

Influence of Coulomb-attenuation on exchange–correlation functional quality

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The dependence of functional quality on the attenuation parameters—which control the limiting ($r_{12} \rightarrow 0, \infty$) values and the rate of attenuation—is investigated for a Coulomb-attenuated exchange–correlation functional. For the attenuation and functional form considered, satisfaction of an exact long-range condition is detrimental for properties such as atomisation energies and bond lengths, but does improve classical reaction barriers and small molecule electronic excitation energies. The functionals considered can provide high quality valence, Rydberg, intramolecular and asymptotic intermolecular charge transfer (CT) excitations, but none are able to provide a simultaneously optimal description of all classes; CT excitations are not necessarily improved compared to those from conventional functionals. The study highlights the need for further development of Coulomb-attenuated functionals.

1. Introduction

There is growing interest in the use of Coulomb-attenuated exchange–correlation functionals in Kohn–Sham density functional theory (DFT).^{1,2} The key to this approach is the separation of the exchange into long- and short-range components through a partitioning of the $1/r_{12}$ operator. Of particular relevance to the present study is the work of Hirao^{3–9} and co-workers, who used a partitioning of the form

$$\frac{1}{r_{12}} \equiv \frac{\text{erf}(\mu r_{12})}{r_{12}} + \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} \quad (1)$$

where μ is a parameter of dimension L^{-1} . The first component gives the long-range exchange, which they evaluated using a modified exact orbital expression. The second component gives the short-range exchange, which they evaluated using a modified generalised gradient approximation (GGA). See ref. 10–16 for related work. Recently, Yanai *et al.*¹⁷ proposed the more general partitioning

$$\frac{1}{r_{12}} \equiv \frac{[\alpha + \beta \text{erf}(\mu r_{12})]}{r_{12}} + \frac{1 - [\alpha + \beta \text{erf}(\mu r_{12})]}{r_{12}} \quad (2)$$

where α and β are dimensionless parameters satisfying $0 \leq \alpha + \beta \leq 1$, $0 \leq \alpha \leq 1$, and $0 \leq \beta \leq 1$. This allows an amount α of exact orbital exchange to remain as $r_{12} \rightarrow 0$, and an amount $(\alpha + \beta)$ to remain as $r_{12} \rightarrow \infty$; the partitioning in eqn (1) corresponds to $\alpha = 0.0$ and $\beta = 1.0$. For the partitioning in

eqn (2), the long-range exchange energy E_X^{LR} is given by

$$E_X^{\text{LR}} = \alpha E_X^0 - \frac{\beta}{2} \sum_{\sigma} \sum_{ij} \int \int \psi_{i\sigma}(\mathbf{r}_1) \psi_{j\sigma}(\mathbf{r}_1) \times \frac{\text{erf}(\mu r_{12})}{r_{12}} \psi_{i\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (3)$$

where E_X^0 is the exact orbital exchange energy. The short-range exchange energy E_X^{SR} is given by

$$E_X^{\text{SR}} = -\frac{1}{2} \sum_{\sigma} \int \rho_{\sigma}^{4/3} K_{\sigma}^{\text{GGA}} \left\{ (1 - \alpha) - \beta \left(\frac{8}{3} a_{\sigma} \left[\sqrt{\pi} \text{erf} \left(\frac{1}{2a_{\sigma}} \right) + 2a_{\sigma}(b_{\sigma} - c_{\sigma}) \right] \right) \right\} d\mathbf{r} \quad (4)$$

where K_{σ}^{GGA} defines the chosen GGA exchange functional

$$E_X^{\text{GGA}} = -\frac{1}{2} \sum_{\sigma} \int \rho_{\sigma}^{4/3} K_{\sigma}^{\text{GGA}} d\mathbf{r} \quad (5)$$

and a_{σ} , b_{σ} and c_{σ} are defined in ref. 17. Using this method, Yanai *et al.* proposed the CAM-B3LYP functional

$$E_{\text{XC}}^{\text{CAM-B3LYP}} = E_X^{\text{LR}} + E_X^{\text{SR}}[\text{Becke88}] + E_C^{\text{B3LYP}} \quad (6)$$

which uses the Becke88 exchange functional¹⁸ in the evaluation of the short-range exchange energy. The correlation component is the B3LYP¹⁹ correlation functional

