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Simultaneous Determination of Structures, Vibrations, and Frontier Orbital Energies from a Self-Consistent Range-Separated Hybrid Functional

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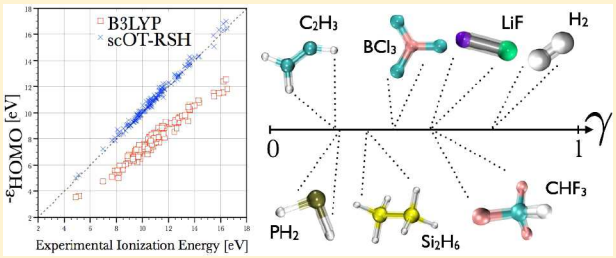
Supporting Information

ABSTRACT: A self-consistent optimally tuned range-separated hybrid density functional (scOT-RSH) approach is developed. It can simultaneously predict accurate geometries, vibrational modes, and frontier orbital energies. This is achieved by optimizing the range-separation parameter, γ, to both satisfy the ionization energy theorem and minimize interatomic forces. We benchmark our approach against an established hybrid functional, B3LYP, using the G2 test set. scOT-RSH greatly improves the accuracy of occupied frontier orbital energies, with a mean absolute error (MAE) of only 0.2 eV relative to experimental ionization energies compared to 2.96 eV with B3LYP. Geometries do not change significantly compared to those obtained from B3LYP, with a bond length MAE of 0.012 Å compared to 0.008 Å for B3LYP, and a 6.5% MAE for zero-point energies, slightly larger than that of B3LYP (3.1%). scOT-RSH represents a new paradigm in which accurate geometries and ionization energies can be predicted simultaneously from a single functional approach.



SECTION: Molecular Structure, Quantum Chemistry, and General Theory

Density functional theory (DFT) is the method of choice for electronic-structure calculations across an unusually wide variety of disciplines,[1] from organic chemistry[2] to condensed matter physics,[3] as it allows for accurate quantum-mechanical calculations at relatively modest computational cost. Practical applications of DFT almost invariably rely on the solution of the Kohn–Sham equation (in either its original[4] or generalized[5] form). Within (generalized) Kohn–Sham theory, the interacting many-electron problem is mapped onto an effective single-particle one. This mapping is exact in principle, as the ground-state density of the original and single-particle description are the same. However, the mapping relies on an exchange-correlation energy, E_{xc}, which is a generally unknown functional of the electron density. The practical success of DFT, therefore, hinges entirely on the existence of suitable approximations for E_{xc}.

Fortunately, approximations sufficiently accurate to predict quantities obtained from the total energy (including its first and second derivatives with respect to atomic positions) have been developed and are in widespread use. In particular, the generalized-gradient approximation (GGA), which expresses E_{xc} in terms of the electron density and its gradient, has become very popular in materials physics[6]—particularly when paired with periodic boundary conditions—and conventional hybrid functionals, which combine a fraction of Fock exchange with a complementary fraction of GGA exchange, have seen similar rates of adoption for applications in chemistry.[2] These have become the standard "workhorse approximations" for accurate prediction of structural quantities such as lattice constants, bond lengths and angles, as well as response properties such as vibrational frequencies, elastic constants, etc.

Unfortunately, neither conventional GGAs nor conventional hybrid functionals do nearly as well in the prediction of electronic excitation spectra of molecular systems.[7] In particular, they usually fail to describe frontier orbital energies.[8−11] Within the (generalized) Kohn–Sham framework, the ionization energy (IE) theorem guarantees that for the exact exchange-correlation functional, the (generalized) Kohn–Sham eigenvalue associated with the highest occupied molecular orbital (HOMO) should correspond to the first vertical IE.[9,12−16] There are, however, no formal constraints on any of the other Kohn–Sham energies; for example, the lowest unoccupied molecular orbital (LUMO) energy computed from

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Kohn−Sham DFT is *not* guaranteed to correspond to the electron affinity (EA). In fact, the LUMO energy and EA differ by the derivative discontinuity, that is, by a finite "jump" in energy associated with an integer increase in the number of electrons in the system that the exact Kohn−Sham potential must possess. With standard GGA approaches, this derivative discontinuity is missing and is erroneously averaged away. Consequently, HOMO and LUMO energies under- and overestimate the IE and EA, respectively.[17−19] The use of a fraction of nonlocal Fock exchange in conventional hybrid functionals mitigates the derivative discontinuity problem, as some of it is "absorbed" into the nonlocal Fock operator. However, HOMO and LUMO energies typically still under- and overestimate the IE and EA, respectively, just like in a GGA, albeit less severely,[9,20] limiting the utility of the (generalized) Kohn−Sham spectrum for predicting and understanding spectroscopy measurements.

