Band structure: Plane wave method, Tight binding method

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.

http://en.wikipedia.org/wiki/File:Erwin_Schr%C3%B6dinger.jpg

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.

Self consistent field

Use a clever approximation that combines the average position of the electrons with the positive ions.

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

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla + U_{mo}(\vec{r})$$

Pseudopotentials

Separation of variables

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla + U_{mo}(\vec{r})$$

The electronic Hamiltonian separates into the molecular orbital Hamiltonians.

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

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

Solving the molecular orbital Hamiltonian

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla + U_{mo}(\vec{r})$$

Band structure calculations:

Plane wave method
Tight binding (LCAO+)

DFT

Plane wave method

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

Write U and ψ as Fourier series.

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

For the molecular orbital Hamiltonian

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

volume of a unit cell

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

Central equations - one dimension

$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_k + \sum_G U_G C_{k-G} = 0$$

$$\begin{bmatrix}
\ddots & & & & & & \\
\frac{\hbar^2 (k-2G_0)^2}{2m} - E & U_{G_0} & U_{2G_0} & U_{3G_0} & U_{4G_0} & U_{5G_0} \\
U_{-G_0} & \frac{\hbar^2 (k-G_0)^2}{2m} - E & U_{G_0} & U_{2G_0} & U_{3G_0} & U_{4G_0} \\
U_{-2G_0} & U_{-G_0} & \frac{\hbar^2 k^2}{2m} - E & U_{G_0} & U_{2G_0} & U_{3G_0} \\
U_{-3G_0} & U_{-2G_0} & U_{-G_0} & \frac{\hbar^2 (k+G_0)^2}{2m} - E & U_{G_0} & U_{2G_0} \\
U_{-4G_0} & U_{-3G_0} & U_{-2G_0} & U_{-G_0} & \frac{\hbar^2 (k+2G_0)^2}{2m} - E & U_{G_0} \\
 & & & & & \ddots
\end{bmatrix}
\begin{bmatrix}
\vdots \\ C_{k+2G_0} \\ C_{k+G_0} \\ C_k \\ C_{k-G_0} \\ C_{k-2G_0} \\ \vdots
\end{bmatrix} = 0$$

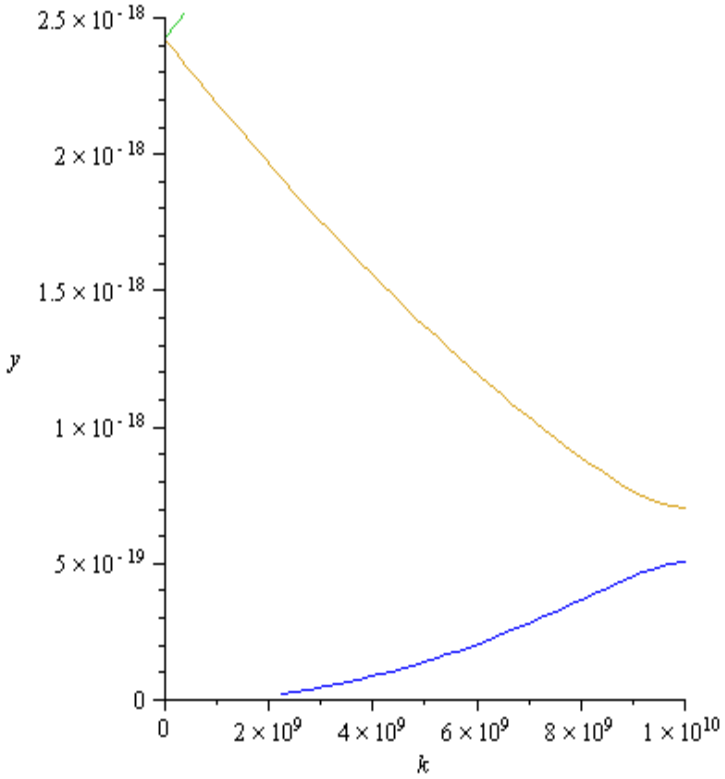
Central equations couple coefficients k to other coefficients that differ by a reciprocal lattice wavevector G.

Central equations - one dimension

$$M4 := \begin{bmatrix} \frac{\mathrm{hbar}^2 \cdot (k + 2 \cdot G)^2}{2m} & U & 0 & 0 \\ U & \frac{\mathrm{hbar}^2 \cdot (k + G)^2}{2m} & U & 0 \\ 0 & U & \frac{\mathrm{hbar}^2 \cdot k^2}{2m} & U \\ 0 & 0 & U & \frac{\mathrm{hbar}^2 \cdot (k - G)^2}{2m} \end{bmatrix} :$$

$V4 := Eigenvalues(M4)$:

$plot([V4[1], V4[2], V4[3], V4[4]], k = 0..1E10, y = 0..2.5E-18);$



Central equations 3d - simple cubic

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

Molecular orbital Hamiltonian

$$U_{\vec{G}} = \frac{-Ze^2}{V_{\text{unit cell}}\varepsilon_0 G^2}$$

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

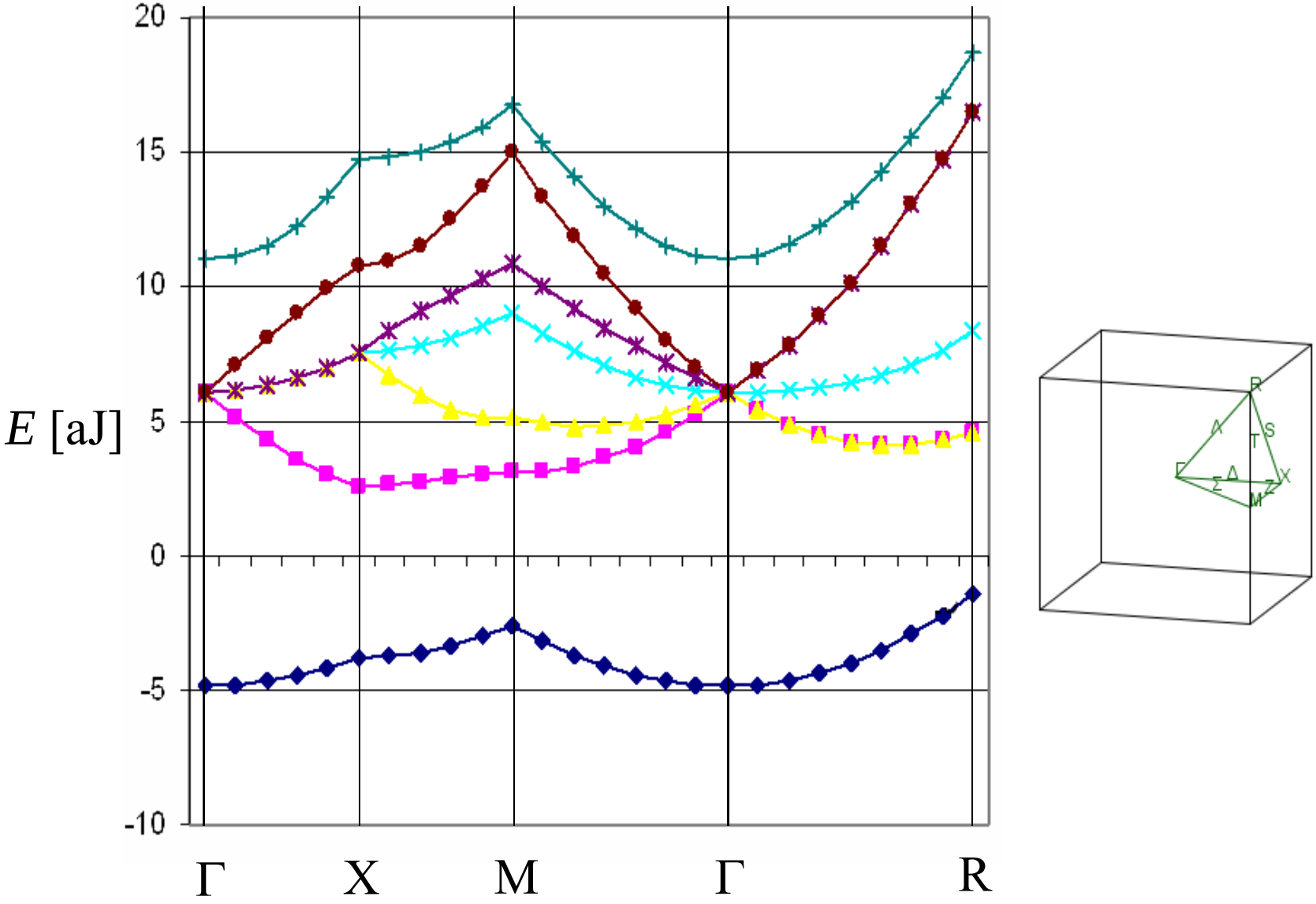
diagonal elements: $$\frac{\hbar^2}{2m}\left(\vec{k} - \vec{G}_i\right)^2$$

