Universiteit Leiden

7D Quantum Scattering Calculations for H2@Cu(111)

Matteo Bonfanti

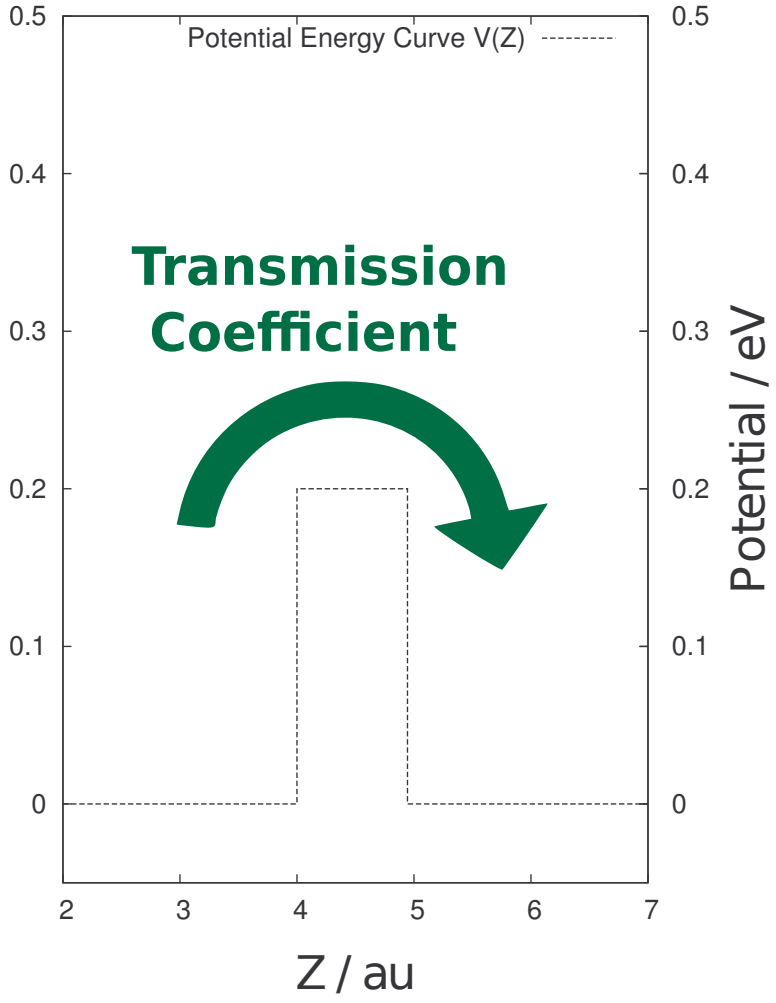
Theoretical Chemistry Group
Leiden Institute of Chemistry

Thursday November 22th, 2012

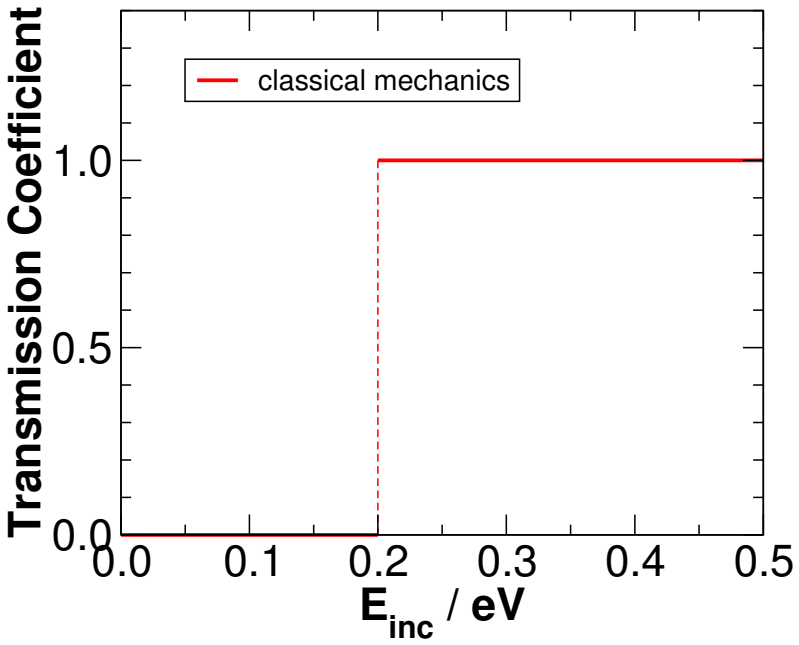
Outline

Outline

The Square Potential Barrier



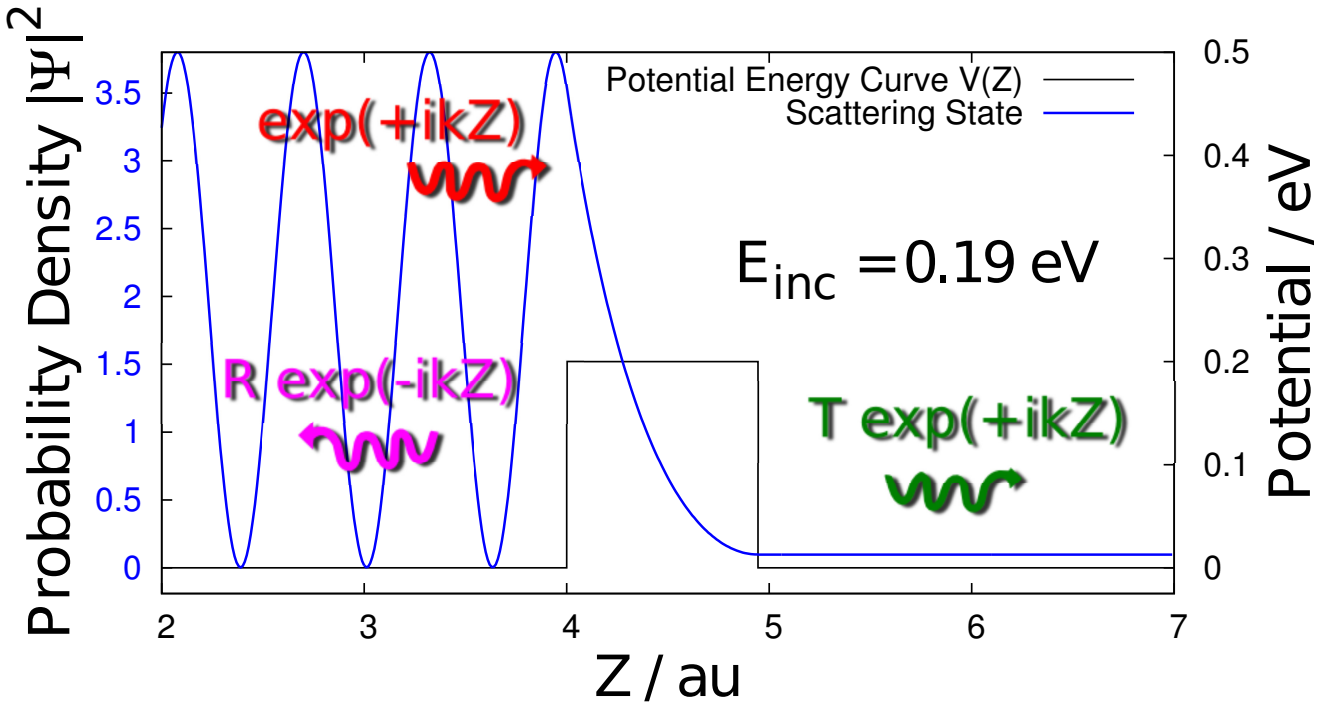
- **particle**: mass 1.0 AMU
  given momentum p
- **square barrier**: $E_{barrier}$ = 0.2 eV
  L = 0.5 Å
- Transmission Coefficient:
  probability to overcome the barrier



Time Independent Quantum Scattering

Scattering States $\psi^+(x, E)$

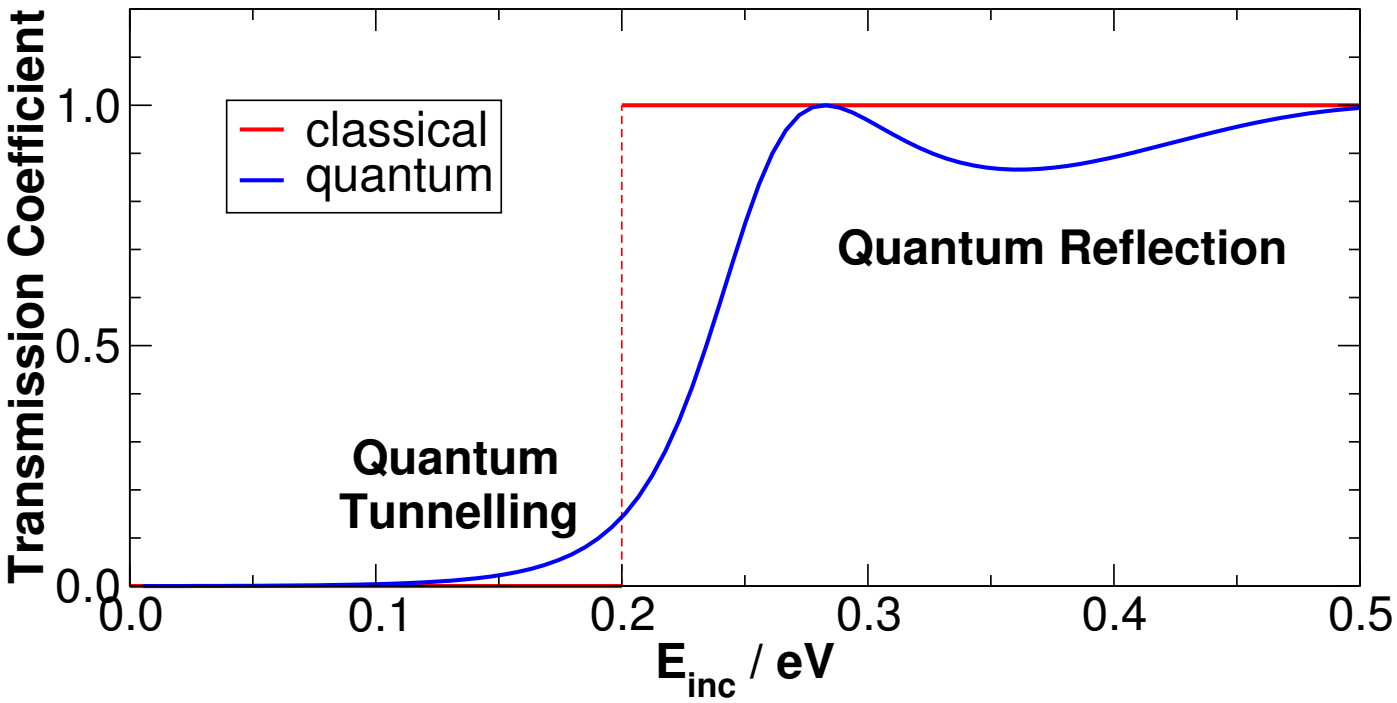
- **Time independent** solutions: $\mathcal{H}\Psi = E\Psi$
  for $Z \to \pm\infty$, plane waves with fixed momentum $p = \hbar k$
- Superposition of waves: **incident**, **reflected** and **transmitted**
- Transmission = $|\text{trasmitted}|^2/|\text{incident}|^2$



Time Independent Quantum Scattering

Scattering States $\psi^+(x, E)$

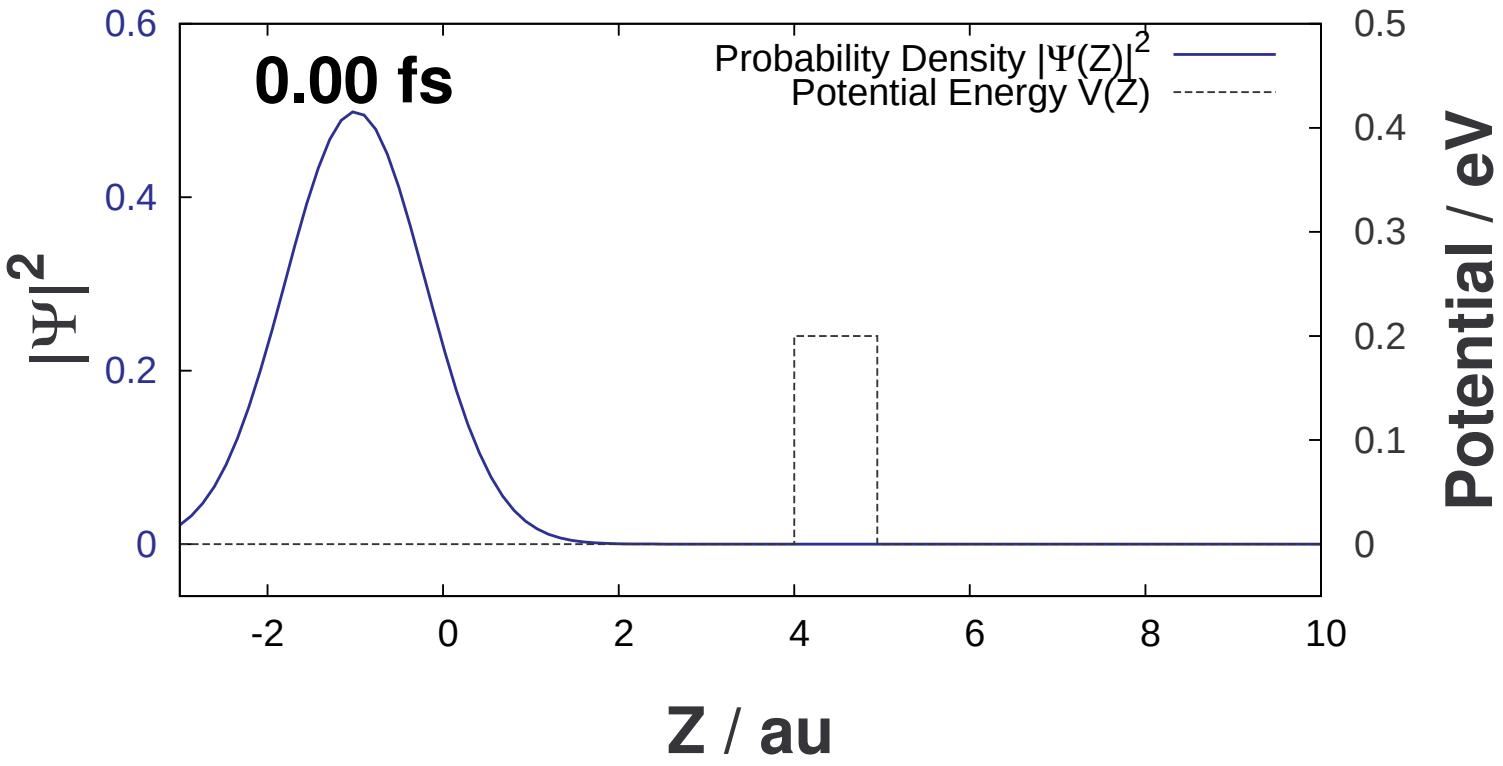
- **Time independent** solutions: $\mathcal{H}\Psi = E\Psi$
  for $Z \to \pm\infty$, plane waves with fixed momentum $p = \hbar k$
- Superposition of waves: **incident**, **reflected** and **transmitted**
- Transmission = $|\text{trasmitted}|^2/|\text{incident}|^2$



