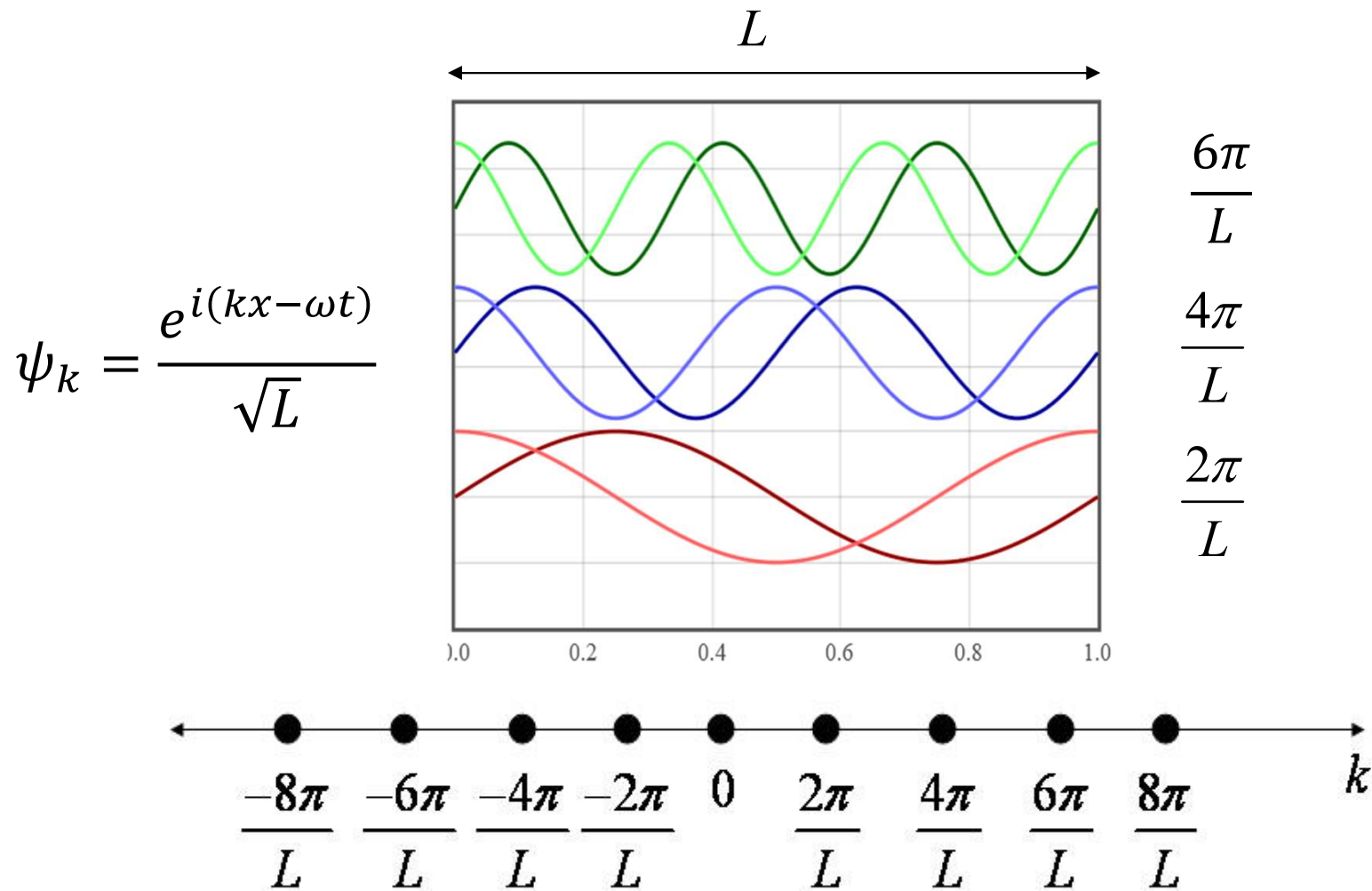


Electrons

Periodic boundary conditions

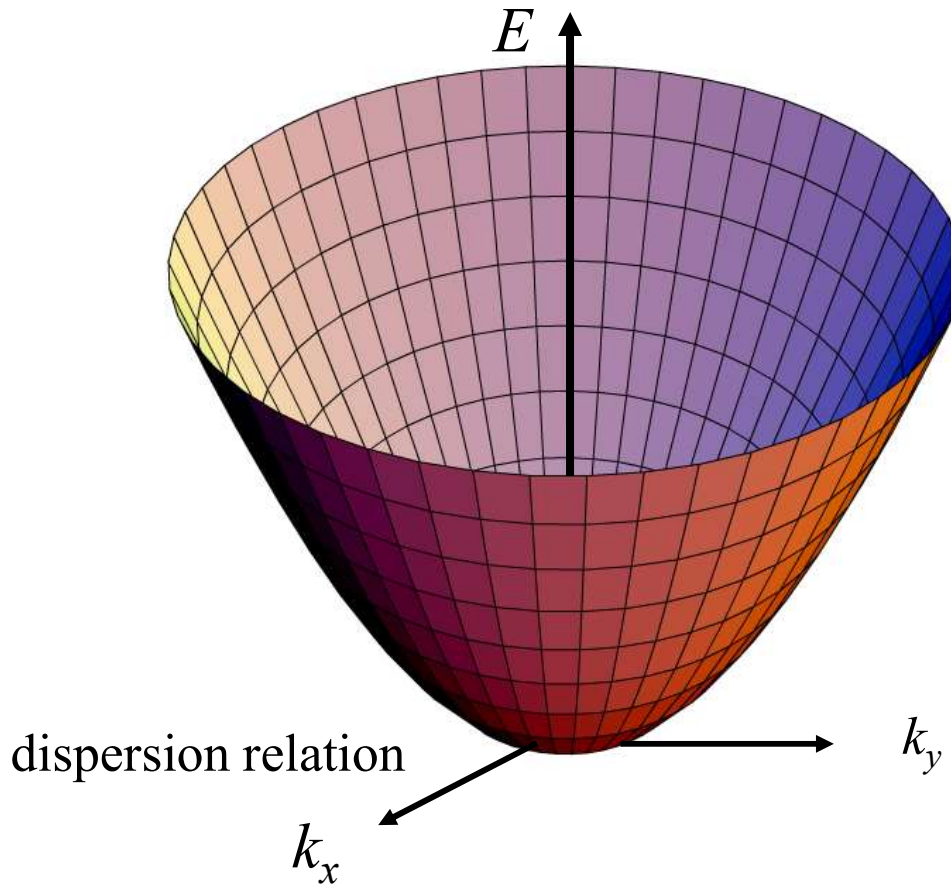
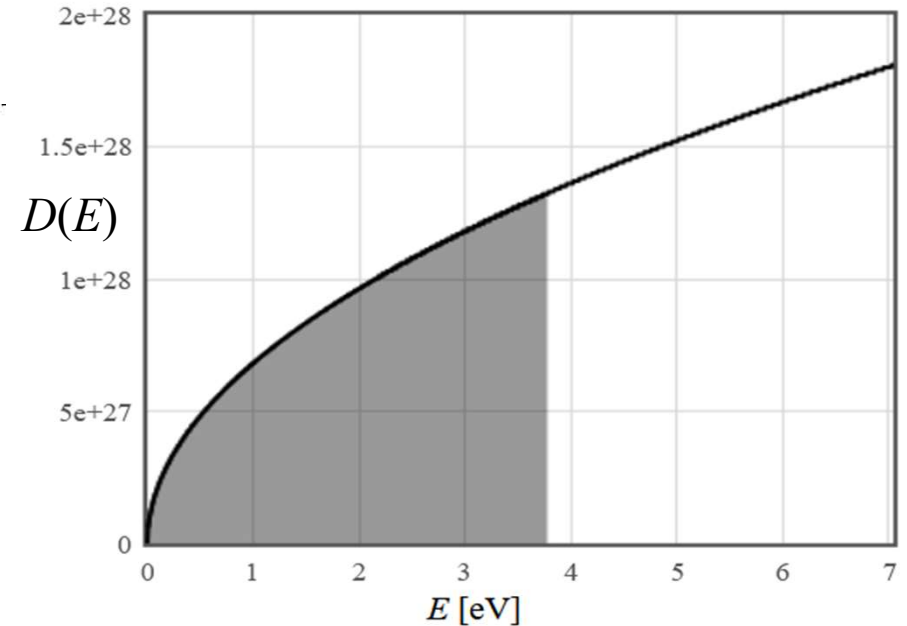


free electrons (simple model for a metal)

$$\vec{p} = \hbar \vec{k}$$

$$E(\vec{k}) = \frac{1}{2} m v^2 = \frac{p^2}{2m} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

