

# Chemisorbtion II - how accurate are calculations

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# Outline

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Electronic structure calculations - summary

CO adsorption puzzle

Chemical reactions

Atomistic thermodynamics

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# THE MOLECULAR SCHRÖDINGER EQUATION

$N$  **electrons** (mass  $m_e$ , charge  $-e$ )

$N_A$  **nuclei** (masses  $M_A$ , charges  $+Z_A e$ ,  $A = 1, \dots, N_A$ )

- Time-independent molecular Schrödinger equation**

$$\left( \hat{T}_e + V_{ee} + V_{ek} + \hat{T}_k + V_{kk} \right) \Psi(r, R) = E \Psi(r, R)$$

$r := \underline{r} = (\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$  electron coordinates

$R := \underline{R} = (\underline{R}_1, \underline{R}_2, \dots, \underline{R}_{N_A})$  nuclear coordinates

$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \Delta_i$  kinetic energy operator electrons

$\hat{T}_k = -\frac{\hbar^2}{2} \sum_{A=1}^{N_A} \frac{1}{M_A} \Delta_A$  kinetic energy operator nuclei

$V_{ee} = \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}}$  electron-electron repulsion ( $r_{ij} = |\underline{r}_i - \underline{r}_j|$ )

$V_{ek} = -\sum_{A=1}^{N_A} \sum_{i=1}^N \frac{Z_A e^2}{4\pi\epsilon_0 R_{iA}}$  electron-nuclear attraction

$V_{kk} = \sum_{A=1}^{N_A} \sum_{B>A}^{N_A} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}$  nuclear-nuclear repulsion

$E$  total molecular energy

$\Psi(r, R)$  total molecular wavefunction

# THE BORN-OPPENHEIMER APPROXIMATION

Electrons much faster than nuclei  $\Rightarrow$  separate nuclear from electronic motion  $\Rightarrow$

- **Born-Oppenheimer approximation, giving:**

- ① **An electronic Schrödinger equation**

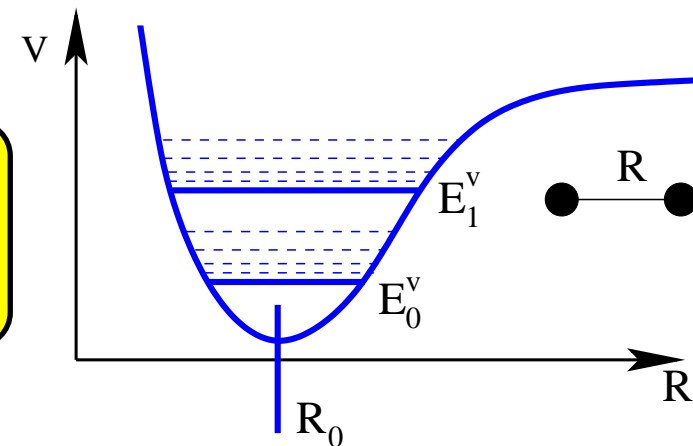
$$\underbrace{\left( \hat{T}_e + V_{ee} + V_{ek} \right)}_{\hat{H}_e} \Psi_e(r; R) = E_e(R) \Psi_e(r; R)$$

$E_e(R)$  = electronic energy (parametrically dependent on  $R$ )

$\Psi_e(r; R)$  = electronic wavefunction (parametrically dependent on  $R$ )

- ② **A nuclear Schrödinger equation**

$$\left( \hat{T}_k + \underbrace{V_{kk}(R) + E_e(R)}_{V(R)} \right) \Psi_k(R) = E \Psi_k(R)$$



