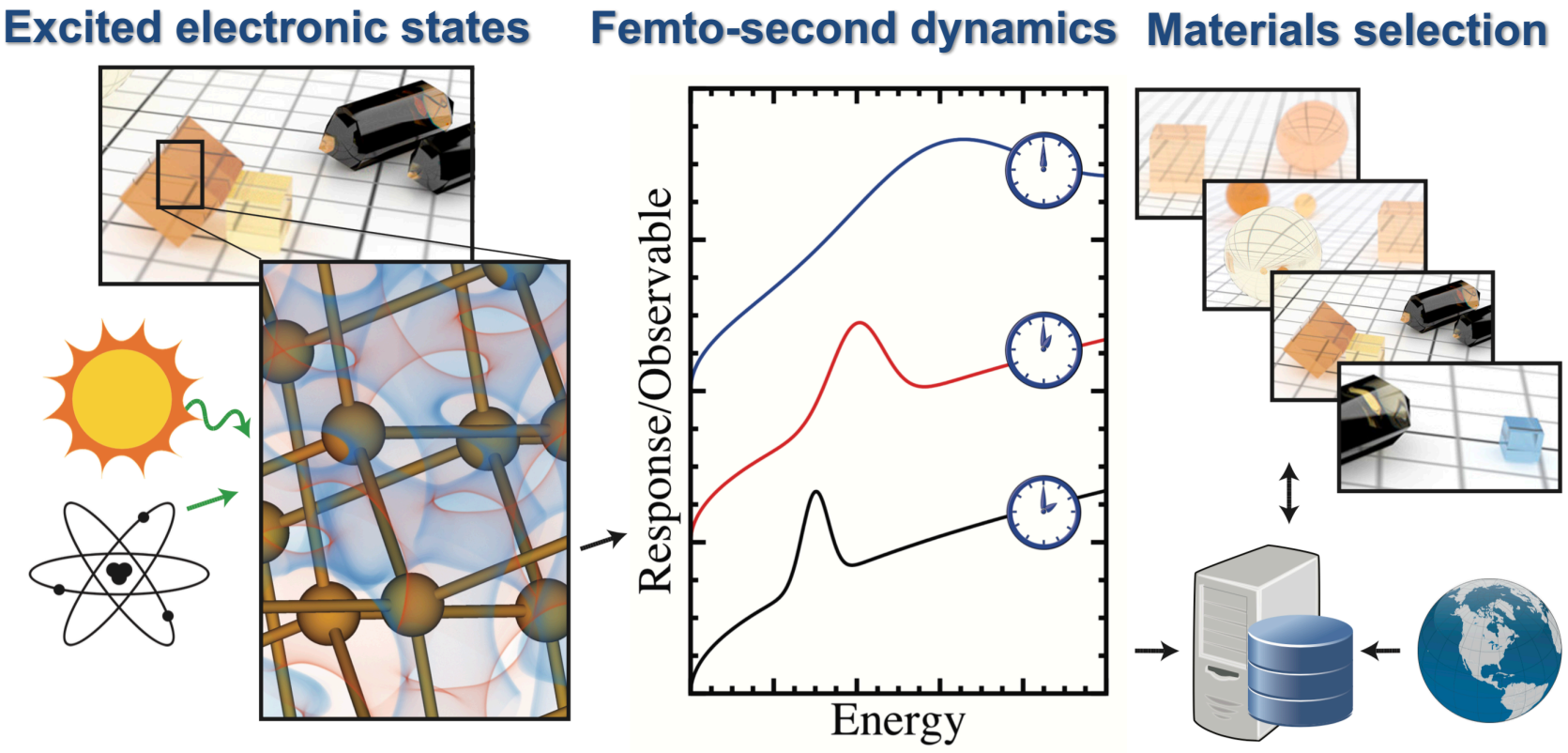
Why … Materials selection?



"Pushing The Frontiers Of Modeling Excited Electronic States And Dynamics To Accelerate Materials Engineering And Design", K. Kang, A. Kononov, C.-W. Lee, J.A. Leveillee, E. Shapera, X. Zhang, A. Schleife, Comp. Mat. Sci. **160**, 207–216 (2019); Finalist "Rising Stars in Computational Materials Science"

Reminders/Introduction: Quantum Mechanics

- Electron described by wave function as basis variable

$$\psi(x,y,z,t)$$

- Square of the wave function describes probability

$$\psi^* \psi$$

- In practice: Solve Schrödinger equation to find wave function

$$\hat{H}\psi = i\hbar \frac{\partial}{\partial t}\psi = E\psi \rightarrow \frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar}(E - V)\psi(x) = 0$$

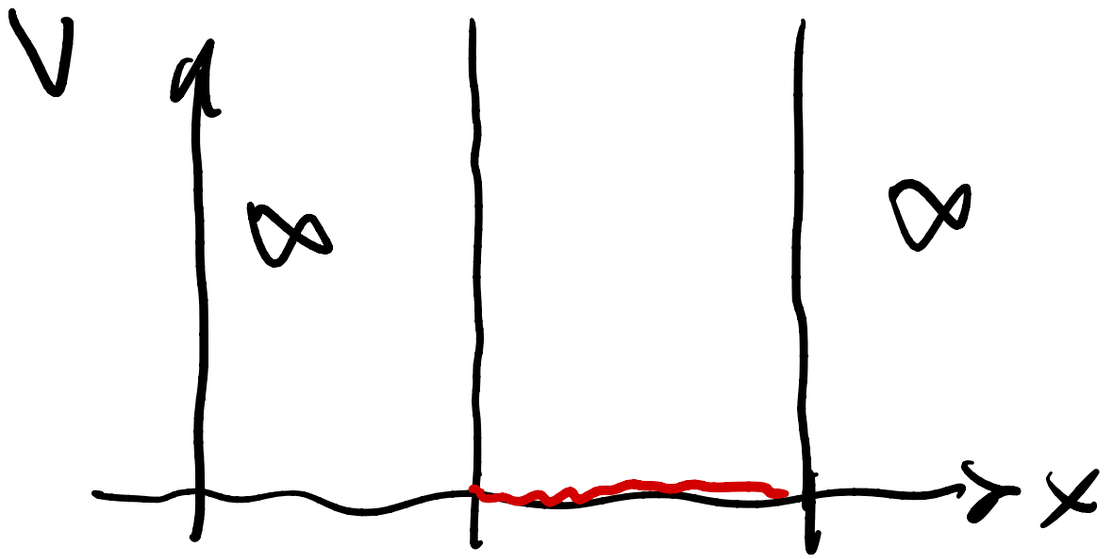
$$\hat{H} = \hat{T} + V$$

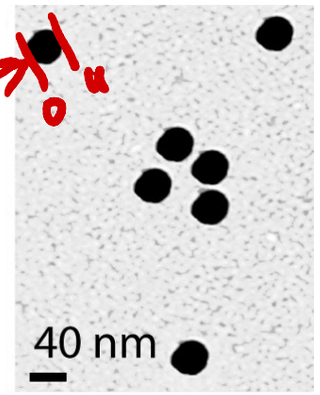
$$k^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0$$

Solution of the Schrödinger Equation: Infinite 1D Well

- infinite well potential looks like this:





- outside: wave fct $= 0$
- inside: free electron
- from math: $\psi(x) = A\exp(ikx) + B\exp(-ikx)$
- $\psi(0) \stackrel{!}{=} 0$ leads to $B = -A$

$$\psi(x) = 2Ai\sin(kx)$$

Solution of the Schrödinger Equation: Infinite 1D Well

$$\psi(x) = 2Ai \sin(kx) \qquad k^2 \equiv \frac{2m}{\hbar^2} E$$

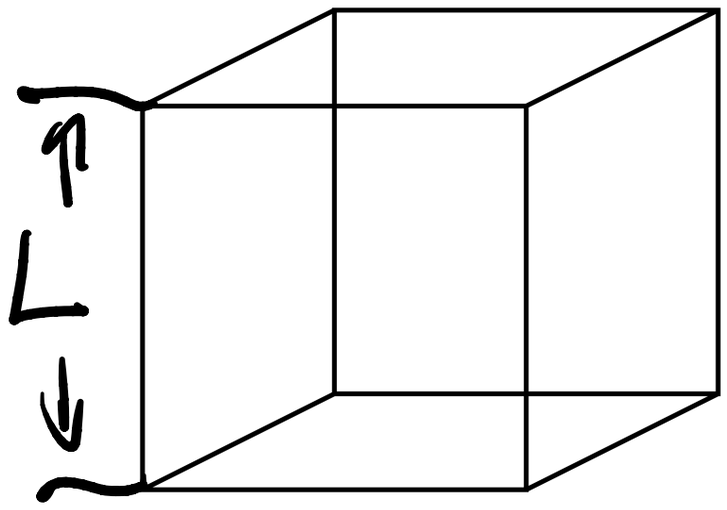
- still have to determine k by fulfilling: $\psi(a) = 0 = 2Ai \sin(ka)$
- this requires: $ka \simeq n\pi \rightarrow k = \frac{n\pi}{a}$

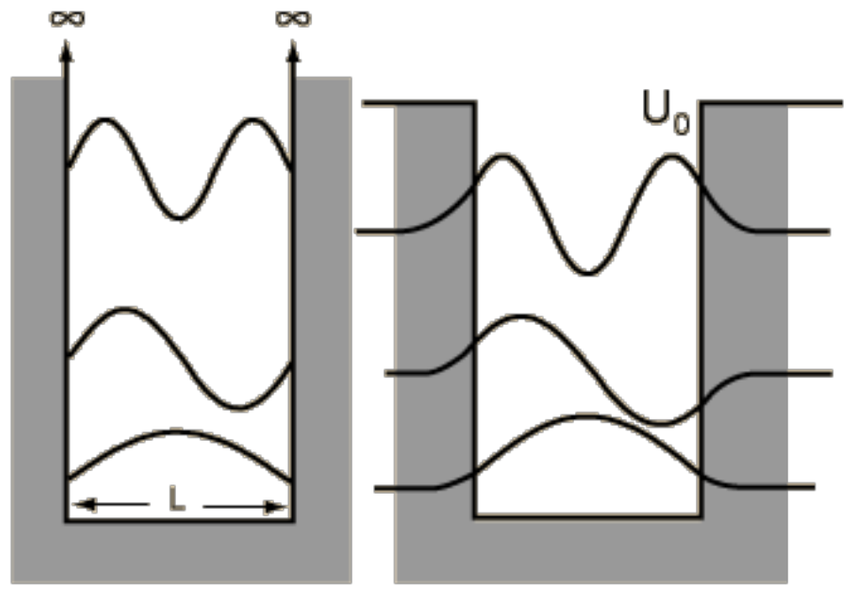
- overall wave function: $\psi(x) = 2Ai \sin\left(\frac{n\pi x}{a}\right)$

$$E = \frac{\hbar^2 n^2 \pi^2}{2ma^2}$$

Solids: Free-electron gas model

- Free-electron gas model of a solid looks like:

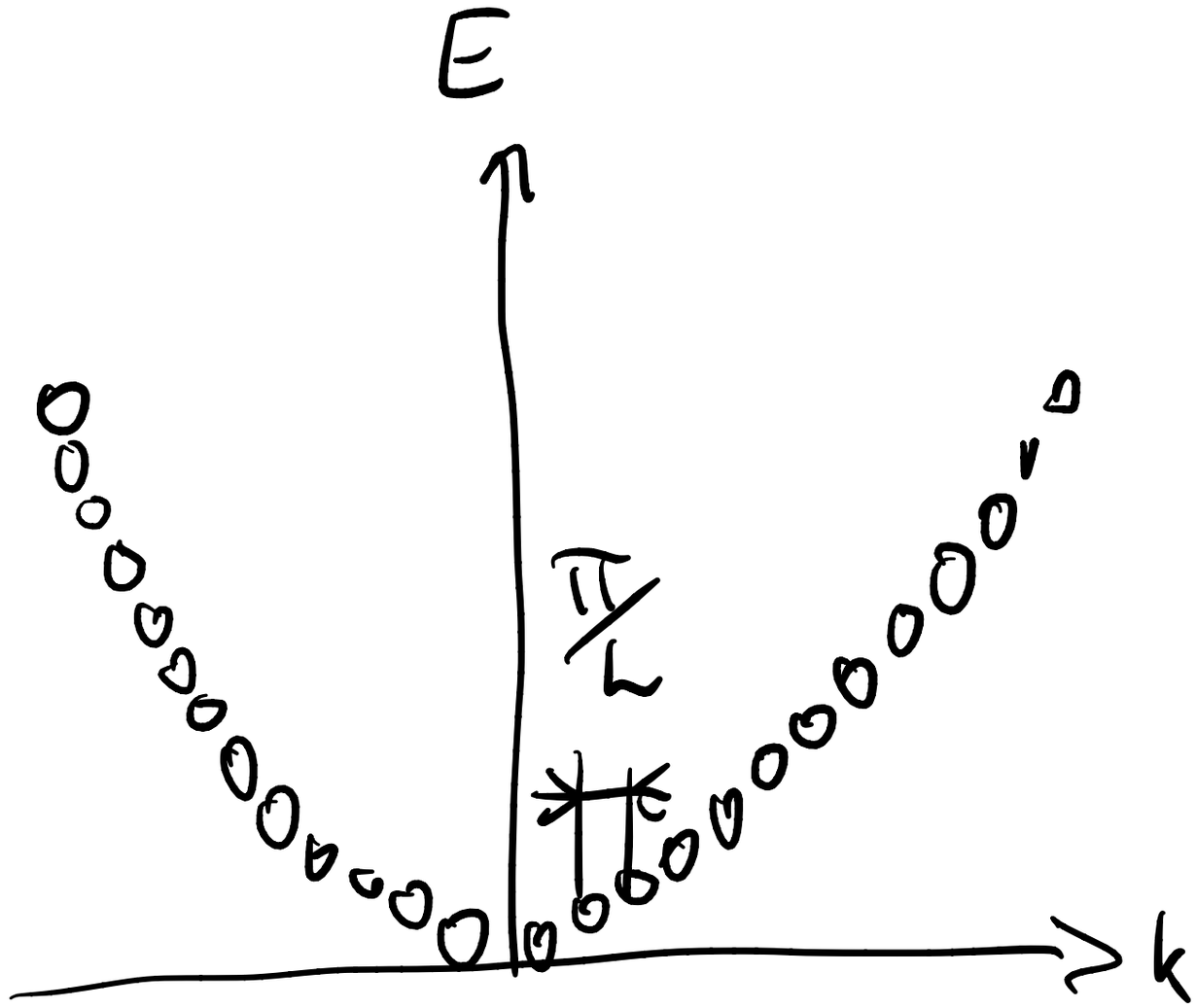




- found for 1D infinite well: $E = \frac{\hbar^2 k^2}{2m}$ $\qquad k^2 = \frac{n^2 \pi^2}{L^2}$
- in 2D: $E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2\right)$
- in 3D: $E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$

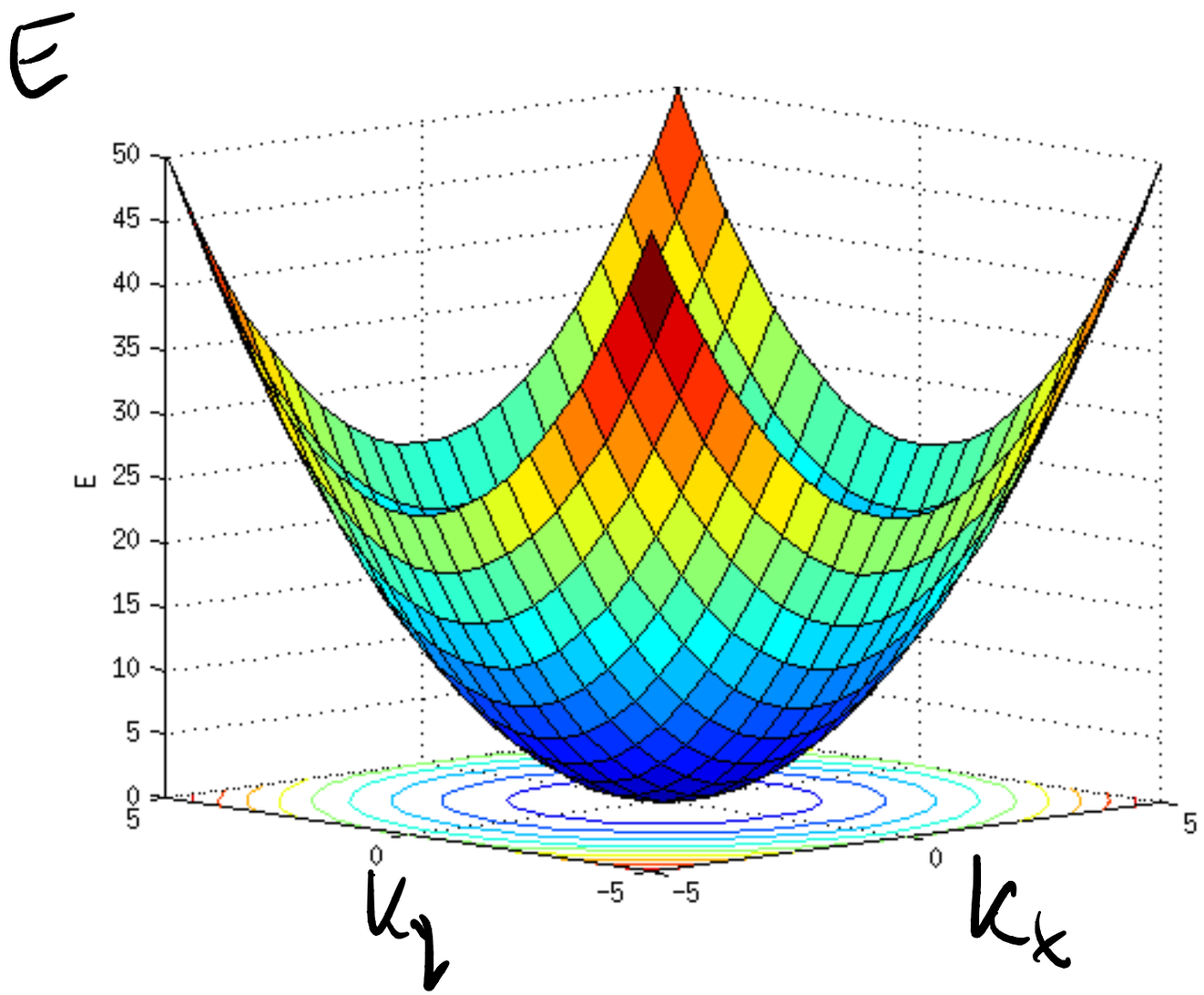
Solids: Free-electron gas model

- energy-momentum relationship (1D):



