5. Tight Binding / Graphene

Oct 15, 2018

Tight binding

Tight binding is a method to calculate the electronic band structure of a crystal. It is similar to the method of Linear Combination of Atomic Orbitals (LCAO) used to construct molecular orbitals. Although this approximation neglects the electron-electron interactions, it often produces qualitatively correct results and is sometimes used as the starting point for more sophisticated approaches.

A wave function is constructed from the valence orbitals of all of the atoms in a primitive unit cell of the crystal.

$$\psi_{\text{unit cell}}\left(\vec{r}\right) = \sum_{a}\sum_{ao} c_{ao,a}\phi_{ao}^{Z_a}\left(\vec{r} - \vec{r}_a\right).$$

Where a sums over the atoms in the basis and ao sums over the atomic orbitals. It is conventional to relabel the atomic orbitals with an index i that sums over the atomic orbitals.

$$\psi_{\text{unit cell}}\left(\vec{r}\right) = \sum_{i} c_i\phi_i\left(\vec{r} - \vec{r}_i\right).$$

The coefficients c_i are determined by substituting the wavefunction into the Schrödinger equation. For instance, for calcium carbonate $CaCO_3$, the valence orbitals would be the 4s orbital for calcium, the 2s and 3 × 2p orbitals for carbon and the 2s and 3 × 2p orbitals for oxygen. In this case there would be 15 terms in the wavefunction for the unit cell, $(i = 1, \cdots, 15)$.

The wave function for the one unit cell is then repeated at every unit cell in the crystal with a complex prefactor.

$$\psi_{\vec{k}}\left(\vec{r}\right) = \frac{1}{\sqrt{N}}\sum_{h,j,l} e^{i\left(h\vec{k}\cdot\vec{a}_1 + j\vec{k}\cdot\vec{a}_2 + l\vec{k}\cdot\vec{a}_3\right)}\psi_{\text{unit cell}}\left(\vec{r} - h\vec{a}_1 - j\vec{a}_2 - l\vec{a}_3\right).$$

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

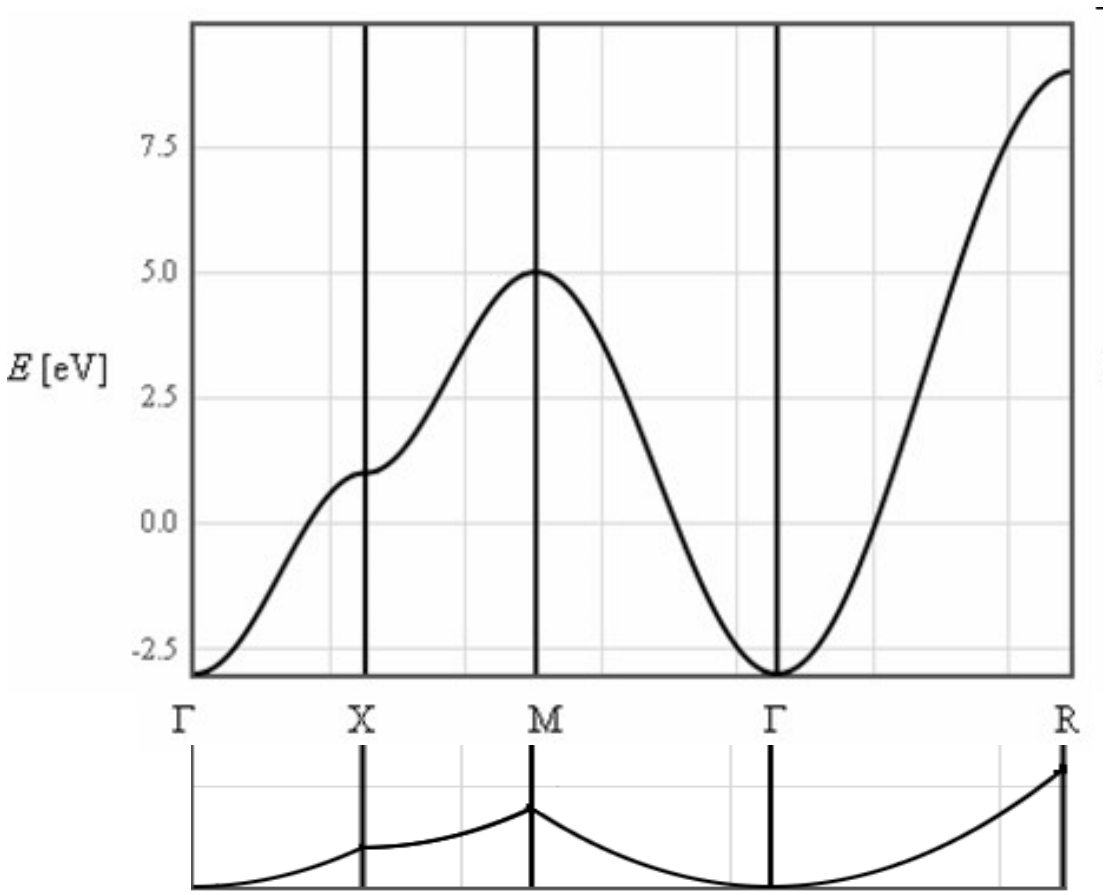
$$\varepsilon = \langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r}) \rangle \qquad t = -\langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r} - \vec{\rho}_m) \rangle$$

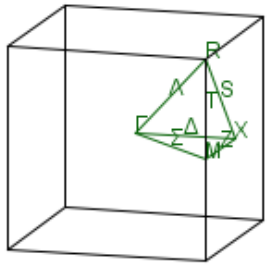
Tight binding, simple cubic

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

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

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

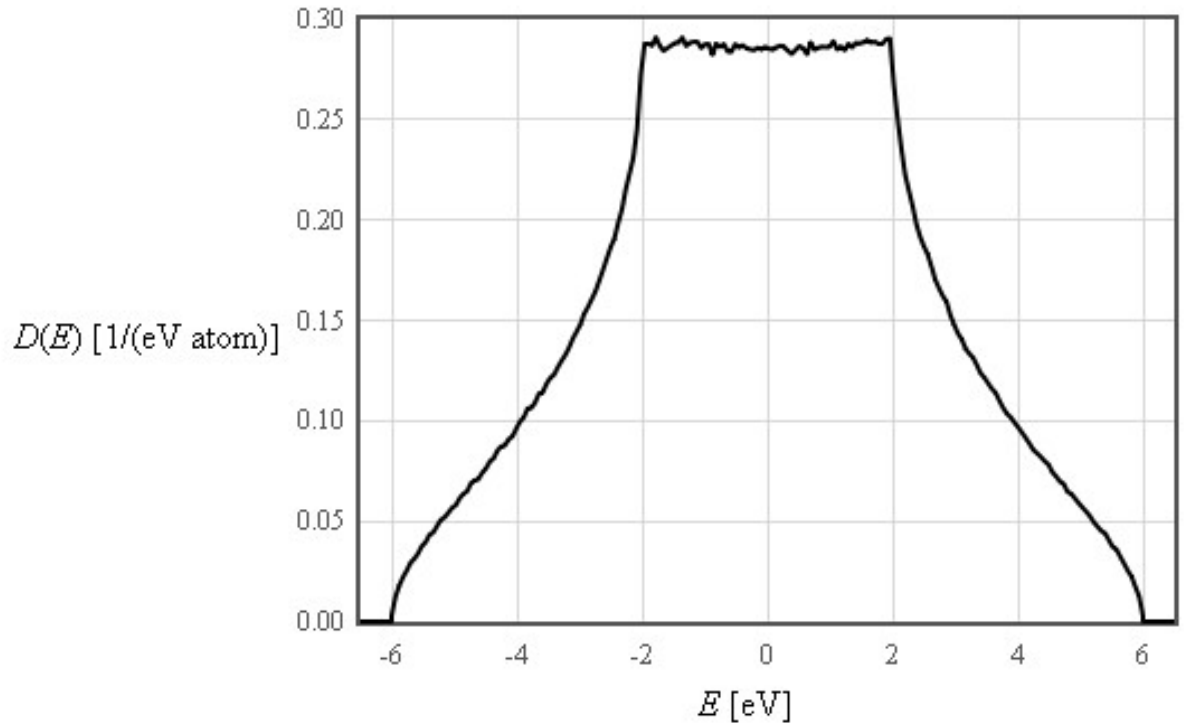




Effective mass $m^* = \dfrac{\hbar^2}{\dfrac{d^2E}{dk^2}} = \dfrac{\hbar^2}{2ta^2}$

Narrow bands → high effective mass

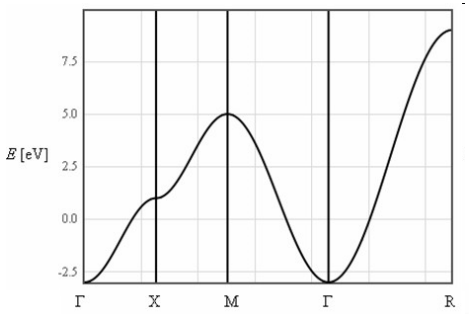
Density of states (simple cubic)



