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**Feature Review**

# Status and Challenges of Density Functional Theory

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We discuss some of the challenges facing density functional theory (DFT) and recent progress in DFT for both ground and excited electronic states. We discuss key aspects of the results we have been able to obtain with the strategy of designing density functionals to have various ingredients and functional forms that are then optimized to accurately predict various types of properties and systems with as much universality as possible. Finally, we make specific recommendations of approximate density functionals that are well suited for particular kinds of applications.

## The Advancement of DFT by Adding Ingredients

Recent advances in the development of **Kohn–Sham DFT (KS-DFT)** (see Glossary) have focused on obtaining more accurate and **universal density** functionals. KS-DFT has been successful in describing numerous properties of atoms, molecules, and solids, and very large systems can be treated accurately at an affordable computational expense. Nevertheless, KS-DFT suffers from limitations. In practical applications of the original theory, these may all be considered to arise from the need to approximate the **exchange-correlation functional**. Most approximate functionals suffer from **self-interaction error**, **delocalization error**, or both and their task is made particularly difficult by the need to make up for the representation of the density as a single-**configuration** reference wave function that corresponds to noninteracting electrons.

Probably the single most influential tactic for improving DFT has been the addition of new ingredients, with each new ingredient leading to improved or broader accuracy. Some historical examples of this have been the introduction of density gradients, Hartree–Fock (HF) exchange, kinetic energy density, various ways to include nonlocal correlation, and range separation. We have attempted to use a combination of ingredients and flexible functional forms to design universal density functionals and we have also proposed some specific-purpose functionals with the intent of understanding what ingredients of a functional affect which properties. In this review, we summarize some recent progress we have made in improving DFT and advancing toward the goal of achieving universality. Because universality is only partially achieved, we also summarize recommendations for functionals well adapted to specific kinds of applications.

## Challenges Facing DFT

Solving the Schrödinger equation for an atom, a molecule, or a solid yields its wave function, which can be used to determine various properties of the system. The two quantum chemistry methods widely used to calculate the properties are DFT and wave function theory (WFT). In WFT, one works explicitly with the wave function, which depends on $3n$ coordinates for an $n$-electron system with fixed nuclear coordinates. In contrast, the basic premise of DFT is that, for a given set of nuclear coordinates, the energy density at a point in space is a functional of the 3D electron density. Therefore, the original formulation of DFT involves only three dimensions. For open-shell systems, we need the up-spin density and the down-spin density, which are each

### Highlights

Density functional theory is in principle exact, but its success depends on improvement and refinement of the exchange-correlation functionals. This is being accomplished by using improved functional forms with more flexibility and more ingredients and by optimization against broader databases. The goal has been to obtain more universally applicable functionals that are simultaneously accurate for as many properties as possible. Recent optimizations also place a premium on smoothness that diminishes problems with self-consistent-field iterations and grid-size convergence.

Density functional theory for ground-state properties has been mainly improved in recent work by optimizing functionals with simultaneously good performance for both main-group and transition-series chemistry, including both bond energies and barrier heights. This can be especially important, for example, when treating catalysis in metal–organic frameworks.

Density functional theory for excited-state properties has been mainly improved in recent work by optimizing functionals with simultaneous good performance for valence excitations, Rydberg excitations, and charge-transfer excitations.

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functions of only three spatial coordinates. For this reason, DFT is practical even for large molecules and complicated materials, whereas accurate WFT is an impractical method for large systems, although it is capable of high accuracy when it is affordable for small systems. Because it is impossible to solve the Schrödinger equation exactly for a many-body system, approximations are made in both WFT and DFT methods, and the type of approximation one enforces determines the usefulness of these methods for various properties. In practice, much progress in DFT has involved adding additional ingredients to the spin densities.

The accurate treatment of electron correlation constitutes a central problem in both DFT and WFT. It is often defined with respect to a HF wave function, which is a single-configuration wave function obtained by using the variational principle to find the orbitals that lead to the lowest energy. Electron correlation energy is often quantified somewhat arbitrarily as the difference between the exact energy and the HF energy of a system at the complete basis set limit. Electron correlation energy can be broadly divided into dynamic and static correlation energy [1]. The correlation energy that can be treated well by adding a small number of nearly degenerate **configuration state functions (CSFs)** to a single-configuration starting point is usually called static correlation energy [2–4]. A prominent example is left–right correlation energy associated with the near degeneracy of bonding and antibonding orbitals when a bond is broken. The remaining correlation energy is then called dynamic. The dynamic correlation energy converges very slowly with respect to the addition of more CSFs to a reference CSF and this is the main reason for the high cost of well-converged WFT calculations. Systems with high static correlation energy are called strongly correlated systems or single-reference (SR) systems and other systems are called weakly correlated or multireference (MR) systems. Independently of the language, the border between strongly correlated and weakly correlated is imprecise. Nevertheless, we can make two generalizations: (i) that dynamic correlation is expected to have a very similar character in all states, while static correlation is expected to be very system-dependent, state-dependent, and even geometry-dependent; and (ii) that systems with high static correlation are hard to treat accurately if one uses a single CSF as a reference function.

KS-DFT, like HF theory, is based on a mean-field formalism and is an SR method, but in KS theory the reference wave function is not a zero-order wave function for perturbation theory or a starting point for adding CSFs by excitations (single, double, triple, etc.) in configuration interaction theory or coupled cluster theory, but rather it is a Slater determinant corresponding to noninteracting electrons that have the same one-electron density as the exact solution to the Schrödinger equation. Thus, this Slater determinant is not a wave function for the real system. Because it corresponds to the same density as the real system, it can be used like a wave function for calculating properties like dipole moments that depend only on the density, but – except for the energy – it should not be used for properties that depend on correlated electron distributions, which are described by the two-particle density. (For example, the many-electron spin $S$ is not a one-electron property, so the KS-DFT determinant should not be used to calculate the expectation value of $S^2$.)

Although KS-DFT has a mean-field formulation and represents the density with a single Slater determinant, it is in principle an exact theory. The energy in KS-DFT is not calculated by adding more CSFs but rather by using an exchange-correlation functional, which is a functional of the density. Although there is an existence theorem for an exact exchange-correlation functional, even for strongly correlated systems, in practice we have to approximate the exchange-correlation functional, and currently available functionals are more accurate for weakly correlated systems than for strongly correlated ones. This is understandable because, in a strongly correlated system, the exchange-correlation functional must account not just for the generic dynamic correlation

## Glossary

**Classical Coulomb energy:** the energy of interaction of an electron with the electrostatic field of the nuclei and all the electrons of the atom or molecule under consideration. By convention this may also include internuclear repulsion.

