

Calculations of ionization energies and electron affinities for atoms and molecules: A comparative study with different methods

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In the present work, we examined the performance of 36 density functionals, including the newly developed doubly hybrid density functional XYG3 (Y. Zhang, X. Xu, and W. A. Goddard III, *Proc. Natl. Acad. Sci. USA*, 2009, 106, 4963), to calculate ionization energies (IEs) and electron affinities (EAs). We used the well-established G2-1 set as reference, which contains 14 atoms and 24 molecules for IE, along with 7 atoms and 18 molecules for EA. XYG3 leads to mean absolute deviations (MADs) of 0.057 and 0.080 eV for IEs and EAs, respectively, using the basis set of 6–311+ G (3df,2p). In comparison with some other functionals, MADs for IEs are 0.109 (B2PLYP), 0.119 (M06-2X), 0.159 (X3LYP), 0.161 (PBE), 0.162 (B3LYP), 0.165 (PBE0), 0.173 (TPSS), 0.200 (BLYP), and 0.215 eV (LC-BLYP). MADs for EAs are 0.090 (X3LYP), 0.090 (B2PLYP), 0.102 (PBE), 0.103 (M06-2X), 0.104 (TPSS), 0.105 (BLYP), 0.106 (B3LYP), 0.126 (LC-BLYP), and 0.128 eV (PBE0).

Keywords ionization energy, electron affinity, DFT, XYG3, B3LYP

1 Introduction

Ionization energy (IE) is defined as the 0 K enthalpy change for the electron detachment reaction, i.e., the energy required to remove an electron from an atom or a molecule [1]:

$$M \rightarrow M^+ + e^-; IE = \Delta_f H_{0K}^\square(M^+) - \Delta_f H_{0K}^\square(M) \quad (1)$$

Analogously, electron affinity (EA) is defined as the negative of the 0 K enthalpy change for the electron attachment reaction [1]:

$$M + e^- \rightarrow M^-; EA = \Delta_f H_{0K}^\square(M) - \Delta_f H_{0K}^\square(M^-) \quad (2)$$

Our present work deals with the adiabatic IEs and EAs, which correspond to the energy differences between the lowest energy states of the neutral species and the corresponding ionic ones.

IE and EA are essential molecular properties [2–5] which define many useful concepts such as electronegativity [6], chemical potential [7], hardness and softness [8], as well as electrophilicity and nucleophilicity [9], etc. IE and EA are of fundamental importance in assessing the electron donating and accepting abilities of a system involved in any redox processes and have been widely employed in understanding the electron transfer and proton transfer processes occurring in gas phase or in condensed phase [10–13]. They are also of great significance in setting up structure-reactivity relationships to aid the design of new materials [14–17].

Many theoretical studies [10–30] have been devoted to the determination of IEs and EAs of atoms or molecules. Nevertheless, accurate calculations of IEs and EAs still present a challenge, as electron detachment and attachment will always lead to change of the spin state of the system, and the theoretical method employed has to be able to treat the charged/neutral (open-shell/closed-shell or vice versa) species on an equivalent footing. For atoms and small molecules made of light elements, highly accurate results can be obtained by using high level wave function based approaches such as W1/W2 [20], $Gn(n = 1-4)$ [21–24], and CBS-QB3 [25,26]. These are coupled-cluster based methods, which scale on the order of N^7 , where N measures the system size. Such methods are not yet available for the routine use of larger molecules.

Density functional theory (DFT) offers a very attractive alternative [10–17,27–30] due to its lower scaling on the system size (generally $N^3 \sim N^4$), being tractable to much larger systems. Early assessment was focused on some new functionals at that time such as BLYP [31,32], BP86 [31,33], BPW91 [31,34], B3LYP [31,32,35–38], B3P86 [31,33,35–38], B3PW91 [31,34–38], giving positive impact on the applications of these DFT methods to calculate IEs and EAs of a wide range of systems [10–17,27–30].

Over decades, new generation of density functionals have appeared. These include the so-called meta-generalized gradient approximation (meta-GGA) functionals [39–43], range-separated functionals [44–49], dispersion corrected

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functionals [49–51], and doubly hybrid density functionals (DHDFs) [47,51–58], etc. It is hoped that higher level of accuracy and therefore greater reliability can be achieved for IE and EA calculations with these new functionals. The task of the present work is to give a systematic assessment of the new generation functionals, highlighting the importance of DHDFs for such applications.

The paper is organized as follows. In Section 2, we briefly describe the computational details. In Sections 3 and 4, we test the performances of 36 functionals for the prediction of IE and EA, respectively, using the well-established G2-1 set where accurate experimental results are available. Results from some *ab initio* methods are also included for comparison. Finally, a summary is given in Section 5.

2 Computational details

Perdew has formulated the hierarchy of various DFT approximations as a “Jacob’s ladder” rising from the “earth of Hartree” to the “heaven of chemical accuracy” [59]. We tested here the performance of some representative functionals of each rung. They are the first rung functionals, SVWN and SVWN5 [35,36], based on the local density approximation (LDA) whose energy density depends only on the value of the density at the very same point for evaluation. The second rung functionals, BLYP [31,32], PW91 [34], PBE [60], BPW91 [31,34], BP86 [31,33], LC-BLYP [44], HCTH407 [61] were constructed based on the generalized gradient approximation (GGA) by using density and its gradients; the third rung is meta-GGA which adds further ingredients of the Laplacian of the density and/or the kinetic energy density. The meta-GGAs tested in this work include: VSXC [39] TPSS [40], M06-L [41], and tHCTH [42]. The forth rung functional was pioneered by B3LYP [31,32,35–38]. This so-called hybrid GGA functional has enjoyed immense popularity since its proposition. It was constructed by introducing Hartree-Fock (HF) like exchange as additional ingredient. There are a large collection of hybrid functionals being available up to now. Some representatives were tested in this work for their performances on IE and EA predictions. These include B3P86 [33,37], B3PW91 [37], B98 [43], LC- ω PBE [45], CAM-B3LYP [46], ω B97X [48], ω B97X-D [49], B97-D [50], BHHLYP [32,62], X3LYP [63,64], PBE0 [65,66], O3LYP [67,68], B97-1 [69], TPSSH [70], HSE06 [71], M06 [72], and M06-2X [72]. A new generation of functionals, DHDFs, have emerged recently. These functionals not only have an HF like component in the exchange part, but also incorporate an MP2 like component in the correlation part, lying on the top rung (the fifth rung) of Perdew’s Jacob’s ladder. There are three types of DHDFs

[73], represented by MC3BB [53], B2PLYP [54], and XYG3 [52], respectively. They differ by how the functionals are constructed, or technically which orbitals and density are used to evaluate each energy component [73]. In addition to these three DHDFs, we tested also other two DHDFs, i.e., B2PLYP-D [51], and B2GP-LYP [55].

