalized to the total number of electrons \( N \). Hohenberg and Kohn justified the use of the density as a variable and thereby laid the foundation of DFT with two theorems as proven next.

### 2.1.1 The Hohenberg-Kohn Theorems

The first Hohenberg-Kohn theorem \([90]\) legitimizes the electron density as a basic variable. It reads:

The external potential \((v(r))\) is determined, within a trivial additive constant, by the electron density \((n(r))\).

Since the electron density determines the number of electrons through normalization, it follows that it also determines all electronic ground state properties of the system. The proof of the theorem is surprisingly simple and only utilizes the minimum energy principle for ground state wave functions.

**Proof:** Consider the electron density \((n(r))\) for a non-degenerate ground state of a \( N \)-electron system (the theorem holds for the degenerate case as well). \( n(r) \) determines \( N \) by normalization. \( n(r) \) also determines \( v(r) \), and therefore all molecular properties. The proof uses a counterargument. Assume that there exist two potentials \((v_1 \text{ and } v_2)\) differing in more than a constant, and each giving rise to the same density \((n(r))\). Consequently, two different Hamiltonians exist \((\hat{H}_1 \text{ and } \hat{H}_2)\) whose ground state densities are the same although their corresponding normalized wave functions \((\Psi_1 \text{ and } \Psi_2)\) are different. Using \( \Psi_2 \) as a trial function for \( \hat{H}_1 \):

\[
E_1 < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle = E_2 + \int n(r)[v_1(r) - v_2(r)] \, dr,
\]

(2.3)

where the variational principle has been used. Here \( E_1 \) and \( E_2 \) are the ground state energies for \( \hat{H}_1 \) and \( \hat{H}_2 \), respectively. The energy, \( E_1 \), is strictly smaller than the expectation value since \( \Psi_1 \neq \Psi_2 \). Similarly, taking \( \Psi_1 \) as a trial function for \( \hat{H}_2 \):

\[
E_2 < \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle = \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle + \langle \Psi_1 | \hat{H}_2 - \hat{H}_1 | \Psi_1 \rangle = E_1 - \int n(r)[v_1(r) - v_2(r)] \, dr.
\]

(2.4)

Adding the inequalities in Eqs. (2.3) and (2.4), the following expression is obtained

\[
E_1 + E_2 < E_2 + E_1,
\]

(2.5)
which constitutes a contradiction. Hence, two potentials differing with more than a constant cannot give the same density for their ground states ■

From this it can be concluded that the density determines both $N$ and $v$, hence all properties of the ground state. For example, the kinetic energy ($T[n]$), the potential energy ($V[n]$), and the total energy ($E[n]$). The total energy can be written as

$$E[n] = T[n] + V_{ne}[n] + V_{ee}[n] = \int n(r)v(r)dr + F_{HK}[n], \quad (2.6)$$

where the Hohenberg-Kohn universal density functional has been introduced

$$F_{HK}[n] = T[n] + V_{ee}[n]. \quad (2.7)$$

In Eq. (2.6) $V_{ne}$ and $V_{ee}$ refers to the potential energies of the electron-nuclei attraction and electron-electron repulsion, respectively, while $T$ refers to the kinetic energy.

The second Hohenberg-Kohn theorem [90] is the density analog to the variational principle for wave functions. It states:

For the trial density ($\tilde{n}(r)$) such that $\tilde{n}(r) \geq 0$ and $\int \tilde{n}(r)dr = N$,

$$E_0 \leq E[\tilde{n}] \quad (2.8)$$

where $E[\tilde{n}]$ is the functional of Eq. (2.6).

Proof: The proof for the theorem uses the first Hohenberg-Kohn theorem, which ensures that $\tilde{n}$ determines its own potential ($\tilde{v}$), Hamiltonian ($\tilde{H}$), and wave function ($\tilde{\Psi}$). This can be used as the trial function for the problem of interest given the external potential $v$. That is,

$$\langle \tilde{\Psi}|\tilde{H}|\tilde{\Psi} \rangle = \int \tilde{n}(r)v(r)dr + F_{HK}[\tilde{n}] = E[\tilde{n}] \geq E[n], \quad (2.9)$$

where $n$ is the ground state density ■

Assuming differentiability of $E[n]$, the variational principle in Eq. (2.8) requires that the ground state density satisfy the stationary principle

$$\delta \left\{ E[n] - \mu \left[ \int n(r)dr - N \right] \right\} = 0, \quad (2.10)$$

giving the Euler-Lagrange equation [3]

$$\mu = \frac{\delta E[n]}{\delta n(r)} = v(r) + \frac{\delta F_{HK}[n]}{\delta n(r)}. \quad (2.11)$$
where $\mu$ is the Lagrange multiplier (also called the chemical potential) associated with the constraint that the density is normalized to $N$. If the exact functional $F_{HK}[n]$ was known Eq. (2.11) would be an exact equation for the ground state electron density. Once an explicit form (in practice approximate) for $F_{HK}[n]$ is obtained, the method can be applied to any system. As will be elucidated next Kohn and Sham made a very clever choice for $F_{HK}[n]$ opening the doors to a new and accurate way of solving quantum mechanical problems.

### 2.1.2 Kohn-Sham Theory

Kohn and Sham turned DFT into a practical tool for rigorous calculations by developing an indirect approach to the kinetic energy functional now known as the Kohn-Sham method [4]. They introduced the orbitals into the problem such that the kinetic energy can be computed simply and with good accuracy leaving a small residual correction that can be handled separately. This is done by introducing a fictitious non-interacting auxiliary reference system, in which there is no electron-electron repulsion term, and for which the ground state electron density is exactly $n$, the density of the “true” system. For the auxiliary system the kinetic energy and density is given by

\begin{equation}
T_s[n] = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle, \tag{2.12}
\end{equation}

\begin{equation}
n(r) = \sum_i \sum_s | \psi_i(r, s) |^2, \tag{2.13}
\end{equation}

respectively. Here the $\psi_i$’s are the $N$ lowest eigenstates. Although $T_s[n]$ is uniquely defined for any density, it is not the exact kinetic energy functional, $T[n]$. The essence of KS theory is setting up the problem in such a way that $T_s[n]$ is exactly the auxiliary system’s kinetic energy component. This will turn out to give us an independent particle model, which is still exact.

To produce the desired separation out of $T_s[n]$ as the kinetic energy component, Eq. (2.7) is rewritten as

\begin{equation}
F[n] = T_s[n] + J[n] + E_{xc}[n], \tag{2.14}
\end{equation}

where

\begin{equation}
E_{xc}[n] \equiv T[n] - T_s[n] + V_{ee}[n] - J[n]. \tag{2.15}
\end{equation}

$E_{xc}[n]$ defined above is called the exchange-correlation (XC) energy and contains the difference between $T$ and $T_s$ (presumably fairly small), and the difference between the classical and the non-classical part of the electron-electron repulsion. In Eq. (2.14), $J[n]$ is the Hartree energy due to the Coulomb repulsion of the electron density

\begin{equation}
J[n] = \int d\mathbf{r}d\mathbf{r}' n(r)n(r') \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \tag{2.16}
\end{equation}
The Euler equation in Eq. (2.11) now takes the form

\[ \mu = v^{\text{eff}}(r) + \frac{\delta T_s[n]}{\delta n(r)}, \]  

(2.17)

where the KS effective potential is defined as

\[ v^{\text{eff}}(r) = v(r) + \frac{\delta J[n]}{\delta n(r)} + \frac{\delta E_{\text{xc}}[n]}{\delta n(r)} = v(r) + \int \frac{n(r')}{|r-r'|} dr' + v_{\text{xc}}(r), \]  

(2.18)

and where the XC potential is given by

\[ v_{\text{xc}}(r) = \frac{\delta E_{\text{xc}}[n]}{\delta n(r)}. \]  

(2.19)

Solving Eq. (2.17), with the constraint that the density is normalized, is exactly the same as solving a system of non-interacting electrons moving in an external potential, \( v_s(r) = v^{\text{eff}}(r) \). Therefore, an analogous solution is found simply by solving the \( N \) one-electron eigenequations

\[ [-1/2 \nabla^2 + v^{\text{eff}}(r)] \psi_i = \epsilon_i \psi_i, \]  

(2.20)

and calculating the density using Eq. (2.13). Since \( v^{\text{eff}} \) depends on \( n(r) \) through Eqs. (2.18) and (2.19), Eqs. (2.20) and (2.13) have to be solved self-consistently. The self-consistent procedure is illustrated in the flow diagram in Fig. 2.2 [97]. Starting from an initial guess for \( n(r) \), \( v^{\text{eff}} \) is constructed using Eq. (2.18), from which a new \( n(r) \) is computed using Eqs. (2.20) and (2.13). When this iterative procedure has reached a given threshold the energy can be computed directly through Eq. (2.6) with \( F[n] \) given in Eq. (2.14). Usually the iterative scheme is repeated until both the energy and the density has reached a specified convergence criteria. Eqs. (2.18)-(2.20) and Eq. (2.13) are the celebrated KS equations. It should be mentioned that in spin-polarized density functional calculations the up and down densities are considered as separate variables. In this case the KS equations are developed analogously with spin-dependent KS potentials.

### 2.1.3 Exchange-Correlation Functionals

The genius of KS theory is setting up the calculations in such a way that the majority of the energy is calculated exactly leaving a small residual term, which in practice needs to be approximated. This is the essence of Eq. (2.14). If the exact XC functional was known, DFT would yield an exact solution to the Schrödinger equation as stated by the first Hohenberg-Kohn theorem. The XC functional is the cardinal point of DFT. Unfortunately, the theorem only proves the existence of the exact functional, it does not provide any explicit form of the functional nor a way to construct it. Therefore, since the introduction of
KS orbitals in the 1960’s, a lot of effort within development of DFT has focused on searching for various approximate XC functionals.

The XC functional corrects for the fact that electrons interact with each other. The Pauli exclusion principle [1] states that two fermions cannot occupy the same quantum mechanical state. In the case of molecules and atoms, it states that electrons with the same spin cannot be at same position in space. The exchange energy ($E_x[n]$) is the energy required to insure this antisymmetric behavior of the wave function associated with the Pauli exclusion principle.\footnote{that is, the many-body wave function must be antisymmetric under the permutation of any two electrons}

The correlation energy ($E_c[n]$) is the energy associated with the description of the electrons mutual repulsion beyond the classical Coulomb interaction. The motions of the electrons are correlated, induced by the instantaneous mutual repulsion. In the absence of this correlated motion an electron in the system would be traveling in a mean-field created by all the electrons of the system. The correlation energy also corrects for the self-interaction energy. This is a classical effect which guarantees that an electron does not interact with itself as is the case in Eq. (2.16). The exchange energy is the dominant term.

The Pauli exclusion principle and the Coulomb interaction reduces the probability of finding two electrons close to each other. This can be described by introducing the XC hole ($h_{xc}(r; r')$) describing the changes in electron density
from the exchange and correlation effects for an electron at the position \( r \) due to a neighboring electron at \( r' \). The XC energy in terms of the XC hole can be expressed as [98]

\[
E_{xc} = \int \text{d}r' \frac{n(r) h_{xc}(r; r')}{|r - r'|},
\]

(2.21)

where

\[
\int \text{d}r' h_{xc}(r; r') = -1.
\]

(2.22)

Eq. (2.22), that XC hole integrates to one missing electron, is known as a sum rule. This is a general condition for the exact XC functional. The exact XC functional is known to satisfy certain conditions such as size-consistency, coordinate scaling relations and the correct limiting value of the XC energy for constant density [98]. Non-empirical functionals can be constructed by mathematical modeling of XC functional using physical arguments to satisfy certain constraints and conditions, which are known to be correct for the exact functional. It should be expected that the more conditions a functional satisfies the more accurate it is. Empirical functionals, on the other hand, contain a number of parameters, which are determined by fitting the functional against a set of experimental and/or \( ab\) \( initio \) data. The empirical functional may not satisfy several of the exact known relations. Nevertheless, the functional often produces reliable results for the property for which it is fitted, especially, if the problem studied chemically resembles the data set used for the fitting. On the contrary, transferability to systems or properties very different from the fitted systems may be questionable. Transferability of semi-empirical XC functionals will be considered in great detail in Chapter 5.

**Approximate Functionals**

The simplest XC functional is the local density approximation (LDA) [4], where the XC energy at a given density is approximated with the XC energy of the uniform electron gas with the same density

\[
E_{xc}^{\text{LDA}}[n] = \int \text{d}r n(r) \epsilon_{xc}[n(r)],
\]

(2.23)

where \( \epsilon_{xc}[n(r)] \) is the XC energy per particle for a uniform electron gas of spin density \( n(r) \). Expressions for both high and low-density limits are known exactly, while intermediate values can be interpolated using quantum Monte-Carlo results. LDA assumes a slowly varying electron density. This local nature makes LDA a good approximation in a few specialized cases for which the density is nearly constant, e.g., simple free-electron like metals. LDA conserves the XC hole and error cancellation occurs when combining the exchange and correlation parts giving surprisingly successful results, even for systems where the crude approximation was not expected to work [99]. Nevertheless, this model cannot in general be used for studying gas phase molecules, since the electron density in this case is inhomogeneous.
The relative success and apparent deficiencies of LDA lead to the inclusion of gradients of the electron density in the gradient expansion approximation (GEA). Unfortunately, GEA does not fulfill a number of sum rules, which are automatically satisfied for LDA due to a spurious tail of the density. This is believed to be the reason that GEA actually worsens the results relative to LDA. This led to the development of the generalized gradient approximation [100] (GGA), which improves on GEA fulfilling exact known limits and properties such as Eq. (2.22). A GGA functional can generally be written as [98]

\[ E_{xc}^{\text{GGA}} = \int dr n(r) \epsilon_{xc}[n(r), \nabla n(r)]. \]  

(2.24)

Since the GGA functionals depend on both the electron density and change in the nearby electron density (the gradients) the method is often referred to as semi-local. Any GGA exchange energy may be written as

\[ E_{x}^{\text{GGA}}[n] = \int dr u_{xc}^{\text{unif}}[n(r)] F_{x}[n(r), \nabla n(r)], \]  

(2.25)

where \( F_{x} \) is the exchange enhancement factor. It expresses how much the exchange is enhanced over the LDA value. Most GGA XC functionals were developed in the late 1980s, and are still popular, since they provide good accuracy and are cost-effective. They are especially popular in solid state physics.

The XC functionals can be divided into five rungs along ”Jacob’s ladder” ascending towards the ”heavens of chemical accuracy” as illustrated in Fig. 2.3. In Perdew’s classification [6], XC functionals are grouped depending on which terms they contain:

1. The first rung is the previously discussed local density approximation. A spin-unrestricted version of LDA called local spin density approximation (LSDA) also exists.

2. Second rung on ”Jacob’s ladder” is the generalized gradient approximation XC functionals as detailed above. An example of a GGA functional is RPBE [7].

3. The third rung in Perdew’s classification is known as meta-GGA (MGGA), in which XC functionals contains information about the Laplacian of the electron density and/or the kinetic energy density of the the occupied KS orbitals. MGGA functionals depend on the orbitals, making the computational cost higher; however, it sometimes improves the accuracy. TPSS is a MGGA XC functional [101].

4. The fourth rung corresponds to hybrid DFT XC functionals (also called hyper-GGA), which contain a fraction of Hatree-Fock (HF) exchange energy [5]. Most hybrid functionals contain both HF and DFT exchange components. The exact fraction is usually determined by fitting. This type of functional is the
Figure 2.3: The five rungs on "Jacob's ladder" acceding towards "chemical heaven". $E_{XX}$ is exact exchange, $\tau$ is the kinetic energy, and $\psi_u$ is the unoccupied KS orbitals.

The most common used in quantum chemistry calculations using localized basis sets. Unfortunately, when using plane wave basis set for XC functionals including non-local HF exchange greatly increases the computational burden due to the numerical details of solving the KS equations. The extremely popular B3LYP [5, 102, 103, 9] is an example of a hybrid XC functional.

The fifth rung on "Jacob's ladder" is a random phase approximation (RPA) type method, which includes terms containing virtual KS orbitals. This allows the treatment of dispersion. The downside of this introduction is that the calculations become significantly more computationally expensive. The fifth generation is currently undergoing a lot of investigation. Application and development are still limited and further development of computational affordable fifth generation functionals are needed.

The vdW XC functionals will be described in the following chapter. The vdW type XC functionals have not been assigned a place on "Jacob's ladder": however, it is the authors opinion that both conceptually and computationally it belongs between rungs 3 and 4. It should be stressed that "Jacobs Ladder" is a way to classify the numerous XC functionals by model complexity, and systematic improvement does not occur when going up the ladder. Furthermore, the picture of a ladder is not the most ideal analog, since higher order functionals do not necessarily include lower order terms. For example, a hybrid does not necessarily depend on the Laplacian of the density. Table 2.1.3 illustrates a number of XC functionals and which terms are included in the functional form.
\[ \nabla n(r) \hat{\nabla}^2 n(r) \tau E_{XX} \psi_u E_{uu}^{nl} \text{ Fitted Reference(s)} \]

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<th>E_{XX}</th>
<th>\psi_u</th>
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Table 2.1: An overview of the XC functionals and the terms they depend on. \( E_{XX} \) is exact exchange, \( \tau \) is the kinetic energy, and \( \psi_u \) is the unoccupied KS orbitals.

### 2.2 DFT Implementation

#### 2.2.1 The Projector-Augmented Wave Method

In chemical reactions, that is, bond breaking and formation, the inner electrons close to the nuclei are less relevant and the process is dominated by the changes in the valence electrons. Since the majority of electrons are core electrons and the wave function displays numerically demanding rapid oscillations near the nuclei, it is a great advantage to approximate this region. Thereby, the computational power is applied where it is most important.

In the pseudopotential approach, the electronic density of the core is replaced by a smoothed density chosen to match various mathematical and physical properties. Based on all-electron calculations, the pseudo wave function and potential match the all-electron wave function and potential outside a chosen radius and are allowed to deviate inside. In this fashion, the core electrons of the isolated atoms are fixed when solids or molecules are formed. This is referred to as the frozen core approximation. This reduces the number of wave functions to be calculated, since the pseudopotential only needs to be computed once and stored for each atom leaving only the valence wave functions. The KS equations only need to be solved for the valence electrons.

In the PAW approach, a linear transformation \( \hat{T} = 1 + \sum_R \hat{T}_R \) from auxiliary smooth wave function to the true all-electron KS wave function is
performed, where only the region close to the nuclei is altered. The original wave function can then be decomposed into auxiliary wave functions, which are smooth everywhere, and rapid oscillating contributions, which only contribute in specific small areas of space. These different contributions can be treated individually facilitating computations. A simple picture of this partitioning is shown in Fig. 2.4. The all-electron KS wave function can be expressed as

$$\psi_n(r) = \tilde{\psi}_n(r) + \sum_a \sum_i \left( \phi_a^i(r) - \tilde{\phi}_a^i(r) \right) \langle \tilde{p}_a^i | \tilde{\psi}_n(r) \rangle,$$

(2.26)

where the partial waves $\phi_a^i(r)$, the smooth partial waves $\tilde{\phi}_a^i(r)$, and the smooth projector functions, $\tilde{p}_a^i | \tilde{\psi}_n(r) \rangle$ has been introduced. This changes the computations of energies, density etc.

In the PAW formalism the variational quantity is the smooth wave function $(\tilde{\psi}_n)$ which is obtained by solving the transformed KS equations [94]

$$\hat{\tilde{H}} \tilde{\psi}_n(r) = \epsilon_n \hat{\tilde{S}} \tilde{\psi}_n,$$

(2.27)

where the transformed Hamiltonian ($\hat{\tilde{H}} = \hat{T}^\dagger \hat{H} \hat{T}$) and the overlap operator ($\hat{\tilde{S}} = \hat{T}^\dagger \hat{T}$) have been introduced. The energy can be expressed as [97]

$$E_{\text{total}} = \hat{E}_{\text{total}} + E_{\text{total}}^1 + \hat{E}_{\text{total}}^1,$$

(2.28)

where $\hat{E}$ is the energy due to the smooth functions evaluated either in Fourier space or on a grid in real space, $E^1$ is the same energy evaluated only in the spheres and $E_{\text{total}}^1$ denotes the energy in the spheres with the full functions.

### 2.2.2 Real Space Grids

In GPAW a multi-grid systems is utilized, where a coarse grid is used for wave functions, while a finer grid (8 times higher grid point density) is used to determine the densities and potentials. Using a grid introduces a new parameter the grid spacing, which needs to be sufficiently fine (more grid points) to insure convergence of the property in question. Normally a grid spacing of around 0.16-0.18 Å is sufficient.
Chapter 3

van der Waals Interactions

Several interactions exist in molecular systems and solids. They generally have different strengths, even though the relative strength of the interactions are very system depend. For example, vdW interactions are negligible in some materials; however, for more sparse matter the interaction becomes relevant. Soft matter is all around us. Polymers, liquids, solids and interacting systems, such as adsorption, water overlayers and hydrogen storage, biostructures, like DNA, protein structure and protein folding are examples of systems, where a proper description of vdW interactions is essential [35]. For decades, vdW interactions was known to be one of DFT’s limitations, so studying such extremely interesting things as DNA or graphene with DFT was simply not an option. The vdW theory development within DFT has made great progress and several options of vdW XC functionals have been proposed [14, 15, 10, 42, 43, 44, 45]. In this chapter, a short explanation of the interactions occurring in molecular systems and solids are given for completeness. The chapter is meant to give a general overview of how vdW interactions can be incorporated in DFT with emphasis on the vdW-DF type XC functionals. The order of the method sections are chosen such that the methods increase in degree of approximation.

3.1 Molecular interactions

3.1.1 Covalent, Ionic and Hydrogen Bonds

Ionic bonds are electrostatic interaction between chemical species with opposite charge. Covalent bonds, on the other hand, are charge sharing between atoms. There is not a clear distinction between the two. There is a gradual move from one type of bond to the other depending on the difference in electron-negativity of the atoms present. These type of electrostatic interaction are by far the most dominant in most molecular systems.

The H-bond is conceptually very easy to understand. For example, in water H-bonds can be thought of as an intermolecular bond generated from electro-
static interaction between the partial plus charge in a hydrogen in one water molecule to a partially negative O in another molecule. Nevertheless, a strict definition of H-bonds is very difficult. Several geometrical definitions exist, each based on physical arguments; however, which one to use is still somewhat arbitrary, and therefore also slightly subjective. Furthermore, some charge transfer will be present in the bond, and it is therefore not clear whether or not vdW interactions should be included in the H-bond. H-bonds are essential not only in water, the interaction also keeps the DNA double helix together. H-bonds are typically weaker than covalent bonds and stronger than vdW interactions [35].

3.1.2 The Lennard-Jones Approximation

vdW interactions, also known as London dispersion interactions, are truly quantum mechanical phenomena, where fluctuating charge spontaneously introduces local dipoles and multipoles in a part of an atomic system. The spontaneously occurring dipole and multipole moments produces an electric field which induces new dipole and multipole moments in the surroundings, thereby correlating the motions of the electrons as illustrated in Fig. 3.1. This phenomenon gives rise to a long-range attractive vdW force. The net effect of this electromagnetic interaction is a lowering of the total energy of the system.

Using classical arguments the asymptotic behavior\(^1\) of the attractive potential can be written as [36]

\[
E_{\text{vdW}}^{\text{asympt}} = -\frac{A}{R^6},
\]

(3.1)

where \(A\) is an empirical constant and \(R\) is the separation between the dipole moments.

\(^1\)where the separations are so large that no overlapping of the wave functions occur and dipole-dipole interactions dominate
The attractive long-range vdW interactions is countered by the short-range repulsive Coulomb interaction, where particles of same charge repel each other. Historically, and still being applied, is a simple and crude mathematical model, where the interaction is considered pairwise from atoms (or selected molecular subgroups) in term of their mutual separation. Empirical forms of the local repulsion of the overlapping electron clouds include an exponential potential and a $R^{-12}$-model \[36\]. The actual form of the repulsive part of the potential is not immensely important, as long as it is very repulsive at short range, thereby dominating the singularity of the $R^{-6}$-term. The combined attractive and repulsive interaction are therefore often modeled using the Lennard-Jones (LJ) potential

$$V_{LJ}(r_i - r_j) = D_{12}^{ij} \frac{1}{|r_i - r_j|} - D_6^{ij} \frac{1}{|r_i - r_j|^6},$$

(3.2)

where $r_i$ is the position of atom $i$ and $D_{12}^{ij}$, $D_6^{ij}$ are positive empirical constants expressing the magnitude of the interaction of atom (or molecular subgroup) $i$ and $j$. This potential is often chosen for analytical simplicity. The parameters are determined at equilibrium, therefore the $D_6^{ij}$ constants does not reflect the asymptotic behavior, and the original physical justification is not valid. The LJ-potential should therefore mostly be considered a simple mathematical model. Since the model is fitted to experimental data, it is bound to give reliable results for the test systems. Nevertheless, the question of transferability to other systems arises. Furthermore, contributions beyond pair-wise interactions may be relevant for systems that are very anisotropic or polarizable \[40\]. In short, this simple scheme is insufficient and more accurate methods are needed.

3.1.3 The Random Phase Approximation

The random phase approximation (RPA) and the non-local term in the vdW-DF have their origin from the adiabatic-connection fluctuation-dissipation (ACFD) theorem \[37\]. The ACFD formula is an exact formal expression for the correlation energy in terms of the response function. Even though the ACFD expression is exact, it is purely formal, and it is not clear how the response function should be approximated. Different approaches have been developed, among them RPA and vdW-DF, where the latter is the crudest of the two. RPA originates from the 1950s many-body treatment for the uniform gas \[38, 39\] and was later introduced into DFT. Details about the various higher order methods for calculating vdW interactions (such as RPA) can be found in the excellent review paper by Dobson and Gould \[40\].

In the most common RPA approach the exchange is treated as exact exchange and the correlation as RPA in the EXX/RPA method \[47\]. This has the advantage that the self-interaction error cancels out with part of the exact exchange. RPA correlation is fully non-local and therefore capable of describing vdW interactions accurately. Since it is an orbital dependent functional RPA is considerably more computationally expensive than the various vdW-DFs and is in general performed non-selfconsistently in a post processing fashion, making
structure optimizations and AIMD simulations unattainable. The large computational cost also limits the method to smaller systems. Nevertheless, the accurate EXX/RPA method can be utilized to access the accuracy of less precise vdW methods. This can help elucidating deficiencies in the current vdW-DFs as performed in Ref. [47]. The RPA method is found on the fifth rung of "Jacob’s ladder" introduced in the Chapter 2.

3.2 vdW Exchange-Correlation Functionals

3.2.1 The Original van der Waals Density Functional

As mentioned, the vdW-DF method is also based on the ACFD theorem; however, it is derived using several more approximations than RPA [40]. Contrary to the exact XC functional, semi-local and local DFT currently per default does not contain non-local vdW interactions. A density functional containing vdW interactions was first developed for layer systems [41] and later for general geometries [14, 41]. In this subsection, the general geometry vdW-DF, where the vdW interactions are accounted for either perturbatively [14, 41] or self-consistently [110], will be described.

The most general expression for a vdW-DF functional is

$$E_{xc} = E_{c}^{\text{new}} + E_{x}^{\text{GGA}},$$

(3.3)

where $E_{x}^{\text{GGA}}$ is an appropriate chosen exchange functional and $E_{c}^{\text{new}}$ is a new correlation functional, which includes vdW effects. In the original general-geometry vdW-DF scheme, the XC functional takes the form [14]

$$E_{xc} = E_{c}^{\text{LDA}} + E_{x}^{\text{GGA}} + E_{c}^{\text{nl}},$$

(3.4)

where $E_{c}^{\text{LDA}}$ is LDA correlation energy and $E_{c}^{\text{nl}}$ is the non-local correlation energy. LDA correlation was chosen to avoid double counting of the non-local vdW interactions. Nevertheless, one of the strengths in LDA is the error cancellation between correlation and exchange, which may not be present when LDA is coupled with GGA exchange [98].

revPBE was used for the exchange part in the original vdW-DF, because, contrary to many GGA functionals, it does not give unphysical 'vdW' binding from exchange [111]. This conclusion was based in a comparison to HF exchange in a study of benzene dimers with a separation in the region 4-4.5 Å [14]. Nevertheless, the same conclusions may not be valid at smaller distances. Furthermore, to produce a valuable XC functional, error cancellation in the composition of exchange and correlation is important. An appropriate match between correlation and exchange functionals needs to be considered and choosing an exchange functional which produces results closest to HF exchange is not necessarily the best approach.

The non-local correlation contribution is smaller than the shorter-ranged local correlation and less sensitive to position. Therefore, it is treated with less
The non-local correlation energy in the vdW-DF is given by [14]

\[
E_{\text{nl}}^c = \frac{1}{2} \int \int n(\mathbf{r}_1) \varphi(q_1, q_2, r_{12}) n(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2,
\]

(3.5)

where \( r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \), \( q_1 \) and \( q_2 \) are values of the universal function \( q[n(\mathbf{r}), |\nabla n(\mathbf{r})|] \) evaluated at \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \), respectively. \( \varphi \) is the interaction kernel and technically only depends on two variables, \( d_1 = q_1 r_{12} \) and \( d_2 = q_2 r_{12} \); however, in practical calculations the three variables \( q_1, q_2 \) and \( r_{12} \) are used [112]. The interaction kernel is seen to indirectly depend on the density and its gradient. The form of the kernel is derived using the plasmon-pole model. Exact known relations are enforced in order to have the non-local term fulfill a) the correct \( R^{-6} \) asymptotic behavior and b) that the non-local term is strictly zero for systems with constant densities [14]. The approximations introduced to calculate the non-local term are described in Ref. [40]. The exact form of the interaction kernel can be seen in Ref. [14] and the details of the algorithm used to calculate the non-local term is described in Ref. [112]. In the limit of large systems the computational cost of the vdW interactions is equivalent to that of a standard GGA functional [112].

In the self-consistent version of the vdW-DF XC functional [110] oscillatory non-localities also occur in the XC potential in the KS equations [14]

\[
V_{\text{nl}}^c (r) = \frac{\delta E_{\text{nl}}^c[n]}{\delta n(r)}.
\]

(3.6)

Including the vdW self-consistently is obviously more complete and proper; however, the extensive computations are in some cases redundant. Comparison of the perturbation vdW scheme with the vdW-SCF method typically gives negligible difference [110, 113]. Nonetheless, vdW-SCF is required when performing such things as structure relaxations and molecular dynamics simulations.

### 3.2.2 Revised vdW Functionals

In recent years several new flavors of vdW XC functionals have been proposed illustrating the great interest in applying DFT to sparse systems, and also suggesting that there is still room for improvement in the current vdW XC functional approximations. An overview of the current vdW functionals and their revisions are given in Table 3.2.2.

The initial efforts for improving the vdW-DF type XC functionals focused on finding suitable exchange functionals. Klimes et al. [10] proposed two new vdW density functionals (optPBE-vdW and optB88-vdW) based on the original functionals of Dion et al. [14]; however, with re-optimized parameters in the exchange enhancement factors using the S22 dataset [46] for training. The optPBE-vdW functional shows promise for the description of dispersive and H-bonded systems as it obtained better-than-chemical-accuracy (typically defined as 1 kcal/mole) for the various configurations of water hexamers. Another exchange proposal to
the vdW-DF functional was made using the Cooper exchange functional, [42] here a reduction in short-range exchange repulsion was introduced. As shall be illustrated later, extreme care has to be taken when modifying the exchange part of an XC functional in order to improve the van der Waals-like bonding as varying, e.g., the exchange enhancement factor of a GGA functional drastically changes the performance of the functional for covalently bonded systems while only modifying the vdW interactions slightly.

Other attempts have aimed at optimizing the correlation part of the vdW XC functionals. The vdW-DF2 [15] for example, has a new parametrization of the interaction kernel for the non-local correlation and uses the PW86 [114] exchange instead of revPBE [19], as the PW86 was argued to give a more consistent agreement with HF [115]. Others have suggested that LDA correlation is not necessarily the best choice [116]. In the vdW-DF family the newly developed functionals VV09 [43, 44] and VV10 [45] simplify the expression of the vdW interactions making them less computationally expensive. VV09 and VV10 both have the right description in the asymptotic limit as the previously vdW-DFs; however, contrary to those functionals it also describes the short-range region adequately [43]. The VV10 method has been assessed on thermochemical data and performs very well [55].

### 3.3 Other Approaches to vdW DFT

#### 3.3.1 Dispersion Corrected Functionals

Two approaches have mainly been used to overcome the neglect of vdW interactions in DFT a) the fundamental development of vdW-DFs outlined above and b) the more pragmatic approach of introducing a damped correction term to account for the dispersion. Simple semi-empirical dispersion corrected XC functionals have been proposed, which include a damped \( C_6 \alpha R^{-6} \) dispersion term [48]. In DFT-D (dispersion) a correction to standard functionals is introduced

\[
E_{xc}^{DFT-vdW} = E_{KS-DFT} + E_{disp},
\]

<table>
<thead>
<tr>
<th>vdW functional</th>
<th>Revision</th>
<th>Reference(s)</th>
</tr>
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<tbody>
<tr>
<td>vdW-DF</td>
<td>the original functional</td>
<td>[14]</td>
</tr>
<tr>
<td>vdW-DF2</td>
<td>PW86 exchange and new non-local parametrization</td>
<td>[15]</td>
</tr>
<tr>
<td>optPBE-vdW</td>
<td>PBE-type exchange fitted functional</td>
<td>[10]</td>
</tr>
<tr>
<td>optB88-vdW</td>
<td>B88-type exchange fitted functional</td>
<td>[10]</td>
</tr>
<tr>
<td>C09-vdW</td>
<td>Cooper exchange</td>
<td>[42]</td>
</tr>
<tr>
<td>VV09</td>
<td>new parametrization of the non-local correlation</td>
<td>[43, 44]</td>
</tr>
<tr>
<td>VV10</td>
<td>new parametrization of the non-local correlation</td>
<td>[45]</td>
</tr>
</tbody>
</table>

Table 3.1: The various flavors of vdW density functionals and a description of how they are revised from the original format.
where $E^{GGA-\text{vdW}}_{xc}$ is the dispersion corrected functional, $E^{KS-DFT}_{xc}$ is the original XC functional and $E_{\text{disp}}$ is an empirical dispersion correction

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{atoms}}-1} \sum_{j=i+1}^{N_{\text{atoms}}} \frac{C_{6}^{ij}}{R_{ij}} f_{\text{damp}}(R_{ij}). \quad (3.8)$$

Here $N_{\text{atoms}}$ is the number of atoms in the system, $C_{6}^{ij}$ is the dispersion coefficient for the atom pair $ij$ with the interatomic distance $R_{ij}$, and $s_6$ is a global scaling factor which only depends on the functional used. A damping function is introduced to avoid singularities in the dispersion energy

$$f_{\text{damp}}(R_{ij}) = \frac{1}{1 + \exp(-d(R_{ij}/R_{r}) - 1)}, \quad (3.9)$$

where $R_r$ is the sum of the atomic vdW radii and $d$ is set to 20. The original functional $E^{KS-DFT}_{xc}$ in Eq. (3.7) is reparametrized in the scheme. These new types of dispersion including XC functionals show very promising results [48, 49] at an affordable cost. An interesting development in the DFT-D functional is that of Tkatchenko and Scheffler, who have developed a method for determining the $C_{6}$ coefficients and vdW radii from a mean-field ground-state electron density for molecules and solids [117]. This makes the method parameter-free and remedies somewhat to the empirical nature. DFT-D has been shown to perform well for non-covalent bounded systems [50, 51]. Particularly promising is the DFT-D3 method [52, 53, 54, 55]. The biggest drawback of the method is that the non-local part is, in general, not density dependent, which could be a problem if the density changes significantly.
Part II

Water
Chapter 4

The Structure of Liquid Water

It is so simple really, three small atoms combined to give the water molecule. Nevertheless, when water goes from gas to liquid phase intermolecular interactions become important. The partial charges of the hydrogens in one molecule are attracted by the partial charges in the oxygens of neighboring molecules giving what is referred to as hydrogen bonds (H-bonds). Furthermore, the isotropic vdw interaction may be a competing factor. The balancing of these two competing interactions makes bulk water a very complex material to study. The complexity is illustrated by the many anomalies of water, e.g., the density maximum at 4°C, the isothermal compressibility and heat capacity minima at 46°C and 35°C, respectively and, lastly, the fact that the microscopic structure of the most important and well-studied liquid in the world still is a matter of great debate [56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82]. As shall be elucidated in this chapter the very fundamental question: "What is the microscopic structure of water?" remains unresolved!

This chapter begins with background information about the controversies surrounding liquid water including the supercooled region, followed by a section explaining MD. After this a discussion of DFT’s description of liquid water is given. In the last sections, results from \textit{ab initio} simulations using the vdW density functionals, optPBE-vdW and vdW-DF2, are presented and interpreted to be consistent with the bimodal model of liquid water. The results are presented in Paper 1 [82].

4.1 Background

The textbook picture of liquid water at ambient conditions is a continuous distribution of distorted tetrahedral structures. Most molecular dynamics simulations gives this; however, at the same time producing over-structured O-O
and O-H pair-correlation functions (PCFs) compared to x-ray and neutron scattering experimental data [65, 69, 85]. On the other hand, it has been shown that diffraction data do not discriminate between differently H-bonded structure models [118, 65, 69], since it is possible to generate a more distorted tetrahedral structure model that is consistent with the diffraction data; however, equivalent agreement is also found for alternative asymmetrical and mixture models.

An alternative model for ambient water has been suggested based on x-ray absorption (XAS) [56, 119, 120, 121, 122, 123] and emission spectroscopy (XES) [124, 125, 126, 127] combined with x-ray Raman scattering (XRS) and small angle x-ray scattering (SAXS) data [70]. In this fluctuating bimodal liquid model a division into contributions from two classes of local instantaneous H-bonded structures is driven by incommensurate requirements of minimizing enthalpy and maximizing entropy [67, 70, 74, 83]. In the proposed picture the dominating class at ambient temperatures consists of a continuum of structures with some resemblance to high-pressure water [70]; however, with a further expanded first shell (more distorted H-bonds) and more disorder in the 2nd shell called high-density liquid (HDL). The second class corresponds to fluctuations, where regions of strongly tetrahedral structures similar to low-density liquid (LDL) appear in different sizes and shapes as the molecules attempt to form enthalpically favored tetrahedral H-bond structures. The competition between the two structures results in a mean length scale of ~1 nm. Naturally many sizes and shapes would appear [70]. Since these are fluctuations no strict boundaries between the two classes are expected. The attosecond (XRS, SAXS) to femtosecond (XES) time scales of the experimental probes are too fast for molecular motion to occur and the experimental data therefore correspond to a statistical sampling of instantaneous frozen local structures in the liquid. No experimental information on the time scale of such fluctuations is currently available [70]. Nevertheless, other opinions exist regarding the interpretation of the new SAXS, XES and XRS data [73, 72, 66, 57, 63, 75, 76, 77, 78, 84].

The disputes about liquid water extend all the way down to the supercooled regime. To fully grasp this, a rudimentary understanding of the various phases surrounding the supercooled region of water is necessary. An overview is displayed in the phase diagram shown in Fig. 4.1 a). The following discussion follows a review about supercooled water by Mishima and Stanley [128]. Supercooled water exists between 0 and -38°C. From -120 to -140°C ultraviscous water is present 1 and under specific conditions and below this temperature glassy water (also called amorphous ice) exists, both of which are metastable phases. These temperatures are all for 1 bar pressure. Even though glassy water is a solid, similar to liquid water, its structure is disordered. Polymorphism is known to exist for glassy water as high-density and low-density amorphous (HDA/LDA) ice has been observed (see Ref. [128] and references therein). HDA resembles liquid water under high pressure. Furthermore, very-high-density amorphous ice (VHDA) was discovered in 1996 by Mishima [129]. The elucidation of supercooled water is further complicated by the fact that below -38°C

1 needs to be rapidly cooled otherwise ice is present
(at 1 bar) water freezes spontaneously, making it inaccessible from experiments. This region is therefore known as "no man’s land", and computer simulations of water are essential here. The connections from the liquid water phase to the glassy phase is as follows; small volumes of water can be supercooled to -38°C (metastable) below this temperature water unavoidably crystalizes on a millisecond timescale. This means that in order to get to the glassy regime the water has to be quenched past the "no man’s land" sufficiently rapidly to avoid crystallization.

Figure 4.1: a) A phase diagram of liquid water assuming the LLPT hypothesis [128]. C is the critical point for the gas phase and C’ is the proposed second critical point in supercooled liquid water. Between the dotted lines is "no man’s land", which is inaccessible to experiments. Below the second critical point liquid water supposedly separates into two phases LDL and HDL, while above a mixture exists. Two phases of glassy water are known to exist below the "no man’s land", LDA and HDA. b) An illustrative picture of how the proposed second critical point in the supercooled region of water may have consequences up into ambient conditions giving rise to structural fluctuations in this region.

The liquid-liquid phase-transition (LLPT) hypothesis stems from a MD simulation of supercooled water [130, 131, 132]. In this hypothesis a second critical point is proposed and estimated to be at $T_c' \approx 220K$, $P_c' \approx 100MPa$ and $\rho_c' \approx 1g/cm^3$. The point terminates the coexistence line of the high-density or low-density liquid phases, and only a single phase remains with properties dominated by either of the two phases, depending on which side of the Widom line the water is (at which pressure and temperature). The Widom line is defined as the line in the temperature-pressure diagram where the correlation length has its maximum and is an extension of the phase coexistence line. Above the second critical point water will fluctuate between the two phases. So when Wernet et al. proposed two structures to coexist at ambient conditions [56], this can be considered an extension of the LLPT hypothesis from the supercooled region.
to ambient conditions as illustrated in Fig. 4.1 b). The LLCP model explains the significant increase in density fluctuations upon supercooling water, which is evidenced by the anomalously increasing isothermal compressibility [133], as resulting from attempts to locally form enthalpically favored open tetrahedrally coordinated H-bond regions. It furthermore connects the deeply supercooled liquid state of water to the polyamorphism seen in ices, i.e., the LDA and HDA ice phases just described.

An illustrative simple picture for bimodal liquid water is a free energy curve with two minima, one shallow at short separation, and another narrow deep minimum at larger separation [128]. Water would on cooling be forced into the shallow minimum at short separations, if a sufficiently high pressure was present. Alternatively, water would obviously go to the deeper and narrow minimum at larger separation if nothing prevented it. At temperatures slightly higher than the critical temperature a fraction of the water molecules would have sufficient kinetic energy to go from one minimum to the other (fluctuate).

Since the second proposed critical point is in the “no man’s land” the LLPT is extremely hard to verify experimentally. Therefore, the only current experimental evidence is circumstantial. As water approaches the second critical point the isothermal compressibility and constant-pressure specific heat start to diverge. The aforementioned properties have a maximum when crossing the Widom line above the second critical point. The LLPT is consistent with water’s known properties; however, it is still a hypothesis. It should be stressed that several alternative models exist, i.e., singularity-free (SF) [131, 134], critical-point-free (CPF) [135] and stability limit (SL) conjecture [136] scenarios have been proposed; however, still building on structural HDL/LDL fluctuations. In this chapter the dispute about water at ambient conditions is investigated using molecular dynamics, which is introduced next.

