Quantum studies of the interaction and of the reaction of hydrogen atoms with silver surfaces[1]

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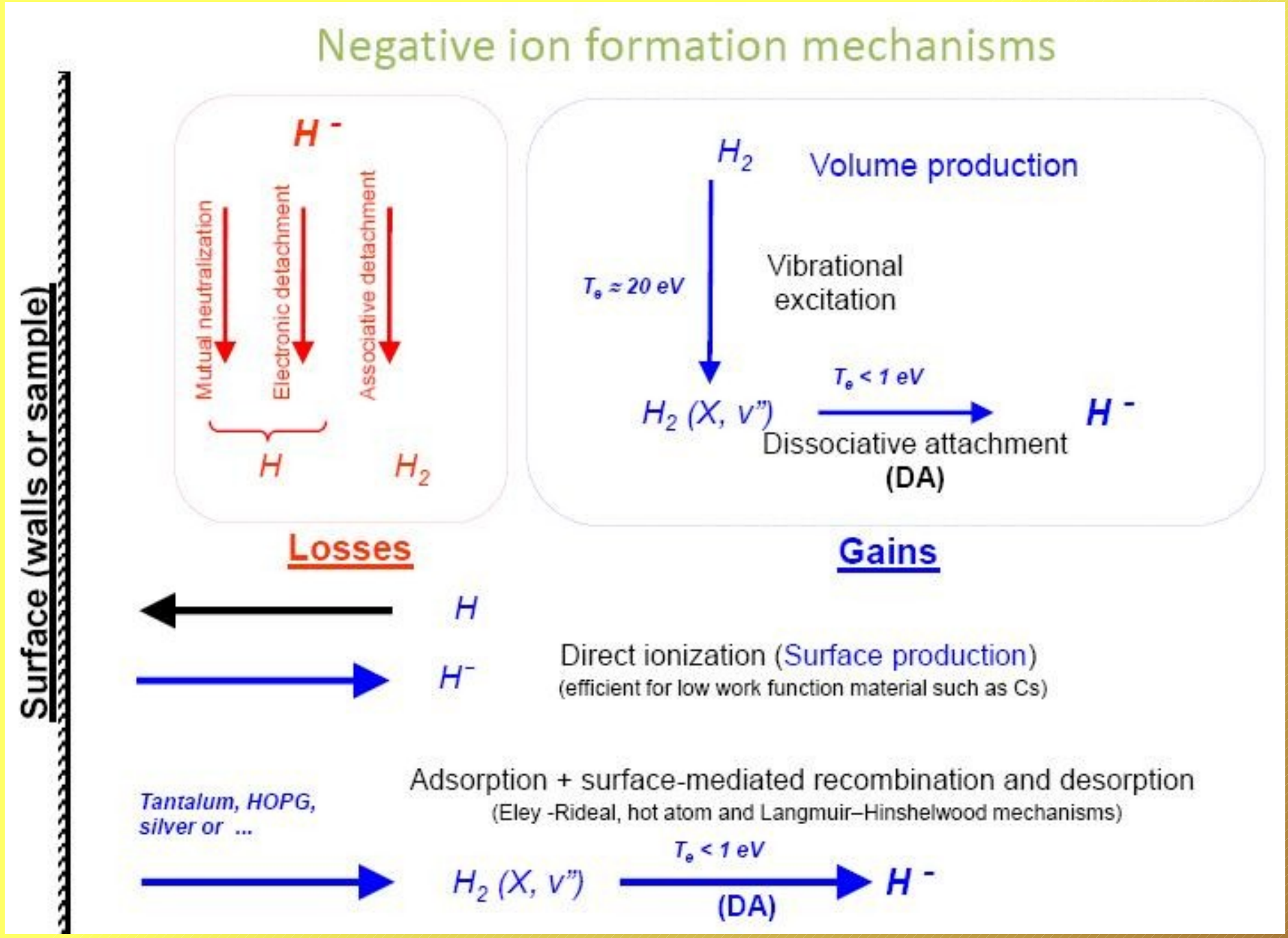
Outline

- General considerations
- Computational details
- H adsorption on Ag(111)
- H+H/Ag(111) interaction
- H adsorption on Ag(100)
- H insertion into the bulk through Ag(100)
- H+H/Ag(100) interaction
- Conclusion & Outlook

Why studying Hydrogen/surface interactions ?

- Understanding of heterogeneous catalysis mechanisms
- Formation of molecular hydrogen in interstellar clouds
- Plasma/wall interactions in tokamaks
- Negative ion source *e.g.* for fusion plasma heating

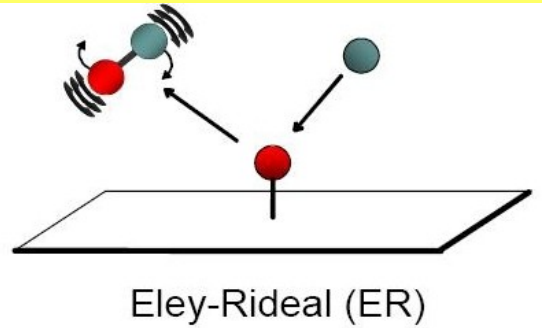
Negative ions with a plasma source



Collisional recombination in the single adsorbate regime

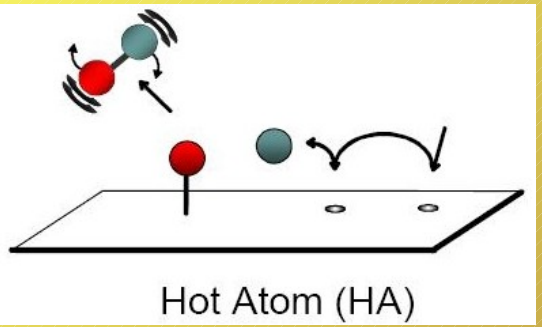
Eley-Rideal (ER)

- Generally exothermic
- Vibrationally excited molecules



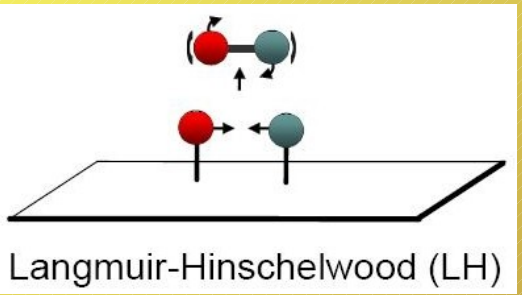
Hot Atom

- Multiple impact at the surface



Diffusion Langmuir-Hinshelwood (LH)

- Generally thermoneutral

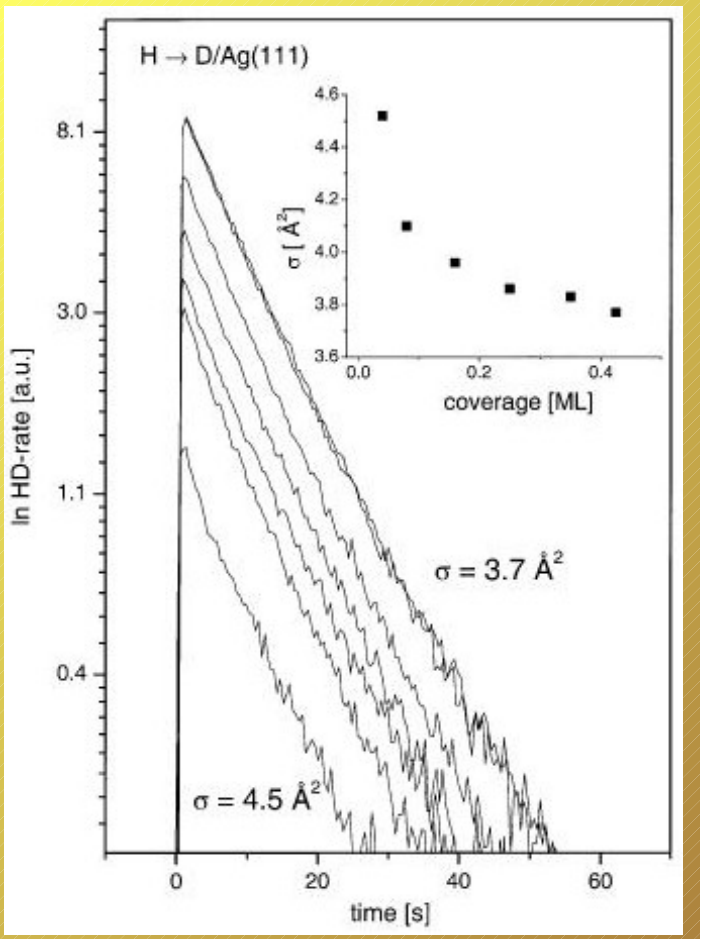


Why studying silver ?

• The weakest H chemisorption energy among transition metals → potential for highly vibrationally excited H_2 molecules (and thus for producing negative ions)

• Experiments of Kolovos-Vellianitis and Küppers [Surf. Sci., **548** (2004) 67]

- → subsurface population with strong isotopic (D vs H) effects for Ag(100)
- → large HD ER-like cross-section particularly for Ag(111) (σ=3.7 Å^2)

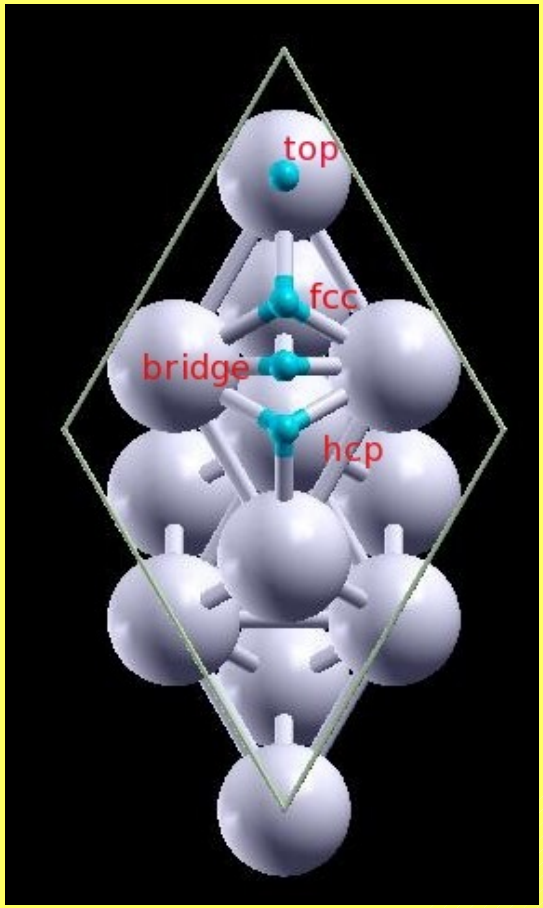


HD kinetics measured during admitting a H flux at D covered Ag(100) surfaces

Computational details

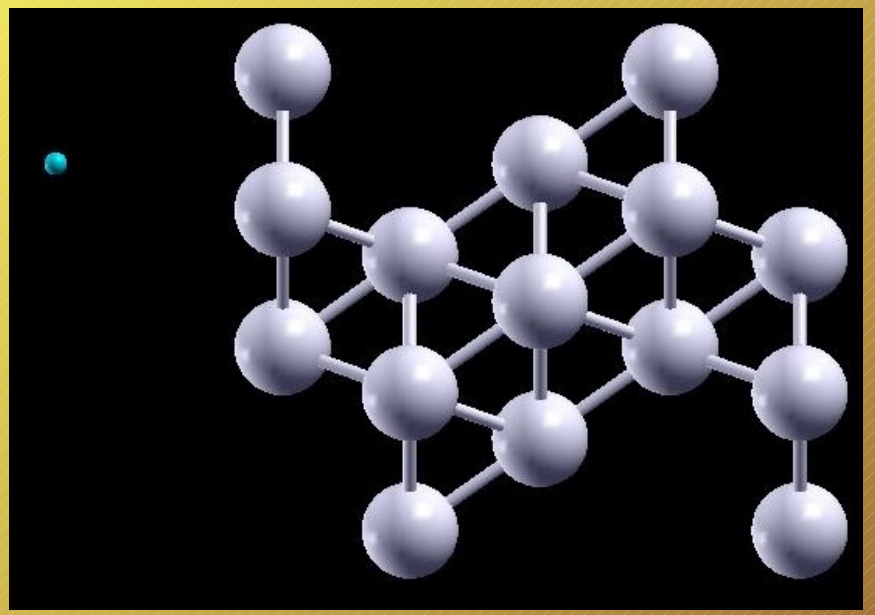
- VASP [http://cms.mpi.univie.ac.at/vasp/] wave-plane calculations with DFT PBE functional and pseudopotentials
- 2X2 supercell defining a 1/4 monolayers coverage
- 5 silver layers
- Automatic K-points mesh generation
- Spin polarisation
- Silver atoms relaxation

