Activities - <u>Realistic Theories of CEM</u>

(O. Andersen, A. Georges, B. Gabriel Kotliar, A. Lichtenstein)

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Testing the accuracy of the xc energy of electronic-structure theories for real materials

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Testing the accuracy of the xc energy of electronic-structure theories for real materials

Example: surface structure and
surface chemical reactions at Si(001)

Silicon is one of the best examples of a nearly free electron material

Thus, correlation is not too important, and approximate xc functionals are doing fine

This assessment is WRONG !!!

Testing the accuracy of the xc energy of electronic-structure theories for real materials

Example: surface structure and surface chemical reactions at Si(001)

Phys. Rev. Lett. 87, 016105 (2001) and Phys. Rev. Lett. 89, 166102 (2002)

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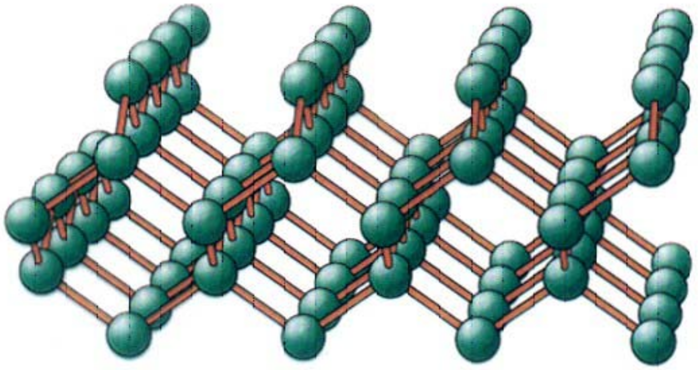
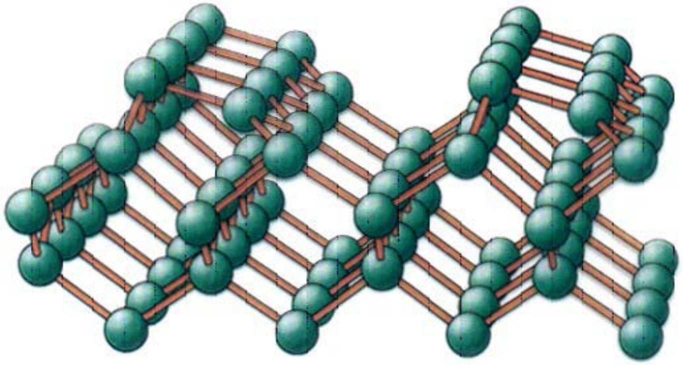
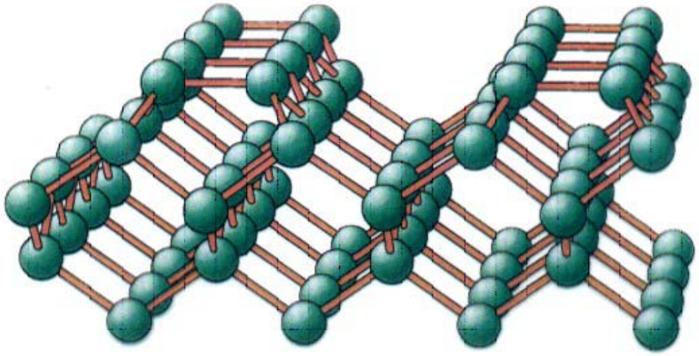
Dimerization and dimer buckling at Si(001)



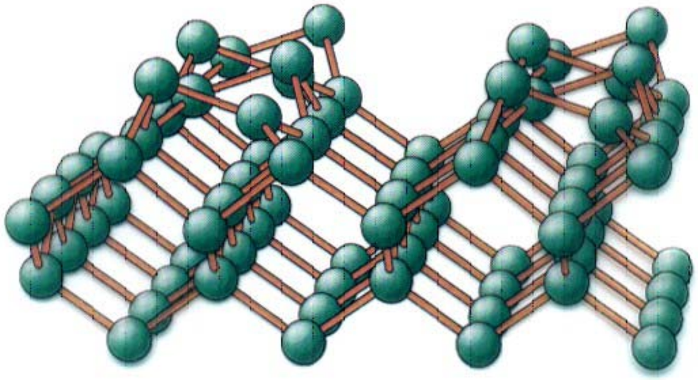
truncated bulk geometry



dimer buckling



formation of dimers

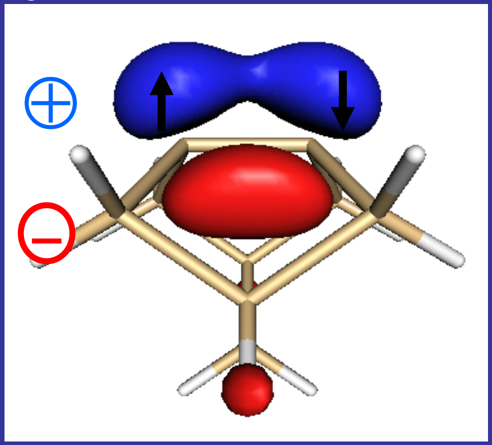


alternating buckling

Buckling at the clean Si(001) surface is sensitive to electron correlation and electron-lattice coupling

"A negative U system" ?

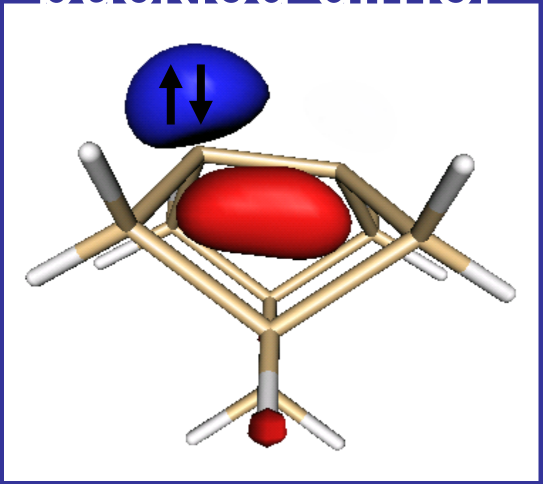
HOMO of
symmetric dimer



favored by MCSCF
(clusters)

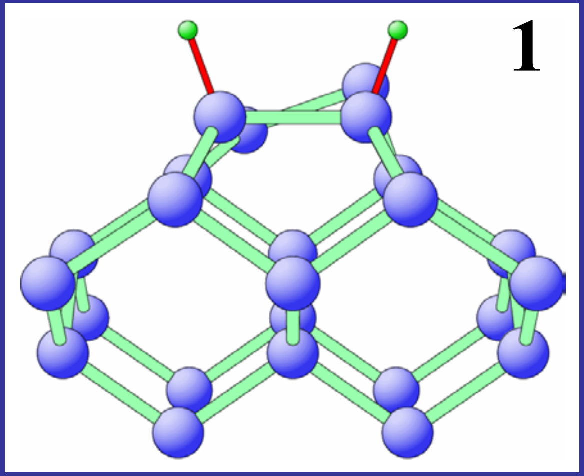
Which configuration is the ground state ?

