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1938-10

Workshop on Nanoscience for Solar Energy Conversion

27 - 29 October 2008

Quantum simulations of electrochemical systems

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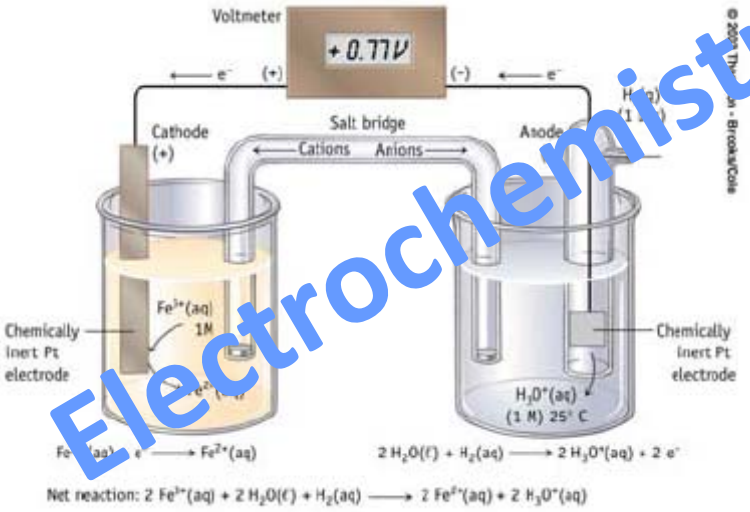
Energy harvesting and conversion: DFT challenges

1. **Oxidation states and charge-transfer excitations (IP/EA catastrophe, long-range self-interactions)**

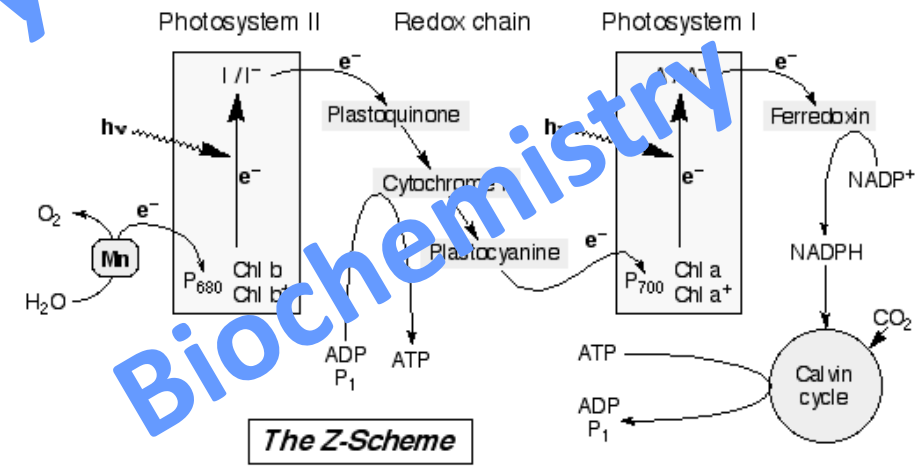
2. **Transition-metal catalysis (localized *d, f* orbitals, short-range self-interactions)**

3. **Realistic electrochemistry: quantum simulations at applied electrochemical potentials**

Electron-transfer reactions



Electrochemistry

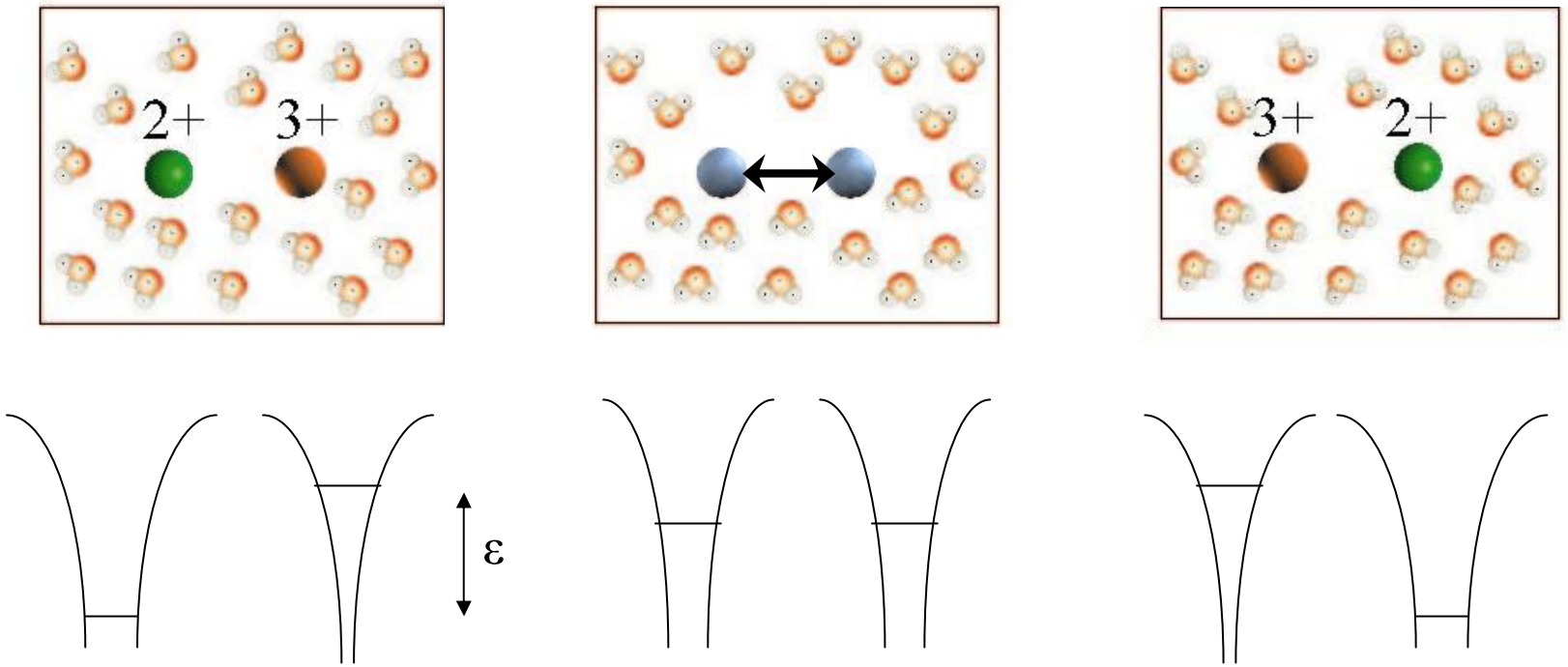


Biochemistry

- **Redox reactions in which an electron moves from a donor to an acceptor (via a bridge, in “inner-sphere” reactions)**
- **Rudolph Marcus (’50s-’60s, Nobel prize in Chemistry, 1992)**
- **Arieh Warshel, David Chandler (’80s)**

Marcus picture of electron transfer

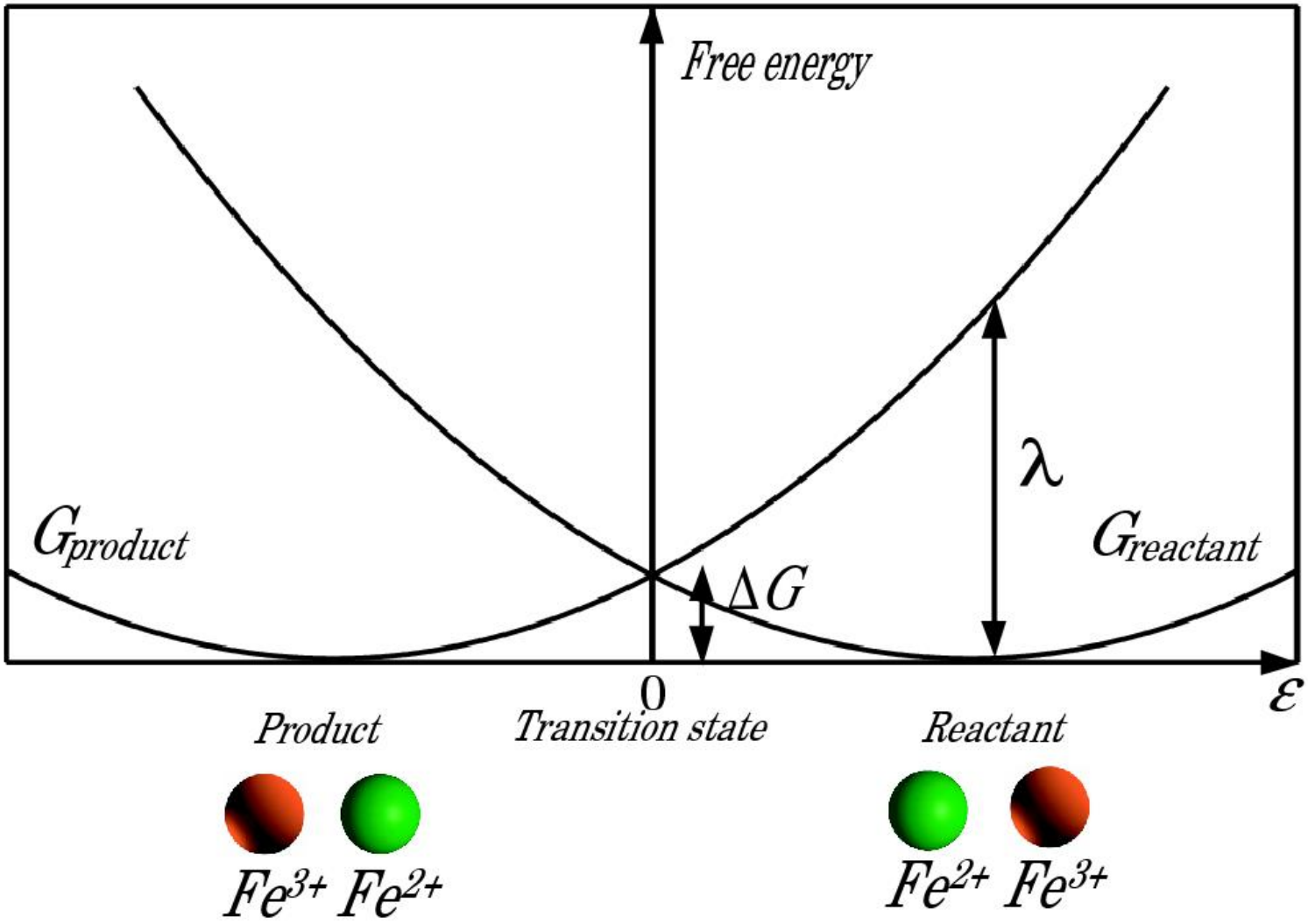
- Electron transfer mediated by polar solvent fluctuations.
- Tunneling can occur when reactant and product are degenerate



