Conceptual Density Functional Theory: Redox Reactions Revisited
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Outline

1. Introduction: Chemical Concepts from DFT
2. Redoxpotentials of $\text{Me}^{n+}/\text{Me}^{(n-1)+}$ couples: the role of electrophilicity.
3. An EEM approach based on the Grand Canonical Ensemble Theory
4. Some disgressions about vertical quantities
5. Conclusions
6. Acknowledgements
1. Introduction: Chemical Concepts from DFT

Fundamentals of DFT: the Electron Density Function as Carrier of Information

Hohenberg Kohn Theorems  

ρ(r) as basic variable

- ρ(r) determines N (normalization)
- "The external potential v(r) is determined, within a trivial additive constant, by the electron density ρ(r)"

![Diagram](image)
\[ \rho(r) \rightarrow H_{op} \rightarrow E = E[\rho] = \int \rho(r)v(r)dr + F_{HK}[\rho(r)] \]

- Variational Principle

\[ v(r) + \frac{\delta F_{HK}}{\delta \rho(r)} = \mu \]

\[ F_{HK} \text{ Universal Hohenberg Kohn functional} \]

\[ \text{Lagrangian Multiplier} \]

\[ \int \rho(r)dr = N \]

- Practical implementation: Kohn Sham equations

\[ \text{Computational breakthrough} \]

That branch of DFT aiming to give precision to often well known but rather vaguely defined chemical concepts such as electronegativity, chemical hardness, softness, ..., to extend the existing descriptors and to use them to describe chemical bonding and reactivity either as such or within the context of principles such as the Electronegativity Equalization Principle, the HSAB principle, the Maximum Hardness Principle ...

Starting with Parr's landmark paper on the identification of \( \mu \) as (the opposite of) the electronegativity.
Starting point for DFT perturbative approach to chemical reactivity

Consider $E = E[N, v]$ Atomic, molecular system, perturbed in number of electrons and/or external potential

$$dE = \left( \frac{\partial E}{\partial N} \right)_{v(r)} dN + \int \left( \frac{\delta E}{\delta v(r)} \right)_{N} \delta v(r) dr$$

Identification first order perturbation theory

$\mu$

Identification

$\rho(r)$


$$= - \chi \text{ (Iczkowski - Margrave electronegativity)}$$
Identification of two first derivatives of E with respect to N and v in a DFT context → **response functions** in reactivity theory

\[
\begin{align*}
E[N,v] & = \mu \\
\left( \frac{\partial E}{\partial N} \right)_{v(r)} & = \mu \\
\left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)} & = \eta \\
\left( \frac{\partial E}{\partial v(r)} \right)_{N} & = \rho(r) \\
\left( \frac{\partial^2 E}{\partial v(r) \partial v(r')} \right)_{N} & = \chi(r,r')
\end{align*}
\]

**Chemical hardness**

\[
S = \frac{1}{\eta} 
\]

**Chemical Softness**

**Fukui function**

**Linear response Function**

\[
Sf(r) = s(r)
\]

**Local softness**
Combined descriptors


energy lowering at maximal uptake of electrons

\[ \Delta E = -\frac{\mu^2}{2\eta} = -\omega \]

Reviews :


• P. Geerlings, F. De Proft, PCCP, 10, 3028 (2008)
Applications until now mostly on (generalized) acid base reactions

- acid/base (Arrhenius, Brønsted-Lowry)
- generalized acid base (Lewis) → complexation reactions
- organic chemistry
  - electrophilic/nucleophilic
  - substitution/addition/elimination

Use of Principles

- EEP (Electronegativity Equalization Principle)
- HSAB (Hard and Soft Acids and Bases Principle; global/local)
- MHP (Maximum Hardness Principle)
Not or nearly not discussed with Conceptual DFT

- Pericyclic Reactions (WATOC talk)

- Redox Reactions

Today’s talk
2. Redox potential of $\text{Me}^{n+}/\text{Me}^{(n-1)+}$ complexes: the role of electrophilicity

- Redox reactions are the Archetypes of reactions involving a change in the number of electrons $\longrightarrow$ perturbative approach $E = E[N,v]$

- Appoprate descriptor?


- Local version?

