Solving the Schrödinger Equation – Simple Examples

The stationary-state wave functions and energy levels of a one-particle, one-dimensional system will be dealt with in this class, by solving the time-independent Schrödinger equation. Let's first review the mathematics of differential equations.

1. Differential Equations

1.1 Ordinary differential equations and partial differential equations

ODE: Only one independent variable
PDE: More than one independent variable.

$$\frac{\partial^2 \Psi(x,y,z,t)}{\partial t^2}=c^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z,t)$$

$$y'''+2x(y')^4+\sin x\cos y=y^5$$

The order of a differential equation is the order of the highest derivative in the equation.

1.2 Linear differential equation

$$A_n(x)y^{(n)}+A_{n-1}(x)y^{(n-1)}+\cdots+A_1(x)y'+A_0(x)y=g(x) \tag{1}$$

where the *A*'s and *g* (some of which may be zero) are functions of *x* only.

If $g(x)=0$, equation (1) is a homogeneous differential equation; otherwise it is inhomogeneous.

The one-dimensional Schrödinger equation is a linear homogeneous differential equation of second order.

Any second order linear homogeneous equation can be written as:

$$y''+P(x)y'+Q(x)y=0 \tag{2}$$

Suppose we have two independent functions y_1 and y_2 each of which satisfy equation (2). Then the general solution of the linear homogeneous differential equation is the linear combination of y_1 and y_2 :

$$y=c_1y_1+c_2y_2 \tag{3}$$

Where c_1 and c_2 are arbitrary constants (use boundary conditions to fix the constants). The general solution of a differential equation of *n*th order usually have *n* arbitrary constants.

1.3 A special linear homogeneous second-order differential equation

$$y''+py'+qy=0 \tag{4}$$

The auxiliary equation: $s^2+ps+q=0$

The general solution:

$$y=c_1e^{s_1x}+c_2e^{s_2x} \tag{5}$$

2. Particle in a Box

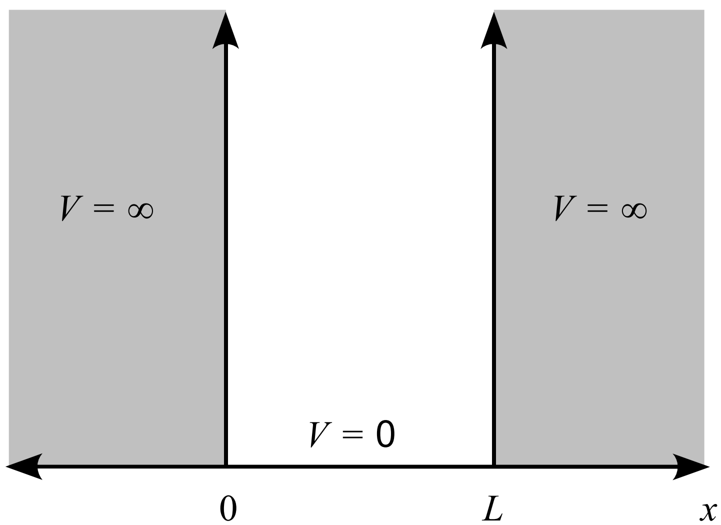
In physics, the particle in a box (a.k.a. the infinite well, or the infinite square well) is a problem consisting of a particle trapped in an infinite potential well, from which it can not escape, and which loses no energy when it collides with the wall of the well. In classical physics, the particle moves at a constant energy in a straight line. How does quantum mechanics explain describe the particle?

The quantum behavior in the box includes: (cf. Classical physics)

Energy quantization: Discreet energy levels

Zero-point energy: Lowest allowable energy

Special nodes: Places where the particle can never be found



2.1 The Schrödinger equation:

$$\frac{-\hbar^2}{2m}\psi''(x) = E\psi(x) \tag{6}$$

General solution:

$$\psi(x) = A\sin(kx) + B\cos(Bx) \tag{7}$$

$$E = \frac{k^2\hbar^2}{2m} \tag{8}$$

A and B can be any complex numbers. k , can be any real number.

