Group of Theoretical Chemical Physics
University of Chile

http://tayrona.ciecias.uchile.cl

cacarden@gmail.com

Diatomic Molecule

$|1\rangle \quad |2\rangle$

Basis

$$\langle i | j \rangle = \delta_{ij}$$

Wave function

$$|\Psi\rangle = c_1|1\rangle + c_2|2\rangle$$

Schrödinger Equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\sum_{j=1}^{2} \hat{H}|j\rangle = E\sum_{j=1}^{2}|j\rangle$$

$$\sum_{j=1}^{2} \langle p|\hat{H}|j\rangle = E$$

Tight binding approximation

$$\langle p|\hat{H}|p\rangle = \alpha \qquad \text{on site energy}$$

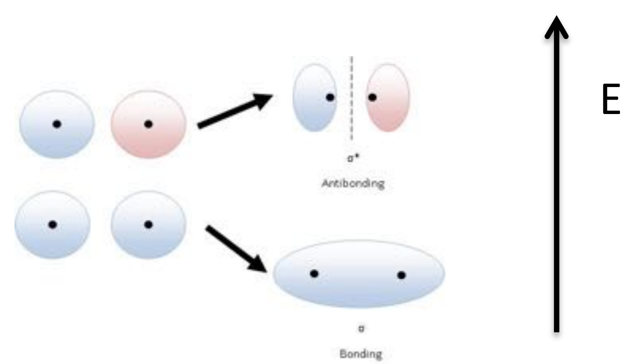
$$\langle 1|\hat{H}|2\rangle = \beta < 0 \quad \text{hopping integral}$$

$$\alpha c_1 + \beta c_2 = E c_1$$

$$\beta c_1 + \alpha c_2 = E c_2$$

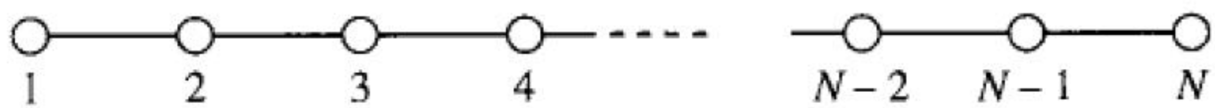
$$E_b = \alpha + \beta$$

$$E_a = \alpha - \beta$$

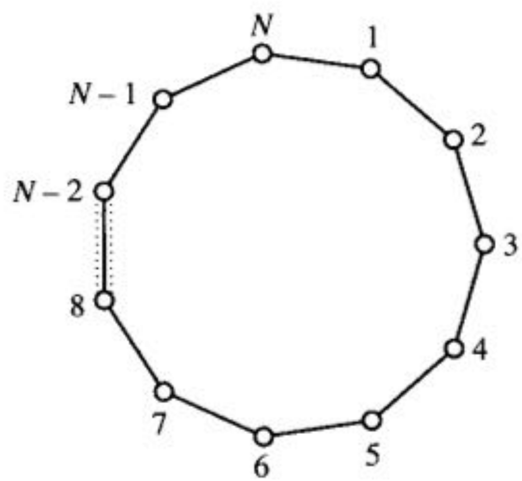


Infinite chain->infinite ring

Linear chain of N Hydrogen atoms

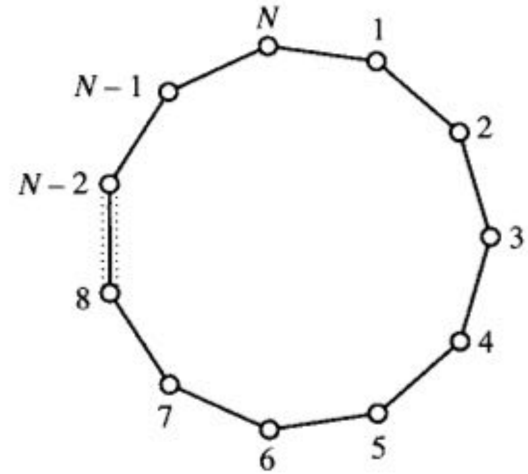


Note that NOT all atoms are equivalent. But if N->∞ there are not edge atoms and all of them should be equivalent: this define **Periodic Boundary Conditions (**Born–von Karman**)**



Sutton, Adrian P. *Electronic structure of materials*. Clarendon Press, 1993.

Infinite ring



Each H atom is associate with an "s" state. Assume that set of these states are orthonormal and form a *complete basis set.*

$$|\Psi\rangle = \sum_{j=1}^{N} c_j |j\rangle, \qquad \langle p|j\rangle = \delta_{pj}$$

Goal: to find the $\mathbf{C}_j$ that solve the Schrödinger equation

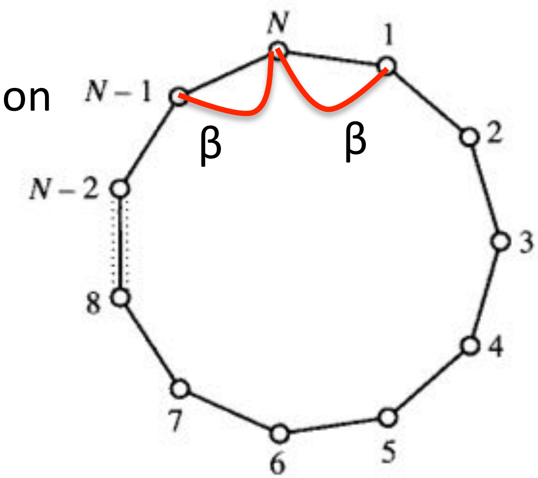
$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\sum_{j=1}^{N} c_j \hat{H}|j\rangle = E\sum_{j=1}^{N} c_j |j\rangle, \quad \text{oparate with the bra} \langle p|$$

$$\sum_{j=1}^{N} c_j \langle p|\hat{H}|j\rangle = E\sum_{j=1}^{N} c_j \langle p|j\rangle$$

Infinite ring

$$\sum_{j=1}^{N} c_j \langle p|\hat{H}|j\rangle = E\sum_{j=1}^{N} c_j \langle p|j\rangle = E\,c_j \qquad (*)$$



Tight binding approximation: neglect electron-electron repulsion and parameterize the matrix elements of the Hamiltonian.

