

Calculation of ionization energies, electron affinities, electronegativities, and hardnesses using density functional methods

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The performance of two exact exchange methods is tested in the calculation of ionization energies, electron affinities, electronegativities, and hardnesses using Dunning's correlation consistent basis sets. Comparison is made to experiment and other density functional methods, including the local density approximation and two gradient corrected functionals. The obtained electronegativities and hardnesses are also compared with high level coupled cluster results. Both the exact exchange methods show an excellent performance in the calculation of all four properties, yielding mean absolute deviations from experiment below 0.20 eV for all basis sets. © 1997 American Institute of Physics. [S0021-9606(97)00906-9]

I. INTRODUCTION

Since the beginning of the nineties, a growing interest has existed for density functional methods as an alternative to traditional *ab initio* MO methods. Density functional theory (DFT)¹⁻⁴ uses the electron density $\rho(\mathbf{r})$ as the basic variable of an atomic or molecular system instead of the wave function Ψ ; due to the Hohenberg-Kohn theorems,⁵ at the basis of the theory, atomic or molecular properties can be expressed as a functional of this electron density directly from a minimization of the atomic or molecular energy functional. Using a variational procedure minimizing the atomic or molecular energy E with the constraint that the integration of the electron density should yield the number of electrons N

$$\delta \left(E - \mu \int \rho(\mathbf{r}) d\mathbf{r} \right) = 0, \quad (1)$$

the famous Euler equation is obtained

$$\mu = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta T}{\delta \rho} + v_{\text{XC}}(\mathbf{r}), \quad (2)$$

with μ the Lagrange multiplier called the electronic chemical potential, $v(\mathbf{r})$ the external potential (i.e., due to the nuclei), T the kinetic energy functional and $v_{\text{XC}}(\mathbf{r})$ the exchange correlation potential, being the functional derivative of the exchange correlation energy E_{XC} with respect to the electron density

$$v_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}}{\delta \rho}. \quad (3)$$

Kohn and Sham⁶ turned this equation into a practical calculation tool by introducing orbitals in the unknown kinetic energy functional. Among others, the performance of density functional methods in the calculation of atomic or molecular properties has received much attention in the last years (see, e.g., Refs. 7-9 and references in these papers).

The implementation of the Kohn-Sham equations in standard quantum chemical programs, together with the development of high-level exchange-correlation functionals,¹⁰ has resulted in numerous studies employing this methodology.

An at least as important aspect of DFT, next to its computational advantages is, in our opinion, the fact that many commonly used chemical concepts receive a precise definition, permitting their nonempirical evaluation and accurate calculation. One of these concepts is the electronegativity¹¹⁻¹³ (denoted hereafter as χ). Introduced by Pauling in the 1930's as the power of an atom in a molecule to attract electrons to itself, this property was shown by Parr *et al.* to be the negative of the Lagrange multiplier μ .¹⁴ Parr *et al.* showed that

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_v. \quad (4)$$

In 1983, the chemical hardness η was introduced by Parr and Pearson as¹⁵

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_v. \quad (5)$$

The hardness measures a chemical species' resistance to charge transfer, whereas the electronegativity expresses its initial attraction towards electronic charge. Both quantities have been shown to be very important in the elucidation and interpretation of chemical reactivity,¹⁶ amongst other acid-base reactions.¹⁷

Using a finite difference approximation and a quadratic relationship between the energy E and the number of electrons N , both definitions (4) and (5) are transformed into the following working equations:

$$\chi = \frac{I + A}{2} \quad (6)$$

and

$$\eta = \frac{I - A}{2}, \quad (7)$$

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TABLE I. Performance of the B3LYP functional with various basis sets in the calculation of ionization energies. All values are in eV.

Molecule	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	Expt. ^a
H	13.64	13.66	13.65	13.67	13.60
He	24.87	24.94	24.59
B	8.76	8.74	8.76	8.74	8.30
C	11.52	11.53	11.57	11.54	11.26
N	14.57	14.69	14.69	14.66	14.54
O	13.92	14.09	14.14	14.14	13.61
F	17.44	17.66	17.78	17.74	17.42
Ne	21.32	21.62	21.81	21.73	21.56
Al	6.03	6.01	6.03	6.02	5.98
Si	8.11	8.11	8.13	8.12	8.15
P	10.37	10.62	10.41	10.39	10.49
S	10.49	10.55	10.55	10.56	10.36
Cl	13.03	13.06	13.10	13.07	12.97
Ar	15.79	15.79	15.86	15.80	15.76
CH ₄	12.33	12.46	12.39	12.45	12.62
NH ₃	9.86	10.08	10.17	10.19	10.18
OH	12.80	13.10	13.20	13.21	13.01
OH ₂	12.11	12.45	12.60	12.60	12.62
FH	15.52	15.91	16.10	16.07	16.04
SiH ₄	10.84	10.89	10.85	10.88	11.00
PH	10.15	10.17	10.19	10.18	10.15
PH ₂	9.89	9.93	9.94	9.93	9.82
PH ₃	9.77	9.82	9.83	9.82	9.87
SH	10.37	10.45	10.46	10.47	10.37
SH ₂ (² B ₁)	10.31	10.39	10.41	10.41	10.47
SH ₂ (² A ₁)	12.52	12.61	12.63	12.63	12.78
CIH	12.64	12.71	12.76	12.73	12.75
HCCH	11.08	11.23	11.18	11.24	11.40
H ₂ CCH ₂	10.16	10.31	10.24	10.29	10.51
CO	14.06	14.15	14.21	14.18	14.01
N ₂ (² Σ _g ⁻)	15.61	15.78	15.80	15.83	15.58
N ₂ (² Π _u)	16.42	16.61	16.56	16.65	16.70
O ₂	12.44	12.50	12.64	12.57	12.07
P ₂	10.75	10.74	10.82	10.76	10.53
S ₂	9.62	9.57	9.67	9.58	9.36
Cl ₂	11.48	11.39	11.51	11.40	11.50
ClF	12.61	12.57	12.76	12.64	12.66
SC	11.45	11.43	11.54	11.46	11.33
	mean absolute deviation				
	0.18	0.15	0.18	0.15	