4.2 Molecular dynamics

Molecular simulations are a great tool in materials science. Molecular simulations are basically a theoretical probe of atom movement in silico. In the quantitative characterization of water, computer simulations play a vital role not just in probing the “no man’s land”, but also at ambient conditions. This will be discussed further below, but first molecular simulations are explained.

By performing molecular simulations a fraction of phase space is explored. In general there are two main simulation methods: Monte Carlo (MC) [137] and molecular dynamics (MD) [137]. MC samples phase space through random moves. A probability factor (exp(−ΔE/RT)) is used if the move raises the energy. MD, on the other hand, is time based and produces a trajectory defined typically by classical mechanics. Phase space is sampled by having a sufficiently long trajectory, which is investigated by taking snapshots of the coordinates at different times. The two simulations should produce the same result for averaged
properties for large sampling as stated by the ergodic hypothesis [96]

\[ \langle X \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{0}^{\tau} X(t)dt = \lim_{M \to \infty} \frac{1}{M} \sum_{i=1}^{M} X_i, \quad (4.1) \]

where \( X \) is the property considered over the infinite time period \( \tau \) or number of samples \( M \). The ergodic hypothesis states that independent of the starting point, any point in phase space can be sampled. Properties are obtained by time averaging for MD simulations and by performing an ensemble average in the case of MC. Here only MD simulations are considered.

MD is based on Newton’s second law of motion \((F = ma)\). Initially starting coordinates and velocities need to be specified. At time step \( n \), given a set of particle coordinates \((r_n)\) the position a small time later \((\Delta t)\) can be found by performing a Taylor expansion [138]

\[ r_{n+1} = r_n + \frac{\partial r_n}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 r_n}{\partial t^2} (\Delta t)^2 + \frac{1}{6} \frac{\partial^3 r_n}{\partial t^3} (\Delta t)^3, \quad (4.2) \]

where the first, second and third derivative is the velocity \((v_n)\), acceleration \((a_n)\), and hyper acceleration \((b_n)\), respectively. Inserting \(-\Delta t\) in Eq. (4.2) the position a time step earlier is obtained

\[ r_{n-1} = r_n - \frac{\partial r_n}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 r_n}{\partial t^2} (\Delta t)^2 - \frac{1}{6} \frac{\partial^3 r_n}{\partial t^3} (\Delta t)^3. \quad (4.3) \]

Addition of Eqs. (4.2) and (4.3) yield a procedure for determining the position at time \( n + 1 \):

\[ r_{n+1} = (2r_n - r_{n-1}) + a_n(\Delta t), \quad (4.4) \]

\[ a_n = \frac{F_n}{m} = -\frac{1}{m} \frac{dV}{dr_n}, \quad (4.5) \]

where \( F_n \) is the force, \( V \) the potential energy and \( m \) is the mass. This is known as the Verlet algorithm [139]. Note that it is correct to the third order in \( \Delta t \), since the hyper acceleration cancels out. To solve Eq. (4.4) the derivative of the potential energy needs to be evaluated at each time step, which is computationally expensive. At the initial point the previous point is not available; however, this can be found by performing a first order approximation. The Verlet algorithm makes the assumption that the time step is so small that the velocity does not change. Having too large time steps will lead to systematical error (a drift in energy). The time step should in general be an order of magnitude smaller than the fastest process in the system. The numerical accuracy can be improved by using the velocity Verlet algorithm [140]

\[ r_{n+1} = r_n + v_n \Delta t + \frac{1}{2} a_n \Delta t^2, \quad (4.6) \]

\[ v_{n+1} = v_n + \frac{1}{2} (a_n + a_{n+1}) \Delta t. \quad (4.7) \]
The velocity Verlet algorithm preserves the particle number (N), the volume (V), and the energy (E), which is known as the micro-canonical ensemble. To change this into a NVT ensemble, the velocities can be scaled by a factor

$$\text{scale factor} = \sqrt{1 + \frac{\Delta t}{\tau} \left( \frac{T_{\text{desired}}}{T_{\text{actual}}} - 1 \right)}.$$ (4.8)

which follows from having an artificial heat bath connected to the ensemble [141]. Here $\tau$ is a coupling parameter, $T_{\text{desired}}$ and $T_{\text{actual}}$ are the desired temperature and the actual temperature, respectively. The actual temperature is calculated at each step from the kinetic energy. At each step the velocities are then scaled giving the NVT ensemble.

Empirical force fields are frequently applied in molecular mechanics; however, with a questionable transferability, since force fields are parameterized against experimental data or against a limited set of quantum chemically computed structures. Furthermore, in the case of water many-body interactions beyond pair-interactions are frequently not taken into account. These deficiencies are eliminated in Car-Parrinello [142] (CP) and Born-Oppenheimer (BO) MD, collectively known as ab initio (AI) MD. In AIMD, the forces are calculated using a first-principles electronic structure method, typically based on DFT. BOMD, used in the present study, minimizes the KS energy functional at each time step, keeping the nuclear positions frozen. Generally, when bond breaking and formation occurs classical simulations are insufficient and AIMD simulations are necessary. Here, AIMD simulations are performed using DFT. The following section argues why the recent optPBE-vdW and vdW-DF2 XC functionals are chosen to evaluate the forces in the AIMD study.

### 4.3 The Description of Liquid Water using DFT

#### 4.3.1 Water Clusters

There is no way to know a priori how well an XC functional describes specific chemical species or properties. It is therefore essential to benchmark the approximate XC functionals against highly accurate methods. Nevertheless, the scaling of the computational burden with the size of the system of these accurate methods limits their applications to small systems, in this case minor water clusters.

The two most commonly used XC functionals for AIMD simulations of water are PBE [13] and BLYP [143], which do not explicitly include vdW interactions. They have been applied to small water clusters and the results have been compared to high accuracy methods such as coupled cluster (CCSD(T)) and Møller-Plesset (MP2). PBE [144] gives near chemical accuracy for the strength of the H-bond in the water dimer, while BLYP consistently under-binds small water clusters [145]. Nevertheless, discrepancies arise and increase with the size
of the water cluster for both PBE and BLYP, which may be ascribed to the lack of a description of vdW forces [145]. It could be argued that obtaining the correct result for the water dimer is essential; however, this does not guarantee the correct description since not all physical interactions relevant for larger clusters are sampled by the dimer.

Two of the recently developed flavors of vdW-DFs, optPBE-vdW and vdW-DF2 (detailed in Chapter 3), show great promise describing the constituents of water. The optPBE-vdW XC functional uses the original vdW-DF [14] non-local term with a refitted exchange component. The functional shows promise in the description of dispersion and H-bonded systems as it reduces the under-binding given by the vdW-DF XC functional to chemical accuracy, while preserving the correct hexamer trends. Nevertheless, this improved behavior is obtained at the cost of poorer performance on the binding energy of small molecules [Paper 2]. A second version of the vdW-DF, called vdW-DF2, has been suggested [15], using a new non-local correlation functional along with a slightly refitted version of the PW86, called PW86R [115] as an appropriate exchange functional. This functional also gets the correct hexamer trends. Both functionals also describe the water dimer excellently as seen in Fig. 4.2 a), where the potential energy curve for the water dimer calculated using PBE, vdW-DF, vdW-DF2 and optPBE-vdW in comparison with the benchmark CCSD(T) curve from Ref. [146] is displayed. Fig. 4.2 a) shows that the vdW functionals are capable of describing this basic constituent of liquid water extremely accurately.

Plotted in Fig. 4.2 b) is the non-local contribution ($E_{nl}^{\text{c}}$) to the dimer binding from the two vdW XC functionals, which reveals that the accuracy of the vdW functionals is obtained for different reasons. The non-local part of the optPBE-vdW functional, which is based on the older approximation, is more attractive [15]. The total energy for the dimer is almost identical for vdW-DF2 and optPBE-vdW even though they have different non-local contributions; the residual of the interaction energy must therefore give a larger contribution for the vdW-DF2 than for optPBE-vdW. The remaining part of the interaction energy includes electrostatic interaction, electronic correlation, and repulsive exchange. Since electrostatic interactions only depend on separation, and local correlation is treated identically with the LDA correlation in both cases, this difference has to come from the different choices for the exchange. The PW86 exchange in vdW-DF2 is hence less repulsive than the optPBE exchange; a possible cause of the reported collapsed second-shell structure was in Ref. [147] suggested to be that the non-local parameterization of exchange used in vdW-DF and optPBE-vdW may be too attractive when used in MD simulations. Nevertheless, this is not the case, as seen from the PCFs, discussed shortly. First the effect of choosing different XC functionals for AIMD simulations of water is discussed.
Figure 4.2: a) The water dimer potential energy curves calculated using the XC functionals PBE, vdW-DF, vdW-DF2 and optPBE-vdW, respectively, are compared to CCSD(T)/CBS wave function results [146]. b) The distance dependence of the non-local contribution to the interaction energy of the water dimer for the XC functionals vdW-DF2 and optPBE-vdW.

4.3.2 Computer Simulations of Water

In nearly all force field and AIMD simulations of water at ambient conditions there seems to be a strong driving force to form highly directional H-bonds, leading to tetrahedral structures that are in general over-structured in terms of the derived PCFs. One exception is the coarse-grained mW water model [148], which has two terms in the interaction potential corresponding to anisotropic tetrahedral interactions and isotropic vdW interactions, respectively, and which gives a maximum peak height of 2.3 in the O-O PCF at room temperature, in close agreement with recent analyses of experimental diffraction results [85, 65, 69, 86, 87, 88]. This model was shown to feature fluctuations between tetrahedral and disordered species resulting in a liquid-liquid transition in the supercooled region [149]. Nevertheless, empirical force field models which have over-structured PCFs in agreement with older determinations [150, 151] have also been shown to exhibit liquid-liquid phase transitions in the supercooled regime [132, 152, 153, 154], indicating that the PCFs are not decisive for general trends in the thermodynamic behavior in water simulations. A recent study suggests that even in the ambient regime the force field model TIP4P [155] has underlying bimodal potential energy surface when investigating the local-structure index [79].

AIMD simulations of water have until recently almost exclusively been performed with the BLYP and PBE XC functionals. These functionals significantly over-structure liquid water [156], producing a too high and narrow first peak in the O-O PCF [85, 65, 86, 69, 87, 88]. The choice of XC functional has been shown to produce different predictions for AIMD simulations of water [157].

45
GGA based MD simulations tend to over-structure liquid water and lead to diffusion constants two to three times smaller than experiment; using hybrid functionals only marginally improves the results [158]. An example of the GGA simulation discrepancies to experiments is the fact that PBE-based AIMD simulations lead to a melting point of ice at 417 K [159]. Contrary, inclusion of vdW forces has been demonstrated to significantly lower the melting point where, e.g., the BLYP-D functional with empirical vdW forces was shown to lower the melting point from >400 K with the BLYP functional down to 360 K [160]. Influences of vdW interactions have been investigated using MD simulations based on empirical potentials [161, 162], e.g., performed with a dispersion-corrected BLYP XC functional [163], or using empirically damped C_6R^−6 corrections [164, 165, 166, 167] to describe the vdW interactions. A more recent AIMD with the more accurate BLYP-D3 [52] has also been performed [168]. A way to introduce vdW forces in DFT from first principles is provided by the vdW-DF [14] XC functional applied for the first time in AIMD on liquid water [147]. The inclusion of vdW forces using the vdW-DF was shown to greatly improve water’s equilibrium density and diffusivity. Nevertheless, the vdW-DF MD also produces a collapsed second coordination shell giving rise to new structural problems, that have been suggested to depend partially on the choice of exchange used in the vdW functional [147].

Most simple rare gas solids and liquids have a nearest-neighbor coordination of 12, whereas hexagonal ice has a coordination of only 4 due to the directional H-bonds. The latter leads to large open volumes in the ice lattice and a resulting low-density. The dispersion in condensed rare gases leads to isotropic interactions and closer packing. Similarly, the inclusion of vdW interactions in ab initio simulations of water may counteract the directional interactions and lead to better agreement with, e.g., experimental PCFs. This balancing act between the directional H-bond and the isotropic vdW interaction was expected to produce less over-structure and this, together with the excellent description of the constituents of water, motivated the AIMD simulations with optPBE-vdW and vdW-DF2 presented below. It should be emphasized that while agreement between theoretical and experimental PCFs could be regarded as a minimum requirement of a water model, it is by no means sufficient for a complete description.

4.4 Computational Protocol

optPBE-vdW, vdW-DF2, and PBE AIMD simulations have been performed in the NVE ensemble using the grid-based real-space projector augmented wave GPAW code [91, 92, 93]. A wave function grid spacing of 0.18 Å and Fermi smearing with a width of 0.01 eV have been used. In the electronic structure calculations a strict energy convergence criterion of 10^{-7} eV per electron is used in order to determine the forces adequately.

Angles are allowed to vary, (i.e., bending vibrations are included); however,
all internal bond lengths are kept fixed at 0.9572 Å (an MP2 optimized gas phase geometry) [169]; eliminating the high-frequency OH-stretch allows longer time steps in the simulations. Albeit this introduces some uncertainty [170] which is not relevant for the large differences observed in the presented simulation results between PBE and the vdW functionals since all simulations have this constraint imposed. 64 water molecules, in a cubic periodic box with side lengths 12.42 Å giving a density of 1 g/cm$^3$, have been optimized to obtain a configuration at zero Kelvin (using PBE). From this initial configuration the MD simulations were started giving the atoms random velocities according to a Maxwell-Boltzmann velocity distribution corresponding to two times 300 K while keeping the center of mass of the box stationary. Approximately half of the kinetic energy converts to potential energy thus giving an average temperature around 300 K. An initial equilibration of 10 ps using the PBE XC functional was performed followed by 2.5 ps vdW equilibration of the simulations using optPBE-vdW and vdW-DF2. For all methods equilibration was followed by production runs for 10 ps, which has been reported as the minimum time necessary due to the slow diffusion of water [171]. Using 64 water molecules has been shown to be adequate to remove the most significant problems concerning finite size effects [172] and is feasible within the current computational capabilities. The Verlet algorithm was employed using a time step of 2 fs in the NVE ensemble. Using this type of ensemble the temperature is allowed to fluctuate and the average temperature of the PBE, vdW-DF2 and optPBE-vdW simulations were 299 K, 283 K and 276 K, respectively. The same computational setup has been used for the PBE and vdW density functional MD simulations in order to allow direct comparison of the different models. Since simulations with PBE at ambient conditions describe a deeply supercooled state relative to its melting point at 417 K [159] the PBE simulations are only performed here to provide a reference for the effects of including vdW interactions through the optPBE-vdW and vdW-DF2 functionals.

4.5 van der Waals Simulations of Ambient Water

4.5.1 Pair-Correlation Functions

The AIMD simulations of liquid water using vdW-DF2 and optPBE-vdW give significantly similar O-O PCFs as illustrated in Fig. 4.3 a) [82]. Nevertheless, the vdW PCFs are very different from the O-O PCF from PBE and furthermore from those derived from experiment using either Empirical Potential Structure Refinement (EPSR) [85] or Reverse Monte Carlo (RMC) [173] to fit the structure factor [65, 69].

The O-O PCFs obtained with the vdW functionals result in the same characteristics as reported in a similar study with the vdW-DF XC functional [147] including a lower first peak shifted to larger O-O separation than for normal GGAs as well as for experiment on ambient water. The second coordination
shell at 4.5 Å is also completely smeared out, where correlations from the region 4.5-5 Å have instead moved into the region 3.3-3.7 Å. The non-local correlation differences in the functionals only affect the O-O PCFs slightly, producing a somewhat higher (2.5) first peak for vdW-DF2 compared to optPBE-vdW (2.3). Since the latter functional gives a slightly stronger non-local contribution this indicates that it is indeed the vdW contribution which strongly affects the first shell structure in the simulations.

On the contrary, by altering the exchange in vdW-DF from revPBE to PBE, the second shell structure again became well defined [147]. Nevertheless, the exchange functionals of revPBE and PBE are quite different, making an explanation in terms of the exchange less likely; also the potential energy curve of the dimer is not reproduced very well using the PBE exchange with LDA and non-local correlation suggesting that substituting revPBE by PBE for the exchange does not lead to consistent improvement in the description. Clearly, the O-O PCF obtained from PBE is severely over-structured, while the simulations including vdW forces have resulted in a significantly less structured PCF compared to what is experimentally observed for ambient liquid water. Neither simulation model gives direct agreement with the experimental O-O PCF even though, in the case of the vdW functionals, small water clusters are described very accurately. This will be addressed in Section 4.6.

![Figure 4.3](image_url)

Figure 4.3: a) Oxygen-oxygen PCFs ($g_{OO}$) obtained from experimental data using EPSR [85] and RMC [69] in comparison with PCFs obtained by DFT MD simulations using PBE, optPBE-vdW and vdW-DF2. b) Oxygen-hydrogen PCFs ($g_{OH}$) obtained from experimental data using EPSR [85] and RMC [69] in comparison with PCFs from PBE, optPBE-vdW and vdW-DF2.

As seen from Fig. 4.3 b) there is a significant difference in the first peak position in the O-H PCF between the EPSR [85] and RMC [69] fits compared to what is found for the O-O PCF. Nevertheless, the relatively lower sensitivity of the neutron data to specifically the O-H correlation in comparison to the sensitivity of x-ray data to the O-O correlation could explain this [69]. By
combining the EPSR [118, 69] and RMC techniques [174] information on the uncertainties and assumptions in the resulting fits can be acquired. Interestingly, the RMC method gives a shift in the first peak of the O-H correlation out to nearly 2 Å [69], which agrees well with the vdW MD simulations presented here. On the contrary, the EPSR solution is closer in position to the PBE, likely reflecting the SPC/E starting force-field in the EPSR fitting procedure. The RMC and EPSR fits both reproduce the experimental scattering data equally well, implying that the position of the first intermolecular OH correlation is not strictly determined by the data, which leaves an uncertainty in the diffraction-derived O-H PCF [175, 69]. The first peak in the PBE O-H PCF is clearly too high and the first minimum at 2.5 Å too low. All three simulations exaggerate the height of the second peak at 3.2 - 3.4 Å; however, by including quantum effects this is expected to be reduced [176].

4.5.2 Hydrogen Bonding Networks and Structural Parameters

Structures with less tetrahedral bonding are obtained with the vdW simulations as demonstrated by the average number of H-bonds per water molecule [82]; where the cone criterion from Ref. [56] has been applied as a geometric H-bond definition:

\[ r_{OO} < r_{OO}^{\text{max}} - 0.00044\delta_{HOO}. \] (4.9)

This defines a cone around each H-bond-donating OH group, where \( r_{OO}^{\text{max}} = 3.3 \) Å is the maximum O-O distance at zero angle \( \delta_{HOO} \), where \( \delta_{HOO} \) is the H-O-\( \cdot \cdot \cdot \)O angle quantifying the angular distortion of the H-bond. Fig. 4.4 shows the H-bond statistics for PBE, optPBE-vdW and vdW-DF2. PBE is seen to prefer a tetrahedral H-bond coordination with a majority of the molecules having 4 H-bonds. Including vdW interactions has a large effect illustrated by the fact that for both optPBE-vdW and vdW-DF2, the H-bond distribution shifts to a predominance of species with two or three. optPBE-vdW has a slightly larger amount of water molecules having two or three H-bonds compared to vdW-DF2, which can be ascribed to the relatively more repulsive exchange and stronger non-local contribution in the former, whereas the vdW-DF2 with its relatively weaker vdW interaction shows slightly higher preference towards forming H-bonds. This analysis suggests that there is a competition between isotropic vdW forces and directional H-bonds, resulting in fewer or more H-bonds per water molecule depending on the applied approximations. Nevertheless, between the vdW models the average number of H-bonds varies only weakly despite differences in vdW strength.

Two useful measures of the local coordination of molecules in water are the tetrahedrality [177, 178] and asphericity [179] parameters. The former quantifies the degree of tetrahedrality in the nearest neighbor O-O-O angles and is defined as

\[ Q = 1 - \frac{3}{8} \sum_{i=1}^{3} \sum_{j>i}^{4} (\cos \theta_{ij} + \frac{1}{3})^2, \] (4.10)
Figure 4.4: A bar chart showing the percentage distribution of hydrogen bonds per water molecule calculated using the cone criterion from Ref. [56].

where \( \theta_{ij0} \) is the angle formed by two neighboring oxygen atoms \( i \) and \( j \) and the central molecule 0. \( Q \) is a very local measure since only the four nearest neighbors are considered. Perfect hexagonal ice gives \( Q = 1 \) for all molecules while the ensemble average over an ideal gas gives \( \langle Q \rangle = 0 \) [178]. The asphericity parameter is defined as

\[
\eta = \frac{A^3}{36\pi V^2},
\]

where \( A \) and \( V \) are the area and volume of the Voronoi polyhedron of the molecule in question. Contrary to \( Q \), \( \eta \) is sensitive also to interstitial molecules outside the first shell and to the second coordination shell since these add surfaces to the Voronoi polyhedron making it more spherical. The two relevant limits for water are that of hexagonal ice, which gives \( \eta = 2.25 \), and that of a perfect sphere which gives \( \eta = 1 \); larger disorder in the local coordination thus gives smaller values of \( \eta \).

Not surprisingly including vdW interactions has a dramatic effect on both the tetrahedrality and asphericity distributions as Fig. 4.5 reveals. At \( Q = 0.8 \) a strong peak is observed for the PBE simulation [82], signifying a dominance of locally tetrahedral O-O-O angles, while both vdW simulations show an attenuation and shift of the high-\( Q \) peak to lower tetrahedrality along with the appearance of a strong low-\( Q \) peak associated with interstitial molecules at non-tetrahedral positions between the first and second coordination shells. optPBE-vdW is seen to be slightly less tetrahedral compared to vdW-DF2, consistent with their differences in H-bond statistics and PCFs discussed above. The average tetrahedrality is 0.692, 0.602 and 0.583 for PBE, vdW-DF2 and optPBE-vdW, respectively, which clearly illustrates this.

The effect of including non-local correlation is even more pronounced in the
4.6 Interpretation of Simulation Results

The promising accuracy of the vdW-DF2 and optPBE-vdW XC flavors when describing the water dimer, water hexamers [180] and the S22 dataset [10], opens the possibility that the interactions between molecules in the simulation box are given sufficiently accurately by the functionals, and that the discrepancy between simulated and experimentally observed O-O PCF is rather due to limitations and constraints in the simulation protocol. Here this possibility is explored and a possible interpretation is proposed [82].

Simulations using PBE lead to tetrahedral H-bond coordination and low-density, while the vdW simulations favor a more close-packed ordering and higher density, as evidenced by the loss of distinction between first and second coordination shells and the reduced number of H-bonds. Fixing the internal OH distances has been shown to lead to somewhat less structured PCFs in earlier work [170]. Nevertheless, since the simulations setup is identical for all AIMD simulations this cannot explain the large effects on the O-O PCF from including the vdW non-local correlation.

In Fig. 4.6 a) the PCFs from the vdW simulations are compared to the results of a neutron diffraction study [181] where LDL and HDL O-O PCFs
were extrapolated from data at different pressures; the resulting PCFs are shown below in Fig. 4.6 b). Several similarities between the EPSR derived HDL PCF and also the PCF obtained using a Fourier transform of x-ray diffraction data at high pressures [182] with that derived from vdW-DF2 and optPBE-vdW MD simulations is seen from the second- and third-shell structure: when increasing pressure the O-O PCF changes such that the 4.5 Å correlation disappears and moves to the 3.3-3.7 Å region and the third shell is shifted down to 6 Å [182]. Similarly, the O-O PCFs obtained using the vdW functionals show a lack of well defined structure at 4.5 Å, an increase in correlations at 3.3-3.7 Å and show a shift towards shorter separations in comparison to PBE of the correlation at 6-6.5 Å. Both are clear indications towards HDL water.

As opposed to the high pressure O-O PCFs, a well defined peak at 3.5 Å is not present in the vdW MD simulations, only an increase in correlations, and instead the first peak position is shifted outwards, contrary to pressurized water. It could be argued that a well-defined peak at 3.5 Å should not be expected for the more compact HDL-like structure from the vdW simulations since HDL-like water at ambient conditions should be thermally excited with a more expanded first shell and therefore further disordered in comparison to HDL water obtained under pressure [67, 70]. Entropy effects from thermal excitations giving a higher disorder should create a structure where both the first shell and, in particular, the collapsed second shell are distributed over a range of distances, giving molecules in interstitial positions and with the first O-O peak appearing at longer distance when not under pressure. In comparison, for the very high-density (VHDA) ice, the second shell moves inwards and a peak at 3.4 Å develops while for amorphous high-density (HDA) ice a peak is found at 3.7 Å and the second peak broadens significantly indicating that various interstitial sites may be occupied making the high-density forms less well-defined [183, 184, 185, 186, 187, 188]. Note that a peak at ~3.7 Å is present in the MD simulation performed by Wang et al. [147] using the earlier vdW-DF [14] formulation of the functional.

As previously stated the vdW simulations do not agree with the experimentally obtained O-O PCF directly. Nevertheless, assuming that the vdW models give HDL water, and assuming the proposed fluctuation model is correct, agreement might be obtained by adding a “missing” LDL contribution. Since the PBE simulated structure is far from its preferred density [147], the experimental LDL PCF from Soper and Ricci [181] is used. Weighting the vdW-DF2 O-O PCF with a model of LDL to a combined PCF and comparing with the PCF derived from experiment using EPSR [85] and RMC [69] agreement is achieved with a 70:30 mixture of vdW-DF2 HDL PCF and the experimentally derived LDL PCF [181] as seen from Fig. 4.7. This ratio is very close to estimations from XAS [56], XES [67, 70], and to an interpretation of infrared data in connection with analysis of a fractional Stokes-Einstein relation in water [189]. Note furthermore that quantum effects have not been included in the simulations, which is expected to bring down and broaden the first O-O correlation additionally [190, 176, 191]. When combining two separate PCFs, it is
important to consider cross-terms [84]. Nevertheless, since both the LDL and HDL local structures give a peak in the region of 2.7 - 3 Å and beyond that the HDL-like PCF is basically without structure, it seems likely that in this particular case, no extra features should be expected from cross contributions to a combined PCF.

Combining experimental LDL and vdW O-O PCFs to quite accurately reproduce the latest O-O PCF of ambient water is of course not a proof that "real water" is a combination of the two. The mixing of PCFs is of course not a long-term viable solution. The real question is: Why does the vdW simulation only show the appearance of HDL-like water and why is there no direct agreement with x-ray diffraction experiments? Nevertheless, the accuracy of the interaction potential obtained with the new vdW functionals indicates that other causes than the non-local interaction are a feasible option to account for the discrepancy between simulated and measured PCF. Furthermore, the large change of structure when including vdW interactions and the similarities to HDL structures is undeniable.

Having two balancing interactions that favor opposite structural properties is a prerequisite for fluctuations. Tuning the importance of H-bonding or the
vdW interaction will affect the preference for either structure in the simulations. A potential explanation could be that the simulation is performed in the NVE ensemble, disabling fluctuations of the density of the box to occur (fixed volume) and that this may penalize LDL to a greater extent than HDL, once the more isotropic vdW interactions are included. Using the NVE ensemble is equivalent to adding a pressure to maintain the box size, which would disfavor fluctuations to lower density assuming that the density at ambient conditions corresponds more closely to that of HDL. In order for spatially separated fluctuations between HDL and LDL to develop fully, it might be necessary to use much larger simulation boxes, in particular, if the fluctuations are of a mean length scale around 1 nm [70, 88]. There is furthermore some experimental evidence from thin water films on slightly hydrophobic surfaces that only an HDL related structure is observed even in the supercooled regime [192], indicating that if the system size becomes very small, indeed only one class of local structure is observed and the formation of LDL-like local regions is suppressed.

4.7 Summary and Conclusions of vdW Water Simulations

The recent vdW density functionals optPBE-vdW and vdW-DF2 show great promise in describing the basic structural constituents of liquid water, exemplified by benchmarking against water dimer and hexamers coupled cluster CCSD(T) results [180, 10, 15]. A softening of the structure of liquid water at ambient conditions is observed when including vdW interactions, consistent with previous work [163, 167, 147]. This is seen from the more disordered tetra-
hedrality and asphericity distributions, and from the much lower and broader first peak of the O-O PCF obtained from the optPBE-vdW and vdW-DF2 models compared to PBE [82]. The lower first peak of the O-O PCF improves the agreement with experiment significantly; however, the outer structure is washed out by the vdW forces. This has been suggested [147] to be related to non-local correlations; however, this study using functionals with different non-local correlation strength did not show any significant difference in the liquid structures, while both were found to be very accurate for the water dimer. On the contrary, the inclusion of the more isotropic vdW interaction shifts the balance over from directional H-bonding towards a more close-packed system, i.e., a competition between directional and isotropic interactions.

The vdW simulations are potentially consistent with a picture of fluctuations between two different water structures instantaneously coexisting in nanoscale patches. Albeit not directly observing fluctuations except in the sense of obtaining two alternative endpoints with vdW forces included (HDL) or excluded (LDL) [82]. The relatively small simulation only gives a picture of the local structure of water, and while PBE predominantly describes an approximation to low-density water, both optPBE-vdW and vdW-DF2, as well as vdW-DF [147], seem to possibly describe an approximation to high-density water. Comparing the O-O PCFs of the vdW models with PCFs extracted from x-ray [182] and neutron [181] diffraction of water at different pressures reveals a resemblance between the vdW models and high-density water in terms of effects on the second- and third-neighbor correlations; the expansion of the first coordination sphere found in the simulations may in experiments be counteracted by the pressure applied to experimentally generate pure HDL. The comparison to HDL is further supported by the reduction of the average number of H-bonds per molecule in the vdW MD simulations, which is a result of the isotropic vdW forces competing with the directional H-bond formation. Varying the strength of the exchange interaction does not result in a significant change in number of bonds once the vdW interaction is included. A 70:30 mixture of vdW-DF2 and the experimentally determined LDL PCF is compatible with the latest x-ray O-O PCF which does not constitute proof of a fluctuating real water structure; however, it indicates the possibility that averaging over a trajectory obeying less restrictive simulation conditions in terms of box size, length of trajectory etc. could result in an O-O PCF directly comparable with experiment [78, 84].

The main result of the simulations performed here is the significant change when including the vdW interactions and the resemblance of these results with the experimental high-density water. The mixing of LDL with vdW simulation structures opens for the possibility that other explanations than simply erroneous XC functionals might exist. The present work does by no means resolve the debate on water structure; however, it suggests the vdW non-local correlation for further investigation. The vdW interaction is a physically sound mechanism which affects the balance between directional H-bonding and higher packing and may thus indicate a way to reconcile the interpretation of recent x-ray spectroscopic data with structures obtained from AIMD simulations of liquid water. It is likely that much larger and longer simulations in the NPT ensemble
are needed to determine whether current vdW models support a temperature-
dependent balance of fluctuations between HDL and LDL-like structures in
ambient water, as suggested by recent x-ray spectroscopic and diffraction re-
sults [70, 83, 80], and which would be enhanced upon cooling, as they must
according to all scenarios for water at supercooled temperatures. From the
present work it is, however, clear that a consistent description of the vdW in-
teraction in AIMD simulations may possibly provide the key to tuning such a
balance.
Part III

Functional Development
Chapter 5

The Baysian Error Estimation Functional

Since the introduction of KS theory one of the main focus point for DFT development has been on the search for continuously improving approximations for the XC functional. As mentioned in Chapter 2, the development can be partitioned into two groups: reductionism and empiricism. Reductionism is understanding the nature of something complex by reducing it to the interactions it consists of. In DFT that is having terms that describe the fundamental physical interactions present at the atomic level, while obeying as many constraints as possible known to be valid for the exact functional. This is arguably the most idealistic and systematic approach, and it is the authors opinion that the biggest quantum leaps within XC development have been obtained using this approach. On the contrary, empiricism is an approach based on knowledge from previous experience. In the case of XC functional development that is the approach of fitting parameters to experimental and/or high-level ab initio results. Often a new term is developed by reductionists and subsequently used in a fitting scheme by empiricists. In either case, choices are inevitably made as to what kind of physics and chemistry that should be described well [11, 107].

Even though an exact functional in principle exists, it is likely so complicated and intractable that solving the Schrödinger equation using brute force might be as "easy a task" as finding and applying the exact functional. This study uses empiricism, and takes a very pragmatic approach with the purpose of obtaining the approximative XC functional that performs best on the properties of interest. The goal in the methodology presented here has been to make an honest and transparent approach that focuses on the two questions: How is the XC functional that performs best for a given XC model space obtained? And how can the inevitable choices be made explicit? The latter question refers to automating and controlling of what properties and chemical systems are described well.

A central issue in the development of empirical DF is overfitting to the
training data and transferability of the optimized DF to systems and material properties not contained in the training data [6, 16, 17]. For example, using polynomial expansions of orders above 4 of GGA exchange and correlation energies in a least squares fitting scheme have been shown to yield increasingly oscillatory and unphysical XC functionals [16]. Nonetheless, semi-empirical DFs containing many parameters have been constructed with little attention to overfitting issues [20, 8, 21]. Transferability of a DF parametrization depends not only on the degree of overfitting to a single set of molecular or condensed matter properties, but also on how many physically different properties the approximate model has been trained on. Optimizing an XC functional to several different properties naturally leads to a ”competition” between the datasets and a compromise has to be reached. This is often done implicitly by assigning weights to each dataset often based on experience [8, 21]. On the contrary, here regularization of a very flexible polynomial GGA exchange expansion is used from machine learning to ”tame” the XC functional and achieve transferability. The three pillars of empirical DF development are considered in detail: datasets, model space and model selection. The details concerning the datasets are given in Chapter 6.

In this chapter, the Bayesian Error Estimation Functional van der Waals (BEEF-vdW) functional will be presented based on Paper 2. The XC functional is based on a number of datasets from literature or assembled here representing gas phase chemistry, surface chemistry, solid state properties and vdW interactions. Using these datasets results in a general-purpose functional particularly useful for surface science and catalysis. The model space used to generate BEEF-vdW is GGA plus a non-local term, which is also applied in the vdW-DF2 functional [15]. The concept of overfitting is explained in the section 5.3 and the model selection developed in Paper 2 is presented. The model selection used here is a two-step process, where the model is first optimized to the individual training sets using machine learning techniques, and subsequently a compromise between the datasets is found. Error estimation is naturally derived for the BEEF-vdW functionals as an ensemble of functionals surrounding the ideal functional is easily obtained.

## 5.1 Other Empirical Functionals

The concept of molecular training or fitting XC functionals was introduced by Becke in the first study where exact exchange was included in an XC functional [5]. This study was the catalyst for several things in DFT: a) hybrid functionals, b) the concept of fitting XC functionals, and c) the prospect of (at the time) remarkable accuracy for quantum chemical systems, suggesting that DFT was a worthy alternative to other more computationally demanding wave function based methods. Fig. 2.1 in Chapter 2 shows the exponential growth of popularity in DFT, which was kickstarted in 1993 by Becke. If Kohn and Sham made DFT into a rigorous tool for calculations, Becke inspired scientist to use it by showing the possible accuracy. The fitting from Becke’s study, later led
to the most popular XC functional in quantum chemistry (B3LYP [9]) which is based on three parameters fitted using a least squares fit to heat of formations for small molecules.

Since the introduction of the very successful non-empirical GGA functional Perdew-Burke-Ernzerhof (PBE) [13] several empirical descendants have been proposed. By fitting a single parameter in the exchange enhancement factor using least squares fit the revPBE XC functional produces atomic total energies 10 times more accurately than PBE [19]. The RPBE XC functional uses the revPBE parameters; however, with a slightly altered functional form, which ensures that the Lieb-Oxford (LO) bound is respected globally [7]. Both RPBE and revPBE are widely used in catalysis. In the same family of functionals is PBEsol [11]. This functional was optimized for lattice properties by altering two parameters from PBE.

Recently several empirical vdW functionals have been presented [42, 10]. The C09-vdW XC functional was constructed using LDA and vdW-DF correlations and a three parameter functional for the exchange enhancement factor that were obtained by fitting to match the high density limit of the gradient expansion approximation for $s < 1.5$ and revPBE exchange for $8.0 < s < 10.0$ [42, 10]. As mentioned earlier, the optPBE-vdW and optB88-vdW have Rutgers-Chalmers and LDA correlations and refitted exchange parameters based on the PBE and B88 functionals forms, respectively, where the interaction energies of the dispersion dominated dimers in the S22 dataset has been used as target values [10]. All three functionals show excellent descriptions of the vdW dominated systems in the S22 dataset [42, 10].

All the above mentioned XC approximations are based on simple models, (i.e., few fitted parameters) and least squares fits. Since the model spaces for these functionals are simple, overfitting should not be expected. Nevertheless, the choice of which material properties and systems chosen as training data is very important in determining what the XC functionals describe well. Transferability to systems different from the training systems may be questionable, and the functionals can potentially be very specialized. Relevant questions are: Could a more complex model describe the systems more accurately? Are the XC functionals underfitted?

Pragmatic approaches for empirical development of XC functional have been performed using many parameters and large amounts of data [22, 23, 8, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34]. Some of these methods have been fitted with little concern with overfitting, and the choice of weight between various datasets containing different properties has been based on trial and error, and personal experience, as opposed to a general, automatic, and less political choice.

Among the functionals that are based on this pragmatic approach are the HTCH series [22, 23, 8]. The original HTCH functional [22] consists of correlation and an exchange enhancement factor expansion also used in the B97 XC functional [16]. The exchange coefficients are found by using the least squares fit method to the atomic energies, ionization potentials, total energies etc. for
the G2/97 dataset [193]. In the first HTCH XC functional the polynomial expansion was truncated at order four to avoid overfitting. New parameterizations of the HTCH functional have since been suggested, using many expansion coefficients (up to 15) to fit larger amount of molecular data with little attention to overfitting [23, 8].

The most extensive work within computational molecular datasets and fitting XC functionals has been done by Truhlar et al. [24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34]. In the last decade, Truhlar et al. have proposed close to 20 generally applicable XC functionals, most of which are on the 4'th rung of “Jacob's ladder” including both exact exchange and the Laplacian of the density, making them relatively computationally expensive. The datasets used in the fitting schemes are typically focussed on such properties as atomic energies, barrier heights, non-covalently bounded species etc.. Initially the Minnesota group only fitted a few parameters [33, 34]; however, more recently the number has grown to as many as 47 in the M08-Hx functional [27]. In the fitting scheme of the functionals several exact known constrains are often satisfied, and a cost function consisting of a sum of root mean signed errors of the properties in question is minimized without regularization, often using a generic algorithm [194]. Since the properties used in the fitting may have different numerical size, weights chosen from experience are used to get them on the same footing in the cost function. As shall be discussed shortly, the combination of a large number of parameters, and the absence of a regularization term can produce overfitted XC functionals. The M06 family of functionals have been reported to be problematic to evaluate in literature [195, 196, 197]. For example, the MGGA M06-L functional [30] has 34 parameters and was unsuccessfully attempted to be applied in the benchmarking study presented in Chapter 6. A more practical issue is that the vast amount of XC functionals produced by the Minnesota group and others can make it hard to navigate for non-experts in the field.

The concept of the functional development presented here resembles the Truhlar and HTCH molecular training approaches; however, it does have distinct and very important differences. Obviously the model space is different including a non-local vdW term. More importantly, the cost function for the BEEF-vdW XC functional contains a regularization term, which controls the model complexity. Furthermore, as shall be shown, the weights are determined in an automated and specific way minimizing the product of the cost function of the individual datasets, contrary to the more common way based on experience.

5.2 Datasets

When fitting a semi-empirical XC functional one of the most obvious and influential decisions made is the choice of training sets. The quality of the data of the target values, and which properties and chemical species are included is important to consider when choosing the training sets. Here the datasets used to train or assess the BEEF-vdW XC functional are chosen to represent gas phase
Table 5.1: An overview of the datasets used for the training and assessment of the BEEF-vdW XC functional. * refers to the datasets that was used to training the BEEF-vdW functional. In parenthesis the number of entries in the dataset are given.

<table>
<thead>
<tr>
<th>Dataset</th>
<th>Subset(s)</th>
<th>Describing</th>
<th>Quantity</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G3-2* (93)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G3-3 (75)</td>
<td></td>
<td></td>
<td>[199]</td>
</tr>
<tr>
<td>RE42* (42)</td>
<td>None</td>
<td>Gas Phase Reactions</td>
<td>Reaction Energy</td>
<td>Paper 2</td>
</tr>
<tr>
<td>DBH24/08* (24)</td>
<td>None</td>
<td>Gas Phase Barriers</td>
<td>Barrier Height</td>
<td>[200]</td>
</tr>
<tr>
<td>S22×5* (110)</td>
<td>S22×5-0.90 (22)</td>
<td></td>
<td>H-Bonds</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S22×5-1.0 (22)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S22×5-1.1 (22)</td>
<td>vdW Interactions</td>
<td>Interaction Energy</td>
<td>[46, 201, 202, 203]</td>
</tr>
<tr>
<td></td>
<td>S22×5-1.25 (22)</td>
<td>Dispersion</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S22×5-1.5 (22)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sol34Ec* (34)</td>
<td>None</td>
<td>Solid State Physics</td>
<td>Cohesive Energy</td>
<td>Paper 2</td>
</tr>
<tr>
<td>Sol27Ec (27)</td>
<td>None</td>
<td>Solid State Physics</td>
<td>Cohesive Energy</td>
<td>Paper 2</td>
</tr>
<tr>
<td>Sol27Lc* (27)</td>
<td>None</td>
<td>Solid State Physics</td>
<td>Lattice Parameter</td>
<td>Paper 2</td>
</tr>
<tr>
<td>CE27 (27)</td>
<td>CE17* (17)</td>
<td>Chemisorption</td>
<td>Adsorption Energy</td>
<td>Paper 2</td>
</tr>
</tbody>
</table>

An overview of the datasets considered is given in Table 5.1. The references reveal which datasets were compiled from the literature and created for this study and the * refers to which datasets are used as training for the fitting scheme (for more details see Chapter 6).

Figure 5.1: Simple models are too crude to be accurate and overly complex models will, if they are not controlled, overfit and have issues with transferability [204].

## 5.3 Overfitting and Bayesian Theory

The concept of overfitting versus underfitting is illustrated in Fig. 5.1. The higher the model complexity is, the better data points included in a fit can be
reproduced. For example, a polynomial of order \( N \) can fit any \( N \) data points perfectly, in the sense that the error on each data point is zero. Nevertheless, the fitted function is an abysmal model for any points not included in the fit. This is known as overfitting. In the other extreme, underfitting, the model is simply too crude to be an accurate model. The ideal model is somewhere in between these two extrema. Transferability is a models’ ability to predict data points that are not included in the training data. The least squares fit, where the individual errors to the data points are minimized, is not ideal when using a very flexible model, since it will lead to overfitting. Instead, the focus should be on minimizing the error to the data points not included in the training data.

