

Density functional approximations for charge transfer excitations with intermediate spatial overlap†

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Density functional theory is now the method of choice for calculating the electronic structure of complex systems, and time-dependent density functional theory (TDDFT) is now the preferred method for calculating spectroscopic properties of large molecules. The validity of the theory depends mainly on the quality of the approximation to the unknown exchange–correlation energy. In the present paper we consider TDDFT calculations of electronic excitation energies and oscillator strengths. We show that the M06-2X and M08-HX density functionals perform as well as and better than the range-separated CAM-B3LYP functional for charge transfer excitations with intermediate spatial overlap but have better performance for bond energies, noncovalent interactions, and chemical reaction barrier heights for representative systems; we conclude that M06-2X and M08-HX should be preferred for studies requiring the exploration of potential energy surfaces as well as electronic excitation energies, provided that those excitations with the longest-range charge transfer are excluded.

Electronic excitations of molecules may be classified in terms of three ideal cases: local valence excitations in which the principal quantum number does not change (e.g., $2sp^2n_O \rightarrow 2p\pi^*_CO$ in acetone),¹ high Rydberg transitions (e.g., excitation of states with principal quantum number > 10),² and charge transfer excitations between charge distributions in different regions of space (e.g., a charge shift between neighboring peptide units in dipeptides).³ However, real excited states are often not purely one of these ideal types. In particular, low Rydberg states often have mixed valence–Rydberg character,^{4,5} and many charge transfer excitations are between orbitals with appreciable spatial overlap (the “spatial overlap” of an excitation from orbital ψ_1 to orbital ψ_2 refers to the overlap of the moduli of the orbitals, $|\psi_1||\psi_2|$, rather than the usual orbital overlap integral, $\langle\psi_2|\psi_1\rangle$).⁶ A challenge for quantum chemistry is to develop accurate methods to calculate electronic excitation energies for both pure and mixed types of transitions, even for large molecules.

Time-dependent density functional theory is a very appealing choice for such calculations because it includes dynamical correlation energy and is much more affordable than post-Hartree–Fock wave function methods.^{7–10} In practice, TDDFT calculations in chemistry are almost always carried out in the adiabatic approximation, using frequency-independent density functional approximations (DFAs) developed for the ground state. Such calculations, although they have been very useful, are known to suffer from a number

of shortcomings.^{11,12} For example, many common DFAs give inaccurate results for Rydberg states. The M06-2X functional¹³ gives accurate results for local valence excitations and for low Rydberg states, but not for the more challenging problem of spatially nonoverlapping charge transfer excitations.¹³ The M06-HF functional¹⁴ is accurate for spatially nonoverlapping charge transfer but less accurate than M06-2X for local valence and low Rydberg states,¹³ and it significantly overestimates the transition energies for $\pi \rightarrow \pi^*$ states.¹⁵ A recent study¹⁵ concluded that “No functional...shows acceptable accuracy for all three of valence, Rydberg, and charge transfer excitations.”

Peach *et al.*⁶ recently presented a diagnostic called Λ that quantifies the degree of spatial overlap in charge transfer excitations, with $\Lambda = 0$ corresponding to no spatial overlap and $\Lambda \cong 1$ corresponding to a local valence excitation. They found that the CAM-B3LYP density functional¹⁶ performs well even for $\Lambda \cong 0$. In a subsequent study¹⁷ of the protonated Schiff base 11-*Z*-*cis*-retinal (**1**) and the analogous 11-*Z*-*cis*-7,8-dihydroretinal (**2**), following upon previous work,¹⁸ they found that the CAM-B3LYP functional performs well for five excitation energies with Λ in the range 0.23–0.72, whereas the popular B3LYP functional¹⁹ performed well for $\Lambda = 0.50$ –0.72 but has large errors for $\Lambda = 0.23$ –0.30.

