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REGULAR ARTICLE

Global hybrid exchange energy functional with correct asymptotic behavior of the corresponding potential

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Abstract A non-empirical global hybrid exchange–correlation energy functional which leads to an exchange potential with correct asymptotic behavior is presented. The exchange functional combines one-fourth of exact exchange with three-fourths of the correct asymptotic potential (CAP) generalized gradient approximation functional. It is combined with the Perdew–Burke–Ernzerhof correlation energy with a slightly modified parameterization so as to cancel the gradient terms of CAP exchange with that of correlation, in the limit of slowly varying density. The resulting global hybrid functional, called CAP0, gives heats of formation, ionization potentials, electron affinities, proton affinities, binding energies of weakly interacting systems, barrier heights for hydrogen and non-hydrogen transfer reactions, bond distances, and harmonic frequencies on standard test sets that are competitive with results from other long-range-corrected, Coulomb-attenuated, or global hybrid functionals. In fact, they are generally superior to or competitive with CAM-PBE0 and, except for heats of formation, with CAM-B3LYP as well. Advantageously, the Rydberg excitation energies from CAP0 are superior to those of other global hybrids and of the long-range-corrected hybrids. They are similar to those from CAM-B3LYP and modestly inferior to the CAM-PBE0 errors. For the valence excitations, we did not find substantial differences for all the hybrid functionals considered, while the oscillator strengths from CAP0 are better to those of other global hybrids and comparable to those obtained with long-range-corrected and Coulomb-attenuated hybrids.

Keywords Density functional theory · Kohn–Sham method · Hybrid exchange–correlation energy functional · Exchange potential asymptotic behavior · Excited states · Time-dependent density functional theory

1 Introduction

The conceptual and practical advantages of density functional theory (DFT) [1], especially in its Kohn–Sham (KS) [2, 3] form, are so well known that rehearsal of those merits is unneeded. The result is wide-spread use to investigate diverse systems [3–13]. Within KS, the primary ingredient which theory must supply is an approximation to the exchange–correlation (XC) energy functional, $E_{\mathrm{XC}}[\rho]$ of useful accuracy and generality, where $\rho(\mathbf{r})$ is the electron density. The distinguishing feature of the KS equations is the XC potential,

$$v_{\mathrm{XC}}[\rho](\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[\rho]}{\delta \rho(\mathbf{r})}, \tag{1}$$

which is a consequence of the variational property of the Hohenberg–Kohn–Levy–Lieb functional. Immediately, it is evident that the accuracy of KS calculations depends

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both upon the quality of the XC energy functional and upon the quality of its functional derivative. This is particularly the case for expressions in which the KS eigenvalues and orbitals are used explicitly, as for example, in computing a response property.

Time-dependent density functional theory (TDDFT) within the KS formulation [1, 2, 14–24] also has been extensively applied to the study of dynamical phenomena. At least formally, one defines an action XC functional, $A_{\rm XC}[\rho]$, that plays a role similar to that of the XC energy functional in the time-independent case. Most commonly the adiabatic approximation is made. In it, the explicitly time-dependent XC potential is approximated by the time-independent XC potential evaluated with the time-dependent density. Introducing the notation ρ_t to denote ρ evaluated at the time t [24],

$$v_{\rm XC}[\rho](\mathbf{r},t) = \frac{\delta A_{\rm XC}[\rho]}{\delta\rho(\mathbf{r},t)} \cong \frac{\delta E_{\rm XC}[\rho_t]}{\delta\rho_t(\mathbf{r})} = v_{\rm XC}[\rho_t](\mathbf{r}). \tag{2}$$

For the calculation of excitation energies, it is common to use linear response theory [24–27] with TDDFT (though there are exceptions [28–33]). The outcome is an eigenvalue equation for which the eigenvalues are the square of the excitation energies and the eigenvectors contain information about the molecular orbitals involved in each excitation and hence can be used to determine the oscillator strengths. Within this approach the so-called XC kernel is determined from the adiabatic XC potential [24],

$$\begin{aligned} f_{\rm XC}[\rho](\mathbf{r},t,\mathbf{r}',t') &= \frac{\delta v_{\rm XC}[\rho](\mathbf{r},t)}{\delta\rho(\mathbf{r}',t')} \\ &\cong \delta(t-t')\frac{\delta v_{\rm XC}[\rho_t](\mathbf{r})}{\delta\rho_t(\mathbf{r}')} \\ &= \delta(t-t')\frac{\delta^2 E_{XC}[\rho_t]}{\delta\rho_t(\mathbf{r}')\delta\rho_t(\mathbf{r})}. \end{aligned} \tag{3}$$

From Eqs. (2) and (3), one can see that the accuracy of excitation energies in adiabatic TDKS calculations is determined by the quality of the first and second functional derivatives of the XC energy functional.

