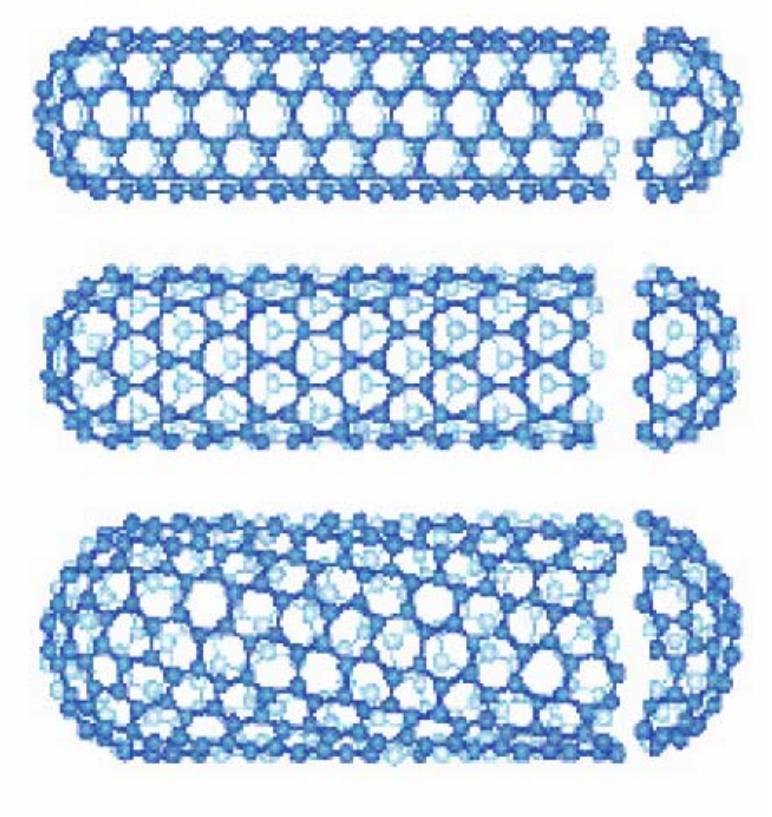
6. Carbon nanotubes / Photoemission

Oct 21, 2019

Carbon nanotubes - rolled up graphene



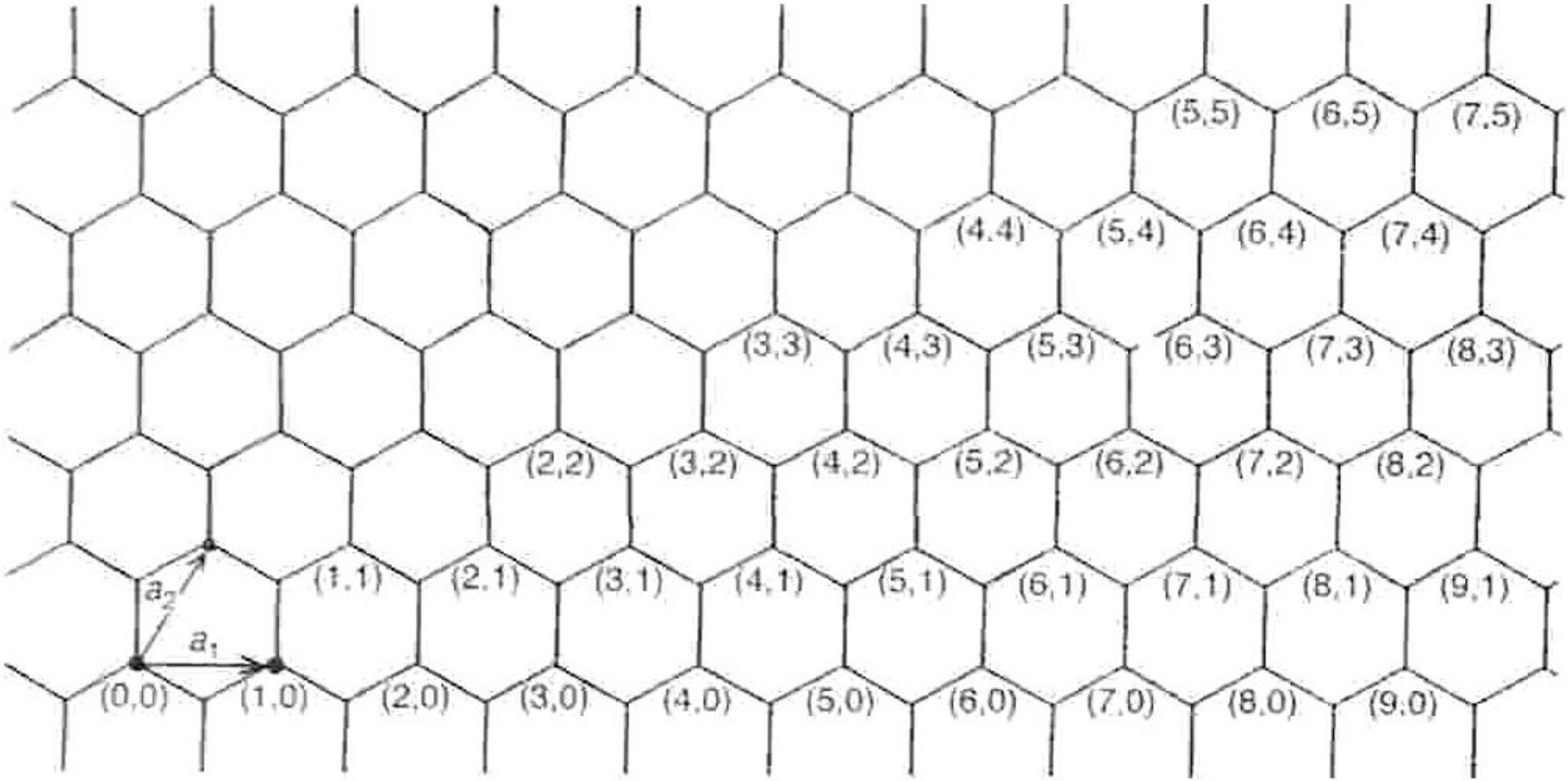
armchair

zig-zag

chiral

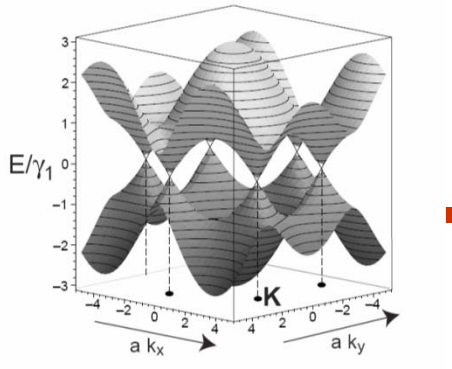
www.physics.umd.edu/courses/Phys732/hdrew/spring07/Schoenenberger%20tutorial%20on%20CNT%20bands.pdf

(*m*,*n*) notation

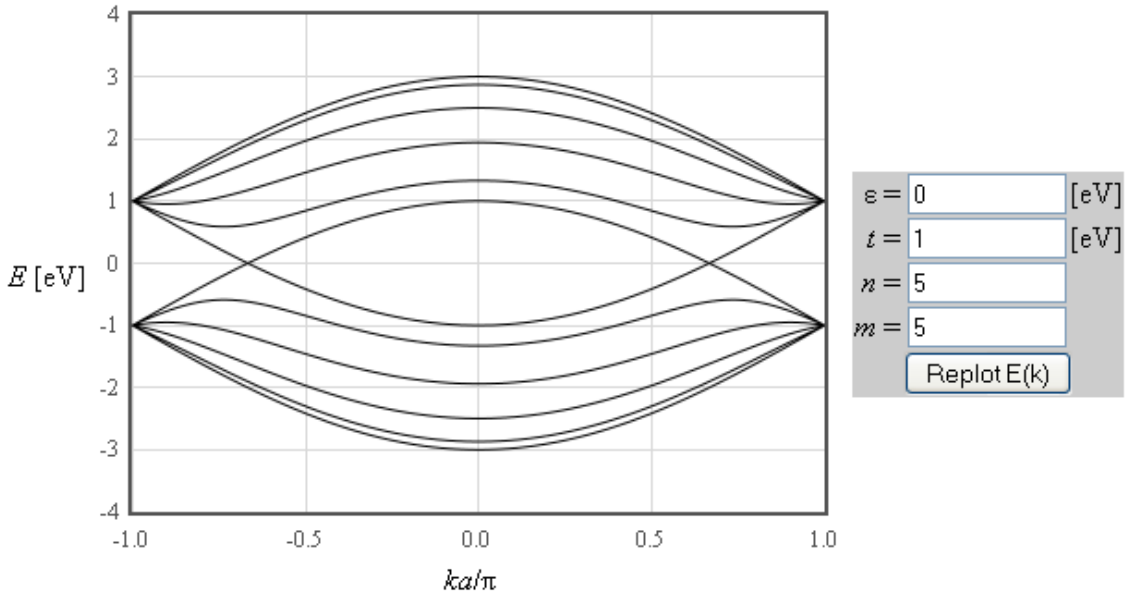


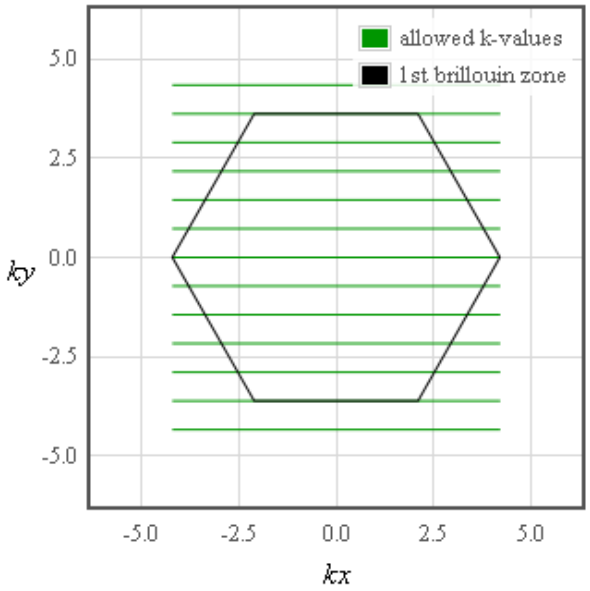
http://www.personal.rdg.ac.uk/~scsharip/tubes.htm

