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Negative Electron Affinities and Derivative Discontinuity Contribution from a Generalized Gradient Approximation Exchange Functional

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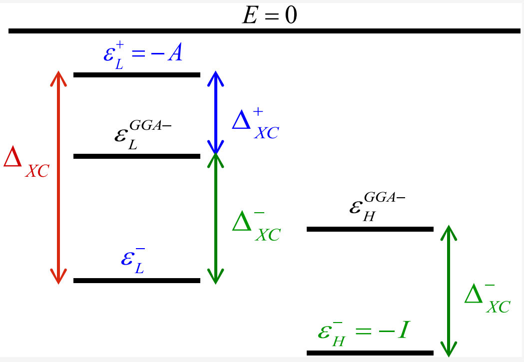
ABSTRACT: Two methods to calculate negative electron affinities systematically from ground-state density functional methods are presented. One makes use of the lowest unoccupied molecular orbital energy shift provided by approximate inclusion of derivative discontinuity in the nearly correct asymptotic potential (NCAP) nonempirical, constraint-based generalized gradient approximation exchange functional. The other uses a second-order perturbation calculation of the derivative discontinuity based on the NCAP exchange-correlation potential. On a set of thirty-eight molecules, NCAP leads to a rather accurate description that is improved further through the perturbation correction. The results presented show the importance of the asymptotic behavior of the exchange-correlation potential in the calculation of negative electron affinities as well as demonstrating the versatility of the NCAP functional.



1. INTRODUCTION

Obtaining well-defined and useful quantitative physical measures of chemical reactivity has been a significant area of investigation for decades. In particular, in describing charge transfer processes in chemical interactions, the original conceptualizations go back to Pauling,[1,2] Mulliken,[3] Sanderson,[4,5] and Pearson,[6,7] among others. Parr[8−12] recognized that those rather qualitative and intuitive ideas could be given a proper quantum mechanical grounding via identification with various partial and functional derivatives in density functional theory (DFT). That grounding of chemical concepts in DFT formalism has come to be known in physical chemistry and chemical physics by the shorthand term "conceptual DFT".[13,14]

Here we readdress a DFT challenge that was recognized some time ago by Geerlings et al.[14] It arises when one asks for a reliable evaluation of the chemical reactivity indices that appear in conceptual DFT.[12−22] The issue is negative electron affinities.[23−34] The context of the problem is two global descriptors, the chemical potential[8] μ and the hardness[9] η. The chemical potential is the negative of the electronegativity χ as defined through the generalization of Iczkowski and Margrave[35] of Mulliken's electronegativity.[3] The DFT definitions of the two are

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} = -\chi \tag{1}$$

and

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} \tag{2}$$

Here $v(\mathbf{r})$ is the total Kohn−Sham external potential (typically for a molecule, the potential generated by the nuclei) and N is the equilibrium total electron number of the neutral system. In the exact theory, analysis of the zero-temperature limit[36−38] of an ensemble composed of systems with $N - 1$, N, and $N + 1$ electrons in their ground states shows that E does not have continuous number derivatives at integer N. Instead, its number dependence consists of a line segment joining $E(N - 1)$ and $E(N)$ and another joining $E(N)$ and $E(N + 1)$ with the slopes of those two being the ionization potential I and electron affinity A, respectively. Evaluation of eqs 1 and 2 by finite differences via those slopes then gives

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$$\mu = -(I + A)/2 = -\chi_M \tag{3}$$

and

$$\eta = I - A \tag{4}$$

where χ_M is Mulliken's electronegativity.

The ionization potential and the electron affinity of a chemical species provide important information about its capacity to donate or accept charge. From the conceptual DFT perspective, these two quantities are foundational in determining the chemical potential and the chemical hardness. Thus, the relationships just discussed are both operationally useful and connect clearly to the conceptual definitions from Mulliken and Pearson. For example, in a charge transfer process between two species the direction of electronic flux is from the species with higher μ to the one with lower μ. The chemical hardness takes the role proposed by Pearson, namely as a resistance to electron flow. Species with large η values are less prone to exchange charge with another species than those with small values. Thus, these two concepts embrace, in a simple but chemically meaningful way, the fundamental aspects of charge transfer processes in chemical interactions.[9,12−22,39−62]

To use these two global descriptors quantitatively via eqs 3 and 4 obviously requires reliable values of I and A for the chemical species of interest. Although both I and A may be measured experimentally, independent prediction via an electronic structure calculation is highly desirable. In this context, the usual, straightforward procedure is to use total energy differences among systems with $N - 1$, N, and $N + 1$ electrons, all of them determined with the N-electron system ground-state geometry. These "vertical" I and A are

$$I = E_{N-1} - E_N \tag{5}$$

and

$$A = E_N - E_{N+1} \tag{6}$$

Experimentally I is a positive definite quantity. In contrast, A may have positive or negative values. Systems with negative electron affinities are a barrier for using eqs 3 and 4. Such systems have transient (i.e., metastable) anionic states that are chemically meaningful, in the sense of being along a reaction path, and they are observable: ref 63 is an early example while ref 64 is much more recent. But as resonances such states are not eigenstates of any time-independent Schrödinger equation. Hence, they are not states that can be treated rigorously by ground state DFT. The utilitarian challenge therefore is to enable general use of eqs 3 and 4, which are rooted in ground-state DFT and work well for $A \geq 0$, by constructing reliable, controlled approximations to handle cases in which $A < 0$ within the framework of ground-state DFT.