H adsorption on Ag(111) (1)



Four high-symmetry adsorption sites:

- on top (t)
- twofold bridge (b)
- threefold hollow fcc (fcc)
- threefold hollow hcp (hcp)

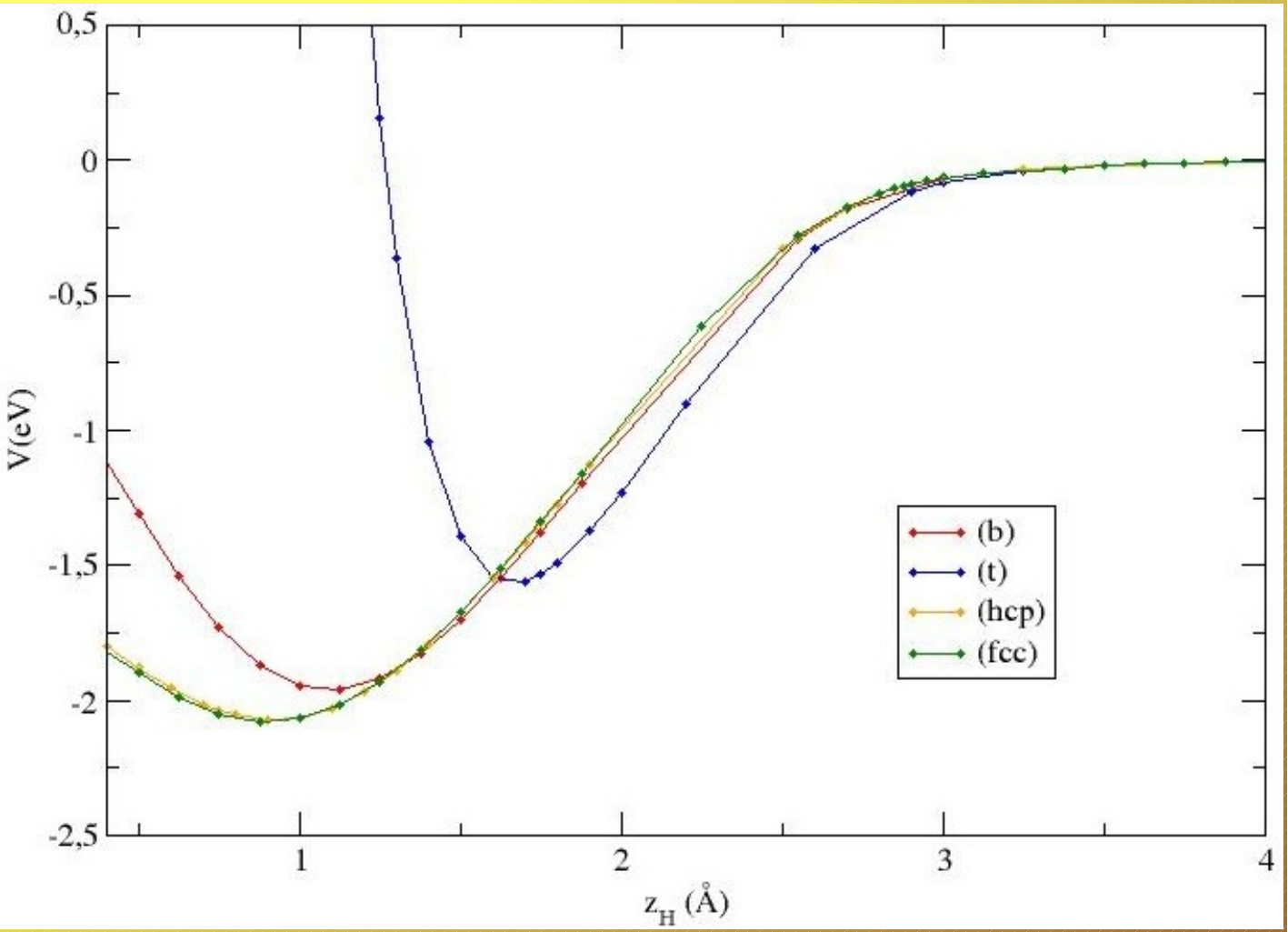


H adsorption on Ag(111) (2)

	fcc	hcp	t	b
$E_{H/Ag}$(eV)	-2.10	-2.09	-1.57	-1.98
d_H (Å)	1.923	1.928	1.664	1.830

- fcc & hcp most favourable & energetically close adsorption sites

- Minimum barrier to H diffusion ≈ 120 meV



H/Ag(111) interaction: modified Morse potential fit

Morse potential modified to better account for the attractive branch of the H/surface interaction

$$V_i(z) = D_i\left(e^{-2\alpha_i(z-z_i^0)} - 2f(z)e^{-\alpha_i(z-z_i^0)}\right)$$

$$f(z) = \exp\left(\frac{\tilde{\alpha}_i(z-z_i^0)}{1+e^{-\beta_i\alpha_i(z-z_i^1)}}\right)$$

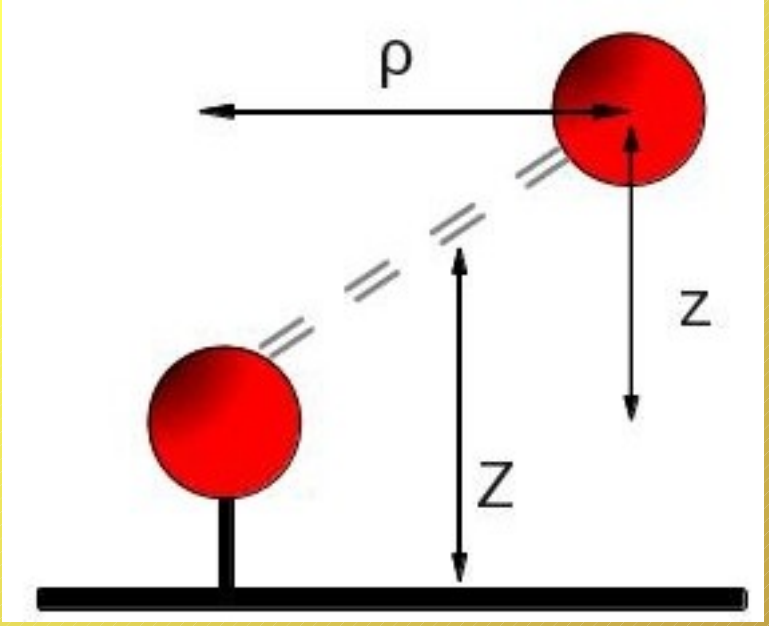
	fcc	hcp	t	b
D_i (eV)	2.066	2.055	1.562	1.912
α_i (Å^{-1})	0.622	0.588	1.764	0.634
z_i^0 (Å)	0.944	0.962	1.658	1.246
$\tilde{\alpha}_i$ (Å^{-1})	0.870	0.859	0.805	0.915
z_i^1 (Å)	2.194	2.152	2.532	2.028
β_i	4.000	4.000	4.000	4.000

Root Mean Square (RMS) error < 1meV

H+H/Ag(111) interaction (1)

$$V(\vec{R},\vec{r}) = V(X,Y,Z,r,\theta,\phi) \rightarrow V(Z,r,\theta) \rightarrow V(Z,\rho,z)$$

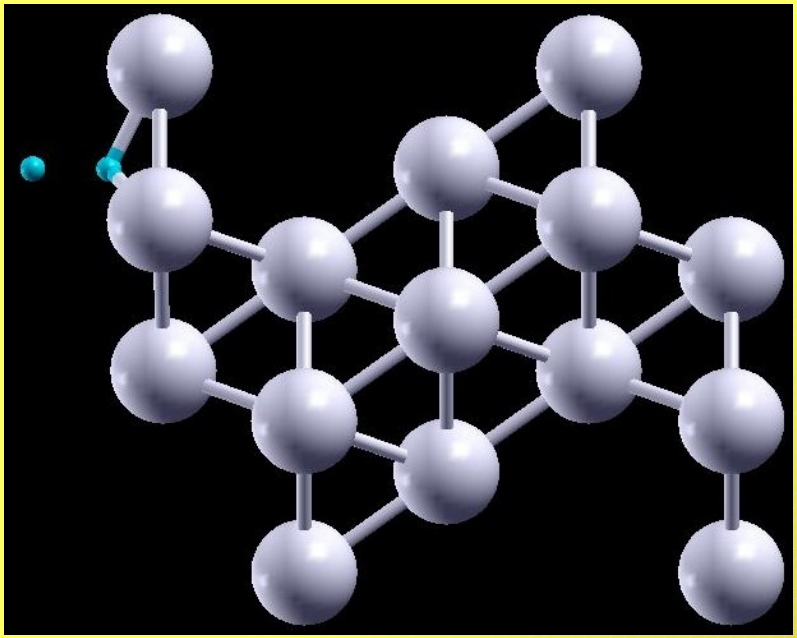
Flat surface approximation



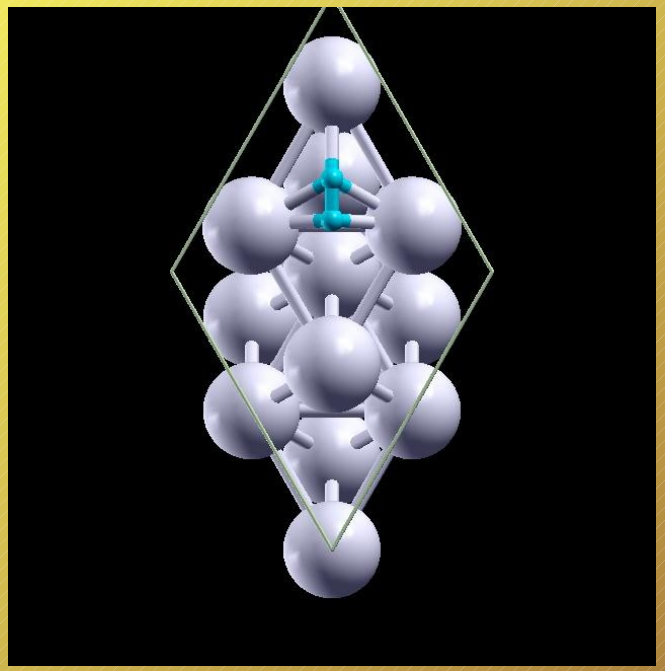
H+H/Ag(111) interaction (2)

