PHY 481/581 Intro Nano-MSE:

Applying simple Quantum Mechanics to nanoscience problems, part I

Time dependent Schrödinger Equation in 3D,

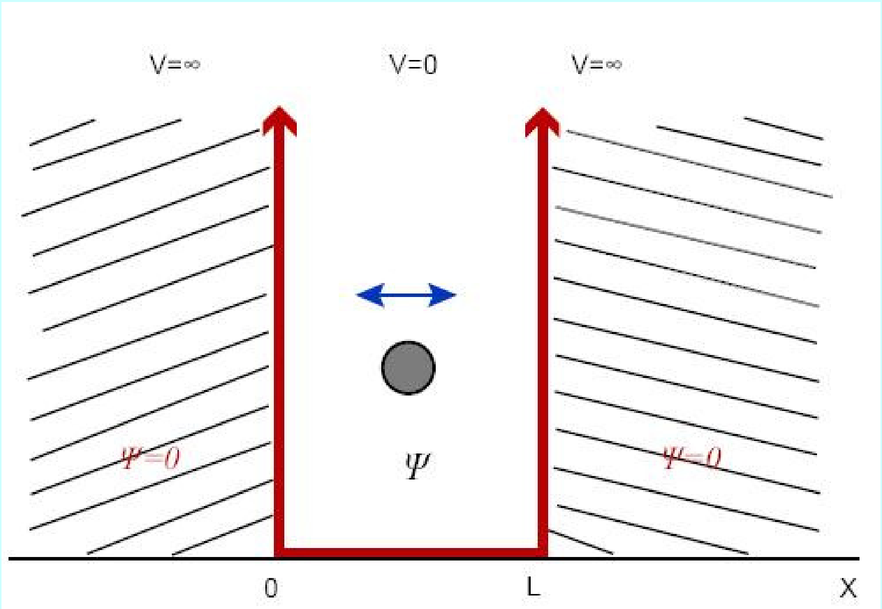
$$-\frac{h^2}{8m\pi^2}\nabla^2\psi + V\psi = i\,\frac{h}{2\pi}\,\frac{d\psi}{dt}$$

Many problems concern stationary states, i.e. things do not change over time, then we can use the much simpler tine independent Schrödinger Equation in 3D, e.g.

Particle in a Potential Box

$$-\frac{h^2}{8m\pi^2}\nabla^2\psi + V\psi = E\psi$$

The potential is infinitely high, equivalently, the well is infinitely deep



Since potential energy V is zero inside the box

$$\frac{d^2\psi}{dx^2} = -k^2\psi \qquad k^2 = \frac{8m\pi^2 E}{h^2}$$

$$\psi(x) = e^{ikx} \text{ and } \psi(x) = e^{-ikx}$$

Since the Schrödinger equation is linear

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

Note that the wavefunction should satisfy the boundary condition that $\psi(x = 0) = 0$, this leads to the requirement that $B = -A$. Hence we have

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

What about the other boundary condition that $\psi(x = L) = 0$? Where does it lead us? We have the following equation

$$\psi(L) = C\sin(kL) = 0$$

Since C cannot be zero (otherwise we will have no wavefunction), therefore $\sin(kL) = 0$ and this implies $kL = n\pi$ where n is an integer. Substituting this equation back

$$E = \frac{n^2h^2}{8mL^2}$$

The number n is known as the Quantum Number.