A quantitative measure of quality of a model is the expected prediction error (EPE), which is defined as follows: If \( \mu_D \) is the best fit model to a dataset \( D \) and \( t(x) \) is the target function that generates the target values of the dataset, then EPE is defined as \([205, 206]\)

\[
\text{EPE}^2 = \langle \langle (\mu_D(x) - t(x))^2 \rangle_D \rangle_x. \tag{5.1}
\]

That is, the mean squared error of a model averaged over all the datasets \( D \) and all the input values \( x \). The concept of overfitting and underfitting can be understood as a competition between bias and variance. Bias is when the calculated results are systematically different from the property in question. This will be high for a simple model. Variance is a parameter which describes the distribution of numbers. Very complex models are very sensitive to the data to which they are fitted, and hence vary significantly with changing data (high variance). In terms of the bias and variance the EPE is given as

\[
\text{EPE}^2 = \text{bias}^2 + \text{variance} \tag{5.2}
\]

with

\[
\text{bias}^2 = \langle \langle (\bar{\mu}(x) - t(x))^2 \rangle_D \rangle_x, \tag{5.3}
\]

\[
\text{variance} = \langle \langle (\mu_D(x) - \bar{\mu}(x))^2 \rangle_D \rangle_x, \tag{5.4}
\]

where the average model \( \langle \bar{\mu}(x) = \langle \mu_D \rangle_D \rangle \) has been introduced. The ideal model complexity is therefore obtained as a compromise, where neither bias nor the variance are too large.

One way to control the model complexity is using Bayesian statistics \([207]\). In Bayesian statistics probability is a measure of plausibility. On the contrary, frequentist define plausibility based on the number of occurrences of the thing in question among other events \([208, 209]\). The probability of a model \( M \) given some data \( D \) can be obtained using Bayes’ theorem

\[
p(M|D) \propto p(D|M)p(M), \tag{5.5}
\]

where the posterior \( p(D|M) \) is the data given the model and the prior \( p(M) \) is the probability that the model \( M \) is good before the data is given. The quantities in Eq. (5.5) can be interpreted in the following way: \( p(M) \) is the probability
that the model $M$ is good a priori (for example, one could limit certain undesirable solutions from the very beginning); $p(D|M)$ is the probability that model $M$ generated the data $D$, given $M$ is a good model; $p(M|D)$ is the probability that $M$ is a good model, after all evidence has been considered. Bayes theorem thus expresses how to find a good model from data, expressed in terms of how well the data is reproduced by the model and what models are considered good initially before any knowledge of the data is used. $p(D|M)$ gives no information of the performance of the model $M$ beyond the data $D$. Therefore, a model $M$ that performs excellent on a dataset $D$ can still perform poorly for new data (overfitting). That leaves the prior $p(M)$ to avoid overfitting. The complexity of the model can be controlled by the introduction of a model complexity parameter $\omega$ in the prior $p(M|\omega)$, which makes some of the model space unlikely and hence inaccessible. There will be one $\omega$ that minimizes the EPE.\footnote{Note that the expected prediction error is a frequentist quantity} The model complexity parameter enters in the cost function through the regularization term as described below.

The cost function is the quantity which is minimized when fitting a function. A least squares fit is a cost function ($C(a)$) containing the sum of errors (target value minus calculated value) squared. To control the model complexity a positive regularization term ($R(a, \omega)$) is added to the least squares cost function

$$\tilde{C}(a) = C(a) + R(a, \omega).$$ (5.6)

By maximizing the information entropy it can be shown that the cost function relates to Bayes theorem \cite{210, 211} such that $p(M|D) \sim \exp(-C(a)/\tau)$ and $p(M) \sim \exp(-R(a, \omega)/\tau)$, where $\tau$ is the effective temperature defined in Eq. (5.26). Therefore, the regularization term is often called the prior. As mentioned earlier, $\omega$ is a strength parameter, which scales the regularization term. The regularization’s purpose is to control the model complexity by effectively reducing the model space by rendering some solutions unlikely (high cost). The choice of regularization decides which solutions are undesirable. A simple choice, for example, could be $\omega^2$, which would add a parabola (with the curvature $\omega^2$) in every direction, effectively removing some of the sloppy directions. The choice of regularization used here and how to find the ideal strength parameter is discussed in section 5.5.

### 5.4 Model Space

The majority of the XC energy is exchange and therefore a flexible description of this term is desirable. A highly flexible exchange model is obtained by expanding the GGA exchange enhancement factor in a basis of Legendre polynomials ($B_m(t(s))$) of order 0 to $M_x$ in a transformed reduced density gradient, denoted...
where $s$ is the reduced density gradient, $\varepsilon_{\text{UEG}}(n)$ is the uniform electron gas exchange energy, $a_m$ is the expansion coefficient, and $E_{\text{GGA-x}}^m$ is the exchange energy corresponding to the Legendre basis function $B_m$. The polynomial basis is constructed such that the boundary limits $t = [-1, 1]$ are zero for all $m > 1$ basis functions making these limits determined by the 0th and 1st order basis functions. The transformation is used since the Legendre polynomials are orthonormal in the region $t \in [-1, 1]$, and furthermore, has the advantage that the lower $s$-region, where most chemistry takes place, is sampled more densely.

The correlation model space has been chosen to be a linear combination of the PBE semi-local correlation functional, purely local Perdew–Wang [12] LDA correlation, and vdW-DF2 [15] type non-local correlation, which has been shown to produce accurate results for several of the interactions and systems considered [116].

The complete XC model space thus consists of GGA exchange expanded in Legendre polynomials, as well as local, semi-local, and non-local correlations:

$$E_{xc} = \sum_{m=0}^{M_x} a_mE_{m}^{\text{GGA-x}} + \alpha_c E^{\text{LDA-c}} + (1 - \alpha_c)E^{\text{PBE-c}} + E^{\text{nl-c}},$$

where $M_x = 30$, giving a total of 31 parameters. None of the commonly imposed constraints on GGA exchange are invoked, e.g., the LDA limit of $F_x(s)$, nor the LO bound [212, 213]; however, the sum of LDA and PBE correlation is constrained to unity.

### 5.5 Model Selection

Here a model selection scheme is presented that a) finds the optimal solution for the individual datasets, and thereafter uses the result to b) find a desired compromise between the solutions for the individual datasets in a combined fit.

#### 5.5.1 Individual Materials Properties

The best fit model for the $i$'th dataset is obtained by finding the expansion coefficient to the cost function defined using the standard Tikhonov regularization
method [18] to avoid overfitting

\[ C_i(a) = (X_i a - y_i)^2 + \omega^2 \Gamma^2 (a - a_p)^2, \quad (5.12) \]

\[ \Gamma^2_{ij} = \int_{-1}^{1} \frac{d^2 B_i(t)}{d t^2} \frac{d^2 B_j(t)}{d t^2} d t, \quad (5.13) \]

where \( X_i \) is a data matrix containing all XC contributions to each data point in the \( i \)'th dataset, \( a \) is the coefficient vector, \( y_i \) is a target vector containing XC contribution of training data, \( \omega \) is a regularization strength, the prior vector \( a_p \) is the origo for the length of the desired solution and \( \Gamma \) is denoted the Tikhonov matrix.

The Tikhonov matrix in Eq. (5.13) is defined from a smoothness criterion: the exchange part of \( \Gamma \) is the overlap of the second derivative of the exchange basis functions with respect to the transformed reduced density gradient, and the correlation part has ones in the diagonal and zeros in the off-diagonal elements. Since increasing orders of Legendre polynomials have increasing curvatures, the Tikhonov matrix effectively scales the regularization strength such that the higher-order basis functions are suppressed. This will give solution vectors with small coefficients for higher-order polynomials, and thereby a preference for smooth exchange enhancement factors. Requiring \( F(s) \) to be smooth is physically sound, and significantly non-smooth exchange enhancement factors have been shown to have poor transferability [214]. Since \( \Gamma \) acts in the transformed \( t(s) \)-space, the transformation in Eq. (5.10) causes the regularization penalty on exchange to be strongest in the large-\( s \) region, where the datasets give little information [7, 215].

The ideal regularization is the minimum in the EPE as a function of \( \omega^2 \). Unfortunately, the EPE has to be approximated. Here it is estimated using bootstrap sampling of the data matrix with the .632 estimator [205, 206], defined as

\[ \text{EPE}_{.632} = \sqrt{0.368 \cdot \hat{err} + 0.632 \cdot \hat{Err}}, \quad (5.14) \]

where \( \hat{err} \) is the variance of the deviation between the target data and the results predicted by the solution \( a \), and \( \hat{Err} \) measures the deviations on samples of data to which solutions were not fitted, all for a given \( \omega^2 \). The latter is given by

\[ \hat{Err} = \frac{1}{N_{\mu}} \sum_{\mu} \frac{1}{N_s | \mu \notin s} \sum_{s | \mu \notin s} (x_{\mu} b_s - y_{\mu})^2, \quad (5.15) \]

where \( \mu \) is an entry in the dataset, \( N_{\mu} \) is the number of data points, \( s \) is a bootstrap sample of \( N_{\mu} \) data points, and \( N_s | \mu \notin s \) is the number of samples not containing \( \mu \). The parenthesis calculates the difference between the prediction \( x_{\mu} b_s \) of the data point \( \mu \) by the best fit coefficient vector \( b_s \) and the \( \mu \)'th target value \( y_{\mu} \). The best fit solution is found by minimizing the cost function with the data in sample \( s \) only. 500 randomly generated data samples are selected independently for each \( \omega^2 \). The exchange part of the prior vector is chosen as
the linear combination of the order 0 and 1 polynomial basis functions that fulfills the LDA limit at \( s = 0 \) and the LO bound for \( s \to \infty \). The origo of correlation is \( \alpha_c = 0.75 \).

The strength parameter of the regularization can be used to express an effective number of parameters of a given model as shown in Eq. (5.23). A large regularization corresponds to few effective parameters. Fig. 5.2 shows how to find the ideal \( \omega \) (and the effective number of parameters) for the G2/97 dataset by minimizing the EPE, essentially showing how to find the ideal function in Fig. 5.1.

![Figure 5.2: Shows the EPE a) as a function of \( \omega \) and b) the effective number of parameters.](image)

The details for the XC models for the individually optimized fits are displayed in Table 5.5.1 and Fig. 5.3, and clearly their features differ significantly. The DBH24/08 set favors exchange that substantially violates the LDA limit (\( F_x(0) = 1.14 \)) and overshooting the LO bound significantly (\( F_x(\infty) = 3.14 \)), along with inclusion of full PBE correlation. The XC model optimized to the G2/97 set behaves similarly for both the exchange and PBE correlation; however, scaled down relative to both. On the contrary, the model optimized to the Sol34Ec dataset favors an exchange enhancement factor starting out slightly below one, then reaching a maximum around \( s = 2 \), after which it declines slowly towards \( F_x = 1.25 \) combined with full PBE and non-local correlations. Density
Table 5.2: Model selection statistics and coefficients of the individually trained XC models of Eq. (5.11) to the 10 different datasets. \( N_{\text{eff}} \) is the effective number of parameters in a model calculated using Eq. (5.23). The \( s = 0 \) and \( s \to \infty \) limits of the obtained exchange enhancement factors are also shown. MSD, MAD and STD are mean signed, mean absolute, and standard deviation, respectively, all in meV. The results are non-selfconsistent.

5.5.2 Several Materials Properties

Considering the large difference in the various fits to the individual datasets the question now arises if they are compatible. A way to investigate the transferability is considering the performance of the XC models from the fits to the individual datasets, on datasets they were not trained for. Fig. 5.4 shows a color map of the relative standard deviation (rSTD), defined as the STD obtained by the used model divided by the STD of the model that was fitted to that dataset, for all combinations of model fits and datasets. Clearly, a fundamental compromise has to be made between how well different materials properties are reproduced. In particular, the S22x5-2.0 model yields rSTD > 5 for all but the DBH24/08 dataset. Furthermore, a 5 × 4 square in the top left corner illustrates that XC models trained on chemical datasets perform significantly worse on vdw type energetics than models fitted to solid state properties. The challenge is to make the mandatory compromise as explicit and transparent as possible, so the XC functional with the most desired properties can be found. Here one route towards such a methodology for optimizing an XC model to simultaneously describe several different materials properties is proposed and
Figure 5.3: Exchange enhancement factors of the individually trained XC models listed in Table 5.5.1 as a function of the reduced gradient density $s$.

**Product Cost Function**

A product cost function for arbitrary numbers of training datasets is defined as

$$\Phi(a) = \prod_i C_i(a)^{w_i},$$  \hspace{1cm} (5.16)

where $w_i$ is a constant weight allowing some training datasets to be considered less important than others. In the case of two datasets, the stationary point between the two individual solutions in model space is found by differentiating the logarithm of $\Phi(a)$ with respect to $a$, and solving

$$\sum_i w_i \frac{dC_i}{da} = 0.$$  \hspace{1cm} (5.17)

The model solution that minimizes Eq. (5.16) is found in terms of the individual solutions by using the method of completing the square,

$$c = \left( \sum_i \frac{w_i}{C_i} H_i^0 \right)^{-1} \left( \sum_i \frac{w_i}{C_i} H_i^0 a_i \right),$$  \hspace{1cm} (5.18)

where $H_i^0$ is the Hessian matrix, $C_i = C_i(c)$, and $w_i$ simply scales the individual cost. Since $C_i$ is evaluated at $c$, the optimum solution is found using $C_i^{-1}$ as an
Figure 5.4: Color map of the relative standard deviations obtained when non-selfconsistently applying all 10 individually trained XC models, listed on the abscissa, to all 10 training datasets along the ordinate.
Figure 5.5: XC model compromises between the G2/97 and S22x5-1.0 datasets. When systematically varying the fraction of joint cost function weights, $W_{G2/97}/W_{S22x5-1.0}$, a range of compromising solutions are obtained, many of which are essentially fitting one dataset only while sacrificing model performance on the other. The product of relative costs display a minimum (blue dot) for a certain combination of joint cost function weights.
Table 5.3: BEEF-vdW XC model compromise. The effective weight in determining the model solution is \( w/C \) for each dataset, as iteratively found from minimizing the product cost function given in Eq. (5.16).

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Dataset} & w & w/C & rCost & rSTD \\
\hline
\text{CE17} & 1.0 & 1.80 & 1.7 & 1.3 \\
\text{RE42} & 0.5 & 0.62 & 2.5 & 1.8 \\
\text{DBH24/08} & 1.0 & 0.65 & 4.9 & 2.3 \\
\text{G2/97} & 0.5 & 0.62 & 2.6 & 1.6 \\
\text{Sol34Ec} & 1.0 & 0.43 & 7.5 & 2.8 \\
\text{S22x5-0.9} & 0.1 & 0.01 & 28.6 & 5.4 \\
\text{S22x5-1.0} & 0.1 & 0.04 & 9.1 & 2.9 \\
\text{S22x5-1.2} & 0.1 & 0.09 & 3.5 & 2.1 \\
\text{S22x5-1.5} & 0.1 & 0.08 & 4.1 & 2.1 \\
\text{S22x5-2.0} & 0.1 & 0.18 & 1.8 & 1.5 \\
\hline
\end{array}
\]

5.6 The BEEF-vdW Functional

The initial calculations for generating the BEEF-vdW functional were performed from RPBE densities. The BEEF-vdW XC functional was designed using the same origo vector as for the combined functional for the individual models and

\[\text{iterator, while searching for a converged minimum of the product cost function, given the constant weights } w_i.\]

The relative cost for each dataset \( (rCost[i]) \) is defined as the individual cost for that set evaluated at the compromising solution \( b \) relative to the individual cost at \( a_i \). It is a simple measure of how far the compromising solution moves in model space in order to accommodate several different datasets. The condition of minimizing the product of relative costs is identical to minimizing the product of costs and is applied henceforth. The condition essentially states that if changing the solution vector \( a \) to \( a + \delta a \) gains a larger relative reduction in cost on one materials property than is lost in total on all other properties considered, then \( a + \delta a \) is preferred.

Fig. 5.5 shows how the product of the relative G2/97 and S22x5-1.0 costs varies with the weight fraction \( W_{G2/97}/W_{S22x5-1.0} \). To the right along the abscissa, where the fraction increasingly favors the G2/97 set, the product of rCost increases rapidly. To the left the increase is much smaller; however, a minimum is located in between. Similar conclusions apply to any combination of two or more datasets that do not favor the same directions in the incomplete model space.

\[\text{The product cost function for two datasets is the sum of two quadratic equations, where the stationary point in the middle will be the global minimum if the two modes are weak. Nevertheless, if one or both the quadratic terms become strong, the two other stationary points can become minima. The middle compromise is chosen.}\]
Figure 5.6: The BEEF-vdW exchange enhancement factor compared to those of a few standard GGA exchange functionals. The corresponding BEEF-vdW correlation functional is composed of 0.6 LDA, 0.4 PBE, and 1.0 nonlocal correlation.
the set of weights $w$ listed in Table 5.6, which also shows the effective dataset weight $w/C$, rCost, and relative standard deviation (rSTD, defined similarly to rCost) for all datasets used in model training. The expansion coefficients of BEEF-vdW can be found in Table III in Paper 2. Especially the S22x5-0.9 interaction energies are difficult to fit along with the other datasets within the used XC model space as seen from the high relative cost. The delicate act of balancing the strong and weak interactions in the S22x5-0.9 complexes is nearly incompatible with at least one of the other sets of materials properties.

The BEEF-vdW’s correlation functional consists of 0.6 LDA, 0.4 PBE, and 1.0 non-local. The qualitative shape of the BEEF-vdW exchange enhancement factor is shown in Fig. 5.6. The limits of BEEF-vdW exchange are $F_x(s = 0) = 1.034$ and $F_x(s \to \infty) = 1.870$. Thus, it does not fully obey the LDA limit for $s \to 0$ being slightly higher. The enhancement factor is above most GGA exchange functionals up to $s \approx 2.5$, from where it approaches the LO bound with a small overshoot in the infinite limit.

### 5.7 Error Estimation

A normal DFT calculation does not provide any information about the uncertainty of the result. A commonly used method to estimate the uncertainty is applying several different functionals for the same system and observing the variations in the results. A more systematic approach is to use an ensemble of XC functionals designed to provide an error estimate, as discussed in Ref. [211]. This method is applied to the BEEF-vdW model, and the adaptation is briefly presented here. Inspired by Bayesian statistics [18] a probability distribution $P$ for the model parameters $a$ is defined as

$$P(a|M) \sim \exp(-C(a)/\tau), \quad (5.19)$$

where $M$ is the model, $D$ is the training data, $C(a)$ is the cost function, and $\tau$ is a cost “temperature”. That is, a given model perturbation $\delta a$ has a certain probability associated with it given the data $D$, and this defines an ensemble of different XC functionals. The temperature ensures that the errors observed when using BEEF-vdW self-consistently is reproduced by the spread of the ensemble model predictions of the training data.

The ensemble is defined through a Hessian scaled with the temperature

$$\Omega^{-1} = \tau H^{-1}, \quad (5.20)$$

$$H = 2 \sum_{i}^{N} \frac{w_i}{C_i(a_p)} \Gamma^{-1} \left( X_i^T X_i + \omega^2 L^2 \right) \Gamma^{-1T}, \quad (5.21)$$

with eigenvalues $w_{\Omega-1}^{i}$, eigenvectors $\mathbf{V}_{\Omega-1}$, and where the sum in the Hessian is over the various training datasets. Using a random ensemble of $k$ vectors ($\mathbf{v}_k$) each of length $M$ with normally distributed elements of zero mean and variance one, the BEEF-vdW ensemble coefficient vectors ($\mathbf{a}_k$) are calculated from

$$\mathbf{a}_k = \mathbf{V}_{\Omega^{-1}} \cdot \mathbf{1} w_{\Omega^{-1}} \cdot \mathbf{v}_k. \quad (5.22)$$
The $\Omega^{-1}$ ensemble matrix is available in the Supplementary Materials of Paper 2.

The temperature is calculated from the effective number of parameters in the BEEF-vdW model

$$N_{\text{eff}} = \sum_m^M \frac{\sum_m' \omega_m^2}{\omega_m^2 I_m^2}, \quad (5.23)$$

$$\omega_{\text{eff}}^2 = \sum_i^N \frac{w_i}{C_i(c)} \omega_i^2, \quad (5.24)$$

$$\Sigma' = \mathbf{V}^T \left( \sum_i^N \frac{w_i}{C_i(c)} X_i' X_i' \right) \mathbf{V}, \quad (5.25)$$

where $\omega_{\text{eff}}$ and $\omega_i^2$ is the effective and individual datasets regularization strengths, respectively, and $\Sigma'$ is the diagonalized combined square of the transformed data matrix. For the BEEF-vdW model the effective number of parameters is 7.11, so the regularization has suppressed more than 75% of the model degrees of freedom.

The temperature is slightly modified from Ref. [211] since a larger error is expected when BEEF-vdW is applied to systems not included in the training datasets

$$\tau = \frac{2 C(c)}{N_{\text{tot}}} \cdot \frac{N_{\text{tot}}}{N_{\text{tot}} - N_{\text{eff}}}, \quad (5.26)$$

where $N_{\text{tot}}$ is the total number of systems in the training datasets. Since $N_{\text{tot}} \gg N_{\text{eff}}$ the second term is close to one. One drawback of the method presented here is that systematic errors in the XC model will not be detected since the ensemble is based on the XC model.

### 5.8 Summary

In this chapter, the GGA+vdW type density functional BEEF-vdW has been presented. The semi-empirical functional is based on the 3 pillars of density functional fitting: i) datasets, ii) model space and iii) model selection.

The datasets representing chemistry, vdW interactions, solid state physics, and chemisorption have been chosen to create a generally applicable functional that works particularly well for surface science and catalysis. Most of the datasets were obtained directly from literature; however, a number of additional datasets were compiled in this study.

The model space used for the XC functional is a linear combination of LDA and PBE to describe the correlation as well as vdW dispersion interaction being accounted by a Rutgers–Chalmers vdW-DF2 type term [15]. The exchange is described at the GGA level using a highly flexible basis set containing 30 Legendre polynomials.
Inspired by machine learning the Tikhonov regularization with non-smoothness penalization and cross-validation was used to avoid overfitting. The model selection scheme is a two-step process. First the model was fitted to the individual training sets, and it was proven possible to make highly optimized smooth functionals for each training dataset. Thereafter, a transparent approach was employed, where the combined optimization was done through weighing the optimizations to the individual datasets and minimizing the product of their costs. Using these method the highly flexible model space has been "tamed" such that the 31 parameters were reduced to effectively only 7.11.

Lastly, from an ensemble of functionals around BEEF-vdW error estimation is naturally derived.
Chapter 6

Benchmarking

In DFT there is no *a priori* knowledge about how an XC functional performs for a specific type of system or property. Therefore, to validate new methods and to find possible applications and limitations it is essential to test the method against high accuracy *ab initio* methods and/or experiments. In this chapter a comprehensive benchmarking study assessing the BEEF-vdW XC functional and various other popular XC functionals ranging from GGA, MGGA, hybrids to vdW-DFs is given. The newly developed BEEF-vdW functional performs excellent overall. An overview of the XC functionals used is given in Table 6. The assessment is performed for the datasets of various properties reported in Table 5.1 in Chapter 5; including the six datasets that the BEEF-vdW functional was fitted to, as well as the independent data of G3-3, CE27, Sol27Lc and Sol27Ec\(^1\). The hybrid functionals are not applied to the extended systems because of the large computational burden. The details about the datasets are presented before the benchmarking results are given. More detailed results can be found in Appendix B.

To assess the XC functionals the statistical measures mean signed error (MSE) and mean absolute deviation (MAD) are considered:

\[
\text{MSE} = \frac{1}{N} \sum_{i}^{N} (\text{DFT}_i - y_i),
\]

\[
\text{MAD} = \frac{1}{N} \sum_{i}^{N} \sqrt{(\text{DFT}_i - y_i)^2},
\]

where \(y_i\) and \(\text{DFT}_i\) are the target value and the calculated DFT value of the \(i\)th element, respectively, and \(N\) is the number of elements in the dataset.

\(^1\)Sol27Ec is not an independent dataset

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Table 6.1: An overview of the XC functionals applied in the benchmark study.

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<tr>
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<th>Reference(s)</th>
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<tr>
<td>PBE0</td>
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6.1 Data handling

Computing the various properties for the many dataset each containing numerous data points requires an extensive amount of calculations. To systematically manage the bulk of input scripts and output data the procedure displayed in Fig. 6.1 has been applied for each dataset: A template file is used to setup scripts with identical computational protocol, which is used as an input to a filemaker script that generates python scripts each calculating a data point in the dataset. A submitting script then submits all the generated scripts simultaneously. Once the calculations finish, a checking script searches for data-files containing the right amount of numbers and gpw-files (the basic storage file in GPAW). The cases that have convergence issues or other problems are handled individually.

The datasets are setup as python lists of systematic names for each constituent, each containing python dictionaries involving geometry, target value, details such as magnetic moments etc. This simplifies generating the calculation scripts and acquiring the target data. An example of a dataset entry is shown in Fig. 6.2. When the BEEF-vdW functional was created in Chapter 5 the output files contain contributions for each basis set in the exchange expansion and the correlation terms for the fit. In the benchmarking study, the output is simply the desired quantity of the dataset listed in Table 5.1 for the XC functional applied.
Figure 6.1: To handle the vast amount of DFT calculations a filemaker script creates the calculation scripts from a template file. A submitting script is used to submit the bulk of calculations, and the results are subsequently followed using a checking script.

6.2 Datasets

6.2.1 Gas Phase Chemistry

Gas Phase Formation Energies

The G3 datasets [198, 193, 199] consist (partially) of formation energies that can be calculated using the difference between molecular and atomic total energies

$$\Delta_f E = E_M - \sum A E_A,$$

(6.3)

where $E_A$ is the ground state energy of atom $A$ in the molecule $M$ with the corresponding ground state energy $E_M$. The 223 experimental formation energies in G3/99 [199] dataset have been extrapolated to zero Kelvin [193] and corrected for thermal and vibrational contributions using thermal corrections and zero-point energies [193, 216] making them directly comparable to electronic structure calculations. The G3/99 dataset can be subdivided into G3-1
g3_1 = ['LiH', 'BeH', 'CH', 'CH3', 'CH4', 'NH', 'NH2', '…]

'LiF': {
    'description': "Lithium Fluoride (LiF), C*v symm.",
    'name': "LiF",
    'enthalpy': -80.1,
    'ZPE': 1.4019,
    'thermal correction': 2.0990,
    'ionization energy': 11.30,
    'symbols': 'LiF',
    'latex name': "LiF",
    'magmoms': None,
    'positions': [[0., 0., -1.174965],
                  [0., 0., 0.391655]]},

Figure 6.2: As an example of how the datasets are implemented the G3-1 python list and the "LiF" element implemented as a dictionary with positions, correction, etc. is displayed.

(55), G3-2 (93) and G3-3 (75) datasets. G3-1 and G3-2 are collectively known as the G2/97 dataset and were used as training data for BEEF-vdW, while the G3-3 subset is only utilized as independent data for assessing the BEEF-vdW functional in the benchmarking study.

Performance of XC Functionals

The Gn datasets are the most commonly used for validating DFT methods in thermochemistry. Fig 6.3 shows the deviation statistics for the various XC functionals for the G2/97 dataset and the expansion the G3-3 dataset.

The G2/97 dataset, which the BEEF-vdW functional was fitted to, is considered first. At the lowest level of "Jacob’s ladder", the LDA is seen to grossly overestimate the formation energies reflecting that the small molecules in the dataset do not have local densities. Including gradient in the GGA functionals drastically improves the description, in particular for the XC functionals designed for molecular systems (RPBE, BLYP, HCTH407), which all have MADs below 0.5 eV. On the contrary, the solid state GGA XC functionals (PBEsol, WC, AM05) systematically overbind as seen by the MSEs. The MGGA functionals TPSS and revTPSS reproduce the formation energies quite well.

The vdW-DF flavors, vdW-DF and vdW-DF2, have relatively small errors
Figure 6.3: Shows the MADs and MSDs for the heat of formation of the a) G2/97 and b) G3-3 datasets.

for the G2/97 dataset. Contrary, the optPBE-vdW, optB88-vdW, and C09-vdW functionals, which all have optimized GGA exchange terms to vdW energetics resulting in overbinding in agreement with Ref. [116]. This illustrates that great care should be taken when altering the exchange (the majority of the XC energy) to describe the small energy differences in the vdW molecular systems, since this comes at the risk of destroying the description of other types of systems.

The fourth rung of "Jacob's ladder", the hybrid functionals (B3LYP and PBE0), are known in quantum chemistry to describe thermochemistry very
well, which is verified in Fig. 6.3. Of all the XC functionals, B3LYP performs the best on the G2/97 dataset. The BEEF-vdW DF also performs very well for the G2/97 dataset with a MAD of 0.16 eV even outperforming the hybrid functional PBE0.

Containing 75 molecules, G3-3 is an expansion of the G2/97 dataset. G3-3 consists of independent data points for the BEEF-vdW functional, since the molecules were not included in the training data. With the exceptions of vdW-DF, vdW-DF2, TPSS and revTPSS the average deviations are larger for the G3-3 dataset compared to G2/97. The BEEF-vdW functional performs very well for these independent data points suggesting transferability of the method. The excellent overall performance on the formation energies of the newly developed functional is further emphasized, when considering the combined dataset G3/99 (G2/97 and G3-3), where the functional has the best overall performance of the tested XC functionals (see Appendix B). On this larger dataset both MGGA functionals, the vdW-DF, and vdW-DF2 also perform well.

**Reaction Energies**

From G2/97 a dataset of reaction energies can be compiled. The reaction energies are computed from the total energies of relaxed molecules in G2/97

\[
\Delta_r E = \sum_P E_P - \sum_R E_R,
\]

where the sums run over the reactant \( R \) and products \( P \). In Table A in Appendix A the RE42 dataset containing 42 reaction energies involving 45 different molecules is presented.

**Performance of XC Functionals**

The benchmarking results for the RE42 dataset is shown in Fig. 6.4. Surprisingly, even though the reaction energies are compiled from the formation energies of G2/97, the conclusions concerning the XC functionals’ performances do not seem to transfer to this dataset. The functionals optPBE-vdW and optB88-vdW that described formation energies poorly describe gas phase reaction energies as reliably as the best GGA functional (RPBE). In general, the GGA, MGGA and vdW-DF type functionals all have comparable accuracy for the gas phase reaction energies independent of their respectively description of the corresponding formation energy. At the highest rung of “Jacob’s ladder” considered here, the hybrid functional B3LYP significantly improves the results for the dataset. For most XC functionals the errors on the reaction energies are higher than the heat of formation, which may partially reflect that more atoms are transferred in the reactions, scaling the errors. Arguably reaction energies better represent chemistry than formation energies, since predicting formation energies is as much about having a correct description of atoms as it is molecules. Therefore it is particular noteworthy that the conclusions from the formation energies datasets do not transfer to the reaction energies. Evaluating
an XC functionals’ predictability for thermochemistry only from formation energies, which is common, might not be ideal. The same idea goes for molecular fitting, which should also focus more on energetics of molecules than atoms for the correct description of chemistry. An interesting study that shows the same sort of trends in energetics of molecules is that of Korth and Grimme [217], who have introduced a non-biased dataset consisting of artificial molecules and their energetics.

**Gas Phase Barrier Heights**

Density functional barrier heights are computed from the transition state total electronic energy ($E_{ts}$) and the initial ($E_i$) and final ($E_f$) state total energies:

$$V_f = E_{ts} - E_i,$$

$$V_b = E_{ts} - E_f.$$  

(6.5)  
(6.6)

The DBH24/08 [200] contains the barrier heights from high-level theory or experiments [200] of 12 forward and backwards reactions. QCISD geometries are used for the ground and transition state molecular geometries [218].

**Performance of XC Functionals**

The benchmarking results of the various XC functionals for the DBH24/08 barrier heights dataset is displayed in Fig. 6.5. It is well known that including
Figure 6.5: Shows the error statistics of the various tested XC functionals for the barrier heights in the DBH24/08 dataset.

a fraction of exact exchange in the XC approximation significantly helps the description of gas phase barrier heights [219, 220]. Not surprisingly, all GGA XC functionals systematically underestimates the barriers. Including the Laplacian of the density in the MGGA functionals or vdW interactions has little effect and the systematic errors pertain. BEEF-vdW is no exception, even though it is among the best non-hybrid functionals. Considering that the functional is fitted to the dataset and still has a large MAD and MSD, it seems that the model space is incapable of accurately describing the property. Fig. 6.5 also confirms that hybrid functionals indeed do perform significantly better than the XC functionals on the lower rungs of ”Jacob’s Ladder”.

6.2.2 Surface Chemistry

Chemisorption Energies

The CE27 dataset and the subset CE17 comprise experimental reaction energies for chemisorption of simple molecules on (111), (100), and (0001) facets of late transition metal surfaces at low coverage derived from temperature programmed desorption experiments or from microcalorimetry. The 27 chemisorption energies, listed in Table A in Appendix A, have been critically chosen from literature with emphasis on reliability as well as coverage of a wide range of substrates and adsorbates.

For the molecular adsorption processes at 0.25 ML coverage (the majority
of CE27) the chemisorption energy is computed using

$$\Delta E = E_{AM} - E_M - xE_A,$$

(6.7)

where $E_{AM}$ is the total electronic energy of the adsorbate $A$ on metal surface $M$, and $E_A$ and $E_M$ are total energies of the isolated adsorbate and metal surface, respectively. The constant $x$ is 1 for molecular adsorption and $N_2$ dissociation on Fe(100), and $x = \frac{1}{2}$ for the dissociative $H_2$ chemisorption reactions. In the special case of NO dissociation on Ni(100) at 0.25 ML coverage the chemisorption energy is calculated using

$$\Delta E = E_{AM} + E_{BM} - 2E_M - E_{AB},$$

(6.8)

where AB is the NO molecule.

**Performance of XC Functionals**

Deviation statistics of the tested XC functionals of the chemisorption energies in the CE27 dataset and the subset CE17 are reported in Fig. 6.6. The CE17 dataset was a training set for the BEEF-vdW XC functional, while the CE27 contains 10 independent chemisorption systems.

As with the gas phase molecules LDA severely overestimates the chemisorption energies. The GGA functionals fall into two groups; the functionals designed for solid state properties or for chemistry (see Table 6). The solid state XC functionals clearly overbind the molecules to the surface as illustrated by the negative MSE. The XC functional that are more specialized for chemistry (RPBE, BLYP, and HCTH407) do not have this issue and especially RPBE performs excellent with a MAD of 0.11 eV for both chemisorption datasets. The two MGGA functionals fall in between these two groups.

The vdW-DF and vdW-DF2 functionals provide fairly reliable methods for studying chemisorption systems. Conversely, the exchange fitted vdW functional, as with the gas phase formation energies, overbind severely, reiterating the point that care has to be taken when fitting exchange to vdW systems. As seen from Fig. 6.6, the BEEF-vdW functional is among the very best for the CE17 dataset. The expansion in CE27 includes systems that BEEF-vdW was not trained for, and since the accuracy to a large extent remains, transferability should be expected also to the breaking and making of chemical bonds on metal surfaces that occurs in catalysis.

**6.2.3 Solid State Properties**

**Cohesive Energies and Lattice Parameters**

The three sets Sol34Ec, Sol27LC, and Sol27Ec contain zero Kelvin experimental solid state data. The SolEc34 comprises 34 zero-point phonon corrected cohesive energies of 34 Period 2–6 bulk solids in fcc, bcc, diamond, and hcp
Figure 6.6: The MSDs and MADs generated from applying the various XC functionals on the chemisorption datasets a) CE17 and b) CE27.

The Sol27LC and Sol27Ec sets contain lattice constants and cohesive energies, respectively, of 27 cubic lattices, both corrected for zero-point vibrational contributions which may be important when benchmarking density functional methods [215]. Experimental zero Kelvin lattice constants and cohesive energies ($E_c$) contain zero-point vibrational contributions, leading to a zero-point anharmonic expansion (ZPAE) of the lattice and zero-point vibrational energy (ZPVE) contributions to $E_c$. The ZPVE may be estimated from...
the Debye temperature, $\Theta_D$, of the solid [221]

$$\text{ZPVE} = -\frac{9}{8}k_B\Theta_D,$$

(6.9)

and subtracted from the cohesive energy, leading to increased stability of the crystal towards atomization. A semi-empirical estimate of the ZPAE contribution to the volume of cubic crystals has been derived [221], and was recently supported by a first principles approach [222]. The Sol27LC and Sol27Ec sets of zero Kelvin lattice constants and cohesive energies are appropriately corrected for zero-point phonon effects unlike Sol34Ec (which is why SolEc27 cannot be considered a subset of SolEc34). Details are given in Table A in Appendix A.

The cohesive energy for a given crystal lattice constant, $a$, is calculated from

$$E_c(a) = E_A - E_B(a),$$

(6.10)

where $E_A$ is the total energy of the free atom and $E_B$ is the bulk total energy per atom. Using this definition, the equilibrium cohesive energy of a stable solid is a positive quantity. Equilibrium lattice constants of cubic crystals, $a_0$, are determined from fitting the SJEOS [221] equation of state to cohesive energies sampled in five points in a small interval around the maximum of the $E_c(a)$ curve.

Performance of XC Functionals

Fig. 6.7 summarizes the deviation statistics for calculations of lattice constants (Sol27LC) and cohesive energies (Sol27Ec).

LDA gives fairly good results for the lattice constants considering the crude approximation. The description of the lattice parameters at the GGA level are clearly best for the PBEsol, AM05 and WC functionals. Also the MGGA functional revTPSS performs well for lattice parameters. Nevertheless, the accuracy for lattice constants seem to come at the price of overestimating cohesive energies. The opposite result is obtained with the vdW-DF and vdW-DF2 functionals that describe cohesive energies well; however, lattice constant less so. In that sense describing these two properties seems to be antagonistic. The vdW-DF functionals with revised exchange perform fairly well for the solids and have statistics that are comparable with PBE and TPSS for both properties.

As seen from Fig. 6.7 the BEEF-vdW performs reasonably well for both cohesive energies and lattice constants; however, still producing softer lattices than the exchange fitted vdW-DFs. Nonetheless, the BEEF-vdW functional accuracy for the two solid state properties studied here is still significantly better than the vdW-DF, vdW-DF2 and GGA functionals focused on chemistry, showing the overall applicability of the functional.

The GGA, MGGA, and vdW-DF results and conclusions presented here for solid state properties are in agreement with recent studies [215, 223, 224, 225, 226].
Figure 6.7: The error statistics of the solid state properties of a) the cohesive energies in the SolEc27 dataset and b) the lattice parameters in the SolLc27 dataset.

6.2.4 van der Waal Interactions

Non-covalently Bounded Systems

The S22 [46] set of CCSD(T) intermolecular interaction energies of non-covalently bonded complexes has become popular for benchmarking [227, 42, 228, 51, 229, 230, 231] and parametrization [228, 10, 15, 45, 52, 21] of vdW type XC func-
tionals. The S22 dataset was expanded to consist of potential-energy curves (PECs) for each S22 complex, with interaction energies at relative interaction distances of 0.9, 1.0, 1.2, 1.5, and 2.0 in what is referred to as the S22x5 [203]. Here the S22x5 is divided into five subsets, e.g., "S22x5-0.9". Geometries of the datasets were reproduced from MP2 or CCSD(T) calculations.

Each interaction energy at the relative interaction distance $d$, is given as the difference between the total electronic energy of the interacting complex, $E_{d}^{0}$, and the two corresponding isolated constituents, $E_{d}^{1}$ and $E_{d}^{2}$:

$$E_{d}^{\text{int}} = E_{d}^{0} - E_{d}^{1} - E_{d}^{2}. \quad (6.11)$$

Employing larger basis sets for the S22 dataset has revealed some inaccuracies in the original dataset and a revised version of energies has been proposed [201, 202]. The S22x5 [203] PECs were reported more recently using the original computational protocol, and the inaccuracies are expected to persist for the S22x5. A modification is here proposed to shift the equilibrium point to the revised S22 energies, and approximately correct the remaining data points on each PEC:

$$E_{d}^{\text{int}} := \varepsilon_{d}^{\text{int}} \times \frac{E_{\text{int}}^{1.0}}{\varepsilon_{\text{int}}} \quad (6.12)$$

where $E_{d}^{\text{int}}$ and $\varepsilon_{d}^{\text{int}}$ denote modified and original S22x5 energies at the relative intermolecular distance $d$, respectively. For $E_{\text{int}}^{1.0} = \varepsilon_{\text{int}}^{1.0}$, Eq. (6.12) obviously reduces to $E_{d}^{\text{int}} = \varepsilon_{d}^{\text{int}}$ for all distances. The obtained corrections can be found in the Appendix of Paper 2. The modified CCSD(T) interaction energies are used henceforth.

**Performance of XC Functionals**

Fig. 6.8 illustrates the deviation statistics of the non-covalently bound dimers in the S22x5 dataset. LDA is completely local in nature and obviously cannot describe the non-local interactions of these types of systems. Similarly, the tested MGGA, hybrids, and the GGA functionals seem to be incapable of describing the interactions of the systems. Exceptions to this are the GGA XC functionals that have low enhancement factors (PBEsol, WC, AM05). Nevertheless, considering the appreciable LDA over-binding of the S22x5 complexes, this is most likely the case of getting it right for the wrong reasons.

The vdw-DFs are designed to describe non-covalent interactions and, in agreement with previous studies, the methods are validated for the purpose [227, 10, 45, 15]. In particular, the exchange fitted vdw-DFs have MADs of 20 meV or less for all 110 points on the 22 potential-energy curves showing a very impressive performance. The vdw-DF2 also predicts the interaction energies very well; however, it does (contrary to the fitted functionals) have a systematic as revealed by the positive MSE. Naturally, the fitted functionals will have MSEs around zero unless the model space does not sufficiently describe the dataset. The BEEF-vdW and vdw-DF have the same type of erroneous tendencies as vdw-DF2, only more enhanced. The results presented here are consistent with
a recent study of the S22 dataset within the computational accuracy from using different codes [45].

Table 6.2.4 shows the s22x5 dataset in greater detail for the vdW functionals. As a whole BEEF-vdW, vdW-DF and vdW-DF2 all perform well for the dataset, although the short separation for \( d = 0.90 \) is troublesome to describe for the functionals (as discussed in Chapter 5). Furthermore, at the equilibrium position the exchange fitted functionals (optPBE-vdW, optB88-vdW and C09-vdW) all perform better.

### 6.3 Summary

In this chapter an extensive benchmarking study has been presented where LDA, GGA, MGGA, vdW and hybrid XC functionals have been applied to numerous datasets. In this section an overview of the many results is given. Fig. 6.9 shows a bar chart of the MADs of selected XC functionals representing each rung on "Jacob’s ladder" for gas phase chemical, surface chemical, solid state, and vdW dominated datasets. The bars are scaled to be of equal size for the various datasets and the actual MADs are computed below.