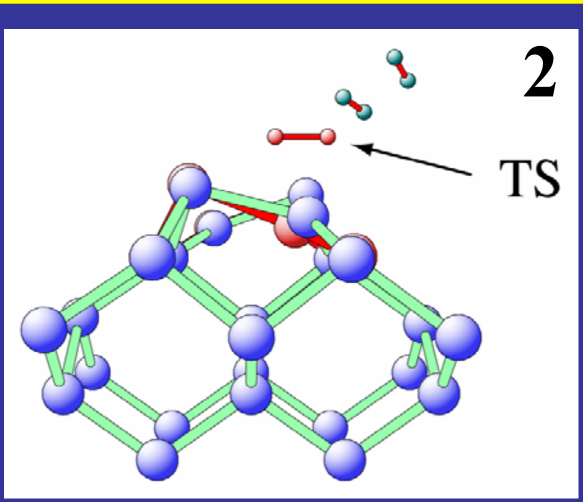
HOMO of
buckled dimer

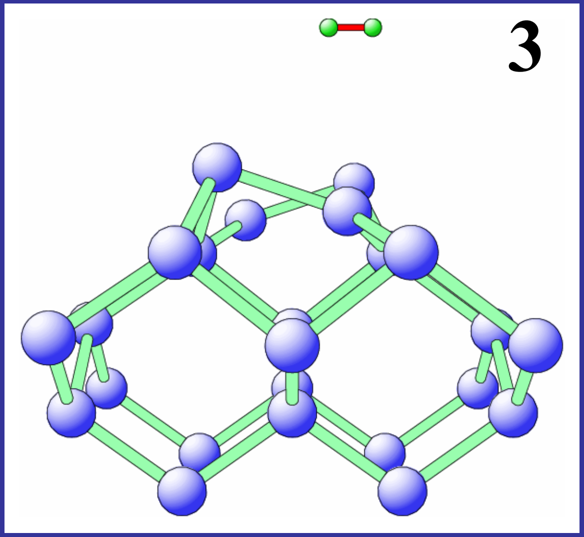


favored by DFT
(slabs)

The H_2 / Si(001) energy barrier puzzle

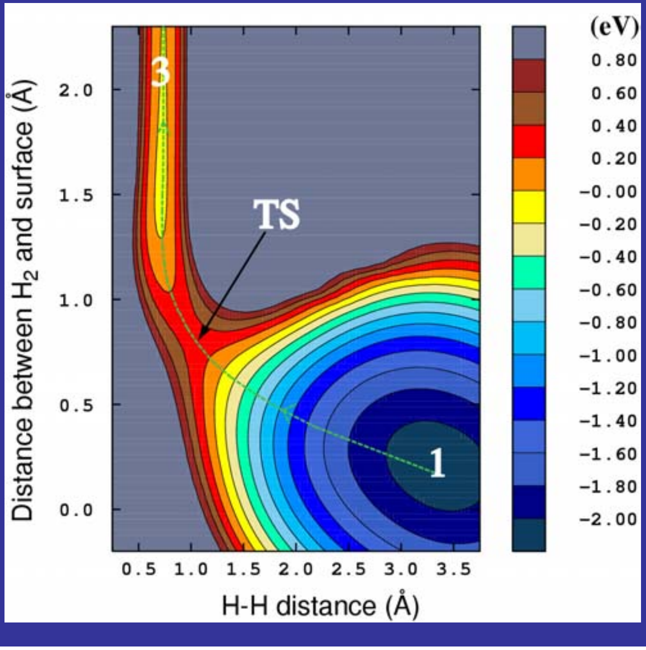






A. Gross, A., M. Bockstedte, M. S., Phys. Rev. Lett. 79 *(1997)*

- Adsorption experiments of H_2 at Si(001) show an adsorption energy barrier (> 0.6 eV).
- Desorption experiments of H_2 from Si(001) show that there is no adsorption barrier.
- CI and DFT calculations give very different descriptions.



Where do we stand with the first-principles description of materials?

- Structure and vibrations are well described by DFT with available xc functionals !? However, for big systems (e.g. surfaces) such calculations are not a black box, and uncritical faith is not recommended [e.g. Si(001) and CO/Pt(111)].
- Errors in total energies can be noticeable. Even for energy *differences* they can be as large as several tenths of an eV.

We need to do better!!

... in particular for reaction energy barriers.

This work: Correct the DFT xc energy by QMC.

Is the *direct* DFT route too complicated?

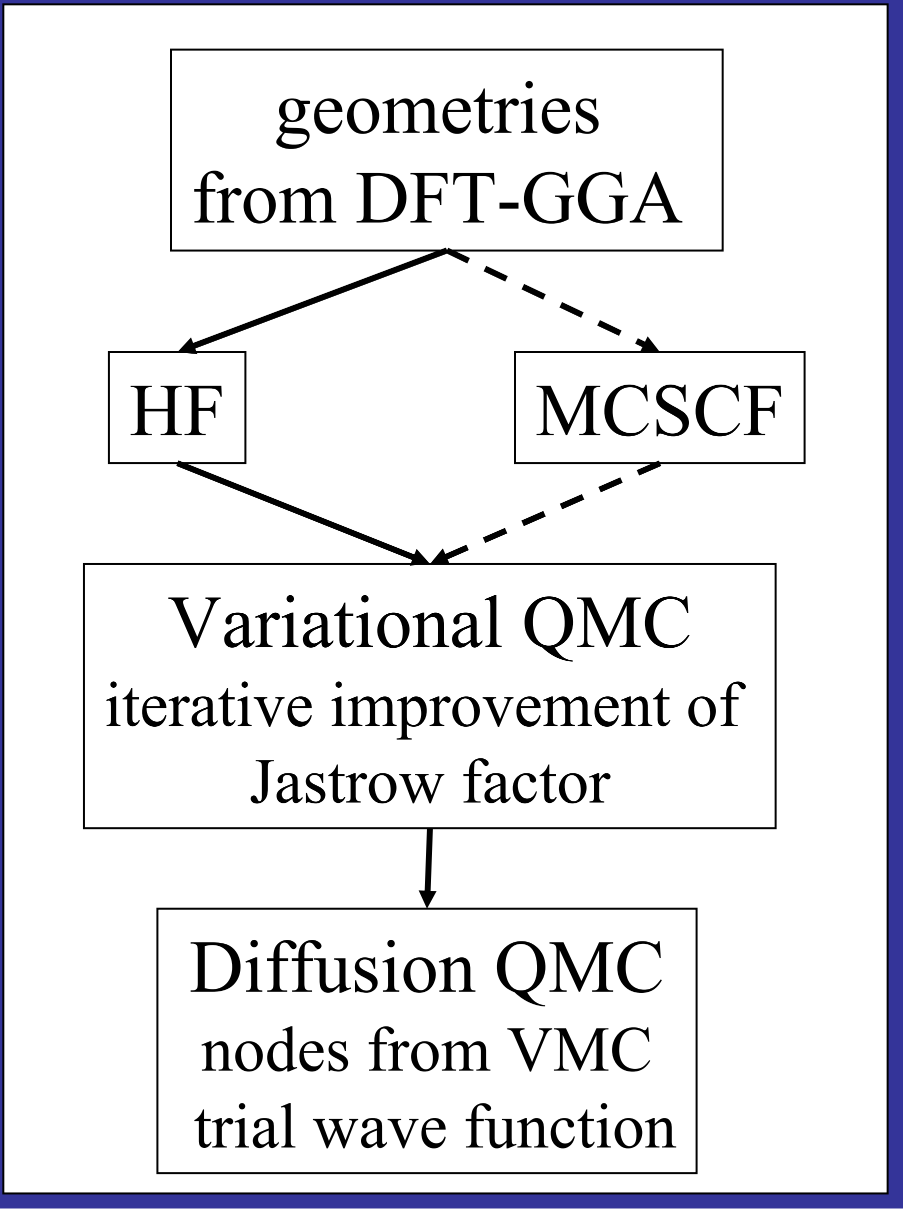
- The xc energy, E_{xc} , stems from many-body theory.
- E_{xc} is a functional of the density, but maybe impossible to handle as such. Maybe, for the accuracy we need, we have to use a "detour" (we do so already for $T_s[n]$).