In general, the calculation of I through eq 5 either with DFT techniques or through wave function methods can be done with reasonable accuracy. However, the calculation of A, especially for $A < 0$, via eq 6 represents a challenge in general, but particularly for calculations that use finite $\mathcal{L}^2$ basis sets.[25] Such calculations can yield an anion energy above that of the neutral system, leading to seemingly reasonable estimates with certain basis sets. However, if one increases the basis set size to enlarge the number of diffuse functions, the results typically deteriorate in quality with electron affinities tending to zero. That behavior resembles more the conjunction of the neutral system with a free electron than the desired anion. Thus, it has been proposed that for systems with negative electron affinities, one should set the value of A to zero for the calculation of the chemical potential and the hardness with eqs 3 and 4. Doing so, however, is an uncontrolled approximation that can lead to underestimation of the hardness, and consequently to overestimation of the charge transferred. The preferable route therefore is to use negative electrons affinities. The issue is how to do that systematically and efficiently.

From the computational effort viewpoint, the evaluation of I and A from eqs 5 and 6 requires three calculations, the ground state of the reference system and the corresponding cation and anion states at the ground-state geometry of the reference system. Thus, an alternative approximation to these quantities comes from a Koopmans type approach in which,

$$I \approx -\varepsilon_H^0 \tag{7}$$

and

$$A \approx -\varepsilon_L^0 \tag{8}$$

where ε_H^0 and ε_L^0 are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) eigenvalues of the N electron system, respectively. In this case one only needs the calculation of the reference system ground state. These expressions commonly are used either with eigenvalues from approximations to the Kohn−Sham exchange-correlation (XC) energy functional, $E_{XC}^{\text{aprox}}[\rho(\mathbf{r})]$, or with Hartree−Fock orbital energies, although they have a quite different behavior.[65] The Hartree−Fock ε_H^{HF} lies close to the experimental ionization potential. But as a consequence of the finite basis set and HF virtual space self-repulsion, ε_L^{HF} in general has a large positive value. That would correspond to a large magnitude negative electron affinity for any system. On the other hand, the LDA, GGA, and meta-GGA approximations to the Kohn−Sham $E_{XC}^{\text{aprox}}[\rho(\mathbf{r})]$ lead, in general, to a value of ε_H^0 that is shifted upward with respect to the exact I (because of self-interaction and derivative discontinuity effects), so that the ionization potential is underestimated by the HOMO eigenvalue. For the same reasons, such functionals give a value of ε_L^0 that, in most cases, is shifted downward with respect to the exact A, so that the electron affinity is, in general, overestimated. Thus, in order to improve the accuracy of the I and A values determined through the HOMO and LUMO eigenvalues (and thereby to determine μ and η), corrections are needed. In the Kohn−Sham case, those usually are based on approximations for the effects of self-interaction and the derivative discontinuity (DD) of the exact XC potential.[27,29,33,66−70]

In this latter context, Tozer and De Proft[27] developed a procedure in which the DD magnitude is estimated through the ionization potential (determined from energy differences), eq 5, and the HOMO eigenvalue of the reference system. That estimate then is used to shift the LUMO eigenvalue, leading to the relationship

$$A = -(\varepsilon_H^0 + \varepsilon_L^0) - I \tag{9}$$

In application to a test set of thirty-eight molecules with negative electron affinities,[28] this expression gave results that lie close to the experimental values.

Recently, Yang et al.[33] have developed a global scaling correction (GSC) that imposes the linear behavior of the energy as a function of the number of electrons upon approximate functionals. The electron affinity is determined by adding this correction to the reference system LUMO eigenvalue, that is,

$$A = -(\varepsilon_{\rm L}^{0} + \Delta\varepsilon_{\rm L}^{\rm GSC}) \tag{10}$$

This procedure leads to an even better description of the test set of thirty-eight molecules than the method proposed by Tozer and De Proft.

On the other hand, Vibert and Tozer[34] proposed an extension to the method that led to eq 9, incorporating density scaling homogeneities to derive two system-dependent XC functionals, one appropriate for the electron deficient side of the integer and one appropriate for the electron abundant side. The electron affinity in this case is expressed as in eq 9, but with I and $\varepsilon_{\rm L}^{0}$ replaced by the eigenvalues of the HOMO and the LUMO, respectively, obtained with the XC functional of the electron deficient side, and $\varepsilon_{\rm H}^{0}$ replaced by the eigenvalue of the HOMO obtained from the XC functional of the electron abundant side. As in the case of the method described by eq 9, one needs to determine I from the energy differences to fix the values of the parameters in the associated XC potentials. However, the results obtained through this approach, for a subset of the thirty-eight molecule test set, show an important improvement over the ones obtained through eq 9, and are similar to the ones obtained from eq 10. A relevant, common aspect in the three procedures is that one does not require the anion energy.

