CHEMICAL REVIEWS
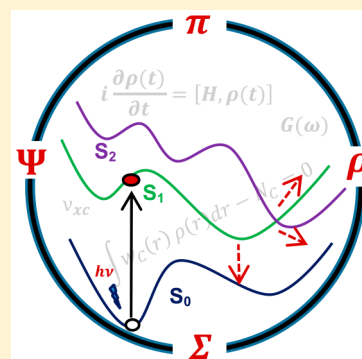
Combining Wave Function Methods with Density Functional Theory for Excited States

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ABSTRACT: We review state-of-the-art electronic structure methods based both on wave function theory (WFT) and density functional theory (DFT). Strengths and limitations of both the wave function and density functional based approaches are discussed, and modern attempts to combine these two methods are presented. The challenges in modeling excited-state chemistry using both single-reference and multireference methods are described. Topics covered include background, combining density functional theory with single-configuration wave function theory, generalized Kohn−Sham (KS) theory, global hybrids, range-separated hybrids, local hybrids, using KS orbitals in many-body theory (including calculations of the self-energy and the GW approximation), Bethe−Salpeter equation, algorithms to accelerate GW calculations, combining DFT with multiconfigurational WFT, orbital-dependent correlation functionals based on multiconfigurational WFT, building multiconfigurational wave functions from KS configurations, adding correlation functionals to multiconfiguration self-consistent-field (MCSCF) energies, combining DFT with configuration-interaction singles by means of time-dependent DFT, using range separation to combine DFT with MCSCF, embedding multiconfigurational WFT in DFT, and multiconfiguration pair-density functional theory.

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1. INTRODUCTION

The Born–Oppenheimer approximation simplifies the solution to the Schrödinger equation[1] by separating the nuclear and electronic motions, but even after this simplification, the electronic Schrödinger equation remains unsolvable for many-electron systems. Because electronic structure is the key to understanding many chemical problems, a variety of approximation techniques have been proposed. For a long time, these approximations were mainly based directly on the Schrödinger equation, and this may be called wave mechanics or wave function theory (WFT). Slower to emerge as a powerful electronic structure method (although it has roots in the early days of quantum theory) was another approach, this one based on electron density rather than electronic wave functions. The second approach is called density functional theory (DFT),[2,3] the most popular version of which is based on the Kohn–Sham (KS) equation. Owing to having more favorable scaling of demand on computational resources with respect to system size, DFT eventually became the most common method for large and complex systems with accuracy for many cases comparable to or better than (affordable) WFT approximations. However, approximate DFT suffers from some generic problems, many of which can be traced to so-called delocalization error[4] (or the closely related problem of self-interaction error). This has motivated many workers to seek hybridized theories that combine the best of both approaches. The present review is about methods that combine WFT and DFT to treat electronic excitation.

A key issue in all electronic structure theories is electron correlation. Electron correlation refers to the situation that the probability of simultaneously finding electron 1 at point $\mathbf{r}_1$ in coordinate space and electron 2 at point $\mathbf{r}_2$ is not simply the probability of finding electron 1 at $\mathbf{r}_1$ times the probability of finding electron 2 at $\mathbf{r}_2$; i.e., the motion of the electrons is correlated. Fully including electron correlation has a huge effect on calculated energies, and it is a bottleneck to high accuracy in WFT. As we shall see, DFT is challenged not only by the treatment of electron correlation but also by the treatment of electron exchange. But DFT is computationally less expensive than WFT, so WFT researchers are motivated to take advantage of the successful aspects of DFT to make WFT more efficient. For small enough systems, WFT can be made more accurate than DFT by increasing the level, so DFT researchers are motivated to incorporate systematic WFT procedures into DFT to improve the treatment of exchange and correlation.

A second key issue is electron density. Note that when we refer to the "density" with no qualifiers, we mean the total electron probability density $\rho(\mathbf{r})$ as a function of coordinate position $\mathbf{r}$ in real space (three-dimensional space). This is also sometimes called the single-particle density to distinguish it from the two-particle density $\rho(\mathbf{r},\mathbf{r}')$ that gives the probability density of simultaneously finding one electron at $\mathbf{r}$ and another at $\mathbf{r}'$. In the absence of antisymmetry and electron correlation, one would have $\rho(\mathbf{r},\mathbf{r}')$ equal to $\rho(\mathbf{r})\rho(\mathbf{r}')$. The most convenient property of KS-DFT is that it is built on $\rho(\mathbf{r})$ and does not require $\rho(\mathbf{r},\mathbf{r}')$, whereas in WFT, the need to calculate electron correlation is the bottleneck to accuracy and computational speed.

DFT, WFT, and the combined DFT and WFT methods have now attained useful accuracy for both ground- and excited-state properties, but progress has been greater for treating ground electronic states than for treating excited electronic states, and we will summarize some of the challenges in treating excited states in section 1.4. First, however, we present some background and language that may be helpful for readers of the review.

1.1. General Background

One of the earliest WFT approximation methods to be developed was Hartree–Fock (HF) theory,[5,6] in which the electronic wave function of the system is represented by a single Slater determinant, and every electron is considered to be moving in an average field of all the other electrons and the nuclei; this is an example of a mean-field approximation. The wave functions of the individual electrons are called orbitals. Because the mean field in which each electron moves depends on the orbitals of all of the other electrons, the solution to the Schrödinger equation must be found by iterating a trial solution to self-consistency, and the field in which the electrons move is called the self-consistent field (SCF). The HF approximation thus transforms the many-body Schrödinger equation into many coupled single-particle equations. The solutions for atoms and molecules are called atomic orbitals (AOs) and molecular orbitals (MOs), respectively, although the term AO is also often used for atom-centered one-electron basis functions. In 1951, Roothaan presented convenient equations for solving the HF equations variationally by representing MOs as a linear combination of atomic orbitals (LCAO),[7] i.e., a linear combination of atomic basis functions. The HF theory showed some success;[8] however, it does not describe electron correlation beyond the minimum required to satisfy the antisymmetry requirement for electronic wave functions, and the resulting approximate electronic energies are not accurate enough for most practical applications in chemistry. Electron correlation arises from the correlated movement of electrons, and the failure of HF theory to describe it properly originates from the inadequacy of its mean-field approximation to treat electron–electron interactions properly.[9]

In electronic structure theory, a configuration is a specific way to assign electrons to orbitals or sometimes to spin-orbitals. A configuration state function (CSF) is a many-electron trial wave function corresponding to a single configuration that has a definite spin symmetry, and sometimes it is also constrained to have a desired point group symmetry.[10] An HF calculation consists in the variational optimization of the orbitals of a single CSF; in the case of a closed-shell singlet (and some, but not all, open-shell cases), this would be a single Slater determinant. To include electron correlation (beyond that due to antisymmetry) in WFT, one must consider a superposition of CSFs. A multiconfigurational wave function is a wave function that is a linear combination of two or more CSFs. Standard multiconfigurational approaches are the configuration interaction

(CI) method, perturbation theory (PT, e.g., Møller−Plesset second-order perturbation theory, MP2[11]), and coupled cluster (CC)[12] methods, each of which has many variants, for example, algebraic-diagrammatic construction[13] (ADC) is a variant of CI or the approximate coupled cluster linear-response model[14] called CC3. One widely applied WFT method for calculating electronically excited states is equation-of-motion (EOM) coupled cluster theory, which is equivalent to linear response theory applied to a CC wave function.[15]

Correlation effects often can be divided into two types of interactions:[16] (i) static correlation, also called nondynamic correlation or left−right correlation,[17,18] and (ii) dynamic correlation, also called dynamical correlation. Although it is practically impossible to differentiate these kinds of correlations in a quantitative way, their origin is different in nature.[19] Static correlation arises from the near degeneracy of several configurations. In such cases, e.g., the singlet ground state of dissociated H_2, a single Slater determinant is inadequate to represent the wave function of the system accurately (although it can represent the density). Dynamic correlation on the other hand is due to the tendency of electrons to avoid one another at short distances to minimize repulsion or due to their correlated motion at longer distances leading to dispersion and dispersion-like forces. The simplest way to include electron correlation is the CI approach.[20−26] In CI methods, the wave function is represented by a linear combination of CSFs, and their coefficients are linear variational parameters optimized by minimizing the total electronic energy. The CSFs are written in terms of one-electron basis functions (also called the orbital basis); variationally optimizing the coefficients of all possible configurations for a given orbital basis leads to full CI (FCI), and full CI for a complete orbital basis (usually called a complete basis set or CBS) is a numerically exact solution of the electronic Schrödinger equation, which is called complete CI (CCI). While CCI corresponds to an exact solution of the electronic Schrödinger equation, it cannot be practically achieved for any but the tiniest of chemical systems. (note that CC calculations also include all CSFs that can be formed from a given orbital basis, but the coefficients of the CSFs are not independently optimized unless one includes all excitations up to the *N*-tuple level for an *N*-electron system. Because the coefficients are different, truncated CC is not equivalent to FCI[27]).

The CI approach not only includes electron correlation in the minimized energy of the ground state, it also extends HF theory to excited states. This is useful because in general one cannot converge self-consistent calculations for excited states of the same symmetry as the ground state. More specifically, excited-state SCF solutions *can* be found by imposing constraints of spin or spatial symmetry if the excited state has a different space and/or spin symmetry than all lower-energy states or by imposing orthogonality constraints, and in favorable instances one may achieve fortuitous convergence with a well-chosen initial guess, but there is no *generally* applicable method of preventing the SCF process from converging to the ground state or to a broken-symmetry solution including the ground state as one of its components. In a CI calculation, though, each eigenvalue of the variational secular equation corresponds to a physical state of the system, and the corresponding eigenvector is orthogonal to the eigenvectors corresponding to approximations to the lower- (and higher-) energy roots.

Although static correlation can be recovered just by including only the degenerate and near-degenerate configurations in the CI expansion, dynamic correlation converges very slowly with

respect to the number of configurations. Furthermore, the cost of the calculation increases rapidly with the number of independently varied CSF coefficients. This is true not just for CI calculations but also for PT and CC calculations. For this reason, performing a WFT calculation with chemical accuracy for complex or large systems is usually impractical, if not impossible (although there has been dramatic recent progress in speeding up single-reference coupled-cluster calculations using schemes that take advantage of the shorter-range character of dynamic correlation[28−31]). This is the main disadvantage of WFT, and DFT attempts to overcome it.

Although DFT has a history almost as old as the Schrödinger equation, the modern form dates back to the paper by Hohenberg and Kohn[32] in 1964 and the extension by Levy in 1979.[33] The theory is usually applied in the form suggested by Kohn and Sham[2] in 1965. In Kohn−Sham density functional theory (KS-DFT), as in HF theory, electrons are treated as formally independent particles in the mean field of all other electrons, but electron correlation is now included by virtue of an extra energy term calculated as a functional of the density called the exchange-correlation (XC) functional. Kohn and Sham calculated the kinetic energy and the classical Coulomb energy from a Slater determinant and approximated the rest of the energy (correction to the kinetic energy, entire exchange energy, and entire correlation energy) by a density functional. KS-DFT would be an exact theory if one used an exact XC functional, but an exact functional is unknown and probably unknowable[34] (note that the classical Coulomb energy depends only on the density and for an atom or molecule in a field-free environment, it equals the sum of the attractive electron interactions with the nucleus or nuclei and the repulsive electron−electron interactions, with the latter calculated by classical electrostatics). Many approximate XC functionals have been proposed. In spite of the less expensive nature of KS-DFT compared to most of the wave function based methods, it is still a single-configuration theory. Thus, even though density functionals are very efficient in recovering dynamic correlation energy for many systems and they can also recover some static correlation energy (one might prefer to say that they avoid some static correlation error), they are unable to treat near degeneracies in a system in a natural way.[35−40] Furthermore, they require time-dependent methods for practical calculations on excited states.

Limitations of both the wave function and DFT based approaches were realized very early, and there has always been interest in combining the two kinds of methods.

1.2. Language

Density functional theory is widely used in both chemistry and physics. As a result, there are many concepts and methods that have more than one name. A simple example is self-consistent field theory, also called mean-field theory. These terms are often used interchangeably. There are some contexts where workers might recognize one language as more general, that A is a special case of B, or B is a special case of A, but we use the words interchangeably. However, in density functional theory, there is a subtlety that does not occur in most other usage of the term, namely that "mean-field theory" is often interpreted as "mean-field approximation," but DFT is in principle exact. So one should not misinterpret "mean-field theory" as "mean-field approximation."

Two names for the same thing is one problem, and a related problem is two meanings for the same term. We have already

seen an example of this with the two different meanings of atomic orbitals.

Another notational issue with multiple names for the same thing is the division of SCF calculations into spin-restricted (a single set of spatial orbitals is used for both α and β spins) calculations and spin-unrestricted (different spatial orbitals for different spins) calculations. Spin-restricted is often just called restricted and is sometimes divided into closed-shell and restricted open-shell. Spin-unrestricted is often called spin-polarized and often shortened to just "unrestricted."

A more complicated situation is the already mentioned division of correlation energy into static and dynamic components. Some systems are said to have only dynamic correlation, while systems with significant static correlation are sometimes called strongly correlated or inherently multi-configurational. Methods that use a multiconfigurational reference state as a preliminary stage are often called multireference methods. Examples of strongly correlated systems are systems with di- or polyradicaloid character, including highly stretched bonds and antiferromagnetically coupled magnetic centers, and, significantly for the present review, most electronically excited states involving excitation to valence-like orbitals. Systems that require a multireference treatment for high accuracy in the absence of including higher-order excitations like quadruple excitations are variously called inherently multiconfigurational systems, multireference systems, or strongly correlated systems. Then systems that do not require such a treatment, i.e., systems with negligible static correlation energy are called single-reference systems. Strong static correlation is usually caused by a near-degeneracy condition, but the borderline between static and dynamic correlation is fuzzy.

A similar division of correlation energy is into internal and external.[41] This is similar but worth distinguishing. If one uses a multiconfigurational SCF calculation to capture the major static correlation, it inevitably also captures some dynamic correlation. The part of the correlation captured by such a calculation is called the internal correlation, and the rest of the dynamic correlation is called the external correlation.

A more complicated language issue is provided by the term random phase approximation (RPA), which sometimes seems to refer to more than one method, some of which can be shown to be identical (even though they look different or are arrived at by different routes) and some of which are actually different. Many chemists use "RPA with exchange" to refer to the time-dependent Hartree–Fock method for calculating excited states,[42,43] whereas its historical roots[44] identify it as an approximation to the correlation energy such that it can be used to approximate the correlation functional in DFT.[45−47] The best attempt we know of to explain the connections and the historical context is a review by Ren et al.,[48] which we will not recapitulate here.

Another case of multiple names is a set of systems variously called uniform electron gas, homogeneous electron gas, free electron gas, and jellium. These terms all refer to the same kind of system, namely a mathematical (or "toy") system with electron density the same everywhere in space, which requires a uniform background of positive charge (although such a system does not much resemble any chemical system, analytical results obtained for the uniform electron gas have played an important historical role in the development of DFT[49]).

Another language issue concerns XC functionals. All available XC functionals are approximate, and some authors would prefer that one refers to them as density functional approximations or approximate XC functionals, but we will follow the common convention of simply calling them XC functionals or density functionals without reminding the reader every time that they are only approximations to the unknown exact XC functional.

In the literature, "spin density" sometimes means $\rho_\alpha - \rho_\beta$, but in DFT, it is conventional to call that the spin density polarization or the net spin density and to call ρ_α and ρ_β the spin densities; we follow the latter conventions here. Some density functionals depend only on the local density or the local spin densities and are called a local density approximation (LDA) or a local spin density approximation (LSDA).[2,50] Other functionals depend also on other local properties like local gradients of the spin densities or local spin-specific kinetic energy densities. Two popular examples that depend on the gradients of the spin densities are BLYP (which combines Becke-88 exchange[51] and Lee–Yang–Parr (LYP) correlation[52]) and PBE (an exchange-correlation functional by Perdew, Burke, and Ernzerhof[53]); an example of a functional that also depends on the local spin-specific kinetic energy densities is M06-L.[54] These and other functionals are often generically referred to as "local" in the chemical literature, but one must be careful to distinguish local approximations from the special subset case of local-density approximations. Physicists and some chemists often label local functionals that are not LDAs or LSDAs as semilocal, but we will not use that term. Functionals in which the local energy density depends on more than just local properties are called nonlocal, and there are many types, including hybrid, doubly hybrid, and van-der-Waals-type; these are explained in later sections.

An important term in the energy expression in DFT is the classical electrostatic energy of the electronic charge density ρ. The complete classical electrostatic energy includes electron–electron, electron–nucleus, and nucleus–nucleus terms, but here we focus on the electron–electron part. In classical electrostatics, the charge density is coarse-grained such that the discrete nature of the charges making up the charge distribution is irrelevant, and there is no correction for the fact that letting the entire ρ interact with itself includes a small part due to the interaction of a given electron with itself, but at the atomic scale the fact that an electron does not interact with itself becomes very significant.

A simple product of one-electron spin orbitals is called a Hartree product, and the electron–electron part of the classical electrostatic energy of a Hartree product is called the Hartree energy or the Coulomb energy. Antisymmetrizing a Hartree product yields a Slater determinant, and the WFT expectation value of the energy of a Slater determinant involves the kinetic energy, the electron–nucleus interaction, the Hartree energy, and a term that cancels the interaction of each electron with itself; this latter term is called the exchange energy. Exchange energy is not a physical observable. Therefore, although exchange energy has a clear meaning in HF theory in which a single Slater determinant is used, exchange energy for a multiconfigurational wave function is not well-defined, and the precise definition of the exchange energy in DFT is arbitrary.[55] We and many others use the term "Hartree–Fock exchange energy" to denote the energy computed by applying the Hartree–Fock energy expression to any Slater determinant, for example, the Kohn–Sham determinant, even though that gives a different result than applying that energy expression to a Hartree–Fock wave function (it might be less confusing to say "Fock exchange" than to say "Hartree–Fock exchange" in this

context, and a few workers use that language; however, we use the more common term "Hartree—Fock exchange"). In the context of KS-DFT, some workers prefer to call this exact exchange, but it cannot be exact for real systems because a single Slater determinant cannot be exact for a system with interacting electrons.

Yet another ambiguous term is "Kohn—Sham theory" itself. The theme of this review is the combination of DFT with WFT. The most common example of this is sometimes called hybrid DFT in which one combines the original version of KS theory involving local potentials and explicit local functionals of the density with HF exchange potentials, which are nonlocal. It is very common in the literature to refer to hybrid Kohn—Sham theory simply as Kohn—Sham theory. From another point of view though, at least for the usual way of solving the equations for hybrid Kohn—Sham theory or any variation of Kohn—Sham theory that involves orbital-dependent functionals (such as meta functionals that depend on local kinetic energy density), such theories have a different justification called generalized Kohn—Sham theory.[56] We will say more about this in section 2, but here it is useful to point out that we will often follow the common convention by which "Kohn—Sham theory" (KS theory or KS-DFT) includes both the original theory and the generalized Kohn—Sham theory.