**Configuration:** an assignment of occupancies (two, one, or zero) to the various orbitals of a system (partial occupancies require a linear combination of CSFs).

**Configuration state function (CSF):** a many-electron wave function corresponding to a particular way to assign electrons to orbitals (for closed-shell singlets, a CSF is a single Slater determinant).

**Delocalization error:** the error due to the electron density or a hole being predicted to be too spread out over more than one atomic center.

**Density:** the one-electron density, which is the reduced single-particle density matrix obtained by integrating the many-electron density over all of the electronic coordinates except one (when one says density without a qualifier, one is referring to this one-electron density; the density gives the probability density for finding an electron at a point in space).

**Exchange-correlation energy:** the energy that KS-DFT adds to the kinetic energy and the classical Coulomb energy to obtain the total electronic energy of an atom, molecule, or material.

**Exchange-correlation functional:** a functional of the spin densities – and, in most cases, of their derivatives and/or of the orbitals and/or their derivatives – that gives the exchange-correlation energy density as a function of an electron's position in an atom, molecule, or material.

**Kohn–Sham density functional theory (KS-DFT):** a theory in which the electron density of a system is represent by a Slater determinant of spin orbitals and the electronic energy is the sum of the kinetic energy of the determinant, the classical Coulomb energy, and the exchange-correlation energy.

**Local functional:** an exchange-correlation functional in which the energy density at a point depends only on local properties at that point, usually on spin densities and their gradients and sometimes also on the kinetic energy density.

but also for the very state-dependent static correlation. One obtains the orbitals of a KS-DFT determinant by self-consistent-field variational calculations and the variational principle sometimes accounts for static correlation (as well as it can) by using a Slater determinant that does not have the same symmetry properties as the exact wave function of that state. For example, even in the absence of spin-orbit coupling, the variationally best Slater determinant for an open-shell system will be spin polarized (sometimes called spin unrestricted or just unrestricted), which means that the spin-up orbitals are not the same as the spin-down ones, and the Slater determinant will not be an eigenfunction of $S^2$ [5]; this is not entirely unexpected since $S^2$ is a not a one-electron property, but it can cause problems in determining whether the KS-DFT calculation has actually approximated the state of interest, and in fact, the state produced by a KS-DFT calculation with presently available functionals for strongly correlated systems is sometimes best interpreted as an approximation to an ensemble of states rather than to a single state.

One way to alleviate the problem with strongly correlated systems is to develop density functional methods that employ a multiconfigurational reference function; a promising approach of this type is multiconfiguration pair DFT (MC-PDFT) [6]. This approach shows great promise and is typically much less computationally demanding than wave function methods of comparable accuracy, but it does raise the cost compared with KS-DFT. This review is therefore restricted to the less-expensive approach based on a single Slater determinant as the reference wave function.

In addition to suffering from the difficulty of treating strongly correlated systems, another important difficulty of the original KS-DFT is self-interaction error. This comes about as follows. A key element of the original KS-DFT method is that the SCF equations for the orbitals involve each electron moving in a **local potential**. The interaction energy with this potential is the **classical Coulomb energy**. In contrast, in the SCF equations of HF theory, the field in which the electrons move is nonlocal because it includes the HF exchange potential, which is an integral operator; that is, at a given point in space, the HF exchange potential involves integration over all space. In both HF theory and KS-DFT, the potential field includes the Coulomb potential, which is the interaction of the electron with the entire electron density of the atom, molecule, or material. That is physically incorrect, because an electron does not interact with itself. In HF theory, the exchange potential cancels the self-interaction part of the Coulomb potential. In KS-DFT this cannot be done exactly because a local potential cannot exactly replace an integral operator. The exchange-correlation potential mimics the exchange potential to some extent (as well as approximating the correlation energy), but the fact that it does not completely cancel self-interaction error is usually considered to be the most important source of error in exchange-correlation functionals, especially for weakly correlated systems.

A specific fundamental source of error in KS-DFT is delocalization, which is sometimes considered to be the same as self-interaction error (because the self-interaction of electrons promotes excessive spreading over multiple centers), but it should probably be considered to be different [7]. Delocalization error can be analyzed in terms of charge delocalization (e.g., in the dissociation of $H_2^+$) and spin delocalization (e.g., in the dissociation of $H_2$) [8]. However, we do not use this kind of analysis in this review.

One strategy to alleviate the self-interaction error is to replace part of the local exchange-correlation functional by nonlocal HF exchange [9–11]. This was originally introduced in an *ad hoc* manner; Parr and Yang call it the Hartree–Fock–Kohn–Sham method [9]. Most often it is now called hybrid KS-DFT. However, the unrealized possibilities of this method are better appreciated by noting that it is a special case of generalized KS (GKS) [12] DFT. In the GKS theory [12], the reference wave function, although still a single Slater determinant, represents the density

**Local potential:** a potential energy function whose value at a point depends only on the identity of that point.
**Self-interaction error:** the error due to an approximate exchange functional not canceling the portion of the classical interaction of an electron with the entire electron density, although part of that density is its own.
**Universal:** being accurate for all possible applications.

of a partially interacting system rather than a noninteracting one. The most common choice of the partial interaction is to put some portion of the two-electron energy of the Slater determinant into the reference system. For example, if we include $X$ percent of the two-electron interaction, the resulting self-consistent-field equations contain $X$ percent of the nonlocal HF exchange, and in fact it is identical to hybrid KS-DFT. One important aspect of the GKS derivation is that it shows that, just as in the original KS-DFT, that there exists in principle an exact exchange-correlation functional; it is different for each choice of interaction included in the reference (e.g., it is different for each $X$). Both HF theory and the original KS-DFT may be considered special cases of GKS theory.

Properties that can be improved with the GKS theory can be as simple as the charge distribution of a molecule [13] and can be as challenging as the excitation energies of molecules [14] and band gaps of solids [15]. In this overview, we focus on our group's work on two kinds of problems: (i) designing new density functionals for ground states that are accurate for both weakly correlated and strongly correlated atoms and molecules; and (ii) designing density functionals that are accurate for both excitation energies of molecules and band gaps of periodic solids.