^aExperimental values taken from Refs. 27 and 28.

with I and A the ionization energy and electron affinity, respectively.

Calculation of the electronegativities and hardnesses for an atom, molecule or molecular fragment as presented by us in the past^{18,19} and used in reactivity studies in organic, inorganic, and biochemistry,^{17,20} thus requires the accurate evaluation of the system's ionization energy and electron affinity. Both of these quantities are known to be largely influenced by the incorporation of electron correlation in the calculation method and require the use of large basis sets,^{21,22} which becomes prohibitive for larger molecular systems. In this aspect, DFT methods are very promising, since they incorporate electron correlation at a much lower (and affordable) cost than traditional wave function correlated calculation methods, such as Møller–Plesset perturbation theory (MP),²³ configuration interaction (CI),²⁴ or coupled cluster methods²⁵ [e.g., the much used CCSD(T)²⁶ method].

Pople *et al.* investigated the performance of the B-LYP exchange correlation functional in the calculation of atomization energies, ionization energies, electron affinities and proton affinities using the 6-31G(*d*), 6-31+G(*d*), 6-311+G(2*df,p*), and 6-311+G(3*df,2p*) basis sets.²⁷ In a test on the molecules of the well-known G2 thermochemical data set,²⁸ a mean absolute deviation of 0.195 eV for the ionization energies (42 molecules) and 0.137 eV for the electron affinities (25 molecules) was found for the largest basis set. Among the Kohn–Sham methods, a lot of interest recently arose for the so-called exact-exchange methods e.g., B3LYP and B3PW91. Based on the adiabatic connection theorem,²⁹ Becke introduced the following form for the exchange correlation energy functional³⁰

$$E_{XC} = E_{XC}^{LSDA} + a_0(E_X^{\text{exact}} - E_X^{LSDA}) + a_X \Delta E_X^B + a_C \Delta E_C^{PW91} \quad (8)$$

with E_{XC}^{LSDA} the uniform electron gas exchange correlation energy, E_X^{exact} the Hartree–Fock exchange energy based on Kohn–Sham orbitals and ΔE_X^B and ΔE_C^{PW91} Becke's 1988³¹ and Perdew and Wang's 1991³² gradient corrections for exchange and correlation respectively. The parameters a_0 , a_X , and a_C were fitted to thermochemical data, consisting of 56 atomization energies, 42 ionization potentials, and 8 proton affinities, thus making it a semiempirical theory. The values for a_0 , a_X , and a_C were 0.20, 0.72, and 0.81, respectively.

The basis set dependence of the B3LYP method in the calculation of atomization energies was recently studied by Bauschlicher, and a comparison was made with high level *ab initio* MO methods. In a test on 55 atomization energies of the G2 molecules, it was found that B3LYP yielded atomization energies superior to CCSD(T) for smaller basis sets, whereas for the larger basis set, CCSD(T) was superior.³³ Furthermore, it was found that B3P86 showed errors similar to B3LYP for geometries and zero-point energies as B3LYP but performed considerably less well than the latter for atomization energies.³⁴

In this contribution, and as a sequel to our previous studies in which we concentrated on the performance of various DFT methods in the calculation of charge distributions, dipole moments, infrared properties, and reactivity descriptors,^{35–37} we will investigate the performance of the B3LYP and B3PW91 exchange correlation functionals in the calculation of ionization energies and electron affinities, using Dunning's correlation consistent basis sets.³⁸ For the largest basis set, a comparison is made with results obtained using the local density approximation (LDA), and two gradient corrected density functionals B-P86 and B-LYP. Finally, electronegativities and hardnesses are calculated for neutral atoms and ions and compared with experiment and CCSD(T) results using the same basis set.

II. COMPUTATIONAL DETAILS

All calculations were performed using the GAUSSIAN94 program³⁹ running on the Cray J916/8-1024 of the Brussels Free Universities Computer Centre. The DFT methods considered were:

TABLE II. Performance of the B3PW91 functional with various basis sets in the calculation of ionization energies. All values are in eV.

