Calculation of redox potentials and pKa's using DFTMD

Jun Cheng
College of Chemistry and Chemical Engineering, Xiamen University, China
Department of Chemistry, University of Aberdeen, UK

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Redox and acid-base chemistry

Redox half reaction

$$\mathrm{X}^{-}(aq) \rightarrow \mathrm{X}^{\bullet}(aq) + \mathrm{e}^{-}(vac)$$

Acid dissociation reaction

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

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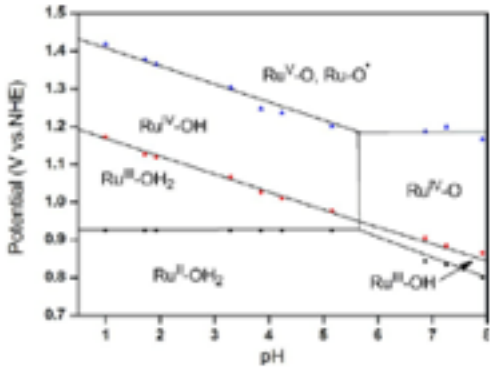
Pourbaix diagram

- Phase diagram of redox species under various conditions of potential and pH in aqueous solutions



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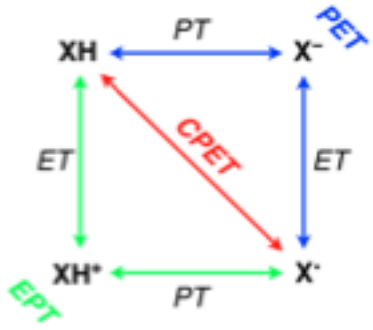
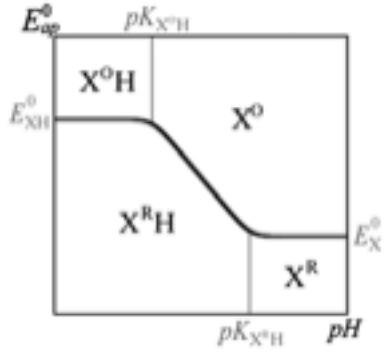
Thermochemistry of proton coupled electron transfer (PCET)





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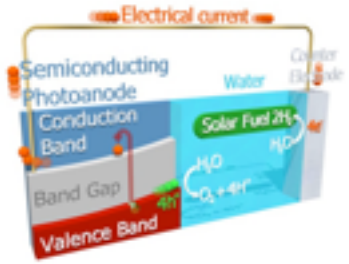
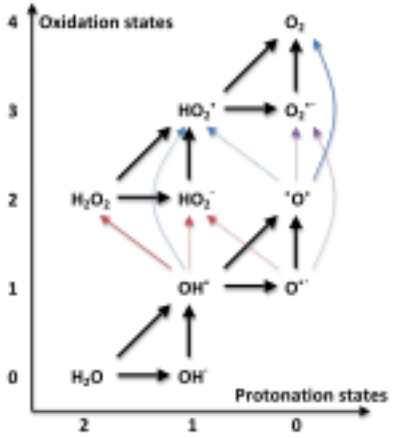
PCET in water oxidation

proton coupled electron transfer (PCET) reaction
decoupled vs concerted





J. Cheng, et al. Angew. Chem. Int. Ed. 2014, 53, 12046.(Frontispiece)

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Computation of redox potentials and pKa's

- Implicit solvation:
  Dielectric continuum
  PCM, SMx, COMSO, SCCS, etc.
  Semi-empirical, effective, accurate (often)
- Explicit solvation:
  - QM/MM: classical water
  - AIMD: treating solutes and solvents at the same level of electronic structure theory (DFT), and accounting for statistical mechanics of solvent dynamic fluctuation.

