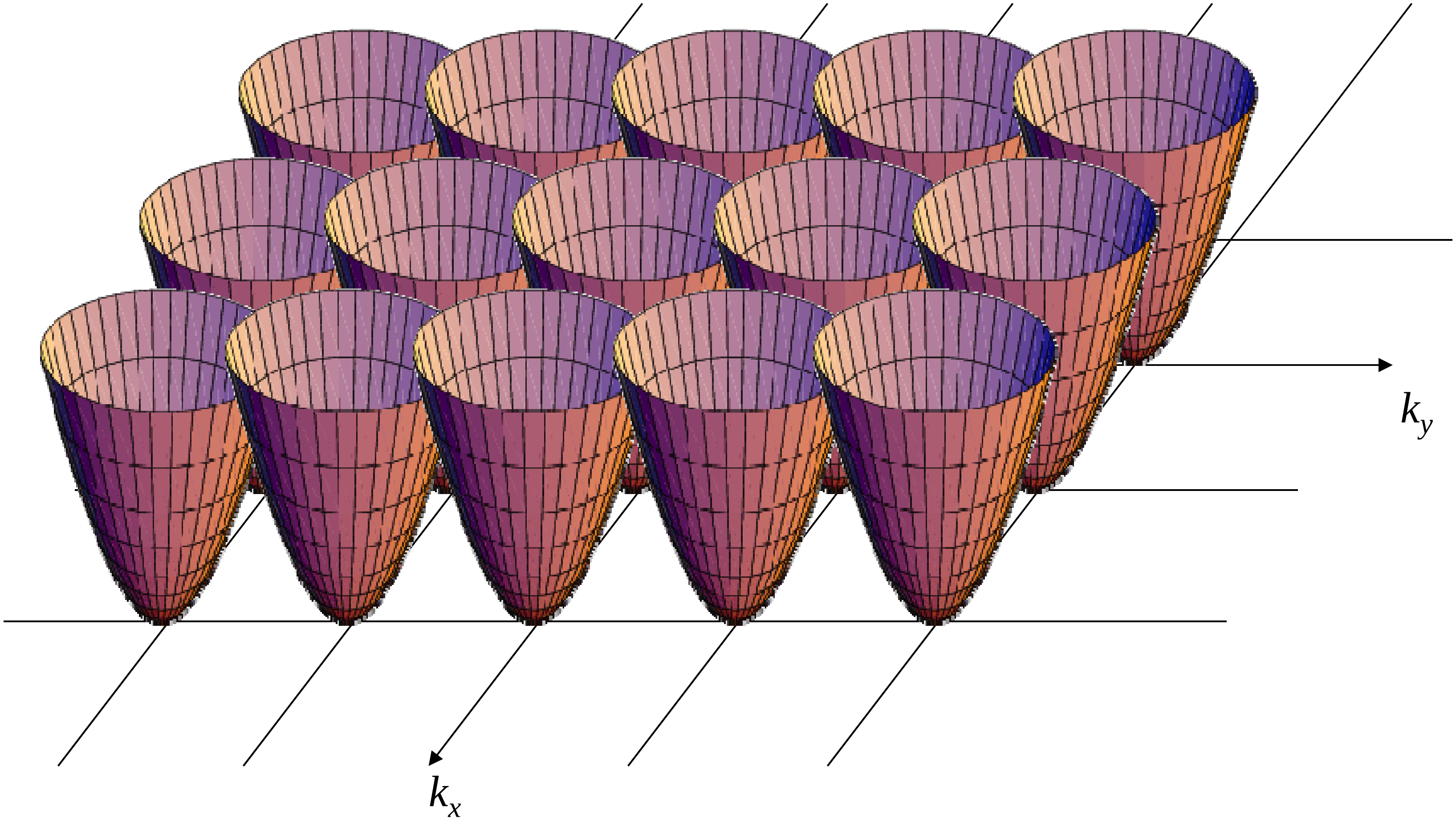
Electrons
Fermi Surfaces

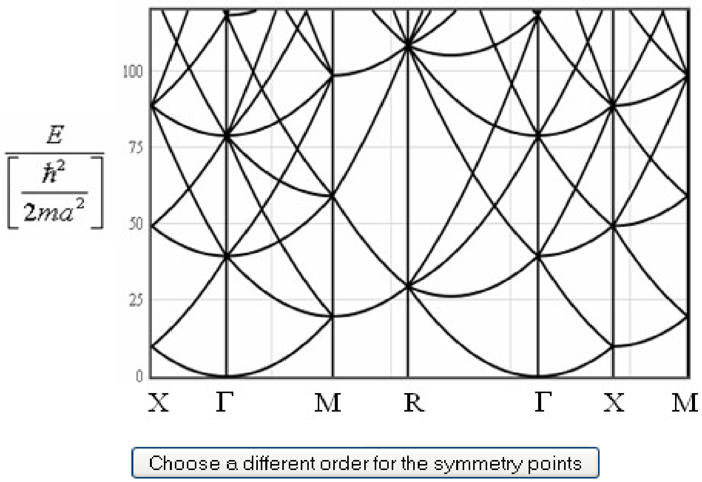
Empty lattice approximation



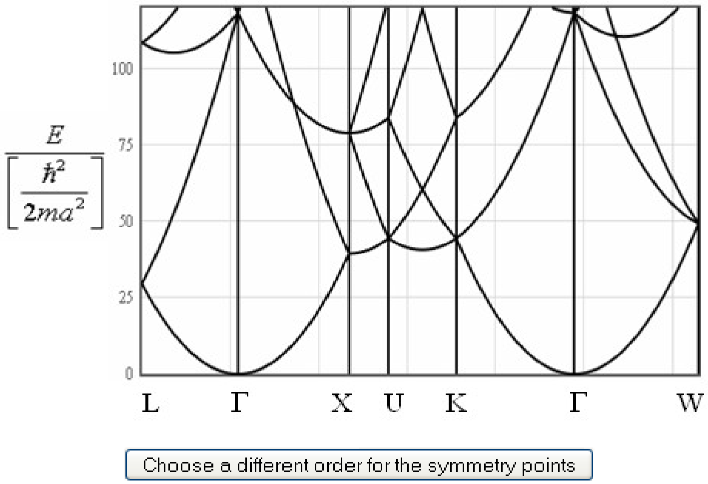
$$e^{i\vec{k}\cdot\vec{r}} = e^{i\vec{k}'\cdot\vec{r}}e^{i\vec{G}\cdot\vec{r}}$$

