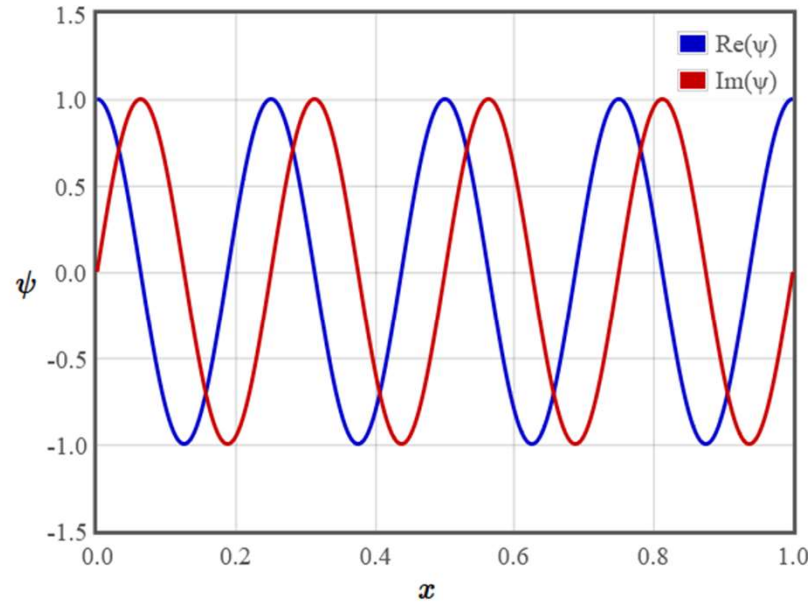# Electron bands

Free-electron model

$n_x = 4$ [+] [-]

Single particle solutions to Schrödinger equation	$\psi(\vec{r}) = \dfrac{1}{\sqrt{L}} e^{ikx} \quad \dfrac{1}{\sqrt{\mathrm{m}}}$	$\psi(\vec{r}) = \dfrac{1}{\sqrt{L^2}} e^{i\vec{k}\cdot\vec{r}} \quad \dfrac{1}{\mathrm{m}}$	$\psi(\vec{r}) = \dfrac{1}{\sqrt{L^3}} e^{i\vec{k}\cdot\vec{r}} \quad \dfrac{1}{\mathrm{m}^{3/2}}$
Allowed k values	$k_x = \dfrac{2\pi n_x}{L} \quad \dfrac{1}{\mathrm{m}}$ $n_x = \cdots - 2,\, -1,\, 0,\, 1,\, 2,\, \cdots$	$\vec{k} = \left[\dfrac{2\pi n_x}{L}, \dfrac{2\pi n_y}{L}\right] \dfrac{1}{\mathrm{m}}$ $n_x, n_y = \cdots - 2,\, -1,\, 0,\, 1,\, 2,\, \cdots$	$\vec{k} = \left[\dfrac{2\pi n_x}{L}, \dfrac{2\pi n_y}{L}, \dfrac{2\pi n_z}{L}\right] \dfrac{1}{\mathrm{m}}$ $n_x, n_y, n_z = \cdots - 2,\, -1,\, 0,\, 1,\, 2,\, \cdots$
Density of electron states in reciprocal space	$D(\vec{k}) = \dfrac{2}{2\pi}$	$D(\vec{k}) = \dfrac{2}{(2\pi)^2}$	$D(\vec{k}) = \dfrac{2}{(2\pi)^3}$
Density of electron states in reciprocal space	$D(k) = \dfrac{2}{}$	$D(k) = \dfrac{k}{} \quad \mathrm{m}^{-1}$	$D(k) = \dfrac{k^2}{} \quad \mathrm{m}^{-2}$

$$u \approx \frac{3}{5}nE_F + \frac{\pi^2}{4}\frac{n}{E_F}(k_BT)^2 \quad \text{J m}^{-3}$$

$$c_v \approx \frac{\pi^2}{2}\frac{n}{E_F}k_B^2T \quad \text{J K}^{-1}\text{m}^{-3}$$

$$s \approx \frac{\pi^2}{2}\frac{n}{E_F}k_B^2T \quad \text{J K}^{-1}\text{m}^{-3}$$

$$f \approx \frac{3}{5}nE_F - \frac{\pi^2}{4}\frac{n}{E_F}(k_BT)^2 \quad \text{J m}^{-3}$$

$$P \approx \frac{2}{5}nE_F + \frac{\pi^2}{6}\frac{n}{E_F}(k_BT)^2 \quad \text{N m}^{-2}$$

$$B \approx \frac{2}{3}nE_F + \frac{\pi^2}{18}\frac{n}{E_F}(k_BT)^2 \quad \text{N m}^{-2}$$

$$h \approx nE_F + \frac{5\pi^2}{12}\frac{n}{E_F}(k_BT)^2 \quad \text{J m}^{-3}$$

$$g \approx nE_F - \frac{\pi^2}{12}\frac{n}{E_F}(k_BT)^2 \quad \text{J m}^{-3}$$

All properties depend on n and m

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} \quad \text{J}$$

Fit data to n amd m

Bloch Theorem

Bloch form $\qquad \psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$

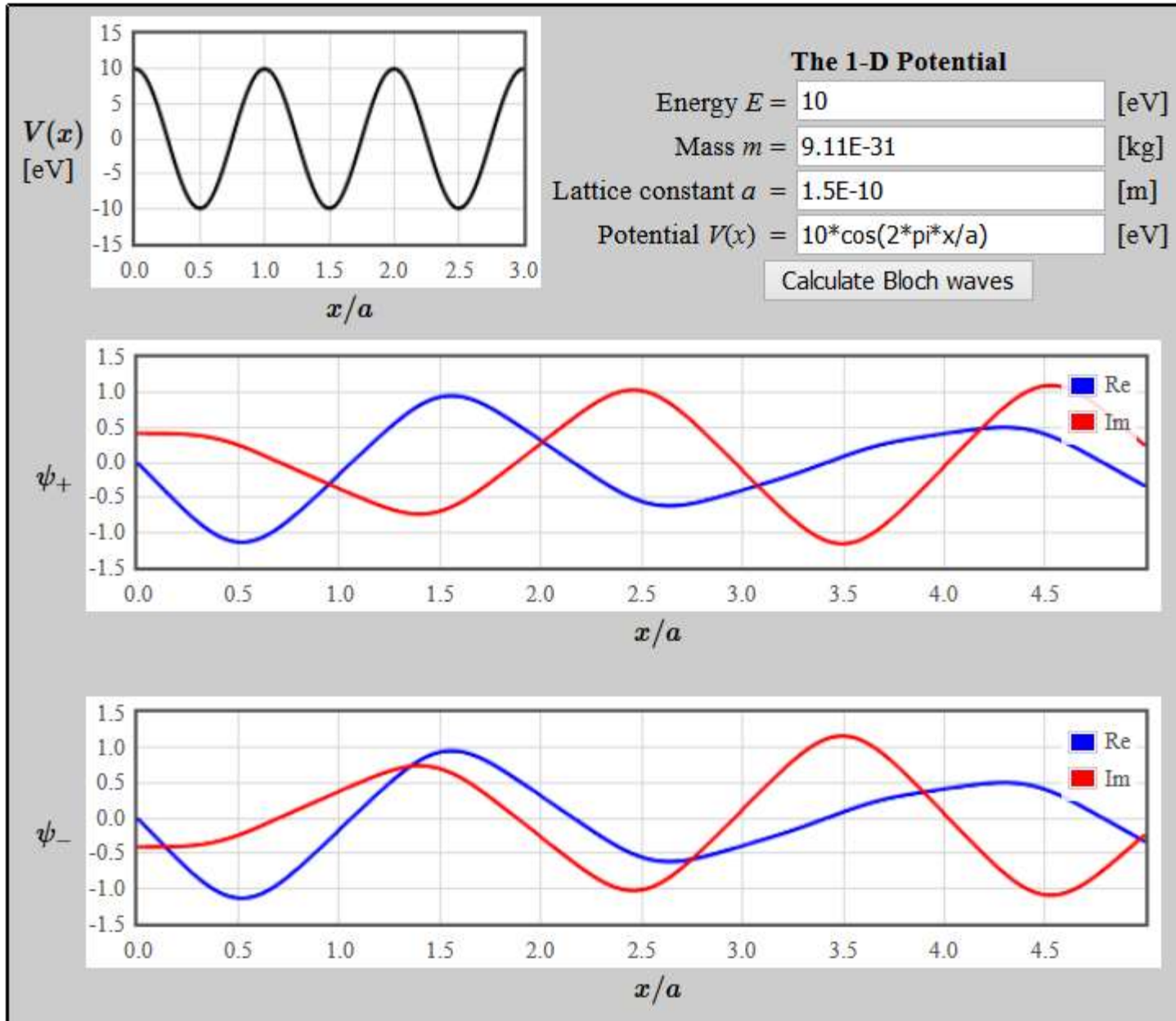$u_{\vec{k}}(\vec{r})$ is a periodic function.

$\vec{k}$ is a wavevector in the first Brillouin zone.

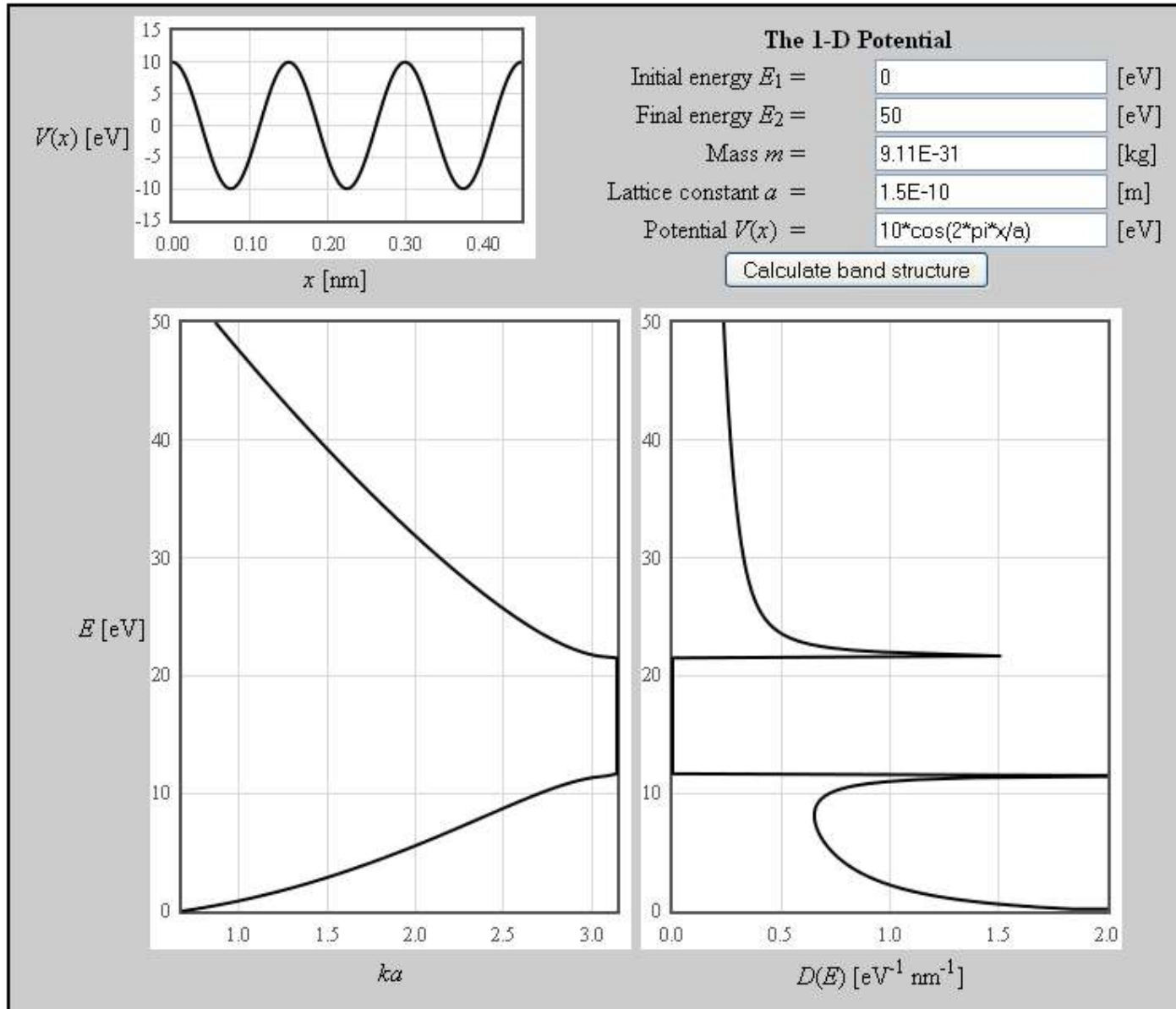Eigenfunction solutions of the Schrödinger equation have Bloch form.