off-diagonal elements: $$\frac{-Ze^2}{V_{\text{unit cell}}\varepsilon_0 \left(\vec{G}_i - \vec{G}_j\right)^2}$$

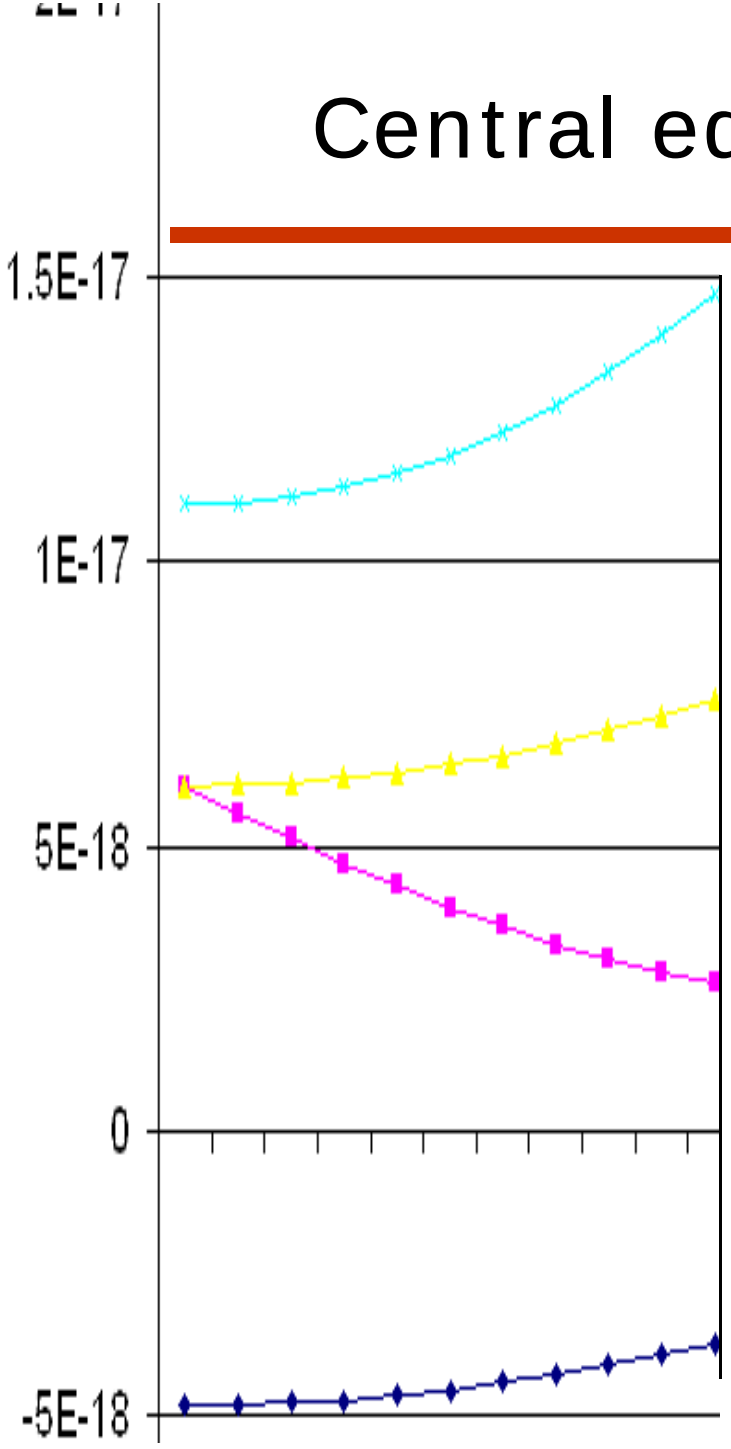
Central equations - simple cubic

$$
\begin{pmatrix}
\frac{\hbar^2\left(\vec{k}+\frac{2\pi}{a}\hat{k}_z\right)^2}{2m} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{16V_{\text{unit cell}}\varepsilon_0\pi^2} \\
\frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{\hbar^2\left(\vec{k}+\frac{2\pi}{a}\hat{k}_y\right)^2}{2m} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{16V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} \\
\frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{\hbar^2\left(\vec{k}+\frac{2\pi}{a}\hat{k}_x\right)^2}{2m} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{16V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} \\
\frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{\hbar^2k^2}{2m} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} \\
\frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{16V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{\hbar^2\left(\vec{k}-\frac{2\pi}{a}\hat{k}_x\right)^2}{2m} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} \\
\frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{16V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{\hbar^2\left(\vec{k}-\frac{2\pi}{a}\hat{k}_y\right)^2}{2m} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} \\
\frac{-Ze^2a^2}{16V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{2V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{\hbar^2\left(\vec{k}-\frac{2\pi}{a}\hat{k}_z\right)^2}{2m}
\end{pmatrix}
$$

