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The Study of Redox Reactions on the Basis of Conceptual DFT Principles: EEM and Vertical Quantities

Jan Moens,[†] Pablo Jaque,[†,‡] Frank De Proft,[†] and Paul Geerlings*[,†]

Eenheid Algemene Chemie, Faculteit Wetenschappen, Vrije Universiteit Brussel (VUB), Pleinlaan 2, Brussels, Belgium, and Laboratorio de Química Teórica Computacional (QTC), Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile

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In this article, two new approaches are introduced which describe redox reactions through descriptors defined within the field of conceptual density functional theory (DFT). One approach starts with the grand canonical ensemble DFT from which a formula is derived for the chemical potential of the electrode in terms of intrinsic properties of oxidized and reduced states of the electroactive species. Second, starting from a Born−Haber scheme, the redox potential is solely expressed in terms of the vertical electron affinity and ionization potential of oxidized and reduced species, respectively. A large collection of 44 organic and inorganic systems are studied in different solvents including implicit and explicit solvation models. Both strategies seem well capable of reproducing experimental values of redox potentials.

1. Introduction

Density functional theory (DFT) is based on the dependence of the energy on the electron density $\rho(\underline{r})$ of the atomic or molecular system.[1] Since this property determines the number of electrons N and the external potential $\nu(\underline{r})$ exerted by the nuclei, the features of the molecular system are characterized by its $\rho(\underline{r})$. From its introduction in the early 1960s on, DFT has shown to be a powerful interpretative and computational tool in many fields of chemistry. Moreover, several intuitive chemical concepts, for example, electronegativity and chemical hardness, received a firm theoretical foundation in the conceptual DFT context.[2,3] In conceptual DFT, reactive indices find their origin as measures of a system's energy change when it is subject to a perturbation in its number of electrons or external potential. The cornerstone of conceptual DFT was laid by Parr et al.[4] with the identification of the electronic chemical potential $\mu = [(\partial E)/(\partial N)]_{\nu(\underline{r})}$ as the Lagrangian multiplier in the Euler equation. From this point on, higher order derivatives such as the chemical hardness η,[5] the Fukui function $f(\underline{r})$,[6,7] the dual descriptor $\Delta f(\underline{r})$,[8] and so forth were derived and applied to different chemical reactivity problems. A comment on the application and value of higher order indices is recently given by Geerlings and De Proft.[9] The application of these descriptors has proven to be a valuable tool to gain insight in many organic and inorganic reactions in gas and condensed phase. Maybe unexpectedly, these DFT descriptors are only recently emerging in the field of redox chemistry. Since redox reactions are the textbook examples of electron-transfer processes, their description in the framework of conceptual DFT seems a logic and valuable next step. Previous work in this field was mainly concentrated on the application of the electrophilicity[10,11] for the description of one electron-transfer process and multi-electron-transfer processes.[12,13] However, it functioned merely as a qualitative estimate of the redox potential taking solely the properties of the oxidized species into account. In a recent paper by the present contributors,[13] the local philicity concept[14] helped to identify the reactive regions during the electron uptake process by triply charged transition metal ions. Accurate calculation of redox potential values is in the field of theoretical electrochemistry mainly dominated by the Born−Haber approach. This methodology links the process in the gas phase to solution through the solvation energy of the oxidized and reduced species.[15–23] Other strategies emerge from a Car−Parrinello molecular dynamics (CPMD) approach such as the grand canonical titration method,[24–26] the constrained MD method,[27] and the thermodynamic integration method.[28] These methods enforce reduced species to be oxidized by modulating, respectively, the electronic chemical potential μ, a suitable order parameter at constant μ, or a coupling parameter. Some accurate predictions of redox potential values can be achieve but at a rather high computational cost. The focus of this work is to examine two other possible pathways to result in an at least approximate determination of the redox potential.

Our first approach is founded within the grand canonical ensemble theory. By minimizing the grand potential Ω, a formula is derived for the chemical potential of the electrode composed of the chemical potentials of oxidized and reduced species. This result is analogous to the electronegativity equalization method (EEM). The principle behind this method, originally formulated by Sanderson, states that when a molecule is formed, the electronegativity of its constituent atoms becomes equal, reaching an averaged value.[29,30] From the late 1980s on, this principle enabled Mortier and co-workers[31–35] to calculate charge distribution in a cheap way, and its refinements are still attracting much interest in recent literature also by some of the present authors.[36,37]

The second approach uses a thermodynamic cycle separating reorganization terms and electronic transitions within the linear response approximation stated by Marcus.[38,39] A simple formula composed of the vertical quantities of oxidized and reduced species is derived.

The two approaches converge in the particular case that the oxidized and reduced species have the same chemical hardness.

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* To whom correspondence should be addressed. E-mail: pgeerlin@vub.ac.be; phone: +32-2-629-3314; fax: +32-2-629-3317.

[†] Vrije Universiteit Brussel.

[‡] Pontificia Universidad Católica de Chile.

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The performance of both methods will be checked as an estimate of the reorganization energy. Organic and inorganic systems are subjects of this research embedded in different kind of solvents described by implicit and explicit/implicit solvation models. This large structurally unrelated group of molecules should prove the significance of the introduced approaches. Moreover, different kinds of charged systems, that is, neutral molecules, cations, as well as anions, are considered in aqueous solution and acetonitrile.

This paper is organized as follows. After the introduction, the theoretical background based on the grand canonical ensemble theory is treated and applied to the particular case of one-electron half-reactions (Ox + e^- $\rightleftharpoons$ Red). This is followed by the second approach which will define the redox potential in terms of the vertical electron affinities and ionization potentials within the Marcus theory. In part 3, the methodology is discussed followed by the results in part 4. Conclusions will be drawn in part 5.