⇨ Calculate a correction to $\boxed{E_{xc}^{..\mathrm{A}}[n]}$ from the many-body wave function Ψ_0. (Recall: Ψ_0 , is a functional of the density, as is the many-body Hamiltonian.)

Methodology of this work

- DFT-GGA slab and cluster calculations
- QMC cluster calculations
- **correction of the DFT-GGA exchange-correlation energy**

$$\Delta E_{\mathrm{corr}} = E_{\mathrm{cluster}}(\mathrm{QMC}) - E_{\mathrm{cluster}}(\mathrm{DFT\text{-}GGA})$$



geometries from DFT-GGA

HF

MCSCF

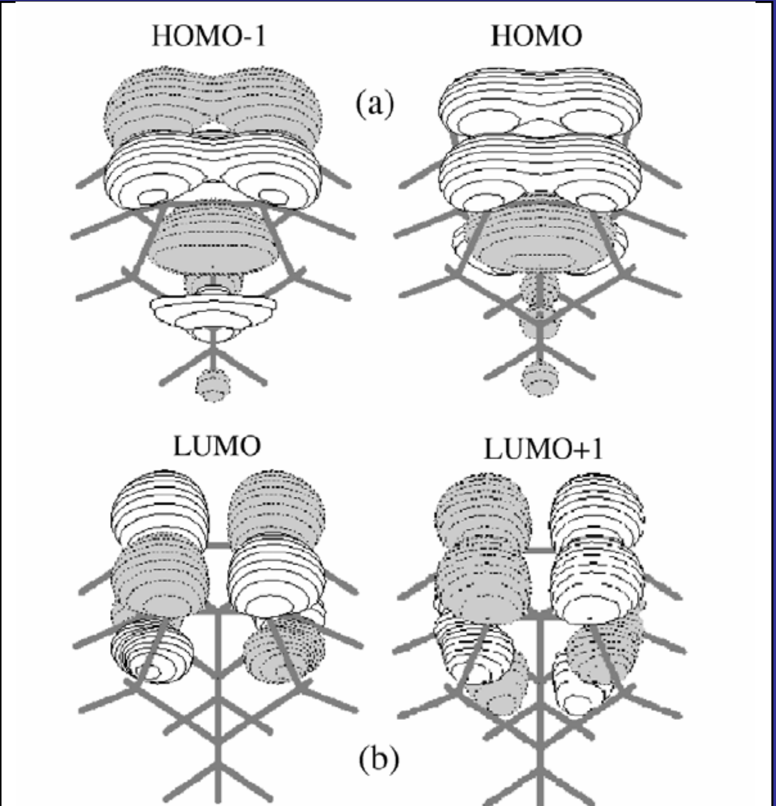
Variational QMC
iterative improvement of Jastrow factor

Diffusion QMC
nodes from VMC trial wave function

Correlated wavefunctions in VMC

Zero-order wave function: Linear combination of Slater determinants (from HF or MCSCF)

$$\Psi_0(r_1, r_2, \ldots r_N) = \Sigma_n\, d_n\, Det_n\{\varphi_\alpha\}\, Det_n\{\varphi_\beta\}$$



Active space for MCSCF

Correlate this Slater wave function:

$$\Psi_T = \Psi_0 \exp(U_{corr})$$

$$U_{corr} = \Sigma_{i,j}\ \Sigma_I\, \Sigma_{k,l,m}\, c_{k,l,m}\, a_k(r_{ij})\, b_l(r_{iI})\, b_k(r_{jI})$$

Variance minimization of the local energy to optimize the parameters

Guess $\Psi_T(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = \Psi_T(\boldsymbol{R})$

Evaluate

$$\begin{aligned} E_T &= \int \Psi_T^*(\boldsymbol{R}) H \Psi_T(\boldsymbol{R}) d\boldsymbol{R} \\ &= \int \left(\frac{H\Psi_T(\boldsymbol{R})}{\Psi_T(\boldsymbol{R})} \right) \left|\Psi_T(\boldsymbol{R})\right|^2 d\boldsymbol{R} \\ &= \int E_L(\boldsymbol{R}) \left|\Psi_T(\boldsymbol{R})\right|^2 d\boldsymbol{R} \end{aligned}$$

using Monte Carlo integration

Adjust Ψ_T to minimize E_T or the variance of E_L .

Beyond VMC: Diffusion Monte Carlo

- iterative projection technique

  $\Psi_{i+1} = \exp(-H\ \tau)\ \Psi_i$

  or

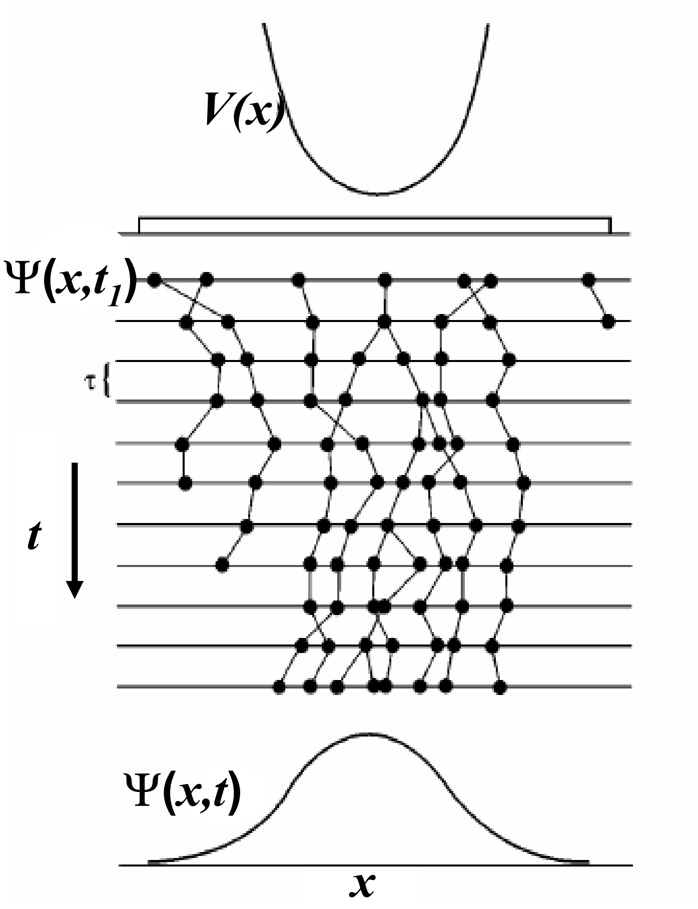
  $\Psi(\boldsymbol{R},\ t+\tau) = \int dR'\ G(\boldsymbol{R}, \boldsymbol{R}', \tau)\ \Psi(\boldsymbol{R}',t)$

