article

Finding electron affinities with approximate density functionals

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There has been a long discussion about the reliability of approximate density functionals for atomic anions. It is well known that the extra electron produces a strong self-interaction error, so strong that the extra electron is unbound. Despite this, electron affinities have been calculated using finite basis sets and very good results have been reported by Schaefer and others. We recently suggested how to resolve the contradicting viewpoints between theory and calculation. We calculate electron affinities using Hartree-Fock or exact exchange DFT densities which bind the extra electron correctly and show excellent results with well-defined basis-set limit. Here we give further data in support of our argument, and explain further how and why accurate densities and total energies of anions may be obtained from approximate density functional theory, despite positive HOMO energies.

Keywords: density functional theory, self-interaction error, electron affinity, Hartree-Fock, localized Hartree-Fock, limited basis set

1. Introduction

Density functional theory (DFT) has become a popular choice for many electronic structure calculations in quantum chemistry[1], providing a useful balance between accuracy and computational cost. This enables much larger systems to be calculated than with *ab initio* methods, while maintaining useful accuracy. Modern DFT was established with the Hohenberg-Kohn[2] theorem in 1964 and the Kohn-Sham (KS)[3] scheme in 1965 for practical application of DFT. KS-DFT is formally rigorous but, still, the exchange-correlation (XC) energy, E_{XC}, must be approximated as a functional of the density in practical calculations. The first approximation to E_{XC} was the local density approximation (LDA)[3–6] derived from the uniform electron gas and using only the density at a given point to find the XC energy density at that point. In the late 1980s and mid 1990s, generalized gradient approximations (GGA) such as B88[7], LYP[8], PW91[9], and PBE[10] were developed, depending on both the density and the gradient of the density at a given point. The mixing of a finite fraction of exact exchange introduced hybrid functionals like B3LYP[8, 11] and PBE0[12]. These standard approximate functionals provide enough accuracy in many areas of chemistry and physics, and are used in most practical calculations.

However, there has been an ongoing argument about the applicability of such approximations to atomic anions[13, 14]. Subsequently, this raises a question about the reliability of DFT for electron affinity (EA) calculations in general. Approximate functionals suffer from a self-interaction error (SIE), and this is particularly

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strong for anions[15]. SIE is due to the fact that self-repulsion of the electron in the Coulomb potential is not exactly canceled by the approximate exchange potential such as LDA and GGA. The LDA or GGA XC potentials decay exponentially rather than as $-1/r$ in an asymptotic region far from the nucleus. This makes the HOMO energy positive even for stable anions, indicating that a valence electron is unbound, and also produces a large barrier in the KS effective potential.

From a formal viewpoint, approximate DFT can not be applied to negative ions unless the HOMO eigenvalues are negative[16], because the HOMO is unbound. Nevertheless, in many papers, EA's have been calculated using approximate functionals with finite basis sets and reasonable results have been reported[13, 17, 18]. These conflicting views are well summarized in Refs [13] and [14]. The former shows that if a large but finite basis set is used with approximate functionals, there is no difficulty in obtaining accurate EA's despite positive HOMO energies. The latter argues why such approximate DFT calculations should be discounted on a formal basis.

In a recent letter[19], we showed that *both* theoretical and practical viewpoints are essentially correct, and how they can be reconciled. Also we suggested a practical, theoretically appealing, method to avoid SIE problems, which produces reasonable (even slightly better) results compared to existing methods. In this paper, we provide more data to support our argument and suggest another way to explain how and why accurate densities and total energies of anions can be obtained from approximate DFT with limited basis set (LBS) approaches.

2.   Background

2.1.   *Exact statements*

We begin with the KS formalism. The KS equations for any atom or ion are

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{s}\sigma}(r)\right]\phi_{i\sigma}(r) = \epsilon_{i\sigma}\phi_{i\sigma}(r)\,,\tag{1}$$

and the spin densities are

$$n_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma}|\phi_{i\sigma}(\mathbf{r})|^2\,,\tag{2}$$

where $v_{\mathrm{s}\sigma}(r)$ is a single, multiplicative spin-dependent KS potential and σ is spin index($\uparrow$ and $\downarrow$). The KS potential is a sum of three contributions:

$$v_{\mathrm{s}\sigma}(r) = v(r) + v_{\mathrm{H}}[n](r) + v_{\mathrm{xc}\sigma}[n_\uparrow, n_\downarrow](r)\,,\tag{3}$$

where $v(r) = -Z/r$ for an atomic system, $v_{\mathrm{H}}(r)$ is the Hartree potential which is given as

$$v_{\mathrm{H}}(r) = \int d^3r'\, \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,,\tag{4}$$

and the XC contribution is

$$v_{\mathrm{xc}\sigma}[n_\uparrow, n_\downarrow](r) = \frac{\delta E_{\mathrm{xc}}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(r)}\,.\tag{5}$$

Since $v_{s\sigma}(r)$ depends on the (spin)-density, we solve the KS equations iteratively, and find a self-consistent solution.

In the asymptotic region far from a nucleus, Eq. (4) shows that the Hartree potential decays as N/r, where N is the number of electrons. The exact XC potential decays as

$$v_{\text{xc}}(r) \rightarrow -1/r, \quad r \rightarrow \infty, \tag{6}$$

which is known to be a pure exchange effect[20]. Thus, the exact KS potential decays in the asymptotic region as

$$v_{\text{s}}(r) \rightarrow -\frac{Z - N + 1}{r}, \quad r \rightarrow \infty. \tag{7}$$

For a neutral atom, the exact $v_{\text{s}}(r)$ decays as $-1/r$ exactly, since $Z = N$. But for an anion, $v_{\text{s}}(r)$ is short-ranged, as seen in Fig. 1. The exact He potential decays as $-1/r$, but that of H^- is short-ranged.
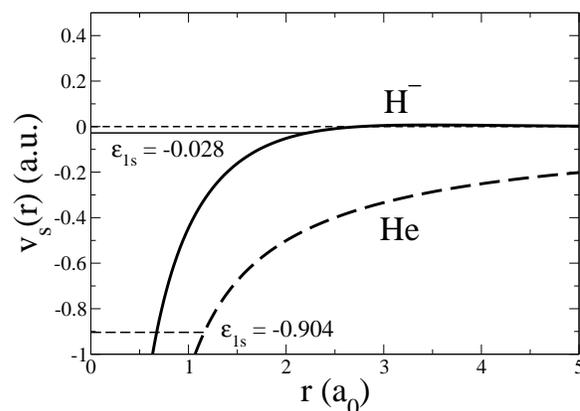

Figure 1. Comparison of essentially exact KS potentials of H^- and He. The exact KS potentials are obtained from the densities of highly accurate quantum Monte Carlo calculations, and by inversions of the KS equations from Umrigar et al[21]

Long ago, in the context of Hartree-Fock (HF) calculations, Koopmans[22] stated that if there is no relaxation in HF orbitals on ionization process, the ionization energy is approximately equal to the HOMO energies of HF.

$$I^{\text{HF}} = E^{\text{HF}}(N - 1) - E^{\text{HF}}(N) \simeq -\epsilon_N \tag{8}$$

However, this includes two kinds of errors. The first one is, as we already said, that it ignores the reorganization of orbitals, and the second one is to ignore the correlation effects. These are often canceled with each other fortuitously. In exact DFT, there is an an analogous theorem to Koopman's. Perdew et al[23, 24] proved that, in exact DFT, the ionization energy is precisely that of the HOMO energy of KS system:

$$I = E(N - 1) - E(N) = -\epsilon_{\text{KS}}^{\text{HOMO}}(N) \tag{9}$$

Thus for He, the last occupied level of the exact KS potential is at $\epsilon = -24.2$ eV, the exact ionization potential (IP) as in Fig. 1. For the anion, the analogous

condition is

$$A = E(N) - E(N+1) = -\epsilon_{\mathrm{KS}}^{\mathrm{HOMO}}(N+1)\,. \tag{10}$$

In Fig. 1, the short-ranged potential for H^- yields a HOMO of only -0.75 eV. These conditions are violated by all standard approximations.