3-d density of states

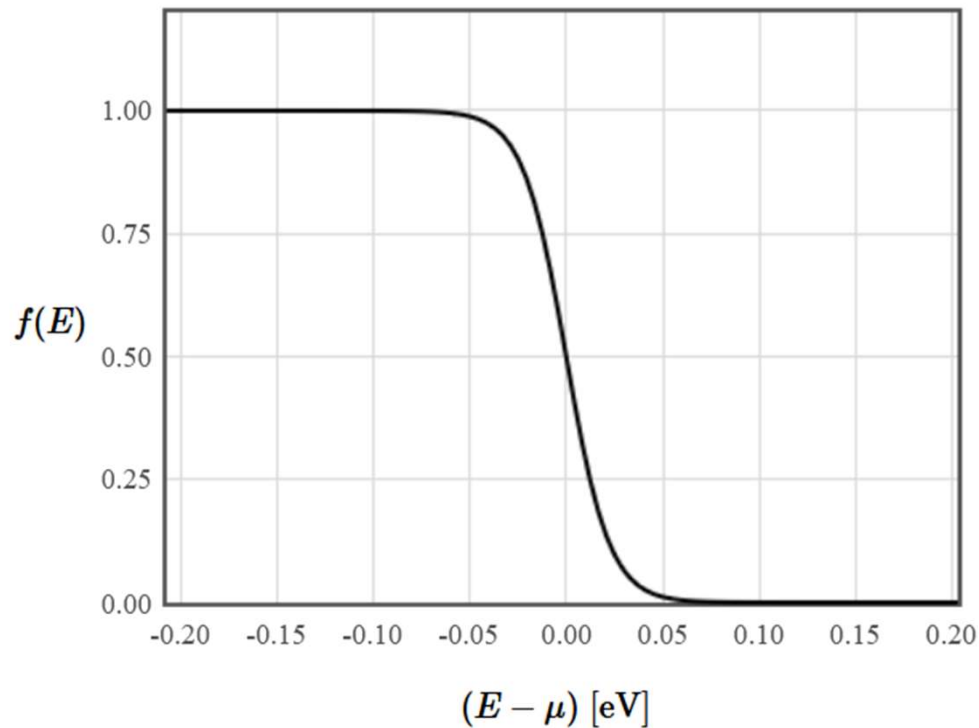


$$D(E) = \begin{cases} 0 & \text{for } E < 0 \\ \frac{(2m)^{3/2}}{2\pi^2 \hbar^3} \sqrt{E} & \text{for } E > 0 \end{cases}$$

Fermi function

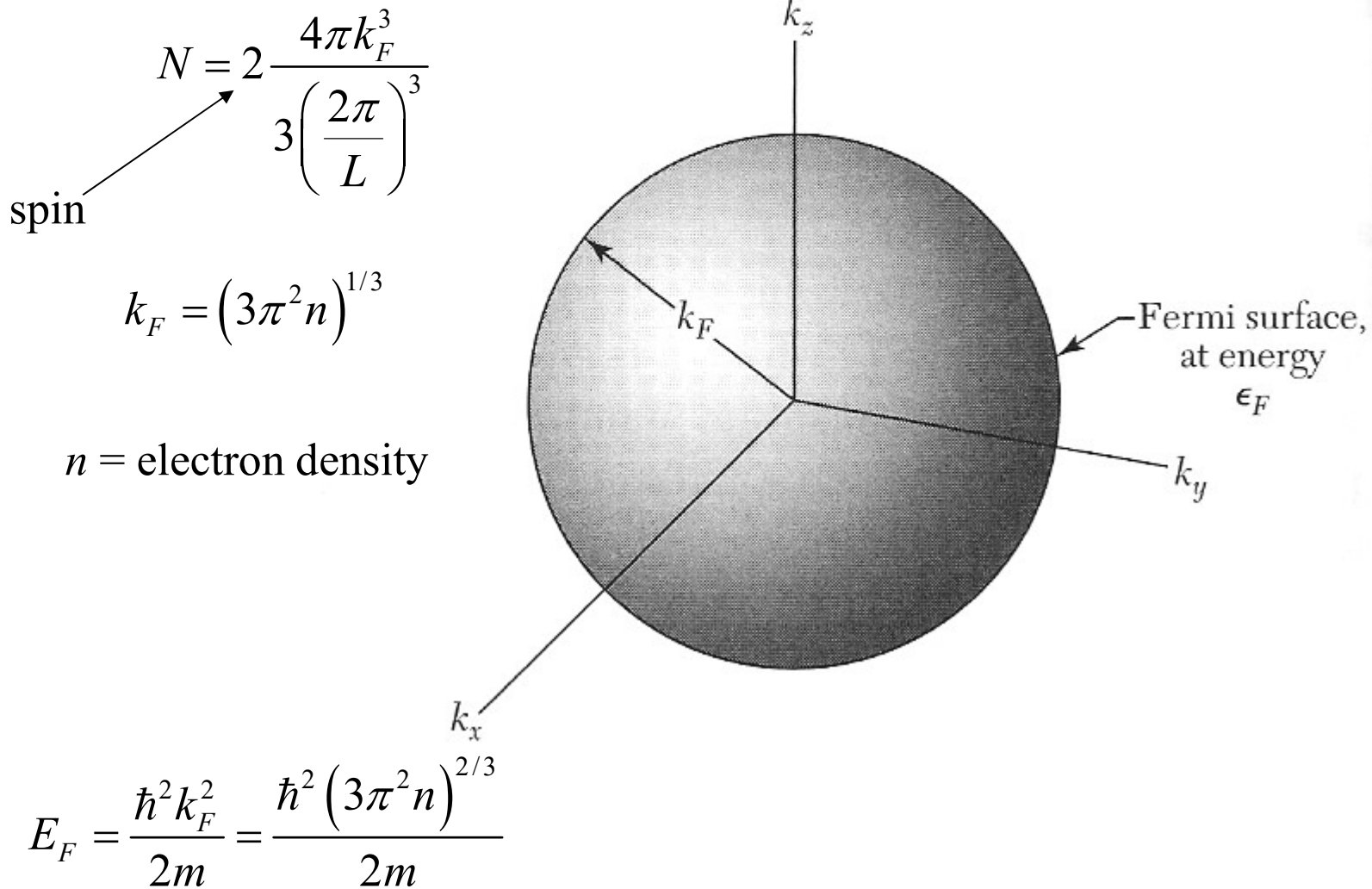
$f(E)$ is the probability that a state at energy E is occupied.

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)}$$



$\mu =$ chemical potential

Fermi sphere



The thermal and electronic properties depend on the states at the Fermi surface.

