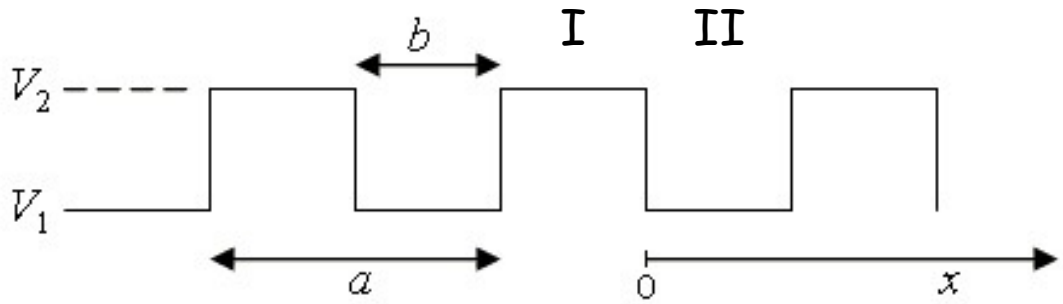
Kronig-Penney model

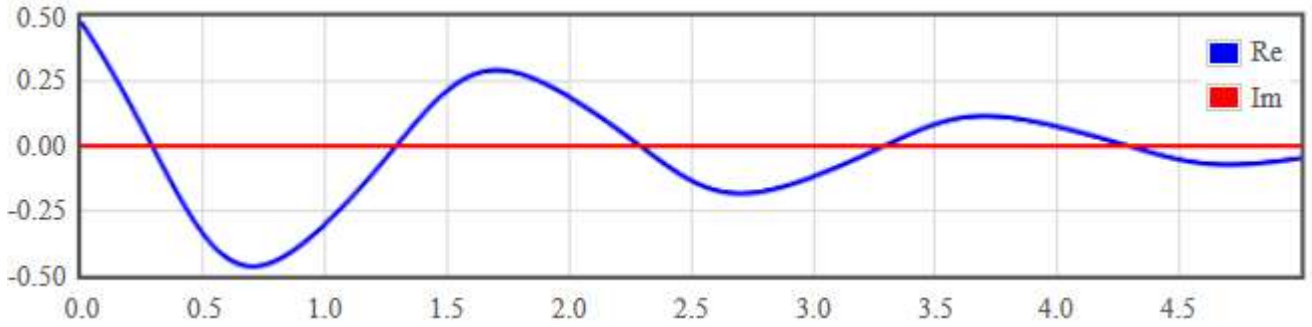


$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi=E\psi$$

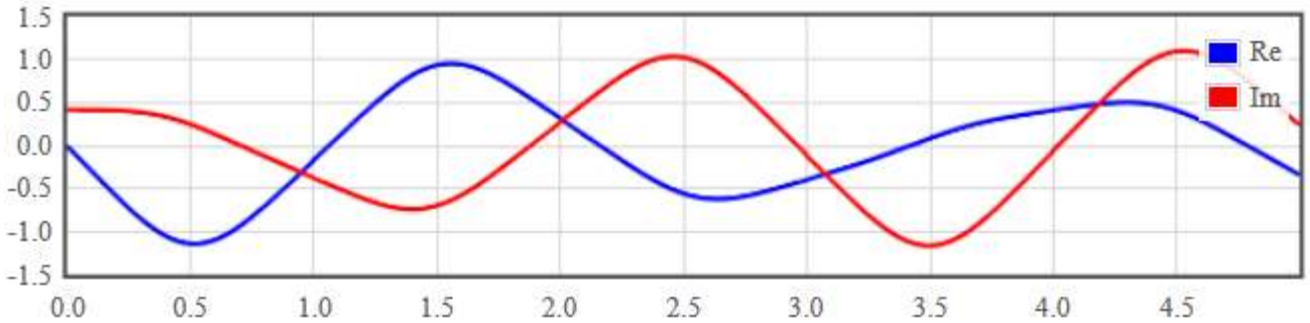
Solutions can be found in region I and region II
Match boundary conditions

Linear differential equations with periodic coefficients

Have exponentially decaying solutions,



or solutions of the form $e^{ikx}u_k(x)$

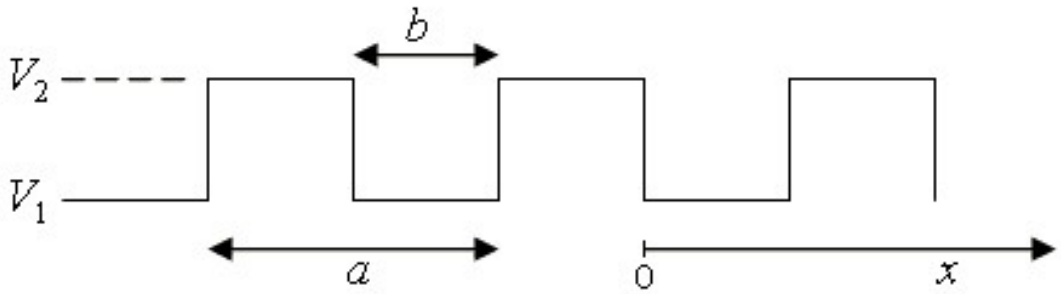


$$T\psi = \lambda\psi$$

$$Te^{ikx}u_k(x) = e^{ik(x+a)}u_k(x+a) = e^{ika}e^{ikx}u_k(x) = e^{ika}\psi$$

$$\lambda = e^{ika}$$

Kronig-Penney model

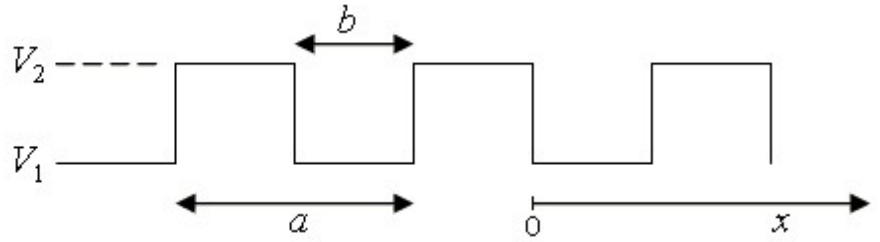


Solutions can be found that are simultaneous eigenfunctions of the Hamiltonian and the translation operator.

Eigenfunctions of the translation operator can be found in terms of any two linearly independent solutions. A convenient choice is:

$$\psi_1(0)=1, \qquad \frac{d\psi_1}{dx}(0)=0, \qquad \psi_2(0)=0, \qquad \frac{d\psi_2}{dx}(0)=1.$$

Kronig-Penney model



for $0 < x < b$

$$\psi_1(x) = \cos(k_1 x), \qquad \psi_2(x) = \frac{\sin(k_1 x)}{k_1}$$

for $b < x < a$

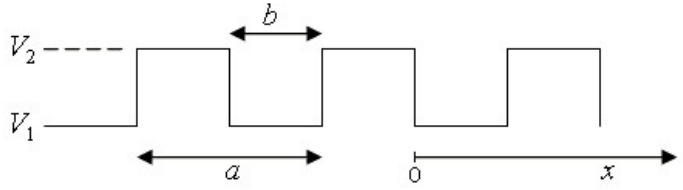
$$\psi_1(x) = \cos(k_2(x-b))\cos(k_1 b) - \frac{k_1 \sin(k_2(x-b))\sin(k_1 b)}{k_2},$$

$$\psi_2(x) = \frac{\cos(k_2(x-b))\sin(k_1 b)}{k_1} + \frac{\sin(k_2(x-b))\cos(k_1 b)}{k_2}.$$

Except for the coefficients, these are the same solutions as we found for light in a layered material.

