Using optimally tuned range separated hybrid functionals in ground-state calculations: Consequences and caveats

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Using optimally tuned range separated hybrid functionals in ground-state calculations: Consequences and caveats

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Optimally tuned range separated hybrid functionals are a new class of implicitly defined functionals. Their important new aspect is that the range separation parameter in these functionals is determined individually for each system by iteratively tuning it until a fundamental, non-empirical condition is fulfilled. Such functionals have been demonstrated to be extremely successful in predicting electronic excitations. In this paper, we explore the use of the tuning approach for predicting ground state properties. This sheds light on one of its downsides – the violation of size consistency. By analyzing diatomic molecules, we reveal size consistency errors up to several electron volts and find that binding energies cannot be predicted reliably. Further consequences of the consistent ground-state use of the tuning approach are potential energy surfaces that are qualitatively in error and an incorrect prediction of spin states. We discuss these failures, their origins, and possibilities for overcoming them. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4807325]

I. INTRODUCTION

Recent years have seen the advent of a new class of functionals in density functional theory (DFT) and time-dependent DFT (TDDFT). Functionals within this class are not and cannot be expressed explicitly, but are defined implicitly, often via a numerical procedure. Such functionals can be general and non-empirical, yet allow for considerably greater flexibility in the functional definition. Therefore, they are a promising route for improving the accuracy of practical DFT and TDDFT calculations without introducing empirical concepts. In the spirit of the famous classification of density functionals into three generations,[1] one may think of numerically defined functionals as the fourth generation. Examples for such functionals include the adiabatically exact approximation,[2] functionals based on inversion arguments,[3] functionals based on the concepts of machine learning,[4] and optimally tuned range separated hybrid (RSH) functionals.[5,6] The latter are examined in this work.

The main idea in RSH functionals is the separation of the Coulomb repulsion term into a short- and a long-range part,[7,8] e.g., in the form

$$\frac{1}{r} = \frac{1 - \mathrm{erf}(\gamma\, r)}{r} + \frac{\mathrm{erf}(\gamma\, r)}{r}, \qquad (1)$$

where γ is a range separation parameter. For short distances, the first term on the right hand side of Eq. (1) is the dominant contribution. For large distances, the second term dominates. They equally contribute at around $0.5\,\gamma^{-1}$, the separation point between short and long-range. The two ranges of electron-electron distances are then treated with different functionals. The most common realization is to treat the short-range exchange with a semi-local functional and the long-range exchange exactly, with the correlation energy described by a semi-local functional without splitting into long-range and short-range parts. RSH functionals have become popu-

lar in recent years because the range separation allows for a self-interaction free description at large electron-electron distances while maintaining a balanced description of exchange and correlation in the short range, based on well known semi-local functional concepts. Different implementations of this idea have been suggested and discussed, e.g., in Refs. 9–14 and more general forms involving a fraction of short-range exact exchange have also been put forth, e.g., in Refs. 15 and 16.

The focus of this work is on investigating the specific way of choosing the range separation parameter γ, which has become known as "optimal tuning." One way of determining γ is by empirical fitting against an appropriate training set.[12,14–17] However, various studies, e.g., Refs. 18–22, have shown that the best value of γ can be strongly system-dependent and that capturing this dependence correctly is crucial for the quality of the results. "Optimal tuning" is a successful strategy for choosing γ in a system-specific but non-empirical way, in which γ is chosen so as to obey a known exact property.[5,6] While other possibilities exist,[23] in the most popular and broadly applicable tuning approach γ is chosen such that the eigenvalue of the highest occupied molecular orbital (HOMO) is as close as possible to the negative ionization potential (IP) computed from total energy differences,[12] often for both the neutral and anionic system.[24] The optimally tuned RSH approach was already successfully employed for a great variety of systems. Two of its notable achievements were the correct prediction of charge transfer excitation energies, also in situations where other functionals designed for charge transfer fail,[21] and fundamental gaps (see, e.g., Refs. 6, 18–21, 24–27 for an overview). For the fundamental gaps, it is particularly important to keep in mind that RSH functionals are implemented within the generalized Kohn-Sham scheme.[28] It is therefore possible to tune the generalized-Kohn-Sham HOMO-LUMO gap to be close to the physically meaningful fundamental gap.[6]

While virtually all applications of the optimal-tuning approach have so far confirmed a distinct system dependence of γ, such a dependence, when incorporated into a global parameter as in the tuning, clearly also possesses conceptual drawbacks, notably the violation of size consistency. It has long been known that this problem exists in principle.[12] With this work, taking seriously the concept of treating the tuned RSH functional as an implicitly defined one, we investigate how the formal drawbacks manifest themselves in errors obtained in practical scenarios. We demonstrate that there are situations in which not only the choice of the range separation parameter but also the choice of the semi-local approximation has a major influence on the results. After a brief description of the underlying methods in Sec. II and a detailed discussion of different tuning conditions in Sec. III, we quantify the size consistency error and examine its impact on binding energies in Sec. IV. In Sec. V, we show how related issues may result in problems with the prediction of electronic spin configuration and potential energy curves. Finally, we analyze and summarize the reasons for the observed failures and close with an outlook on approaches for overcoming these problems.

II. METHODOLOGY

As mentioned above, this work aims to quantify the size consistency error and to calculate the binding energies of molecules with optimally tuned RSH approaches in a comparative study of different tuning conditions and short-range exchange expressions. In order to keep the analysis – which is in fact quite involved – as transparent as possible, we focus on diatomic molecules. Of the various RSH functionals that are available we here examine two specific choices: the Baer-Neuhauser-Livshits (BNL) functional,[11,12] which employs a short-range version of the local density approximation (LDA) exchange functional and Lee-Yang-Parr (LYP) semi-local correlation, and the ωPBE functional of Scuseria and co-workers[13] which employs a short-range version of the Perdew-Burke-Ernzerhof (PBE) semi-local exchange functional[29] and semi-local PBE correlation.

For our calculations we used the program package QChem,[30] which has both the BNL and the ωPBE functionals implemented. All calculations were carried out using the aug-cc-pVQZ basis set, unless explicitly stated otherwise. Most of the results presented below change considerably if a cc-pVQZ basis set is used without diffuse functions, because calculations with anions are incorporated as part of the tuning procedure. Further details on basis set dependence are given in Sec. III.

