Quantum box with infinite well potential

Masatsugu Sei Suzuki
Department of Physics, State University of New York at Binghamton
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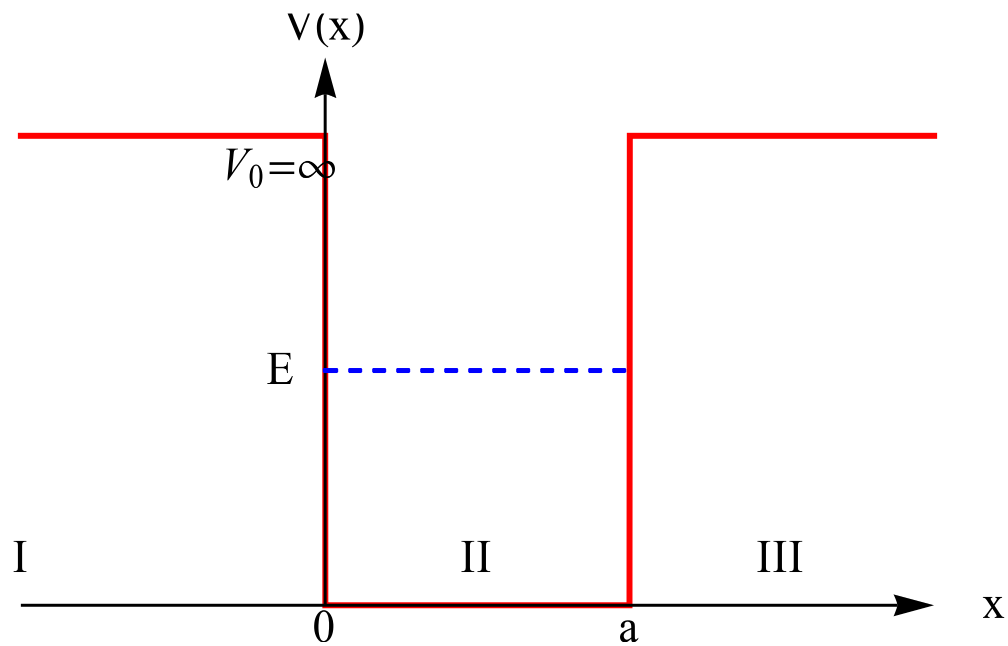
1. 1D one-dimensional well potential



$$\hat{H}=\frac{\hat{p}^2}{2m}$$

$$H\varphi(x)=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\varphi(x)=E\varphi(x)=\frac{\hbar^2k^2}{2m}\varphi(x)$$

The solution of this equation is

$$\varphi(x)=A\sin(kx)+B\cos(kx)$$

where

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

Using the boundary condition:

$$\varphi(x=0)=\varphi(x=a)=0$$

we have

$B = 0$ and $A \neq 0$.

$$\sin(ka) = 0$$

$$ka = n\pi \quad (n = 1, 2, \ldots)$$

Note that $n = 0$ is not included in our solution because the corresponding wave function becomes zero. The wave function is given by

$$\varphi_n(x) = \langle x | \varphi_n \rangle = A_n \sin(\frac{n\pi x}{a}) = \sqrt{\frac{2}{a}} \sin(\frac{n\pi x}{a})$$

with

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2$$

((**Normalization**))

$$1 = \int_0^a A_n{}^2 \sin^2(\frac{n\pi x}{a}) dx = \frac{a}{2} A_n{}^2$$

2. Mathematica

$$|\varphi_n(x)|^2 = [\sqrt{\frac{2}{a}} \sin(\frac{n\pi x}{a})]^2 = \frac{2}{a} \sin^2(\frac{n\pi x}{a})$$

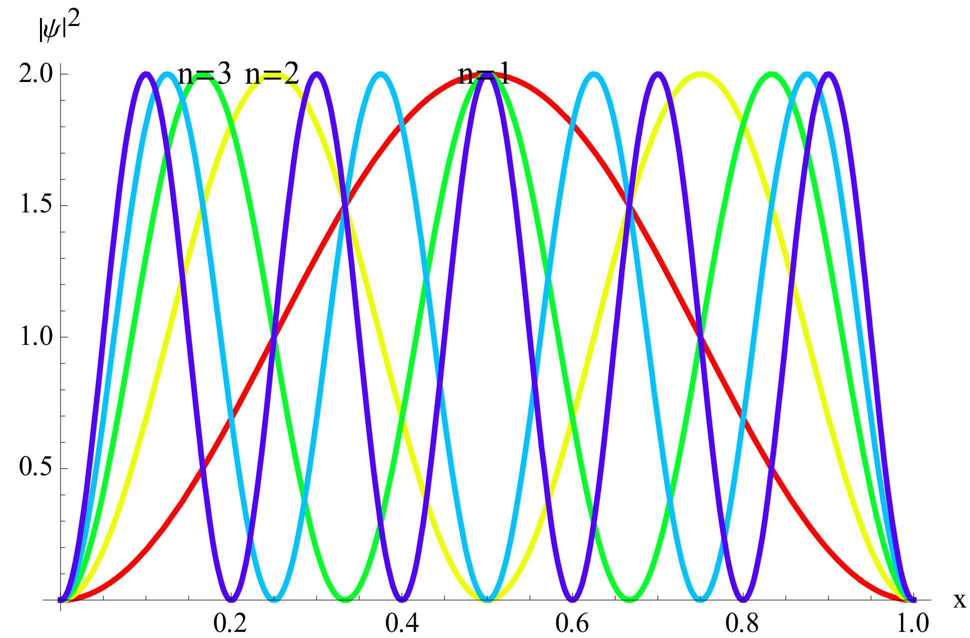


Fig. Plot of $\left|\varphi_n(x)\right|^2$ with $a = 1$, as a function of x. $n = 1$ (red), 2 (yellow), 3 (green), 4 (blue), and 5 (dark blue). There are n peaks for the state $\left|n\right\rangle$.