2.2. *Density functional approximations*

Approximate XC functionals such as LDA or GGA do not reproduce the exact asymptotic behavior. For spin-unpolarized LDA, the exchange potential is given by

$$v_{\mathrm{x}}^{\mathrm{LDA}}(r) = 4A_{\mathrm{x}}/3\,n^{1/3}(r)\,, \quad A_{\mathrm{x}} \simeq -0.738\,. \tag{11}$$

In the asymptotic region of an atomic system, a density decays exponentially. Thus the LDA exchange potential also decays exponentially rather than as $-1/r$. GGA includes the gradient of the density, but still decays exponentially. Although this asymptotically wrong decay has a small effect on a density itself, this produces incorrect KS eigenvalue structure and does not reproduce a Rydberg series in either approximation, as seen in Fig. 2. It also leads to very poor HOMO levels in
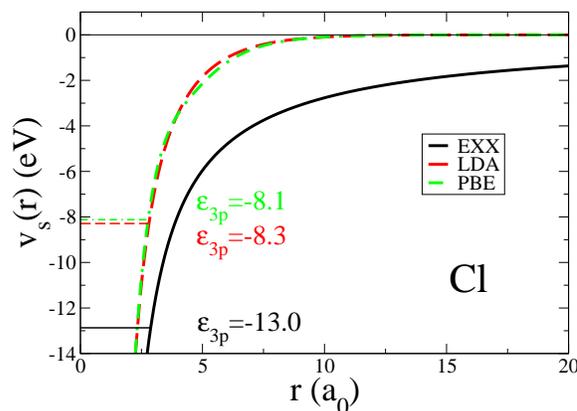

Figure 2.   Comparison of KS potentials of Cl. The black line is the exact exchange only (EXX) $v_{\mathrm{S}}(r)$. The red (dashed) and green (dot and dash) line are the $v_{\mathrm{S}}^{\mathrm{LDA}}(r)$ with LDA and PBE. The horizontal lines are the HOMO (3p orbital) energies. All calculations are performed with an atomic OEP code[25].

approximate DFT calculations (For Cl, ϵ^{HOMO}=-8.21 eV with LDA, -8.13 eV with PBE, and -9.25 eV with B3LYP, but $I = 12.97$ eV). These are all manifestation of the SIE.

   For neutral atoms or cations, this SIE is not that severe. One can calculate total energies by evaluating energy functionals on self-consistent KS densities. And corresponding total energies and energy differences are known to have chemically useful accuracy with sophisticated XC functionals[26]. However, the SIE becomes devastating in atomic anions. Due to the extra electron in the system, the sum of $v(r)$ and $v_{\mathrm{H}}(r)$ decays as $1/r$ in the asymptotic region, and this is not canceled by the exponential decay of LDA or GGA exchange potentials. Thus, $v_{\mathrm{S}}(r)$ in anions behaves as

$$v_{\mathrm{S}}(r) \to +1/r, \quad r \to \infty, \ \text{(anions in LDA/GGA)} \tag{12}$$

with approximate XC functionals. The effect of SIE can be reduced in a big molecule due to the spatial charge distribution but, especially for small systems, this causes a large positive bump in the KS potential, and makes the HOMO positive, as shown in Fig. 3. In Fig. 3, we plot the Kohn-Sham (KS) potential for Cl^- which
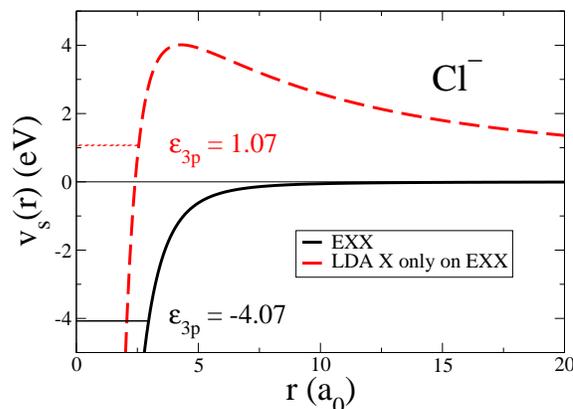

Figure 3. Comparison of KS potentials of Cl^-. The black line is the EXX $v_S(r)$, obtained from an atomic OEP code[25]. The red (dashed) line is the $v_S^{LDA}(r)$ with LDA exchange only on the EXX density. The two horizontal lines are the HOMO (3p orbital) energies.

is obtained from the exact exchange only (EXX) calculation (see Sec. 2.3) and the LDA X (exchange only) KS potential on the EXX density, illustrating this. From the LDA X/aug-cc-pV5Z calculation, the HOMO energy of Cl^- is 1.07 eV, and the 3p orbital becomes a sharp shape resonance. Hybrid functionals mix about 25% of exact exchange with a GGA, but this will only reduce the barrier by about 25%, not solving the SIE problem.

   More than two decades ago, Shore et al[15] showed the instability of H^- with LDA. They calculated the total energy and HOMO energy, ϵ_{1s}, of the H^- ground state in a self-consistent LDA calculation by confining electrons in a spherical cavity and varying the radial size of the cavity. They found the asymptotic solution of the ground state by placing the spherical hard wall at $R = 25$ a.u. and varying the number of core electrons. The energy minimum was found when the 1.7 electrons remained in the core and 0.3 electron escaped into the asymptotic region, and then ϵ_{1s} became zero.

   In the more recent chemistry literature, Galbraith and Schaefer[13] state that, if a large basis set such as Dunning's augmented correlation consistent polarized valence X-tuple zeta basis set (aug-cc-pVXZ, X=D, T, Q, and 5, AVXZ in this paper)[27, 28] is used, approximate DFT can be used to calculate accurate EA. They calculate the total energies of neutral atoms and anions using approximate functionals with finite basis sets and show calculated EA's are very accurate compared to highly accurate *ab initio* method or experimental EA's although the HOMO energies are still positive. Rösch and Trickey[14] point out that approximate DFT methods can not describe the negative ions properly as shown in Fig. 3, although DFT (KS-DFT) does not have any problem to handle small negative ions in theory. They argue that approximate DFT calculation for small anions produces the positive HOMO, and only the usage of a finite Gaussian basis set makes the outermost orbital artificially normalizable and masks the positive HOMO eigenvalue problem.

   After these two successive papers about the negative ions, Jarecki and Davidson[16] show that, for F^-, there are two plateau regions in the energy curve as

a function of a basis-set size by adding more diffuse functions. In the first plateau, both total energy and HOMO eigenvalue seem to converge. If more diffuse functions are added to the basis set, and the basis set spans the outside area of outer turning point ($\sim 17 \text{Å}$) in Fig. 3, then HOMO energy suddenly drops to near zero due to the escape of fractional number of an electron. Despite this leakage, the total density is not changed much, thus the total energy is hardly changed. With more diffuse functions, the HOMO energy level finally drops down below 0.