$V(R)$  = **potential energy surface**  $\Rightarrow$  molecular structure

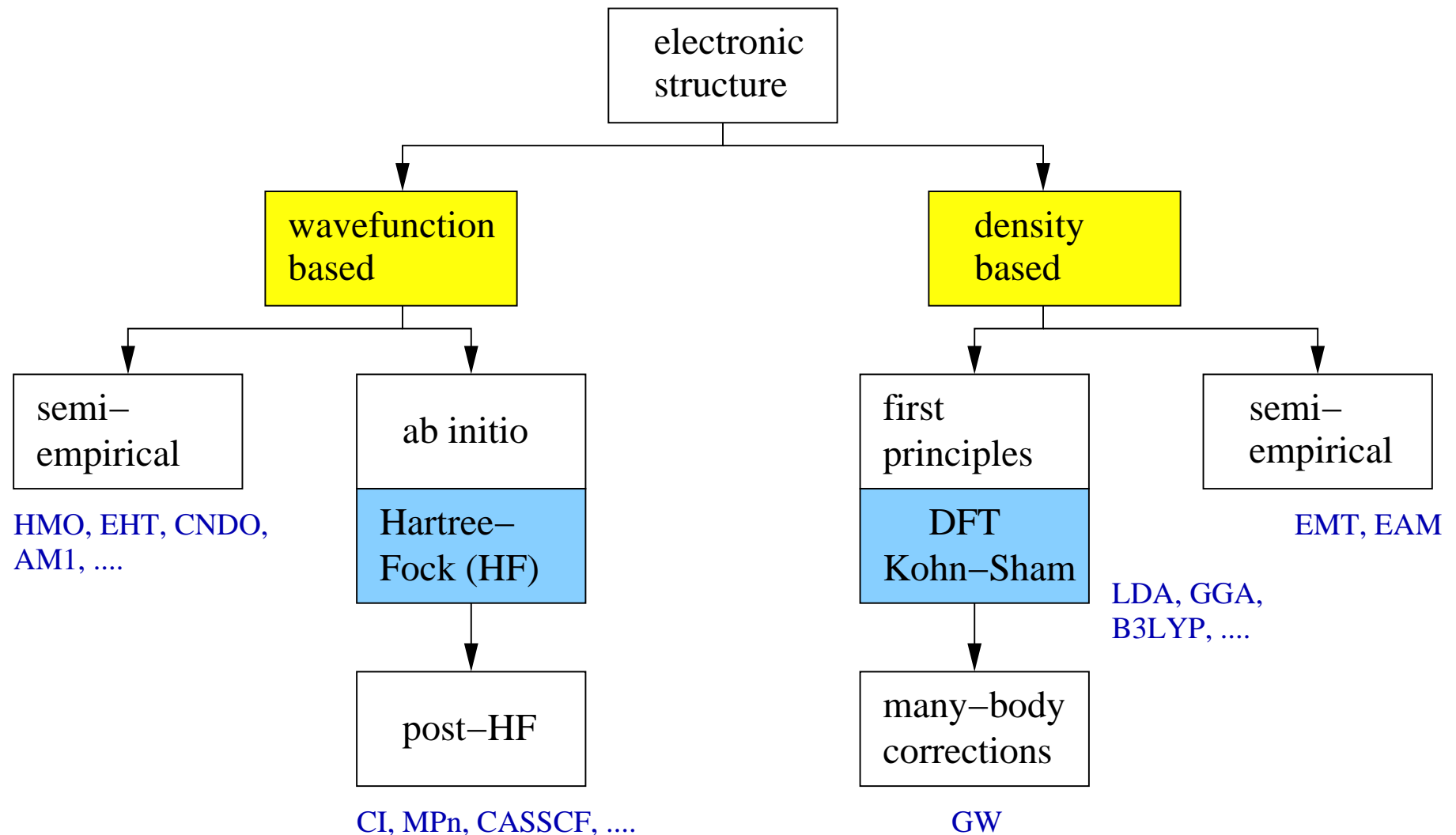
$\Psi_k$  = nuclear wavefunction, with  $\Psi = \Psi_k \cdot \Psi_e$



# ELECTRONIC STRUCTURE METHODS

$$\hat{H}_e \Psi_{e,n}(r; R) = E_{e,n}(R) \Psi_{e,n}(r; R)$$

$n = 0$  (ground state),  $n > 0$  (excited states)



# ELECTRONIC STRUCTURE METHODS

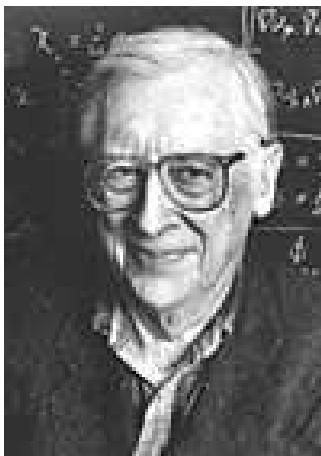
- The “wavefunction” world

$$E_e = E_e[\Psi_e(\underline{r}_1, \dots, \underline{r}_N)] = \langle \Psi_e | \hat{H}_e | \Psi_e \rangle$$

variational principle:

$$E_e^{opt} = \min_{\Psi_e} E_e[\Psi_e(\underline{r}_1, \dots, \underline{r}_N)]$$

⇒ 3N-dimensional variational problem!



John Pople



- The “density” world

$$E_e = E_e[n_e(\underline{r})]$$

variational principle:

$$E_e^{opt} = \min_{n_e} E_e[n_e(\underline{r})]$$

⇒ 3-dimensional variational problem!



Walter Kohn

# THE WAVEFUNCTION WORLD: WAVEFUNCTIONS

## • Orbitals: Eigenfunctions of 1-electron Hamiltonians

$$\chi(\underline{x}) = \underbrace{\psi(\underline{r})}_{\text{spatial}} \cdot \underbrace{\gamma(\omega)}_{\text{spin function}}$$

$$\gamma(\omega) = \alpha(\omega) \text{ or } \beta(\omega)$$

$$\omega = \text{spin coordinate } (\pm 1/2 \hbar)$$

$$\underline{x} = (\underline{r}, \omega)$$

$$\hat{h}(\underline{x}_1) \chi_a(\underline{x}_1) = \varepsilon_a \chi_a(\underline{x}_1)$$

