

A fast doubly hybrid density functional method close to chemical accuracy using a local opposite spin ansatz

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We develop and validate the XYGJ-OS functional, based on the adiabatic connection formalism and Görling-Levy perturbation theory to second order and using the opposite-spin (OS) ansatz combined with locality of electron correlation. XYGJ-OS with local implementation scales as N^3 with an overall accuracy of 1.28 kcal/mol for thermochemistry, bond dissociation energies, reaction barrier heights, and nonbonded interactions, comparable to that of 1.06 kcal/mol for the accurate coupled-cluster based G3 method (scales as N^7) and much better than many popular density functional theory methods: B3LYP (4.98), PBE0 (4.36), and PBE (12.10).

ACM | DHDF | GGA | LDA | MAD

Obtaining chemical accuracy (~ 1 kcal/mol) to quantify key chemical quantities (e.g., heats of formation, bond dissociation energies, and reaction barrier heights) using quantum mechanics (QM) has been a major focus in the development of the theory. This has led to, for example, the Gn method (1, 2) that approaches this chemical accuracy. Because G3 is a coupled-cluster based method, it scales on the order of N^7 , where N measures the system size, limiting to fairly small species for routine use.

The desire to predict unique physiochemical phenomena (e.g., solvation, catalysis, self-assembly, and drug design) in practical (large) systems has brought about a second major focus of theoretical development, leading, for example, to divide-and-conquer formulations to attain more efficient scaling (3), but with much lower accuracy than Gn.

Density functional theory (DFT) in the framework of Kohn-Sham (KS) scheme (4, 5) provides a “shortcut” to the many-body problem. Many density functional approximations (DFAs), provide typical scaling of $N^3 \sim N^4$, while yielding significantly more accurate results than Hartree-Fock (HF) theory, the lowest level wave function based method with similar scaling, but they still lead to significant errors for some systems. For example, current DFAs lead to a poor description of London dispersion (van der Waals attraction), which is essential to predict the packing of molecules into solids, and the binding of drug molecules to proteins. These DFAs are also poor in predicting the magnitude of reaction barriers.

In this article, we develop and present a unique functional, XYGJ-OS, that provides a good combination of high accuracy and speed. XYGJ-OS involves a doubly hybrid density functional (DHDF), containing both a nonlocal orbital-dependent component in the exchange term (HF-like exchange), and also information about the unoccupied KS orbitals in the electron correlation part (PT2, perturbation theory up to second order) using the opposite-spin (OS) ansatz to include the locality of electron correlation. XYGJ-OS provides accuracy comparable to that of Gn for the test datasets and speed with $N^2 \sim N^3$ for the local implementation. Hence XYGJ-OS is both accurate and fast.

Theory

The Holy Grail in KS-DFT is to find the exact, yet unknown, exchange-correlation functional $E_{xc}[\rho]$ using density ρ as the basic variable (4, 5). In practice, an approximate E_{xc} must be adopted, which is often partitioned into the exchange and correlation parts

$$E_{xc}[\rho] \approx E_x^{DFA}[\rho] + E_c^{DFA}[\rho]. \quad [1]$$

E_x^{DFA} has been extended to include a portion of nonlocal E_x^{HF} , where the superscript “HF” emphasizes that the exchange part has the same form as in Hartree-Fock theory (6). The exchange-correlation potential v_{xc} in the n th cycle of the self-consistent-field (SCF) process to solve the KS equation is obtained as a functional of ρ of the previous cycle.

On the other hand, Görling and Levy (GL) (7, 8) argued that the same KS scheme should work as well in terms of KS orbitals φ_i and eigenvalues ε_i . GL proposed a formally exact KS scheme based on perturbation theory, where E_{xc} was expressed as:

$$E_{xc}[\rho] = E_x^{HF}[\{\varphi_i\}] + \sum_{j=2}^{\infty} E_{c,j}[\{\varphi_i\}, \{\varepsilon_i\}, \{v_1(r), v_2(r), \dots, v_{j-1}(r)\}], \quad [2]$$

$$E_{c,2} = E_c^{GL2} = \sum_{i=1}^{\infty} \frac{|\langle \Phi_{s,0} | \hat{V}_{ee} - v_1 | \Phi_{s,i} \rangle|^2}{E_{s,0} - E_{s,i}}. \quad [3]$$

