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Computation of the Hardness and the Problem of Negative Electron Affinities in Density Functional Theory

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The absolute hardness in density functional theory (DFT) is discussed, emphasizing the charge-transfer excitation interpretation. Direct evaluation from the computed ionization potential and electron affinity is intrinsically problematic when the affinity is negative; the calculated affinity exhibits a strong basis set dependence, becoming near zero as diffuse functions are added. An alternative Koopmans-based approximation using local functional eigenvalues uniformly and significantly underestimates the hardness. A simple correction to the Koopmans expression is highlighted on the basis of a consideration of the integer discontinuity. The resulting hardness expression does not require the explicit computation of the affinity and has a straightforward interpretation in terms of the electronegativity. The correction eliminates the underestimation and gives hardness values that do not degrade as the electron affinity becomes more negative. For systems with large negative affinities, the values are an improvement over those from the other approaches. The success can be traced to an implicit, unconventional approximation for the electron affinity, which outperforms the standard approach when the affinity is significantly negative and which does not break down as the basis set becomes more diffuse.

1. Introduction

In the conceptual approach to density functional theory (DFT), chemical properties are identified as response functions of the electronic energy E with respect to the number of electrons N and the external (i.e., due to the nuclei) potential $v(\mathbf{r})$ or both.[1−6] Chemical concepts such as electronegativity,[7,8] hardness,[9−11] and softness,[9,10,12] which are often defined on an empirical basis, thus acquire a mathematical definition, permitting their calculation from first principles. A series of chemical principles such as Sanderson's electronegativity equalization principle[13] and Pearson's hard and soft acids and bases (HSAB)[9,10,14] and maximum hardness principles (MHP)[10,15] receive theoretical justification (for an overview, see ref 6). A recent derivation of the HSAB principle has been presented by Ayers.[16]

The absolute hardness is an important quantity, as it serves as input in HSAB and MHP studies of chemical reactivity and stability. The concept was introduced by Pearson in the 1960s within the framework of the classification of Lewis acids and bases.[9] The absolute hardness η was quantified by Parr and Pearson as the second derivative of the electronic energy of the system with respect to the number of electrons at a constant external potential.[11]

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} \tag{1}$$

The operational definition of the exact, absolute hardness is obtained by finite difference, assuming a quadratic relationship between E and N.

$$\eta^\circ = \frac{I^\circ - A^\circ}{2} \tag{2}$$

where I° and A° are the experimental vertical ionization potential and electron affinity, respectively; the need for vertical quantities reflects the differentiation at the constant external potential in eq 1. Throughout this study, all ionization potentials and electron affinities (calculated and experimental) refer to vertical rather than adiabatic quantities. The hardness is therefore (half) an exact charge-transfer (CT) vertical excitation energy between two identical, infinitely separated molecules. A large number of experimental hardness values have been compiled and used by Pearson.[10,17−19]

The natural way to approximate the hardness in DFT is to evaluate it directly from the calculated ionization potential and electron affinity as

$$\eta = \frac{I - A}{2} \tag{3}$$

where I and A are obtained from total electronic energy calculations on the $N - 1$, N, and $N + 1$ electron systems at the neutral geometry

$$I = E_{N-1} - E_N \tag{4}$$

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

In the context of excitations, this represents a "delta SCF" approximation to the CT excitation in eq 2. The experimental ionization potential is positive and can typically be reproduced to within a few tenths of an electronvolt by standard DFT

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functionals. A positive experimental electron affinity indicates that the anion is stable with respect to electron loss, and in such cases, the affinity, and thus the hardness, can generally be calculated to a similar accuracy. It is important to observe, however, that the highest occupied molecular orbital (HOMO) eigenvalue is often positive for atomic and small molecular anions, and this has been discussed in terms of self-interaction error.[20−23] A positive eigenvalue formally corresponds to a nonnormalizable, continuum orbital, although in practice, the orbital is constrained to be normalized by the finite basis set. Note that this does not imply that expanding the basis set through the addition of diffuse functions would cause the electron to completely leave the system because this would raise the energy to that of the neutral species, which would be energetically unfavorable. As demonstrated by Jarecki and Davidson,[24] particular care is required when performing and interpreting calculations on bound anions. Specifically, they demonstrated that accurate numerical evaluation of Kohn−Sham matrix elements involving diffuse basis functions leads to a negative HOMO eigenvalue in F^-, whereas it had previously been calculated to be positive.[22]

