

Pair-Wise and Many-Body Dispersive Interactions Coupled to an Optimally Tuned Range-Separated Hybrid Functional

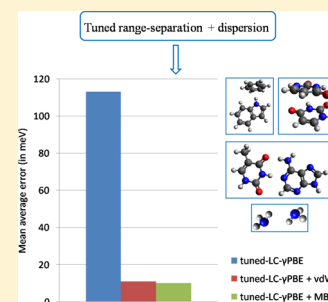
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S Supporting Information

ABSTRACT: We propose a nonempirical, pair-wise or many-body dispersion-corrected, optimally tuned range-separated hybrid functional. This functional retains the advantages of the optimal-tuning approach in the prediction of the electronic structure. At the same time, it gains accuracy in the prediction of binding energies for dispersively bound systems, as demonstrated on the S22 and S66 benchmark sets of weakly bound dimers.



I. INTRODUCTION

Density-functional theory (DFT) is an approach to the many-electron problem, in which the electron density, rather than the many-electron wave function, plays the central role.^{1,2} In recent years, DFT has become the method of choice for electronic-structure calculations across an unusually wide variety of disciplines,³ from organic chemistry⁴ to condensed matter physics,⁵ as it allows for fully quantum-mechanical calculations at a relatively modest computational cost. Practical applications of DFT are usually achieved by solving the Kohn–Sham equations (in either original⁶ or generalized form⁷), which map the original many-electron problem into an equivalent single-electron Hamiltonian. Although exact in principle, this mapping is approximate in practice. Its practical success depends critically on the nature of the approximate density functional employed for describing the energy and potential associated with electron exchange and correlation.^{8,9}

One class of approximate density functionals which has gained considerable interest recently is that of the range-separated hybrid (RSH) functionals.¹⁰ In the simplest realization of this idea, the repulsive Coulomb potential is split into a long-range (LR) and short-range (SR) term, for example, via

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\gamma r_{12})}{r_{12}} + \frac{\text{erf}(\gamma r_{12})}{r_{12}} \quad (1)$$

where γ is the range-separation parameter and $r_{12} \equiv r - r'$ is the relative electron coordinate. The LR exchange is then treated via an “explicit” or “exact” Fock-like term, whereas the SR part is treated using a semilocal approximation. Together with a semilocal expression for correlation, this leads to the following equation

$$\left(-\frac{\nabla^2}{2} + V_{\text{ext}}(r) + V_{\text{H}}([n]; r) + \hat{V}_{\text{F}}^{\text{LR},\gamma} + v_{\text{x}}^{\text{SR},\gamma}([n]; r) + v_{\text{c}}^{\text{sl}}([n]; r) \right) \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad (2)$$

where V_{H} is the Hartree potential, v_{c}^{sl} is the semilocal correlation, $\hat{V}_{\text{F}}^{\text{LR},\gamma}$ is the long-range Fock-like operator

$$\hat{V}_{\text{F}}^{\text{LR},\gamma} \varphi_i(r) = \sum_j \varphi_j(r) \int \text{d}r' \frac{\text{erf}(\gamma|r - r'|)}{|r - r'|} \varphi_j^*(r') \varphi_i(r') \quad (3)$$

and $v_{\text{x}}^{\text{SR},\gamma}([n]; r)$ is the SR, semilocal exchange potential. The RSH approach is useful because on the one hand RSH functionals employ 100% Fock exchange in the long-range of the interaction, leading to the correct form of the asymptotic potential, which is not obtained in conventional semilocal or hybrid functionals. On the other hand, they maintain the delicate balance of exchange and correlation in the short-range, thereby retaining the advantages of conventional functionals in the description of chemical bonding.^{8,11,12}

Usually, the range-separation parameter, γ , which provides a characteristic length scale for the transition from the short-range to the long-range, is determined semiempirically.^{13–18} Recently, it was suggested that γ can be tuned from first principles instead.^{11–13,19} This can be achieved by insisting that the ionization potential theorem^{20–23} (sometimes known as the “DFT version of Koopmans’ theorem”) be fulfilled. This means that

