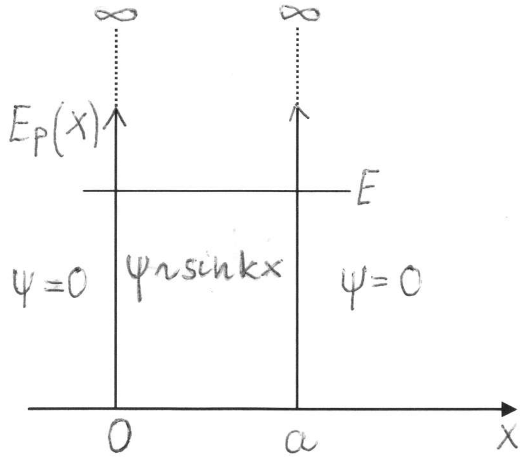
Potential box

E.g.: free particle in a container, electron in metal (ignore interaction with ions)

$E_p(x) = 0 \qquad 0 < x < a$

$\quad = \infty \qquad$ outside

$\rightsquigarrow \psi(x) = 0$ ~~out~~ outside



Inside:

Schr. e.: $\dfrac{d^2\psi}{dx^2} + k^2\psi = 0$

$k^2 = \dfrac{2mE}{\hbar^2}$

$\psi(x) = Ae^{ikx} + Be^{-ikx}$

Boundary conditions: $\psi(x) = 0 \quad x = 0$ and $x = a$

$\longrightarrow \psi(0) = A + B = 0 \rightsquigarrow A = -B \rightsquigarrow$

$\psi(x) = (A e^{ikx} - e^{-ikx}) = 2iA \sin kx = C' \sin kx \qquad C = 2iA$

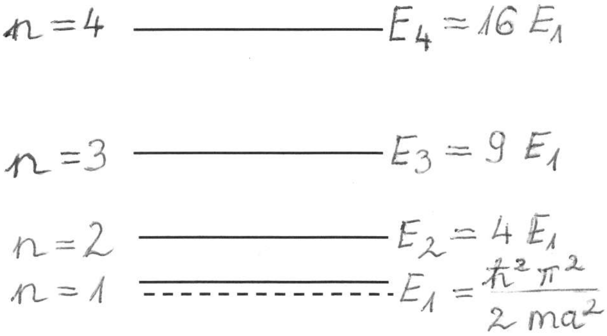
$\longrightarrow \psi(a) = C' \sin ka = 0 \rightsquigarrow \sin ka = 0 \rightsquigarrow$

$k = n\dfrac{\pi}{a}$ $\quad$ n = integer! $\quad p = \hbar\dfrac{n\pi}{a}$ momentum

The energy:

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

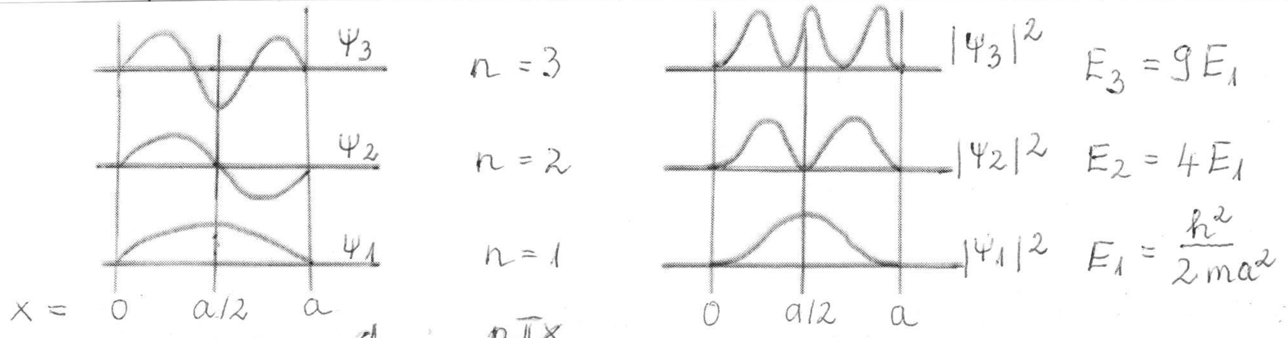
$E_n \sim n^2$



Discrete energy values

This is ↑ when motion of the particle is limited in space.