Empty lattice approximation

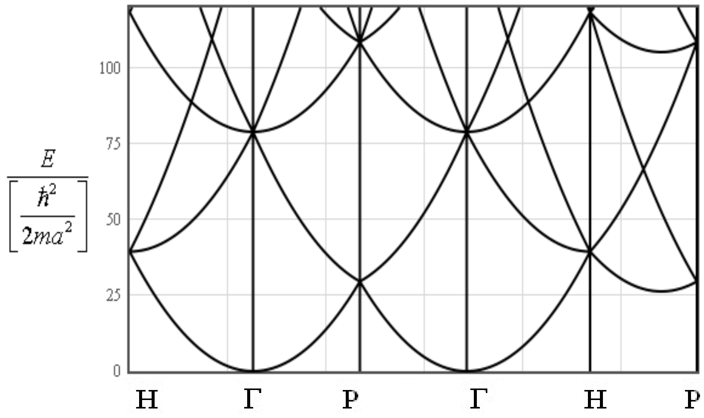
Simple cubic



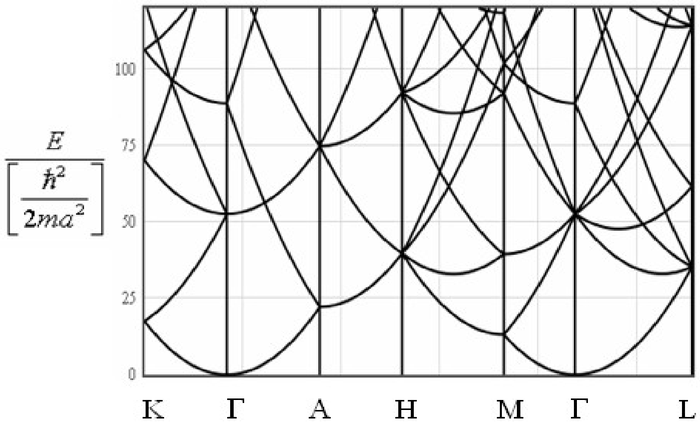
Face centered cubic



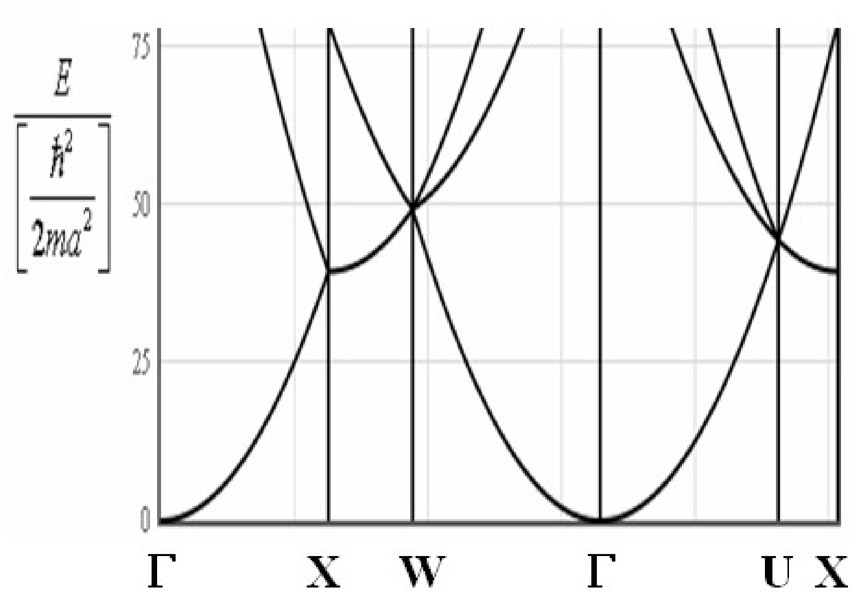
Body centered cubic

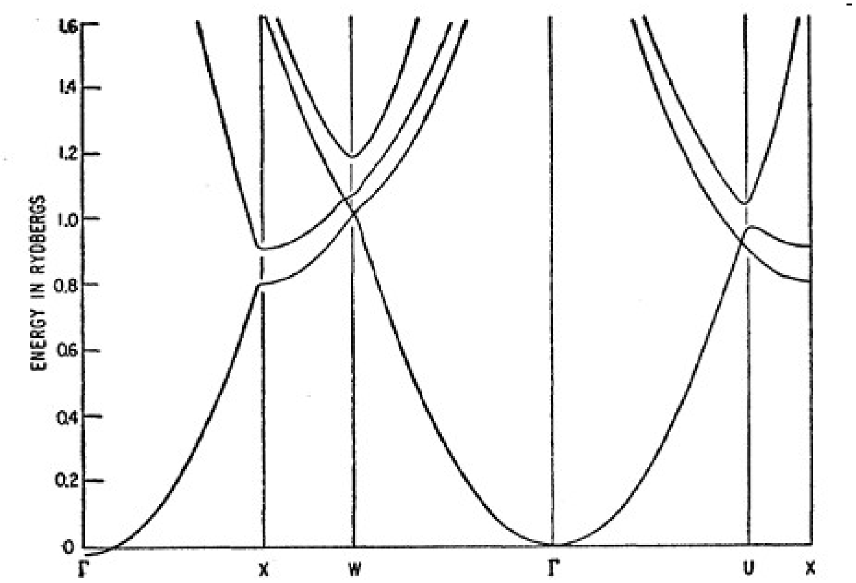


Hexagonal



Empty lattice approximation





W. Harrison, Phys. Rev. 118 p. 1182 (1960)

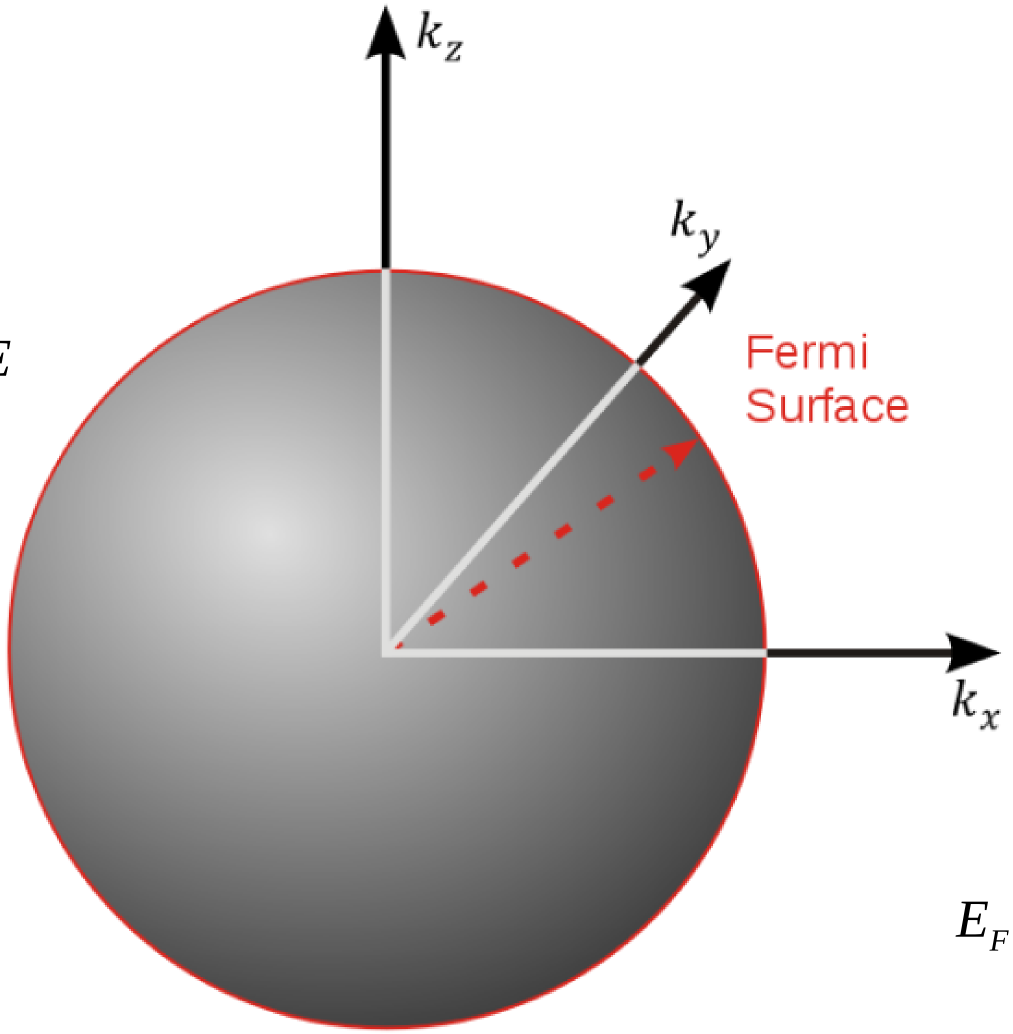
aluminum

Fermi surface for free electrons

$$n = \int_{-\infty}^{E_F} D(E)\,dE$$

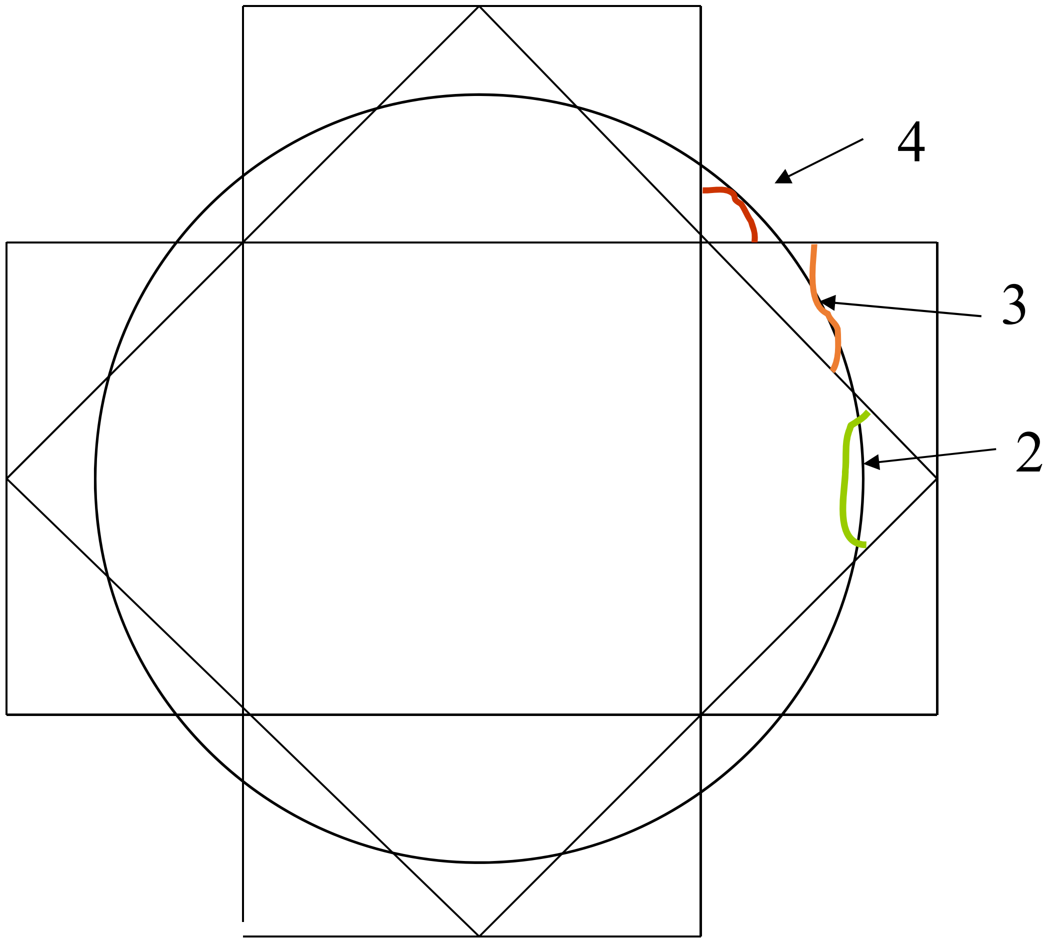
$$n = \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3}\int_{-\infty}^{E_F}\sqrt{E}\,dE$$