## Data Used for Evaluation

A key aspect in designing density functionals is the development of broad databases [14,16]. Compilation of accurate data from accurate experimental measurements or high-level quantum mechanical calculations (in the absence of accurate experimental data) is important in testing the accuracy of existing and newly designed density functionals. For widely testing the performance of density functionals, one would like to include data that are disparate and data that are seemingly incongruent; for example, data on: molecular and solid-state properties; ground-state and excited-state properties; various types of excitation energies such as valence, Rydberg, and charge transfer (CT); short-range and long-range CT; SR and MR species; and so on. In our recent work, we put together 56 diverse databases to make Minnesota Database 2019 [14,17]. Minnesota Database 2019 can be broadly divided into subdatabases for ground-state and excited-state properties; see Figure 1 for properties represented in this database. Within ground-state properties, it includes both geometries and energies. The geometric data include transition-state geometries, transition-metal dimer bond lengths, and main-group bond lengths. The energetic data include bond energies, reaction energies, proton affinities, electron affinities, ionization potentials, noncovalent interaction energies, reaction barrier heights, and total atomic energies.

In various tests performed by us and by others, one finds that there are properties that correlate with each other and that there are properties that do not correlate with each other. For instance, the properties that might not correlate with each other could be: (i) properties of the ground state versus those for an excited state; (ii) energies versus geometries; (iii) energies of SR systems versus energies of MR systems; and (iv) atomic versus molecular versus solid-state properties. Therefore, finding a balanced density functional that provides good results for as many properties as possible is a formidable challenge. In the remainder of this review we discuss how well we have been able to achieve this goal with our most recently developed functionals and we discuss which functionals perform best for various properties. Although our discussion here is focused rather tightly on functionals developed at Minnesota, we have presented extensive comparisons to other functionals in the papers where we published new functionals. The reader is also referred to the recent work of Grimme and coworkers in testing a large set of density functionals against main-group [16] and transition-metal [18] databases, as well as the review by Laurent and Jacquemin [19] of tests of DFT for electronic excitation energies.
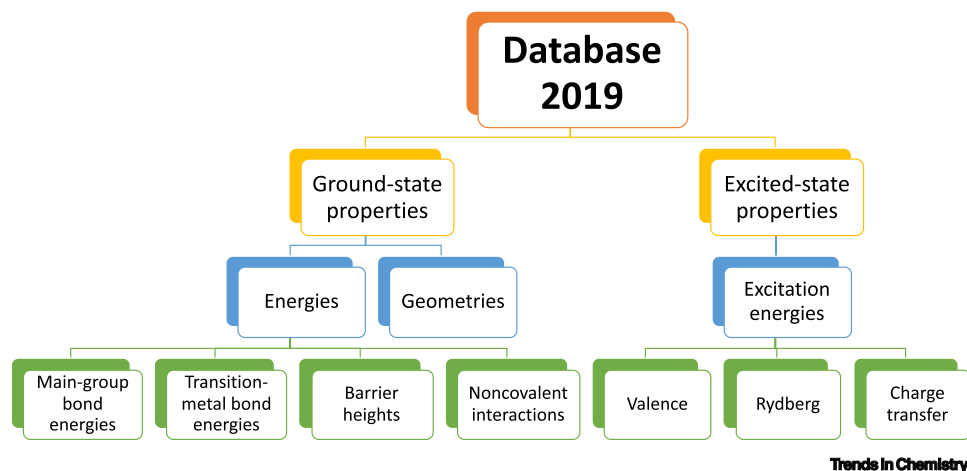
Figure 1. Key Properties Represented by Minnesota Database 2019. The database can be further divided into 56 subdatabases [14].

## Design of New Density Functionals for Ground States

An early forerunner of DFT was the density-based Thomas–Fermi model [20,21]. Decades later, two seminal papers – one by Hohenberg and Kohn in 1964 [22] (that gave us the first and second Hohenberg–Kohn theorems) and another by Kohn and Sham in 1965 [23] – put forth DFT as we now know it. The most widely used formulation of DFT implemented in most quantum chemistry packages and currently used for performing electronic structure calculations is the one by Kohn and Sham [23]. The unknown quantity in KS-DFT is the exchange-correlation functional, and the **exchange-correlation energy** contribution to KS equations can be approximated in more than one way as discussed next.

In what follows, we will often divide exchange-correlation functionals into two classes, local and nonlocal. A **local functional** depending only on the spin densities and their gradients is called a gradient approximation (GA). Functionals depending also on the local kinetic energy density are called meta functionals. Any local functional may be augmented with nonlocal elements, the most common of which are nonlocal HF exchange (which has already been discussed), nonlocal orbital-dependent correlation [24,25], nonlocal density-dependent correlation [26], or so-called rung-3.5 terms [27], which are nonlocal correlation terms that attempt to mimic static correlation.

An exchange-correlation functional that depends only on the local spin densities is called a local-spin-density approximation, which is not accurate enough for most purposes. Adding local gradients of the spin densities leads to a GA, adding local kinetic energy density leads to a meta functional, and adding some percentage of orbital-dependent nonlocal HF exchange leads to a hybrid functional. Examples of GAs are BLYP [28,29] and PBE [30], of meta functionals TPSS [31] and M06-L [32], and of hybrid functionals B3LYP [33], M06 [34], and M06-2X [34].

Based on their percentage (called $X$) of HF exchange, hybrid functionals may be subclassified into various classes; in this review we consider four such classes: global-hybrid functionals in which $X$ is a constant; long-range-corrected (LRC) hybrid functionals in which $X$ depends on the inter-electronic separation and increases to 100% at large separation; Coulomb-attenuated-hybrid functionals in which $X$ increases with interelectronic separation but to less than 100% at large separation; and screened-exchange-hybrid functionals in which $X$ decreases to zero with

increasing interelectronic separation. This review does not include functionals with nonlocal correlation terms other than rung-3.5 terms.

Most (but not all) density functionals have been developed with the developers' eyes on ground-state properties and the functionals were only later tested for molecular excitation energies and solid-state band gaps.

Next we discuss the performance of the following density functionals on the NCCE30/18 [35–42], MR-TMD-BE3 [38,43], DGL6 [35,38], TMDBL10 [44], and TSG48 [45] databases, which are part of Minnesota Database 2019:
- GAs: PBE [30], GAM [38]
- meta approximations: M06-L [32], revM06-L [46], MN15-L [47]
- global-hybrid GA: B3LYP [33]
- global-hybrid meta approximations: PW6B95 [48], M05 [49], M05-2X [50], M06 [34], M06-2X [34], revM06 [51], MN15 [52]
- LRC-hybrid meta approximations: M11 [53], revM11 [14]
- LRC-hybrid meta approximation with rung-3.5 ingredients: M11plus [54].

PBE and B3LYP are chosen based on their popularity and the rest of the density functionals are the ones developed at Minnesota. The databases to be discussed include some of the most challenging ones for ground-state DFT and we will discuss whether the popular functionals or the recent functionals are able to give good accuracy. The two energetic databases – NCCE30/18 and MR-TMD-BE3 – are discussed with all of the 16 functionals above and the three geometric databases – DGL6, TMDBL10, and TSG48 – are discussed with all of the functionals except M11plus.