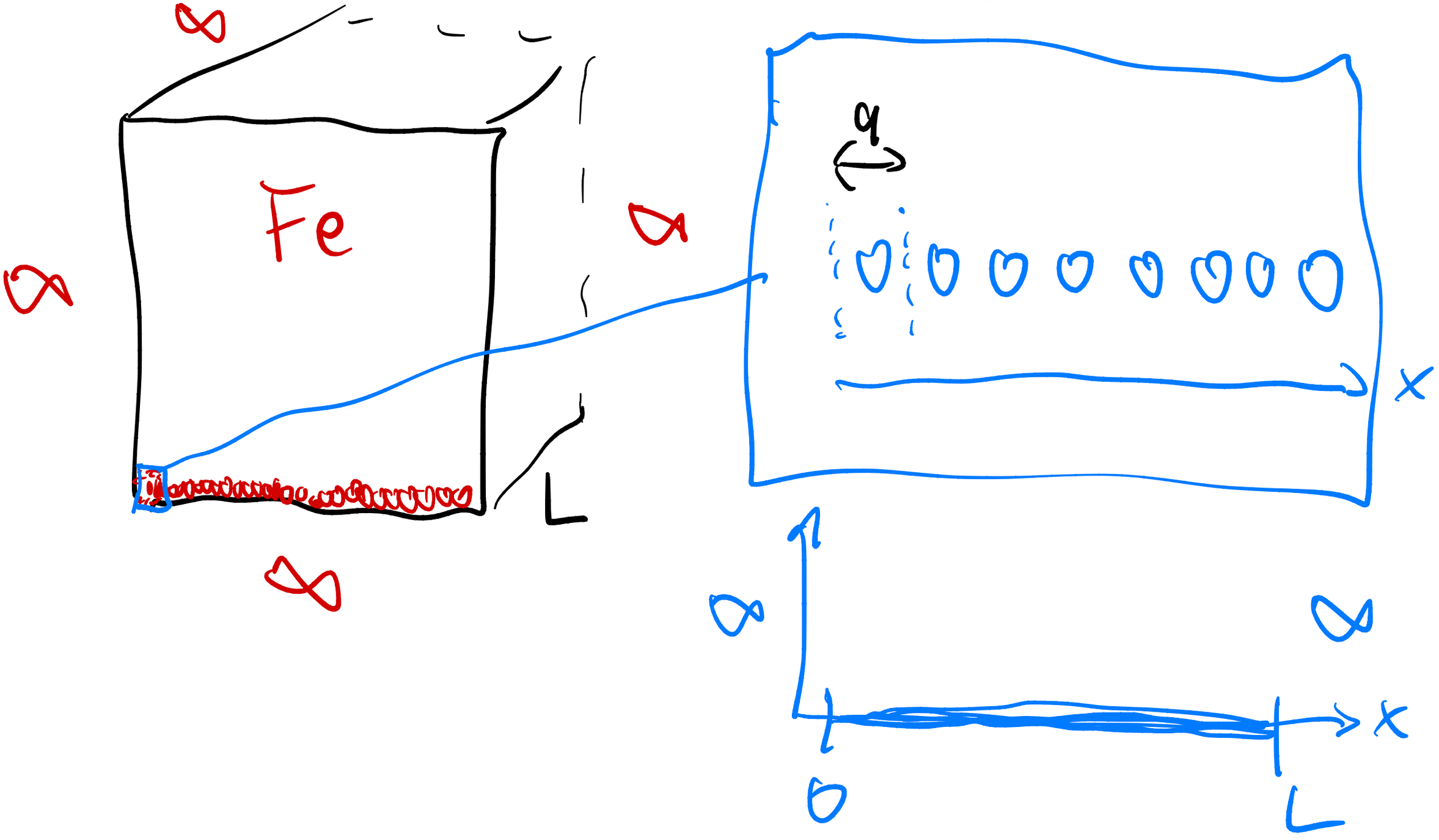
Solids: Free-electron gas model

- energy-momentum relationship (2D):



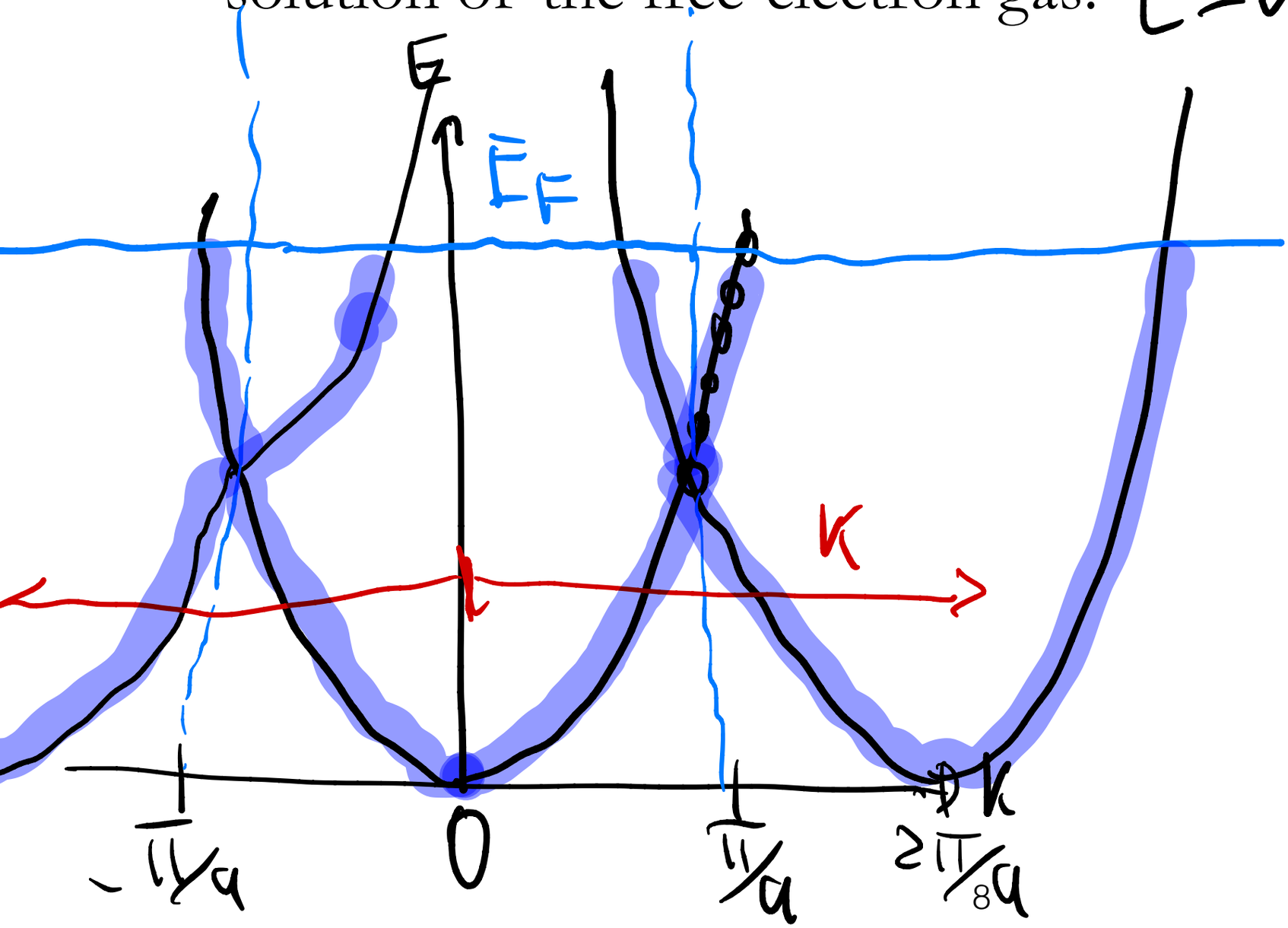
Towards a Band Theory of Solids: Periodic Potential

- we assume: all atoms sit on equilibrium positions
- this leads to a *periodic* lattice of atoms (potential for electrons)



Towards a Band Theory of Solids: Periodic Potential

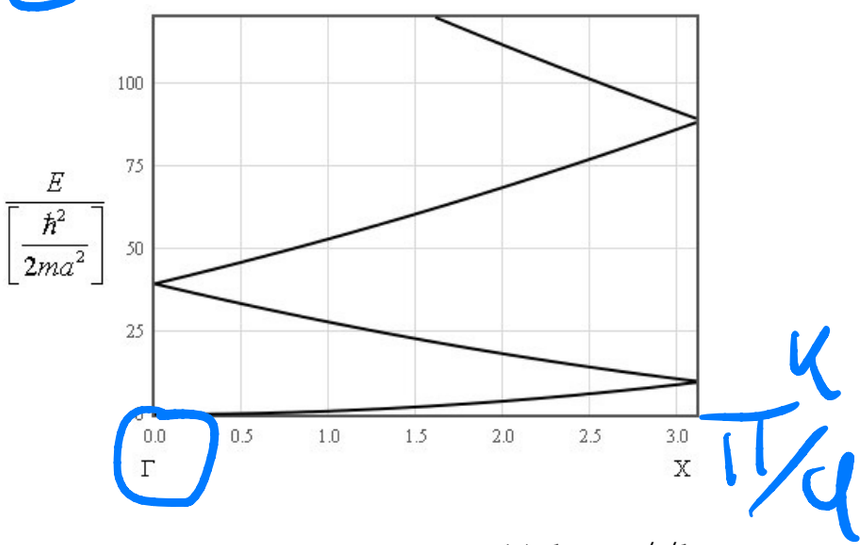
- we assume: all atoms sit on equilibrium positions
- this leads to a *periodic* lattice of atoms (potential for electrons)
- Bloch theorem (for all periodic potentials)
- solution of the free-electron gas: $E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (k_{reduced} + K)^2}{2m}$



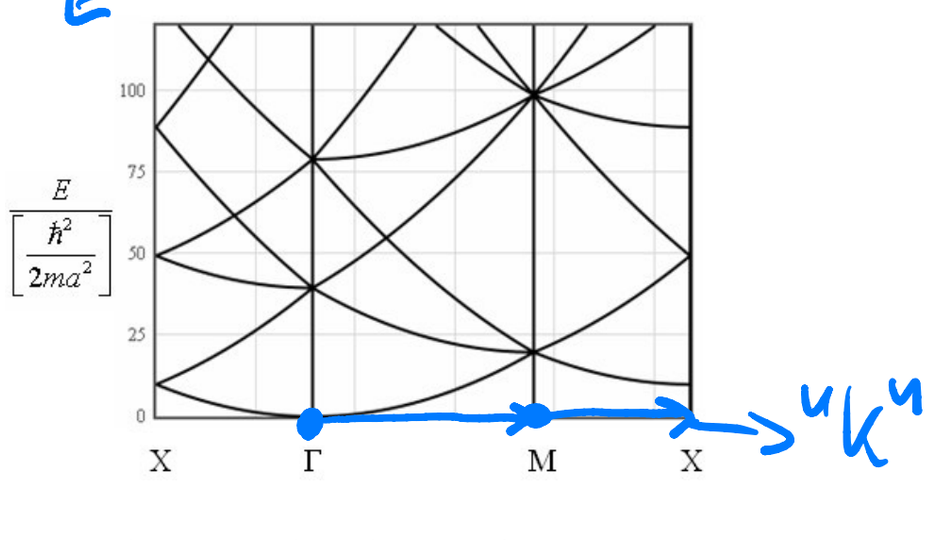
Towards a Band Theory of Solids: Empty Lattice Approximation

- lattice is periodic, but no atoms are present
- plot solutions for different lattice types: don't show periodicity