Internal energy density at $T = 0$

$$u = \int_{-\infty}^{\infty} ED(E)dE = \int_0^{E_f} ED(E)dE$$

$$D(E) = \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3} \sqrt{E} \quad \text{J}^{-1} \text{m}^{-3}$$

$$u = \int_0^{E_f} \frac{(2m)^{\frac{3}{2}}}{2\pi^2\hbar^3} E^{3/2} dE = \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3} E_f^{\frac{5}{2}}$$

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad u(T=0) = \frac{3}{5} n E_F$$

$$u(T=0) = \frac{\pi^{\frac{4}{3}} \hbar^2}{10m} (3n)^{\frac{5}{3}} = \frac{\pi^{\frac{4}{3}} \hbar^2}{10m} \left(\frac{3N}{V} \right)^{\frac{5}{3}}$$

Pressure 3-D

$$P = - \left(\frac{\partial U}{\partial V} \right)_N$$

$$u(T = 0) = \frac{\pi^{\frac{4}{3}} \hbar^2}{10m} (3n)^{\frac{5}{3}} = \frac{\pi^{\frac{4}{3}} \hbar^2}{10m} \left(\frac{3N}{V} \right)^{\frac{5}{3}}$$

$$U = Vu \propto V^{-2/3}$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_N = \frac{2}{3} \frac{U}{V} = \frac{2}{5} n E_F = \frac{\hbar^2 (9\pi^4 n^5)^{\frac{1}{3}}}{5m}$$

Bulk modulus

$$B = -V \frac{\partial P}{\partial V}$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_N = \frac{\hbar^2 (9\pi^4 N^5 / V^5)^{\frac{1}{3}}}{5m}$$

$$P \propto V^{-5/3}$$

$$B = \frac{5}{3} P = \frac{10}{9} \frac{U}{V} = \frac{2}{3} n E_F = \frac{\hbar^2 (3\pi^4 n^5)^{\frac{1}{3}}}{m} \quad \text{N/m}^2$$

See: Landau and Lifshitz, Statistical Physics 1
or Ashcroft and Mermin, Solid State Physics

Bulk modulus

Table 2.2
BULK MODULI IN 10^{10} DYNES/CM² FOR SOME
TYPICAL METALS^a

METAL	FREE ELECTRON B	MEASURED B
Li	23.9	11.5
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9
Al	228	76.0

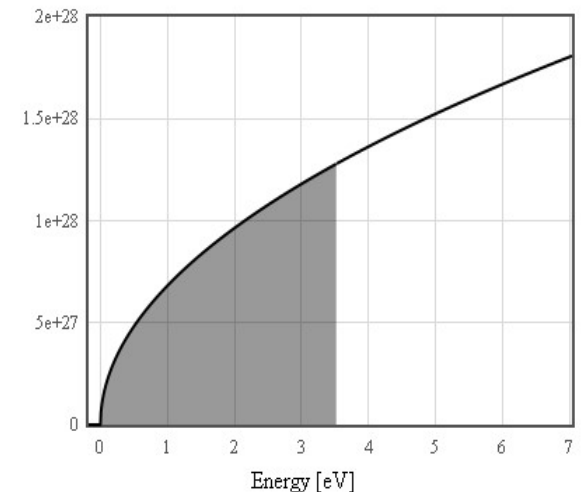
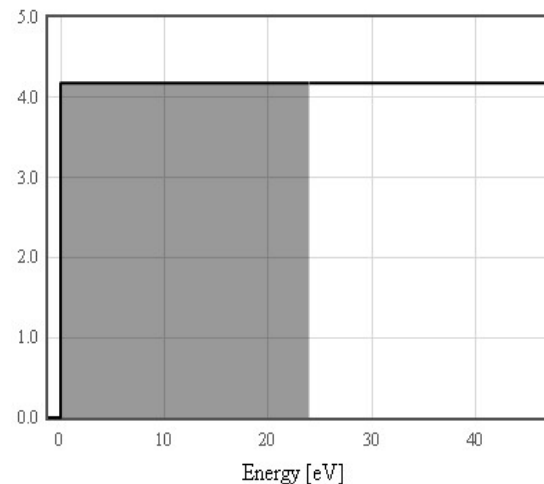
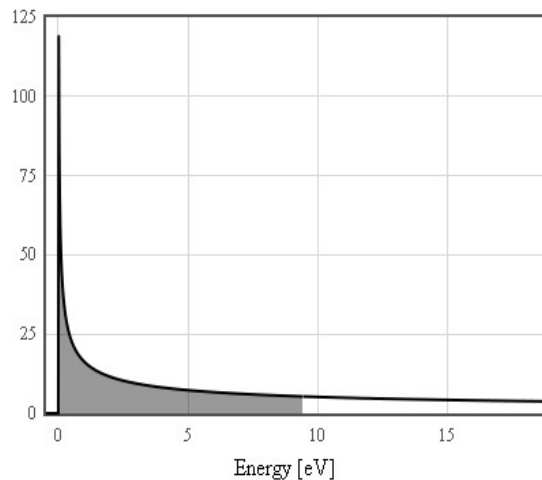
^a The free electron value is that for a free electron gas at the observed density of the metal, as calculated from Eq. (2.37).

Free electron Fermi gas

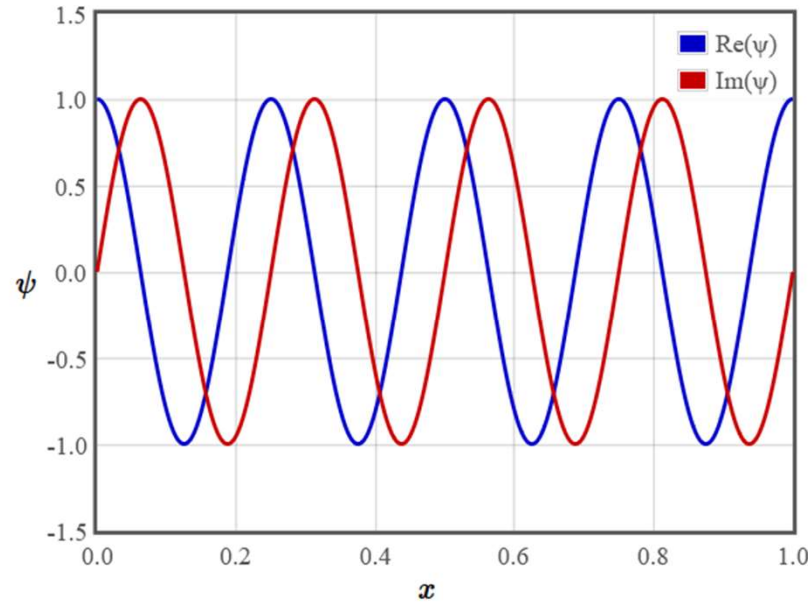
$$1 - d \quad D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} = \frac{n}{2\sqrt{E_F E}} \quad \text{J}^{-1} \text{m}^{-1}$$

$$2 - d \quad D(E) = \frac{m}{\hbar^2 \pi} = \frac{n}{E_F} \quad \text{J}^{-1} \text{m}^{-2}$$

$$3 - d \quad D(E) = \frac{\pi}{2} \left(\frac{2m}{\hbar^2 \pi^2} \right)^{3/2} \sqrt{E} = \frac{3n}{2E_F^{3/2}} \sqrt{E} \quad \text{J}^{-1} \text{m}^{-3}$$



Free-electron model



$n_x = 4$

Single particle solutions to Schrödinger equation	$\psi(\vec{r}) = \frac{1}{\sqrt{L}} e^{ikx} \frac{1}{\sqrt{m}}$	$\psi(\vec{r}) = \frac{1}{\sqrt{L^2}} e^{i\vec{k}\cdot\vec{r}} \frac{1}{m}$	$\psi(\vec{r}) = \frac{1}{\sqrt{L^3}} e^{i\vec{k}\cdot\vec{r}} \frac{1}{m^{3/2}}$
Allowed k values	$k_x = \frac{2\pi n_x}{L} \frac{1}{m}$ $n_x = \dots - 2, -1, 0, 1, 2, \dots$	$\vec{k} = \left[\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L} \right] \frac{1}{m}$ $n_x, n_y = \dots - 2, -1, 0, 1, 2, \dots$	$\vec{k} = \left[\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L} \right] \frac{1}{m}$ $n_x, n_y, n_z = \dots - 2, -1, 0, 1, 2, \dots$
Density of electron states in reciprocal space	$D(\vec{k}) = \frac{2}{2\pi}$	$D(\vec{k}) = \frac{2}{(2\pi)^2}$	$D(\vec{k}) = \frac{2}{(2\pi)^3}$
Density of electron states in reciprocal space	$D(k) = \frac{2}{\pi}$	$D(k) = \frac{k}{\pi} \text{ m}^{-1}$	$D(k) = \frac{k^2}{\pi} \text{ m}^{-2}$