In general, these correction terms have been developed for GGA XC expressions, the functional form of which in terms of the electron density does not incorporate DD effects. However, we have recently proposed a GGA XC functional,[71] named nearly correct asymptotic potential (NCAP), which introduces approximate DD effects explicitly. An important consequence is that the NCAP functional derivative leads to an XC potential that tends asymptotically to a constant. That constant depends on the HOMO eigenvalue. This approximate DD correction motivates the present work. Specifically, the main objective of this work is to analyze the DD for NCAP type XC functionals in terms of its consequences for the calculation of negative electron affinities. For comparison, we also analyze the performance of a perturbation approach designed to estimate the DD magnitude.[72]

2. THEORETICAL DEVELOPMENT

As discussed already, at zero temperature the DFT energy is a pair of lines joining the energies for $N - 1$, N, and $N + 1$ electron systems with N being the number of electrons of the reference system.[36−38,73,74] An important consequence of this behavior is that the exact Kohn−Sham XC potential has a discontinuity as N crosses an integer value,[75,76] that is

$$\Delta_{\rm XC} = v_{\rm XC}^{+}(\mathbf{r}) - v_{\rm XC}^{-}(\mathbf{r}) \tag{11}$$

Here $\Delta_{\rm XC}$ is the magnitude of the DD, which is assumed to be constant,[77] and $v_{\rm XC}^{-}(\mathbf{r})$ and $v_{\rm XC}^{+}(\mathbf{r})$ correspond to the XC potential evaluated from the electron deficient and the electron abundant sides, respectively.

Thus, according to the ionization potential theorems[78] for the exact XC energy functional, the HOMO eigenvalue of the N electron system, obtained with $v_{\rm XC}^{-}(\mathbf{r})$, denoted as $\varepsilon_{\rm H}^{-}$, is equal to the negative of the ionization potential, that is

$$\varepsilon_{\rm H}^{-} = -I \tag{12}$$

while the LUMO eigenvalue of the same system, obtained with $v_{\rm XC}^{+}(\mathbf{r})$, denoted as $\varepsilon_{\rm L}^{+}$, satisfies the relationship

$$\varepsilon_{\rm L}^{+} = -A \tag{13}$$

It is important to note that the eigenvalues used in eqs 7 and (8) are associated with some specified XC functional approximation, $E_{\rm XC}^{\rm aprox}[\rho(\mathbf{r})]$, and hence lead to approximate I and A values. In contrast, if the eigenvalues used in eqs 12 and 13 were determined with the exact XC potential, they would yield the exact vertical values of I and A.

Recognizing that the LUMO associated with $v_{\rm XC}^{-}(\mathbf{r})$ can be expressed as $\varepsilon_{\rm L}^{-}$, and that eq 11 shows that the difference between $v_{\rm XC}^{+}(\mathbf{r})$ and $v_{\rm XC}^{-}(\mathbf{r})$ is the constant $\Delta_{\rm XC}$, one finds that

$$\Delta_{\rm XC} = \varepsilon_{\rm L}^{+} - \varepsilon_{\rm L}^{-} \tag{14}$$

A closer analysis of these relationships follows from a seemingly trivial rewriting of the exact eqs 12 and 13 in the form

$$\varepsilon_{\rm H}^{-} = -I = \varepsilon_{\rm H}^{-} - (\varepsilon_{\rm H}^{-} + I) \tag{15}$$

and

$$\varepsilon_{\rm L}^{+} = -A = \varepsilon_{\rm L}^{-} - (\varepsilon_{\rm L}^{-} + A) \tag{16}$$

where $\varepsilon_{\rm H}^{-}$ and $\varepsilon_{\rm L}^{-}$ correspond to a Kohn−Sham calculation of the reference system using some approximate or the exact XC potential. The rewritten form suggests that the terms in parentheses may be interpreted as the shifts one has to perform on the approximate eigenvalues, to obtain the exact values for I or A, so that one may define

$$\Delta_{\rm XC}^{-} = -(\varepsilon_{\rm H}^{-} + I) \tag{17}$$

and

$$\Delta_{\rm XC}^{+} = -(\varepsilon_{\rm L}^{-} + A) \tag{18}$$

Subtracting these two equations gives

$$I - A = \varepsilon_{\rm L}^{-} - \varepsilon_{\rm H}^{-} + \Delta_{\rm XC}^{+} - \Delta_{\rm XC}^{-} \tag{19}$$

so that

$$\Delta_{\rm XC} = \Delta_{\rm XC}^{+} - \Delta_{\rm XC}^{-} \tag{20}$$

This follows because if $\varepsilon_{\rm H}^{-}$ and $\varepsilon_{\rm L}^{-}$ are the exact eigenvalues, then substitution of eqs 12, 13, and 20 in eq 19 leads to eq 14, which corresponds to the exact definition of the magnitude of the XC DD. Also, one can see, from eqs 17 and 18, that for the exact eigenvalues, $\Delta_{\rm XC}^{-} = 0$ and $\Delta_{\rm XC}^{+} = \Delta_{\rm XC}$. However, if the eigenvalues arise from an approximate XC potential, eqs 17 and 18 indicate that the shift for $\varepsilon_{\rm H}^{-}$ is negative and is different from the shift for $\varepsilon_{\rm L}^{-}$, which is positive. Therefore, according to eq 20, it is through the difference of these two shifts that one obtains the approximate value of $\Delta_{\rm XC}$. It is important to note that the present approach, which is based on the ionization potential theorems, agrees with the observations of Teale, De Proft, and Tozer,[29] who derived those relationships through the analysis of the dependence of the energy as a function of the number of electrons of an approximate XC functional with respect to the exact one.

