FIRST-PRINCIPLES MODELING OF MOLECULES AND MATERIALS



Energy conversion processes at heterogeneous interfaces: a quantum chemical perspective

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outline

- motivation & theoretical tools
- **CASE 1**: *dye-electrode interface in dye-sensitized solar cells*
- **CASE 2**: proton-conducting solid oxide fuel cells
 - electrode based on mixed proton-electron conductor
 - bifunctional electrocatalyst for ORR and OER
- CASE 3: electrocatalysis at oxide surface, the role of defects
 - Fe-doped ZrO₂ for low temperature FCs
 - Cu-Fe delafossite oxide for CO₂ reduction
- **method development**: Density Functional Embedding Theory



challenges in renewable energy technologies

• renewable energy sources are discontinuous

- peaks can exceed grid capabilities => energy loss
- downs prevent sufficient energy supplies



• many of the current technologies are efficient, but this is not enough...

next generation of energy conversion device must rely on purposely tailored high-performance functional materials

experiment - theory - simulations



hierarchy of computational models



Time scales

ab initio

- *ab initio* from the beginning *The Oxford Dictionary*
- ab initio calculation a method of calculating atomic and molecular structures directly from the first principles of quantum mechanics (QM), without using any quantities derived from experiment as parameters.

A Dictionary of Chemistry, Oxford University Press 2001

- The most chemically accurate, physically precise computation possible
- The holy grail of computational chemists
- No empirical input

PREDICTIVE POWER

the many-body problem

time-independent Schrödinger equation

$$\hat{H}\Psi(\vec{r}_{1},\vec{r}_{2},...,\vec{r}_{N}) = E\Psi(\vec{r}_{1},\vec{r}_{2},...,\vec{r}_{N})$$

$$\hat{H} = -\sum_{\mu} \frac{1}{2M_{\mu}} \nabla_{\mu}^{2} - \sum_{i} \frac{1}{2} \nabla_{i}^{2} + \sum_{i,j>i} \frac{1}{r_{ij}} - \sum_{i,\mu} \frac{Z_{\mu}}{r_{i\mu}} + \sum_{\mu,\nu>\mu} \frac{Z_{\mu}Z_{\nu}}{R_{\mu\nu}}$$

Schrödinger eq. is exactly solvable only for:

- two particles (analytically)
- *few particles* (numerically)

=> WE NEED APPROXIMATIONS

ab initio calculations: the main tool

PES - Potential Energy Surface



- Molecular structures and dynamics - PES minima and trajectories
- Internal motions and free energy

 PES curvature
- Chemical reactivity - PES saddle points
- Molecular properties
 - Linear response theory

** On the basis of the Born-Oppenheimer approximation

=> the many-electron problem

$$\hat{H}^{el}_{\{\vec{R}_{\mu}\}} = -\sum_{i} \frac{1}{2} \nabla_{i}^{2} + \sum_{i,j>i} \frac{1}{r_{ij}} + V^{ext}_{\{\vec{R}_{\mu}\}}(\{\vec{r}_{i}\})$$

OLD and EXTREMELY hard problem to solve !

- all first-principles methods used today are **APPROXIMATE** after all, even if considered **EXACT** !!!
- they provide approximate solutions to the electronic Schrödinger eq.

some are more approximate than others

first-principles approaches

QM Wave-Function methods

- Hartree-Fock (HF) theory (mean-field) HF: 99% of the true energy of the system
- Moeller-Plesset (MP) perturbation theory MP2: 80% of the last 1% (the correlation energy)
- Coupled Cluster (CC) theory CCSD(T): 95% of the correlation - Chemical Accuracy
- Multi Reference Configuration-Interaction (MRCI) full-CI: exact wave-function

MP2, CC, CI are very accurate but very expensive !!!

