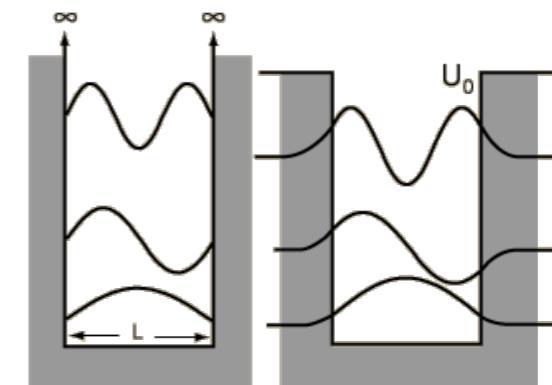
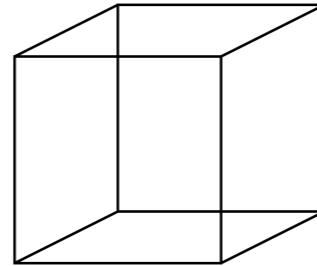
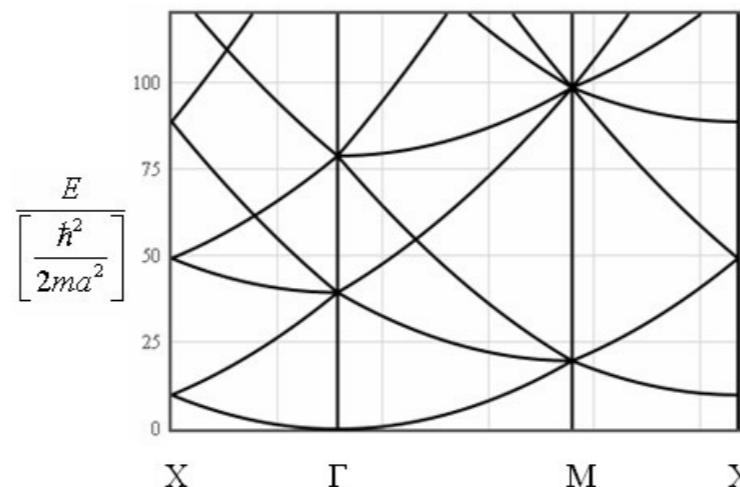
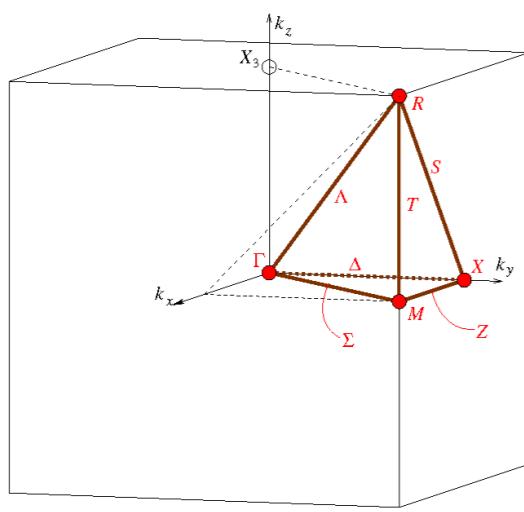