$$\mathbf{T}\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot(\vec{r}+\vec{T})} u_{\vec{k}}(\vec{r}+\vec{T}) = e^{i\vec{k}\cdot\vec{T}} e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{T}} \psi_{\vec{k}}(\vec{r})$$
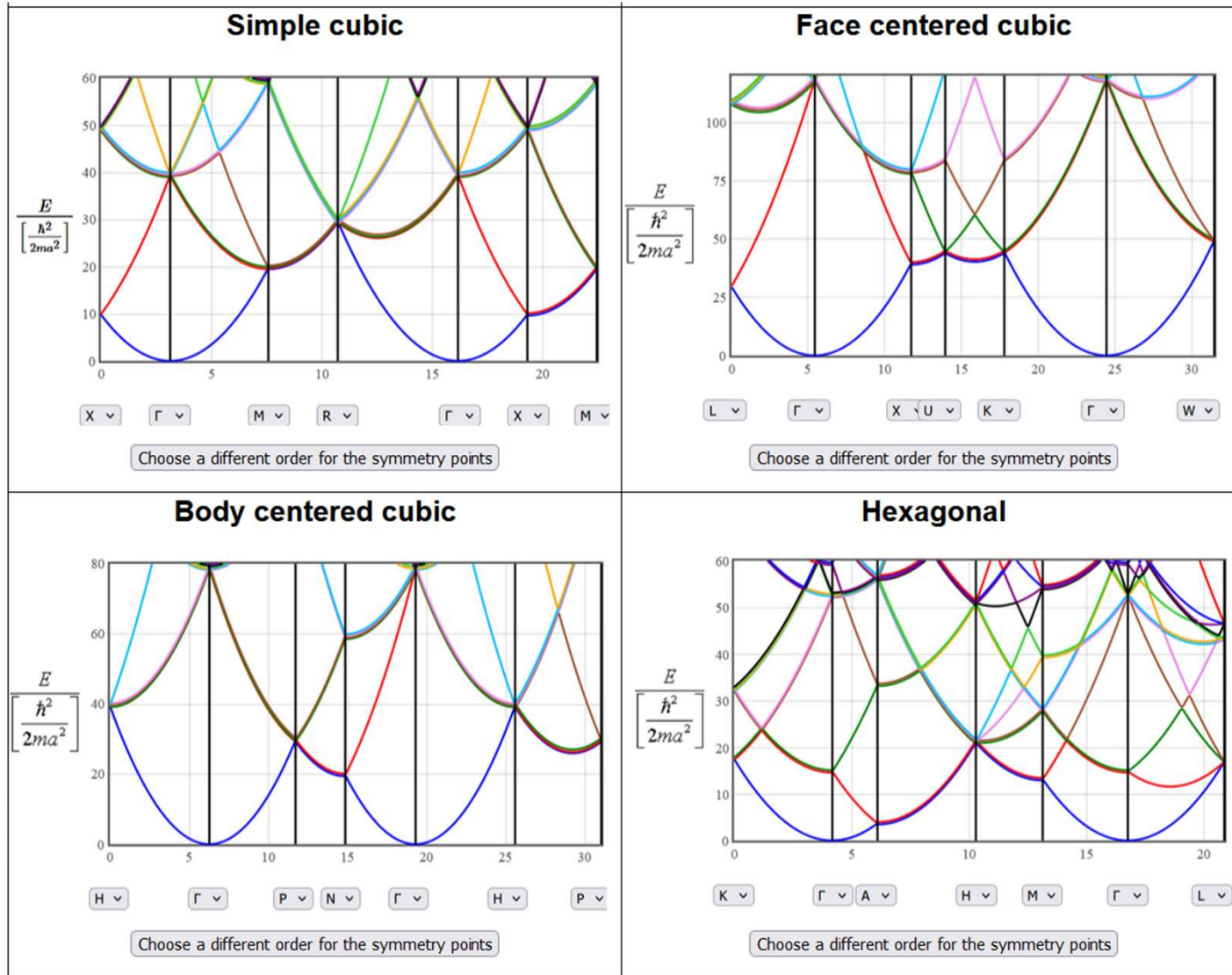
Bloch waves in 1-D
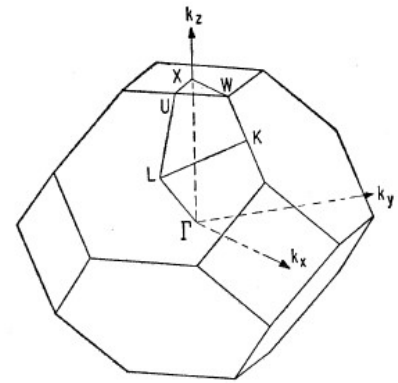
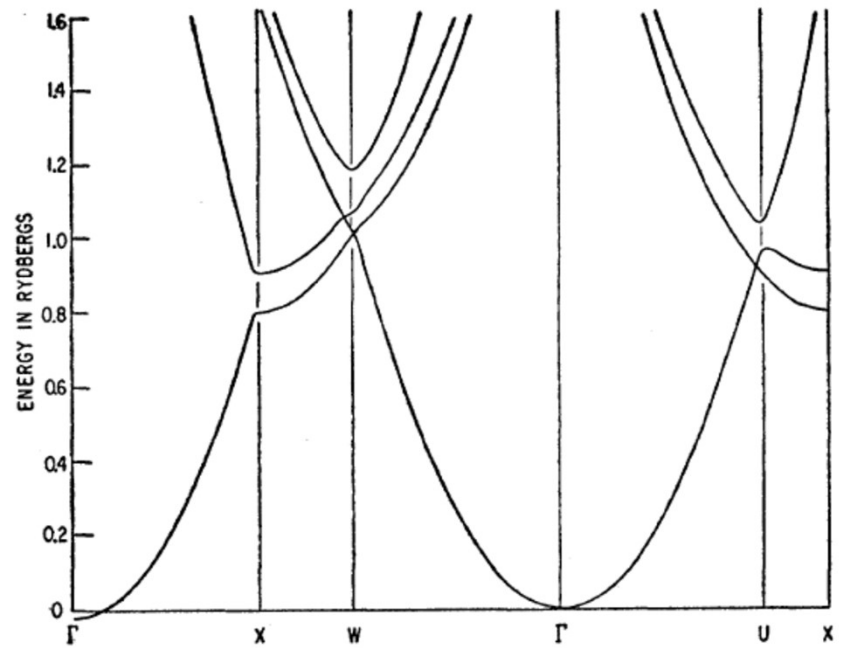$$\psi = e^{ikx} u_k(x)$$

Band structure in 1-D

The 1-D Potential

Initial energy E_1 =	0	[eV]
Final energy E_2 =	50	[eV]
Mass m =	9.11E-31	[kg]
Lattice constant a =	1.5E-10	[m]
Potential $V(x)$ =	10*cos(2*pi*x/a)	[eV]

Calculate band structure

Empty lattice approximation

Band Structure of Aluminum

WALTER A. HARRISON

General Electric Research Laboratory, Schenectady, New York
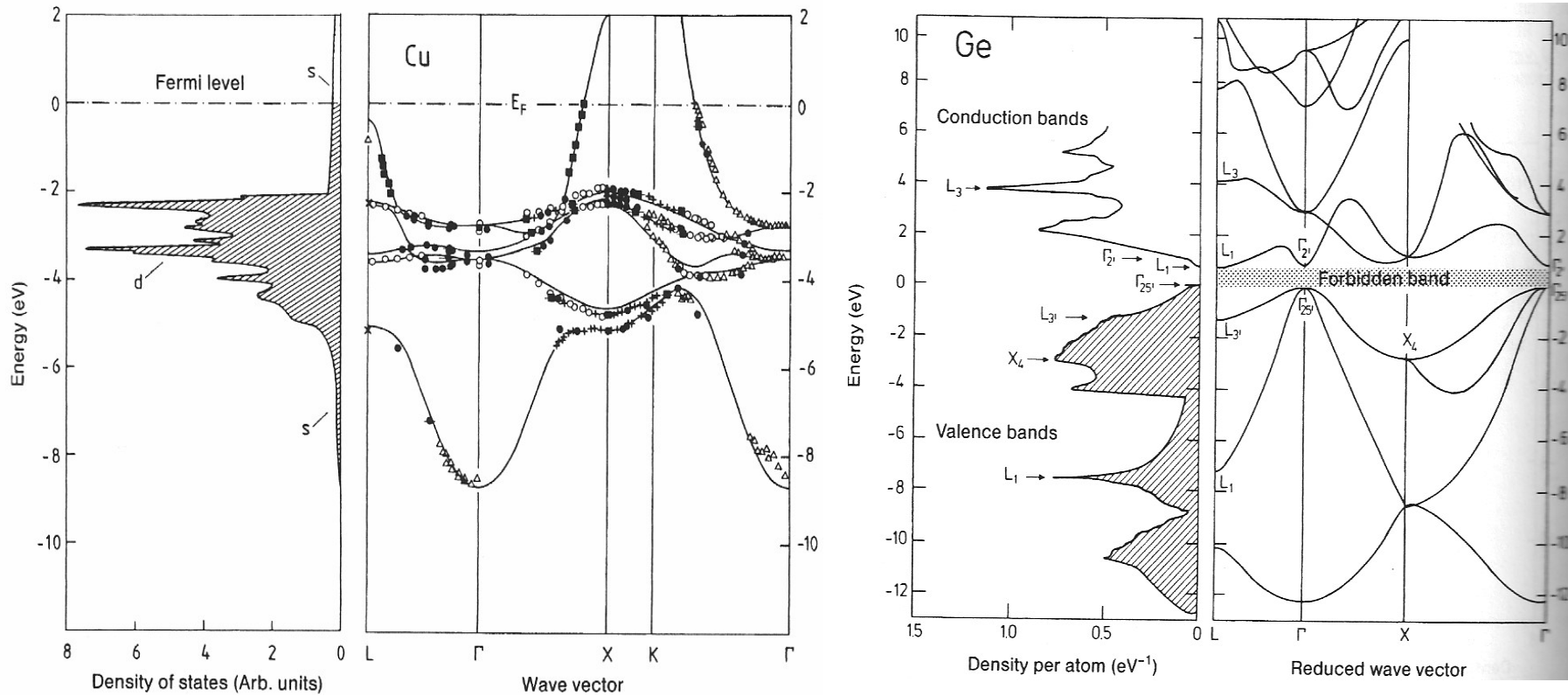
empty lattice approximation
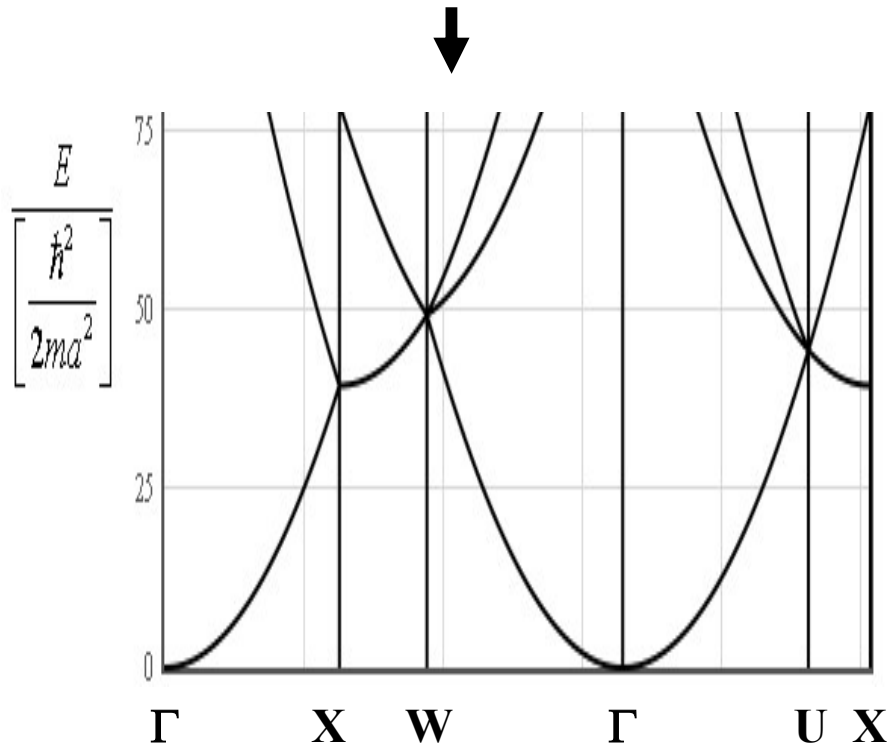
Metals, semiconductors, and insulators