In many cases, the experimental electron affinity is negative rather than positive, as measured by electron transmission spectroscopy methods.[25,26] Such systems pose a fundamental problem; the anion is unstable with respect to electron loss and cannot be described by a standard DFT ground-state total energy calculation (or, indeed, a ground-state calculation from any electronic structure method). In practice, medium-sized basis set DFT calculations on the anion do give energies above that of the neutral species so reasonable estimates for the negative affinity can be obtained. However, this simply reflects an artificial binding of the electron by the finite basis set. The addition of more diffuse functions allows the electron to leave the system to dipole-bound or continuum states, and the anion energy becomes close to that of the neutral species; the electron affinity becomes near zero, and the hardness becomes $\sim I/2$. See refs 22 and 27−31 and references therein for further discussion. This basis set dependence makes eq 3 a less-attractive approach for calculating the hardness of a system with a significant negative experimental electron affinity, although it is often used in studies of chemical reactivity.

An alternative DFT approximation, originating from Koopmans' theorem,[32,33] is

$$\eta = \frac{\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}}{2} \tag{6}$$

where ϵ_{LUMO} and ϵ_{HOMO} are Kohn−Sham one-electron eigenvalues associated with the lowest unoccupied molecular orbital (LUMO) and the HOMO, respectively, from an approximate DFT calculation on the neutral species. Unless otherwise stated, we shall assume that all Kohn−Sham eigenvalues in the present study are associated with local exchange-correlation approximations, such as generalized gradient approximations (GGA). In the context of excitations, eq 6 then represents[34] the adiabatic time-dependent DFT (TDDFT) approximation to the CT excitation in eq 2. The expression is appealing as it is equally applicable to systems with positive and negative electron affinities and only requires a single Kohn−Sham calculation. However, it is well-known that it uniformly underestimates the hardness; for an example, see ref 31, where the underestimation is typically several electronvolts. Other methodologies to compute the chemical hardness have also been proposed. These have been reviewed in ref 6; more recent contributions include refs 35 and 36 and references therein.

In a recent study,[37] we demonstrated that the failure of local functional TDDFT to describe CT excitations between infinitely separated systems can be attributed to the influence of the integer discontinuity in the exact exchange-correlation potential. It follows that the same analysis explains the failure of the Koopmans approximation, eq 6 (TDDFT), to represent the exact hardness, eq 2 (CT). In section 2, we summarize the analysis and use it to highlight a simple correction to eq 6. The resulting hardness expression does not require the explicit computation of the electron affinity and has a simple interpretation in terms of the electronegativity. In section 3, the expression is used to calculate the hardness of 14 small molecules, which have increasingly negative experimental electron affinities. Results are compared with those determined using eqs 3 and 6, together with experimental values from eq 2. A scheme for computing negative electron affinities is highlighted. Conclusions are presented in section 4.

2. Theory

Using an ensemble treatment, Perdew et al.[38] have demonstrated that a plot of the exact electronic energy vs the number of electrons comprises a series of straight-line segments. The derivative discontinuities at integer N lead to integer discontinuities in the exact exchange-correlation potential. The exact potentials on the electron deficient and electron abundant sides of the integer, denoted v_{XC}^- and v_{XC}^+, respectively, differ by some system-dependent positive constant Δ_{XC} at all points in space

$$v_{\text{XC}}^+ - v_{\text{XC}}^- = \Delta_{\text{XC}} \tag{7}$$

where Δ_{XC} is typically on the order of several electronvolts for small, main-group molecules.[39,40] For experimental $I°$ and $A°$ values corresponding to the removal of an electron from the HOMO and the addition of an electron to the LUMO, respectively, it can be shown[38] that the HOMO eigenvalue associated with the exact v_{XC}^- is

$$\epsilon_{\text{HOMO}}^- = -I° \tag{8}$$

(this condition has been widely discussed; for example, see refs 40−47) and the LUMO eigenvalue associated with the exact v_{XC}^+ is

$$\epsilon_{\text{LUMO}}^+ = -A° \tag{9}$$

Equations 8 and 9 are exact DFT analogues of the original, approximate Koopmans theorem.[33] In the spirit of eq 6, the exact hardness, eq 2, is given by

$$\eta° = \frac{\epsilon_{\text{LUMO}}^+ - \epsilon_{\text{HOMO}}^-}{2} \tag{10}$$