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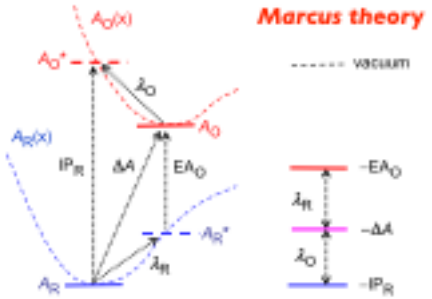
From vertical to adiabatic



Marcus theory

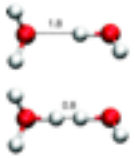
Linear response approximation

$$\lambda_R = \lambda_O = \lambda$$

$$\Delta A = \tfrac{1}{2}\left(IP_R + EA_O\right)$$

$$\lambda = \tfrac{1}{2}\left(IP_R - EA_O\right)$$

Generalisation to vertical proton insertion



Switch on/off the proton charge

M. Sulpizi, M. Sprik, PCCP, 2008, 10, 5238.

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Thermodynamic integration

Mapping potential:

$$E_\eta = (1-\eta)E_0 + \eta E_1$$

Redox $\quad E_\eta = (1-\eta)E_{red} + \eta E_{ox}$

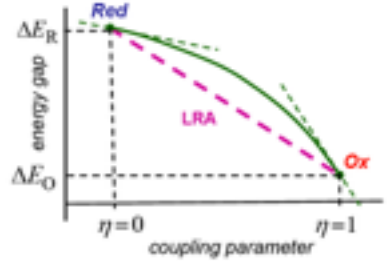
(De)protonation $\quad E_\eta = (1-\eta)E_{AH} + \eta E_{A^-}$

Vertical energy gap:

$$\frac{\partial E_\eta}{\partial \eta} = E_1 - E_0 = \Delta E$$

Adiabatic (free) energy:

$$\Delta A = A(\eta=1) - A(\eta=0) = \int_0^1 d\eta \langle \Delta E \rangle_\eta$$



J. Blumberger, I. Tavernelli, M.L. Klein, M. Sprik, JCP 2006, 124, 064507.
M. Sulpizi, M. Sprik, PCCP, 2008, 10, 5238.
J. Cheng, M. Sulpizi, M. Sprik, JCP, 2009, 131, 154504.
F. Costanzo, M. Sulpizi, R. G. Della Valle, M. Sprik, 2011, 134, 244508.

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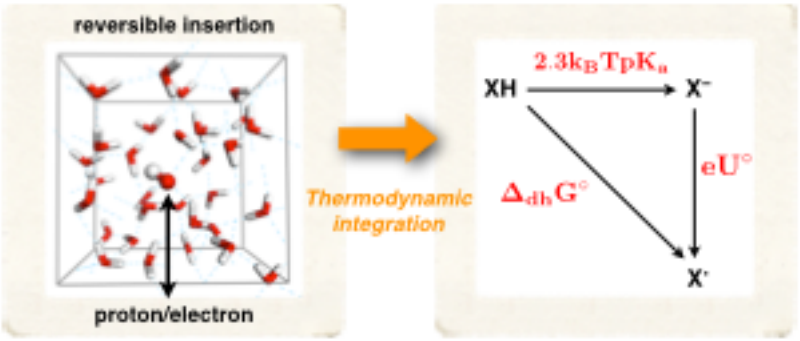
CP2K

- Standard 32/64 water cubic box under full PBC
- GGA, hybrid, RPA, double hybrid
- ADMM for HFX
- RI-GPW for MP2 term, RPA
- (O(N^4) with small prefactor)
- MD trajectories of 5~10 ps

J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, Comp. Phys. Comm. 2005, 167, 103.
M. Guidon, J. Hutter, J. VandeVondele, JCTC, 2010, 6, 2348.
M. Del Ben, J. Hutter, J. VandeVondele, JCTC, 2012, 8, 4177; 2013, 9, 2654; JCP 2015, 143, 054506.

Reversible insertion of proton/ electron



Multiple_Force_Evals

```
! generic parameters
@SET ETA 0
@SET a 0

&GLOBAL
  PROJECT water-${ETA}
  RUN_TYPE MD
  PRINT_LEVEL medium
  FLUSH_SHOULD_FLUSH T
  WALLTIME 10500
&END GLOBAL

&MULTIPLE_FORCE_EVALS
  FORCE_EVAL_ORDER 1 2 3 4
  MULTIPLE_SUBSYS T
&END MULTIPLE_FORCE_EVALS

@SET METHOD MIXED
@include input.inc
```

```
! force_eva for Red/Pro
@SET METHOD QS
@SET a 1
@include input.inc

! force_eva for Ox/Depr
@SET METHOD QS
@SET a 2
@include input.inc

! force_eva for restraining
water
@SET METHOD FIST
@include input.inc

&MOTION
  &MD
    .. ..
  &END MD
&ENDMOTION
```

usual MD section

input.inp

MIXED

```
&FORCE_EVAL
  METHOD  ${METHOD}

  &MIXED
    GROUP_PARTITION  24 24
    MIXING_TYPE GENMIX
    &GENERIC
      # X: Energy force_eval 2 (Red/Pro)
      # Y: Energy force_eval 3 (Ox/Depr)
     MIXING_FUNCTION (1-k)*X+k*Y
      VARIABLES X Y Z
      PARAMETERS k
      VALUES ${ETA}
    &END
    &PRINT
      &DIPOLE OFF
      &END
    &END
  &END MIXED
.. .. ..
```