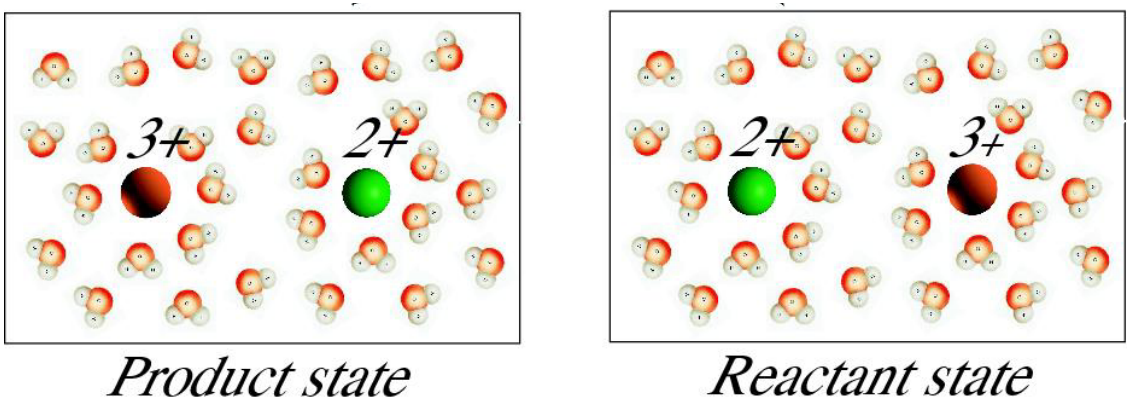
- $\varepsilon = \varepsilon_{product} - \varepsilon_{reactant}$ is the energy gap or reaction coordinate

R. A. Marcus, J. Chem. Phys. 43, 679 (1965)
A. Warshel, J. Chem. Phys. 86, 2218 (1982)
D. Chandler, Classical and Quantum Dynamics in Condensed Phase Simulations, pp. 25-49 (1998)

Ferrous-ferric self-exchange

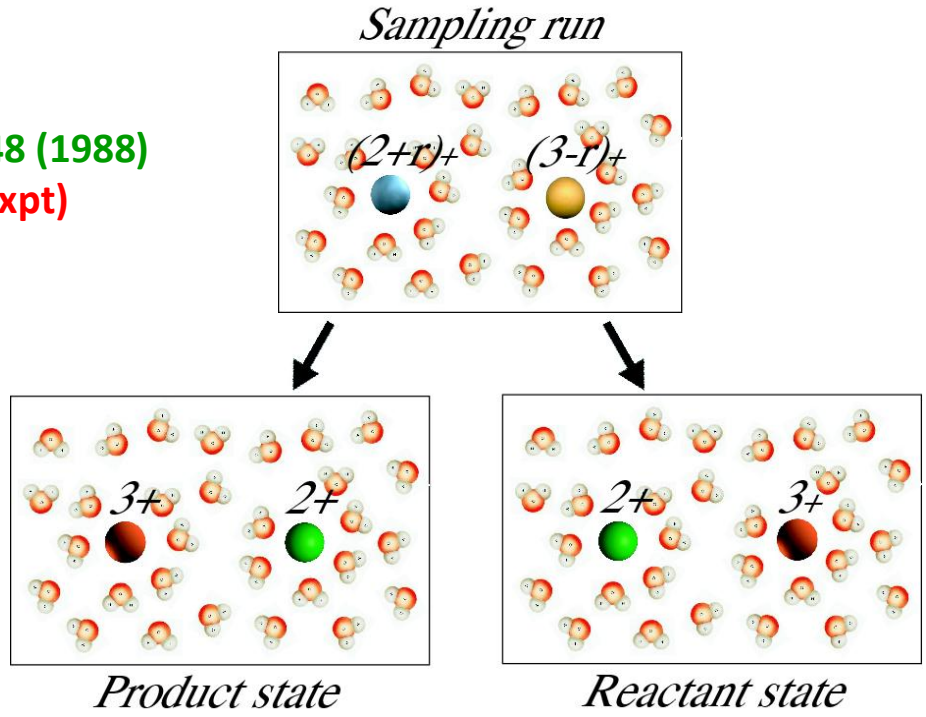


Sampling ε across the phase space



Calculation of the energy gap

R. A. Kuharski et al.
J. Chem. Phys. 89, 3248 (1988)
λ = 3.6 eV (vs 2.1 eV expt)



1. **Umbrella sampling runs:** Car-Parrinello simulations with fractional charged irons

2. **Constrained runs:** Car-Parrinello simulations constrained on the stored trajectories, and constrained on the reactant state and in the product state

Umbrella sampling

3. **Statistics**: $\varepsilon(t) = \varepsilon_{product}(t) - \varepsilon_{reactant}(t)$ is the reaction coordinate at each time step;

4. $G_{reactant}(\varepsilon) = -k_B T \ln(P(\varepsilon))$ **is the free energy, where** $P(\varepsilon)$ is the probability distribution of ε, after corrections for **non-Boltzmann statistics** in the umbrella sampling

When sampling Hamiltonian is not same as reactant Hamiltonian

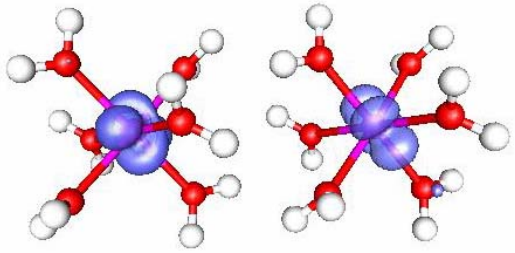
$$P(\varepsilon) = \frac{\int \delta(\varepsilon(\{r\}) - \varepsilon) \exp[-\beta E_r(\{r\})] dr_1 \cdots dr_N}{\int \exp[-\beta E_r(\{r\})] dr_1 \cdots dr_N}$$

$$= \frac{\int \exp[-\beta E_s(\{r\})] \delta(\varepsilon(\{r\}) - \varepsilon) \exp[-\beta [E_r(\{r\}) - E_s(\{r\})]] dr_1 \cdots dr_N}{\int \exp[-\beta E_s(\{r\})] \exp[-\beta [E_r(\{r\}) - E_s(\{r\})]] dr_1 \cdots dr_N}$$

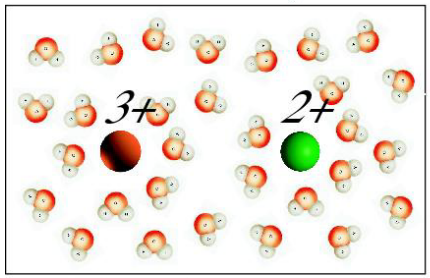
$$= \frac{\sum_t \delta_{\varepsilon,\varepsilon(t)} \exp[-\beta [E_r(t) - E_s(t)]]}{\sum_t \exp[-\beta [E_r(t) - E_s(t)]]}$$

DFT shortcomings: ground and excited states

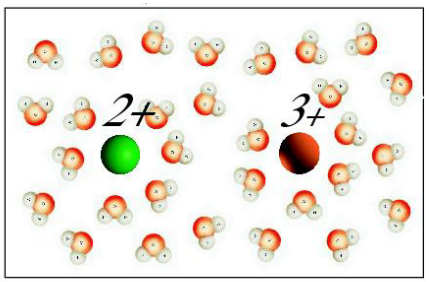
a) The transferring electron (minority spin 3d electron for iron ions) splits between two ions – **the ground state is incorrect**



b) The energy gap is an **excited state property**



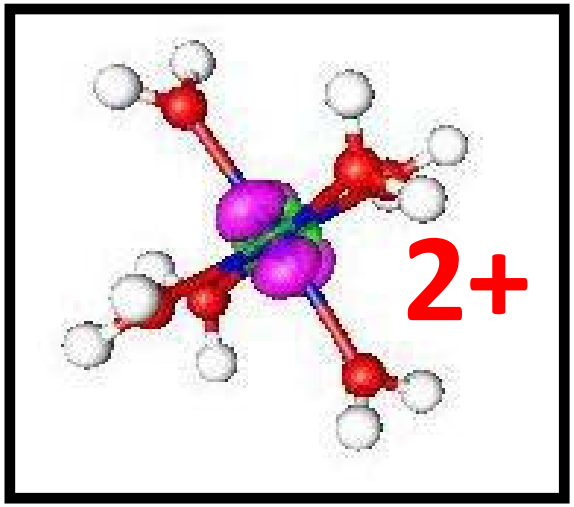
Product state

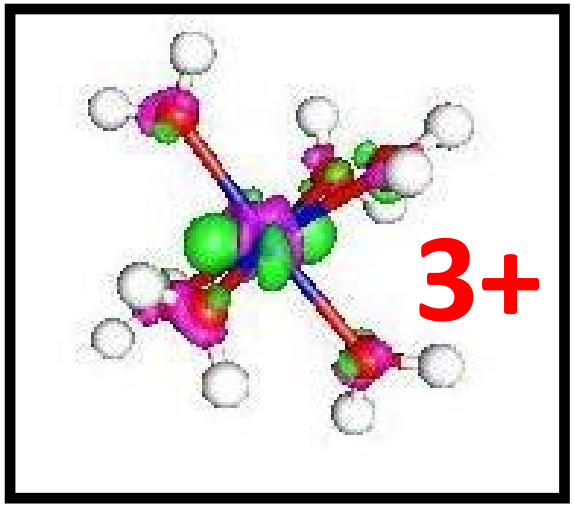


Reactant state

A penalty-functional for oxidation-reductions

You know the electronic structure you want





You capture it by measuring the occupation of target orbitals:

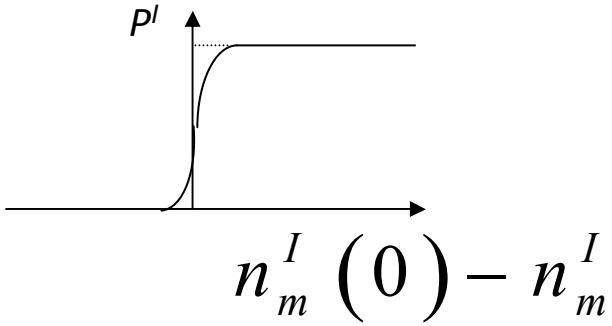
$$n^{I\sigma}_{mm'} = \sum_i \langle \psi^{\sigma}_i \mid \varphi^{I}_{m'} \rangle \langle \varphi^{I}_{m} \mid \psi^{\sigma}_i \rangle$$

A penalty-functional for oxidation-reductions

Penalize electronic states that have not the target occupation

$$E\left[\{\psi_i\}\right] \Rightarrow E\left[\{\psi_i\}\right] + E_{penalty}\left[n^{I\sigma}(0)\right]$$

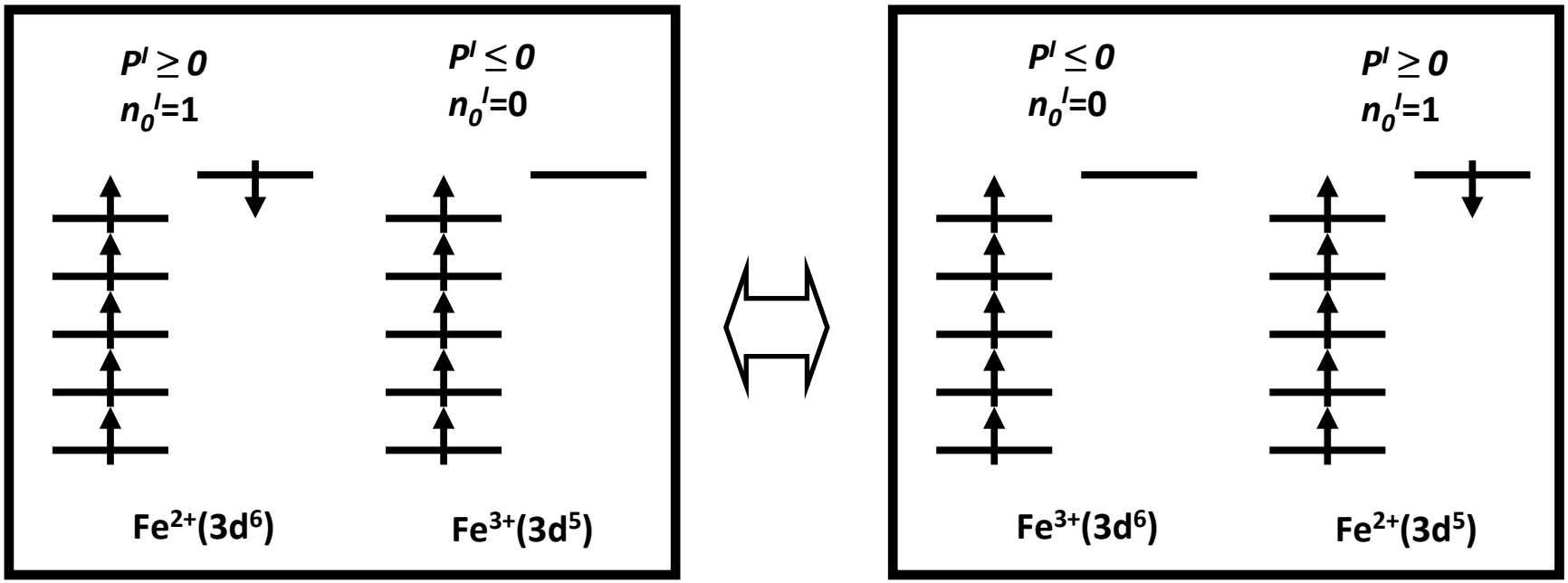
$$= E\left[\{\psi_i\}\right] + \sum_I \frac{P^I}{\sigma_I\sqrt{2\pi}} \int_{-\infty}^{n^{I\sigma}(0)-n^{I\sigma}} \exp\left(-\frac{x^2}{2\sigma_I^2}\right) dx$$



Constrained DFT - see also:

P. Dederichs et al, PRL 53, 2512 (1984)
T. Van Voorhis, PRA 72, 024502 (2005)
P. H. L. Sit, M Cococcioni and N. Marzari, PRL 97, 028303 (2006)
J. Boehler et al, PRB 75, 115409 (2007)

Controlling oxidation states



$f_0{}^l$ is a COMPACT PHOTOGRAPH of the electronic structure you want

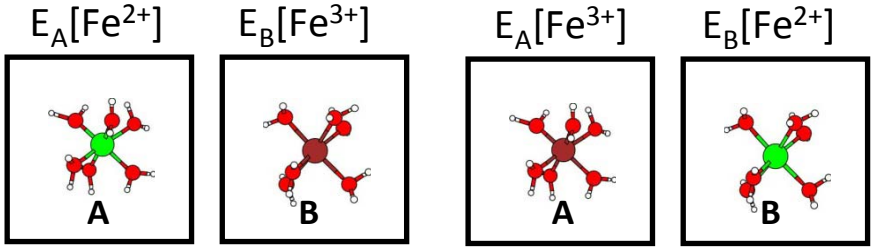
In aqueous environment, to reproduce the correct ferrous, ferric picture:

	P^l	$n_0{}^l$	σ_l
ferrous	**0.54 eV**	**0.95**	**0.01**
ferric	**-0.54 eV**	**0.28**	**0.01**

Is it correct ? (Quantitative picture)

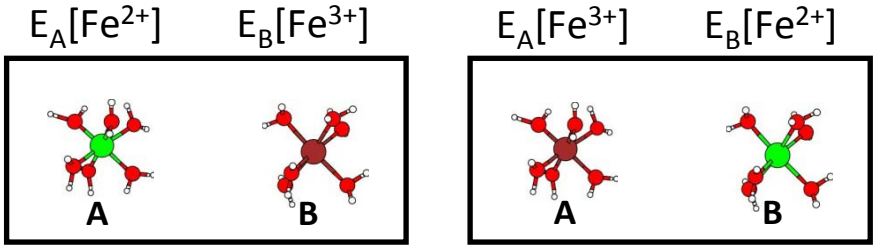
Exact DFT calculations:

$\varepsilon = \{E_A[Fe^{3+}] + E_B[Fe^{2+}]\} - \{E_A[Fe^{2+}] + E_B[Fe^{3+}]\}$



Penalty functional:

$\varepsilon = E_{AB}[Fe^{3+} - Fe^{2+}] - E_{AB}[Fe^{2+} - Fe^{3+}]$



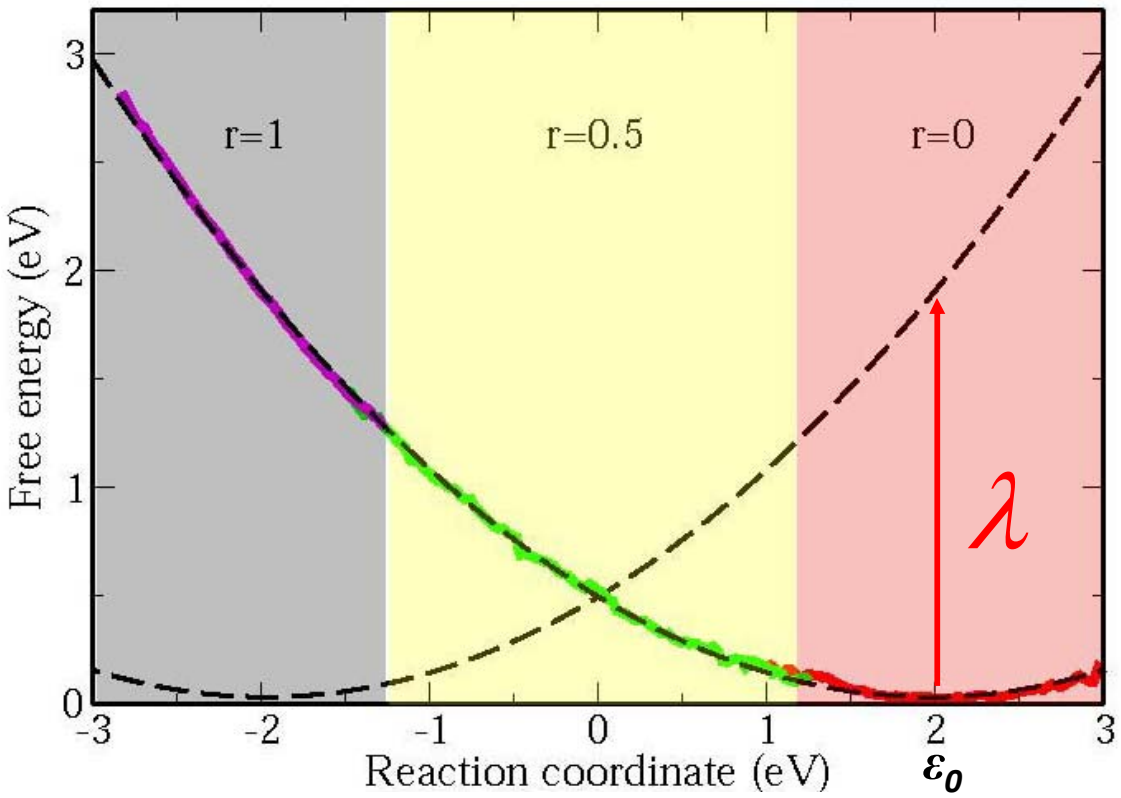
Exact DFT	Penalty functional
0.622 eV	0.632 eV
0.542 eV	0.569 eV
0.769 eV	0.769 eV
1.012 eV	1.027 eV

Take home message ☺

Standard LDA/GGA DFT predicts excited states with 0.01 eV accuracy !