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$$\varepsilon_{\text{H}} = -I \quad (4)$$

that is, the highest occupied eigenvalue, ε_{H} , is equal and opposite to the ionization potential obtained from total energy differences, I . It was further shown that if the above condition is demanded for both neutral and anion systems, for example, in the form

$$J^2(\gamma) = [\varepsilon_{\text{homo}}(N; \gamma) + IP(N; \gamma)]^2 + [\varepsilon_{\text{homo}}(N + 1; \gamma) + IP(N + 1; \gamma)]^2 \quad (5)$$

then one can identify the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the DFT calculation with the ionization potential and electron affinity, respectively, thereby mimicking successfully, within DFT, the quasi-particle picture of many-body perturbation theory.²⁴ The same approach was found to be useful for the prediction of optical gaps from time-dependent DFT,^{25,26} notably for cases that are typically beyond the reach of conventional functionals, including full,^{19,27,28} partial,^{29,30} or implicit^{31,32} charge transfer excitations. Similar and related approaches were also found to be beneficial for a variety of electron and optical spectroscopies (see, e.g., refs 33–38).

One important issue which RSH functionals (with or without a tunable range parameter) fail to address is the description of dispersive interactions. Such interactions result from density fluctuations and dominate in regions where there is no or little overlap of electron densities.^{39,40} Although they are significantly weaker than a typical covalent bond, they still play an important and often crucial role in determining the structure and properties of a large variety of systems. From the DFT point of view, dispersive interactions require nonlocal correlation expressions,^{41–43} which are trivially missing from all standard functionals, including the RSH expression of eq 2.

Advanced DFT approaches that can capture dispersive interactions are a highly active field of research.^{41–43} A simple strategy, which is one of the most exploited ones in practice, is to add pair-wise dispersion corrections in the form

$$E_{\text{disp}} = - \sum_{j>i} f_{\text{damp}}(R_{ij}, R_{ij}^0) C_{\delta ij} R_{ij}^{-6} \quad (6)$$

where C_6 is the dispersion coefficient, R_{ij}^0 is the sum of equilibrium van der Waals (vdW) radii for the pair, and R is the interatomic distance, to the total energy obtained from the DFT calculation. These correction terms are damped in the short-range by the damping function f_{damp} , so that the successful description of strong chemical bonds is retained, but at the same time the long-range attraction essential to dispersive interactions is explicitly enforced. Several useful forms of such corrections have been put forth^{44–50} and have found widespread use. In particular, several forms for dispersive corrections of RSH functionals have also been presented.^{51–55}

An additional advantage of pair-wise dispersive corrections is that they allow one to overcome the thorny problem of obtaining a reliable description of both geometry and electronic structure.⁵⁶ Normally, this is difficult because the electronic structure is highly sensitive to Fock exchange, and determining long-range correlation expressions that are compatible with exact exchange is a very difficult task.⁹ Pair-wise dispersive corrections circumvent this difficulty by decoupling the two issues.⁵⁶ First, one chooses a functional that is appropriate to the electronic structure, but does not include a good description of dispersive interactions. Then, one augments it

with corrections for the leading terms of the dispersion interaction. Ideally, one would therefore like to augment optimally tuned RSH functionals with dispersive corrections and enjoy their superior electronic structure prediction without sacrificing their applicability to systems where dispersive interactions are important. However, because the range-separation parameter is system-dependent, and because the pair-wise correction depends on the details of the underlying functional, it is not clear how or even whether a suitable dispersive correction can be obtained.

To examine this question, we focus here on a specific form of pair-wise corrections, known as the Tkatchenko-Scheffler van der Waals (TS-vdW) method.⁴⁹ We have chosen this form for two reasons: First, distinctly from other pair-wise corrections schemes, in the TS-vdW scheme, the C_6 coefficients are determined from first principles, based on atomic polarizabilities that are renormalized by considering the environment-induced changes in the effective volume of each atom. The TS-vdW scheme is therefore largely free of adjustable parameters. It only contains one adjustable parameter, which is introduced in the Fermi–Dirac-like damping function,

$$f_{\text{damp}}(R_{ij}, R_{ij}^0) = \left[1 + \exp \left(-d \left(\frac{R_{ij}}{s_{\text{R}} R_{ij}^0} - 1 \right) \right) \right]^{-1} \quad (7)$$

where d and s_{R} are free parameters. The value of d is kept as a constant 20, which was found suitable for the noncovalent interaction and adjusts the steepness of the damping function. The semiempirical parameter is s_{R} , a range-separation parameter for the dispersion correction, which is determined on the basis of the vdW correction needed for a particular xc-functional. This allows the TS-vdW correction to yield results of useful and uniform accuracy for a wide range of underlying density functionals, as shown in refs 56, 57. Furthermore, in this way the first principles aspect of the optimally tuned RSH approach is retained inasmuch as possible even after dispersive corrections. In fact, because in the TS-vdW scheme the vdW parameters are functionals of the electron density, this scheme can be implemented self-consistently as a minimally empirical density functional for long-range correlation.⁵⁸

