20.Electron Bands

June 7, 2018

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

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

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

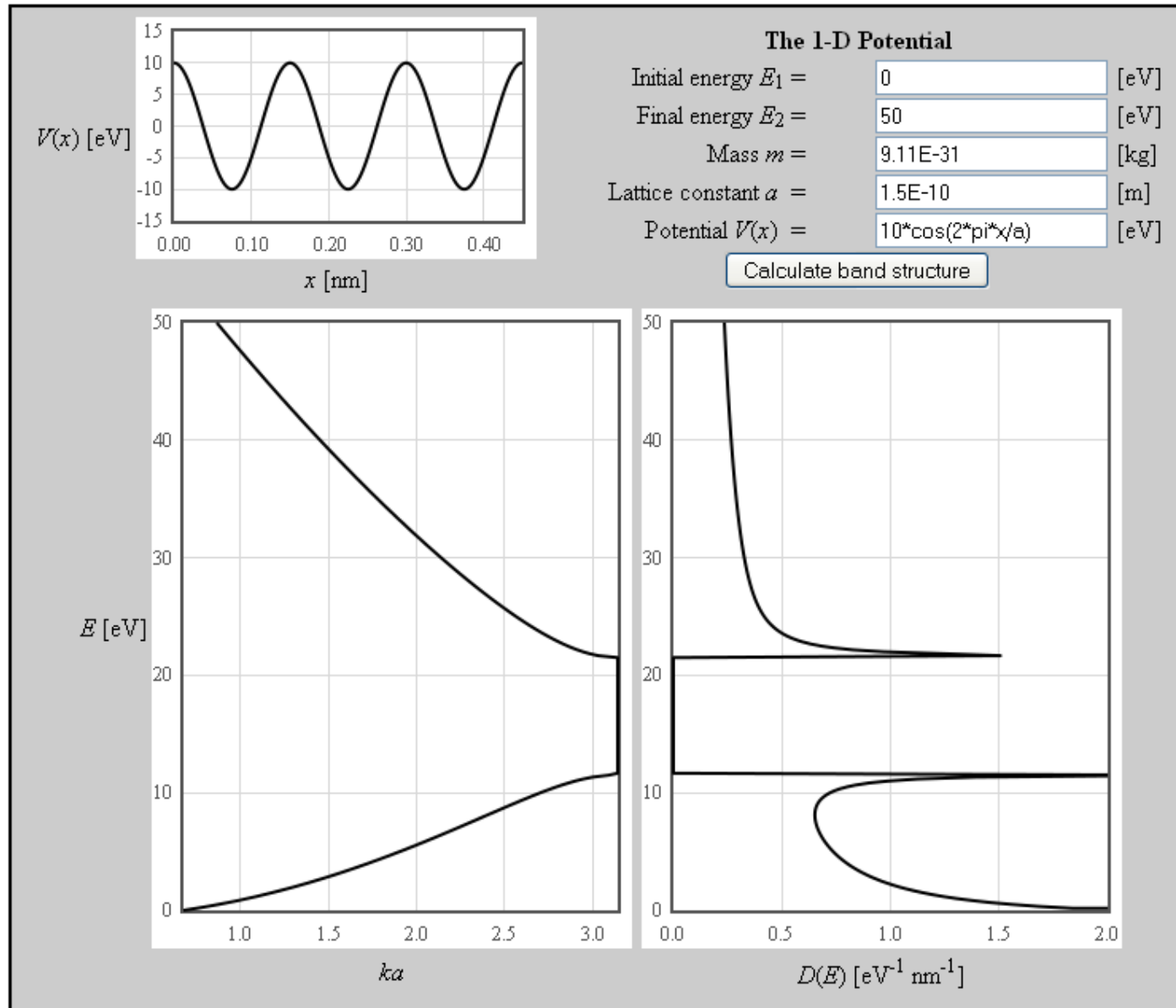These k's label the symmetries

periodic function

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

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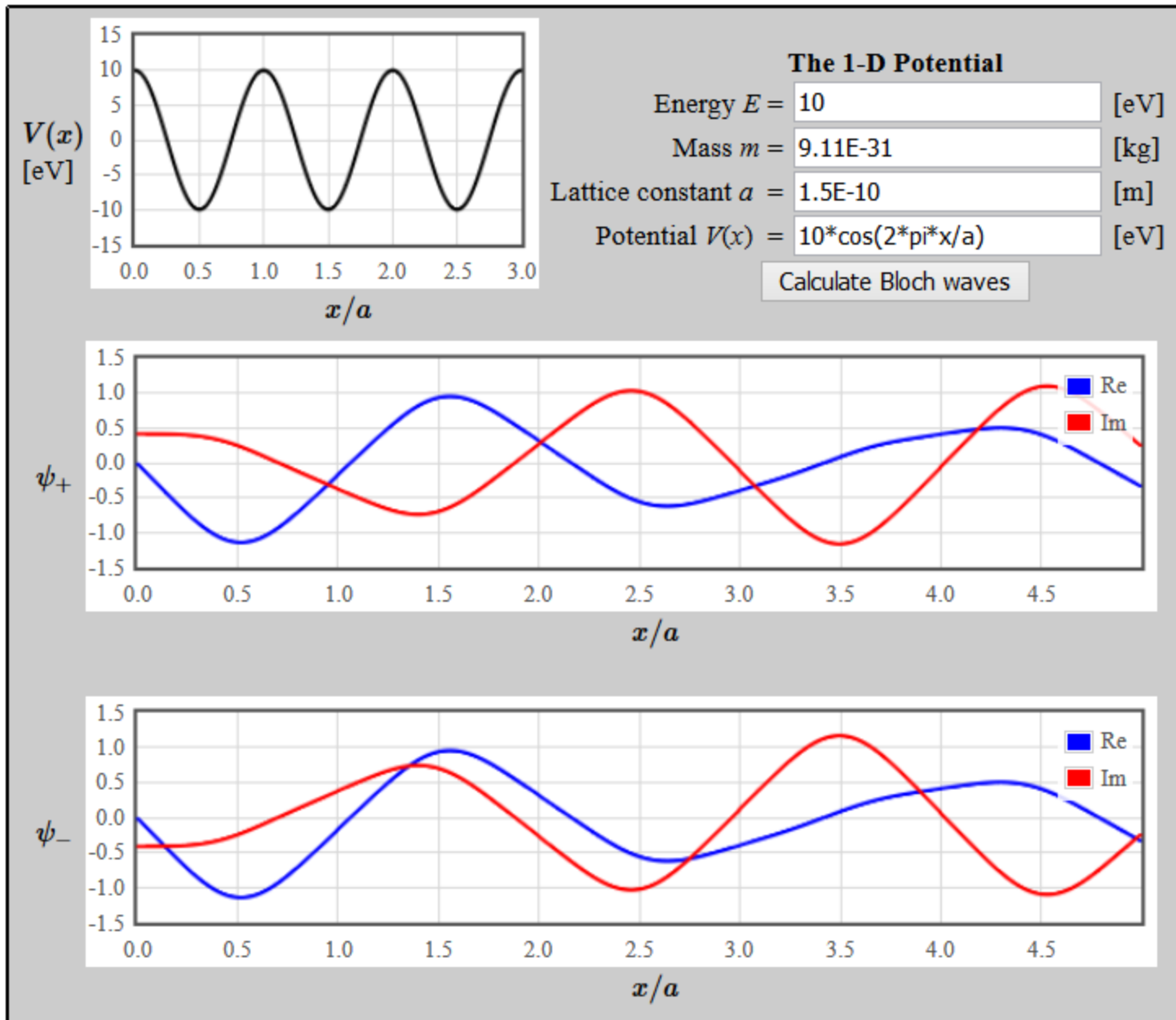
Bloch form $\qquad \psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$