The LDA is too crude an approximation for almost all of the datasets. Especially the gas phase molecules are not represented well. The best description by this method is the solid state properties, where the density is more homogeneous. The GGA functionals can very broadly be grouped into two specializa-
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Table 6.2: Detailed statistics on the deviations of calculated S22x5 interaction energies from a CCSD(T) benchmark, using vdW density functionals in all five points along the intermolecular PEC. Mean signed and mean absolute deviations are in meV. Mean signed relative (MSRD) and mean absolute relative (MARD) deviations are also listed. Negatively signed deviations mean overbinding on average.
tions: chemistry and solid state physics. The first describes gas phase chemistry well in the form of formation energies, while the latter reproduces experimental cohesive energies well. Surprisingly, the conclusions from the formation energies do not transfer to the reaction energies. The XC functionals predict reaction energies in the RE42 dataset almost equally well independent of their performance on the formation energies. This may cast doubt to the approach of evaluating the predictability of thermochemistry of a method only from formation energies, since the errors may be in the energetics of the atoms. Including exact exchange in the XC functional improves the prediction of reaction energies significantly. 

vdW interactions are surprisingly reliably computed by a few of the GGA functionals that have soft exchange enhancement factors, even though the correct physics to describe the interaction is not included in the functional form. This is most likely a case of getting it right for the wrong reasons. Barrier heights are well known to be underestimated by GGA functionals, which is confirmed in this study. The chemisorption systems are best described by the "chemistry" GGA functionals and RPBE stands out as an excellent option for studying these types of systems, whereas solid state GGA gives large errors.

Including the Laplacian of the density in the MGGA XC functionals give good results for formation energies; however, as for the GGAs, the reaction energies and barrier heights are not well reproduced. The MGGA functionals are not capable of describing the vdW dispersion; however, do perform fairly well for the solids. Although the revTPPS and TPSS functionals are not among the worst functionals for the chemisorption systems, several alternatives at the GGA level are preferred.

The vdW-DF flavors can be partitioned into two: those where the exchange is fitted and those where it is not. The vdW-DF and vdW-DF2, where the exchange has not been fitted reproduce formation energies and the vdW system reasonably well (with the exception of the short separation $d = 0.90$). The exchange fitted vdW functionals (optPBE-vdW, optB88-vdW and C09-vdW) have an excellent description of the non-covalently bound dimers; however, this comes at a cost of severely overestimating the formation and chemisorption energies. As with GGA, all vdW-DFs underestimate the barriers of gas phase reactions. The vdW functionals that describe lattice parameters well (vdW-DF and vdW-DF2) have issues with cohesive energies and vice versa (optPBE-vdW and optB88-vdW). The C09-vdW falls in between.

The highest level of "Jacob's ladder" considered in this benchmark study is the hybrid functionals. The higher computational cost gives an improved description for several chemical properties such as formation and reaction energies, as exemplified by the B3LYP functional. Nevertheless, because of the large computational burden the hybrid functionals have not been applied to the bulk systems. The hybrids are not able to describe vdW interactions.

The newly developed BEEF-vdW is a truly general-purpose XC functional as seen from Fig. 6.9. The average BEEF-vdW error is not among the largest for any of the datasets, while several other functionals are highly biased towards certain types of materials properties. Especially vdW-DF2 and optB88-vdW, show severely erroneous description of binding energetics for bulk solids and
Figure 6.9: Bar plot comparison of the accuracy of different density functionals in predicting various materials properties. For each dataset, the bars represent proportionally scaled mean absolute deviations. The datasets represent intermolecular bond energetics (G3), chemisorption energetics of molecules on surfaces (CE27), molecular reaction barrier heights (DBH24/08), molecular reaction energies (RE42), bulk solid cohesive energies (Sol27Ec) and lattice constants (Sol27Lc), and interaction energies of weakly interacting complexes (S22x5). Hybrid functionals have not been applied to the extended systems.
Part IV

Functional Application
Chapter 7

CO desorption from Ru(0001)

This chapter begins with a brief background on precursor states in catalysis followed by a succinct description of a very recent pump-probe experiment at Linac Coherent Light Source (LCLS), that indicates the existence of a precursor state for CO on Ru(0001). The bulk of this chapter is focused on the calculation of the potential of mean force (PMF), which is a free energy potential curve where all degrees of freedom except the reaction coordinate have been thermally averaged. This is the main support in interpreting the spectroscopic results, since the PMF starts to develop an adsorption/desorption barrier for increasing temperatures and a second minimum occurs at larger surface separations. To adequately represent the desorption process, it is essential to have the correct description of chemistry and vdW interactions as well as the transition between the two wells. As shall be shown, common GGAs are incapable of this, whereas the non-local vdW interactions in BEEF-vdW are essential for a correct description. The results presented here originate from Paper 3.

7.1 Precursor State

In catalysis, reactant species are chemisorbed on solid surfaces and chemical reactions occur, after which the products desorb leaving the surface unaltered. When a molecule or atom approaches a surface an attraction starts to occur from long-range vdW interactions [232]. At extended surface separation the interaction is weak and insensitive to adsorption site, making the adsorbate free to diffuse and rotate. A trapping in such a transient, weakly bound, mobile state, preceding the more strongly bound chemisorption state, is known as a precursor state [233, 234, 235]. The concept was initially proposed in 1933 by Taylor and Muir [233]. A distinction is made between intrinsic and extrinsic precursor states, where the first is a weakly bound molecule above an empty site and the latter is above an occupied site. The extrinsic precursor state has been
observed at low temperature using shadowed field-emitter tip experiments [236]. Empirical evidence of the existence of the intrinsic precursor state has been difficult to obtain because the lifetime is typically shorter than the timescale of the actual measurement. Therefore most experimental evidence has been circumstantial. The fact that the sticking probability often decreases with increasing substrate temperature has often been argued as consistent with a precursor state [237, 238, 239]. Molecular beam studies also provide an indication of the existence of an intrinsic precursor state [240, 241]. In this chapter, new femtosecond experiments capable of probing the time evolution of the desorption of CO from Ru(0001) will be discussed and supported by theoretical calculations.

Theoretical investigations of the properties of precursor states have been performed by Doren and Tully [242, 243]. From liquid state theory they introduced the PMF [244], which is equivalent to the free energy as a function of reaction coordinate (in this case the surface-adsorbate separation distance), where the remaining degrees of freedom have been thermally averaged. It is temperature dependent, and can be quite different from the minimum energy path potential, since entropic effects are included. In fact, one of the major conclusions from Doren and Tully is: "wells and barriers may appear in the reduced potential which are not evident from the simple cut through the [ground state electronic] hyper-surface". The PMF has been used to investigate properties of precursor state models for CO on Ni(111) [243]. It should be emphasized that models were used for the sole purpose of finding characteristics of precursor states, meaning that no "true potential" was applied. The main feature found for the precursor models was a strong rotational polarization allowing only cartwheel rotations as opposed to helicopter rotations [243]. The general picture of a precursor state in Ref. [243] is freely rotating and diffusing CO molecules, contrasted by the chemisorbed state where the CO molecules are constrained to be oriented vertically. Using this picture the reduced sticking probability at higher temperatures can be explained by the "wrong" orientation of the incoming CO molecules. The precursor state can be thought of much like a funnel that only allows the upright CO molecule to proceed to the chemisorption sites. In this chapter, Doren and Tully’s approach is utilized to interpret new femtosecond experiments of CO desorption on Ru(0001). Instead of using an effective fitted potential, phase space of the CO on Ru(0001) is sampled using the new BEEF-vdW functional.

7.2 The Pump-Probe CO Desorption on Ru(0001) Experiment

When an adsorbate is physisorbed to a substrate there is only little overlap of wave functions and therefore only small changes in the electronic structure, producing a weak interaction. On the contrary, for chemisorption there is a larger rearrangement of molecular levels usually giving rise to a broadening and
shifting of the energy levels, and sometimes new levels may appear that were not present in the gas phase molecule [245]. CO is chemisorbed in the on top position on Ru(0001) in an upright configuration with the C atom closest to the surface. The molecular orbitals generated on the surface are denoted with a tilde and can be considered as perturbations of the gas phase molecular orbitals. The CO molecules' interaction to a metal surface is rather weak, as illustrated by the fact that chemisorption energy is only around 10-15% of the molecular dissociation energy [245]. The bonding of the CO molecule to the surface comes from minimizing the σ repulsion and maximizing the attractive π-bonding, where both the 1π and 2π* orbitals are involved as the d-electron states are moved towards the Fermi level. As the 1π and 2π* orbitals couple to the d-band in the metal, the π states change slightly in energy and a new band, \( \tilde{d}_{\pi} \), appears. The \( \tilde{d}_{\pi} \) band is a unique feature of the CO molecule on the surface. For greater detail about the CO bonding to the surface see Ref. [245].

Very recently the LCLS free-electron x-ray laser was used to probe the electronic structure of CO molecules as their chemisorption state changes upon exciting the Ru(0001) substrate using a femtosecond optical laser pulse [Paper 3]. To measure the time evolution of the electronic structure in real time oxygen resonant XAS and XES were utilized. The principle of core-level excitation (XAS) and de-excitation (XES) together with the static spectra from the oxygen atom for CO chemisorbed on Ru(0001) are illustrated in Fig. 7.1 [246]. The advantages of these spectroscopic methods are the ability to provide atom-specific probes of the electronic structure through the involvement of the local O1s level [247, 248], and since both XAS and XES measure on an attosecond and femtosecond timescale, respectively, they provide an almost instantaneous picture. The latter is essential if a transient state has to be captured. XAS measures the energy spectrum of the CO photon absorption from the O1s core level to the 2π* state, while XES measures the fluorescence when a core-excited CO molecule relaxes into a lower-energy state.

The overall interpretation of the experimental results is illustrated in Fig. 7.2. The spectroscopic results are consistent with a weakening of the CO-substrate interaction; however, without significant desorption [Paper 3]. This indicates that around half of the molecules become trapped in a transient precursor state prior to desorption. After a period of 25 ps approximately 1/3 of the molecules are desorbed while the remaining are re-adsorbed. The observation of a short-lived intermediate is the first direct spectroscopic observation of a precursor state in desorption and (by time-reversal) in adsorption. The details of the experimental results can be found in Paper 3. The rest of this chapter is devoted to the theoretical support and interpretation of the experiment.

7.3 The Potential of Mean Force

The PMF is a free energy potential curve including contributions from entropy where all degrees of freedom except the reaction coordinate have been thermally...
Figure 7.1: Schematic illustration of the excitation process from the O1s level to the unoccupied $2\pi^*$ resonance in XAS and the core hole decay process from occupied $4\sigma$, $5\tilde{\sigma}$, $1\tilde{\pi}$ and $d_{\pi}$ molecular orbitals back to the O1s in XES. The displayed XES spectrum is a representation of the measured static CO on Ru(0001) data [246]. $E_F$ is the Fermi level.

averaged by integration. The following sections explain how the PMF has been calculated for CO on Ru(0001).

### 7.3.1 Computational Protocol

The electronic structure calculations are performed using the grid-based real-space projector-augmented wave GPAW code. A wave function grid-spacing of 0.18 Å, 0.01 eV Fermi smearing and a 4x4x1 k-point sampling has been applied. For the relaxations in the minimum energy path (MEP) the criterion of 0.05 eV/Å as maximum force on each relaxed atom was used. The Ru(0001) slab was set up in a 2x2 cell using periodic boundary conditions and containing 3 layers where the bottom layer was fixed. On top a CO molecule was placed having 10 Å vacuum to the top of the box giving a 1/4 monolayer adsorption. The equilibrium Ru-C distance for on-top adsorption was obtained as 1.94 Å with the BEEF-vdW functional.

O K edge x-ray emission spectra were calculated in the same framework [124] using ground state orbitals and summed over $p_{xy}$ and $p_z$ symmetries. To com-
Figure 7.2: A schematic of the recent pump-probe experiment at LCLS. Initially a laser excites the surface atoms. Energy transfers from the surface to the CO molecules which weakens their bonds to the surface and after 10 ps approximately half of them seem to be captured in a transient state at an extended separation compared to the chemisorbed state. After 25 ps 1/3 of the molecules have desorbed and the rest are re-adsorbed.

In order to compare with the experimental spectra, a broadening with a Gaussian function of 1 eV at full-width at half-maximum (FWHM) was employed. Geometries of the chemisorbed state and the precursor state were taken from the MEP of desorption. To obtain an absolute energy scale, the computed spectra were shifted so that the energy position of the calculated state is aligned with that of the corresponding experimental spectrum.

The potential energy curves (PECs) for the PMF described below have been fitted using the least squares method and the integral defined in Eq. (7.3) was solved using these fits as well as numerical integration using Gaussian quadrature as implemented in the python library "Matplotlib".

7.3.2 Exchange-Correlation Functionals

The BEEF-vdW XC functional was chosen to describe the CO desorption from Ru(0001), since it is capable of describing both the chemical and vdW interactions [Paper 2] unlike the commonly used GGA XC functionals PBE [13] and RPBE [7]. Fig. 7.3 shows the PECs as function of the Ru-C distance using the three XC functionals RPBE, PBE and BEEF-vdW. As is clearly seen from Fig. 7.3 PBE goes to zero exponentially for increasing surface distances of the CO molecule, while RPBE actually produces a barrier after which it trails off to zero. Only BEEF-vdW is able to get an attractive plateau starting at a C-Ru...
distance around 3.5 Å. As shall be shown from the PMF this attractive plateau is essential in the theoretical interpretation of the experimental results. Other vdw XC functionals have been tested and give similar results as BEEF-vdW. For the spectrum calculations the RPBE functional was chosen.

Figure 7.3: Shows the MEP potential of the CO desorption from the Ru(0001) surface using the PBE, RPBE and BEEF-vdW functionals.

### 7.3.3 Potential of Mean Force

To estimate the PMF it is assumed that the potential energy is separable in the translational and rotational degrees of freedom

\[
V_{\text{tot}} = V_0 + V_x + V_y + V_{\text{rot1}} + V_{\text{rot2}} \approx V_0 + 2V_{\text{trans}} + V_{\text{rot1}} + V_{\text{rot2}}, \tag{7.1}
\]

where the rotational potentials \(V_{\text{rot1}}\) and \(V_{\text{rot2}}\), translational degrees of freedom potentials \((V_x\text{ and } V_y)\) and the potential of the minimum energy path \((V_0)\) have been introduced. The high-frequency internal CO vibration is assumed not to be excited and is therefore neglected. The approximation equality sign in Eq. (7.1) refers to the assumption that the two translational degrees of freedom on the surface are equivalent. As proposed by Doren and Tully [242] the PMF can be written as

\[
W(s) = -k_BT g(s) + k_BT g(\infty), \tag{7.2}
\]

where \(k_B\) is Boltzmann’s constant, \(T\) is the temperature, \(s\) is the distance from the surface to the center of mass of the CO molecule and \(g(s)\) is given by the integral

\[
g(s) = \Gamma^{-1} \int \exp \left(-\frac{V(s,q)}{k_BT}\right) dq, \tag{7.3}
\]

here \(q\) represents the four independent degrees of freedom discussed above and \(\Gamma\) is an arbitrary normalization constant, the choice of which is irrelevant when
the PMF is set to zero at infinite separation. \( g(s) \) is the position distribution function and \( g(s)ds \) is proportional to the probability that a molecule is between the surface distances \( s \) and \( s + ds \) analog to a radial distribution function. It should be stressed, that Eq. (7.3) assumes that all degrees of freedom can be treated classically, which is a rather crude approximation especially at low temperatures. The experimental temperature has (with great uncertainties) been estimated to be 1500-2000 K [Paper 3]. Inserting Eq. (7.1) into Eq. (7.3) the following is obtained

\[
    g(s) = \Gamma^{-1} \int \exp \left( - \frac{V_0(s) + 2V_{\text{trans}}(s,x) + V_{\text{rot1}}(s,\theta) + V_{\text{rot2}}(s,v)}{k_B T} \right) dx dv dr, \tag{7.4}
\]

\[
    = \Gamma^{-1} g_{\text{trans}}(s)g_{\text{rot1}}(s)g_{\text{rot2}}(s). \tag{7.5}
\]

By adding and subtracting the potential of the minimum energy path (MEP), \( V_0 \), to each degree of freedom, the PMF can be written as a correction for each degree of freedom

\[
    W_{\text{tot}}(s) = V_0 - \sum_{i=1}^{N} W_i - V_{\text{fit},i}, \tag{7.6}
\]

where \( W_i \) is the PMF and \( V_{\text{fit},i} \) is the fit to \( V_0 \) for the \( i \)’th degree of freedom, respectively. \( V_{\text{fit}} \) only differs from \( V_0 \) to the extent that our mathematical representation of the potential in this direction is not perfect. By subtracting it in each degree of freedom this error cancels out. To calculate the individual contributions, the degrees of freedom have been sampled by calculating the potential energy of the two rotations (cartwheel and helicopter) and a translation (counted twice) of the CO molecule at fixed surface distances using the new BEEF-vdW XC functional. The PECs for each degree of freedom have been fitted to functions for each surface distance and inserted in the integral to obtain the PMF. The detailed fitting procedure is described below.

### 7.3.4 Fitting the Potential Energy

The potential energy of the translational motion has been fitted to the function

\[
    f_1(x) = a_0 + a_1 \cos(d \pi x) + a_2 x^8. \tag{7.7}
\]

The periodicity \( d \) in the cosines function is the distance from one on-top position to another. It is assumed that all CO molecules are transferred into the precursor state, which is simulated by having a 2x4 unit cell containing two CO molecules at the same surface distance. Here one CO molecule is fixed, while the other is moved in the surface plane between the neighboring CO molecules at the same surface distance confining it. This gives a particle in a box-like potential with a cosines bottom as illustrated in Fig. 7.4 a) and b). The fitting procedure for the translational motion is as follows: First all the coefficients are determined by fitting to all data points. \( a_0 \) and \( a_2 \) are then fixed to the obtained values, while \( a_1 \) is refitted to the non-repulsive points (excluding the potential energy points where the CO molecules are too close to their neighbors). This is done to avoid destroying the description of the interesting low potential energy
region. A fit of the translational potential energy for the CO surface distance 2.75 Å is shown in Fig. 7.4 b).

**Figure 7.4**: Shows a) the translational motion of the CO on the surface confined by neighboring CO molecules. The distance $d$ is the periodicity in the fitting function for the potential energy in Eq. (7.7). b) shows the fit to the translational potential energy of the CO on the surface with a surface distance of 2.75 Å.

Both the cartwheel and helicopter rotational modes were computed for a single CO in a 2x2 periodic cell. The cartwheel rotation can be approximated with a cosines series

$$f_2(x) = a_0 + a_1 \cos(x) + a_2 \cos(2x) + a_3 \cos(3x) + a_4 \cos(4x) + a_5 \cos(5x).$$ (7.8)

The cartwheel rotation and a fit of the corresponding potential energy is given in Fig. 7.5.

The helicopter rotational degree of freedom is simply given by

$$f_3(x) = V_0 + \Delta E \cos(6v) + \frac{\Delta E}{2},$$ (7.9)

where $v$ is the angle of periodicity, $V_0$ is the lowest potential energy and $\Delta E$ is the difference between the highest and lowest potential energy. The helicopter rotation and a fit of the potential energy is similarly given in Fig. 7.6 a) and b), respectively.
The helicopter rotation is not a normal mode when the CO molecule is close to the surface. As shall be shown later, the parallel orientation of the CO molecule is very unstable close to the surface. In this region, the cartwheel rotation is counted twice in the PMF. At 4 Å surface distance and above, where the parallel CO orientation becomes as stable as the perpendicular, the contributions from both rotations are used instead.

Figure 7.5: Illustrates a) the cartwheel rotational degree of freedom and b) the fitted functional of the cartwheeling rotation potential at 2.75 Å surface distance.

Figure 7.6: Shows a) the helicopter rotational degree of freedom. $\nu$ is the angle of periodicity. b) shows a plot of the potential energy of the helicopter rotational degree of freedom at 2.75 Å surface separation.
7.3.5 Contributions

Figs. 7.7, 7.8 and 7.9 display the translational, cartwheel and helicopter rotational contributions to the PMF, respectively, for 300, 500, 1500 and 2000 K. The translational motion (Fig. 7.7) destabilizes the CO molecule on the surface relative to the gas phase, when temperature is increased in the PMF. Furthermore, as the temperature rises the contribution to the PMF from the degree of freedom starts to create a barrier. Similar results are obtained for the cartwheel rotational contribution (Fig. 7.8) only more enhanced. The low temperature plots barely show a barrier for both rotations, contrary to the higher temperatures. For the helicopter rotation the plot is made using $V_0$ (the MEP potential energy) as a reference, since $V_0^{\text{fit}}$ deviates grossly from the MEP potential, due to the fact that the CO parallel to the surface is a highly unstable orientation. Since the helicopter rotation is not a normal mode in this region the rotational cartwheel contribution is counted twice and only for surface separations of 4 Å and above, where the helicopter potential (and PMF) is as stable as the cartwheel, is the contribution added. The most noteworthy thing about the helicopter rotational contribution to the PMF is that it seems to be completely independent of temperature.

![Figure 7.7: Shows the contribution from the translational motion to the PMF for 300, 500, 1500 and 2000 K.](image-url)
Figure 7.8: Shows the PMF for the cartwheel rotations at 300, 500, 1500 and 2000 K.

7.3.6 Discussion of PMF

As can be seen from the total PMF curves in Fig. 7.10, when the temperature increases two minima start to develop: the chemisorption minimum and a second minimum associated with a precursor state for adsorption or desorption [242, 243]. At high temperature the loss of entropy in the strongly adsorbed state, where the rotations and translations of the CO molecule are frustrated, means that the free energy increases substantially relative to the gas phase. Contrary, in the precursor state the CO molecule is nearly free to rotate and to move parallel to the surface, only limited by the coverage. Here, the entropy loss is minimal. In other words, there are fewer accessible degrees of freedom available to contribute to the entropy for CO molecules at the surface compared to in the precursor state. The insert in Fig. 7.10 shows the PECs of the parallel and perpendicular orientations of the CO molecule. The rotational polarization, which has previously been suggested to be important for the precursor state [243], is clearly seen to be present for the CO desorption/adsorption on Ru(0001). Note that the chemisorbed state is found with an adsorption energy of 1.4 eV, in good agreement with the experimentally determined value of 1.6 eV [249]. Furthermore, the free energy differences, \( \Delta G \), of the extrema for instance, directly give the transition-state-theory rate constant for desorption (or
Figure 7.9: shows the helicopter rotation contribution to the PMF for 300, 500, 1500 and 2000 K. Note that $V_0$ from the MEP has been used here instead of the fitted potential energy since the perpendicular CO configuration deviates grossly from the MEP potential.

adsorption).

Fig. 7.10 is consistent with the following qualitative picture of the experiment. After the initial laser pulse the adsorbate temperature increases to a value in the range 1500-2000 K [Paper 3 supporting material], where the free energy of the precursor state becomes comparable to that of the chemisorbed state and a substantial fraction of the adsorbed CO molecules shift to this state.

The calculated XES spectra [250] in the precursor state are displayed in Fig. 7.11 [Paper 3]. As observed experimentally [250], the $d_\pi$ intensity vanishes and the $\sigma_\pi$ orbital shifts towards the gas phase position at higher energy; hence the experimentally observed weak remaining $d_\pi$ intensity indicates a fraction of molecules is trapped in the inner chemisorbed well [Paper 3]. The major spectroscopic difference between the gas phase and the precursor state is in the XAS resonance position, where the shift from the gas phase value is still distinct, as seen in Fig. 7.11. The result shows that in the precursor state the anti-bonding CO orbitals, which have a large spatial extent, still interact significantly with the metal states. Half of the $d_\pi$ intensity disappears after a while indicating that at least half of the molecules are pumped into the precursor
state consistent with the two states having comparable free energies [Paper 3].

Some of the CO molecules desorb during the experiment; however, as the system cools down the free energy barrier for entering the chemisorption state decreases and molecules can re-adsorb.

![Figure 7.10: The PMF for CO adsorption/desorption on Ru(0001) at 0 K (minimum energy path, MEP) and 300, 500, 1500 and 2000 K [Paper 3]. The insert shows the PEC (0 K) of the CO molecule with orientation parallel and perpendicular to the Ru(0001) surface. The surface distance is measured between the CO center-of-mass and the surface. At 0 K and distances smaller than 2.5 Å CO moves from on-top to bridge and hollow sites giving less strong repulsion compared to the finite temperatures where more repulsive orientations are sampled.]

### 7.4 Summary

The theoretical results presented in this chapter support and help interpret a very recent pump-probe experiment at LCLS. In the experiment a Ru(0001) crystal was excited by a laser pulse and the CO adsorbate was subsequently studied using XAS and XES. These core-level spectroscopy methods were chosen to study the time evolution of the electronic structure of CO since they give element-specific results and the measurements are performed on a femtosecond
Figure 7.11: Computed XES spectra of CO on Ru(0001) at distances corresponding to the minimum in the chemisorption state (blue) and at the precursor state (red and dashed) in Fig. 7.10 [Paper 3]. The spectra are resolved in $p_{xy}$ and $p_z$ components to clarify. S indicates the distance from the Ru surface to the center of mass of the CO molecule. The calculated spectra are shifted so that the energy position of the $1\tilde{\pi}$ state is aligned with that of the corresponding experimental spectrum. As the molecule moves to the precursor state we observe a shift of the $5\tilde{\sigma}$ component towards higher energy and the $\tilde{d}_{\pi}$ state vanishes as the interaction with the substrate decreases.
timescale. The experimental results indicate an initial weakening of the CO to substrate binding without desorbing. After 25 ps around 30% of the molecules have desorbed while the remaining re-adsorb.

To understand this the PMF has been considered. The PMF is a classical expression for the free energy, where all degrees except the surface separation are integrated out to give a thermal average. The PMF is temperature dependent and includes entropic effects. The PMF was calculated by sampling the cartwheel and helicopter rotations, as well as the translational degree of freedom using the newly developed BEEF-vdW functional. The correct description of the long-range interactions is essential in order to get a stable plateau at large surface separations for the potential, which in the PMF becomes a second minimum at high temperatures. When temperature rises, the PMF starts to build a barrier between 3 and 3.5 Å surface separation. The barrier stems from the translational degree of freedom and the cartwheel rotation. The qualitative picture of the experiment can be understood as follows: initially the CO molecules are hot from the laser pulse and the chemisorbed minimum is comparable with the precursor minimum, and therefore approximately half of the CO molecules are transferred to the outer minimum where some desorb; however, most get trapped. When the temperature decreases so does the barrier of the PMF allowing the molecule to return to the chemisorption minimum. This picture is consistent with the experimental observations, and the calculated XES spectra. The experiment provides the first direct spectroscopic observation of a transient precursor state in desorption and in adsorption.
Part V

Conclusions
Chapter 8

Future Challenges

Doing material design and development in vdW density functional theory has the advantage that the unemployment line is short; however, the disadvantage is that spare time is scarce. In short, there are many challenges and interesting ideas to pursue. This short chapter gives an overview of which problems and limitations that occurred during my PhD process, as well as what ideas have been sparked. There are plenty other issues to investigate, I have merely chosen to discuss the challenges directly resulting from my project.

8.1 Water

The current dispute concerning the structure of liquid water at ambient conditions is by no means resolved. The AIMD vdW-DF type water simulations presented here open the door to even more interesting investigations. The question: "What is the microscopic structure of water?" still remains. More specific and less grandeur questions are also very relevant, such as: "What is the ideal density for water simulations using various vdW-DFs?" How does the water structure simulated using vdW-DF XC functionals change as a function of density?" Other interesting studies could be AIMD simulations of water at ambient conditions using the newly developed BEEF-vdW functional, large scale AIMD simulations, and simulations using the NVT or NPT ensemble. Many of these studies are unfortunately not presently feasible due to the limitations in the current implementation of the vdW functionals (only parallelizes up to 20 CPUs).

8.2 Exchange-Correlation Functionals

Further development of semi-empirical functionals could be based on the three pillars model space, datasets and fitting procedure, described in Chapter 5. The three pillars and suggestions on how to proceed are illustrated in Fig. 8.1.
The fitting procedure gives a robust and general framework for creating future semi-empirical functionals. It is the author’s opinion that the BEEF-vdW XC functional has pushed the model space, GGA plus vdW, to its limit. To make any drastic improvement in performance or include new properties, without severely worsening the performance on the currently included properties, the complexity of the model space needs to be increased. Fortunately, multiple options for expanding the model by adding other physical terms currently exist. Examples are: including a plus U term [251, 252], self-interaction correction term [253], or inclusion of a fraction of exact exchange [254]. The next step on "Jacob’s ladder", and also the most logical choice to pursue, is MGGA [101].

Two of the current limitations in the BEEF-vdW functional are the performance on gas phase reactions and barriers. It is well known that hybrid functionals perform much better on gas phase barrier heights [255], and from this study it is clear, that the same holds true for gas phase reactions. This makes including exact exchange an appealing option. Conversely, the computational burden for exact exchange makes it less applicable for for studying surface science.

Fitting to several datasets simultaneously is a compromise between the various properties included in the fit. Creating a functional with focus on other datasets would produce a different XC functional with other capabilities. BEEF-vdW was developed to be a generally applicable functional for chemistry on surfaces and vdW interactions. So, choosing other datasets, the same procedure could be an option if another focus is desired. As the model complexity increases, it is natural to include more datasets or expand on the ones included, thereby creating better statistics to obtain an improved fit. S66×8 is an example of of an expanded dataset [256]. Lastly, the fitting procedure can still be improved. A more explicit method for weighing the datasets is desired. Even though the weights of the datasets were found using the product of cost functions, somewhat arbitrary weights were still chosen to politically decide that one property was more important than others. A more unbiased and automatic approach could be developed.

All three pillars: model complexity, datasets and fitting procedure, go hand in hand. Improvement in one area will prompt improvement in the other. With that being said, it seems evident that expanding the model complexity first is essential. This will undoubtedly induce further development in the two remaining areas.

8.3 Applications

When a new approximation for the XC functional is introduced, it needs to be thoroughly tested to probe strengths, weaknesses and discover suitable applications. In this study, the BEEF-vdW has been tested on numerous datasets. Nevertheless, to fully understand the functional, more examinations are required. In particular, testing on independent datasets, which were not used in the training of the functional, is essential in order to get a proper assessment.
Figure 8.1: The three pillars of semi-empirical development of XC functionals and possible future options to include for each.
of the transferability of BEEF-vdW. This should include properties and chemical species that are significantly different from the ones used to obtain the fit. Lastly, the BEEF-vdW XC functional was made for first-principle usage. The benchmarking in this study shows that it performs overall very well on a wide range of systems making it highly applicable. The possible interesting applications are too numerous to list here; however, the accuracy on chemical and - at the same time - vdW systems makes it relevant for systems in which the balance or transition between these two interactions is central.
Chapter 9

Summary

In this thesis novel results have been presented within the field of van der Waals interactions in density functional theory.

The two new van der Waals exchange-correlation functionals vdW-DF2 and optPBE-vdW show promising description of small water clusters, i.e., the PEC for the water dimer and the energetics of water hexamers. The latter has until now been incorrectly described in density functional theory. This motivated a study where the exchange-correlation functionals were applied in ab initio molecular dynamics simulations of ambient water to help resolve the current dispute in the field, where two opposing water models currently exist. Including van der Waals interactions was seen to produce much softer water structures in the simulations. This was clear from the fewer number of hydrogen bonds and the lowering of the first peak in the O-O pair-correlation function. Nevertheless, the structure from the second solvation shell is completely smeared out in the O-O pair-correlation functions and the third peak is pushed inwards to shorter distances. The O-O pair-correlation functions resembles high-density liquid significantly. Similarly, the structures obtained without the van der Waals interactions using the PBE exchange-correlation functional resembles low-density liquid water. A mixture of 30% low-density liquid and 70% vdW-DF2 (with high-density liquid-like structure) gives direct agreement with recent experimental O-O pair-correlation functions. Interestingly, this is the same fraction estimated by x-ray emission spectroscopy studies showing that the van der Waals simulation results potentially could be consistent with the bimodal model of water. In this way, the directional hydrogen bond and the isotropic van der Waals interactions could act as antagonists producing fluctuations between the high-density and low-density liquid structures.

A pragmatic molecular fitting approach has been used to produce a new van der Waals functional termed BEEF-vdW. The model space consisted of a flexible generalized gradient approximation basis set of Legendre polynomials for the dominant exchange part, and a linear combination of LDA, PBE and vdW-
DF2 non-local correlations. A number of diverse datasets representing gas phase chemistry, dispersion dominated systems, solid state physics, and chemisorption were used as training data in order to produce a generally applicable exchange-correlation function. The model selection used for the BEEF-vdW functional is a two-step process. First the function is fitted to the individual datasets, and subsequently the compromise between the various dataset fits is found. To control the model complexity, a fitting scheme originating from Bayesian statistics was presented. A regularization term was added to the least squares fit in the cost function, which punished non-smooth functions. The regularization strength was determined by using the .632 Bootstrap method to minimize the expected prediction error. To find the compromise between the individual fits, the weighed product of relative cost functions was minimized. Minimizing the relative product of cost functions means, that if the compromising solution vector is changed, the relative cost increase on one dataset must result in a larger corresponding decrease in the relative cost functions of the complimentary datasets to be preferred. The final functional ended up having reduced the number of effective parameters from 31 to only 7.11.

An attractive property of the BEEF-vdW functional is that error estimation is easily obtained from a distribution of functionals around the ideal solution. In this way a calculation can be presented with an estimate of how much the number should be trusted. Unfortunately, the systematical errors pertaining to the incomplete model space cannot be revealed by the method, since it is solely based on the model.

The BEEF-vdW functional was benchmarked along with various other exchange-correlation functionals ranging from LDA, generalized gradient approximation, meta generalized gradient approximation, hybrids to vdW-DFs. The study confirmed that BEEF-vdW is a generally applicable functional, non-biased towards any of the studied properties as opposed to most other exchange-correlation functionals. Furthermore, including independent data points in expansions of the datasets used in the fitting scheme indicates transferability of the functional. The BEEF-vdW functional also reveals the limitation of the model space as gas phase barrier heights are systematically underestimated and gas phase reaction energies are predicted less accurately than formation energies.

The BEEF-vdW functional was applied to a study of desorption of CO from Ru(0001). The study was motivated by a novel pump-prope experiment at Stanford Linear Accelerator Center resulting in a spectroscopic measurement of a precursor state. In this experiment, a laser was used to excite the surface heating it locally. x-ray absorption and x-ray emission spectroscopies where used to measure the time evolution of the system. The experiment indicated that the CO molecules on the surface get heated, and after 10 ps around half of the molecules are trapped in a transient state, where they are not quite desorbed, but the bonding to the surface is greatly weakened. After 25 ps 30 % of the CO molecules are re-adsorbed, while 70 % are desorbed completely. To fully understand the experiment the potential of mean force has been calculated using the BEEF-vdW exchange-correlation functional. The potential of mean
force is an estimation of the Gibbs free energy, where all degrees of freedom except the reaction coordinate have been thermally averaged. It is essential that the functional can describe both chemical region and long-range region correct in order to calculate the desorption. Contrary to common generalized gradient approximation exchange-correlation functionals, BEEF-vdW is able to describe an attractive plateau in the potential energy curve, which is crucial for the theoretical interpretation of the experiment. When temperature rises the potential of mean force develops a barrier and the attractive plateau at large surface separations becomes a shallow well corresponding to the precursor state. The barrier arises from the loss of a degree of freedom, since the CO parallel to the surface is highly unstable. The experiments can be understood in the following way: initially, when the surface and CO molecules are hot, the chemisorbed and precursor minima are similar in energy and around half the CO molecules are transferred to the outer minima. As the temperature decreases so does the barrier and the CO molecules that have not yet desorbed are re-adsorbed to the chemisorbed state.
Bibliography


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[93] The gpaw and ase codes are available as parts of the CAMPOS software: http://www.camd.dtu.dk/Software.


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[204] June 2012.


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Appendix A

Datasets
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<th>Reaction</th>
<th>$\Delta_e E$</th>
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<td>$N_2 + 2H_2 \rightarrow N_2H_4$</td>
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<td>$N_2 + O_2 \rightarrow 2NO$</td>
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</tr>
<tr>
<td>$N_2 + 3H_2 \rightarrow 2NH_3$</td>
<td>-1.68</td>
</tr>
<tr>
<td>$O_2 + 2H_2 \rightarrow 2H_2O$</td>
<td>-5.45</td>
</tr>
<tr>
<td>$N_2 + 2O_2 \rightarrow 2NO_2$</td>
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</tr>
<tr>
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</tr>
<tr>
<td>$2N_2 + O_2 \rightarrow 2N_2O$</td>
<td>1.57</td>
</tr>
<tr>
<td>$2CO + O_2 \rightarrow 2CO_2$</td>
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</tr>
<tr>
<td>$CO + 3H_2 \rightarrow CH_4 + H_2O$</td>
<td>-2.80</td>
</tr>
<tr>
<td>$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$</td>
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</tr>
<tr>
<td>$CH_4 + NH_3 \rightarrow HCN + 3H_2$</td>
<td>3.32</td>
</tr>
<tr>
<td>$O_2 + 4HCl \rightarrow 2Cl_2 + 2H_2O$</td>
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</tr>
<tr>
<td>$2OH + H_2 \rightarrow 2H_2O$</td>
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</tr>
<tr>
<td>$O_2 + H_2 \rightarrow 2OH$</td>
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</tr>
<tr>
<td>$SO_2 + 3H_2 \rightarrow SH_2 + 2H_2O$</td>
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</tr>
<tr>
<td>$H_2 + O_2 \rightarrow H_2O_2$</td>
<td>-1.68</td>
</tr>
<tr>
<td>$CH_4 + 2Cl_2 \rightarrow CCl_4 + 2H_2$</td>
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<td>$CH_4 + 2F_2 \rightarrow CF_4 + 2H_2$</td>
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</tr>
<tr>
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</tr>
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<td>$CH_4 + CO_2 \rightarrow 2CO + 2H_2$</td>
<td>3.11</td>
</tr>
<tr>
<td>$3O_2 \rightarrow 2O_3$</td>
<td>2.92</td>
</tr>
<tr>
<td>methylamine + $H_2 \rightarrow CH_4 + NH_3$</td>
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</tr>
<tr>
<td>thioethanol + $H_2 \rightarrow H_2S + ethane$</td>
<td>-0.71</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
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<td>$4CO + 9H_2 \rightarrow$ trans – butane + $4H_2O$</td>
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<tr>
<td>ethanol → dimethylether</td>
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<tr>
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<td>propyne + $H_2 \rightarrow$ propene</td>
<td>-2.00</td>
</tr>
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<td>propene + $H_2 \rightarrow$ propane</td>
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<tr>
<td>allene + $2H_2 \rightarrow$ propane</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>$CH_2 + CO_2 \rightarrow$ aceticacid</td>
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</tr>
<tr>
<td>$CH_4 + CO + H_2 \rightarrow$ ethanol</td>
<td>-0.91</td>
</tr>
<tr>
<td>$1,3 - cyclohexadiene \rightarrow 1,4 - cyclohexadiene$</td>
<td>-0.01</td>
</tr>
<tr>
<td>benzene + $H_2 \rightarrow 1,4 -$ cyclohexadiene</td>
<td>-0.01</td>
</tr>
<tr>
<td>$1,4 - cyclohexadiene + 2H_2 \rightarrow$ cyclohexane</td>
<td>-2.94</td>
</tr>
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</table>

Table A.1: Gas phase reactions and the corresponding reaction energies (in eV) constituting the RE42 dataset. The experimental reaction energies are compiled from the G2/97 static-nuclei formation energies. Negative reaction energies are exothermic.
Table A.2: Experimental reaction energies, $\Delta E$, for chemisorption on late transition metal surfaces in the CE27 dataset. Reactions in the subset CE17 are marked with a "$\star$". All chemisorption energies are in eV per adsorbate at a surface coverage of 0.25 monolayers (ML), except where otherwise noted. The adsorption mode is indicated by "m" (molecular) or "d" (dissociative), along with the adsorption site. Chemisorption energies for O have been evaluated as $\frac{1}{2}(\Delta E(O_2) - E_b(O_2))$ with $E_b(O_2) = 118$ kcal/mol [267] for the dioxygen bond energy.

<table>
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<th>Mode</th>
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<th>Reference(s)</th>
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</tr>
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<td>hollow</td>
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<td>CO/Rh(111)</td>
<td>$\star$</td>
<td>m</td>
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<tr>
<td>CO/Pd(111)</td>
<td>$\star$</td>
<td>m</td>
<td>fcc -1.48</td>
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<tr>
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<td>m</td>
<td>top -1.58</td>
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<td>m</td>
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<td>m</td>
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<td>N$_2$/Fe(100)$^2$</td>
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Table A.3: Experimental solid-state properties of 27 cubic bulk solids. The ZPAE exclusive Sol27LC zero Kelvin lattice constants, $a_0$ (Å), are adapted from Ref. [223]. Zero Kelvin Sol27Ec cohesive energies, $E_c$ (eV/atom), from Ref. [36] are corrected for ZPVE contributions. Strukturbericht symbols are indicated in parenthesis for each solid. A1: fcc, A2: bcc, A3: hcp, A4: diamond.

<table>
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Appendix B

Benchmarking
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</tr>
<tr>
<td>vDW-DF</td>
<td>-0.54</td>
<td>0.60</td>
</tr>
<tr>
<td>vDW-DF2</td>
<td>-0.58</td>
<td>0.64</td>
</tr>
<tr>
<td>optPBE-vdW</td>
<td>-0.12</td>
<td>0.27</td>
</tr>
<tr>
<td>optB88-vdW</td>
<td>0.01</td>
<td>0.25</td>
</tr>
<tr>
<td>C99-vdW</td>
<td>0.42</td>
<td>0.43</td>
</tr>
<tr>
<td>BEEF-vdW</td>
<td>-0.37</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Table B.1: Deviation statistics for the Sol27Ec cohesive energies (eV/atom) and Sol27LC lattice constants (Å). Zero-point vibrational effects have been removed from both experimental datasets.
vdW interactions in simulations of water Ab initio van der Waals interactions in simulations of water alter structure from mainly tetrahedral to high-density-like


Ab Initio van der Waals Interactions in Simulations of Water Alter Structure from Mainly Tetrahedral to High-Density-Like


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ABSTRACT: The structure of liquid water at ambient conditions is studied in ab initio molecular dynamics simulations in the NVE ensemble using van der Waals (vdW) density-functional theory, i.e., using the new exchange--correlation functionals optPBE-vdW and vdW-DF2, where the latter has softer nonlocal correlation terms. Inclusion of the more isotropic vdW interactions counters highly directional hydrogen bonds, which are enhanced by standard functionals. This brings about a softening of the microscopic structure of water, as seen from the broadening of angular distribution functions and, in particular, from the much lower and broader first peak in the oxygen–oxygen pair-correlation function (PCF) and loss of structure in the outer hydration shells. Inclusion of vdW interactions is shown to shift the balance of resulting structures from open tetrahedral to more close-packed. The resulting O–O PCF shows some resemblance with experiment for high-density water (Soper, A. K.; Ricci, M. A. Phys. Rev. Lett. 2000, 84, 2881), but not directly with experiment for ambient water. Considering the accuracy of the new functionals for interaction energies, we investigate whether the simulation protocol could cause the deviation. An O–O PCF consisting of a linear combination of 70% from vdW-DF2 and 30% from low-density liquid water, as extrapolated from experiments, reproduces near-quantitatively the experimental O–O PCF for ambient water. This suggests the possibility that the new functionals may be reliable and that instead larger-scale simulations in the NPT ensemble, where the density is allowed to fluctuate in accordance with proposals for supercooled water, could resolve the apparent discrepancy with the measured PCF.

