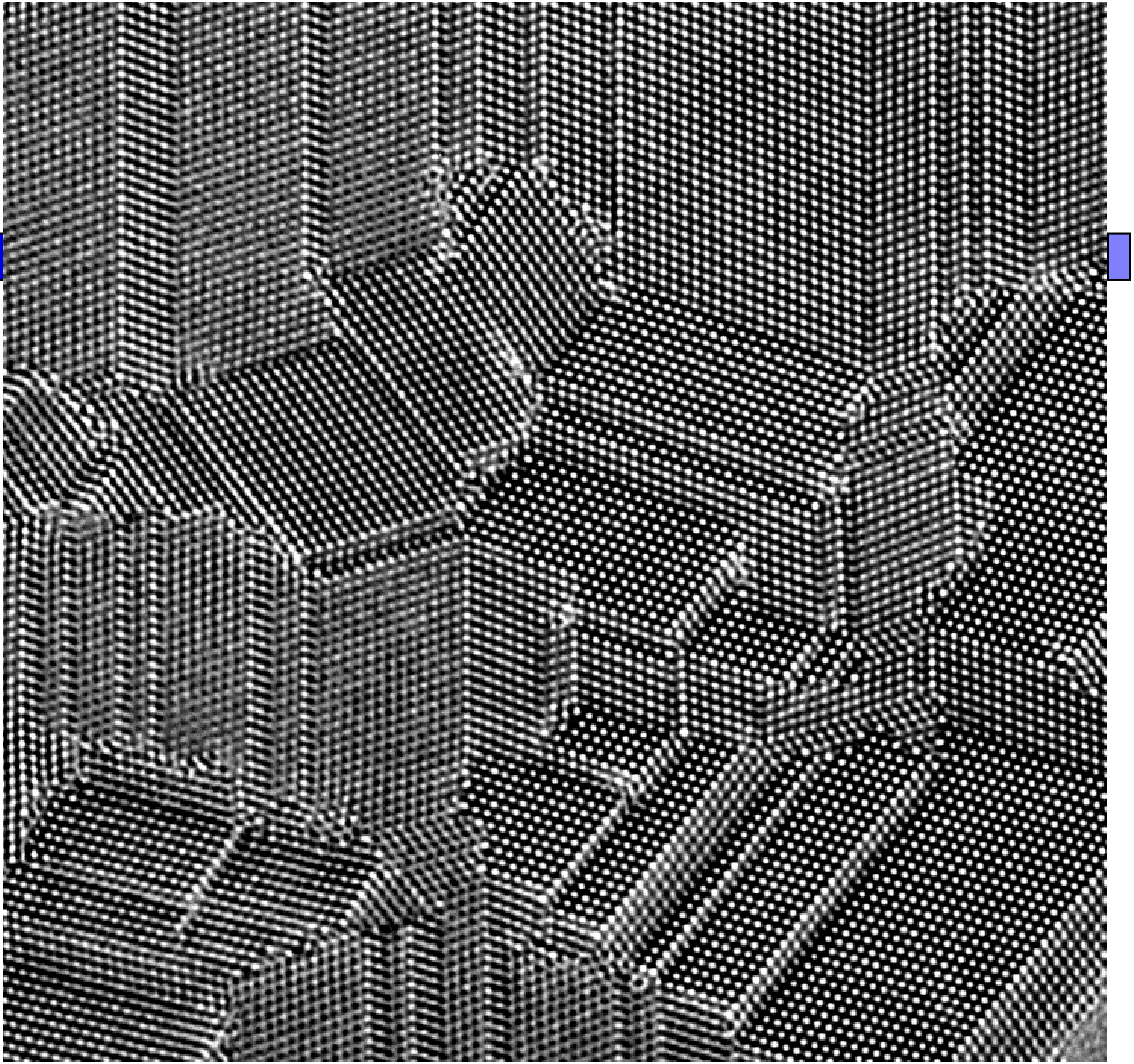
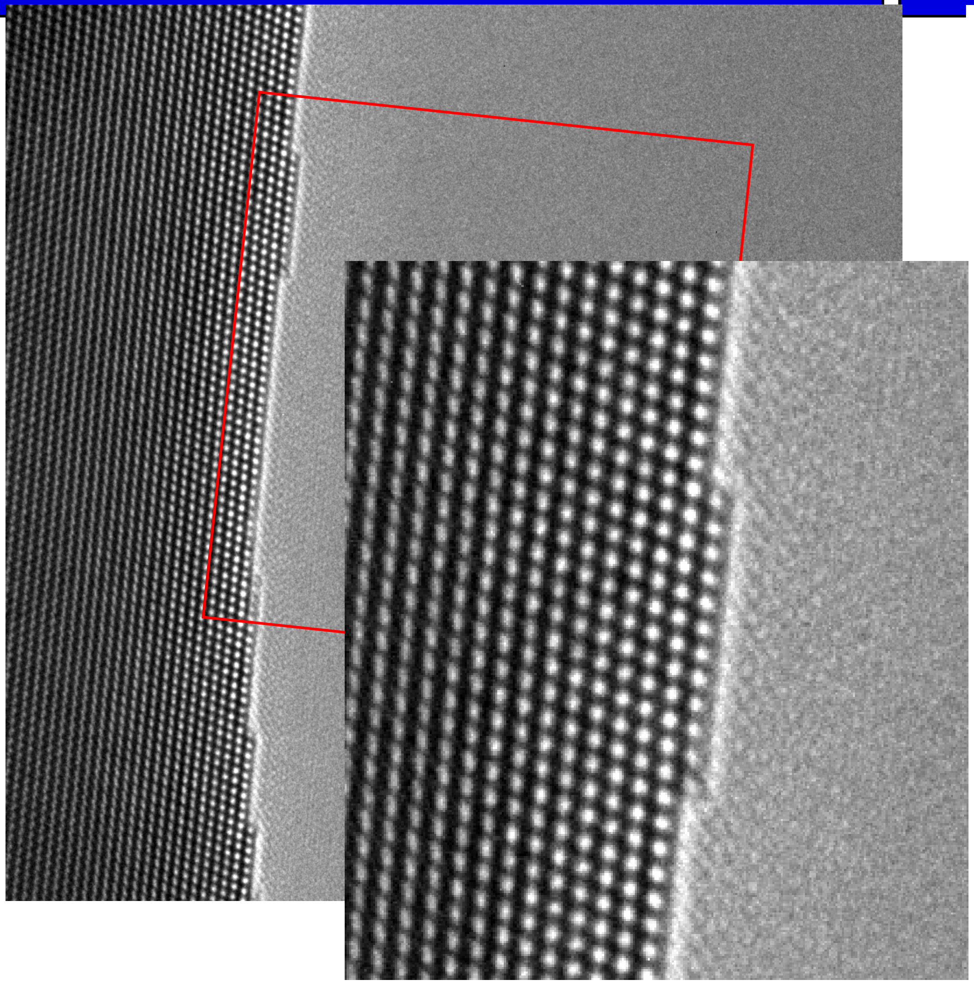
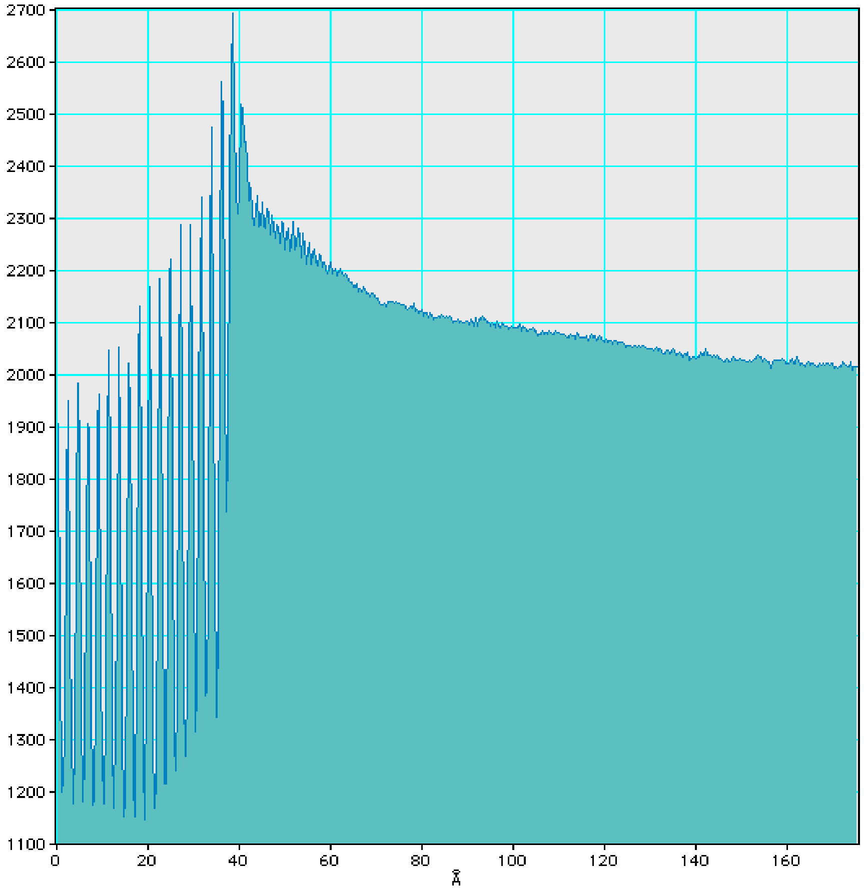


