

# Hybrid functionals with system-dependent parameters: Conceptual foundations and methodological developments

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## Funding information

National Key Research and Development Program of China, Grant/Award Number: 2016YFB0701100; National Natural Science Foundation of China, Grant/Award Numbers: 21673005, 21621061

## Abstract

Approximate density-functional theory (DFT) has become the major workhorse of modern computational chemistry and materials science, but the most widely used DFT approaches, local-density approximation (LDA) and generalized gradient approximation (GGA), suffer from some fundamental deficiencies, including, in particular, the band gap problem. As a relatively cheap way to overcome the difficulty confronted by LDA/GGA, hybrid functional methods have attracted tremendous interest, first in molecular quantum chemistry, and more recently also in computational materials science. While early hybrid functionals use fixed parameters that are determined either by fitting some standard experimental database or based on theoretical arguments, recent studies have clearly indicated that the hybridization parameters carry on the physical significance and therefore should be system-dependent. Developing theoretical methods to evaluate those parameters in a first-principles manner has become one of the most active frontiers in theoretical chemistry community, and various schemes have been proposed. In this article, we aim at giving a systematic overview on the main theoretical concepts underlying various strategies and review major methodological developments in the recent years.

This article is categorized under:

Structure and Mechanism > Computational Materials Science

Electronic Structure Theory > Ab Initio Electronic Structure Methods

Electronic Structure Theory > Density Functional Theory

## KEYWORDS

Density-functional theory, Hybrid functionals, Band gap problem, Dielectric dependent hybrid functionals, Screened exchange, Piece-wise linearity condition, Range separated hybrid functional

## 1 | INTRODUCTION

Kohn–Sham (KS) density-functional theory (DFT)<sup>1–4</sup> has become the most widely used theoretical tool to calculate electronic structure of a large variety of systems including complex molecules, clusters, bulk materials, surfaces, and interfaces, due to its favorable trade-off between accuracy and cost.<sup>5–7</sup> The essence of KS-DFT is to map the ground state of an interacting many-electron system to that of a non-interacting system with the same electron density, which converts

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the complex many-body problem formally into a greatly simplified one-body problem.<sup>8,9</sup> All many-body effects are included in the exchange-correlation (xc) functional ( $E_{xc}$ ), whose exact form is unknown and has to be accessed by some density-functional approximation (DFA).<sup>10</sup> Being the earliest practiced DFAs, local-density approximation (LDA) and generalized-gradient approximation (GGA) are able to give accurate description for many properties, especially those related to ground state total energy or electron density, such as equilibrium lattice constant, compressibility, and phase stability, with relatively low computational cost.<sup>11</sup>

However, the accuracy of electronic band structure obtained from KS-DFT based on LDA/GGA suffers from the so-called band gap problem.<sup>12</sup> In principle, the major properties with explicit physical meaning which KS-DFT can offer are electron density and the ground-state total energy, but a set of single-particle wave functions with particular energies are also given by solving the KS equation. The latter, while not physically meaningful except for the highest occupied one, which will be elaborated in the next section, is compatible with the electronic band structure theory in the mean-field picture and is employed to interpret the electronic structure properties of materials and molecules under certain conditions.<sup>13</sup> Although the KS spectrum in LDA/GGA can often offer a good qualitative description for many materials, it is not satisfactory from a quantitative point of view. For semiconductors such as Si and GaAs, the bandgap obtained by using energies of frontier orbitals from LDA/GGA-based KS-DFT is systematically underestimated, and many narrow-gap semiconductors, for example, Ge and InN, are wrongly predicted to be semi-metallic or metallic.<sup>14</sup> This problem can be partly attributed to the self-interaction error (SIE) in LDA/GGA, namely, the error that results from the spurious interaction of an electron with itself, and in turn raises and lowers the energies of orbitals in the occupied and unoccupied regime, respectively.<sup>15</sup>

In the past decades, significant developments have been made to fully understand the physical origin of the band gap problem and overcome it within the DFT framework. Notably, hybrid functionals, which admix a certain fractional portion of Hartree–Fock (HF) exact exchange (EXX) in  $E_{xc}$ , have achieved remarkable success.<sup>16–20</sup> The early development of the hybrid functionals<sup>21,22</sup> was motivated by the adiabatic connection formalism of the exact exchange-correlation functional,<sup>23</sup> which will be discussed in more details in the following section. The success of the hybrid functionals to the band gap problem can be partly attributed to the error cancellation between LDA/GGA, which usually underestimates the band gaps, and the HF method, which tends to overestimate the band gaps of solids dramatically.<sup>16,24</sup> One can expect that an appropriate admixture of EXX and LDA/GGA may lead to a compromised band gap in better agreement with experiment. Moreover, since HF is self-interaction free, the SIE can be partially alleviated when EXX is built into  $E_{xc}$ . In 1990, Bylander and Kleinman introduced the EXX with a short-ranged screened Coulomb interaction, instead of a bare one. This method, later termed as SX-LDA,<sup>25</sup> predicts the band gaps of semiconductors in greatly improved agreement with experiment compared to LDA/GGA.<sup>16,25</sup> In a different context, Becke proposed a hybrid functional with equal fractions of EXX and LDA/GGA, based on the adiabatic connection formulation of the xc functional.<sup>21</sup> While different approaches to include EXX were suggested, the theoretical justification for the use of the nonlocal xc potential, as typically practiced in hybrid functionals, was missing in the DFT framework. The KS framework requires  $V_{xc}$  being a local potential, and for hybrid functionals that are explicit functionals of KS orbitals, and therefore implicit functionals of density, it is necessary to use the optimized effective potential (OEP) approach to obtain the local  $V_{xc}$ .<sup>26–28</sup> This conceptual difficulty was solved by the generalized KS (GKS) theory proposed by Seidl et al. in 1996,<sup>25</sup> in which a nonlocal effective potential is allowed by making use of the constrained-search technique. GKS lays the foundation for manipulating and optimizing orbital-dependent density functionals to approach the exact limit in a more flexible way.<sup>28</sup>

A hybrid functional that is universally applicable for a wide range of systems is then in order. Early strategies in searching for the optimal hybrid functional mainly involve the determination of the global fraction of Fock exchange. This is done either by theoretical analysis along with empirical observation,<sup>29</sup> or parameterizing against some experimental data sets to obtain minimal training error in the predictions for particular properties, for example, atomization energy and enthalpy of formation.<sup>22,30,31</sup> Range-separation is also introduced for the independent treatment of exchange interaction in short- and long-range, which takes account of the effective screening and provides additional degree of freedom for the balance of exchange and correlation functionals as well as parameterization.<sup>32,33</sup> The parameters are typically fixed to simplify the implementation and improve usability. The hybrid functionals with fixed parameters are generally capable of giving good description of the band structures of different materials. However, there are also cases where these approaches fail. For example, the screened hybrid functional HSE06 systematically underestimates the bandgap of insulators.<sup>34</sup> While pyrite and marcasite  $\text{FeS}_2$  are semiconductors with bandgap about 1 eV,<sup>35,36</sup> both B3LYP and HSE06 methods overestimate this value by more than 1 eV.<sup>37,38</sup> The failure is due to the deficiencies of these functionals. First of all, certain hybrid functionals break the apparent constraints for the exact functional. For example, B3LYP does not

recover the local density approximation in the high-density limit due to the use of LYP correlation.<sup>39</sup> Second, in the determination of fixed parameters, for example, the fraction of EXX and range-separation parameter, arbitrariness arises due to the confined coverage of systems in the chosen dataset and the properties against which the parameters are fitted. Last but not least, the portion of EXX should be system-dependent in principle. This is understood qualitatively with the observation that the exact functional can be appropriately recovered by a linear combination of EXX and semi-local XC functional according to mean-value theorem.<sup>28</sup> Apparently, the ratio between EXX and semi-local XC functional varies in different landscapes of electron gas, and hence represents the nature of the investigated system.

In sight of the limited applicability with fixed parameters, great efforts have been devoted during the past two decades to build the hybrid functionals with system-dependent parameters in the aim to improve the predictive power of theory within the DFT framework. New functionals are proposed with different combinations of parameters and strategies to decide them, for example, using quantities obtained empirically from experiments or extracted from nonempirical on-the-fly calculations. These new methods are benchmarked and analyzed in various systems, ranging from simple cases like bulk semiconductors and isolated molecules, to complex ones such as liquid water, surfaces, and interfaces. Here may come the time to review the progress which has been achieved toward the universal hybrid functional. We first discuss briefly the ideas underlying system-dependent parameters, including generalized KS theory and many-body perturbation theory. Then explicit examples for the newly developed functionals are presented, with an overview of the methods. Finally, we present our perspectives on further development of the hybrid functionals, where new lands can be explored.

## 2 | IDEAS BEHIND SYSTEM-DEPENDENT HYBRID FUNCTIONALS

### 2.1 | Overview of KS DFT

To put the main topic of this review in the context, we first give a brief overview of KS DFT and its major approximations in practice. The theoretical foundation of DFT is the Hohenberg–Kohn (HK) theorems<sup>8</sup>: (a) for a given form of electron–electron (e–e) interaction  $v_{ee}(r_{12})$ , physically Coulomb interaction  $v_{ee}(r_{12}) \equiv 1/r_{12}$ , there is a one-to-one correspondence between the ground state electron density  $\rho(\mathbf{x})$  ( $\mathbf{x}$  is a collective coordinate of spatial and spin degrees of freedom, as explained in more details below) and the local external potential  $V_{\text{ext}}(\mathbf{x})$  up to an additive constant, and (b) the ground state total energy for a given system defined by the external potential  $V_{\text{ext}}(\mathbf{x})$  can be uniquely represented as a functional of  $\rho(\mathbf{x})$ , which satisfies the variational principle and gives the exact ground state total energy by taking the minimum of the functional with respect to all physically allowed electron density. In this article, we consider the general case that the external potential can be spin-dependent,<sup>40</sup> and use  $\mathbf{x} \equiv (\mathbf{r}, \sigma)$  to denote collectively the spatial coordinate ( $\mathbf{r}$ ) and the spin index ( $\sigma$ ). Therefore,  $\rho(\mathbf{x}) \equiv \rho_{\sigma}(\mathbf{r})$  denotes the spin-dependent density and  $\rho(\mathbf{r}) = \int d\sigma \rho(\mathbf{x}) \equiv \sum_{\sigma} \rho_{\sigma}(\mathbf{r})$  denotes the total density. Based on the assumption that the ground state electron density  $\rho(\mathbf{x})$  of the interacting system is also that of a fictitious  $N$ -electron noninteracting system, Kohn and Sham (KS)<sup>9</sup> proposed the following ansatz for the ground state total energy (atomic units are used through the paper)

$$E[\rho(\mathbf{x})] = \sum_i^N \left\langle \psi_i \left| -\frac{1}{2} \nabla^2 \right| \psi_i \right\rangle + \int d\mathbf{x} V_{\text{ext}}(\mathbf{x}) \rho(\mathbf{x}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\rho(\mathbf{x})]. \quad (1)$$

$\psi_i(\mathbf{x})$ , termed KS orbitals, are eigen-solutions of the following single-particle KS equation

