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Advances in Density-Functional Calculations for Materials Modeling

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Abstract

During the past two decades, density-functional (DF) theory has evolved from niche applications for simple solid-state materials to become a workhorse method for studying a wide range of phenomena in a variety of system classes throughout physics, chemistry, biology, and materials science. Here, we review the recent advances in DF calculations for materials modeling, giving a classification of modern DF-based methods when viewed from the materials modeling perspective. While progress has been very substantial, many challenges remain on the way to achieving consensus on a set of universally applicable DF-based methods for materials modeling. Hence, we focus on recent successes and remaining challenges in DF calculations for modeling hard solids, molecular and biological matter, low-dimensional materials, and hybrid organic-inorganic materials.

1. INTRODUCTION

The materials research community has been fundamentally transformed by electronic-structure calculations based on density-functional theory (DFT) (1). The Kohn-Sham scheme of DFT is now used in at least 30,000 scientific publications per year to solve the electronic-structure problem in a wide variety of scientific fields (2–5). Novel materials discovery and molecular-level characterization rely heavily on density-functional (DF) calculations and form a central part of international research portfolios, as evidenced by the US Materials Genome Initiative and the European Centres of Excellence NOMAD and MAX. With the rise in popularity of DFT has come the need to clearly establish methodological best practices (6) and the important factors that define the accuracy and precision of the method, such as the reliability of the underlying basis sets and other numerical approximations (7, 8).

In light of the omnipresent use of DFT in materials research, it is important to continuously assess the ability of density-functional approximations (DFAs) to accurately predict relevant materials properties, such as their composition, structure, stability, and mechanical, electronic, and optical response, among many others. Continuous improvements in approximations to the true exchange-correlation (xc) functional are required to ensure that the predictive capabilities of DF calculations grow with the increase in complexity of modern materials.

The advances in DFT capabilities over the years are best measured by challenging contemporary benchmark systems, which have continuously increased in complexity over time. These so-called hard systems expose the shortcomings of DFAs and provide tangible milestones that have to be overcome to extend the applicability of DFAs to increasingly more complex and relevant materials. The evolving challenges at this moment in time compared to 15 years ago are a sign of the tremendous progress in this field. For example, silicon and transition-metal oxides—the challenging hard materials 15 years ago—have been replaced by strongly correlated materials and superconductors. At the beginning of the twenty-first century, the so-called CO puzzle—the inability of generalized gradient approximation (GGA) functionals to correctly describe the adsorption-site trend across the transition metals—dominated the description of catalytic materials (9). In contrast, modern challenges for DFT are represented by hybrid inorganic-organic materials (HIOMs) and molecular materials composed of large and complex molecular adsorbates, where long-range van der Waals (vdW) dispersion interactions play a very important role in addition to strong covalent bonds and charge transfer processes (10–12). Important insights from considering these benchmark systems are that DFAs perform very differently for different materials classes and that the pace of progress to find optimal DFAs differs between materials.

DFT: density-functional theory

DF: density functional

DFAs: density-functional approximations

xc: exchange-correlation

GGA: generalized gradient approximation

vdW: van der Waals

LDA: local density approximation

Only a decade ago, the applicability of DFT to the modeling of even the simplest biological molecules and other noncovalently interacting systems was seriously questioned. The lack of accuracy of the local density approximation (LDA) and GGA functionals for noncovalent interactions is disheartening. However, since the early 2000s many different complementary methods have been devised to overcome the deficiencies of semilocal functionals, and today, dispersion-inclusive hybrid functionals often yield results that are starting to challenge experimental uncertainties for molecular crystals and biological materials.

The objectives of this review are to analyze the advances in the predictive capabilities of DFT for materials applications during the last 15 to 20 years, to assess the current state of the art of DF calculations in materials applications, and to identify the remaining challenges for the future. In the following sections, we review DF calculations and methodological advances and current best practices for different materials classes, and we conclude with an outlook on the future of DFT and other electronic-structure methods in materials research.

2. AN OVERVIEW OF DFT FOR MATERIALS RESEARCH

While the ambition of DFT is to provide a reliable description of electronic structure with the help of an exact and universal xc functional, in practice this functional is not known, and approximations have to be made. Sometimes these approximations are physically motivated and based on some known limits of the exact functional; sometimes these approximations are pragmatic and driven by the desire to provide an improved description of target properties for a particular materials class.

A widely invoked classification of DFAs was made by John Perdew with the Jacob's ladder analogy of DFT (see **Figure 1**). Herein, DF calculations are systematically improved upon by

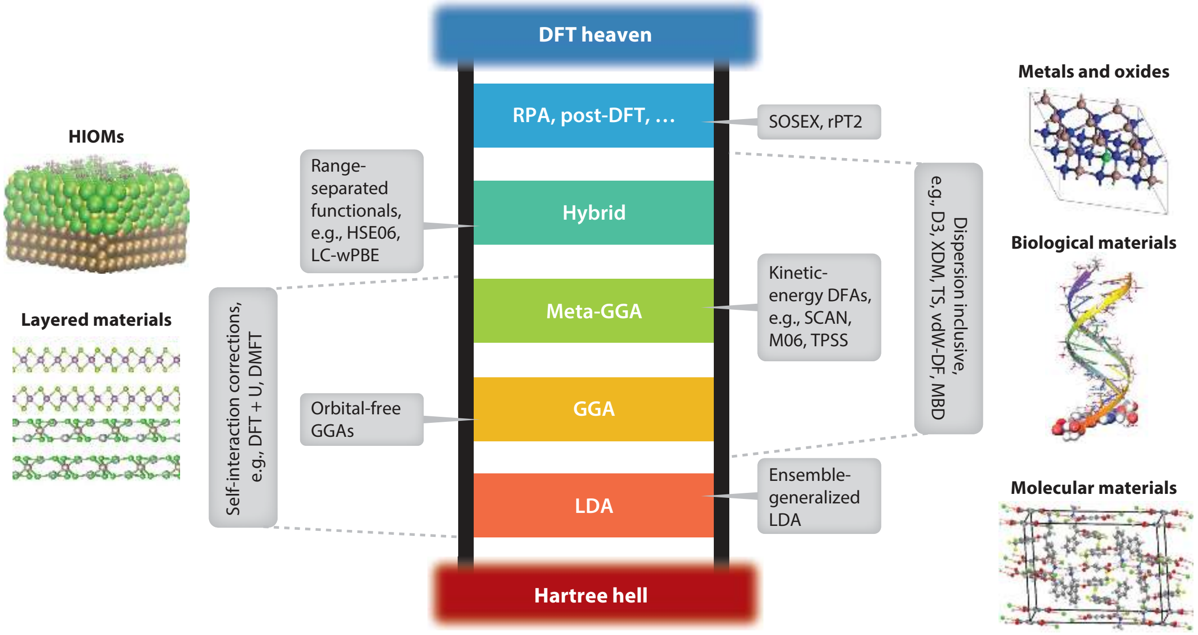

DFT heaven
RPA, post-DFT, ...
Hybrid
Meta-GGA
GGA
LDA
Hartree hell
SOSEX, rPT2
Range-separated functionals, e.g., HSE06, LC-wPBE
Kinetic-energy DFAs, e.g., SCAN, M06, TPSS
Orbital-free GGAs
Ensemble-generalized LDA
Self-interaction corrections, e.g., DFT + U, DMFT
Dispersion inclusive, e.g., D3, XDM, TS, vdW-DF, MBD
HIOMs
Layered materials
Metals and oxides
Biological materials
Molecular materials

Figure 1

Jacob's ladder provides a guidance for improving density-functional approximations (DFAs) by ascending rungs of approximations from Hartree theory toward the exact functional, in the following order (from *bottom* to *top*): local density approximation (LDA), generalized gradient approximations (GGAs), meta-GGA functionals that incorporate higher-order derivatives, hybrid functionals that admix exact exchange, and the random-phase approximation (RPA) and higher-level corrections from many-body perturbation theory (so-called post-DFT methods). The gray boxes show developments of the last 15 to 20 years in DFT with relevance to modeling of the different materials classes shown in the periphery of the figure. Abbreviations: DFT + U, DFT with Hubbard-U self-interaction correction; DMFT, dynamical mean-field theory; HIOM, hybrid inorganic-organic material; MBD, many-body dispersion; SOSEX, second-order screened exchange; TS, Tkatchenko-Scheffler method; vdW-DF, nonlocal van der Waals density functional; XDM, exchange-hole dipole moment.

ascending rungs of different approximations. At the bottom is the LDA, which assumes that the xc functional depends only on the local value of the electron density. Despite its known problem of underestimating band gaps, LDA has been successfully applied to conventional hard materials such as metals and doped semiconductors. An interesting aspect of DF development in the last 15 years is that development has occurred not only on more recent, nominally more accurate rungs but also on lower rungs such as the LDA. In addition to many conceptual works, there have been developments based on LDA with direct relevance to materials research. These include ensemble-generalized versions of LDA that remedy the self-interaction error in LDA (13), as well as Koopman's compliant functionals (14), which impose the derivative discontinuity condition onto LDA.