**Example:** H atom (atomic units)

$$\hat{h}(\underline{x}_1) = -\frac{1}{2}\Delta_1 - \frac{1}{r_1}$$

$$\psi_a(\underline{r}_1) = \psi_{nlm}(\underline{r}_1) = \text{s, 2p}_x, \dots \text{ orbitals}$$

$$\varepsilon_a = \varepsilon_n = -\frac{1}{2n^2} \quad (n = 1, 2, \dots)$$

## • N-electron wavefunctions: Slater determinants

$$\Psi(\underline{x}_1, \dots, \underline{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\underline{x}_1) & \chi_2(\underline{x}_1) & \cdots & \chi_N(\underline{x}_1) \\ \chi_1(\underline{x}_2) & \chi_2(\underline{x}_2) & & \vdots \\ \vdots & & \ddots & \vdots \\ \chi_1(\underline{x}_N) & \chi_2(\underline{x}_N) & \cdots & \chi_N(\underline{x}_N) \end{vmatrix} = |\chi_1(1), \dots, \chi_N(N)\rangle$$

❶ antisymmetric

❷ Pauli principle

❸ normalized

❹ approximate

▷ Every Slater determinant represents an **electron configuration**, e.g.  $(1s^2 2s^2 2p^2)$  for C

# THE WAVEFUNCTION WORLD: HARTREE-FOCK

## • The Hartree-Fock equations

- Use single determinant  $|\Psi_0\rangle = |\chi_1(1), \dots, \chi_N(N)\rangle$  as trial wavefunction for ground state
- Use full electronic Hamiltonian  $\hat{H}_e$
- Determine orbitals  $\chi_i$  from **variational principle**  $E_0^{HF} = \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle = \min!$

$\implies$  **Hartree-Fock equations**

$$\hat{f}(1) \chi_i(1) = \varepsilon_i^{HF} \chi_i(1) \quad ; i = 1, 2, \dots, N$$

## • Properties

- Coupled single-electron equations, with **Fock operator**

$$\hat{f}(1) = -\frac{1}{2}\Delta_1 - \sum_{A=1}^{N_A} \frac{Z_A}{r_{1A}} + \underbrace{\sum_{b=1}^N \left( \underbrace{\hat{J}_b(1)}_{\text{Coulomb}} - \underbrace{\hat{K}_b(1)}_{\text{exchange}} \right)}_{\text{HF potential} \quad \hat{V}^{HF}(1)}$$

- Nonlinear equations  $\implies$  iterative (self consistent field, SCF) solution
- Self-interaction free

# THE ROOHTHAAN-HALL METHOD: LCAO-MO

## • LCAO-MO

Spatial orbitals (MOs) are expanded in a set of  $K$  “atomic orbitals”  $\{\phi_\nu\}$  (AOs):

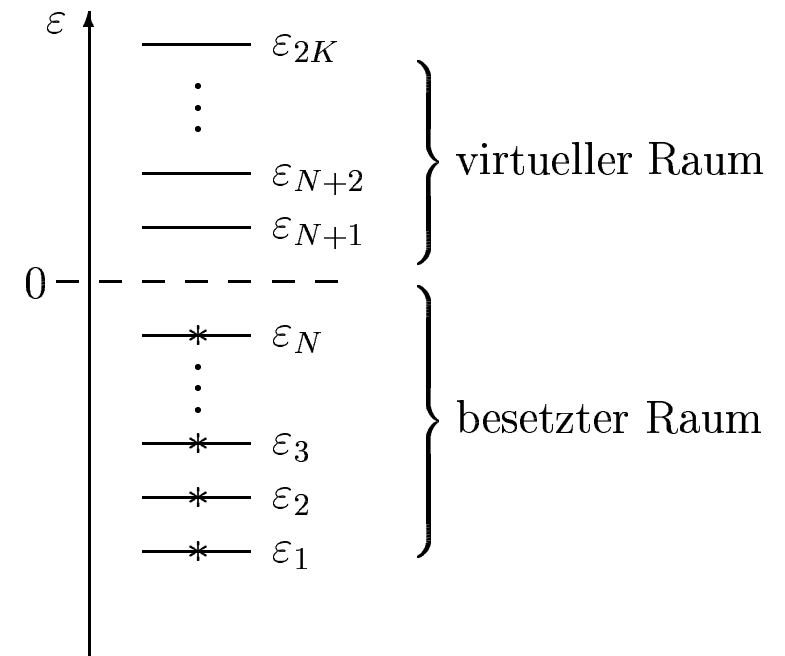
$$\psi_j(\underline{r}) = \sum_{\nu=1}^K C_{\nu j} \cdot \phi_\nu(\underline{r}) \quad ; \quad \nu = 1, 2, \dots, K$$

$\Rightarrow$  linear variation problem for  $C_{\nu j}, \varepsilon_j$

## • Roothaan-Hall equations

$$\sum_{\nu=1}^K C_{\nu j} \underbrace{F_{\mu\nu}}_{\langle \phi_\mu | \hat{f} | \phi_\nu \rangle} = \varepsilon_j \sum_{\nu=1}^K C_{\nu j} \underbrace{S_{\mu\nu}}_{\langle \phi_\mu | \phi_\nu \rangle}$$

closed- and open-shell variants



## • Basis sets $\{\phi_\nu\}$

- ❶ Slater functions:  $e^{-\zeta r}$
- ❷ Slater-type linear comb. of Gaussians: STO-3G, 6-31G\*, ...; cc-pVDZ, cc-pVTZ, ...
- ❸ Plane waves:  $e^{ikr}$ , cutoff  $V_c = k_{\max}^2 / 2$

