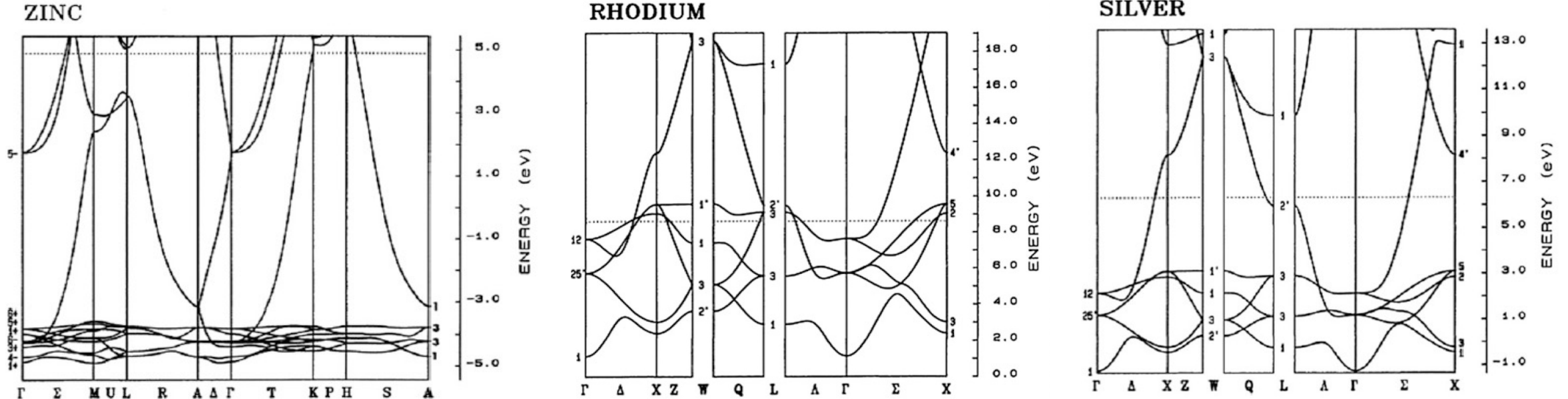


1. Band structures and DOS

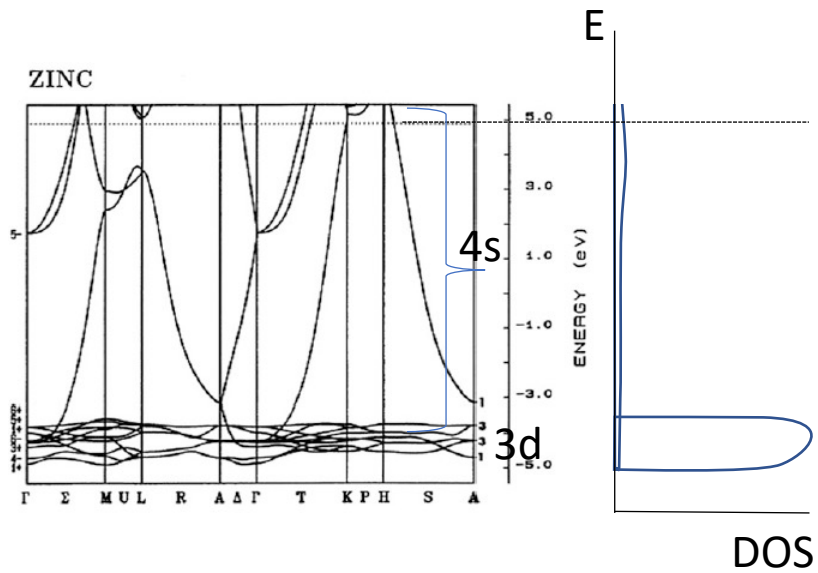
The calculated band structure of three metals is shown in the figures below. The Fermi energy is indicated by the dotted line. For each of them:

- use the periodic table to find the atomic electron configuration
- identify the atomic states that form the bands in the solid, and identify the bands in the band diagram
- sketch the density of states (DOS)