Insulators: band gap > 3 eV

From Ibach & Lueth

2N states per Brillouin zone

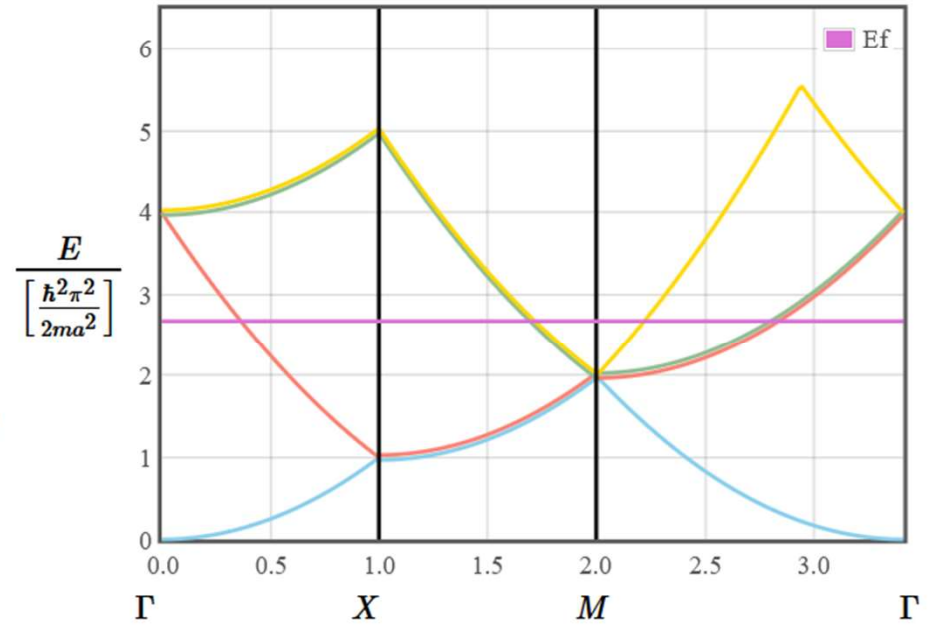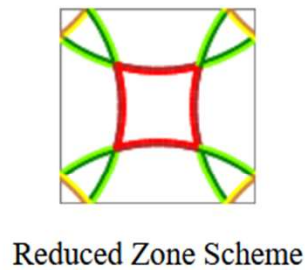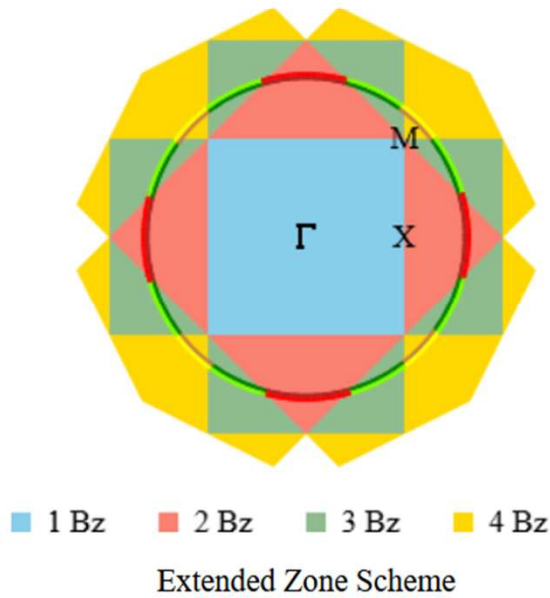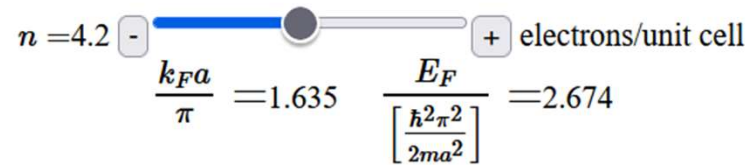A crystal $L \times L \times L$ has $N = \dfrac{L^3}{a^3}$ primitive unit cells.

The first Brillouin zone contains $\quad N = \dfrac{\left(\dfrac{2\pi}{a}\right)^3}{\left(\dfrac{2\pi}{L}\right)^3} = \dfrac{L^3}{a^3} \quad$ k points.

Each k state can hold 2 electrons (spin).

There are $2N$ electron states per Brillouin zone.

$2N$ electron states per band

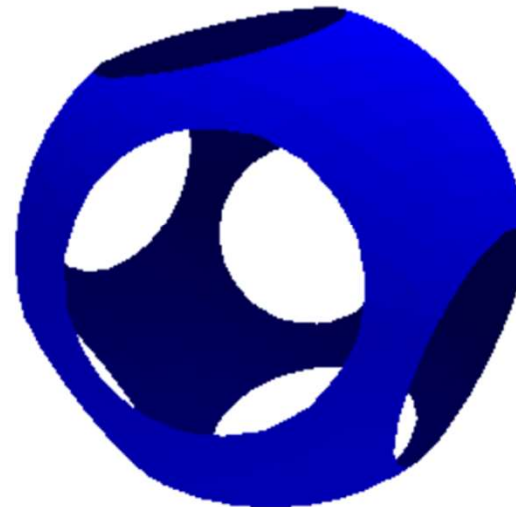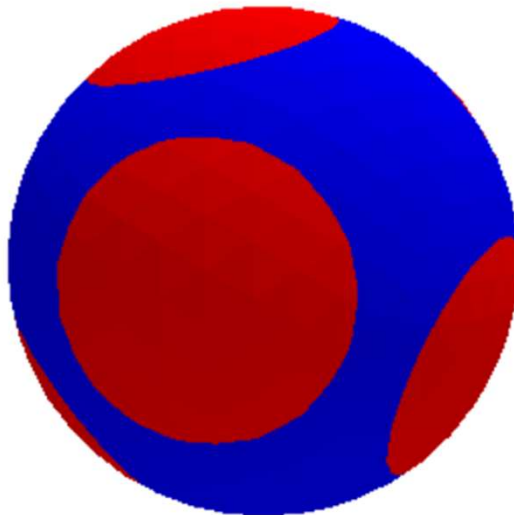# Fermi surface of a two-dimensional square lattice

$n = 4.2$ [-] [====●====] [+] electrons/unit cell

$$\frac{k_F a}{\pi} = 1.635 \qquad \frac{E_F}{\left[\frac{\hbar^2 \pi^2}{2ma^2}\right]} = 2.674$$

1 Bz   2 Bz   3 Bz   4 Bz

Extended Zone Scheme

Reduced Zone Scheme

$$\frac{E}{\left[\frac{\hbar^2 \pi^2}{2ma^2}\right]}$$

http://lampx.tugraz.at/~hadley/ss2/fermisurface/2d_fermisurface/2dsquare.php

Fermi Surfaces

$n = 2$ [-] ———●——— [+] electrons/unit cell

$$k_F = (3\pi^2 n)^{1/3} = 3.90$$

Lattice: ○ Simple Cubic ○ Body Centered Cubic ◉ Face Centered Cubic ○ Hexagonal Close Pack $\frac{c}{a} = \sqrt{\frac{8}{3}}$

[Show 1st Brillouin zone] [Stop Rotation]

Brillouinzone	1	2	3	4
Outside Color	■	■	■	■
Inside Color	■	■	■	■
Show	☑	☐	☑	☑

http://lampx.tugraz.at/~hadley/ss2/fermisurface/3d_fermisurface/index.html

Band structure calculations

Knowing how the atoms are arranged, calculate the electron states
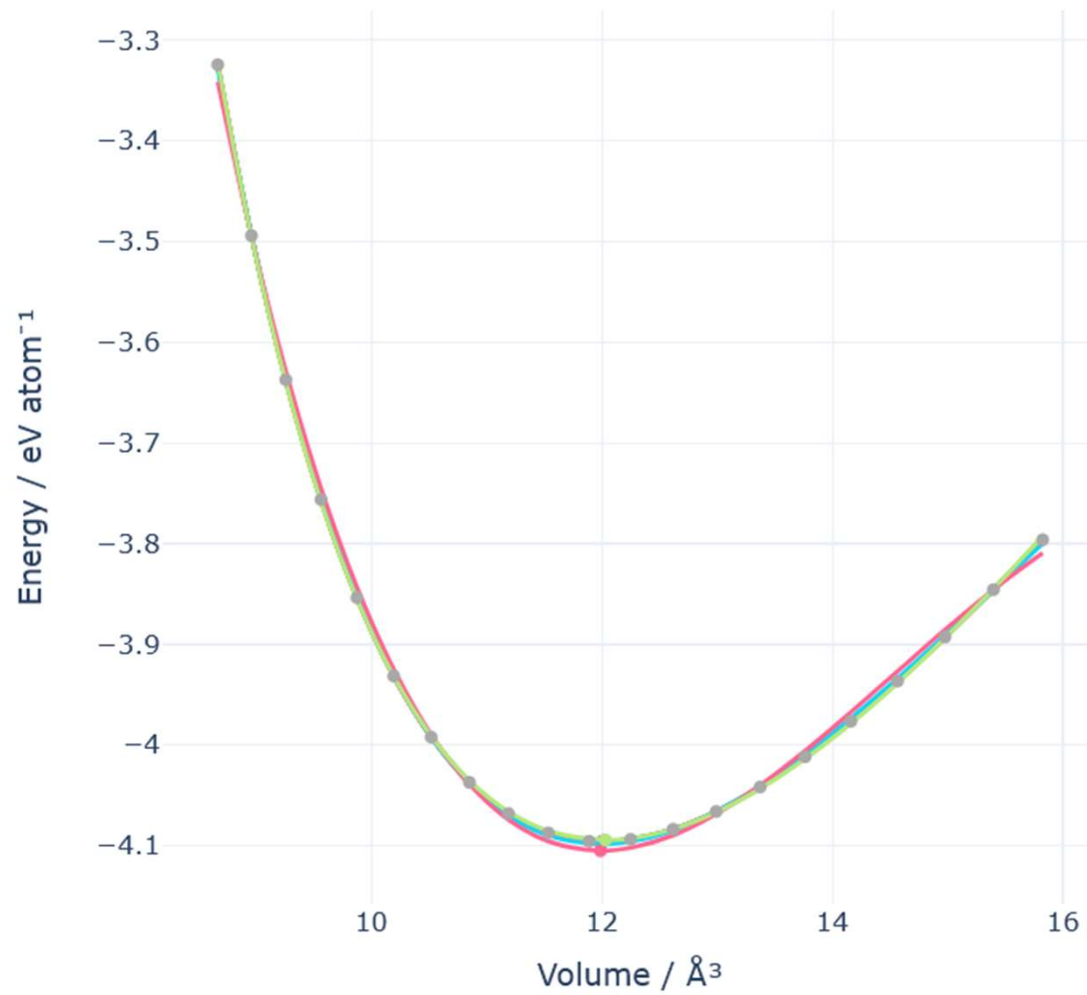
Density Functional Theory (DFT)
Plane wave method
Tight binding

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a} \nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}$$

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Band structure calculations

Plane wave method

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}} + U(\vec{r})\psi_{\vec{k}} = E\psi_{\vec{k}}.$$

The potential is periodic

$$U(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Bloch form

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}'} C_{\vec{G}'} e^{i\vec{G}'\cdot\vec{r}}$$

$$\sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = \sum_{\vec{G}'} C_{\vec{G}'} e^{i\vec{G}'\cdot\vec{r}}$$

We can relabel the reciprocal lattice vectors since we sum over them.

