Evaluation of hardness in Kohn-Sham theory with local density and generalized gradient approximations

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By making use of Janak’s interpolation in the Kohn-Sham method, together with an explicit and differentiable functional of the density for the exchange-correlation energy, like LDA or GGA, the second derivative of the energy with respect to the number of electrons, $N$, is evaluated from the derivative of the highest occupied molecular orbital (HOMO) with respect to $N$ (left derivative), or from the derivative of the lowest unoccupied molecular orbital (LUMO) with respect to $N$ (right derivative). Both cases lead to expressions that may be evaluated from a single post-SCF calculation that avoids the use of the frontier orbitals eigenvalues. The results obtained for two test sets of molecules and for several atoms indicate that both provide a better description than the LUMO-HOMO eigenvalue difference and that the left derivative seems to lead to more confident results than the right derivative.

**Keywords:** Theoretical chemistry, Density functional calculations, Kohn-Sham theory, Chemical reactivity, Chemical potential, Hardness, Softness

The advances in electronic structure calculations in the last decades have been very important to get a better understanding of the behavior of physical, chemical and biological systems at the microscopic level. The development of methods to determine the many electron wavefunction, together with the advancement in computing capabilities, has made it possible to carry out electronic structure calculations of a wide variety of systems. The role played by the Kohn-Sham method of density functional theory (DFT) has been fundamental.\textsuperscript{1-6} Also, the development of tools to convert the complex information contained in the wavefunction into chemically significant information, has accompanied the growth in theoretical studies of electronic structure. In this aspect, the role played by density functional theory has also been very important.\textsuperscript{1,7-14}

The basis for chemical reactivity in density functional theory (CR-DFT) departs from the identification of the chemical potential ($\mu$) and the hardness ($\eta$) as the first\textsuperscript{15} and second\textsuperscript{16} derivatives of the energy ($E$) with respect to the number of electrons ($N$), at constant external potential ($V(\mathbf{r})$), that is,

$$\mu = \left( \frac{\partial E}{\partial N} \right)_V$$

and

$$\eta = \left( \frac{\partial^2 E}{\partial N^2} \right)_V = \left( \frac{\partial \mu}{\partial N} \right)_V$$

Electronegativity\textsuperscript{17-19} ($\chi$) is the negative of the chemical potential.\textsuperscript{15,19} Through these identifications, it has been possible to construct a language in chemistry,\textsuperscript{20} which involves global,\textsuperscript{15,16,21} local\textsuperscript{22-27} and non-local quantities.\textsuperscript{28,29} The global quantities provide information on the chemical reactivity of the molecule as a whole, while the local and non-local quantities provide information about site selectivity within a molecule. The contributions from Prof. Swapan K. Ghosh to the theoretical foundations of these concepts, in the early days of CR-DFT have been very important.\textsuperscript{24,25,30,31}

Now, it is relevant to mention that according to the grand canonical formulation for fractional $N$, the energy as a function of the number of electrons is given by a series of straight lines connecting the integer values of $N$.\textsuperscript{32-34} This situation implies that the first derivative from the left, $\mu_\ell$, is different from the first derivative from the right, $\mu_r$, and that the second derivative is zero when evaluated from the left or from the right, and it is not defined when $N$ is an integer. Thus, in the case of the chemical potential,\textsuperscript{35}
\[ \mu^-(N) = -I = E(N_0) - E(N_0 - 1) \]

for \( N_0 - 1 < N < N_0 \) \quad \text{and} \quad \mu^+(N) = -A = E(N_0 + 1) - E(N_0)

for \( N_0 < N < N_0 + 1 \)

where \( I \) is the vertical first ionization potential, \( A \) is the vertical electron affinity and \( N_0 \) is an integer. On the other hand, in the case of the hardness, due to the difficulties associated with the second derivative, one generally adopts the definition

\[ \eta = [E(N_0 - 1) - E(N_0)] - [E(N_0) - E(N_0 + 1)] \]

\[ = I - A \]

that may be also obtained from the derivative discontinuity, as the difference between the right and left derivatives, that is,

\[ \eta = \mu^+ - \mu^- \]