Time Dependent Quantum Scattering

Time Dependent Wavepacket $\psi(x,t)$

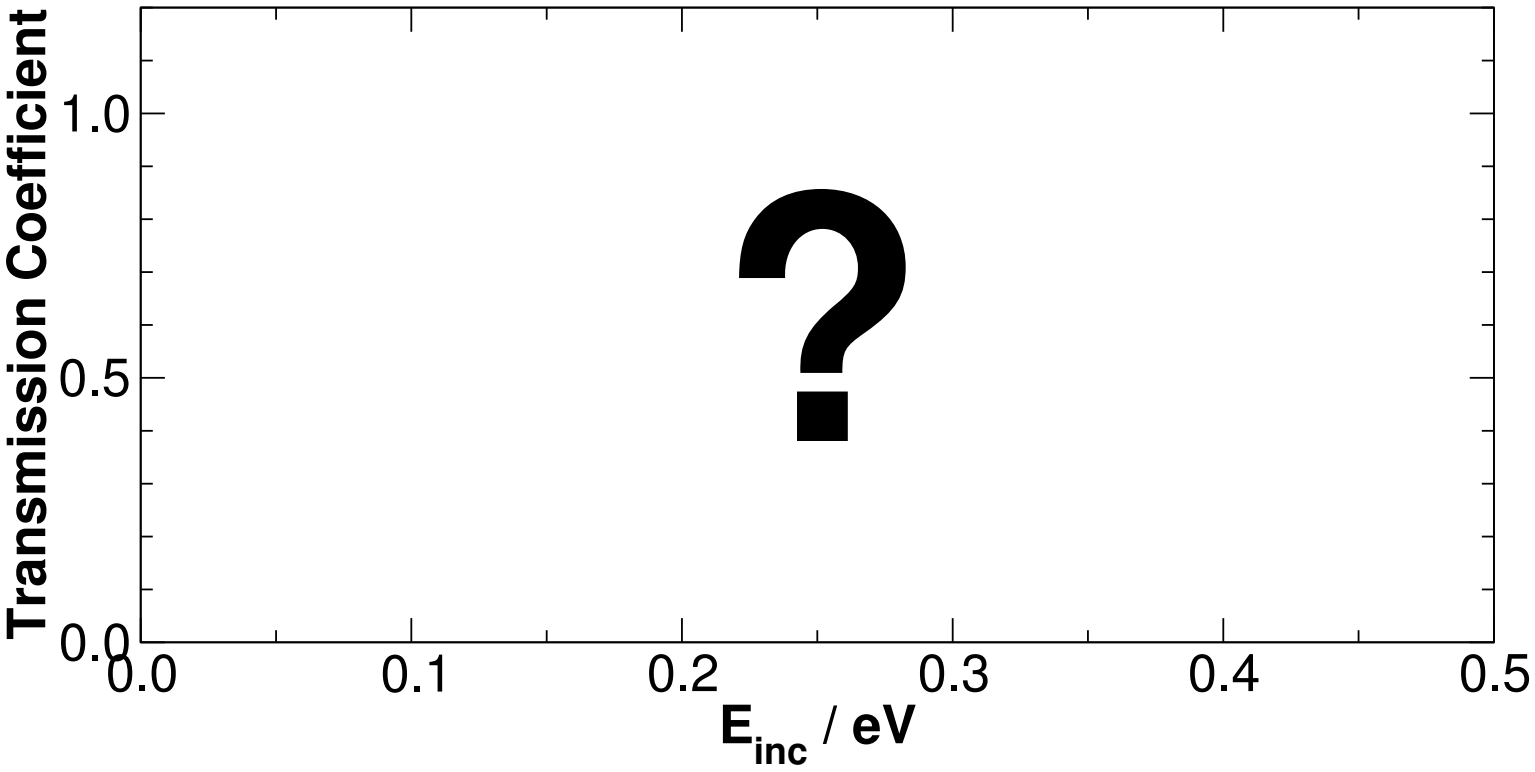
- **Time dependent** solutions: $\imath\hbar\frac{\partial}{\partial t}\Psi = \mathcal{H}\Psi$
  at t=0, gaussian wavepacket with **gaussian p distribution**
- Continous E_{inc} distribution: how to extract Trasmission vs E_{inc} ?



Time Dependent Quantum Scattering

Time Dependent Wavepacket $\psi(x,t)$

- **Time dependent** solutions: $\imath\hbar\frac{\partial}{\partial t}\Psi = \mathcal{H}\Psi$
  at t=0, gaussian wavepacket with **gaussian p distribution**
- Continous E_{inc} distribution: how to extract Trasmission vs E_{inc} ?

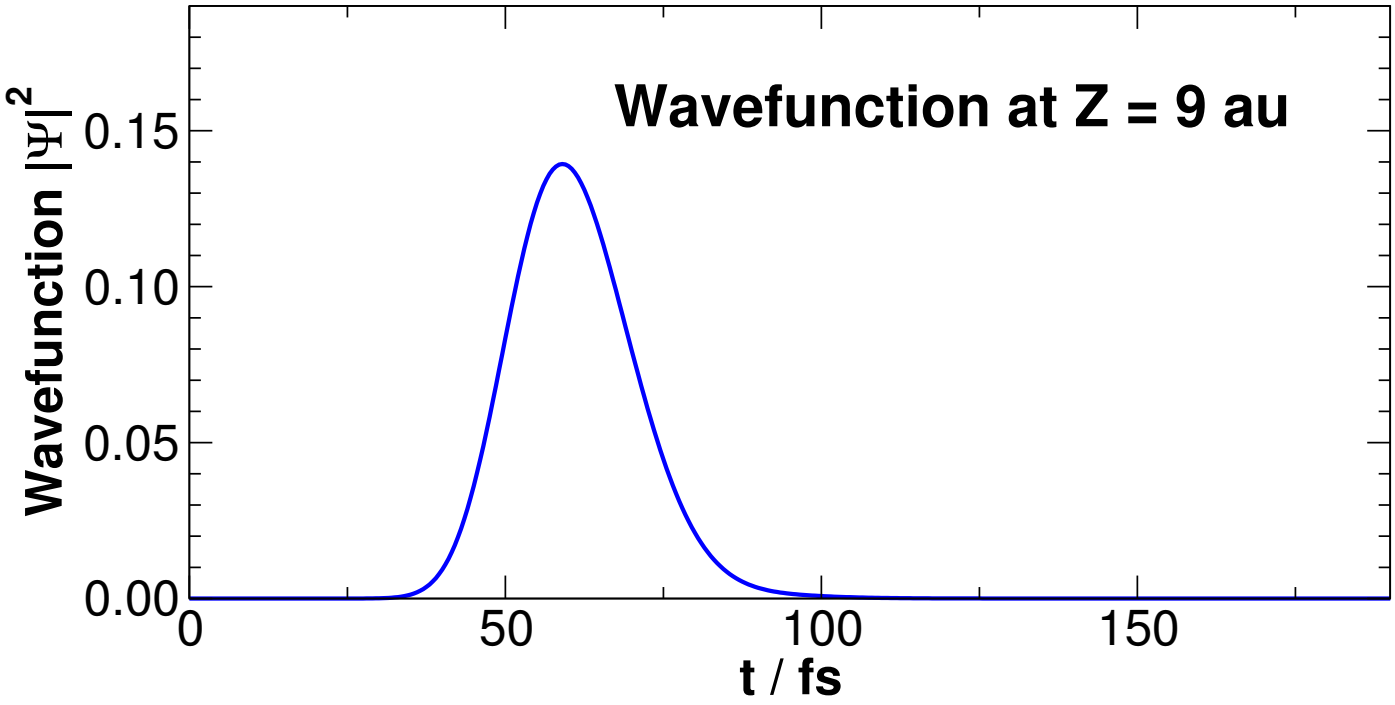


Time-Energy Mapping

Time-Energy Fourier Trasform $\psi^+(x,E) \Leftrightarrow \psi(x,t)$

time-dependent wavepacket and **scattering states** are related by FT

$$\psi^+(\tilde{x},E) = \frac{\sqrt{E}}{\pi\sqrt{2M}\phi(E)} \int_{-\infty}^{+\infty} dt\, e^{\frac{i}{\hbar}Et} \psi(\tilde{x},t)$$

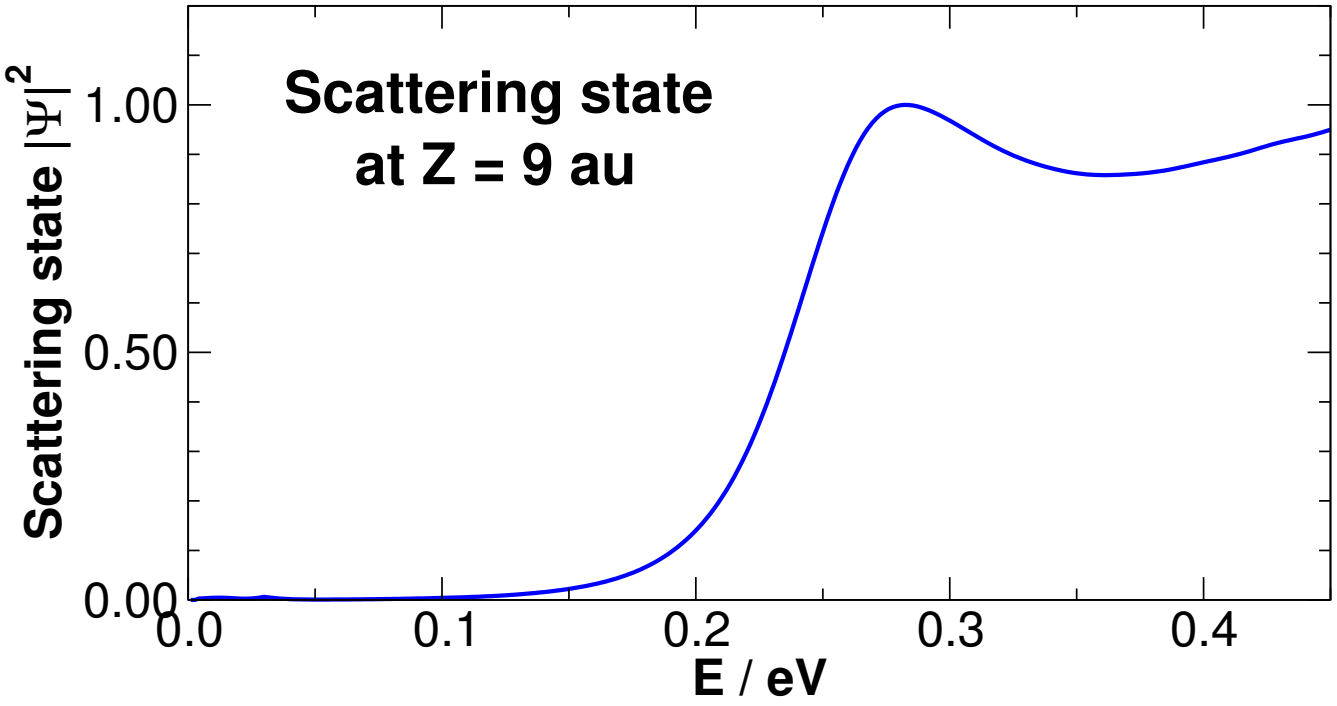


Time-Energy Mapping

Time-Energy Fourier Trasform $\psi^+(x,E) \Leftrightarrow \psi(x,t)$

time-dependent wavepacket and **scattering states** are related by FT

$$\psi^+(\tilde{x},E) = \frac{\sqrt{E}}{\pi\sqrt{2M}\phi(E)} \int_{-\infty}^{+\infty} dt\, e^{\frac{i}{\hbar}Et}\psi(\tilde{x},t)$$



Quantum Scattering Methods

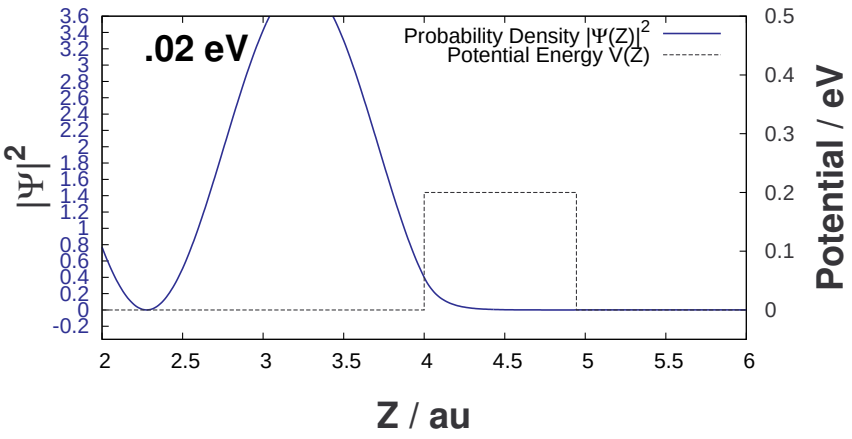
Time Independent

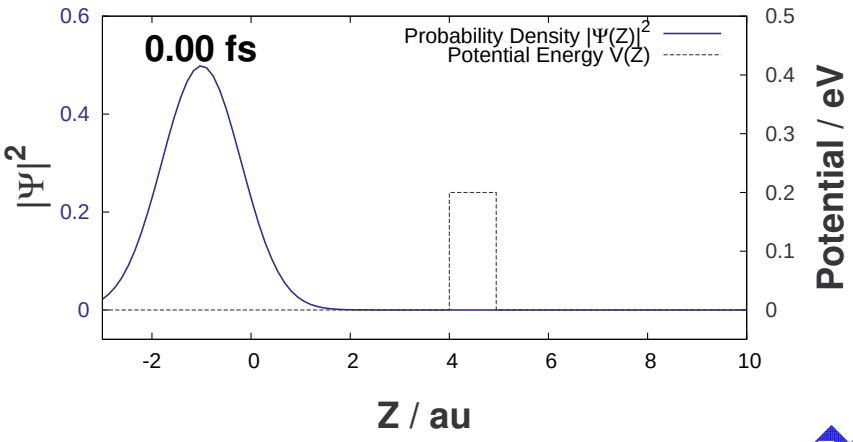
- Scattering states
- Time Indep SE: $\mathcal{H}\Psi = E\Psi$
- Asymptotic condition, $x \to \infty$