2. Theoretical Background

2.1. The Electronegativity Equalization Method (EEM). An open system with a fluctuating number of particles is described in quantum mechanics not by a pure state but through a statistical mixture or ensemble. Within the grand canonical ensemble, a large collection of pure states is in equilibrium with an external reservoir of electrons at a fixed chemical potential μ. The individual states of the ensemble are capable of exchanging electrons and energy when μ is altered whereas the external potential $\nu(\underline{r})$ and temperature are kept constant. The chemical environment of the oxidized and reduced species is simulated by this external reservoir at constant chemical potential which we will call $\mu_{\text{electrode}}$. This reservoir is analogous to the electrode in experimental electrochemistry. Within a CPMD approach, this quantity is used as a thermodynamic control parameter to govern reduction and oxidation on the basis of a grand canonical DFT approach.[24] As was pointed out by Gázquez et al.,[40] this chemical potential can be seen as a property of a bath of electrons, it is linearly proportional to the chemical potential of the chemical species, and it drives the flow of electrons. The grand canonical ensemble is characterized by the grand potential Ω that within the finite-temperature grand canonical ensemble theory is expressed as

$$\Omega[\rho(\underline{r})] = A[\rho(\underline{r})] - \mu_{\text{electrode}}N \qquad (1)$$

in which $A[\rho(\underline{r})]$ is the Helmholtz free energy functional.[41]

The equilibrium point in the grand potential Ω will be achieved when the first derivative of the grand potential with respect to the number of exchanged electrons is vanished.

$$\left(\frac{\partial \Omega}{\partial N}\right)_{T,\,\nu(\underline{r})} = \left(\frac{\partial A[\rho(\underline{r})]}{\partial N}\right)_{T,\,\nu(\underline{r})} - \mu_{\text{electrode}} = 0 \qquad (2)$$

$$\mu_{\text{electrode}} = \left(\frac{\partial A}{\partial N}\right)_{T,\,\nu(\underline{r})} = \left(\frac{\partial E}{\partial N}\right)_{T,\,\nu(\underline{r})} - T\left(\frac{\partial S}{\partial N}\right)_{T,\,\nu(\underline{r})} \qquad (3)$$

At zero temperature, the chemical potential $\mu_{\text{electrode}}$ of the ensemble becomes equal to the electronic chemical potential of the studied system.

$$\mu_{\text{electrode}} = \left(\frac{\partial E}{\partial N}\right)_{T,\,\nu(\underline{r})} = \mu \qquad (4)$$

The curve of E versus N is a series of straight-line segments at zero temperature.[42] The curve itself is continuous, but its derivative has possible discontinuities at integral values of N. The linear interpolation scheme neglects second-order effects, which can be taken into account by means of a second-order interpolation scheme around the reference molecule. The energy change of oxidized and reduced species can be written in a second-order Taylor expansion in function of the number of exchanged electrons ($\Delta N = N - N_0$)

$$E = E(N_0) + \mu^0\Delta N + \frac{1}{2}\eta^0\Delta N^2 \qquad (5)$$

in which μ^0 is the chemical potential of the studied system measuring the escaping tendency of an electronic cloud, and η^0 is the chemical hardness indicating the system's resistance to a change in its number of electrons. The derivative of the electronic energy to the number of electrons becomes

$$\left(\frac{\partial E}{\partial N}\right)_{\nu(\underline{r})} = \mu = \mu^0 + \eta^0\Delta N \qquad (6)$$

in which a second-order correction arises because of the parabolic fitting procedure. At equilibrium, the chemical potential of the electrode becomes equal to $\mu^0 + \eta^0\Delta N$ of the respectively pure states, that is, the oxidized or reduced state. The process of oxidation and reduction is controlled by altering the chemical potentials of the different states through the number of exchanged electrons. The condition for a minimum in the grand canonical potential for the oxidized species at oxidized geometry ($\nu = \nu_{\text{Ox}}$) becomes

$$\mu_{\text{electrode}} = \mu^0_{\text{Ox}} + \eta^0_{\text{Ox}}\Delta N_{\text{Ox}} \qquad (7)$$

In analogy to the previous equation, the expression for the reduced species at the reduced species' geometry ($\nu = \nu_{\text{Red}}$) gives

$$\mu_{\text{electrode}} = \mu^0_{\text{Red}} + \eta^0_{\text{Red}}\Delta N_{\text{Red}} \qquad (8)$$

Oxidation and reduction reactions take place at the same chemical potential of the electrode $\mu_{\text{electrode}}$, which results in an equalization of eqs 7 and 8.

The number of electrons that the reduced species will give and that the oxidized species takes up is equal and is given by eq 9

$$\Delta N_{\text{Ox}} = -\Delta N_{\text{Red}} = \frac{\mu^0_{\text{Red}} - \mu^0_{\text{Ox}}}{\eta^0_{\text{Red}} + \eta^0_{\text{Ox}}} \qquad (9)$$

As such, the electron transfer is governed by the chemical hardness and chemical potentials of oxidized and reduced species. Differences in chemical potential drive electron transfer. A lower value of μ_{Ox} (a higher electronegativity) and a higher value of μ_{Red} (a lower electronegativity) favor the electron uptake process. On the contrary, the second-order effects included by the chemical hardnesses moderate electron transfer.

Combining eqs 7–9 results in the formulation of the $\mu_{\text{electrode}}$ in terms of reactivity indices of the oxidized and reduced species

$$\mu_{\text{electrode}} = \frac{\mu^0_{\text{Ox}}\eta^0_{\text{Red}} + \mu^0_{\text{Red}}\eta^0_{\text{Ox}}}{\eta^0_{\text{Ox}} + \eta^0_{\text{Red}}} \qquad (10)$$

This equation indicates that the oxidized species becomes less prone for an electron uptake when it takes up a fractional charge during the reduction process, while the reduced species becomes more electrophilic when losing fractional charge during oxidation.