Thus, to build an approximate XC energy functional that could give a satisfactory description of total energies, energy differences (e.g., atomization energies or activation barriers), and response properties (e.g., static and dynamic polarizabilities and hyperpolarizabilities) or excitation energies, one needs to consider both the exact properties of $E_{\rm XC}[\rho]$, and the exact properties of its first and second functional derivatives. The first functional derivative, which is the XC potential, has a direct effect upon the occupied and unoccupied KS orbitals and eigenvalues. For the total energies and energy differences, the correct description of the orbitals in the physically important regions is crucial, while the asymptotic behavior (far from the nuclei) is of little consequence. However, for response properties and excitation energies the asymptotic behavior of the orbitals becomes crucial. This situation implies that the XC potential needs to be correctly described in both the region important for binding and in the asymptotic region [34–36]. In the latter, for a neutral system, the exact exchange (X) potential adopts the form

$$v_{\rm XC}[\rho](\mathbf{r}) = \frac{\delta E_{\rm XC}[\rho]}{\delta\rho(\mathbf{r})} \longrightarrow [r\to\infty] - \frac{1}{r}. \tag{4}$$

This behavior has important consequences in the occupied and unoccupied KS orbitals and eigenvalues, particularly the highest occupied and lowest unoccupied molecular orbital (HOMO, LUMO, respectively). This is relevant in time-dependent systems because the electrons can explore regions far from the nuclei. Another significant feature that is closely related with the behavior of the KS orbitals and eigenvalues is the discontinuity of the XC potential with respect to electron number N [37–41]. Incorporation of this behavior in approximate XC functional is a difficult task that we do not undertake here.

Current expressions for the XC functional, like the local density approximations (LDA) [42, 43] or generalized gradient approximations (GGA) such as PBE [44] with its different parameterizations [45–48], RPBE [49], BLYP [50, 51], OLYP [51, 52], VMT [53], VT{8,4} [54], PBE-LS [55], SOGGA11 [56], lsRPBE [57], and others, all yield an X potential that decays exponentially with distance from the nuclei. This asymptotic behavior limits the applicability of these functionals for the calculation of excited states. In particular, Casida [58] has shown that the LDA does not give a good description of excitation energies for high-lying excited states. Those excitation energies tend to be severely underestimated with respect to experimental values, a failure traceable to the incorrect asymptotic behavior of the LDA X potential. The GGA results are similar for the same reason. The underestimation can be alleviated by introducing corrections directly to the X potential. Examples include GGA-type potentials asymptotically corrected [59], model potentials with both correct asymptotic behavior and derivative discontinuity [37–39, 60], exact local potentials [61, 62], and non-local potentials with the correct asymptotic behavior [63–70]. But because these all are direct modifications of the X potential, the corresponding X functional $E_{\rm X}[\rho]$ in general is unknown. Though there have been efforts [71–75] to establish a procedure to obtain the X functional (or correlation functional, C) that corresponds to a model potential, the resulting total energies must be interpreted with caution, because the reconstructed density functional is unique only if its KS potential is a functional derivative. Conversely, it has been shown [76] that the

quality of calculated excitation energies is severely limited in the case that $v_{XC}[\rho](\mathbf{r})$ is not the functional derivative of $E_{XC}[\rho]$.

There have been efforts, beyond the level of the GGA, to construct an X functional with a functional derivative that describes the binding region well and that has correct asymptotic behavior. Some incorporate the Laplacian of the density [77–79], others the Fermi-Amaldi term [80]. In contrast, we recently proposed [81] a non-empirical GGA X functional, CAP, whose functional derivative leads to the correct asymptotic potential. In combination with the PBE correlation energy, CAP leads to a good description of energy differences, when compared to other GGA functionals and gives improved description of response properties like static and dynamic polarizabilities and hyperpolarizabilities through the use of time-dependent auxiliary density perturbation theory (TDADPT) [82–86].

However, it is known that global, long-range-corrected and Coulomb-attenuated hybrid exchange energy functionals, which combine exact X with a GGA X, provide, in general, better descriptions of energy differences and excitation energies than GGA X functionals alone, although the computational effort is increased. Thus, the object of the present work is to study the non-empirical global hybrid built from CAP for the GGA component, combined with one-fourth of exact exchange [87], to assess the capability to predict the properties just mentioned.

