Lecture in the course “Surface Physics and Nano Physics” 2008

Quantum wells and Dots on surfaces

Bo Hellsing
Department of Physics, Göteborg University, Göteborg, S

Collaborators:

QW

Johan Carlsson, Göteborg University
Lars Walldén, Chalmers

QD

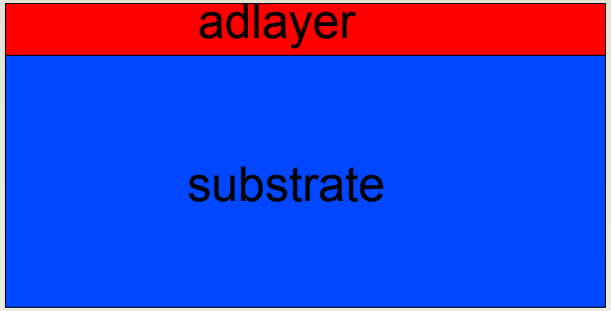
V. Lindberg, Växjö University
T. Petersson, Växjö University

T. Torsti, Helsinki University of Technology
M.J. Puska, Helsinki University of Technology

Nano scale electron confinement - quantum phenomena

1D – Quantum well

Atomic layers on a substrate

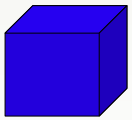


2D – Quantum wire

Chain of atoms

3D – Quantum dot

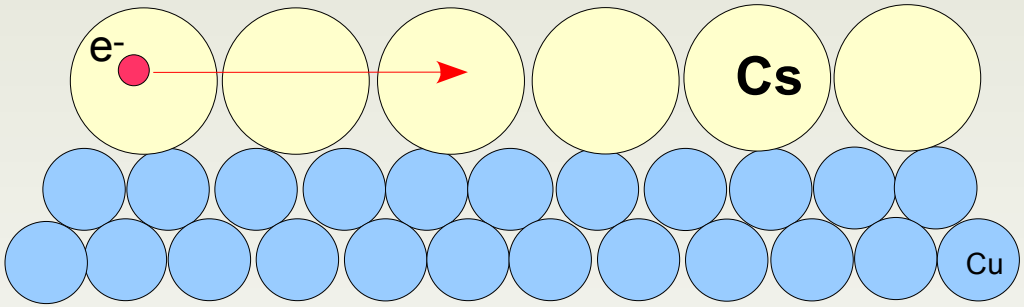
Custer of atoms on surfaces, 5-20 atoms



Quantum well

Monolayer of Na on Cu(111)

Example: 1 ML (2x2) Cs on Cu(111)

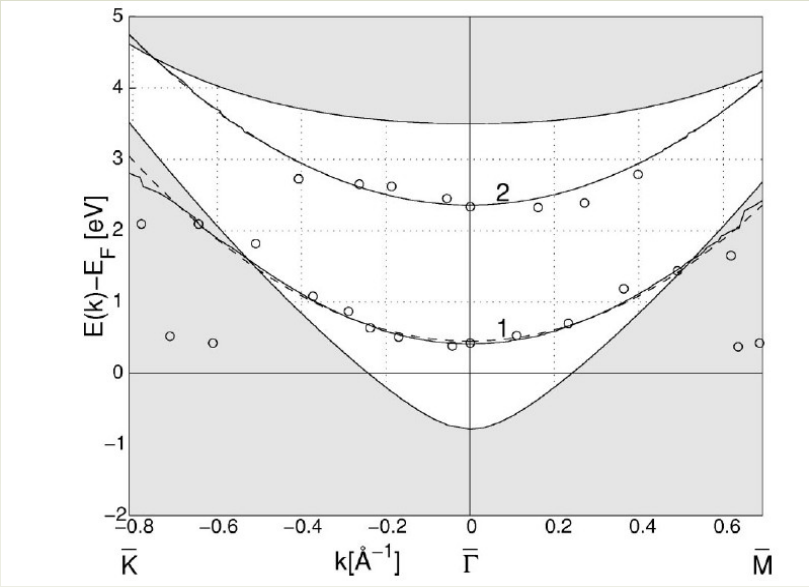


QWS bands in bulk band gap

Low Na coverage

$\theta = 0.25$

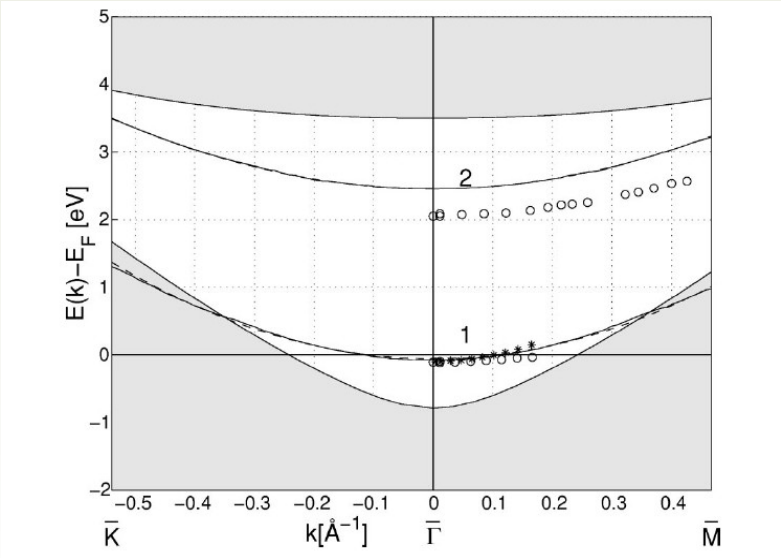
(2x2 structure)



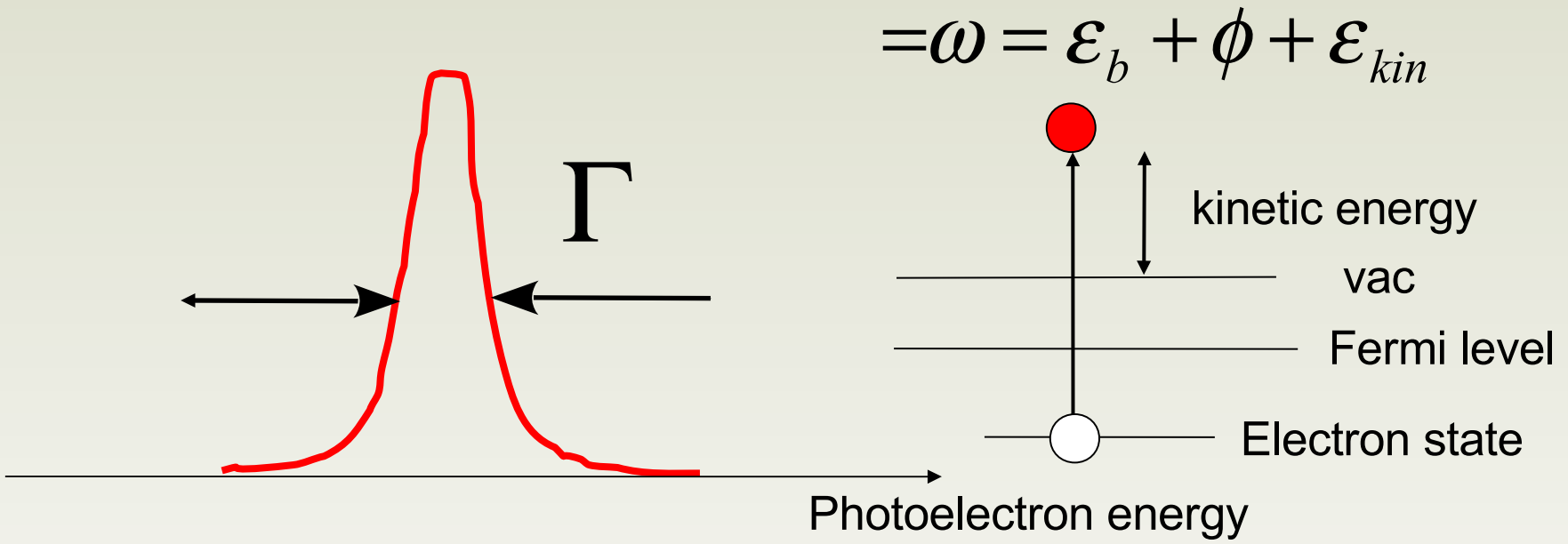
Complete Na monolayer coverage

$\theta = 0.44$

(3/2 x 3/2 structure)



Line width in a PES experiment



$$\Gamma = \Gamma_{in\,\mathrm{hom}} + \Gamma_{elast} + \Gamma_{e-e} + \Gamma_{e-p}$$

Γ_{elast} = elastic broadening (resonance broadening)

$\Gamma_{in\,\mathrm{hom}}$ = inhomogeneous broadening (inperfections)

