Quantum Chemistry meets Solid State: HOMO-LUMO gap in proximity of metal surface

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VŠB TECHNICKÁ UNIVERZITA OSTRAVA | IT4INNOVATIONS NÁRODNÍ SUPERPOČÍTAČOVÉ CENTRUM

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Motivation

Corrosion

- Rust-resistant alloys
- Galvanization
- Coatings and painting
- Bluing
- Humidity control
- **Inhibitors**

Chemistry

- exact methods
- electronic correlations
- real-space wavefunctions
- small systems

Physics

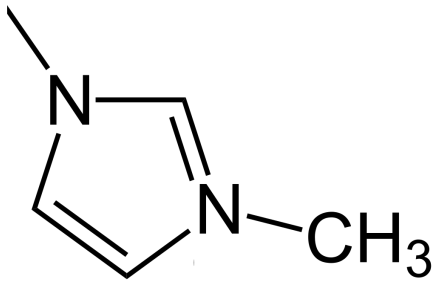
- large systems
- magnetism
- metallicity
- approximate correlations

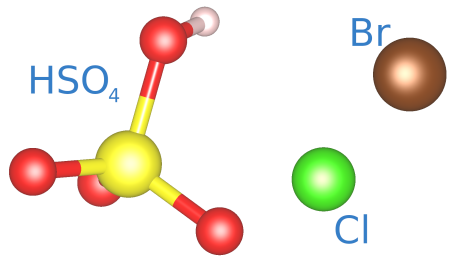
Theoretical modelling

Hypothesis I

Imidazole ionic liquid derivative compound will inhibit corrosion.

C_4H_9 C_6H_{13} C_8H_{17}





Hypothesis II

Inhibitor quality depends on its HOMO-LUMO gap on surface.

We need:

Metallic surface

Easy using DFT

Molecular [BHO]MI[øBCS]

Easy using Hartree-Fock + vdW

DFT using *exact-exchange* information

α-Iron surfaces

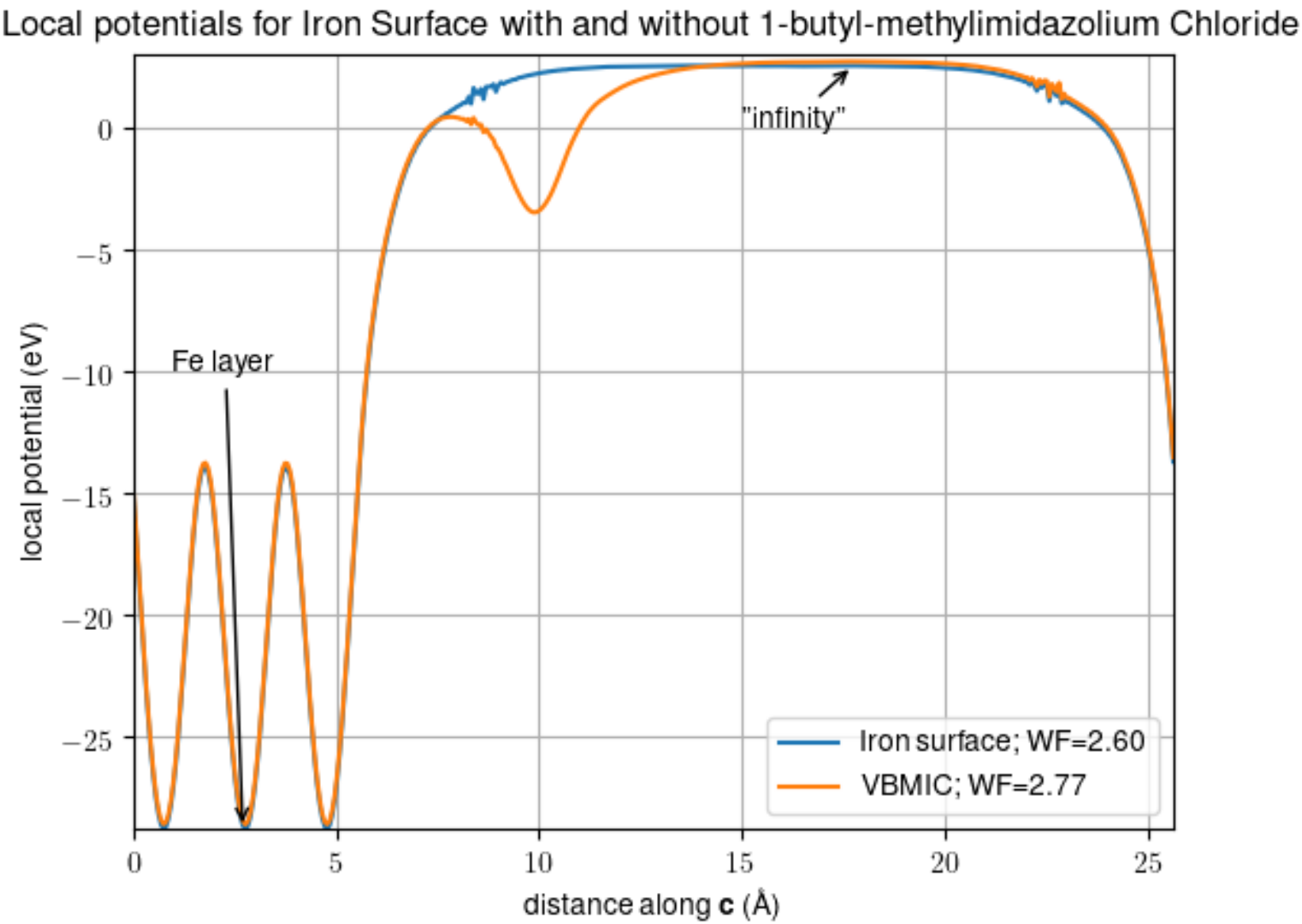
Surfaces: [100],[110],[111] towards the 30 Å vacuum $\|\hat{z}$
Surface energy