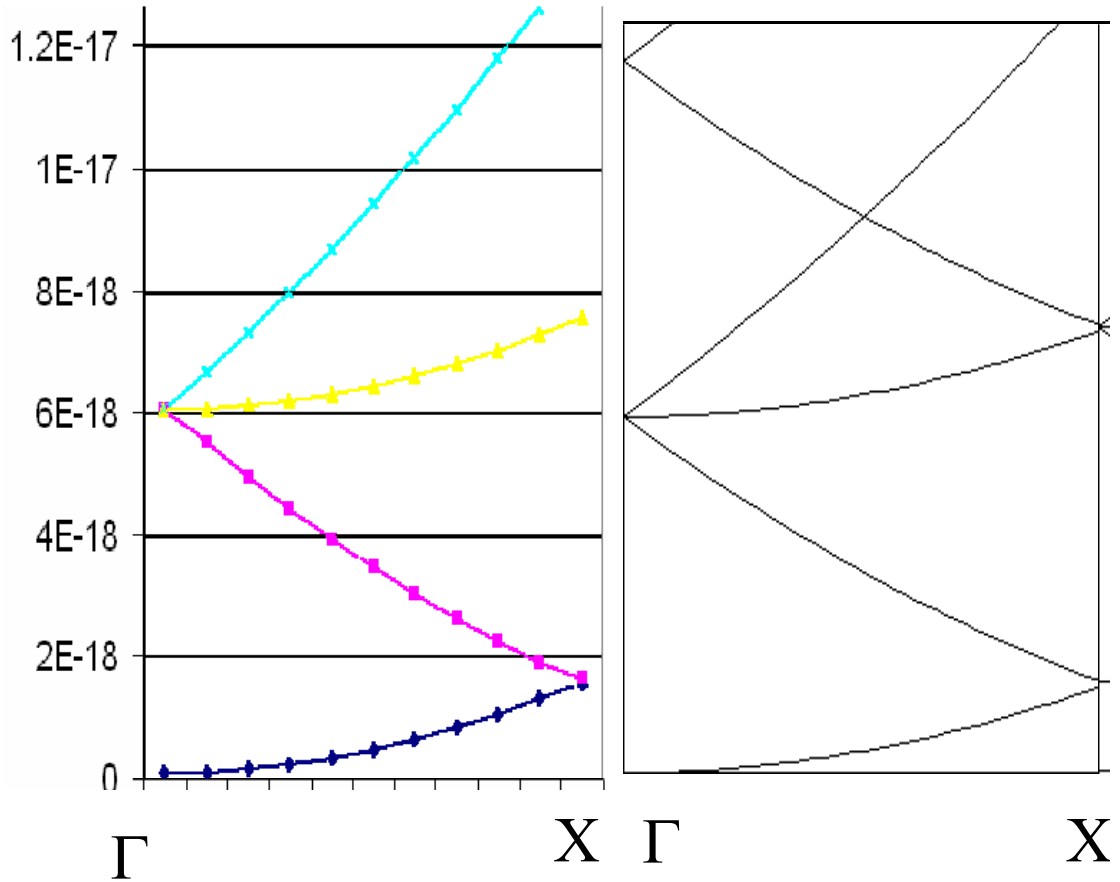
Central equations - simple cubic



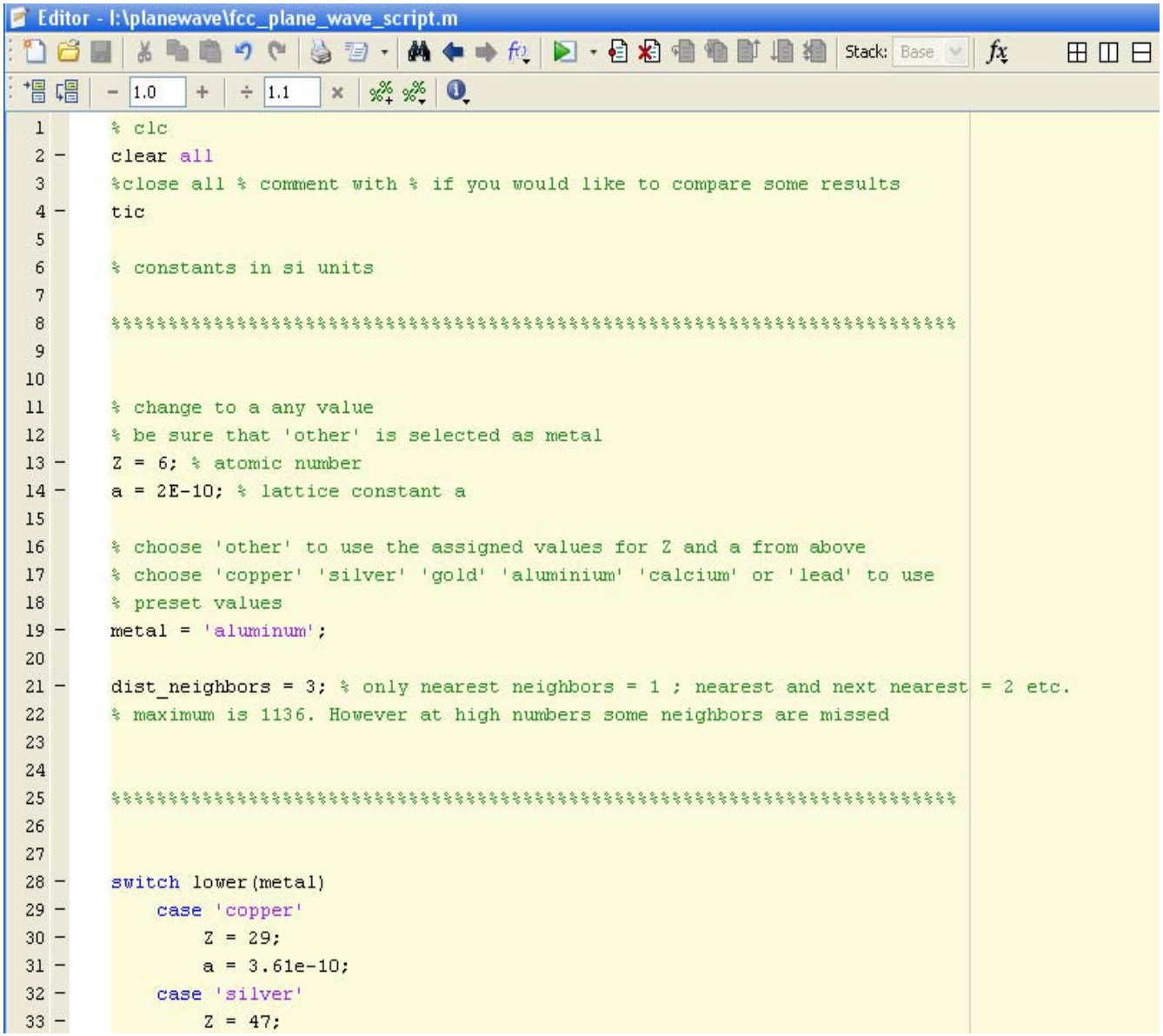
Central equations - simple cubic



empty lattice



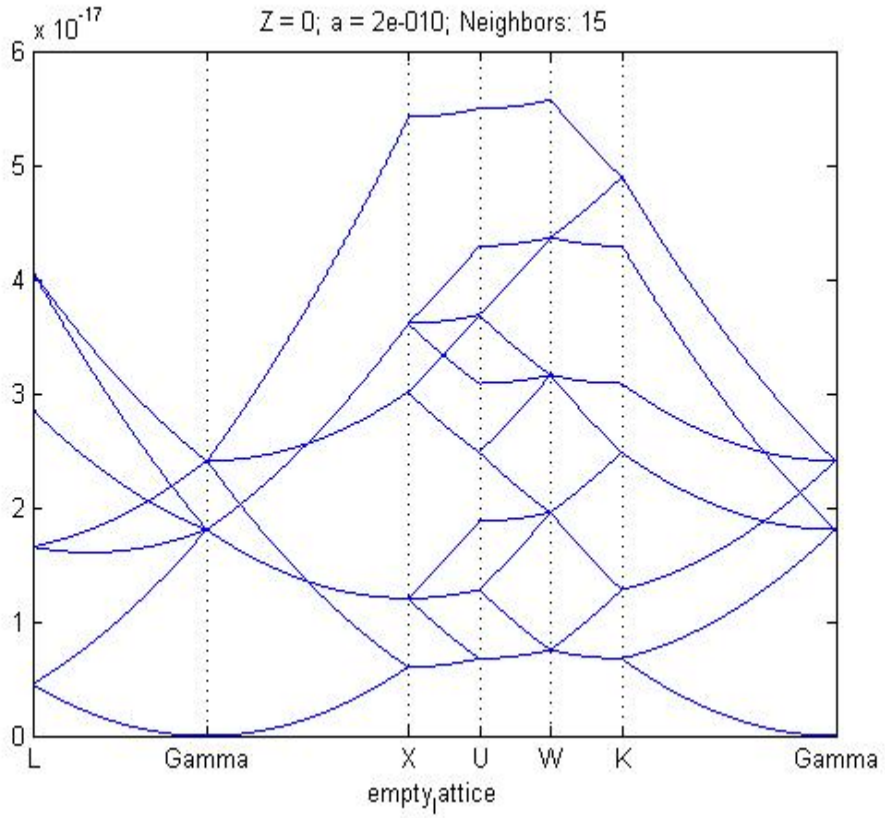
Plane wave method



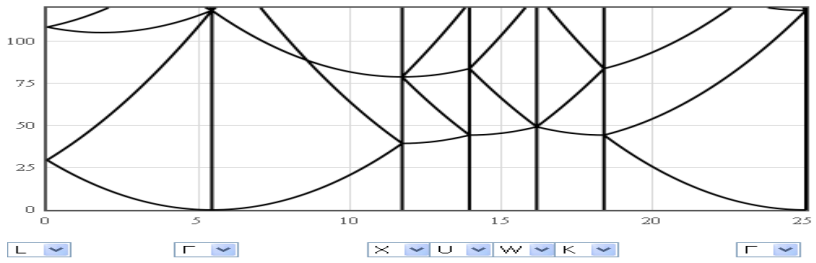

```
% clc
clear all
%close all % comment with % if you would like to compare some results
tic

% 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

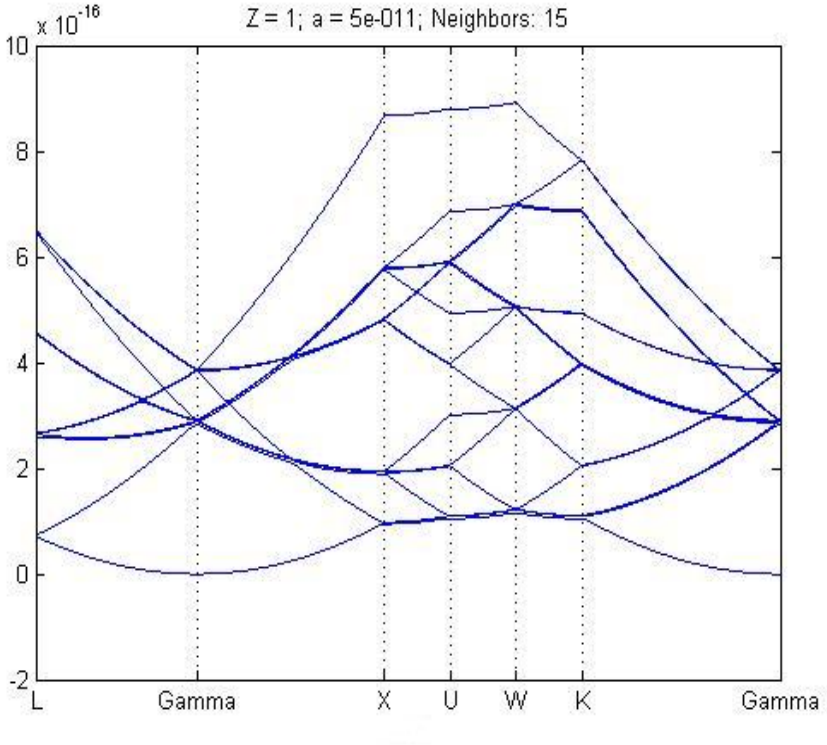


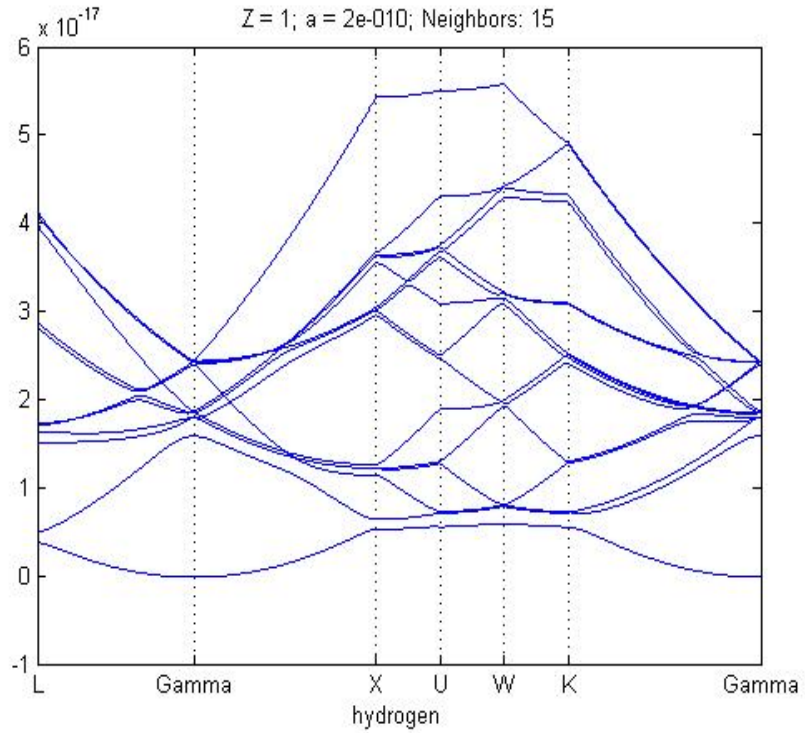
empty lattice



Plane wave method

fcc hydrogen