Calculate the energy for every allowed k in the Brillouin zone

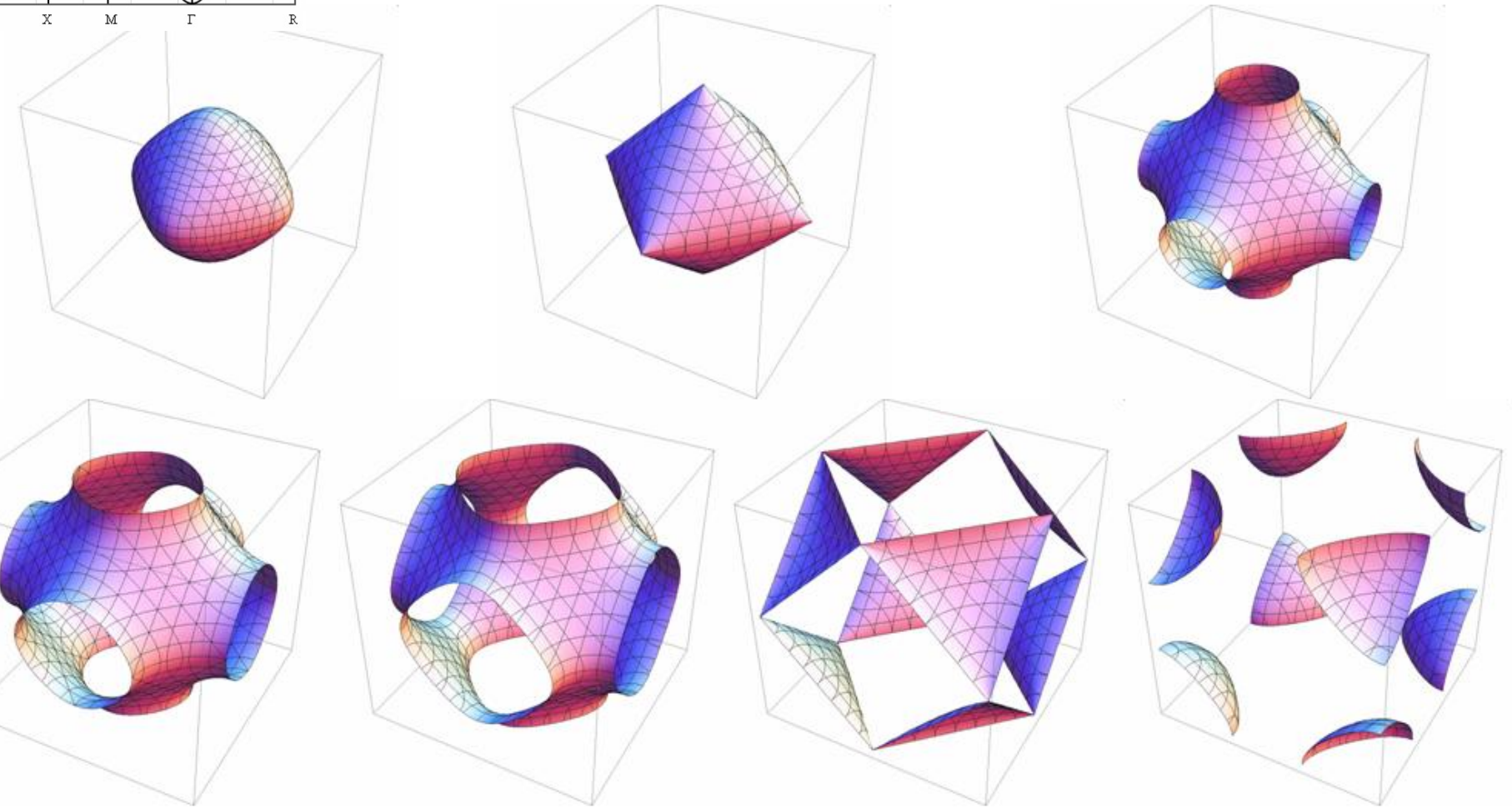
$$E = \varepsilon - 2t\left(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right)$$

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



Tight binding, simple cubic

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

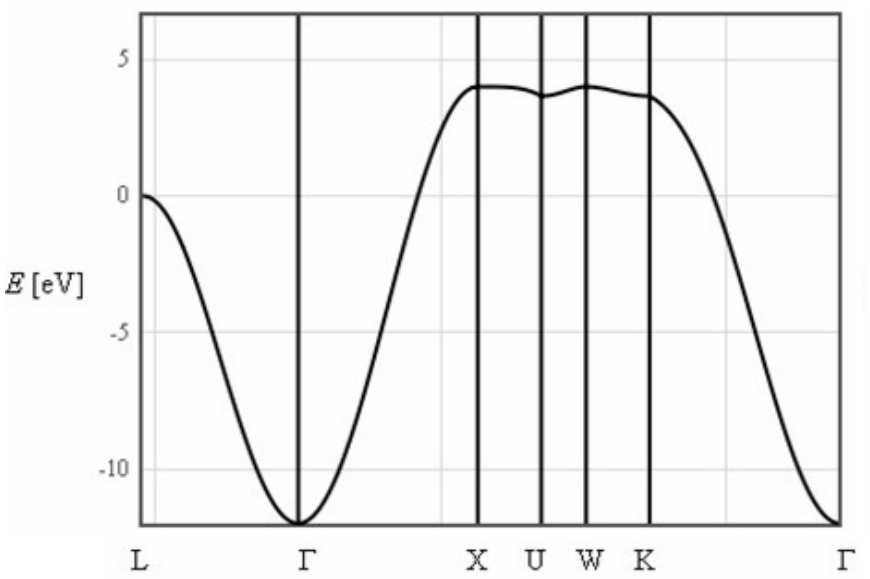


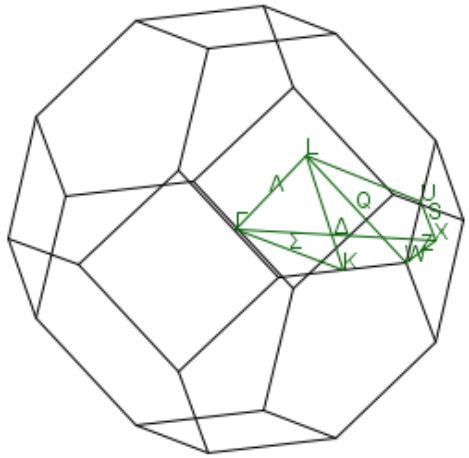
Christian Gruber, 2008

Tight binding, fcc

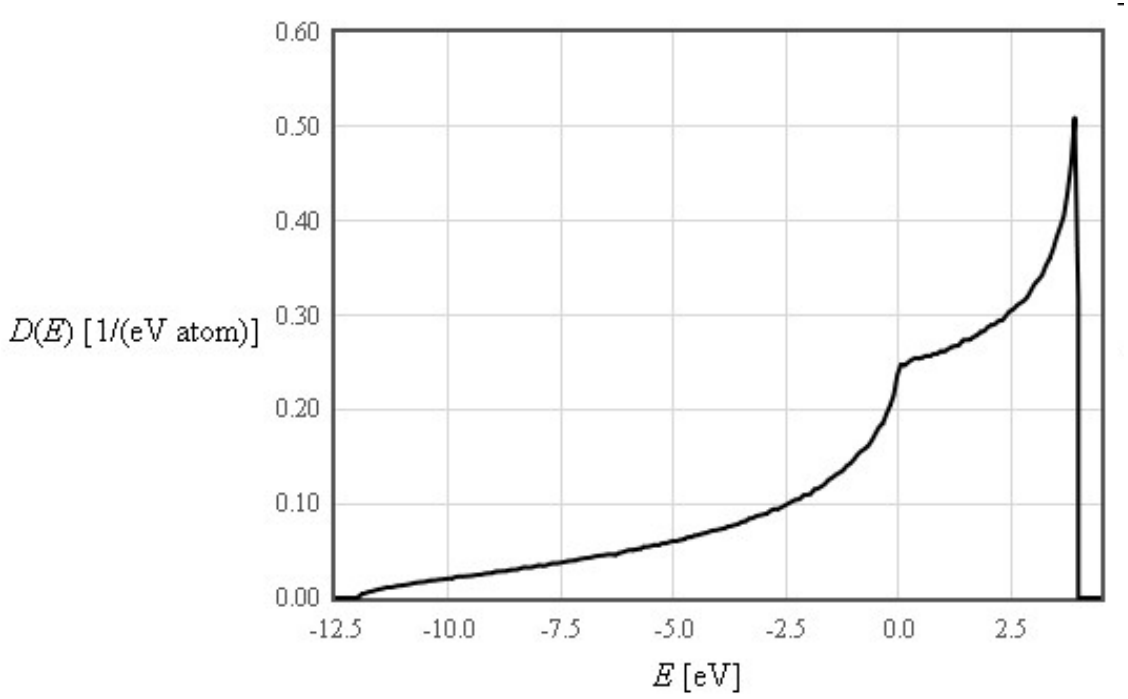
$$E = \varepsilon - t\sum_{m} e^{i\vec{k}\cdot\vec{\rho}_m}$$

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





Density of states (fcc)