Carbon nanotubes



$$E = \varepsilon \pm t\sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$

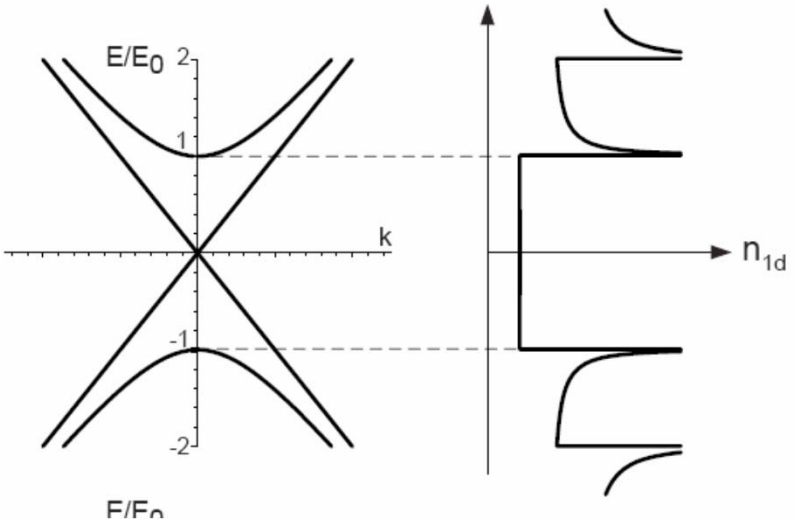


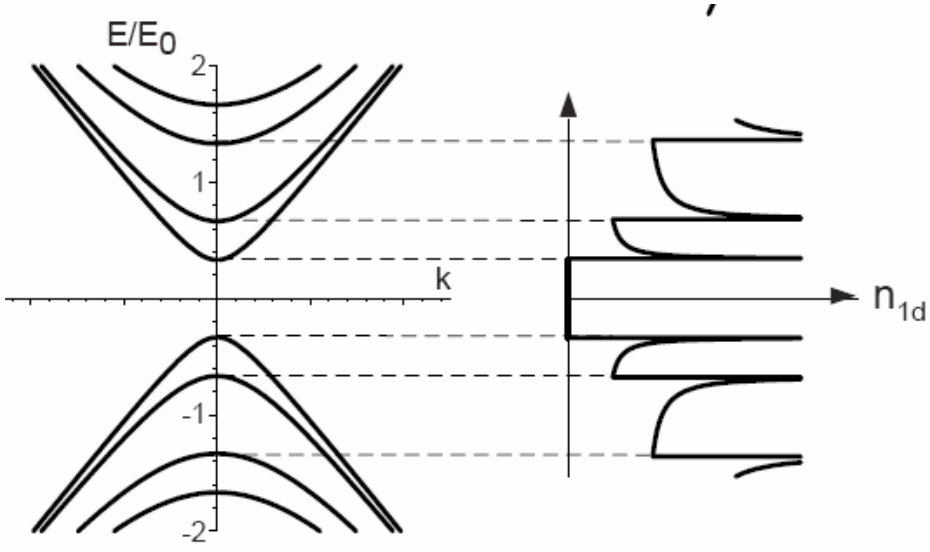


metallic (5,5) armchair tube

http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tbtable/CNTs.html

Carbon nanotubes



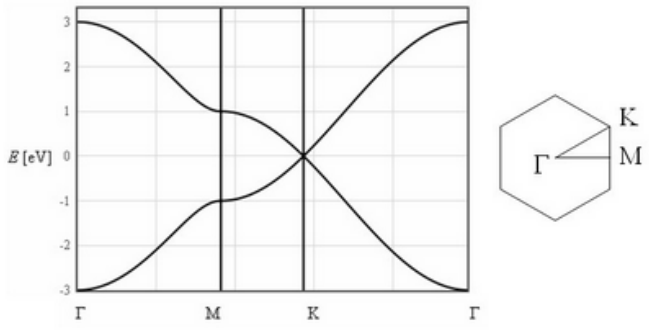
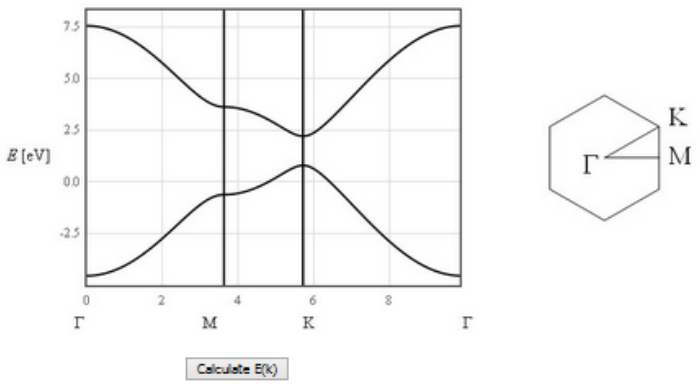
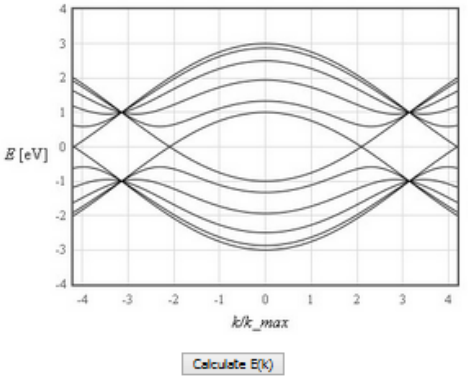
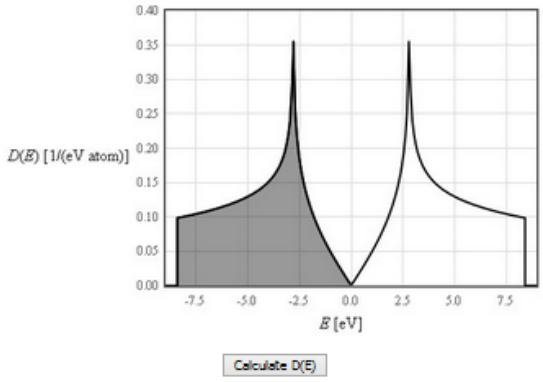
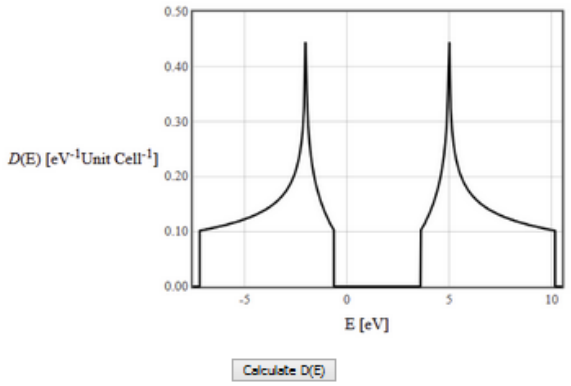
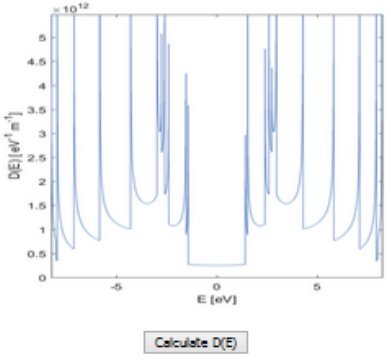


metallic $m - n = 3Z$

semiconducting

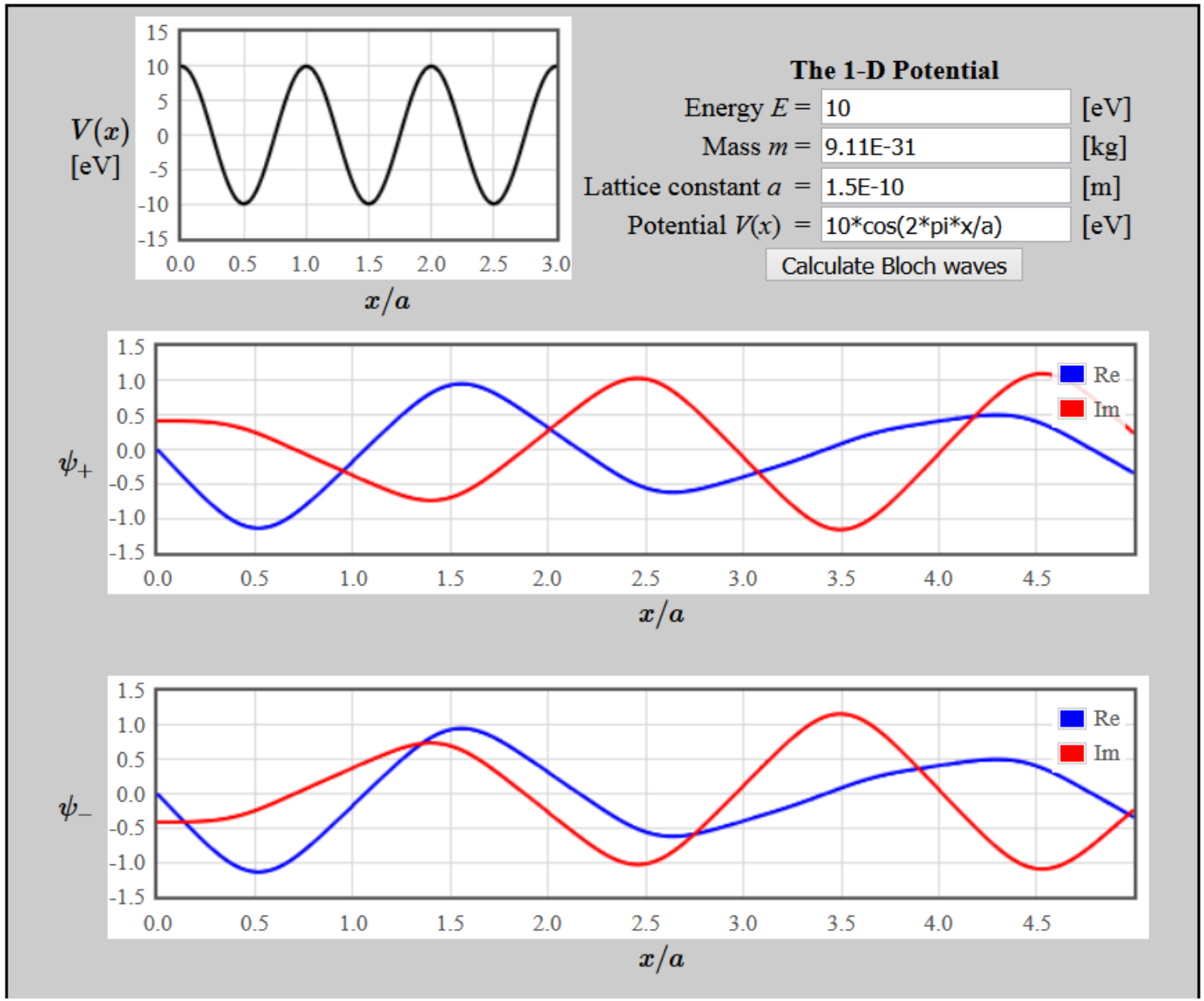
www.physics.umd.edu/courses/Phys732/hdrew/spring07/Schoenenberger%20tutorial%20on%20CNT%20bands.pdf