2.2 Boundary conditions:

For the case of an infinite potential, $\psi(x)$ must be zero (do you know why?)

$$\psi(0) = \psi(L) = 0 \tag{9}$$

$$\psi(x) = A\sin(kx) \tag{10}$$

$$\psi(L)=A\sin(kL)=0 \tag{11}$$

$$k=\frac{n\pi}{L} \tag{12}$$

Where $n\in\mathbb{Z}^{+}$.

2.3 Wavefunction normalization

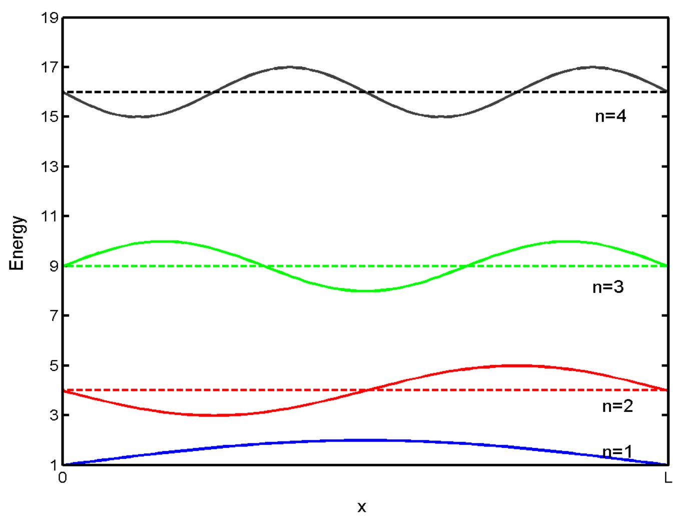
$$1=\int_{-\infty}^{\infty}|\psi(x)|^2 d\,x=|A|^2\int_0^L \sin^2(kx)\,dx=|A|^2\frac{L}{2} \tag{13}$$

$$|A|=\sqrt{\frac{2}{L}} \tag{14}$$

A may be any complex number with absolute value of $\sqrt{2/L}$.

$$\psi_n(x)=\sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L}) \tag{15}$$

$$E_n=\frac{n^2\hbar^2\pi^2}{2mL^2}=\frac{n^2h^2}{8mL^2} \tag{16}$$



The zero-point energy can be explained using Heisenberg's uncertainty rule.

- Quantum numbers
- ground state, excited states
- bound state

2.4 Heuristic derivation of eigen-energies

The wavefunctions must have nodes at the boundary of the box.

$$n\frac{\lambda}{2}=L \tag{17}$$

Using the de Broglie equation, the momentum of the particle is:

$$p = \frac{h}{\lambda} = \frac{nh}{L} \tag{18}$$

The energy:

$$E = \frac{p^2}{2\mathrm{m}} = \frac{n^2 h^2}{8mL^2} \tag{19}$$

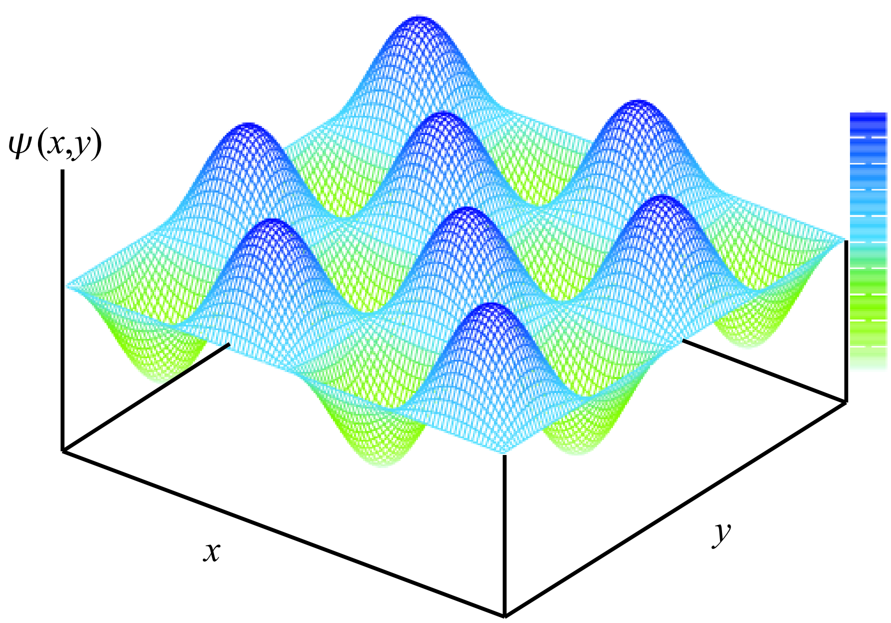
2.5 Quantum wells (semiconductors)

