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Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States

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We present a new density functional called M06-HF. The new functional has full Hartree−Fock exchange, and therefore it eliminates self-exchange interactions at long range. This leads to good performance in TDDFT calculations of both Rydberg and charge-transfer states. In addition, the functional satisfies the uniform electron gas limit, and it is better than the popular B3LYP functional, on average, for ground-electronic-state energetics.

Introduction

Density functional theory (DFT) is now the electronic structure method of choice for accurate calculations of the properties of large molecules in their ground electronic state.[1] Wave function theory (WFT) methods of competitive accuracy have computational costs that scale less favorably with system size[2] and typically become unaffordable for many kinds of applications when the number of atoms reaches 15−25.

Time-dependent DFT (TDDFT) with the linear response approximation provides a way to extend DFT to excited electronic states dominated by single excitations,[3−9] and when it works well, e.g., for localized valence excitations, it provides many of the same computational efficiencies that DFT provides for ground electronic states.[9] For both ground and excited electronic states, the efficiencies of DFT and TDDFT ultimately derive from its ability to treat electron correlation within a convenient set of equations, the Kohn−Sham equations,[10] for one-electron orbitals.

Unfortunately, both DFT and TDDFT fail for certain kinds of systems. For example, many density functionals are unable to treat the polarizability of conjugated systems,[11] and thus they fail for the ground-state energy of systems such as protonated polyenes.[12] This failure may be attributed to an incorrect long-range behavior of the effective potentials generated by the density functionals that have been popularly used because of their accuracy for broad areas of other thermochemical predictions. This incorrect long-range behavior results from self-interaction error in local DFT exchange functionals (including so-called semilocal functionals like GGAs). The breakdown for systems with medium-range electron−electron coupling can be ameliorated by employing improved functionals,[12] although it remains a concern. For large classes of excited electronic states though, one often cannot avoid the problems caused by the incorrect long-range behavior of DFT effective potentials, and this is a very serious limitation to the usefulness of TDDFT.[9]

Two important classes of excited states that have proved troublesome in this regard are Rydberg states and charge-transfer states. In fact, for both of these classes of excitation, a variety of specialized functionals and ad hoc algorithms have been proposed.[13−24] For example, Dreuw and Head-Gordon[16] have suggested a method for treating charge transfer by combining DFT with wave function configuration interaction calculations. Various authors have suggested asymptotic correction schemes for treating Rydberg states[14,15,17] and charge-transfer states,[22−24] and methods based on partitioning the Coulomb operator have also been proposed.[18−21] Although these ad hoc solutions have considerable value for practical work, they are not well suited to many practical applications where valence, Rydberg, and charge-transfer excitations occur in the same energy range or even mix or where one needs simultaneously accurate treatments of ground and excited states.

One way to correct the long-range errors in DFT effective potentials is to mix full Hartree−Fock exchange with DFT correlation. Unfortunately, exchange and correlation functionals in DFT must be well matched, and so far functionals containing full Hartree−Fock exchange, although they eliminate the most severe errors in TDDFT for Rydberg and charge-transfer states, do not have satisfactory performance in most of the other areas that make DFT useful. Because the most popular general-purpose density functional is B3LYP,[25−28] a reasonable objective would be to develop a functional that has full Hartree−Fock exchange, thereby eliminating long-range self-interaction error, but that also has overall average performance as good as or better than B3LYP. The present letter presents such a functional, which will be called M06-HF.

The M06-HF approximation to the exchange−correlation energy has the following functional form

$$E_{\mathrm{XC}}^{\mathrm{M06-HF}} = E_{\mathrm{XC}}^{\mathrm{M06}} + E_{\mathrm{X}}^{\mathrm{HF}} \tag{1}$$

where $E_{\mathrm{XC}}^{\mathrm{M06}}$ is the same functional form (but with different values of the parameters) as for the local M06-L[29] functional and $E_{\mathrm{X}}^{\mathrm{HF}}$ is the nonlocal Hartree−Fock exchange energy. Both terms in eq 1 are functionals of the occupied Kohn−Sham orbitals, which are optimized self-consistently to minimize the total energy. The total energy is the sum of the Kohn−Sham