Band structure diagram of a semiconductor

$$\hat{H}\Psi = i\hbar \frac{\partial}{\partial t} \Psi = E\Psi$$

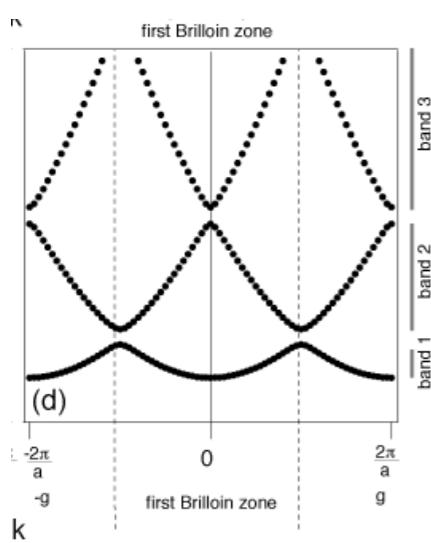


free electron
in a box



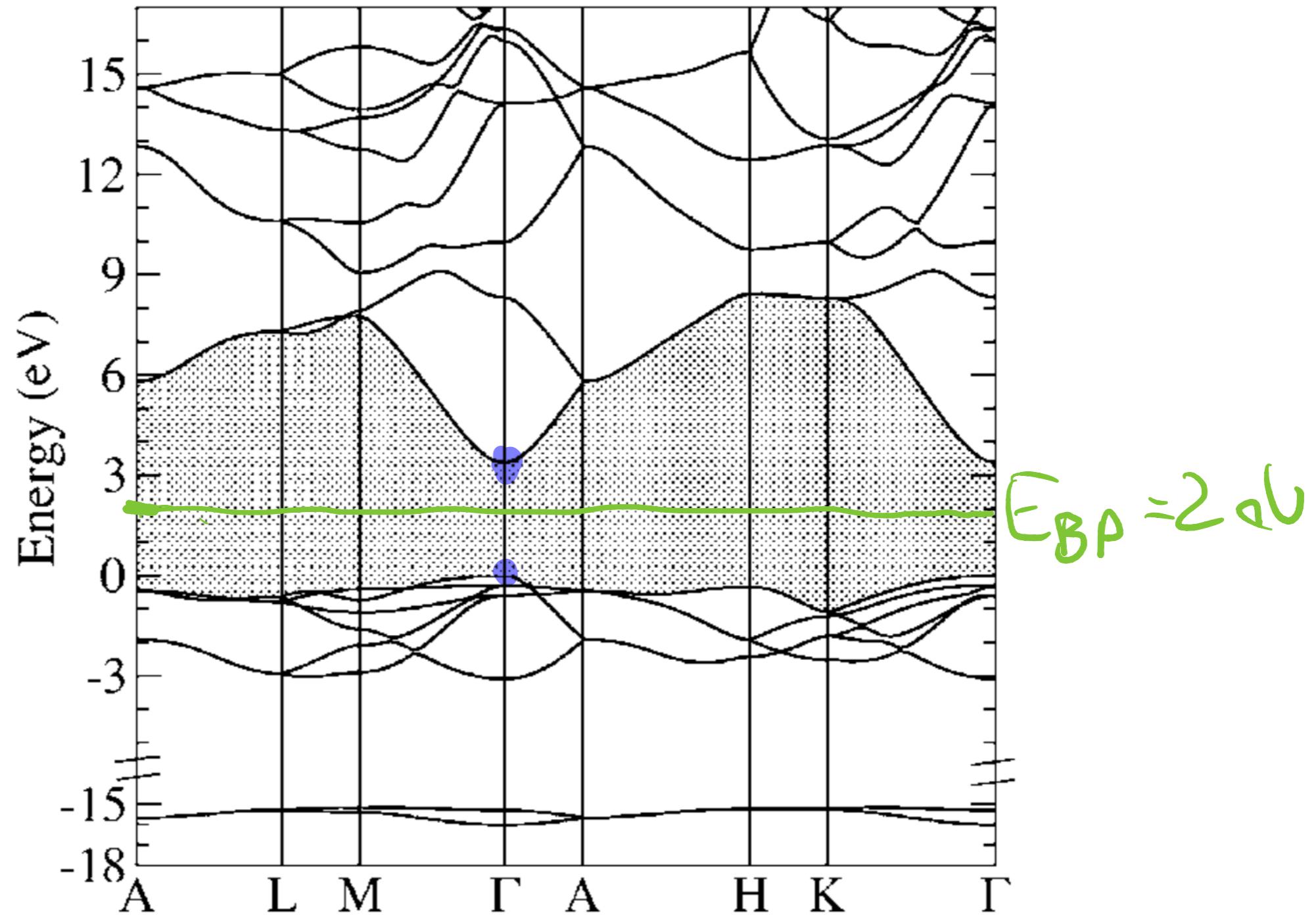
- periodicity of atomic
lattice

- empty lattice approx



- atoms cause small perturbations
- nearly free electrons

Band structure diagram of a semiconductor



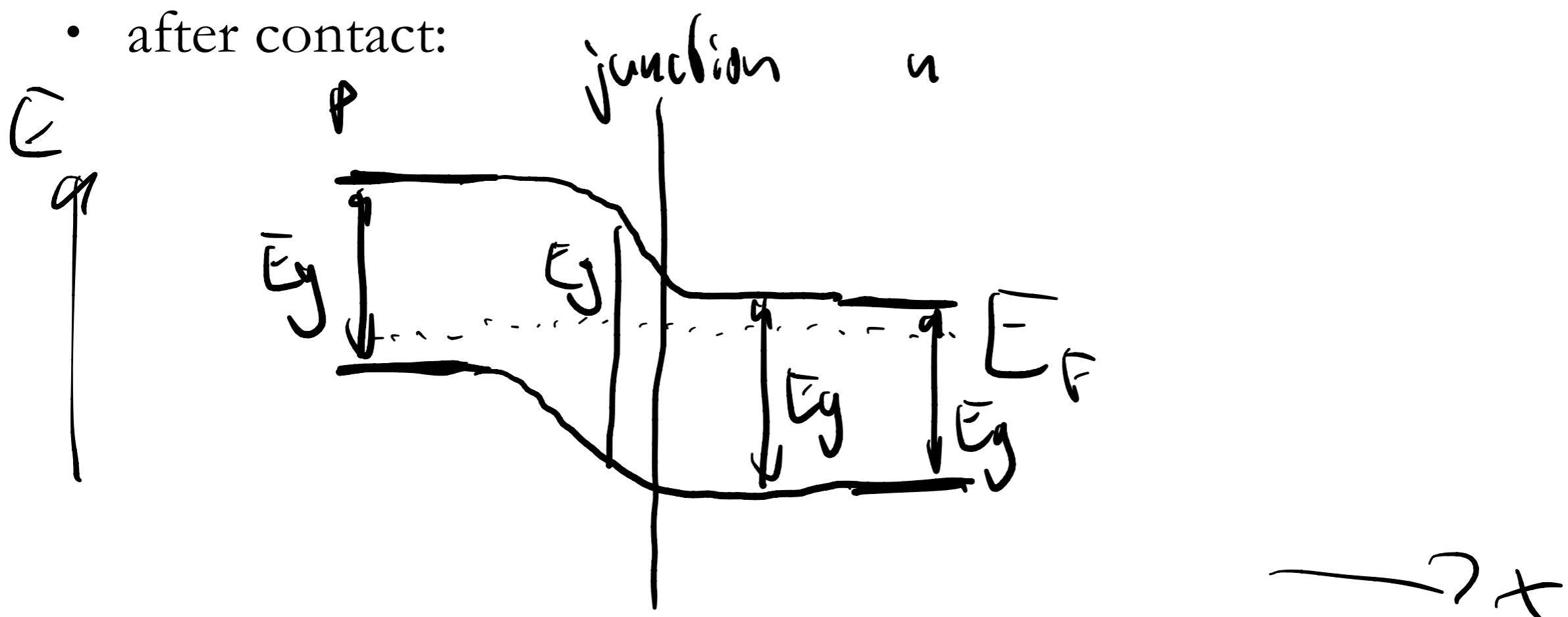
(c) Phys. Rev. B 73, 245212 (2006)