One may classify DFAs in various ways, and for the present discussion we distinguish three classes: local DFAs, global hybrids (including doubly hybrids), and range-separated hybrids. Local DFAs depend on the local spin-up and spin-down electron densities (here called the spin densities), and possibly on their local gradients or higher derivatives, and/or on the local spin kinetic energies (calculated from the local values of the spin-orbitals, which are themselves functionals of the spin densities). Examples include BP86^{20,21} and M06-L.²² Local hybrid DFAs include a fixed percentage of nonlocal Hartree–Fock (HF) exchange²³ or fixed percentages of HF exchange and of nonlocal correlation functionals that depend

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on the occupied values of the spin-orbitals over all space. The percentage of nonlocal Hartree–Fock exchange is called X , and the percentage of nonlocal correlation is called Y . Examples are B3LYP,¹⁹ M06-HF,¹⁴ M06,¹³ M06-2X,¹³ and M08-HX,²⁴ all with $Y = 0$ and with $X = 20, 100, 27, 54$, and 52.23 , respectively. Range-separated functionals²⁵ are a generalization of local hybrids in which the percentages of local dependency and nonlocal dependency depend on the value of the interelectronic separation (and perhaps also on local variables). Examples of range-separated functionals are discussed below.

It is widely appreciated that local DFAs and local hybrids (with the exception of local hybrids like M06-HF that include 100% HF exchange), although often giving useful accuracy for valence excited states, are often inaccurate for Rydberg states and are very inaccurate for excitations involving charge transfer between nonoverlapping charge densities. The reason for the failure of local DFAs and most global hybrids for Rydberg states and the failure of all local DFAs and all global hybrids with $X < 100\%$ for long-range charge transfer is well understood, namely the incorrect behavior of the Kohn–Sham effective potential at large interelectronic distances due to unphysical self-interaction of electrons in these approximations.¹²

Long-range corrected (LC) functionals,²⁶ including the Coulomb-attenuating method (CAM),¹⁶ are range-separated hybrids²⁵ that were developed to eliminate or reduce the spurious long-range interaction. LC and CAM functionals have $X \geq 65$ at large values of the interelectronic distance and much smaller X at small interelectronic distance. Here we examine three published LC functionals, namely CAM-B3LYP,¹⁶ LC- ω PBE,²⁷ and ω B97X-D,²⁸ and two unpublished ones, LC-BP86 and LC-M06-L. LC- ω PBE has $X = 0$ at short range and $X = 100$ at long range, and ω B97X-D and CAM-B3LYP have $X = 22.2036$ and 19 , respectively, at short range and $X = 100$ and 65 , respectively, at long range. LC-BP86 and LC-M06-L are obtained by simply applying the long-range correction of Hirao and coworkers²⁶ to the BP86 and M06-L functionals; thus these DFAs have $X = 0$ at short range and $X = 100$ at long range.

We have mentioned 12 different DFAs, and in this article we applied all 12 of them to the five excitation energies of **1** and **2** for which accurate results were calculated by coupled cluster (CC) calculations by Zaari and Wong.¹⁸ The structures of **1** and **2** are shown in Fig. 1 and 2, respectively. Table 1 gives the excitation energies, and Table 2 gives the oscillator

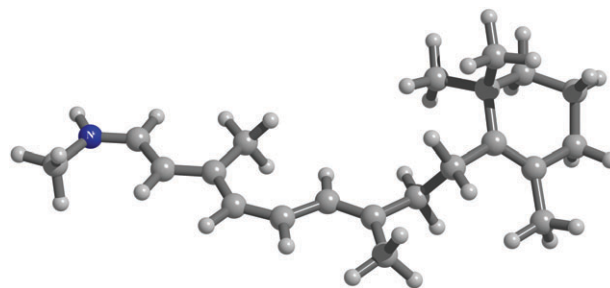


Fig. 2 Structure of **2**

Table 1 Vertical excitation energies (eV), mean unsigned errors (eV), and A diagnostics (unitless)