III. TUNING CONDITIONS

The general idea behind the tuning approach is to demand that the HOMO is the negative of the IP – a condition that has to be fulfilled for the exact functional.[31–34] One possibility for obtaining an approximation to the IP is the calculation of the difference between the total energies of the $N-1$ and the N electron system. This leads to the tuning condition[12]

$$T_N(\gamma) = \left| \epsilon^\gamma_{\text{HOMO}}(N) + E^\gamma(N-1) - E^\gamma(N) \right| = \min. \quad (2)$$

The minimum of T_N defines an optimal γ_N for which the HOMO energy is as close as possible to the approximate IP. γ_N has to be determined in an iterative procedure with successive ground state energy calculations for the N and the $N-1$ electron system. For the ultimate functional, the condition of Eq. (2) would be perfectly fulfilled. For approximate functionals the approach is still approximate as per construction, even when $T_N(\gamma) = 0$ is reached, it is limited to the predictive power of the IP approximation—a price to pay for having a non-empirical tuning approach.

In order to obtain the fundamental gap from quasiparticle energy differences, it is tempting to use a similar condition for connecting the LUMO (lowest unoccupied molecular orbital) and the electron affinity (EA). However, there is no rigorous theoretical basis for such a connection. A convenient way around this problem is to apply the IP tuning to the $N+1$ electron system. This leads to the second tuning condition[24]

$$T_{N1}(\gamma) = \left| \epsilon^\gamma_{\text{HOMO}}(N+1) + E^\gamma(N) - E^\gamma(N+1) \right| = \min. \quad (3)$$

To obtain the optimal fundamental gap it would be necessary to enforce both conditions T_N and T_{N1} at the same time. However, this is not possible with just one parameter γ and therefore both conditions have to be combined in a least square approach to minimize the resulting error. This leads to the third condition[6]

$$T_{LS}(\gamma) = \sqrt{T_N^2(\gamma) + T_{N1}^2(\gamma)} = \min. \quad (4)$$

The optimal γ obtained from this tuning condition, γ_{LS}, lies between γ_N and γ_{N1}, i.e., the optimal γ's that result from using T_N and T_{N1} as tuning conditions. It is thus a compromise between these both conditions. We note that a related, fourth tuning condition, used in some of our earlier publications[19,21,24,25] combines the absolute values of T_N and T_{N1},

$$T_{J2}(\gamma) = |T_N(\gamma)| + |T_{N1}(\gamma)| = \min. \quad (5)$$

We do not consider this tuning condition in the following because it tends to produce γ_{J2} which is very close to either γ_N or γ_{N1}, depending on how the total and the HOMO energies vary with γ.

A first step in our work is to find the optimized γ-values and energies for representative atoms and diatomic molecules with these tuning conditions. A technical but important prerequisite to this task is to determine the basis set sensitivity of the method. Generally, the basis set quality required for a certain calculation strongly depends on the employed method and the property of interest. Because RSH functionals are in many ways similar to hybrid functionals, one could naively expect equivalent basis set requirements. For an RSH without tuning this is indeed the case, as demonstrated in Fig. 1 for the BNL functional, using the oxygen atom as an example. In these two graphs we compare different basis sets with the aug-cc-pVQZ basis set and plot the respective differences for the total energy and the HOMO-LUMO gap. As expected, data points obtained from B3LYP,[35] a popular conventional hybrid functional, are close to the "BNL without tuning" data points (where we used $\gamma = 0.6$). If we perform the T_{LS} tuning for each basis set separately, however, we observe severe
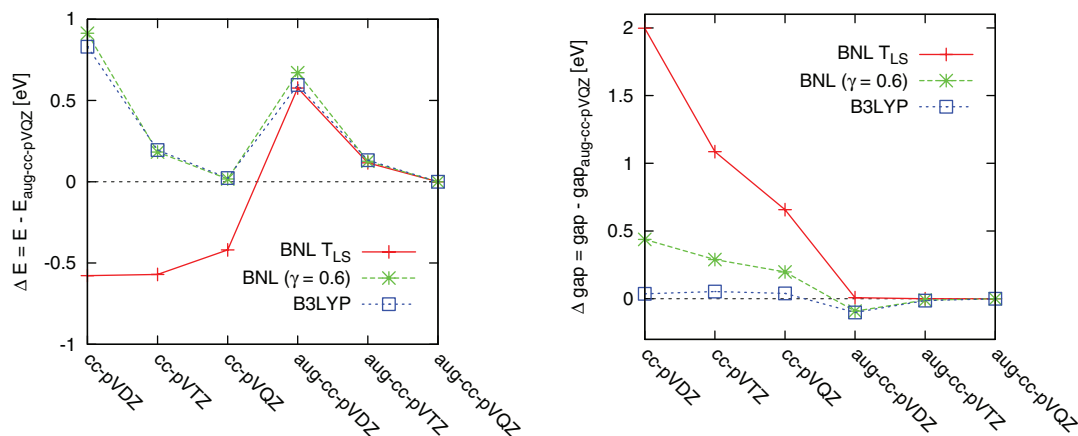
FIG. 1. Basis set dependence for the oxygen atom: Tuned BNL calculations with T_{LS} (solid line), BNL calculations with a constant $\gamma = 0.6$ (dashed line), and B3LYP calculations (dotted line). (Left) Difference of the ground-state energies obtained with the particular basis set and the aug-cc-pVQZ basis set. (Right) HOMO-LUMO gap difference obtained with the particular basis set and the aug-cc-pVQZ basis set.

deviations from the calculations with constant γ. There are two reasons for this increased basis set dependence. First, the tuning depends on the anion and the cation, which themselves have a basis set sensitivity (especially the anion). Second, changes due to the basis set enter a calculation twice. On the one hand due to the RSH calculation itself and on the other hand due to the tuning process. Hence it is necessary to choose the basis set carefully if doing a tuned RSH calculation and to use or compare to a basis set with diffuse functions if using the T_{N1} or the T_{LS} tuning, as both depend on the anion.

Having addressed the basis set issue, we turn to evaluating the tuning procedure itself. The upper part of Fig. 2 shows the optimized γ values for diatomic molecules composed of first and second row atoms. All three tuning conditions exhibit

FIG. 2. (Upper part) Optimized γ values for diatomic molecules. The tuning conditions of Eqs. (2)–(4) were used. (Lower part) Inverse experimental[36] bond lengths.

a similar behavior. With only a few exceptions, the BNL γ's are just slightly larger than the ωPBE ones. As mentioned in earlier work,[18,20,21] the range separation parameter depends inversely on the system size. Our calculations confirm this finding, as seen by comparing γ to the inverse of the bond length in the lower part of Fig. 2. As a corollary, γ_N is larger than γ_{N1}, the latter being obtained for the (larger) anion, and consequently γ_{LS} is between γ_N and γ_{N1}. However, note that there is one clear exception: the BeS molecule. This exception is related to tuning problems with alkali and earth alkali atoms and is discussed in the following. We also note that this behavior is very sensitive to the basis set. If we use the cc-pVQZ instead of the aug-cc-pVQZ basis set, we obtain much smaller γ_N and γ_{LS} for BeS; however, γ_N of Be$_2$ is then considerably larger. That data points are missing for some systems indicates that the calculations in these cases lead to unstable anions. Therefore, the tuning conditions T_{N1} and T_{LS} are not well defined and are neglected in this graph and all other graphs of this work.

