Università degli Studi di Milano

Modelling Surface Motion in H_2 Dissociation on $Cu(111)$

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Outline

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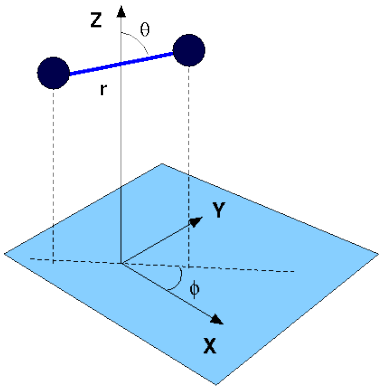
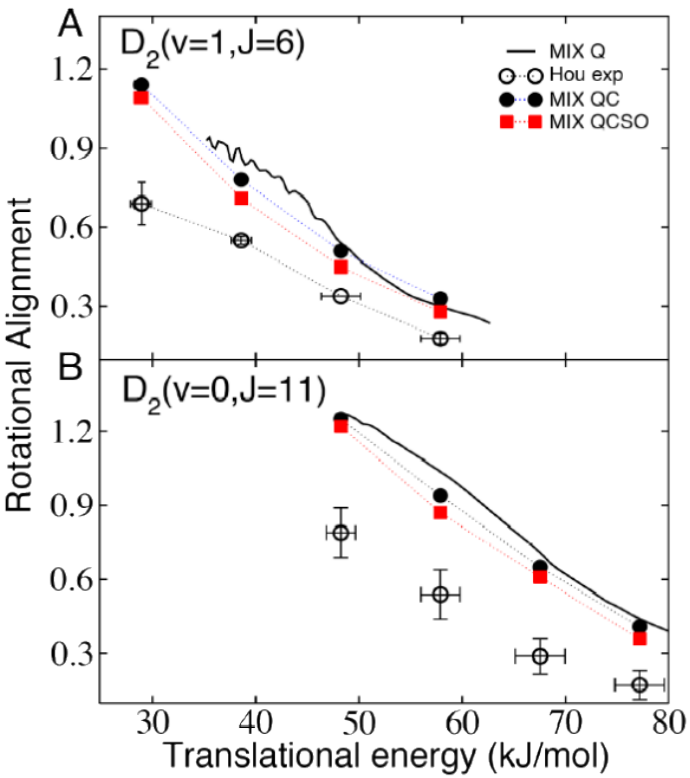
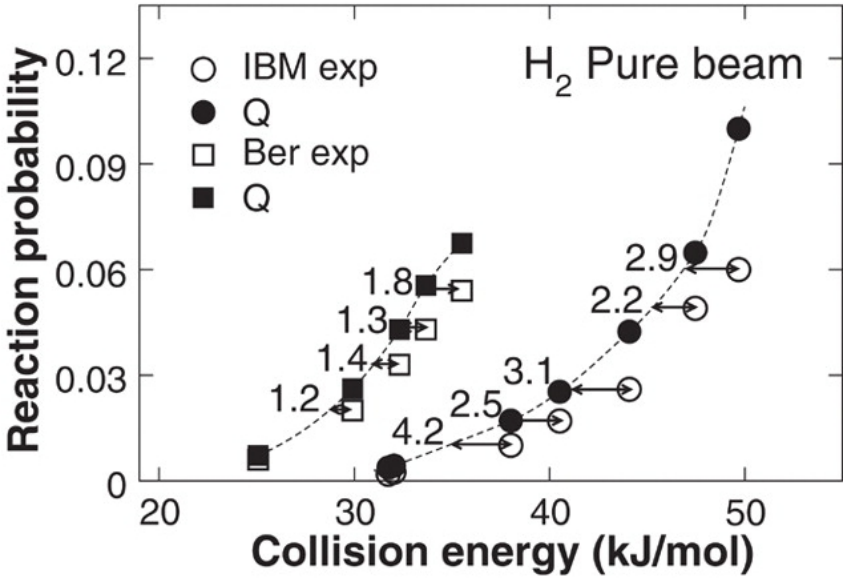
$H_2/Cu(111)$: previous results



C. Díaz et. Al., Science *326*, 832-834, **2009**
"Chemically Accurate Simulation of a Prototypical Surface Reaction: H_2 Dissociation on Cu(111)"

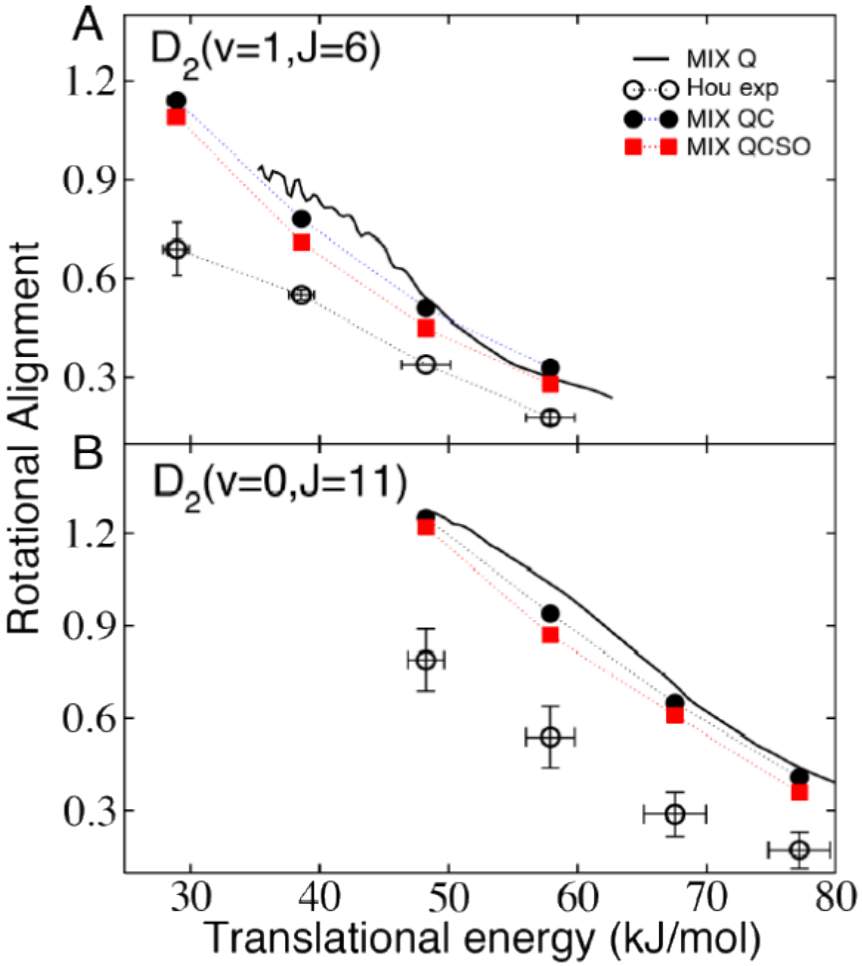


- Accurate results for **reaction probabilities**
- Still some improvements are needed, e.g. **rotational alignment**



