2269-25

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

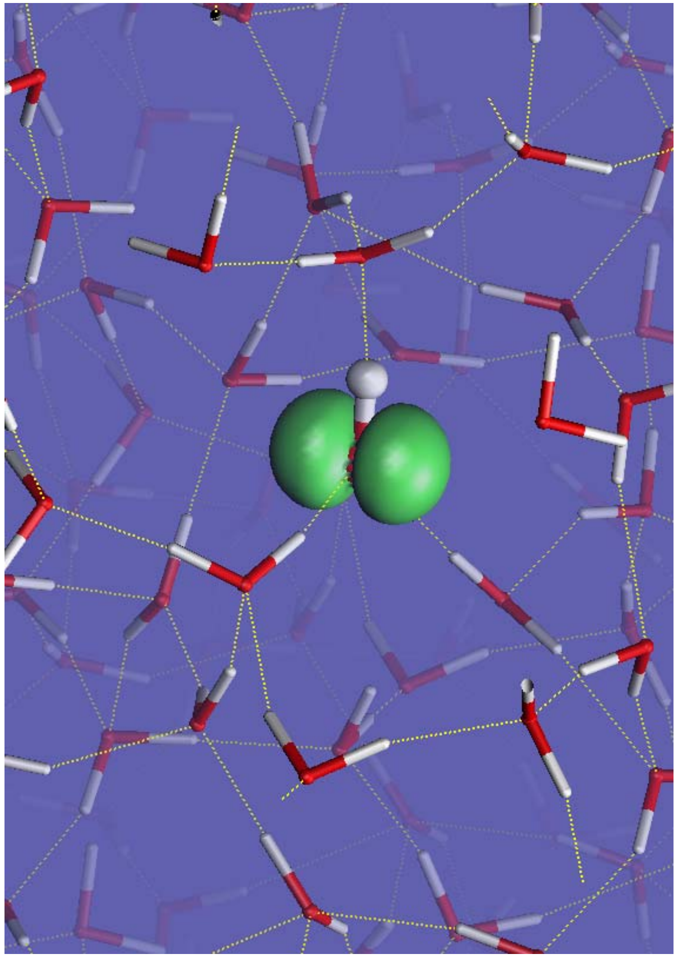
All-atom density functional thoery of the O2 Latimer series of dioxygen

Michiel SPRIK

Dept. of Chemistry, University of Cambridge
U.K.

All-atom DFT of the O_2 Latimer series

using a molecular dynamics normal hydrogen electrode



Collaboration:

Jun Cheng

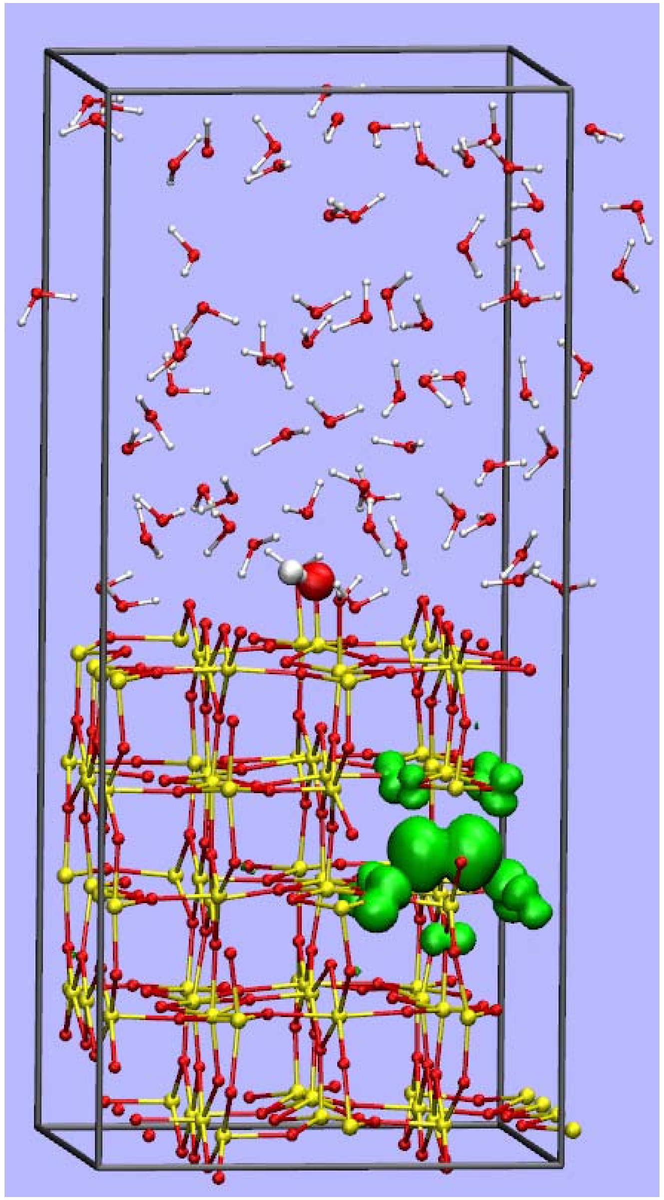
Marialore Sulpizi

Joost VandeVondele

***Funding:* EPSRC, UKCP**

Department of Chemistry
University of Cambridge

Motivation: formation of a surface hydroxyl group



Oxidative dehydrogenation of water

$$*\mathrm{OH}_2 \rightarrow *\mathrm{OH}^{\bullet} + \mathrm{H}^{+} + e^{-}$$

Hole trapping by surface hydroxide

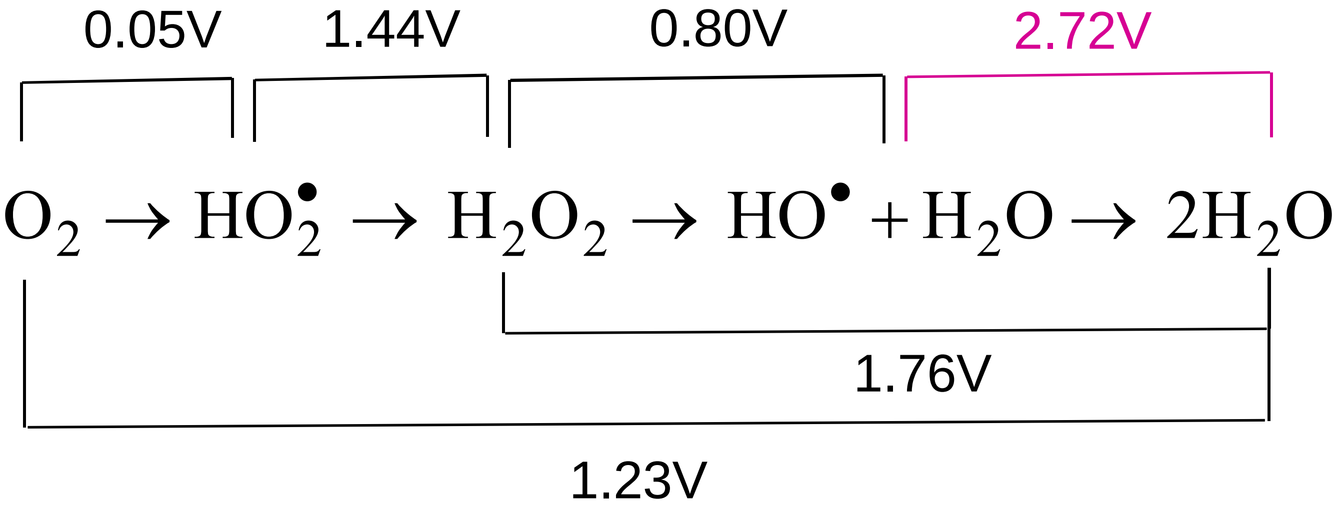
$$\boxed{*\mathrm{OH}^{-} + \mathrm{h}^{+} \rightarrow *\mathrm{OH}^{\bullet}}$$

Spin density in TiO_2

(*Jun Cheng*)

Reduction O_2 ↔ oxidation H_2O in solution

Successive addition/removal of ***e***$^-$ and **H**$^+$.



0.05V 1.44V 0.80V 2.72V

$$\mathrm{O_2 \rightarrow HO_2^{\bullet} \rightarrow H_2O_2 \rightarrow HO^{\bullet} + H_2O \rightarrow 2H_2O}$$

1.76V

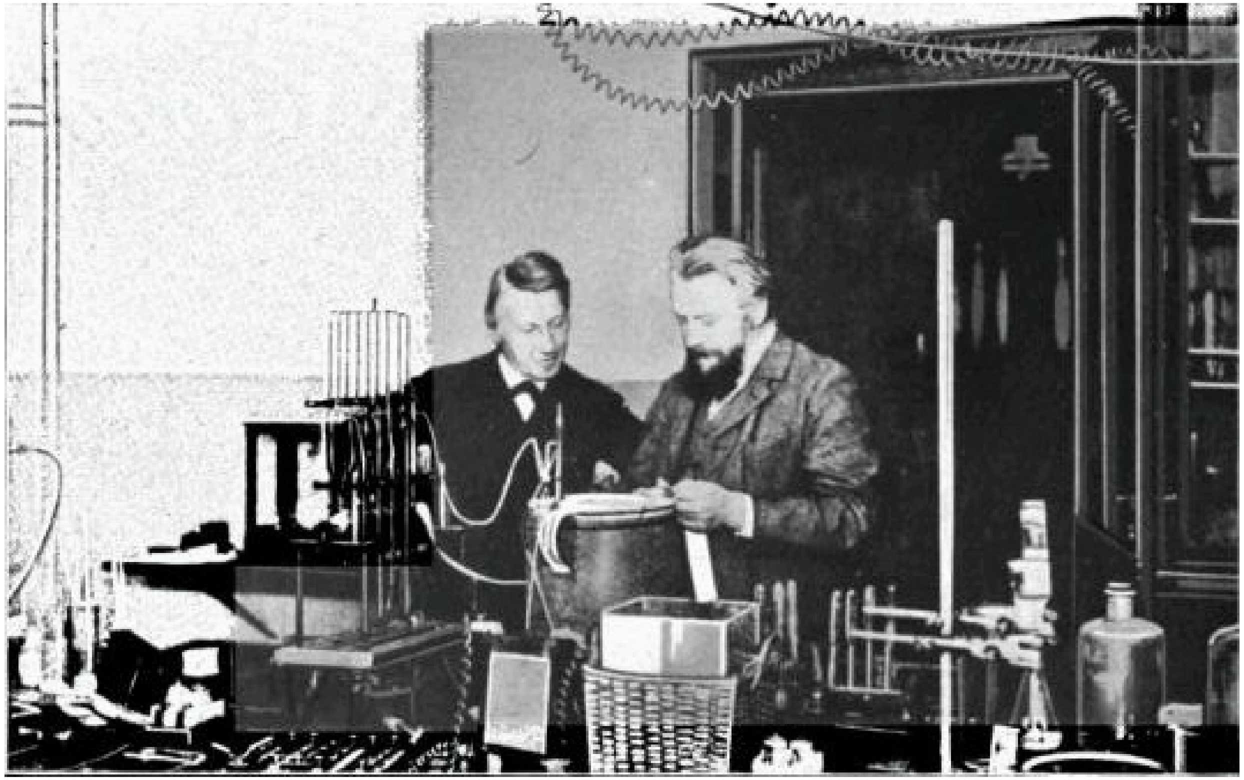
1.23V

$$\boxed{E^{o} = -\frac{\Delta G^{o}}{Fn}}$$

First H abstraction the most costly

Interfacial Electrochemistry:

Is molecular simulation finally ready for 19th century science?



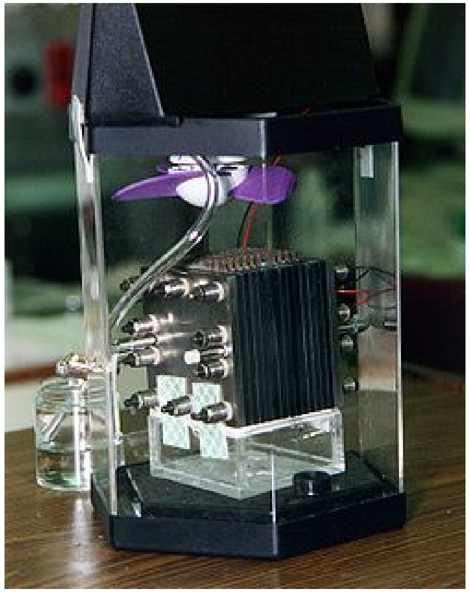
Ostwald and van’t Hoff
Founding fathers of
Physical Chemistry

Electrochemistry in the 19th century: highlights

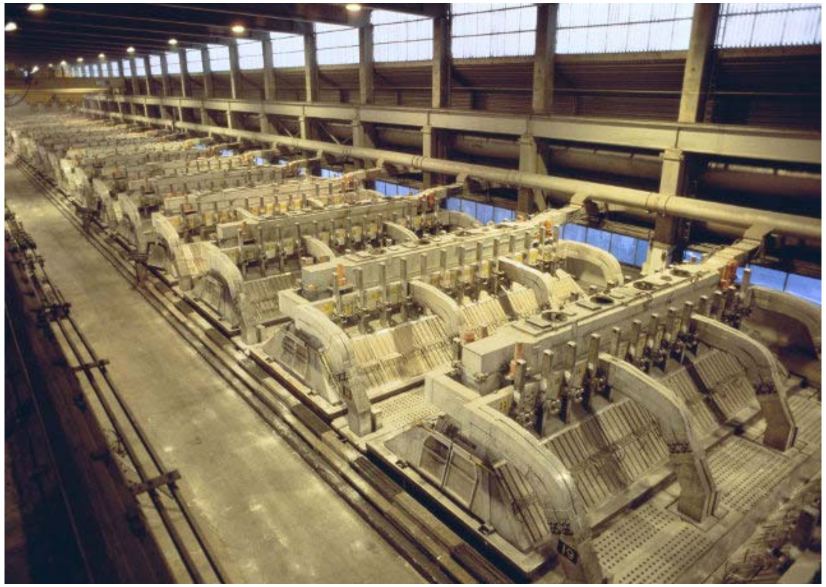
Volta	1800	Volta pile, first electrochemical device
Nicholson and Carlisle	1800	Electrolysis of water
Von Grotthuss	1805	Mechanism of conductance
Faraday	1834	Laws of electrolysis
Daniell	1836	Chemical cells
Grove	1839	Fuel Cells
Hittorf	1853	Migration of ions
Clausius	1857	Existence of free ions
Kohlrausch	1869	Conductance-concentration relationships
Helmholtz	1871	Fixed double layer
Lippmann	1873	Electrocapillary effect
Planté	1879	Storage battery
Ostwald	1883	Definition of electrode potential
Van ‘t Hoff	1887	Osmotic pressure of electrolyte solutions
Arrhenius	1888	Electrolytic dissociation
Tafel	1905	Overvoltage

What is Electrochemistry?

Chemical reactions generating electricity
and electricity driving chemical reactions