The wavefunctions and the probability densities



$$\psi_n(x) = C' \sin\frac{n\pi x}{a}$$

The particle can exist only with energy larger than a minimal energy

If $n = 0 \rightsquigarrow k = 0 \rightsquigarrow \psi(x) \equiv 0 \rightsquigarrow |\psi|^2 = 0 \rightarrow$ no particle

$n = 1 \quad E_1 = \frac{\hbar^2\pi^2}{2ma^2} = E_{min}$

This is the so called <u>0-point energy</u>

It follows from Heisenberg's uncertainty principle

$\Delta x \, \Delta p \geq \hbar$ now: $\Delta x \sim a \quad \Delta p \sim 2p$ (moving back & forth)

$$a \cdot 2p \geq h \rightarrow p \geq \frac{\pi\hbar}{a} \rightarrow E = \frac{p^2}{2m} \geq \frac{\pi^2\hbar^2}{a^2}\frac{1}{2m} = E_{min} = E_1$$

$C \rightarrow$ from normalization

$$\int_{-\infty}^{\infty} |\psi_n|^2 dx = \int_0^a |\psi_n|^2 dx = C'^2 \underbrace{\int_0^a \sin^2\frac{n\pi x}{a}\, dx}_{1/2\, a} = 1 \rightsquigarrow C' = \sqrt{\frac{2}{a}}$$

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}$$

The wavefunctions are <u>orthogonal</u> i.e

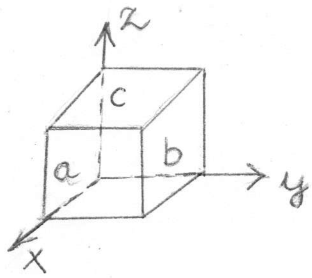
$$\int_{-\infty}^{\infty} \psi_n^* \psi_{n'}\, dx = 0 \quad \text{if} \quad n \neq n'$$

since

$$\int_0^a \sin\frac{n\pi x}{a} \sin\frac{n'\pi x}{a}\, dx = \frac{1}{2}\int_0^a \left[\cos\frac{(n-n')\pi x}{a} - \cos\frac{(n+n')\pi x}{a}\right] dx = 0$$

– Three dimensional / spatial / potential box

$$p_x = \frac{\pi \hbar n_1}{a} \; ; \quad p_y = \frac{\pi \hbar n_2}{b} \; ; \quad p_z = \frac{\pi \hbar n_3}{c}$$



$$E = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) =$$

$$= \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

$$\psi = C' \sin\frac{n_1 \pi x}{a} \sin\frac{n_2 \pi y}{b} \sin\frac{n_3 \pi z}{c}$$

Cube box: $E = \frac{\pi^2 \hbar^2}{2ma^2}\left(n_1^2 + n_2^2 + n_3^2\right) = \frac{\pi^2 \hbar^2}{2ma^2} \varkappa^2 = E_1 \varkappa^2$

$$\varkappa^2 = n_1^2 + n_2^2 + n_3^2$$

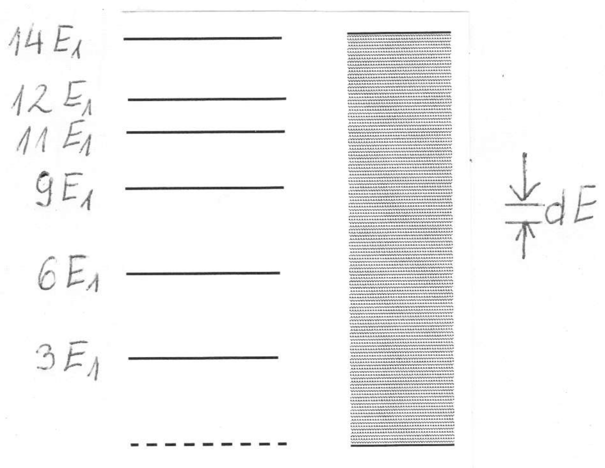
The same $\varkappa$ with different n_1, n_2, n_3 → <u>degeneracy</u>

Possible energy	n_1, n_2, n_3 combination	degree of degeneracy (g)
$3 E_1$	(1, 1, 1)	1
$6 E_1$	(2, 1, 1) (1, 2, 1) (1, 1, 2)	3
$9 E_1$	(2, 2, 1) (2, 1, 2) (1, 2, 2)	3
$11 E_1$	(3, 1, 1) (1, 3, 1) (1, 1, 3)	3
$12 E_1$	(2, 2, 2)	1
$14 E_1$	(1, 2, 3) (3, 2, 1) (2, 3, 1) (1, 3, 2) (2, 1, 3) (3, 1, 2)	6