Work previously done by the present authors was about the use of the electrophilicity descriptor as measure of the system's ability to accept electrons.[12,13] This descriptor encompasses the decrease in energy associated with a process of maximum electron uptake between a ligand and a perfect electron donor.[10] This perfect electron donor can be seen as a bath of electrons

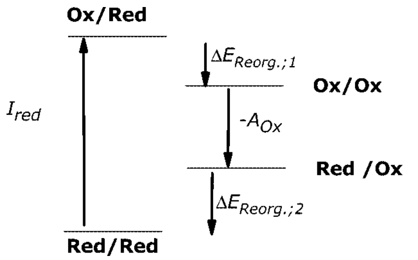

Figure 1. Energy scheme for oxidized and reduced states for an electroactive species. The left-hand side in the notation *i*/*j* ($i, j =$ Ox, Red) refers to the electronic state and the right-hand side refers to the optimized geometry. The ionization potential *I* and electron affinity *A* mentioned are vertical quantities.

with zero chemical potential. Within the grand canonical approach, this would result in a grand potential that becomes the electronic energy. The change in the grand potential corresponding to a maximum transfer of electrons is set equal to the electrophilicity. We have shown that at least a qualitative correlation is possible between the electrophilicity and the redox potential. The present approach is based on the measurement of the chemical potential of the electrode through the chemical potential and the hardness of oxidized and reduced species. Equation 10 is derived assuming a second-order perturbation and equal transfer of electronic charge at 0 K. Entropic and thermal contributions are not considered.

Since $\mu_{\text{electrode}}$ measures the change in Helmholtz free energy at 0 K with a corresponding change in electronic energy, this quantity can function as an approximation of the Gibbs free energy related to the one-electron half-reaction. From the Nernst equation, the expression for the standard redox potential becomes

$$E^\circ = -\frac{\mu_{\text{electrode}}}{F} - E_{\text{NHE}}{}^\circ \tag{11}$$

The calculated value of E° is related to the reduction potential of a reference electrode, in this case, the normal hydrogen electrode (NHE, H^+ (aq) + $e^- \rightarrow {}^1/_2H_2$ (g)) with an associated free-energy change of −4.28 eV in aqueous solution[43,44] and −4.48 eV in acetonitrile.[45] All systems studied in this work are one-electron half-reactions, and the processes are reversible.

2.2. Vertical Quantities: Ionization Potential and Electron Affinity. The most common approach to the calculation of a redox potential is by using the aforementioned thermodynamic scheme which links the process in the gas phase with the solution phase. The main difficulty lies in the treatment of solvent effects during the electron-transfer process. Accurate determination of the solvation energy of the reduced and oxidized species is therefore of utmost importance in this context. Electron transfer takes place rapidly, while the geometric relaxation will proceed after the electron transition. The redox reaction can therefore be split into two steps, an electron uptake and a reorganization step.

As shown in Figure 1, the oxidized species has a higher energy than the reduced one. The change in energy for the transition between oxidized and reduced species can be written in terms of vertical electron affinities and ionization potentials accompanied by the respective reorganization energies. These expressions become:

for the forward reaction: Ox/Ox + $e^- \rightarrow$ Red/Red

$$\begin{gathered} E_{\text{Red/Red}} - E_{\text{Ox/Ox}} = E_{\text{Red/Red}} - E_{\text{Red/Ox}} + E_{\text{Red/Ox}} - E_{\text{Ox/Ox}} \\ \Delta E_{\text{Red}} = \Delta E_{\text{reorganization,2}} - A_{\text{Ox}} \end{gathered} \tag{12}$$

for the backward reaction: Red/Red → Ox/Ox $+e^-$

$$\begin{gathered} E_{\text{Ox/Ox}} - E_{\text{Red/Red}} = E_{\text{Ox/Ox}} - E_{\text{Ox/Red}} + E_{\text{Ox/Red}} - E_{\text{Red/Red}} \\ \Delta E_{\text{Ox}} \equiv -\Delta E_{\text{Red}} = \Delta E_{\text{reorganization,1}} + I_{\text{Red}} \end{gathered} \tag{13}$$

Since both eqs 12 and 13 describe the inverse process, the energy differences are equal on a sign difference. This leads to a single equation in which both reorganization energies 1 and 2 are written

$$\Delta E_{\text{reorganization,1}} + \Delta E_{\text{reorganization,2}} = A_{\text{Ox}} - I_{\text{Red}} \tag{14}$$

By assuming that $\Delta E_{\text{reorganization, 1}}$ and $\Delta E_{\text{reorganization, 2}}$ are equal, eq 14 becomes

$$\Delta E_{\text{reorganization}} = \frac{1}{2}(A_{\text{Ox}} - I_{\text{Red}}) \tag{15}$$

This assumption is based on the linear free energy relationship proposed by Marcus.[38,39,46] The Marcus model, which is of great importance within the electron-transfer reaction theory, predicts that the free-energy functions depend quadratically on the solvent electrostatic potential; the force constants describing the curvature for the products and the reactants are supposed to be equal regardless of the nature of the products and reactants. As such, the energies of reorganization for a process going from reactant to product or vice versa are the same.[46] This statement is based on the fact that the change in the charge of the reacting species results in a linearly proportional change in the dielectric polarization of the solvent medium. After a slight rearrangement of eq 15, the reorganization energy can be seen as a pair hardness or intermolecular hardness as defined by Pearson[57] ($\Delta E_{\text{reorganization}} = -{}^1/_2\eta_{\text{Red Ox}}$) between reduced and oxidized species. This remark can be seen as a starting point to link Marcus theory with conceptual DFT.