Kronig-Penney model

at $x = a$



$$\psi_1(a) = \cos(k_2(a-b))\cos(k_1 b) - \frac{k_1 \sin(k_2(a-b))\sin(k_1 b)}{k_2},$$

$$\psi_2(a) = \frac{\cos(k_2(a-b))\sin(k_1 b)}{k_1} + \frac{\sin(k_2(a-b))\cos(k_1 b)}{k_2}.$$

The translation operator translates the function a distance *a*.

$$\begin{bmatrix} \psi_1(x+a) \\ \psi_2(x+a) \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \end{bmatrix}.$$

The elements of the translation operator can be evaluated at $x = a$.

Kronig-Penney model

$$\begin{bmatrix} \psi_1(x+a) \\ \psi_2(x+a) \end{bmatrix} = \begin{bmatrix} \psi_1(a) & \frac{d\psi_1}{dx}(a) \\ \psi_2(a) & \frac{d\psi_2}{dx}(a) \end{bmatrix} \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \end{bmatrix}$$

The eigen functions and eigen values are

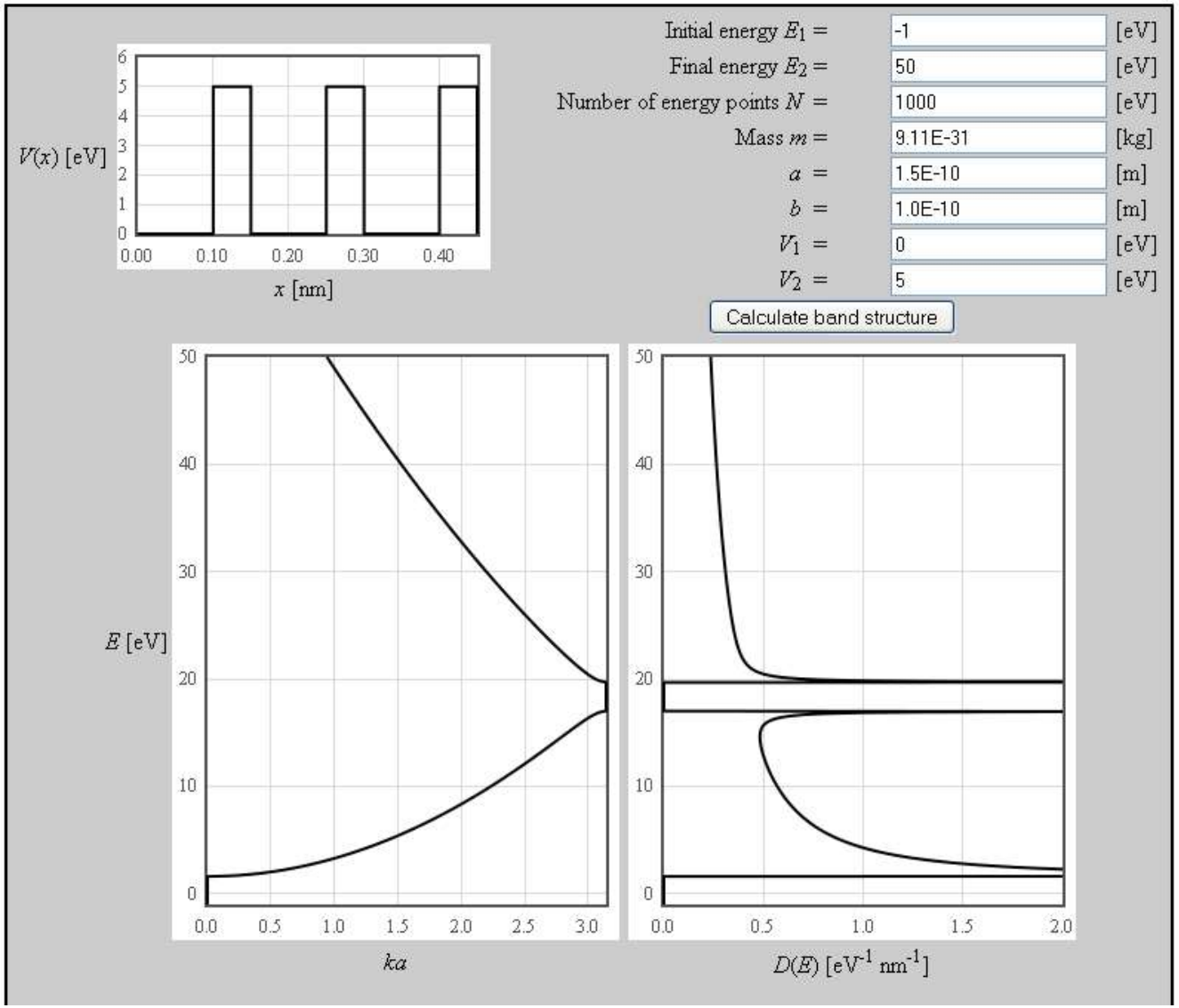
$$\psi_{\pm}(x) = \frac{2\psi_2(a)}{\frac{d\psi_2(a)}{dx} - \psi_1(a) \pm \delta}\psi_1(x) + \psi_2(x), \qquad \lambda\pm = \frac{1}{2}(\alpha \pm \delta),$$

$$\delta = \sqrt{\alpha^2 - 4}$$

$$\alpha = \psi_1(a) + \frac{d\psi_2(a)}{dx} = 2\cos\left(k_2(a-b)\right)\cos(k_1 b) - \left(\frac{k_2}{k_1} + \frac{k_1}{k_2}\right)\sin\left(k_2(a-b)\right)\sin(k_1 b).$$