Approximate solution near the Bz boundary

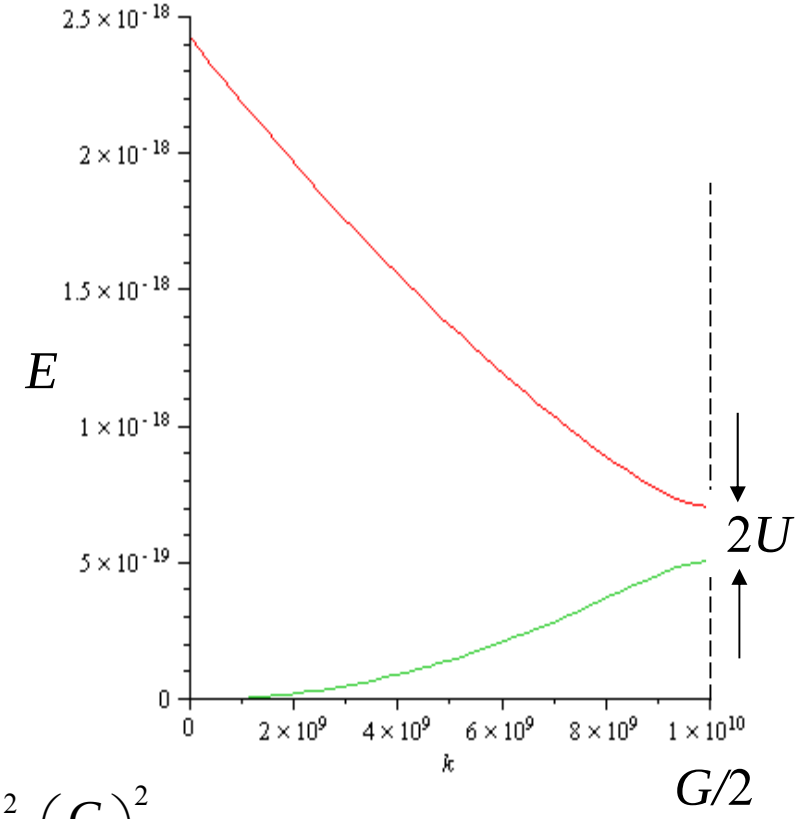
$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_k + \sum_G U_G C_{k-G} = 0$$

For just 2 terms

$$\begin{bmatrix} \frac{\hbar^2 k^2}{2m} - E & U \\ U & \frac{\hbar^2 (k-G)^2}{2m} - E \end{bmatrix} \begin{bmatrix} C_k \\ C_{k+G} \end{bmatrix} = 0$$

Near the Brillouin zone boundary $k \sim G/2$

$$\begin{bmatrix} \frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2 - E & U \\ U & \frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2 - E \end{bmatrix} \begin{bmatrix} C_k \\ C_{k+G} \end{bmatrix} = 0$$