2.3.   *Orbital dependent approximations*

There are several cures to self-interaction errors. One of them is to use the self-interaction corrected LDA or GGA[29]. This removes the self-interaction artificially by subtracting the part of E_H and E_XC^LDA (or E_XC^GGA) which depends on the spin-dependent KS orbital density. But, in this scheme, the total energy is not invariant under the unitary transformation of KS orbitals. The energy difference is about 0.1 H in the ground state according to the choice of basis set representations[30]. The other remedy in DFT is to use the optimized effective potential (OEP) method[31], which finds the exchange potential as an *orbital*-dependent exchange functional, often denoted EXX, producing a KS potential with the correct asymptotic $-1/r$ behavior and a HOMO that is close to $-I$ for neutral systems which was used to create the black line of Fig. 3. A practical and accurate approximation to OEP was developed by Görling and co-workers [32, 33], called localized Hartree-Fock (LHF). In Fig. 3, the EXX HOMO is at -4.07 eV, too low by 0.5 eV. Simple HF itself can be an alternative treatment for SIE but is not a KS-DFT method, because it does not produce a single multiplicative potential. EXX total energies are almost identical to those of HF, and the ϵ^HOMO values are also very close[34]. However, the electron affinities calculated from total energy differences with these methods often have negative values even for stable anions, since the correlation effects are large.

2.4.   *Adjusting the constant in the XC potential*

If the extra electron of an anion is not bound by approximate DFT, how can we get those reasonable EA's in Refs. [17] and [18] (also, see Table 2 in Sec. 3.2 from our calculation) by a traditional limited basis-set approach?

In KS DFT[3], $v_\text{s}(r)$ is defined only for a fixed number of particles, and, by HK theorem[2], $v_\text{s}(r)$ is only determined up to an arbitrary constant. Adding a constant to $v_\text{s}(r)$ does not affect the density. In this case, all KS orbital eigenvalues are shifted by that amount. According to the magnitude of the constant, the orbital eigenvalues can be positive. So a positive orbital energy does not imply that a density or a total energy must be discarded. But, in approximate DFT calculations, we usually

set $v_\text{s}(r)$ to be zero as $r \rightarrow \infty$. Then, if the HOMO is positive, the extra electron of an anion is not in a bound state as shown in Fig. 3. But now, for fun, consider adding a very small correction to any approximate XC functional:

$$\Delta E_\text{XC} = -\Delta\epsilon \int d^3r \, (n^\text{T} - n(r))\Theta(n^\text{T} - n(r)), \tag{13}$$

where $\Delta\epsilon$ is some constant, a few eV, and n^T is a very small density value, and Θ is a step function. Adding it to, e.g. density functional approximations (DFA)

$$E_\text{XC} = E_\text{XC}^\text{DFA} + \Delta E_\text{XC}, \tag{14}$$
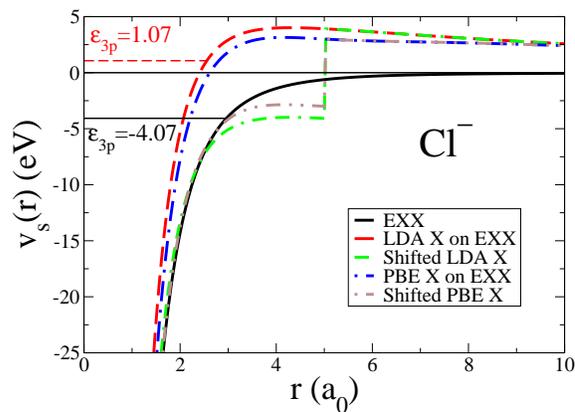
Figure 4. Shifted approximate $v_{\rm S}(r)$ potentials (eV) in Cl^-. The HOMO from EXX is -4.07 eV, and the HOMO from LDA X/AV5Z is 1.07 eV. We shift the LDA X and PBE X $v_{\rm S}(r)$ by choosing $\Delta\epsilon = 8.0$ and $\Delta\epsilon = 6.0$ repectively. $n^{\rm T}$ is chosen as 8×10^{-5} arbitrarily.

will barely change the energy if $n_{\rm T}$ is chosen small enough. But the XC potential is changed dramatically:

$$v_{\rm xc}(r) = v_{\rm xc}^{\rm DFA}(r) - \Delta\epsilon \left[\Theta(n^{\rm T} - n(r)) - 1\right]. \tag{15}$$

where the constant in the XC potential has been chosen to vanish as $r \to \infty$. This kind of shift is well-known in the literature for neutral atoms[35–37].

We now apply this arbitrary correction to the approximate $v_{\rm s}(r)$ of Cl^- in Fig. 4. The constant, $\Delta\epsilon$, is chosen as 8.0 for LDA X and 6.0 for PBE X, and $n^{\rm T} = 8\times 10^{-5}$, which is chosen arbitrarily. This shifted $v_{\rm s}(r)$ has almost the same density as the original approximation for Cl^- everywhere except in the asymptotic region, but has a negative HOMO energy.
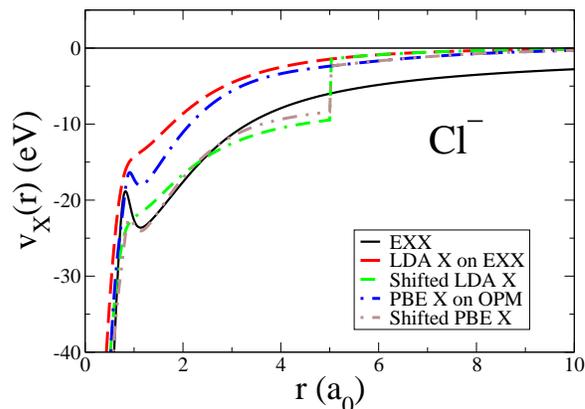
Figure 5. Shifted approximate $v_{\rm X}(r)$ potentials (eV) in Cl^-. We shift the LDA and PBE $v_{\rm X}(r)$ by choosing $\Delta\epsilon = 8.0$ and $\Delta\epsilon = 6.0$ repectively. $n^{\rm T}$ is chosen as 8×10^{-5} arbitrarily.

Can approximate DFT with self-interaction errors reproduce the EXX KS potential? We plot the exchange potentials using our model in Fig. 5. These shifted LDA X and PBE X potentials follow the EXX KS potential quite faithfully compared to the original LDA and PBE X KS potentials before 5 a.u.. Then, can this approximate DFT provide the accurate density and total energy? This is generally true, if the approximate functional gives the accurate description of a density in the core shell, except for the asymptotic region (tail of the density).

To confirm our argument, we define an electron affinity density as a difference between radial densities of a negative ion and a neutral atom and plot the electron affinity density of Cl^- in Fig. 6. To calculate the density of Cl^-, we use LDA and PBE functionals with AV5Z via TURBOMOLE v6.2[38]. For non-spherical Cl and EXX calculation, we use a fully numerical OEP[25] code with spherical approximations. We suspect that the approximate functionals yield more accurate
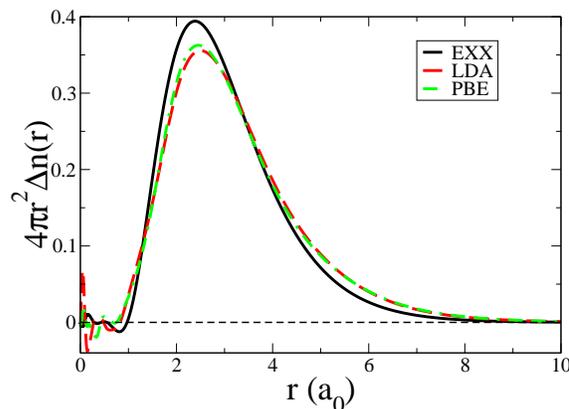
Figure 6.   Plot of electron affinity densities (anion - neutral) for Cl. For EXX and non-spherical cases, an atomic OEP code was used. For Cl^-, we use LDA and PBE with AV5Z.