Quantum wells are formed in semiconductors by having a material, like GaAs sandwiched between two layers of a material with a wider bandgap like AlAs. These structures (called "heterostructures") can be grown by molecular beam epitaxy or chemical vapor deposition with control of the layer thickness down to monolayers. This is now common in industry, in research.

The effects of quantum confinement take place when the quantum well thickness becomes comparable at the de Broglie wavelength of the carriers (generally electrons and holes), leading to energy levels called "energy subbands", i.e., the carriers can only have discrete energy values.

Blue laser (applications in HD-DVD, Blue-ray DVD)

2.6 Particles in 2D and 3D wells



The wavefunction of a particle in a 2D box: $n_x = 4$, $n_y = 4$

Derivation:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi(x, y) = \frac{-2\mathrm{mE}}{\hbar^2}\psi(x, y) \tag{20}$$

Using the variable separation method,

$$\psi(x,y)=X(x)Y(y) \tag{21}$$

Substituting equation (21) into equation (20):

$$Y X''+X Y''=\frac{-2\text{mE}}{\hbar^2}XY \tag{22}$$

$$\frac{X''}{X}+\frac{Y''}{Y}=\frac{-2\text{mE}}{\hbar^2} \tag{23}$$

X''/X and Y''/Y must be constant. We have two separate equations:

$$\frac{X''}{X}=\frac{-2\text{mE}_x}{\hbar^2};\frac{Y''}{Y}=\frac{-2\text{mE}_y}{\hbar^2} \tag{24}$$

$$X(x)=\sqrt{\frac{2}{L_x}}\sin(\frac{n_x\pi x}{L_x}) \tag{25}$$

$$Y(y)=\sqrt{\frac{2}{L_y}}\sin(\frac{n_y\pi y}{L_y}) \tag{26}$$

The solutions:

$$\psi(x,y)=\sqrt{\frac{4}{L_x L_y}}\sin(\frac{n_x\pi x}{L_x})\sin(\frac{n_y\pi y}{L_z}) \tag{27}$$

$$E_{n_x,n_y}=\frac{\hbar^2\pi^2}{2\text{m}}\left[(\frac{n_x}{L_x})^2+(\frac{n_y}{L_y})^2\right] \tag{28}$$

Degeneracy: different eigenstates correspond to the same energy
(e.g. $n_x=1, n_y=2$ and $n_x=2, n_y=1$)

Doubly degenerated, triply degenerated... On the other hand, if there is only one wavefunction corresponding to a certain energy, the state and the energy level are said to be *non-degenerate.*

Q: Derive the wavefucntion and energy equations of a 3D infinite well.

3. Free particle

The classical free particle is characterized by its velocity (momentum, kinetic energy):

$E=\frac{1}{2}mv^2$

The quantum description of a free particle is (Schrödinger's equation):

$$\frac{-\hbar^2}{2\text{m}}\psi''(x)=E\psi(x) \tag{29}$$

$$\psi''(x)+\frac{2\mathrm{mE}}{\hbar^2}\psi(x)=0 \tag{30}$$

The auxiliary equation:

$$s^2+\frac{2\mathrm{mE}}{\hbar^2}s=0 \tag{31}$$

$$s=\pm\sqrt{\frac{-2\mathrm{mE}}{\hbar^2}}=\pm i\sqrt{\frac{2\mathrm{mE}}{\hbar^2}} \tag{32}$$

E must be negative. Two solutions:

$$\psi(x)=e^{ikx};\psi(x)=e^{-ikx};k=\sqrt{\frac{2\mathrm{mE}}{\hbar^2}} \tag{33}$$

