

Cohesive energy in metals: study on Kronig-Penney model of 1D periodic square well potential, with the use of Mathematica

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Frederick Seitz (July 4, 1911– March 2, 2008) was an American physicist and a pioneer of solid state physics. Seitz was the 4th president of Rockefeller University from 1968–1978, and the 17th president of the United States National Academy of Sciences from 1962–1969. Seitz was the recipient of the National Medal of Science, NASA's Distinguished Public Service Award, and other honors. He founded the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana–Champaign and several other material research laboratories across the United States

Seitz studied metals under Eugene Wigner in the Princeton University, gaining his PhD in 1934. He and Wigner pioneered one of the first quantum theories of crystals, and developed concepts in solid-state physics such as the Wigner–Seitz unit cell used in the study of crystalline material in solid-state physics.



(a)



(b)

(a)

https://en.wikipedia.org/wiki/Frederick_Seitz

(b)

http://cache.boston.com/resize/bonzai-fba/Globe_Photo/2008/03/06/1204862320_7365/300h.jpg

((Main purpose of this note))

In Spring semester of 2019, we had an opportunity to teach Phys.472-572 (Solid State Physics). We used a textbook of Charles Kittel Introduction to Solid State Physics (8-th edition). Among so many interesting topics, we are interested in the explanation of the cohesive energy of metals. The Wigner-Seitz method was originally developed for the understanding of cohesive energy of sodium metal, by Wigner and Seitz around 1933-1934. It is a typical example of the application for quantum mechanics (the Bloch theorem). The introduction of the Wigner-Seitz cell is essential in this model. It is shown that the energy eigenvalue for the electrons in the system with the specified boundary condition at the Wigner-Seitz cell is much lower than that of the electron of the isolated atom. However, it seems rather difficult for undergraduate students to understand the derivation of energy eigenvalue in the Wigner-Seitz method, without any specific calculation of wavefunction based on the Schrodinger equation. In the original Wigner-Seitz model, only the Bloch state with $k = 0$ was considered for the sake of simplicity. The Bloch state with $k \neq 0$ can be discussed. by using the perturbation theory with $k \cdot p$ as a perturbing Hamiltonian.

In the textbook of Kittel (Introduction to Solid State Physics, 8-th edition), we find a very interesting figure (**Fig.20**, p.238) for the evaluation of the ground state energy of electron in a periodic (attractive) square well potential of the depth U with the width a and the separation b , where the wavenumber k is equal to zero. We guess that this figure was originally obtained by C.Y. Fong. We tried to find a possible original paper of Fong, but we could not find so far. Note that our note presented here is motivated mainly from reproducing the result of **Fig.20** using the Kronig-Penney model.

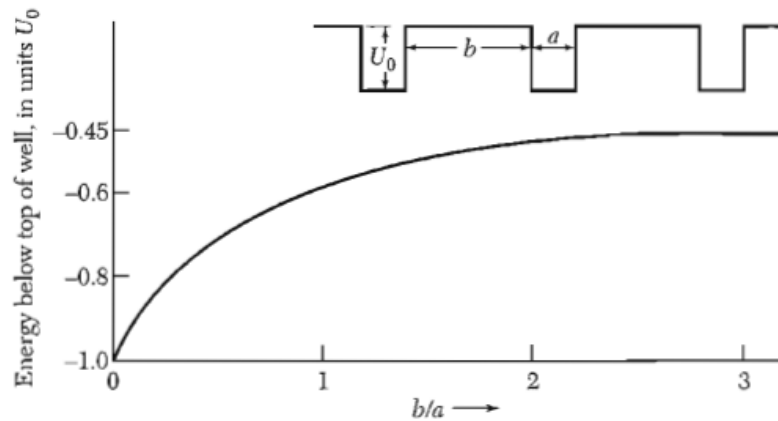


Fig.1 Ground orbital ($k = 0$) energy for an electron in a periodic square well potential of depth $|U_0| = 2\hbar^2 / (ma^2)$. The energy is lowered as the wells come closer together. Here a is hold constant and b is varied. Large b/a corresponds to separated atoms. (Courtesy of C.Y. Fong). [**Fig.20**, p.238, C. Kittel, Introduction to Solid State Physics, 8-th edition (John-Wiley & Sons, 2005).

