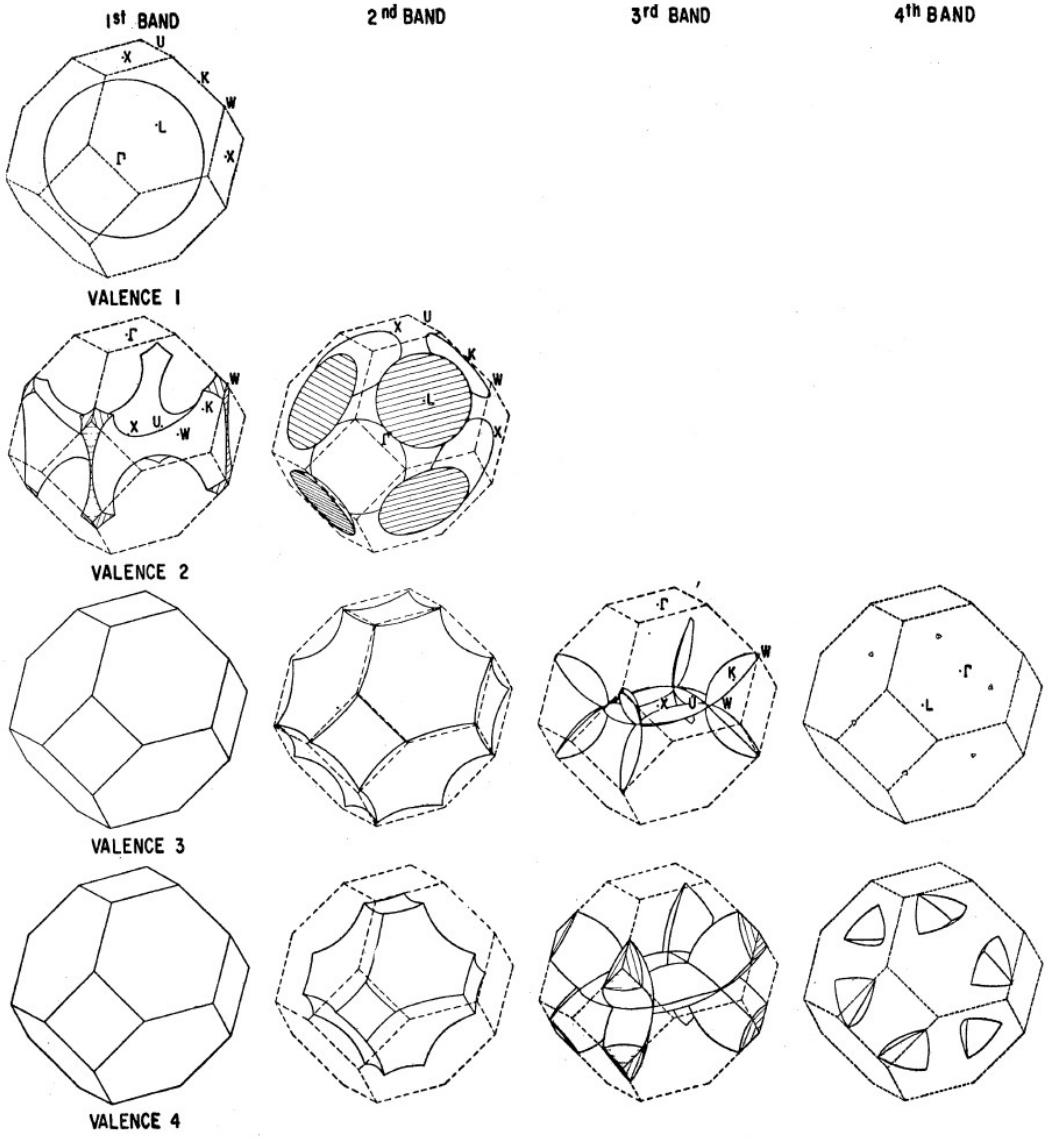
Review: Metals

The simplest model is the free electron model:

Thermodynamic properties depend on electron states near the Fermi surface.
The Fermi surface is spherical.
In 3-D the density of states grows like $\sqrt{E}$
The dispersion relation is given by the empty lattice approximation.

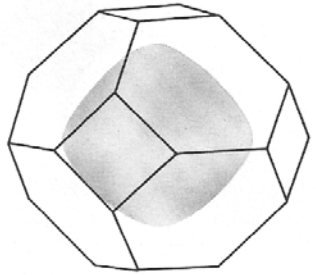
When the periodicity of the lattice is included, the electron waves diffract at the Brillouin zone boundaries. The Fermi surface must meet the Brillouin zone boundaries at 90° and the Fermi surface distorts from the spherical shape.

