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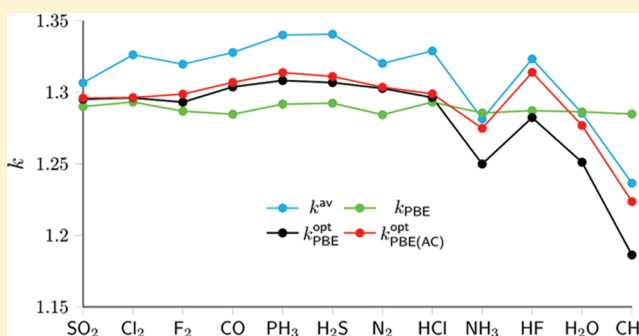
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Negative Electron Affinities from DFT: Influence of Asymptotic Exchange-Correlation Potential and Effective Homogeneity under Density Scaling

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ABSTRACT: The influence of the asymptotic exchange-correlation potential and density-scaling homogeneity on negative electron affinities determined using the approach of Tozer and De Proft [*J. Phys. Chem. A* **2005**, *109*, 8923] is investigated. Application of an asymptotic correction to the potential improves the accuracy for several of the systems with the most negative affinities, reflecting their diffuse lowest unoccupied orbitals. For systems with modest affinities, it reduces the accuracy marginally. Enforcing a near-exact effective homogeneity through a simple shift in the potential leads to improved correlation with experimental values but significantly overestimated affinities. Optimal effective homogeneities are therefore determined, and a simple scheme is proposed for enforcing an average optimal value. Application of the scheme to a series of organic molecules maintains the excellent correlation with the experimental values while significantly reducing the absolute errors.



INTRODUCTION

Many neutral molecules have negative experimental vertical electron affinities, as measured by electron transmission spectroscopy (ETS),^{1,2} meaning the energy of the anion is above that of the neutral. These temporary anions or shape resonances are unstable with respect to electron loss, making the calculation of negative affinities a challenge for electronic structure methods. A number of approaches to estimate negative electron affinities have been proposed and applied.^{3–24} Tozer and De Proft (TDP)¹⁷ suggested that the negative affinity of an N -electron system be estimated in Kohn–Sham density functional theory (DFT) using

$$A^{\text{TDP}} = -(\epsilon_{\text{LUMO}}^{\text{local}} + \epsilon_{\text{HOMO}}^{\text{local}}) - I \quad (1)$$

where $I = E_{N-1} - E_N$ is the vertical ionization energy, and $\epsilon_{\text{LUMO}}^{\text{local}}$ and $\epsilon_{\text{HOMO}}^{\text{local}}$ are the lowest unoccupied and highest occupied molecular orbital energies of the system, determined from a conventional Kohn–Sham calculation using a local (e.g., LDA, GGA) exchange-correlation functional.

The key assumption that underlies eq 1 is that

$$v_{\text{xc}}^{\text{local}}(\mathbf{r}) \approx v_{\text{xc}}^{\text{av}}(\mathbf{r}) \quad (2)$$

where $v_{\text{xc}}^{\text{local}}(\mathbf{r})$ is the exchange-correlation potential of the N -electron system determined using the local functional, and $v_{\text{xc}}^{\text{av}}(\mathbf{r})$ is the average of the exact exchange-correlation potentials on either side of the integer discontinuity,²⁵ where the discontinuity is computed using the negative ETS affinity. This exact average potential is

$$v_{\text{xc}}^{\text{av}}(\mathbf{r}) = v_{\text{xc}}^-(\mathbf{r}) + \frac{\Delta_{\text{xc}}}{2} \quad (3)$$

where $v_{\text{xc}}^-(\mathbf{r})$ is the exact potential on the electron deficient side of the integer and

$$\Delta_{\text{xc}} = (I^0 - A^{\text{ETS}}) - (\epsilon_{\text{LUMO}}^- - \epsilon_{\text{HOMO}}^-) \quad (4)$$