Some other language and methodological concepts are so pervasive in this review that it is useful to get a set of related definitions established at the very beginning. Consider for example the phrase "orbital-dependent" used in the previous paragraph. In the DFT literature, this refers to a functional that depends on the orbitals, but depending on the density (which in KS-DFT is the sum of the squares of the occupied orbitals) or its derivatives does not count as orbital dependent, nor does the dependence of the KS kinetic energy (the so-called non-interacting kinetic energy, sometimes denoted T_S) on the orbitals count as orbital dependence in this language. However, a similar sounding phrase "orbital-free DFT" is used to refer to versions of DFT that do not involve orbitals at all,[57] not even the noninteracting kinetic energy. The present review does not include orbital-free DFT.

1.3. Introduction to MCSCF and Multireference Methods

A more advanced SCF method that will be prominent in this review is the multiconfiguration self-consistent field (MCSCF) method, which is also (especially in the older literature) sometimes called multiconfiguration Hartree—Fock. In such a calculation, the trial wave function is a linear combination of CSFs, and one optimizes the linear parameters (the CI coefficients mentioned earlier) as well as the orbitals. There are many special cases, corresponding to different choices of which configurations to include: complete-active-space SCF[58] (CASSCF), which is also called the fully optimized reaction space (FORS) method,[59] restricted active space SCF[60,61] (RASSCF), generalized active space SCF[62,63] (GASSCF), occupation-restricted multiple active space[64–66] (ORMAS), generalized valence bond[67] (GVB), separated pair (SP) approximation,[68] etc. The CASSCF method divides the orbitals into orbitals that are doubly occupied in all CSFs (these may be called inactive orbitals), active orbitals, and virtual orbitals. The virtual orbitals are unoccupied in all CSFs. One also specifies a given number of active electrons, and one performs FCI of the active electrons in the active orbitals. In RASSCF, one divides the active space orbitals into three subspaces called RAS1, RAS2, and RAS3. One performs full CI of a given number of active

electrons in the RAS2 orbitals, and one also includes configurations involving a restricted number of holes in RAS1 and a restricted number of electrons in RAS3. The methods discussed so far in this paragraph are referred to as MCSCF methods. There are also non-SCF variations, for example, CASCI and RASCI, in which the configuration lists are put together the same way as in CASSCF or RASSCF, but the orbitals are not self-consistently optimized for this configuration list; rather, the orbitals are optimized with a HF theory, by an MCSCF calculation with a smaller active space, or even by DFT.

A critical issue is the choice of the active space, which involves specification of how many active electrons, how many active orbitals, and, for a given number of active orbitals, *which* orbitals are active. A second critical issue is which configurations to include. In CASSCF, one includes all CSFs that can be obtained by distributing the active electrons in active orbitals in all possible ways (full CI in the active space). One can select the active orbitals on a case-by-case basis or by using certain systematic schemes, for example, the full valence CAS scheme[59,69] or one of the correlated participating orbitals schemes.[70–76] In RASSCF, GASSCF, and ORMAS, one does not include all the CSFs that can be formed in the active space; rather, one eliminates the "deadwood" (CSFs that do not contribute significantly). In GASSCF, one does this by dividing the active space into subspaces, and there are various ways to partition subspaces, e.g., various kinds of frontier orbital partitioning.

Often the MCSCF calculation is just stage 1 of a two-stage calculation. The second stage, sometimes called the post-MCSCF stage, is very important because one cannot usually obtain quantitative accuracy unless one includes external correlation. A common wave function approach is to build on an MCSCF wave function by second-order perturbation theory (PT2), which is sometimes called multireference-PT2 (MRPT2) or MRMP2;[77] when building on a CASSCF space, it may be called CASPT2,[78,79] and when building on a RASSCF calculation, it may be called RASPT2. This is a separate stage after the SCF calculation, and one often calls it a post-SCF step for this reason. The first stage, i.e., the SCF stage, of such a calculation is often called the diagonalization step, and MRPT2 methods are sometimes called "diagonalize, then perturb" methods. A more central topic in this review will be combining MCSCF with DFT, either intimately as a single-stage calculation or post-SCF as a two-stage calculation.

In "standard" MCSCF or CASSCF, one variationally optimizes a single state, which may be the ground state or an excited state. To get a more balanced treatment of several states, one may optimize the orbitals and CI coefficients to minimize the average energy of a set of states; this is called state-averaged MCSCF[80] (SA-MCSCF, for example, SA-CASSCF, SA-GASSCF, etc.). In WFT, one often builds on this by a perturbation calculation that considers several states at once. This too has various names including multiconfiguration quasidegenerate perturbation theory (MC-QDPT)[81] and multi-state CASPT2 (MS-CASPT2).[82] Such a calculation uses perturbation theory to build a nondiagonal CI Hamiltonian in a subspace of the full CSF space; this subspace is called the model space, and this approach is sometimes called a "perturb, then diagonalize" approach. Such an approach is necessary for treating closely coupled excited states.

Another multireference method to treat a spectrum of excited states is multireference configuration interaction with single and double excitations (MRCISD) in which one builds CSFs from

MCSCF orbitals and includes all single and double excitations out of the MCSCF reference state in a large CI calculation.[83−89] This is more expensive than MS-CASPT2 but not necessarily more accurate because it is not size extensive.

1.4. Challenges in Modeling Excited States

The first challenge in modeling excited-state chemistry is that almost all excited states are open-shell states, and those involving excitation to valence-like orbitals are usually inherently multi-configurational.

The second challenge comes from the difficulty of converging an SCF solution to an excited state, as has already been discussed. When one can converge an SCF solution for an excited state, the difference of its energy from the ground-state SCF energy is usually called the ΔSCF approximation.[90−94]

The best general methods for overcoming these first two challenges in WFT are the SA-MCSCF methods, as defined above. The CI step in these methods provides a direct extension to excited states, while HF and KS-DFT can be extended to excited states by using time-dependent formalisms like time-dependent HF (TD-HF) and time-dependent DFT (TDDFT).[95−98] In TD-HF and TDDFT, one identifies the excited states as the poles of the linear-response frequency-dependent generalized polarizability of the ground state.

The third challenge is that a suitable method for excited states should describe not only the vertical excitation spectra but also adiabatic transitions and emission spectra. For photochemistry applications, it is not enough for a method to be accurate at a certain point on the potential energy surface, it has to be accurate for the entire excited-state potential energy surface as well. Even though conventional XC functionals show good accuracy for ground-state equilibrium structures of most chemical systems, their accuracy for entire excited-state potential energy surfaces can be questionable. Indeed, in parts of the ground-state potential energy surface where near degeneracies of states are more prominent, unrestricted KS-DFT converges to broken symmetry solutions that are often highly spin contaminated. Excited-state calculations on top of these highly spin contaminated ground states do not always produce meaningful results.

A fourth challenge comes from the fact that a universally accurate method for excited states would have to be accurate for all classes of excitations. We often classify electronic excitations into three ideal cases: (i) valence excitations that involve localized orbitals and do not have especially large effects on local moments of the charge distribution, (ii) Rydberg excitations that involve transition from localized to diffuse orbitals, and (iii) charge-transfer excitations in which net charges in different parts of the system change to a significant degree. In the prior definitions, "significant" is, of course, a subjective term, and some excitations are not readily assigned to a single category. Nevertheless, an ideal electronic structure method designed for excited states should be accurate for all these types of excitations as well as for excitations that are a mixture of these ideal cases. If we look at the performance of density functionals for these excitations, it is well-known that local density functionals underestimate excitation energies that involve transitions between two orbitals having very small spatial overlap[99] because they do not produce the correct asymptotic behavior of the effective potential.[100−103] Approaches based on CI do not suffer from such problems. However, the underestimation of dynamic electron correlation in truncated-CI methods with a small number of CSFs means that one does not obtain quantitatively

accurate results. As dynamic correlation has different stabilizing effects on different types of excitations, even the relative ordering of the excited states produced by small CI calculations can be wrong.

Modeling conical intersections poses another important challenge in the study of excited states, and it occurs commonly when a large part of the potential energy surface is studied including multiple excited states. Conical intersections are the points of a potential energy surface where two electronic states are exactly degenerate. The single-reference KS-DFT has had mixed success in producing accurate potential energy surfaces in regions near conical intersections,[104−106] and among multi-reference methods, state average (SA)-CASSCF is one of the most widely used methods for conical intersection studies.[107−113] However, the missing dynamic correlation in SA-CASSCF can often provide wrong conical intersections as well as wrong geometries at the conical intersection.

So far, of the quantum mechanical tools available, on many occasions multistate complete active space second-order perturbation theory (MS-CASPT2) is considered to be the most accurate method for studying excited-state properties. It not only produces a correct wave function (i.e., one of proper spin and possibly spatial symmetry) using CASSCF as a starting point, but it also recovers some remaining dynamic correlation using perturbation theory. However, expensive methods like MS-CASPT2 (or CASPT2) are (at least with conventional techniques) only applicable to small systems and only small regions of excited-state potential energy surfaces can be studied. Moreover, MS-CASPT2 analytical gradients are available only in a few packages.[114]

In light of the challenges mentioned above and the limitations of the existing methods in qualitatively and quantitatively modeling excited-state chemistry, this chemistry becomes an ideal area to successfully combine WFT and DFT methods to exploit the best features of both the methods. By using a multideterminant wave function obtained from a WFT calculation, the excited and ground states can be represented with correct spin and spatial symmetry, and by using an appropriate density functional, the missing dynamic electron correlation can be recovered in an efficient manner. There exist several ways of combining WFT and DFT in the literature, and the various choices made for the WFT and DFT methods and their application to excited states are the focus of the present review.

2. MINGLING DFT WITH WFT: AN OVERVIEW

As described in the previous section, besides having their own limitations, both single-configuration methods (i.e., KS-DFT and HF) and multireference methods can be separately useful for selected properties, and this was a key motivation early on for exploring combinations of the two to see if a hybrid approach might fix the limitations of either or both without degrading their utility where already useful. One particularly straightforward way to accomplish this is to add a correlation potential to a HF wave function, and this was shown in 1983 to give an improved treatment of electron affinities of atoms.[115] Another simple idea is to employ KS orbitals for the evaluation of WFT operators. While a single KS determinant must have a higher energy expectation value than the variationally optimized single HF determinant, the use of the KS orbitals to evaluate expectation values employed in the computation of *post*-HF energies may lead to improved results, including for excited-state energies,[116] as elaborated in much greater detail below.

In many cases, KS-DFT and HF theory have opposite errors; for just one example, KS-DFT often underestimates chemical reaction barrier heights and HF theory often overestimates them. This led some workers to ask whether some combination of the two methods might be better. Becke,[117] for example, on the basis of a two-point quadrature of the adiabatic connection formula[46,47,118] of KS-DFT, argues that a 50:50 mixture of local exchange (also referred to as density functional exchange) and HF exchange would be appropriate when combined with a local density approximation for electron correlation. Becke built on previous use of the adiabatic connection,[119] where it was proved that the adiabatic connection integrand is essentially linear for a small coupling constant and is exactly linear as the coupling constant approaches zero. Becke took it further and assumed linearity from zero to unity. From this point of view, one is obtaining a more accurate approximation to the unknown exact KS XC functional by combining density functional local exchange, HF nonlocal exchange, and density functional local correlation.[117,120]

An alternative point of view was provided by Levy and co-workers,[56,121] who formulated generalized Kohn−Sham (GKS) theory. Kohn−Sham theory maps the Born−Oppenheimer electronic wave function of a system to that of a noninteracting system described by a Slater determinant. GKS theory maps the Born−Oppenheimer electronic wave function of a system to that of an interacting system described by a Slater determinant.[56,121] In both KS and GKS theories, the electronic energy is written as the energy of the model system (computed from the orbitals of the Slater determinant) and a remainder. In KS theory, because the model system is noninteracting, the model system energy is just the kinetic energy of the Slater determinant. The remainder may be written as the sum of the classical electrostatic energy (both electron−electron and electron−nucleus interactions computed classically from the electronic density) and an XC functional that accounts for everything else. In GKS theory, the model energy can be assigned in a very flexible fashion. For example, it may be the fully interacting energy of the Slater determinant (by which we mean the energy computed with the HF energy expression, even though the orbitals do not minimize the energy of this expression), or it could be a $(100 - X):X$ mixture of the noninteracting model energy and the energy of a fully interacting system described by a Slater determinant (which is not the same as the fully interacting real system, which is multiconfigurational). The $(100 - X):X$ model leads to and justifies the equations for hybrid Kohn−Sham theory with a percentage X of HF exchange. But more importantly, as emphasized and clearly explained by Korzdorfer, Kümmel, Kronik, and others,[122−125] it leads to a different interpretation of hybrid Kohn−Sham theory. For example, each choice of model potential has its own exact density functional. We never use an exact density functional (because nobody knows one), but it is usually viewed as an important justification for Kohn−Sham theory that an exact functional can be proven to exist. From this point of view, it is equally important to recognize that the exact functional is different for different choices of the model potential; thus, for example, different hybrid approximations are approximations to different exact functionals.

In GKS theory, HF exchange is treated as a nonlocal operator in solving the KS equations, which then become coupled integrodifferential equations rather than coupled differential equations. Furthermore, the multiplicative local potentials derived by functional derivatives of the XC energy with respect to the density are replaced by functional derivatives with respect to the spin-orbitals, resulting in nonlocal potentials.[126−128]

One subfield of DFT research is to devise algorithms to obtain optimized effective potentials (OEPs)[129] (the algorithms can involve difficulties and instabilities, but that is not our concern here). The OEPs are local potentials that allow one to obtain almost the same total energy as a GKS calculation but staying with the original KS framework of multiplicative potentials. If one instead accepts the justification of orbital-dependent functionals (of which HF exchange is one special case) by GKS theory, then the need for OEPs is diminished. The original motivation for finding optimized effective potentials was to place hybrid KS-DFT into the original KS framework involving local potentials, and there was some question about whether there are practical advantages to do so. In this context, it is important to recognize that even if one finds an OEP that yields a similar total energy to a GKS calculation, the orbital energy spectrum can be quite different, especially for hybrids with a substantial fraction of HF exchange; the GKS orbital eigenvalues are better approximations to the particle energies (i.e., to the energies required to remove or add an electron to the system).[122] The difference between the two eigenvalue spectra has been discussed in terms of self-interaction and a "particle correction".[122,130]

Functionals with some admixture of HF exchange generally lead to more accurate predictions than local functionals for bond energies, barrier heights, molecular interactions, band gaps, and electronic excitations of various kinds, but they introduce static correlation error,[131] especially for multireference systems, molecular geometries, and vibrational frequencies, and they increase the cost for large systems.

The above discussion is mainly focused on mixing HF exchange with local density functionals. More broadly, a large component of the quest for improved XC functionals in DFT centers on which ingredients to employ, including the question of whether to include ingredients based on WFT. For the purpose of this review, DFT methods, including mingled methods, can be broadly divided into various classes and subclasses depending on the ingredients in the density functional for the energy density at a point **r** in real space. The classification of the most commonly encountered methods is as follows:

I. Unmingled DFT methods (all based on a single Slater determinant).

I.A. Local.

I.A.1. Local spin-density approximation (LSDA, with the special case for a closed-shell system being called LDA):[132,133] The energy density is a simple function (not functional) of the density (sum of the squares magnitudes of the occupied orbitals) at a point **r**. There is more than one LSDA, but when most workers say LSDA they mean the spin-polarized version of the Gáspár−Kohn−Sham approximation for exchange combined with one or another LSDA approximation (a review is available[134]) for correlation. LSDAs have been widely and successfully used for a long time for solid-state applications but are now obsolete for most purposes.

I.A.2. Gradient approximation: The energy density is an ordinary function of the density and the magnitude of its gradient. Subclasses are generalized gradient approximations (GGAs),[135,136] which involve functional forms designed to separately approximate exchange and correlation, and non-separable gradient approximations (NGAs),[137,138] where one does not separate the functional into these categories.

I.A.3. Local orbital-dependent: the energy density depends not only on the spin densities and their gradients but also more generally on the local values of the KS orbitals and their derivatives (formally the KS orbitals are functionals of the density). The meaning of "local" in this context is that the density functional approximation to the energy density at a point $\mathbf{r}$ depends only on properties of the orbitals at point $\mathbf{r}$, and in particular it does not involve integration over all space. The commonly encountered example is called a meta-functional (a meta-GGA or a meta-NGA), which depends on the local kinetic energy density as computed from the derivatives of the KS orbitals by the following formula

$$\tau = \frac{1}{2} \sum_i^{\text{occ}} |\nabla \varphi_i(\mathbf{r})|^2 \tag{1}$$

where φ_i represents the ith occupied KS orbital (technically one should say the local noninteracting kinetic energy density because the kinetic energy computed from the KS orbitals represents the kinetic energy of a system of noninteracting electrons with the same density as the real system, but usually we just say kinetic energy density). The class of meta functionals also includes nonorbital-dependent functionals that depend on the Laplacians of spin densities, but these are in less wide use (because such functionals are prone to instability problems).

I.B. Nonlocal.

An example would be the so-called van der Waals functionals (a better name, based on the senior author of the original paper on this subject,[139] might be Langreth-type functionals). These are nonlocal functionals of the density designed to give a nonzero approximation to the interaction energy of two subsystems whose densities have negligible overlap. This kind of approximation was originally proposed by Langreth and co-workers, as in the vdW139 and vdW2[140] functionals, and has also been advanced by Vydrov and Van Voorhis, as in the VV10 correlation functional[141] (the border between methods combining DFT and WFT can be ambiguous, but in this review, we will not include van der Waals functionals as they may be considered to reside entirely in DFT).

II. DFT mingled with single-configuration WFT.

II.A. Hybrid functionals: These have already been introduced above. The HF exchange is mixed with local exchange. The reference wave function is still a single Slater determinant. These functionals are nonlocal because HF exchange involves integration over all space, and they are orbital dependent because the HF exchange formula depends on orbitals (or on the off-diagonal elements of the density matrix, which is equivalent).

II.B. Quasiparticle methods built on Dyson's equation, the GW approximation, and/or the Bethe−Salpeter approximation.

III. Multiconfigurational extensions of DFT.

III.A. Doubly hybrid density functionals (abbreviated as DHDFs, also called double hybrid functionals or multi-coefficient extrapolated DFT methods): One augments the correlation functional with a nonlocal contribution based on WFT, for example, perturbation theory, configuration interaction, or coupled cluster theory. While this typically involves computing only an energy correction, consistent multiconfigurational wave functions may in principle be assembled.

III.B. Configuration interaction calculations with Hamiltonian matrix elements obtained by using one or another element of DFT.

III.C. Methods that add additional density functional correlation energy to an MCSCF energy.

III.D. Combining DFT with configuration-interaction singles (CIC-TDA, b-D-TDDFT).

III.E. Using range separation to combine DFT with MCSCF wave functions.

III.F. Combining density functionals with WFT kinetic energies and densities.