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kinetic energy, the Coulomb energy (nucleus−nucleus, nucleus-electron, and electron−electron), and the exchange−correlation energy. Note that the M06-L exchange−correlation functional, like other "hybrid meta" functionals,[30−33] depends on local spin density, the reduced gradient of local spin density, and spin kinetic energy density. Functionals that depend on the latter quantities as well as local spin density are sometimes called "semilocal", although mathematically there is only "local" and "nonlocal", and in this mathematical classification they are local, which is the language we use here. Hartree−Fock exchange, however, is nonlocal. Note that E_X^{HF} is not scaled down (as, for example, in B3LYP,[25,26,28] TPSSh,[32] or M05-2X,[33] where it is multiplied by 0.2, 0.1, or 0.56, respectively); therefore we call this full Hartree−Fock exchange.

At this point some comments are in order. First of all, we note that the Coulomb energy includes both the interaction of the electron distribution with the external potential (Coulomb attraction to the nuclei) and its interaction with itself. The later term is calculated classically and so it includes the interaction of a given electron with itself; the exchange part of the exchange−correlation functional must cancel this self-interaction, but this is impossible for a local functional. This is one reason why local functionals cannot be exact.[34] Hartree−Fock exchange corrects this error, and full Hartree−Fock exchange in eq 1, in the absence of exchange in E_{XC}^{M06}, would correct it completely.

Because the E_{XC}^{M06} contains both local exchange and local correlation energy, M06-HF has both local and nonlocal exchange. One might question whether including full Hartree−Fock exchange plus a certain amount of local exchange is "double counting." In this respect, we note that semiempirical exchange−correlation density functionals are sometimes optimized under various constraints (correct asymptotic limits, correct uniform electron gas limit, exact limit for one-electron systems, and so forth) but sometimes are optimized without such constraints or, usually, with only some of them (a review is provided elsewhere[35]); the present functional, like most other functionals, does not attempt to enforce all known constraints, but we do enforce the correct uniform electron gas limit for M06-HF. We also note that E_{XC}^{M06} enforces the condition of being free of self-correlation and that Hartree−Fock exchange is longer range than the local exchange functional used here. Therefore the M06-HF functional tends to the Hartree−Fock result at long range, and it therefore eliminates self-interaction in that limit. It does not eliminate self-exchange at short range for nonuniform densities, and therefore, like most functionals, it has a small amount of exchange even for one-electron systems. By incorporating additional dependence on spin kinetic energy density, it is not difficult to modify the exchange functional to make the self-exchange vanish completely for one-electron systems, and we explored this possibility; however, it generally degrades the performance for many-electron systems, and so we abandoned that approach—the issue of short-range self-exchange is an interesting subject for future work.

The use of an unnormalized exchange potential at short range is reminiscent, in some respects, of the Hartree−Fock−Slater approximation for which Slater,[36] averaging the exchange potential over the entire Fermi sphere, derived an exchange potential 1.5 times larger than the uniform-electron-gas value derived by applying the variational method to the energy of a uniform electron gas by Gáspár,[37] Kohn and Sham,[10] and Cowan et al.[38] The averaging procedure may be generalized[39,40] for energies above the Fermi level. It is well-known that the uniform electron-gas approximation underestimates the exchange energies of atoms.[41] In the exact functional, the corrections must come from more complicated terms such as those that depend on gradients or nonlocal terms. Nevertheless, in the absence of such terms, it has been argued that increasing the exchange functional, although its effect vanishes exponentially at long range, provides a better approximation to the correct self-interaction-free exchange physics at medium range, especially for calculations of ionization potentials, optical spectra, and polarizability.[42] It is not clear if these arguments are relevant to the success of M06-HF, which includes gradients, kinetic energy density, a correlation functional, and nonlocal exchange as well as strictly local exchange, but they illustrate that a wide variety of approaches are available for modeling the unknown exact nonlocal exchange−correlation functional.