Since we know k

$$k^2 = \frac{8m\pi^2 E}{h^2}$$

$$\psi(x) = C\sin(n\pi x/L)$$

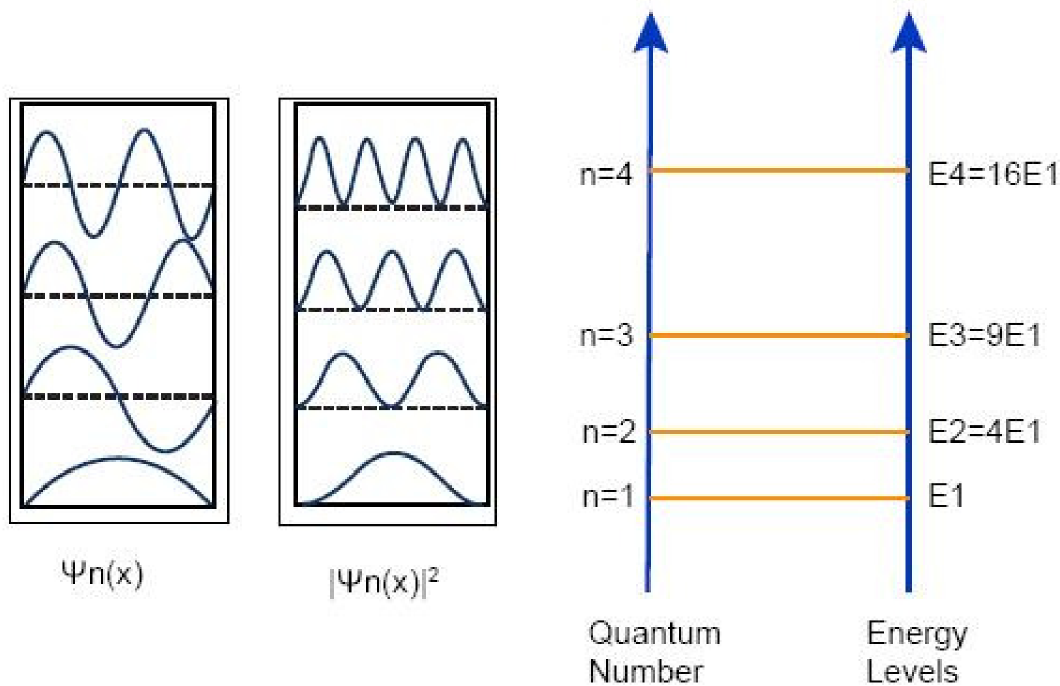
Now we need to normalize

$$\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1$$

This sets the scale for the wave function, we need to have it at the right scale to calculate expectation values, this condition means that the particle definitely exist (with certainty, probability 100 %) in some region of space, in our case in between x = 0 and L

$$\int_0^L |\psi(x)|^2\,dx = 1 \text{ and so } \int_0^L C^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$



$$E = \frac{n^2 h^2}{8mL^2}$$

There are infinitely many energy levels, their spacing depends on the size of the box, there is on E0 = 0 as this is forbidden by the uncertainty principle

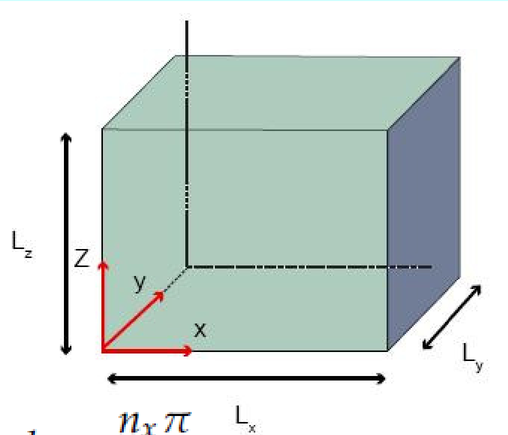
Generalisation to 3D Potential Box

Again, the potential is infinitely high, equivalently, the 3D well is infinitely deep

Generalization to three dimensions is straightforward, kind of everything is there three times because of the three dimensions,

not particularly good approximation for a quantum dot (since the potential energy outside of the box is assumed to infinite, which does not happen in physics, also the real quantum dot may have some shape with some crystallite faces, while we are just assuming a rectangular box or cube

$$L_x \times L_y \times L_z$$



$$\psi(x,y,z) = D\sin(k_x x)\sin(k_y y)\sin(k_z z)$$

set of integer quantum numbers (n_x, n_y, n_z)

$$E = \frac{h^2}{8m\pi^2}\left[k_x^2 + k_y^2 + k_z^2\right] = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

$$k_x = \frac{n_x \pi}{L_x}$$

(3.29)