Excitation spectra with DFT are typically calculated within the framework of linear response time-dependent DFT[142] (LR-TDDFT) or the associated Tamm−Dancoff approximation (TDA)-TDDFT, although real-time TDDFT approaches also find use,[143−147] with the latter formalism offering an interesting approach to compute electronic excitation spectra for already excited electronic states.[148−150] The Tamm−Dancoff approximation is widely used in WFT where it is usually called configuration interaction singles (CIS),[151−156] which is a CI calculation including only the ground state and CSFs generated from the ground state by single excitations. If the ground state is a HF wave function, the single excitations are not coupled to the ground state.

For large systems, the LR and TDA formalisms based on KS-DFT can be computationally much more efficient than the possibly more accurate wave function-based post-HF methods. Besides LR versus TDA, the choice of density functional is of great importance in predicting various types of excitations, as discussed below.

As already mentioned, because KS-DFT is intrinsically a ground-state theory (although the theory may be generalized to excited states that are the lowest-energy states of their symmetry[46]), excited states are usually handled by linear response (as in time-dependent DFT). The present review is concerned with merging features of KS-DFT with features of WFT, where configuration interaction provides a very natural way to treat excited states. However, it should be mentioned that there are time-independent methods for handling excited states entirely within DFT, although not within traditional KS-DFT. Chief among these is ensemble DFT, which may be traced back to the work of Theophilou[157] and Gross, Oliviera, and Kohn;[158] ensemble DFT treats excited states in terms of fractional orbital occupations analogous to those in a multiconfiguration wave function. Ensemble DFT has been developed in various (partially divergent) ways since then. We consider ensemble DFT to be outside the scope of the present review, but we give some recent references to illustrate the state-of-the-art, and earlier work may be traced back from these references.[159−170] Another closely related subject not covered in this review is density matrix functional theory; recent reviews are available.[171,172]

Although the theme of this review is mixing WFT and DFT for electronically excited states, to fully explain the methods we discuss, we will also have to review some ground-state theory and applications because most of the methods used for excited states were developed originally, in whole or in part, for ground states, so a certain amount of ground-state material is necessary background.

3. DFT WITH SINGLE-CONFIGURATION WFT: GENERALIZED KOHN−SHAM THEORY

In this section, we will focus on the successes and failures of some of the hybrid methods for excited-state chemistry; we will consider only hybrid methods that involve mingling DFT with the simplest single-configuration WFT method, namely the nonlocal HF method.

Hybrid functionals have been very successful for ground-state properties (some of the most popular ones include Becke, 3-parameter, Lee−Yang−Parr (B3LYP),[120,173−175] Coulomb-attenuating method-B3LYP (CAM-B3LYP),[176] PBE with one empirical parameter (PBE0, also called PBE1PBE),[177] Heyd−Scuseria−Ernzerhof (HSE06),[178,179] M06,[180] and M06-2X),[180] and they also have proven to be systematically more accurate than local functionals for excited-state properties such as photoelectron spectroscopy, band gaps of solids, and excitation energies of atoms and molecules.[123,150,180,181] The poor performance of local density functionals can be partly attributed to self-interaction energy, which arises from the Coulomb interaction of the electron density of one electron with itself and which generally cannot be exactly canceled by a local exchange approximation. Yang and co-workers[4] have argued, though, that errors often attributed to self-interaction can be better understood as delocalization errors. Self-interaction error and delocalization error are usually decreased by adding an admixture of HF exchange to the functional, and this is a principal reason for the success of hybrid functionals.

Hybrid functionals can be based on combining HF exchange with various kinds of local ingredients of a density functional, leading to hybrid GGAs, hybrid NGAs, hybrid meta-GGAs, and hybrid meta-NGAs. The way that HF exchange is incorporated leads to another way to classify them; this incorporation can be done in more than one way as described in the next three subsections where we discuss global hybrids, range-separated hybrids, and local hybrids.

The performance of global hybrids for excited-state properties such as electronic excitation of molecules calculated within the framework of time-dependent DFT is very widely studied.[180−198] Only some key conclusions will be reviewed below.

While local approximations to density functionals may sometimes be good for valence excitations, they can significantly underestimate Rydberg excitations, intra- and intermolecular charge-transfer excitations, and core excitation energies. Hybrid functionals are often useful in predicting these properties, and of the available hybrid functionals, the range-separated ones with long-range correction are among the most popular ones. However, the optimum range parameters for the long-range corrected functionals are system-dependent, and the best results are obtained when the range-separation parameter ω is tuned according to the system,[199−202] as discussed below.

3.1. Global Hybrids

The simplest way of generating a hybrid functional by combining single-configuration WFT with DFT is by replacing a fraction X of local DFT exchange with nonlocal HF exchange. When X is a constant, and a single value of X is used for all interelectronic separations, such hybrids are called global hybrids.

Typically, values of X between 20 and 30 (X is always given as a percentage, so this means 20−30%) are used for general purpose functionals, but one might prefer lower X for applications to inherently multiconfigurational systems, and one might prefer higher X for applications to barrier heights[203] or to excited states in order to improve the treatment of Rydberg and charge-transfer excitations, although most excited states are inherently multiconfigurational, so there is a trade-off.[204,205] Global hybrids often give improved description of reaction energies, ionization energies, electron and proton affinities, and noncovalent complexation energies.[186,206−208] They also give improved solid-state and molecular excitation energies.

Jacquemin et al.[186] tested the performance of various classes of density functionals for their ability to predict 190 valence excitations, 20 Rydberg excitations, and 16 charge-transfer states, and they found that functionals such as B3LYP, PBE0, and M06 with a modest amount of HF exchange (20−30%) work well for valence excited states, functionals with relatively high HF exchange (>50%; e.g., M05-2X and M06-2X) work well for Rydberg states, and M06-HF with 100% HF exchange was found to be the best for charge-transfer states. Besides showing the importance of including an admixture of HF exchange for electronic excitations, this work[186] also showed that no particular hybrid functional is good for all the three types of excitations. Similar conclusions have been drawn in other studies.[180,189,192] One conclusion of this work is that functionals with higher HF exchange tend to be better for Rydberg excitations, but changes that make a functional better for Rydberg states often make it worse for valence excitations.

Although the performance of global hybrid functionals has been very impressive, their inability to simultaneously provide useful accuracy for all kinds of properties, especially all kinds of excited states, and their enormous computational cost for calculations with plane-wave basis sets, led to the search for alternative options. One such alternative is the class of range-separated hybrid functionals.

3.2. Range-Separated Hybrids

Another possible way of generating a hybrid functional is to replace local density functional exchange by nonlocal HF exchange such that the value of X is a function of interelectronic separation. In these functionals, the interelectronic separation, r_{12}, in the electron−electron Coulomb interaction term is divided into two or more terms, for example, one can divide it into two parts, short-range and long-range, by using the complementary error function (erfc) and the error function (erf), where erfc = 1 − erf. Thus, the Coulomb operator can be written as follows:

$$\frac{1}{r_{12}} = \frac{\text{erf}(\omega r_{12})}{r_{12}} + \frac{\text{erfc}(\omega r_{12})}{r_{12}} \tag{2}$$

Here the first term corresponds to long-range and the second term corresponds to short-range; ω is an adjustable parameter that determines the range over which the separation occurs (in some work discussed in a later section, ω is called μ). An ω value of zero makes the long-range term zero, and $\omega \to \infty$ makes the short-range term zero. Typical values of ω used in literature lie in the range 0.15−0.50 a_0^{-1}, where 1 a_0 = 1 bohr $\cong$ 0.5292 Å.

Three ways discussed in the literature for achieving range separation are

(1) X (which is given as a percentage) decreases from short-range to long-range interelectronic separation in such a way that it vanishes at long-range; these are referred to as screened exchange hybrids. Some examples include HSE03, HSE06,[178,179] N12-SX,[209] MN12-SX,[209] and HSEB,[210] in all of which X decreases from 25 to 0.

(2) X increases from short-range to long-range interelectronic separation such that it goes to 100% HF exchange or to a finite value; these are referred to as long-range corrected (LC) hybrids. Some examples include LC-ωPBE ($X = 0-100$),[211] ωB97 ($X = 0-100$),[212] ωB97X ($X = 15.7706-100$),[211] ωB97X-D ($X = 22.2036-100$),[213] CAM-B3LYP ($X = 19-65$),[212] and M11 ($X = 42.8-100$).[214]

(3) X increases from short-range to a maximum value at medium-range and then decreases to zero at long-range. An example includes Henderson–Izmaylov–Scuseria–Savin (HISS).[215,216] The X value of HISS increases from zero at $r_{12} = 0$ to 35.81 at $r_{12} = 1.47$ a_0 (where r_{12} is the interelectronic distance) and then decreases to 15 at 4.07 a_0 and to 5 at 6.12 a_0, eventually going to zero in the long-range limit.

The first two approaches are widely used, while the third one has not gained much attention so far.

The first approach, screened exchange, is designed mainly for use in condensed-phase calculations. The motivation in these calculations is 2-fold. The first motivation is that the long-range part of HF exchange is very expensive in plane wave codes. Thus, if one wants to get some of the advantage of HF exchange (e.g., better band gaps, structures, or thermodynamic properties) but decrease the cost compared to global hybrids, one can use screened exchange.[209,217] The cost savings clearly depend on the system and the software, but in some plane-wave applications where this kind of functional has been employed the cost of a global hybrid is 3 orders of magnitude larger than the cost of a local functional, while the cost of a screened exchange functional is only 2 orders of magnitude more expensive. The second motivation for screened exchange is to eliminate a problem of the HF approximation itself for metals, namely the divergence of the group velocity at the Fermi level. This can be shown to come from the HF treatment of the slowly decaying long-range Coulomb potential; replacing the Coulomb potential ($\propto 1/r_{12}$) by a screened Coulomb potential ($\propto e^{-\omega r_{12}}/r_{12}$) eliminates this problem.[218,219] This is not just a mathematical fix, but rather it follows from the physics. The electron–electron interaction is screened by the correlated motion of the other electrons in the medium between the two interacting electrons, and this changes the long-range form of their effective interaction. Thus, screening the long-range exchange corresponds to introducing an electron correlation effect that is not present in HF theory. Using another language, we can say that introducing screening corresponds to giving the medium a dielectric constant different from unity.

The second approach, long-range-corrected range-separated functionals, where X increases with interelectronic separation and often includes 100% of HF exchange at large r_{12}, is motivated by a different class of phenomena, namely those where it is important to have the correct asymptotic behavior of the unscreened exchange potential for properties such as nonlinear optics, polarizabilities of long chain molecules, charge transfer, and Rydberg excitation energies.[217,220–223] Therefore, this kind of functional is often called a "long-range corrected" functional and indicated by the prefix LC or ω. Although highly successful in some respects, the LC hybrids have limitations owing to the sensitivity of the range-separation parameter ω to the system and property, and therefore, schemes for tuning ω have been suggested and discussed.[122,199,224] Examples of an optimally tuned functional are the Baer, Neuhauser, and Livshits (BNL) range-separated hybrid functional[225] or the long-range corrected ωPBE0 (LC-ωPBE0) functional,[226] which have been applied to fundamental and optical gaps of organic photovoltaics.[199,227] The review of Kronik and Neaton[124] and the recent work of Kronik and co-workers[228–231] may be consulted for further discussion of optimally tuned functionals; the latest of these includes a discussion of some pros and cons of this approach. One possible way to avoid the issue of using a universal parameter ω for all systems is to use position-dependent ω, which was proposed by Krukau et al.[232] and which led to the so-called locally range-separated (LRS) functionals (also known as local hybrids) and was shown to be better for kinetics and thermochemistry as compared to a functional that used constant ω.[232] In this way, one may be able to remove the size consistency problem of tuned range-separated hybrids.

The goal of the third approach, for example, the HISS middle-range functional, is to combine the computational efficiency of screened exchange functionals with the physical-modeling advantages of functionals in which X increases with r_{12}.

Bartlett and co-workers[233–236] have developed the Quantum Theory Project (QTP) family of range-separated exchange-correlation density functionals with 100% HF exchange for long-range interelectronic interactions. They are motivated by the objective of creating an accurate correlated orbital theory with Kohn–Sham eigenvalues of the occupied orbitals equal the vertical ionization energies. These functionals have been applied to calculate vertical excitation energies of valence and Rydberg states.

3.3. Local Hybrids

Local hybrid functionals have generated considerable interest[237,238243,245,247,249,251–255,257–261,262,267,268] owing to some of the limitations of the hybrid density functionals summarized above. While the hope for the global hybrid functionals and the range-separated hybrid functionals is that they strike a good balance between elimination of one-electron self-interaction error (which can be achieved with a high amount of HF exchange) and adequate treatment of static correlation (which can best be achieved by minimizing HF exchange), their form is not flexible enough to introduce the optimum mixture of nonlocal exchange for each region of a molecule. The local hybrids show great potential for overcoming this limitation by allowing the percentage X of HF exchange to vary with position.

The XC energy for a local hybrid functional can be written in terms of a local mixing function (LMF), $f(\mathbf{r})$,[237,248,269] which determines the admixture of HF exchange at point $\mathbf{r}$ (thus the X of global hybrids is replaced by $f(\mathbf{r})$ in local hybrids). The LMF is designed to satisfy conditions for the uniform electron gas as well as to give correct long-range asymptotic behavior by having s-dependent and/or τ-dependent terms. An example is

$$f(\mathbf{r}) = \frac{\tau_W(\mathbf{r})}{\tau(\mathbf{r})} \tag{3}$$

where τ_W is the von Weizsäcker kinetic energy density

$$\tau_W = \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho(\mathbf{r})} \tag{4}$$

and τ is the actual kinetic energy defined by eq 1. In regions dominated by a single electron, one traditionally expects that τ_W and τ become equal, making $f(\mathbf{r})$ equal to one, and in regions dominated by uniform electron density, $\nabla\rho$ becomes zero, making $f(\mathbf{r})$ equal to zero. Additionally, both τ_W and τ are positive and $\tau \geq \tau_W$; therefore, $0 \leq f(\mathbf{r}) \leq 1$. In the limit of $f(\mathbf{r}) \to 0$, the nonlocal HF exchange term drops out resulting in a local density functional, and in the limit of $f(\mathbf{r}) \to 1$, the local DFT exchange term drops out leaving behind the nonlocal HF exchange term, which has no one-electron self-interaction.

A caveat to the above expectations is that even in regions one might consider to be one-electron regions, τ_W/τ may differ from 1 when the system has an orbital nodal plane.[270]

Local hybrid functionals were first tested[237] for bond lengths and binding energies of A_2^+ dimers (A = H, He, Ne, Ar, HF, H_2O, and NH_3), barrier heights, and atomization energies using a local hybrid of the BLYP functional labeled as Lh-BLYP and using a local hybrid of PBE exchange and Perdew–Kurth–Zupar–Blaha (PKZB) correlation,[271] which is labeled as Lh-PBEPKZB. Both the local hybrids of ref 237 were tested nonself-consistently and were based on either HF or LSDA densities, which are labeled as post-HF or post-LSDA densities, respectively, in ref 237. The A_2^+ cations are particularly interesting as test cases for DFT because the bond lengths predicted by most density functionals tend to be quite long compared to experiment due to self-interaction error. Because of the way local hybrid functionals are designed, they tend to minimize the effect of self-interaction error, and it was found that the two local hybrid functionals (Lh-BLYP and Lh-PBEPKZB) give shorter and therefore better estimates of bond lengths compared to the local functional, BLYP, and the popular global hybrid functional, B3LYP.[237] The binding energies of the A_2^+ cations (calculated by subtracting the energy of the dimeric cation from the separated cation and the neutral atom or molecule) also showed significant improvement with the local hybrid functionals,[237] as did the energy barrier for the reaction $H_2 + H \rightarrow H + H_2$. However, average errors for atomization energies of the 55 molecules in the G2 test set were not encouraging,[237] indicating that improvements in the local mixing function $f(\mathbf{r})$, examples of which were suggested in ref 237, were required.

In 2006, Arbuznikov et al.[239] built upon the work of Scuseria and co-workers[237] by (i) implementing a self-consistent version of local hybrid functionals and (ii) testing sensitivity to the choice of LMF. Arbuznikov et al.[239] were the first ones to implement a self-consistent version of local hybrid functionals by generating localized potentials from them by using a common energy denominator or localized HF approximations, approximations that are used for orbital-dependent functionals. The resulting localized potential was labeled as a localized local hybrid potential in ref 239. It was shown that using Becke-88 exchange and Perdew–Wang-91 (PW91) correlation[272] for the self-consistent implementation gave lower total electronic energies compared to the nonself-consistent one, and the results for atomization energies were found to be similar to the nonself-consistent case. The choice of the local mixing function LMF can be an important factor in deciding the accuracy of the functional, and one test evaluated in ref 239 was the use of higher powers of the LMF. Thus, the LMF $[f(\mathbf{r})]^2$ was considered, which, like $f(\mathbf{r})$, satisfies the condition that it lies in the range $[0, 1]$. However, both $[f(\mathbf{r})]^2$ and $f(\mathbf{r})$ were found to give poor performance for atomization energies owing to the high average amount of HF exchange.[239] This suggested that further improvements in LMF were necessary to take into account a balanced inclusion of HF exchange, which strongly affects the static correlation in a system.

In 2007, a local hybrid functional, namely Lh-SVWN, was proposed by Kaupp and co-workers[240] that was shown to be as good as the popular B3LYP hybrid functional for atomization energies of 55 molecules.[273,274] The LSDA was used for local exchange and local correlation. This work[240] also tested other LMFs besides the ones already suggested in refs 237 and 239, as well as a still more general form:

$$f(\mathbf{r}) = \sum_{j=0}^{j_{max}} a_j \left[\frac{\tau_W(\mathbf{r})}{\tau(\mathbf{r})} \right]^j \tag{5}$$

Tests were performed for values of j_{max} up to four, but ultimately $j_{max} = 1$ was chosen, as higher values of j did not yield significant improvements.[240] Subsequently, the scaling factor a_1 was varied, and a strong dependence of mean unsigned error (MUE) on a_1 was found for the atomization energies of a database of 55 atomization energies (see Figure 1 of ref 240.); a value of $a_1 = \sim 0.5$ was found to be the optimum value, although this does not eliminate self-interaction error in long-range regions dominated by a single electron, as $f(\mathbf{r})$ itself has its upper bound a_1, rather than 1.[240] The MUE was found to be more sensitive to a_1 than to the percentage X of HF exchange of a global hybrid functional having the same exchange and correlation components as Lh-SVWN.

Arbuznikov and Kaupp[241] proposed a family of LMF functional forms that depend on the reduced gradient of the density, s (as opposed to those given by eqs 3 and 5, which are τ-dependent). These were designed to achieve the correct asymptotic behavior in long-range regions dominated by a single electron as well as to obtain improved thermochemical performance on the 55 atomization energies using the same Slater–Dirac exchange and VWN correlation as used in ref 240. Some of the functionals forms of s-dependent LMFs suggested in ref 241 that satisfy the condition $0 \leq f(s(\mathbf{r})) \leq 1$ are

$$f(s(\mathbf{r})) = \left[\frac{s}{a + s} \right]^2 \tag{6}$$

$$f(s(\mathbf{r})) = [1 - e^{-as}]^2 \tag{7}$$

$$f(s(\mathbf{r})) = \left[\frac{2(\tan^{-1}(as))}{\pi} \right]^2 \tag{8}$$

$$f(s(\mathbf{r})) = [\text{erf}(as)]^2 \tag{9}$$

Here a is a parameter, which is positive and is optimized to determine the most suitable LMF for certain properties, and s is the reduced density gradient.