In recent years, a promising new class of hybrid functionals has emerged—that of range-separated hybrid (RSH) functionals,[21,22] which are based on partitioning the Coulomb interaction in space. Many such partitioning schemes exist.[23−28] Perhaps the simplest one distinguishes between short- and long-range contributions through use of the error function, namely, using the relation $(1/r) = (1/r)\mathrm{erfc}(\gamma r) + (1/r)\mathrm{erf}(\gamma r)$, where r is the interelectron coordinate and γ is an adjustable length-scale. The two interaction ranges are then treated differently: in the functional used here, the short-range term is handled in a GGA manner, allowing for a local balance between exchange and correlation contributions. Meanwhile, the long-range term is handled in a Fock-like manner, which guarantees the correct $\sim -1/r$ asymptotic behavior for isolated molecules, crucial for processes involving electron removal (ionization).

It has been recently demonstrated[9,29,30] that the RSH approach can improve the DFT eigenvalue prediction if the range separation parameter, γ, is optimally tuned (OT) so as to obey the IE theorem, that is, it minimizes the function

$$j(N;\gamma) = \varepsilon^{\gamma}_{\mathrm{HOMO}}(N) + [E_{\mathrm{gs}}(N-1;\gamma) - E_{\mathrm{gs}}(N;\gamma)] \tag{1}$$

where $\varepsilon^{\gamma}_{\mathrm{HOMO}}(N)$ is the eigenvalue of the highest occupied generalized Kohn−Sham state for the N-electron system, and $E_{\mathrm{gs}}(N;\gamma)$ and $E_{\mathrm{gs}}(N-1;\gamma)$ are the total energies of the original system and its cation, respectively, for a specific choice of γ. The function j then represents the remaining deviation from the IE theorem, where $j = 0$ implies that the HOMO level is equal (and opposite in sign) to the IE, as expected from the exact functional. Simultaneous excellent agreement between the LUMO and EA can be obtained by applying the above condition not only on the neutral system but also on its anion,[9,29] for example, to minimize

$$J(N;\gamma) = \sqrt{[j(N;\gamma)]^2 + [j(N+1;\gamma)]^2} \tag{2}$$

This double-tuning procedure has been used successfully for predicting fundamental (with time-independent DFT) and optical gaps (with time-dependent DFT) in a variety of systems (see, for example, refs 30−42). Additionally, it was shown to be useful in the prediction of other optical properties such as (full, partial, or implicit) charge-transfer excitations[29,43−47] and optical rotations.[48] It has also proven to be helpful beyond the frontier orbital energies in approximating the outer valence excitation spectra.[49,50] It should be noted, however, that the double-tuning procedure should not be applied when the EA is negative.[31]

Despite this impressive range of successes, structural information in most of the above-mentioned OT-RSH research was obtained using conventional semilocal or hybrid functionals, with the relaxed geometry "frozen" for the sake of the subsequent OT-RSH calculation. Very little work has been devoted to structural predictions from OT-RSH calculations.[33,51−53] Apart from our preliminary results,[54] and the work of Körzdörfer et al.,[55] which focused on the specific case of bond-length alternation in polyenes, tuning of γ and structural optimization have been treated as unrelated tasks.

Generally speaking, obtaining a functional that offers predictions of sufficient accuracy for quantities derived from *both* the total energy and the frontier orbital eigenvalues is known to be a very difficult task.[56−60] Therefore, it is of great interest to examine whether, and to what extent, OT-RSH functionals can balance these two requirements. Specifically, we ask whether OT-RSH functionals can supply accurate predictions for both frontier orbital eigenvalues on the one hand and structures and vibrational frequencies on the other hand.

In this Letter, we develop a self-consistent (scOT-RSH) approach for a nonempirical range-separated hybrid density functional that can simultaneously predict accurate geometries, vibrational modes, and frontier orbital energies of molecules. Starting with a range-separated hybrid functional, we introduce a scheme by which the range separation parameter γ can be simultaneously optimized to both satisfy the IE theorem and minimize the forces acting on atoms for molecular structures.