Molecule	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	Expt.	$\Delta(\text{aug-cc-pVTZ})$	$\Delta(\text{Becke})$
B	8.73	8.71	8.73	8.71	8.30	0.41	0.41
C	11.58	11.58	11.61	11.58	11.26	0.32	0.32
N	14.72	14.76	14.81	14.78	14.54	0.24	0.24
O	13.79	13.92	13.97	13.96	13.61	0.35	0.34
F	17.37	17.53	17.65	17.59	17.42	0.17	0.16
Ne	21.32	21.54	21.73	21.62	21.56	0.06	0.04
Al	6.12	6.11	6.13	6.12	5.98	0.14	0.14
Si	8.25	8.25	8.26	8.25	8.15	0.10	0.10
P	10.56	10.58	10.58	10.56	10.49	0.07	0.08
S	10.45	10.48	10.48	10.49	10.36	0.13	0.12
Cl	13.04	13.03	13.07	13.04	12.97	0.07	0.07
Ar	15.83	15.79	15.87	15.79	15.76	0.03	0.04
CH ₄	12.30	12.38	12.33	12.38	12.62	-0.24	-0.15
NH ₃	9.84	10.02	10.10	10.11	10.18	-0.07	-0.06
OH	12.75	13.00	13.08	13.09	13.01	0.08	0.08
OH ₂	12.11	12.40	12.53	12.53	12.62	-0.09	-0.08
FH	15.55	15.86	16.04	15.99	16.04	-0.05	-0.05
SiH ₄	10.82	10.83	10.80	10.83	11.00	-0.17	-0.15
PH	10.30	10.30	10.32	10.31	10.15	0.16	0.16
PH ₂	10.01	10.03	10.03	10.03	9.82	0.21	0.21
PH ₃	9.75	9.77	9.78	9.78	9.87	-0.09	-0.06
SH	10.36	10.41	10.41	10.42	10.37	0.05	0.06
SH ₂ (² B ₁)	10.33	10.38	10.40	10.39	10.47	-0.08	-0.05
SH ₂ (² A ₁)	12.54	12.59	12.62	12.61	12.78	-0.17	-0.14
CIH	12.69	12.71	12.76	12.72	12.75	-0.03	-0.01
HCCH	11.10	11.21	11.16	11.21	11.40	-0.19	-0.17
H ₂ CCH ₂	10.17	10.30	10.22	10.26	10.51	-0.25	-0.15
CO	13.97	14.03	14.07	14.04	14.01	0.03	0.04
N ₂ (² Σ_g)	15.61	15.73	15.75	15.76	15.58	0.18	0.19
N ₂ (² Π_u)	16.47	16.61	16.56	16.63	16.70	-0.07	-0.07
O ₂	12.43	12.43	12.56	12.48	12.07	0.41	0.39
P ₂	10.82	10.78	10.85	10.79	10.53	0.26	-0.12
S ₂	9.71	9.62	9.72	9.63	9.36	0.27	0.22
Cl ₂	11.53	11.39	11.51	11.39	11.50	-0.11	-0.15
ClF	12.64	12.54	12.73	12.58	12.66	-0.08	-0.11
SC	11.43	11.36	11.48	11.38	11.33	0.05	0.01
			mean absolute deviation				
		0.20	0.15	0.17	0.15		

^aExperimental values taken from Refs. 27 and 28.

- (1) The local density approximation (LDA), which actually uses Slater's expression for exchange (S)⁴⁰ and Vosko, Wilk, and Nusair's expression for the correlation energy of the uniform electron gas⁴¹ (VWN), parametrized using Ceperly and Alders quantum Monte Carlo results.⁴²
- (2) The gradient corrected B-LYP and B-P86 functionals, using Becke's 1988 gradient correction for exchange³¹ and Lee, Yang, and Parr's⁴³ or Perdew's 1986⁴⁴ expression for the correlation energy functional.
- (3) The exact exchange functionals B3LYP and B3PW91,³⁰ using the implementation of this functional in the GAUSSIAN94 program,⁴⁵ which is a slightly altered expression as compared to the original proposed by Becke [Eq. (8)].

Ionization energies were calculated using the following basis sets: the cc-pVDZ (correlation-consistent polarized valence double zeta), which is a $[3s2p1d/2s1p]$ contraction of a $(9s4p1d/4s1p)$ primitive set, and the cc-pVTZ (cor-

relation-consistent polarized valence triple zeta), a $[4s3p2d1f/3s2p1d]$ contraction of a $(10s5p2d1f/5s2p1d)$ primitive set.³⁸ Next to these two basis sets, we also considered the aug-cc-pVDZ and aug-cc-pVTZ basis sets to calculate this property, where a diffuse function of each angular momentum is added to the original set.⁴⁶ The geometries of both the neutral systems and the ions were fully optimized at all DFT levels and with all basis sets. Furthermore, the zero-point vibrational energy obtained from a vibrational frequency calculation at the corresponding level was included (using unscaled vibrational frequencies).

Atomic and ionic electronegativities and hardnesses finally were obtained using the the Pople 6-311++G(3df,2p)⁴⁷ and Dunning aug-cc-pVTZ basis sets. For these quantities, also CCSD(T) calculations were performed in which all the electrons were included in the correlation treatment.

TABLE III. Performance of the different density functional methods with the aug-cc-pVTZ basis set in the calculation of ionization energies. All values are in eV.