Plane wave method

$$\sum_{\vec{G}'} \frac{\hbar^2(\vec{k}+\vec{G}')^2}{2m} C_{\vec{G}'} e^{i(\vec{k}+\vec{G}')\cdot\vec{r}} + \sum_{\vec{G}}\sum_{\vec{G}''} U_{\vec{G}} C_{\vec{G}''} e^{i(\vec{k}+\vec{G}+\vec{G}'')\cdot\vec{r}} = E \sum_{\vec{G}'} C_{\vec{G}'} e^{i(\vec{k}+\vec{G}')\cdot\vec{r}}$$

Only the terms with the same wavelength can be equal to each other.

$$\vec{G}'' = \vec{G}' - \vec{G}$$

Central equations: $$\frac{\hbar^2(\vec{k}+\vec{G}')^2}{2m} C_{\vec{G}'} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{G}'-\vec{G}} = E C_{\vec{G}'}$$

There is one equation for each $\vec{G}'$ vector.

+ - **Body Centered Cubic with a Comb Potential**

If all of the components of a Fourier series are real and have the same amplitude, there is constructive interference at the Bravais lattice points and this produces a comb function with one large amplitude peak per Bravais lattice point. Below is python code to calculate the band structure of a bcc comb potential. One hundred twenty five reciprocal lattice points are included in the calculation where h, k, and l are in the range -2, -2, 0, 1, 2.

Every band is drawn in a different color and there must be an energy for that band for every k. If a color is not visible for some range of k that band must be degenerate in energy with another band.
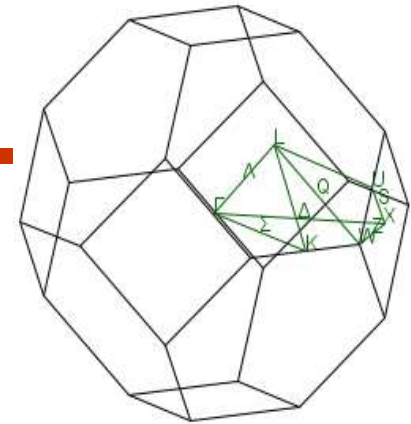
Tight binding

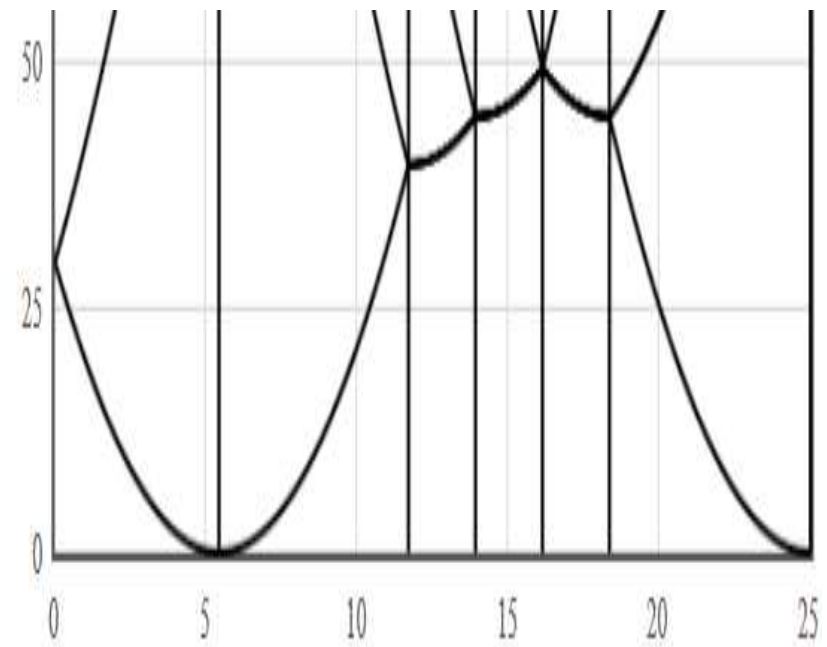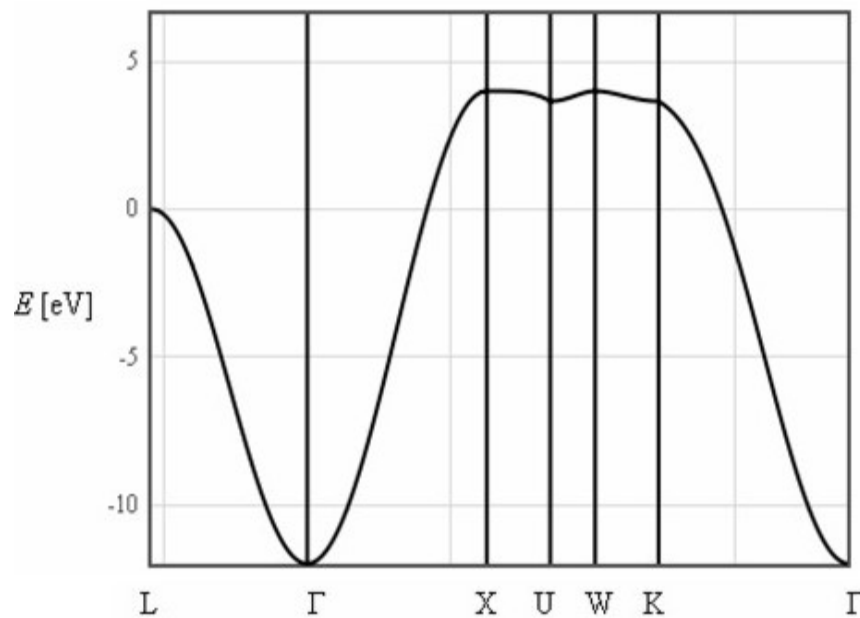Atoms (large internuclear distance)   Bonds (smaller internuclear distance)
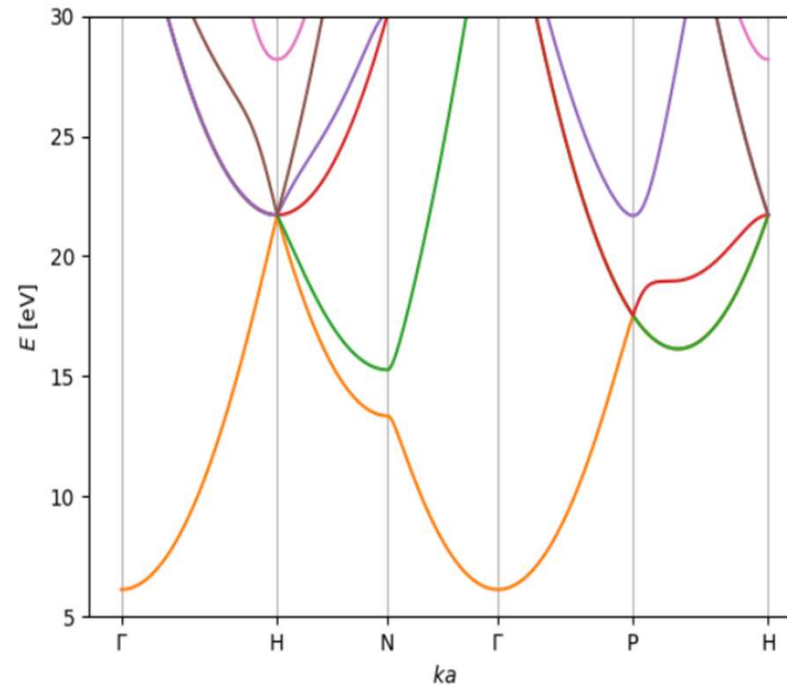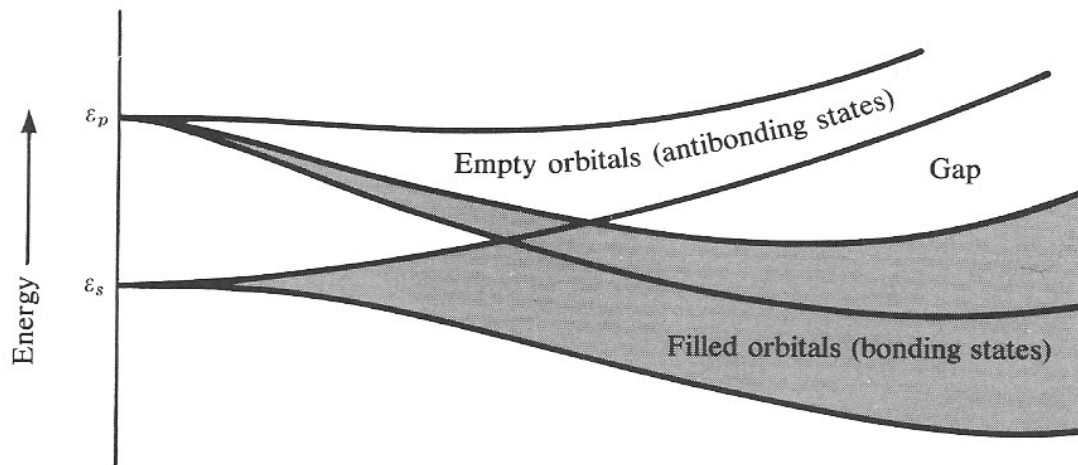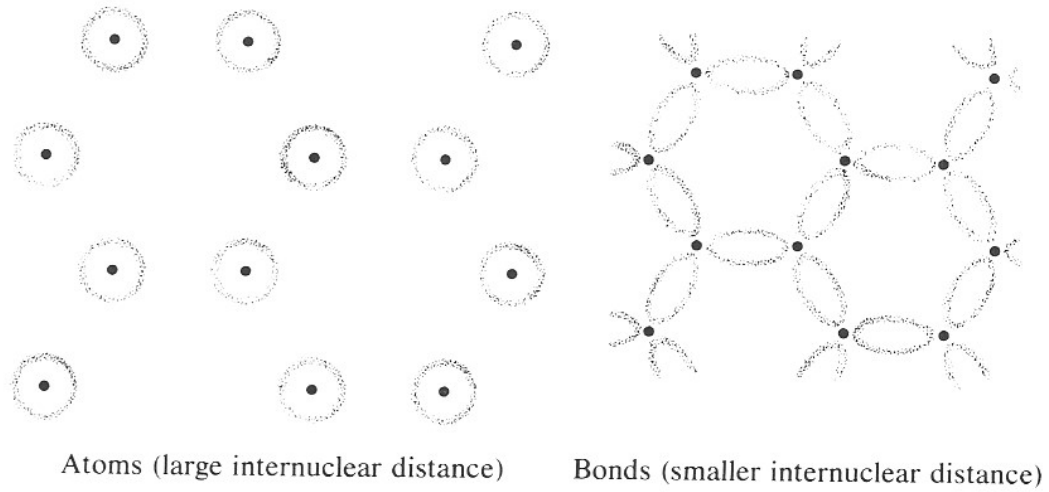
Harrison, Electronic Structure, Freeman 1980
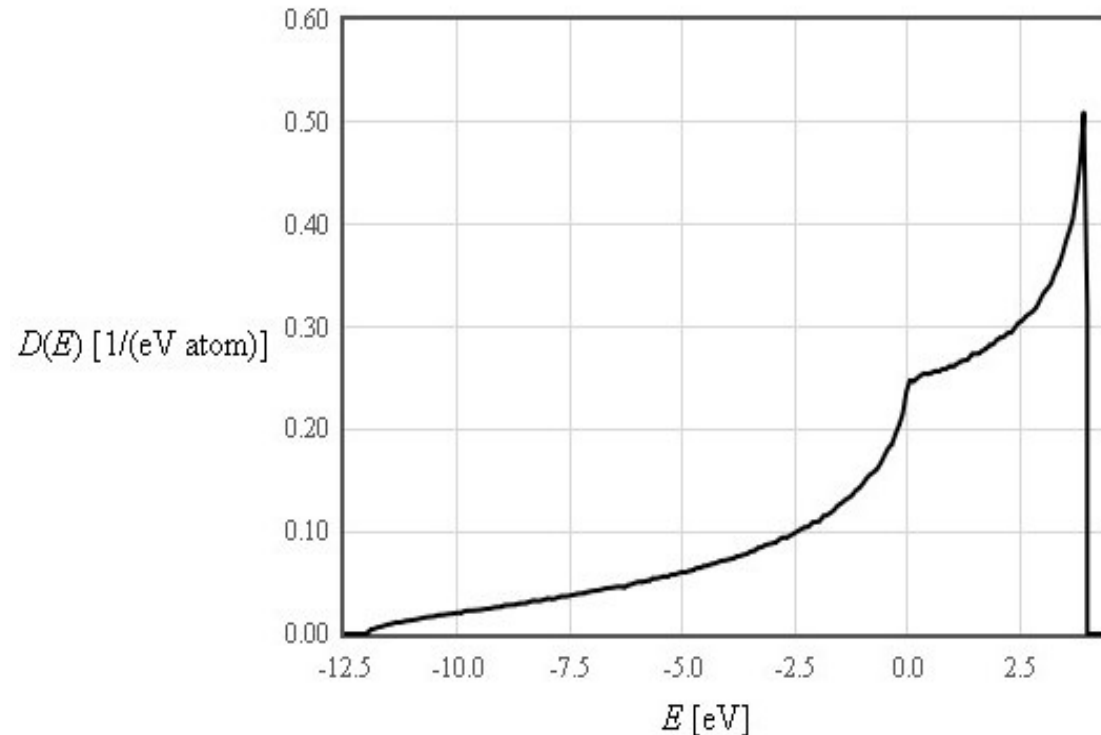
Tight binding, fcc