METHOD: MIXED, QS(DFT), or FIST(MM)

$$E_\eta = (1-\eta)E_0 + \eta E_1$$

ETA: coupling parameter

input.inc

Insert/remove an electron

```
&DFT
.. ..
@IF ${a}==1
    CHARGE  1
    UKS T
@ENDIF
@IF ${a}==2
    CHARGE  0
    UKS T
@ENDIF
.. ..
&END DFT
```

Change the total charge of the box
Caution: Restricted/unrestricted Kohn Sham and multiplicity

Switch on/off dummy H atom

```
&DFT
.. ..
@IF ${a}==1
    &KIND H1
      BASIS_SET TZV2P-GTH
      POTENTIAL GTH-BLYP-q1
    &END KIND
@ENDIF
@IF ${a}==2
    &KIND H1
      BASIS_SET NONE
      POTENTIAL GTH-BLYP-q1
      GHOST T
    &END KIND
@ENDIF
.. ..
&END DFT
```

Label the special H atom

Restraining potential

```
&FORCE_EVAL
  METHOD  ${METHOD}

  &MIXED
    GROUP_PARTITION  24 24 4
    MIXING_TYPE GENMIX
    &GENERIC
      # X: Energy force_eval 2 (Red/Pro)
      # Y: Energy force_eval 3 (Ox/Depr)
      # Z: Energy force_eval 4 (restraints)
      MIXING_FUNCTION k*X+(1-k)*Y+Z
      VARIABLES X Y Z
      PARAMETERS k
      VALUES ${ETA}
    &END
    &PRINT
      &DIPOLE OFF
      &END
    &END
  &END MIXED
```

Combine with FIST(MM)

```
&MM
  &FORCEFIELD
    DO_NONBONDED F
    &BOND
      ATOMS   H1 O
      KIND    CHARMM
      K       0.1
      R0      1.89
    &END BOND
    .. .. ..
&END MM
```


Vertical energy gaps

MIXING_FUNCTION k*X+(1-k)*Y

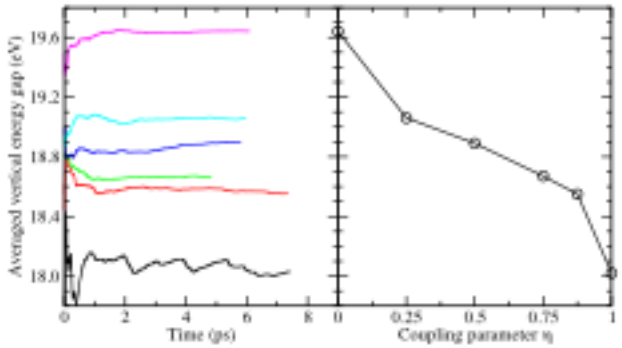
		Mixed	X	Y	Cons. Qty
0	0.000	-561.626813843	-572.638745466	-572.199760517	-561.475983453
1	0.500	-563.519939382	-572.595935868	-572.184378722	-562.968878699
2	1.000	-564.938824374	-572.452695885	-571.968382717	-564.787698777
3	1.500	-566.570562194	-572.503488425	-572.018397585	-566.419374492
4	2.000	-568.011433853	-572.594648898	-572.101393683	-567.868189417
5	2.500	-569.111375323	-572.689625958	-572.116242980	-568.968083598
6	3.000	-569.943387930	-572.594537952	-572.102148725	-569.792858677
7	3.500	-570.575298712	-572.573985867	-572.084787580	-570.423926636
8	4.000	-571.050249333	-572.553882423	-572.071224324	-570.898857347
9	4.500	-571.399981295	-572.536529301	-572.063039613	-571.248565626
10	5.000	-571.647584981	-572.521685602	-572.061881683	-571.496149168
11	5.500	-571.804524167	-572.508963778	-572.051381701	-571.653871533
12	6.000	-571.857444166	-572.444827758	-571.999668823	-571.785978515
13	6.500	-571.812523575	-572.335851587	-571.885285874	-571.698833941
14	7.000	-571.859518246	-572.325738343	-571.874311431	-571.694182219
15	7.500	-571.984427888	-572.435982829	-571.976282176	-571.832924888