Recall that the general solution is:

$$\psi(x)=c_1 e^{ikx}+c_2 e^{-ikx} \tag{34}$$

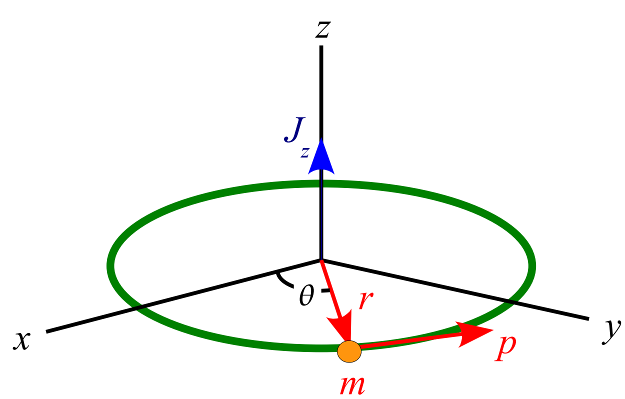
For an ***unbound*** particle, c_1 and c_2 cannot be determined (no appropriate boundary conditions). Likewise, the wavefunciton cannot be normalized.

- Propagation directions (momentum) $p=-\sqrt{(2\mathrm{mE})}$ and $p=\sqrt{(2\mathrm{mE})}$
- Two eigenstates
- No energy quantization (Energy is continuous).

4. Particle in a Ring

4.1 The classical rotation

A particle undergoes rotation at constant speed.



Angular velocity $\omega=\frac{v}{r}$, v is linear velocity.

The kinetic energy : $E_k=\frac{mv^2}{2}=\frac{m\omega^2 r^2}{2}$

The moment of intertia: $I=mr^2$

The angular momentum (a vector, the right hand rule): $\vec{J}_z=\vec{r}\times\vec{p}$ here, $J_z=x\,p_y-y\,p_x$

In the present case $J_z=m\,\omega\,r^2$

The kinetic energy $E_k=\frac{J_z^2}{2I}$ (compare this with linear motion: $E_k=\frac{p^2}{2\mathrm{m}}$

4.2 The quantum description of the particle in a ring

Treatment 1: The free particle with the periodic boundary condition. (In crystal solids, it is called the Born-von Karman boundary condition)

$$\psi(x)=\psi(x+L) \tag{35}$$

$$\psi(x)=A e^{\pm kx}=A e^{\pm k(x+L)} \tag{36}$$

$$k=\frac{2n\pi}{L}, n\in\mathbb{Z} \tag{37}$$

Recall $E=\frac{\hbar^2 k^2}{2m}$, $L=2\pi r$,

$$E=\frac{n^2\hbar^2}{2mr^2}, n=1,2,3 \tag{38}$$

In addition, there is one special state:

$$\psi(x)=A e^{2\pi} \tag{39}$$

After normalization, the 2n+1 eigenstates below the energy indexed by *n* are:

$$\psi(x)=\frac{1}{\sqrt{2\pi}} e^{\pm in\frac{x}{L}}=\frac{1}{\sqrt{2\pi}} e^{\pm in\theta} \tag{40}$$

and

$$\psi(x)=\frac{1}{\sqrt{2\pi r}} \tag{41}$$

Treatment 2: Using polar coordinates on the 1-D ring $\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial\theta^2}$, the Schrödinger equation becomes:

$$\frac{1}{r^2}\frac{\partial}{\partial\theta^2}\psi(\theta)=\frac{-2mE}{\hbar^2}\psi(\theta) \tag{42}$$

with conditions: $\psi(\theta)=\psi(\theta+2\pi)$ and $1=\int_0^{2\pi}|\psi|(\theta)^2 d\theta$

The solutions:

$$E=\frac{n^2\hbar^2}{2mr^2}, n=1,2,3 \tag{43}$$

$$\psi(\theta)=\frac{1}{\sqrt{2\pi}} e^{in\theta}, n=0,\pm1,\pm2\ldots \tag{44}$$

Q: What does $n=0$ mean? What is the physical meaning of $n>0$ and $n<0$?

The case of a particle in a one-dimensional ring is an instructive example when studying the quantization of angular momentum for, say, an electron orbiting the nucleus. The azimuthal wavefunctions in that case are identical to the energy eigenfunctions of the particle on a ring.