(for some charge-transfer reactions…)

Realistic Marcus free energy surface



Two ions, separated 5.5 Å apart, solvated in 62 water molecules at 400 K

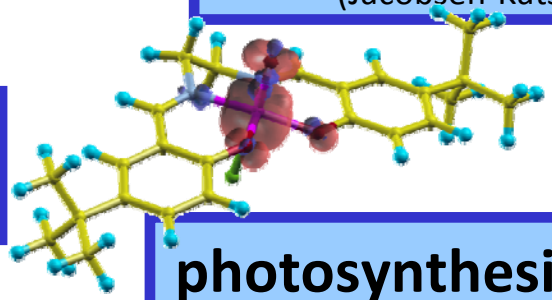
$\lambda = G_{product}(\varepsilon_0) - G_{reactant}(\varepsilon_0) =$ **1.93 eV (expt. 2.1 eV)**

P. H. L. Sit, M Cococcioni and N. Marzari, Phys. Rev. Lett. 97, 028303 (2006)

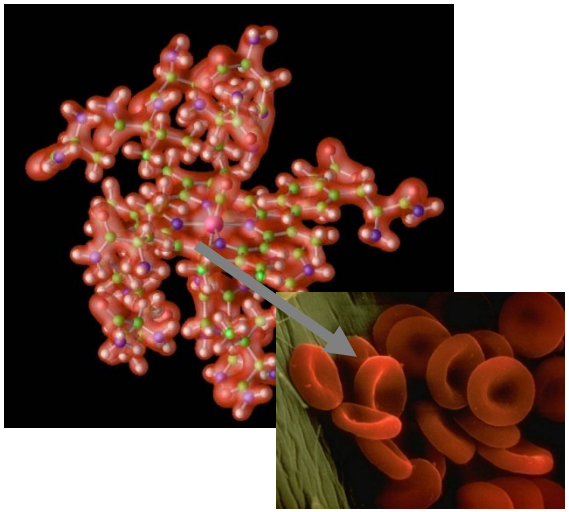
Transition-metal chemistry

Transition metals are reactive centers of fundamental natural and synthetic reactions:

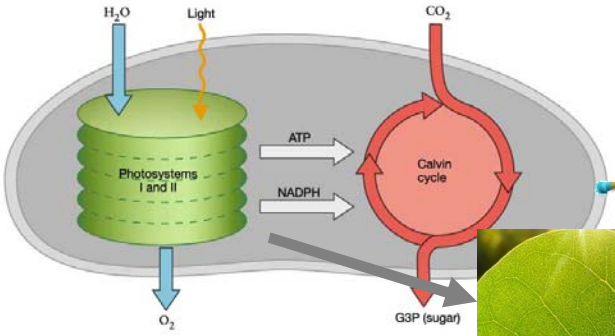
chiral epoxidation
(Jacobsen-Katsuki catalyst).

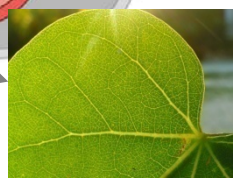


hemeproteins
(Myoglobin pictured).

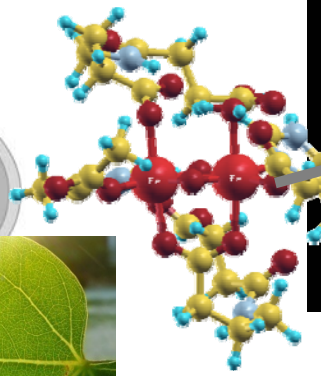


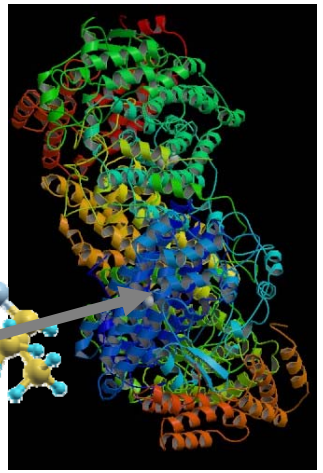
photosynthesis
(Photosystems I/II).





oxidoreductases
(Methane monooxygenase).





But *most* electronic-structure approaches *fail* to describe transition metal chemistry accurately!

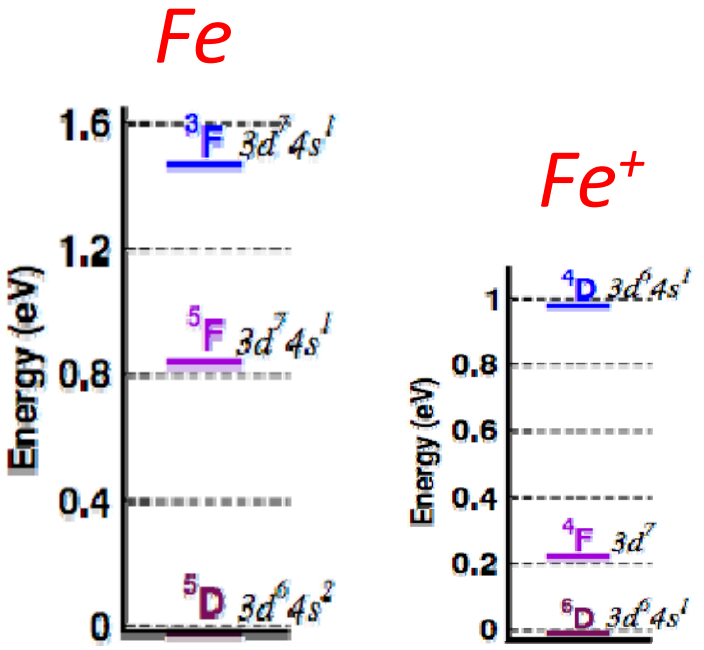
Transition-metal chemistry

d,f electrons are challenging

1)localized

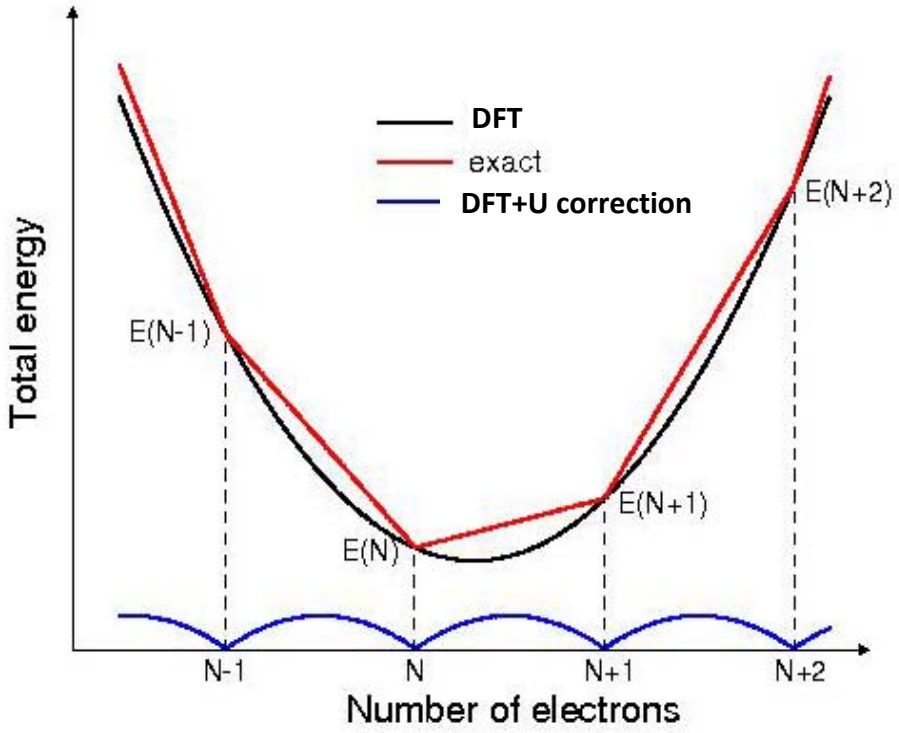
2)closely spaced levels

3)open shell: several configurations and spins



A DFT + Hubbard U approach

$$\frac{U}{2}\sum_{I,\sigma}\sum_{mm'}[n^{I\sigma}_{mm'}(\delta_{m'm}-n^{I\sigma}_{m'm})]$$



GGA energy has *unphysical curvature*

the exact solution *is piecewise linear*

correction reproduces exact solution

U is the *intrinsic* unphysical curvature of the GGA solution;

U is a FIRST-PRINCIPLES linear-response property:

$$U=\frac{d^2E^{LDA}}{d(n^{Id})^2}-\frac{d^2E_0^{LDA}}{d(n^{Id})^2}$$

U and rotationally-invariant U: V.I. Anisimov and coworkers PRB (1991), PRB (1995).

