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Revisiting the Half-and-Half Functional

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Cite This: J. Phys. Chem. A 2025, 129, 3969–3982 ACCESS I III Metrics & More III Article Recommendations Supporting Information ABSTRACT: Hybrid density functionals typically provide significantly better accuracy than semilocal functionals. Conventional wisdom holds that incorporating more than 20–25% exact exchange

wisdom holds that incorporating more than 20–25% exact exchange is deleterious to thermochemical properties and should only be used as a last resort, for problems that are dominated by self-interaction error. In such cases, the Becke–Lee–Yang–Parr "half-and-half" functional (BH&H-LYP) has emerged as a go-to choice, especially in timedependent density functional theory calculations for excitation energies. Here, we examine the assumption that 50% Hartree–Fock exchange sacrifices thermochemical accuracy. Using a sequence of functionals B(α)LYP, with different percentages of exact exchange (0 $\leq \alpha \leq 100$), we find that BH&H-LYP (with $\alpha = 50$) is nearly optimal



and affords accuracy similar to B3LYP for thermochemistry, barrier heights, and excitation energies. Although BH&H-LYP is significantly less accurate than B3LYP for atomization energies, this emerges as the sole rationale for the taboo against values $\alpha > 25$. Overall, BH&H-LYP is a reasonable choice for problems that are dominated by self-interaction error, including charge-transfer complexes and core-level excitation energies. While B3LYP remains more accurate for valence excitation energies, the use of 50% exact exchange appears to be an acceptable compromise, and BH&H-LYP can be used without undue concern over its diminished accuracy for ground-state properties.

intensity

1. INTRODUCTION

In 1993, Becke introduced one of the first hybrid density functionals, based on equal mixing of Hartree–Fock (HF) exchange with the local spin density approximation (LSDA),¹

$$E_{\rm xc}^{\rm BHandH} = \frac{1}{2} (E_{\rm x}^{\rm HF} + E_{\rm xc}^{\rm LSDA}) \tag{1}$$

The construction of Becke's "half-and-half" functional (BHandH) in eq 1 is justified by a simple approximation to the adiabatic connection formula.^{1,2} The half-and-half recipe was quickly modified,³ swapping out LSDA in favor of a generalized gradient approximation (GGA). Using semilocal B88 exchange for that purpose (E_x^{B88}) ,⁴ and adding the Lee–Yang–Parr (LYP) correlation functional (E_c^{LYP}) ,⁵ one obtains a modern version of the half-and-half functional:

$$E_{\rm xc}^{\rm BH\&H-LYP} = \frac{1}{2} (E_{\rm x}^{\rm B88} + E_{\rm x}^{\rm HF}) + E_{\rm c}^{\rm LYP}$$
(2)

We will call this functional BH&H-LYP, although it sometimes goes by other names including BHLYP, BHHLYP, and BHandH-LYP.⁶ Half-and-half functionals were quickly eclipsed by Becke's three-parameter "B3" *ansatz*,⁷ leading to the B3LYP functional in 1994.⁸ As a result, BH&H-LYP never saw widespread deployment. B3LYP contains 20% exact exchange $(E_x^{\rm HF})$, a fraction that was determined empirically but is close to the 25% that would later be suggested by appeal to Görling-Levy perturbation theory.⁹ That argument is used to justify including 25% exact exchange in the PBE0 functional.¹⁰

B3LYP quickly displaced most competing functionals. According to one estimate,¹¹ BH&H-LYP was used in a mere 1% of density functional theory (DFT) calculations up to 2007, as compared to 80% that used B3LYP. Today, there are undoubtedly better-performing functionals than B3LYP,¹² yet many of them involve complexity of at least the meta-GGA variety. When augmented with an empirical dispersion correction,¹³ B3LYP remains a respectable functional.^{12–14} Comparatively recent attempts to reoptimize the B3 parameters have landed on very nearly the same numerical values originally suggested by Becke.^{15,16} This is a remarkable tribute to his insight, given the paucity of data in the original parametrization: 42 ionization energies, 8 proton affinities, and 10 first-row total atomic energies, representing the so-called G1 data set.^{17,18}

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Even as hybrid GGAs have given way to meta-GGAs and double-hybrid functionals as the most accurate instruments in the density-functional toolkit, BH&H-LYP has persisted. It tends to be used when there is concern regarding artifacts originating in self-interaction error (SIE), often manifesting as anomalous delocalization of charge.^{19–21} Thus, BH&H-LYP has long been used to study charge-transfer (CT) complexes^{3,22–30} and systems with extended π conjugation,^{31–33} both of which are sensitive to delocalization error. For similar reasons, BH&H-LYP is a standard approach for computing electron affinities of neutral molecules and electron detachment energies for anions,^{34–45} where the open-shell species is more sensitive to SIE. Finally, BH&H-LYP has been demonstrated to improve the behavior of DFT calculations in cases where convergence is hampered by charge oscillations.^{46–48}

For excited-state calculations using time-dependent (TD-) DFT,^{49,50} BH&H-LYP is often used to investigate systems where spurious low-energy CT states may be problematic.^{30,51-56} Functionals such as B3LYP (with 20% exact exchange) and PBE0 (with 25%) systematically underestimate excitation energies for states with charge-separated character,⁵⁷⁻⁶² including core-to-valence transitions.⁶³⁻⁶⁹ This is primarily a consequence of SIE and becomes less severe as the fraction of exact exchange is increased. The BH&H-LYP functional performs well in benchmark tests of small-molecule valence excitation energies,⁷⁰⁻⁷² although it does overestimate excitation energies in some cases.⁷¹⁻⁷⁵ (This is especially true for large conjugated molecules,⁷³⁻⁷⁵ where 40% exact exchange may be preferable.⁷³) BH&H-LYP has also become the *de facto* standard for spin-flip TD-DFT calculations,⁷⁶⁻⁹⁶ for reasons explained elsewhere.⁹⁷ It shows up in other spectroscopic contexts as well.⁹⁸⁻¹⁰²

