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Theoretical study of electron affinities for selected diatomic molecules

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Ab initio Hartree–Fock (HF) methods and different hybrid density functional theories (DFT), *i.e.*, LSDA, BPV86, B3LYP, B3PV91, MPW1PW91, PBEPBE, PBE1PBE, HCTH, THCTH and TPSSTPSS, have been used to evaluate electron affinities (EAs) for selected diatomic molecules. Computations have also been made at the high level *ab initio* quadratic complete basis set (CBS-Q) method. The results show that HF calculations underestimate and DFT overestimate EA's values in comparison to experimental data. We obtain the best agreement with experimental values of EA's in DFT calculations with PBE1PBE, TPSSTPSS, THCTH and PBE1PBE functionals for OH, NaBr, LiBr and F_2 molecules, respectively.

Keywords: electron affinity, DFT methods.

1. Introduction

Accurate values of electron affinities (EAs) for various chemical systems are important for many problems in plasma physics and chemistry. In gas discharges, an admixture of electron attaching gases changes drastically electron-energy distribution functions and electron densities. Recent environmental requirements to substitute traditional electro-attaching gases (like SF_6) with gases with less greenhouse warming potential makes it necessary to study new systems. However, experimental data are rather difficult to obtain for many molecular species, although the studies of the fundamental collision processes of slow electrons and gaseous molecules have been made for more than 100 years [1–4]. In recent years, quantum chemical methods have become more and more popular for calculations of such fundamental quantities as electron affinities of atoms or molecules. In particular, various density functional theory (DFT) methods have recently been used in those calculations. This is due to their less time consuming and, for many systems, more accurate results than *ab initio* methods. However, different DFT methods give sometimes diametrically different results [5]. In this work we have tested ten out of the most popular DFT approaches to calculations of electron affinities for homonuclear and heteronuclear diatomic molecules in comparison with *ab initio* Hartree–Fock (HF) and quadratic complete basis set (CBS-Q) methods and experimental data for diatomic systems: fluorine, lithium bromide, sodium bromide and hydroxyl radical.

The extreme hygroscopic character of LiBr makes it useful for a desiccant in certain air conditioning systems. NaBr is used in organic synthesis as a source of the bromide nucleophile to convert alkyl chlorides to more reactive alkyl bromides. In the past, it was used as a hypnotic, anticonvulsant, and sedative medicament. Hydroxyl radical is highly reactive and consequently short-lived. However, OH is important in radical chemistry. F_2 is a supremely reactive and poisonous gas. Moreover F_2 is an interesting case because HF calculations for this molecule give the negative binding energy.

2. Methods

The adiabatic EAs have been computed as differences in total energies (*i.e.*, electronic and zero point vibrational energies) of fully optimized neutral and negatively charged diatomic molecules, *i.e.*, F_2, OH, LiBr, NaBr. All computational studies have been performed with the Gaussian 03W computational package [6]. We have examined several different methods to calculations of EA's values:

1) The Hartree–Fock method with the 6-311++G(3*df*, 3*pd*) basis set [7].

2) Hybrid DFT methods with the 6-311G++(3*df*, 3*pd*) basis sets:

– Local spin density approximation (LSDA) [8],

– BPV86 – which uses Perdew's 1986 functional with local correlation replaced by that suggested by Vosko *et al.* (VWN) [9–11],

– B3LYP – the dynamical functional of Lee, Yang, and Parr (LYP), coupled with Becke's three-parameter pure DFT exchange functional (B3) [9, 12],

– MPW1PW91 – modified Perdew–Wang exchange and Perdew–Wang 91 correlation functionals [13–18],

– PBEPBE – the gradient-corrected correlation functional of Perdew, Burke and Ernzerhof,

– PBE1PBE hybrid functional of Perdew, Burke and Ernzerhof which uses 25% exchange and 75% correlation weighting [19, 20],

– HTCH and THCTH – Handy's family functionals including gradient-corrected correlation [21–23]

– TPSSTPSS – the meta-GGA (generalized gradient approximation) functional of Tao, Perdew, Staroverov, and Scuseria [24]

3) CBS-Q – high levels of *ab initio* computational studies with the quadratic complete basis set [25].

As the HF method overestimated vibrational energies of molecules, thermodynamic functions obtained through frequency calculations have been multiplied by the scaling factor of 0.89 suggested by Hout *et al.* [26].