With respect to the definitions given by Eqs (1) and (2), the smooth interpolation for the energy between the \( N_0 - 1, N_0 \) and \( N_0 + 1 \) systems, through a second order Taylor series expansion, namely,

\[ \Delta E = \mu^0 \Delta N + \frac{1}{2} \mu^0 (\Delta N)^2 \]

leads, through a finite differences approach, to the relationships,

\[ \mu^0 = -(I + A) / 2 \]

and

\[ \eta^0 = I - A \]

where the superscript “0” is used to indicate that the first and second derivatives are evaluated at \( N = N_0 \).

Equations (8) and (9) have provided strong support to the interpretation of the first and second derivatives of the energy as the chemical potential (minus the electronegativity) and the hardness, because when one calculates these two quantities through them, one finds that they show, in general, the same trends of the qualitative scales originally developed by Pauling for \( \chi \) and by Pearson for \( \eta \). Equation (8) corresponds to the definition given by Mulliken for electronegativity. Also, Eq. (7) has proven to be a quite useful approximation to describe many aspects of charge transfer processes in molecules, underscoring the relevance of the chemical potential and the chemical hardness concepts, and the importance of their quantification to study the interaction between chemical species. 

Equation (8) is the average of the left and right derivatives of Eqs (3) and (4), while Eq. (9) is identical to Eq. (5), except that in Eq. (9) the quantity \( I - A \) is interpreted as an approximation to the second derivative.

Thus, from a theoretical perspective, the determination of \( \mu \) and \( \eta \) requires to calculate the first ionization potential and the electron affinity through an energy differences procedure, in which one needs to perform the calculation of the \( N_0 \) electron reference system with geometry optimization, and the calculations of the \( N_0 - 1 \) and the \( N_0 + 1 \) electron systems at the geometry of the \( N_0 \) electron reference system. In the case of the electron affinity, when the reference system is a neutral or a negatively charged species, the calculation of the anion, may present convergence problems. An alternative approach is to use Koopmans theorem, which for Hartee-Fock establishes that \( I = -\epsilon_h \) and \( A = -\epsilon_L \), where \( \epsilon_h \) and \( \epsilon_L \) are the eigenvalues of the highest occupied and lowest unoccupied molecular orbitals, respectively. Therefore, within this approximation, \( \mu = (\epsilon_h + \epsilon_L) / 2 \) and \( \eta = \epsilon_L - \epsilon_h \). An advantage of this procedure is that \( \epsilon_h \) and \( \epsilon_L \) are obtained from a single calculation. These expressions have also been used in Kohn-Sham DFT calculations. However, in this case there are several factors that need to be taken into account when dealing with an approximate expression of the exchange-correlation energy functional. This is true, particularly in the case of the hardness, because explicit and differentiable exchange-correlation energy functionals of the density, like the local density approximation (LDA) or the generalized gradient approximation (GGA), are known to underestimate the hardness when evaluated with the expression \( \eta = \epsilon_L - \epsilon_h \), since for these functionals the derivative discontinuity of the exchange-correlation potential is equal to zero. This perspective has been amply analyzed and several procedures have been proposed to incorporate the effects of the derivative discontinuity in calculations of the hardness.

The objective of this work is to analyze the evaluation of the hardness in Kohn-Sham theory and to derive an approximate expression that allows one
to estimate its value from a post-SCF calculation which avoids the use of the frontier orbitals eigenvalues.