In order to assess our approach, we focus on the G2 test set,[61] which contains 148 small organic molecules. We have chosen this particular test set for two reasons. First, experimental gas-phase structural, vibrational, and ionization energy data have been extensively recorded for this set, making a comprehensive comparison between theory and experiment meaningful. Second, we compare our calculations to those obtained from the popular conventional hybrid functional, B3LYP.[62,63] In its construction, B3LYP was explicitly fit against thermochemistry data of this set and is therefore at its best by definition. This makes the burden of proof on the accuracy of our approach particularly high.

Our nonempirical range-separated hybrid density functional scheme proceeds as follows. First, following the existing OT-RSH approach,[9,29] for fixed geometry, we obtain the range separation parameter γ such that the molecule, in its fixed configuration, satisfies eq 1. Ten independent calculations (in parallel) for both the neutral and cationic species were performed at the initial geometry over a range of γ values. From these, the two values of γ most closely satisfying eq 1 were identified and then used as the upper and lower bound for a second trial set of ten γ values. All molecules exhibited a clear minimum of $j(N;\gamma)$. We note, however, that some molecules within the set require careful identification of their (neutral or cationic) ground-state spin configurations[50,64,65] (which can be quite sensitive to initial geometries, as discussed below).

Second, we optimize the positions of the nuclei in the ground state, that is, we eliminate any residual Hellmann−Feynman forces. For the new geometry, we then recompute γ. This procedure continues until we converge on a γ for which all forces are negligible. This results in an optimized geometry obtained without resorting to empirical parameters. For most molecules in the set, self-consistency was achieved in a single

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iteration. Throughout the entire set, self-consistency was always reached in less than four iterations. Our parallel implementation results in an additional factor of 2−3 in the time-to-solution compared to that of standard DFT functionals.

We used B3LYP/6-31G*-optimized structures[66,67] as initial geometries for our scheme. To rule out any bias B3LYP may have imposed on our results, we randomly selected several molecules from the set, optimized their structure using the unified force field,[68] and confirmed that this did not impact the final results. All calculations were performed using the QChem 3.2 package.[69] The "G3Large"[70] basis set was used throughout. This basis set was chosen as it is defined for all atom types present in G2 and is also compatible with the G3/99 and G3/05 test sets. We additionally ascertained that results obtained with this basis set are consistent with those obtained using Dunning's cc-pVTZ basis set.[71] The largest differences found between the two basis-sets were of the order of 1% for the HOMO levels, 0.1% for bond lengths, and 1% for vibrational frequencies. We used an OT-RSH functional of the form given in eq 1 based on the LC-ωPBE functional,[25] which employs a short-range version of the Perdew−Burke−Ernzerhof (PBE) GGA exchange functional[72] and PBE-GGA correlation.

We emphasize that any structural relaxation within DFT typically requires two nested self-consistent procedures: an outer one for the geometry and an inner one for the self-consistent solution of the electronic structure at a fixed geometry.[73] Here, an additional self-consistency cycle, nested in between the usual inner and outer ones, is the self-consistency in the choice of γ. This allows the functional to adapt itself to both the instantaneous geometry and electronic structure of the system. Thus, one may think of our approach as a special case of a nonempirical "fourth generation" density functional, where the functional is not and cannot be expressed explicitly, but rather is defined implicitly with the aid of a uniquely defined numerical procedure.[64]

Most molecules in the G2 set have a negative EA (our calculations indicate that this is the case for 116 out of the 148 molecules in the data set). For many of the molecules that have a positive EA, experimental data for the vertical EA are sparse and not always reliable. Therefore, we use the single HOMO-tuning condition of eq 1, rather than the double-tuning procedure of eq 2. Nevertheless, the consequences of double tuning are discussed further below.

A first and crucial test of the suggested approach is the comparison of HOMO eigenvalues to experimental IEs. In particular, the question is whether, as in the above-mentioned previous work, the method still facilitates the prediction of the IE or whether the simultaneous geometry optimization reduces the level of agreement between theory and experiment. Our comparison to experimental IEs is based primarily on the database of the National Institute of Standards and Technology.[74] However, some of the examined systems have multiple reported reference values, with a large deviation among these values. For other systems, the data set contains two different spin configurations, but only one reference value exists. In other cases yet, values reported in the database as vertical ionization energies are in fact adiabatic. For these cases, we used values collected directly from the literature. A detailed report is tabulated in the Supporting Information. Nevertheless, we caution that some errors in the experimental data may remain. With this in mind, a comparison of HOMO eigenvalues from our self-consistent RSH functional and from B3LYP, against the experimental gas-phase ionization energies, is given graphically in Figure 1 and is summarized in Table 1.