Combining eq 15 and eq 12 or 13, we find two equivalent expressions for ΔE_{Red}

$$\Delta E_{\text{Red}} = -I_{\text{Red}} - \frac{1}{2}(A_{\text{Ox}} - I_{\text{Red}}) \tag{16}$$

$$\Delta E_{\text{Red}} = -A_{\text{Ox}} + \frac{1}{2}(A_{\text{Ox}} - I_{\text{Red}}) \tag{17}$$

Conclusively, both eq 16 and eq 17 are equal and give one expression for ΔE_{Red}

$$\Delta E_{\text{Red}} = -\frac{1}{2}(A_{\text{Ox}} + I_{\text{Red}}) \tag{18}$$

This final equation states that the energy change for the reduction process can be approximated by, respectively, the vertical electron affinity and the ionization potential taking into account a constant reorganization term, which is identical for the oxidation and reduction reactions. A larger electron affinity of the oxidized species indicates that it will easily accept an electron while a larger ionization potential measures a more difficult ionization process of the reduced species. Equation 18 bears some analogy with eq 11 of ref 42 in which I_{min} is now seen as I_{red} and A_{max} is now seen as A_{ox}. Conclusively, the reduction process becomes energetically more favorable when the oxidized species is highly prone to an electron uptake and the reduced species is not readily ionized. Redox potential values are calculated on the basis of the Nernst equation with the energy of reaction approximated by eq 18.

$$E^\circ = -\frac{\Delta E_{\mathrm{Red}}}{F} - E_{\mathrm{NHE}}{}^\circ \tag{19}$$

The electronic energy replaces the Gibbs free energy in eq 19 by neglecting entropic contributions and intermolecular interactions in the redox system.

2.3. Link between EEM and Vertical Quantities. Equation 10 coincides with eq 18 in the particular case that the hardness of oxidized and reduced species is equal. Then, eq 10 is simplified to

$$\mu_{\mathrm{electrode}} = \frac{\mu^0_{\mathrm{Ox}} + \mu^0_{\mathrm{Red}}}{2} \tag{20}$$

which can be written in terms of vertical electron affinity and ionization potential as

$$\mu_{\mathrm{electrode}} = \Delta E_{\mathrm{Red}} = -\frac{1}{2}(A_{\mathrm{Ox}} + I_{\mathrm{Red}}) \tag{21}$$

Therefore, we can state that eq 18 is an approximation of eq 10. It is possible to split eq 10 into a term concerning the electron transition and a reorganization term as has been done in the previous section.

$$\mu_{\mathrm{electrode}} = \frac{\mu^0_{\mathrm{Ox}}\eta^0_{\mathrm{Red}} + \mu^0_{\mathrm{Red}}\eta^0_{\mathrm{Ox}}}{\eta^0_{\mathrm{Ox}} + \eta^0_{\mathrm{Red}}} \tag{22}$$

$$\mu_{\mathrm{electrode}} = -I_{\mathrm{Red}} - \Delta E_{\mathrm{reorganization,1}} \tag{23}$$

$$\mu_{\mathrm{electrode}} = -A_{\mathrm{Ox}} + \Delta E_{\mathrm{reorganization,2}} \tag{24}$$

This will result in the following form for the reorganization terms in the context of the EEM

$$\Delta E_{\mathrm{reorganization,1}} = \frac{2\eta^0_{\mathrm{Red}}\Delta E_{\mathrm{reorganization}}}{\eta^0_{\mathrm{Ox}} + \eta^0_{\mathrm{Red}}} \tag{25}$$

$$\Delta E_{\mathrm{reorganization,2}} = \frac{2\eta^0_{\mathrm{Ox}}\Delta E_{\mathrm{reorganization}}}{\eta^0_{\mathrm{Ox}} + \eta^0_{\mathrm{Red}}} \tag{26}$$

$$\frac{\eta^0_{\mathrm{Ox}}\Delta E_{\mathrm{reorganization}}}{\eta^0_{\mathrm{Ox}} + \eta^0_{\mathrm{Red}}} + \frac{\eta^0_{\mathrm{Red}}\Delta E_{\mathrm{reorganization}}}{\eta^0_{\mathrm{Ox}} + \eta^0_{\mathrm{Red}}} = \Delta E_{\mathrm{reorganization}} \tag{27}$$

in which the division of the reorganization energy is based on the weight factors involving the chemical hardness of the oxidized and reduced species. As previously shown in the section of the EEM, the curvatures of the energy profile with respect to the number of electrons, identified as the chemical hardness, are different for both oxidized and reduced species. Within Marcus theory, equal force constants for both curves in the profile of E versus the reaction coordinate are assumed. Deviations from the linear solvent response can have different origins such as strong molecular interactions and considerable influence of one solute on the solvent polarization of the other. Within conceptual DFT, the difference in chemical hardness values can now be supposed to figure as a measure of the different reorganization energies of oxidized and reduced species.

3. Methodology

The chemical hardness and the chemical potential of oxidized and reduced species are computed using vertical electron affinities and ionization potentials as defined in eqs 28 and 29. Through a finite difference approximation in the quadratic E versus N model, the expressions of the chemical potential and the hardness are

$$\mu = -\frac{I + A}{2} \tag{28}$$

$$\eta = I - A \tag{29}$$

Structures were optimized, and frequency calculations were done to ensure that a minimum in the potential energy surface was reached. A large range of organic and inorganic systems in different solvents were examined. To establish a large range of positive and negative redox potentials, positive as well as negative and neutral reactants were studied. The total ensemble of 44 species was divided in four different groups:

(a) The aliphatic group includes alkanes, alkenes, and substituted alkanes such as alcohols, nitroalkanes, and amines. The redox reaction between the positively charged ion and the neutral molecule was examined. In the case of 2-methyl-2-nitroproprane, the reduced species is negatively charged.

(b) The aromatic group is composed of benzene and substituted benzenes. In the case of nitrobenzene, benzaldehyde, and acetophenone, reduced species are negatively charged. Solvent effects were included using PCM[47] to serve as a model for acetonitrile for molecules from groups a and b. The spheres centered on each atom were constructed from Bondi's atomic radii and were scaled with an electrostatic factor of 1.20. This scaling factor, though not rigorously defined for acetonitrile in the default PCM model, was based on a previously made optimization by Fu et al.[21] to approximate the pK_a values of 15 organic molecules. Sixty tesserae were used to build up the spheres.