$$\langle p|\hat{H}|p\rangle = \alpha \qquad \text{on site energy}$$

$$\langle p|\hat{H}|p\pm 1\rangle = \beta < 0 \qquad \text{hopping integral}$$

$$c_1\alpha + c_N\beta + c_2\beta = Ec_1 \qquad (p=1)$$

$$c_1\beta + c_2\alpha + c_3\beta = Ec_2 \qquad (p=2)$$

$$\vdots$$

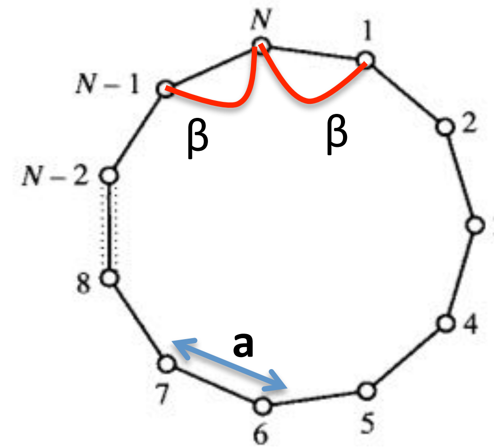
$$(*) \qquad c_{j-1}\beta + c_j\alpha + c_{j+1}\beta = Ec_j \qquad (p=j)$$

$$\vdots$$

$$c_{N-1}\beta + c_N\alpha + c_1\beta = Ec_N \qquad (p=N)$$

Do not try to solve the secular equation because N->∞

Infinite ring



solve:

$$c_{j-1}\beta + c_j\alpha + c_{j+1}\beta = Ec_j$$

$$c_{j-1} - xc_j + c_{j+1} = 0, \quad x = \tfrac{E-\alpha}{\beta}$$

with the boundary conditions:

$$c_{N+1} = c_1$$

a good guess for the solution is: $c_j = e^{ijka}$, $i = \sqrt{-1}$

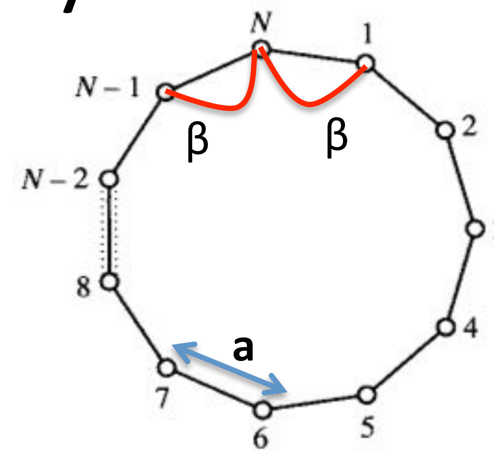
$$e^{i(N+1)ka} = e^{i(1)ka}$$

$$kNa = 2\pi m$$

$$k = \frac{2\pi m}{Na}, \; m = 0,1,2,\ldots,N-1$$

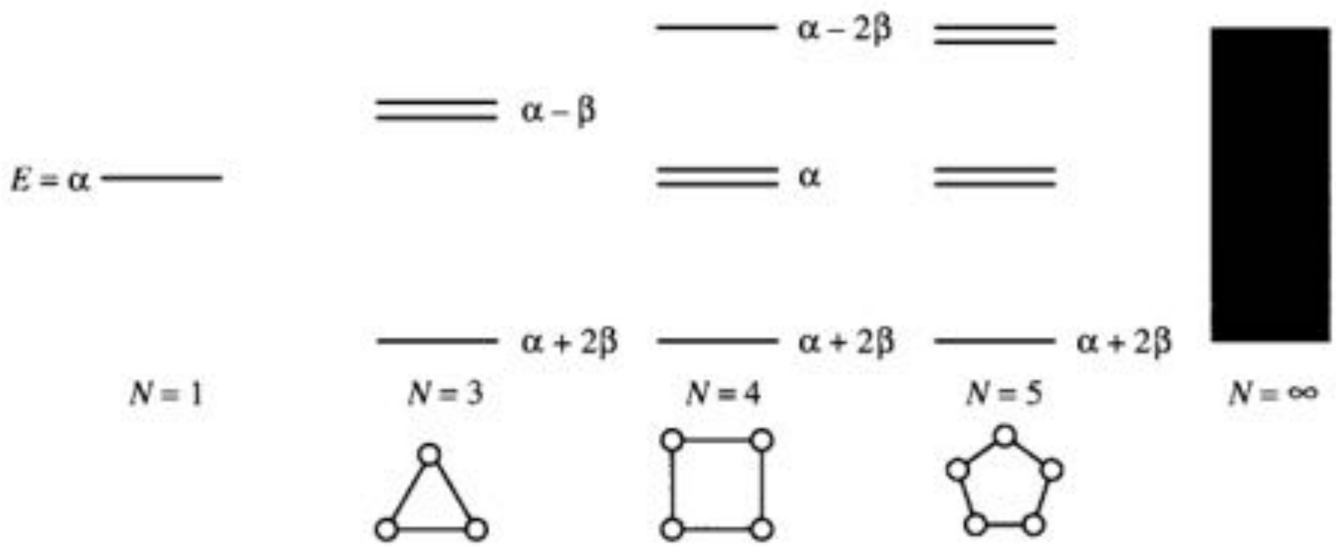
$$c_j^m = \frac{1}{\sqrt{N}}\exp\left(i\frac{2\pi jm}{N}\right) = \frac{1}{\sqrt{N}}\exp\left(ik_m ja\right)$$

Infinite ring: Summary



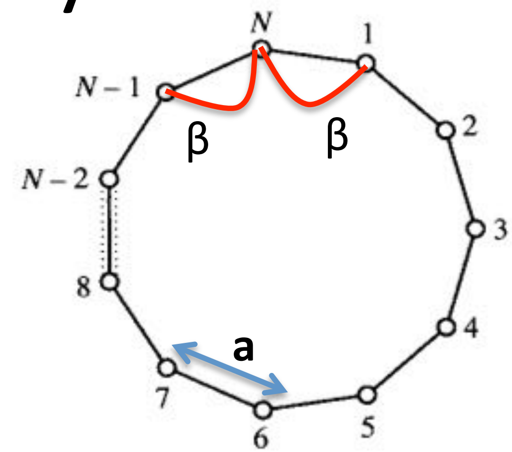
$$\left|\Psi_k\right\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{(ikja)} \left| j \right\rangle$$

$$E_k = \alpha + 2\beta \cos(ka) = \alpha + 2\beta \cos\left(\frac{2\pi m}{N}\right)$$



Band!