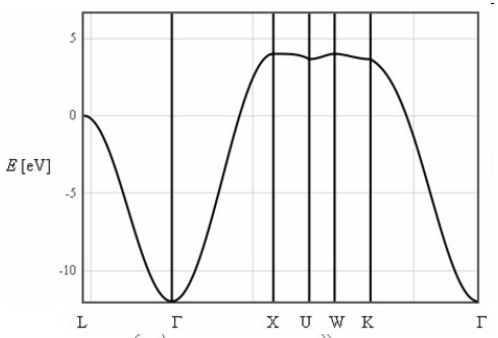


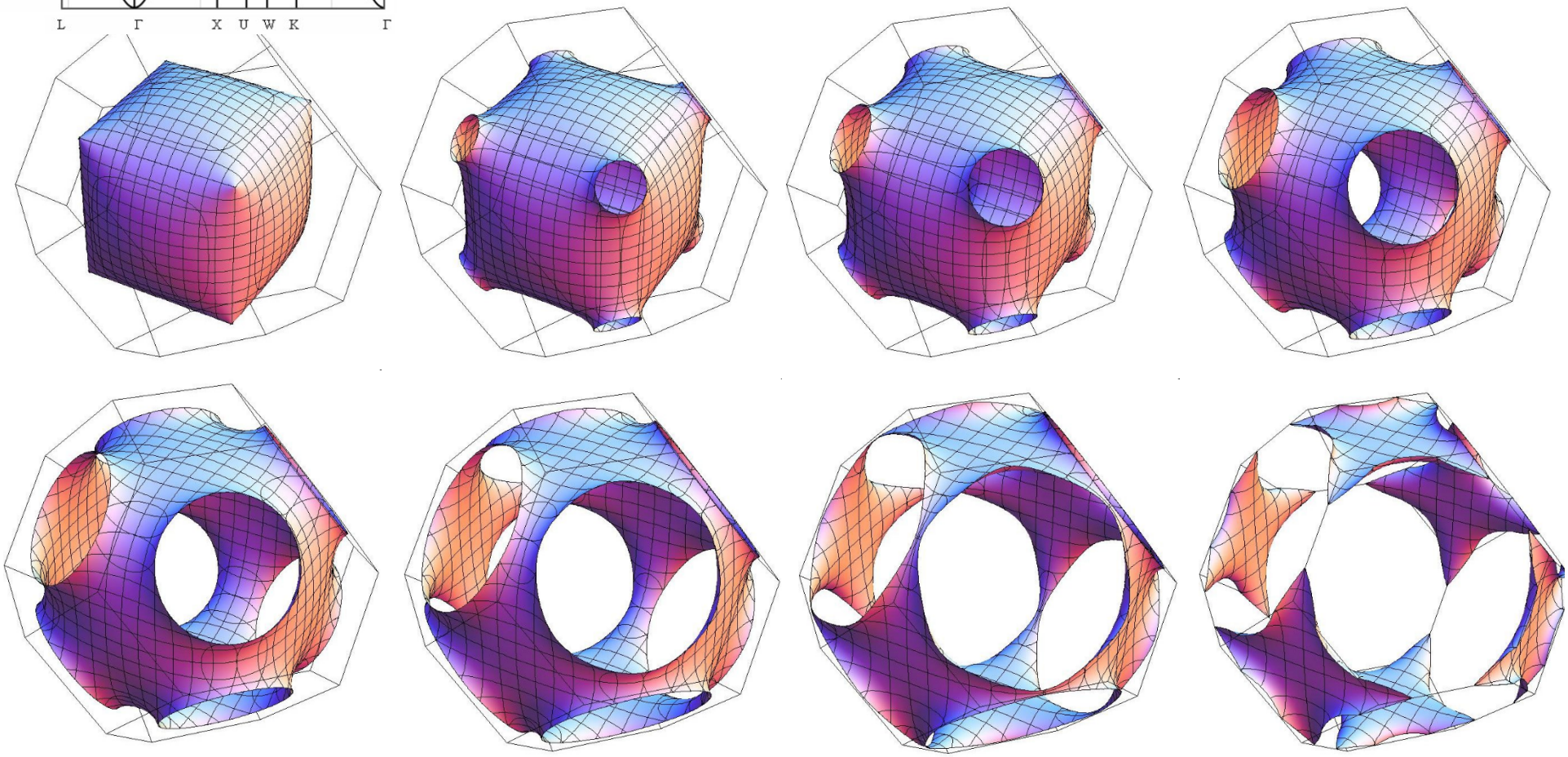
Calculate the energy for every allowed *k* in the Brillouin zone

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

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

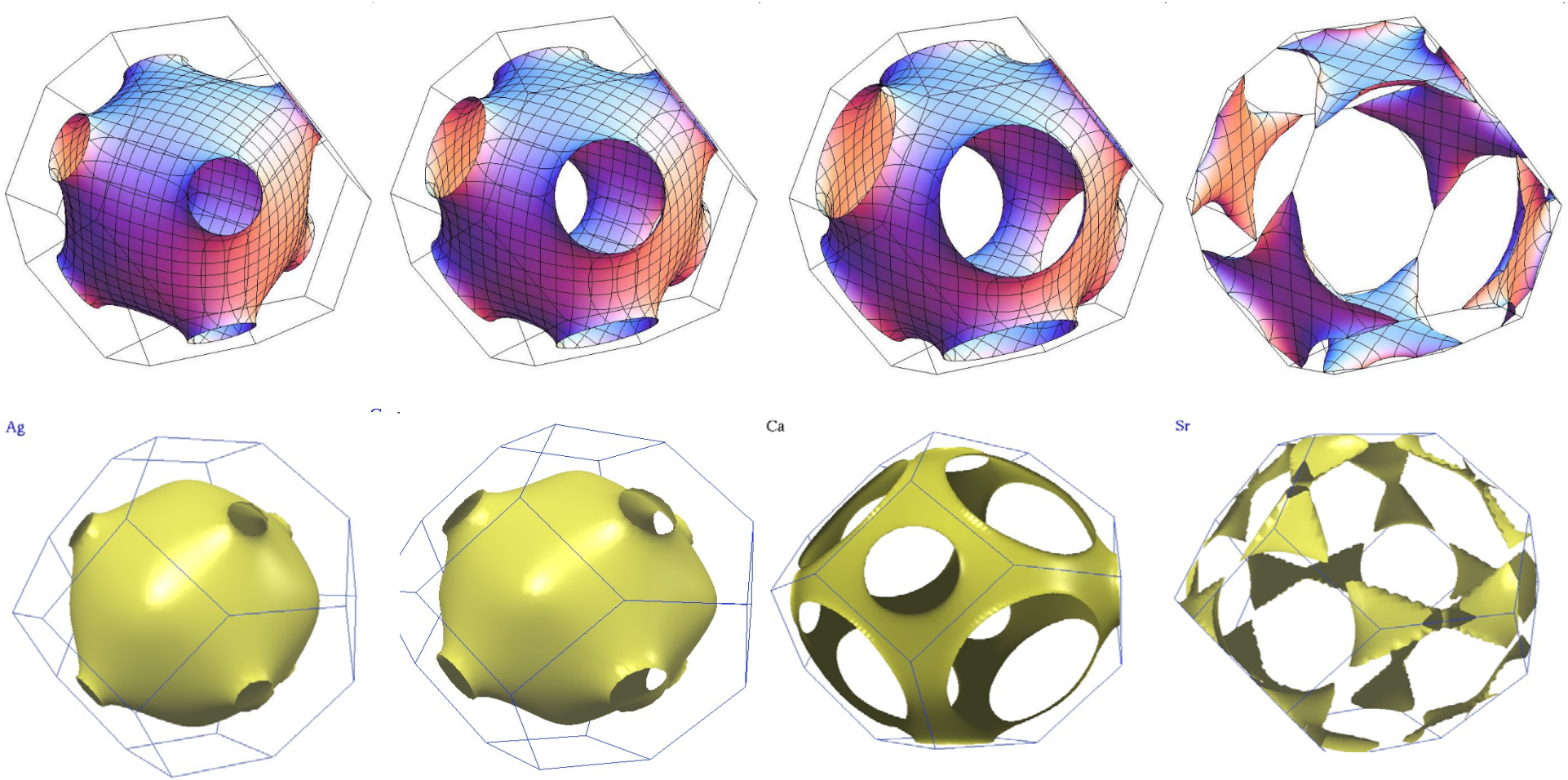
Tight binding, fcc





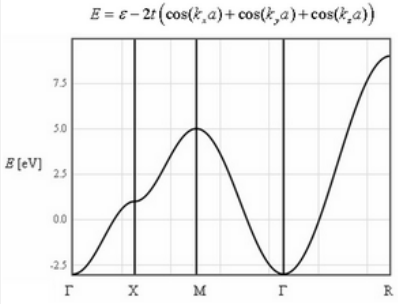
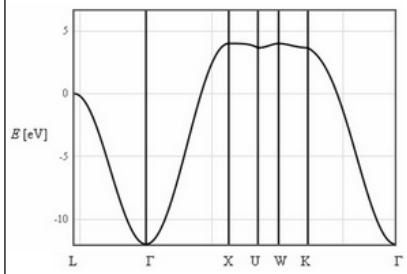
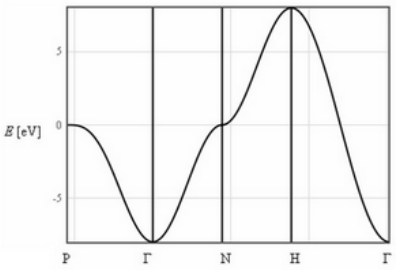
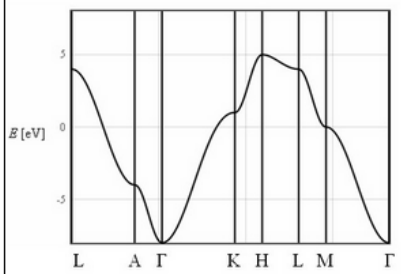
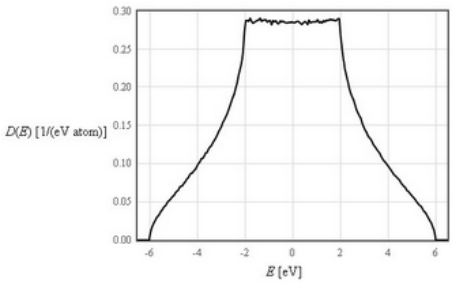
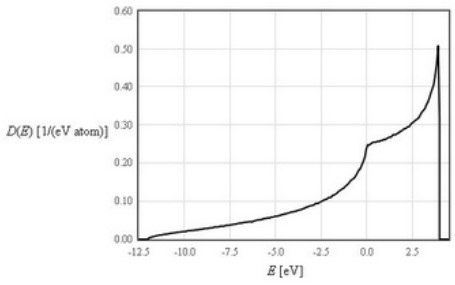
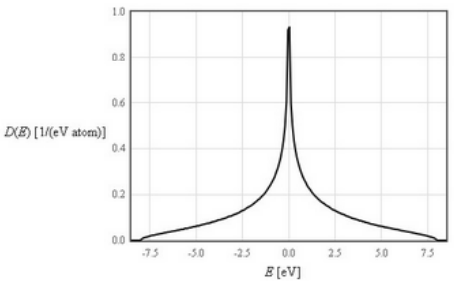
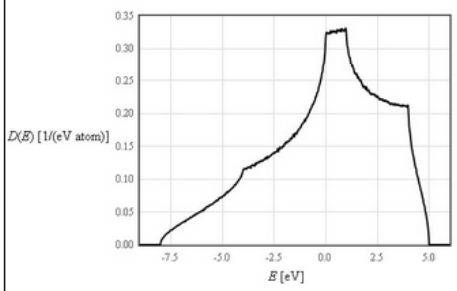
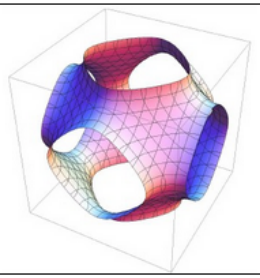
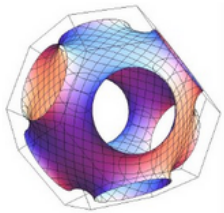
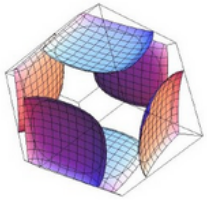
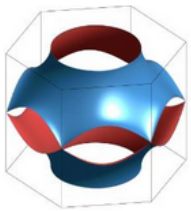
Christian Gruber, 2008