Eigen function solutions of the Schrödinger equation have Bloch form.

Band structure in 1-D

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.

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

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

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

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

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

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

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

Central equations - one dimension

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

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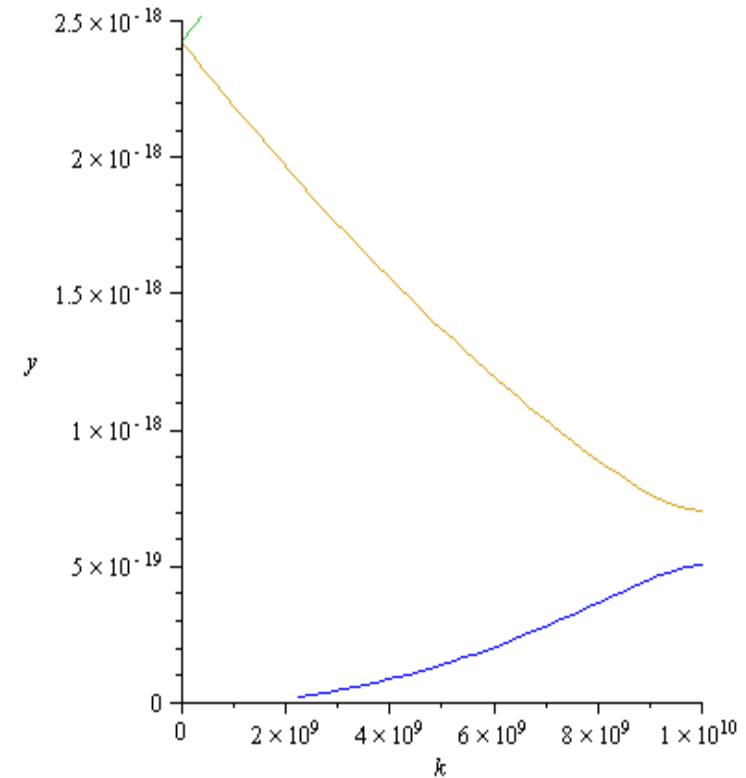C_k \\
C_{k-G_0} \\
C_{k-2G_0} \\
\vdots
\end{bmatrix} = 0
$$

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

Central equations - one dimension

$$M4 := \begin{bmatrix} \dfrac{\text{hbar}^2 \cdot (k + 2 \cdot G)^2}{2\,m} & U & 0 & 0 \\[2mm] U & \dfrac{\text{hbar}^2 \cdot (k + G)^2}{2\,m} & U & 0 \\[2mm] 0 & U & \dfrac{\text{hbar}^2 \cdot k^2}{2\,m} & U \\[2mm] 0 & 0 & U & \dfrac{\text{hbar}^2 \cdot (k - G)^2}{2\,m} \end{bmatrix} :$$