# METHODS TO TREAT ELECTRON CORRELATION

- Form of exact wavefunction and configuration interaction (CI) methods

$$\Psi = \underbrace{\underbrace{D_0 \Psi_0}_{\text{HF}} + \sum_{a=1}^N \sum_{r=N+1}^{N_{\text{virt}}} D_a^r \Psi_a^r}_{\text{CI Singles}} + \underbrace{\sum_{a < b}^N \sum_{r < s}^{N_{\text{virt}}} D_{ab}^{rs} \Psi_{ab}^{rs} + \dots \text{N-excitations}}_{\text{CI Singles Doubles, Full CI, FCI}}$$

❶ correlation energy

❷ excited states:  $\underline{\underline{H}}^{CI} \underline{D}_n = E_n \underline{D}_n$

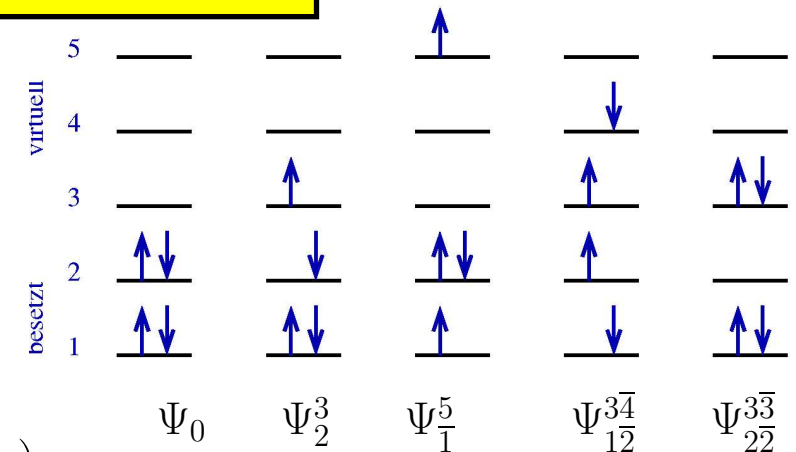
- Variants of CI-type methods

- MCSCF and CASSCF (vary amplitudes and orbitals)

- Coupled Cluster (CC) methods:

$$\Psi = \underbrace{\exp(\hat{T}_1 + \hat{T}_2 + \dots \hat{T}_N)}_{\text{Full CI}} \Psi_0$$

CCS  
CCSD



- Non-variational: Møller-Plesset perturbation theory (MP2, MP3, ...)

# THE DENSITY WORLD: DFT

- The Hohenberg-Kohn theorems

- ① Ground state electronic energy  $E_0$  completely determined by electron density  $n(\underline{r})$ :

$$E_0[n(\underline{r})] = \underbrace{T[n]}_{\text{kin. en. el}} + \underbrace{V_{ke}[n]}_{\text{nuc-el attr.}} + \underbrace{J[n]}_{\text{Coulomb el/el}} + \underbrace{\tilde{E}_{xc}[n]}_{\text{exchange-correlation}}$$

- ② Variational principle for densities

$$E_0^{opt} = \min_n E_0[n(\underline{r})]$$

- The Kohn-Sham equations

$$\left[ -\frac{1}{2}\Delta - \sum_{A=1}^{N_A} \frac{Z_A}{|\underline{r} - \underline{R}_A|} + \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' + \underbrace{\frac{\delta E_{xc}}{\delta n}}_{\text{xc potential } v_{xc}(\underline{r})} \right] \psi_i^s(\underline{r}) = \varepsilon_i^s \psi_i^s(\underline{r})$$

- single-particle equations (like HF), self-consistent solution
- contain electron correlation (unlike HF), exact if exchange-correlation functional exact
- $n(\underline{r}) = \sum_i^N |\psi_i^s(\underline{r})|^2$ ;  $T = \sum_i^N \langle \psi_i^s | -\frac{1}{2}\Delta \psi_i^s \rangle$ ;  $\tau(\underline{r}) = \sum_i^N \frac{1}{2} |\nabla \psi_i^s(\underline{r})|^2$  (kin.-energy dens.)

# EXCHANGE-CORRELATION FUNCTIONALS

- Levels of approximation:  $E_{xc} = E_x + E_c$

type	definition ( $A = E_x, E_c$ )	exchange	correlation
❶ Null	$A = 0$	—	—
❷ LDA	$A = \int a(n) n d\underline{r}$	S	VWN
❸ GGA	$A = \int a(n, \nabla n) n d\underline{r}$	B88, PW91	P86, PW91, LYP
❹ meta-GGA	$A = \int a(n, \nabla n, \tau) n d\underline{r}$	TPSS, BR, VSXC	TPSS, B95, VSXC

LDA= Local Density Appr.; GGA= Generalized Gradient Appr.;  $a$  = energy per electron

E.g.: **NullNull** (=Hartree); **SNull** (=X $\alpha$ ); **SVWN** (=LDA); **BLYP**, **BP86** (both GGA)

- “Jacob’s ladder”: Systematically improvable DFT (?)

