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SUPPLEMENTARY INFORMATION

Electronegativity and redox ractions

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Here we perform the same analysis shown in the manuscript, regarding the performance of the different studied models at the time of predicting oxidation potentials. The difference is that now we will approximate the ionization energies and electron affinities using the Kohn-Sham HOMO and LUMO energies, respectively. Tables 1-6 and Figure 1 are analogous to those presented in the manuscript. Equation numbers are referred to the manuscript.

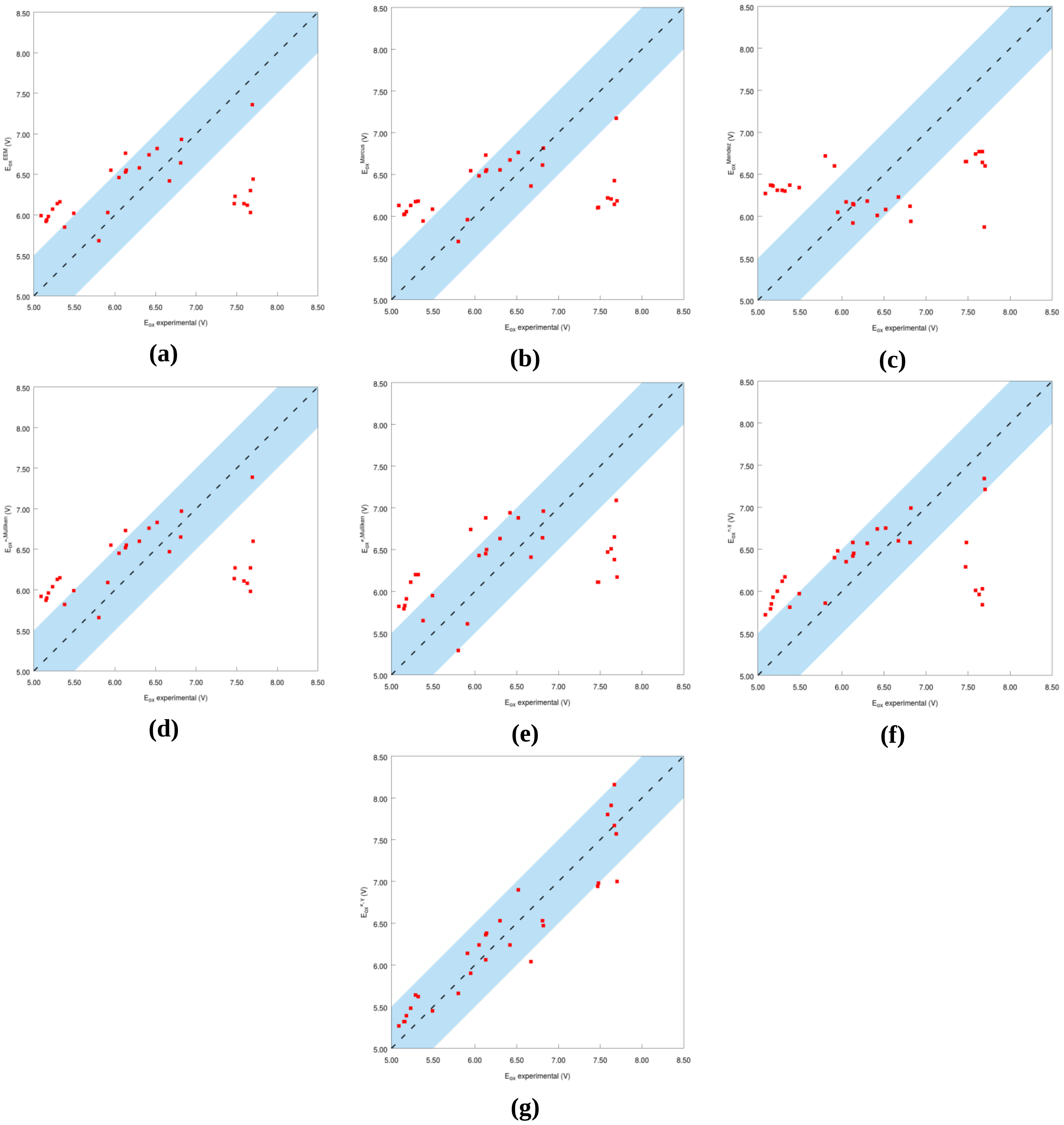
Table 1. Ionization energies, electron affinities and chemical hardnesses of the reduced (I_R, A_R, η_R) and oxidized (I_O, A_O, η_O) species in the training set, calculated using finite differences. The PCM solvent model is specified as either water (w) or acetonitrile (a). All energy values are in electron volts.