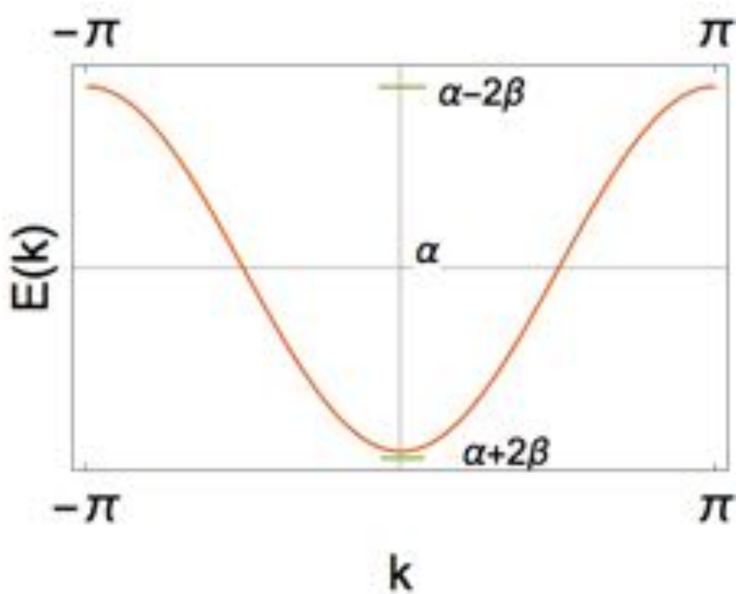
Infinite ring: Summary



$$\left|\Psi_k\right\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{(ikja)} \left| j \right\rangle$$

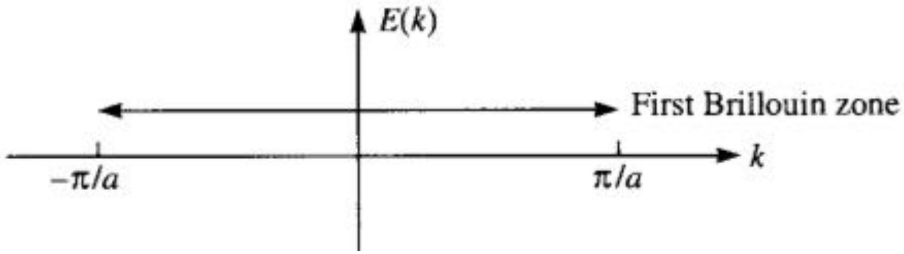
$$E_k = \alpha + 2\beta \cos(ka)$$

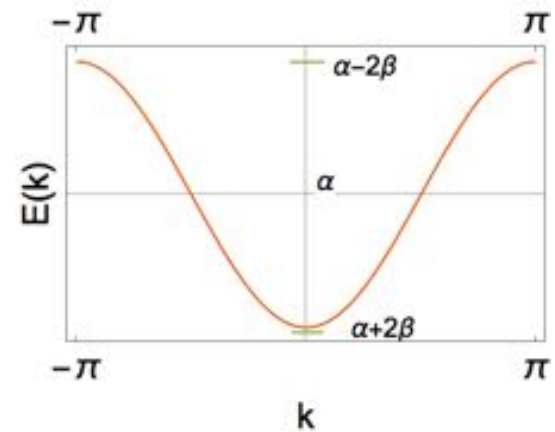
$$-\frac{\pi}{a} < k\frac{m}{N} < \frac{\pi}{a}, \quad \lim_{N\to\infty} \frac{m}{N} = 1$$



First Brillouin Zone:k-space

$$-\frac{\pi}{a} < k\frac{m}{N} < \frac{\pi}{a}$$





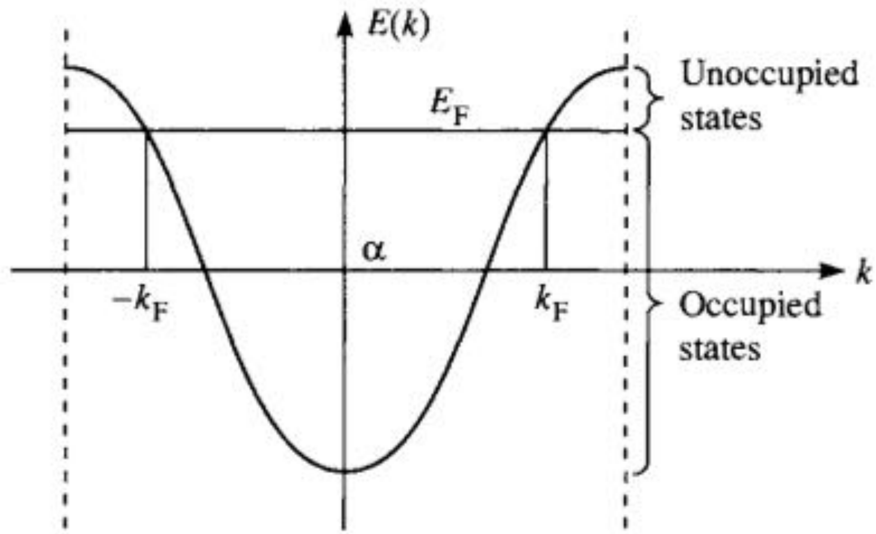
- For finite N the reciprocal space is discrete. k has to be a multiple of 2π/Na
- The numbers of states that fit in a unit distance of k-space is Na/2π
- Density of states in the k-space is

$$DOS(k) = \frac{Na}{2\pi} = \frac{L}{2\pi}$$

What states are occupied?