One big challenge for ground-state properties has been to obtain physically meaningful van der Waals interaction energies for complexes. The first functional to gain widespread use in chemistry was B3LYP, which often incorrectly predicts repulsion where there should be van der Waals attraction. Sometimes this is overcome for practical work by adding attractive molecular mechanics terms to the density functional [55], but this is not necessary with many hybrid meta functionals that predict reasonable amounts of attraction at van der Waals minima [34,50,53]. In Figure 2, the performance of the 16 functionals listed earlier is shown for the noncovalent complexation energies database, NCCE30/18. The NCCE30/18 database comprises 30 organic and inorganic complexes (e.g., water dimer, ammonia dimer, benzene dimer). The largest mean unsigned errors (MUEs) are by the local functional PBE (1.43 kcal/mol) and the global hybrid functional B3LYP (1.25 kcal/mol). Another local functional, GAM, also gives MUE > 1 kcal/mol. Of the remaining 13 density functionals in Figure 2, the best local functional is revM06-L and the best hybrid functional is M11. This figure shows that adding kinetic energy density or HF exchange can improve noncovalent complexation energy, with most of the recent Minnesota functionals giving an error of <0.5 kcal/mol.

Transition-metal chemistry is another application area that can be difficult for DFT [56], especially the treatment of inherently multiconfigurational systems and especially for hybrid functionals. In Figure 3, the error in bond energies of three transition-metal dimers ($V_2$, $Cr_2$, and $Fe_2$) is presented. These three dimers are MR in nature and are grouped into the MR-TMD-BE3 database. The figure shows that this database is particularly difficult for DFT, with some of the density functionals giving an error >100 kcal/mol. The large errors for M05-2X and M06-2X functionals can be attributed to their high percentages of HF exchange: $X = 56\%$ and $54\%$, respectively. Because high $X$ tends to improve many other properties, this presented a challenge: can we obtain a high-$X$ functional that is not so inaccurate for transition-metal chemistry? This challenge has now been met successfully to some extent by the two more recent Minnesota functionals with
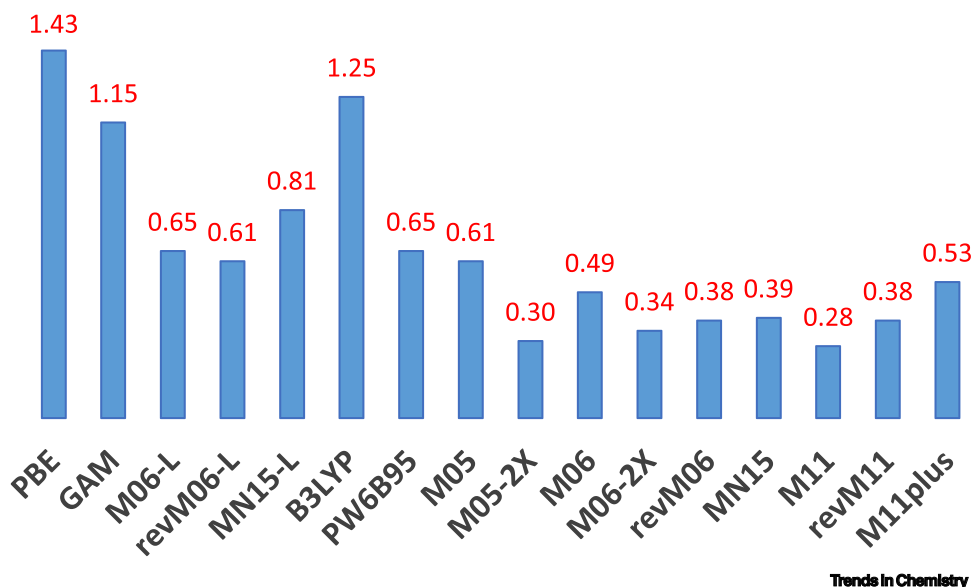
Figure 2. Mean Unsigned Error (MUE) (in kcal/mol) for the NCCE30/18 Database of Noncovalent Complexation Energies Calculated Using 16 Density Functionals.