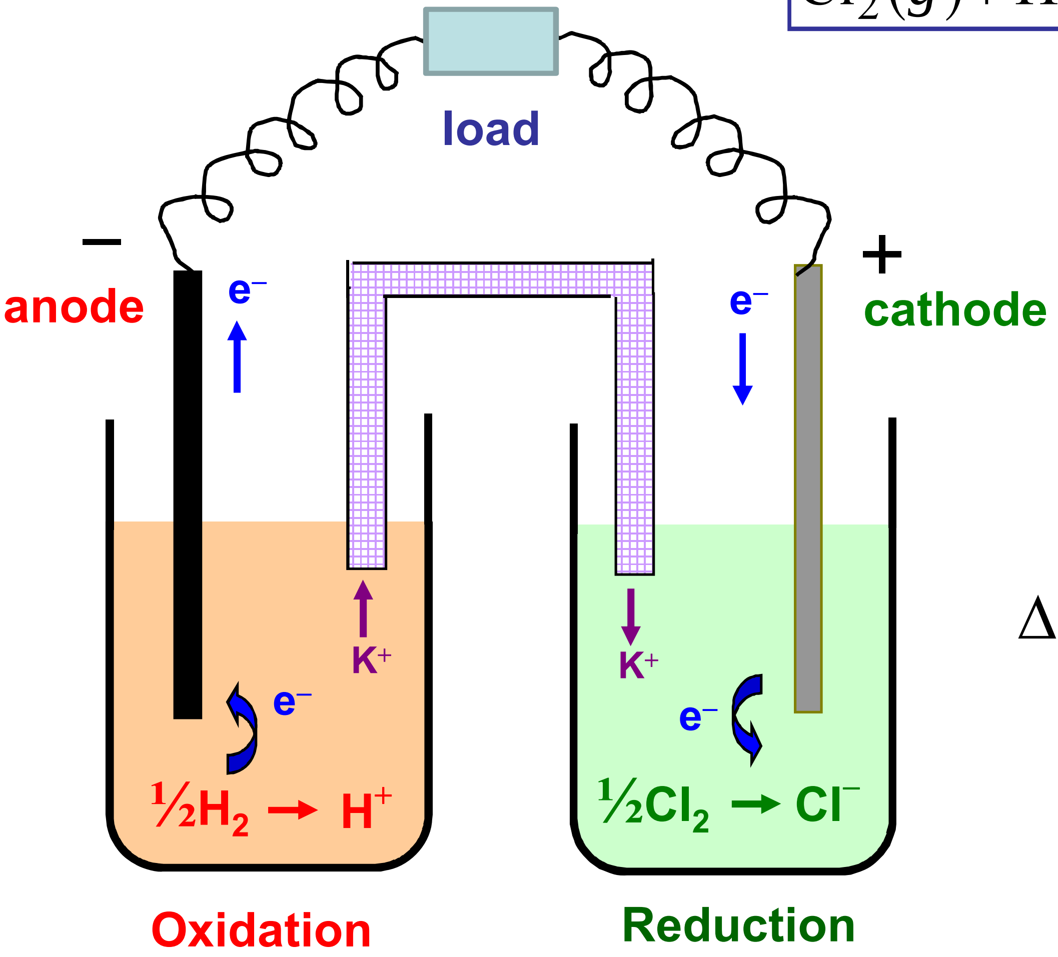
Direct methanol fuel cell



Industrial electrolysis of aluminium oxide

Chemical reactions generating electricity

$$\boxed{Cl_2(g) + H_2(g) \rightarrow 2Cl^-(aq) + 2H^+(aq)}$$



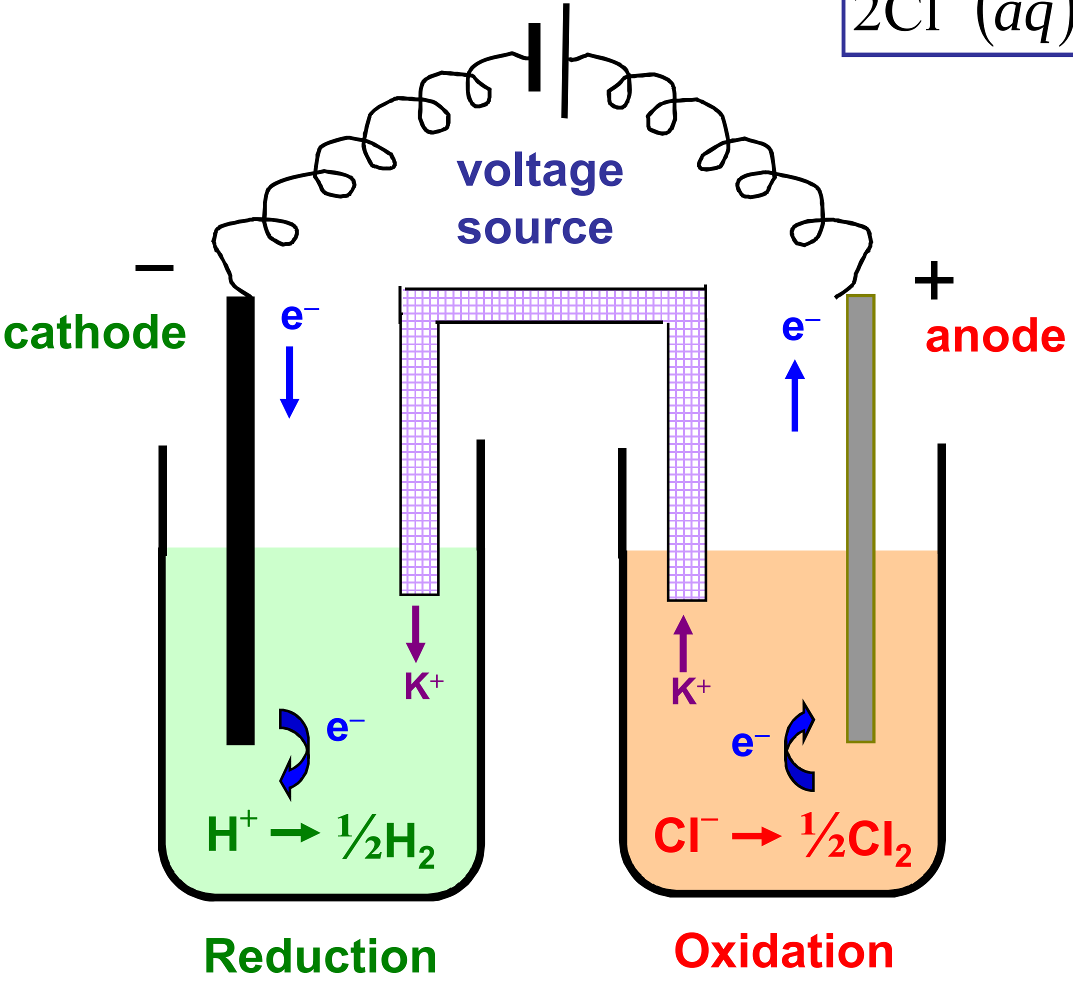
$$E^o = 1.36\,\mathrm{V}$$

$$\Delta_r G^o = -2eE^o_{\mathrm{cell}} = -2.72\,\mathrm{eV}$$

Chlorine fuel cell

Electricity driving chemical reactions

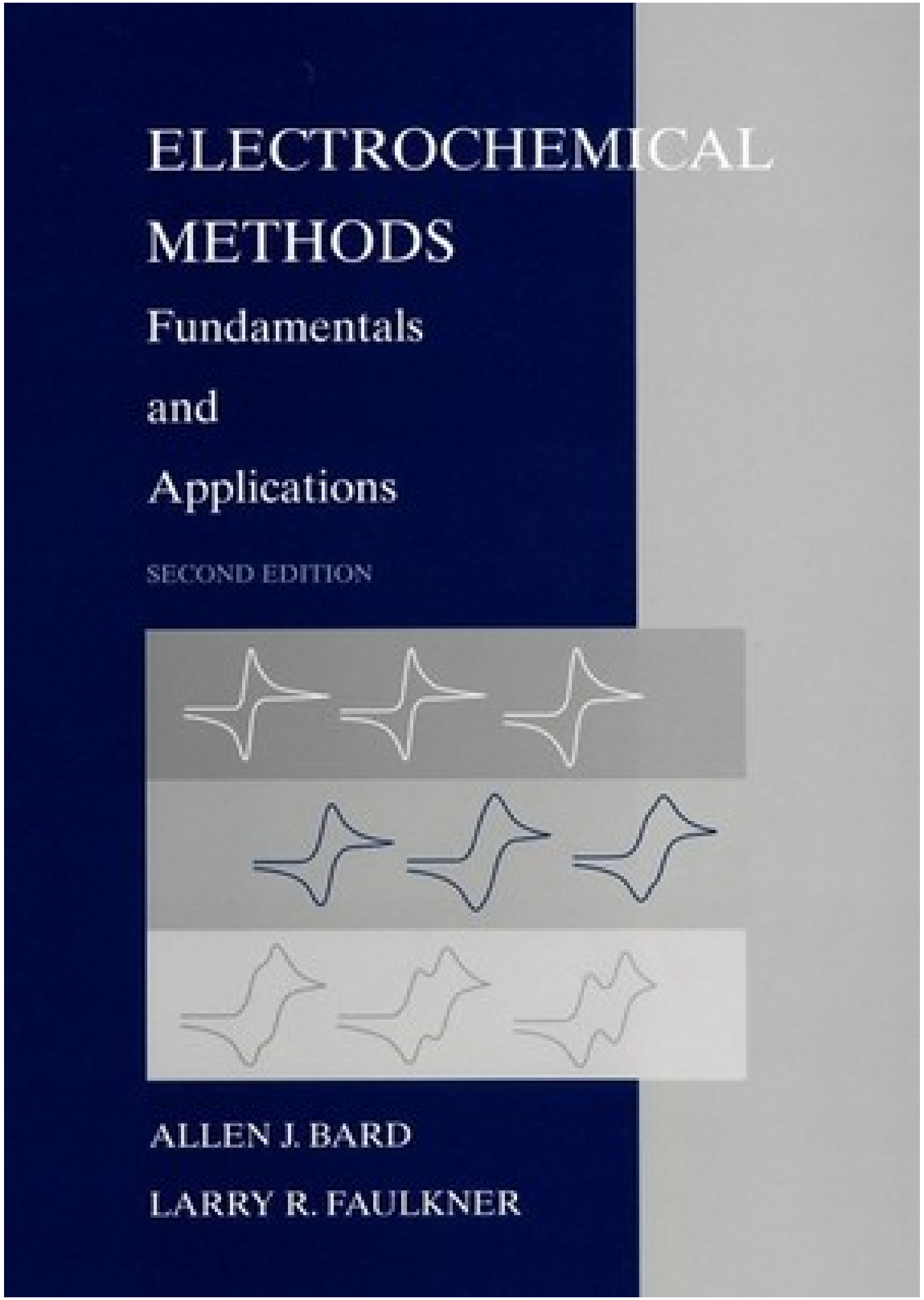
$$\boxed{2\mathrm{Cl}^-(aq) + 2\mathrm{H}^+(aq) \rightarrow \mathrm{Cl}_2(g) + \mathrm{H}_2(g)}$$



$$E^{\mathrm{o}} = 1.36\,\mathrm{V}$$

$$\Delta_r G^{\mathrm{o}} = 2eE^{\mathrm{o}}_{\mathrm{cell}} = 2.72\,\mathrm{eV}$$

Chloride oxidation

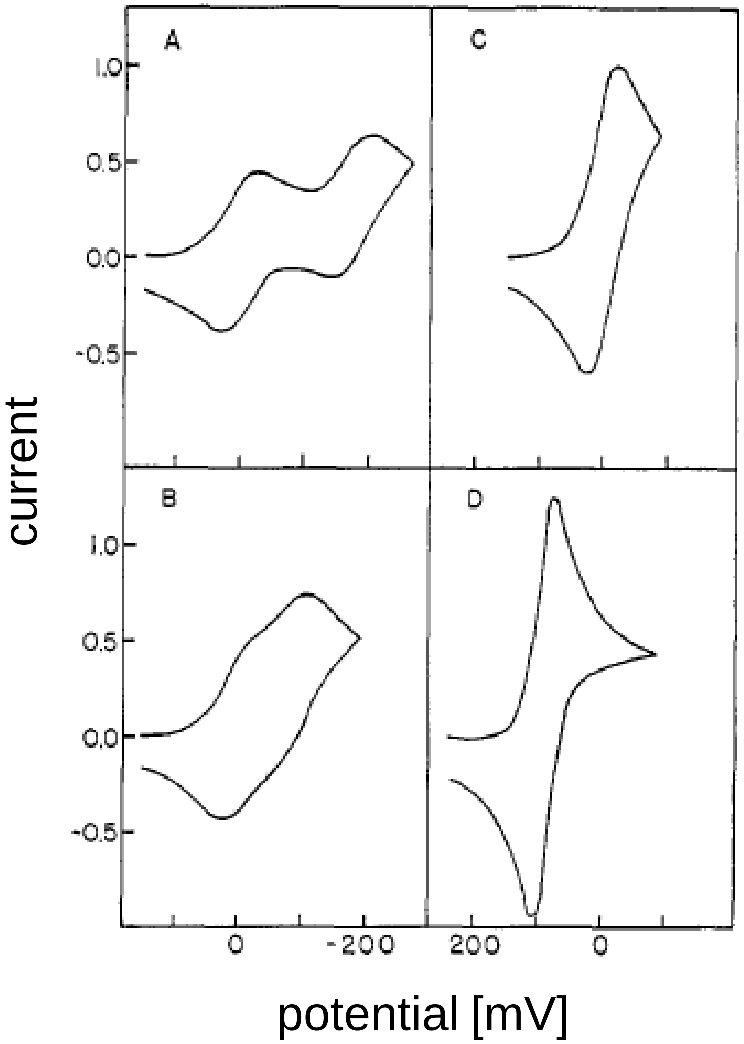


ELECTROCHEMICAL
METHODS
Fundamentals
and
Applications

SECOND EDITION

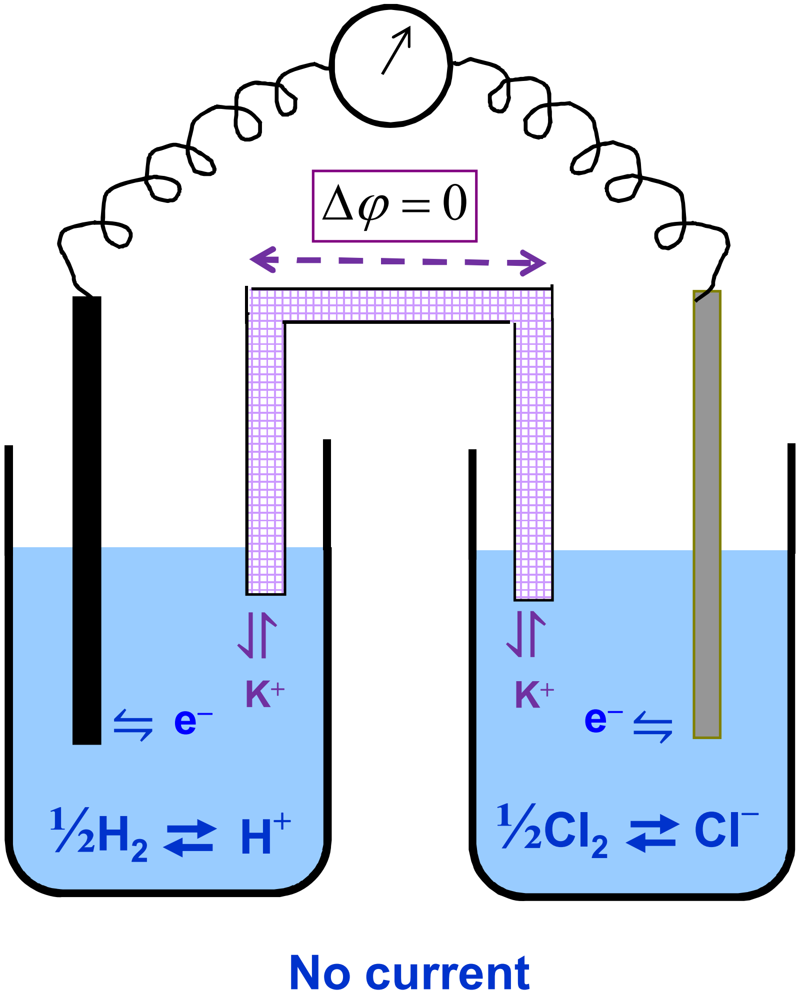
ALLEN J. BARD
LARRY R. FAULKNER

Cyclic Voltammetry



Not ready for this yet

Open circuit voltage of redox electrodes



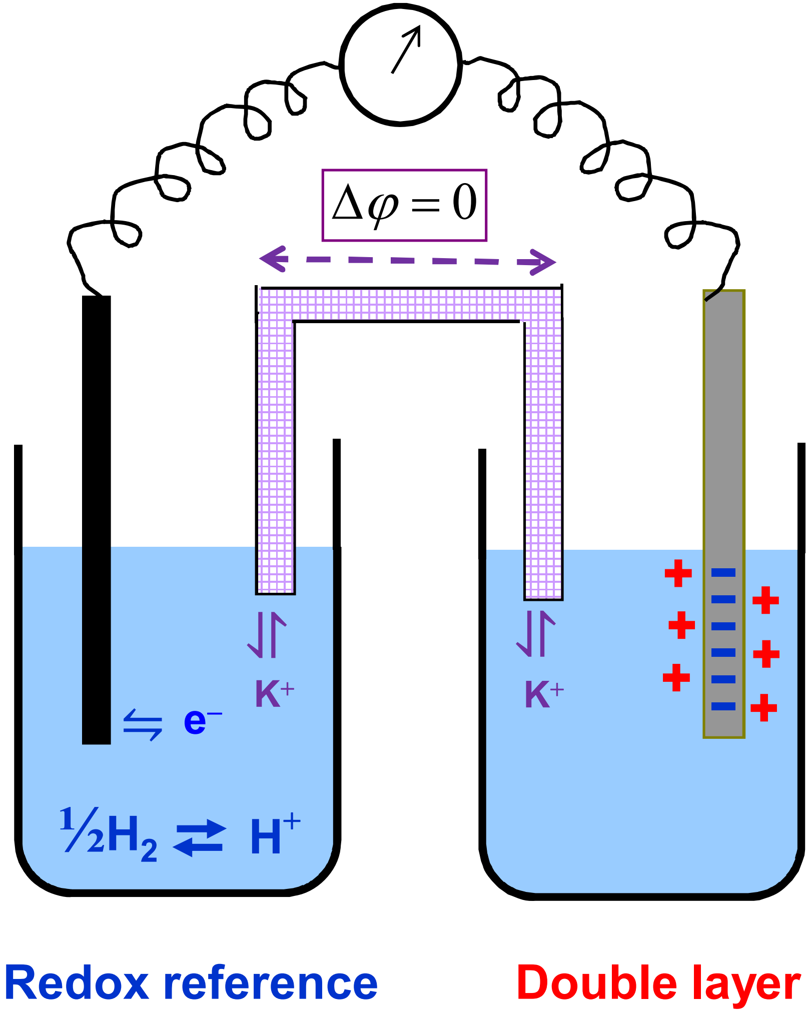
Electrode reactions in equilibrium

$$E = -\frac{\Delta_r G}{2e}$$

$$E = E^o + \frac{k_B T}{2e} \ln \frac{p_{H_2} p_{Cl_2}}{[H^+]^2 [Cl^-]^2}$$

Nature of electrodes irrelevant

No control by a redox process



Electrode acts as a capacitor

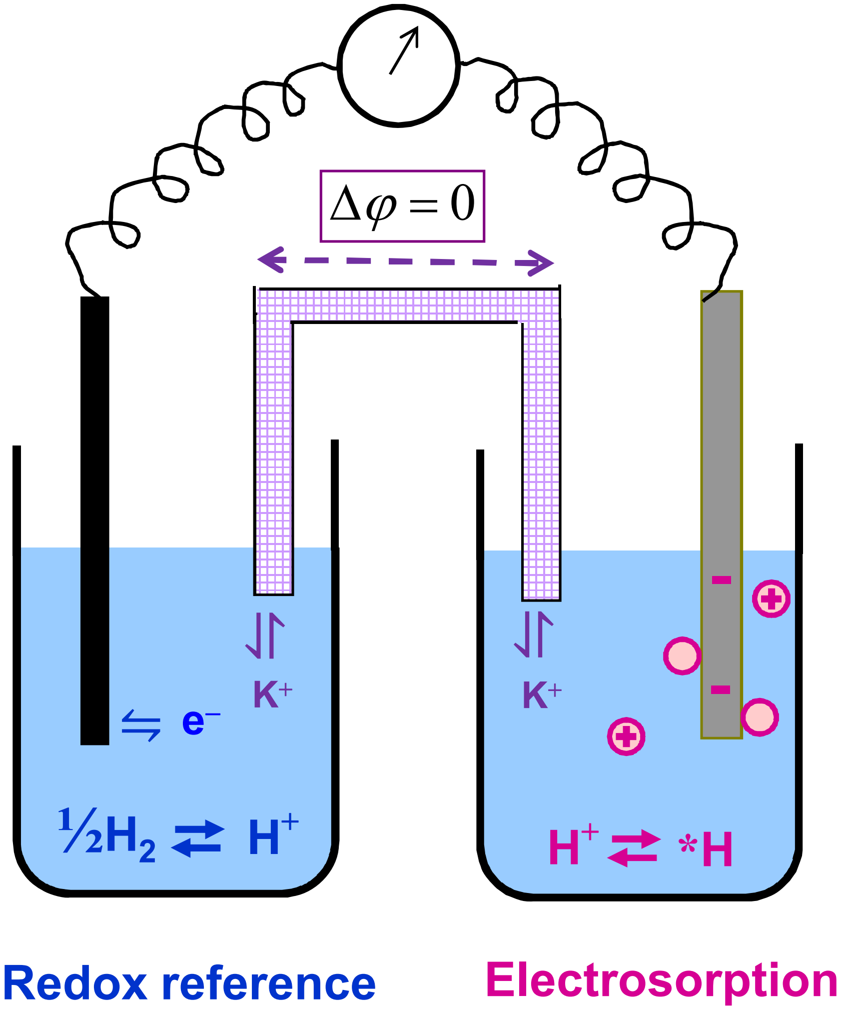
$$E = \varphi_{\text{pzc}} + \frac{Q}{C(Q)}$$

Nature of electrode matters.