p-n junction: Energy Band diagram

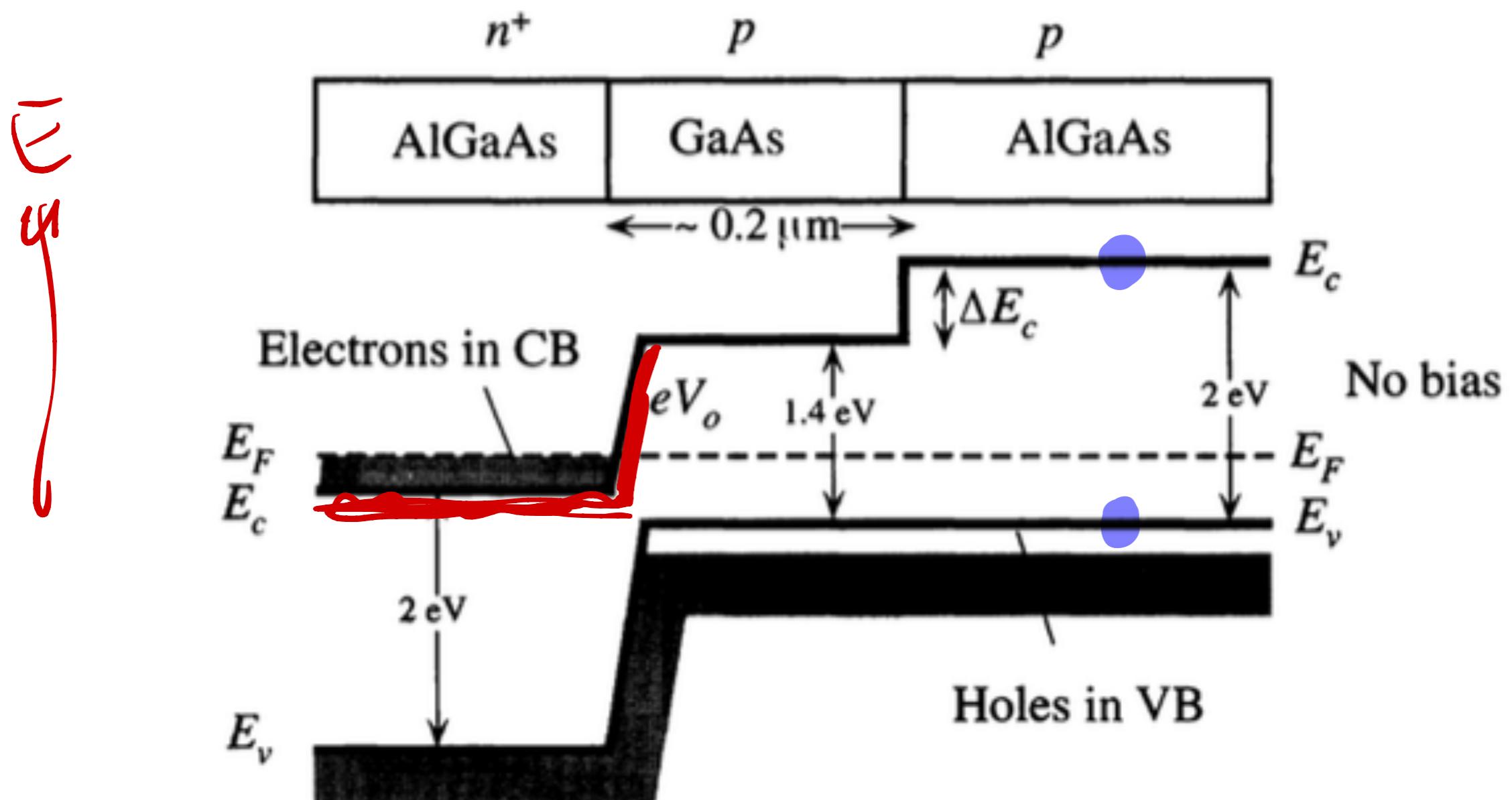
- before contact:



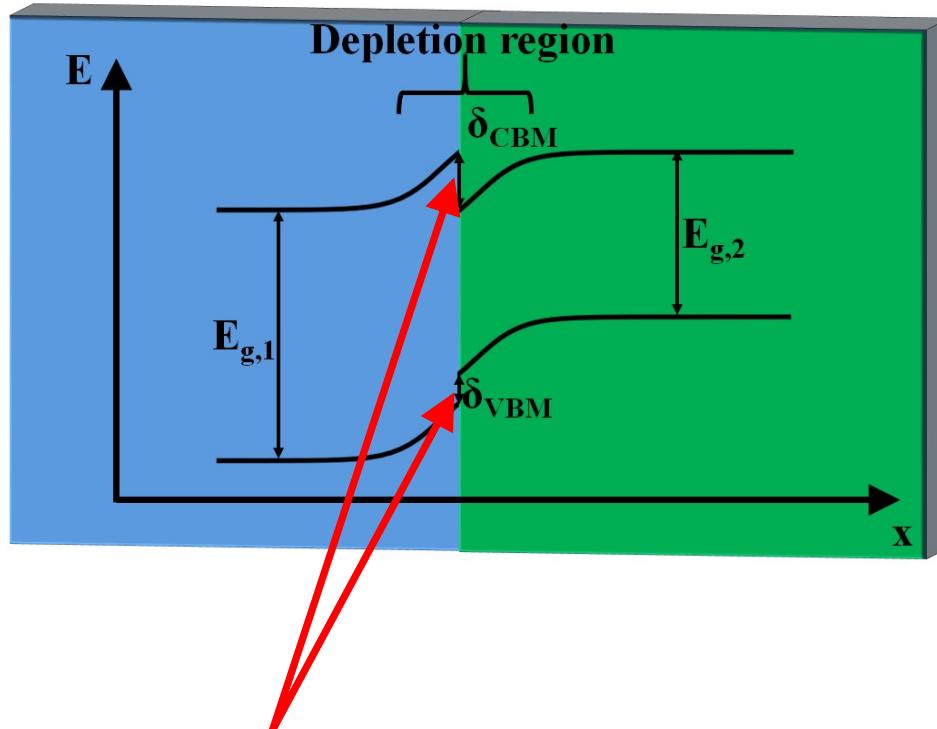
- after contact:



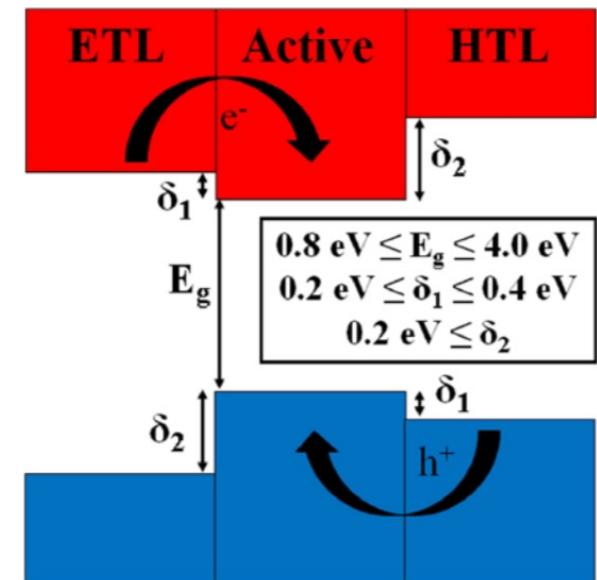
Heterojunction LED:



Materials Selection for Semiconductor Heterojunctions



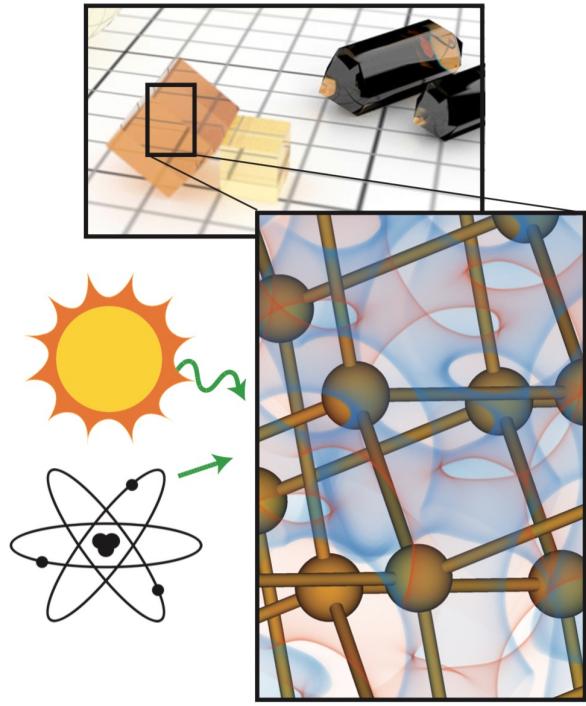
Energy discontinuities at interface for band offsets