At least two distinct ρ configurations need to be considered
in order to generate the potential energy surface

- Collinear case (ρ=0 Å)

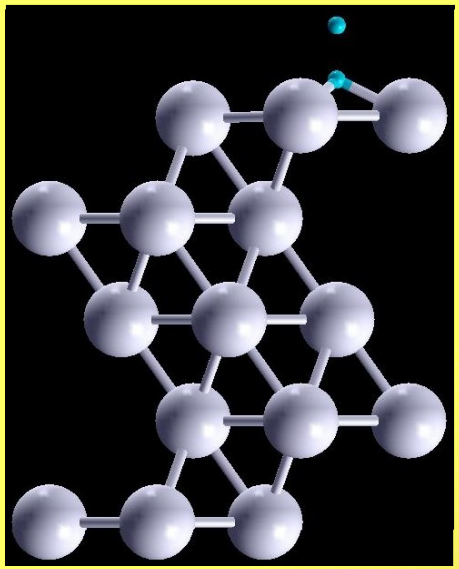


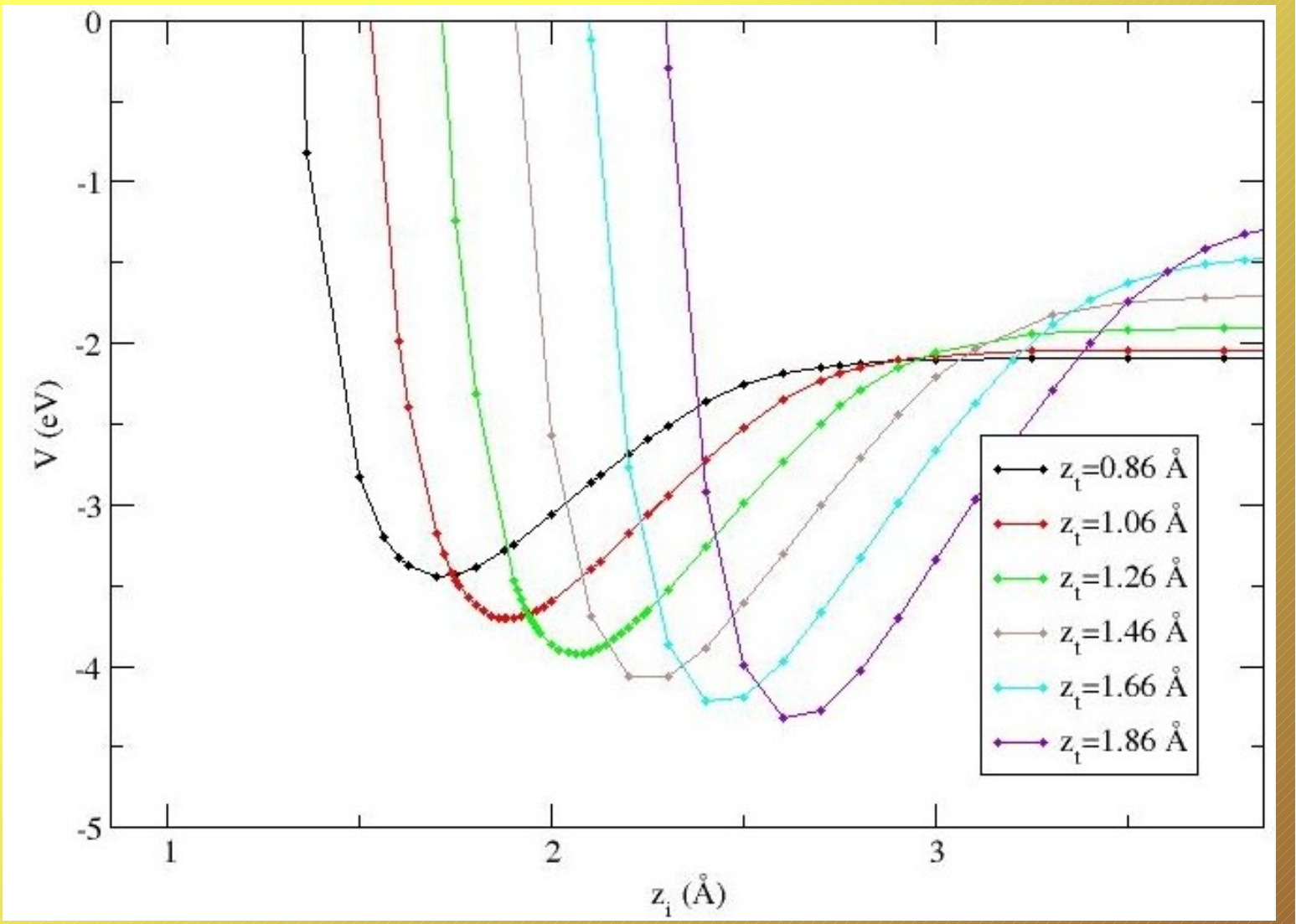
- Quasi-collinear case (ρ=0.75 Å)



H+H/Ag(111) interaction: collinear case

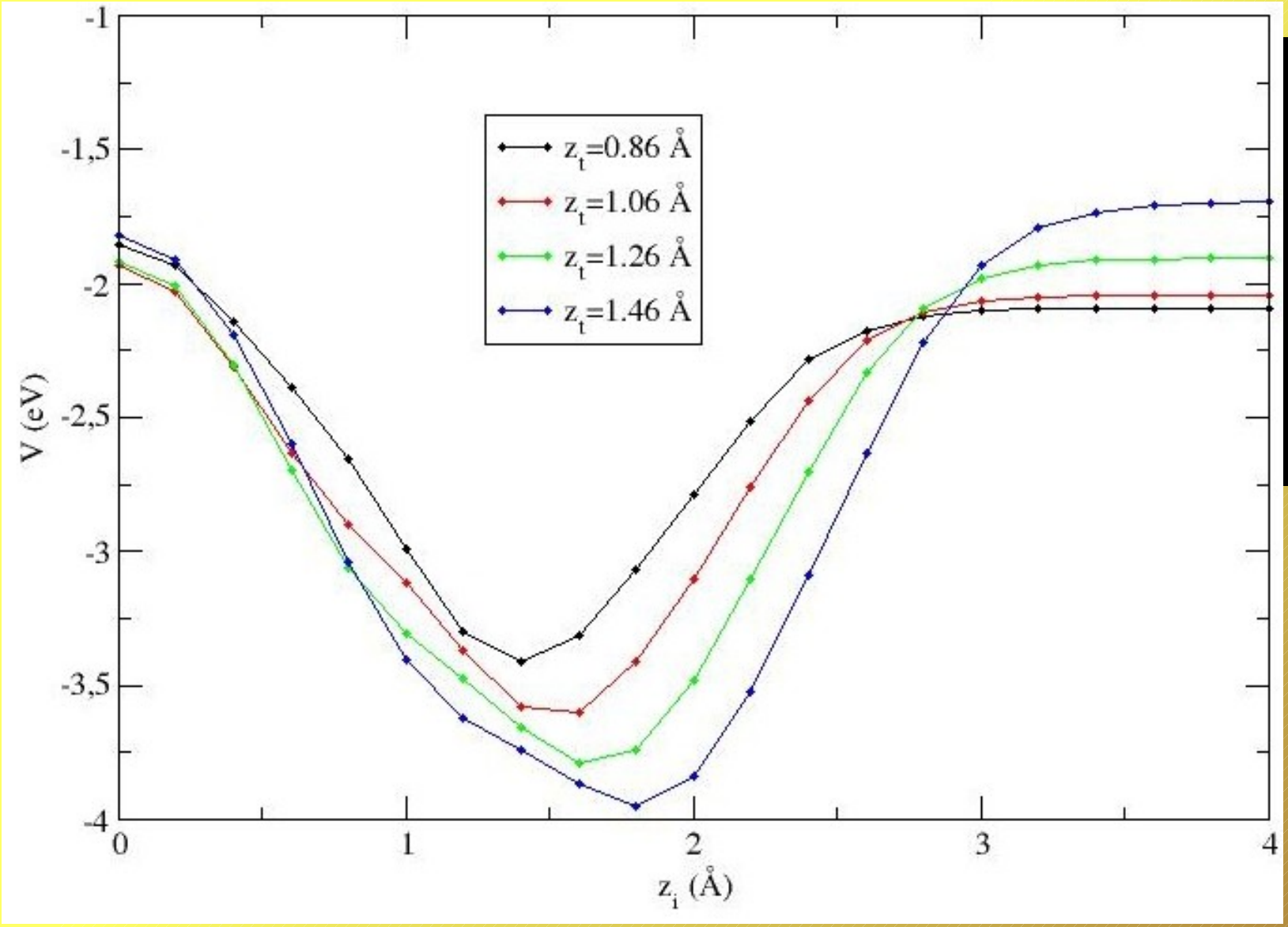
- Target H initially located over the fcc site, at different heights
- Incident H impinging directly over the target H

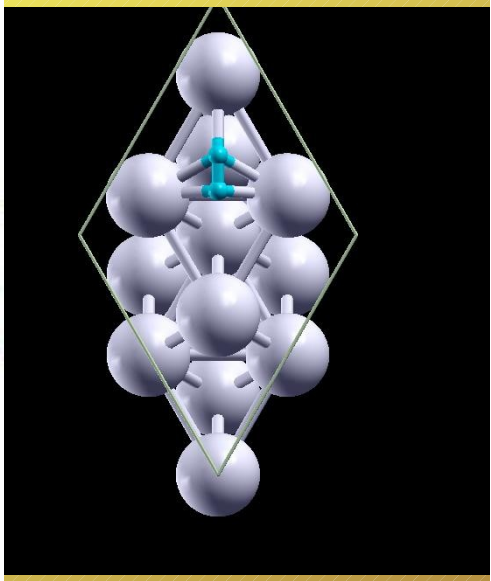




H+H/Ag(111) interaction: quasi-collinear case

- Target H initially located over the fcc site
- Incident H located at ρ=0.75 Å





H+H/Ag(111) interaction: modified LEPS[1] potential

$$V(\rho, z, Z) = U_i(z_i) + U_t(z_t) + U_m(r) + \sqrt{Q_m(r)^2 + (Q_i(z_i) + Q_t(z_t))^2 - (Q_t(z_t) + Q_i(z_i))\,Q_m(r)}$$

$$\begin{cases} U_i(r) = \dfrac{D_i}{4(1+\Delta_i)}\left[(3+\Delta_i)e^{-2(\alpha_i(r-r_i^0))} - (2+6\Delta_i)f(r)e^{-2\alpha_i(r-r_i^0)}\right] \\ Q_i(r) = \dfrac{D_i}{4(1+\Delta_i)}\left[(1+3\Delta_i)e^{-2(\alpha_i(r-r_i^0))} - (6+2\Delta_i)f(r)e^{-2\alpha_i(r-r_i^0)}\right] \end{cases}$$