$\Gamma_{e-e} + \Gamma_{e-p}$ = Inelastic broadening

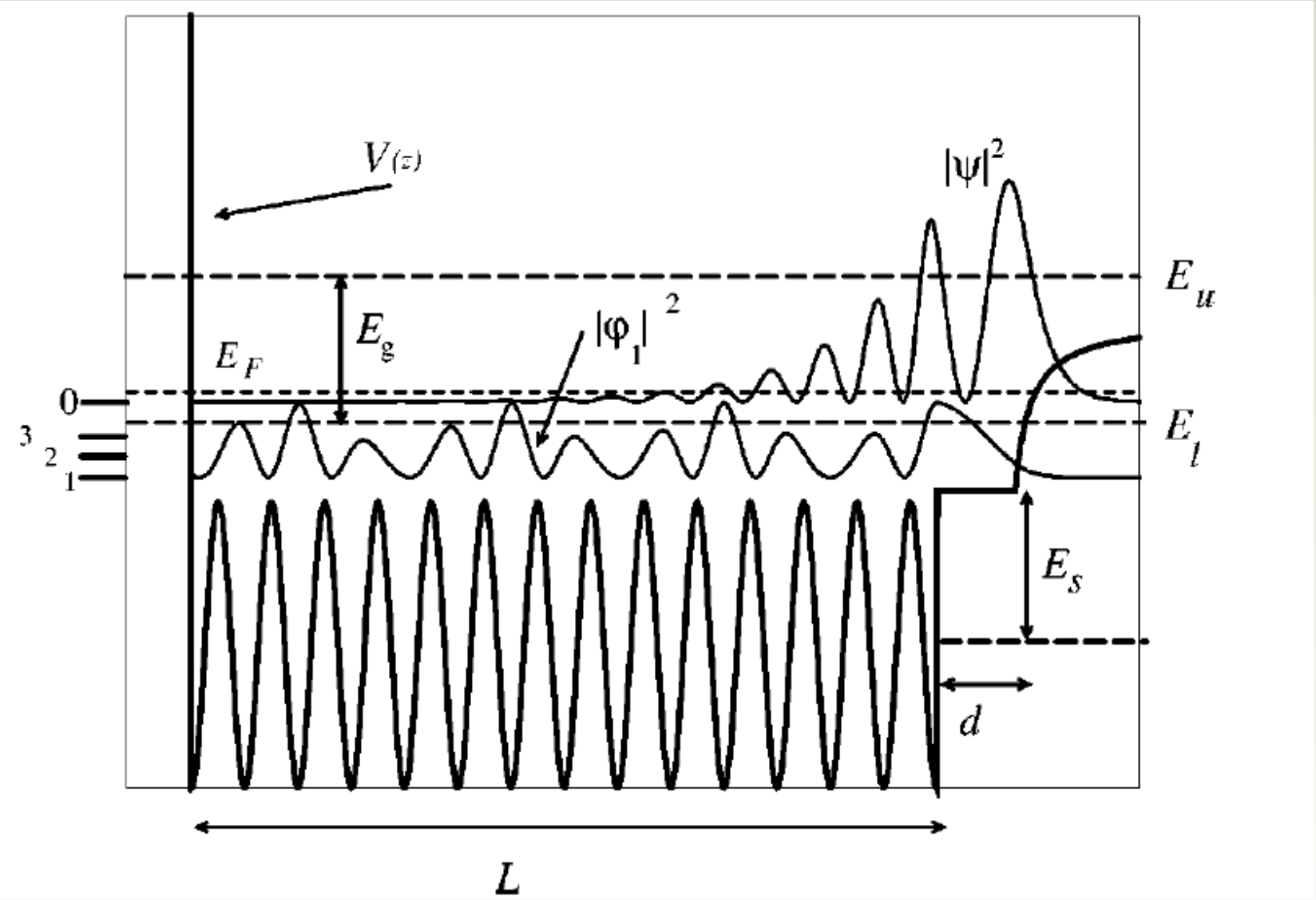
Decay of QW state holes

(electron-electron and electron-phonon scattering)

LIFETIME BROADENING (inverse lifetime τ) :

$$\Gamma = \frac{\tau}{\tau} \quad , \quad \begin{aligned} 1\,meV &\Leftrightarrow 0.6\,ps \\ 10\,meV &\Leftrightarrow 60\,fs \\ 1\,eV &\Leftrightarrow 0.6\,fs \end{aligned}$$

Model calculation



Density functional theory (DFT) calculation

Quanum well state wave function

$$|\psi_{QWS}(\vec{x})|^2$$

Adsorbate induced electron charge density

$$\Delta\rho(\vec{x})$$

z

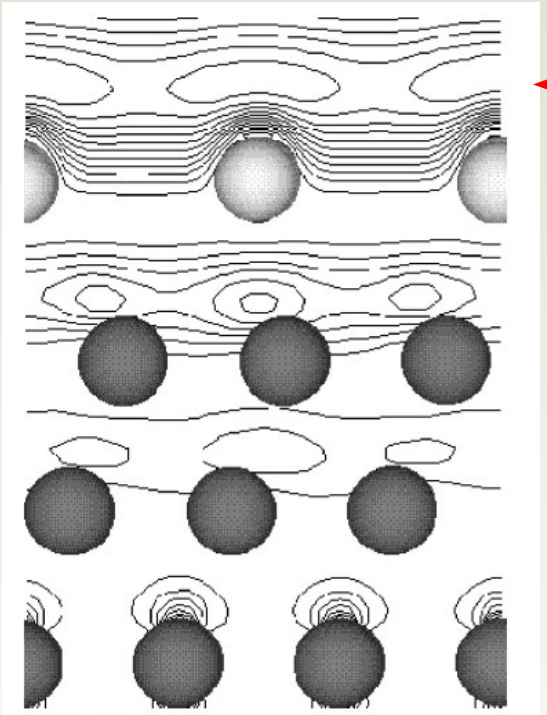


FIG. 10. The local density of states $\rho_{\mathbf{k},\epsilon}(\mathbf{r})$ of the quantum-well state at the $\bar{\Gamma}$ point for the saturated monolayer. The Cu atoms are dark gray and the Na atoms are light gray. The isodensity lines have a line spacing of 5×10^{-5} $e/\text{Å}^3$ and the contour line of lowest value corresponds to 5×10^{-5} $e/\text{Å}^3$. The peak amplitude of this state is localized at the boundary between the Na layer and the vacuum boundary and the amplitude decays rapidly into the Cu substrate.

MAX

MIN

MAX

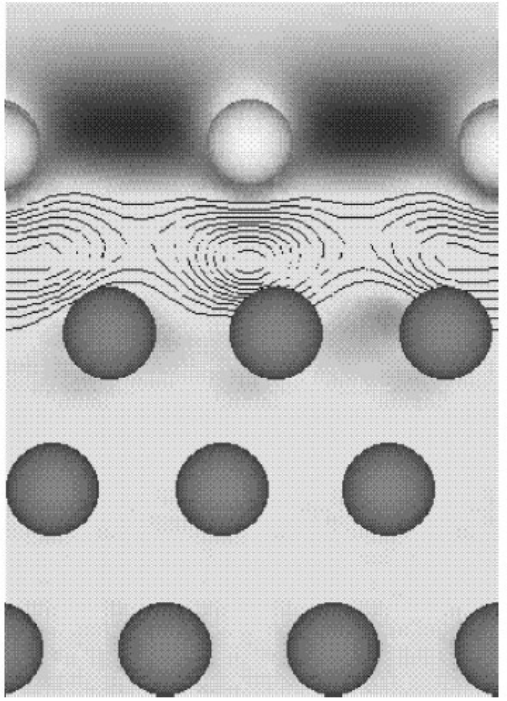


FIG. 4. The adsorbate-induced charge density $\Delta\rho$ of the (3/2 $\times$3/2) structure. The Cu atoms are dark gray and the Na atoms are light gray. The cut passes through the sodium adatoms. The charge accumulation is shown by isodensity lines of spacing 2.5×10^{-3} $e/\text{Å}^3$ and the contour line of lowest value corresponds to 2.5×10^{-3} $e/\text{Å}^3$. The charge depletion is indicated by shading from black to white in the density range $[-0.01,0]$ $e/\text{Å}^3$.

QW physics

Catalysis: Manipulation of surface localized electrons

Fundamentals: Lifetimes of photo-holes generated in Photoemission gives information about the importance of fundamental scattering processes electron-electron and electron-phonon scattering.

REFERENCES

High- Resolution Photoemission from Tunable Quantum Well: Cu(111)/Na. Phys. Rev. B, 56(1997)1593 A. Carlsson, B. Hellsing, S.-Å Lindgren and L. Walldén

First-principles invetsigation of the quantum-well system Na on Cu(111) Phys. Rev. B, 61(2000)13973 J. Carlsson and B. Hellsing.