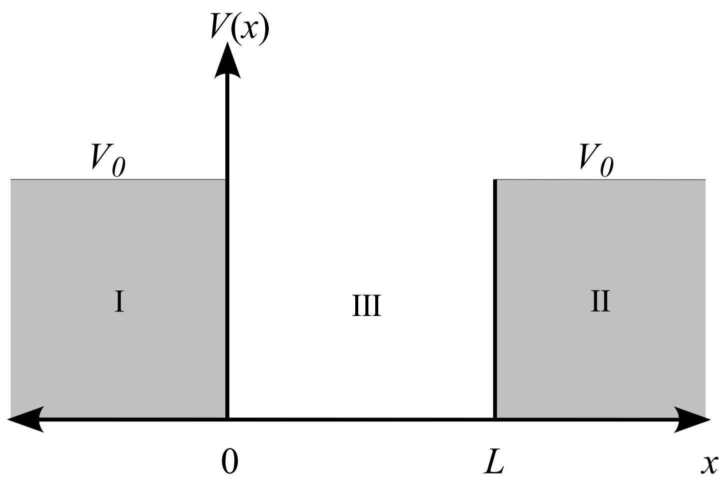
4.3 Application

In organic chemistry, aromatic compounds contain atomic rings, such as benzene rings consisting of five or six, usually carbon atoms (also, the surface of buckballs). These molecules are exceptionally stable.

The ring behaves like a circular wave guide. The valency electrons spin around in both directions. To fill all energy levels up to n requires $2\times(2n+1)$ electrons, as electrons have two possible orientations of their spins. The rule that $4n + 2$ excess electrons in the ring produces an exceptionally stable ("aromatic") compound, is known as the Hückel's rule.

5. Particle in a Finite potential well

5.1 The solutions



In region I:

$$\psi''=\frac{-2\mathrm{m}(E-V_0)}{\hbar^2}\psi \tag{45}$$

The general solution of this is:

$$\psi=A_1e^{\alpha x}+B_1e^{-\alpha x} \tag{46}$$

where A_1 and B_1 are arbitrary constants, and

$$\alpha=\sqrt{\frac{-m(E-V_0)}{\hbar^2}} \tag{47}$$

In region II:

$$\psi=A_2e^{\alpha x}+B_2e^{-\alpha x} \tag{48}$$

In region III:

$$\psi''=\frac{-2\mathrm{mE}}{\hbar^2}\psi \tag{49}$$

With the general solution:

$$\psi=A_3\sin(\beta x)+A_3\cos(\beta x) \tag{50}$$

where $\beta = \sqrt{\frac{2mE}{\hbar^2}}$.

Considering the conditions on wavefunctions: nowhere infinite, continuous, and smooth, we obtain

$$\psi = A_1 e^{\alpha x}, x < 0, \tag{51}$$

$$\psi = A_3 \cos(\beta x) + B_3 \sin(\beta x), 0 \le x \le L \tag{52}$$

$$\psi = B_2 e^{-\alpha x} \tag{53}$$

The continuity of ψ at $x=0$ gives

$$A_1 = A_3 \tag{54}$$

and that of $d\psi/dx$ gives

$$\alpha A_1 = \beta A_3 \tag{55}$$

Similarly, the continuity of ψ at $x=L$ gives

$$A_3 \cos(\beta L) + B_3 \sin(\beta L) = B_2 e^{\alpha L} \tag{56}$$

and

$$-\beta A_3 \sin(\beta L) + \beta B_3 \cos(\beta L) = \alpha B_2 e^{\alpha L} \tag{57}$$

Dividing equation (57) by (56)

$$\frac{A_3 \sin(\beta L) - B_3 \cos(\beta L)}{A_3 \cos(\beta L) + B_3 \sin(\beta L)} = \frac{\alpha}{\beta} \tag{58}$$