In the upper part of Fig. 3 we plot the γ values for atoms calculated again with both BNL and ωPBE. In the lower part of the same Figure we plot the inverse of the calculated atomic radii to demonstrate the system size dependence of γ as we would expect it. Clearly, the BNL γ_N and the BNL γ_{LS} values of all alkali and earth alkali atoms of this plot do not follow the general trend. Their γ values are out of scale, just as in the case of the BeS molecule. The reason is that for these systems $T_N(\gamma)$ of Eq. (2) never intersects the zero line, whereas a zero is found for all other systems that the authors know about. Moreover, $T_N(\gamma)$ exhibits just a shallow minimum at very large γ, or it has no minimum and converges to a small positive constant c, as in the case of Li. It is noteworthy that in these cases the minimum value (or the constant c) is very small (<0.5 eV) and therefore even in these cases the tuning approach predicts the fundamental gap reliably as demonstrated in Ref. 18. However, other properties, such as the total energy in the ground state, may differ from reference values by up to several 10 eV.
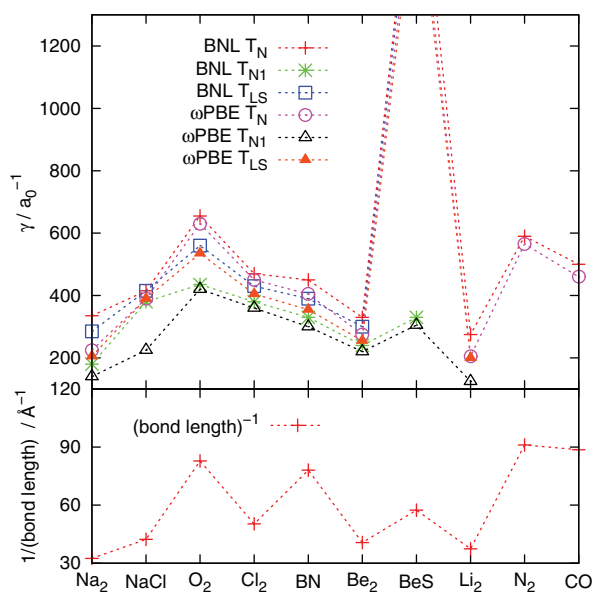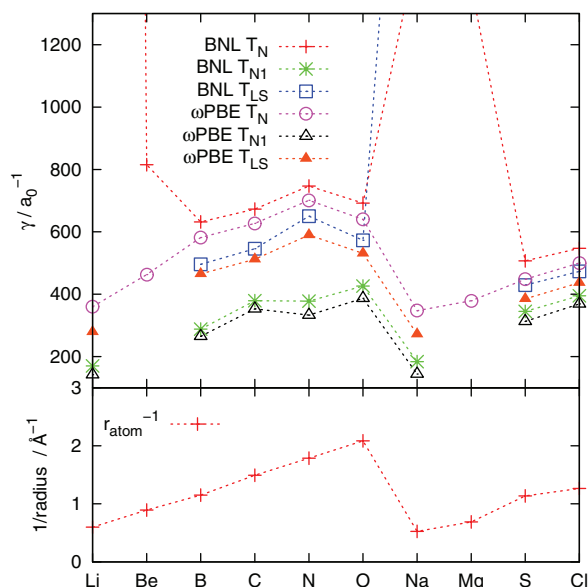
FIG. 3. (Upper part) Optimized γ values for selected atoms. The tuning conditions of Eqs. (2)–(4) were used. (Lower part) Inverse calculated[37] atomic radii.

IV. SIZE CONSISTENCY

A. Size consistency error

The size consistency criterion is a fundamental constraint that applies to any electronic structure approach, and thus also to approximations in DFT. It states that the sum of the energies E_A and E_B of two well-separated, independent subsystems A and B should be equal to the energy E that one obtains when A and B are considered as one large combined system. The RSH functional itself is expected to be properly size consistent if no tuning is performed, because all of its exchange and correlation ingredients are. Nevertheless, by construction a tuned RSH functional is not size consistent,[12] because due to its implicit definition it generally has different γ values for the whole system and the two separate subsystems. As a consequence

$$\Delta_{SC} = E_{\gamma_A}(A) + E_{\gamma_B}(B) - E_{\gamma_{A+B}}(A + B) \neq 0, \quad (6)$$

with Δ_{SC} defining the size-consistency error. While this argument establishes that the tuning procedure in principle violates the size consistency condition, we do not know of any study so far that systematically quantified the error. Therefore, we examine it here in the transparent, hallmark test case of two atoms that are far from each other. In this situation we expect large γ differences due to the large γ variations seen in Fig. 3. Our theoretical setup is a system of two atoms with a distance of 20 Å, large enough such that all orbitals are localized on either one of the two atoms A or B with vanishing orbital overlap. Consider, for example, the simple T_N or T_{N1} tuning criteria. If we assume that the HOMO of the whole (neutral or anionic, respectively) system, A+B, is localized on atom A, we obtain $\gamma_{A+B} = \gamma_A$ as the range separation parameter for the whole system. The size consistency error can then be expressed as

$$\Delta_{SC} = E_{\gamma_A}(A) + E_{\gamma_B}(B) - E_{\gamma_A}(A + B) \quad (7)$$

and therefore reduces to $E_{\gamma_B}(B) - E_{\gamma_A}(B)$ owing to the size-consistency of the RSH functional itself. Whether the resulting size consistency error is negligible or worrisome depends on the difference $\gamma_A - \gamma_B$ and how strongly the total energy of B varies with γ.