In this note, we calculate exactly the energy eigenvalue for the one-dimensional square well potential by the Kronig-Penney model with the use of Mathematica 12.0. This calculation clearly supports that the result from the Wigner-Seitz model is valid. We use ContourPlot and FindRoot program of the Mathematica.

There are so many articles of calculations on the Kronig-Penney model. As far as we know there have few systematic studies of this model for the 1D periodic square well potential with the width a (kept constant) and the separation b . Here, here we discuss the detail by using Mathematica (version 12.0): the energy eigenvalue as a function of wave number k , the ratio b/a , the depth of potential U . We also discuss the effective mass (derived from the perturbation theory) as a function of the ratio b/a , from the least-squares fit of the energy dispersion in the small value of $ka \rightarrow 0$ [the energy is proportional to $(ka)^2$]. We think that our calculation may be helpful to our understanding the essential of the Wigner-Seitz method.

This note consists of two parts.

Part I: Introduction of Wigner-Seitz method (mainly, summary of various textbooks)

Part II. Kronig-Penney model of the 1D periodic square potential. We solve the problem exactly without any approximation by using the Kronig-Penney model. We also solve the energy eigenvalue and wavefunction of the 1D square well potential of electron in a isolated atom directly from the Schrodinger equation. These results will be compared with those obtained from the Kronig-Penney model (mainly our calculation with the use of Mathematica; ContourPlot pogram).

Part I Wigner-Seitz model

1. Introduction

There are two approximations to obtain the Bloch orbital: first an approximation that starts from plane waves and, second a method based on the linear combination of atomic orbitals. However, these are two limiting cases on the linear combination of atomic orbitals. However, these are not sufficient enough to discuss real materials. A method which is closer to reality was proposed by Slater, and Wigner and Seitz. This became the basis for the band calculations that are presently carried out for many materials. Further, Wigner and Seitz clarified the essential nature of the metallic bond based on the results of this calculation.

We consider the alkaline metals, sodium (Na) for example. We specify the mean field that a conduction electron is subject to the periodic potential of the crystal as follows. First, the whole crystal is divided into atomic polyhedral (Wigner-Seitz cell, or WS cell). When an electron is in an atomic WS cell, it is subject to the atomic potential of the atom that is contained in the WS cell. When the electron moves to a neighboring atomic WS cell, it is then subject to the atomic potential of the atom that is contained therein. As a result, we obtain the potential that is illustrated in **Fig.2**

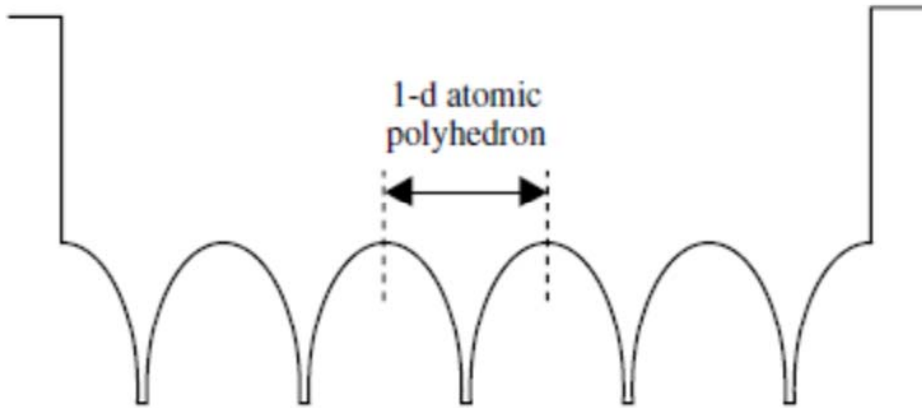


Fig.2 Wigner-Seitz potential (in one dimension). (from the book written by J. Kondo).