is the magnitude of the integer discontinuity, determined using the experimental ionization potential I^0 , the ETS affinity A^{ETS} , and the orbital energies associated with $v_{\text{xc}}^-(\mathbf{r})$. The HOMO and LUMO energies associated with $v_{\text{xc}}^{\text{av}}(\mathbf{r})$ are

$$\epsilon_{\text{HOMO}}^{\text{av}} = -I^0 + \frac{\Delta_{\text{xc}}}{2} \quad (5)$$

$$\epsilon_{\text{LUMO}}^{\text{av}} = -A^{\text{ETS}} - \frac{\Delta_{\text{xc}}}{2} \quad (6)$$

and so it trivially follows that if the approximation in eq 2 becomes an equality, then $\epsilon_{\text{HOMO}}^{\text{local}} = \epsilon_{\text{HOMO}}^{\text{av}}$ and $\epsilon_{\text{LUMO}}^{\text{local}} = \epsilon_{\text{LUMO}}^{\text{av}}$, and the evaluation of eq 1 using the local orbital energies and I^0 will yield the ETS affinity exactly. For further discussion on the validity of eq 1, see ref 26.

Several studies^{17–22} have illustrated that eq 1 yields negative affinities that correlate well with ETS values, although quantitative accuracy is not achieved. For example, the affinities reported by Sablon et al.¹⁹ exhibit a correlation coefficient of

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$R^2 = 0.94$, but the values are consistently too low, as reflected by the linear relationship between the calculated and experimental values of $A^{\text{TDP}} = 1.05A^{\text{ETS}} - 0.46$ eV.

The aim of the present study is to consider the influence of two factors on the accuracy of eq 1. The first factor is the asymptotic behavior of the exchange-correlation potential. It is well-known that the potentials of conventional local functionals break down in asymptotic regions. This affects the orbital energies, particularly the LUMO,²⁶ which is a component in eq 1. We shall asymptotically correct (AC) the potential using the scheme of Tozer and Handy²⁷ and quantify the influence on the negative affinities from eq 1. The second factor is the effective homogeneity of the exchange-correlation functional under density scaling, defined by

$$k = \frac{\int \rho(\mathbf{r}) v_{\text{xc}}(\mathbf{r}) d\mathbf{r}}{E_{\text{xc}}} \quad (7)$$

where $\rho(\mathbf{r})$, $v_{\text{xc}}(\mathbf{r})$, and E_{xc} are the electron density, exchange-correlation potential, and exchange-correlation energy, respectively. In a recent study, Borgoo et al.²⁸ used the Wu–Yang approach²⁹ with coupled cluster singles and doubles (CCSD) densities, together with experimental ionization potentials and ETS affinities, to determine near-exact average potentials $v_{\text{xc}}^{\text{av}}(\mathbf{r})$ (eq 3) for a series of atoms and small molecules. They then evaluated eq 7 using these average potentials, together with the CCSD densities and near-exact exchange-correlation energies, to yield near-exact average homogeneities, which we denote k^{av} . They found that k^{av} was close to 4/3 and relatively system independent for all but the molecules with the most negative affinities. We shall use homogeneity considerations to apply simple shifts to the exchange-correlation potential and quantify the influence on the negative affinities from eq 1.

RESULTS

Figure 1a presents electron affinities from eq 1, determined using Perdew–Burke–Ernzerhof (PBE)³⁰ GGA orbital energies and vertical ionization potentials, for the molecules of ref 28. Following that earlier work, the aug-cc-pCVQZ basis set is used together with the same geometries. For molecules with affinities less negative than -4 eV, values from eq 1 are systematically too low, which is consistent with the work of Sablon et al.¹⁹ For molecules with affinities more negative than -4 eV, however, eq 1 instead overestimates the ETS values. Figure 1 also presents affinities from eq 1, determined using the same PBE ionization potentials but orbital energies from asymptotically corrected PBE(AC) calculations; for the AC calculations, the PBE ionization potential was used, and the α and β parameters were set to 3.0 and 4.0, respectively.³¹ For the four systems with the most negative affinities, the AC significantly influences the affinities, which is to be expected given the diffuse nature of the LUMOs in these systems; three of the values improve notably although one (HF) degrades. For the systems with less negative affinities, the influence of the AC is less pronounced, and the affinities degrade marginally. In all cases, the effect of the AC is to make the affinities more negative because the LUMO energy becomes less negative. Figure 1a also presents the linear correlation data; the inclusion of the AC improves the slope and R^2 , at the expense of a marginally less accurate intercept.