LDA, GGA, meta-GGA, hyper-GGA, ...

- DFT with “exact” (HF-like) exchange  $E_x^{ex}$ : Hybrid functionals

E.g.:  $E_{xc}^{B3LYP} = (1 - a) E_x^{LDA} + a E_x^{ex} + b \Delta E_x^{B88} + (1 - c) E_c^{LDA} + c E_c^{LYP}$  ( $a = 0.2$ )



# PERFORMANCE: ELECTRONIC ENERGIES

- Atomic energies: Ground states

	HF	X $\alpha$	SVWN (=LDA)	BVWN	BLYP (= GGA)	MP2	QCISD ( $\approx$ CCSD)	exact
H	0.4982	0.4540	0.4760	0.5178	0.4954	0.4982	0.4982	0.5000
He	2.8552	2.7146	2.8267	2.9672	2.8978	2.8664	2.8702	2.9037
C	37.6809	37.0950	37.4537	38.0318	37.8320	37.7365	37.7552	37.8450
O	74.7839	73.9544	74.4884	75.3238	75.0470	74.8820	74.8977	75.067
Ne	128.4744	127.3950	128.1419	129.2442	128.8796	128.6262	128.6285	128.939

6-31G\* basis; in atomic units (1 Hartree=27.21 eV) (Gill, 1993)

- Ionization potentials  $IP = -\epsilon_{\text{HOMO}}$

Atom	HF	LDA	LDA-SIC	exp.
H	13.6	7.3	13.6	13.6
Li	5.3	3.2	4.4	5.4
Na	5.0	3.1	5.1	5.1
N	15.4	8.3	14.9	14.5
P	10.7	6.3	10.0	10.5
Cr	6.5	4.0	6.7	6.8

num. sol. of KS equations; in eV (Zunger, 1984)

- Comparison to experiment

Method	MAD	max. AD
G2	1.6	8.2
G2(MP2)	2.0	10.1
SVWN	90.9	228.7
BLYP	7.1	28.4
B3LYP	3.1	20.1
B3PW91	3.5	21.8

G2-2; in kcal/mol; Jenssen (1999)

# PERFORMANCE: MOLECULAR GEOMETRIES

- Main group compounds

		HF	SVWN	BVWN	BLYP	MP2	QCISD	Expt.
H <sub>2</sub>	$R_0(\text{H-H})$	1.379	1.446	1.398	1.414	1.395	1.410	1.401
HF	$R_0(\text{H-F})$	1.722	1.776	1.778	1.786	1.782	1.765	1.733
H <sub>2</sub> O	$R_0(\text{O-H})$	1.790	1.844	1.842	1.850	1.829	1.831	1.810
	$\theta_0(\text{H-O-H})$	105.5	103.6	102.9	102.7	104.0	104.0	103.9
NH <sub>3</sub>	$R_0(\text{N-H})$	1.891	1.938	1.937	1.944	1.920	1.925	1.910
	$\theta_0(\text{H-N-H})$	107.2	106.0	105.8	104.8	106.4	106.0	106.0
CH <sub>4</sub>	$R_0(\text{C-H})$	2.046	2.078	2.071	2.076	2.057	2.065	2.092
$\overline{E}$	$R_0(44)$	-0.010	0.014	0.018	0.020	0.010	0.012	—
$ \overline{E} $	$R_0(44)$	0.020	0.021	0.018	0.020	0.014	0.013	—

6-31G\* (Gill, 1993); 32 molecules; in Å and °

- Rules of thumb

- ❶ LDA (HF) bond lengths slightly too long (short)
- ❷ Gradient corrections and post-HF slightly better



# PERFORMANCE: TRANSITION METALS

- Geometries:  $M(CO)_6$

method	HF	MP2/ECP	CCSD(T)	SVWN	BP86	B3LYP	exp.
Cr(CO) <sub>6</sub>	1.970-2.010	1.862	1.939	1.865	1.910	1.921	1.918
Mn(CO) <sub>6</sub>	—	2.031	—	2.035	2.077	2.068	2.063
W(CO) <sub>6</sub>	—	2.047	—	2.060	2.116	2.078	2.058

M-C distance (in Å); extended basis sets, most at least of TZ quality; Koch /Holthausen (1999)

- Dissociation energies  $MH^+ \rightarrow M+H^+$ ; excitation energies  $M \rightarrow M^*$

	SVWN	BP86	B3LYP	MCPF	PCI-80	exp.
MAD diss. en. (kcal/mol)	12	8	4-5	6	2	±2
MAD exc. en. (eV)	0.75		0.33			

M=Sc-Cu; details see Koch / Holthausen, *A Chemist's Guide to DFT* (1999)