high $X$; namely MN15 and M11plus, which give much lower MUEs of 23 and 16 kcal/mol, respectively. The MN15 functional has $X = 44\%$ and the M11plus functional also has a high $X$ that varies from 42.8% at short interelectronic distances to 100% at long interelectronic distances. An important feature of the M11plus functional is that it contains rung-3.5 ingredients that help in reducing errors for MR systems. The two parent functionals of M11plus – M11 and revM11 – give large MUEs of 83 and 49 kcal/mol, respectively, which demonstrates the power of rung-3.5 terms. As opposed to the hybrid functionals, the five local functionals (PBE, GAM, M06-L, revM06-L, and
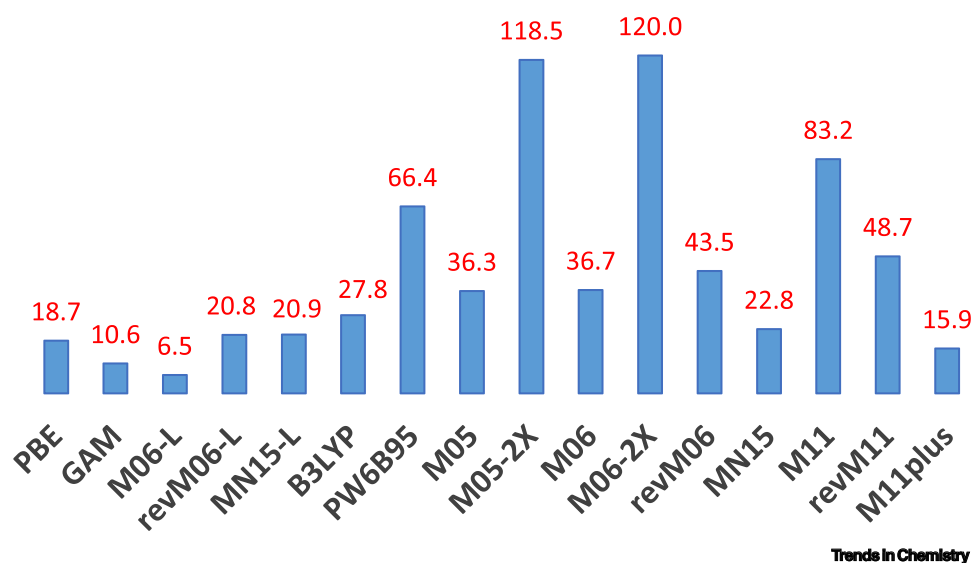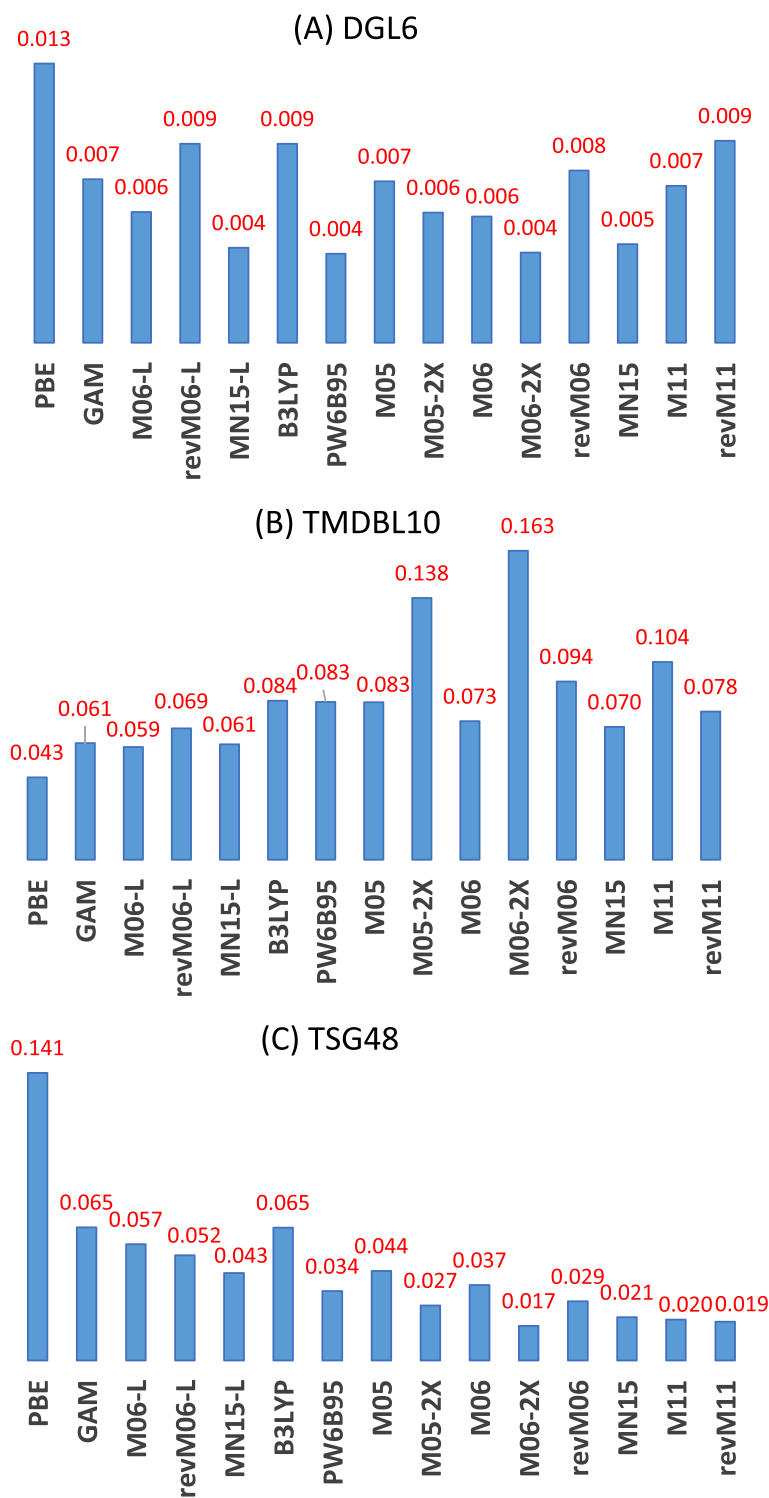


Figure 3. Mean Unsigned Error (MUE) (in kcal/mol) for the MR-TMD-BE3 Database Containing Multireference Transition-Metal Dimer Bond Energies Calculated Using 16 Density Functionals.

Figure 4. Mean Unsigned Error (MUE) (in Å) for Three Geometric Databases Calculated Using 15 Density Functionals. (A) The DGL6 database of diatomic geometries of light-atom molecules; (B) the TMDBL10 database of transition-metal dimer bond lengths; and (C) the TSG48 database of transition state geometrical data.

MN15-L) of Figure 3 give much smaller errors, where the best local functional is M06-L with an MUE of only 6.5 kcal/mol.

Figure 4 presents MUEs for three geometric databases; namely, DGL6, TMDBL10, and TSG48. The DGL6 database comprises bond lengths of $Cl_2$, $H_2$, HF, MgS, $N_2$, and OH; the TMDBL10 database comprises bond lengths of $Ag_2$, $Au_2$, $Cu_2$, $Fe_2$, FeC, $Ir_2$, $Ni_2$, $Os_2$, $Pd_2$, and $Pt_2$; and the TSG48 database comprises 16 transition structure geometries, where for each structure we consider three bond distances. These three databases are very different from each other and the rationale for presenting them is to see how well the 15 density functionals perform on such diverse geometric sets and whether the same functional works well for all three of them.

For the DGL6 database (Figure 4A), the maximum MUE is 0.013 Å due to PBE and the minimum MUE is 0.004 Å due to MN15-L, PW6B95, and M06-2X, the difference between the maximum and minimum being a factor of 3. For the TMDBL10 transition-metal database (Figure 4B), the maximum MUEs are due to M05-2X and M06-2X (0.138 and 0.163 Å, respectively) – the same two functionals that gave maximum errors for the transition-metal bond energy database (MR-TMD-BE3) considered in the previous paragraph. In general, the local functionals predict errors smaller than the hybrid functionals for this database, with the best-performing functional being PBE (MUE = 0.043 Å). Among the hybrid functionals, the best performance is by MN15 that has an MUE of 0.070 Å. It is important to note here that the errors for the TMDBL10 database are higher than those for the DGL6 database, which has main-group diatomics. For the TSG48 database (Figure 4C), the maximum error is due to PBE (MUE = 0.141 Å) and the minimum error is due to M06-2X (MUE = 0.017 Å, a factor of 8 smaller). The hybrid functionals in general give better results than the local functional for these transition-structure geometries.

In the search for a functional that does well on all parts of Figure 4, the only functional among the very best functionals for all three is MN15.

## Design of New Density Functionals for Excited States

Next we turn our attention to excitation energies in molecules and band gaps in solids. In this regard, we can raise several questions. (i) Can we develop better methods to treat molecular spectra with time-dependent density functional theory (TDDFT)? (ii) How well can we treat band gaps in solids in terms of KS orbital energies? (iii) How well can we develop universal functionals that have useful accuracy for both of these properties as well as for chemical properties like noncovalent interaction energies, reaction energies, and barrier heights for chemical reactions?

