Pair-wise dispersive corrections of an optimally-tuned range-separated hybrid functional

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By

PIYUSH AGRAWAL

20071057

Under the guidance of

Prof. Leeor Kronik

Head, Materials and Interfaces Department

Weizmann Institute of Science

Department of Chemistry

Indian Institute of Science Education and Research Pune

Certificate

This is to certify that this dissertation entitled *"Pair-wise dispersive corrections of an optimally-tuned range-separated hybrid functional"* towards partial fulfilment of 5 year dual BS-MS program at the Indian Institute of Science Education and Research, Pune, represents original research carried out by Piyush Agrawal under the supervision of Prof. Leeor Kronik at Weizmann Institute of Science during the academic year "2012-2013".

PIYUSH AGRAWAL
(20071057)

Supervisor [Head, Materials and Interfaces]

Date: 16-03-2013

Place:

Declaration

I hereby declare that the matter embodied in the report entitled "Pair-wise dispersive corrections of an optimally-tuned range-separated hybrid functional" is the results of the investigations carried out by me at the Department of Materials and Interfaces, at Weizmann Institute of Science, Israel, under the supervision of Prof. Leeor Kronik and the same has not been submitted elsewhere for any other degree.

PIYUSH AGRAWAL

Date
Place

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Abstract

We propose a non-empirical, pairwise-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.

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1. Introduction

1.1 Density Functional Theory

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 chemistry[4] 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 equation (in either original[6] or generalized form[7]), which maps 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]

1.2 Range-Separated Hybrid Functional

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, e.g., via

$$\frac{1}{r_{12}} = \frac{1-\mathrm{erf}(\gamma r_{12})}{r_{12}} + \frac{\mathrm{erf}(\gamma r_{12})}{r_{12}}, \tag{1}$$

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 semi-local approximation. Together with a semi-local expression for correlation, this leads to the following equation:

$$(-\frac{\nabla^2}{2} + V_{ext}(r) + V_H([n];r) + \hat{V}_F^{\mathrm{lr},\gamma} + v_x^{sr,\gamma}([n];r) + v_c^{sl}([n];r))\Phi_i(r) = \varepsilon_i\Phi_i(r) \tag{2}$$

where V_H is the Hartree potential, v_c^{sl} is the semilocal correlation, $\hat{V}_F^{lr,\gamma}$ is the long-range Fock-like operator

$$\hat{V}_F^{lr,\gamma}\Phi_i(r) = \sum_j \Phi_j(r) \int dr' \frac{\text{erf}(\gamma|r-r'|)}{|r-r'|} \Phi_j^*(r')\Phi_i(r') \tag{3}$$

and $v_x^{sr,\gamma}([n];r)$ 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 semi-local 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]

1.3 Optimal γ Tuning

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 semi-empirically.[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

$$\varepsilon_H = -I, \tag{4}$$

i.e., 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, e.g., in the form

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

then one can identify the HOMO and 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] notably for cases that are typically beyond the reach of conventional functionals, including full[19], partial[26,27], or implicit[28] charge

transfer excitations. Similar and related approaches were also found to be beneficial for a variety of electron and optical spectroscopies (see, e.g. (29-34)).

1.4 Motivation of Study and Dispersion Correction

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.[35,36] 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 large variety of systems. From the DFT point of view, dispersive interactions require non-local correlation expressions,[37-39] 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.[38-39] A simple strategy, which is one of the most exploited ones in practice, is to add pair-wise dispersion corrections in the form

$$E_{disp} = - \sum_{j>i} f_{damp}\left(R_{ij}, R_{ij}^0\right) C_{6ij} R_{ij}^{-6} \tag{6}$$

where C_6 is the dispersion coefficient, R_{ij}^0 is the sum of equilibrium 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, 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[40-45] and have found widespread use. Moreover, several forms for dispersive corrections of RSH functionals have also been presented.[46-49]

