Quantum box with infinite well potential
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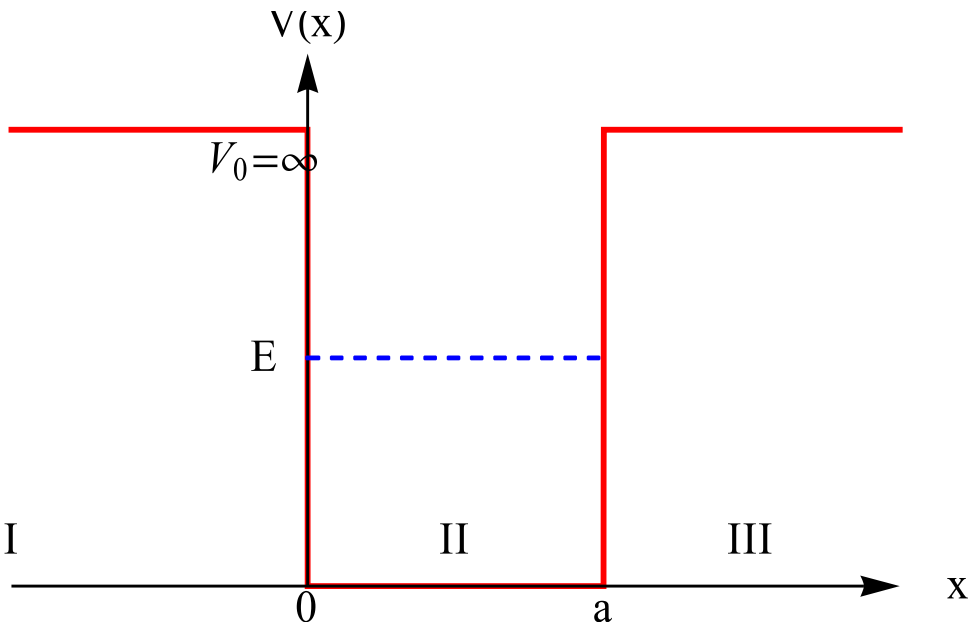
1. 1 Done-dimensional well potential



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

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

The solution of this equation is

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

where

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

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

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

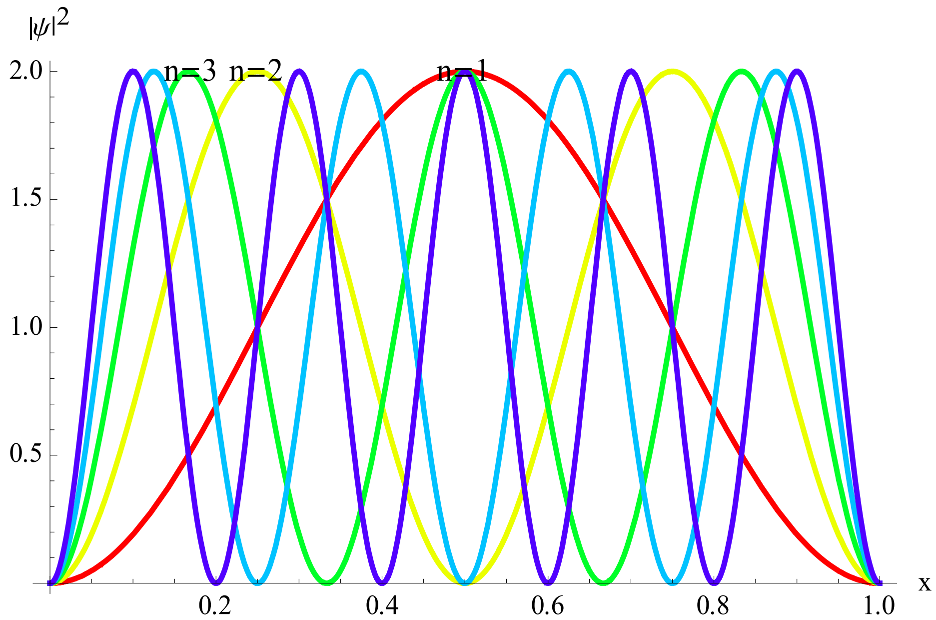


Fig. Plot of $|\varphi_n(x)|^2$ with a = 1, as a function of *x*. $n = 1, 2, 3, 4$, and 5. There are *n* peaks for the state $|n\rangle$.