Atomic resolution micrograph of multiply-twinned nanocrystalline film of Si. (C. Song)

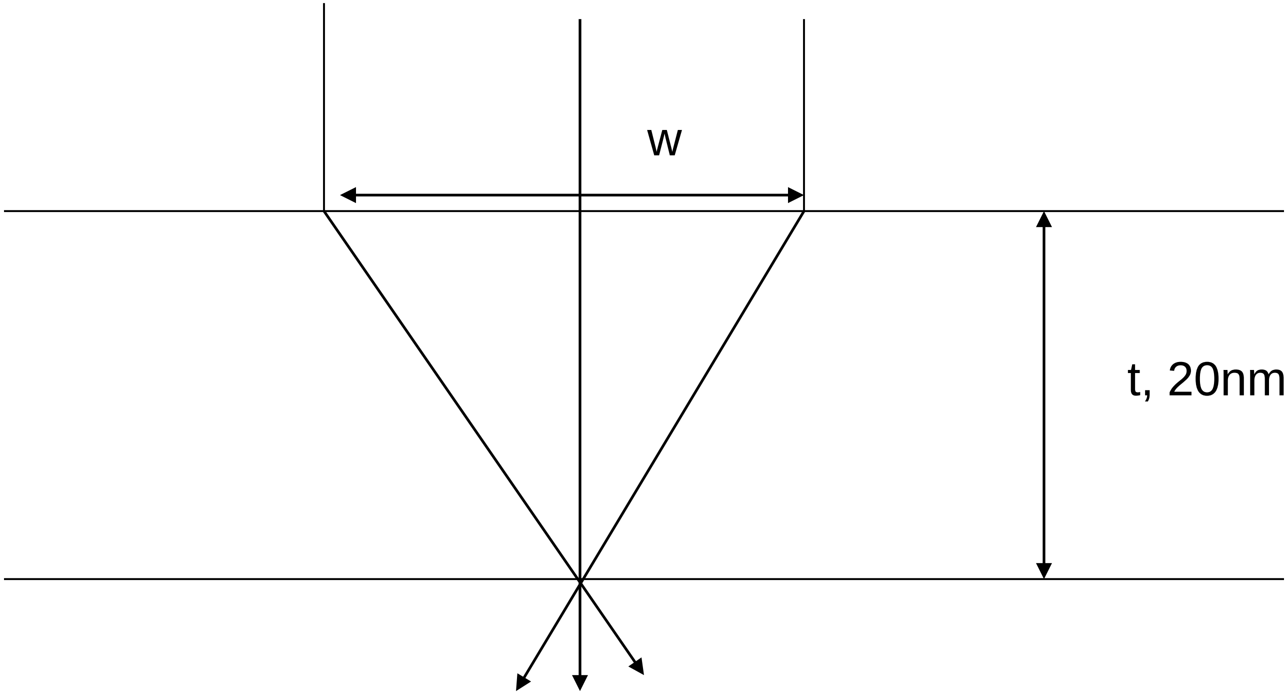
Au [110] – Vacuum wave





Courtesy C. Kisielowski, J.R. Jinschek (NCEM, Berkeley)

But…column approximation?



w = 2tθ. Take θ=10 mRad, t=20nm, w=4 Angstroms

Basis Sets

- Plane waves
  - Solutions in vacuum
  - Used in kinematical theory
- Bloch waves
  - Used in 2-beam theory (and beyond)
  - Combinations of plane waves
- Tight-binding model
  - Uses atom-like orbitals (similar to chemistry, MO)

Basis Sets Continued

- What to use?
- No simple answer
- The one which gives the simplest explanation with the least complications (KISS = Occam’s Razor) is normally best
- Often this changes depending upon the type of problem/property of interest…

Channeling: Real-Space model

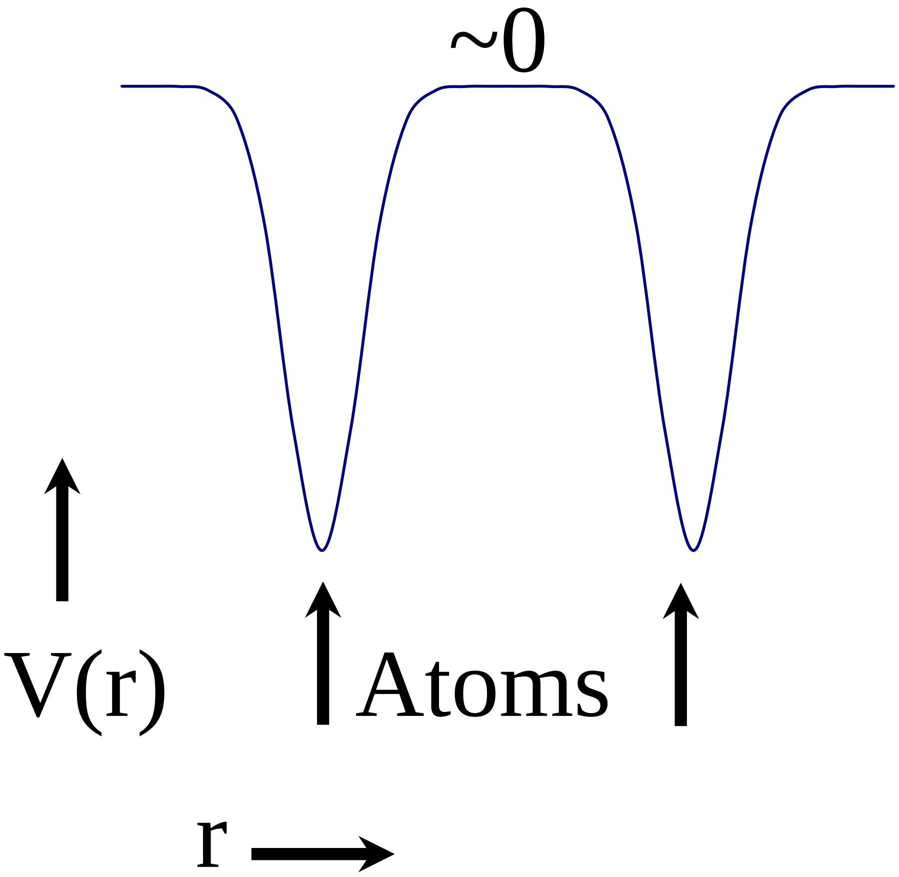
- Electron channeling approximation*:
  - 1) Ignore all but ZOLZ interactions (high energy)
  - 2) Assume sample orientation so that one has well separated atomic columns along z (in initial expansion only)
  - 3) Use atomic-column based tight-binding model

* Fujimoto, phys. stat. sol. (1978) + many others

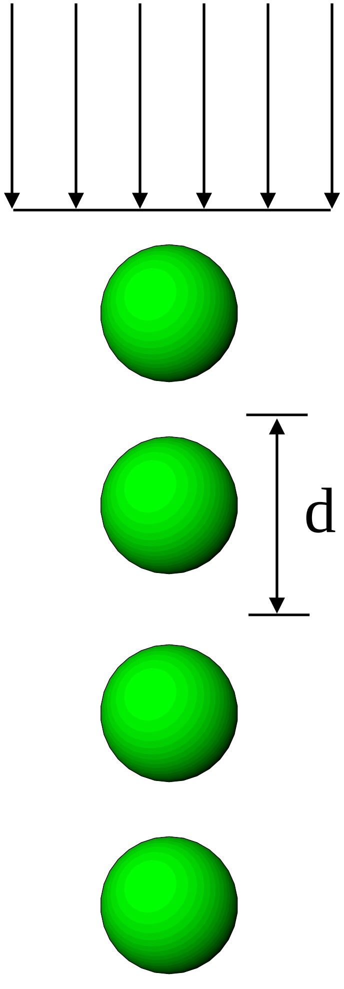
Van Dyck and Op de Beeck, *Ultramicroscopy* (1996)

Channeling Concept

- For many zone axes, in projection atoms are well separated
- Potential large near columns
- Small between columns



Consider an isolated column: I



$$V(\underline{R}) = V(x,y) = \frac{1}{d}\int_{-d/2}^{d/2} V_0(\underline{R},z)\,dz$$