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{x}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{x}) \right] \psi_i(\mathbf{x}) = \varepsilon_i \psi_i(\mathbf{x}), \quad (2)$$

where  $V_{\text{H}}(\mathbf{r}) \equiv \int v_{ee}(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r}'$  is the Hartree potential and  $V_{\text{xc}}(\mathbf{x}) \equiv \delta E_{\text{xc}} / \delta \rho(\mathbf{x})$  is the exchange-correlation potential. The KS equation is derived by requiring that the electron density of the original interacting system can be calculated from the  $N$ 's lowest eigen-orbitals

$$\rho(\mathbf{x}) = \sum_i f_i |\psi_i(\mathbf{x})|^2, \quad (3)$$

in which  $f_i$  denotes the occupation number of the  $i$ -th orbital, equal to 1 for  $N$ -lowest energy orbitals and 0 otherwise at zero-temperature. On the right-hand side of Equation (1), the first three terms denotes respectively the kinetic energy of the KS noninteracting system, the interaction energy between electrons and nuclei and the classical Coulomb interaction between electrons (also termed as the Hartree energy). The last term is the exchange-correlation energy, which is the only one whose exact form is unknown. Physically, it consists of two major contributions,

$$E_{xc}[\rho(\mathbf{x})] = [\langle \Psi_\rho | \hat{T} | \Psi_\rho \rangle - \langle \Phi_\rho | \hat{T} | \Phi_\rho \rangle] + \left[ \langle \Psi_\rho | \hat{V}_{ee} | \Psi_\rho \rangle - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \right], \quad (4)$$

where  $\hat{T} \equiv \sum_i^N -\frac{1}{2}\nabla_i^2$  and  $\hat{V}_{ee} \equiv \sum_{i<j}^N v_{ee}(|\mathbf{r}_i - \mathbf{r}_j|)$  denote the kinetic energy operator and the electron–electron interaction operator of  $N$ -electron system, respectively.  $\Psi_\rho$  denotes the  $N$ -electron anti-symmetric wave function that gives the electron density  $\rho(\mathbf{x})$  and minimizes the expectation value of  $\hat{T} + \hat{V}_{ee}$ , which can be formally written as

$$\Psi_\rho = \arg \min_{\Psi \rightarrow \rho(\mathbf{x})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \quad (5)$$

Similarly,  $\Phi_\rho$  denotes the single determinant  $N$ -electron wave function that gives the electron density  $\rho(\mathbf{x})$  and minimizes the expectation value of  $\hat{T}$ , formally written as

$$\Phi_\rho = \arg \min_{\Phi \rightarrow \rho(\mathbf{x})} \langle \Phi | \hat{T} | \Phi \rangle. \quad (6)$$

Here we use  $\operatorname{argmin}_x f(x)$  to represent taking  $x$  that minimizes the function (or functional)  $f(x)$  to simplify the notation, which will be also used later in the paper. The first bracketed term in Equation (4) represents the difference between the ground state kinetic energy of the interacting system and the noninteracting KS system, both corresponding to the same ground state electron density, and the second bracketed term is the difference between the full electron–electron Coulomb interaction energy and its classical counterpart (i.e., the Hartree energy). The exchange-correlation functional  $E_{xc}$  can be represented in a more concise and in the meanwhile more inspiring form via the adiabatic connection (AC) formalism,<sup>23</sup>

$$E_{xc}[\rho] = \int_0^1 d\lambda \left[ \langle \Psi_\rho^\lambda | \hat{V}_{ee} | \Psi_\rho^\lambda \rangle - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \right] \equiv \int_0^1 d\lambda U_{xc}^\lambda[\rho], \quad (7)$$

where

$$\Psi_\rho^\lambda = \arg \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle. \quad (8)$$

It is straightforward to see that  $U_{xc}^{\lambda=0} \equiv E_x^{\text{HF}}$  is the HF exchange energy calculated by the KS orbitals,

$$E_x^{\text{HF}} = -\frac{1}{2} \sum_{i,j} f_i f_j \int d\mathbf{x} \int d\mathbf{x}' \psi_i^*(\mathbf{x}) \psi_j^*(\mathbf{x}') v_{ee}(\mathbf{r}_1, \mathbf{r}_2) \psi_j(\mathbf{x}) \psi_i(\mathbf{x}'), \quad (9)$$

which is often termed as the exact exchange in the DFT literature. Introducing the (first-order reduced) density matrix,<sup>3</sup>

$$\rho(\mathbf{x}, \mathbf{x}') = \sum_i f_i \psi_i(\mathbf{x}) \psi_i^*(\mathbf{x}'), \quad (10)$$

the HF exchange energy can be written more concisely as

$$E_x^{\text{HF}} \equiv E_x^{\text{HF}}[\{\psi_i\}; v_{ee}] = \int d\mathbf{x} \int d\mathbf{x}' |\rho(\mathbf{x}, \mathbf{x}')|^2 v_{ee}(\mathbf{r}, \mathbf{r}'). \quad (11)$$

In the notation for Equation (11), we have indicated explicitly the functional dependence on the orbitals and the bare electron–electron interaction  $v_{ee}$  used for the HF exchange. Similar notations will be used in generalized hybrid functionals based on other forms of e–e interaction. If not explicitly denoted, the original HF exchange energy is assumed. Although the formally exact AC formalism of  $E_{xc}$  can be not used for practical calculation, it is of great importance theoretically and is the starting point of many important developments of approximate DFT methods.<sup>41</sup>

The KS DFT provides an in-principle-exact theoretical framework for solving the ground state total energy of many-electron interacting systems by solving a set of single-electron Schrödinger equations. Compared to the wavefunction theory formulated in terms of  $N$ -electron many-body wavefunction, DFT uses electron density  $\rho(\mathbf{x})$  as the basic variational quantity, and is therefore formally a dramatic simplification.<sup>1</sup> On the other hand, the complexity of solving the many-body problem of  $N$ -electron interacting systems is transformed into the construction of the exchange–correlation functional, and the fundamental principles underlying DFT have not provided any straightforward guidelines regarding how to build approximations to  $E_{xc}$  in practice. Fortunately, partly because  $E_{xc}$  accounts for only a small fraction of the total energy, even some kind of “crude” approximation to  $E_{xc}$  can already deliver rather reasonable results. However, it is also important to emphasize the crucial role played by  $E_{xc}$ , which is indispensable for correct description of any types of bonding, and can be regarded as the nature’s glue therefore.<sup>42</sup>

In the past decades, a great amount of effort has been invested in the development of approximate exchange correlation functionals.<sup>5,43,44</sup> The functionals developed so far can be categorized in terms of Jacob’s ladder proposed by Perdew.<sup>45</sup> The first rung in Jacob’s ladder is LDA, in which  $E_{xc}$  is a local functional of electron density, in the sense that the integrand in the functional depends on density locally (or is a function of density), with a functional form taken from the simplest many-electron interacting system, the homogeneous electron gas (HEG),

$$E_{xc}^{\text{LDA}}[\rho(\mathbf{x})] = \int \varepsilon_{xc}^{\text{HEG}}(\rho(\mathbf{x}))\rho(\mathbf{x})d\mathbf{x}, \quad (12)$$

where  $\varepsilon_{xc}^{\text{HEG}}(\rho)$  is the exchange–correlation energy per electron for the HEG model system. Although apparently being a very crude approximation, the LDA is surprisingly successful in theoretical description of many inhomogeneous electron systems, including, in particular, metals,<sup>43</sup> which can be partially attributed to the fact that  $E_{xc}$  in the LDA satisfies several exact relations that can be derived for the exact  $E_{xc}$ .<sup>46</sup> The second rung of Jacob’s ladder refers to GGA functionals, which can be formally written as

$$E_{xc}^{\text{GGA}}[\rho(\mathbf{x})] = \int \varepsilon_{xc}^{\text{HEG}}(\rho(\mathbf{x}))\rho(\mathbf{x})f(\rho(\mathbf{x}), \nabla\rho(\mathbf{x}))d\mathbf{x}. \quad (13)$$

$f$  is the correction factor with respect to the HEG xc energy density, which have different forms in different GGAs. Among the most widely used GGA functionals are the B88 exchange functional,<sup>47</sup> the LYP correlation functional,<sup>39</sup> PW91<sup>48</sup> and PBE exchange–correlation functional.<sup>49</sup> The approximate functionals in the third rung are termed as meta-GGA(mGGA),<sup>50,51</sup>

$$E_{xc}^{\text{mGGA}}[\rho(\mathbf{x})] = \int \varepsilon_{xc}^{\text{HEG}}(\rho(\mathbf{x}))\rho(\mathbf{x})f(\rho(\mathbf{x}), \nabla\rho(\mathbf{x}), \tau(\mathbf{x}))d\mathbf{x}, \quad (14)$$

where  $\tau(\mathbf{x}) \equiv \sum_i^N \frac{1}{2} |\nabla\psi_i(\mathbf{x})|^2$  is the KS kinetic energy density. The functionals up to the second and third rung are often called semilocal approximations in the literature,<sup>43</sup> and they are computationally very efficient and therefore widely used in first-principles materials research. One of the recent important developments in DFT is the SCAN meta-GGA functional<sup>52</sup> that has introduced remarkable improvement with respect to previous semilocal functionals,<sup>53</sup> and therefore have attracted a lot of interest.

The functionals in the fourth rung are called hyper-GGA, which depend on occupied orbitals.<sup>45</sup> The most commonly used hyper-GGA functionals are hybrid functionals that are usually obtained by mixing the HF exchange, also named exact exchange, with LDA, GGA, or mGGA.<sup>21,29</sup> For molecular systems, the most widely used hybrid functional is

B3LYP,<sup>22,39,54</sup> and for materials systems (crystals or surfaces), the most widely used hybrid functionals are PBE0<sup>29</sup> and HSE06.<sup>32,33</sup> The development of hybrid functionals, which is the main focus of this article, will be elaborated in details in the following section. While the fourth-rung functionals depend on occupied orbitals via the exact exchange, the fifth-rung functionals are more sophisticated and depend on both occupied and unoccupied states. A variety of fifth-rung functionals have been proposed, including, in particular, the correlation energy from the random phase approximation (RPA) in the adiabatic connection fluctuation–dissipation theorem (ACFDT) framework,<sup>55,56</sup> and the doubly hybrid functionals.<sup>57,58</sup> While the fifth-rung functionals can provide significantly improved accuracy for many properties,<sup>55,57,59,60</sup> they are also computationally much more expensive than semilocal and hybrid functionals, and therefore their application is currently limited to relatively simple molecules and solids. It should also be mentioned that there have been continuing efforts to develop more accurate and efficient treatments of van der Waals type weak interactions in the DFT framework.<sup>61,62</sup>