Reduced species	I_R	A_R	I_O	A_O	η_R	η_O
aniline(a)	5.66	0.20	7.38	1.39	5.46	5.99
aniline(w)	5.67	0.21	7.32	1.33	5.46	5.99
benzene(w)	7.02	0.30	8.82	2.76	6.72	6.06
1,3-butadiene(w)	6.51	0.93	8.74	3.45	5.58	5.28
diethylamine(w)	6.13	-1.34	8.78	-0.53	7.47	9.31
ethanol(w)	7.41	-1.29	10.17	-0.19	8.70	10.36
ethylene(w)	7.56	-0.10	10.43	3.81	7.66	6.63
m-cloroaniline(a)	5.87	0.48	7.53	1.63	5.38	5.90
methanol(w)	7.40	-1.34	11.58	0.12	8.74	11.46
m-toluidine(a)	5.60	0.12	7.22	1.28	5.48	5.94
m-xylene(w)	6.54	0.21	8.33	2.42	6.32	5.92
naphthalene(w)	6.10	1.30	7.55	2.98	4.80	4.57
n-heptane(w)	8.24	-1.34	8.77	-0.78	9.59	9.55
n-hexane(w)	8.37	-1.35	8.91	-0.77	9.72	9.68
N, N-dimethyl-benzenamine(w)	5.29	0.16	7.15	1.26	5.13	5.89
n-octane(w)	8.15	-1.33	8.63	-0.79	9.48	9.43
n-pentane(w)	8.55	-1.36	9.02	-0.10	9.90	9.12
n-propylamine(w)	6.54	-1.35	9.21	-0.47	7.89	9.68
o-chloroaniline(a)	5.89	0.48	7.42	1.58	5.41	5.84
1-ethylbenzene(w)	6.71	0.27	8.52	2.43	6.44	6.08
1-(prop-1-en-2-yl)benzene(w)	6.33	0.94	7.87	2.98	5.40	4.89
o-toluidine(a)	5.60	0.07	7.15	1.25	5.53	5.90
o-xilene(w)	6.52	0.14	8.33	2.37	6.38	5.96
p-chloroaniline(a)	5.75	0.51	7.17	1.56	5.24	5.61
phenol(w)	6.25	0.35	8.17	2.03	5.90	6.15
p-toluidine(a)	5.51	0.20	6.96	1.30	5.31	5.66
p-xilene(w)	6.42	0.24	8.10	2.26	6.18	5.84
styrene(w)	6.33	1.18	7.96	3.09	5.15	4.87
toluene(w)	6.70	0.27	8.59	2.46	6.42	6.13
2-methylnaphtalene(w)	6.02	1.21	7.39	2.90	4.80	4.49
1-methyletanol(w)	7.36	-1.17	9.45	-0.17	8.53	9.62

Table 2. Experimental ($\Delta E_{\mathrm{ox}}^{\mathrm{exp}}$) and predicted ($\Delta E_{\mathrm{ox}}^{\mathrm{EEM}}$, $\Delta E_{\mathrm{ox}}^{\mathrm{Marcus}}$, $\Delta E_{\mathrm{ox}}^{\mathrm{Mendez}}$, $\Delta E_{\mathrm{ox}}^{=,\mathrm{Mulliken}}$, $\Delta E_{\mathrm{ox}}^{\neq,\mathrm{Mulliken}}$, $\Delta E_{\mathrm{ox}}^{=,\gamma}$, $\Delta E_{\mathrm{ox}}^{\neq,\gamma}$) absolute oxidation potentials for the half-reactions in the training set. The solvent is indicated in parenthesis: either water (w) or acetonitrile (a). Ionization energies and electron affinities were calculated using the finite-difference data from Table 1. All potentials are in volts.