**Chemical Potential and Hardness in Kohn-Sham Theory**

The total energy in the spin polarized version of Kohn-Sham DFT, for an $N$ electron system with $N_{\alpha}$ and $N_{\beta}$ electrons with spin $\alpha$ and $\beta$, such that $N = N_{\alpha} + N_{\beta}$, is given by Eq. (10),

$$E[\rho_{\alpha}, \rho_{\beta}] = T_{S}[\rho_{\alpha}, \rho_{\beta}] + J[\rho] + E_{XC}[\rho_{\alpha}, \rho_{\beta}] + \int dr \rho(r) v(r)$$  

... (10)

where $\rho_{\alpha}(r)$ and $\rho_{\beta}(r)$ are the electron densities of the $\alpha$ and $\beta$ spin electrons, respectively, $\rho(r) = \rho_{\alpha}(r) + \rho_{\beta}(r)$ is the total electron density, $T_{S}[\rho_{\alpha}, \rho_{\beta}]$ is the non-interacting kinetic energy functional, $J[\rho] = \int \int dr \, \rho(r) \rho(r')/|r-r'|$ is the Coulomb energy and $E_{XC}[\rho_{\alpha}, \rho_{\beta}]$ is the exchange-correlation energy functional. In terms of the KS spin-orbitals, $\psi_{\sigma,i}(r)$, the total electron density is given by Eq. (11),

$$\rho(r) = \sum_{\sigma=\alpha, \beta} \rho_{\sigma}(r) = \sum_{\sigma=\alpha, \beta} \sum_{i=1}^{N_{\sigma}} n_{\sigma,i} \psi_{\sigma,i}^{*}(r) \psi_{\sigma,i}(r)$$

$$= \sum_{\sigma=\alpha, \beta} \sum_{i=1}^{N_{\sigma}} n_{\sigma,i} \rho_{\sigma,i}(r)$$

... (11)

while the non-interacting kinetic energy is given by Eq. (12),

$$T_{S}[\rho_{\alpha}, \rho_{\beta}] = \sum_{\sigma=\alpha, \beta} \sum_{i=1}^{N_{\sigma}} n_{\sigma,i} \int dr \psi_{\sigma,i}^{*}(r) (-\frac{1}{2} \nabla^{2}) \psi_{\sigma,i}(r)$$

... (12)

where $n_{\sigma,i}$ are the occupation numbers such that $\sum_{i=1}^{N_{\sigma}} n_{\sigma,i} = N_{\sigma}$.

The minimization of the total energy with respect to the spin-orbitals, subject to the orthonormality constraints, leads to the KS self-consistent equations, i. e., Eq. (13),

$$\begin{pmatrix}
-\frac{1}{2} \nabla^{2} + v(r) \\
+ \int dr' \rho(r')/|r-r'| \\
+ v_{XC}(r)
\end{pmatrix} \psi_{\sigma,i}(r) = \epsilon_{\sigma,i} \psi_{\sigma,i}(r)$$

... (13)

where $v_{XC}(r) = \delta E_{XC} [\rho_{\alpha}, \rho_{\beta}]/\delta \rho_{\sigma}(r)$  

... (14)

is the exchange-correlation potential. In Eqs (11) and (12), the sum over $i$ goes over the lowest $N_{\alpha}$ and the lowest $N_{\beta}$ solutions of Eqs (11). For the exact $E_{XC}[\rho_{\alpha}, \rho_{\beta}]$, the self-consistent solutions of Eq. (13), with $n_{\sigma,i} = 1$ for all the occupied spin orbitals and $n_{\sigma,i} = 0$ for all the unoccupied ones, leads to the exact ground-state electronic density of the system, from which one can determine the exact ground state energy.

Janak$^{34}$ has shown that a suitable generalization of the theory can be constructed by allowing the occupation numbers to adopt non-integral values. Thus, one can make a continuous connection between the ground-state energies of the $N_{0}$ and $N_{0}+1$ electron system, by gradually increasing, from zero to one, the occupation number of the lowest unoccupied level of the $N_{0}$ electron system, or one can make a continuous connection between the ground state energies of the $N_{0}$ and the $N_{0} - 1$ electron system, by gradually decreasing, from one to zero, the occupation number of the highest occupied level of the $N_{0}$ electron system. Additionally, Janak showed that for continuous occupation numbers, and allowing the orbitals to relax, $\partial E/\partial n_{\sigma,i} = \epsilon_{\sigma,i}$.