2 Global hybrid exchange energy functional with correct asymptotic potential

Global hybrid functionals arose via analysis of the adiabatic connection between the non-interacting system and the fully interacting real system [88–92]. The basic concept is that XC energy functionals could be composed of a fraction of exact X, $E_X^{exact}[\rho]$, combined with GGA XC. Originally, Becke [93] suggested a three-parameter formula involving the B88 X functional and the Perdew–Wang C functional [94, 95] correlation. That proposal gave rise to the well-known empirical XC energy functional B3LYP [96, 97], in which the PW91 C energy functional was replaced by the LYP C energy functional. Later, Becke [98] produced a simplified one-parameter expression

$$E_{XC}^{hyb}[\rho] = E_{XC}^{GGA}[\rho] + a_0(E_X^{exact}[\rho] - E_X^{GGA}[\rho]) \tag{5}$$

Subsequently, Perdew et al. [87] used DF perturbation theory [99, 100] to rationalize a non-empirical value of $a_0 \approx 1/4$. When the GGA used in Eq. (5) is the PBE XC functional one is led to the also well-known, non-empirical, hybrid functional PBE0 [101–103], where the zero indicates that there are no adjustable parameters.

Both hybrids, B3LYP (empirical) and PBE0 (non-empirical), lead to a rather reasonable description of energy differences and excitation energies [104–107], among other properties. In general, it is found that global hybrids perform better, over a wide range of properties, than their GGA counterparts, indicating that the fraction of exact exchange included plays an important role. However, in both cases, the X potential determined from the functional derivative of the GGA X energy functional component of the hybrid does not lead to correct asymptotic behavior of the X potential. Moreover, the fraction of exact exchange, according to Eq. (5), leads asymptotically to $-a_0/r$, which underestimates the $-1/r$ behavior, because $a_0 < 1$. Thus one is motivated to construct a global hybrid with the correct asymptotic potential, i.e., one in which the GGA contribution yields an asymptotically correct potential. The CAP X functional fits that specification. Observe that, unless the optimized effective potential procedure is used [108], hybrid functionals do not give simple multiplicative potentials, and hence, it is customary to implement hybrids via the generalized Kohn–Sham procedure. We do so here.

Conventionally, a GGA X energy functional is written in terms of an enhancement factor with respect to local X, $F_X(s)$, as

$$E_X^{GGA}[\rho] = \int \rho(\mathbf{r})\left(e_X^{LDA}[\rho](\mathbf{r})\right)F_X(s)\mathrm{d}\mathbf{r} = \int e_X[\rho](\mathbf{r})\mathrm{d}\mathbf{r}, \tag{6}$$

where $e_X^{LDA}[\rho](\mathbf{r}) = A_X\rho(\mathbf{r})^{1/3}$, with $A_X = -3(3\pi^2)^{1/3}/4\pi$, and $s(\mathbf{r}) = |\nabla\rho(\mathbf{r})|/2k_F(\mathbf{r})\rho(\mathbf{r})$, is the reduced density gradient, with $k_F(\mathbf{r}) = (3\pi^2\rho(\mathbf{r}))^{1/3}$.

The CAP X energy enhancement factor is [81]

$$F_X^{CAP}(s) = 1 - \frac{\alpha}{A_X}\frac{s\ln(1+s)}{1+c\ln(1+s)}, \tag{7}$$

where α and c are determined from constraint satisfaction. That is, by requiring that

$$F_X(s) \longrightarrow [s \to \infty] - \frac{(3\pi^2)^{1/3}}{A_X}s, \tag{8}$$

one finds that the functional derivative of $E_X^{CAP}[\rho]$ gives an asymptotically correct X potential. This implies that $c = \alpha/(3\pi^2)^{1/3}$. On the other hand, since for small values of s one has that,

$$F_X(s) \longrightarrow [s \to 0]1 + \mu s^2 + \cdots, \tag{9}$$

where the constant μ may be fixed through several non-empirical procedures, one finds that $\alpha = -A_x\,\mu$. Thus, a given value of μ fixes α, which in turn fixes c. We have found that by using the value $\mu = 0.2195$ (as in the PBE