$$E_C^{\text{B3LYP}} = 0.81 E_C^{\text{LYP}} + 0.19 E_C^{\text{VWN}} \quad (7)$$

where E_C^{LYP} and E_C^{VWN} are the Lee–Yang–Parr (LYP)²⁰ and Vosko–Wilk–Nusair (VWN)²¹ correlation functionals, respectively. Using $\mu/a_0^{-1} = 0.33$, as previously recommended by Tawada *et al.*,⁵ they determined optimal values of α and β through a fit to the atomisation energies of (essentially) the G2-1²² set of molecules, obtaining $\alpha = 0.19$ and $\beta = 0.46$. The

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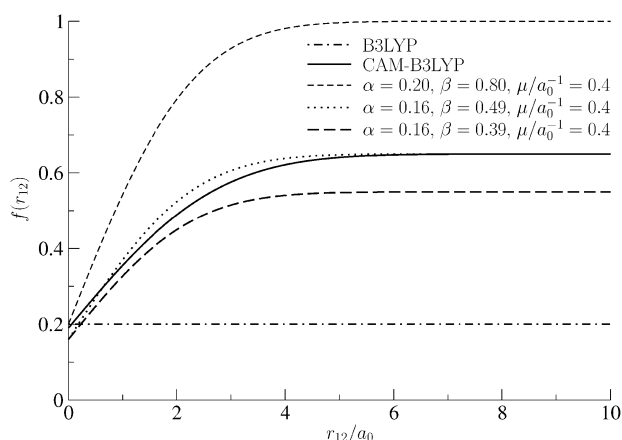


Fig. 1 Plots of $f(r_{12}) = \alpha + \beta \text{erf}(\mu r_{12})$ (exact orbital exchange contribution) for Coulomb-attenuated functionals. B3LYP corresponds to $\alpha = 0.2$, $\beta = 0.0$.

partitioning is illustrated in Fig. 1. This completely defines CAM-B3LYP.¹⁷

The CAM-B3LYP functional has been shown to provide promising results for electronic excitation energies, particularly those of Rydberg^{23,24} and charge-transfer (CT) character,^{17,24,25} two- and three-photon absorptions,^{26–29} optical rotation,³⁰ and electric field-induced second harmonic generation.³¹ This is to be expected, given the improved long-range characteristics of this functional. However, we recently demonstrated²⁴ that despite using a value of $\alpha = 0.19$ —thereby imposing conventional hybrid functional characteristics for small valued r_{12} —there is still room for improvement in other properties such as atomisation energies, ionisation potentials, and vibrational frequencies.

The aim of the present study is to provide a thorough analysis of the dependence of functional quality on the parameters in eqn (2), in order to establish the limits of what can be achieved. In particular, Yanai *et al.* did not consider the dependence on the parameter μ , which governs how rapidly the large r_{12} limit is attained; larger values result in faster attainment. Furthermore, the CAM-B3LYP parameters sum to $\alpha + \beta = 0.65$, and so the functional does not satisfy the exact long-range exchange condition

$$\alpha + \beta = 1 \quad (8)$$

the importance of which has been highlighted.^{24,31} We shall explicitly investigate the influence of both these factors on functional quality. We commence in section 2 by quantifying the influence of α , β , and μ on atomisation energies when eqn (8) is satisfied. We consider atomisation energies because Yanai *et al.* used these quantities to optimise the CAM-B3LYP parameters α and β ; this is a common procedure in semi-empirical functional development. An optimal functional is identified and its performance is assessed for a range of chemical quantities. The effect of reducing $\alpha + \beta$ is then investigated. We complete the study by considering vertical electronic excitation energies in more detail, investigating the influence of the parameters on valence, Rydberg, and CT excitations; deficiencies are highlighted. Conclusions are presented in section 3.

2. Results and discussion

2.1. Computational details

In our previous study,²⁴ we used the implementation of Coulomb-attenuated functionals in a development version of the DALTON program;³² a restricted formalism was used for both closed- and open-shell systems. In the present study, we continue to use DALTON for the restricted closed-shell calculations, but instead use a more theoretically rigorous³³ unrestricted formalism for open-shell systems, as implemented in a development version of the CADPAC program.³⁴ We have confirmed that closed-shell total energies from the two programs agree to within negligible numerical integration grid error.