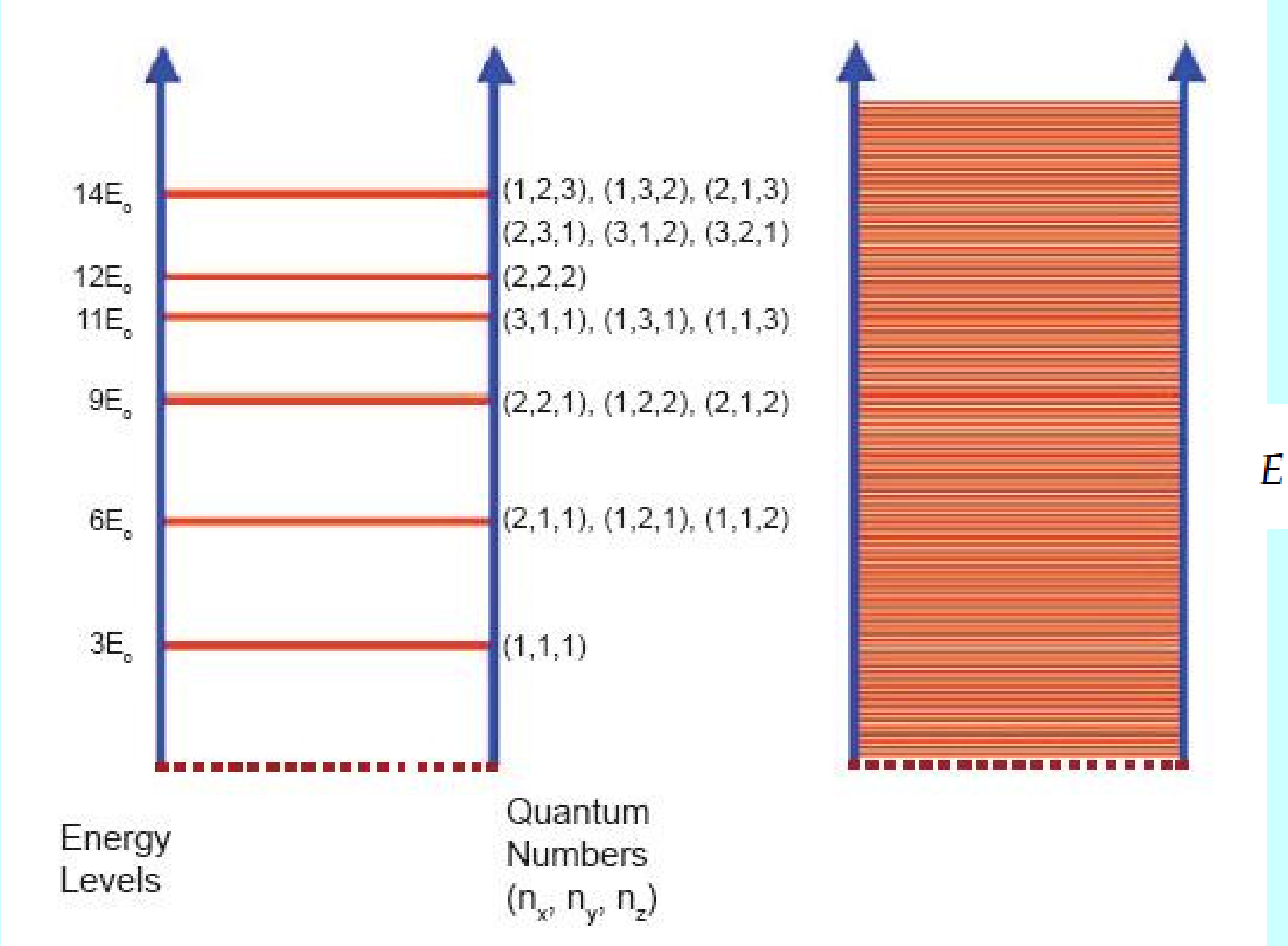
$$k_y = \frac{n_y \pi}{L_y}$$

$$k_z = \frac{n_z \pi}{L_z}$$

Case 1: $L_x = L_y = L_z = L$

$$E = \frac{(n_x^2 + n_y^2 + n_z^2)h^2}{8mL^2}$$

Particle in a cube, there will be degenerate energy levels, i.e. wave functions with different sets of quantum numbers will correspond to the same energy eigenvalue, this is due to the symmetry of the potential



$$E = \frac{(n_x^2 + n_y^2 + n_z^2)h^2}{8mL^2}$$

Potential in 3D box (infinitely deep well) with small edges (L) for potential energy function with cubic symmetry