X functional [44]), CAP X combined with PBE C gives a rather good description of the heats of formation of the G3 test set [109]. We note that in PBE the value of μ, which is associated with the second-order term of the X gradient expansion [Eq. (9)], was fixed to cancel the second-order term of the C gradient expansion so as to recover the benefits of LSDA linear response. The C gradient is dependent on a parameter β. The cancelation implies that

$$\mu = \pi^2\beta/3. \tag{10}$$

The value of $\mu = 0.2195$ was obtained by using the value [110] $\beta_{\mathrm{PBE}} = 0.066725$. However, it has become common practice to use Eq. (10) instead to fix β from a given μ. Here we propose a new global hybrid XC energy functional based in Eq. (5), with $a_0 = 1/4$, where the GGA X functional is CAP [Eqs. (6), (7)], and the C functional is PBE C with $\beta = (3/4)\beta_{\mathrm{PBE}}$, in order to achieve second-order gradient cancelation. This new hybrid is named CAP0, because as in the case of PBE0 it has no adjustable parameters. We note that the CAP potential has somewhat unusual properties, including a pragmatically valuable but anomalous localization of the LUMO. Details are in Ref. [80]. The focus here is not on those properties but upon the extent to which CAP X yields a broadly accurate global hybrid functional.

A relevant aspect of the assessment of CAP0 is its performance compared with long-range-corrected or Coulomb-attenuated hybrid XC functionals [111–116]. In those, the two-electron operator $1/r_{12}$ is separated into short-range and long-range parts via the standard error function,

$$\frac{1}{r_{12}} = \frac{1-(a+b\,\mathrm{erf}(\eta r_{12}))}{r_{12}} + \frac{a+b\,\mathrm{erf}(\eta r_{12})}{r_{12}}, \tag{11}$$

where a, b and η are parameters, that must satisfy the relations $0 \le a+b \le 1$, $0 \le a \le 1$ and $0 \le b \le 1$. To obtain a functional with the correct asymptotic potential, the long-range part (the second term in the right hand side of Eq. (11) is associated with exact exchange, whereas the short-range effects are obtained with conventional-type XC functionals adapted to the range-separated interaction. For $a = 0$ and $b = 1$ this kind of functional is commonly called long-range-corrected (LC), while other combinations lead to the so-called Coulomb attenuating method (CAM) [117, 118].

3 Results and discussion

The performance of CAP0 is assessed on the basis of results for energy differences, bond distances, and excitation energies for molecules in standard data sets designed for each property. All calculations were done with a developmental version of the program NWChem-6.0 [119].

For various energy differences the properties studied for the dataset indicated in parenthesis were heats of formation (G3/99) [109, 120], ionization potentials (IP13/3) [121], electron affinities (EA13/3) [122], proton affinities (PA8) [120, 123–126], binding energies of weakly interacting systems (HB6/04 [127], CT7/04 [127], D16/04 [127], W17/05 [128], and PPS5/05 [128]), and barrier heights for forward and backward transition states of hydrogen and non-hydrogen transfer reactions (HTBH38/04 and NHTBH38/04 [128–131]). In the case of geometries, the properties were bond distances (T-96R [132, 133]) and harmonic frequencies (T-82F [132–135]). The detailed protocols used in all these cases can be found in Ref. [48].

We treated the new hybrid functional CAP0, the global hybrids PBE0, B3LYP, and M06-2X [136], the long-range-corrected hybrids LC-BLYP, LC-PBE, and the Coulomb-attenuated CAM-B3LYP and CAM-PBE0. All but PBE0 and CAP0 rely upon empirically adjusted parameters. The functional M06-2X provides a reference to the improvement achieved by the other functionals, since the 32 adjustable parameters in M06-2X were determined to minimize the deviations for several of the test sets considered here. The parameters of Eq. (11) are for LC-BLYP [137] $a = 0$, $b = 1.0$ and $\eta = 0.33$, for LC-PBE [118] $a = 0$, $b = 1.0$ and $\eta = 0.30$, for CAM-B3LYP [117] $a = 0.19$, $b = 0.46$ and $\eta = 0.33$, and finally, for CAM-PBE0 [118] $a = 0.25$, $b = 0.75$ and $\eta = 0.30$.