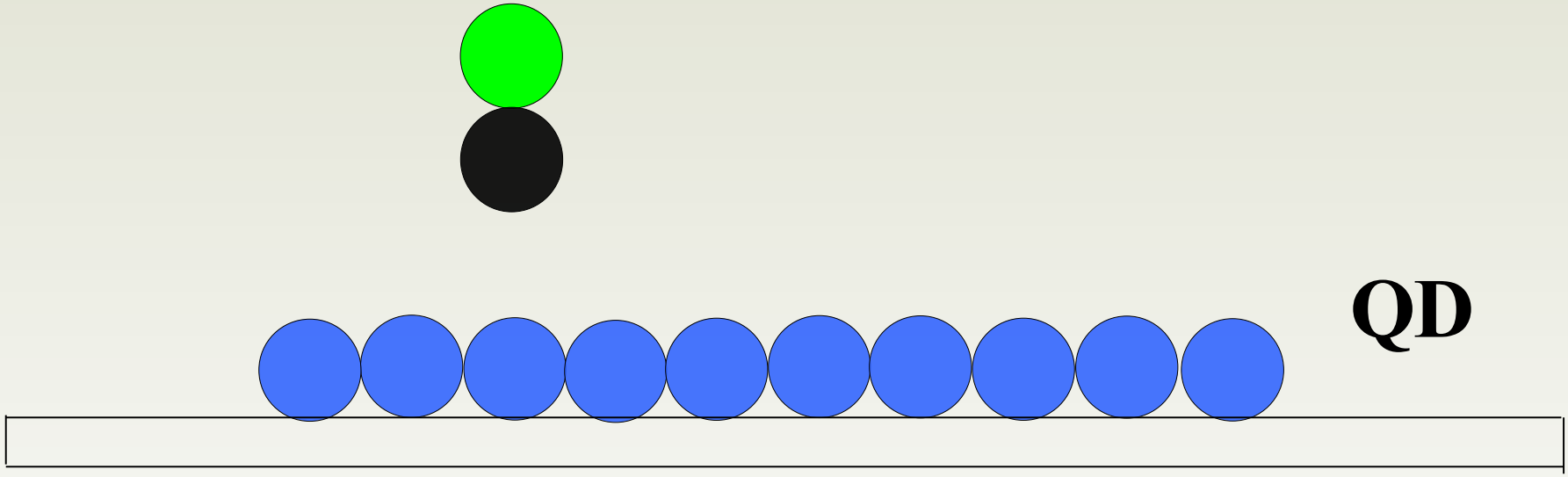
Phonon-induced decay of a quantum-well hole: One monolayer of Na on Cu(111) Phys. Rev. B, 61(2000)2343 B. Hellsing, J. Carlsson, L. Wallden and S.Å Lindgren.

Two dimensional localization of fast electrons in p(2x2)-Cs/Cu(111) Phys. Rev. B 76 (2007) 1 , V. Chis, S. Caravati, G. Butti, M.I. Trioni, P. Cabrera-Sanfelix, A. Arnau and B. Hellsing

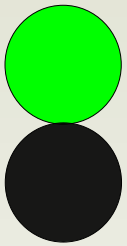
Overlayer resonance and quantum well state of Cs/Cu(111) studied with angel-resolved photoemission, LEED and first principles calculations Physical Review B 75(2007)155403, M. Breitholtz, V. Chis, B. Hellsing, S.-Å. Lindgren and L. Wallden

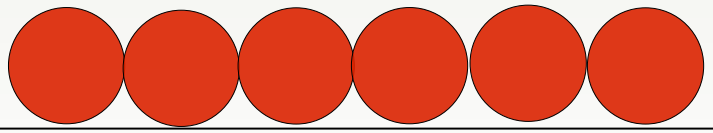
Quantum Dot

Non-reactive Quantum Dot



Reactive Quantum Dot





QD

Adsorbed Quantum Dots

- Low dimensional structures
- Relatively stable at low temperatures
- Quantum size effects of reactivity ?

Right: Na/Cu(111) 590 x 590 $Å^2$, Kliewer and Berndt 2000.

Step 1 :

Electron structure of the QD

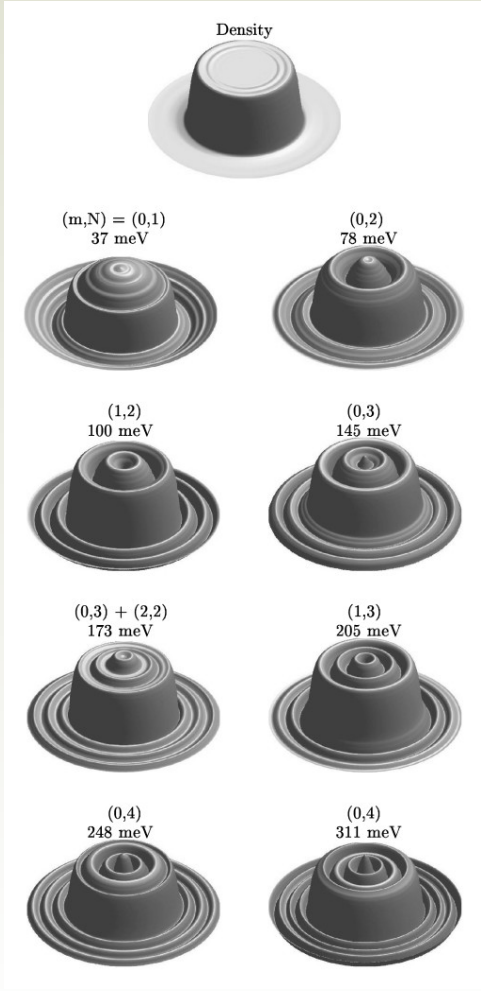
Na Quantum Dot on Na/Cu(111)

MIKA-DFT calculation for a cylindrical QD

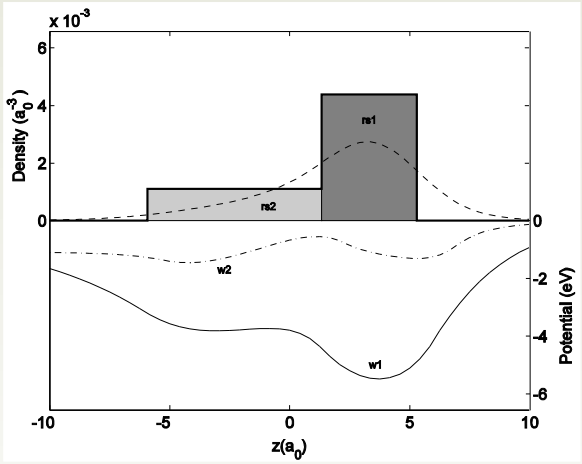
LDOS

QD: 550 electrons

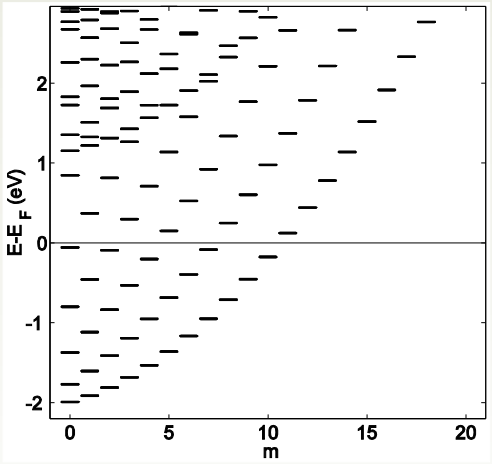
Diameter = 6 nm



Jellium model



Energy spectra



REFERENCES:

Phys. Rev. B **61**, 13973 (2000)

Surf. Science **506**, 297 (2002)

Phys. Rev. B **66**, 235420 (2002)

Local density of states (LDOS):

$$\rho(\vec{x},\varepsilon) = \sum_{\substack{n \\ occ}} |\psi_n(\vec{x})|^2 \, \delta(\varepsilon - \varepsilon_n)$$

Density of states:

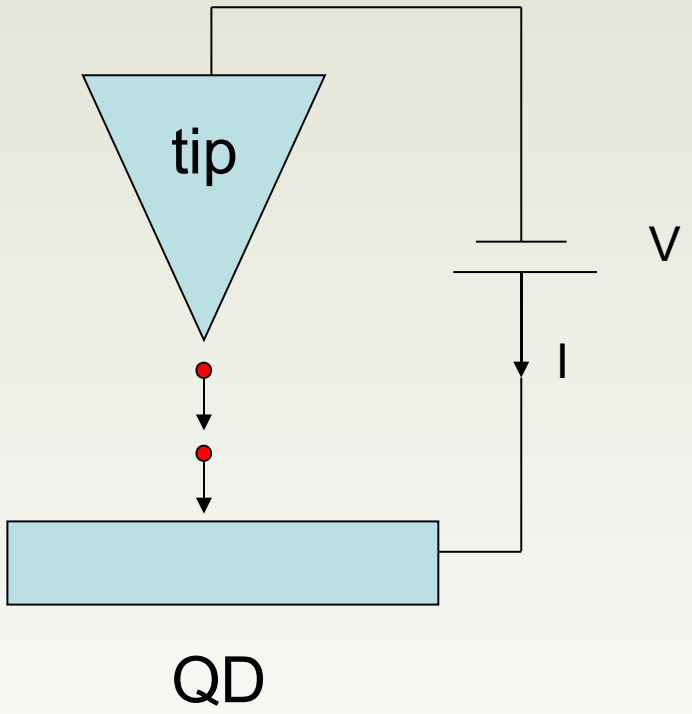
$$\rho(\varepsilon) = \int \rho(\vec{x},\varepsilon)\, d\vec{x} = \int \sum_{\substack{n \\ occ}} |\psi_n(\vec{x})|^2 \, \delta(\varepsilon - \varepsilon_n)\, d\vec{x} =$$

$$\sum_{\substack{n \\ occ}} \{ \int |\psi_n(\vec{x})|^2 \, d\vec{x} \} \, \delta(\varepsilon - \varepsilon_n) = \sum_{\substack{n \\ occ}} 1 \, \delta(\varepsilon - \varepsilon_n) = \sum_{\substack{n \\ occ}} \delta(\varepsilon - \varepsilon_n)$$