This is a rather ingenious idea. In reality, there are contributions in the form of the atomic potentials of the atoms in other polyhedra than in which the electron is located, and also the potential due to the other electrons. However, since, on the average, there is one electron in each polyhedron, each atomic polyhedron is charge neutral, and therefore exerts only a weak potential. Hence we may neglect them altogether. When an electron moves to a neighboring atomic polyhedron, the electron that was lying there moves away to somewhere, so that all of the atomic polyhedra other than that in which the electron that is presently under attention has entered can again be assumed to be charge neutral. This potential is thus able to account for much of the electronic correlation.

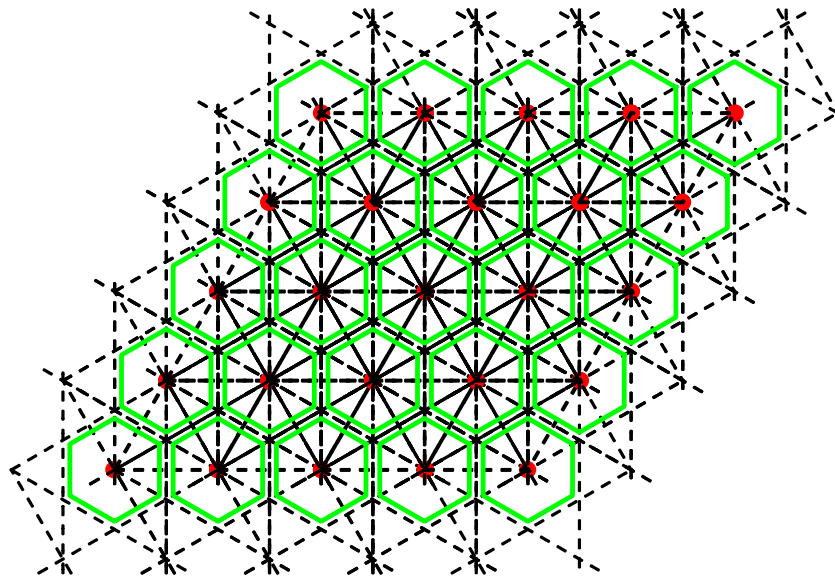


Fig.3 Typical example of the Wigner-Seitz cell (one of the primitive cells). The dotted line denotes the perpendicular bisector. The case of two-dimensional lattice.

2. Wigner-Seitz method

Wigner and Seitz showed that for the alkali metals there is no inconsistency between the electron wavefunctions of free atom and the nearly free electron model of the band structure of a crystal. Over most of a band the energy may depend on the wavevector nearly as for a free electron. However, the Bloch wavefunction, unlike a plane wave, will pile up charge on the positive ion cores as in the atomic wavefunction.

A Bloch function satisfies the wave equation

$$\left(\frac{1}{2m} \mathbf{p}^2 + U(\mathbf{r}) \right) e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}),$$

where $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the lattice. With the momentum $\mathbf{p} = -i\hbar\nabla$, we have

$$\mathbf{p}[e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})] = \hbar\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{p}u_{\mathbf{k}}(\mathbf{r}),$$

$$\mathbf{p}^2[e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})] = (\hbar\mathbf{k})^2 e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}} (2\hbar\mathbf{k} \cdot \mathbf{p})u_{\mathbf{k}}(\mathbf{r}) + e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{p}^2 u_{\mathbf{k}}(\mathbf{r}).$$

Thus the above equation can be written as an equation for $u_{\mathbf{k}}(\mathbf{r})$

$$\left[\frac{1}{2m} (\mathbf{p} + \hbar\mathbf{k})^2 + U(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}).$$