  Systems: $\text{Me}^{3+}/\text{Me}^{2+}(aq)$ redox couples

  First row transition metals: Sc $\rightarrow$ Zn
\( \omega = \text{electrophilicity} \)

= energy lowering at maximal uptake of electrons

\[
\Delta E = -\frac{\mu^2}{2\eta} = -\omega
\]

Interaction with a perfect electron donor

**Quadratic model of Energy versus \( N \)**
• Quadratic model:

\[ \omega = \frac{\mu^2}{2\eta} = \frac{(I + A)^2}{8(I - A)} = A + \frac{(I - 3A)^2}{8(I - A)} \]

\[ \Delta N_{ideal} = -\frac{\mu}{\eta} = \frac{(I + A)}{2(I - A)} \]

• \( \text{Me}^{3+} \): highly prone to electron uptake \( \Delta N_{ideal} \gg 1 \)

\[ \implies \text{System readily accepts more than one electron} \]

\[ \Downarrow \text{Use of } \omega_{Scaled}: \]

\[ \omega_{Scaled} = \frac{2\omega}{1 + \Delta N_{ideal}} \]
• System in aqueous solution
  • First (6) and second (12) solvation sphere
  • PCM

First solvation sphere

First +second solvation sphere
## Correlation analysis $E^\circ$ vs. $\omega$

<table>
<thead>
<tr>
<th>Correlation Coefficient $R^2$</th>
<th>Gas</th>
<th>6 H$_2$O</th>
<th>6 H$_2$O + PCM</th>
<th>18H$_2$O</th>
<th>18 H$_2$O + PCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega$</td>
<td>0.76</td>
<td>0.88</td>
<td>0.76</td>
<td>0.87</td>
<td>0.79</td>
</tr>
<tr>
<td>$\omega_{Scaled}$</td>
<td>0.83</td>
<td>0.95</td>
<td>0.95</td>
<td>0.90</td>
<td>0.91</td>
</tr>
</tbody>
</table>
Absolute values of $E^\circ_{Abs}$ versus $\omega_{Scaled}$ for metal ions embedded in PCM and a first solvation sphere.

$E^\circ_{Abs} = 0.99 \omega_{Scaled}$

$R^2 = 0.94$

- Low spin $\text{Co}^{3+}$ & $\text{Ni}^{3+}$
Local Level (e.g. Fe$^{3+}$/Fe$^{2+}$)

\[ \omega_k = \omega f_k^+ \quad \text{Local electrophilicity (} f^+ \text{: electron uptake)} \]

<table>
<thead>
<tr>
<th></th>
<th>Bare atom</th>
<th>6 H$_2$O First solvation sphere</th>
<th>12 H$_2$O Second solvation sphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge (NPA)</td>
<td>2.136</td>
<td>0.240</td>
<td>0.625</td>
</tr>
<tr>
<td>Fukui function $f^+$</td>
<td>0.524</td>
<td>0.324</td>
<td>0.152</td>
</tr>
</tbody>
</table>

- Two electrophilic regions
  - Central metal ion
  - First solvation sphere

- Second solvation sphere: “take-and-give”, acts as a continuum
<table>
<thead>
<tr>
<th></th>
<th>Bare atom</th>
<th>6 H₂O</th>
<th>12 H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>First solvation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sphere</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second solvation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sphere</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Local ω</strong></td>
<td>0.263</td>
<td>0.163</td>
<td>0.076</td>
</tr>
<tr>
<td>(ω⁺)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Graph showing the local philicity of transition metal cations](image)
• Local electrophilicity (condensed) $\omega_k^+$

• Additive $\sum_k \omega_k^+ = \omega$

Group Philicity

$$\omega_{\text{group}} = \omega_{\text{Metal}} + \sum_i \omega_{\text{First shell }, i}$$

• Completely mimics the redox potential ($R^2=0.90$)

3. An EEM Approach based on the Grand Canonical Ensemble Theory

Previous Approach
- Electrophilicity: interaction between a system and a perfect electron donor ⇒ ideal system with zero chemical potential.
- Now: simulation of chemical environment of oxidized and reduced species by an electron bath with constant chemical potential $\mu_{\text{electrode}} = \text{electrode in experimental electrochemistry}$
- Open systems: exchange of electrons when $\mu_{\text{electrode}}$ is changed

Grand Potential $\Omega = \Omega[\rho(r)] = A[\rho(r)] - \mu_{\text{electrode}}N$

$A =$ Helmholtz free energy functional

Equilibrium $\left(\frac{\partial \Omega}{\partial N}\right)_{T,V} = 0$  $\iff$ $\left(\frac{\partial A}{\partial N}\right)_{T,V} = \mu_{\text{electrode}}$

$\mid T=0$

$\left(\frac{\partial E}{\partial N}\right)_{T,V} = \mu_{\text{electrode}}$
Second order model $\mu = \mu^0 + \eta^0 \Delta N$