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{\frac{2}{3}}$$



$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

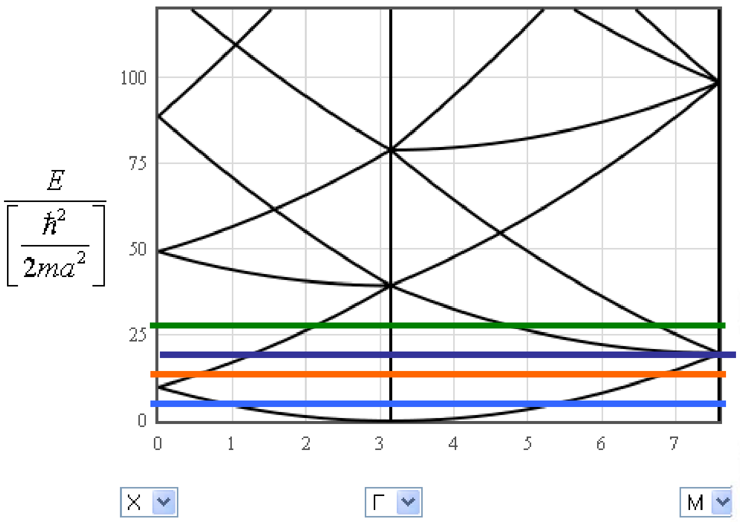
Constructing Fermi surface

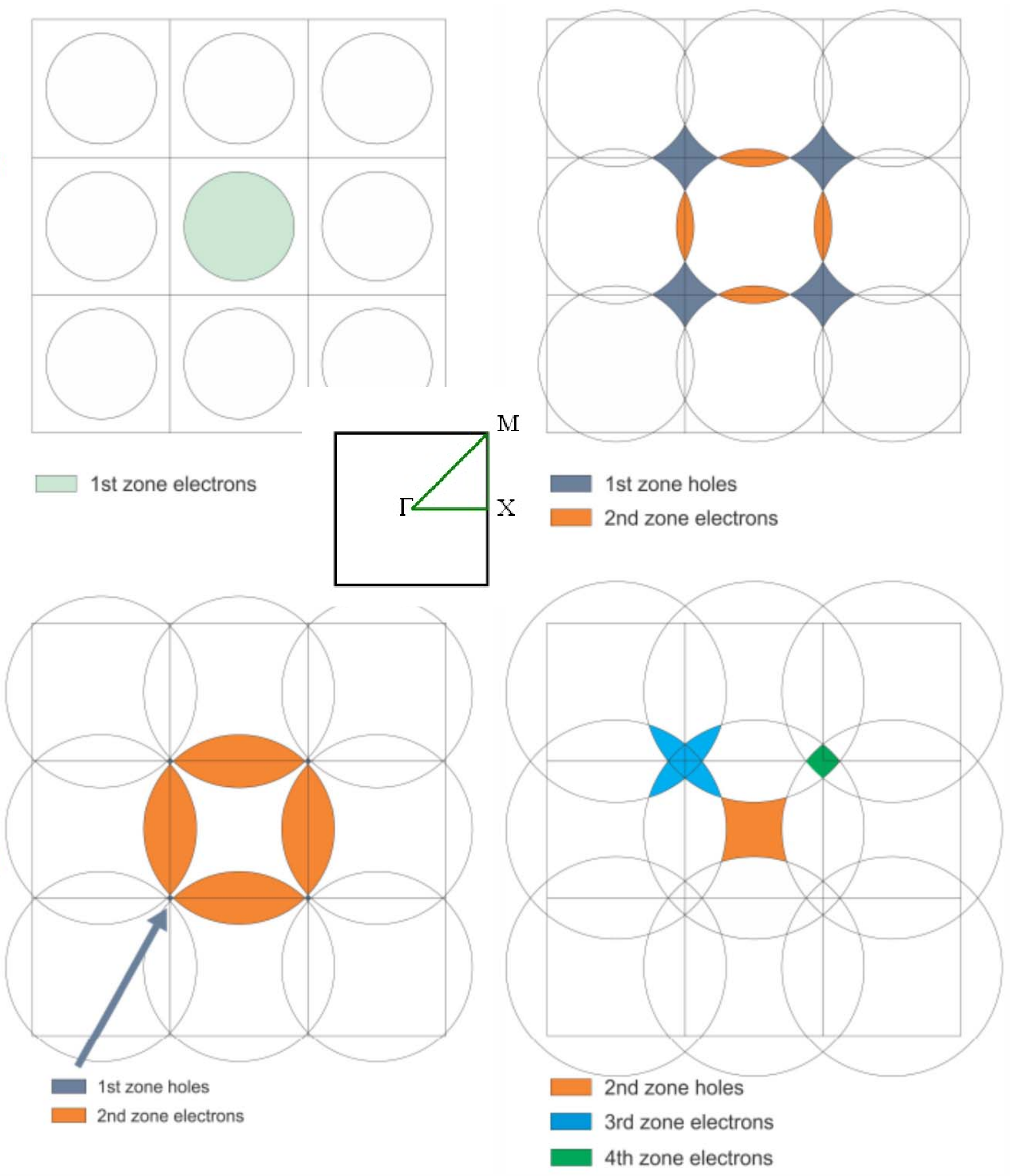


No Fermi surface in the 1st Brillouin zone

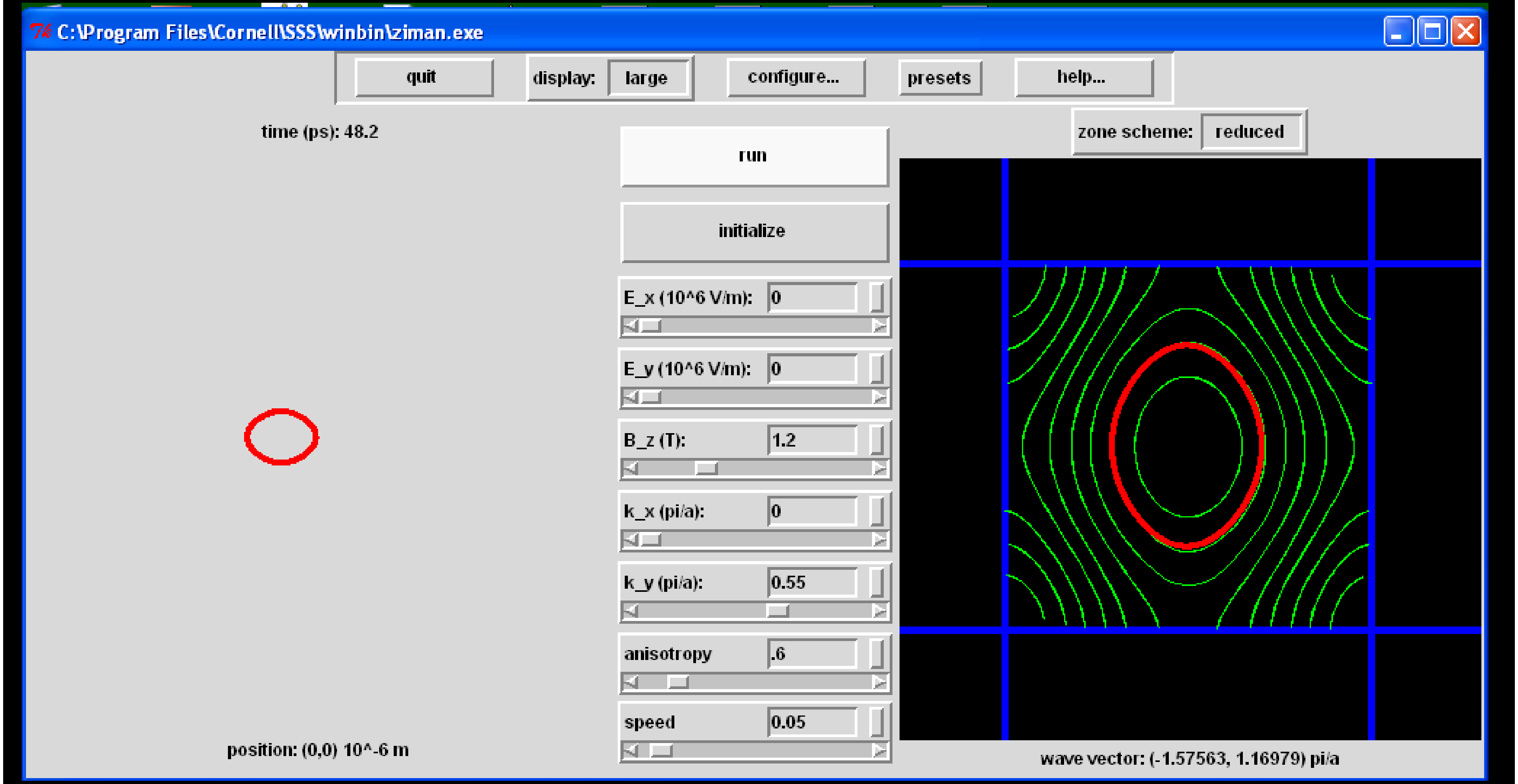
2d square

2N electron states in a Brillouin zone





The Fermi surface strikes the Brillouin zone boundary at 90$^{\text{o}}$.