$V4 := Eigenvalues(M4) :$

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

Central equations 3d - simple cubic

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

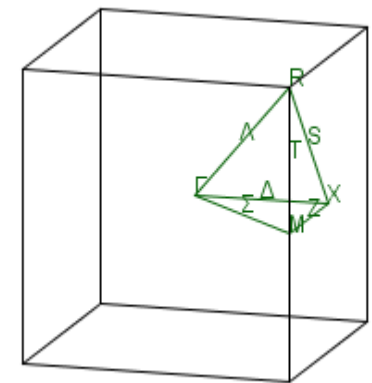Molecular orbital Hamiltonian
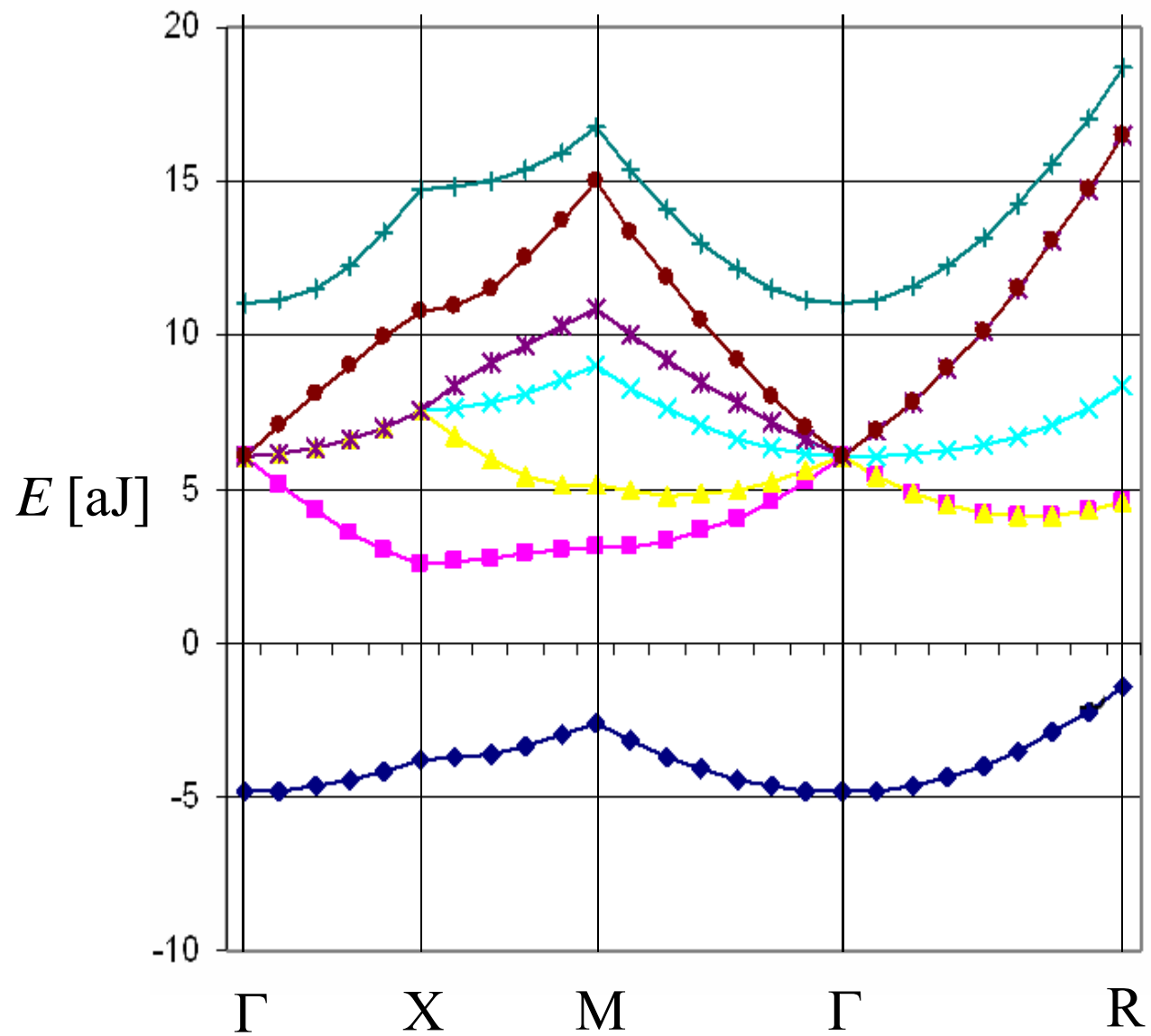
$$U_{\vec{G}} = \frac{-Ze^2}{V_{\text{unit cell}}\varepsilon_0 G^2}$$

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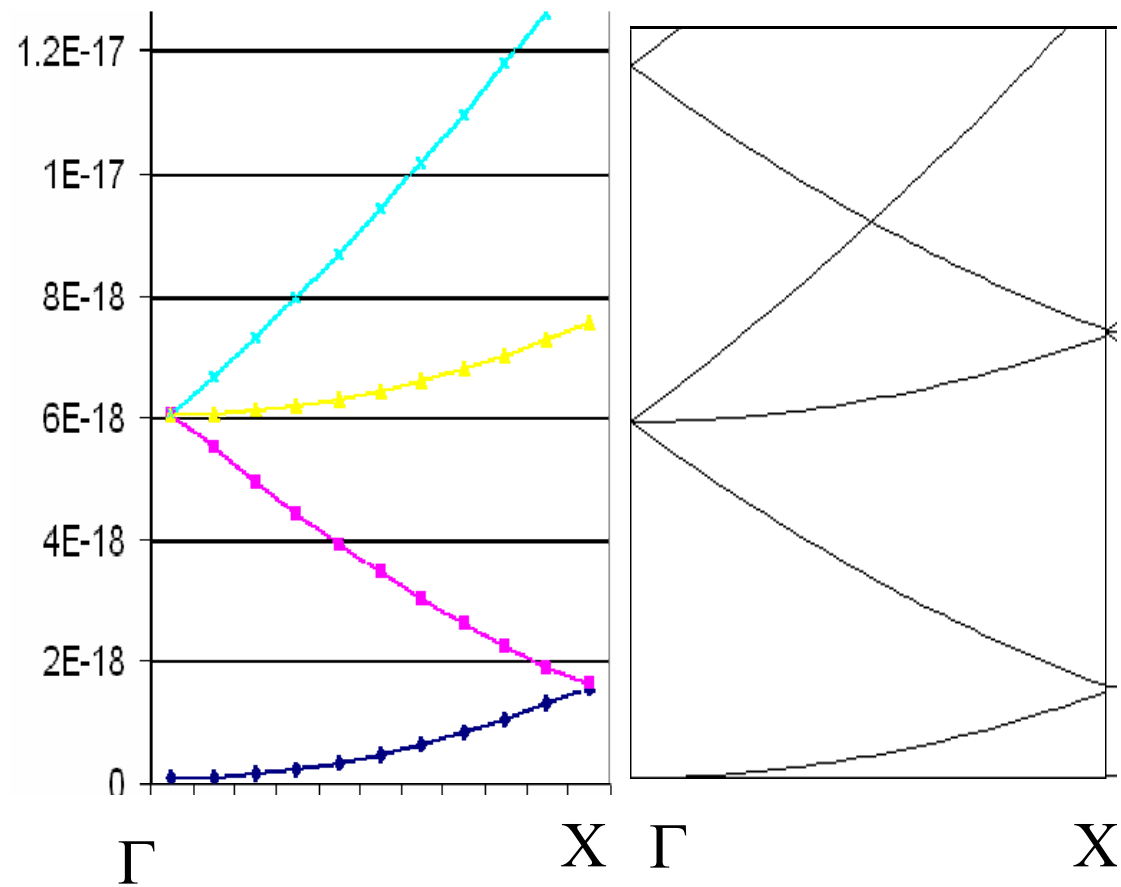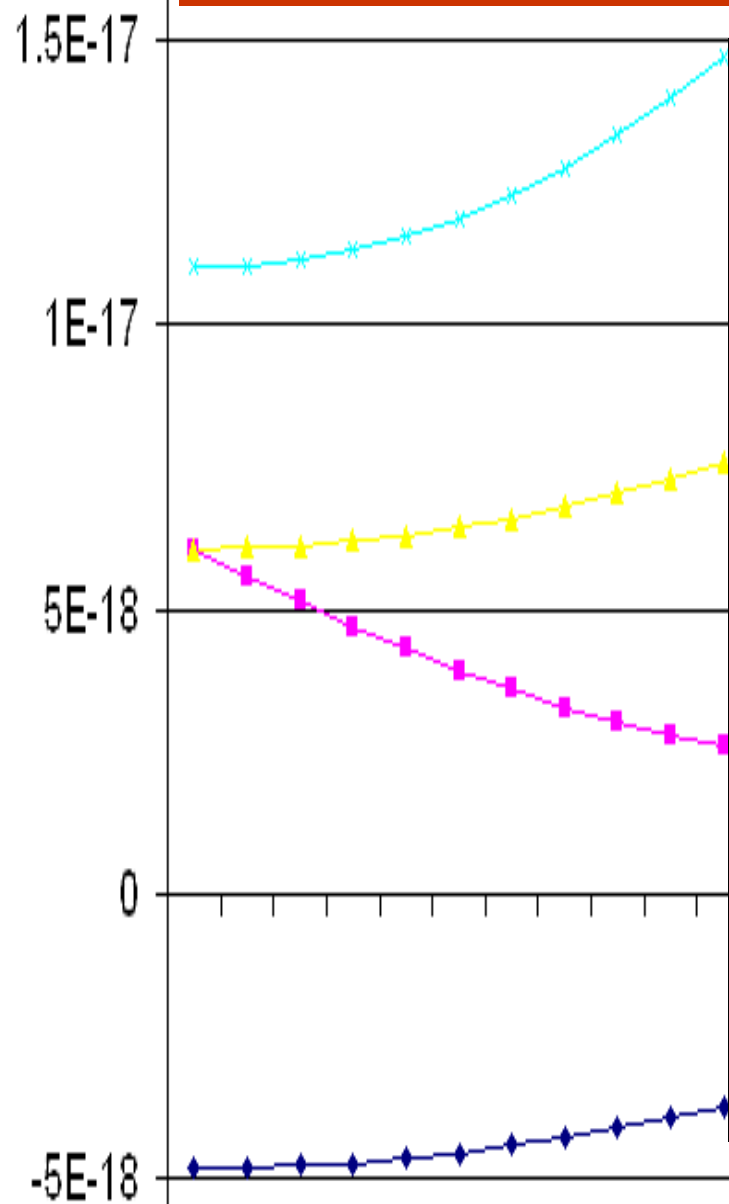$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} = 0$$