Note that the functionals with their names ended with -D are the dispersion corrected methods [49–51], while the functionals with their names containing ω are the range-separated methods [45,47–49]. LC- and CAM-, as well as HSE [71], also stand for the range-separated methods [44–46]. We also included results from some wave function based methods, HF, UMP2, MP4SDQ, and QCISD(T), for comparison.

For IEs, and EAs calculations (at 0 K), the so-called G2-1 set [22,23,27] was used as references. They were calculated as energy differences between the neutral species and the corresponding ionic species according to Eq. (1) and Eq. (2), respectively. As in the G2 and G3 methods [22,23,27], the geometries were optimized using MP2(full) with the 6-31G(d) basis set. Analytical vibrational frequencies were calculated at the level of HF/6-31G(d) and scaled by 0.8929 to estimate zero-point energies. Single point DFT calculations were performed with the 6-311 + G(3df,2p) basis set. This is the target basis set of the G2 method [22,27] and has been frequently used for DFT functional evaluations [27,39,52, 63,64,66,68,73].

All calculations reported in this paper were performed using the Gaussian 09 suite of program [74].

3 Calculations of ionization energies

Table 1 lists the experimental IEs [22,23,27] and the theoretical deviations of 11 popular methods for 14 atoms and 24 molecules in the G2-1 set. The statistics for the total 38 systems of 36 DFT methods and 4 *ab initio* methods are presented in Table 2. We note that some results have appeared in the literature for some functionals [27,39,52,63,64,66, 68,73]. Our present results essentially confirm the previous ones when available.

Generally, charged species are more inhomogeneous than the corresponding neutral systems. Thus it is expected that LDA leads to the worst results for IE calculations. This is indeed true for SVWN, but not necessary so for SVWN5. This reflects the important role played by the correlation functional and presents a vivid example that the IE performances of these two related functionals [36] differ dramatically. Previously, Curtiss et al. [27] and Ernzerhof and Scuseria [66] have independently examined the LDA performance for charged species and have reached different conclusions. While the

Table 1 Experimental ionization energies ^{a)} (IEs, eV) at 0 K and theoretical errors ^{b)} for the G2-1 Set (38 systems)

Species	Expt.	BLYP	B3LYP	PBE	PBE0	TPSS	TPSSH	M06-L	M06-2X	XYG3	MP2	QCISD(T)
Li	5.39	-0.13	-0.23	-0.18	-0.17	-0.10	-0.09	0.36	-0.01	-0.07	0.04	0.03
Be	9.32	0.34	0.20	0.32	0.34	0.25	0.25	0.44	0.25	0.17	0.50	0.03
B	8.3	-0.33	-0.44	-0.37	-0.34	-0.45	-0.44	-0.31	-0.02	-0.15	0.02	0.07
C	11.26	-0.15	-0.29	-0.28	-0.26	-0.19	-0.19	-0.18	-0.07	-0.06	-0.01	0.06
N	14.54	0.03	-0.13	-0.20	-0.17	-0.13	-0.13	-0.26	-0.03	0.03	-0.07	0.04
O	13.61	-0.56	-0.55	-0.46	-0.25	-0.42	-0.34	-0.25	-0.11	-0.06	0.28	0.20
F	17.42	-0.32	-0.34	-0.26	-0.06	-0.02	0.04	-0.07	-0.14	0.01	0.10	0.15
CH ₄	12.62	0.25	0.06	0.24	0.22	0.24	0.23	0.09	0.05	0.01	0.07	0.06
NH ₃	10.18	0.06	-0.01	0.01	0.15	0.21	0.24	0.11	-0.02	0.06	0.03	0.12
OH	13.01	-0.18	-0.23	-0.16	0.01	0.09	0.13	0.03	-0.04	0.00	0.09	0.15
H ₂ O	12.62	0.07	0.00	0.03	0.17	0.22	0.26	0.17	0.02	0.04	-0.07	0.13
HF	16.04	0.00	-0.06	-0.03	0.14	0.16	0.21	0.13	0.04	0.02	-0.13	0.09
Na	5.14	-0.21	-0.28	-0.21	-0.14	-0.03	-0.01	0.64	-0.01	-0.06	0.07	0.05
Mg	7.65	0.02	-0.08	0.03	0.11	0.11	0.12	0.14	-0.12	0.02	0.31	0.07
Al	5.98	0.11	-0.04	-0.09	-0.11	-0.17	-0.17	0.11	0.20	0.06	0.18	0.06
Si	8.15	0.21	0.04	-0.05	-0.07	-0.07	-0.08	0.10	0.16	0.09	0.12	0.06
P	10.49	0.31	0.11	0.00	-0.04	-0.02	-0.03	-0.04	0.18	0.09	0.03	0.06
S	10.36	-0.05	-0.19	-0.07	-0.04	-0.10	-0.08	0.17	-0.05	0.04	0.42	0.27
Cl	12.97	0.06	-0.10	-0.01	0.01	0.01	0.02	0.11	-0.03	0.04	0.25	0.26
SiH ₄	11	0.33	0.09	0.30	0.20	0.17	0.15	-0.06	0.28	0.00	0.21	0.11
PH	10.15	0.17	-0.02	-0.10	-0.14	-0.12	-0.13	-0.05	0.04	0.01	0.04	0.06
PH ₂	9.82	0.06	-0.12	-0.17	-0.20	-0.18	-0.20	-0.05	0.01	-0.04	0.07	0.08
PH ₃	9.87	0.15	0.03	0.09	0.14	0.14	0.15	0.06	0.12	0.08	0.21	0.11
HS	10.37	0.05	-0.10	-0.02	0.01	0.01	0.02	0.09	-0.01	0.01	0.21	0.18
H ₂ S(² B ₁ cation)	10.47	0.20	0.04	0.09	0.12	0.12	0.13	0.14	0.03	0.06	0.14	0.17
H ₂ S(² A ₁ cation)	12.78	0.30	0.12	0.22	0.20	0.19	1.73	0.22	0.15	0.07	0.14	0.16
HCl	12.75	0.17	0.00	0.06	0.07	0.09	0.09	0.07	-0.01	0.02	0.08	0.17
C ₂ H ₂	11.4	0.28	0.16	0.16	0.25	0.31	0.32	0.30	0.14	0.01	-0.08	0.10
C ₂ H ₄	10.51	0.23	0.15	0.10	0.23	0.28	0.31	0.20	0.21	0.08	0.02	0.06
CO	14.01	0.10	-0.13	0.14	0.08	0.15	0.12	0.33	-0.04	0.01	-0.18	0.12
N ₂ (² Σ cation)	15.58	0.22	-0.27	0.20	-0.18	0.19	0.04	0.08	-0.57	0.20	0.27	0.13
N ₂ (² Π cation)	16.7	0.27	0.07	0.15	0.16	0.29	0.28	0.23	-0.03	-0.12	-0.32	0.13
O ₂	12.07	-0.40	-0.79	-0.38	-0.68	-0.41	-0.53	-0.59	-0.82	-0.16	0.35	-0.11
P ₂	10.53	0.39	0.21	0.18	0.17	0.16	0.16	-0.25	-0.54	-0.07	-0.08	0.13
S ₂	9.36	0.08	-0.23	-0.10	-0.29	-0.16	-0.23	-0.10	-0.25	-0.04	0.14	0.08
Cl ₂	11.5	0.43	0.11	0.34	0.15	0.30	0.22	0.28	-0.06	0.01	0.11	0.14
ClF	12.66	0.33	0.05	0.29	0.16	0.27	0.21	0.23	-0.08	0.05	0.03	0.16
SC	11.33	0.06	-0.11	0.03	0.03	0.04	0.04	0.27	-0.01	-0.07	-0.69	0.05