Another question arises: to what extent is useful accuracy possible only by the cancellation of large errors for individual physical aspects of the problem. This is important because such cancellation of errors may be much more prevalent in some kinds of systems or for some kinds of properties than others, so a method that works by cancellation of errors is not likely to have universal accuracy. Considerable investigation of this problem has occurred in the context of comparing approximate exchange-correlation functionals to known or expected properties of the unknown exact KS functional. However, this is not the only way forward. One may instead think of approximate exchange-correlation functionals as generalized approximations to the self-energy, which does not have some of the limitations of the KS theory. Furthermore, one may study the quality of approximate exchange-correlation functionals by testing their ability against experiment rather than against known or expected properties of the unknown exact KS functional.

One important step forward has been the introduction of orbital-dependent ingredients into the exchange-correlation functionals. The most straightforward examples are functionals incorporating HF exchange and/or kinetic energy density [57,58]. Orbital-dependent functionals are often considered to be *ad hoc* ways to improve the original KS local potentials that were obtained from functionals of the density and/or its derivatives. However, a better justification, as mentioned earlier, is provided by the GKS theory [12,59]. The GKS justification frees the theory from some of the constraints of KS theory and the introduction of new ingredients or functional forms not constrained by the properties of the unknown exact KS functional allows a broader exploration of the possibilities for more universal functionals. For example, the GKS formalism provides a foundation for screened exchange (SX) functionals introduced by Bylander and Kleinman [60] and popularized by Heyd and colleagues [61].

Important approaches used by chemists to study excited-state chemistry and to obtain reference data are coupled-cluster theory or configuration interaction methods with large basis sets [62,63]. The coupled-cluster theory can be extended to excited states either by using the equation-of-motion coupled-cluster methods or by using the linear response theory [62–68]. When high-order excitations are included – for example, connected triple excitations in coupled-cluster theory – these methods can provide accuracy similar to ground-state coupled-cluster theory with similar computational cost; however, they work best in the realm of SR systems or properties. One can also make progress by combining DFT with WFT, as discussed in a recent review article [69], and this is a particularly promising avenue for treating excited states because excited states tend to have MR character. Here, however, we focus on the possibilities for improved density functionals in KS-DFT and GKS theory. Modeling excited states with DFT also poses challenges, but one is relieved of the enormous computational cost associated with obtaining accurate results with either SR or MR WFT methods. Again, the important challenge for DFT is choosing an appropriate density functional for the excitation(s) one is interested in.

Within excited-state properties of molecules, we here consider only excitation energies databases (and not the geometries of the excited states). We evaluate accuracy by comparison with experiment or, when available, with well-converged benchmarks obtained by WFT methods. The excitation energies are calculated with each density functional by either the ΔSCF approach or by linear-response TDDFT. The databases in Minnesota Database 2019 that involve the ΔSCF approach are 3dEE8 [43,70,71], 4dAEE5 [72], and pAEE5 [73], which correspond to excitation energies involving 3d orbitals, 4d transition-metal atomic excitation energies, and p-block atomic excitation energies, respectively. The excitation energies calculated by linear-response TDDFT are subdivided into valence, Rydberg, and CT excitations, with the CT excitations subcategorized into short-to-medium-range and long-range CT. A strong dependence on the percentage of HF exchange is found for excitation energies, which is most pronounced in the case of CT excitations [14].

In solids, the most common way of gauging accuracy for excitations is by calculating band gaps. For plane-wave calculations of band gaps (or any other plane-wave calculations), local functionals are orders-of-magnitude less expensive than hybrid functionals. A tremendous amount of work has been devoted to understanding which, if any, local functionals can predict accurate band gaps for a variety of solids at a reasonable computational cost. Recent benchmark studies [74,75] on large datasets of a variety of solids such as covalent-, ionic-, and van der Waals-bonded solids are available.

One way to obtain improved band gaps has been the development of local functionals employing high local exchange for all regions of the density and interelectronic separation with the motivation that completely local functionals are much less expensive in plane wave codes. Two such functionals were proposed – HLE16 [76] and HLE17 [77] – and they show promise in improving the band gaps of solids and excitation energies of molecules at a computational cost that is very low even for plane-wave periodic calculations. In conventional functionals, the exchange-correlation energy is correct for an infinite uniform electron gas (UEG) with uniform positive and negative charge densities. However, this approximation to the energy is poor for materials and molecules that, unlike a UEG, have finite energy gaps between the occupied and unoccupied orbitals. The HLE attempts to be more realistic for real materials at the cost of being less realistic for a UEG. Although both of these functionals were designed to be nonuniversal but simple, they do have competitive accuracy compared with some popular local functionals for selected properties besides band gaps and molecular excitation energies; for example, chemical reaction barrier heights and noncovalent interaction energies [77]. It is an open question whether one can make this kind of functional more universal while retaining the relatively good accuracy for band gaps. In the rest of this section we focus on more complicated functionals designed with universality as an objective.

For band gaps of solids, we have benchmarked density functionals using the SBG31 [15,78] and the TMOBG4 [79] databases, where the former has solids that are closed shell (with band gaps in the range 0.23–5.48 eV) and the latter has transition-metal oxides that are open shell (with band gaps in the range 2.4–4.2 eV). We have also benchmarked widely used local functionals for complex materials such as metal–organic frameworks, covalent organic frameworks, perovskites, and zeolites [80]. Our tests show that HLE17 is a good compromise between cost and accuracy for these solids.

We have mentioned that hybrid functionals are more expensive in plane wave codes, and this is mainly due to the inclusion of long-range exchange. One can make the hybrid functionals less expensive in plane wave codes by using SX. This is a range-separated exchange in which $X$ decreases to zero at large interelectronic separation. Not only does this lower the cost, it is also theoretically more justified because long-range electron exchange is screened by dielectric effects in condensed media [81]. Figure 5 shows the performance on the SBG31 database using:
- seven local functionals: PBE, GAM, M06-L, MN15-L, revM06-L, HLE16, HLE17
- five SX functionals: HSE06 [82,83], N12-SX [84], MN12-SX [84], HISS [85,86], M06-SX [87].

As expected, the local functionals except HLE16 and HLE17 give large errors for band gaps in the SBG31 database and the hybrid functionals reduce the errors significantly, with all of the five SX functionals giving MUE ≤ 0.4 eV. Among the local functionals, the revised M06-L functional (revM06-L) gives an MUE of only 0.45 eV, which is closer to HLE16 and HLE17 than the other local functionals of Figure 5. This is important because revM06-L is a reasonable choice for a universal functional when one considers both molecular and solid-state properties.