2.2. Functional form

We continue to use the CAM-B3LYP exchange form, *i.e.* we use the Becke88 exchange functional in the evaluation of the short-range exchange energy. As highlighted in ref. 24, even if α is set to 0.2, the CAM-B3LYP functional does not reduce to B3LYP for the case of zero attenuation ($\beta = 0$), due to differing pre-factors of the exchange gradient correction. It follows that the use of the B3LYP correlation functional of eqn (7) has little justification and—as was noted by Yanai *et al.*¹⁷—we find that a fraction of VWN correlation reduces atomisation energy quality. We therefore replace the B3LYP correlation with LYP correlation. All new functionals in the present study take the form

$$E_{\text{XC}} = E_{\text{X}}^{\text{LR}} + E_{\text{X}}^{\text{SR}}[\text{Becke88}] + E_{\text{C}}^{\text{LYP}} \quad (9)$$

2.3. Dependence on α , β , μ

We commence by considering the influence of the three parameters on the atomisation energies of a small, representative subset of the G2 molecules.^{22,35} Specifically, we consider C_2H_2 , C_2H_4 , CH_3NH_2 , CH_3OH , CH_4 , CO , CO_2 , H_2O , H_2O_2 , LiH , N_2 , N_2O , NH_3 , and NO_2 at MP2/6-31G* geometries using the 6-311+(3df,2p) basis set. Fig. 2(a) presents a plot of the mean absolute error for a range of α and μ values, with $0 \leq \alpha \leq 0.4$, in intervals of 0.04, and $0 \leq \mu/a_0^{-1} \leq 1$, in intervals of 0.1. In all cases, we constrain $\beta = 1 - \alpha$ in order to satisfy eqn (8).

The figure highlights a strong dependence on the choice of μ . The minimum along the $\alpha = 0$ path occurs near $\mu/a_0^{-1} = 0.5$, where the error is approximately 4.8 kcal mol⁻¹. This is indicative of the accuracy that can be achieved for these molecules with a connection of the form of eqn (1). Using the recommended value of $\mu/a_0^{-1} = 0.33$ increases this error by more than a factor of three. Our observations are consistent with those of Gerber and Ángyán,¹⁶ who considered the μ -dependence for the special case of $\alpha = 0.0$ and $\beta = 1.0$, using the local density approximation in the short-range exchange. The introduction of a non-zero α has the desired effect of reducing the atomisation energy error. Fig. 2(a) exhibits three distinct minima; the two combinations $\alpha = 0.2$, $\beta = 0.8$, $\mu/a_0^{-1} = 0.4$ and $\alpha = 0.28$, $\beta = 0.72$, $\mu/a_0^{-1} = 0.3$ give