  $G(\boldsymbol{R}, \boldsymbol{R}', \tau) = < \boldsymbol{R} \mid e^{-H\tau} \mid \boldsymbol{R}' >$

- represent $\Psi(\boldsymbol{R}, t)$ by an ensemble of 'walkers' that evolves according to the above equations

- constraint: Ψ must have unique sign in each nodal pocket
  $\rightarrow$ fixed node approximation

schematic example
for harmonic potential



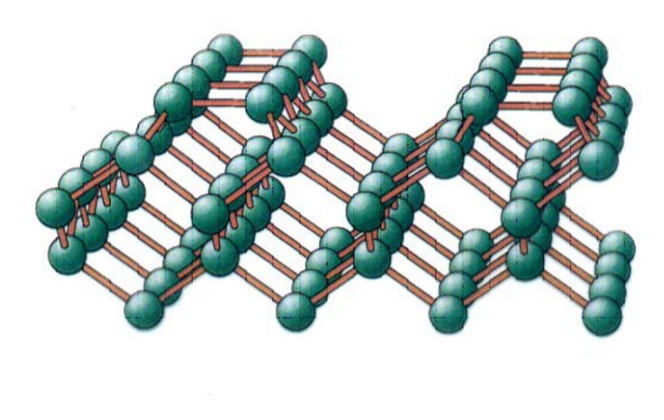
Example:

The importance of correlations for Si(001) and H_2 adsorption and desorption at Si(001)

Clean Si(001): experimental Results

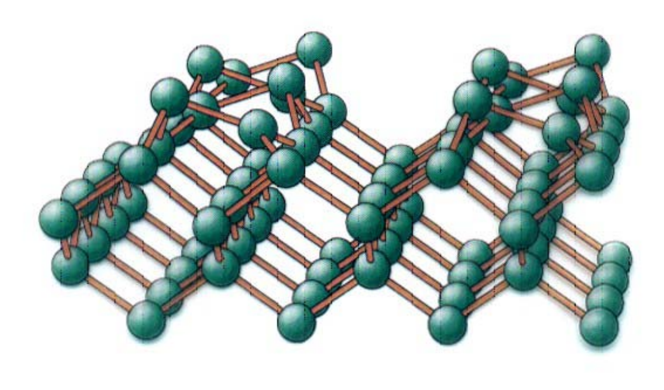
STM

- Room temperature: symmetric dimers
- below 120 K: buckled dimes
- below 20 K: symmetric dimers