## 2.2 | Origin of the band gap problem

DFT is in principle an exact many-body theory only for the ground state total energy and electron density. KS DFT also provides a set of single-electron orbital energies and wave-functions, which have no direct physical meanings theoretically, but they are widely used to describe the electronic band structure of materials. The KS-DFT in LDA/GGA actually has severe problems. The general performance of LDA/GGA for the description of electronic band structure of materials can be summarized as the following: (a) In general, the band gaps obtained from LDA/GGA KS orbital energies are systematically underestimated compared to experiment, and the degree of underestimation is system-dependent instead of a simple proportional relation.<sup>63</sup> (b) For systems with similar chemical bonding, the underestimation of the band gap is similar. Therefore, although there is a significant quantitative deviation, DFT with LDA/GGA can still predict a reasonable qualitative trend of the band gaps in the materials of similar chemical nature. (c) For many simple semiconductors, the band dispersion (the dependence of the band energy on the wave-vector  $\mathbf{k}$ ) predicted by LDA/GGA is in good agreement with angular resolved photo-emission spectroscopy data or more accurate theoretical results, although the band gap values deviate greatly from the experiment values. Therefore, in practical applications, the LDA/GGA results are often corrected by adding a rigid movement to the conduction band, that is, so-called “scissor operator” method. (d) For materials containing *d* or *f* open-shell electrons, such as transition metal oxides, due to the severe self-interaction error (SIE) of LDA/GGA for spatially localized *d/f* electrons, many insulating systems are predicted to be metallic.<sup>64,65</sup> For those systems, LDA/GGA cannot give any physically meaningful prediction of the electronic band structure.<sup>66,67</sup>

The difficulty of DFT in LDA/GGA to accurately describe electronic band structure of materials, including in particular, the significant underestimation of the band gaps, is often termed as the DFT band gap problem.<sup>12</sup> The physical origin of the band gap problem has now been well-understood thanks to a series of seminal works published about three decades ago.<sup>12,68–70</sup> To properly address the band gap issue, it is necessary to generalize the domain in which the energy functional (including both the total energy and its components) is defined to the one that includes systems with fractional number of electrons, so that the number of electrons  $N$  can be continuously changed, and the derivative of the total energy with respect to  $N$  can be properly defined. That can be realized by generalizing DFT to the finite temperature regime in the grand canonical ensemble formalism,<sup>3,71</sup> and then taking the zero-temperature limit.<sup>3,12</sup> For systems with  $N = M + \omega$  electrons ( $M$  is an integer and  $\omega$  is a fractional number between 0 and 1), the total energy of the ground state satisfies the following relation

$$E(M + \omega) = (1 - \omega)E(M) + \omega E(M + 1), \quad (15)$$

which is often termed as the piece-wise linearity (PWL) condition.<sup>12</sup> The chemical potential for the system at the integer number of electrons at zero temperature is therefore given by

$$\mu(N) \equiv \frac{\partial E}{\partial N} = \begin{cases} -I(M) & (N = M - \delta) \\ -A(M) & (N = M + \delta) \end{cases} \quad (16)$$

where  $\delta$  denotes a positive infinitesimal. Equation (16) indicates that at zero temperature the chemical potential  $\mu$  as a function of electron number is discontinuous for insulating systems, and the discontinuity is just the fundamental gap.

$$\mathcal{E}_{\text{gap}} \equiv \mu(N = M + \delta) - \mu(N = M - \delta) \equiv I - A. \quad (17)$$

Such discontinuity guarantees that any neutral diatomic molecules will always dissociate into two neutral atoms.<sup>12</sup> The fundamental band gap can be related to the KS gap, the energy difference between lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), based on the so-called the KS Koopmans' theorem, which states that for a finite system, by taking the vacuum level, that is, the energy in the region infinitely (in the microscopic sense) far away from the system as the energy zero, the minus of the HOMO energy in the exact KS theory corresponds to the ionization energy of the system,<sup>72–75</sup>

$$I = -\varepsilon_N(N) \quad \text{for exact } E_{\text{xc}} \quad (18)$$

where  $\varepsilon_i(N)$  represents the  $i$ -th KS orbital energy of the  $N$ -electron system. It should be noted that KS Koopmans' theorem is conceptually different from the original Koopmans' theorem in the HF theory: the latter, relating the HF orbital energies with ionization potentials or electron affinities, is intrinsically of approximate nature since it is only valid by assuming orbital relaxation upon electron removal or addition is negligible, while the former is exact under the condition that the exact xc functional is known. On the other hand, the HF Koopmans' theorem applies to all orbitals, but the KS Koopmans' theorem is only valid for the highest occupied KS orbital.

Using KS Koopmans' theorem and the fact that the electron affinity of the  $N$ -electron system is equal to the ionization potential of the  $N + 1$ -electron system with the same external potential, that is, with the fixed nuclear geometry, one can relate the fundamental gap to the KS gap  $\varepsilon_g^{\text{KS}}$  between highest occupied orbital and the lowest unoccupied orbital as the followings

$$\begin{aligned} \mathcal{E}_{\text{gap}} &= I - A \\ &= [-\varepsilon_N(N)] - [-\varepsilon_{N+1}(N+1)] \\ &= [\varepsilon_{N+1}(N) - \varepsilon_N(N)] + [\varepsilon_{N+1}(N+1) - \varepsilon_{N+1}(N)] \\ &= \varepsilon_g^{\text{KS}} + \Delta_{\text{xc}} \end{aligned} \quad (19)$$

where the second term  $\Delta_{\text{xc}} \equiv \varepsilon_{N+1}(N+1) - \varepsilon_{N+1}(N)$  can be derived as<sup>12,69</sup>

$$\Delta_{\text{xc}} = \left. \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{x})} \right|_{N+\delta} - \left. \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{x})} \right|_{N-\delta}, \quad (20)$$

therefore, often termed as the derivative discontinuity of the xc functional.

The analysis above indicates that the KS gap is not equal to the fundamental gap even with the exact exchange-correlation functional, and the contribution of  $\Delta_{\text{xc}}$  must be included. In LDA/GGA,  $E_{\text{xc}}$  is an explicit functional of electron density, and the electron density itself is a continuous function of  $N$ , such that  $\Delta_{\text{xc}}$  vanishes. This is the origin of the LDA/GGA band gap problem. The analysis above also indicates that to solve the DFT band gap problem it is necessary to consider xc functionals that depend on electron density in a more complicated manner than standard LDA/GGA.

### 2.3 | Generalized KS theory

The basic characteristic of the KS method is that the KS equation is a single-electron Schrödinger equation corresponding to a *local multiplicative* effective potential, which is formally even simpler than the HF equation that uses nonlocal exchange potential. The local potential, determined by the electron density, thus indirectly makes the KS orbitals a functional of electron density. One can develop an approximate xc functional that explicitly depends on KS orbitals, and is therefore an implicit functional of density.<sup>27</sup> The introduction of the orbital-dependence greatly

broadens the scope for the development of approximate xc functionals. However, the locality requirement makes the calculation of the corresponding xc potential much more complicated, and involves solving an integral equation, often termed as the optimized potential method (OPM) or optimize effective potential (OEP) approach.<sup>27,28,76</sup> In practice, for implicit exchange-correlation functionals that depend on occupied orbitals, a much simpler strategy is to relax the locality requirement and use the nonlocal potential in a similar way as in the HF method. The use of the nonlocal potential in the DFT community emerged in different forms during the 1990s. In quantum chemistry of molecular systems, Becke developed the idea of hybrid functionals,<sup>21,22</sup> that is, the HF exchange (exact exchange) is mixed with the LDA/GGA xc energy in a certain fraction. In the meanwhile, Bylander and Kleinman developed the so-called SX-LDA method<sup>16</sup> by combining the screened exchange (SX) with LDA in the field of condensed matter physics. Later, Seidl et al.<sup>25</sup> systematized such nonlocal potential methods in a theoretically more rigorous manner and unified these methods into the DFT framework by introducing the GKS formalism.<sup>25</sup>

The basic idea of the GKS method is to incorporate a part of the Coulomb interaction (denoted as  $v_{ee}^\lambda$  and the corresponding two-electron operator is denoted as  $\hat{V}_{ee}^\lambda$  in the following text) in the definition of the single-particle reference system (i.e., still using the Slater determinant wave function). The parameter  $\lambda$  here is used to represent the interaction strength. Using the Levy's constrained search formalism,<sup>77</sup> the ground state energy can be obtained as

$$E_0 = \min_{\rho \rightarrow N} \left\{ \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} + \hat{V}_{ee}^\lambda | \Phi \rangle + \int \rho(\mathbf{x}) V_{\text{ext}}(\mathbf{x}) d\mathbf{x} + E_{\text{R}}^\lambda[\rho] \right\} \quad (21)$$

where

$$\begin{aligned} E_{\text{R}}^\lambda[\rho] &= \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee}^\lambda | \Psi \rangle - \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} + \hat{V}_{ee}^\lambda | \Phi \rangle \\ &\equiv \langle \Psi_\rho | \hat{T} + \hat{V}_{ee}^\lambda | \Psi_\rho \rangle - \langle \Phi_\rho | \hat{T} + \hat{V}_{ee}^\lambda | \Phi_\rho \rangle \end{aligned} \quad (22)$$

is the residual energy contribution that can be approximated by some explicit density functional. The minimization over the electron density in the above formula can be realized by requiring the variation of the energy functional defined on the right-hand side of Equation (21) with respect to the orbital wave-functions to vanish,<sup>25,78</sup> which leads to the following GKS equation,

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{x}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc},\lambda}^{\text{DFA}}(\mathbf{x}) \right] \psi_i(\mathbf{x}) + \int d\mathbf{x}' V_{\text{xc},\lambda}^{\text{NL}}(\mathbf{x}, \mathbf{x}') \psi_i(\mathbf{x}') = \varepsilon_i \psi_i(\mathbf{x}) \quad (23)$$

where the nonlocal potential in the last term on the left-hand side of Equation (23) is defined as,

$$V_{\text{xc},\lambda}^{\text{NL}}(\mathbf{x}, \mathbf{x}') = - \sum_j^N v_{\text{ee}}^\lambda(\mathbf{x}, \mathbf{x}') \psi_j(\mathbf{x}) \psi_j^*(\mathbf{x}') \quad (24)$$

and  $V_{\text{xc},\lambda}^{\text{DFA}} \equiv \delta E_{\text{R}}^\lambda / \delta \rho(\mathbf{x})$  is the explicit exchange-correlation potential. Depending on the definition of  $v_{\text{ee}}^\lambda$ , GKS can have many different variants, and therefore GKS can be regarded as a general strategy or framework to develop new approximate exchange-correlation functionals, rather than a unified theory.

In the past two decades, a lot of different methods have been developed within the GKS framework.<sup>5,6,41</sup> Here we will briefly summarize the basic ideas behind various GKS methods.