$$E = \varepsilon - t \sum_{lmn} e^{i\vec{k} \cdot \vec{\rho}_{lmn}}$$

$$E = \varepsilon - 4t \left(\cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) \right)$$
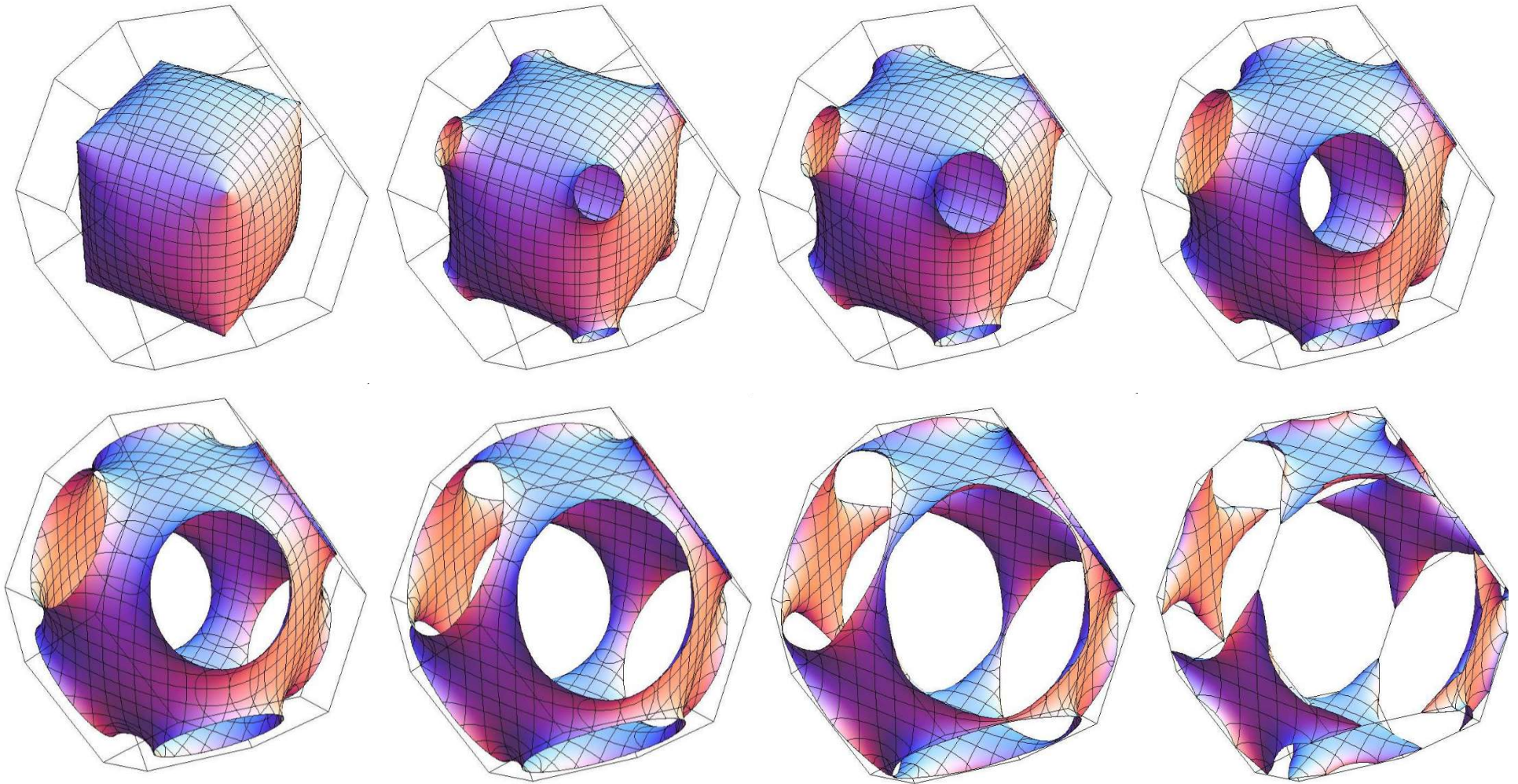
Density of states (fcc)

Calculate the energy for every allowed k in the Brillouin zone

$$E = \varepsilon - 4t \left(\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right) \right)$$
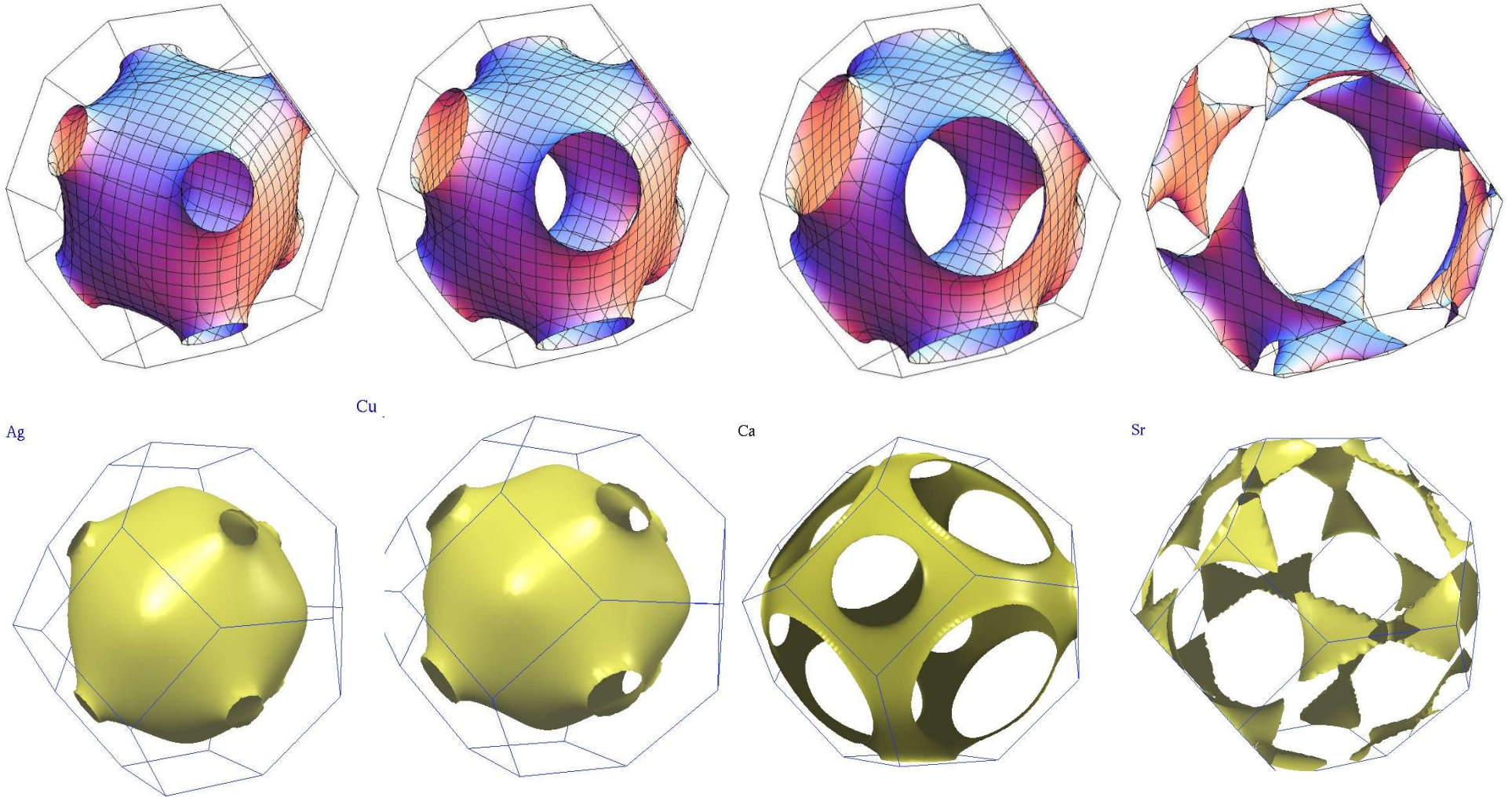
http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tbtable/tbtable.html

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

Linear Chain	2-D square lattice	

$$E = \varepsilon - 2t\cos(k_x a)$$

$$E = \varepsilon - 2t\left(\cos(k_x a) + \cos(k_y a)\right)$$

$$E = \varepsilon - 2t\left($$

relation

Calculate E(k)

Calculate E(k)

of states

$$D(k) = \frac{2}{\pi}$$

$$D(k) = \frac{k}{\pi} \quad \text{m}^{-1}$$

of states

$$D(E) = \frac{1}{at\sqrt{1 - \left(\dfrac{\varepsilon - E}{2t}\right)^2}} \quad \text{J}^{-1}\text{m}^{-1}$$

$D(E)$ [eV^{-1} nm^{-1}]

$D(E)$ [1/(eV atom)]

$D(E)$ [1/(eV

Tight binding, fcc

Christian Gruber, 2008

Tight binding, fcc

Ag
Cu
Ca
Sr

http://www.phys.ufl.edu/fermisurface/

1A	2A	3B	4B	5B	6B	7B		8		1B	2B	3A	4A	5A	6A	7A	NG
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Feup	Coup	Niup	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

magnets :

Feup	Fedn	Coup	Codn	Niup	Nidn

native Structures :

sc	Ti_bcc	Fe_bcc	Zr_bcc		Ti_fcc	Mn_fcc	Co_fcc	Ni_fcc	Zn_fcc	Y_fcc	Zr_fcc	Tc_fcc	Ru_fcc	Cd_fcc		Co_hcp

[Simple Periodic Table with the electronic band structure of each element]

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

[png images, less than about 20 kb](Start 2/2, 2006)(Update 7/30, 2020)
[NPT2][Copyright and No warranty][Top]

Materials Explorer
App by Materials Project

References

Search for materials information by chemistry, composition, or property.