Electronic specific heat

$$c_{v,electrons} = \frac{du}{dT} \approx \left(\frac{\pi}{3}\right)^{\frac{2}{3}} \frac{mn^{\frac{1}{3}}}{\hbar^2} k_B^2 T \quad \text{J K}^{-1} \text{m}^{-3}$$

$$c_{v,total} = \underbrace{\gamma T}_{\text{electrons}} + \underbrace{AT^3}_{\text{phonons}}$$

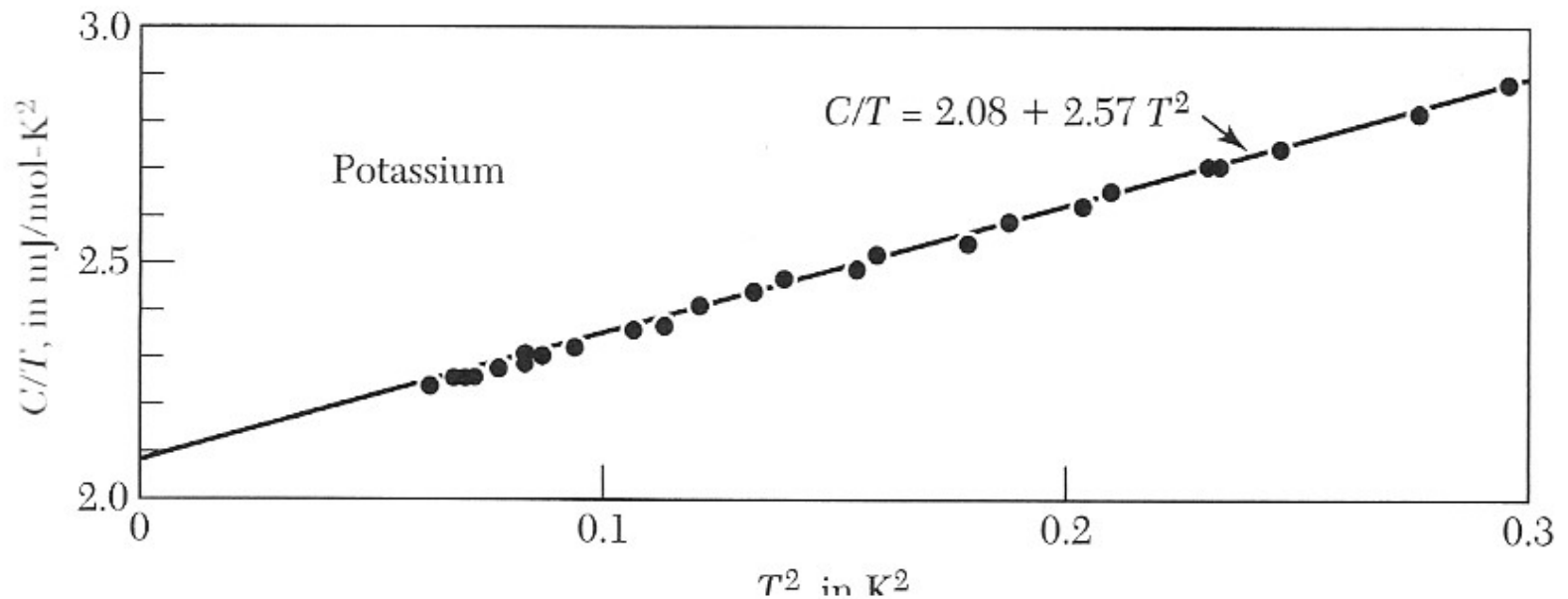


Table 2 Experimental and free electron values of electronic heat capacity constant γ of metals

(From compilations kindly furnished by N. Phillips and N. Pearlman. The thermal effective mass is defined by Eq. (38).)

Li		Be											B	C	N
1.63	0.17														
0.749	0.500														
2.18	0.34														
Na		Mg											Al	Si	P
1.38	1.3										1.35				
1.094	0.992										0.912				
1.26	1.3										1.48				
Observed γ in $\text{mJ mol}^{-1} \text{K}^{-2}$.															
Calculated free electron γ in $\text{mJ mol}^{-1} \text{K}^{-2}$.															
$m_{th}/m = (\text{observed } \gamma)/(\text{free electron } \gamma)$.															
K	Ca	Sc	Ti	V	Cr	Mn(γ)	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	
2.08	2.9	10.7	3.35	9.26	1.40	9.20	4.98	4.73	7.02	0.695	0.64	0.596		0.19	
1.668	1.511									0.505	0.753	1.025			
1.25	1.9									1.38	0.85	0.58			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn ^(w)	Sb	
2.41	3.6	10.2	2.80	7.79	2.0	—	3.3	4.9	9.42	0.646	0.688	1.69	1.78	0.11	
1.911	1.790									0.645	0.948	1.233	1.410		
1.26	2.0									1.00	0.73	1.37	1.26		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg(α)	Tl	Pb	Bi	
3.20	2.7	10.	2.16	5.9	1.3	2.3	2.4	3.1	6.8	0.729	1.79	1.47	2.98	0.008	
2.238	1.937									0.642	0.952	1.29	1.509		
1.43	1.4									1.14	1.88	1.14	1.97		

from Kittel

All properties depend on n and m

$$u \approx \frac{3}{5}nE_F + \frac{\pi^2}{4} \frac{n}{E_F} (k_B T)^2 \quad \text{J m}^{-3}$$

$$c_v \approx \frac{\pi^2}{2} \frac{n}{E_F} k_B^2 T \quad \text{J K}^{-1} \text{m}^{-3}$$

$$s \approx \frac{\pi^2}{2} \frac{n}{E_F} k_B^2 T \quad \text{J K}^{-1} \text{m}^{-3}$$

$$f \approx \frac{3}{5}nE_F - \frac{\pi^2}{4} \frac{n}{E_F} (k_B T)^2 \quad \text{J m}^{-3}$$

$$P \approx \frac{2}{5}nE_F + \frac{\pi^2}{6} \frac{n}{E_F} (k_B T)^2 \quad \text{N m}^{-2}$$

$$B \approx \frac{2}{3}nE_F + \frac{\pi^2}{18} \frac{n}{E_F} (k_B T)^2 \quad \text{N m}^{-2}$$

$$h \approx nE_F + \frac{5\pi^2}{12} \frac{n}{E_F} (k_B T)^2 \quad \text{J m}^{-3}$$