The expectation values and uncertainty

$$\left\langle x^m \right\rangle = \int_0^a \varphi_n^*(x) x^m \varphi_n(x) dx = \int_0^a \frac{2}{a} x^m \sin^n(\frac{n\pi x}{a}) dx$$

$$\left\langle p^m \right\rangle = \int_0^a \varphi_n^*(x) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^m \varphi_n(x) dx$$

Since

$$\left\langle x \right\rangle = 0, \qquad \left\langle x^2 \right\rangle = \frac{a^2}{6}(2 - \frac{3}{n^2\pi^2})$$

$$\left\langle p \right\rangle = 0, \qquad \left\langle p^2 \right\rangle = \frac{n^2\pi^2\hbar^2}{a^2}$$

we have

$$\Delta x = \sqrt{\left\langle x^2 \right\rangle - \left\langle x \right\rangle^2} = a\sqrt{\frac{1}{6}(2 - \frac{3}{n^2\pi^2})}$$

$$\Delta p = \sqrt{\left\langle p^2 \right\rangle - \left\langle p \right\rangle^2} = \frac{n\pi\hbar}{a}$$

Then

$$\Delta p \Delta x = n\pi\hbar\sqrt{\frac{1}{6}(2 - \frac{3}{n^2\pi^2})}$$

When $n = 1$,

$$\Delta p \Delta x = 1.67029\ \hbar > 0.5\ \hbar$$

((**Mathematica**))

```
Clear["Global`*"]; ϕ[n_, x_] := Sqrt[2/a] Sin[n π x/a];

xav1 = ∫_0^a x ϕ[n, x]^2 ⅆx // Simplify[#, n ∈ Integers] &
```

$$\frac{a}{2}$$

```
xav2 = ∫_0^a x^2 ϕ[n, x]^2 ⅆx // Simplify[#, n ∈ Integers] &
```

$$\frac{1}{6} a^2 \left(2 - \frac{3}{n^2 \pi^2}\right)$$

```
pav1 = ℏ/ⅈ ∫_0^a ϕ[n, x] D[ϕ[n, x], x] ⅆx //
  Simplify[#, n ∈ Integers] &
```

0

```
pav2 = (ℏ/ⅈ)^2 ∫_0^a ϕ[n, x] D[ϕ[n, x], {x, 2}] ⅆx //
  Simplify[#, n ∈ Integers] &
```

$$\frac{n^2 \pi^2 \hbar^2}{a^2}$$

```
ΔxΔp = Sqrt[xav2] Sqrt[pav2] // Simplify[#, {ℏ > 0, a > 0}] &
```

$$\frac{\sqrt{n^2} \sqrt{-\frac{3}{n^2} + 2 \pi^2}\ \hbar}{\sqrt{6}}$$

```
ΔxΔp/ℏ /. n → 1 // N
```

1.67029

3. Exercise: Townsend 6-16 problem

A particle of mass m is in lowest energy (ground) state of the infinite potential energy well

$V(x) = 0$ for $0<x<L$ and ∞ elsewhere.

At time $t = 0$, the wall located at $x = L$ is suddenly pulled back to a position at $x = 2L$. This change occurs so rapidly that instantaneously the wave function does not change.

(a) Calculate the probability that a measurement of the energy will yield the ground-state energy of the new well. What is the probability that a measurement of the energy will yield the first excited energy of the new well?

(b) Describe the procedure you would use to determine the time development of the system. Is the system in a stationary state?

((**Solution**))

The old wave function of the ground state is given by

$$\varphi_1(x) = \sqrt{\frac{2}{a}}\sin(\frac{\pi x}{a}) \qquad \text{only for } 0<x<a \qquad \text{(0 otherwise).}$$

The new wave function is given by

$$\psi_{new}{}^{(n)}(x) = \sqrt{\frac{2}{2a}}\sin(\frac{n\pi x}{2a}) = \sqrt{\frac{1}{a}}\sin(\frac{n\pi x}{2a})$$

with the energy of

$$E_{new}{}^{(n)} = \frac{\hbar^2}{2m}\left(\frac{\pi n}{2a}\right)^2$$

(a)

$$\varphi_1(x) = \sum_n c_n \psi_{new}{}^{(n)}(x)$$

$$\begin{aligned} c_n &= \int_0^{2a} \psi_{new}{}^{(n)*}(x)\varphi_1(x)dx \\ &= \frac{\sqrt{2}}{a}\int_0^a \sin(\frac{n\pi x}{2a})\sin\left(\frac{\pi x}{a}\right)dx \\ &= \frac{4\sqrt{2}}{\pi(4-n^2)}\sin(\frac{n\pi}{2}) \end{aligned}$$

Note that

$$c_2 = \frac{1}{\sqrt{2}}$$

$$|c_1|^2 = \frac{32}{9\pi^2} = 0.360253, \qquad |c_2|^2 = \frac{1}{2} = 0.5$$

(b)