Now, consider local exchange-correlation functionals such as GGA, which do not exhibit an integer discontinuity; they are continuum approximations. In regions where the HOMO and LUMO are located, they approximately average over the discontinuity[44,48]

$$v_{\text{XC}} \approx \frac{v_{\text{XC}}^+ + v_{\text{XC}}^-}{2} \tag{11}$$

although this breaks down at larger distances from the system.[49] It follows from eq 11 that the HOMO and LUMO eigenvalues from a local functional are approximately shifted from the exact values in eqs 8 and 9

$$\epsilon_{\mathrm{HOMO}} \approx \epsilon^{-}_{\mathrm{HOMO}} + \frac{\Delta_{\mathrm{XC}}}{2} \qquad (12)$$

$$\epsilon_{\mathrm{LUMO}} \approx \epsilon^{+}_{\mathrm{LUMO}} - \frac{\Delta_{\mathrm{XC}}}{2} \qquad (13)$$

and so do not satisfy the Koopmans relationships; see ref 40 for numerical examples of the former. Rearranging eqs 12 and 13 and substituting them into eq 10 gives

$$\eta^{\circ} \approx \frac{\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}}{2} + \frac{\Delta_{\mathrm{XC}}}{2} \qquad (14)$$

and so the Koopmans approximation, eq 6, underestimates the exact hardness by approximately half the integer discontinuity. This explains the systematic underestimation observed in ref 31. Following Chan,[39] the latter contribution in eq 14 can be termed a "hardness shift", highlighting the fact that a single Kohn−Sham calculation is not sufficient to determine the hardness (see, also, ref 50). Equation 14 is nothing more than a statement of the well-known band gap problem of local DFT[48,51] (e.g., see eq 10 of ref 48).

It is clear from eq 14 that an improved approximation to the hardness could be obtained if Δ_{XC} was known. This quantity can be approximated from correlated electron densities,[39,40] but this is not a practical way to go forward. A more appealing route is to use the fact that $\Delta_{\mathrm{XC}}/2$ is the exact asymptotic potential for a functional that averages over v^{+}_{XC} and v^{-}_{XC}. It is therefore approximately equal to the exact asymptotic potential, $v_{\mathrm{XC}}(\infty)$, of the local functional associated with the eigenvalues in eq 14, which in turn can be well approximated by[49]

$$v_{\mathrm{XC}}(\infty) \approx \epsilon_{\mathrm{HOMO}} + I \qquad (15)$$

where ϵ_{HOMO} and I are determined from the local functional calculations. Hence,

$$\frac{\Delta_{\mathrm{XC}}}{2} \approx \epsilon_{\mathrm{HOMO}} + I \qquad (16)$$

(this can also be derived by substituting eq 8 into eq 12 and setting $I^{\circ} \approx I$). Equation 16 can then be combined with eq 14 to give an alternative approximation for the hardness,

$$\eta = \frac{\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}}{2} + \epsilon_{\mathrm{HOMO}} + I \qquad (17)$$

The hardness can therefore be approximated as *half the HOMO−LUMO gap plus the near-exact local functional asymptotic potential*. Equation 17 has a simple interpretation in terms of the electronegativity. To see this, we rewrite it as

$$\eta = \frac{\epsilon_{\mathrm{LUMO}} + \epsilon_{\mathrm{HOMO}}}{2} + I \qquad (18)$$

