Die Verzwergten :

Confinement of free-electron states in 1,2,3 dimensions

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June 2016

We consider a (nano-)object in which the electronic states are strictly confined, i.e., that with infinite-well boundary conditions. The potential inside is flat, the wave functions are plane waves, the dispersion law is that of free electrons (in any dimensionality):

$$E = \frac{\hbar^2 k^2}{2m^*}\,, \tag{1}$$

assuming, in general case, the electron effective mass m^*. In the following exmples, the confinement results in quantization of one, two or three components of $\mathbf{k}$; those not affected by quantization are free (continuous).

Confinement in one dimension ("quantum well")

The width of the box (potential well) is L; the wave function is $\psi(x_{\sim}\sin(kx)$, with the k values quantized:

$$k = \frac{\pi}{L},\ \frac{2\pi}{L},\ \dots\ \frac{N\pi}{L},\ \dots\ . \tag{2}$$

We note a difference from the case of imposing the Born – von Kármán periodic boundary conditions on a finite crystal consisting of N usits of length a. In this case, the only condition imposed is that $\psi(x)$ be periodic, its value not pinned anywhere, and the quantization yields N distinct values of k along the Brillouin zone length, $2\pi/a$. In our analysis, there is *a priori* no need to presume any regularity in the inner structure of the nanoobject; the quantization step is imposed by its total size. However, it can be convenient to take into account the number of unit cells throughout the nanoobjects, in order to easily count the electrons and to make practical estimations. Whereas in the periodic case the k values are usually counted $[-\pi/a, \pi/a]$, in our case of confined object, because of the boundary condition $\psi(x) = 0$, the solutions are $\sim\sin(kx)$ and hence identical for $k \leftrightarrow -k$. Consequently it suffices to consider only $k \geq 0$ (also in higher dimensions). The discrete energy levels are

$$E_n = \frac{\hbar^2}{2m^*}\left(\frac{\pi}{L}\right)^2 = \frac{h^2}{8m^* L^2}\,n^2 \tag{3}$$

and become more dense as L increases.

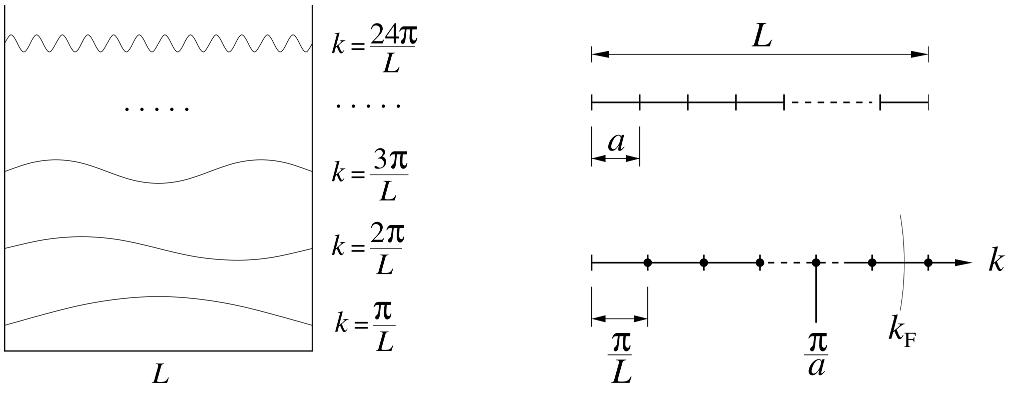

Figure 1: 1-dim. wave functions (left panel); schema of 1-dim. quantum well with total length L and lattice parameter a (right panel, top); schema of counting the states for $k \leq k_{\rm F}$ (right panel, bottom).