Note that

$$(\mathbf{p} + \hbar\mathbf{k})^2 = \mathbf{p}^2 + \hbar^2 \mathbf{k}^2 + 2\hbar\mathbf{k} \cdot \mathbf{p},$$

$$\left[\frac{1}{2m} \mathbf{p}^2 + \frac{\hbar^2 \mathbf{k}^2}{2m} + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + U(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}),$$

or

$$\left[\frac{1}{2m} \mathbf{p}^2 + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + U(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = \left(E_{\mathbf{k}} - \frac{\hbar^2 \mathbf{k}^2}{2m} \right) u_{\mathbf{k}}(\mathbf{r}).$$

((The case of $k = 0$))

It is much easier to find a solution at $\mathbf{k} = 0$ than at a general \mathbf{k} , because at $\mathbf{k} = 0$ a nondegenerate solution will have the full symmetry of $U(\mathbf{r})$, that is, of the crystal. We can then use $u_0(\mathbf{r})$ to construct the approximate solution

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_0(\mathbf{r}).$$

This is of the Bloch form, but it is much easier to find a solution at $\mathbf{k} = 0$ than at a general \mathbf{k} , because at $\mathbf{k} = 0$ a nondegenerate solution will have the full symmetry of $U(\mathbf{r})$, that is, of the crystal. We can then use $u_0(\mathbf{r})$ to construct the approximate solution

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_0(\mathbf{r}).$$

This is of the Bloch form, but $u_0(\mathbf{r})$ is not an exact solution. It is a solution only if we drop the term in $\mathbf{k} \cdot \mathbf{p}$. This term is treated as a perturbation. The $\mathbf{k} \cdot \mathbf{p}$ perturbation theory is especially useful in finding the effective mass m^* .

3. Boundary condition for $u_0(x)$ in the Wigner-Seitz cell

(I) Continuity of wave function

$$\psi_{x=\frac{1}{2}a-0} = \psi_{x=\frac{1}{2}a+0}, \quad \psi_{x=-\frac{1}{2}a-0} = \psi_{x=-\frac{1}{2}a+0} \quad (\text{continuity of } \psi)$$

(II) Bloch theorem

$$\psi(x+a) = e^{ika} \psi(x).$$

(III) Continuity of the derivative of the wave function with respect to x ,

$$\left(\frac{d\psi}{dx}\right)_{x=\frac{1}{2}a-0} = \left(\frac{d\psi}{dx}\right)_{x=\frac{1}{2}a+0}, \quad \left(\frac{d\psi}{dx}\right)_{x=-\frac{1}{2}a-0} = \left(\frac{d\psi}{dx}\right)_{x=-\frac{1}{2}a+0} \quad (\text{continuity of } \frac{d\psi}{dx})$$

From the condition (I), we get

$$\psi_{x=\frac{1}{2}a+0} = e^{\frac{ika}{2}} u_{x=\frac{1}{2}a+0}, \quad \psi_{x=-\frac{1}{2}a-0} = e^{\frac{ika}{2}} u_{x=-\frac{1}{2}a-0}$$

$$\psi_{x=-\frac{1}{2}a+0} = e^{-\frac{ika}{2}} u_{x=-\frac{1}{2}a+0}, \quad \psi_{x=-\frac{1}{2}a-0} = e^{-\frac{ika}{2}} u_{x=-\frac{1}{2}a-0}$$

leading to

$$u_{x=\frac{1}{2}a+0} = u_{x=\frac{1}{2}a-0}, \quad (1)$$

$$u_{x=-\frac{1}{2}a-0} = u_{x=-\frac{1}{2}a+0}. \quad (2)$$

From the condition (II, Bloch theorem), we get

$$\psi_{x=\frac{a}{2}-0} = e^{ika} \psi_{x=\frac{a}{2}-0}, \quad u_{x=\frac{a}{2}-0} = u_{x=\frac{a}{2}-0} \quad (3)$$