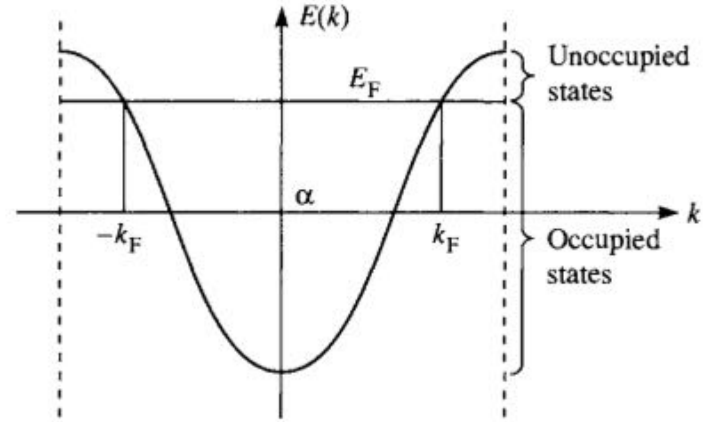
- Depends on the number of electrons per atom, ν
- The Pauli principle say that every state can be occupied by at most 2 electrons.
- Then, for a given number of electrons per atom, there will be M states occupied such that

$$\nu = \frac{2M}{N}$$



Fermi Level and Fermi Energy

$$2\frac{Na}{2\pi}k_F = M \rightarrow \boxed{k_F = \frac{\nu\pi}{2a}}$$



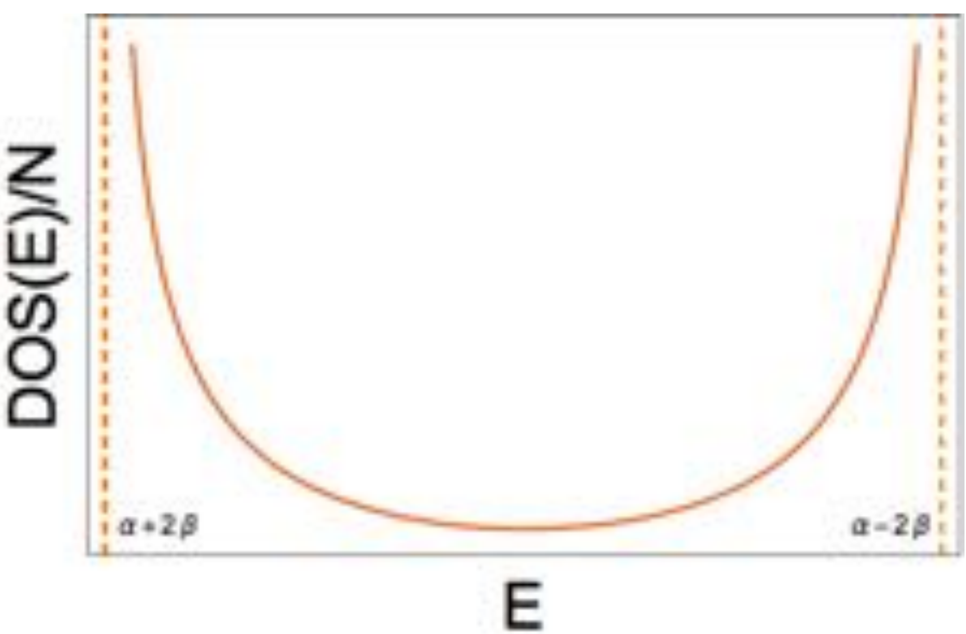
$$E_F = \alpha + 2\beta\cos\left(k_F a\right)$$

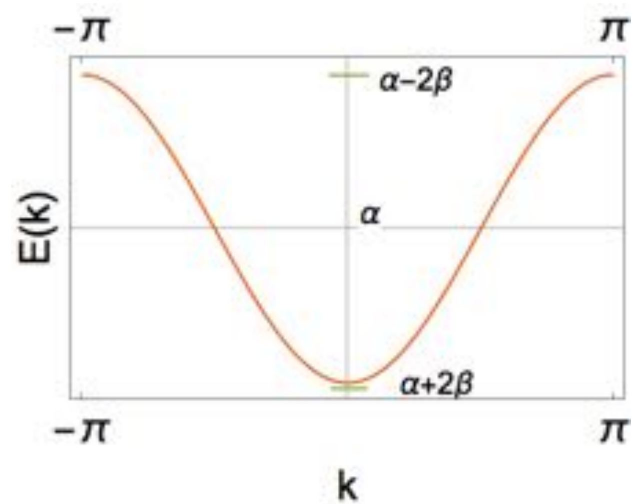
Density of states

Density of states in the k-domain $$DOS(k)=\frac{Na}{2\pi}=\frac{L}{2\pi}$$

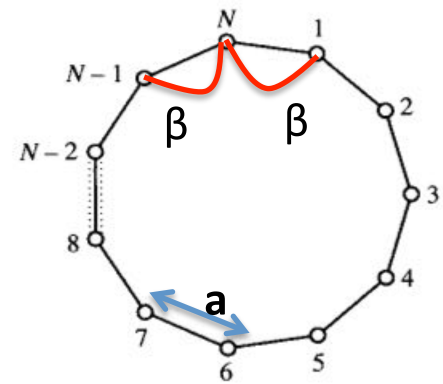
Density of states in the energy domain: number of states in ***E*** and ***E+dE.***

$$DOS(E)=DOS(k)\left|\frac{dk}{dE}\right|=2\frac{Na}{2\pi}\frac{1}{2\beta\sin(ka)}=\frac{N}{\pi}\frac{1}{\sqrt{\left(4\beta^2-(E-\alpha)^2\right)}}$$





Bloch's Theorem



$$\left|\Psi(x+ma)\right|^2 = \left|\Psi(x)\right|^2$$

therefore, $\Psi(x)$ and $\Psi(x+ma)$ differ in a phase

$$\Psi(x+ma) = e^{i\phi ma}\Psi(x)$$

expand $\Psi(x)$ in the atomic base

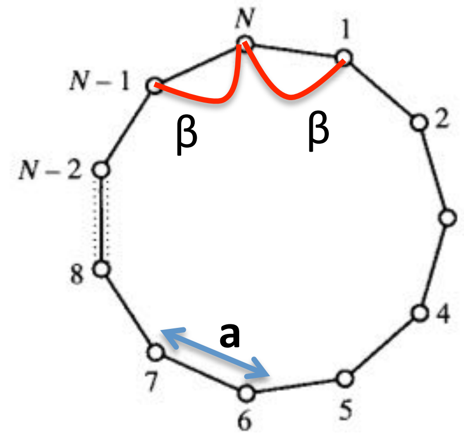
$$\Psi(x) = \sum_{j=1}^{N} c_j \langle x | j \rangle \quad and \quad \Psi(x+ma) = \sum_{j=1}^{N} c_j \langle x+ma | j \rangle = \sum_{j=1}^{N} c_j \langle x | j-m \rangle = \sum_{j=1}^{N} c_{j+m} \langle x | j \rangle$$

then

$$\sum_{j=1}^{N} c_{j+m} \langle x | j \rangle = e^{i\phi} \sum_{j=1}^{N} c_j \langle x | j \rangle \Rightarrow c_{j+m} \left(c_j\right)^{-1} = e^{i\phi ma}$$