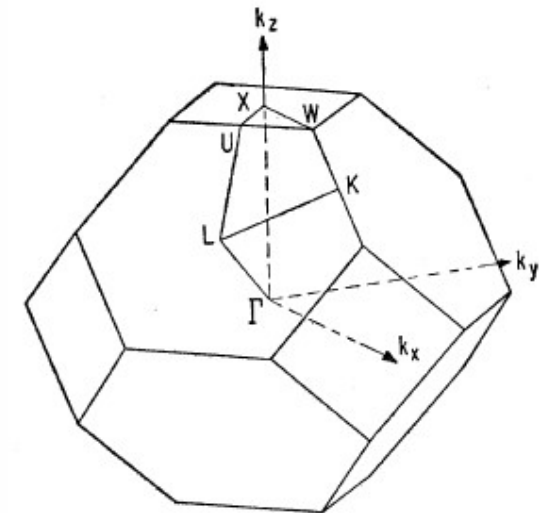
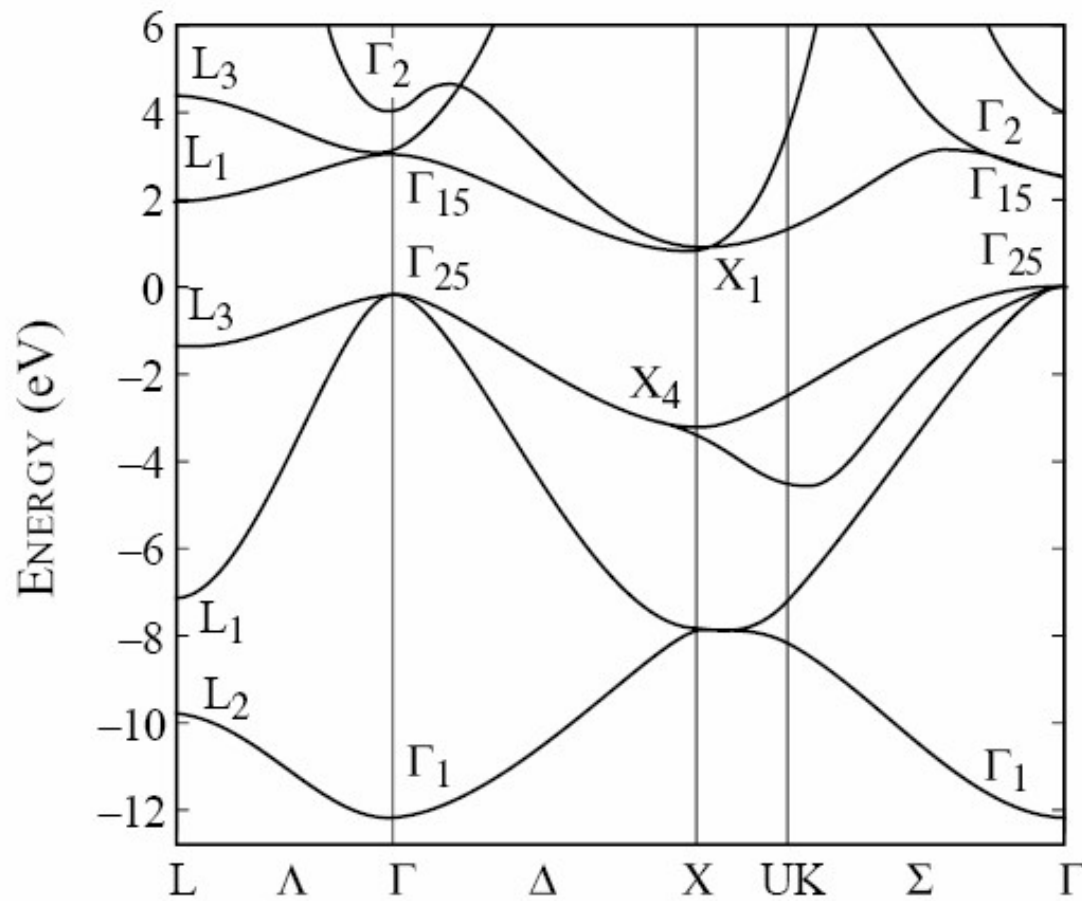
$$g \approx nE_F - \frac{\pi^2}{12} \frac{n}{E_F} (k_B T)^2 \quad \text{J m}^{-3}$$

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad \text{J}$$

Fit data to n and m

Electron Band Theory

Calculate the dispersion relation for electrons in a crystal



silicon

Bloch Theorem

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

$u_{\vec{k}}(\vec{r})$ is a periodic function.

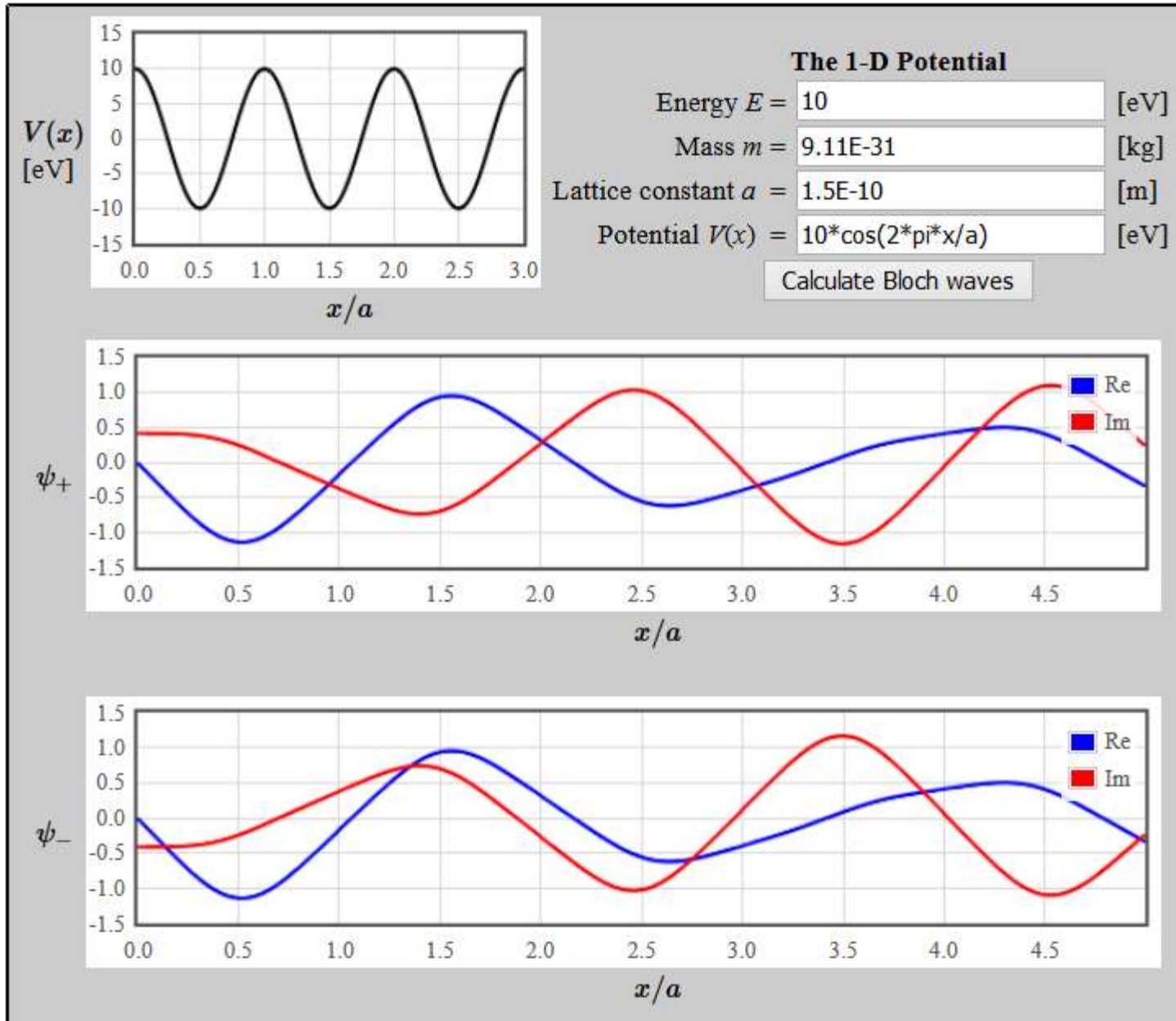
\vec{k} is a wavevector in the first Brillouin zone.

Eigenfunction solutions of the Schrödinger equation have Bloch form.