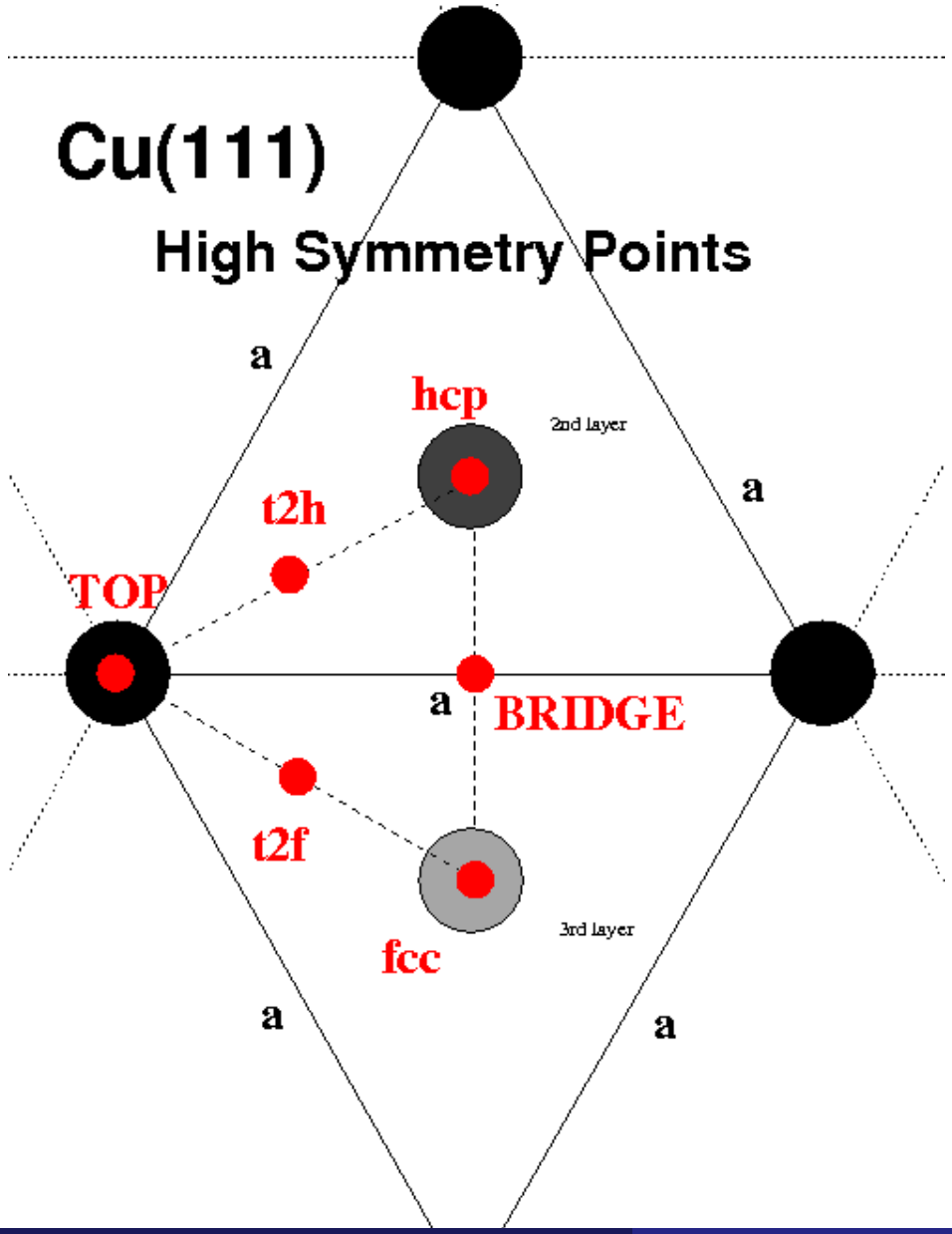
Surface Oscillator Model

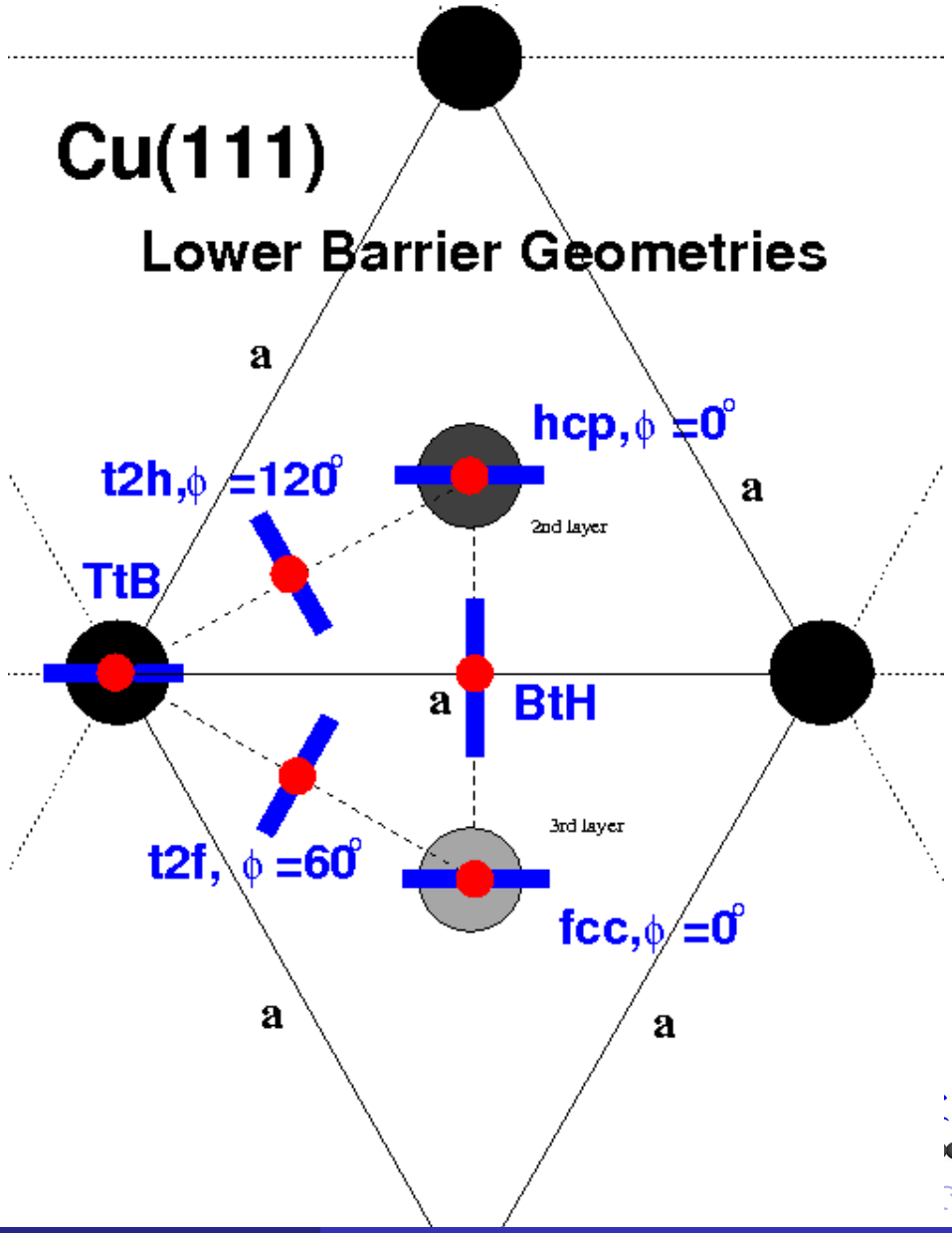
$$V_{SO}(X, Y, Z, r, \vartheta, \varphi, Q) = V_{6D}(X, Y, Z - Q, r, \vartheta, \varphi) + \frac{1}{2}\mu\omega^2 Q^2$$



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

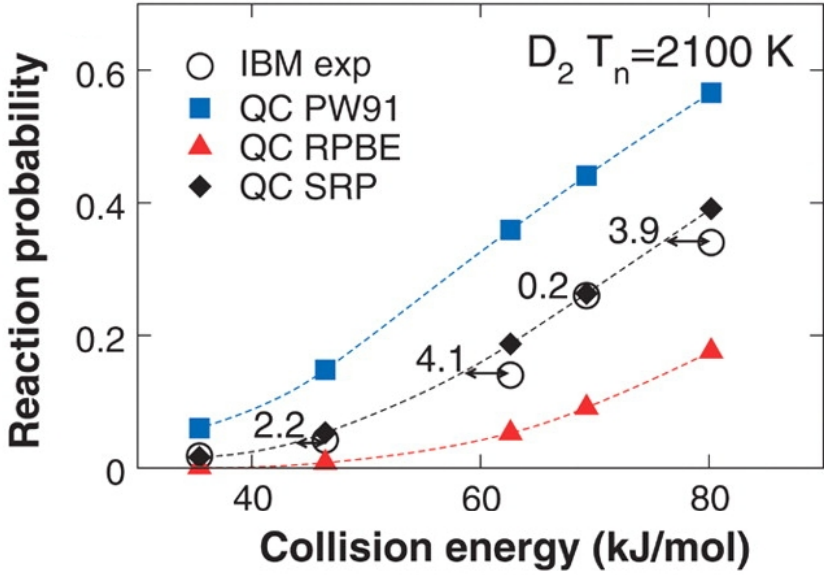
$H_2/Cu(111)$: sites and barriers