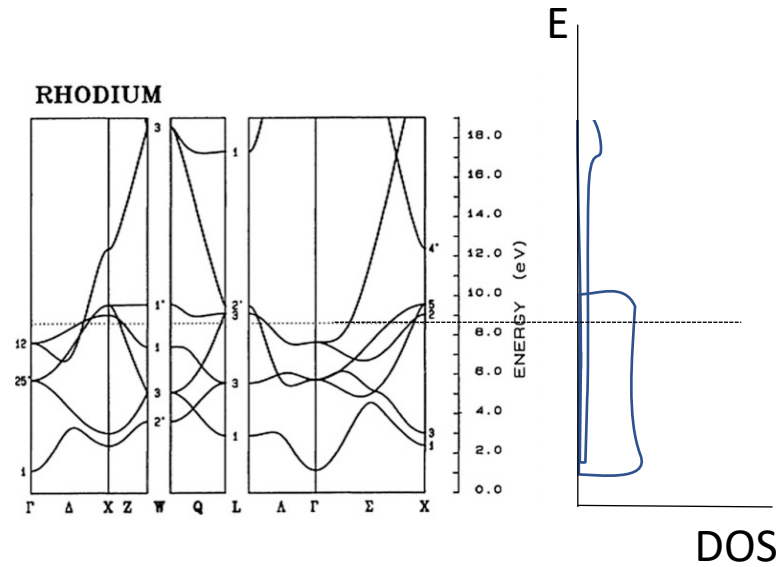


1. Solution - Band structures and DOS

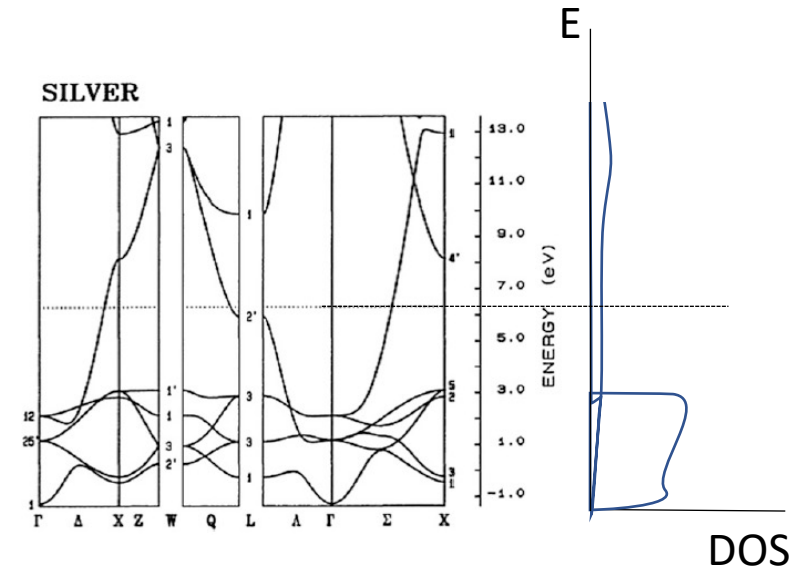
Zn: [Ar] 3d¹⁰ 4s²
3d and 4s



Rh: [Kr] 4d⁸ 5s¹
4d and 5s



Ag: [Kr] 4d¹⁰ 5s¹
4d and 5s



2. STM tips: DOS at the Fermi level

We have seen in the lecture that standard STM tips are made from W or from PtIr alloys (for example Pt₉₀Ir₁₀).

Using the calculated orbital-resolved DOS for Pt and Ag shown in the figures below, estimate the relative contribution of s, p and d states to the total DOS at the Fermi level, indicated by the dotted line.