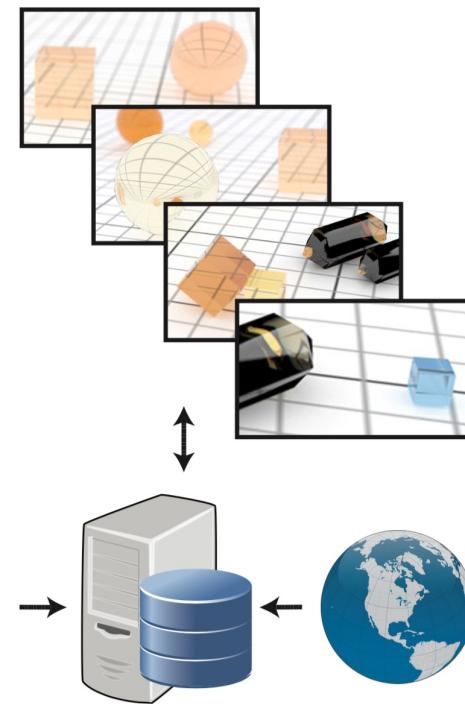
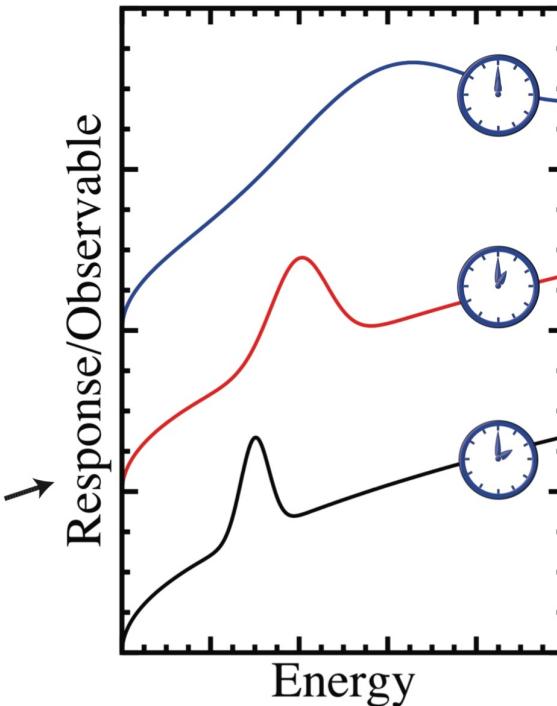
Why ... Materials selection?



Excited electronic states



Femto-second dynamics

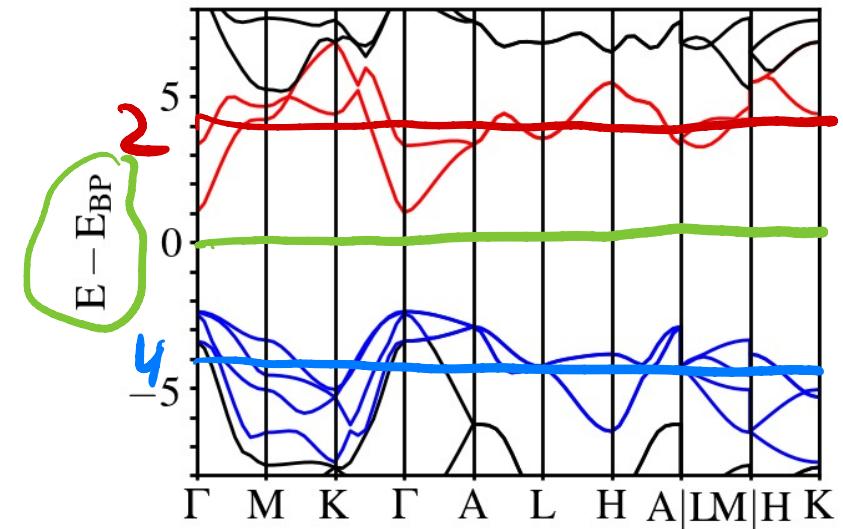


"Pushing The Frontiers Of Modeling Excited Electronic States And Dynamics To Accelerate Materials Engineering And Design", K. Kang, A. Kononov, C.-W. Lee, J.A. Leveillee, E. Shapera, X. Zhang, A. Schleife, Comp. Mat. Sci. **160**, 207–216 (2019); Finalist "Rising Stars in Computational Materials Science"