In Fig. 4, we plot the size consistency errors of several diatomic molecules calculated with the BNL (left graph) and ωPBE functional (right graph). The error strongly depends on the system and the applied tuning condition. The largest errors are observed for (Na+Cl) and (Be+S). This is related to the fact that in these atom pairs the differences between the atomic γ values are the largest (compare Fig. 3). It is exacerbated by the fact that one atom dominates the ionization potential and therefore T_N, whereas the other atom dominates the electron affinity and therefore T_{N1}. The monoatomic systems (O+O) and (N+N) exhibit no size consistency error since the combined system has the same γ as its subsystems. Using an RSH approach without tuning is size consistent and is
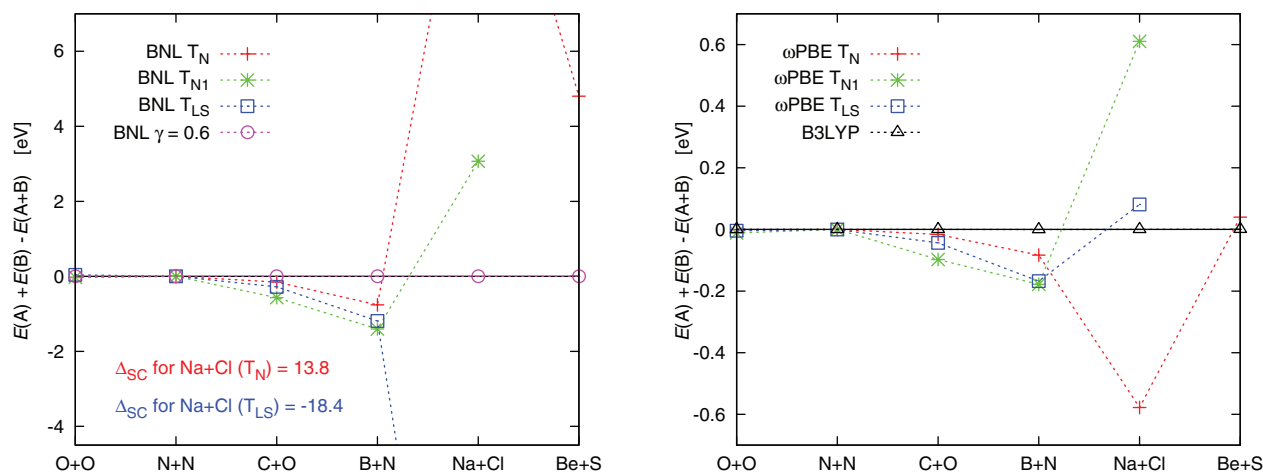

FIG. 4. The size consistency error according to Eq. (6) for atom pairs calculated with the BNL (left) and the ωPBE functional (right). The distance between the two subsystems is 20 Å. Note that B3LYP data points exhibit no size consistency error, which proves that the calculations were properly set up. The data points "BNL $\gamma = 0.6$" (no tuning, γ constant for all systems) are also all zero, confirming that the RSH approaches itself (without tuning) are size consistent (the same applies to ωPBE). Note the different scales on the energy axes in the left and right viewgraph.
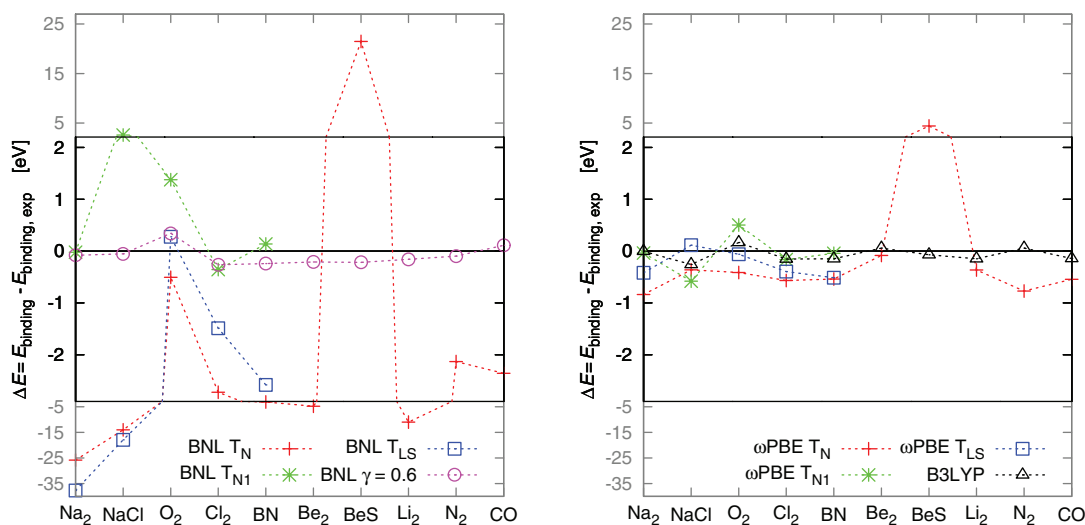
FIG. 5. Differences of calculated binding energies (according to Eq. (8)) and experimental binding energies. The calculations were performed with all three tuning conditions for the BNL functional (left) and the ωPBE functional (right). It also shows B3LYP data points (*right*) and data points for the case of BNL without tuning ("BNL $\gamma = 0.6$", *left*). Note the change of scale in the energy axis. Missing T_{N1} and T_{LS} data points indicate that either the anion of the molecule or at least one of its atoms is unstable (cf. Sec. III).

demonstrated with the data points "BNL $\gamma = 0.6$" in the left part of Fig. 4 where we used a constant $\gamma = 0.6$ in all calculations. The comparison of the BNL and the ωPBE functional is the most noteworthy aspect of Fig. 4. The size consistency errors of both methods differ substantially, with the BNL error being one order of magnitude larger than the ωPBE one. (Na+Cl) is the most extreme case that we encountered, with an error of 18 eV for the T_{LS} tuning of BNL. We attribute this to the above-discussed abnormal tuning behavior of the sodium atom. Even when such extreme cases are disregarded, the size consistency violation for BNL is nevertheless generally severe, as a consequence of the strong γ dependence of the total energy (compare Fig. 7). This γ dependence is smaller for ωPBE (compare Fig. 7) resulting in a moderate error. However, even for ωPBE it may be considerably large, as in the case of (Na+Cl).

B. Binding energies of diatomic molecules

In this section, we address an important consequence of the violation of size consistency: the incorrect prediction of binding energies. As in Secs. III and IV A, we focus our analysis on diatomic molecules. In order to calculate their binding energies with the implicitly defined tuned RSH functionals, we have to conduct the tuning process for the atoms and the molecules separately. Therefore, we obtain a difference in the γ values of the molecule (γ_{AB}) and its constituent atoms (γ_A and γ_B). Due to this difference the resulting binding energy,

$$E_{\text{binding}} = E_{\gamma_A}(A) + E_{\gamma_B}(B) - E_{\gamma_{AB}}(AB), \quad (8)$$

incorporates an error that is closely connected to the size consistency error. We calculated these binding energies for diatomic molecules composed of first and second row elements with all three tuning approaches for the BNL and the ωPBE functional. In Fig. 5 we plot the differences of our calculated binding energies and the experimental binding energies.[38] The

graph shows severe deviations of the BNL calculations (left part of Fig. 5) from the experiment. A binding energy error of 1–3 eV is the normal case, but 10 eV and more are observed for the molecules containing alkali and earth alkali atoms. By using a constant range separation parameter, $\gamma = 0.6$ (chosen without specific optimization, but considered "reasonable" for thermochemistry[12]), the deviations from the experiment are less than 0.3 eV. This is the same order of error as observed for the B3LYP data points presented in the right part of Fig. 5. This part of Fig. 5 also shows the ωPBE calculations with a binding energy error smaller than 0.8 eV, consistent with the more moderate size consistency error of this functional. The only exception is BeS, with an error of 4.4 eV. This large error is related to the above-discussed abnormal tuning behavior of this system (cf. Sec. III).