Fermi surface for fcc in the empty lattice approximation

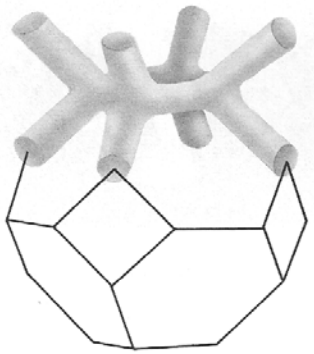


Valence 4

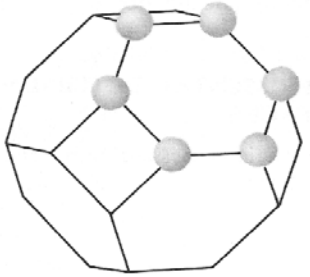
2nd zone holes



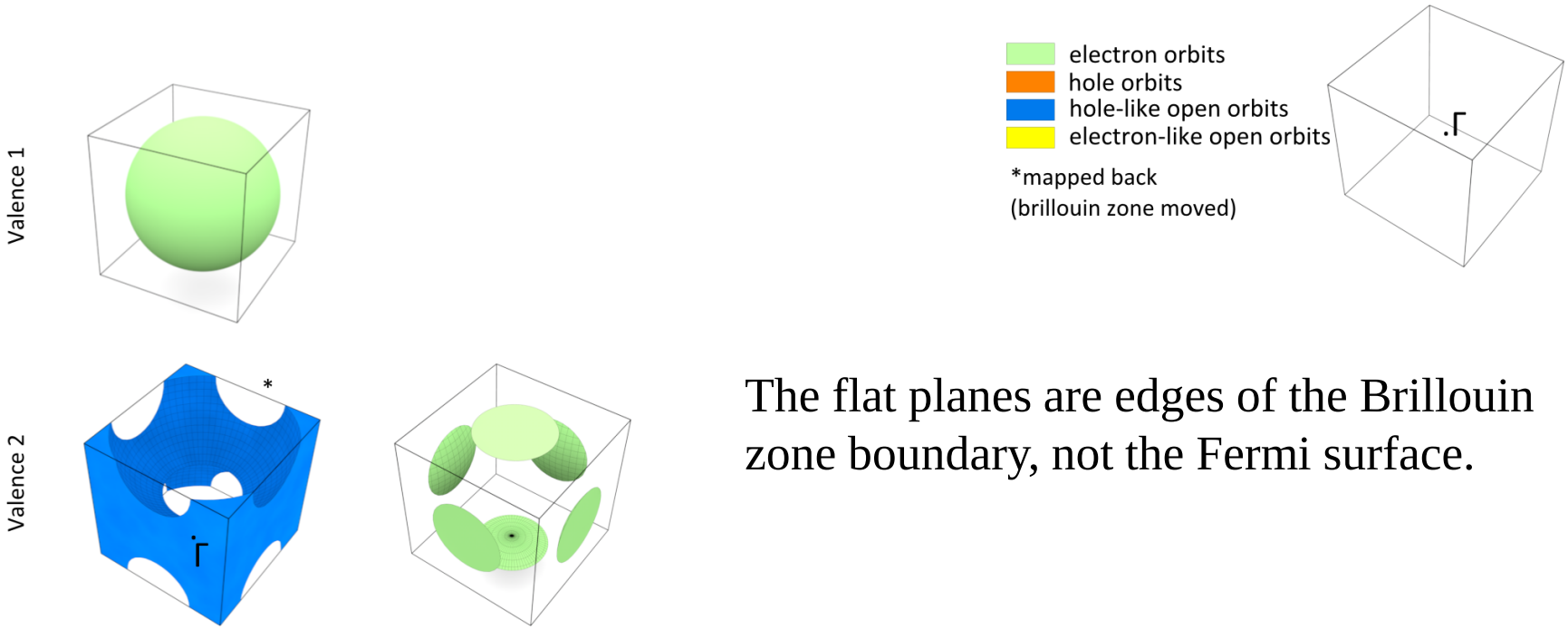
3rd zone monster



4th zone electrons

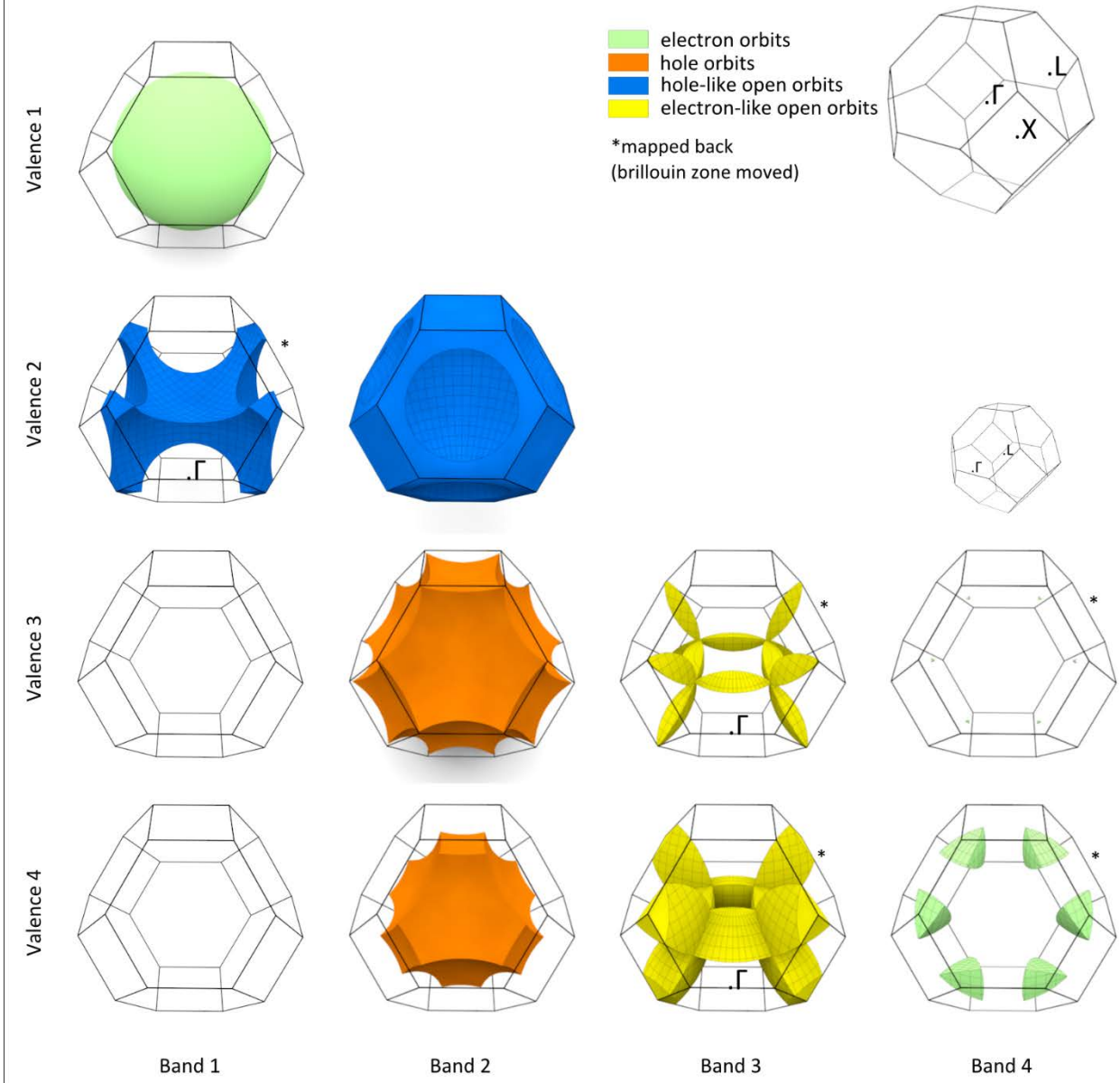


SC - Fermi surfaces in the empty lattice approximation



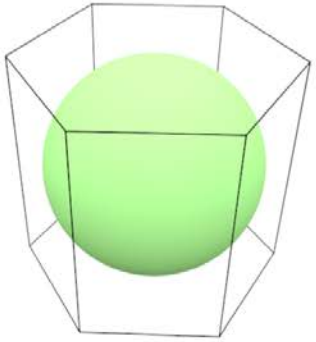
The flat planes are edges of the Brillouin zone boundary, not the Fermi surface.

FCC - Fermi surfaces in the empty lattice approximation

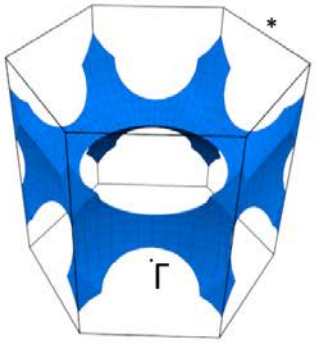


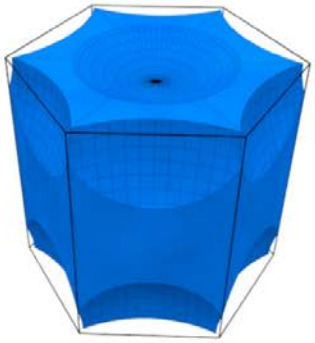
Hexagonal - Fermi surfaces in the empty lattice approximation

Valence 1



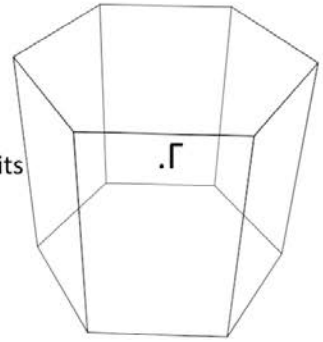
Valence 2





electron orbits
hole orbits
hole-like open orbits
electron-like open orbits

*mapped back
(brillouin zone moved)



Band structure calculations

Start with the full Hamiltonian.