a) Experimental data are from Refs. [22,23,27];

b) Error = (Expt. - Calc.)

former used SVWN, the latter calculations were based on SVWN5. As shown in Table 2, the mean absolute deviation (MAD) for IEs in the G2-1 set is 0.663 eV for SVWN and 0.224 eV for SVWN5, the latter being 0.44 eV (or 10.1 kcal/mol) better than the former.

Starting from that of SVWN, one may see that the second rung functionals of GGAs dramatically improve the prediction of IEs over LDA. Actually, GGAs on average give an MAD of 0.22 eV, being close to that of SVWN5, while PBE and PW91 give an MAD around 0.16 eV, which are slightly

better. If one compares the performance of PW91 and BPW91, the former is 0.06 eV (or 1.5 kcal/mol), better than the latter, suggesting that the exchange functional also plays a role in IE prediction. As ionization may create or quench a singly occupied orbital, the IE error may therefore be related to the self-interaction error [75] which differs on the amount between the neutral and the corresponding charged species. Hence, one sees, from Table 2, a steady improvement for IE prediction along the ladder up to hybrid functionals, possibly due to the mitigation of the self-interaction error because of

Table 2 Statistic theoretical errors ^{a)} for ionization energies (IEs, eV) at 0 K for the G2-1 Set (38 systems)

		MAD ^{b)}	AD ^{c)}	RMS ^{d)}	Max + ^{e)}	Max - ^{f)}
1st Rung	SVWN	0.663	-0.663	0.698	NA ^{g)}	-1.15 (F→F ⁺)
	SVWN5	0.224	-0.175	0.269	0.30 (Be→Be ⁺)	-0.56(O ₂ →O ₂ ⁺)
2nd Rung	BLYP	0.200	0.078	0.240	0.43(Cl ₂ →Cl ₂ ⁺)	-0.56(O→O ⁺)
	PBE	0.161	-0.004	0.200	0.34(Cl ₂ →Cl ₂ ⁺)	-0.46(O→O ⁺)
	PW91	0.165	-0.059	0.209	0.29(Cl ₂ →Cl ₂ ⁺)	-0.53(O→O ⁺)
	BPW91	0.229	0.064	0.377	1.71 (H ₂ S→H ₂ S + ² A ₁)	-0.46(O→O ⁺)
	BP86	0.231	-0.040	0.367	1.60 (H ₂ S→H ₂ S + ² A ₁)	-0.63(O→O ⁺)
	HCTH407	0.245	-0.083	0.380	1.57 (H ₂ S→H ₂ S + ² A ₁)	-0.61(N→N ⁺)
3rd Rung	LC-BLYP	0.215	-0.149	0.298	0.26 (Be→Be ⁺)	-0.92(O ₂ →O ₂ ⁺)
	M06-L	0.193	0.077	0.239	0.64 (Na→Na ⁺)	-0.59(O ₂ →O ₂ ⁺)
	TPSS	0.173	0.037	0.205	0.31(C ₂ H ₂ →C ₂ H ₂ ⁺)	-0.45(B→B ⁺)
	VSXC	0.192	0.046	0.346	1.64 (H ₂ S→H ₂ S + ² A ₁)	-0.33(N→N ⁺)
4th Rung	tHCTH	0.220	-0.023	0.365	1.62 (H ₂ S→H ₂ S + ² A ₁)	-0.50(Mg→Mg ⁺)
	B3LYP	0.162	-0.087	0.226	0.20 (Be→Be ⁺)	-0.79(O ₂ →O ₂ ⁺)
	X3LYP	0.159	-0.040	0.214	0.24 (Be→Be ⁺)	-0.76(O ₂ →O ₂ ⁺)
	PBE0	0.165	-0.001	0.204	0.34 (Be→Be ⁺)	-0.68(O ₂ →O ₂ ⁺)
	B3PW91	0.159	-0.056	0.208	0.32 (Be→Be ⁺)	-0.72(O ₂ →O ₂ ⁺)
	B3P86	0.616	-0.616	0.646	NA ^{g)}	-1.28(O ₂ →O ₂ ⁺)
	BHHLYP	0.213	0.076	0.281	0.47(C ₂ H ₄ →C ₂ H ₄ ⁺)	-0.99(O ₂ →O ₂ ⁺)
	TPSSH	0.214	0.074	0.347	1.73 (H ₂ S→H ₂ S + ² A ₁)	-0.53(O ₂ →O ₂ ⁺)
	O3LYP	0.141	0.037	0.180	0.30(SiH ₄ →SiH ₄ ⁺)	-0.57(O ₂ →O ₂ ⁺)
	B98	0.130	-0.024	0.178	0.24 (Be→Be ⁺)	-0.71(O ₂ →O ₂ ⁺)
	HSE06	0.166	0.004	0.206	0.34 (Be→Be ⁺)	-0.68(O ₂ →O ₂ ⁺)
	CAM-B3LYP	0.165	-0.097	0.238	0.22(P ₂ →P ₂ ⁺)	-0.85(O ₂ →O ₂ ⁺)
	LC-ωPBE	0.194	-0.111	0.255	0.29 (Be→Be ⁺)	-0.70(O ₂ →O ₂ ⁺)
	B97-1	0.130	0.015	0.169	0.29 (Be→Be ⁺)	-0.62(O ₂ →O ₂ ⁺)
	B97-D	0.161	0.057	0.200	0.35(Cl ₂ →Cl ₂ ⁺)	-0.52(O ₂ →O ₂ ⁺)
	ωB97X	0.135	0.007	0.187	0.46 (Be→Be ⁺)	-0.63(O ₂ →O ₂ ⁺)
	ωB97X-D	0.132	-0.006	0.187	0.49 (Be→Be ⁺)	-0.67(O ₂ →O ₂ ⁺)
	M06-2X	0.119	-0.011	0.196	0.28(SiH ₄ →SiH ₄ ⁺)	-0.82(O ₂ →O ₂ ⁺)
	M06	0.159	0.027	0.211	0.39 (Be→Be ⁺)	-0.76(O ₂ →O ₂ ⁺)
5th Rung	XYG3	0.057	0.010	0.075	0.20(N₂→N₂⁺, ²Σ_g)	-0.16(O₂→O₂⁺)
	MC3BB	0.120	0.070	0.150	0.42 (Be→Be ⁺)	-0.40(O ₂ →O ₂ ⁺)
	B2PLYP	0.109	0.049	0.130	0.31 (Be→Be⁺)	-0.31(O₂→O₂⁺)
	B2PLYP-D	0.110	0.054	0.131	0.31 (Be→Be ⁺)	-0.31(O ₂ →O ₂ ⁺)
	B2GP-PLYP	0.101	0.050	0.123	0.33 (Be→Be⁺)	-0.31(O₂→O₂⁺)
<i>Ab initio</i>	HF	1.005	0.954	1.135	1.82 (Be→Be ⁺)	-0.84(O ₂ →O ₂ ⁺)
	UMP2	0.163	0.077	0.218	0.50 (Be→Be ⁺)	-0.69 (CS→CS ⁺)
	MP4SDQ	0.150	0.116	0.173	0.33 (S→S ⁺)	-0.38 (CS→CS ⁺)
	QCISD(T)	0.111	0.106	0.125	0.27 (S→S ⁺)	-0.11 (CS→CS ⁺)