A second and significant reason for focusing on the TS-vdW scheme is that it has been recently extended to obtain the full many-body dispersive (MBD) energy in the dipole approximation,^{59,60} allowing it to seamlessly account for both solid and gas-phase interactions with chemical accuracy.⁶¹ This makes the question of MBD compatibility to an underlying RSH functional equally intriguing. Briefly, the MBD scheme proceeds from the TS-vdW one in two steps. In the first step, long-range screening is included by modeling each TS-vdW polarizable atom as a quantum harmonic oscillator and solving self-consistently the classical electrodynamics equations arising from dipolar interaction between the oscillators. In the second step, N -body interactions are accounted for by coupling the self-consistent oscillators obtained from the previous step using a many-body Hamiltonian that yields all orders of dipole interaction. As with the original TS-vdW scheme, the MBD method only requires one adjustable parameter, which is determined once and for all for a particular xc-functional. Furthermore, the MBD method can be cleanly derived from the exact adiabatic connection fluctuation–dissipation theorem for a system of coupled quantum harmonic oscillators.⁶⁰ Here the sole adjustable parameter is introduced via the dipole–dipole

interaction term, which (to avoid double counting of effects already present in the underlying functional) is based on a long-range Coulomb operator, in the form:

$$W(R_{ij}) = \{1 - \exp[-(R_{ij}/R_{ij}^0)^\beta]\}/R_{ij} \quad (8)$$

where β is a semiempirical parameter.

Here, the TS-vdW and MBD are coupled to optimally tuned RSH calculations for the well-known S22⁶² and S66 sets⁶³ of benchmark data for dispersive interactions. We find that, despite strong variations in the optimal value of the range-separation parameter, γ , a level of accuracy that is comparable to and even slightly better than that achieved with conventional semilocal or hybrid functionals is obtained. In addition, we find that this is achieved with universal values for the range-separation parameters of the dispersive corrections, s_R and β , that do not depend on the optimal exchange range-separation parameter, γ . Therefore, we find TS-vdW and MBD corrections to be inherently suitable to optimally tuned RSH calculations and to allow for their simple, reliable, and meaningful extension to dispersively bound systems.

II. METHODOLOGICAL AND COMPUTATIONAL DETAILS

All DFT calculations presented in this article were performed using version 6.0 of the NWChem package.⁶⁴ We used an optimally tuned RSH functional, of the form given in eq 1, based on the LC- ω PBE functional⁶⁵ which employs a short-range version of the Perdew–Burke–Ernzerhof (PBE) semilocal exchange functional⁶⁶ and semilocal PBE correlation. We shall refer to this functional here as LC- γ PBE, to emphasize that, unlike in the original functional, here the range-separation parameter is not a universal constant. The aug-cc-pvtz basis set was used throughout, with the counterpoise (CP)^{67,68} method employed to correct for basis set superposition errors (BSSE) in the evaluation of binding energies. All binding energies values reported below are the average of the uncorrected and CP-corrected values, which typically over- and underestimate, respectively, the binding energy. The average difference between the uncorrected and CP-corrected values was found to be ~ 4 meV for both the S22 and S66 sets. This serves as a useful measure of remaining basis-set-related errors.

Optimal γ values were deduced for each dimer structure using eq 5. Subsequently, dispersion corrections of the form given in eq 6 were added to the total energy. The binding energy of each dimer was then obtained from the total energy difference of the dimer and the isolated monomers. Note that the optimal tuning parameter of the monomer is not necessarily the same as that of the dimer. However, subtracting energies obtained from different γ values may introduce severe size-consistency errors.^{13,69} Therefore, the optimal γ value determined for the dimer was also used for the monomer species in the calculation of the binding energy. Finally, optimization of the TS-vdW and MBD semiempirical parameters (s_R and β of eqs 7 and 8, respectively) was performed based on the S22 set, as discussed below.