The s-dependent LMFs have advantages over both the scaled (eq 5) and unscaled (eq 3) τ-dependent LMFs in terms of ease of implementation of self-consistent versions because they have density-dependent terms instead of orbital-dependent terms. Also, when used with LSDA, the most promising s-dependent LMFs give performances similar to that of the scaled τ-dependent LMF and the global hybrid functional, B3LYP, for the database of 55 atomization enrgies.[241]

With the objective of validating the performance of local hybrid functionals on multiple properties, Kaupp and co-workers also tested them on heats of formation[244] of the G3/99 database of enthalpies of formation, ionization potentials, electron affinities and proton affinities,[275] barrier heights[244] of 38 hydrogen transfer reactions (HTBH38)[276,277] and 38 non-hydrogen transfer reactions (NHTBH38),[278] and other interesting nonthermochemical properties such as nuclear shielding constants[242] of light main-group containing molecules. Both s-dependent and scaled and unscaled τ-dependent LMFs were tested with SVWN (referred to as Lh-SVWN), and the performance of Lh-SVWN with specific forms of LMFs was found to be better or at par with widely used methods. Additionally, an interesting conclusion drawn from ref 244 was

that gradient corrections to LSDA such as GGAs give less improvement compared to adding position-dependent HF exchange to LSDA.

Further modifications to local hybrid functionals involved translation of its formulation (referred to as a full-range local hybrid hereafter), which in the original form mimics the way a global hybrid is written to the range-separated formalism.[248] The local mixing function used here is the scaled τ-dependent function, and the long-range corrected one has 100% HF exchange at long-range. Self-consistent implementations of both of them give performance similar to full range local hybrids for thermochemistry and kinetics.[248]

More recently, Kaupp and co-workers have made considerable progress as compared to the work (up to 2008) reviewed above, and a review is available.[279] The currently best local hybrids in their TDDFT tests are those from ref 256. A key aspect in the improvement is the use of a "common τ-LMF" rather than a "spin-channel τ-LMF", where ingredients are derived from the total τ rather from the spin-channel τ; this brings in some spin cross terms into the nondynamical part. The two best functionals in the TDDFT tests use modified LSDA correlation functionals, where short-range self-correlation is removed either fully ("sif") or is reduced ("sir"). This allows the use of a larger prefactor for the common t-LMF, which leads to improved performance.

A fundamental problem with local hybrids that has likely deterred many workers from entering the field much earlier, is the so-called gauge problem, i.e., the ambiguity of exchange-energy densities. That is, one may add a calibration function (CF) that integrates to zero when integrated over all space. While this does not matter for global hybrids, it does for local hybrids, and considerable effort has gone into finding the best calibration function and testing its effect on excited-state energies and noncovalent interactions.[246,260,264,266]

In another approach of developing a local hybrid functional, Haunschild et al.[250] proposed adding a portion of HF exchange to a global hybrid functional perturbatively near the nuclei. This is achieved by using[250]

$$f(\mathbf{r}) = X + (1 - X)\mathrm{erf}\left(C \sum_A e^{-\gamma|\mathbf{r}_A|^2}\right) \tag{10}$$

Here X, C, and γ are positive constants, and r_A is the distance between a point in space and nucleus A. The parameter γ was optimized against two representative databases,[278] namely atomization energies of six molecules (AE6 database) and barrier heights of six reactions (BH6 database).

The discussion above shows that local hybrid functionals have evolved in the last 15 years to adequately describe various properties, which are primarily ground-state properties.

Because of their greater flexibility, local hybrid functionals can be potentially useful for various types of excitations, and a TDDFT implementation of them was carried out by Maier et al.[263] in 2015. Subsequently, in 2016, Maier et al.[265] performed extensive tests on various types of vertical excitations using four local hybrid functionals, which were initially optimized to accurately predict ground-state properties. The valence excitations test suite consisted of 166 excitations of which 103 were singlet and 63 were triplet, all taken from the Thiel test set of diverse organic molecules.[182,280,281] Intermolecular charge-transfer was investigated using the ethylene–tetrafluoroethylene complex at various intermonomer distances, intramolecular charge-transfer and Rydberg excitations were assessed for test

systems taken from the work of Tozer and co-workers,[282,283] and core excitations were assessed for test systems taken from a separate work of Tozer and co-workers.[284] The local hybrids were found to give good performance for all types of excitations except for charge-transfer excitations, but if one ranks local hybrids based on across-the-board performance for excitation energies, then LMFs with τ-dependence gave the best compromise for all types of excitations.[265]

In another work, Grotjahn et al.[268] tested the performance of a local hybrid functional, Lh12ct-SsifPW92, within the framework of TDDFT for predicting vertical excitations in chromophores having the potential to undergo singlet fission in the solid state. The chromophores in ref 285 were used as a test set, and Lh12ct-SsifPW92 was found to be a promising method for predicting T_1 excitation energies using the ΔSCF method and S_1 and T_2 excitation energies by LR means.

The self-consistent implementation of local hybrids is difficult to accomplish in a computationally efficient manner, as is their implementation within the framework of TDDFT. This has been partly responsible for their slow adoption. However, recent progress has reduced the cost,[263] and this will likely affect future work on excited states. Further improvements are needed, as local hybrid functionals do not yet work well for a wide range of properties.

Arbuznikov and Kaupp[128] have generalized the concept of local hybrids to a broader class of occupied-orbital dependent functionals, including, for example, the Becke's 2005 non-dynamical-correlation functional[286,287] (B05). Janesko and co-workers[288] presented a simplified version of the B05 functional; the simplification allows the implementation of analytic fourth derivatives and TDDFT excited-state geometry optimization.[289] This new works builds on Janesko's simplification of local hybrids that he calls "rung 3.5" functionals.[290,291] Rung 3.5 functionals have been applied to several properties, including band gaps, band structures, and molecular excitation energies; a broad summary of the accuracy is that it is between that of local functions and global hybrids but with lower cost than global hybrids.[289]

4. USING KOHN–SHAM ORBITALS IN MANY-BODY THEORY

The central element of DFT involves solving a set of self-consistent equations in which single-particle functions (orbitals or spin orbitals) evolve in an effective potential, which is a functional derivative of the XC energy. The effective potential includes many-body electron correlation effects within the framework of independent-particle equations. Including many-body correlation effects using an independent-particle or mean-field framework has a long history, which predates DFT,[292−296] and so it is not surprising that there are attempts to combine DFT and WFT to make connections between these approaches. In scattering theory, the accurate effective potential is called the optical potential. In condensed-matter theory, it is called the self-energy. The self-energy is often discussed using Green's function theory rather than by working directly with wave functions; nevertheless, when we classify all electronic structure methods as either WFT or DFT, it clearly lands on the WFT side.

Although Green's function theory as a method of electronic structure was originally developed in the context of condensed-matter physics[297] (and the language of solid-state physics permeates the field), it is also applicable to atomic and molecular physics and is starting to be applied more widely there. An

important distinction to keep in mind is that Green's function theory is a generalization of the traditional Green's functions of mathematical physics that are defined in terms of differential equations, and a "Green's function" in the context of electronic structure theory is actually a field-theoretic propagator; in fact, in quantum chemistry, one often finds Green's function theory referred to as propagator theory[298−301] (Green's functions are also called Green functions). The connection between Green's function theory and conventional quantum chemistry has been reviewed before.[302] The connection between Green's function theory and DFT has also been reviewed.[303−305]

A key concept in approximate Green's function theory is the screened Coulomb potential. As mentioned above, the screening accounts for the fact that the effective interaction between charged particles is reduced by the other electrons acting as an atomic-scale dielectric medium (a macroscale analogue is the dielectric constant of Debye−Hückel theory). Note that the screening is "dynamical", which simply means that it depends on energy or frequency. At high frequency, the screening is ineffective and one recovers the unscreened Coulomb interaction.

Another key concept in Green's function theory is the quasiparticle, originally introduced by Landau in the context of Fermi liquid theory. A quasiparticle is sometimes described as a bare particle or hole and its surrounding screening charge.[297,306] A more formal way to think about quasiparticles is that they are elementary excitations acting like particles (electrons or holes) with nearly additive energies.[218,219] This provides a way to explain and calculate many-body physics in a single-particle framework. The basic equation describing the energy of a quasiparticle is the Dyson equation in the frequency (ω) domain:

$$G(r_1, r_2; \omega) = G_0(r_1, r_2; \omega)$$
$$+ \iint G_0(r_1, r'; \omega)\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon)G(r'', r_2; \omega)$$

(11)

where G_0 and G are the one-particle Green's functions for a noninteracting system and the interacting system, respectively, Σ is the self-energy operator that includes exchange and correlation, and ε is the quasiparticle eigenvalue. Quasiparticle energies are directly related to photoemission and inverse photoemission processes; that is, they refer to the energy to remove an electron from the system or add an electron to the system. For example, in photoemission, a photon of energy $h\nu$ (where h is the Planck's constant and ν is the frequency) produces an electron of lower kinetic energy E_{kin}, and the difference ($h\nu - E_{kin}$) is the quasiparticle energy of a hole. Photoexcitations of neutral excited states are considered to be two-quasiparticle processes involving both a quasihole and a quasielectron (as if an outgoing electron were captured in an unoccupied orbital); the interacting pair is called an exciton. Describing this interaction requires an effective two-particle equation.

4.1. Self-Energy and the GW Approximation

One way to map the many-body problem into a quasiparticle framework is the self-energy formulation,[307]

$$\left(-\frac{\nabla^2}{2} + V^{ext}(\mathbf{r}) + V^{Hartree}(\mathbf{r})\right)\phi^{QP}(\mathbf{r})$$
$$+ \int d\mathbf{r}'\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon)\phi^{QP}(\mathbf{r}') = \varepsilon\phi^{QP}(\mathbf{r})$$

(12)

where ε and ϕ^{QP} are the quasiparticle eigenvalues and eigenfunctions, respectively. In general, the self-energy operator is nonlocal, energy-dependent, and non-Hermitian, where the non-Hermitian character follows from the fact that quasiparticles are not eigenstates of the many-electron Hamiltonian but rather have a finite lifetime. The exact self-energy, like the exact XC functional, is essentially incalculable, so one seeks good approximations.[308−311]

Because a quasielectron corresponds to the composite of an electron and the polarization, it induces in its neighborhood, the quasiparticles interact via a screened Coulomb potential. The most commonly used approximation is Hedin's GW method,[312] where the name follows from its approximation of the self-energy as iGW (or GW, depending on definitions), where $i = \sqrt{-1}$, G is the single-particle Green's function, and W is the screened Coulomb interaction. The higher-order terms neglected in self-energy may be included by replacing iGW by $iGW\Gamma$, where Γ is the vertex function; setting $\Gamma = 1$ yields the GW approximation. Neglecting the vertex function corresponds to keeping only the first-order term in a power series of the screened Coulomb interaction; vertex corrections account for second- and higher-order powers in the screened potential expansion. Hedin's equations would be formally exact if the full vertex function were included. Detailed description of the theory can be found elsewhere.[297,313−317] In brief, though, by using Dyson's equation[318] for the one-particle Green's function, the equations can be solved iteratively. Originally, the iterations were started with HF wave functions, but now most works use KS eigenfunctions as a mean-field approximation.

In many cases, rather than solving the equations iteratively, a single-shot calculation is performed where the initial-guess orbitals and orbital energies are used to construct the self-energy. This is referred to as $\Sigma = G_0W_0$. When using Kohn−Sham orbitals in G_0W_0 theory, the many-body problem is not solved iteratively; instead, ε is obtained by perturbatively correcting KS-DFT eigenvalues (ε^{KS-DFT}) to first order.[319]

Although this non-self-consistent approximation has the advantage of being more computationally affordable than self-consistent versions,[320] it violates some important sum rules like particle conservation. These problems can be solved by iteratively updating the screened coulomb potential W and Green's function G, and this yields the self-consistent GW (scGW) method.[321] In discussing GW self-consistency, one must be very careful about which type of self-consistent scheme one is assessing, especially to differentiate between fully self-consistent calculations (involving iteration in G) and eigenvalue self-consistency.[322] The accuracy of the self-consistent GW approach and effect of different levels of self-consistency are ongoing areas of research.[323−328] To avoid the high computational cost of scGW, Barth and Holm proposed a scheme where G is calculated self-consistently but W is not,[329−331] i.e., one iterates the eigenvalues in the Green's function but not the orbitals in the dielectric function of W.[332] This scheme is called GW_0 (sometimes it is called partial scGW). Another partially self-consistent scheme is quasiparticle self-consistent GW (QP-scGW), where the one-particle wave function is updated.[333−335] Although it was found for fully self-consistent treatments of the homogeneous electron gas that the description of the quasiparticle spectrum deteriorates with increasing levels of self-consistency,[336,337] eigenvalue self-consistency and QP-scGW have been shown to improve the ionization potential and energy gap significantly for a large set of organic molecules.[322,338] Very recently, the accuracy of different levels

of self-consistent GW methods have been tested for the ionization energies of the *GW*100 test set[339] that is composed of 100 molecules of different bonding types, chemical composition, and ionization energies.[340] The accuracy of the QP-scGW method has been tested for electronic properties of TiO_2 nanoclusters,[341] atoms,[342] and small molecules.[335]

Although it was found for some applications that scGW results are independent of the mean-field starting point,[343,344] that is not true for the more affordable nonself-consistent or partially self-consistent GW methods. The dependence of G_0W_0 results on the starting point is now fairly well-known for both organic[345−349] and inorganic[331,350,351] molecules. Calculations starting from HF are found to overestimate the HOMO−LUMO gap significantly. This problem is ameliorated by using LDA XC functionals; however, G_0W_0 calculations with LDA functionals still underestimate the HOMO−LUMO gap significantly. This error can be eliminated to some extent by using global and range-separated hybrid functionals as a starting point.[352−354] Because the amount of HF exchange included in an XC functional varies from functional to functional, some research has been devoted to schemes to evaluate the amount of HF exchange to be included.[227,352,355−361] Nevertheless, the dependence on the starting point is worse than in TD-DFT when using G_0W_0 in a Bethe−Salpeter equation (BSE) context; BSE is introduced in the next subsection, but we note here that this dependence limits the usefulness of G_0W_0 for excited-state modeling.

In an iterative procedure, after the first iteration, one can recompute the new G and go through the iteration again. In that case, due to nonvanishing $\frac{\delta\Sigma}{\delta G}$, one would obtain a correction to the bare vertex Γ. Because of its computational expense, the GW approximation ignores this step. Although this approximation is justified only when a Hartree reference state is used, and then only in the first iteration of the scheme,[362] it has nevertheless been widely used for both HF and DFT starting points. The often-seen deterioration of GW results with self-consistency can be linked to this approximation.[363] However, it has been suggested in the literature that the vertex correction and self-consistency are competing effects[364] and that they tend to cancel each other to a large extent. In other cases, vertex corrections have been found to play a large role, especially for band gap calculations.[365,366] Efficiently including the vertex correction to improve GW calculations is an active area of research.[367−371]

Very recently, renormalized second-order perturbation theory has been used to add an additional self-energy term for the electron correlation energy.[372] This approach was tested against the ionization potentials of the G2 test set, and improved results were obtained.

Kananenka et al.[373] presented a framework that combines a short-range density functional approximation with a long-range single-particle Green's function method.

Even after long research, several aspects of GW calculations still need to be explored in a systematic way in the context of applications to molecular systems. These areas include self-consistency, vertex corrections, the dependence on starting point, and static correlation error.[374]

By starting with DFT orbitals and using perturbation theory in a post-SCF step, the G_0W_0 theory bears a resemblance to doubly hybrid theories, which are discussed in section 5.1.

4.2. Bethe−Salpeter Equation

GW calculations with one-particle Green's functions can accurately predict photoemission, but photoabsorption involv-

ing excitation to a bound state is a two-quasiparticle property, and it is more properly treated by a theory involving the two-particle Green's function, in particular, the Bethe−Salpeter equation (BSE),[303,305,314,316,375−377] which is typically employed on top of the results from a GW calculation.

A two-particle Green's function (G^2) represents propagation of two quasiparticles at the same time. It can be used to represent two holes or two electrons as well as one hole and one electron (neutral excitation). To calculate optical absorption spectra, then, one needs to calculate two-particle correlation functions,

$$L(r_1, r_2; r'_1, r'_2) = -G^2(r_1, r_2; r_1, r'_1, r'_2) + G(r_1, r'_1)G(r_2, r'_2) \tag{13}$$

The correlation function satisfies the BSE,

$$L(r_1, r_2; r_1, r'_1, r'_2) = G(r_1, r'_2)G(r_2, r'_1)$$
$$+ \int d(r_3 r_4 r_5 r_6)G(r_1, r_3)G(r_4, r'_1)\Xi(r_3, r_5; r_4, r_6)L$$
$$(r_6, r_2; r_5, r'_2) \tag{14}$$

where the Kernel Ξ is the derivative of the self-energy with respect to a one-particle Green's function. The problem of absorption spectra can then be solved by searching for poles of two-particle correlation functions in the complex energy plane, whose positions provide the excitation energies. The BSE can be reduced to an eigenvalue problem,[375,378]

$$H_{exc}|\lambda\rangle = E_\lambda|\lambda\rangle \tag{15}$$

where H_{exc} is the excitonic Hamiltonian which is a non-Hermitian matrix, $|\lambda\rangle$ represents the electronic state, and E_λ is the energy of the state $|\lambda\rangle$. In many of the recent implementations, the matrix H_{exc} is constructed using an electron−hole basis set.[379−385] Because of the non-Hermitian nature of the H_{exc} matrix, it cannot be solved iteratively. To reduce the computational cost, Hermiticity is often enforced, however, by neglecting the off-diagonal elements of H_{exc}. This approximation is known as the Tamm−Dancoff approximation (TDA). The TDA approximation has been successfully used for predicting the absorption spectra of several solids.[379−381,386−388] However, while off-diagonal terms are smaller than diagonal terms, they can affect absorption spectra significantly,[389,390] especially in the case of plasmons in solids[390] and confined systems such as nanotubes or π-conjugated molecules.[391,392]

Especially for molecular and finite systems, solving the full BSE (non-Hermitian matrix) has been found to be important. Various algorithms have been used in the literature to solve the non-Hermitian BSE.[392−397] BSE has been successfully used to study both intermolecular[398] and intramolecular[394,399,400,398,401−403] charge-transfer excitations. BSE has also been used to study excited states relevant to singlet fission in acenes[404,405] and the optical gaps in small transition metal molecules[406] and the singlet[407−410] and triplet[408,409,411] excited states and oscillator strengths[412] in a large set of organic molecules. The BSE results are more accurate than TD-DFT for systems with some multiexcitation character, but the accuracy is not good enough to be called successful for triplet states and singlet−triplet splittings.