Table of tight-binding calculations

Graphene	2-D boron nitride	Carbon nanotubes
$E = \varepsilon \pm t\sqrt{1+4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)+4\cos^2\left(\frac{k_y a}{2}\right)}$	$E = \frac{\varepsilon_1+\varepsilon_2}{2} \pm \sqrt{\frac{(\varepsilon_1-\varepsilon_2)^2}{2}+4t^2\left(\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)+\cos^2\left(\frac{k_y a}{2}\right)+\frac{1}{4}\right)}$	
		
$D(k) = \frac{k}{\pi}$ m^{-1}	$D(k) = \frac{k}{\pi}$ m^{-1}	$D(k) = \frac{2}{\pi}$
		

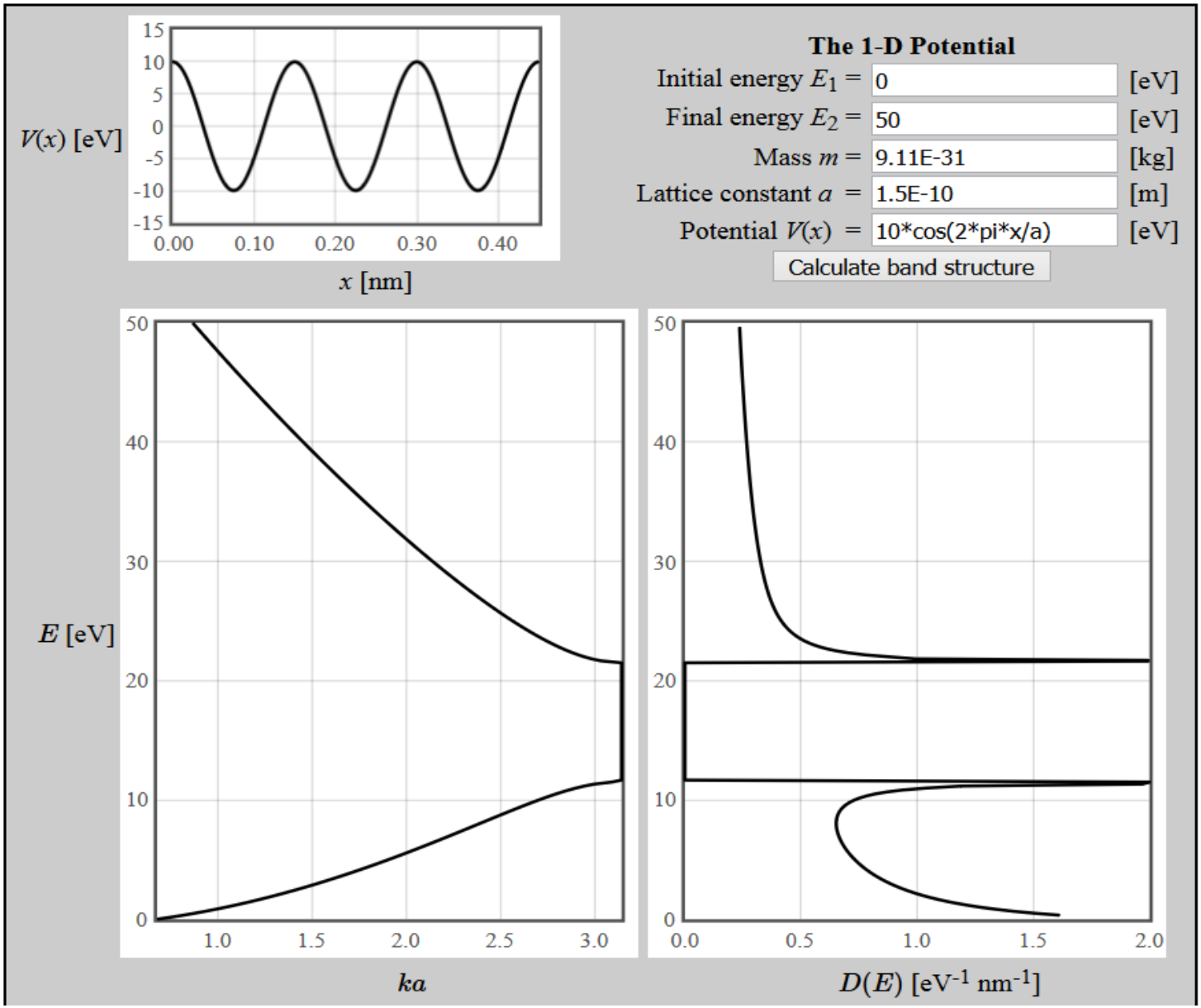
http://lampx.tugraz.at/~hadley/ss1/bands/tbtable/tbtable.html

Bloch waves in one dimension



http://lampx.tugraz.at/~hadley/ss1/bloch/bloch.php

Band Structure in one dimension



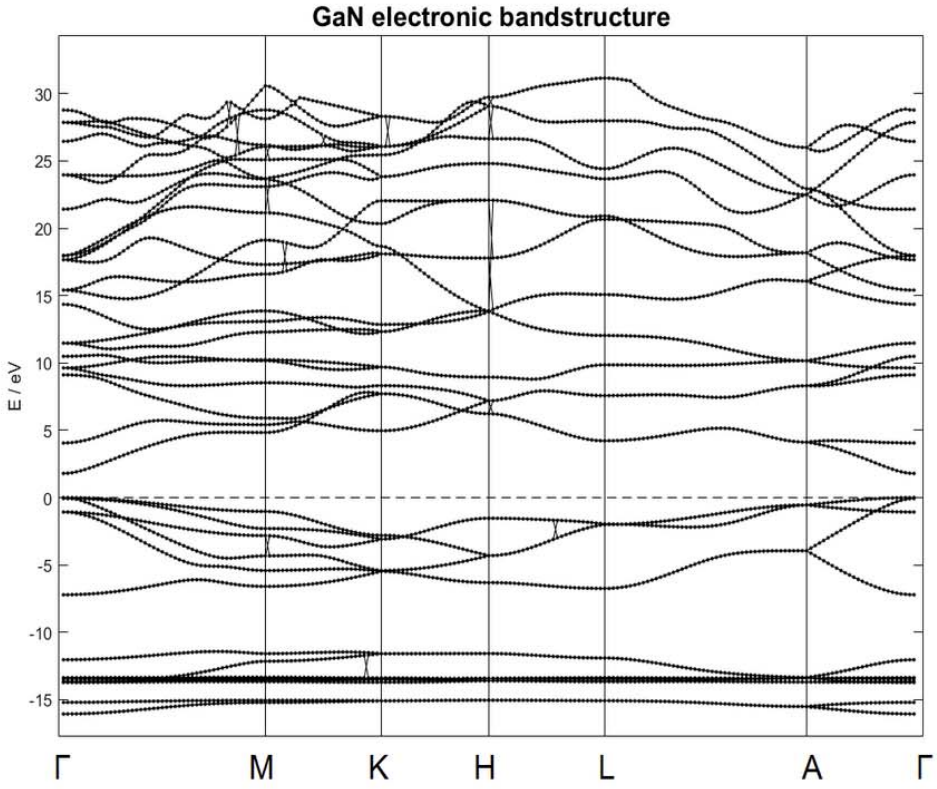
http://lampx.tugraz.at/~hadley/ss1/bloch/bloch.php

Photoemission

- Band structure calculations: GaN, 6H SiC, GaAs, GaP, Ge, InAs
- Calculated electron density of states
  - Al fcc, Au fcc, Cu fcc, Na bcc, Pt fcc, W bcc, Si diamond, Fe bcc, Ni fcc, Co fcc, Mn bcc, bcc, Gd hcp, Pd fcc, Pd_3Cr, Pd_3Mn, PdCr, PdMn , GaN, 6H SiC, GaAs, GaP, Ge, InAs

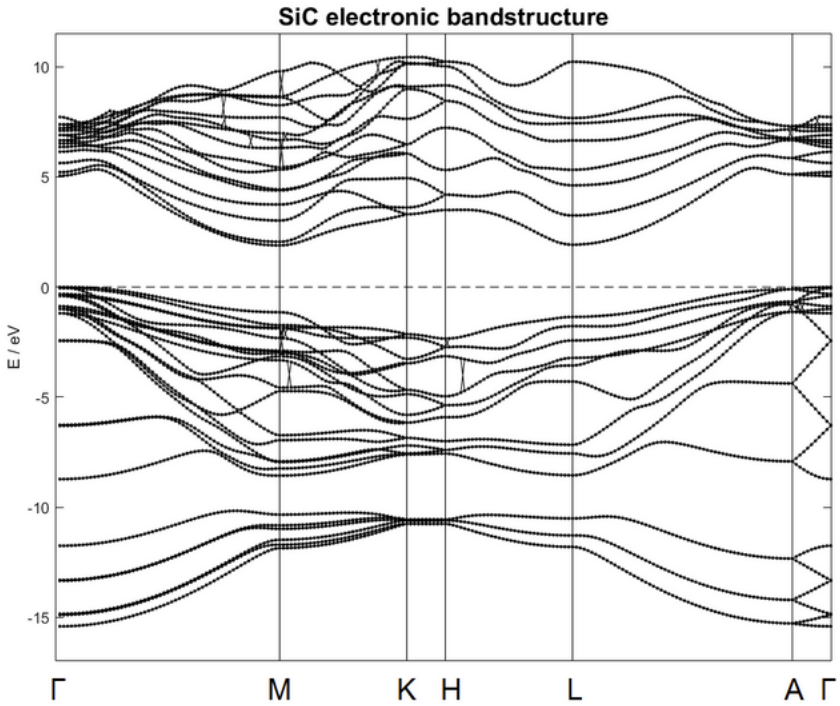
Bandstructure of hexagonal gallium nitride (GaN)

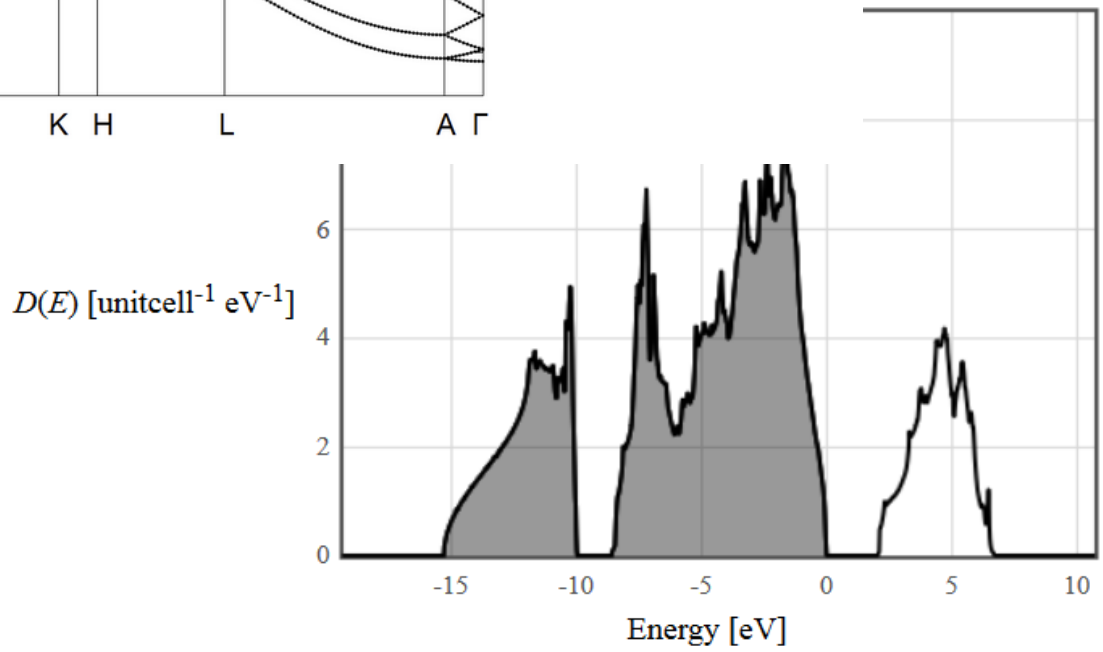
The bandstructure calculation for gallium nitride was calculated using the program Quantum Espresso (version 5.2.1) and the pseudopotentials for Ga and N.