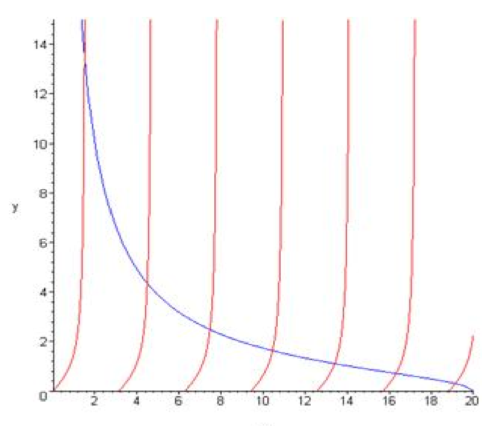
After rearrangement, this yields

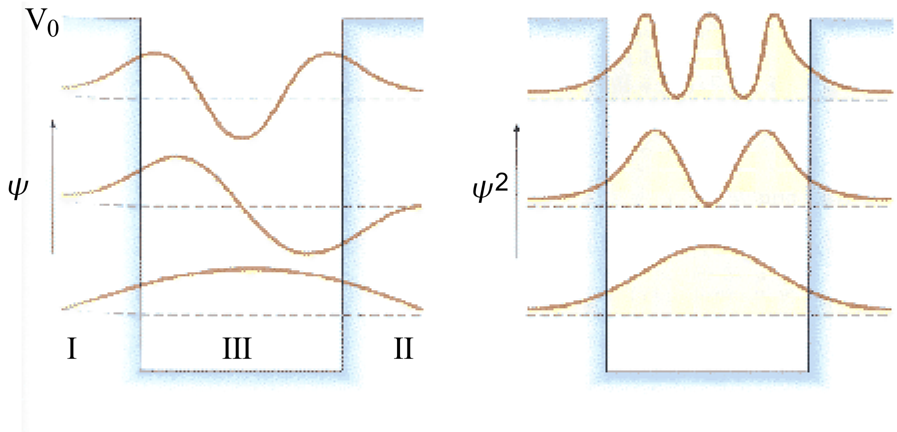
$$\tan(\beta L) = \frac{2\alpha\beta}{\beta^2 - \alpha^2} \tag{59}$$

Or,

$$\tan L \sqrt{\frac{2mE}{\hbar^2}} = \frac{2\sqrt{E(V_0 - E)}}{2E - V_0} \tag{60}$$

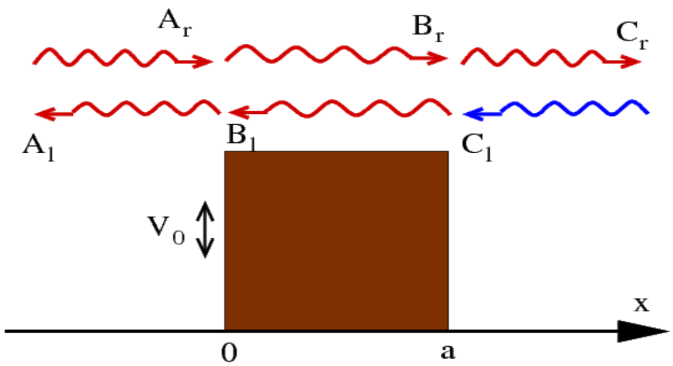
Q: How to solve this problem graphically?

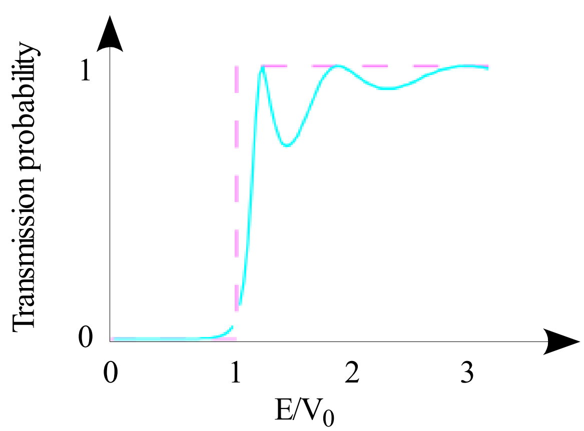




5.2 Quantum tunneling

In quantum mechanics, quantum tunneling is a phenomenon in which a particle violates the principles of classical mechanics by penetrating or passing through a potential barrier or impedance higher than the kinetic energy of the particle.





- α - particle radio-active decay.
- superconductor physics
- scanning-tunneling microscope (measuring the tunneling electron current)
- Field emission (cold emission)
- enzyme reactions

6. Important Properties of Wavefunctions

6.1 Parity of wavefunctions (symmetry and anti-symmetry)

In general, if ψ is the wavefunction for a nondegenerate state, it must be *symmetric* or *antisymmetric* under any transformation that leaves H unchanged.