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

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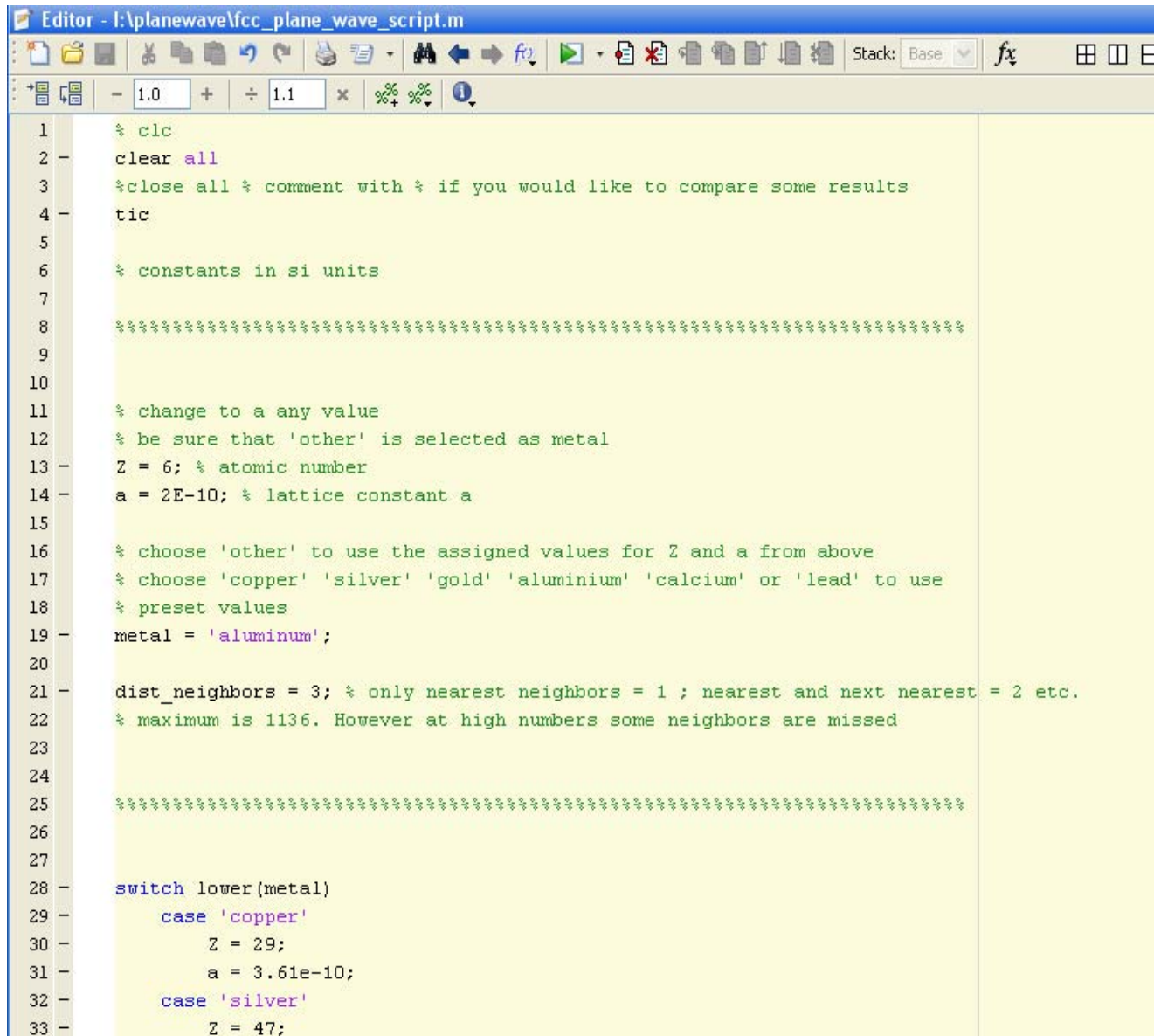$$\frac{-Ze^2}{V_{\text{unit cell}}\varepsilon_0 \left(\vec{G}_i - \vec{G}_j\right)^2}$$

