Simple and accurate correlation of experimental redox potentials and DFT-calculated HOMO/LUMO energies of polycyclic aromatic hydrocarbons.

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Abstract: The ability to accurately predict the oxidation and reduction potentials of molecules is very useful in various fields and applications. Quantum mechanical calculations can be used to access this information, yet sometimes the usefulness of these calculations can be limited because of the computational requirements for large systems. Methodologies that yield strong linear correlations between calculations and experimental data have been reported, however the balance between accuracy and computational cost is always a major issue. In this work, linear correlations (with an R^2 value of up to 0.9990) between DFT-calculated HOMO/LUMO energies and seventy redox potentials from a series of fifty-one polycyclic aromatic hydrocarbons (obtained from the literature) are presented. The results are compared to previously reported linear correlations that were obtained with a more expensive computational methodology based on a Born-Haber thermodynamic cycle. It is shown in this article that similar or better correlations can be obtained with a simple and cheaper calculation.

Keywords: HOMO, LUMO, reduction, oxidation, linear correlation

I. Introduction

Determination of the reduction and oxidation potentials of a given molecule at an interface is important in many research areas such as dye sensitized solar cells (DSSC), organic photovoltaics (OPV), and artificial photosynthesis, where tuning the thermodynamic properties of every component of a system is essential for it to work in

the desired way [1-6]. The perturbation of the HOMO and LUMO energies (HLE) is also of interest in the context of designing both novel and efficient molecules for harnessing solar energy in artificial photosynthesis and photocatalysis [3-6]. Ideally one would like to know with accuracy the redox properties of a compound of interest before embarking on an often difficult, expensive and time-consuming synthetic procedure.

The simplest way to rationalize an approximate linear relationship between HLE and oxidation/reduction potentials is to consider the Marcus Relation for interfacial electron transfer

$$\Delta G^{\#} = \frac{\left(\Delta_r G^0 + \lambda\right)^2}{4\lambda}$$
(**1**)

where $\Delta G^{\#}$ is the free energy of activation and $\Delta_r G^o$ and λ are the reaction free energy and the total reorganization energy, respectively. Solving for $\Delta_r G^0$ in equation (**1**) gives

$$\Delta_r G^0 = \sqrt{4\lambda\Delta G^{\#}} - \lambda$$
(**2**)

Further we introduced the thermodynamic relation between $\Delta_r G^o$ and the electrochemical cell potential

$$\Delta_r G^0 = -nF(E - E^0)$$
(**3**)

The reorganization energy is generally decomposed into two contributions, λ_i and λ_0, coming from the molecule and from the solvent, respectively

$$\lambda = \lambda_i + \lambda_o$$
(4)

This decomposition leads to the following equation

$$\Delta_r G^0 = \sqrt{4(\lambda_i + \lambda_o)\Delta G^{\#}} - \lambda_o - \lambda_i \tag{5}$$

Up to this point equation (**5**) is formally exact. To proceed, one has to invoke that in many reactions $\lambda_i = \lambda_o$ [7] and that the first two terms in (**5**) are approximately constant within a family of chemically related molecules, while λ_i is proportional to the energy of the HOMO or the LUMO depending on whether oxidation or reduction is considered [8]. Combining these two approximations and using equations (**3**) and (**5**) leads to the linear relationship

$$E_{OX/RED} = a + b\varepsilon_{HOMO/LUMO} \tag{6}$$

where $E_{OX/RED}$ is the experimental redox potentials, $\varepsilon_{HOMO/LUMO}$ the calculated HLE, and a and b are constants.

Maccoll showed for the first time in 1949 that a good correlation could be obtained between Huckel LUMO energies and experimental reduction potentials [9]. Nevertheless, in the computational electrochemistry literature [10-12], efforts to predict redox potentials steer away from this methodology mainly because of the assumptions involved (e.g. molecular and solvent reorganization energies are not included in the calculation). Instead, a Born-Haber thermodynamic cycle is preferred as the free energies are directly calculated and solvation energies are accounted for, which are significant as has been observed when electrochemistry is done under different solvents and conditions [13]. Unfortunately, the main drawback for this methodology is that when applied to large molecules (e.g. polycyclic aromatic hydrocarbons (PAHs), porphyrins, phthalocyanines) the computations are very expensive.