at $x = -\frac{a}{2} - 0$, and

$$\psi_{x=\frac{a}{2}+0} = e^{ika} \psi_{x=-\frac{a}{2}+0}, \quad u_{x=\frac{a}{2}+0} = u_{x=-\frac{a}{2}+0} \quad (4)$$

at $x = -\frac{a}{2} + 0$

From the condition III (continuity in $\frac{d\psi}{dx}$)

$$\psi = e^{ikx} u(x)$$

$$\frac{\partial \psi}{\partial x} = ik\psi_k(x) + e^{ikx} \frac{\partial u_k}{\partial x}$$

$$\left(\frac{\partial \psi}{\partial x} \right)_{x=\frac{a}{2}+0} = \left(\frac{\partial \psi}{\partial x} \right)_{x=\frac{a}{2}-0}, \quad \left(\frac{\partial \psi}{\partial x} \right)_{x=-\frac{a}{2}+0} = \left(\frac{\partial \psi}{\partial x} \right)_{x=-\frac{a}{2}-0} \quad (\text{Continuity})$$

or

$$\begin{aligned}\left(\frac{\partial \psi}{\partial x}\right)_{x=\frac{a}{2}+0} &= ik\psi_{x=\frac{a}{2}+0} + e^{\frac{ika}{2}} \left(\frac{\partial u_k}{\partial x}\right)_{x=\frac{a}{2}+0} \\ &= ike^{\frac{ika}{2}} u_{x=\frac{1}{2}a+0} + e^{\frac{ika}{2}} \left(\frac{\partial u_k}{\partial x}\right)_{x=\frac{a}{2}+0}\end{aligned}$$

$$\begin{aligned}\left(\frac{\partial \psi}{\partial x}\right)_{x=\frac{a}{2}-0} &= ik\psi_{x=\frac{a}{2}-0} + e^{\frac{ika}{2}} \left(\frac{\partial u_k}{\partial x}\right)_{x=\frac{a}{2}-0} \\ &= ike^{\frac{ika}{2}} u_{x=\frac{1}{2}a-0} + e^{\frac{ika}{2}} \left(\frac{\partial u_k}{\partial x}\right)_{x=\frac{a}{2}-0}\end{aligned}$$

at $x = \frac{a}{2}$.

$$\begin{aligned}\left(\frac{\partial \psi}{\partial x}\right)_{x=-\frac{a}{2}+0} &= ik\psi_{x=-\frac{a}{2}+0} + e^{-\frac{ika}{2}} \left(\frac{\partial u_k}{\partial x}\right)_{x=-\frac{a}{2}+0} \\ &= ike^{-\frac{ika}{2}} u_{x=-\frac{1}{2}a+0} + e^{-\frac{ika}{2}} \left(\frac{\partial u_k}{\partial x}\right)_{x=-\frac{a}{2}+0}\end{aligned}$$

$$\begin{aligned}\left(\frac{\partial \psi}{\partial x}\right)_{x=-\frac{a}{2}-0} &= ik\psi_{x=-\frac{a}{2}-0} + e^{-\frac{ika}{2}} \left(\frac{\partial u_k}{\partial x}\right)_{x=-\frac{a}{2}-0} \\ &= ike^{-\frac{ika}{2}} u_{x=-\frac{1}{2}a-0} + e^{-\frac{ika}{2}} \left(\frac{\partial u_k}{\partial x}\right)_{x=-\frac{a}{2}-0}\end{aligned}$$

at $x = -\frac{a}{2}$.

$$\left(\frac{\partial u}{\partial x}\right)_{x=\frac{a}{2}+0} = \left(\frac{\partial u}{\partial x}\right)_{x=\frac{a}{2}-0}, \quad (5)$$

$$\left(\frac{\partial u}{\partial x}\right)_{x=-\frac{a}{2}-0} = \left(\frac{\partial u}{\partial x}\right)_{x=-\frac{a}{2}+0} \quad (6)$$