EA densities than EXX, despite the unbounded HOMO, for the reasons we have described. We see that the radial EA densities from LDA and PBE are very close to the EXX calculation except in the region $r > 5$.

3.   Detailed numerical results

Our suggestion is to use the density from an exact exchange calculation which binds the extra electron correctly[19]. Then we evaluate the approximate functional on that density to find the total energies of neutral atoms and/or negative ions. This scheme has its own disadvantages but, at least, we can avoid all problems from unbound electrons. All computational details can be found in our recent letter[19].
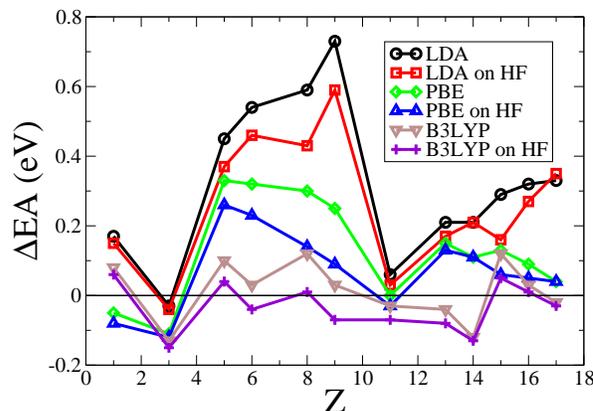
Figure 7.   Comparison of errors (Δ) in electron affinities in the first 2 rows of periodic table. Total energies are calculated with LDA, PBE and B3LYP functionals, evaluated on self-consistent densities and HF densities for both neutral atoms and anions with AVTZ basis set.

We summarize our results using LDA[4–6], PBE[10], and B3LYP[8, 11] functionals in Fig. 7 for EA's to show our method briefly. The traditional EA's, which are obtained from self-consistent field (SCF) calculations with LBS, are much more accurate than the corresponding ionization potentials (IP, typically by about a factor of 2), with mean absolute errors below 0.1 eV. Results with our method are very similar to LBS, but generally a little better. These results with LBS vary a little when the basis set is increased by either larger valence space or more diffuse functions. The results from our new method almost do not change with the size of basis sets. The method has a well-defined basis-set limit, if we are evaluating approximate functionals on Hartree-Fock (HF) densities for both neutral atoms and anions. Also we can find similarly good results for PBE0[12], and meta-GGA (TPSS)[39] on HF densities.

3.1. *Ionization potential*

First of all, to benchmark our methods, we study ionization potentials according to basis sets from AVDZ to AV5Z in Table 1. The ionization potentials converge already at the AVDZ basis set. All approximate functionals follow their usual behaviors. The LDA exchange energy is generally underestimated by 10 %, and the LDA correlation energy is overestimated by a factor of 2-3. But the magnitude of LDA exchange is 4 times bigger than that of LDA correlation. Thus, LDA generally underestimates the total energy of an atom. LDA underestimates total energies of positive ions more than those of neutral atoms, so IP from LDA is largely overestimated. Non-empirical functionals (PBE, PBE0, and TPSS) show more systematic errors than B3LYP. Interestingly, the mean absolute errors (MAE) of PBE and B3LYP are almost identical regardless of mixing of exact exchange. PBE0 with 25% exact exchange mixing and TPSS give the best results (total MAE, $\sim$0.13 eV).

3.2. *Limited basis set approach*

In Table 2, we report the results of traditional LBS methods, whose LDA, PBE, and B3LYP numbers with AVTZ are plotted in Fig. 7. Without concerning the positive HOMO eigenvalues of anions, these results are better than IP calculations except LDA in Table 1. The EA's are also converged already in AVDZ basis set. LDA functional is the worst case for EA calculations and consistently overestimates the electron affinity except H and Li. PBE reduces the overestimation in comparison with LDA except for H and Li. However, still, the MAE of PBE is not within chemical accuracy. PBE0 with the quarter of exact exchange improves the EA's compared to the result of PBE. B3LYP and TPSS functionals give the best total MAE ($\sim$0.07 eV). TPSS is slightly better for the second-row atoms (0.01 eV difference). TPSS systematically reduces the overestimations, and is the best functional in the LBS approach for atomic EA calculations without any input from exact exchange.

3.3. *HOMO of anions*

Although the LBS approaches produce accurate EA's, the HOMO energies of anions are still positive in most cases. We show the ϵ_{HOMO} with AV5Z basis set in Table 3. PBE0 gives negative ϵ_{HOMO} for F and Cl (B3LYP for Cl), but these eigenvalues are much smaller than the corresponding EA's.

Table 1.   Ionization potentials (eV). Total energies for both neutral atoms and positive ions are calculated by SCF procedure.

	IP[a]	Δ IP																		
		LDA				PBE				B3LYP				PBE0				TPSS			
		DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z
H	13.60	-0.59	-0.58	-0.58	-0.57	-0.02	0.00	0.00	0.01	-0.04	-0.02	-0.02	-0.02	0.02	0.04	0.04	0.04	0.00	0.01	0.01	0.01
Li	5.39	0.06	0.08	0.08	0.08	0.19	0.19	0.19	0.20	0.15	0.16	0.16	0.16	0.17	0.18	0.18	0.18	0.11	0.11	0.11	0.11
B	8.30	0.35	0.34	0.34	0.35	0.39	0.37	0.37	0.37	0.38	0.35	0.35	0.36	0.36	0.34	0.35	0.35	0.48	0.47	0.47	0.47
C	11.26	0.44	0.43	0.43	0.43	0.31	0.28	0.28	0.28	0.22	0.19	0.19	0.20	0.28	0.25	0.25	0.25	0.21	0.20	0.20	0.20
O	13.62	0.38	0.39	0.38	0.38	0.43	0.44	0.44	0.44	0.41	0.42	0.41	0.41	0.23	0.23	0.23	0.23	0.40	0.42	0.43	0.42
F	17.42	0.58	0.55	0.54	0.54	0.28	0.25	0.24	0.23	0.25	0.21	0.20	0.20	0.09	0.04	0.03	0.02	0.05	0.02	0.02	0.01
Na[b]	5.14	0.19	0.22	0.23	0.23	0.19	0.22	0.22	0.22	0.18	0.21	0.22	0.22	0.13	0.15	0.16	0.16	0.02	0.04	0.04	0.04
Al	5.99	0.05	0.04	0.04	0.05	0.09	0.08	0.09	0.09	-0.04	-0.05	-0.05	-0.05	0.11	0.10	0.11	0.11	0.16	0.16	0.17	0.17
Si	8.15	0.10	0.09	0.08	0.08	0.06	0.05	0.05	0.05	-0.10	-0.11	-0.12	-0.12	0.08	0.07	0.07	0.07	0.07	0.06	0.07	0.07
P	10.49	0.11	0.10	0.09	0.09	0.02	0.01	0.00	0.00	-0.16	-0.18	-0.19	-0.19	0.06	0.05	0.04	0.04	0.03	0.02	0.02	0.01
S	10.36	0.19	0.21	0.21	0.21	0.05	0.07	0.07	0.07	0.09	0.10	0.10	0.10	0.03	0.05	0.05	0.04	0.08	0.10	0.10	0.10
Cl	12.97	0.25	0.24	0.23	0.23	0.03	0.01	0.00	0.00	0.03	0.00	0.00	0.00	0.03	-0.01	-0.01	-0.02	0.00	-0.01	-0.02	-0.02
1st		0.40	0.39	0.39	0.39	0.27	0.26	0.26	0.26	0.24	0.23	0.22	0.23	0.19	0.18	0.18	0.18	0.21	0.20	0.21	0.20
2nd		0.15	0.15	0.15	0.15	0.08	0.07	0.07	0.07	0.10	0.11	0.11	0.11	0.08	0.07	0.07	0.07	0.06	0.06	0.07	0.07
MAE		0.27	0.27	0.27	0.27	0.17	0.17	0.16	0.16	0.17	0.17	0.17	0.17	0.13	0.13	0.13	0.13	0.13	0.13	0.14	0.14

[a]available from http://cccbdb.nist.gov/

[b]For Na, AV5Z is not available, so we used the AVQZ result for AV5Z to compare MAE's.