Here E_c^{GL2} stands for the GL perturbation theory up to the second order, $\{\Phi_{s,0}, E_{s,0}\}$ and $\{\Phi_{s,i}, E_{s,i}\}$ are the wave function and energy for the ground state and the i th excited state of an N -electron KS system, respectively; \hat{V}_{ee} is the operator of electron-electron repulsion, and the v_1 potential may be determined from the “exchange-only” KS equation (8). With knowledge of the potentials $v_j(r)$, Eq. 2 gives the formally exact exchange-correlation energy as functional of the KS orbitals φ_i and eigenvalues ε_i , with which the approximate $E_{xc}^{DFA}[\rho]$ defined in [1] can be compared. However, in practice, such a procedure is difficult to apply to higher than second order due to the unfavorable scaling with the system size, and in many cases perturbation theory is nonconvergent. Thus the scheme must be simplified to make it applicable for including higher-order contributions.

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The adiabatic connection method [(ACM), ref. 9, 10], which defines a family of partially interacting N -electron systems with a coupling constant for a fixed ρ , provides a powerful tool for developing and understanding E_{xc} (6, 11–13). ACM suggests that Eq. 2 up to second order, while being more appropriate for coupling close to zero, is only exact if the potential energy of exchange-correlation depends linearly on the coupling strength, whereas [1] is more associated with full electron-electron coupling (13, also see *SI Text* for more discussion). To go beyond the linear approximation and to take advantages of both [1] and Eq. 2, we define an empirical DHDF that combines Eq. 2 ($j = 2$) with [1]:

$$E_{xc}^{DHDF}[\rho] = c_1 E_x^{LDA} + c_2 \Delta E_x^{GGA} + c_3 E_x^{HF} + c_4 E_c^{LDA} + c_5 \Delta E_c^{GGA} + c_6 E_c^{PT2}. \quad [4]$$

Here $\{E_x^{LDA}, E_c^{LDA}\}$ are the exchange and correlation components within the local density approximation (LDA), and $\{\Delta E_x^{GGA}, \Delta E_c^{GGA}\}$ are the corresponding correction terms to LDA within the generalized gradient approximation (GGA). The meta-GGA functionals that include kinetic energy density or the Laplacian of density can also be used in place of GGAs. Such a combination suggests that only the energetically most important double excitation PT2 term in Eq. 2 need be calculated explicitly, the higher-order correlations are embedded into the parameterized terms such as $(E_x^{DFA} - E_x^{HF})$ (12). Other examples of DHDFs include MC3BB (14), B2PLYP (15), B2GP-PLYP (16), and ω B97X-2 (17), which are derived and constructed differently (see below and *SI Text* for more discussion).

Several key issues distinguish our approach from GL perturbation theory (7, 8) and other DHDFs (14–23).

- i. Instead of seeking for $\{\varphi_i, \varepsilon_i, v_j\}$ self-consistently and order by order via Eq. 2, we use a conventional DFA defined in [1] to generate $\{\varphi_i, \varepsilon_i\}$ and to evaluate E_{xc} defined in Eq. 4 in a post-SCF manner. In fact, the GL perturbation theory, Eq. 2, was built on KS orbitals with a local effective potential, while we have extended it to include hybrid functionals with generalized KS orbitals (12, 13).
- ii. E_c^{PT2} differs from E_c^{GL2} in that the singles contribution is not explicitly calculated, but we argue (12, 13) that it can be reasonably absorbed into the parameterization in Eq. 4. Higher-order contributions $E_{c,j}$ ($j > 2$) are also implicitly included via the parameterization.
- iii. Neglecting the nonlocal exchange-correlation effects (E_x^{HF}, E_c^{PT2}) in Eq. 4 leads to a pure DFA, while neglecting the local exchange-correlation effects, Eq. 4 gives an approximation to GL2. Hence our DHDF may be regarded as an interpolation approach between a pure DFA and GL2, while both of them are in the framework of the KS scheme. As different orbitals are used to construct the PT2 term, neglecting the local exchange-correlation effects in other DHDFs (14–23) will bring back the conventional MP2, such that these DHDFs may be regarded as an interpolation approach between a DFA and MP2, the wave function based lowest level correlation method. These functionals go beyond the framework of the KS scheme (23).