- t stands for the target (initially chemisorbed) hydrogen
- i for the incident atom
- m for the hydrogen molecule
- $\Delta_i, \Delta_t, \Delta_m$ are the Sato (reactivity) parameters
- 21 parameters

[1]: Sha, X. and Jackson, B. and Lemoine, D., J. Chem. Phys., **116** (2002) 7158

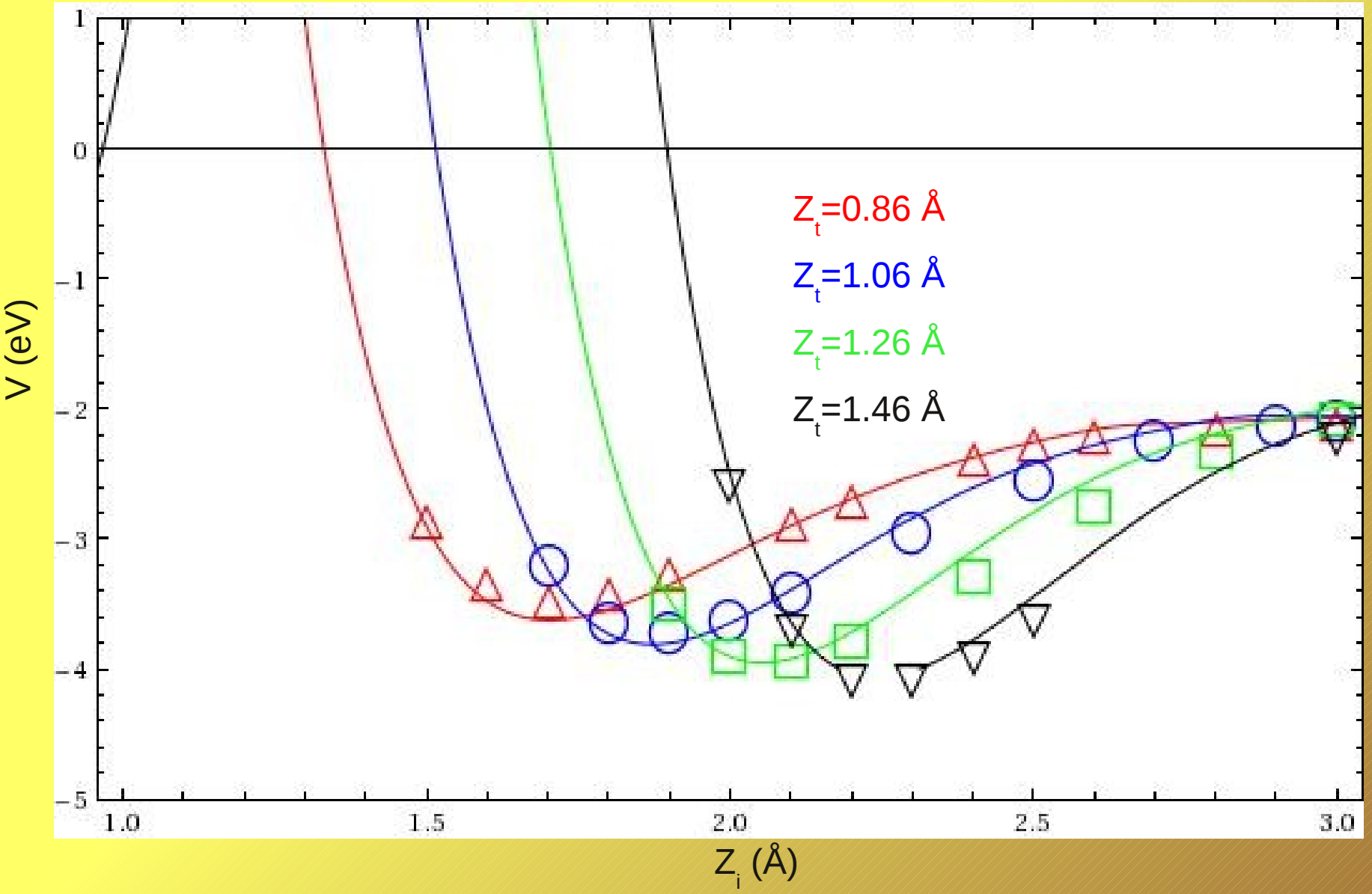
H+H/Ag(111) interaction: Modified LEPS fit

- 70 points (collinear & quasi-collinear) fit
- Incident H interaction averaged over four impact sites (flat surface approximation)
- Target H initially chemisorbed over the fcc site
- Fixed molecular Morse parameters
- Target and incident parameters allowed to slightly change (up to 6%)

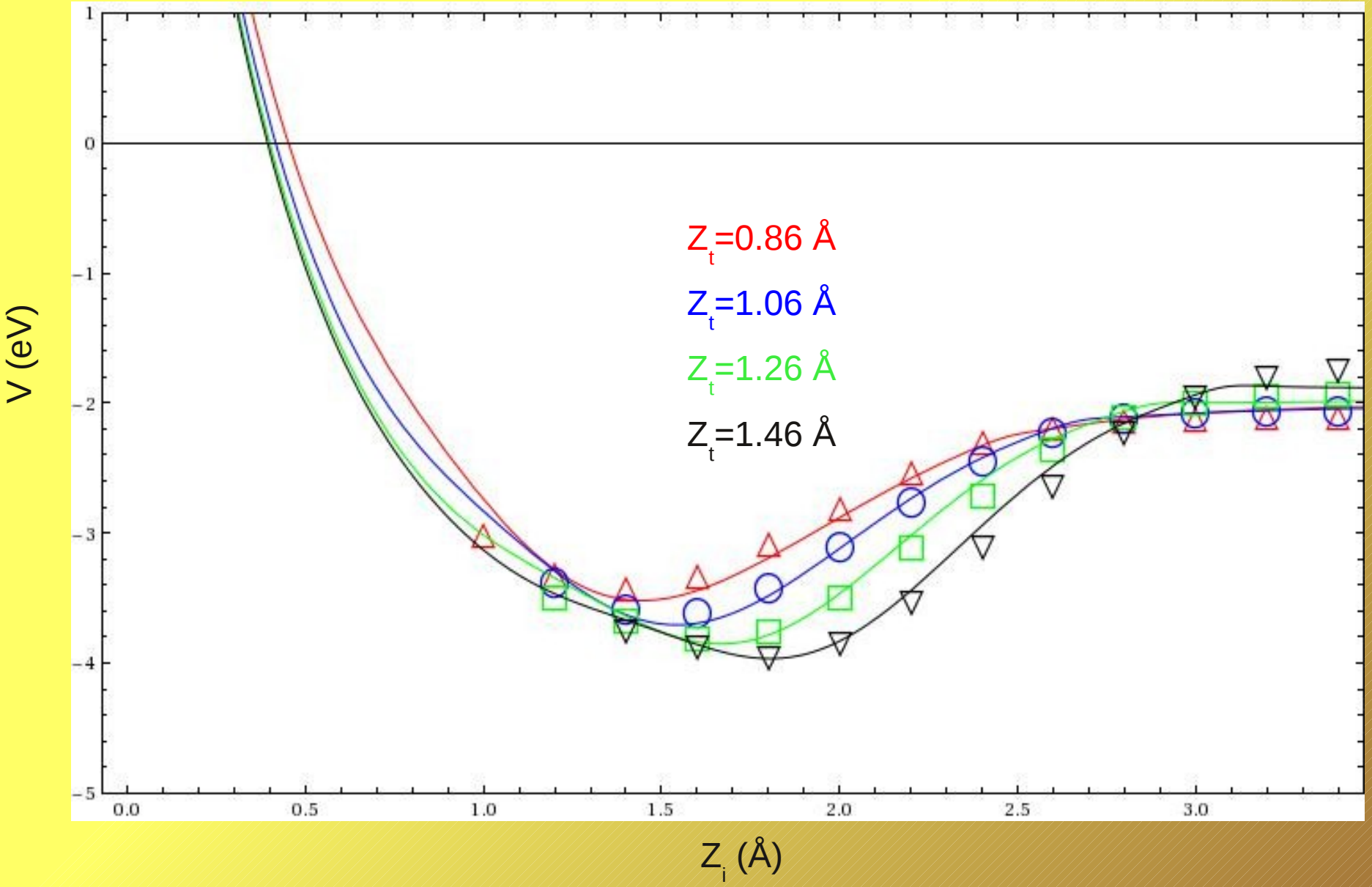
	D_i (eV)	r_i^0 (Å)	α_i (Å^{-1})	$\tilde{\alpha}_i$ (Å^{-1})	r_i^1 (Å)	β_i	Δ_i
H_i	1.683	1.262	0.992	0.884	2.320	3.050	-0.057
H_t	2.018	1.001	0.659	0.819	2.326	9.518	0.223
H_2	4.510	0.755	2.030	1.036	1.819	9.464	-0.056

RMS error of 82 meV

H+H/Ag(111) interaction: collinear fit



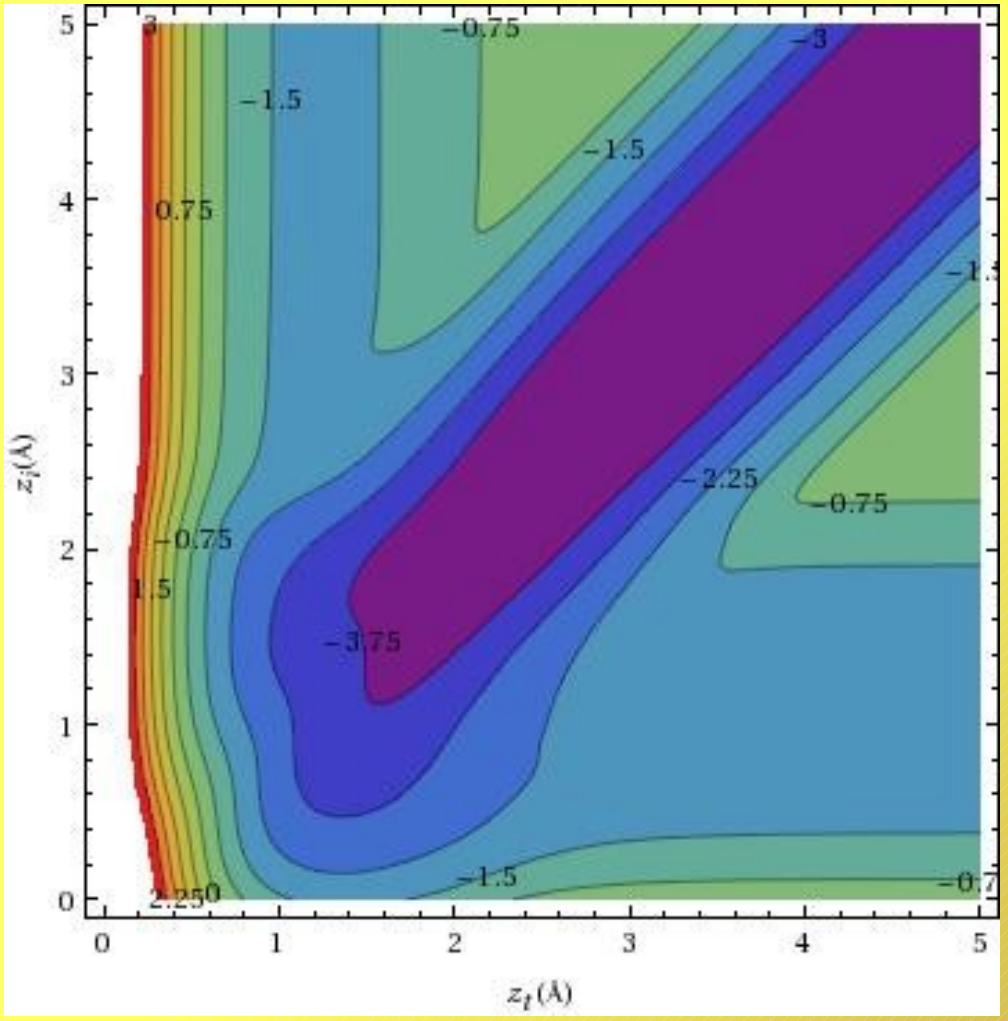
H+H/Ag(111) interaction: quasi-collinear fit