LRT U: M. Cococcioni and S. de Gironcoli. PRB (2005)

Isooelectronic FeO^+ series

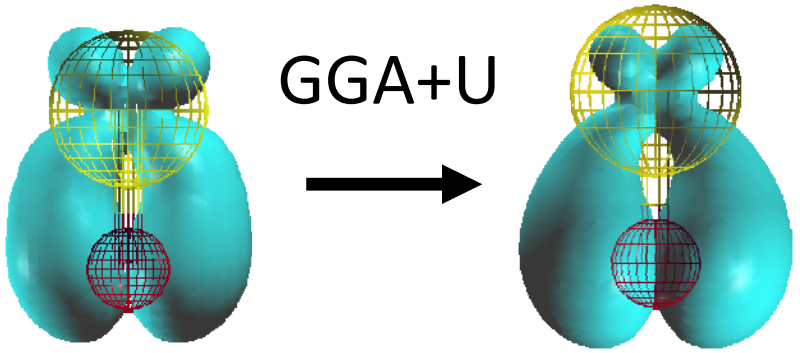
$^6\Sigma^+$

FeO^+	5.50
FeN	4.38
MnO	3.41
CrO^-	2.85
CrF	2.00

Structural Parameters: FeO^+

	$^6FeO^+$			$^4FeO^+$		
Method	R_e	ω_e	$\omega_e x_e$	R_e	ω_e	$\omega_e x_e$
GGA	1.62	901	328	1.56	1038	332
GGA+U	1.66	749	432	1.75	612	172
CCSD(T)	1.66	724	434	1.70	633	188

Delocalized minority spin π bond of $^4FeO^+$

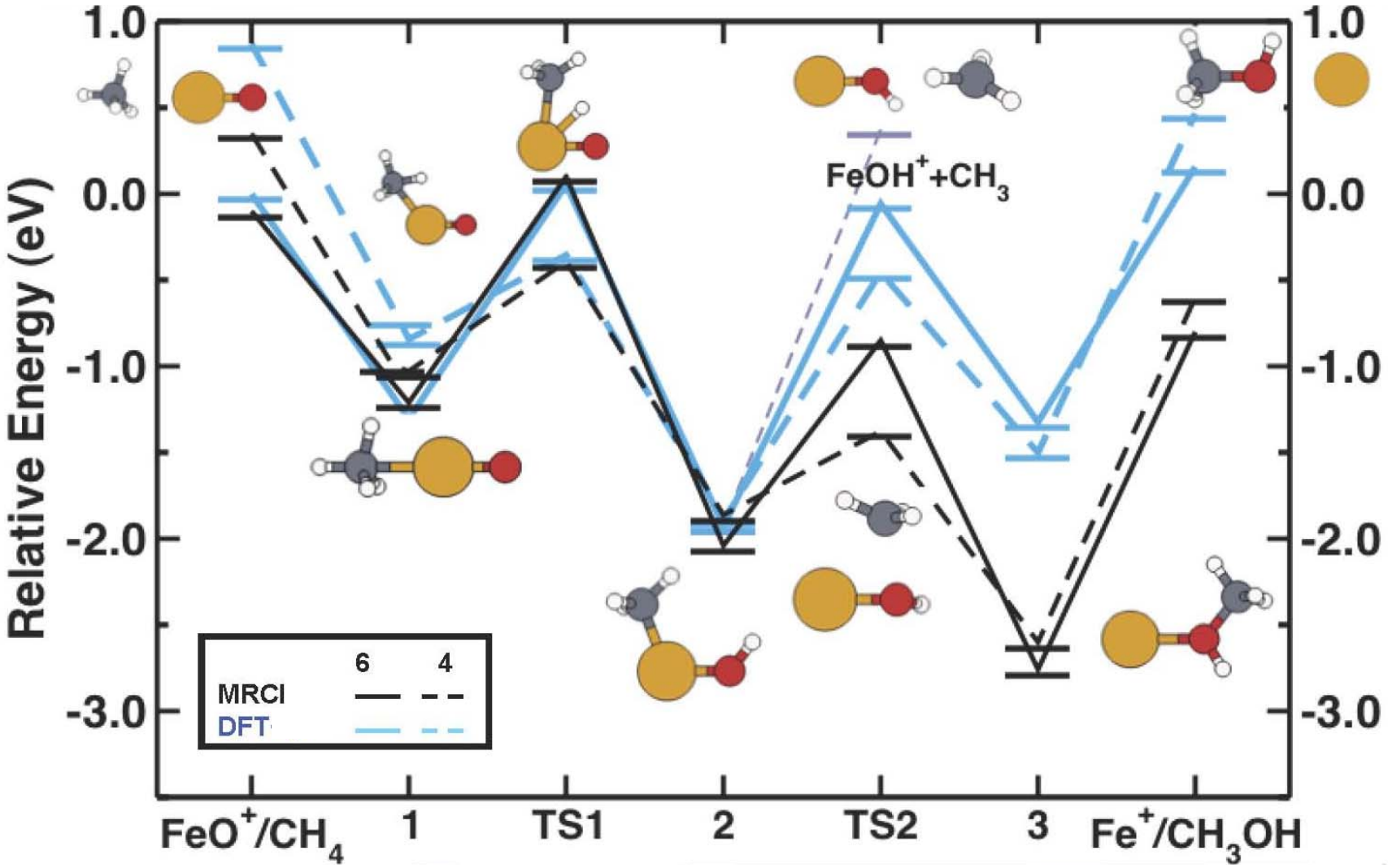


Multiplet Splittings: Fe_2 and Fe_2^-

State	B3LYP	GGA	$+U_0$ (2eV)	$+U_{scf}$ (3eV)	CCSD(T)	MRCI[a]
$^8\Sigma_g^-$	0.00	0.00	0.00	0.00	0.00	0.00
$^8\Delta_g$	0.14	-0.52	0.04	0.38	0.40	0.45
$^9\Sigma_g^-$	0.00	0.00	0.00	0.00	0.00	0.00
$^7\Sigma_g^-$	0.34	0.65	0.66	0.60	0.55	0.62
$^7\Delta_u$	0.18	-0.12	0.48	0.72	0.86	0.69
$^9\Delta_g$	0.36	0.28	0.36	0.41	0.38	0.45

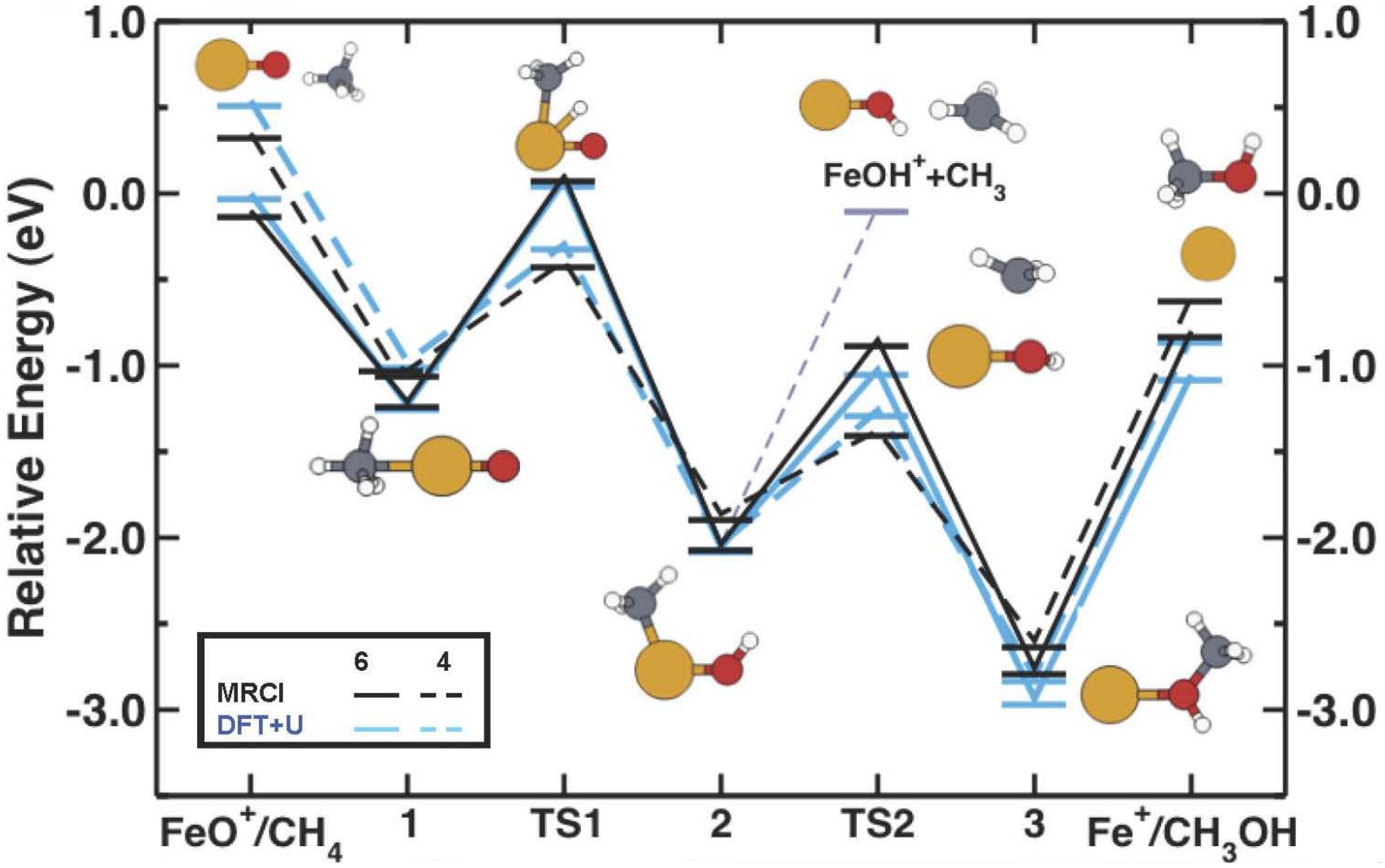
H.J. Kulik, M. Cococcioni, D.A. Scherlis, and N. Marzari, Phys. Rev. Lett. (2006)

CH_4 on FeO^+: GGA



H.J. Kulik and N. Marzari, JCP in press (2008)

CH_4 on FeO^+: GGA+U



H.J. Kulik and N. Marzari, JCP in press (2008)

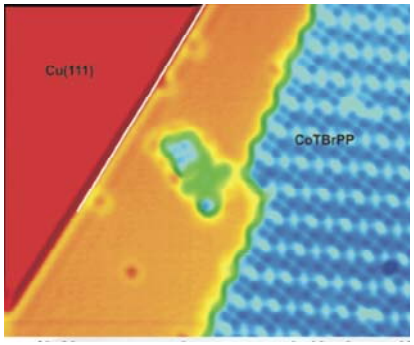
Multiplet splittings

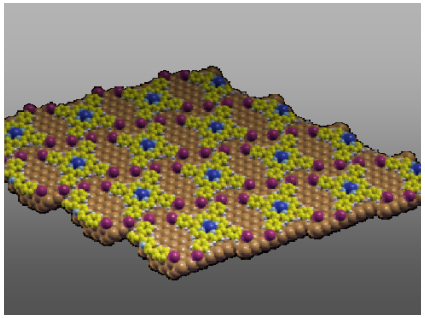
Mean Absolute Errors

	GGA	GGA+U	B3LYP
Bond length (10^{-2} Å)	4.3	2.2	1.3
Multiplet splitting (eV)	0.20	0.04	0.30

Co-Porphyrin SAM on Cu(111)

Experiments show net spin on the outer ring of the molecule, not on Co when in SAM on Cu(111) surface (in collaboration with S-W Hla, Ohio U.)