### 2.3.1 | Hybridization

For many physical or chemical properties, the performances of LDA/GGA and HF often exhibit opposite trends. For electronic band structure properties of insulating materials, LDA tends to underestimate the band gap while the HF always predicts greatly overestimated band gaps. Based on such empirical observation, one can expect that by properly mixing LDA/GGA with HF, it is possible to reach a compromise and therefore a more accurate description. The idea of



hybrid functionals can be theoretically formulated in a more rigorous way based on the adiabatic connection formalism for the xc energy. By introducing a linear approximation to the adiabatic connection formula, that is, assuming  $U_{xc, \lambda}$  given in Equation (7) is a linear function of  $\lambda$ , Becke proposed<sup>21</sup> the following hybrid functional

$$E_{xc}^{\text{BeckeHH}} = \frac{1}{2}(E_x^{\text{HF}} + E_{xc}^{\text{DFA}}), \quad (25)$$

which is often called Becke half-half (BeckeHH) functional. However, BeckeHH was not very successful in practical calculations of molecular systems.<sup>22</sup> More commonly used is the so-called Becke three-parameter (B3) hybrid functional,<sup>22</sup>

$$E_{xc}^{\text{B3}} = E_{xc}^{\text{LDA}} + \alpha_{\text{HF}}\Delta E_x^{\text{HF}} + \alpha_x\Delta E_x^{\text{GGA}} + \alpha_c\Delta E_x^{\text{GGA}} \quad (26)$$

where  $\Delta E_x^{\text{HF}} \equiv E_x^{\text{HF}} - E_x^{\text{LDA}}$  is the difference between HF and LDA (i.e., Slater) exchange energy, and  $\Delta E_x^{\text{GGA}}$  ( $\Delta E_c^{\text{GGA}}$ ) is the difference between the exchange (correlation) energy of GGA and LDA, and parameters  $\alpha_{\text{HF}} = 0.20$ ,  $\alpha_x = 0.72$ , and  $\alpha_c = 0.81$  are chosen by fitting experimental data. The most widely used B3-type hybrid functional is the B3LYP,<sup>54</sup> which uses the Becke88 GGA exchange<sup>47</sup> and the Lee–Yang–Parr<sup>39</sup> GGA correlation functional. B3LYP has become the most widely used DFT method in molecular quantum chemistry.<sup>44</sup> Perdew et al. obtained the following (partially) non-empirical hybrid functional PBE0.<sup>29</sup>

$$E_{xc}^{\text{PBE0}} = \alpha_{\text{HF}}(E_x^{\text{HF}} - E_x^{\text{PBE}}) + E_{xc}^{\text{PBE}}, \quad (27)$$

where  $\alpha_{\text{HF}} = 1/4$  is determined by some theoretical analysis based on the adiabatic connection formalism.

Approximate functionals like B3LYP or PBE0 that mix the HF exact exchange and LDA/GGA is sometimes called scaled hybrid functional,<sup>78</sup> which can be generally written as

$$E_{xc}^{\text{SH}} = \alpha_{\text{HF}}(E_x^{\text{HF}} - E_x^{\text{DFA}}) + E_{xc}^{\text{DFA}}. \quad (28)$$

Here we use “DFA” henceforth to denote a particular explicit density functional approximation (LDA or GGA). The scaled hybrid functional approach achieved remarkable success in molecular systems and can deliver comparable accuracy to high-level quantum chemistry methods for many properties but with much lower computational cost. It has become widely used in the field of molecular quantum chemistry since 1990s. In contrast, the use of hybrid functional methods in computational materials science lagged behind for many years due to the computational difficulties of the HF exchange for extended systems.<sup>32</sup> With the rapidly increasing high-performance computational facility and the development of new computational methods, especially with the consideration of screening effects,<sup>19,32,33</sup> the hybrid functionals has also become increasingly popular in condensed matter physics community.<sup>19,79</sup>

### 2.3.2 | Screening

Almost at the same time as Becke proposed the idea of the hybrid functional, Bylander and Kleinmann developed a correction to LDA/GGA from a different perspective, that is, the so-called screened exchange (SX).<sup>16</sup> For solid-state materials, one of the most severe problems of the HF theory is its lack of screening, the effect that the effective interaction between two electrons is weakened due to the presence of other electrons. The screening effect is intrinsically a correlation effect, and under certain conditions, it can have a very simple and intuitive expression in solids. The simplest one is the so-called Thomas–Fermi screening model,<sup>80</sup> where the effective interaction between electrons can be simply expressed as a Yukawa potential,

$$v_{\text{sc}}^{\text{TF}}(r_{12}) = \frac{\exp(-q_{\text{TF}}r_{12})}{r_{12}} \quad (29)$$

where  $q_{\text{TF}}$  is the Thomas–Fermi wave vector, which is determined by the electron density for the uniform electron gas.<sup>81</sup> For nonuniform electron systems, it is usually determined by the averaged valence electron density ( $n_{\text{val}}$ ). Based on the above idea, Bylander and Kleinman proposed the following approximate functional, which was called modified LDA,<sup>16,82</sup> or more commonly as SX-LDA,<sup>83</sup>

$$E_{\text{xc}}^{\text{SX-LDA}} = E_{\text{x}}^{\text{HF,SX}}[\{\psi_i\}; q_{\text{TF}}] - E_{\text{x}}^{\text{LDA,SX}}[\rho; q_{\text{TF}}] + E_{\text{xc}}^{\text{LDA}}[\rho] \quad (30)$$

where  $E_{\text{x}}^{\text{HF,SX}}$  is the HF exact exchange energy corresponding to  $v_{\text{sc}}^{\text{TF}}(r_{12})$  and  $E_{\text{x}}^{\text{LDA,SX}}$  is the screened exchange energy under local density approximation, which is explicitly available as a functional of electron density.

Closely related to the SX-LDA method, the so-called screened hybrid functional<sup>32</sup> has been proposed. To overcome the difficulty of implementing hybrid functionals for solids that is related to the long-range nature of bare Coulomb interaction, Heyd et al. proposed to use a short-range screened Coulomb interaction, represented by the complementary error function  $\text{erfc}(x) \equiv 1 - \text{erf}(x)$  as  $v_{\text{sc}}(r_{12}) = \text{erfc}(\mu r_{12})/r_{12}$ , in the computation of the exact exchange part in the PBE0-like hybrid functional<sup>32</sup>

$$E_{\text{xc}}^{\text{HSE}} = \frac{1}{4} (E_{\text{x}}^{\text{HF, SR}}[\{\psi_i\}; \mu] - E_{\text{x}}^{\text{PBE, SR}}[\rho; \mu]) + E_{\text{xc}}^{\text{PBE}}[\rho]. \quad (31)$$

The parameter  $\mu$  is the parameter that defines the range in which the exact exchange correction is effective. In Heyd et al.'s original work,  $\mu$  is determined by fitting experimental data in the G2 data set.<sup>32</sup> In practice,  $\mu$  in the range of 0.2–0.3 Å<sup>-1</sup> is often used.<sup>17,32</sup> Although originally developed as an “approximation” to PBE0, the HSE functional performs better PBE0 in many cases, especially for the band gap of narrow- and middle-gap semiconductors.<sup>17</sup> The success of HSE can be attributed to the screening effects taken into account by using the short-range Coulomb interaction, which are physically very important for accurate description of electronic band structure of semiconductors.<sup>79,84</sup>

### 2.3.3 | Long-range correction

Qualitatively speaking, many errors of LDA/GGA, especially for molecular systems, can be attributed to its failure to describe the long-range correlation well, which is closely related to their self-interaction error. As an indication of this problem, the xc potential in LDA/GGA decays exponentially in the asymptotic region, which is qualitatively different from the exact  $-1/r$  behavior. As a result, LDA/GGA fails to describe anions correctly. This is also one of the main causes for significant errors in LDA/GGA-based TDDFT calculations of excited-state properties, especially those related to charge-transfer excitation (see, e.g., Reference [85] and references therein). Savin and coworkers proposed the idea of combining wave-function based quantum chemistry methods and DFT in local or semi-local approximation (LDA/GGA) to treat long- and short-range correlation, respectively.<sup>86,87</sup> The method, to some extent, can not only overcome the shortcomings of LDA/GGA in the description of long-range correlation, but also reduce the high computational cost of the full quantum chemistry treatment.<sup>86</sup> As the simplest combined approach, one treats the long-range interaction at the HF level,

$$E_{\text{xc}}^{\text{LC}} = \alpha (E_{\text{x}}^{\text{HF, LR}}[\{\psi_i\}; \mu] - E_{\text{x}}^{\text{DFA, LR}}[\rho; \mu]) + E_{\text{xc}}^{\text{DFA}}[\rho], \quad (32)$$

which is often called long-range corrected (LC)<sup>88</sup> or range-separated (RS)<sup>89</sup> hybrid functional approximation. One should note the difference between the screened hybrid functionals like HSE and the long-range corrected hybrid functionals, which treat the short-range and long-range interaction in the HF-like way, respectively.

### 2.3.4 | System-dependence of hybridization and/or screening parameters

Most of the approaches discussed above are based on a combination of HF and LDA/GGA with some system-independent global parameters that are often determined by fitting experimental data of some chemical or

physical properties, which introduces a certain empiricism to the methodology. Even for the so-called non-empirical hybrid functional like PBE0, the validity of setting the fraction of the exact exchange to be 0.25 still depends on some assumptions about the nature of the systems.<sup>29</sup> The use of global parameters makes these methods relatively simple in practical applications, but its limitations are also very obvious. From a physical point of view, some parameters, such as the effective screening length ( $\mu$ ), or the fraction of the exact exchange ( $\alpha_{\text{HF}}$ ), are closely related to intrinsic properties of the system. One can therefore expect that different values should be used for systems of different nature. In addition, the most popular hybrid functionals, such as B3LYP, whose parameters are obtained by fitting a series of experimental data on the thermochemistry of small organic molecules, might not provide equally satisfactory results for large organic molecules, inorganic molecules, electronic structure, or magnetic properties.<sup>90</sup>

To overcome the above difficulties, system-dependent hybridization/screening methods have been developed, in which the hybridization parameters are related to the properties of the system under study. We will discuss some representative methods in more detail in the next section.

## 2.4 | Perspective from many-body perturbation theory

The formalism of the hybrid functional can also be “derived” in some sense from the perspective of many-body perturbation theory.<sup>91,92</sup> In the Coulomb hole and screened exchange (COHSEX) approximation,<sup>91</sup> the exchange-correlation self-energy that describes all nonclassical electron–electron interactions beyond the Hartree approximation in single excitation (electron removal or addition) processes is expressed as

$$\begin{aligned} \Sigma_{\text{xc}}(\mathbf{x}, \mathbf{x}') &= -\frac{1}{2}\delta(\mathbf{x}-\mathbf{x}') \left[ \frac{1}{|\mathbf{r}-\mathbf{r}'|} - W(\mathbf{x}, \mathbf{x}'; \omega=0) \right] - \sum_{i \in \text{occ}} \psi_i(\mathbf{x}) \psi_i^*(\mathbf{x}') W(\mathbf{x}, \mathbf{x}'; \omega=0) \\ &\equiv \Sigma_{\text{COH}}(\mathbf{x}, \mathbf{x}') + \Sigma_{\text{SEX}}(\mathbf{x}, \mathbf{x}'). \end{aligned} \quad (33)$$