Molecule	LDA	B-P86	B-LYP	Expt.
H	13.50	13.61	13.54	13.60
B	9.90	8.75	8.62	8.30
C	12.14	11.59	11.40	11.26
N	15.46	14.76	14.50	14.54
O	14.51	14.22	14.15	13.61
F	18.54	17.79	17.72	17.42
Ne	22.76	21.77	21.69	21.56
Al	6.46	6.15	5.87	5.98
Si	8.68	8.26	7.95	8.15
P	11.03	10.54	10.19	10.49
S	11.09	10.61	10.42	10.36
Cl	13.73	13.11	12.91	12.97
Ar	16.52	15.82	15.61	15.76
CH ₄	12.82	13.04	12.22	12.62
NH ₃	10.96	10.27	10.12	10.18
OH	13.91	13.27	13.17	13.01
OH ₂	13.45	12.68	12.54	12.62
FH	17.01	16.15	16.02	16.04
SiH ₄	11.29	10.79	10.62	11.00
PH	10.75	10.30	9.98	10.15
PH ₂	10.44	10.04	9.75	9.82
PH ₃	10.44	9.88	9.70	9.87
SH	11.08	10.51	10.32	10.37
SH ₂ (² B ₁)	11.08	10.46	10.25	10.47
SH ₂ (² A ₁)	13.18	12.64	12.44	12.78
CIH	13.43	12.77	12.56	12.75
HCCCH	12.09	11.31	11.12	11.40
H ₂ CCH ₂	11.01	10.34	10.15	10.51
CO	14.59	14.01	13.90	14.01
N ₂ (² Σ _g ⁻)	16.14	15.49	15.35	15.58
N ₂ (² Π _u)	17.59	16.63	16.44	16.70
O ₂	12.85	12.37	12.30	12.07
P ₂	11.30	10.74	10.49	10.53
S ₂	9.96	9.54	9.30	9.36
Cl ₂	11.80	11.28	11.08	11.50
ClF	13.06	12.50	12.34	12.66
SC	11.96	11.42	11.25	11.33
	mean absolute deviation			
	0.69	0.17	0.19	

^aExperimental values taken from Refs. 27 and 28.

III. RESULTS AND DISCUSSION

A. Ionization energies

In a first part, the performance of B3LYP and B3PW91 in the calculation of ionization energies is investigated, using the molecules from the G2 thermochemical data set. An introductory remark concerning this point has to be made. As it was stated in the introduction, the parameters a_0 , a_X , and a_C were fitted to thermochemical data, among which are ionization energies of the molecules that will be studied in this work. The reader might therefore rightly wonder whether our results would not be a foregone conclusion. However, the results obtained by Becke result from numerical Kohn–Sham orbitals and the performance of the methods using finite Gaussian basis sets has to our knowledge never been investigated. Therefore in this work we will study the basis set dependence and compare with Becke’s “basis set free” nu-

merical results. Furthermore, since electron affinities were not included at all in Becke’s analysis and consequently neither electronegativities nor hardnesses were calculated, these properties definitely merit investigation.

Tables I and II list the obtained ionization energies for the B3LYP and B3PW91 methods, for the four basis sets, together with the experimental values, taken from Refs. 27 and 28. At the bottom of the Table, the mean absolute deviation from experiment is listed for each basis set. As can be seen from these Tables, the B3LYP and B3PW91 functionals show a comparable performance in the calculation of the ionization energies. The cc-pVDZ and aug-cc-pVDZ bases nearly show the same mean absolute deviation from experiment as do the cc-pVTZ and aug-cc-pVTZ basis sets. However, some remarks should be made. Comparing with the other three basis sets, the cc-pVDZ basis sets performs considerably worse for hydrogen fluoride. The absolute deviations of 0.52 for B3LYP and 0.49 eV for B3PW91 are among the largest of all species for this basis set. This feature is also encountered for H₂O, NH₃, and OH. Finally, focusing on the largest basis sets, the worst performances occur for the first row atoms and the diatomics N₂, O₂, P₂, and S₂, as was also found in the original work by Becke. From these results, it can however be decided, that, apart from some exceptions, the cc-pVDZ basis set already gives reliable results in the calculation of ionization energies; extending the basis set to *spdf* quality further reduces the error. As compared to the native cc-pVXZ (with $X=D$ or T) basis set, introducing augmented functions has a minor influence. Exceptions to this statement are the first row hydrides HF, H₂O, OH, and NH₃ for the cc-pVDZ and the aug-cc-pVDZ, where indeed the incorporation of augmented functions results in a dramatic improvement of the ionization energy. This effect is much less pronounced for the cc-pVTZ and aug-cc-pVTZ basis set, an indication that the quantity is indeed converging with respect to basis set extension. Finally, a comparison can be made between B3LYP and B3PW91. Concentrating on the largest basis set, there really is not much to choose between these two levels of theory. However, there are some differences. B3PW91 seems to perform considerably better for some molecules containing a triple bond, namely CO, N₂, CS, and O₂, whereas B3LYP performs better for CH₄ and NH₃. No obvious reason exists for this behavior; however, in a previous study, we have already shown that B3PW91 performs slightly better than B3LYP for charge distributions where a considerable pile-up of electrons in certain molecular regions, such as e.g., triple bonds, occurs. Finally, we list in Table II the deviation from experiment for the aug-cc-pVTZ basis set, together with the Δ values, the deviations from experiment obtained by Becke from a numerical implementation, which was then used to fit the three “ a ” parameters. As can be seen, all deviations have the same sign as Becke’s, the only noticeable exception being P₂. Since the mean absolute deviations are almost always equal to the ones obtained by Becke, it can thus be concluded that using a basis set of *spdf* quality (being the cc-pVTZ or aug-cc-pVTZ basis set), one has essentially arrived at the point of basis set convergence. Moreover, the mean

TABLE IV. B3LYP and B3PW91 electron affinities of some selected molecules with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. All values are in eV.