H+H/Ag(111) interaction: some contour plots for fun

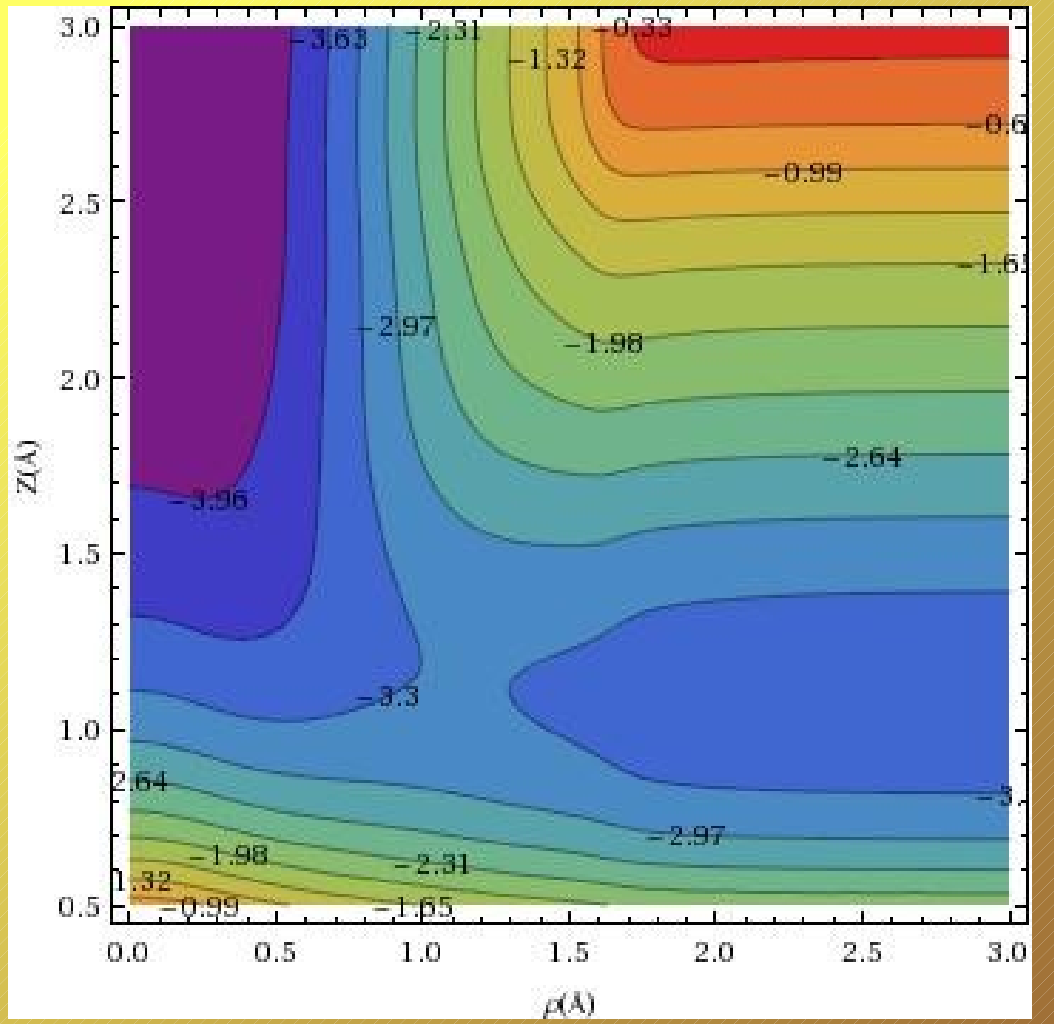
$V(\rho=0.75,z_i,z_t)$

ER “helicopter” product channel



$V(\rho,z=0.75,Z)$

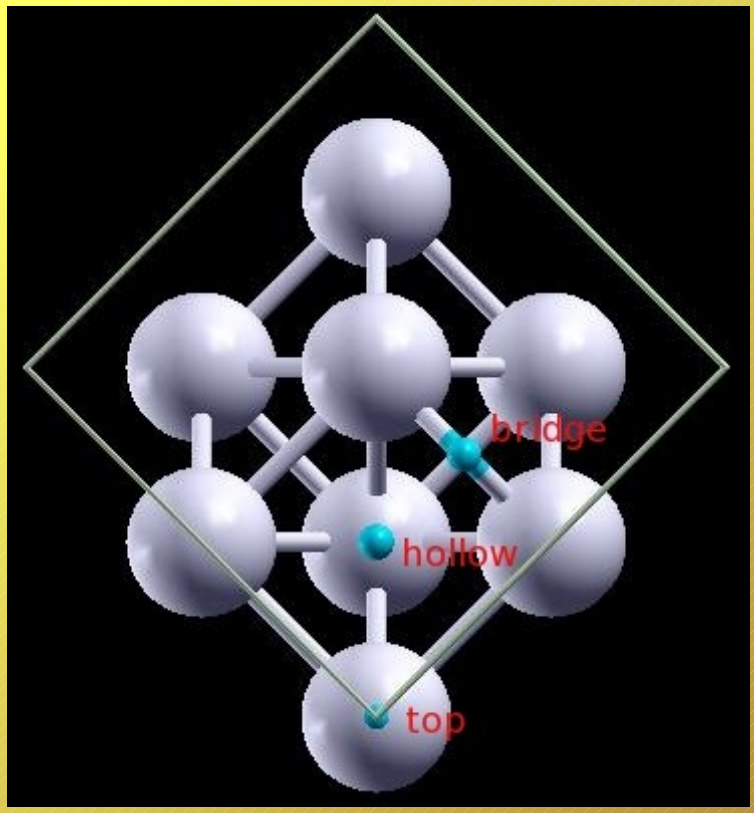
HA J=0 product channel



H adsorption on Ag(100) (1)

Three high-symmetry adsorption sites:

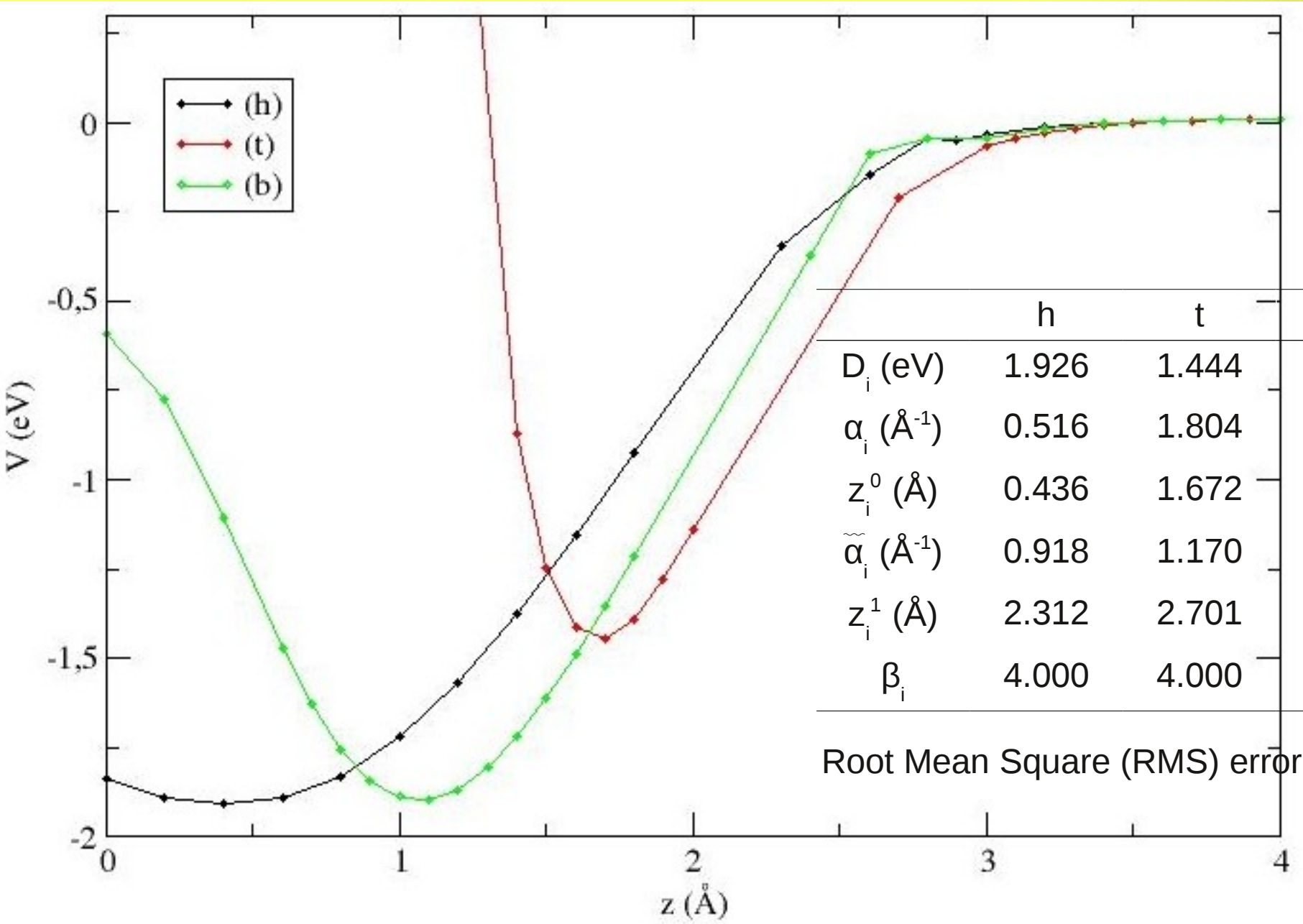
- on top (t)
- twofold bridge (b)
- fourfold hollow (h)



	h	t	b
$E_{H/Ag}$(eV)	-1.94	-1.46	-1.92
d_H (Å)	2.113	1.675	1.819

- hollow site: most favourable adsorption site
- Minimum barrier to H diffusion: 20 meV