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

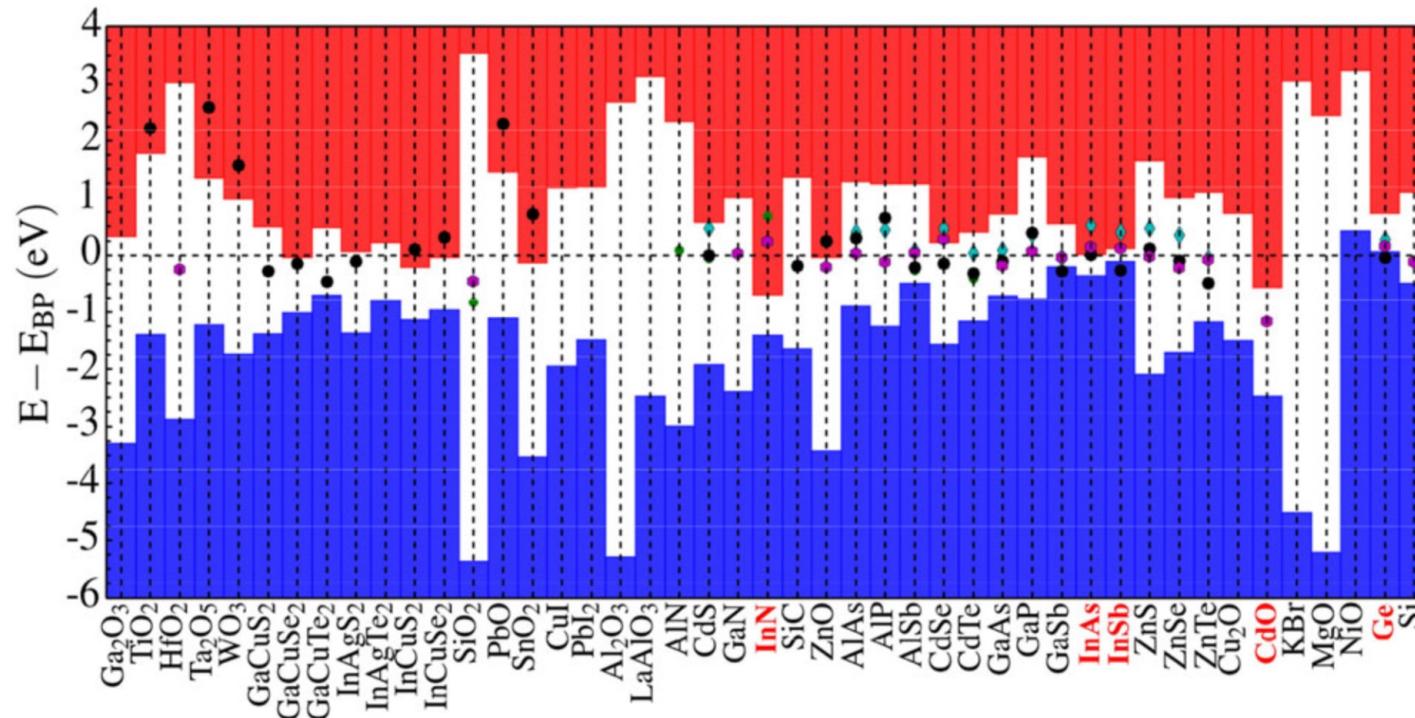
$$E_{BP} = \frac{1}{2N_k} \left(\frac{1}{N_c} \sum_{c_i}^{N_c} \varepsilon_{c_i}^{\text{QP}}(\mathbf{k}) + \frac{1}{N_v} \sum_{v_i}^{N_v} \varepsilon_{v_i}^{\text{QP}}(\mathbf{k}) \right)$$



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

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)