xxx-mix-1.ener

$$\frac{\partial E_\eta}{\partial \eta} = E_1 - E_0 = \Delta E$$

$$\Delta A = A(\eta = 1) - A(\eta = 0) = \int_0^1 d\eta \langle \Delta E \rangle_\eta$$

Thermodynamic integration

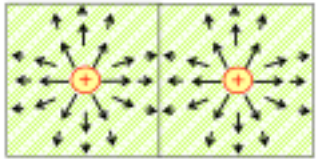


dehydrogenation of a water molecule
in a 32 water box (HSE06 functional)

Electrostatics under PBC: potential reference

Open boundary condition

$$\varphi(\infty) = 0$$



Periodic boundary condition
(Ewald sum)

$$\frac{1}{V_{cell}} \int_{cell} \varphi(r) dr = 0$$

$$E_{\infty} = \sum_i q_i \varphi_i \stackrel{?}{=} \sum_i q_i (\varphi_i + C) = \sum_i q_i \varphi_i + \sum_i q_i C$$

Kleinman, Phys. Rev. B 1981, 24, 7412.

Standard hydrogen electrode (SHE)

Reference electrode

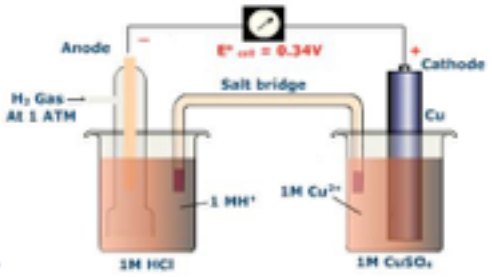
$H^+(aq) + e \rightarrow \frac{1}{2} H_2(g)$

Working electrode

$Cu^{2+}(aq) + 2\,e \rightarrow Cu\,(s)$

$H^+(aq) \rightarrow H^+(g)$

$H^+(g) + e \rightarrow \frac{1}{2} H_2(g)$



J. Cheng, M. Sulpizi, M. Sprik, JCP, 2009, 131, 154504.

Redox potentials

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

$$X^-(aq) \rightarrow X^{\bullet}(aq) + e^-(vac) \qquad \Delta_{ox}A_{X^{\bullet}}$$

$$1/2H_2(g) \rightarrow H^+(aq) + e^-(vac)$$

$$H_3O^+(aq) \rightarrow H_2Od(aq) \qquad \Delta_{dp}A_{H_3O^+}$$

$$1/2H_2(g) \rightarrow H^+(g) + e^-(vac) \qquad \mu^{g,\circ}_{H^+}$$

pKa's

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

$$\mathrm{XH}(aq) + \mathrm{H_2O}(aq) \rightarrow \mathrm{X}^-(aq) + \mathrm{H_3O}^+(aq)$$

$$\mathrm{XH}(aq) \rightarrow \mathrm{Xd}^-(aq) \qquad \Delta_{\mathrm{dp}}A_{\mathrm{XH}}$$

$$\mathrm{H_3O}^+(aq) \rightarrow \mathrm{H_2Od}(aq) \qquad \Delta_{\mathrm{dp}}A_{\mathrm{H_3O}^+}$$

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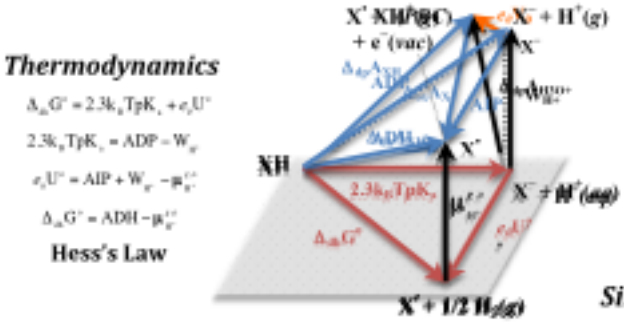
Computational SHE