Define the reflection operation:

$$R f(x) = f(L-x) \tag{61}$$

$$R\nabla^2 = \frac{\partial^2}{\partial (L-x)^2} = \frac{\partial^2}{\partial x^2} \tag{62}$$

$$RH = H \tag{63}$$

Applying this operator to Schrödinger's equation ($H\psi = E\psi$):

$$(RH)(R\psi) = (RE)(R\psi) \tag{64}$$

For a constant energy E , ψ and $R\psi$ both are eigenstates, which means $R\psi$ is linearly dependent on ψ , that is:

$$R\psi = c\psi \tag{65}$$

with the condition:

$$\int_0^{inf} |c\psi^2| d\tau = 1 \tag{66}$$

$$R\psi = \pm\psi \tag{67}$$

$$\psi(x) = \pm\psi(L-x) \tag{68}$$

Parity of wavefunctions:

symmetric ⇔ even parity (*gerade* σ_g)
antisymmetric ⇔ odd parity (*ungerade* σ_u)

6.2 Orthogonality of wavefunctions

If ψ_1 and ψ_2 are wavefunctions of a particle moving in three dimensions corresponding to the different energy levels E_1 and E_2 respectively, then

$$\int \psi_1^* \psi_2 d\tau = 0 \tag{69}$$

The integration being throughout all space, and the functions are said to be orthogonal.

Q: How to derive this? [Hint: Use Green's theorem to convert a volume integral to a surface integral according to $\int_{vol} (\psi\nabla^2\phi - \phi\nabla^2\psi) dr = \int_S (\psi\nabla\phi - \phi\nabla\psi)\vec{n}\, dS$]

$$\psi_2 \nabla^2 \psi_1^* = \psi_2 \frac{-2\mathrm{m}(E_1 - V(x))}{\hbar^2} \psi_1^* \tag{70}$$

$$\psi_1 \nabla^1 \psi_2^* = \psi_1 \frac{-2\mathrm{m}(E_2 - V(x))}{\hbar^2} \psi_2^* \tag{71}$$

$$\frac{2\mathrm{m}}{\hbar^2}(E_1 - E_2) \int \psi_1^* \psi_2 \, d\tau = 0 \tag{72}$$

If ψ_m and ψ_n have

$$\int_a^b \psi_m^* \psi_n \, d\tau = \delta_{mn} \tag{73}$$

δ_{nm} having the value unity if $m=n$ and zero if $m \neq n$ (Kronecker notation), ψ_m ψ_n are orthonormal.

Q: If ψ_1 and ψ_2 are degenerate wavefunctions of the energy level E , can we create a wavefunction, say, ψ_3 that is orthogonal to ψ_1 ? and how?

7. Harmonic Oscillators

7.1 Classical harmonic oscillators

kinetic energy $V(x) = m\omega^2 x^2/2$

7.2 Quantum harmonic oscillators

$$\frac{-\hbar^2}{2\mathrm{m}} \frac{d^2\psi}{dx^2} + \frac{m\omega^2 x^2}{2} = E\psi \tag{74}$$

$$\psi'' = \frac{-2\mathrm{m}(E - m\omega^2 x^2/2)}{\hbar^2} \psi \tag{75}$$

Let's consider the function:

$$\psi_0 = e^{-\alpha x^2} \tag{76}$$

we obtain

$$E = \frac{\alpha \hbar^2}{m} \quad \text{and} \quad \alpha = \frac{m\omega}{2\hbar} \tag{77}$$

$$E_0 = h\omega/2 \tag{78}$$

Do you think ψ_0 is possibly the ground state of the oscillator and $E_0 = \hbar\omega/2$ is the lowest energy? Why?