The expectation values and uncertainty:

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

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

Since

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

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

we have

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = a\sqrt{\frac{1}{6}(2 - \frac{3}{n^2\pi^2}) - \frac{1}{4}} = \frac{1}{\sqrt{12}}\sqrt{1 - \frac{6}{n^2\pi^2}}$$

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

Then

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

When $n = 1$,

$$\Delta p \Delta x = \hbar > 0.567862\ \hbar > \frac{\hbar}{2}$$

3. 2D well potential

Next we consider a particle in a 2D well potential

The potential:

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

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

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

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

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

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

4. Mathematica

A particle in a two dimensional box

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

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prb = ψ^2 /. {a → 1, b → 1};
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p13D1 = Plot3D[prb /. {n → 4, m → 4}, {x, 0, 1}, {y, 0, 1},
  PlotPoints → 100]
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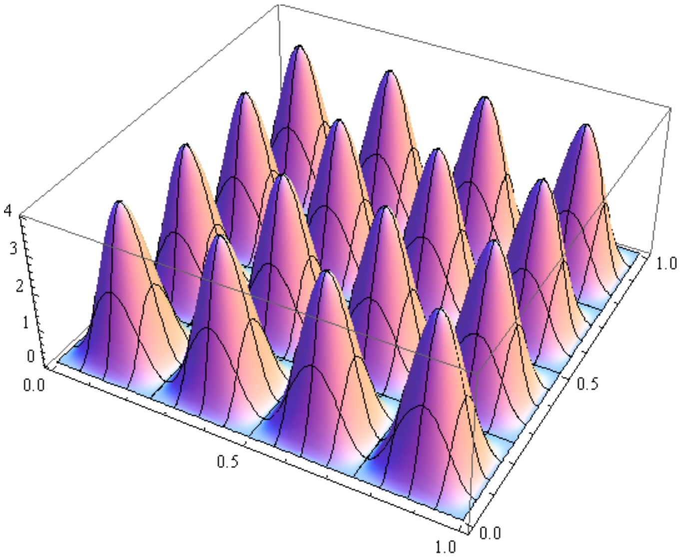


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cont1 = ContourPlot[prb /. {n → 4, m → 4}, {x, 0, 1},
  {y, 0, 1}, PlotPoints → 100]
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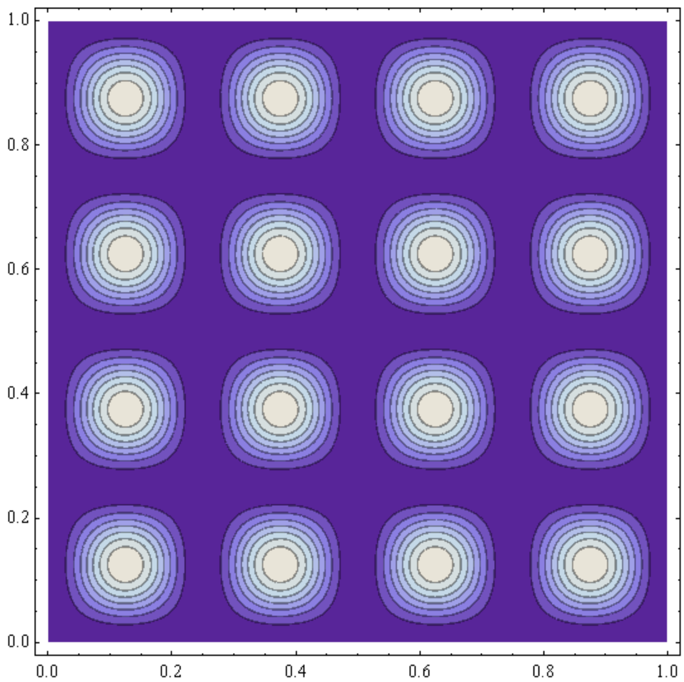