A relevant aspect that arises from the present analysis concerns the relationship of approximate KS HOMO and LUMO eigenvalues to the exact I and A already mentioned. The way that the KS scheme is developed (aubau prinzip) means that conventional Kohn−Sham eigenvalues and orbitals for a neutral system are calculated from the electron deficient side, so the relevant potential is $v_{\mathrm{XC}}^{-}(\mathbf{r})$. Most GGA XC functionals lead to potentials that decay asymptotically faster than $-1/r$, lack the derivative discontinuity correction, and are not self-interaction free. As a result, the occupied Kohn−Sham levels are pushed up with respect to the exact Kohn−Sham levels. That upward shift is larger for $\varepsilon_{\mathrm{H}}^{-}$ than for $\varepsilon_{\mathrm{L}}^{-}$, a fact responsible for the well-known problem of underestimation of the Kohn−Sham HOMO−LUMO gap from such functionals. Therefore, relative to the exact value of $-I$, $\varepsilon_{\mathrm{H}}^{-}$ always is shifted upward. However, since the GGA HOMO−LUMO gap is too small, it also is plausible that $\varepsilon_{\mathrm{L}}^{-}$ will be shifted downward with respect to $-A$. This downward shift argument is supported by experience in many cases, though as far as we are aware it is not universally valid.

In consideration of such shifts, the expression proposed by Tozer and De Proft, eq 9, may be obtained from eq 19 by assuming that $\Delta_{\mathrm{XC}}^{+} = -\Delta_{\mathrm{XC}}^{-}$, and that $\Delta_{\mathrm{XC}}^{-} = -(\varepsilon_{\mathrm{H}}^{0} + I)$, where the ionization potential, as previously mentioned, is determined through energy differences, eq 5. This procedure leads to a reasonably good description of ionization potentials and electron affinities with the PBE GGA XC functional.[27,28] Two calculations are required, one for the ground state of the reference system, another for the corresponding cation at the reference system geometry. Explicit calculation of the anion is not needed. Thus, it seems that for GGA XC expressions, the functional form of which in terms of the electron density does not incorporate DD effects, the assumption $\Delta_{\mathrm{XC}}^{+} = -\Delta_{\mathrm{XC}}^{-}$ is approximately valid. However, matters are different for a GGA that includes DD effects by construction.

A GGA exchange energy functional usually is written in terms of the reduced density gradient, $s(\mathbf{r}) = |\nabla\rho(\mathbf{r})|/2k_F(\mathbf{r})\rho(\mathbf{r})$, where $k_F = (3\pi^2\rho(\mathbf{r}))^{1/3}$, through the enhancement factor, $F_{\mathrm{X}}(s)$, as

$$E_{\mathrm{X}}^{\mathrm{GGA}}[n] = \int n(\mathbf{r})\varepsilon_{\mathrm{X}}^{\mathrm{LDA}}(n(\mathbf{r}))F_{\mathrm{X}}(s)\,\mathrm{d}\mathbf{r} \tag{21}$$

Here $\varepsilon_{\mathrm{X}}^{\mathrm{LDA}}(n(\mathbf{r})) = A_{\mathrm{X}}(n(\mathbf{r}))^{1/3}$ is the local density approximation for the exchange energy per particle with $A_{\mathrm{X}} = -3(3\pi^2)^{1/3}/4\pi$. Recently, we have presented and validated a nonempirical GGA XC functional, NCAP, the enhancement factor for the exchange energy of which is given by[71]

$$F_{\mathrm{X}}^{\mathrm{NCAP}}(s) = 1 + \mu\tanh(s)\sinh^{-1}(s)\frac{1 + \alpha((1-\zeta)s\ln(1+s) + \zeta s)}{1 + \beta\tanh(s)\sinh^{-1}(s)} \tag{22}$$

where $\mu = 0.219515$, $\alpha = 0.345112$, $\beta = 0.018086$, and $\zeta = 0.304121$, values that were determined through constraint satisfaction. When this exchange energy functional is combined with the Perdew-86 correlation energy functional, one finds that the combination leads to a reasonable description of thermodynamic, kinetic, structural, and response properties, and that it also provides a good description of excitation energies. While the descriptions of the first three properties largely are determined from the values of the enhancement factor in the interval $0 \le s \le 3$, the latter two properties have a strong dependence on the limit of $F_{\mathrm{X}}(s)$ as $s \to \infty$. Attention to that limit is particularly important to correct the asymptotic exponential decay of the XC potential of most GGAs. Such exponential decay leads in part, to the problems associated with the HOMO and LUMO eigenvalues mentioned before. By construction, the NCAP X functional has its X potential (the functional derivative with respect to density) behaving asymptotically as

$$v_{\mathrm{X}}^{\mathrm{NCAP}}(\mathbf{r}) \xrightarrow[r\to\infty]{} -v_{\mathrm{X}}^{\mathrm{DD}} - c/r \tag{23}$$

where $c \sim 0.3$, instead of $c = 1$ which is the exact value that it should have, and $-v_{\mathrm{X}}^{\mathrm{DD}}$ is a positive quantity.