$$\gamma = \frac{E_{\text{slab}} - N \cdot E_{\text{bulk}}}{2A},$$

where E_{slab} is the energy of a slab of N atoms with area A exposed on vacuum, and E_{bulk} is energy (per atom) of bulk bcc iron.

	N	$\frac{E_G}{N}$ (eV)	A (Å^2)	γ (eV Å^{-2})	γ (J m^{-2})
bulk	54	-8.34069			
$Fe_{[100]}$	108	-8.12508	74.132	0.157	2.52
$Fe_{[111]}$	108	-7.92548	128.401	0.175	2.80
$Fe_{[110]}$	72	-8.04459	69.893	0.153	2.44
W.R. Tyson and W.A. Miller, Surface Science **62**, 267 (1977)					2.41
I. H. Sahputra *et al.*, Phys. Status Solidi B **254**, 1600408 (2017)					2.44

Local potential



1-*-3-methylimidazolium [BHO]MIM: HOMO | LUMO

$$\eta \equiv \frac{1}{2}\left(-E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}\right) \quad \sigma \equiv \frac{2}{-E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}} \quad \chi \equiv -\frac{1}{2}\left(E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}\right)$$

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	η (eV)	σ (eV^{-1})
BMIM up:	-3.006	-0.113	2.893	1.446	0.691
HMIM up:	-2.984	-0.096	2.887	1.443	0.692
OMIM up:	-2.798	-0.004	2.794	1.397	0.715
BMIM do:	-6.050	-0.113	5.936	2.968	0.336
HMIM do:	-6.024	-0.098	5.926	2.963	0.337
OMIM do:	-5.910	-0.038	5.871	2.935	0.340

1-*-3-methylimidazolium +[Br Cl HSO] [BHO]MI[BCS]

$$\eta \equiv \frac{1}{2}\left(-E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}\right) \quad \sigma \equiv \frac{2}{-E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}} \quad \chi \equiv -\frac{1}{2}\left(E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}\right)$$

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	η (eV)	σ (eV^{-1})	χ (eV)
BMIB	-4.137	-1.968	2.169	1.084	0.922	3.053
HMIB	-4.146	-2.130	2.016	1.008	0.992	3.138
OMIB	-4.200	-2.158	2.042	1.021	0.979	3.179
BMIC	-4.318	-1.884	2.434	1.217	0.822	3.101
HMIC	-4.410	-2.001	2.409	1.204	0.830	3.205
OMIC	-4.449	-2.068	2.381	1.191	0.840	3.259
BMIS	-4.483	-2.827	1.656	0.828	1.208	3.655
HMIS	-4.337	-2.749	1.588	0.794	1.259	3.543
OMIS	-4.172	-2.660	1.512	0.756	1.323	3.416