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A}\nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 r_{AB}}$$

Everything you can know is contained in this Hamiltonian.

Usually this is too difficult to solve.

Electrons in a crystal

Fix the positions of the nuclei (Born Oppenheimer approximation) and consider the many electron Hamiltonian.

$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

This is still too difficult. Neglect the electron-electron interactions.

Separation of variables

$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \cancel{\sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}}$$

The electronic Hamiltonian separates into the molecular orbital Hamiltonians.

$$H_{\text{elec}}(r_1,r_2,...r_n) = H_{\text{MO}}(r_1) + H_{\text{MO}}(r_2) + ... H_{\text{MO}}(r_n)$$

$$\Psi_{\text{elec}}(r_1,r_2,...r_n) = |\psi_{\text{MO}}(r_1)\psi_{\text{MO}}(r_2) \ ... \ \psi_{\text{MO}}(r_n)>$$

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla - \sum_A \frac{Z_A e^2}{4\pi\varepsilon_0 \left|\vec{r} - \vec{r}_A\right|}$$

Solving the molecular orbital Hamiltonian

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla - \sum_A \frac{Z_A e^2}{4\pi\varepsilon_0 \left|\vec{r} - \vec{r}_A\right|}$$

Band structure calculations:

Plane wave method
Tight binding (LCAO+)

Plane wave method

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U_{MO}(\vec{r})\psi = E\psi$$

Write U and ψ as Fourier series.

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

For a periodic lattice of Coulomb potentials:

$$U_{MO}(\vec{r}) = \frac{-Ze^2}{4\pi\varepsilon_0}\sum_j \frac{1}{\left|\vec{r}-\vec{r}_j\right|} = \frac{-Ze^2}{V\varepsilon_0}\sum_{\vec{G}} \frac{e^{i\vec{G}\cdot\vec{r}}}{G^2}$$

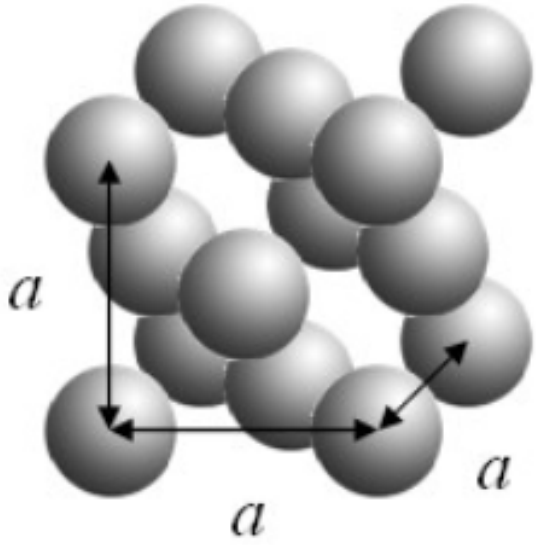
volume of a unit cell

Expressing a 3-D periodic function as a Fourier Series

Example 2: spheres on an fcc lattice

Spheres of radius R are arranged on a fcc lattice.

$$f(\vec{r}) = \frac{4\pi C}{V} \sum_{\vec{G}} \frac{\sin\left(|G|R\right) - |G|R\cos\left(|G|R\right)}{|G|^3} \exp\left(i\vec{G}\cdot\vec{r}\right).$$



http://lampx.tugraz.at/~hadley/ss1/crystaldiffraction/fourier.php

Plane wave method

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

$$U_{MO}(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \qquad \psi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$

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

Must hold for each Fourier coefficient.

$$\vec{k}' + \vec{G} = \vec{k} \qquad \Rightarrow \qquad \vec{k}' = \vec{k} - \vec{G}$$

$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} = 0$$

Central equations (one for every *k* in the first Brillioun zone)

Plane wave method

The central equations can be written as a matrix equation.

$$M\vec{C} = E\vec{C}$$

Diagonal elements: $$M_{ii} = \frac{\hbar^2}{2m}\left(\vec{k} - \vec{G}_i\right)^2$$

Off-diagonal elements: $$M_{ij} = -\frac{Ze^2}{V\varepsilon_0\left(\vec{G}_i - \vec{G}_j\right)^2}$$

For $Z = 0$, this results in the empty lattice approximation.

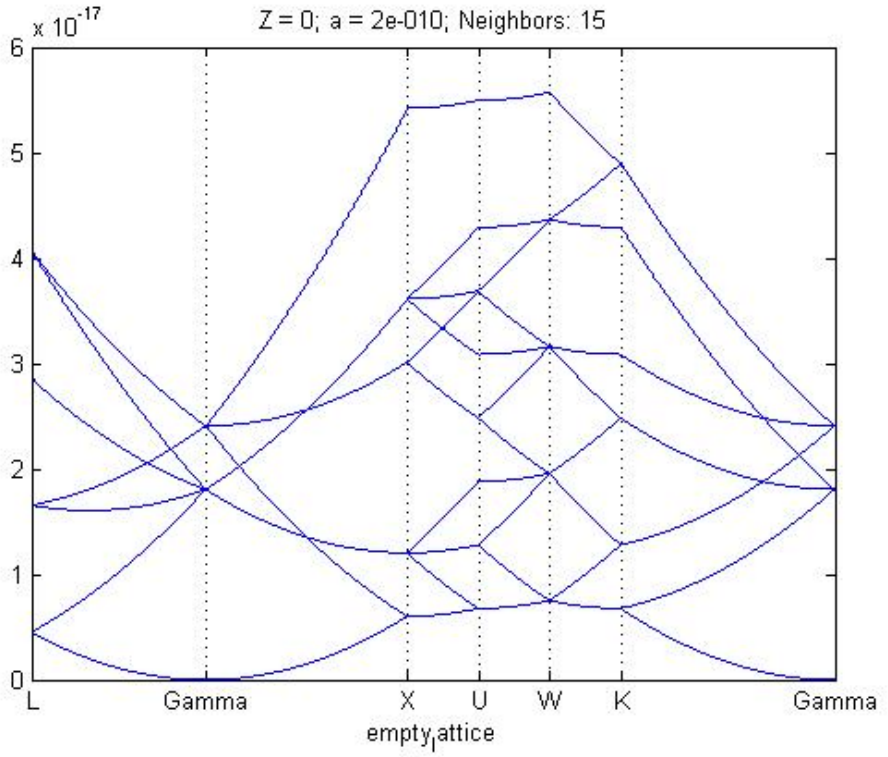
Plane wave method

Editor - I:\planewave\fcc_plane_wave_script.m

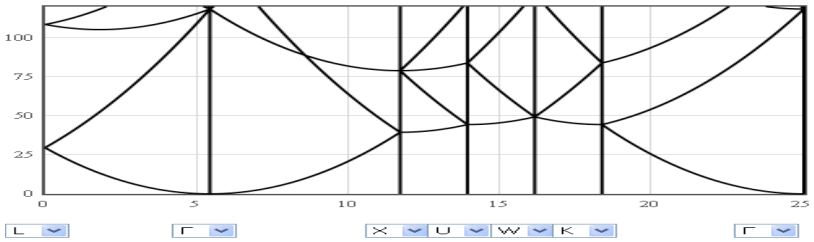
```
% clc
clear all
%close all % comment with % if you would like to compare some results
tic

% constants in si units

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% change to a any value
% be sure that 'other' is selected as metal
Z = 6; % atomic number
a = 2E-10; % lattice constant a

% choose 'other' to use the assigned values for Z and a from above
% choose 'copper' 'silver' 'gold' 'aluminium' 'calcium' or 'lead' to use
% preset values
metal = 'aluminum';

dist_neighbors = 3; % only nearest neighbors = 1 ; nearest and next nearest = 2 etc.
% maximum is 1136. However at high numbers some neighbors are missed


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%


switch lower(metal)
    case 'copper'
        Z = 29;
        a = 3.61e-10;
    case 'silver'
        Z = 47;
```