Average potential

$$\nabla^2\psi(\mathbf{r})+\frac{2m}{\hbar^2}\left[E+V(\mathbf{r})\right]\psi(\mathbf{r})=0$$

$$\nabla^2\psi(\mathbf{r})=\nabla_R^2\psi(\mathbf{r})+\partial^2\psi(\mathbf{r})/\partial z^2$$

$$\psi(\mathbf{r})=\exp(-2\pi ikz)\Omega(R)$$

$$\nabla^2\psi(\mathbf{r})=\exp(-2\pi ikz)\{\nabla_R^2\Omega(\mathbf{r})+\xcancel{\partial^2\Omega(\mathbf{r})/\partial z^2}$$

$$-4\pi ik\partial\Omega(\mathbf{r})/\partial z-4\pi^2k^2\Omega(\mathbf{r})\}$$

$$\updownarrow$$

$$\nabla^2\psi(\mathbf{r})=\exp(-2\pi ikz)\{\nabla_R^2\Omega(\mathbf{r})-E\Omega(\mathbf{r})-4\pi ik\partial\Omega(\mathbf{r})/\partial z\}$$

$$\nabla_R^2\Omega(\mathbf{r})-4\pi ik\partial\Omega(\mathbf{r})/\partial z+\frac{2m}{\hbar^2}\left[V(\mathbf{r})\right]\Omega(\mathbf{r})=0$$

$$\nabla_R^2 \Omega(\mathbf{r}) - 4\pi i k \partial \Omega(\mathbf{r}) / \partial z + \frac{2m}{\hbar^2}\left[V(\mathbf{r})\right]\Omega(\mathbf{r}) = 0$$

$$4\pi i \partial \Omega(\mathbf{r}) / \partial z = (1/k)\nabla_R^2 \Omega(\mathbf{r})$$ Spreading of information

$$4\pi i \partial \Omega(\mathbf{r}) / \partial z = -\frac{2m}{\hbar^2 k}\left[V(\mathbf{r})\right]\Omega(\mathbf{r})$$ Diffraction

$$\nabla_R^2 \Omega(\mathbf{r}) - 4\pi i k \partial \Omega(\mathbf{r}) / \partial z + \frac{2m}{\hbar^2}\left[V(\mathbf{r})\right]\Omega(\mathbf{r}) = 0$$

$$\Omega(\mathbf{r}) = (m / 2\pi k \hbar^2)\Phi(R)\exp(-i\varepsilon z)$$

$$\nabla_R^2 \Phi(\mathbf{R}) + \frac{2m}{\hbar^2}\left[\varepsilon + V(\mathbf{R})\right]\Phi(\mathbf{R}) = 0$$

Consider an isolated column: II

- Problem reduces to 2-D Schrödinger's Eqn

$$\nabla^2_{\mathbf{R}}\Phi(\mathbf{R}) + \frac{2m}{h^2}\left[\varepsilon \;\; + V(\mathbf{R})\right]\Phi(\mathbf{R}) = 0$$

“Transverse Energy”

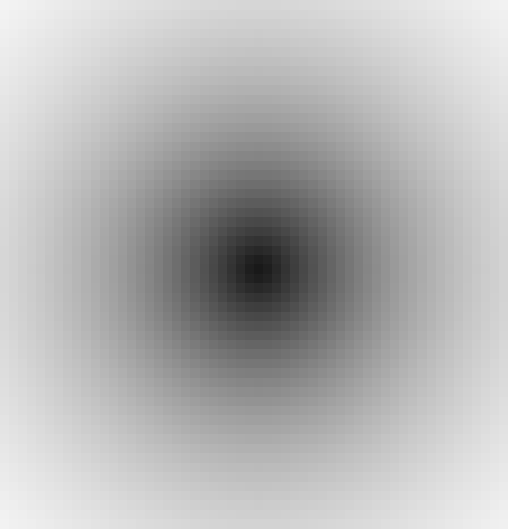
- Solutions have form:

$$\psi(\mathbf{r}) = \sum_n C_n \Phi_n(\mathbf{R}) \exp\{-i\pi\varepsilon_n z\}$$

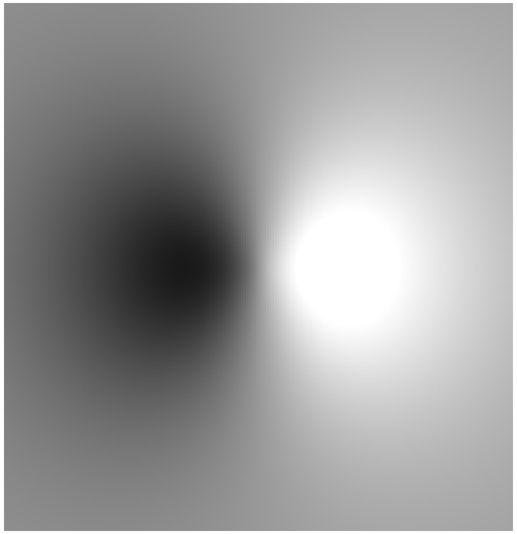
2D orbitals

Character of States

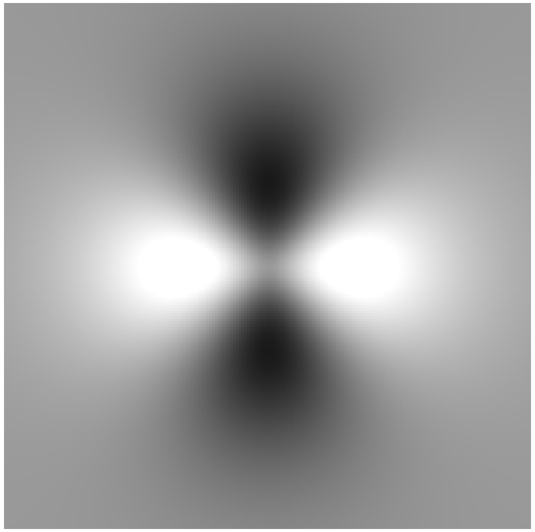
- 2D analogues of 3D atomic orbitals



1s



2p



3d

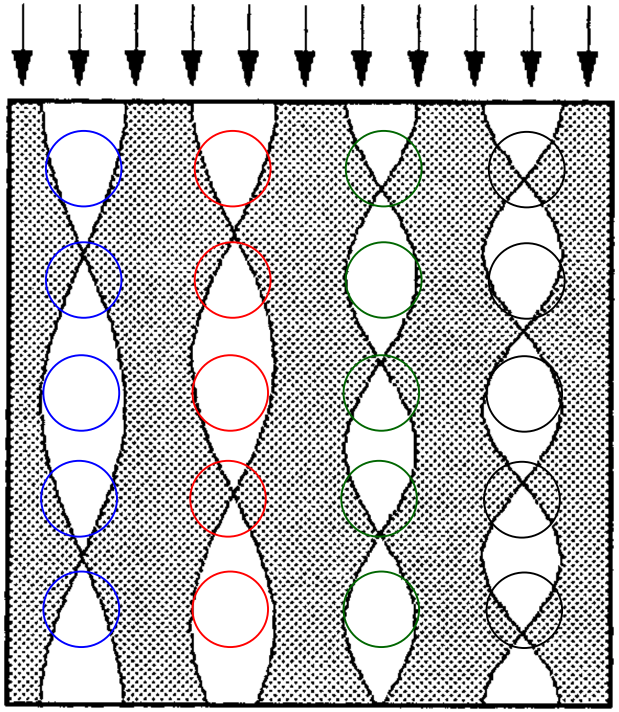
Dynamical Solutions: many columns

- General solution

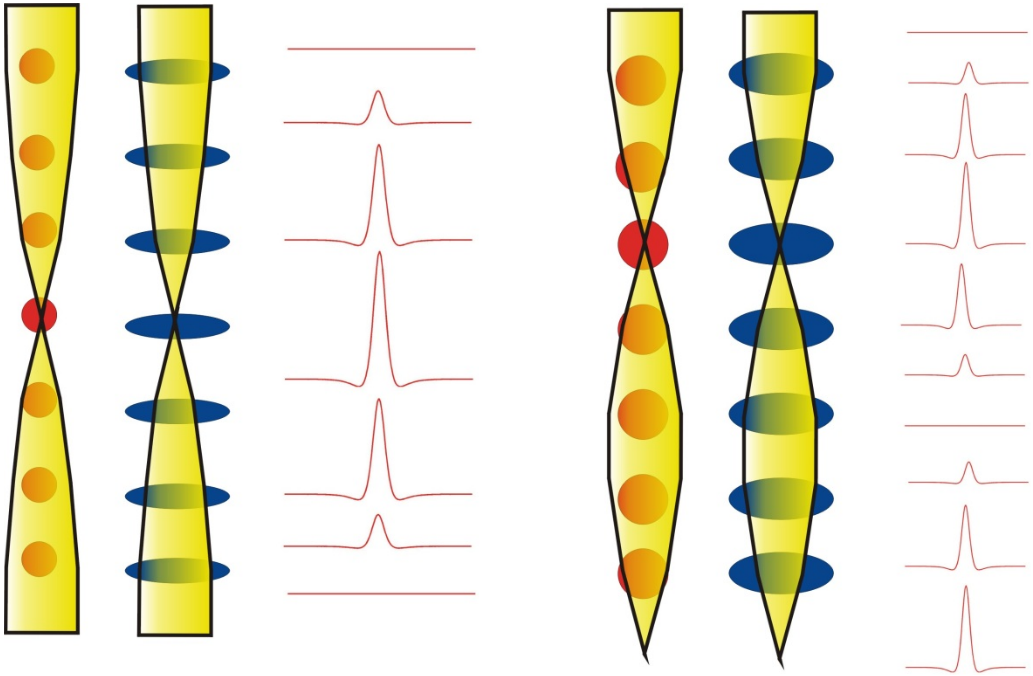
$$\psi(\mathbf{R},z)-1\approx\sum_{i,j}C_i\Phi_i(\mathbf{R}-\mathbf{R}_j)\left(\exp(-i\pi\varepsilon_n z)-1\right)$$