1D



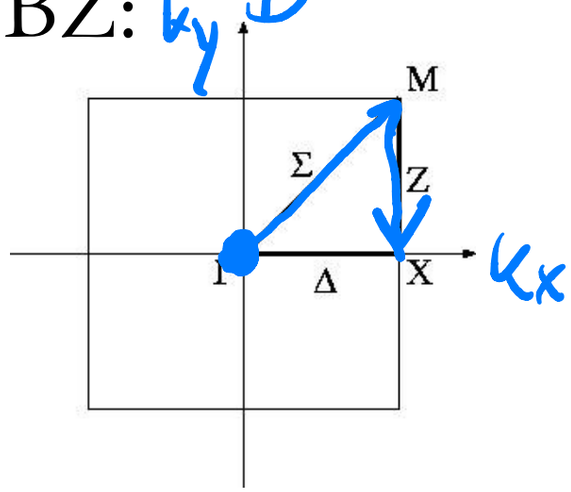
2D (square)



(c) http://lamp.tu-graz.ac.at/~hadley/ss1/empty/empty.php

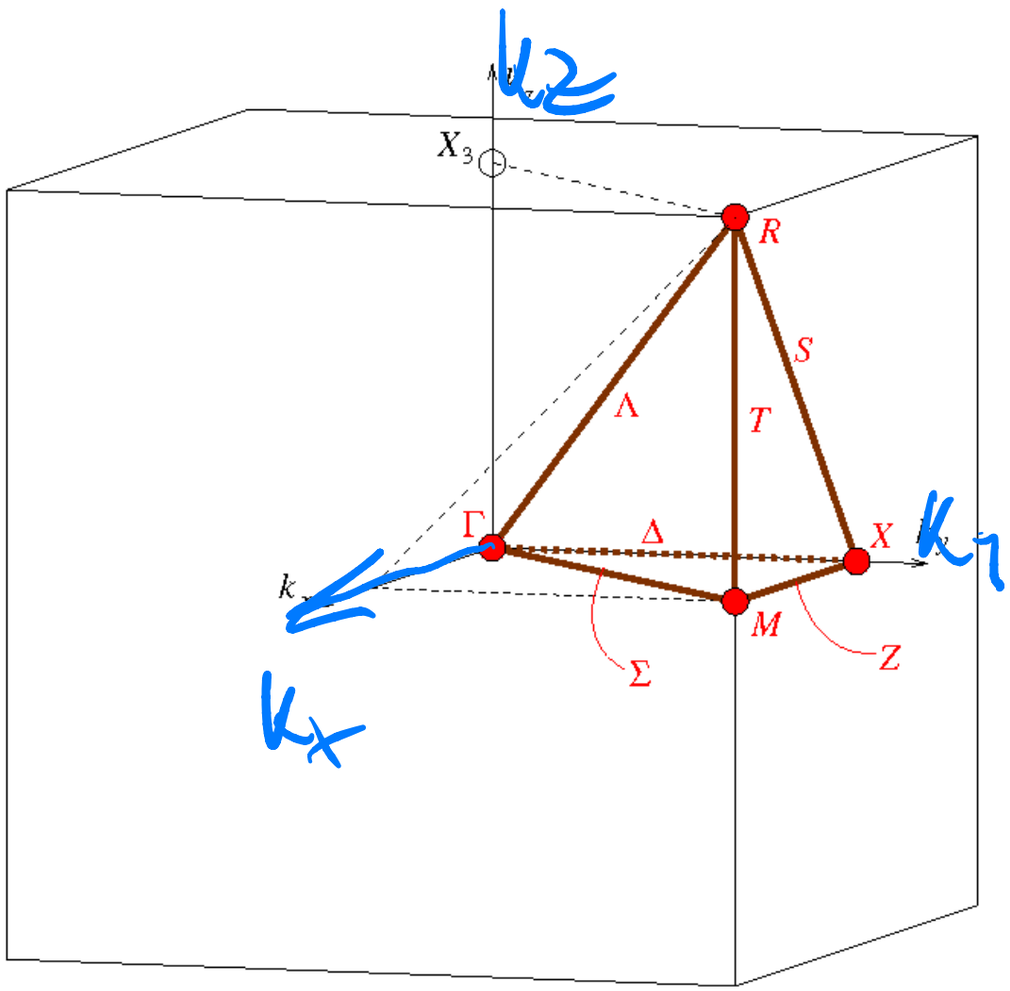
$$E(\mathbf{k}) = \hbar^2 \frac{\mathbf{k}^2}{2m} = \hbar^2 \frac{(\mathbf{k}_{\text{reduced}} + \mathbf{K})^2}{2m}$$

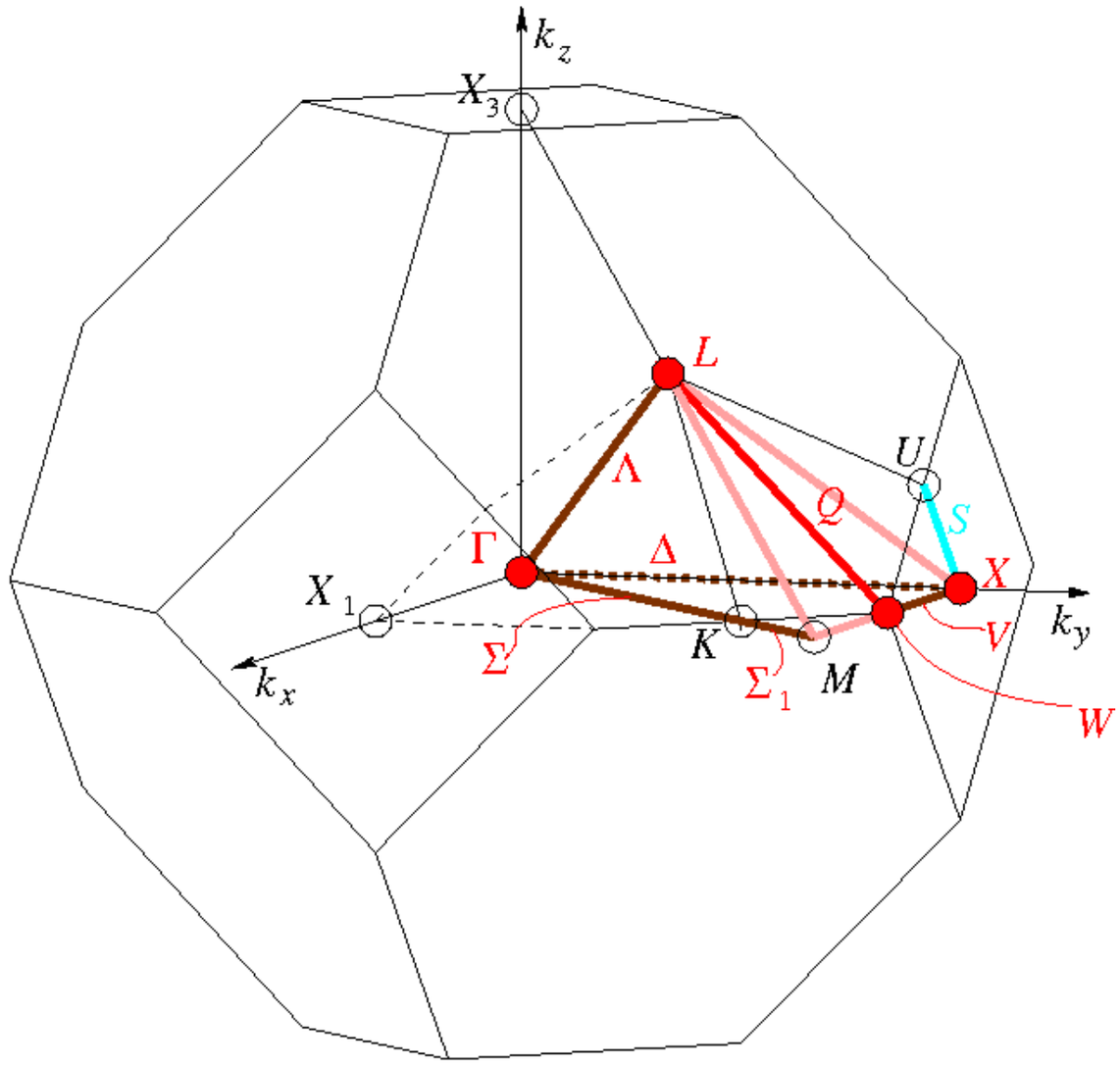
BZ:



Towards a Band Theory of Solids: Reciprocal Lattice

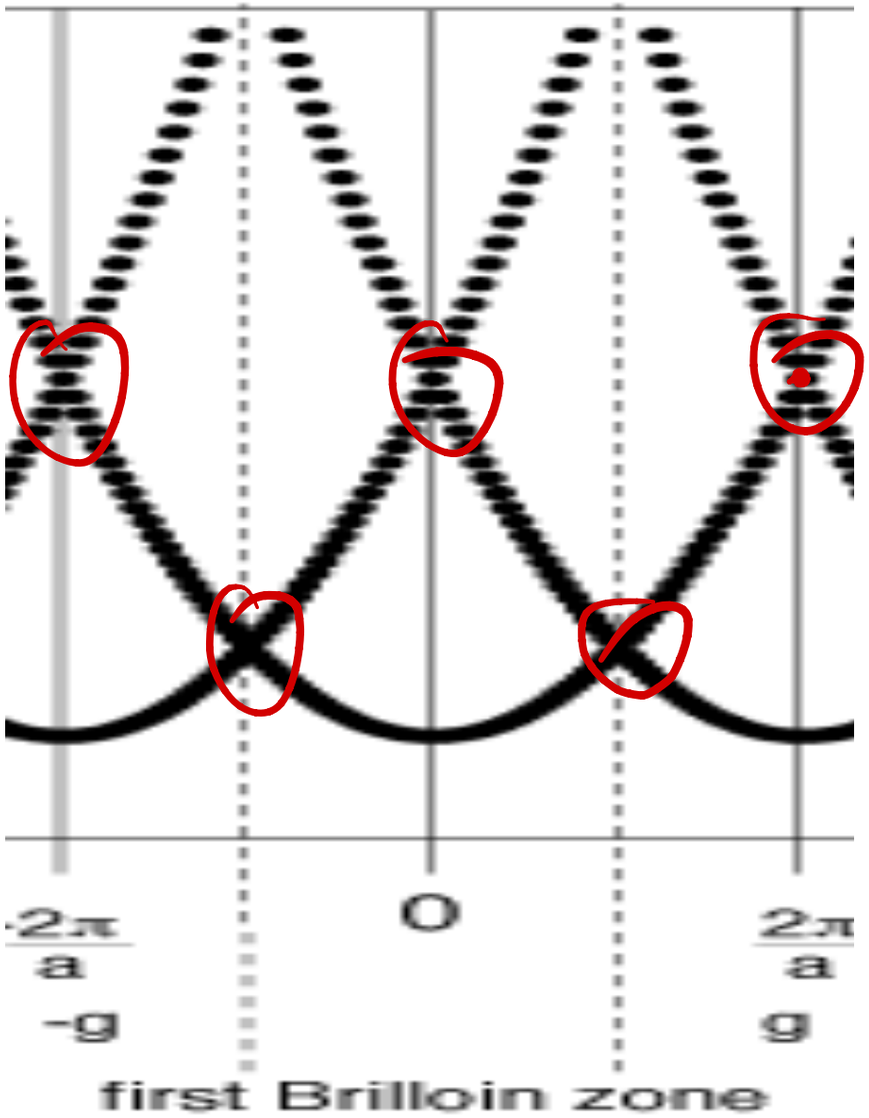
- Wigner-Seitz cell of reciprocal lattice: Brillouin zone