(c) The aniline group consists of aniline and several monosubstituted anilines all calculated in aqueous solution. Previous work by Winget and co-workers[17,20] concerning these compounds in aqueous solution resulted in a mean unsigned error (MUE) of 0.24 V for a group of molecules composed of aniline and 12 monosubstituted anilines when their computationally most complete protocol was used. Yu et al.[48] reported MUE as high as 0.304 eV for the calculation of redox potentials of neutral anilines in dimethylsulfoxide (DMSO). They assigned this error mainly to the inaccuracy of the calculated solvation energies of the aniline radical cations. Their results improved by changing the size of the cavity.

(d) The inorganic group consists of first-row transition-metal ions. The reduction reaction of a triply charged metal ion to the doubly charged ion was studied. The methodology was previously published by the present authors.[13] Metal ions were surrounded by a second solvation sphere built up from two sets of nine water molecules interacting on two parallel planes. This complex was further embedded in a PCM model.

All calculations were performed with the Gaussian03 software.[49] Structures of groups a−c were optimized on a 6-31+G(d,p) basis set using the three-parameter fitted B3LYP[50,51] exchange-correlation functional. Single-point energy calculations were done with the elaborate 6-311++G(d,p) basis set. For group d optimizations, single-point energy calculations were performed on a 6-311G(d) level also with B3LYP as the exchange-correlation functional. No optimization of the structures in solvent was done since in good approximation this relaxation energy is small. All the reported redox potential values are relative to the normal hydrogen electrode (NHE). Experimentally determined values which are relative to the saturated calomel electrode (SCE) are converted to NHE values by adding 0.27 V.

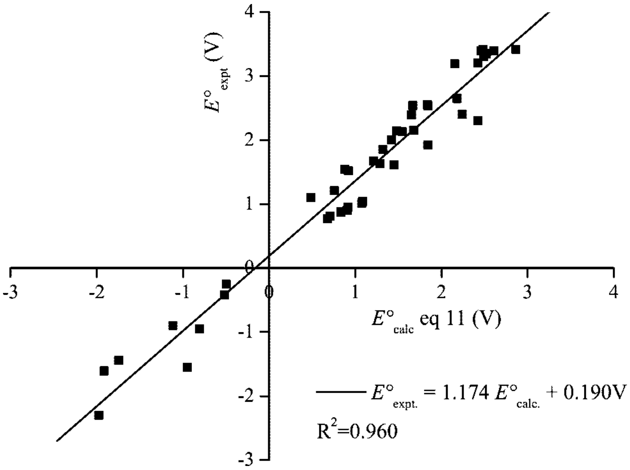

Figure 2. Calculated values of the redox potentials on the basis of the chemical potential derived from a grand canonical approach, through eq 11.

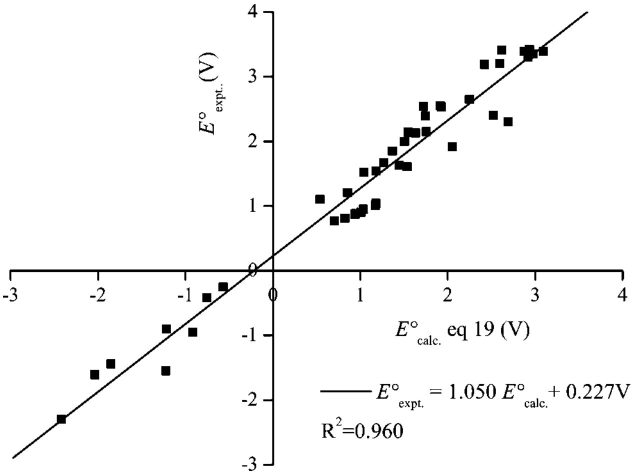

Figure 3. Calculated values of the redox potential using vertical electron affinities and ionization potentials. Redox potentials are computed through eq 19.

4. Results and Discussion

4.1. Performance of the EEM and Vertical Quantities. The above-introduced methods were checked against experimentally known redox potentials. Figures 2 and 3 report the performance of eqs 11 and 19 in respect to experimental values. Correlation coefficients (R^2) as high as 0.96 confirm the accuracy of the introduced methodologies and their performance as estimates of redox potential values. For the thermodynamic cycle method (eq 19), the slope is close to unity deviating only by a margin of 5%. The chemical potential corresponding to the principle of equal electronegativity equally well performs in regard to experimental results with a small systematic error and a slightly more elevated slope. Results are summarized in Table 1.

Both methods seem to underestimate systematically experimental redox potential values. Calculations based on eq 11 lead to smaller systematic errors compared to the thermodynamic cycle method. The group of the anilines is well described by eq 19 with an MUE under 0.1 V; redox potentials computed by eq 11 result in an MUE under 0.05 V. For the transition-metal ions, these values are around 0.22 and 0.24 V, respectively. Reactions which take place in acetonitrile, namely, species from the aliphatic and aromatic group, have more elevated MUE compared to the redox reactions studied in aqueous solution. Taking into account the large spread of organic and inorganic systems and different solvents, the overall performance of eq 19 is reasonably good with an MUE of 0.360 V and with an elevated error of 0.437 V for results computed from eq 11. An explanation of this increased error and a possible solution for this problem will be given in the following sections. These numbers nonetheless convince us of the usefulness of both methods for the approximated calculation of redox potentials.