C:\Program Files\Cornell\SSS\winbin\ziman.exe

time (ps): 48.2

zone scheme: reduced

E_x (10^6 V/m): 0

E_y (10^6 V/m): 0

B_z (T): 1.2

k_x (pi/a): 0

k_y (pi/a): 0.55

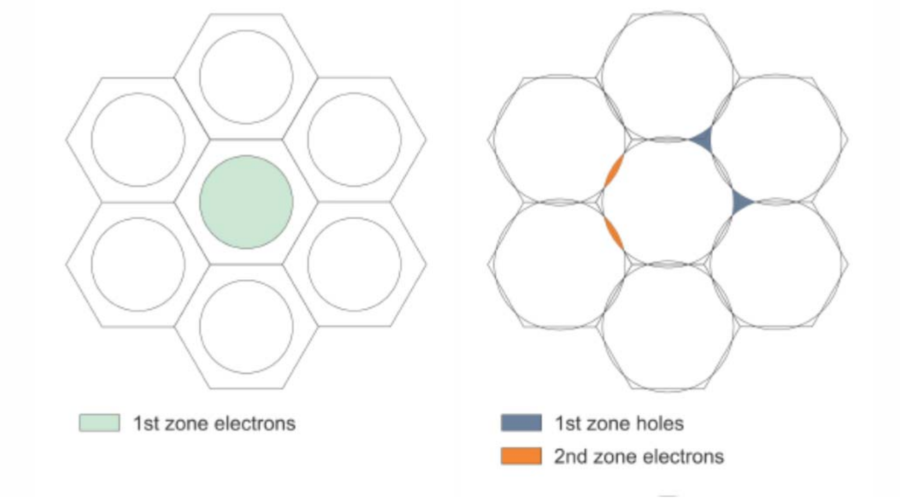
anisotropy .6

speed 0.05

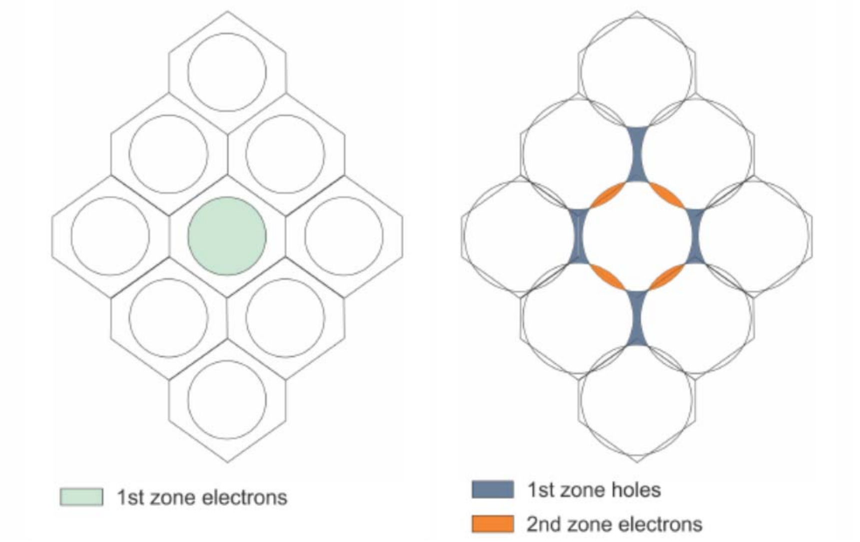
position: (0,0) 10^-6 m

wave vector: (-1.57563, 1.16979) pi/a

2d hexagonal



2d centered rectangular

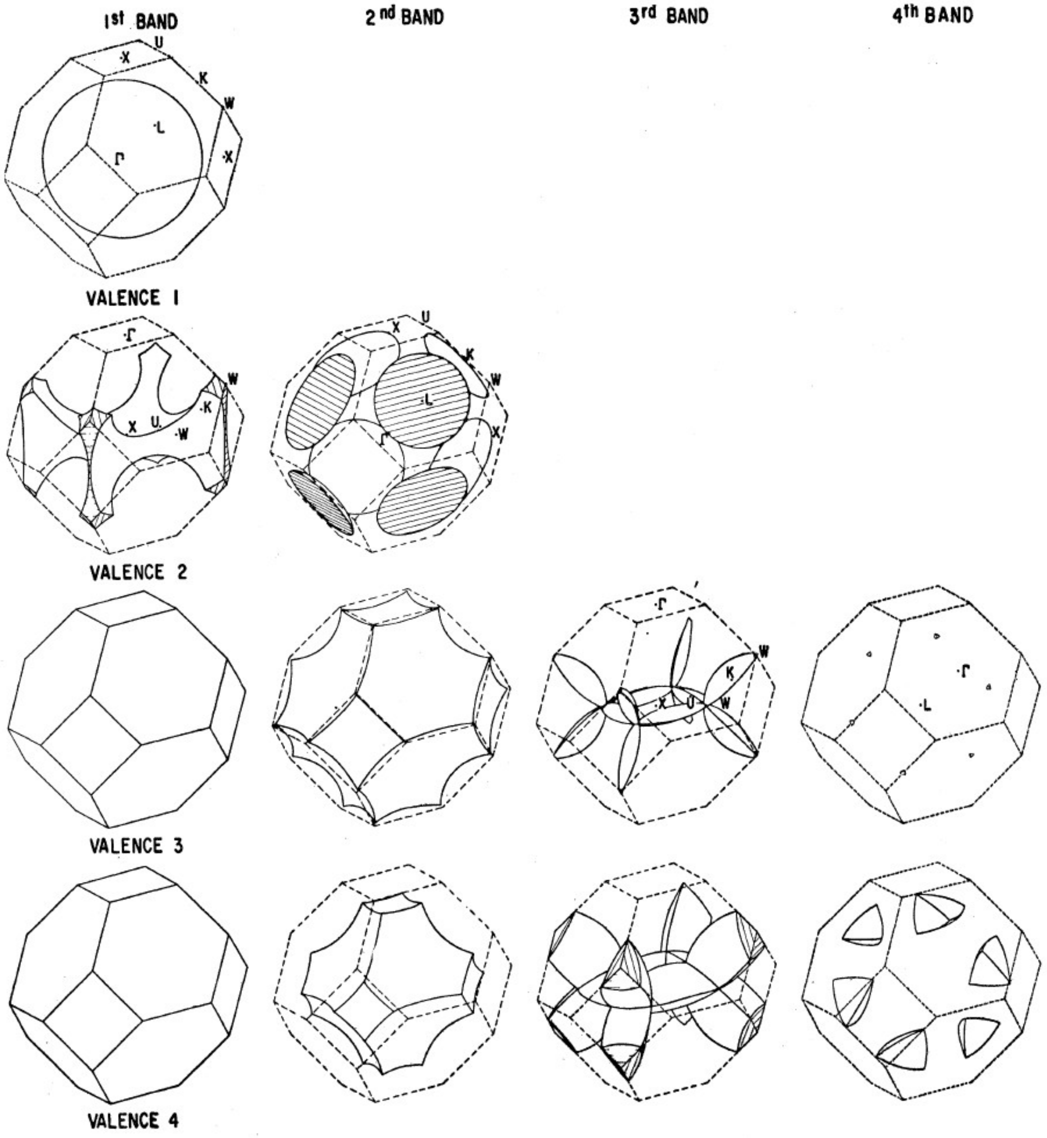


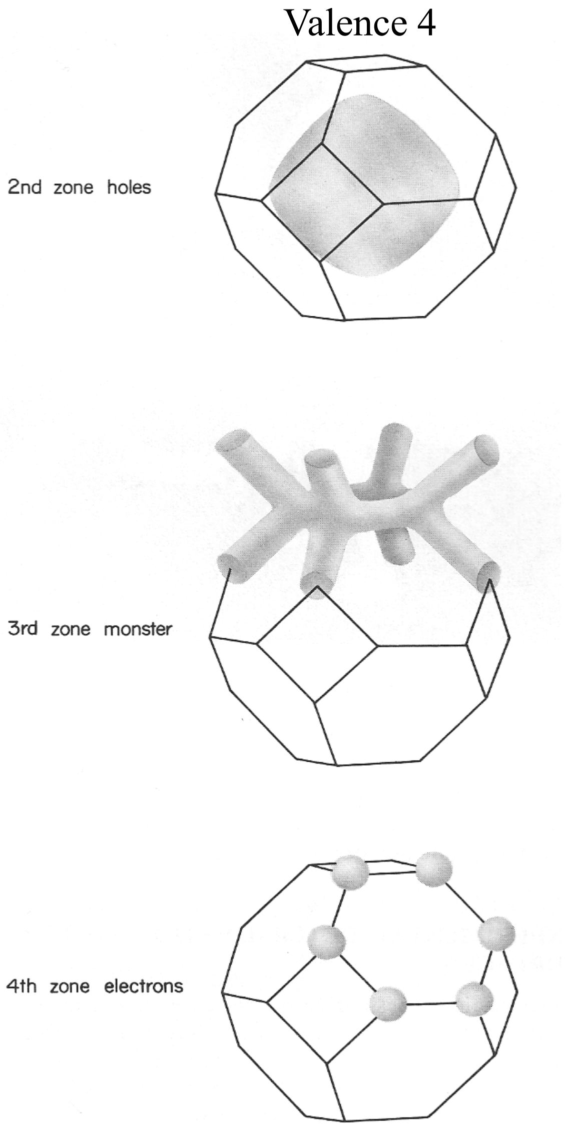
Student project

Replot the Fermi surfaces in 2-D plotting just the surface.

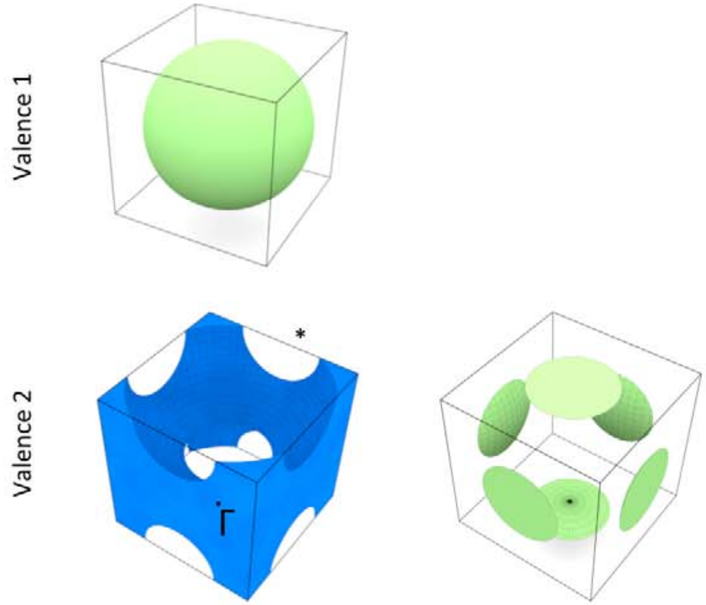
It would be best if we use a program to draw the Fermi surfaces dynamically.

Fermi surface for fcc in the empty lattice approximation



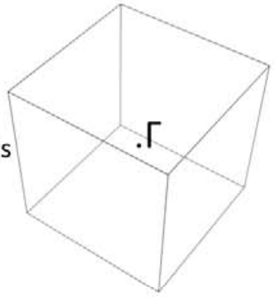


SC - Fermi surfaces in the empty lattice approximation



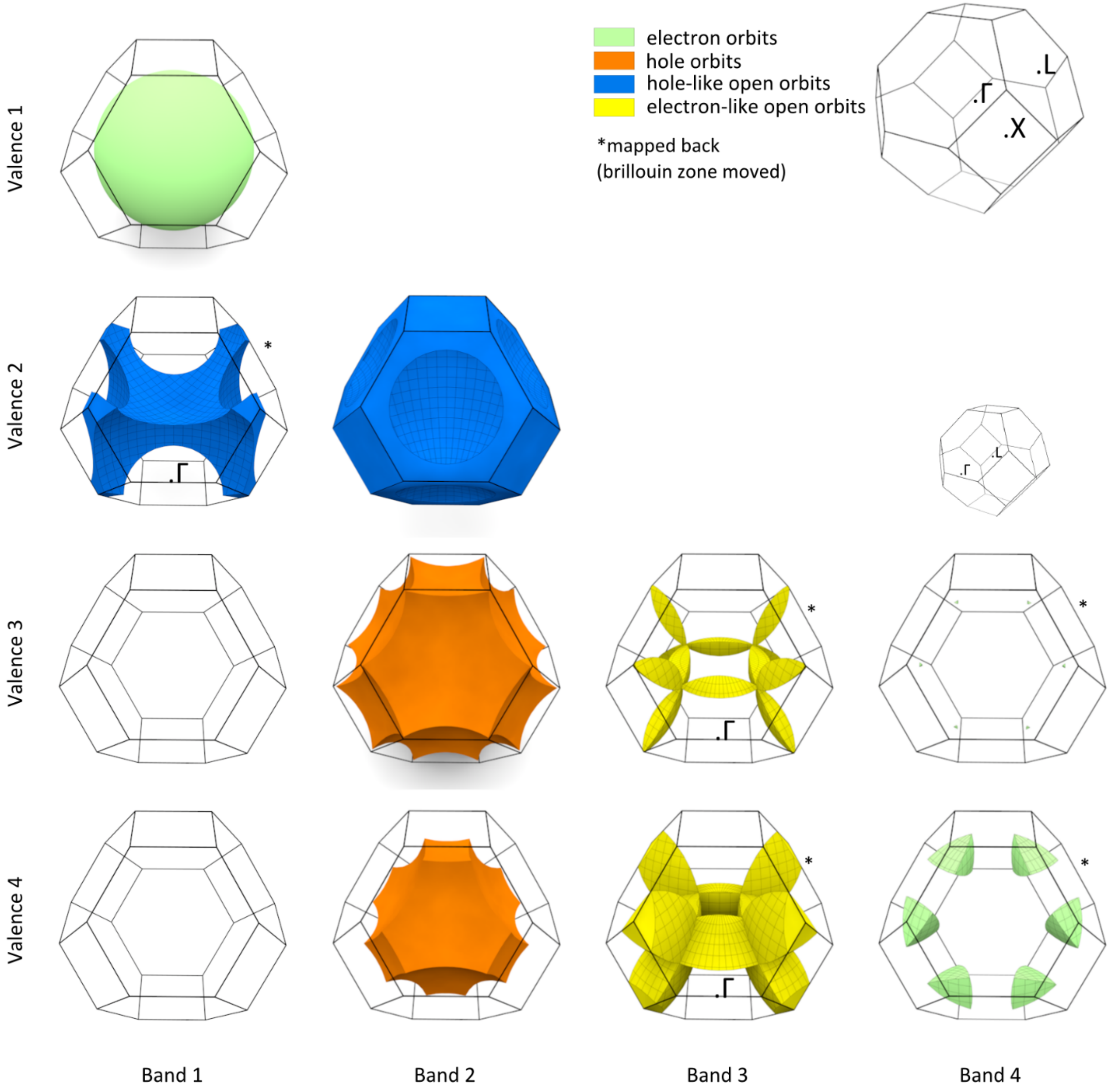
🟩 electron orbits
🟧 hole orbits
🟦 hole-like open orbits
🟨 electron-like open orbits

*mapped back
(brillouin zone moved)



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

FCC - Fermi surfaces in the empty lattice approximation



🟩 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

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

The electronic Hamiltonian separates into the molecular orbital Hamiltonians.