$$\varphi_{\text{pzc}} \propto \varepsilon_{\text{fermi}}$$

Point of zero charge for metals

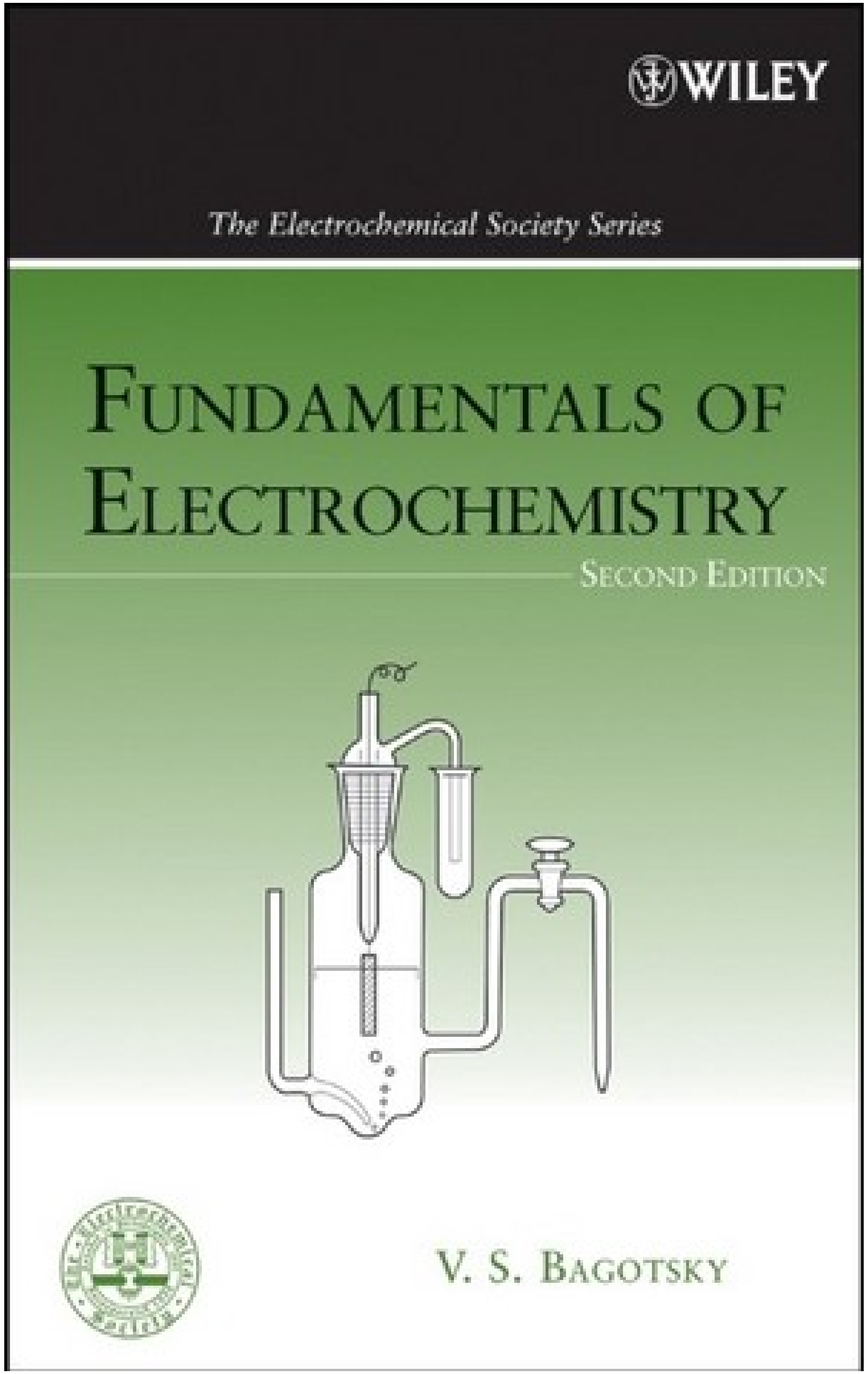
Redox active species adsorbed on surface



Example: Volmer reaction

$$H^+(aq) + e^-(m) \rightarrow *H$$

Step in Hydrogen Evolution Reaction


WILEY

The Electrochemical Society Series

FUNDAMENTALS OF ELECTROCHEMISTRY

SECOND EDITION

V. S. BAGOTSKY

We need a common energy reference

Normal hydrogen electrode (NHE)

$$X^- + H^+(aq) \rightarrow X^\bullet + \tfrac{1}{2} H_2(g)$$

Oxidation free energy of X^- by H^+

$$eE^o_X = \Delta_{ox} G^o_{X^-}$$

How to construct a molecular dynamics normal hydrogen electrode?

NHE half cell

Priorities in computational electrochemistry

Development of

- A computational normal hydrogen electrode.
- Methods for constant potential simulation.

Some of the leading groups

Norskov, Rossmeisl (Stanford, Lyngby)

Neurock (Virginia)

Sugino, Morikawa (Tokyo, Osaka)

Anderson (Cleveland)

Gross (Ulm)

Marzari (EPFL)

Liu (Fudan)

All of them starting from a computational surface science perspective

Our starting point: Solution chemistry

Proton coupled oxidation (PCET)

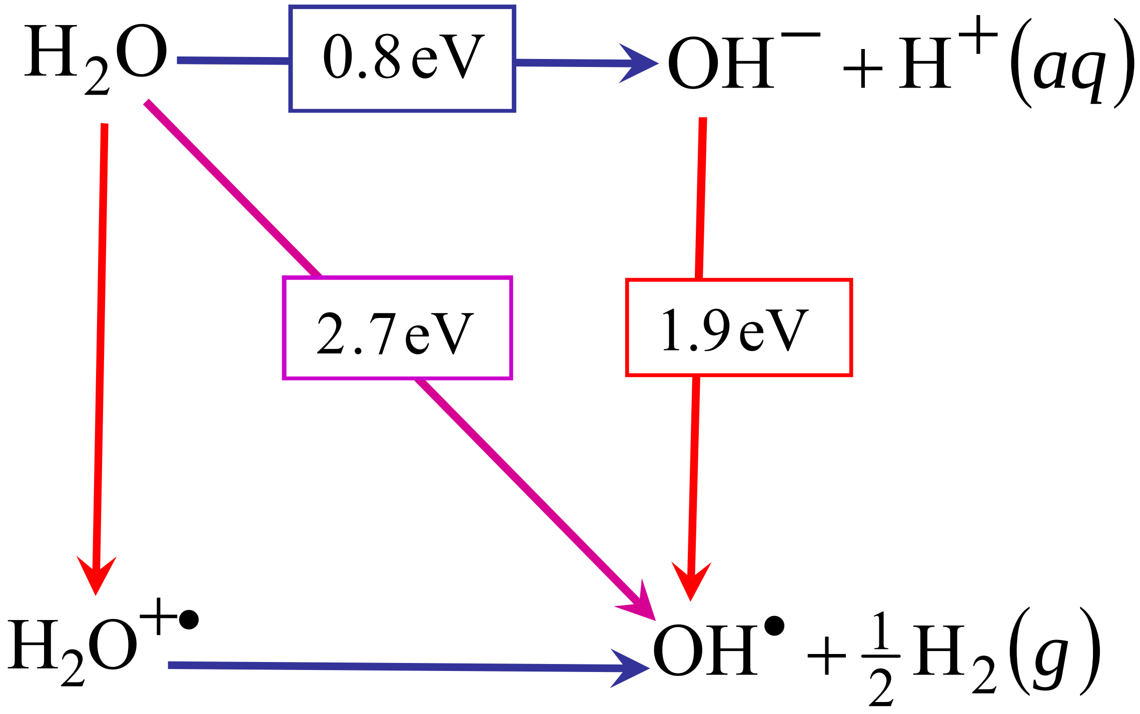
$$\begin{tikzcd}
\mathrm{XH} \arrow[r, "2.3k_{\mathrm{B}}T\,\mathrm{p}K_a"] \arrow[d] \arrow[dr, "\Delta_{\mathrm{dh}}G^{\mathrm{o}}" description] & \mathrm{X}^{-} + \mathrm{H}^{+}(aq) \arrow[d, "eE^{\mathrm{o}}" description, "\textbf{NHE}"] \\
\mathrm{XH}^{+\bullet} \arrow[r] & \mathrm{X}^{\bullet} + \tfrac{1}{2}\mathrm{H}_2(g)
\end{tikzcd}$$

$$\Delta_{\mathrm{dh}}G^{\mathrm{o}} = 2.3k_{\mathrm{B}}T\,\mathrm{p}K_a + eE^{\mathrm{o}}$$

Abstracting the first hydrogen from water

$$H_2O(l) \rightarrow OH^{\bullet}(aq) + \tfrac{1}{2}H_2(g)$$

Experiment



$$\begin{tikzcd}
H_2O \arrow[rr, "\boxed{0.8\,\mathrm{eV}}"] \arrow[d] \arrow[drr, "\boxed{2.7\,\mathrm{eV}}"] & & OH^{-} + H^{+}(aq) \arrow[d, "\boxed{1.9\,\mathrm{eV}}"] \\
H_2O^{+\bullet} \arrow[rr] & & OH^{\bullet} + \tfrac{1}{2}H_2(g)
\end{tikzcd}$$

Density functional molecular dynamics method

Credo

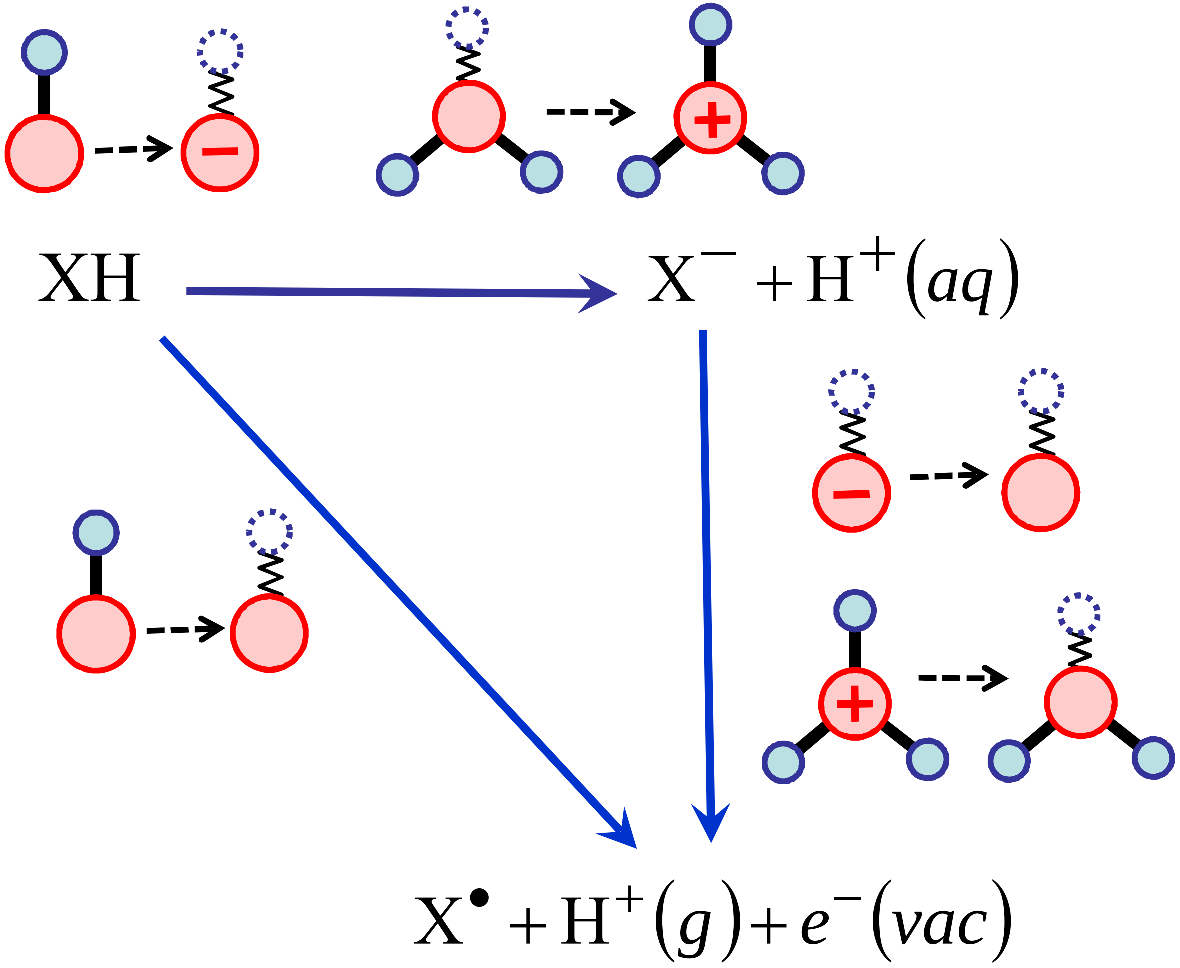
Treat solute and solvent at the same level of density functional theory

Code **CP2K** (cp2k.berlios.de)

- Gaussian basis set (+ plane waves for density)
- GGA and now also Hybrid functionals
- Born-Oppenheimer dynamics
- Free energy calculation

*J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, Comp. Phys. Comm. (2005), **167**, 103.*

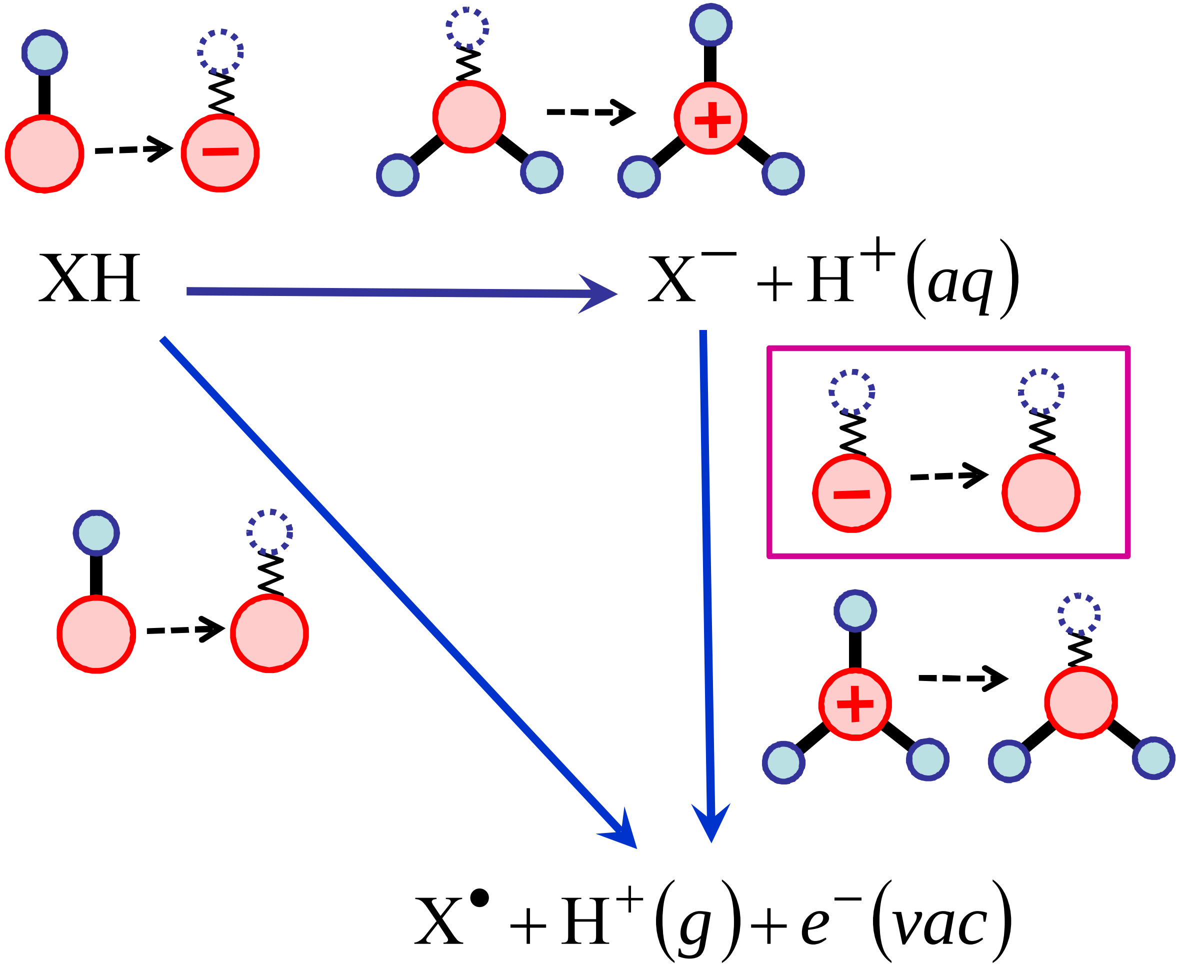
Reversible discharge of proton + electron



$$\begin{tikzcd}
\mathrm{XH} \arrow[r] \arrow[dr] & \mathrm{X}^{-} + \mathrm{H}^{+}(aq) \arrow[d] \\
 & \mathrm{X}^{\bullet} + \mathrm{H}^{+}(g) + e^{-}(vac)
\end{tikzcd}$$

Free energy perturbation plus analytical thermochemical corrections

Dehydrogenation by double reversible discharge



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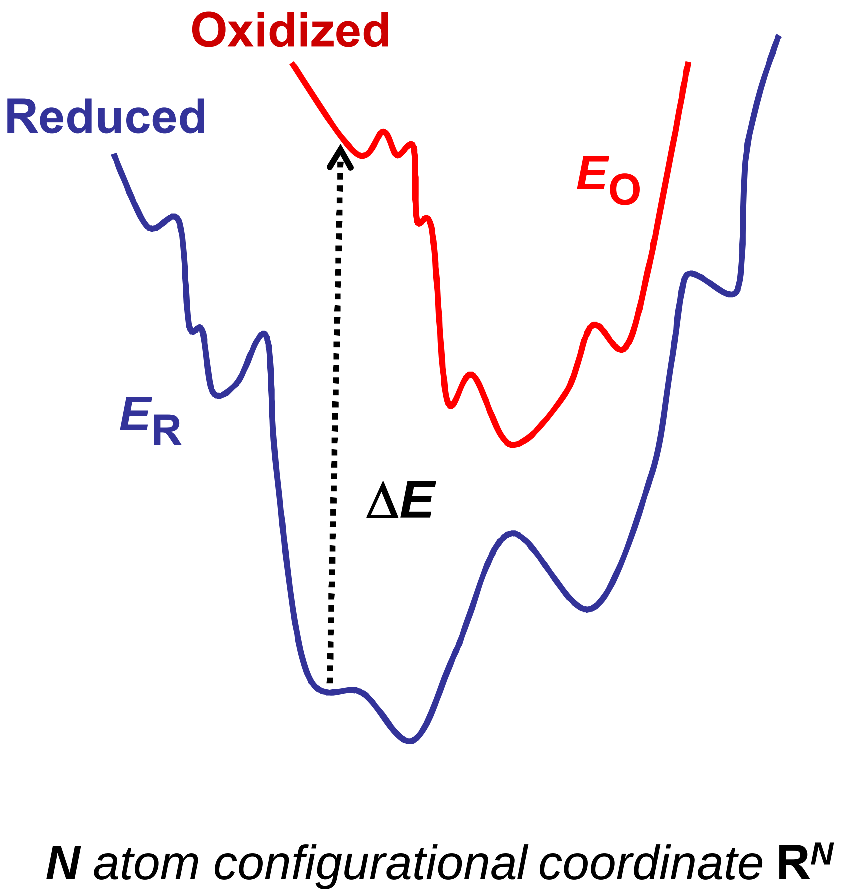
 & \mathrm{X}^{\bullet}+\mathrm{H}^{+}(g)+e^{-}(vac)
\end{tikzcd}$$