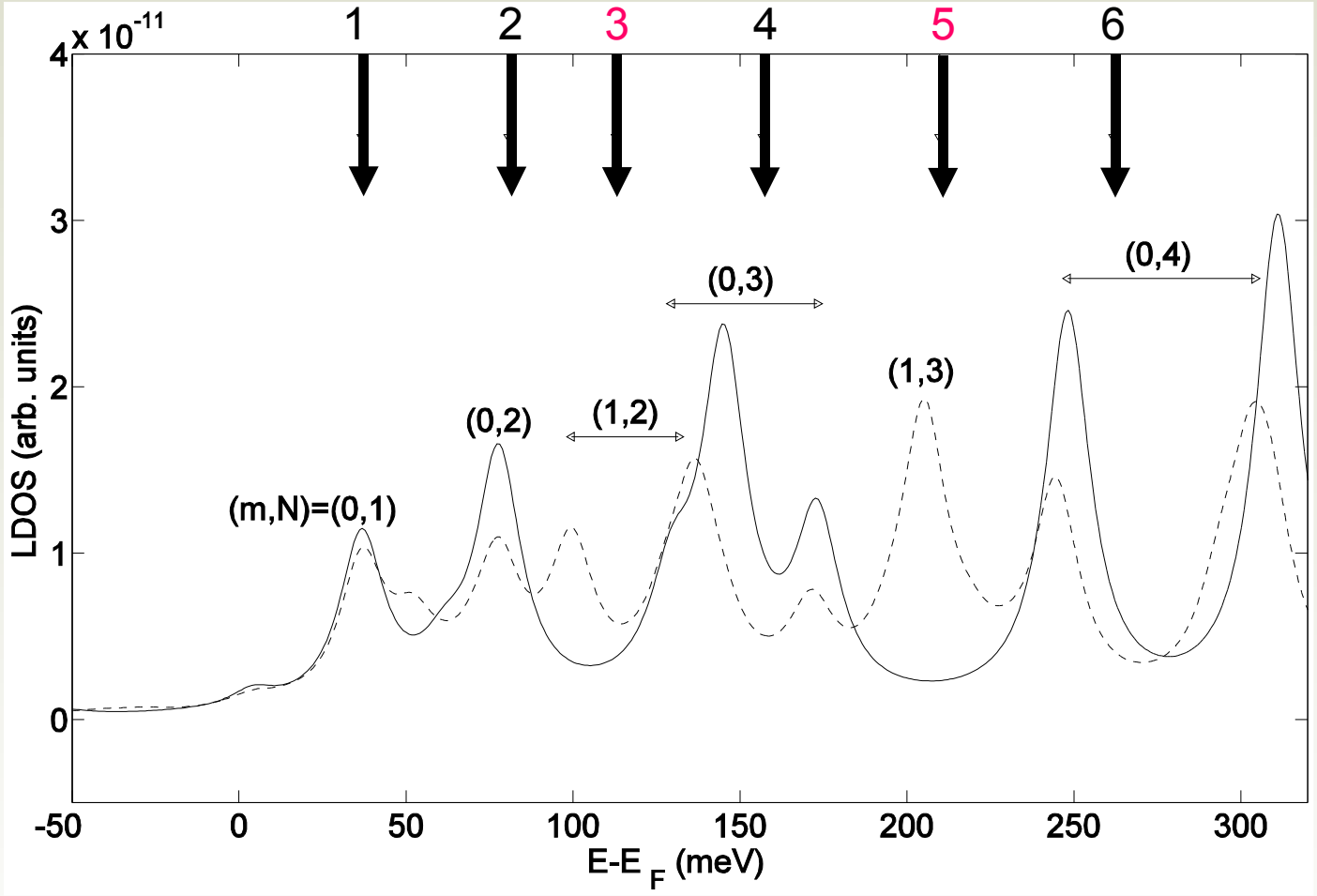
Scanning Tunneling Spectroscopy STS

The differential current is proportional to the LDOS

$$\frac{dI}{dV} \propto \rho(\vec{x}, \varepsilon_F \pm eV)$$



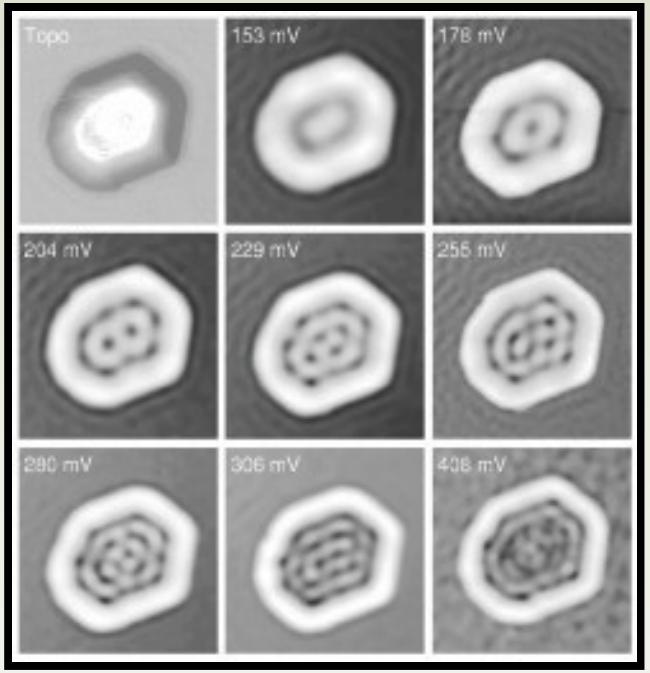
LDOS 6 Å above the QD

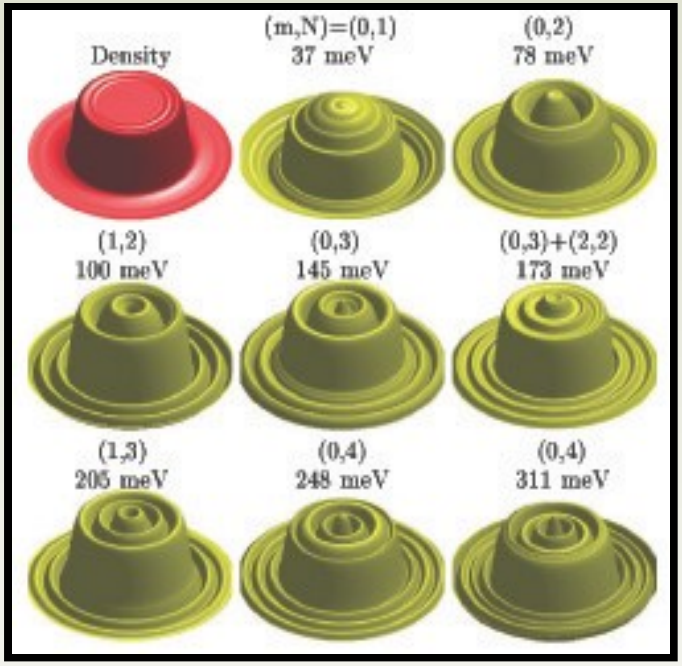


STM DATA

CALCULATION

Electron Density and LDOS





Left: STM topographic scan and dI/dV recordings, Kliewer and Berndt 2000.

Right: Calculations of the Electron Density and LDOS.