Time - Energy Fourier Transform

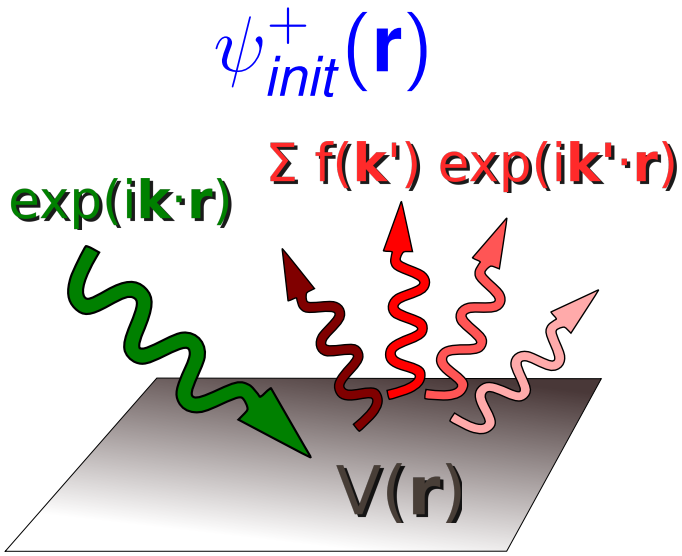
Time Dependent

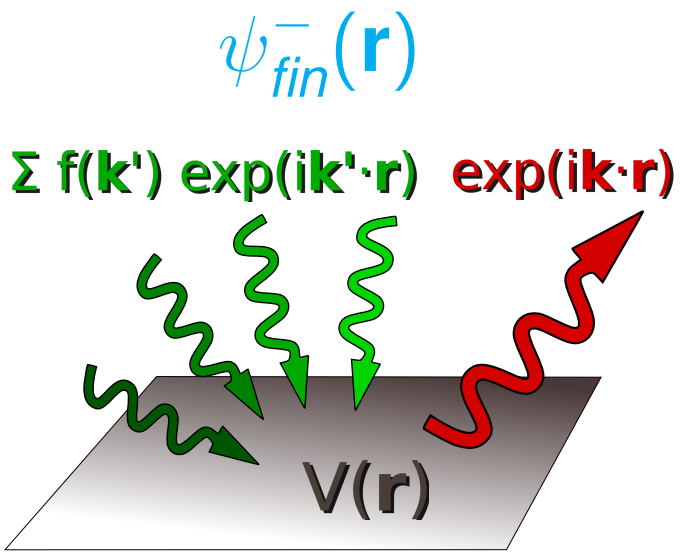
- Wavepackets
- Time Dep SE: $\imath\hbar\frac{\partial}{\partial t}\Psi = \mathcal{H}\Psi$
- Initial condition, $\psi(t=0) = \psi_0$





Scattering Matrix





Scattering Matrix $S(fin \leftarrow init)$

- the S-matrix is the **overlap of in and out** scattering states

$$S(\text{fin} \leftarrow \text{init}) = \int d\mathbf{r}\, \psi^{-}_{fin}(\mathbf{r})^{\star} \psi^{+}_{init}(\mathbf{r}) = \langle \psi^{-}_{fin} | \psi^{+}_{init} \rangle$$

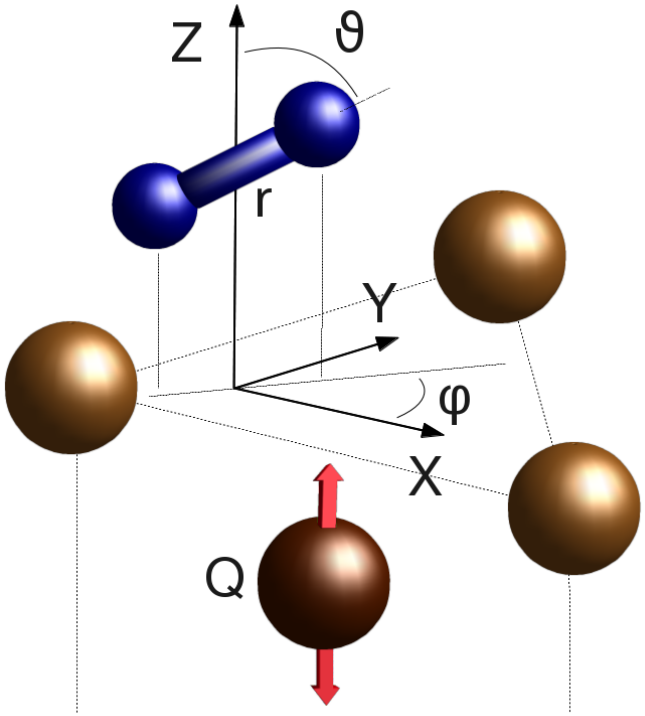
- The **scattering probability** $P(\text{fin} \leftarrow \text{init})$ is given by

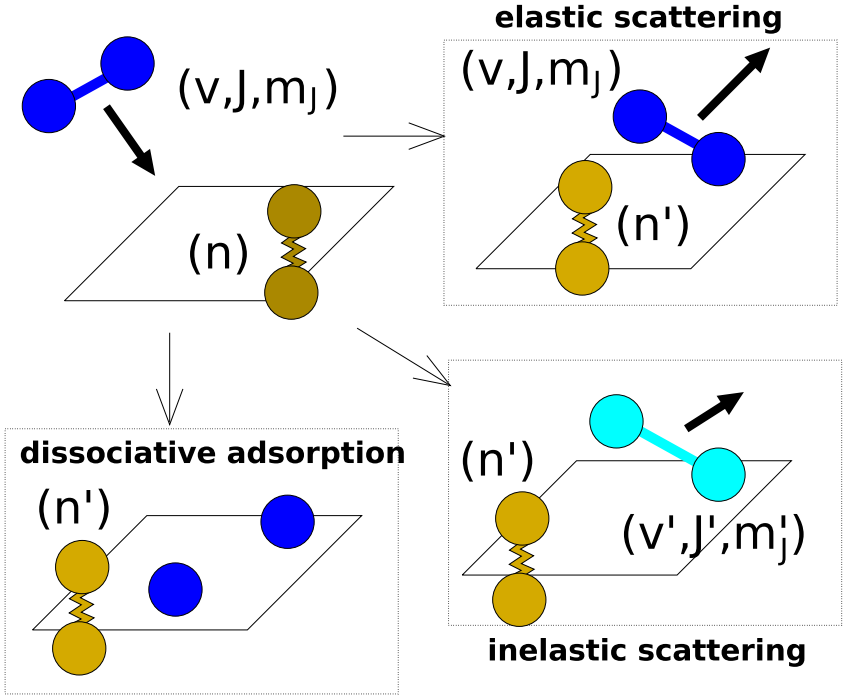
$$P(\text{fin} \leftarrow \text{init}) = \| S(\text{fin} \leftarrow \text{init}) \|^2$$

Outline

The Dynamical Model

- 7 DoF model
  1. 6 DoF of H_2: (r,Z,X,Y,ϑ,φ)
  2. 1 Dof of Cu surface: 2nd layer, $\perp$ direction
- Quantum Wavepacket Calculations

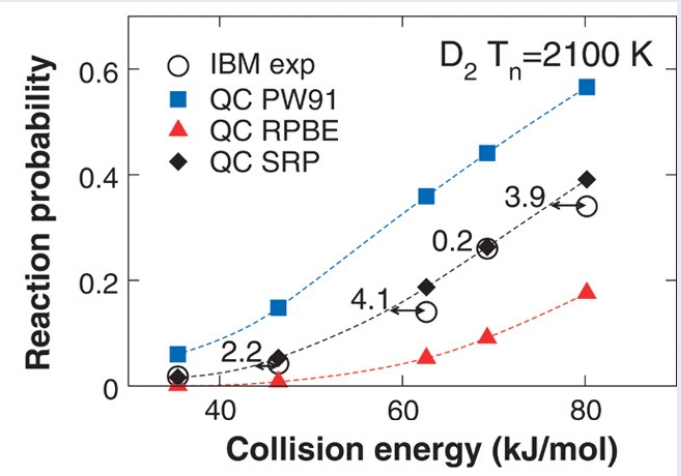




Potential Energy Surface

DFT method

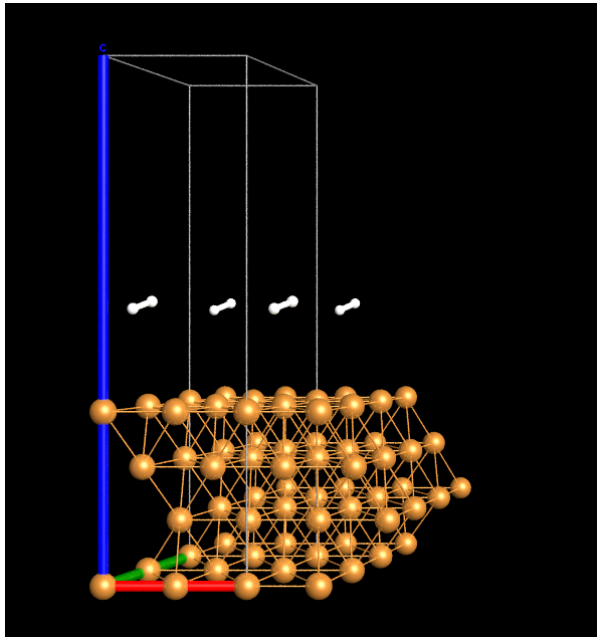
- **2x2 Supercell**
- **Plane Waves**: cutoff 350 eV, 8x8x1 **k** points
- **Functional**: mixed PW91/RPBE Specific Reaction Parameter



- Calculations with DACAPO code

PES

- **6D Potential** at fixed Q = -0.2 Å, 0.0 Å, 0.2 Åwith Corrugation Reducing Procedure
- **Q interpolation** with parabola

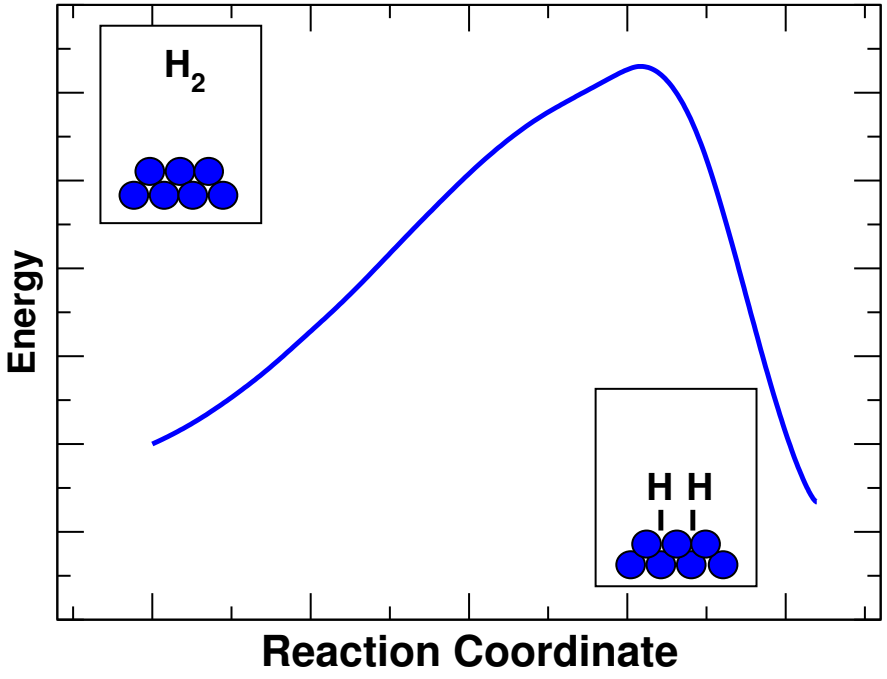


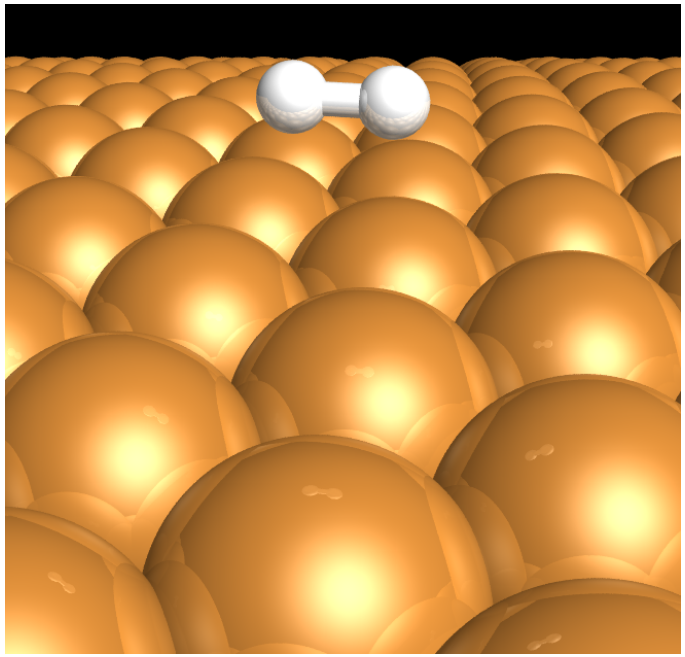
[a] C. Díaz *et al.* Phys. Chem. Chem. Phys. **12**, 6499 (2010)
[b] H.F. Busnengo *et al.* J. Chem. Phys. **112**, 7641 (2000)