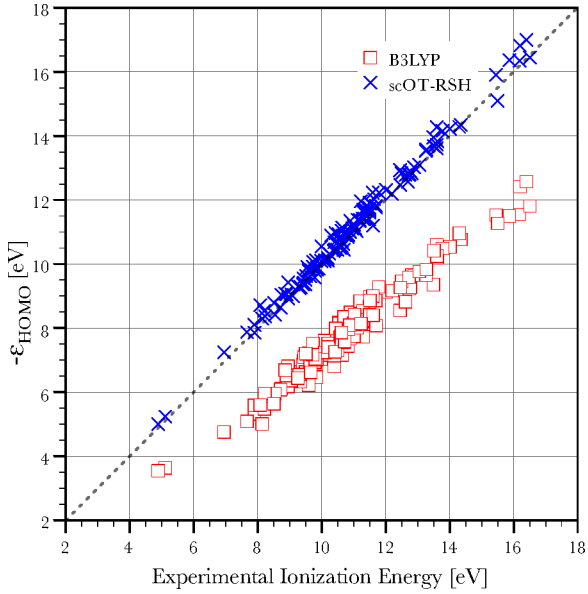

Figure 1. Comparison of the calculated generalized Kohn−Sham HOMO eigenvalues for the neutral species, calculated with B3LYP (red squares) and scOT-RSH (blue × marks), with the experimental vertical ionization energy, in eV. Points lying on the 45° dashed line indicate agreement between theory and experiment (within the accuracy of the latter).

Table 1. Comparison of Bond Lengths, HOMO Energies, and Zero-Point Energies Calculated Using B3LYP and the New scOT-RSH Scheme, with Experimental Values Across the G2 Set

		HOMO [eV]	Bond length [Å]	ZPE [cm^{-1}]
scOT-RSH	MAE	0.20	0.012	379.31
	STD	0.17	0.014	299.4
	% error	1.84	1.02	6.49
B3LYP	MAE	2.96	0.008	250.73
	STD	0.52	0.011	258.4
	% error	27.24	0.61	3.10

Overall, and especially when considering the above-discussed difficulties in the comparison to experiment, the resulting mean absolute error (MAE) of the self-consistent functional HOMO energies with respect to experiment is excellent. The MAE is 0.2 eV, corresponding to a relative error of 1.84% from experiment, with a standard deviation (STD) of 0.17 eV. For comparison, B3LYP results severely underestimate the experimental values (as is well known and expected) and yield a MAE of 2.96 eV (i.e., a relative error of 27.24%) and a standard-deviation of 0.52 eV. Interestingly, recent work[75] explored the IEs of a subset of 55 molecules from the G2 set by applying various flavors of Koopmans' corrections.[16,76] We note that our results are on par with the best results obtained from such corrections and slightly outperform the many-body perturbation theory results reported in ref 77 for a further subset of 34 of these 55 molecules.

It is important to note that IE predictions based on the B3LYP-optimized geometry, namely, a standard, nonself-consistent OT-RSH, differ from the scOT-RSH IE results by a very small amount (less than 0.01 eV). Importantly, although

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the change in γ is modest in this case (less than 5%), all information can be extracted from one fully self-consistent DFT calculation without any empiricism. The fact that we observe only small differences between self-consistent and nonself-consistent calculations in this case may then serve as a validation of the assumption made in previous calculations, i.e., that it is acceptable to base the OT-RSH calculations on geometries optimized with standard functionals. One can certainly envision, however, that for more complex molecules quantitative and even qualitative differences may arise.