Despite its utility in mitigating delocalization error, BH&H-LYP was long ago judged to be unfit for general-purpose DFT calculations.^{103,104} Early studies demonstrated that half-and-half functionals exhibit somewhat larger errors (as compared to B3LYP) for atomization energies^{7,104} and reaction enthalpies,^{105,106} although BH&H-LYP affords slightly smaller errors for barrier heights.^{106–108} The notion that BH&H-LYP is greatly inferior to B3LYP, and thus inferior to improved functionals developed over the past 30 years, has become entrenched. As such, BH&H-LYP tends to be regarded as a functional of last resort, which should only be used in the context of certain SIE-dominated problems (including TD-DFT), because it will substantially degrade the accuracy of ground-state thermochemical properties.

Much of this conventional wisdom, however, is based on older literature and benchmarks using much smaller data sets than what has subsequently become standard in quantum chemistry. Prompted by another recent example where BH&H-LYP affords a solution to SIE-driven errors,⁴⁸ which are amplified by the DFT-based many-body expansion,^{48,109} we decided to reconsider and quantify the accuracy of BH&H-LYP versus B3LYP and related functionals with intermediate fractions of exact exchange.

To do so, we define a sequence of functionals $B(\alpha)LYP$,

$$E_{\rm xc}^{\rm B(\alpha)LYP} = \frac{\alpha}{100} E_{\rm x}^{\rm HF} + \frac{(100 - \alpha)}{100} E_{\rm x}^{\rm B88} + E_{\rm c}^{\rm LYP}$$
(3)

where α is the percentage of exact exchange $(E_x^{\rm HF})$. Our intention is not to carefully optimize α but rather to understand whether $\alpha = 50$, corresponding to the BH&H-

LYP functional in eq 2, is merely a point along a continuum or something worthy of special consideration. Because the functionals BHandH and BH&H-LYP are available by name in many quantum chemistry programs, one should consider the possibility that their recurring presence in the literature simply reflects available keywords. In the end, however, we find that 50% exact exchange does seem to have advantages compared to slightly larger or smaller values of α .

2. METHODS

2.1. Data Sets. The data sets used to benchmark groundstate properties (thermochemistry and barrier heights) are described in Section 2.1.1, while those used for vertical excitation energies are discussed in Section 2.1.2.

2.1.1. Ground-State Benchmarks. Geometries and reference energies for all thermochemical calculations were obtained from the GMTKN55 database.¹¹⁰ (The same geometries are used for each functional.) GMTKN55 is an amalgam of 55 distinct data sets and a description of each one can be found in Table S1. We group these into three subsets, the first of which consists of reaction barrier heights and includes the data sets BH76,¹¹⁰ BHPERI,¹¹¹ BHDIV10,¹¹⁰ INV24,¹¹² BHROT27,¹¹⁰ PX13,¹¹³ and WCPT18.¹¹⁴ (See Table S1 for brief descriptions, which are taken from ref 110.) The second subset contains basic thermochemical properties for small systems, including reaction energies, and consists of the data sets W4-11,¹¹⁵ G21EA,¹¹⁶ G21IP,¹¹⁶ DIPCS10,¹¹⁰ PA26,^{110,116–118} SIE4×4,¹¹⁰ YBDE18,¹¹⁹ AL2×6,¹¹⁰ NBPRC,¹¹⁰ ALK8,¹¹⁰ G2RC,¹¹⁰ BH76RC,¹¹⁰ FH51,^{120,121} TAUT15,¹¹⁰ and DC13.^{110,122} The ALKBDE10¹²³ and HEAVYSB11¹¹⁰ data sets, which are part of the reaction barrier data in GMTKN55, are excluded here because they contain atoms that are not supported by the def2-TZVPD basis set. Finally, we examine reaction and isomerization energies for large systems, including data sets MB16-43,¹¹⁰ DARC,¹¹⁰ RSE43,¹¹⁰ BSR36,¹¹⁰ CDIE20,¹²⁴ ISO34,¹²⁴ ISOL24,^{110,125} and PArel.¹¹⁰ The C60ISO data set,¹²⁶ consisting of isomerization reactions involving C₆₀, was excluded due to erratic convergence behavior for functionals with small fractions of exact exchange.

The parts of GMTKN55 that are dedicated to intermolecular and noncovalent interactions are not used here, as this would mostly be testing the dispersion correction. However, we will examine interaction energies for a set of $F^{-}(H_2O)_n$ clusters where ion-water delocalization error could be problematic. For that purpose we extracted cluster configurations from a classical molecular dynamics simulation, which were then trimmed to contain n = 3-7 water molecules. Benchmark interaction energies for removing the ion, while keeping the $(H_2O)_n$ geometry fixed, were computed at the level of second-order Møller-Plesset perturbation theory (MP2) within the resolution-of-identity (RI) approximation. To obtain complete basis-set RI-MP2 energy estimates, we combined the HF/aug-cc-pVQZ energy with a two-point extrapolation of the RI-MP2 correlation energy,¹²⁷ using augcc-pVTZ and aug-cc-pVQZ.^{128,129}

2.1.2. TD-DFT Benchmarks. For valence excitation energies, we employ a data set consisting of 23 local excitations and 8 CT excitations that was assembled by Tozer and co-workers (Table S14).⁶¹ Geometries for this data set can be found elsewhere.¹³⁰ For core-excited transition energies at the carbon, nitrogen, and oxygen K-edges, we use a benchmark data set from ref 131 (Table S15), with geometries from ref 69.