Table 2.   Errors in electron affinities (eV). Total energies for both neutral atoms and anions are calculated by SCF procedure.

| | EA[a] | Δ EA | | | | | | | | | | | | | | | | | | | |
| | | LDA | | | | PBE | | | | B3LYP | | | | PBE0 | | | | TPSS | | | |
		DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z
H	0.75	0.15	0.17	0.18	0.18	-0.07	-0.05	-0.04	-0.03	0.06	0.08	0.09	0.09	-0.16	-0.14	-0.13	-0.13	0.02	0.04	0.05	0.05
Li	0.62	-0.03	-0.03	-0.03	-0.03	-0.11	-0.11	-0.11	-0.11	-0.12	-0.13	-0.13	-0.13	-0.13	-0.13	-0.12	-0.13	-0.04	-0.04	-0.03	-0.04
B	0.28	0.44	0.45	0.46	0.48	0.32	0.33	0.34	0.36	0.10	0.10	0.11	0.12	0.19	0.19	0.20	0.20	0.16	0.17	0.18	0.19
C	1.26	0.53	0.54	0.55	0.55	0.31	0.32	0.33	0.34	0.03	0.03	0.03	0.04	0.15	0.15	0.15	0.16	0.18	0.18	0.18	0.19
O	1.46	0.58	0.59	0.60	0.61	0.30	0.30	0.32	0.33	0.12	0.12	0.12	0.13	-0.07	-0.08	-0.07	-0.07	0.03	0.03	0.04	0.05
F	3.40	0.74	0.73	0.73	0.73	0.28	0.25	0.25	0.26	0.06	0.03	0.03	0.03	-0.11	-0.16	-0.16	-0.16	0.05	0.01	0.01	0.02
Na	0.55	0.07	0.06	0.06	0.06	0.01	0.00	0.00	0.00	-0.02	-0.03	-0.03	-0.03	-0.03	-0.04	-0.04	-0.04	0.04	0.03	0.03	0.03
Al	0.43	0.21	0.21	0.21	0.22	0.15	0.15	0.16	0.16	-0.04	-0.04	-0.04	-0.04	0.11	0.11	0.10	0.11	0.09	0.08	0.08	0.08
Si	1.39	0.20	0.21	0.20	0.20	0.11	0.11	0.10	0.11	-0.12	-0.12	-0.12	-0.12	0.08	0.07	0.07	0.07	0.07	0.04	0.04	0.04
P	0.75	0.25	0.29	0.28	0.29	0.09	0.13	0.13	0.14	0.09	0.12	0.12	0.13	0.00	0.04	0.03	0.04	0.07	0.10	0.10	0.10
S	2.08	0.31	0.32	0.31	0.31	0.10	0.09	0.09	0.09	0.04	0.03	0.03	0.03	0.01	-0.01	-0.01	-0.01	0.03	0.02	0.01	0.02
Cl	3.61	0.35	0.33	0.32	0.32	0.09	0.04	0.04	0.04	0.02	-0.02	-0.03	-0.03	0.02	-0.04	-0.04	-0.04	0.02	-0.02	-0.02	-0.02
1st		0.41	0.42	0.42	0.43	0.23	0.23	0.23	0.24	0.08	0.08	0.08	0.09	0.13	0.14	0.14	0.14	0.08	0.08	0.08	0.09
2nd		0.23	0.24	0.23	0.23	0.09	0.09	0.09	0.09	0.06	0.07	0.06	0.06	0.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05
MAE		0.32	0.33	0.33	0.33	0.16	0.16	0.16	0.16	0.07	0.07	0.07	0.08	0.09	0.10	0.10	0.10	0.07	0.06	0.06	0.07

[a]available from http://cccbdb.nist.gov/

Table 3.   HOMO eigenvalues (eV) for negative ions with AV5Z basis set.

Atom	LDA	PBE	B3LYP	PBE0	TPSS	HF	-Exact
H	1.55	1.65	1.05	0.87	1.65	-1.25	-0.75
Li	0.80	0.86	0.62	0.46	0.85	-0.39	-0.62
B	1.61	1.67	1.31	1.11	1.76	-0.78	-0.28
C	1.72	1.81	1.18	0.86	1.87	-2.12	-1.26
O	2.30	2.38	1.36	1.17	2.41	-2.17	-1.46
F	1.28	1.47	0.08	-0.17	1.48	-4.92	-3.40
Al	1.18	1.24	0.97	0.77	1.32	-0.61	-0.43
Si	1.06	1.12	0.70	0.37	1.15	-1.69	-1.39
P	1.69	1.75	1.17	1.01	1.74	-0.67	-0.75
S	1.00	1.10	0.34	0.11	1.08	-2.33	-2.08
Cl	0.10	0.24	-0.71	-0.99	0.20	-4.09	-3.61

Table 4.   HOMO eigenvalues of negative ions and
total energy differences (ΔE) between neutral and
negative atoms with HF/AVDZ and LHF/AVDZ.
(eV unit)

		$-\epsilon^{\text{HOMO}}$		ΔE	
	EA	HF	LHF	HF	LHF
H	0.75	1.22	1.26[a]	-0.34	-0.33[a]
Li	0.62	0.38	0.38	-0.14	-0.14
B	0.28	0.76	0.75	-0.30	-0.31
C	1.26	2.11	2.11	0.47	0.47
O	1.46	2.15	2.12	-0.52	-0.53
F	3.40	4.93	4.92	1.28	1.29
Na	0.55	0.35	0.35	-0.11	-0.12
Al	0.43	0.60	0.57	0.02	0.01
Si	1.39	1.68	1.66	0.87	0.87
P	0.75	0.55	0.51	-0.37	-0.38
S	2.08	2.26	2.23	0.92	0.91
Cl	3.61	4.10	4.08	2.47	2.48

[a]Obtained   from   an   atomic   OEP   code

Since HF or LHF self-consistent calculations produce the negative HOMO eigen-values, one can try Koopmans' theorem for EA's using $-\epsilon_{\text{HOMO}}$ of HF or LHF as the estimate. As shown in Table 4, this gives relatively reasonable results, in the sense that they are all negative, but, the MAE's (0.48 eV for both HF and LHF) are much larger than the limited basis set approaches. As we already mentioned in Sec. 2.3, the EA's from HF and LHF are not sufficiently accurate. Correlation effects are relatively larger than in neutrals.

3.4.   *(Localized) Hartree-Fock densities for anions*

We calculate the total energy of a neutral atom using the approximate functional on its self-consistent density, and the total energy of a negative ion by evaluating an approximate energy functional on the LHF self-consistent density. In Table 5, we show EA's using the above scheme. The results for all functionals are much *better* than those for ionization potentials, and even better than limited basis set approaches. They also follow the usual trends of approximate functionals. We com-pare MAE's with those in the LBS calculations with AVQZ. LDA gives 0.16 eV better EA than LBS approach for the first row, 0.15 eV for the second row. PBE gives 0.13 and 0.04 eV for the first and the second rows, and they are the half of MAE's in the LBS calculations. The MAE's of PBE0 are almost the same to the results of Table 2. B3LYP at AVQZ level becomes slightly worse than in the LBS result. TPSS gives a slightly worse result for the first row, but it improves the second row EA's. Hence, the total MAE of TPSS does not change much. Inter-estingly, with our LHF method for the anions, PBE does as well as either B3LYP or PBE0: Mixing of exact exchange does *not* improve results, but the meta-GGA, TPSS, does do slightly better.