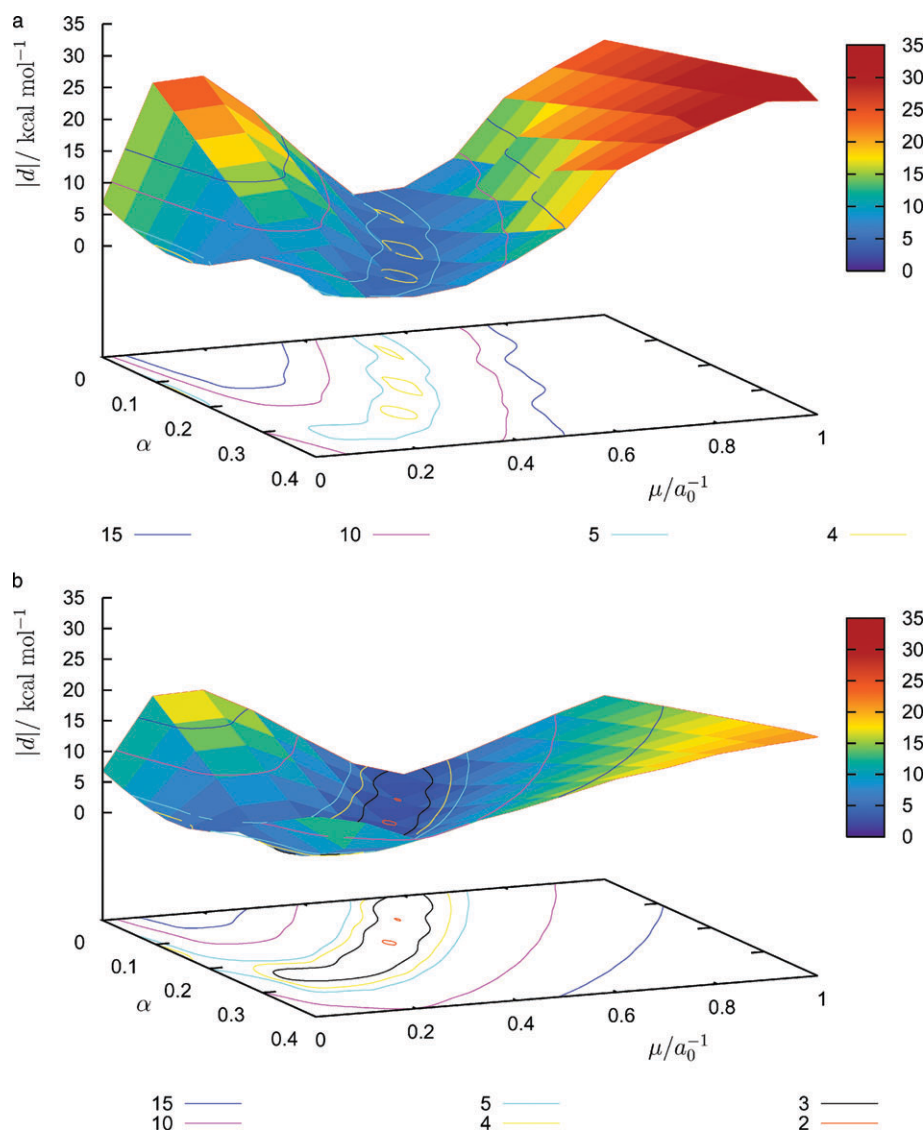


Fig. 2 Mean absolute error $|d|$ in atomisation energies of the representative subset, as a function of α and μ for (a) $\beta = 1.0 - \alpha$; and (b) $\beta = 0.65 - \alpha$.

the lowest errors, both at $3.4 \text{ kcal mol}^{-1}$. The corresponding error for CAM-B3LYP is $2.2 \text{ kcal mol}^{-1}$.

Next we consider the performance for a range of chemical properties. Specifically we examine 90 atomisation energies, 21 ionisation potentials, 23 classical reaction barriers, 37 vibrational wavenumbers, and 13 electronic polarisabilities. These correspond to the molecules considered previously in ref. 24, omitting $(\text{CH}_3)_3\text{C}$ from the atomisation energies and reaction 13 from the barriers, due to computational limitations. We also consider bond lengths in 66 molecules, which are a composite of the three bond length assessments of ref. 24 (diatomics, G2, and hydrogen bonds). For full details of geometries and basis sets, see this earlier work. We also consider the combined singlet vertical electronic excitation energies of CO, N_2 , C_2H_4 , and H_2CO , determined at near-experimental geometries using the Sadlej basis set,³⁶ augmented with additional diffuse functions as described in ref. 37. For atomisation energies, ionisation potentials, vibrational wavenumbers, and excitation energies, the reference values

are experimental. For barriers and bond lengths, a combination of theory and experiment is used. Polarisabilities are from high-level *ab initio* calculations. See ref. 24 for full details.

Table 1 lists mean and mean absolute errors, relative to reference values. The first two columns present errors for the B3LYP and CAM-B3LYP functionals, respectively. For atomisation energies, CAM-B3LYP errors are marginally smaller than those of B3LYP, which is fully consistent with the original findings of Yanai *et al.*¹⁷ We note that a different conclusion was reached in ref. 24, where it was found that CAM-B3LYP was notably less accurate than B3LYP. These conflicting observations reflect the different formalisms used for open-shell species—unrestricted in the present study and restricted in ref. 24. The ionisation potential and reaction barrier errors in Table 1 are also different to those of ref. 24, for the same reason, but the difference is less pronounced. All other results in Table 1 relate to closed-shell species.