Now, from eqs 8, 9, 12, and 13,

$$\frac{\epsilon_{\mathrm{LUMO}} + \epsilon_{\mathrm{HOMO}}}{2} \approx -\chi^{\circ} \qquad (19)$$

where χ° is the exact electronegativity,

$$\chi^{\circ} = \left(\frac{I^{\circ} + A^{\circ}}{2}\right) \qquad (20)$$

Hence, an alternative interpretation is that we *approximate the negative of the electronegativity as the average of the HOMO and LUMO eigenvalues and then add an approximate ionization potential to give an approximate hardness* (because $\eta^{\circ} = -\chi^{\circ} + I^{\circ}$). The key point is that the electronegativity can be approximated using eq 19 because taking the sum approximately cancels the contributions from Δ_{XC} in eqs 12 and 13; this has been known for some time, e.g., see ref 48.

Equation 17 or, equivalently, eq 18 is a hardness approximation that does not explicitly involve the electron affinity. It would therefore appear to be an attractive method for computing the hardness in systems with negative affinities, where the direct computation using eq 3 is problematic. Of course, such an application would strictly be a departure from the ground-state requirement because the negative affinity corresponds to an anion that is not in its ground state. In the next section, we use this expression to determine the hardness of a series of small molecules, comparing the results with those from the standard approaches in eqs 3 and 6, together with experimental values from eq 2.

3. Results and Discussion

We consider the following set of representative, neutral closed-shell molecules, containing first and second row atoms: F_2, Cl_2, H_2CO, C_2H_4, CO, PH_3, H_2S, HCN, HCl, CO_2, NH_3, HF, H_2O, and CH_4. The experimental electron affinity is positive for the first two molecules but becomes increasingly negative across the series. Where possible, calculations were performed at near-experimental reference geometries, taken from ref 52; for the molecules where no sufficiently accurate reference geometry was available, MP2/aug-cc-pVTZ geometries were instead used. We have confirmed that the results have little sensitivity to geometry; the same conclusions are obtained when optimized geometries are used. All hardness calculations were performed using the aug-cc-pVTZ basis set;[53] see later for further discussion. All calculations were performed using the CADPAC[54] program. Experimental values for the absolute hardness were determined using eq 2, with vertical ionization potentials and electron affinities from ref 55. Again, we stress the importance of using vertical quantities; many experimentally available ionization potentials and positive electron affinities are adiabatic rather than vertical.

We determined the hardness using eqs 3, 6, and 17, using four GGA functionals: PBE,[56] OLYP,[57,58] KT3,[59] and 1/4.[60] The eigenvalues, ionization potentials (calculated using eq 4), and electron affinities (calculated using eq 5) in the three expressions were all determined using the respective functionals. The variations in the results due to the choice of functional were minimal and were significantly smaller than the variations due to the different hardness expressions. The conclusions regarding the relative accuracy of the three hardness expressions are therefore not dependent on the choice of functional. For the present study, we present PBE results because this functional is widely available in electronic structure codes. (In practice, the best results from eq 17 were obtained using the 1/4 functional, which reflects the fact that this functional was determined with an emphasis on exchange-correlation potentials; however, the improvement over PBE is minimal and 1/4 is not a globally applicable nor widely available functional.)

Table 1 presents hardness values calculated using eqs 3, 6, and 17 with the PBE functional. The final column lists

TABLE 1: Hardness Values (eV), Determined Using the Three Approaches with the PBE Functional and the aug-cc-pVTZ Basis Set, Compared to Experimental Values Determined Using the Data in Reference 55[a]

molecule	eq 3 $\eta = (I - A)/2$	eq 6 $\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2$	eq 17 $\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2 + \epsilon_{HOMO} + I$	exptl: eq 2 $\eta° = (I° - A°)/2$
F_2	7.36	1.83	7.72	7.2
Cl_2	5.16	1.54	5.42	5.2
H_2CO	5.66	1.79	6.29	6.2
C_2H_4	5.58	2.84	6.74	6.2
CO	7.44	3.52	8.34	7.9
PH_3	5.44	3.05	6.84	6.2
H_2S	5.38	2.73	6.82	6.3
HCN	7.17	3.97	8.88	8.0
HCl	6.56	3.47	8.15	8.0
CO_2	7.20	4.10	8.69	8.8
NH_3	5.70	2.73	7.51	8.2
HF	8.39	4.34	11.01	11.1
H_2O	6.61	3.16	8.71	9.5
CH_4	7.22	4.55	9.06	10.7
d/eV	−1.3	−4.7	+0.1	
$\|d\|$/eV	+1.4	+4.7	+0.5	
m	+1.41	+1.48	+1.16	
c/eV	−1.30	+3.21	−1.31	
R^2	0.64	0.64	0.87	