Analytical gradients within BSE are not yet available. However, Ismail-Beigi and Louie proposed an approximate approach for calculating excited-state forces[413] and used that approach to explore the formation of self-trapped excitons in silicon dioxides.[414] BSE has recently been used to calculate intermolecular dispersion and induction energies.[415]

4.3. Algorithms to Accelerate GW Calculations

Despite several attractive features of the family of GW methods, due to its high computational cost, only very recently has it been applied to medium and large size systems. Over the years, many approaches have been proposed to reduce the computational cost of GW calculations without compromising the accuracy. Early GW calculations were done using plane-wave basis sets. For complex systems, a large numbers of basis functions are required for accurate GW calculations. To overcome this bottleneck, use of localized Gaussian-orbital basis sets has been proposed.[416−419] However, calculated quasiparticle energies converge only very slowly with basis set size when Gaussian type orbitals are used.[339] Recently, it has been shown that basis set extrapolated results obtained from Gaussian-orbital basis set calculations show similar accuracy as plane-wave basis set calculations.[420] The computational cost of studying systems requiring d and f functions using plane-wave basis sets is enormous. Projected augmented-wave methods can be used to solve that problem.[421−423]

One of the major bottlenecks of GW calculations is the calculation of self-energy. Self-energy in the GW framework can be separated into two contributions: exchange (Σ^X) and correlation (Σ^C). In practice, computing Σ^C involves a summation over both occupied and unoccupied states, which presents two major drawbacks. First, this approach does not scale well with system size, and second, in principle, the summation involves an infinite number of unoccupied orbitals. Approaches have been proposed to reduce the scale of this problem by including only a few low-lying states in the summation.[424,425] Such an approach has been used by Tiago and Chelikowsky to study optical excitations in organic molecules, Si clusters, and LiCl (using BSE).[426] Many algorithms have been proposed to avoid consideration of unoccupied orbitals completely in GW calculations.[427−429]

Another computationally expensive part of GW calculations is the calculation and storage of large dielectric matrices and their inverses. The dielectric matrix appears in the calculation of the screened Coulomb potential and self-energy calculations. An early solution to this issue was proposed by using the solid-state analogue of the self-consistent Sternheimer equation for atomic polarizabilities.[430] In this approach, the inversion of the dielectric matrix is avoided using an iterative approach. It also eliminates time-consuming sums over the conduction band. Galli and co-workers used a similar approach, where truncation of the summation over occupied and unoccupied orbitals is determined by a single parameter that can be determined by a convergence test.[431−433] Using this approach, GW calculations have been possible on large solid-state systems with more than 1000 valence electrons in a unit cell. Galli and co-workers calculated quasiparticle energies of Si nanocrystals and solid/liquid interfaces using this approach.[433]

Neuhauser and co-workers have developed a stochastic GW algorithm and applied it to silicon nanocrystals with more than 3000 electrons.[434,435] They have also developed a real-time stochastic approach to describe neutral excitations in finite extended systems based on BSE and applied it to large Si and CdSe nanocrystals.[436]

## 5. COMBINING DFT WITH MULTICONFIGURATIONAL WFT

5.1. Orbital-Dependent Correlation Functionals Based on Multiconfigurational WFT

Doubly hybrid density functionals (also called double-hybrid density functionals and abbreviated here as DHDFs) are functionals in which the estimation of correlation energy includes a WFT-based treatment of excited-state configurations; in that sense the method involves a multiconfigurational treatment of correlation. One should be careful not to confuse this with multireference methods: the reference function is still single-configurational, and the multiconfigurational character is still single-configurational, and the multiconfigurational character is added in a post-SCF fashion in most cases. DHDFs were developed with the same motivation as hybrid functionals. In addition to recovering orbital-dependent nonlocal exchange or a portion of it by WFT, one recovers orbital-dependent correlation energy or a portion of it by wave function theory.[277,437−447] Just as hybrid exchange energy naturally involves integrals over occupied orbitals, doubly hybrid correlation energy naturally involves integrals over unoccupied orbitals, and so it is nonlocal. The earliest schemes of DHDFs involved second-order perturbation theory, and divergences were obtained when the orbitals were optimized in the presence of the correlation functional.[439,443] These divergences can be overcome by a closure approximation[439] or by another method discussed below, but more progress has been made with post-SCF correlation functionals (which are analogous to G_0W_0, which is the most widely used form of GW theory), and we shall discuss these first.

Post-SCF Orbital-Dependent Correlation Functionals. Doubly hybrid functionals in the form most commonly encountered at present were introduced in 2004 by using a multicoefficient approach to mix scaling-all-correlation (SAC) theory with hybrid DFT methods.[442] In the original paper, the added correlation energy was calculated by second-order perturbation theory. One must choose whether to calculate the correlation energy with HF orbitals or with KS orbitals (the KS orbitals being evaluated without the PT1 term). There are pros and cons associated with both choices. With KS orbitals, there should be first-order terms, which are not included in standard Møller−Plesset theory because they vanish with HF orbitals (Brillouin's theorem). In our original work,[442] we did the calculations both ways. We found that we got very similar results with the two kinds of orbitals, and therefore we published only the results with HF orbitals because this did not involve neglecting the first-order term. In the published version of the method, the DFT part was calculated with a polarized triple-ζ basis set and the MP2 part with a polarized double-ζ basis set to keep the cost of the MP2 step low. Despite having two sets of orbitals and two basis sets, the method has analytical gradients and Hessians.

Doubly hybrid methods can be considered in two different ways. They can be considered either to be an extension of density functional methods to include correlation in terms of unoccupied orbitals or an extension of multicoefficient wave function methods based on scaling (for example, SEC,[448] SAC,[449,450] MCG2,[451] MCG3,[452] G3S,[453] and G3SX[454]) to include components of density functional exchange and correlation. The first doubly hybrid methods, combining hybrid DFT with MP2, were named as the multicoefficient three-parameter Becke88-Becke95 (MC3BB) method and multi-
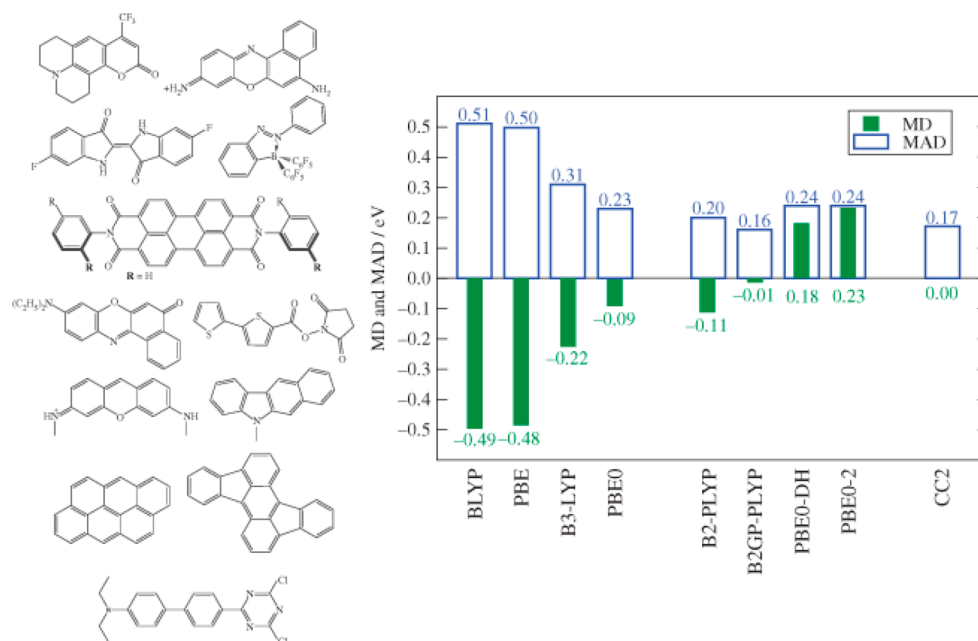
Figure 1. (right) Mean absolute deviations (MADs) and mean deviations (MDs) for electronic excitations in (left) 12 dye molecules computed using different density functionals and the CC2 method. Reprinted with permission from ref 472. Copyright 2014 John Wiley and Sons.

coefficient three-parameter modified Perdew−Wang (MC3MPW) methods.[277,455] A followup[442] to the first doubly hybrid paper went beyond the combination of DFT with second-order perturbation theory and also considered hybridizing DFT with other forms of WFT, like MP4(DQ),[456] QCISD,[457] and coupled cluster theory including CCSD(T), and the inclusion of higher-order correlation greatly improved the accuracy.[458] This work showed that for many problems of interest in chemistry, the doubly hybrid methods yielded higher accuracy for a given cost than either hybrid DFT or conventional WFT, although it did lead to higher basis set superposition error than hybrid DFT. Post-MP2 terms have also ben considered by Chan et al.,[459] who, in contrast to the work discussed above,[442] found that higher-order terms did not improve the results in the way that they included them.

Although the original published work[277,442,460] used HF orbitals for the post-SCF terms, later work by other workers usually used KS orbitals (computed with the truncated energy expression omitting the MP1 term). However, this does not seem to be a major distinction. For example, in a comprehensive test involving 13 nonmetal databases (atomization energies, ionization potentials, electron affinities, hydrogen-atom transfer barriers, heavy-atom transfer barriers, nucleophilic substitution barriers, unimolecular association barriers, alkyl bond energies, hydrogen bonding, charge-transfer, dipole complexes, π−π stacking, and weak interactions), with the M06 density functional for exchange and local correlation, MP2 nonlocal correlation, and a polarized double-ζ basis set, performed as part of the original studies, the mean unsigned error was found to be 0.87 kcal/mol with HF orbitals and 0.90 kcal/mol with KS orbitals; a polarized triple-ζ basis set reduced this to 0.79 kcal/mol with KS orbitals, which compared to 0.94 kcal/mol for straight M06 with the same basis set.[461,462]

Grimme introduced a slightly different approach to DHDF theory by combining KS-DFT and perturbation theory by using separate scaling parameters for the exchange and correlation components of the hybrid KS portion.[445] Exchange-correlation energy (E_{xc}) in this formalism is given by,

$$E_{xc} = (1 - a_x)E_x^{GGA} + a_x E_X^{HF} + bE_c^{GGA} + cE_c^{MP2} \quad (16)$$

where a_x is the HF-exchange scaling parameter, b and c scale the GGA and perturbative correlation contributions, respectively, E_x^{GGA} and E_X^{HF} are local GGA and HF exchange, respectively, E_c^{GGA} is local GGA correlation, and E_c^{MP2} is nonlocal correlation. If $a_x = c = 1$ and $b = 0$, this is MP2; if $a_x = c = 0$ and $b = 1$, this is a GGA. For the local exchange and correlation, Grimme used the B88 exchange functional and the LYP correlation functional. The parameters a_x and c have the values 0.53 and 0.27, respectively. Because there is only 27% of MP2 correlation and the local functional used is poor for noncovalent interactions, this doubly hybrid functional underestimates noncovalent interaction energies. This functional was named B2-PLYP. Grimme and Neese later extended the DHDF method to excited states by adding an excited-state perturbative correlation correction similar to CIS with PT2 treatment of double excitations (CIS(D)).[463,464,446] Analytic gradients were developed for this approach.[465] Variations of the B2-PLYP functional were later reported with different values for the scale parameters.[466−468] Assessments and reviews of these methods are available.[469−473]

Chai and Head-Gordon combined the spin-component-scaled MP2 (SCS-MP2)[474] and long-range corrected functional to develop a doubly hybrid functional called ωB97X-2.[475] SCS-MP2 involves separate scaling of the same-spin component (E_C^{SS}) and the opposite-spin component (E_C^{OS}) in order to increase the accuracy. The total energy for ωB97X-2 can be expressed as,

$$E_{total} = E_{LC-DFT} + C_{ss}E_C^{SS} + C_{os}E_C^{OS} \quad (17)$$

Following the same approach as B2-PLYP, E_{LC-DFT} is computed using the ωB97X KS-DFT functional and nonlocal correlation is added in a post-KS way using the PT2 method. The method provides significant improvement for atomization energies, base-stacking interactions, and symmetric homonuclear radical cations.

In spin-opposite-scaled PT2 (SOS-PT2),[476] the scale factor for same-spin correlation is set to zero to reduce the computational cost. Goerigk and Grimme developed the first DHDF that uses the SOS-PT2 approach; they developed two doubly hybrid meta-GGA functionals: PTPSS (based on the TPSS functional for exchange and correlation) and PWPB95 (based on PW91 exchange and B95 correlation functionals).[477] The functional form is,

$$E_{XC}^{SOS-DHDF} = (1 - a_X)E_X^{DFT} + a_X E_X^{HF} + (1 - c_0)E_C^{DFT} + c_0 E_C^{OS}$$

(18)

where E_X^{DFT} is a local meta-GGA exchange, E_X^{HF} is a nonlocal HF exchange, and E_C^{DFT} is a local meta-GGA correlation. E_C^{OS} is opposite-spin (OS) correlation. Goerigk and Grimme pointed out that including only opposite spin correlation from perturbation theory works for TPSS and B95 correlations as they already include same-spin correlation, but it is important to add both opposite- and same-spin correlations if the LYP functional is used, as it does *not* contain same-spin correlation.

Several variations of SCS-DHDF have been proposed by many groups,[478−481] and very recently a time-dependent approach was implemented for SCS- and SOS-DHDF.[482]

Zhang et al.[483] developed the XYG3 model based on adiabatic connections. Assuming a linear coupling constant dependence of the XC energy, as Becke[117] had done in developing hybrid DFT, one can evaluate E_{XC} using the trapezoidal rule to integrate between 0 and 1. Because the accurate functional for a given value of the coupling constant is not known, they used the value and slope at zero coupling, as determined by second-order Gorling -Levy perturbation theory.[437,438] Zhang et al.[483] obtained good results for heat of formation, reaction barrier heights, and noncovalent interactions. Su et al.[484] applied the XYG3 functional to calculate ionization potentials, electron affinities, and their differences (the fundamental band gaps) by energy derivatives and obtained good results. Su and Xu[485] used the adiabatic connection and scaling constraints to derive a DHDF called PBE-ACDH. Su and Xu also reviewed the performance of XYG3 and PBE-ACDH and earlier methods.[486,487]

Martin and co-workers[488−490] have developed functionals with SCS-MP2 and molecular mechanics dispersion. They used the form,

$$E_{XC}^{DSD-DFT} = (1 - a_X)E_X^{DFT} + a_X E_X^{HF} + c_C E_C^{DFT} + c_0 E_C^{OS} + c_s E_C^{SS} + E_D$$

(19)

In this approach, the scaling factor c_C for local correlation (E_C^{DFT}) is independent of the PT2 correlation scaling factors, c_0 and c_s. All parameters are optimized in the presence of the molecular mechanics damped dispersion term E_D. These approaches are called dispersion-corrected, spin-component scaled doubly hybrid (DSD) DFT. They carried out extensive tests on a large number of different kinds of data and obtained good accuracy.[490]

Sharkas et al. developed functionals based on a single parameter.[491] These functionals may be called density-scaled one-parameter doubly hybrid (DS1DH) and one-parameter doubly hybrid (1DH). DS1DH has the functional form,

$$E_{xc}^{DS1DH} = \lambda E_x^{HF} + (1 - \lambda)E_x + E_c - \lambda^2 E_{c,n_{1/\lambda}} + \lambda^2 E_c^{MP2}$$

(20)

where $E_{c,n_{1/\lambda}}$ is the correlation functional for scaled density $\rho_{1/\lambda}(r) = \left(\frac{1}{\lambda}\right)^3 \rho\left(\frac{r}{\lambda}\right)$. For 1DH, the functional form reduces to

$$E_{xc}^{1DH} = \lambda E_x^{HF} + (1 - \lambda)E_x + (1 - \lambda^2)E_c + \lambda^2 E_c^{MP2}$$

(21)

Later this formula was revised for the high-density limit, and a cubic dependence on λ was introduced.[492] This functional may be called linearly scaled one-parameter doubly hybrid (LS1-DH), and it is expressed as follows:

$$E_{xc}^{1DH} = \lambda E_x^{HF} + (1 - \lambda)E_x + (1 - \lambda^3)E_c + \lambda^3 E_c^{MP2}$$

(22)

Shortly thereafter, Fromager developed a two-parameter generalization of the theory, thus rationalizing a larger class of double hybrid approximations.[493] This work was then used in the formulation of the first CAM-B3LYP-type double hybrid.[494]

Grimme et al. used RPA correlation to develop a functional named PWRB95[495] (use of RPA was also explored earlier in a DFT context[47,496]). The reason for using RPA rather than MP2 is that RPA was believed to be more robust. The general expression for this functional is

$$E_{xc} = aE_X^{HF} + (1 - a)E_x^{GGA} + bE_c^{RPA} + cE_C^{mGGA} + (1 - b)E_c^{NL}$$

(23)

where E_c^{RPA} is the RPA correlation energy, E_x^{GGA} and E_C^{mGGA} are the GGA local exchange and meta-GGA local correlation energies, respectively, and E_c^{NL} is the nonlocal dispersion correction to energy. Here, local and RPA correlations are scaled independently to introduce more flexibility. Core electrons are frozen during the RPA treatment. Because RPA correlation includes long-range correlation leading to dispersion interactions, this part is excluded from E_c^{NL}. They used the PW91 GGA exchange functional and the Becke95 (B95) meta-GGA correlation functional. For nonlocal correlation the VV10 functional is used.

Orbital-Optimized Doubly Hybrid Density Functionals. The doubly hybrid methods discussed so far add wave function correlation in a post-SCF fashion. Another approach is to optimize the orbitals in the presence of the added correlation functional. Orbital optimized second-order perturbation (OO-MP2) theory was developed to optimize HF orbitals in the presence of dynamic correlation.[497] The same approach has been used in the framework of doubly hybrid functionals. Peverati et al. applied this approach to two such functionals, PBE0-DH and PBE0-2.[498] The orbital optimized forms of these functionals are called OO-PBE0-DH and OO-PBE0-2. These functionals show qualitative improvement over conventional DHDFs for the properties of open-shell systems. This approach has been applied to other DHDF functionals as well.[499]

Another approach for self-consistent DHDF was introduced in the framework of the optimized effective potential. This is based on optimizing orbitals in the presence of a fully local potential corresponding to the complete XC energy expression, including the MP2 contribution, of a DHDF.[500] Thus, the KS-DFT one-electron equation becomes,

$$\left(-\frac{1}{2}\nabla^2 + v^{ext}(r) + v_H(r) + v_{xc}^{OEP}(x)\right)\phi(x) = \varepsilon\phi(x)$$

(24)

where v_{xc}^{OEP} is a fully local potential obtained by taking the functional derivative with respect to the density of all energy terms,

$$v_{xc}^{OEP}(x) = \lambda v_x^{HF}(x) + (1 - \lambda)v_x^{DFT}(x)$$
$$+ (1 - \lambda^2)v_c^{DFT}(x) + v_c^{MP2}(x) \quad (25)$$

where λ is a scaling parameter, and v_x^{HF}, v_x^{DFT}, v_c^{DFT}, and v_c^{MP2} are the HF exchange, local exchange, local correlation, and MP2 correlation potentials, respectively. Śmiga et al. applied a one-parameter version of this approach with the BLYP exchange-correlation functional;[500] they found improved accuracy for electron affinities but not for total energies and ionization potentials.