The third column in Table 1 presents errors for the $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$ functional, which provides the

Table 1 Mean error d and mean absolute error $|d|$, relative to reference values

	B3LYP	CAM-B3LYP	$\alpha = 0.2$ $\beta = 0.8$ $\mu/a_0^{-1} = 0.4$	$\alpha = 0.16$ $\beta = 0.49$ $\mu/a_0^{-1} = 0.4$	$\alpha = 0.16$ $\beta = 0.39$ $\mu/a_0^{-1} = 0.4$
Atomisation energies					
$d/\text{kcal mol}^{-1}$	−2.9	1.5	5.5	1.5	−0.3
$ d /\text{kcal mol}^{-1}$	3.6	3.3	7.5	3.2	2.4
Ionisation potentials					
d/eV	0.00	0.11	0.10	0.04	0.02
$ d /\text{eV}$	0.17	0.17	0.19	0.17	0.18
Classical barriers					
$d/\text{kcal mol}^{-1}$	−3.7	−2.6	−1.3	−2.6	−2.8
$ d /\text{kcal mol}^{-1}$	3.8	2.7	1.7	2.7	2.9
Bond lengths					
$d/\text{\AA}$	0.009	−0.009	−0.027	−0.012	−0.007
$ d /\text{\AA}$	0.015	0.016	0.027	0.017	0.015
Vib. wavenumbers					
d/cm^{-1}	6	34	66	39	31
$ d /\text{cm}^{-1}$	22	37	66	41	34
Excitation energies					
d/eV	−0.82	−0.40	0.07	−0.34	−0.45
$ d /\text{eV}$	0.84	0.43	0.24	0.37	0.48
Polarisabilities					
$d/\text{a.u.}$	0.36	0.15	−0.18	0.12	0.20
$ d /\text{a.u.}$	0.45	0.30	0.31	0.28	0.33

joint-lowest error in Fig. 2(a); the corresponding partitioning is illustrated in Fig. 1. Overall, the performance of this functional is disappointing. Atomisation energies, bond lengths, and vibrational wavenumbers are significantly less accurate than those of CAM-B3LYP. Ionisation potentials and polarisabilities also degrade slightly. The only properties predicted more accurately than with CAM-B3LYP are the excitation energies and reaction barriers; this is to be expected—the former property is sensitive to long-range behaviour whilst the latter is known to improve when the amount of exact orbital exchange is increased.³⁸ We have confirmed (results not presented) that this functional also accurately describes the asymptotic R -dependence of the intermolecular CT excitation in the $\text{C}_2\text{H}_4 \cdots \text{C}_2\text{F}_4$ model system of Dreuw *et al.*³⁹ since this is governed entirely by the value of $\alpha + \beta$; see ref. 24 for illustration. We do not explicitly present results from the other minimum functional of Fig. 2(a) since atomisation energy errors for this more extensive assessment are notably larger than those from the $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$ functional.

The reasonable performance of CAM-B3LYP for properties such as atomisation energies and bond lengths is therefore closely related to the violation of eqn (8). To illustrate this, Fig. 2(b) presents the mean absolute error in atomisation energies of the representative subset, as a function of α and μ , for the case $\beta = 0.65 - \alpha$, as in CAM-B3LYP. The plot exhibits a similar shape to that of Fig. 2(a), but the errors are smaller. The minimum error of $1.8 \text{ kcal mol}^{-1}$ (now below that of CAM-B3LYP) is obtained with the functional $\alpha = 0.16$, $\beta = 0.49$, and $\mu/a_0^{-1} = 0.4$. As demonstrated in Table 1, the majority of errors from this functional reduce compared to those of $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$. The only quantities that degrade are the excitation energies and reaction barriers; the asymptotic intermolecular CT excitation of Dreuw *et al.*³⁹ is also less accurate. Overall the performance of the functional is close to that of CAM-B3LYP. Fig. 1

highlights the similarity between this partitioning and that of CAM-B3LYP.

Given the improvement obtained upon relaxation of the condition in eqn (8), it is pertinent to ask what combination of parameters provides the lowest atomisation energy error. Guided by our observations in Fig. 2, we have varied the parameters over the relevant range of parameter space and find that our lowest error for the representative subset, $1.6 \text{ kcal mol}^{-1}$, is obtained using $\alpha = 0.16$, $\beta = 0.39$, and $\mu/a_0^{-1} = 0.4$; see Fig. 1. Table 1 demonstrates that this functional has a similar overall performance to CAM-B3LYP, but notably improved atomisation energies.