Assuming LDA and GGA in Eq. 4 are SVWN (24, 25) and BLYP (26, 27), respectively, we previously developed XYG3 (12), a DHDF which is remarkably accurate for a wide range of systems and important chemical properties (12, 13, 28–31). Nevertheless, the PT2 term in XYG3 and other DHDFs is evaluated in a way similar to MP2:

$$E_c^{PT2} = \frac{1}{4} \sum_{ij} \sum_{ab} \frac{|\langle \varphi_i \varphi_j | \varphi_a \varphi_b \rangle - \langle \varphi_i \varphi_j | \varphi_b \varphi_a \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \quad [5]$$

where the subscripts (i, j) and (a, b) denote the occupied and unoccupied KS spin-orbitals, respectively, leading to a formal scaling as N^5 , as opposed to a formal scaling of N^4 as in B3LYP (24–27, 32, 33). This unfavorable scaling raises an issue for the practicality to apply DHDFs to large systems.

Density fitting approximations have often been used in electronic structure theories to reduce computational expense. In the so-called “resolution-of-the-identity” RI-MP2 method (34, 35), the product of occupied and virtual orbitals (ia pair) is expanded with auxiliary functions, such that numerous 4-center 2-electron integrals based on molecular orbitals (MO) are replaced by fewer 3 and 2-center integrals with cheaper transformation from atomic orbitals (AO) to MO. RI-MP2 is about 5–20 times faster than conventional MP2 (36, 37). Nevertheless, RI-MP2 reduces only the prefactor, it does not change the scaling. Similarly, we have RI-XYG3, which retains the original accuracy but is faster for small systems with large basis sets.

Here we propose a unique OS ansatz for DHDF, that yields a balanced description of nonlocal correlation effects while considerably reducing computational time. Our OS ansatz is motivated by the observation that the most important electron correlation effects involve correlations of the OS electrons in the same orbital. The OS ansatz leads to N^4 scaling (36, 37) [using auxiliary basis expansions (34, 35) and Laplace quadrature approximations (38)]. It should be emphasized that as the same-spin (SS) correlation is very important in accurate description of open-shell systems and magnetic properties, such contributions cannot be simply neglected. In XYGJ-OS, the SS correlation effects are included within the standard DFA.

In recognition of the “nearsightedness of electron correlation” as emphasized by Kohn (39), we then build upon XYGJ-OS to introduce the local approximation for the OS electron correlation by utilizing the sparsity of the RI expansion coefficients, integral matrices, and Laplace transform matrices. The local implementation of XYGJ-OS scales as N^3 while retaining the accuracy of the original XYGJ-OS (see *SI Text* for more discussion).

Thus our proposed functional form (XYGJ-OS) is

$$E_{xc}^{XYGJ-OS}[\rho] = e_x E_x^{HF} + (1 - e_x) E_x^S + (e_{VWN} E_c^{VWN} + e_{LYP} E_c^{LYP}) + e_{PT2} E_{c,OS}^{PT2}. \quad [6]$$

In Eq. 6 we normalize the HF exchange and Slater exchange (24), while eliminating the ΔE_x^{GGA} contribution. The correlation part consists of E_c^{VWN} (25), E_c^{LYP} (27), and $E_{c,OS}^{PT2}$, where the first term includes both the SS and OS effects while the second and third terms include only OS components. Our concept is that the combination of VWN, LYP, and PT2-OS yields a balanced description of both local and nonlocal spin dependent correlation terms. To determine the optimal four parameters in Eq. 6, we use the experimental heats of formation (HOF) data for the G3/99 set of 223 molecules (1, 2) as the training set, leading to $\{e_x, e_{VWN}, e_{LYP}, e_{PT2}\} = \{0.7731, 0.2309, 0.2754, 0.4364\}$.