MBPT: many-body perturbation theory

RPA: random-phase approximation

ACFDT: adiabatic connection fluctuation-dissipation theorem

SOSEX: second-order screened exchange

Functionals based on the GGA depend on the local density and the local density gradient. The idea of improving functionals by continuing the local gradient expansion to second derivatives or higher-order dependencies has further given rise to meta-GGAs. The most notable developments here have been the TPSS functional (15), M06L (16), and the recent SCAN functional (17), which make use of the Kohn-Sham orbital kinetic-energy density. Very recent work to provide an orbital-free description of the kinetic-energy density has led to a reduced-cost version of SCAN (18) and to promising new GGA functionals such as LKT (19).

Hybrid functionals on the next rung admix a certain predefined amount of exact exchange into the xc functional, and range-separated hybrid functionals do so with different mixing parameters for different interaction ranges of the Coulomb potential. These functionals notably remedy a significant portion of the self-interaction error and the band-gap problem that persist in lower rungs, but at the same time, the functionals include parameters (the mixing parameter and range-separation parameters) for which a choice has to be made. The more recent developments in the context of materials are range-separated functionals such as HSE06 (20), LC-wPBE (21), and RS-DDH (22).

The fifth rung in Jacob's ladder of DFT is a bit more elusive, as it collects a number of approaches that include either a dependence of the functional on unoccupied Kohn-Sham states or a dependence on more general response functions from which explicit electron correlation contributions are calculated. These methods are formally grounded in many-body perturbation theory (MBPT) and are often referred to as post-DFT methods. The most common approach is the random-phase approximation (RPA) (23). On the basis of the adiabatic connection fluctuation-dissipation theorem (ACFDT) employing the electron-density response function, one can obtain an expression for the correlation energy. This response function can be constructed from a variety of perturbative expansions, with RPA being one of them. This is a very active field of development, with several works exploring the realm beyond RPA, including second-order screened exchange (SOSEX) (24, 25), the inclusion of single excitations (26), renormalized RPA (27), and second-order corrections to RPA (28). Also on this rung are double-hybrid DFs, where nonlocal correlation methods are coupled with the semilocal xc functional (29). Although retaining some level of empiricism, double-hybrid DFs compute some chemical and physical properties with higher accuracy than do other listed rungs (30).

At all rungs, a choice for the flexible exchange and correlation enhancement factors, i.e., the deviation from the LDA expression, has to be made. This can be done by fulfilling as many exact constraints as possible [PBE (31), SCAN (17), PBE0 (32)], by having a small set of parameters (3–10) that are optimized on reference data [B97D (33), B3LYP (34, 35)], or by disregarding several known constraints in favor of higher flexibility with more parameters and large databases for optimizing them [M06L (36), MN15 (37)]. With increasing flexibility, the global optimization within the parameter space can become a combinatorial problem, as shown in the recent DF ωB97M-V (38).

Many of the known shortcomings of DFT, most notably the lack of long-range correlation or dispersion interactions and the spurious self-interaction error, have sparked several specialized developments to address specific materials challenges. These developments are not easily summarized within the Jacob's ladder framework, as they are relevant for several of the rungs. As such, they are visualized in **Figure 1** alongside the rungs and are discussed in more detail in the relevant subsequent sections. In particular, explicit self-interaction corrections have been proposed for correlated materials such as the DFT + U methods and dynamical mean-field theory (DMFT) (39, 40), as well as numerous methods to incorporate long-range correlation into existing functionals. Several recent reviews provided a detailed discussion of these methods (41–46). Most of the currently used dispersion-inclusive methods can be classified into a posteriori corrections on top of existing functionals, explicit nonlocal correlation functionals, and effective one-particle potentials. The first class features a variety of developments that have led from empirical to less empirical atom-pairwise (sometimes including atom-triples) methods often referred to as DFT + vdW. These include a series of methods developed by Grimme and colleagues (-D1, -D2, -D3) (33, 47, 48), density- and property-derived methods such as the exchange-hole dipole moment (XDM) (49, 50), and the Tkatchenko-Scheffler method (51), to name just a few. Recent developments include corrections for use on metal surfaces (52), incorporation of charge information into the Grimme scheme (53), and full many-body dispersion (MBD) at the coupled fluctuating dipole level (54). The second class features nonlocal pairwise DF formulations to capture long-range correlation effects (44) and build on the work of Dion et al. (55). Methods in the third class are empirically driven and try to incorporate long-range correlation effects into the one-electron xc functional by fitting to appropriate reference sets (36) or by adjusting the atom core potential (56).

DFT + U: DFT with Hubbard-U self-interaction correction

DMFT: dynamical mean-field theory

DFT + vdW: DFT with long-range dispersion correction

MBD: many-body dispersion

Recent DFT developments over the past 10 years have shown an increasingly splintered field of research, with a focus on addressing the major shortcomings of existing DF approximations in the context of certain materials classes. In the next few sections, we show that the predictive capabilities of the current state of the art of DF calculations show a wide spread across materials and that, while there are some material-specific challenges, many of the remaining problems are universal. Future convergence of various approximate approaches within DFT is thus possible and indeed desirable.

3. HARD SOLIDS: METALS AND SEMICONDUCTORS

3.1. DFT: The Workhorse of Quantitative Theory in Solids

Ever since its early days, DFT has been applied to crystalline hard-matter solids such as metals, semiconductors, and ceramics. Today, there is hardly any materials class within that group that has not been studied with DF-based approaches. Tremendous experience has been accumulated on how accurately the total energy, the electronic structure, and derived properties can be computed and how the various challenges posed by different materials can be met. This development is not over yet, but the use of DF calculations for hard solids can be considered a mature field. DF calculations have therefore become a routine tool to carry out simulations for up to ~1,000 atoms, providing lattice constants, atomic positions, energy differences, band structures, phonons, response properties, and many more, within a few percent of their experimental values. In many cases, DF calculations are combined with phenomenological theories beyond the electronic-structure scale, providing essential input parameters for such simulations.

This progress in applications has been driven equally (*a*) by improvements in the theory itself, notably through better approximations to the xc functional (30, 57); (*b*) by advances in practical implementations and their availability (8); and (*c*) by the tremendous increase in computer power. Improvements in the functionals have gone hand in hand with applications: Whenever the widespread use of DFT revealed that a particular property was not calculated well (e.g., band gaps, lattice constants, surface energies, adsorption energies, and their site dependence, to name but a few problems), DF developers analyzed the physical origin of the failure and tried to come up with better solutions in a physically motivated or semiempirical way. Also, the methodology around the computational realization of DFT should be appreciated. Better algorithms to solve the Kohn-Sham equations (58–60), density mixing and preconditioners throughout the self-consistent iterations (58), and novel schemes to treat the atomic cores (61), to incorporate electric and magnetic fields (62, 63), to calculate derivatives via perturbation theory (64), to explore potential energy surfaces, or to accelerate dynamical simulations by extrapolation have contributed to making DFT a Swiss Army knife for increasingly complex materials.

A large proportion of DF calculations for hard solids focus on predicting basic structural and thermodynamic properties, notably heats of formation. In conjunction with more easily accessible, functional properties (such as elastic constants, dielectric tensors, and electronic band structures), high-throughput DF calculations have helped to accelerate novel materials discovery for specific applications, including batteries, hydrogen storage, solar cells, and thermoelectrics. Large databases containing such data have been built in recent years. Two prominent examples are the Materials Project (65) and the NOMAD repository (66). The Materials Project database, as of 2018, contained data for more than 80,000 solid compounds calculated within a standardized DFT scheme and many more in other materials classes. The NOMAD repository provides free access to more than 50 million calculations, mostly from DFT in various flavors.