Oxidized species \hspace{1cm} Reduced species

Equilibrium point:

$\mu_{\text{ox}} = \mu_{\text{electrode}} = \mu_{\text{ox}}^0 + \eta_{\text{ox}}^0 \Delta N_{\text{ox}}$

$\mu_{\text{red}} = \mu_{\text{electrode}} = \mu_{\text{red}}^0 + \eta_{\text{red}}^0 \Delta N_{\text{red}}$

with $\Delta N_{\text{ox}} = -\Delta N_{\text{red}} = \frac{\mu_{\text{red}}^0 - \mu_{\text{ox}}^0}{\eta_{\text{red}}^0 + \eta_{\text{ox}}^0}$

Cfr. Electronegativity, Equalization
\[ \mu_{\text{electrode}} = \frac{\mu_{\text{ox}}^0 \eta_{\text{red}}^0 + \mu_{\text{red}}^0 \eta_{\text{ox}}^0}{\eta_{\text{ox}}^0 + \eta_{\text{red}}^0} \]

Now, \( \mu_{\text{electrode}} \) : change in Helmholtz Free Energy at 0K \( \cong \) Gibbs Free Energy related to one-electron half reaction

\[ E^0 = -\frac{\mu_{\text{electrode}}}{F} - E^0_{\text{NHE}} \]

One-electron redox potential for 44 different organic and inorganic systems:
- aliphatic group (acetonitril (PCM)) (12)
- aromatic group (acetonitril (PCM)) (16)
- aniline group (water(PCM)) (7)
- inorganic systems: First row transition metal ions (18 \( \text{H}_2\text{O} + \text{water(PCM)} \)) (9)

• Remarkable accuracy is achieved based on solely vertical quantities (I and A used to evaluate \( \mu^0 \) and \( \eta^0 \) of oxidized and reduced species) and neglecting entropic and thermal contributions.
• No problems with scaling of highly electrophilic species as in previous method.
4. Some disgression about vertical quantities

- More common approach in the calculation of redox potentials is a Thermodynamic cycle: linking processes in gas phase and solution
  - Treatment of solvent effects during the electron transfer processes
  - Accurate determination of solvation energy of reduced and oxidized species
  - Electron transfer takes place rapidly $\iff$ geometric relaxation after the electron transfer

- Electron uptake / loss step
- Reorganization step

- How can the vertical quantities I and A used in the first method be exploited in this approach?
\[ \Delta E_{\text{red}} = E_{\text{red/Red}} - E_{\text{Ox/Ox}} = -A_{\text{Ox}} + \Delta E_{\text{Reorg.2}} \]

\[ \Delta E_{\text{Ox}} = E_{\text{Ox,Ox}} - E_{\text{Red,Red}} = +I_{\text{Red}} + \Delta E_{\text{Reorg.1}} = -\Delta E_{\text{Red}} \]

\[ \Delta E_{\text{reorg.1}} + \Delta E_{\text{reorg.2}} = A_{\text{Ox}} - I_{\text{Red}} \]

**Hypothesis**

\[ \Delta E_{\text{reorg.1}} = \Delta E_{\text{reorg.2}} \]

\[ \Delta E_{\text{reorg}} = \frac{1}{2} \left( A_{\text{Ox}} - I_{\text{Red}} \right) \]

\[ \Delta E_{\text{Red}} = -I_{\text{Red}} - \frac{1}{2} \left( A_{\text{Ox}} - I_{\text{Red}} \right) \]

\[ \Delta E_{\text{Red}} = -A_{\text{Ox}} + \frac{1}{2} \left( A_{\text{Ox}} - I_{\text{Red}} \right) \]

\[ \Delta E_{\text{Red}} = -\frac{1}{2} \left( A_{\text{Ox}} + I_{\text{Red}} \right) = -\Delta E_{\text{Ox}} \]

→ Reduction/Oxidation process can be approximated by **vertical** electron affinity and ionization energy taking into account a constant reorganisation term, identical for oxidation and reduction.
$E^0 = -\frac{\Delta E_{\text{Red}}}{F} - E_{\text{NHE}}^0$

Slope close to unity deviating only by 5%
Avoiding the hypothesis \( \Delta E_{\text{reorg},1} = \Delta E_{\text{reorg},2} \)

\[
\mu_{\text{electrode}} = \frac{\mu_{\text{ox}}^0 \eta_{\text{red}}^0 + \mu_{\text{red}}^0 \eta_{\text{ox}}^0}{\eta_{\text{ox}}^0 + \eta_{\text{red}}^0}
\]

\[
\Delta E_{\text{red}} = -\frac{1}{2} (A_{\text{ox}} + I_{\text{red}})
\]