III. RESULTS AND DISCUSSION

Because dispersive corrections, by definition, only affect total energies, they do not affect the electronic structure and therefore we focus here solely on assessing their success in describing binding energies. As a first step, optimal γ values were determined for all dimers in the S22 and S66 set, with the

values found given in the Supporting Information. They were found to vary between 0.25 and 0.5 (in atomic units), underscoring yet again the importance of a nonuniversal value for γ (see, e.g., refs 11, 12 for a detailed overview of this issue). Mean absolute errors (MAE) for the binding energies, obtained from the optimally tuned RSH in the absence of dispersion corrections, are given in Table 1 and 2 for the S22

Table 1. Mean Absolute Error (in meV) for the S22 Set of Dimers, for Binding Energy before and after TS-vdW Correction with Optimal γ Value, for the Overall Optimal s_R of the Set ($s_R = 0.95$) and with the Optimal s_R for Each Dimer

functional	TS-vdW correction	Hbond	vdW	mixed	total
tuned LC- γ PBE	without correction	86	205	95	132
tuned LC- γ PBE	with correction $s_R = 0.95$	25	8	7	13
tuned LC- γ PBE	with s_R per γ	24	8	6	12
PBE	without correction	53	208	87	118
PBE	with correction $s_R = 0.94$	16	14	7	12
PBEh	without correction	41	191	78	107
PBEh	with correction $s_R = 0.96$	22	10	7	17

Table 2. Mean Absolute Error (in meV) for the S66 Set of Dimers, for Binding Energy before and after TS-vdW Correction with Optimal γ Value, for the Overall Optimal s_R of the Set ($s_R = 0.95$) and with the Optimal s_R for Each Dimer

functional	TS-vdW correction	Hbond	vdW	mixed	total
tuned LC- γ PBE	without correction	65	172	104	113
tuned LC- γ PBE	with correction $s_R = 0.95$	13	12	7	11
tuned LC- γ PBE	with s_R per γ	12	14	8	11
PBE	without correction	37	159	93	96
PBE	with correction	20	26	12	19
PBEh	without correction	32	156	87	91
PBEh	with correction	21	20	11	17

and S66 sets, respectively. For comparison, the same tables also reproduce previously published⁵⁷ binding energies obtained from the semilocal PBE functional,⁶⁶ as well as from the conventional hybrid functional based on PBE,⁷⁰ which we denote here as PBEh. It is readily observed that for van der Waals bonded systems, the performance of the RSH functional is similar to that of PBE and PBEh, whereas for the hydrogen-bonded complexes it is worse. In any case, and as expected, the performance of any of those functionals in the absence of dispersive corrections is unacceptable.

For the conventional functionals, an optimal value of the damping range parameter, s_R , was obtained previously by determining the value that minimizes errors with respect to the reference data across the S22 set. As a first step, the same procedure was employed for the optimally tuned RSH calculations, despite the system-dependent value of γ . The value obtained was $s_R = 0.95$, which compares very well with the previously determined s_R values of 0.94 and 0.96 for PBE and PBEh, respectively.⁵⁷ The same parameter was then used, as is, for the S66 set, without further optimization. This allows us to ascertain that the quality of the results is not merely a trivial outcome of the fitting procedure and that it persists outside of the original training set.

Results obtained with these dispersive corrections for both the S22 and the S66 set are also given in Tables 1 and 2, respectively. As already known, a significant improvement is obtained with dispersion corrections using any of the underlying exchange-correlation functionals. In particular, the MAEs drop from the order of ~ 100 meV to 10–20 meV. Satisfyingly, the errors obtained from the optimally tuned LC- γ PBE functional for the larger and more diverse S66 set are as good as those obtained for the S22 set and even somewhat better.

To examine whether further accuracy can be obtained by allowing s_R to depend on γ , rather than being a universal parameter, we performed the following additional calculations. First, binding energies were obtained across a range of (nontuned) γ values for each of the dimers in the S22 set. Specifically, γ was varied from 0 to 1 in steps of 0.1. MAEs obtained from this procedure are shown in Figure 1. It is readily