DF calculations can also be employed to construct thermodynamic databases and phase diagrams (67, 68). It had long been believed that the predictive power of DFT fell short of experiment [which certainly continues to be true for room-temperature formation enthalpies, despite some progress (69)] unless error cancellation was exploited (70). However, in conditions that limit direct experimental measurements (high temperature, high pressure, kinetic hindrance), theoretical predictions can match or even exceed experimental precision (68, 71, 72). For direct comparison to experiment going beyond the $T = 0$ K ground state, it is necessary to systematically address finite-temperature effects. Formally, this is achieved by taking into account all possible excitation mechanisms—primarily due to atomic vibrations (phonons) but also electronic, magnetic, and configurational excitations.

3.2. Toward Accurate Thermodynamics Beyond $T = 0$: Excitations

For phonons, the harmonic approximation gives the leading contribution at low to moderate temperatures. It is obtained from the Hessian matrix (the second derivative of the total energy) and is therefore directly accessible from DFT via numerical derivatives of the forces or from perturbation theory (67, 73). For higher temperatures, recent years have seen tremendous progress via T-dependent potentials (74) or via thermodynamic integration over the coupling constant between a harmonic potential and the full DFT system in accelerated schemes (72, 75, 76). These new methods allow one to reproduce heat capacities in excellent agreement with experiment up to the melting point (75). Electronic excitations are significant for bulk metals with a high electronic density of states at the Fermi level but do not pose major difficulties within standard Kohn-Sham DFT (77). More challenging are the ground-state and electronic excitations in strongly correlated materials, e.g., f metals and correlated transition-metal oxides. These materials contain atoms with partially filled, localized f and d shells, respectively. Due to the dynamic localization of electrons on single atoms, such materials show a Mott-Hubbard gap in the single-particle spectrum. The mean-field Kohn-Sham Hamiltonian underlying standard DFT is unable to capture this effect and therefore exhibits a metallic electronic structure. Augmenting the DFT energy by a Hubbard-U correction, so-called DFT + U, is necessary to get the electronic spectrum qualitatively right in these cases (39). The additional computational cost of the Hubbard-U correction is negligible, rendering DFT + U very attractive for complex systems or high-throughput calculations (65). DFT + U collapses the true many-body state into a representative broken-symmetry electron configuration. However, correlated materials with localized electrons may exhibit a large number of energetically almost degenerate realizations in DFT + U. For estimating the associated entropy, the electronic configuration can be mapped to a lattice model and be treated (similar to alloys; see below) with appropriate methods like cluster expansion (78).

GW: Green's function (G)–screened interaction (W) approximation to Hedin's equations within MBPT

As a computationally more involved but also more powerful symmetry-conserving alternative, DMFT (40) for the correlated subspace, in combination with DFT for the other electrons, has developed into a practical DFT + DMFT scheme, particularly since forces have become available (79). DMFT treats correlations within one site (typically the localized orbitals of a single atom) at the many-body level and embeds the site into a bath of electronic states representing the surrounding solid (the Anderson impurity model). The Green's function for the bath is then constructed self-consistently from the single sites. Since DFT + DMFT covers a wide range of strong-correlation phenomenology in a unified framework (40), it has been applied to novel superconductors, catalysts, thermoelectrics, pigments, and more.

For weakly correlated semiconductors and insulators, electronic excitations do not play an important role for thermodynamic stability at typical processing temperatures. Nevertheless, the band gap as well as the alignment of electronic states at interfaces between different materials, or between defect states and the host material, is of utmost interest for applications (80) (see also Section 7 on HIOMs). Kohn-Sham DFT with local or semilocal (e.g., GGA) functionals systematically underestimates experimental band gaps by typically 50–100%, which is known as the band-gap problem. Within DFT, it can be overcome by hybrid functionals, which from a pragmatic point of view interpolate between the underestimation of gaps with GGAs and the overestimation of the gap at the (uncorrelated) Hartree-Fock level. The amount of exact exchange admixed (typically 25% or 30%) can even be tuned to reproduce the gap for a specific material. While such tuning may be justified for a particular application, notably for the successful calculation of defect levels within the gap, it hinders comparative studies across different materials. In contrast, the partial inclusion of nonlocal exchange within hybrid functionals approximates the screened exchange of many-body theory (80) and improves upon other failures of DFT such as the localization of excess electrons in these materials. For solid semiconductors, range-separated HSE-type functionals (20, 81) have become the method of choice because they provide an improved description of band gaps, energies, structures, and phonons at the same time (81). This is particularly important if DFT is used as a tool to characterize different aspects of a material, e.g., as part of an integrated materials science simulation approach.

For a rigorous treatment of electronic excitations, one must go beyond ground-state DFT. For weakly correlated solids, which constitute the vast majority of conventional semiconductors and insulators, MBPT in the GW approximation (82) is the method of choice. In MBPT, the mean-field xc potential from DFT is replaced by a nonlocal, energy-dependent self-energy. In GW, this self-energy is the product of the electronic Green's function G and the screened interaction W, hence the name GW. GW yields dramatically improved electronic band structures compared to standard DFT and has no empirical tuning parameters, unlike hybrid functionals. GW calculations are, at present, computationally feasible on a routine basis for up to a hundred atoms. For more strongly correlated systems, DFT + DMFT methods yield electronic excitations and response functions in good agreement with experiment on a sound theoretical footing.

Magnetic excitations become thermodynamically important near and beyond the critical ordering temperature for ferromagnets (the Curie temperature) and antiferromagnets (the Néel temperature). Fundamentally, these are low-energy collective electronic excitations inaccessible to ground-state DFT in the Kohn-Sham formalism in principle. In most transition-metal compounds, however, the magnetic state can be coarse grained to the atomic level, assigning a single atomic spin to each magnetic atom. DFT is then very effective in parameterizing model spin-lattice Hamiltonians because magnetic configurations at the coarse-grained level often turn out to be metastable solutions of the DFT (or DFT + U) self-consistent equations. Excitations and the associated thermodynamic properties are then obtained from the model Hamiltonians (83, 84). These Hamiltonians can also be used for spin dynamics simulations; see Reference 85 for a recent example.

While the different excitation mechanisms discussed so far are usually treated additively in a first approximation, their interplay has also been investigated. Vibrations at high temperatures smear out sharp features in the electronic density of states by breaking translational symmetries responsible for van Hove singularities (77). Conversely, electron and phonon modes may couple dynamically at low temperatures, redressing both the phononic and electronic excitations. Calculating the interactions and the resulting polarons in strongly ionic materials based on DFT is a field of active research (86, 87). Magneto-vibrational couplings are even more complex (85) but can be effectively interpolated across magnetic phase transitions (88).

3.3. Alloys

Most applied solid materials are not pure compounds but are alloys with some degree of chemical disorder since this opens a huge chemical space for property tuning. Understanding the influence and interplay of alloying elements is increasingly being addressed using DFT-based approaches, although a direct simulation of disordered alloys remains prohibitive. For ideal random alloys, special quasi-random structures (89) continue to be an efficient approach to simulate average properties that are sensitive to short-range correlations. However, most alloys show some degree of temperature-dependent short-range ordering from chemical or elastic interactions. To address these interactions in a systematic way, effective lattice Hamiltonians such as the cluster expansion (90) are parameterized from a set of DFT configurations. These chemical-configuration lattice Hamiltonians then yield configurational contributions to the free energy (usually via grand canonical Monte Carlo simulations and thermodynamic integration in μ-T space) and derived thermodynamic quantities (91). Within the alloy formalism, off-stoichiometric compounds can also be treated by including vacancies.

One challenge in coherent multiphase materials or in epitaxial alloys (such as optoelectronic materials) is the interplay between (*a*) strain and (*b*) vacancy, chemical, or magnetic ordering (92, 93). Such questions are amenable to DFT modeling today. For instance, nanoscale coherent precipitates in complex alloys may exhibit a thermodynamically stable off-stoichiometric distribution of elements, e.g., in κ carbides in Fe-Mn-Al steels (93).