5.2. Building Multiconfigurational Wave Functions from Kohn−Sham Configurations

All the methods explained so far begin with a single-configuration reference state, but they use different approaches to try to recover most of the correlation energy. Although these approaches can be very effective in recovering dynamic correlation energy, they still have difficulty in properly describing static correlation occurring due to near degeneracies. Systems with degenerate or nearly degenerate configurations are inherently multiconfigurational, and starting with a single-configuration reference state is often inadequate with practical methods for including electron correlation (if one used complete configuration interaction, the results would be independent of the reference function, but that is impractical for systems with more than a few electrons). However, a multiconfigurational reference wave function contains not only static correlation but also inevitably some dynamic correlation. Conventional correlation functions are designed to estimate the entire correlation energy, so combining a conventional correlation functional with the energy of a multiconfiguration wave function could involve double counting a portion of the correlation energy. Grafenstein and Cremer[501] used the Colle−Salvetti correlation functional as an anchor point for the derivation of a multireference DFT method and discussed the double counting problem in detail.

DFT/MRCI. An early example[502] of a configuration interaction calculation with Hamiltonian matrix elements obtained using information from DFT is a method called density functional theory with multireference configuration interaction (DFT/MRCI). In this method, information obtained by KS-DFT is used to evaluate an effective Hamiltonian for a multireference configuration interaction calculation. The choice of CSFs to include is based on a simple energy gap criterion. The method has been used successfully for many excited-state calculations,[503−506] although difficulties have also been noted.[507] The method has been extended in various ways.[508,509]

Constrained DFT Configuration Interaction (CDFT-CI). The most straightforward example of adding multiconfigurational wave function features to DFT is to use DFT to generate Hamiltonian matrix elements for a valence-bond-like configuration interaction calculation. This is possible in the framework of constrained DFT (CDFT).[510,511] In KS-DFT, if one uses symmetry constraints, it is possible to optimize not only ground state of a system but also lowest-energy state of any spatial symmetry and multiplicity. Akai and co-workers used this to demonstrate that by using more general constraints, problems related to charge and magnetization fluctuations in solids can be treated.[512]

The basic idea of CDFT is to add a constraint on the electron density such as

$$\int w_C(r)\rho(r)\, dr - N_C = 0 \quad (26)$$

where w_C is a weight function that defines the constraints and N_C is the number of electrons in domain C. For example, w_C can have a value of 1 in the domain C and be 0 everywhere else. Using a Lagrange multiplier to add the constraint to the KS equations yields an extra potential (to be called the constraint potential) in those equations. Wu et al. used this concept to develop a method called CDFT configuration interaction (CDFT-CI).[513] In this approach, different localized states are created using spin and/or charge constraints, and they are used as basis states for CDFT-CI calculations. Once the basis states are chosen, the CDFT-CI calculation can be reduced to

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E\begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \quad (27)$$

in the two-state case. Here $|1\rangle$ and $|2\rangle$ are the two constrained nonorthogonal states and S_{12} is the overlap. These states are nonorthogonal because they are created by using two different constraint potentials. Specific assumptions are needed to evaluate H_{12}. CDFT-CI has had some success in problems where static correlation plays an important role.[514] Figure 2 shows that for the symmetric stretch and bend vibrational modes of the water molecule, single-functional TDDFT fails to describe the conical intersection, while CDF-CI gives results comparable to CASSCF. CDFT-CI has also been successfully used to study mechanisms of singlet-fission in acenes and acene derivatives.[515]
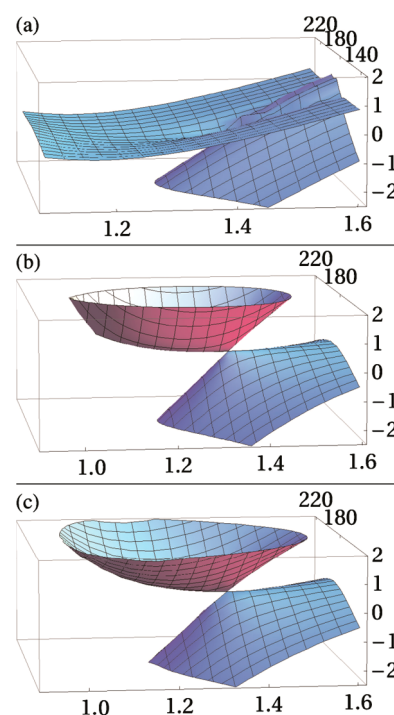
Figure 2. Symmetric water energy manifolds as computed by (a) TDDFT, (b) CDFT-CI, (c) CAS(6,9). Reprinted with permission from ref 514. Copyright 2010 AIP Publishing.

Related approaches were proposed by Mo et al.[516] and Gao et al.,[517] in which they have used block localized wave functions to create initial localized states. A block-localized determinant can be written using block-localized Kohn–Sham (BLKS) orbitals on the fragments m. These BLKS orbitals are linear combinations of the atomic orbitals assigned to the corresponding blocks. Ionic and covalent states are represented by spin-adapted CSFs by combining several determinants. Each state is optimized variationally using KS-DFT, and the resulting states are used as basis states in a CI calculation. Off-diagonal elements are determined by using a transition density functional. In this theory, ground and excited states are treated at the same level, and the method can be useful to study conical intersections and other excited-state properties.[518−520]

5.3. Adding Correlation Functionals to MCSCF Energies

One potential way to improve density functionals is to increase the number of Slater determinants used in the wave function to represent the density. This can be done by an active space method, but first, one has to choose an orbital space, and making such a choice is not straightforward. One of the first such approaches was introduced by Lie and Clementi[521,522] who introduced a correlation functional into an MCSCF wave function that was chosen to give proper dissociation of bonds. More recently, Perez-Jimenez and Perez-Jorda adopted a similar approach incorporating a correlation functional that evaluates a pair of densities obtained from the natural orbitals and occupation numbers as an alternative to the usual spin densities;[523] they obtained good results for the diradical automerization barrier of cyclobutadiene and for energy differences between triplet states and open-shell singlet states.

Colle and Solvetti (CS) proposed a functional for adding correlation to a wave function based on the one- and two-particle density matrices for closed and open-shell systems.[524,525] The correlation energy of this functional correctly goes to zero when the wave function is exact. It was found that this functional produces a total correlation energy with remarkable accuracy although there is significant error in the pair correlations. In spite of this deficiency, the CS method has received considerable attention due to its simple form.[526] The CS functional was found to give accurate results for the excited potential energy surfaces of N_2.[527]

Hartree–Fock Density Functional Theory (HF-DFT). Corongiu proposed the idea to combine HF theory with the Heitler–London (HL) approximation to compute qualitatively correct potential curves for bond dissociation.[528] This HF-HL method accounts for nondynamical correlation and explicitly considers avoided crossings. In a post-HF-HL approach, Clementi and Corongiu proposed the idea of using a density functional to recover the missing dynamical correlation.[529] This HF-HL-DFT approach provided quantitative results for several diatomic bond dissociations.

Gill and co-workers proposed that correlation energy can be calculated using a Wigner intracule.[530] Fondermann et al. extended the idea to calculate correlation energies for light diatomic molecules using HF densities.[531] The method showed only limited accuracy for these systems.

Generalized Valence Bond-Density Functional Theory (GVB-DFT). Kraka combined perfect-pairing generalized valence bond (GVB-PP) multiconfigurational wave functions with the local Vosko–Wilk–Nusair (VWN)[132] LSDA correlation functional to calculate bond dissociation energies of several small molecules.[532] She found that although the GVB method describes homolytic bond dissociation qualitatively correctly, it still shows large errors for dissociation energies, but GVB with LSDA correlation improved the results considerably. Even though this method improved the dissociation energy compared to HF, HF-LSDA, and GVB, it still showed an average error close to 4 kcal/mol.

Natural Orbital Occupation Functional. Following the work of Lie and Clementi,[521,522] Savin developed a method to combine CI and density functional methods.[533] Savin followed an approach where the CI calculation is performed in an orbital space whose composition is based on natural orbital occupation numbers.[533] His method involves a small CI to include near-degeneracy effects, and he added to the CI energy an additional correlation energy that depends in an approximate way on the highest natural orbital occupation number of any of the orbitals not included in the CI. For diatomic C_2, the error in the dissociation energy is 0.1 hartree. To improve the theory, one needs a better approximation for how the additional correlation energy decreases when the size of the CI increases.

CAS-DFT. To develop a theory combining CASSCF with DFT, Savin and co-workers built on two main strategies.[534,535] The first was the use of the on-top pair density Π as an independent variable of the density functional. The on-top pair density is defined as the probability of finding two electrons at a point $\mathbf{r}$, where the two electrons must be of opposite spin in order for the wave function to be antisymmetric when two electrons are permuted. A discussion of the properties of on-top pair densities has been presented by Staroverov and Davidson.[536] Conventional density functionals are based on total density ρ and spin polarization ζ, which is defined at a point $\mathbf{r}$ in real space as

$$\zeta = \frac{\rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r})}{\rho(\mathbf{r})} \tag{28}$$

where ρ_α and ρ_β are the up-spin and down-spin electron densities. If a singlet spin eigenfunction is used, then $\zeta(\mathbf{r})$ is identically zero, and a description based on ρ and ζ would not be able to describe the open-shell singlet that is produced by homolytic bond dissociation. For example, a true singlet has $\zeta = 0$ at all points in space, even for a diradical singlet. KS-DFT describes a diradical singlet only by having excess up-spin at one radical center and excess down-spin at the other, which is not the correct physics. Conventional KS-DFT uses ρ and ζ as independent variables, and conventional functionals use these densities to describe open-shell systems (such as high-spin transition-metal centers or homolytically dissociating bonds) in terms of Slater determinants with broken spin symmetry, but MCSCF wave functions are written in terms of spin-adapted configuration state functions, and for wave functions with the correct spin symmetry, ρ and ζ do not generally provide a useful description of open-shell character. Therefore, ρ and Π are preferred variables when one uses approaches involving spin eigenfunctions, as in conventional multiconfiguration methods.

The second strategy was to use a correlation functional whose magnitude is cut back to account for the correlation energy already presented in the CASSCF calculation. The new correlation functional was developed from a free-electron gas model as in the earlier work[533] of Savin. The XC energy per particle becomes a functional of ρ, Π, and a quantity interpreted as the highest excitation energy included in the CASSCF calculations. Savin and co-workers used this approach to

calculate correlation energies for He and Be atoms and their isoelectronic systems and the potential energy curve of H_2.[535]

The scheme just described was further modified by Grafenstein and Cremer.[537] They focused on the way in which, in a scheme of this type, the correlation functional, ε_c, must depend on the size of the active space (because as the active space increases, it recovers not only static correlation but increasingly more dynamic correlation). For this purpose, Grafenstein and Cremer introduced a scaling factor.[537] To establish an indicator for the size of the active space, they calculated the reference density as,

$$\rho_{ref}(\mathbf{r}) = \sum_i^{occ} 2\phi_i(\mathbf{r})\phi_i(\mathbf{r}) \tag{29}$$

where all the occupied orbitals are considered to be doubly occupied. Then the ratio $\frac{\rho_{ref}(\mathbf{r})}{\rho(\mathbf{r})}$, where $\rho(\mathbf{r})$ is the actualy density, is greater than or equal to 1. The DFT correlation energy is scaled by a factor f (where $0 \le f \le 1$) to avoid double counting. To calculate f, first the correlation energy, $\varepsilon_c(\rho_{ref}(\mathbf{r}),\rho(\mathbf{r}))$ is calculated using $\rho_{ref}(\mathbf{r})$ as the density of the active space. Then all the virtual orbitals are added in the active space, and the correlation energy is recalculated as $\varepsilon_c(\rho_{ref}(\mathbf{r}), \infty)$. The scaling factor is

$$f = 1 - \frac{\varepsilon_c(\rho_{ref}(\mathbf{r}), \rho(\mathbf{r}))}{\varepsilon_c(\rho_{ref}(\mathbf{r}), \infty)} \tag{30}$$

So far in the analysis, the theory assumes that all occupied orbitals are in the active space, but in most conventional CASSCF calculations, there are also inactive occupied orbitals, and with such orbitals, there could be some inconsistencies in the model. Although the scaling factor introduced for the correlation energy eliminates the double counting of some excitations, at the same time it eliminates excitations from inactive to active orbitals. These inconsistencies are ameliorated by adding an extra term to the DFT correlation energy for inactive orbitals by using the core density and the on-top pair density. Then the total correlation energy becomes

$$E_C = E_C^{no\text{-}core} + E_C^{core} \tag{31}$$

This method was applied to study the ring opening of dioxirane and the singlet−triplet splitting in methylene. It was realized that the scaling factor did not entirely remove the double counting, and better definitions of the scaling factor would be needed for more consistent results.[538] Other groups also explored the possibility of using pair-density functionals while trying to avoid double counting in CAS-DFT formalisms.[539,540]

On the basis of sample calculations for carbenes and organic biradicals, Grafenstein and Cremer[541] discussed the advantages and limitations of restricted open-shell singlet DFT and CAS-DFT and gave guidelines for future improvements of DFT methods for multireference problems.

Building on the ideas of Savin[534,535] and Grafenstein and Cremer,[537] Yamaguchi and co-workers introduced an orbital-dependent correlation correction method for CAS-DFT based on the CASPT2 method.[542] Instead of just improving the CASSCF energy with a density functional correction, Yamaguchi and co-workers also modified the CAS-DFT method by self-consistently optimizing both the CI and MO coefficients.[543] Their self-consistent CAS-DFT theory was applied to study excitation energies in atoms and transition metal complexes and magnetic properties of organic radicals and a bimetallic Cu complex.[544−546]

Alternative Density Functionals. Another approach that has been proposed to combine MCSCF methods with DFT is in terms of alternative spin densities.[523,547,548] If we consider a singlet spin eigenfunction, we will have at every position in space

$$\rho_\alpha = \rho_\beta = \frac{1}{2}\rho \tag{32}$$

where ρ_α, ρ_β, and ρ are the alpha, beta, and total densities, respectively. Now consider the H_2 molecule. In the case of MCSCF, the relation 32 is satisfied over the entire H_2 dissociation curve, but if unrestricted HF is used and one scans the internuclear distance in the direction of increasing distance, there occurs at some point an unphysical spin polarization as the single determinant wave function "breaks symmetry" (this is often called the Coulson−Fischer[549] point). To treat this problem, the use of a new kind of expression for the correlation functional has been suggested.[549] For example, for the H_2 dissociation problem, at equilibrium the correlation functional would be $E_C[\rho/2,\rho/2]$, and at the dissociation limit it would be $E_C[\rho, 0]$. To decide when to switch between these two equations, natural orbital occupations are used. The total density can be expressed in terms of natural orbital occupations as

$$\rho = \sum_{i=1}^N n_i \phi_i^2 \tag{33}$$

where ϕ_i is the ith natural orbital, and n_i is its occupation number. Two new densities are defined,

$$\rho_> = \sum_{i,n_i \ge 1} (n_i - 1)|\phi_i|^2 \tag{34}$$

$$\rho_< = \rho - \rho_> = \sum_{i,n_i \ge 1} |\phi_i|^2 + \sum_{i,n_i < 1} n_i |\phi_i|^2 \tag{35}$$

Then the correlation functional is expressed as a functional of these two densities. The total energy is then written as

$$E = E_{MCSCF} + E_C[\rho_<, \rho_>] \tag{36}$$

The LYP correlation functional was used with this approach to calculate magnetic coupling for four materials: NiO, $KNiF_3$, K_2NiF_4, and La_2CuO_4.[547] This alternative electron density approach shows significant improvement over the unrestricted formalism. It has also been applied to several diatomics to calculate their dissociation curves.[547]

Valence Bond-Density Functional Theory (VB-DFT). Valence bond (VB) theory represents a wave function as a linear combination of configurations representing various spin couplings between atom-centered orbitals.[550,551] In the early days of computational chemistry, it was not widely used for quantitative calculations because of the difficulties of handling nonorthogonal configurations, but these difficulties have been largely overcome by the implementation of new algorithms.[552−556] Wu and Shaik combined VB theory with DFT to develop a new method called VB-DFT.[557] In VB theory, the wave function can be expressed as

$$\psi = \sum_K C_K \Phi_K \tag{37}$$

where the Φ_K are CSFs corresponding to VB structures. The energy of the VB-DFT wave function is expressed as,

$$E = E^{\text{DFT}} + E^{\text{VBT}} + E^{\text{int}} \tag{38}$$

where E^{DFT} and E^{VBT} are the DFT and VB energies, respectively, and E^{int} is an interaction term. Effective integrals are built using KS-DFT orbitals to optimize VB orbitals. This method was applied with the B3LYP functional to study the bond dissociation energies of F_2, F_2^-, dihalides, hydrogen peroxide, and dihydrogen dichalcogenides and the retrocyclization of cyclobutadiene.

Ying et al.[558] proposed a method called density functional valence bond (DFVB) in which a DFT correlation term is added to the WFT energy of a VB wave function that accounts for static correlation. They based the approach on the LYP and PW91 correlation functionals. They used this method to calculate singlet−triplet gaps in diradical systems, including C, CH_2, NF, O, O_2, and trimethylenemethane. While some KS-DFT calculations failed to predict the singlet−triplet gap accurately in these molecules, DFVB showed remarkable success, especially with the PW91 functional.

Recently, Wu and co-workers proposed a Hamiltonian matrix correction-based VB-DFT approach where dynamical correlation is recovered by correcting the VB Hamiltonian using DFT XC functionals.[559] This approach was found to improve the accuracy of VB-DFT method when compared with previous approaches.