Step 2:

Molecule - QD charge transfer

Model calculation

CO molecule approaching the QD
Newns-Anderson model

$$H = \varepsilon_a c_a^+ c_a + \sum_k \varepsilon_k c_k^+ c_k + \sum_k \{V_{ak} c_k^+ c_a + V_{ak}^+ c_a^+ c_k\}$$

$|a> = 2\pi^*$ *orbital of CO*

$|k> =$ *QD states*

The hopping matrix elements between the $2\pi^*$ *orbital and the QD states*:

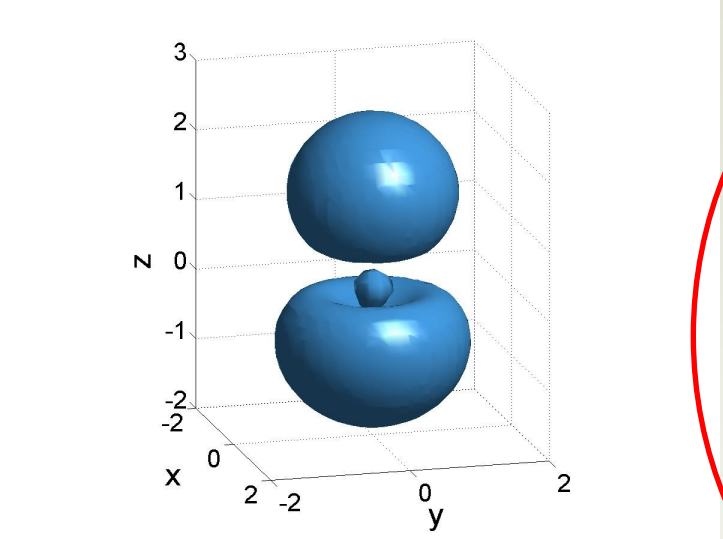
$$V_{ak} = <a|V|k> \approx V_0 <a|k>$$

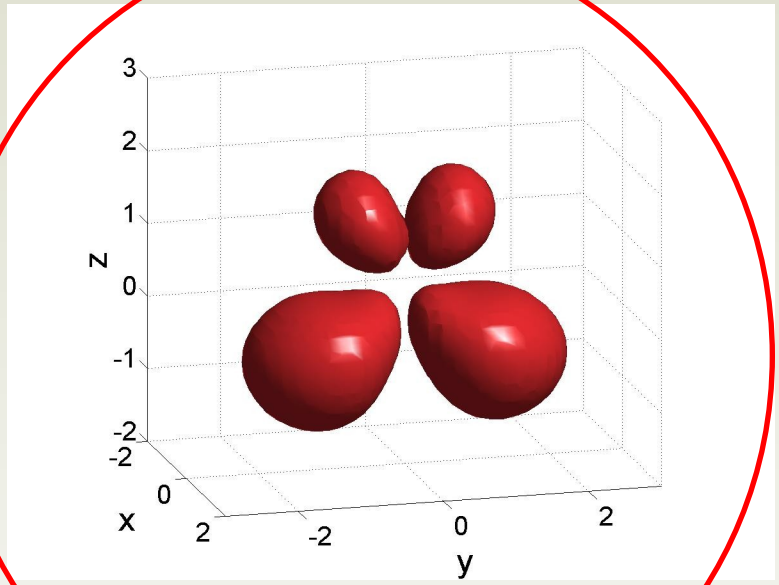
|k> states of the QD

- Cylindrical step potential

$$V(r,z,\phi)=\begin{cases}0, & r<a,\ -\dfrac{L}{2}<z<\dfrac{L}{2}\\ V_0, & elsewhere\end{cases}$$

|a> state of CO

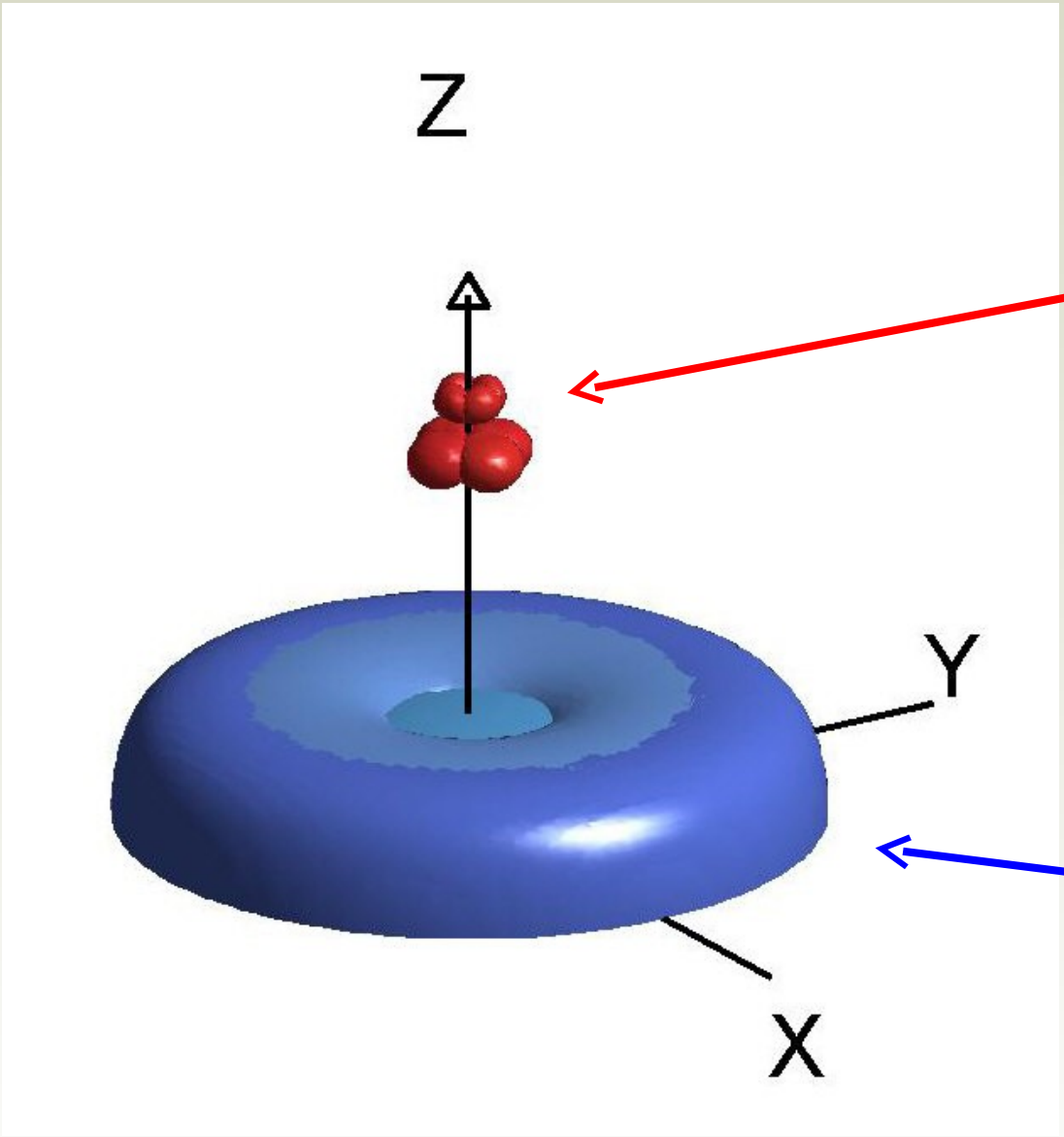




5σ orbital

$2\pi^*$ orbital **LUMO**

Electron affinity: -1.5 eV



LUMO of CO
$2\pi^*$ orbital (m=1)

QD

Charge transfer

- Projected density of states

$$\rho_{aa}^{\sigma}(\epsilon)=\frac{1}{\pi}\frac{\Delta(\epsilon)}{\left[\epsilon-\epsilon_{\sigma}-\Lambda(\epsilon)\right]^2+\Delta^2(\epsilon)}$$

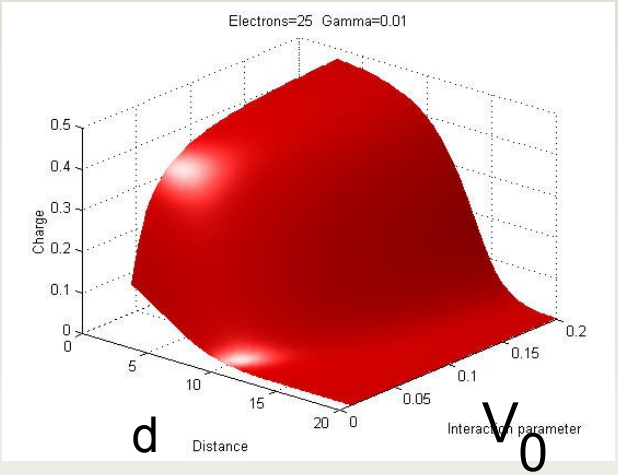
$$\Delta(\epsilon)=\pi\sum_k\left|V_{ak}\right|^2\delta(\epsilon-\epsilon_k)$$

$$\Lambda(\epsilon)=\frac{1}{\pi}P\int_{-\infty}^{\infty}\frac{\Delta(\epsilon')d\epsilon'}{\epsilon-\epsilon'}$$