Tight binding, fcc



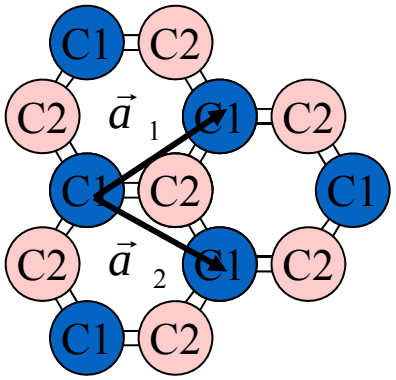
http://www.phys.ufl.edu/fermisurface/

Table of tight-binding calculations

simple cubic 3-D	fcc	bcc	hexagonal
$E = \varepsilon - 2t\left(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right)$	$E = \varepsilon - 4t\left(\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right)\right)$	$E = \varepsilon - 8t\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right)$	$E = \varepsilon - t\left(2\cos(k_x a) + 4\cos\left(\frac{\sqrt{3}k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right) + 2\cos(k_z c)\right)$
 Calculate E(k)	 Calculate E(k)	 Calculate E(k)	 Calculate E(k)
$D(k) = \frac{k^2}{\pi^2}$ m^{-2}	$D(k) = \frac{k^2}{\pi^2}$ m^{-2}	$D(k) = \frac{k^2}{\pi^2}$ m^{-2}	$D(k) = \frac{k^2}{\pi^2}$ m^{-2}
 Calculate D(E)	 Calculate D(E)	 Calculate D(E)	 Calculate D(E)
			

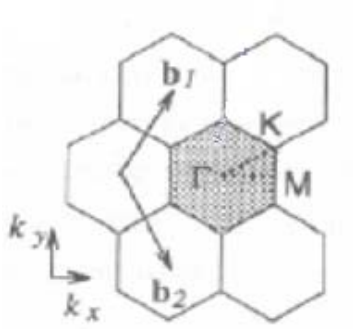
http://lampx.tugraz.at/~hadley/ss1/bands/tbtable/tbtable.html

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

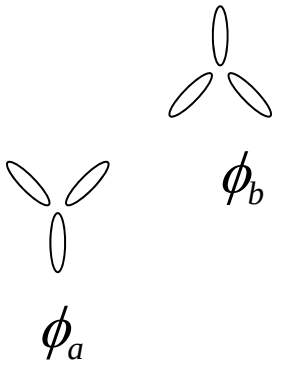
Graphene has an unusual dispersion relation in the vicinity of the Fermi energy.

2 carbon atoms / unit cell

The standard guess for the wave function in the tight binding model is

$$\psi_k = \sum_{j,l} \exp\left(i\left(j\vec{k}\cdot\vec{a}_1 + l\vec{k}\cdot\vec{a}_2\right)\right)\left(c_a\phi_{p_z a}\left(\vec{r} - j\vec{a}_1 - l\vec{a}_2\right) + c_b\phi_{p_z b}\left(\vec{r} - j\vec{a}_1 - l\vec{a}_2\right)\right)$$

For graphene, the valence orbitals are p_z orbitals



Substitute this wave function into the Schrödinger equation

$$H\psi_k = E\psi_k$$

2 carbon atoms / unit cell

$$\psi_k = \sum_{j,l} \exp\left(i\left(j\vec{k}\cdot\vec{a}_1 + l\vec{k}\cdot\vec{a}_2\right)\right)\left(c_a\phi_{p_z a}\left(\vec{r} - j\vec{a}_1 - l\vec{a}_2\right) + c_b\phi_{p_z b}\left(\vec{r} - j\vec{a}_1 - l\vec{a}_2\right)\right)$$

$$H\psi_k = E\psi_k$$

Multiply by $\phi^*_{p_z a}(\vec{r})$ and integrate

the orbital for the atom at $j = 0$, $l = 0$.

$$c_a\langle\phi_a|H|\phi_a\rangle + c_b\langle\phi_a|H|\phi_b\rangle\sum_m e^{i\vec{k}\cdot\vec{\rho}_m} + \text{small terms}$$

$$= E\left(c_a\langle\phi_a|\phi_a\rangle + c_b\langle\phi_a|\phi_b\rangle\sum_m e^{i\vec{k}\cdot\vec{\rho}_m} + \text{small terms}\right)$$

1 0

m sums over the nearest neighbors

2 carbon atoms / unit cell

To get a second equation for c_a and c_b

Multiply $H\psi_k = E\psi_k$ by $\phi^*_{p_z b}(\vec{r})$ and integrate

the orbital for the atom at $j = 0$, $l = 0$.

$$c_a \langle \phi_b | H | \phi_a \rangle \sum_m e^{-i\vec{k}\cdot\vec{\rho}_m} + c_b \langle \phi_b | H | \phi_b \rangle + \text{small terms}$$

$$= E\left(c_a \langle \phi_b | \phi_a \rangle \sum_m e^{i\vec{k}\cdot\vec{\rho}_m} + c_b \langle \phi_b | \phi_b \rangle + \text{small terms} \right)$$

$\langle \phi_b | \phi_a \rangle \to 0$ $\qquad$ $\langle \phi_b | \phi_b \rangle \to 1$

Write as a matrix equation

Tight binding graphene

$$\begin{bmatrix} \langle \phi_a | H | \phi_a \rangle - E & \langle \phi_a | H | \phi_b \rangle \sum_m e^{i\vec{k}\cdot\vec{\rho}_m} \\ \langle \phi_b | H | \phi_a \rangle \sum_m e^{-i\vec{k}\cdot\vec{\rho}_m} & \langle \phi_b | H | \phi_b \rangle - E \end{bmatrix} \begin{bmatrix} c_a \\ c_b \end{bmatrix} = 0$$

m sums over the nearest neighbors.

There will be two eigen energies for every *k*.

N orbitals / unit cell results in *N* bands

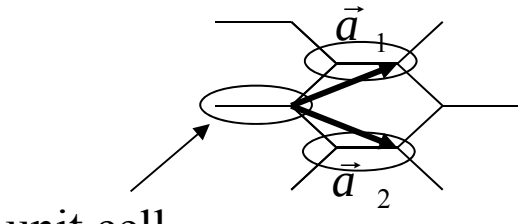
$$\varepsilon = \langle \phi_a | H | \phi_a \rangle$$
$$t = -\langle \phi_a | H | \phi_b \rangle$$

Tight binding graphene

$$\begin{vmatrix} \varepsilon - E & -t\sum_m e^{i\vec{k}\cdot\vec{\rho}_m} \\ -t\sum_m e^{-i\vec{k}\cdot\vec{\rho}_m} & \varepsilon - E \end{vmatrix} = 0$$

$$\sum_m e^{i\vec{k}\cdot\vec{\rho}_m} = \left(1 + \exp\left(i\left(\frac{\sqrt{3}k_x a}{2} + \frac{k_y a}{2}\right)\right) + \exp\left(i\left(\frac{\sqrt{3}k_x a}{2} - \frac{k_y a}{2}\right)\right)\right)$$

$\vec{k}\cdot\vec{a}_1$ $\qquad$ $\vec{k}\cdot\vec{a}_2$



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

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

There will be two eigen energies for every *k*.