$$E = \frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2 \pm U$$

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

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

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

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

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

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

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

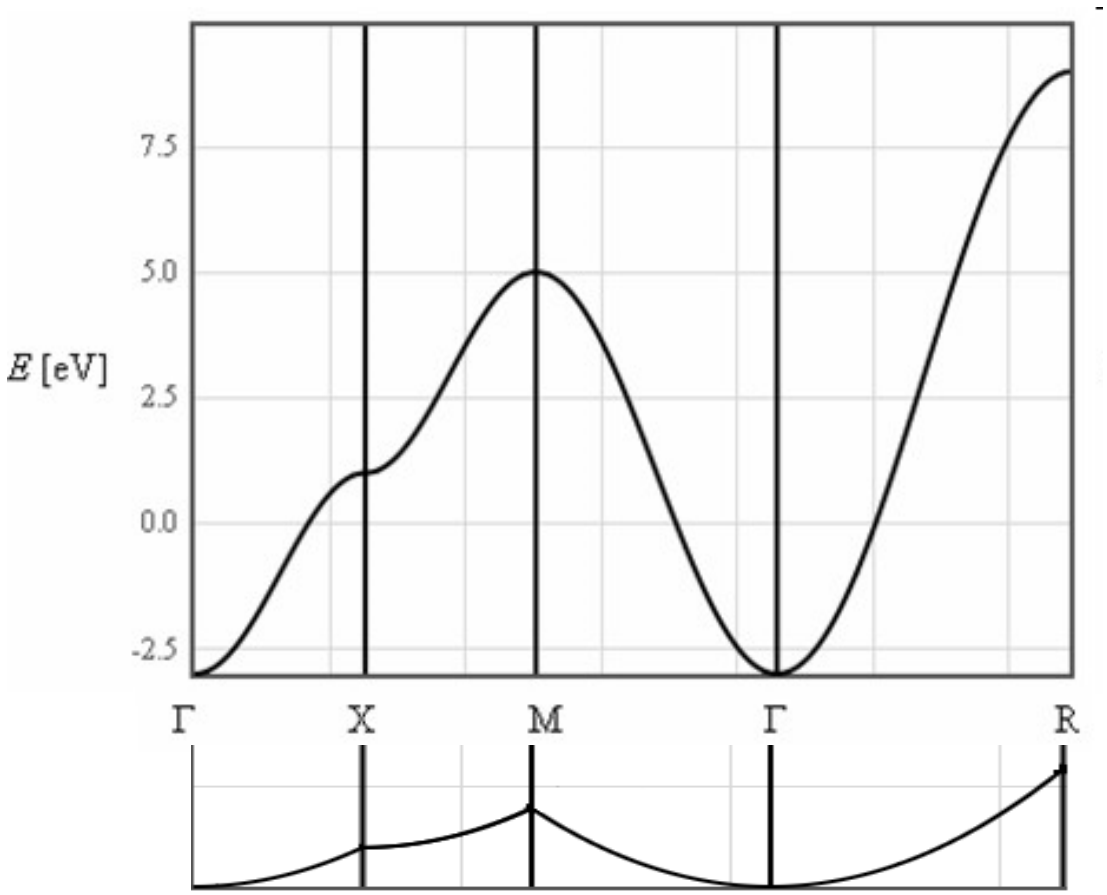