The parameters in the first term of eq 1 were optimized against a training set of benchmark data. In particular, we optimized the parameters to minimize the following training function:

$$Q = [\mathrm{RMSEPB(MGAE109)} + \mathrm{RMSE(IP13)} + \mathrm{RMSE\ (EA13)} + \mathrm{RMSE(PA8)} + \mathrm{RMSE(BH76)} + \mathrm{RMSE(ABDE4)} + \mathrm{RMSE(AE17)} + \mathrm{RMSE}(\pi 13) + 10\mathrm{RMSE(NCCE31)}\ ]/8 \quad (2)$$

where the terms are defined as follows: the root-mean-squared error (RMSE) per bond (PB) for the MGAE109 database[43] of 109 main-group atomization energies, the RMSE for the IP13 database[44] of 13 main-group ionization potentials, the RMSE for the EA13 database[44] of 13 main-group electron affinities, the RMSE for 8 small-molecule proton affinities (PA8),[12] the RMSE for the 76 barrier heights in the HTBH38 (hydrogen-transfer barrier heights) and NHTBH38 (other barrier heights) databases.[45] The RMSE for 4 energies of bond dissociations producing alkyl and alkoxy radicals (ABDE4),[46] the RMSE for the 17 total atomic energies of from H to Cl,[47] the RMSE for the 13 energetic data in the πIE3[12] (isomerizatiion energies of π systems), PA-P5[12] (proton affinities of conjugated polyenes), and PA-SB5[12] (proton affinities of conjugated Schiff bases) databases, and the RMSE for the 31 noncovalent complexation energies in the HB6/04[48] (hydrogen-bonding pairs), CT7/04[48] (ground-state charge-transfer complexes), DI6/04[48] (complexes bound by dipole forces), WI7/05[46] (complexes bound by weak interactions due to medium-range correlation energy), and PPS5/05[46] ($\pi-\pi$ stacks) databases.

All parameter optimizations and tests of density functionals in the present Letter are carried out at fixed geometries taken from previous work;[29,33,46] our experience indicates that when reasonably accurate geometries are used (as they are here) this is not a serious limitation for parametrization and testing of density functionals. The geometries and basis sets used for all calculations presented here are specified in Supporting Information.

In optimizing the parameters, we constrained M06-HF to satisfy the uniform electron-gas limit. All optimized parameters for M06-HF are listed in Table 1; the notation is defined in our previous paper.[29]

The performance of M06-HF was then tested for spectroscopy. We judge the performance for spectroscopy primarily in terms of the mean unsigned errors (MUEs) for non-charge-transfer (non-CT) and charge-transfer (CT) excitations in a test set. The first of these is defined as

$$\mathrm{MUE(non\text{-}CT)} = 0.5{*}\mathrm{MUE(valence)} + 0.5{*}\mathrm{MUE(Rydberg)} \quad (3)$$

TABLE 1: Optimized Parameters in the M06-HF Methods

	M06-HF					
parameters	a_i	$c_{C\alpha\beta,i}$	$c_{C\sigma\sigma,i}$	d_i	$d_{C\alpha\beta,i}$	$d_{C\sigma\sigma,i}$
0	1.179732E−01	1.674634E+00	1.023254E−01	−1.179732E−01[a]	−6.746338E−01[a]	8.976746E−01[a]
1	−1.066708E+00	5.732017E+01	−2.453783E+00	−2.500000E−03	−1.534002E−01	−2.345830E−01
2	−1.462405E−01	5.955416E+01	2.913180E+01	−1.180065E−02	−9.021521E−02	2.368173E−01
3	7.481848E+00	−2.311007E+02	−3.494358E+01		−1.292037E−03	−9.913890E−04
4	3.776679E+00	1.255199E+02	2.315955E+01		−2.352983E−04	−1.146165E−02
5	−4.436118E+01					
6	−1.830962E+01					
7	1.003903E+02					
8	3.864360E+01					
9	−9.806018E+01					
10	−2.557716E+01					
11	3.590404E+01					

[a] A parameter that was constrained during the optimization; other parameters were optimized without constraints. The constraints are $a_0 + d_0 = 0$; $c_{C\alpha\beta,0} + d_{C\alpha\beta,0} = 1$; $c_{C\sigma\sigma,0} + d_{C\sigma\sigma,0} = 1$. The latter two constraints serve the same normalization purpose as in ref 29, but the first constraint is different. In ref 29 we required $a_0 + d_0 = 1$ to normalize the local exchange in the uniform electron gas limit, whereas here, because we use full Hartree−Fock exchange, these two coefficients are constrained to sum to zero so that the local exchange vanishes in the uniform electron gas limit.