Solve for the dispersion relation

$$\begin{vmatrix} \varepsilon - E & -t\left(1+\exp\left(i\left(\frac{\sqrt{3}k_x a}{2}-\frac{k_y a}{2}\right)\right)+\exp\left(i\left(\frac{\sqrt{3}k_x a}{2}+\frac{k_y a}{2}\right)\right)\right) \\ -t\left(1+\exp\left(-i\left(\frac{\sqrt{3}k_x a}{2}-\frac{k_y a}{2}\right)\right)+\exp\left(-i\left(\frac{\sqrt{3}k_x a}{2}+\frac{k_y a}{2}\right)\right)\right) & \varepsilon - E \end{vmatrix} = 0$$

$$\left(\varepsilon - E\right)^2 - t^2 \begin{pmatrix} 1+\exp\left(i\left(\frac{\sqrt{3}k_x a}{2}-\frac{k_y a}{2}\right)\right)+\exp\left(i\left(\frac{\sqrt{3}k_x a}{2}+\frac{k_y a}{2}\right)\right) \\ +\exp\left(-i\left(\frac{\sqrt{3}k_x a}{2}-\frac{k_y a}{2}\right)\right)+1+\exp\left(-i\left(\frac{\sqrt{3}k_x a}{2}-\frac{k_y a}{2}\right)+i\left(\frac{\sqrt{3}k_x a}{2}+\frac{k_y a}{2}\right)\right) \\ +\exp\left(-i\left(\frac{\sqrt{3}k_x a}{2}+\frac{k_y a}{2}\right)\right)+\exp\left(-i\left(\frac{\sqrt{3}k_x a}{2}+\frac{k_y a}{2}\right)+i\left(\frac{\sqrt{3}k_x a}{2}-\frac{k_y a}{2}\right)\right)+1 \end{pmatrix} = 0$$

Graphene dispersion relation

$$(\varepsilon - E)^2 - t^2\left(3 + 2\cos\left(\frac{\sqrt{3}k_x a}{2} - \frac{k_y a}{2}\right) + 2\cos\left(\frac{\sqrt{3}k_x a}{2} + \frac{k_y a}{2}\right) + 2\cos\left(k_y a\right)\right) = 0$$

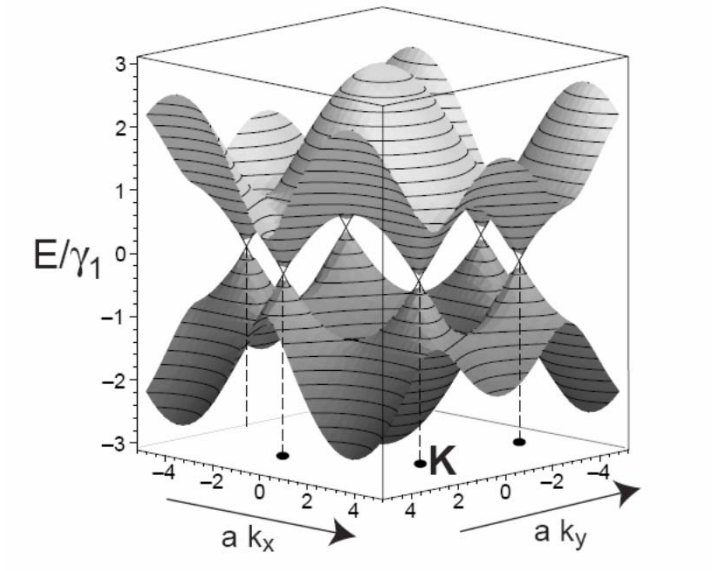
$$\cos(a+b) = \cos a \cos b - \sin a \sin b$$
$$\cos(a-b) = \cos a \cos b + \sin a \sin b$$
$$\cos 2a = 2\cos^2 a - 1$$

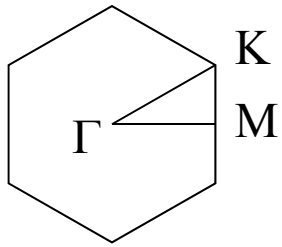
$$(\varepsilon - E)^2 - t^2\left(1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)\right) = 0$$

$$E = \varepsilon \pm t\sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$

Tight binding, graphene

$$E = \varepsilon \pm t\sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$



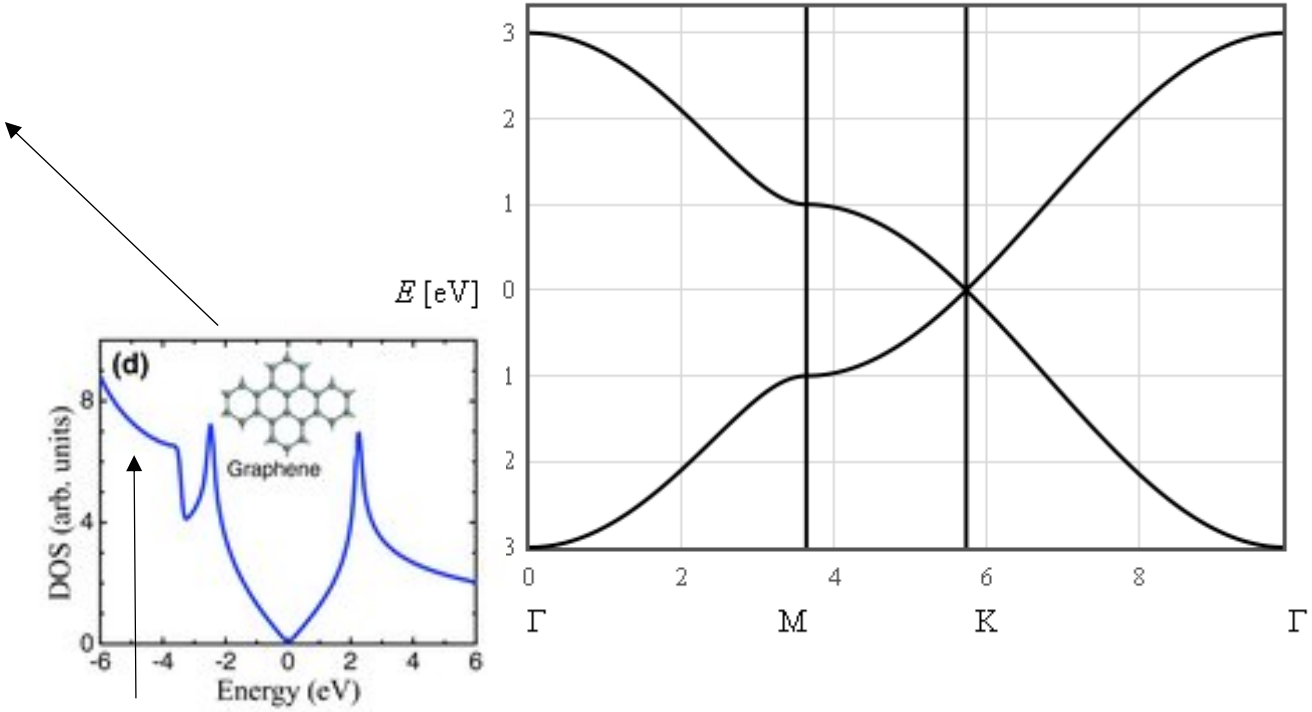


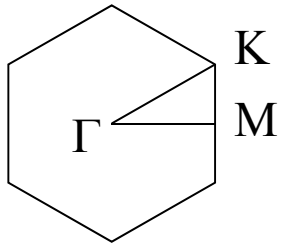
www.physics.umd.edu/courses/Phys732/hdrew/spring07/Schoenenberger%20tutorial%20on%20CNT%20bands.pdf

http://onlinelibrary.wiley.com/doi/10.1002/adfm.201101241/full

Tight binding dispersion relation for graphene

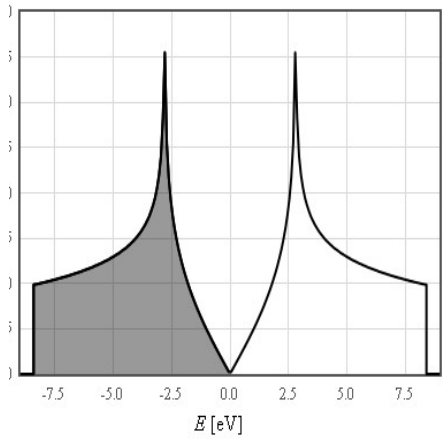
$$E = \varepsilon \pm t\sqrt{1+4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)+4\cos^2\left(\frac{k_y a}{2}\right)}$$





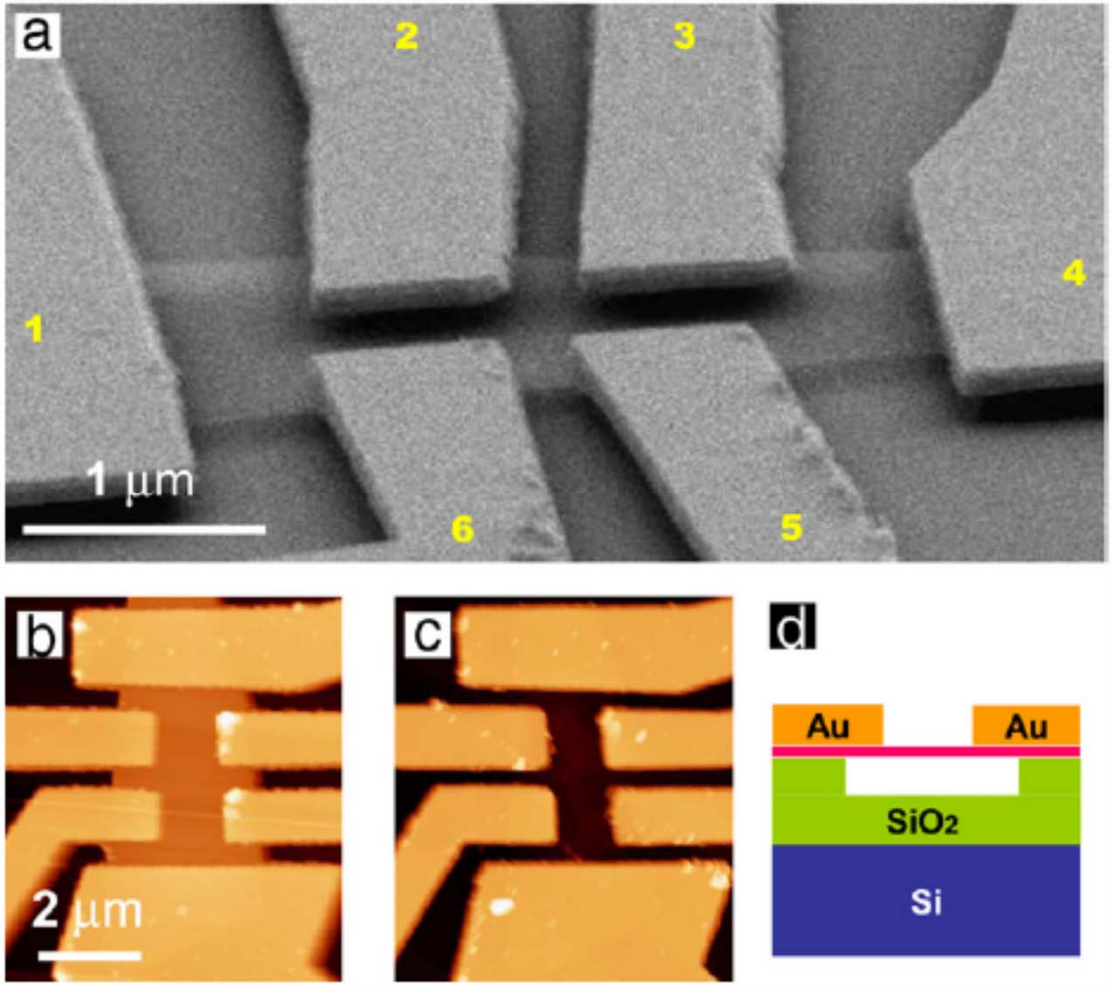
ε = 0 [eV]
t = 2.8 [eV]
Replot E(k)