first-principles approaches

Density Functional Theory (**DFT**) $\Psi(\{\vec{r}_i\}) \rightarrow \rho(\vec{r})$

$$E[\rho_{GS}(\vec{r})] \equiv \int d^3 \vec{r} V_{ext}(\vec{r}) \rho(\vec{r}) + F[\rho(\vec{r})] = E_{GS}$$

- The functional of the electron density is UNKNOWN
- Kohn-Sham approach

kinetic energy of non-interacting electrons

$$E[\rho] = T_0[\rho] + \int d^3 \vec{r} \rho(\vec{r}) [V_{ext}(\vec{r}) + \frac{1}{2} \Phi(\vec{r})] + E_{xc}[\rho]$$

• Approximations for the XC functional LDA, GGA (PBE, PW91, BLYP), hybrid HF-DFT (B3LYP, PBE0)

first-principles approaches

DFT provides the best **ACCURACY:COST** ratio

- state-of-the-art method for extended materials
 - Periodic Boundary Conditions (super-cell approach)
 - Plane-wave basis set and pseudopotential
- workhorse method for molecular sciences
 - Localized basis set (GTO, Gaussian Type Orbitals)
- but XC approximations come with few known flaws
 - excited states (feasible via TD-DFT), self-interaction error
 - vdW dispersion, charge transfer, strong-correlated systems

ab initio calculations: why?

- electrons have a leading role in many processes
 => charge tranfer, chemical reactions, excited states
- when high degree of accuracy is required
 => thermochemical and kinetics studies
- to avoid extensive parameterization
 => non-standard systems (e.g. defects, radicals)

ab initio calculations: why?

Renewable enegry conversion and storage technologies

- devices made of layered functional materials
- energy conversion occurs via complex processes of charge and mass transport across several heterogeneous interfaces

Development of new devices must be based on solid scientific grounds

• rational design strategies need reliable and accurate assessments of structure-property-function relationships for any complex materials

Computational modelling offers several valuable tools

- photo-excitations, chemical reactions, electrochemical processes depend all on the **quantum mechanical** behaviour of electrons
- *first-principles* methods based on **Density Functional Theory** provide the best balance between accuracy and feasibility

CASE 1: solar energy and dye-sensitized solar cells



- sunlight is the most abundant renewable energy source



Merits of DSSCs:

- cheap materials
- flexible and transparent
- good for indoor light recycling

since early 90s - Dye-Sensitized Solar Cells
cost-effective alternative to solid-state Si-based PV
heterogeneous photo-anodes (n-type SC + dye)
liquid electrolyte (I⁻/I₃⁻ in ACN solution)
metallic counter-electrode



B. O'Regan, M. Grätzel, *Nature* 353, 737 (1991)

solar energy and dye-sensitized solar cells

Best Research-Cell Efficiencies



- most of DSSC research groups have shifted to PSC => what future for DSSC ?

what future for dye sensitized solar cells?





need to improve photocathode efficiency!

A. Hagfeldt et al., Chem. Rev. 110, 6595 (2010)

F. Odobel et al., Acc. Chem. Res. 43, 1063 (2010)

photo-cathode: p-type DSSC functioning scheme



limits of current p-DSSCs

- too slow hole injection
- fast charge recombination

desired processes

- electron injection from dye to electrolyte
- hole injection from Dye to VB

undesired processes

- charge recombination
- hole transfer to the electrolyte

DESIGN GUIDELINES

- **dye**: good sunlight adsorption
- dye-electrode interface:
 - strong dye-electrode binding
 - good driving force for hole injection (ΔE)
- **electrode**: low VB edge absolute position (V_{oc})

p-DSSC systems: dyes on NiO p-type SC









nickel oxide - NiO

- rocksalt structure
- CT band gap (≈3.5 eV)
- AFM along 111 planes
- DFT-PBE+U
- *ab initio* U-J(Ni *d*)= 3.8 eV