Results and Discussion

We emphasize that we use the fully optimized B3LYP orbitals to generate the density and to calculate each term in Eqs. 4 or 6 (12, 13, 29–31). But the choice of LDA = SVWN and GGA = BLYP in Eqs. 4 or 6, as well as using B3LYP orbitals as input, is not unique. We find that any conventional DFAs defined in [1] can also serve the same purpose, leading to similar performance, albeit with a reoptimized set of mixing parameters. In our method, we assume that our KS wave function is the zeroth-order wave function in the GL perturbation theory that gives the correct ground-state electron density. Instead, MC3BB is a multicoefficient method, which mixes the total energies from the conventional MP2 and a conventional DFA calculation. Hence there are two independent SCF calculations in the MC3BB type of

DHDFs, which lead to two sets of different orbitals, yielding two different densities. In MC3BB, the SCF-HF orbitals are used for MP2 evaluation (14), while it is well known that HF wave function is the one-determinantal wave function which gives the lowest expectation value with the fully interacting Hamiltonian. It has been shown recently (23) that the B2PLYP family of functionals works in a way which is technically similar to MP2. These functionals adopt orbitals that minimize the one-determinantal wave function based on the so-called density-scaled one parameter hybrid approximation. Hence, the density from the B2PLYP type of functionals is by construction not meant to be the true density. In contrast to what was originally proposed (15), there is no singles' contribution by construction in the B2PLYP family of functionals, and its theoretical basis is provided by the multidefinant extension of the Kohn-Sham scheme (23). On the other hand, the key idea of the XYG3 type of functionals is to combine the GL perturbation theory and the standard KS scheme in the framework of ACM. In XYG3, only the energetically most important double excitation PT2 term in Eq. 2 is calculated explicitly using orbitals generated from a conventional DFA in [1]. Our present OS ansatz further reduces the computational cost by only calculating the most important electron correlation effects contributed by the OS electrons in the same orbital. XYGJ-OS presents a unique combination of speed and accuracy. Hence, we propose that the current DHDFs shall be categorized into three types (13), as represented by MC3BB (14), B2PLYP (15), and XYG3 (12). The former two go beyond the KS scheme.

It is possible to carry out a SCF calculation for any orbital-dependent E_{xc} using, for example, the direct optimization approach to compute the optimized effective potential (OEP) as proposed by Yang and coworkers (40). It was found that such a SCF procedure can often lead to unphysically unbound state with too low total energy mainly due to the near-degeneracy of the orbitals in the single excitation terms. This unbound issue can be largely remedied by calculating only the double excitation terms in the post-SCF manner (40). This procedure is indeed the calculation approach adopted by the XYG3 type of functionals. Furthermore, we note that extra terms will appear when formu-

lating the analytical gradients for doing geometry optimization with our functionals, which, however, will not impose any practical difficulty in implementation as compared to other types of DHDFs.

We find that XYGJ-OS is remarkably accurate for a broad range of systems and important chemical properties (1, 2, 41–45) other than HOF which are *not used in fitting the parameters*. Table 1 (more details are in *SI Text*) compares the overall performance of some representative DFT methods, showing that XYGJ-OS is the best or nearly best for essentially all properties, leading to chemical accuracy (1.28 kcal/mol) comparable to the G3 theory (which contains four empirical parameters involving the number of electron pairs) (1.06) and much better than MP2 (7.49 kcal/mol).

Heats of Formation. The 223 molecule G3/99 set (1, 2) provides a test of accuracy for the main group covalent systems. XYGJ-OS gives mean absolute deviation (MAD) of 1.65 kcal/mol, lying between those of G2 (1.89) and G3 (1.06) theories. Note that the MADs for HOF listed in Table 1 associated with XYG3, B2PLYP, B2PLYP-D, and ω B97X-2(LP) are taken from the original refs. 12, 17, 22, which were obtained by using the way these functionals were parameterized. It was shown that HOF calculations with DHDFs are most prone to the basis set effects (29). The results with the G3Large basis set (1) used for optimization of the XYGJ-OS functional can be found in *SI Text*, where severe basis set dependences are clearly shown.