From Eqs.(1) – (4), we have

$$u_{x=-\frac{a}{2}-0} = u_{x=-\frac{a}{2}+0} = u_{x=\frac{a}{2}-0} = u_{x=\frac{a}{2}+0}$$

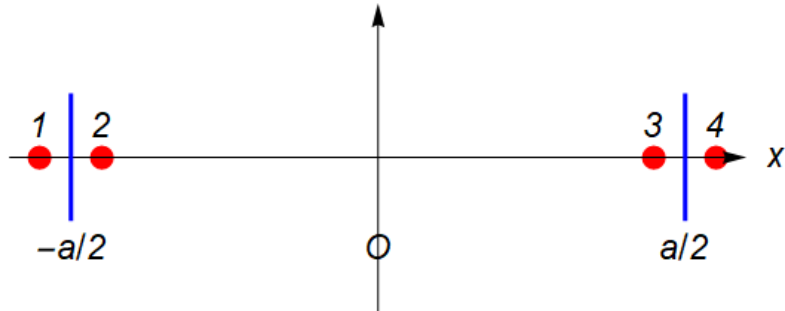


Fig.4 Continuity of wave function I. The boundary condition.

$$u_1 = u_2 = u_3 = u_4$$

We note that

$$\left(\frac{du}{dx}\right)_{x=a/2} = \lim_{\Delta x \rightarrow 0} \left(\frac{u_4 - u_3}{\Delta x}\right) = 0$$

$$\left(\frac{du}{dx}\right)_{x=-a/2} = \lim_{\Delta x \rightarrow 0} \left(\frac{u_2 - u_1}{\Delta x}\right) = 0$$

((General case))

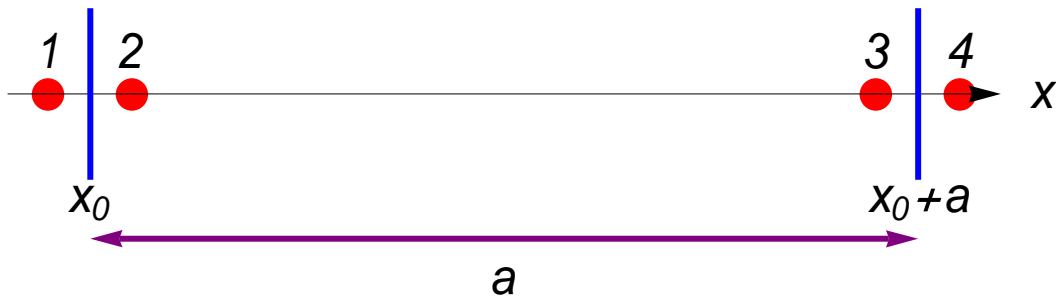


Fig.5 Continuity of wave function II. The boundary condition.