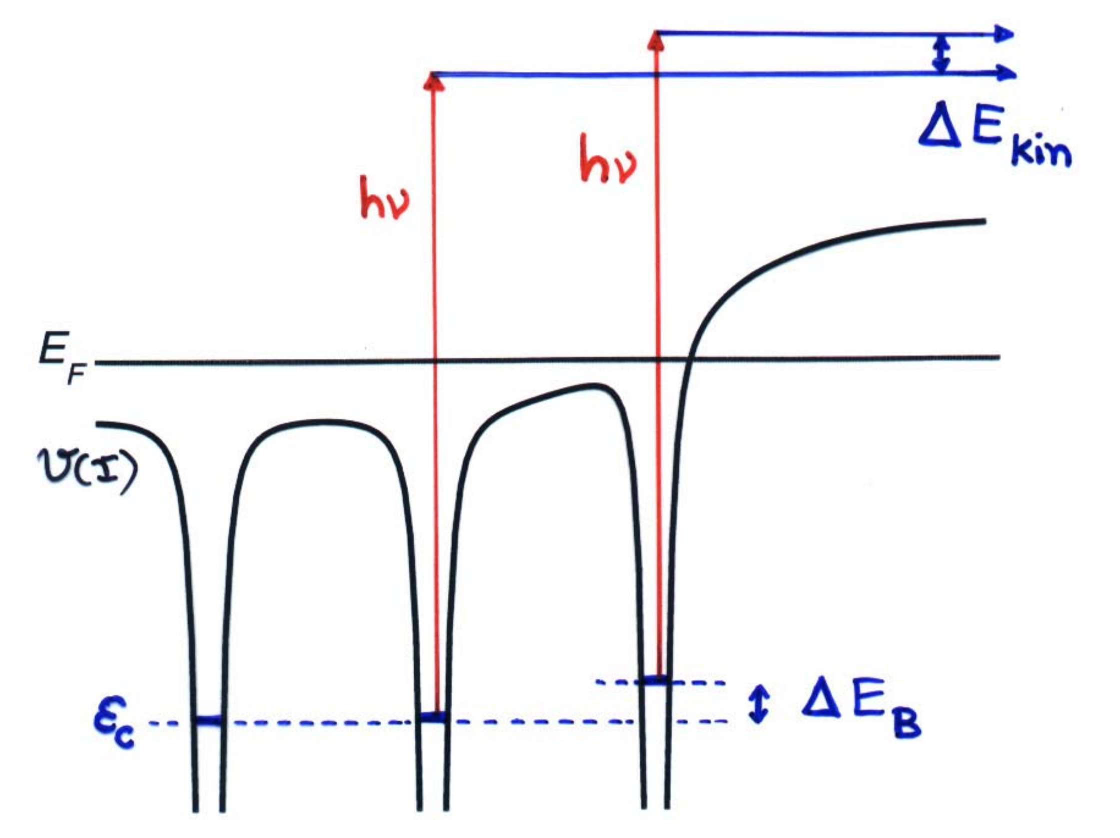
SLCS

- buckled dimers



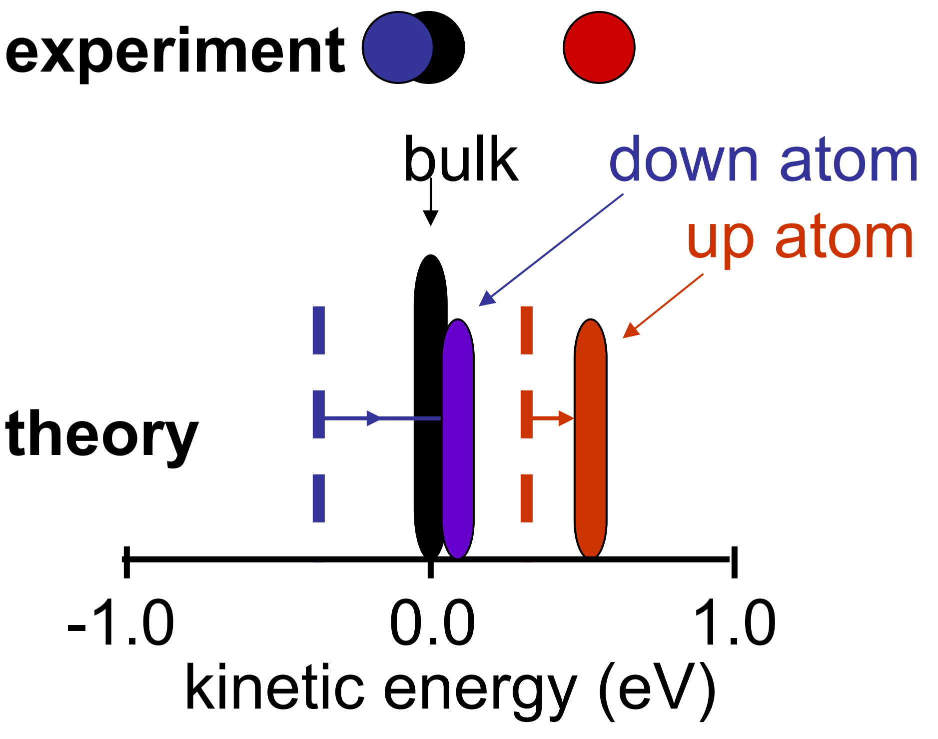
Surface core level shifts (SCLS or ESCA)

Important tool for surface analysis (identification of atoms, electronic structure, nature of bonding).



Often surface core-level shifts are interpreted as an initial-state effect.

Si *2p* SCLS for Si(001) p(2x2)



For this system: screening at the surface is better than in the bulk

Theory

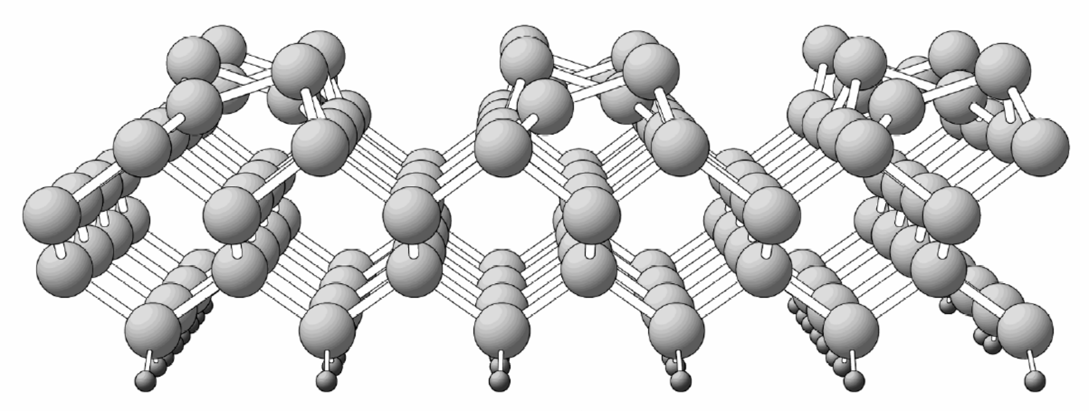
dashed: initial-state effect only

bars: including also final-state screening (*by total-energy differences or transition-state theory*)

E. Pehlke and M.S., PRL ***71****, 2338 (1993).*

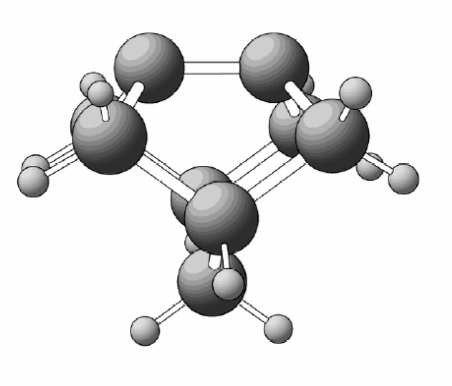
Two peaks = clear proof for the buckling

DFT-GGA cluster calculations for Si(001)

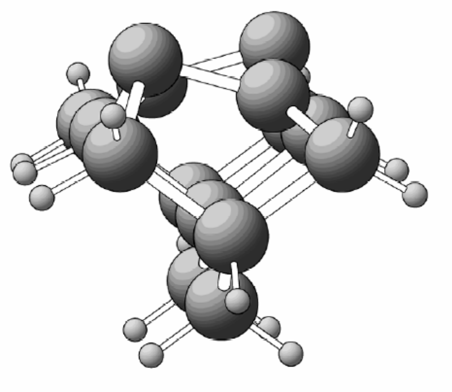


	angle (deg)	bond (Å)	ΔE (eV)	gap (eV)
Si_9	4.9	2.24	0.0	1.1
Si_{15}	15.7	2.32	0.1	0.9
Si_{21}	18.0	2.40	0.2	0.7
slab	18.3	2.40	0.2	0.0

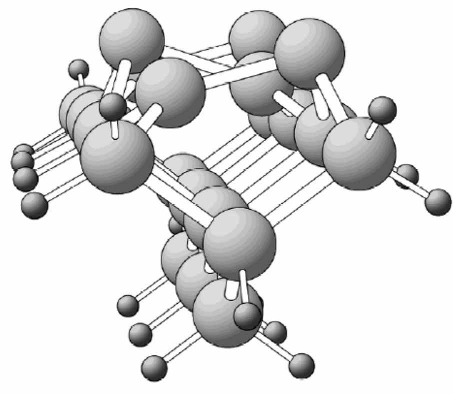
The buckling only develops fully in bigger clusters.