Effect of Lattice DoF on Activated Chemisorption

Effects of lattice displacement on reaction path

1. electronic coupling: barrier height
2. mechanical coupling: barrier position





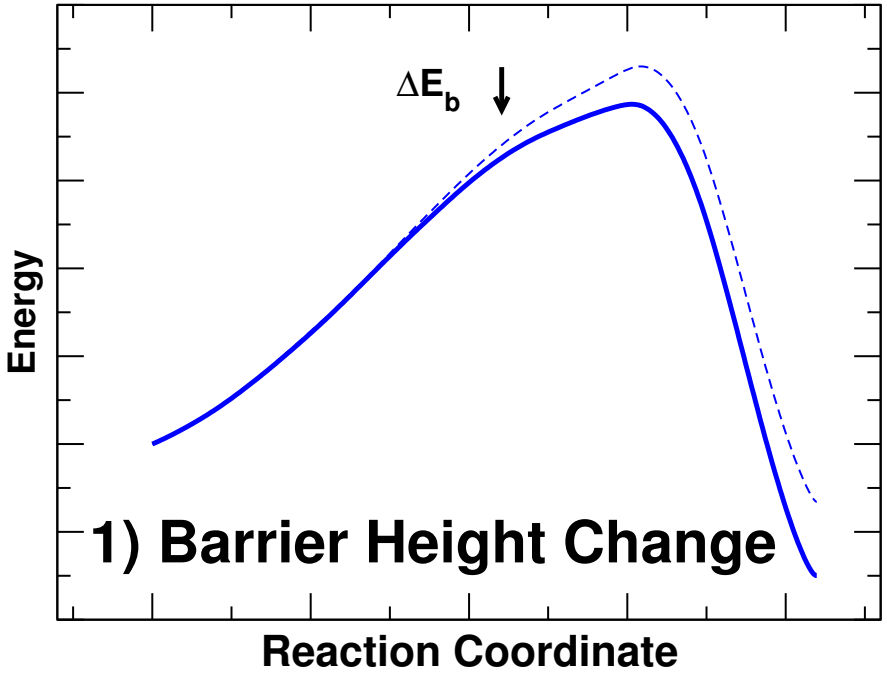
[a] S. Nave and B. Jackson, J. Chem. Phys. **130**, 054701 (2009)

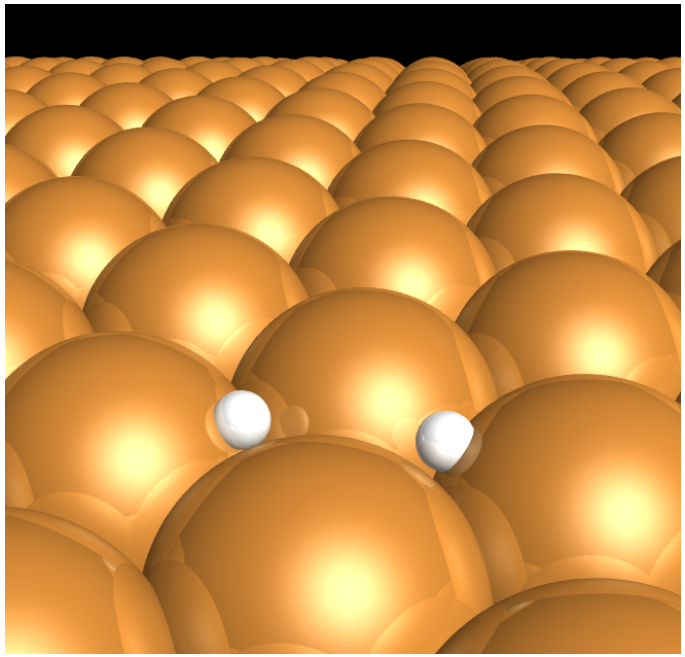
[b] M.Bonfanti, C.Díaz, M.F.Somers and G.J. Kroes, PCCP, **13**, 4552 (2011)

Effect of Lattice DoF on Activated Chemisorption

Effects of lattice displacement on reaction path

1. electronic coupling: barrier height
2. mechanical coupling: barrier position





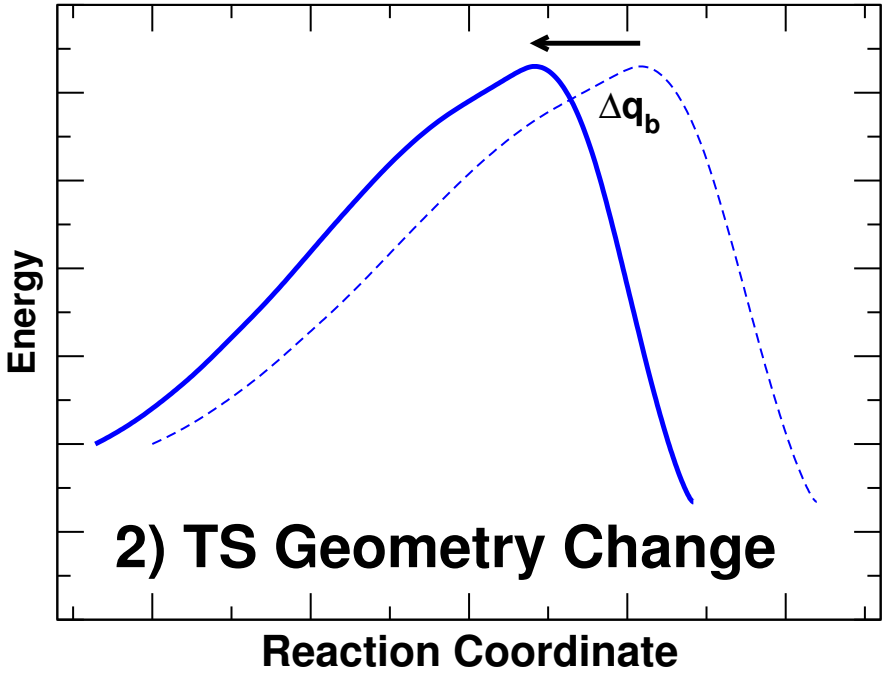
[a] S. Nave and B. Jackson, J. Chem. Phys. **130**, 054701 (2009)

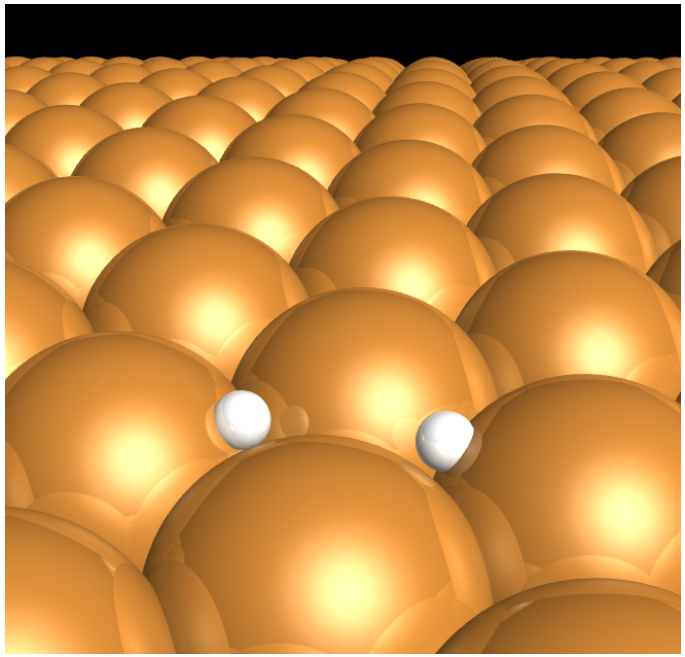
[b] M.Bonfanti, C.Díaz, M.F.Somers and G.J. Kroes, PCCP, **13**, 4552 (2011)

Effect of Lattice DoF on Activated Chemisorption

Effects of lattice displacement on reaction path

1. electronic coupling: barrier height
2. mechanical coupling: barrier position



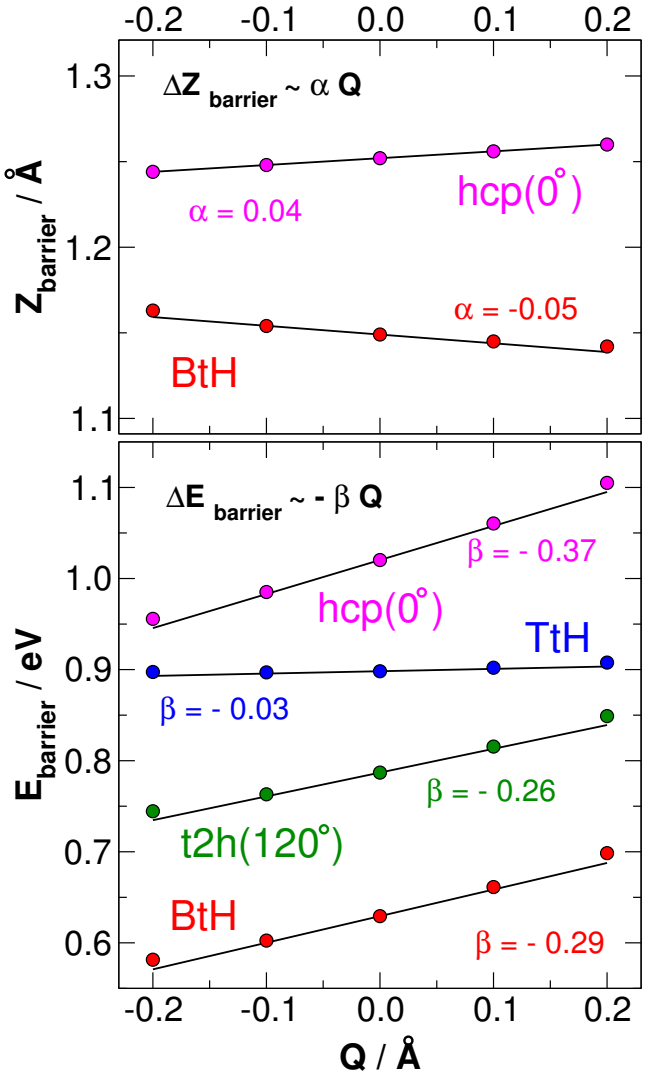


[a] S. Nave and B. Jackson, J. Chem. Phys. **130**, 054701 (2009)

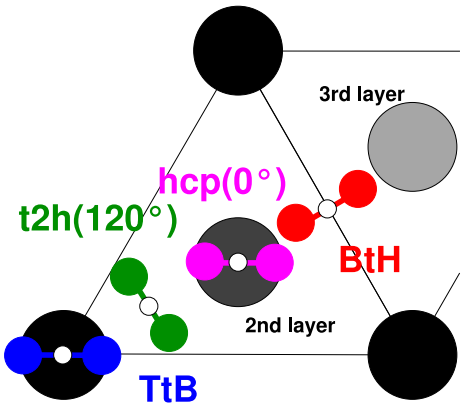
[b] M.Bonfanti, C.Díaz, M.F.Somers and G.J. Kroes, PCCP, **13**, 4552 (2011)

Effect of 2nd Layer Cu ⊥ motion

Barrier	Q (Å)	Geometry Θ (°)	Δr (Å)	ΔZ (Å)	ΔE (meV)
BtH	-0.2	90.	-0.03	0.01	-48.
	0.2	90.	0.03	-0.01	69.
t2h	-0.2	90.	-0.02	0.00	-42.
	0.2	90.	0.02	0.00	62.
TtH	-0.2	90.	-0.01	0.00	-1.
	0.2	90.	0.00	0.00	10.
hcp	-0.2	90.	-0.01	-0.01	-65.
	0.2	90.	0.00	0.01	85.



- Negligible change in barrier geometry
- Displacement mainly in bond length *r*



[a] M.Bonfanti, C.Díaz, M.F.Somers and G.J. Kroes, PCCP, **13**, 4552 (2011)

Vibrational Sudden Approximation

- VSA scattering matrix

$$S_{\text{sudden}}(\mathbf{f}, n' \leftarrow \mathbf{i}, n) = \int dQ\, \chi^{\star}_{n'}(Q)\, S_{\text{frozen Q}}(\mathbf{f} \leftarrow \mathbf{i}, Q)\, \chi_n(Q)$$

- Summing over the final vibrational state n'

$$P_{\text{sudden}}(\mathbf{i}, n) = \int dQ\, |\chi_n(Q)|^2\, P_{\text{frozen Q}}(\mathbf{i}, Q)$$

- We expect VSA to hold with **small coupling** and **slow vibrations**

From a practical point of view...

- **Compute 6D S-matrix** on a set of fixed Q (tipically 20)
- Evaluate average with **Q quadrature**

[a] J.M. Bowman *et al.*, J. Chem. Phys. **71**, 2270 (1979)

Outline

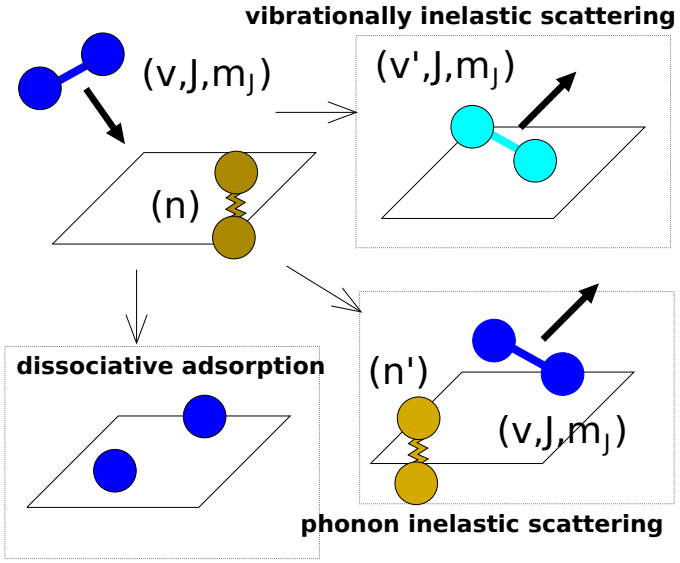
Results

Dynamical models

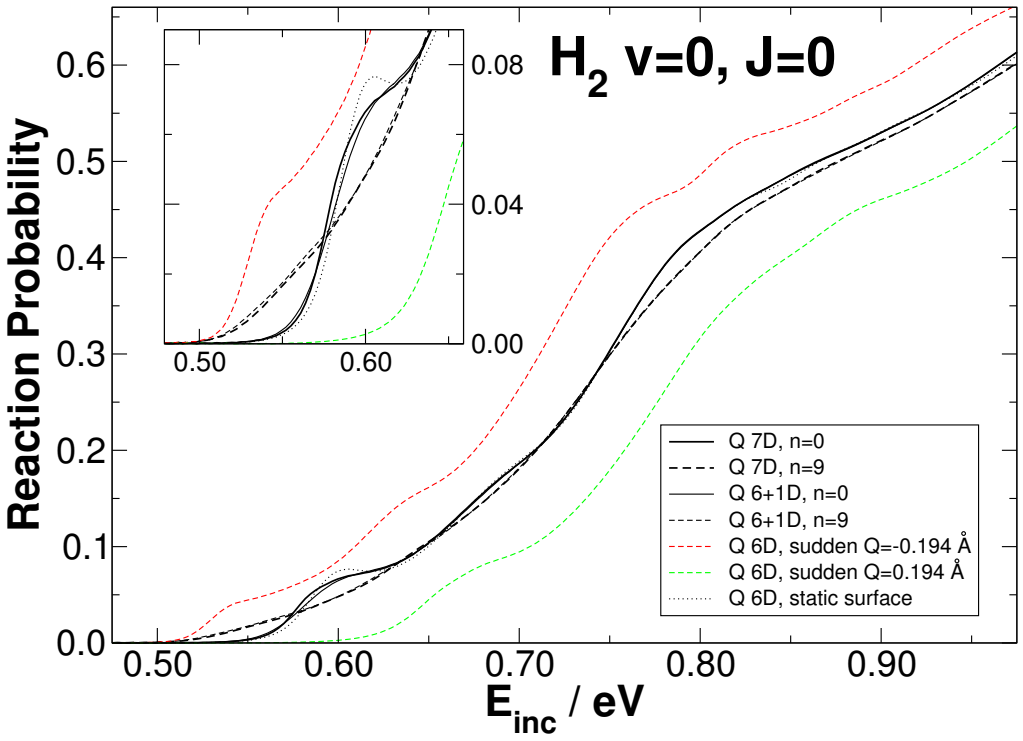
- **BOSS**: quantum dynamics with static surface, Q frozen in equilibrium position
- **7D**: quantum dynamics with full 7D model, Q motion explicitly included in the dynamics
- **VSA**: quantum dynamics with Vibrational Sudden Approximation for the 7th DoF