DFT has become an integral part of materials simulations in bottom-up approaches, directly providing atomic-scale properties, as well as reliable input parameters for phenomenological descriptions that are capable of addressing larger timescales and length scales (94, 95). Second, extensions and corrections to conventional DFT have become available within the last two decades and have widened its applicability to more materials classes and properties. While the choice of an appropriate scheme crucially requires a good understanding of material-specific challenges, going against the old dream of a universal solution of electronic-structure theory, we obtain a valuable practical tool to make reliable predictions that complement and sometimes even replace experimental measurements. Lastly, further pushing the theoretical description of bulk properties in so-called problematic hard-matter materials continues to be an important driver for methodological advances in theory and simulation, and DFT often appears as part of the solution with regard to making quantitative predictions for specific materials from first principles.

4. MOLECULAR MATERIALS

Molecular materials, like hard solids, are also at the heart of many new technologies and advances, and their faithful in silico design is the holy grail of materials modeling (96, 97). The polymorphism of molecular crystals, i.e., the ability of a molecule (or molecules) to crystallize into different metastable configurations in the solid state, is important in many areas of chemistry and physics (98, 99) but makes such in silico design both particularly challenging and important. This challenge arises because these different polymorphs can be very similar in stability (sometimes varying with thermodynamic conditions) but can feature quite different properties that can impact their application, such as solubility and mechanical response. For instance, most market-active pharmaceutical ingredients are administered or manufactured as solid or crystalline forms. Theoretical crystal-structure prediction (100) would be of particular value in drug development to foresee situations in which properties might be impacted by the late appearance of a different solid form that is as yet experimentally unobserved.

Beyond pharmaceuticals, many modern materials include organic components, e.g., organic electronics, energetic materials (explosives), polymers, protein crystals, and layered materials, and design of functional molecular materials with tailored absorption properties, conductivities, optical behavior, mechanical response, solubility, etc., would be of enormous benefit and application. Experimentally there are close to 1 million organic and metal-organic crystal-structure determinations in the Cambridge Structural Database (101). These molecular crystals exhibit a huge diversity of molecular and crystal structures and covalent and noncovalent interactions, all of which impact their properties. The prediction and design of materials with tailored properties require predicting the (meta)stable crystal structures of a set of molecules, but the challenge is to get all aspects, in terms of structure, stability, and properties, correct. Achieving this goal requires a first-principles description in which each of these aspects can be treated seamlessly and on an equal footing, but molecular materials have posed specific difficulties for DF-based methods.

4.1. Challenges in the Modeling of Molecular Crystals

There are two major challenges in modeling molecular crystals with DF-based methods. First, the crystallographic unit cells of even small molecules can be significantly larger than those of hard solids, with typically hundreds of atoms per unit cell and often a small number of symmetry elements. Second, accurately understanding and modeling the assembly and stability of molecular crystals require a seamless description of the range of covalent and noncovalent interactions, including electrostatics, hydrogen bonding, and vdW dispersion interactions.

The stability of molecular crystals is often assessed (to a first approximation) using their lattice energy, i.e., the electronic energy per molecule gained in forming the crystal with respect to the molecule(s) being in the gas phase. To make reliable predictions, we are aiming for an accuracy in lattice energies significantly below chemical accuracy (4 kJ/mol, or approximately 43 meV), which is necessary to distinguish competing polymorphs (102). For example, a survey of 508 pairs of organic polymorphs estimated the lattice-energy difference to be below 21 meV for half of the polymorphs, and only 5% had an energy difference greater than 75 meV (103). Additionally, molecular crystals can feature multiple molecules per unit cell (e.g., cocrystals, hydrates, salts, and solvates) that require accurately modeling the competition between a wide range of different compositions, limiting error-cancellation effects. Some key properties (such as solubility) require the ability to model molecules in solution or potentially at interfaces.

While DFT is becoming more widely used in complementing experimental studies of organic polymorphism (104), the ultimate aim is to guide experiment toward the most stable or interesting materials. This requires a combination of high accuracy for a range of properties and the ability to tractably calculate thousands of putative structures within the timeframe of experimental solid form screening, which can be only a few weeks, depending on the target molecules (99).

4.2. Extending DF Methods to Molecular Materials

In the context of the stringent challenge that molecular materials pose, standard local and semilocal GGA functionals can have serious qualitative deficiencies, often leading to severe errors. In terms of structure and stability, these errors are largely due to the neglect of the contribution and correct form of London dispersion interactions (105), which are key for cohesion and properties in even relatively simple molecular crystals. These dispersion interactions are also known as the attractive part of the vdW interactions. It is well established that a (semi)local description cannot correctly describe many relevant electron correlation effects, including vdW dispersion interactions (105). Therefore, many early applications of DFT to molecular crystals fixed unit cells at experimental volumes and focused on crystals held together by hydrogen-bonding networks.

Fortunately, the introduction of dispersion-inclusive methods in the past decade has led to a plethora of different approaches that have significantly improved on the underlying xc functionals, extending the applicability of DF methods to this important class of materials. As a result, DF calculations are becoming one of the most widely used methods for studying molecular crystals and polymorphism, particularly in the context of crystal-structure prediction calculations (98, 100), with notable advances (100). The self-assembly of porous organic cages has also been predicted on the basis of DF calculations, saving considerable synthetic time (106).

The vdW methods employ a range of approaches that enable them to capture the local chemical environment or hybridization effects (46), as well as electrodynamic screening and many-body contributions that are very sensitive to the molecular environment within the material, and such methods are hence important for modeling and understanding polymorphism and self-assembly (107). A detailed overview of the different aspects of combining a semilocal DFA with long-range vdW contributions can be found in recent reviews (42, 44, 45) (see Section 2 for more detail).

Alongside developments in methods for modeling vdW interactions, there have been improvements that have extended the availability of hybrid and meta-GGA DFAs. Exact constraints on the form of the DF have been combined with various degrees of parameterization (ranging from nonempirical to highly empirical) to improve the short- to medium-range electron correlation (17, 108, 109). These DFAs can improve the modeling of hydrogen-bonding interactions, short-range repulsion, and electrostatics, all of which are essential to having a balanced picture of cohesion in molecular materials. They can additionally improve band gaps and other electronic properties.

4.3. What Can DFT + vdW Do Today for Molecular Materials?

DF calculations have been used in a number of current and emerging applications to molecular materials. The accuracy of dispersion-inclusive DFT methods is sufficiently good to reproduce and even validate single-crystal and powder X-ray diffraction structures (110)—with, for example, DFT-optimized structures in the most recent blind test having root mean squared deviations (RMSDs) of less than 0.4 Å—with respect to experimental structures (100). DF calculations of nuclear magnetic resonance spectra and coupling constants are also sufficiently accurate and robust to be used to characterize and elucidate the structure of crystals without single-crystal X-ray data (111). As even low-temperature experimental crystal structures can have appreciable contributions from zero-point vibrations, obtaining closer RMSD agreement with experimental geometries would require going beyond a static 0 K model with DFT, potentially using quasi-harmonic calculations (112, 113).

In terms of absolute lattice energies, recent dispersion-inclusive DFT methods are capable of obtaining agreement with experimental benchmark data of the order of 4 kJ/mol and better (114–116). This has translated into more accurate modeling of polymorphism (i.e., relative lattice energies), but the small relative energy differences (1–2 kJ/mol) are reaching the point where both nuclear quantum and thermal effects (including anharmonicity) (117, 118) could play a pivotal role in understanding any given polymorphic system. It should also be stressed that the underlying DFA and not only the vdW treatment plays a key role, with more computationally demanding hybrid functionals proving important for lattice-energy benchmarks and a number of archetypal polymorphic systems (114–116).

The more accurate modeling of energies further translates to related properties such as phonon or terahertz spectra and elastic properties. However, such properties (even though calculated with static DF calculations) can be much more sensitive to vibrational contributions than to lattice parameters and energies, as quasi-harmonic calculations have illustrated (112). Beyond thermodynamic stability and energy-related properties, the crystal packing can affect many other properties, for example, excitonic properties (119, 120) and the spin state of spin-crossover compounds (121).