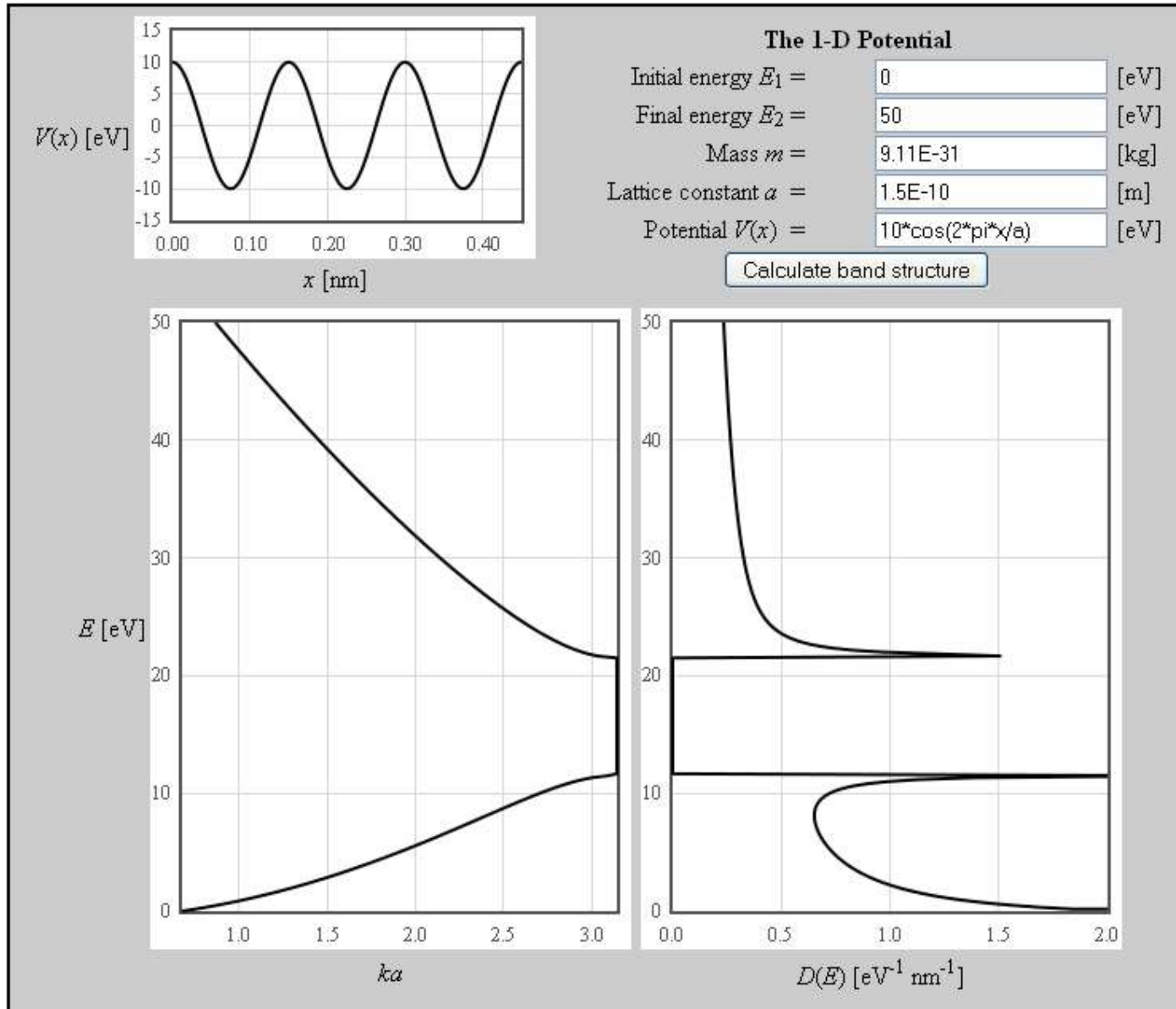
$$\mathbf{T}\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot(\vec{r}+\vec{T})} u_{\vec{k}}(\vec{r} + \vec{T}) = e^{i\vec{k}\cdot\vec{T}} e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{T}} \psi_{\vec{k}}(\vec{r})$$