Molecule	B3LYP		B3PW91		Expt.
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	
C	1.37	1.37	1.47	1.47	1.26
CH	1.36	1.36	1.43	1.43	1.24
CH ₂	0.80	0.79	0.63	0.62	0.65
CH ₃	0.11	0.11	0.00	0.00	0.08
CN	4.04	4.05	3.94	3.94	3.82
NH	0.46	0.50	0.31	0.34	0.38
NH ₂	0.75	0.76	0.63	0.64	0.74
NO	0.42	0.36	0.34	0.28	0.02
O	1.68	1.68	1.51	1.50	1.46
OH	1.85	1.84	1.72	1.71	1.83
O ₂	0.57	0.56	0.41	0.38	0.44
F	3.56	3.53	3.43	3.39	3.40
Si	1.35	1.35	1.49	1.48	1.39
SiH	1.29	1.28	1.40	1.39	1.28
SiH ₂	1.20	1.19	1.28	1.27	1.12
SiH ₃	1.65	1.62	1.56	1.54	1.44
P	0.93	0.64	0.82	0.86	0.75
PH	1.09	1.11	1.01	1.03	1.00
PH ₂	1.26	1.27	1.21	1.22	1.26
PO	1.36	1.28	1.38	1.31	1.09
S	2.21	2.21	2.15	2.13	2.08
SH	2.36	2.34	2.32	2.29	2.31
S ₂	1.77	1.71	1.73	1.66	1.66
Cl	3.72	3.68	3.69	3.64	3.62
Cl ₂	3.06	2.87	2.93	2.70	2.39
BO	2.61	2.60	2.47	2.46	2.84
N ₃	2.66	2.65	2.63	2.61	2.76
	mean absolute deviation				
	0.15	0.12	0.13	0.11	

^aAll experimental values were taken from Refs. 27 and 28 except the ones for BO and N₃ taken from *Handbook of Chemistry and Physics*, 75th ed. (CRC, Boca Raton, FL, 1995).

absolute deviation found in the work of Becke is 0.14 eV, whereas, in this work and for the largest basis sets, 0.15 eV is found.

Table III lists the ionization energies for the species with the largest basis set for the LDA method together with the B-P86 and B-LYP methods. The largest mean absolute deviation is found for the LDA method. For the B-LYP method, a mean absolute deviation of 0.197 eV is found, which is essentially the same as the 0.195 eV of Gill and co-workers found for this functional using the 6-311++G(3df,2p) basis set. However, in their work, the additional systems He, Li, Be, Na, and Mg were considered, which were not calculated in the present work since correlation consistent basis sets have not been reported for these atoms yet. The smallest mean absolute deviation however is found for the BP86 method; it thus appears that the P86 correlation functional is performing somewhat better in the calculation of ionization energies than the LYP functional.

B. Electron affinities

In a second part, electron affinities were calculated for some selected atomic or molecular systems, again the molecules from the G2 thermochemical data set, and two addi-

tional molecules, BO and N₃. For this property, only the aug-cc-pVDZ and aug-cc-pVTZ basis sets were considered since it is generally accepted that the accurate calculation of anionic systems demands for the inclusion of diffuse functions. In Becke's original work, electron affinities were not considered due to the fact that the LSDA method does not bind negative ions.³⁰ However, very recently, Galbraith and Schaefer concluded in a study on F⁻ and F₂ using DFT calculation methods and Dunning's correlation consistent basis sets, that there was "no conclusive evidence to support the claims of negative ion instability."⁴⁸ However, the performance of DFT methods in the calculation of electron affinities remains relatively unstudied and it would be interesting to see if anionic instability occurs for other systems. The results for B3LYP and B3PW91 with the aforementioned basis sets can be found in Table IV. As can be seen, all electron affinities are positive, indicating a more stable anion with respect to the neutral system. The differences occurring between the aug-cc-pVDZ and aug-cc-pVTZ basis set are minor, the only noticeable exception being Cl₂. Looking at the mean absolute deviations, it appears that B3PW91 performs slightly better than B3LYP, the mean difference only being 0.02 eV. One can however conclude that the perfor-

TABLE V. Calculated electron affinities (eV) for the LDA, BP86, and B-LYP levels.

Molecule	LDA		BP86		BLYP	
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ
C	2.21	2.22	1.63	1.63	1.34	1.34
CH	2.13	2.14	1.59	1.60	1.32	1.33
CH ₂	1.54	1.43	0.93	0.92	0.83	0.83
CH ₃	0.90	0.91	0.28	0.28	0.13	0.14
CN	4.47	4.49	3.90	3.90	3.75	3.76
NH	1.24	1.27	0.65	0.69	0.95	0.57
NH ₂	1.64	1.66	0.93	0.95	0.79	0.81
NO	0.86	0.82	0.43	0.39	0.32	0.28
O	2.55	2.63	1.89	1.90	1.80	1.81
OH	2.83	2.84	2.06	2.07	1.94	1.94
O ₂	1.01	1.02	0.59	0.59	0.55	0.55
F	4.64	4.63	3.78	3.76	3.69	3.67
Si	2.00	2.01	1.56	1.56	1.23	1.23
SiH	1.90	1.89	1.48	1.47	1.17	1.16
SiH ₂	1.76	1.75	1.37	1.36	1.08	1.07
SiH ₃	1.11	2.20	1.71	1.54	1.56	1.53
P	1.46	1.50	1.03	1.07	0.86	0.90
PH	1.71	1.74	1.19	1.22	1.01	1.04
PH ₂	1.94	1.96	1.37	1.38	1.17	1.18
PO	1.81	1.75	1.41	1.35	1.18	1.12
S	2.87	2.87	2.32	2.32	2.13	2.13
SH	3.07	3.06	2.47	2.45	2.27	2.25
S ₂	2.22	2.18	1.78	1.73	1.59	1.54
Cl	4.44	4.42	3.82	3.78	3.61	3.57
Cl ₂	3.15	2.97	2.99	2.81	2.95	2.79
BO	3.09	3.08	2.58	2.57	2.47	2.46
N ₃	3.54	3.55	2.81	2.80	2.62	2.62
	mean absolute deviation					
	0.76	0.77	0.25	0.23	0.16	0.14