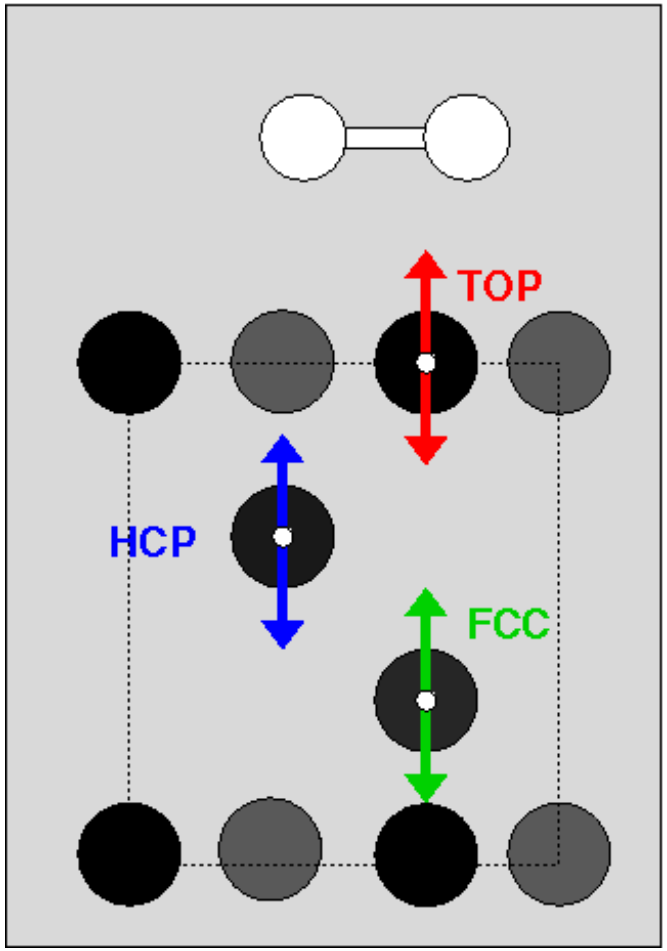
DFT method

- **Supercell**: 2x2 unit cell, 4 Cu layers and 5 vacuum layers
- **Plane Waves**: cutoff 350 eV, 8x8x1 **k** points
- **Functional**: GGA mixed PW91/RPBE
  Specific Reaction Parameter (SRP) approach
  $E^{MIX} = xE^{RPBE} + (1-x)E^{PW91}$ $x = 0.43$
- Calculations with DACAPO code