$$\varepsilon = \langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r}) \rangle \qquad t = -\langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r} - \vec{\rho}_m) \rangle$$

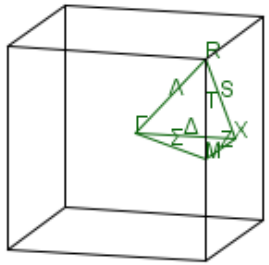
Tight binding, simple cubic

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

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

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

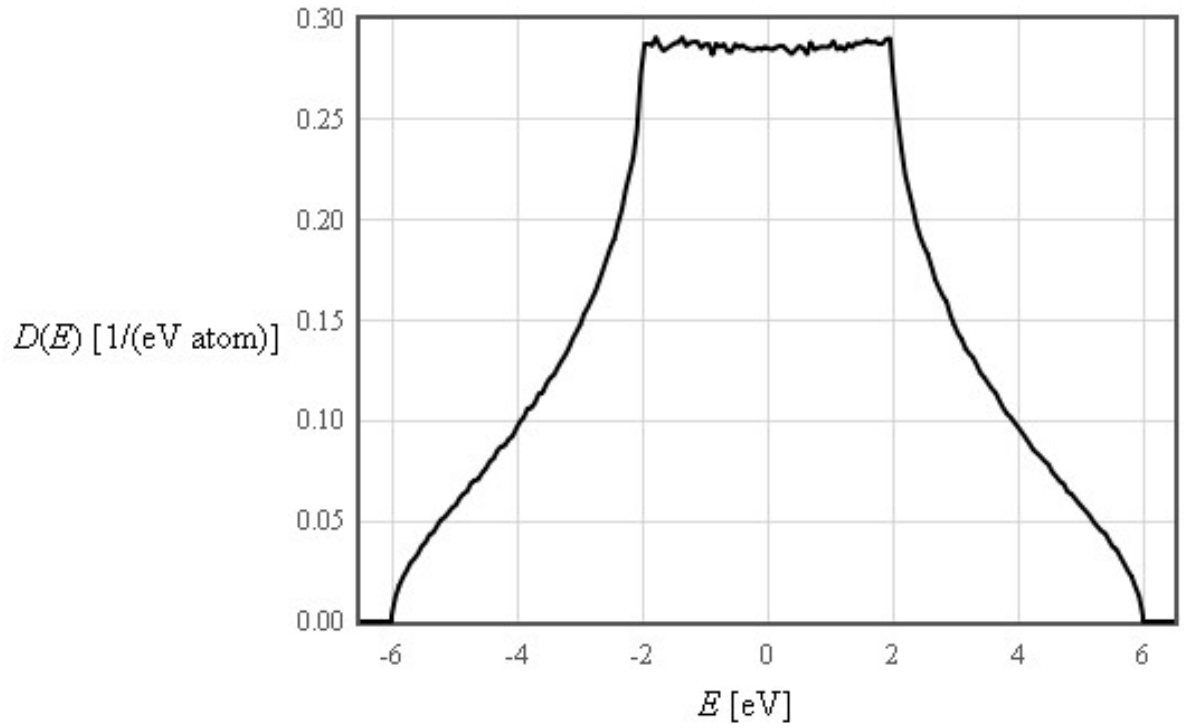




Effective mass $m^* = \dfrac{\hbar^2}{\dfrac{d^2E}{dk^2}} = \dfrac{\hbar^2}{2ta^2}$

Narrow bands → high effective mass