Free energy perturbation plus analytical thermochemical corrections

Vertical ionization energy

Atomic position fixed



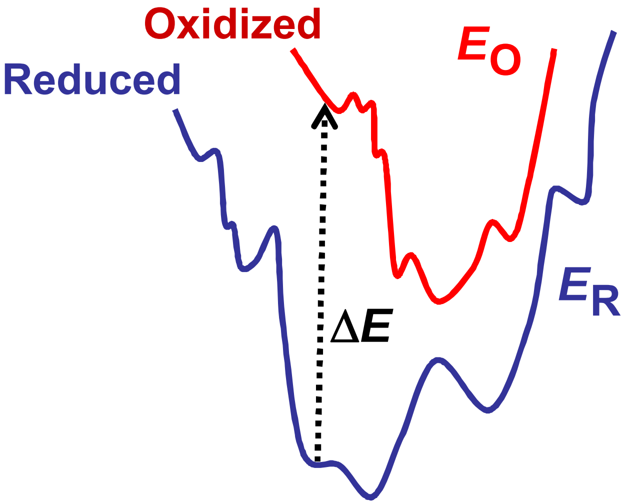
$$\Delta E\left(\mathbf{R}^N\right) = E_O\left(\mathbf{R}^N\right) - E_R\left(\mathbf{R}^N\right)$$

$E_R\left(\mathbf{R}^N\right)$: PES **reduced**

$E_O\left(\mathbf{R}^N\right)$: PES **oxidized**

However we also need the adiabatic ionization potential

Free energy perturbation method



Two potential energy surfaces

$E_R(\mathbf{R}^N)$: PES **reduced**

$E_O(\mathbf{R}^N)$: PES **oxidized**

Vertical energy gap

$$\Delta E(\mathbf{R}^N) = E_O(\mathbf{R}^N) - E_R(\mathbf{R}^N)$$

Mapping potential

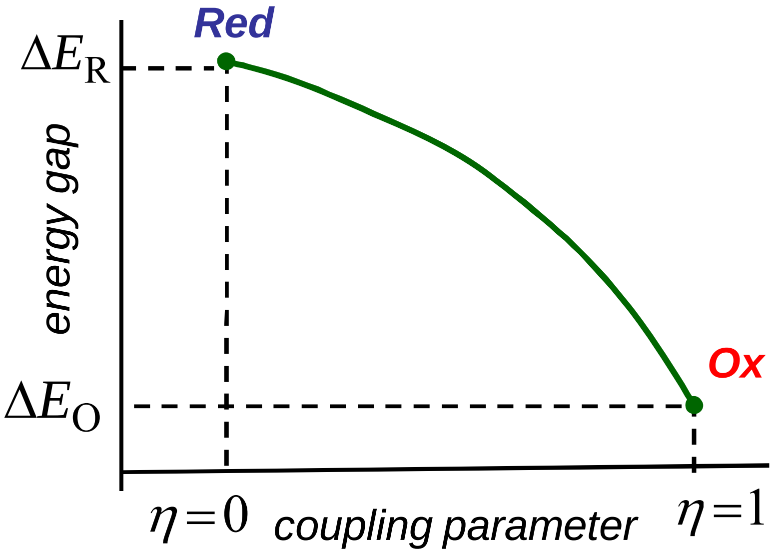
$$E_\eta(\mathbf{R}^N) = \eta\, E_O(\mathbf{R}^N) + (1-\eta) E_R(\mathbf{R}^N)$$

Coupling parameter derivative

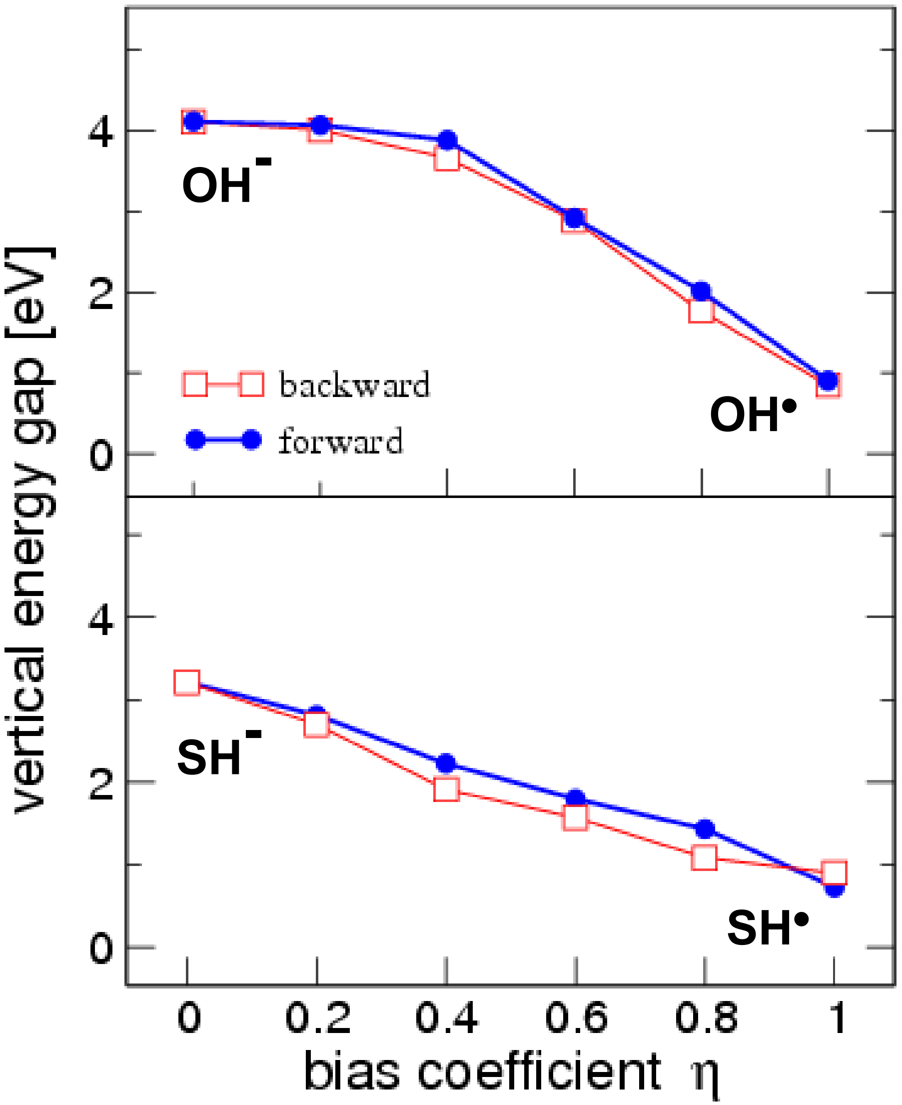
$$\frac{\partial}{\partial \eta} E_\eta(\mathbf{R}^N) = \Delta E(\mathbf{R}^N)$$

Oxidation free energy

$$\Delta A = A_O - A_R = \int_0^1 d\eta \left\langle \Delta E(\mathbf{R}^N) \right\rangle_\eta$$



Example: two aqueous radicals



$OH^- \rightarrow OH^\bullet + e^-$

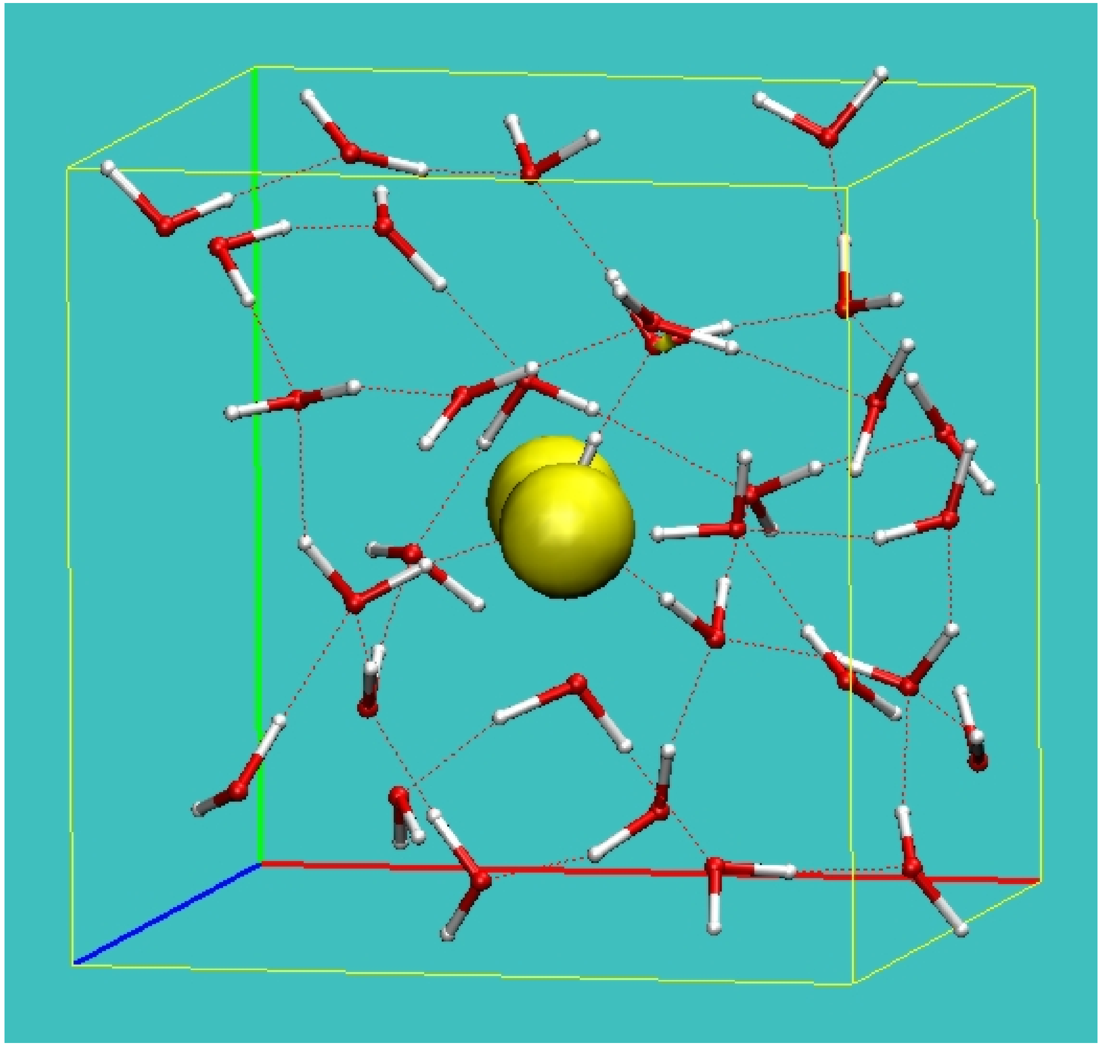
Non-linear solvent response:

$SH^- \rightarrow SH^\bullet + e^-$

Linear solvent response

Run length ≈ 10 ps per data point

DFTMD model system for homogeneous $OH^{\bullet}/H_2O$



DFTMD Model

1 $OH^{\bullet}$ radical

31 H_2O

In cubic box of

L = 9.86 Å

(periodic boundaries)

10-50 ps MD runs

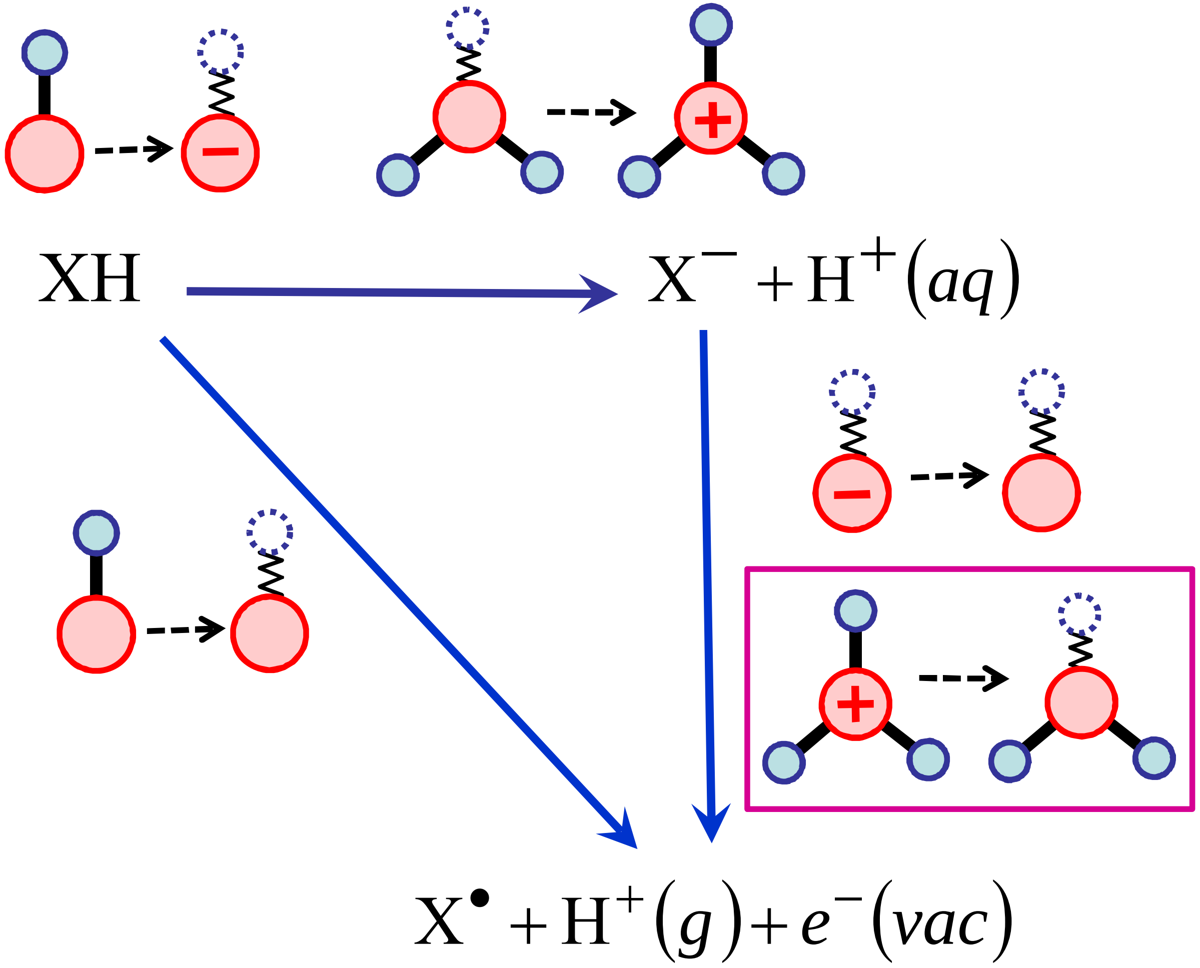
Electronic structure

TZV2P basis,

280 Ry (density cutoff)

No explicit counterion

Dehydrogenation by double reversible discharge



XH

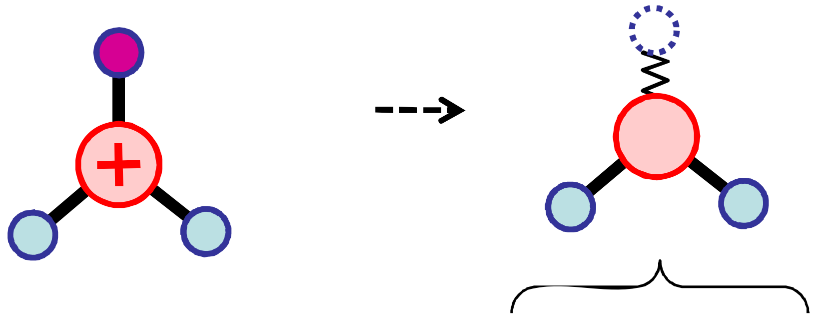
$\mathrm{X}^{-} + \mathrm{H}^{+}(aq)$

$\mathrm{X}^{\bullet} + \mathrm{H}^{+}(g) + e^{-}(vac)$

Free energy perturbation plus analytical thermochemical corrections

Reversible deprotonation

Switching the proton charge off and on again



BO surface ***protonated*** *system*

BO surface ***deprotonated*** *system*

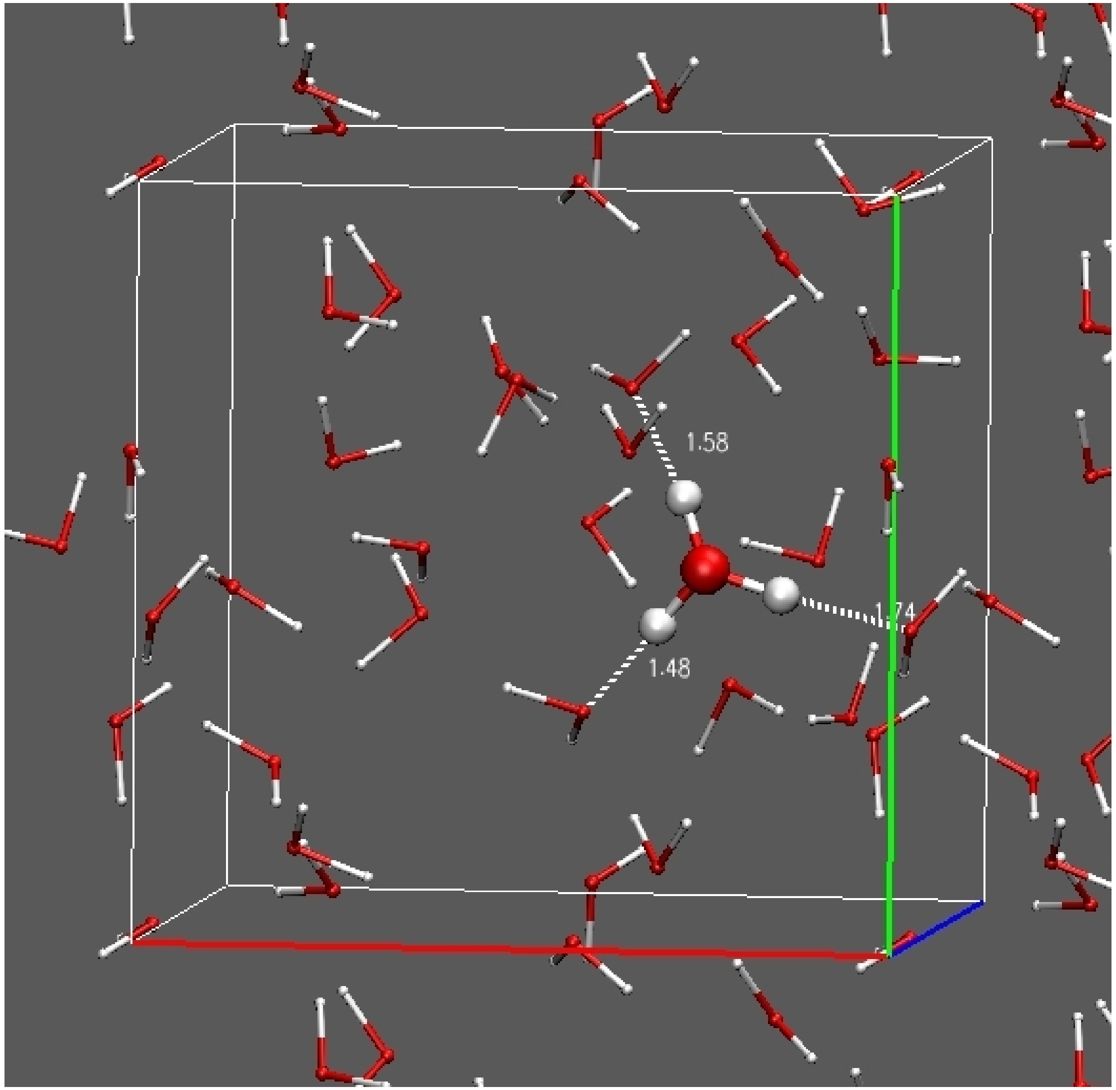
Harmonic potential holding ***dummy*** *in place*