INTRODUCTION

Liquid water plays a crucial role in all biological and numerous chemical processes, which has provided the incentive for many detailed experimental and theoretical studies probing both structural and dynamical properties of the fluid. However, the microscopic structure of ambient liquid water is still a matter of current debate.1–27 In particular, two classes of models are currently being considered, where the traditional model of water is based on a continuous distribution of distorted tetrahedral structures. This is typical of what most molecular dynamics simulations currently give. However, most of these simulations give overstructured O–O and O–H pair-correlation functions (PCFs) and show discrepancies in comparison to X-ray and neutron scattering experimental data.11,15 It is, however, possible to generate a more distorted tetrahedral structure model that is consistent with the diffraction data, but equivalent agreement is seen also for alternative asymmetrical and mixture models illustrating that diffraction data do not discriminate between differently hydrogen-bonded (H-bonded) structure models.11,15,28

Based on recent findings correlating X-ray emission spectroscopy (XES) with X-ray Raman scattering (XRS) and small-angle X-ray scattering (SAXS) data,16 a model has been suggested where a division into contributions from two classes of local instantaneous H-bonded structures is driven by incommensurate requirements for minimizing enthalpy and maximizing entropy; in particular, the XES data show two well-separated peaks that interconvert but do not broaden with changes in temperature.15,16,20,25 In the proposed picture the dominating class at ambient

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temperatures consists of a continuum of structures with some resemblance to high-pressure water, but with a further expanded first shell (more distorted H-bonds) and more disorder in the second shell; this was based on the temperature dependent shift of the dominating peak in the XES spectra, indicating more thermal distortion and disorder with increasing temperature. The second class corresponds to fluctuations where regions of strongly tetrahedral structures (similar to low-density water) appear in different sizes and shapes as the molecules attempt to form enthalpically favored tetrahedral H-bond structures, resulting in mean size interpreted from the SAXS data as \( ~1 \text{nm} \), but naturally many sizes and shapes would appear. It should be emphasized that, because these are fluctuations, no strict boundaries between the two classes should be expected.

The attosecond (XRS, SAXS) to femtosecond (XES) time scales of the experimental probes are too fast for molecular motion to be followed and the experimental data thus correspond to a statistical sampling of instantaneous, frozen local structures in the liquid; no experimental information on the time scale of such fluctuations is thus currently available. Besides being consistent with both neutron and X-ray diffraction, this picture was recently also shown to bring a consistency between X-ray diffraction and extended X-ray absorption fine structure (EXAFS) data, requiring both disordered structures and a fraction of molecules with straight, strong hydrogen bonds. However, other opinions exist regarding the interpretation of the new SAXS, XES, and XRS data. On the other hand, recent SAXS data extending into the supercooled regime and supported by theoretical simulations as well as recent high-quality X-ray diffraction data resolving shell structure out to 12 \( \AA \) even in ambient and hot water, but contributed by a minority species, provide support for the original interpretation in this debate.

Most simple rare gas solids and liquids have a nearest-neighbor coordination of 12 whereas hexagonal ice, due to the directional H-bonds has a coordination of only 4. The latter leads to large open volumes in the ice lattice and a resulting low density. The dispersion, or van der Waals (vdW) force, in condensed rare gases leads to nondirectional, isotropic interactions, and closer packing. Similarly, the inclusion of vdW interactions in ab initio simulations of water may counteract the directional interactions and lead to better agreement with, e.g., experimental PCFs. Here it should be understood that, while this could be regarded as a minimum requirement of a water model, it is by no means sufficient for a complete description. Interestingly, it has been argued on thermodynamic grounds that over a large range of the liquid—vapor coexistence line the averaged water interaction potential should resemble that of liquid Argon, i.e., not be determined by directional H-bonding.

Water shows many anomalies in its thermodynamic properties, such as compressibility, density variation, and heat capacity. In attempts to explain this, directional H-bonds and more isotropic vdW forces are key concepts. While vdW forces are well-defined as results of nonlocal electronic correlations, there is no unique way to characterize H-bonds in terms of topology or interaction strength. And yet “the H-bond governs the overall structure and the dynamics of water”.

One of the models to explain the enhanced anomalies in supercooled water is the liquid—liquid critical-point (LLCP) hypothesis, with the most substantial role played by cooperative H-bond interactions among the water molecules. The LLCP model explains the significant increase in density fluctuations upon supercooling water, which is evidenced by the anomalously increasing isothermal compressibility, as resulting from attempts to locally form enthalpically favored open tetrahedrally coordinated H-bond regions. It furthermore connects the deeply supercooled liquid state of water to the polymorphism seen in ices, i.e., the distinct low-density and high-density amorphous ice phases (LDA/HDA). A high-density liquid (HDL) phase transforms to an ordered low-density phase (LDL) in the deeply supercooled region through a first-order phase transition at high pressures above the LLCP and through a continuous smooth transition upon crossing the Widom line at pressures below the critical. There are differences in their respective local structures; in pure HDL the local tetrahedrally coordinated H-bond structure is perturbed by a partially collapsed second coordination shell, while in the LDL a more open and locally “bulk-ice-like” H-bond network is realized.

The combined XES, XAS, and SAXS results described above, which indicate nanoscale density and structural fluctuations, can be easily interpreted as reflections of this “competition” between the two local forms, HDL (maximizing entropy) and LDL (minimizing enthalpy) and thus viewed as extending an established picture of supercooled water into the ambient regime. Whether HDL and LDL can exist as pure phases, accompanied by a liquid—liquid phase transition and a critical point, is still unresolved and alternative models, e.g., singularity-free (SF), critical-point-free (CPF), and stability limit (SL) conjecture scenarios have been proposed, however, still building on structural HDL/LDL fluctuations.

In the quantitative characterization of water, computer simulations play a vital role. Empirical force fields are frequently applied but with questionable transferability, because force fields are parametrized against experimental data or against a, by necessity, limited set of quantum chemically computed structures. Furthermore, many-body interactions beyond pair-interactions are frequently not taken into account.

These deficiencies are eliminated in Car–Parrinello (CP) and Born–Oppenheimer (BO) molecular dynamics (MD), collectively known as ab initio (AI) MD. In AIMD, the forces are calculated using a first-principles electronic structure method, typically based on density functional theory (DFT). BOMD, used in the present study, minimizes the Kohn–Sham energy functional at each time step, keeping the nuclear positions frozen. In nearly all force field and AIMD simulations of water at ambient conditions there seems to be a strong driving force to form highly directional H-bonds, leading to tetrahedral structures that are in general overstructured in terms of the derived PCFs. One exception is the coarse-grained mW water model, which has two terms in the interaction potential corresponding to anisotropic tetrahedral interactions and isotropic vdW interactions, respectively, and which gives a maximum peak height of 2.3 in the O–O PCF at room temperature, in close agreement with recent analyses of experimental diffraction results. This model was shown to feature fluctuations between tetrahedral and disordered species resulting in a liquid—liquid transition in the supercooled region. Empirical force-field models that have overstructured PCFs in agreement with older determinations have, however, also been shown to exhibit liquid—liquid phase transitions in the supercooled regime, e.g., refs 40, 59, 60, and 61, indicating that the PCFs are not decisive for general trends in the thermodynamic behavior in water simulations.

Until recently, AIMD simulations of water have almost exclusively been performed with the BLYP and PBE exchange–correlation (XC) functionals. However, these functionals are...
shown to significantly overstructure liquid water, as seen from the maximum value and sharpness of the first peak in the oxygen–oxygen PCF compared to recent data and analyses. MD simulations of water have furthermore been shown to depend on which functional is applied and to give different predictions for different XC functionals. MD simulations performed using functionals based on the generalized gradient approximation (GGA) tend to overstructure liquid water and lead to diffusion constants 2–3 times too small compared to experiment; using hybrid functionals only marginally improves the results. In addition, it has been shown that PBE-based AIMD simulations lead to a melting point of ice at 417 K and therefore simulations at ambient conditions with this functional will describe a deeply supercooled state that is strongly overstructured with respect to real liquid water at ambient conditions. However, inclusion of vdW forces has been demonstrated to significantly lower the melting point where, e.g., the BLYP-D functional with empirical vdW forces was shown to lower the melting point from >400 K with the BLYP functional to 360 K, this is still significantly higher than the 273 K observed for real water, which indicates that, with further improvement, the melting point in ab initio based simulations should approach the observed solid–liquid equilibrium state point from above and simulations at a given temperature are thus likely to represent a cooler, rather than hotter, state than the real liquid. Due to computational cost we have not endeavored to determine the melting-points of ice with the used functionals that account for vdW forces. However, as we will show in the following, inclusion of the more isotropic vdW interaction balances the directional forces allowing a partial breakdown of the H-bond network with significant consequences leading to a much less structured liquid.

**METHODS**

Role of van der Waals (vdW) Forces. Small water clusters have been studied using the PBE and BLYP XC functionals, which do not explicitly include vdW interactions, and the results compared to high accuracy methods such as coupled cluster (CCSD(T)) and Møller–Plesset (MP2). With PBE near chemical accuracy for the strength of the H-bond for the water dimer is obtained while BLYP consistently underbinds small water clusters. However, discrepancies arise and increase with the size of the water cluster for both PBE and BLYP. This has been ascribed to the lack of a description of vdW forces. One could thus argue that obtaining the correct result for the water dimer is essential but no guarantee for a correct description because not all physical interactions relevant for larger clusters are sampled by the dimer.

While it is well established that at low temperatures H-bonds give the major contributing factor to the dynamics and structure of water, vdW interactions have also been suggested to be important. In line with this, thermodynamic considerations have led to the suggestion that at higher temperatures the averaged water interaction potential should resemble that of liquid argon. The angular dependence of the H-bond is anticipated to have a big impact on the PCF and self-diffusion coefficient. If, for example, it is too difficult to bend a DFT H-bond, the diffusion coefficient should come out too small, which it does. Many other suggestions to explain the too small diffusion coefficient exist however, but balancing the directional H-bond interactions with more isotropic vdW forces would intuitively contribute to softening the H-bond network and allow more efficient diffusion. Traditional local and semilocal DFT do not, however, contain nonlocal vdW interactions, e.g., BLYP being especially incapable of describing dispersion. Influences of vdW interactions have been investigated using MD based on empirical potentials, e.g., performed with a dispersion-corrected BLYP XC functional, or using empirically damped \( C_{6} R^{-6} \) corrections to describe the vdW interactions.

A way to introduce vdW forces in DFT from first principles is provided by the van der Waals density functional vdW-DF, recently used for the first time in AIMD on liquid water. The inclusion of vdW forces using the vdW-DF was shown to greatly improve water’s equilibrium density and diffusivity. However, the vdW-DF MD also produces a collapsed second coordination shell, giving rise to new structural problems that have been suggested to depend partially on the choice of exchange used in the vdW functional.

The vdW-DF method proposed by Dion et al. accounts for exchange by a functional that gives Hartree–Fock-like repulsion at relevant separations and that includes nonlocal correlation, and thus vdW forces, by calculating the dielectric response in a plasmon-pole approximation. It gives the correct stability trend for low-lying water hexamers but returns a significant underbinding for most H-bonds. The underbinding can be remedied by using an exchange functional that gives more binding at typical H-bond separations, like the PW86, optPBE, and C09 exchange functionals. Recently Klimes et al. proposed a new vdW density functional, optPBE-vdW, based on the original vdW-DF functional. This scheme shows promise in the description of dispersion and H-bonded systems, as it reduces the underbinding given by the vdW-DF down to chemical accuracy while preserving the correct hexamer trends. However, this improved behavior is obtained at the cost of poorer performance on the binding energy of small molecules. Very recently a second version of the vdW-DF, called vdW-DF2, was suggested, using a new nonlocal correlation functional along with a slightly refitted version of the PW86, called PW86R as an appropriate exchange functional. Both optPBE-vdW and vdW-DF2 give chemical accuracy for the water dimer, albeit with a slightly different balance between nonlocal correlation and exchange contributions. In the present study we therefore wish to investigate the microscopic structure of liquid water by performing AIMD using both the new optPBE-vdW and vdW-DF2 XC functionals to also investigate the importance of the balance between correlation and exchange in liquid water AIMD simulations.

optPBE-vdW and vdW-DF2 Exchange—Correlation Functionals. In general a vdW-DF functional takes the form

\[
E_{xc} = E_{xc}^{GGA} + E_{xc}^{LDA} + E_{xc}^{nl}
\]

where \( E_{xc}^{GGA} \) is an exchange functional using the generalized gradient approximation (GGA) and \( E_{xc}^{LDA} \) accounts for the local correlation energy by using the local density approximation (LDA). LDA is chosen to avoid double counting of correlation. The nonlocal correlation energy describing the vdW interaction is given by the six-dimensional integral

\[
E_{xc}^{nl} = \frac{1}{2} \int \int n(r) \phi(r,r') n(r') \, dr \, dr'
\]

where \( \phi(r,r') \) is the interaction kernel and depends on the density and its gradient. The nonlocal term is calculated as suggested in...
ref 93. In the original vdW-DF from Dion et al.,\textsuperscript{81} the exchange functional from revPBE\textsuperscript{94} is utilized.

The optPBE-vdW functional is constructed like vdW-DF\textsuperscript{81} but uses an alternative exchange functional. The latter takes the same form as both the PBE and RPBE exchange, but the parameters of the exchange enhancement factor are optimized against the S22 database.\textsuperscript{89,95} The S22 database\textsuperscript{95} is a set of 22 weakly interacting dimers, mostly of biological importance, including the water dimer.

The vdW-DF2\textsuperscript{92} has the form of eq 1 and uses the PW86 exchange,\textsuperscript{96} which is argued in ref 87 to give the most consistent agreement with Hartree–Fock (HF) exact exchange, and with no spurious exchange binding. Furthermore, a new approximation for $E_\text{nl}$ is used to calculate the value of the interaction kernel in eq 2.\textsuperscript{92} This new functional has been shown to give very accurate results for the water dimer as compared to benchmark CCSD(T) calculations\textsuperscript{92,97} and to compare closely to the S22 benchmark.\textsuperscript{98}

**Computational Protocol.** Ab initio molecular dynamics simulations are performed in the NVE ensemble with optPBE-vdW, vdW-DF2, and PBE, using the grid-based real-space projector augmented wave GPAW code.\textsuperscript{99,100} A wave function grid spacing of 0.18 Å and Fermi smearing with a width of 0.01 eV have been used. The grid spacing has been determined by comparing DFT calculations of water hexamers with CCSD(T) results. In the electronic structure calculations a strict energy convergence criterion of $10^{-7}$ eV per electron is used to determine the forces adequately.

All internal bond lengths are kept fixed at 0.9572 Å (an MP2 optimized gas phase geometry obtained from the G2-database)\textsuperscript{101} but angles are allowed to vary (i.e., bending vibrations are included); eliminating the high-frequency OH-stretch allows longer time steps in the simulations albeit introducing some uncertainty,\textsuperscript{102} which, however, is not relevant for the large differences observed in our simulations between the PBE on the one hand and the vdW functionals on the other because all simulations have this constraint imposed. In the initial configuration, 64 water molecules are placed in a simple cubic lattice with random orientations in a cubic periodic box with side lengths 12.42 Å, to reproduce a water density of 1 g/cm$^3$. The geometry is then optimized to obtain a configuration at zero Kelvin (using PBE), from which the MD is started, giving the atoms random velocities according to a Maxwell–Boltzmann velocity distribution corresponding to 2 times 300 K, keeping the center of mass of the box stationary.

Approximately half of the kinetic energy converts to potential energy, thus giving an average temperature around 300 K. An initial equilibration of 10 ps using the PBE XC functional is performed followed by 2.5 ps vdW equilibration of the simulations using optPBE-vdW and vdW-DF2. For all methods equilibration was followed by production runs for 10 ps, which is the minimum time reported necessary due to the slow diffusion of water.\textsuperscript{103} Using 64 water molecules has been shown to be adequate to remove the most significant problems concerning finite size effects\textsuperscript{104} and is feasible within the current computational capabilities. The Verlet algorithm is employed using a time step of 2 fs in the NVE ensemble. With this type of ensemble the temperature is allowed to fluctuate and the average temperature of the PBE, vdW-DF2, and optPBE-vdW simulations were 299, 283, and 276 K, respectively. The same computational setup has been used for the PBE and vdW density functional MD simulations to allow direct comparison of the different models. Because simulations with PBE at ambient conditions describe a deeply supercooled state relative to its melting point at 417 K\textsuperscript{97} the PBE simulations are only performed here to provide a reference for the effects of including vdW interactions through the optPBE-vdW and vdW-DF2 functionals.

**RESULTS**

**Water Dimer.** Before discussing the MD results, we compare the functionals for a simpler but still relevant system: the water dimer. Figure 1a illustrates the potential energy curve for the water dimer calculated using PBE, vdW-DF, vdW-DF2, and optPBE-vdW in comparison with the benchmark CCSD(T) curve from ref 97. Figure 1a shows that the vdW functionals are capable of describing this basic constituent of liquid water extremely accurately, however for different reasons. The nonlocal contribution ($E_\text{nl}$) to the dimer binding from the two functionals is plotted in Figure 1b. The nonlocal part of the optPBE-vdW functional, which is based on the older approximation, is more attractive as mentioned in ref 92. Because less attraction stems from the nonlocal interaction in the vdW-DF2, while the total energy for the dimer is almost identical to that of optPBE-vdW, the remaining part of the interaction energy must give a larger contribution for the vdW-DF2 than for optPBE-vdW. The remaining part of the interaction energy includes electrostatic interaction, electronic correlation, and repulsive exchange.

![Figure 1](dx.doi.org/10.1021/jp2040345)
Because electrostatic interactions only depend on separation, and local correlation is treated identically with the LDA correlation in both cases, this difference has to come from the different choices for the exchange. The PW86 exchange in vdW-DF2 is hence less repulsive than the optPBE exchange in optPBE-vdW; a possible cause of the reported collapsed second-shell structure was in ref 82 suggested to be that the nonlocal parametrization of exchange used in vdW-DF and optPBE-vdW may be too attractive when used in MD. This is, however, not the case, as seen from the pair-correlation functions (PCFs), to be discussed next.

**Pair-Correlation Functions.** Figure 2a illustrates that AIMD simulations of liquid water using vdW-DF2 and optPBE-vdW give very similar O–O PCFs which are, however, very different from the O–O PCF from PBE and, furthermore, from those derived from experiment using either empirical potential structure refinement (EPSR)53 or reverse Monte Carlo (RMC)105 to fit the structure factor. In the simulations both vdW functionals result in the same characteristics as reported in ref 82, including a lower first peak shifted to larger O–O separation than for normal GGAs as well as for experiment on ambient water. The second coordination shell at 4.5 Å is also completely smeared out where correlations from the region 4–5 Å have instead moved into the region 3.3–3.7 Å. The nonlocal correlation differences in the functionals do not, however, result in significantly different O–O PCFs, but we note a somewhat higher (2.5) first peak for vdW-DF2 compared to that for optPBE-vdW (2.3). Because the latter gives a slightly stronger nonlocal contribution, we take this as an indication that it is indeed the vdW contribution that so strongly affects the first shell structure in the simulations.

In contrast, the very recent vdW-DF MD simulation showed that by changing the exchange in vdW-DF from revPBE to PBE, the second shell structure again became well-defined.82 However, the exchange functionals of revPBE and PBE are quite different, making an explanation in terms of the exchange less likely; the potential energy curve of the dimer is furthermore not reproduced very well using the PBE exchange with LDA and nonlocal correlation, suggesting that substituting revPBE by PBE for the exchange does not lead to consistent improvement in the description.

Compared to the experimentally derived O–O PCFs, it is clear that the PCF obtained from PBE is severely overstructured while the simulations including vdW forces have resulted in a significantly less structured PCF than what is experimentally observed for ambient liquid water. Clearly neither simulation model gives direct agreement with the experimental O–O PCF even though, in the case of the vdW functionals, small water clusters are described very accurately. We will address this aspect in the Discussion below.

Some discrepancy in the O–H PCF for the vdW XC functionals compared to experiment is seen in Figure 2b, which we shall now consider. The O–O correlations can be obtained from a Fourier transform of the X-ray diffraction data, if a large enough k-range has been measured and the data can be properly normalized; X-ray scattering is strongly dominated by the electron-rich oxygens. Neutron diffraction data, on the other hand, contain simultaneous information on the H–H, O–H, and to some extent, the O–O PCFs, making a direct Fourier transform to extract a specific PCF inapplicable. Various fitting schemes of structure models to the experimental structure factors have therefore been developed, and we show two such fits to the same experimental data using the EPSR53 and RMC methods, respectively.

There is a significant difference in the first peak position in the intermolecular O–H PCF between the EPSR and RMC fits compared to what is found for the O–O PCF. This can be understood from the relatively lower sensitivity of the neutron data to specifically the O–H correlation in comparison to the sensitivity of X-ray data to the O–O correlation. The EPSR technique uses the assumed reference pair-potential to provide structural aspects not included in the experimental data, while structural aspects not determined by the experimental data, or imposed constraints, will in the RMC technique simply result in a phase-space weighted sampling of structures consistent with the experimental structure factors, combining the two methods thus gives additional information on the uncertainties and assumptions in the resulting fits. It is interesting to note that the RMC method gives a shift in the first peak of the O–H correlation out to nearly 2 Å, which agrees well with the vdW MD simulations presented here, while the EPSR solution is closer in position to the PBE, likely reflecting the SPC/E starting...
force-field in the EPSR fitting procedure. Note that both the RMC and EPSR fits reproduce the experimental scattering data equally well, implying that the position of the first intermolecular OH correlation is not strictly determined by the data, which leaves an uncertainty in the diffraction-derived O–H PCF.\textsuperscript{1,5,107} The first peak in the PBE O–H PCF is clearly too high and the first minimum at 2.5 Å too low, however, while all three simulations exaggerate the height of the second peak at 3.2–3.4 Å; this can, however, be expected to be reduced by including quantum effects, e.g., ref. 108.

Angular Distribution Functions and Hydrogen-Bonding Analysis. The van der Waals functionals provide a smoother angular structure with less tetrahedral bonding, as demonstrated by the angular distribution functions and the average number of H-bonds per water molecule; here we use the cone criterion from ref.2 as a geometric H-bond definition: $r_{\text{OO}} < r_{\text{OO}}^\text{max} - 0.00044 \delta_{\text{HOO}} \cdot$. This defines a cone around each H-bond-donating OH group, where $r_{\text{OO}}^\text{max}$ is the maximum OO distance at zero angle $\delta_{\text{HOO}}$ where $\delta_{\text{HOO}}$ is the H–O–O angle quantifying the angular distortion of the H-bond. Table 1 shows the H-bond statistics for PBE, optPBE-vdW, and vdW-DF2. PBE is seen to prefer a tetrahedral H-bond coordination with a majority of the molecules having 4 H-bonds. Including nonlocal correlation has a large effect where, for both optPBE-vdW and vdW-DF2, the H-bond distribution shifts from a majority with four H-bonds to instead a predominance of species with two or three. Comparing the two vdW functionals, we observe that the optPBE-vdW has a slightly larger amount of water molecules having two or three H-bonds compared to vdW-DF2 which we ascribe to the relatively more repulsive exchange and stronger nonlocal contribution in the former. The vdW-DF2 with its relatively weaker vdW interaction shows slightly higher preference toward forming H-bonds. This analysis suggests that there is a competition between isotropic vdW forces and directional H-bonds, resulting in fewer or more H-bonds per water molecule depending on the applied approximations; however, between the vdW models the average number of H-bonds varies only weakly despite differences in vdW strength.

In this context, where the simulated structure exhibits a large number of broken H-bonds, we need to emphasize the difference between H-bonded structure dynamics and that of individual H-bonds. It has been shown using pump–probe spectroscopy that individual H-bonds are “broken only fleetingly,”\textsuperscript{109} but this has been interpreted incorrectly as also pertaining to dynamics in terms of structure in the liquid. However, the fact that individual hydrogen bonds are broken only fleetingly does not necessarily result in any change of H-bond coordination or even structure. In an asymmetric H-bond-donated situation the two hydrogens can exchange which of the two is bonded and which is free. This leads to only fleetingly broken H-bonds in an HDO vibrationally localized experiment but does not correspond to a fleeting structural situation: the bonding is still asymmetric after the exchange of which of the two, OH or OD, makes the single H/D-bond. Thus, dynamics can occur on different levels and a large number of nonstrongly-H-bonded OH groups in ambient water are thus not excluded by femtosecond pump–probe spectroscopy while they are strongly indicated by X-ray spectroscopy as discussed in the Introduction.

We note in particular the low number of double-donor, double-acceptor tetrahedral molecules according to the cone criterion\textsuperscript{2} for the two vdW models. In fact, the large number of broken H-bonds in the vdW simulations suggests that these models are in closer agreement with predictions from X-ray spectroscopies\textsuperscript{1,2,13,16,23–27} compared to most other AIMD models and future calculated X-ray spectra based on optPBE-vdW and vdW-DF2 structures may provide an interesting opportunity to obtain further insight regarding the interpretation of these spectra.

The angular distribution functions (ADFs) of the H-bonds are shown in Figure 3. The ADFs of H-bond acceptor and donor give information on the orientational flexibility of the water molecules. In the ADFs only the angles between a central molecule and the molecules of the first solvation shell are considered by using a cutoff distance corresponding to the first minimum in the PBE O–O PCF; this distance was applied also to the vdW MDs where the second shell is smeared out and no minimum is visible. Figure 3a displays the distributions of donor angles $\alpha = \angle O–H \cdot \cdot \cdot O$ for the various simulations. The first peak in Figure 3b is $\beta$, the deviation of the O–H···O bond from linearity, which gives information on the flexibility of donor H-bonds, while the second peak is the acceptor angle $\theta = \angle H \cdot \cdot \cdot O–H$. The distribution of angles has been found to depend on the choice of water model.\textsuperscript{16} The picture of a competition between nondirectional vdW interactions and directed H-bonds seems to be supported by the ADFs, as illustrated by the fact that the model without vdW forces (PBE) has no incentive to deviate from a structure of
strong H-bonds, thus resulting in a relatively straight H-bond angle. When vdW forces are included, the H-bonds become significantly more bent. In general, a softening of the structure is seen from the broader ADFs obtained in the case of the vdW-DFs.

**Tetrahedrality and Asphericity.** Two useful measures of the local coordination of molecules in water are the tetrahedrality and asphericity parameters. The former quantifies the degree of tetrahedrality in the nearest neighbor O–O–O angles and is defined as

\[
Q = 1 - \frac{3}{8} \sum_{i<j} \cos \theta_{ij} + \frac{1}{3}
\]

where \(\theta_{ij}\) is the angle formed by two neighboring oxygen atoms \(i\) and \(j\) and the central molecule 0. Only the four nearest neighbors are taken into account, which makes \(Q\) a very local measure. Perfect hexagonal ice gives \(Q = 1\) for all molecules while the ensemble average over an ideal gas gives \(Q = 0\).\footnote{Note} The asphericity parameter is defined as

\[
\eta = \frac{A^3}{36\pi V^2}
\]

where \(A\) and \(V\) are the area and volume of the Voronoi polyhedron of the molecule in question. Contrary to \(Q\), \(\eta\) is sensitive also to interstitial molecules outside the first shell and to the second coordination shell because these add surfaces to the Voronoi polyhedron, making it more spherical. The two relevant limits for water are that of hexagonal ice, which gives \(\eta = 2.25\), and that of a perfect sphere, which gives \(\eta = 1\); larger disorder in the local coordination thus gives smaller values of \(\eta\).

As Figure 4 shows, the inclusion of the vdW interaction not surprisingly has a dramatic effect on both the tetrahedrality and asphericity distributions. The PBE simulation displays a strong peak at \(Q = 0.8\), signifying a dominance of locally tetrahedral O–O–O angles, while both vdW simulations show an attenuation and shift of the high-Q peak to lower tetrahedrality along with the appearance of a strong low-Q peak associated with interstitial molecules at nontetrahedral positions between the first and second coordination shells. Out of the two vdW models, optPBE-vdW is seen to be somewhat less tetrahedral, consistent with their differences in H-bond statistics and PCFs discussed above. This is clearly illustrated by the average tetrahedrality which is 0.692, 0.602, and 0.583 for PBE, vdW-DF2, and optPBE-vdW, respectively. In comparison, the average tetrahedrality has been estimated to be 0.576 using the ESR method;\footnote{Note} note, however, that the tetrahedrality parameter is experimentally rather uncertain; i.e., the same diffraction data have been shown to support tetrahedrality values ranging from 0.488 to 0.603.

An even larger difference is seen in the asphericity distributions; the two vdW models show sharper peaks centered at lower asphericity values compared to PBE. This directly reveals the large disorder in second-shell correlations in the vdW models, resulting from the tendency to form more isotropic local structures when vdW forces are included. Similarly to the comparison between the PCFs of the two vdW models discussed above, it can be seen here that despite nonlocal differences between vdW-DF2 and optPBE-vdW their respective liquid water structures turn out to be rather comparable in terms of both first- and second-shell correlations. The average asphericity is 1.681, 1.552, and 1.552 for PBE, vdW-DF2, and optPBE-vdW, respectively.

**DISCUSSION**

Considering the accuracy of the present versions of nonlocal correlation functionals, as calibrated against benchmark MP2 and CCSD(T) calculations for water dimer, water hexamers,\footnote{Note} the S22 database,\footnote{Note} we will here explore the possibility that the interactions between molecules in the simulation box are given sufficiently accurately by the functionals and that the resulting discrepancy between simulated and observed O–O PCF is rather due to limitations and constraints in the simulation protocol.

Comparison of the results from the simulations using PBE with those including the vdW interactions shows a strong shift in the balance between directional H-bonding and more isotropic interactions; the former leads to tetrahedral H-bond coordination and low density while the latter favors a more close-packed ordering and higher density, as evidenced by the loss of distinction between first and second coordination shells and the reduced number of H-bonds. The simulations have in all cases...
been performed with internal OH distances fixed to the gas phase value; eliminating the high-frequency OH stretch allows longer time steps to be used in the AIMD, but not allowing the internal OH distance to vary according to H-bond situation has been shown to lead to somewhat less structured PCFs in earlier work.102 However, because the simulations with PBE, optPBE-vdW, and vdW-DF2 were all run with the same constraint in terms of internal OH distance this cannot explain the large effects on the O–O PCF from including the vdW nonlocal correlation.

We note that recent, high-precision X-ray diffraction measurements32 of ambient (25 °C) and hot (66 °C) water resolve shell-structure out to ~12 Å, in agreement with conclusions from SAXS,16 shell structure out to the fifth neighbor distance has been resolved before but only for supercooled water.65,114 On the basis of the analysis of large-scale simulations with the TIP4P/2005 force-field115 using the local structure index (LSI),116–119 the shell structure could be assigned as due to an instantaneous LDL-like minority species.32 The observed spatial extent of the correlation (12 Å) is similar to the size of the present simulation box (12.42 Å), making it unlikely that the simulation box is sufficiently extended to support such experimentally observed instantaneous structures.

We compare the PCFs from the simulations performed using the vdW-DF2 and optPBE-vdW XC functionals (Figure 5a), respectively, with the results of a neutron diffraction study47 where LDL and HDL O–O PCFs were extrapolated from data at different pressures; the resulting PCFs are shown in Figure 5b. The EPSR derived HDL PCF is rather similar to the PCF obtained using a Fourier transform of X-ray diffraction data at high pressures120 and furthermore seen to be very similar in terms of the second- and third-shell structure to that derived from vdW-DF2 and optPBE-vdW MD simulations; the effect of increasing pressure on the O–O PCF is that the 4.5 Å correlation disappears and moves to the 3.3–3.7 Å region and the third shell is shifted down to 6 Å120 The O–O PCFs obtained using the vdW functionals similarly show a lack of well-defined structure at 4.5 Å, an increase in correlations at 3.3–3.7 Å, and a shift toward shorter separations in comparison to PBE of the correlation at 6–6.5 Å, as is seen from Figure 5. Both are clear indications toward HDL water. However, in contrast to the high pressure PCFs, a well-defined peak at 3.5 Å is not present in the vdW MD simulations, but only an increase in correlations, and the first peak position is shifted outward, which is not observed for pressurized water.

Assuming that the AIMD simulations with nonlocal correlation and more isotropic interactions have led to a more compact, HDL-like structure, it could be argued that a well-defined peak at 3.5 Å should not be expected because, as deduced from XES spectra at different temperatures,13,16 HDL-like water at ambient conditions should be thermally excited with a more expanded first shell and therefore further disordered in comparison to HDL water obtained under pressure. In particular, entropy effects due to thermal excitations leading to higher disorder can be expected to create a structure where both the first shell and, in particular, the collapsed second shell are distributed over a range of distances, leading to molecules in what is often denoted interstitial positions and with the first O–O peak appearing at longer distance when not under pressure. In this respect a comparison with the amorphous high-density (HDA) and very high-density (VHDA) ices is of interest, where, for VHDA, the second shell moves inward and a peak at 3.4 Å develops while for HDA a peak is found at 3.7 Å and the second peak broadens significantly. This indicates that various interstitial sites may be occupied by making the high-density forms less well-defined.121–126 It should be mentioned that a peak at ~3.7 Å is present in the MD simulation performed by Wang et al.58 using the earlier vdW-DF1 formulation of the functional.

If we consider the proposed model of fluctuations between HDL and LDL,16,127,128 it could well be that the vdW models under the present conditions only generated HDL-like structures while without including vdW the resulting structure is clearly more LDL-like. Having two balancing interactions that favor opposite structural properties is a prerequisite for fluctuations; it is clear that by tuning either the importance of H-bonding or the vdW interaction the preference for either structure will be affected in the simulations. However, if the two proposed structures of liquid water truly do coexist as end points of fluctuations in nanosized patches of different local density, as suggested in ref 16, then an AIMD with only 64 water molecules in a fixed volume may not be suitable to observe this behavior; a much larger box size and an NPT ensemble simulation allowing the box size to vary would be required. The relatively small simulation (12.42 Å box length) and short run time (10 ps) may only observe a local structure of water which, in this picture, is either approximating LDL- or HDL-like. It should be noted that the simulations are run in the NVE ensemble with density fixed to correspond to ambient conditions which, under the assumption that ambient water is dominated by HDL, should furthermore favor an HDL-like structure over fluctuations toward LDL, if energetically allowed, as seems to be the case with vdW interactions included.

Exploring the hypothesis that the experimentally measured O–O PCF in reality is the result of a spatial or temporal average over fluctuating structures as suggested in, e.g., ref 16, and that the vdW-DF2 and optPBE-vdW functionals actually provide a sufficiently accurate interaction potential, we will consider what additional contribution would be required to achieve agreement with the measured O–O PCF. The PCFs are, however, not directly measurable but derived from experimental data and we first need to discuss specifically the choice of O–O PCF for the comparison because different reference PCFs are used in the literature.

Figure 5. (a) Oxygen–oxygen PCFs (gOO) obtained by MD simulations from DFT with PBE, optPBE-vdW, and vdW-DF2 functionals. (b) Experimental PCFs for high- and low-density water.57
X-ray and neutron diffraction data treated in conjunction, either by the technique of empirical-potential structure refinement (EPSR)\textsuperscript{53} or by reverse Monte Carlo (RMC) simulations\textsuperscript{11,15} as well as by directly Fourier transforming the latest high-quality X-ray diffraction data sets\textsuperscript{54,55,32} and the early data set of Narten and co-workers\textsuperscript{128,129} all give a broad and slightly asymmetric first O—O peak with height 2.1—2.3, which is significantly lower than from standard MD simulations (height ~3) and from previous analyses of either only neutron diffraction data using EPSR\textsuperscript{57} or analysis of the total X-ray scattering \(I(k)\) in terms of comparison to computed \(I(k)\) from MD simulations.\textsuperscript{58,130}

There were, however, problems with both the latter approaches\textsuperscript{57,58,130} because neutron diffraction mainly measures H—H and O—H correlations and thus contain insufficient information to modify the initial SPC/E force-field guess in EPSR to a solution that also describes the O—O PCF, which is mainly determined by X-ray diffraction. The assumption by Hura et al.\textsuperscript{58,130} was that some existing MD force-field should describe the total \(I(k)\); the best agreement was found for the TIP4P-pol2 potential from which pair-correlation functions were subsequently extracted to represent experiment. However, the internal molecular scattering strongly dominates \(I(k)\) in X-ray scattering and masks the more relevant intermolecular scattering such that small, but significant, discrepancies in phase and amplitude at higher \(k\),\textsuperscript{11} which determine the shape and height of the first O—O peak, were not observed and taken into account. Because the two independent studies based on, respectively, neutron and X-ray diffraction data arrived simultaneously at similar peak height and shape, this was understandably taken as proof that the O—O PCF had been determined correctly; however, both studies reproduced in a sense the force-field used for the analysis and neither was strictly correct.

This state of affairs was analyzed more deeply in subsequent work by Soper, who in two seminal papers\textsuperscript{26,53} first showed that diffraction data do not contain enough information to discriminate between structure models of strongly different H-bond topology and then that a combination of X-ray (sensitive to O—O and O—H correlations) and neutron diffraction data (sensitive to O—H and H—H correlations) is required to obtain reliable estimates of the three PCFs. Considering the significantly reduced height of the first O—O peak, it was concluded that softer MD potentials were called for;\textsuperscript{121} similar conclusions were reached on the basis of RMC fits to the same data sets.\textsuperscript{11,15,17} Indeed, actually fitting the Hura et al. data set using either EPSR\textsuperscript{53} or RMC\textsuperscript{11,15} gives a first peak height (2.3) and position (2.82—2.85 Å) in agreement with the analysis by Narten and co-workers\textsuperscript{128,129} of their earlier data as well as with the Fourier transforms of recent more extended data sets.\textsuperscript{32,54,55}

We now test whether the obtained O—O PCF from the vdW models, with their low and asymmetric first peak at long distance and smeared out second shell, can be compatible with the PCF for ambient water under the assumption that the interactions are sufficiently well described, but that the simulation protocol may have introduced too strong constraints on possible structures. That HDL-like water would dominate the liquid under ambient conditions, i.e., the structure found with the vdW functionals, would be in agreement with what has been suggested from X-ray spectroscopy, as well as obtained from all scenarios for supercooled water.\textsuperscript{12,16,131,132} In those scenarios fluctuations between HDL and LDL forms are assumed and, in view of the vdW functionals seemingly giving only HDL-like solutions, we explore whether adding a “missing” LDL contribution, as postulated in these scenarios, could give consistency with experiment in terms of the O—O PCF. We thus weigh together the vdW-DF2 O—O PCF with a model of LDL to a combined PCF and compare with the PCF derived from experiment using EPSR\textsuperscript{53} and RMC.\textsuperscript{15} Because the PBE simulated structure is far from its preferred density,\textsuperscript{82} it can be assumed to have too large distortions from the “real” LDL that could appear as fluctuations in the otherwise HDL dominated liquid, and we thus compare with the experimental LDL PCF from Soper and Ricci.\textsuperscript{47}

In fitting to the experimental O—O PCF we obtain agreement (Figure 6) with a 70:30 mixture between vdW-DF2 HDL PCF and the experimentally derived LDL PCF.\textsuperscript{47} This ratio is most interesting, because it is very close to the original estimate of Wernet et al.\textsuperscript{2} and the estimation based on X-ray emission spectroscopy,\textsuperscript{13,16} as well as to that from interpreting infrared data in connection with analysis of a fractional Stokes—Einstein relation in water.\textsuperscript{134} Note, furthermore, that quantum effects have not been included in the simulations that would be expected to bring down and broaden the first O—O correlation additionally.\textsuperscript{108,133,134}

As has been pointed out by Soper,\textsuperscript{24} when combining two separate PCFs, one must also consider the cross-terms between the two, i.e., whether the contribution to the total PCF from considering pairs of atoms, one from each distribution, could change the picture. This would be expected from a combination of two highly structured PCFs with well-defined peaks occurring at different interparticle separations in the two distributions. However, considering that both the LDL and HDL local structures give a peak in the region of 2.7—3 Å and beyond that the HDL-like PCF is basically without structure, it seems likely that in this particular case no extra features should be expected from cross contributions to a combined PCF.

The question is naturally why the vdW simulation only shows the appearance of HDL-like water and why, to obtain agreement with X-ray diffraction experiments, it is necessary to artificially add an LDL component. The fact that a combination of an experimental LDL O—O PCF and that from vdW quite accurately reproduces the latest O—O PCF of ambient water is of course no proof that real water is a combination of the two. However, the increased accuracy of the interaction potential obtained with these latest generation vdW functionals indicates that other causes than the nonlocal interaction should be explored to account for the discrepancy between simulated and measured PCF.

One potential explanation could be related to the fact that the simulation is performed in the NVE ensemble, which keeps the

![Figure 6](https://journals.iucr.org/)
volume fixed and thus does not allow fluctuations of the density of the box and that this penalizes LDL to a greater extent than HDL, once the more isotropic vdW interactions are included; the NVE ensemble is equivalent to adding a pressure to maintain the box size, which would disfavor fluctuations to lower density assuming that the density at ambient conditions corresponds more closely to that of HDL. The box is furthermore rather limited with only 64 molecules. For spatially separated fluctuations between HDL and LDL to develop fully, it might be necessary to use much larger simulation boxes, in particular if the fluctuations are of a mean length scale around 1 nm as suggested in refs 16 and 32. There is furthermore some experimental evidence from thin water films on slightly hydrophobic surfaces that only an HDL related structure is observed even in the supercooled regime, indicating that if the system size becomes very small, indeed only one class of local structure is observed and the formation of LDL-like local regions is suppressed.

**CONCLUSIONS**

The new van der Waals density functionals optPBE-vdW and vdW-DF2 show great promise in describing the basic structural constituents of liquid water, as seen from comparing calculations of water dimer and hexamers with benchmark coupled cluster CCSD(T) results. A softening of the structure of liquid water at ambient conditions is observed when vdW interactions are included, consistent with previous work. This is seen from the broader angular distributions, the more disordered tetrahedrality and asphericity distributions, and the much lower first peak of the oxygen–oxygen PCF obtained from the optPBE-vdW and vdW-DF2 models compared to PBE. The lower first peak of the O–O PCF improves the agreement with experiment significantly. However, the outer structure is washed out by the vdW forces. This has been suggested to be related to nonlocal correlations, but our study of functionals with different nonlocal correlation strength did not show any significant difference in the liquid structures, while both were found to be very accurate for the water dimer. Instead, we find that the inclusion of the more isotropic vdW interaction shifts the balance over from directional H-bonding toward a more close-packed system, i.e., a competition between directional and isotropic interactions.

The vdW simulations seem to be potentially consistent with a picture of fluctuations between two different water structures instantaneously coexisting in nanoscale patches albeit not directly observing fluctuations except in the sense of obtaining two alternative end points with vdW forces included (HDL) or excluded (LDL). The relatively small simulation can only give a picture of the local structure of water, and while PBE predominantly describes an approximation to low-density water, both optPBE-vdW and vdW-DF2, as well as vdW-DF, describe an approximation to high-density water. By comparing the O–O PCFs of the vdW models with PCFs from X-ray and neutron diffraction of water at different pressures, we note a resemblance between the vdW models and high-density water in terms of effects on the second- and third-neighbor correlations while the expansion of the first coordination sphere found in the simulations may in experiments be counteracted by the pressure applied to experimentally generate pure HDL. The comparison to HDL is further supported by the reduction of the average number of H-bonds per molecule in the vdW MD simulations, which is a result of the isotropic vdW forces competing with the directional H-bond formation. Varying the strength of the exchange interaction does not result in a significant change in number of bonds once the vdW interaction is included. A 70:30 mixture of vdW-DF2 and the experimentally determined LDL PCF is compatible with the latest X-ray O–O PCF which, however, does not constitute proof of a fluctuating real water structure but indicates the possibility that averaging over a trajectory obeying less restrictive simulation conditions in terms of box size, length of trajectory, etc. could result in an O–O PCF directly comparable with experiment.