Bandstructure of hexagonal silicon carbide (SiC)

The bandstructure calculation for silicon carbide was calculated using the program Quantum Espresso (version 5.3.0) and the pseudopotentials for Si and C.



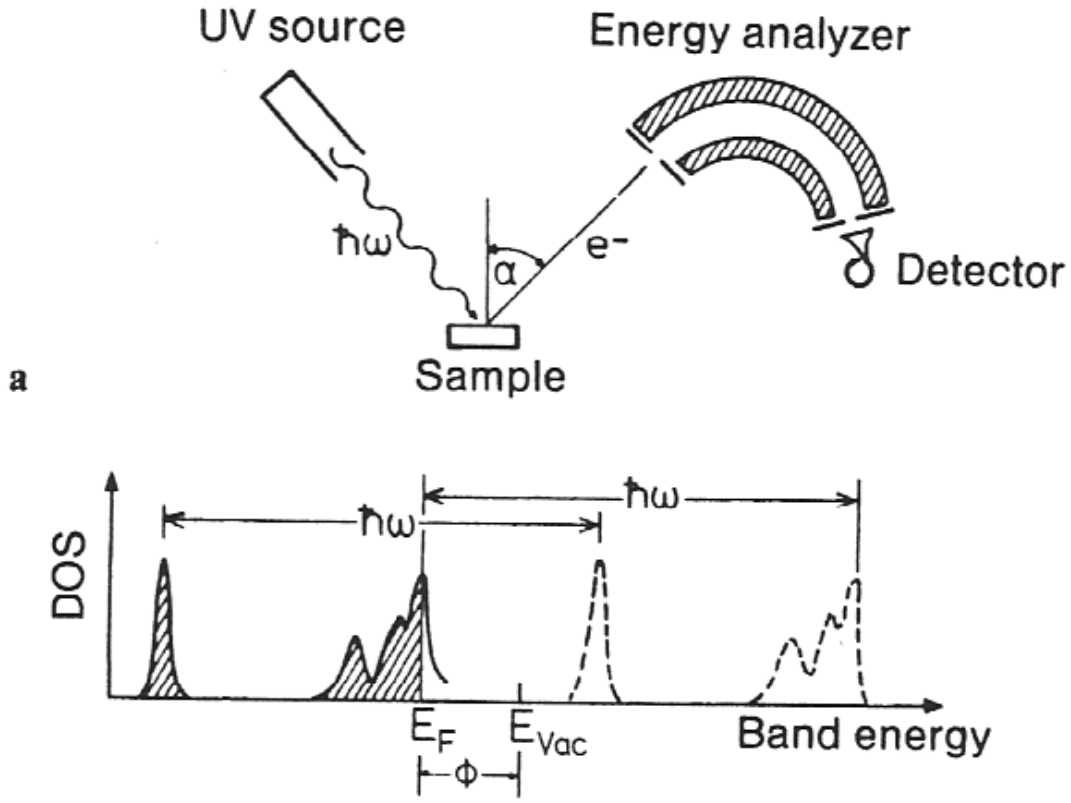


Photoemission spectroscopy

UPS - Ultraviolet photoemission spectroscopy

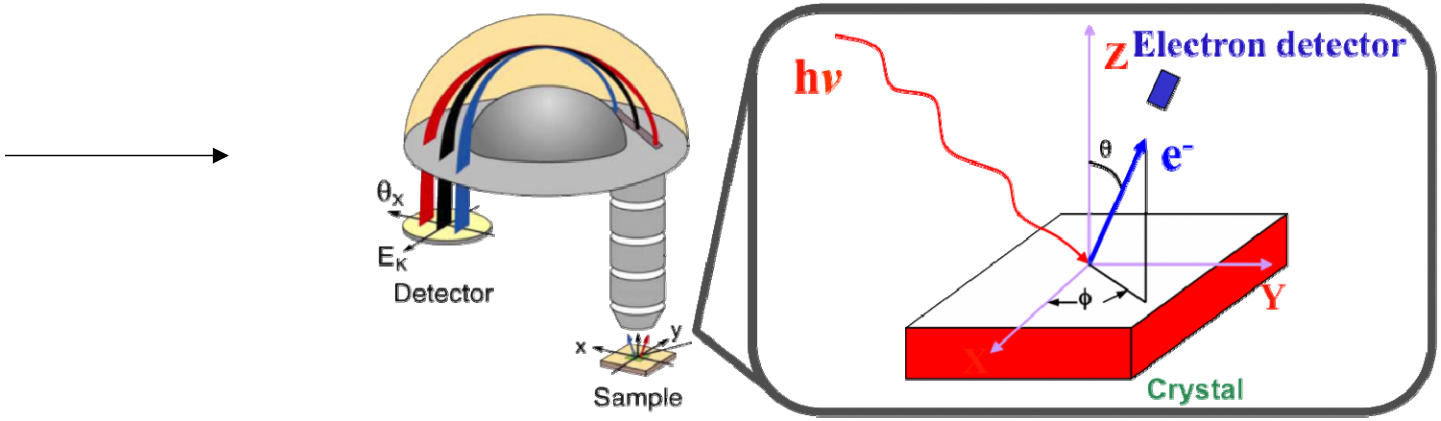
XPS - X-ray photoemission spectroscopy

Measure the density of states with photoemission spectroscopy

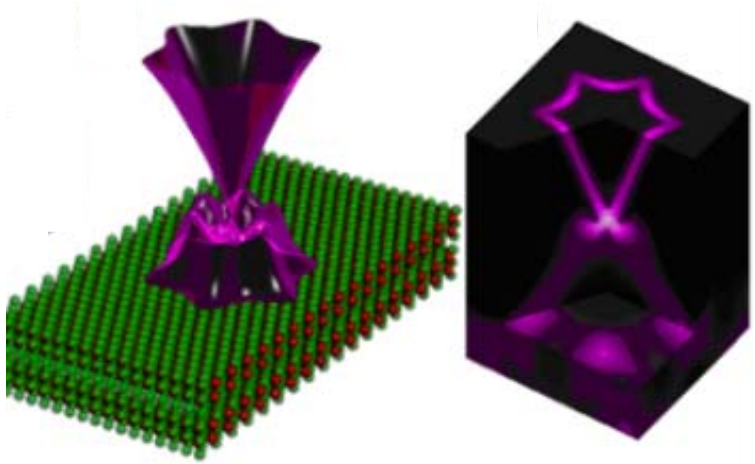


From: Ibach & Lueth

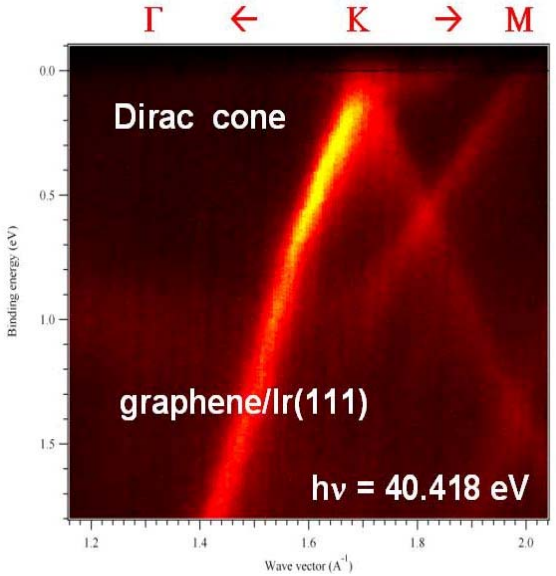
Angle resolved photoemission spectroscopy (ARPES)



