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

Neil Qiang SU1, Igor Ying ZHANG1,2, Jianming WU (✉)2 and Xin XU1,2

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 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]:

\[ M \rightarrow M^+ + e^-; \quad \text{IE} = \Delta_f H_{0K}^\circ (M^+) - \Delta_f H_{0K}^\circ (M) \]  (1)

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

\[ M + e^- \rightarrow M^-; \quad \text{EA} = \Delta_f H_{0K}^\circ (M^-) - \Delta_f H_{0K}^\circ (M) \]  (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], G2(n = 1–4) [21–24], and CBS-QB3 [25,26]. These are coupled-cluster based methods, which scale on the order of N7, 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 N3–N4), 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], 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
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-oPBE [45], CAM-B3LYP [46], oB97X [48], oB97X-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 $\omega$ 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