The screened Coulomb interaction  $W$  is defined as

$$W(\mathbf{x}, \mathbf{x}'; \omega) = \int d\mathbf{x}'' \varepsilon^{-1}(\mathbf{x}, \mathbf{x}''; \omega) \frac{1}{|\mathbf{r}''-\mathbf{r}'|} \quad (34)$$

where  $\varepsilon^{-1}(\mathbf{x}, \mathbf{x}''; \omega)$  is the inverse microscopic dielectric function accounting for dynamic electronic screening. For insulating systems, especially wide-gap insulators, the main effect of the inverse dielectric function is to reduce the effective strength of electron–electron interaction, and the simplest approximation is to replace  $\varepsilon^{-1}(\mathbf{x}, \mathbf{x}'')$  by a constant scaling factor equal to the inverse of the optical dielectric constant  $1/\varepsilon_{\infty}$ , that is,

$$\varepsilon^{-1}(\mathbf{x}, \mathbf{x}''; \omega) \simeq \frac{1}{\varepsilon_{\infty}} \delta(\mathbf{x}, \mathbf{x}''), \quad (35)$$

which leads to

$$\Sigma_{\text{SEX}}(\mathbf{r}, \mathbf{r}') \approx -\frac{1}{\varepsilon_{\infty}} \sum_{i \in \text{occ}} \psi_i(\mathbf{x}) \psi_i^*(\mathbf{x}') v_{\text{ee}}(\mathbf{r}, \mathbf{r}'). \quad (36)$$

When approximating the COH term by LDA or GGA, one obtains the scaled hybrid functional, and therefore  $\alpha_{\text{HF}} = 1/\varepsilon_{\infty}$ . Alternatively, one can approximate the dielectric function in the Thomas–Fermi screening model, which is expected to be more accurate than Equation (35) for metallic or narrow-gap insulating systems, and then one can obtain SX-LDA presented above. The link between COHSEX and hybrid functionals has proven to be a fruitful route to develop new hybrid functionals with system-dependent parameters.<sup>79,93,94</sup>

### 3 | RECENT METHODOLOGICAL DEVELOPMENTS

In this work, we review in some details recent methodological developments on system-dependent hybrid functionals in which main parameters are system-specific and determined either based on physical considerations or by imposing some exact conditions. The SX-LDA method<sup>16</sup> discussed above can be regarded as the first system-dependent hybrid functional since the screening parameter  $q_{\text{TF}}$  is calculated from the averaged valence electron density that is system-dependent.<sup>25,95</sup> It is found that the SX-LDA can predict the band gaps of many insulating systems remarkably well.<sup>16,25,82,83,95,96</sup>

#### 3.1 | Overview of hybrid functionals with system-dependent parameters

We first give an overview of the various system-dependent hybrid functionals in a unified framework. One should note that different notations and terms are often used in the literature regarding various hybrid functionals even though many of them are identical or closely related to each other. Here we try to use consistent notations to clarify the essence of different methods. We note that Yanai et al. first generalized hybrid functionals with different fractions of short- and long-range exact exchange,<sup>97</sup> and Liu et al. presented a similar unified formulation of different hybrid functionals as in this work.<sup>98</sup>

One starts with the decomposition of the Coulomb interaction into the short- and long-range components, often called as range-separation (RS) in the literature,<sup>78</sup>

$$v_{\text{ee}}(r_{12}) \equiv \frac{1}{r_{12}} = v_{\text{ee}}^{\text{sr}}(r_{12}; \mu) + v_{\text{ee}}^{\text{lr}}(r_{12}; \mu), \quad (37)$$

where  $\mu$  is the range separation parameter. There are several different ways to make such range-separation. Physically the short-range part corresponds to a screened Coulomb interaction, and it is therefore natural to choose the Yukawa potential, which is the form of the screened Coulomb interaction that can be derived in the Thomas–Fermi model,<sup>81</sup> as the short-range component,

$$v_{\text{ee}}^{\text{sr-Yuk}}(r_{12}; \mu) = \frac{e^{-\mu r_{12}}}{r_{12}}. \quad (38)$$

Alternatively one can also use the error function (erf) and its complement (erfc) for the range separation,<sup>32,86</sup> in which the short-range contribution reads

$$v_{\text{ee}}^{\text{sr-erf}}(r_{12}; \mu) = \frac{\text{erfc}(\mu r_{12})}{r_{12}} \quad (39)$$

One can also use the Gaussian function to do the range separation.<sup>99</sup>

$$v_{\text{ee}}^{\text{sr-Gau}}(r_{12}; \mu) = \frac{e^{-\mu^2 r_{12}^2}}{r_{12}} \quad (40)$$

It should be pointed out that different ways of range separation have little effects on the final results. For example, using the error function and the exponential function leads to essentially the same results if the corresponding range separation parameters are related by  $\mu_{\text{erf}} = 2\mu_{\text{Yuk}}/3$ .<sup>100,101</sup> Using the error function for the range-separation is advantageous especially when implemented in the Gaussian-based codes since two-electron integrals can be analytically calculated.

Based on the range separation, a further re-partitioning of bare Coulomb interaction can be introduced in a form that was originally suggested by Yanai et al.<sup>97</sup> in the Coulomb attenuation method (CAM) approach,

$$\begin{aligned}
 v_{ee}(r_{12}) &= [\alpha_{sr}v_{ee}^{sr}(r_{12}) + \alpha_{lr}v_{ee}^{lr}(r_{12})] + [(1-\alpha_{sr})v_{ee}^{sr}(r_{12}) + (1-\alpha_{lr})v_{ee}^{lr}(r_{12})] \\
 &= v_{sc}(r_{12}; \alpha_{sr}, \alpha_{lr}, \mu) + \bar{v}_{sc}(r_{12}; \alpha_{sr}, \alpha_{lr}, \mu).
 \end{aligned}
 \tag{41}$$

Correspondingly, the total xc energy is decomposed into two contributions, one calculated in the form of the HF exact exchange with  $v_{sc}(r_{12})$  as electron–electron interaction, and the other one including contributions to the xc energy corresponding to  $\bar{v}_{sc}(r_{12}) \equiv v_{ee}(r_{12}) - v_{sc}(r_{12})$  that is approximated by a certain LDA/GGA-like density-functional approximation,

$$E_{xc} = E_x^{HF}[\rho(\mathbf{x}, \mathbf{x}'); v_{sc}] - E_x^{DFA}[\rho(\mathbf{x}); v_{sc}] + E_{xc}^{DFA}[\rho(\mathbf{x})]. \tag{42}$$

In the GKS framework, the corresponding XC potential is nonlocal, and takes the following form

$$\begin{aligned}
 V_{xc}(\mathbf{x}, \mathbf{x}'; \alpha_{sr}, \alpha_{lr}, \mu) &= \alpha_{sr} [V_x^{HF, sr}(\mathbf{x}, \mathbf{x}'; \mu) - V_x^{DFA, sr}(\mathbf{x}; \mu)\delta(\mathbf{x} - \mathbf{x}')] \\
 &+ \alpha_{lr} [V_x^{HF, lr}(\mathbf{x}, \mathbf{x}'; \mu) - V_x^{DFA, lr}(\mathbf{x}; \mu)\delta(\mathbf{x} - \mathbf{x}')] \\
 &+ V_{xc}^{DFA}(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')
 \end{aligned}
 \tag{43}$$

where  $V_x^{HF, sr}$  ( $V_x^{DFA, sr}$ ) and  $V_x^{HF, lr}$  ( $V_x^{DFA, lr}$ ) are the HF (LDA/GGA) exchange potential corresponding to short- and long-range interactions, respectively. Obviously when  $\alpha_{sr} = \alpha_{lr} = \alpha_{HF}$ , the scaled (or full-range) hybrid functional is recovered.

TABLE 1 summarizes various hybrid functionals with different range-separation schemes and different choices of parameters ( $\alpha_{sr}$ ,  $\alpha_{lr}$  and  $\mu$ ) that have been recently developed. We will discuss them in more detail in the remaining part of this section.

### 3.2 | Dielectric-dependent hybrid functionals

As mentioned above, the global hybrid functionals with a fixed fraction of the HF exchange ( $\alpha_{HF}$ ) like PBE0 and B3LYP exhibit some systematic trends for many properties.<sup>110</sup> In particular for the band gaps of insulating systems, PBE0, although showing dramatic improvement with respect to common LDA/GGA functionals, tends to overestimate the

**TABLE 1** Available functionals represented in terms of the notation defined in Equation (43)

Functional	RS	$\alpha_{sr}$	$\alpha_{lr}$	$\mu$	References
PBE0	NA	0.25	0.25	NA	29
HSE	erf	0.25	0.0	0.2–0.3 Å <sup>-1</sup>	32,33
SX-LDA	Yuk	1	0.0	$q_{TF}$	16
YS-PBE0 $\alpha_{opt}$	Yuk	$A + B\epsilon_{\infty}^{-1}$	0	0.165 bohr <sup>-1</sup>	102
DDH	NA	$\epsilon_{\infty}^{-1}$	$\epsilon_{\infty}^{-1}$	NA	94
RS-DDH	erf	0.25	$\epsilon_{\infty}^{-1}$	(in terms of $n_{val}$ or by fitting $\epsilon_s(q \rightarrow 0)$ )	103
DD-RSH-CAM	erf	1	$\epsilon_{\infty}^{-1}$	(by fitting $\epsilon_s(q \rightarrow 0)$ )	104
DSH	erf	1	$\epsilon_{\infty}^{-1}$	(in terms of $n_{val}$ Equation (51))	105
OT-RSH ( $\mu$ )	Yuk	1	0	KOT	106
OT-RSH ( $\alpha, \mu$ )	Yuk	0.2	1	KOT	107
OT-SRSH ( $\alpha, \mu$ )	Yuk	0.2	$\epsilon_{\infty}^{-1}$	KOT	108,109

Notes: “RS” indicates the scheme used for range-separation. “KOT” means Koopmans’ condition-based optimal tuning (Equation (61)). Other symbols:  $q_{TF}$ , the Thomas–Fermi wave-vector;  $\epsilon_{\infty}$ , optical dielectric constant;  $\epsilon_s$ , the ion-clamped macroscopic dielectric function; “NA”, not applicable.

band gap for narrow-gap semiconductors and underestimate the band gap for wide-gap insulators.<sup>17</sup> The screened hybrid functional HSE significantly improves the treatment of narrow- and middle-gap semiconductors with respect to PBE0, but also shows significant underestimation for wide-gap insulators.<sup>17,19</sup> These systematic trends can be easily rationalized by recognizing that the value of  $\alpha_{\text{HF}}$  should be related to the screening strength of the system under study, which becomes obvious by linking the hybrid functional approach to the COHSEX approximation as already discussed in the preceding section.<sup>93,110</sup> Neglecting the spatial and frequency dependence of dielectric function, the simplest characterization of electronic screening in insulating systems is the optical dielectric constant  $\epsilon_{\infty}$  (we note in the literature this quantity is also denoted as  $\epsilon_{\text{M}}^{105}$  or  $\epsilon_{\text{s}}^{100}$ ), which suggests that physically  $\alpha_{\text{HF}}$  should be related to  $1/\epsilon_{\infty}$ .<sup>93,100,110</sup> The link between  $\alpha_{\text{HF}}$  and  $1/\epsilon_{\infty}$  was first suggested by Alkauskas et al. in their theoretical study of band offset in semiconductor-oxide hetero-junctions,<sup>110</sup> in which it was found that the optimal  $\alpha_{\text{HF}}$  determined by fitting experimental band gaps for Si, SiC, SiO<sub>2</sub> and HfO<sub>2</sub> follows qualitatively the relation  $\alpha_{\text{HF}}^* \simeq 1/\epsilon_{\infty}$ . In a more systematic study that considers about 20 insulating systems, Marques et al.<sup>93</sup> found that  $\epsilon_{\infty}$  calculated at the PBE level is approximately inversely proportional to the optimal  $\alpha_{\text{HF}}$  that is determined by fitting experimental band gaps. By using the PBE0-like hybrid functional with  $\alpha_{\text{HF}}$  set to  $1/\epsilon_{\infty}$ (PBE), which was denoted as PBE0 $\epsilon_{\infty}$ , the average percentage error for the band gaps of selected set is significantly reduced (16.5% compared to 29.4% in PBE0 and 47.3% in PBE).