Si_9H_{12}

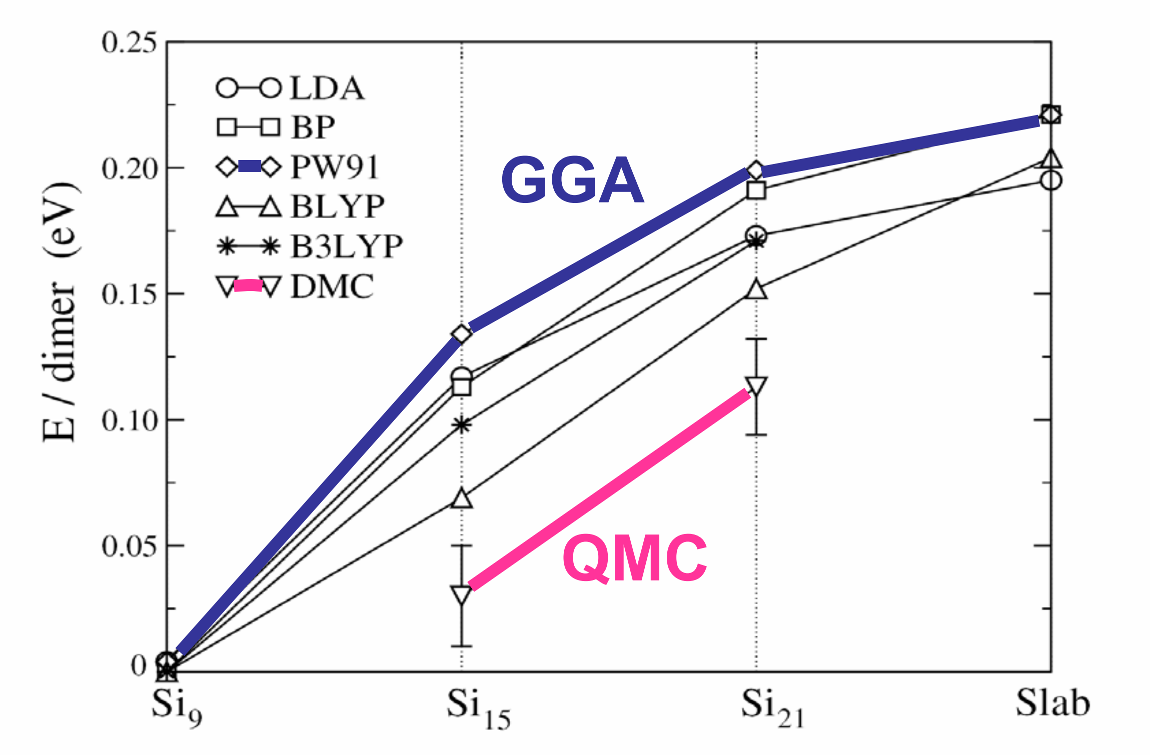


$Si_{15}H_{16}$



$Si_{21}H_{20}$

Energy gain from Si-dimer buckling



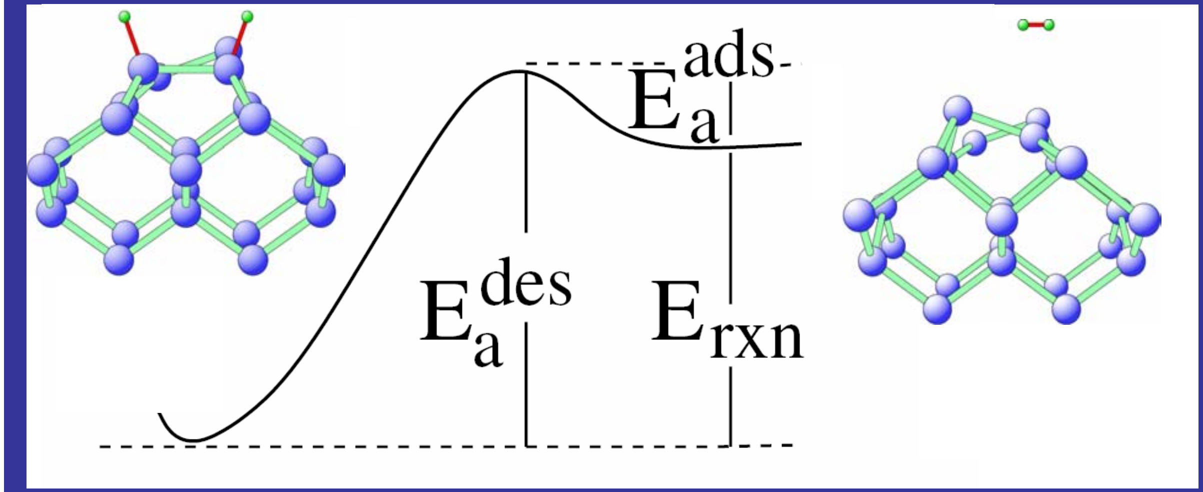
*S. B. Healy,
C. Filippi,
P. Kratzer,
E. Penev & M. S.,
Phys. Rev. Lett.* ***87*** *(2001).*

- QMC calculations confirm the buckled ground state, though with a smaller energy gain than DFT.
- It needs a large cluster with 3 dimers ($Si_{21}H_{20}$) to identify the effect.
- $\Delta E_{\mathrm{corr}} = E_{\mathrm{cluster}}(\mathrm{QMC}) - E_{\mathrm{cluster}}(\mathrm{GGA}) \approx 0.1\ \mathrm{eV}$

Explanation of the experimental results for clean Si(001)

- Room temperature: The symmetric dimers seen in STM are due to dynamic (fast) flipping
- Below 120 K: STM sees buckled dimes; thus, the exp. energy barrier is approx. 0.15 eV, in good agreement with our QMC extrapolation to infinitely large clusters.
- Below 20 K: STM sees symmetric dimers. This is possibly induced by the STM electrons.

H_2 / Si(001)



experiments:

$E^{ads} > 0.6$ eV

$E_{rxn} = 1.9 \pm 0.3$ eV

$E^{des} = 2.5 \pm 0.1$ eV

DFT calculations (slabs)

	E_{rxn}[eV]	E_{des}[eV]	E_{ads}[eV]
PW91	1.90	2.27	0.37

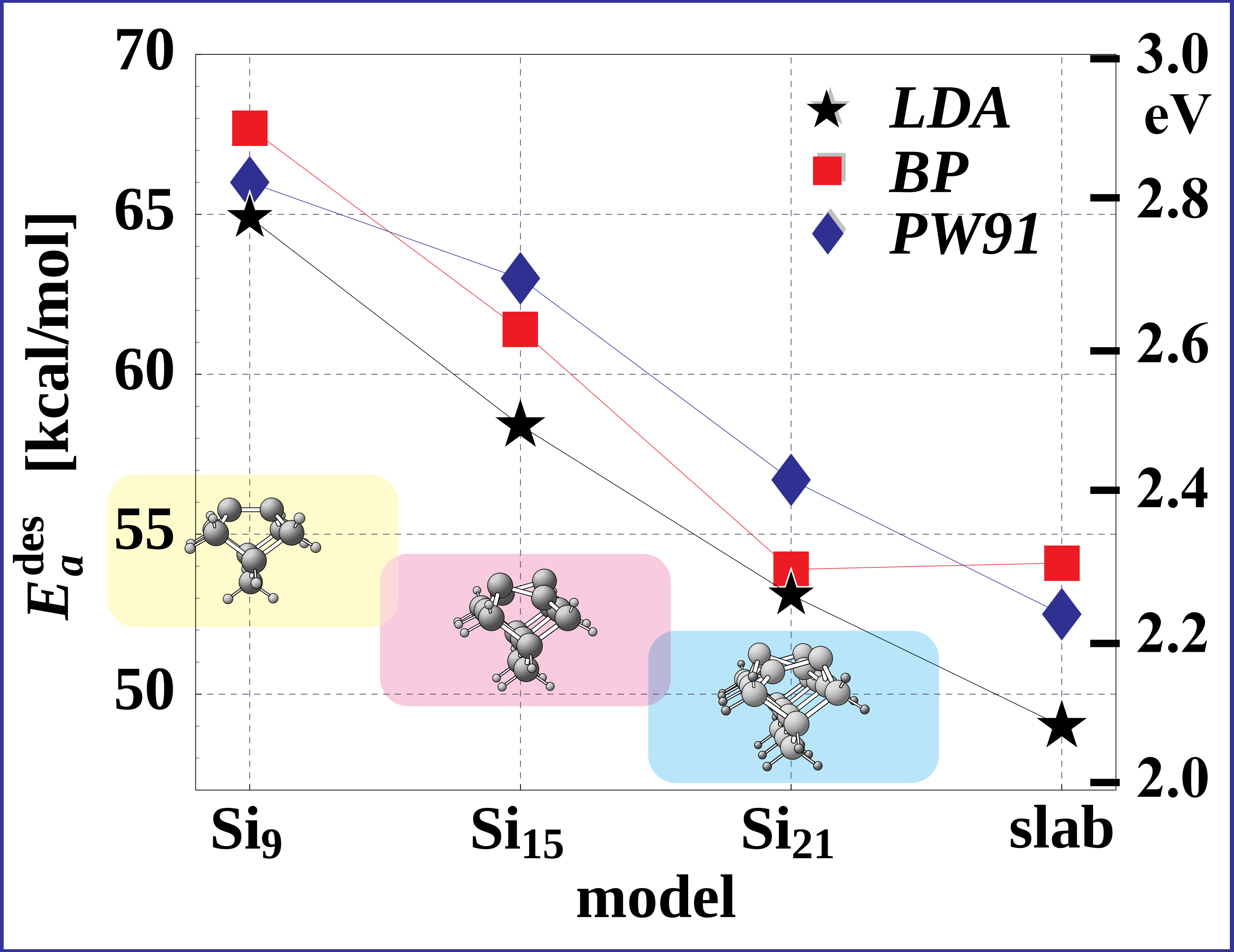
CI calculations (Si_9 clusters)