Table 5.   Electron affinities (eV) and errors. Total energies for neutral atoms are calculated by SCF procedure and for anions are evaluated on self-consistent LHF densities.

	EA	Δ EA LDA			PBE			B3LYP			PBE0			TPSS[b]		
		DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ
H[a]	0.75	0.14	0.14	0.14	-0.09	-0.09	-0.09	0.07	0.07	0.07	-0.14	-0.14	-0.14	-	-	-
Li	0.62	-0.05	-0.09	-0.09	-0.13	-0.13	-0.13	-0.15	-0.15	-0.15	-0.14	-0.14	-0.14	-0.05	-0.05	-0.05
B	0.28	0.32	0.28	0.28	0.23	0.23	0.23	0.02	0.02	0.02	0.16	0.15	0.15	0.12	0.12	0.11
C	1.26	0.38	0.33	0.33	0.18	0.16	0.16	-0.07	-0.09	-0.09	0.09	0.08	0.08	0.09	0.08	0.08
O	1.46	0.33	0.26	0.25	0.08	0.05	0.05	-0.04	-0.07	-0.07	-0.16	-0.19	-0.19	-0.13	-0.16	-0.16
F	3.40	0.46	0.36	0.34	0.02	-0.05	-0.06	-0.12	-0.18	-0.19	-0.22	-0.29	-0.29	-0.14	-0.22	-0.23
Na	0.55	0.00	-0.04	-0.07	-0.03	-0.06	-0.08	-0.08	-0.10	-0.12	-0.05	-0.07	-0.08	0.02	0.00	-0.01
Al	0.43	0.10	0.07	0.01	0.10	0.09	0.06	-0.10	-0.11	-0.14	0.08	0.07	0.06	0.05	0.03	0.01
Si	1.39	0.11	0.08	0.04	0.06	0.05	0.03	-0.17	-0.18	-0.20	0.06	0.05	0.04	0.03	0.00	-0.01
P	0.75	0.12	0.10	0.08	0.02	0.05	0.04	0.02	0.04	0.03	-0.03	0.00	-0.01	0.03	0.05	0.04
S	2.08	0.19	0.13	0.11	0.03	0.00	-0.01	-0.02	-0.04	-0.05	-0.02	-0.04	-0.05	-0.01	-0.03	-0.04
Cl	3.61	0.26	0.18	0.16	0.03	-0.03	-0.04	-0.04	-0.09	-0.10	0.00	-0.06	-0.07	-0.01	-0.06	-0.07
1st		0.31	0.26	0.26	0.13	0.12	0.13	0.08	0.10	0.10	0.16	0.17	0.17	0.11	0.13	0.13
2nd		0.13	0.10	0.08	0.04	0.05	0.04	0.07	0.09	0.11	0.04	0.05	0.05	0.03	0.03	0.03
MAE		0.21	0.17	0.16	0.08	0.08	0.08	0.08	0.10	0.11	0.09	0.10	0.11	0.06	0.07	0.07

[a]Obtained from an atomic OEP code. We used the definition of the exchange-correlation functionals (B3LYP and PBE0) to evaluate total energies.

[b]We calculated the MAE using 5 atoms for the first row, and 6 atoms for the second row.

What if we use HF densities for the anions only? Here, we obtain total energies of anions evaluating approximate functionals on HF self-consistent densities. In Table 6, we report the EA's using HF densities for anions, but self-consistently minimize the approximate density functionals for the neutral. An interesting feature is that, for the first row, MAE's are decreasing as we increase the basis set size, but the MAE's for the second row are increasing. Convergence becomes a problem, presumably because of the unbalanced treatment of a neutral atom and an anion. This trend does not appear in Tables 2 and 5. Hence, we investigate the densities of HF and LHF for a negative ion in the second row. We calculate the density of Cl^- using PBE functional as a reference, since we only need to see the different behaviors between HF and LHF. In Figs. 8 and 9, we plot the difference of a radial
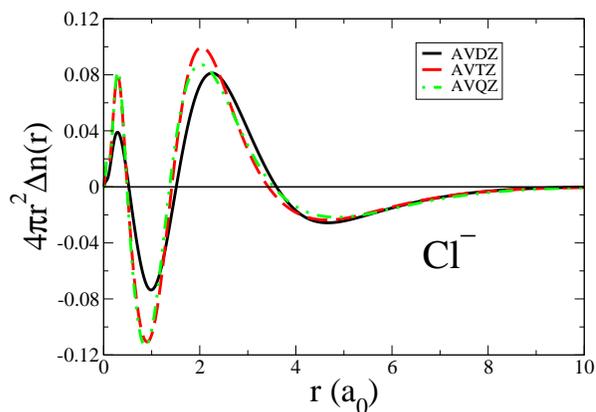
Figure 8. Plot of the radial density difference of Cl^- between HF and PBE according to the basis sets.
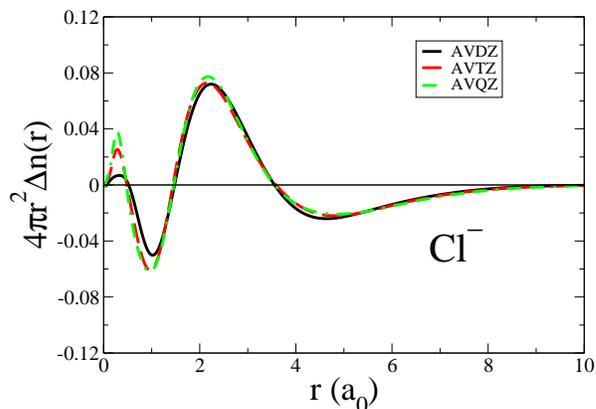
Figure 9. Plot of the radial density difference of Cl^- between LHF and PBE according to the basis sets.

density between (L)HF and PBE for Cl^-. As we increase basis sets from AVDZ to AVQZ, the HF density shows large fluctuation in the core shell structure, whereas as the LHF density converges. We conclude that, if using HF, it is best to use HF densities for both neutral and anion. If using LHF, it makes little difference, because it is a KS method with a true $v_s(r)$.

Table 6.   Electron affinities (eV) and errors. Total energies for neutral atoms are calculated by SCF procedure and for anions are evaluated on self-consistent HF densities.