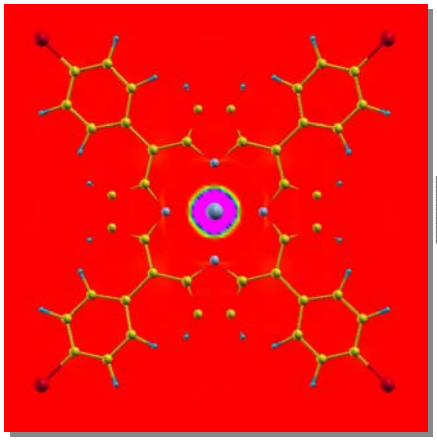




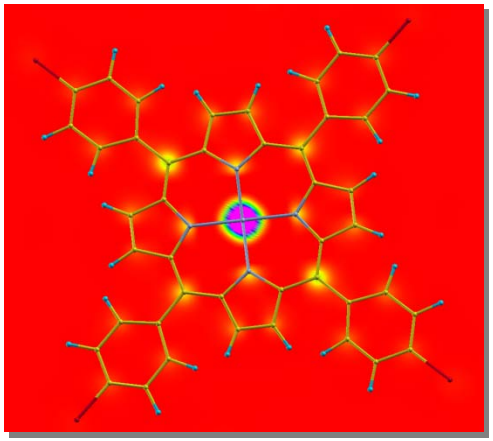
Unit cell: *Co-TBrPP on Cu(111) slab (177 atoms, 1357 e^-).*

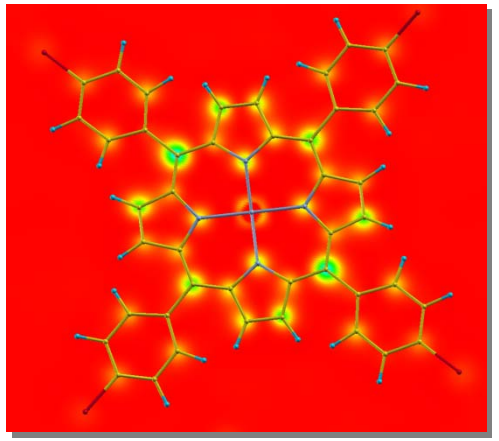
CPU Time: *20hrs on 6 2.40GHz Intel Core 2 Duos.*

isolated molecule ***SAM on Cu(111)***



atop Cu(111)





GGA and GGA+U **GGA** **GGA+U**

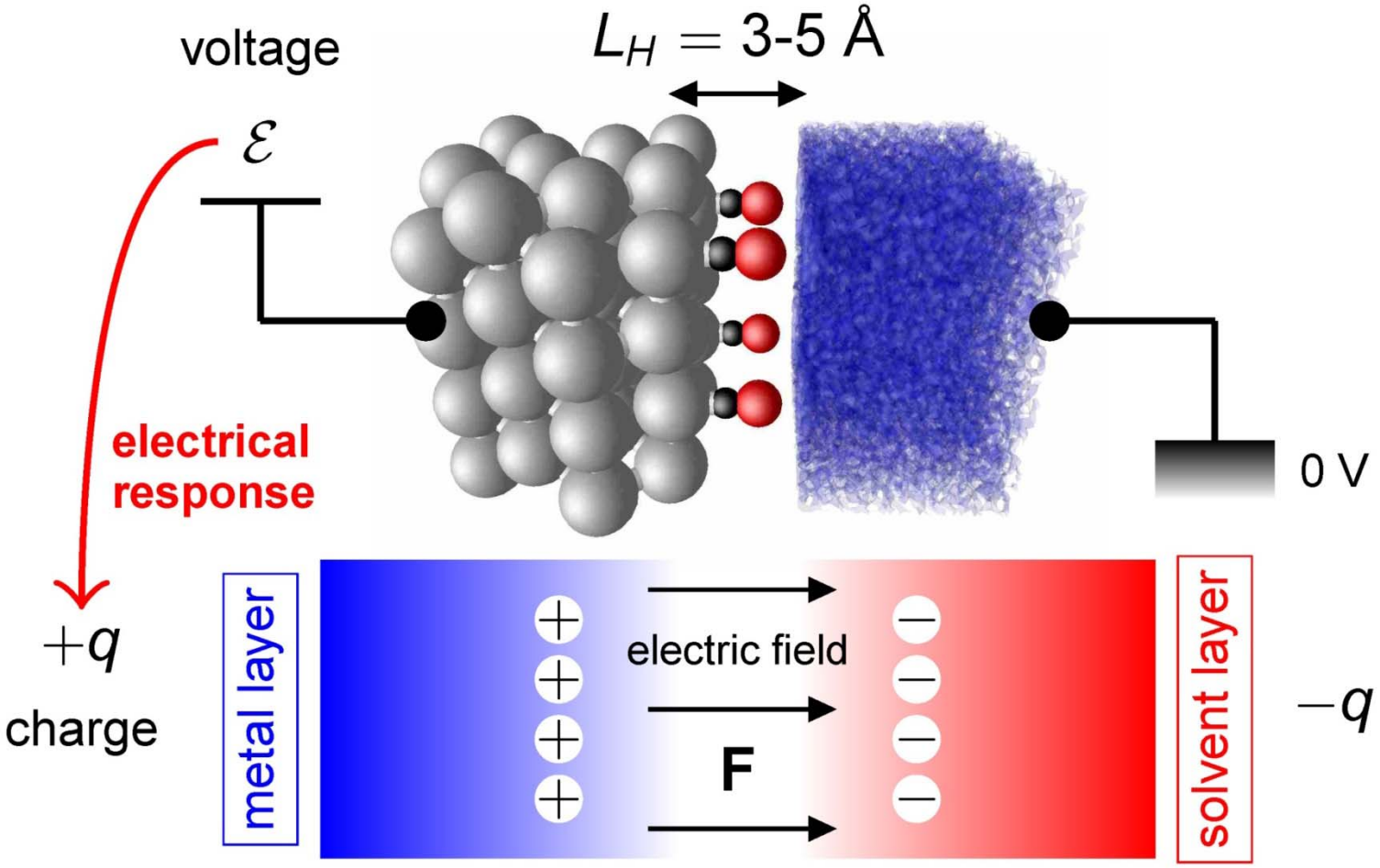
First-principles electrochemistry

Quantum-simulations in a realistic electrochemical environment:

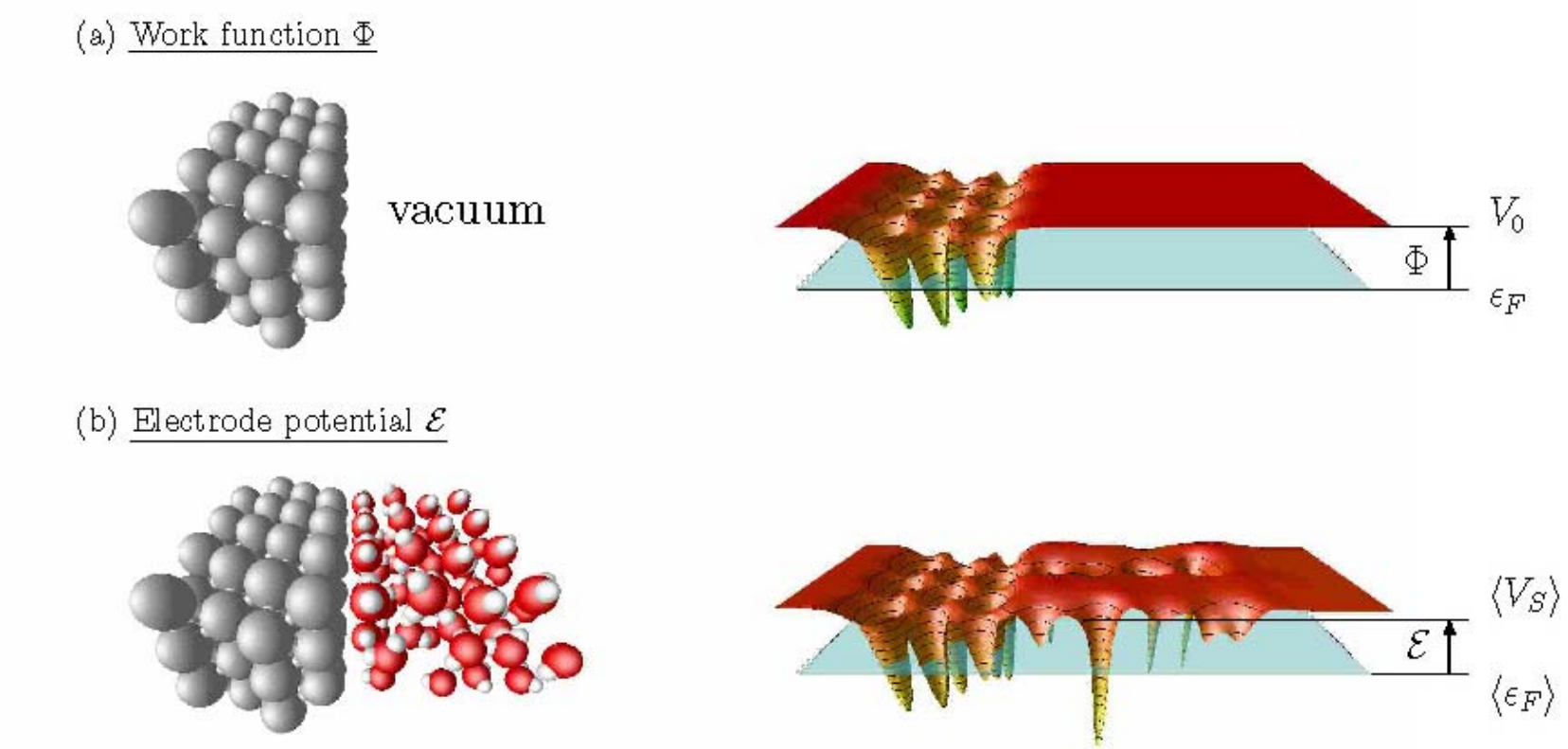
1. **solvent**
2. **counterions**
3. **applied potential**