TABLE 2: Excitation Energies (eV) for N_2, CO, HCHO, Tetracene, $NH_3\cdots F_2$, and $C_2H_4\cdots C_2F_4$[a]

molecule	type	state	transition	TPSSh	B3LYP	B98	PBE0	BMK	M05-2X	M06-HF	HF	accurate[b]
N_2	Rydberg	$^1\Pi_u$	$\pi_u \rightarrow 3s\sigma_g$	11.91	12.04	12.20	12.32	12.72	13.36	13.48	14.05	13.24
		$^1\Sigma_u^+$	$\sigma_g \rightarrow 3p\sigma_u$	11.20	11.62	11.81	11.87	12.60	13.16	13.40	14.83	12.98
		$^1\Pi_u$	$\sigma_g \rightarrow 3p\pi_u$	11.46	11.78	11.97	11.99	12.59	13.16	12.45	13.21	12.90
		$^1\Sigma_g^+$	$\sigma_g \rightarrow 3s\sigma_g$	10.90	11.24	11.44	11.47	12.19	12.75	12.99	13.98	12.20
		$^3\Sigma_g^+$	$\sigma_g \rightarrow 3s\sigma_g$	10.72	10.99	11.15	11.17	11.92	12.32	12.06	13.05	12.00
	valence	$^3\Pi_u$	$\sigma_u \rightarrow \pi_g$	10.75	10.63	10.85	10.74	11.30	11.10	11.25	11.28	11.19
		$^1\Delta_u$	$\pi_u \rightarrow \pi_g$	9.94	9.72	9.75	9.89	9.92	10.19	10.20	8.77	10.27
		$^1\Sigma_u^-$	$\pi_u \rightarrow \pi_g$	9.72	9.31	9.32	9.34	8.85	8.35	6.47	7.93	9.92
		$^3\Sigma_u^-$	$\pi_u \rightarrow \pi_g$	9.72	9.31	9.32	9.34	8.85	8.35	6.47	7.93	9.67
		$^1\Pi_g$	$\sigma_g \rightarrow \pi_g$	9.32	9.24	9.30	9.31	9.28	9.15	8.71	9.77	9.31
		$^3\Delta_u$	$\pi_u \rightarrow \pi_g$	7.97	7.97	8.10	7.90	8.39	8.82	9.51	7.62	8.88
		$^3\Pi_g$	$\sigma_g \rightarrow \pi_g$	7.48	7.55	7.69	7.50	7.76	7.63	7.55	5.85	8.04
		$^3\Sigma_u^+$	$\pi_u \rightarrow \pi_g$	7.03	7.06	7.07	6.93	7.27	7.24	7.53	3.45	7.75
CO	Rydberg	$^1\Sigma^+$	$\sigma \rightarrow 3d\sigma$	10.14	10.47	10.59	10.68	11.38	11.99	12.99	13.55	12.40
		$^1\Pi$	$\sigma \rightarrow 3p\pi$	10.06	10.27	10.45	10.49	10.99	11.61	11.62	12.59	11.53
		$^3\Pi$	$\sigma \rightarrow 3p\pi$	10.01	10.24	10.35	10.42	10.90	11.46	11.28	12.37	11.55
		$^1\Sigma^+$	$\sigma \rightarrow 3p\sigma$	9.96	10.21	10.38	10.42	10.95	11.53	11.68	12.56	11.40
		$^3\Sigma^+$	$\sigma \rightarrow 3p\sigma$	9.93	10.19	10.29	10.35	10.86	11.41	11.24	12.28	11.30
		$^1\Sigma^+$	$\sigma \rightarrow 3s$	9.64	9.83	10.02	10.05	10.55	11.09	10.98	11.88	10.78