5. Standing wave solutions with a fixed boundary condition

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

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

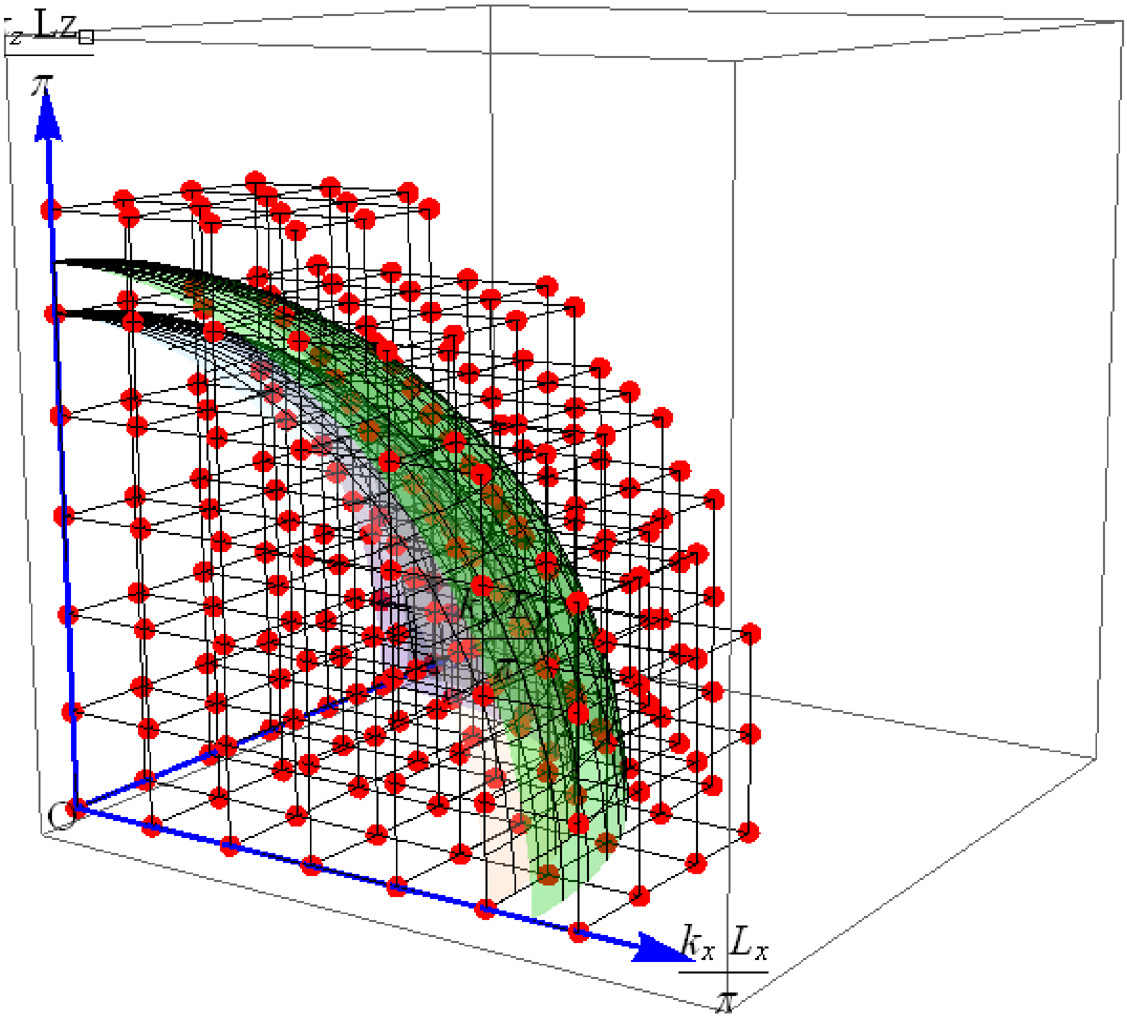
where n_x, n_y, and n_z are positive integers.

((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

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

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

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

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

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

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6. 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

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

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

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

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 $n = 0, \pm 1, \pm 2, \ldots$, 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.

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

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.

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

with

$k_x = (2\pi/L)\, n_x$, ($n_x = 0, \pm 1, \pm 2, \pm 3, \ldots..$),
$k_y = (2\pi/L)\, n_y$, ($n_y = 0, \pm 1, \pm 2, \pm 3, \ldots..$),
$k_z = (2\pi/L)\, n_z$, ($n_z = 0, \pm 1, \pm 2, \pm 3, \ldots..$).

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

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

Here

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

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

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

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

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

The Fermi wavenumber k_F is given by

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

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

$\varepsilon_F = 3.64645\text{x}10^{-15}\, n^{2/3}$ [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].