Our approach

The electrode potential is measured from the screened response of the quantum, solvent, and counterion fields

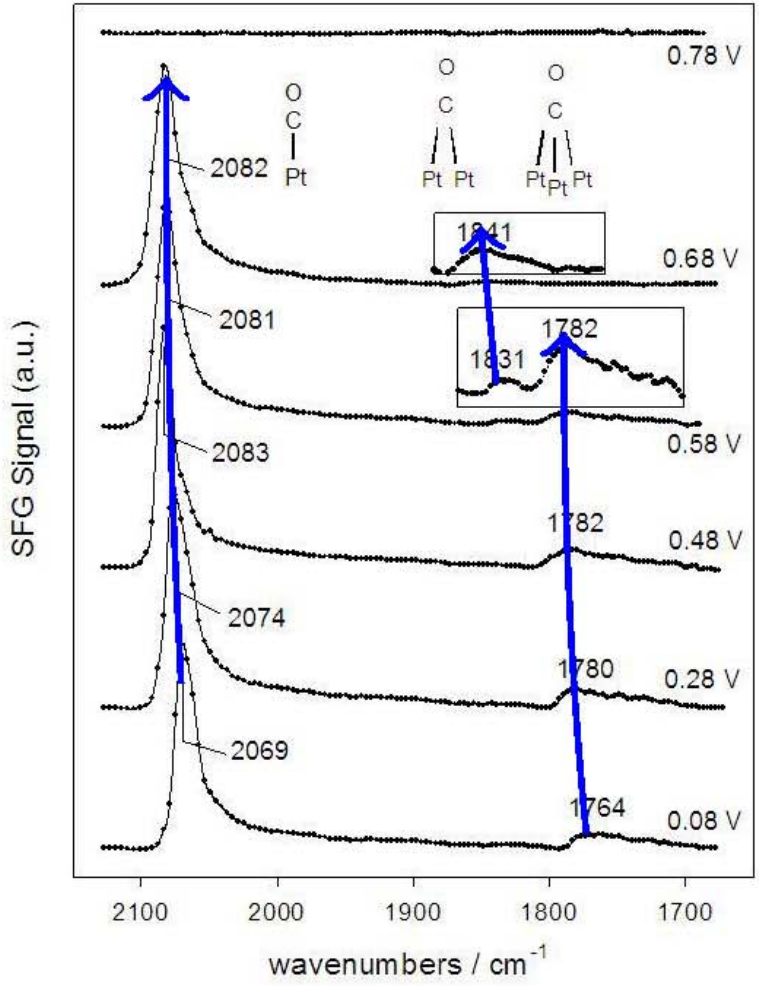


Work function and absolute electrode potential



1. **Work Function**: Difference between the Fermi energy and the vacuum reference energy ($q = 0$ only)
2. **Electrode Potential**: Difference between the Fermi energy and the reference energy in the bulk of the solvent ($q = 0$ and $q \neq 0$)

Our probe: Stark tuning shifts

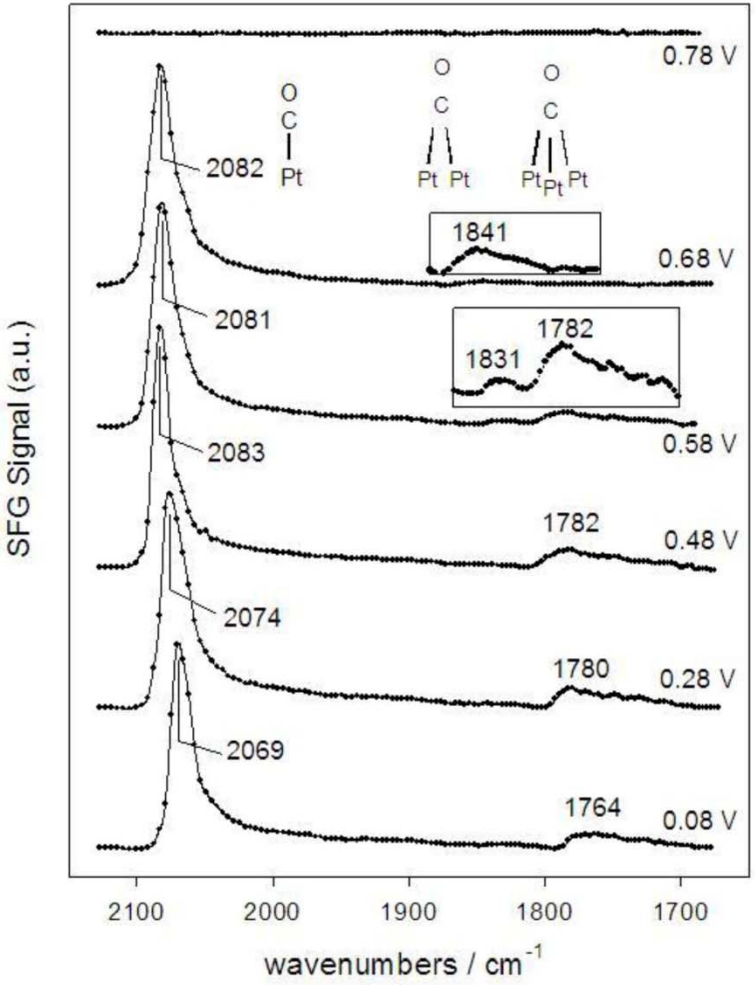


$$\frac{d\nu(\mathrm{C{-}O})}{d\mathcal{E}} = 28\text{-}32\ \mathrm{cm^{-1}\cdot m^2/C}$$

- Technogically important system (CO poisoning).
- Accurate experimental data.
- Highly sensitive to electrochemical conditions.
- No comprehensive first-principles model.

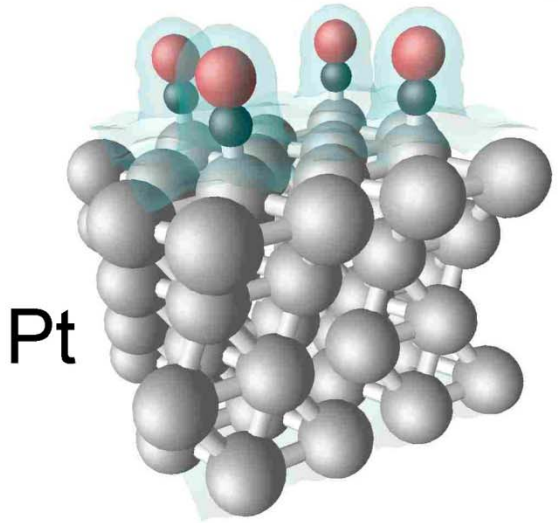
Vibrational properties from DFT

I. Dabo, A. Wieckowski, N. Marzari, JACS 129, 11045-11052 (2007)



$$\nu(C-O)$$

	DFT	(Exp.)
atop	2050 cm^{-1}	(2070 cm^{-1})
bridge	1845 cm^{-1}	(1830 cm^{-1})
hcp	1752 cm^{-1}	(1760 cm^{-1})
fcc	1743 cm^{-1}	(1760 cm^{-1})