Figure 1. Error statistics for barrier heights. (a) MAEs for individual data sets in GMTKN55. (b) MAEs (in color), considering all of the barrier height data, and average maximum errors (in gray), where the latter is the average of the maximum errors for each of the seven data sets that are listed in (a). The def2-TZVPD basis set was used for all calculations.

All of these benchmark calculations employ full linear response in the TD-DFT calculations, meaning that the Tamm-Dancoff approximation⁴⁹ (TDA) is not invoked. This helps to identify the transitions for which reference data are available, by comparison to previously published benchmarks.¹³² Core-tovalence excitation energies are computed using the core/ valence separation (CVS) technique.^{133,134}

A data set containing 22 donor–acceptor complexes was used to compute S_1 excitation energies having CT character.¹³⁵ Benchmark excitation energies for this data set were computed for the present work, using configuration interaction singles corrected for double excitations, [CIS(D)].¹³⁶ (This method has elsewhere been used to benchmark CT excitation energies.¹³⁷) Reference values computed at the CIS(D)/augcc-pVTZ level can be found in Table S16. For TD-DFT calculations on this data set, we do employ the TDA.

TD-DFT(TDA) calculations are also reported for models of the hydrated electron, $e^{-}(aq)$. These calculations use structures obtained from quantum mechanics/molecular mechanics (QM/MM) trajectory data, originally from ref 138. Following established protocols,¹³⁹ these $e^{-}(aq)$ models consist of a DFT region extending to a radius of 7.5 Å and containing 68–76 QM water molecules, depending on the particular snapshot. In addition, an average of 6,140 additional water molecules are included as classical point charges. Geometries and point charges for these models can be found in ref 132.

2.2. Functionals. All functionals considered in this work are either dispersion-corrected or dispersion-inclusive,¹⁴⁰ as proper treatment of dispersion interactions is necessary in order to obtain competitive thermochemical benchmarks in modern DFT.^{140–146}

At the heart of this work is an examination of the $B(\alpha)LYP$ sequence defined in eq 3. This includes the GGA functional BLYP as a special case when $\alpha = 0$. At the other limit ($\alpha = 100$) is the HF-LYP functional,

$$E_{\rm xc}^{\rm HF-LYP} = E_{\rm x}^{\rm HF} + E_{\rm c}^{\rm LYP} \tag{4}$$

However, we find that errors are sufficiently large by $\alpha = 70$ that we will not report data for $\alpha > 70$.

We also consider the B3LYP functional,⁸ as a historical baseline and a point of contact that remains widely used and quite effective, especially for TD-DFT applications.^{49,70–72,147–151} The B3LYP functional does not fit within the B(α)LYP *ansatz*, and is instead given by

$$E_{xc}^{B3LYP} = a_0 E_x^{HF} + (1 - a_0 - a_x) E_x^{Slater} + a_x E_x^{B88} + (1 - a_c) E_c^{VWN} + a_c E_c^{LYP}$$
(5)

with $a_0 = 0.20$, $a_x = 0.72$, and $a_c = 0.81$.⁷ Note that different implementations of B3LYP may use different interpolation formulas to implement electron-gas correction, E_c^{VWN} .¹⁵² Occasionally, the *ansatz* in eq 5 has been used to implement a type of half-and-half functional, using $a_0 = 0.50$ and $a_x = 0.42$ (leaving $a_c = 0.81$),¹⁵³ but that functional is not examined here.

B3LYP is included in our testing due to its historical and ongoing significance, yet we find that its performance is generally similar to the B(20)LYP that uses the same fraction of exact exchange but fits within the *ansatz* defined in eq 3. We also considered the CAM-B3LYP functional,¹⁵⁴ which substantially mitigates problems with spurious CT states in TD-DFT,^{154–157} albeit sometimes erring too far in the opposite direction.¹⁵⁸ All ground-state B3LYP, CAM-B3LYP, and B(α)LYP calculations include the D3 dispersion correction in its original, "zero-damping" form.¹⁵⁹ As shown in Figure S2, ground-state error statistics for B3LYP+D3 and CAM-B3LYP+D3 are extremely similar, so the latter functional will not be considered in detail although we will make some further remarks on its accuracy for TD-DFT excitation energies.

In addition to B3LYP+D3 and B(α)LYP+D3, we also consider the meta-GGA functional ω B97M-V.¹⁶⁰ It is unrelated to B(α)LYP but is arguably the best all-around density-functional approximation available today.¹² Here, it serves to set a baseline for how small the errors can be made for modern DFT calculations of reaction barriers and thermochemistry.

Finally, we considered the M06-HF functional that includes 100% exact exchange and has been advertised as a density functional for spectroscopy, with better ground-state properties



Figure 2. Error statistics for thermochemical properties. (a) MAEs for individual data sets in GMTKN55. (b) WTMAD2 values (eq 6) for each functional, for the same data sets. All calculations used the def2-TZVPD basis set.

than B3LYP.¹⁶¹ While that statement is statistically true for the data sets considered in ref 161, we find that M06-HF is significantly inferior to B3LYP (and to BH&H-LYP) for the much more extensive data sets that are examined here. M06-HF data can be found in Table S6, which should be compared with the corresponding B3LYP data in Table S3. The M06-HF functional will not be discussed any further.