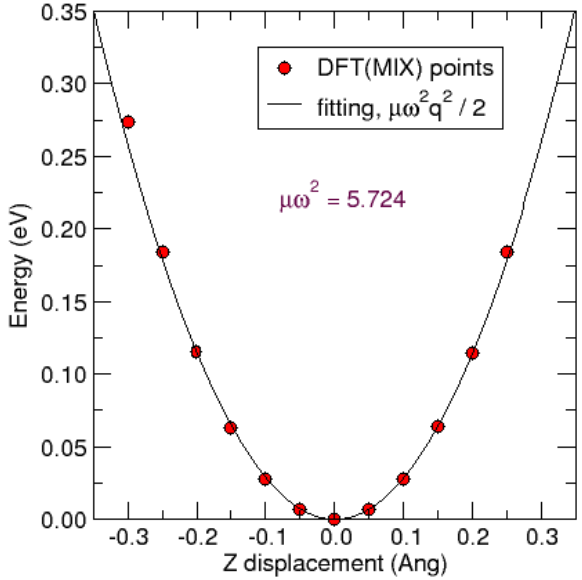


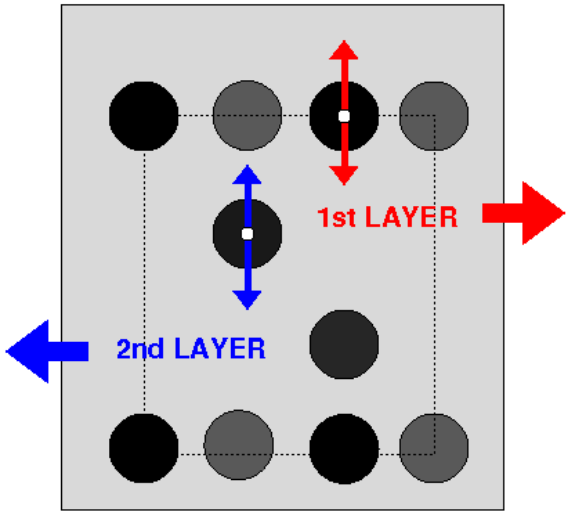
Vibrational Degrees of Freedom of the surface

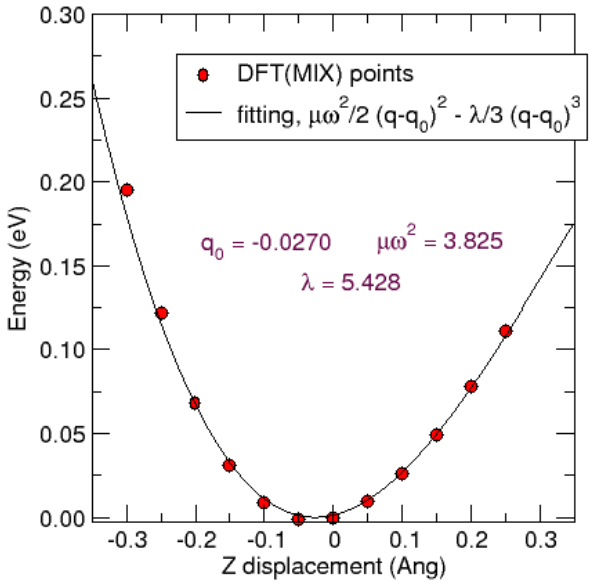
- **Localized** DOF, not collective
- For each layer (up to the 3rd) motion of the **nearest Cu atoms**
- Cu atoms displacement **perpendicular to the surface** (Z direction)



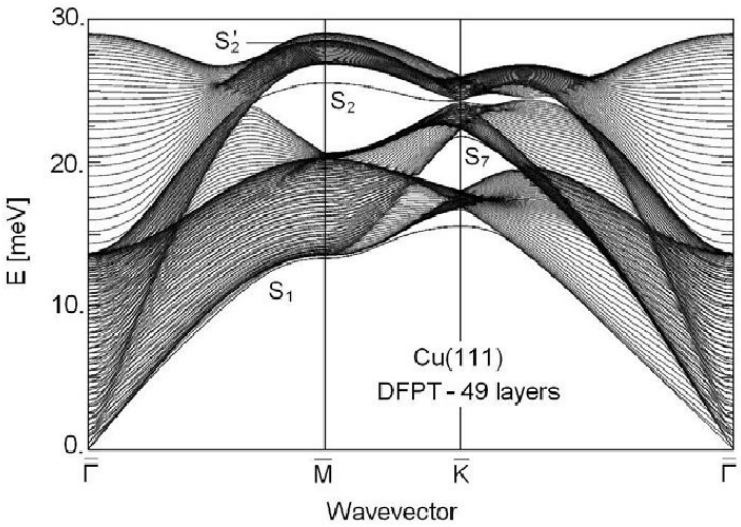
Surface DOF: Potential Energy Curves







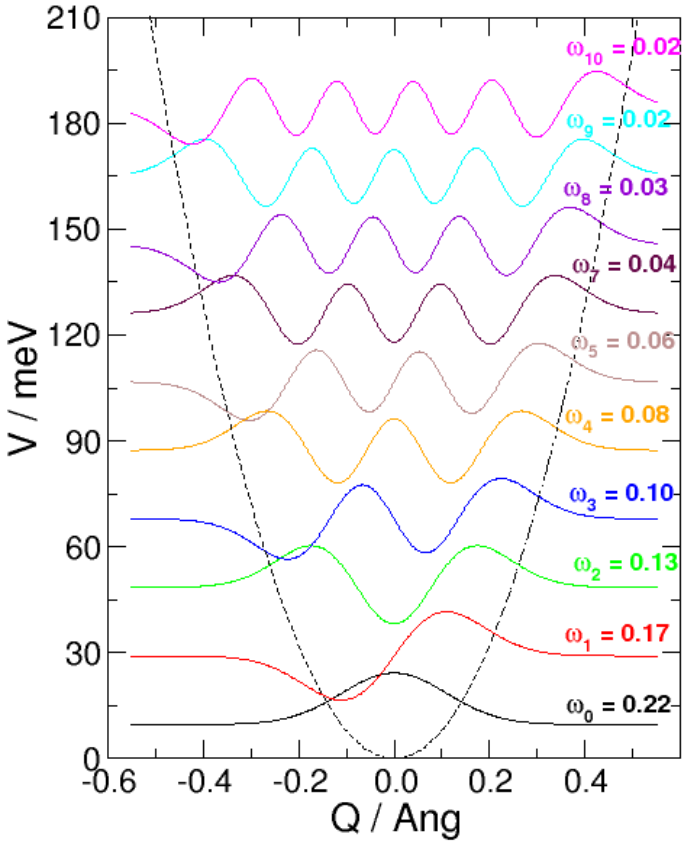
- 1st layer: ω = 16 meV
- 2nd layer: ω = 19 meV
- Debye Model: ω = 14 meV