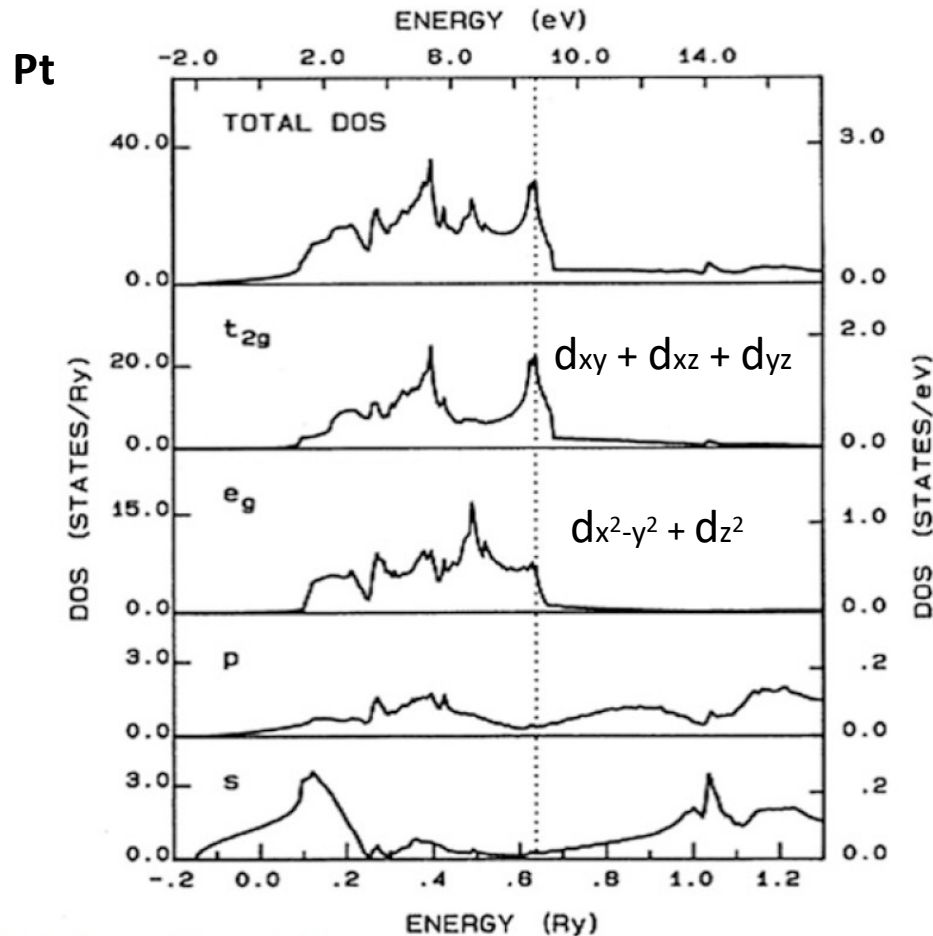


Fig. 6.21 Density of states for Pt

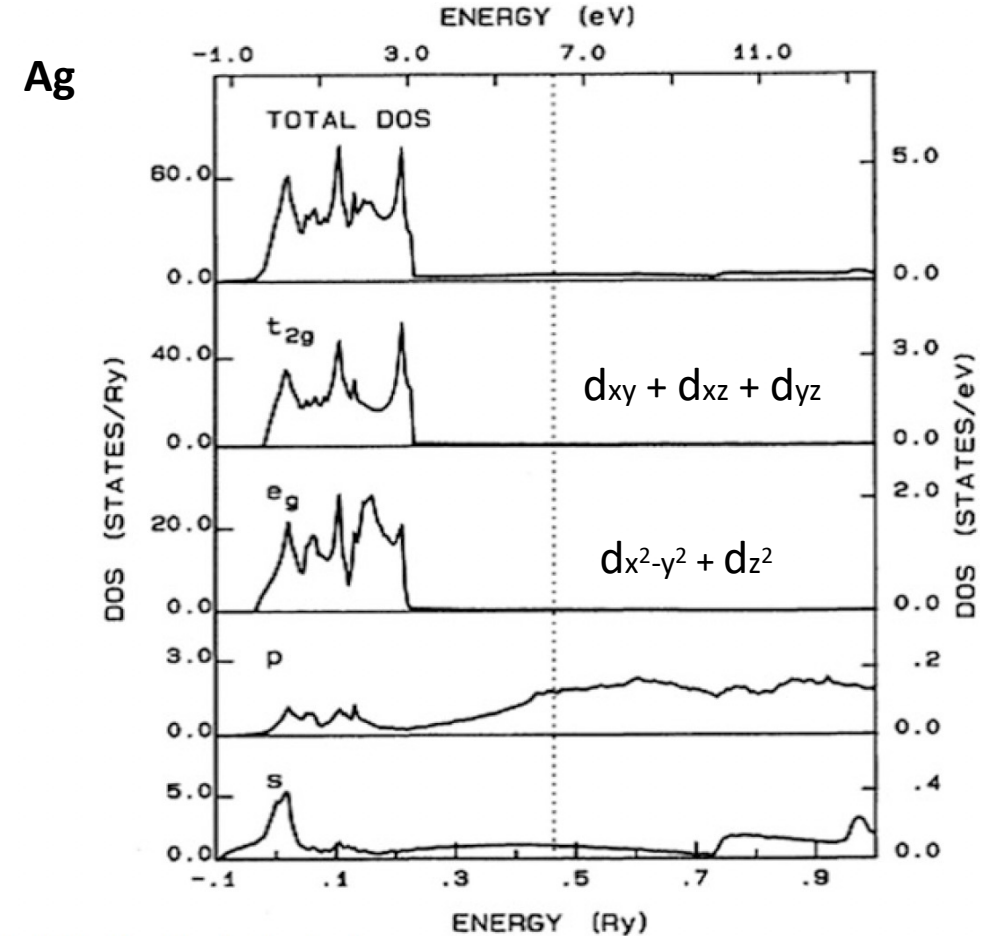


Fig. 5.21 Density of states for Ag

2. Solution - STM tips: DOS at the Fermi level

Pt	(states/eV)	Ag	(states/eV)
s	< 0.02	s	~ 0.07
p	~ 0.02	p	~ 0.13
d	~0.5 + 1.5= 2	d	0
tot	2.04	tot	~ 0.20