Central equations - simple cubic

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

Central equations - simple cubic

Central equations - simple cubic

empty lattice

Plane wave method
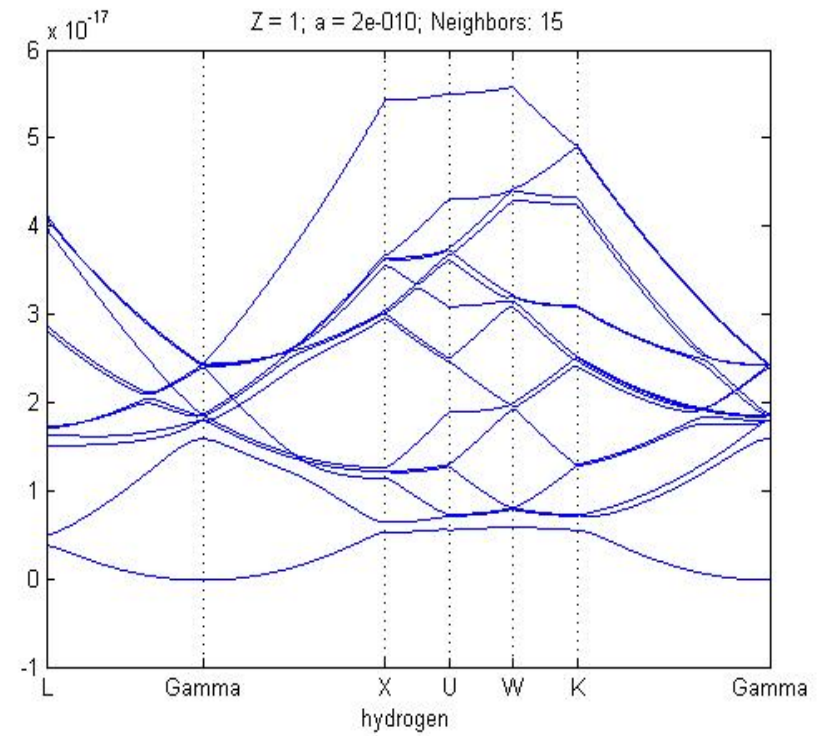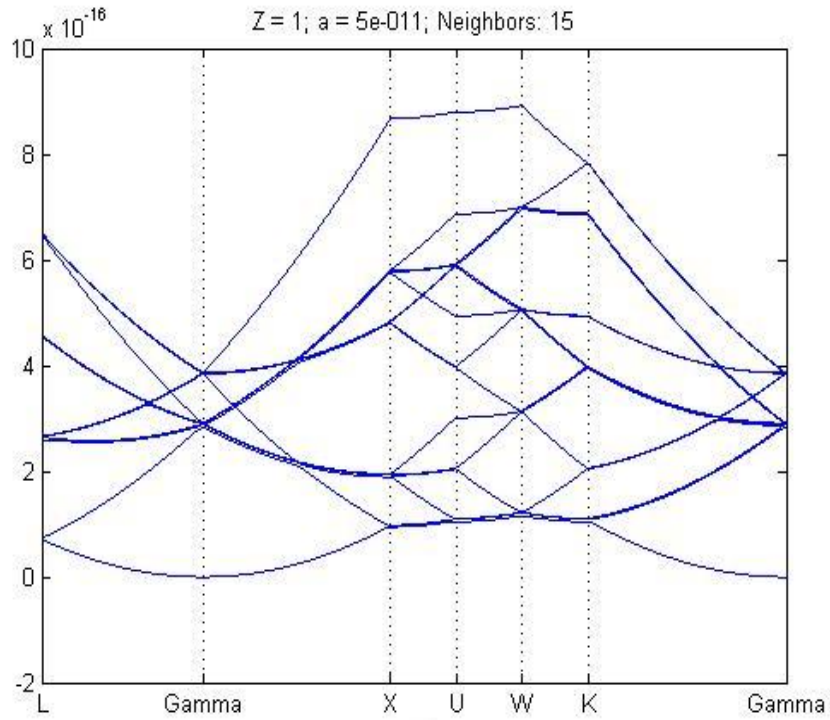
Plane wave method

fcc *Z*= 0

empty lattice

Plane wave method

fcc hydrogen
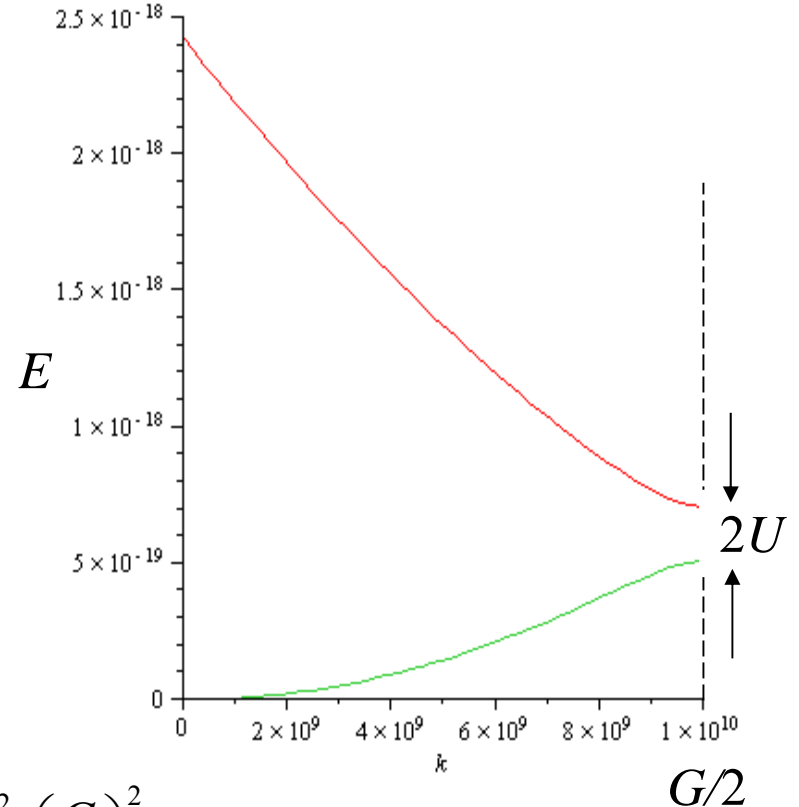
Approximate solution near the Bz boundary

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

For just 2 terms

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

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

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

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

E

$2U$

$G/2$

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}.