Quantum effects are not included in the current simulations but including them should not qualitatively change the consistency with the presented picture. The internal O–O bond distance is kept fixed during the simulations, which might affect the hydrogen bonding, but not the comparison between PBE and the vdW functionals. Lastly, the possibility that the vdW interaction is not completely accounted for by the current vdW functionals still exists although calibrations against various benchmarks indicate a quite reliable representation.

The present work does not resolve the debate on water structure but it suggests for further investigation the van der Waals interaction as a physically sound mechanism that affects the balance between directional H-bonding and higher packing and may thus indicate a way to reconcile the interpretation of recent X-ray spectroscopic data with structures obtained from AIMD simulations of liquid water. It is likely that much larger and longer simulations in the NPT ensemble are needed to determine whether current vdW models support a temperature-dependent balance of fluctuations between HDL- and LDL-like structures in ambient water, as suggested by recent X-ray spectroscopic and diffraction results, which would be enhanced upon cooling, as they must according to all scenarios for water at supercooled temperatures. From the present work it is, however, clear that a consistent description of the vdW interaction in AIMD simulations may possibly provide the key to tuning such a balance.

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Paper 2

Density functionals for surface science: Exchange–correlation model development with Bayesian error estimation

Density functionals for surface science: Exchange–correlation model development with Bayesian error estimation

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A methodology for semi-empirical density functional optimization, using regularization and cross-validation methods from machine learning, is developed. We demonstrate that such methods enable well-behaved exchange–correlation approximations in very flexible model spaces, thus avoiding the overfitting found when standard least squares methods are applied to high-order polynomial expansions. A general-purpose density functional for surface science and catalysis studies should accurately describe bond breaking and formation in chemistry, solid state physics, and surface chemistry, and should preferably also include van der Waals dispersion interactions. Such a functional necessarily compromises between describing fundamentally different types of interactions, making transferability of the density functional approximation a key issue. We investigate this trade-off between describing the energetics of intra- and inter-molecular, bulk solid, and surface chemical bonding, and the developed optimization method explicitly handles making the compromise based on the directions in model space favored by different materials properties. The approach is applied to designing the Bayesian Error Estimation Functional with van der Waals correlation (BEEF-vdW), a semilocal approximation with an additional nonlocal correlation term. Furthermore, an ensemble of functionals around BEEF-vdW comes out naturally, offering an estimate of the computational error. An extensive assessment on a range of datasets validates the applicability of BEEF-vdW to studies in chemistry and condensed matter physics. Applications of the approximation and its Bayesian ensemble error estimate to two intricate surface science problems support this.

I. INTRODUCTION

Kohn–Sham density functional theory1,2 (KS-DFT) is a widely celebrated method for electronic structure calculations in physics, chemistry, and materials science.3,4 Indeed, modern DFT methods have proven valuable for elucidating mechanisms and fundamental trends in enzymatic and heterogeneous catalysis,5–13 and computational design of chemically active materials is now within reach.14–17 Successful use of DFT often relies on accurate but computationally tractable approximations to the exact density functional for the exchange–correlation (XC) energy. The generalized gradient approximation (GGA) is very popular due to a high accuracy-to-cost ratio for many applications, but suffer from a range of shortcomings. Thus, common GGA functionals are well-suited for computing many important quantities in chemistry and condensed matter physics, but appear to be fundamentally unable to accurately describe the physics and chemistry of a surface at the same time.18 Moreover, van der Waals (vdW) dispersion interactions are not accounted for by GGAs,19 and spurious self-interaction errors can be significant.20–22 The interest in applying DFT to more and increasingly complex problems in materials science is not likely to decrease in the years to come. Much effort is therefore devoted to improve on current density functional approximations.

The five rung "Jacob's ladder" of Perdew23 represents a classification of the most popular density functional methods. Each rung adds new ingredients to the density functional approximation (DFA), and so should enable better approximations, but also adds to the computational cost. In order of increasing complexity, the ladder consists of the local spin-density approximation (LDA), GGA, meta-GGA (MGGA), hyper-GGA, and finally the generalized random phase approximation (RPA). The LDA uses only the local density as input, while rungs 2 and 3 introduce semilocal dependence of the density (GGA) and the KS orbitals (MGGA).24 Hyper-GGAs introduce nonlocal dependence of the occupied KS orbitals in the exact exchange energy density, and fifth rung approximations calculate correlation energies from the unoccupied KS orbitals. The latter is computationally heavy, but RPA type methods are the only DFAs in this five rung hierarchy that can possibly account for vdW dispersion between nonoverlapped densities.24

The failure of lower-rung DFAs in capturing dispersion forces has spurred substantial developments in recent years.19 Such interactions are spatially nonlocal in nature, and several different approaches to add "vdW terms" to lower-rung DFAs now exist.25–28 The vdW-DF nonlocal correlation25 is a particularly promising development in this field. It is a fully nonlocal functional of
the ground state density, and has proven valuable in a wide range of sparse matter studies. However, the vdW-DF and vdW-DF2 methods yield much too soft transition metal crystal lattices, and the correct choice of GGA exchange functional to use in vdW-DF type calculations is currently investigated. One approach to choosing GGA exchange is comparison to Hartree–Fock exchange and consideration of the behaviour of the exchange functional in the limit of large density gradients. Where does the vdW-DF approximation belong in a hierarchy such as Jacob’s ladder? In terms of computational complexity, the method contains fully nonlocal density–density information without explicit use of the KS orbitals. From this point of view it should fit between rungs 3 and 4, and we assign it here to rung 3.5. Note that nonlocal exchange approximations, designed to partially mimic exact exchange at a reduced computational cost, have recently been proposed as belonging to a rung 3.5.

Put in simple terms, two paradigms for developing density functionals are dominant: that of constraint satisfaction by reduction and that of fitting to empirical data. Both have contributed greatly to the success of DFT. Reductionists impose constraints based on analytic properties of the exact density functional, and strive for nonempirical functionals that fulfill as many constraints as possible on each rung of Jacob’s ladder. Empirically oriented DFA developers use experimental or high-level theoretical training data to optimize the DFA description of one or more materials properties. Reduction is arguably the most systematic approach to density functional development, and has had a significant impact on the field of KS-DFT. However, choices are often made as to what types of physics and chemistry the DFA should describe well. The empirical approach is fundamentally a matter of explicitly making these choices, and parametrize an XC model to suit personal preferences for computational performance. This makes overfitting the training data and transferability of the optimized DFA to systems and materials properties not contained in the training data a central issue.

The risk of overfitting was realized early on by Becke and others. Using polynomial expansions of GGA exchange and correlation in least squares fitting procedures, polynomial orders above 4 were found to yield increasingly oscillatory and unphysical XC functionals, that is, “a transition to mathematical nonsense”. Nevertheless, semi-empirical DFAs containing many parameters have been constructed with little attention to the overfitting issue. Transferability of a DFA parametrization depends not only on the degree of overfitting to a single set of molecular or condensed matter properties, but also on how many physically different properties the approximate model was trained on. Optimizing XC parameterizations to several different properties naturally leads to a “competition” between datasets in determining the model solution, i.e., an XC model compromise. Implicitly acknowledging this, each dataset is often assigned more or less arbitrary weights. In our view, such an approach is not guaranteed to yield the optimum model compromise.

In this study, we apply machine learning methods to avoid the above mentioned pitfalls of semi-empirical density functional development. Regularization of a very flexible polynomial GGA exchange expansion is at the heart of the developed approach. We furthermore investigate the characteristics of XC model compromises in a GGA+vdW model space, and formulate and apply an explicit principle for how an XC model trade-off should be composed. Using several training datasets of quantities representing chemistry, solid state physics, surface chemistry, and vdW dominated interactions, the BEEF-vdW exchange–correlation model is generated. The three most important aspects of semi-empirical DFA design are thus considered in detail: datasets, model space, and model selection. The developed approach furthermore leads to an ensemble of functionals around the optimum one, allowing an estimate of the computational error to be calculated. Lastly, BEEF-vdW is evaluated on systems and properties partly not in the training sets, and is also applied in two small surface science studies: Calculating potential-energy curves for graphene adsorption on the Ni(111) surface, and investigation of the correlation between theoretical chemisorption energies and theoretical surface energies of the substrate.

II. DATASETS

Several sets of energetic and structural data describing bonding in chemical and condensed matter systems are used throughout this study. These datasets are either adapted from literature or compiled here from published works, and are briefly presented in the following. Additional information is found in the Appendix.


b. Molecular reaction energies Molecular formation energies lend themselves well to compilation of gas-phase reaction energies. The RE42 dataset of 42 reaction energies involves 45 different molecules from G2/97.

c. Molecular reaction barriers The DHB24/08 set of Zheng et al., comprising 12 forward and 12 backward benchmark barriers, is chosen to represent gas-phase reaction barriers.

d. Noncovalent interactions The S22 and S22x5 sets of CCSD(T) intermolecular interaction energies of noncovalently bonded complexes were compiled by Hobza and co-workers. Particularly the S22 set has become popular for assessment and parametrization of density functional methods for vdW
type interactions. The S22x5 set consists of potential-energy curves (PECs) for each S22 complex, with interaction energies at relative distances \( d \) of 0.9, 1.0, 1.2, 1.5, and 2.0 as compared to S22, totaling 110 data points. For convenience, this study divides S22x5 into five subsets according to interaction distance, e.g., "S22x5-0.9".

The accuracy of the original S22 and S22x5 energies have certain deficiencies, so the revised S22x5-1.0 energies of Takatani et al.\(^{65}\) are used instead. The remaining (non-equilibrium) data points on each CCSD(T) PEC are correspondingly corrected according to the difference between original and revised S22x5-1.0 energies, as elaborated on in the Appendix.

e. Solid state properties  
Three sets of zero Kelvin experimental solid state data are used, here denoted Sol34Ec, Sol27LC, and Sol27Ec. The first comprises cohesive energies of 34 Period 2–6 bulk solids in fcc, bcc, diamond, and hcp lattices. Zero-point phonon effects have not been corrected for. Conversely, the Sol27LC and Sol27Ec sets contain lattice constants and cohesive energies, respectively, of 27 cubic lattices, both corrected for zero-point vibrational contributions.

f. Chemisorption on solid surfaces  
The CE17 and CE27 datasets comprise experimental reaction energies for chemisorption of simple molecules on the (111), (100), and (0001) facets of late transition metal surfaces at low coverage. The CE17 set is a subset of CE27.

### III. COMPUTATIONAL DETAILS

Self-consistent density functional calculations are performed using GPAW.\(^{62–64}\) a real-space grid implementation of the projector-augmented-wave method.\(^{65}\) The ASE\(^{64,66}\) package provides a convenient interface to GPAW.

Grid-point spacings of 0.16 Å are employed for high-quality computations of simple properties such as molecular binding energies. Properties of bulk solids are calculated using somewhat denser grids with a spacing of 0.13 Å. Real-space structure relaxation is applied to the G3/99 molecules and CE27 chemisorption systems with 0.05 eV/Å as the criterion of maximum force on each relaxing atom. Molecular and single-atomic systems are placed in a box with at least 7 Å vacuum to the box boundaries, except for the S22x5 complexes for which the vacuum width is 10 Å.

Further details on the computational procedure employed are found in the Appendix.

### IV. MODEL SPACE

The GGA exchange energy density \( \varepsilon_x^{\text{GGA}}(n, \nabla n) \) is conveniently expressed in terms of the exchange energy density of the uniform electron gas, \( \varepsilon_x^{\text{UEG}}(n) \), and an exchange enhancement factor \( F_x(s) \), depending on the local density as well as its gradient through the reduced density gradient \( s \),

\[
s = \frac{|\nabla n|}{2k_F n} - 1, \quad 0 \leq s \leq \infty,
\]

\[
\varepsilon_x^{\text{GGA}}(n, \nabla n) = \varepsilon_x^{\text{UEG}}(n) F_x(s(n, \nabla n)),
\]

\[
E_x^{\text{GGA}}[n, \nabla n] = \int \varepsilon_x^{\text{UEG}}(n) F_x(s(n, \nabla n)) \mathrm{d}r,
\]

where \( n = n(\mathbf{r}) \), \( k_F = (3\pi^2 n)^{1/3} \) is the Fermi wave vector of the UEG, and \( E_x^{\text{GGA}} \) is the semilocal GGA exchange energy.

In this study, a highly general exchange model space is obtained by expanding the GGA exchange enhancement factor in a basis of \( M_x \) Legendre polynomials \( B_m(t(s)) \) of orders 0 to \( M_x - 1 \) in a transformed reduced density gradient, denoted \( t(s) \),

\[
t(s) = \frac{2s^2}{4 + s^2} - 1, \quad -1 \leq t \leq 1,
\]

\[
F_x^{\text{GGA}}[s] = \sum_m a_m B_m(t(s)),
\]

\[
E_x^{\text{GGA}}[n, \nabla n] = \sum_m a_m \int \varepsilon_x^{\text{UEG}}(n) B_m(t(s)) \mathrm{d}r,
\]

where \( a_m \) are expansion coefficients, and \( E_x^{\text{GGA}} \) is the exchange energy corresponding to the Legendre basis function \( B_m \). The polynomial basis is constructed such that the boundary limits, \( t = [-1, 1] \), are zero for all \( m > 1 \) basis functions. Therefore, these limits are determined by the order 0 and 1 basis functions only.

Semilocal approximations to electron correlation effects beyond GGA exchange are not easily cast in terms of a single variable, such as \( s \). The correlation model space is chosen to be a linear combination of the PBE\(^{67}\) semilocal correlation functional, purely local Perdew–Wang\(^{68}\) LDA correlation, and vdW-DF\(^{30}\) type nonlocal correlation. The latter is calculated from a double integral over a nonlocal interaction kernel \( \phi(\mathbf{r}, \mathbf{r}') \),

\[
E_{\text{nl-c}}[n] = \frac{1}{2} \int n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \mathrm{d}r \mathrm{d}r',
\]

which is evaluated using the fast Fourier transformation method of Román-Pérez and Soler,\(^{69}\) implemented in GPAW as described in Ref. 70.

In total, the XC model space consequently consists of GGA exchange expanded in Legendre polynomials as well as local, semilocal, and nonlocal correlation,

\[
E_{xc} = \sum_{m=0}^{M_x-1} a_m E_x^{\text{GGA}}[s] + \alpha_c E_{\text{LDA-c}} + (1 - \alpha_c) E_{\text{PBE-c}} + E_{\text{nl-c}},
\]

where \( M_x = 30 \), and the total number of parameters is \( M = M_x + 1 = 31 \).
None of the commonly imposed constraints on GGA exchange are invoked, e.g., the LDA limit of $F_x(s)$ and recovery of the correct gradient expansion for slowly varying densities, nor the Lieb–Oxford (LO) bound\textsuperscript{71,72} for large electron density gradients. However, as seen from Eq. (4), the sum of LDA and PBE correlation is constrained to unity.

V. MODEL SELECTION

Choices are made when developing a semi-empirical density functional. These are both explicit and implicit choices pertaining to what the functional is to be designed for, that is, for the selection of an optimum exchange–correlation model that captures the materials properties of main interest when applying the approximation. This study aims to explicate the choices, and to develop a set of principles for the model selection process. These principles are used to guide the inevitable compromise between how well significantly different quantities in chemistry and condensed matter physics are reproduced by an incomplete XC model space.

Development of an XC functional is in this approach divided into two steps. First an individual model selection for a number of datasets is carried out, and subsequently a simultaneous model selection is made, compromising between the individual fits.

A. Individual materials properties

1. Regularizing linear models

Model training is formulated in terms of finding the expansion coefficient vector that minimizes a cost function without overfitting the data. This may be viewed as determining the optimum trade-off between bias and variance of the model.\textsuperscript{73}

The cost function contains two terms, a squared error term and a regularization term. One simple regularization suitable for varying the bias-variance ratio is one that "penalizes" the cost function for model solutions that differ from a suitably chosen prior solution. This effectively removes sloppy\textsuperscript{74} eigenmodes of the cost function by adding curvature to all modes, and thereby limits the effective number of parameters in the model solution. As the regularization strength is continuously decreased from infinity towards zero, the model parameters that minimize the cost function are allowed to differ increasingly from the prior solution. In a sufficiently large model space the solution that reproduces the data best without overfitting is in general found for intermediate regularization strength. A slightly more elaborate regularization is used in this study, as outlined later on.

Finding the optimum model is then a matter of determining the optimum regularization strength. This may be done by minimizing the estimated prediction error (EPE) for varying regularization strength. The EPE provides a statistical estimate of the validity of a model outside the space of its training data, and can be obtained by a large variety of resampling methods. We obtain it using bootstrap resampling.\textsuperscript{75} Even though common error quantities, such as the standard deviation (STD), will in general decrease for regularization strengths smaller than that which minimizes the EPE, the corresponding model solutions are likely to be increasingly overfitted. Minimizing the EPE and not the STD is therefore preferred for determining well-behaved XC functionals.

2. Details of the procedure

The standard Tikhonov regularization method\textsuperscript{73} is chosen to control overfitting. A cost function for the $i$’th dataset is therefore defined as

$$C_i(a) = (X_i a - y_i)^2 + \omega^2 \Gamma^2 (a - a_p)^2,$$

where $X_i$ is a data matrix, $a$ the coefficient vector, $y_i$ a target vector of training data, $\omega^2$ the regularization strength, $\Gamma$ is denoted the Tikhonov matrix, and the prior vector $a_p$ is the origo for regularization.

In accordance with Eq. (4), the data matrix consists of XC contributions to a materials property for each system in the $i$’th dataset from the $M$ basis functions. These are evaluated non-self-consistently on RPBE\textsuperscript{76} densities. The target vector contains the target XC contribution to each quantity in the set.

The Tikhonov matrix is defined from a smoothness criterion on the basis functions. The exchange part of $\Gamma$ is the overlap of the second derivative of the exchange basis functions with respect to the transformed reduced density gradient,

$$\Gamma^2_{ij} = \int_{-1}^{1} \frac{d^2 B_i(t)}{dt^2} \frac{d^2 B_j(t)}{dt^2} dt.$$  (6)

Defined this way, the Tikhonov matrix directly penalizes the integrated squared second derivative of the exchange fit for finite regularization strength. This can be understood as penalizing a measure of non-smoothness of the fitted exchange enhancement factor. In effect, the $\Gamma$ matrix scales the regularization strength acting on each exchange basis function, such that higher-order basis functions are suppressed when minimizing the cost function. This leads to a model selection preference for solution vectors with small coefficients for higher-order polynomials, unless they are essential for obtaining a satisfactory fit. Physically, it is very reasonable to require $F_x(s)$ to be a smooth and preferably injective function of $s$, and significantly non-smooth exchange solutions have been shown to degrade transferability of fitted exchange functionals to systems outside the training data.\textsuperscript{77} The correlation part of $\Gamma$ has one in the diagonal and zeros in the off-diagonal elements.
Since $\mathbf{\Gamma}$ acts in the transformed $t(s)$-space, the transformation in Eq. (2) causes the regularization penalty on exchange to be strongest in the large-$s$ regime, where information from the data matrix about the optimum behavior of $F_x(s)$ is expected to be scarce.\cite{76,78}

In order to minimize the cost function in Eq. (5), it is transformed by $\mathbf{\Gamma}^{-1}$. Ones are therefore inserted in the first two diagonal elements of $\mathbf{\Gamma}$ to avoid numerical issues. The solution vector $\mathbf{a}$, that minimizes $C_t$ is written

$$
\mathbf{a}_t = \mathbf{\Gamma}^{-1} \left( \mathbf{X}_t^T \mathbf{X}_t + L^2 \omega^2 \right)^{-1} \left( \mathbf{X}_t^T \mathbf{y}_t + \omega^2 L^2 \mathbf{a}_p \right),
$$

where $\mathbf{X}_t = \mathbf{X}_t \mathbf{\Gamma}^{-1}$, $\mathbf{a}_p = \mathbf{\Gamma} \mathbf{a}_p$, and $L^2$ is the identity matrix with zeros in the first two diagonal elements. Singular value decomposition of $\mathbf{X}_t^T \mathbf{X}_t$ is used to calculate the inverse matrix. The LDA and PBE correlation coefficients in the XC model are constrained to be between zero and one, implying $\alpha_c \in [0, 1]$ for the correlation coefficient in Eq. (4). In the cases this is not automatically fulfilled, it is enforced by recalculating the solution while fixing $\alpha_c$ to the nearest bound of the initial solution.

The exchange part of the prior vector is chosen as the inverse matrix. The LDA and PBE correlation coefficients in the XC model are constrained to be between zero and one, implying $\alpha_c \in [0, 1]$ for the correlation coefficient in Eq. (4). In the cases this is not automatically fulfilled, it is enforced by recalculating the solution while fixing $\alpha_c$ to the nearest bound of the initial solution.

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As previously mentioned, the optimum regularization is found by minimizing the estimated prediction error for varying $\omega^2$. Bootstrap resampling of the data matrix with the .632 estimator\cite{75,79} is used. It is defined as

$$
\text{EPE}_{.632} = \sqrt{0.368 \cdot \hat{\text{Err}} + 0.632 \cdot \bar{\text{Err}}},
$$

where $\hat{\text{Err}}$ is the variance between the target data and the prediction by the optimal solution $\mathbf{a}_t$, and $\bar{\text{Err}}$ measures the variance on samples of data to which solutions were not fitted in the resampling. Both are determined as a function of $\omega^2$, and $\bar{\text{Err}}$ is given by

$$
\bar{\text{Err}} = \frac{1}{N} \sum_{s} \frac{1}{N_{s}^{\mu \neq s}} \sum_{s_{\mu \neq s}} \left( x_{\mu} b_{s_{\mu}} - y_{\mu} \right)^2,
$$

where $\mu$ is an entry in the dataset, $N_{\mu}$ the number of data points, $s$ a bootstrap sample of $N_{\mu}$ data points, and $N_{s_{\mu \neq s}}$ the number of samples not containing $\mu$. The parenthesis calculates the difference between the prediction $x_{\mu} b_{s_{\mu}}$ of the data point $\mu$ by the best-fit coefficient vector $b_{s_{\mu}}$ and the $\mu$’th target value $y_{\mu}$. The best-fit solution is found by minimizing the cost function with the data in sample $s$ only.

In the bootstrap resampling procedure, 500 randomly generated data samples are selected independently for each $\omega^2$. The regularization strength that minimizes the .632 estimator is found by a smooth fitting of the slightly scattered estimator plot near the minimum. To properly regularize the S2x5 subsets with long interaction distances, a condition $F_x(s = \infty) \geq 1$ is enforced.

### 3. Individually trained XC models

Table I and Fig. 1 show details and statistics for the optimized XC models obtained when the procedure outlined above is applied to molecular, solid state, surface chemical, and vD.$\text{W}$ dominated energetics. Each model is therefore trained on a single materials property only, and their features differ significantly.

The DBH24/08 set appears to favor GGA exchange that substantially violates the LDA limit ($F_x(0) = 1.14$) along with inclusion of full PBE correlation ($\alpha_c = 0$; no LDA correlation). The model furthermore overshoots

<table>
<thead>
<tr>
<th>$\alpha_c$</th>
<th>$M_{\text{eff}}$</th>
<th>$F_x(0)$</th>
<th>$F_x(\infty)$</th>
<th>MSD</th>
<th>MAD</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE17</td>
<td>0.90</td>
<td>4.7</td>
<td>0.97</td>
<td>2.15</td>
<td>-10</td>
<td>96</td>
</tr>
<tr>
<td>RE42</td>
<td>1.00</td>
<td>4.2</td>
<td>1.06</td>
<td>1.21</td>
<td>19</td>
<td>168</td>
</tr>
<tr>
<td>DBH24/08</td>
<td>0.00</td>
<td>3.7</td>
<td>1.14</td>
<td>3.14</td>
<td>1</td>
<td>116</td>
</tr>
<tr>
<td>G2/97</td>
<td>0.27</td>
<td>7.2</td>
<td>1.10</td>
<td>2.53</td>
<td>-13</td>
<td>109</td>
</tr>
<tr>
<td>Sol34Ec</td>
<td>0.00</td>
<td>7.7</td>
<td>0.97</td>
<td>1.25</td>
<td>-4</td>
<td>168</td>
</tr>
<tr>
<td>S22x5-0.9</td>
<td>0.81</td>
<td>3.2</td>
<td>0.96</td>
<td>1.68</td>
<td>0</td>
<td>9</td>
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<tr>
<td>S22x5-1.0</td>
<td>0.82</td>
<td>3.1</td>
<td>0.98</td>
<td>1.87</td>
<td>0</td>
<td>8</td>
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<tr>
<td>S22x5-1.2</td>
<td>0.40</td>
<td>5.7</td>
<td>1.04</td>
<td>2.38</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>S22x5-1.5</td>
<td>0.85</td>
<td>4.0</td>
<td>1.02</td>
<td>1.91</td>
<td>-1</td>
<td>3</td>
</tr>
<tr>
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<td>3.3</td>
<td>0.95</td>
<td>1.37</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

FIG. 1. (Color online) Exchange enhancement factors of the individually trained XC models listed in Table I.
the LO bound $F_{x,LO}^s = 1.804$ significantly ($F_x(\infty) = 3.14$). The XC model optimized to the G2/97 set shows similar trends with respect to GGA exchange and PBE correlation, but is less extreme.

In the other end of the spectrum is the model optimized to the Sol34Ec cohesive energies. These favor GGA exchange and PBE correlation. The occurrence of a maximum in exchange enhancement factor should, however, not be overemphasized. It has been shown\textsuperscript{76,78} that only small GGA exchange contributions to chemical and solid state binding energetics can be attributed to reduced density gradients above 2.5. In the region of large $s$, where the smoothness criterion on exchange is strongly enforced, the regularization term in the cost function, Eq. (5), will therefore dominate in determining the solution for such systems. The regularization may therefore well determine the behavior of $F_x(s)$ for large density gradients.

For the remaining datasets in Table I, the optimized XC models appear reasonable, with all exchange enhancement factors starting out near the LDA limit.

It is illustrative to investigate how the XC models perform for datasets on which they were not trained. The standard deviation is a natural measure of performance. Defining the relative standard deviation, rSTD, on some dataset with some XC model, as the STD obtained by that model divided by the STD of the model that was fitted to that dataset, rSTD is a measure of transferability. Figure 2 shows a color map of the rSTD for all 10 training datasets with all 10 trained models. The diagonal from bottom left to top right is, by definition, ones. In a background of blue and yellow-green squares, the map features two distinct areas of mostly reddish squares. To the far right, the S22x5-2.0 model yields rSTD $> 5$ for all other sets than DBH24/08, and rSTD $\approx 28$ for S22x5-0.9. Furthermore, a $5 \times 4$ square in the top left corner illustrates that XC models trained on chemical or solid state datasets perform significantly worse on vdW type energetics, than models fitted to the latter. It is also interesting to see that the S22x5-2.0 rSTDs are largely unaffected by changing XC models. With little or no density–density overlap between many of the S22x5-2.0 complexes, the constant nonlocal correlation in all 10 models is likely the main XC contribution to intermolecular binding.

In summary, the deviation statistics in Table I illustrate that the XC model space considered here most certainly spans the model degrees of freedom necessary to obtain well-performing density functionals with smooth exchange enhancement factors and sound correlation components. However, a high degree of transferability between the datasets should not be expected for several of the models.

B. Several materials properties

Fundamentally, a compromise has to be made between how well different materials properties are reproduced by the same semi-empirical density functional. This is expressed as a compromise between how well the functional quantitatively performs on different training datasets. What the compromise should be can only be determined by the target applications of the functional, and one challenge is to make this choice as explicit as possible. This section presents one route towards a methodology for optimizing an XC model to simultaneously describe several different materials properties.

First the nature of the model comprise is illustrated for the case of simultaneously fitting two datasets using a summed cost function with varying weights on the two sets. However, in the end a product cost function is found more convenient for determining the optimum weights according to the directions in model space favored by different datasets.

1. Model compromise

Consider first the problem of simultaneously fitting two datasets, and let the model compromise be described through the total cost function, given as the sum of the two individual cost functions,

$$\Lambda(\mathbf{a}) = W_1 C_1(\mathbf{a}) + W_2 C_2(\mathbf{a}), \quad (10)$$
Thus defined, the relative cost for each training dataset is a simple measure of how unfavorable it is for each dataset to be fitted by the compromising solution \( b \) instead of the individual solutions \( a_i \).

The main panel of Fig. 3 illustrates XC model compromises between the G2/97 and S22x5-1.0 datasets. The curve maps out the relative costs on both datasets obtained from model solutions \( b \) when systematically varying the weights in \( \Lambda(a) \). The weight fraction \( f \) is introduced, see the figure caption. A wide range of poorly compromising models can obviously be produced, sacrificing a lot of relative cost on one set while gaining little on the other. However, if both materials properties represented by the two datasets are considered important, the optimum weighting is somewhere midway between the asymptotic extrema.

The insert in Fig. 3 shows how the product of the relative costs varies with \( f \). To the right along the abscissa, where the fraction increasingly favors the G2/97 set, the rCost product increases rapidly. To the left the increase is much smaller, but a minimum is located in between. At least one intermediate minimum is always present, since the slopes in the two asymptotic regions are \(-\infty\) and \(0\), respectively. This property is induced by the variational property around the two original minima of the individual cost functions. Similar conclusions apply to any combination of two or more datasets that do not favor the same directions in the incomplete model space.

We find in general that the condition of minimizing the product of relative costs is well-suited for choosing cost function weights for arbitrary numbers of training datasets, if the aim is a general-purpose model. This condition, which is identical to minimizing the product of costs, is applied henceforth.

### 2. Product cost function

A product cost function for arbitrary numbers of training datasets is here defined, such that the minimizing solution \( c \) yields a desired minimum of the product of costs. The cost function is written

\[
\Phi(a) = \prod_i C_i(a)^{w_i},
\]

where \( w_i \) is a constant weight, and \( C_i \) is again an individual cost function. The constant weight is an important feature of \( \Phi(a) \), since it allows inclusion of training datasets which are perceived significantly less important than others. It is thus chosen from personal preferences given the purpose of the functional, and we shall see that \( c \) minimizes the product of costs given this choice.

For the case of two datasets, the stationary point between the two individual solutions in model space is
therefore lowered to 0.5. The same reasoning applies to is based on G2/97 molecules, the data in RE42 is corre-
tions between some of the datasets have led us to lower
In principle these should all equal one, however, correla-
tion functional is composed of 0.6 LDA, 0.4 PBE, and 1.0 nonlocal correlation.

TABLE II. The BEEF-vdW model compromise. The effective weight in determining the XC model solution is \( w/C \) for each dataset, as iteratively found from minimizing the product cost function, Eq. (14). The relative standard deviation (rSTD) is the ratio of the STD at the BEEF-vdW compromise to the STD at the regularized individual solution in Table I. The relative cost (rCost) are defined similarly, but includes regularization, see Eq. (13).

<table>
<thead>
<tr>
<th>Dataset</th>
<th>( w )</th>
<th>( w/C )</th>
<th>rCost</th>
<th>rSTD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE17</td>
<td>1.0</td>
<td>1.80</td>
<td>1.7</td>
<td>1.3</td>
</tr>
<tr>
<td>RE42</td>
<td>0.5</td>
<td>0.62</td>
<td>2.5</td>
<td>1.8</td>
</tr>
<tr>
<td>DBH24/08</td>
<td>1.0</td>
<td>0.65</td>
<td>4.9</td>
<td>2.3</td>
</tr>
<tr>
<td>G2/97</td>
<td>0.5</td>
<td>0.62</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Sol34Ec</td>
<td>1.0</td>
<td>0.43</td>
<td>7.5</td>
<td>2.8</td>
</tr>
<tr>
<td>S22x5-0.9</td>
<td>0.1</td>
<td>0.01</td>
<td>28.6</td>
<td>5.4</td>
</tr>
<tr>
<td>S22x5-1.0</td>
<td>0.1</td>
<td>0.04</td>
<td>9.1</td>
<td>2.9</td>
</tr>
<tr>
<td>S22x5-1.2</td>
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<td>0.09</td>
<td>3.5</td>
<td>2.1</td>
</tr>
<tr>
<td>S22x5-1.5</td>
<td>0.1</td>
<td>0.08</td>
<td>4.1</td>
<td>2.1</td>
</tr>
<tr>
<td>S22x5-2.0</td>
<td>0.1</td>
<td>0.18</td>
<td>1.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

found by differentiating the logarithm of \( \Phi(\mathbf{a}) \) with respect to \( \mathbf{a} \) and solving

\[
\sum_i w_i \frac{dC_i}{C_i} \frac{d\mathbf{a}}{\mathbf{a}} = 0. \tag{15}
\]

Using the method outlined above, the model solution that minimizes \( \Phi(\mathbf{a}) \) is found in terms of the individual solutions as

\[
c = \left( \sum_i \frac{w_i}{C_i} \mathbf{H}_i \right)^{-1} \left( \sum_i \frac{w_i}{C_i} \mathbf{H}_i \mathbf{a}_i \right), \tag{16}
\]

where \( C_i = C_i(c) \), and \( w_i \) simply scales the individual costs. We see that this solution corresponds to letting \( W_i \) in Eq. (11) equal \( w_i/C_i \). Thus, minimizing the product of costs has introduced a natural weight \( C_i^{-1} \), while \( w_i \) still leave room for deliberately biasing the model solution.

From here on, the product solution is therefore used to find the desired XC model solution: Since \( C_i \) is evaluated at \( c \), the optimum solution is found iteratively, using \( C_i^{-1} \) as an iterator while searching for a converged minimum of the product cost function, given the constant weights \( w_i \).80

3. BEEF-vdW density functional

The BEEF-vdW exchange–correlation functional was designed using the set of weights \( w \) listed in Table II. In principle these should all equal one, however, correlations between some of the datasets have led us to lower the constant weight on some of them: Since the RE42 set is based on G2/97 molecules, the data in RE42 is correlated with some of the data in G2/97. Both weights were therefore lowered to 0.5. The same reasoning applies to the S22x5 subsets, where the same complexes are found in all the five sets, albeit at different interaction distances. A weight of \( 1/5 = 0.2 \) on each S22x5 subset would therefore be natural, but for reasons of performance of the final functional, constant weights of 0.1 were chosen. The origo vector was the same for the combined functional as for the individual models.

The resulting model compromise is also tabulated in Table II, showing the effective dataset weight \( w/C \), rCost, and rSTD for all datasets used in model training. It is clearly seen that especially the S22x5-0.9 interaction energies are hard to fit simultaneously with the other datasets within the XC model space employed here: The relative cost for the set is high, allowing the model to adapt mostly to the other datasets by lowering \( w/C \)

![FIG. 4. (Color online) The BEEF-vdW exchange enhancement factor compared to those of a few standard GGA exchange functionals. The corresponding BEEF-vdW correlation functional is composed of 0.6 LDA, 0.4 PBE, and 1.0 nonlocal correlation.](image)
for this set. This is furthermore reflected in the rSTD of 5.4, indicating that the BEEF-vdW performance on this dataset is significantly worse than obtained in the individual fit to the S22x5-0.9 systems reported in Table I. Even so, the remaining S22x5 subsets appear to share XC model space with the datasets representing formation and rupture of interatomic bonds to a significantly greater extent. Thus, accurate description of the balance of strong and weak interactions in the S22x5-0.9 complexes is nearly incompatible with at least one of the other sets of materials properties, when demanding well-behaved exchange and correlation functionals in the present model space.

Table III lists the BEEF-vdW expansion coefficients. The correlation functional consists of 0.6 LDA, 0.4 PBE, and 1.0 nonlocal correlation. The qualitative shape of the BEEF-vdW exchange enhancement factor is shown in Fig. 4, with $s = 0$ and $s \to \infty$ limits of 1.034 and 1.870, respectively. Thus, BEEF-vdW exchange does not exactly obey the LDA limit for $s = 0$, but is 3.4% higher. The enhancement factor is above most GGA exchange functionals up to $s \approx 2.5$, from where it approaches the LO bound with a small overshoot in the infinite limit.

The lack of exact fulfillment of the LDA limit for exchange indicates a conflict between this limit, the training data, and the employed preference for smooth exchange. However, completely removing such features require overly strong regularization.

### VI. ENSEMBLE ERROR ESTIMATION

A normal DFT calculation does not provide any information about the uncertainty of the result from using an approximate XC functional. One method to obtain an estimate of the uncertainty is performing several calculations using different functionals, and observe the variations in the prediction of the quantity of interest. Another more systematic approach is to use an ensemble of functionals designed to provide an error estimate, as discussed in Ref. 81. This method is applied to the BEEF-vdW model, and the adaptation is briefly presented here.

Inspired by Bayesian statistics, we define a probability distribution $P$ for the model parameters $a$ given the model $\theta$ and training data $D$,

$$P(a|\theta D) \sim \exp(-C(a)/\tau),$$  

where $C(a)$ is the cost function, and $\tau$ is a cost “temperature”. Given the data $D$, a model perturbation $\delta a$ has a certain probability associated with it, and this defines an ensemble of different XC functionals. The temperature is to be chosen such that the spread of the ensemble model predictions of the training data reproduces the errors observed when using BEEF-vdW self-consistently. This approach to constructing the probability distribution is closely related to the maximum entropy principle. The ensemble is defined through a Hessian scaled with the temperature. The Hessian is calculated directly from

$$ H = 2 \sum_i^N \frac{w_i}{C_i(a_p)} \Gamma^{-1} \left(X_i^T X_i' + \omega_i^2 L^2 \right) \Gamma^{-1T}, $$  

where the sum is over training datasets. The temperature is related to the effective number of parameters in the model, calculated from the effective regularization

$$ \omega_{\text{eff}}^2 = \sum_i^N \frac{w_i}{C_i(c)} \omega_i^2, $$  

where $\omega_i^2$ is the regularization strengths for the individual datasets. Additionally, diagonalization of the combined square of the transformed data matrix

$$ \Sigma' = V^T \left( \sum_i^N \frac{w_i}{C_i(c)} X_i^T X_i \right) V, $$  

where $\Sigma'$ contains the eigenvalues along the diagonal and $V$ the eigenvectors, allows the effective number of parameters left in the model after regularization, $M_{\text{eff}}$, to be computed as

$$ M_{\text{eff}} = \sum_m^M \frac{\Sigma_m' \omega_m^2 + \omega_{\text{eff}}^2 \Sigma_m'}{\Sigma_m' \omega_m^2 + \omega_{\text{eff}}^2 \Sigma_m'}. $$  

Since $M_{\text{eff}} = 7.11$ in the BEEF-vdW model compromise, more than 75% of the initially 31 model degrees of freedom have been suppressed by regularization.

The temperature calculation is slightly modified from the method in Ref. 81 in order to construct an unbiased error estimation. This reflects that a larger error is expected when BEEF-vdW is applied to systems not included in the training datasets. The temperature is therefore calculated as

$$ \tau = 2 \frac{C(c)}{M_{\text{eff}}} \cdot \frac{N_{\text{tot}}}{N_{\text{tot}} - M_{\text{eff}}}, $$  

where $N_{\text{tot}}$ is the total number of systems in the training sets. The second term is close to unity since $N_{\text{tot}} \gg M_{\text{eff}}$

An ensemble matrix is now found as

$$ \Omega^{-1} = \tau H^{-1}, $$  

with eigenvalues $\omega_{\Omega^{-1}}^2$ and eigenvectors $V_{\Omega^{-1}}$. 

The distribution of correlation parameters in an ensemble containing 20,000 samples. The distribution is centered around the distribution of the exchange model perturbations that yield DFT results ±1 standard deviation away from BEEF-vdW results. The insert shows a histogram of the distribution of correlation parameters in an ensemble containing 20,000 samples. The distribution is centered around $\alpha_c = 0.6$.

Finally, using an ensemble of $k$ vectors $v_k$, each of length $M$ with elements randomly drawn from a normal distribution of zero mean and variance one, the BEEF-vdW ensemble coefficient vectors $a_k$ are calculated from

$$a_k = V_{\Omega^{-1}} \cdot 1w_{\Omega^{-1}} \cdot v_k.$$  \hspace{1cm} (24)\]

The BEEF-vdW ensemble matrix is provided in the Supplemental Material.\cite{83}

An illustration of the BEEF-vdW ensemble is shown in Fig. 5. For each data point in each dataset this ensemble may be applied non-self-consistently to BEEF-vdW electron densities. The standard deviation of the ensemble predictions of a quantity is then the ensemble estimate of the BEEF-vdW standard deviation on that quantity. The exchange enhancement ensemble expands after $s \approx 2$, where most of the chemistry and solid state physics have already happened.\cite{76,78}

The predictive performance of the ensemble has been evaluated using 20,000 ensemble functionals. In practice, however, a few thousand ensemble functionals suffice for well-converged error estimates at a negligible computational overhead. Estimated standard deviations on the training datasets are compared to those from self-consistent calculations in Table IV. The ensemble performance on the dataset level should be assessed in combination with observing the error predictions on a system-to-system basis. Figure 6 illustrates the BEEF-vdW ensemble error estimates for the RE42 molecular reaction energies, and compares BEEF-vdW results to those of other functionals. Similar figures for more datasets are found in the Supplemental Material.\cite{83}

On the dataset level, the overall predictive performance of the ensemble is satisfactory. The ensemble standard deviations in Table IV are slightly underestimated for the G2/97, CE17, and S22x5-0.9 datasets, while the ensemble underestimates the errors for RE42, DBH24/08, and Sol34Ec. For the remaining S22x5 subsets the error estimates are too large.

Importantly, Fig. 6 illustrates strengths and weaknesses of the present approach to error estimation. Many of the reaction energies are accurately reproduced by BEEF-vdW and the ensemble estimates a relatively small error on those data. However, some of the reactions for which BEEF-vdW has larger errors are assigned too small error bars. The water-gas shift reaction $\text{CO} + \text{H}_2 \rightarrow \text{CO}_2 + \text{H}_2$ is one of these. The reason for this is indicated by the fact that all tested GGA, MGGA and vdW-DF type functionals yield nearly identical reaction energies for this reaction. One simply has to move rather far in XC model space to find a functional that predicts a reaction energy significantly different from the BEEF-vdW result. This causes the ensemble to underestimate the actual error for that reaction. Since the hybrid functionals appear to break the overall trends observed for the lower-rung functionals in Fig. 6, inclusion of exact exchange in the model space might remedy such limitations of the BEEF-vdW functional and its Bayesian ensemble.

### VII. BENCHMARKS

The following is a comparative assessment of BEEF-vdW and a selection of literature XC functionals of the LDA, GGA, MGGA, vdW-DF, and hybrid types. These are listed in Table V. The benchmark datasets used are the six sets to which BEEF-vdW was trained, except Sol34Ec, as well as the G3-3, CE27, Sol27Ec, and Sol27LC datasets. The latter sets were introduced in Section II. Statistics on deviations of computed quantities from experimental or high-level theoretical references are reported for each density functional in terms of the mean signed (MSD), mean absolute (MAD), and standard deviations to those predicted by the ensemble of functionals around BEEF-vdW. All energies in meV.