	EA	Δ EA																		
		LDA				PBE				B3LYP				PBE0				TPSS			
		DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z
H	0.75	0.11	0.13	0.13	0.13	-0.11	-0.09	-0.09	-0.09	0.03	0.05	0.05	0.05	-0.17	-0.15	-0.15	-0.15	0.01	0.03	0.03	0.03
Li	0.62	-0.06	-0.11	-0.11	-0.13	-0.14	-0.15	-0.15	-0.17	-0.15	-0.17	-0.17	-0.19	-0.15	-0.15	-0.15	-0.16	-0.06	-0.06	-0.06	-0.07
B	0.28	0.26	0.19	0.19	0.18	0.19	0.17	0.17	0.15	-0.01	-0.03	-0.03	-0.04	0.13	0.12	0.11	0.11	0.09	0.09	0.08	0.07
C	1.26	0.34	0.25	0.25	0.23	0.15	0.12	0.11	0.09	-0.09	-0.13	-0.13	-0.14	0.08	0.06	0.05	0.04	0.08	0.06	0.05	0.05
O	1.46	0.25	0.12	0.11	0.10	0.03	-0.03	-0.03	-0.05	-0.08	-0.13	-0.14	-0.15	-0.19	-0.23	-0.24	-0.25	-0.16	-0.21	-0.21	-0.22
F	3.40	0.41	0.23	0.21	0.19	-0.01	-0.11	-0.13	-0.15	-0.14	-0.24	-0.26	-0.27	-0.24	-0.32	-0.34	-0.35	-0.16	-0.26	-0.28	-0.29
Na	0.55	-0.02	-0.13	-0.18	-0.18	-0.06	-0.12	-0.16	-0.16	-0.09	-0.15	-0.18	-0.18	-0.07	-0.10	-0.12	-0.12	0.00	-0.04	-0.06	-0.06
Al	0.43	0.01	-0.08	-0.19	-0.22	0.04	-0.01	-0.08	-0.11	-0.16	-0.20	-0.26	-0.29	0.05	0.02	-0.01	-0.03	0.00	-0.03	-0.07	-0.09
Si	1.39	0.03	-0.08	-0.12	-0.21	0.00	-0.05	-0.08	-0.15	-0.22	-0.27	-0.29	-0.36	0.02	-0.01	-0.02	-0.06	-0.01	-0.06	-0.07	-0.12
P	0.75	0.01	-0.09	-0.11	-0.21	-0.06	-0.08	-0.09	-0.17	-0.05	-0.07	-0.08	-0.15	-0.08	-0.07	-0.08	-0.12	-0.03	-0.03	-0.04	-0.09
S	2.08	0.06	-0.09	-0.11	-0.22	-0.07	-0.14	-0.16	-0.24	-0.10	-0.17	-0.18	-0.25	-0.08	-0.13	-0.14	-0.18	-0.08	-0.13	-0.14	-0.20
Cl	3.61	0.15	-0.03	-0.06	-0.16	-0.05	-0.16	-0.18	-0.25	-0.10	-0.20	-0.22	-0.29	-0.04	-0.13	-0.15	-0.19	-0.07	-0.15	-0.17	-0.22
1st		0.24	0.17	0.17	0.16	0.11	0.11	0.11	0.12	0.08	0.13	0.13	0.14	0.16	0.17	0.18	0.18	0.09	0.12	0.12	0.12
2nd		0.04	0.08	0.13	0.20	0.04	0.09	0.12	0.18	0.12	0.18	0.20	0.25	0.06	0.08	0.09	0.12	0.03	0.07	0.09	0.13
MAE		0.14	0.13	0.15	0.18	0.08	0.10	0.12	0.15	0.10	0.15	0.17	0.20	0.11	0.12	0.13	0.15	0.06	0.10	0.10	0.13

3.5.   *EA with (L)HF densities*

As we see Table 6 and Fig. 8, using HF density only for anions is not a proper procedure to get accurate EA's. We repeat the HF calculations to obtain the densities of both neutral atoms and anions, and then obtain total energies in either cases by calculating the approximate energy functionals on HF densities. Again, the EA results are better than IP for sophisticated functionals in all basis sets. The total MAE's of LDA are almost identical to those of IP. But PBE and PBE0 give the same MAE's which are larger than B3LYP and TPSS results, but much smaller than LDA. B3LYP and TPSS on HF densities produce the best MAE's. MAEs from this procedure are almost the same (slightly better than) to those in LBS method, and individual differences are almost all within the MAE of the given functional. The important aspect is that we have well-define basis-set limit in this method. As we increase basis sets from AVDZ to AV5Z in Table 7, the errors (Δ eV) of EA in individual atoms remain almost same for a given functional.

Fig. 7 shows the more systematic (and often larger) errors of the non-empirical GGA versus the empirical hybrid B3LYP. We also use LHF densities instead of HF for both species, and we find almost identical results in Table 8.

3.6.   *Other DFT estimates*

As we have discussed, there are many possible routes to electron affinities with approximate functionals. Tozer et al[40] suggest the calculation of negative EA's from the discussion of the derivative discontinuity in $v_{\mathrm{xc}}(r)$ and the lack of discontinuity in standard approximations. We test this method to evaluate the positive EA's of atoms:

$$\mathrm{EA} = -(\epsilon_{\mathrm{HOMO}}^{\mathrm{DFA}} + \epsilon_{\mathrm{LUMO}}^{\mathrm{DFA}}) - \mathrm{IP}^{\mathrm{DFA}} \tag{16}$$

where ϵ_{HOMO} and ϵ_{LUMO} are obtained from SCF calculations of neutral atoms with approximate functionals. IP's are the energy differences between positive ions and neutral atoms with AVXZ (X = D, T, Q, and 5) basis set. The results already converge at AVDZ basis set. In Table 9, we summarize the results. Most functionals give negative EA's except for a few atoms. Despite the positive EA's of those atoms with the correct (+) sign, the errors are significantly larger than those of the LBS approach. However, these results are not so surprising given the underlying assumptions used in the method. Eq. (16) was designed to estimate negative EA's, which can not be determined with LBS method when the basis set is diffuse.

3.7.   *Halide ions*

We calculate electron affinities of halide atoms using AVDZ. Since iodine has an effective-core potential basis set for AVDZ, we do not include this atom in the calculation. In Table 10, we report EA's using the LBS method and HF densities with AVDZ basis set.

Up to Cl, we have slightly better EA's if we are using HF densities for neutral atoms and anions. But, for Br, the results from our method are almost the same (slightly worse than) those in the LBS method.

Table 7. Errors in electron affinities (eV). Total energies for both neutral atoms and anions are obtained by evaluating approximate functionals on HF densities.

| | EA | Δ EA | | | | | | | | | | | | | | | | | | | |
| | | LDA | | | | PBE | | | | B3LYP | | | | PBE0 | | | | TPSS | | | |
		DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z	DZ	TZ	QZ	5Z
H	0.75	0.13	0.15	0.14	0.16	-0.11	-0.08	-0.09	-0.08	0.03	0.06	0.05	0.06	-0.17	-0.15	-0.15	-0.15	0.01	0.03	0.03	0.03
Li	0.62	-0.04	-0.04	-0.04	-0.04	-0.12	-0.12	-0.12	-0.12	-0.14	-0.15	-0.15	-0.15	-0.14	-0.14	-0.14	-0.14	-0.05	-0.05	-0.05	-0.05
B	0.28	0.36	0.37	0.37	0.37	0.26	0.26	0.26	0.26	0.04	0.04	0.04	0.04	0.17	0.17	0.17	0.17	0.12	0.12	0.12	0.12
C	1.26	0.45	0.46	0.47	0.47	0.23	0.23	0.23	0.24	-0.04	-0.04	-0.04	-0.03	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
O	1.46	0.41	0.43	0.43	0.43	0.14	0.14	0.15	0.15	0.01	0.01	0.02	0.02	-0.14	-0.15	-0.15	-0.15	-0.09	-0.11	-0.10	-0.10
F	3.40	0.59	0.59	0.58	0.58	0.12	0.09	0.09	0.09	-0.04	-0.07	-0.07	-0.07	-0.18	-0.23	-0.23	-0.23	-0.07	-0.13	-0.13	-0.13
Na	0.55	0.04	0.03	0.03	0.03	-0.01	-0.03	-0.02	-0.02	-0.05	-0.07	-0.07	-0.07	-0.05	-0.06	-0.05	-0.05	0.03	0.02	0.02	0.02
Al	0.43	0.17	0.17	0.17	0.17	0.13	0.13	0.13	0.13	-0.08	-0.08	-0.08	-0.08	0.10	0.10	0.09	0.09	0.06	0.05	0.05	0.05
Si	1.39	0.21	0.21	0.21	0.21	0.11	0.11	0.10	0.10	-0.13	-0.13	-0.13	-0.14	0.09	0.08	0.08	0.08	0.07	0.04	0.04	0.04
P	0.75	0.13	0.16	0.16	0.16	0.03	0.06	0.06	0.06	0.02	0.05	0.05	0.05	-0.03	-0.00	-0.00	-0.00	0.03	0.05	0.05	0.05
S	2.08	0.27	0.27	0.27	0.27	0.06	0.05	0.05	0.05	0.01	0.01	0.01	0.01	0.00	-0.02	-0.02	-0.02	0.01	-0.01	-0.01	-0.01
Cl	3.61	0.36	0.35	0.34	0.34	0.08	0.04	0.04	0.03	0.01	-0.03	-0.03	-0.03	0.03	-0.03	-0.03	-0.04	0.02	-0.02	-0.03	-0.03
1st		0.33	0.34	0.34	0.34	0.16	0.15	0.16	0.16	0.05	0.06	0.06	0.06	0.15	0.16	0.16	0.16	0.08	0.09	0.09	0.09
2nd		0.20	0.20	0.20	0.20	0.07	0.07	0.07	0.07	0.05	0.06	0.06	0.06	0.05	0.05	0.05	0.05	0.04	0.03	0.03	0.03
MAE		0.26	0.27	0.27	0.27	0.12	0.11	0.11	0.11	0.05	0.06	0.06	0.06	0.10	0.10	0.10	0.10	0.06	0.06	0.06	0.06