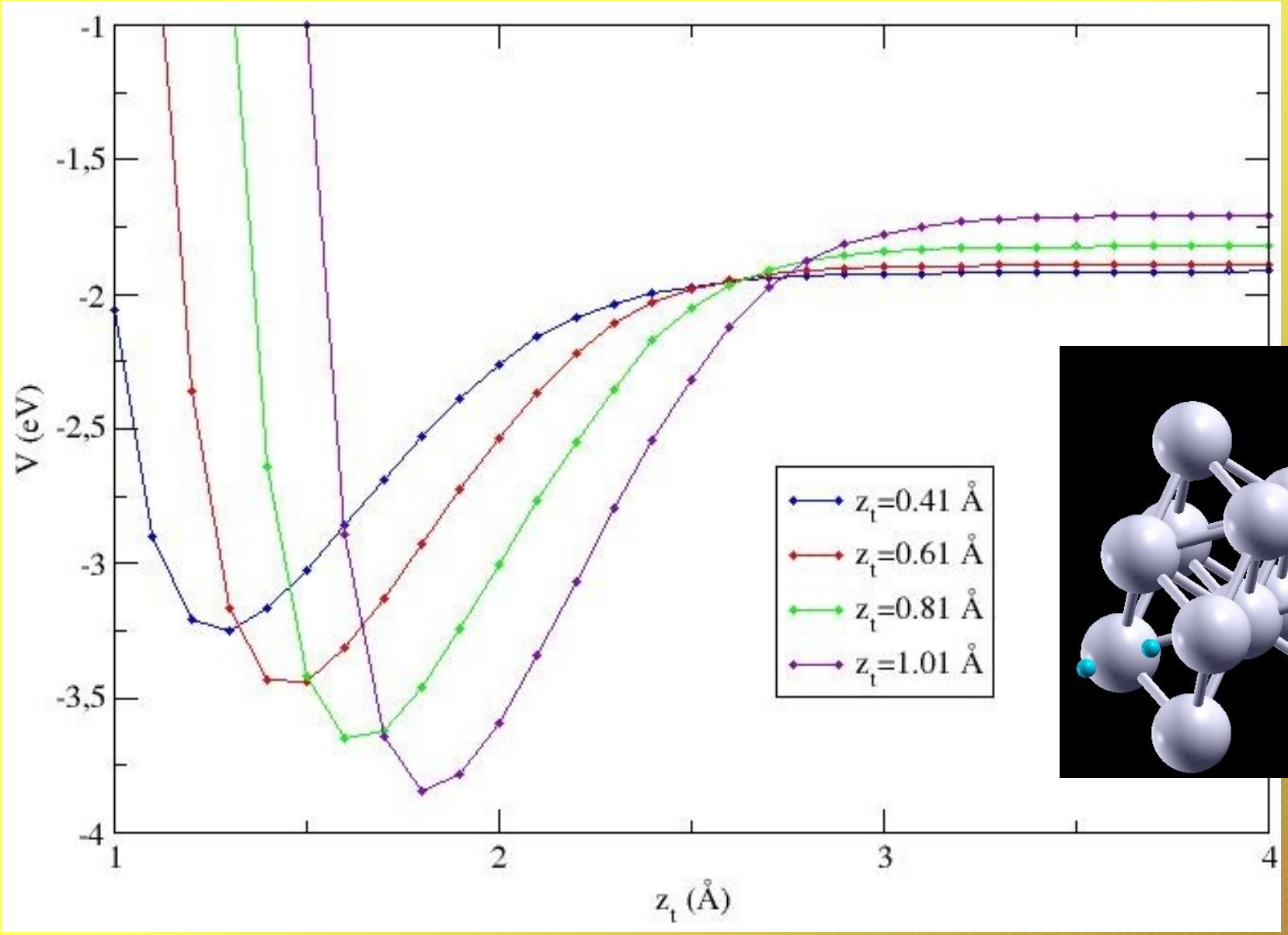
H adsorption on Ag(100) (2)

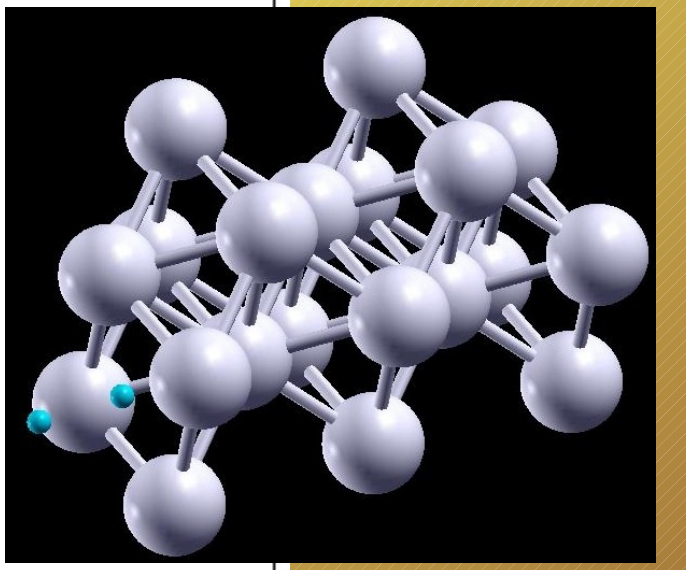


	h	t	b
D_i (eV)	1.926	1.444	1.881
α_i (Å^{-1})	0.516	1.804	0.862
z_i^0 (Å)	0.436	1.672	1.048
$\tilde{\alpha}_i$ (Å^{-1})	0.918	1.170	1.069
z_i^1 (Å)	2.312	2.701	2.363
β_i	4.000	4.000	4.000