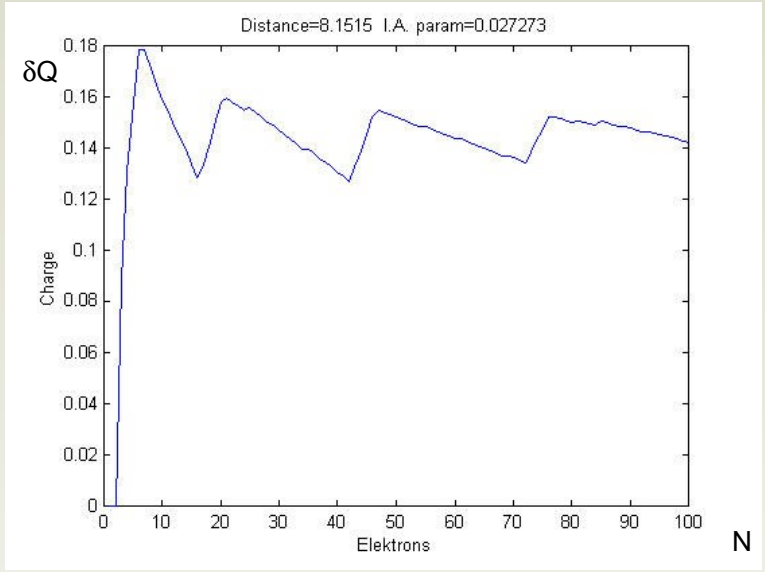
- Total occupation for the $2\pi^*$ orbital

$$N_a^{\sigma}=2\int_{-\infty}^{\epsilon_F}\rho_{aa}^{\sigma}(\epsilon)d\epsilon$$

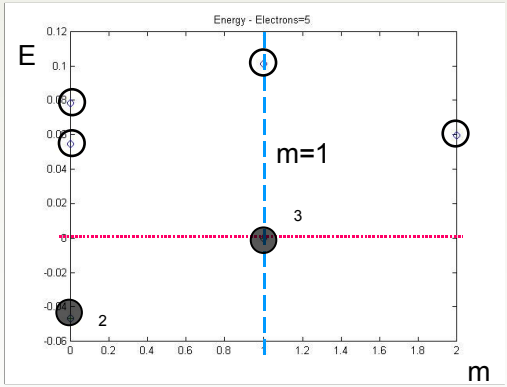
Quantum and Symmetry effects in charge transfer



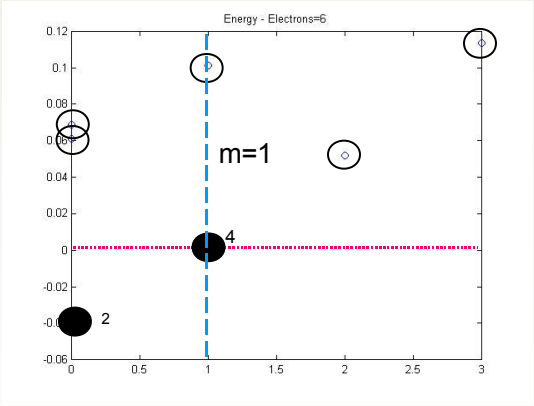
Charge transfer (V_0,d)



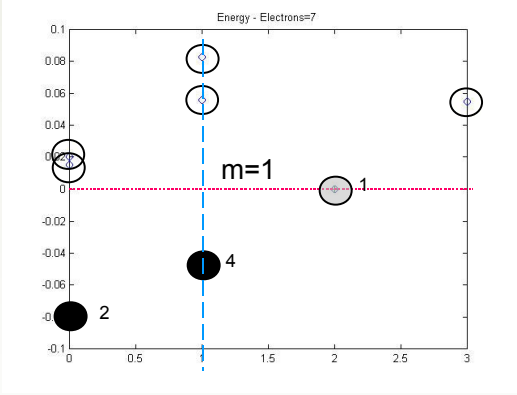
Quantum effect of charge transfer



5 electron QD



6 electron QD



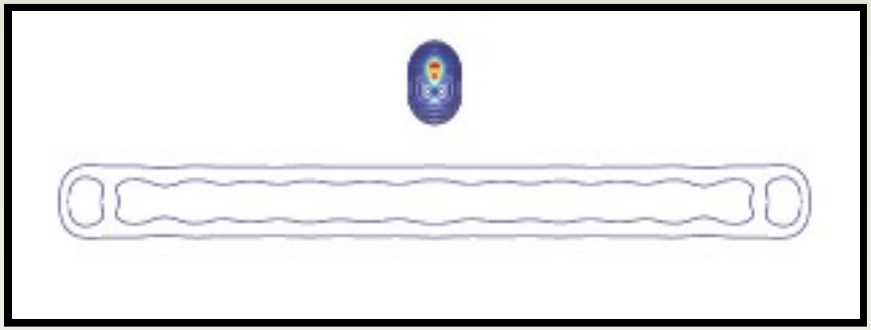
7 electron QD

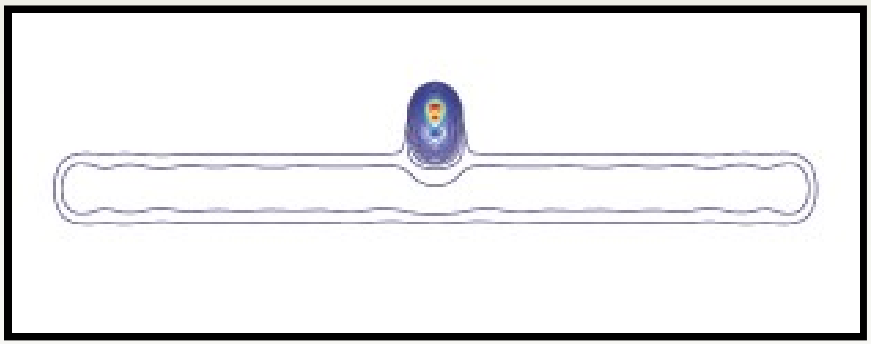
Step 2:

Molecule - QD interaction

DFT calculation

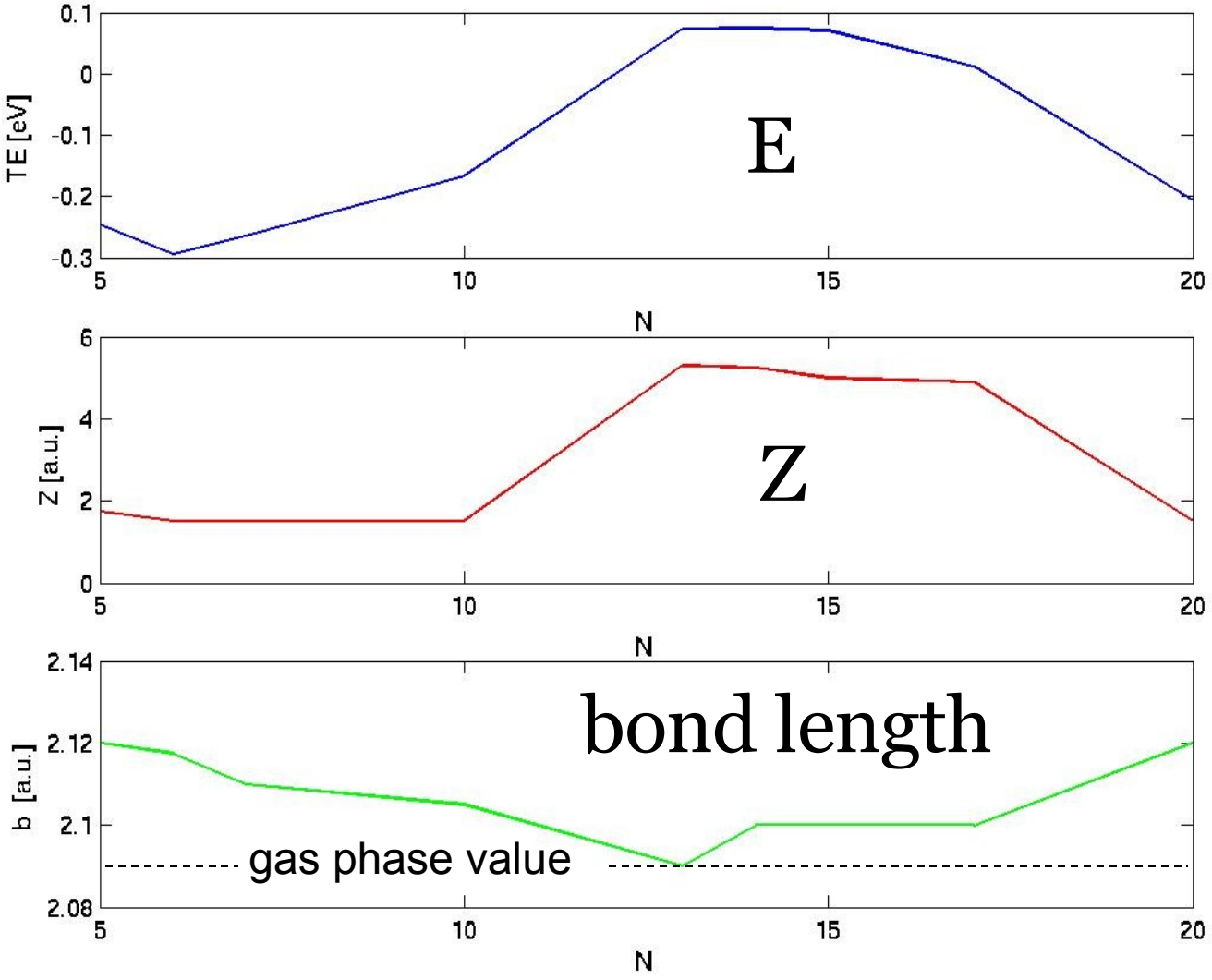
CO-QD interaction (DFT calculation)