mance of the exact-exchange functionals in the calculation of electron affinities is exceptionally good, taking into consideration the fact that electron affinities were *not* considered in Becke's data set for the determination of the three "a" parameters. Finally, the calculated electron affinities using the LDA, B-P86, and B-LYP methods using the aug-cc-pVTZ basis set are depicted in Table V. Again, no negative electron affinities are observed. LDA shows the worst performance; in this case, it is the B-LYP functional that yields overall somewhat more accurate results than B-P86. However, B3LYP and B3PW91 show the lowest mean absolute deviation from experiment.

The overall very good performance of the density functional methods in the calculation of ionization energies and electron affinities is obviously very promising for the accurate determination of electronegativities and hardnesses [cf. Eqs. (6) and (7)], a problem that will be tackled in the next section.

C. Electronegativities and hardnesses

The calculation of electronegativities and hardness is subject to the following error sources:

(1) The finite difference approximation, due to the fact that a

numerical derivation with respect to the number of electrons can only be performed using a finite number of electrons (i.e., $\Delta N = \pm 1$).

- (2) The form of the energy curve $E = E(N)$ chosen; when considering a N , $N-1$, and $N+1$ system, only a quadratic and exponential curve can be fitted. Only when other systems with different (integral N) values are considered, other relationships can be looked for. The difficulty rises that almost all second electron affinities are negative, so that the curve to the $N+1$ electron side becomes less well described and that one usually sticks to the N and $N \pm 1$ cases for proper balancing.
- (3) The accuracy of the calculated energy values, due to the lack of a complete description of electron correlation effects and basis set incompleteness.

It is only the last item that will be considered in this section. Electronegativities and hardnesses for the first and second row atoms and some positive ions were calculated using both the Pople type 6-311+G(3df,2p) basis set and Dunning's aug-cc-pVTZ basis. In addition, CCSD(T) calculations were performed on the same systems, in which all the electrons were correlated. The results are summarized in Tables VI–IX. Concentrating on the electronegativities obtained with the 6-311+G(3df,2p) basis set, it can be seen that the worst performance is put in by the LDA method, as

TABLE VI. Electronegativities calculated at the different DFT levels and with the CCSD(T) method, using the 6-311++G(3df,2p) basis set, together with the experimental values. All values are in eV.

Atom/Ion	LDA	BP86	BLYP	B3LYP	B3PW91	CCSD(T)	Expt.
H	7.38	7.29	7.17	7.27	...	7.07	7.18
Li	3.40	3.09	2.99	3.09	3.03	3.19	3.01
Be	4.85	4.52	4.34	4.45	4.41	4.40	4.9
B	5.08	4.68	4.49	4.57	4.59	4.21	4.29
C	7.18	6.60	6.36	6.45	6.52	6.20	6.27
N	8.10	7.56	7.38	7.41	7.38	7.05	7.30
O	8.54	8.03	7.94	7.88	7.71	7.32	7.54
F	11.56	10.75	10.65	10.61	10.48	10.24	10.41
Na	3.37	2.99	2.93	3.00	2.89	2.83	2.85
Mg	4.18	3.82	3.66	3.75	3.70	3.63	3.75
Al	3.71	3.37	3.07	3.20	3.31	3.13	3.23
Si	5.32	4.89	4.57	4.72	4.85	4.71	4.77
P	6.25	5.79	5.53	5.66	5.69	5.48	5.62
S	6.96	6.45	6.26	6.37	6.30	5.98	6.22
Cl	9.08	8.45	8.24	8.38	8.34	8.09	8.30
Li ⁺	40.52	40.75	40.70	40.83	...	40.19	40.52
Na ⁺	27.14	26.44	26.39	26.51	26.41	26.02	26.21
Be ²⁺	85.62	86.30	86.31	86.43	...	85.72	86.05
Mg ²⁺	48.58	47.81	47.84	47.98	47.84	47.34	47.59
Cl ⁺	19.11	18.55	18.36	18.52	18.48	18.08	18.39
B ³⁺	147.72	148.91	148.96	149.05	...	148.32	148.65
Al ³⁺	75.26	74.46	74.56	74.71	74.54	73.99	74.22
	mean absolute deviation						
	0.66	0.23	0.18	0.21	0.15	0.25	

^aExperimental values taken from Ref. 1.

TABLE VII. Hardnesses calculated at the different DFT levels and with the CCSD(T) method, using the 6-311++G(3df,2p) basis set, together with the experimental values. All values are in eV.