On the whole, these results reflect the size consistency errors of Sec. IV A. The differences between the two applied RSH approaches are consistent with our finding that the total energies depend more strongly on γ for the BNL functional than for the ωPBE functional. This is reflected in Fig. 6, which shows the difference of γ_{AB} (molecule AB) to the mean atomic γ, i.e., the average of γ_A and γ_B. Although these differences are very similar for BNL and ωPBE (except for molecules containing alkali and earth alkali atoms), the binding energy errors are much larger for the BNL functional. Note that the general structure of the graphs in Fig. 6 (γ differences) and Fig. 5 (binding energy errors) is very similar. This falls in line with the other arguments in this section, i.e., the differences in the γ values obtained for molecules and atoms in the tuning approach are the main reason for the notable errors.

V. TUNING-RELATED SHORTCOMINGS

In this section, we address some situations where the tuning approach leads to problems in an indirect way that is not
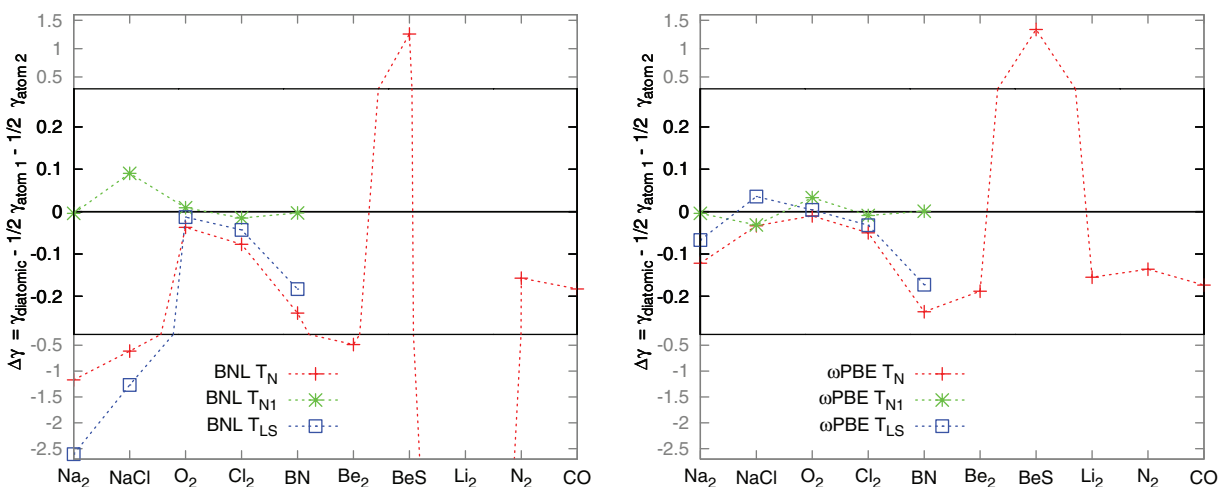
FIG. 6. Difference $\Delta\gamma$ between γ_{AB} (molecule) and $1/2(\gamma_A + \gamma_B)$ (average over atoms) for the BNL functional (left) and the ωPBE functional (right). Systems with a large $\Delta\gamma$ are expected to have a large binding energy error if calculated with tuned RSH functionals. Note the change of scale in the ordinate. Missing T_{N1} and T_{LS} data points indicate that either the anion of the molecule or at least one of its atoms is unstable (cf. Sec. III).

strictly related to the violation of size consistency. In these situations, tuning has to be conducted with great care, or not at all.

A. Spin configuration

Spin multiplicity introduces an additional problematic aspect of tuning. Generally, a modification of the spin configuration may modify the optimal value of γ and, in turn, introduce changes in the energy that go beyond the physical energy changes demanded by the changes in the spin configuration. To explore this effect, consider the prototypical example of the O_2 molecule, well-known to possess a triplet ground state. Fig. 7 shows the energy of the O_2 molecule, at the experimental bond length, as a function of γ. For both the BNL and the ωPBE functionals, the triplet energy is correctly identified as lower than the singlet energy, for any choice of γ.

For the BNL functional, however, the T_{LS} optimally tuned γ of the singlet state (solid vertical line) is larger than that of the triplet state (dashed vertical line). Due to the strong γ-dependence of the energy, the tuned singlet energy is lower than the tuned triplet energy, i.e., the triplet and singlet energy ordering at their respective optimal γ values (solid and dashed horizontal line, respectively) is erroneous. Note that due to the weaker γ-dependence of its energy, the ωPBE functional predicts the correct order of the singlet and the triplet energy (the singlet and triplet γ of ωPBE are close to the solid and dashed vertical line). However, the same quantitative limitation remains in force, even if it does not translate into a qualitative difference in this case. Thus, if one constructs the energy at optimal tuning as a function of bond length, as shown in Fig. 8, the equilibrium bond length is obtained correctly, at least qualitatively, but the predicted spin configuration itself is incorrect. For a system with a spin state that is unknown prior to calculation, a naive tuned-RSH approach may therefore be
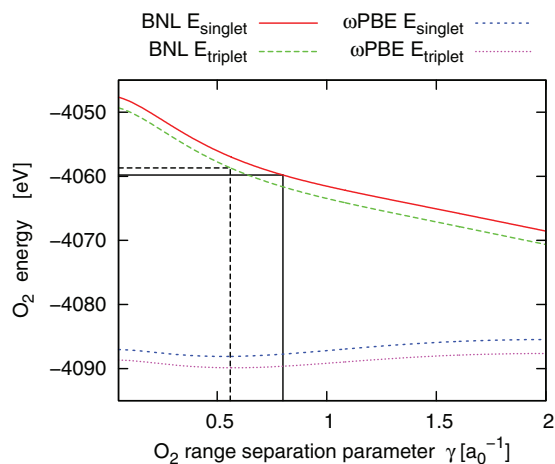