Split up \( \mu_{\text{electrode}} = -I_{\text{red}} - \Delta E_{\text{reorg},1} \) \( \Rightarrow \) \( \Delta E_{\text{reorg},1} = \frac{2\eta_{\text{red}}^0}{\eta_{\text{ox}}^0 + \eta_{\text{red}}^0} \Delta E_{\text{reorg}} \)

\[
\mu_{\text{electrode}} = -A_{\text{ox}} + \Delta E_{\text{reorg},2} \]

\( \Rightarrow \)

\( \Delta E_{\text{reorg},2} = \frac{2\eta_{\text{ox}}^0}{\eta_{\text{ox}}^0 + \eta_{\text{red}}^0} \Delta E_{\text{reorg}} \) \( \ast \)

As \( \eta_{\text{red}}^0 \neq \eta_{\text{ox}}^0 \) \( \rightarrow \) difference between two reorganization energies

\[
\text{Different } E = E[N] \text{ curves for oxidized and reduced species}
\]

It turns out that the reorganization energy of the oxidized species is largely underestimated (compare with exact adiabatic calculations)
\[ \Delta E_{\text{reorganization}} = 0.668 \cdot (\text{Equation (*)}) - 0.174 \text{ eV} \]

\[ R^2 = 0.632 \]

Reorganization Energy Oxidized Species
Solution

- Refinement of the $E = E[N]$ curves for oxidized and reduced species


\[
\mu^+ = -\frac{1}{4}(I + 3A) \quad \text{Electron uptake; right derivative, more emphasis on A}
\]

\[
\mu^- = -\frac{1}{4}(3I + A) \quad \text{Electron release; left derivative, more emphasis on I}
\]
\[ \Delta E_{\text{reorganization};1} = \frac{\mu_{\text{red}}(A_{\text{ox}} - I_{\text{red}})}{\mu_{\text{ox}} + \mu_{\text{red}}} \] (eV)

\[ R^2 = 0.938 \]

Insertion in $\Delta E_{\text{reorg}}$ (justification: $\mu^\pm$ instead of $\eta$)

\[ \Delta E_{\text{reorg},1} = \frac{2\mu_{\text{red}}}{\mu_{\text{ox}} + \mu_{\text{red}}} \Delta E_{\text{reorg}} \]

\[ \Delta E_{\text{reorg},2} = \frac{2\mu_{\text{ox}}^+}{\mu_{\text{ox}}^+ + \mu_{\text{red}}^-} \Delta E_{\text{reorg}} \]
Insertion

\[ \mu_{\text{electrode}} = -I_{\text{red}} - \Delta E_{\text{reorg},1} \]

\[ = -A_{\text{ox}} + \Delta E_{\text{reorg},2} \]

\[ \Delta E_{\text{reorg},1} = \frac{2\mu^-_{\text{red}} \Delta E_{\text{reorg}}}{\mu^+_{\text{ox}} + \mu^-_{\text{red}}} = \frac{2\mu^-_{\text{red}} (A_{\text{ox}} - I_{\text{red}})}{\mu^+_{\text{ox}} + \mu^-_{\text{red}}} \]

with

\[ \begin{align*}
\mu^+_{\text{ox}} &= -\frac{1}{4}(I_{\text{ox}} + 3A_{\text{ox}}) \\
\mu^-_{\text{red}} &= -\frac{1}{4}(3I_{\text{red}} + A_{\text{red}})
\end{align*} \]

(No problem with stability of cations)
Excellent correlation
Slope still only 5% deviating from 1

Individual reorganization energy for oxidized and reduced form show fair correlation with exact adiabatic values.

\[ E^\circ_{\text{expt.}} = 1.052 E^\circ_{\text{calc.}} + 0.184 \text{ V} \]
\[ R^2 = 0.958 \]
5. Conclusions

• Conceptual DFT offers a framework for the interpretation of redox chemistry

• The **electrophilicity** turns out to be a key descriptor to get insight into the redox behaviour of $\text{Me}^{n+}/\text{Me}^{(n-1)+}$ couples and gives quantitative information about a system’s ability to accept 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 disgression about **vertical quantities** $(A,I)$ combined with Gazquez’s recent expressions for $\mu^+$ and $\mu^-$ leads to an excellent correlation between calculated and experimental Redox potentials with fair account for reorganisation effects.
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