The def2-TZVPD basis set¹⁶² is used for all calculations on the GMTKN55 data set, as it provides accuracy rivaling def2-QZVPD for DFT thermochemistry and barrier heights.¹⁶³ All DFT calculations used the SG-1 quadrature grid,¹⁶⁴ except that ω B97M-V calculations used SG-2¹⁶⁵ and M06-HF calculations used SG-3.¹⁶⁵

3. RESULTS AND DISCUSSION

The following discussion presents error statistics for various functionals in graphical form. For the barrier heights (Section 3.1) and thermochemical data (Section 3.2), complete error statistics for each individual data set can be found in Tables S3-S13. TD-DFT data are presented in Section 3.4 and the numerical data can be found in Tables S14-S16.

3.1. Barrier Heights. Figure 1 examines errors for barrier heights, using the functionals described in Section 2.2. In Figure 1a, these errors are separated according to the various data sets that comprise the barrier height data in GMTKN55. The BHROT27 data set, consisting of 27 different rotational barriers around a single bond, is clearly an outlier insofar as the errors are very small for every functional examined. Although rotational barriers can manifest SIE problems in molecules with extended conjugation,¹⁶⁶ the BHROT27 molecules do not fall into that category. The transition states in question do not involve incipient bonds or fractional charges, and the errors are insensitive to the fraction of exact exchange.

For the other barrier height data sets, error statistics vary more widely from one functional to another, with MAEs ranging from 1 to 9 kcal/mol. Standard deviations (Tables S3– S13) are smaller than 2 kcal/mol except for the B(60)LYP +D3, B(70)LYP+D3, and BLYP+D3 functionals, where they range from 2.5 to 3.0 kcal/mol. Those three functionals will emerge as the least accurate of the ones examined here, and they are included mostly to set goalposts on the performance of B(α)LYP. Even so, the spread of the errors is sufficiently tight so that MAEs provide a reasonable way to analyze the error statistics.

The well-established functionals B3LYP+D3 and ω B97M-V afford MAEs of 2.5 and 1.5 kcal/mol, respectively. The "average maximum errors" that are reported in Figure 1b represent averages of the maximum errors for each of the barrier height data sets that are considered in Figure 1a; these values are 6.0 kcal/mol for B3LYP+D3 and 4.0 kcal/mol for ω B97M-V. Together, the errors for these two functionals set a baseline for what constitutes good performance. For B(20)LYP, which uses the same fraction of exact exchange as in B3LYP, the MAE is 2.3 kcal/mol and the average maximum error is 6.0 kcal/mol. These statistics are quite similar to those for B3LYP+D3, whereas the B(30)LYPfunctional performs slightly better with a MAE of 1.8 kcal/mol. The BLYP+D3 functional is not expected to perform well for problems where SIE is important and is included here simply to set a boundary, representing poor performance.

We are most interested in B(α)LYP for 20 $\leq \alpha \leq$ 50, which is the range that extends from something B3LYP-like ($\alpha = 20$), up to BH&H-LYP ($\alpha = 50$). Within that range, we observe no serious deterioration in accuracy relative to B3LYP+D3, and even one very small improvement for $\alpha = 30$. Although the statistical significance of this decrease is unclear, at the very least the MAE for barrier heights does not increase in any meaningful way, up to $\alpha = 50$. When compared to B3LYP+D3, the $\alpha = 50$ functional looks very similar except that the average maximum error is somewhat larger, at 7.0 kcal/mol (BH&H-LYP+D3) versus 6.0 kcal/mol (B3LYP+D3). When the percentage of exact exchange is increased beyond 50%, however, the MAEs do begin to increase somewhat, while the average maximum errors increase significantly.

3.2. Thermochemistry. We next consider the data sets in GMTKN55 consisting of thermochemical properties. For this discussion, we separate out isomerization energies from the broader thermochemical subset of GMTKN55, and reserve those data for Section 3.2.2.

Reference energies in the thermochemical data sets span two orders of magnitude so it is deceptive to consider average errors, as we did for barrier heights where the reference energies are more similar. Instead, we use the weighted total



Figure 3. Error statistics for large-molecule isomerization energies. (a) MAEs for individual data sets in GMTKN55. (b) MAEs (in color), considering all of the data sets except for MB16-43, and average maximum errors (in gray). The latter statistic is the average of the maximum errors over seven data sets, again excluding MB16-43. The def2-TZVPD basis set was used for all calculations.

mean absolute deviation, version 2 (WTMAD2), which was introduced for this purpose in ref 110. This metric is defined as

WTMAD2 =
$$\frac{1}{N} \sum_{i} \left[N_i (\text{MAE})_i \frac{|\overline{\Delta E}|_{\text{all}}}{|\overline{\Delta E}|_i} \right]$$
 (6)

where the summation runs over 15 thermochemical data sets. The quantity $(MAE)_i$ is the MAE for the *i*th data set, containing N_i data points whose average absolute reference data value is $|\overline{\Delta E}|_i$. The total number of data points in all 15 data sets is $N = \sum_i N_i$ and $|\overline{\Delta E}|_{all} = 56.84$ kcal/mol is the average absolute reference value across all N data points.

Average reference energies $|\overline{\Delta E}|_i$ span a range from 3 kcal/ mol (TAUT15) to 645 kcal/mol (DIPCS10), which is why error statistics for these myriad data sets require a weighted metric to make them comparable. It also means that the numerical value of WTMAD2 in eq 6 should not be taken as an actual error statistic, although it does have units of energy, but instead should be used simply to rank the performance of the different functionals examined.¹¹⁰ Error statistics within each individual data sets can be found in Tables S3–S13, and the MAEs for individual data sets are provided in Figure 2.

3.2.1. Basic Thermochemical Properties. The "basic" thermochemical data set¹¹⁰ consists of atomization energies (W4-11 data set), electron and proton affinities (G21EA and PA26 sets), ionization energies (G21IP and DIPCS10), bond dissociation energies (YBDE18 and AL2×6), and reaction energies (NBPRC, ALK8, G2RC, BH76RC, FH51, and TAUT15). Two other data sets, SEI4×4 and DC13, contain problems that are known to be particularly challenging for DFT. Error statistics are shown in Figure 2, with MAEs for the individual data sets provided in Figure 2a and WTMAD2 values in Figure 2b.