NiO (100) surface

- supercell slab model
- 5 atomic layers (tested up to 9)
- $(\sqrt{2} \times \sqrt{2})$ along the xy plane (80 atoms)
- vacuum > 30 Å along the z direction
- dipole correction

p-NiO(001)/Coumarin interface: **anchoring modes**



A. B. Muñoz-García, M. Pavone Phys. Chem. Chem. Phys. 17, 12238 (2015)

p-NiO(001)/Coumarin interface: anchoring modes



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p-NiO(001)/dye interface: *push-pull dye*



- intramolecular charge tansfer (ICT) upon photoexcitation
- LUMO is far from the anchoring groups
- two possible conformations on Ni(100)



p-NiO(001)/dye interface: *push-pull dye*



- polar solvents improve the hole injection driving force
- LUMO far from p-SC avoids charge recombination

p-NiO(001)/dye - tuning dye molecular features



TD-DFT (CAM-B3LYP) calculations in ACN

Dye	λ _{max} (nm)	f	Е ₀₋₀ (eV)	Е _{номо} (eV)	E _{LUMO} (eV)
C1	361	1.347	3.10	-6.06	-2.96
C2	389	1.626	2.75	-6.00	-3.25
C3	425	1.165	2.57	-5.85	-3.28

ICT metrics: D_{CT} in Å and q_{CT} in e^{-1}

D	D _{ct} (Å)		q _{c⊤} (e⁻)		Dipole (D)	
Dye	S ₀	$S_0 S_1 S_0 S_1$		S ₁	S ₀	S ₁
C1	2.65	2.23	0.601	0.536	7.652	5.740
C2	2.83	1.16	0.642	0.500	8.722	2.797
C3	3.45	2.62	0.694	0.593	11.495	7.454

- the electron acceptor group changes optical and electronic properties

p-NiO(001)/dye - tuning dye molecular features

PV performances (in collaboration with UNITO and POLITO)

Dvo	V _{oc} (mV)		J _{sc} (mA cm ⁻²)		FF (%)		PCE (%)	
Dye	1d	50d	1d	50d	1d	50d	1d	50d
C1	132	141	0.942	0.946	37.0	37.0	0.0460	0.0494
C2	104	118	0.380	0.280	44.8	51.7	0.0177	0.0171
C3	93	132	0.620	0.590	35.2	34.4	0.0203	0.0268





- the hole-injection driving force is a key feature

p-NiO(001)/dye - tuning dye molecular features

PV performances (in collaboration with UNITO and POLITO)



- dye conformation is crucial to avoid charge recombination

p-type DSSC: conclusions and perspectives

- p-type DSSC can be improved with tailored modification at the dye-electrode interfaces
- push-pull dyes are promising, but it is important to control the dye orientation with respect to the electrode surface
- DFT-based approaches (DFT+U, hybrid HF-DFT) are playing a pivotal role in guiding the experimental design of new systems
- electrode-dye-electrolyte interactions in aqueous solution
- charge transfer processes (excited states, non equilibrium solvation at heterogeneous interfaces)
- electrochemical reactions (HER/OER) for photo-catalysis of water splitting

CASE 2: *H*₂ *fuel cells => clean electric power generation*

 FCs are electrochemical devices that convert fuels (chemical energy) into electrical energy



some examples:

- Alkaline FC
- PEM FC
- Solid Oxide FC







Proton-Conducting Electrochemical Cells

low cost oxides (no Pt) Intermediate Temperatures (~500°C):

- higher mobility of H⁺ wrt O²⁻
- minimize degradation
- H_2 + fuels (FC)
- less electric demand than Low T (EC)

Proton-Conducting Solid Oxide Electrochemical Cells

ELECTROLYTES

insulator proton conductor

- oxygen vacancies V_o
- low H⁺ migration barrier

 $H_2O + M-V_O-M + M-O-M => 2 \cdot M-O(H)-M$



e⁻ (metal) or composite IDEAL ELECTRODE MIEC (mixed e^{-}/O^{2-}) electrode mixed e^{-}/H^{+} e⁻ conductor catalytic activity proton conductor - Oxygen vacancies V_{0} - Low H⁺ migration barrier PC-Electrolyte **PC-Electrolyte PC-Electrolyte TCOs MPECs** state-of-the-art target system