Bi_2Te_3



Topological insulator

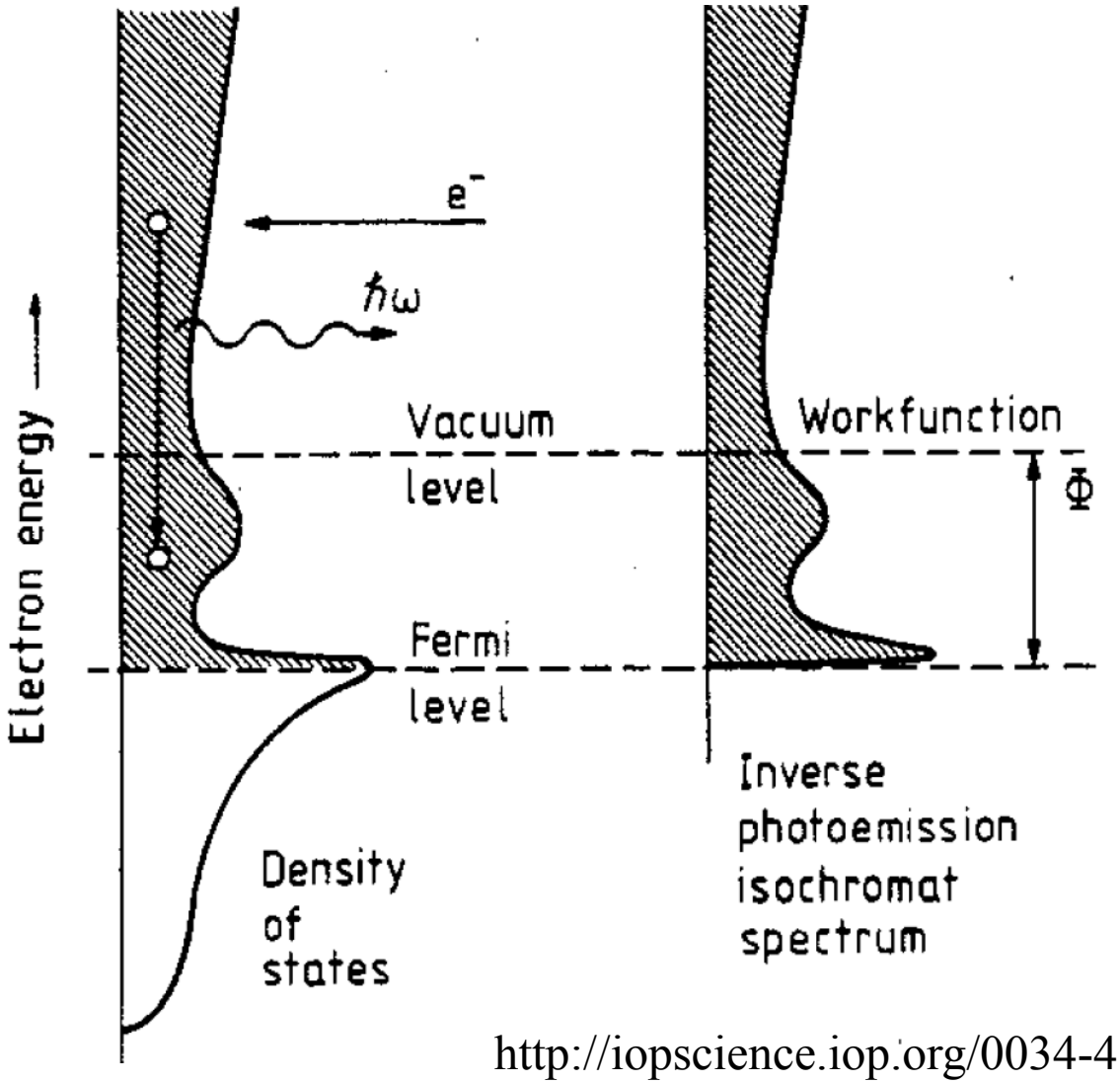


Measure the dispersion relation with angle resolved photoemission

https://arpes.stanford.edu/research/tool-development/angle-resolved-photoemission-spectroscopy

http://server2.phys.uniroma1.it/gr/lotus/Instrumentation1_M.htm

Inverse photoemission spectroscopy (IPES)



http://iopscience.iop.org/0034-4885/51/9/003

k-resolved Inverse Photoemission Spectroscopy (KRIPES)

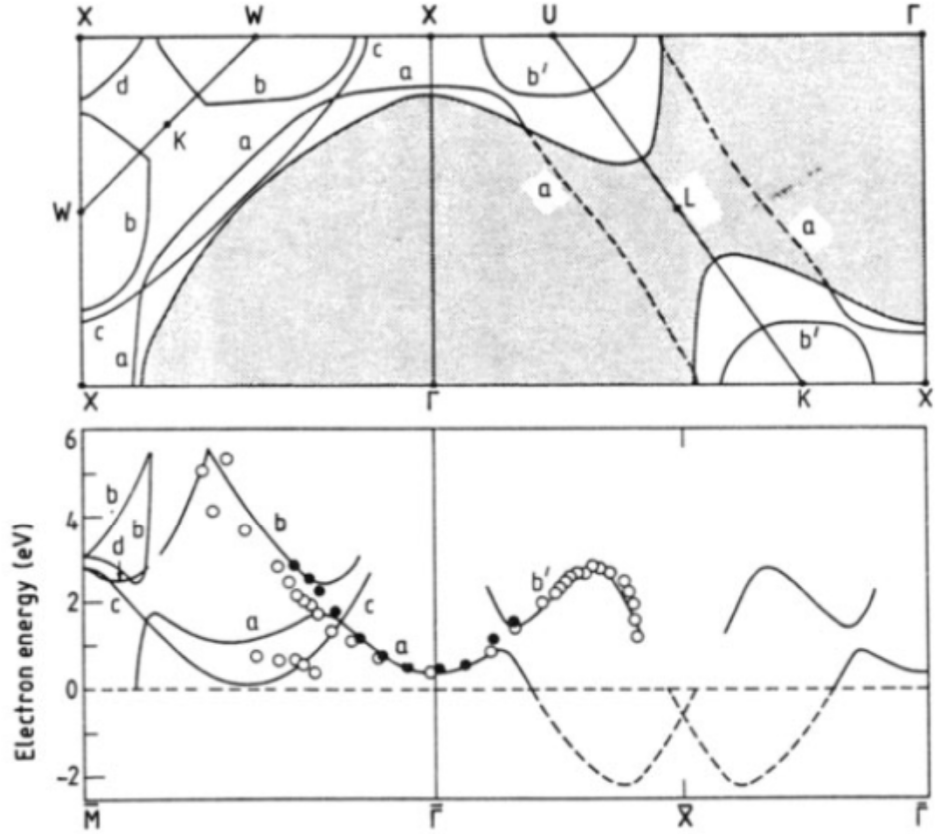
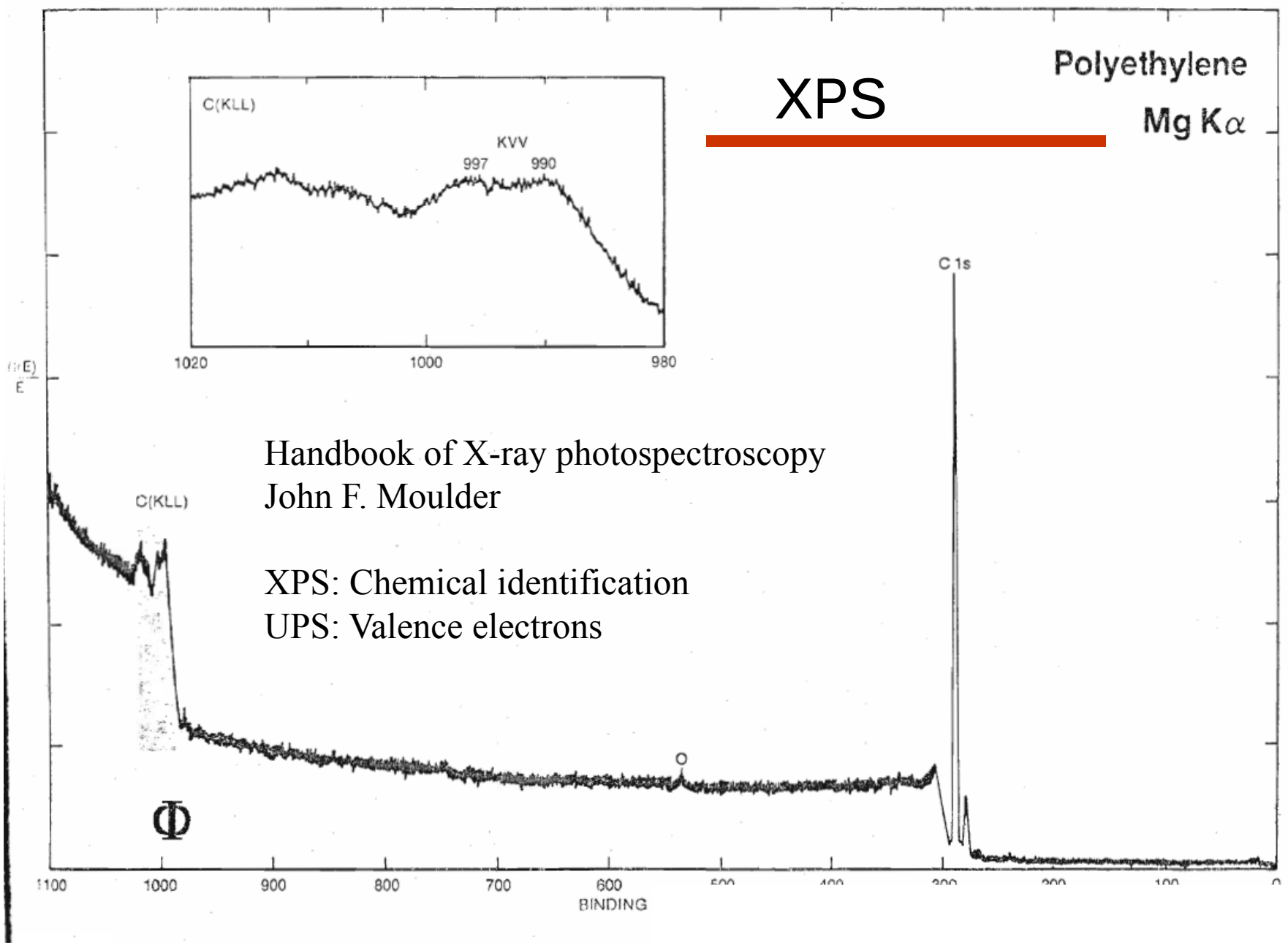


Figure 9. Band calculations and data for bulk direct transitions in the two principal azimuths $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{X}$ and Cu(001). Upper panel shows the Fermi surface and isochromat curves at $\hbar\omega = 9.7$ eV for transitions into band 6. Lower panel shows the corresponding $E_f(k_\parallel)$ projections. Computations and filled data circles are from Woodruff *et al* (1982); open circles are data from Jacob *et al* (1986).

http://iopscience.iop.org/0034-4885/51/9/003

XPS



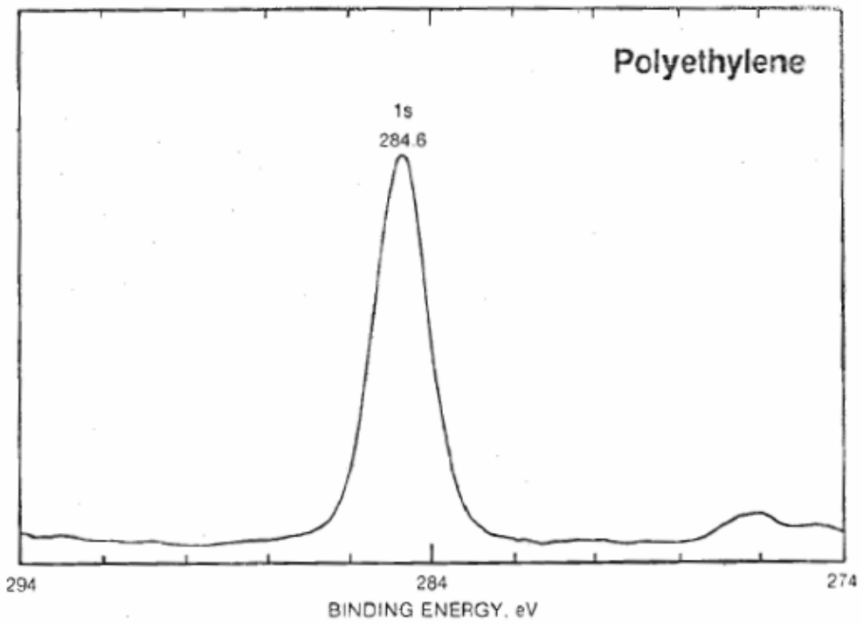
Handbook of X-ray photospectroscopy
John F. Moulder