It is useful to first compare the general performance of the functionals examined. As a baseline, B3LYP+D3 has a WTMAD2 value of 4.5 kcal/mol whereas the best-performing functional remains ω B97M-V, with a WTMAD2 value of 2.5 kcal/mol. For BLYP+D3, the WTMAD2 is 6.9 kcal/mol. Any

acceptable member of the $B(\alpha)LYP+D3$ family ought to fall within the range delineated by these limiting cases.

Similar to what was observed for barrier heights, the performance of B(α)LYP+D3 shows little variation across the range 20 $\leq \alpha \leq$ 50, with WTMAD2 values of 5.3 kcal/mol ($\alpha = 20$) and 5.2 kcal/mol ($\alpha = 50$) for the end points. All of the functionals in this range perform slightly worse than B3LYP +D3, corresponding to WTMAD2 values that are ~ 0.6 kcal/mol larger and MAEs that are about 1 kcal/mol larger (see Tables S3–S11). At the same time, these B(α)LYP+D3 functionals are superior to BLYP+D3, by ~1.6 kcal/mol in the WTMAD2 metric. In contrast, values $\alpha \geq$ 60 afford errors that are comparable to (or even larger than) those exhibited by BLYP+D3, which is unacceptable for a hybrid functional.

Three data sets are worth examining in detail: W4-11, SIE4×4, and DC13, each of which exhibits a broad spectrum of errors (Figure 2a). The W4-11 data set consists of 140 atomization energies and exhibits the largest variation in the errors, among the set of functionals examined. Atomization energies make for a rigorous test of performance because there is no opportunity for error cancellation, and it is clear from the W4-11 data that increasing the fraction of exact exchange has a direct and detrimental impact on the accuracy of $B(\alpha)LYP+D3$ for this particular property. The B3LYP+D3 functional performs substantively better even than B(20)LYP+D3, whose MAE is 7 kcal/mol, and all functionals with $\alpha \ge 30$ perform worse for the W4-11 atomization energies than does BLYP+D3. On the other hand, because atomization energies are rarely an observable of interest, poor performance of $B(\alpha)LYP+D3$ for this property may not be an obstacle to deploying a given functional in practice.

We next consider the SIE4×4 data set, which consists of dissociation energies for H_2^+ , He_2^+ , $(NH_3)_2^+$, and $(H_2O)_2^+$ at intermolecular distances $R = R_e$ (equilibrium separation) and also $R = 1.25R_e$, $1.50R_e$, and $1.75R_e$. These are challenging systems for many functionals, due to SIE problems. The data for SIE4×4 in Figure 2a reflect the anticipated trend, with errors decreasing as the fraction of exact exchange increases, starting from BLYP+D3 that exhibits the largest errors. The BH&H-LYP functional ($\alpha = 50$) outperforms ω B97M-V for

SIE4×4, as does B(60)LYP+D3, while B(40)LYP+D3 is on par with ω B97M-V. For these SIE-dominated problems, there is clear merit in enhancing the fraction of exact exchange and it is precisely for these type of CT complexes where BH&H-LYP has often been deployed in the past.^{3,26,29,30}

The final data set that we examine in detail is DC13, consisting of 13 large-system reaction and isomerization energies that are considered to be challenging for DFT.¹¹⁰ MAEs for all of the B(α)LYP+D3 functionals lie within about 4 kcal/mol of one another. Each is superior to BLYP+D3 and comparable to B3LYP+D3, except (arguably) for the $\alpha = 20$ functional whose error is a bit larger. Of the B(α)LYP+D3 functionals, however, BH&H-LYP+D3 is the best, outperforming even B3LYP+D3 and suggesting that 50% exact exchange is beneficial for these challenging cases.

Our overall assessment is that increasing exact exchange beyond 20% has benefits on the order of \sim 1 kcal/mol for many properties, with atomization energies as a notable exception. Further increases in the fraction of exact exchange are beneficial for problems where SIE plays a significant role but such increases have a deleterious effect on the accuracy of atomization energies. Setting the latter property aside, BH&H-LYP+D3 exhibits performance that is similar to B3LYP+D3 in most cases and superior in SIE-dominated cases. However, 50% exact exchange appears to be something of an upper bound, beyond which the errors increase significantly.

3.2.2. Isomerization Energies. We next consider largemolecule isomerization energies, whereas the isomerization energy data sets considered in Section 3.2.1 correspond to smaller molecules. Error statistics are presented in Figure 3. As for the barrier height data in Figure 1b, the maximum errors presented as gray bars in Figure 3b are averages of the maximum errors across the separate data sets, except that in the present case we exclude the MB16-43 data set from the average. This data set comes from "mindless benchmarking",¹⁶⁷ consisting of 43 reactions created at random and having 16 atoms each.¹¹⁰ The reference energies for this data set are quite large, with an average of $|\overline{\Delta E_{MB16-43}}| = 414.7 \text{ kcal}/$ mol, which is an order of magnitude larger than $|\overline{\Delta E}|_{i}$ for any other data set considered in Figure 3. This significantly skews the error statistics, so we remove MB16-43 from the averages that are given in Figure 3b. This is an alternative to using WTMAD2 and allows us to consider actual MAEs, by

eliminating the one data set that would otherwise swamp the averages. Excluding MB16-43, B3LYP+D3 has a MAE of 3.3 kcal/mol for the remaining seven data sets that are considered in Figure 3. (That MAE increases to 7.2 kcal/mol if MB16-43 is included.) The ω B97M-V functional has a MAE of 2.9 kcal/mol if MB16-43 is excluded or 4.9 kcal/mol if it is included. For comparison, BLYP+D3 has a MAE of 4.2 kcal/mol (sans