It is surprising to see that although entropic and thermal contributions are neglected a still remarkable accuracy is achieved on the basis solely of vertical quantities of oxidized and reduced species. Our previous methodologies within conceptual DFT were based on the electrophilicity descriptor. As positively defined, this descriptor turned out to give some merely qualitative information about a system's ability to accept electrons. Moreover, problems arose for highly electrophilic species; for a discussion, see ref 13. Now, instead of coupling the studied system to an ideal bath of electrons, the introduction of the chemical potential of the electrode resulted in a quantitative estimate of the redox potential for reversible one-electron half-reactions. The present work can therefore be seen as a next valuable step to redox chemistry from conceptual DFT.

From eq 10, extra properties of the oxidized and reduced species enter the formula of the redox potential. Some structural information of the oxidized and reduced systems is enclosed through the inverse proportionality between the size of a reactive site and its hardness. Increasing the size of reactants and products decreases the chemical potential of equilibrium, and consequently, conforming to eq 11, the system's redox potential augments. The solvent influences the hardness and chemical potential of oxidized and reduced species.[53,54] As shown by Pérez et al.,[55] the chemical hardness decreases when molecules are embedded in a solvent environment. We noticed a qualitative correlation between difference in chemical hardness between oxidized and reduced species and their redox potential. In general, it seems that negative redox potentials are linked to oxidized species which are harder than the reduced ones, while for positive $E°$ values the oxidized systems are softer than the reduced ones.

4.2. Reorganization Energy and the Proportionalities of Hardness. On the basis of the thermodynamic cycle approach, the reorganization energy is counted by the difference of the electron affinity of the oxidized and the ionization potential of reduced species within the Marcus linear approximation. The prediction of the reorganization energy using this methodology compared to the exact reorganization energy as calculated by energetic differences gives an estimate of the performance of this method.

As can be seen from Figures 4 and 5, high correlation coefficients ensure the correctness of the approximation of the reorganization energy by $^1/_2(A_{Ox} - I_{Red})$. Some scattering points in these figures can be linked to larger errors in calculated redox potential values with respect to experimental ones. Concerning the EEM, the reorganization energy calculated by the previous methodology is scaled by the weight factors involving the hardness values of oxidized and reduced species. The insertion of the chemical hardness is a result of the conceptual DFT approach wherein the second-order energy change is related to the chemical hardness. Considering the reduction reaction, it seems that the uptake of one electron is less energetically favorable when the chemical hardness of the oxidized species is larger resulting in a more important reorganization term. In the case of the oxidation reaction, losing one electron will be an energetically more demanding process for a harder reduced

TABLE 1: One-Electron Redox Potential Values Estimated by Eqs *11* and *19* for Different Organic and Inorganic Systems[a]

	$E°$ expt	$E°$ calcd (eq 11)	$E°$ calcd (eq 19)
Aliphatic Group* ($E°$ Expt See Ref 21)			
n-pentane	3.39	2.610	3.096
n-hexane	3.35	2.522	2.979
n-heptane	3.31	2.490	2.920
n-octane	3.39	2.462	2.873
ethylene	3.41	2.485	2.614
1,3-butadiene	2.54	1.669	1.722
methanol	3.42	2.863	2.936
ethanol	3.2	2.423	2.596
1-methylethanol	3.19	2.154	2.420
diethylamine	1.52	0.921	1.038
n-propylamine	1.63	1.288	1.444
2-methyl-2-nitropropane(−)	−1.55	−0.947	−1.225
Aromatic Group* ($E°$ Expt. See Ref 21)			
styrene	2.14	1.482	1.545
1-(prop-1-en-2-yl)benzene	2.00	1.422	1.507
benzene	2.65	2.182	2.248
toluene	2.55	1.838	1.916
o-xylene	2.15	1.678	1.756
m-xylene	1.61	1.452	1.537
p-xylene	−0.95	−0.805	−0.918
phenol	2.39	1.654	1.742
nitrobenzene(−)	2.13	1.544	1.631
1-ethylbenzene	2.53	1.845	1.929
naphthalene	1.85	1.322	1.366
2-methylnaphthalene	1.67	1.213	1.269
aniline	1.21	0.757	0.856
N, *N*-dimethyl-benzenamine	1.1	0.487	0.540
benzaldehyde(−)	−1.44	−1.745	−1.853
acetophenone(−)	−1.61	−1.914	−2.037
Aniline† ($E°$ Expt See Ref 52)			
aniline	0.90	0.907	1.009
o-toluidine	0.87	0.833	0.939
m-toluidine	0.88	0.836	0.942
p-toluidine	0.81	0.708	0.825
o-chloroaniline	1.01	1.075	1.172
m-chloroaniline	1.04	1.084	1.178
p-chloroaniline	0.95	0.917	1.035
Inorganic Systems† ($E°$ Expt See Ref 13)			
$Sc^{3+}\|Sc^{2+}$	−2.3	−1.977	−2.422
$Ti^{3+}\|Ti^{2+}$	−0.9	−1.116	−1.214
$V^{3+}\|V^{2+}$	−0.255	−0.497	−0.568
$Cr^{3+}\|Cr^{2+}$	−0.42	−0.515	−0.754
$Co^{3+}\|Co^{2+}$	1.54	0.880	1.182
$Fe^{3+}\|Fe^{2+}$	0.77	0.678	0.706
$Mn^{3+}\|Mn^{2+}$	1.92	1.841	2.054
$Ni^{3+}\|Ni^{2+}$	2.3	2.423	2.690
$Cu^{3+}\|Cu^{2+}$	2.4	2.242	2.523

[a] Groups indicated by * are calculated in acetonitrile, while groups with † are calculated in aqueous solution. The (−) sign refers to a negatively charged reduced species. All values are given in volts.