Therefore, by recognizing that a change in the number of electrons corresponds, in this approach, to a change in the occupation of one of the frontier orbitals, then, for the left derivative,

$$\mu^{-} = \epsilon_{H}$$

... (15)

and for the right derivative,

$$\mu^{+} = \epsilon_{L}$$

... (16)

Although these relationships seem to be identical to the KS expressions for the exact exchange-correlation functional, there are important differences. In the case of the exact KS theory,$^{35}$ $\mu_{KS} = \epsilon_{H} = -I$, for any
average electron number between \( N-1 \) and \( N \), while \( \mu_{KS} = \varepsilon_L + \Delta_{XC} = -A \), for any average electron number between \( N \) and \( N+1 \) (\( \Delta_{XC} \) represents the discontinuity of the exchange-correlation potential), so that in this case the hardness, according to Eq. (6), is given by \( \eta = \varepsilon_L - \varepsilon_H + \Delta_{XC} \). This means that the exact exchange-correlation energy functional cannot be an explicit and differentiable functional of the density, a condition that has been implicitly assumed in the derivation of Eqs (15) and (16), as it has been shown by Yang and collaborators \(^{38} \) through an analysis based on the potential functional formulation.

Equations (15) and (16), in the case of the approximate interpolation of Janak, may be used to estimate the hardness from \( \eta = (\partial \mu / \partial N) \), Eq. (2), because in this theoretical framework the frontier orbital energies are also continuous functions of the occupation numbers. Therefore, multiplying Eq. (13) by \( \psi_{\sigma,i}(r) \), integrating over \( r \), and taking the derivative with respect to \( n_{\sigma,i} \), one can show that, for the left derivative,

\[
\eta^- = \int dr \, dr' \rho_h(r) f^-(r') / |r - r'|
\]

\[
+ \int dr \, dr' \rho_h(r) f^-(r') \left( \frac{\delta^2 E_{XC}[\rho_a,\rho_\beta]}{\delta \rho_\sigma(r') \delta \rho_\sigma(r)} \right)
\]

... (17)

while for the right derivative,

\[
\eta^+ = \int dr \, dr' \rho_L(r) f^+(r') / |r - r'|
\]

\[
+ \int dr \, dr' \rho_L(r) f^+(r') \left( \frac{\delta^2 E_{XC}[\rho_a,\rho_\beta]}{\delta \rho_\sigma(r') \delta \rho_\sigma(r)} \right)
\]

... (18)

where \( \rho_h(r) = \psi_h^*(r) \psi_h(r) \) and \( \rho_L(r) = \psi_L^*(r) \psi_L(r) \) are the charge densities associated with the HOMO and the LUMO, and \( f^-(r) = (\partial \rho(r) / \partial N)^- \) and \( f^+(r) = (\partial \rho(r) / \partial N)^+ \) are the left and right Fukui functions.\(^{22} \)

The calculation of these quantities, when one includes the relaxation effects associated with the addition or removal of charge, through a finite differences approximation, implies that one needs to calculate, in addition to the \( N_0 \) electron system, the \( N_0-1 \) and the \( N_0+1 \) electron systems. Thus, in order to estimate the hardness from a single calculation, one can make use of Eq. (11) to calculate the directional derivatives of the density with respect to \( N \), through the derivative with respect to the occupation of the corresponding frontier orbital \(^{27,35} (n_i) \), and neglect the relaxation effects on the orbitals associated with the changes in \( n_i \), so that the left and right Fukui functions are approximated by \( \rho_h(r) \) and \( \rho_L(r) \), respectively. Accordingly, from Eqs (17) and (18) one finds that,

\[
\eta^- = \int dr \, dr' \rho_h(r) \rho_h(r') / |r - r'|
\]

\[
+ \int dr \, dr' \rho_h(r) \rho_h(r') \left( \frac{\delta^2 E_{XC}[\rho_a,\rho_\beta]}{\delta \rho_\sigma(r') \delta \rho_\sigma(r)} \right)
\]