The connection between  $\alpha_{\text{HF}}$  and  $\epsilon_{\infty}$  was exploited in a semi-empirical way by Koller et al.<sup>102</sup> Working in the framework of the HSE-like screened hybrid functional using the Yukawa potential for range-separation with a fixed screening parameter  $\mu_{\text{Yuk}} = 0.165 \text{ bohr}^{-1}$ , Koller et al. first determined the optimal value of  $\alpha_{\text{HF}}$  by fitting experimental band gaps for a selected set of insulating systems, denoted as  $\alpha_{\text{exp}}$ , and calculated the dielectric constant  $\epsilon_{\infty}$  using YS-PBE0 with  $\alpha_{\text{exp}}$ , denoted as  $\epsilon^*$ ; based on a least-square fitting procedure for the  $\alpha_{\text{exp}}$  and  $\epsilon^*$  data, the optimal value of  $\alpha_{\text{HF}}$  is related to  $\epsilon_{\infty}$  by  $\alpha_{\text{HF}} = A + B/\epsilon_{\infty}$  with  $A = 0.147$  and  $B = 0.634$ ; this relation is then used for other systems with  $\epsilon_{\infty}$  recalculated self-consistently.

Also building on Marques et al.'s work, Skone et al.<sup>94</sup> further suggested a self-consistent hybrid functional approach in which the relation  $\alpha_{\text{HF}} = 1/\epsilon_{\infty}$  is implemented self-consistently. This approach is termed as the dielectric dependent hybrid (DDH) henceforth. In Skone et al.'s work, the static dielectric constant  $\epsilon_{\infty}$  is calculated by coupled perturbed KS (CPKS) method, which takes into account local-field effects and is therefore more accurate than the methods used in other related works.<sup>93,102</sup> For a set of more than 20 insulating systems including typical semiconductors, transition metal oxides and ionic insulators, the self-consistent DDH approach leads to significant improvement with respect to PBE0. The mean absolute error is reduced to 0.18 eV compared to 0.43 eV in PBE0. In a later study,<sup>103</sup> the same authors found that the DDH tends to over-correct the errors in PBE0: PBE0 tends to over-estimate the band gap for systems with  $\epsilon_{\infty}$  larger than 4, which usually correspond to narrow-gap systems, but underestimate the band gap for systems with  $\epsilon_{\infty}$  smaller than 4, which correspond to wide-gap systems; in contrast, the DDH approach exhibits the opposite trend, although the absolute error is significantly smaller. As a remedy to this problem, Skone et al. further developed the range-separated DDH (RS-DDH) approach,<sup>103</sup> in which the interaction treated in the EXX part takes the form of

$$v_{\text{sc}}(r_{12}) = \frac{\epsilon_{\infty}^{-1}}{r_{12}} + (\beta - \epsilon_{\infty}^{-1}) \frac{\text{erfc}(\mu r_{12})}{r_{12}} \quad (44)$$

where the parameter  $\beta = 1/4$ . The authors proposed several different approaches to calculate the system-specific range-separation parameter  $\mu$ , including: (a) relating  $\mu$  to the Wigner-Seitz (WS) radius ( $r_{\text{s}}$ ) corresponding to the average valence electron density  $n_{\text{val}}$ ,

$$\mu = \mu_{\text{WS}} \equiv 1/r_{\text{s}} = \left( \frac{4\pi n_{\text{val}}}{3} \right)^{1/3}, \quad (45)$$

(b) relating  $\mu$  to the Thomas–Fermi screening parameter,

$$\mu = \mu_{\text{TF}} \equiv \frac{1}{2} q_{\text{TF}} = \left( \frac{3n_{\text{val}}}{6} \right)^{1/6}, \quad (46)$$

and (c) determining  $\mu$  by fitting the long-range decay of the diagonal elements of the calculated dielectric matrix. It was found that different schemes to evaluate  $\mu$  lead to very similar results.<sup>103</sup> Overall, the RS-DDH can further improve the results of the DDH for both inorganic insulating systems and organic molecular crystals.<sup>103</sup>

From a physical point of view, the DDH approach only grasps one type of screening in real solids, that is, the dielectric screening, which is dominant in wide-gap insulators. The most significant improvement of the DDH approach with respect to PBE0 is indeed observed in systems with large band gaps<sup>94</sup> for which the PBE0 approach often underestimates the band gap.<sup>93,94</sup> On the other hand, the DDH approach still exhibits significant errors for systems with narrow band gaps.<sup>103,111</sup> Physically, it can be attributed to the fact that other screening mechanisms can become important for narrow-gap semiconductors. In the limit of metallic systems, the Thomas–Fermi screening, which is taken into account in the SX-LDA,<sup>16</sup> becomes dominant. To describe the band gaps of materials of different nature in the hybrid functional framework, it is necessary to consider both dielectric and metallic screenings with system-dependent screening parameters, which essentially combines SX-LDA and DDH. The RS-DDH approach<sup>103</sup> discussed above can be regarded as an ad hoc way to do that.

Generalized dielectric dependent hybrid functionals that consider different screening mechanisms can also be developed in a more systematic way by exploiting the link between hybrid functionals and the COHSEX approximation. Instead of replacing the dielectric function by the dielectric constant, one can consider model dielectric functions in the reciprocal space that have been developed in the *GW* framework.<sup>112</sup> It is helpful to note that the Thomas–Fermi screened interaction in Equation (29) corresponds to a model dielectric function in reciprocal space as

$$\epsilon_{\text{TF}}(q) = 1 + \frac{q_{\text{TF}}^2}{q^2}. \quad (47)$$

To obtain hybrid functionals that can treat wide-gap insulators and narrow-gap semiconductors with comparable accuracy, it is crucial to consider a more general model dielectric function that accounts for both dielectric and Thomas–Fermi metallic screening simultaneously. In the context of simplifying the *GW* approach<sup>63,92,112</sup> for semiconductors, Bechstedt et al. proposed the following model dielectric function,<sup>113,114</sup>

$$\epsilon(q) = 1 + \left[ (\epsilon_{\infty} - 1)^{-1} + \alpha \left( \frac{q}{q_{\text{TF}}} \right)^2 + \frac{q^4}{4\omega_{\text{pl}}^2} \right]^{-1} \quad (48)$$

where  $\omega_{\text{pl}} = (4\pi n_{\text{val}})^{1/2}$  is the plasmon frequency corresponding to the valence electron density  $n_{\text{val}}$ , and  $\alpha$ , taking the value of 1.563, is a fitting parameter introduced by Bechstedt et al. to better reproduce directly calculated dielectric function for typical semiconductors.<sup>114</sup> We note that this model dielectric functional has recently attracted a lot of interest in the model Bethe–Salpeter equation (mBSE) or other related approaches in the framework of time-dependent DFT (TDDFT) with hybrid functionals<sup>115,116</sup> as an effort to reduce the computational cost of the standard BSE calculations of optical properties of materials. The Bechstedt model dielectric function has the nice features that it reproduces the Thomas–Fermi screening model when  $\epsilon_{\infty}$  is large and  $q$  is small, and in the long-range limit ( $q = 0$ ),  $\epsilon(0) = \epsilon_{\infty}$ . Thus both limiting cases (the dielectric and metallic screening) can be recovered. Shimazaki and coworkers developed the hybrid functionals based on the Bechstedt model dielectric function in a series of papers.<sup>100,117–119</sup> They proposed to use the simplified version of the Bechstedt dielectric function that neglects the  $q^4$  term,<sup>100</sup> and the corresponding screened Coulomb interaction in the real space has the following simple analytic form

$$v_{\text{sc}}(r_{12}) = \frac{\epsilon_{\infty}^{-1}}{r_{12}} + \frac{(1 - \epsilon_{\infty}^{-1}) \exp(-\tilde{q}_{\text{TF}} r_{12})}{r_{12}} \quad (49)$$

with  $\tilde{q}_{\text{TF}}$  being an effective Thomas–Fermi screening parameter defined by  $\tilde{q}_{\text{TF}}^2 = \frac{q_{\text{TF}}^2}{\alpha} \left( \frac{1}{\epsilon_{\infty} - 1} + 1 \right)$ . They suggested to replace the Yukawa potential by the complementary error function (erfc) to facilitate the implementation in the Gaussian basis,<sup>100</sup>

$$v_{\text{sc}}(r_{12}) = \frac{\epsilon_{\infty}^{-1}}{r_{12}} + \frac{(1 - \epsilon_{\infty}^{-1}) \text{erfc}(\mu r_{12})}{r_{12}}, \quad (50)$$

with

$$\mu \equiv 2\tilde{q}_{\text{TF}}/3 = \frac{2}{3} \sqrt{\frac{q_{\text{TF}}^2}{\alpha} \left( \frac{1}{\epsilon_{\infty} - 1} + 1 \right)}. \quad (51)$$

There are two system-dependent parameters in this generalized dielectric dependent hybrid functional, the Thomas–Fermi screening parameter  $q_{\text{TF}}$ , which can be easily evaluated in terms of the average valence electron density, and the dielectric constant. In Reference 100, the authors used the experimental value of  $\epsilon_{\infty}$ . In References 117 and 118, the authors proposed to calculate  $\epsilon_{\infty}$  self-consistently in terms of the simplified Penn model to the dielectric function,<sup>112,120</sup>

$$\epsilon_{\infty} \approx 1 + \left( \frac{\hbar\omega_{\text{pl}}}{\bar{E}_{\text{gap}}} \right)^2, \quad (52)$$

where  $\bar{E}_{\text{gap}}$  is the k-averaged band gap,

$$\bar{E}_{\text{gap}} \equiv \frac{1}{N_k} \sum_{\mathbf{k}} [\epsilon_{\text{LUMO}}(\mathbf{k}) - \epsilon_{\text{HOMO}}(\mathbf{k})]. \quad (53)$$

They applied the method to several typical semiconductors, and found that the self-consistent screened hybrid functional can well reproduce experimental band gaps.<sup>118</sup> In Reference 119, the authors further suggested to calculate the dielectric constant in a first-principles way by the independent particle approximation. They also explored the use of the Gaussian-based cutoff scheme for screened hybrid functionals.<sup>121,122</sup>