Materials e.g. Li-Fe or Li,Fe or Li3Fe or mp-19017

| Only Elements | At Least Elements | Formula |

* Select elements to search for materials with **only** these elements

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

| La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

Lithium bcc

$$\frac{E}{\left[\frac{\hbar^2}{2ma^2}\right]}$$

Γ   H   N   Γ   P   N   H

LITHIUM

Γ Δ H G N Σ Γ Λ P D N P F H

Density of states
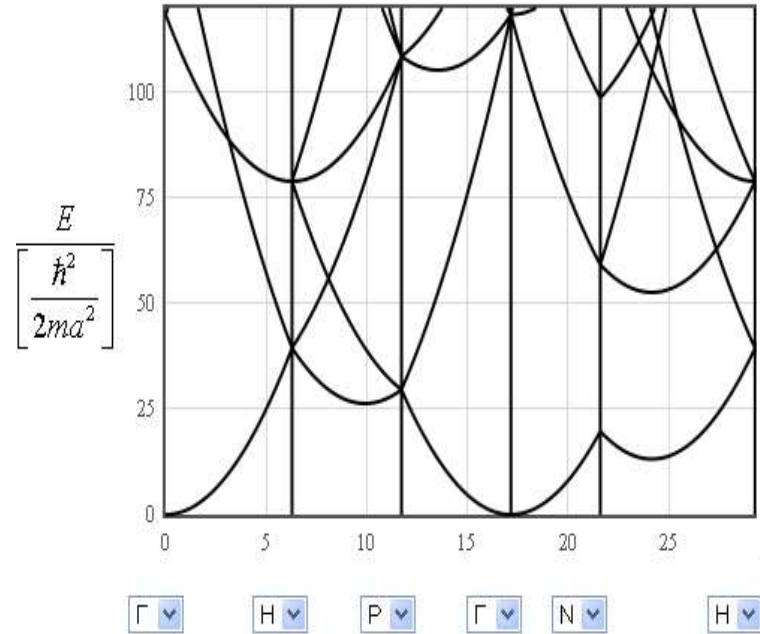
Li

E_f

ENERGY (eV)

TOTAL DOS

Sodium

Fig. 6. Na (bcc). Energy bands calculated using the APW method by Gupta (quoted in [73Haq]).

$$\frac{E}{\left[\frac{\hbar^2}{2ma^2}\right]}$$

Γ H P Γ N H
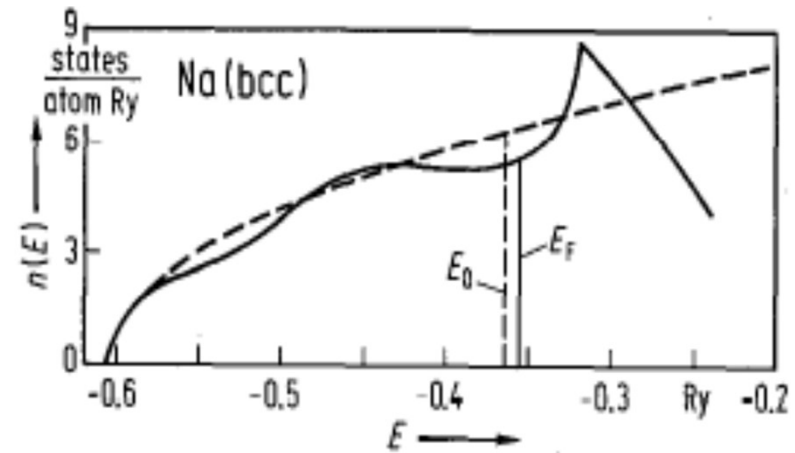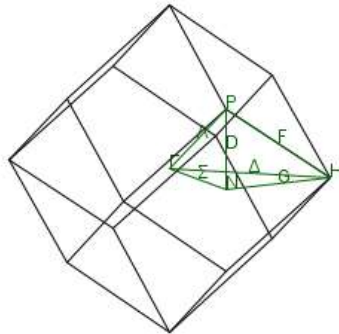
Bandstructure of bcc chromium (Cr)

Transition metals

Ti (hcp)   V (bcc)   Cr (bcc)   Fe (bcc)   Co (fcc)   Ni (fcc)   Cu (fcc)

Density of States for VANADIUM

Density of States for COPPER

d band metals, transition metals

f band metals, rare earths

hydrogen 1 **H** 1.0079		helium 2 **He** 4.0026

lithium 3 **Li** 6.941 beryllium 4 **Be** 9.0122 boron 5 **B** 10.811 carbon 6 **C** 12.011 nitrogen 7 **N** 14.007 oxygen 8 **O** 15.999 fluorine 9 **F** 18.998 neon 10 **Ne** 20.180

sodium 11 **Na** 22.990 magnesium 12 **Mg** 24.305 aluminium 13 **Al** 26.982 silicon 14 **Si** 28.086 phosphorus 15 **P** 30.974 sulfur 16 **S** 32.065 chlorine 17 **Cl** 35.453 argon 18 **Ar** 39.948

potassium 19 **K** 39.098 calcium 20 **Ca** 40.078 scandium 21 **Sc** 44.956 titanium 22 **Ti** 47.867 vanadium 23 **V** 50.942 chromium 24 **Cr** 51.996 manganese 25 **Mn** 54.938 iron 26 **Fe** 55.845 cobalt 27 **Co** 58.933 nickel 28 **Ni** 58.693 copper 29 **Cu** 63.546 zinc 30 **Zn** 65.39 gallium 31 **Ga** 69.723 germanium 32 **Ge** 72.61 arsenic 33 **As** 74.922 selenium 34 **Se** 78.96 bromine 35 **Br** 79.904 krypton 36 **Kr** 83.80

rubidium 37 **Rb** 85.468 strontium 38 **Sr** 87.62 yttrium 39 **Y** 88.906 zirconium 40 **Zr** 91.224 niobium 41 **Nb** 92.906 molybdenum 42 **Mo** 95.94 technetium 43 **Tc** [98] ruthenium 44 **Ru** 101.07 rhodium 45 **Rh** 102.91 palladium 46 **Pd** 106.42 silver 47 **Ag** 107.87 cadmium 48 **Cd** 112.41 indium 49 **In** 114.82 tin 50 **Sn** 118.71 antimony 51 **Sb** 121.76 tellurium 52 **Te** 127.60 iodine 53 **I** 126.90 xenon 54 **Xe** 131.29

caesium 55 **Cs** 132.91 barium 56 **Ba** 137.33 57-70 ✱ lutetium 71 **Lu** 174.97 hafnium 72 **Hf** 178.49 tantalum 73 **Ta** 180.95 tungsten 74 **W** 183.84 rhenium 75 **Re** 186.21 osmium 76 **Os** 190.23 iridium 77 **Ir** 192.22 platinum 78 **Pt** 195.08 gold 79 **Au** 196.97 mercury 80 **Hg** 200.59 thallium 81 **Tl** 204.38 lead 82 **Pb** 207.2 bismuth 83 **Bi** 208.98 polonium 84 **Po** [209] astatine 85 **At** [210] radon 86 **Rn** [222]

francium 87 **Fr** [223] radium 88 **Ra** [226] 89-102 ✱✱ lawrencium 103 **Lr** [262] rutherfordium 104 **Rf** [261] dubnium 105 **Db** [262] seaborgium 106 **Sg** [266] bohrium 107 **Bh** [264] hassium 108 **Hs** [269] meitnerium 109 **Mt** [268] ununnilium 110 **Uun** [271] unununium 111 **Uuu** [272] ununbium 112 **Uub** [277] ununquadium 114 **Uuq** [289]
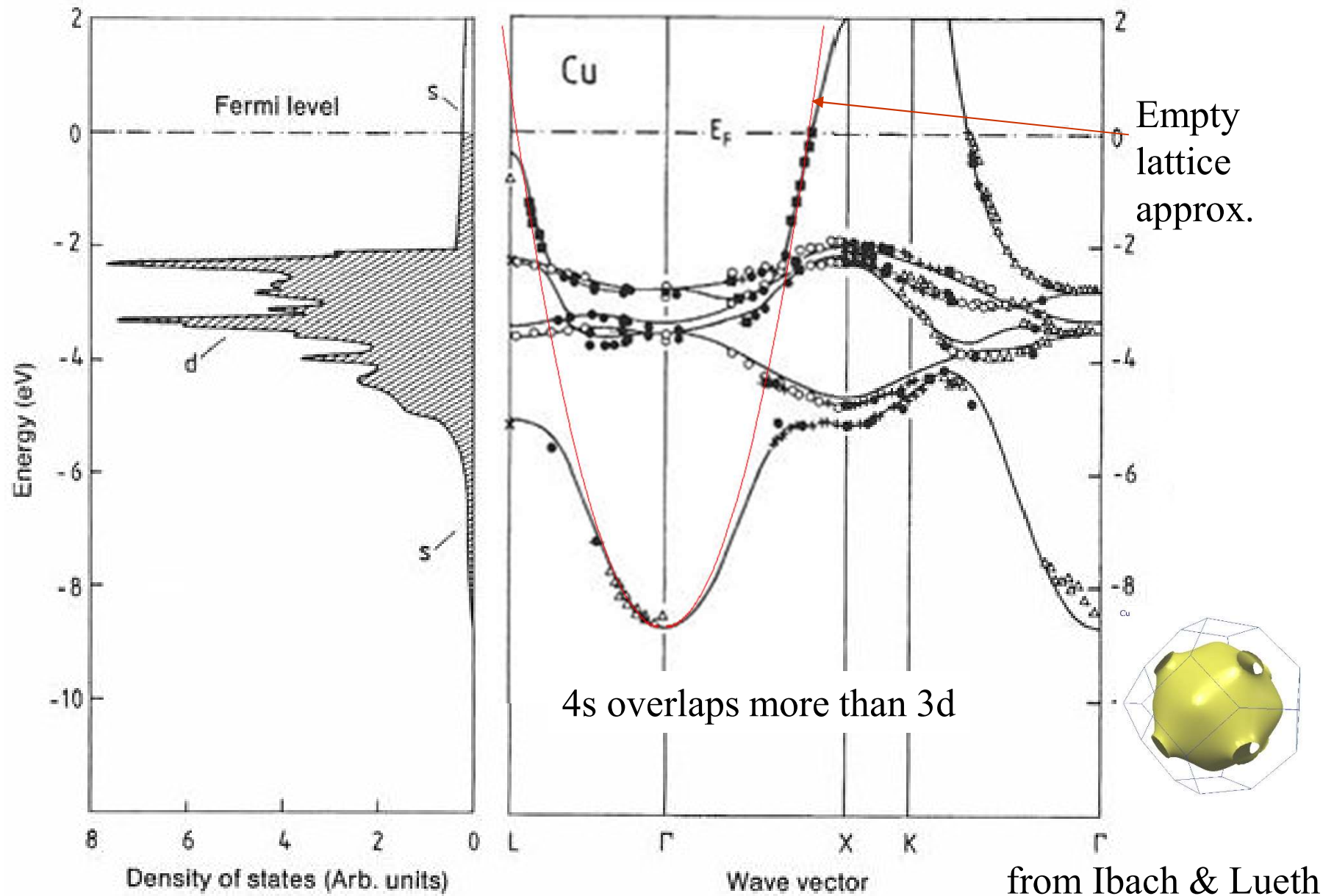
✱ Lanthanide series

lanthanum 57 **La** 138.91 cerium 58 **Ce** 140.12 praseodymium 59 **Pr** 140.91 neodymium 60 **Nd** 144.24 promethium 61 **Pm** [145] samarium 62 **Sm** 150.36 europium 63 **Eu** 151.96 gadolinium 64 **Gd** 157.25 terbium 65 **Tb** 158.93 dysprosium 66 **Dy** 162.50 holmium 67 **Ho** 164.93 erbium 68 **Er** 167.26 thulium 69 **Tm** 168.93 ytterbium 70 **Yb** 173.04

✱✱ Actinide series

actinium 89 **Ac** [227] thorium 90 **Th** 232.04 protactinium 91 **Pa** 231.04 uranium 92 **U** 238.03 neptunium 93 **Np** [237] plutonium 94 **Pu** [244] americium 95 **Am** [243] curium 96 **Cm** [247] berkelium 97 **Bk** [247] californium 98 **Cf** [251] einsteinium 99 **Es** [252] fermium 100 **Fm** [257] mendelevium 101 **Md** [258] nobelium 102 **No** [259]

Copper dispersion relation and density of states

Fermi level

Empty lattice approx.