Bloch waves in 1-D

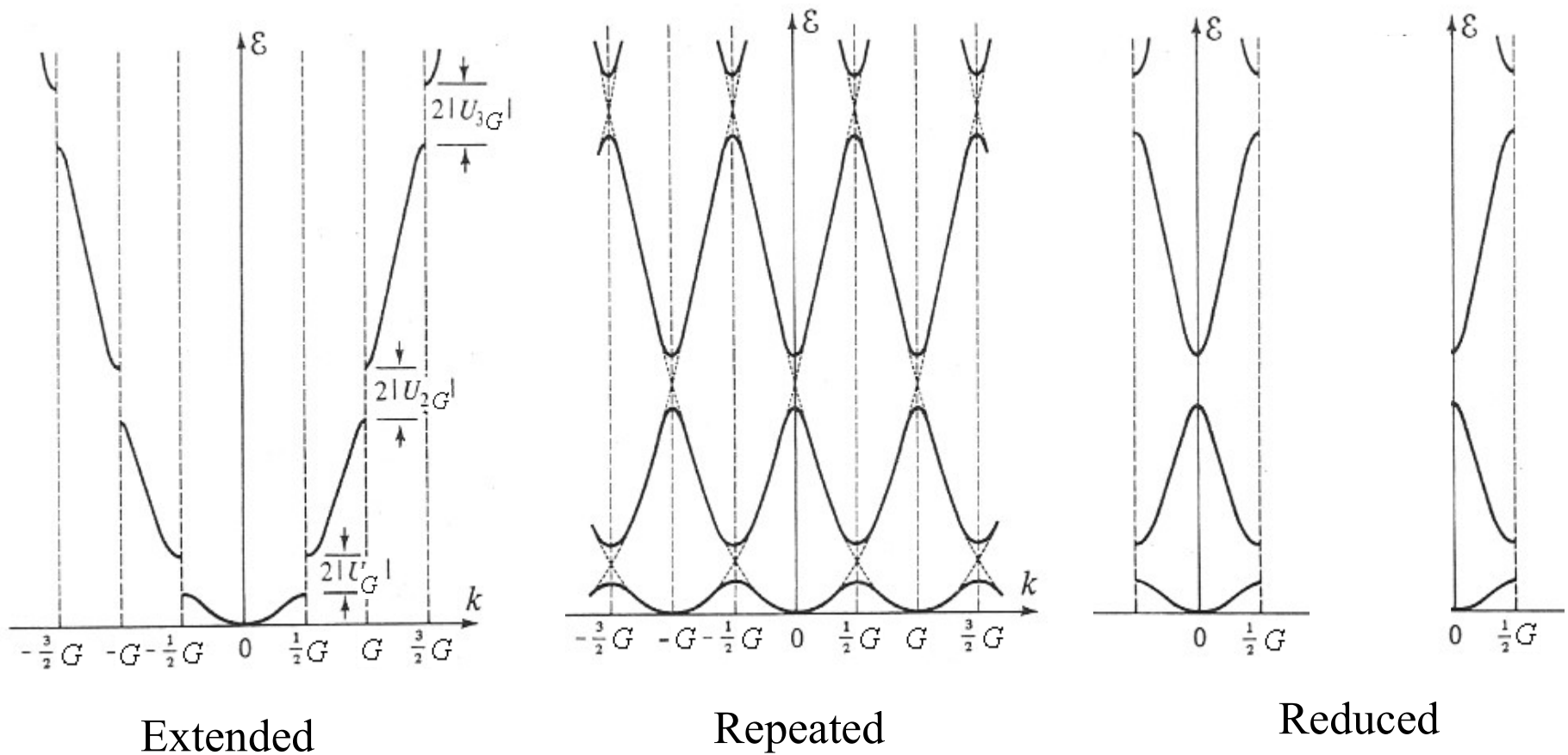
$$\psi = e^{ikx} u_k(x)$$



Band structure in 1-D

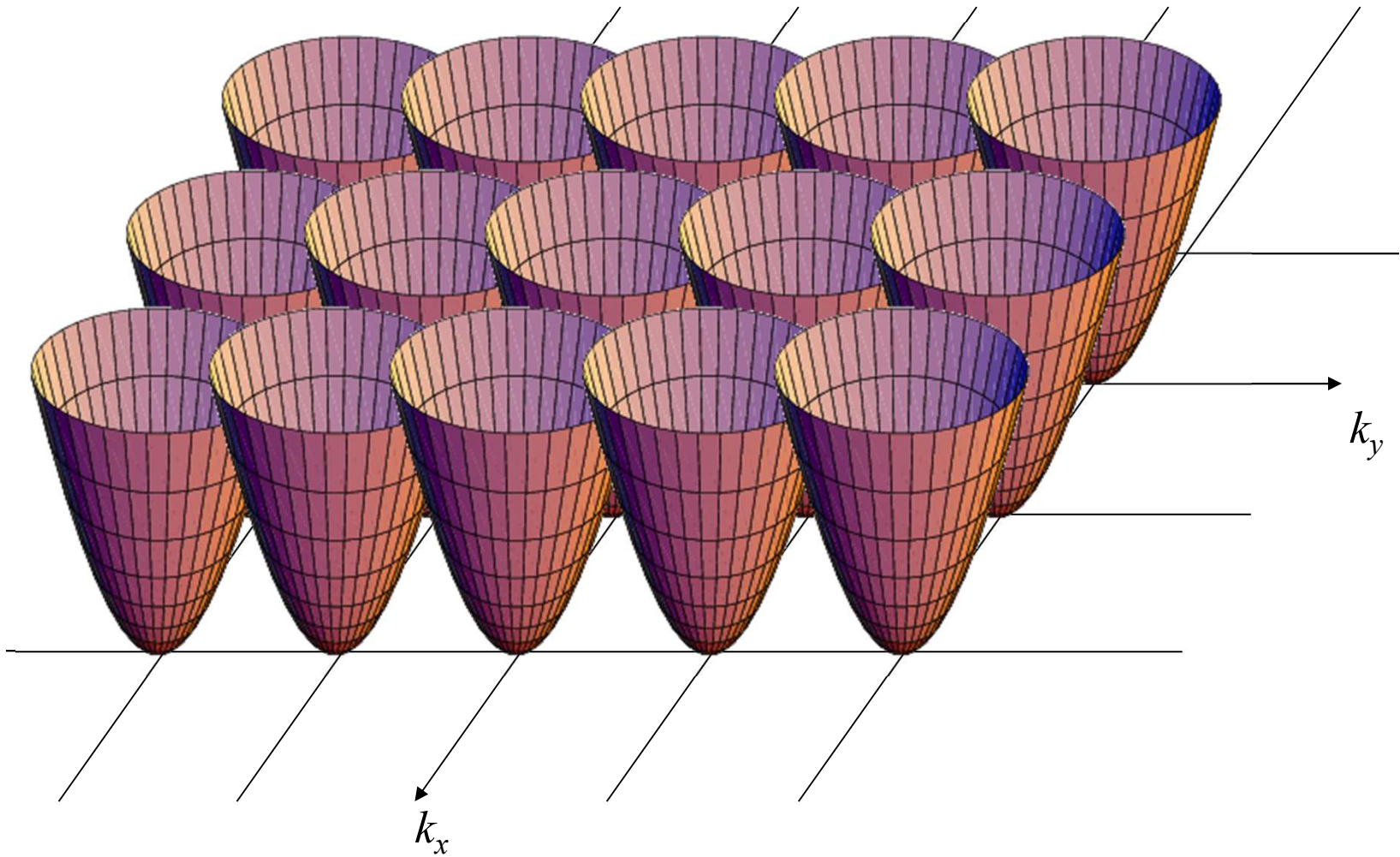


Empty lattice approximation

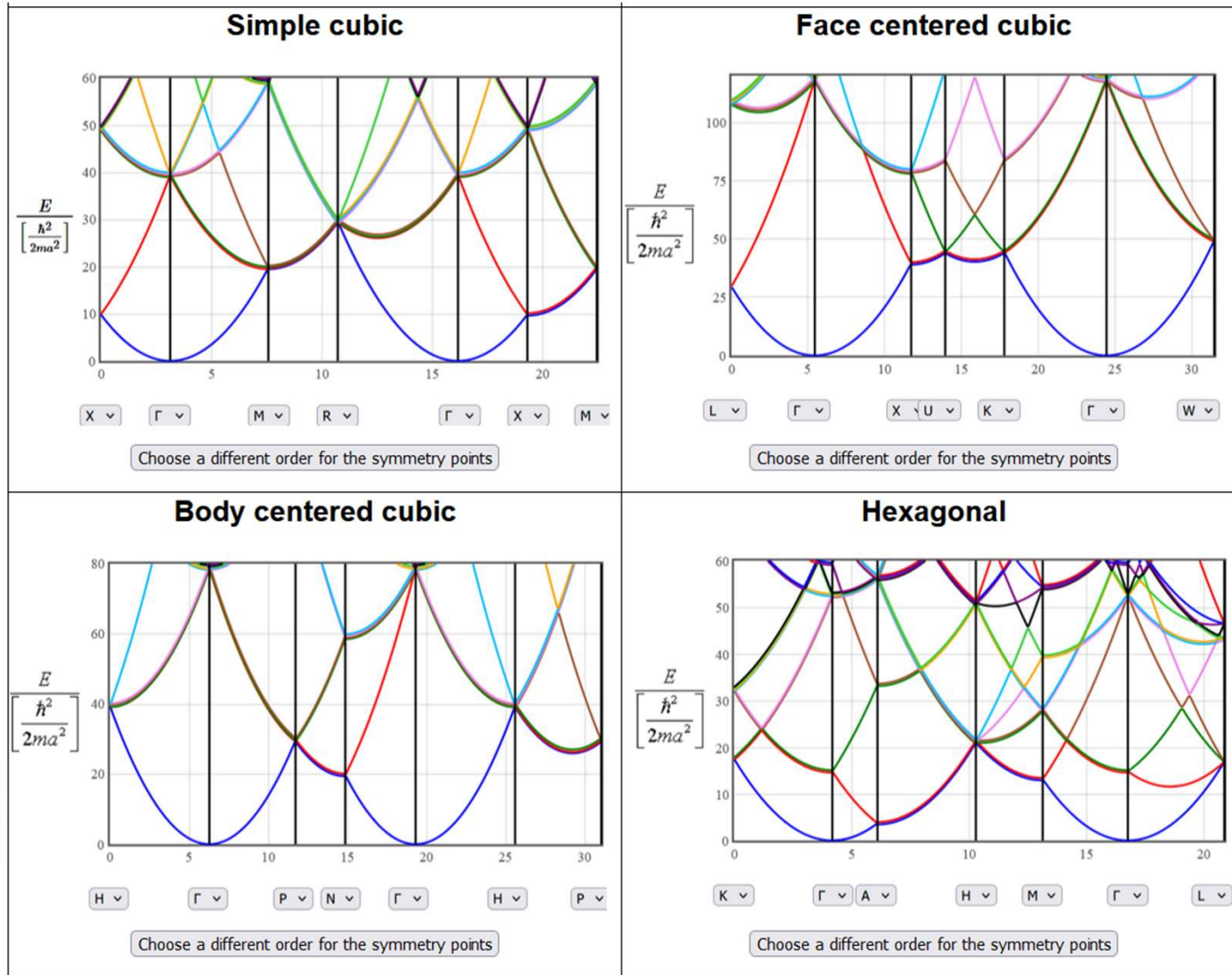


$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{r}} \underbrace{e^{i\vec{G}_0\cdot\vec{r}} e^{-i\vec{G}_0\cdot\vec{r}}}_1 \sum_{\vec{G}} C_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} = e^{i(\vec{k}+\vec{G}_0)\cdot\vec{r}} \sum_{\vec{G}} C_{\vec{G}} e^{i(\vec{G}-\vec{G}_0)\cdot\vec{r}}$$