Mapping potential $$E_\eta\left(\mathbf{R}^N\right) = (1-\eta)\,\boxed{E_{\mathrm{XH}}\left(\mathbf{R}^N\right)} + \eta\,\boxed{E_{\mathrm{X}^-}\left(\mathbf{R}^{N-1}\right)} + \boxed{V_r\left(\mathbf{R}^N\right)}$$

Vertical proton gap: $$\frac{\partial}{\partial\eta}E_\eta\left(\mathbf{R}^N\right) = E_{\mathrm{X}^-}\left(\mathbf{R}^{N-1}\right) - E_{\mathrm{XH}}\left(\mathbf{R}^N\right) = \Delta E\left(\mathbf{R}^N\right)$$

Restrained deprotonation free energy $$\Delta A = A_{\mathrm{X}^-} - A_{\mathrm{XH}} = \int_0^1 d\eta \left\langle \Delta E \right\rangle_{r\eta}$$

H_3O^+/H_2O model system



DFTMD Model

$32\ H_2O \pm H^+$

In cubic box of

L = 9.86 Å

(periodic boundaries)

20-50 ps MD runs

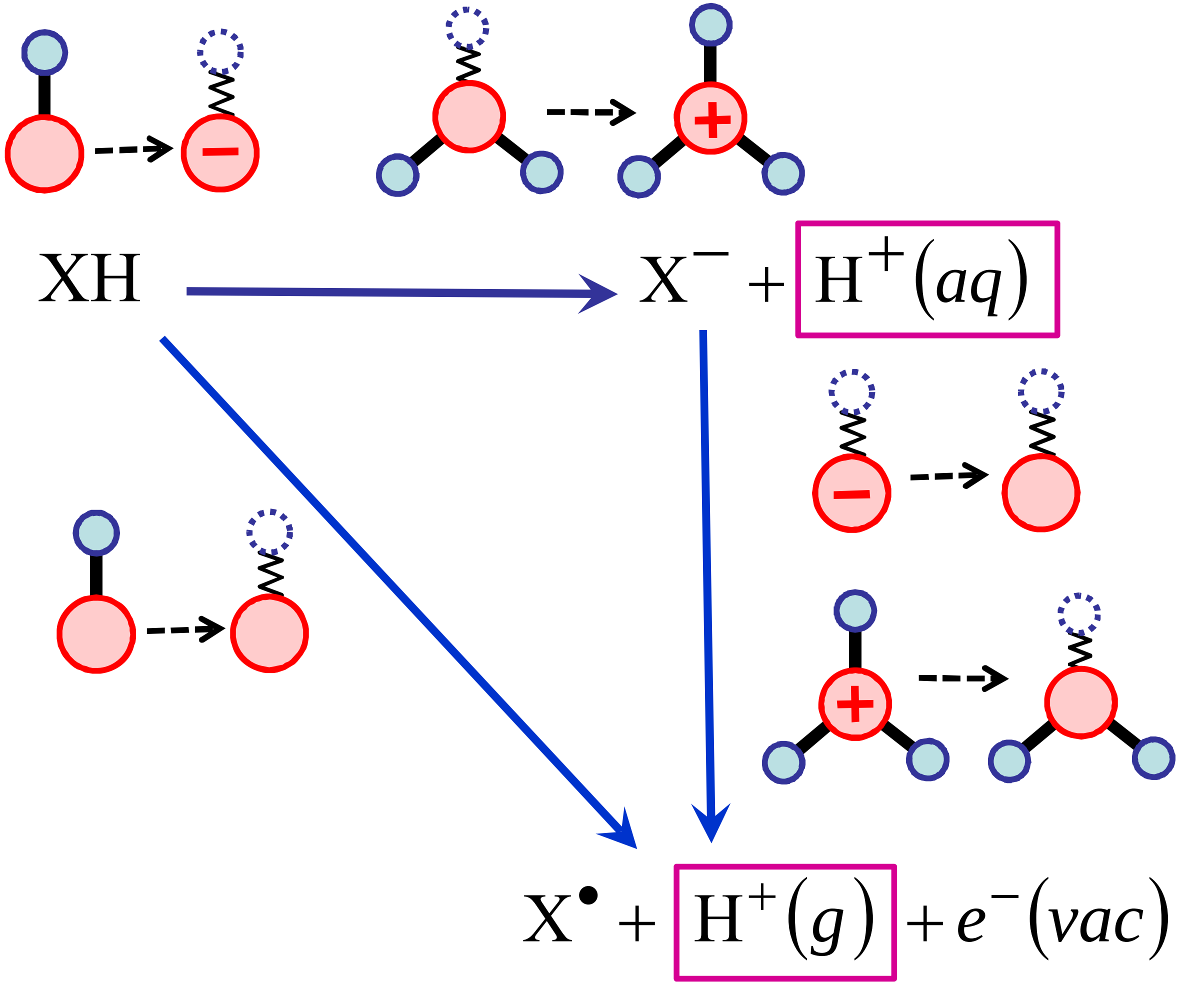
Electronic structure

TZV2P basis,

280 Ry (density cutoff

No explicit counter ion

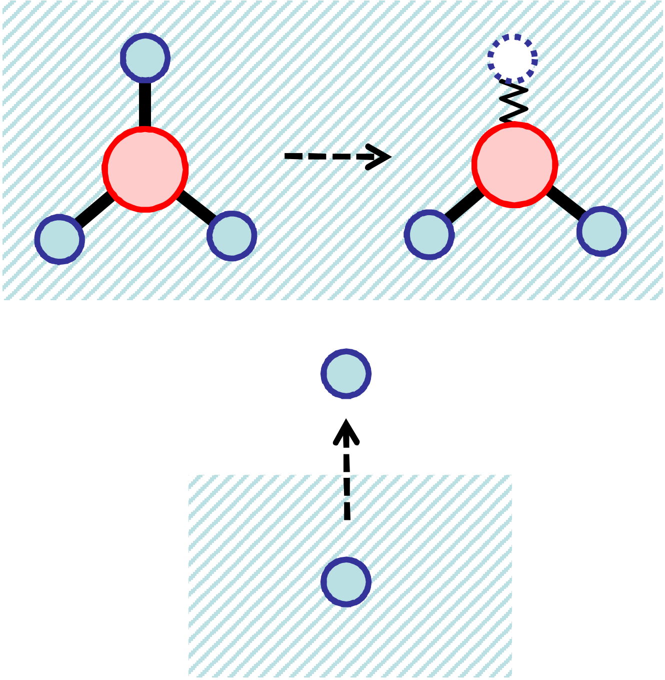
Dehydrogenation by double reversible discharge



$$\begin{tikzcd} \mathrm{XH} \arrow[r] \arrow[dr] & \mathrm{X}^- + \boxed{\mathrm{H}^+(aq)} \arrow[d] \\ & \mathrm{X}^\bullet + \boxed{\mathrm{H}^+(g)} + e^-(vac) \end{tikzcd}$$

Free energy perturbation plus **analytical thermochemical corrections**

Desolvating H^+ by deprotonating H_3O^+



What we calculate: discharge energy

$$\int_0^1 d\eta \left\langle \Delta E_{\mathrm{H_3O^+}} \right\rangle_{r\eta}$$

What we want: desolvation energy

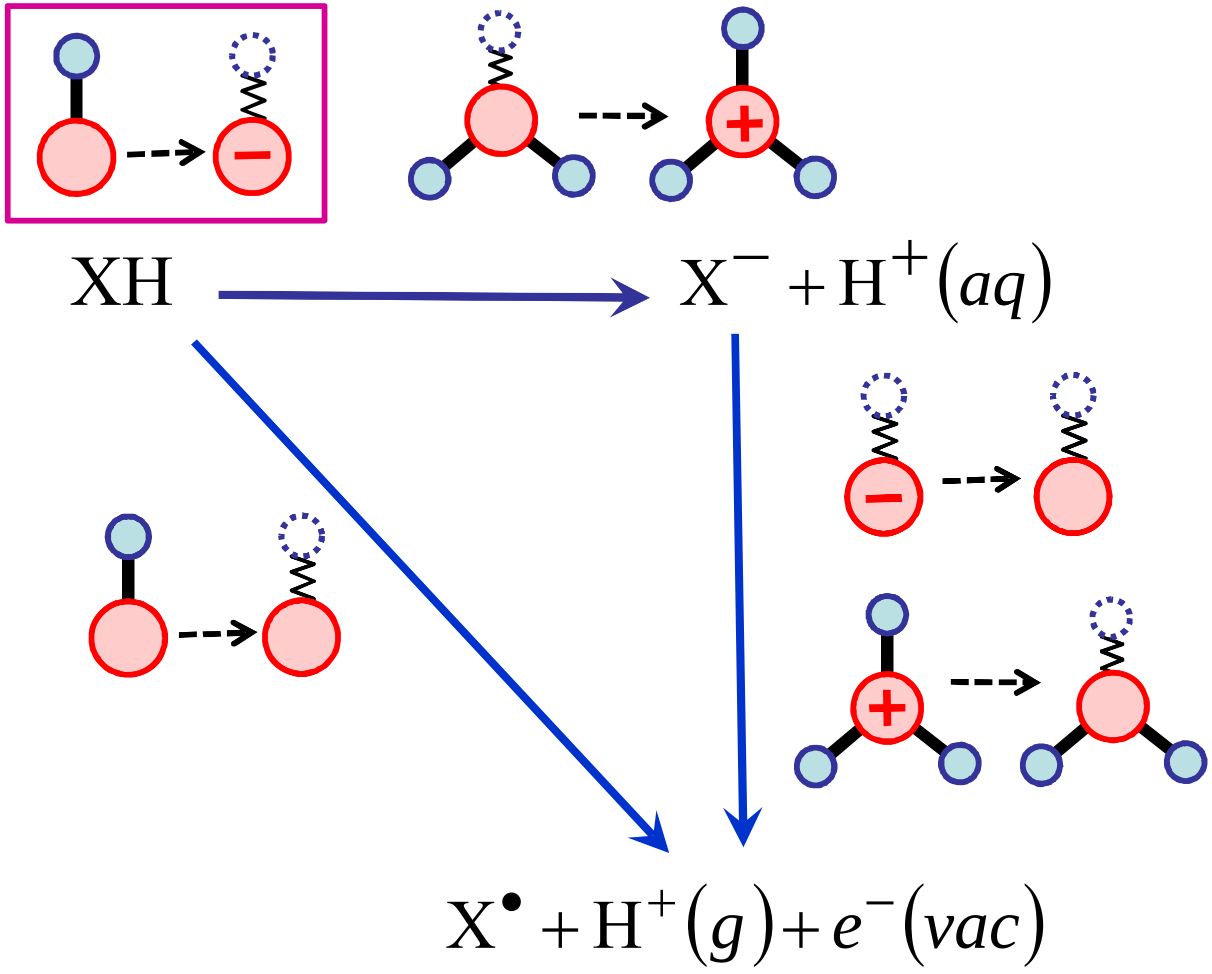
$$-\Delta_s G_{\mathrm{H^+}} > 0$$

Desolvation free energy (in 0 order approximation)):

$$-\Delta_s G_{\mathrm{H^+}} = \int_0^1 d\eta \left\langle \Delta E_{\mathrm{H_3O^+}} \right\rangle_{r\eta} - \boxed{\Delta_{\mathrm{zp}} E_{\mathrm{H^+}}}$$

Zero point motion correction ≈ 350 meV

Dehydrogenation by double reversible discharge



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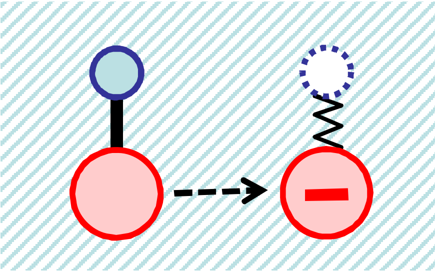
 & \mathrm{X}^{\bullet} + \mathrm{H}^{+}(g) + e^{-}(vac)
\end{tikzcd}$$

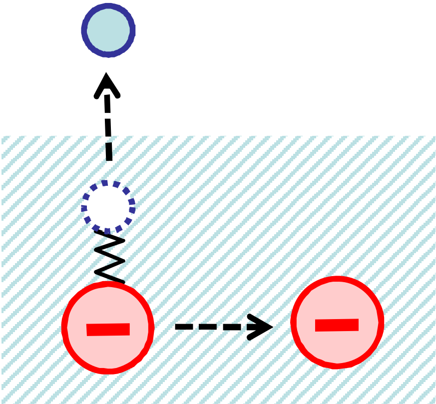
Free energy perturbation plus analytical thermochemical corrections

Proton transfer to virtual gas-phase



Discharging integral

$$\int_0^1 d\eta \left\langle \Delta E_{\mathrm{XH}} \right\rangle_{r\eta}$$



Thermochemical correction

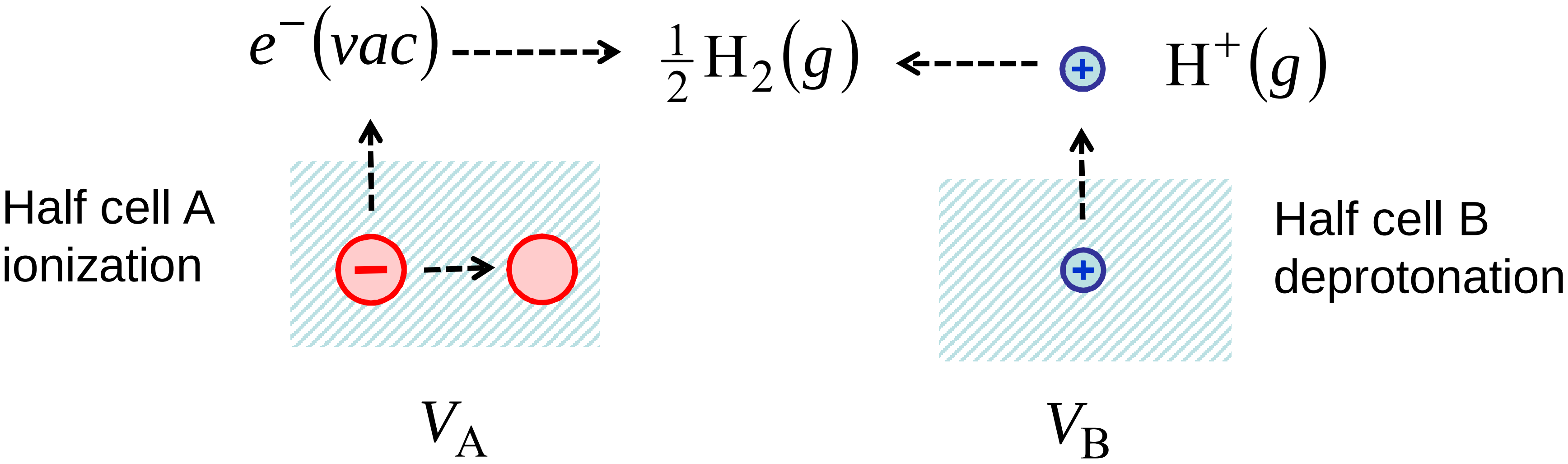
$$\boxed{k_{\mathrm{B}} T \ln\left[c^{\mathrm{o}} \Lambda^{3}_{\mathrm{H}^+}\right]} - \Delta_{\mathrm{zp}} E_{\mathrm{H}^+}$$

***ideal chemical potential* H$^+$ ≈ –190 meV**

Deprotonation free energy (in 0 order approximation)

$$\Delta_{\mathrm{dp}} G_{\mathrm{XH}} = \int_0^1 d\eta \left\langle \Delta E_{\mathrm{XH}} \right\rangle_{r\eta} + k_{\mathrm{B}} T \ln\left[c^{\mathrm{o}} \Lambda^{3}_{\mathrm{H}^+}\right] - \Delta_{\mathrm{zp}} E_{\mathrm{H}^+}$$