Core−Valence Electron Correlation. McDouall and co-workers proposed decomposing the total energy in terms of core and valence electron correlation.[560] For a full-CI wave function ψ, they propose dividing the total correlation energy as,

$$E_C = E_C^{\text{core}} + E_C^{\text{valence}} + E_C^{\text{core/valence}} \tag{39}$$

where E_C^{core} is the correlation energy obtained by exciting all the core electrons into all the virtual orbitals, E_C^{valence} is obtained similarly for valence electrons, and $E_C^{\text{core/valence}}$ is obtained from coupled excitations from the core and valence sets. They proposed obtaining E_C^{valence} from an MCSCF calculation and the rest by DFT, using

$$E_{\text{total}} = E_{\text{MCSCF}}(\psi) + E_C(\rho) - E_C(\rho_{\text{valence}}) \tag{40}$$

This method double counts part of the core/valence coupled correlation, but this part is assumed to be small. This method was applied for bond dissociation of several small molecules.[560,561] Later, a scaling factor was added to the total DFT correlation energy,

$$E_{\text{total}} = E_{\text{MCSCF}}(\psi) + E_C(\rho)\left[1 - \frac{N_{\text{valence}}}{N}\right] \tag{41}$$

This approach was applied to the excitation energies of the first-row transition metals, Sc−Cu.[562]

In a similar approach, Hohenstein and co-workers proposed to use CASCI type formalisms and to recover dynamic correlation energy for core orbitals using DFT.[563] In general, in the CASCI formalism, the core orbitals are treated at the HF mean-field level. In their DFT-corrected CASCI approach, they add dynamical correlation of core orbitals by DFT but leave the interactions of active electrons unchanged from the MCSCF wave function. The method was used to study excited-state proton transfer reactions for 10-hydroxybenzo-[h]quinoline[563] and 2-(2-hydroxyphenyl)benzothiazole[564,565] (Figure 3).
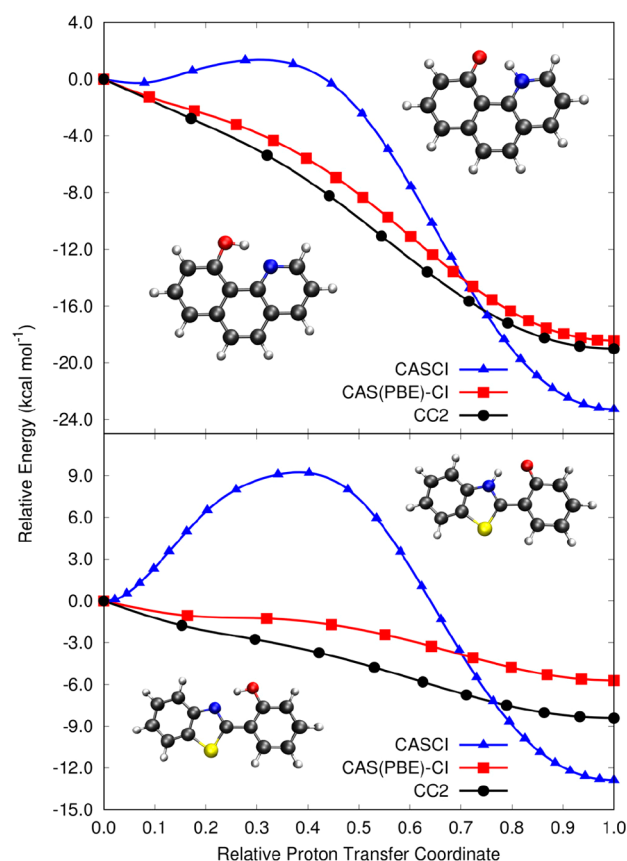
Figure 3. Minimum energy proton transfer path of hydroxybenzo-[h]quinolone (upper panel) and 2-(2-hydroxyphenyl)benzothiazole (lower panel) on the S_1 state computed at the CC2/cc-pVDZ, CISNO-CAS(2,2)-CI, and PBE-corrected CISNO-CAS(2,2)-CI/6-31G* levels of theory. Reprinted with permission from ref 563. Copyright 2017 American Chemical Society.

5.4. Combining DFT with Configuration-Interaction Singles (CIC-TDA, b-D-TDDFT)

An early example[566] of combining the CIS method with DFT is a method called density functional theory with singles configuration interaction (DFT/SCI). This method is basically an empirical predecessor of TDA-TDDFT.

TDDFT, in either the full linear-response formalism or with the TDA, does not yield potential surfaces with the correct topology at S_0−S_1 conical intersections (S_0 denotes the lowest singlet state, and S_1 denotes the first excited singlet state.). The reason for this failure is that the theory explicitly includes only single excitations, and the coupling of the ground state to single excitations vanishes by Brillouin's theorem.

The KS-TDA equations for excited singlet states constitutes an eigenvalue problem,

$$\mathbf{AZ} = \omega\mathbf{Z} \tag{42}$$

where ω is the excitation energy, $\mathbf{Z}$ is the amplitude vector for singly excited configurations, and the matrix elements of $\mathbf{A}$ are,

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (ai|jb) - \frac{X}{100}(ab|ji)$$
$$+ \left(1 - \frac{X}{100}\right)(ai|f_{xc}|jb) \tag{43}$$

where X is the percentage of HF exchange in a hybrid functional, ε_a is a KS orbital eigenvalue, and $(ai|jb)$ is a two-electron integral.

Maitra et al. proposed a scheme called dressed TDDFT (D-TDDFT), where one or a few double excitations are included by going beyond the adiabatic approximation.[567,568] Now, the matrix **A** will have blocks **A**$_{11}$, **A**$_{12}$, and **A**$_{22}$ that are single−single, single−double, and double−double coupling blocks, respectively, and the coupling to double excitations not only corrects the topology of the surfaces but also in principle makes the calculations more accurate. This method has been assessed for excited states in 28 organic chromophores.[569]

Li et al. proposed that the coupling term between ground and excited states be calculated by WFT.[570] Then the coupling term is not zero. This method is called configuration interaction corrected TDA (CIC-TDA). This method was applied to study conical intersections in two systems, ammonia and protonated penta-2,4-dieniminium cation. CIC-TDA removes the unphysical double crossing obtained in both the systems when KS-TDA is used.

In later work, a simpler way was proposed to accomplish this, namely calculate the orbitals with one XC functional and calculate the response with another XC functional.[571,572] This is called the dual-functional TDA (DF-TDA). When the functional used to obtain the orbitals differs from the one used to calculate the response only by replacing local exchange with HF exchange, this is called DF100, and it was used successfully to study the conical intersection regions in ammonia.[572]

5.5. Using Range Separation to Combine DFT with MCSCF Wave Functions

Another way to combine multiconfigurational wave functions with DFT is to use range separation. It has been proposed to represent the short-range interactions with DFT[573] and the long-range interactions by a multiconfiguration wave function. In this approach, the two-electron interaction is divided into short- and long-range terms,

$$\frac{1}{r_{12}} = w_{ee}^{lr,\mu}(r_{12}) + w_{ee}^{sr,\mu}(r_{12}) \tag{44}$$

Both terms depend on a parameter μ (with units of a_0^{-1}) that controls the range separation; this is the same parameter as was called ω in eq 2 in section 3.2 The energy of the system is obtained from the variational principle as

$$E_0^{\mu} = \min_{\Psi}\{\langle\Psi|\hat{T} + \hat{V}_{ne} + w_{ee}^{lr,\mu}|\Psi\rangle + E_{HXc}^{sr,\mu}[\rho(\Psi)]\} \tag{45}$$

where $\hat{T}$ is the kinetic energy operator, $\hat{V}_{ne}$ is the electron−nuclear attraction potential, and $E_{HXc}^{sr,\mu}$ is the short-range Hartree + XC energy which not only depends on density but also on μ.

Leininger et al.[574] expressed the XC functional for the short-range electron−electron interaction in terms of a single determinant and treated the long-range part by a multiconfigurational wave function. This method was applied to Be and Ne atoms and to the dissociation of H_2, N_2, and F_2 molecules, and they found that the short-range local density approximation gave a reasonably reliable estimate of dynamic correlation energy.

Pollet et al. later proposed a scheme for choosing the range parameter μ and the configurations in the CI expansion.[575] For the CI expansion, they wanted to find the smallest configuration space that provides good accuracy. One of the proposed methods is to use natural orbital occupations and use cutoffs to decide which orbitals are to be included in the CI calculations. They used their CI-DFT approach to study dissociation curves of several binuclear molecules with mixed results.

Savin and co-workers[220,576] proposed various possible long-range−short-range separations and assessed their accuracies for various limiting cases. Jensen and co-workers explored the possibility of using a universal μ parameter for all systems.[577] To find an optimal μ value, Jensen and co-workers performed numerical investigations using a small set of systems with and without static correlation, and $\mu = 0.4$ was found to give the best results. Later, a μ value of 0.4 was used to study H_2, N_2, the symmetric dissociation of water,[577] and properties of f^0 actinide systems.[578]

Casanova[579] combined an exchange-correlation functional for short range with a RASCI wave function at long range and used this method in a state interaction mode to calculate excitation energies of organic molecules with a mean unsigned error of 0.3 eV.

Choices of the Wave Function Method for the Long-Range Interaction. Various WFT methods have been combined with DFT using range separation. Toulouse and co-workers proposed a range-separated hybrid MP2 type scheme for studying van der Waals forces using density functionals.[580] This MP2-srDFT approach was found to show remarkable improvement over conventional XC functionals when applied to potential energy curves of rare gas dimers, even when LDA was used for the short-range part. Stoll and co-workers implemented a range-separated hybrid scheme for coupled cluster (CCSD and CCSD(T)) models and studied rare gas dimers with this CCSD(T)-srDFT method.[581] With a triple-ζ basis set, the results with CCSD(T)-srDFT are more accurate than those with CCSD(T).

Jensen and co-workers have combined many-body perturbation theory (MBPT) with short-range DFT with special attention to the update of the srDFT contributions due to the deviation of the density from its zeroth-order approximation, induced by the long-range interaction.[582,583] They also extended the MBPT-srDFT method for MCSCF wave functions using strongly contracted n-electron valence perturbation theory[584] (sc-NEVPT2).[585]

Reiher and co-workers have combined the density matrix renormalization group (DMRG) for long-range interactions with short-range DFT.[586] DMRG is used here basically as a way to perform a CASSCF calculation with a very large active space. This DMRG-srDFT method was applied to study stretched H_2O and N_2 and ligand binding energies to two transition metals. It was found that the effect of active space truncation was much lower for DMRG-srDFT than for DMRG itself. They also used DMRG-srDFT together with polarizable embedding for excited states.[587]

Time-Dependent Range-Separated Methods and Excited States. Time-dependent MC-srDFT (TD-MC-srDFT) was developed where the long-range interaction was described by TD-MCSCF and the short-range interaction by TDDFT.[588] In this way, it is possible to explicitly model double excitations because the wave function becomes multideterminantal. The TD-MC-srDFT method was applied with LDA and GGA functionals for short-range interaction to stretched H_2 and to the 1^1D doubly excited state of Be. The method was also applied with a short-range GGA functional to study low-lying singlet excited states in d^6 metallocene ferrocene. When compared with experiments, TD-MC-srDFT performs well for both valence and charge-transfer excitations. The accuracy of TD-MC-srDFT depends on the short-range functional used. Using the μ-dependent short-range exchange-correlation functional of Goll et al.,[589] which is based on the PBE functional, the accuracy of the method has been tested[588] for some valence and charge-transfer excitations in hydrogen chloride and for some

organic chromophores: a dipeptide, a β-dipeptide, a tripeptide, N-phenyl pyrrole, 4-(N,N-dimethylamino)benzonitrile, and retinal chromophore.[590] This TD-MC-srPBE method performs better than KS calculations with the B3LYP global hybrid density functional, especially for charge-transfer excitations, but it is less accurate than the range-separated functional CAM-B3LYP. TD-MC-srDFT has also coupled with polarizable embedding (PE) model to study solvatochromic effect on electronic spectra.[591] PE-TD-MC-srDFT was used to study the solvent effect on low-lying excitations in acetone, uracil, and channel rhodopsin protein. The performance of TD-MC-srDFT has also been tested for singlet valence excitations in a larger set of organic molecules (Figure 4).[592]
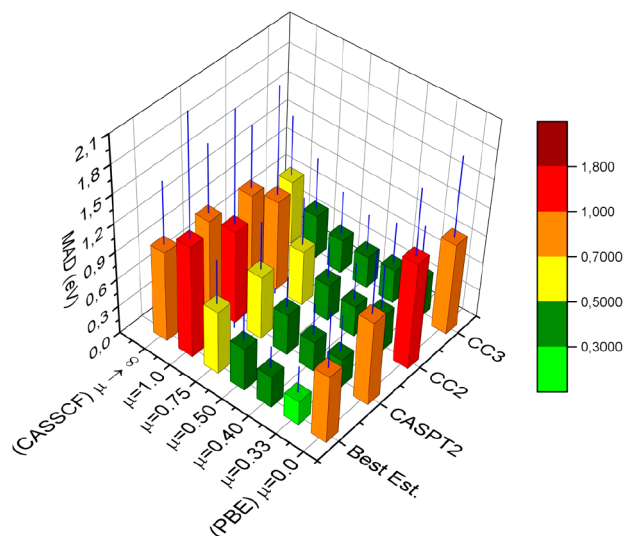
Figure 4. Mean absolute deviation for CAS-srPBE with various values of μ (defined in eq 2) against CC2, CC3, and CASPT2 methods for electronic excitations in organic molecules. Reprinted with permission from ref 592. Copyright 2016 American Chemical Society.

5.6. Embedding Multiconfigurational WFT in DFT

A quite different way to combine a multiconfiguration wave function with DFT is to use embedding theory.[315,593−595]

Govind et al. developed an embedding scheme that is capable of treating an embedded region with correlated WFT methods in a periodic DFT framework.[596,597] This embedding method was later used to study local excitation of a carbon monoxide molecule adsorbed on Pd surface.[598,599]

Gomes et al. used a coupled cluster wave function for embedded systems in a nonperiodic framework to study the solvatochromic shift of acetone in water and $f−f$ spectrum of NpO_2^{2+} embedded in a $Cs_2UO_2Cl_4$ crystal.[600] The approach they use can allow for a seamless approach of WFT to a region treated as a frozen density.[601]

Goodpaster, Manby, Miller, and co-workers[602−607] developed general quantum-embedding theories that treat different regions of the system at different levels of accuracy, including the possibility of a correlated WFT calculations in a small region, such as an active site of a catalyst, and a less accurate, but more computationally efficient description of the remainder; these methods can then be used to perform first-principles studies on large, reactive, and condensed-phase systems. The method has recently been applied to calculate excited electronic states of a ruthenium nitrosyl model.[608] In another application,[609] coupled cluster calculations were carried out for the $S_0−S_1$ excitation of

acrolein in up to 37 water molecules (involving 1737 basis functions), where the water molecules were treated by KS theory; this calcualtion was labeled eEOM-CCSD to denote embedded EOM-CCSD. For a smaller cluster with only four water moecules, eEOM-CCSD agrees with full EOM-CCSD within 0.01 eV.

Daday et al. developed an embedding scheme with CASSCF, CASPT2, coupled cluster, and quantum Monte Carlo wave functions for nonperiodic systems and applied the method to study electronic excitations in p-nitroaniline, s-cis-acrolein, methylenecyclopropane, and anionic p-nitro-phenolate in the presence of solvent molecules.[610,611]

Prager et al.[612,613] combined frozen-density embedding theory with the second-order and third-order ADC scheme for calculating electronic excitation energies. Höfener and Visscher[614,615] combined frozen-density embedding theory with the CC theory for calculating electronic excitation energies. The frozen density can be obtained by either WFT or DFT.

Dresselhaus et al.[616] embedded a self-consistent DMRG calculation (basically a CASSCF calculation) in a frozen-density environment treated by DFT; this embedding scheme is also suitable for excited states.

Hégely et al.[617] compared several strategies for combining WFT and DFT by embedding.

5.7. Combining Density Functionals with WFT Kinetic Energies and Densities

A radically different approach to combining WFT and DFT is to extend the original ansatz of Kohn and Sham, applied by them to a Slater determinant, to a multiconfigurational wave function as explained next. Kohn and Sham calculated the kinetic energy and the classical Coulomb energy from a Slater determinant and approximated the rest of the energy (correction to the kinetic energy, entire exchange energy, and entire correlation energy) by a density functional. The analogue used in the method discussed in this subsection is to calculate the kinetic energy and the classical Coulomb energy from a multiconfigurational wave function and approximate the rest of the energy (correction to the kinetic energy, entire exchange energy, and entire correlation energy) by a density functional. A key aspect of this approach is that the multiconfigurational wave function should be a spin eigenfunction (eigenfunction of S^2 as well as S_z, where S is total electron spin). Because the conventional XC functionals of KS-DFT give reasonable results for many open-shell systems only by utilizing unphysical ρ_α and ρ_β densities obtained from unrestricted (i.e., spin-polarized) Slater determinants with broken spin symmetry, they are not appropriate for use with spin eigenfunctions. Therefore, the density functional in the approach discussed in this section is based on the total density ρ (the sum of ρ_α and ρ_β) and the on-top pair density Π. The use of on-top pair densities in various ways in the context of DFT has a long history.[534,535,540,575,618−623] The method described in this paragraph is called multiconfiguration pair-density functional theory (MC-PDFT),[624,625] and the density functionals expressed in terms of ρ and Π are called on-top functionals.

In KS-DFT, the total density is

$$\rho = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r}) \tag{46}$$

the spin magnetization density is given by

$$m = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r}) \tag{47}$$

and the spin polarization is given by eq 28, which can be also be written as

$$\zeta = m(\mathbf{r})/\rho(\mathbf{r}) \qquad (48)$$

As introduced in the previous paragraph, instead of using spin-labeled densities, the MC-PDFT method uses $\rho(\mathbf{r})$ and $\Pi(\mathbf{r})$ as fundamental variables for density functionals,[534,618,626,627] where $\Pi(\mathbf{r})$ represents the on-top two-particle density at a point $\mathbf{r}$ in space. A discussion of the properties of on-top pair densities has been presented by Staroverov and Davidson.[628] For a single Slater determinant, we have the relation

$$\zeta = \left(1 - \frac{\Pi(\mathbf{r})}{[\rho(\mathbf{r})/2]^2}\right)^{1/2} \qquad (49)$$

and this is used to motivate well-defined protocols to translate a standard spin-polarized XC functional, which is expressed in terms of ρ and m and the magnitudes of their gradients, into a pair-density functional. The GGA that has been most extensively tested for translation is PBE, and the resulting on-top functional is labeled as tPBE; it includes the gradients of ρ and Π, which has a discontinuous derivative. To include the gradient of Π, another kind of translation was proposed.[629] Functionals with the latter kind of translation are called fully translated or "ft" functionals.

Running an MC-PDFT calculation involves the following five steps:

(1) One- and two-body density matrices are obtained from a standard MCSCF calculation or other CI calculation (e.g., RASCI).

(2) The density is calculated from the one-body density matrix, and the on-top density is calculated from the two-body density matrix.

(3) The MCSCF wave function of step (i) is used to calculate the kinetic energy of electrons, and the electron−nuclear attraction energy and the classical electron−electron repulsion energy are calculated from the density of step (ii).

(4) The on-top energy is calculated as an integral over all space of the product of the density and the on-top energy density functional, which is a function of the density, the on-top density, and their gradients (in future work, one could include more ingredients in the on-top density functional).

(5) The energies of steps (iii) and (iv) are summed to obtain the total MC-PDFT energy.

The cost of an MC-PDFT calculation is dominated by the cost of an MCSCF calculation. In one study, the timing and memory requirements of CASPT2 and MC-PDFT were compared with respect to system size;[630] while CASPT2 has larger memory and time requirements, MC-PDFT is similar to CASSCF in this regard for the same system size (Figure 5). In another study,[71] comparisons were made for the NF diatomic molecule, using CASSCF with an active space of 12 electrons in 14 orbitals. This involves 2.1 M CSFs. Adding external correlation by CASPT2 required 61 min of computer time and 1.3 GB of storage; in contrast, the post-SCF step of MC-PDFT required 1 min of computer time and 1 MB of storage.