Fig. 1 depicts the lowest allowed $\psi(k)\sim\sin(kx)$ solutions along with the accepted geometry in direct and reciprocal space. The states numbered by k values multiple of π/L are occupied up to the Fermi wavevector $k_{\rm F}$. The latter can be placed before, or after, the π/a "boundary"; the role of this k-value is that up to it, the $N = L/a$ states are occupied, so it has an analogy with one band being fully occupied in a periodic system. Assume that each "unit cell" of length a hosts Z electrons.[1] The number of states available up to $k_{\rm F}$ is $2{\times}k_{\rm F}/(\frac{\pi}{L})$ (the factor 2 due to spin degeneracy); it must equal the number of available electrons, i.e., $(L/a){\times}Z$, hence

$$k_{\rm F} = \frac{\pi Z}{2a} \qquad \text{and} \quad E_{\rm F} = \frac{\hbar^2\pi^2 Z}{8m^* a^2}\,. \tag{4}$$

The number of states per given interval dk is

$$dN = 2{\times}\frac{dk}{(\pi/L)} = \frac{2L}{\pi}dk\,;$$

on the other side, from Eq. (1)

$$dE = \frac{\hbar^2}{m^*}k\,dk\,,$$

hence the density of states (DOS) is

$$\frac{dN}{dE} = \frac{dN/dk}{dE/dk} = \frac{(2L/\pi)}{(\hbar^2 k/m^*)} = \frac{\sqrt{2m^*}}{\pi\hbar}\,\frac{L}{\sqrt{E}}\,. \tag{5}$$

Integrating this DOS up to $E_{\rm F}$ from Eq. (4) yields

$$\int\limits_0^{E_{\rm F}} \frac{dN}{dE}dE = \frac{\sqrt{2m^*}L}{\pi\hbar}\int\limits_0^{E_{\rm F}}\frac{dE}{\sqrt{E}} = \frac{L}{a}Z\,, \quad \text{as expected.} \tag{6}$$

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[1] The number of atoms that provide these electrons is irrelevant. E.g., for the case of aluminium wire with nominal fcc lattice parameter $a = 4.050$ Å, we would count $Z = 12$.

Confinement in two dimensions (“quantum wire”)

We consider a cross-section of linear dimensions (L_x, L_y); the boundary condition $\psi(x, y) = 0$ everywhere at the (rectangular) boundary yields the quantisation rules

$$k_x = \frac{\pi}{L_x},\ \frac{2\pi}{L_x},\ \ldots \qquad k_y = \frac{\pi}{L_y},\ \frac{2\pi}{L_y}, \ldots \quad \text{etc.} \tag{7}$$

The number of occupied states within k_F is

$$2\times\frac{\pi k_\mathrm{F}^2/4}{(\pi/L_x)(\pi/L_y)} = \frac{L_x}{a}\frac{L_y}{b}Z$$

($2\times$ accounts for spin, Z is number of electrons per unit cell), whence

$$k_\mathrm{F} = \sqrt{\frac{2\pi Z}{ab}} \qquad \text{and} \qquad E_\mathrm{F} = \frac{\hbar^2 \pi Z}{m^* ab}\,. \tag{8}$$

The number of states, i.e. of the rectangles in the (k_x, k_y) plane added on increasing the radius from k to $k + dk$, is

$$dN = 2\times\frac{2\pi k}{4}\,dk\,\frac{L_x L_y}{\pi^2},$$

then the DOS is

$$\frac{dN}{dE} = \frac{dN/dk}{dE/dk} = 2\frac{(\pi k/2)(L_x L_y/\pi^2)}{\hbar^2 k/m^*} = \frac{L_x L_y m^*}{\pi\hbar^2}\,. \tag{9}$$

hence not energy dependent. This means that the individual states (peaks) are equidistant along the energy axis. The energy interval between adjacent peaks $\Delta E^{(2\mathrm{D})}$ follows from the condition