Empty lattice approximation

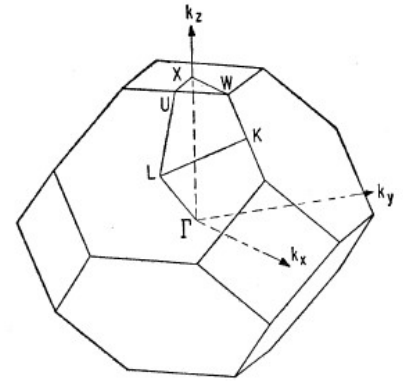


Empty lattice approximation

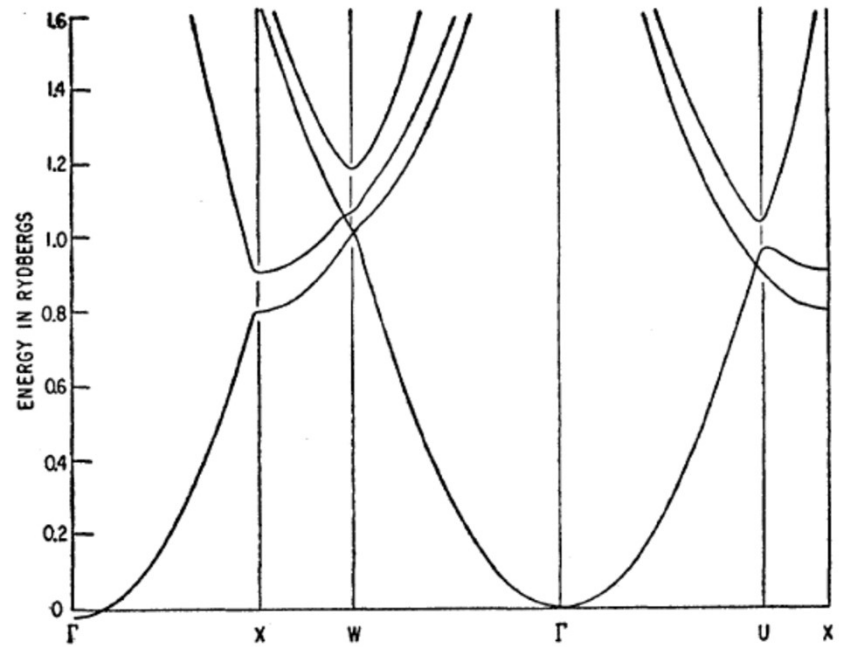
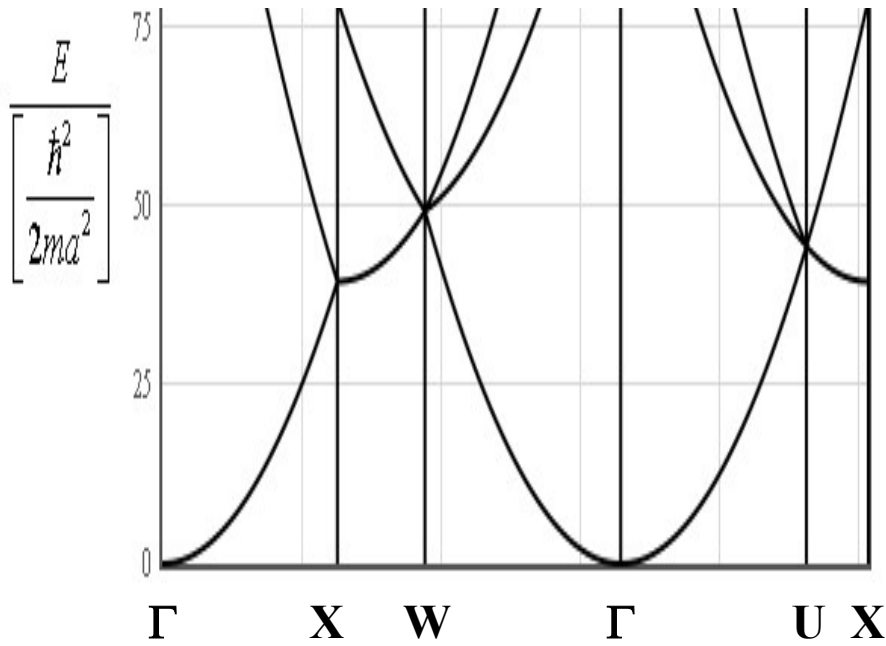


Band Structure of Aluminum

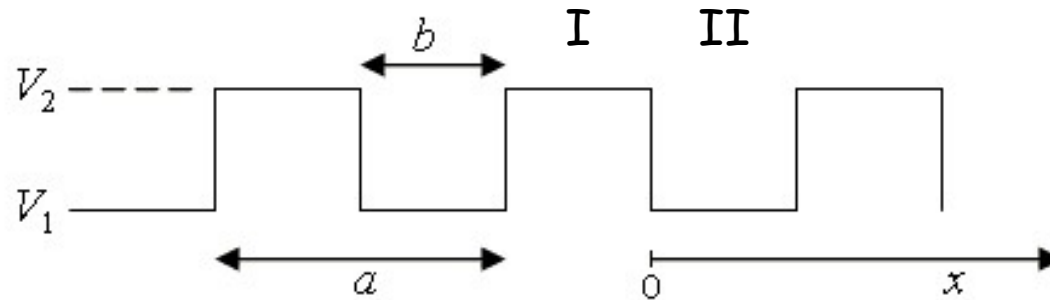
WALTER A. HARRISON
General Electric Research Laboratory, Schenectady, New York



empty lattice approximation



A separable potential

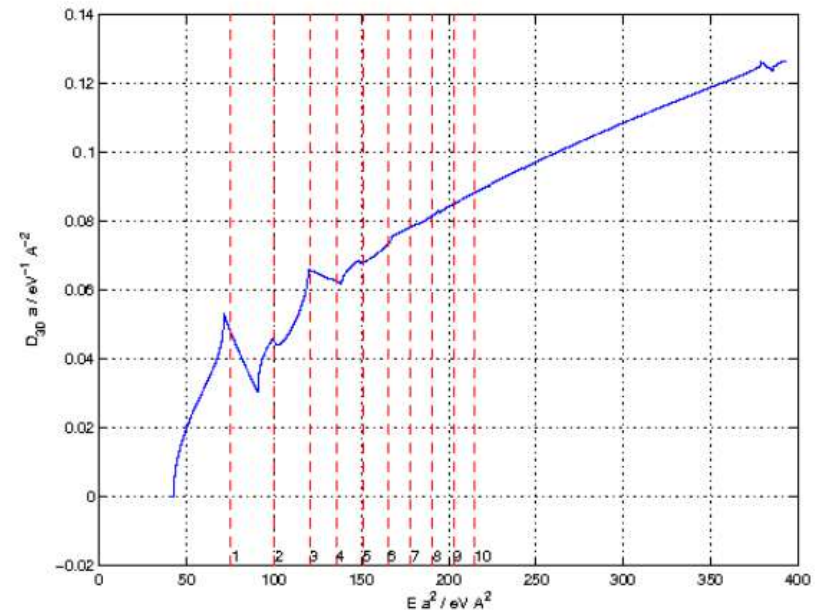
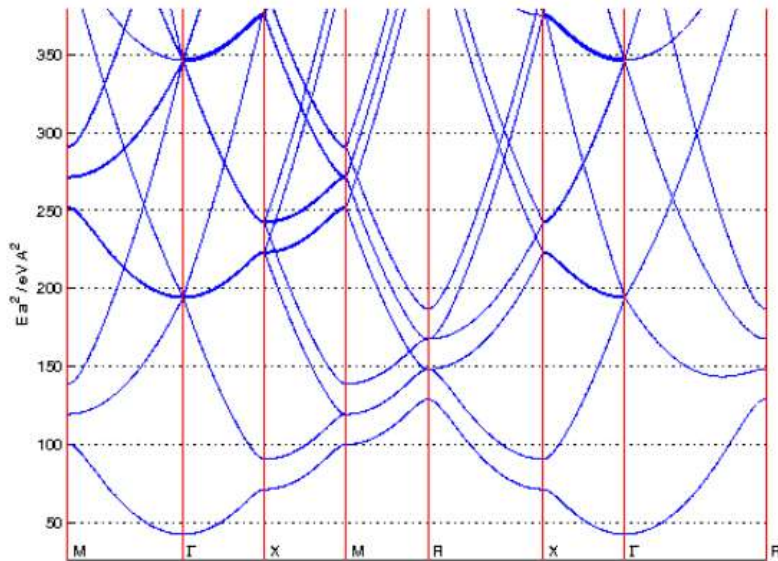
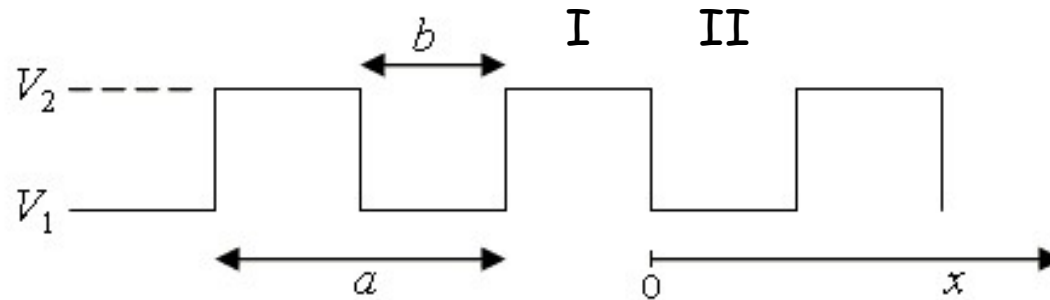


$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + (V(x) + V(y) + V(z)) \Psi = E \Psi$$

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>