PlotAlignment.ipynb

Comment

Share



File Edit View Insert Runtime Tools Help All changes saved

+ Code

+ Text

RAM
Disk

Editing

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')
```

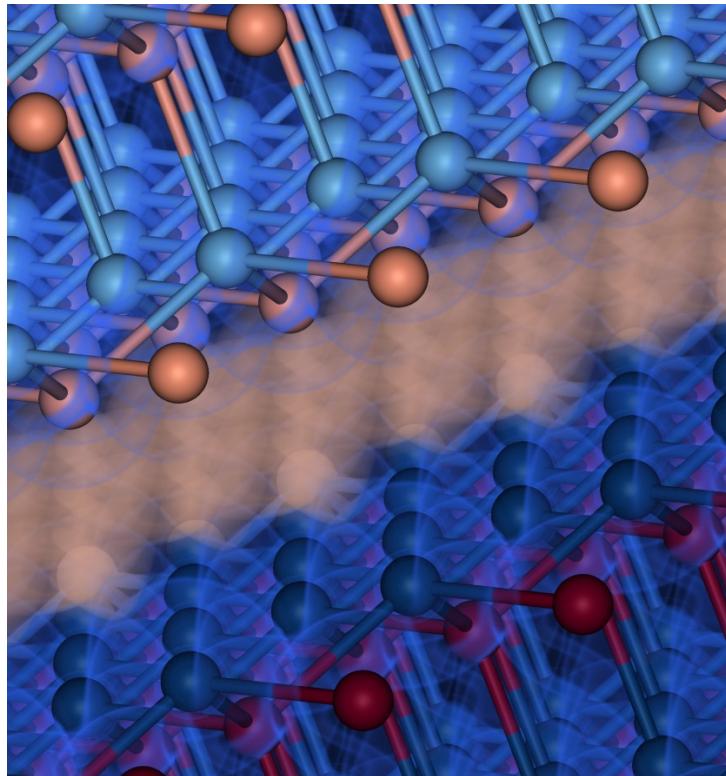
Drive already mounted at /content/drive; to attempt to forcibly remount, call drive.mount("/content/drive", force_remount=True).

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

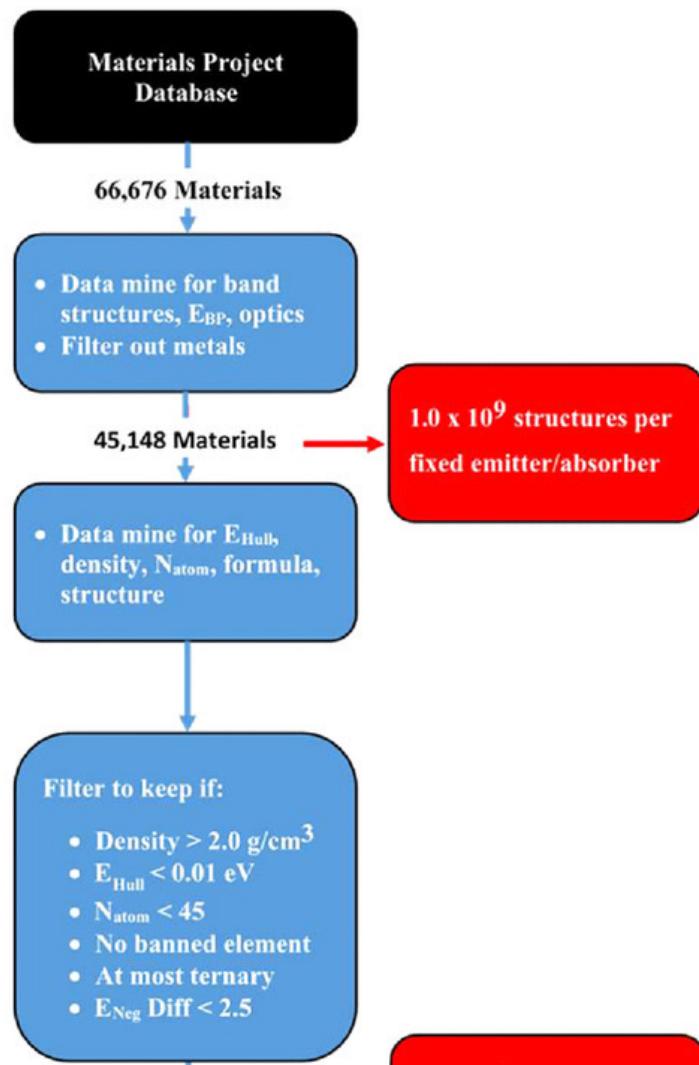
```
[ ] #IDsToPlot=[886,554278,352,10390,19342,5238,4840,3839,19833,22386,22736,22811,546794,19921,856,570136,22883,1143,2920,
#       661,672,804,22205,7631,2133,2172,1550,2624,2691,406,2534,2490,1156,20305,20012,10695,1190,2176,361,1132,
#       23251,1265,715434,32,149]
IDsToPlot=[886,554278,352,10390]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

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



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.