a) Experimental data are from Refs. [22,23,27]. The best three are in the bold face; b) Mean absolute deviations; c) Averaged deviations (Expt. – Calc.); d) Root-mean-square errors; e) Maximum positive deviations; f) Maximum negative deviations; g) Not applicable

the introduction of the HF exchange. The majority of the 4th rung functionals give an MAD around 0.16 eV, while some hybrid functionals, (e.g., B97-1, ωB97X and ωB97X-D) give an MAD around 0.13 eV. M06-2X is outstanding, giving an MAD of only 0.119 eV for the G2-1 set. B3P86 is a surprising failure, whose MAD is as high as 0.616 eV! The -D

functionals do not affect the accuracy of the calculated IEs as compared to the corresponding precedents without -D. Interestingly, it is found that the LC scheme does not necessary help to improve the numerical accuracy for IE prediction (e.g., BLYP (0.200 eV) vs. LC-BLYP (0.215 eV) and B97-1 (0.130 eV) vs. ωB97X (0.135 eV), shown in Table

2). As it should be expected, the 5th rung functionals should further improve the accuracy because of the further improvement on the correlation part. Indeed, all DHDFs give MADs below 0.12 eV. Significantly, XYG3 gives an MAD of only 0.057 eV for the G2-1 set.

It is worthwhile to make a comparison with the IE performances of the wave function based methods. Clearly, HF (MAD = 1.005 eV) is useless for the IE prediction, emphasizing again the importance of correlation effects. MP2 has dramatically reduced MAD to 0.163 eV, which has been further reduced to 0.150 eV for MP4SDQ and to 0.111 eV for QCISD(T). It should be emphasized that basis set requirement is generally higher for wave function based methods. With larger basis set than 6-311 + G(3df,2p) used here, we expect that QCISD(T) will lead to more satisfactory results, albeit at higher expense.

Very accurate experimental IEs for atoms are known, providing a good test for the ability of the functionals to handle the positively charged systems. For 14 atomic systems listed in Table 1, MADs are 0.181 (PBE), 0.151 eV (PBE0), 0.147 (TPSS), and 0.142 (TPSSh). Results from the popular functionals BLYP and B3LYP are actually not very satisfactory, giving MADs = 0.201 and 0.216 eV, respectively. Results from the recently developed M06-2X is quite good, giving MAD of only 0.099 eV. In accordance with the general trend, the performance degrades from M06-2X to M06-L for a lack of the HF exchange. MAD for the latter is 0.226 eV. DHDFs, although at a similar cost of MP2, whose MAD is 0.173 eV, are better performers. In particular, XYG3 is outstanding, giving an MAD of only 0.066 eV.

For 24 molecular systems, MADs for IE calculations are generally smaller than those for atomic IE calculations using the corresponding functionals. The exceptions are those of M06-2X, PBE0, TPSS, TPSSh, which perform worse in molecular IE calculations. MADs are 0.131 (B3LYP), 0.173 (PBE0), 0.256 (TPSSh), 0.149 (M06-2X) and 0.052 eV (XYG3). As shown in Table 2, IE of O₂ is a problematic case for many functionals. The MP2 geometry for O₂ is very bad ($R_{\text{OO}} = 1.246 \text{ \AA}$ rather than the experimental value of 1.207 Å [76]), which partly accounts for this error.

Figure 1 shows the histogram of deviations (Expt. – Calc.) for 38 IEs in the G2-1 set. They are on average the best functionals currently available for IE predictions. B3LYP errors actually scatter around a wide range with more negative deviations, indicating that neutral species are substantially overbound relative to the ions. Errors on B98, ω B97X-D and M06-2X are more evenly distributed, although ions are directly involved in the training sets to optimize the parameters in the functionals, and there still exist some outliers. The good behaviors with DHDFs are clearly displayed in Fig. 1. Outstandingly, 25 out of 38 entries are

within the 0.0 to 0.1 eV error range for XYG3, showing the predictive power of this functional. We emphasize that ions were not included in the training set for XYG3. The three mixing parameters in XYG3 were optimized by using only heats of formation of the G3 set where all species are neutral.