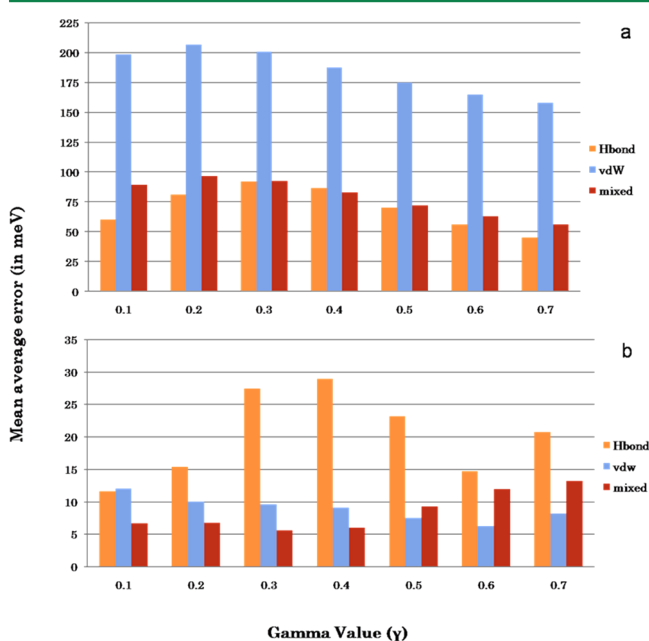


Figure 1. Mean absolute error (in meV) for the S22 set at different values of γ , without (a) and with (b) TS-vdW corrections, with respect to CCSD(T) reference values.

observed that while there is some dependence of the results on the value of γ , the general picture is the same one reported above. Following this, the s_R parameter of the TS-vdW approach was optimized separately for each value of γ . The dispersion-corrected results are shown in Figure 1b, with the dependence of s_R on γ given in Figure 2 (and see the Supporting Information for a detailed table of values). As expected, errors are diminished considerably for any choice of γ . The calculations of Tables 1 and 2 were then revisited, with the $s_R(\gamma)$ curve of Figure 2 used to select s_R per each value of optimally tuned γ . These results are also reported in the tables and are essentially of the same quality as that obtained with a fixed s_R value. This is helpful, because it means that per- γ optimization of s_R is unnecessary, which makes the practical application of the dispersive corrections easier.

Encouraged by these results, we examined the extent to which further improvement can be obtained from the inclusion of the many-body dispersive (MBD) energy. As a first step, we fitted the optimal value of the MBD range-separation

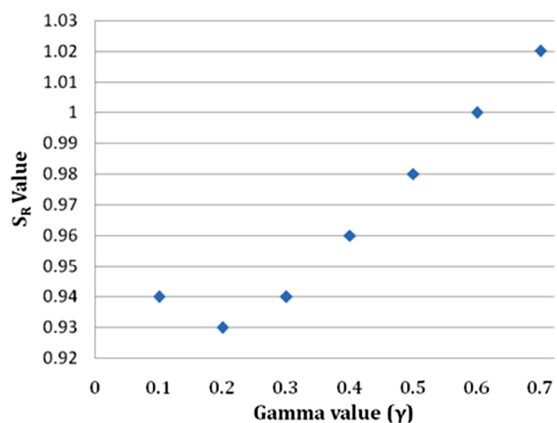


Figure 2. Optimal van der Waals range separation parameter, s_R , as a function of the hybrid functional range separation parameter, γ .

parameter, β of eq 8, using the Tuned-LC- γ PBE RSH results for the S22 set. We obtained a value of 2.59, which again compares very well with the previously determined values of 2.56 and 2.53 for the PBE and PBEh functionals, respectively.⁵⁹ MBD-corrected calculations were then performed for the S66 set using this value. A comparison of TS-vdW and MBD corrections for the PBE, PBEh, and tuned-LC- γ PBE functionals is given in Table 3. As expected, MBD corrections provide

Table 3. Comparison of Mean Absolute Error (in meV) for the Binding Energies of the S66 \times 1.0 and S66 \times 0.9 Sets of Dimers, Obtained with Tkatchenko–Scheffler and Many-Body Dispersion Corrections of the PBE, PBEh, and Tuned-LC- γ PBE Functionals

set	functional	Hbond	vdW	mixed	total
S66 \times 1.0	PBE + TS	20	26	12	19
	PBEh + TS	21	20	11	17
	tuned-LC- γ PBE + TS	13	12	7	11
	PBE + MBD	16	16	8	13
	PBEh + MBD	18	12	7	13
	tuned-LC- γ PBE + MBD	13	9	8	10
S66 \times 0.90	PBE + TS	26	29	15	23
	PBEh + TS	31	28	12	24
	tuned-LC- γ PBE + TS	15	28	19	21
	PBE + MBD	25	28	16	23
	PBEh + MBD	32	23	12	23
	tuned-LC- γ PBE + MBD	13	18	14	15