From eq 23 one can see that at very large distances the exchange potential of NCAP reaches a constant value $-v_{\mathrm{X}}^{\mathrm{DD}}$, which comes from the presence of the term $s\ln(1+s)$ in the limit as $s \to \infty$. However, the ionization potential theorem requires the potential to be realigned to zero.[78] One therefore needs to add the constant to obtain the X potential, the eigenvalue of which will be approximately equal to the negative of the exact ionization potential, that is

$$v_{\mathrm{X}}^{-}(\mathbf{r}) = v_{\mathrm{X}}^{\mathrm{NCAP}}(\mathbf{r}) + v_{\mathrm{X}}^{\mathrm{DD}} \tag{24}$$

The constant $v_{\mathrm{X}}^{\mathrm{DD}}$ is related to the asymptotic behavior of the electron density,[78−81] $\rho(\mathbf{r}) \to C\exp(-2\sqrt{-2\varepsilon_{\mathrm{H}}^{-}})$, where $\varepsilon_{\mathrm{H}}^{-}$ is the eigenvalue associated with the X potential $v_{\mathrm{X}}^{-}(\mathbf{r})$, explicitly

$$v_{\mathrm{X}}^{DD} = A_{\mathrm{X}}Q_{\mathrm{X}}\sqrt{-\varepsilon_{\mathrm{H}}^{-}} \tag{25}$$

where A_{X} has been defined in eq 21, and $Q_{\mathrm{X}} = (\sqrt{2}/3(3\pi^2)^{1/3})\gamma$ with $\gamma = 4\pi(1-\zeta)/3$. However, following Armiento and Kümmel,[82] it is more useful to express the constant in terms of the eigenvalues associated with $v_{\mathrm{X}}^{\mathrm{NCAP}}(\mathbf{r})$, because those are the ones that are known from the Kohn−Sham calculation. Thus, from eq 24, one finds that

$$\varepsilon_{\mathrm{H}}^{-} = \varepsilon_{\mathrm{H}}^{\mathrm{NCAP}} + v_{\mathrm{X}}^{\mathrm{DD}} \tag{26}$$

which when combined with eq 25 leads to a quadratic equation for $v_{\mathrm{X}}^{\mathrm{DD}}$ with two solutions,

$$v_{\mathrm{X}}^{\mathrm{DD}\mp} = -\frac{1}{2}A_{\mathrm{X}}^{2}Q_{\mathrm{X}}^{2}\left(1 \pm \sqrt{1 - 4\frac{\varepsilon_{\mathrm{H}}^{\mathrm{NCAP}}}{A_{\mathrm{X}}^{2}Q_{\mathrm{X}}^{2}}}\right) \tag{27}$$

As expected from the discussion that led to eq 20, this result indicates that there are two different shifts that can be applied to the NCAP eigenvalues. In the case of $\varepsilon_{\mathrm{H}}^{\mathrm{NCAP}}$ the solution with the plus sign satisfies the condition $\Delta_{\mathrm{XC}}^{-} < 0$, which will make the value of $\varepsilon_{\mathrm{H}}^{-}$ closer to $-I$ because in this case $v_{\mathrm{X}}^{\mathrm{DD}} = v_{\mathrm{X}}^{\mathrm{DD}-} \approx \Delta_{\mathrm{XC}}^{-}$ is a negative quantity, therefore

$$\varepsilon_{\mathrm{H}}^{-} = -I = \varepsilon_{\mathrm{H}}^{\mathrm{NCAP}} + v_{\mathrm{X}}^{\mathrm{DD}-} \tag{28}$$

On the other hand, in the case of $\varepsilon_{\mathrm{L}}^{\mathrm{NCAP}}$ the solution with the minus sign satisfies the condition $\Delta_{\mathrm{XC}}^{+} > 0$, which will make the value of $\varepsilon_{\mathrm{L}}^{+}$ closer to $-A$, because in this case $v_{\mathrm{X}}^{\mathrm{DD}} = v_{\mathrm{X}}^{\mathrm{DD}+} \approx \Delta_{\mathrm{XC}}^{+}$ is a positive quantity, and

$$\varepsilon_{\mathrm{L}}^{+} = -A = \varepsilon_{\mathrm{L}}^{\mathrm{NCAP}} + v_{\mathrm{X}}^{\mathrm{DD}+} \tag{29}$$

It is interesting to note that since the shift $v_{\mathrm{X}}^{\mathrm{DD}-}$ applies for all the orbitals obtained with $v_{\mathrm{X}}^{\mathrm{NCAP}}(\mathbf{r})$, in particular for $\varepsilon_{\mathrm{L}}^{\mathrm{NCAP}}$ to obtain $\varepsilon_{\mathrm{L}}^{-}$, then substituting this result together with eq 29 in eq 14, one finds that

$$\Delta_{\mathrm{XC}}^{\mathrm{NCAP}} = v_{\mathrm{X}}^{\mathrm{DD}+} - v_{\mathrm{X}}^{\mathrm{DD}-} \tag{30}$$

That is, the difference of the two solutions of eq 27 provides an estimate of the DD.

Thus, through a single calculation of the reference system ground state, one determines the shifts that must be applied to $\varepsilon_{\mathrm{H}}^{\mathrm{NCAP}}$ and $\varepsilon_{\mathrm{L}}^{\mathrm{NCAP}}$ to estimate I and A, respectively. However, NCAP establishes a different magnitude for the shift of $\varepsilon_{\mathrm{H}}^{\mathrm{NCAP}}$ and the shift of $\varepsilon_{\mathrm{L}}^{\mathrm{NCAP}}$, as a consequence of the two solutions given by eq 27.