<table>
<thead>
<tr>
<th>Functionals</th>
<th>MSD (meV)</th>
<th>MAD (meV)</th>
<th>Standard Deviation (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE17</td>
<td>143</td>
<td>209</td>
<td>209</td>
</tr>
<tr>
<td>RE42</td>
<td>372</td>
<td>253</td>
<td>253</td>
</tr>
<tr>
<td>DBH24</td>
<td>331</td>
<td>144</td>
<td>144</td>
</tr>
<tr>
<td>G2/97</td>
<td>242</td>
<td>312</td>
<td>312</td>
</tr>
<tr>
<td>SolEc34</td>
<td>576</td>
<td>436</td>
<td>436</td>
</tr>
<tr>
<td>s22x5-0.9</td>
<td>171</td>
<td>197</td>
<td>197</td>
</tr>
<tr>
<td>s22x5-1.0</td>
<td>94</td>
<td>181</td>
<td>181</td>
</tr>
<tr>
<td>s22x5-1.2</td>
<td>36</td>
<td>137</td>
<td>137</td>
</tr>
<tr>
<td>s22x5-1.5</td>
<td>8</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>s22x5-2.0</td>
<td>5</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>
violation (STD). The sign convention is

\[ \text{deviation} = \text{DFT} - \text{reference}. \] (25)

Computed deviations for all systems in all datasets considered are tabulated in the Supplemental Material,\(^83\) which also provides the raw DFT data.

All data are further available online in the Computational Materials Repository (CMR).\(^95\) The repository contains all information about the individual DFT calculations which form the basis for the results presented here, including atomic configurations and GPAW specific parameters. Access to search, browse, and download these data is provided through the CMR web-interface.\(^96\)

### A. Molecular formation energies

The G2/97 and G3/99 thermochemical test sets have become standards for validating density functional methods, and the present calculations are well in line with published benchmark data\(^94\) for these sets. Statistics are reported in Table VI.

Considering first G2/97, the LDA grossly overestimates the molecular formation energies. Significant improvements are found with GGA's, where XC functionals designed to capture molecular energetics (RPBE, BLYP, HCTH407) yield STDs below 0.5 eV, while those targeted at solid state properties (PBEsol, WC, AM05) perform significantly worse: their MSEs are large and negative.
TABLE V. A selection of density functionals at the LDA (1), GGA (2), MGGA\(^b\) (3), vdW-DF (3.5), and hybrid\(^b\) (4) rungs of Jacob's ladder.

<table>
<thead>
<tr>
<th>Type</th>
<th>Target(^c)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>1</td>
<td>68</td>
</tr>
<tr>
<td>PBE</td>
<td>2</td>
<td>general 67</td>
</tr>
<tr>
<td>RPBE</td>
<td>2</td>
<td>chemistry 76</td>
</tr>
<tr>
<td>BLYP</td>
<td>2</td>
<td>chemistry 87,88</td>
</tr>
<tr>
<td>HCTH407</td>
<td>2</td>
<td>chemistry 46</td>
</tr>
<tr>
<td>PBEsol</td>
<td>2</td>
<td>solid state 43</td>
</tr>
<tr>
<td>WC</td>
<td>2</td>
<td>solid state 89</td>
</tr>
<tr>
<td>AM05</td>
<td>2</td>
<td>solid state 90</td>
</tr>
<tr>
<td>TPSS</td>
<td>3</td>
<td>general 91</td>
</tr>
<tr>
<td>revTPSS</td>
<td>3</td>
<td>general 44</td>
</tr>
<tr>
<td>vdW-DF</td>
<td>3.5</td>
<td>vdW 25</td>
</tr>
<tr>
<td>vdW-DF2</td>
<td>3.5</td>
<td>vdW 30</td>
</tr>
<tr>
<td>optPBE-vdW</td>
<td>3.5</td>
<td>vdW 33</td>
</tr>
<tr>
<td>optB88-vdW</td>
<td>3.5</td>
<td>vdW 33</td>
</tr>
<tr>
<td>C09-vdW</td>
<td>3.5</td>
<td>vdW 34</td>
</tr>
<tr>
<td>B3LYP</td>
<td>4</td>
<td>chemistry 92</td>
</tr>
<tr>
<td>PBE0</td>
<td>4</td>
<td>chemistry 93</td>
</tr>
</tbody>
</table>

\(^a\) Attempts to apply the M06-L\(^47\) MGGA were unsuccessful due to convergence issues for a wide range of systems from almost all considered datasets. Note that problems of evaluating MGGA potentials, especially for the M06 family of functionals, are discussed in recent literature.\(^84-86\)

\(^b\) Hybrid functionals have not been applied to extended systems.

\(^c\) Should be understood as a very general characterization of the main target of a functional, and does not consider underlying principles of design.

indicating severe overbinding. The TPSS and revTPSS MGGA approximations perform quite well on this set.

Turning to the vdW-DF variants, good description of the G2/97 formation energies is also found for vdW-DF and vdW-DF2. This, however, is not the case for the optPBE-vdW, optB88-vdW, and C09-vdW functionals, for which the GGA exchange components are optimized with vdW dominated energetics in mind. This approach apparently leads to intramolecular overbinding, as previously noted in Ref. 31.

For comparison, Table VI also includes statistics for the B3LYP and PBE0 hybrids. As the wide application of hybrid XC functionals in the quantum chemistry community suggests, B3LYP and PBE0 accurately describe molecular bond energetics, and the B3LYP parametrization is found to be the best DFA for the G2/97 dataset. Table VI furthermore shows that also the BEEF-vdW functional performs very well in predicting molecular formation energies. With a MAD of 0.16 eV, BEEF-vdW is highly accurate on the G2/97 thermochemical set, and even outperforms the PBE0 hybrid on these systems.

Now, let us switch attention to the G3-3 set of 75 molecules, which the BEEF-vdW model was not trained on. For most XC functionals tested here, the average deviations on G3-3 are larger than on G2/97. It is, however, noteworthy that TPSS, revTPSS, vdW-DF, and vdW-DF2 are exceptions to this trend. Benchmarking BEEF-vdW on G3-3 validates its good performance in predicting molecular bond energetics. This conclusion is underlined by the BEEF-vdW deviation statistics on the full G3/99 compilation. With a MAD of 0.19 eV, it is the most accurate DFA tested on G3/99, closely followed by B3LYP. Both MGGA functionals as well as vdW-DF and vdW-DF2 also perform well on this set.

### B. Molecular reaction energies

The last column of Table VI summarizes deviation statistics for the RE42 dataset. Even though the reaction energies are derived from the G2/97 formation energies, the reaction energies appear difficult to capture accurately with GGA, MGGA, and vdW-DF type functionals. None of them yield a STD less than 0.3 eV. The B3LYP hybrid proves significantly more accurate in this respect. Interestingly, the optPBE-vdW and optB88-vdW functionals, which both severely overestimate the G2/97 formation energies, prove as reliable for calculating gas-phase reaction energies as the best GGA (RPBE), and compare well to TPSS and BEEF-vdW.

### C. Chemisorption on solid surfaces

Deviation statistics for the CE17 and CE27 datasets are reported in the first two columns of Table VII. The BEEF-vdW model was trained on CE17, while CE27 contains 10 extra entries, mostly covering dissociative H\(_2\) chemisorption on late transition metal surfaces.

With MADs ≥ 0.7 eV, LDA and the GGAs designed for solid state applications are clearly overbinding simple adsorbates to solid surfaces (negative MSEs). The RPBE, BLYP, and HCTH407 functionals are significantly more reliable for calculation of chemisorption energies, RPBE performing best with a MAD of 0.11 eV for both CE17 and CE27. Also vdW-DF and vdW-DF2 yield MADs of 0.20 eV of less on CE27, while the two MGGA overbind on average. Again, a significant overbinding is found for the three exchange-modified vdW-DF flavors.

Lastly, it is seen from the CE17 column in Table VII that BEEF-vdW is among the DFAs offering most accurate predictions of chemisorption energies of simple adsorbates on solid surfaces. Since much of this accuracy is retained when moving to CE27, good transferability is expected when applying BEEF-vdW to other types of surface processes involving rupture and formation of chemical bonds.

### D. Molecular reaction barriers

The DBH24/08 reaction barrier heights belong to a class of systems for which a fraction of exact exchange is known to increase computational accuracy significantly
over GGA's. This is supported by the DBH24/08 data in Table VII, where the two hybrids clearly outperform the lower-rung XC functionals. Considering the corresponding statistics for BEEF-vdW as well as for the individual DBH24/08 XC model reported in Table I, where a MAD of 0.12 eV was obtained, it is clear that the BEEF-vdW model has moved significantly away from the part of model space favored by gas-phase reaction barrier heights. Nevertheless, BEEF-vdW is among the best non-hybrid functionals for such quantities.
E. Noncovalent interactions

The last column of Table VII lists deviation statistics for the S22x5 interaction energies. As previously found in several studies of the original S22 dataset, vdW dominated interactions are well described by vdW-DF type density functionals, especially those with an optimized exchange component. With MADs of 20 meV or less over all 110 points on the 22 potential-energy curves, the optPBE-vdW, optB88-vdW, and C09-vdW functionals prove highly accurate in this respect. The vdW-DF functional also captures vdW interactions well, but the positive MSE signifies that most of the deviations from the CCSD(T) reference energies stem from underbinding.

Concerning computational accuracy, the vdW-DF2 MSE of 43 meV and MAE of 44 meV for S22x5-1.0 obtained here compare very well to the MSE and MAE of 40 and 41 meV, respectively, found in a recent study for a revised S22 dataset.

TABLE IX. Deviation statistics for the Sol27Ec cohesive energies (eV/atom) and Sol27LC lattice constants (Å). Zero-point vibrational effects have been removed from both experimental datasets.

<table>
<thead>
<tr>
<th>Method</th>
<th>Sol27Ec (27)</th>
<th></th>
<th>Sol27LC (27)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MSD</td>
<td>MAD</td>
<td>STD</td>
<td>MSD</td>
</tr>
<tr>
<td>LDA</td>
<td>-0.89</td>
<td>0.89</td>
<td>1.08</td>
<td>-0.07</td>
</tr>
<tr>
<td>PBE</td>
<td>-0.10</td>
<td>0.27</td>
<td>0.38</td>
<td>0.05</td>
</tr>
<tr>
<td>RPBE</td>
<td>-0.54</td>
<td>0.58</td>
<td>0.71</td>
<td>0.11</td>
</tr>
<tr>
<td>PBEsol</td>
<td>0.43</td>
<td>0.45</td>
<td>0.63</td>
<td>-0.01</td>
</tr>
<tr>
<td>BLYP</td>
<td>-0.79</td>
<td>0.80</td>
<td>0.89</td>
<td>0.11</td>
</tr>
<tr>
<td>AM05</td>
<td>0.25</td>
<td>0.36</td>
<td>0.51</td>
<td>0.01</td>
</tr>
<tr>
<td>WC</td>
<td>0.37</td>
<td>0.41</td>
<td>0.57</td>
<td>0.00</td>
</tr>
<tr>
<td>HCTH407</td>
<td>-0.59</td>
<td>0.67</td>
<td>0.82</td>
<td>0.08</td>
</tr>
<tr>
<td>TPSS</td>
<td>0.08</td>
<td>0.27</td>
<td>0.36</td>
<td>0.05</td>
</tr>
<tr>
<td>revTPSS</td>
<td>0.31</td>
<td>0.37</td>
<td>0.50</td>
<td>0.03</td>
</tr>
<tr>
<td>vdW-DF</td>
<td>-0.54</td>
<td>0.60</td>
<td>0.72</td>
<td>0.12</td>
</tr>
<tr>
<td>vdW-DF2</td>
<td>-0.58</td>
<td>0.64</td>
<td>0.75</td>
<td>0.12</td>
</tr>
<tr>
<td>optPBE-vdW</td>
<td>-0.12</td>
<td>0.27</td>
<td>0.38</td>
<td>0.06</td>
</tr>
<tr>
<td>optB88-vdW</td>
<td>0.01</td>
<td>0.25</td>
<td>0.36</td>
<td>0.04</td>
</tr>
<tr>
<td>C09-vdW</td>
<td>0.42</td>
<td>0.43</td>
<td>0.59</td>
<td>0.01</td>
</tr>
<tr>
<td>BEEF-vdW</td>
<td>-0.37</td>
<td>0.45</td>
<td>0.59</td>
<td>0.08</td>
</tr>
</tbody>
</table>

F. Solid state properties

Table IX reports a summary of deviation statistics for calculations of lattice constants (Sol27LC) and cohesive
energies (Sol27Ec).

The lattice constant statistics are in clear favor of the PBEsol, AM05, WC, and revTPSS functionals. Their standard deviations are small and the MSEs are close to zero Å. On average, however, these remarkably accurate predictions of equilibrium crystal volumes come at the price of overestimated cohesive energies.

The picture is opposite for vdW-DF and vdW-DF2. Lattice constants are overestimated and more so than with any other XC functional tested, vdW-DF2 yielding a standard deviation of 0.18 Å. Furthermore, those two DFAs notably underestimate cohesive energies. The less repulsive exchange functionals of the modified vdW-DF variants lead in general to statistics similar to those of PBE and TPSS for the two materials properties in question.

These findings closely match those reported in recent studies assessing the performance of GGA, MGGA, and vdW-DF type XC functionals for solid state properties.

Benchmarking finally BEEF-vdW, we find in Table IX that it performs reasonably well for cohesive energies and lattice constants, though still predicting softer crystal lattices than the optimized vdW-DF variants. With BEEF-vdW these two bulk materials properties are, however, significantly closer to agreement with experiments than predictions by vdW-DF, vdW-DF2, and most of the GGAs designed mainly for chemistry.

**VIII. APPLICATIONS**

Two applications of BEEF-vdW to problems of current interest in the surface science community are here presented; graphene adsorption on the close-packed Ni(111) surface, and the trends observed when applying lower-rung density functionals in calculations of the binding energy of CO to Pt(111) and Rh(111) substrates as well as the surface energy of those substrates.

A. Graphene adsorption on Ni(111)

The remarkable electronic properties of monolayer graphene and its potential application in electronics technology motivate investigation of the interactions between graphene sheets and metallic surfaces. The nature of graphene adsorption on metals is highly metal-dependent, some surfaces binding graphene only weakly and others forming strong covalent bonds to the carbon sheet. The Ni(111) surface belongs to the latter group, graphene forming a (1 x 1) overlayer at a graphene–metal distance of d = 2.1 Å. Furthermore, a bandgap is induced in graphene upon adsorption, underlining the strong hybridization responsible for changing the electronic structure of the carbon sheet.

Several theoretical studies have investigated the graphene/Ni(111) potential-energy curve, with mixed results. However, based on RPA calculations, it is by now established that this particular adsorption process is a delicate competition between strong interactions close to the surface and vdW forces further from the surface.

Figure 7 shows calculated PECs for graphene adsorption on Ni(111) using LDA, MGGA, and vdW-DF type density functionals, as well as BEEF-vdW. Computational details are given in the Appendix. Additionally, two sets of RPA data are shown for comparison, indicating that graphene adsorption on Ni(111) is characterized by a physisorption minimum at d = 3.0–3.5 Å and a chemisorbed state at d ≈ 2.2 Å, the latter in good agreement with experiments. However, as previously found, rung 1–3 DFAs, as well as vdW-DF and vdW-DF2, fail to simultaneously describe both qualitative features. Conversely, the optPBE-vdW and optB88-vdW PECs are increasingly closer to RPA data. The BEEF-vdW PEC shows qualitatively similar features, but the local minimum at d = 2.25 Å is very shallow and yields a positive adsorption energy.

Figure 7 also shows ensemble error estimates along the...
BEEF-vdW PEC. Especially two aspects of these are of interest. First of all, the error bars do not straddle the zero line for large graphene–metal distances, indicating that confidence in the presence of a physisorption minimum is high. Secondly, the error bars enlarge notably at smaller distances from \( d = 2.6 \) Å and inwards, reflecting that these BEEF-vdW data points are associated with a significantly larger uncertainty. Recalling how the ensemble error estimate is designed (Sec. VI), the error estimates indicate that the graphene/Ni(111) PEC is very sensitive to the choice of XC functional in the chemically interesting range. Put differently, the ensemble suggests that we should not trust the BEEF-vdW prediction of a positive PEC for \( d < 2.7 \) Å as a definite result, the estimated errors are simply too large in this region of the PEC.

B. Surface chemistry and stability

Chemisorption energies of molecules on surfaces are obviously important quantities in heterogeneous catalysis and surface science. However, accurate computation of surface energies, \( E_\gamma \), can be critical as well, since minimization of surface energy is a driving force determining the morphology and composition of surfaces, interfaces, and nanoparticles.\(^{123}\) GGA density functionals, however, often underestimate \( E_\gamma \), and the GGAs yielding most accurate surface energies also vastly overbind molecules to surfaces.\(^{119}\) It thus appears that accurate computation of chemisorption energies on a surface as well as the stability of that surface is not possible with the same GGA approximation, underscoring a fundamental incompleteness of the GGA XC model space.

The issue is here investigated for vdW-DF variants and BEEF-vdW. Figure 8 shows atop chemisorption energies of CO on Pt(111) and Rh(111) against surface energies of those substrates, calculated using GGA, MGGA and vdW-DF type functionals, and BEEF-vdW with error estimation. These are compared to RPA results and experimental data.

As previously reported,\(^{119,124}\) the GGA data points fall along an approximately straight line, which is significant offset from the experimental data, thus illustrating the issue discussed above. This is here shown to be the case for vdW-DF variants also: The dashed vdW-DF lines are parallel to the solid GGA lines, and are only slightly offset from the latter, especially for Rh(111). The vdW-DF and vdW-DF2 data points are quite close to RPBE. Larger surface energies are found with the exchange-modified vdW-DF variants, albeit at the expense of overestimated chemisorption energies. Note that such a correlation should be expected from Tables VII and IX and a linear relation between \( E_\gamma \) and the solid cohesive energy.\(^{123}\)

Though BEEF-vdW contains the vdW-DF2 nonlocal correlation functional as an essential component, the former predicts larger surface energies than the latter with-

We expect that this ability of BEEF-vdW to ”break” the vdW-DF line is due to the expanded GGA model space as compared to vdW-DF, the latter of which pairs nonlocal correlation with LDA correlation. Significant inclusion of semilocal correlation in vdW-DF type calculations was also found in Ref. 31 to broadly improve accuracy for several materials properties.

The BEEF-vdW error estimates furthermore appear out sacrificing accuracy of the CO–metal binding energy.

![FIG. 8. (Color online) Atop CO chemisorption energies \( \Delta E \) versus surface energies \( E_\gamma \) for Pt(111) and Ru(111). Red and blue lines are linear fits to GGA and vdW-DF type data points, respectively. MGGA data in green, and yellow RPA data adapted from Ref. 119. Estimated standard deviations are indicated by error bars around the orange the BEEF-vdW data points. All points \( (E_\gamma, \Delta E) \) inside the gray areas are within one standard deviation from the BEEF-vdW point for both quantities. Experimental surface energies from liquid-metal data (Refs. 120 and 121), and experimental CO chemisorption energies from Ref. 122.](https://example.com/figure8.png)
very reasonable. The experimental CO chemisorption energies are straddled for both Pt(111) and Rh(111), and the error estimates along $E_a$ almost fill out the gap between the GGA lines to the left and the RPA and C09-vdW surface energies to the right.

Lastly, it is seen from the green TPSS and revTPSS data points in Fig. 8, as also reported in Ref. 124, that the third rung of Jacob's ladder may offer the possibility of quite accurate surface energies with only moderately overbound surface adsorbates.

IX. DISCUSSION

The presented approach to semi-empirical DFA development fundamentally considers XC functionals as more or less accurate models of the exact density functional. From this point of view, the XC model space expansion and model selection procedure are essential. As datasets for calibrating or benchmarking XC models.

The concept of an ensemble of model solutions is intrinsic to the present model selection procedure. The cost function for a single dataset has both weak (sloppy) and strong (important) eigenmodes in a sufficiently flexible model space. Regularization is used to suppress the weak modes in order to facilitate a physically sensible model and maximize transferability. The regularized ensemble thus contracts around the strong modes, and the optimum model can, to some extent, be regarded as an average of the ensemble solutions. Without Tikhonov regularization of exchange, all XC approximations obtained in this work would have 31 parameters and wildly oscillating GGA exchange solutions, corresponding to a least squares fit of an order 30 polynomial in the reduced density gradient. Instead, well-behaved models with 3–8 effective parameters are obtained.

It is important to note that model selection is intrinsically connected to the model space. The reduced density gradient transformation $f(s)$ defines the expansion of GGA exchange. It thereby also determines how hard the regularization punishes non-smoothness in different regions of $s$-space, as well as how the exchange part of the prior solution transforms to $s$-space. As previously stated, the prior is the origo for the XC model solution. Many different priors may be chosen, but we find it convenient that it transforms to a reasonable exchange approximation. Then, decreasing regularization from infinity towards zero leads to increasingly non-smooth variations away from this initial guess.

The linear combination correlation model space of local, semilocal, and nonlocal correlation was anticipated to enable highly accurate calculations for several, if not all, of the datasets considered. The individually trained models in Table I confirm this, some sets favoring full LDA correlation in addition to nonlocal ditto, other sets preferring full PBE correlation, while most sets are fitted best by a combination of both. The corresponding exchange functionals are also significantly different, so the sets of strong eigenmodes for the regularized cost functions are very materials property dependent. We argue here that explicitly considering transferability among different materials properties is important for producing a single DFA composed of the most important modes for the combined datasets, that is, the optimum model compromise must be found.

One approach to this task is minimizing a weighted sum of the individual cost functions. This is somewhat similar to weighted training functions used in least squares fitting procedures, but with the critically important addition of regularization. The summed cost function is elegantly minimized using the individual solutions only, but gives no information regarding how the weights should be chosen. Clearly, an XC model trade-off is inevitable, so the weights should be the ones yielding an optimum compromise. For just two datasets, a wide range of poor choices of weights can be made, and the complexity of this choice increases with the number of datasets. In line with the statistical approach taken in the bulk of this work, we believe that such choice should not be made based on experience or intuition alone. Rather, a systematic methodology for locating one or more points in XC model space, where a well-behaved and properly compromising solution resides, is desirable. The condition of minimizing the product of relative costs for each dataset is a reasonable requirement for the model solution, philosophically as well as in practice: The condition essentially states, that if changing the solution vector $a$ to $a + \delta a$ gains a larger relative reduction in cost on one materials property than is lost in total on all other properties considered, then $a + \delta a$ is preferred.

Extensive benchmarking of BEEF-vdW against popular GGA, MGGA, vdw-DF type, and hybrid XC functionals shows that the developed methodology is able to produce truly general-purpose XC approximations. Results are summarized in Fig. 9, where error statistics for representative functionals on gas-phase chemical, surface chemical, solid state, and vdW dominated datasets are illustrated by bars. The BEEF-vdW model compromise is indeed a very agreeable one. For none of the datasets is the average BEEF-vdW error among the largest, while several other functionals are highly biased towards certain types of materials properties. This is especially true for vdW-DF2 and optB8S-vdW, displaying severely erroneous description of binding energetics for bulk solids and molecules, respectively. Furthermore, the figure shows an overall performance equivalence of BEEF-vdW and the original vdw-DF for gas-phase and surface chemical properties, though the former more accurately predicts bonding in the solid state. Further testing of the functional might, however, prove interesting. Systems such as ionic solids, semiconductors, and transition metal complexes are not included in the present benchmark, nor are the BEEF-vdW predictions of molecular ionization potentials and electron affinities tested. This will be addressed in future work.

We emphasize the strengths and weaknesses of the
BEEF-vdW ensemble error estimate. The ensemble functionals are based on a probability distribution for the model parameters, which limits the ensemble to the BEEF-vdW model space only. This space is incomplete in the sense that it can not accommodate a physically reasonable XC model yielding zero error on all systems in all datasets considered, hence the model trade-off. The BEEF-vdW computational errors are in general reasonably well estimated, but the energetics of certain systems is rather insensitive to the choice of XC approximation within the GGA, MGGA, and vdW-DF type model spaces. This leads to relatively small error estimates for these systems, even though the actual computational error may be substantial.

Meanwhile, we find BEEF-vdW and the Bayesian ensemble highly useful in surface science related applications. The fact that BEEF-vdW appears to yield more accurate surface energies than GGA or vdW-DF type XC approximations of similar accuracy for adsorbate–surface bond strengths is very promising. The error estimate proves very useful in this case, even though the kinetic energy density of MGGA type functionals may be needed in the model space if the surface energy error bars are to span the experimental data. This again illustrates that the ensemble does not give information beyond its model space, as it is solely based on it. However, the error estimate is carries important information in the BEEF-vdW study of graphene adsorption on Ni(111). The PEC is qualitatively wrong in the region of chemical bonding for this intricate case of “solid state adsorption”, and the estimated errors indeed indicate that this part of the BEEF-vdW PEC is poorly determined. BEEF-vdW calculations can therefore not predict with any confidence whether graphene should form chemical bonds to the Ni(111) substrate in a low-temperature experiment. It is encouraging that the ensemble is able to capture this.

X. SUMMARY AND CONCLUSIONS

We have presented and evaluated a machine learning inspired approach to semi-empirical density functional development. Focus has been on general applicability of the resulting density functional to both strong and weak interactions in chemistry and condensed matter physics, including surface chemistry. Transferability and avoiding overfitting are thus key issues, leading the presented methodology to rely primarily on 1) a variety of datasets chosen to represent vastly different interactions and bonding situations, 2) a very flexible XC model space expansion at a computationally feasible GGA+vdW level of approximation, and 3) XC model selection procedures designed to “tame” the flexible model space and yield XC approximations which properly compromise between describing different types of physics and chemistry.

To conclude, we have shown that regularization and cross validation methods are very useful for semi-empirical density functional development in highly flexible model spaces. It is furthermore clear that computationally efficient general-purpose functionals, targeted at accurately describing several physically and chemically different materials properties, necessarily must compromise between those properties in an incomplete XC model space. However, the optimum model trade-off is
not easily found from simple intuition. A simple but powerful principle for determining the position in model space of a properly compromising XC approximation is therefore formulated.

Application of the developed methodology has yielded the BEEF-vdW density functional, and a benchmark of BEEF-vdW against popular GGA, MGGA, vdW-DF type, and hybrid XC functionals for energetics in chemistry and condensed matter physics has been conducted. This benchmark validates BEEF-vdW as a general-purpose XC approximation, with a reasonably reliable description of van der Waals forces and quantitatively accurate prediction of chemical adsorption energies of molecules on surfaces, while avoiding large sacrifices on solid state bond energetics. This should make it a valuable density functional for studies in surface science and catalysis.

Furthermore, an error estimation ensemble of functionals around BEEF-vdW comes out naturally of the developed fitting methodology. The ensemble is designed to provide an easily obtainable estimate of the XC approximation error. It is based on a probability distribution for the XC model parameters, and has been applied in the BEEF-vdW benchmark and qualitative assessments for molecular surface adsorption, surface energies, and graphene adsorption on Ni(111).

Finally, the methods developed here should lend themselves well to other XC model spaces also, including the MGGA level of theory or self-interaction correction schemes.

ACKNOWLEDGMENTS

The authors are grateful for the helpful suggestions and comments by Nicola Marzari, Frank Abild-Pedersen and Joost VandeVondele. This work was supported by the Danish Center for Scientific Computing. The Center for Atomic-scale Materials Design is sponsored by the Lundbeck Foundation. The work at SUNCAT/SLAC has been supported by the US Department of Energy, Basic Energy Sciences.
### TABLE X. Gas-phase molecular reactions and reaction energies (in eV) constituting the RE42 dataset. The experimental reaction energies are compiled from the G2/97 static-nuclei formation energies. \( \Delta V, E < 0 \) means exothermic.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 + 2\text{H}_2 \rightarrow \text{N}_2\text{H}_4 )</td>
<td>0.41</td>
</tr>
<tr>
<td>( \text{N}_2 + 2\text{O} \rightarrow 2\text{NO} )</td>
<td>1.88</td>
</tr>
<tr>
<td>( \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 )</td>
<td>-1.68</td>
</tr>
<tr>
<td>( \text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O} )</td>
<td>-5.45</td>
</tr>
<tr>
<td>( \text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2 )</td>
<td>0.62</td>
</tr>
<tr>
<td>( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 )</td>
<td>-0.31</td>
</tr>
<tr>
<td>( 2\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{N}_2\text{O}_2 )</td>
<td>1.57</td>
</tr>
<tr>
<td>( 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 )</td>
<td>-6.06</td>
</tr>
<tr>
<td>( \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} )</td>
<td>-2.80</td>
</tr>
<tr>
<td>( \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} )</td>
<td>-2.50</td>
</tr>
<tr>
<td>( \text{CH}_4 + \text{NH}_3 \rightarrow \text{HCN} + 3\text{H}_2 )</td>
<td>3.32</td>
</tr>
<tr>
<td>( \text{O}_2 + 4\text{HCl} \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O} )</td>
<td>-1.51</td>
</tr>
<tr>
<td>( 2\text{OH} + \text{H}_2 \rightarrow 2\text{H}_2\text{O} )</td>
<td>-6.19</td>
</tr>
<tr>
<td>( \text{O}_2 + \text{H}_2 \rightarrow 2\text{OH} )</td>
<td>0.74</td>
</tr>
<tr>
<td>( \text{SO}_2 + 3\text{H}_2 \rightarrow \text{SH}_2 + 2\text{H}_2\text{O} )</td>
<td>-2.62</td>
</tr>
<tr>
<td>( \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 )</td>
<td>-1.68</td>
</tr>
<tr>
<td>( \text{CH}_4 + 2\text{Cl}_2 \rightarrow \text{CCl}_4 + 2\text{H}_2 )</td>
<td>0.19</td>
</tr>
<tr>
<td>( \text{CH}_4 + 2\text{F}_2 \rightarrow \text{CF}_4 + 2\text{H}_2 )</td>
<td>-8.60</td>
</tr>
<tr>
<td>( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{methanol} + \text{H}_2 )</td>
<td>1.33</td>
</tr>
<tr>
<td>( \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 )</td>
<td>3.11</td>
</tr>
<tr>
<td>( 3\text{O}_2 \rightarrow 2\text{O}_3 )</td>
<td>2.92</td>
</tr>
<tr>
<td>methylamine + ( \text{H}_2 \rightarrow \text{CH}_4 + \text{NH}_3 )</td>
<td>-1.15</td>
</tr>
<tr>
<td>thioethanol + ( \text{H}_2 \rightarrow \text{H}_2\text{S} + \text{ethane} )</td>
<td>-0.71</td>
</tr>
<tr>
<td>2\text{CO} + \text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2 )</td>
<td>-7.94</td>
</tr>
<tr>
<td>( \text{CO} + 2\text{H}_2 \rightarrow \text{methanol} )</td>
<td>-1.48</td>
</tr>
<tr>
<td>( \text{CO}_2 + 3\text{H}_2 \rightarrow \text{methanol} + \text{H}_2\text{O} )</td>
<td>-1.17</td>
</tr>
<tr>
<td>2\text{methanol} + \text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2 )</td>
<td>-3.11</td>
</tr>
<tr>
<td>4\text{CO} + 9\text{H}_2 \rightarrow \text{trans-butane} + 4\text{H}_2\text{O} )</td>
<td>-9.00</td>
</tr>
<tr>
<td>ethanol \rightarrow \text{dimethylether} )</td>
<td>0.53</td>
</tr>
<tr>
<td>ethyne + ( \text{H}_2 \rightarrow \text{ethene} )</td>
<td>-2.10</td>
</tr>
<tr>
<td>ketene + ( \text{H}_2 \rightarrow \text{ethene} + \text{H}_2\text{O} )</td>
<td>-1.92</td>
</tr>
<tr>
<td>oxirane + ( \text{H}_2 \rightarrow \text{ethene} + \text{H}_2\text{O} )</td>
<td>-1.56</td>
</tr>
<tr>
<td>propyne + ( \text{H}_2 \rightarrow \text{propene} )</td>
<td>-2.00</td>
</tr>
<tr>
<td>propene + ( \text{H}_2 \rightarrow \text{propane} )</td>
<td>-1.58</td>
</tr>
<tr>
<td>allene + ( \text{H}_2 \rightarrow \text{propene} )</td>
<td>-3.64</td>
</tr>
<tr>
<td>iso-butane \rightarrow \text{trans-butene} )</td>
<td>0.08</td>
</tr>
<tr>
<td>( \text{CO} + \text{H}_2\text{O} \rightarrow \text{formic acid} )</td>
<td>-0.39</td>
</tr>
<tr>
<td>( \text{CH}_4 + \text{CO}_2 \rightarrow \text{acetic acid} )</td>
<td>0.28</td>
</tr>
<tr>
<td>( \text{CH}_4 + \text{CO} + \text{H}_2 \rightarrow \text{ethanol} )</td>
<td>-0.91</td>
</tr>
<tr>
<td>1,3-cyclohexadiene \rightarrow 1,4-cyclohexadiene</td>
<td>-0.01</td>
</tr>
<tr>
<td>benzene + ( \text{H}_2 \rightarrow 1,4)-cyclohexadiene</td>
<td>-0.01</td>
</tr>
<tr>
<td>1,4-cyclohexadiene + ( \text{H}_2 \rightarrow \text{cyclohexane} )</td>
<td>-2.94</td>
</tr>
</tbody>
</table>

### Appendix: Details of datasets and computations

1. **G2/97 and G3/99**

In accordance with the procedure of Ref. 49 the G3/99 formation enthalpies are corrected for thermal and vibrational contributions using thermal corrections and zero-point energies from Refs. 49 and 94. The G3/99 set is divided into three subsets denoted G3-1, G3-2, and G3-3 comprising 55, 93, and 75 molecules, respectively. The G3-1 and G3-2 subsets constitute G2/97. The G3-3 subset contains a significant fraction of larger carbon-rich molecules as compared to G2/97.

Theoretical G3/99 formation energies \( \Delta_f E \) are calculated from the difference between molecular and atomic total energies as

\[
\Delta_f E = E_M - \sum_A E_A, \quad (A.1)
\]

where \( A \) runs over all atoms in the molecule \( M \), while \( E_M \) and \( E_A \) are ground state molecular and atomic total energies at 0 K, respectively.
TABLE XII. Experimental solid-state properties of 27 cubic bulk solids. The ZPAE exclusive Sol27LC zero Kelvin lattice constants \( a_0 \) (Å) are adapted from Ref. 98. Zero Kelvin Sol27Ec cohesive energies \( E_c \) (eV/atom) from Ref. 125 are corrected for ZPVE contributions. Strukturbericht symbols are indicated in parenthesis for each solid. A1: fcc, A2: bcc, A3: hcp, A4: diamond.

<table>
<thead>
<tr>
<th>Solid</th>
<th>Sol27LC</th>
<th>Sol27Ec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li (A2)</td>
<td>3.451</td>
<td>1.66</td>
</tr>
<tr>
<td>Na (A2)</td>
<td>4.209</td>
<td>1.05</td>
</tr>
<tr>
<td>K (A2)</td>
<td>5.212</td>
<td>0.94</td>
</tr>
<tr>
<td>Rb (A2)</td>
<td>5.577</td>
<td>0.86</td>
</tr>
<tr>
<td>Ca (A1)</td>
<td>5.565</td>
<td>1.86</td>
</tr>
<tr>
<td>Sr (A1)</td>
<td>6.040</td>
<td>1.73</td>
</tr>
<tr>
<td>Ba (A2)</td>
<td>5.092</td>
<td>1.91</td>
</tr>
<tr>
<td>V (A2)</td>
<td>3.024</td>
<td>5.35</td>
</tr>
<tr>
<td>Nb (A2)</td>
<td>3.294</td>
<td>7.60</td>
</tr>
<tr>
<td>Ta (A2)</td>
<td>3.299</td>
<td>8.12</td>
</tr>
<tr>
<td>Mo (A2)</td>
<td>3.141</td>
<td>6.86</td>
</tr>
<tr>
<td>W (A2)</td>
<td>3.160</td>
<td>8.94</td>
</tr>
<tr>
<td>Fe (A2)</td>
<td>2.853</td>
<td>4.33</td>
</tr>
<tr>
<td>Rh (A1)</td>
<td>3.793</td>
<td>5.80</td>
</tr>
<tr>
<td>Ir (A1)</td>
<td>3.831</td>
<td>6.98</td>
</tr>
<tr>
<td>Ni (A1)</td>
<td>3.508</td>
<td>4.48</td>
</tr>
<tr>
<td>Pd (A1)</td>
<td>3.876</td>
<td>3.92</td>
</tr>
<tr>
<td>Pt (A1)</td>
<td>3.913</td>
<td>5.86</td>
</tr>
<tr>
<td>Cu (A1)</td>
<td>3.596</td>
<td>3.52</td>
</tr>
<tr>
<td>Ag (A1)</td>
<td>4.062</td>
<td>2.97</td>
</tr>
<tr>
<td>Au (A1)</td>
<td>4.062</td>
<td>3.83</td>
</tr>
<tr>
<td>Pb (A1)</td>
<td>4.912</td>
<td>2.04</td>
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<tr>
<td>Al (A1)</td>
<td>4.019</td>
<td>3.43</td>
</tr>
<tr>
<td>C (A4)</td>
<td>3.544</td>
<td>7.59</td>
</tr>
<tr>
<td>Si (A4)</td>
<td>5.415</td>
<td>4.69</td>
</tr>
<tr>
<td>Ge (A4)</td>
<td>5.639</td>
<td>3.89</td>
</tr>
<tr>
<td>Sn (A4)</td>
<td>6.474</td>
<td>3.16</td>
</tr>
</tbody>
</table>

ZPVE corrections are calculated according to Eq. (A.6) using Debye temperatures from Ref. 125.

2. RE42

The 42 molecular reaction energies \( \Delta_r E \) of the RE42 set are listed in Table X. Theoretical reaction energies are calculated from the total energies of G2/97 molecules after full geometry relaxation as

\[
\Delta_r E = \sum_P E_P - \sum_R E_R, \quad (A.2)
\]

where the sums run over reactant (\( R \)) and product (\( P \)) molecules.

3. DBH24/08

Forward (\( V_f \)) and backward (\( V_b \)) benchmark reaction barriers from high-level theory or experiments are adapted from Ref. 50. Ground and transition state molecular QCISD geometries are from Ref. 136.

Density functional barrier heights are computed from the transition state total electronic energy (\( E_{ts} \)) and the initial (\( E_i \)) and final (\( E_f \)) state total energies as

\[
V_f = E_{ts} - E_i, \quad V_b = E_{ts} - E_f. \quad (A.3)
\]

4. S22x5

The original S22 publication\(^{51}\) from 2006 reported CCSD(T) interaction energies of 22 noncovalently
bonded complexes with extrapolation to the complete basis-set (CBS) limit. However, different basis sets were used for small and large complexes. Geometries were determined from MP2 or CCSD(T) calculations. Later works\textsuperscript{61,137} have revised the S22 interaction energies, employing larger and identical basis sets for all complexes without changing the geometries. For the larger complexes the reported basis-set effects are significant, so we use here the CCSD(T)/CBS energies of Takatani \textit{et al.}\textsuperscript{61} as the current best-estimate of the true S22 interaction energies.

The S22x5\textsuperscript{52} CCSD(T)/CBS potential-energy curves were reported more recently. The computational protocol was, however, not updated from that used for S22, so we expect the aforementioned interaction-energy inaccuracies to persist for S22x5. In order to shift the equilibrium point on each PEC to the revised S22 energies, and approximately correct the remaining data points, a modification of the (possibly) slightly inaccurate S22x5 CCSD(T) interaction energies is here introduced as

\[ E_{\text{int}}^d := \varepsilon_{\text{int}}^d \times E_{\text{int}}^{1.0} \]

where \( E_{\text{int}}^d \) and \( \varepsilon_{\text{int}}^d \) denote modified and original S22x5 energies at the relative intermolecular distance \( d \), respectively. For \( E_{\text{int}} = \varepsilon_{\text{int}} \) Eq. (A.4) obviously reduces to \( E_{\text{int}}^d = \varepsilon_{\text{int}}^d \) for all distances. The obtained corrections to \( \varepsilon_{\text{int}}^d \) are listed in Table XI. The maximum correction of 11.4\% amounts to 25.6 meV for the indole–benzene complex in a stacked geometry, while the total mean signed correction to all the 110 interaction energies is 0.1 meV.

The modified CCSD(T) interaction energies are used throughout this study for the S22x5 dataset and subsets. Each density functional interaction energy \( E_{\text{int}}^d \) is calculated as the difference between the total electronic energy of the interacting complex, \( E_0^d \), and those of its two isolated molecular constituents, \( E_1^d \) and \( E_2^d \):

\[ E_{\text{int}}^d = E_0^d - E_1^d - E_2^d. \]

Computational accuracy is enhanced by keeping all atoms in the molecular fragments in the same positions in the box as those atoms has when evaluating the total energy of the complex.

5. **Sol27LC and Sol27Ec**

It was recently shown\textsuperscript{78} that removal of thermal and zero-point contributions to experimentally determined lattice constants and bulk moduli may be important when benchmarking density functional methods. Experimental zero Kelvin lattice constants and cohesive energies (\( E_c \)) contain zero-point vibrational contributions, leading to zero-point anharmonic expansion (ZPAE) of the lattice and zero-point vibrational energy (ZPVE) contributions to \( E_c \). As discussed in Ref. 138, an estimate of the ZPVE may be obtained from the Debye temperature \( \Theta_D \) of the solid according to

\[ \text{ZPVE} = -\frac{9}{8} k_B \Theta_D. \]  

The vibrational contribution is subtracted from the cohesive energy, leading to increased stability of the crystal towards atomization. The same reference derived a semi-empirical estimate of the ZPAE contribution to the volume of cubic crystals. A recent study\textsuperscript{18} calculating the ZPAE from first principles largely validates this approach.

The Sol27LC and Sol27Ec sets of zero Kelvin lattice constants and cohesive energies of 27 fcc, bcc, and diamond structured bulk solids are appropriately corrected for zero-point phonon effects. Details are given in Table XII.

Density functional computation of total energies of the extended bulk solids are done using a 16\( \times \)16\( \times \)16 \( \mathbf{k} \)-point mesh for sampling reciprocal space of the periodic lattice and 0.1 eV Fermi smearing of the electron occupation numbers. Calculations for bulk Fe, Ni, and Co are spin polarized. The cohesive energy for a given crystal lattice constant \( a \) is calculated from

\[ E_c = E_A - E_B, \]

where \( E_A \) is the total energy of the free atom and \( E_B \) is the bulk total energy per atom. By this definition, the equilibrium cohesive energy of a stable solid is a positive quantity. Equilibrium lattice constants of cubic crystals, \( a_0 \), are determined from fitting the SJEOS\textsuperscript{138} equation of state to cohesive energies sampled in five points in a small interval around the maximum of the \( E_c(a) \) curve.