Plane wave method

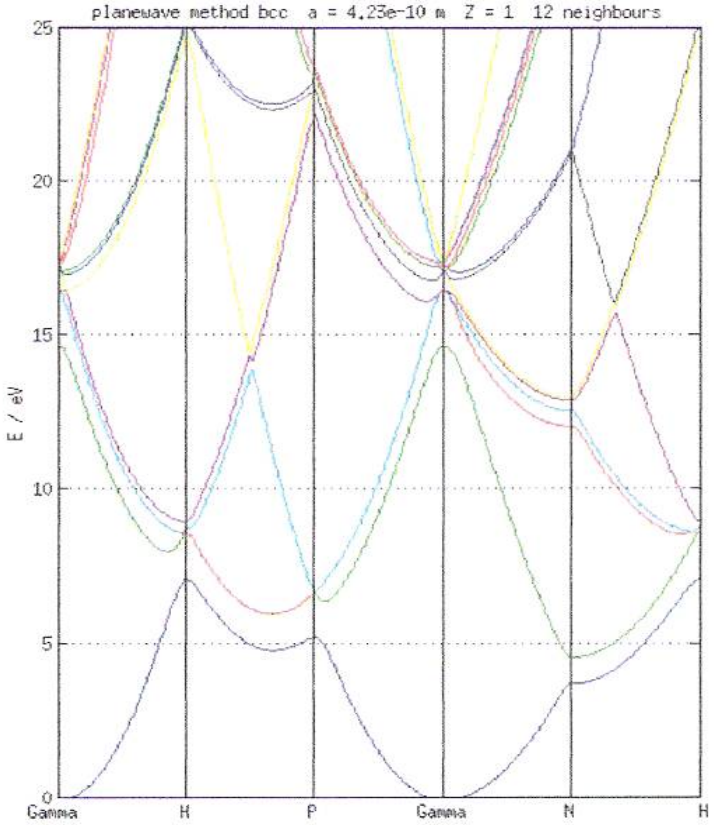
fcc Z= 0



empty lattice



Plane wave method bcc



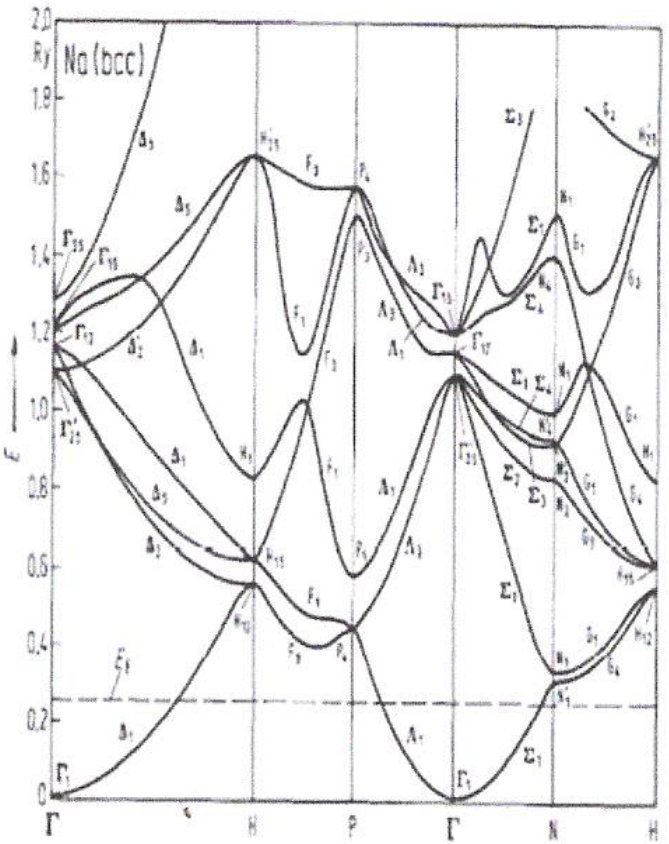


Abbildung 4: Planewave-Methode angewandt an Natrium vs. Literaturberechnung [1]

Muffin tin potentials, pseudopotentials

$$U(\vec{r}) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$ inside a radius R and is constant outside

$$U(\vec{r}) = \frac{Ze^2}{V\varepsilon_0}\sum_{\vec{G}}\left(\frac{\cos(|G|R)-1}{|G|^2}+\frac{\sin(|G|R)-|G|R\cos(|G|R)}{|G|^3}\right)\exp(i\vec{G}\cdot\vec{r}).$$

SEARCH

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Forum

PSEUDOPOTENTIALS

- Admin PP Database
- More about pseudopotentials
- Naming convention for the pseudopotential
- Unified Pseudopotential Format

PSEUDOPOTENTIALS

Ready-to-use pseudopotentials are available from the periodic table below. Choose the options you desire from the menus (pseudopotentials from PSlibrary are recommended), then press "Filter". Elements for which at least a pseudopotential is available will appear in red. Click on the element entry and follow the link to access the pseudopotentials and a minimal description of their characteristics.

More information about pseudopotentials in general, the naming convention adopted for pseudopotential files, the Unified Pseudopotential Format , and on other pseudopotential databases, can be found via the links of the menu at the left.

Important Note: although most of these pseudopotentials were published or used with satisfactory results in published work, we cannot give any warranty whatsoever that they fit your actual needs.