Where Physics meets Chemistry

Equivalent quantities

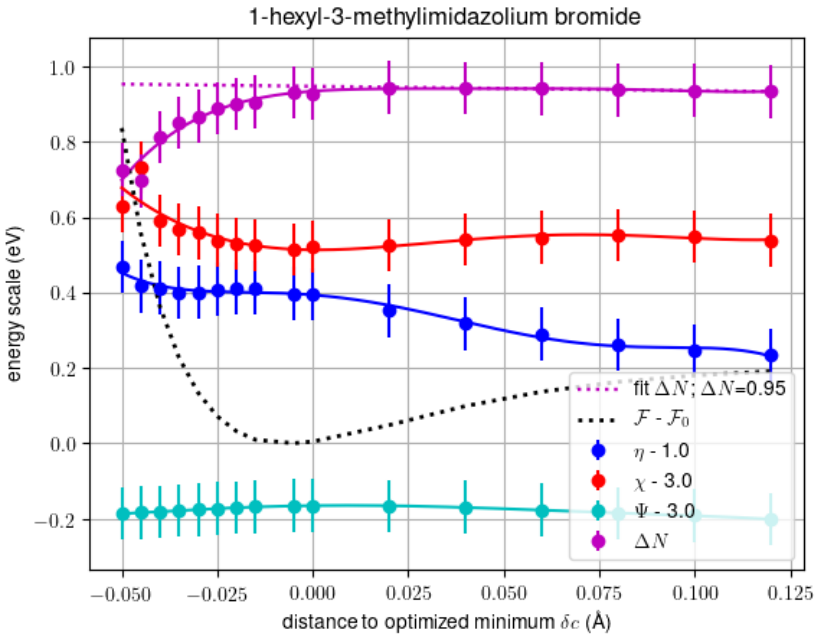
Chemistry	Physics
Hardness η	derivative of chemical potential
$\eta = \frac{1}{2}(-E_{HOMO} + E_{LUMO})$	$\eta = \frac{d\mu}{dN}$

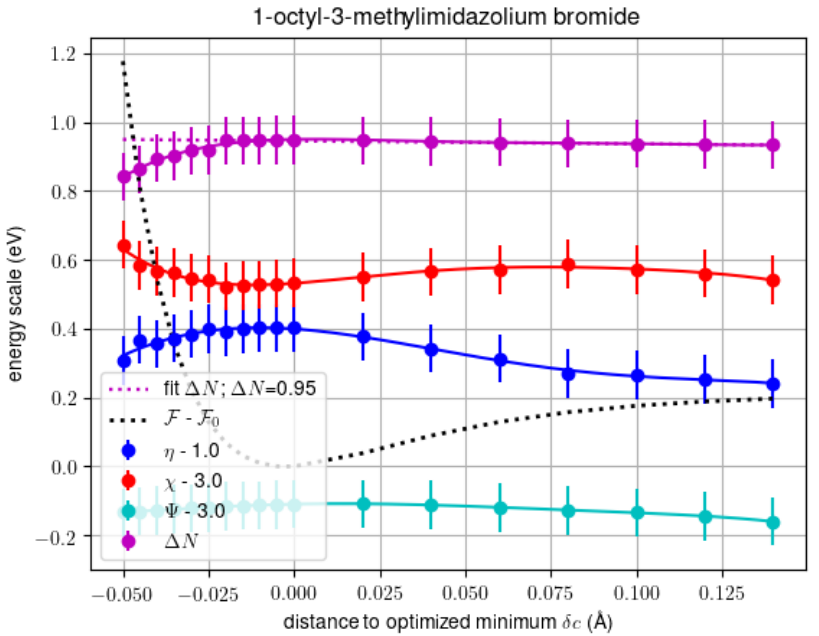
1-*-3-methylimidazolium: hardness & electronegativity

$$\chi \equiv -\frac{1}{2}\left(E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}\right); \quad \eta \equiv \frac{1}{2}\left(-E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}\right); \quad \sigma \equiv \frac{2}{-E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}}. \tag{1}$$

Compound	HOMO	LUMO	ΔE (eV)	η (eV)	σ (eV^{-1})	χ (eV)	ΔN
BMIC	-4.843	-2.291	2.552	1.276	0.784	3.567	0.47
HMIC	-4.973	-2.423	2.550	1.275	0.784	3.698	0.47
OMIC	-5.030	-1.999	3.031	1.515	0.660	3.514	0.47
BMIB	-4.988	-2.057	2.931	1.465	0.682	3.522	0.76
HMIB	-5.011	-2.119	2.892	1.446	0.692	3.565	0.85
OMIB	-5.092	-2.131	2.960	1.480	0.676	3.612	0.85
BMIM	-8.046	-3.174	4.872	2.436	0.411	5.610	-0.55
HMIM	-7.942	-2.881	5.061	2.531	0.395	5.411	-0.43
OMIM	-7.661	-2.928	4.733	2.367	0.423	5.294	-0.40
BMIS	-7.302	-2.313	4.989	2.494	0.401	4.807	-0.08
HMIS	-8.156	-2.625	5.531	2.766	0.362	5.391	-0.31
OMIS	-7.911	-2.495	5.417	2.708	0.369	5.203	-0.28

