

Improved Adsorption Energetics within Density Functional Theory using revised Perdew-Burke-Ernzerhof Functionals

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Outline

- Theoretical Background
 - Hohenberg-Kohn Theorem
 - Kohn-Sham Equations
 - Exchange-Correlation Functional
- Results
 - Comparison of Different XC Functionals with Experiments
 - Mathematical Form of GGA XC Functionals
- Summary

The Hohenberg-Kohn Theorem

- The basis of DFT is the HK theorem (1964).
 - One-to-one correspondence between the *potential* and *electron density* of the *ground state*.
 - The total energy of a quantum mechanical electron gas is a unique functional of its density

$$E[\rho] = \langle \Psi[\rho] | H | \Psi[\rho] \rangle$$

- Raleigh-Ritz *variational* principle:

$$E_{\text{gs}} = \min_{\rho(\mathbf{r})} (E[\rho(\mathbf{r})])$$

minimize the energy to find the exact *ground state*
energy and density

The Kohn-Sham Equations

One electron wave function:
$$\left\{ -\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

v_{eff} and ϕ_i unknown \Rightarrow solved *self-consistently*

The *effective potential* is written:
$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r})$$

where $v(\mathbf{r})$ is the sum of the *kinetic & ionic* potentials and $v_{\text{H}}(\mathbf{r})$ is the Hartree potential and:

$$v_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})} \quad \text{where :} \quad E_{\text{XC}}[\rho] = \int d^3r \epsilon_{\text{XC}}[\rho, \mathbf{r}] \rho(\mathbf{r})$$

The XC functional is a local functional describing the *e-e interaction*

The Exchange-Correlation Functional

The KS eq. are in principle exact, however, in practice the $E_{xc}[\rho]$ has to be approximated as its *exact functional is unknown*.

XC energy at the point \mathbf{r} is taken to be that of a *homogeneous* electron gas at a density of $\rho = \rho(\mathbf{r})$:

$$E_{XC}^{LDA}[\rho] = \int d^3r \epsilon_{XC}^{LDA}[\rho(\mathbf{r})]\rho(\mathbf{r})$$

W. Kohn and L.J. Sham, Phys. Rev. **140** (1965)

Another approximation (GGA) includes the gradient of the density in the XC functional :

$$E_{XC}^{GGA}[\rho] = \int d^3r \epsilon_{XC}^{GGA}[\rho(\mathbf{r}), s(\mathbf{r})]\rho(\mathbf{r})$$

where $s(\mathbf{r})$ is the *reduced density gradient* :

$$s(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{2\sqrt{3\pi^2\rho(\mathbf{r})\rho(\mathbf{r})}}$$

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Atomic & Molecular Chemisorption Energies on Transition-Metal Surfaces

Atomic chemisorption energy:

$$E_{chem} = E_{AM} - E_A - E_M$$

**Dissociative chemisorption
of molecules:**

$$E_{chem} = E_{AM} + E_{BM} - E_{AB} - 2E_M$$

**Self-consistent PW91 densities &
volumes are used as inputs for the
non-self-consistent energies.**

	$E_{chem,\beta}$					E_{chem}^{exp}
	LDA	PW91	PBE	revPBE	RPBE	
O(fcc)/Ni(111)	-6.68	-5.38	-5.27	-4.83	-4.77	-4.84 ^a
O(hol)/Ni(100)	-6.97	-5.66	-5.55	-5.10	-5.03	-5.41 ^a
O(hol)/Rh(100)	-6.64	-5.34	-5.23	-4.77	-4.71	-4.56 ^a
O(fcc)/Pd(111)	-5.34	-4.08	-3.98	-3.54	-3.49	
O(hol)/Pd(100)	-5.39	-4.14	-4.04	-3.59	-3.53	
σ_O	1.84	0.57	0.47	0.22	0.24	
CO(fcc)/Ni(111)	-2.85	-1.99	-1.88	-1.52	-1.49	-1.35 ^a
CO(hol)/Ni(100)	-3.05	-2.11	-2.00	-1.62	-1.58	-1.26 ^a
CO(brd)/Rh(100)	-3.02	-2.28	-2.16	-1.84	-1.81	-1.19 ^a
CO(fcc)/Pd(111)	-2.95	-2.07	-1.96	-1.59	-1.56	(-1.47) ^b
CO(brd)/Pd(100)	-2.77	-1.98	-1.87	-1.53	-1.50	-1.69 ^a
σ_{CO}	1.58 (1.49)	0.78 (0.64)	0.67 (0.54)	0.39 (0.25)	0.37 (0.23)	
NO(hol)*/Ni(100)	-6.31	-4.52	-4.41	-3.79	-3.68	-3.99 ^a
NO(brd)/Rh(100)	-3.73	-2.76	-2.67	-2.31	-2.28	
NO(fcc)/Pd(111)	-3.27	-2.20	-2.12	-1.72	-1.67	(-1.86) ^c
NO(hol)/Pd(100)	-3.19	-2.12	-2.04	-1.63	-1.58	-1.61 ^d
σ_{NO}	1.98	0.52	0.43	0.14	0.22	
σ_{tot}	1.76 (1.76)	0.66 (0.58)	0.56 (0.48)	0.30 (0.21)	0.30 (0.23)	