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, by decoupling the two issues.[50] 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 first principles 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 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) correction.[45] 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. The only parameter which is empirical is introduced in the Fermi-Dirac-like damping function,

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

where d and s_R are the free parameters. The value of d is kept as a constant 20, which was found suitable for the non-covalent interaction and adjusts the steepness of the damping function. The only empirical parameter remaining is s_R, which is determined on the basis of the vdW correction needed for a particular xc-functional. This way, the first principles aspect of the optimally-tuned RSH approach is retained in as much as possible. Second, the TS-vdW correction has previously been shown to yield results of useful and uniform accuracy for a wide range of underlying density functionals.[50,51]

Here, we apply TS-vdW corrections to optimally-tuned RSH calculations for the well-known S22[52] and S66 sets[53] of benchmark data for dispersive interactions. We find that, despite strong variations in the optimal value of the exchange range-separation, parameter, γ, a level of accuracy that is comparable and even slightly better than that achieved with conventional semi-local or hybrid functionals is obtained. Furthermore, it was found that seeking an optimal relation between the two range separation parameters, γ and s_R, does not increase the accuracy further. Therefore, we find TS-vdW corrections to be inherently suitable

to optimally-tuned RSH calculations and to allow for their reliable extension to dispersively-bound systems.

2. Methodological and Computational Details

All DFT calculations presented in this article were performed using version 6.0 of the NWChem package.[54] We used an optimally-tuned RSH functional, of the form given in Eq. (1) based on the LC-ωPBE functional[55] which employs a short-range version of the Perdew-Burke-Ernzerhof (PBE) semi-local exchange functional[56] and semi-local PBE correlation. The aug-cc-pvtz basis set was used throughout. Optimal γ values were deduced for the 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.[13,57] Therefore, for calculating binding energies, the optimal γ value determined for the dimer was also used for the monomer species.

3. Results and Discussions

Optimal γ values for all dimers studies are given in the table 1 and 2. Optimal gamma values were found to vary between 0.25 and 0.5 for dimers in both the S22 and S66 sets, underscoring the importance of a non-universal value for γ. Mean absolute errors (MAE) for the binding energies, obtained from the optimally-tuned RSH in the absence of dispersion corrections, are given in Table I and II for the S22 and S66 sets, respectively. For comparison, the same tables also reproduce previously published[51] binding energies obtained from the semi-local PBE functional,[56] as well as from the conventional hybrid functional based on PBE,[58] 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 somewhat worse. In any case, and as expected, the performance of any of those functionals in the absence of dispersive corrections is unacceptable.

Table 1. Optimal-tuned gamma value for all monomers of S22 set.

Ammonia_dimer	0.428
water_dimer	0.498
formicacid_dimer	0.395
formamide_dimer	0.370
uracil_dimer	0.291
2_pyrodoxine_aminopyridine	0.258
adenine_thymine WC	0.253
methane dimer	0.462
ethene dimer	0.343
benzene_methane	0.275
benzene dimer	0.248
pyrazine dimer	0.292
uracil dimer	0.260
indole benzene	0.245
adenine thymine stack	0.245
ethene_ethyne	0.335
benzene_water	0.280
benzene_ammonia	0.300
benzene_HCN	0.273
benzene_dimer	0.262
indole_benzene_tshape	0.255
phenol dimer	0.264

Table 2. Optimal-tuned gamma value for all dimers of S66 set.