To resolve this issue, Fry *et al*. have reported a methodology that accurately predicts the redox potentials of PAHs with a simplified approach to the Born-Haber thermodynamic cycle [14]. This methodology involves the optimization of molecules in both the ground state and the reduced or oxidized state (radical anion or radical cation respectively) with a

continuum based solvent model in order to account for reorganization energies. This approach removes the optimization step in the gas phase that is part of the Born-Haber thermodynamic cycle, thus decreasing the number of calculations, from six to three (in order to obtain both oxidation and reduction potentials). This methodology was tested with fifty-one PAHs, whose experimental redox potentials (which were obtained from the literature) were measured under similar conditions. They were able to obtain a very strong correlation, up to $R^2 = 0.9981$, between the calculated and the experimental values.

Before Fry, in 2008, Gillmore *et al.* introduced a further simplified methodology. It consists of a molecular energy optimization in gas phase, followed by a single point calculation in the presence of a continuum solvent model [15]. This increases again the number of calculations to six (in order to obtain both oxidation and reduction potentials), but the computational time is reduced because four of them (the ones that involve the solvent) are single point calculations. They found a very good correlation between the calculated energy difference and the reduction potentials of quinones, cyanoaromatics and N-metyl heteroaromatic cations [15], and later expanded their methodology to PAHs, flexible aromatic molecules and heterocyclic amines [16].

In searching for a methodology to calculated redox potentials accurately and that is computationally less expensive than Gillmore's approach but at least as accurate as Fry's, reported herein is a good correlation between HLE (calculated at the DFT level using the B3LYP/6-31G(d) functional) and experimental redox potentials. This follows Maccoll's methodology and significantly reduces the complexity of the required calculations. The advantage of this approach is that just one optimization calculation is required, thus it can be applied to large molecules with a relatively low computational cost.

II. Computational method

To test this methodology and compare it to previously reported correlations, the library of PAHs collected by Fry *et al.* [14], which include data from six different references, was used. The literature redox potentials were measured in acetonitrile and are reported in V vs. ferrocene/ferrocenium (Fc/Fc$^+$), which was used as an internal reference.

All PAHs were optimized using Gaussian 09 [17] at the B3LYP/6-31G(d) level of theory [18-23] in the gas phase and in the presence of acetonitrile simulated using the Conductor-like Polarizable Continuum Model (CPCM) [24-25]. The calculated HLE were plotted against the experimental oxidation and reduction potentials respectively.

III. Results

Plots for the calculated HLE of a series of fifty-one PAHs against their experimental oxidation and reduction potentials are shown in **Figure 1** and **2**. When using acetonitrile as the solvent a very strong correlation (R^2=0.9989) is observed between the calculated and experimental values. It is noteworthy that there is also a very strong correlation between HLE and redox potentials when the molecules are optimized in the gas phase (R^2=0.9990). The reason why this is true in this specific case is because solvent reorganization energies are very similar for the set of PAHs under study, resulting in a cancelation of the error obtained by not including the solvent in the calculation. A summary of the results obtained from the method used in this work as well as the results obtained by Fry *et al.* can be found in **Table 1.**