Table 1 displays the mean absolute deviation (MAD) for all these properties, for the specific datasets mentioned. One sees that for heats of formation PBE0 and B3LYP perform slightly better than CAP0, whereas CAM-B3LYP improves upon them, but LC-BLYP, LC-PBE, and CAM-PBE0 show very large errors. For ionization potentials, CAP0 has the lowest MAD. In the case of electron affinities all functionals give similar errors. For the proton affinities, the global hybrid functionals show similar results, while long-range-corrected and Coulomb-attenuated hybrid functionals lead to slightly worst results. For binding energies of weakly interacting systems CAP0 shows a relatively larger deviation from experiment than the other functionals. In the case of the barrier heights for forward and backward transition states of hydrogen transfer reactions, CAP0 improves upon all the other functionals. For the non-hydrogen transfer reaction barrier heights, CAM-B3LYP and CAM-PBE0 provide improvements over the other functionals. However, both CAP0 and the LC functionals provide a better description than B3LYP and PBE0. For bond distances CAP0, PBE0, and B3LYP lead to similar results, whereas the LC and CAM approximations tend to give larger deviations from the experimental values. In frequencies

Table 1 Mean absolute deviation (MAD) for several global, long-range-corrected (LC), and Coulomb-attenuated (CAM) hybrid functionals, for several properties

	Global				Long-range-corrected and Coulomb-attenuated			
	PBE0	B3LYP	M06-2X	CAP0	LC-BLYP	LC-PBE	CAM-B3LYP	CAM-PBE0
Heats of formation	5.72	5.69	2.52	7.90	31.78	47.89	3.16	25.18
Ionization potentials	3.44	4.76	3.01	3.10	4.98	6.14	5.04	5.82
Electron affinities	2.91	3.26	2.84	3.48	3.39	3.44	2.86	2.84
Proton affinities	1.16	1.31	2.05	1.56	5.57	4.06	2.47	3.00
Binding energies of weakly interacting systems	1.05	1.17	0.62	1.90	1.67	1.61	0.96	1.21
Reaction barrier heights								
Hydrogen transfer forward	4.05	4.29	1.04	2.58	6.73	8.00	3.36	3.50
Hydrogen transfer backward	4.90	4.65	1.38	3.11	6.31	7.82	3.48	4.00
Non-hydrogen transfer forward	6.68	7.81	1.76	5.51	5.39	4.96	4.17	2.51
Non-hydrogen transfer backward	6.22	6.67	1.92	5.42	5.89	6.69	3.57	4.06
Bond distances	0.0103	0.0108	0.0155	0.0126	0.0199	0.0186	0.0136	0.0232
Frequencies	45.26	35.20	70.17	45.39	64.75	67.31	52.58	91.23

Energies in kcal/mol, bond distances in Å, and frequencies in cm^{-1}

Table 2 Exchange energies (in hartrees) of noble gas atoms, and MAEs with respect to Hartree–Fock values, for several global, long-range-corrected (LC) and Coulomb-attenuated (CAM) hybrid functionals

Atom	Global				Long-range-corrected and Coulomb-attenuated				HF
	PBE0	B3LYP	M06-2X	CAP0	LC-BLYP	LC-PBE	CAM-B3LYP	CAM-PBE0	
He	−1.00688	−1.00415	−1.02110	−1.00390	−0.96617	−0.96112	−0.99419	−0.97629	−1.02577
Ne	−12.02891	−11.99477	−12.03450	−11.92814	−11.91472	−11.86400	−12.00771	−11.92017	−12.10835
Ar	−30.00862	−29.94231	−29.98939	−29.77546	−29.87605	−29.74905	−30.01651	−29.85266	−30.18499
Kr	−93.45709	−93.37439	−93.39108	−92.91900	−93.42121	−93.02668	−93.62642	−93.22290	−93.85605
Xe	−178.40557	−178.32743	−178.48413	−177.55500	−178.53529	−177.80974	−178.79616	−178.11956	−179.09757
Rn	−386.23252	−386.23713	−387.08154	−384.85364	−386.80444	−385.35630	−387.13068	−385.87459	−387.50381
MAD	0.439	0.483	0.296	0.957	0.376	0.835	0.201	0.635	

Exchange-only calculations with a universal Gaussian basis [150]

B3LYP is better than PBE0 and CAP0. Nonetheless, the LC and CAM approximations give larger deviations than B3LYP, PBE0 and CAP0. One also can see in Table 1 that the functional M06-2X provides the best description for all the properties considered, except for bond distances and frequencies. However, as already mentioned, M06-2X is heavily parametrized to minimize the deviations for several of the test sets utilized here. Hence M06-2X serves here simply as a reference to attainable accuracy. In the Supplementary Material, we present the individual deviations of the properties reported in Table 1.

To analyze the performance of CAP0 in the calculation of the X energy, Table 2 shows results for X-only calculations on the noble gas atoms. One can see that the MAD for CAP0 is slightly larger than for all the other functionals. This situation is similar to the one for CAP itself in comparison with other GGA functionals. It seems that the constraint given by Eq. (8) induces small changes in the binding region that lead to an underestimation of the X energy. That underestimation is partially canceled when calculating energy differences, as shown by properties reported in Table 1.