The system is not stationary since $|\psi(t=0)\rangle$ is not an eigenstate of the new Hamiltonian $\hat{H}_{new}$, but is a superposition of the eigenstates $|\psi_{new}{}^{(n)}\rangle$ with various kinds of *n*.

$$|\psi(t=0)\rangle = |\varphi_1\rangle = \sum_n c_n |\psi_{new}{}^{(n)}\rangle$$

$$\begin{aligned}|\psi(t)\rangle &= \exp(-\frac{i}{\hbar}\hat{H}_{new}t)|\psi(t=0)\rangle \\ &= \sum_n c_n \exp(-\frac{i}{\hbar}\hat{H}_{new}t)|\psi_{new}{}^{(n)}\rangle \\ &= \sum_n c_n \exp(-\frac{i}{\hbar}E_{new}{}^{(n)}t)|\psi_{new}{}^{(n)}\rangle\end{aligned}$$

or

$$\psi(x,t) = \langle x|\psi(t)\rangle = \sum_n c_n \exp(-\frac{i}{\hbar}E_{new}{}^{(n)}t)\psi_{new}{}^{(n)}(x)$$

where c_n are determined as in (a)

$$c_n = \frac{4\sqrt{2}}{\pi(4-n^2)}\sin(\frac{n\pi}{2})$$

and

$$E_{new}{}^{(n)} = \frac{\hbar^2}{2m}\left(\frac{\pi n}{2a}\right)^2,$$

$$\psi_{new}{}^{(n)}(x) = \sqrt{\frac{2}{2a}}\sin(\frac{n\pi x}{2a}) = \sqrt{\frac{1}{a}}\sin(\frac{n\pi x}{2a})$$

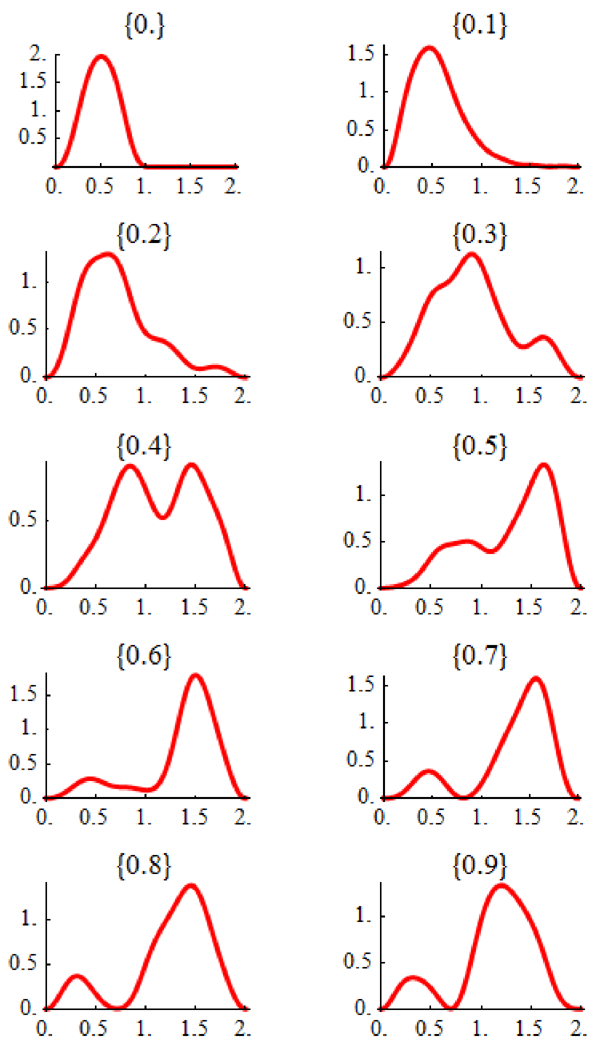
Then we get

$$|\psi(x,t)|^2 = \sum_m c_m{}^* \exp(\frac{i}{\hbar}E_{new}{}^{(m)}t)\psi_{new}{}^{(m)^*}(x)\sum_n c_n \exp(-\frac{i}{\hbar}E_{new}{}^{(n)}t)\psi_{new}{}^{(n)}(x)$$
$$= \sum_{n,m} c_m{}^* c_n \psi_{new}{}^{(m)^*}(x)\psi_{new}{}^{(n)}(x)\exp[-\frac{i}{\hbar}(E_{new}{}^{(n)} - E_{new}{}^{(n)})t]$$