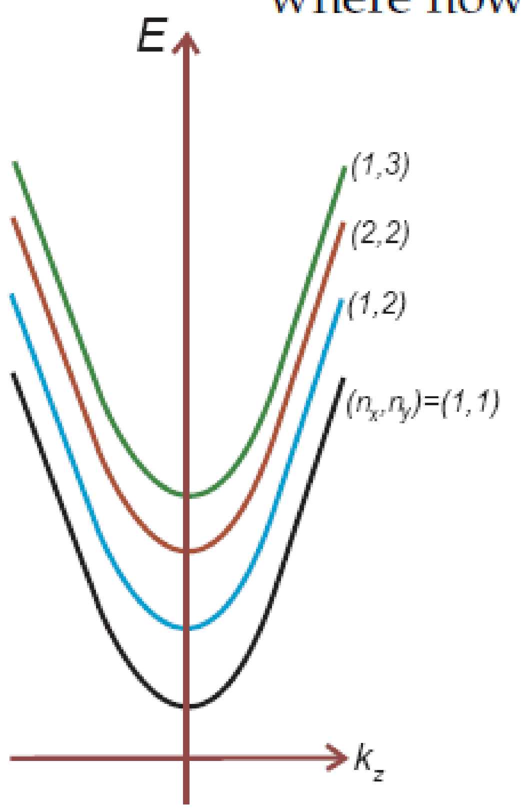
Same scenario if dimensions/edges L of the box are large, Bohr's correspondence principle, the spacing of the energy level gets too small to be detected in classical physics

Case 2: $L_x = L_y = L$ and $L_z \gg L_x, L_y$. In such a case, the quantisation condition (3.29) along the z-direction becomes essentially continuous, i.e. there is only a small difference in k_z and energy for n_z and $n_z + 1$. Thus we can write the energy of the particle as

$$E = \frac{h^2}{8m}\left[\frac{n_x^2}{L^2} + \frac{n_y^2}{L^2} + k_z^2\right]$$

Note that we still have a square (2D) potential, hence there is again degeneracy

where now we have the quantised band characterised by n_x and n_y while k_z is essentially a continuous variable



Such a potential system where the particle is confined by potential wells in two dimensions but free in the third dimension is known as a *quantum wire*.

Case 3: $L_y, L_z \gg L_x = L$. In such a case, the quantisation condition (3.29) along both y- and z-directions becomes essentially continuous. Thus we can write the energy of the particle as

$$E = \frac{h^2}{8m}\left[\frac{n_x^2}{L^2} + k_y^2 + k_z^2\right]$$

where the quantised band is characterised by n_x while k_y and k_z are essentially continuous variables. Such a potential system where the particle is confined by potential wells in one dimension but free in the other two dimensions is known as a *quantum well*.

One may approximate this this then as a 1D problem, for large L in 2D there is essentially only quantization in x, the thickness of the quantum well

Note that quantum mechanics thrives on approximations, one can make these approximations, as precise as necessary for a desired purpose,

This is similar to specification in an engineering context

1D Potential well, created by a finite square potential

- The finite square-well potential is

$$V(x) = \begin{cases} V_0 & x \le 0 & \text{region I} \\ 0 & 0 < x < L & \text{region II} \\ V_0 & x \ge L & \text{region III} \end{cases}$$

- The Schrödinger equation outside the finite well in regions I and III is

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} = E - V_0 \qquad \text{regions I, III}$$