Another way to use eq 14 in combination with approximate determination of $\varepsilon_{\mathrm{L}}^{+}$ from information obtained through the ground state calculation of the N electron system was proposed by some of us a while ago.[72] The idea is to approximate the density of the $N + 1$ electron system, using the density of the N electron system together with the density associated with the LUMO, which would be the orbital occupied by the additional electron, that is, $\rho_{N+1}(\mathbf{r}) \approx \rho_N(\mathbf{r}) + \rho_L(\mathbf{r})$. The full Kohn–Sham potential, $v_{\mathrm{KS}}[\rho(\mathbf{r})] = v_{\mathrm{External}}(\mathbf{r}) + v_{\mathrm{Coulomb}}[\rho(\mathbf{r})] + v_{\mathrm{XC}}[\rho(\mathbf{r})]$, then may be estimated through the expression $v_{\mathrm{KS}}[\rho_{N+1}] \approx v_{\mathrm{KS}}[\rho_N + \rho_{\mathrm{L}}]$. That, in turn, may be combined with second-order perturbation theory to yield the approximate magnitude of the XC DD as

$$\begin{aligned}\Delta_{\mathrm{XC}}^{\mathrm{PT}} &= \varepsilon_{\mathrm{L}}^{+} - \varepsilon_{\mathrm{L}}^{-}\\ &\approx \int \mathrm{d}\mathbf{r}\, \phi_{\mathrm{L}}^{*}(\mathbf{r})(v_{\mathrm{KS}}[\rho_N + \rho_{\mathrm{L}}] - v_{\mathrm{KS}}[\rho_N])\phi_{\mathrm{L}}(\mathbf{r})\\ &\quad + \sum_{i\neq \mathrm{L}} \frac{\left|\int \mathrm{d}\mathbf{r}\, \phi_{\mathrm{L}}^{*}(\mathbf{r})(v_{\mathrm{KS}}[\rho_N + \rho_{\mathrm{L}}] - v_{\mathrm{KS}}[\rho_N])\phi_i(\mathbf{r})\right|^2}{\varepsilon_{\mathrm{L}} - \varepsilon_i}\end{aligned} \tag{31}$$

where $\phi_i(\mathbf{r})$ is the ith Kohn–Sham orbital and i runs over all occupied and unoccupied orbitals obtained for a given basis set.

To use this approach with NCAP, it is important to note that the perturbation theory just described allows one to estimate the value of the total magnitude of the DD $\Delta_{\mathrm{XC}}^{\mathrm{PT}}$. But as we have just showed, a consequence for a variational potential that goes to a positive constant in the asymptotic limit, is that $\Delta_{\mathrm{XC}}^{\mathrm{NCAP}}$, eq 30, is composed of two shifts. Therefore, we must partition $\Delta_{\mathrm{XC}}^{\mathrm{PT}}$ into two shifts that preserve the same proportion obtained for NCAP, because the sets of eigenvalues and orbitals used in eq 31 have been determined with the NCAP XC potential. Thus, for the perturbation theory approach in NCAP, from eqs 28–31, one finds that

$$\varepsilon_{\mathrm{H}}^{-} = -I = \varepsilon_{\mathrm{H}}^{\mathrm{NCAP}} + \frac{v_{\mathrm{X}}^{\mathrm{DD}-}}{\Delta_{\mathrm{XC}}^{\mathrm{NCAP}}}\Delta_{\mathrm{XC}}^{\mathrm{PT}} \tag{32}$$

and

$$\varepsilon_{\mathrm{L}}^{+} = -A = \varepsilon_{\mathrm{L}}^{\mathrm{NCAP}} + \frac{v_{\mathrm{X}}^{\mathrm{DD}+}}{\Delta_{\mathrm{XC}}^{\mathrm{NCAP}}}\Delta_{\mathrm{XC}}^{\mathrm{PT}} \tag{33}$$

It may be seen that all the information required to evaluate I and A from these two expressions comes from an NCAP calculation of the ground state of the reference system.

3. RESULTS AND DISCUSSION

To test the performance of the perturbation theory and the direct NCAP approaches, we have made use of a set of thirty-eight molecules with negative electron affinities. The ground state geometries for all the molecules are the ones used in ref 33, where the optimization was done with the B3LYP hybrid XC functional[83−85] and a 6-311+G** basis,[86] using the Gaussian 09 suite of programs.[87] All the single-point calculations for the present work utilized those geometries, both for the reference system and its corresponding cation and anion. The calculations used a modified version of NWChem 6.5.[88] This modified version includes the calculation of $\Delta_{\mathrm{XC}}^{\mathrm{PT}}$ through eq 31. The aug-cc-pVTZ basis set[89,90] was used. The rationale is that previous work[28,33] on the 38 systems with the PBE XC functional showed, by comparison with the results obtained with the cc-pVTZ basis set, that inclusion of diffuse functions is important for the determination of the electron affinity through eq 6. That relationship requires one to perform the calculation of the corresponding anion. However, the inclusion of diffuse functions did not show a significant change in the frontier eigenvalues of the reference system, so that going beyond the aug-cc-pVTZ basis set would not lead to substantial changes.