Reduced species	$\Delta E_{\mathrm{ox}}^{\mathrm{exp}}$	$\Delta E_{\mathrm{ox}}^{\mathrm{EEM}}$ Eq. (30)	$\Delta E_{\mathrm{ox}}^{\mathrm{Marcus}}$ Eq. (31)	$\Delta E_{\mathrm{ox}}^{\mathrm{Mendez}}$ Eq. (32)	$\Delta E_{\mathrm{ox}}^{=,\mathrm{Mulliken}}$ Eq. (21)	$\Delta E_{\mathrm{ox}}^{\neq,\mathrm{Mulliken}}$ Eq. (22)	$\Delta E_{\mathrm{ox}}^{=,\gamma}$ Eq. (28)	$\Delta E_{\mathrm{ox}}^{\neq,\gamma}$ Eq. (29)
aniline(a)	5.49	6.02	6.08	6.34	5.99	5.95	5.97	5.45
aniline(w)	5.18	5.98	6.05	6.36	5.96	5.91	5.93	5.39
benzene(w)	6.52	6.82	6.76	6.08	6.83	6.88	6.75	6.90
1,3-butadiene(w)	6.82	6.93	6.81	5.94	6.97	6.96	6.99	6.47
diethylamine(w)	5.80	5.68	5.70	6.72	5.66	5.29	5.86	5.66
ethanol(w)	7.48	6.23	6.11	6.65	6.27	6.11	6.58	6.98
ethylene(w)	7.69	7.36	7.17	5.87	7.39	7.09	7.34	7.57
m-cloroaniline(a)	5.32	6.16	6.18	6.30	6.15	6.20	6.17	5.62
methanol(w)	7.70	6.44	6.18	6.60	6.60	6.17	7.21	7.00
m-toluidine(a)	5.16	5.94	6.03	6.37	5.90	5.83	5.85	5.32
m-xylene(w)	6.14	6.55	6.55	6.14	6.55	6.50	6.45	6.38
naphthalene(w)	6.13	6.76	6.73	5.92	6.73	6.88	6.58	6.06
n-heptane(w)	7.59	6.14	6.22	6.74	6.11	6.47	6.01	7.80
n-hexane(w)	7.63	6.12	6.21	6.77	6.08	6.51	5.96	7.91
N, N-dimethyl-benzenamine(w)	5.38	5.85	5.94	6.37	5.82	5.65	5.81	4.99
n-octane(w)	7.67	6.03	6.14	6.77	5.98	6.38	5.84	7.67
n-pentane(w)	7.67	6.30	6.42	6.64	6.27	6.65	6.03	8.16
n-propylamine(w)	5.91	6.03	5.96	6.60	6.09	5.61	6.40	6.14
o-chloroaniline(a)	5.29	6.14	6.18	6.31	6.13	6.20	6.12	5.64
1-ethylbenzene(w)	6.81	6.64	6.61	6.12	6.65	6.64	6.58	6.53
1-(prop-1-en-2-yl)benzene(w)	6.28	6.60	6.53	6.12	6.64	6.79	6.71	6.18
o-toluidine(a)	5.15	5.92	6.02	6.37	5.87	5.79	5.79	5.32
o-xilene(w)	6.13	6.53	6.54	6.15	6.52	6.45	6.42	6.36
p-chloroaniline(a)	5.23	6.07	6.13	6.31	6.04	6.11	6.00	5.48
phenol(w)	6.67	6.42	6.36	6.23	6.47	6.41	6.60	6.04
p-toluidine(a)	5.09	5.99	6.13	6.27	5.92	5.82	5.72	5.27
p-xilene(w)	6.05	6.46	6.48	6.17	6.45	6.43	6.35	6.24
styrene(w)	6.42	6.74	6.67	6.01	6.76	6.94	6.74	6.24
toluene(w)	6.30	6.58	6.55	6.18	6.60	6.63	6.57	6.53
2-methylnaphtalene(w)	5.95	6.55	6.54	6.05	6.55	6.74	6.48	5.90
1-methyletanol(w)	7.47	6.14	6.10	6.65	6.14	6.11	6.29	6.94