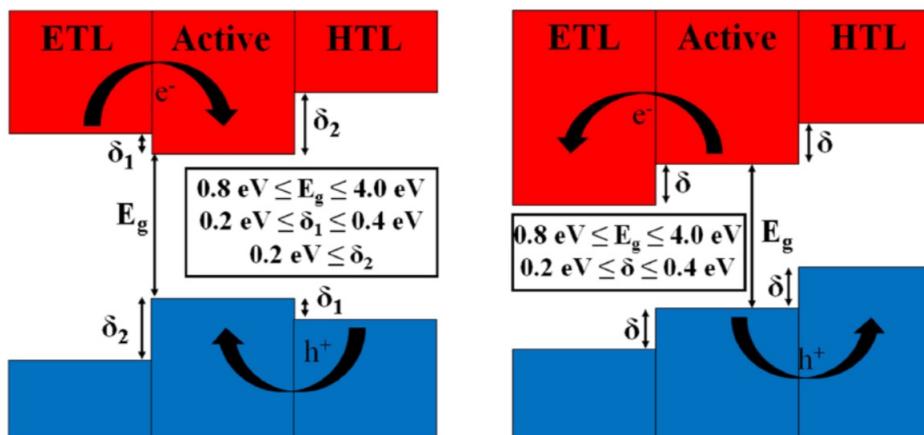
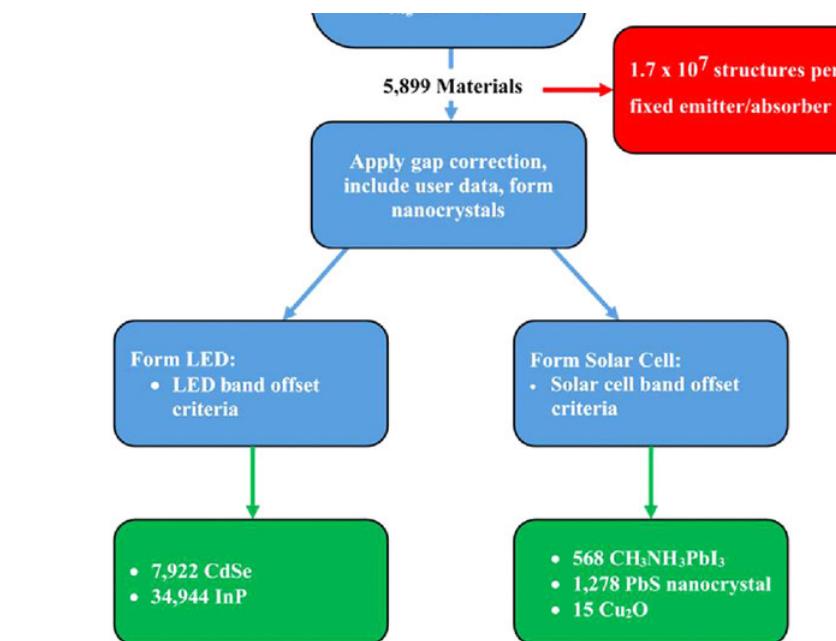
```
In [ ]: IDFfilename='idlist.txt'  
fID=open(IDFfilename,'w')  
  
data = mp.query(criteria={}, properties=["task_id"])  
AllIDs=[]  
for i in data:  
    AllIDs.append(int(i['task_id'].split('-')[1]))  
IDList=list(set(AllIDs))  
IDList.sort()  
for i in IDList:  
    fID.write(str(i)+'\n')  
fID.close()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

The next cell sets up the output files.

```
In [ ]: filename2='CNDdata.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_NUmer'+'\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.

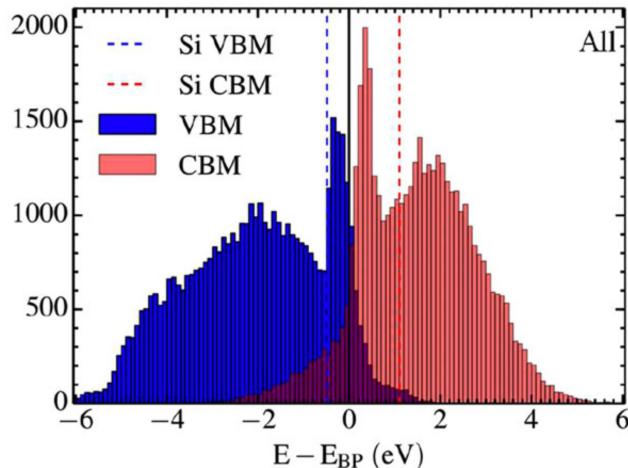
```
In [1]: import numpy as np
import copy
import scipy.constants as cons
import os
import bisect
import re
import itertools
#from sklearn import svm
#from sklearn.model_selection import cross_validate as cross_validation
from shutil import copyfile
import collections
import random
import sys
```

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 ($\text{CH}_3\text{NH}_3\text{PbI}_3$)	144	568
Solar Cell (PbS nanoparticle $R = 5 \text{ nm}$)	212	1278
Solar Cell (Cu_2O HTL)	4	15

Example	ETL	Active	HTL
LED	Ca_3N_2 , Mg_3N_2 , ZnSeO_4	CdSe	$\text{CdS}^{[83]}$ $\text{WO}_3^{[84]}$ $\text{MoO}_3^{[85]}$ $\text{SiC}^{[86]}$
LED	$\text{ZnSe}^{[87]}$ CuI , $\text{NaBiS}_2^{[88]}$	InP	GaSe , $\text{V}_2\text{O}_5^{[89]}$ $\text{SrCuO}_2^{[90]}$
Solar cell	WO_3 , $\text{In}_2\text{S}_3^{[91]}$	$\text{CH}_3\text{NH}_3\text{PbI}_3$	Mn_3O_4 , $\text{Cr}_2\text{O}_3^{[92]}$
Solar cell	PdS , $\text{Fe}_3\text{Si}^{[93]}$	PbS , $R = 5 \text{ nm}$	MnP , Cr_3S_4
Solar cell	$\text{Ca}_2\text{Cu}_2\text{O}_5$	$\text{CdS}^{[94]}$	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