$H_{\mathrm{elec}}(\mathrm{r}_1,\mathrm{r}_2,\ldots\mathrm{r}_\mathrm{n}) = H_{\mathrm{MO}}(\mathrm{r}_1) + H_{\mathrm{MO}}(\mathrm{r}_2) + \ldots H_{\mathrm{MO}}(\mathrm{r}_\mathrm{n})$

$\Psi_{\mathrm{elec}}(\mathrm{r}_1,\mathrm{r}_2,\ldots\mathrm{r}_\mathrm{n}) = |\psi_{\mathrm{MO}}(\mathrm{r}_1)\psi_{\mathrm{MO}}(\mathrm{r}_2)\ \ldots\ \psi_{\mathrm{MO}}(\mathrm{r}_\mathrm{n})>$

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

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

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.

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

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

↗

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

Plane wave method

The central equations can be written as a matrix equation.

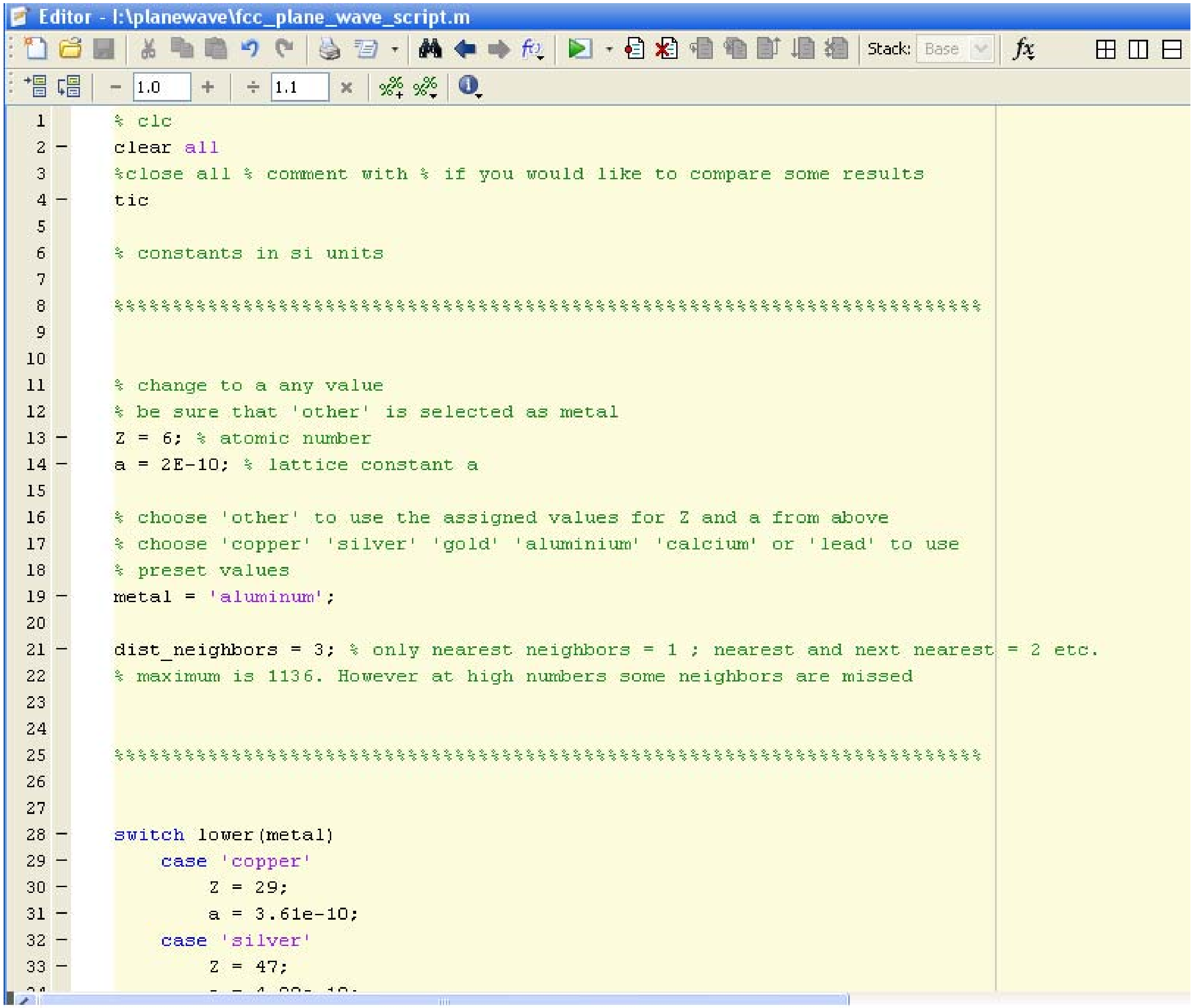
$$M\vec{C} = E\vec{C}$$

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.