Figure 1: Predicted vs. experimental values of the oxidation potential for the $\Delta E_{\text{ox}}^{\text{EEM}}$ (a), $\Delta E_{\text{ox}}^{\text{Marcus}}$ (b), $\Delta E_{\text{ox}}^{\text{Mendez}}$ (c), $\Delta E_{\text{ox}}^{=,\text{Mulliken}}$ (d), $\Delta E_{\text{ox}}^{\neq,\text{Mulliken}}$ (e), $\Delta E_{\text{ox}}^{=,\gamma}$ (f) and $\Delta E_{\text{ox}}^{\neq,\gamma}$ (g) models. The blue regions enclose the predicted values that differ from the experiments in less than 0.5 V.



(a) **(b)** **(c)**

(d) **(e)** **(f)**

(g)

Table 3. The fit parameters for the linear free energy relation, $\Delta E_{\mathrm{ox}} = m\varepsilon + b$ (Eq. (18)), for the different models for the electronegativity dependence, ε .

Method	*m* (eV/C)	*b* (V)	β	γ
$\Delta E_{\mathrm{oxd}}^{\mathrm{EEM}}$	0.706	3.443	-	-
$\Delta E_{\mathrm{oxd}}^{\mathrm{Marcus}}$	0.514	4.252	-	-
$\Delta E_{\mathrm{oxd}}^{\mathrm{Mendez}}$	-0.197	6.618	-	-
$\Delta E_{\mathrm{ox}}^{=,\mathrm{Mulliken}}$	0.398	3.066	-	-
$\Delta E_{\mathrm{ox}}^{\neq,\mathrm{Mulliken}}$	0.108	2.184	10.300	-
$\Delta E_{\mathrm{ox}}^{=,\gamma}$	0.486	2.287	-	0.051
$\Delta E_{\mathrm{ox}}^{\neq,\gamma}$	0.108	-0.534	9.451	1487.710

Table 4. Correlation coefficient (R^2), average error (AE), mean absolute error (MAE), standard deviation (STD), root mean square deviation (RMSD), maximum absolute error (MaxErr) and number of observations that differ from the experimental in more than 0.5 V (#>|0.5|) for all the methods considered, over the training set. All potentials are in volts.

Method	R^2	*AE*	*MAE*	*STD*	*RMSD*	*MaxErr*	*#>|0.5|*
ΔE_{ox}^{EEM}	0.1651	$-4.02*10^{-11}$	0.69	0.837	0.824	1.64	17
ΔE_{ox}^{Marcus}	0.1225	$-3.50*10^{-11}$	0.71	0.858	0.844	1.53	19
ΔE_{ox}^{Mendez}	0.0854	$-1.50*10^{-11}$	0.75	0.877	0.862	1.82	21
$\Delta E_{ox}^{=,Mulliken}$	0.1840	$-1.97*10^{-11}$	0.68	0.828	0.814	1.69	17
$\Delta E_{ox}^{\neq,Mulliken}$	0.2431	$-1.83*10^{-5}$	0.69	0.797	0.784	1.53	20
$\Delta E_{ox}^{=,\gamma}$	0.2184	$-4.10*10^{-6}$	0.64	0.810	0.797	1.83	14
$\Delta E_{ox}^{\neq,\gamma}$	0.8800	$-1.50*10^{-5}$	0.26	0.317	0.312	0.70	4

Table 5. The experimental absolute oxidation potential, $\Delta E_{\text{ox}}^{\text{exp}}$, along with the ionization energies and electron affinities the reduced ($I_{\text{R}}, A_{\text{R}}$) and oxidized ($I_{\text{O}}, A_{\text{O}}$) species in the training set, calculated using finite differences. The PCM solvent model is specified as either water (w) or acetonitrile (a). All energy values are in electron volts and the oxidation potential is reported in volts.