Observables

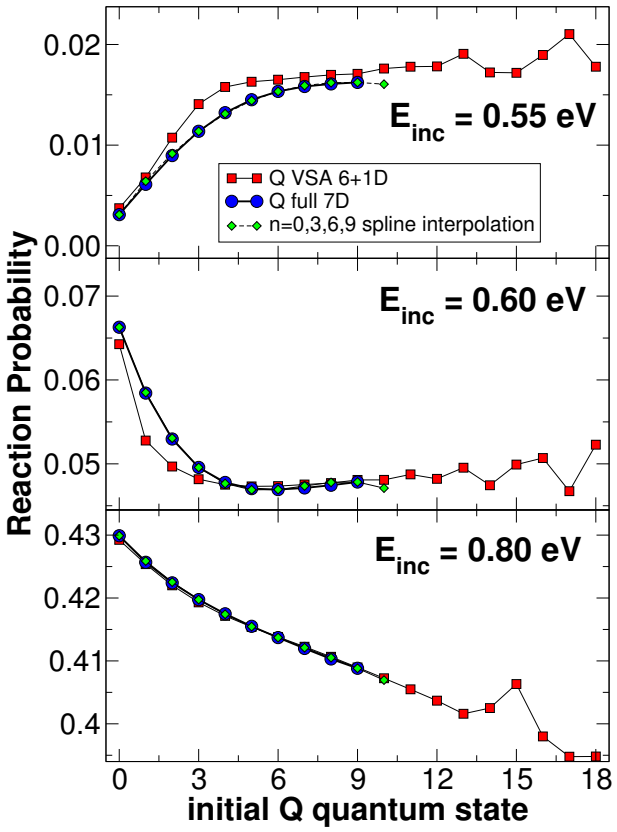
- Dissociative chemisorption
- Vibrationally Inelastic Scattering
- Phonon Inelastic Scattering



Dissociative Chemisorption: BOSS, 7D and VSA



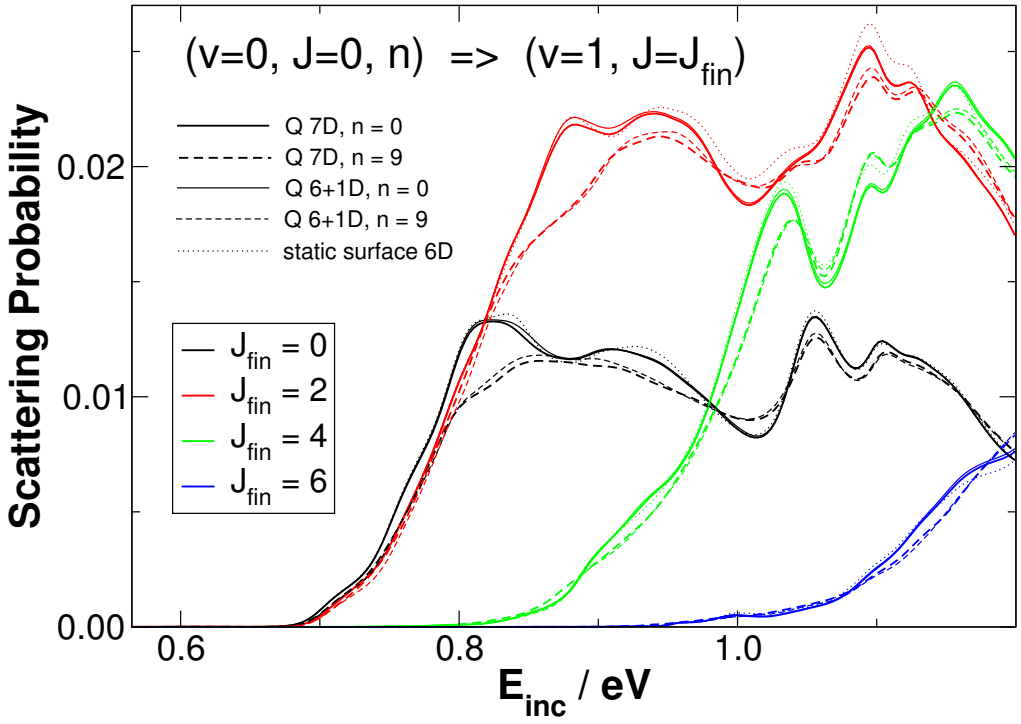
- H_2 v=0, J=0
- **Static** surface vs **moving** surface
- 7D and VSA



- Very small difference between static surface and Q ground state
- Broadening and smoothening with vibrational excitation
- VSA and 7D in very good agreement

Vibrationally Inelastic Scattering: BOSS, 7D and VSA

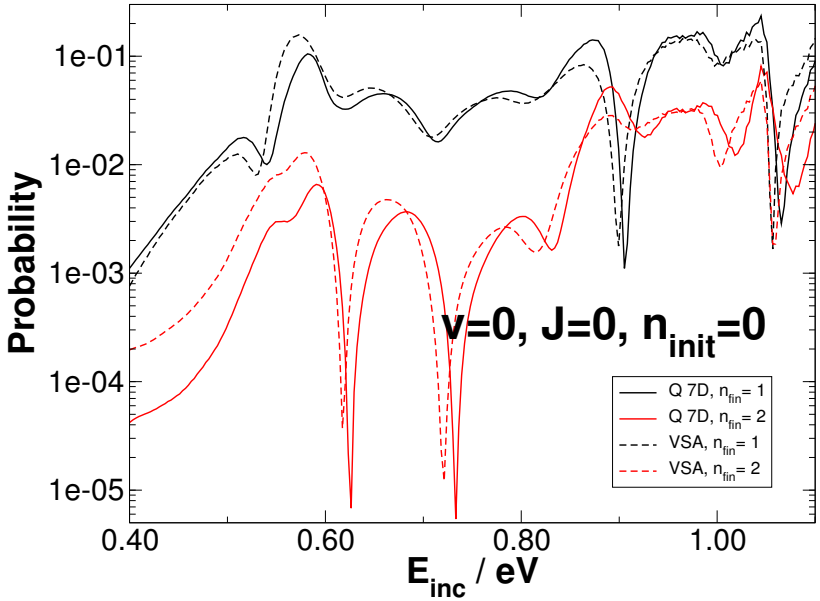
H_2 **(v=0, J=0)** $\Rightarrow$ H_2 **(v=1, J=0/2/4/6)**

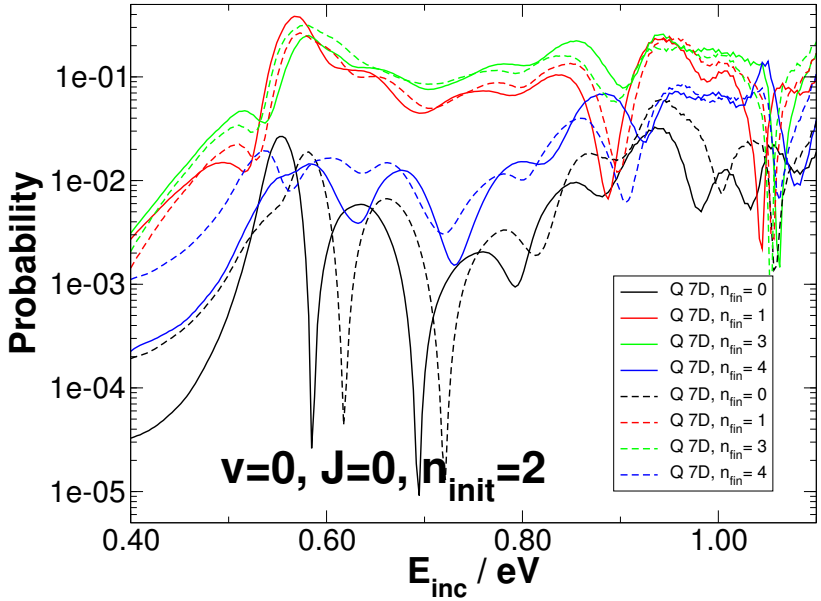


- Small difference between static surface and Q ground state
- Slight decrease of the probabilities with vibrational excitation
- VSA and 7D in very good agreement

Phonon Inelastic Scattering: 7D and VSA

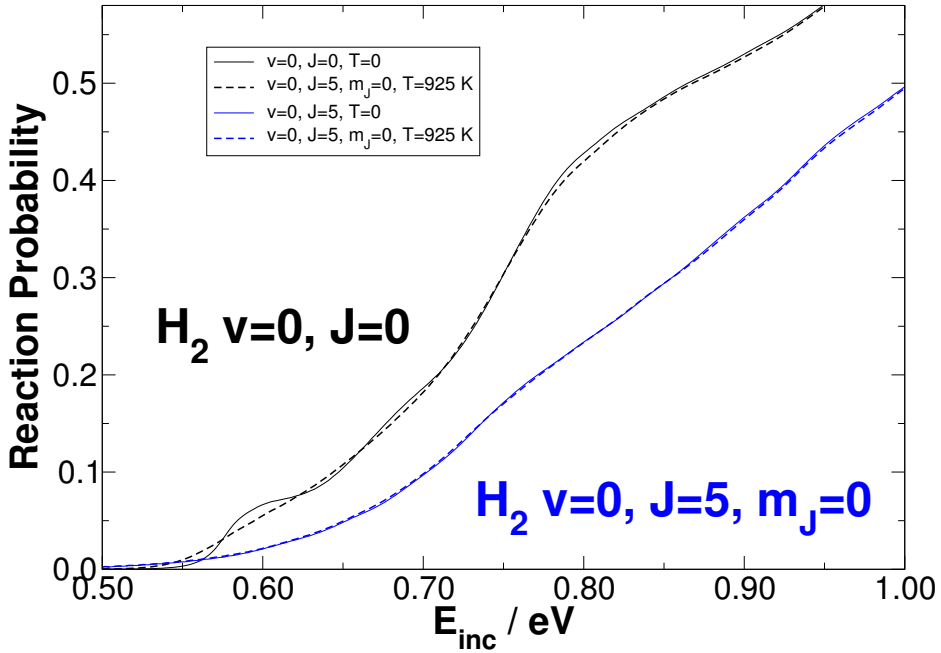
H_2 **(v=0, J=0)** + Cu **(n=0/2)** $\Rightarrow$ H_2 **(v=0, J=0)** + Cu **(n′)**





- stricter test on VSA: molecule-surface energy transfer
- reasonable agreement, behaviour well reproduced but some quantitative mismatch

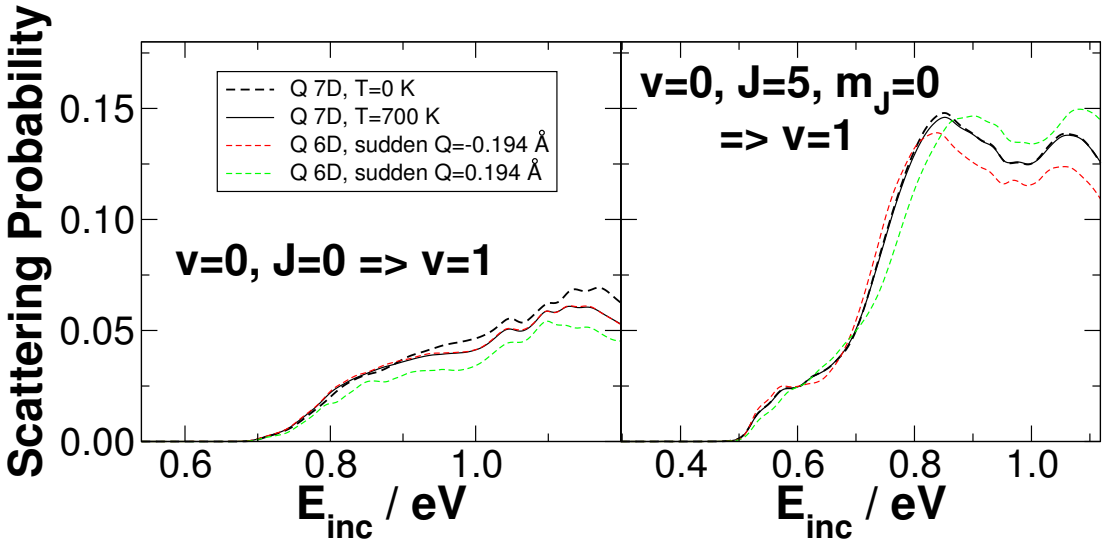
Thermal Averaged Results



Thermal distribution of initial n states:

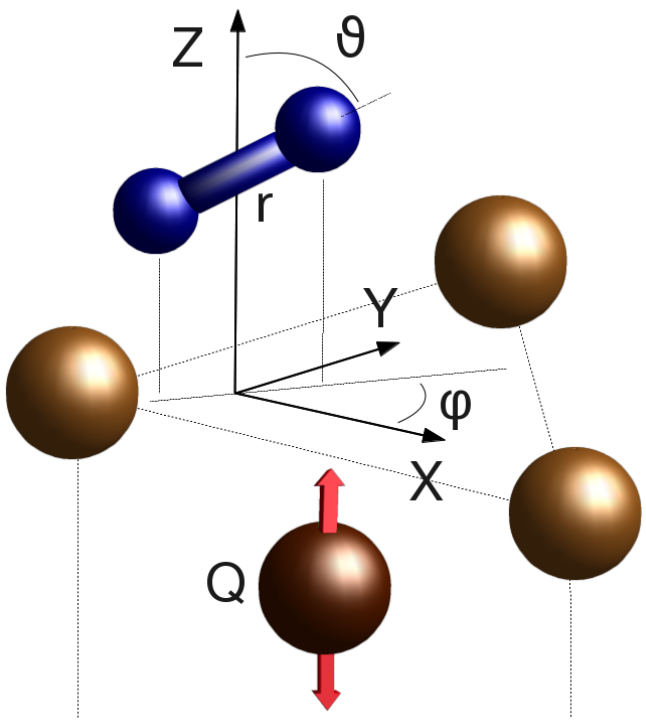
$$P = \sum_n \omega_n p_n \qquad \omega_n = \frac{e^{-\beta E_n}}{Z}$$