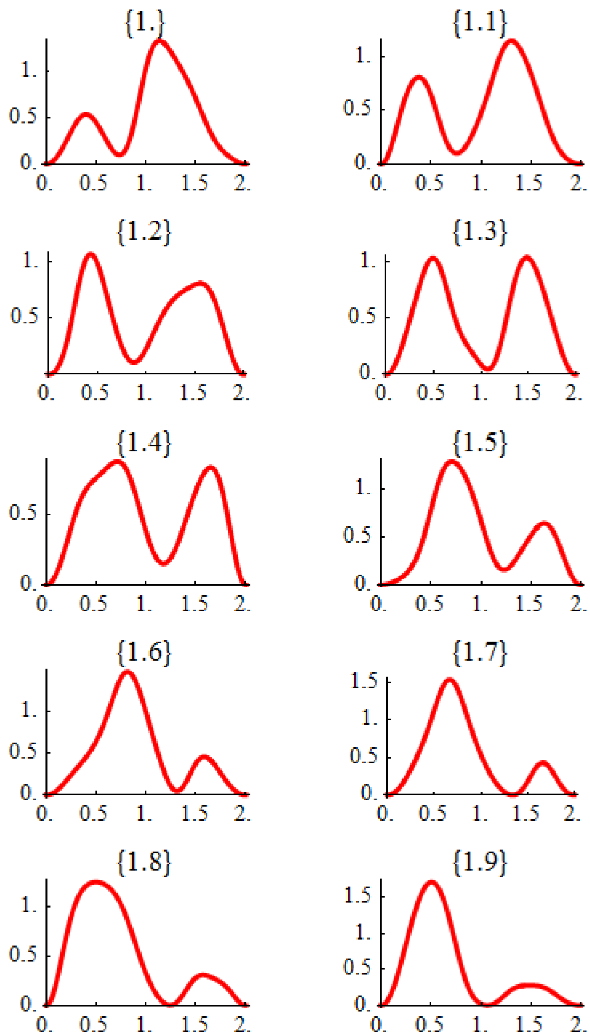
((**Mathematica**))

We use $m = \hbar = 1$. $a = 1$. Red (At $t = 0$). The Plot of $|\psi(x,t)|^2$ as a function of x ($0<x<2a$), where t is changed as parameter; $t = 0$ - 3 with $\Delta t = 0.1$. The summation over n (n = 1 – 10).

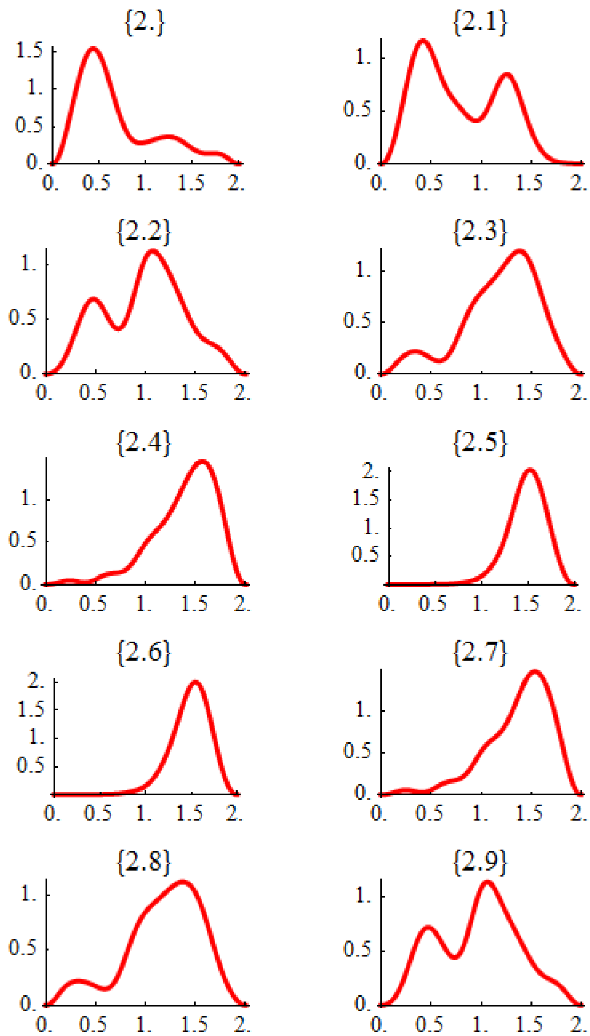
(a) t = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9



(b) t = 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9



(c) $t = 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9$



4. 2D well potential

Next we consider a particle in a 2D well potential

The potential:

$V(x,y) = 0$ for $0 \le x \le a$ and $0 \le y \le a$. $V(x,y) = \infty$ otherwise.

$$H\varphi(x,y) = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right)\varphi(x,y) = E\varphi(x,y) = \frac{\hbar^2 k^2}{2m}\varphi(x,y)$$

$$E = \frac{\hbar^2}{2m}(k_x{}^2 + k_y{}^2)$$

$$\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right)\varphi(x,y) = -(k_x{}^2 + k_y{}^2)\varphi(x,y)$$

We use the method of the separation variables. Suppose that

$$\varphi(x,y) = X(x)Y(y)$$

$$\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} = -(k_x{}^2 + k_y{}^2)$$

We assume that

$$X''(x) = -k_x{}^2 X(x)$$

$$Y''(y) = -ky^2 Y(y)$$

Using the boundary condition

$$X(x=0) = X(x=a) = 0$$

and

$$Y(y=0) = Y(y=a) = 0$$

Then we have

$$\varphi_{nx,ny}(x,y) = \left(\sqrt{\frac{2}{a}}\right)^2 \sin(\frac{n_x \pi x}{a})\sin(\frac{n_y \pi y}{a})$$