The correlations obtained with the method used in this paper are comparable or better than the ones obtained by Fry. When analyzing the oxidation and reduction potentials together Fry obtained a mean absolute deviation (MAD) of 0.056 V while we get a MAD of 0.046 V. When the data is split in two sets (only reduction or oxidation potentials), Fry's correlation is better than ours for both reductions and oxidations, but the error is of the same order of magnitude for both approaches. In general, both methods are in very good agreement with the experimental values, our method having the advantage that it consists of only one optimization rather than three.
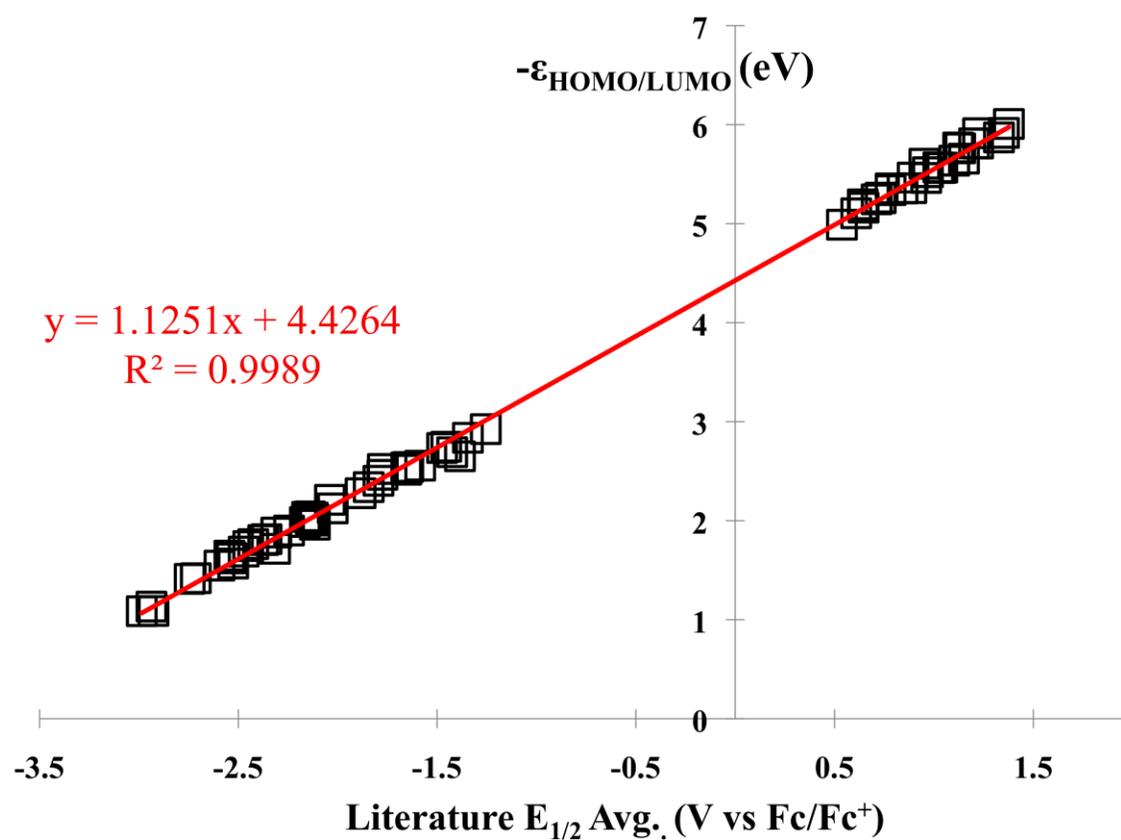
Fig. 1 Plot of computed HOMO/LUMO energies (eV) using acetonitrile as the solvent vs. experimental $E_{1/2}$ avg. obtained from [14] and references therein.
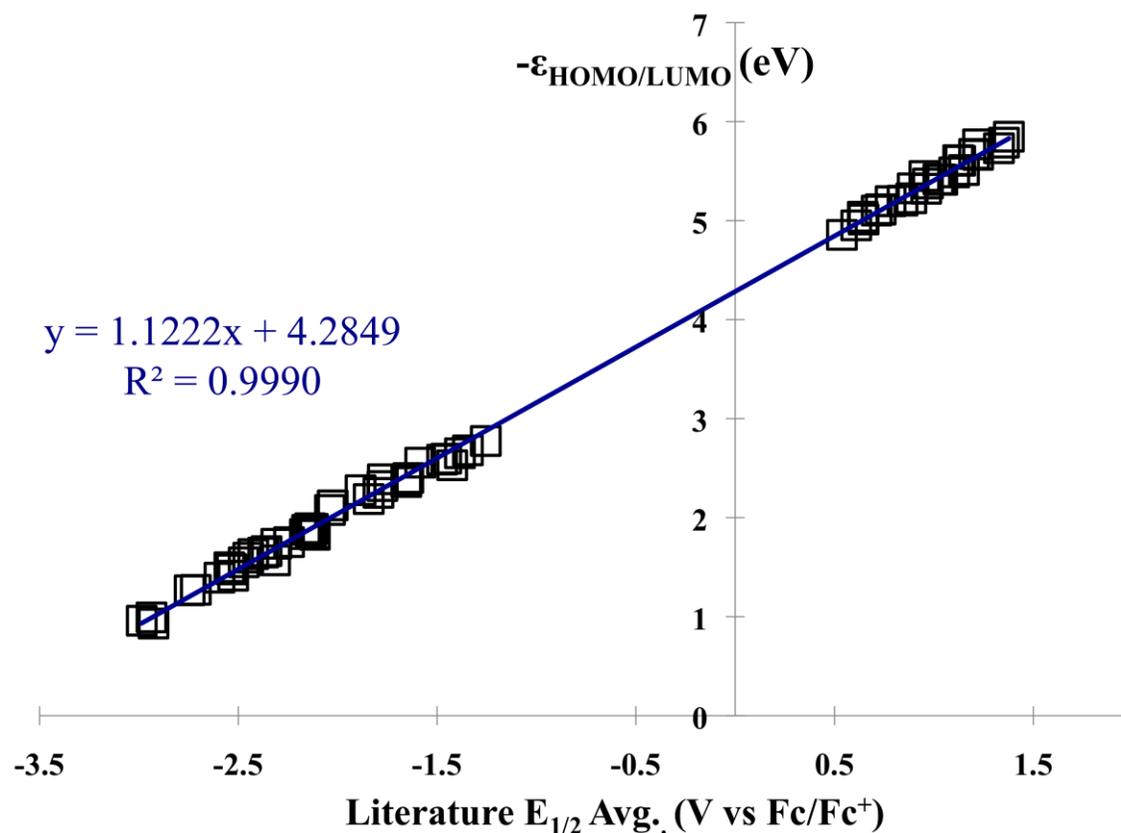
Fig. 2 Plot of computed HOMO/LUMO energies (eV) in the gas phase vs. experimental $E_{1/2}$ avg. obtained from [14] and references therein.