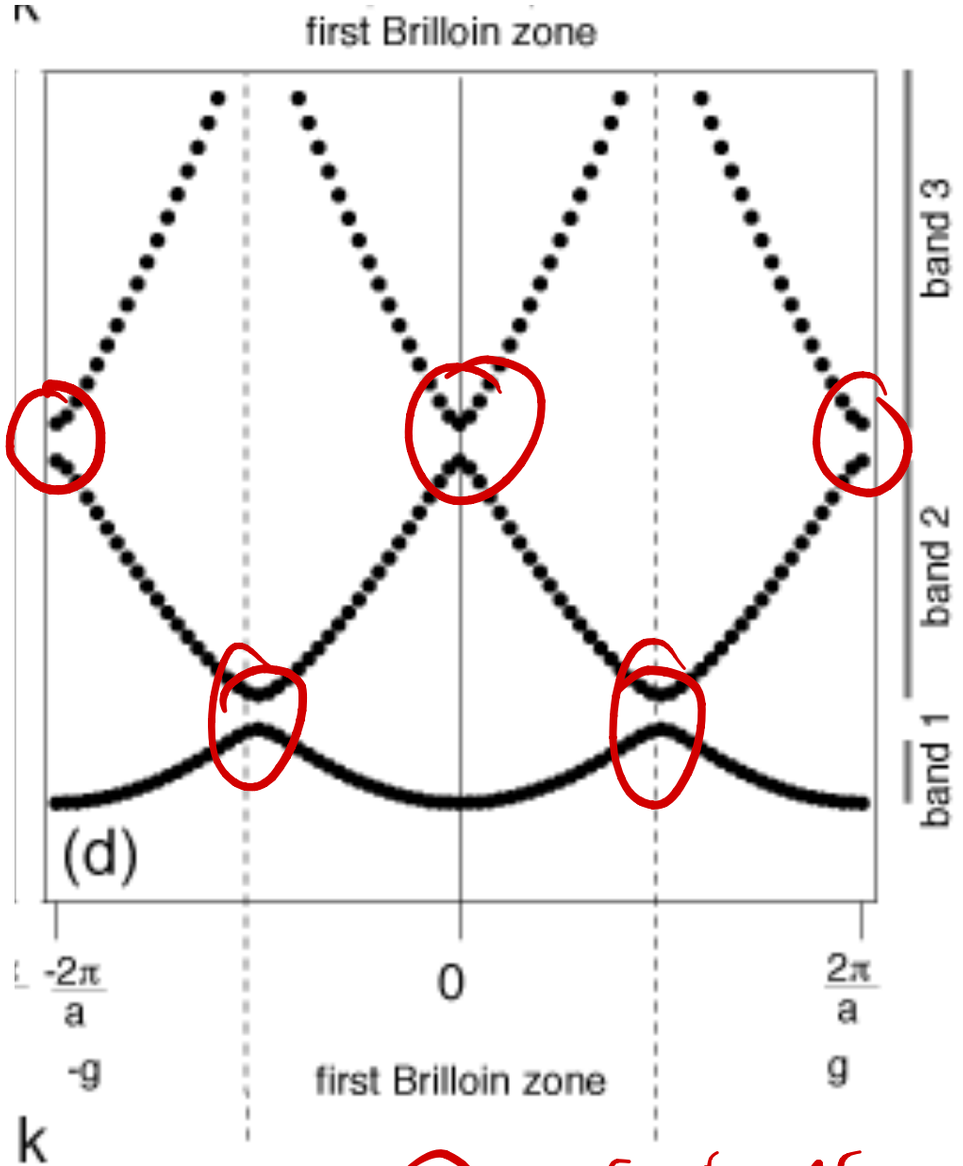


Towards a Band Theory of Solids: Nearly Free Electrons

- these results allow us to draw the following energy diagram for nearly free electrons