some further improvement on the TS-vdW ones for any underlying functional. Importantly for the present discussion, the slightly better performance of the tuned-LC- γ PBE functional, observed with the TS-vdW pair-wise corrections, persists with the MBD corrections as well. With this in mind, it is interesting to make the same comparison for the related S66 \times 0.9 set, where the geometry is compressed by 10% with respect to the original set, because the errors at the shorter intermolecular distances are expected to be larger owing to the steepness of the potential energy curves.⁶³ This comparison, with optimal γ values calculated anew for the new geometry (see Supporting Information for details), is also given in Table 3. Indeed, the MAE for the S66 \times 0.9 set is ~ 25 –50% larger than that for the S66 \times 1.0 set for each of the underlying functionals. But even so, the optimally tuned RSH-based calculation outperforms all others. In fact, for the S66 \times

0.9 set the tuned-LC- γ PBE+MBD offers essentially the same accuracy as that obtained with PBE(h)+MBD for the uncompressed $S66 \times 1.0$ set.

The following picture emerges from the above detailed comparison between the various uncorrected and dispersion-corrected results: (1) The (pair-wise or many-body) dispersion-corrected optimally tuned RSH functional performs at least as well as, and possibly slightly better than, the dispersion-corrected conventional functionals; (2) It does so with dispersion-related range-separation parameters that are very close to those of its ancestor functionals, PBE and PBEh; (3) It does so without requiring that the dispersion parameters be adjusted to the range-separation parameter in the underlying functional; (4) It offers improved accuracy for cases of compressed geometry.

What are the physical origins of this behavior? A key observation here is that PBE, PBEh, and LC- γ PBE only differ in the partition between semilocal and nonlocal exchange. However, as mentioned above, dispersion is primarily a nonlocal correlation phenomenon from a DFT point of view. Therefore, the pair-wise or many-body corrections should be similar in value for all of them. The similar values of s_R and β obtained for all functionals confirm this assertion. Interestingly, Figure 2 shows that s_R tends to increase (weakly, but clearly) with increasing γ . As can be gleaned from eq 2, in the limit of $\gamma \rightarrow 0$ the GGA (in this case, PBE) expression is retrieved, whereas for $\gamma \rightarrow \infty$ Hartree–Fock plus GGA correlation is obtained. An increased value of s_R means that the range at which dispersive interactions need to be added is larger and therefore that more midrange dispersive interaction is already contained in the underlying functional.⁵⁷ Generally, semilocal exchange functionals with an asymptotic exchange-hole potential weaker than $\sim 1/r$ are expected to overbind with respect to Fock exchange and therefore produce spurious dispersive attraction.⁷¹ But in this case, the increase of s_R with γ suggests that PBE exchange actually underbinds with respect to Fock exchange and that the well-documented residual binding, obtained from the application of PBE to dispersively bound systems,^{56,57} is coming from the PBE correlation. We hypothesize that the optimal-tuning of the range-separation in the RSH functional assists in the balance of the midrange correlation and therefore slightly improves performance for the $S66$ set, especially in its compressed form. However, it is too soon to tell whether this is a systematic observation or one that is particular to this benchmark data set. In any case, the usefulness of combining pair-wise or many-body dispersive corrections with an optimally tuned range-separated hybrid functional is clearly established.

IV. CONCLUSIONS

In this study, we have shown that the optimally tuned RSH functional approach can be combined successfully with Tkatchenko–Scheffler pair-wise and many-body methods for the dispersion energy. Therefore, one can use the optimal-tuning idea, with all its benefits in the description of the electronic structure, without sacrificing the ability to treat weakly bound systems, in particular their geometry and binding energy. Furthermore, this is achieved with the same form of correction as for simpler functionals and with the optimal tuning introducing no complication whatsoever as far as the damping function of the dispersive corrections is concerned. We expect this combined approach to be useful in future

studies of the electronic structure and optical properties of weakly bound systems.

■ ASSOCIATED CONTENT

Supporting Information

Mean absolute errors before and after dispersive correction, as a function of range-separation parameter, γ ; Optimal γ value for each in the $S22$, $S66 \times 1.0$, and $S66 \times 0.90$ sets. 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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