Charged Species. Charged species are not included in our training set. The G2-1 set (2) for ionization potential (IP) contains 14 atoms and 24 molecules. XYGJ-OS gives a MAD of 1.23 kcal/mol, being one of the best DFT methods for calculating IP. Over the 25 cases in the G2-1 set for electron affinity (EA) (2), XYGJ-OS leads to MAD = 1.97 kcal/mol. Generally, increasing the size of the basis set will increase the accuracy for EA calculation with DHDFs. For the eight systems for proton affinity in the G2 and G3 sets (1), XYGJ-OS leads to MAD = 1.68 kcal/mol, comparable to the performance of conventional DFAs.

Table 1. MAD, (in kcal/mol) for various benchmarks

Methods	HOF (223)	IP (38)	EA (25)	PA (8)	BDE (92)	NHTBH (38)	HTBH (38)	NCIE (31)	All (493)	Time*	
										C ₁₀₀ H ₂₀₂	C ₁₀₀ H ₁₀₀
<i>DFT methods</i>											
SVWN (LDA)	130.88	15.14	17.30	5.68	18.14	12.53	17.95	3.29	67.28		
BLYP	10.16	6.02	2.47	1.75	7.00	8.29	7.68	1.49	7.84		
PBE	20.71	5.13	2.40	1.56	3.91	8.57	9.48	1.17	12.10		
TPSS	5.01	5.36	2.41	1.66	5.88	9.04	8.26	1.14	5.33		
B3LYP	6.08	3.74	2.45	1.40	5.51	4.84	4.26	0.98	4.98	2.8	12.3
B3LYP-D3	4.15	3.77	2.47	1.18	4.29	5.17	4.97	0.64	3.93		
PBE0	5.64	3.84	2.97	1.25	3.67	3.56	4.38	0.71	4.36		
M06-2X	2.26	2.72	2.37	1.94	1.40	1.26	1.25	0.28	1.86		
XYG3 [†]	1.81	1.31	1.84	1.61	1.57	1.29	0.75	0.32	1.51	200.0	81.4
XYGJ-OS	1.65	1.23	1.97	1.68	0.71	1.18	0.88	0.35	1.28	7.8	46.4
MC3BB	3.28	2.78	4.01	1.03	2.43	1.44	0.80	0.58	2.58		
B2PLYP [‡]	2.74	2.48	2.15	1.52	2.95	2.23	1.73	0.55	2.45		
B2PLYP-D [‡]	1.67	2.48	2.15	1.34	2.27	2.47	2.11	0.45	1.88		
ω B97X-2(LP) [§]	1.52	1.73	1.56	1.09	1.62	1.67	0.74	0.47	1.44		
<i>Wavefunction based methods</i>											
HF	213.42	23.19	26.46	3.09	32.70	9.08	13.51	2.37	107.71		
MP2	10.63	3.49	3.59	2.13	7.73	5.42	3.91	0.60	7.49		
G2	1.89	0.97	1.31	1.34	1.80	0.97	1.24	0.57	1.56		
G3	1.06	1.27	1.13	1.06	1.08	0.97	1.24	0.57	1.06		

HOF is heat of formation (1, 2), IP is ionization potential (2), EA is electron affinity (2), PA is proton affinity (2), BDE is bond dissociation energy (40), NHTBH and HTBH are barrier heights for reactions (42, 43), NCIE is the binding in molecular clusters (42, 43). The basis sets used for final energetics are G3Large unless otherwise stated. See *SI Text* for computational details.

*The time is single CPU hours on 2.5 GHz Xeon for linear alkane C₁₀₀H₂₀₂ and the C₁₀₀H₁₀₀ diamond structure. The basis sets used are cc-pVDZ.

[†]Taken from ref. 12 with 6-311+G(3df,2p).

[‡]HOF are taken from ref. 22 with very large basis set of CQZV3P. BDEs are calculated using the corresponding HOF.

[§]Taken from ref. 17 or calculated with 6-311++G(3df,3pd). BSSE corrections are included for the NCIE set.

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