... (19)

and

\[
\eta^+ = \int dr \, dr' \rho_L(r) \rho_L(r') / |r - r'|
\]

\[
+ \int dr \, dr' \rho_L(r) \rho_L(r') \left( \frac{\delta^2 E_{XC}[\rho_a,\rho_\beta]}{\delta \rho_\sigma(r') \delta \rho_\sigma(r)} \right)
\]

... (20)

Hence, the hardness may be estimated from each one of these two equations or from their average.

\[
\eta^0 = \frac{1}{2} \left( \eta^- + \eta^+ \right)
\]

... (21)

The second functional derivatives are to be taken with respect to the spin density that corresponds to the spin of the HOMO or LUMO, respectively.

Therefore, through this procedure one needs to perform the calculation of the reference system with \( N_0 \) electrons, and the hardness may be estimated from Eqs (19) – (21) in a post-SCF calculation, which do not depend on the frontier orbital eigenvalues.

It is important to note that even though the exchange-correlation energy functional has been assumed to be an explicit and differentiable functional of the density, and that as a consequence of this approximation \( \Delta_{XC} \) is equal to zero, the expressions given by Eqs (15) and (16) indicate that the left and right first derivatives of the energy with respect to \( N \) are different, so that the hardness as defined by Eq. (6) is given by \( \eta = \varepsilon_L - \varepsilon_H \). That is, these functionals do lead to a discontinuity of the first derivative with respect to \( N \), but the hardness thus obtained is largely underestimated with respect to...
the values obtained from the experimental values of \( I \) and \( A \), or from the energy differences (Eq. (5)) obtained from total energies calculated with the same type of functionals. However, since by the present approach, based on Janak’s interpolation, each of the first left and right derivatives is also a continuous function of the number of electrons, one can calculate separately the second derivative for each case, and associate it to the concept of hardness through the identification given by Eq. (2). Thus, the three expressions given by Eqs (19)–(21) are each one of them a different approximation to the hardness as a consequence of the discontinuity of the first derivative for this type of functionals, and they provide an alternative approach to estimate this property without using the HOMO and LUMO eigenvalues.

Results and Discussion

In order to evaluate the hardness through the procedure described in the previous section, we made use of the density functional deMon2k computational package.\(^{56,57}\) All calculations were carried out at the spin-polarized level (unrestricted KS). We carried out calculations with several exchange-correlation energy functionals and with different basis sets, in order to analyze the sensitivity of the values of the integrals in Eqs (19) and (20) with respect to them.

The exchange-correlation functionals considered were LDA,\(^ {58,59}\) PBE,\(^ {60}\) BLYP\(^ {61,62}\) and PW91.\(^ {63}\) Selecting these functionals allows one to cover the main differences in the behavior of the enhancement function of the GGA exchange energy functional as a function of the reduced density gradient \( s(\mathbf{r}) = |\nabla \rho(\mathbf{r})| / [(2 \pi^2)^{1/3} \rho^{4/3}(\mathbf{r})] \). The three enhancement functions have a value of 1 at \( s = 0 \). However, as \( s \) grows, PBE grows to reach a limiting value associated with the local Lieb-Oxford bound\(^ {64}\) and when \( s \to \infty \), PW91 grows up to a maximum that is also associated with the local Lieb-Oxford bound and then decays to zero as \( s \to \infty \), while the Becke exchange functional of BLYP diverges in this limit. Thus, although the three functionals have, grossly, a similar behavior in the interval \( 0 \leq s \leq 3 \), which is very important for the total energy, they show a rather different behavior as \( s \) grows.

The basis set used were DZVP,\(^ {65}\) TZVP\(^ {66,67}\) and DZ-ANO\(^ {68}\) in combination with a GEN-A2* auxiliary basis set.\(^ {69}\) The molecular calculations were carried out at the experimental geometry.