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

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

Linear combination of atomic orbitals

Guess that the solution to H_{mo} can be written as a linear combination of atomic orbitals.

$$\psi_{mo} = c_1 \phi_{1s,A}^{H} + c_2 \phi_{1s,B}^{H} + c_3 \phi_{2s,A}^{H} + c_4 \phi_{2s,B}^{H} + \cdots$$
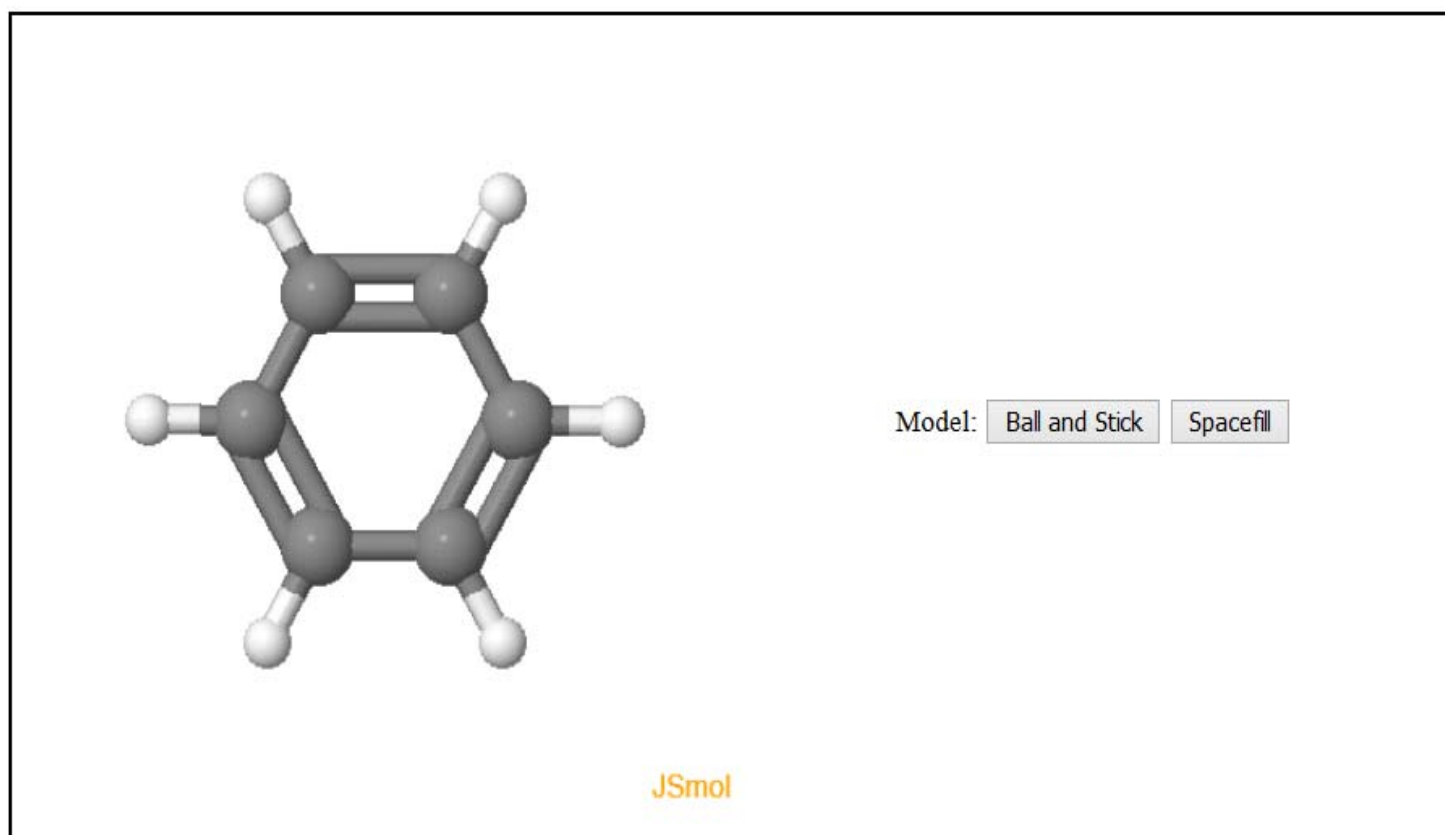
Construct the Hamiltonian matrix.

$$\begin{bmatrix} \langle \phi_{1s,A}^{H} | H_{mo} | \phi_{1s,A}^{H} \rangle & \langle \phi_{1s,A}^{H} | H_{mo} | \phi_{1s,B}^{H} \rangle \\ \langle \phi_{1s,B}^{H} | H_{mo} | \phi_{1s,A}^{H} \rangle & \langle \phi_{1s,B}^{H} | H_{mo} | \phi_{1s,B}^{H} \rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} \langle \phi_{1s,A}^{H} | \phi_{1s,A}^{H} \rangle & \langle \phi_{1s,A}^{H} | \phi_{1s,B}^{H} \rangle \\ \langle \phi_{1s,B}^{H} | \phi_{1s,A}^{H} \rangle & \langle \phi_{1s,B}^{H} | \phi_{1s,B}^{H} \rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$$S \approx \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Molecular orbitals of benzene

Benzene (C_6H_6) consists of 6 carbon atoms in a ring. A hydrogen atom is attached to each carbon atom. The carbon-carbon bond length is 1.40 Å and the carbon-hydrogen bond length is 1.10 Å.

Model: Ball and Stick   Spacefill

JSmol

$$\psi_{\mathrm{mo},j} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \exp\left(\frac{i2\pi nj}{N}\right) \phi_{2pz}^{C}(\vec{r} - \vec{r}_n) \qquad j = 1, 2, \cdots, N.$$

Tight binding: 1-D chain

$$\psi_k\left(x\right) = \frac{1}{\sqrt{N}} \sum_n e^{inka} \phi\left(x - na\right)$$

Substitute the tight-binding wave function into the time independent Schrödinger equation.