If $\alpha > 2$, the potential acts like a mirror for electrons

Kronig-Penney model



$$E \rightarrow k_1, k_2$$

$$\alpha(k_1, k_2, V_1, V_2, a, b)$$

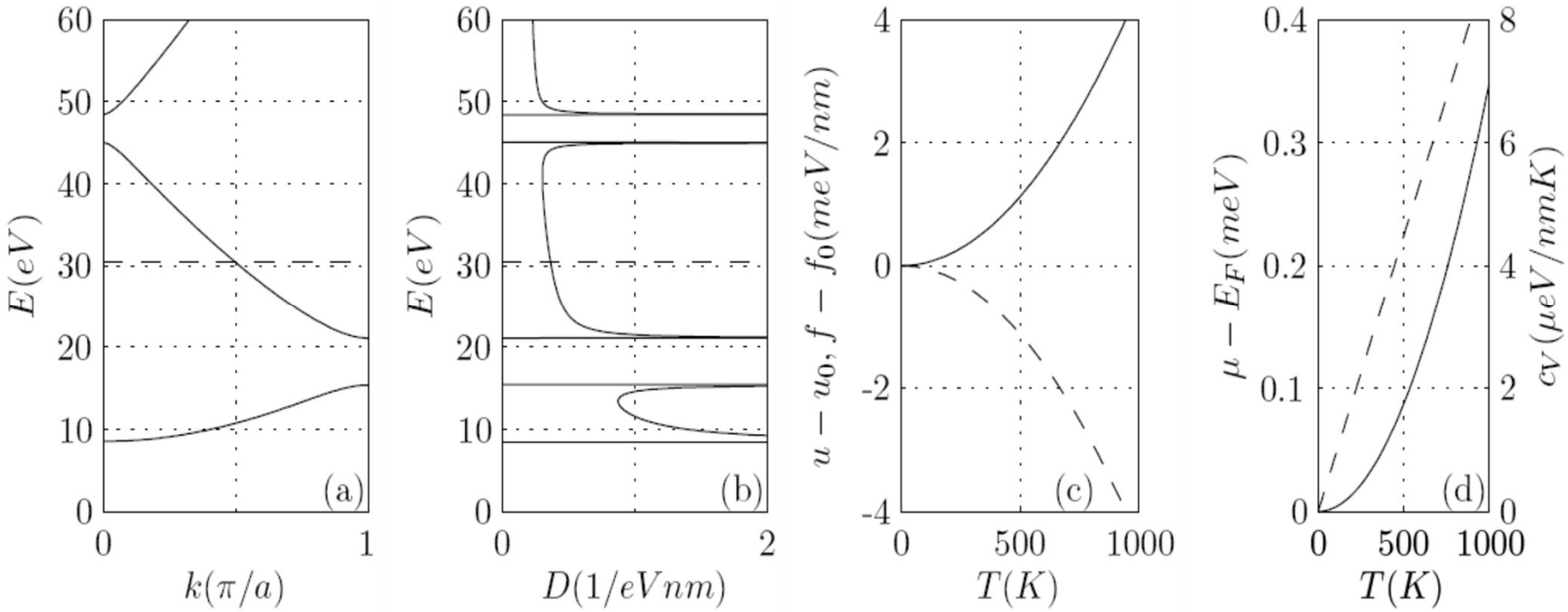
$$\delta = \sqrt{\alpha^2 - 4}$$

$$\lambda\pm = \frac{1}{2}(\alpha \pm \delta)$$

$$\lambda = e^{ika}$$

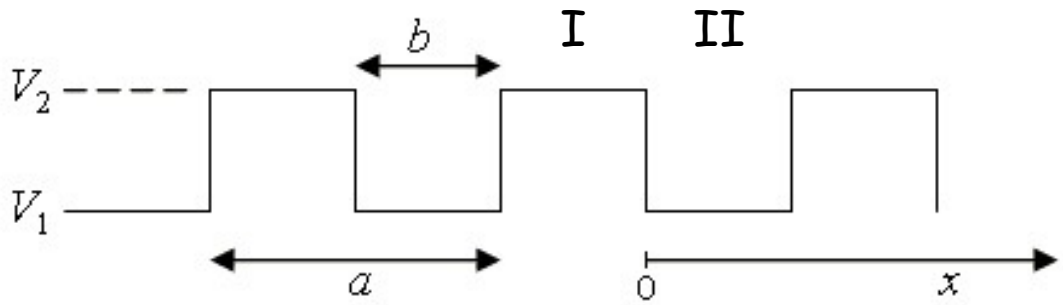
$$k = \pm\frac{1}{a}\tan^{-1}\left(\frac{\sqrt{4-\alpha^2}}{\alpha}\right)$$

Kronig-Penney model



(a) The energy-wave number dispersion relation. The dashed line is the Fermi energy. (b) The density of states. (c) The internal energy density (solid line) and Helmholtz free energy density (dashed line). (d) The chemical potential (solid line) and the specific heat (dashed line). All of the plots were drawn for a square wave potential with the parameters: $V = 12.5$ eV, $a = 2 \times 10^{-10}$ m, $b = 5 \times 10^{-11}$ m, and an electron density of $n = 3$ electrons/primitive cell.

A separable potential

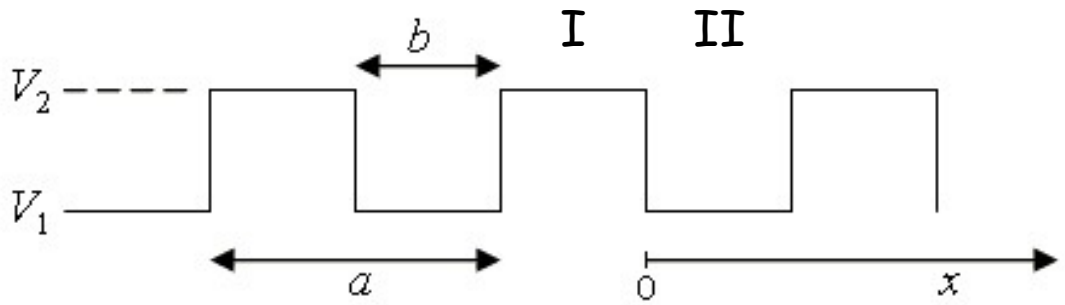


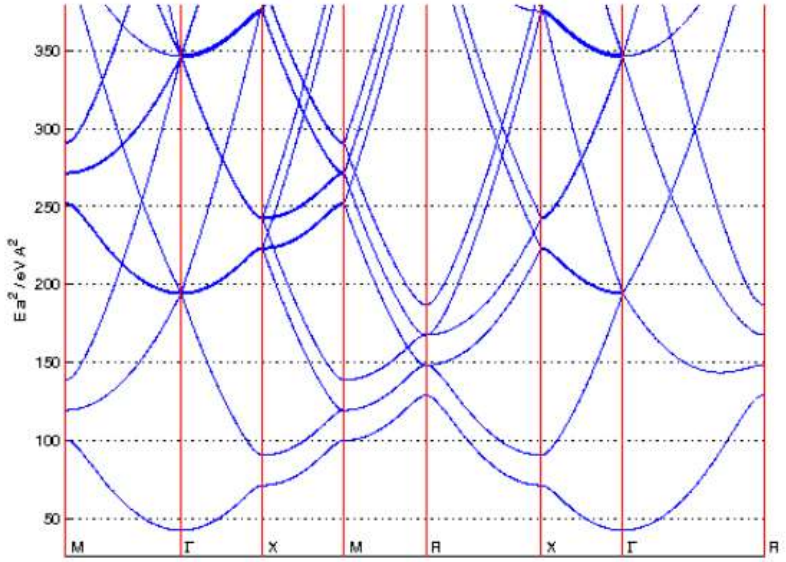
$$-\frac{\hbar^2}{2m}\nabla^2\Psi+(V(x)+V(y)+V(z))\Psi=E\Psi$$

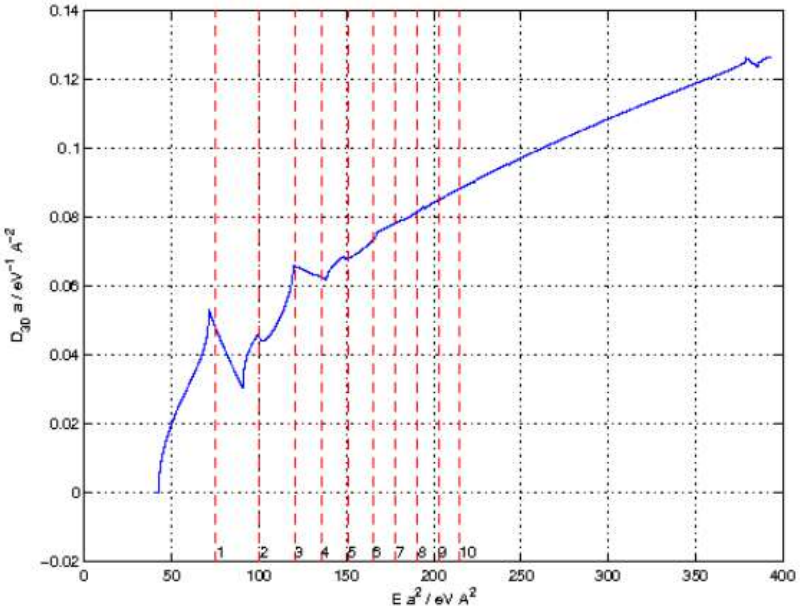
Ψ is the product of the solutions to the Kronig-Penney model.