	E_{rxn}[eV]	E_{des}[eV]	E_{ads}[eV]
CCSD(T) ‡	2.65	3.26	0.61
CAS(4,4)+MRCI*	2.60	3.75	1.15

‡ J.A.Steckel et al., J. Phys. Chem. B ***105****, 4031 (2001)*

Z. Jing & J.L. Whitten, J. Chem. Phys.* ***98**, 7466 (1993)*

Cluster models: H_2 dissociative adsorption



Convergence with cluster size is slow.

E. Penev, P. Kratzer and M. Scheffler, J. Chem. Phys. ***110****, 3986 (1999)*

QMC -- reliability checks

- geometries, in particular transition states
- pseudopotential error
- other technical aspects
  - basis set in HF
  - angular integration grid for non-local pseudopot.
- comparison to CI calculations for small clusters

Si_9, intra-dimer pathway (H2*)

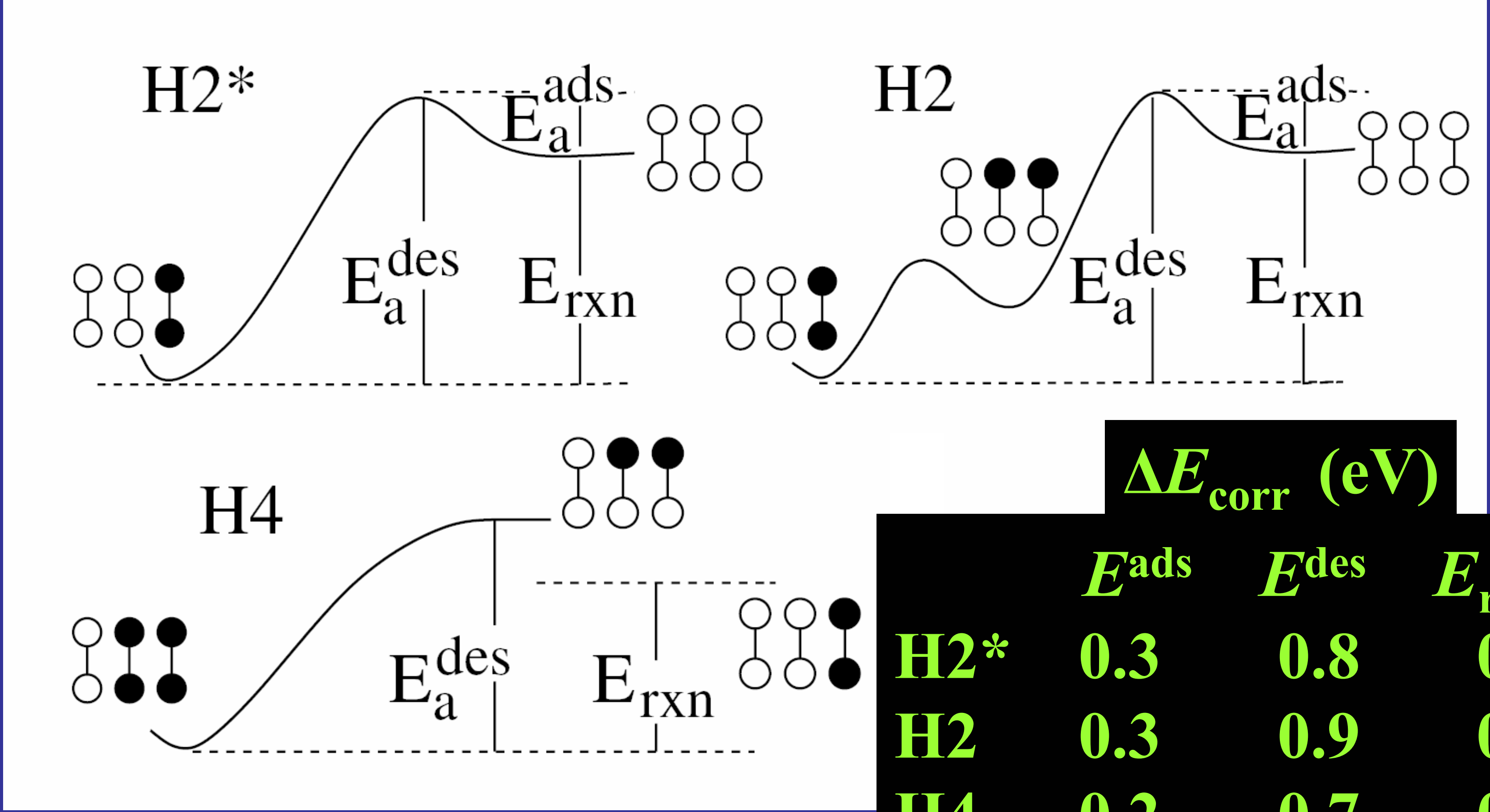
method	E_{rxn}[eV]	E_{des}[eV]	E_{ads}[eV]
DMC (±0.06)	2.64	3.65	1.01
CAS(4,4)+MRCI*	2.60	3.75	1.15