The Local Exchange Enhancement Factor

Exchange energy functional:

Hammer *et al.*, PRB, **59** (1999)

$$E_X[n] = \int n(\mathbf{r}) \epsilon_X(\mathbf{r}) d\mathbf{r} = \int n(\mathbf{r}) \epsilon_X^{LDA}(n(\mathbf{r})) F_X(s(\mathbf{r})) d\mathbf{r}$$

where $n(\mathbf{r}) \epsilon_X^{LDA}(n(\mathbf{r}))$ is the *local exchange energy density* from the LDA, and s is the *reduced density gradient*:

$$s(\mathbf{r}) = |\nabla n(\mathbf{r})| / [2(3\pi^2)^{1/3} n(\mathbf{r})^{4/3}]$$

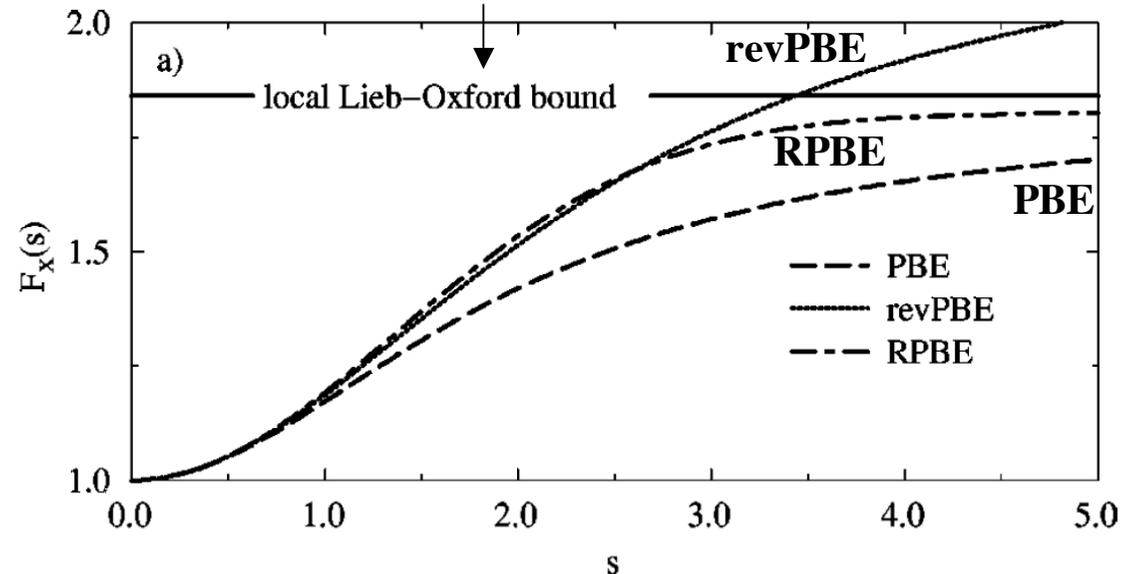
and F_X is a *local exchange enhancement factor*.

PBE and revPBE:

$$F_X(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa}$$

with $\kappa = 0.804$ in PBE but $\kappa = 1.245$ in revPBE

Upper bound: 1.804



RPBE:

$$F_X(s) = 1 + \kappa(1 - e^{-\mu s^2 / \kappa})$$

with $\kappa = 0.804$

All these functionals are constructed to have the same behavior for small s :