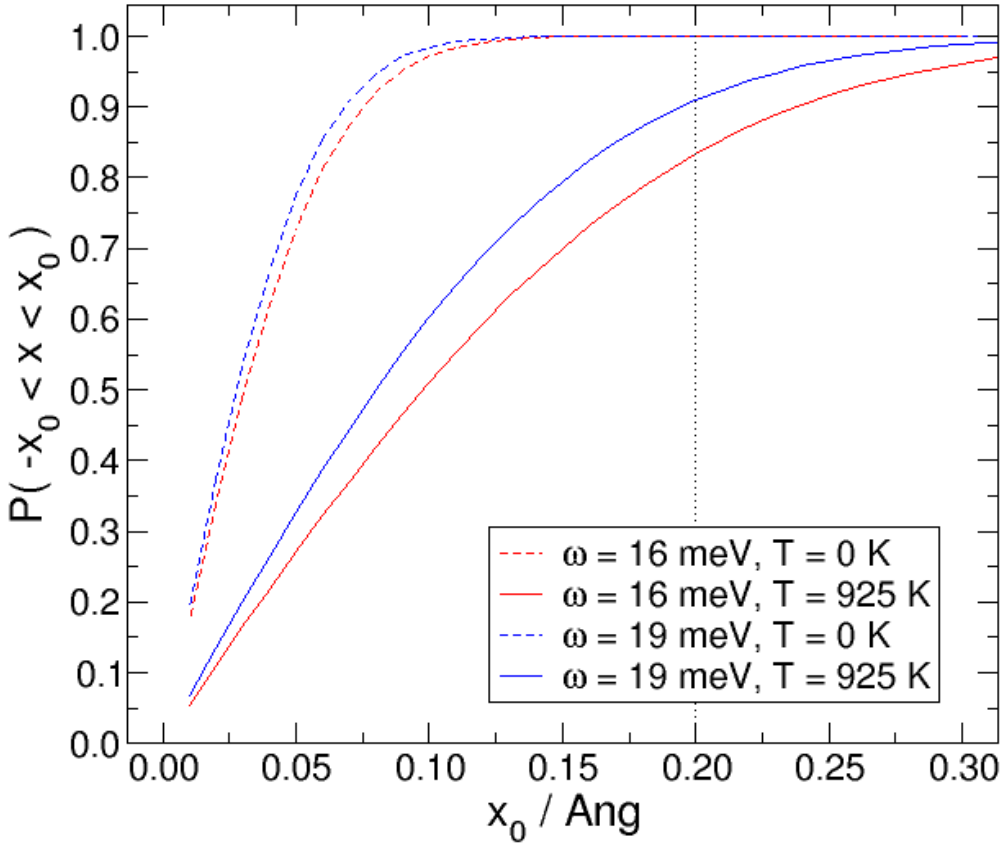


Surface DOF: Position Distribution

$$\mathcal{H}_{HO}\,|n\rangle = E_n\,|n\rangle \qquad \omega_n = \frac{e^{-\beta E_n}}{Z} \qquad \hat{\rho} = \sum_n |n\rangle\,\omega_n\,\langle n|$$

$$P(-x_0 \le x \le x_0) = \sum_n \omega_n\, p_n \qquad p_n = \int_{-x_0}^{x_0} dx\,|\psi_n(x)|^2$$





H_2 - Surface Coupling Potential

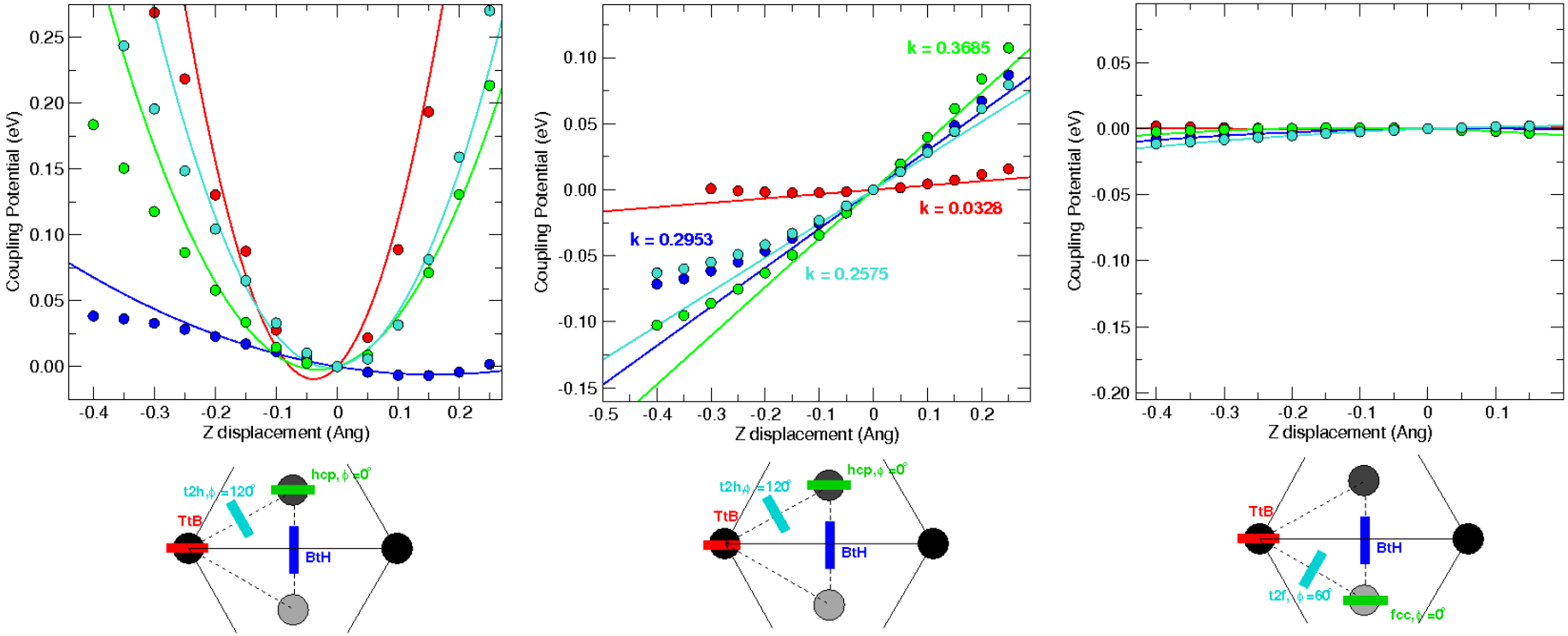
$$V_{7D}(\xi, Q) = V_{H2@Cu}(\xi) + V_{phonon}(Q) + V_{coupling}(\xi, Q)$$