- Rules of thumb

- ① LDA (HF) bond lengths too short (long)
- ② Gradient corrections and post-HF perform better
- ③ Errors generally larger than for main group compounds
- ④ Accurate low-spin / high-spin splittings very difficult (role of exact exchange)



# PERFORMANCE: ATOMIZATION ENERGIES

- Atomization (dissociation) energies:  $A-B \rightarrow A+B$

	HF	SVWN	BVWN	BLYP	MP2	QCISD	Expt.
H <sub>2</sub>	75.9	107.5	110.8	103.2	86.6	91.2	103.3
LiH	30.4	57.5	60.3	54.9	39.8	44.1	56.0
Li <sub>2</sub>	2.2	22.5	20.5	19.8	14.1	20.9	24.0
F <sub>2</sub>	-34.3	83.6	47.4	54.4	36.8	27.9	36.9
H <sub>2</sub> O	131.7	240.8	209.1	207.3	188.8	183.7	219.3
CH <sub>4</sub>	300.4	436.8	396.0	389.9	354.2	353.9	392.5
$\overline{E}$ (32)	-85.8	35.6	0.1	1.0	-22.4	-28.8	—
$ \overline{E} $ (32)	85.9	35.7	4.4	5.6	22.4	28.8	—

32 molecules; 6-31G\*; in kcal/mol (Gill, 1993)

G2 set/6-311+G(3df,2p), MADs: 74.5 (HF); MP2 (7.3); BLYP (5.0); BP86 (10.3)

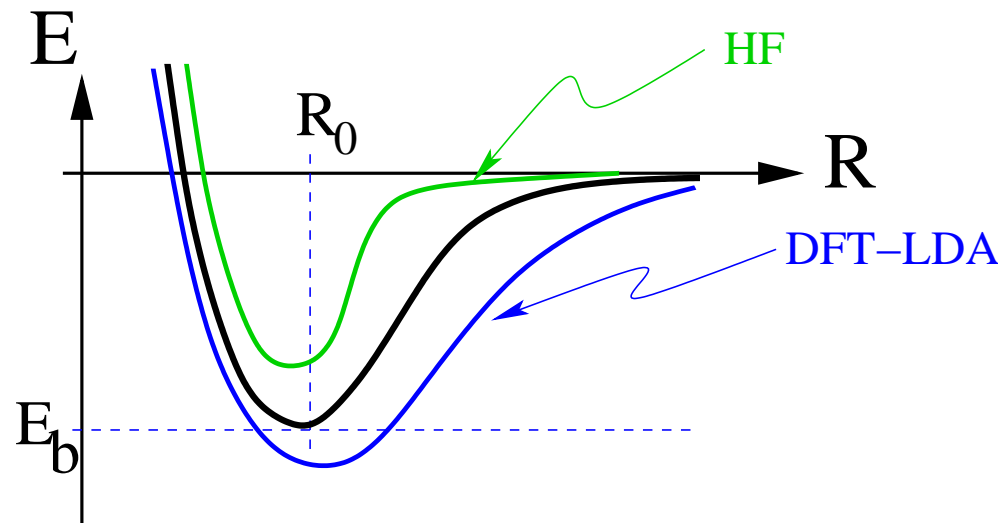
- Rules of thumb

- 1 LDA (HF) too large (much too small)
- 2 Improvement by gradient corrections or post-HF



# PERFORMANCE: POTENTIAL CURVES

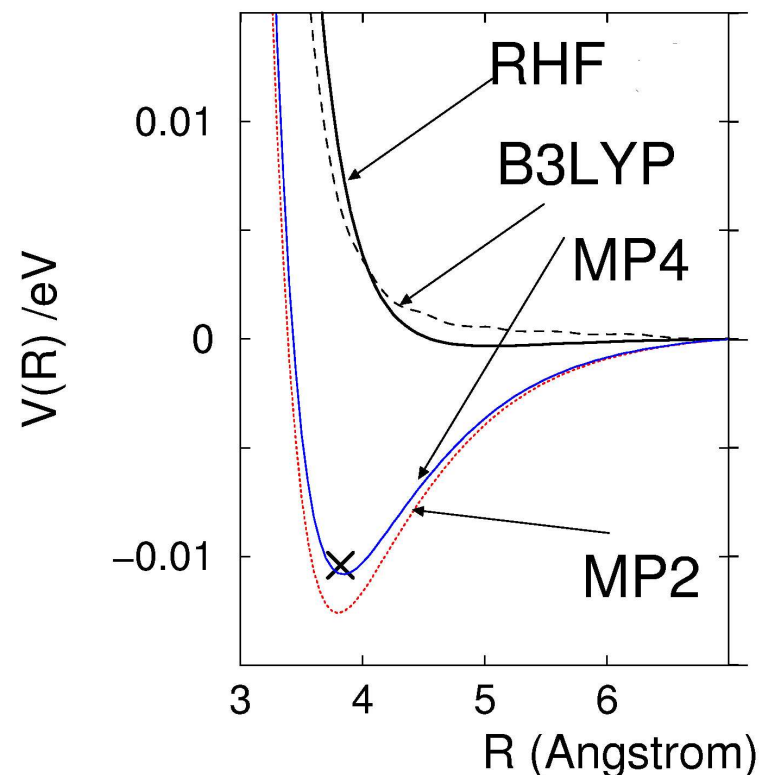
## • Chemical bond: Summary



- ❶ HF too shallow, too steep
- ❷ LDA too deep, too flat
- ❸ GGA and post-HF perform better