3. Results and discussion

Electron affinity of fluorine molecule and hydroxyl radical was measured by the use of different methods, for example by measuring the formation enthalpy of anion relationship [27], kinetic method [28], electron impact appearance energy [29] or laser photodetachment techniques [30]. According to our knowledge, the experimental data of EA for lithium bromide do not exist. We referred to the value extrapolated by polarizability and radius [31]. Electron affinity of sodium bromide was measured by using the laser photoelectron spectroscopy [31]. We have chosen the recommended values from NIST Standard Reference Database Number 69 [32] and compared our results with these data.

Results of EAs calculations for diatomic molecules, *i.e.*, F_2, LiBr, NaBr and OH, are presented in the Table.

Table. Electron affinities of F_2, LiBr, NaBr and OH (in eV) for 6-311G++(3*df*, 3*pd*).

	EA [eV]			
Method	EA(F_2)	EA(LiBr)	EA(NaBr)	EA(OH)
HF	2.84	0.59	0.71	–0.27
LSDA	3.80	1.09	1.25	2.75
BPV86	3.87	0.81	0.94	1.93
B3LYP	3.72	0.76	0.92	1.75
B3PV91	3.54	0.76	0.88	1.65
MPW1PW91	3.49	0.75	0.87	1.54
PBEPBE	3.64	0.76	0.89	1.84
PBE1PBE	3.43	0.71	0.88	1.53
HCTH	3.81	0.75	0.90	1.95
THCTH	3.68	0.63	0.68	1.89
TPSSTPSS	3.47	0.69	0.79	1.63
CBS-Q	2.04	0.70	0.81	1.78
Exp*	3.08	0.66	0.788	1.83

*NIST Standard Reference Database Number 69 [32].

For F_2 the Hartree–Fock method slightly underestimates the EA value in comparison to experimental data (see Fig. 1). The CBS-Q method also underestimates the EA value, but the difference between this EA and experimental one is higher (1.04 eV). All DFT methods overestimate EA. The best agreement with the experiment in the midst of these techniques is for PBE1PBE functionals. The use of TPSSTPSS, MPW1PW91 and B3PV91 functionals gives differences below 0.5 eV. The worst agreement with experimental data is in case of BPV86 functional.

Differences between calculated and experimental data of electron affinity for lithium bromide are shown in Fig. 2. In this case, two methods – HF and DFT/THCTH – slightly underestimate the values of EA about 0.07 and 0.03 eV, respectively. Other

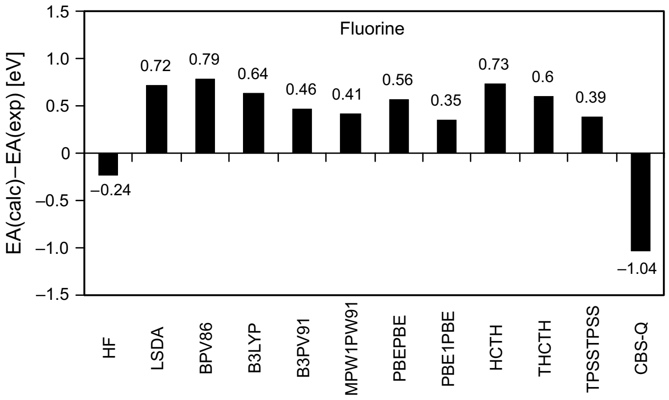

Fig. 1. Differences between computed electron affinity values using *ab initio* (HF and CBS-Q) and DFT methods and experimental values for fluorine.

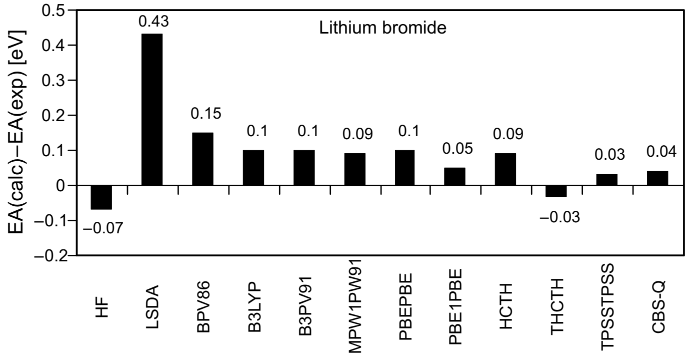

Fig. 2. Differences between computed EA values using *ab initio* (HF and CBS-Q) and DFT methods and experimental values for lithium bromide.

calculation techniques give higher values than experimental ones. We have obtained very good results for TPSSTPSS and CBS-Q methods, where differences with experiment are 0.03 and 0.05 eV, so about 5% and 6%, respectively. Higher disagreement is observed for LSDA method – 0.43 eV, *i.e.*, 65%.