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Redox potentials and pKa's

Deprotonation	GGA/BLYP ΔA	GGA/BLYP ΔG	GGA/BLYP pK$_a$	Hybrid/HSE06 ΔA	Hybrid/HSE06 ΔG	Hybrid/HSE06 pK$_a$	Exp. ΔG	Exp. pK$_a$
$H_2O^+ \rightarrow H_2O^{\bullet}$	15.58	-0.19	-3.2	15.28	-0.19	-3.2	-8.10	-1.7
$H_2O(l) \rightarrow OH^{\bullet}$	16.34	0.70	11.9	16.28	0.71	12.0	0.85	14.0
$H_2O_2 \rightarrow HO_2^{\bullet}$	16.11	0.57	9.7	16.08	0.61	10.3	0.69	11.7
$HO_2^{\bullet} \rightarrow O_2^{\bullet-}$	15.73	0.19	3.2	15.74	0.26	4.4	0.21	3.6
$HCl \rightarrow Cl^-$	15.1	-0.4	-7.5				-0.41	-7.0
$HCOOH \rightarrow HCOO^-$	15.8	0.5	4.4				0.22	3.8
$NH_4^+ \rightarrow NH_3$	16.2	0.7	11.2				0.54	9.2
$H_2S \rightarrow HS^-$	16.0	0.5	7.8				0.41	7.0
$HS^- \rightarrow S^{2-}$	16.5	1.0	17.1				1.0	17
$CH_3SH \rightarrow CH_3S^-$	16.2	0.7	11.2				0.61	10.3
PheA	16.3	0.8	12.9				0.80	13.5
PheB	16.1	0.6	9.5				0.55	9.3
$H_2Q \rightarrow HQ^-$	16.28		8.6				0.58	9.8
$H_2Q^{\bullet+} \rightarrow HQ^{\bullet}$	15.76		1.2				-0.06	-1.0
$HQ^{\bullet} \rightarrow Q^{\bullet-}$	15.94		4.2				0.24	4.1
$HQ^{\bullet} \rightarrow Q$	15.23		-7.8				-0.41	-8.9
TyrOH$^{\bullet+} \rightarrow$TyrO$^{\bullet}$	15.78		8.2				0.80	10.1
TyrpH$^{\bullet+} \rightarrow$Tyr$^{\bullet}$	15.54		4.2				0.25	4.3
MUE		0.67	1.0		0.69	1.4		
MAE		0.01	-0.1		-0.06	-1.0		

pKa

GGA Hybrid

Oxidation	GGA/BLYP ΔA	GGA/BLYP U^0	Hybrid/HSE06 ΔA	Hybrid/HSE06 U^0	Exp. U^0
$OH^- \rightarrow OH^{\bullet}$	2.1	1.3	2.52	1.65	1.90
$HO_2^- \rightarrow HO_2^{\bullet}$	1.1	0.3	1.33	0.46	0.75
$O_2^{\bullet-} \rightarrow O_2$	0.3	-0.5	0.52	-0.35	-0.16
$Cl^- \rightarrow Cl^{\bullet}$	2.3	1.5	2.73	1.87	2.41
$HS^- \rightarrow HS^{\bullet}$	1.5	0.5	1.71	0.84	1.08
$CO_2^{\bullet-} \rightarrow CO_2$	-1.26	-2.07	-1.09	-1.96	-1.90
$H_2Q \rightarrow H_2Q^{\bullet+}$	1.12	0.40			1.10
$HQ^- \rightarrow HQ^{\bullet}$	0.54	-0.12			0.46
$HQ^{\bullet} \rightarrow HQ^+$	1.23	0.57			0.76
$Q^{\bullet-} \rightarrow Q$	0.48	-0.18			0.10
TyrO$^- \rightarrow$Ty	1.5	0.6			0.72
TyrpH$\rightarrow$TyrH$^{\bullet+}$	1.55	0.41			1.15
MUE			-0.51		-0.26
MAE			0.51		0.26