While there has been significant progress in computing various materials properties, many studies concentrate solely on thermodynamic and static properties. However, the kinetics of crystal growth can play a pivotal role in determining the crystal morphology and which materials are experimentally accessible. Hence, true in silico materials discovery and design will require models of crystal growth and kinetics at a first-principles DFA + vdW level. Here, a brute-force first-principles approach will likely be too computationally demanding. To address this issue, DF calculations are increasingly being used in parameterizing empirical potentials or in developing coarse-grained models. For instance, the area of machine-learning potential interpolation is a very active and promising field that is enabling large-scale simulations with DFT accuracy (see, for example, 122–124).

Beyond the actual target of calculations, there has been a significant improvement in the ease of use and availability of dispersion-inclusive DFT methods for studying molecular materials. The methods themselves are parameterized (where required) for a wider range of elements, chemical environments, and underlying DFAs. Their computational cost (depending on the specific implementation) is typically less than, or at worst on par with, the DFA part of total-energy calculations (46). Furthermore, the most widely used approaches are available in multiple DFT codes. In contrast to bulk solids (8), however, few systematic studies of reproducibility of results with different implementations, codes, and basis sets have been performed for molecular materials. Such studies would be timely, given the increased use and importance of DF modeling of molecular materials.

5. WATER AND BIOLOGICAL MATERIALS

Many challenges of modeling biological materials with DF methods [either in so-called clean room conditions (125) or in the presence of water] resemble those encountered when modeling

CCSD(T): coupled cluster approach with single, double, and perturbative triple excitations

molecular materials. Reliable modeling of biological materials imposes stringent requirements on the accuracy and efficiency of methods for describing a broad range of covalent and noncovalent interactions. For example, covalent bond stretching and torsional degrees of freedom interplay with electrostatics, hydrogen bonding, and vdW dispersion interactions in most biological systems. In addition, the extended structures of amino acids and base pairs present in proteins and DNA lead to the important and hard-to-describe phenomenon of cooperativity (126). Quantitative description of these effects with DF methods requires (*a*) the employment of hybrid functionals that mitigate the self-interaction error found in standard GGA functionals and (*b*) a reliable description of vdW dispersion interactions that goes beyond the widely used interatomic or electron density–based pairwise approximation.

The relevant energy scale in biology is set by kT, which is 2.5 kJ/mol at room temperature. Achieving such accuracy for conformational energy differences is not trivial, even when using the most sophisticated quantum-chemical methods, such as the coupled cluster approach with single, double, and perturbative triple excitations [CCSD(T)], which is considered the gold standard in quantum chemistry. Such accuracy is even harder to obtain with DF methods, although many recent studies on increasingly larger biological molecules yield very promising results. In the case of polyalanine homopeptides, DFT + vdW methods come close to CCSD(T) accuracy for relative conformational energies, while DFT + vdW molecular-dynamics simulations yield quantitative agreement in unfolding temperature when compared to gas-phase experiments (127). More recently, heteropeptides have been studied with DFT + vdW in isolation and in microsolvation environments, with remarkably good agreement with experiment in terms of structures and conformational stabilities of these systems, provided that the hybrid PBE0 functional is used in conjunction with the MBD method for vdW interactions (128, 129). In what follows, we highlight a few recent studies that nicely illustrate the current capabilities of and remaining challenges for DF methods applied to water and biological materials.

5.1. Advances in DF Modeling of Water

Before modeling biomolecules under physiological conditions (solvated in water, at room temperature, at standard pH), it is important to assess the reliability of DF methods for pristine water. This seemingly simple task is unexpectedly challenging (130–132). A quantitative description of the structural properties of water (as measured by its radial distribution function) necessitates an accurate treatment with a hybrid PBE0 functional, a nonempirical treatment of vdW dispersion interactions, and the inclusion of nuclear quantum effects (133). Even after all of these important effects are included, the field is not free from controversy (132). Many of the anomalous properties of water, such as diffusion coefficients, the coexistence of several phases, and others, demand convincing explanations from first-principles DF calculations.

In addition to modeling pristine water, accurately describing ion solvation is highly relevant. This field has seen substantial advances, but many unsolved challenges remain. For example, ion coordination numbers can be accurately modeled using DF-based molecular-dynamics simulations (134). A recent study using state-of-the-art DF calculations unraveled the origins of the difference between hydroxide and hydronium ion diffusion in water, attributing this difference to correlated proton transfer (135). In addition, ionic electrostatic fields can strongly affect intermolecular vdW interactions by making them either repulsive or attractive (136).

5.2. Advances in DF Modeling of Biological Molecules

First-principles calculations have been applied to the modeling of biological molecules from the early days of DFT (126). While these early calculations were done in the gas phase, they were often compared to experiments carried out on solvated biomolecules. This led to disagreements or occasional coincidental agreement regarding DF calculations and experimental measurements of structures and relative stabilities of biomolecular conformations. The situation has much improved since the development of electrospray ionization techniques, which now enable experimental characterization of biomolecules in the gas phase and in microsolvated environments (137).

Baldauf & Rossi (125) reviewed the current situation of DF modeling of peptides up to 20 residues in the gas phase. Most advanced DF calculations are now able to produce structures and relative stabilities of peptide conformations in remarkable agreement with experiments. Such calculations are also able to suggest peptide sequences with challenging energy landscapes by combining different levels of theory, from classical force fields to PBE0 + MBD. DF-based molecular-dynamics simulations are now possible up to timescales of hundreds of picoseconds for peptides with up to 1,000 atoms. Such dynamics explore only local energy landscapes, and hence explicit folding simulations are not yet achievable with direct DF dynamics. In addition, while microsolvated peptides have been successfully studied (125), full solvation remains too computationally demanding for the moment.

5.3. Toward Fully Solvated Biomolecules with DF Calculations

The complete folding dynamics of solvated biomolecules can currently be studied only by using classical molecular dynamics with empirical force fields. While many seminal advances have been made in this way (138), the many shortcomings of empirical force fields are well recognized (139). Thus, there is much interest in modeling fully solvated biomolecules with first-principles calculations. As explained above, direct DF simulations of solvated biomolecules are not feasible. Hence, there has been a strong push toward the development of coarse-grained models for addressing long-timescale biomolecular dynamics (140) and for constructing accurate hierarchical models for water interacting with biomolecules.

Even the fundamental balance between water-water and water-biomolecule interactions remains poorly understood (141). Understanding such a balance from first principles requires a quantitative description of all relevant enthalpic and entropic contributions for solvated biomolecules. While the DF calculations described in Section 5.2 would, in principle, yield an accurate description of energetics for systems with a few thousand atoms, vibrational enthalpic and entropic contributions would require the development of coarse-grained empirical potentials. The construction of such potentials could rely on machine-learning techniques parameterized using first-principles DF calculations on smaller model systems (142, 143).

6. LOW-DIMENSIONAL AND LAYERED MATERIALS

There is no universal definition in materials physics and chemistry of where one- or two-dimensionality begins. A simple rule of thumb in atomistic contexts, such as DF calculations, is to say that a two-dimensional (2D) material has one length scale smaller than approximately 1 nm (the thickness) and two length scales much larger than 1 nm (the in-plane length scale). To maintain structural integrity as an atomistic 2D system, in-plane bonding has to be strongly covalent, while stability also dictates that there cannot be out-of-plane dangling bonds. The 2D system is thus characterized by in-plane ionic-covalent bonding and vdW-dominated out-of-plane bonding. In nature, 2D systems are primarily found in the form of weakly bonded layered systems; the canonical case is graphite, which consists of sheets of graphene, the first 2D material to be studied in controlled circumstances (144, 145).

6.1. The Importance of vdW Interactions

vdW-DF: nonlocal van der Waals density functional

The primary challenge for DFAs in 2D and layered systems is the description of weak vdW-dominated out-of-plane bonding. Low-dimensional systems pose a particular challenge in the context of vdW interactions since the high anisotropy of the system means that the dielectric response is very different along the various directions. A 2D system will behave like a molecule out of plane and like a bulk solid in plane, and the resulting screening properties will somehow interpolate between these extremes, depending on the system studied. Thus, the systems are difficult to model, particularly so when one is constructing a general-purpose DF.