Half cells with virtual gas-phase interface



$e^{-}(vac)$

$\frac{1}{2}\mathrm{H}_2(g)$

$\mathrm{H}^{+}(g)$

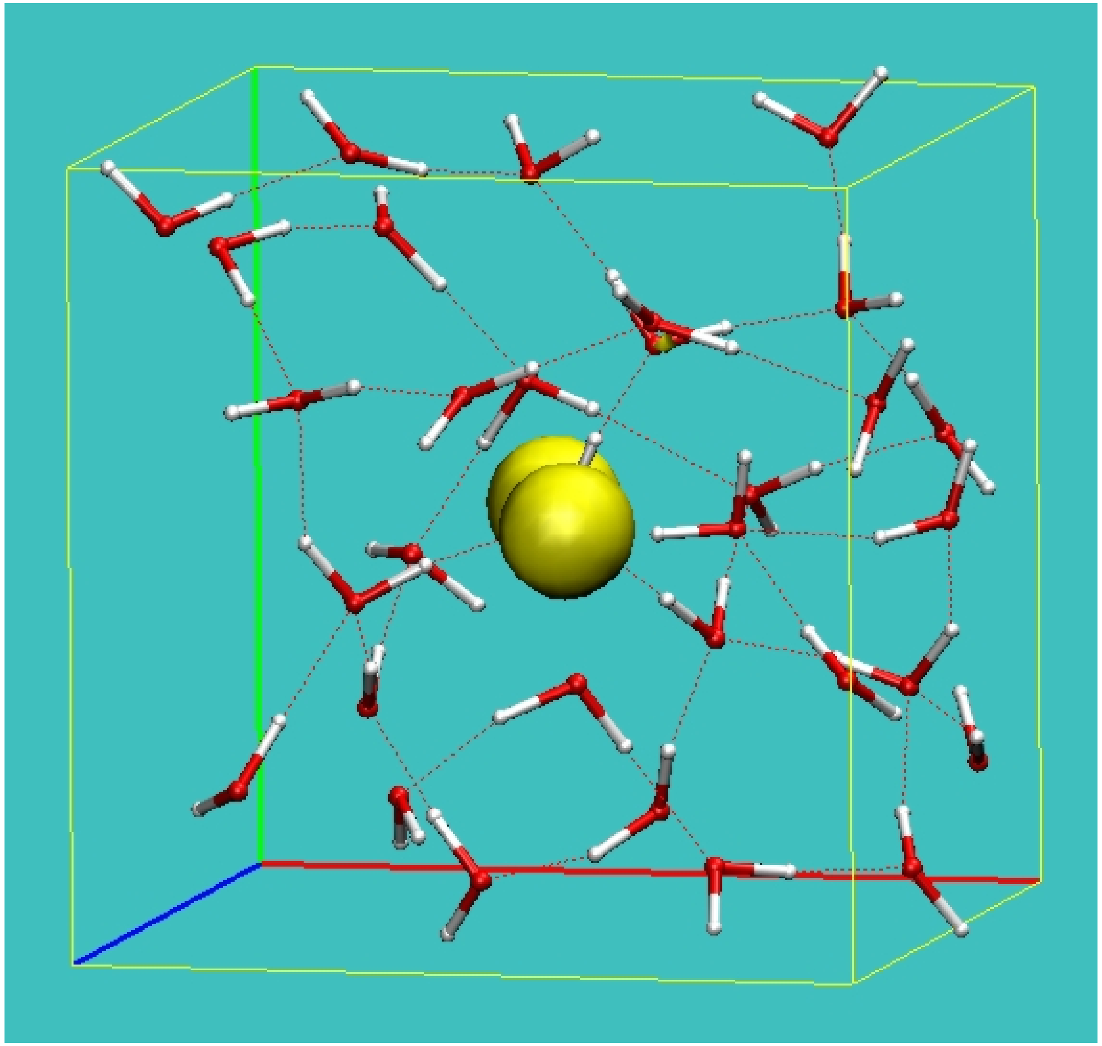
Half cell A
ionization

Half cell B
deprotonation

V_A

V_B

Half cell for OH^- /$OH^\bullet$ oxidation



DFTMD Model

1 $OH^\bullet$ radical

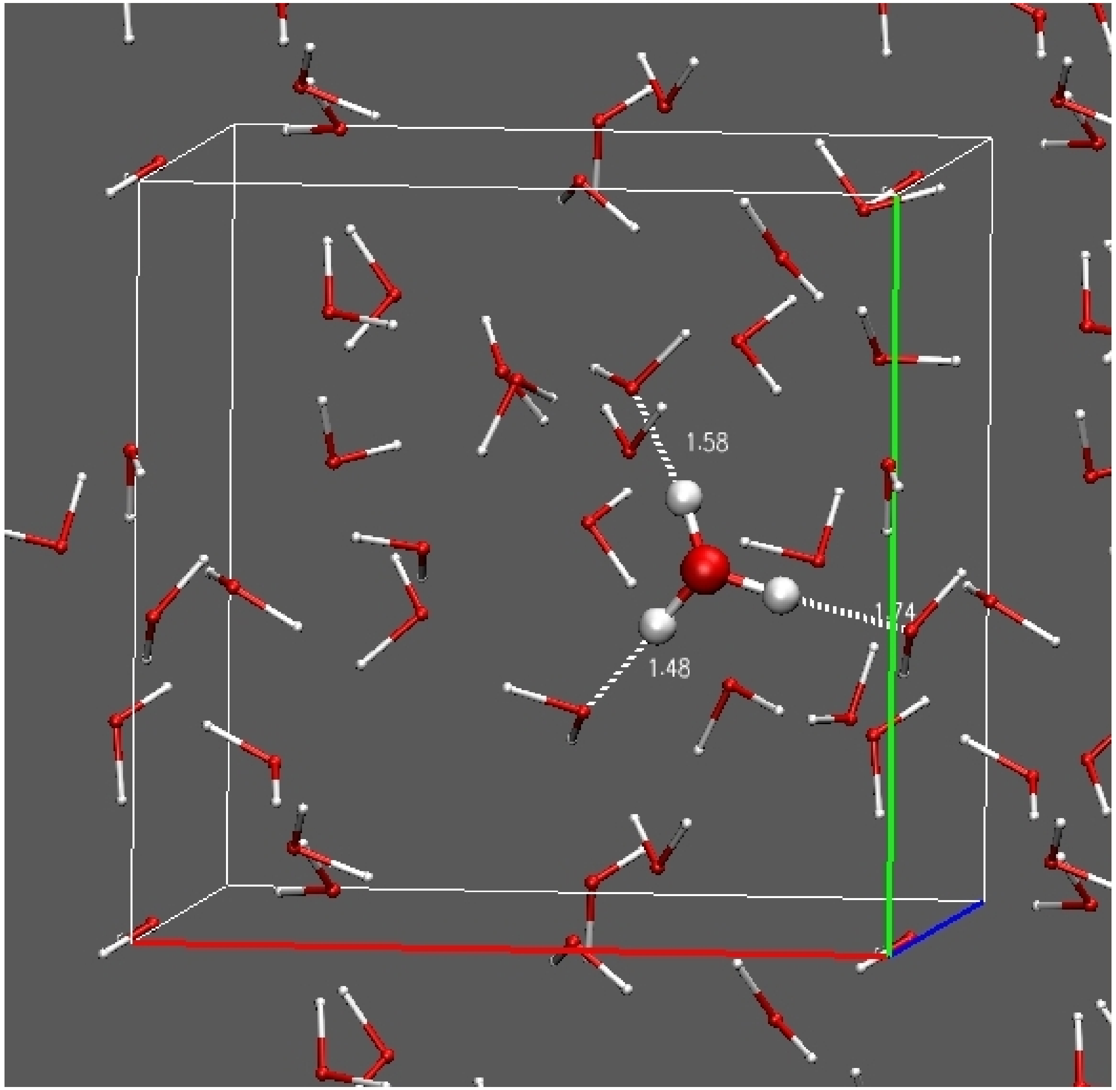
31 H_2O

In periodic cubic box of

L = 9.86 Å

No explicit counter ion

Half cell for H_3O^+/H_2O deprotonation



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$32\ H_2O \pm H^+$

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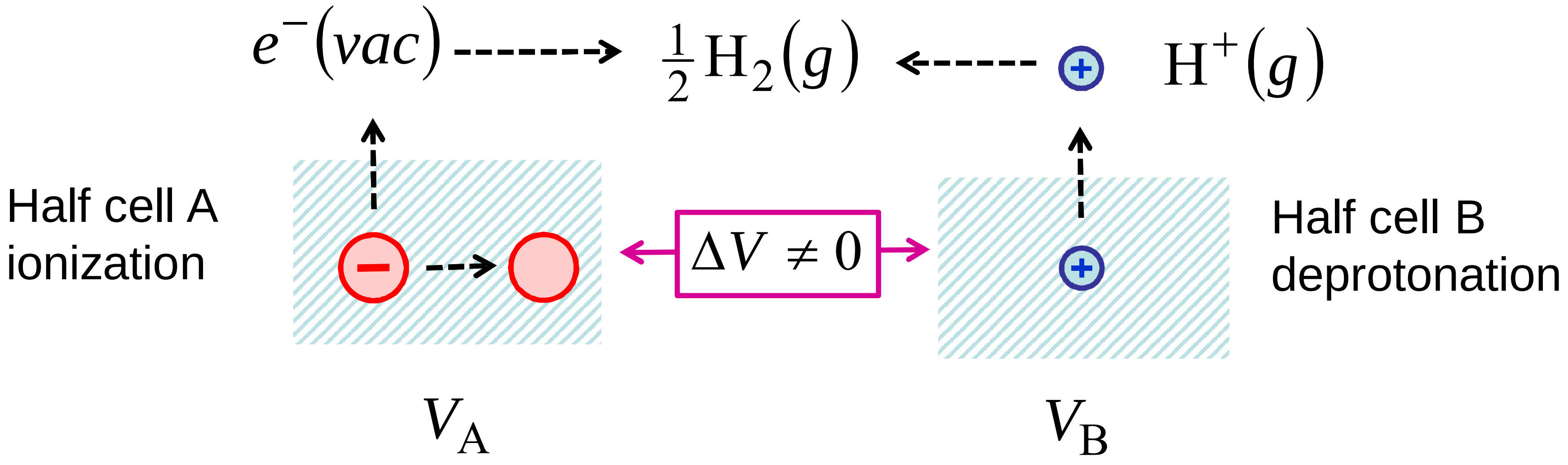
Half cells with virtual gas-phase interface



$e^-(vac) \dashrightarrow \tfrac{1}{2}\mathrm{H}_2(g) \dashleftarrow \mathrm{H}^+(g)$

Half cell A
ionization

$\Delta V \neq 0$

Half cell B
deprotonation

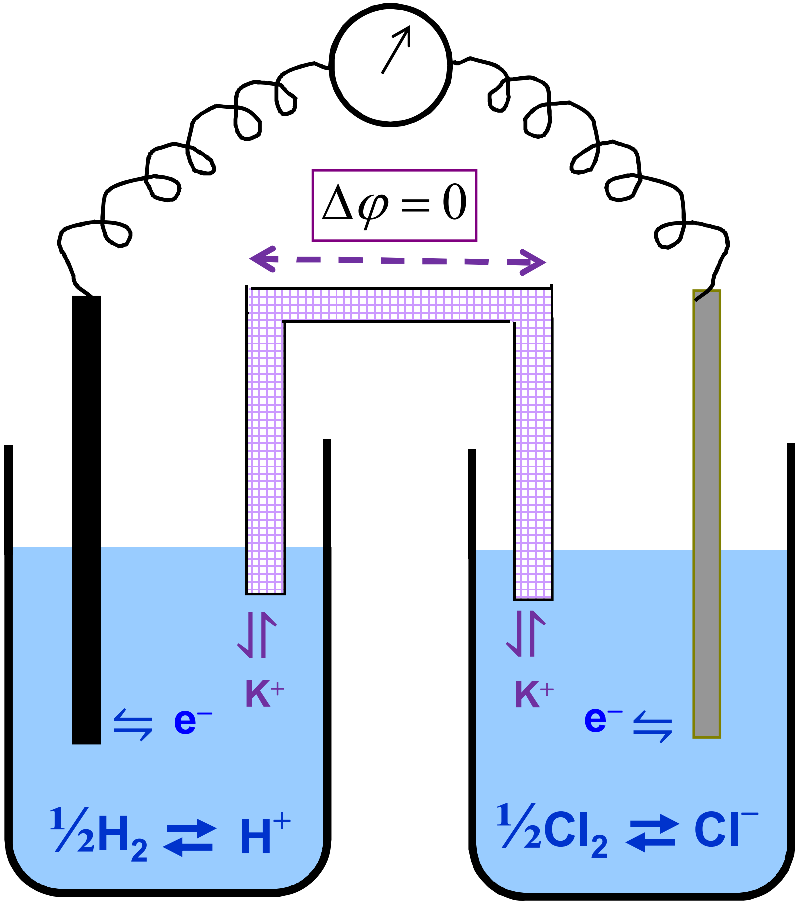
V_A

V_B

Reference for electrostatic potential in cell A and B may not be the same

Level alignment (band offset) problem under periodic boundary conditions

Open circuit voltage of redox electrodes



No current

Electrode reactions in equilibrium

$$E = -\frac{\Delta_r G}{2e}$$

$$E = E^{o} + \frac{k_B T}{2e} \ln \frac{p_{H_2}\, p_{Cl_2}}{\left[H^+\right]^2 \left[Cl^-\right]^2}$$

Nature of electrodes irrelevant

Electrochemical potential

For a **finite charged conducting phase**

$$\frac{\partial G}{\partial n_i} = \overline{\mu}_i$$

- $\overline{\mu}_i$ the **electrochemical potential** of the phase

$$\overline{\mu}_i = \mu_i + z_i e \varphi$$

- μ_i the **chemical potential** of component *i*

$$\mu_i = \mu_i^\circ + k_\mathrm{B} T \ln a_i$$

- φ the **inner or Galvani potential** of the phase

Separation in chemical and electrostatic terms experimentally not possible

Chemical equilibrium at anode and cathode

$$\boxed{\mathrm{H}_2(g) \leftrightarrow 2\mathrm{H}^+(s_A) + e^-(m_A)}$$

$$\mu^{g}_{\mathrm{H}_2} = 2\bar{\mu}^{s_A}_{\mathrm{H}^+} + 2\bar{\mu}^{m_A}_{e^-}$$

$$\mu^{g}_{\mathrm{H}_2} = 2\left(\mu^{s_A}_{\mathrm{H}^+} + e\varphi^{s_A}\right) + 2\bar{\mu}^{m_A}_{e^-}$$

$$-2\bar{\mu}^{m_A}_{e^-} = 2\mu^{s_A}_{\mathrm{H}^+} - \mu^{g}_{\mathrm{H}_2} + 2e\varphi^{s_A}$$

$$\boxed{\mathrm{Cl}_2(g) + e^-(m_C) \leftrightarrow 2\mathrm{Cl}^-(s_C)}$$

$$\mu^{g}_{\mathrm{Cl}_2} + 2\bar{\mu}^{m_C}_{e^-} = 2\bar{\mu}^{s_C}_{\mathrm{Cl}^-}$$

$$\mu^{g}_{\mathrm{Cl}_2} + 2\bar{\mu}^{m_C}_{e^-} = 2\left(\mu^{s_C}_{\mathrm{Cl}^-} - e\varphi^{s_C}\right)$$

$$2\bar{\mu}^{m_C}_{e^-} = 2\mu^{s_C}_{\mathrm{Cl}^-} - \mu^{g}_{\mathrm{Cl}_2} - 2e\varphi^{s_C}$$

Adding

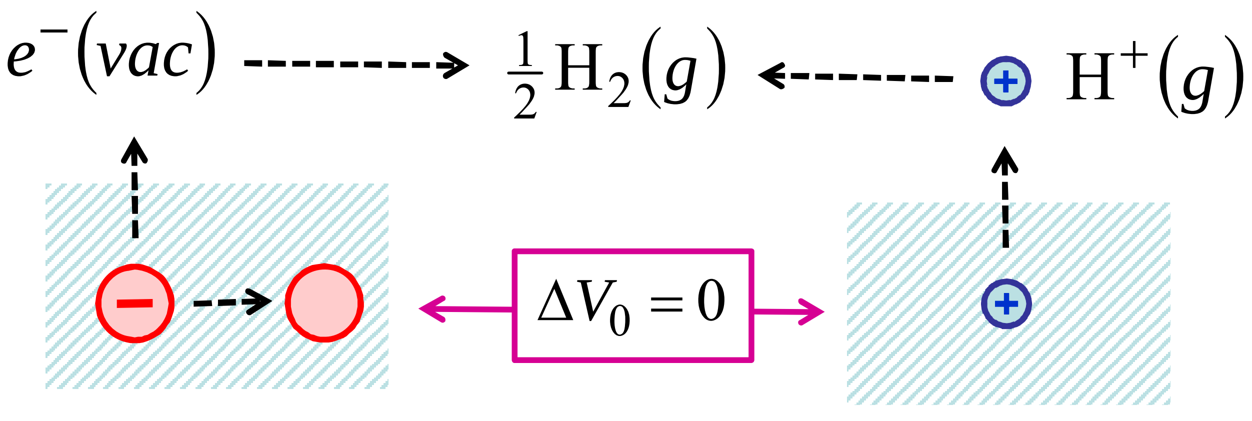
$$2\left(\bar{\mu}^{m_C}_{e^-} - \bar{\mu}^{m_A}_{e^-}\right) = 2\mu^{s_C}_{\mathrm{Cl}^-} + 2\mu^{s_A}_{\mathrm{H}^+} - \mu^{g}_{\mathrm{Cl}_2} - \mu^{g}_{\mathrm{H}_2} + 2e\left(\varphi^{s_A} - \varphi^{s_C}\right)$$

$$-2eE = \Delta_r G + 2e\boxed{\left(\varphi^{s_A} - \varphi^{s_C}\right)}$$

= 0 electrical equilibrium between anode and cathode

$$E = -\frac{\Delta_r G}{2e}$$

Average potential half cells determined by solvent



$e^-(vac) \dashrightarrow \tfrac{1}{2}\mathrm{H}_2(g) \dashleftarrow \mathrm{H}^+(g)$

$\Delta V_0 = 0$

$\Delta_{\mathrm{ip}} A - \boxed{V_0}$

$-\Delta_{\mathrm{s}} G_{\mathrm{H}^+} + \boxed{V_0}$

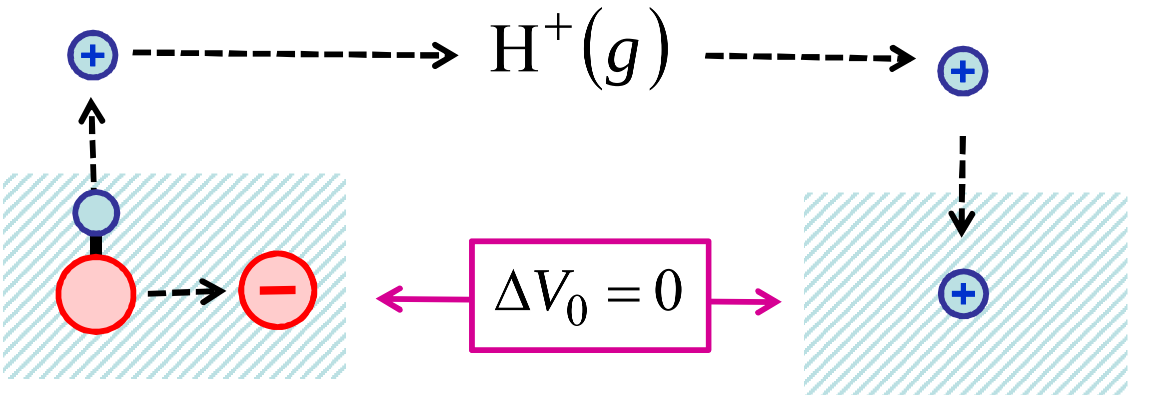
Adiabatic ionization potential

Desolvation free energy H^+

$$eE^\circ = \int_0^1 d\eta \left\langle \Delta_{\mathrm{ip}} E_{\mathrm{X}^-} \right\rangle_\eta + \int_0^1 d\eta \left\langle \Delta_{\mathrm{dp}} E_{\mathrm{H_3O^+}} \right\rangle_{r\eta} - \Delta_{\mathrm{zp}} E_{\mathrm{H}^+} - \Delta_f G_{\mathrm{H}^+(g)}$$