The first integral that appears in Eqs (19) and (20), is evaluated using the same technique that it is implemented in this computational package for Coulomb-type integrals. For the second integral, which involves the second functional derivative of the exchange-correlation functional, we made use of finite differences expansions of the form

\[
E_{xc}[\rho_a + \lambda \rho_s, \rho_s] = E_{xc}[\rho_a, \rho_s] + \lambda \int dr \rho_s(\mathbf{r}) \frac{\delta E_{xc}[\rho_a, \rho_s]}{\delta \rho_s(\mathbf{r})} + \frac{1}{2} \lambda^2 \int d\mathbf{r} d\mathbf{r}' \rho_s(\mathbf{r}) \rho_s(\mathbf{r}') \frac{\delta^2 E_{xc}[\rho_a, \rho_s]}{\delta \rho_s(\mathbf{r}) \delta \rho_s(\mathbf{r})}
\]

which, when evaluated at three values of lambda, namely \( -\lambda, 0 \) and \( \lambda \), leads to a three point formula for the second derivative,

\[
\frac{\delta^2 E_{xc}[\rho_a, \rho_s]}{\delta \rho_s(\mathbf{r})} = (E_{xc}[\rho_a + \lambda \rho_s, \rho_s] + E_{xc}[\rho_a - \lambda \rho_s, \rho_s] - 2 E_{xc}[\rho_a, \rho_s]) / \lambda^2
\]

The basis set used were DZVP,\(^ {65}\) TZVP\(^ {66,67}\) and DZ-ANO\(^ {68}\) in combination with a GEN-A2* auxiliary basis set.\(^ {69}\) The molecular calculations were carried out at the experimental geometry.
that all these values are lower than 1 eV, together with the fact that the values in each column are close to each other, implies that the variations in the values of the hardness obtained from Eqs (19)–(21), with respect to the GGA functional used are rather small.

Table 3 shows the RMS of the differences between the value obtained for the given basis set and the values obtained with the DZVP basis set. The calculations were done with the PBE exchange-correlation energy functional and \( \lambda = 0.001 \). The fact that all these values are rather small, together with the fact that the values in each column are close to each other, implies in this case, that the variations in the values of the hardness obtained from Eqs (19)–(21), with respect to the basis set are practically negligible.

Hence, in Table 4 we present the results obtained for the PBE functional with the DZVP basis set and \( \lambda = 0.001 \), for \( \eta^+ \), \( \eta^- \) and \( \eta^0 \) determined from Eqs (19)–(21), the results obtained from the eigenvalues difference, \( \epsilon_I - \epsilon_A \), the results provided by Eq. (5) with the energy differences to calculate the ionization potential and the electron affinity determined from the calculation of the cation and the anion, respectively, and the results corresponding to the difference between the experimental values of \( I \) and \( A \). One can note that the mean absolute error (MAE) with respect to \( I - A \), when this quantity is evaluated with the experimental values is very large for the eigenvalues difference, while it lies between approximately 1.5 and 2.6 eV for Eqs (19)–(21). On the other hand, the MAE with respect to the calculated vertical energy differences determined with the PBE functional and the DZVP basis set lies between 0.6 and 1.2 eV for Eqs (19)–(21) and it is also rather large for the eigenvalues difference. Thus, although \( \eta^0 \) provides a slightly better description than \( \eta^+ \), in both cases it may be considered that Eqs (19) and (20) separately, and their average Eq. (21), provide a good description for the test set considered in this work, much better than the direct eigenvalue difference.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \epsilon_I - \epsilon_A ) (eV)</th>
<th>( \eta^+ ) (eV)</th>
<th>( \eta^- ) (eV)</th>
<th>( \eta^0 ) (eV)</th>
<th>MAE1a (eV)</th>
<th>MAE2b (eV)</th>
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<td>12.92</td>
<td>9.40</td>
<td>9.40</td>
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<td>13.17</td>
<td>11.54</td>
<td>9.61</td>
<td>9.70</td>
</tr>
<tr>
<td>CH3</td>
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<td>9.62</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>10.01</td>
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<td>7.80</td>
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Table 4.—Comparison of the hardness values obtained from Eqs (19)–(21) with the values obtained from the eigenvalues difference, with the values obtained from Eq. (5) through energy differences (calculated) and through the experimental values of \( I \) and \( A \), for the PBE exchange-correlation energy functional, with the DZVP basis set and \( \lambda = 0.001 \).