s < 1%	s ~ 35%
p ~ 1%	p ~ 65%
d ~ 98%	d ~ 0%

In general, material with high d density of states at the Fermi level are chosen as materials to produce tips, for example W, as well as PtIr alloys, where the role of Ir is to make the material less soft.

In particular, z-oriented orbitals of p and of d states increase the corrugation measured in STM images, leading more easily to high resolution images.

For some specific applications, different materials might be used, for example Au tips for their plasmonic properties, and Cr or MnNi tips for their magnetic properties.

2. Solution - STM tips: DOS at the Fermi level

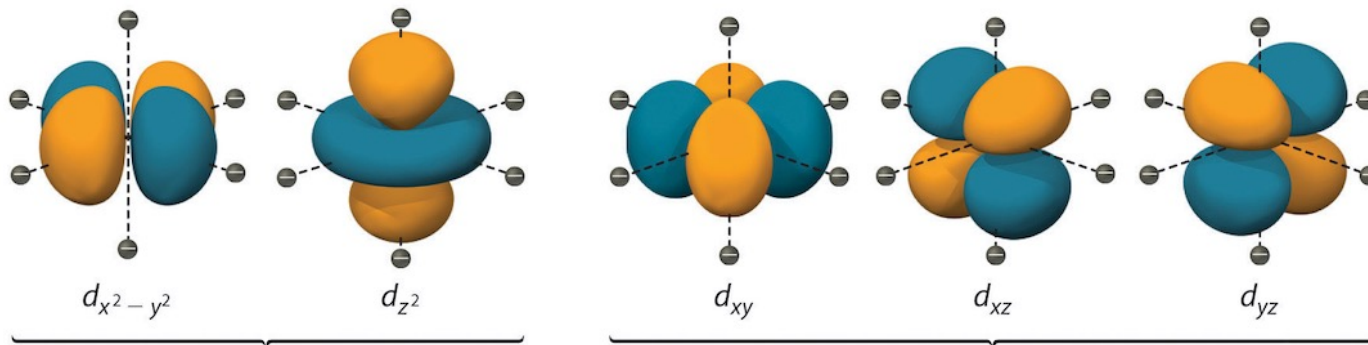
Supplement: Why in the orbital-resolved DOS presented in the figures of the exercise the d states are separated into two?

In an octahedral crystal field, the degeneracy of the five d orbitals of a transition metal atom is partially lifted. This is due to the orientation of the different d orbitals, and to the position of the surrounding negative charges due to the presence of the nearest neighbor atoms in the crystal. It's the crystal field splitting.

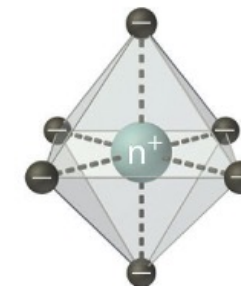
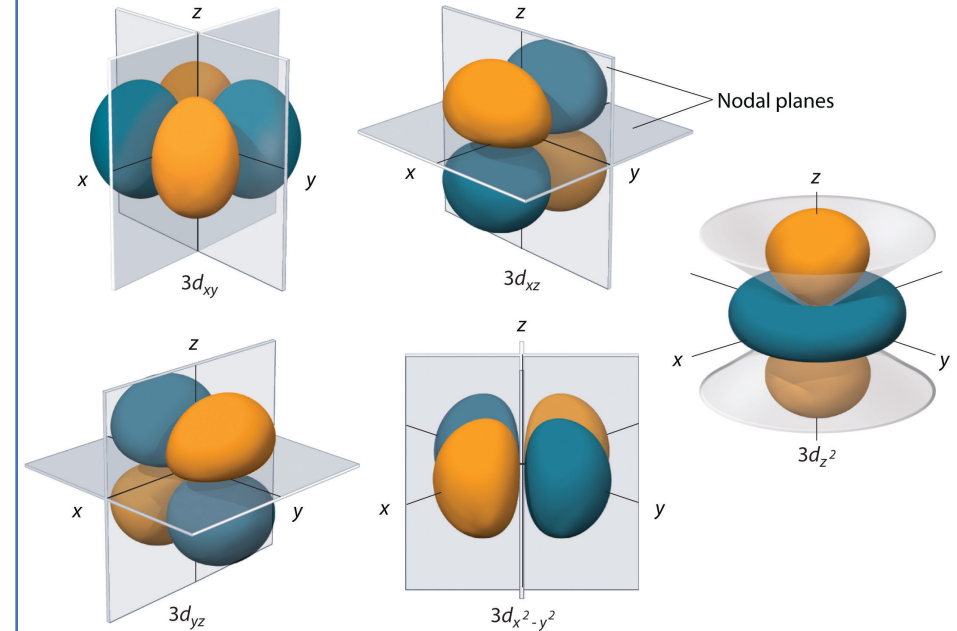
For the $d_{x^2-y^2}$ and d_{z^2} orbitals, the surrounding charges are aligned with the "lobes" of the orbitals, i.e. with the regions in space where the probability of finding the electrons is high, resulting in some repulsion. As a consequence the energy of the states derived from these 2 orbitals is higher.