Figure 2 compares the PBE effective homogeneities, k_{PBE} , obtained by evaluating eq 7 using PBE quantities, with the near-exact average homogeneities, k^{av} , from ref 28. The PBE values are uniformly below 4/3, illustrating the effect of the terms

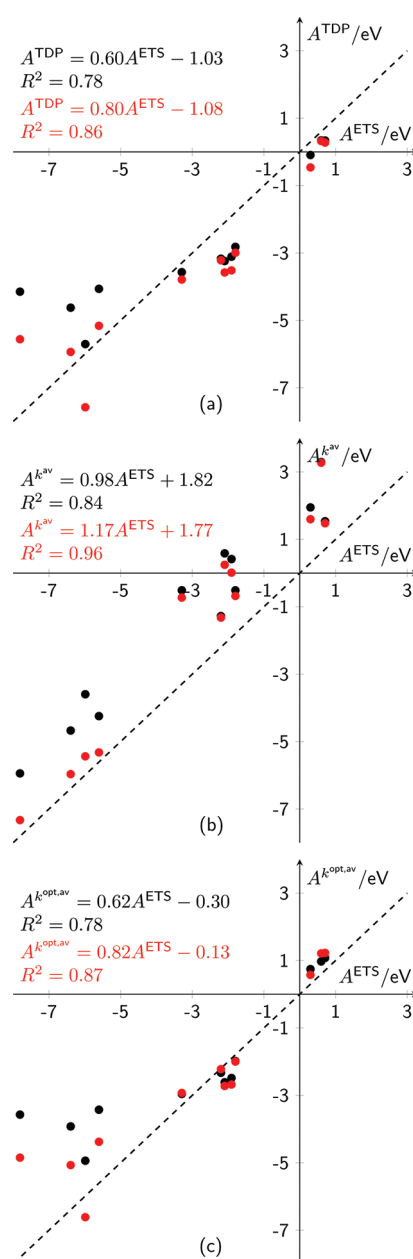


Figure 1. Electron affinities determined using PBE (black) and PBE(AC) (red), compared to experimental ETS affinities, for the set of molecules in ref 28.

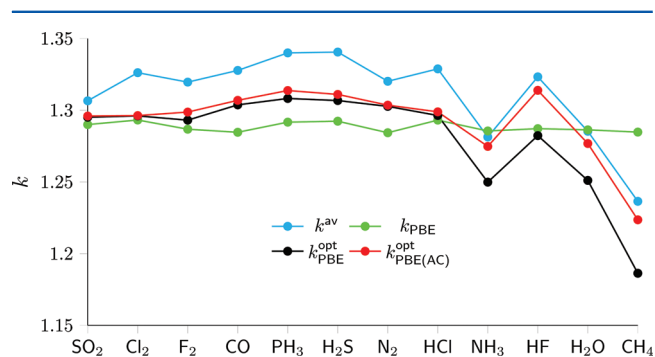


Figure 2. Effective homogeneities for the set of molecules in ref 28.

added to the Dirac exchange functional, which is exactly homogeneous of degree 4/3. The k_{PBE} values are in rather poor

agreement with k^{av} . Replacing the PBE density and exchange-correlation potential in eq 7 with the PBE(AC) values yields effective homogeneities (not shown) that are indistinguishable from the PBE values on the scale of Figure 2.