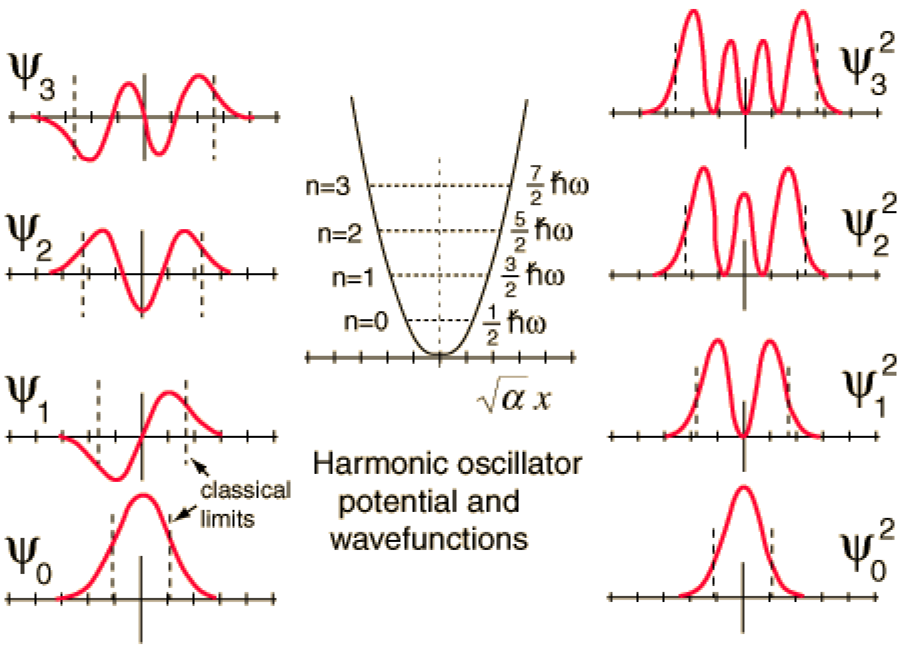
The first excited energy: antisymmetric, one node. Let's consider

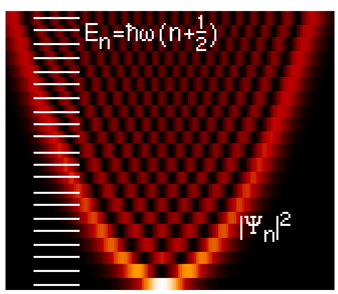
$$\psi_1 = x e^{-\alpha x^2} \tag{79}$$

Now

$$E_1 = 3\hbar\omega/2 \tag{80}$$

Next $\psi_2 = (1 - x^2) e^{-\alpha x^2}$, $E_2 = 5\hbar\omega/2$
In general, $E_n = (n + 1/2)\hbar\omega \, , n = 0, 1, 2, \ldots$





7.3 Zero-point energy

- **Interpretation:** the energy that remains when all other energy is removed from a system.
- **Can we remove the zero-point energy?** ("free-energy" device)
- **Importance:** Solid-state physics, liquid helium at absolute zero temperature, Casimir effect

PROBLEMS: (due Feb. 5 2005)

1. The benzene molecule contains a ring of six carbon atoms around which six delocalized π electrons can circulate. Adapting the particle-in-a-ring model, estimate the longest wavelength absorption in the benzene spectrum. [Hint: the C-C distance in benzene is around 1.39 Å. Make use of the six delocalized π electrons.]

2. Two atoms bonded together in a diatomic molecule, vibrating back and forth, can be considered as an oscillator. Using m_1 and m_2 to represent the masses of the two atoms, write down the effective (reduced) mass of the oscillator. The strongest infrared band of $H^{35}Cl$ occurs at 2992 cm^{-1}. Find the force constant of $H^{35}Cl$. State any approximation made. (10 points)

3. For many potential-energy functions $V(x)$, the one-particle, 1D Schrödinger equation can not be solved exactly. There are numerical methods available for computer solution of the one-particle 1D Schrödinger equation to obtain accurate eigenfunctions and eigenenergies for an arbitrary $V(x)$. One method is called the **Numerov Method.** Explain this method, and use this method to find the lowest 4 stationary-state energies for a one-particle system with $V(x)=1/|x|$. The Numerov method can be performed using Mathmetica or Matlab packages available on wk18.cos.gmu.edu. Alternatively, you can log onto class_qcm@glass.gmu.edu, and get the numerov code - ~/codes/schord1d.f90. (This problem is optional. However, if you solve it correctly, there will be 10 bonus points).