$$\alpha^2 = 2m(V_0 - E)/\hbar^2$$

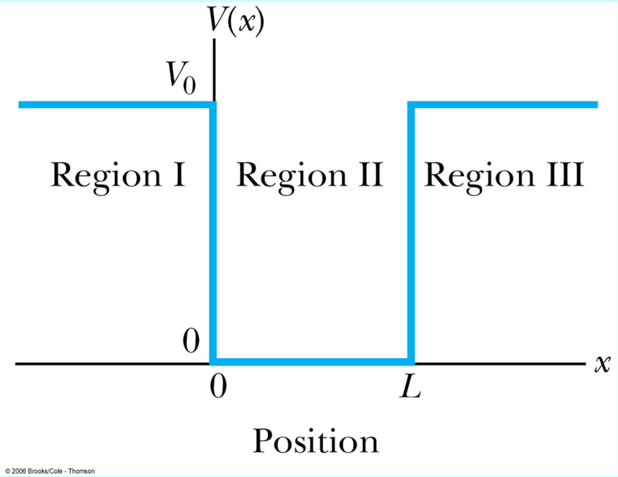
$$\frac{d^2\psi}{dx^2} = \alpha^2\psi$$

the wave function must be zero at infinity, the solutions for this equation are

$$\psi_{\mathrm{I}}(x) = Ae^{\alpha x} \qquad \text{region I, } x < 0$$

$$\psi_{\mathrm{III}}(x) = Be^{-\alpha x} \qquad \text{region III, } x > L$$

The wave function from one region to the next must match and so must its slope (derivative)



Finite Square-Well Solution

- Inside the square well, where the potential V is zero, the wave equation becomes $\frac{d^2\psi}{dx^2} = -k^2\psi$ where $k = \sqrt{(2mE)/\hbar^2}$
- Instead of a sinusoidal solution we have

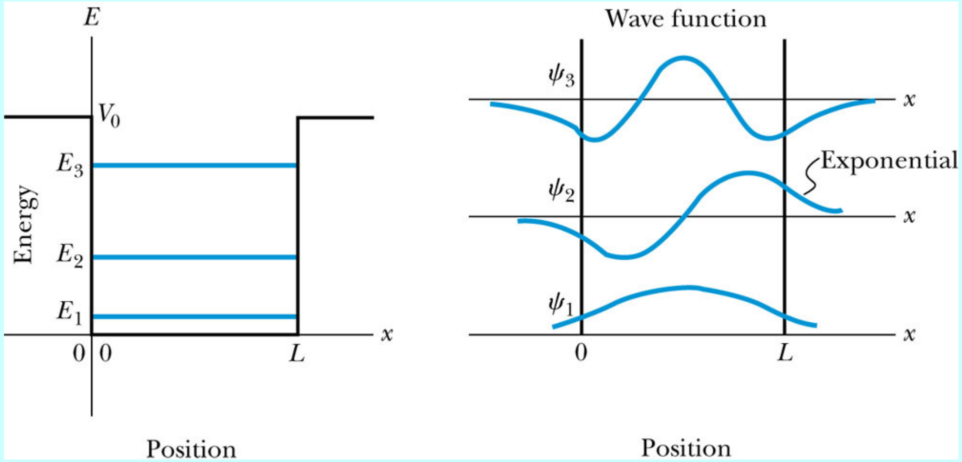
$$\psi_{\mathrm{II}} = Ce^{ikx} + De^{-ikx} \qquad \text{region II, } 0 < x < L$$

- The boundary conditions require that

$$\psi_{\mathrm{I}} = \psi_{\mathrm{II}} \text{ at } x = 0 \text{ and } \psi_{\mathrm{II}} = \psi_{\mathrm{III}} \text{ at } x = L$$

and the wave function must be smooth where the regions meet.

- Note that the wave function is nonzero outside of the box.



Penetration Depth

- The penetration depth is the distance outside the potential well where the probability significantly decreases. It is given by

$$\delta x \approx \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0 - E)}}$$