In Table 1 we present the results for the electron affinities determined through eqs 6, 8, 29, and 33, together with the experimental values. As expected, the poorest description comes from the results calculated as simply the negative of the LUMO eigenvalue, eq 8. This behavior is a result of the downward shift that is characteristic, in general, as explained before, of $\varepsilon_{\mathrm{L}}^{\mathrm{GGA}}$ that leads to an overestimation of the electron affinities. In fact, eq 8 yields $A > 0$ in all the cases considered. The results with energy differences, eq 6, requiring calculation for the anion, lie closer to zero. In general this leads to an overestimation with respect to the experimental values, with a mean average deviation (MAD) of 0.84 eV, very similar to the value reported for the PBE XC functional with the same basis set, 0.91 eV. Although the sign is correct for both functionals, for all the cases, it is spurious. That outcome means that the anions are found to have higher energies than the corresponding neutral species. Hence the anions are unstable. The positive sign is a consequence of the finite $\mathcal{L}^2$ basis set, which converts the unstable scattering state into an artificially normalizable one.

The results for eq 29 give the correct sign and follow the experimental trends while avoiding treatment of the anions, leading to a MAD of 0.50 eV. This is greater precision than the energy differences. One important aspect of this result is that the calculations for NCAP may be considered to be approximately equivalent to those with PBE reported by De Proft et al.,[28] in the following sense. In the latter, the assumption of equal shifts in opposite directions for $\varepsilon_{\mathrm{H}}^{\mathrm{PBE}}$ and $\varepsilon_{\mathrm{L}}^{\mathrm{PBE}}$ may be seen to be approximately valid for GGA XC expressions the functional form of which does not incorporate a DD correction. The former corresponds to the case in which the variationally obtained XC potential tends to a positive constant, and requires different shifts for $\varepsilon_{\mathrm{H}}^{\mathrm{NCAP}}$ and $\varepsilon_{\mathrm{L}}^{\mathrm{NCAP}}$. This seems to explain the similar values of the MAD of 0.49 eV obtained, with PBE and the same basis set, by De Proft et al., and the one reported here with NCAP of 0.50 eV.

Finally, one can see that the perturbation theory calculations with eq 33 lead to results of the same quality as those obtained by Wang et al.[33] through eq 10. In the case of the latter, the MAD obtained with a value of an electron affinity of −3.45 eV for the chloromethane molecule is 0.24 eV, while in our case it is 0.21 eV. However, their discussion of the electron affinity for chloromethane suggests a value closer to −1.3 eV, which led them to a MAD of 0.18 eV, while in our case the value obtained is 0.15 eV.

To get an overall picture of the four sets of results, Figure 1 compares the calculated and the experimental electron affinities. One can see that the energy differences approach does not follow the experimental trend. Rather, as already emphasized, the energy differences tend to be near zero. Of the other three methods, only two bear a useful quantitative relation with the experimental values. NCAP itself, eq 29,

Table 1. Calculated and Experimental Electron Affinities in eV for a Test Set Composed of Thirty-Eight Molecules[a]

	ΔE	$-\varepsilon_L^{NCAP}$	NCAP	NCAP-PT	
system	eq 6	eq 8	eq 29	eq 33	expt
1,1-dichloroethylene	−0.402	1.661	−1.487	−1.061	−0.75
1,3-cyclohexadiene	−0.374	1.682	−1.012	−0.587	−0.80
acetaldehyde	−0.377	1.966	−0.995	−1.401	−1.19
adenine	−0.125	1.605	−1.202	−0.430	−0.64
bromobenzene	−0.888	1.568	−1.445	−0.757	−0.70
chlorobenzene	−0.952	1.545	−1.492	−0.791	−0.75
chloroethylene	−0.457	1.362	−1.775	−1.391	−1.29
chloromethane	−0.376	0.610	−2.722	−1.185	−3.45
cis-dichloroethylene	−0.381	1.555	−1.537	−1.275	−1.12
cytosine	−0.016	1.947	−0.928	−0.521	−0.36
ethylene	−0.516	0.998	−2.226	−1.716	−1.78
fluorobenzene	−1.093	1.472	−1.569	−0.879	−0.87
naphthalene	−0.232	2.043	−0.758	0.142	−0.20
norbornadiene	−0.373	1.304	−1.478	−0.814	−1.04
pyrazine	−0.228	2.587	−0.347	−0.053	−0.07
pyridazine	−0.290	2.540	−0.224	−0.003	−0.32
pyrimidine	−0.464	2.333	−0.631	−0.242	−0.25
styrene	−0.283	2.003	−0.870	0.011	−0.25
thiophene	−1.206	1.361	−1.577	−0.978	−1.17
trans-dichloroethylene	−0.975	1.687	−1.398	−1.098	−0.82
trichloroethylene	−0.411	1.847	−1.238	−0.935	−0.58
uracil	−0.044	2.337	−0.724	−0.194	−0.21
1,2,4-trimethylbenzene	−0.317	0.922	−1.911	−1.197	−1.07
acetone	−0.322	1.596	−1.270	−1.536	−1.51
aniline	−0.391	1.011	−1.614	−1.158	−1.13
anisole	−0.327	1.121	−1.647	−1.116	−1.09
cis-butene	−0.442	0.319	−2.596	−2.294	−2.22
cyclohexene	−0.405	0.391	−2.507	−1.606	−2.07
furan	−0.437	0.797	−2.069	−1.678	−1.76
m-xylene	−0.394	1.038	−1.873	−1.121	−1.06
o-xylene		0.948	−1.964	−1.277	−1.12
phenol		1.217	−1.604	−1.044	−1.01
propene	−0.474	0.669	−2.393	−1.921	−1.99
pyrrole	−0.308	0.058	−2.629	−2.226	−2.38
trans-butene	−0.457	0.368	−2.548	−2.183	−2.10
trimethylethylene	−0.423	0.390	−2.428	−1.824	−2.24
CO_2	−0.767	0.238	−3.657	−3.769	−3.80
guanine	0.016	1.293	−1.436	−0.843	−0.46
MAD	0.835	2.527	0.499	0.211	
MAD[b]	0.775	2.470	0.517	0.155	