- Very small effect on reaction probability
- Cannot explain the observed increase of inelastic scattering



Conclusions

1. VSA is a very promising approach
   - Very good agreement for reaction and scattering probability
   - Even qualitative description of phonon-inelastic scattering
2. Model is not sufficient to describe experimental observations
   - Very small broadening of reaction probability
   - No increase of vibrationally inelastic scattering

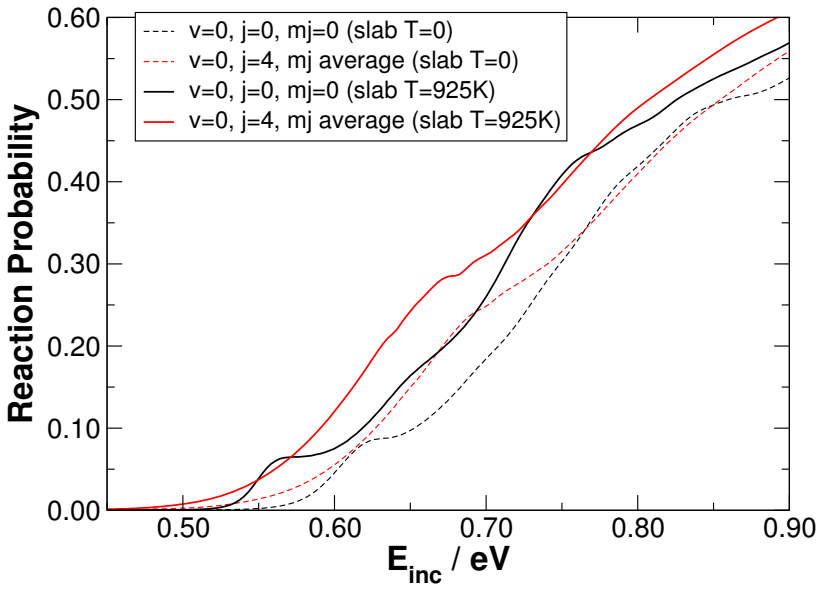


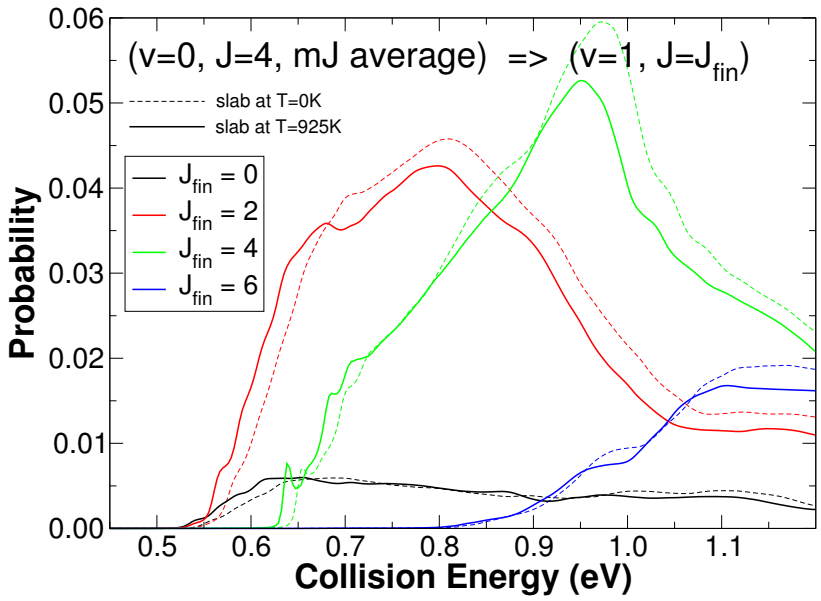
Outline

Thermal Expansion

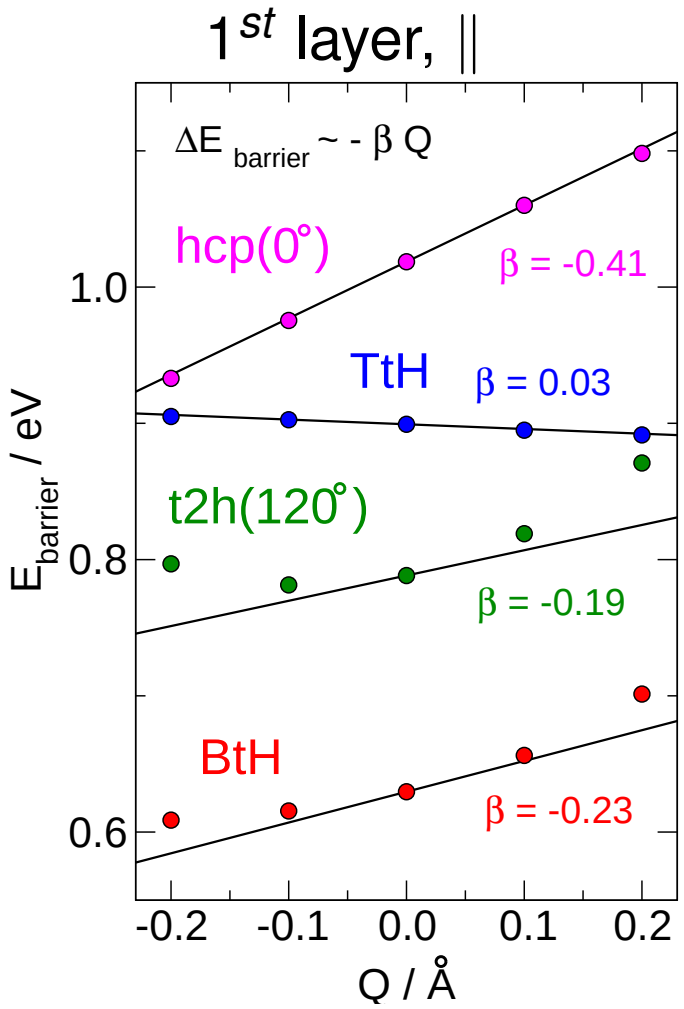
Reaction and scattering probability with two 6D PES:

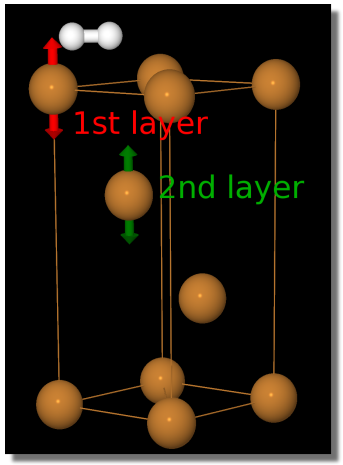
- Cu atoms in equilibrium position (0 K)
- Expanded unit cell according to the experimental thermal expansion at 925 K

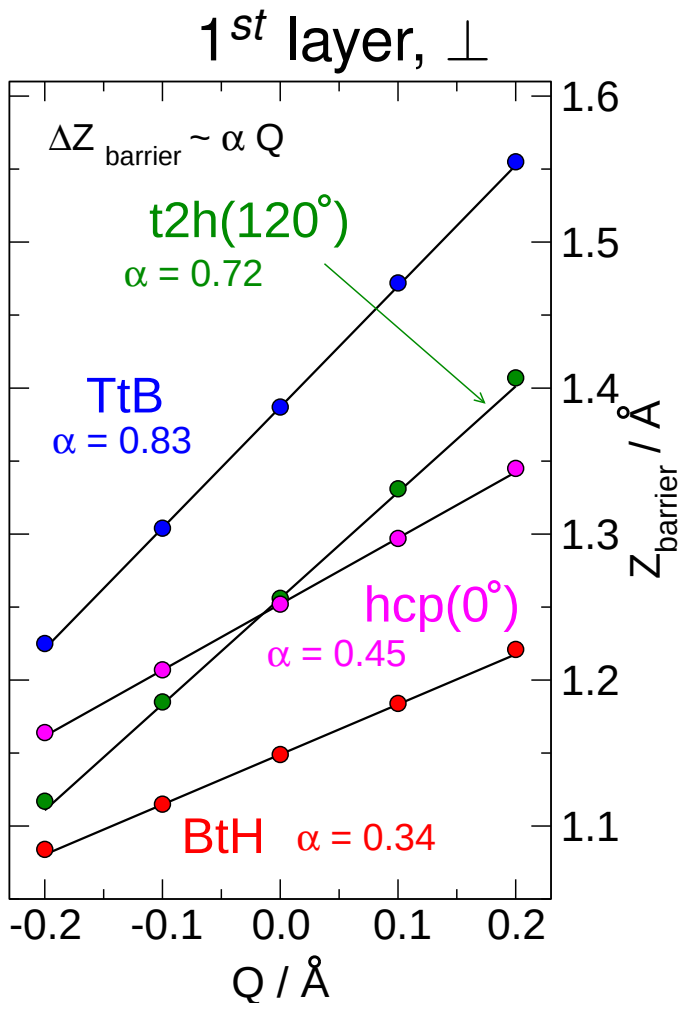




First layer atom motion





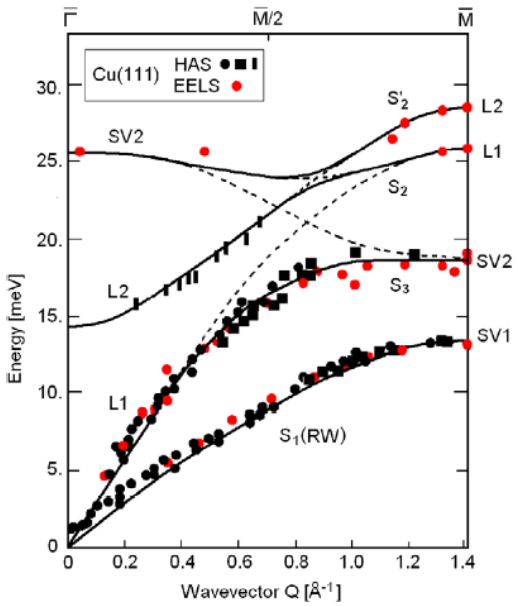


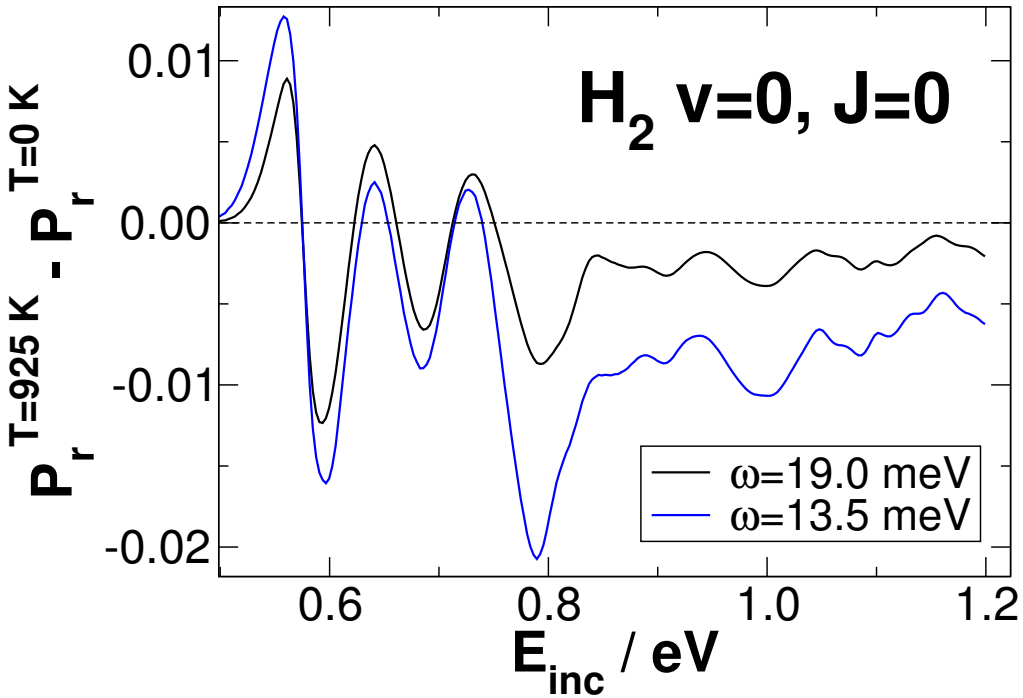
- Both mechanical (⊥) and electronic (||) effects

[a] M.Bonfanti, C.Díaz, M.F.Somers and G.J. Kroes, PCCP, **13**, 4552 (2011)

Vibrational Frequency of the DoF

- Ambiguous definition of ω in localized picture
- "Antisymmetric" surface phonon modes with lower ω ($\sim$ 13 meV)
- Simulation with ω=13 meV instead of 19 meV





Acknowledgments

- Geert-Jan Kroes
- Mark Somers
- Cristina Díaz
- Fabio Busnengo
- Mark Wijzenbroek
- Arobendo Mondal

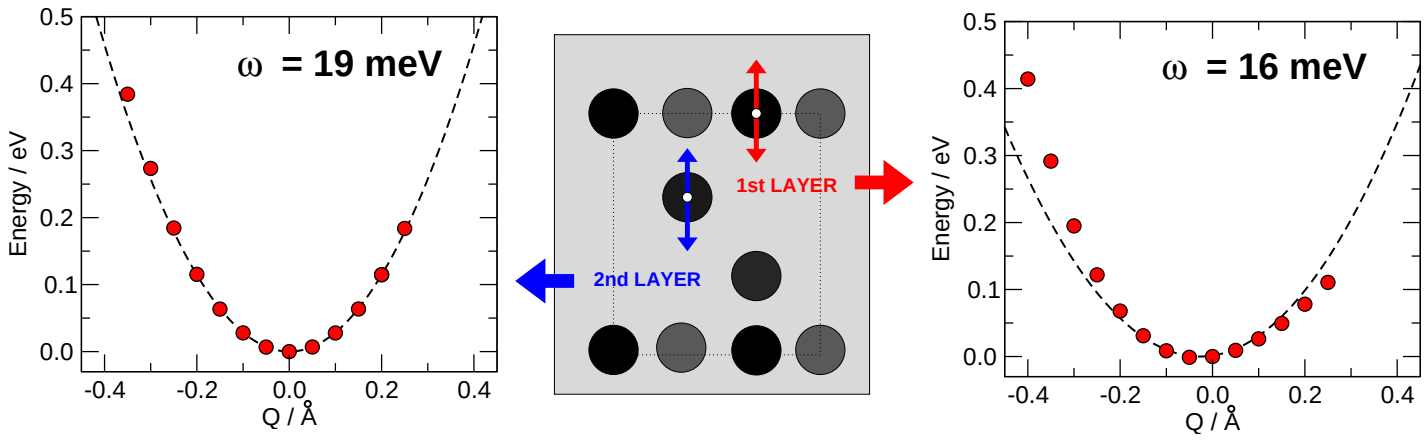
... and thank you, for your attention!