Reduced specie	$\Delta E_{\text{ox}}^{\text{exp}}$	I_{R}	A_{R}	I_{O}	A_{O}
4-CO_2-Me-biphenyl (a)	6.38	6.57	1.77	7.95	2.87
biphenyl (a)	6.23	6.35	1.05	7.82	2.36
tert-butylbenzene (a)	6.56	6.69	0.27	8.48	2.24
piperidine (a)	5.82	6.12	-1.25	8.44	-0.61
mesitylene (a)	6.33	6.50	0.10	8.06	2.35
dimethylsulfide (w)	5.94	6.05	-1.31	9.57	0.79
4-cyanophenol (w)	5.99	7.06	1.33	8.68	2.89
indole (w)	5.52	5.64	0.59	7.45	1.95
dimethyldisulfide (w)	5.67	5.39	0.53	7.89	2.28
thioanisole (w)	5.73	6.96	0.77	7.78	2.02

Table 6. Average error (AE), mean absolute error (MAE), standard deviation (STD), root mean square deviation (RMSD), maximum absolute error (MaxErr) and number of observations that differ from the experimental in more than 0.5 V (#>|0.5|) for all the methods considered, over the test set. All potentials are in volts.

Method	*AE*	*MAE*	*STD*	*RMSD*	*MaxErr*	*#>|0.5|*
ΔE_{ox}^{EEM}	0.38	0.27	0.374	0.519	0.97	4
ΔE_{ox}^{Marcus}	0.36	0.27	0.350	0.486	0.83	4
ΔE_{ox}^{Mendez}	0.23	0.21	0.460	0.491	0.92	3
$\Delta E_{ox}^{=,Mulliken}$	0.40	0.28	0.395	0.548	1.05	4
$\Delta E_{ox}^{\neq,Mulliken}$	0.43	0.36	0.695	0.789	1.46	5
$\Delta E_{ox}^{=,\gamma}$	0.44	0.30	0.407	0.586	1.16	5
$\Delta E_{ox}^{\neq,\gamma}$	0.10	0.31	0.502	0.487	1.04	2

From the data presented above it is evident that the quality of the predictions decreases notably if we use orbital energies in our calculations. This is to be expected, since we are using an approximated density functional, in which case there is no rigorous relation between the Kohn-Sham energies and the ionization potentials and electron affinities. This is particularly obvious for the approximation $A \approx -\varepsilon^{LUMO}$, since we are not taking into account the derivative discontinuity of the exchange-correlation functional. In fact, as we can see if we compare Tables 1 from the manuscript and this Supplementary Information, the biggest differences appear in the estimates of the electron affinities.

In this case, as shown in Table 4, the model $\Delta E_{ox}^{\neq,\gamma}$ outperforms all the other approaches. Nonetheless, this is most certainly a case of over fitting, due to the greater number of parameters present in this model. This is obvious if we analyze Table 6, where we see that the overall performance of all methods is, again, quite similar and far from the general accuracy obtained with the use of N-electron energies.

Besides the purely quantitative difficulties that this entails, these errors also have qualitative importance in some cases. For example, as can be seen in Table 1, if we use Kohn-Sham energies it is no longer evident that the reorganization energies are almost identical for the involved species. Moreover, one could erroneously assume that the seemingly equivalence between the studied methods is a consequence of the similar Parr-Pearson hardnesses. Other qualitative problem can be found in Table 3, where we see that the monotonic dependency of the oxidation potential with the electron affinity in $\Delta E_{\mathrm{oxd}}^{\mathrm{Mendez}}$ has reversed, with respect to that shown in Table 3 of the manuscript. The fact that this is the most affected model agrees with the fact that this is the model that depends the most on the electron affinities.

All these problems indicate that all the analysis presented in terms of approximated Kohn-Sham orbital energies should be taken with a grain of salt. In general, the picture of HOMO/LUMO orbitals at the time of studying redox reactions is quite useful from a qualitative point of view, but we have shown here that its quantitative scope is quite limited. Quantitative correlations obtained in this case are, in general, of poor value, and is certainly preferable to use ionization energies and electron affinities calculated using N-electron energies.