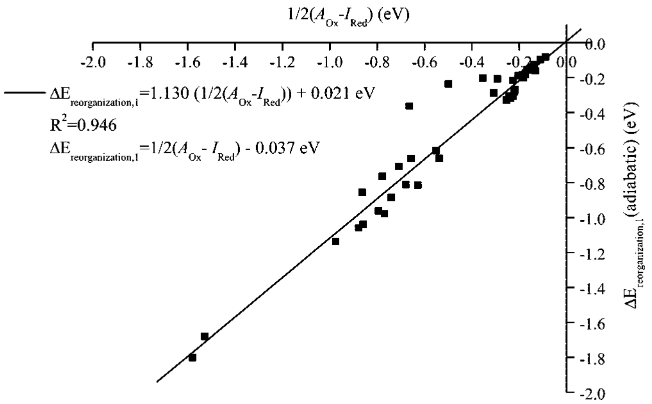

Figure 4. Regression line of $\Delta E_{\mathrm{reorganization},1}$ (adiabatic) in function of $^1/_2(A_{\mathrm{Ox}} - I_{\mathrm{Red}})$.

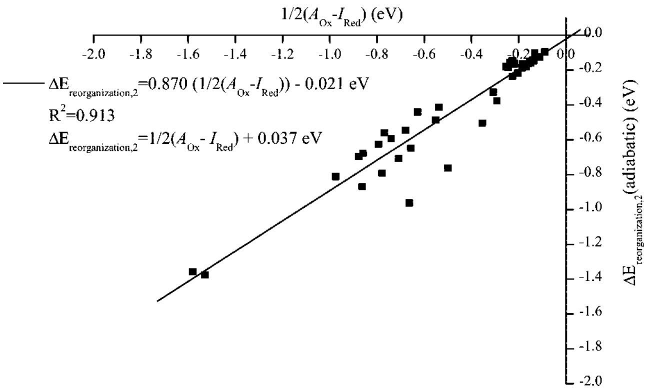

Figure 5. Regression line of $\Delta E_{\mathrm{reorganization},2}$ (adiabatic) in function of $^1/_2(A_{\mathrm{Ox}} - I_{\mathrm{Red}})$.

species. This vertical transition will as a result be accompanied by a larger reorganization energy when relaxing to the optimized geometry of the oxidized structure. As such, the weight factor composed of the chemical hardnesses is surely linked to the correct trend in the reorganization energy.

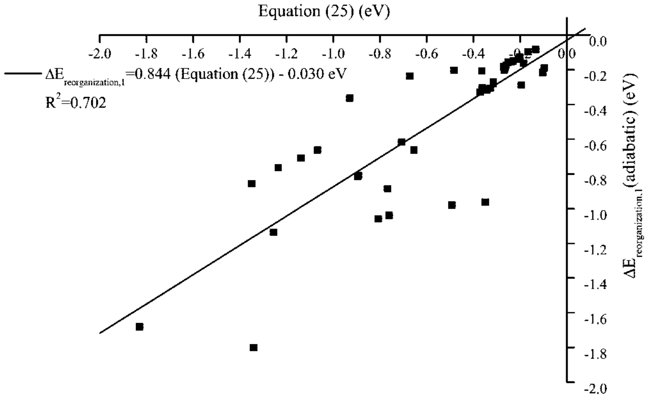

Figure 6. Regression line of $\Delta E_{\text{reorganization},1}$ (adiabatic) in function of eq 25.

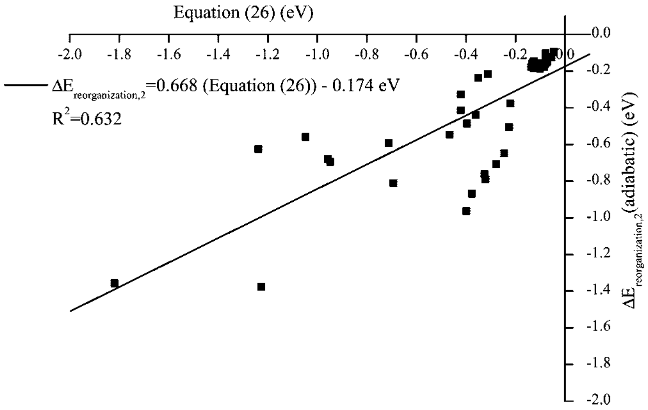

Figure 7. Regression line of $\Delta E_{\text{reorganization},2}$ (adiabatic) in function of eq 26.

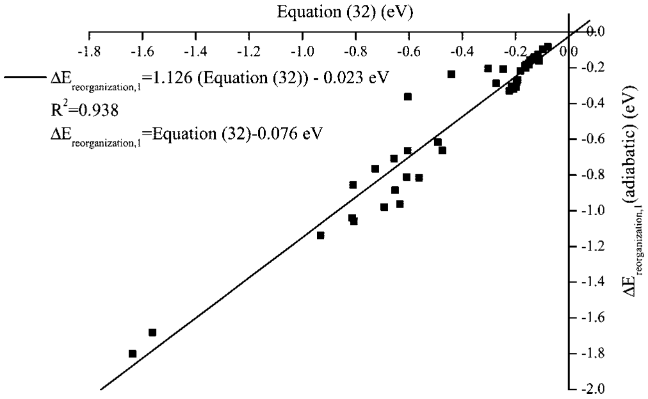

Figure 8. Regression line of $\Delta E_{\text{reorganization},1}$ (adiabatic) in function of eq 32.

From Figures 6 and 7, it is clear that the reorganization energy is poorly subdivided in terms of the hardness weight factors. In the case of positive redox potentials, the low hardness values of oxidized species with respect to reduced ones result in a large underestimation of reorganization energies. This effect is a result of the lowering of the chemical hardness in solvent. The thermodynamic Born−Haber approach is, however, able to estimate correct trends in the reorganization energies suggesting that the study of the redox systems is valid within the Marcus approximation.