<u>Big box</u>

a is large → gap between energy levels is small

dense energy states



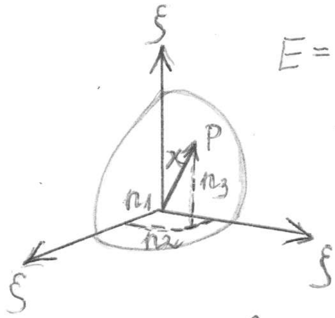
Number of states between energies $0 - E \equiv N(E)$

Volume of $\frac{1}{8}$-th of sphere with radius $\varkappa$

$$N(E) = \frac{1}{8}\,\frac{4\pi\varkappa^3}{3} = \frac{1}{8}\,\frac{n\pi}{3}\left(\frac{E}{E_1}\right)^{3/2} =$$

$$= \frac{\pi}{6}\,a^3\left(\frac{2mE}{\pi^2\hbar^2}\right)^{3/2} =$$

$$= \frac{8\pi V}{3h^3}\,(2m^3)^{1/2}\,E^{3/2}$$



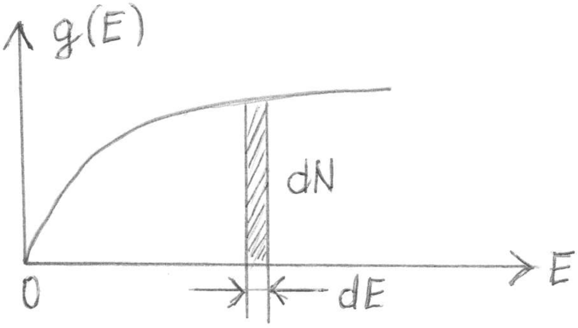
$E = E_1\varkappa^2$

$\varkappa = \sqrt{\frac{2mE}{\pi^2\hbar^2}} \cdot a$

$V = a^3$

Density of states:

$$g(E) = \frac{dN(E)}{dE} = \frac{4\pi V(2m^3)^{1/2}}{h^3}\,E^{1/2}$$



Harmonic oscillator

E.g. vibration of atoms in molecules or solids

$$E_p = \frac{1}{2}kx^2$$

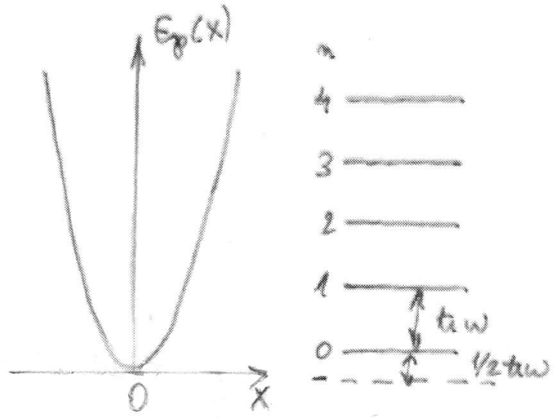
Schr. eq.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\frac{1}{2}kx^2\psi = E\psi$$

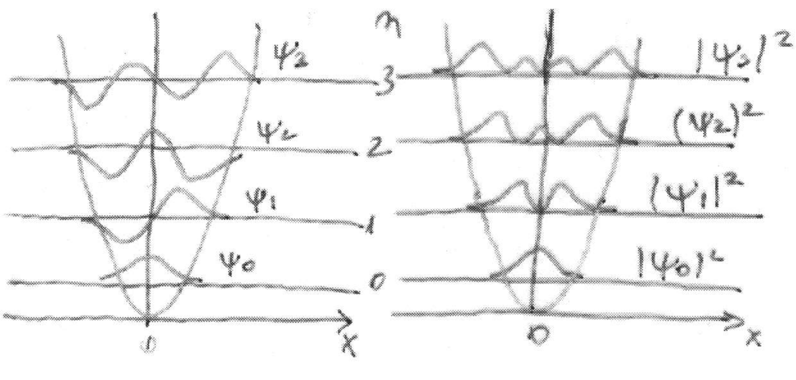
$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega$$