		$^3\Sigma^+$	$\sigma \rightarrow 3s$	9.43	9.56	9.68	9.70	10.23	10.62	9.83	10.96	10.40
	valence	$^1\Delta$	$\pi \rightarrow \pi^*$	10.17	10.04	10.11	10.20	10.37	10.35	10.18	9.96	10.23
		$^1\Sigma^-$	$\pi \rightarrow \pi^*$	10.01	9.71	9.76	9.78	9.55	9.13	7.61	9.38	9.88
		$^3\Sigma^-$	$\pi \rightarrow \pi^*$	10.01	9.71	9.76	9.78	9.55	9.13	7.61	9.38	9.88
		$^3\Delta$	$\pi \rightarrow \pi^*$	8.61	8.64	8.79	8.61	9.11	9.12	9.45	7.88	9.36
		$^1\Pi$	$\sigma \rightarrow \pi^*$	8.52	8.40	8.46	8.44	8.45	8.30	7.91	8.80	8.51
		$^3\Sigma^+$	$\pi \rightarrow \pi^*$	7.87	7.92	7.99	7.84	8.25	7.98	8.00	6.34	8.51
		$^3\Pi$	$\sigma \rightarrow \pi^*$	5.77	5.85	6.04	5.73	6.15	6.04	6.19	5.28	6.32
H_2CO	Rydberg	$^1A_2$	$n \rightarrow 3db_1$	7.57	7.94	8.04	8.12	8.59	9.40	9.87	11.22	9.22
		$^1A_2$	$n \rightarrow 3db_1$	7.03	7.35	7.48	7.54	7.97	8.76	8.86	9.69	8.38
		$^1B_2$	$n \rightarrow 3pa_1$	6.93	7.16	7.32	7.37	7.82	8.41	8.44	9.28	8.12
		$^3B_2$	$n \rightarrow 3pa_1$	6.89	7.10	7.23	7.27	7.72	8.26	8.01	8.93	7.96
		$^1A_1$	$n \rightarrow 3pb_2$	6.87	7.15	7.31	7.37	7.67	8.54	8.71	9.52	7.97
		$^3A_1$	$n \rightarrow 3pb_2$	6.84	7.10	7.21	7.28	7.58	8.41	8.33	9.18	7.79
		$^1B_2$	$n \rightarrow 3sa_1$	6.29	6.43	6.62	6.67	7.19	7.68	7.69	8.54	7.09
		$^3B_2$	$n \rightarrow 3sa_1$	6.17	6.32	6.47	6.49	7.06	7.58	7.25	8.13	6.83
	valence	$^1B_1$	$\sigma \rightarrow \pi^*$	9.14	9.03	9.09	8.90	9.08	9.00	8.50	9.71	8.68
		$^3A_1$	$\pi \rightarrow \pi^*$	5.43	5.48	5.59	5.29	5.83	5.49	5.74	2.21	5.53
		$^1A_2$	$n \rightarrow \pi^*$	4.08	3.92	3.96	3.94	3.90	3.72	3.16	4.42	3.94
		$^3A_2$	$n \rightarrow \pi^*$	3.26	3.20	3.28	3.15	3.24	3.11	2.72	3.45	3.50
tetracene	valence	B_{2u}	L_a	3.40	3.45	3.48	3.52	3.66	3.71	3.79	3.90	3.39
	CT	B_{3u}	L_b	2.34	2.41	2.44	2.48	2.68	2.74	3.04	2.95	2.88
$NH_3\cdots F_2$	CT	$^3A_1$	$n \rightarrow \sigma^*$	1.49	2.22	2.59	2.83	4.29	5.38	9.36	11.12	9.46
$C_2H_4\cdots C_2F_4$	CT	$^3B_2$	$\pi \rightarrow \pi^*$	6.36	7.03	7.19	7.41	8.73	9.60	12.62	13.88	12.63