$$\boxed{c_j = Ae^{ij\phi ma} = \frac{1}{\sqrt{N}} e^{ijkma}}$$

Bloch's Theorem



$$\Psi(x+ma) = e^{ik(ma)}\Psi(x) = e^{ikR}\Psi(x)$$

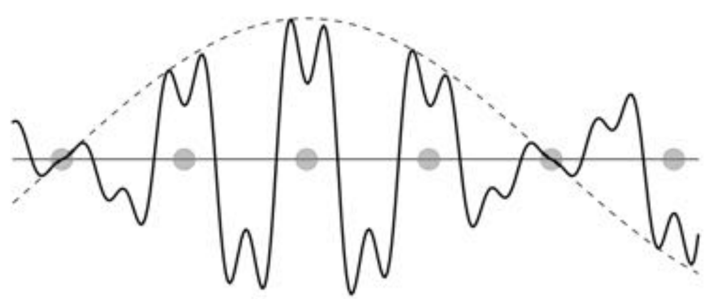
R is a "latice vector"

or

$$\Psi(x) = e^{ikx}u(x)$$

Plane wave with wave vector k

Periodic function: Bloch functions



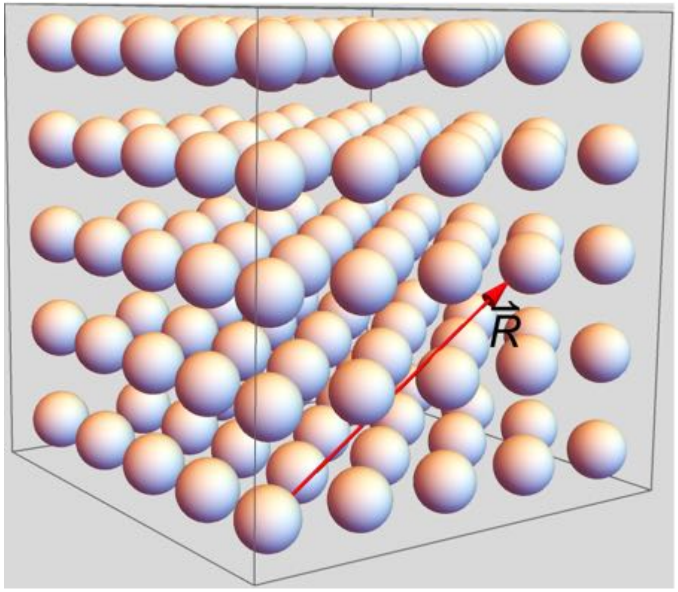
3D: Cubic Solid

$$\left|\Psi_{\vec{k}}\right\rangle = \frac{1}{\sqrt{N_x N_y N_z}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \left|\vec{R}\right\rangle$$

$$\vec{R} = a(l,m,n)$$

$$\vec{k} = (k_x, k_y, k_z)$$

$$E(\vec{k}) = \alpha + 2\beta\left(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right)$$

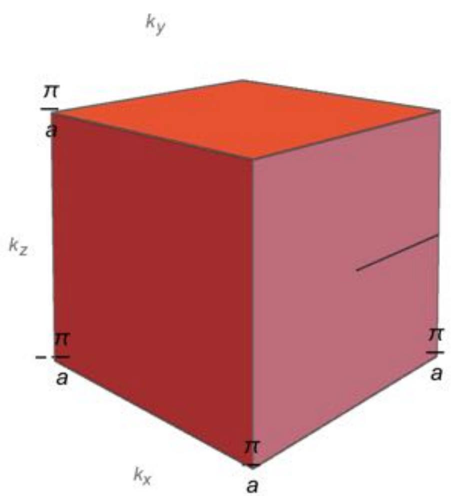


First Brillouin Zone:

$$-\frac{\pi}{a} < k_x < \frac{\pi}{a}$$

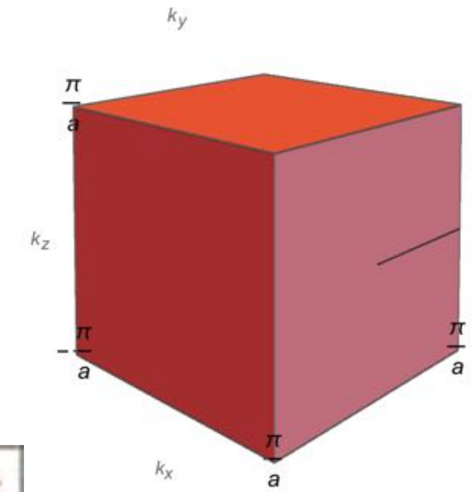
$$-\frac{\pi}{a} < k_y < \frac{\pi}{a}$$