	1 S ₁	1 S ₂	2 S ₁	2 S ₂	2 S ₃	MUE
BP86	2.16	2.58	1.02	2.23	2.53	1.01
M06-L	2.33	2.79	1.16	2.55	2.88	0.69
B3LYP	2.30	3.04	1.54	3.07	3.22	0.54
M06	2.34	3.15	1.81	3.13	3.50	0.44
M06-2X	2.45	3.49	2.73	3.23	4.48	0.19
M08-HX	2.42	3.54	2.68	3.20	4.46	0.17
M06-HF	2.92	4.27	3.20	4.61	5.30	0.97
LC- ω PBE	2.80	4.10	3.25	4.32	5.38	0.88
LC-BP86	2.87	4.27	3.33	4.63	5.42	1.01
LC-M06-L	2.39	4.06	3.34	4.69	5.41	0.89
CAM-B3LYP	2.52	3.62	2.87	3.29	4.69	0.31
ω B97X-D	2.54	3.72	3.05	3.44	4.99	0.46
CC ^a	2.10	3.30	2.62	3.03	4.40	0.00 ^b
A	0.68	0.72	0.23	0.54	0.30	—

^a Ref. 18. ^b By definition.

Table 2 Oscillator strengths and their mean unsigned errors (unitless)

	1 S ₁	1 S ₂	2 S ₁	2 S ₂	2 S ₃	MUE
BP86	0.95	0.36	0.13	0.04	0.001	0.40
M06-L	1.14	0.23	0.11	0.05	0.01	0.34
B3LYP	1.17	0.34	0.09	0.86	0.43	0.26
M06	1.09	0.31	0.09	1.22	0.02	0.27
M06-2X	1.14	0.29	0.32	1.04	0.01	0.17
M08-HX	1.25	0.26	0.27	1.10	0.004	0.16
M06-HF	1.16	0.15	1.23	0.02	0.03	0.38
LC- ω PBE	1.33	0.17	1.41	0.01	0.03	0.38
LC-BP86	1.35	0.19	1.31	0.02	0.04	0.38
LC-M06-L	1.37	0.34	1.18	0.04	0.07	0.32
CAM-B3LYP	1.25	0.28	0.40	1.02	0.003	0.13
ω B97X-D	1.26	0.26	1.02	0.37	0.01	0.22
CC ^a	1.47	0.26	0.64	0.88	0.01	0.00 ^b

^a Ref. 18. ^b By definition.

strengths. All density functional calculations in these tables employed the 6-31++G(d,p) basis set as used by Dwyer and Tozer.¹⁷ The last column of each table gives the mean unsigned error (MUE) in the five quantities, relative to the benchmark coupled cluster calculations. The last row of Table 1 gives A .

All calculations in this article were carried out with Gaussian 09.²⁹

The first two rows of Tables 1 and 2 give results for functionals with $X = 0$. As in our previous study of the accuracy of DFAs for spectroscopy,¹⁵ M06-L is more accurate than BP86, but neither functional is accurate enough for routine use in spectroscopy.