$$\frac{2}{\Delta E^{(2\mathrm{D})}} = \frac{dN}{dE}$$

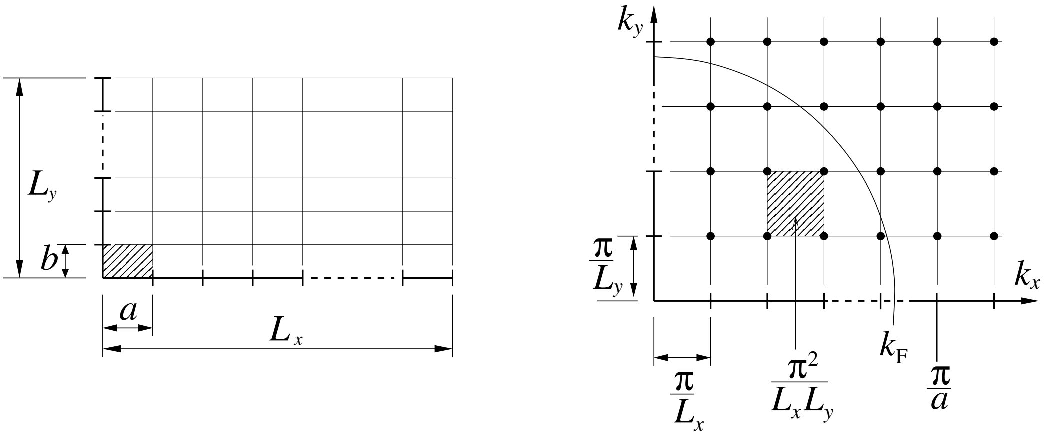

Figure 2: Schema of 2-dim. cross-section with linear dimensions (L_x, L_y) and unit cell dimensions (a, b) (left panel); quantization of (k_x, k_y) values and counting the states with $|k| < k_\mathrm{F}$ (right panel).

(as each peak hosts two states due to spin), hence

$$\Delta E^{(2\mathrm{D})} = \frac{2\pi\hbar^2}{L_x\,L_y\,m^*}\,. \tag{10}$$

The integration of the DOS to E_F (Eq. 8) yields

$$\int_0^{E_\mathrm{F}} \frac{dN}{dE}dE = \frac{L_x}{a}\frac{L_y}{b}Z\,, \tag{11}$$

as expected.

Confinement in three dimensions ("quantum dot")

Generalization over three dimensions is straightforward; the number of states included within an octant of sphere with radius k_F is

$$2\times\frac{(4\pi k_\mathrm{F}^3/3)(1/8)}{(\pi/L_x)(\pi/L_y)(\pi/L_z)} = \frac{L_x}{a}\frac{L_y}{b}\frac{L_z}{c}Z\,, \quad \text{then}$$

$$k_\mathrm{F} = \sqrt[3]{\frac{Z}{abc}\,3\pi^2}\,; \qquad E_\mathrm{F} = \frac{\hbar^2}{2m^*}\left(\frac{3\pi^2 Z}{abc}\right)^{2/3}\,. \tag{12}$$

The number of states / cubes $(\pi/L_x)(\pi/L_y)(\pi/L_z)$ added on increasing the radius from k to $k+dk$ is

$$dN = 2\times\frac{4\pi k^2}{8}\,dk\,\frac{L_xL_yL_z}{\pi^3},$$

then the DOS is

$$\frac{dN}{dE} = \frac{dN/dk}{dE/dk} = 2\frac{(\pi k^2/2)(L_xL_yL_z/\pi^3)}{\hbar^2 k/m^*} = \frac{L_xL_yL_z m^*}{\pi^2\hbar^2}k = \frac{L_xL_yL_z m^*}{\pi^2\hbar^3}\sqrt{2m^*E}\,. \tag{13}$$

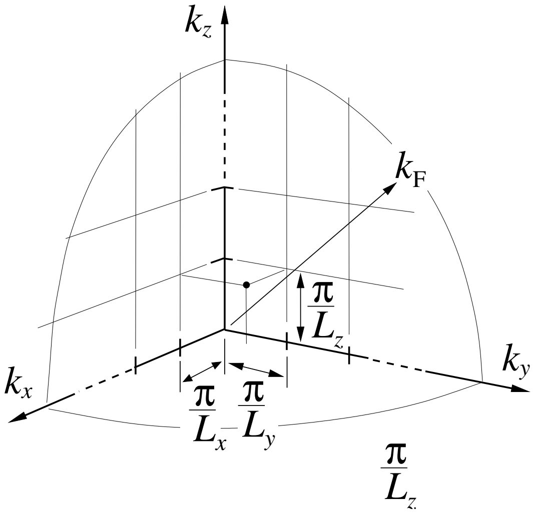

Figure 3: Counting occupied states $k \le k_\mathrm{F}$ in case of 3-dim. confinement.