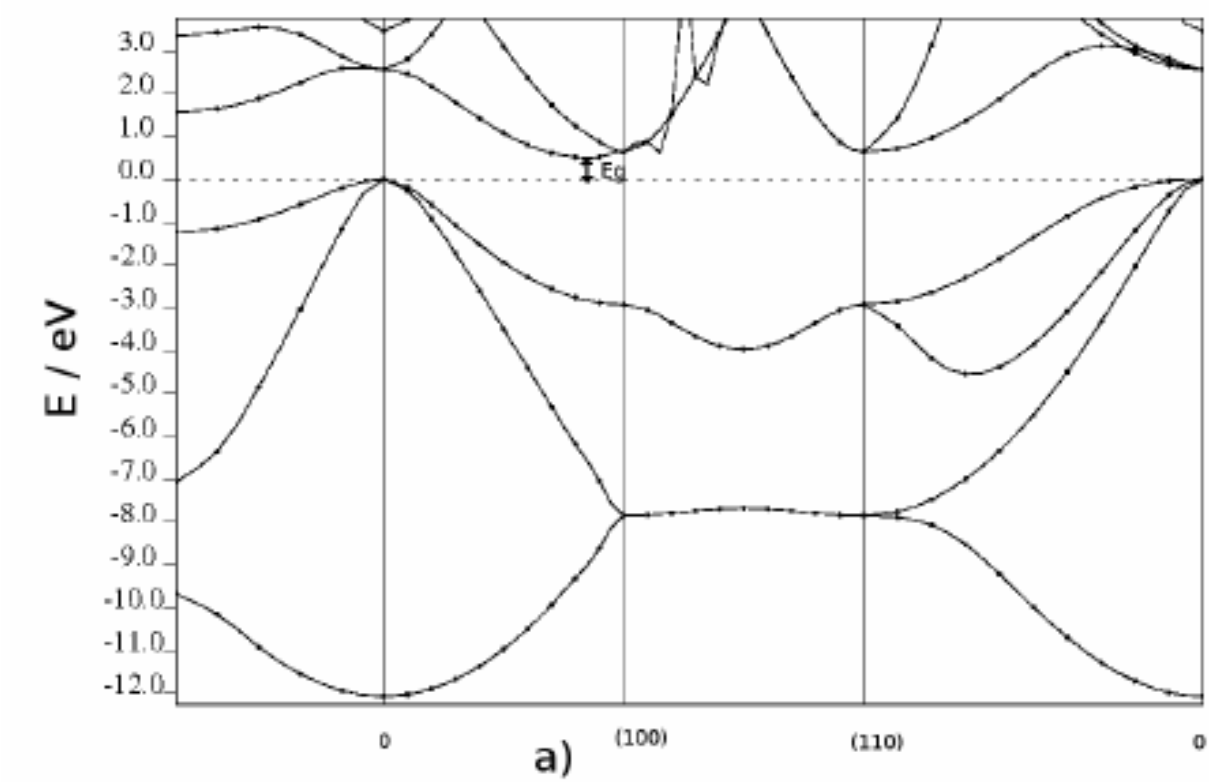
ANY FUNCTIONAL | ANY TYPE | Apply Filter

ANY PP LIBRARY | OTHER OPTIONS

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-70 *	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

Si

Bachelor thesis Benedikt Tschofenig



QUANTUMESPRESSO

http://www.quantum-espresso.org/

Tight binding

Tight binding does not include electron-electron interactions

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla + V(\vec{r}) = \frac{-\hbar^2}{2m_e}\nabla - \sum_A \frac{Z_A e^2}{4\pi\varepsilon_0 \left|\vec{r} - \vec{r}_A\right|}$$

Assume a solution of the form.

$$\psi_k = \sum_{l,m,n} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3\right)\right)\sum_a c_a\phi_a\left(\vec{r} - l\vec{a}_1 - m\vec{a}_2 - n\vec{a}_3\right)$$

atomic orbitals: choose the relevant valence orbitals

http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tightbinding/tightbinding.php

Tight binding

$$\psi_k = \sum_{l,m,n} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3\right)\right)\sum_a c_a\phi_a\left(\vec{r} - l\vec{a}_1 - m\vec{a}_2 - n\vec{a}_3\right)$$

$$H_{MO}\psi_k = E_k\psi_k$$

$$\left\langle\phi_a\middle|H_{MO}\middle|\psi_k\right\rangle = E_k\left\langle\psi_a\middle|\psi_k\right\rangle$$

$$c_a\left\langle\phi_a\middle|H_{MO}\middle|\phi_a\right\rangle + \sum_{\text{nearest neighbors } m} c_m\left\langle\phi_a\middle|H_{MO}\middle|\phi_m\right\rangle\exp(i(h\vec{k}\cdot\vec{a}_1 + j\vec{k}\cdot\vec{a}_2 + l\vec{k}\cdot\vec{a}_3)) + \text{small terms}$$

$$= E_k c_a\left\langle\phi_a\middle|\phi_a\right\rangle + \text{small terms}$$

There is one equation for each atomic orbital

Tight binding, one atomic orbital

$$c_a \langle \phi_a | H_{MO} | \phi_a \rangle + \sum_{\text{nearest neighbors } m} c_m \langle \phi_a | H_{MO} | \phi_m \rangle \exp(i(h\vec{k}\cdot\vec{a}_1 + j\vec{k}\cdot\vec{a}_2 + l\vec{k}\cdot\vec{a}_3)) + \text{small terms}$$

$$= E_k c_a \langle \phi_a | \phi_a \rangle + \text{small terms}$$

For only one atomic orbital in the sum over valence orbitals

$$E_k c_a \langle \phi_a | \phi_a \rangle = c_a \langle \phi_a | H_{MO} | \phi_a \rangle + \sum_{\text{nearest neighbors } m} c_a \langle \phi_a | H_{MO} | \phi_m \rangle \exp(i(h\vec{k}\cdot\vec{a}_1 + j\vec{k}\cdot\vec{a}_2 + l\vec{k}\cdot\vec{a}_3))$$

one atomic orbital
$E_k = \varepsilon - t\sum_m e^{i\vec{k}\cdot\vec{\rho}_m}$

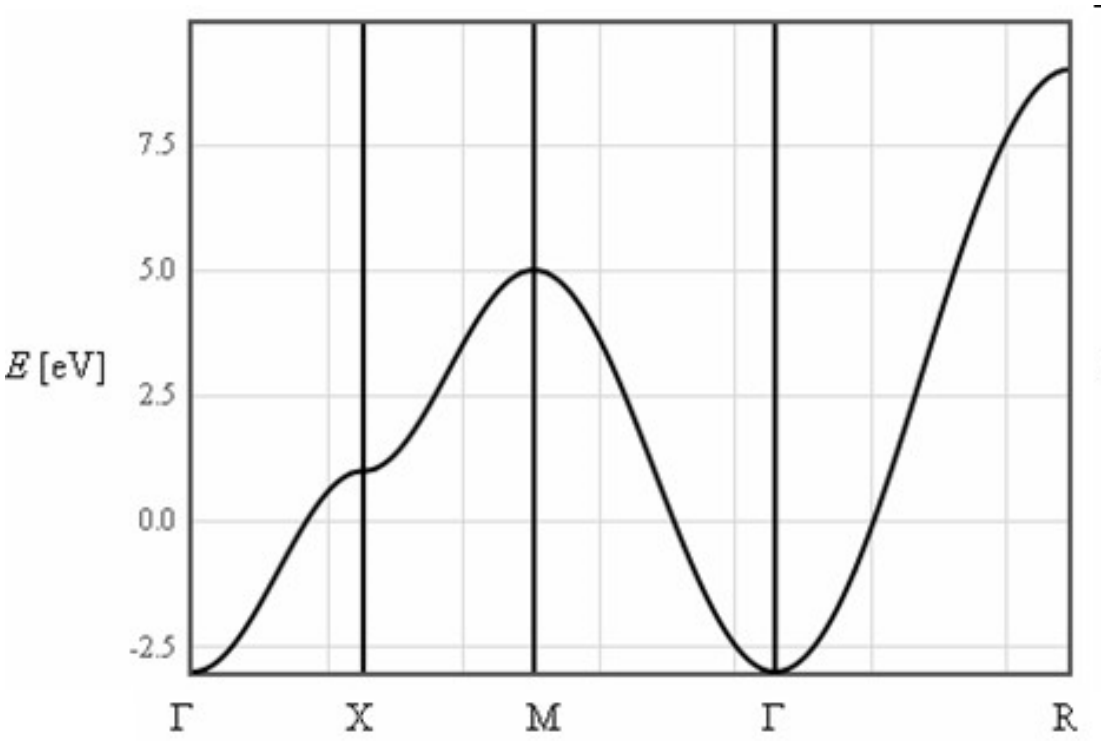
$$\varepsilon = \langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r}) \rangle \qquad t = -\langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r} - \vec{\rho}_m) \rangle$$