[a] The augmented Sadlej pVTZ basis set[13,61] was employed for the calculations of the N_2, CO, and HCHO molecules; the 6-31+G(d,p) basis set was employed for the calculations of $NH_3\cdots F_2$; the 6-31G* basis set was employed for the $C_2H_4\cdots C_2F_4$ complex; and the 6-311G(2d,p) basis set was employed for tetracene. [b] The accurate data for N_2,[49] CO,[50] HCHO,[51] and tetraacene[52] were taken from experimental studies, the accurate charge-transfer excitaion energy for $C_2H_4\cdots C_2F_4$ was taken from a previous paper by Tawada et al.,[18] and the accurate charge-transfer excitation energy for the $NH_3\cdots F_2$ complex was calculated at the SAC-CI/6-31+G(d,p) level of theory. The accurate excitation energies for tetracene were taken from Grimme.[62]

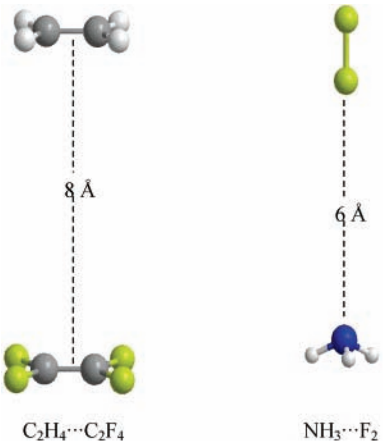

Figure 1. Structures of $C_2H_4\cdots C_2F_4$ and $NH_3\cdots F_2$ complexes.

TABLE 3: Mean Unsigned Errors (eV) for Excitation Energies

type	TPSSh 10[a]	B3LYP 20	B98 19	PBEh 25	BMK 42	M05-2X 56	M06-HF 100	HF 100
valence	0.24	0.28	0.24	0.29	0.30	0.37	0.71	1.08
Rydberg	1.33	1.07	0.92	0.86	0.35	0.31	0.39	1.18
non-CT	0.78	0.67	0.52	0.58	0.33	0.34	0.55	1.13
CT	4.93	4.44	4.25	4.08	3.10	2.42	0.09	0.99
all[b]	2.17	1.93	1.80	1.75	1.25	1.03	0.40	1.08

[a] The number below each functional is the percentage of Hartree−Fock exchange. [b] MUE (all) = [MUE(valence) + MUE(Rydberg) + MUE(CT)]/3.

where MUE(valence) is the mean unsigned error for the 20 valence transitions of N_2, CO, formaldehyde, and tetracene in Table 2 and MUE(Rydberg) is the mean unsigned error for the 20 Rydberg transitions of N_2, CO, and formaldehyde in Table 2. The second is

$$\mathrm{MUE(CT)} = [|\text{error in CT transition of tetracene}| + |\text{error in } \mathrm{NH_3\cdots F_2} \text{ at 6 Å}| + |\text{error in } \mathrm{C_2H_4\cdots C_2F_4} \text{ at 8 Å}|]/3 \tag{4}$$

The distances of the two CT pairs of eq 4 are defined in Figure 1, which also shows the orientation of the subunits. The results for the all transitions are in Table 2, along with accurate results[18,49−52] to which we compare. The MUEs are in Table 3.

Tables 2 and 3 also contain results for B3LYP and five other high-quality functionals: TPSSh,[32] B98,[53] PBEh,[54] BMK,[55] and M05-2X.[33] Finally, Tables 2 and 3 contain results for the time-dependent Hartree−Fock approximation[9] (equivalent to the random-phase approximation[56−58]), which is here abbreviated as HF (just as, for example, TDB3LYP is here abbreviated as B3LYP).

Table 3 shows that M06-HF performs better than HF for all three classes of excitation. However, it is not as good as other high-quality density functionals for valence excitations. The situation turns around, however, for Rydberg transitions, where M06-HF has an MUE of 0.39 eV, much better than the 0.86−1.33 eV of TPSSh, B3LYP, B98, and PBEh and almost as good as the 0.31−0.35 eV of M05-2X and BMK. In fact, averaged over an equal number of valence and Rydberg transitions, M06-HF still outperforms TPSSh, B3LYP, and PBEh. As a side point, we note that Table 3 shows truly excellent performance for BMK and M05-2X for non-CT transitions; these methods have not previously been applied in the context of TDDFT, and they can be highly recommended when there are no long-range charge-transfer states.

The situation for the second to last row of Table 3 is entirely different. M06-HF is excellent for CT transitions, and no other method gives useful results. In fact, the table shows that high Hartree−Fock exchange is not the entire story, because M06-HF is much better than HF. Therefore, in the last row of Table 3 where all three types of transition are weighted 1/3, M06-HF is a factor of more than 2.5 better than the second best method, which is M05-2X.