Atom/Ion	LDA	BP86	BLYP	B3LYP	B3PW91	CCSD(T)	Expt.
H	6.12	6.32	6.38	6.40	...	6.53	6.43
Li	2.47	2.46	2.53	2.53	2.52	2.57	2.39
Be	4.61	4.59	4.64	4.67	4.59	4.88	4.5
B	4.01	4.06	4.14	4.17	4.12	4.02	4.01
C	4.97	4.99	5.05	5.10	5.06	5.00	5.00
N	7.38	7.21	7.13	7.26	7.41	7.45	7.23
O	6.06	6.22	6.23	6.28	6.27	6.09	6.08
F	7.01	7.08	7.09	7.15	7.15	7.02	7.01
Na	2.40	2.34	2.43	2.42	2.38	2.29	2.30
Mg	3.98	3.89	3.97	3.97	3.84	3.95	3.90
Al	2.75	2.78	2.80	2.82	2.79	2.79	2.77
Si	3.35	3.36	3.38	3.40	3.39	3.37	3.38
P	4.77	4.74	4.65	4.72	4.86	4.96	4.88
S	4.11	4.15	4.15	4.18	4.18	4.10	4.14
Cl	4.65	4.66	4.67	4.69	4.69	4.62	4.68
Li ⁺	34.65	35.20	35.19	35.22	...	34.42	35.12
Na ⁺	21.37	21.10	21.04	21.09	21.14	20.90	21.08
Be ²⁺	66.94	67.93	67.80	67.83	...	67.58	67.84
Mg ²⁺	32.80	32.57	32.42	32.52	32.63	32.44	32.55
Cl ⁺	5.39	5.45	5.45	5.45	5.45	5.37	5.42
B ³⁺	109.37	110.83	110.57	110.60	...	110.48	110.72
Al ³⁺	46.01	45.80	45.58	45.71	45.87	45.72	45.77
	mean absolute deviation						
	0.21	0.05	0.09	0.08	0.08	0.13	

^aExperimental values taken from Ref. 1.

TABLE VIII. Electronegativities calculated at the different DFT levels and with the CCSD(T) method, using the aug-cc-pVTZ basis set, together with the experimental values. All values are in eV.

Atom/Ion	LDA	BP86	BLYP	B3LYP	B3PW91	CCSD(T)	Expt. ^a
H	7.41	7.31	7.19	7.29	7.23	7.16	7.18
B	5.05	4.71	4.53	4.60	4.61	4.23	4.29
C	7.18	6.61	6.37	6.46	6.52	6.21	6.27
N	8.13	7.59	7.42	7.44	7.40	7.10	7.30
O	8.57	8.06	7.98	7.91	7.73	7.38	7.54
F	11.58	10.77	10.69	10.64	10.49	10.30	10.41
Al	3.74	3.40	3.12	3.24	3.34	3.18	3.23
Si	5.34	4.91	4.59	4.73	4.86	4.75	4.77
P	6.27	5.81	5.55	5.68	5.71	5.54	5.62
S	12.19	6.46	6.27	6.38	6.31	6.05	6.22
Cl	9.07	8.44	8.24	8.38	8.34	8.14	8.30
Cl ⁺	19.12	18.56	18.37	18.53	18.49	18.14	18.39
B ³⁺	147.81	149.03	149.10	149.17	...	148.26	148.65
Al ³⁺	75.29	74.47	74.85	74.73	74.53	73.77	74.22
	mean absolute deviation						
	1.15	0.27	0.20	0.20	0.14	0.19	

^aExperimental values taken from Ref. 1.

could be expected. However, all gradient corrected methods and the exact exchange methods perform better, compared to experiment, than the very powerful CCSD(T) method. The lowest mean absolute deviation is found for the B3PW91 method (which also showed the overall best performance in the calculation of I and A), followed by B-LYP. All of the methods perform considerably less well in the calculation of ionic electronegativities; however, since these values are larger in magnitude anyway, the relative error is of the same magnitude as for the calculation of atomic electronegativities. Moreover, the general trend seems to exist that the first row atoms are considerably less well described than the second row atoms. This could be due to the fact that, due to their smaller size and thus larger effective nuclear charge and average external potential, the density falls off more rapidly, giving rise to a higher density gradient, a situation that is

perhaps less well described by the gradient corrected or the exact exchange functionals. Within the second row elements, the electron density can be expected to behave much more smoothly. In that case, the gradient corrected and exact exchange methods may behave considerably better. As can be seen, the performance of the DFT methods is around 0.05 eV worse than their average performance in the calculation of I and A . In most of the atomic cases, all the DFT methods overestimate the ionization energy and the electron affinity, thus giving rise to error amplification when the electronegativity is calculated as the mean of I and A . When this is indeed the case, calculated hardnesses should be closer to experiment. It can be seen from Table VII that this is indeed the case. The mean absolute deviation for the local density approximation is reduced to one-third as compared to the electronegativities; the best performance is now due to

TABLE IX. Hardnesses calculated at the different DFT levels and with the CCSD(T) method, using the aug-cc-pVTZ basis set, together with the experimental values. All values are in eV.