$$n = 0, 1, 2 \ldots, \quad \omega = \sqrt{\frac{k}{m}}$$

$$\Delta E = E_{n+1} - E_n = \hbar\omega = h\nu$$



0-point energy $= \frac{1}{2}\hbar\omega$



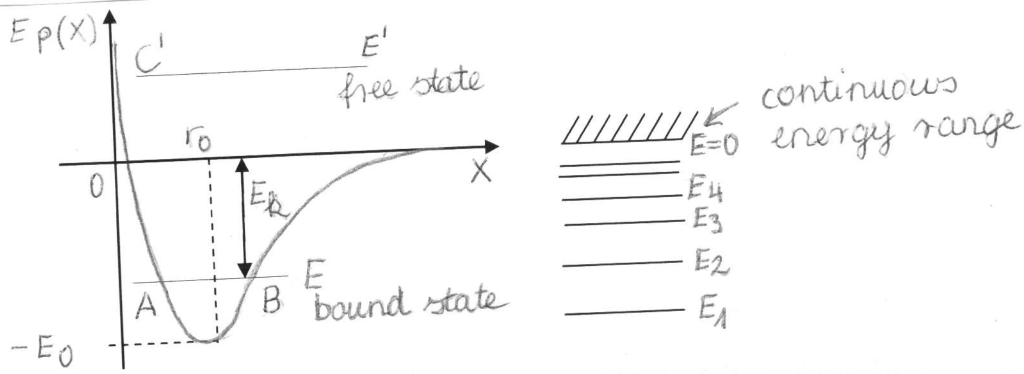
$|\psi|^2_s$ extends beyond the limits of classical motion but they decay rapidly.

In three dimensions: spatial harmonic oscillator

$$E_n = \left(n+\frac{3}{2}\right)\hbar\omega$$

- Real potential

E.g. central force



Large x → Ep = constant = 0

smaller x → Ep falls — attraction force

very small x Ep increases — repellent force

- Classically:

  E < 0 → bound motion (oscillation between A and B)

  E > 0 → reflection (C is point of return)

- Quantum mechanically

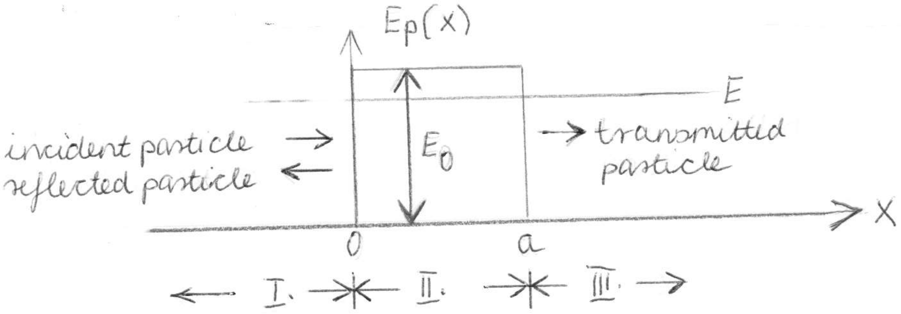
  E < 0 → discreet solutions for bound states (discreet energy spectrum) 2 boundary conditions

  E > 0 → only one boundary condition at C (continuous energy spectrum)

Binding energy E_k ≡ energy needed to take the particle far (E = 0) away from the bound state

Dissociation, ionization etc. energy

Transition through a potential barrier



- $E < E_0$

Classically: reflection
Quantum mechanically: partial transmission
For the ranges I, II and III the solutions of the Schrödinger eq.,

$$\Psi_1 = Ae^{ikx} + Be^{-ikx}$$

$$\Psi_2 = Ce^{\alpha x} + De^{-\alpha x}$$

$$\Psi_3 = A'e^{ikx}$$

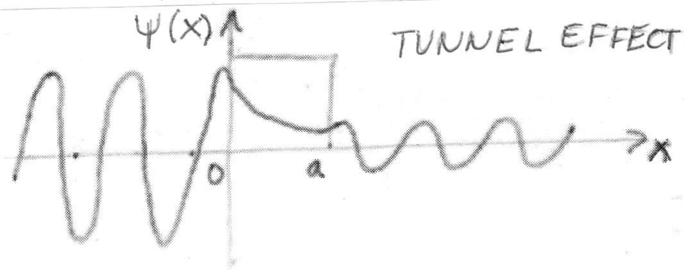
A, B, C, D, A' from the boundary conditions