[a] d and $|d|$ denote the mean and mean absolute errors, respectively, relative to experimental data. m, c, and R^2 denote the gradient, the intercept, and the correlation parameters, respectively, of the correlation plots, relative to experimental data.

TABLE 2: Ionization Potentials (I), Calculated Using Eq 4 with the aug-cc-pVTZ Basis Set, Compared to Experimental Values ($I°$)[a]

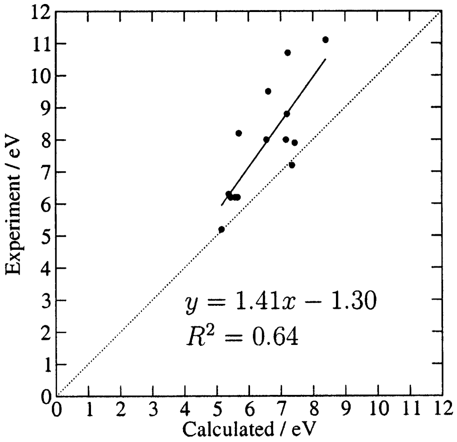
molecule	eq 4 I^b	$I°$	eq 5 A^b	eq 5 A^c	eq 22 A^b	$A°$
F_2	15.34	15.70	+0.63	−0.43	−0.10	+1.24
Cl_2	11.18	11.49	+0.87	+0.47	+0.34	+1.02
H_2CO	10.75	10.9	−0.58	−1.51	−1.84	−1.5
C_2H_4	10.66	10.68	−0.50	−2.46	−2.82	−1.8
CO	13.85	14.01	−1.02	−2.34	−2.82	−1.8
PH_3	10.52	10.59	−0.37	−2.59	−3.16	−1.9
H_2S	10.40	10.5	−0.37	−2.30	−3.24	−2.1
HCN	13.95	13.61	−0.38	−3.47	−3.81	−2.3
HCl	12.73	12.75	−0.39	−2.21	−3.58	−3.3
CO_2	13.67	13.77	−0.72	−3.31	−3.70	−3.8
NH_3	10.96	10.82	−0.44	−2.65	−4.06	−5.6
HF	16.32	16.12	−0.47	−2.91	−5.70	−6.0
H_2O	12.80	12.62	−0.42	−2.71	−4.62	−6.4
CH_4	13.97	13.6	−0.47	−2.75	−4.15	−7.8

[a] Also listed are the electron affinities calculated using the standard approach, eq 5, with the aug-cc-pVTZ and cc-pVTZ basis sets; the electron affinity calculated using eq 22 with the aug-cc-pVTZ basis; and the experimental electron affinity, $A°$. All calculated quantities were obtained using the PBE functional. All quantities are in eV. [b] Values were calculated using the aug-cc-pVTZ basis set. [c] Values were calculated using the cc-pVTZ basis set.

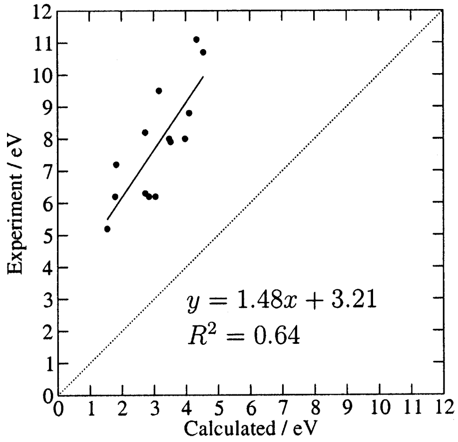
experimental values from eq 2. Mean and mean absolute errors, relative to experimental data, are denoted d and $|d|$, respectively. First, we consider the results from eq 3, which uses the calculated I and A values. The hardness is accurately reproduced for F_2 and Cl_2, both of which have positive electron affinities (as anticipated, the anion HOMO eigenvalues are positive in both cases). However, the results degrade as the table is descended, reflecting the increasingly negative experimental electron affinity. To quantify this, we list, in Table 2, the calculated and experimental ionization potentials and electron affinities, which are the components of the hardness. The first two columns of Table 2 compare the calculated and experimental ionization potentials. In all cases, the computation is of reasonable quality. The next column lists the calculated electron affinities, which should be compared to the experimental values in the final column. As the table is descended, the computed affinities degrade; they are not sufficiently negative. The hardness values in Table 1 become close to $I/2$, significantly underestimating experimental values, with a mean absolute error of 1.4 eV.