$$-\frac{\pi}{a} < k_z < \frac{\pi}{a}$$

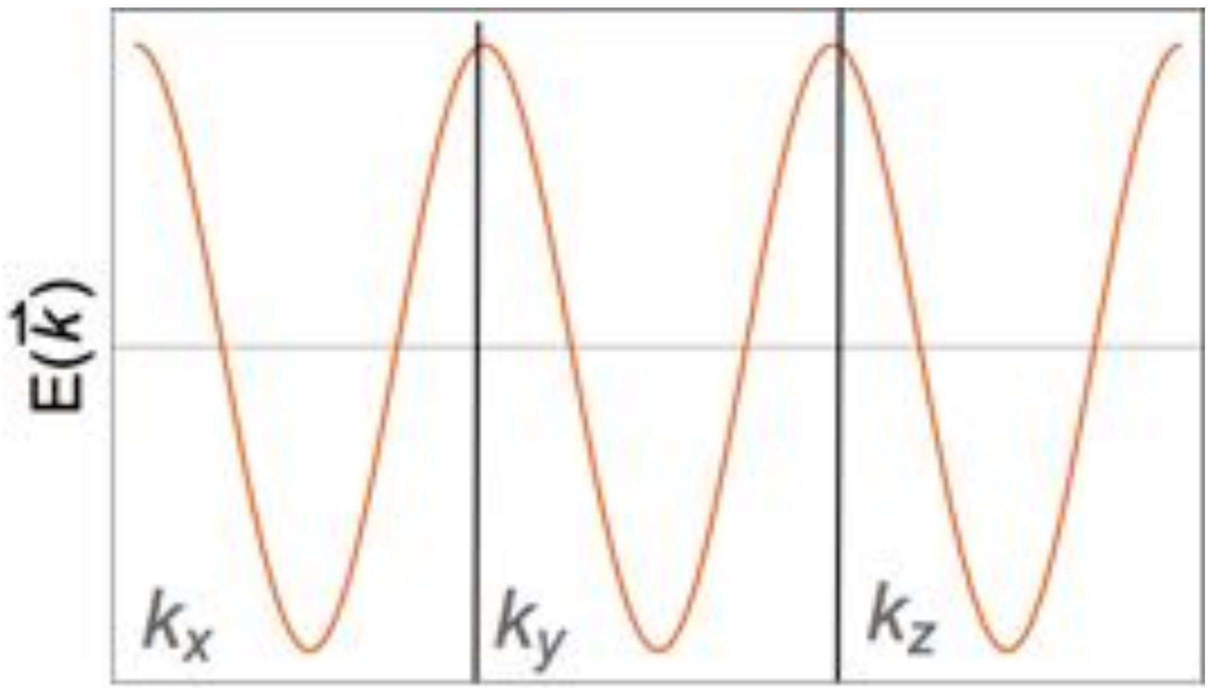


Cubic Solid: Bands

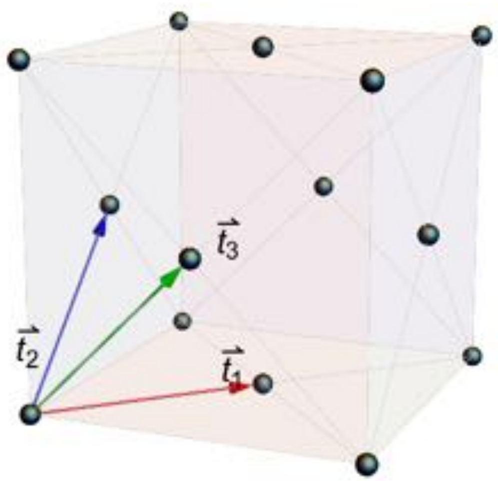
$$E\left(\vec{k}\right) = \alpha + 2\beta\left(\cos\left(k_x a\right) + \cos\left(k_y a\right) + \cos\left(k_z a\right)\right)$$



First Brillouin Zone:



FCC: Lattice and Reciprocal Space

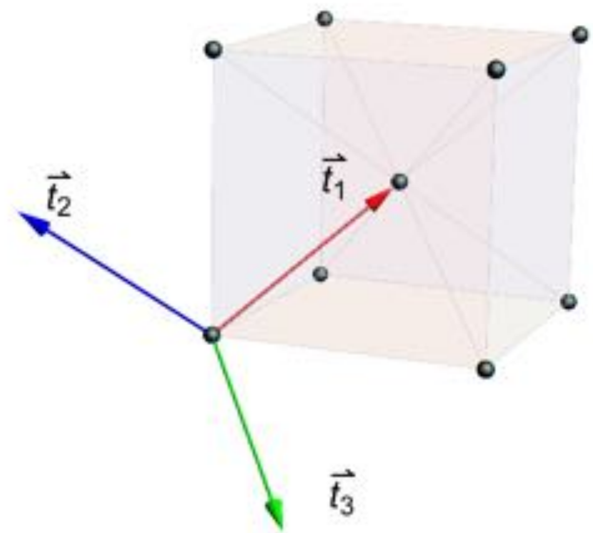


Lattice

$$\vec{t}_1^{\,*} = \frac{2\pi\,\vec{t}_2 \times \vec{t}_3}{\vec{t}_1 \cdot \left(\vec{t}_2 \times \vec{t}_3\right)}$$

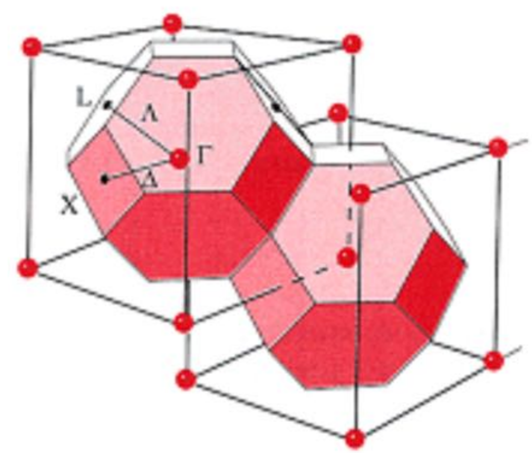
$$\vec{t}_2^{\,*} = \frac{2\pi\,\vec{t}_3 \times \vec{t}_1}{\vec{t}_1 \cdot \left(\vec{t}_2 \times \vec{t}_3\right)}$$

$$\vec{t}_3^{\,*} = \frac{2\pi\,\vec{t}_1 \times \vec{t}_2}{\vec{t}_1 \cdot \left(\vec{t}_2 \times \vec{t}_3\right)}$$



Reciprocal Space

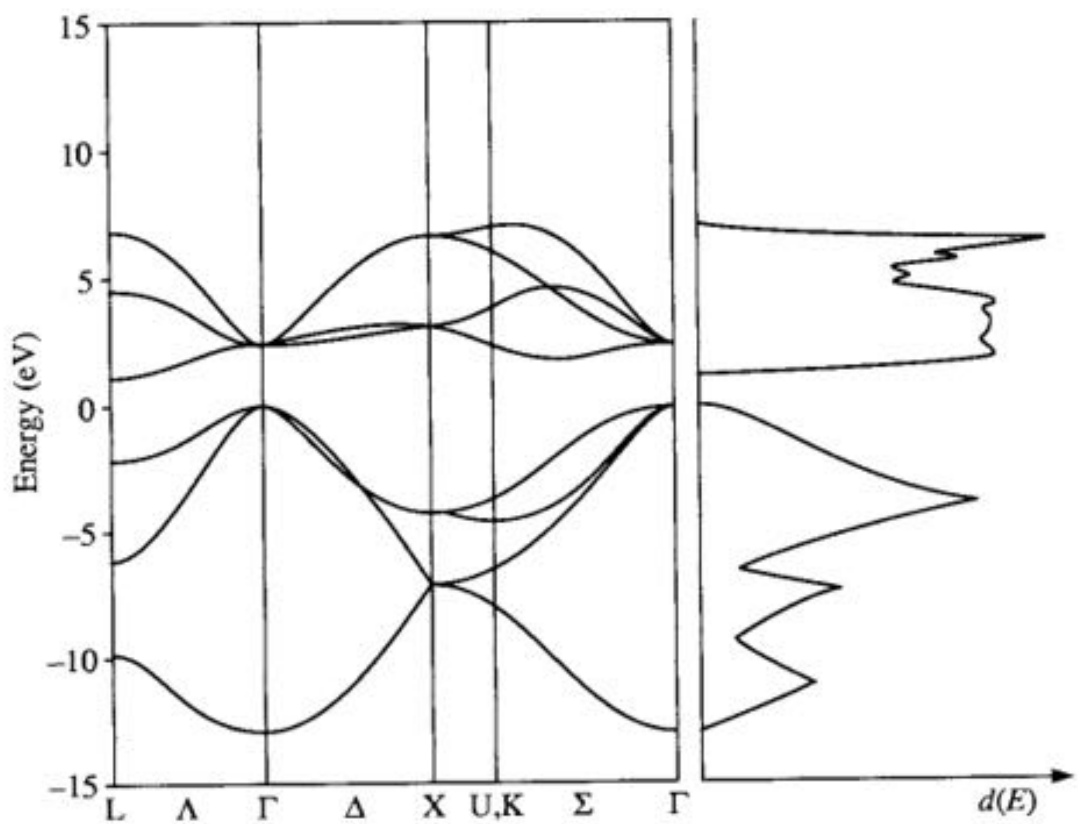
First Brillouin Zone:



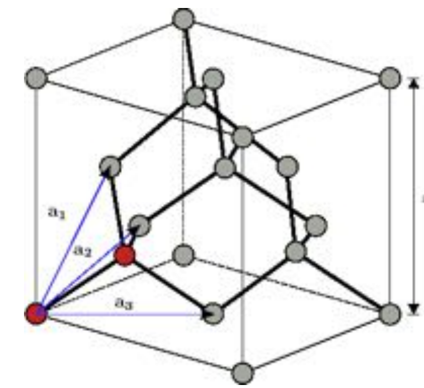
Silicon Mininal Basis set.

each atom has AO: 2s,2px,2py, 2pz

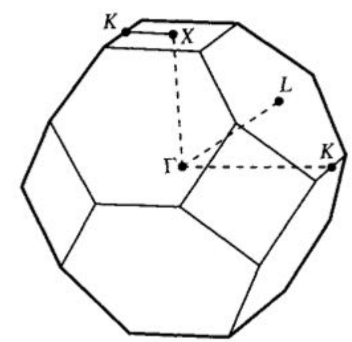
$$\left|\Psi_{n,\vec{k}}\right\rangle = \frac{1}{\sqrt{N}} \sum_{m} \sum_{j=1,2} c^{n}_{j,AO}\, e^{i\vec{k}\cdot\left(\vec{R}_m - \vec{b}_j\right)} \left|m, j, AO\right\rangle$$



Lattice



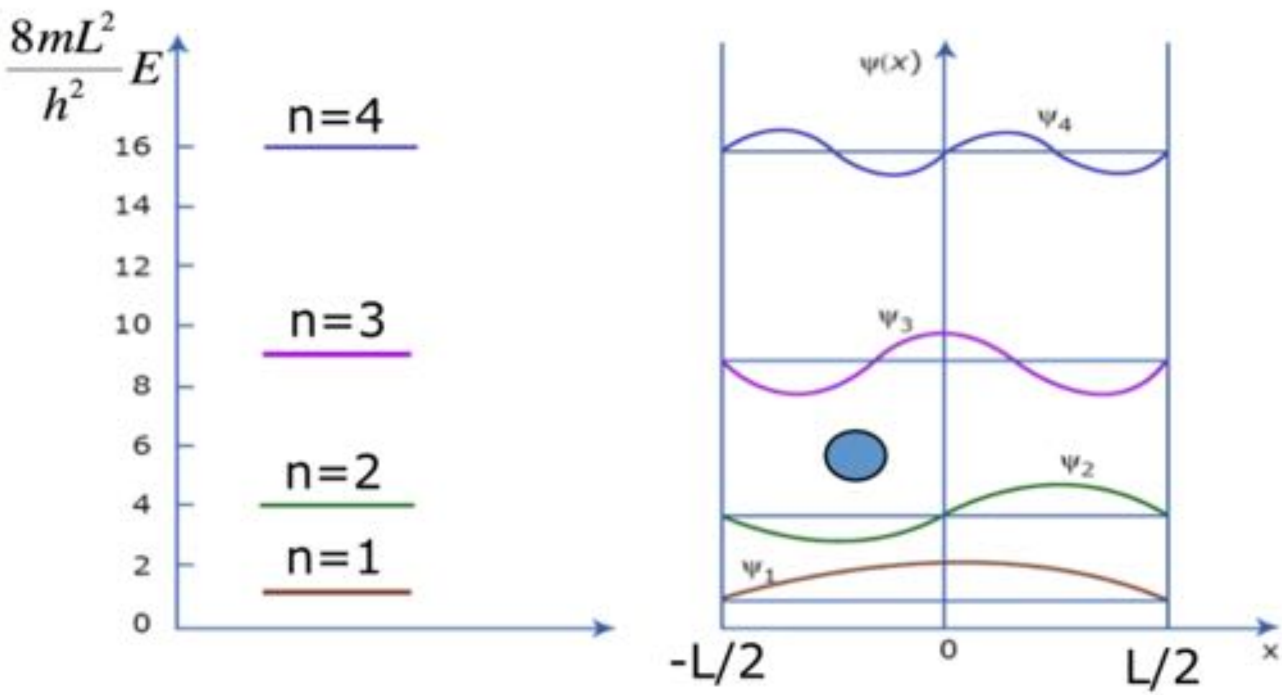
First Brillouin Zone:



A particle in a box: 1D Case

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n(x)+V(x)\psi_n(x)=E_n\psi_n(x) \qquad V(x)=\begin{cases}0, -L/2<x<L/2\\ \infty, outside\end{cases}$$

$$\psi_n(x)=\sqrt{\frac{2}{L}}\sin(k_n x), \quad k_n=\frac{n\pi}{L}, n=0,1,2,... \qquad E_n=\frac{\hbar^2 k_n{}^2}{2m},$$