The k^{av} values from ref 28 are the homogeneities associated with the near-exact average potential. As noted in the introduction, if the local potential were to equal the average potential, then eq 1 would become exact. It is therefore tempting to simply shift the PBE and PBE(AC) potentials by an amount δ_1 (different for the two approaches) to enforce these values

$$\frac{\int \rho(\mathbf{r})(v_{\text{xc}}(\mathbf{r}) + \delta_1) d\mathbf{r}}{E_{\text{xc}}} = k^{\text{av}} \quad (8)$$

and then re-evaluate eq 1 using the HOMO and LUMO energies associated with the shifted potentials. This corresponds to the affinity

$$A^{k^{\text{av}}} = A^{\text{TDP}} - 2\delta_1 \quad (9)$$

where A^{TDP} is the value from eq 1, and δ_1 is obtained by rearranging eq 8. Figure 1b compares the resulting affinities with the ETS values. The R^2 values are notably improved over the A^{TDP} values in Figure 1a, but both PBE and PBE(AC) significantly overestimate the ETS values. The failure of this approach is a simple consequence of the fact that the PBE and PBE(AC) quantities are not exact.

In order to ascertain what the optimal homogeneity is for PBE and PBE(AC), in the sense of an accurate eq 1, we define a new quantity

$$\delta_2 = \frac{A^{\text{TDP}} - A^{\text{ETS}}}{2} \quad (10)$$

for both PBE and PBE(AC). Shifting the potential by the amount δ_2 and re-evaluating eq 1 yields, by construction, the ETS affinity. The effective homogeneity associated with this shifted potential is

$$k^{\text{opt}} = \frac{\int \rho(\mathbf{r})(v_{\text{xc}}(\mathbf{r}) + \delta_2) d\mathbf{r}}{E_{\text{xc}}} \quad (11)$$

and the PBE and PBE(AC) values, denoted $k_{\text{PBE}}^{\text{opt}}$ and $k_{\text{PBE(AC)}}^{\text{opt}}$, respectively, are compared with the near-exact k^{av} values in Figure 2. The PBE and PBE(AC) values are now distinguishable due to their different values of A^{TDP} in eq 10. The latter are uniformly closer to k^{av} ; the agreement is particularly striking for the systems with the most negative affinities. Both the PBE and PBE(AC) values exhibit a similar system-dependence to k^{av} .

For molecules with modest negative affinities (less negative than -4 eV, which are often of most chemical interest), the values of k^{opt} in Figure 2 do not exhibit a significant system dependence, and they have average values that we denote $k_{\text{PBE}}^{\text{opt,av}} = 1.300$ and $k_{\text{PBE(AC)}}^{\text{opt,av}} = 1.303$. We can therefore also consider shifting the PBE and PBE(AC) potentials by an amount δ_3 to enforce these values

$$\frac{\int \rho(\mathbf{r})(v_{\text{xc}}(\mathbf{r}) + \delta_3) d\mathbf{r}}{E_{\text{xc}}} = k^{\text{opt,av}} \quad (12)$$

and then evaluate the affinities using

$$A^{k^{\text{opt,av}}} = A^{\text{TDP}} - 2\delta_3 \quad (13)$$

Affinities determined using this approach are presented in Figure 1c. The linear correlation data is improved over that in Figure 1a, with the improvement most marked (by construction) for the systems with modest negative affinities.

To test the predictive usefulness of the approach in eqs 12 and 13 for systems with modest negative affinities, we have also used it to determine the affinities for the set of molecules considered in ref 19, omitting cyclohexadiene, thiophene, uracil, naphthalene, and chloromethane due to convergence problems. That earlier study used the aug-cc-pVTZ basis set, but we use aug-cc-pCVTZ in order to ensure an accurate description of the core, which is necessary for the evaluation of effective homogeneities. Results determined using the conventional evaluation in eq 1 and the new evaluation in eq 13, using $k_{\text{PBE}}^{\text{opt,av}} = 1.300$ and $k_{\text{PBE(AC)}}^{\text{opt,av}} = 1.303$, are presented in Figure 3a,b. The