Water-Water	0.495	Uracil-Pentane	0.262
Water-MeOH	0.430	Uracil-Cyclopentane	0.263
Water-MeNH2	0.375	Uracil-Neopentane	0.267
Water-Peptide	0.318	Ethene-Pentane	0.330
MeOH-MeOH	0.405	Ethyne-Pentane	0.355
MeOH-MeNH2	0.457	Peptide-Pentane	0.283
MeOH-Peptide	0.376	Benzene-Benzene_TS	0.262
MeOH-Water	0.415	Pyridine-Pyridine_TS	0.296
MeNH2-MeOH	0.375	Benzene-Pyridine_TS	0.313
MeNH2-MeNH2	0.364	Benzene-Ethyne_CH-pi	0.269
MeNH2-Peptide	0.455	Ethyne-Ethyne_TS	0.380
MeNH2-Water	0.375	Benzene-AcOH_OH	0.284
Peptide-MeOH	0.338	Benzene-AcNH2_NH-pi	0.314
Peptide-MeNH2	0.329	Benzene-Water_OH-pi	0.287
Peptide-Peptide	0.312	Benzene-MeOH_OH-pi	0.291
Peptide-Water	0.330	Benzene-MeNH2_NH-pi	0.340
Uracil-Uracil_BP	0.291	Benzene-Peptide_NH-pi	0.300
Water-Pyridine	0.296	Pyridine-Pyridine_CH-N	0.320
MeOH-Pyridine	0.350	Ethyne-Water_CH-O	0.391
AcOH-AcOH	0.336	Ethyne-AcOH_OH-pi	0.360
AcNH2-AcNH2	0.324	Pentane-AcOH	0.356
AcOH-Uracil	0.271	Pentane-AcNH2	0.340
AcNH2-Uracil	0.268	Benzene-AcOH	0.272
Benzene-Benzene_pi-pi	0.250	Peptide-Ethene	0.330
Pyridine-Pyridine_pi-pi	0.270	Pyridine-Ethyne	0.321
Uracil-Uracil_pi-pi	0.250	MeNH2-Pyridine	0.335
Benzene-Pyridine_pi-pi	0.252		
Benzene-Uracil_pi-pi	0.267		
Pyridine-Uracil_pi-pi	0.265		
Benzene-Ethene	0.270		
Uracil-Ethene	0.273		
Uracil-Ethyne	0.276		
Pyridine-Ethene	0.306		
Pentane-Pentane	0.253		
Neopentane-Pentane	0.312		
Neopentane-Neopentane	0.288		
Cyclopentane-Neopentane	0.305		
Cyclopentane-Cyclopentane	0.319		
Benzene-Cyclopentane	0.258		
Benzene-Neopentane	0.260		

Table 3. 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 optimal s_R for each dimer.

functional	TS-vdW correction	Hbond	vdW	mixed	Total
tuned LC-γPBE	without correction	80	196	92	126
tuned LC-γPBE	with correction s_R =0.95	24	8	7	13
tuned LC-γPBE	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 4. 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 optimal s_R for each dimer.

functional	TS-vdW correction	Hbond	vdW	mixed	Total
tuned LC-γPBE	without correction	62	168	101	110
tuned LC-γPBE	with correction s_R =0.95	11	13	7	11
tuned LC-γPBE	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

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, a value that compares very well with the previously determined s_R values of 0.94 and 0.96 for PBE and PBEh, respectively.[51] 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 3 and 4, respectively. As already known, a significant improvement is obtained with dispersion correction using either PBE or PBEh. In particular, the MAEs drop from the order of ~100 meV to 10-20 meV. Satisfyingly, the errors obtained from the PBE-based RSH functional are as good for the S22 set and even somewhat better for the larger and more diverse S66 set.

Table 5. Mean absolute error (in meV) for the S22 set at different values of ω, with and without TS-vdw corrections with respect to CCSD(T) reference values.