$$\Psi(x,y,z)=\psi_{KP}(x)\psi_{KP}(y)\psi_{KP}(z)$$

A separable potential

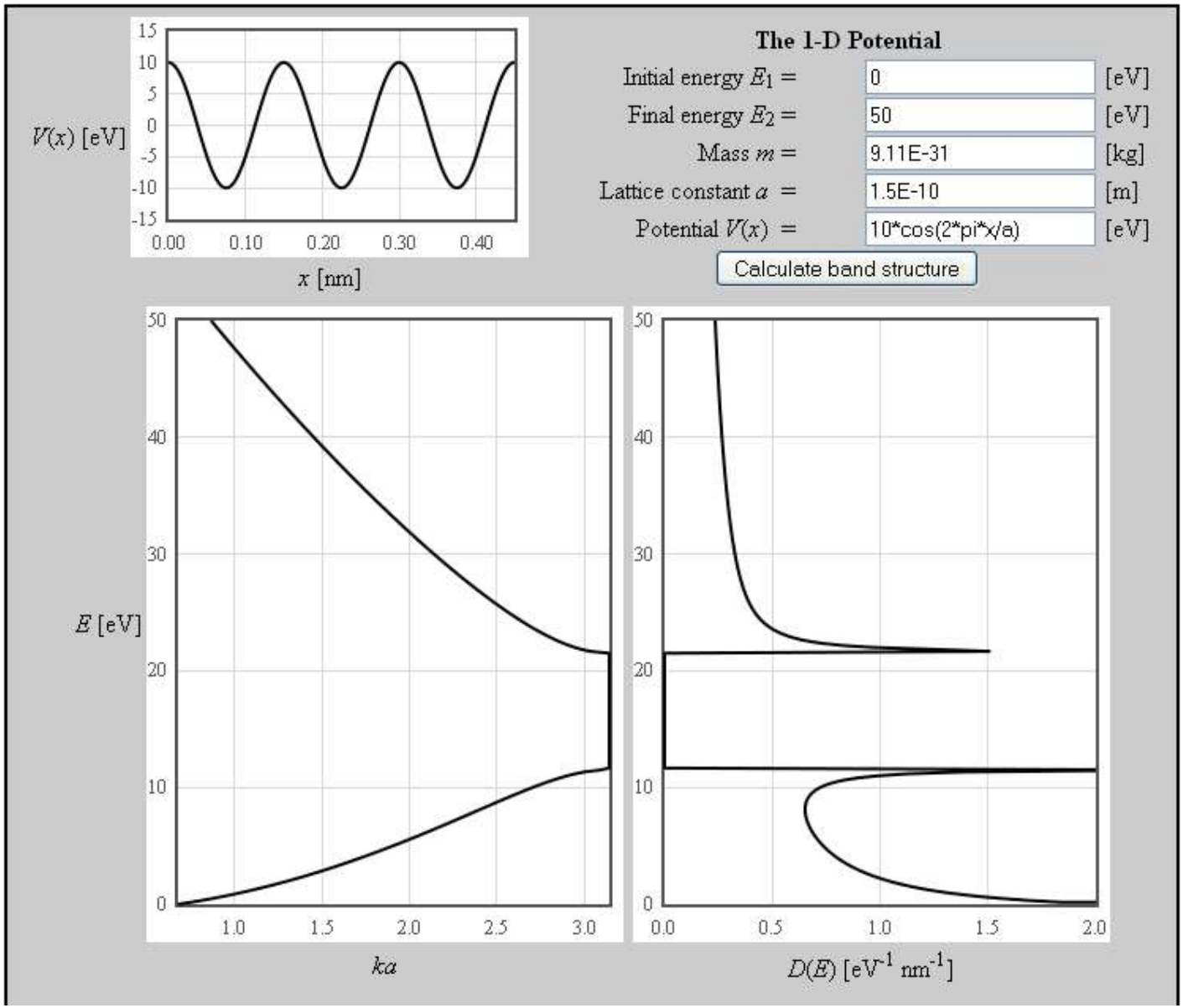






http://lampx.tugraz.at/~hadley/ss1/separablecrystals/thermo.html

Band structure in 1-D



Bloch Theorem

$$\psi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$ ← Any wave function that satisfies periodic boundary conditions

$$\psi(\vec{r}) = \sum_{\vec{k}\in 1Bz} \sum_{\vec{G}} C_{\vec{k}+\vec{G}} e^{i\left(\vec{k}+\vec{G}\right)\cdot\vec{r}}$$