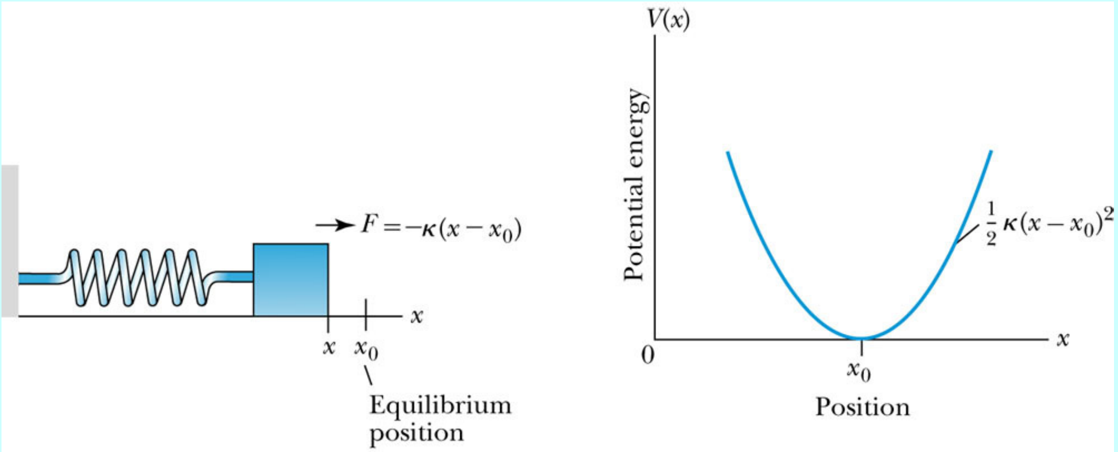
- It should not be surprising to find that the penetration distance that violates classical physics is proportional to Planck's constant.

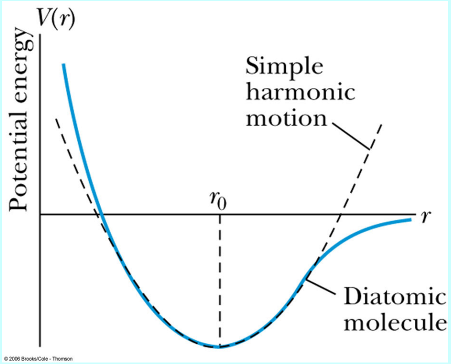
For the Energy of the lowest energy level, a good approximation is the formulae for the infinitely deep well modified by the penetration depth

$$E_n \approx \frac{n^2 \pi^2 \hbar^2}{2m(L + 2\partial x)}$$

Simple Harmonic Oscillator

- Simple harmonic oscillators describe many physical situations: springs, diatomic molecules and atomic lattices.





- Consider the Taylor expansion of a potential function:

$$V(x) = V_0 + V_1(x - x_0) + \tfrac{1}{2}V_2(x - x_0)^2 + \ldots$$

Redefining the minimum potential and the zero potential, we have

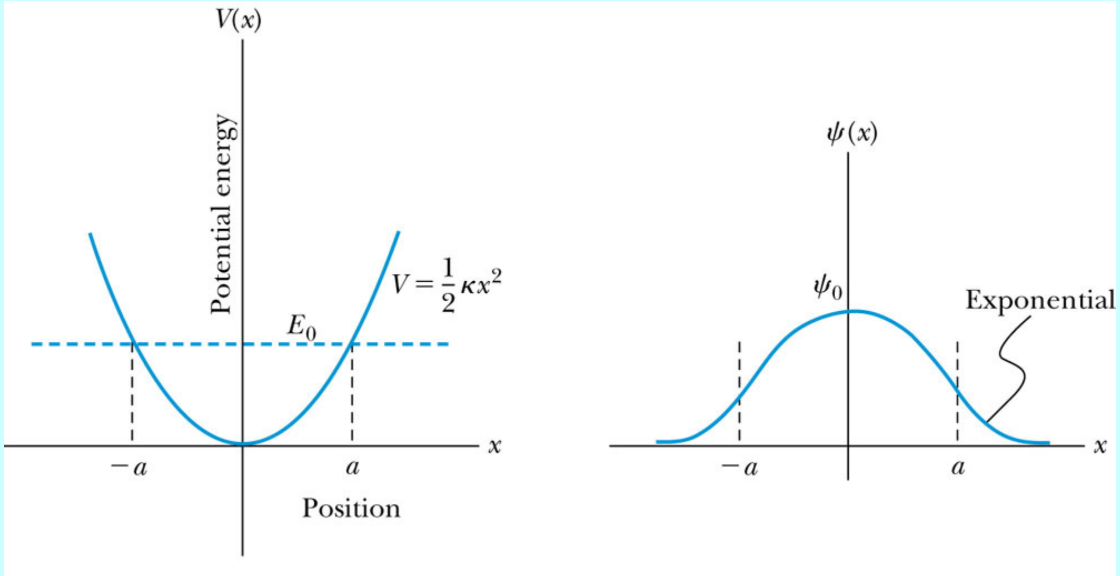
$$V(x) = \tfrac{1}{2}V_2(x - x_0)^2$$

Substituting this into the wave equation:

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(E - \frac{\kappa x^2}{2}\right)\psi = \left(-\frac{2mE}{\hbar^2} + \frac{m\kappa x^2}{\hbar^2}\right)\psi$$

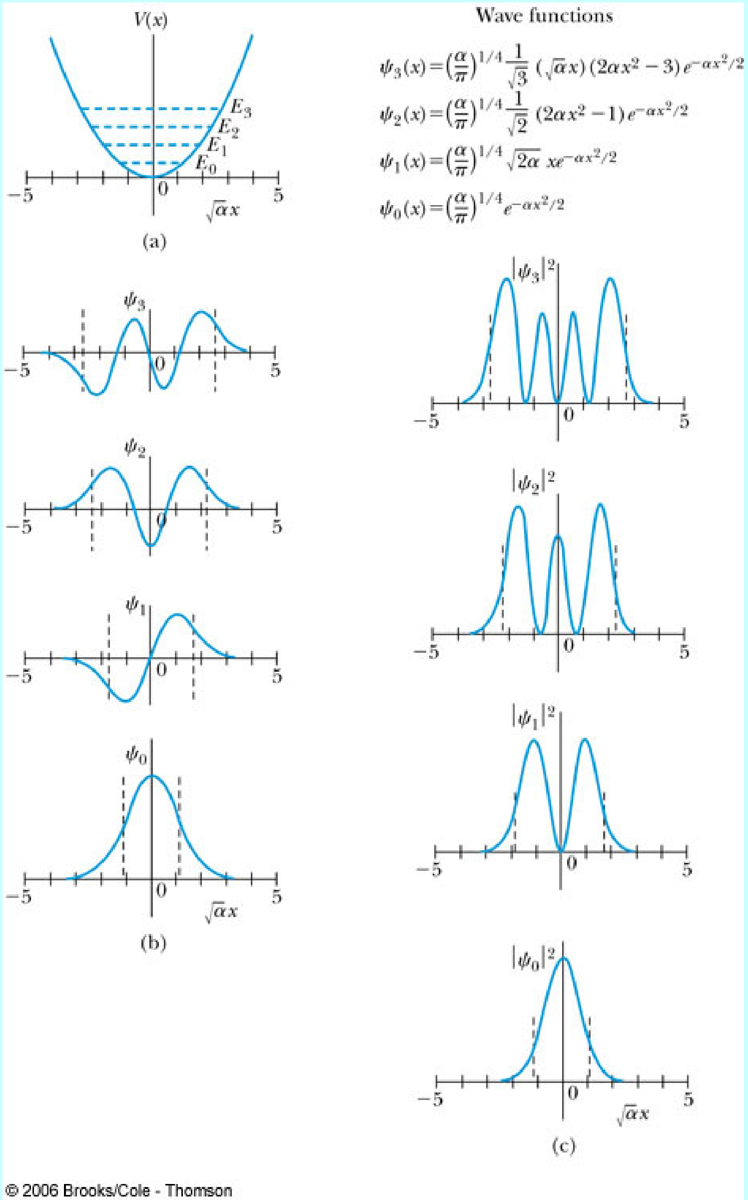
Let $\alpha^2 = \frac{m\kappa}{\hbar^2}$ and $\beta = \frac{2mE}{\hbar^2}$ which yields $\frac{d^2\psi}{dx^2} = (\alpha^2 x^2 - \beta)\psi$