4s overlaps more than 3d
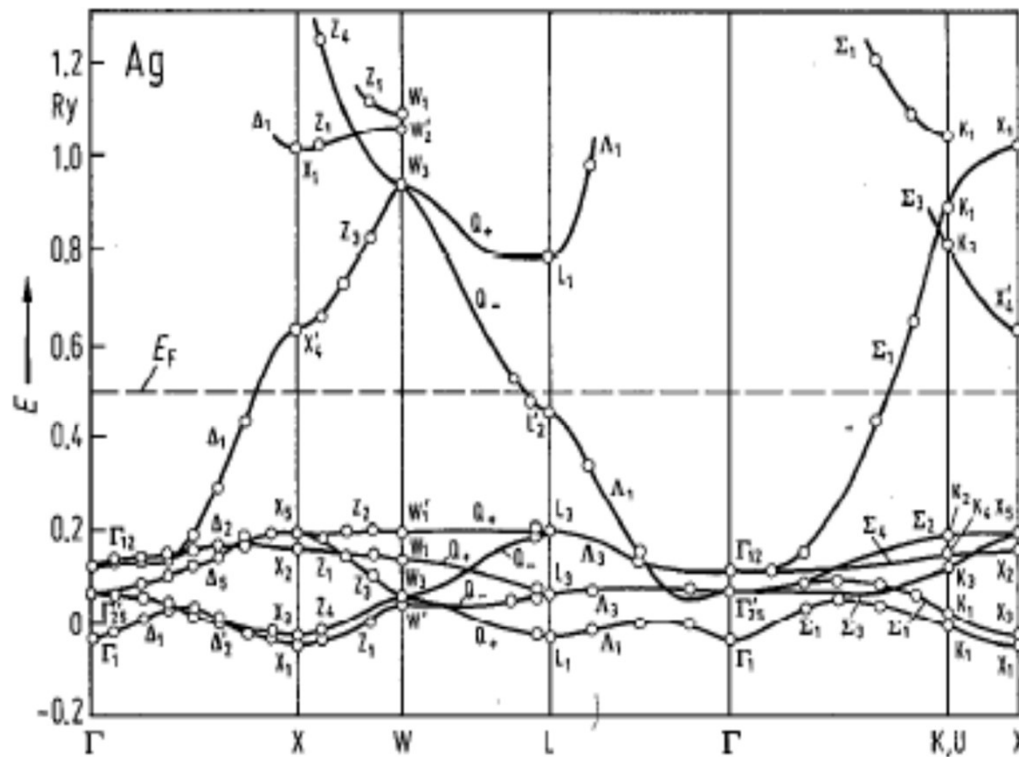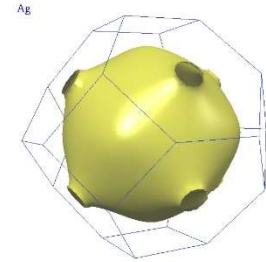
from Ibach & Lueth

Silver

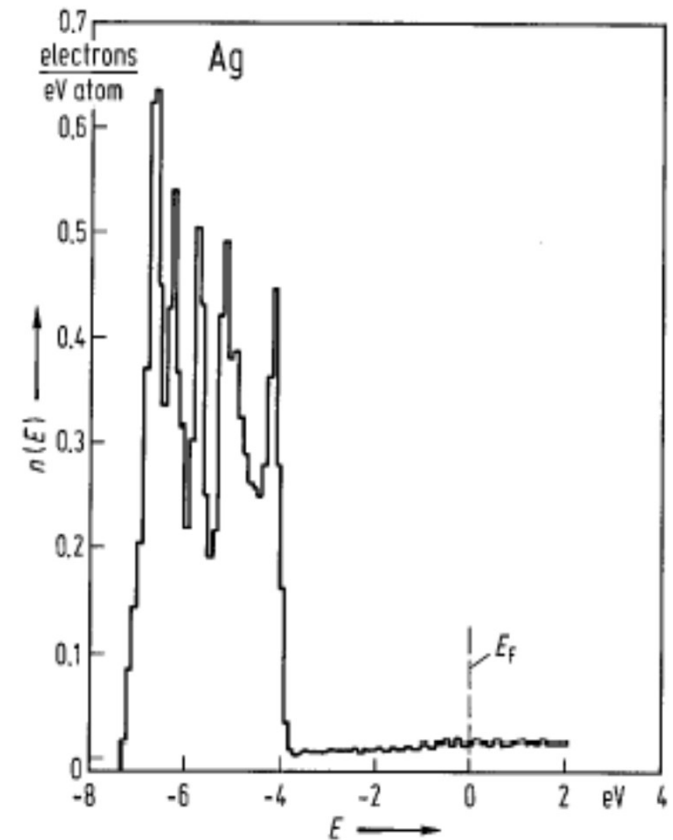Fig. 3. Ag. Energy bands calculated using the APW method [69Chr].

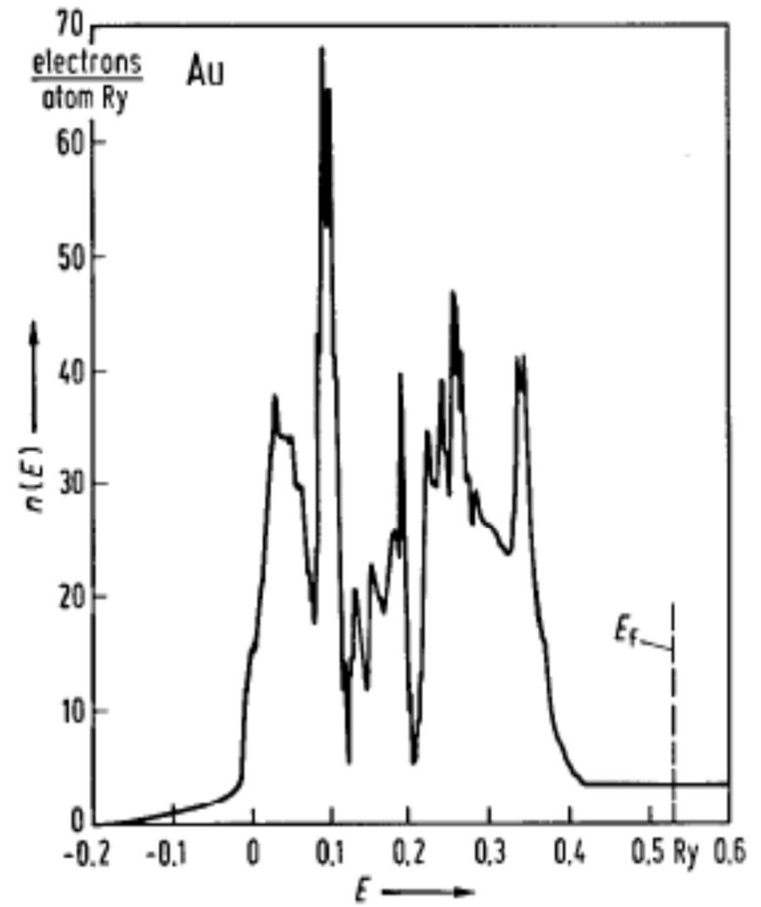Fig. 15. Ag. Density of states calculated from the energy bands in Fig. 10. Ag [75Fon].
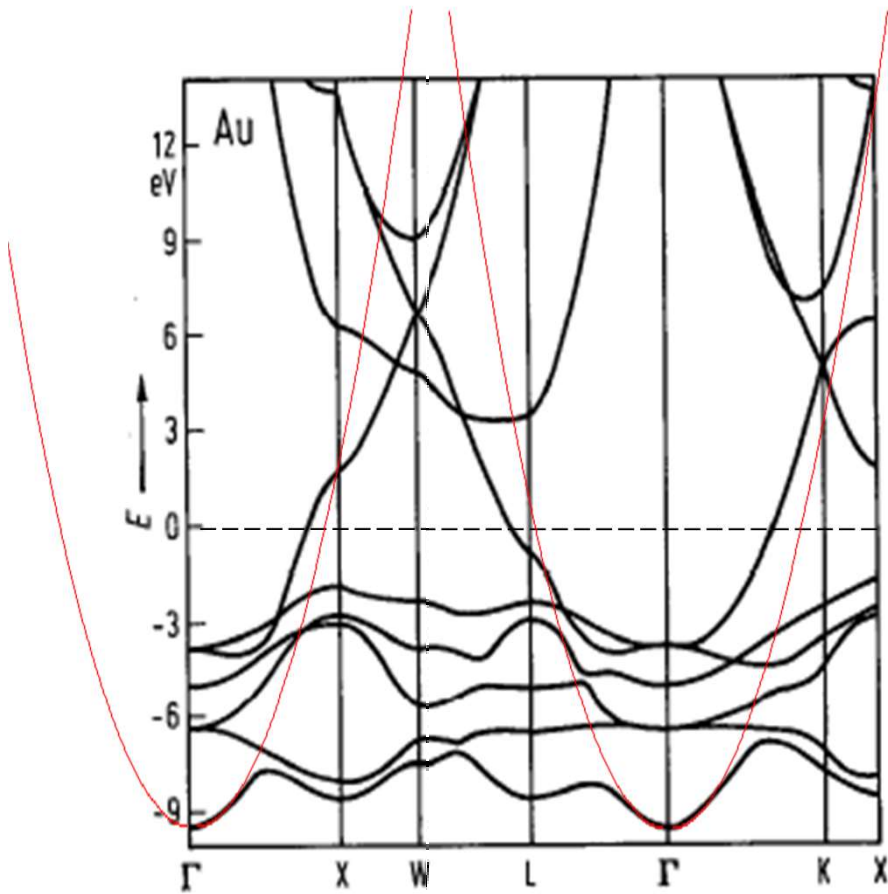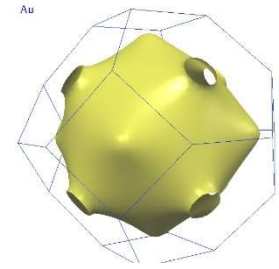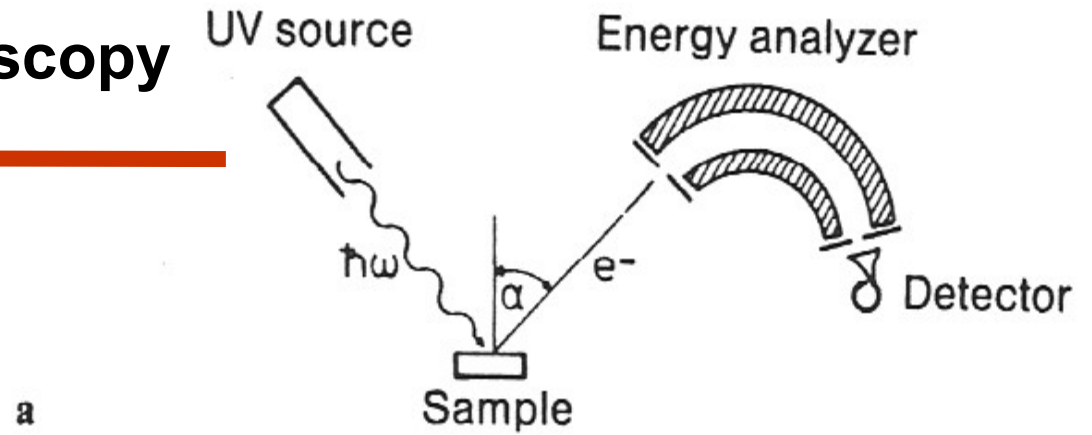
Gold

Fig. 9. Au. Density of states calculated from the energy bands in Fig. 4b. Au [71Chr2].
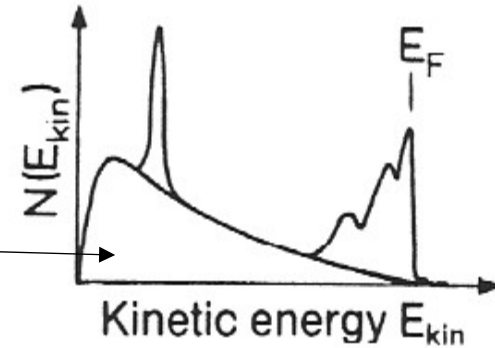
Photoemission spectroscopy

UPS - Ultraviolet
photoemission spectroscopy

Measure the density of states
with photoemission
spectroscopy
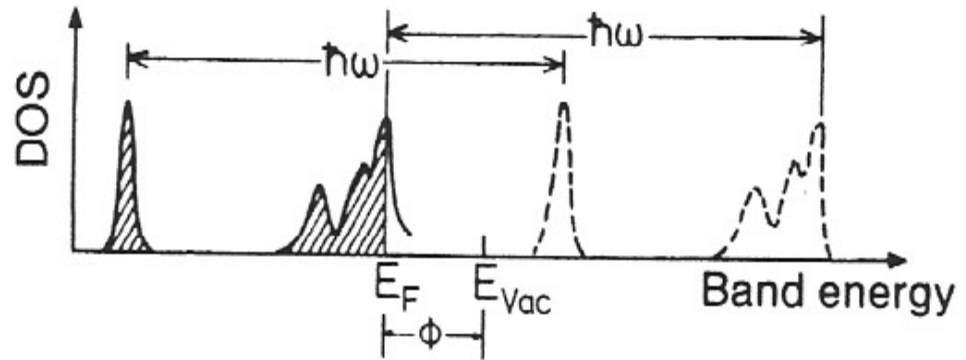
Secondary
electrons