These *k*'s label the symmetries

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

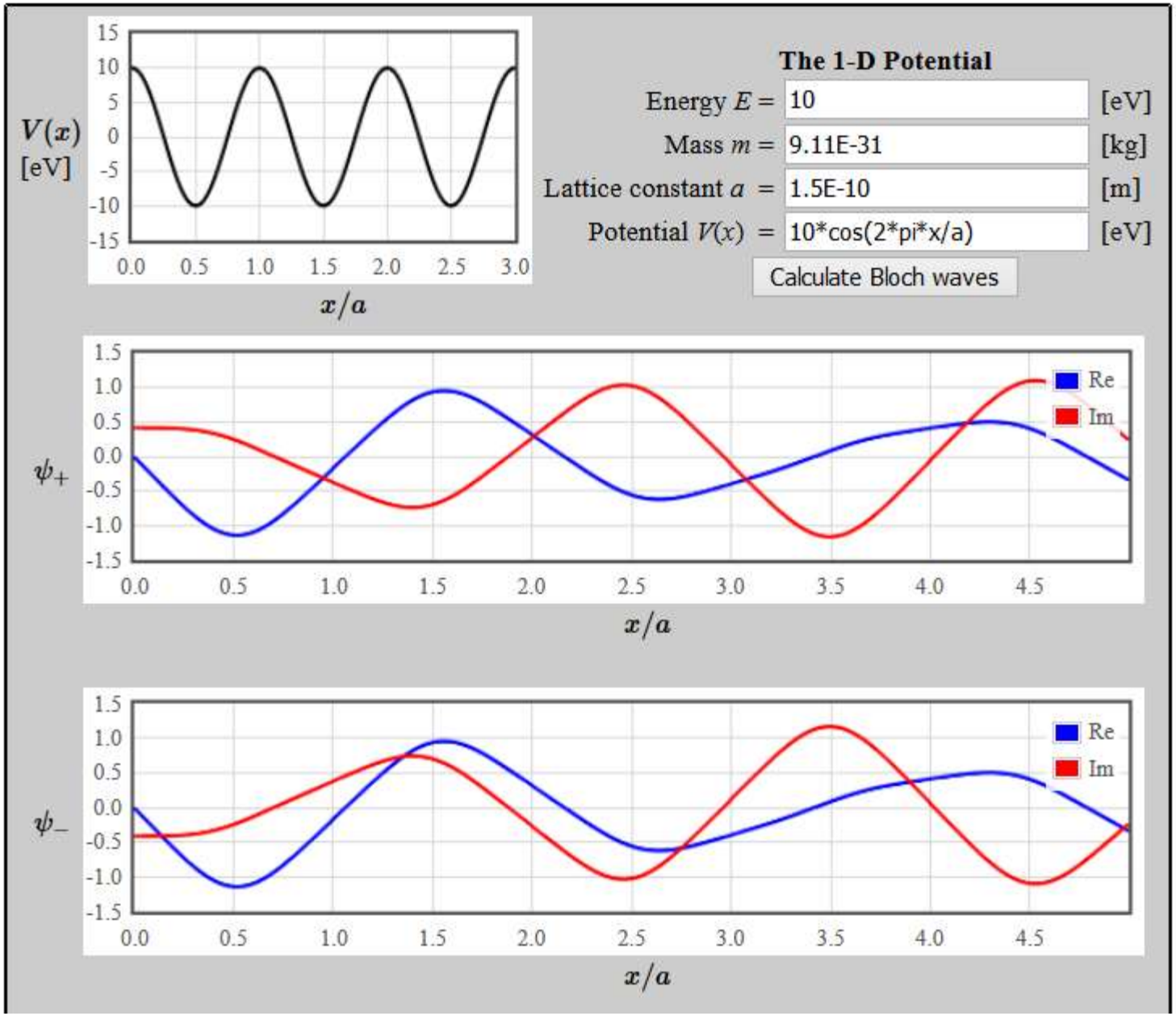
periodic function

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

$$T_{mnl}\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot(\vec{r}+m\vec{a}_1+n\vec{a}_2+l\vec{a}_3)} u_{\vec{k}}(\vec{r}+m\vec{a}_1+n\vec{a}_2+l\vec{a}_3) = e^{i\vec{k}\cdot(m\vec{a}_1+n\vec{a}_2+l\vec{a}_3)}\psi_{\vec{k}}(\vec{r})$$

Eigen function solutions of the Schrödinger equation have Bloch form.

Bloch waves in 1-D



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

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

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

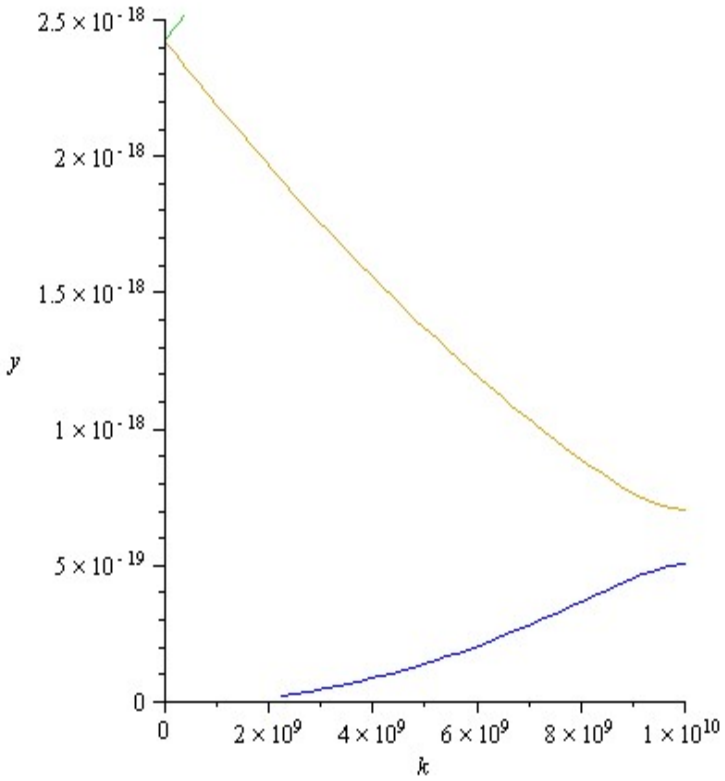
Central equations couple coefficients k to other coefficients that differ by a reciprocal lattice wavevector G.

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

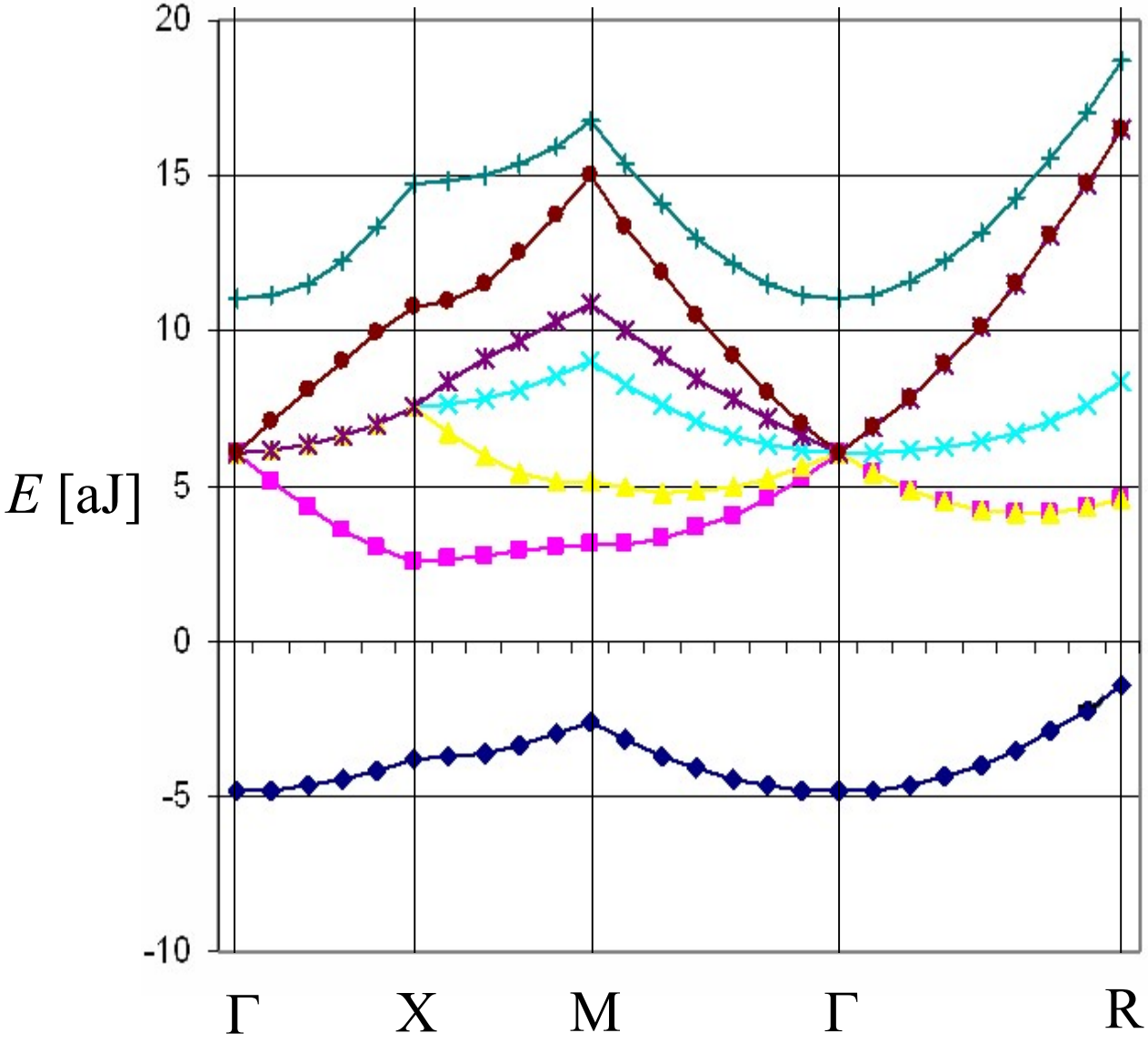
diagonal elements: $$\frac{\hbar^2}{2m}\left(\vec{k} - \vec{G}_i\right)^2$$