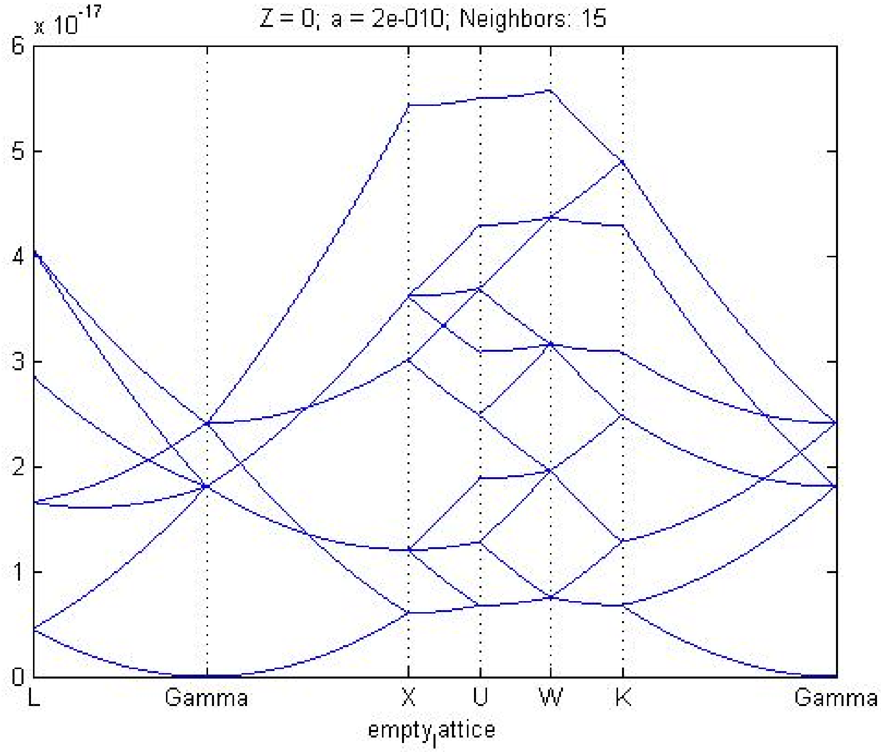
Plane wave method



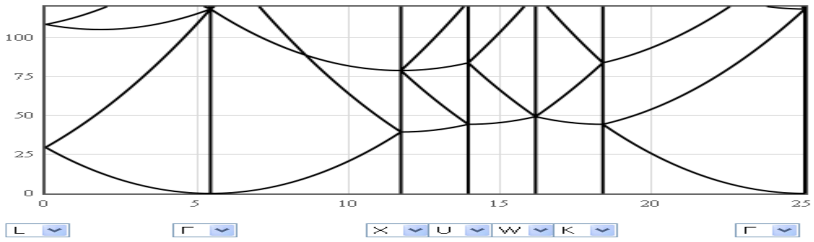
```
% clc
clear all
%close all % comment with % if you would like to compare some results
tic

% 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

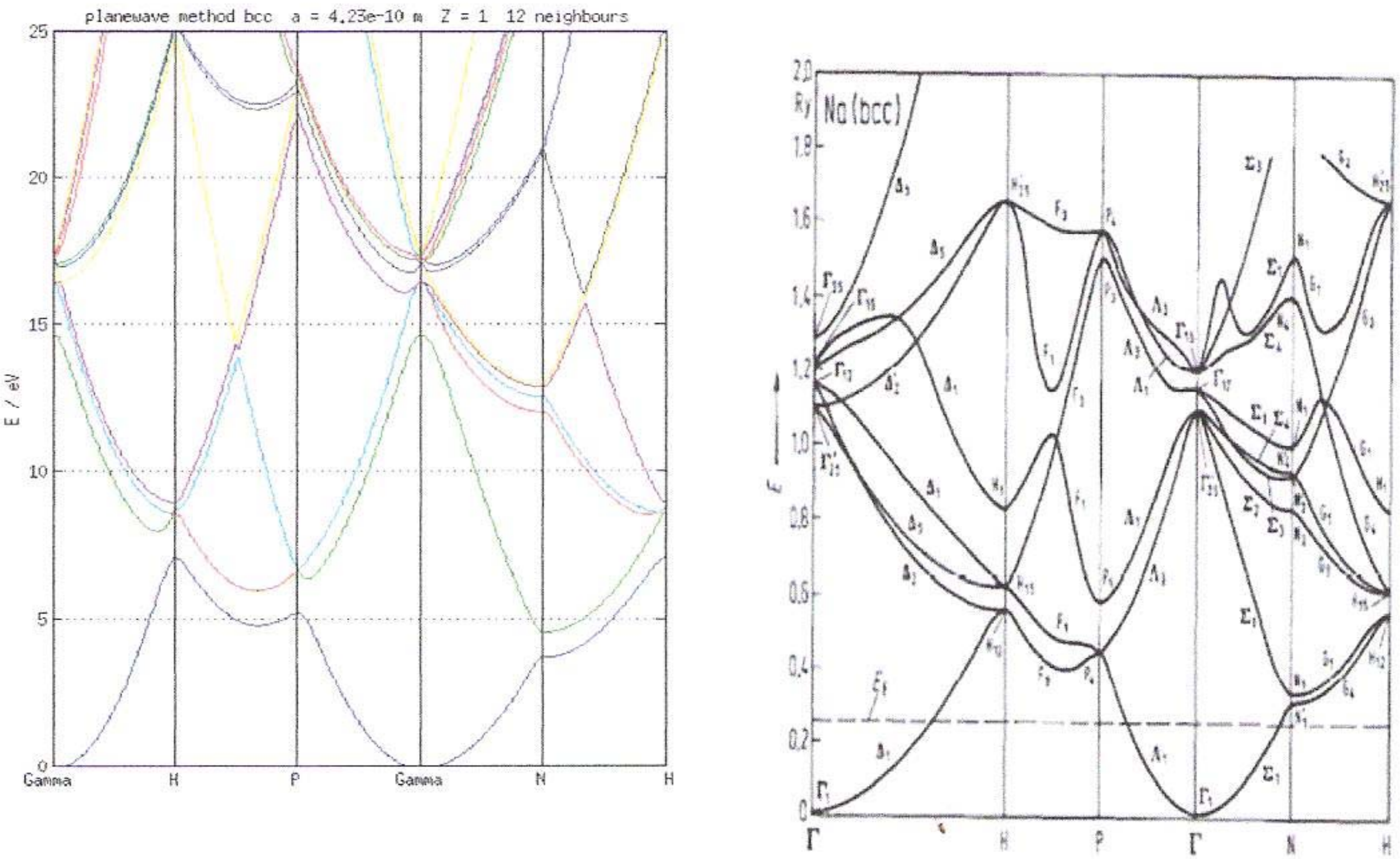


Abbildung 4: Planewave-Methode angewandt an Natrium vs. Literaturberechnung [1]

Muffin tin potentials, pseudopotentials

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

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

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- Naming convention for the pseudopotential
- Unified Pseudopotential Format

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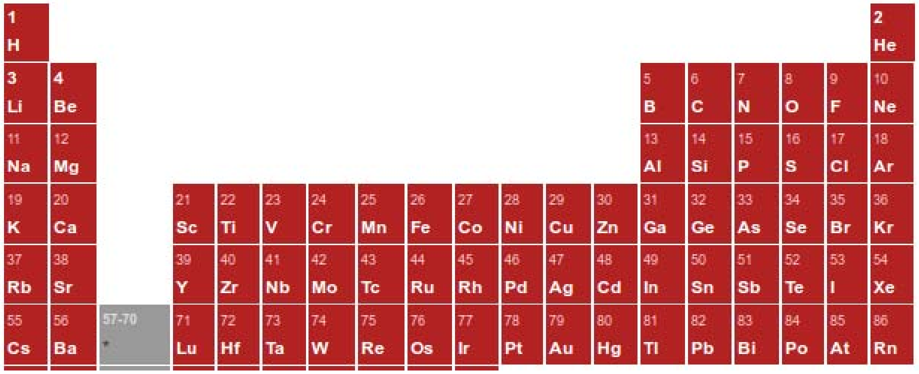
Ready-to-use pseudopotentials are available from the periodic table below. Choose the options you desire from the menus (pseudopotentials from PSlibrary are recommended), then press “Filter”. Elements for which at least a pseudopotential is available will appear in red. Click on the element entry and 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

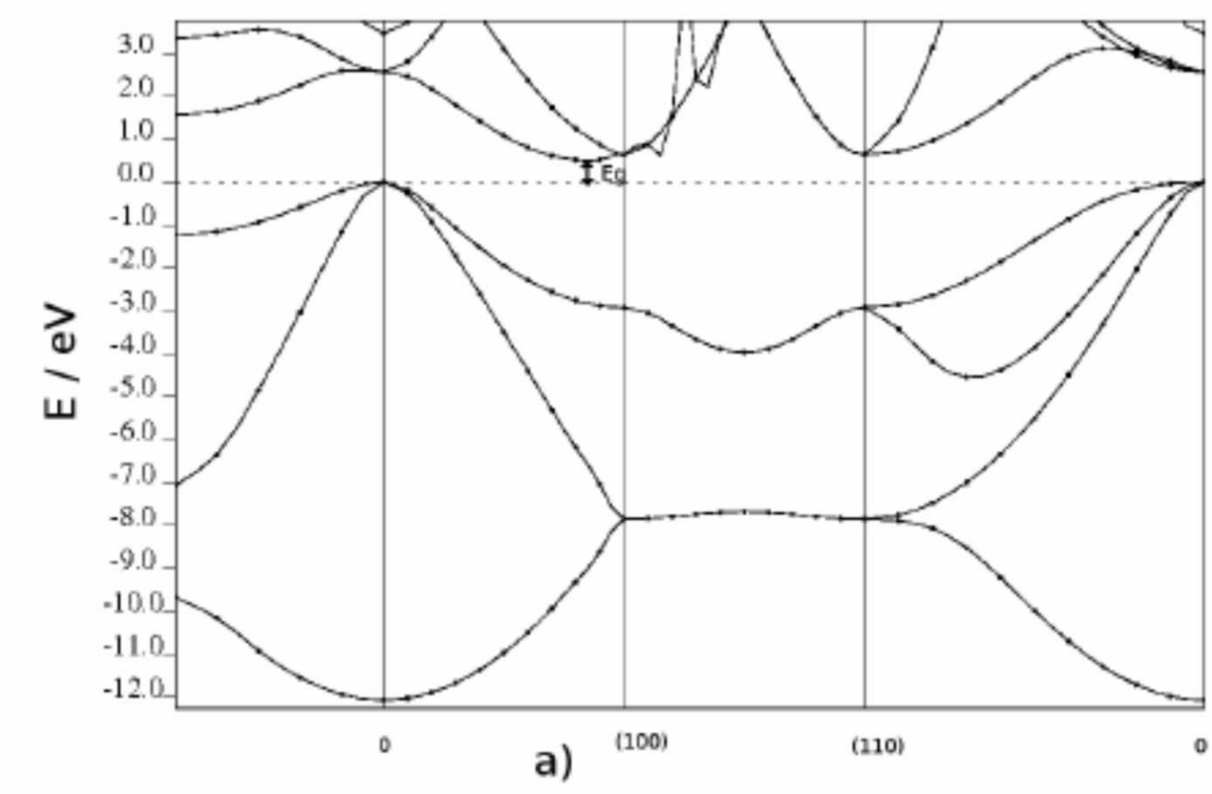
ANY PP LIBRARY ▾ OTHER OPTIONS ▾