5. Mathematica

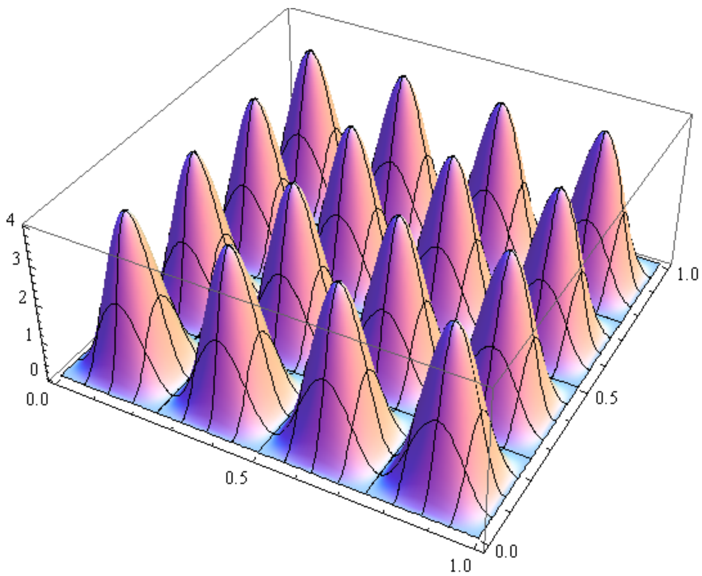
A particle in a two dimensional box

```
Clear["Global`*"];
```

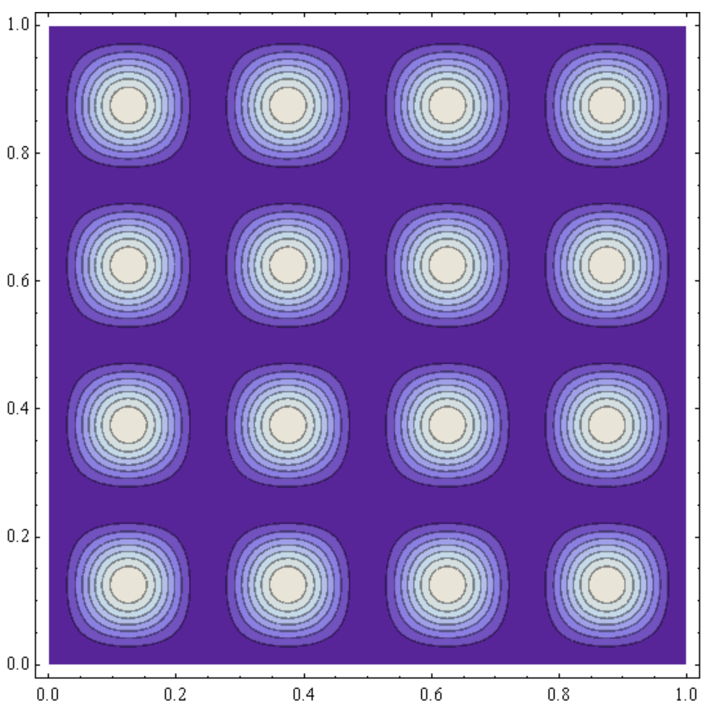
$$\psi = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{b}}\ \mathrm{Sin}\left[\frac{n\,\pi\,x}{a}\right]\mathrm{Sin}\left[\frac{m\,\pi\,y}{b}\right];$$

```
prb = ψ^2 /. {a → 1, b → 1};
```

```
p13D1 = Plot3D[prb /. {n → 4, m → 4}, {x, 0, 1}, {y, 0, 1},
  PlotPoints → 100]
```




```
cont1 = ContourPlot[prb /. {n → 4, m → 4}, {x, 0, 1},
  {y, 0, 1}, PlotPoints → 100]
```



6. Standing wave solutions with a fixed boundary condition

We consider a free particle inside a box with length L_x, L_y, L_z along the x, y, and z axes, respectively. The Schrödinger equation of the system is given by

$$H\psi(x,y,z) = -\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z)$$

under the boundary condition;

$$\psi(x = L_x, y, z) = \psi(x = 0, y, z) = 0$$
$$\psi(x, y = L_z, z) = \psi(x, y = 0, z) = 0$$
$$\psi(x_x, y, z = L_z) = \psi(x, y, z = 0) = 0$$

We use the method of separation variables. We assume that

$$\psi(x,y,z) = X(x)Y(y)Z(z)$$

with

$$X(0) = X(L_x) = 0, \qquad Y(0) = Y(L_y) = 0, \qquad Z(0) = Z(L_z) = 0$$

The substitution of the solution into the Schrödinger equation yields

$$\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)} = -\frac{2mE}{\hbar^2}$$

We assume that

$$\frac{X''(x)}{X(x)} = -k_x^{\ 2}, \qquad \frac{Y''(y)}{Y(y)} = -k_y^{\ 2}, \frac{Z''(z)}{Z(z)} = -k_z^{\ 2}$$

The solution of these differential equations can be obtained as a standing wave solution,

$$X(x) = \sin(k_x x), \qquad Y(y) = \sin(k_y y), \qquad Z(z) = \sin(k_z z)$$

under the boundary conditions, where k_x, k_y, and k_z are constants. The resulting wave function is

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

The condition that $\psi = 0$ at $x = L_x$ requires that

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

The values for the k_x, k_y, and k_z are

$$k_x = \frac{n_x \pi}{L_x}, \qquad k_y = \frac{n_y \pi}{L_y}, \qquad k_z = \frac{n_z \pi}{L_z}$$

where n_x, n_y, and n_z are positive integers.