Induce e⁻ conductivity in PC-electrolytes Induce PC in MIEC materials

SFMO as TCO candidate

Sr(Fe,Mo)O₃



Outstanding electrocatalytic performance in symmetric OC-SOFCs

Redox stability, no poisoning

Excellent MIEC properties

- Non-stoichiometric Sr₂Fe_{1.5}Mo_{0.5}O_{6- δ} (δ =0.10)
- Low O²⁻ migration barrier (~0.3 eV)

Is also a good proton conductor ?

A-substitutions



Ionic Ra	adii (Å)
Sr ²⁺	1.44
Ba ²⁺	1.61
K+	1.64

Ba²⁺ structural effects

K⁺ structural/electronic effects (p-doping)

Ana B. Muñoz-García et. al *J. Am. Chem. Soc. 134,* 6826 (2012) Ana B. Muñoz-García et. al *Phys. Chem. Chem. Phys.,* **15,** 6250 (2013) Ana B. Muñoz-García et. al *Acc. Chem. Res.,* **47,** 3340 (2014)

computational strategy







structure and energetics

Material a(Å)		8	∕ ∕E _{form}	ΔE_{hydr}	
Iviacentai	۵(۲)	U	Fe-O-Fe	Mo-O-Fe	(eV)
SFMO	7.872	0.125	-0.090	1.28	-0.328
BSFMO	7.948	0.25	0.023	1.42	-0.353
KSFMO	7.917	0.25	-0.297	0.619	-1.166





 $\delta_{\text{KSFMO}} > \delta_{\text{BSFMO}} > \delta_{\text{SFMO}}$



Solid State ionics , **259,** 1 (2014)



SFMO and **BSFMO**

- Mo-O(H)-Fe unstable
- Only Outwards Fe-O(H)-Fe



KSFMO

- Mo-O(H)-Fe stabilized by K
- Both Outwards and Inwards Fe-O(H)-Fe

electronic structure



dry

fully hydrated

dry SFMO, BSFMO, KSFMO MIEC hydration affects carrier mobility in SFMO and BSFMO

fully hydrated KSFMO likely performs as good electron conductor

Ana B. Muñoz-Garcia, Michele Pavone Chem. Mater. 2016, 28, 490

proton migration



electrocatalytic capabilities

oxygen reduction reaction (ORR)
$O_2 + 2H_2 \rightarrow 2H_2O$
$*O_2 + 1H^+ + 1e^- \rightarrow *OOH$
$*OOH + 1H^+ + 1e^- \rightarrow *O + H_2O$
$*O + 1H^+ + 1e^- \rightarrow *OH$
$*OH + 1H^+ + 1e^- \rightarrow * + H_2O$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Nørskov computational NHE U=0 $\mu(H^+) + \mu(e^-) = \frac{1}{2}\mu(H_2)$ U≠0 $\mu(H^+) + \mu(e^-) = \frac{1}{2}\mu(H_2) - eU$ $E_{H_2O/O_2}^O = 1.23V \Longrightarrow E_{H_2O/O_2}^{DFT} = 1.11V$ oxygen evolution reaction (OER) $2H_2O \rightarrow O_2 + 2H_2$ $* + H_2O \rightarrow *OH + 1H^+ + 1e^ *OH \rightarrow *O + 1H^+ + 1e^ *O + H_2O \rightarrow *OOH + 1H^+ + 1e^ *OOH \rightarrow *O_2 + 1H^+ + 1e^ 2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$$\begin{split} \Delta G_{1-4} &= \Delta E + (\Delta ZPE - T\Delta S) - eU \\ U_{ONSET} \implies \Delta G_{1-4}^{ORR/OER} \leq 0 \\ \eta^{ORR} &= 1.11V - U_{ONSET} \\ \eta^{OER} &= U_{ONSET} - 1.11V \end{split}$$