FIG. 7. Energy of the O_2 molecule at its experimental bond length[36] for different RSH approaches and spin configurations. The solid vertical and horizontal line illustrate the optimally tuned BNL γ_{LS} and its corresponding energy $E(\gamma_{LS})$ for the singlet state. The dashed vertical and horizontal line indicate γ_{LS} and $E(\gamma_{LS})$ of BNL for the triplet state.
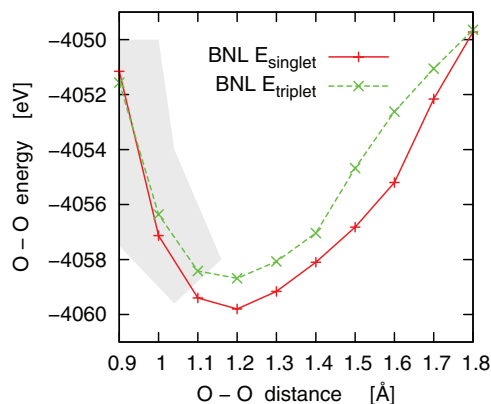
FIG. 8. Singlet (solid) and triplet (dashed) energy of the O_2 molecule as a function of the bond length calculated with the BNL functional with T_{LS} tuning. For the parts of the curves that are within the shaded area the tuning approach is not well defined. Although the neutral system is stable at these bond lengths the anion is unstable as the HOMO value of the anion calculated with the optimally tuned γ_{LS} is slightly positive.
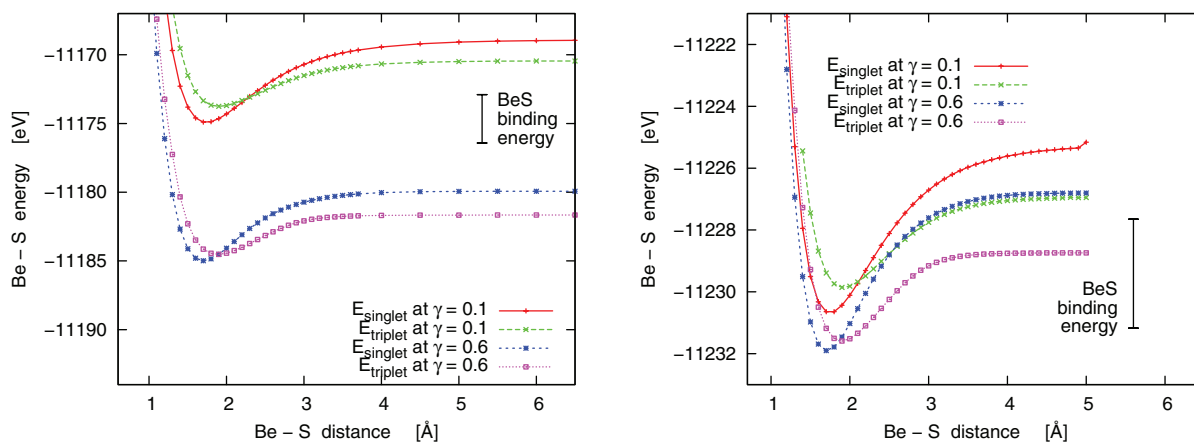
FIG. 9. BNL (left) and ωPBE (right) energy as a function of distance between Be and S for a singlet and a triplet spin configuration and for two different γ values.

misleading and the correct spin state has to be determined by considering a range of γ values (as in Fig. 7) and/or with a different functional beforehand.

B. Potential energy curve

In this subsection, we analyze how the tuning approach performs for the calculation of potential energy surfaces. We again focus on diatomic molecules as these allow for a transparent analysis. The discussion is motivated by and related to the effects reported in Sec. V A for O_2 close to its equilibrium bond length. However, here we discuss two additional conceptual problems.

In Subsection V A we pointed out possibly spurious spin-related issues of the neutral species. But even if no such issue arises, the energy of the neutral system may still exhibit a spurious dependence of the energy on the multiplicity of the anion and the cation of the system under consideration. By going from the equilibrium bond length to a very large one, the multiplicity of the system may change at a specific distance where a different spin configuration becomes more favorable, e.g., the systems could go from a singlet to a triplet state. The dilemma is that the anion and cation of the sys-

tem could also change their spin states and this could happen at a different distance or even several times, e.g., the multiplicity could change from 2 to 4 and than again from 4 to 6. For a specific example, consider the heterodimer comprised of beryllium (Be) and sulfur (S) with the following configuration:

	Neutral	Anion	Cation
Molecule (multiplicity)	1	2	2
Well separated (multiplicity)	3	2	4

For a common functional one would calculate a singlet and a triplet energy curve that would intersect at a certain bond length. The same applies to RSH functionals without tuning. Fig. 9 displays these singlet and triplet energy curves for Be and S for the BNL and ωPBE functionals (without tuning), for two different values of the range separation parameter. For both γ values, both functionals behave correctly and predict the correct binding energy of 3.5 eV,[38] as the difference of the triplet energy at large internuclear separation and the singlet energy at the equilibrium bond length. A different situation, however, occurs when either

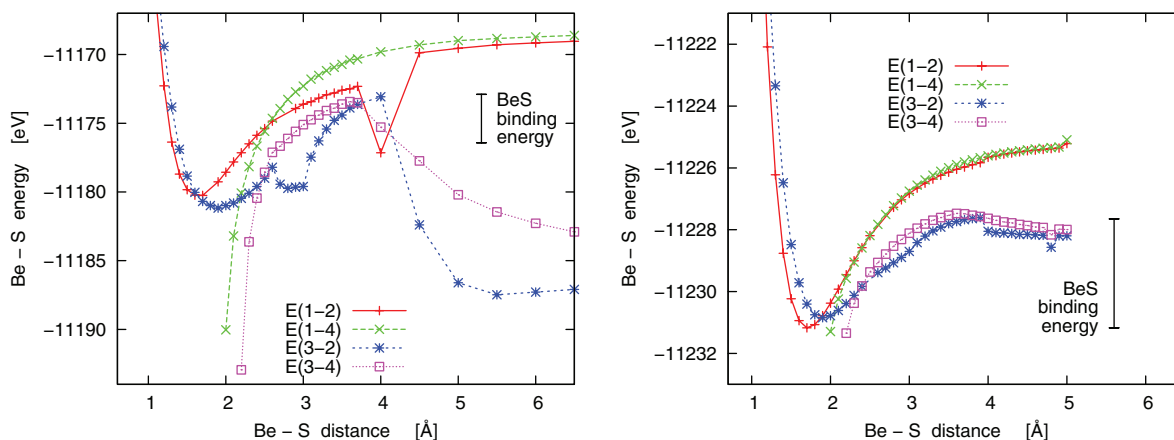FIG. 10. Tuned BNL (left) and ωPBE (right) energies of Be-S as a function of distance between Be and S for four different spin configurations. The T_N tuning was applied at each distance separately. "E($x - y$)" encodes the energy of the four different spin configurations according to E(<*multiplicity of the neutral system*> − <*multiplicity of the cation*>). The multiplicity of the anion is always 2.