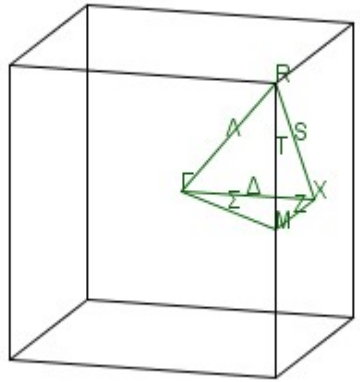
off-diagonal elements: $$\frac{-Ze^2}{V_{\text{unit cell}}\varepsilon_0 \left(\vec{G}_i - \vec{G}_j\right)^2}$$

Central equations - simple cubic

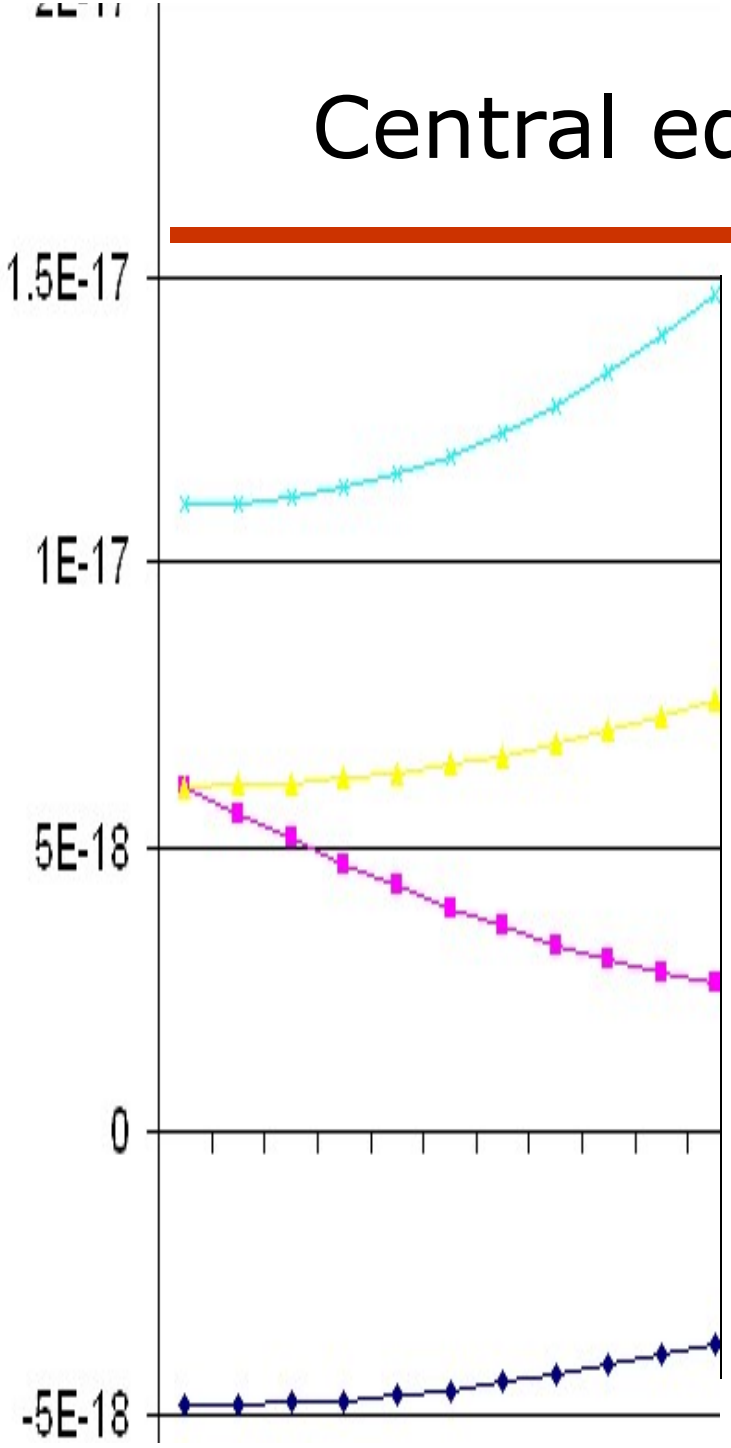
$$
\begin{pmatrix}
\frac{\hbar^2\left(\vec{k}+\frac{2\pi}{a}\hat{k}_z\right)^2}{2m} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{4V_{\text{unit cell}}\varepsilon_0\pi^2} & \frac{-Ze^2a^2}{8V_{\text{unit cell}}\varepsilon_0\pi^2}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