Table 8.   Electron affinities (eV) and errors. Total energies for neutral atoms and anions are evaluated on self-consistent LHF densities.

	EA	ΔEA																
		LDA			PBE			B3LYP			PBE0			TPSS[b]					
		DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ		
H[a]	0.75	0.14	0.14	0.14	-0.09	-0.09	-0.09	0.07	0.07	0.07	-0.14	-0.14	-0.14	-	-	-		
Li[a]	0.62	-0.04	-0.04	-0.04	-0.12	-0.12	-0.12	-0.25	-0.25	-0.25	-0.15	-0.15	-0.15	-	-	-		
B	0.28	0.37	0.38	0.38	0.26	0.27	0.27	0.04	0.05	0.05	0.17	0.17	0.17	0.13	0.13	0.13		
C	1.26	0.43	0.45	0.45	0.22	0.22	0.23	-0.05	-0.04	-0.04	0.11	0.11	0.11	0.11	0.12	0.11		
O	1.46	0.43	0.45	0.45	0.15	0.16	0.16	0.02	0.02	0.03	-0.13	-0.14	-0.14	-0.08	-0.09	-0.08		
F	3.40	0.57	0.58	0.58	0.11	0.08	0.08	-0.05	-0.07	-0.08	-0.19	-0.23	-0.23	-0.08	-0.12	-0.13		
Na[a]	0.55	0.03	0.03	0.03	-0.02	-0.02	-0.02	-0.06	-0.06	-0.06	-0.05	-0.05	-0.05	-	-	-		
Al	0.43	0.18	0.18	0.18	0.14	0.14	0.13	-0.07	-0.07	-0.07	0.10	0.10	0.10	0.07	0.06	0.06		
Si	1.39	0.19	0.21	0.20	0.10	0.10	0.10	-0.14	-0.13	-0.14	0.08	0.08	0.07	0.06	0.04	0.04		
P	0.75	0.18	0.21	0.20	0.06	0.09	0.09	0.05	0.08	0.08	-0.01	0.02	0.01	0.05	0.08	0.07		
S	2.08	0.28	0.29	0.28	0.08	0.06	0.06	0.02	0.02	0.02	0.01	-0.01	-0.01	0.02	0.01	0.00		
Cl	3.61	0.33	0.33	0.32	0.06	0.03	0.02	-0.01	-0.03	-0.04	0.01	-0.04	-0.04	0.01	-0.03	-0.03		
1st		0.33	0.34	0.34	0.16	0.16	0.16	0.08	0.08	0.09	0.15	0.16	0.16	0.10	0.12	0.11		
2nd		0.20	0.21	0.20	0.08	0.07	0.07	0.06	0.07	0.07	0.04	0.05	0.05	0.04	0.04	0.04		
MAE		0.26	0.27	0.27	0.12	0.12	0.11	0.07	0.07	0.08	0.10	0.10	0.10	0.07	0.08	0.07		

[a]Obtained from OPMKS code. We used the definition of the exchange-correlation functionals (B3LYP and PBE0) to evaluate total energies.

[b]We calculated the MAE using 4 atoms for the first row, and 5 atom for the second row.

Table 9.   Electron affinities (eV) from Eq. (16) in conjunction with AVDZ.

Atom	Exp	LDA	PBE	B3LYP	PBE0	TPSS
H	0.75	-3.01	-6.60	-3.76	-5.49	-6.09
Li	0.62	-0.15	-0.97	-0.44	-0.88	-1.00
B	0.28	-0.64	-0.89	-0.99	-0.82	-1.05
C	1.26	0.45	0.12	-0.02	0.16	0.08
O	1.46	0.55	0.01	0.14	-0.06	-0.26
F	3.40	2.63	1.97	2.03	1.86	1.86
Na	0.55	0.02	-0.72	-0.15	-0.65	-0.77
Al	0.43	-0.11	-0.21	-0.35	-0.17	-0.25
Si	1.39	0.93	0.78	0.61	0.84	0.77
P	0.75	-0.19	-0.47	-0.11	-0.32	-0.39
S	2.08	1.71	1.39	1.46	1.41	1.35
Cl	3.61	3.30	2.95	2.99	2.97	2.91

Table 10.   Comparison of errors in electron affinities (eV) using LBS and HF densities with AVDZ basis set.

Atom	EA	Δ EA (LBS)				
		LDA	PBE	B3LYP	PBE0	TPSS
F	3.40	0.74	0.28	0.06	-0.11	0.05
Cl	3.61	0.35	0.09	0.02	0.02	0.02
Br	3.36	0.44	0.19	0.14	0.15	0.18
		Δ EA (HF density)				
F	3.40	0.46	0.02	-0.12	-0.22	-0.14
Cl	3.61	0.26	0.03	-0.04	0.00	-0.01
Br	3.36	0.46	0.19	0.15	0.17	0.20

4.   Summary

Defying formal theory at the time, Schaefer and co-workers showed that approximate DFT could produce accurate electron affinities of atoms[13, 18]. Our letter and this work show why such methods, using limited basis sets, actually work. The constant in the KS potential of an approximate functional can be easily shifted, so that the sign of the HOMO is ambiguous. But we have also suggested a simple and practical way to evaluate electron affinities which has an unambiguous basis-set limit and avoids positive HOMO energies of anions due to approximate functionals. We calculate electron affinities using HF or LHF SCF densities which properly bind the extra (valence) electron and have negative HOMO energies. This procedure allows us to obtain accurate and reasonable results (even slightly better than the traditional limited basis-set approaches of Schaefer). The advantage of our method is its well-defined basis-set limit. From AVDZ to AV5Z, the errors in electron affinities remain almost constant. We have also shown and explained that accurate densities and total energies of anions can be obtained using limited basis sets for SCF calculations within approximate density functionals despite positive HOMO energies of anions. However, the limited basis-set approach becomes ill-defined if the potential barrier due to SIE is too narrow or inadequately high, so it is impossible to find the energy convergence by increasing the size of basis sets.

If we evaluate the total energy on one functional, while calculating the potential on another functional, various well-known problems do arise, such as in the calculation of force, which needs the input of potentials. We also mention that our method will obviously fail if HF or LHF densities are not accurate enough or the approximate functionals do not provide sufficiently accurate energies for the system under study.

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