For excitation energies of molecules, we have benchmarked density functionals using the EE23 [36,76,77,88–91] and the LRCTEE9 [92] databases. Both of these databases involve calculations with linear-response TDDFT. The EE23 database comprises 23 vertical excitation energies of which 18 are valence excitations (VEE18), two are Rydberg excitations (REE2), and three are CT excitations (CTEE3). The LRCTEE9 database comprises nine CT excitation energies of the
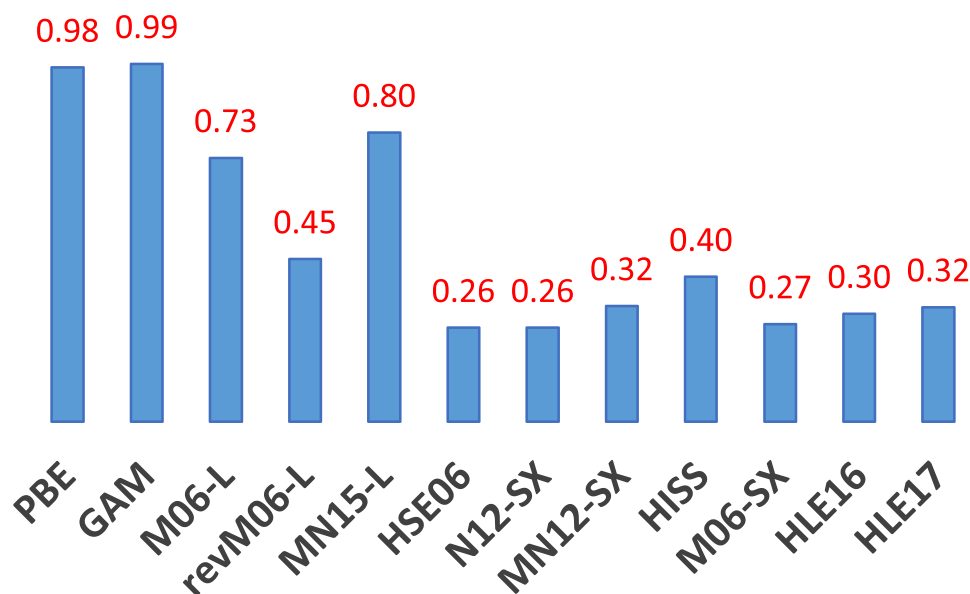
Figure 5. Mean Unsigned Error (MUE) (in eV) of the SBG31 Database of Semiconductor Band Gaps Calculated Using 12 Density Functionals.

$NH_3 \cdots HNO_2$ complex calculated at nine intermonomer distances; we look at the $\pi \rightarrow \pi^*$ $^1A_1$ excitation of this complex at all distances. Figure 6 shows the performance on both these databases using the functionals:

- GA: PBE
- global-hybrid GA: B3LYP
- global-hybrid meta approximations: M06-2X, revM06, MN15
- LRC-hybrid meta approximations: M11, revM11
- LRC-hybrid meta approximation with rung-3.5 ingredients: M11plus
- LRC-hybrid GAs: LC-$\omega$PBE [93], $\omega$B97 [94], $\omega$B97X [94]
- Coulomb-attenuated-hybrid GA: CAM-B3LYP [95].

The functionals, M11, revM11, M11plus, LC-$\omega$PBE, $\omega$B97, $\omega$B97X, and CAM-B3LYP are range-separated hybrid functionals for which the percentage of HF exchange increases with interelectronic separation, and they are well suited to study excitations in molecules.

In Figure 6, the largest error on EE23 is due to the only local functional, PBE, which is an expected result, and the second largest error is due to the global hybrid functional B3LYP. All of the post-B3LYP density functionals give smaller errors. In Figure 6B there is a large variation in MUE with the choice of the functional for the LRCTEE9 database. The functionals with high HF exchange tend to give lower errors for this database. As can be seen from Figure 6B, a number of density functionals give errors of several electronvolts. The best LRC hybrid functional for long-range CT is revM11, which gives an MUE of only 0.39 eV, which is a significant reduction in error from its parent functional, M11, which gives an MUE of 1.08 eV.

## Recommended Density Functionals for Various Types of Properties
In the design of approximate density functionals, one may target a range of properties or a specific property. In this section, we provide recommendations for density functionals developed at