$$k^2 = \frac{2mE}{\hbar^2}$$

$$\alpha^2 = 2m\frac{(E_0 - E)}{\hbar^2}$$

Since at $x = 0$ Ψ_2 is non-0 $\rightsquigarrow$

$\Psi_3 \neq 0$
particle is transmitted
TUNNEL EFFECT



- $E > E_0$

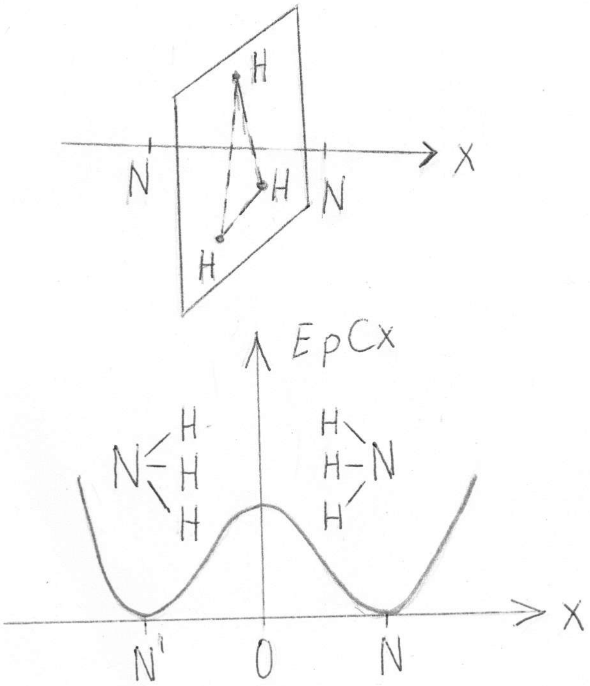
Unlike classically there is reflection, too.
At discreet energies no reflection: resonance transmission
Condition: for the wavelength of the particle above the barrier

$$\lambda' = \frac{2\pi}{k'} \quad \text{where } k'^2 = \frac{2m(E - E_0)}{\hbar^2}$$

$$n \cdot \frac{\lambda'}{2} = a \qquad \text{must hold.}$$

Examples

1. Inversion of the molecule ammonia NH_3



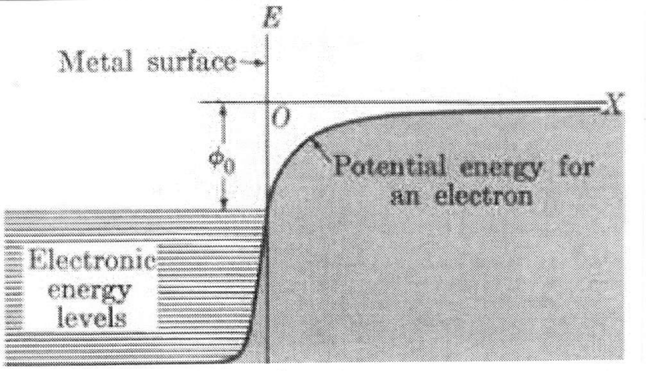
N atom has two symmetric positions: 2 equivalent minima of potential energy

The motion is the superposition of 2 oscillation:

1. oscillation around N (or N')
2. slower oscillation between the two states crossing the potential barrier

NH_3 : $2{,}38 \cdot 10^{10}$ Hz (time standard).

2. Emission of electron from metal

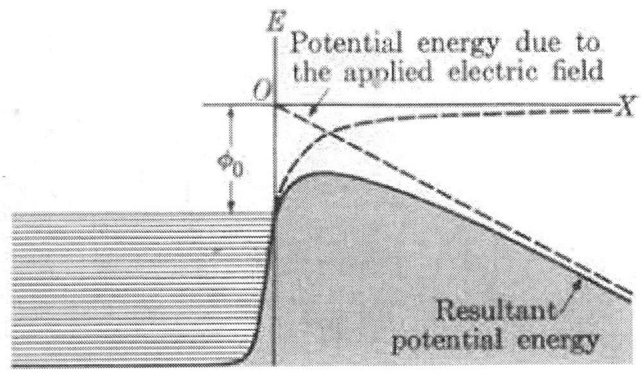


For emission energy $\geq \phi_0$ is required.

Energy feed:
heat – thermoemission
light – photoelectric effect

Other solution

With external electric field modification of the potential to a potential barrier



Electron emitted by tunneling:

field emission

(Cold cathodes)