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



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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.

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

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

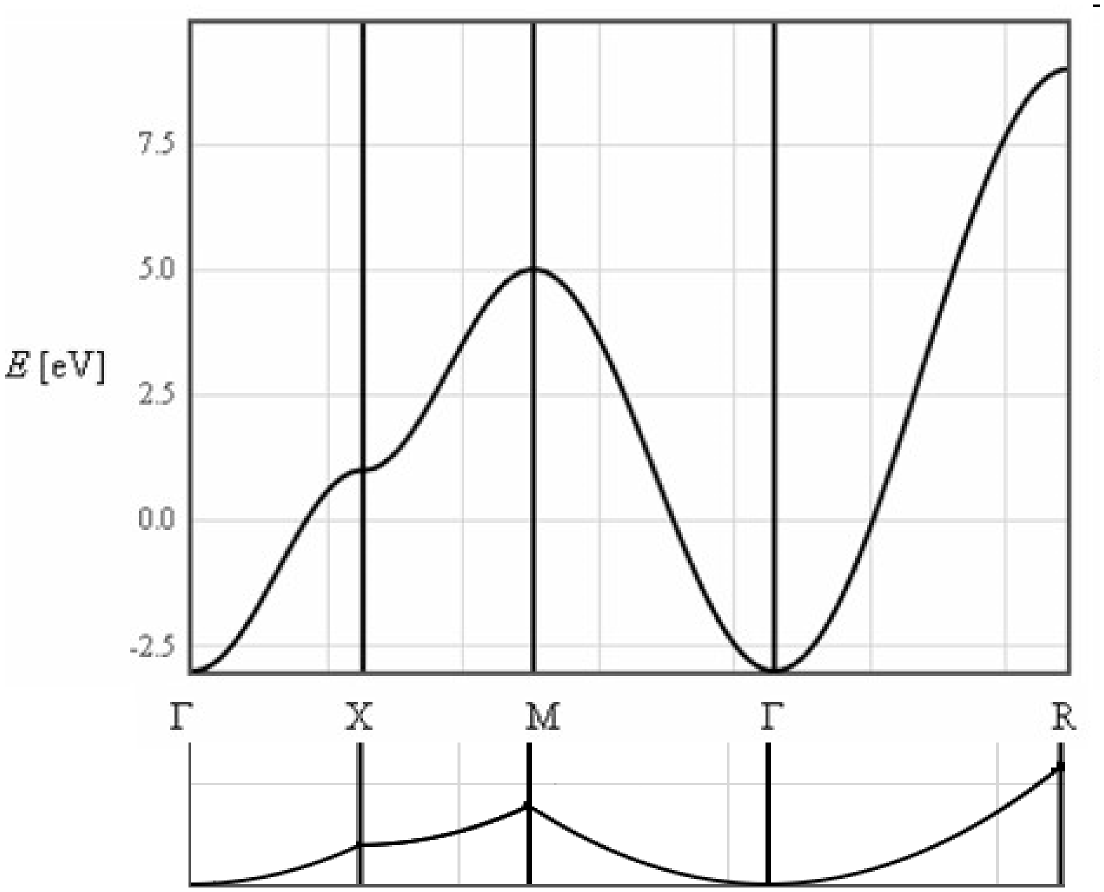
$$\varepsilon = \langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r}) \rangle \qquad t = -\langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r} - \vec{\rho}_m) \rangle$$

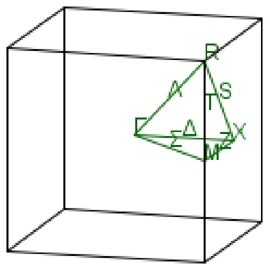
Tight binding, simple cubic

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

$$E=\varepsilon-t\left(e^{ik_xa}+e^{-ik_xa}+e^{ik_ya}+e^{-ik_ya}+e^{ik_za}+e^{-ik_za}\right)$$

$$=\varepsilon-2t\left(\cos(k_xa)+\cos(k_ya)+\cos(k_za)\right)$$

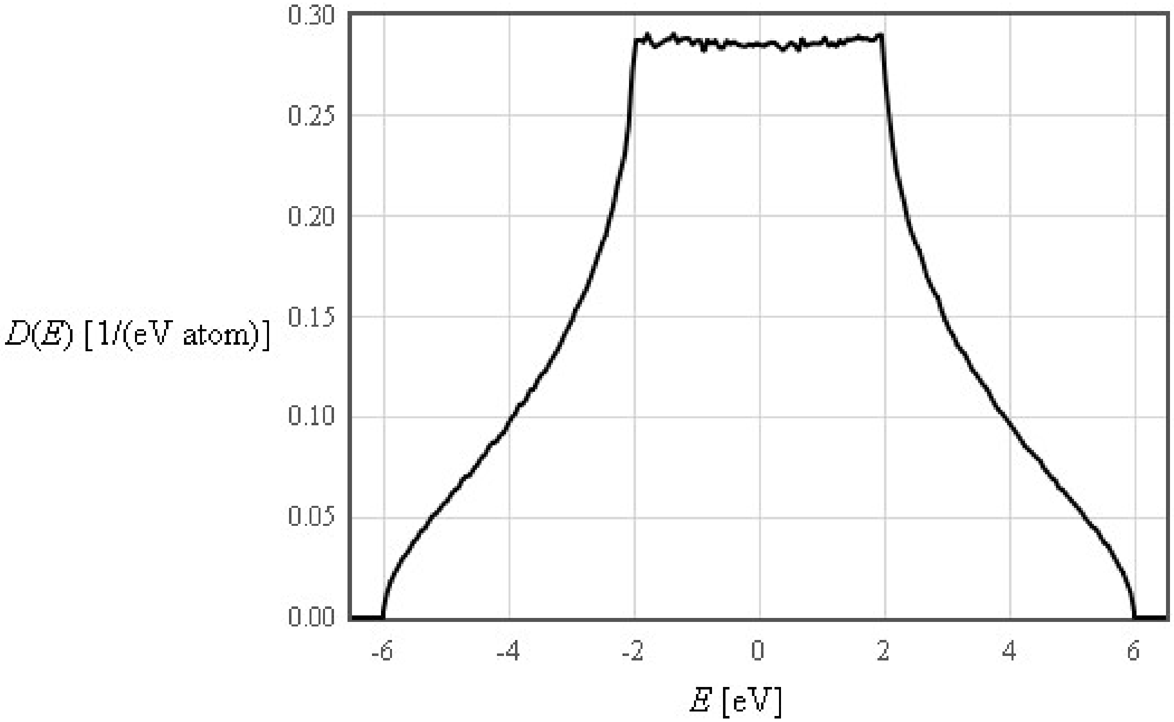




Effective mass $m^*=\frac{\hbar^2}{\frac{d^2E}{dk^2}}=\frac{\hbar^2}{2ta^2}$

Narrow bands → high effective mass

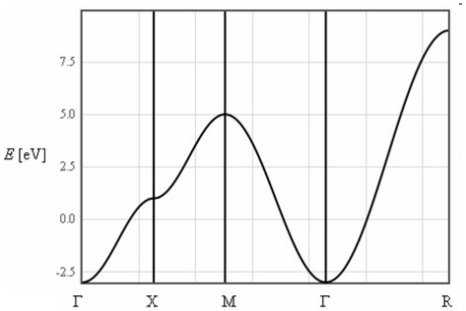
Density of states (simple cubic)



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

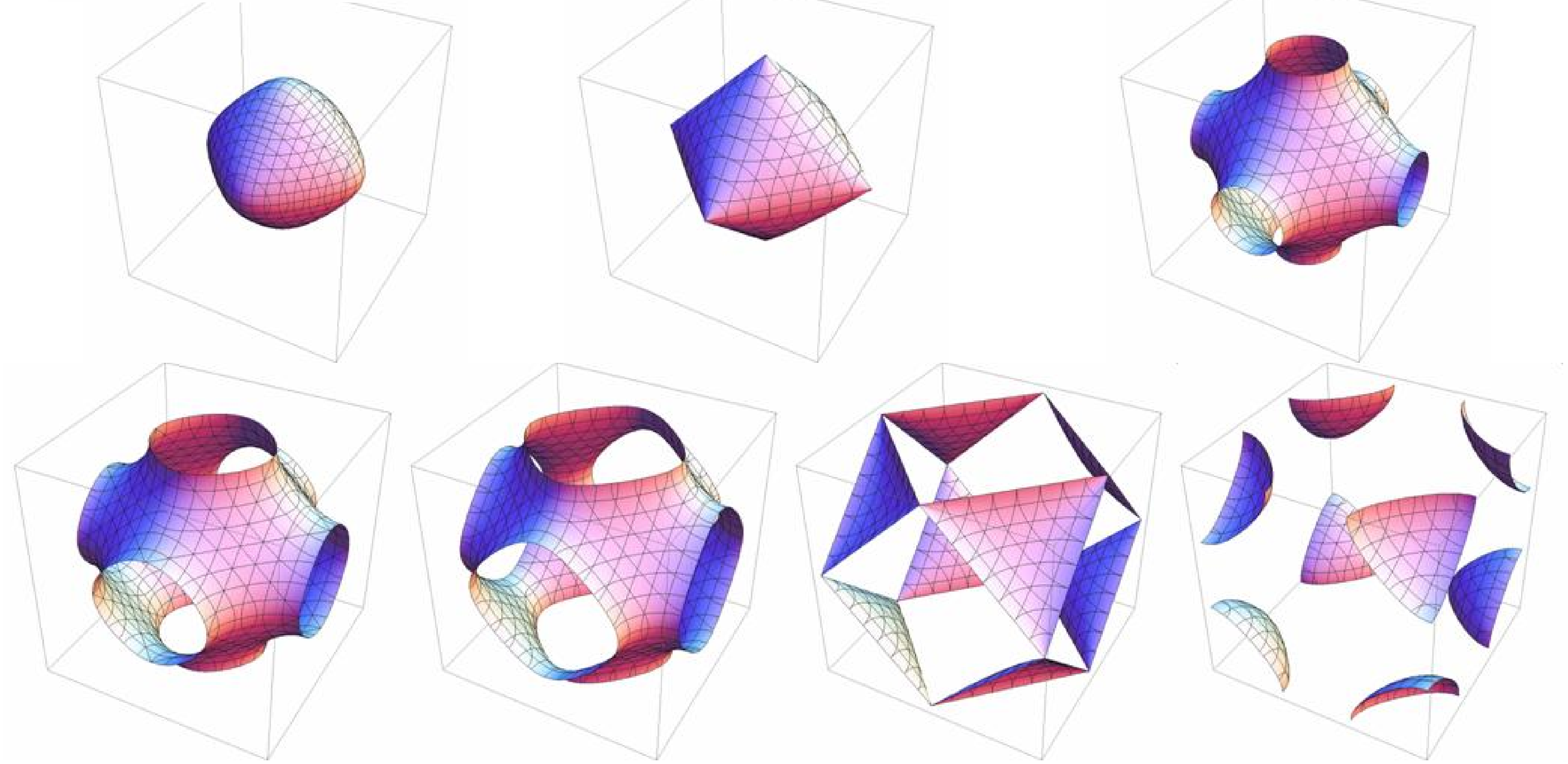
$$E = \varepsilon - 2t\left(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right)$$