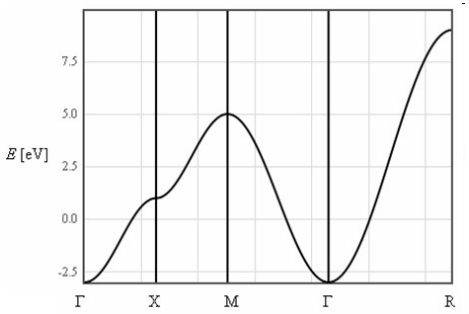
Density of states (simple cubic)



Calculate the energy for every allowed k in the Brillouin zone

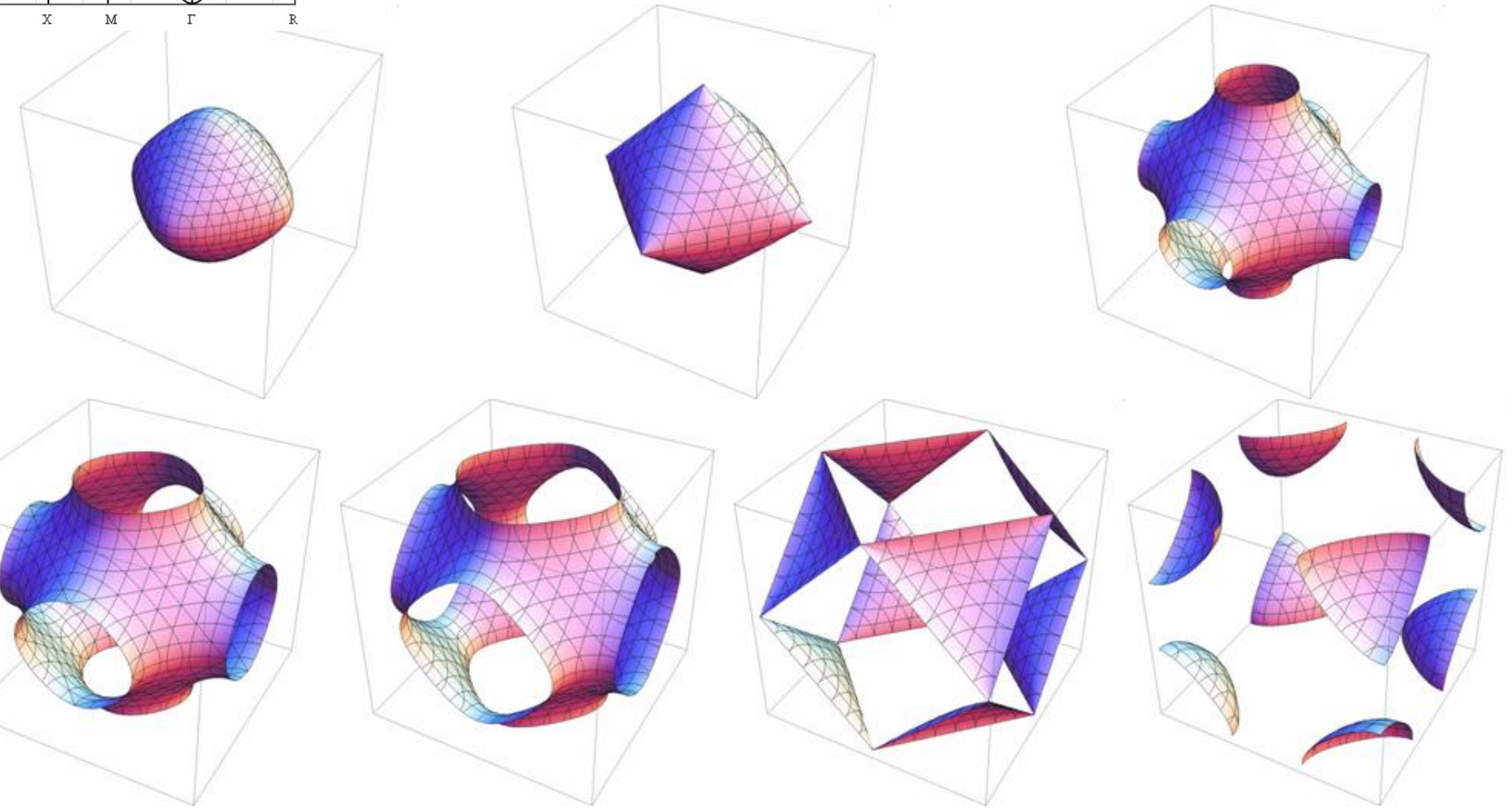
$$E = \varepsilon - 2t\left(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right)$$

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



Tight binding, simple cubic

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

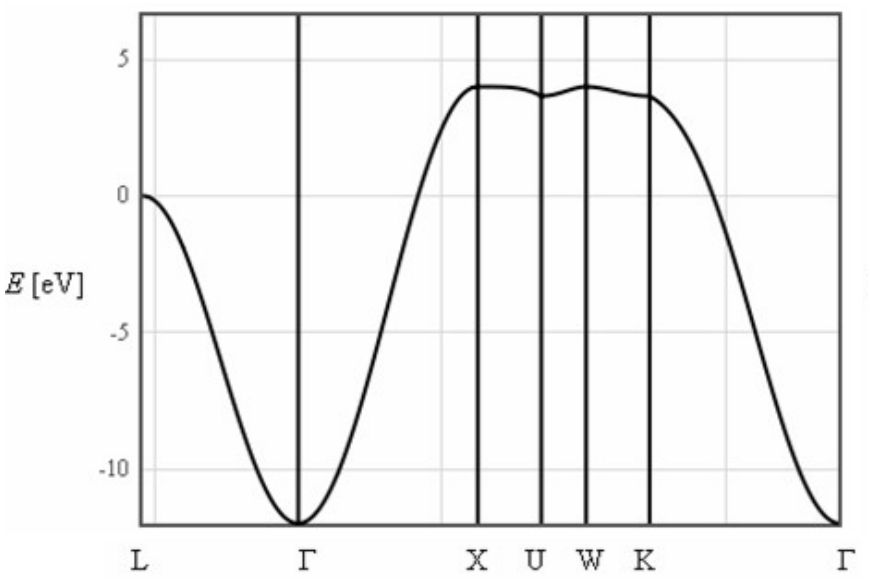


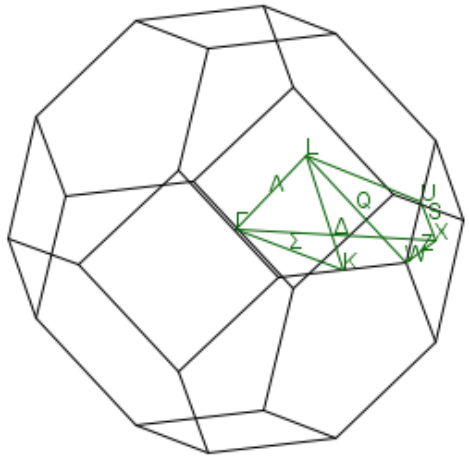
Christian Gruber, 2008

Tight binding, fcc

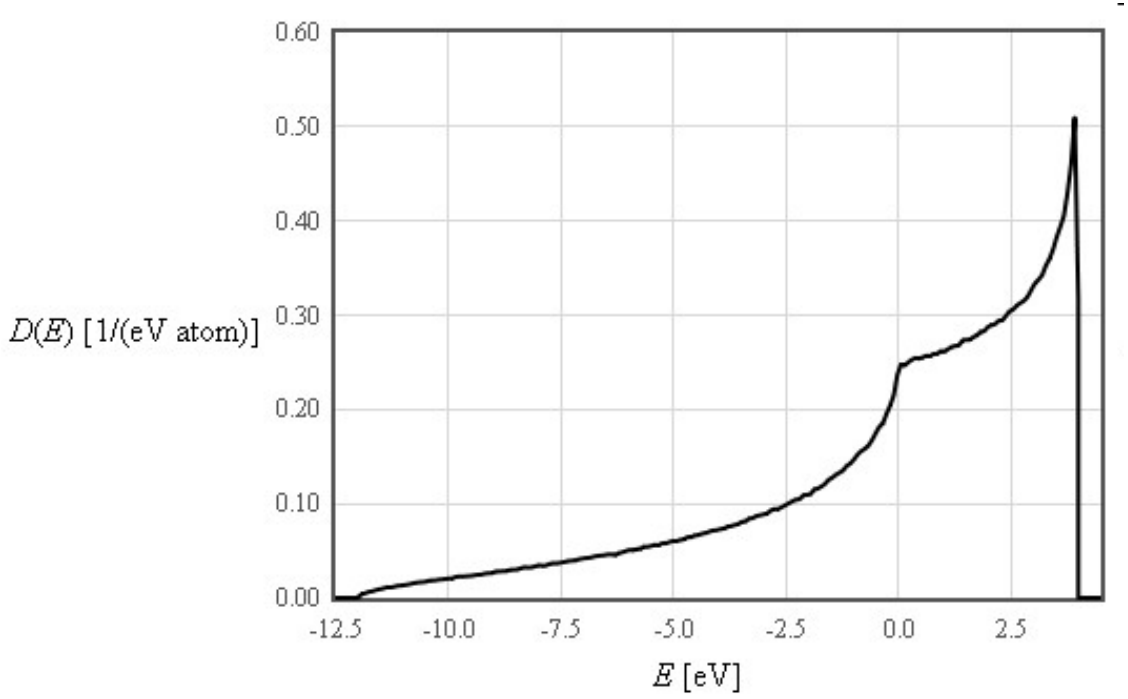