Table 1.—RMS deviation (eV) of the exchange integral given by Eq. (23) as a function of \( \lambda \) with respect to the values for \( \lambda = 0.001 \) for the set of sixteen molecules described in the text for the PBE exchange-correlation energy functional and the DZVP basis set.

<table>
<thead>
<tr>
<th>( \lambda ) (eV)</th>
<th>( \eta^+ ) (eV)</th>
<th>( \eta^- ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>4.64E-01</td>
<td>1.02E-01</td>
</tr>
<tr>
<td>0.500</td>
<td>3.21E-01</td>
<td>1.97E-02</td>
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<td>0.100</td>
<td>6.13E-02</td>
<td>7.60E-04</td>
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<tr>
<td>0.010</td>
<td>2.38E-03</td>
<td>7.47E-06</td>
</tr>
<tr>
<td>0.001</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
</tbody>
</table>

Table 2.—RMS deviation (eV) of the hardness values obtained from Eqs (19)–(21) with different GGA functionals with respect to the values for LDA for the set of sixteen molecules described in the text for the basis set DZVP and \( \lambda = 0.001 \).

<table>
<thead>
<tr>
<th>Functional</th>
<th>( \eta^+ ) (eV)</th>
<th>( \eta^- ) (eV)</th>
<th>( \eta^0 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>0.73</td>
<td>0.15</td>
<td>0.42</td>
</tr>
<tr>
<td>BLYP</td>
<td>0.51</td>
<td>0.12</td>
<td>0.29</td>
</tr>
<tr>
<td>PW91</td>
<td>0.74</td>
<td>0.54</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Table 3.—RMS deviation (eV) of the hardness values obtained from Eqs (19)–(21) with different basis sets with respect to the values for the DZVP basis set for the set of sixteen molecules described in the text for the PBE exchange-correlation energy functional and \( \lambda = 0.001 \).

<table>
<thead>
<tr>
<th>Basis</th>
<th>( \eta^+ ) (eV)</th>
<th>( \eta^- ) (eV)</th>
<th>( \eta^0 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TZVP</td>
<td>0.17</td>
<td>0.07</td>
<td>0.11</td>
</tr>
<tr>
<td>DZ-ANO</td>
<td>0.35</td>
<td>0.10</td>
<td>0.22</td>
</tr>
</tbody>
</table>

\( ^a \)Mean absolute error with respect to the experimental values.

\( ^b \)Mean absolute error with respect to the calculated energy differences.
As an additional test, in Table 5 we present the results for a test set conformed by fourteen closed shell molecules. In this case we only present the comparison with energy differences, because the experimental electron affinities are not well established. One can see again that the eigenvalues difference leads to a poor description, and that for this test set $\eta^-$ is better than $\eta^+$ by almost a factor of three. We believe that these discrepancies between $\eta^-$ and $\eta^+$ are related to the use of the LUMO for $\eta^+$ (Eq. (20)), versus the use of the HOMO for $\eta^-$ (Eq. (19)). In general, we have found that calculations with the HOMO are more stable and provide more confident results.

Finally, in Fig. 1 we present the plot of the hardness determined from $\eta^-$, Eq. (19), for the neutral atoms with $1 \leq Z \leq 36$. In these cases, there were numerical instabilities for Li, Na and K for $\eta^+$, and the general description was rather poor, indicating that a more detailed numerical study for the integral with $\rho_i(r)$ is required. The numerical instabilities may probably be associated with the asymptotic behavior of this orbital. However, the general trends predicted by $\eta^-$ are rather good, with a MAE with respect to the hardness calculated from the experimental values of $I^1$ and $A^2$ of 1.54 eV.