Next, we compare computed bond lengths and angles to experimental gas-phase structure, again taken from the NIST database.[74] The results are given graphically in Figure 2 and summarized in Table 1. As expected, B3LYP bond-length predictions are within a highly satisfactory MAE of 0.008 Å from experiment (corresponding to a relative error of 0.61%), with a standard-deviation of 0.011 Å. The predicted bond lengths obtained from our self-consistent scheme exhibit a very similar accuracy, with a MAE of 0.012 Å from experiment (corresponding to a relative error of 1.02%) and a standard deviation of 0.014 Å. We additionally compared the self-consistent scheme predicted angles to experimental values. Again, in order to confine ourselves to well-established experimental data, we have limited our examination of angles to "central" ones within each molecule (see Supporting Information for further details). Here too, our results show a satisfying MAE of 0.52° from experiment, corresponding to a relative error of 0.48%. B3LYP results are very similar, with a MAE of 0.59° from experiment, corresponding to a relative error of 0.53%.

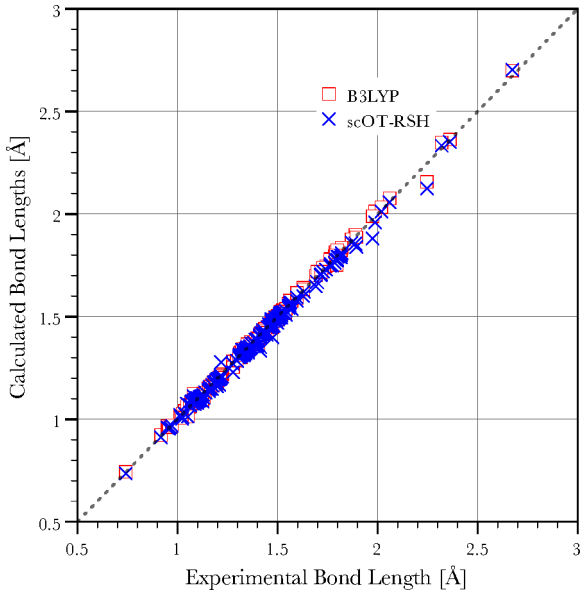

Figure 2. Comparison of theoretical bond lengths across the G2 test set, calculated with B3LYP (red squares) and scOT-RSH (blue × marks), with experimental values.[74] Points lying on the 45° dashed line indicate agreement between theory and experiment (within the accuracy of the latter).

To further explore the capabilities of our suggested scheme, we examined molecular vibrational properties. For these calculations, γ was held fixed at the optimized value. This can be justified by assuming that γ is a weak function of the atomic positions (an assumption already verified above) so that its change in the course of small-amplitude molecular vibrations can be neglected. Furthermore, allowing γ to change during the vibration raises difficulties associated with size-consistency issues, as discussed in detail below. To reduce the number of degrees of freedom and avoid spurious comparison of frequencies corresponding to different normal modes, we considered the zero-point energy (ZPE), calculated for each molecule by ZPE = $1/2\ \hbar \sum_{\nu=0}^{M-1} \omega_\nu$, where $\hbar$ is the reduced Planck constant and ω_ν is the vibrational frequency for mode ν, out of a total of M normal modes per molecule. The results, compared to ZPEs obtained from experimentally derived harmonic freqencies, are reported graphically in Figure 3 and summarized in Table 1. We find that B3LYP yield a MAE of 250.7 cm^{-1}, corresponding to a relative error of 3.10% from experiment. Our self-consistent scheme yields a somewhat larger, but still useful, MAE of 379.3 cm^{-1}, corresponding to a relative error of 6.49%.

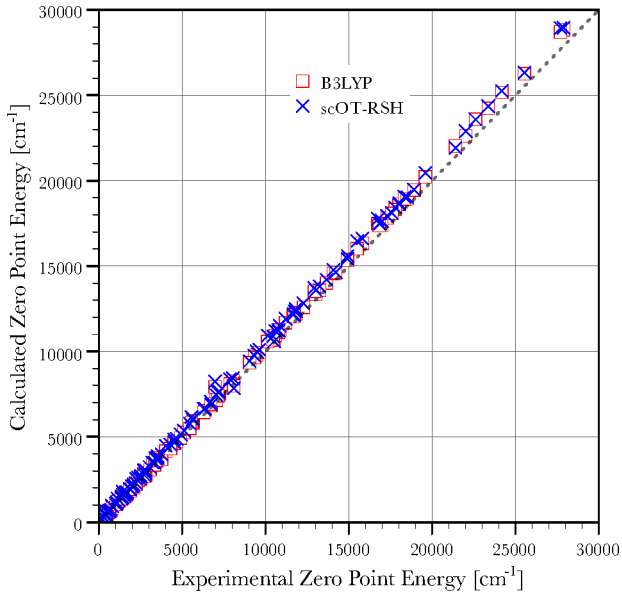

Figure 3. Comparison of theoretical zero-point energies across the G2 test set, calculated with B3LYP (red squares) and the new scOT-RSH scheme (blue × marks), with experimental values.[74] Points lying on the 45° dashed line indicate agreement between theory and experiment (within the accuracy of the latter).