## (A) EE23
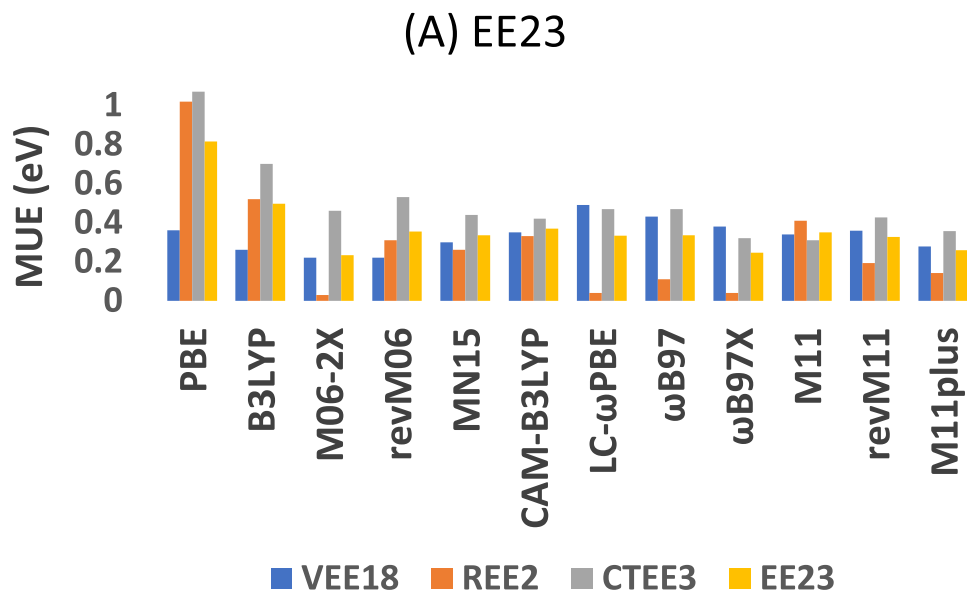


## (B) LRCTEE9
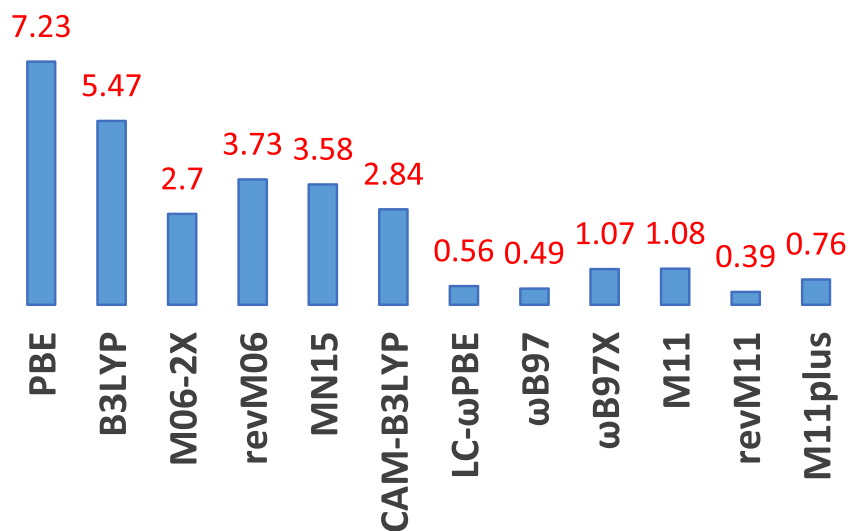


Figure 6. Mean Unsigned Error (MUE) (in eV) for Excitation Energies of Molecules Calculated Using 12 Density Functionals. (A) The EE23 database of molecular excitation energies and its subdatabases: VEE18 of valence excitation energies, REE2 of Rydberg excitation energies, and CTEE3 of charge-transfer excitation energies; and (B) the LRCTEE9 database of excitation energies of long-range charge-transfer complexes.

Minnesota since 2005 for various properties. These recommendations are based on benchmark tests; however, a word of caution needs to apply here: it is hard to estimate the reliability of functionals for applications significantly different from the test data, although we have found that optimization against a broad set of data usually results in good performance for an even broader set of data.

Table 1. Classification of Selected Functionals Developed at Minnesota into General Purpose, Specific Purpose, and with Smoothness Restraints[a]

| Type of functional | Name of approximation |
|---|---|
| General purpose | GA: **GAM**<br>Meta approximations: M06-L, **MN15-L, revM06-L**<br>Global-hybrid GA: SOGGA11-X [97]<br>Global-hybrid meta approximations: M06, **revM06, MN15**<br>SX-hybrid GA: N12-SX<br>LRC-hybrid meta approximations: M11, **revM11**<br>LRC-hybrid meta approximation plus rung-3.5 terms: **M11plus**<br>SX-hybrid meta approximations: MN12-SX, **M06-SX** |
| Specific purpose | GAs: SOGGA [98], HLE16<br>Meta approximation: HLE17<br>Global-hybrid meta approximations: M06-HF, M06-2X, M08-HX, M08-SO |

[a]The functionals in bold incorporate smoothness restraints.

In Table 1, we classify the functionals developed at Minnesota since 2005 [96] into general-purpose functionals (that in principle provide accuracy for a broad set of systems and properties) and specific-purpose functionals (that were designed to provide accuracy for specific properties or a more limited range of systems). The functionals in bold are the ones that were developed incorporating smoothness restraints to aid in better numerical convergence (of SCF iterations and grid sizes for integration of the exchange-correlation energy), but we note that the extent of smoothness being enforced is not the same for all of them. The most recent ones – revM11, M11plus, and M06-SX – have higher values for the smoothness restraint parameter than the

Table 2. Recommended Use of Functionals Developed at Minnesota since 2005

| Property | Highly recommended functionals |
|---|---|
| Ground-state properties | |
| Molecular geometries | PW6B95, M06-L, M11, MN12-SX, MN15, revM06, revM11 |
| Dipole moments | PW6B95, M06-L, M06, GAM, revM06-L, revM06, M06-SX |
| Main-group bond energies | MN15, revM06-L, revM06, M11plus, M06-SX |
| Transition-group bond energies | M06, MN15-L, MN15, M06-SX |
| Main-group isomerization energies | M06, M08-HX, M08-SO, M11, MN15, revM06 |
| Main-group barrier heights | M06-2X, M08-HX, M08-SO, MN15, revM06 |
| Noncovalent interaction energies | M06-2X, M11, MN15, revM06, revM11, M06-SX |
| Ionization potentials | MN15-L, MN15, revM06, M11plus |
| Electron affinities | M08-HX, M11, SOGGA11-X, MN15, revM06, M11plus |
| Proton affinities | PW6B95, M08-HX, M11, MN12-SX, MN15, M06-SX |
| MR systems | MN15-L, MN15, revM06-L, M06-L, M11plus, M06-SX |
| Excited-state properties | |
| Valence excitations | M06-L, M06-2X, N12-SX, MN15, revM06, M11plus, M06-SX |
| Rydberg excitations | M06-2X, MN15, revM06, revM11, M11plus |
| CT excitations | M08-HF, M11, revM11, M11plus |
| Solid-state properties | |
| Lattice constants | SOGGA, N12-SX, MN12-SX, revM06-L |
| Band gaps | N12-SX, MN12-SX, HLE16, HLE17, revM06-L, M06-SX |

older ones. In Table 2, we recommend functionals for various properties based on considering the tests we have done in the papers where our functionals were published.

For many of the properties there are several other functionals almost as good as the ones listed in Table 2, but we limited ourselves to listing just a few for each property. If we consider both ground and excited states, MN15, MN15-L, revM11, M11plus, revM06, and revM06-L all show good progress in one way or another in being simultaneously good for SR and MR systems, and revM06-L will be especially useful if we want to consider a local universal density functional.

## Concluding Remarks

Designing new density functionals is an ongoing process because it still has unmet challenges. It is a quantum nightmare to get all of the properties right at a reasonable computational cost. To take advantage of the opportunities offered by DFT of relatively high accuracy with relatively low computational cost, further work (see Outstanding Questions) will focus on the design both of even more universally accurate density functionals and of density functionals of less universal accuracy but higher accuracy for specific applications. The opportunities for further improvements remain tempting.

### Outstanding Questions

Will further developments involving rung-3.5 ingredients allow better universality by improving the treatment of static correlation without degrading other properties?

Can exchange-correlation functionals be improved for the treatment of spin splitting and magnetic properties?

Can inexpensive exchange-correlation functionals be developed that are simultaneously more accurate for the band structures and lattice constants of solid-state systems?

Can the high accuracy of some exchange-correlation functionals for excitations of valence electrons be extended to core excitations for treating X-ray absorption spectroscopy?

Will multiconfiguration pair-density functional theory, which is powerful for ground-state and excited-state properties of multireference systems, be able to compete with Kohn–Sham density functional theory for treating large systems?

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