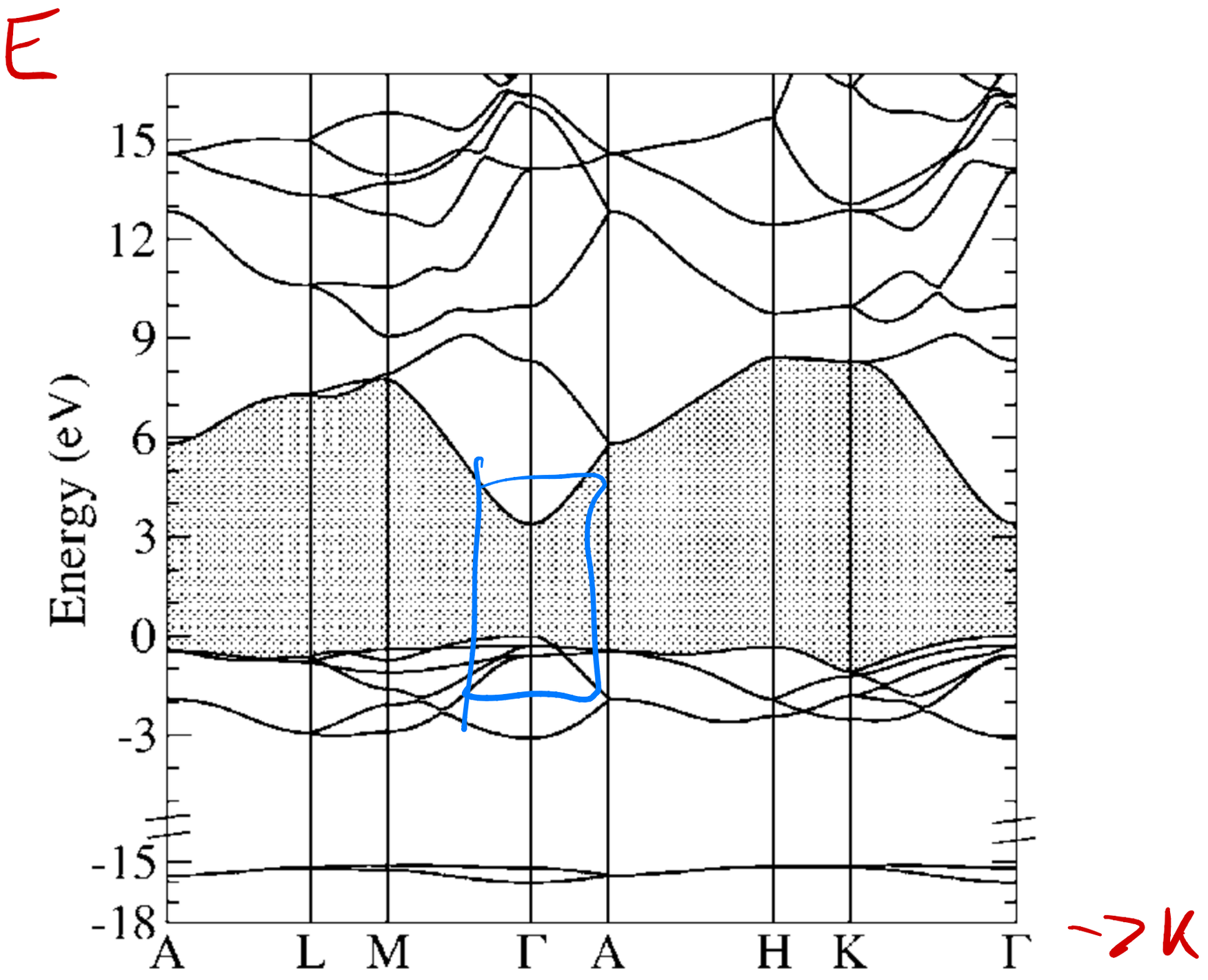


V = 0



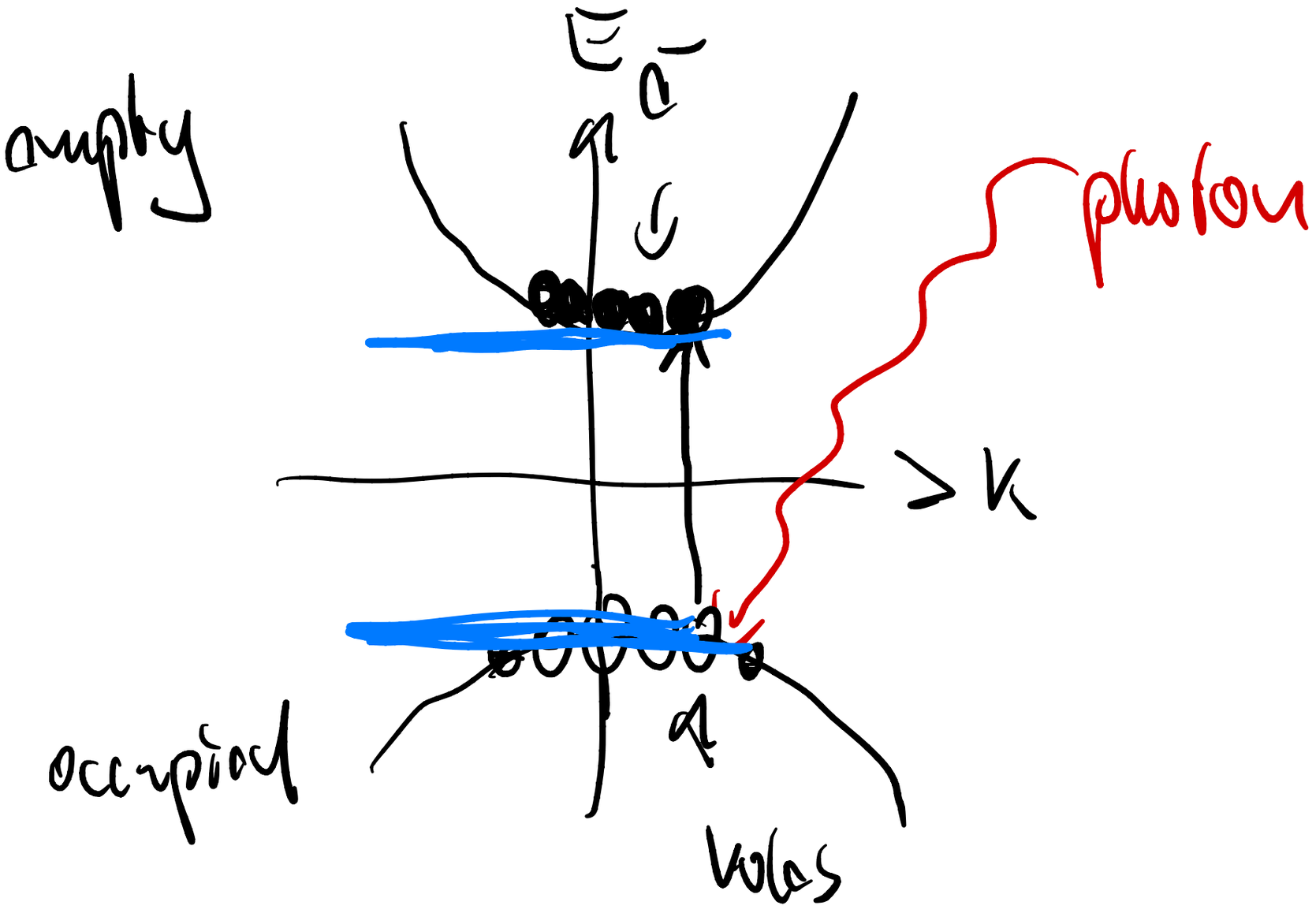
V ≠ 0 (atoms present)

Band Structure for a real material



(c) Phys. Rev. B **73**, 245212 (2006)

Semiconductors: Conductivity and Absorption

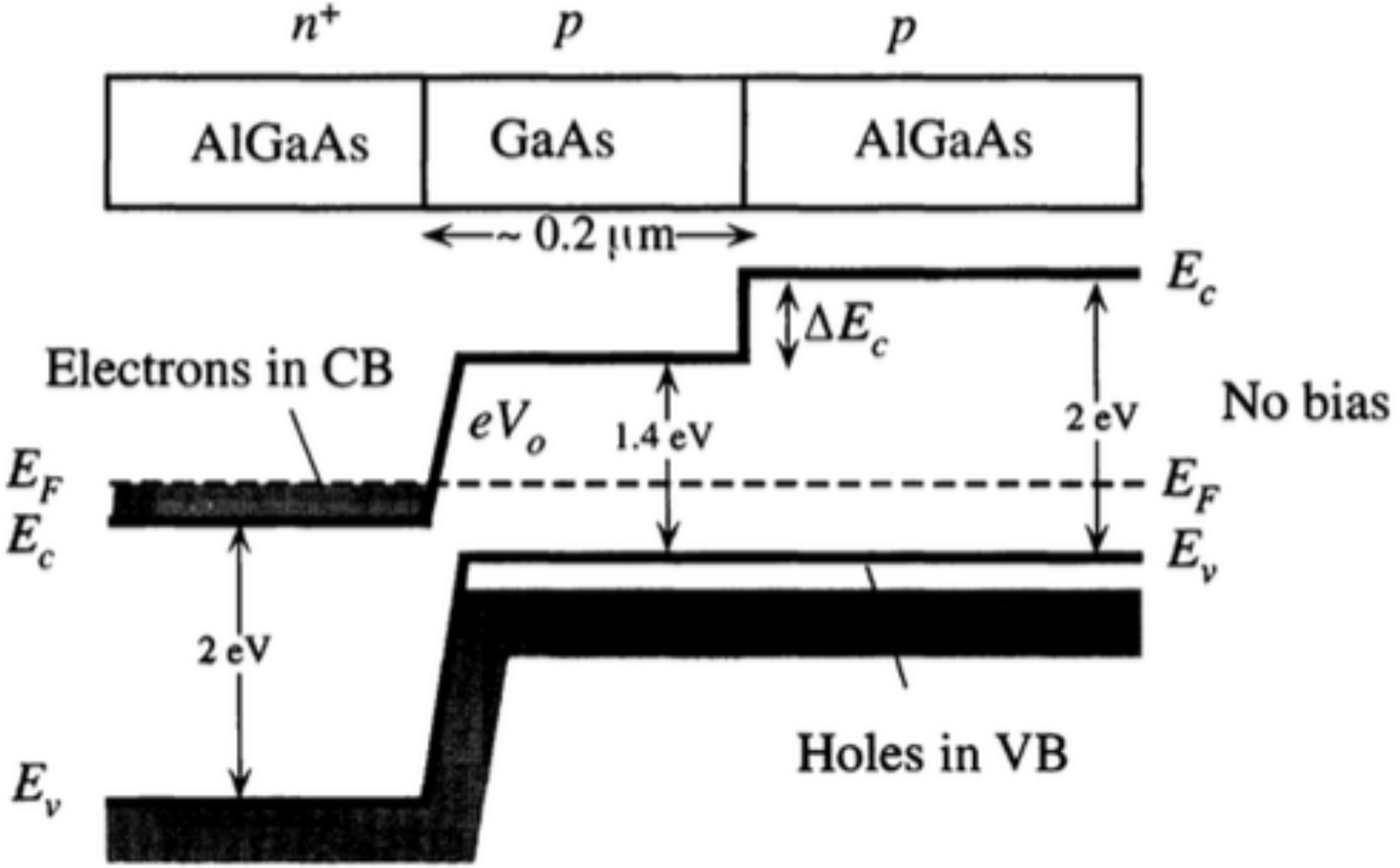


p-n junction: Energy Band diagram

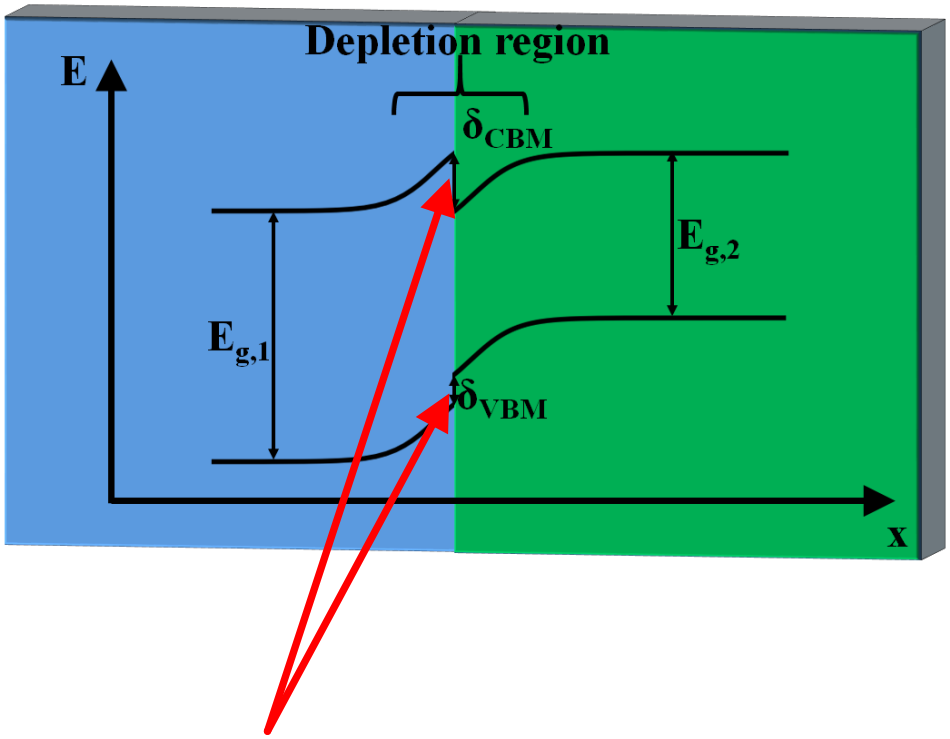
- before contact:

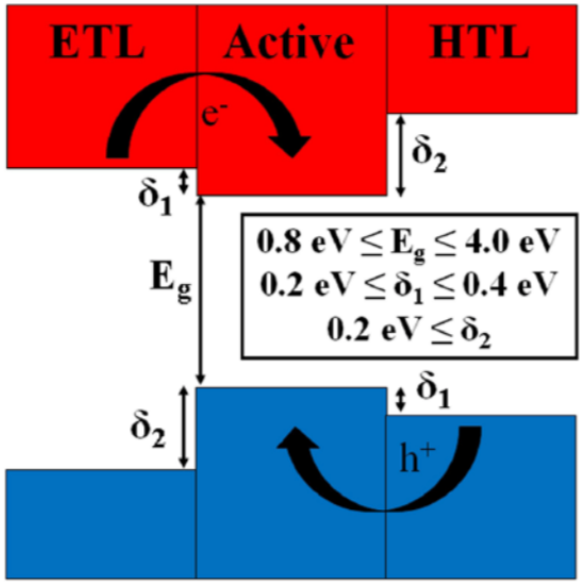
- after contact:

Heterojunction LED:



Materials Selection for Semiconductor Heterojunctions



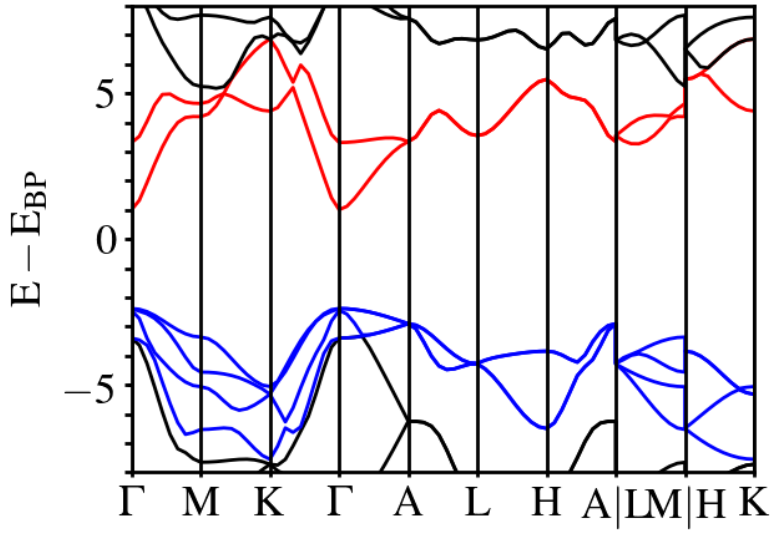


Energy discontinuities at interface for band offsets

Heterojunctions: Branch-point energy

- Experimentally and computationally difficult to determine how bands bend and align at interface between materials
- Calculate alignment with branch point energy from online electronic structure data in existing databases

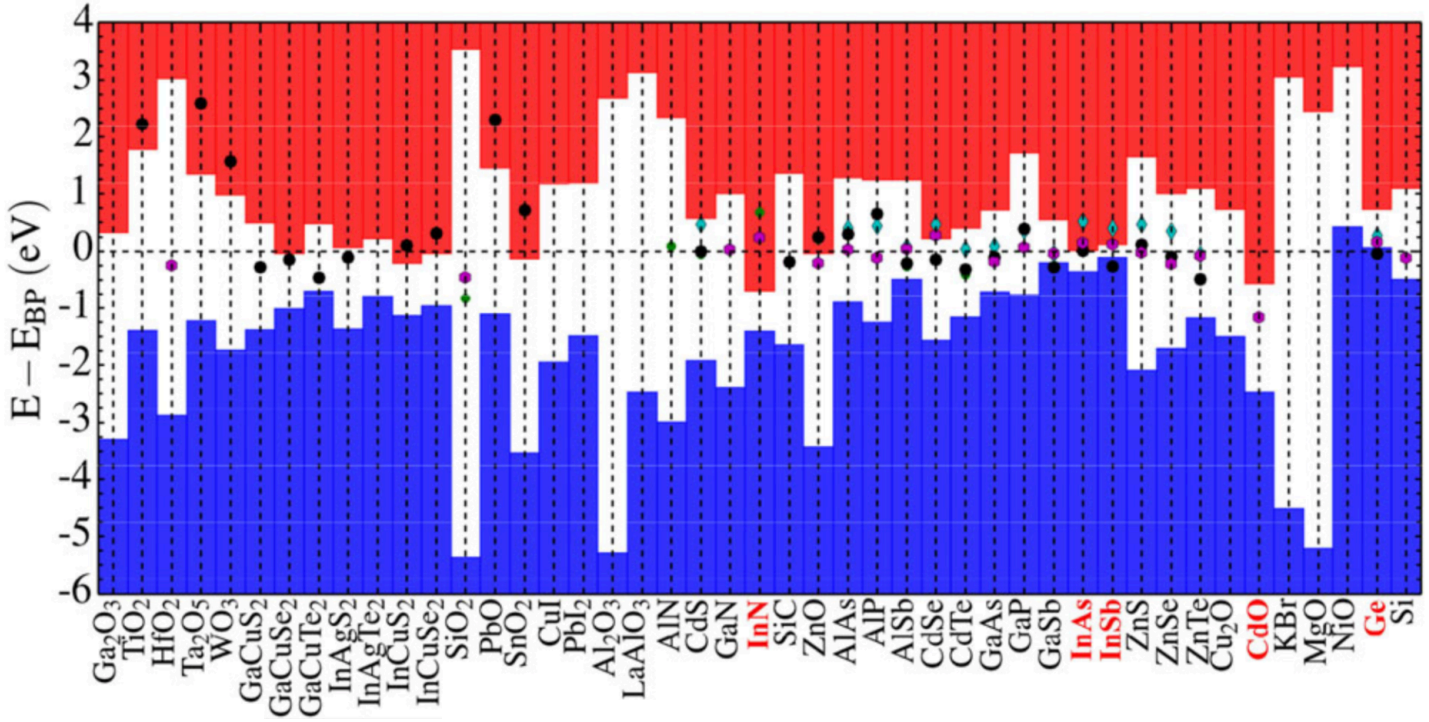
$$E_{BP} = \frac{1}{2N_{\boldsymbol{k}}}\left(\frac{1}{N_c}\sum_{c_i}^{N_c}\varepsilon_{c_i}^{\mathrm{QP}}(\boldsymbol{k}) + \frac{1}{N_v}\sum_{v_i}^{N_v}\varepsilon_{v_i}^{\mathrm{QP}}(\boldsymbol{k})\right)$$



- Band gap corrected with two-tiered scheme
  - Use experimental values if available
  - Linear band-gap correction (Curtarolo) otherwise: $\mathrm{E_g^{corr}} = 1.348\mathrm{E_g^{DFT}} + 0.913\ \mathrm{eV}$
- Use Brus equation for nanocrystals: $\Delta\mathrm{E_g} = \frac{\hbar^2\pi^2}{2\mathrm{R}^2}\left(\frac{1}{\mathrm{m_e^*}} + \frac{1}{\mathrm{m_h^*}}\right)$

E. Shapera and A. Schleife; Adv. Theor. and Simulations **1**, 1800075 (2018)

Heterojunctions: Branch-point energy



- Visual comparison of band alignment to different experimental (purple, black) and theoretical techniques (green, cyan), 45 semiconductors
- Comparing to Exp. for 21 materials: Mean absolute error = 0.19 eV
- Vacuum-level alignment for 17 materials: MAE = 0.28 eV (us: 0.12 eV)
- Hydrogen-level alignment: MAE = 0.32 eV (us: 0.31 eV)

E. Shapera and A. Schleife; Adv. Theor. and Simulations **1**, 1800075 (2018)

This notebook plots the band alignment of materials using the data from Materials Project.

```
import math
import numpy as np
import matplotlib.pyplot as plt
import bisect
import itertools
import copy
import operator
from matplotlib.ticker import AutoMinorLocator
import matplotlib as mpl
mpl.rcParams['axes.linewidth'] = 2.0
csfont = {'fontname':'Times New Roman'}
from google.colab import drive
drive.mount('/content/drive')
```

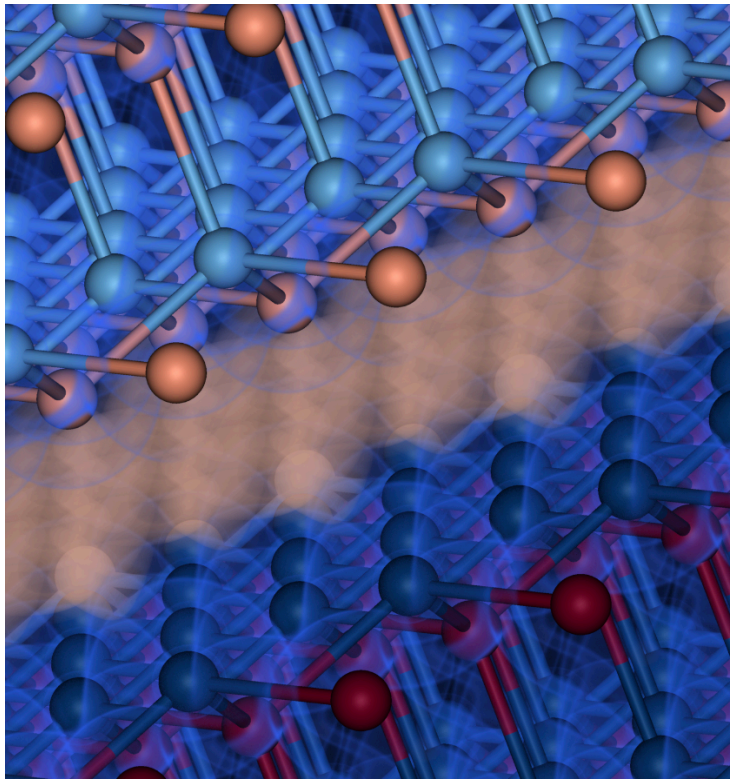
```
Drive already mounted at /content/drive; to attempt to forcibly remount, call drive.mount("/content/drive", force_remount=True).
```

In the next cell, specify the MPIDs for he desired materials. Order is not important, they will be sorted automatically.

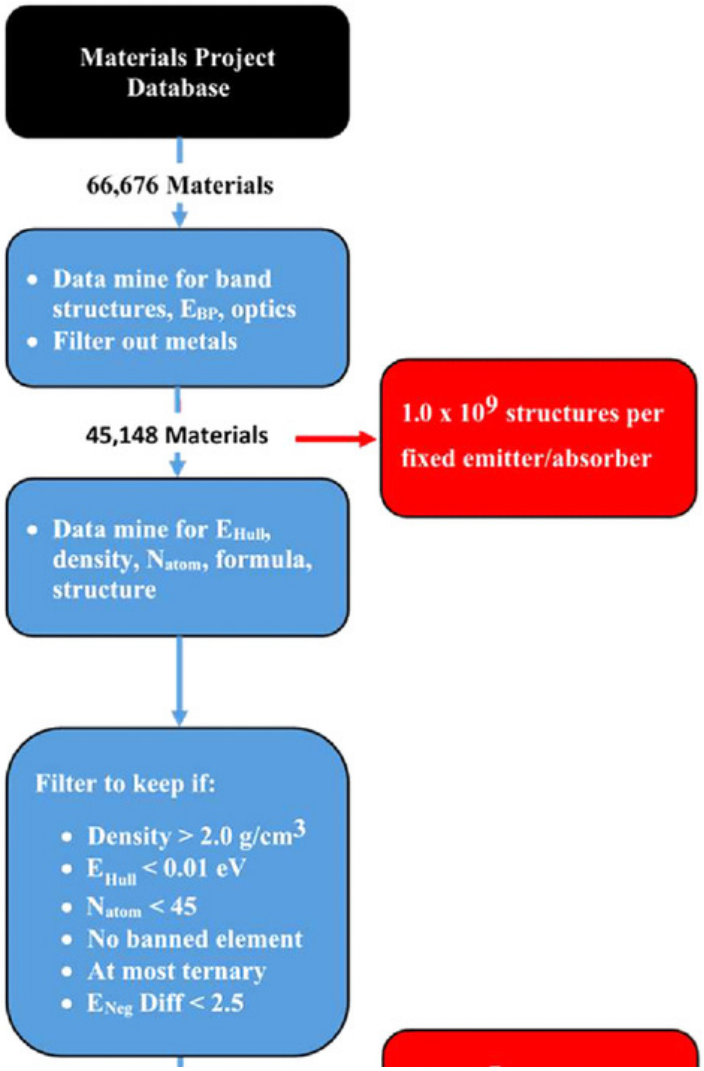
```
[ ] #IDsToPlot=[886,554278,352,10390,19342,5238,4840,3839,19833,22386,22736,22811,546794,19921,856,570136,22883,1143,2920,
    #           661,672,804,22205,7631,2133,2172,1550,2624,2691,406,2534,2490,1156,20305,20012,10695,1190,2176,361,1132,
    #           23251,1265,715434,32,149]
    IDsToPlot=[886,554278,352,10390]
```

The next slide is the main section.