Redox potential

Dehydrogenation	GGA/BLYP ΔA	GGA/BLYP ΔG	Hybrid/HSE06 ΔA	Hybrid/HSE06 ΔG	Exp. ΔG
$H_2CO(l) \rightarrow OH^{\bullet}$	18.54	2.10	18.89	2.45	2.72
$H_2O_2 \rightarrow HO_2^{\bullet}$	17.19	0.84	17.45	1.08	1.44
$HO_2^{\bullet} \rightarrow O_2$	16.16	-0.19	16.27	-0.08	0.05
$H_2Q \rightarrow HQ$	16.83	0.50			1.04
$HQ^{\bullet} \rightarrow Q$	16.57	0.24			0.55
TyrO$^- \rightarrow$Ty	17.21	0.89			1.32
TyrpH$\rightarrow$Tyr$^{\bullet}$					1.41
MUE		-0.48		-0.26	
MAE		0.48		0.26	

dehydr. potential

J. Chang, X.-D. Liu, J. VandeVondele, M. Sulpizi, M. Sprik, Acc. Chem. Res, 2014, 47, 3522 (invited perspective).

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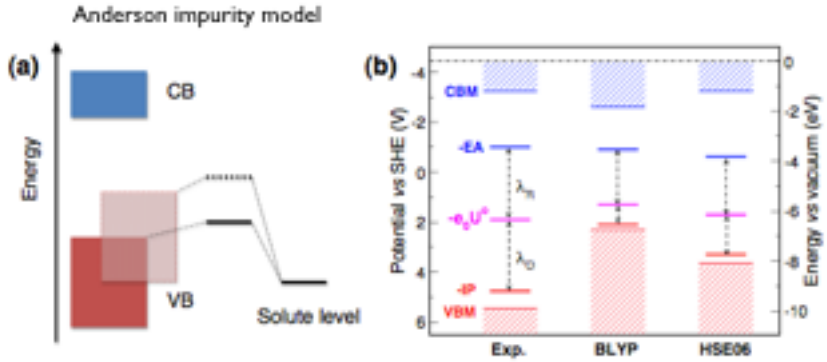
Delocalisation error in DFA



C. Adriaanse, J. Chang, V. Chau, M. Sulpizi, J. VandeVondele, M. Sprik, JPCL, 2012, 3, 3411.

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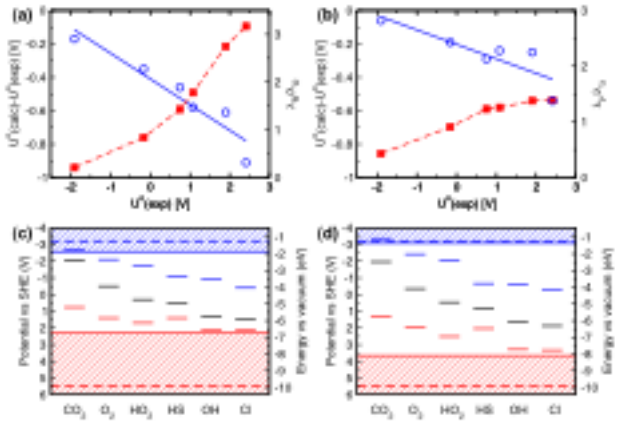
Vertical and adiabatic levels



J. Cheng, X.-D. Liu, J. VandeVondele, M. Sulpizi, M. Sprik, Acc. Chem. Res, 2014, 47, 3522 (invited perspective).

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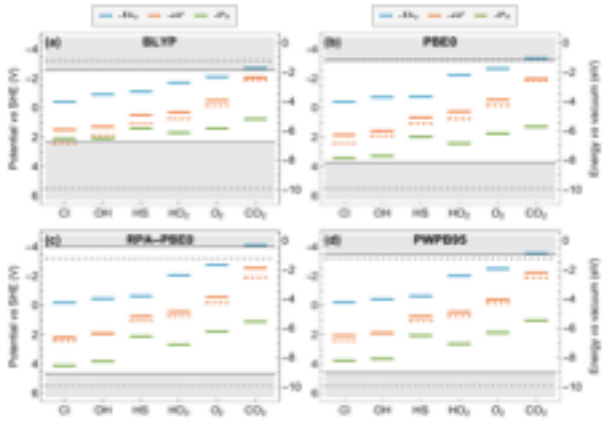
Energy levels from MBPT



L. Goerigk, S. Grimme, JCTC, 2011, 7, 291.

RPA and double hybrid calculations use HSE06/PBE0 MD trajectories.

J. Cheng, J. VandeVondele, PRL, 2016, 116, 086402.

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- Dr. Aron Cohen (Cambridge)

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Thank you for your attention!

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