Another band is included here.



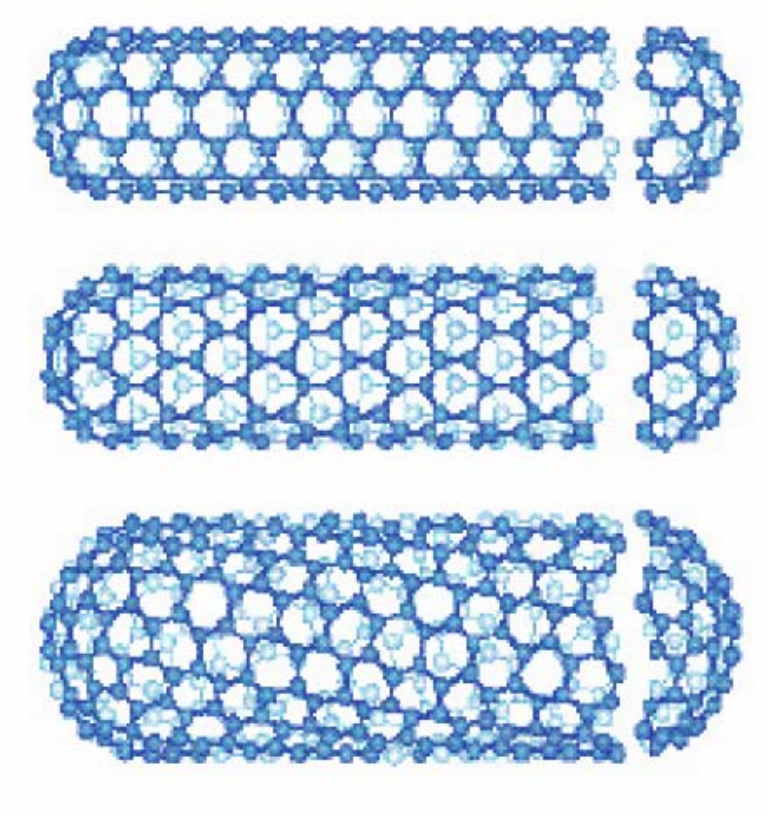
http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tbtable/dispgraphene.html

Graphene



Mobility: 200000 cm^2 /V s suspended, ~20000 cm^2 /V s otherwise

Carbon nanotubes - rolled up graphene



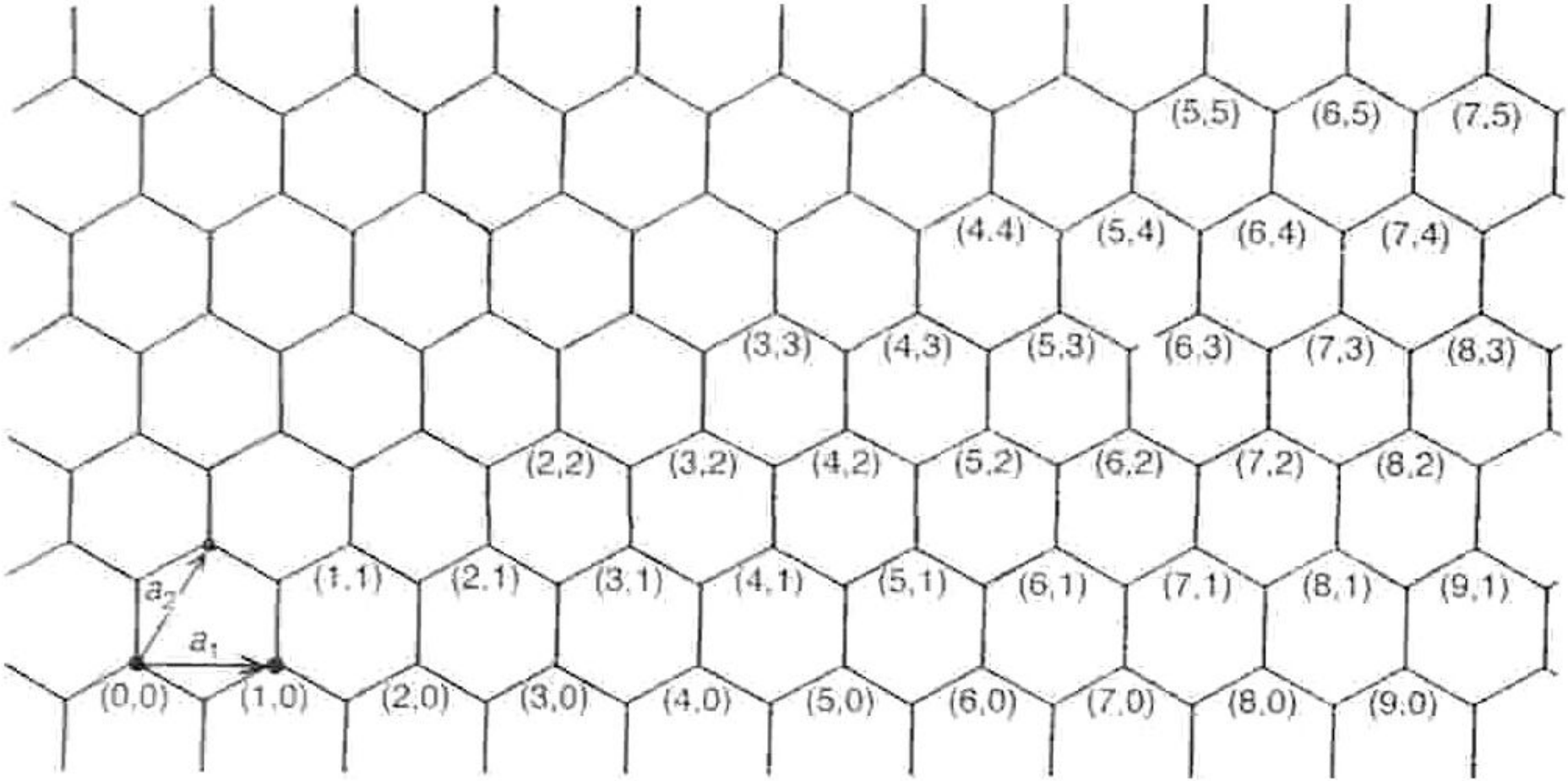
armchair

zig-zag

chiral

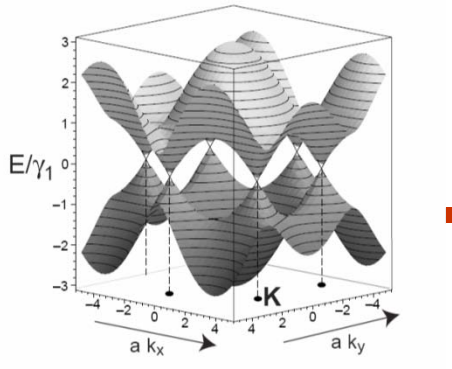
www.physics.umd.edu/courses/Phys732/hdrew/spring07/Schoenenberger%20tutorial%20on%20CNT%20bands.pdf