The message from this analysis is clear and intuitive. A non-zero value of α does reduce atomisation energy errors compared to $\alpha = 0$; this was the original impetus for considering the attenuation function (2) in ref. 17. However, the results are very sensitive to the precise choice of the parameter μ . Satisfaction of eqn (8) is detrimental for properties such as atomisation energies and bond lengths, but is beneficial for the excitation energy and reaction barrier assessments. Reducing the value of $\alpha + \beta$ returns CAM-B3LYP quality. For this combination of GGA and attenuation function, it is not possible to simultaneously achieve optimal accuracy for all these quantities.

2.4. Electronic excitation energies

The real potential of Coulomb-attenuated functionals lies in their ability to describe long-range properties accurately. For the remainder of this study, we therefore concentrate on vertical excitation energies, which are amongst the most important properties calculated within DFT. We pay particular attention to the $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$ functional, since it is theoretically appealing and it provides the highest quality excitations in Table 1. The excitation energy errors tabulated in Table 1 are combined errors for CO, N_2 , H_2CO ,

Table 2 Vertical excitation energy errors for CO, N₂, H₂CO, and C₂H₄, and combined errors for valence and Rydberg excitations, in eV

	B3LYP	CAM-B3LYP	$\alpha = 0.2$ $\beta = 0.8$ $\mu/a_0^{-1} = 0.4$
CO excitations			
d/eV	−0.77	−0.37	0.08
$ d /eV$	0.77	0.37	0.16
N ₂ excitations			
d/eV	−0.86	−0.53	−0.13
$ d /eV$	0.86	0.54	0.30
H ₂ CO excitations			
d/eV	−0.66	−0.24	0.28
$ d /eV$	0.76	0.37	0.28
C ₂ H ₄ excitations			
d/eV	−0.94	−0.40	0.12
$ d /eV$	0.94	0.40	0.22
Combined valence			
d/eV	−0.23	−0.20	−0.15
$ d /eV$	0.29	0.28	0.33
Combined Rydberg			
d/eV	−1.14	−0.51	0.18
$ d /eV$	1.14	0.51	0.19
Combined total			
d/eV	−0.82	−0.40	0.07
$ d /eV$	0.84	0.43	0.24

and C₂H₄. To further analyse the results, Table 2 lists errors for the individual molecules. For all four systems, the errors reduce uniformly from B3LYP to CAM-B3LYP to the $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$ functional. The table also lists combined errors, for these four molecules, in valence and Rydberg excitations. The former are relatively insensitive to functional, whereas the latter improve significantly, reflecting the long-range nature of Rydberg excitations. The increased accuracy associated with Coulomb-attenuation is very encouraging.

Another class of excitation that is of considerable interest is charge-transfer. Many studies have highlighted significant underestimation of CT excitation energies with conventional DFT functionals; for examples and discussion see ref. 39–45. For asymptotic intermolecular excitations, this underestimation can be understood⁴² in terms of the integer discontinuity in the exchange–correlation potential. We now consider two molecules that exhibit CT excitations. The first is a model dipeptide, where we have previously highlighted⁴⁰ a significant CT error for conventional functionals. Table 3 lists vertical excitation energies determined using B3LYP, CAM-B3LYP, and the $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$ functional,

comparing with the complete-active-space second-order perturbation theory (CASPT2) values from ref. 40. CT denotes charge-transfer; W and NV denote more localised valence excitations. Following ref. 17, we determine excitation energies with the TZ2P⁴⁶ basis set at the 6-31G* BP86^{18,47} geometry. One of the key observations of Yanai *et al.*¹⁷ was the improvement relative to B3LYP in the CT excitations of this system, when CAM-B3LYP was employed. As shown in Table 3, B3LYP significantly underestimates the two CT excitations. These excitation energies increase with CAM-B3LYP, significantly improving agreement with CASPT2. However, it is worth noting that the NV excitations, already much higher than CASPT2 with B3LYP, further increase with CAM-B3LYP. The W excitations are comparable with both functionals. In moving to the $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$ functional, there is a further uniform increase in all the excitation energies, leading to a significant degradation, relative to CASPT2, for the NV and CT excitations. The ¹A'' CT excitation is significantly overestimated. The W excitations are described to a similar accuracy as in the small molecules.