The integration to E_{F} (Eq. 12) yields the total number of electrons N_e:

$$N_e = \int\limits_0^{E_{\mathrm{F}}} \frac{dN}{dE} dE = \frac{L_x L_y L_z m^*}{\pi^2 \hbar^3} \sqrt{2m^*} \cdot \frac{2}{3} E_{\mathrm{F}}^{3/2} = \frac{L_x L_y L_z}{a\, b\, c} Z\,. \tag{14}$$

As was argued above for 2-dim case, the energy interval between the adjacent levels can be related to DOS, namely,

$$\frac{2}{\Delta E^{(3\mathrm{D})}} = \frac{dN}{dE}\,; \qquad \Delta E^{(3\mathrm{D})} = \frac{2\pi^2 \hbar^3}{L_x L_y L_z m^* \sqrt{2m^* E}}\,. \tag{15}$$

Obviously, the levels become more dense as the energy increases. In immediate vicinity of the Fermi level, combining Eq. (15) and Eq. (14),

$$\Delta E^{(3\mathrm{D})} = \frac{4}{3} \frac{E_{\mathrm{F}}}{N_e}\,, \tag{16}$$

that is the Kubo formula.

A practical calculation: an Al islet

Consider the quantization conditions in an islet of metallic aluminium, of thickness L_z=1.5 nm and lateral size $L_x = L_y = 25$ nm (an example from “our response to Referee”). We find for aluminium – see, e.g., PRB **27**(2), 727 (1983):

$$\begin{aligned}
m^* &= 1.1{\times}(m_e = 9.109{\cdot}10^{-31}\,\mathrm{kg}) = 1.002{\cdot}10^{-30}\,\mathrm{kg}\,; \\
E_{\mathrm{F}} &= 11.7\,\mathrm{eV} = 1.762{\cdot}10^{-18}\,\mathrm{J}\,; \\
\hbar &= 1.0546{\cdot}10^{-34}\,\mathrm{J{\cdot}s}\,; \\
k_{\mathrm{F}} &= = \frac{1}{\hbar}\sqrt{2m^* E_{\mathrm{F}}} = 1.782{\cdot}10^{10}\,\mathrm{m}^{-1}.
\end{aligned}$$

For reference, the lattice constant of fcc aluminium is $a = 4.050$ Å; the farthest from Γ point of the fcc Brillouin zone is $W = \left[\frac{\pi}{a}, \frac{2\pi}{a}, 0\right]$, hence at the distance $k_W = \pi\sqrt{5}/a = 1.735{\cdot}10^{10}$ m^{-1}, i.e., slightly yet fully inside the Fermi sphere, as it should be for Al.

In the geometry considered, the strongest confinement is one-dimensional due to L_z, so that the quantization step along k_z is (after Eq. 2) $\pi/L_z = 0.209{\cdot}10^{10}$ m^{-1}. We see that k_{F} falls between the quantized k_z values

$$\begin{aligned}
8{\times}0.209{\cdot}10^{10}\,\mathrm{m}^{-1} &\;\rightarrow\; 1.676{\cdot}10^{10}\,m^{-1} \equiv k_- \quad \text{and} \\
9{\times}0.209{\cdot}10^{10}\,\mathrm{m}^{-1} &\;\rightarrow\; 1.885{\cdot}10^{10}\,m^{-1} \equiv k_+\,;
\end{aligned}$$

the corresponding energy values are

$$E_- = E_{\mathrm{F}} \left(\frac{k_-}{k_{\mathrm{F}}}\right)^2 = 10.34\ \mathrm{eV}\,; \qquad E_+ = E_{\mathrm{F}} \left(\frac{k_+}{k_{\mathrm{F}}}\right)^2 = 13.09\ \mathrm{eV}\,;$$