4 Calculations of electron affinities

Even though the actual numerical performances demonstrate that DFT methods predict electron affinities with an accuracy comparable to, or even better than, conventional *ab initio* calculations with the same basis set of reasonably large size [27,39,52,63,64,66,68,73,77], there has been debate in the literature, concerning whether conceptually DFT methods are suitable for calculating electron affinities [28,66,78,79]. It has been argued that two artifacts combine fortunately in the right way for error cancellation. On one hand, the ‘self-interaction error’ causes the Kohn-Sham orbital energies to be shifted upwards artificially, leading to a positive (unstable) orbital energy for the highest occupied orbital of the anion. On the other hand, an artificial stabilization is provided by employing a finite basis set with functions localized at the anion. This debate continues [80].

Table 3 lists the experimental EAs [22,23,27] and the theoretical deviations of 11 popular methods for 7 atoms and 18 molecules in the G2-1 set. The statistics for the total 25 systems of 36 DFT methods and 4 *ab initio* methods are presented in Table 4. And the histograms of deviations (Expt. – Calc.) for 6 best functionals for EA predictions are displayed in Fig. 2, which are compared with those of wave function methods MP2 and QCISD(T).

As with IE calculations, SVWN and SVWN5 also show dramatically different behaviors for EA calculations. SVWN displays an MAD = 0.750 eV, significantly worse than MAD = 0.289 eV associated with SVWN5. Unlike IE performance for DFT methods, data in Table 4 clearly demonstrate that GGAs and meta-GGAs can considerably improve the predictions of EAs over LDA. The best GGA and meta-GGAs lead to MADs of 0.094 (BPW91) and 0.104 eV (TPSS, VSXC). Some hybrid functionals (e.g., B98, ω B97X-D) and DHDFs (e.g., XYG3) can still improve the accuracy to some amount, giving MADs around 0.08 eV. Note that, even though B3P86 was found to be better than B3LYP for bond dissociation energy calculations [81], which also involves energy difference between closed shell and open shell species, this functional is of little practical value for EA calculations with MAD = 0.595 eV.

It has been argued that DFTs should perform better in EA calculations for molecules than for atoms, as molecules have larger spaces to delocalize the extra electrons [78]. This argument seems to be supported only by low rung functionals

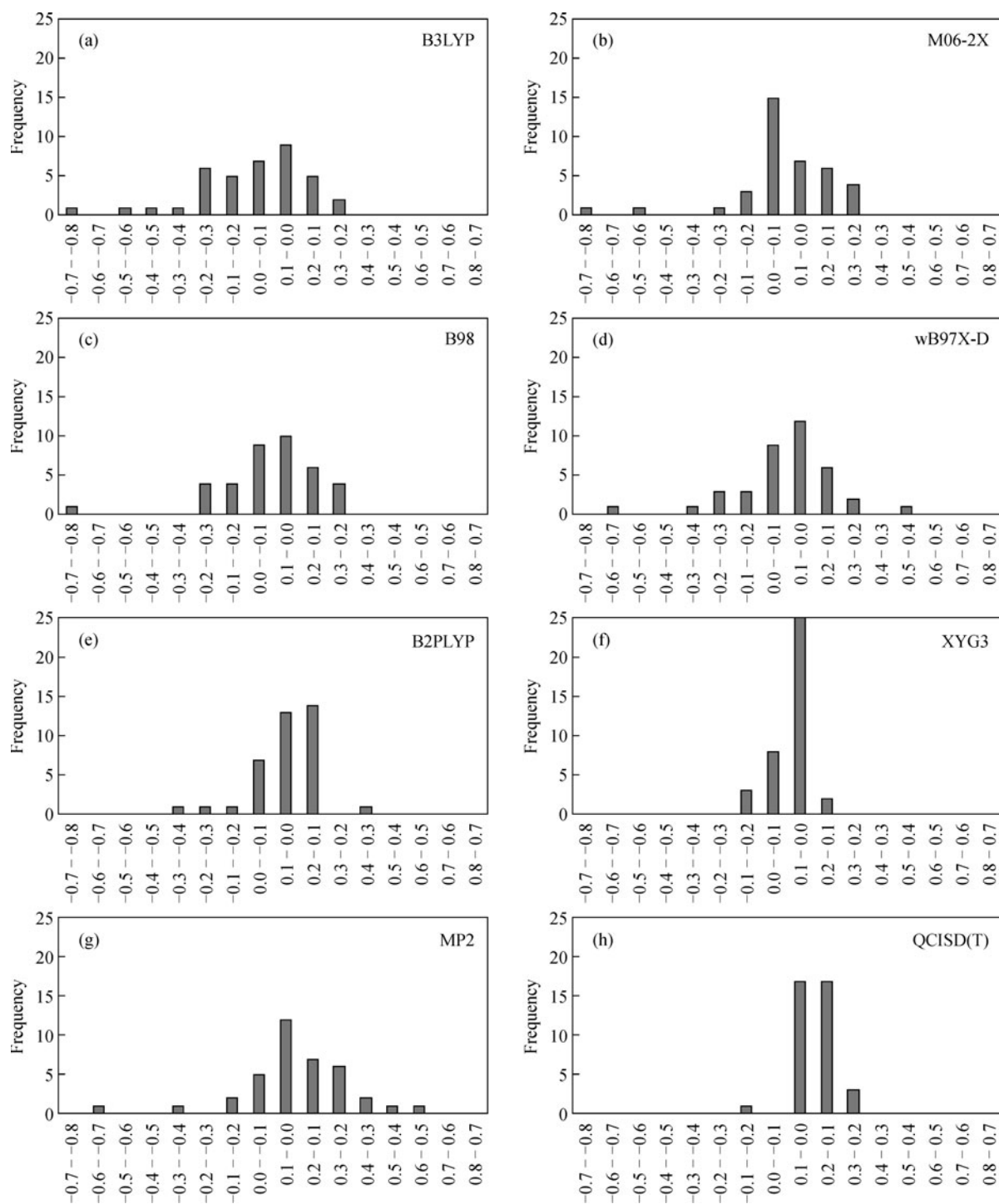


Figure 1 Histogram of deviations (Expt. – Calc.) for 38 ionization energies (IEs) in the G2-1 set. Each vertical bar represents deviations in a 0.1 eV range.

of LDAs and GGAs, as well as two hybrid functionals (i.e., B3P86 and BHHLYP), which do not have good performance for EA calculations. All other functionals listed in Table 4 show a better performance in atomic systems than that in the molecular systems. For example, TPSS yields MAD = 0.060 eV for atoms and 0.121 eV for molecules, and TPSSH gives