As it is shown in Fig. 3, calculations of electron affinity for sodium bromide have given similar results like in the case of lithium bromide (EA for NaBr is higher than for LiBr about 0.1 eV, probably in view of differences in physical properties of those species, for example in dipole moments – 7.1 D for LiBr and 9.6 for NaBr from our B3LYP calculations). What is more, only HF and DFT/THCTH methods underestimate the values of EA about 0.08 and 0.1 eV, respectively. We obtained directly ideal values for TPSSTPSS functionals in DFT method. The CBS-Q technique has also given very good results – the deviation from the experimental value is only 0.02 eV, *i.e.*, about 3% and higher disagreement is for LSDA method – 0.46 eV, *i.e.*, about 60%.

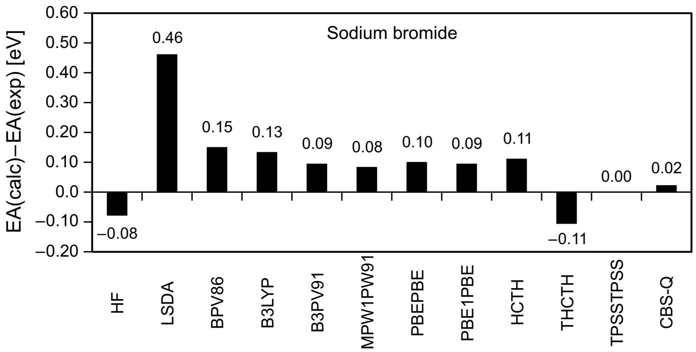

Fig. 3. Differences between computed and experimental values of EA for sodium bromide.

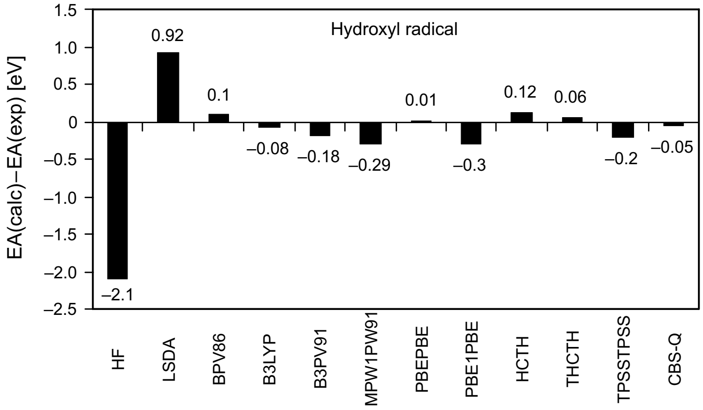

Fig. 4. Differences between computed and experimental values for hydroxyl radical.

Calculations for hydroxyl radical have showed that HF, B3LYP, B3PV91, MPW1PW91, PBE1PBE, TPSSTPSS and CBS-Q methods underestimate EA value but the deviation is the highest in the case of the first one, *i.e.*, 2.1 eV (more than 110%) for which EA adopts negative value (see Fig. 4). In other cases EA is overestimated, most in the LSDA method – the difference with recommended experimental values is 0.92 eV (50%). The best agreements with the experiment we have obtained for PBEPBE, THCTH and B3LYP DFT methods and the CBS-Q technique – in these cases agreements with the recommended values are better than 5%.

To sum up, we can ascertain that the HF method gives a wrong sign of the electron affinity for the OH radical. In this method, the best consistence with the experiment is that for the NaBr molecule. The similar situation is in the case of BPV86, PBEPBE and HCTH, though the correspondence with the experiment is much better. B3LYP, B3PV91, MPW1PW91, PBE1PBE and TPSSTPSS methods overestimate the values, with the exception of the OH molecule. The EA data that have been gained by the use of the THCTH are overestimated for the F_2 and OH molecules and lowered for LiBr and NaBr. CBS-Q method gives good results for LiBr, NaBr and OH molecules, however, in the case of F_2 the EA value is lower than the experimental one, by a little more than 1 eV.

4. Conclusions

Our results show that the HF/6-311G++(3*df*, 3*pd*) method generally underestimates EAs, in particular for OH molecule, where it gives negative values (–0.27 eV). All DFT methods slightly overestimate electron affinities with the exception of B3LYP, B3PW91, MPW1PW91 and PBE1PBE for OH, where we obtained 1.75, 1.65, 1.54 and 1.53 eV, respectively, in comparison with 1.83 eV experimental value. For the F_2 molecule the CBS-Q method seems to be the best one – we have obtained 3.04 eV with comparison with the experimental value of 3.08 eV.

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