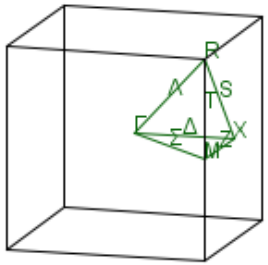
Tight binding, simple cubic

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

$$E = \varepsilon - t\left(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a} + e^{ik_z a} + e^{-ik_z a}\right)$$

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

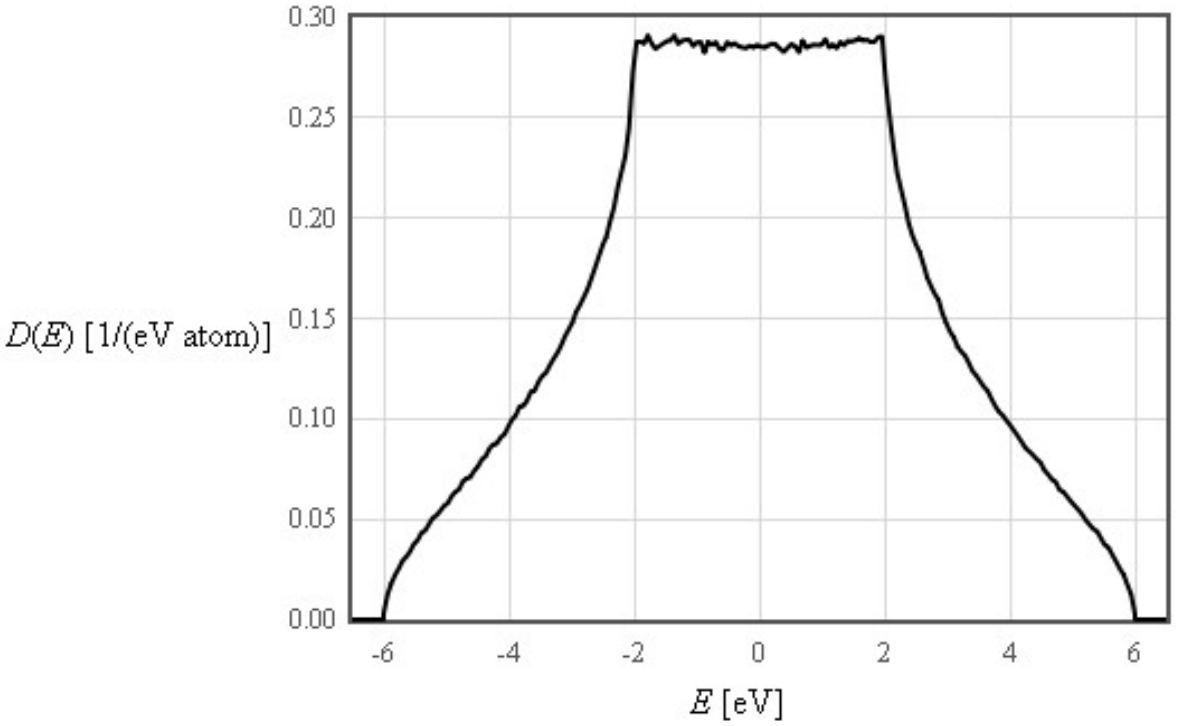




Effective mass $m^* = \dfrac{\hbar^2}{\dfrac{d^2E}{dk^2}} = \dfrac{\hbar^2}{2ta^2}$

Narrow bands → high effective mass

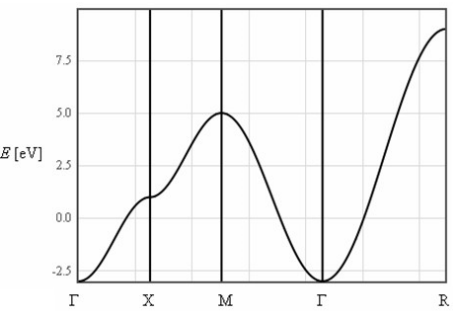
Density of states (simple cubic)



Calculate the energy for every allowed *k* in the Brillouin zone

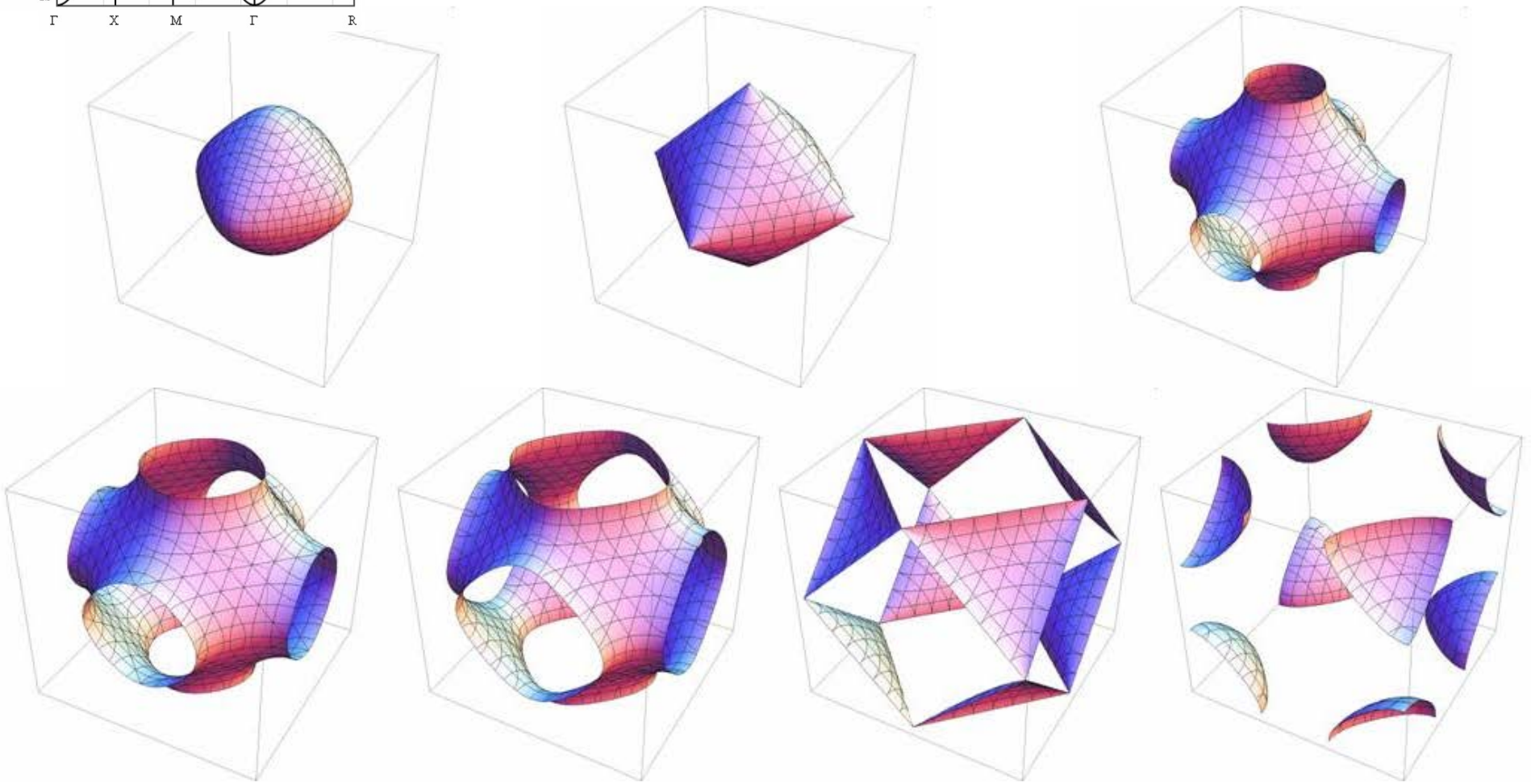
$$E = \varepsilon - 2t\left(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right)$$