- On a zone (symmetry), s-type orbitals dominate
- Not so simple if the zone axis is complicated – not a solved problem

$$\psi(\mathbf{R},z)-1\approx\sum_{i,j}C_i\Phi_i(\mathbf{R}-\mathbf{R}_j)\left(\exp(-i\pi\varepsilon_n z)-1\right)$$



light atoms heavy atoms



light atoms heavy atoms

Curtesy D. Van Dyck

A Quick Comparison

- Bloch Wave
    - Different States
    - Oscillate with Depth
- Interference
    - Thickness Fringes,etc

- Tight Binding
    - Atomic States
    - Oscillate with Depth
- Interference
    - Atomic contrast

Note: ignore overlap of states

OPW

- Suppose we have some atomic-like state, $\Phi(r)$ and also add a plane-wave like term
- The two must be orthogonal – a plane wave is not
- Instead use

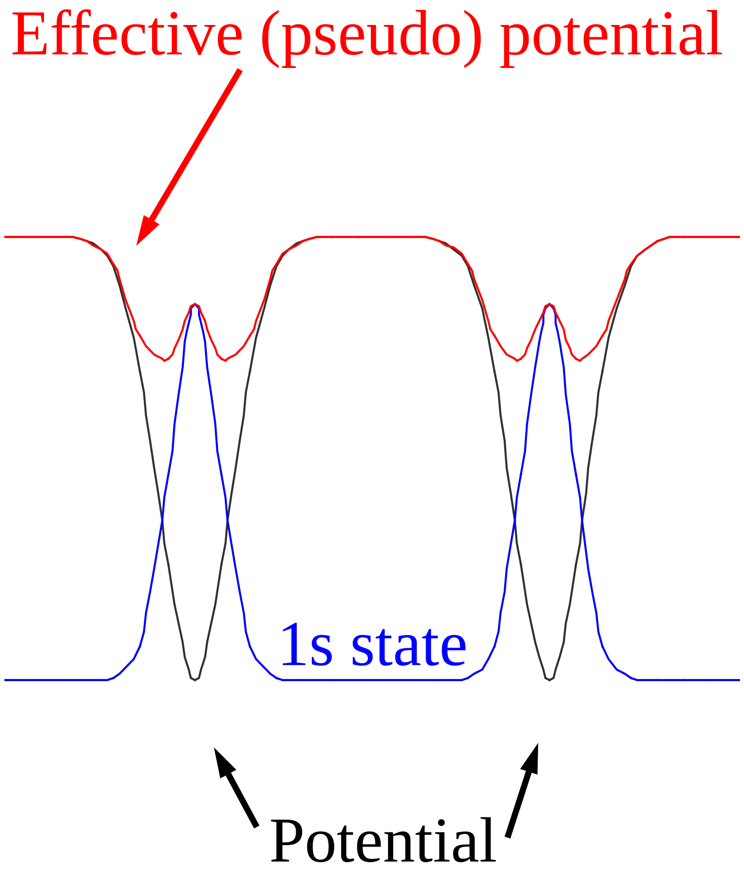
$$\exp(2\pi ik.r) - \Phi(r)\int \Phi(r)^* \exp(2\pi ik.r)\,dr$$

- This is small when $\Phi(r)$ is large, misses the core

So what does this gain us?

- First core state (1s) cancels most of potential (OPW)
- Only need to consider a few states, unlike classic Bloch-wave methods