XPS: Chemical identification
UPS: Valence electrons

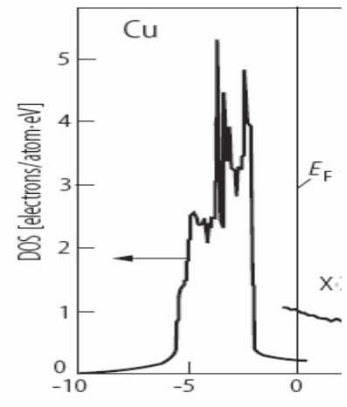
XPS

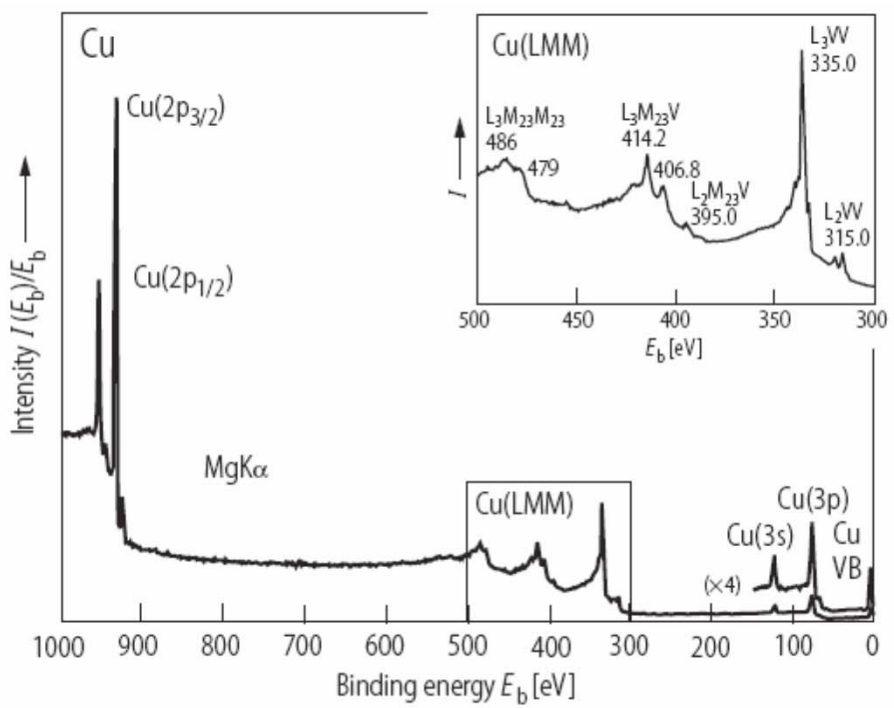
Carbon, C Atomic Number 6

COMPOUND	1s BINDING ENERGY, eV (280 / 284 / 288 / 292 / 296)	REF.
HfC		RH1
TiC		RH1
WC		RH1
C (graphite)		HJG
$(CH_2)_n$		Φ
$Mn(C_5H_5)_2$		BCD
$SnPh_4$		BAL
$MeCH_2NH_2$		GHH
$Cr(C_6H_6)_2$		PFD
$MeCH_2Cl$		GHH
$MeCH_2OH$		GHH
$MeCH_2OEt$		GHH
$MeCH_2OOCMe$		GHH
CS_2		GHH
$Fe(CO)_5$		BC1
Me_2CO		GHH
$(NH_2)_2CO$		GHH
C_6F_6		GHH
MeCOONa		GHH
MeCOOEt		GHH
MeCOOH		GHH
Na_2CO_3		GHH
$NaHCO_3$		GHH
CO		BC1
CO_2		GHH
$(CHFCH_2)_n$		CFK
$(CHFCHF)_n$		CFK
$(CHFCF_2)_n$		CFK
$(CF_2CH_2)_n$		CFK
$(CF_2CHF)_n$		CFK
$(CF_2)_n$		CFK
CF_3COONa		GHH
CCl_4		GHH
CF_3COMe		GHH
CF_3COOEt		GHH

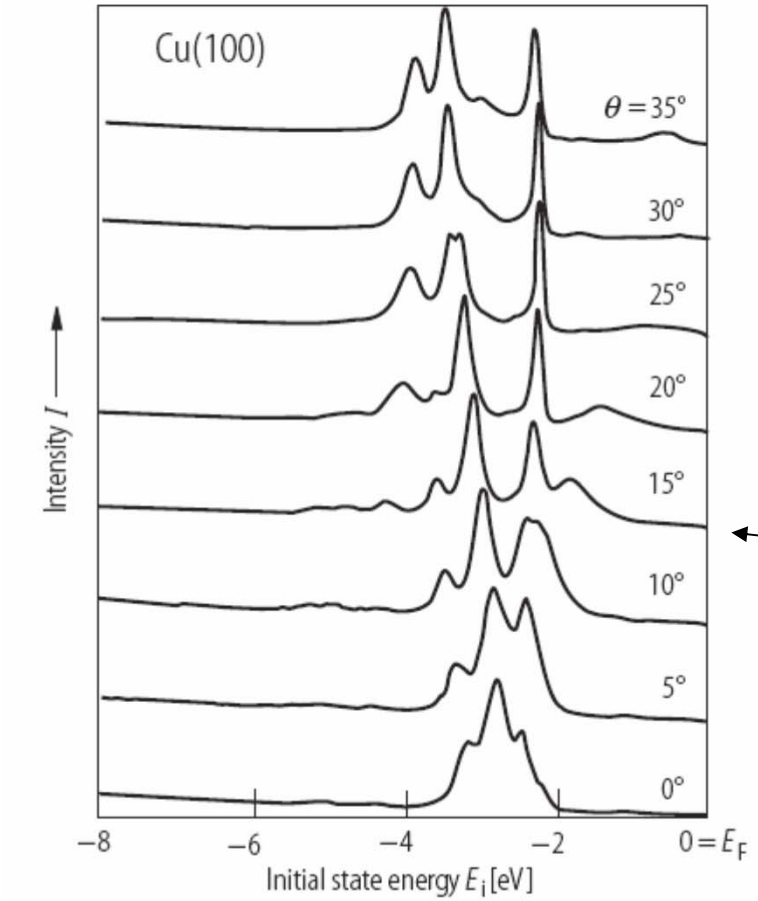


Cu





XPS

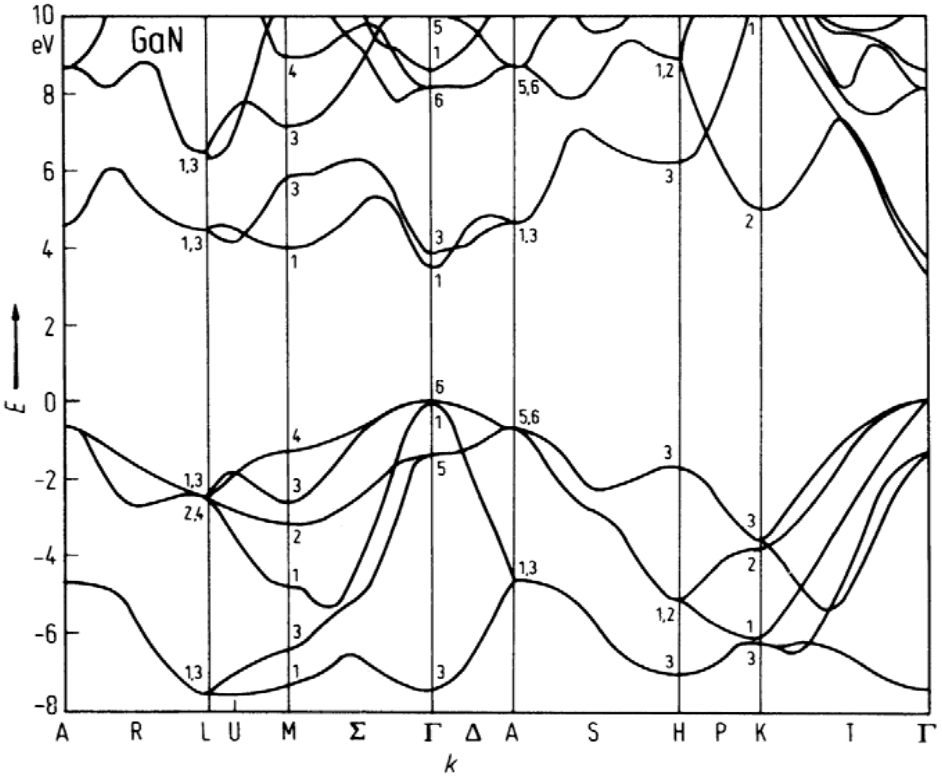


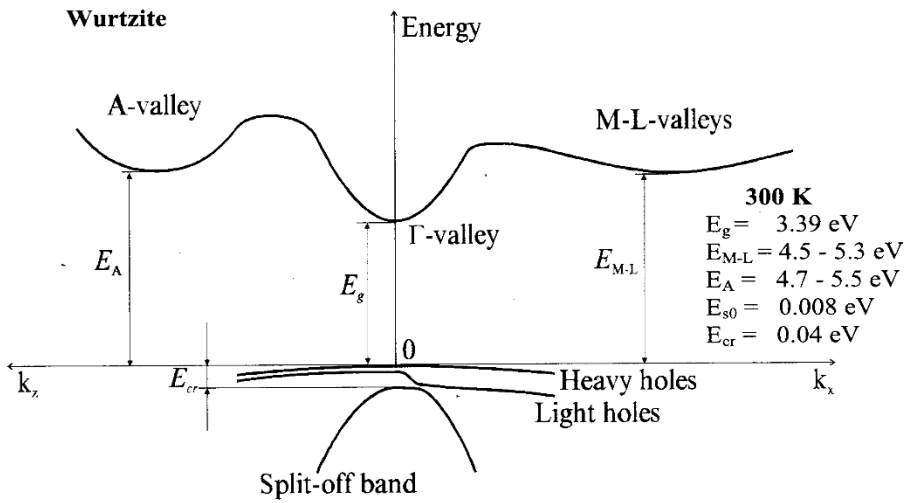
ARPES

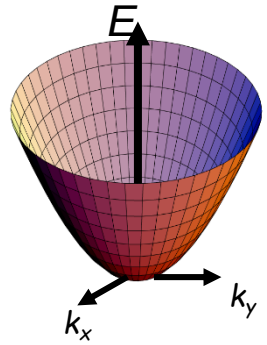
Fig. 28. Cu(100). Angle-resolved photoelectron spectra taken at different polar angles θ along the ΓXUL bulk mirror plane. Photon energy $h\nu$ = 21.2 eV, sample temperature T = 50 K [93M1]. For further data taken at room temperature see [79H1]. For data taken with linear-polarized photons at $h\nu$ = 40° see [83G].