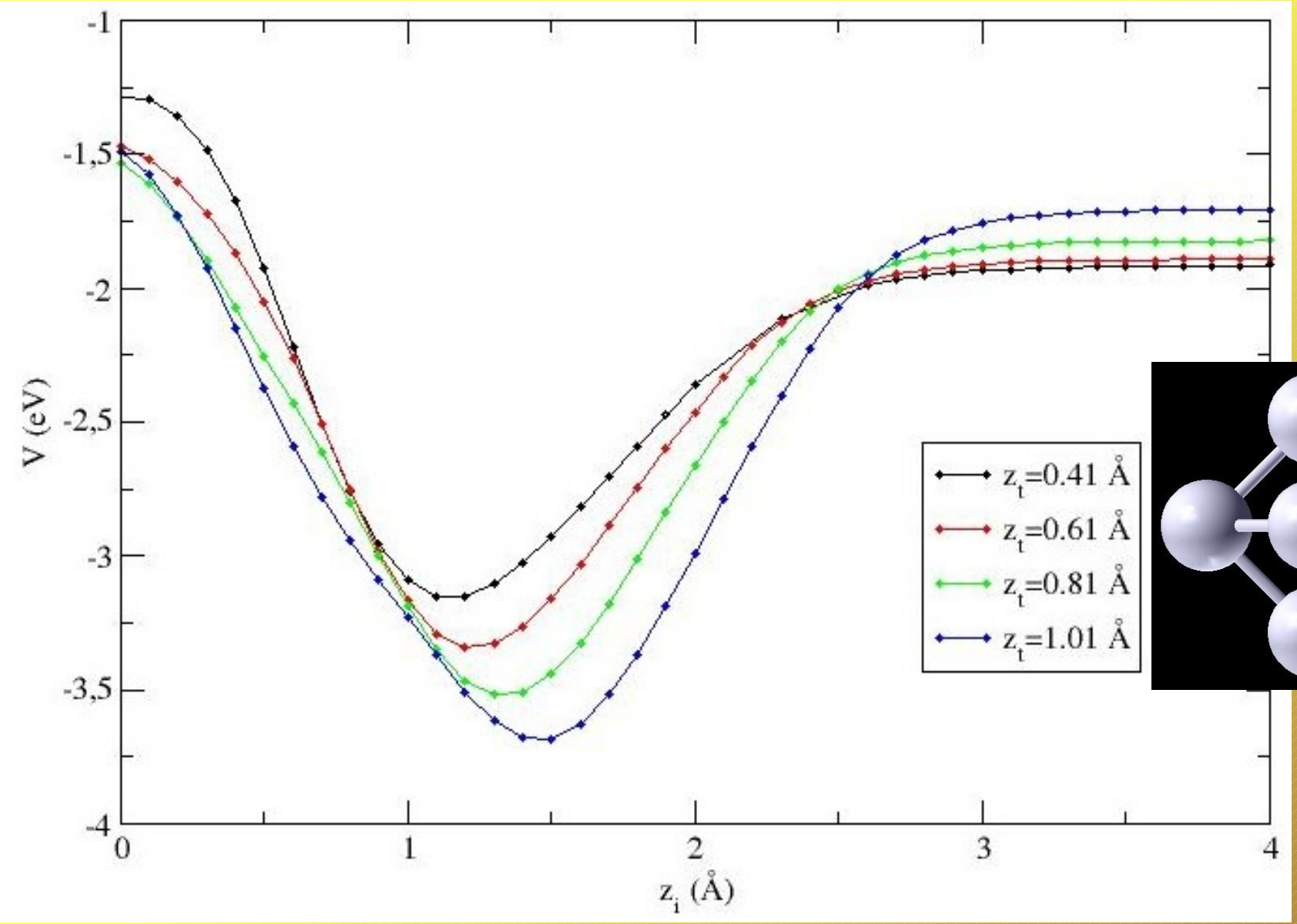
Root Mean Square (RMS) error < 1meV

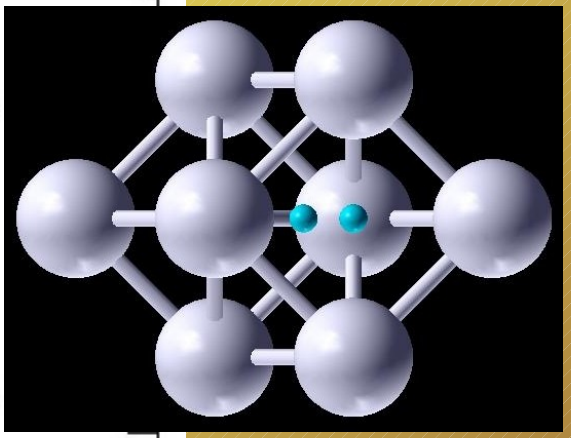
H+H/Ag(100) interaction: collinear case





H+H/Ag(100) interaction: quasi-collinear case





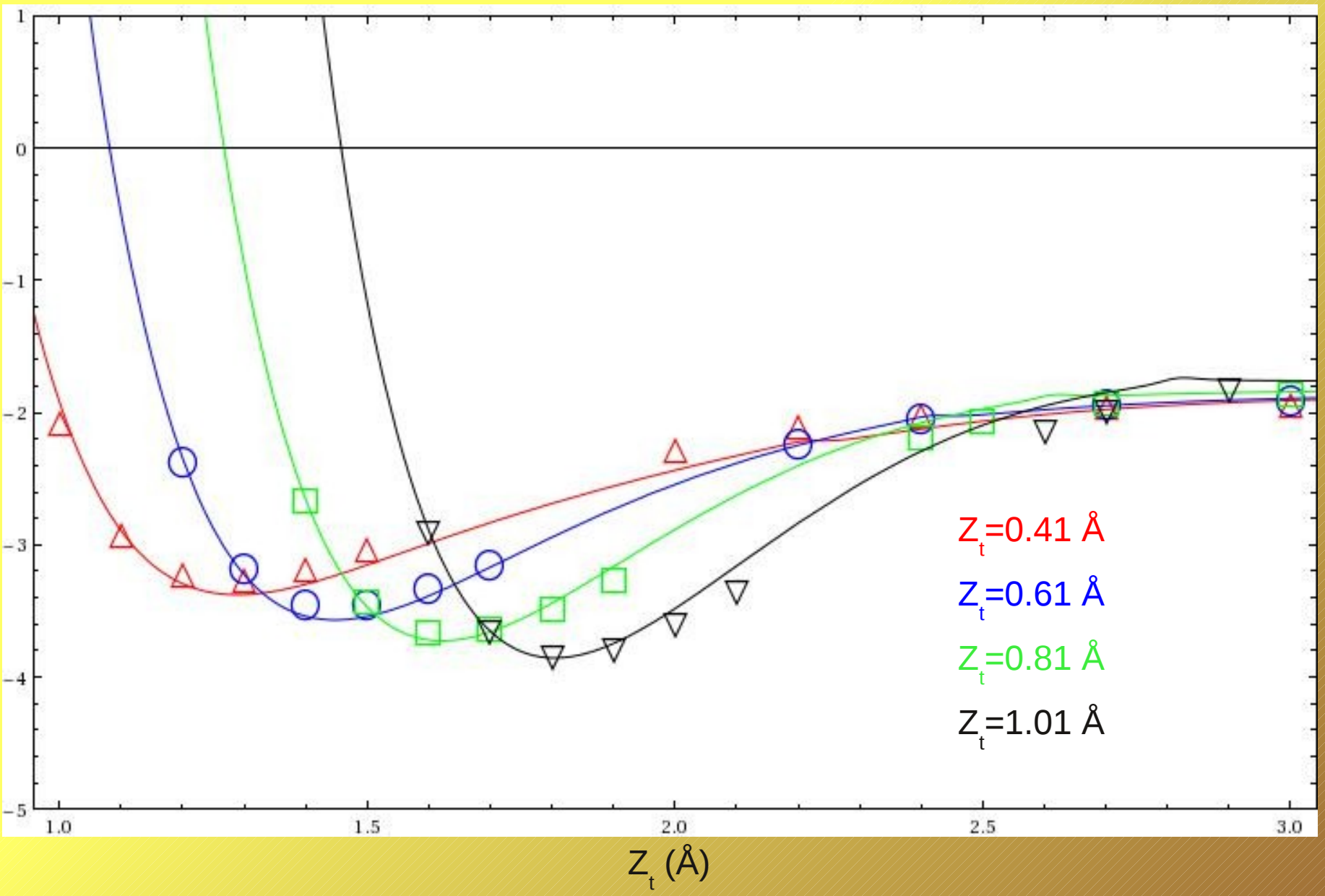
H+H/Ag(100) interaction: Modified LEPS fit

- 100 points (collinear & quasi-collinear) fit
- Incident H interaction averaged over three impact sites (flat surface approximation)
- Target H initially chemisorbed over the hollow site
- Fixed molecular Morse parameters
- Target and incident parameters allowed to slightly change (up to 6%)

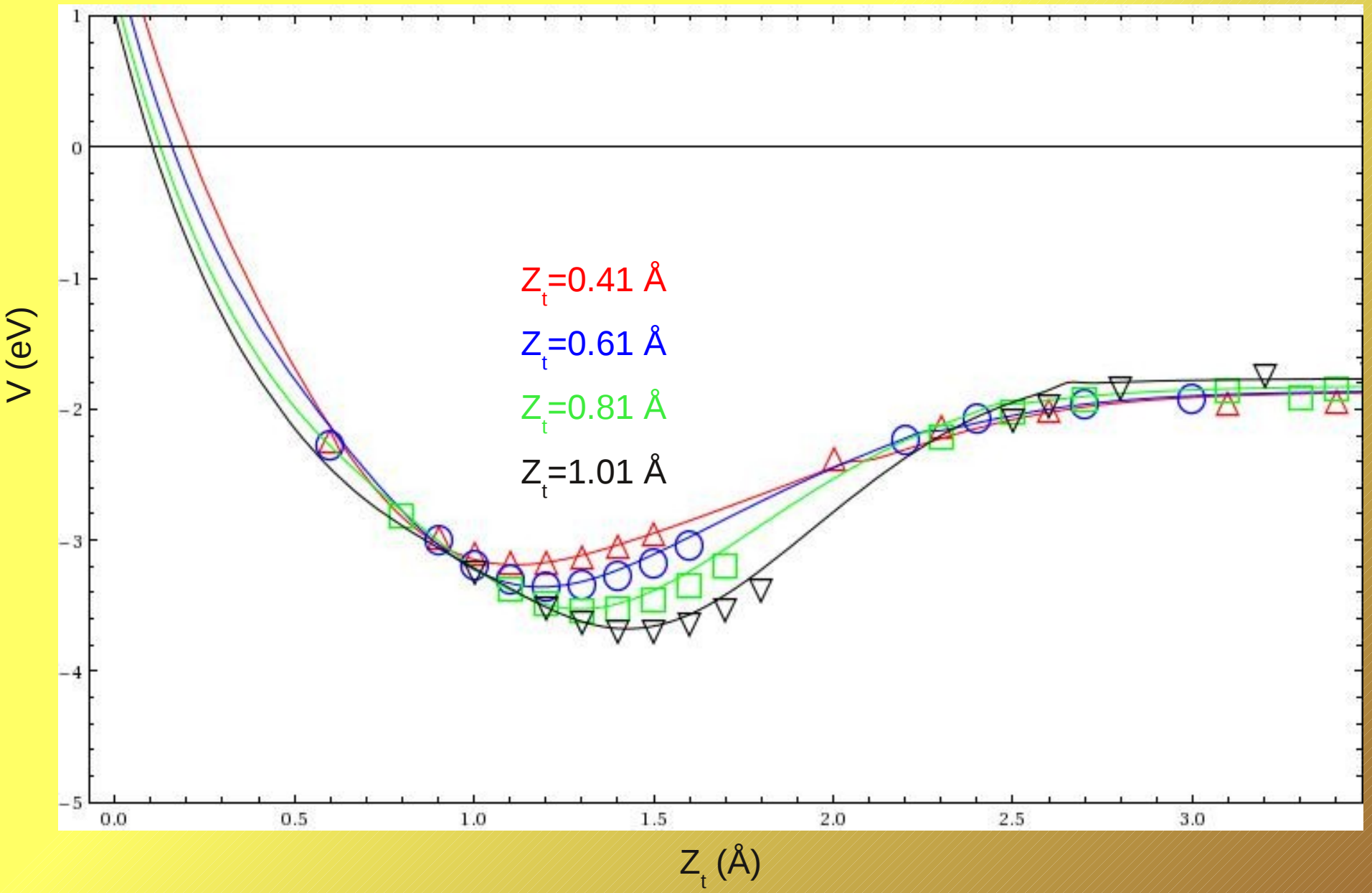
	D_i (eV)	r_i^0 (Å)	α_i (Å^{-1})	$\tilde{\alpha}_i$ (Å^{-1})	r_i^1 (Å)	β_i	Δ_i
H_i	1.658	0.977	0.940	0.983	2.416	3.023	-0.089
H_t	1.863	0.466	0.482	0.918	2.349	15.178	0.170
H_2	4.510	0.755	2.030	1.036	1.819	25.550	-0.119

RMS error of 89 meV

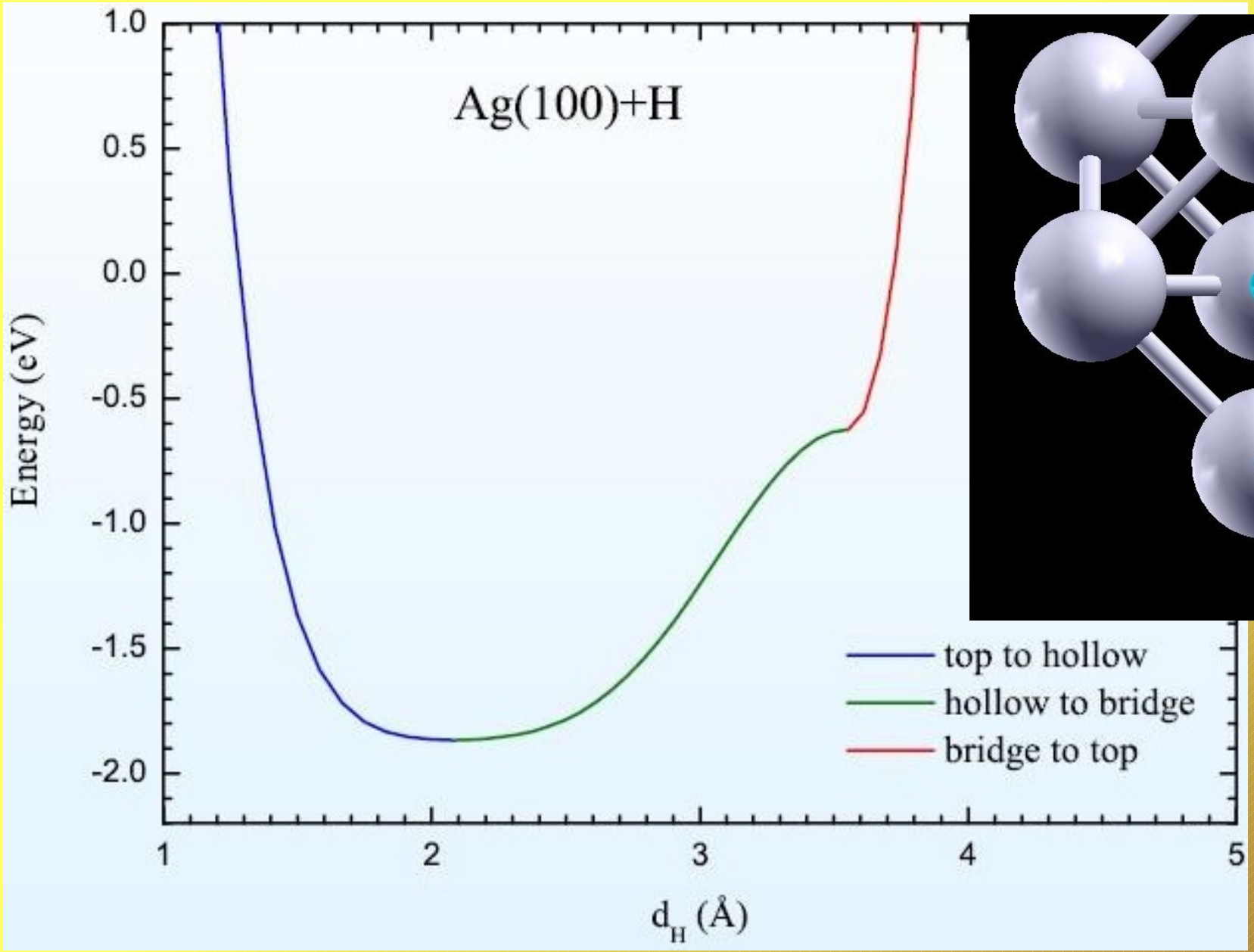
H+H/Ag(100) interaction: collinear fit

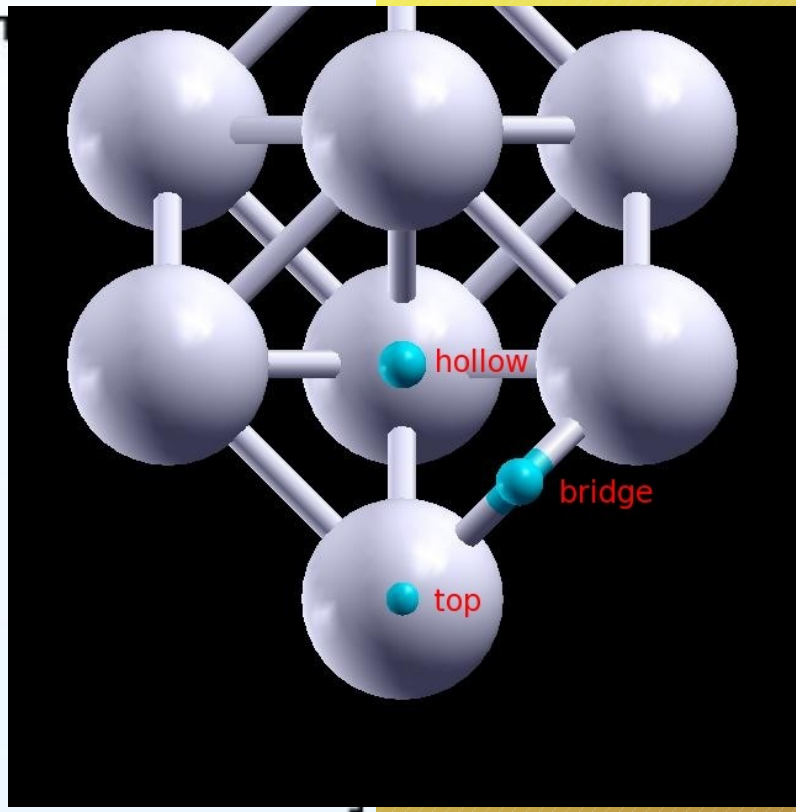


H+H/Ag(100) interaction: quasi-collinear fit



Ag(100): H in the surface plane





Ag(100) subsurface H population

TDS experiments of Kolovos-Vellianitis and Küppers, Surf. Sci., **548** (2004) 67