N.B. Tight-binding



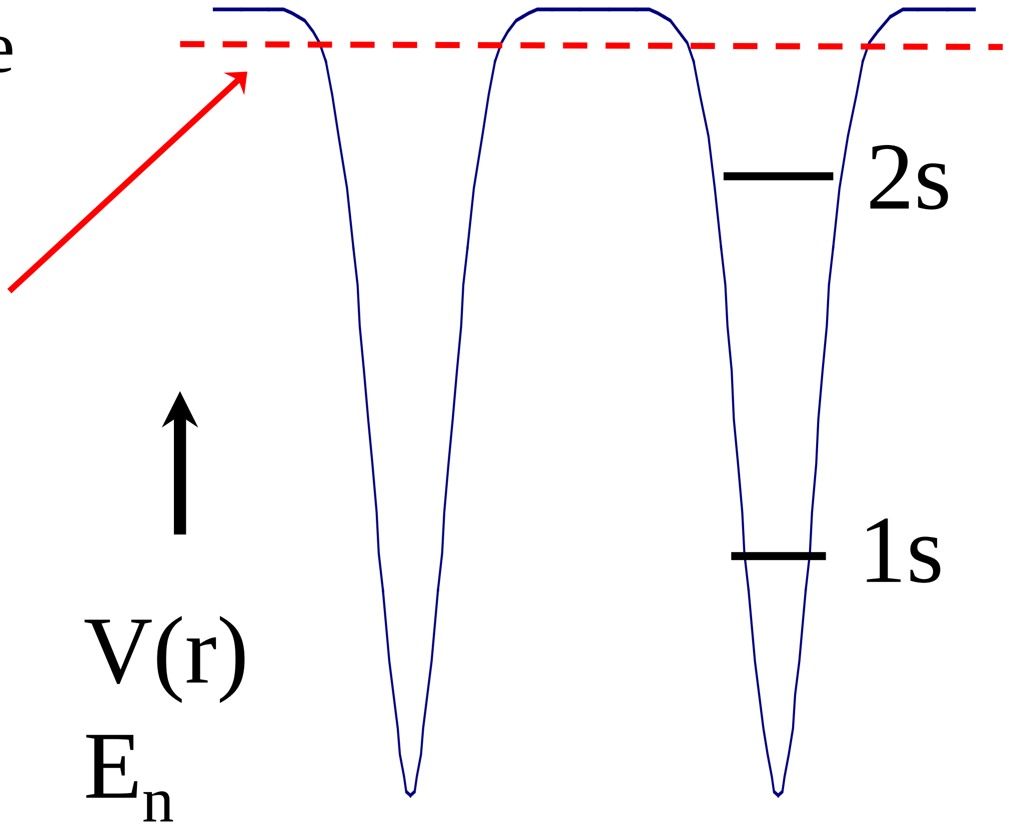
Effective (pseudo) potential

1s state

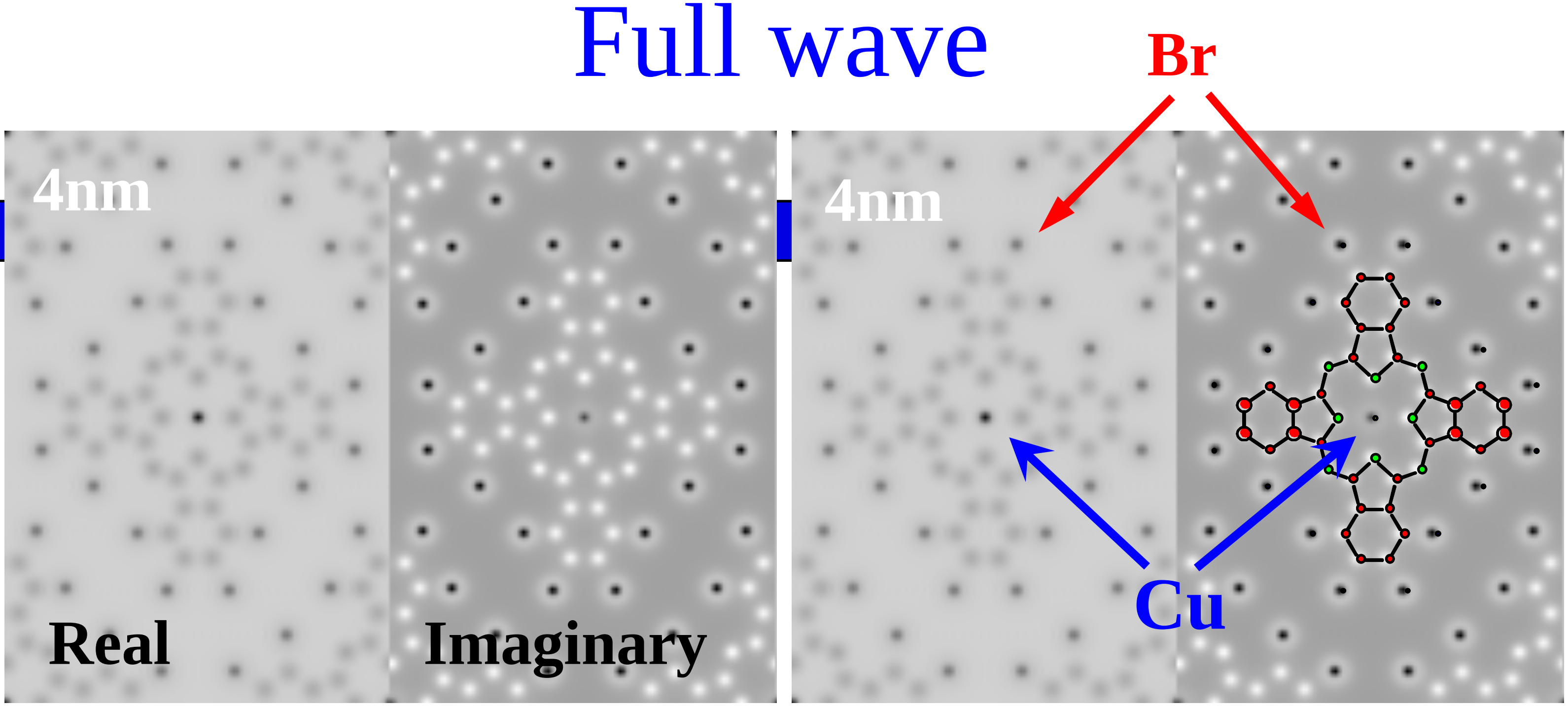
Potential

Channeling Concept

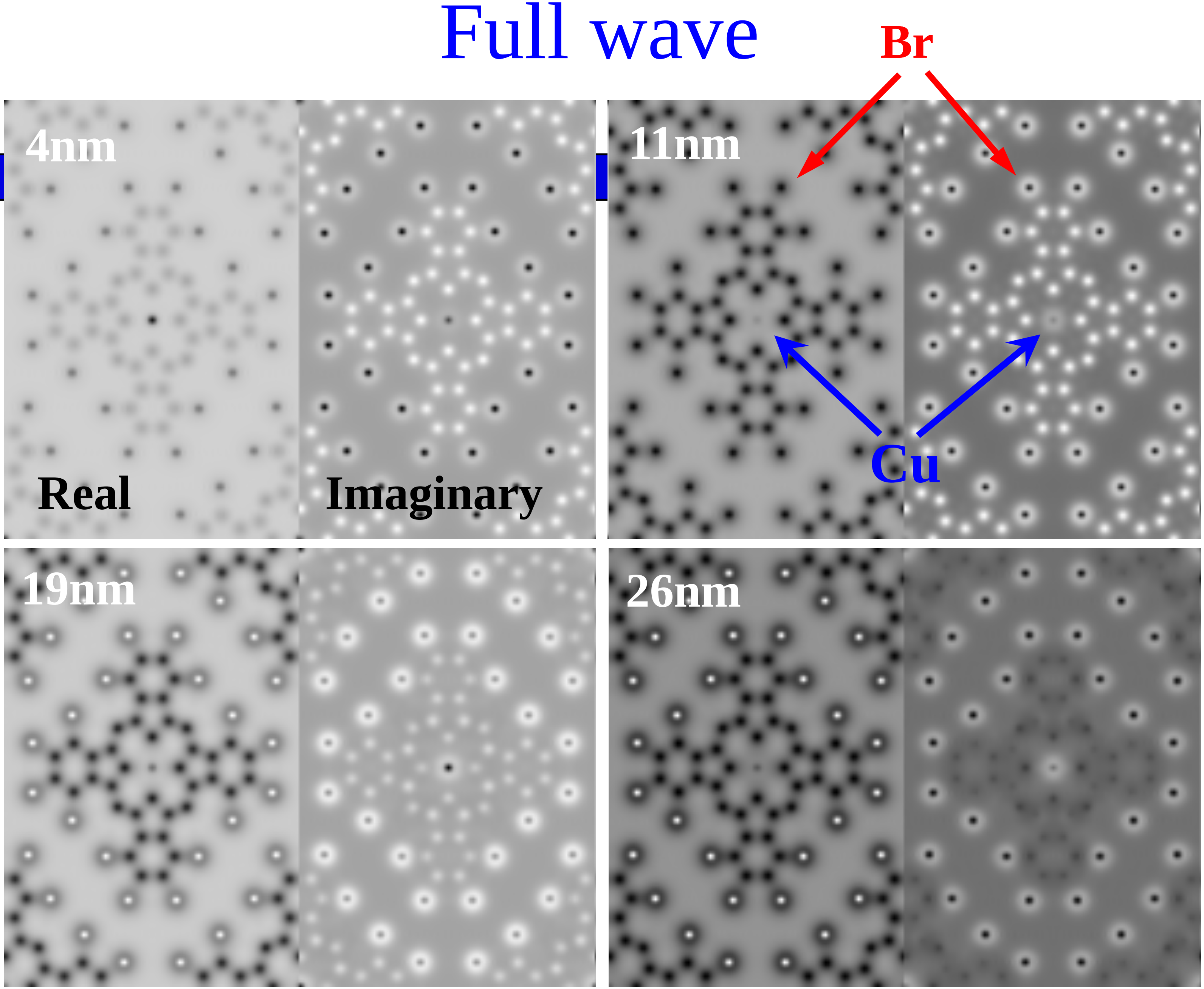
- Lowest Transverse Energy states (1s) dominate
- Can ignore (to 2nd order) delocalized states



Full wave



Full wave



Dynamical Solutions: many columns

$$\psi(\mathbf{R},z)-1\approx\sum_{i,j}C_i\Phi_i(\mathbf{R}-\mathbf{R}_j)\left(\exp(-i\pi\varepsilon_n z)-1\right)$$

$$|\psi(\mathbf{R},z)-1|$$

Peaked atom-like term, localized at columns in projection

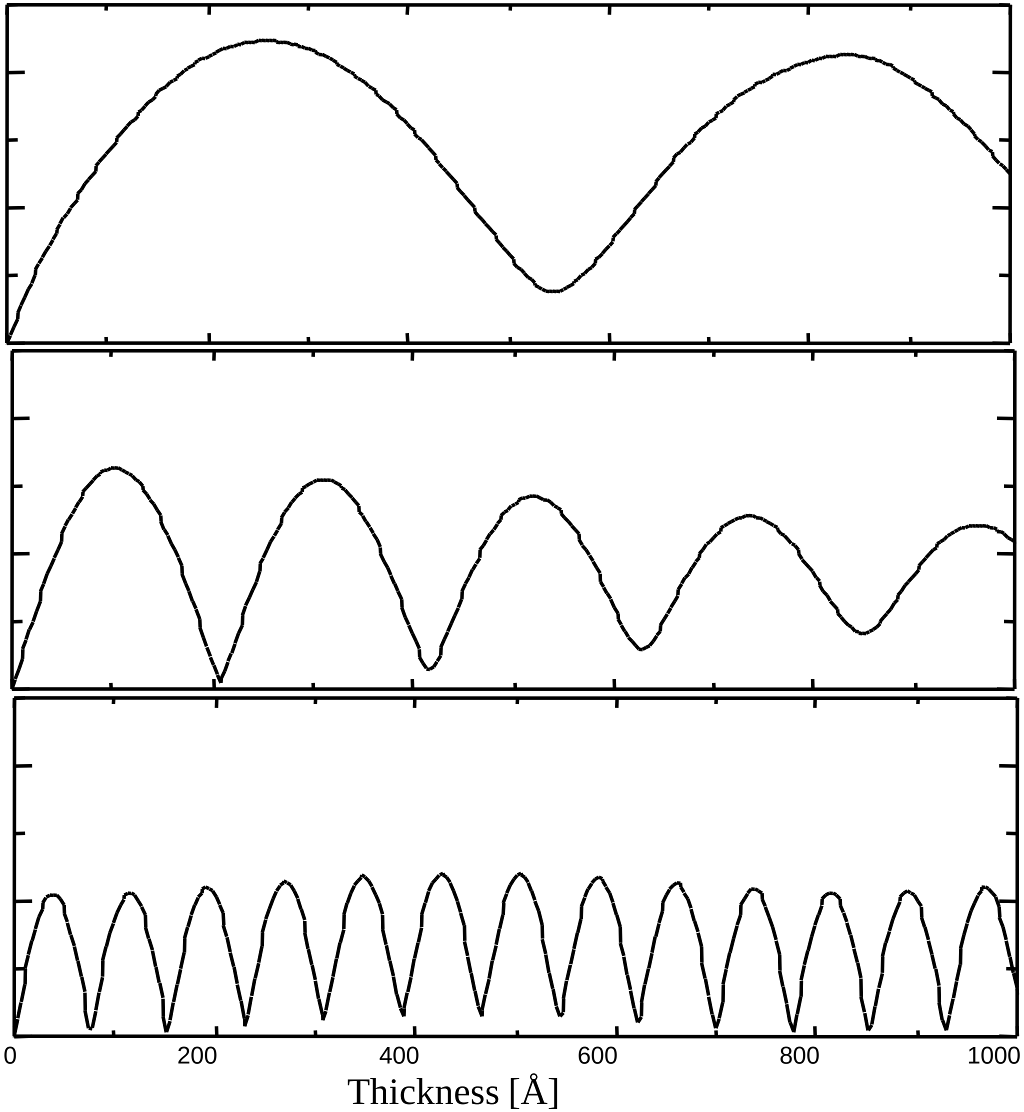
Depth dependence by atom type

|1-ψ(r)|
at atom

O

Al

Ga



Why?

$$\psi(\mathbf{R},z)-1\approx\sum_{i,j}C_i\Phi_i(\mathbf{R}-\mathbf{R}_j)\left(\exp(-i\pi\varepsilon_n z)-1\right)$$

z small

$$\psi(\mathbf{R},z)-1\approx\sum_{i,j}C_i\Phi_i(\mathbf{R}-\mathbf{R}_j)\left(-i\pi\varepsilon_n z\right)$$