Cui et al.<sup>105</sup> developed the hybrid functional based on the Bechstedt model dielectric function in combination with PBE for the corresponding semi-local approximation, which is termed as doubly screened hybrid (DSH) functional to emphasize both dielectric screening and metallic screening have been taken into account. The exchange-correlation energy in DSH reads

$$E_{\text{xc}} = E_{\text{x}}^{\text{HF}}[\rho(\mathbf{x}, \mathbf{x}'); v_{\text{sc}}] - E_{\text{x}}^{\text{PBE}}[\rho(\mathbf{x}); v_{\text{sc}}] + E_{\text{xc}}^{\text{PBE}}[\rho(\mathbf{x})], \quad (54)$$

where the first and second terms are the HF and PBE exchange energy calculated using the screened Coulomb interaction  $v_{\text{sc}}$ , respectively. The corresponding nonlocal exchange-correlation potential in DSH reads<sup>105</sup>

$$V_{\text{xc}}^{\text{DSH}}(\mathbf{x}, \mathbf{x}') = \epsilon_{\infty}^{-1} V_{\text{x}}^{\text{HF}}(\mathbf{x}, \mathbf{x}') + (1 - \epsilon_{\infty}^{-1}) V_{\text{x}}^{\text{HF, sr}}(\mathbf{x}, \mathbf{x}'; \mu) + [(1 - \epsilon_{\infty}^{-1}) V_{\text{x}}^{\text{PBE, lr}}(\mathbf{x}; \mu) + V_{\text{c}}^{\text{PBE}}(\mathbf{x})] \delta(\mathbf{x}, \mathbf{x}'), \quad (55)$$

where

$$V_{\text{x}}^{\text{HF, sr}}(\mathbf{x}, \mathbf{x}'; \mu) = -\rho(\mathbf{x}, \mathbf{x}') \frac{\text{erfc}(\mu|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}, \quad (56)$$

and  $V_{\text{x}}^{\text{PBE, lr}}(\mathbf{x})$  is the long-range part of the PBE exchange functional (the same one as that used in the HSE functional<sup>32</sup>), which is introduced to compensate the missing long-range contribution corresponding to the second term. The consideration of the third term ( $V_{\text{x}}^{\text{PBE, lr}}$ ), which is neglected in previous works,<sup>100,117,119</sup> is important to obtain a consistent description of both the potential and the total energy in the generalized KS framework.<sup>25,78</sup> Cui et al. investigated the performances of the DSH method for a set of semiconductors and insulators, and they considered both self-consistent DSH and the one-shot scheme that used the dielectric constant from the PBE calculation as the input without further updating. All insulating systems with wide, moderate or narrow band gaps can be well described by the DSH functional. In particular, for *sp* systems with moderate or wide band gaps, both the one-shot (with PBE as the starting point) and self-consistent DSH can reproduce experimental results very well with a mean absolute relative error less than 10%, an accuracy that is comparable to numerically converged all-electron  $GW_0$ @PBE.<sup>123</sup> They also compared



the performances of the self-consistent DDH and DSH, and found that DDH and DSH perform similarly in describing the electronic band structure of typical *sp* semiconductors with moderate and wide gaps. For narrow-gap semiconductors the DDH approach tends to significantly underestimate the band gaps, and in some cases has difficulty in reaching convergence during iterative determination of dielectric constants. In contrast, the DSH still works very well, not only in terms of good convergence behavior, but also in terms of quantitatively good agreement with experimental results. The overall remarkable performances of the DSH approach clearly indicates the importance of considering two limiting screening mechanisms, the global dielectric (insulator) screening, embodied in the scaling of the Coulomb interaction by  $1/\epsilon_\infty$ , and the short-range metallic screening, represented in the Yukawa potential, for accurate description of electronic band structure of materials of different nature.

Following a similar line of thinking, Chen et al. developed the DD-RSH-CAM method.<sup>104</sup> The authors started with partitioning the bare Coulomb interaction as introduced in the Coulomb attenuation method (CAM)<sup>97</sup>

$$\frac{1}{r_{12}} = \frac{\alpha + \beta \operatorname{erf}(\mu r_{12})}{r_{12}} + \frac{1 - \alpha - \beta \operatorname{erf}(\mu r_{12})}{r_{12}}. \quad (57)$$

Assuming that the first-term, which corresponds to the electron–electron interaction treated in the EXX form, can be related to the inverse dielectric function, one can obtain

$$\epsilon^{-1}(q) = \alpha + \beta e^{-\frac{q^2}{4\mu^2}}. \quad (58)$$

Imposing the conditions  $\epsilon^{-1}(q \rightarrow \infty) = 1$  and  $\epsilon^{-1}(q=0) = \epsilon_\infty^{-1}$  leads to  $\alpha = 1$  and  $\beta = \epsilon_\infty^{-1} - 1$ , and the effective interaction,

$$v_{\text{sc}}(r_{12}) = \frac{1 + (\epsilon_\infty^{-1} - 1) \operatorname{erf}(\mu r_{12})}{r_{12}}, \quad (59)$$

which, by using  $\operatorname{erfc}(x) \equiv 1 - \operatorname{erf}(x)$ , is actually the same as the one used in the DSH method (Equation (50)). However, the range-separation parameter  $\mu$  is determined in a different way than that in DSH. Similar to the RS-DDH,<sup>103</sup>  $\mu$  is determined by fitting the calculated dielectric function  $\epsilon^{-1}(q, \omega = 0)$  in the long-wavelength limit. The authors considered 32 semiconductors and insulators, and found that overall the DD-RSH-CAM method outperforms the DDH and RS-DDH, especially when the dielectric function is evaluated with both the local field effect and the vertex correction  $f_{\text{xc}}$  included. Obviously DSH and DD-RSH-CAM are essentially same except that the parameters  $\epsilon_\infty$  and  $\mu$  are determined in different ways. Liu et al.<sup>98</sup> compared the performance of DSH and DD-RSH-CAM, and their results show that these two approaches are similar.

As obvious from the discussion above, the optical dielectric constant  $\epsilon_\infty$  plays a crucial role in dielectric dependent hybrid functional methods developed for bulk materials. Theoretically the optical dielectric constant can be calculated from the microscopic dielectric function  $\epsilon(\mathbf{x}, \mathbf{x}'; \omega)$ , and its complete formulation requires evoking many-body perturbation theory in terms of Green's function,<sup>124–126</sup> which is out of the scope of this review. Here we briefly summarize several different approaches that have been widely used for the calculation of optical dielectric constant, especially in the context of hybrid functionals with system-dependent parameters. The simplest approach to calculate  $\epsilon_\infty$  is the independent particle approximation (IPA) in which a mean-field (or KS) response function is calculated via the summation over states (SOS), and the optical dielectric constant is obtained by taking the macroscopic limit.<sup>127</sup> The correlation effects beyond IPA can be taken into account at different approximation levels, either in the time-dependent density-functional theory (TDDFT)<sup>126</sup> or Bethe–Salpeter equation (BSE)<sup>125</sup> frameworks. If we focus only on the static and macroscopic limit, the corresponding dielectric tensor  $\epsilon_\infty$  can also be calculated by the density functional perturbation theory (DFPT),<sup>128,129</sup> and finite field approach.<sup>130</sup> These methods compute the derivative of macroscopic polarization  $\mathbf{P}$  with respect to a perturbative electric field. Among them, the DFPT computes the analytic response of density (matrix) through the first-order perturbation theory self-consistently. The finite field approach utilizes the modern theory of polarization<sup>131–134</sup> to represent the (change of) macroscopic polarization under a finite but small electric field and then the dielectric tensor is evaluated through the minimization of electric enthalpy and finite difference of polarization.<sup>130,135</sup>

### 3.3 | Optimally tuned hybrid functionals with physical constraints

Various hybrid functionals reviewed above are mainly developed by taking into account system-dependent screening effects that are dominant for condensed matter systems. For molecular systems, there have been also very active developments of hybrid functionals with system-dependent parameters, but often with very different strategies. In many of those hybrid functionals for molecules, the hybridization parameters are determined by imposing some physical or theoretical constraints. In this part, we briefly review some available strategies.

We first discuss hybrid functionals in which parameters are determined by enforcing Koopmans' theorem. As we have discussed in the preceding section, in the exact (generalized) KS theory the first ionization potential (IP) is equal to the negative of the highest occupied molecular orbital energy  $\epsilon_{\text{HOMO}}$ , that is,  $\text{IP} = -\epsilon_{\text{HOMO}}$ .<sup>12,25,136</sup> However, the Koopmans' theorem is usually violated in LDA/GGA in finite systems, where the calculated KS HOMO energy is generally much smaller than the IP calculated by the  $\Delta$ -SCF approach.<sup>137</sup> This is related to the convex behavior of the total energy as a function of the fractional electron number in LDA/GGA in contrast to the exact piece-wise linear behavior,<sup>15</sup> as a result of which the orbital energies in the valence regime are spuriously raised up. On the other hand, although hybrid functional with the Fock exchange is proved to be able to alleviate SIE to some extent, the magnitude to which the orbital suffers from SIE is not only dependent on the system, but also on the spatial characteristic of the orbital itself.<sup>138</sup> Hence it requires different fraction of the Fock exchange to alleviate SIE and restore the Koopmans' theorem for different electronic systems. And therefore Koopmans' condition can be used to determine the system-dependent hybridization parameters in hybrid functionals.

Enforcing Koopmans' condition for molecular systems is relatively straightforward. Baer, Kronik and coworkers have undertaken comprehensive research in developing optimally tuned range-separated hybrid (OT-RSH) functionals based on Koopmans' condition,<sup>78,139,140</sup> formulated in the Baer–Neuhauser–Livshits RSH functional,<sup>89,141</sup> in which the exchange energy is decomposed to the HF nonlocal exchange corresponding to long-range interaction and explicit semi-local exchange functional (LDA/GGA) for short-range interaction, using the error function for range separation,

$$E_x = E_x^{\text{HF,sr}}[\{\psi_i\}; \mu] + E_x^{\text{DFA,lr}}[\rho(\mathbf{r})]. \quad (60)$$

The range-separation parameter  $\mu$  is determined by minimizing the deviation from the Koopmans' condition for the neutral and anionic states of the system under study,

$$\mu^* = \arg \min_{\mu} \sum_{i=0,1} |\epsilon_{\text{H}}^{\mu}(N+i) + \text{IP}^{\mu}(N+i)|, \quad (61)$$

where  $\text{IP}^{\mu}(M)$  denotes the ionization potential of the  $M$ -electron system calculated by the  $\Delta$ -SCF method. The OT-RSH method has been applied to various molecular systems with remarkable performances in theoretical prediction of ionization potentials, electron affinities, optical excitation gaps (in combination with time-dependent DFT) and nonlinear optical properties of many molecular systems.<sup>106,137,142–147</sup>

Kronik and coworkers<sup>107</sup> have extended the optimal tuning strategy to the more general partitioning of Coulomb interaction, that is, that of CAM (Equation (57)). Here the requirement of  $\alpha + \beta = 1$  is imposed to guarantee correct asymptotic behavior of the xc potential, which is crucial for finite systems. For a given  $\alpha$ , the optimal range-separation parameter  $\mu^*$  is determined in terms of Equation (61). It was found that the energies corresponding to delocalized orbitals are insensitive to  $\alpha$ , but localized orbitals are highly sensitive to  $\alpha$ , and therefore the optimal value of  $\alpha$  is also system-dependent, and should be determined by enforcing some theoretical constraints. In Reference 107 the authors proposed to determine the optimal  $\alpha$  by imposing the piece-wise linearity condition. In practice, this is realized by choosing  $\alpha$  that minimizes the curvature of the total energy as a function of the fractional number of electrons  $E(N + \delta)$ . Using this method, which is termed as OT-RSH( $\alpha, \mu$ ), the full quasi-particle spectrum for occupied states of four important benchmark organic molecules can be well predicted in good agreement with experimental gas-phase photoemission spectra. Similar good performances of OT-RSH( $\alpha, \mu$ ) were also observed for theoretical prediction of outer-valence electron spectra of a set of prototypical aromatic heterocycles.<sup>138</sup>