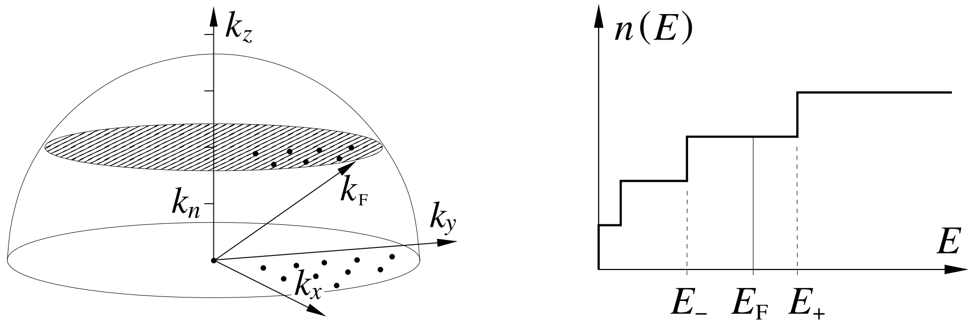

Figure 4: Inclusion of further electronic states as the k-radius increases and reaches new k_n planes of k_z quantized values (left panel); stepwise density of states corresponding to 2-dim. electron gas (right panel).

Between these two values (or between any others, say E_n and E_{n+1}, at which the isoenergy surface in the **k** space touches the quantized k_z values), the density of states is flat. The number of states increases as the radius $k = 1/\hbar\sqrt{2m^*E}$ increases, and more states in the plane $k_z = k_n$ fall within the circle of radius $\sqrt{k^2 - k_n^2}$, see Fig. 4. Every new touch $k = k_n$ adds a new plane and hence a step in the density of states.

For a given ($k_z\!=\!\text{const}$) plane, the energy interval between adjacent energy levels is, according to Eq. (10): $\Delta E^{(2\text{D})} = 1.116{\cdot}10^{-22}$ J $= 0.62$ meV. We note that this result follows from the state density within a single plane; an inclusion of n planes within the (octant of the) Fermi sphere (see Fig. 4), divides this interval by n and, correspondingly, raises the 2-dim. DOS to the nth step. We note that

Further in in the context of our exercise concerning aluminium, we'll consider the lateral size as variable, and adjust it so that the ΔE would match the major (longitudinal acoustic) peak in the phonon spectrum, that is, $h\nu = 35$ meV $= 5.61{\cdot}10^{-21}$ J. Taking Eq. (10) in the form $\Delta E^{(2)}/n = 2\pi\hbar^2/(L_x L_y m^*)$, we get

$$L_{x,y} = \hbar\sqrt{\frac{2\pi n}{\Delta E^{(2)} m^*}} = 3.5 \text{ nm (for } n\text{=1), or } 10.0 \text{ nm } (n\text{=8}). \tag{17}$$

This means that for the islets of smaller size, the transitions between discrete electron levels cannot be induced by highest-frequency available longitudinal phonons. As the lateral size exceeds $\sim$10 nm, the electronic levels become more dense, and such transitions become possible.

It seems important to note that for systems with strongly non-uniform confinement, the Kubo formula (16) is not valid even approximately. The problem is not only that the interlevel distance in the case of 2-dim. confinemnent remains constant throughout the given step whereas it should grow according to the Kubo formula. For the Al islet as considered above, $L_x = L_y\!=\!25$ nm, $L_z\!=\!1.5$ nm, the number of electrons is

$$N_e = \frac{L_x L_y L_z}{a^3}{\cdot}(4\,\text{at.}{\times}3\,\text{el.}) = 14.11{\cdot}10^3\,;$$

hence $\Delta E^{(3\text{D})} = 1.11$ meV instead of $\Delta E^{(2\text{D})} = 0.62$ meV. In fact, taking instead of

E_{F} its bordering values “on the step”, $E_{-} = 10.34$ eV and $E_{+} = 13.09$ eV, yields the $\Delta E^{(3\mathrm{D})}$ values of 0.98 meV and 1.24 meV, correspondingly. They are much larger than $\Delta E^{(2\mathrm{D})} = 0.62$ meV because the Kubo formula effectively assumes the nanoparticle to be a “round” one for which the 3-dim. confinement is valid.