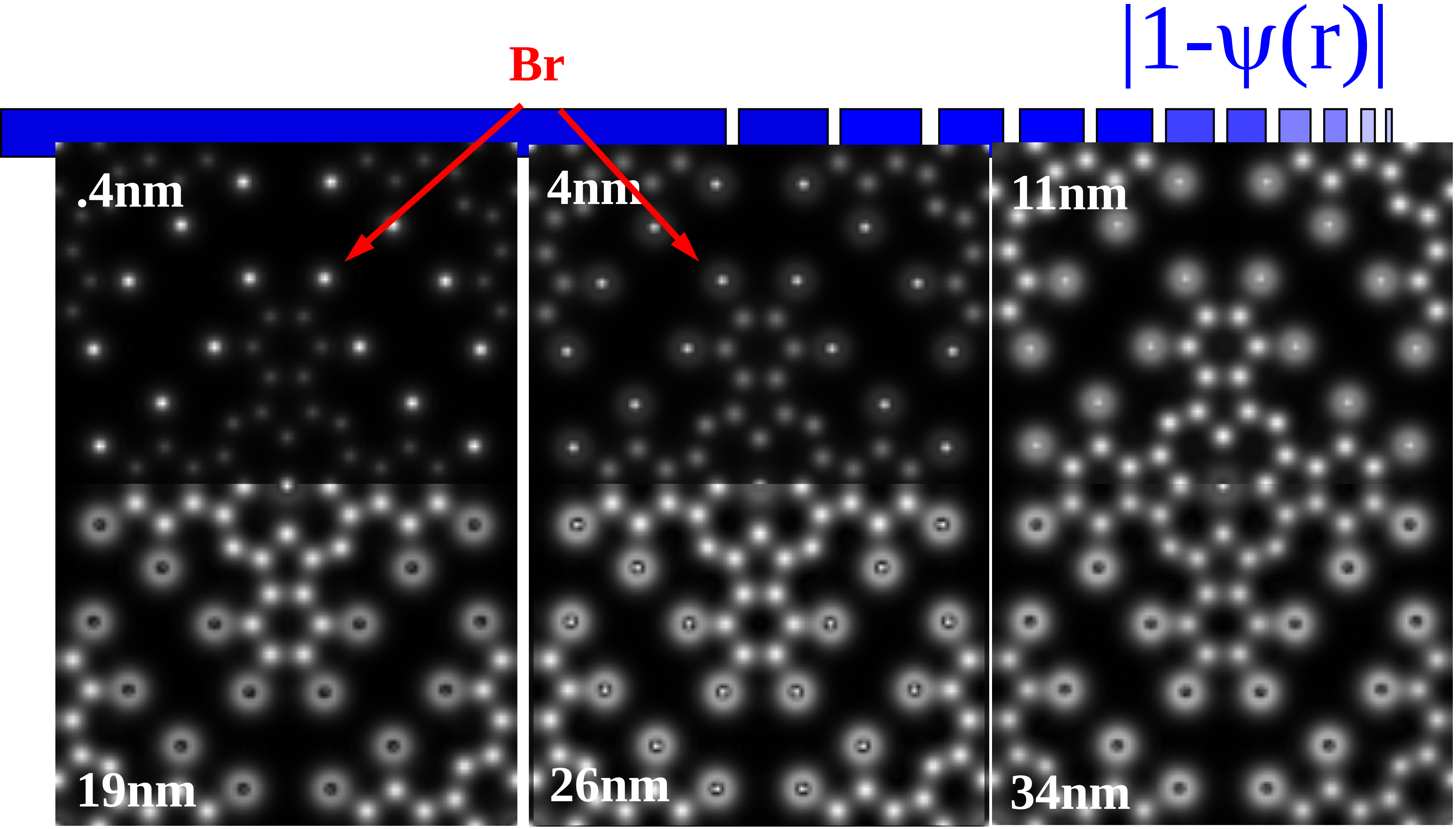
Phase grating approximation

$$\psi(\mathbf{R},z)\approx\exp(i\sigma zV(\mathbf{R}))$$

$$\psi(\mathbf{R},z)-1\approx i\sigma zV(\mathbf{R})$$

$$C\approx\sigma/\varepsilon_n$$

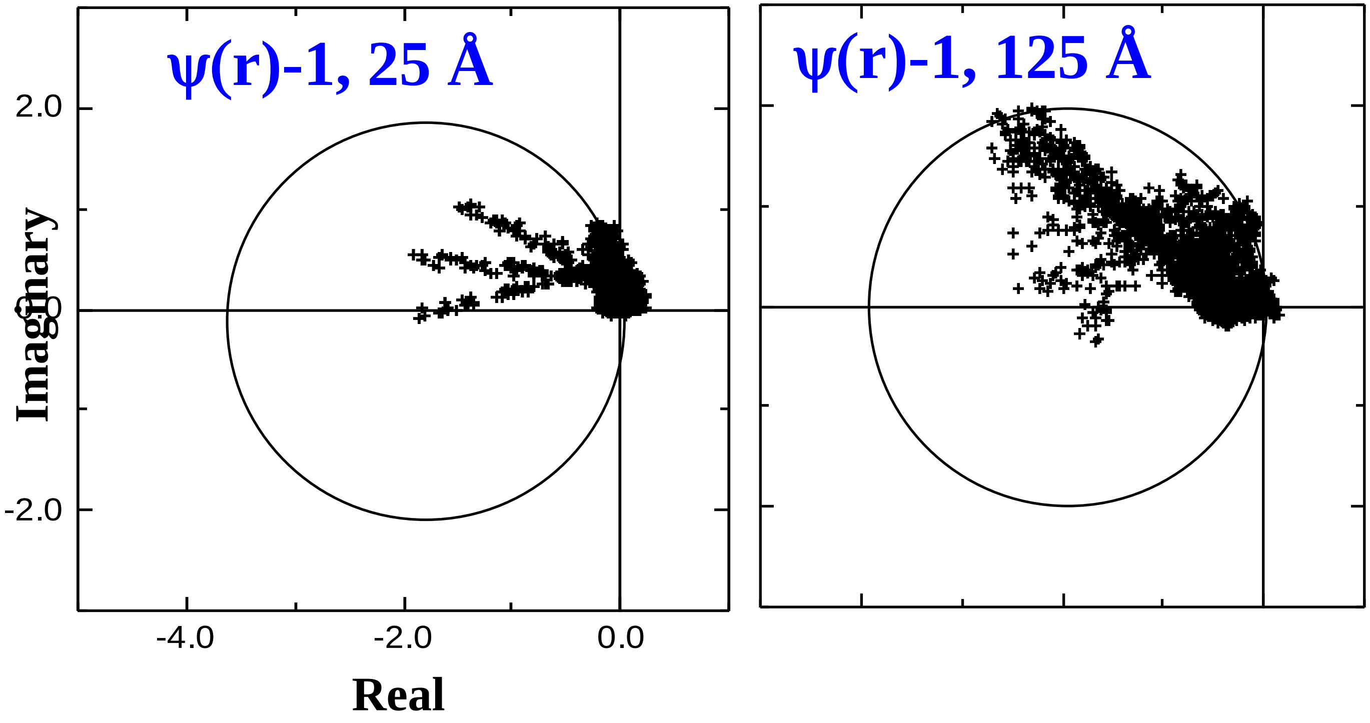
ε_n is larger for heavier atom



Carbon is more important than Bromine for ~ 10nm

Sinkler Plots: Quasi-Kinematical

ψ(r)-1 has atom-like peaks with species-dependent oscillation



Note: if the points lay on a straight line the result is pseudo-kinematical, i.e. it walks and talks like kinematical even though it is not

Thickness Movie

Oxygen 1s States

▶

Metal 1s States

Bloch-wave formulation (dynamical theory)

Schroedinger equation

↓

Wave function of the incident electron:

$$\Psi(\mathbf{r}) = \Sigma_j \, \varepsilon^{(j)} \, b^{(j)}(\mathbf{r})$$

Bloch state (eigen state):

$$b^{(j)}(\mathbf{r}) = \Sigma_g C_g^{(j)} \exp[2\pi i(\mathbf{k}^{(j)}+\mathbf{g})\cdot\mathbf{r}]$$