**Table 5—Comparison of the hardness values obtained from Eqs (19)–(21) with the values obtained from the eigenvalues difference and with the values obtained from Eq. (5) through energy differences (calculated), for the PBE exchange-correlation energy functional, with the DZVP basis set and $\lambda = 0.001$**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\epsilon_L - \epsilon_H$</th>
<th>$\eta^+$</th>
<th>$\eta^-$</th>
<th>$\eta^0$</th>
<th>$(I-A)_{calc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_2$</td>
<td>3.59</td>
<td>17.93</td>
<td>16.67</td>
<td>17.30</td>
<td>15.59</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>3.02</td>
<td>10.01</td>
<td>10.01</td>
<td>10.01</td>
<td>10.90</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>3.61</td>
<td>11.60</td>
<td>14.07</td>
<td>12.83</td>
<td>12.25</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>5.69</td>
<td>9.48</td>
<td>11.32</td>
<td>10.40</td>
<td>13.09</td>
</tr>
<tr>
<td>CO</td>
<td>7.02</td>
<td>11.82</td>
<td>14.47</td>
<td>13.14</td>
<td>16.26</td>
</tr>
<tr>
<td>PH$_3$</td>
<td>6.75</td>
<td>7.38</td>
<td>10.54</td>
<td>8.96</td>
<td>13.58</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>5.92</td>
<td>8.33</td>
<td>11.55</td>
<td>9.94</td>
<td>13.46</td>
</tr>
<tr>
<td>HCN</td>
<td>6.27</td>
<td>11.11</td>
<td>12.76</td>
<td>11.93</td>
<td>14.80</td>
</tr>
<tr>
<td>HCl</td>
<td>7.63</td>
<td>8.66</td>
<td>13.18</td>
<td>10.92</td>
<td>15.90</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>8.77</td>
<td>11.92</td>
<td>12.92</td>
<td>12.42</td>
<td>17.66</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>7.31</td>
<td>6.85</td>
<td>15.81</td>
<td>11.33</td>
<td>15.28</td>
</tr>
<tr>
<td>HF</td>
<td>10.09</td>
<td>6.69</td>
<td>22.00</td>
<td>14.34</td>
<td>20.72</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>7.93</td>
<td>7.57</td>
<td>18.54</td>
<td>13.06</td>
<td>17.01</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>11.01</td>
<td>6.37</td>
<td>12.38</td>
<td>9.38</td>
<td>18.26</td>
</tr>
<tr>
<td>MAE$^*$</td>
<td>8.58</td>
<td>5.98</td>
<td>2.22</td>
<td>3.81</td>
<td></td>
</tr>
</tbody>
</table>

$^*$Mean absolute error with respect to calculated energy differences.

![Fig. 1 — Comparison of the hardness values obtained from Eq. (19), $\eta^-$ (dashed line), with the values obtained from Eq. (5) through the experimental values of $I$ and $A$ (continuous line), for the PBE exchange-correlation energy functional, with the DZVP basis set and $\lambda = 0.001$. The mean average error with respect to the experimental value is 1.54 eV.](image-url)
integer values of \( N \), as Eqs (15) and (16) show, and in fact, it is this discontinuity which led to three expressions for the hardness, Eqs (19)–(21). However, this discontinuity severely underestimates the experimental hardness and the one calculated through energy differences according to Eq. (5), because it predicts that \( \Delta_{xc} \) is equal to zero.

On the other hand, the fact that \( \Delta_{xc} \) is equal to zero also implies that in the SCF equations, the left and right exchange-correlation potentials for this type of functionals are equal, so that the frontier orbitals and the second derivative of the exchange-correlation energy thus determined do not have the influence of this contribution. Nevertheless, it seems that its impact in the evaluation of the integrals given by Eqs (19)–(21) is smaller, because the estimation of the hardness is better than when using the HOMO and LUMO eigenvalues.

The overall situation indicates that the present approach may be a useful procedure to estimate the hardness of chemical species without using the frontier eigenvalues of LDA or GGA calculations. However, although the left derivative given by Eq. (19) seems to provide a reasonable description, it is important to analyze and to improve upon the possible numerical instabilities associated with the right derivative, to obtain a more complete description of this important property.

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References