Studies have concluded that weakly vdW-bonded layered solids, such as graphite, have remarkably similar interlayer binding energies, without strong dependence of the chemical elements that make up the layers (146, 147). This lack of variation is explained by the vdW interaction making up nearly all of the attractive part of the interaction between the layers, resulting in the interlayer binding being a quasi-constant of this particular geometric arrangement. However, if the geometric criteria of what constitutes a weakly bonded layered solid are relaxed, a more complex picture emerges, and a continuum of binding energies is seen (148). This continuum is presumably due to an increasing intermixture of covalency in the bonding, since electrostatic interactions between layers are mostly expected to be small (149).

6.2. DF Calculations for Two-Dimensional Materials

Just as for other materials types dominated by vdW bonds, plain GGA-type functionals produce binding energies that are far too small in weakly bonded layered solids, in some cases failing to produce any binding (150, 151). The LDA will produce binding, sometimes reproducing equilibrium properties, but typically combining a too low binding energy with too short vdW bond lengths (150). For an average DFT user, the often much-too-short bond lengths are the primary problem since bad geometries will tend also to impact the electronic structure in the form of too small band gaps.

The de facto standard for higher-order techniques capable of describing vdW interactions (152) in 2D and layered systems is RPA within the ACFDT since it is a realistically applicable technique that includes some of the many-body contributions important in dispersion interactions (152). For instance, the RPA was used to study the cohesive properties of hexagonal boron nitride (153) and of graphite (154). The RPA is currently also the highest-order explicit many-body theory that is still computationally feasible for enabling large-scale calculations to produce benchmark sets in layered systems. For example, a benchmark set consisting of 26 layered solids, since its publication in 2012 (147), has served as the main theoretical benchmark for interlayer binding energies. Studies using methods beyond the RPA have so far provided at most small corrections to binding energies in layered and 2D systems (155–157).

6.2.1. Nonlocal correlation functionals. Nonlocal correlation functionals (44) come in two main flavors: (*a*) the original formulation, vdW-DF, of Dion et al. (55) and its successors and (*b*) the more recent VV10 functional of Vydrov & van Voorhis (158). The origin of these was a conceptual functional designed specifically to capture the dielectric response of layered solids (159). However, today none of the original versions of these functionals can be recommended for layered systems; the original vdW-DF has much too large vdW bond lengths, and the unmodified VV10 functional is fairly strongly overbinding (150). However, over the years since their initial formulations, the different flavors have gradually been improved, following varying paths and design philosophies. Most of these later methods describe layered materials well, as discussed in recent reviews, investigations, and developments (44, 151, 160, 161).

The main tendency of these DFs is to produce larger interlayer binding energies than does RPA, although not drastically so for the best performing versions. Equilibrium geometries tend to vary in the expected way with binding energies; i.e., the stronger the binding, the shorter is the interlayer distance. For the second-generation versions of these functionals, the typical errors in interlayer distances are an order of magnitude smaller (of the order of 1%) than errors in the interlayer binding energies relative to RPA (of the order of 10%), although coupling the revised VV10 functional to the SCAN meta-GGA functional has produced even better results (160).

6.2.2. Pairwise interatomic methods and beyond. A variety (33, 48, 51) of pairwise approaches aim to correct local and semilocal DFs for missing vdW interactions. They usually give a reasonable description of layered systems, although most of them do not reach a precise description of both the distance and the binding energy between layers. For instance, the PBE + D2 method was applied (162–164) to layered systems, and in the case of graphite and hexagonal boron nitride (h-BN), it predicted an interlayer distance that was too short, while the binding energy was too large in comparison with the RPA values. The Tkatchenko-Scheffler method has been used (165–168) to calculate the properties of several layered materials. This method provides excellent equilibrium geometries but overestimates interlayer binding energies relative to the RPA. The D3 correction (48) has been used as well (169) for those systems; similarly, the obtained equilibrium geometries are reasonable, but the interlayer binding energies are overestimated. One step further can be taken by including many-body effects (54, 170) in the description of the vdW interactions between the layers. When these methods are applied to layered systems (168, 171), both the RPA geometries and binding energies can be reproduced quite well, which means that those methods can be used as a reliable computational tool to study layered systems.

6.3. Relation to Experimental Data

The available experimental data, such as lattice constants of solids and adsorption heights of 2D layers deposited or grown on surfaces, are primarily geometrical. However, experimentally extracted values of binding energies in 2D systems are unfortunately both rare and plagued with uncertainties since no direct measurement method is currently known, and results have to be inferred indirectly, involving modeling of the interaction. It has been demonstrated for experimentally estimated cleavage energies for graphite that different reasonable choices for these interaction models can result in differences in binding energies of up to 100% (172). Since other experimental values of the interlayer binding of graphene sheets (173–175) also depend on an underlying model of the interaction, one may reasonably ask to what extent these experimental values can be trusted. For the interlayer binding of graphite, the experimentally reported numbers fall in the range of 35–52 meV/atom, close to the best available calculations. This is clearly an encouraging consistency, but whether the calculated values underpin the experimental ones or vice versa is a somewhat open question.

Not all ways of measuring the interlayer binding give agreement between DFT and experiment. On the basis of the optimal surface energies of surfactants in liquid-phase exfoliation, Cunningham et al. (146) concluded that a range of well-known layered materials, including graphene, h-BN, and various transition-metal dichalcogenides, had very similar surface energies. The surface energy is by definition half the cleavage energy of the bulk compound, and for weakly bonded layered solids, this number is close to the interlayer binding energy (147). On the basis of RPA and VV10 calculations, Björkman et al. (147) computationally arrived at the same result, with binding energies falling in a fairly narrow range. What has not yet been resolved, however, is the fact that the surface energies inferred from exfoliation data are only approximately half of what is expected on the basis of the calculated interlayer binding energies. The reason for this discrepancy is presently not understood.

7. HYBRID INORGANIC-ORGANIC MATERIALS AND INTERFACES

7.1. What Are Hybrid Inorganic-Organic and Metal-Organic Materials?

Composites of traditional molecular and inorganic materials classes, HIOMs are emerging materials, in terms of not only basic materials processing and application areas but also novel characteristics and properties that arise at the organic-inorganic interface. These applications include organic semiconductor thin films in contact with metals and oxides (176), novel display devices (177), sensors, and nanocatalysts. It is therefore not surprising that HIOMs come with a diverse range of morphologies, including multilayered thin films, polymer-nanoparticle composites, molecularly doped frameworks, and molecularly functionalized metal nanoparticles (178).

The coexistence of localized molecular and extended metallic states in HIOMs means that neither successful xc functionals for molecules nor successful functionals for pristine metal and semiconductor materials are particularly well suited for the prediction of HIOMs. In the following, we discuss the recent advances in and capabilities of existing functionals and the remaining challenges in describing prototypical HIOMs to gauge the current state of DF approximations.

7.2. Dominant Interactions in Hybrid Inorganic-Organic Materials and State-of-the-Art DFAs

When one is discussing the performance of different DF approximations for HIOMs, it is useful to break down the interactions in HIOMs at equilibrium geometries into three distinct, physically meaningful contributions that are discussed below.

First, hybridization and orbital overlap at the interface give rise to covalent chemical bonds, which are the dominant form of interaction at HIOMs. Most functionals are designed with covalent interactions in molecules in mind (15, 179, 180). At the same time, since LDA and GGAs are based on the physics of the homogeneous electron gas, they also yield a reasonably accurate description of the cohesive properties of metals (181). However, GGAs still face notable problems. For example, the bond-length alternation, i.e., the difference in bond length between a single bond and a double bond in aromatic molecules, is underestimated and is more accurately described at the hybrid and range-separated hybrid levels (182). In metals, in contrast, admixture of exact exchange into the xc functional leads to a deterioration of the description of cohesive properties, which is connected to the fact that unscreened exchange leads to a finite band gap in many metals and to the removal of the often advantageous error cancellation at the semilocal DFT level (183).

Second, extended polarizable materials and adsorbate molecules exhibit vdW or dispersion forces. Although it is a nominally weak interaction, in large systems the accumulated interaction due to dispersion interactions can be equal to or larger than covalent chemical interactions, and at metal-organic interfaces, these forces generally cannot be neglected. Due to the large intrinsic length scales, HIOMs require an efficient treatment of such long-range dispersion interactions—a requirement that is shared with molecular, biological, and low-dimensional materials (see Sections 4, 5, and 6).