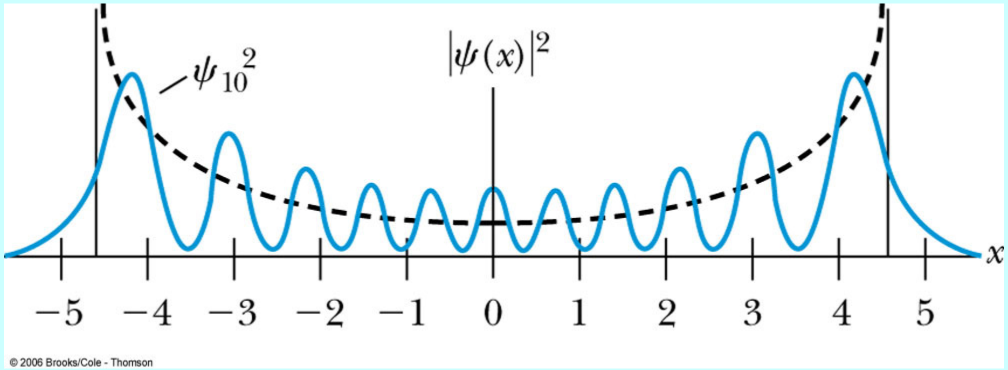
Parabolic Potential Well



- If the lowest energy level is zero, this violates the uncertainty principle.
- The wave function solutions are $\psi_n = H_n(x)e^{-\alpha x^2/2}$ where $H_n(x)$ are Hermite polynomials of order n.
- In contrast to the particle in a box, where the oscillatory wave function is a sinusoidal curve, in this case the oscillatory behavior is due to the polynomial, which dominates at small x. The exponential tail is provided by the Gaussian function, which dominates at large x.

Analysis of the Parabolic Potential Well





- The energy levels are given by

$$E_n = (n + \tfrac{1}{2})\hbar\sqrt{\kappa / m} = (n + \tfrac{1}{2})\hbar\omega$$

- The zero point energy is called the Heisenberg limit:

$$E_0 = \frac{1}{2}\hbar\omega$$

- Classically, the probability of finding the mass is greatest at the ends of motion and smallest at the center (that is, proportional to the amount of time the mass spends at each position).
- Contrary to the classical one, the largest probability for this lowest energy state is for the particle to be at the center.

If it is a charged particle that is vibrating around an equilibrium position, then there would be emission and absorption of electromagnetic radiation connected to transitions from one energy level to another

This is modeled by an oscillating expectation value: $x_{m,n}$ times a constant charge

$$e < x_{m,n} >= e\int \psi^*_m \, x \psi_n dx \neq 0$$

For the harmonic oscillator, these integrals are zero, i.e. the oscillating expectation values are zero, i.e. the transition is forbidden unless $m = n \pm 1$

just as Max Planck needed to postulate for the derivation of the black body radiation formulae

A single electromagnetic mode is completely specified by the parameters of its associated photon, i.e. E, p, (alternatively ω, λ or k) and acts like a simple harmonic oscillator of circular frequency ω,

The number of photons in a given mode is not limited (the photons are bosons with spin 1), this allows for the operation of a laser

The zero point energy of the harmonic oscillator is equivalent to the “vacuum fluctuation” that cause the Casimir force and also for the spontaneous emission of electromagnetic radiation from an excited state

Useful approximation due to Wentzel, Kramers and Brillion, WKB

$$\frac{1}{\lambda(x)} = \frac{\sqrt{2m[E - U(x)]}}{h}$$

Wavelength is considered to depend on position rather than being constant, there can be smooth changes in the wavelength with position

$$\int_a^b \frac{\sqrt{2m[E - U_0]}}{h} dx = 1/2, 1, 3/2$$

Condition for standing wave (other than sine or cosine) between integration limits a and b, where λ(x) is smoothly varying as one often obtain for large quantum numbers

In case of harmonic oscillator, a = -b, penetration into the barriers is ignored, will be a better approximation for large quantum numbers

$$\frac{1}{\lambda(x)} = \frac{\sqrt{2m[E - 1/2\, m\omega_0^{\,2} x^2]}}{h} \qquad b = \sqrt{\frac{2E}{m\omega_0^{\,2}}}$$

E_n = n h f, n = 1, 2, 3, .. by WKB, also ΔE = hf is correct

Solution of the Schrödinger equation gives correct quantization $E_n = (n + ½)\, h f$, n = 0, 1, 2, 3, … with zero point energy $E_0 = ½\, h f$