## • Van-der-Waals bond

$\text{Ar}_2$ , 6-311++G(3df,3dp)



- ❶ HF and B3LYP fail,  
the former because lack of correlation,  
the latter because  $\lim_{r \rightarrow \infty} v_c(r)$  wrong
- ❷ Good basis sets needed

# Non bonding interactions

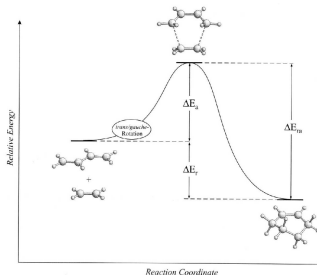
## Types

- ▶ Hydrogen-Bonded systems
- ▶ Charge-Transfer systems
- ▶ Dipole-Interacting systems
- ▶ Weak Interactions (VdW, ...)

There are systems where special care is recommended.

# Chemical reactions - gas example

- An example: Diels-Alder reaction



	Exp.	G2	HF	SVWN	BLYP	B3LYP
$\Delta E_a$ (kcal/mol)	27±2	25	51	5	26	28
$\Delta E_r$ (kcal/mol)	-38	-38	-30	-59	-14	-29

HF and DFT with 6-311+G(d,p), zero-point corrected

- Rules of thumb

- ❶ LDA (HF) activation energies much too small (much too high)
- ❷ LDA (HF) overbinds (underbinds)
- ❸ Gradient corrections and post-HF perform better

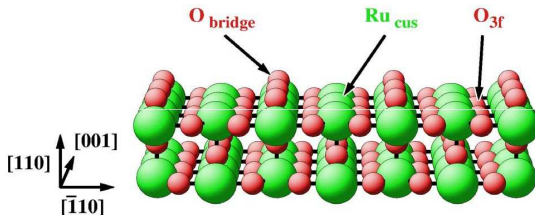
# Catalytic applications of surface science

- *A prerequisite for understanding the function of surfaces is detailed knowledge of the surface composition and geometry.*
- *UHV surface science help - sometimes UHV results can be related to high-pressure applications. Nevertheless, often structures dominating these application may be impossible to stabilize under UHV conditions.*
- *The theoretical determination of a  $(T,p)$  phase diagram, covering the surface phases from UHV to realistic conditions, is critical for bridging of the pressure gap, enabling to investigate real high-pressure problems.*
- *From the surface phase diagram a coexistence of different surface phases can be found, leading to an enhanced dynamics and enabling a reaction mechanism not playing a role otherwise.*

**The concept of first-principles atomistic thermodynamics enables us to calculate such surface phase diagrams.**



# CO on RuO<sub>2</sub>



## STM: in UHV stable state

There are no vacancies in the O<sub>bridge</sub> rows.

## STM: in an environment containing O<sub>2</sub> and CO

- bridge sites are occupied by only  $\approx 90\%$  oxygen atoms,
- Ru<sub>cus</sub> sites are occupied by  $\approx 70\%$  CO and  $\approx 30\%$  O.

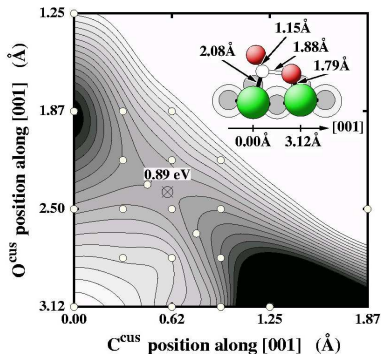


TABLE Calculated binding energies in  $(1 \times 1)$  phases on  $\text{RuO}_2(110)$ . The values are given with respect to the free  $\text{O}_2$  and  $\text{CO}$  molecule respectively, zero-point vibrations not included.

Species	Phase	Binding energy
$\text{O}^{\text{br}}$	$\text{O}^{\text{br}}/-$	-2.44 eV/atom
$\text{O}^{\text{br}}$	$\text{O}^{\text{br}}/\text{O}^{\text{cus}}$	-2.23 eV/atom
$\text{O}^{\text{br}}$	$\text{O}^{\text{br}}/\text{CO}^{\text{cus}}$	-2.37 eV/atom
$\text{O}^{\text{cus}}$	$\text{O}^{\text{br}}/\text{O}^{\text{cus}}$	-0.99 eV/atom
$\text{O}^{3\text{f}}$	$\text{O}^{\text{br}}/-$	-3.59 eV/atom
$\text{CO}^{\text{cus}}$	$\text{O}^{\text{br}}/\text{CO}^{\text{cus}}$	-1.26 eV/atom
$\text{CO}^{\text{cus}}$	$\text{CO}^{\text{br}}/\text{CO}^{\text{cus}}$	-1.26 eV/atom
$\text{CO}^{\text{br}}$	$\text{CO}^{\text{br}}/\text{CO}^{\text{cus}}$	-1.58 eV/atom