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

Multiply from the left by the atomic orbitals.

$$\langle \phi\left(x\right)|\hat{H}|\psi_k\left(x\right)\rangle = E\langle \phi\left(x\right)|\psi_k\left(x\right)\rangle$$

$$\langle \phi\left(x\right)|\hat{H}|\phi\left(x - a\right)\rangle e^{-ika} + \langle \phi\left(x\right)|\hat{H}|\phi\left(x\right)\rangle + \langle \phi\left(x\right)|\hat{H}|\phi\left(x + a\right)\rangle e^{ika} + \text{small terms}$$

$$= E + \text{small terms}.$$

$$\epsilon = \langle \phi\left(x\right)|\hat{H}|\phi\left(x\right)\rangle \text{ and } t = -\langle \phi\left(x\right)|\hat{H}|\phi\left(x - a\right)\rangle$$

$$E = \epsilon - t\left(e^{-ika} + e^{-ika}\right) = \epsilon - 2t\cos(ka).$$

Tight binding: 1-D chain

$$E = \epsilon - 2t \cos(ka).$$

Tight binding

Tight binding does not include electron-electron interactions

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

$$\psi_k = \frac{1}{\sqrt{N}}\sum_{l,m,n} \exp\left(i\left(l\vec{k}\cdot\vec{a}_1 + m\vec{k}\cdot\vec{a}_2 + n\vec{k}\cdot\vec{a}_3\right)\right)\psi_{\text{unit\_cell}}\left(\vec{r}-l\vec{a}_1 - m\vec{a}_2 - n\vec{a}_3\right)$$

$$\psi_{\text{unit\_cell}}\left(\vec{r}\right) = \sum_i c_i\phi_i\left(\vec{r}-\vec{r}_i\right)$$

Atomic wave functions

This is the tight-binding wave function.

$$T_{pqs}\psi_k = \exp\left(i\left(p\vec{k}\cdot\vec{a}_1 + q\vec{k}\cdot\vec{a}_2 + s\vec{k}\cdot\vec{a}_3\right)\right)\psi_k$$

Tight binding, one atomic orbital

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

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

For only one atomic orbital in the sum over valence orbitals

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

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

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

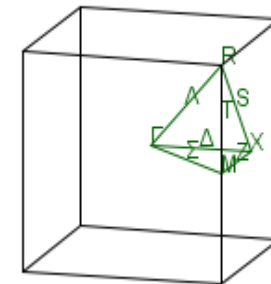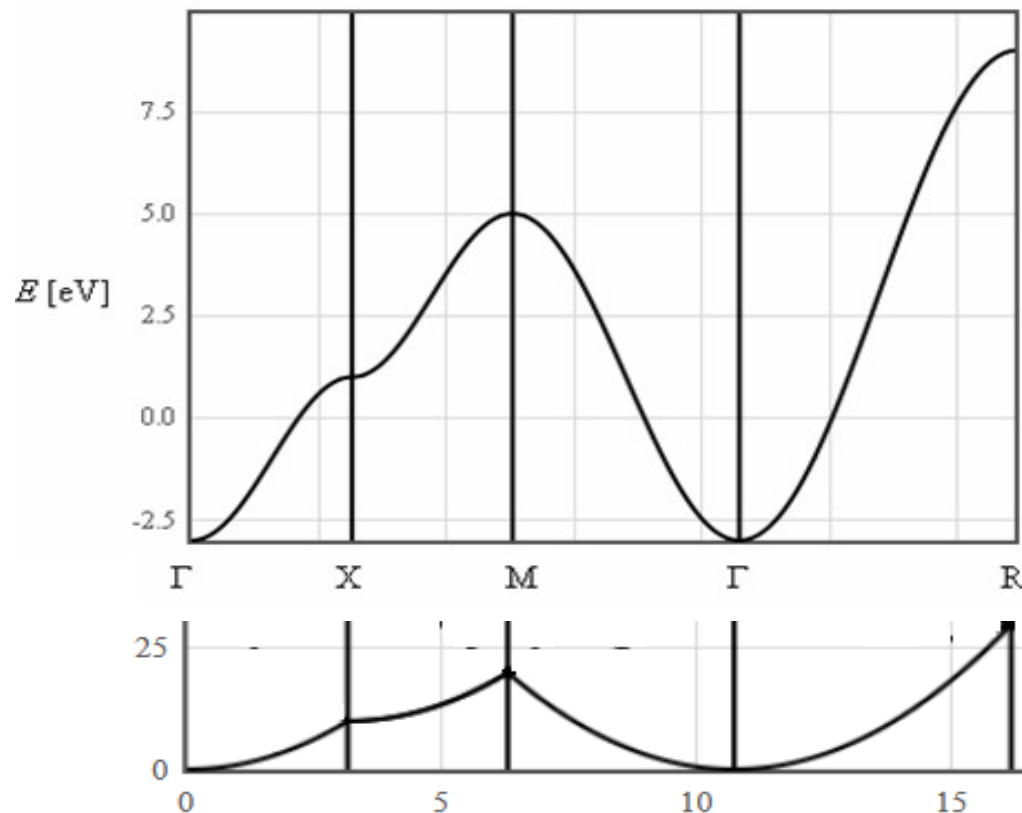On-site energy   Overlap integral