1-*-3-methylimidazolium bromide

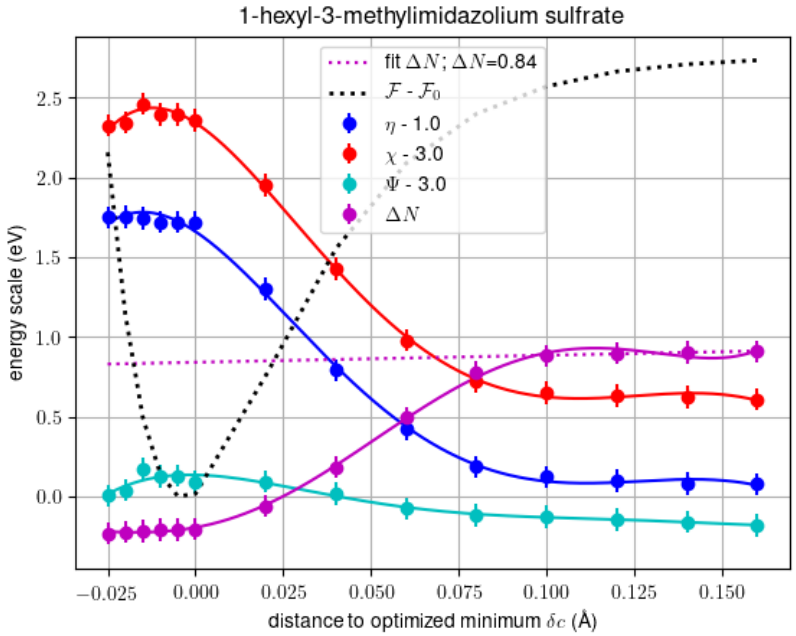


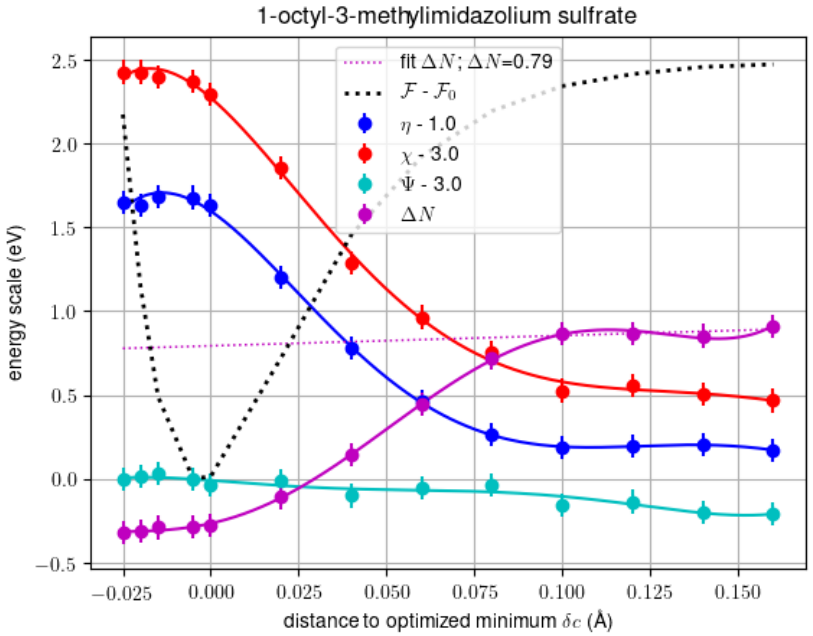


Note

Near-to linear dependence of ΔN in proximity of the surface.

butyl





Extrapolated values

compound	charge transfer ΔN
BMIS	0.94
HMIS	0.84
OMIS	0.79

1-*-3-methylimidazolium: Adsorption energy

$$E_{ads} = E_{Fe+MIM} - E_{MIM} - E_{Fe}$$

$$E_{ads;WF} = E_{ads} - \Phi_{Fe+MIM} + \Phi_{MIM} + \Phi_{Fe}$$

Compound	E_{Fe+MIM} (eV)	E_{MIM} (eV)	E_{Fe} (eV)	E_{ads} (eV)	Φ_{Fe+MIM} (eV)	Φ_{MIM} (eV)	Φ_{Fe} (eV)	$E_{ads;WF}$ (eV)
BMIB	-1249.057	-145.925	-1102.743	-0.389	2.733	0.170	2.599	-0.354
HMIB	-1281.939	-178.917	-1102.743	-0.279	2.833	0.286	2.599	-0.228
OMIB	-1314.937	-211.910	-1102.743	-0.284	2.890	0.362	2.599	-0.214
BMIC	-1249.310	-146.391	-1102.743	-0.176	2.766	0.180	2.599	-0.164
HMIC	-1282.304	-179.374	-1102.743	-0.187	2.864	0.314	2.599	-0.139
OMIC	-1315.305	-212.351	-1102.743	-0.211	2.927	0.395	2.599	-0.145
BMIM	-1247.002	-142.140	-1102.743	-2.118	2.702	0.128	2.599	-2.095
HMIM	-1280.269	-175.202	-1102.743	-2.325	2.712	0.152	2.599	-2.287
OMIM	-1313.327	-208.218	-1102.743	-2.366	2.761	0.178	2.599	-2.351