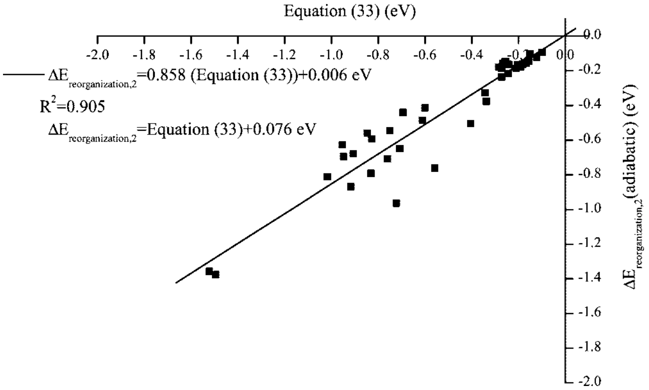

Figure 9. Regression line of $\Delta E_{\text{reorganization},2}$ (adiabatic) in function of eq 33.

4.3. A New Approach. The main problem with the weight factors composed of the chemical hardness values is the large underestimation of the reorganization energy of oxidized species. A solution to this problem is the introduction of the system's response to an electron uptake and release process. As previously stated by Gómez et al.[56] and Gázquez et al.,[40] left and right derivatives of the energy with respect to the number of electrons are different. Instead of using a single value of μ, different definitions are useful to describe electron donating and accepting powers. Since electron transfer is mainly driven by the chemical potential, two new relationships for μ are derived by Gázquez et al.[40]

$$\mu^{+} = -\frac{1}{4}(I + 3A) \tag{30}$$

$$\mu^{-} = -\frac{1}{4}(3I + A) \tag{31}$$

Clearly, more emphasis is given to the electron affinity in the definition of μ^+ while the ionization potential is more stressed in μ^-. Both quantities can now be inserted in the equations of the reorganization energies of oxidized and reduced species, namely, μ^+ for the oxidized species and μ^- for the reduced species. This substitution is chemically sound since less negative values of μ^- with respect to μ^+ corresponds to a less energy demanding electron release process. Consequently, the $\Delta E_{\text{reorganization},1}$ term becomes less negative and smaller in absolute value. By taking these two chemical potentials relative to each other into account, an estimate of the partitioning of the reorganization energy, comparable to the hardness values, can be achieved. This strategy fundamentally approaches the quadratic curve of the energy versus the number of electrons as straight lines for electron uptake and release close to N_0. Formulas for the reorganization energies will now become

$$\Delta E_{\text{reorganization, 1}} = \frac{2\mu^{-}_{\text{Red}}\Delta E_{\text{reorganization}}}{\mu^{+}_{\text{Ox}} + \mu^{-}_{\text{Red}}} \tag{32}$$

$$\Delta E_{\text{reorganization, 2}} = \frac{2\mu^{+}_{\text{Ox}}\Delta E_{\text{reorganization}}}{\mu^{+}_{\text{Ox}} + \mu^{-}_{\text{Red}}} \tag{33}$$

The comparison of the estimated reorganization energies by, respectively, eqs 32 and 33 to the exact values is shown in Figures 8 and 9.

Remarkable improvement of this methodology over the hardness proportionality is clearly seen in Figures 8 and 9. Estimates of the redox potential can be calculated by inserting eqs 32 and 33 into the expressions for eqs 23 and 24. As a consequence, estimates of redox potential values are improved when using these new scaled reorganization energies as shown in Figure 10. The problem with the weight factor composed of the hardness is the low hardness values of oxidized species in solvent. This results in reorganization energies for the oxidized

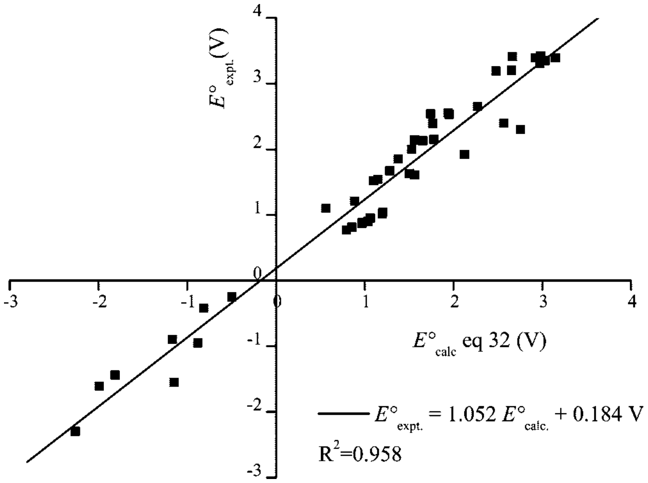

Figure 10. Calculated values of the redox potential on the basis of eqs 32 and 33 for the reorganization energies.

species which are too low compared to exact values. By comparing now the relative size of μ^{+}_{Ox} and μ^{-}_{Red}, this problem is avoided and trends in reorganization energies are fairly well reproduced.

5. Conclusions

This paper addresses the problem of redox reactions in the context of conceptual DFT. We have introduced two methodologies which express redox properties in terms of vertical quantities of oxidized and reduced systems. The first approach starts from the grand canonical ensemble theory which has led to an equation of the redox potential in terms of the chemical potential of the electrode. The chemical potential formulated as a weighted average of hardness and chemical potentials of oxidized and reduced species is shown to act as a descriptor of a one-electron transfer process. The second approach starts from a Born−Haber scheme in which the redox potential was solely expressed in terms of the vertical electron affinity of the oxidized and the ionization potential of the reduced species. The success of both approaches is clearly shown for a large class of chemically unrelated organic and inorganic systems in different solvents. Larger errors in the EEM approach were assigned to a problem in the estimate of reorganization energies by the chemical hardness proportionalities. However, improvement could be achieved when instead of the chemical hardness, the response of the chemical potential to an electron uptake or release is taken into account. This step can be seen as a refinement of the second-order model to achieve a better estimate of energy changes for small alterations in the number of electrons. Conclusively, this paper clearly supports the use of conceptual DFT principles such as the EEM in the field of electrochemistry.

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