MB16-43) or 8.3 kcal/mol (with MB16-43). For the B(α)LYP+D3 functionals, values 30 $\leq \alpha \leq$ 40 exhibit errors that are comparable to, or slightly smaller than, B3LYP+D3 errors, suggesting that these are adequate functionals for reaction energies. In fact, BH&H-LYP+D3 and B(60)LYP+D3 exhibit MAEs of 2.4 and 2.3 kcal/mol, respectively, either of which improves upon B3LYP+D3 by nearly 1 kcal/mol. However, values $\alpha \geq 60$ significantly exacerbate outliers, as evidenced by larger average maximum errors when compared to BH&H-LYP+D3. The particular choice $\alpha = 50$ does seem to be superior to values that are somewhat larger or smaller.

Overall, we find that the general performance of BH&H-LYP is never truly poor, except for atomization energies. Moreover, this functional improves upon B3LYP in key cases where SIE is significant. For those cases, the use of 50% exact exchange does appear to be nearly optimal, at least within the one-parameter $B(\alpha)LYP$ ansatz. As such, the persistence of BH&H-LYP in the literature may reflect a genuine performance benefit rather than a residual consequence of being a named functional in many electronic structure codes.

3.3. Ion–Water Interactions. We next consider interaction energies for a data set consisting of 131 configurations of $F^{-}(H_2O)_n$, n = 3-7, where benchmark interaction energies for the ion were computed at the RI-MP2/aug-cc-pV[T/Q]Z level as described in Section 2.1.1. These benchmarks range from $\Delta E = -55$ kcal/mol to $\Delta E = -105$ kcal/mol across the data set. Error distributions for various DFT calculations, relative to these benchmarks, are presented in Figure 4 in the form of histograms over the 131 configurations. The ω B97M-



Figure 4. Signed errors in $F^{-}\cdots(H_2O)_n$ interaction energies with respect to benchmarks computed at the RI-MP2/aug-cc-pV[T/Q]Z level. Positive errors indicate values of $|\Delta E|$ that are larger than the benchmark and the shaded region represents ± 1 kcal/mol error. Vertical black lines indicate the mean error for each functional. All DFT calculations used the aug-cc-pVTZ basis set.

V functional affords excellent agreement with the benchmarks, with a mean error in $|\Delta E|$ of only 0.4 kcal/mol (tending toward overestimation) and a narrow distribution of errors. B3LYP +D3 also affords good agreement with the benchmarks, with a mean error in ΔE of 0.7 kcal/mol in the opposite direction.

Using $B(\alpha)LYP+D3$, we observe a consistent trend toward larger interaction energies (i.e., larger values of $|\Delta E|$) as α increases. In Figure 4, we have included data for functionals with α = 5 and α = 15 that were not considered above, in order to emphasize that this trend is quite systematic. In contrast to thermochemical properties, where there was often little variation in accuracy over the range $30 \le \alpha \le 50$, here there are systematic shifts within that range. An essentially linear shift in the mean value of $|\Delta E|$, as α increases, reflects delocalization of the ion's density into frontier molecular orbitals (MOs) of the neighboring water molecules,¹⁹ and the GGA functional BLYP+D3 underestimates $|\Delta E|$ by about 3.4 kcal/mol. The B(20)LYP+D3 errors are not dissimilar from the B3LYP+D3 errors albeit shifted slightly so that the mean error is nearly zero. For $\alpha \geq 30$, the ion is increasingly overbound as α increases. For BH&H-LYP, the mean error is 4.2 kcal/mol (toward overbinding). In percentage terms, however, the mean error for BH&H-LYP+D3 is <10% because $|\Delta E|$ is quite large.

3.4. Excitation Energies. We next consider TD-DFT results for excitation energies. This discussion is separated into K-edge ($1s \rightarrow valence$) excitation energies for second-row elements, which are considered in Section 3.4.1, whereas valence excitation energies are discussed in Section 3.4.2. In Section 3.4.3 we consider the absorption spectrum of the hydrated electron, $e^{-}(aq)$.

3.4.1. Core-to-Valence (K-Edge) Transitions. Unlike the situation for wave function methods, core-level excitations in TD-DFT need not require specialized basis sets or modifications to the core functions,¹³⁴ although we do invoke the CVS approximation.^{133,134} Errors in TD-DFT/def2-TZVPD excitation energies for a set of small organic molecules,¹³¹ at the K-edges of carbon, nitrogen, and oxygen, are provided in histogram form in Figure 5 for the B(α)LYP functionals.

Previous work demonstrates that hybrid functionals including B3LYP, PBE0, and CAM-B3LYP consistently underestimate core-to-valence excitation energies,^{69,102} with errors that increase as a function of atomic number for the elemental K-edge in question. This trend can be understood in terms of differential SIE between core and valence orbitals, with greater SIE for the 1s orbitals of heavier elements.¹⁶⁸ Meanwhile, the CIS method overestimates these same transition energies.⁶⁹ This is mostly an effect of incomplete orbital relaxation,¹⁰² a shortcoming that is shared by TD-DFT but exposed in the CIS case because SIE is absent. This points to orbital relaxation errors partially canceling SIE for core-to-valence TD-DFT calculations, as quantified elsewhere.¹⁰²

Using the one-parameter B(α)LYP *ansatz*, Besley and coworkers suggested $\alpha = 57$ as the optimal value to cancel SIE and minimize errors in K-edge transition energies, ^{65,169} although others have suggested that 70% HF exchange is optimal for K-shell excitations, as compared to 50% for L-shell transitions and 20% for valence excitations.¹⁷⁰ For the present data set, the value $\alpha = 60$ in Figure 5 leads to signed errors that are approximately symmetric about zero, whereas smaller values systematically underestimate the transition energies (suggesting residual SIE that is more significant than neglected



Figure 5. Errors in TD-DFT/def2-TZVPD values for K-edge excitation energies in a set of 20 organic molecules, as compared to theoretical best estimates from ref 131. Negative errors correspond to underestimated transition energies and the shaded region corresponds to \pm 1 eV error.

orbital relaxation), whereas larger values of α lead to overestimated excitation energies whose errors are likely dominated by the missing orbital relaxation effects.