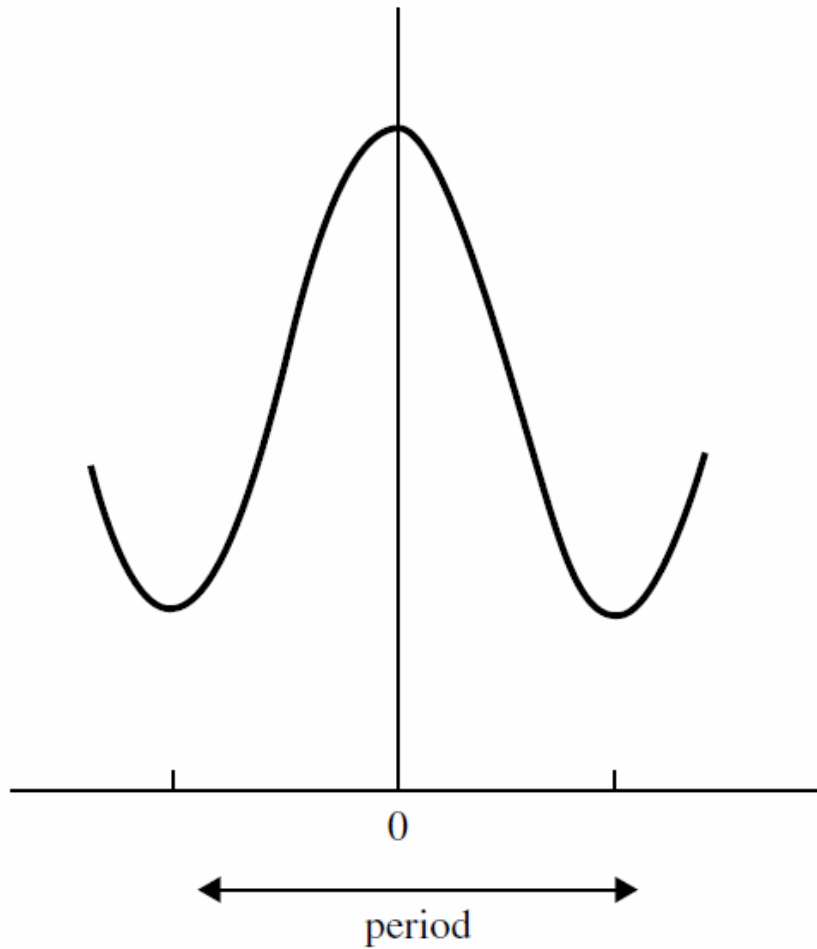


Fig.6 Example of wave function in the Wigner-Seitz cell. (from the book written by J. Kondo). The wavefunction is symmetric with respect to x around the origin.

4. Result from Wigner-Seitz method for sodium (Na)

Here is a result of sodium Na atom obtained from the Wigner-Seitz method.

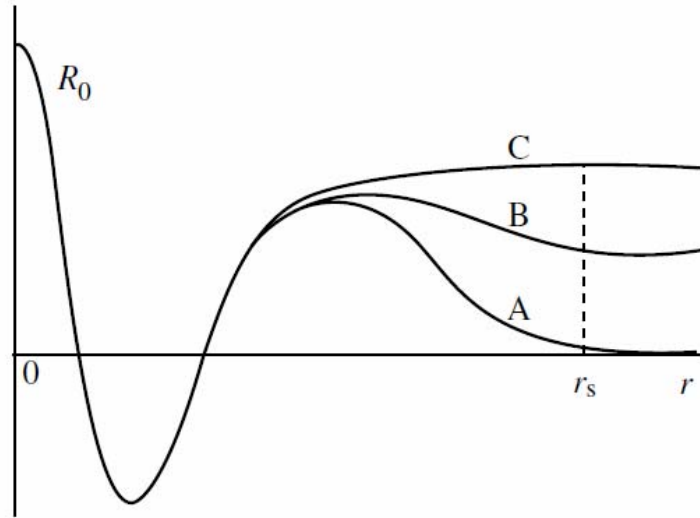


Fig.7 A schematic diagram for the 3s orbital of Na. The curve A is for $E=E_{3s}$. Curves B and C are for deeper (more negative) energies. The derivative of C vanishes at $r=r_s$. (From the book of C. Kittel, Introduction to Solid State Physics, 4-th edition).

In **Fig.7**, we first show the values of u_0 when E is set equal to E_{3s} of the isolated atom as curve A. This satisfies $u_0 \rightarrow 0$ as $r \rightarrow \infty$. When the value of E is decreased slightly, we obtain curve B. With further decrease of E at certain value, the curve C, that is, the solution that satisfies $u_0' \rightarrow 0$ as $r=r_s$, is obtained. This value corresponds to the energy of the 3s band at $\mathbf{k}=0$, that is, it represents the position of the bottom of the conduction band. We call this energy E_0 . As is seen from Fig. it undergoes a large oscillation in the vicinity of $r=0$, and this is influenced by the strong atomic potential. On the other hand, it is almost constant in the vicinity of $r=r_s$, so that, in this sense, it behaves like a plane wave with $\mathbf{k}=0$.