The MC-PDFT method has been applied to a variety of applications for calculating both ground- and excited-state properties. The ground-state applications include potential energy curves,[624] main-group bond energies,[68,629,631] transition-metal bond energies,[72,75,629,631] proton affinities,[629,631] hydrogen bonding,[629,631] chemical reaction barrier heights,[631] reaction energies,[629−631] and charge-transfer complexes.[632] The excited-state properties include atomic excitation ener-
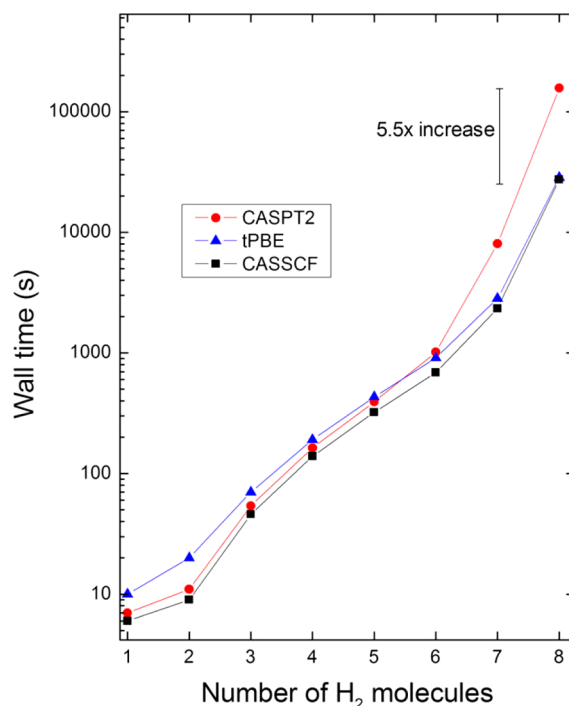
Figure 5. Timing information for calculations on hydrogen molecule systems. A $(2n,2n)$ active space, where n is the number of hydrogen molecules, is used. The MC-PDFT and CASPT2 times are cumulative, containing both the time used to calculate the MCSCF wave function and the time used during the post-SCF step. The cc-pVQZ basis set was used. Reprinted with permission from ref 630. Copyright 2017 AIP Publishing.

gies,[624,633] molecular excitation energies of valence, Rydberg, and charge-transfer states for both main-group and transition-metal compounds,[74,624,629,632−638] spin-splittings,[71,76,639,640] and excited-state geometries.[74]

MC-PDFT has been applied to long-range intermolecular charge-transfer excitations (Figure 6) and ground-state charge-transfer complexes. In both the cases, MC-PDFT performs remarkably well compared to KS-DFT with the parent density
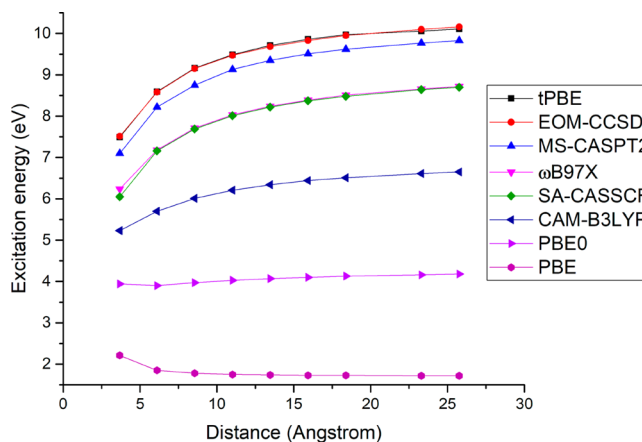
Figure 6. Distance dependence of $^1A_1$ charge-transfer excitation energies for $NH_3\cdots HNO_2$. Note that the tPBE curve is visually indistinguishable from and hidden by the EOM-CCSD curve, and the ωB97X curve is visually indistinguishable from and hidden by the SA-CASSCF curve. This is a modified (for clarity) version, used with permission from ref 632. Copyright 2015 American Chemical Society.

X

functional, from which the translated functional for MC-PDFT was obtained. Particularly for intermolecular charge-transfer excitations, where PBE severely underestimates excitation energies, tPBE gives accurate results and also shows the correct asymptotic behavior.[632] When MC-PDFT was tested for a larger data set of 23 electronic excitations for 18 organic molecules, overall it was found to perform as well as CASPT2. While TDDFT shows instability when larger basis sets with more diffuse functions are used, it was shown MC-PDFT results is not nearly as strongly affected by this increase in basis set size for atomic excitations.[633]

Three other applications of MC-PDFT to electronic excitations involving charge-transfer character were also carried out. Ensemble-averaged calculations were carried out for a retinal molecule with 64 atoms, and they reproduced the experimentally determined absorption bandwidths and peak positions better than CASPT2.[635] For MnO_4^-, MC-PDFT accurately predicts the spectrum at a significantly reduced cost as compared to RASPT2.[637] For organic photoredox catalysts (each with 56 atoms), MC-PDFT was applied with a RASCI reference state because CASSCF wave functions with the required large size of the active space would be too large; the calculations gave an accurate description of the experimental optical absorption spectra.[638]

Various active space choices have been proposed to reduce the cost of the MCSCF calculations without significantly diminishing the accuracy of the MC-PDFT. One of such active space choice proposed in the framework of GASSCF is called the separated pair (SP) approximation.[68] The SP approximation is a special case of GASSCF in which no more than two orbitals are included in any GAS subspace and intersubspace excitations are excluded. The SP approximation typically leads to far fewer configurations than CASSCF for the same number of electrons and orbitals in the active space. SP-PDFT (MC-PDFT based on an SP wave function) reproduces the accuracy of CAS-PDFT (MC-PDFT based on the CASSCF wave function) for predicting singlet−triplet gaps in open-shell singlet systems, methylene and ozone. GASSCF reference wave functions were also used to study singlet-triple gaps in acene series. By using GAS partition, it was possible to extend the active space size to 50 electrons in 50 orbitals for dodecacene with much lesser number of CSFs compared to full CASSCF wave function.[639] When compared with available literature values, MC-PDFT gives remarkably accurate results even with simplified wave functions for these systems.

MC-PDFT was also applied to spin-state ordering in iron complexes with 13−25 atoms. MC-PDFT was able to reproduce the spin-state ordering found in more computationally demanding CASPT2 WFT calculations in four out of five cases, and the dependence on the ligand field strength was also reproduced.[640]

Additional applications to electronic excitation energies were also successful. A test on 23 electronic excitations valence, Rydberg, and charge-transfer character give a mean unsigned deviation from best estimates of only 0.20 eV compared to 0.21 eV for CASPT2.[634] For a test on the first three doublet excitation energies of the doublet CN radical, the tPBE calculation gave a smaller mean unsigned error than all three EOM coupled cluster methods (including one with quasiperturbative triple excitations), than all 10 TDDFT methods tested and than CASSCF, MRCISD, and MS-CASPT2; results for the fourth excited state were less accurate.[73] A final application to be mentioned addressed the important issue of the selection of the active space.

An automatic three-step selection scheme was proposed and applied to the first five excitation energies of a set of 10 doublet radicals.[636] The scheme was successful for MC-PDFT calculations on all 10 systems; one is cautioned that the automation will not necessarily work on other kinds of systems; further study of this aspect is required.

MC-PDFT is currently available in the *Molcas* code.[641] Analytic gradients are available.[642]

Theoretical analysis has included a study of the on-top pair density as a measure of on-top correlation energy[643] and a study of the active space dependence of the components of the MC-PDFT energy.[644] It has been shown that MC-PDFT suffers less from delocalization error, which is a big source of error in KS-DFT.[645] It was also shown that MC-PDFT with local on-top functionals has smaller errors for systems prone to self-interaction error than does CASSCF, which has no self-interaction error.[646]

Scuseria and co-workers followed the same approach used in MC-PDFT, but to avoid the cost of MCSCF calculations, they obtained their density from pair coupled cluster doubles (pCCD)[647] calculations.[648] The pCCD method does not apply to open shells, but for closed shells, it works well for multireference systems, while it shows polynomial scaling with the system size.[647] Range separation technique is also used in the pCCD-DFT method.[649,650] The pCCD-DFT methods have been used to study bond dissociation in small molecules, for example, the dissociation of the C−O bond in form-aldehyde.[647−650]

6. CONCLUDING REMARKS

The shortcomings of methods based either solely on wave functions, and of methods based solely on density functionals, have led to the emergence of an interesting new class of hybridized methods that combine the cost-efficiency of DFT with the potentially higher accuracy of WFT. This review considered various types of combined DFT and WFT approaches, with special emphasis on methods that are useful (or potentially useful) for excited states. Excited states tend to be multiconfigurational in nature, and hence modeling them is challenging from both the qualitative and quantitative points of view. The qualitative aspect can be taken care of by using a multideterminant wave function such that the multiconfigurational excited state is treated properly with correct spin symmetry (and, optionally, also correct spatial symmetry), and the quantitative aspect can be taken care of by combining multiconfigurational WFT with DFT such that both static and dynamic correlation are treated in a balanced way.

One of the major challenges for these theories is the double counting of electron correlation. Recently developed MC-PDFT tries to solve this problem by using only the kinetic energy, density, and on-top pair density from a multiconfigurational wave function and recovering electron correlation and exchange energies entirely from a density functional. Building on previous work, MC-PDFT has been developed in terms of functionals that depend on both the density and the on-top pair-density. The first such functionals have been derived from KS-DFT functionals, but future development of the theory may involve developing new functionals specifically based on both the density and pair density.

Efforts to combine WFT and DFT have seen intense evolution in last two decades. Development of these new combined theories has also benefited both DFT and WFT in their uncombined forms by having introduced new ideas that

have extended their individual applicabilities. As researchers propose new ideas, it is also important to re-evaluate some old concepts that were underestimated, forgotten, or abandoned. We hope that this review sheds some light on both the old and the new.

It is not only that new theories have been developed in the past decade; computational power and algorithmic efficiency have increased as well. Many theories that were only applicable to small or model systems are now applied regularly to medium or large chemical systems. For example, one theory that has probably received the most attention in this respect is the GW method, where new algorithms have made it possible to apply the GW method to systems with hundreds of atoms in a (solid-state periodic) unit cell. More and more publicly available software packages are now supporting GW calculations for molecular systems, and this availability is an important aspect of making this theory more popular among chemists and physicists.

We conclude by noting that while various ways to combine WFT and DFT have been proposed and implemented over recent decades, many of the concepts still remain at a developmental stage. New ideas are being introduced to make these theories more accurate and more widely applicable to a variety of problems in chemistry and materials science. With the availability of ever growing computational resources and the introduction of new algorithms, we anticipate continued progress in this area.

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Notes

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Laura Gagliardi obtained her Ph.D. degree from the University of Bologna, Italy, in Theoretical Chemistry. After a postdoctoral appointment at Cambridge, U.K., she began her independent career as an Assistant Professor in Italy at the University of Palermo. She then moved as Associate Professor to the University of Geneva, Switzerland. In 2009, she moved to the University of Minnesota as Professor of Chemistry, and since 2014 she has been a Distinguished McKnight University of Minnesota Professor. She has been recognized as a fellow by the American Physical Society and by the Royal Society of Chemistry. Her scientific interests involve the development of novel quantum chemical methods for strongly correlated systems and the combination of first-principle methods with classical simulation techniques. The applications are focused on the computational design of novel materials and molecular systems for energy-related challenges. Special focus is devoted to modeling catalysis and spectroscopy in molecular systems, catalysis and gas separation in porous materials, photovoltaic properties of organic and inorganic semiconductors, and separation of actinides. She serves as associate editor of the ACS *Journal of Chemical Theory and Computation* and as Director of the Chemical Theory Center at the University of Minnesota.

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LIST OF ABBREVIATIONS AND ACRONYMS

1DH	one-parameter doubly hybrid functional
a_0	bohr $\cong$ 0.5292 Å
ACDH	adiabatic connection doubly hybrid density functional
ADC	algebraic diagrammatic construction scheme
AE6	atomization energies of six molecules
AOs	atomic orbitals
B3LYP	Becke, 3-parameter, Lee–Yang–Parr density functional
B05	Becke's 2005 nondynamical-correlation functional
B95	Becke's 1995 density functional
BH6	barrier heights of six reactions
BLKS	block-localized Kohn–Sham
BLYP	Becke-Lee–Yang–Parr exchange-correlation functional
BNL	Baer, Neuhauser, and Livshits
BSE	Bethe–Salpeter equation
CAM-B3LYP	Coulomb-attenuating method B3LYP
CASCI	CI where the configuration list is defined as in CASSCF but the orbitals are not optimized self-consistently
CAS-PDFT	complete-active-space pair-density functional theory
CASPT2	complete-active-space PT2
CASSCF	complete-active-space SCF
CBS	complete basis set, i.e., complete orbital basis
CC	coupled cluster
CCI	complete configuration interaction
CCSD	coupled cluster singles and doubles
CCSD(T)	coupled cluster singles doubles with connected triple excitations included noniteratively
CCSD(T)-srDFT	CCSD(T) with short-range DFT
CDFT	constrained DFT
CDFT-CI	constrained DFT configuration interaction
CI	configuration interaction
CIC-TDA	configuration interaction corrected Tamm–Dancoff approximation
CIS	configuration interaction with single excitations
CS	Colle and Solvetti
CSF	configuration state function
DAC	diabatic-at-construction
DFT	density functional theory

DFT/MRCI	density functional theory with multireference configuration interaction
DFT/SCI	density functional theory with singles configuration interaction
DF-TDA	dual-functional TDA
DF100	DF-TDA where the functional used to obtain the orbitals is obtained from the functional used to compute the response by replacing local exchange with 100% HF exchange
DFVB	density functional valence bond
DHDFs	doubly hybrid density functionals
DMRG	density matrix renormalization group
DMRG-srDFT	density matrix renormalization group with short-range DFT
DS1DH	density-scaled one-parameter doubly hybrid density functional
DSD	dispersion-corrected, spin-component scaled doubly hybrid density functional
D-TDDFT	dressed time-dependent DFT
EOM	equation-of-motion (linear response method)
erf	error function
erfc	complementary error function
FCI	full configuration interaction
FORS	fully optimized reaction space
G3X	Gaussian-3 extended dual-level method
GASSCF	generalized active space SCF
GGA	generalized gradient approximation
GKS	generalized KS
GVB	generalized valence bond (usually used as shorthand for GVB-PP)
GVB-PP	GVB with the perfect-pairing restriction
GW	Green's function (G) screened Coulomb (W) approximation (to the self-energy)
GW_0	partial scGW method
G_0W_0	single-shot GW method in which KS-DFT orbitals and orbital energies are used to construct the self-energy noniteratively
HBT	2-(2-hydroxyphenyl)benzothiazole
HF	Hartree–Fock
HF-DFT	Hartree–Fock DFT
HISS	Henderson–Izmaylov–Scuseria–Savin
HL	Heitler–London
HSE06	Heyd–Scuseria–Ernzerhof
HTBH38	hydrogen transfer barrier heights of 38 reactions
KS	Kohn–Sham
KS-DFT	Kohn–Sham DFT
LC	long-range corrected
LCAO	linear combination of atomic orbitals
LDA	local density approximation (the special case of LSDA for closed-shell singlets)
Lh-BLYP	local hybrid functional based on Becke-88 exchange and Lee–Yang–Parr correlation
LMF	local mixing function
LRS	locally range-separated
LR-TDDFT	linear response time-dependent DFT
LS1-DH	linearly scaled one-parameter doubly hybrid
LSDA	local spin-density approximation
LYP	Lee–Yang–Parr
MAD	mean absolute deviation

MBPT	many-body perturbation theory (same as Møller–Plesset perturbation theory)
MBPT-srDFT	many-body perturbation theory with short-range DFT
MC3BB	multicoefficient three-parameter Becke88–Becke95 density functional
MC3MPW	multicoefficient three-parameter modified PW91 density fictional
MC-PDFT	multiconfiguration pair-density functional theory
MC-QDPT	multiconfiguration quasidegenerate perturbation theory
MCSCF	multiconfiguration SCF
MDs	mean deviations
MO	molecular orbital
MP2	Møller–Plesset PT2 (same as second-order MBPT)
MRCISD	multireference CI with (all) single and double excitations
MRPT2	multireference PT2
MS-CASPT2	multistate complete active space PT2
MUE	mean unsigned error
NGA	nonseparable gradient approximation
NHTBH38	non-hydrogen-transfer barrier heights of 38 reactions
OEP	optimized effective potential
OO-MP2	orbital optimized PT2
ORMAS	occupation-restricted multiple active space
OS	opposite-spin
PBE	Perdew–Burke–Ernzerhof exchange-correlation functional
pCCD	pair coupled cluster doubles
PDFT	pair-density functional theory
PE	polarizable embedding
PKZB	Perdew–Kurth–Zupar–Blaha exchange-correlation functional
PT	perturbation theory
PT1	first-order perturbation theory
PT2	second-order perturbation theory
PTPSS	reoptimized TPSS exchange and correlation; SOS-PT2 correlation, fitted together with DFT-D3 dispersion correction
PW91	Perdew–Wang 1991 density functional
PWPB95	reoptimized PW91 exchange and B95 correlation, SOS-PT2 correlation, fitted together with DFT-D3 dispersion correction
QP-scGW	quasiparticle self-consistent GW method
RASCI	CI where the configuration list is defined as in RASSCF but the orbitals are not optimized self-consistently
RASSCF	restricted active space SCF
RASPT2	restricted-active-space PT2
RPA	random phase approximation
SAC	scaling-all-correlation
SA-CASSCF	state-averaged complete-active-space SCF
SA-GASSCF	state-averaged generalized active space SCF
SA-MCSCF	state-averaged multiconfiguration SCF
SCF	self-consistent field
scGW	self-consistent GW method
sc-NEVPT2	strongly contracted n-electron valence perturbation theory (second order)
SCS-MP2	spin-component-scaled MP2
SOS-PT2	spin-opposite-scaled PT2
SP	separated pair
SS	same-spin
SVWN	"Slater–Vosko–Wilk-Nusair", a misnomer for the density functional consisting of Gáspár–Kohn–Sham exchange and VWN correlation
TDA	Tamm–Dancoff approximation
TDDFT	time-dependent DFT
TD-HF	time-dependent Hartree–Fock
TD-MC-srDFT	time-dependent multiconfiguration with short-range DFT
TPSS	Tao–Perdew–Staroverov–Scuseria density functional
VB	valence bond
VB SCF	valence-bond SCF
VV10	Vydrov–Van Voorhis 2010 density functional
VWN	Vosko–Wilk–Nusair correlation functional
WFT	wave function theory
XC	exchange-correlation
XYG3	Xu–Zhang–Goddard 3-parameter density functional

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