The second column of values in Table 1 lists the hardness determined using the Koopmans approximation, eq 6. (For all systems, the HOMO and LUMO eigenvalues are negative.) The hardness values are significantly and uniformly underestimated, reflecting the absence of the discontinuity term in eq 14. The mean absolute error is 4.7 eV. The third column of values in Table 1 is determined from eq 17, through the simple correction of the Koopmans values. The uniform underestimation is eliminated (the mean error is near zero), and the mean absolute error is significantly reduced to 0.5 eV. Admittedly, this error is larger than can be obtained from direct evaluation using eq 3 on systems with positive electron affinities, and this can be traced to the inherent approximations used in the derivation of eq 17. However, hardness values determined using this expression do not degrade as the table is descended; they are as accurate for systems near the bottom of the table as they are for F_2 and Cl_2.

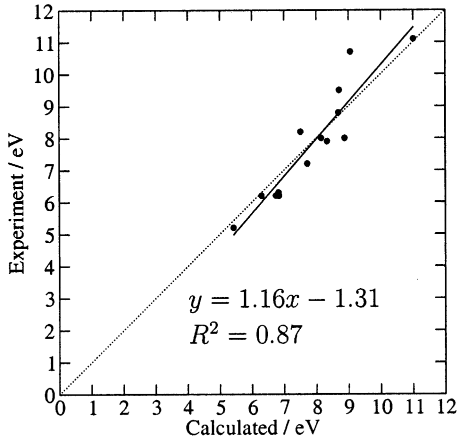
It is pertinent to comment on the basis set dependence of the results. The values in Table 1 were determined using the aug-cc-pVTZ basis set. As discussed in section 1, the calculation of electron affinities for systems with negative experimental values benefits from the use of compact basis sets to enhance the artificial binding of the electron. We have therefore also performed calculations using the more compact (nonaugmented) cc-pVTZ basis set. In line with the observations in refs 22, 27, 28, 30, and 31, the electron affinities of systems with negative experimental values do improve, although the errors remain very significant. The affinities are presented in Table 2. Ionization potentials determined using this smaller basis set barely change from the aug-cc-pVTZ values;[61] the typical change is less than 0.1 eV. It follows that the hardness values determined using eq 3 do improve, although the mean absolute error (0.8 eV) remains large. Even the moderate cc-pVTZ basis set is therefore not capable of sufficiently binding the electron in systems with large negative affinities. Furthermore, we observe that reducing the basis set in this manner reduces the accuracy of the affinity,



(a) Eqn. (3)



(b) Eqn. (6)



(c) Eqn. (17)

Figure 1. Correlation of the hardness, calculated using (a) eq 3, (b) eq 6, and (c) eq 17, with experimental values. Data are taken from Table 1.

and hence the hardness, of F_2 and Cl_2. The artificial improvement of systems lower in the table is therefore achieved at the expense of the systems at the top of the table. Hardness values determined using eq 17 are much less affected by the reduction in the basis set; the mean absolute error increases slightly to 0.6 eV. We have also performed calculations using a doubly augmented daug-cc-pVTZ basis set, which is obtained by augmenting the aug-cc-pVTZ basis set (used in Table 1) with additional diffuse functions, with exponents determined from the geometric progression. Hardness values from eq 17 are essentially identical to those of Table 1, demonstrating that basis set convergence is reached without the need for double augmentation. By contrast, the results from eq 3 are different from those of Table 1, which can be traced to the calculated electron affinities. For F_2 and Cl_2, the calculated affinities increase to approximately one electronvolt whereas for the remaining molecules the affinities are very close to zero. For five of the molecules, convergence problems prevented the computation of the anion energy, demonstrating the difficulty of using such diffuse basis sets for anion calculations.