(*m*,*n*) notation

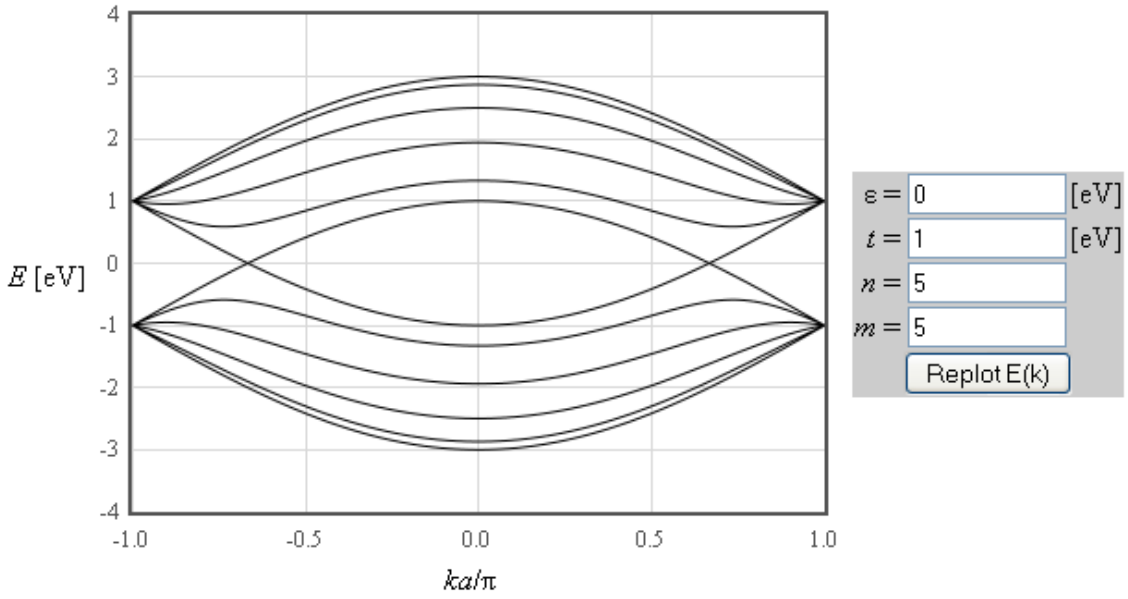


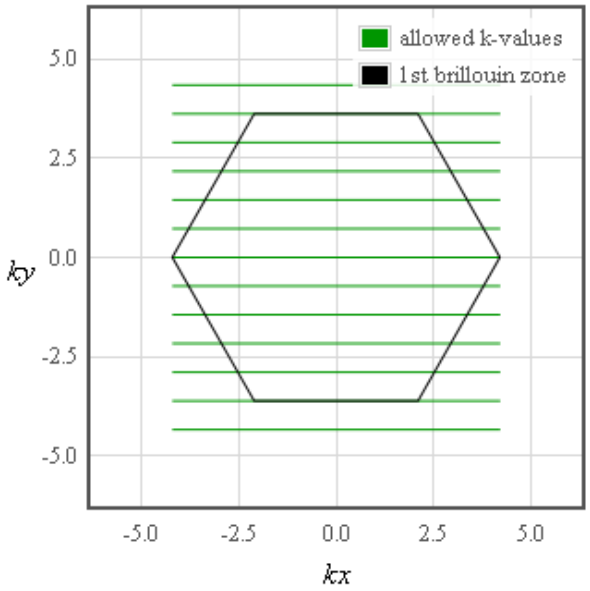
http://www.personal.rdg.ac.uk/~scsharip/tubes.htm

Carbon nanotubes



$$E = \varepsilon \pm t\sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$

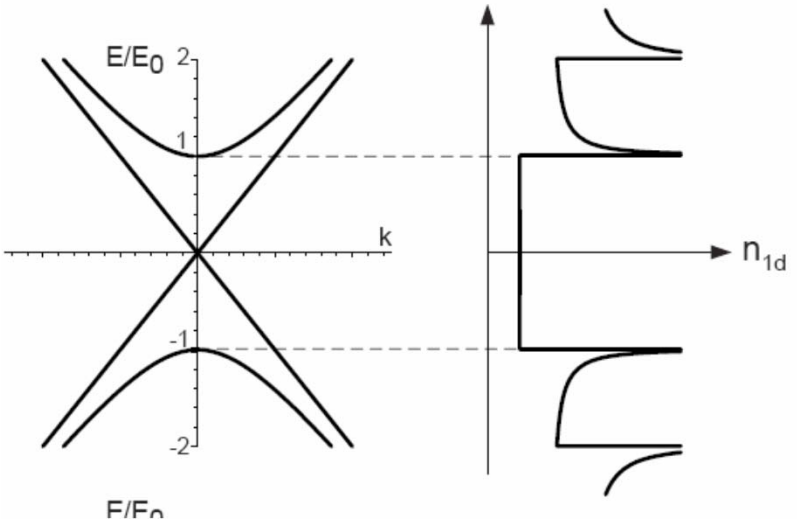


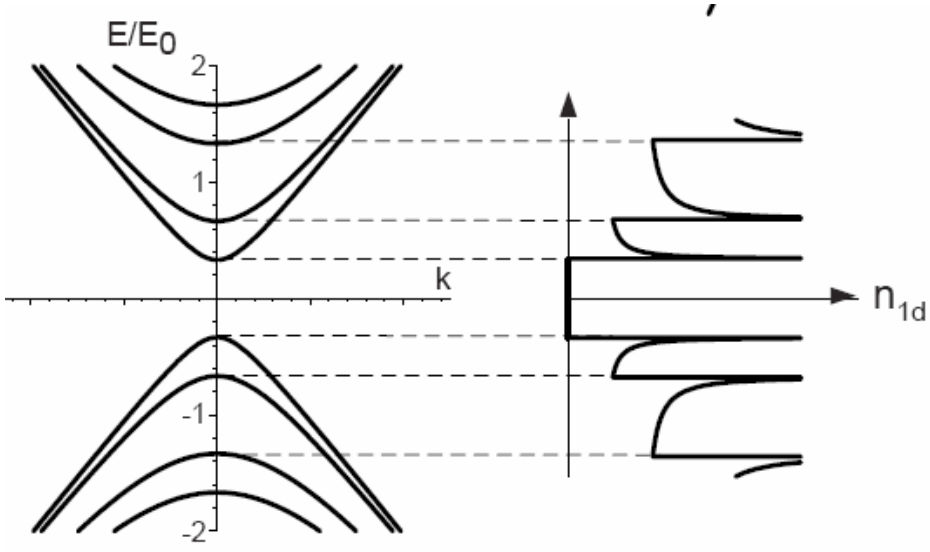


metallic (5,5) armchair tube

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

Carbon nanotubes



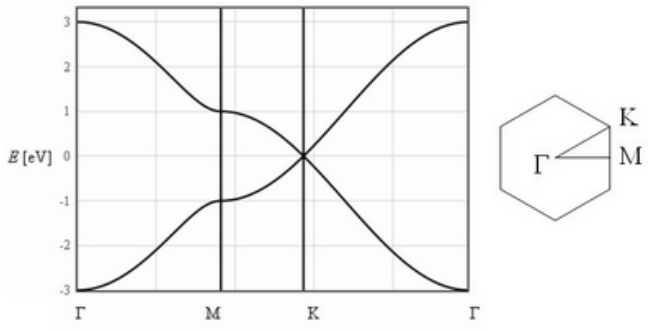
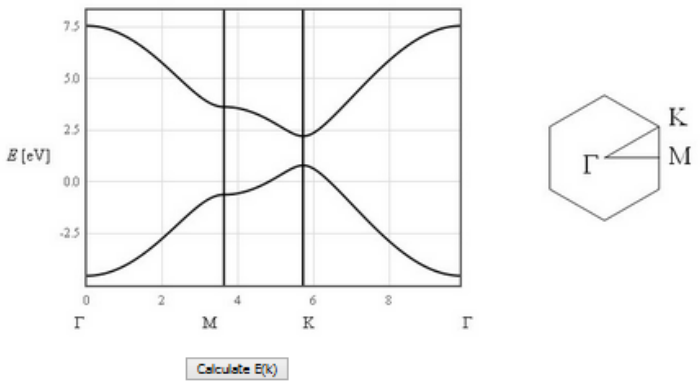
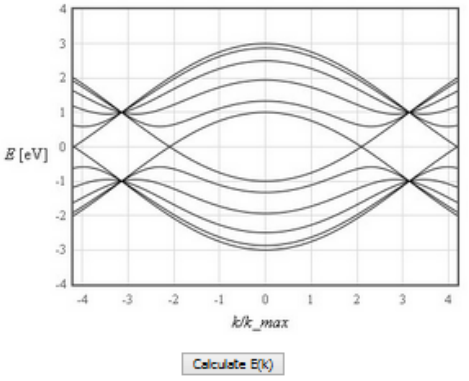
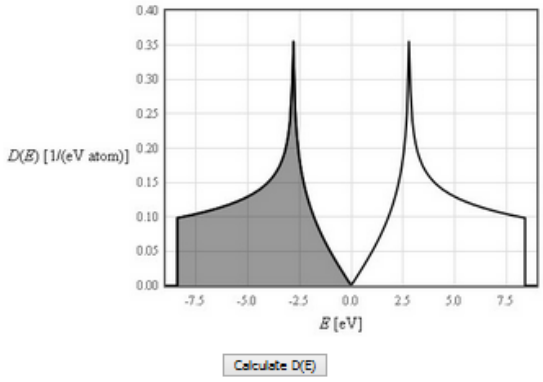
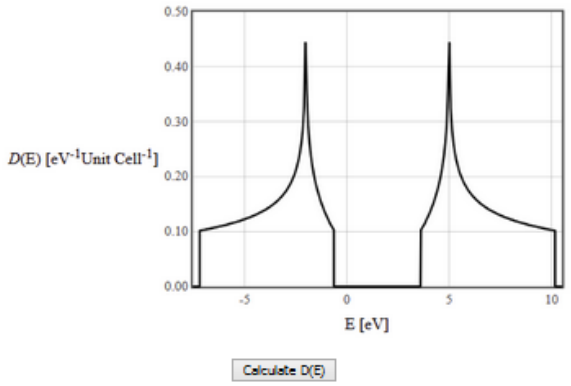
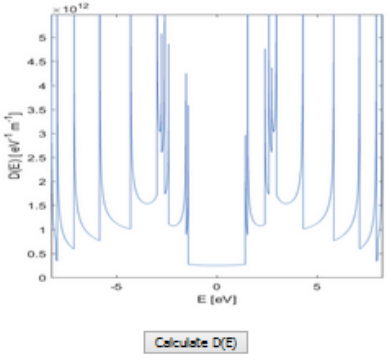