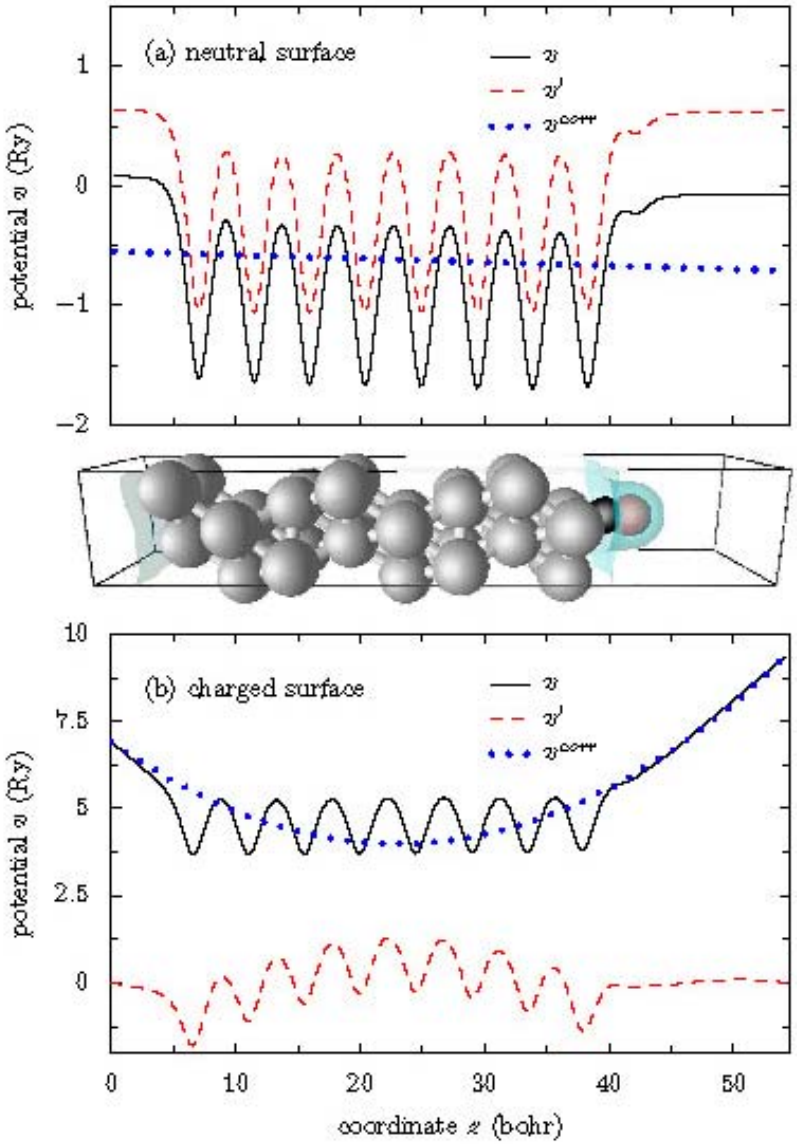


First ingredient: arbitrary boundary conditions

$$d^2v/dz^2 = -4\pi\rho$$

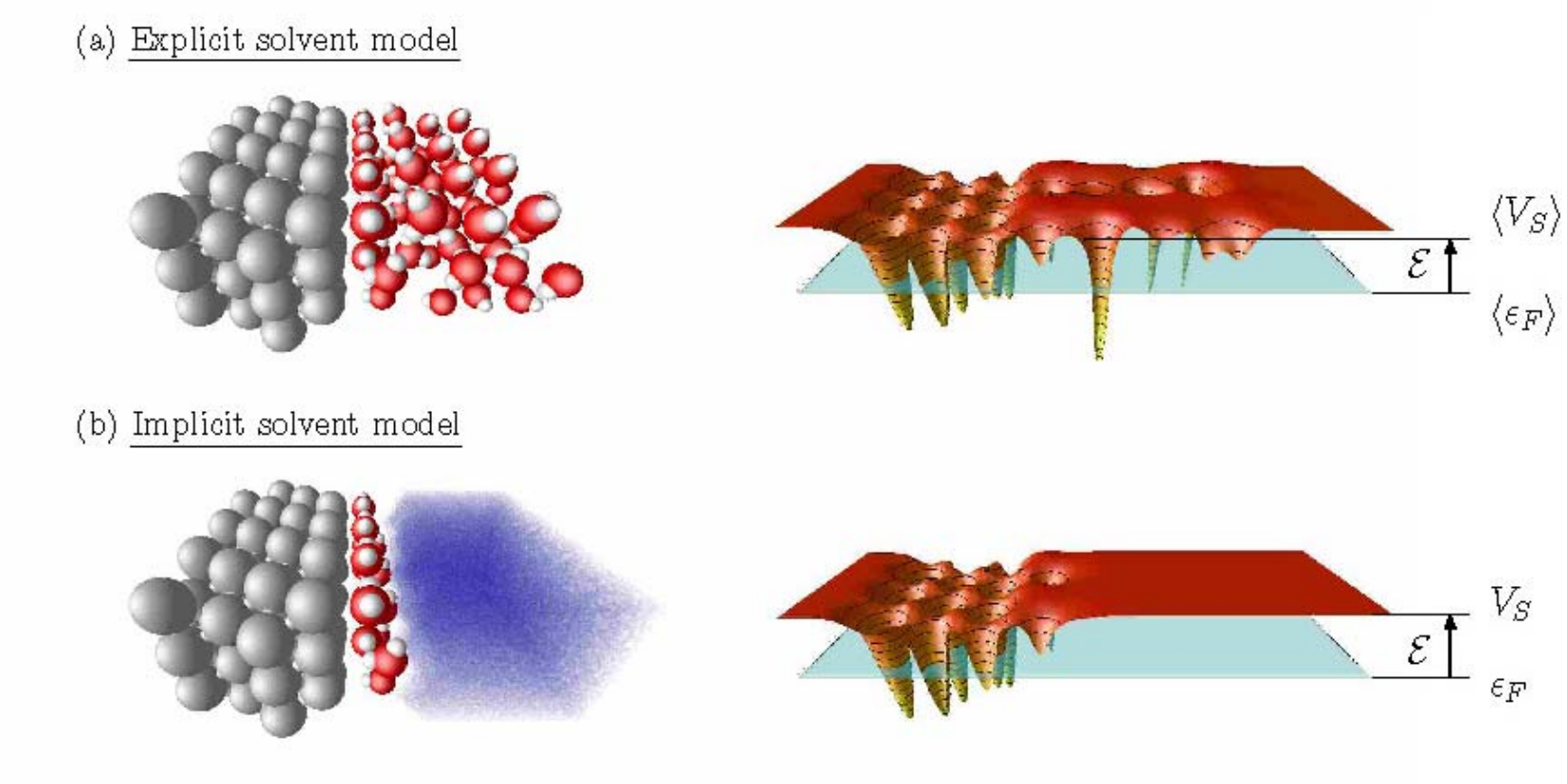
$$-\quad d^2v'/dz^2 = -4\pi(\rho - \langle\rho\rangle)$$

$$d^2v^{corr}/dz^2 = -4\pi\langle\rho\rangle$$



I. Dabo, B. Kozinsky, N. E. Singh-Miller, and N. Marzari, Phys. Rev. B. 77, 115139 (2008)

Second ingredient: solvent

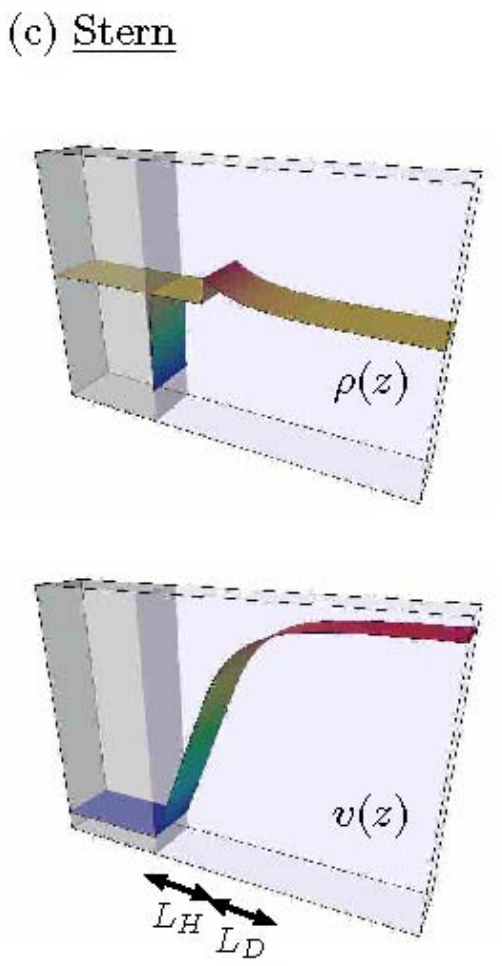


D. Scherlis, J.-L Fattebert, F. Gygi, M. Cococcioni, and N. Marzari, J. Chem. Phys (2006)

Third ingredient: self-consistent field of counterions

$$\begin{cases} \nabla \cdot \epsilon \nabla v^{corr} = -4\pi(\langle\rho\rangle + \rho'_p + \rho_d) \\ \rho'_p = \nabla \cdot \chi \nabla v' \\ \rho_d = z_d c_d \left(e^{-\frac{z_d v}{k_B T}} - e^{+\frac{z_d v}{k_B T}} \right) \text{ if } \rho < \rho_1 \end{cases}$$

$\Rightarrow$ ionic solvent reaction field



Fourth ingredient:
Electrochemical Boundary Conditions
(unpublished)

Electrochemical vibrational Stark effect (unpublished)

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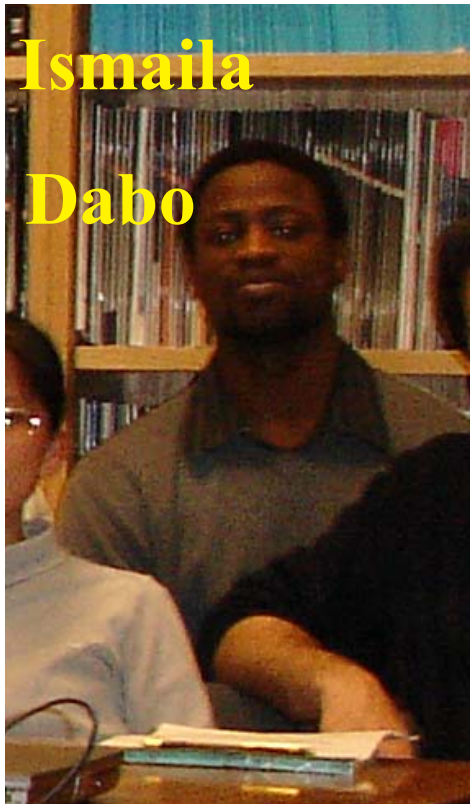
Acknowledgments



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Conclusions

- **Charge transfer reactions / long-range self-interactions: penalty functionals**
  - **Marcus diabatic surfaces**
- **Transition-metal catalysis / short-range self-interactions: DFT+ Hubbard U**
  - **Addition/elimination of hydrogen, methane to methanol, porphyrin/heme chemistry…**
- **First-principles electrochemistry: solvent, electrochemical boundary conditions, counterions**
  - **Fuel cell electrodes**