MAD = 0.089 eV for atoms and 0.146 eV for molecules. Many functionals perform significantly better for the second row atoms than for the first row atoms. Hence, MADs with TPSSH are 0.160 and 0.035 eV for EAs of the first row and the second row atoms, respectively. Performances of some high rung functionals (e.g., B3LYP, M06, B2PLYP) do not fit into

Table 3 Experimental electron affinities ^{a)} (EAs, eV) at 0 K and theoretical errors ^{b)} for the G2-1 Set (25 systems)

Species	Expt.	BLYP	B3LYP	PBE	PBE0	TPSS	TPSSh	M06-L	M06-2X	XYG3	MP2	QCISD(T)
C	1.26	-0.06	-0.10	-0.29	-0.14	-0.17	-0.12	-0.07	0.02	0.13	0.01	0.06
CH	1.24	-0.08	-0.12	-0.29	-0.15	-0.14	-0.10	-0.01	0.01	0.07	0.01	0.10
CH ₂	0.65	-0.16	-0.13	-0.11	0.11	0.11	0.17	0.13	0.16	0.06	0.22	0.13
CH ₃	0.08	0.05	0.06	0.01	0.22	0.19	0.25	0.20	0.14	0.16	0.17	0.20
NH	0.38	-0.13	-0.07	-0.10	0.18	0.16	0.24	0.16	0.18	0.12	0.19	0.23
NH ₂	0.74	0.00	0.04	-0.03	0.23	0.17	0.25	0.30	0.13	0.06	-0.05	0.16
O	1.46	-0.24	-0.14	-0.20	0.14	0.05	0.17	0.18	0.15	0.11	0.14	0.22
OH	1.83	-0.01	0.06	-0.03	0.29	0.19	0.29	0.37	0.24	0.07	-0.11	0.19
F	3.4	-0.16	-0.06	-0.14	0.22	0.07	0.19	0.28	0.25	0.08	-0.14	0.16
O ₂	0.44	-0.06	-0.12	0.04	0.16	0.04	0.09	0.26	0.07	0.07	0.21	0.13
NO	0.02	-0.23	-0.30	-0.22	-0.14	-0.19	-0.16	-0.10	-0.09	-0.03	0.19	0.08
CN	3.82	0.00	-0.21	0.00	-0.05	0.06	0.03	0.18	-0.17	-0.07	-0.78	-0.00
Si	1.38	0.19	0.06	-0.08	-0.06	-0.03	-0.02	0.04	0.14	0.12	0.03	0.04
P	0.75	-0.12	-0.19	-0.10	-0.01	-0.07	-0.03	0.07	-0.08	0.05	0.37	0.23
S	2.08	-0.02	-0.11	-0.06	0.03	0.00	0.03	0.08	-0.02	0.05	0.21	0.20
Cl	3.62	0.05	-0.06	-0.03	0.04	0.03	0.05	-0.06	-0.03	0.00	0.02	0.16
SiH	1.28	0.15	0.03	-0.10	-0.07	-0.04	-0.04	0.13	0.10	0.11	0.11	0.10
SiH ₂	1.12	0.07	-0.05	-0.15	-0.13	-0.10	-0.09	0.15	0.07	0.07	0.14	0.12
SiH ₃	1.44	0.10	0.02	0.04	0.13	0.13	0.15	0.25	0.16	0.12	0.26	0.13
PH	1.00	-0.01	-0.09	-0.05	0.04	0.03	0.06	0.07	0.02	0.05	0.21	0.17
PH ₂	1.26	0.10	0.01	0.02	0.10	0.10	0.12	0.13	0.05	0.07	0.14	0.15
SH	2.31	0.08	-0.02	-0.01	0.08	0.07	0.09	0.12	0.00	0.04	0.06	0.15
PO	1.09	0.03	-0.17	-0.12	-0.20	-0.11	-0.14	0.07	-0.09	0.05	0.15	0.09
S ₂	1.66	0.16	-0.01	0.10	0.08	0.10	0.09	0.31	-0.02	0.07	0.16	0.16
Cl ₂	2.39	-0.36	-0.45	-0.23	-0.20	-0.27	-0.26	-0.28	-0.16	-0.18	0.04	0.02

a) Experimental data are from Refs. [22,23,27]; b) Error = (Expt. - Calc.)

Table 4 Statistic theoretical errors ^{a)} for electron affinities (EAs, eV) at 0 K for the G2-1 Set (25 systems)

		MAD ^{b)}	AD ^{c)}	RMS ^{d)}	Max + ^{e)}	Max - ^{f)}
1st Rung	SVWN	0.750	-0.750	0.766	NA ^{g)}	-1.15 (F←F ⁻)
	SVWN5	0.289	-0.289	0.269	NA ^{g)}	-0.63 (F←F ⁻)
2nd Rung	BLYP	0.105	-0.026	0.135	0.19 (Si←Si ⁻)	-0.36 (Cl ₂ ←Cl ₂ ⁻)
	PBE	0.102	-0.086	0.133	0.10 (S ₂ ←S ₂ ⁻)	-0.29 (C←C ⁻)
	PW91	0.133	-0.128	0.164	0.06 (S ₂ ←S ₂ ⁻)	-0.33 (C←C ⁻)
	BPW91	0.094	-0.060	0.123	0.12 (S ₂ ←S ₂ ⁻)	-0.27 (C←C ⁻)
	BP86	0.211	-0.211	0.232	NA ^{g)}	-0.39 (Cl ₂ ←Cl ₂ ⁻)
	HCTH407	0.167	-0.156	0.213	0.12 (O ₂ ←O ₂ ⁻)	-0.47 (Cl ₂ ←Cl ₂ ⁻)
	LC-BLYP	0.126	-0.038	0.163	0.22 (CH ₃ ←CH ₃ ⁻)	-0.38 (CN←CN ⁻)
3rd Rung	M06-L	0.160	0.118	0.186	0.37 (OH←OH ⁻)	-0.28 (Cl ₂ ←Cl ₂ ⁻)
	TPSS	0.104	0.015	0.122	0.19 (OH←OH ⁻)	-0.27 (Cl ₂ ←Cl ₂ ⁻)
	VSXC	0.104	-0.017	0.148	0.25 (O ₂ ←O ₂ ⁻)	-0.54 (Cl ₂ ←Cl ₂ ⁻)
	tHCTH	0.109	-0.097	0.154	0.08 (O ₂ ←O ₂ ⁻)	-0.42 (Cl ₂ ←Cl ₂ ⁻)
	B3LYP	0.106	-0.084	0.144	0.06 (OH←OH ⁻)	-0.45 (Cl ₂ ←Cl ₂ ⁻)
4th Rung	X3LYP	0.090	-0.035	0.123	0.12 (OH←OH ⁻)	-0.40 (Cl ₂ ←Cl ₂ ⁻)
	PBE0	0.128	0.036	0.146	0.29 (OH←OH ⁻)	-0.20 (Cl ₂ ←Cl ₂ ⁻)
	B3PW91	0.103	-0.030	0.126	0.17 (OH←OH ⁻)	-0.29 (Cl ₂ ←Cl ₂ ⁻)
	B3P86	0.595	-0.595	0.604	NA ^{g)}	-0.83 (Cl ₂ ←Cl ₂ ⁻)
	BHHLYP	0.248	0.198	0.285	0.58 (OH←OH ⁻)	-0.29 (Cl ₂ ←Cl ₂ ⁻)
	TPSSh	0.130	0.053	0.153	0.29 (OH←OH ⁻)	-0.26 (Cl ₂ ←Cl ₂ ⁻)
	O3LYP	0.108	0.068	0.123	0.25 (O ₂ ←O ₂ ⁻)	-0.19 (Cl ₂ ←Cl ₂ ⁻)
	B98	0.078	-0.004	0.103	0.17 (OH←OH⁻)	-0.29 (Cl₂←Cl₂⁻)