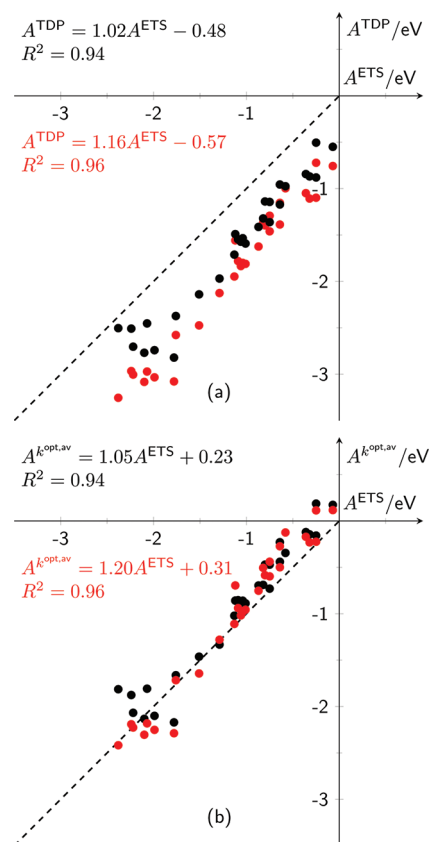


Figure 3. Electron affinities determined using PBE (black) and PBE(AC) (red), compared to experimental ETS values, for the set of molecules in ref 19.

slopes of the linear regression and the R^2 values are very similar for eqs 1 and 13, although the intercepts reduce notably, validating the proposed approach. Mean absolute errors from eq 13 are 0.21 and 0.17 eV from PBE and PBE(AC), respectively, compared to errors of 0.51 and 0.75 eV from eq 1. It is worth noting, however, that the results are highly sensitive to the choice of $k^{\text{opt,av}}$.

The reason why the approach works well for this set of molecules is evident from Figure 4, which plots the $k_{\text{PBE}}^{\text{opt}}$ and $k_{\text{PBE(AC)}}^{\text{opt}}$ values for these systems. The values are relatively system independent, with average values of $k_{\text{PBE}}^{\text{opt,av}} = 1.297$ and $k_{\text{PBE(AC)}}^{\text{opt,av}} = 1.302$, which are close to the values 1.300 and 1.303 obtained using the set of molecules above. Using these former optimal values would further improve the results.

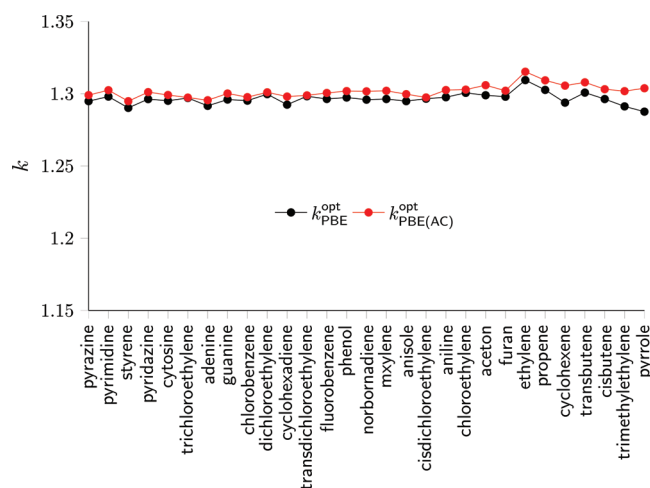


Figure 4. Effective homogeneities for the set of molecules in ref 19.

CONCLUSION

We have considered the influence of the asymptotic exchange-correlation potential and density-scaling homogeneity on electron affinities determined using eq 1. For the set of molecules considered in ref 28, application of an asymptotic correction to the potential improves the accuracy for several of the systems with the most negative affinities, reflecting their diffuse LUMO orbitals. For systems with modest affinities, it reduces the accuracy marginally. Enforcing the near-exact effective homogeneity through a simple shift in the potential leads to an improved correlation with experimental values but significantly overestimated affinities. Optimal effective homogeneities were therefore determined, and a simple scheme was proposed for enforcing an average optimal value. Application of the scheme to the set of molecules considered previously by Sablon et al.¹⁹ maintains the excellent correlation with the experimental values, while significantly reducing the absolute errors.

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Notes

The authors declare no competing financial interest.

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