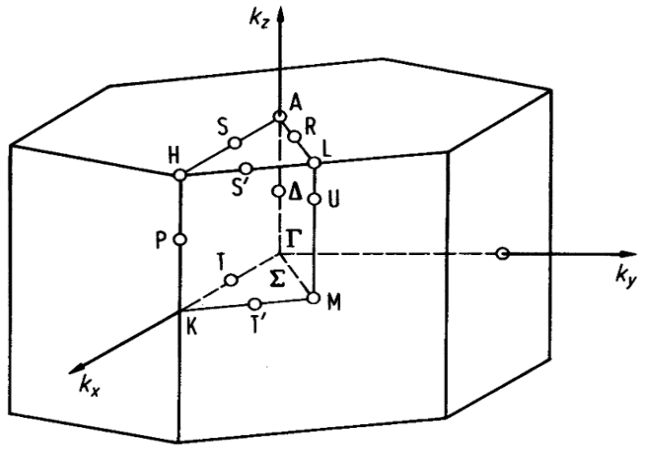
Semiconductors

GaN





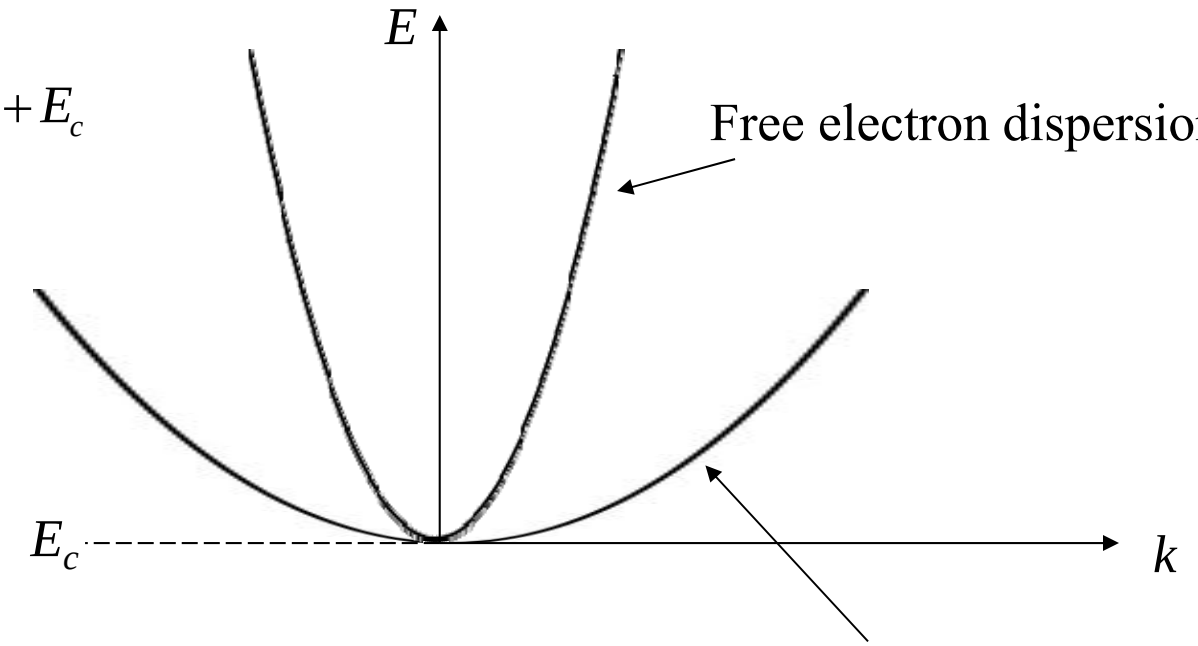




1st Brillioun zone of hcp

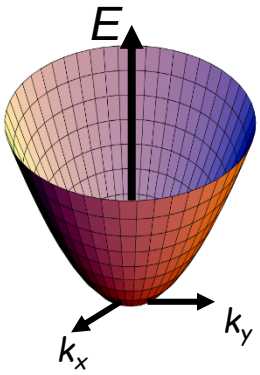
Conduction band minimum

$$E = \frac{\hbar^2 \left(\vec{k} - \vec{k}_0\right)^2}{2m^*} + E_c$$



Near the conduction band minimum, the bands are approximately parabolic.

Effective mass



$$E = \frac{\hbar^2 \left(\vec{k} - \vec{k}_0\right)^2}{2m^*} + E_c$$

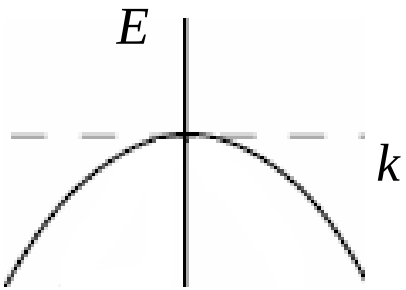
The parabola at the bottom of the conduction band does not have the same curvature as the free-electron dispersion relation. We define an effective mass to characterize the conduction band minimum.

$$m^* = \frac{\hbar^2}{\dfrac{d^2 E(\vec{k})}{dk_x^2}}$$

This effective mass is used to describe the response of electrons to external forces in the particle picture.

Top of the valence band

In the valence band, the effective mass is negative.



$$m^* = \frac{\hbar^2}{\frac{d^2E(\vec{k})}{dk_x^2}} < 0$$

Charge carriers in the valence band are positively charged holes.

$$m^*_h = \frac{-\hbar^2}{\frac{d^2E(\vec{k})}{dk_x^2}}$$

m^*_h = effective mass of holes

Holes

A completely filled band does not contribute to the current.

$$\vec{j} = \int_{\text{filled states}} -e\vec{v}(\vec{k})D(\vec{k})f(\vec{k})d\vec{k}$$

$$= \int_{\text{band}} -e\vec{v}(\vec{k})D(\vec{k})f(\vec{k})d\vec{k} - \int_{\text{empty states}} -e\vec{v}(\vec{k})D(\vec{k})f(\vec{k})d\vec{k}$$

$$= \int_{\text{empty states}} e\vec{v}(\vec{k})D(\vec{k})f(\vec{k})d\vec{k}$$

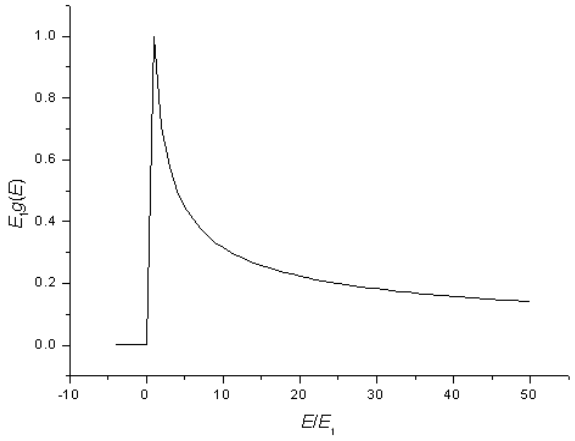
Holes have a positive charge and a positive mass.

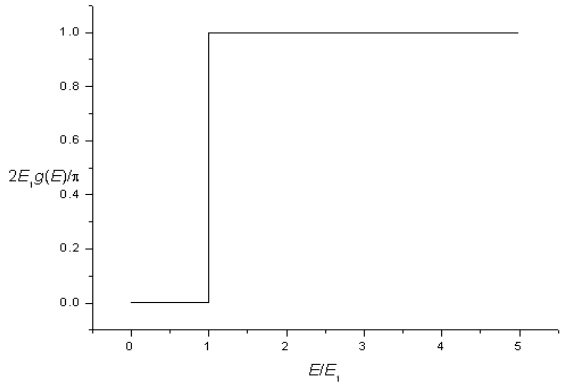
Free electron Fermi gas

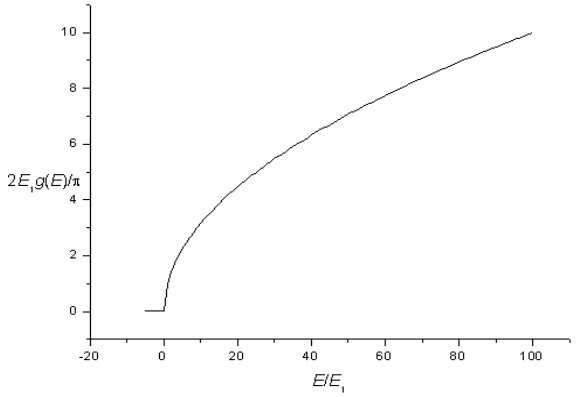
1 - d $$D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} = \frac{n}{2\sqrt{E_F E}} \qquad \mathrm{J^{-1}m^{-1}}$$

2 - d $$D(E) = \frac{m}{\hbar^2 \pi} = \frac{n}{E_F} \qquad \mathrm{J^{-1}m^{-2}}$$

3 - d $$D(E) = \frac{\pi}{2}\left(\frac{2m}{\hbar^2 \pi^2}\right)^{3/2} \sqrt{E} = \frac{3n}{2E_F^{3/2}} \sqrt{E} \qquad \mathrm{J^{-1}m^{-3}}$$