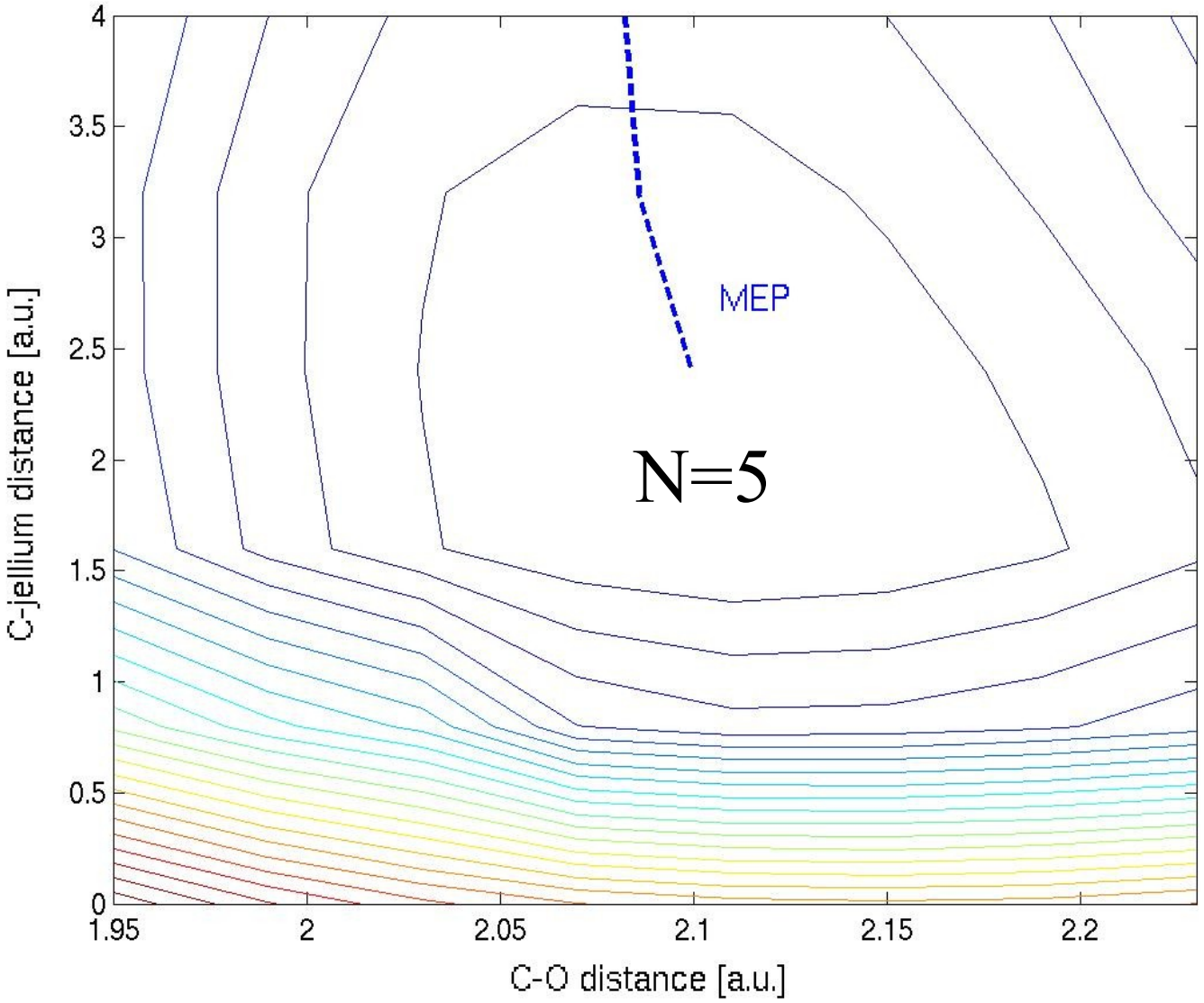


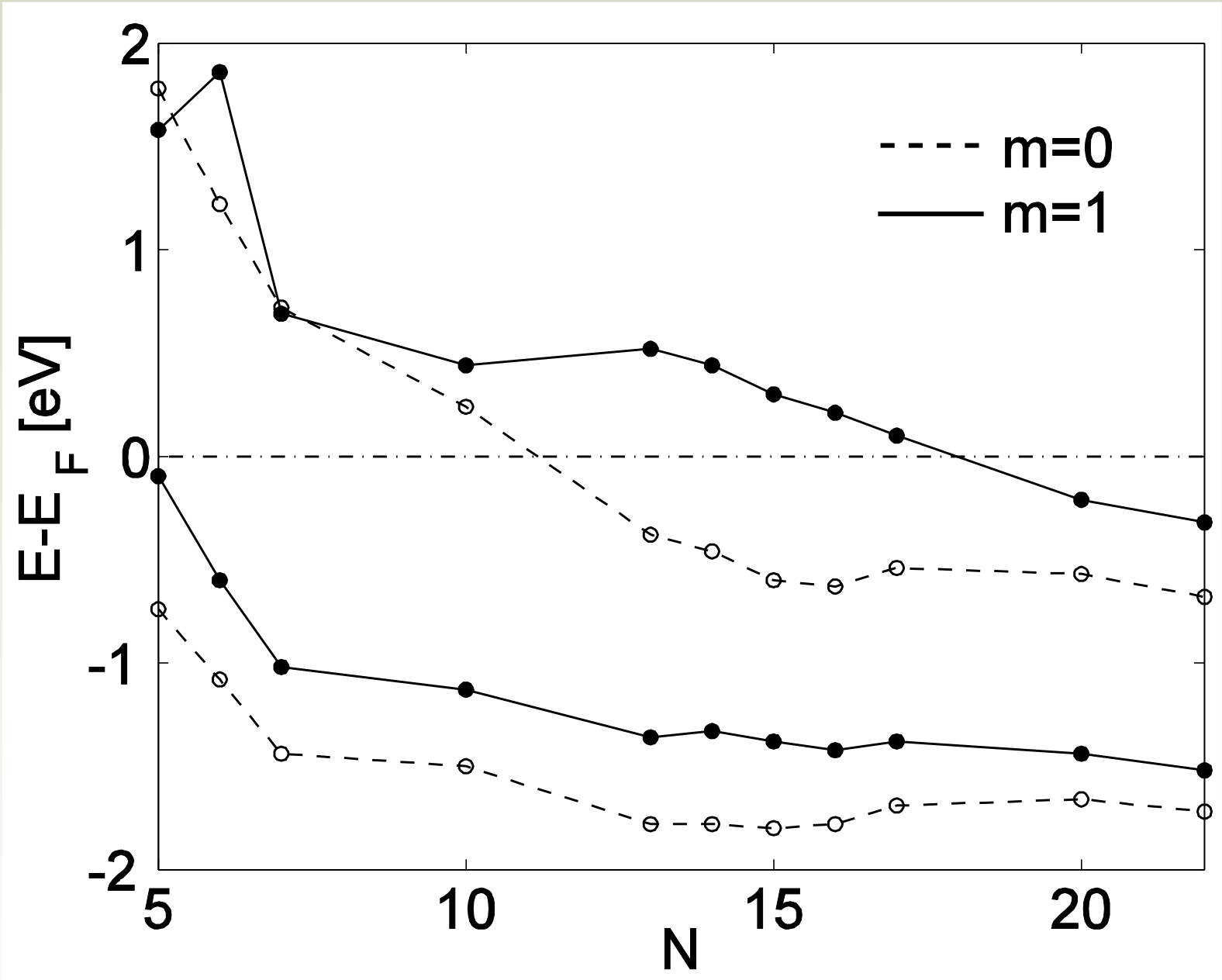
- Quantum size effect ?
- Mechanism ?