Bias V_0 in the electrostatic reference should cancel

Half cell method for determination pKa



$\Delta_{\mathrm{dp}} A + \boxed{V_0}$

$\Delta_{\mathrm{s}} G_{\mathrm{H}^+} - \boxed{V_0}$

Adiabatic deprotonation energy

Solvation free energy H^+

$$2.3\, k_{\mathrm{B}} T\, \mathrm{p}K_a = \int_0^1 d\eta \left\langle \Delta_{\mathrm{dp}} E_{\mathrm{XH}} \right\rangle_{r\eta} - \int_0^1 d\eta \left\langle \Delta_{\mathrm{dp}} E_{\mathrm{H_3O^+}} \right\rangle_{r\eta} + k_{\mathrm{B}} T \ln\left[c^{\mathrm{o}} \Lambda^3_{\mathrm{H}^+} \right]$$

Bias V_0 in the electrostatic reference should cancel

Small acids: Comparison to experiment

Energies eV	$\Delta_{\mathrm{dp}}A_{\mathrm{XH}}$	$\mathrm{p}K_a$	exp.	$\Delta\mathrm{p}K_a$
HCl	15.1	–7	–7	0
H_3O^+	15.35	–3.2	–1.74	–1.5
HCOOH	15.8	5	3.75	1
H_2S	16.0	8	7.0	1
CH_3SH	16.1	11	10.3	1
NH_4^+	16.1	11	10.2	1
Errrors	statistical uncertainty < 0.1 eV			**MUE =1**

$$\Delta_{\mathrm{dp}}A_{\mathrm{XH}} = \int_0^1 d\eta \left\langle \Delta_{\mathrm{dp}}E_{\mathrm{XH}} \right\rangle_{r\eta}$$

(*Sulpizi*)

Homogeneous $H_2O \rightarrow OH + H$: our benchmark

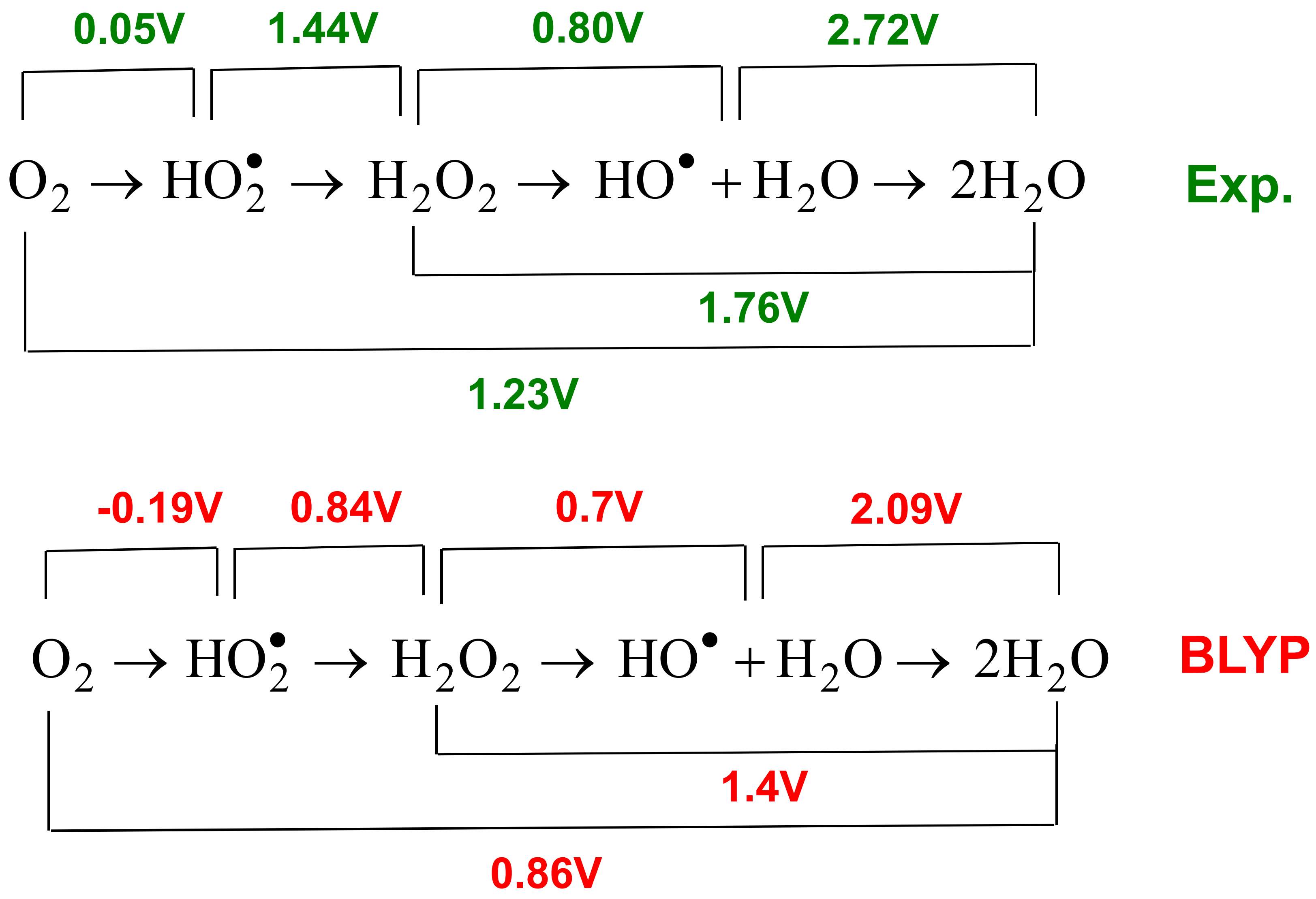
$$\begin{tikzcd}
H_2O \arrow[r, "\mathbf{0.8}"] \arrow[dr, "\text{exp.}", "\boxed{\mathbf{2.7}}"'] & OH^- + H^+ \arrow[d, "\mathbf{1.9}"] \\
 & OH^\bullet + \frac{1}{2}H_2
\end{tikzcd}$$

$$\begin{tikzcd}
H_2O \arrow[r, "\mathbf{0.7}"] \arrow[dr, "\text{BLYP}", "\boxed{\mathbf{2.1}}"'] & OH^- + H^+ \arrow[d, "\mathbf{1.3}"] \\
 & OH^\bullet + \frac{1}{2}H_2
\end{tikzcd}$$

Finite size and time errors "under control"

$$\begin{tikzcd}
H_2O \arrow[r, "\text{charge separation}"] \arrow[dr, "\text{neutral species only}"'] & OH^- + H^+ \arrow[d, "\text{charge recombination}"] \\
 & OH^\bullet + \frac{1}{2}H_2
\end{tikzcd}$$

Reduction O_2 : BLYP/DFTMD performance



0.05V 1.44V 0.80V 2.72V

$$O_2 \rightarrow HO_2^\bullet \rightarrow H_2O_2 \rightarrow HO^\bullet + H_2O \rightarrow 2H_2O$$

Exp.

1.76V

1.23V

-0.19V 0.84V 0.7V 2.09V

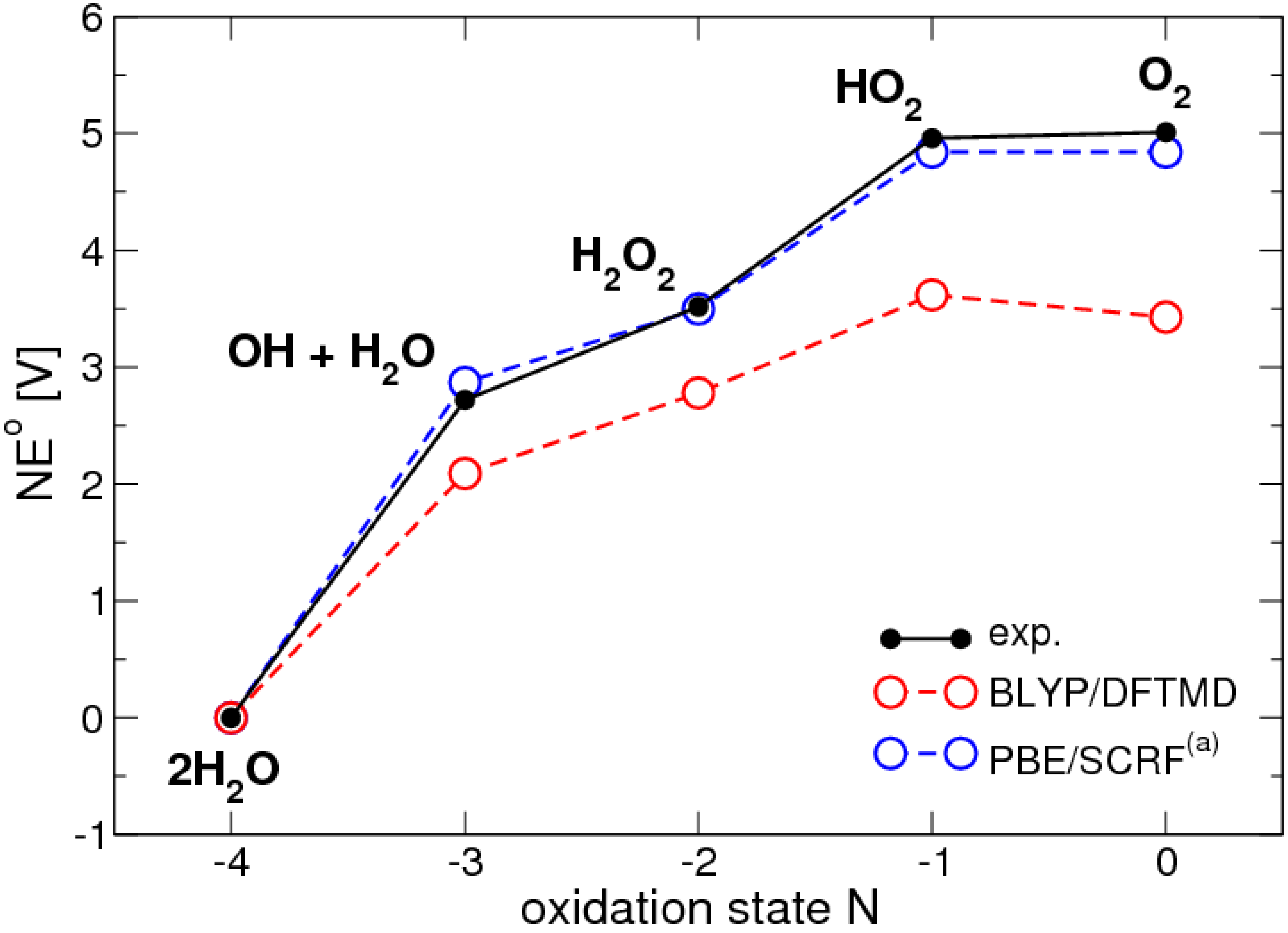
$$O_2 \rightarrow HO_2^\bullet \rightarrow H_2O_2 \rightarrow HO^\bullet + H_2O \rightarrow 2H_2O$$

BLYP

1.4V

0.86V

Frost diagram reduction O_2



[a] R. Jinouchi and A. B. Anderson, *Phys. Chem. C* **112** (2008), 8747

$H_2O \rightarrow OH$ + H in solution: Effect of HF exchange

exp.

$$\begin{tikzcd}
H_2O \arrow[r, "0.8"] \arrow[dr, swap, "\boxed{2.7}"] & OH^- + H^+ \arrow[d, "1.9"] \\
 & OH^\bullet + \frac{1}{2}H_2
\end{tikzcd}$$

BLYP

$$\begin{tikzcd}
H_2O \arrow[r, "0.7"] \arrow[dr, swap, "\boxed{2.1}"] & OH^- + H^+ \arrow[d, "1.3"] \\
 & OH^\bullet + \frac{1}{2}H_2
\end{tikzcd}$$

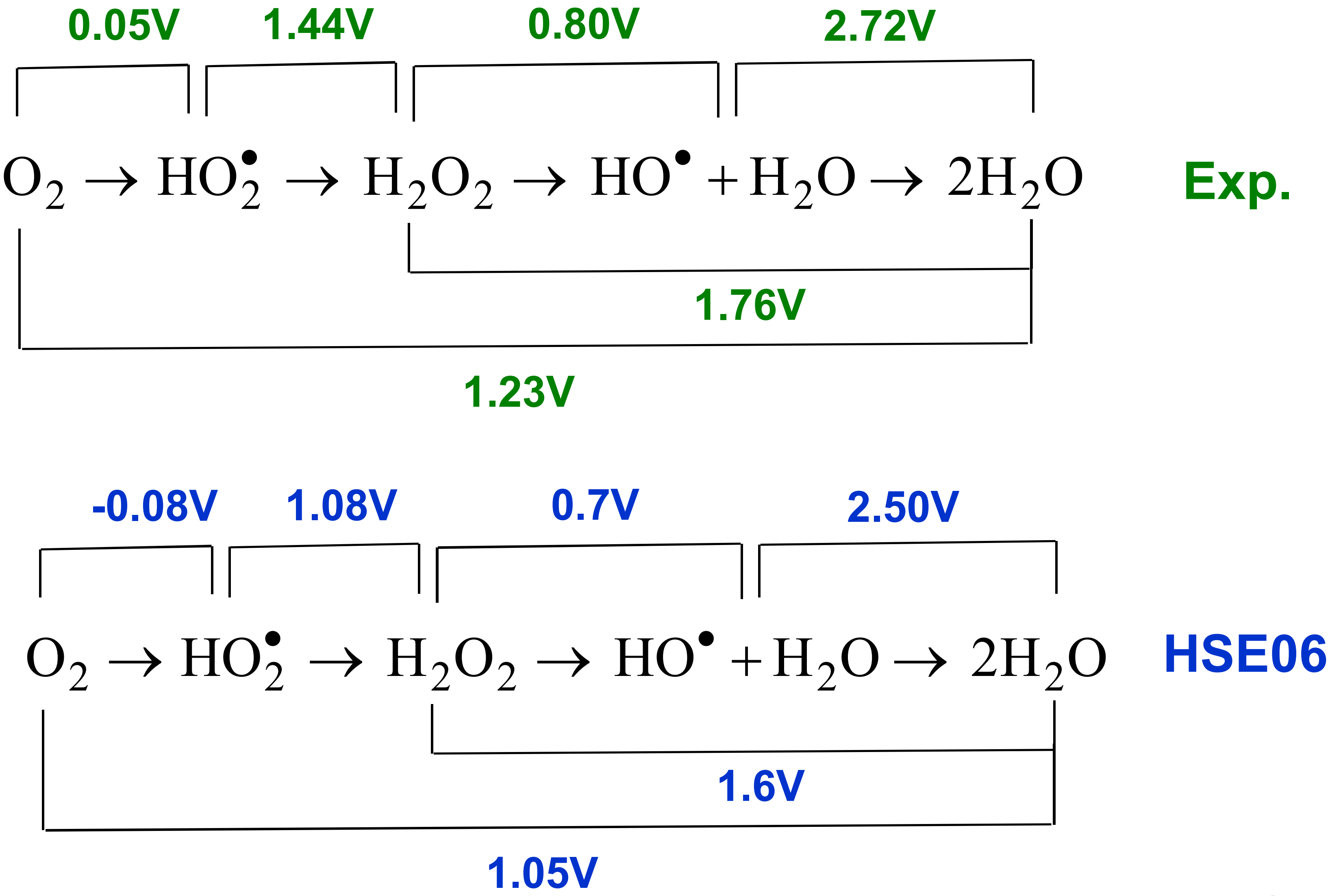
Energies in eV

HSE*

$$\begin{tikzcd}
H_2O \arrow[r, "0.7"] \arrow[dr, swap, "\boxed{2.5}"] & OH^- + H^+ \arrow[d, "1.7"] \\
 & OH^\bullet + \frac{1}{2}H_2
\end{tikzcd}$$

*Guidon, M.; Hutter, J.; VandeVondele, J.
"Auxiliary Density Matrix Methods for
Hartree-Fock Exchange Calculations."
J. Chem. Theory Comput.(**2010**),*6,* 2348.