From: Ibach & Lueth

Angle resolved photoemission spectroscopy (ARPES)
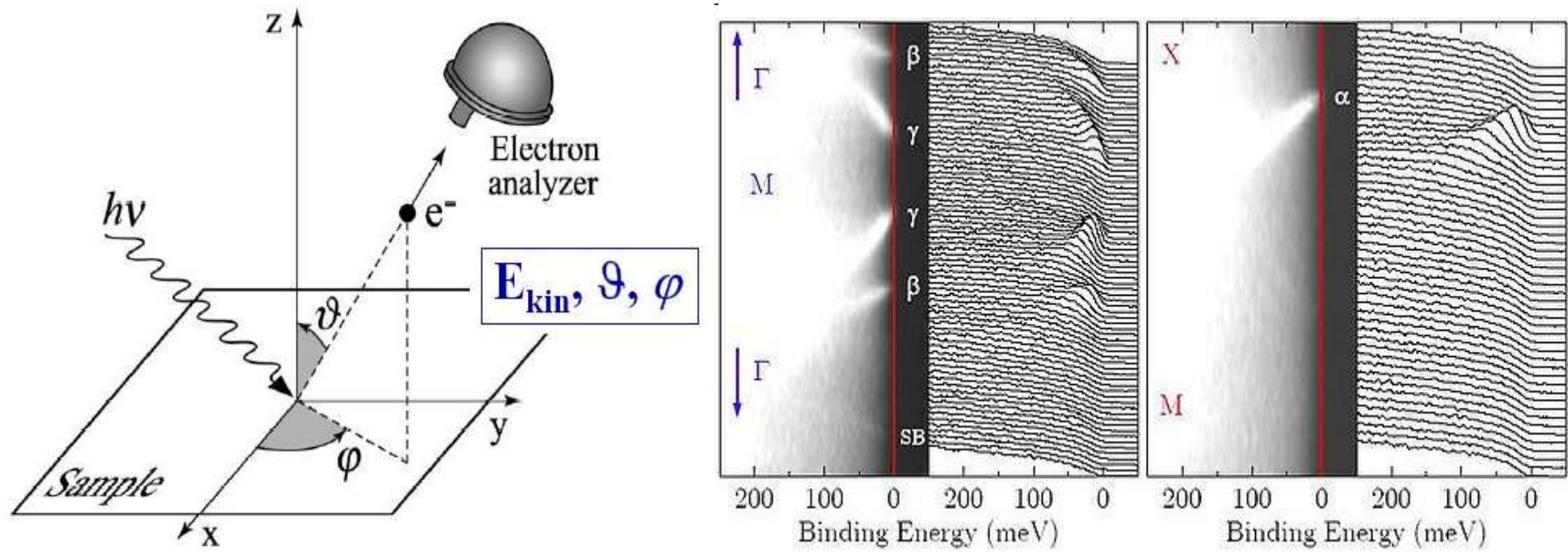
Measure the dispersion relation with angle resolved photoemission
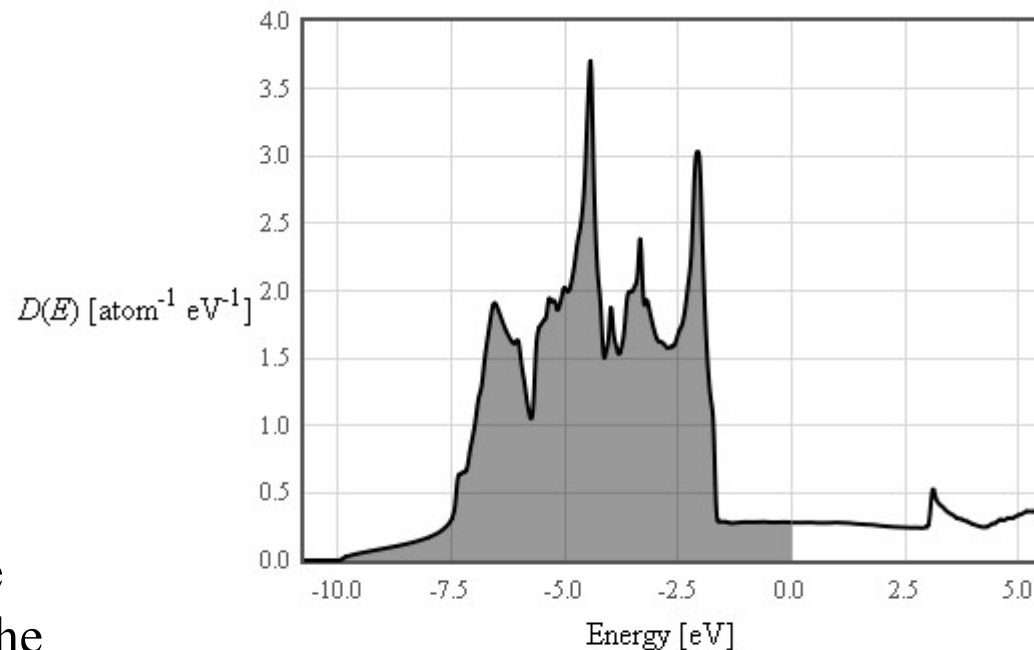
Optical absorption
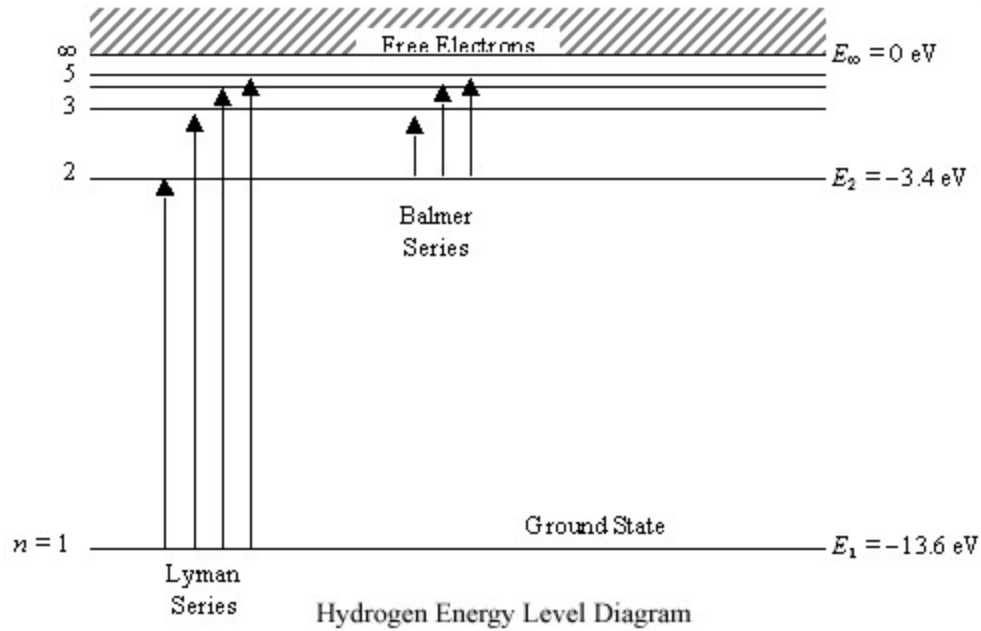
Hydrogen atom
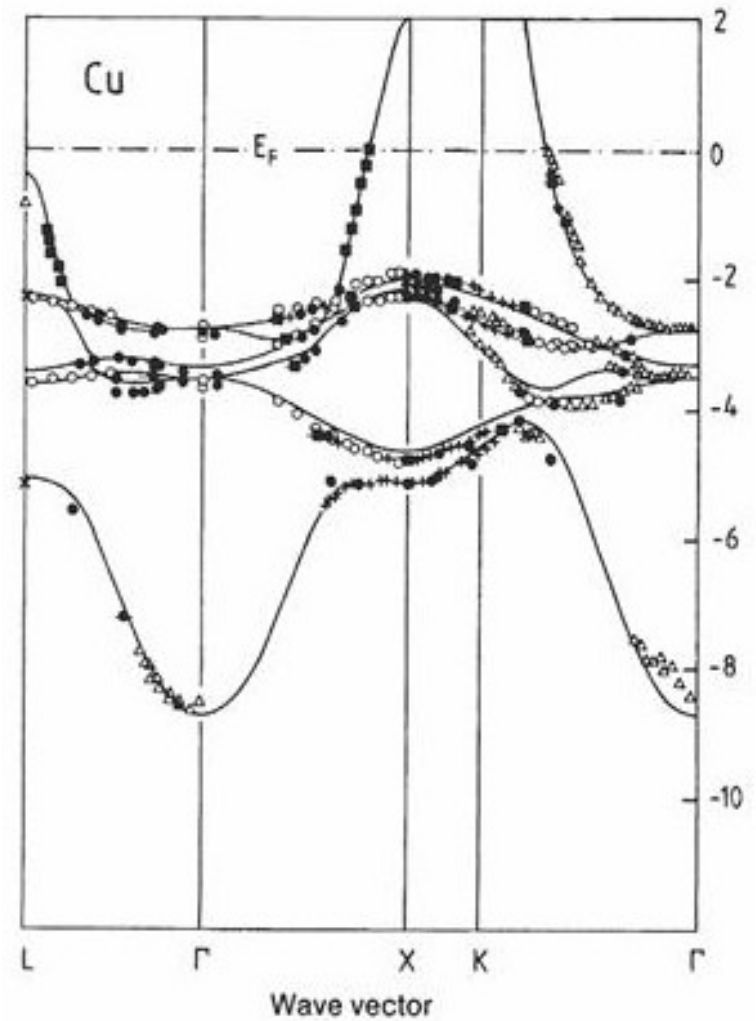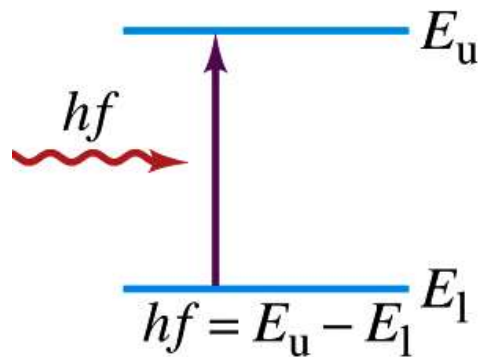
Copper fcc crystal

Thermodynamic properties of metals

From the band structure measurements, we obtain the electron density of states.

Electron density of states for fcc gold

Thermodynamic properties can be calculated from the tabulated data for the density of states

E [eV]	$D(E)$ [atom^{-1} eV^{-1}]
-10.74913	0
-10.73552	0
-10.72192	0

Thermodynamic properties of metals

Chemical potential μ	
Implicitly defined by $$n = \int_{-\infty}^{\infty} D(E)f(E)\,dE$$	$$\mu \approx E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{D'(E_F)}{D(E_F)} \ [\mathrm{J}]$$
Internal energy $$u = \int_{-\infty}^{\infty} E D(E)f(E)\,dE$$	$$u \approx \int_{-\infty}^{E_F} E D(E)\,dE + \frac{\pi^2 D(E_F)}{6}(k_B T)^2 \ [\mathrm{J\,m^{-3}}]$$
Specific heat $$c_v = \left(\frac{du}{dT}\right)_{V=\mathrm{const}}$$	$$c_v \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T \ [\mathrm{J\,m^{-3}\,K^{-1}}]$$

Entropy	
$$s = \int \frac{c_v}{T}\,dT$$	$$s \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T \ [\mathrm{J\,m^{-3}\,K^{-1}}]$$
Helmholtz free energy $$f = u - Ts$$	$$f \approx \int_{-\infty}^{E_F} E D(E)\,dE - \frac{\pi^2 D(E_F)}{6}(k_B T)^2 \ [\mathrm{J\,m^{-3}}]$$

SGTE data for pure elements

http://www.sciencedirect.com/science/article/pii/036459169190030N