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



Tight binding, simple cubic

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

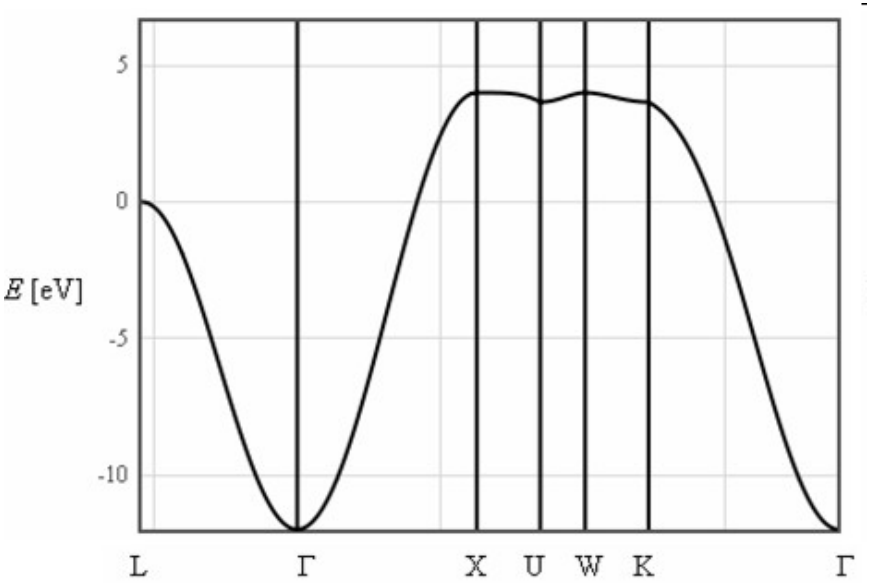


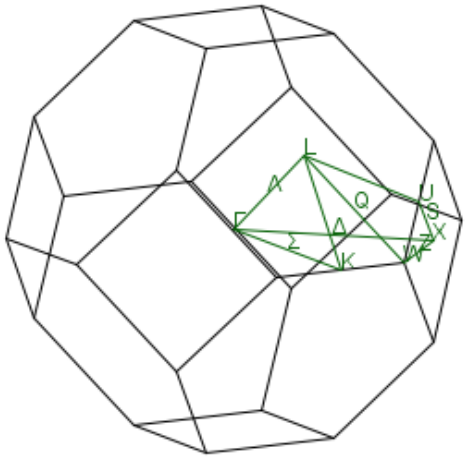
Christian Gruber, 2008

Tight binding, fcc

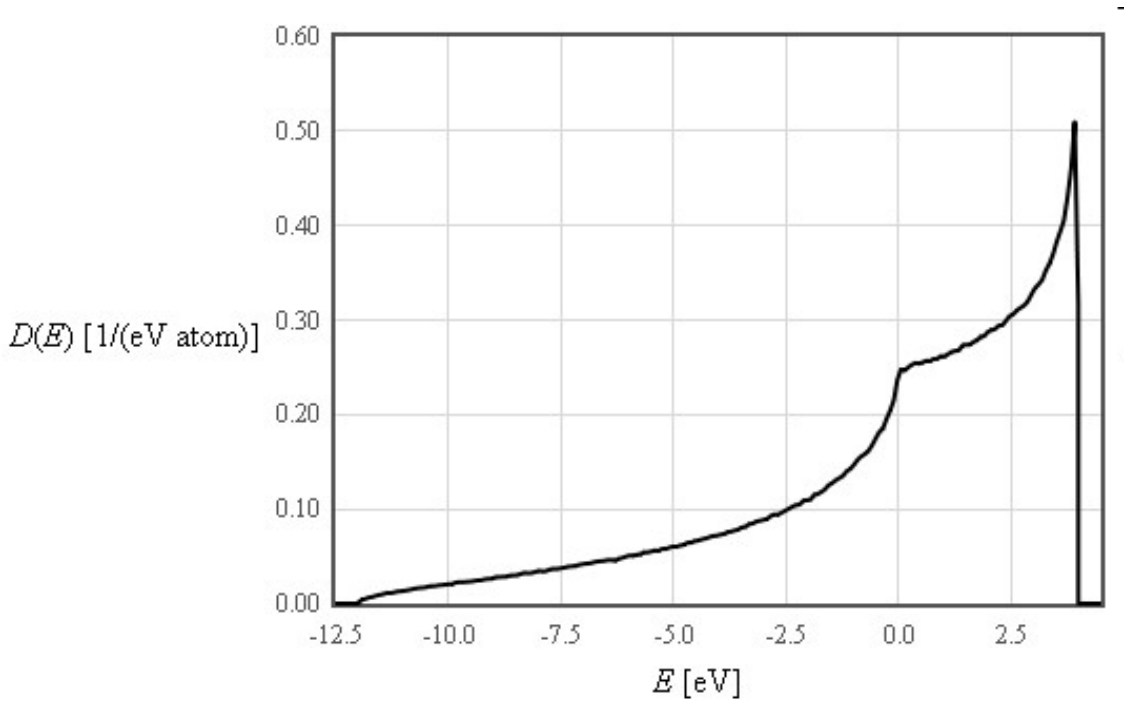
$$E = \varepsilon - t\sum_{m} e^{i\vec{k}\cdot\vec{\rho}_m}$$

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





Density of states (fcc)