Potential energy surface for the reaction  $\text{CO}^{\text{cus}} + \text{O}^{\text{cus}} \rightarrow \text{CO}_2$ . The actually calculated points are indicated by white circles. The lateral positions of  $\text{C}^{\text{cus}}$  and  $\text{O}^{\text{cus}}$  along the  $[001]$  direction have been fixed, fully relaxing all remaining degrees of freedom. The energy zero corresponds to the initial state at (0.00 Å, 3.12 Å). [From Reuter and Scheffler, PRB 2003.](#)

# Statistical mechanics of catalysis from first principles

- ▶ Analysis of all *possibly relevant* processes using **density-functional theory**
  - ▶ Calculate the rates of all important processes
$$\Gamma^{(i)} = \Gamma_0^{(i)} \exp(-\Delta E^{(i)} / k_B T)$$
  - ▶ Statistical mechanics approach to describe
    - adsorption/desorption of O<sub>2</sub> and CO
    - diffusion of O and CO
    - surface reactions between  $\text{CO}^{br} + \text{O}^{cus}$ ,  $\text{CO}^{cus} + \text{O}^{cus}$ ,  $\text{CO}^{br} + \text{O}^{br}$ ,  $\text{CO}^{cus} + \text{O}^{cus}$
- Althogether 26 processes!  $\implies$  Kinetic Monte Carlo**

*Reuter, Stampfl and Scheffler in Handbook of Materials Modeling, Springer, 2005.*

# Ab initio surface phase diagram

Combination of thermodynamics and density-functional theory enables to construct a (T,p) diagram of the stability regions of different surface phases.

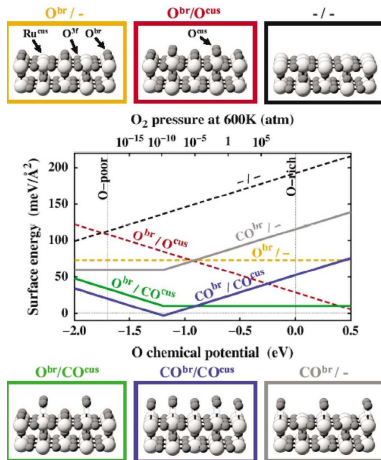
## Example: CO oxydation on the RuO<sub>2</sub> surface

Surface energy per unit area:

$$\gamma(T, \{p_i\}) = G(T, \{p_i\}) - \sum_i N_i \mu_i(T, p_i)$$

- ▶ The surface free energy depends only on two chemical potentials (O, CO), the O<sub>2</sub> and CO gas phase are independent *reservoirs*.
- ▶ The vibrational contribution to the Gibbs free energy,  $G(T, \{p_i\})$ , are for RuO<sub>2</sub> nearly equal to these of bulk oxide  $\Rightarrow$  it will be replaced by the corresponding total energies.
- ▶ High accuracy calculation of energy *differences* ( $\pm 5$  meV).

# CO + O on RuO<sub>2</sub>



Surface free energies,  $\gamma(T, \{p_i\})$ , in the experimentally accessible range of the oxygen chemical potential.

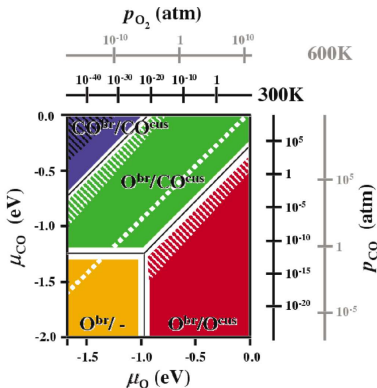
There are used relations  $\mu_{\text{O}}(T, p_{\text{O}_2}) = \frac{1}{2}\mu_{\text{O}_2}(T, p^0) + \frac{1}{2}k_B T \ln(p_{\text{O}_2}/p^0)$  and

$\mu_{\text{CO}}(T, p_{\text{CO}}) = \mu_{\text{CO}}(T, p^0) + k_B T \ln(p_{\text{CO}}/p^0)$  to relate the chemical potential to temperature and partial pressure. The chemical potentials of O<sub>2</sub> and CO at  $p^0=1$  atm are tabulated.

In the CO-rich limit and if the O chemical potential is below -1.2 eV,  $\text{CO} \rightarrow \text{C} + 1/2 \text{O}_2$  (kink in  $\gamma$ ). From Reuter and Scheffler, PRL 2003.

## CO + O on RuO<sub>2</sub>

Phase diagram of surface structures of RuO<sub>2</sub>(110) in constrained equilibrium with gas phase of O<sub>2</sub> and CO. Depending on the temperature and partial pressures of these reactants, several stable surface phases are found with uncertainty  $\pm 100$  K.



Regions of the lowest-energy structures in the ( $\mu_{\text{O}}$ ,  $\mu_{\text{CO}}$ ) space. The additional axes give the corresponding pressure scales at T=300 and T=600 K. [From Reuter and Scheffler, PRL 2003.](#)