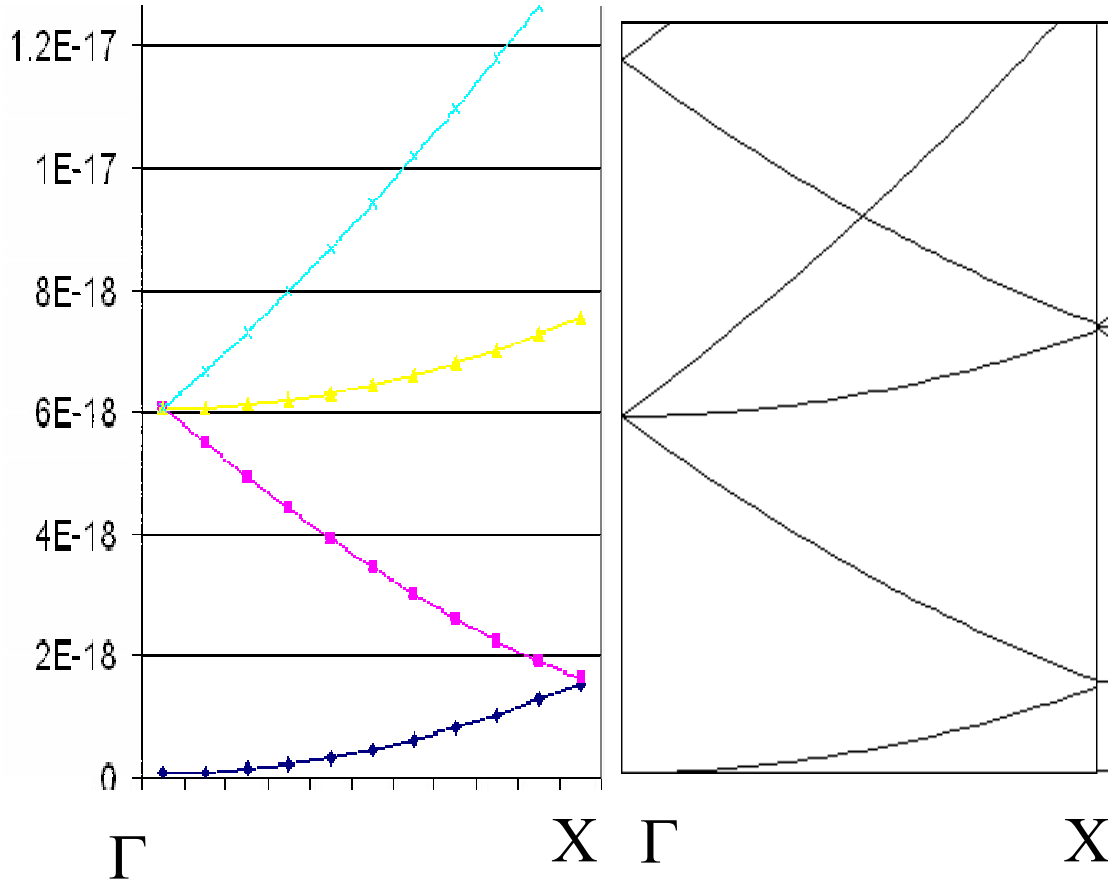




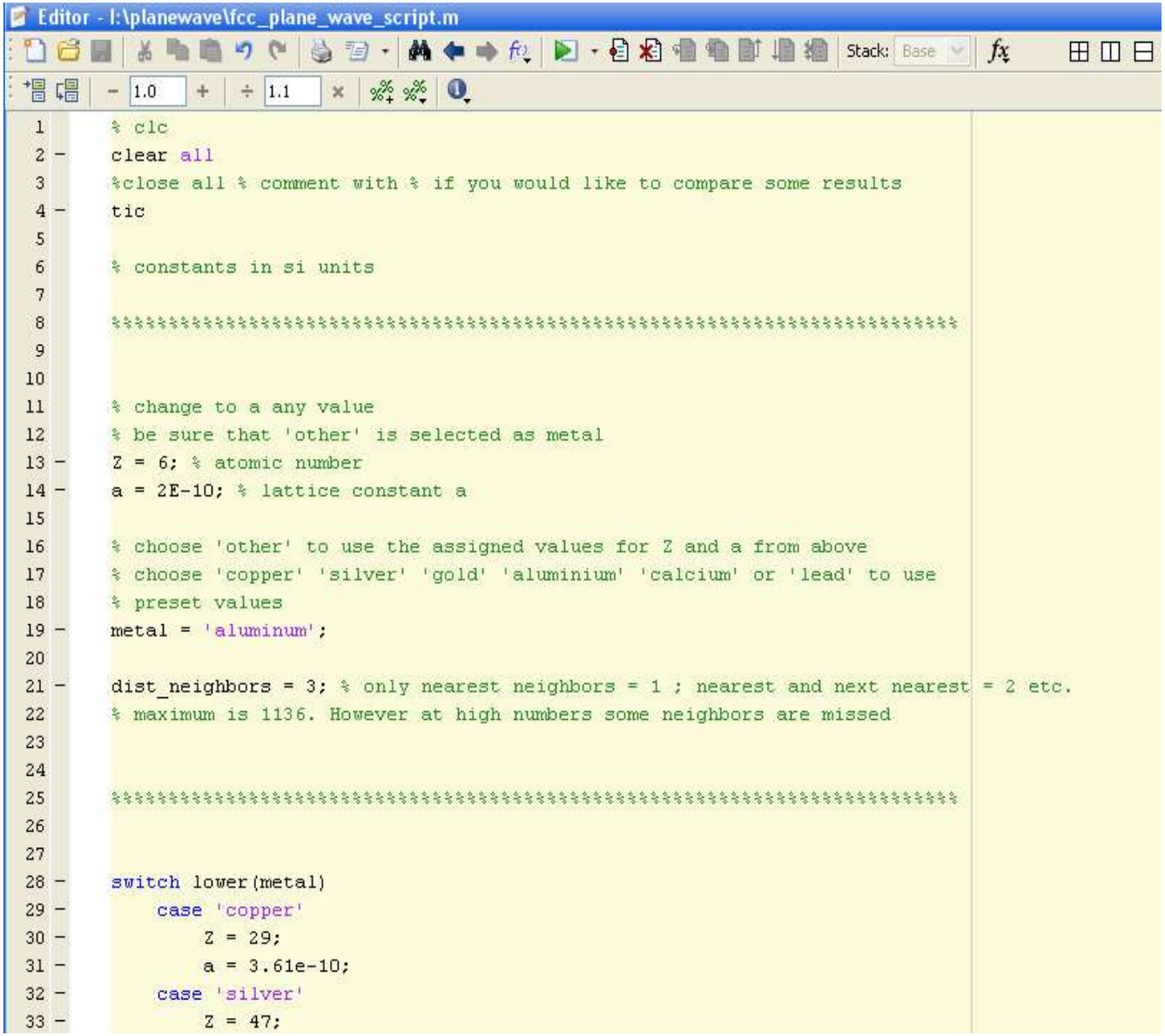
Central equations - simple cubic



empty lattice



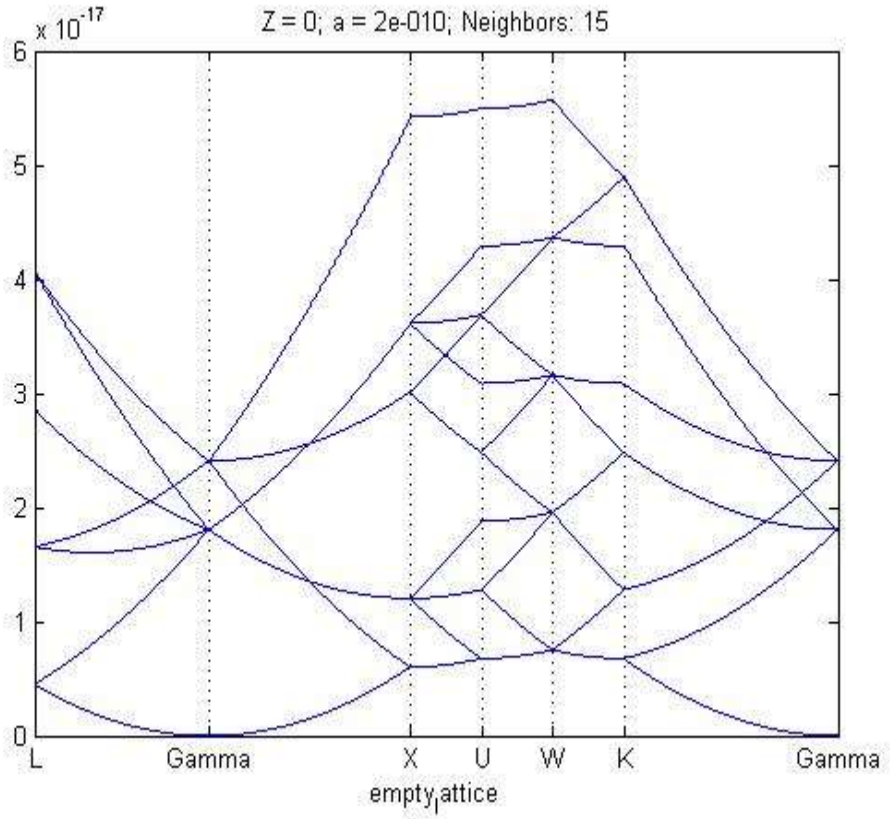
Plane wave method



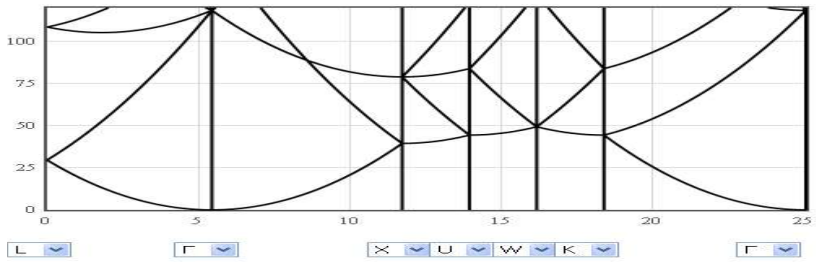

```
% clc
clear all
%close all % comment with % if you would like to compare some results
tic

% 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

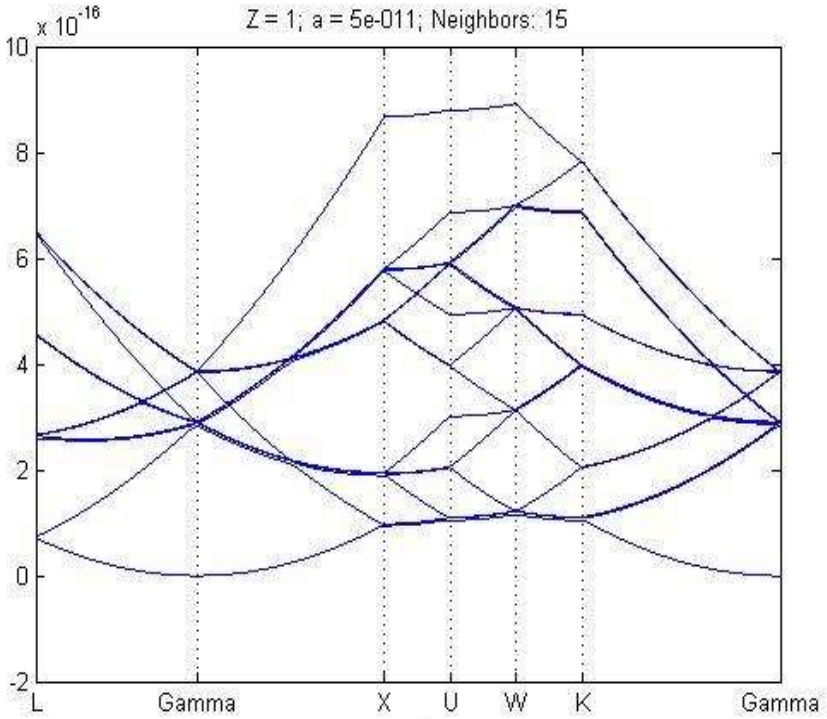


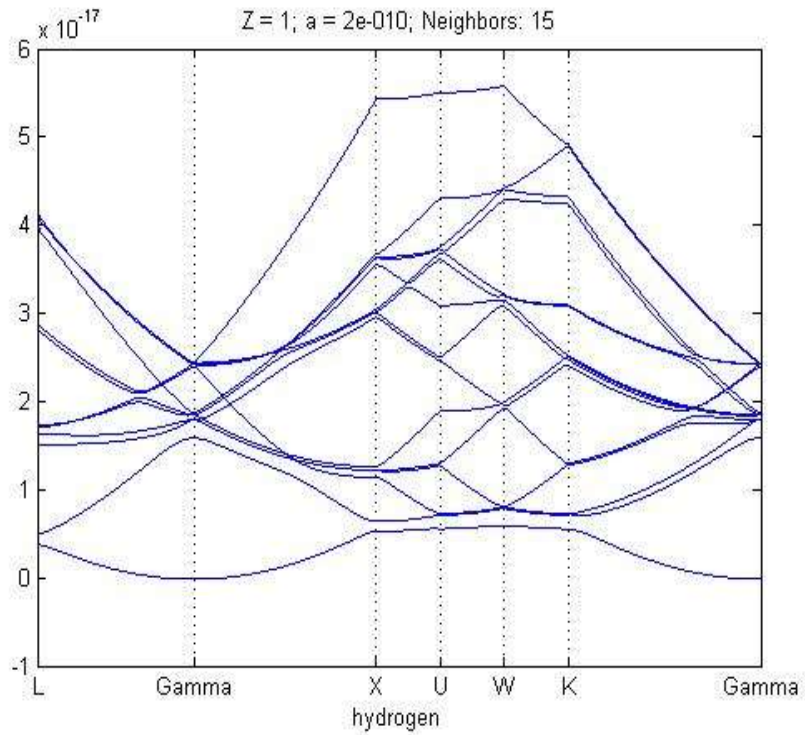
empty lattice



Plane wave method

fcc hydrogen





Approximate solution near the Bz boundary

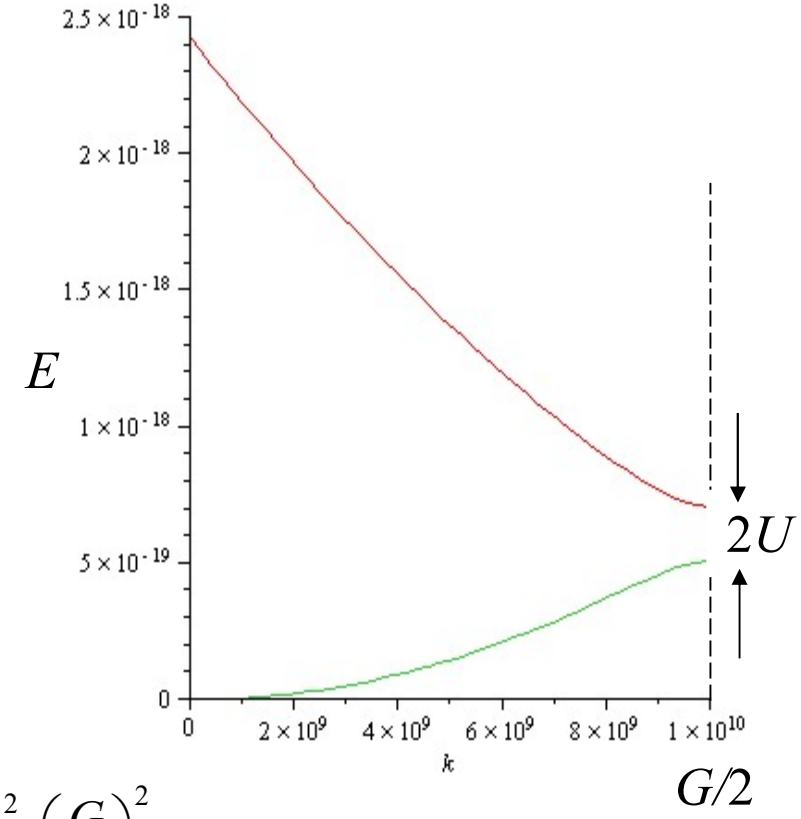
$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_k + \sum_G U_G C_{k-G} = 0$$

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 $k \sim G/2$

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



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

Review: Molecules

Start with the full Hamiltonian

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

Use the Born-Oppenheimer approximation

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

Neglect the electron-electron interactions. H_{elec} is then a sum of H_{MO}.

$$H_{MO} = \frac{-\hbar^2}{2m_e}\nabla_1^2 - \sum_A \frac{Z_A e^2}{4\pi\varepsilon_0 \left|r_1 - r_A\right|}$$

The molecular orbital Hamiltonian can be solved numerically or by the Linear Combinations of Atomic Orbitals (LCAO)