- Surface peaks at 140-150 K
- Subsurface H population increases with coverage
- Subsurface peaks at 100-120 K
- Strong isotopic effects:
  - Subsurface peak in addition to surface peak for D
  - Subsurface peak at the expense of surface peak for H
    → diffuse (2x2) reconstruction evidenced by LEED

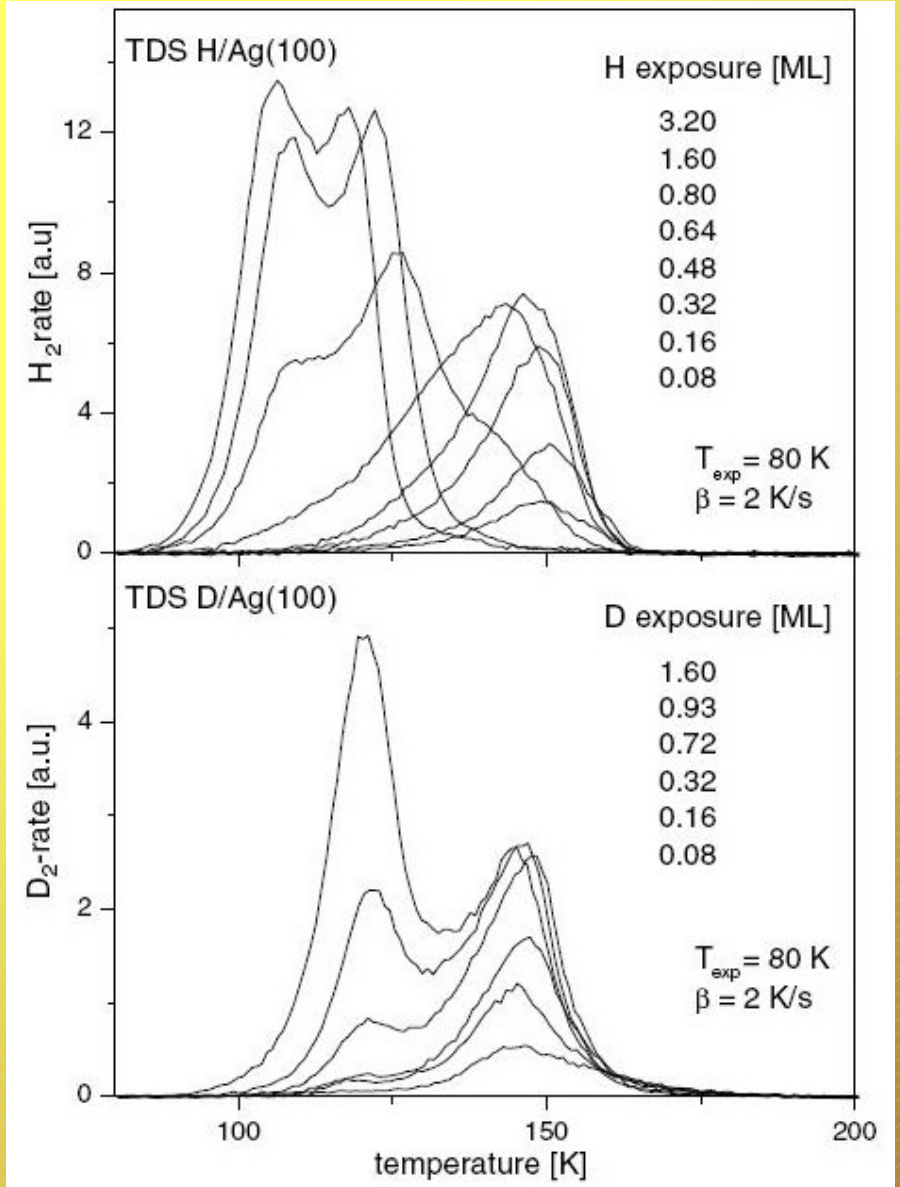
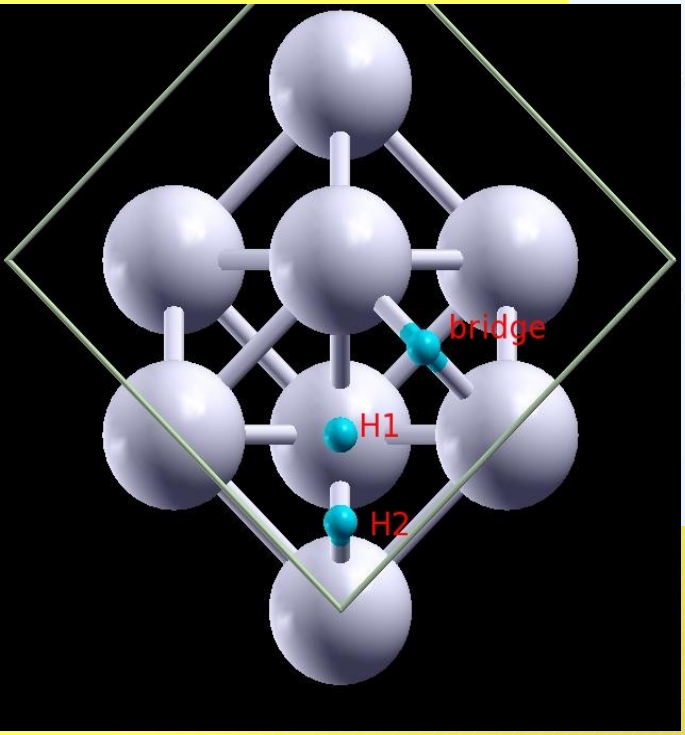
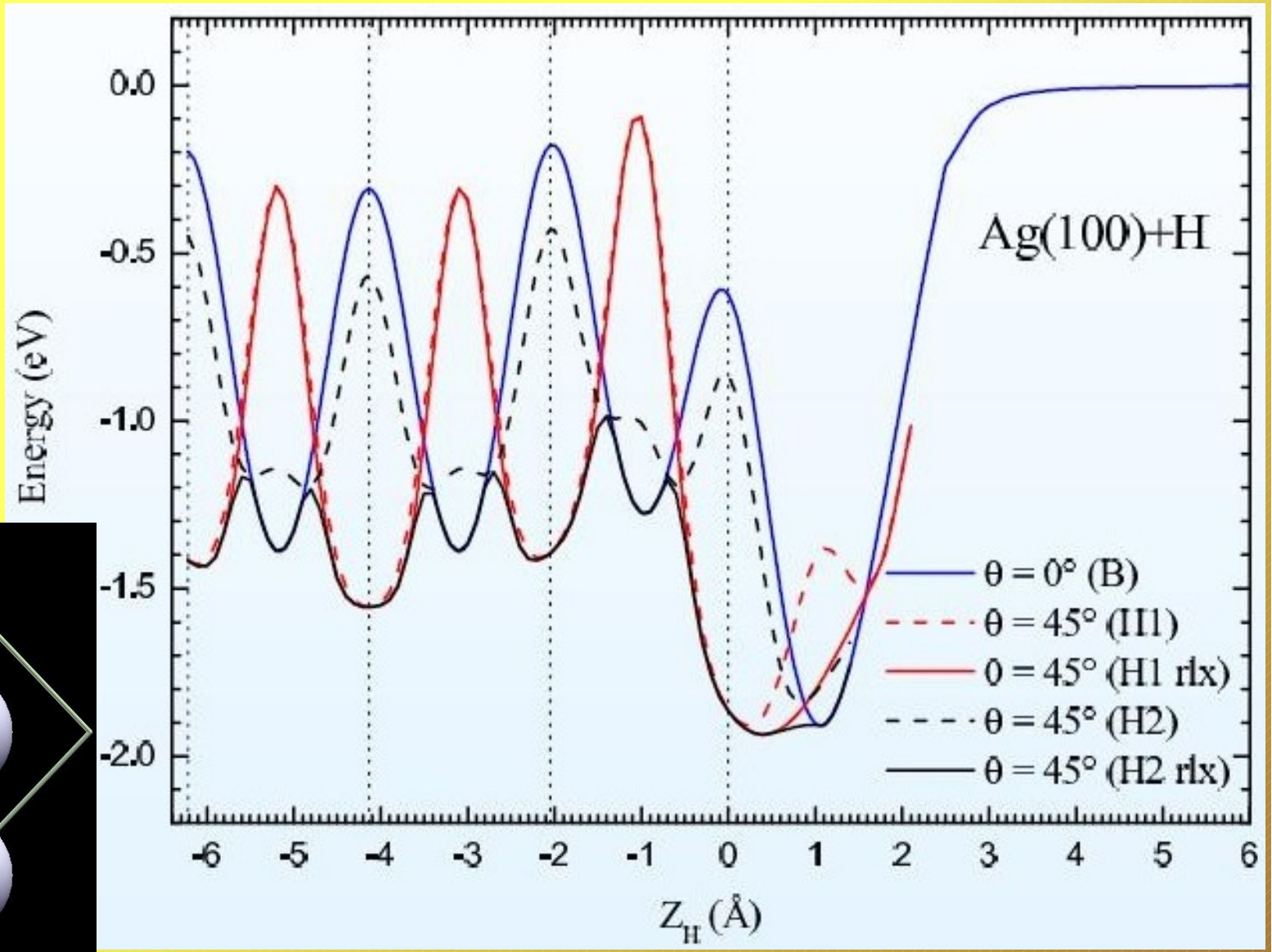


Fig. 1. Thermal desorption spectra of hydrogen and deuterium measured after admitting increasing fluences of H or D to clean Ag(1 0 0) surfaces.

H insertion into the bulk through Ag(100)





Conclusion

- Potential energy surface for H+H/Ag(111)
- Potential energy surface for H+H/Ag(100)
- Facile H insertion into the bulk for Ag(100)

Outlook

- ER dynamics on Ag(111)
- ER dynamics on Ag(100)
- Modelling of TDS spectra

Thank you for your attention !