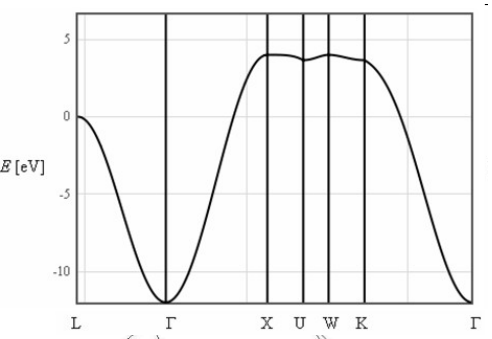


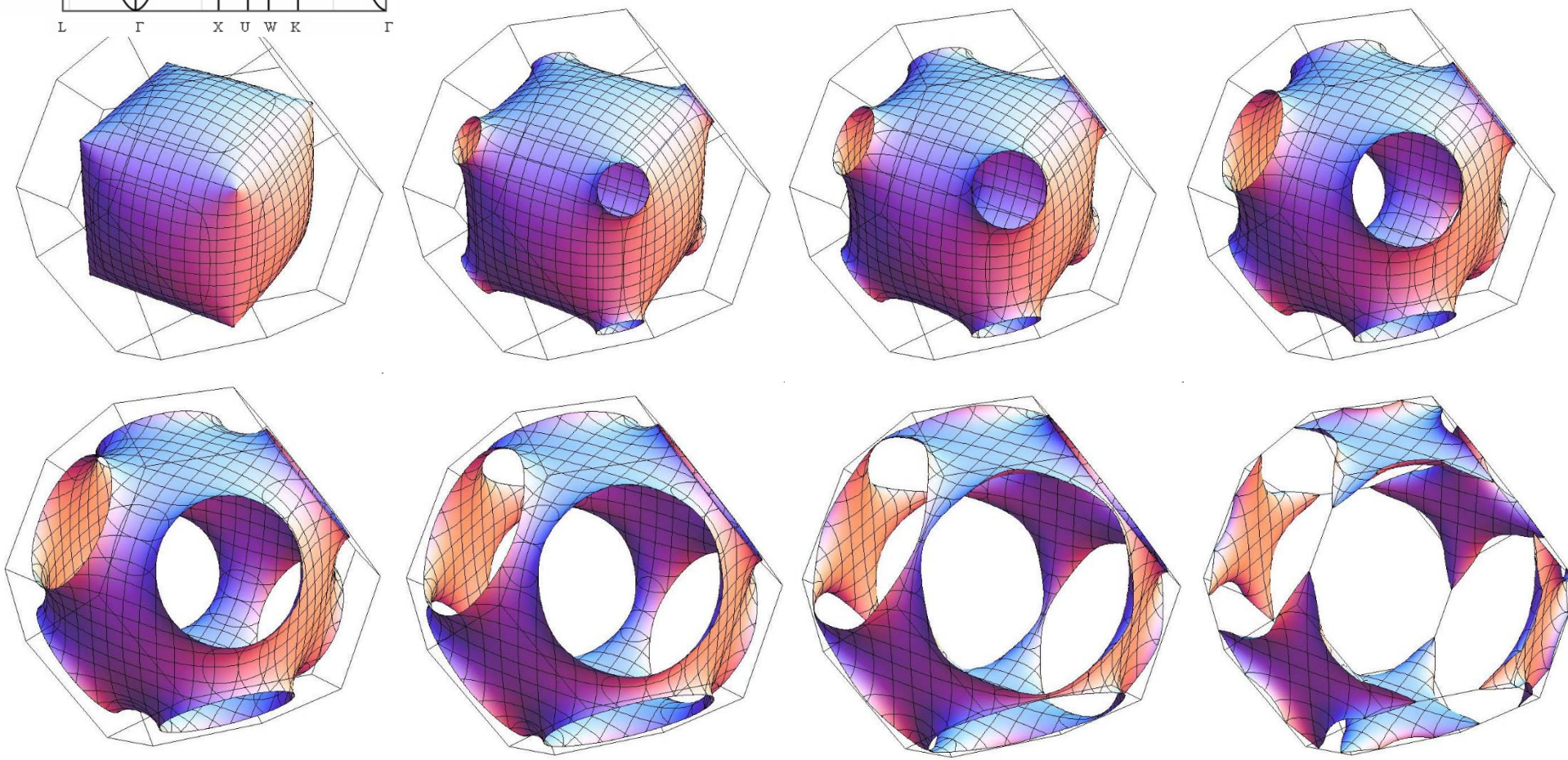
Calculate the energy for every allowed *k* in the Brillouin zone

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

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

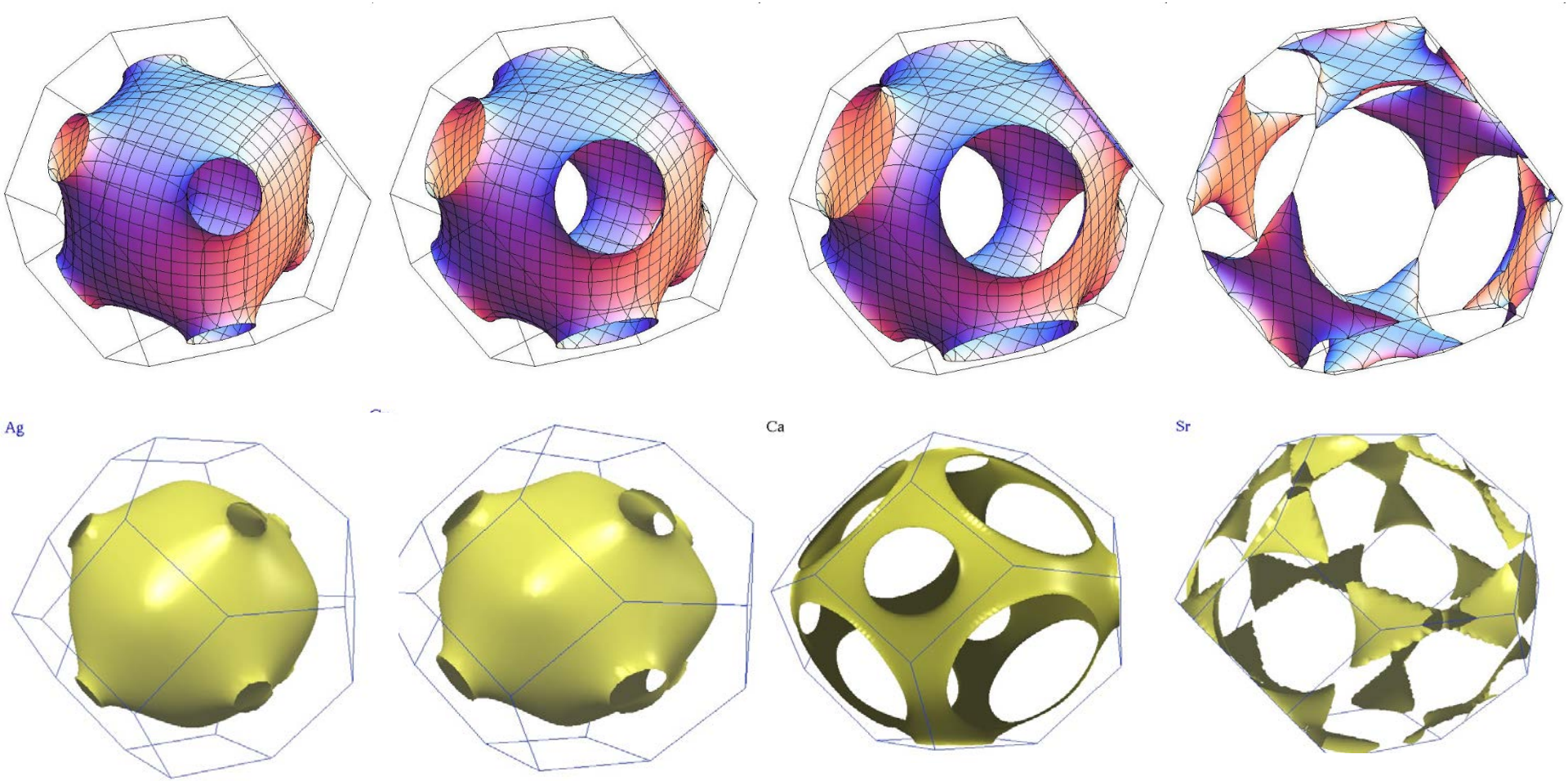
Tight binding, fcc





Christian Gruber, 2008

Tight binding, fcc



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