((**Mathematica**)) ContourPlot3D

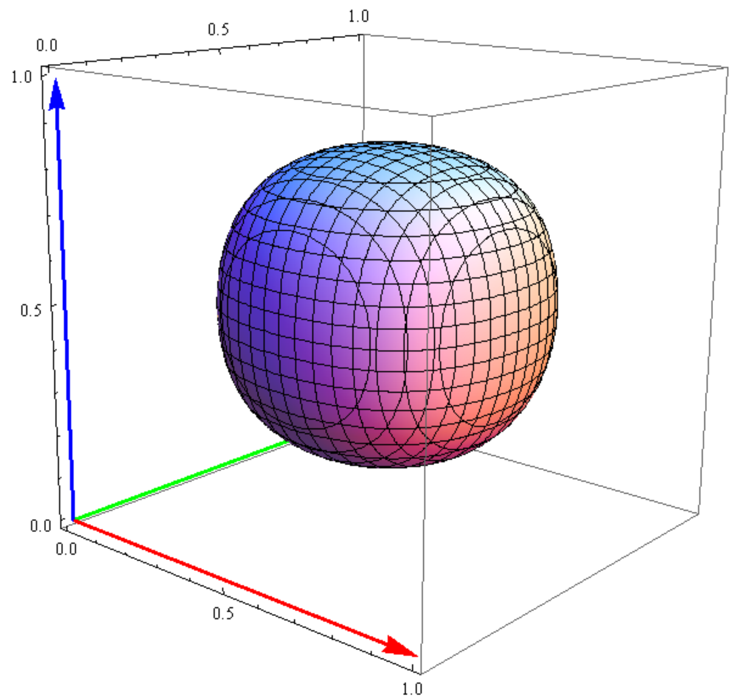


Fig. ContourPlot3D of $\sin^2(k_x x)\sin^2(k_y y)\sin^2(k_z z) = const$ in the 3D real space. $k_x x = \frac{n_x \pi}{L} x$. $k_y y = \frac{n_y \pi}{L} y$. $k_z z = \frac{n_z \pi}{L} z$. $L = 1$ for simplicity. $n_x = 1$, $n_y = 1$, $n_z = 1$