Third, electrostatic interactions [charge transfer, (de)polarization, and image charge effects] play a big role in both dominantly covalently bound (chemisorbed) and vdW-bound (physisorbed) HIOM systems. Electrostatic interactions not only affect the structure and stability of the adsorbate but also lead to the formation of interface dipoles, which affect the HIOMs' work function and other electronic properties that can be directly measured.

7.3. Predicting the Structure and Stability of Hybrid Inorganic-Organic Materials

An important prerequisite for studying the materials properties of HIOMs is to correctly predict the stability and structure of inorganic-organic interfaces. LDA- and GGA-level functionals provide a description of orbital overlap, charge induction, and dispersion that is too unbalanced to accurately describe molecule-metal and molecule-semiconductor interfaces. LDA strongly overestimates organic-inorganic binding, yielding too high adsorption energies and too low adsorption distances. In contrast, PBE and several other GGAs predict little to no bonding with strongly overestimated adsorption distances. This is nicely shown by the example of PTCDA (perylenetetracarboxylic dianhydride) on Ag(111) (11, 52). Otherwise successful dispersion-correction methods, such as the Grimme D3 method (48) and the Tkatchenko-Scheffler method (51), provide systematically overestimated interaction energies and adsorption height errors in the range of 0.1 to 0.5 Å at molecule-metal interfaces (11). A similar trend has been observed for nonlocal vdW correlation functionals such as vDW-DF (55), optPBE-vdW, and optB88-vdW (184).

The increased errors are rooted in the physical nature of vdW interactions in HIOMs and in particular at metal-organic interfaces, where the dielectric function of the metal effectively screens long-range dispersion interactions and the nonlocal collective polarizability leads to a breakdown of the pairwise atom approximation of dispersion. More recent methods that account for these effects, such as the screened Tkatchenko-Scheffler method vdW^{surf} (52) and the MBD method (54), have provided systematically improved adsorption heights with errors within 0.1 Å from experiment (11, 185, 186). Whereas PBE + vdW^{surf} predicts accurate heights, it significantly overestimates binding energies. For several systems, this effect can be remedied by the MBD method (185, 187). The latest generation of vdW-DF methods (vdW-DF-cx) (188) has also shown promising results in that direction (189).

Few reported geometry optimizations with dispersion-corrected hybrid functionals exist, and therefore a fully conclusive picture of their performance has not been established. HSE06 (20) and other range-separated functionals have yielded some progress (185), but a choice has to be made regarding the parameter that defines the range separation.

Explicit treatment of correlation at the level of the RPA has been computationally very demanding but has yielded a reliable description of short-range bonds for small and large molecular adsorbates at metal surfaces, which has been shown for the prototypical systems of PTCDA on Ag(111) (190) and single-sheet graphene on metals (156).

7.4. Predicting the Electronic Properties of Hybrid Inorganic-Organic Materials

Most simulations of HIOMs are performed with specific electronic properties in mind. For surface science studies, these are often spectroscopic properties such as core-level spectra, which provide insight into the chemical bonding and electrostatic potential at the interface. Studies in the context of organic electronics focus more on the interfacial level alignment and the adsorption-induced interface dipole, which is crucial for optimizing charge injection in these devices (191). There is, moreover, interest in the optoelectronic properties at interfaces (192).

In practice, core-level spectra of HIOMs are mostly calculated via their Kohn-Sham energies. Semilocal functionals have a good track record of reproducing relative shifts (193), even if the absolute binding energies are underestimated (194). Physically, this so-called initial-state approach neglects the screening of the induced core hole. A final-state approach, in which a full or half core hole is explicitly modeled in a self-consistent DF calculation (195, 196), can capture these screening effects and has provided highly accurate predictions of core-level photoemission and photoabsorption (197). Nevertheless, problems can arise from artificial dipoles in the unit cell that introduce spurious shifts and energy contributions. A way to avoid this problem would be to employ *GW*, which yields results at the same level of accuracy as the final-state approximation (198, 199). However, *GW* is too expensive to routinely apply to HIOMs.

The situation is similarly unsatisfactory for optical excitations. Ideally, we would like to rely on MBPT, such as the Bethe-Salpeter equation (200). However, with a few notable exceptions (e.g., 201), this approach is usually computationally too expensive. Time-dependent DFT would be a cheaper solution, but implementations for range-separated hybrid functional kernels, which would be required for charge-transfer excitations, are scarce in condensed matter electronic-structure codes. Thus, the present state of the art is to compute the dielectric response of HIOMs (202). This approach, however, neglects excitonic effects that may be important, especially within the organic component. An alternative approach is to use variational constrained DFT (203) or Δ-self-consistent field–based approaches (204) to calculate excitations.

For the discussion of the interfacial level alignment, it is useful to discriminate between systems that are Fermi-level pinned and those that are not. Here, we define Fermi-level pinned systems as those in which charge transfer into or out of a state with a distinct molecular character occurs.

For non–Fermi-level pinned systems, the computed interface dipole is governed by the accuracy of the molecular dipole, the adsorption-induced image potential, and the eventual covalent bonding of the HIOM. Although semilocal functionals have the tendency to underestimate the magnitude of dipole moments and to overestimate molecular polarizabilities (205), the overall interface dipole tends to be very well reproduced (206). For nonpinned systems, the computed work function changes are usually much better described than absolute work functions, in particular for adsorption on nonmetallic substrates.

Fermi-level pinning occurs when the lowest unoccupied molecular orbital of the organic component would be below the Fermi energy of the inorganic substrate (or, conversely, the highest occupied molecular orbital above it), shifting the levels until they are in resonance with the Fermi level. Due to the infamous band-gap problem, one might expect semilocal functionals to yield poor results. However, this is not the case (207), for a number of reasons:

- The band-gap renormalization upon adsorption that is absent in semilocal or hybrid functionals (208) is typically on the same order as the band-gap underestimation by semilocal functionals (209). This leads to a fortuitous cancellation of errors.
- The band-gap problem vanishes for half-filled orbitals. Thus, fractionally occupied orbitals, as observed in Fermi-level pinned systems, suffer far less from band-gap underestimation than do the orbitals of the isolated molecules.

The situation is fundamentally different for adsorption on semiconductors or more inert substrates, in which no hybrid bands are formed. There, the molecular orbitals retain their orbital character and can be filled only in integer quantities. Unfortunately, semilocal DFT overdelocalizes charges and leads to fractional filling of orbitals, even in situations in which noninteger occupations are clearly unphysical (210). The spurious delocalization can be solved using nonlocal hybrid functionals. A problem in this context is that the ideal amount of exchange may be system dependent, and different values are optimal for the free molecule, the adsorbed molecule, and the substrate (211). Despite promising efforts (208, 212), it remains unclear whether a single, global parameter, as used, e.g., in PBE0 or HSE06, can provide a satisfactory solution for both the inorganic component and the organic component at the same time (192, 213).

So far we have focused most of the discussion on metal-organic interfaces. These are the simpler HIOMs—for theory, because the metal is close to the model concept of a homogeneous electron gas, and for experiment, because the conductivity of the metal is a prerequisite for many experimental techniques. From an application viewpoint, however, there is also particular interest in semiconductor/organic HIOMs. We refrain here from an in-depth discussion but say briefly that, beyond the problems that are discussed above for metal interfaces, two aspects particularly require the DFT user's attention. First, the level alignment problem is much more pronounced for semiconducting substrates than for metallic substrates, leading easily to spurious charge transfer (192). Hence, in contrast to metal interfaces, hybrid functionals, which are often computationally much more expensive, are required to achieve qualitatively correct results (211, 214). Second, semiconductors are almost always doped, leading to (long-ranged) bulk-to-interface charge transfer upon HIOM formation. To correctly capture the physics, it is necessary to include dopants either explicitly (214) or via embedding schemes (215, 216).

8. CONCLUSIONS AND REMAINING CHALLENGES

Although, at first sight, the current predictive capabilities of existing xc functionals seem somewhat limited and dependent on the system under study, it is important to realize that the current state of the art has drastically improved from 15 years ago.