Tight binding, simple cubic

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

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

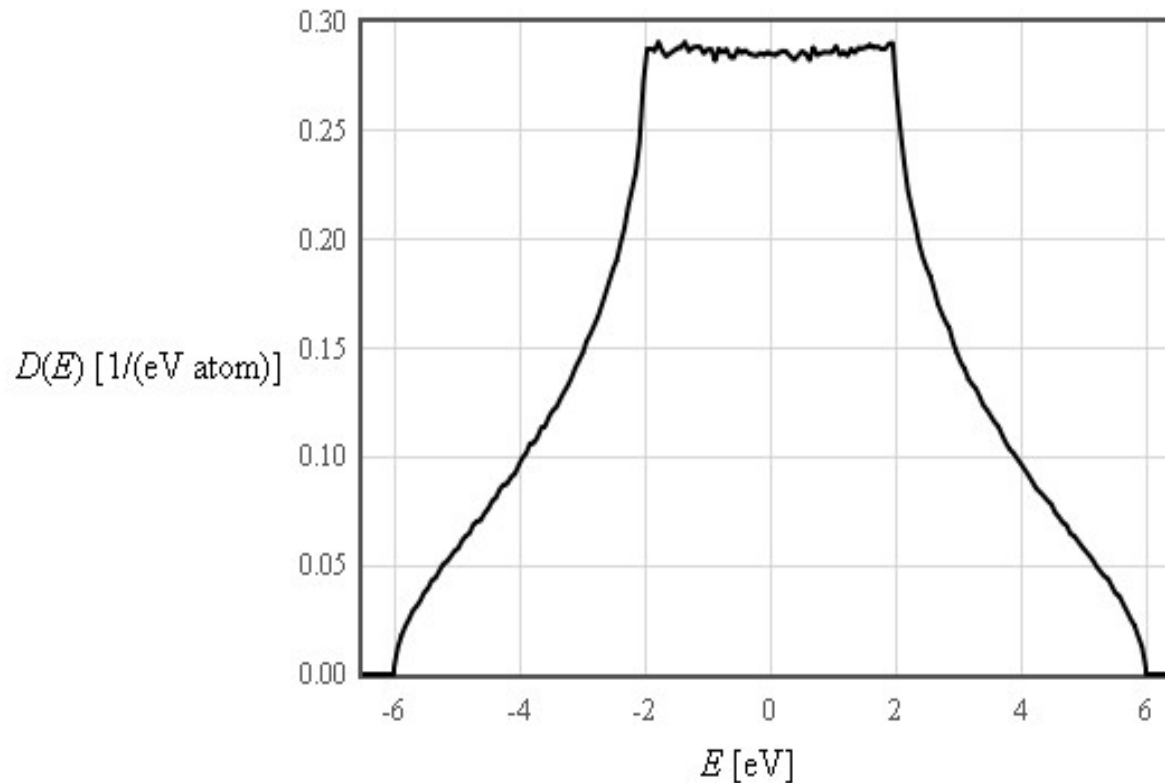$$= \varepsilon - 2t\left(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right)$$

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

Narrow bands $\rightarrow$ high effective mass

Density of states (simple cubic)

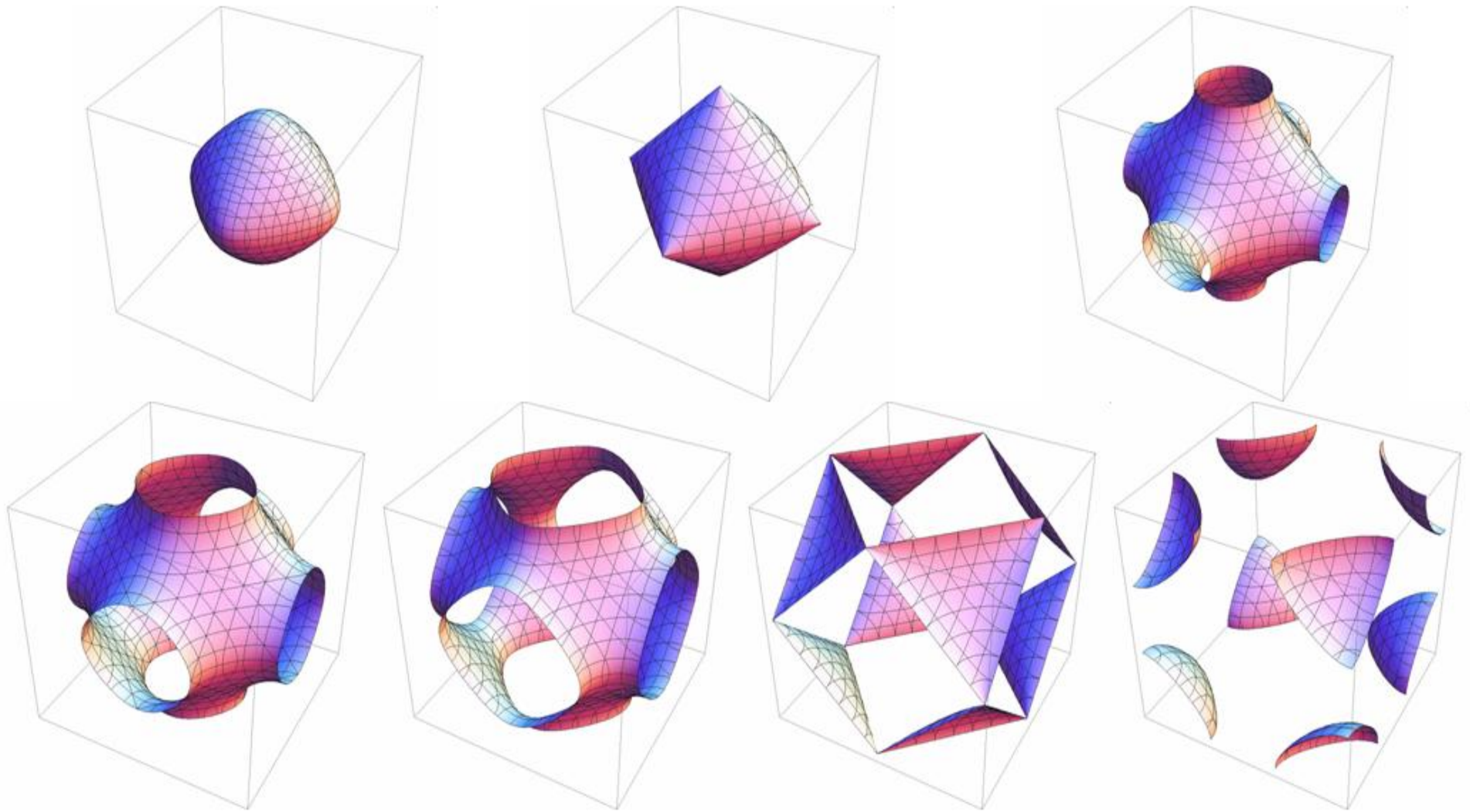

Calculate the energy for every allowed *k* in the Brillouin zone

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

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