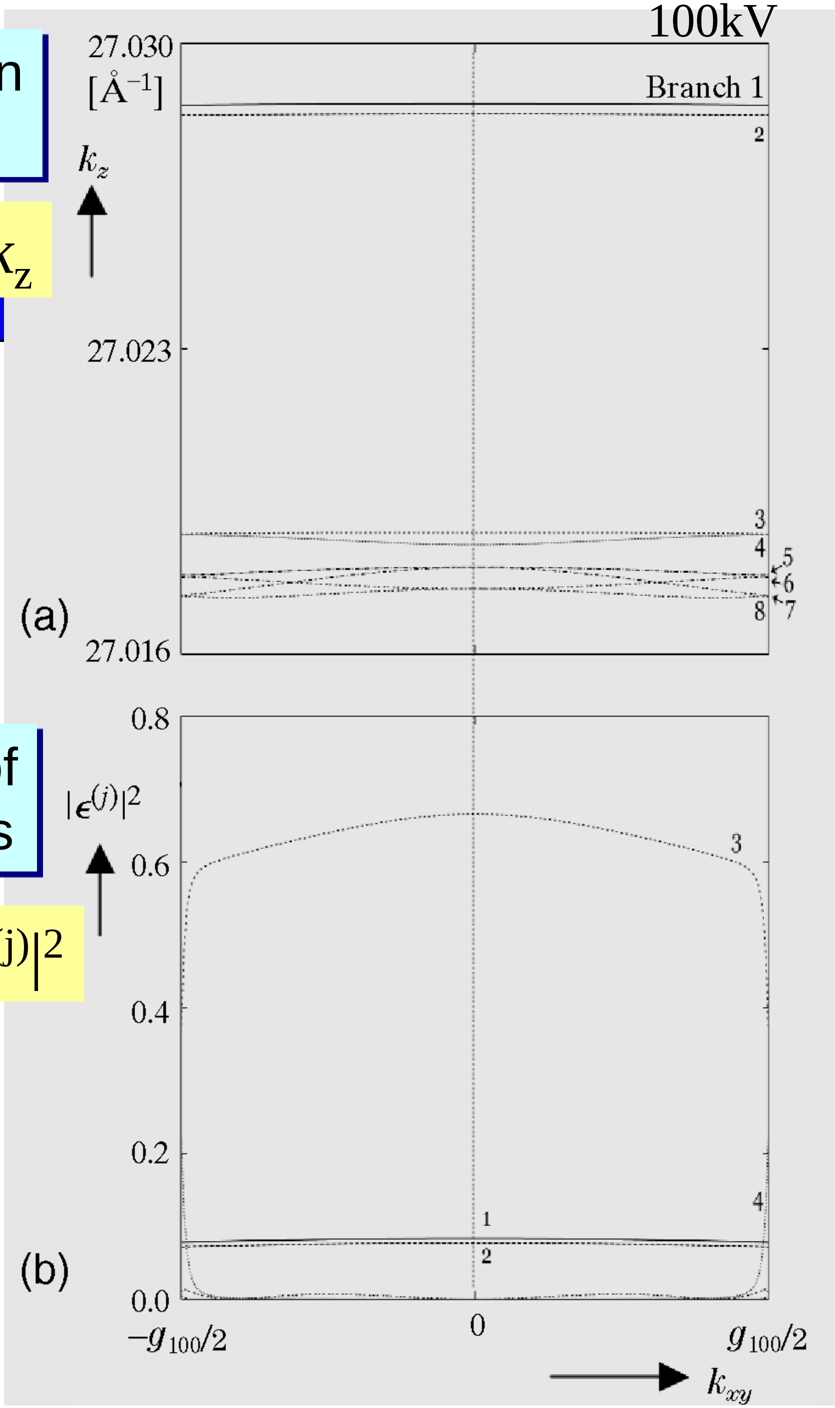
- Electron density distribution of the Bloch state: $|b^{(j)}(\mathbf{r})|^2$

- Excitation of the Bloch states: $\varepsilon^{(j)}$

Dispersion surface and Excitations of Bloch states $SrTiO_3$ [001]

Dispersion surface

k_z



Excitations of the branches

$|\varepsilon^{(j)}|^2$

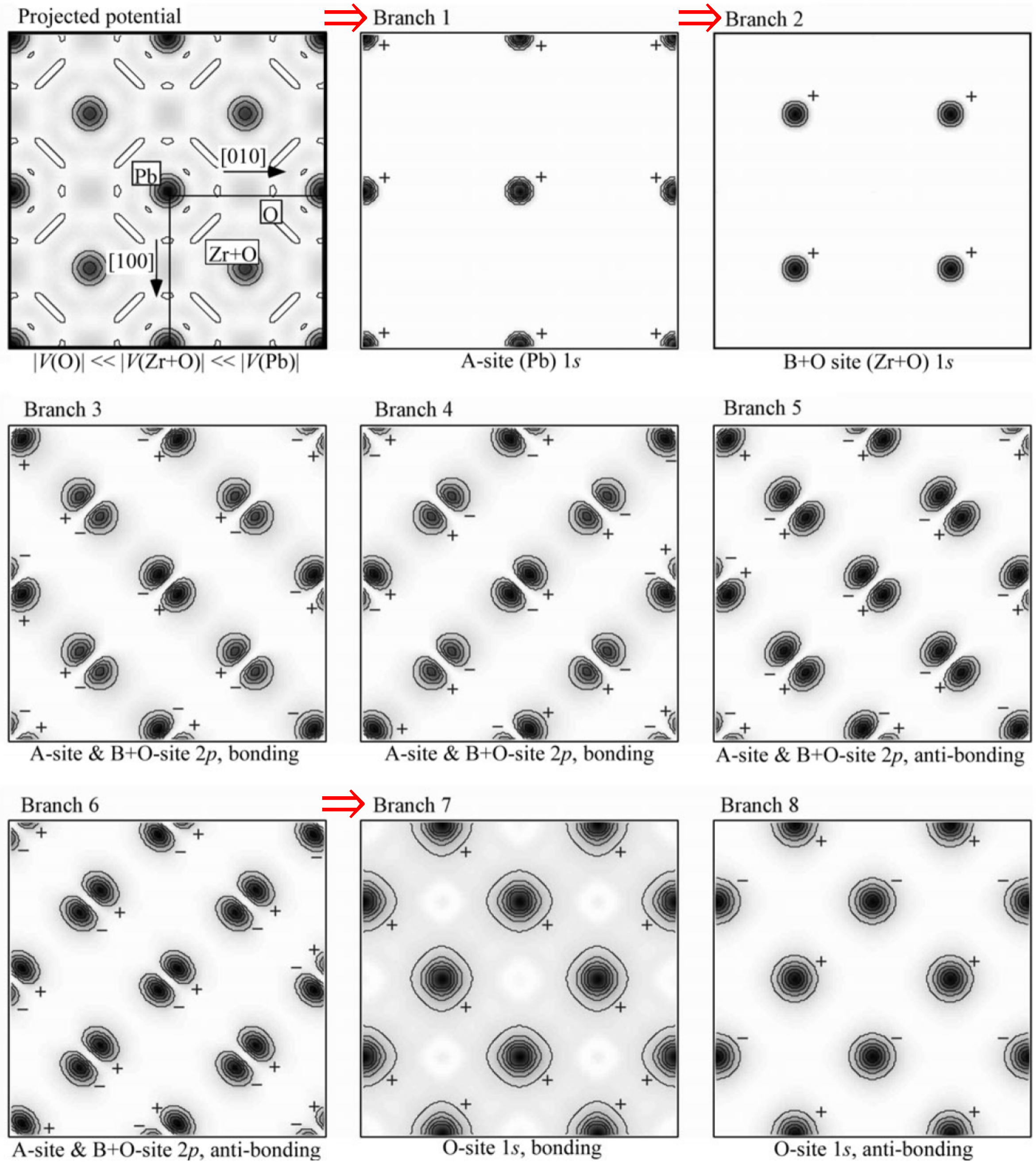
Branches with lower potential energy
➔Higher kinetic energy (*k*)

(Energy conservation)

Curtesy of K. Tsuda

$PbZrO_3$ [001] Bloch-state simulations

100kV



⇒ : well-excited at ZA

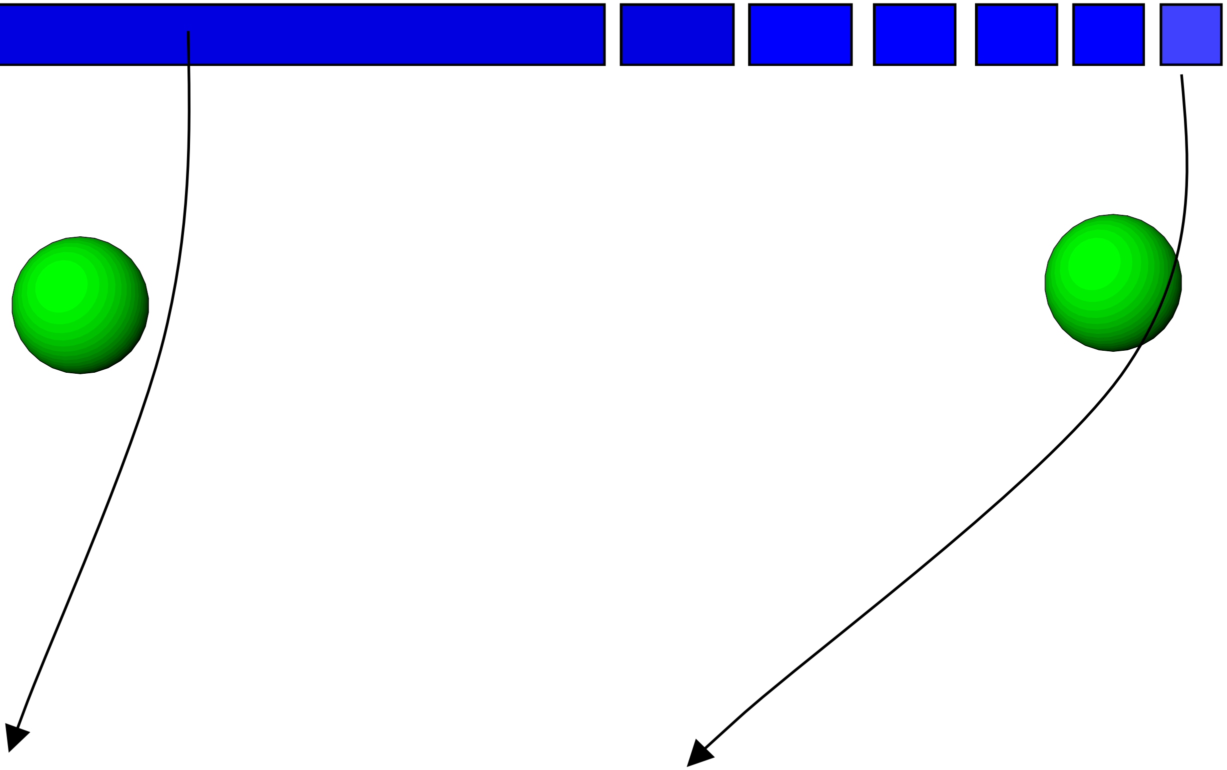
Caveats

- In a thick crystal, must include all states
- Higher E_n states not so “atomic”
- Overlap of states on different columns can be important
- Tilt off zone axis → excites more p, d states
- Strain=tilt, hence may destroy simple picture