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

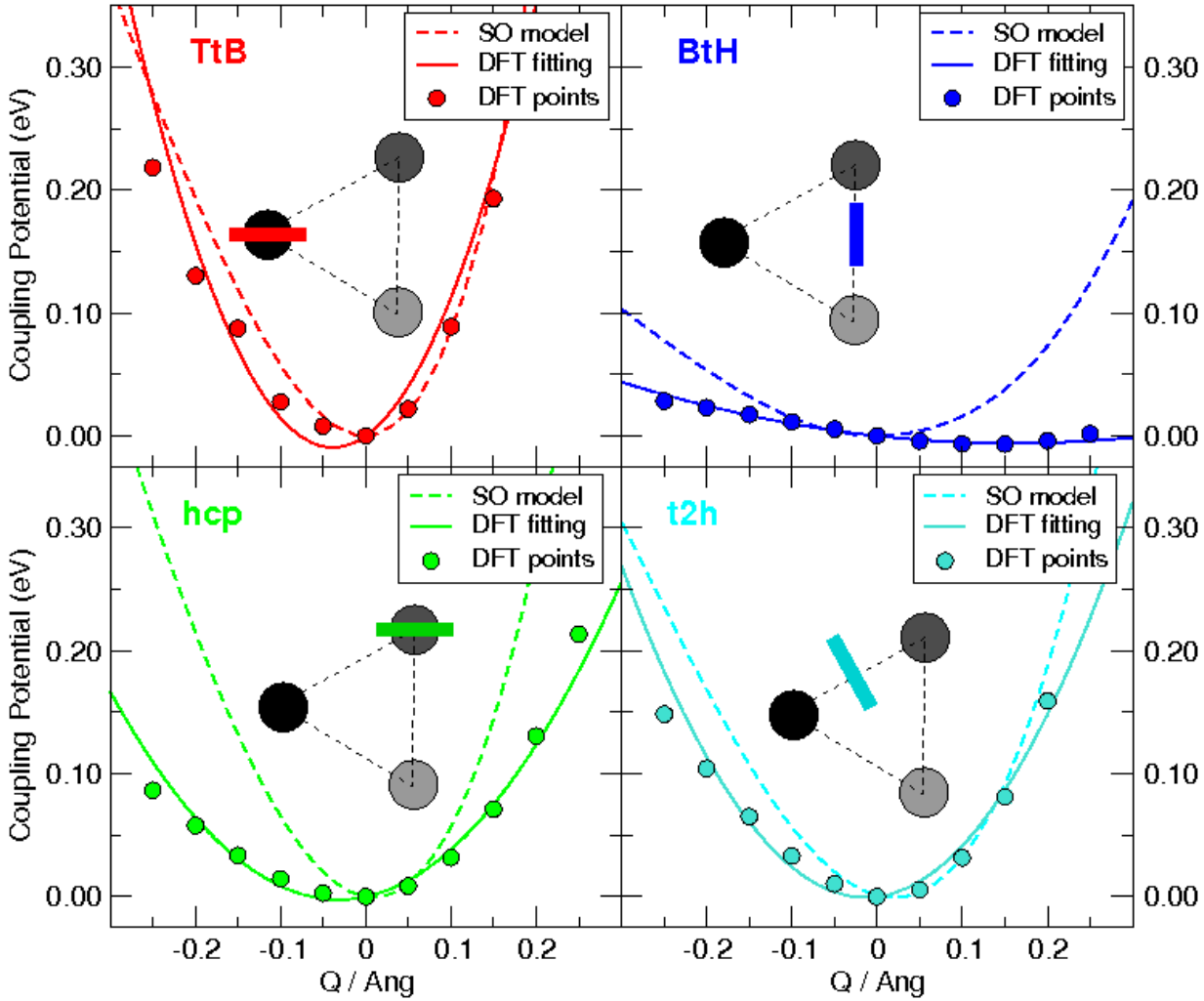
compare different surface DOF by comparing

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

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

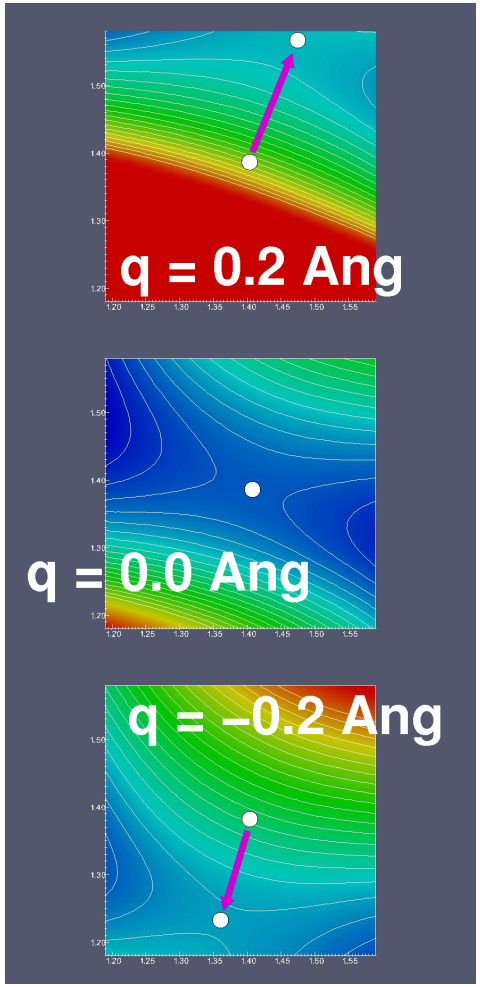


SO Model Coupling



Agreement between SO Model and 1st layer atom motion

Barrier Displacement - 1st Layer Cu motion



Barrier: TtB
Moving Cu atom: TOP

Barrier	Q (Å)	Geometry			
		θ (°)	Δr (Å)	ΔZ (Å)	displ (Å)
BtH	-0.2	90.0	0.01	-0.07	0.07
	0.2	90.0	0.02	0.07	0.07
t2h	-0.2	90.0	-0.04	-0.14	0.14
	0.2	90.0	0.05	0.15	0.16
TtB	-0.2	90.0	-0.04	-0.16	0.16
	0.2	90.0	0.07	0.17	0.18
hcp	-0.2	83.0	-0.05	-0.08	0.09
	0.2	97.0	0.05	0.10	0.11