Total Energy analysis

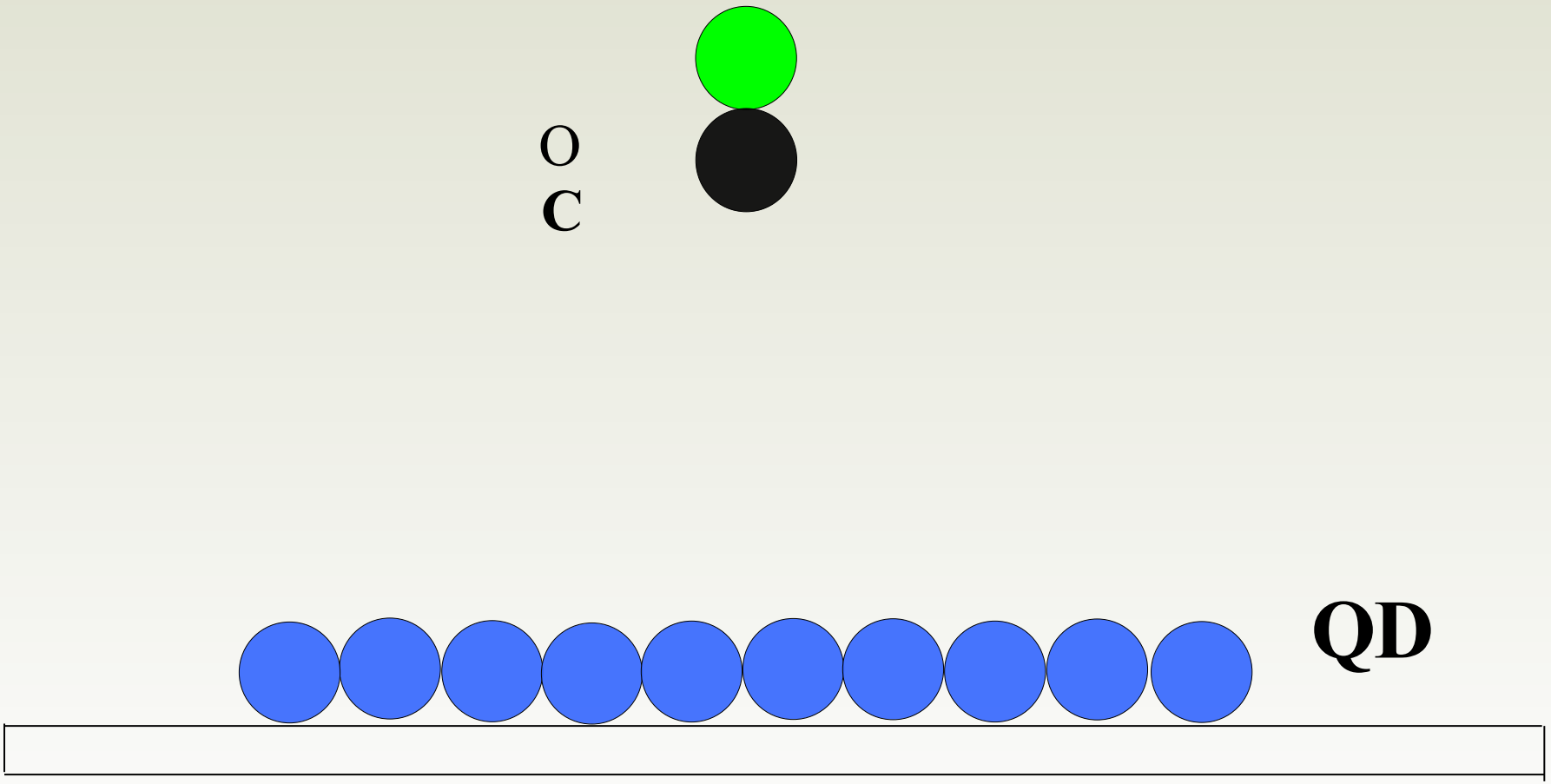


Potential Energy Surface

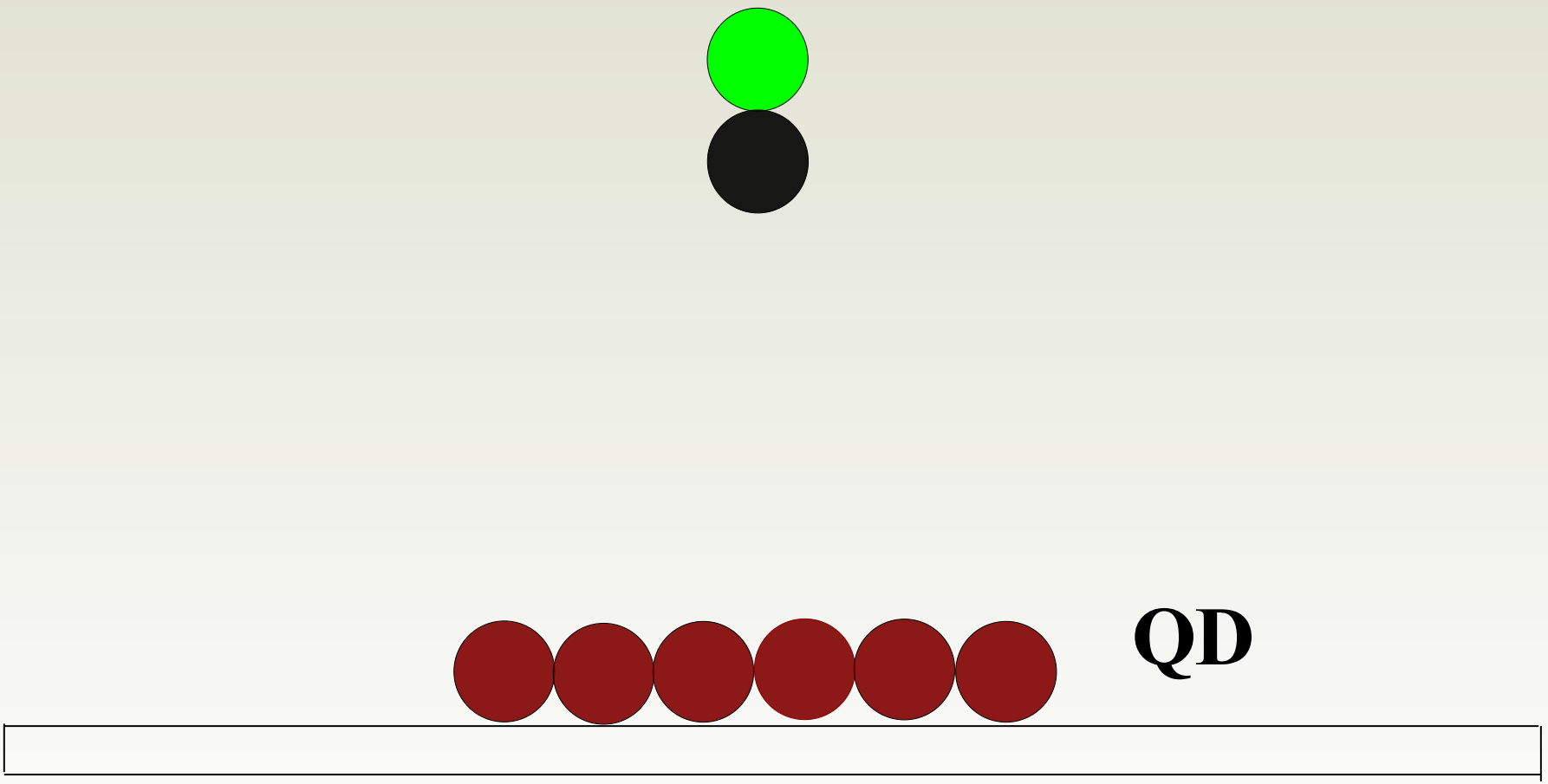



m=0
m=1
E-E_F [eV]
N
2
1
0
-1
-2
5
10
15
20

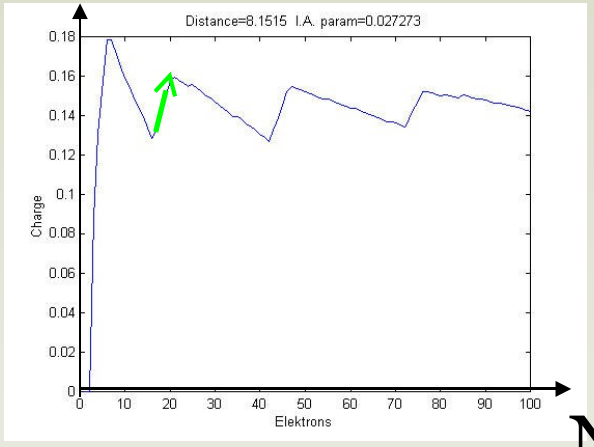
Non-reactive Quantum Dot



Reactive Quantum Dot



Resonant electron charge transfer



Q

N

$2\pi^*$ (m=1)

m=1

E_F

QD

CO

NANO CATALYSIS

- Quantum-size effects in QD-molecule charge transfer
- Matching of wave functions at the Fermi level

Nano-scale catalysis - High selectivity

REFERENCES (and references therein)

- **Model study of Quantum Dots** *Surface Science 506(2002)297 V. Lindberg and B. Hellsing*
- **Model study of adsorbed metallic quantum dots: Na on Cu(111)** *Phys. Rev. B 66(2002)235420 T. Torsti, V. Lindberg, M.J. Puska and B. Hellsing.*
- **Metallic quantum dots** *J. Phys: Condens. Matter, 17 (2005) S1075 V. Lindberg and B. Hellsing.*
- **Quantum size effects of CO reactivity on metallic quantum dots** *Surface Science 600(2006)6 V. Lindberg, T. Petersson and B. Hellsing*