Next, we consider 4-(*N,N*-dimethylamino)benzonitrile (DMABN), which has been the subject of many theoretical studies due to its dual fluorescence.⁴⁸ Table 4 lists vertical excitation energies determined using B3LYP, CAM-B3LYP, and the $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$ functional, comparing with the CASPT2 values of Serrano-Andrés *et al.*,⁵⁰ the similarity transformed equation-of-motion coupled-cluster singles and doubles (STEOM-CCSD) values of Parusel *et al.*,⁵¹ and the DFT single excitation configuration interaction (DFT/SCI) values of Bulliard *et al.*⁴⁹ The CASPT2, STEOM-CCSD, and DFT/SCI excitations were determined at planar geometries and so for consistency our DFT calculations also use a planar conformation. Following Serrano-Andrés *et al.*,⁵⁰ we use the same complete-active-space self-consistent-field (CASSCF) structural parameters, with the amino wagging angle adjusted to 0.0°. We also use the same ANO basis.⁵² We have confirmed that the results are relatively insensitive to changes in the basis set and planar structure. For example, calculations with the more extensive 6-311+G(2d,p) basis set used by Jamorski *et al.*⁵³ reduce the excitation energies by less than one-tenth of an electronvolt; replacing the CASSCF geometry with an optimised planar B3LYP geometry gives a similar change. Table 4 also lists experimental excitation energies⁴⁹ from gas phase electron energy loss spectroscopy. The experimental structure is non-planar, with an out of plane amino wagging angle of

Table 3 Vertical excitation energies of the model dipeptide of ref. 40, in eV

			CASPT2 ^a	B3LYP	CAM-B3LYP	$\alpha = 0.2$ $\beta = 0.8$ $\mu/a_0^{-1} = 0.4$
¹ A''	$n_1 \rightarrow \pi_2^*$	CT	7.92	6.28	7.88	9.72
¹ A'	$\pi_1 \rightarrow \pi_2^*$	CT	6.92	6.07	6.94	7.56
¹ A'	$\pi_1 \rightarrow \pi_1^*$	NV	6.32	7.06	7.32	7.61
¹ A'	$\pi_2 \rightarrow \pi_2^*$	NV	6.29	7.11	7.53	8.36
¹ A''	$n_1 \rightarrow \pi_1^*$	W	5.61	5.54	5.65	5.81
¹ A''	$n_2 \rightarrow \pi_2^*$	W	5.82	5.74	5.88	6.04

^a Ref. 40.

Table 4 Vertical excitation energies of DMABN, in eV

		Expt ^a	CASPT2 ^b	STEOM-CCSD ^c	DFT/SCI ^a	B3LYP	CAM-B3LYP	$\alpha = 0.2$ $\beta = 0.8$ $\mu/a_0^{-1} = 0.4$
¹ B	LE	4.25	4.05	4.15	4.09	4.37	4.66	4.93
¹ A	CT	4.56	4.41	4.73	4.55	4.69	4.96	5.17

^a Ref. 49. ^b Ref. 50. ^c Ref. 51.

12–15°. ^{54,55} However, the calculated excitations are only marginally affected by variation in this angle⁵⁶ and we have confirmed this in the present study. We consider two singlet excited states—a locally excited (LE) state [HOMO → LUMO + 1] and a CT state [HOMO → LUMO].

The CASPT2, STEOM-CCSD, DFT/SCI, and experimental excitations lie in the range of 4.05–4.25 eV for the LE state and 4.41–4.73 for the CT state. The B3LYP LE excitation (4.37 eV) is slightly higher than these reference values, whilst the CT excitation (4.69 eV) is at the upper end of the range. As with the dipeptide, both excitation energies increase notably in moving to CAM-B3LYP and the $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$ functional, leading to a degradation, rather than improvement, with Coulomb-attenuation for both the LE and CT excitations.