Reduction O_2 :HSE06/DFTMD performance



$$O_2 \rightarrow HO_2^\bullet \rightarrow H_2O_2 \rightarrow HO^\bullet + H_2O \rightarrow 2H_2O$$

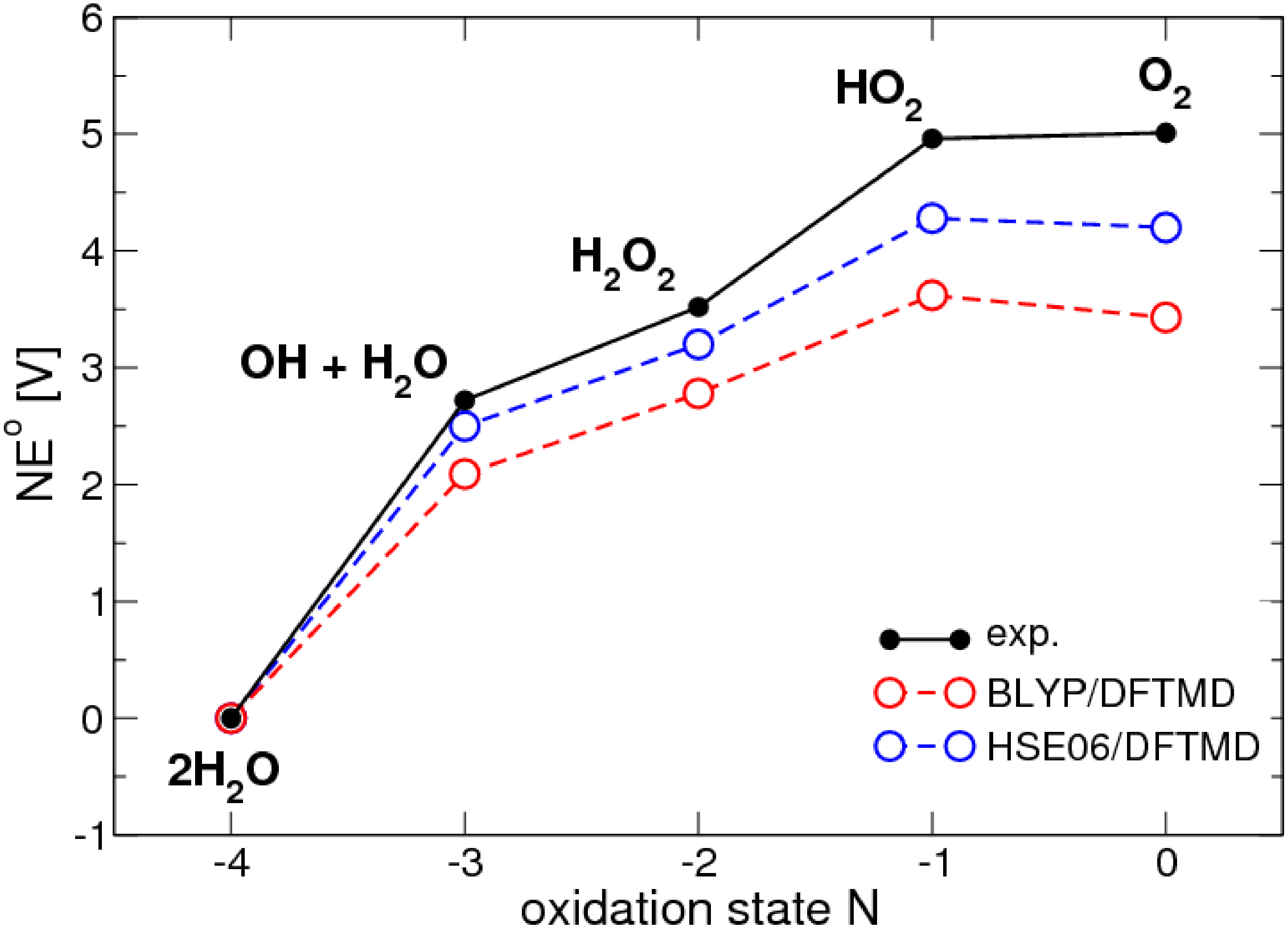
Exp.

$$O_2 \rightarrow HO_2^\bullet \rightarrow H_2O_2 \rightarrow HO^\bullet + H_2O \rightarrow 2H_2O$$

HSE06

(Cheng)

Frost diagram reduction O_2



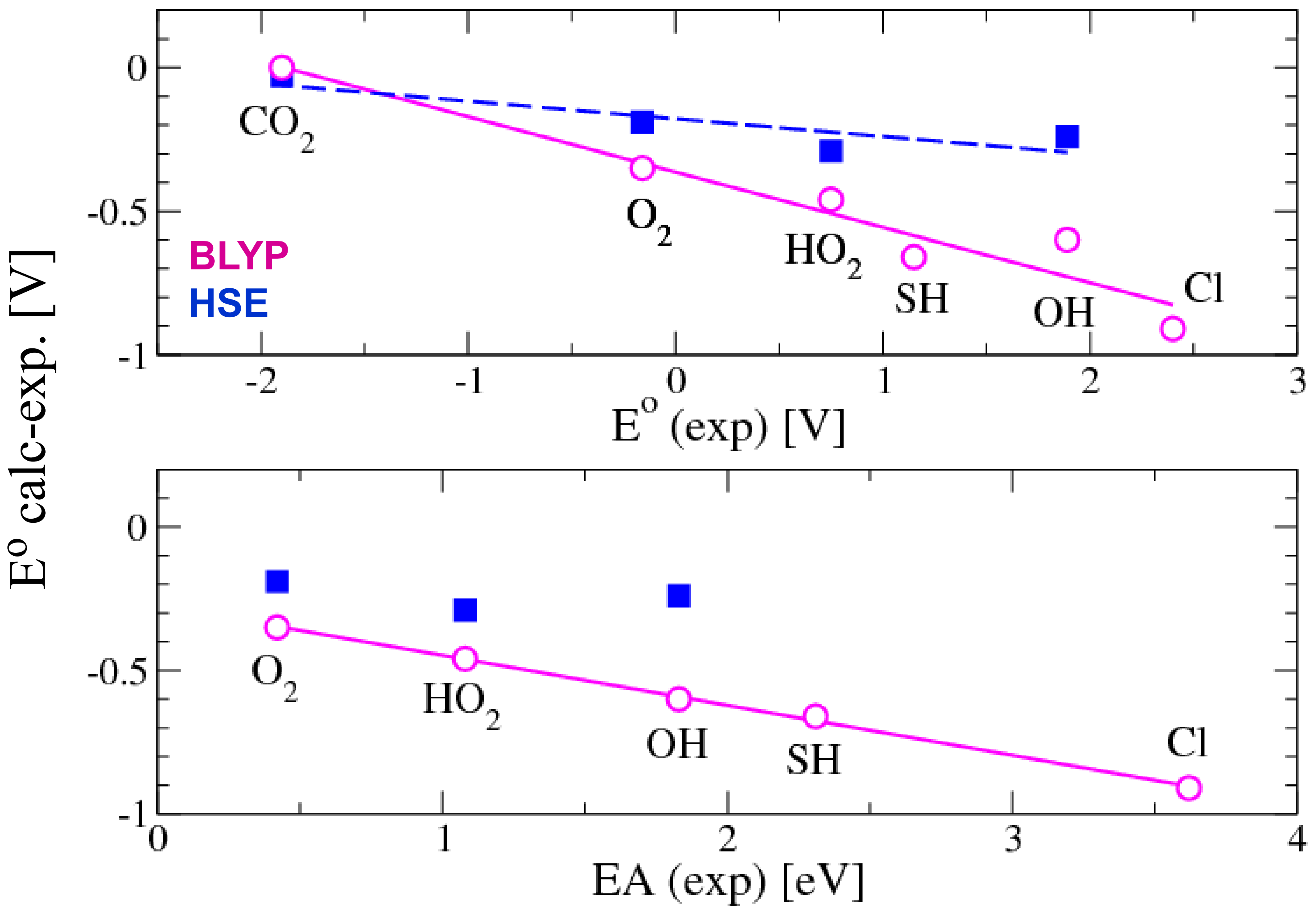
BLYP electron affinities in vacuum and solution

Units V	*EA* vacuum (eV)		Reduction potential *vs* NHE (V)		
	BLYP	exp.	BLYP	exp.	diff.
O_2/O_2^-	0.52	0.42	–0.5	–0.16	–0.4
$OOH^\bullet/OOH^-$	0.96	1.08	0.3	0.75	–0.5
$OH^\bullet/OH^-$	1.80	1.83	1.3	1.89	–0.6
$SH^\bullet/SH^-$	2.19	2.31	0.5	1.15	–0.6
$Cl^\bullet/Cl^-$	3.52	3.62	1.5	2.4	–0.9
MUE	0.09				**0.5**

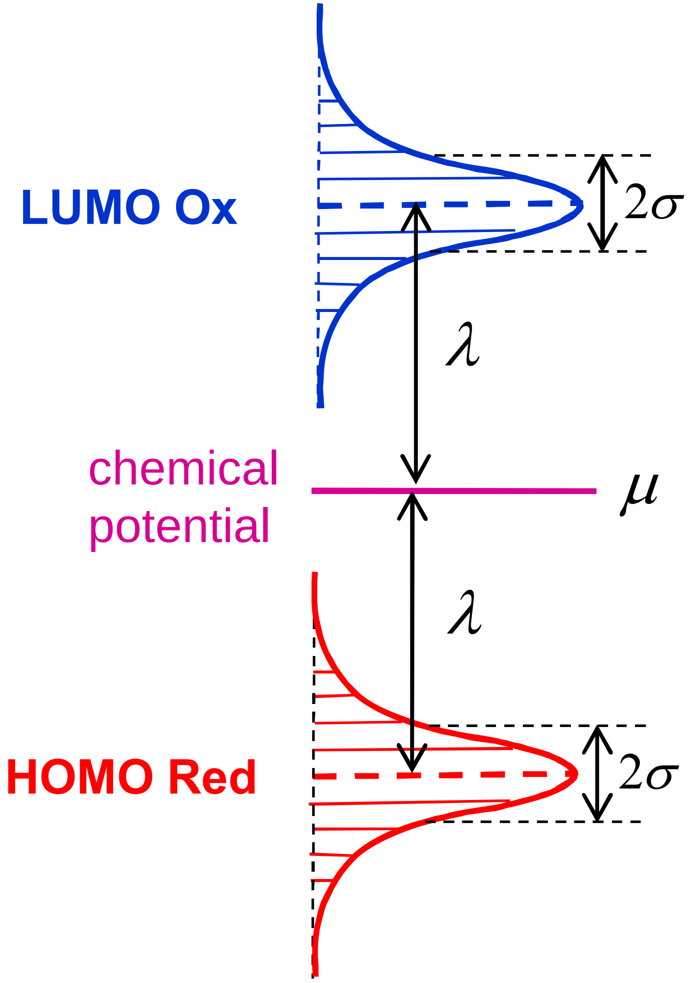
Why the much larger error in solution?

(*Adriaanse*)

Correlating the DFT error



One-electron orbital picture (Marcus-Gerischer)



Electronic chemical potential

$$\mu = \frac{1}{2}\left(\varepsilon_{\mathrm{HOMO}} + \varepsilon_{\mathrm{LUMO}}\right)$$

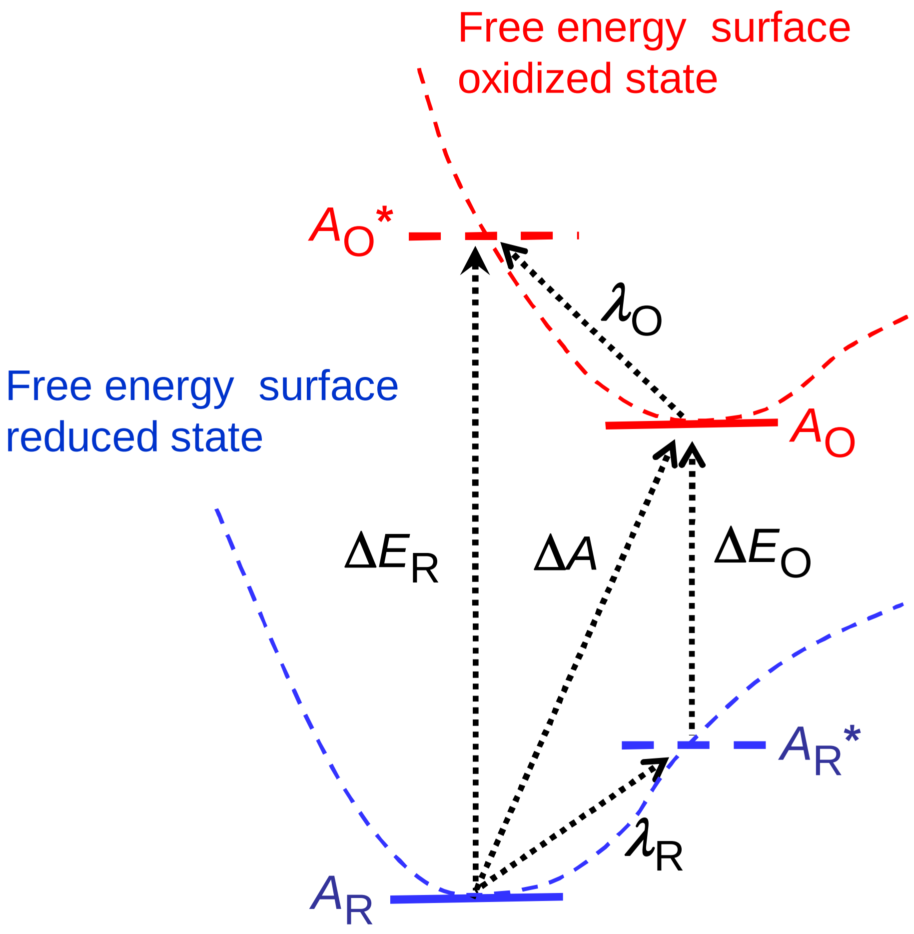
Reorganization energy

$$\lambda = \frac{1}{2}\left(\varepsilon_{\mathrm{LUMO}} - \varepsilon_{\mathrm{HOMO}}\right)$$

Solvent fluctuations

$$\sigma^2 = 2k_{\mathrm{B}}T\lambda$$

Total enery (potential of mean force) picture



Non-linear solvent response

$$\Delta E_{\mathrm{R}} = \Delta A + \lambda_{\mathrm{O}}$$

$$\Delta A = \lambda_{\mathrm{R}} + \Delta E_{\mathrm{O}}$$

Linear response approximation

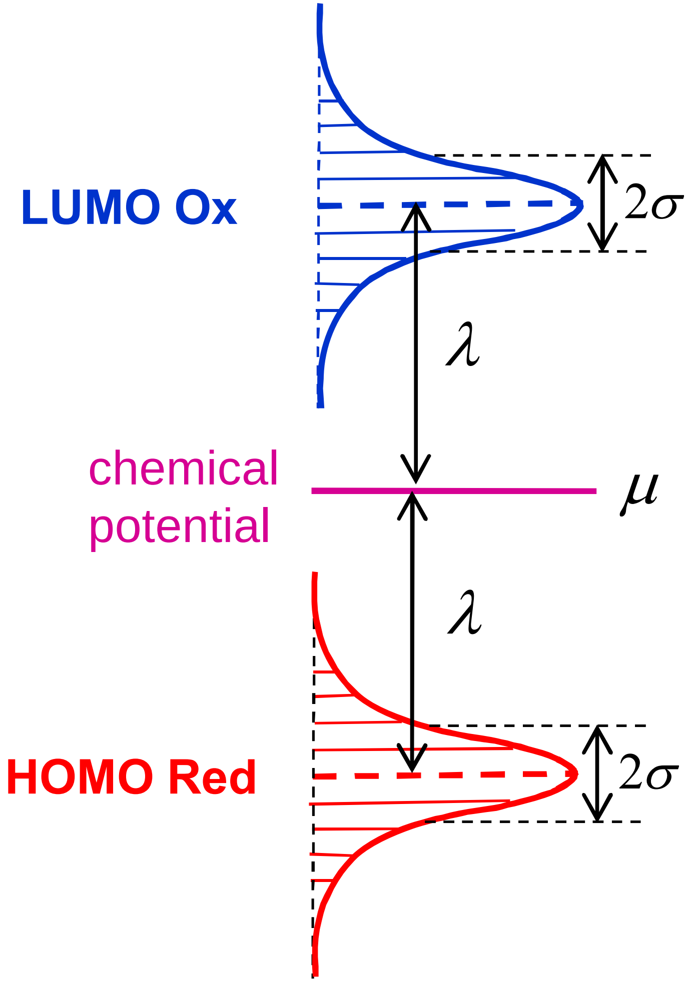
$$\lambda_{\mathrm{R}} = \lambda_{\mathrm{O}} = \lambda$$

$$\lambda = \tfrac{1}{2}\left(\Delta E_{\mathrm{R}} - \Delta E_{\mathrm{O}}\right)$$

$$\Delta A = \tfrac{1}{2}\left(\Delta E_{\mathrm{R}} + \Delta E_{\mathrm{O}}\right)$$

(Zhou and Szabo, JCP 1995)

One-electron orbital picture (Marcus-Gerischer)



Electronic chemical potential

$$\mu = \frac{1}{2}\left(\varepsilon_{\mathrm{HOMO}} + \varepsilon_{\mathrm{LUMO}}\right)$$

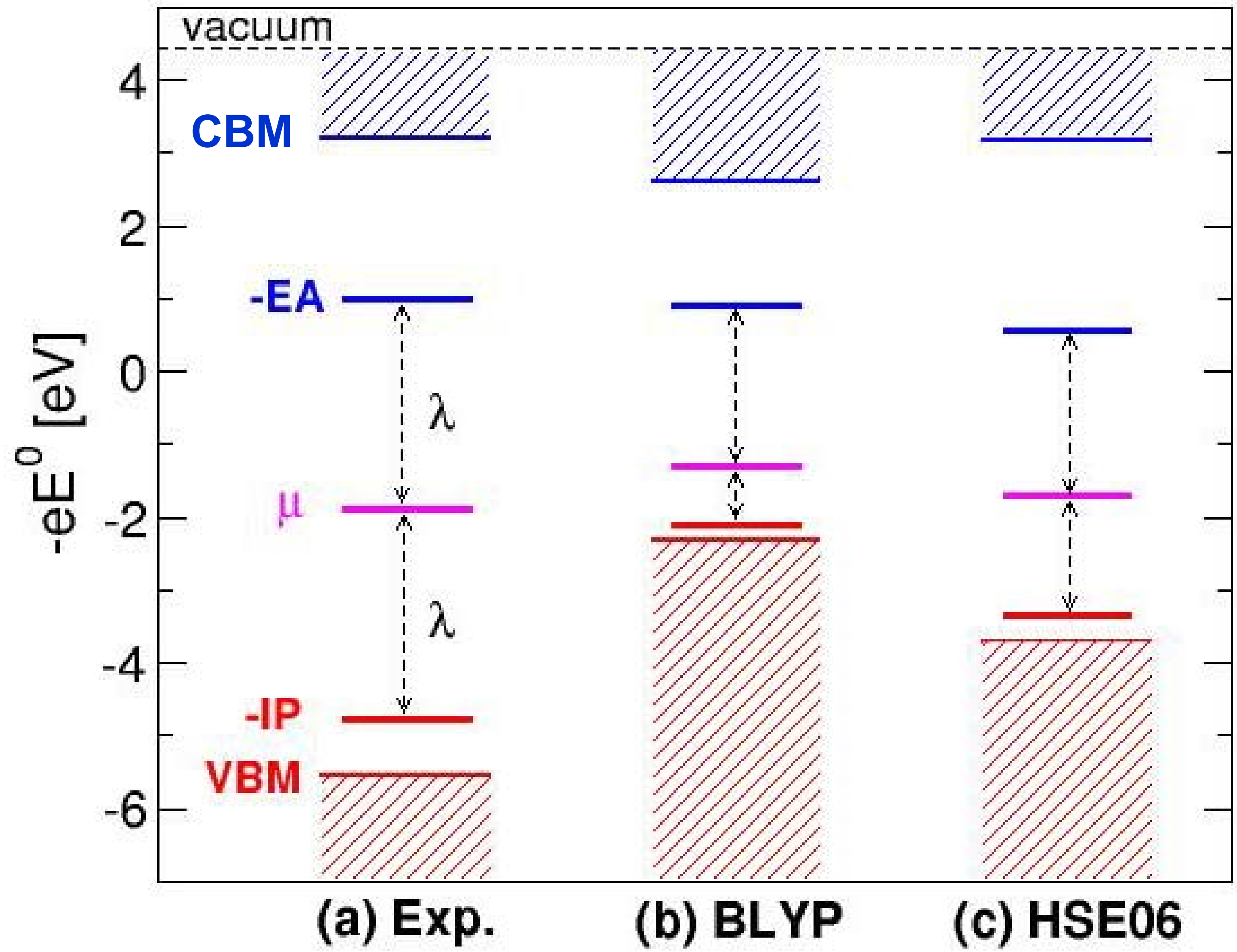
Reorganization energy

$$\lambda = \frac{1}{2}\left(\varepsilon_{\mathrm{LUMO}} - \varepsilon_{\mathrm{HOMO}}\right)$$

Solvent fluctuations

$$\sigma^2 = 2k_{\mathrm{B}}T\lambda$$

Vertical and adiabatic levels OH/water



Interfacial Electrochemistry:

Is molecular simulation finally ready for 19th century science?

We have made a start

Jun Cheng

Marialore Sulpizi

Joost VandeVondele

Regla Ayala

Francesca Costanzo

John Kattirzi