In most applications, the hardness is used to discuss trends in chemical reactivity and stability. Thus, it is important that calculated values exhibit a good correlation with experimental values. To investigate this, we present, in Table 1, the line parameters m (gradient), c (intercept), and R^2 (square of the correlation coefficient) describing the correlation of the three hardness expressions with the experimental values. Calculations using the conventional approaches (eqs 3 and 6) have similar slopes ($m = +1.41$ to $+1.48$) and correlation parameters ($R^2 = 0.64$), which are far from unity. The intercept is particularly large ($c = +3.21$ eV) when eq 6 is used. The correlation is much better for the third approach, with an improved slope ($m = +1.16$) and correlation parameter ($R^2 = 0.87$). The improved correlation is clearly evident in Figure 1, which presents the correlation plots for the three methods.

It is informative to consider the two contributions in eq 17. In a previous study,[40] we determined near-exact HOMO−LUMO eigenvalue differences from high-quality, correlated electron densities using the Zhao−Morrison−Parr (ZMP) approach.[62] These were then subtracted from experimental $I - A$ values to calculate Δ_{XC}. These earlier calculations allow us to judge the accuracy of the two components of the hardness in eq 17. For a subset of 10 of the present 14 molecules, we compared the first and second terms in eq 17 with the corresponding reference values from ref 40. The mean absolute error for the first term (half of the HOMO−LUMO gap) is 0.3 eV, and the error for the second term (half of the discontinuity) is 0.6 eV. Errors in both terms are therefore significant, although that for the latter is larger.

Next, we comment on hybrid functionals. Our derivation of eq 17 assumed that the potential approximately averages over the discontinuity in the exact potential, which is appropriate for functionals such as GGA (and the local density approximation, LDA) but not for hybrids, which include a fraction of exact orbital exchange. Nevertheless, we have observed that the expression does still work reasonably well with hybrids, such as B3LYP.[58,63] The explanation lies in eq 18: HOMO eigenvalues from hybrids are more negative than those of GGAs, but there is a compensating increase in the LUMO eigenvalue, such that the sum is approximately equal to the GGA value, a reasonable approximation to minus the electronegativity. To quantify accuracy, we have determined hardness values, using eq 17 with the B3LYP functional, that have the following mean absolute errors and correlation parameters:

$$\begin{aligned} |d| &= 0.7 \text{ eV} \\ m &= +1.23 \\ c &= -1.52 \text{ eV} \\ R^2 &= 0.78 \end{aligned} \tag{21}$$

Although these results are more accurate than the corresponding

B3LYP values from eqs 3 and 6, they are still inferior to the third column of PBE results in Table 1 and are not recommended.

All the molecules in Table 1 are closed-shell, neutral species. We have also considered the closed-shell cations Li^+, Na^+, Be^{2+}, Mg^{2+}, B^{3+}, and Al^{3+}. For such systems, it is well known that eq 3 provides very accurate hardness estimates because one only needs to compute the higher ionization potentials of the neutral species and not the electron affinities.[61] For example, for B^{3+}, eq 3 is equivalent to subtracting the third and forth ionization potentials of the B atom. As anticipated, results from eq 17 are an improvement over the Koopmans values from eq 6 but are unable to compete with the direct evaluation using eq 3. We have also considered closed-shell anions. For such systems, the HOMO and LUMO eigenvalues tend to be positive and so the results exhibit an unacceptable sensitivity to the basis set. In future work, we shall investigate the hardness of open-shell molecules. Generalization of eq 17 will lead to spin-dependent hardness values.[39] The analogue of Koopmans' theorem with spin-polarized DFT for systems with an open-shell ground state has been discussed by Gritsenko et al.[64,65]