The OT-RSH method is also generalized to calculate the band structure of molecular crystals.<sup>108</sup> Since the direct computation of the ionization potential by the total energy is problematic in solid-state calculation with periodic boundary condition, the optimal parameters  $\alpha$  and  $\mu$  need to be first determined by calculating the molecule in gas phase. The same  $\alpha$  and  $\mu$  are used in the calculation of molecular crystal. This is justified by the fact that the inter-molecular interaction in molecular crystals is weak and does not alter the short-range exchange significantly. However, a direct application of the OT-RSH

approach with such determined parameters fails badly, and misses completely the gap renormalization effects caused by electronic polarization. The authors therefore proposed the following screened range-separation hybrid (SRSH) approach that incorporates the optical dielectric constant to account for electronic polarization,

$$E_{xc}^{SRSH} = \alpha E_x^{HF,sr} + (1 - \alpha) E_x^{DFA,sr} + \epsilon_\infty^{-1} E_x^{HF,lr} + (1 - \epsilon_\infty^{-1}) E_x^{DFA,lr}. \quad (62)$$

Formally the SRSH is very similar to generalized dielectric-dependent hybrid functionals that are reviewed in the preceding section. The authors found that the results from the OT-SRSH approach for several typical molecular crystals including  $C_6H_6$ , pentacene, and  $C_{60}$  agree very well to those from the *GW* method. Recently, the OT-SRSH approach is applied to calculate quasi-particle (fundamental) gaps and optical absorption spectra (in the framework of TDDFT) for a set of 23 noncovalently bound molecular solids, known as the X23 set, which shows a remarkable agreement with the results obtained from many-body perturbation theory in the *GW*-BSE approximation.<sup>148</sup> An overview of recent development along this direction was given in Reference 149.

It should be noted that the OT-SRSH approach in the current form cannot be used for general solids with ionic or covalent bonding characters since the optimal tuning condition Equation (61) cannot be applied easily for extended systems. It is, however, interesting to mention recent works by Kronik and workers,<sup>109,150,151</sup> in which the SRSH functional with the range separation parameter  $\mu$  determined by either fitting experimental band gaps,<sup>109</sup> or *GW* band gaps at one specific high-symmetry point of the Brillouin zone,<sup>150</sup> when applied in the TDDFT framework, was found to be able to predict optical spectra of several prototypical covalent and ionic solids in good agreement with *GW* + BSE.

As we have mentioned before, enforcing the Koopmans' condition is not straightforward for extended systems, which have severely restricted the use of optimally tuned hybrid functionals for materials. Koopmans' theorem can be derived from the more general piece-wise linearity condition (Equation (15)). Combining the PWL condition with Janak's theorem<sup>68</sup> leads to the useful conclusion that for a system with fractional number of electrons, the frontier orbital energy should be constant as the occupation of the orbital varies,<sup>12,152</sup> which is sometimes termed as generalized Koopmans' condition.<sup>153</sup> Using the PWL to determine the optimal fraction of the Fock exchange has been used for finite systems.<sup>154–156</sup> Recently, this has been extended to material systems, especially for theoretical study of defects in solids.<sup>153,157–159</sup>

We finally comment on several methods in which the hybridization parameter is determined by requiring the consistency in the results from hybrid functional calculations and those from *GW* or TDDFT calculations that use the hybrid functional calculation as the input.

In recent works by Atalla et al.,<sup>160,161</sup> the mixing parameter  $\alpha_{HF}$  in the PBE0 form is obtained by imposing the constraint that the self-energy correction to the highest occupied orbital with respect to that from the hybrid functional calculation vanishes, that is,

$$\alpha^* = \arg \min_{\alpha} | \langle \psi_H(\alpha) | \Sigma(\alpha) - V_{xc}(\alpha) | \psi_H(\alpha) \rangle |. \quad (63)$$

With such determined  $\alpha^*$ , the PBE0( $\alpha$ ) method is able to remedy the deviation of straight-line error existing in PBE and PBE0, and hence significantly improves the description of the ionization potential of molecular systems and the electron transfer between donor and acceptor.<sup>161</sup> Theoretically, this method can be regarded as a variant to the optimally tuned hybrid functional based on the Koopmans' theorem.

Inspired by the optimal tuning strategy adopted in the development of the OT-RSH method, Lin and Van Voorhis<sup>162</sup> proposed the triplet tuning approach, in which the optimal hybridization parameters are determined by enforcing the equality of the lowest triplet excitation energies ( $T_1$ ) from the spin-unrestricted DFT and TDDFT using the same hybrid functional. They applied the triplet-tuned hybrid functional to four sets of large organic molecules, and found that not only the triplet excitation energies  $E_T$  but also other key spectroscopic and photo-chemical properties like optical band gaps, singlet-triplet gaps and vertical ionization potentials can all be accurately predicted.

### 3.4 | Empirical system-tuned hybrid functionals

Finally we mention a few system-tuned hybrid functionals that involves more empiricism than the methods we have reviewed above. To avoid the calculation of optical dielectric constant  $\epsilon_\infty$ , which can be expensive, especially for large

systems, Marques et al.,<sup>93</sup> following the practice in the modified Becke–Johnson approach,<sup>163</sup> related the optimal mixing parameter  $\alpha$  to the averaged electron density gradient in the following empirical relation,

$$\alpha = \alpha_1 + \alpha_2 \bar{g}^m \quad (64)$$

where the quantity  $\bar{g}$  is defined as

$$\bar{g} = \frac{1}{\Omega} \int d\mathbf{r} \sqrt{\frac{|\nabla n(\mathbf{r})|}{n(\mathbf{r})}}. \quad (65)$$

$\alpha_1$ ,  $\alpha_2$  and  $m$  are empirical parameters obtained by fitting experimental band gaps of typical semiconductors and insulators, and take the values of  $\alpha_1 = -1.00778$ ,  $\alpha_2 = 1.10507$ , and  $m = 1$  for the PBE0-type global hybrid functional, and  $\alpha_1 = -0.121983$ ,  $\alpha_2 = 0.130711$ , and  $m = 4$  for the HSE-type screened hybrid functional. These methods may be prone to the valence-core partitioning of electron density that is necessary for the use of pseudopotentials.<sup>93,102</sup>

## 4 | CONCLUDING REMARKS

In this work, we have presented a comprehensive overview of recent theoretical developments in the framework of hybrid functionals with system-dependent parameters, with the special emphasis on their conceptual foundation and recent methodological developments. Conceptually there are several inter-related routes or perspectives that lead to hybrid functionals, including: (a) empirical observation that LDA/GGA and HF tend to exhibit opposite errors for many physical or chemical properties, (b) the adiabatic connection formulation of the exact exchange–correlation energy functional, (c) the link between the exchange–correlation potential and the self-energy in many-body perturbation theory in the *GW* approximation, and (d) the exact conditions like the piece-wise linearity of the exact ground state total energy as a function of fractional number of electrons and Koopmans' theorem for the relation between the highest occupied KS orbital energy and the ionization potential. These are conceptual foundations that most of the recent developments in hybrid functionals can be traced back to. Two classes of hybrid functional approaches are especially fruitful, that is, dielectric dependent hybrid functionals that are mainly motivated by the link with the COHSEX approximation in the *GW* theory,<sup>93,94,100,102–105,117,118</sup> and optimally tuned functionals that are based on enforcing exact conditions to determine hybridization parameter.<sup>106,137,139,141</sup> It is noteworthy that these two types of approaches are originally developed with different target systems, the former aiming at solids, and the latter targeting molecular systems. Both have been extended to go beyond their original target systems, but with mixed success.<sup>109,148,164,165</sup>

We close this review by making some general remarks on the open questions and challenges facing the hybrid functionals with system-dependent parameters and other related issues.

- 1 Up to now, system-tuned hybrid functionals are mainly used to obtain more accurate description of electronic properties of materials and molecules. It is obviously desirable to use the same method to treat other properties as well. But for the properties that involves the total energy difference between the structures that are chemically very different, hybrid functionals with system-tuned parameters, which will lead to different hybridization parameters for different systems, can have severe difficulty. The study by Karolewski et al.<sup>166</sup> found that using the optimally tuned parameters in the hybrid functional approach can lead to violation of size consistency; for diatomic molecules, size-consistency errors can be as large as a few electron volts, which results in total failure of properly predicting molecular binding energies. Similar difficulties can be expected for the calculation of cohesive energy or the formation energy of solids, which requires the total energies of a compound solid and its elemental components.
- 2 In most cases, the parameters used in those hybrid functionals are global ones, which can have difficulty to accurately describe heterogeneous complex systems, for example, the hetero-junctions of two chemically distinct materials, solid–molecule or solid–solution interfaces. For such systems, local hybrid functionals,<sup>167</sup> in which the mixing or screening parameters are position-dependent, are highly promising (see Reference 168 for comprehensive review of the current status of local hybrid functionals). Up to now, local hybrid methods have been mainly developed for molecular systems.<sup>168</sup> In a recent study by Borlido et al.,<sup>169</sup> the authors proposed a local hybrid functional based on their previous work that determines the system-dependent  $\alpha$  based on electron density gradient, and applied the method to investigate band-edge alignment at semiconductor interfaces with overall promising results.

- 3 In this article, we have mainly focused on hybrid functionals that mix the HF-exchange and LDA/GGA. Recent years have seen the active development of a new class of hybrid functionals that mix fifth-rank functionals, including in particular MP2 and RPA correlation energy, with the HF exchange and LDA/GGA, which are generally known as double hybrid (DH) functionals (see, for example, References 41, 57, 58 and 170 for comprehensive reviews of recent developments). Many of the ideas and methodologies discussed in this work have been also used for the development of DH functionals. Up to now, the DH functionals are mainly developed and calibrated for molecular systems, and their applications to materials are much more challenging, and therefore their performances for the prediction of material properties, including in particular, electronic band structure properties, remain to be established.
- 4 The last but not least issue we want to comment on is the computational cost problem. Hybrid functionals are much more expensive compared to LDA/GGA, especially for applications to extended systems, which poses severe limitation to the systems that can be accessed by these methods. Obviously, it is still highly desirable to develop more efficient algorithms for the implementation of hybrid functionals, building on great progress that has been made recently on this aspect.<sup>171–176</sup>

## ACKNOWLEDGMENTS

This work is partly supported by the National Key Research and Development Program of China (No. 2016YFB0701100) and National Natural Science Foundation of China (Project Numbers 21673005 and 21621061).

## CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

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**How to cite this article:** Zhang M-Y, Cui Z-H, Wang Y-C, Jiang H. Hybrid functionals with system-dependent parameters: Conceptual foundations and methodological developments. *WIREs Comput Mol Sci.* 2020;e1476.

<https://doi.org/10.1002/wcms.1476>