- **Bigger ΔZ** than Δr
- ΔZ **similar to Q** near the TOP Cu atom
- Tilting angle for hcp barrier, mostly **geometrical effect**

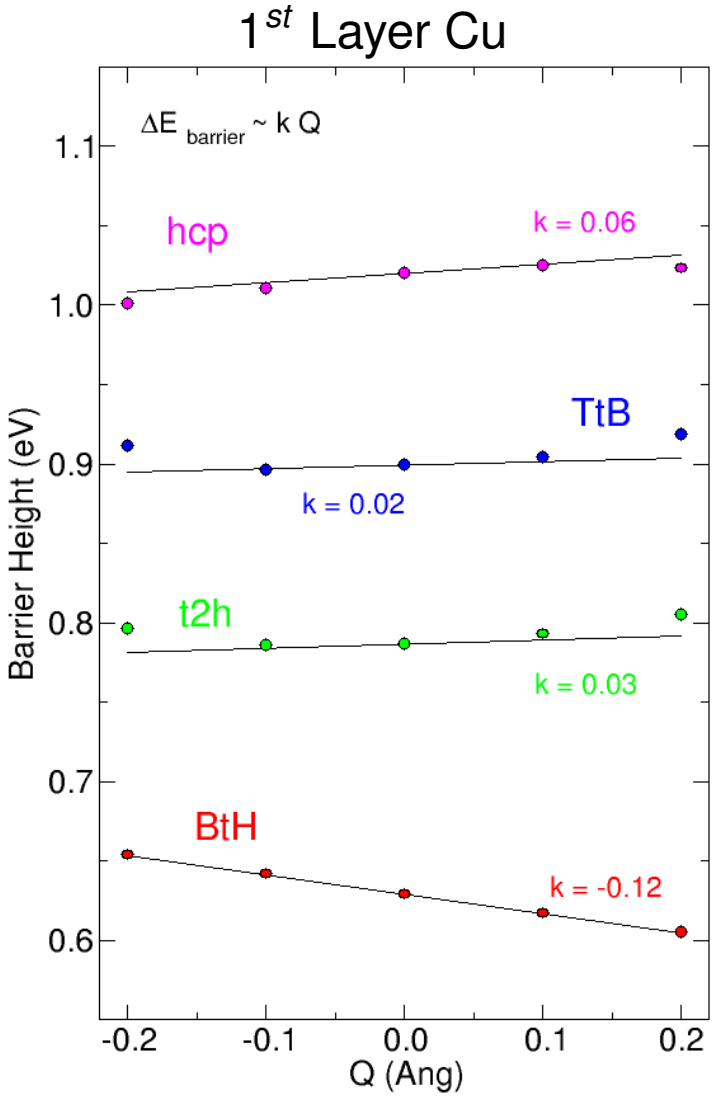
  $\Delta\theta_{geom} = 4.4^\circ$

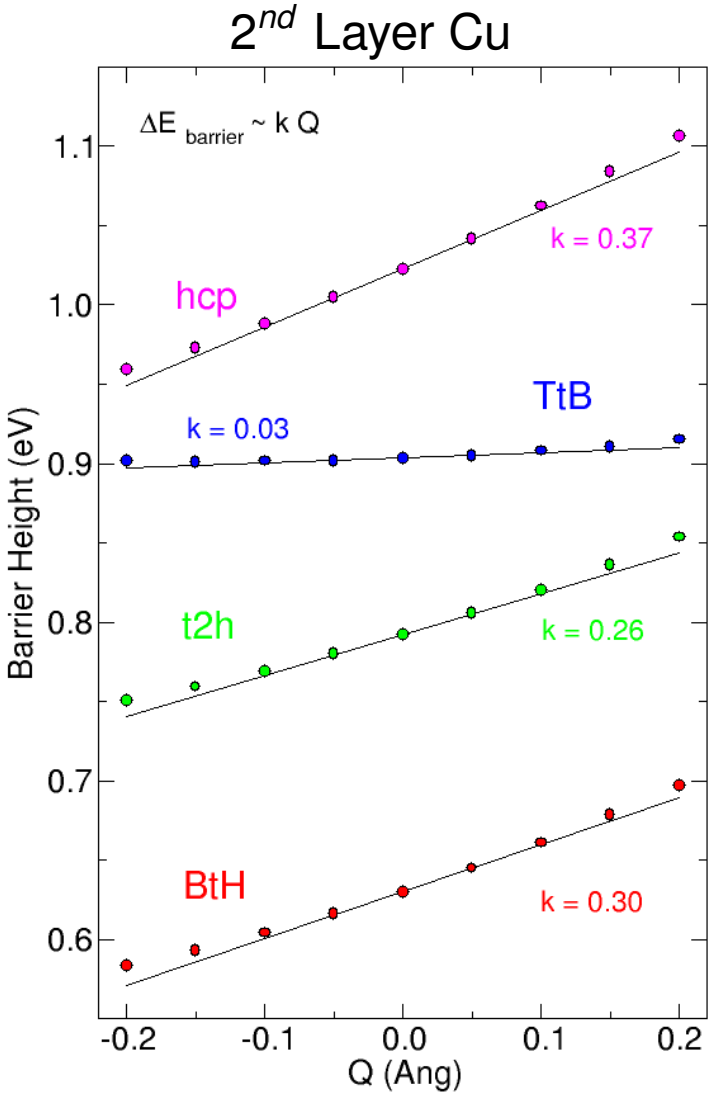
Barrier Displacement - 2nd Layer Cu motion