The dipeptide and DMABN results therefore contrast those of the small molecules in Table 2. Insight into this observation is provided by consideration of the μ -dependence of excitation energies from the $\alpha = 0.2$, $\beta = 0.8$ functionals. We have determined excitations for a range of μ values and observe that $\mu/a_0^{-1} = 0.4$ (the value used in Tables 1–4) simultaneously provides optimal excitations for each of CO, N₂, C₂H₄, and H₂CO. By contrast, a value of $\mu/a_0^{-1} = 0.2$ is required to provide optimal excitations for the dipeptide (errors equivalent to those of CAM-B3LYP) and a value of $\mu/a_0^{-1} = 0.0$ is necessary for DMABN. Such an analysis also helps answer the question of whether a non-zero value of α is actually beneficial for excitation energies—recall that Yanai *et al.* originally introduced this parameter to improve atomisation energies. We have examined excitation energies from the functional $\alpha = 0.0$, $\beta = 1.0$ as a function of μ and observe that, as above, a much smaller μ value is required for the dipeptide and DMABN. In contrast to the above, however, the optimal value of μ varies more between CO, N₂, H₂CO, and C₂H₄. A non-zero value does therefore appear beneficial for excitation energies, as well as atomisation energies.

In section 2.3, we highlighted the performance of the $\alpha = 0.16$, $\beta = 0.39$, and $\mu/a_0^{-1} = 0.4$ functional. We have also applied this functional to the dipeptide and DMABN and observe that the excitation energies are of a similar quality to those of CAM-B3LYP, demonstrating that comparable excitation energies can be obtained from rather different α , β , and μ parameterisations.

3. Conclusions

We have presented a detailed investigation into the influence of the parameters α , β , and μ in eqn (2) on the quality of functionals defined by eqn (9). The approach is pragmatic

but—given the current interest in such functionals^{24–31}—necessary. Our conclusions are as follows:

1. Atomisation energies are very sensitive to the choice of μ . The variation of this quantity has not previously been considered for the attenuation of eqn (2); see ref. 16 for a special case. The use of a non-zero α is beneficial.

2. Enforcing the condition $\alpha + \beta = 1$ is detrimental for properties such as atomisation energies and bond lengths. The acceptable performance of CAM-B3LYP for these properties is closely related to the violation of this condition by reducing to $\alpha + \beta = 0.65$. Enforcing the exact condition does, however, lead to notably improved small molecule excitations (see point 3 below) and classical reaction barriers; the latter is consistent with the well-known observation that increasing the amount of exact orbital exchange is beneficial for the reactions considered.³⁸

3. None of the functionals investigated provides a simultaneously optimal description of all the different classes of vertical electronic excitation energy. For example, using the theoretically appealing $\alpha = 0.2$, $\beta = 0.8$, and $\mu/a_0^{-1} = 0.4$ functional gives very high quality excitations in CO, N₂, C₂H₄, and H₂CO, which can be traced primarily to improved Rydberg excitations. This functional also correctly reproduces the asymptotic intermolecular CT excitation behaviour in the model system of Dreuw *et al.*³⁹ However, the same parameters provide a poor description of CT dipeptide excitations, compared to CASPT2. Reducing μ improves the dipeptide to the detriment of the small molecules. None of the functionals considered simultaneously describe the NV and CT excitations accurately in the dipeptide. For the LE and CT excitations in DMABN, the non-attenuated B3LYP functional provides results closest to CASPT2, STEOM-CCSD, DFT/SCI, and experiment; Coulomb-attenuation degrades the quality.

4. Existing Coulomb-attenuated functionals therefore do not provide a rigorous solution to the well-known problem of CT excitations in DFT. Attenuation does significantly affect such excitations, which is unsurprising given their long-range nature. In cases where conventional functionals underestimate the excitation (as is commonly observed, for example in the dipeptide and in ref. 25), attenuation can provide a significant improvement. However, in other cases (*e.g.* DMABN) conventional functionals provide a surprisingly good quality description and attenuation can then lead to a significant overestimation of the excitation energy. In both cases, the results will be sensitive to the choice of α , β , and μ .

The inability to provide a simultaneously optimal description of the different classes of excitation, together with other properties such as atomisation energies and bond lengths, highlights the need for further investigation. We are presently

investigating alternative GGA forms and attenuation functions.

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