To test the reliability of the new X functional in the calculation of excited states, we employed TDDFT within the adiabatic approximation for calculating oscillator strengths and excitation energies. In particular we used the TDDFT module of NWChem-6.0, which calculates single vertical excitations through the linear response of TDDFT. Valence and Rydberg excited states were determined for a set of four molecules [58], N_2, CO, CH_2O, and C_2H_4 at experimental geometries [134, 138]. These excited states were calculated with the aug-cc-pVDZ+ basis set [60], which has an additional set of diffuse functions with exponents set at 1/3 of the most diffuse function exponents of the original

Table 3 Mean absolute deviation (MAD) with respect to experimental values, in eV, for the valence and Rydberg (in parenthesis) excitations of small molecules calculated with LDA and GGA functionals in TDDFT

Molecule	LDA	PBE	BLYP	CAP
N_2	0.24	0.34	0.41	0.32
8 Val, 2 Ryd	(1.59)	(1.83)	(1.91)	(1.62)
CO	0.29	0.46	0.46	0.44
4 Val, 6 Ryd	(1.72)	(1.88)	(1.88)	(1.71)
CH_2O	0.47	0.29	0.26	0.25
3 Val, 7 Ryd	(1.40)	(1.53)	(1.64)	(1.36)
C_2H_4	0.29	0.28	0.34	0.24
2 Val, 8 Ryd	(0.80)	1.02	(1.23)	(0.73)

The number of valence and Rydberg excitations considered is given below each molecule

aug-cc-pVDZ basis sets [139, 140]. Such diffuse functions are mandatory for treating Rydberg excited states. Note that this combination of basis sets has already proven to be reliable [60]. In addition, we calculated some of the lowest-energy valence excitations that dominate the UV/visible absorption spectra of several aromatic molecules. For this purpose, we selected molecules for which accurate experimental excitation energies as well as gas phase oscillator strengths have been published. The structures of benzene, naphthalene, anthracene, phenol, aniline, and fluorobenzene were optimized at the LDA level of approximation, with the DZVP basis sets [141] and frequency analysis was performed. TDDFT calculations were done with the 6-311++G** basis sets [142], that has proven, in a recent work [143], to be a good choice.

In Table 3 we show the MAD with respect to the experimental values [134, 144–147] for the valence and Rydberg excitations, from TDDFT calculations on the N_2, CO, CH_2O and C_2H_4 for the LDA and several GGA functionals. Although the results are rather similar for the four functionals considered, CAP and LDA lead to somewhat better results than PBE and BLYP. It may also be noted that the description of valence excitations is better than the description of Rydberg excitations. In Table 4 we present the same information for the global, long-range-corrected and Coulomb-attenuated hybrid functionals. One can see from the analysis of the MAD that, in comparison with the other global hybrids, CAP0 gives a substantial improvement over PBE0 and B3LYP in the case of the Rydberg excitations, and gives a slightly better description in this case than the highly parameterized M06-2X functional. Note also that for the Rydberg excitations CAP0 provides a better description than the LC functionals, and it delivers also slightly better results than CAM-B3LYP, but is modestly inferior to CAM-PBE0 performance. The description of the valence excitations by CAP0 is similar to what is obtained with the long-range-corrected and Coulomb-attenuated functionals, is slightly better than PBE0 and B3LYP, but is worse than M06-2X. The Supplementary Material contains the excitation energies that lead to the values reported in Tables 3 and 4.

In Table 5 we present excitation energies and corresponding oscillator strengths for some low-energy valence excitations of benzene, naphthalene, anthracene, phenol, aniline, and fluorobenzene, calculated with LDA and GGA functionals, and compare them with experimental values. With respect to the excitation energies, one can see that in general these are underestimated by all the functionals, but CAP leads systematically to larger values that lie closer to the experimental ones. Notice that in the case of aniline, the functionals LDA, PBE, and BLYP show a splitting which is not present in the experimental results. However, for the oscillator strengths, they all lead to rather similar results (in the case of the split excitations, one needs to add all the oscillator strengths).