For the d_{xy} , d_{xz} and d_{yz} orbitals, the surrounding charges are not aligned with the "lobes" of the orbitals, so there is no repulsion. This lowers the energy of these 3 states.

When analyzed in the frame of group theory, the wave functions for these two groups fall into different symmetry groups, designated by e_g (2 states) and t_{2g} (three states).



The lobes of d_{xy} , d_{xz} and d_{yz} orbitals are at 45° with respect to the axes (check the nodal planes), while for $d_{x^2-y^2}$ and d_{z^2} the lobes are aligned with the x and y axes



Negative charges located at vertices of an octahedron

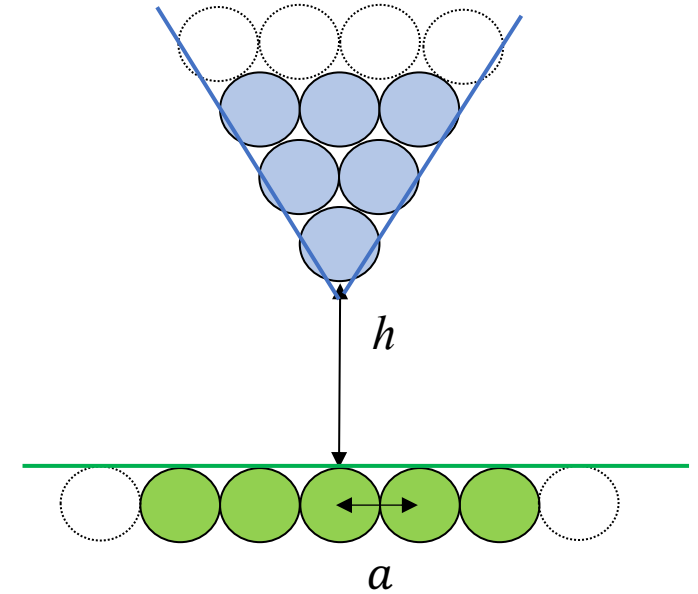
3. STM lateral resolution

We want to evaluate the lateral resolution of an STM tip in the simplified unidimensional model sketched in the figure.

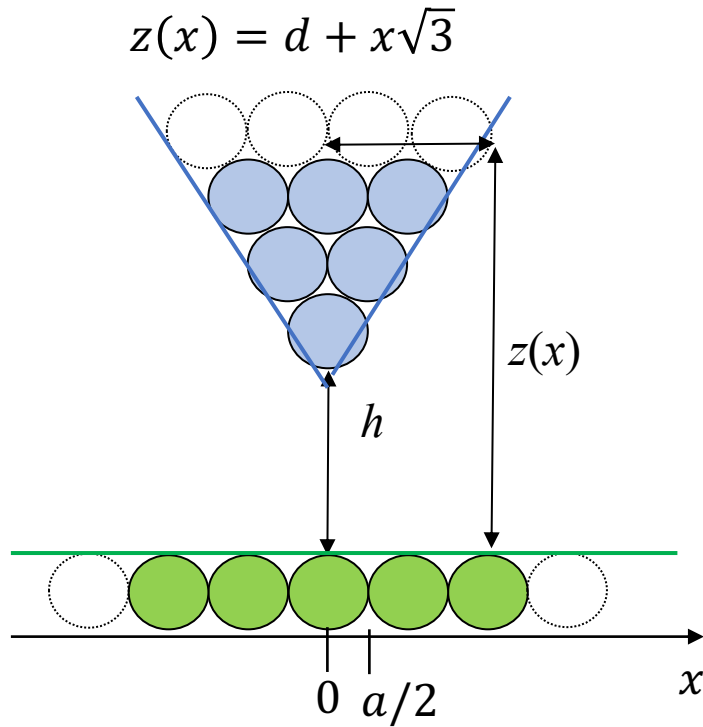
a) Calculate the total tunneling current assuming that electrons can tunnel only perpendicularly to the surface and assuming both tip and surface as having a spatially constant DOS. What is the contribution of the apex atom with respect to the total current? Consider that the distance between the atoms in the surface is $a = 2 \text{ \AA}$.