metallic $m - n = 3Z$

semiconducting

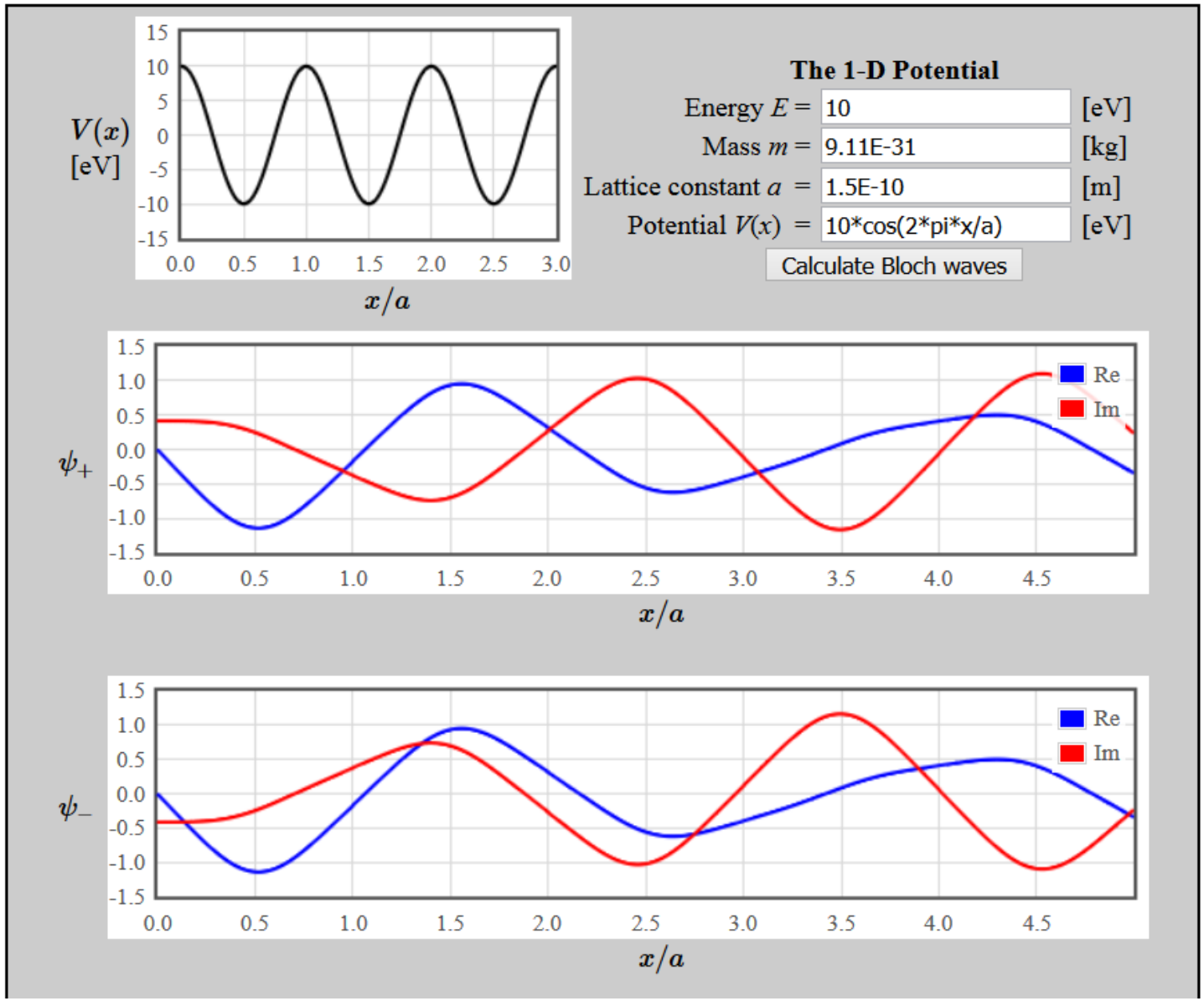
www.physics.umd.edu/courses/Phys732/hdrew/spring07/Schoenenberger%20tutorial%20on%20CNT%20bands.pdf

Table of tight-binding calculations

Graphene	2-D boron nitride	Carbon nanotubes
$E = \varepsilon \pm t\sqrt{1+4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)+4\cos^2\left(\frac{k_y a}{2}\right)}$	$E = \frac{\varepsilon_1+\varepsilon_2}{2} \pm \sqrt{\frac{(\varepsilon_1-\varepsilon_2)^2}{2}+4t^2\left(\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)+\cos^2\left(\frac{k_y a}{2}\right)+\frac{1}{4}\right)}$	
		
$D(k) = \frac{k}{\pi}$ m^{-1}	$D(k) = \frac{k}{\pi}$ m^{-1}	$D(k) = \frac{2}{\pi}$
		

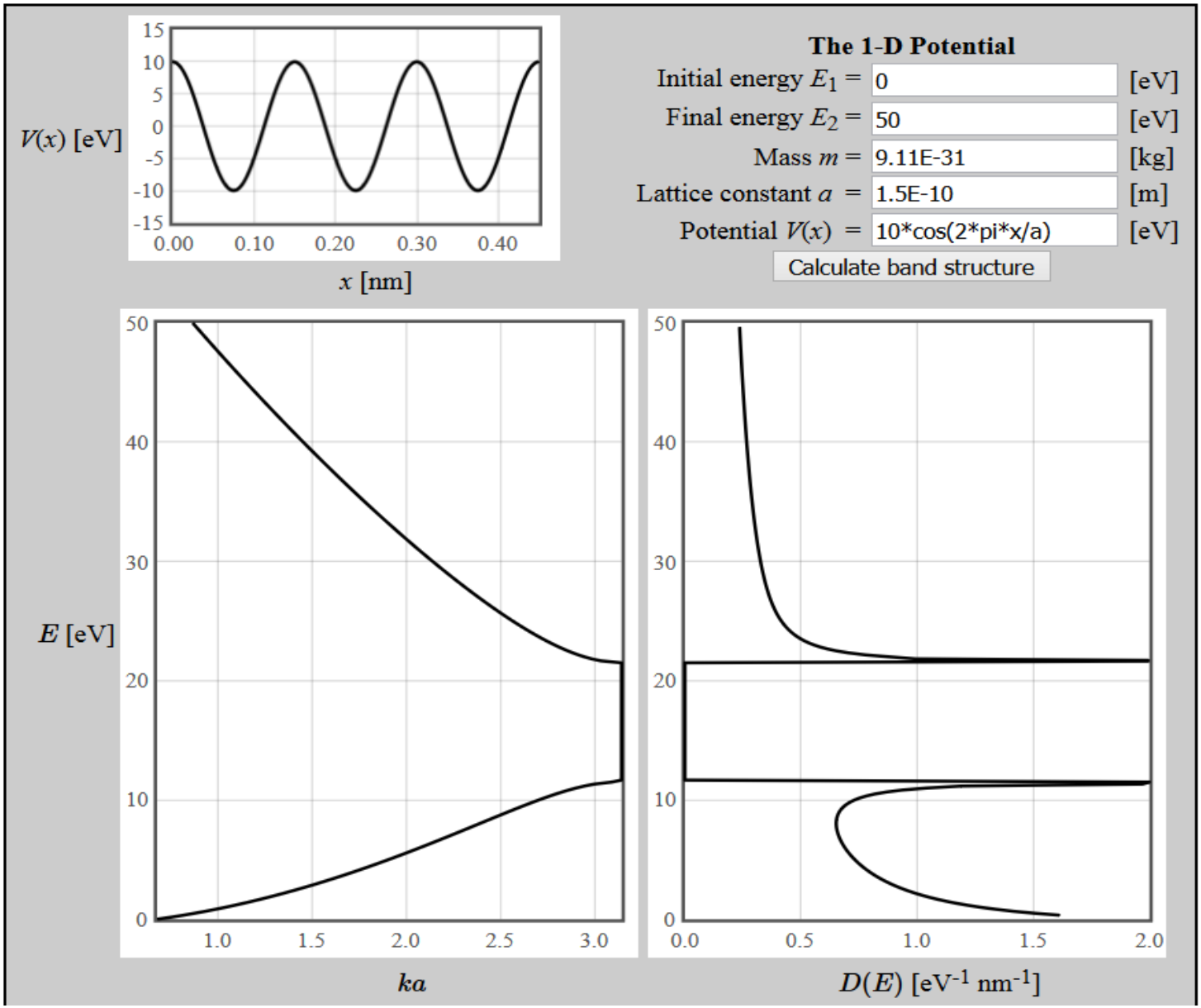
http://lampx.tugraz.at/~hadley/ss1/bands/tbtable/tbtable.html

Bloch waves in one dimension



http://lampx.tugraz.at/~hadley/ss1/bloch/bloch.php

Band Structure in one dimension



http://lampx.tugraz.at/~hadley/ss1/bloch/bloch.php

- Band structure calculations: GaN, 6H SiC, GaAs, GaP, Ge, InAs
- Calculated electron density of states
  - Al fcc, Au fcc, Cu fcc, Na bcc, Pt fcc, W bcc, Si diamond, Fe bcc, Ni fcc, Co fcc, Mn bcc, bcc, Gd hcp, Pd fcc, Pd_3Cr, Pd_3Mn, PdCr, PdMn , GaN, 6H SiC, GaAs, GaP, Ge, InAs

Bandstructure of hexagonal gallium nitride (GaN)

The bandstructure calculation for gallium nitride was calculated using the program Quantum Espresso (version 5.2.1) and the pseudopotentials for Ga and N.