[a] All calculations correspond to the NCAP exchange-correlation energy functional defined in eqs 21 and 22 with the aug-cc-pVTZ basis set. The experimental values were taken from ref 33. [b] Calculated with a value of the experimental electron affinity of chloromethane of −1.3 eV instead of −3.45 eV.

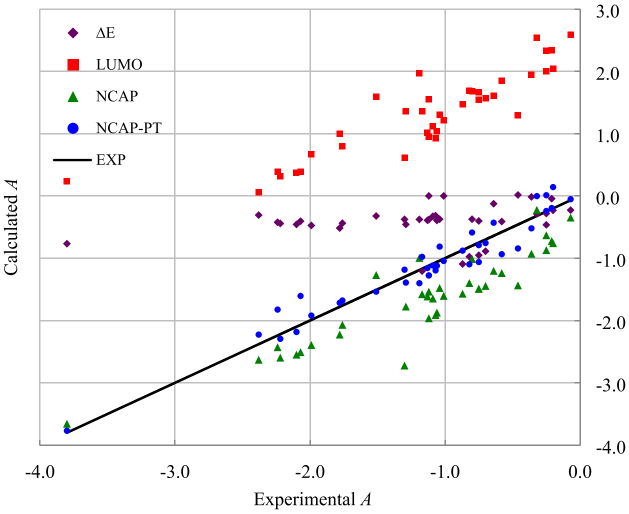

Figure 1. Comparison between the calculated electron affinities and the experimental values of the test set of thirty-eight molecules considered in this work in eV. The black solid line corresponds to the hypothetical equality between the experimental and the calculated values. See Table 1 for the equation used in each case. The experimental value of chloromethane in this plot is −1.3 eV.

predicts values that are slightly more negative than experiment. Perturbation theory corrections applied to NCAP, eq 33, lead to results that lie very close to the experimental ones. For the third method, ε_L^- values, the signs are wrong (positive instead of negative) although the rough trend parallels the experimental one.

4. CONCLUSIONS

The results presented for NCAP and the perturbation theory based on NCAP show the importance of the asymptotic behavior of the XC potential and its relationship to the derivative discontinuity in the calculation of negative electron affinities. The analysis performed indicates that for GGAs, the shifts for ε_H^{GGA} and ε_L^{GGA} are different, although for GGA XC expressions, for which the functional form does not incorporate any approximate DD correction, it seems that the assumption $\Delta_{XC}^+ = -\Delta_{XC}^-$ can lead to a good description of the negative electron affinities. However, one cannot, in those cases, estimate the shift from the information obtainable solely from calculation of the ground state of the reference system. In this respect, XC functionals such as NCAP, which yield a variational X potential decaying asymptotically to a positive constant, have an advantage, because they predict the two required shifts directly from the information on the reference system. As we have shown, at least in the case of NCAP, the proportion of the one shift with respect to the other one seems to be appropriate. Thus, even though the results obtained for NCAP are practically equal to those of Tozer and De Proft with PBE, the NCAP case only requires calculation of the ground state of the neutral N electron system.

The similarity between the results obtained by the GSC and the perturbation theory described in the present work, may be understood by considering that they are addressing the same problem, but with a different approach. That is, the GSC is derived to impose the linear behavior of the energy as a function of the number of electrons to approximate functionals, while the perturbation theory is designed to impose the DD, which is a result of the linear behavior, also upon approximate functionals.

Regarding the differences between NCAP and the perturbation theory based on NCAP, we remark that those basically come from the fact that NCAP tends to overestimate the DD magnitude. That leads to slightly larger values of I and to slightly smaller values of A, with respect to the experimental ones. On the other hand, the perturbation theory based on NCAP provides smaller DD magnitudes than NCAP itself, so that the values of I and A lie closer to the experimental ones.

The results presented here and those of previous work, indicate that through corrections of the LUMO eigenvalue that avoid the calculations for the anion, one can get a rather accurate description of negative electron affinities. We also confirm that the calculation of the unstable anion with finite, square-integrable basis sets leads to an unphysical and therefore incorrect description of these systems.

With respect to the original motivation regarding the determination of the chemical potential and the hardness of chemical systems with negative electron affinities, one can see that, indeed, the approach presented here gives a better description of those descriptors by providing rather accurate A values from a single ground-state calculation and a simple perturbative correction, instead of setting A to zero. That advantage is practical as well as conceptual because of the ease of implementation. Both NCAP itself and the perturbative correction, eqs 31−33 are straightforward to implement in any molecular electronic structure code. In addition to providing the advantages of NCAP itself, such implementation provides, at almost no extra computational cost, trustable values for the two most important global reactivity indices, the chemical potential and the global hardness.

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Notes

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