| ω	S_R	Before TS-vdW Correction					After TS-vdW correction			
		Hbond	vdW	mixed	Total		Hbond	vdW	mixed	Total
0.05	0.95	48.22	190.16	82.53	110.75		14.43	14.86	5.59	11.76
0.10	0.95	55.69	194.69	86.42	116.02		12.12	11.69	6.29	10.11
0.20	0.94	76.79	202.70	93.17	127.79		14.92	7.77	6.68	10.11
0.30	0.95	87.70	196.64	89.54	127.90		25.95	7.48	5.33	12.67
0.40	0.97	82.35	183.13	79.42	118.06		27.70	7.44	6.44	13.57
0.50	0.99	65.78	169.88	68.33	104.44		21.80	7.36	10.32	12.91
0.60	1.01	53.23	159.66	58.81	93.71		14.10	6.97	13.24	11.23
0.70	1.03	42.14	152.50	51.44	85.24		23.47	9.70	14.72	15.68
0.80	1.04	35.42	147.77	46.22	79.71		38.09	10.64	17.47	21.55
0.90	1.04	37.69	144.65	44.05	78.61		51.33	8.73	21.38	26.31
1.00	1.05	41.70	142.62	42.50	78.67		59.77	11.60	21.86	30.19
1.50	1.05	50.80	139.41	39.85	79.54		120.60	11.20	21.86	50.94
optimal	0.95	80.17	196.47	91.59	126.09		23.35	8.35	7.17	12.95
optimal	s_R per γ	80.17	196.47	91.59	126.09		23.97	8.64	6.79	12.93
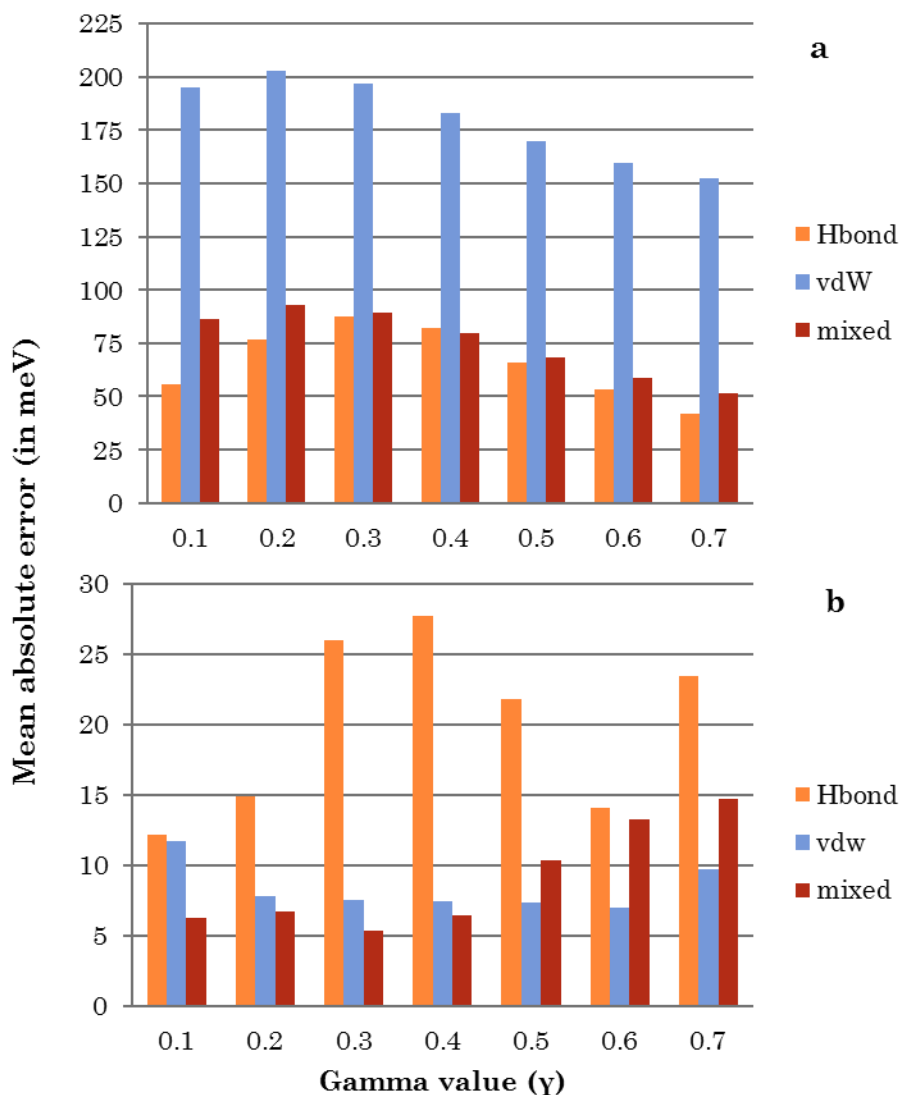
Fig 1: Mean absolute error in (meV) for the S22 set at different values of γ, with (b) and without (a) TS-vdW corrections with respect to CCSD(T) reference values.