The combined results of Figures 1−3 indicate that the suggested self-consistent scheme is indeed successful in predicting accurate HOMO energy levels across the G2 benchmark data set, without compromising the accuracy of structural predictions and with very little compromise on the accuracy of vibrational frequencies. Having established this overall success, we now turn to discussing present-day limitations of the approach.

First of all, trivially, the self-consistent approach hinges on success in finding an optimally tuned range-separation parameter, γ. This was possible for all molecules in the G2 data set. In some cases, issues with competing spin configurations arise, which manifest themselves in $j(N;\gamma)$ with no minima. Special care must be taken in these instances to ensure that the spin configurations being used are indeed the optimized ones, namely, that they lead to the minimal total energy among all possible configurations.

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Next, we address the issue of the detailed choice of tuning criterion. Specifically, we consider the difference between the single-tuning procedure of eq 1, recommended for determining ionization energies,[26] and the double-tuning procedure of eq 2, recommended for determining fundamental gaps as well as optical excitations.[9,30] As mentioned above, for most systems in the G2 data set the electron affinity is negative and eq 2 is inapplicable. However, for 32 molecules the self-optimized scheme based on eq 1 predicted a bound LUMO level. For these, we further investigated the effect of applying the double-tuning procedure. Recall that the minimal value of J in eq 2 may serve as a figure of merit for the expected remaining error in eigenvalues.[78] For 15 of the 32 examined molecules, the double-tuning procedure resulted in an optimal J smaller than 0.2 eV, that is, the prediction of both HOMO and LUMO energies is satisfactory. For 6 molecules, the double-tuning procedure led to a somewhat larger, but still tolerable, error of J = 0.2−0.3 eV. For the remaining 11 molecules, the error was larger and in the range of J = 0.3−0.6 eV, with one exception—OH—where the minimal J was 0.77 eV. Interestingly, among those 11 molecules, 10 are spin-polarized. In all these cases, we could easily find a value of γ such that the HOMO or LUMO tuning succeeds individually, that is, the first or second terms on the right-hand side of eq 2 are minimized separately. However, the value of γ needed for these two minimizations was too different to allow for a satisfactory least-squares compromise. Such behavior is typical for very small systems (and has been pointed out previously[30,64] for atoms and dimers), where the addition or removal of a single electron may change the chemical nature of the system strongly. This is typically much less of an issue for larger systems.[9,30,50] The good news is that the tuning procedure itself provides a warning sign when the reliability of the result may be suspect.

Generally speaking, the approximation we employ assumes an adequate choice for semilocal exchange and correlation expressions. If this is not the case, for example, due to significant contributions from static correlation[55] or long-range correlation,[9,27,33,79] results may suffer. This may be responsible for the slightly reduced accuracy in the description of molecular vibrations. Indeed, we found larger errors (of the order of 10%) for diatomic molecules, where left−right static correlation is important.[80] The combination of semilocal exchange and correlation is known to provide a mimic of static correlation effects.[81,82] In the RSH scheme, some of the semilocal exchange is replaced by Fock exchange by definition, which may explain some of the error. With B3LYP, however, molecules requiring more static correlation are part and parcel of the training set and the treatment is somewhat more accurate owing to the partial incorporation of such effects via the choice of semiempirical parameters.

Up to this point, we have discussed structural parameters and vibrational frequencies, which are related to the first and second derivative of the total energy, respectively. We have not, however, discussed atomization or reaction energies. These are related to finite total energy differences. In this case, the OT-RSH approach is at a disadvantage because of the size-consistency problem. The size consistency criterion is a fundamental constraint in DFT, which states that the total energy E_{AB} of a system comprised of two well-separated, independent subsystems A and B with energies E_A and E_B must be given by $E_{AB} = E_A + E_B$.[6] Nontuned RSH functionals are size consistent (as are all of their exchange and correlation ingredients). However, by construction, a tuned RSH functional is not size consistent because, due to its implicit definition, it generally has different γ values for the whole system and the two separate subsystems. The size consistency error, defined as $E_A + E_B - E_{AB}$, where each of the energies is calculated with its own γ, tuned for the A, B, or AB system separately, was found to be as large as a few electronvolts for several diatomic molecules.[64] This drawback is particularly problematic for protonoation/deprotonation processes, owing to the large γ associated with the hydrogen atom. Although in practice this is much less of an issue for larger fragments, theoretically this is a serious problem that is inherent in the methodology presented here.