$$F_x(s) \rightarrow 1 + \mu s^2, \quad \text{for } s \rightarrow 0$$

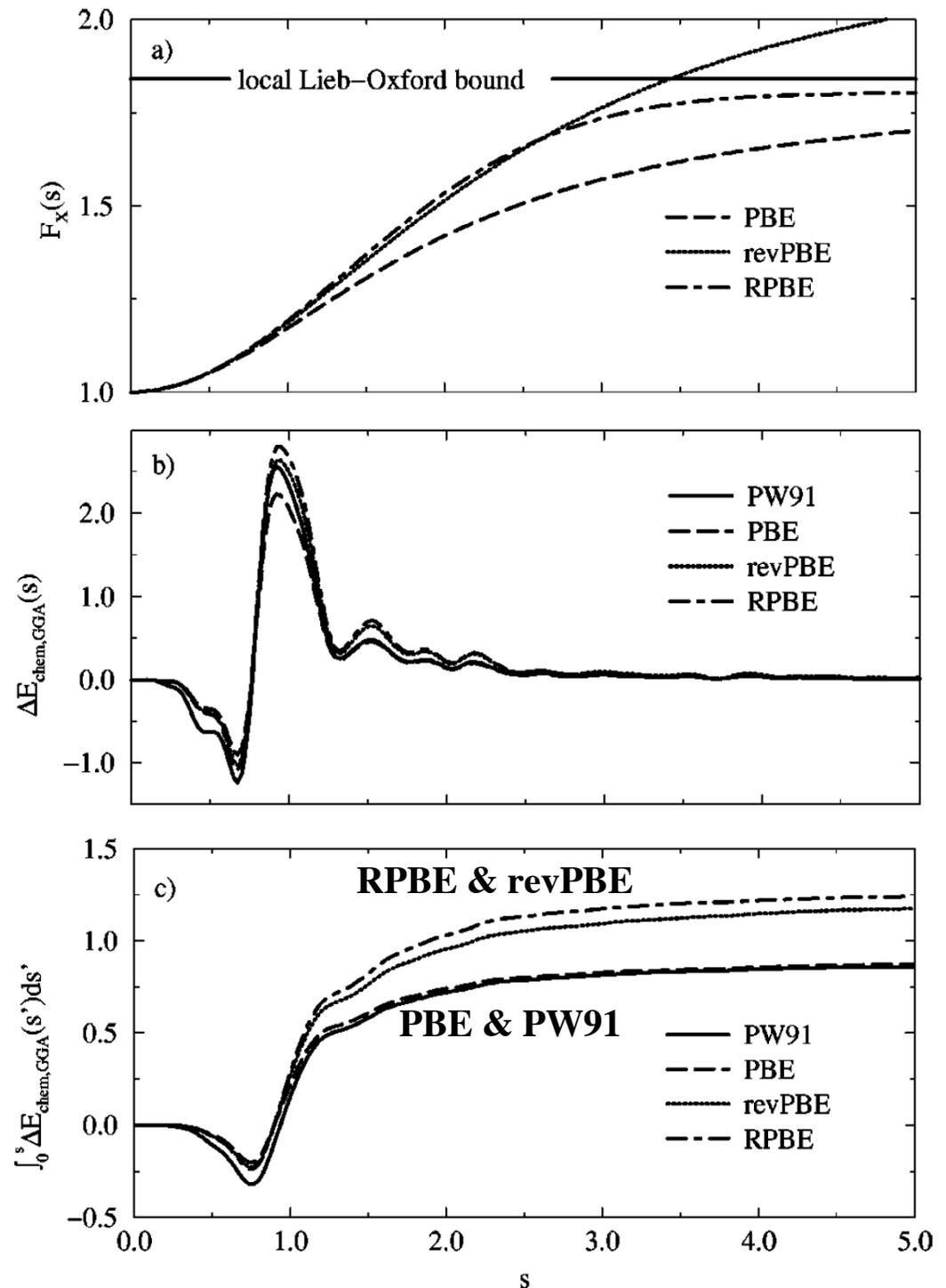
Which values of s give rise to the improvement of the chemisorption energies?

System: CO/Pd(100)

Fig b) Where does the chemisorption energy (relative to LDA) change with s ?

=> Between $s = 0.5 - 2.5$

Fig c) Non-negligible difference between $\Delta E_{\text{chem,PBE}}(s)$ and $\Delta E_{\text{chem,revPBE}}(s)$ lies in this range also.



Summary

- Theoretical background of DFT and XC functionals was briefly illustrated.
- Results of *chemisorption* energies of *atoms* and *molecules* on *transition-metal* surfaces were presented for different XC functionals :
 - LDA: chemisorption energies ca. 1.5 eV too large
 - PW91 & PBE: overbinding reduced too ca. 0.5 eV
 - revPBE & RPBE: overbinding ca. 0.2 eV
- The RPBE functional only differs from the PBE functional in the choice of the *mathematical form* for the *exchange energy enhancement factor*.