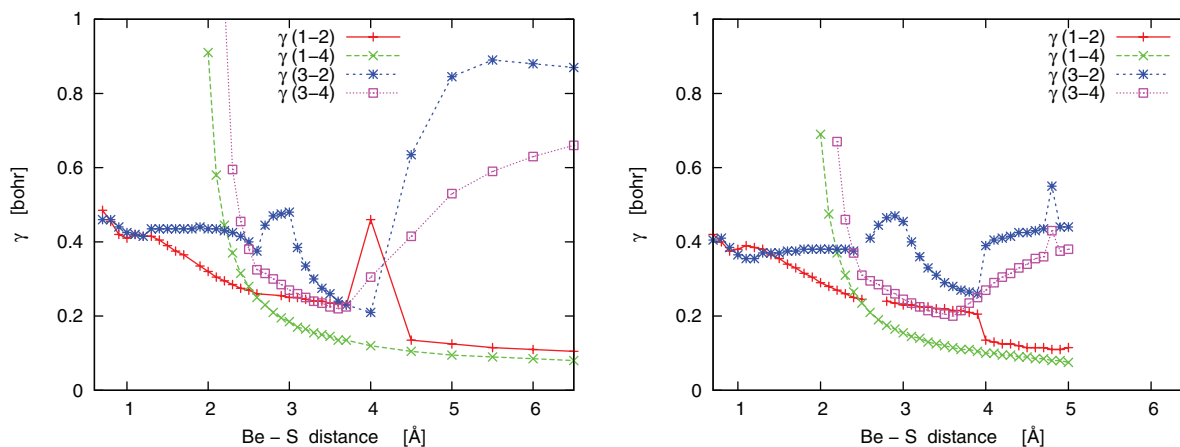FIG. 11. γ values from T_N tuning for Be-S as a function of distance between Be and S for four different spin configurations, for the BNL (left) and ωPBE (right). The T_N tuning was applied at each distance separately. "$\gamma(x-y)$" means $\gamma(<multiplicity\ of\ the\ neutral\ system> - <multiplicity\ of\ the\ cation>)$. The multiplicity of the anion is always 2.

functional is used in combination with the tuning approach. Because the tuning procedures depend on the anion and/or the cation, the spin states of the latter also affect the results. This means one would not simply get a singlet and triplet curve, but a singlet(neutral)-duplet(cation), a singlet(neutral)-quartet(cation), a triplet(neutral)-duplet(cation), and a triplet(neutral)-quartet(cation) curve (if we neglect the anion because its spin state does not change in the case of Be and S). The mere existence of these curves is physically incorrect. For Be and S they are depicted in Fig. 10 for the T_N tuning.

A second conceptual failure is connected to the basic concept of the tuning itself – the system dependence of the range separation parameter. It leads to a change of γ as a function of the distance between the two atoms. Fig. 11 demonstrates this dependence for Be and S for the different spin configurations. The consequence is that the potential energy curves exhibit unphysical trends, as seen in Fig. 10. The curve that one would obtain by choosing the lowest possible energy at each internuclear separation (not explicitly shown in Fig. 10 for reasons of clarity) zig-zags up and down and finally results in a negative binding energy for the optimally tuned BNL functional. The largest change occurs around 4 Å. This may be related to the transition from orbitals that are delocalized over the molecule to orbitals that are localized on the separate atoms. The unphysical curves can be understood by considering Fig. 9 again. Because γ mainly varies in the range between 0.1 and 0.6, the energy "jumps" between the curves of these two different γ values. In contrast to all other calculations in this paper, here we used the cc-pVQZ basis set because then the tuning is more well behaved than with the aug-cc-pVQZ basis set. However, the same effects can be observed for other basis sets as well. Furthermore, we found a similar behavior for all other tuning conditions and other diatomic systems such as BN, NaCl, CO, and O_2; sometimes the failures were not as pronounced as in this case and sometimes even more severe. For the ωPBE functional the curves are, again, generally better behaved because the γ dependence of the total energy is smaller. However, the conceptual problems remain for this functional too.

These results once more demonstrate that energies from calculations with different range separation parameters cannot be compared. Viewing γ as a system dependent quantity and performing the tuning for each configuration of a potential energy curve separately, generally leads to spurious results. As mentioned above, an alternative would be to apply the tuning procedure to molecules at their equilibrium bond length and to use the resulting γ also for all other bond lengths. However, this would be in contradiction to the general philosophy of regarding γ as an implicit density functional and in practice would lead to irreconcilable inconsistencies in the limit of large inter-nuclear separation. Clearly, this calls for a size consistent extension of the current tuning approach.

VI. SUMMARY

The main aim of this work was to analyze the tuning of RSH functionals with respect to the question of size consistency. For this purpose we examined diatomic systems at large distances, where we observed large size consistency errors – up to several electron volts. In the rest of the paper we discussed consequences of the size consistency violation. Likely the most prominent one is that the tuning approach may fail in predicting binding energies correctly and that a strict definition of potential energy surfaces is not possible. We also demonstrated that due to the tuning procedure, spin configurations might be predicted incorrectly and that tuning results depend also on the anion and/or cation of a system and their spin configurations. This, in fact, is an additional factor that can adversely influence potential energy surfaces.

The scenario considered throughout this work – a very small system with a very large difference in the optimal γ between its sub-systems – is in some sense a deliberately constructed "worst case scenario" for the optimal tuning method. It may well be that larger and/or more homogeneous systems, where the dependence on γ may be less pronounced, will exhibit more modest errors. This, in fact, has also been observed in some of the examples studied. We believe the information given here to be useful, as these extreme examples teach us most about potential pitfalls and allow us maximal

caution in the application of the method and the interpretation of its results. Specifically, a re-tuning during static or dynamic processes that changes the electronic configuration (including the case of reaction barriers) should be avoided if energetic changes are of interest. In cases where a tuned long-range correction is beneficial, it is advisable to conduct a tuning step just once. This procedure is not consistent with the interpretation of the tuning procedure as making the range-separation parameter an implicit density functional, but may lead to pragmatically more useful results. Interestingly, while all optimally tuned RSH functionals are subject to these limitations, they do not necessarily suffer from them to the same extent. In our case, ωPBE and BNL were found to perform very differently under identical tuning procedures. The size consistency errors for the ωPBE functional were nearly an order of magnitude smaller than the ones for the BNL functional, with a similar observation for binding energy errors. We attribute this behavior to the improved compatibility of the semi-local correlation and short-range exchange in the ωPBE functional.