Acknowledgments

- Geert-Jan Kroes
- Mark Somers
- Cristina Díaz
- Fabio Busnengo
- Mark Wijzenbroek
- Arobendo Mondal

... and thank you, for your attention!

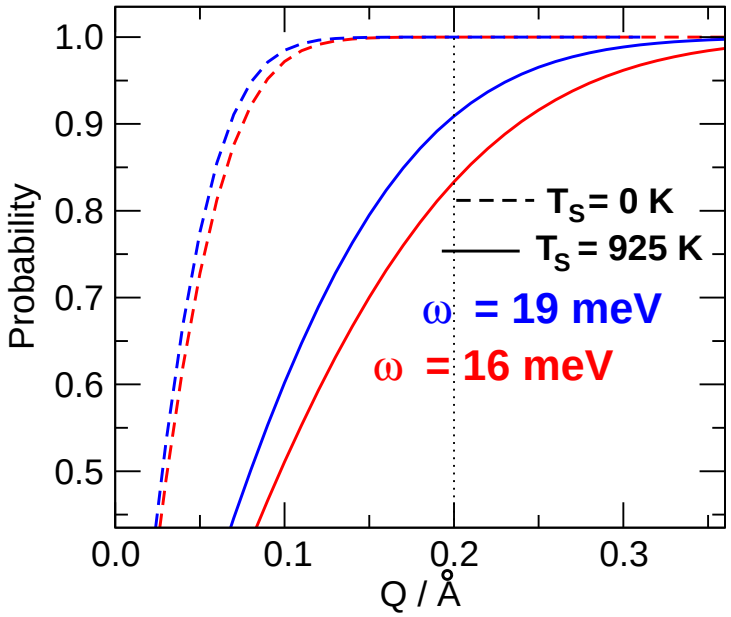
Vibrations of Cu atoms



Assuming an harmonic model and Boltzmann's distribution:

$$P = \sum_n \omega_n p_n \qquad \omega_n = \frac{e^{-\beta E_n}}{Z}$$

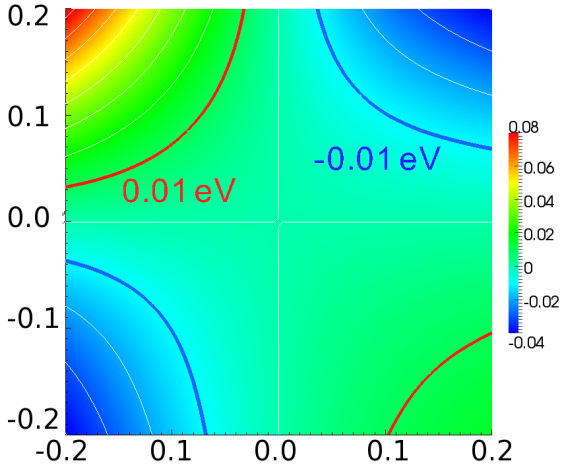
$$p_n = \int_{-x_0}^{x_0} |\psi_n|^2 dx$$



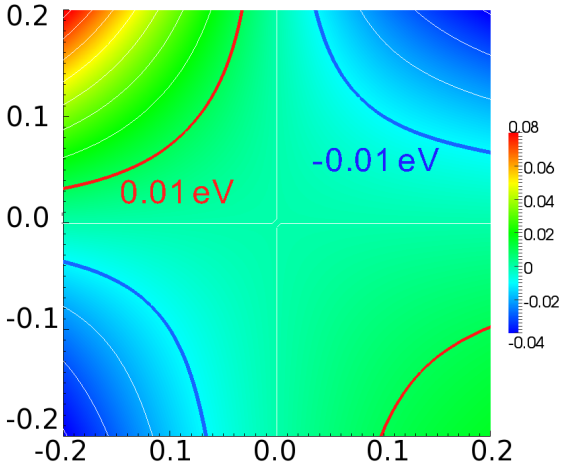
Surface DOF: Potential Energy Coupling

$$V_{2D}(Q_1, Q_2) = V_{1D}(Q_1) + V_{1D}(Q_2) + V_{coupling}(Q_1, Q_2)$$

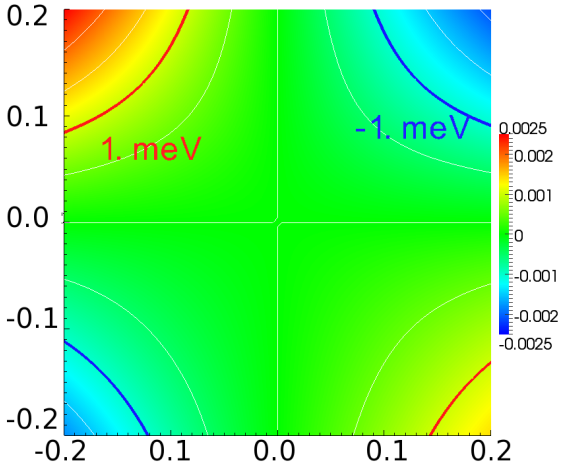
Contour plots of $V_{coupling}$



$Q_1 \rightarrow 1^{st}$ layer
$Q_2 \rightarrow 2^{nd}$ layer



$Q_1 \rightarrow 2^{nd}$ layer
$Q_2 \rightarrow 3^{rd}$ layer



$Q_1 \rightarrow 1^{st}$ layer
$Q_2 \rightarrow 3^{rd}$ layer

H_2-Surface Coupling Potential

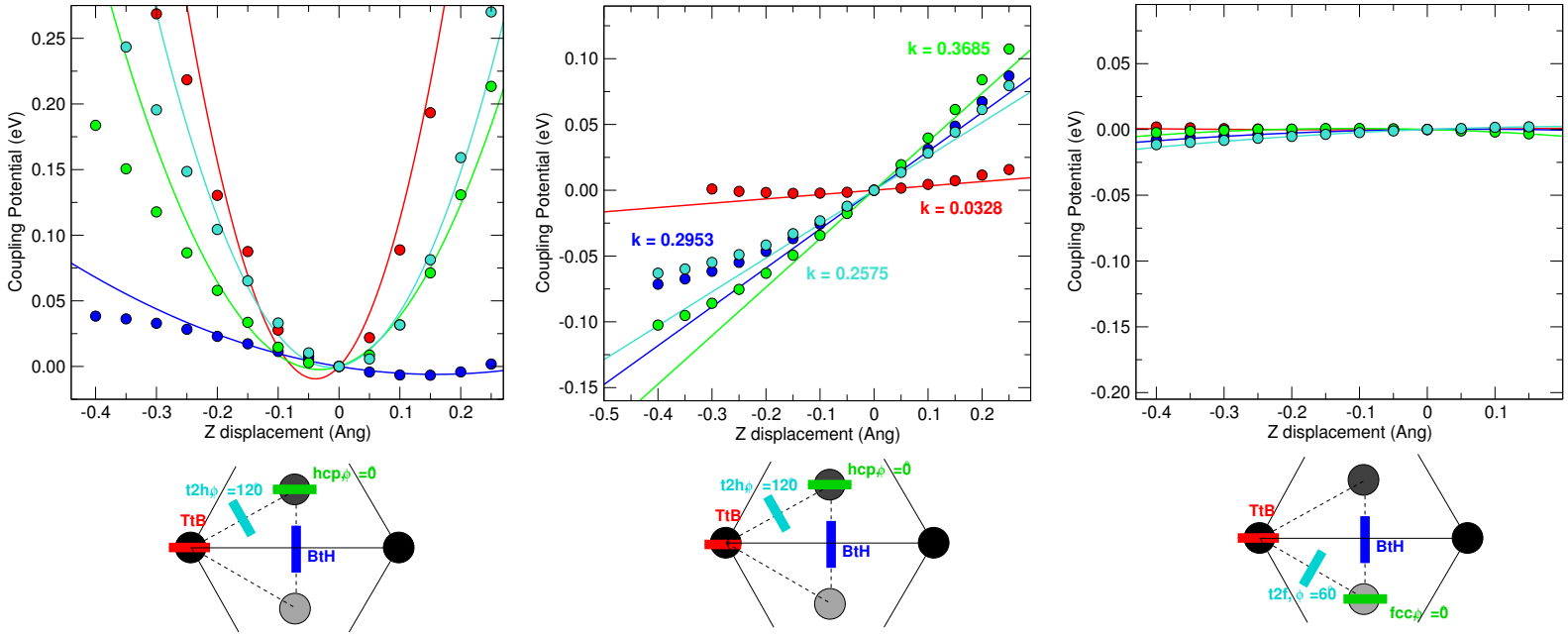
$$V_{7D}(\xi, Q) = V_{H2@Cu}(\xi) + V_{strain}(Q) + V_{coup}(\xi, Q)$$

$$\xi = (X, Y, Z, r, \vartheta, \varphi)$$

compare different surface DOF by comparing

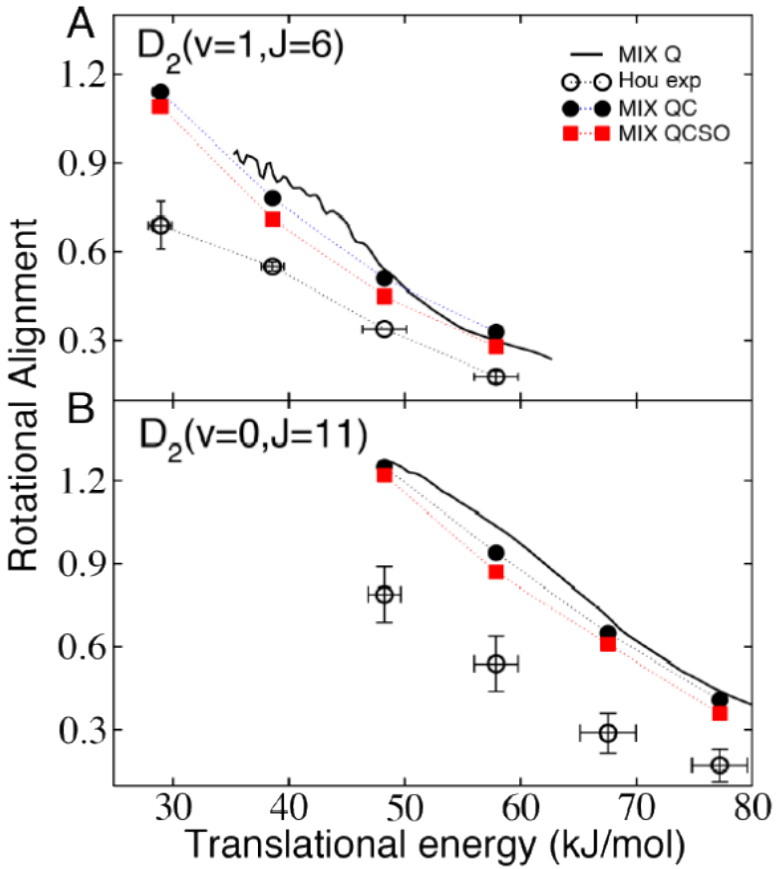
$V_{coup}(\xi_{bar}, Q)$ vs Q $\qquad$ $\xi_{bar} \rightarrow$ lowest barrier geometry

1st Layer Cu **2nd Layer Cu** **3rd Layer Cu**



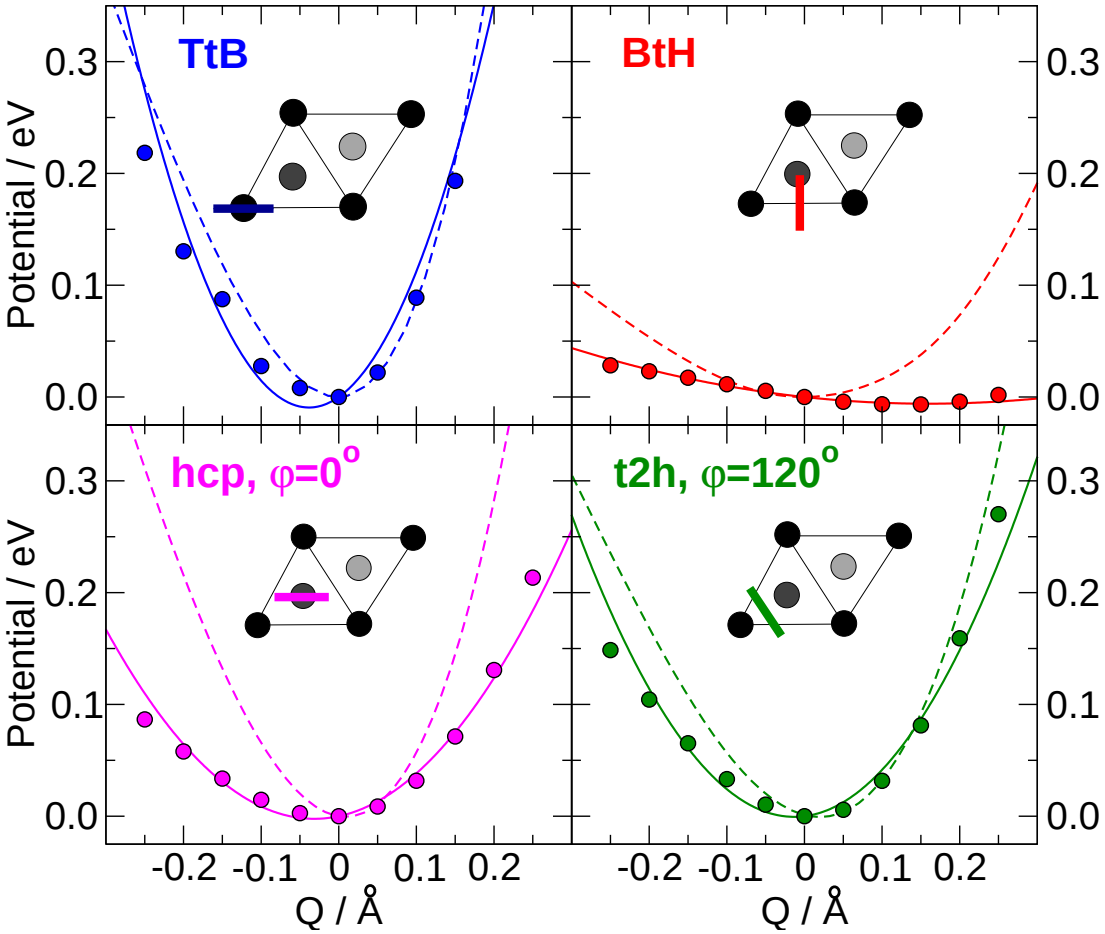
Lattice Motion: Surface Oscillator Model

$$V_{SO}(X, Y, Z, r, \vartheta, \varphi, Q) = V_{6D}(X, Y, Z - Q, r, \vartheta, \varphi) + \frac{1}{2}\mu\omega^2 Q^2$$