Atom/ion	LDA	BP86	BLYP	B3LYP	B3PW91	CCSD(T)	Expt.
H	6.10	6.30	6.35	6.38	...	6.44	6.43
B	4.85	4.03	4.09	4.14	4.10	4.00	4.01
C	4.96	4.98	5.03	5.08	5.06	4.99	5.00
N	7.33	7.16	7.08	7.22	7.38	7.39	7.23
O	5.94	6.16	6.17	6.23	6.23	6.05	6.08
F	6.95	7.01	7.02	7.11	7.10	6.98	7.01
Al	2.72	2.75	2.75	2.78	2.78	2.76	2.77
Si	3.34	3.35	3.36	3.39	3.38	3.36	3.38
P	4.77	4.73	4.64	4.71	4.85	4.93	4.88
S	-1.10	4.15	4.15	4.18	4.18	4.10	4.14
Cl	4.65	4.67	4.67	4.70	4.70	4.64	4.68
Cl ⁺	5.39	5.45	5.45	5.46	5.45	5.37	5.42
B ³⁺	109.43	110.94	110.67	110.69	...	110.42	110.72
Al ³⁺	46.03	45.81	45.37	45.72	45.86	45.65	45.77
	mean absolute deviation						
	0.61	0.06	0.09	0.06	0.06	0.06	

^aExperimental values taken from Ref. 1.

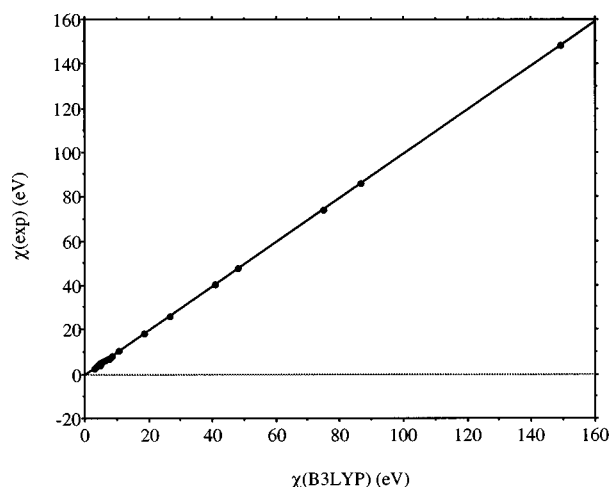


FIG. 1. Correlation of the B3LYP/6-311++G(3df,2p) electronegativities with experiment ($r^2=0.999\ 98$, $n=22$).

B-P86, followed by B3LYP, B3PW91, and B-LYP. Again, all the DFT methods perform better than the CCSD(T). These results are very hopeful indeed for calculating electronegativities and hardnesses to a very good accuracy at an acceptable computational cost. From the results obtained in the calculation of electronegativities and hardnesses of 22 atoms and ions, B3LYP and B3PW91 emerge as the best DFT methods to calculate the properties, when a basis set of *spdf* zeta quality is used. Figures 1 and 2 show a plot of the B3LYP electronegativities and hardnesses with respect to the experimental values, showing indeed a very good correlation.

Tables VIII and IX summarize the results for the electronegativities and hardness obtained using Dunning's aug-cc-pVTZ basis set, for a less extended set of atoms and ions. Exactly the same conclusions can be drawn. For this basis set however, the CCSD(T) methods seems able to keep up the performance with the DFT methods. This could be due to a

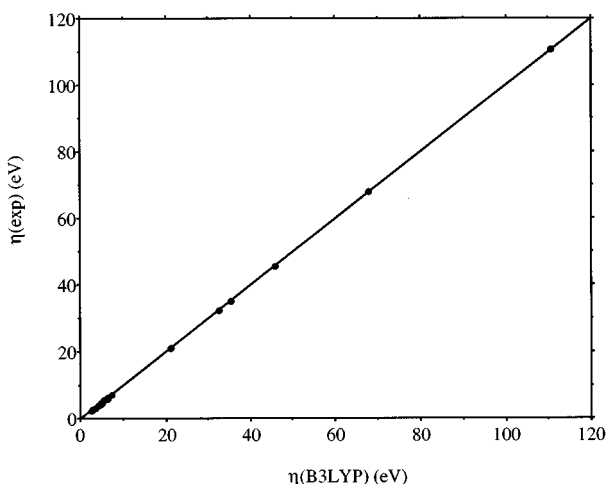


FIG. 2. Correlation of the B3LYP/6-311++G(3df,2p) hardnesses with experiment ($r^2=0.999\ 99$, $n=22$).

more effective description of electronic correlation effects with this basis set. The LDA method however performs considerable less well in the calculation of electronegativities as compared to the Pople type basis set. The same can be said for the hardnesses. The same general conclusions hold for the Pople basis set, the best overall performance being due to B3LYP and B3PW91.

IV. CONCLUSIONS

The performance of two exact exchange density functionals B3LYP and B3PW91 in the calculation of ionization energies and electron affinities was investigated using Dunning's correlation consistent basis sets. Comparison was made with other DFT methods and experiment. In the calculation of ionization energies, there is not much to choose between the two functionals, both giving a mean absolute deviation of 0.15 eV for a basis set of *spdf* quality. However, mean absolute deviations of this magnitude are also found for the electron affinities, not previously included in Becke's work. Finally, electronegativities and hardnesses were calculated for some atoms and cations using both a Pople and Dunning type of basis set; the results were compared with both experiment and high level CCSD(T) calculations. Again, B3LYP and B3PW91 evolve as the methods to be preferred in the calculation of these properties.

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