Another possible difficulty with the new suggested scheme is the fact that while applying the self-consistent procedure, the resulting geometry may be affected by the specific value of γ, so that the self-consistent procedure can get "stuck" at a point that does not correspond to the stable ground-state configuration. If the total energy changes gradually with γ, which is usually found to be the case, this issue is not found to be a problem in practice. This can be learned from cases discussed above, where initial geometries from the unified force field led to exactly the same results as B3LYP initial geometries. However, this could be a severe issue for systems where different choices of γ lead to an abrupt change in the energy, typically owing to an abrupt change of electronic configuration.[64] For example, we found the optimal tuning of the P_2 molecule to be highly affected by the initial P−P bond length. Above some critical bond length, the tuning procedure did not succeed at all, likely due to a problematic configurations of the charged species within this larger separation. However, when starting with a smaller bond length the self-consistent procedure was normally applied and led to results that are well within the overall spread.

Even with these caveats, the results reported in Figures 1−3 represent, in our opinion, a major step forward. Our approach manages to obtain quantitatively useful information for quantities related to *both* eigenvalues and energies. The unique value of γ, obtained for each molecule, can be viewed as a descriptor for the character of the various electronic environments exhibited across the data set. Some selected molecules are shown and sorted by their optimal γ value in Figure 4. It has been pointed out previously (e.g., in 30−32) that, within classes of chemically similar molecules, γ generally decreases with molecular size. This is a clear reflection of the fact that with increased electron delocalization the system emphasizes correlation over exchange. This immediately explains several additional features of our approach: First, the lack of a universal and arbitrary division between the relative importance of exchange and correlation, together with the fact that we wish to keep the expression for either one simple, is a strong driving

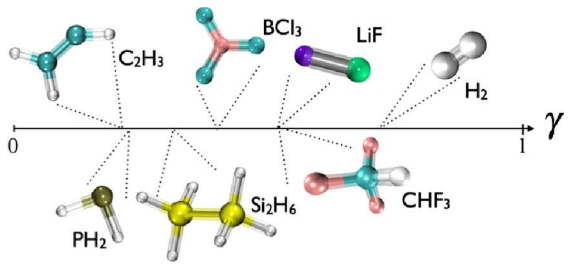

Figure 4. Selected molecules sorted by the optimal value of γ obtained through the scOT-RSH procedure.

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force for the use of a tuning procedure. Moreover, this immediately explains the repeated observation that results of a similar quality are not obtained with a fixed-γ approach.[9] Second, the choice of γ from a physical consideration, rather than through fitting a data set, explains why we can approach the level of accuracy afforded by semiempirical functionals, even when the latter are given the "home field advantage", that is, the comparison is made on the very data set used to parametrize the semiempirical approach. The obvious advantage is that, on general physical grounds, we expect the accuracy of our approach to remain similar for systems far removed from the benchmark data set, whereas this is not guaranteed for semiempirical approaches. In practice, one may still use initial geometries from other functionals in certain cases, but here we show that a fully self-consistent cycle is of the same level of accuracy. Finally, we note that in this self-consistent optimization approach, if long-range correlation is not essential, we can also expect other response properties to be well predicted.[83]

In conclusion, we have introduced and demonstrated the success of a self-consistent functional at describing geometrical and electronic properties across the 148 molecules in the G2 test set. Given that this approach contains no empirical or fitting parameters, its success at predicting experimental results establishes a new performance standard. Our implementation is fully parallelized and typically adds no more than a factor of 2 or 3 to the time-to-solution on a modern computing platform. Finally, the self-consistent procedure naturally produces an electronic order parameter that describes the varied nature of the electronic environment observed within the test set.

■ ASSOCIATED CONTENT

Supporting Information

Examples of internal angles considered, as well as alterations to ionization energies reported in the NIST database. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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