6. **CE17 and CE27**

The CE17 and CE27 data are derived from temperature programmed desorption experiments or from microcalorimetry, most often at low coverage. The 27 chemisorption energies have been critically chosen from literature with emphasis on reliability as well as covering a reasonably wide range of substrates and adsorbates. All data is listed in Table XIII along with details regarding adsorption mode, adsorption site, and references. Most of the CE27 surface reactions are molecular adsorption processes at 0.25 ML coverage. In that case the chemisorption energy is computed according to

\[ \Delta E = E_{AM} - E_M - x E_A, \]

where \( E_{AM} \) is the total electronic energy of the adsorbate \( A \) on metal surface \( M \), and \( E_A \) and \( E_M \) total energies of the isolated adsorbate and metal surface, respectively. The constant \( x \) equals 1 for molecular adsorption and \( N_2 \) dissociation on Fe(100), while \( x = \frac{1}{2} \) for the dissociative \( H_2 \) chemisorption reactions. In the case of NO dissociation on Ni(100) at 0.25 ML coverage the chemisorption energy is

\[ \Delta E = E_{AM} + E_{BM} - 2E_M - E_{AB}. \]
where $AB$ is the NO molecule.

With these definitions of chemisorption energies we consider extended surface slab models with $2 \times 2$ atoms in each layer and 5 layers in total. The slab models are periodic in the surface plane and a vacuum width of 20 Å separates periodically repeated slabs perpendicularly to the surface planes. Calculations involving Fe, Ni, and Co are spin polarized. Well-converged chemisorption energies are obtained using a $10 \times 10 \times 1$ k-point mesh and a real-space grid spacing around 0.16 Å. The self-consistently determined lattice constant of the slab solid obviously determines the $xy$-dimensions of the slab simulation cell. Since the number of real-space grid points employed in each direction is discrete, a grid spacing of exactly 0.16 Å in the $x$- and $y$-directions is rarely possible for slab calculations. Instead, it may be slightly smaller or larger, which should not affect the computational accuracy significantly. During structure relaxations the bottom two layers of the $2 \times 2 \times 5$ slab models are fixed in the bulk structure as found from bulk calculations.

7. Graphene adsorption on Ni(111)

Adsorption of graphene on Ni(111) was modelled using a $1 \times 1 \times 5$ surface slab, a Ni(fcc) lattice constant of 3.524 Å as determined with the PBE density functional, and 20 Å vacuum width. The top three atomic layers were fully relaxed with PBE using a grid spacing of 0.15 Å and a $(20 \times 20 \times 1)$ k-point mesh. Carbon atoms were placed in atop and fcc adsorption sites, respectively.
If one or more of the individual cost functions have very strong modes, several stationary points of the product cost function can exist. In this case one must carefully determine all stationary points, and select the one which represents the best compromise. For the subsequent fitting of the BEEF-vdW, this was a minor issue.

The GPaw and ase codes are available as parts of the CAMPOS software: http://www.cams.dtu.dk/Software.

The CMR web-interface is found at http://cmr.fysik.dtu.dk.

See Supplemental Material at [URL] for 1) Figures comparing the performance of representative XC functionals at system level for all datasets considered in benchmarking, and including BEEF-vdW ensemble error estimates, 2) Tables of those quantities, which are also used for the benchmark statistics, 3) CSV files containing the raw DFT data for benchmarking, and 4) the BEEF-vdW $\Omega^{-1}$ ensemble matrix in CSV format. All the CSV files contain header information.

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Paper 3

Real-Time Observation of Surface Bond Breaking with an X-ray Laser

Title: Real-Time Observation of Surface Bond Breaking with an X-ray Laser

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**Abstract:**

We use the Linac Coherent Light Source free-electron x-ray laser to probe the electronic structure of CO molecules as their chemisorption state changes upon exciting the Ru(0001) substrate using a femtosecond optical laser pulse. We observe electronic structure changes consistent with a weakening of the CO interaction with the substrate, but without significant desorption. This indicates that a large fraction of the molecules becomes trapped in a transient precursor state prior to desorption. The free energy of the molecule as a function of the desorption reaction coordinate is estimated using density functional theory including non-local correlation to describe van der Waals interactions. We find two distinct adsorption wells, chemisorbed and precursor state, separated by an entropy barrier which explains the anomalously high prefactors often observed in desorption of molecules like CO from metals. The present work is the first direct spectroscopic transient observation of a precursor state in desorption and, by time-reversal, in adsorption, and shows that the precursor is characterized by bonding CO states that interact weakly with the metal while the anti-bonding $2\pi^*$ states still couple significantly.

**Main Text:**

In heterogeneous catalysis, reactants adsorbed on surfaces are converted by the catalyst to products, which eventually desorb via various intermediates. It is a chemist’s dream to follow such a surface chemical reaction in real time. Many surface reaction intermediates are, however, transient species with a short residence time making their observation a challenge. For the most fundamental elementary surface chemical process, the adsorption or (by time reversal) desorption of a molecule, it has been proposed since half a century that a weakly bound “precursor” state exists (1-4), but this transient state has never been directly detected in terms of a spectroscopic signature. Ultrafast vibrational spectroscopy measurements with pump-probe techniques have the potential to detect short-lived transient species on surfaces (5-10). A shift of the vibrational frequency of desorbing CO molecules was detected using pump-probe sum frequency generation spectroscopy (SFG), but this was mostly attributed to excitation of frustrated rotational motion, leading to diffusive motion parallel to the surface, rather than to a weakly adsorbed state (6-8).

Here we demonstrate that a transient state in CO desorption from a Ru(0001) surface can be observed using ultrafast pump-probe techniques based on an x-ray free-electron laser, the Linac Coherent Light Source (LCLS). With an optical laser pump pulse we increase the phonon temperature of the substrate on a picosecond timescale, allowing for a rapid population of the adsorbate transient state as an intermediate prior to desorption. With the use of oxygen resonant x-ray emission spectroscopy (XES) and x-ray absorption spectroscopy (XAS), the time evolution of the electronic structure around the adsorbed CO molecule on Ru(0001) could be followed in an element-specific way during the desorption process. In particular, the CO molecules in the transient state are found to have an electronic structure closer to the gas phase than to the chemisorbed state; however, the occupied states are still significantly affected by the interaction with the surface. We propose to characterize this transient state as a two-dimensional gas of CO molecules weakly attached to the surface. The experimental results are complemented by density
functional theory (DFT) calculations of the potential energy surface with a new functional that includes van der Waals interactions through non-local correlation.
The principle of core-level excitation (XAS) and de-excitation (XES) together with the static spectra from the oxygen atom for CO chemisorbed on Ru(0001) is illustrated in Fig. 1. Core-level spectroscopies have the ability to provide atom-specific probes of the electronic structure, both the occupied (XES) and unoccupied (XAS) states, through the involvement of the local O 1s level. The chemical bonding of CO to late transition metal and noble metal surfaces has been investigated in great detail with XES in combination with DFT calculations. What is important in the bond formation between CO and a transition metal surface is the interaction between theπ-orbitals of the molecule and the metal d-states as well as the polarization of the 5σ-orbital away from the surface. In particular, the 5σ orbital interaction with the surface leads to a shift to higher binding energy and an orbital polarization from the carbon to the oxygen atom in comparison to gas phase. Theπ-interaction with the surface involves both the CO 1π and 2π* levels together with d-states in the metal resulting in an allylic configuration. The lowest in energy of the resulting three orbitals is the 1π̃ orbital in a bonding configuration with the metal; the tilde indicates that the orbital is different from gas-phase as a result of mixing in the bond-formation to the surface. The middle orbital (denoted 1dπ) is non-bonding with mainly d-character with a lone-pair contribution on the oxygen atom while the highest orbital is the 2π* level in an antibonding configuration with respect to the metal. The 2π* level lies mainly above the Fermi level but is shifted down towards the Fermi level upon adsorption on the surface through mixing with 1π.

Figure 2 presents dynamic information on the electronic structure obtained with the LCLS x-ray free-electron laser before and 12 ps after inducing a surface temperature jump with a 400 nm optical laser pulse. There are four major spectral changes that can be directly observed from the data. First we note that the peak containing the 5σ̃ and 1σ̃ orbitals becomes sharper with a decrease in intensity of the shoulder at 523.5 eV and seems to shift to higher emission energies. The dip between the 4σ and 5σ spectral features thereby becomes more resolved. Secondly the broad shoulder around 527 eV, where the 1dπ is observed in the XES spectra, becomes vanishingly small. Thirdly the peak corresponding to elastic scattering of the incident beam centered around 535 eV increases in intensity. In the XAS spectra we observe both a shift towards higher absorption energies and higher intensities of the 2π* resonance. All the observed spectral changes in the electronic structure are consistent with a significant amount of CO molecules being more weakly bound to the surface.

All these spectral observations are refined using peak fitting and the evolution of the peaks with pump-probe delay time is shown in Fig. 3. We have chosen to display only the average of the 5σ̃ and 1σ̃ peak positions in Fig. 3A in order to have a parameter that becomes independent of the details of the fitting procedure of each of the two components. We observe that all the changes evolve on a timescale of a few ps and reach a maximum after 6-10 ps, after which they are nearly constant. With a weakening of the bond between CO and metal, the 5σ̃ orbital should shift towards the gas phase 5σ position at higher emission energy and lose intensity since the orbital would polarize back towards the carbon atom and we are probing the electron density around the oxygen. This would explain the overall shift of the combined 5σ̃ and 1σ̃ peak where we assume that the change in the shoulder of the combined 5σ̃ and 1σ̃ peak is mostly due to changes in the 5σ̃ position. A bond weakening is also consistent with the decrease
in the intensity of the $\tilde{d}_s$ spectral feature where only 50% of the intensity remains after long delay times, as shown in the bottom of Fig. 3B. The shift in the $2\tilde{\pi}^*$ level, shown in Fig. 3A, is also towards the gas phase $2\pi^*$ value indicating a bond weakening. However, it is important to note that the intensity at the gas phase energy position is still low indicating that few molecules have completely desorbed. The bonding to the surface leads to partial occupation of CO $2\pi^*$ character in the $\tilde{d}_s$ orbital resulting in a decrease of the $2\tilde{\pi}^*$ XAS resonance intensity (14, 15).

We observe in Fig. 3B that the gas phase $2\pi^*$ resonance intensity is partly restored with increasing delay time, again indicating a bond weakening. The latter is also directly related to the observed increase in the elastic peak since we use O1s $\rightarrow$ $2\tilde{\pi}^*$ excitation and, for a weaker interaction with the surface, the excited electron is less likely to couple to the metal and delocalize. This results in a higher probability for the direct recombination process involving the $2\tilde{\pi}^*$ excited electron giving emission at the same energy as the exciting photon (16).

Surface reactions driven by a laser pulse typically proceed via the underlying surface (9); the absorption cross section of a single adsorbate monolayer is too small to efficiently drive a reaction. Instead, hot electrons are excited in the substrate, which couple to the adsorbate within the first ps (16). We observe some changes at early times (1 ps), as seen in Fig. 3, which we attribute to hot electrons leading to excitation of frustrated rotations and translation of the CO molecule on the surface in accordance with previous studies (6, 7, 17). However, more relevant to the present study, the hot electron bath excites phonons within a few ps, and these phonons, in turn, couple to the CO molecule. Since the major bond weakening occurs only after a few ps we can directly relate this to an increase in the surface temperature (16).

Could a rapid increase in the substrate temperature lead to excitation of the adsorbate motion on the surface that mimics a bond weakening? We know from the XAS spectra in Fig. 2B that only a rather small amount of molecules has desorbed to the gas phase after 10-15 ps. This means that most of the spectral changes should be related to CO molecules still residing in the surface region. Furthermore, translational motion from the top-site to more highly-coordinated bridge and hollow sites leads to stronger interaction and spectral changes opposite to those observed after a few ps (18).

In order to understand the nature of the transient state observed in the experiment we have performed density functional theory calculations of the adsorption energy of a $\frac{1}{4}$ monolayer CO on a Ru(0001) surface using the BEEF functional (19), which includes the non-local correlation effects giving rise to long-range van der Waals interactions (20). When plotted as a function of the distance of the CO molecule to the surface, see Fig. 4, a chemisorbed state is found with an adsorption energy of 1.4 eV in good agreement with the experimentally determined value of 1.6 eV (21). Further away from the surface a shallow region of attraction is found which we associate with a weakly adsorbed state. The importance of this region for the dynamics at elevated temperatures is conveniently brought out following Doren and Tully (3, 22) by calculating $W(s)$, the potential of mean force (PMF), which is a free energy potential curve including the contribution from entropy along the reaction coordinate:

$$W(s) = -k_BT \ln(g(s)) + k_BT \ln(g(\infty)), \quad (1)$$
Here \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, \( s \) is the distance from the surface to the center of mass of the CO molecule, \( q \) represents all degrees of freedom except the reaction coordinate, \( s, V(s,q) \) is the interaction potential and \( \Gamma \) is an arbitrary normalization constant. The PMF is a free energy potential curve where all degrees of freedom except the reaction coordinate have been thermally averaged. The PMF is obtained for a range of temperatures along the minimum energy path for adsorption/desorption in Fig. 4 by approximately evaluating the integral in Equation (2) on the basis of the DFT-BEEF calculations. It should be stressed that Equation (1) assumes that all degrees of freedom can be treated classically, which is a rather crude approximation especially at low temperatures. It does, however, bring out important qualitative features of the dynamics of the system. The free energy differences, \( \Delta G \), of the extrema for instance, directly give the transition-state-theory rate constant for desorption (or adsorption).

In Fig. 4 it can be observed that as the temperature increases two minima develop in the potential of mean force: the chemisorption minimum and another minimum, which is associated with a precursor state for adsorption or desorption (3, 22). At high temperature the loss of entropy in the strongly adsorbed state, where the rotations and translations of the CO molecule are frustrated, means that the free energy increases substantially. In the precursor state, on the other hand, the CO molecule is nearly free to rotate and to move parallel to the surface to the extent allowed by the finite coverage. Here the entropy loss is minimal.

Figure 4 suggests the following qualitative picture of the experiment. After the laser pulse the adsorbate temperature increases to a value in the range 1500-2000 K (16). Here the free energy, \( W(s) \), of the precursor state becomes comparable to that of the chemisorbed state and a substantial fraction of the adsorbed CO molecules shift to this state. Calculating the XES spectra (23) in the precursor state we indeed find that the \( \tilde{d}_x \) intensity vanishes and the \( 5\bar{g} \) orbital shifts towards the gas phase position as observed experimentally (16), see Fig. 5; the experimentally observed weak remaining \( \tilde{d}_x \) intensity thus indicates a fraction of molecules trapped in the inner, chemisorbed well. The major spectroscopic difference between the gas phase and the precursor state is in the XAS \( 2\pi \) resonance position where the shift from the gas phase value is still distinct, see Fig. 2A. The result shows that in the precursor state the unoccupied orbitals, which have a large spatial extent still interact significantly with the metal states.

Since half of the \( \tilde{d}_x \) intensity disappears at long delay times this would indicate that at least half of the molecules are pumped into the precursor state supporting the notion that the two states have comparable free energies. Some of the molecules desorb during the experiment, but when the system cools down molecules can return to the chemisorbed state because the energy of that state again shifts down and the barrier for entering it decreases as the surface temperature decreases. This picture can explain the previous SFG results where the C-O stretch intensity was reduced by 1-2 orders of magnitude after the pump pulse (7). Here we can relate the loss of intensity to a large fraction of the molecules being pumped into the precursor state where the SFG signal disappears due to orientational disorder of the CO molecules (24, 25). The SFG
intensity partly recovered after 70 ps consistent with the notion that a fraction of the molecules readSORb into the chemisorbed state (7).

The identification of the precursor to adsorption and desorption in the present work solves an interesting puzzle in surface dynamics with direct relevance to reaction kinetics. It is well-known that prefactors in Arrhenius expressions for desorption rates of molecules like CO are often found to be anomalously large (26). For instance, the prefactor for CO desorption on Ru(0001) has been found to be of the order $10^{14}$-$10^{19}$ s$^{-1}$ depending on coverage (21). This is much larger than normal prefactors, typically in the range $10^{12}$-$10^{13}$ s$^{-1}$. This has generally been explained by differences in entropy between the initial (adsorbed) state and the final (gas) state (21). However, the present work suggests that it is actually the reduced entropy at the free energy barrier between initial and precursor state that gives the prefactor. An estimate based on the free energy diagram in Fig. 4 indeed gives a prefactor, which is of the order $10^{17}$ s$^{-1}$.

The present observation of short-lived intermediates in surface reactions opens the possibility of understanding surface-catalyzed chemical processes at a deeper level. With the present work we demonstrate the feasibility of coupling ultra-fast laser excitation to initiate a reaction with ultra-fast, atom-specific probing of the electronic structure changes as the reaction proceeds. Heterogeneous catalysis is filled with postulates of intermediates that have not been observed. One important example is the dissociation of CO, which is the starting point in Fisher-Tropsch catalysis used in making synthetic fuels. This process has been suggested to proceed through an adsorbed COH intermediate (27, 28) that has not been observed experimentally. Confirming the nature and understanding the dynamics of such transient intermediates will put heterogeneous catalysis and catalyst design on a considerably firmer basis.

References and Notes:

16. Details of the materials and methods, and supporting analysis of the experimental and theoretical data, are available at *Science* Online.
Acknowledgments:
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Fig. 1. Schematic illustration of the excitation process from the O1s level to the unoccupied $2\pi^*$ resonance in XAS and the core hole decay process from occupied $4\tilde{\sigma}$, $5\tilde{\sigma}$, $1\tilde{\pi}$, and $d_\pi$ molecular orbitals back to the O1s in XES. The displayed XES spectrum is a representation of the measured static CO on Ru(0001) data (II).
Fig. 2. Oxygen K-edge XES (Fig. 2A) and XAS (Fig. 2B) spectra (markers) of CO/Ru(0001) and corresponding fits (solid lines) measured at two selected pump-probe delays ($\Delta t = -1$ ps and $\Delta t = 12$ ps). At the bottom of the two panels the peak deconvolution resulting from the fit of the spectra acquired at $\Delta t = -1$ ps is shown. The XAS data have been fitted with a Gaussian peak for the O1s $\rightarrow 2\pi^*$ resonance (red filled peak). The XES spectra have been fitted with three peaks of Voigt lineshape for the $1\pi$ (light green), $5\sigma$ (dark green), $4\sigma$ (blue) orbitals and an asymmetric Gaussian for the $\tilde{d}_\pi$ states (black); the elastic peak is indicated in light blue around 535 eV. The fit of the spectra at $\Delta t = 12$ ps has been performed by varying only intensity and position of the previously determined components. In the upper part of the figure, the positions of the fitted components measured in previous gas phase experiments are also indicated for resonant and non-resonant conditions (29).
Fig. 3. Experimental observations indicating the population of a less strongly adsorbed precursor state in the desorption of CO from Ru(0001). The $2\tilde{n}^*$ resonance in the XAS spectra shifts to higher excitation energy (upper left, panel A) and increases in intensity (upper right, panel B) after several picoseconds. The shift is towards the gas phase $2\pi^*$ resonance at 534.2 eV. The $d_\pi$ states in the XES spectra decrease in intensity (lower right, panel B) on the same timescale as the changes in the XAS spectra, indicating a decreased hybridization. Moreover the main peak in the XES spectra, that is the center of mass of the $1\tilde{\sigma}$ and $5\tilde{\sigma}$ components (lower left, panel A), moves towards higher emission energy, in the same direction as for gas phase CO. The intensities in the upper right and bottom right plots have been normalized to the unpumped data ($\Delta t=-1$ ps). Since the pump-probe delay was continuously scanned during the measurement, the error bars in the plots along the time axis indicate the length of the time interval in which the data have been summed to produce the spectra of Fig. 2. The error bars on the other axis are evaluated from the fits (1σ), where each point in the measured spectrum has been statistically weighted.
Fig. 4. The potential of mean force for CO adsorption/desorption on Ru(0001) at 0 K (minimum energy path, MEP) and 300, 500, 1500 and 2000 K. The inset shows the potential energy curve (0 K) of the CO molecule with orientation parallel and perpendicular to the Ru(0001) surface. The surface distance is measured between the CO center-of-mass and the surface. At 0 K and distances smaller than 2.5 Å CO moves from on-top to bridge and hollow sites giving less strong repulsion compared to the finite temperatures where more repulsive orientations are sampled.
Fig. 5. Computed XES spectra of CO on Ru(0001) at distances corresponding to the minimum in the chemisorption state (blue) and at the precursor state (red and dashed) in Fig. 4. The spectra are resolved in pxy and pz components to clarify. S indicates the distance from the Ru surface to the center of mass of the CO molecule. The calculated spectra are shifted so that the energy position of the $^1\tilde{\pi}$ state is aligned with that of the corresponding experimental spectrum. As the molecule moves to the precursor state we observe a shift of the $^5\tilde{\sigma}$ component towards higher energy and the $^\tilde{\sigma}_\pi$ state vanishes as the interaction with the substrate decreases.
Supplementary Materials:

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Supplementary Materials:

1. Experimental Details

1.1 Pump-Probe Scheme. The optical pump – x-ray probe experiment was conducted at the Surface Chemistry End Station (SSE) of the soft x-ray materials science instrument (SXR) (30, 31) of the LCLS facility (32). In figure S1 the schematics of the pump-probe set-up is depicted.

X-ray photons (probe) of around 533 eV energy (2.33 nm) were delivered at a repetition rate of 60 Hz by the LCLS, which was operated with an electron bunch charge of 250 pC. The electron bunch compression was set to yield a single pulse duration of 100 fs (determined from electron bunch measurements) with an average energy of about 0.74 mJ/pulse (before the monochromator) (32). The bandwidth of the x-ray FEL fundamental for LCLS at soft x-ray photon energies was 1.1% (32), therefore, by using the first order of the 100 lines/mm grating (I) and an exit slit of 125 µm (corresponding to an energy resolution E/ΔE = 3000), it was possible to probe the oxygen K-edge (range from 531.5 to 536 eV) without further changes to the LCLS machine set-up. At the sample position (120 mm behind the nominal focus of the Kirkpatrick-Baez mirror pair) the beam spot size was about 50 µm (horizontal) x30 µm (vertical) FWHM (1,2) and it was incident on the sample at a grazing angle of 1°, leading to a spot profile of about 50 µm x1800 µm. By taking into account the SXR beamline transmission and the transmission of a thin film 10 nm Al/ 200 nm polyimide/ 10 nm Al used in the x-ray beam path during the experiments as reference-current measurement, the estimated average pulse energy at the sample position was 1.1 µJ (corresponding to a fluence of 12 J/m² on the sample).
Delayed optical pulses (pump) with 30 Hz repetition rate and 400 nm central wavelength and a pulse energy up to 350 µJ were delivered from a frequency-doubled 50 fs Ti:Sapphire laser amplifier, coupled and propagated collinearly with the x-rays. At the sample position the transverse optical laser spot size was about 100 µm (1/e²). The absorbed fluence was set close to the damage threshold of the Ru crystal in order to maximize the CO desorption yield and was estimated to be 140 J/m² (1/e²) with a Gaussian beam shape. The temporal overlap between the optical pump and the x-ray probe at the Ru(0001) position was determined to within 110 fs by measuring the X-ray induced change of the optical reflectivity of a silicon nitride (Si₃N₄) sample, as described in (33). In figure S2 the reflectivity change is presented as a function of pump-probe delay. The data were modeled with a step function, taking into account the drop due to the rapid initial electronic response of the system, and an exponential function for the slow recovery of the signal due to slow lattice dynamics. This model was convolved with a Gaussian to account for the relative arrival time jitter of both pulses (33). The temporal resolution (FWHM of the Gaussian) is determined to be 420 ± 100 fs. The zero in the Pump-Probe delay axis was fixed to the position of the reflectivity signal drop for all plots.

The soft x-ray emission spectra (XES) were monitored with a high-resolution (about 1 eV) slitless Rowland-circle grazing incidence soft x-ray spectrometer (34). As depicted in figure S1, the optical axis of the x-ray spectrometer was at 84° from the surface normal. The x-rays emitted from the sample entering the x-ray spectrometer were dispersed onto an intensifying screen imaged by an OPAL 1000 Adimec camera synchronized with LCLS. During the measurements the delay stage (pump-probe delay) and the monochromator (excitation energy) were continuously scanned over the entire range and for each x-ray pulse (60 Hz) their position as well as an image of the screen was acquired. The data were subsequently sorted as described in section 2.1. To probe the same initial conditions with each shot, the sample was continuously translated parallel to the surface. After finishing one scan line, the pump laser shutter was closed while the sample was moved back to the beginning of the same line to allow for redosing the surface coverage by a CO background with P_{CO} = 1 x 10⁻⁸ torr.

1.2 Sample Preparation. A 10x10 mm commercial Ru(0001) single-crystal (Matek, Germany) was cleaned in ultrahigh vacuum (chamber base pressure of 3x10⁻¹⁰ torr) by Ne⁺ sputtering and repeated cycles of oxygen treatment at temperatures ranging from 800 K and 1200 K. Finally the crystal, was flashed to 1500 K, cooled down to 300 K and exposed to CO (35, 36). The CO background pressure was constantly 1 x 10⁻⁸ torr during the entire experiment.

2. Data Analysis

2.1 Extraction of the spectra. As described in section 1.1 the position of the delay stage (pump-probe delay), the excitation energy (determined from the monochromator position) and an OPAL image of the dispersed x-rays emitted from the sample was recorded for each x-ray pulse (60 Hz). Each image was corrected for the curvature due to the Rowland geometry and integrated in the direction normal to the dispersion (emission energy axis) (34). The emission energy scale was calibrated by determining the energetic position of elastically scattered light at different known photon energies. Oxygen K-edge resonant inelastic x-ray scattering (RIXS) maps (upper panel of Figure S4) were obtained for several pump-probe delay intervals by accumulating the
spectra and sorting with respect to excitation energy (y-axis) and finally normalizing them to the number of x-ray pulses contributing to each excitation energy interval.

At selected pump-probe delays the x-ray absorption spectra (XAS) of Figure S3 were obtained by plotting the total number of emitted photons measured as a function of the excitation energy, which was performed by integrating the RIXS map over the emission energy axis. The XAS spectra were subsequently normalized to the total number of x-ray shots at each time delay. Due to the low statistics, the XES spectra presented in Figure S3 was extracted by summing the RIXS maps over a 2.8 eV broad ([532.7,535.5] eV) interval of excitation energies centered at 534.1 eV (resonant condition), as performed in the bottom graph of Figure S4 for the spectrum labelled XES A. The spectra labelled XES B and XES SSRL are displayed for comparison. XES B was obtained at LCLS during a long acquisition at excitation energy 532.6 eV in a measurement with fixed monochromator position, while the XES SSRL spectrum was measured with the same endstation (but lower resolution) at the SSRL synchrotron source. The three spectra show the same emission lines and differ only in the elastic peak region between 532 eV and 538 eV and in spectral resolution. While for XES B and XES SSRL the width of the elastic peak is limited only by the resolution, the broadening of the elastic peak in XES A is due to the integration performed to extract the spectrum. The XES spectra obtained at each pump-probe delay were normalized to the total area underneath the $1\bar{\pi}$, $5\tilde{\sigma}$, $4\tilde{\sigma}$ and $\vec{d}_\pi$ peaks.

The presented fits were obtained using the built-in functions of the Igor Pro 6.0 software. The XAS data were fitted with one peak of Gaussian lineshape for the transition O1s→ $2\bar{\pi}^*$ . Three peaks of Voigt lineshape for the $1\bar{\pi}$ (light green), $5\tilde{\sigma}$ (dark green), $4\tilde{\sigma}$ (blue) orbitals and an asymmetric Gaussian for the $\vec{d}_\pi$ states (black) convolved with a Gaussian experimental resolution of 1 eV were used for the XES spectra at Δt=1 ps (see Figure S3). The line widths determined (respectively 3.1 eV for $\vec{d}_\pi$, 1.8 eV for $4\tilde{\sigma}$, 1.4 eV for $1\bar{\pi}$ and 1.5 eV for $5\tilde{\sigma}$ similar to (14, 11) ) as well as the energy position of the $1\bar{\pi}$ and $\vec{d}_\pi$ states (524.9 eV and 527.3 eV respectively) were kept fixed for all the fits at consecutive pump-probe delays. The error bars in Figure 3 of the main paper were obtained from the fitting routine by using a statistical weight (1/σ) on the data. In figure S5 an alternative fitting approach is shown, where the shape of the main feature in the spectra comprising the $1\bar{\pi}$ and $5\tilde{\sigma}$ peaks was kept fixed to the unpumped value (fixed $5\tilde{\sigma}/1\bar{\pi}$ height ratio and distance at 0.5 and 1.5 eV respectively) while its intensity and position were fitted. This approach was suggested by the fact that in the grazing emission geometry used in the experiment it is not possible to selectively probe the $5\tilde{\sigma}$ and $1\bar{\pi}$ components as was done in the angle-dependent measurements in ref. (11). As shown in the right graphs of Figure S5 the trends of the $\vec{d}_\pi$ decrease in intensity as function of pump-probe delay (upper right) as well as the shift towards higher emission energy of the center of mass of the $1\bar{\pi}$ and $5\tilde{\sigma}$ components (lower left) are well reproduced also for this fitting approach, confirming the results presented in Figure 3.

2.2 Elastic Peak. In Fig S6 the Oxygen K-edge XES spectra in the emission energy region corresponding to the elastically scattered photons are displayed. The contribution of the elastically scattered light to the fit of the XES spectra (elastic peak) is described by peak E with Gaussian lineshape. The elastic peak is quite broad (FWHM ~3 eV) since the presented XES
spectra were obtained by integrating RIXS maps in a 2.8 eV excitation energy interval (see Figure S4). In the fits the width, position and intensity of the elastic peak determined at Δt=−1 ps are kept fixed for all delays since a change in the intensity of the scattered light as a function of pump-probe delay is not expected. However to fit the data an additional component (dark blue) with Gaussian lineshape (peak P) is required at 533.7 eV. The intensity of this peak increases as a function of pump-probe delay. This feature resembles the participator peak, i. e. the radiative decay of the core-excited state to the ground state of the molecule, which has been observed in the gas phase (29). This decay channel is strongly suppressed for strongly interacting chemisorbed molecules due to ultrafast charge transfer out of the resonance into the metal substrate (37). The presence of the decay channel and its increase as a function of pump-probe delay further supports the conclusion of population of a less chemisorbed state by photoexcitation prior to desorption.

2.3 Two-Temperature Model. The optical laser pulses (hν = 400 nm) that are used to initiate the reaction are absorbed by the metal substrate causing excitation of substrate electrons that thermalize on the time-scale of ~100 fs (38), after which a temperature can be defined for the electrons. The hot electrons subsequently heat up the lattice via electron-phonon coupling and may also couple to the adsorbate vibrational degrees of freedom. Finally the system equilibrates to an elevated temperature. The time-dependent temperatures of the electrons (Te) and phonons (Tp) can be modeled within the two-temperature model of Anisimov (39) where the electron and phonon systems are treated as two coupled heat baths using the same formalism and material parameters as in ref. (40):

\[ C_{el} \frac{\partial}{\partial t} T_{el} = \nabla (\kappa \nabla T_{el}) - g(T_{el} - T_{ph}) + S(z,t) \]

\[ C_{ph} \frac{\partial}{\partial t} T_{ph} = \nabla g(T_{el} - T_{ph}) \]

The heat capacity of the electron system is \( C_{el} = \gamma T_{el} \) with electron specific heat \( \gamma = 400 \frac{J}{m^3 K^2} \) while the heat capacity \( C_{ph} \) of the phonon system is given by the Debye model. The thermal conductivity is \( \kappa = \kappa_0 \frac{T_{el}}{T_{ph}} \) with \( \kappa_0 = 117 \frac{W}{K m} \) and the electron-phonon coupling is \( = 1.85 \times 10^{18} \frac{W}{m^3 K} \). The laser excitation is given as a function of depth z and time t by

\[ S(z,t) = I(t) \lambda^{-1} e^{-\frac{z}{\lambda}} \]

where \( I(t) \) is the time-dependent absorbed intensity of the laser pulse and \( \lambda \) the penetration depth. Using the two-temperature model we computed the electron and phonon temperatures assuming a Gaussian time-dependence with a full-width at half maximum of 50 fs and an absorbed fluence of 140 J/m², which yields an electron-phonon equilibration time of 1.3 ps and a temperature at this time of 1800 K. The modeled time-evolution of the electron and lattice temperatures at the surface during the first 10 ps is shown in Figure S7.

3. Computational Method
3.1 Computational Protocol. The electronic structure calculations are performed using the grid-based real-space projector-augmented wave GPAW code (41, 42, 43). A wave function grid spacing of 0.18 Å, 0.01 eV Fermi smearing and a 4×4×1 k-point sampling has been applied. For the relaxations in the minimum energy path (MEP) the criterion of 0.05 eV/Å as maximum force on each relaxed atom was used. The Ru(0001) slab is set up in a 2×2 cell using periodic boundary conditions and containing 3 layers where the bottom layer has been fixed, on top a CO molecule is placed having 10 Å vacuum to the top of the box giving a 1/4 monolayer adsorption. The equilibrium Ru-C distance for on-top adsorption was obtained as 1.94 Å.

O K edge x-ray emission spectra are calculated in the same framework (44) using ground state orbitals and summed over $p_{xy}$ and $p_z$ symmetries. To compare with the experimental spectra a broadening with a Gaussian function of 1 eV at full-width at half-maximum (FWHM) is employed. Geometries of the chemisorbed state and the precursor state are taken from the MEP of desorption and to obtain an absolute energy scale the computed spectra were shifted so that the energy position of the $\Gamma$ state is aligned with that of the corresponding experimental spectrum.

The potential energy curves for the potential of mean force described below have been fitted using the least squares method and the integral is solved using these fits and numerical integration using the Matlab quad function.

3.2 Exchange-Correlation Functionals. The BEEF-vdW exchange-correlation functional has been chosen to describe the CO desorption from Ru(0001), since it is capable of describing both the chemical and van der Waals interactions (19) unlike the commonly used generalized gradient approximation (GGA) exchange-correlation functionals PBE (45) and RPBE (46). As is clearly seen from Fig. S8 PBE goes to zero exponentially for increasing surface distances of the CO molecule, while RPBE actually produces a barrier after which it trails off to zero. Only BEEF-vdW is able to get an attractive plateau starting at a C-Ru distance around 3.5 Å. As we shall see from the potential of mean force (PMF) this attractive plateau is essential in the theoretical interpretation of the experimental results. For the spectrum calculations the RPBE functional was chosen.

3.3 Potential of Mean Force (PMF). To estimate the PMF it is assumed that the potential energy is separable in the translational and rotational degrees of freedom

$$V_{\text{rot}} = V_0 + V_x + V_y + V_{\text{rot1}} + V_{\text{rot2}} = V_0 + 2V_{\text{trans}} + V_{\text{rot1}} + V_{\text{rot2}},$$

(1)

where the rotational potentials ($V_{\text{rot1}}$ and $V_{\text{rot2}}$), translational degrees of freedom ($V_x$ and $V_y$) and the potential of the minimum energy path ($V_0$) have been introduced. The internal CO stretch vibration is neglected, since it is assumed to be not excited. In the second equation it is also assumed that the two translational degrees of freedom on the surface are equivalent. As Doren and Tully proposed (3, 22) the PMF, $W(s)$, can be written as

$$W(s) = -k_BT \ln(g(s)) + k_BT \ln(g(\infty)).$$

(2)
where \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, \( s \) is the distance from the surface to the center of mass of the CO molecule and \( g(s) \) is given by the integral

\[
g(s) = \Gamma^{-1} \int e^{-\frac{V(s,q)}{k_BT}} dq,
\]

(3)

here \( q \) represents the independent degrees of freedom and \( \Gamma \) is an arbitrary normalization constant, the choice of which is irrelevant when the PMF is set to zero at infinite separation through equation (2).

Inserting Eq. (1) into Eq. (3) the following is obtained

\[
g(s) = \Gamma^{-1} \int e^{-\frac{V(s,q)}{k_BT}} dx d\theta dq = \Gamma^{-1} 2g_{trans}(s)g_{rot1}(s)g_{rot2}(s)
\]

(4)

By adding and subtracting the potential of the minimum energy path (MEP), \( V_0 \), to each degree of freedom, the PMF can be written as a correction for each degree of freedom

\[
W_{rot}(s) = V_0 - \sum_i^N (W_i - V_{0,i}),
\]

(5)

where \( V_0 \) is the energy of the MEP (effectively the z-direction), \( W_i \) is the PMF and \( V_{0,i} \) is the minimum value of the fitted potential (which is very close to \( V_0 \)) for the \( i \)'th degree of freedom, respectively.

To calculate the individual contributions the degrees of freedom have been sampled by calculating the potential energy of the two rotations (cartwheel and helicopter) and a translation of the CO molecule at fixed surface distances using the new BEEF-vdW exchange-correlation functional. The potential energy curves for each degree of freedom have been fitted to functions for each surface distance and inserted in the integral in Eq. (2). The detailed fitting procedure is described below.

**3.4 Fitting the Potential Energy.** The potential energy of the translational motion has been fitted to the function

\[
f1(x) = a_0 + a_1 \cos(dx) + a_2 x^8.
\]

(6)

The periodicity \( d \) in the cosines function is the distance from one on-top position to another. It is assumed that the CO molecules are transferred into the precursor state, which is simulated by having a 2x4 units cell containing two CO molecules at the same surface distance where one CO molecule is fixed while the other is moved in the surface plane between the neighboring CO molecules at the same surface distance confining it and giving a “particle in a box”-like potential with a cosines bottom. The fitting procedure for the translational motion is as follows: First all the coefficients are determined by fitting to all points. \( a_0 \) and \( a_2 \) are then fixed to the obtained values, while \( a_1 \) is refitted to the non-repulsive points (excluding the potential energy points where the CO molecules are too close to their neighbors). This is done in order to avoid destroying the description in the interesting low potential energy region, which would be the case
if the unimportant extremely high potential energy values as the CO molecules get too close to its neighbor were included when fitting the cosines function.

Both the cartwheel and helicopter rotational modes were computed for a single CO in a $2\times2$ cell. The cartwheel rotation can be approximated with a cosines series

$$f_3(x) = a_0 + a_1 \cos(x) + a_2 \cos(2x) + a_3 \cos(3x) + a_4 \cos(4x) + a_5 \cos(5x).$$

(7)

The helicopter rotational degree of freedom is simply given by

$$f_4(x) = \frac{\Delta E}{2} \cos(6\nu) + \frac{\Delta E}{2} + V_0,$$

(8)

where $\nu$ is the angle of periodicity, $V_0$ is the lowest potential energy and $\Delta E$ is the difference between the highest and lowest potential energy.

The helicopter rotation is not a normal mode when the CO molecule is close to the surface. As is also seen from the potential energy in the insert of Fig. 4 of the main paper the parallel orientation of the CO molecule is very unstable close to the surface. In this region the cartwheel rotation is counted twice in the PMF. At 4 Å surface distance and above, where the parallel CO orientation becomes as stable as the perpendicular, the contributions from both rotations are added.
Fig. S1. Scheme of the experiment. The synchronized x-ray (60 Hz) and optical (400 nm, 30 Hz) pulses are coupled and propagate collinearly to the sample. They illuminate the sample at a grazing incidence angle of 1° (as shown in the XES side inset). The incoming x-rays are linearly polarized at 52° from the surface normal (~ magic angle for XAS measurements), while the optical laser is polarized out of the surface plane (as shown in the Beam side inset). The photons emitted and scattered by the sample enter the x-ray Spectrometer along its optical axis at 84° from the surface normal. For each x-ray pulse an image of the photons dispersed by the grating x-ray Spectrometer (34) is acquired with an OPAL camera operating at 60 Hz.
**Fig. S2.** Transient x-ray induced optical reflectivity of a Si₃N₄ sample. x-ray FEL pulses (536 eV, 100 fs) induce a drop in the 400 nm optical light reflected from a Si₃N₄ sample. The drop is associated with a rapid initial electronic response of the system, while the slow recovery of the signal at later times is attributed to slow lattice dynamics (33). The timescale of the fast electronic response is below 100 fs, therefore the initial drop in optical reflectivity is mainly determined by the temporal resolution and was fitted with an erf function. The temporal resolution (FWHM of the Gaussian) is determined to be 420±100 fs. The bin size of the pump probe delay is 100 fs for display reasons. The fit has been performed on data binned in 40 fs steps.
**Fig. S3** Oxygen K-edge XES (left graph) spectra (markers) of CO/Ru(0001) and relative fits (solid lines) measured at selected pump-probe delays ($\Delta t$) presented in the paper.
**Fig. S4.** Oxygen K-edge RIXS map (upper panel) of CO/Ru(0001) measured at pump-probe delays -1.5ps < Δt < 0ps. The 2D-plot was obtained by accumulating all XES spectra (y-profiles) acquired in the selected time interval sorted with respect to excitation energy (monochromator energy, y-axis) and normalizing to the number of x-ray pulses contributing to each excitation energy interval. The XES spectrum labelled XES A (bottom panel), obtained by integrating the RIXS map in the excitation energy range [532.7, 535.5] eV, was used for the data analysis and fitting. The same procedure was repeated for all time intervals of the pump-probe delays presented. The spectra XES B and XES SSRL are displayed for comparison. XES B was obtained at LCLS for excitation energy 532.6 eV in a measurement at fixed monochromator position, while the XES SSRL spectrum was measured with the same endstation at a synchrotron source. The three spectra show the same emission lines and differ only in the elastic peak region between 532 eV and 538 eV and spectral resolution.
Fig. S5. Oxygen K-edge XES (left graph) spectra (markers) of CO/Ru(0001) and corresponding fits (solid lines) measured at selected pump-probe delays ($\Delta t$). For each spectrum the peak deconvolution resulting from the fit is also shown as filled areas. The spectra were fitted with three peaks of Voigt lineshape for the $1\tilde{\sigma}$ (light green), $5\tilde{\sigma}$ (dark green), $4\tilde{\sigma}$ (blue) orbitals and an asymmetric Gaussian for the $\tilde{d}_\pi$ states (black). The adopted fitting approach differs from the one in Figure 2. In particular the area ratio $5\tilde{\sigma}/1\tilde{\sigma}$ and their relative distance were fixed at 0.5 and 1.5 eV respectively. The trends of the $\tilde{d}_\pi$ decrease in intensity as function of pump-probe delay (upper right) as well as the shift towards higher emission energy of the center of mass of the $1\tilde{\sigma}$ and $5\tilde{\sigma}$ components (lower right) are well reproduced also for this fitting approach.
**Fig. S6.** Oxygen K-edge XES spectra and fits (left) in the emission energy region corresponding to elastically scattered photons (between 532 eV and 538 eV) measured at selected pump-probe delays (Δt). In the spectrum at Δt=-1 ps, peak E (at 534.4 eV, FWHM 2.5 eV) is the contribution from the elastic scattering. Its intensity and position is kept fixed in the fitting procedure at all delay times. Peak P (at 533.2 eV, FWHM 1.6 eV), which appears at later delays, is the participator contribution and its intensity increases as a function of pump-probe delay (right panel). This contribution, which has been well characterized in gas phase measurements (29), is an indication of the development of a population of molecules less bound to the surface.
**Fig. S7.** Modeled time-evolution of electron- and phonon-temperatures of the ruthenium surface following absorption of a 140 J/m² laser pulse with a pulse length of 50 fs (FWHM) and wavelength 400 nm at a base temperature of 300 K.

**Fig. S8.** Minimum energy path of the CO desorption from the Ru(0001) surface using the PBE, RPBE and BEEF-vdW exchange-correlation functionals.