(Continued)					
	MAD ^{b)}	AD ^{c)}	RMS ^{d)}	Max + ^{e)}	Max - ^{f)}
5th Rung	HSE06	0.126	0.034	0.145	0.28 (OH←OH ⁺) -0.23 (Cl ₂ ←Cl ₂ ⁻)
	CAM-B3LYP	0.103	-0.052	0.135	0.12 (Si←Si ⁺) -0.36 (Cl ₂ ←Cl ₂ ⁻)
	LC- ω PBE	0.125	-0.006	0.147	0.28 (CH ₃ ←CH ₃ ⁻) -0.28 (PO←PO ⁻)
	B97-1	0.081	0.029	0.099	0.20 (OH←OH ⁺) -0.23 (Cl ₂ ←Cl ₂ ⁻)
	B97-D	0.081	-0.004	0.116	0.17 (S ₂ ←S ₂ ⁻) -0.39 (Cl ₂ ←Cl ₂ ⁻)
	ω B97X	0.083	0.009	0.106	0.17 (Si←Si ⁺) -0.25 (CN←CN ⁻)
	ωB97X-D	0.079	-0.013	0.100	0.15 (OH←OH⁺) -0.22 (Cl₂←Cl₂⁻)
	M06-2X	0.103	0.051	0.126	0.25 (F←F ⁺) -0.17 (CN←CN ⁻)
	M06	0.095	0.048	0.116	0.24 (SiH ₂ ←SiH ₂ ⁻) -0.23 (NO←NO ⁻)
	XYG3	0.080	0.058	0.090	0.16 (CH₃←CH₃⁻) -0.18 (Cl₂←Cl₂⁻)
	MC3BB	0.175	0.132	0.188	0.29 (NH←NH ⁺) -0.26 (CN←CN ⁻)
	B2PLYP	0.090	0.056	0.102	0.17 (CH ₃ ←CH ₃ ⁻) -0.22 (Cl ₂ ←Cl ₂ ⁻)
	B2PLYP-D	0.091	0.056	0.104	0.17 (CH ₃ ←CH ₃ ⁻) -0.23 (Cl ₂ ←Cl ₂ ⁻)
<i>Ab initio</i>	B2GP-PLYP	0.114	0.083	0.124	0.21 (CH ₃ ←CH ₃ ⁻) -0.19 (CN←CN ⁻)
	HF	1.148	1.148	1.283	2.21 (F←F ⁺) NA ^{g)}
	UMP2	0.166	0.079	0.224	0.37 (P←P ⁺) -0.78 (CN←CN ⁻)
	MP4SDQ	0.208	0.175	0.229	0.36 (NH←NH ⁺) -0.41 (CN←CN ⁻)
	QCISD(T)	0.135	0.135	0.148	0.23 (NH←NH ⁺) NA ^{g)}

a) Experimental data are from Refs. [22,23,27]. The best three are in the bold face; b) Mean absolute deviations; c) Averaged deviations (Expt. - Calc.); d) Root-mean-square errors; e) Maximum positive deviations; f) Maximum negative deviations; g) Not applicable

this observation, leading to slightly poor EAs for the second row atoms as compared to those of the first row atoms.

It would be expected that the LC scheme should be of help for EA prediction. Numerically, we found that LC-BLYP (MAD = 0.126 eV) is worse than BLYP (MAD = 0.105 eV); while MADs (~ 0.10 eV) from B3LYP and CAM-B3LYP are similar, and MADs (~ 0.08 eV) from B97-1, B97-D, ω B97X, ω B97X-D are also comparable. In fact, these B97 type functionals are the best performers in predicting EAs in terms of MAD, i.e., 0.078 eV for B98 and 0.079 eV for ω B97X-D. XYG3 is similarly good for EA calculations (MAD = 0.080 eV). We would like to repeat that ions were included in the training set of these B97 type of functionals and more than 19 parameters were optimized to ensure a flexible form of the functionals. On the other hand, no ionic species were used for the optimization of three mixing parameters in XYG3. Indeed, the error histograms displayed in Fig. 2 suggest that XYG3 is the most satisfactory DFT for EA predictions.

From a practical point of view, it is encouraging to have seen from Table 4 that many DFT methods outperform MP2 (MAD = 0.166 eV) and QCISD(T) (MAD = 0.135 eV) for EA calculations. With larger basis set than 6-311 + G(3df,2p) used here, there is no doubt that QCISD(T) will lead to more satisfactory results, although its steep scaling will prevent its applications to larger systems.