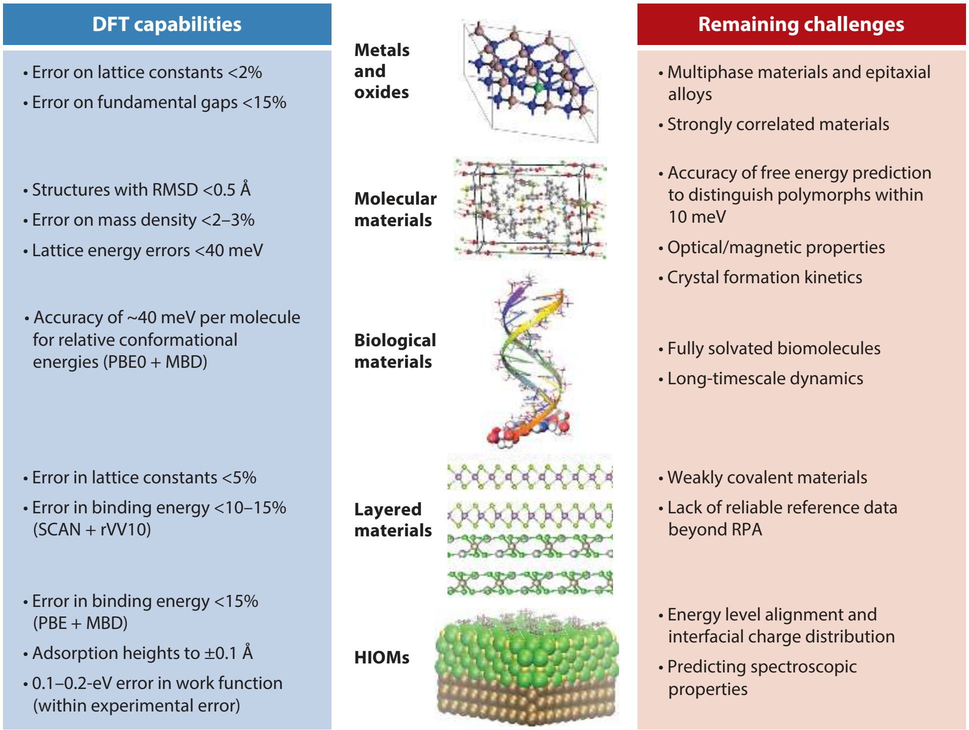
The main drivers of progress are:

- the advent of efficient and reliable long-range dispersion-corrected functionals;
- the development of range-separated hybrid functionals that address the band-gap problem at manageable computational cost; and
- the increasing access to highly accurate experimental or theoretical reference data on the structure, stability, and electronic properties of idealized benchmark systems.

Figure 2 summarizes the results of these developments for the materials classes discussed here. While the accuracies vary considerably across different materials, the common picture is that the structure and stability of materials can be simulated and predicted with high accuracy, in many cases to within the experimental uncertainties.

Although the advancement of DF calculations for materials research over the past decade has been remarkable, many challenges remain. A particular problem that unifies all applications discussed in this review is the lack of good benchmark data from higher-level theory and from experiment. Accurate quantitative measurements of structure and stability are becoming more accessible and, especially in the case of HIOMs, have been real drivers of DFT predictive capabilities (11). A joint experimental and theoretical effort will be required to convince funding agencies and the community to push for more standardized and well-characterized benchmark systems that challenge a particular functionality of DFT. Unfortunately, the strong coupling of structure, temperature, and optoelectronic properties in most interesting modern materials provides a challenge for the direct comparison between electronic-structure theory and experiment.

The progress in DF developments can be most straightforwardly measured against higher-level theory. Here, exciting progress has been made. On the one hand, embedding techniques (217, 218) and local approaches of coupled cluster theories (219, 220) have made the gold standard of quantum chemistry applicable to molecular systems with a few hundred atoms and molecular crystals of small molecules (221). On the other hand, new algorithmic developments in the field of quantum Monte Carlo have made the computation of chemically accurate lattice energies of small molecular crystals feasible with reasonable computational effort (222). Nevertheless, the routine high-level description of systems with more than 100 atoms remains challenging. At the moment, despite its high computational cost, RPA remains the most accessible higher-level method for materials research. Unfortunately, in several cases, it has already been found to be insufficiently accurate, e.g., for molecular materials cohesion energies (222), and it is notoriously difficult to converge with respect to all numerical parameters.



DFT capabilities		Remaining challenges
• Error on lattice constants <2% • Error on fundamental gaps <15%	**Metals and oxides**	• Multiphase materials and epitaxial alloys • Strongly correlated materials
• Structures with RMSD <0.5 Å • Error on mass density <2–3% • Lattice energy errors <40 meV	**Molecular materials**	• Accuracy of free energy prediction to distinguish polymorphs within 10 meV • Optical/magnetic properties • Crystal formation kinetics
• Accuracy of ~40 meV per molecule for relative conformational energies (PBE0 + MBD)	**Biological materials**	• Fully solvated biomolecules • Long-timescale dynamics
• Error in lattice constants <5% • Error in binding energy <10–15% (SCAN + rVV10)	**Layered materials**	• Weakly covalent materials • Lack of reliable reference data beyond RPA
• Error in binding energy <15% (PBE + MBD) • Adsorption heights to ±0.1 Å • 0.1–0.2-eV error in work function (within experimental error)	**HIOMs**	• Energy level alignment and interfacial charge distribution • Predicting spectroscopic properties

Figure 2

Summary of method capabilities and the remaining challenges for different materials classes. Many of the remaining challenges apply across the different materials classes. The given estimates of accuracy are based on empirical knowledge of the authors for particular sets of systems within the respective materials classes, and there are many systems in which errors can be exceptionally higher or lower than what is given. Abbreviations: HIOM, hybrid inorganic-organic material; MBD, many-body dispersion; RMSD, root mean squared deviation; RPA, random-phase approximation.

More efficient, lower-rung xc functionals have gradually approached high-level binding energies and experimental geometries to the point at which these can be considered to be accurate (161), and further improvements will most likely be achieved by accounting for fluctuations and disorder at finite temperatures and pressures. However, to further bridge the gap between experiments and materials modeling, the computational cost and turnaround of DF calculations need to be further improved to enable the direct simulation of measurable observables at realistic experimental conditions. For example, the timescale of key experimental methods, such as crystal polymorph screening, is of the order of weeks. More efficient implementations of state-of-the-art DFAs will be required, exploiting the latest developments in computer hardware.

As we advance with the above challenges, it will become clearer that new DFAs will be required to accurately model specific properties, such as dynamic observables and transport properties in materials, as well as more complex molecular materials, such as multicomponent salts. There are a number of areas in which methodological development can be focused. For example, researchers could develop methods that address the challenge of mid-range correlation in which the underlying DFA and vdW contributions overlap; another possibility is DFAs that can reliably and seamlessly model different types of charge (and proton) transfer within molecular materials. Furthermore, all of the currently used vdW methods rely on local response models that might not be justified for conductors, and further developments might be needed. As the DF developments further splinter toward tackling strong correlation or long-range correlation, new efforts will need to emerge to bring these developments back together and to identify more general solutions.

One challenge in the context of the development of new functionals is that improvements in one property or quantity can often lead to decreased performance for others. For instance, combining new DFAs with vdW contributions is not always straightforward (223, 224). This particular example, in which the semilocal DFAs are becoming more long ranged while the vdW corrections are increasingly capturing short-range effects, is prototypical, as it highlights the challenge to electronic-structure theory when interaction ranges and length scales are not clearly separable.

The current state of the art for predicting structure and stability provides the foundation for a further push toward optoelectronic materials properties, dynamic and kinetic observables, transport properties of materials, and large-scale materials screening efforts. These efforts will see the need to combine specialized methods and software and to develop code interoperability and generalized workflows. Definitions of universal file formats and projects such as the Atomic Simulation Environment (225) and LibXC (226) will gain more and more traction.

Despite these many challenges, recent developments in DF methods and codes have greatly enhanced the applicability and usability of DFT. In combination with advances in simulation and structure-prediction algorithms, DF calculations can now augment and complement experimental studies (but not substitute for them) for a number of challenges, such as interface characterization, polymorphism, and structure prediction. For true computational materials prediction based on DFT to guide the development of new materials, we should provide not only accurate structure and property prediction but also a confidence measure of the uncertainty that is intrinsic to computational modeling.

DISCLOSURE STATEMENT

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