*Z. Jing & J.L. Whitten, J. Chem. Phys **98** (1993)

xc-energy correction for surface reactions

QMC calculations for Si_9, Si_{15}, Si_{21}, Si_{27} clusters

$$\Delta E_{corr} = E_{cluster}(\mathrm{QMC}) - E_{cluster}(\mathrm{PW91})$$

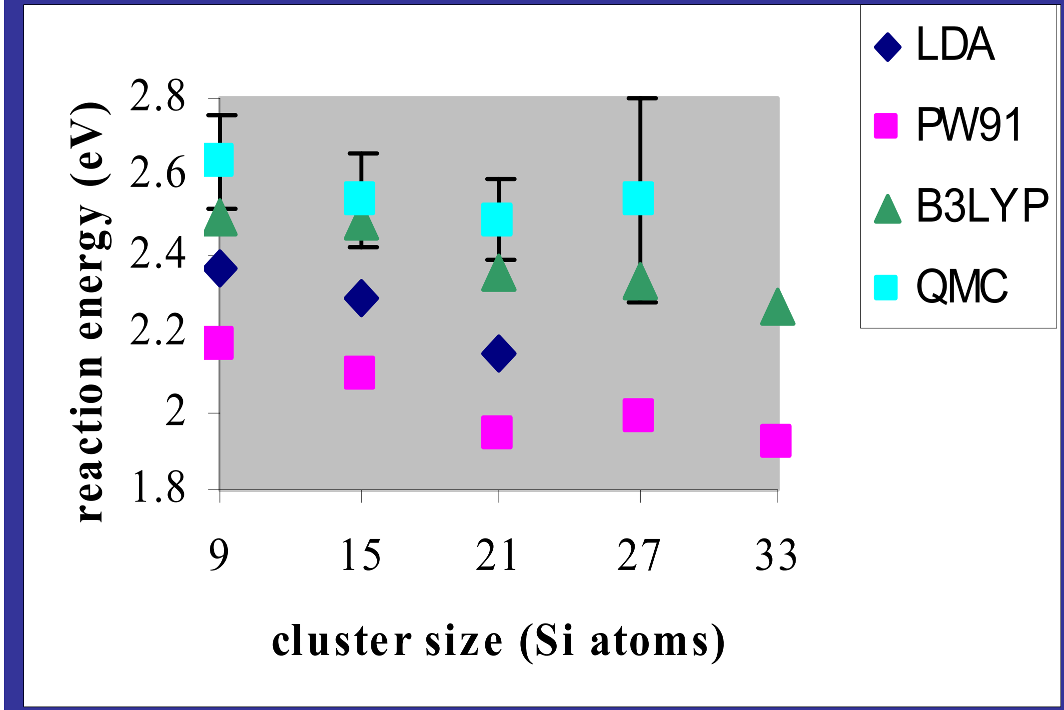


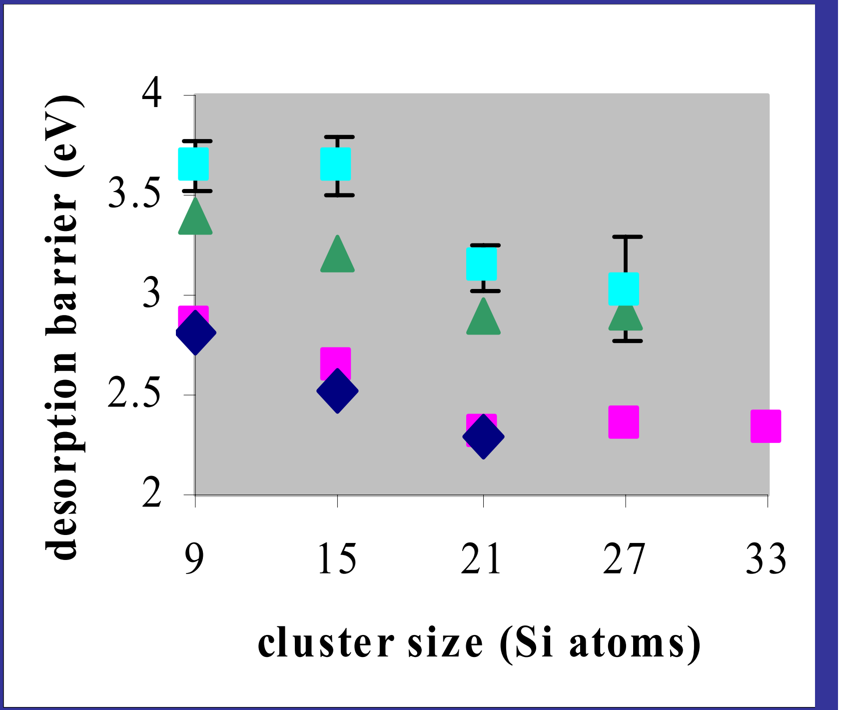
ΔE_{corr} (eV)

	E^{ads}	E^{des}	E_{rxn}
H2*	0.3	0.8	0.5
H2	0.3	0.9	0.5
H4	0.2	0.7	0.5

Cluster size convergence

- Both the reaction energy and the barriers are underestimated by the PW91 functional.
- B3LYP comes close to the QMC results, but still gives slightly lower values.





Results (slab)

	E^{ads}(eV)	E^{des}(eV)	E_{rxn}(eV)
H2* mechanism			
$E^{PW91\text{-}slab}$	0.46	2.16	1.70
ΔE_{corr} (±0.05)	+0.29	+0.80	+0.50
E_{QMC} (±0.05)	0.75	2.96	2.20
exp.	>0.6	2.5±0.1	1.9±0.3
H2 mechanism			
$E^{PW91\text{-}slab}$	0.29	2.04	1.75
ΔE_{corr} (±0.09)	+0.34	+0.87	+0.53
E_{QMC} (±0.09)	0.63	2.91	2.28
exp.	>0.6	2.5±0.1	1.9±0.3
H4 mechanism			
$E^{PW91\text{-}slab}$	0.00	2.12	1.81
ΔE_{corr} (±0.12)	+0.19	+0.72	+0.48
E_{QMC} (±0.12)	0.19	2.84	2.29
exp.	--	2.5±0.1	--

- QMC gives higher adsorption barrier, improving agreement with experiments.
- The inter-dimer path for desorption competes with the intra-dimer path -- in agreement with recent experiments.
- The absolute value of the desorption barrier in QMC is higher then the experimental data (from isothermal desorption).

Conclusions

- Corrections to $\boxed{E_{xc}^{..\mathrm{A}}[n]}$ can be significant -- much of the error is due to self interaction, but correlation is important as well.
- The QMC approach to evaluate such corrections is feasible (and accurate).
- Cluster approximations: The size is crucial.
- Comparison to experiment :
  - clean Si(001): buckled ground state persists at low temperatures.
  - QMC adsorption for H_2 / Si(001) in better agreement with experiment than previous calculations.

www.fhi-berlin.mpg.de/th/Meetings/FHImd2003/

Announcement: "hands on" Workshop

Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics,Chemistry, Engineering and Biology

Ψ_k

21-30 July 2003
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Berlin, Germany

Organisers

- Catherine Stampfl (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin and The University of Sydney, Australia)
- Jörg Neugebauer (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)
- Peter Kratzer (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)
- Arno Schindlmayr (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)
- Matthias Scheffler (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin)

Purpose of the Workshop

The main objectives of the workshop is to introduce density-functional theory calculations to a level such that the participants obtain a thorough understanding of what DFT can offer and are able to perform such calculations. The computer program SFHIngX developed at the Fritz-Haber-Institut, will be used for the