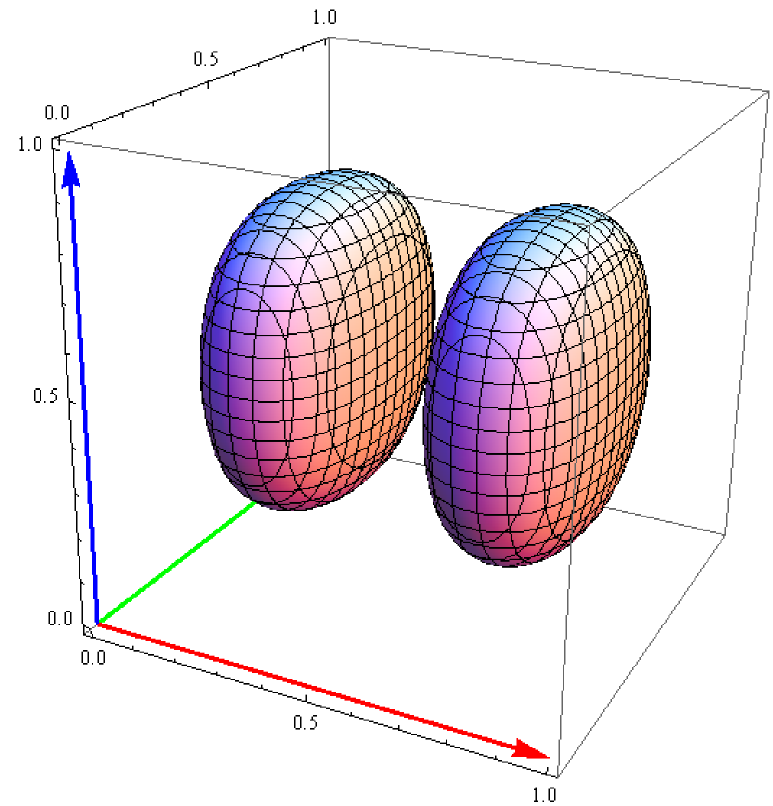


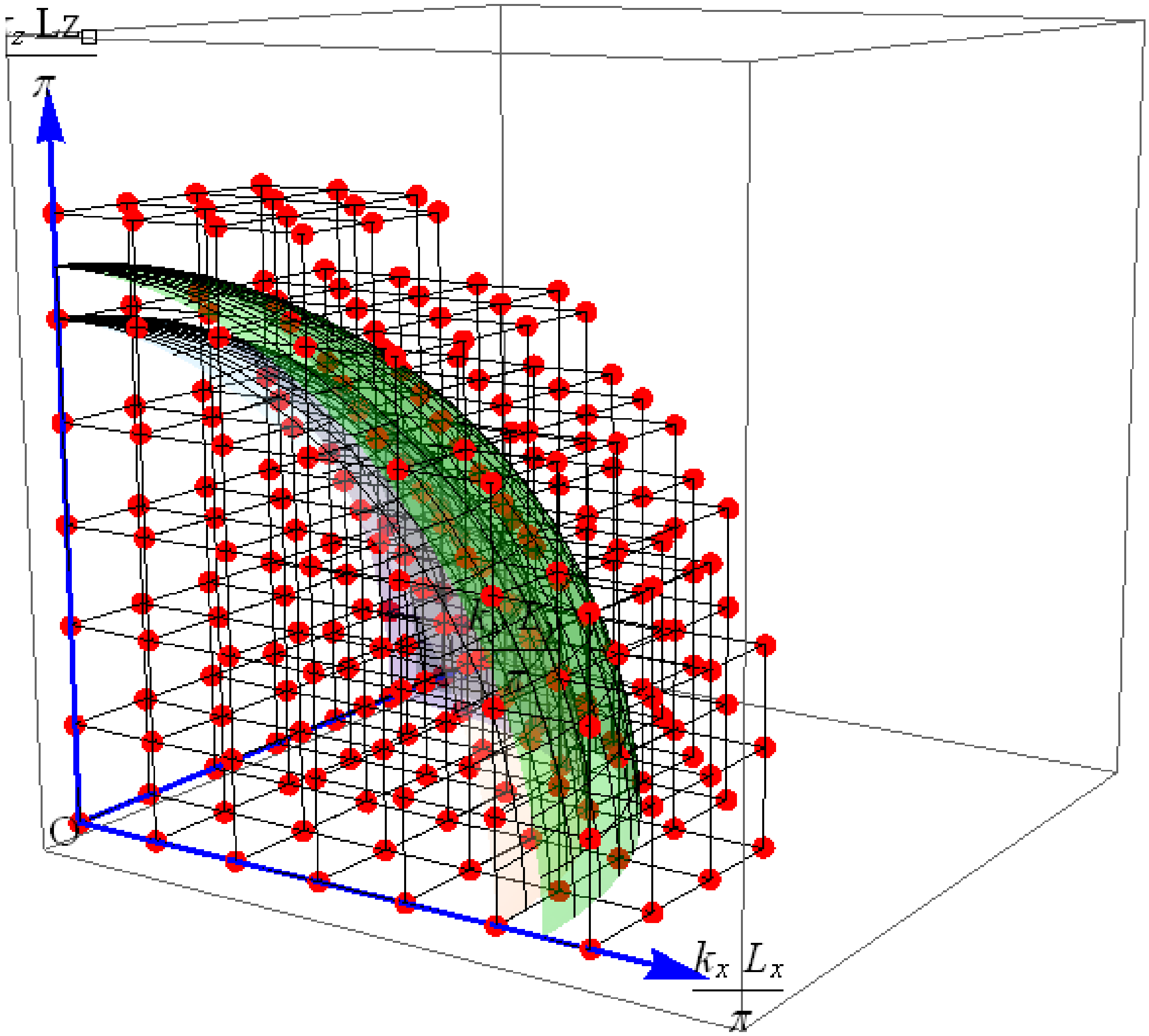
Fig. ContourPlot3D of $\sin^2(k_x x)\sin^2(k_y y)\sin^2(k_z z) = const$ in the 3D real space. $k_x x = \dfrac{n_x \pi}{L} x$. $k_y y = \dfrac{n_y \pi}{L} y$. $k_z z = \dfrac{n_z \pi}{L} z$. $L = 1$ for simplicity. $n_x = 2$, $n_y = 1$, $n_z = 1$

((**Density of states**))

$$
\begin{aligned}
E(k_x, k_y, k_z) = \varepsilon &= \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} (k_x{}^2 + k_y{}^2 + k_z{}^2) \\
&= \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x{}^2}{L_x{}^2} + \frac{n_y{}^2}{L_y{}^2} + \frac{n_z{}^2}{L_z{}^2}\right)
\end{aligned}.
$$

There is one state per volume of the ***k***-space;

$$
\frac{\pi}{L_x} \frac{\pi}{L_y} \frac{\pi}{L_z}.
$$



In the region of k - k + dk, the number of states is

$$D(\varepsilon)d\varepsilon = 2\frac{1}{8}\frac{4\pi k^2 dk}{\dfrac{\pi^3}{L_x L_y L_z}}$$
$$= 2\frac{V}{(2\pi)^3}4\pi k^2 dk$$
$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}d\varepsilon$$

where the factor 2 comes from the two allowed state $|+\rangle$ and $|-\rangle$ for the spin quantum number (S = 1/2); fermions such as electron. The density of state $D(\varepsilon)$ is obtained as

The total particle number N and total energy E can be described by

$$N = \int_0^{\varepsilon_F} D(\varepsilon)d\varepsilon = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\varepsilon_F}\sqrt{\varepsilon}d\varepsilon = \frac{2}{3}\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon_F^{\ 3/2}$$

and

$$E = \int_0^{\varepsilon_F} \varepsilon D(\varepsilon)d\varepsilon = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\varepsilon_F}\varepsilon^{3/2}d\varepsilon = \frac{2}{5}\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon_F^{\ 5/2} .$$

Then we have

$$\frac{E}{N} = \frac{\frac{2}{5}\varepsilon_F^{\ 3/2}}{\frac{2}{3}\varepsilon_F^{\ 3/2}} = \frac{3}{5}\varepsilon_F$$

((Note)) Fermi-Dirac distribution function

The Fermi-Dirac distribution gives the probability that an orbital at energy ε will be occupied in an ideal gas in thermal equilibrium

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}, \tag{12}$$

where μ is the chemical potential and $\beta = 1/(k_BT)$.

(i) $\lim_{T\to 0}\mu = \varepsilon_F$.

(ii) $f(\varepsilon) = 1/2$ at $\varepsilon = \mu$.

(iii) For $\varepsilon - \mu \gg k_BT$, $f(\varepsilon)$ is approximated by $f(\varepsilon) = e^{-\beta(\varepsilon-\mu)}$. This limit is called the Boltzman or Maxwell distribution.