5 Concluding remarks

Recently, we proposed a doubly hybrid functional, XYG3

[52], which shows a very good performance for the calculations of the standard heats of formation, reaction barrier heights, as well as non-bonded interaction [58,73,81,82]. In the present work, we examined the XYG3 performance to calculate IEs and EAs. We used the well-established G2-1 set as a reference, which contains 14 atoms and 24 molecules for IE, along with 7 atoms and 18 molecules for EA. We compared the XYG3 results with a wide range of 35 DFT methods such as doubly hybrid functional (B2PLYP-D, B2PLYP B2GP-PLYP), hybrid meta-GGAs (M06-2X, M06, B98, and TPSSh), hybrid GGAs (BHHLYP, B3LYP, PBE0, B3P86, B3PW91, X3LYP, O3LYP, B97, B97-D, CAM-B3LYP), meta-GGAs (M06-L, TPSS, VSXC), GGAs (HCTH, BLYP, OLYP, PBE, BP86, BPW91, LC-BLYP) and LDA (SVWN, SVWN5). DFT results were also compared with those from the wave function based methods of HF, MP2, MP4SDQ and QCISD(T). We found that:

(1) For the first rung functionals of SVWN and SVWN5, the performance of the latter is significantly better than that of the former, showing the important role played by the correlation functional for both IE and EA calculations.

(2) Along the rung up, the functional performance is generally improved. Such improvement is more significant for IE calculations than for EA calculations. For IEs, the best performers are PBE (MAD = 0.161 eV) for the second rung, TPSS (MAD = 0.173 eV) for the third rung, M06-2X (MAD = 0.119 eV) for the fourth rung, and XYG3 (MAD = 0.057 eV) for the fifth rung. For EAs, the best performers are BPW91 (MAD = 0.094 eV) for the second rung, TPSS and VSXC

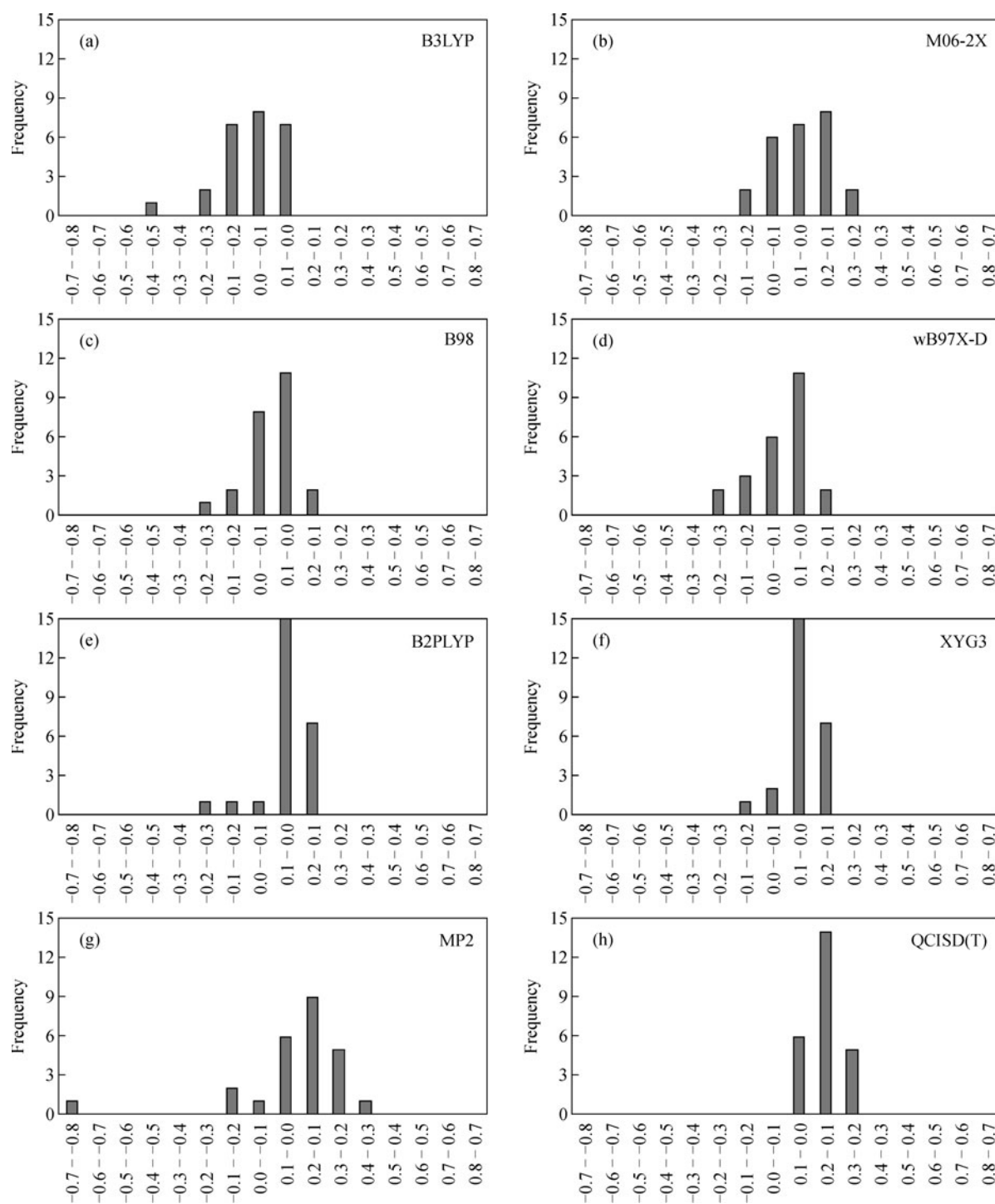


Figure 2 Histogram of deviations (Expt. – Calc.) for 25 electron affinities (EAs) in the G2-1 set. Each vertical bar represents deviations in a 0.1 eV range.

(MAD = 0.104 eV) for the third rung, B98 (MAD = 0.078 eV) for the fourth rung, and XYG3 (MAD = 0.080 eV) for the fifth rung. Notably, B3P86 is a surprising failure, whose MAD is as high as 0.616 eV for IE and 0.595 eV for EA predictions. The LC or -D schemes do not necessary help to improve the numerical accuracy for either IE or EA predictions.

(3) XYG3 is quite satisfactory for IE and EA calculations, displaying a well-behaved error distribution. In comparison, MP2 and QCISD(T) give MADs of 0.163 and 0.111 eV, respectively, for IEs; while the corresponding MADs for EAs are 0.166 (MP2) and 0.135 eV (QCISD(T)) with the same 6-311 + G(3df,2p) basis set used in the present DFT calcula-

tions. Notably, GGA scales formally with the system size N as N^3 , hybrid GGA scales formally as N^4 , whereas the scalings for wave function based methods are significantly higher, with the MP2 scaling formally as N^5 and the QCISD(T) method as N^7 . It is encouraging to see that XYG3 is competitive with the coupled-cluster based method for accuracy at the expense of MP2. We anticipate that XYG3 is a viable method for accurate prediction of IE and EA of medium-sized systems consisting of a hundred atoms.

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