This work		slope (eV/V)	y-intercept (eV)	R^2	MAD (V)	RMSD[a] (V)	x-intercept[b] (V)
acetonitrile	All	1.1251	4.4264	0.9989	0.046	0.058	-3.93
	Oxidation	1.1288	4.4311	0.9700	0.037	0.047	-3.93
	Reduction	1.0444	4.2499	0.9882	0.039	0.053	-4.07
gas phase	All	1.1222	4.2849	0.9990	0.046	0.056	-3.82
	Oxidation	1.1318	4.2813	0.9740	0.035	0.043	-3.78
	Reduction	1.0658	4.1616	0.9864	0.044	0.058	-3.90
Reference [14]							
	All	0.8591	4.442	0.9981	0.056	---	-5.17
	Oxidation	1.073	4.227	0.9847	0.032	---	-3.94
	Reduction	0.947	4.64	0.9924	0.023	---	-4.90

Table 1. Summary of the results from the linear correlations. a) Root-mean-square deviation b) calculated with x-intercept $= -b/a$.

IV. Conclusions

A very strong linear correlation of DFT-calculated HLE and redox potentials of PAHs is shown. It is important to emphasize that only one optimization calculation per molecule is required to obtain both HLEs. In contrast, at least three (and up to six) optimizations per molecule are required to obtain a theoretical approximation of the potentials by the other methods described above. This can be a powerful tool to use when one needs to quickly and accurately predict oxidation and reduction potentials of new compounds given that one have a series of similar compounds whose redox potential are already known.

The strong correlation obtained from HLE and redox potentials of PAHs was independent of whether the solvent model was included in the calculations. This may not be the case when including in the correlation other groups of molecules that have different solvent reorganization energies. For future work this methodology will be extended to quinones, cyanoaromatics, porphyrins, phthalocyanines and perylenes.

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