Barrier	Q (Å)	Geometry			
		θ (°)	Δr (Å)	ΔZ (Å)	displ (Å)
BtH	-0.2	89.7	-0.03	0.01	0.03
	0.2	90.0	0.03	-0.01	0.03
t2h	-0.2	90.0	-0.02	0.00	0.02
	0.2	90.0	0.02	0.00	0.02
TtB	-0.2	90.0	-0.01	0.00	0.01
	0.2	90.1	0.01	0.00	0.01
hcp	-0.2	90.0	0.00	-0.01	0.01
	0.2	90.0	0.00	0.01	0.01

- Very **small displacements**, mainly Δr
- Small tilting (not reliable)

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



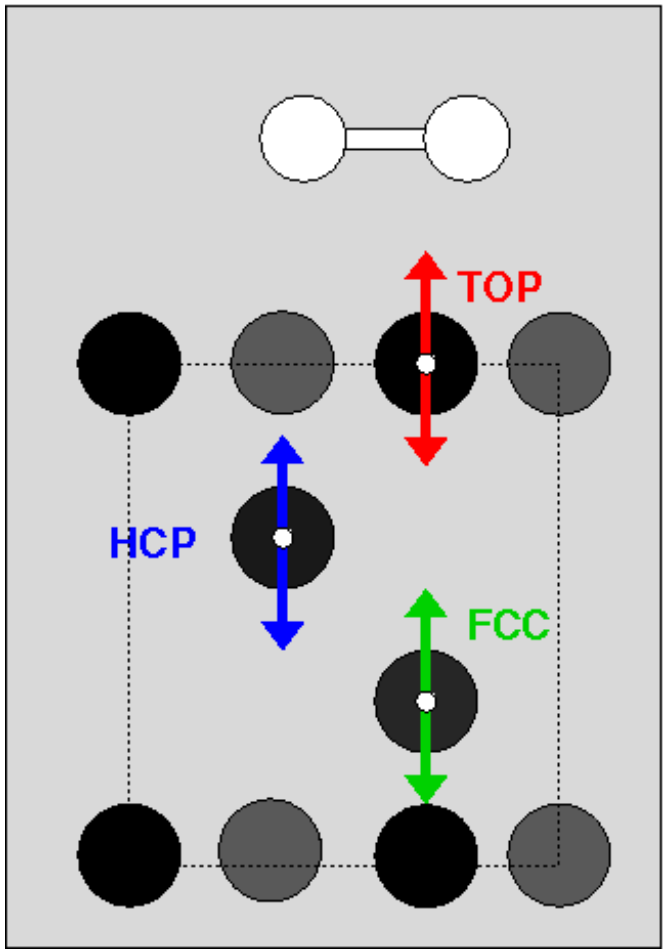


$E_{barrier}$ more sensitive to **2nd Layer motion**!

Conclusions

- 1st layer Cu motion
  - **Shift along Z** of the barrier position
  - **Small changes** in barrier heigth
- 2nd layer Cu motion
  - **Small displacement** of the barriers
  - **Linear dependence** of barrier height on Q
- 3rd layer Cu motion
  - **No coupling** to H_2@$Cu(111)$

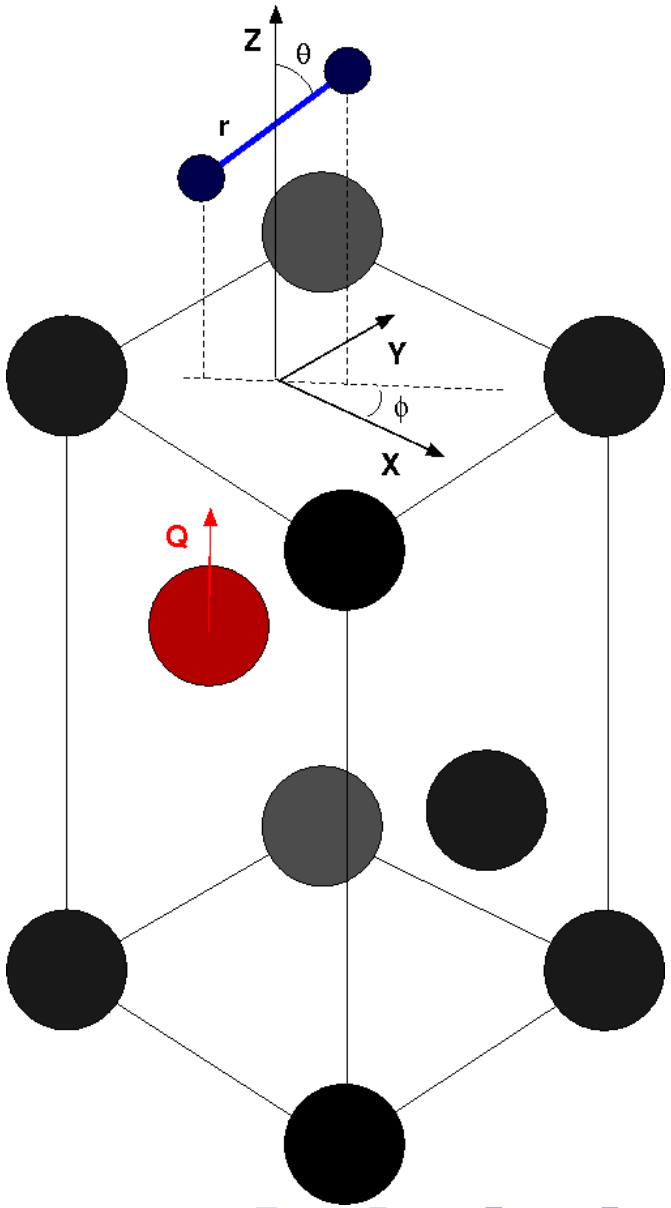
- **SO Model** reproduce the effect of the 1st Layer Cu motion



Further developments

- Investigate the effect of the 2nd layer Cu motion in H_2 dissociation with dynamics
  - Extend the SRP **Potential Energy Surface** including another DOF
  - Compute dynamical properties with **7D Quantum Dynamics**
  - Check the validity of **Vibrational Sudden Approximation**:

$$P_{\nu_r\, j\, m_j\, \nu_Q}(\mathbf{k}) = \left\langle \phi_{\nu_Q}(Q) \middle| P_{\nu_r\, j\, m_j}(\mathbf{k}; Q) | \phi_{\nu_Q}(Q) \right\rangle$$



Acknowledgments

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... and you, for your attention!

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