In Table 6 we present global, long-range-corrected and Coulomb-attenuated hybrid results for the same excitations as in Table 5 and compare them with both coupled-cluster singles and doubles (CCSD) results and with experimental

Table 4 Mean absolute deviation (MAD) with respect to experimental values, in eV, for the valence and Rydberg (in parenthesis) excitations of small molecules calculated with global, long-range-corrected (LC) and Coulomb-attenuated (CAM) hybrid functionals in TDDFT

Molecule	Global				Long-range-corrected and Coulomb-attenuated			
	PBE0	B3LYP	M06-2X	CAP0	LC-BLYP	LC-PBE	CAM-B3LYP	CAM-PBE0
N_2	0.48	0.49	0.42	0.46	0.40	0.31	0.52	0.51
8 Val, 2 Ryd	(0.74)	(0.95)	(0.43)	(0.38)	(0.76)	(0.85)	(0.51)	(0.15)
CO	0.51	0.46	0.15	0.48	0.33	0.34	0.42	0.44
4 Val, 6 Ryd	(1.26)	(1.11)	(0.71)	(0.60)	(0.76)	(0.82)	(0.67)	(0.31)
CH_2O	0.20	0.13	0.33	0.19	0.26	0.29	0.17	0.24
3 Val, 7 Ryd	(0.60)	(0.78)	(0.22)	(0.29)	(0.56)	(0.57)	(0.36)	(0.17)
C_2H_4	0.39	0.35	0.20	0.35	0.27	0.23	0.38	0.41
2 Val, 8 Ryd	(0.55)	(0.76)	(0.45)	(0.26)	(0.23)	(0.15)	(0.36)	(0.16)

The number of valence and Rydberg excitations considered is given below each molecule

Table 5 Comparison of LDA and GGA TDDFT excitation energies (in eV) and oscillator strengths (in parenthesis) with the experimental values for several molecules

Molecule	State	LDA	PBE	BLYP	CAP	Exp.
Benzene	$^1E_{1u}$	6.86 (1.13)	6.78 (1.12)	6.79 (1.12)	6.92 (1.12)	6.96 (0.90)[a]
	$^1E_{1u}$					6.92 (1.20)[b]
Naphthalene	$^1B_{2u}$	5.67 (1.16)	5.62 (1.15)	5.62 (1.15)	5.72 (1.16)	5.89 (1.30)[c]
Anthracene	$^1B_{2u}$	4.91 (1.78)	4.88 (1.77)	4.87 (1.78)	4.94 (1.78)	5.24[d]
Phenol	^1B_a	6.63 (0.55)	6.61 (0.55)	6.55 (0.55)	6.69 (0.56)	6.70 (0.64)[e]
Phenol	^1B_b	6.45 (0.25)	6.44 (0.25)	6.39 (0.26)	6.52 (0.24)	6.93 (0.47)[e]
Aniline	^1B_a	6.29 (0.11)	6.41 (0.36)	6.28 (0.06)	6.48 (0.47)	6.88 (0.57)[e]
		6.43 (0.24)	6.47 (0.11)	6.35 (0.39)		
		6.51 (0.14)				
Fluorobenzene	$^1E_{1u}$	6.82 (1.00)	6.84 (0.98)	6.73 (1.01)	6.85 (1.00)	7.00 (1.43)[e]
	$^1E_{1u}$					6.98 (1.27)[f]
	$^1E_{1u}$					6.99 (0.88)[g]

[a] Ref. [151], [b] Ref. [152], [c] Ref. [153], [d] Ref. [154], [e] Ref. [155], [f] Ref. [156], [g] Ref. [157]

values. Clearly the excitation energies obtained from CAP0, PBE0, LC, and CAM-B3LYP are very similar. All give small overestimations with respect to the experiment, while B3LYP gets closer to the experimental values, and CAM-PBE0, as well CCSD also overestimates them. One can also see that for aniline, all functionals except CAP0 and LC-PBE generate a splitting which is not present in the experimental results. In the case of the oscillator strengths, all the functionals show similar behavior, except for CAM-PBE0 and CCSD, which yield generally larger values.

4 Concluding remarks

The results reported in Sect. 3 show that the global hybrid of CAP with one-fourth exact exchange, CAP0, yields a description of properties depending on energy differences that is competitive in quality with other global functionals like PBE0 and B3LYP. This confirms again that for thermodynamic, kinetic, and structural properties the GGA contribution depends basically on the behavior of the enhancement factor in the physically important region of reduced gradients ($0 \leq s \leq 3$). For the Rydberg excitation energies, however, among the global hybrids, CAP0 leads to a much better description than PBE0 and B3LYP. In fact, CAP0 provides better results than the long-range-corrected hybrids, of a quality similar to those obtained from CAM-B3LYP, though not as good as CAM-PBE0. Both, CAP0 and the long-range-corrected and CAM-PBE0 have in common a fraction of exact exchange and the correct asymptotic behavior of the exchange potential, indicating that both contributions can be rather important in TDDFT. However, it is important to note that correct asymptotic behavior of CAP occurs at very large distances from the molecule, so that the fraction of CAP that enters into CAP0 also reaches the full asymptotic behavior far away. Thus, it would seem desirable to reach the full $-1/r$ behavior at smaller distances, in order to obtain a better description of the Rydberg excitations.