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



Tight binding, simple cubic

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

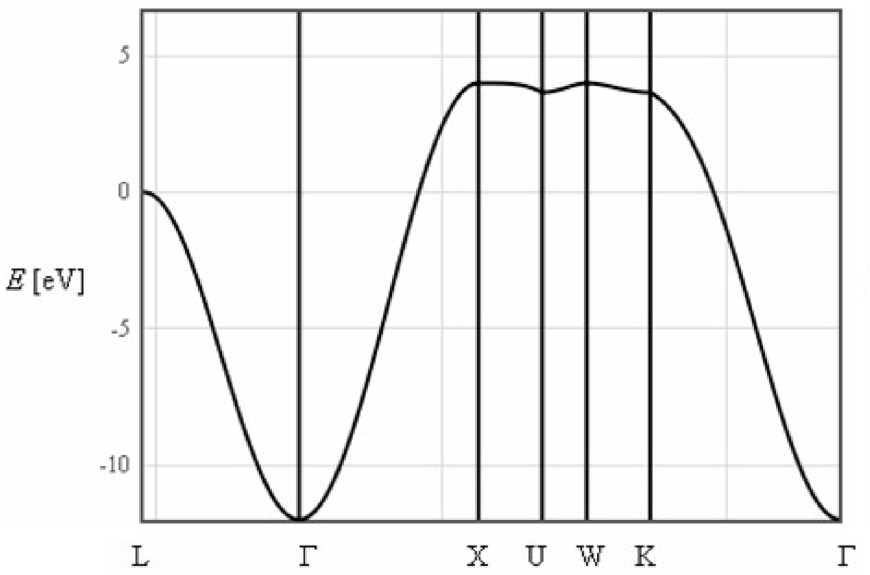


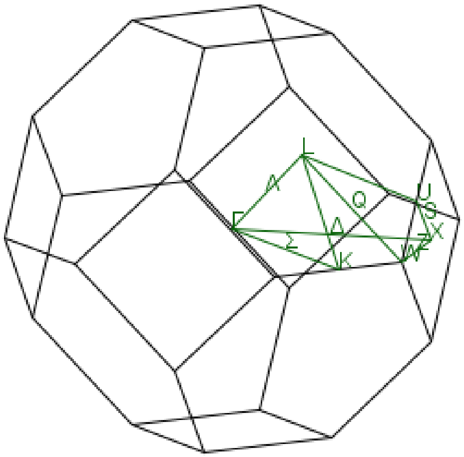
Christian Gruber, 2008

Tight binding, fcc

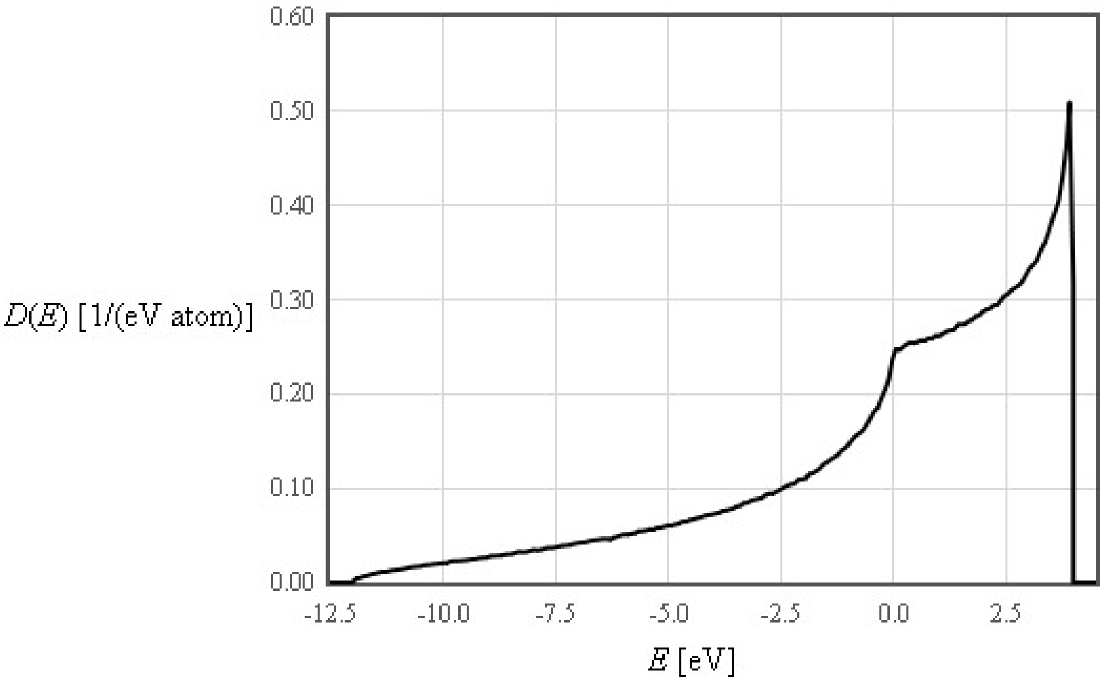
$$E = \varepsilon - t\sum_{m} e^{i\vec{k}\cdot\vec{\rho}_m}$$

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





Density of states (fcc)

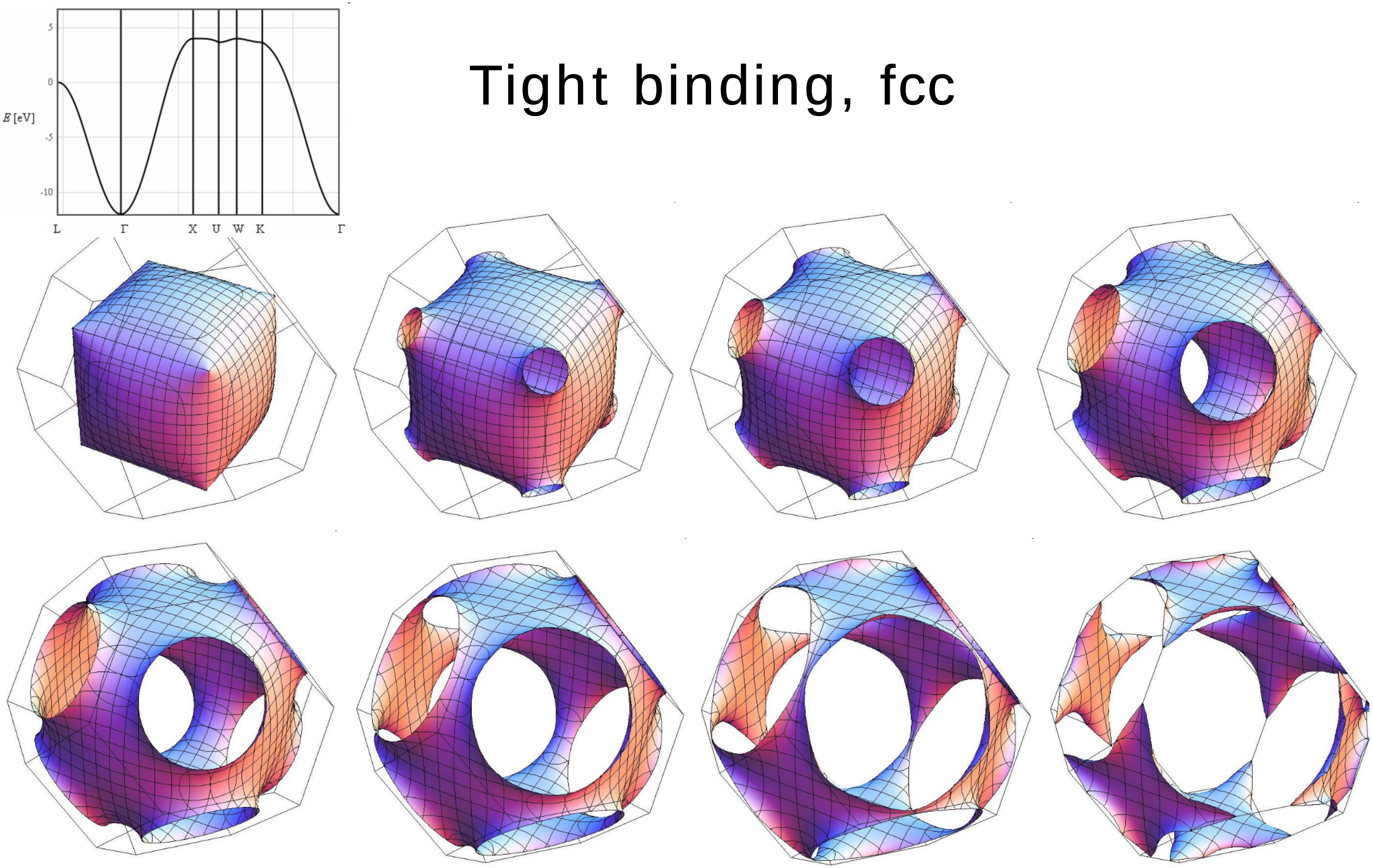


Calculate the energy for every allowed *k* in the Brillouin zone

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

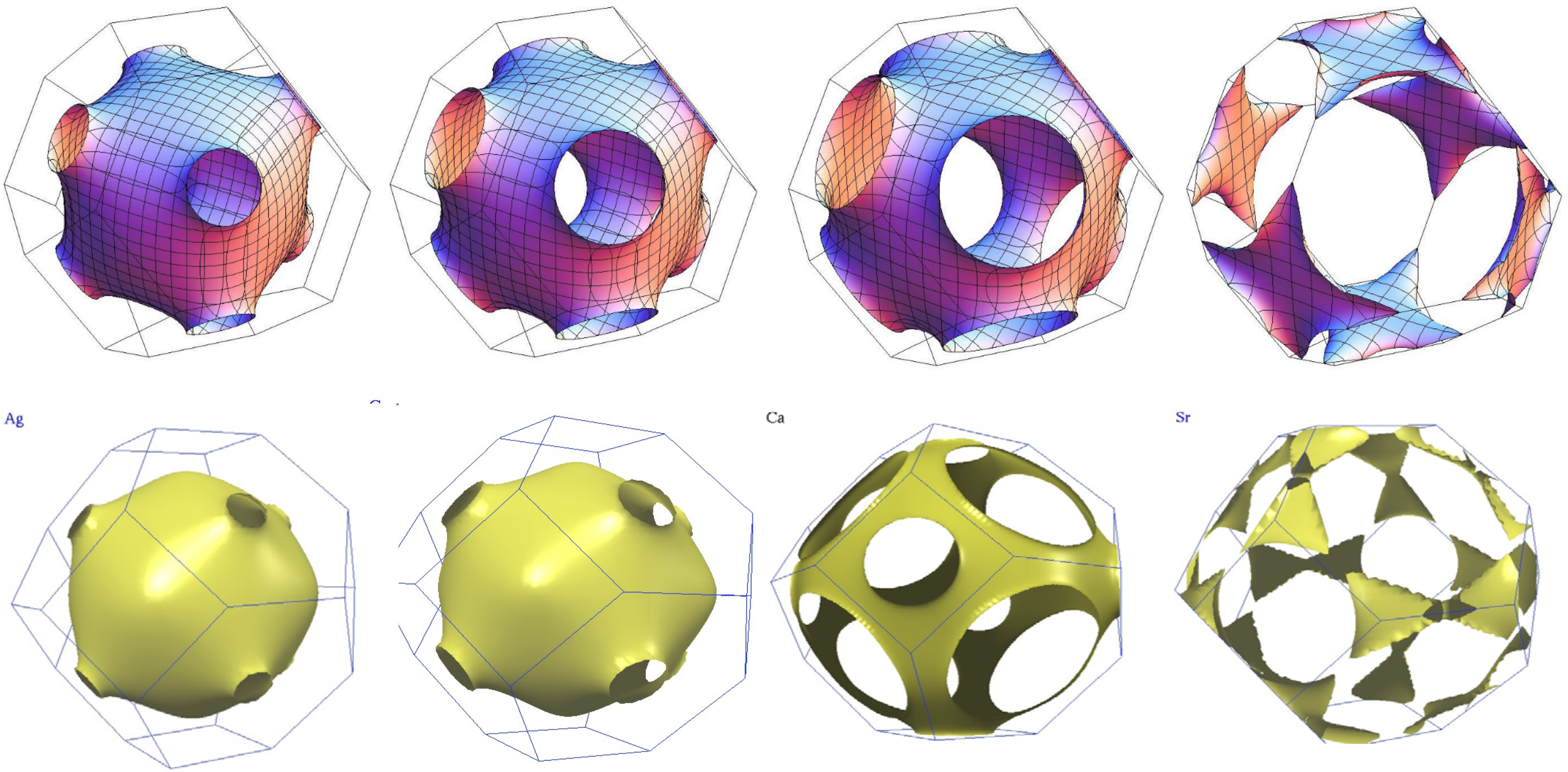
http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tbtable/tbtable.html

Tight binding, fcc



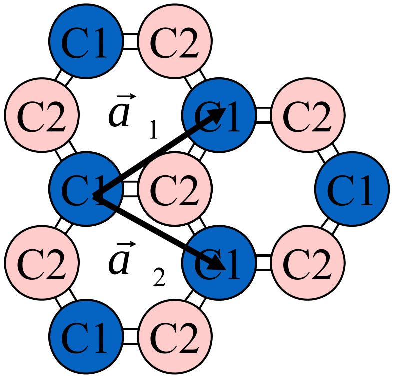
Christian Gruber, 2008

Tight binding, fcc



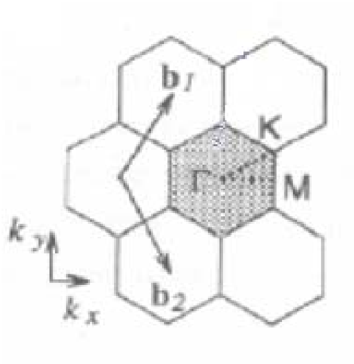
http://www.phys.ufl.edu/fermisurface/

Graphene



$$\vec{a}_1 = \frac{\sqrt{3}}{2} a\hat{x} + \frac{1}{2} a\hat{y}$$

$$\vec{a}_2 = \frac{\sqrt{3}}{2} a\hat{x} - \frac{1}{2} a\hat{y}$$



Two atoms per unit cell

Graphene has an unusual dispersion relation in the vicinity of the Fermi energy.