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 (non-tuned) 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 Fig. 1 and values are tabulated in table 5. 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 Fig. 1b, with the dependence of s_R on γ given in Fig. 2. As expected, errors are diminished considerably for any choice of γ. The calculations of Tables I and II were then revisited, with the s_R (γ) curve of Fig. 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.
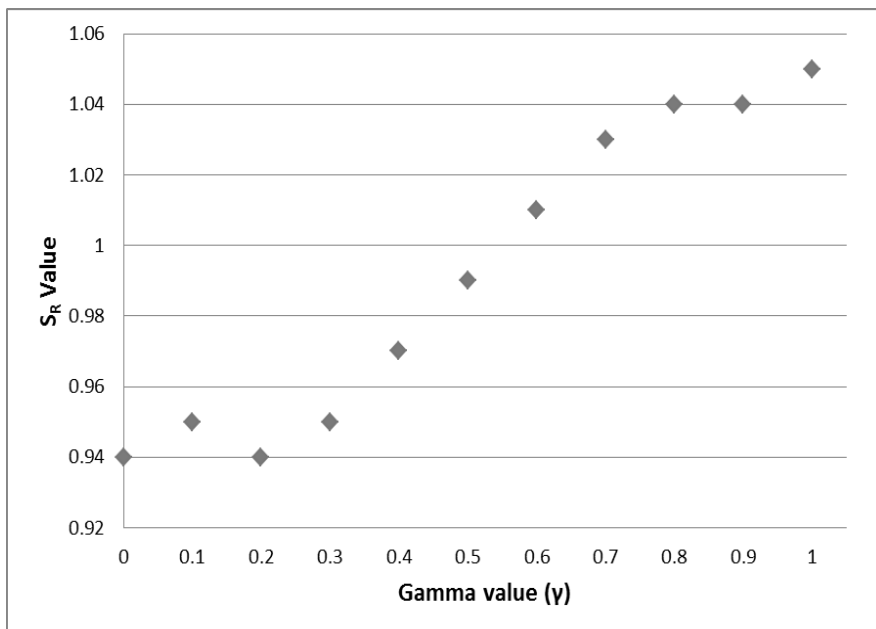

Fig 2: Optimal van der Waals range separation parameter, s_R, as a function of the hybrid functional range separation parameter, γ.

The following picture emerges from the detailed comparison between the various uncorrected and dispersion-corrected results: (1) The dispersion-corrected optimally-tuned RSH functional performs at least as well, if not better, than the dispersion-corrected conventional functionals. (2) It does so with a damping parameter that is very close to that of its ancestor functionals PBE and PBEh. (3) Further tuning of the damping parameter, per tuning of the RSH functional, is neither helpful nor harmful, which makes it redundant in practice.

What are the physical origins of this behavior? A key observation here is that PBE, PBEh, and LC-ωPBE only differ in the partition between semi-local and non-local exchange. However, as mentioned above, dispersion is primarily a

non-local correlation phenomenon from a DFT point of view. Therefore, the same correction should be of similar value to all of them. Possibly the range-splitting in the RSH functional assists some of the mid-range correlation and therefore slightly improves performance for the S66 set, although it is too soon to tell whether this is systematic or particular to this benchmark data set.

4. Conclusions

In this study, we have shown that the optimally-tuned tuned RSH functional approach can be combined successfully with Tkatchenko-Scheffler dispersive corrections. Therefore, one can use the optimal-tuning idea, with all its associated 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.

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