Semiconductor heterojunctions: Results



Semiconductor Heterojunctions: Materials selection



- Data-mine Materials Project database for electronic, crystal properties
- Filtering based on experimental criteria

E. Shapera and A. Schleife; Adv. Theor. and Simulations (2018)

jupyter CollectMaterialsProjectData (autosaved)

File Edit View Insert Cell Kernel Widgets Help Not Trusted

Run Code

In the next cell enter your API key for Materials Project.

In [ ]:
```
API_Key=
mp=MPRester(API_Key)
```

The following cell collects the used MPIDs in Materials project and writes to file.

In [ ]:
```
IDFilename='idlist.txt'
fID=open(IDFilename,'w')

data = mp.query(criteria={}, properties=["task_id"])
AllIDs=[]
for i in data:
    AllIDs.append(int(i['task_id'].split('-')[1]))
IDList=list(set(AllIDs))
IDList.sort()
for i in IDList:
    fID.write(str(i)+'\n')
fID.close()
print('Done')
```

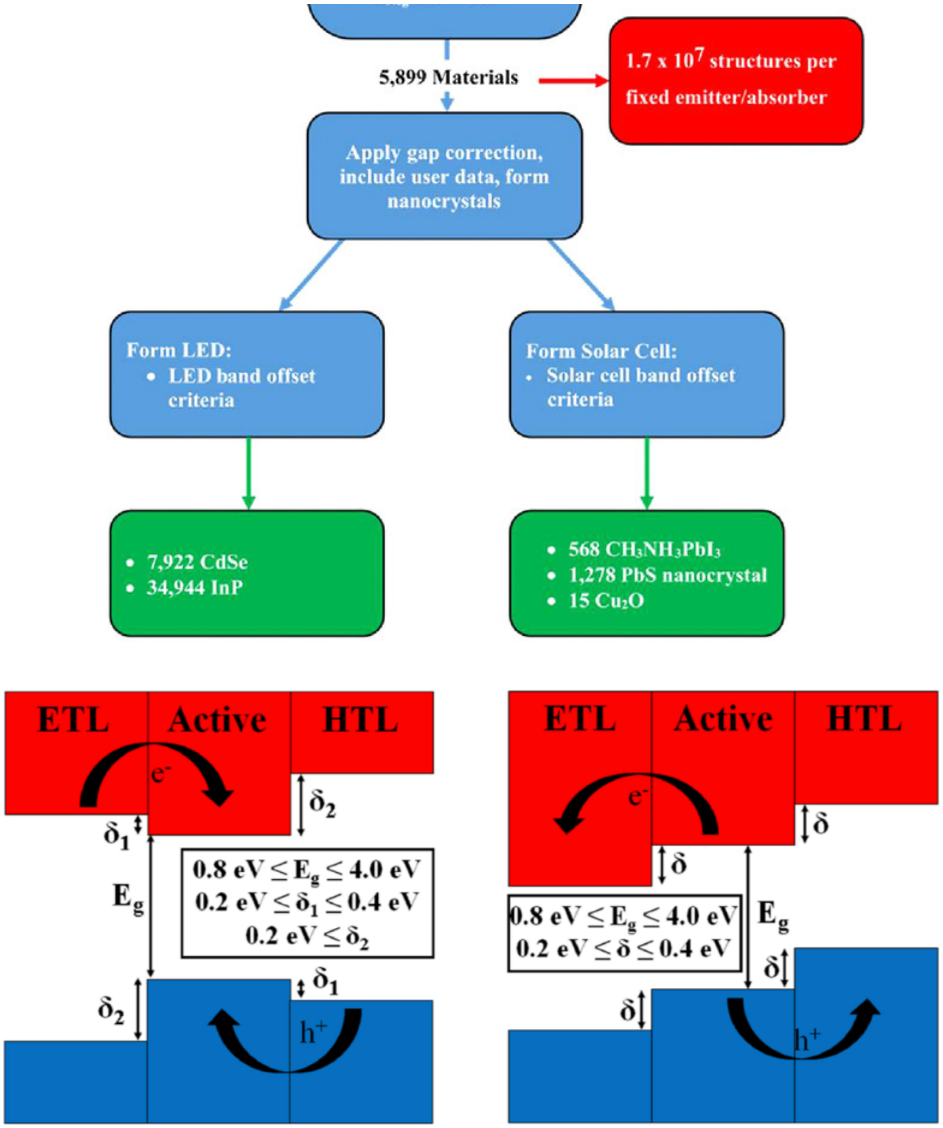
The next cell sets up the output files.

In [ ]:
```
filename2='CNData.txt'
g=open(filename2,'w')
g.write('#MP_Number'+'\t'+'CNL'+'\t'+'EG'+'\t'+'EFermi'+'\t'+'ValenceMax'+'\t'+'CondMin'+'\n')

filename3='OpticalProperties.txt'
h=open(filename3,'w')
h.write('#MP_NUmber'+'\t'+'Eps10'+'\t'+'Meff_El'+'\t'+'Meff_hole'+'\t'+'ExcitonEb'+'\t'+'EdgeJDOS'+'\n')
```

The next cell is collects. This will take several hours.

Semiconductor Heterojunctions: Materials selection



- Impose band offset requirements, determined by application
- Layered structure of semiconductors, electron transport layer, active layer, and hole transport layer
- Rank by figure of merit: Drude model conductivity
- Published as jupyter notebook

E. Shapera and A. Schleife; Adv. Theor. and Simulations (2018)

This is the notebook for designing semiconductor heterostructures based on Materials Project data.

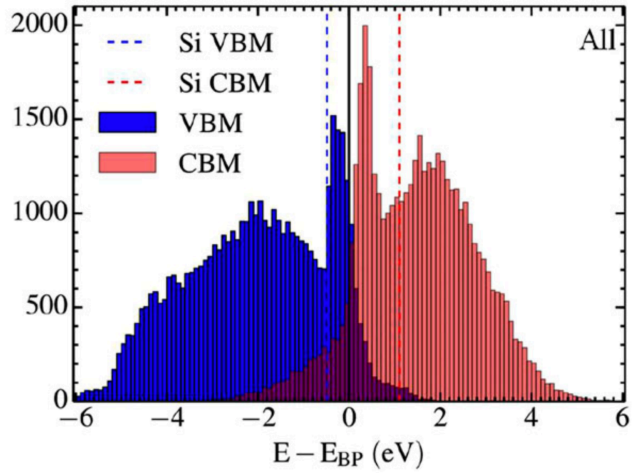
In [1]:
```
import numpy as np
import copy
import scipy.constants as cons
import os
import bisect
import re
import itertools
#from sklearn import svm
#from sklearn.model_selection import cross_validate as cross_validation
from shutil import copyfile
import collections
import random
import sys
```

The next section performs preprocessing of data.

In [2]:
```
def CostFunction(CostName):
    CostVal=0.0
    ENegC=[]
    for k in range(0,len(CostName),2):
        ElementIndex=Elements.index(CostName[k])
        CostVal+=float(CostName[k+1])/Abundances[ElementIndex]

        OrderedElementIndex=OrderedElements.index(CostName[k])
        ENegC.append(Electronegativity[OrderedElementIndex])
    ENegDif=max(ENegC)-min(ENegC)
```

Semiconductor Heterojunctions



- More than 500 materials available for any branch-point energy between 0 and 3.5 eV below the CBM as well as 0 and 4.3 eV above the VBM
- Many candidates! Explore?

Example	Binary	Ternary
LED (CdSe)	264	7922
LED (InP)	1764	34 944
Solar Cell ($CH_3NH_3PbI_3$)	144	568
Solar Cell (PbS nanoparticle $R = 5$ nm)	212	1278
Solar Cell (Cu_2O HTL)	4	15

Example	ETL	Active	HTL
LED	Ca_3N_2, Mg_3N_2, $ZnSeO_4$	CdSe	CdS,[83] WO_3,[84] MoO_3,[85] SiC[86]
LED	ZnSe,[87] CuI, $NaBiS_2$[88]	InP	GaSe, V_2O_5,[89] $SrCuO_2$[90]
Solar cell	WO_3, In_2S_3[91]	$CH_3NH_3PbI_3$	Mn_3O_4, Cr_2O_3[92]
Solar cell	PdS, Fe_3Si[93]	PbS, $R = 5$ nm	MnP, Cr_3S_4
Solar cell	$Ca_2Cu_2O_5$	CdS[94]	Cu_2O

- Found materials that are actually used in practice!
- Found new candidates! Test?
- Problems: Sensitively depends on band-gap correction, branch-point energy, and alignment criteria
- Currently: Fixable by user input

E. Shapera and A. Schleife; Adv. Theor. and Simulations **1**, 1800075 (2018)

Tasks:

- Plot existing data in colab (using colab sheet/files)

- Generate new colab sheet:
  - Connect to MP and download band structures for a few materials
  - Correct the band gap (optional)
  - Compute the branch-point energy
  - Include in your plot