(iv) For $k_BT \ll \varepsilon_F$, the derivative $-df(\varepsilon)/d\varepsilon$ corresponds to a Dirac delta function having a sharp positive peak at $\varepsilon = \mu$.

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7. Plane wave solution with a periodic boundary condition

A. Energy level in 1D system

We consider a free electron gas in 1D system. The Schrödinger equation is given by

$$H\psi_k(x) = \frac{p^2}{2m}\psi_k(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi_k(x)}{dx^2} = \varepsilon_k\psi_k(x) , \tag{1}$$

where

$$p = \frac{\hbar}{i}\frac{d}{dx},$$

and ε_k is the energy of the electron in the orbital.

The orbital is defined as a solution of the wave equation for a system of only one electron: ⟨⟨one-electron problem⟩⟩.

Using a periodic boundary condition: $\psi_k(x+L) = \psi_k(x)$, we have the plane-wave solution

$$\psi_k(x) \sim e^{ikx}, \tag{2}$$

with

$$\varepsilon_k = \frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}n\right)^2,$$

$$e^{ikL} = 1 \text{ or } k = \frac{2\pi}{L}n,$$

where $n = 0, \pm1, \pm2,\ldots$, and L is the size of the system.

B. Energy level in 3D system

We consider the Schrödinger equation of an electron confined to a cube of edge L.

$$H\psi_{\mathbf{k}} = \frac{\mathbf{p}^2}{2m}\psi_{\mathbf{k}} = -\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}} = \varepsilon_{\mathbf{k}}\psi_{\mathbf{k}}. \tag{3}$$

It is convenient to introduce wavefunctions that satisfy periodic boundary conditions.

Boundary condition (Born-von Karman boundary conditions).

$$\psi_{\mathbf{k}}(x+L,y,z) = \psi_{\mathbf{k}}(x,y,z),$$
$$\psi_{\mathbf{k}}(x,y+L,z) = \psi_{\mathbf{k}}(x,y,z),$$
$$\psi_{\mathbf{k}}(x,y,z+L) = \psi_{\mathbf{k}}(x,y,z).$$

The wavefunctions are of the form of a traveling plane wave.

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{4}$$

with

$k_x = (2\pi/L)\, n_x$, ($n_x = 0, \pm1, \pm2, \pm3,\ldots..$),
$k_y = (2\pi/L)\, n_y$, ($n_y = 0, \pm1, \pm2, \pm3,\ldots..$),
$k_z = (2\pi/L)\, n_z$, ($n_z = 0, \pm1, \pm2, \pm3,\ldots..$).

The components of the wavevector ***k*** are the quantum numbers, along with the quantum number m_s of the spin direction. The energy eigenvalue is

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2}{2m}(k_x{}^2 + k_y{}^2 + k_z{}^2) = \frac{\hbar^2}{2m}\mathbf{k}^2 . \qquad (5)$$

Here

$$\mathbf{p}\psi_k(\mathbf{r}) = \frac{\hbar}{i}\nabla_{\mathbf{k}}\psi_k(\mathbf{r}) = \hbar\mathbf{k}\psi_k(\mathbf{r}) . \qquad (6)$$

So that the plane wave function $\psi_{\mathbf{k}}(\mathbf{r})$ is an eigenfunction of ***p*** with the eigenvalue $\hbar\mathbf{k}$. The ground state of a system of *N* electrons, the occupied orbitals are represented as a point inside a sphere in ***k***-space.

Because we assume that the electrons are noninteracting, we can build up the *N*-electron ground state by placing electrons into the allowed one-electron levels we have just found.

((The Pauli's exclusion principle))

The one-electron levels are specified by the wavevectors ***k*** and by the projection of the electron's spin along an arbitrary axis, which can take either of the two values $\pm\hbar/2$. Therefore associated with each allowed wave vector k are two levels:

$$\left|\mathbf{k},\uparrow\right\rangle,\ \left|\mathbf{k},\downarrow\right\rangle .$$

In building up the *N*-electron ground state, we begin by placing two electrons in the one-electron level $k = 0$, which has the lowest possible one-electron energy $\varepsilon = 0$. We have

$$N = 2\frac{L^3}{(2\pi)^3}\frac{4\pi}{3}k_F{}^3 = \frac{V}{3\pi^2}k_F{}^3 , \qquad (7)$$

where the sphere of radius k_F containing the occupied one-electron levels is called the Fermi sphere, and the factor 2 is from spin degeneracy.

The electron density *n* is defined by

$$n = \frac{N}{V} = \frac{1}{3\pi^2}k_F{}^3 . \qquad (8)$$

The Fermi wavenumber k_F is given by

$$k_F = \left(3\pi^2 n\right)^{1/3} . \qquad (9)$$

The Fermi energy is given by

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}. \tag{10}$$

The Fermi velocity is

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(3\pi^2 n\right)^{1/3}. \tag{11}$$

((Note))

The Fermi energy ε_F can be estimated using the number of electrons per unit volume as

$\varepsilon_F = 3.64645 \times 10^{-15}\, n^{2/3}$ [eV] $= 1.69253\, n_0^{2/3}$ [eV],

where n and n_0 is in the units of (cm^{-3}) and $n = n_0 \times 10^{22}$. The Fermi wave number k_F is calculated as

$k_F = 6.66511 \times 10^7\, n_0^{1/3}$ [cm^{-1}].

The Fermi velocity v_F is calculated as

$v_F = 7.71603 \times 10^7\, n_0^{1/3}$ [cm/s].

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