b) Using the previous result and assuming the atoms as point-like objects, calculate the tunneling current due to the 5 green surface atoms and compare it with the value due to the surface atom directly below the apex atom. Consider the two cases with $h = 0.5a$ and $h = 10a$.

c) You are running your STM in the topographic mode (scanning with constant tunnel current) and you aim achieving atomic resolution. Do you choose a high or a low value of the tunneling current? Why?



3. Solution -STM lateral resolution



a) $I(x) \propto \exp(-2\kappa z(x))$

$$I_{tot} \propto 2 \int_0^{\infty} e^{-2\kappa z(x)} dx = \frac{e^{-2\kappa h}}{\kappa\sqrt{3}}$$

$$I_{apex} \propto 2 \int_0^{a/2} e^{-2\kappa z(x)} dx = \frac{1 - e^{-\kappa a\sqrt{3}}}{\kappa\sqrt{3}} e^{-2\kappa h}$$

with $\kappa \sim 1 \text{ \AA}^{-1}$ and $a = 2 \text{ \AA}$,

$$I_{apex} = 97\% I_{tot}$$

→ We can just consider the tunneling current due to the apex atom

b) $I_{5 \text{ atoms}} \propto e^{-2\kappa h} + 2e^{-2\kappa\sqrt{h^2+a^2}} + 2e^{-2\kappa\sqrt{h^2+(2a)^2}}$

$h = 0.5a \rightarrow \text{ratio} \sim 80\%$

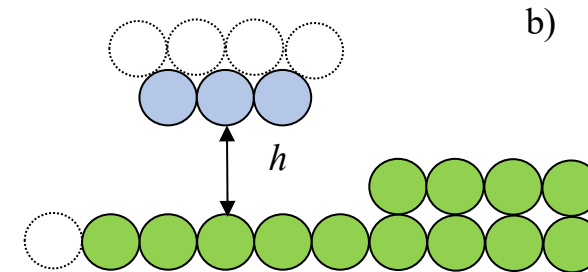
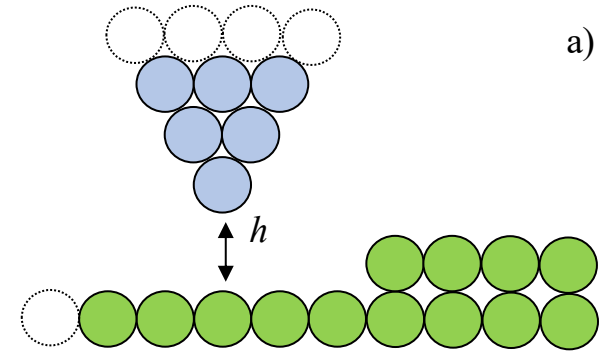
$h = 10a \rightarrow \text{ratio} = 20\%$ (each of the 5 atoms contribute roughly the same)

c) To achieve atomic resolution we want to maximize the contribution of the surface atom just under the tip. This means that the tip has to be close to the surface or equivalently that high tunneling current ($\sim 10 \text{ nA}$) has to be used

4. Effect of the tip apex shape on the lateral resolution

Consider the cases sketched in the figure.

Using the results of the previous exercise, trace the step profile measured by the STM when the tip is moved close to the surface



4. Solution - Effect of the tip apex shape on the lateral resolution

We know that when the tip moves close to the surface only the apex atom and the surface atom closest to the tip contribute to the tunneling current

In case b) the tunneling current on the terraces is given by the three apex atoms. This implies that only when the three apex atoms have climbed the step, the tunneling current on the two terraces is the same. Thus, the step is seen with a very smooth profile with a width comparable to the tip size.

Indeed, in general the recorded topography is the **convolution** of the surface features and tip atomic structure