$$E = \varepsilon - t\sum_{m} e^{i\vec{k}\cdot\vec{\rho}_m}$$

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





Density of states (fcc)

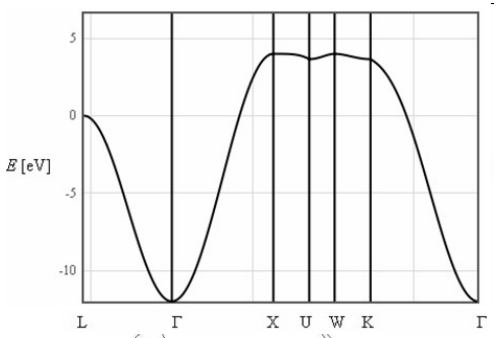


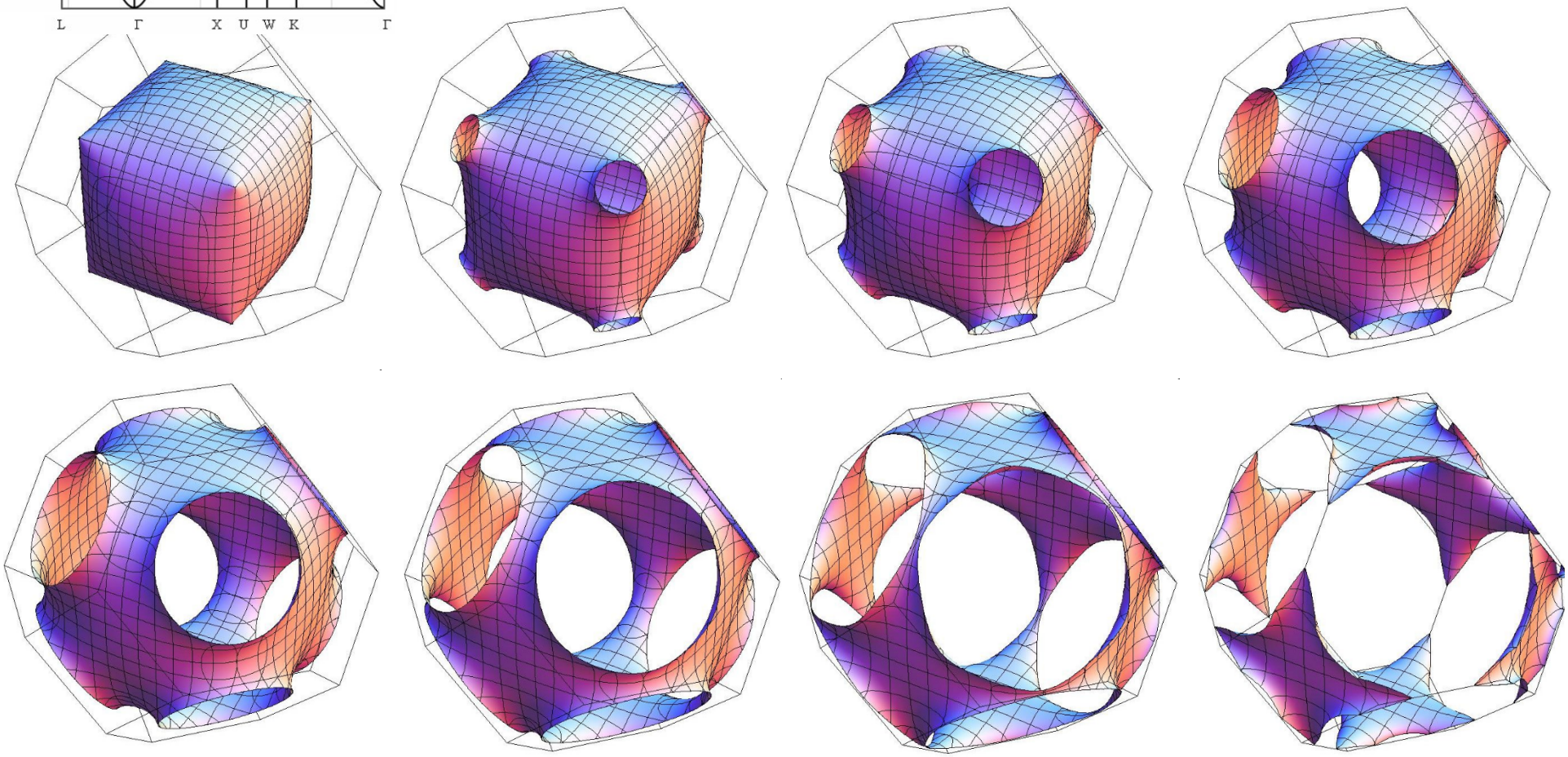
Calculate the energy for every allowed *k* in the Brillouin zone

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

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

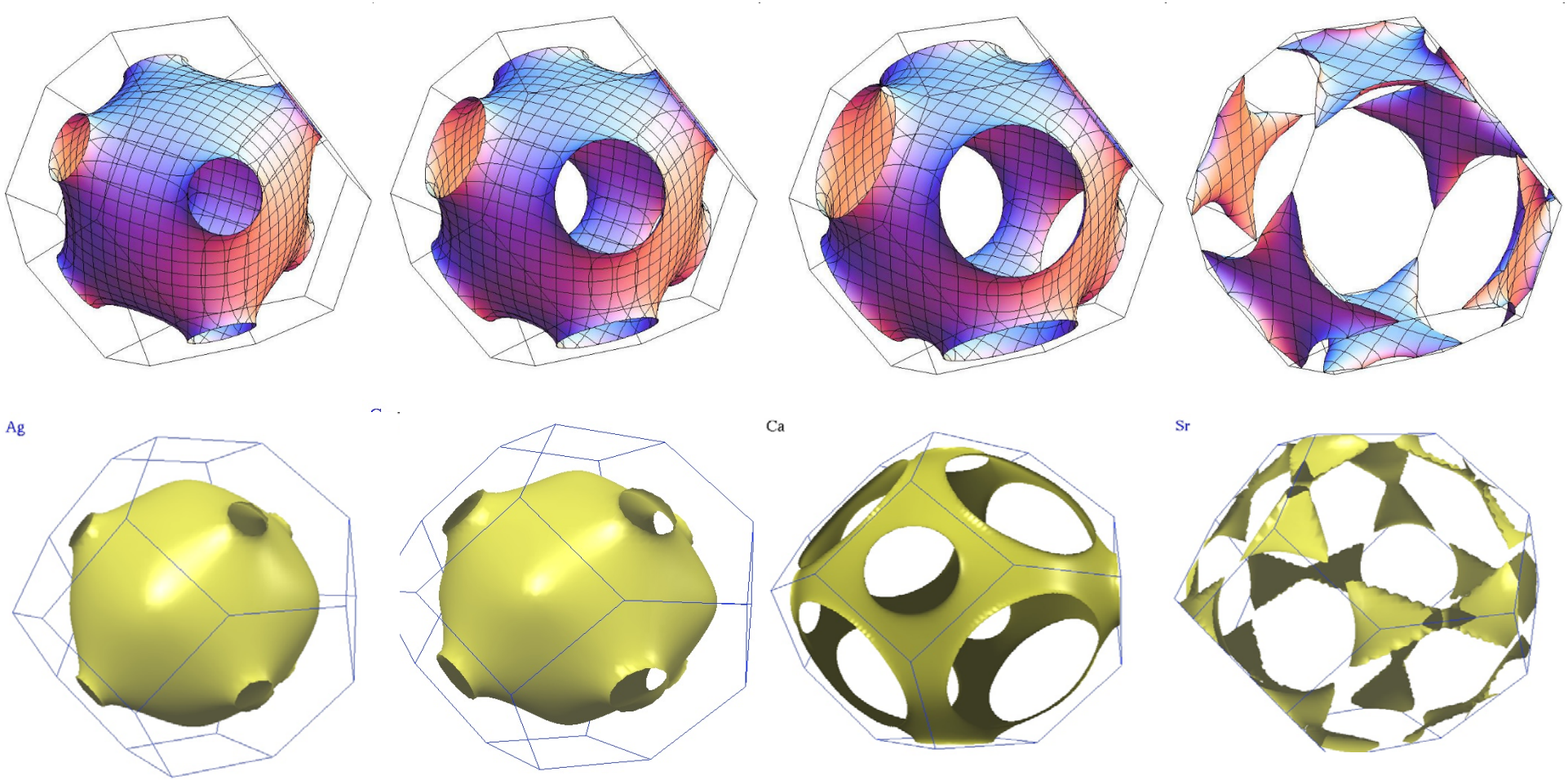
Tight binding, fcc





Christian Gruber, 2008

Tight binding, fcc



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