Explicit Computation of Negative Electron Affinities. The focus of this paper has been the evaluation of the hardness without the explicit computation of the electron affinity. This has been achieved by implicitly approximating the affinity in terms of the Kohn−Sham eigenvalues and the ionization potential. Specifically, eq 17 is exactly equivalent to a direct evaluation of the hardness using eq 3, with a conventional ionization potential but an electron affinity given by

$$A = -(\epsilon_{\mathrm{LUMO}} + \epsilon_{\mathrm{HOMO}}) - I \qquad (22)$$

This can be easily verified: substituting eq 22 into eq 3 gives eq 17. Equation 22 can also be derived from eqs 9, 13, and 16 (see, also, eq 19 of the present study and eq 11 of ref 48). The differences between the hardness values in the first and third columns of Table 1 can therefore be regarded as arising entirely because of the different electron affinity approximations. The former uses the standard evaluation, eq 5, and the latter uses eq 22; both use the ionization potential from eq 4. The improved hardness values from the latter approach simply reflect more accurate affinities, on average, from eq 22. To quantify this, we present, in Table 2, electron affinities determined using this expression with the aug-cc-pVTZ basis set; values using the daug-cc-pVTZ basis set are essentially identical. For systems with significant negative experimental affinities, the results are a notable improvement over both the aug-cc-pVTZ and cc-pVTZ results from eq 5. The new results exhibit a correlation parameter of 0.76, compared to values of 0.30 and 0.48 from the standard expression with the large and small basis sets, respectively. The computation of negative electron affinities is an important research area (e.g., see refs 29 and 30). Equation 22 may be useful for providing qualitative predictions in such studies, overcoming the fundamental basis set breakdown of the standard approach.

4. Conclusions

The calculation of the absolute hardness is an important aspect of conceptual DFT. The conventional approach, where the hardness is evaluated directly from computed DFT ionization potentials and electron affinities, works reasonably well for molecules with positive electron affinities (however, see refs 20−24). This direct approach is less appropriate for systems with a significant negative experimental electron affinity. In such cases, the extra electron is only bound in the DFT calculation by the finite basis set. For the systems in the lower part of Table 1, even the modest cc-pVTZ basis set is completely unable to provide quantitative estimates of the affinity. Enhancing the basis set with diffuse functions allows the electron to leave the system to dipole-bound or continuum states; so, the electron affinity becomes near zero, and the hardness is close to $I/2$.

Using an analysis based on earlier studies,[38,48] we have reiterated why an alternative approximation, based on Koopmans' theorem[33] using local functional eigenvalues, significantly underestimates the hardness. We have then used this analysis to highlight a hardness approximation that can be interpreted as a simple correction to the Koopmans expression (see eq 17) or as the addition of an approximate ionization potential to the negative of an approximate electronegativity (see eq 18 and the discussion below). Only the eigenvalues and the ionization potential from a local functional are required; the electron affinity does not need to be computed. The correction eliminates the uniform underestimation of the Koopmans expression. For the molecules in Table 1, the inherent approximations in the derivation lead to relatively large errors of 0.5 eV on average; however, the results do not degrade as the electron affinity becomes more negative, and the correlation with experimental values is good. For systems with large negative experimental electron affinities, the results are an improvement over those from the conventional approaches. The scheme may prove useful in conceptual DFT studies.

A third interpretation of the scheme is that it evaluates the hardness directly using eq 3, with a conventional approximate ionization potential from eq 4 but an unconventional electron affinity from eq 22. This unconventional electron affinity expression may be useful in studies of negative affinities, overcoming the fundamental basis set breakdown of the standard approach.

Finally, we reiterate the link between the present work and the calculation of the electronegativity, the direct calculation of which is also problematic when the affinity is negative. As indicated in eq 19, the discontinuity contributions approximately cancel for the electronegativity and so it can be approximated as minus the average of the HOMO and LUMO eigenvalues (which is equivalent to the addition of an approximate I to the affinity in eq 22). The accuracy of the electronegativity calculated in this manner will be close to that of the hardness in eq 17 because the two quantities differ only by the ionization potential, which can be calculated to good precision.

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