Relevance 1: HREM

- For a thin sample the 1s states dominate – simple
- The scattering is pseudo-kinematical, easy to interpret
- In thicker samples (> 20nm) not quite so simple

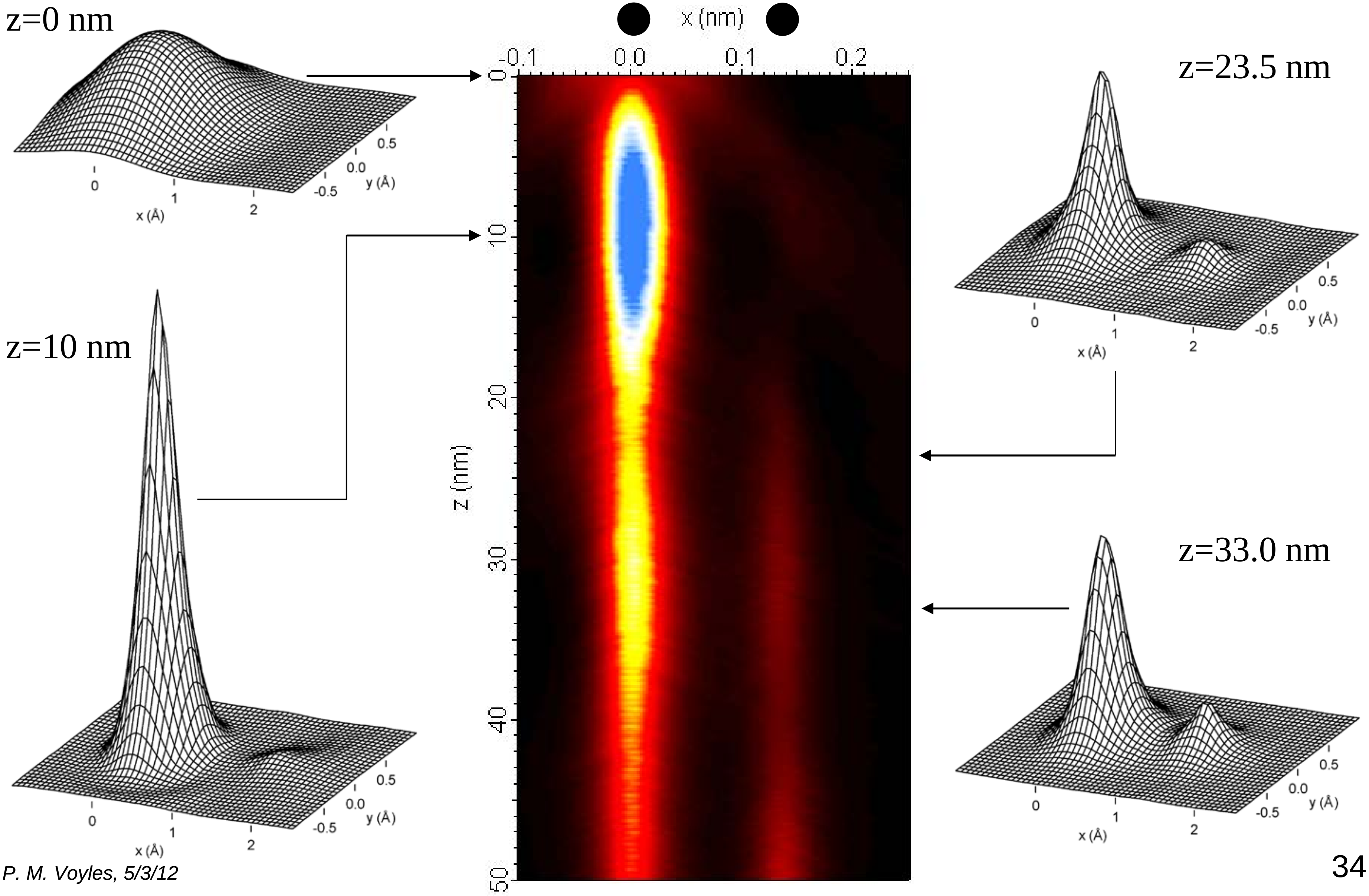
Relevance 2: ADF



The closer the electron comes to the nucleus, the higher the probability of high-angle scattering (elastic or inelastic)

1s states dominate the high-angle scattering

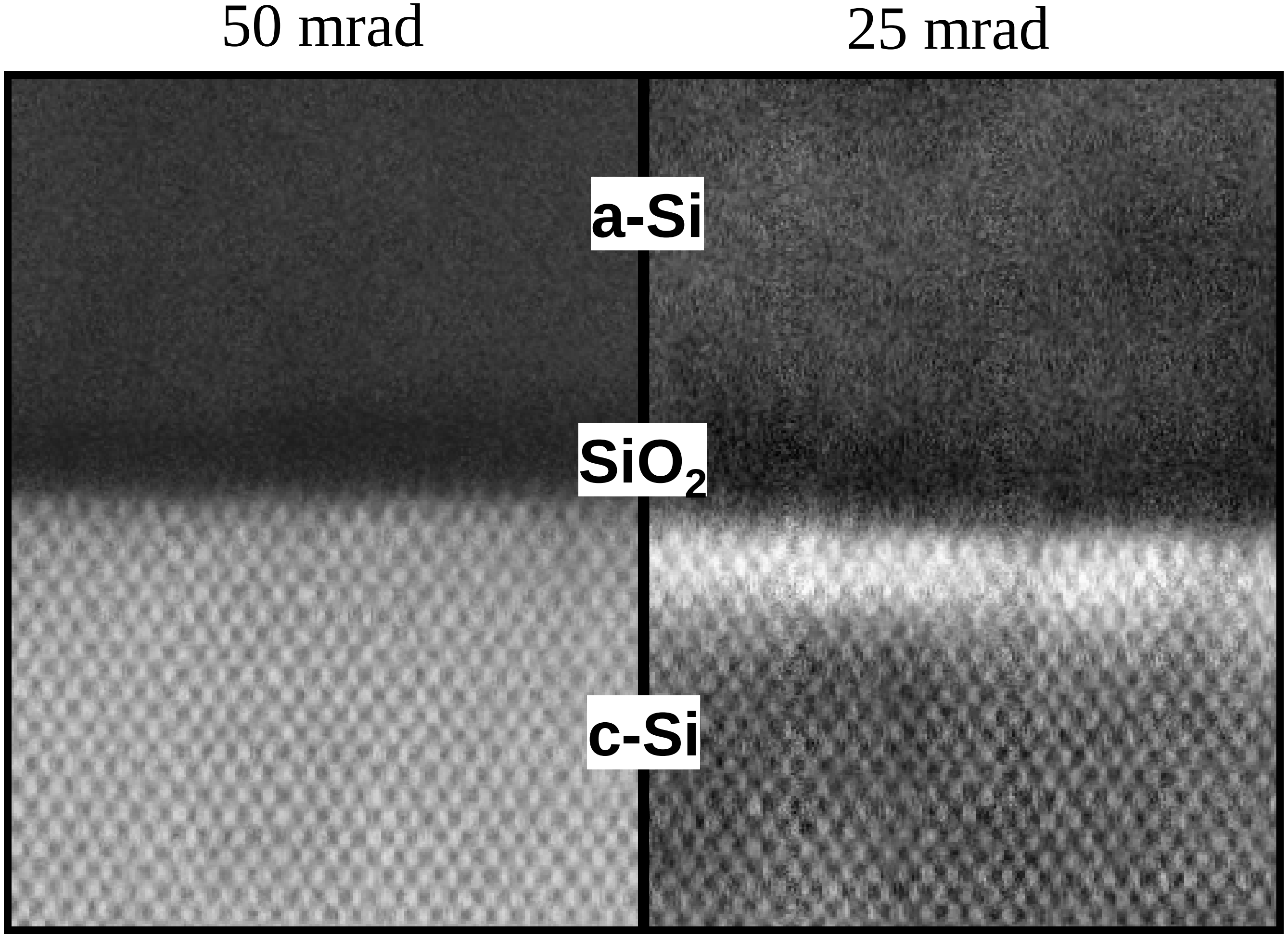
Probe Channeling



Strain Contrast at Si/SiO$_2$ Interfaces

(JEOL 2010F, 200 kV, C_s=1mm)

ADF Inner angle:



Strain Fields cause dechanneling (and scattering to small angles)

Z. Yu, D. A. Muller, and J. Silcox, *J. Appl. Phys.* **95**, 3362 (2004).

When Does the Simple Picture Work?

- Simple incoherent, $Z^{1.7}$ theory works well:
  - for an amorphous specimen
  - for randomly-oriented polycrystalline specimens
  - (mostly) for single crystals tilted between major zone axes
- It doesn't work for single crystals oriented on a zone axes – i.e. when you get atomic-place resolution.