What are the underlying reasons for the failures described above? A first observation is that with the tuning approach the functional is able to adjust its range separation parameter to a specific system. This adjustment has proven to be very important for the prediction of spectroscopic properties. The price to pay for this system dependence of γ are the limitations described in this work. They originate from the implicit construction of the functional itself. The tuning of γ, when being regarded as turning the range-separation parameter into an implicit density functional, must be seen as a definition of a highly non-local functional and global non-localities frequently lead to size-consistency violations.[39]

A second observation is that one could simply think about γ as a parameter that is fixed anew for each system. From this perspective, different values for γ correspond to different functionals and it is therefore immediately obvious that energies obtained from the tuning approach cannot be compared. This perspective, however, is too simplistic. Due to the tuning, one is in fact using a system dependent range separation parameter that can in principle be seen as a functional of the density $\gamma[n]$. However, in taking the functional derivative to derive the exchange potential from the exchange energy, γ has been treated as a constant here as well as in all other applications of the optimally tuning idea that we know of. Yet, if one would take the concept of viewing γ as an implicit density functional seriously, then one should obtain an additional term in the exchange potential of the form

$$\frac{\partial E}{\partial \gamma} \frac{\delta \gamma[n]}{\delta \phi_i}, \tag{9}$$

that is not present if γ is held constant. The latter expression refers to a generalized Kohn-Sham approach,[28] where the exchange energy derivative has to be taken with respect to the generalized Kohn-Sham orbitals ϕ_i, i.e.,

$$\frac{\delta E[n, \gamma[n]]}{\delta \phi_i(\vec{r})}. \tag{10}$$

From this perspective, the optimally tuned calculations that have been done so far used an inconsistent combination of energy and potential, or, in other words, a potential that does not rigorously minimize the energy, because they neglected the term of Eq. (9). Energy-potential inconsistencies are known to generally lead to problems[40,41] and the present case can be seen as a somewhat more subtle manifestation of this general principle.

VII. OUTLOOK

Which conclusions can we draw for the future use and development of tuned functionals in view of the presented findings on the size consistency error and related problems? One conclusion could be to avoid tuned functionals, at least in circumstances when ground-state energetics are relevant, and resort to other approaches. For example, it has been demonstrated that self-interaction free functionals based on exact Kohn-Sham exchange[42,43] or a self-interaction correction (SIC) used in the Kohn-Sham framework[44–46] tremendously improve on many of the deficiencies of semi-local functionals and lead to, e.g., occupied eigenvalues that are much more amenable to physical interpretation[47–54] and an accurate description of charge transfer[45,55] and charge transfer excitations.[56,57] Some of these improvements may even be achieved with semi-local functionals.[58,59]

Yet, in our opinion, avoiding tuned functionals altogether would be a serious misconception. The tuned RSH functionals and approaches such as the Kohn-Sham SIC each have their individual strengths and neither one makes the other superfluous. Rather, each offers specific advantages and one may choose one of the approaches depending on the requirements of the problem at hand. Advantages of, e.g., the Kohn-Sham SIC are the availability of a consistent energy-potential combination and the lack of the requirement to do many calculations to tune a parameter. On the other hand, the tuned RSH functionals offer opportunities that are beyond what can be reached with any Kohn-Sham approach. For example, recent work showed that tuning based on Eq. (4) results in a very good prediction of both fundamental gaps and IP's for both atoms[18,60] and organic systems.[18,20] Consequently, the derivative discontinuity – the discrepancy between the HOMO-LUMO gap and the fundamental gap – is nearly vanishing in the generalized Kohn-Sham system selected due to the tuning, also allowing for a successful mimicking of exciton binding when comparing the HOMO-LUMO gap to the optical gap obtained from time-dependent DFT.[6] This can be a significant advantage in practical applications, in addition to the successful treatment of charge transfer energies.[21,24,25,61–64]

Thus, it is worthwhile to discuss the possibilities for improving concepts of RSH functionals with a system dependent range separation. Some suggestions towards this goal were already made in the literature.[65] Here, we present some further thoughts, based on the perspective that the limitations of the current tuning process and the strong violation of size consistency could be rooted in the dependence of the tuning procedure only on the frontier orbitals. All the different tuning conditions, from Eq. (2) to Eq. (4), address frontier orbitals, which is of course related to the intention of producing reliable results for fundamental gaps and optical (in particular charge-transfer) excitations. Other properties, like the total

energy, that depend on the entire system may be described poorly, as discussed in the present work. The reason for this is that γ enters the functional via the well known long-range exchange energy expression

$$E_x^{LR} = -\frac{1}{2} \sum_\sigma \iint dr_1^3 dr_2^3 \frac{\text{erf}(\gamma |\vec{r}_1 - \vec{r}_2|)}{|\vec{r}_1 - \vec{r}_2|}$$
$$\times \sum_{ij} \phi_{i\sigma}^*(\vec{r}_1)\phi_{j\sigma}^*(\vec{r}_2)\phi_{j\sigma}(\vec{r}_1)\phi_{i\sigma}(\vec{r}_2) \qquad (11)$$

and in this way influences all orbital-orbital interactions (see, e.g., Eq. (4) of Ref. 9), despite having been adjusted only for the frontier orbitals. Because the orbitals of a specific system have various shapes and sizes, the description of their interaction may require distinct separations into long and short-range. This is especially true if we compare inner shell with outer shell or binding orbitals. One possibility could be to assign a range separation parameter γ_{ij} to each orbital pair $\{ij\}$ in order to describe their interaction accurately by a mix of semi-local short-range and exact long-range exchange. Consequently we would obtain

$$E_x^{LR} = -\frac{1}{2} \sum_\sigma \iint dr_1^3 dr_2^3 \sum_{ij} \frac{\text{erf}(\gamma_{ij}^\sigma |\vec{r}_1 - \vec{r}_2|)}{|\vec{r}_1 - \vec{r}_2|}$$
$$\times \phi_{i\sigma}^*(\vec{r}_1)\phi_{j\sigma}^*(\vec{r}_2)\phi_{j\sigma}(\vec{r}_1)\phi_{i\sigma}(\vec{r}_2) \qquad (12)$$

for the long-range exchange energy expression with orbital pair-dependent γ_{ij}^σ's. Because the semi-local short-range expression, which is also γ-dependent, does not depend on orbital-orbital exchange directly, we could use the mean value $\gamma_{SR} = \sum_{ij\sigma} \frac{\gamma_{ij}^\sigma}{2N^2}$ instead. The question is how to determine the values for these γ_{ij}^σ's. One approach may be to assign them according to the spatial extension of the orbitals that form the pair $\{ij\}$ and the distance between their centers of mass. The advantages of such an approach would be a generalization of the range separation in principle and a possible elimination of the time-consuming tuning step involving the anions and cations. Whether such a scheme can be realized in practice and how accurate it may be needs to be left to future work. In any case, considerations such as this one show that the idea of implicitly, numerically defined functionals does hold the potential for extensions that may increase the application range of concepts such as the optimal tuning.

ACKNOWLEDGMENTS

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