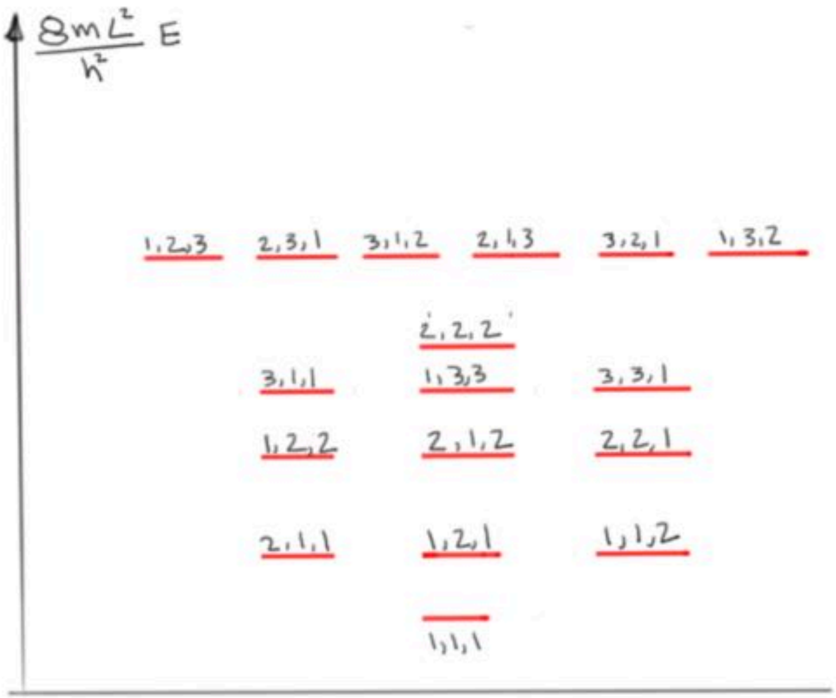
A particle in a box: 3D Case

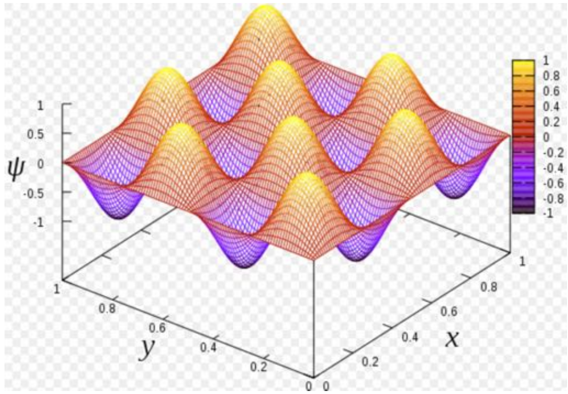
$$-\frac{\hbar^2}{2m}\nabla^2\psi_n(\mathbf{r})+V(\mathbf{r})\psi_n(\mathbf{r})=E_n\psi_n(\mathbf{r})$$

$$\psi_{n_x,n_y,n_z}=\psi_{n_x}(x,L_x)\psi_{n_y}(y,L_y)\psi_{n_z}(z,L_z)$$

$$E_{n_x,n_y,n_z}=\frac{\hbar^2 k^2_{n_x,n_y,n_z}}{2m}$$

$$\mathbf{k}_{\mathbf{n_x},\mathbf{n_y},\mathbf{n_z}}=k_{n_x}\hat{\mathbf{x}}+k_{n_y}\hat{\mathbf{y}}+k_{n_z}\hat{\mathbf{z}}=\frac{n_x\pi}{L_x}\hat{\mathbf{x}}+\frac{n_y\pi}{L_y}\hat{\mathbf{y}}+\frac{n_z\pi}{L_z}\hat{\mathbf{z}}$$

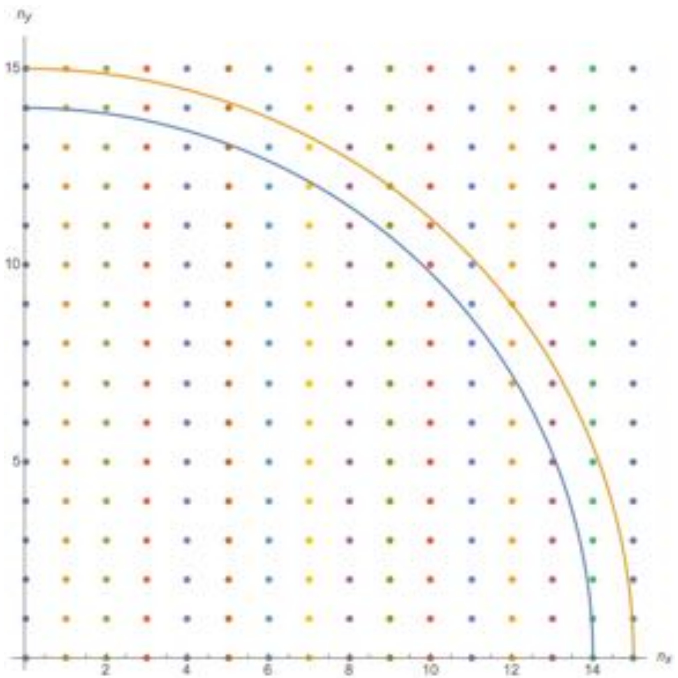




The Density of States: DOS

Be the number of states per unit volume $G := \frac{Number\ of\ states}{Volume} = \frac{N}{V}$

$$DOS = g(E) = \frac{dG}{dE} = Number\ of\ states\ in\ E\ and\ E + dE$$



$$E_{n_x, n_y, n_z} = \frac{\hbar^2 k^2_{n_x, n_y}}{2m}$$

$$k^2_{n_x, n_y} = k^2_{n_x} + k^2_{n_y} = \left(\frac{n_x \pi}{L_x}\right)^2 + \left(\frac{n_y \pi}{L_y}\right)^2$$

$$G = \frac{k^2}{4\pi} = \frac{2mE}{4\pi\hbar^2}$$

$$g(E) = \frac{2m}{4\pi}$$

The Density of States: DOS

$$DOS = g(E) = \frac{dG}{dE} = Number\ of\ states\, in\, E\, and\, E + dE$$

1-Dimension

$$g_{1D}(E) = \sqrt{\frac{m}{2\pi^2\hbar^2 E}}$$

2-Dimensions

$$g_{2D}(E) = \frac{m}{2\pi\hbar^2}$$

3-Dimensions

$$g_{3D}(E) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{3/2}$$