These conclusions can also be observed through the comparison of the results obtained for the GGAs, particularly CAP, which has the correct asymptotic behavior, with the global, long-range-corrected and Coulomb-attenuated hybrids. Tables 3 and 5 show that the GGAs tend to underestimate the excitation energies. Tables 4 and 6 show that global hybrids such as PBE0 (25 % of exact X) and B3LYP (20 % of exact X) increase the excitation energies because of the inclusion of exact exchange, as had already been observed [103, 143, 148, 149]. But Tables 4 and 6 also show that CAP0 (25 % of exact X) and the long-range-corrected and Coulomb-attenuated hybrids (which contain a fraction of exact X) increase the values even more, perhaps because of the correct asymptotic behavior. The global hybrid M06-2X does not have the correct asymptotic behavior, but since it incorporates 54 % of exact X, it gets closer to the $-1/r$ behavior required for the exchange potential than PBE0 and B3LYP.

Thus, one may conclude that the non-empirical CAP0 provides a good description of a wide range of properties, leading, in general, to better results than the non-empirical hybrid PBE0. Also, CAP0 provides a similar description to that of the empirical M06-2X hybrid except for the heats of formation and the barrier heights for the non-hydrogen transfer reactions. However, M06-2X depends upon a large number of fitted parameters and incorporates slightly more than twice the amount of exact exchange of CAP0.

Table 6 Comparison of global, long-range-corrected (LC) and Coulomb-attenuated (CAM) hybrids TDDFT excitation energies (in eV) and oscillator strengths (in parenthesis) with other theoretical calculations and with experimental values for several molecules

Molecule	State	Global				Long-range-corrected and Coulomb-attenuated				CCSD[a]	Exp.[b]
		PBE0	B3LYP	M06-2X	CAP0	LC-BLYP	LC-PBE	CAM-B3LYP	CAM-PBE0		
Benzene	$^1E_{1u}$	7.04 (1.21)	6.95 (1.20)	7.06 (1.20)	7.09 (1.22)	7.05 (1.24)	7.09 (1.21)	7.05 (1.24)	7.22 (1.27)	7.44 (1.32)	6.96 (0.90)
	$^1E_{1u}$										6.92 (1.20)
Naphthalene	$^1B_{2u}$	5.93 (1.28)	5.84 (1.25)	6.02 (1.28)	5.97 (1.29)	6.05 (1.32)	6.06 (1.30)	6.03 (1.32)	6.21 (1.37)		5.89 (1.30)
Anthracene	$^1B_{2u}$	5.21 (2.03)	5.13 (1.99)	5.33 (2.06)	5.23 (2.04)	5.39 (2.11)	5.39 (2.08)	5.34 (2.11)	5.52 (2.18)		5.24
Phenol	^1B_a	6.87 (0.62)	6.77 (0.61)	6.92 (0.60)	6.92 (0.62)	6.90 (0.56)	6.93 (0.59)	6.90 (0.57)	7.08 (0.66)	7.28 (0.66)	6.70 (0.64)
Phenol	^1B_b	6.84 (0.40)	6.72 (0.38)	6.95 (0.44)	6.91 (0.41)	6.89 (0.51)	6.92 (0.45)	6.91 (0.51)	7.12 (0.48)	7.21 (0.48)	6.93 (0.47)
Aniline	^1B_a	6.63 (0.30)	6.56 (0.23)	6.74 (0.24)	6.73 (0.58)	6.74 (0.45)	6.79 (0.54)	6.70 (0.37)	6.90 (0.37)	7.06 (0.09)	6.88 (0.57)
		6.73 (0.23)	6.61 (0.26)	6.80 (0.33)		6.80 (0.12)		6.76 (0.18)	6.95 (0.27)	7.12 (0.49)	
Fluorobenzene	$^1E_{1u}$	7.05 (1.15)	6.95 (1.12)	7.10 (1.14)	7.10 (1.15)	7.05 (1.17)	7.08 (1.15)	7.08 (1.18)	7.25 (1.22)	7.50 (1.28)	7.00 (1.43)
	$^1E_{1u}$										6.98 (1.27)
	$^1E_{1u}$										6.99 (0.88)

[a] Ref. [143], [b] see Table 5 for the references of the experimental values

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