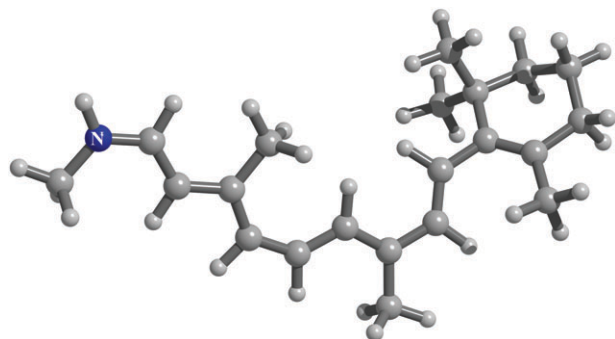


Fig. 1 Structure of **1**

The next four functionals in Tables 1 and 2 have $20 \leq X \leq 54$. We see excellent accuracy for both M06-2X and M08-HX with poorer accuracy for B3LYP and M06, neither of which is accurate for $\lambda \leq 0.30$. Since the M06-2X and M08-HX functionals perform well, it is useful to briefly indicate how these functionals were determined. By the time that M06-HF and M06-2X were designed, Zhao and one of the authors, building on previous work by others,^{23,30–36} had developed considerable experience about what kind of functional form and parametrization scheme is required for a density functional approximation to be broadly accurate,^{14,22,37–39} and that experience was used to design new functional forms depending on spin-up and spin-down kinetic energy densities and Hartree–Fock exchange as well as the spin-up and spin-down electron densities and their reduced gradients. Because these functionals have high percentages of Hartree–Fock exchange (52.23% for M08-HX and 54% for M06-2X) they are not designed for treating transition metal chemistry, and so they were parametrized against data for main-group chemistry, in particular against atomization energies, bond energies, proton affinities, ionization potentials, electron affinities, barrier heights, atomic energies, isomerization energies of π systems, and noncovalent interaction energies—all for ground electronic states.^{13,24}

M06-HF is the only functional in the tables with $X = 100$ for the entire range of internuclear separations. Unfortunately the

Table 3 Mean signed errors and mean unsigned errors (kcal mol⁻¹ per bond) in two bond energy databases

	AE6 ^a		ABDE4 ^b		MGBE10 MUE
	MSE	MUE	MSE	MUE	
M06-2X	-0.17	0.27	0.29	0.75	0.46
M08-HX	-0.31	0.57	-0.46	0.62	0.59
CAM-B3LYP	-0.10	0.36	-5.44	5.44	2.39

^a Basis set is MG3S; geometries are from ref. 42 and are given in the ESI†; accurate values of the atomization energies are from ref. 41; spin-orbit contributions were added to the density functional calculations as described in ref. 46. ^b Basis set is 6-311 + G(3df,2p); geometries are from ref. 43; the accurate bond energies are tabulated in ref. 22.

Table 4 Mean unsigned errors (kcal mol⁻¹) for noncovalent binding energies^a

	HB7A		D8A		M7A		S22A	
	No CpC	CpC	No CpC	CpC	No CpC	CpC	No CpC	CpC
M06-2X	0.81	0.88	0.23	0.25	0.36	0.38	0.46	0.49
M08-HX	0.67	0.90	0.25	0.54	0.42	0.43	0.44	0.62
CAM-B3LYP	0.93	1.03	4.18	4.57	1.54	1.94	2.30	2.61

^a Basis set: def2-TZVP; geometries from ref. 44.

Table 5 Mean signed errors and mean unsigned errors (kcal mol⁻¹) in 24 barrier heights of the DBH24/08 database^a

Method	HATBH6		NSBH6		UABH6		HTBH6		DBH24/08 MUE
	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	
M06-2X	-0.02	0.73	0.60	0.86	0.37	1.09	-0.49	1.24	0.98
M08-HX	0.07	1.13	0.74	1.37	0.73	1.30	-0.49	0.67	1.12
CAM-B3LYP	-3.54	3.54	-1.02	1.02	-0.44	1.97	-3.73	3.73	2.57

^a Basis set: MG3S; geometries from ref. 45.

performance is poor, consistent with our previous assessment.¹⁵ This is unfortunate because M06-HF has been shown to be very accurate for long-range charge transfer transitions,¹³ where most local DFAs and global hybrids fail abysmally. A key conclusion here is that it is not sufficient to have high Hartree–Fock exchange at large interelectronic separations in order to predict accurate results for charge transfer excitations. This point has also been made previously.¹³

The next three functionals in the tables have $X = 100$ for large interelectronic separations and $X = 0$ for small interelectronic separations. Unfortunately the simple expedient of only removing long-range self-interaction by range separation does not give accurate results and cannot be recommended.

CAM-B3LYP and ω B97X-D represent a more sophisticated strategy in which $X \geq 65$ at large interelectronic distance, and $19 \leq X \leq 22.2036$ at small interelectronic separation. The tables show that CAM-B3LYP performs excellently, with a mean error in excitation energies only a factor of 1.8 larger than M08-HX and 63% larger than M06-2X, and with a mean error in oscillator strengths 19–24% lower than those methods. The ω B97X-D method is not quite as accurate as the three best methods, but is comparable to M06, which has $X = 27$ at all interelectronic separations.