Although B3LYP data are not provided in Figure 5, that functional's MAE for this data set is 13.3 eV, which is slightly larger than that for B(30)LYP and thus consistent with the trend (as a function of α) that is evident in Figure 5. The MAE decreases to 2.0 eV for B(60)LYP. A slightly smaller MAE of 0.7 eV was reported by Besley et al.⁶⁵ for K-edge transitions, using a functional with 58% exact exchange applied to a different data set. We regard this as comparable to the present results, given the scale of the errors (as a function of α) that is documented in Figure 5. The short-range correction (SRC) functionals that were introduced in ref 65, in order to improve on these results, employ 50% (SRC1) and 55% (SRC2) exact exchange at the shortest length scale (≤ 1 Å) in a tripartite range separation scheme. This reduces the MAEs to 0.3-0.6 eV. These observations from ref 65 suggest that 50-60% exact exchange works very well for core-to-valence excitation energies, which is indeed what we observe in Figure 5.

3.4.2. Valence Transitions. Errors in valence excitations are considered in Figure 6, using B3LYP and B(α)LYP. Because transitions that exhibit charge-separated character are more sensitive to the fraction of exact exchange, we have set these apart from the localized transition energies in the data set. Even so, the localized transitions (Figure 6a) show a slight uptick in the errors as α increases, although this trend is much more pronounced for CT excitations (Figure 6b,c). Previous work has shown that TD-CAM-B3LYP affords similar errors as TD-B3LYP for valence excitation energies (even while it significantly improves CT and Rydberg excitation energies),^{61,154} so the CAM-B3LYP functional is not considered in detail.

B3LYP exhibits the smallest errors, centered around zero, for the localized valence transitions (Figure 6a), although B(30)LYP is somewhat more accurate for the donor \rightarrow

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Figure 6. TD-DFT error statistics for valence excitation energies. (a) Small-molecule transition energies as compared to reference values from ref 61. (b) S₁ excitation energies for donor-acceptor complexes¹³⁵ with respect to CIS(D)/aug-cc-pVTZ benchmarks. (c) CT excitation energies, using reference values from ref 61. Colored boxes extend from the first to the third quartile of the data, with a horizontal line indicating the median. Whiskers extend to the farthest data point within 1.5× of the interquartile range, which represents a 99% confidence interval in the case of normal distribution of errors. Black circles indicate MAEs for each functional. All calculations used the cc-pVTZ basis set except for the Rydberg transitions, for which the doubly augmented d-aug-cc-pVTZ basis set was used, as in ref 61.

acceptor transitions in Figure 6b. Favorable performance of B3LYP and PBE0 for other valence excitation energies suggests that 20-25% exact exchange works well for localized valence transitions.^{49,70,72,147,148} In contrast, smaller fractions of exact exchange lead to significant underestimation of the transition energies, culminating in significant and systematic underestimation of valence transition energies by GGA functionals.^{49,70,72,147,148} In the present data, this trend manifests as a MAE of 0.3 eV for B(10)LYP as compared to 0.2 eV for both B3LYP and B(20)LYP.

The donor-acceptor data set consists of 22 complexes whose $S_0 \rightarrow S_1$ transitions primarily involve excitation from the highest occupied MO (HOMO) of a donor molecule into the lowest unoccupied MO (LUMO) of an acceptor,¹³⁵ in a van der Waals complex. Although these are CT states in principle, the quantitative extent of CT in these complexes is not large,¹³⁵ due to orbital delocalization, and B3LYP continues to perform well (see Figure 6b). It exhibits a MAE of 0.3 eV as compared to CIS(D)/aug-cc-pVTZ benchmarks. Larger fractions of exact exchange lead to upshifted excitation energies, although B(30)LYP and B(40)LYP remain accurate with MAEs of 0.2 eV in both cases. However, for $\alpha = 40$ the excitation energies are all overestimated, whereas the range of errors spans zero for $\alpha = 30$. For $\alpha = 50$ (BH&H-LYP), the MAE is 0.35 eV and it increases to 0.54 eV for $\alpha = 60$.

Data in Figure 6c correspond to Rydberg transitions and longer-range charge separation.⁶⁵ Here, B3LYP significantly underestimates the excitation energies, with a MAE of 1.0 eV, whereas BH&H-LYP moves the average error closer to zero and exhibits a smaller error as compared to B(30)LYP. Larger fractions of exact exchange are not beneficial; functionals $B(\alpha)LYP$ with $\alpha = 60-70$ overestimate all, or nearly all, of the transition energies. This is consistent with the behavior of CIS.^{49,137} Thus, 50% exact exchange emerges once again as a special value that works well even in comparison to similar mixing coefficients.