One might wonder whether it is meaningful to compare errors as large as 2.42 and 4.93 eV, both of which are too large for the methods yielding them to be useful. However, in other and more complex molecules one might encounter states with partial CT character, and the methods with smaller errors for these prototype test cases would be expected to do better for such molecules. However, in such a case it would be best to employ M06-HF, which is the only method to have errors below 1.0 eV for both non-CT and CT transitions.

One might ask whether this improved performance for spectroscopy has been achieved at a cost of unacceptably poor performance for ground-electronic-state energetics. This is answered by Table 4, which compares the performance of M06-HF for such energetic quantities to the performance of the other high-quality density functionals for several databases based on ground-state main-group energetics. These databases were explained below eq 2.

TABLE 4: Mean Unsigned Errors (kcal/mol) for Energetics in the Ground Electronic State

database	TPSSh	B3LYP	B98	PBEh	BMK	M05-2X	M06-HF	HF
MGAE109 (PB)	0.98	0.91	0.64	0.91	0.47	0.48	0.64	30.83
IP13	3.17	4.72	3.21	3.23	4.21	3.54	3.76	17.92
EA13	2.81	2.29	1.84	2.76	1.56	2.03	2.35	26.96
PA8	2.78	1.02	1.44	1.19	1.07	1.23	2.21	3.19
ABDE4	9.35	8.62	4.87	4.98	1.67	0.61	4.56	35.17
NHTBH38	6.84	4.59	3.37	3.61	1.33	1.75	2.48	9.12
HTBH38	5.97	4.23	4.16	4.22	1.32	1.34	2.06	6.28
πIE3[a]	7.21	6.24	6.26	5.65	3.89	2.99	1.13	2.67
PA-P5[a]	8.57	5.79	7.25	5.73	4.29	2.07	3.89	12.70
PA-SB5[a]	7.82	5.90	7.29	6.53	5.08	3.90	0.77	10.90
HB6	0.60	0.76	0.55	0.34	0.82	0.30	0.52	2.44
CT7	1.30	0.63	0.79	0.90	0.52	0.38	0.49	3.94
DI6	0.54	0.86	0.37	0.37	0.88	0.29	0.63	2.45
WI7	0.22	0.35	0.14	0.15	0.81	0.06	0.16	0.37
PPS5	2.59	3.06	2.02	1.96	2.47	0.60	0.35	3.54
av[b]	4.05	3.33	2.95	2.84	2.02	1.44	1.73	11.23

[a] These three databases are components of the π13 database [b] Average over all the databases in this table; each row of this table is weighted equally.

The success of the present exchange−correlation functional is ultimately derived from the functional form used for $E_{\mathrm{XC}}^{\mathrm{M06}}$ being compatible with high Hartree−Fock exchange, even full Hartree−Fock exchange. This property is inherited from its precursor, the M05 functional,[33,59] which is specifically designed to have this property and in fact to be more compatible than previous functionals with a range of values of the percentage of Hartree−Fock exchange.

Because the M06-HF exchange−correlation functional has the correct[60] long-range behavior, behaving at long range for neutral systems as $-R^{-1}$ in atomic units, it avoids many of the qualitatively wrong (in fact, embarrassingly wrong) predictions of conventional density functionals that are due to long-range self-interaction error. And yet the new exchange−correlation functional achieves this improvement without losing the advantages that have made DFT preferable to Hartree−Fock theory, which also has the correct asymptotic behavior. In fact, the new functional is on average better than the very popular B3LYP functional, as measured by performance (Table 4) on a diverse set of databases. The excellent performance for barrier heights, π systems, and noncovalent interactions is especially noteworthy. The new functional also retains the key formal property of satisfying the uniform-electron-gas limit at both short range and long range, and it includes short-range static-correlation effects that are missing in functionals that combine Hartree−Fock exchange and DFT correlation without any DFT exchange.

Now that it has been demonstrated that one can obtain a functional with all the properties mentioned in the title of this paper, there may be some interest in improving the performance for valence excited states (no excited-state data were used in parametrization) or in deriving this kind of functional from first principles and with a smaller number of parameters. These are interesting subjects for future work.

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Supporting Information Available: Description of the geometries and basis sets employed for all databases and Cartesian coordinates for all molecules in the TDDFT calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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