- V_{6D} is shifted along Z, as if the whole surface move with Q
- the potential for the surface vibration is quadratic

1st Layer vs SO Model

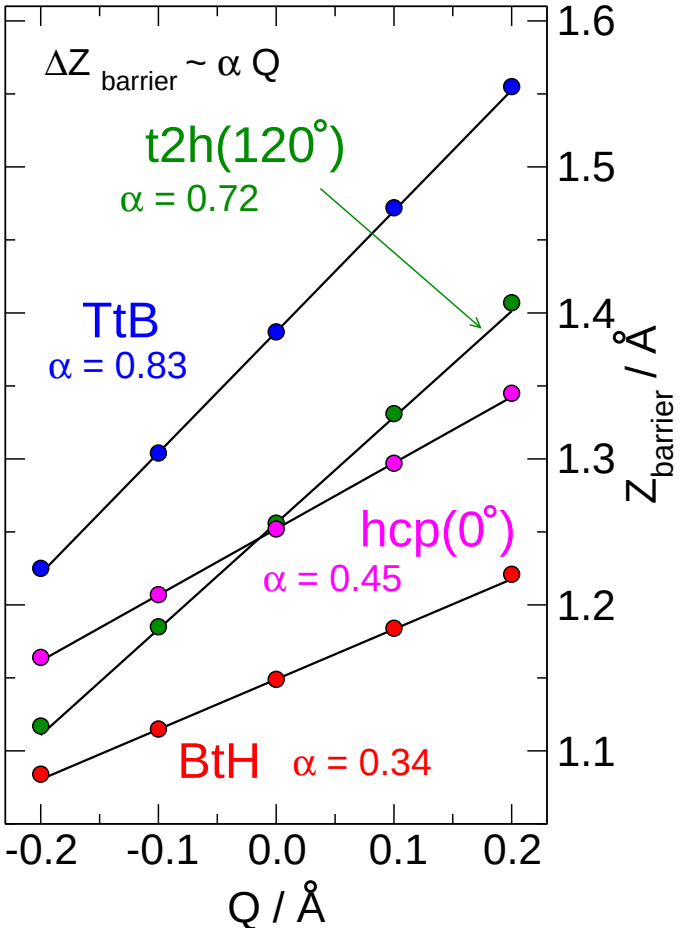


Agreement between SO Model and 1st layer atom motion

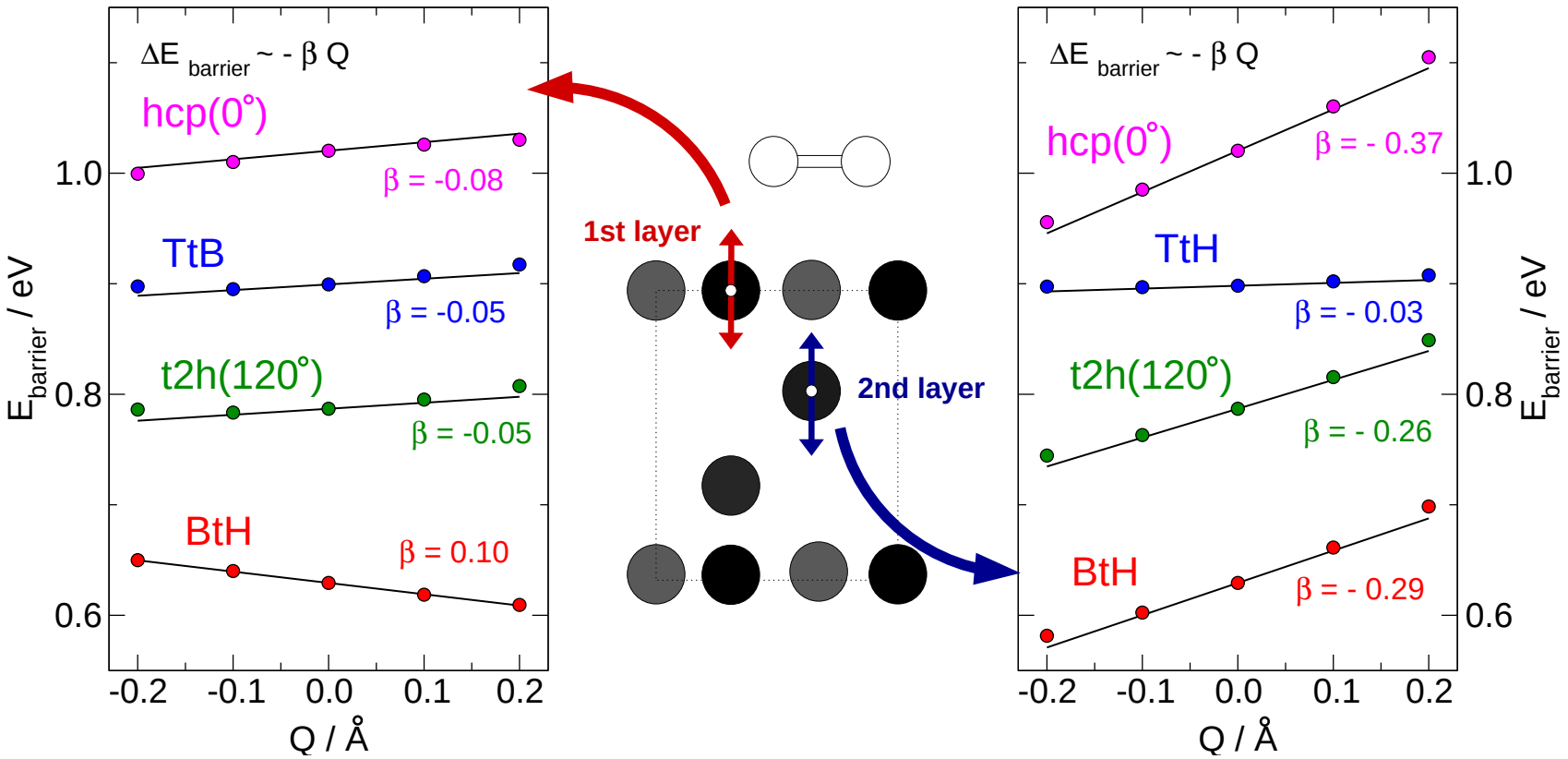
Barrier Displacement - 1st Layer Cu motion

Barrier	Q (Å)	Geometry θ (°)	Δr (Å)	ΔZ (Å)	ΔE (meV)
BtH	**-0.2**	90.	0.01	-0.06	21.
	0.2	90.	0.01	0.07	-20.
t2h	**-0.2**	90.	-0.04	-0.14	-1.
	0.2	90.	0.06	0.15	21.
TtB	**-0.2**	90.	-0.04	-0.16	-2.
	0.2	90.	0.06	0.17	18.
hcp	**-0.2**	83.	-0.04	-0.09	-21.
	0.2	96.	0.06	0.09	10.

- **Bigger ΔZ** than Δr
- ΔZ **similar to Q** near the TOP Cu atom
- Tilting angle for hcp barrier, mostly **geometrical effect** $\Delta\theta_{geom} = 4.4°$

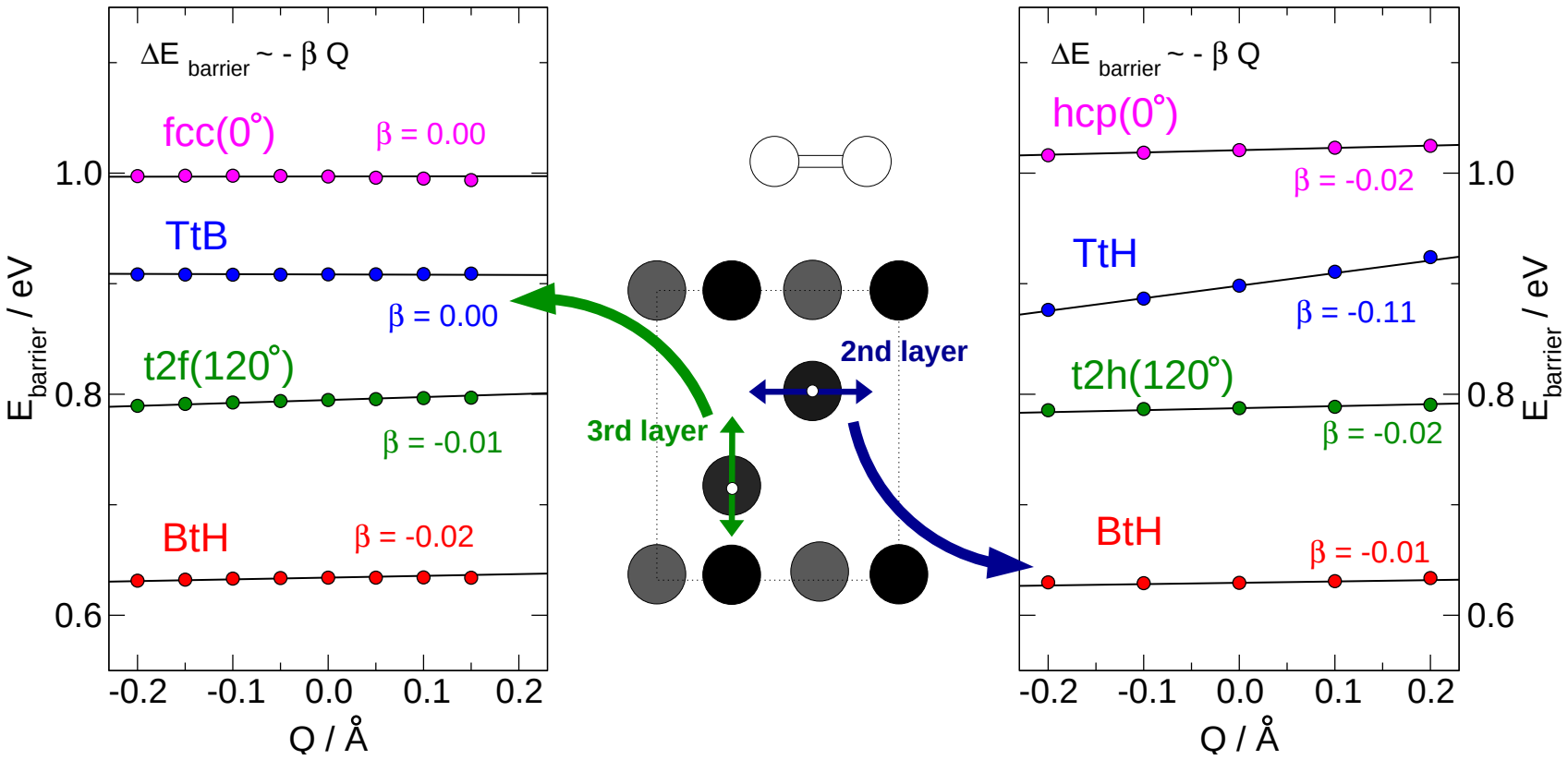


Barrier Height - 1st Layer vs 2nd Layer Cu motion



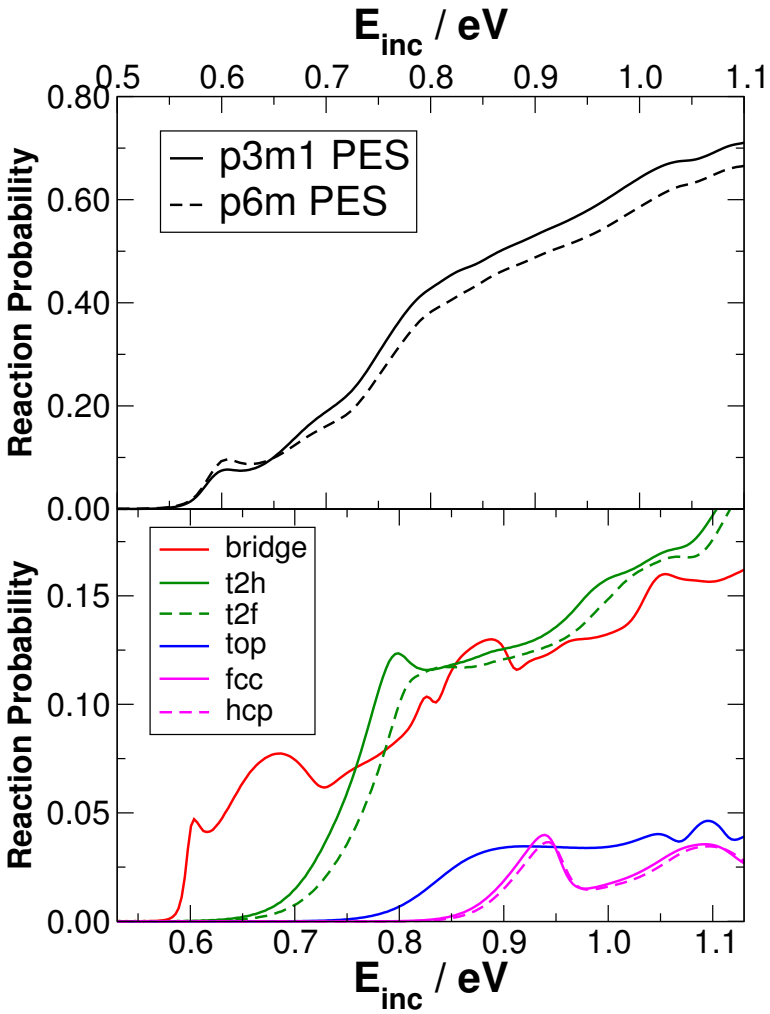
$E_{barrier}$ more sensitive to **2nd Layer motion**!

Other lattice coordinates



$E_{barrier}$ mostly independent of other lattice coordinates

Reaction Probability: 6D and 4D calculations



1. **Static Surface** $P_{reaction}$, comparison between **p6m** (previous PES with hcp = fcc) and **p3m1** (current PES)
2. 4D calculations with **X,Y fixed** in high symmetry sites, weighted and with Dai-Light ZPE correction

- p6m / p3m1 difference is consistent with t2h / t2f
- t2f, t2h and bridge are the most reactive sites

[a] C. Díaz *et al.* Phys. Chem. Chem. Phys. **12**, 6499 (2010)
[b] J. Dai and J.C. Light, J. Chem. Phys. **107**, 1676 (1997)