3.4.3. Hydrated Electron. The aqueous or hydrated electron, $e^{-}(aq)$, $^{171-175}$ has a characteristic absorption spectrum peaked at 1.72 eV, 176 which has long been used as a test for theoretical models. 174 This includes different exchange-correlation functionals in TD-DFT calculations. $^{139,177-180}$ Here, absorption spectra are computed using

seven well-spaced snapshots from a DFT-based QM/MM simulation of $e^{-}(aq)$,¹³⁸ which is sufficient to converge the envelope of the spectrum.¹³² TD-B(α)LYP(TDA)/6-31++G* calculations were performed on these QM/MM snapshots, then the vertical transition energies were weighted by oscillator strength and broadened using a Gaussian function whose standard deviation is 0.2 eV.

Simulated absorption spectra in Figure 7a include just three excited states per snapshot, representing the s \rightarrow p transitions of a particle in a quasi-spherical cavity.^{174,177} Spectra in Figure 7b include additional excited states and exhibit a "blue tail" at higher excitation energies, which is characteristic of the spectrum of $e^{-}(aq)$.^{176,177} These spectra demonstrate, on the one hand, how exquisitely tunable TD-DFT excitation energies are with respect to the fraction of HF exchange, as the maximum in the absorption spectrum is shifted by ≈ 1 eV from $\alpha = 20$ to $\alpha = 70$.

Regardless of how many states are included in the calculation, 20% exact exchange affords a spectrum that peaks much too far to the red, likely as a result of CT character in the excited states.¹³⁹ Values $\alpha = 40-50$ afford a much better match to the experimental absorption maximum. Because the original QM/MM trajectories were performed using a different functional (BLYP with a self-interaction correction),¹³⁸ we do not want to overemphasize which particular value of α matches the experimental absorption maximum, as this is certainly affected by the solvent structure that is obtained from the ground-state molecular dynamics. That said, values $\alpha \gtrsim 60$ are clearly too strongly blue-shifted. This reinforces the view that BH&H-LYP ($\alpha = 50$) is a good choice for TD-DFT applications.

4. CONCLUSIONS

For thermochemistry, our results demonstrate that the BH&H-LYP+D3 functional (with 50% exact exchange) often exhibits satisfactory accuracy as compared to B3LYP+D3. In particular, errors for the former are <1 kcal/mol for many thermochemical data sets. Meanwhile, for problems that are dominated by SIE the half-and-half functional may outperform the best contemporary density-functional approximations, exemplified here by ω B97M-V. A notable exception is that atomization energies are significantly less accurate for the entire one-



Figure 7. QM/MM absorption spectrum of $e^{-}(aq)$ computed at the TD-B(α)LYP(TDA)/6-31++G* level. (a) Spectra obtained using only the lowest 3 excited states for each snapshot, representing $s \rightarrow p$ excitations. (b) Spectra including 15 excited states for each snapshot, exhibiting a pronounced tail at higher excitation energies. A vertical line indicates the experimental absorption maximum at 1.7 eV. To obtain these spectra, vertical transition energies were weighted by oscillator strengths and then broadened using a Gaussian function with a standard deviation of 0.2 eV.

parameter $B(\alpha)LYP+D3$ family of functionals, even as compared to B3LYP+D3. For interaction energies of $F^-(H_2O)_n$ clusters, where GGA functionals such as BLYP +D3 significantly underestimate interaction energies, BH&H-LYP+D3 errs in the opposite direction. For these systems, better accuracy is obtained using fractions of exact exchange that are smaller than 50%.

For excitation energies, TD-BH&H-LYP exhibits superior results in cases where TD-B3LYP fares poorly. Examples include core-to-valence excitations at elemental K-edges, which are effectively a type of CT state, as well as transition energies for Rydberg excitations and other charge-separated states. For these systems, 50–60% exact exchange affords the best results. The BH&H-LYP functional also affords a reasonable absorption spectrum for the hydrated electron, a problem that is exquisitely sensitive to the fraction of exact exchange. In contrast, functionals with \approx 20% exact exchange afford spectra for $e^-(aq)$ that are significantly red-shifted due to CT contamination. Conversely, B(α)LYP with 60% HF exchange affords a significantly blue-shifted spectrum.

Overall, our assessment is that the "half-and-half" choice (50% exact exchange) behaves particularly well for problems that are known to be affected by SIE. As such, it is not happenstance that BH&H-LYP tends to find its most widespread utilization in TD-DFT calculations, and in ground-state applications where CT character is potentially an issue. Neither is it the case that BH&H-LYP simply benefits from being a "named" functional in standard quantum

chemistry programs, which happens to have a large fraction of exact exchange. Rather, BH&H-LYP exhibits favorable performance even as compared to other functionals in the oneparameter B(α)LYP family. BH&H-LYP also outperforms the M06-HF functional,¹⁶¹ which was designed with 100% exact exchange for spectroscopic applications using TD-DFT. Other functionals with 100% exact exchange have been suggested,^{181–193} which are SIE-free by construction, but none of these is yet in widespread use.

Recently, it was suggested that BH&H-LYP may be a "compromise" functional for systems that are beset by SIE and otherwise unapproachable with DFT.^{48,109} The present results indicate that such a compromise sacrifices less than one might have anticipated. Therefore, one may imagine using BH&H-LYP for an entire workflow, obviating the need to swap functionals when SIE rears its head. Although errors for barrier heights and for thermochemistry will likely be somewhat larger than what could be achieved using the best modern meta-GGA functionals, those larger errors may still be comparable to what would be obtained using B3LYP+D3. The latter remains a widely used, all-purpose density-functional approximation and we suggest that BH&H-LYP+D3 can safely be afforded the same status for applications that are sensitive to SIE.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.5c01402.

Detailed thermochemical and excitation energy data (PDF)

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Notes

The authors declare the following competing financial interest(s): J.M.H. is part owner of Q-Chem Inc. and serves on its board of directors.

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