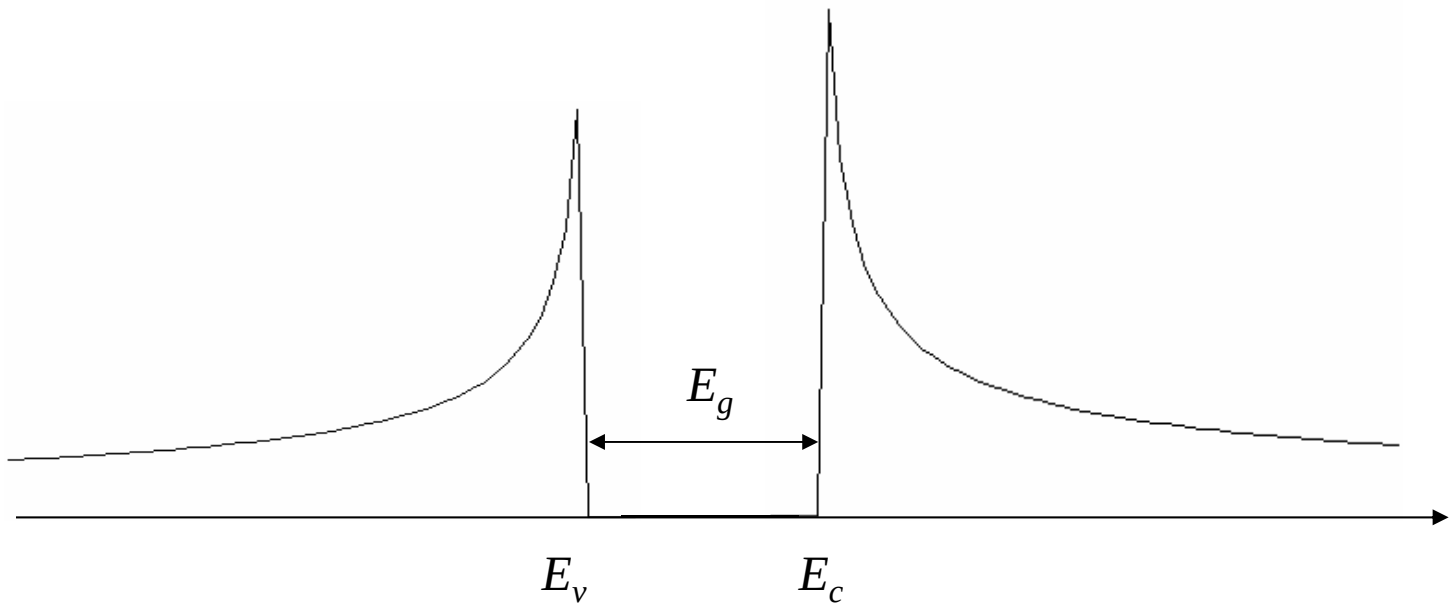




Semiconductors and insulators - 1d

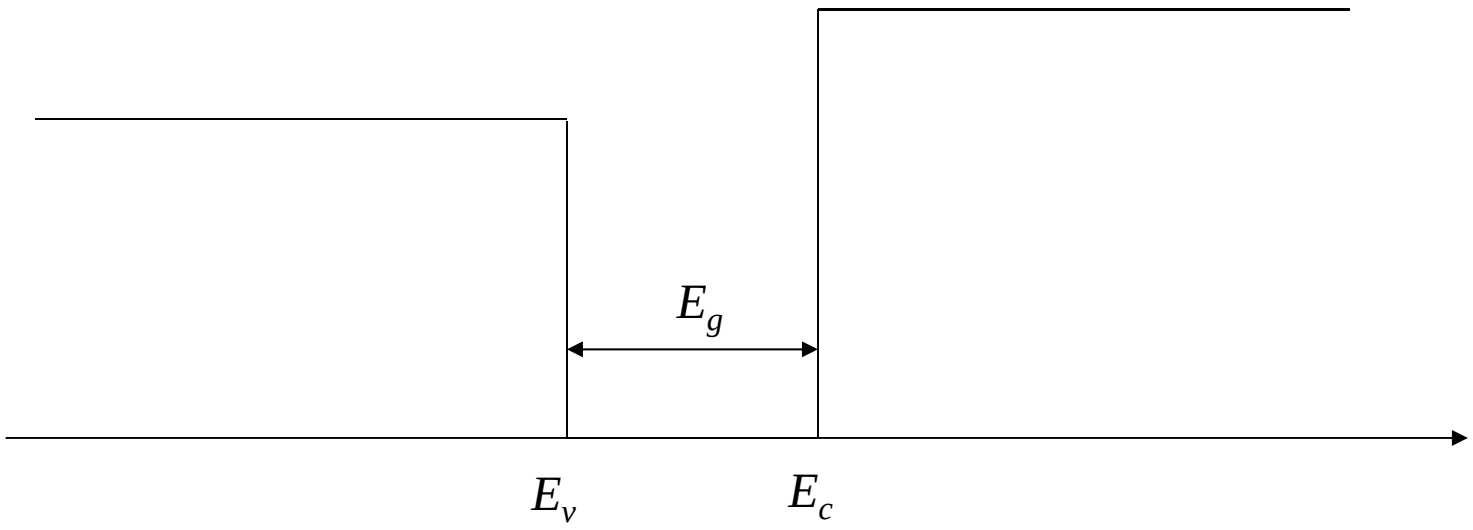
$$E = \frac{\hbar^2 (\vec{k} - \vec{k}_0)^2}{2m^*}$$

$$D(E) = \begin{cases} \dfrac{D_v}{\sqrt{(E_v - E)}} & E < E_v \\ 0 & E_v < E < E_c \\ \dfrac{D_c}{\sqrt{(E - E_c)}} & E_c < E \end{cases} \quad \mathrm{J^{-1}m^{-3}}$$



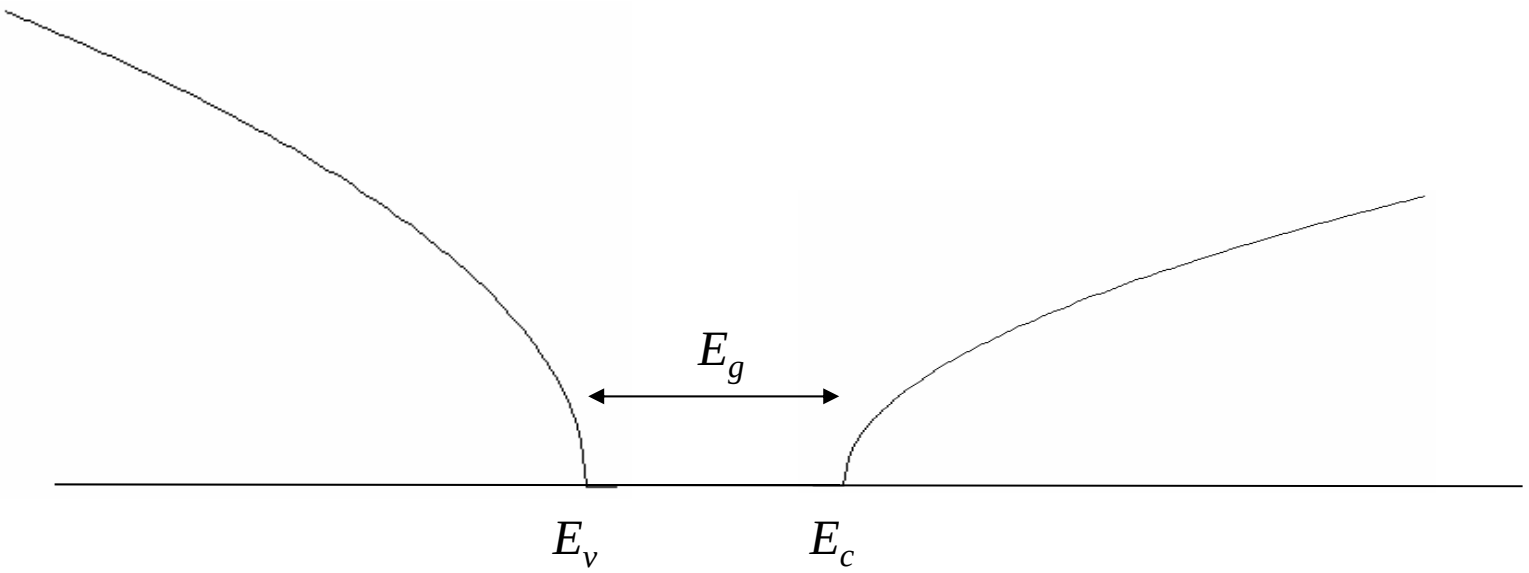
Semiconductors and insulators - 2d

$$D(E) = \begin{cases} D_v & E < E_v \\ 0 & E_v < E < E_c \\ D_c & E_c < E \end{cases} \quad \mathrm{J^{-1}m^{-3}}$$



Semiconductors and insulators - 3d

$$D(E) = \begin{cases} D_v \sqrt{E_v - E} & E < E_v \\ 0 & E_v < E < E_c \\ D_c \sqrt{E - E_c} & E_c < E \end{cases} \quad \mathrm{J^{-1}m^{-3}}$$



The electrical contribution to the thermodynamic properties of insulators depend on band edges

Boltzmann approximation

The table below gives the contribution of electrons in intrinsic semiconductors and insulators to some thermodynamic quantities. These results where calculated in the Boltzmann approximation where it is assumed that the chemical potential lies in the band gap more than $3k_BT$ from the band edge. The electronic contribution to the thermodynamic quantities are usually much smaller than the contribution of the phonons and thus the electronic components are often simply ignored.

	1-d	2-d
Density of states m_e^* and m_h^* are 'density of states' effective masses	$D(E) = \begin{cases} \frac{1}{\hbar\pi}\sqrt{\frac{2m_h^*}{(E_v - E)}} & E < E_v \\ 0 & E_v < E < E_c \\ \frac{1}{\hbar\pi}\sqrt{\frac{2m_e^*}{(E - E_c)}} & E > E_c \end{cases}$ J^{-1} m^{-1}	$D(E) = \begin{cases} \frac{m_h^*}{\hbar^2\pi} H(E_v - E) & E < E_v \\ 0 & E_v < E < E_c \\ \frac{m_e^*}{\hbar^2\pi} H(E - E_c) & E > E_c \end{cases}$ J^{-1} m^{-2} $H(x) = 0$ for $x < 0$ and $H(x) = 1$ for $x > 0$
Density of states N_V and N_C are the effective densities of states	$D(E) = \begin{cases} N_v(300)\sqrt{\frac{2}{300\pi k_B(E_v - E)}} & E < E_v \\ 0 & E_v < E < E_c \\ N_c(300)\sqrt{\frac{2}{300\pi k_B(E - E_c)}} & E > E_c \end{cases}$ J^{-1} m^{-1}	$D(E) = \begin{cases} \frac{N_v(300)}{300k_B} H(E_v - E) & E < E_v \\ 0 & E_v < E < E_c \\ \frac{N_c(300)}{300k_B} H(E - E_c) & E > E_c \end{cases}$ J^{-1} m^{-2}
Density of electrons in the conduction band $n = \int_{E_c}^{\infty} D(E) f(E) dE$	$n = \sqrt{\frac{m_e^* k_B T}{\hbar^2\pi}} \exp\left(\frac{\mu - E_c}{k_B T}\right)$ m^{-1} $= N_c \exp\left(\frac{\mu - E_c}{k_B T}\right)$	$n = \frac{m_e^* k_B T}{\hbar^2\pi} \exp\left(\frac{\mu - E_c}{k_B T}\right)$ m^{-2} $= N_c \exp\left(\frac{\mu - E_c}{k_B T}\right)$
Density of holes in the valence band $p = \int_{-\infty}^{E_v} D(E)(1 - f(E)) dE$	$p = \sqrt{\frac{m_h^* k_B T}{\hbar^2\pi}} \exp\left(\frac{E_v - \mu}{k_B T}\right)$ m^{-1} $= N_v \exp\left(\frac{\mu - E_c}{k_B T}\right)$	$p = \frac{m_h^* k_B T}{\hbar^2\pi} \exp\left(\frac{E_v - \mu}{k_B T}\right)$ m^{-2} $= N_v \exp\left(\frac{\mu - E_c}{k_B T}\right)$