The most striking conclusion of this study is that, even though they do not have $X = 100$ at long range and do not employ range separation, M06-2X and M08-HX perform well even for a transition with λ as low as 0.23; thus these functionals can be recommended for all but the longest-range charge transfer excitations. This is important because these functionals have very broad accuracy for ground-state properties.^{13,24,40} To illustrate this broad accuracy, Tables 3–5 give additional results for the three DFAs that perform best in Tables 1 and 2. These additional results are single-point energy calculations on standard databases. The sources of the geometries used for these databases are specified elsewhere,^{41–45} and the AE6 geometries are given in ESI.†

Table 3 gives the mean signed and unsigned errors for two bond energy databases, AE6^{41,42,46} and ABDE4.^{22,39,43} AE6 contains six molecules with representative atomization

energies, namely SiH₄, SiO, S₂, propyne, glyoxal, and cyclobutane, and, as in previous work,^{13,41} the results are divided by the average number of bonds per molecule to put them on a per-bond basis. ABDE4 contains the following four bond energies: methyl–methyl, methyl–methoxy, methyl–isopropyl, and isopropyl–methoxy. To make the overall conclusion more clear we also combine the errors of AE6 and ABDE4 into a database called MGBE10 (which denotes *ten* main-group molecules used to evaluate predicted bond energies) by weighting the MUEs as 6 : 4::AE6 : ABDE4. The mean unsigned errors in M06-2X and M08-HX are factors of 5.2 and 4.1 smaller, respectively, than those for CAM-B3LYP.

Table 4 shows a comparison for noncovalent interactions. For this comparison we use the S22 update⁴⁷ of the S22A database of Jurecka *et al.*⁴⁴ This database has three subsets: HB7A with seven hydrogen-bonded complexes (*e.g.*, formamide dimer), D8A with eight complexes bound predominantly by dispersion-like interactions, including π – π stacking (*e.g.*, adenine–thymine stack), and M7A with seven complexes bound by a mixture of hydrogen bonding and dispersion-like interactions (*e.g.*, phenol dimer). Since there is no general agreement⁴⁸ on whether to add a counterpoise correction⁴⁹ (CpC) in such calculations, we present the errors both ways. By using a triple- ζ quality basis set, def2-TZVP,⁵⁰ the counterpoise corrections are quite small for these density functionals. M06-2X and M08-HX have much smaller MUEs than CAM-B3LYP. In particular, CAM-B3LYP significantly underestimates dispersion-like interactions.

Table 5 presents the performance of the three density functionals (M06-2X, M08-HX, and CAM-B3LYP) for chemical reaction barrier heights in the DBH24/08 database,⁵¹ which is based on earlier work.^{42,45,52–55} This database contains 24 diverse barrier heights, which are divided into four subgroups, HATBH6, NSBH6, UABH6 and HTBH6. HATBH6 has six barrier heights for three heavy-atom transfer reactions (*e.g.*, H + N₂O → OH + N₂); NSBH6 contains six barrier heights for three nucleophilic substitution reactions (*e.g.*, OH[−] + CH₃F → CH₃OH + F[−]); UABH6 has six barrier heights for unimolecular and association reactions (*e.g.*, H + C₂H₄ → C₂H₅); and HTBH6 contains six barrier heights for three hydrogen transfer reactions (*e.g.*, H + H₂S → H₂ + HS). The calculations used the MG3S basis set.^{56–63} Table 5 shows that M06-2X and M08-HX have similar performance for the DBH24/08 database with MUEs of 0.98 and 1.12 kcal mol^{−1}, respectively. However, CAM-B3LYP has a much larger MUE (2.57 kcal mol^{−1}) for the DBH24/08 database with errors larger than 3.5 kcal mol^{−1} for both HATBH6 and HTBH6.

We conclude that the M06-2X and M08-HX functionals are well suited for applications in photochemistry and exploring the topography of coupled potential energy surfaces because they have good performances both for ground-state properties and for all three classes electronic excitation energies except for those depending on the longest-range interelectronic separations ($A \lesssim 0.2$).

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