((Kittel, Introduction to Solid State Physics, 8-th edition))

The Fermi energy is 3.1 eV. The average kinetic energy per electron is 0.6 (= 3/5) of the Fermi energy, or 1.9 eV. The ground-state energy calculated for sodium with $\partial u_0 / \partial r = 0$ at $r_s = 3.96 a_B$ is about -8.2 eV, as compared with the experimental atomic ground-state energy of -5.16 eV. Thus the 3s energy at $\mathbf{k}=0$ is lower by 3.1 eV in the metal than in the atom. But the conduction electrons at finite \mathbf{k} in the metal have extra kinetic energy; the mean Fermi energy per electron is $\frac{3}{5} E_F = 3.1 \times 0.6 = 1.86$ eV. Thus we have $\langle E_k \rangle = -8.2 + 1.9 = -6.3$ eV, compared with -5.15 eV for

the valence electron of the free atom. We therefore estimate that Na metal is stable by about 1.1 eV with respect to the free atom. This result agrees well with the experimental value 1.13 eV.

The cohesive energy: $6.3 - 5.15 = 1.15$ eV

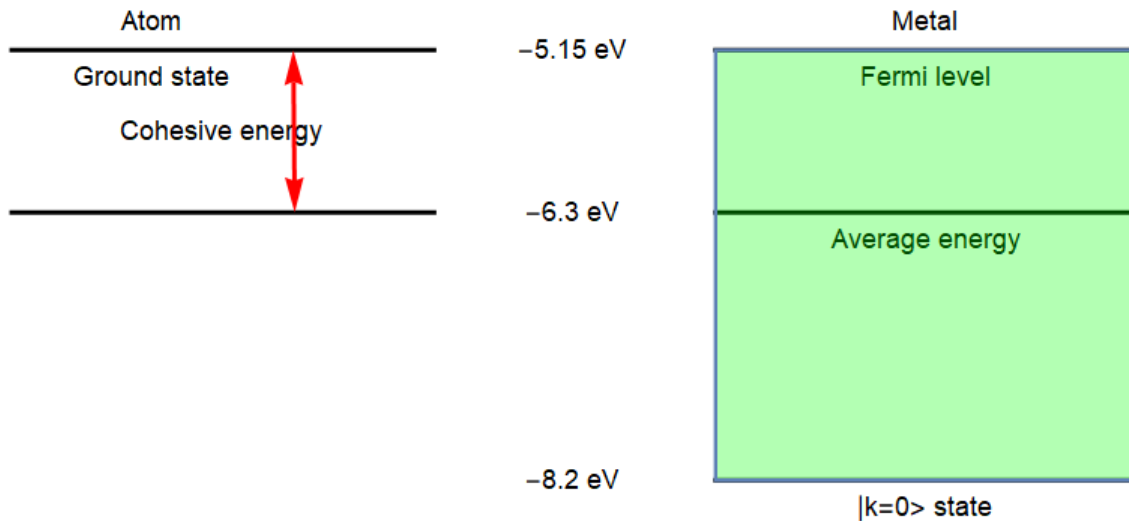


Fig.8 Cohesive energy of sodium (Na) metal is the difference between the average energy of an electron in the metal (-6.3 eV) and the ground state energy (-5.15 eV) of the valence 3s electron in the free atom, referred to an Na^+ ion plus free electron at infinite separation. (from the book of C. Kittel, Introduction to Solid State Physics, 8-th edition).

((Note)) Na metal (bcc)

Conventional cubic lattice constant

$$a = 4.225 \text{ \AA}.$$

There are two atoms per unit cell (a^3).

$$\frac{a^3}{2} = \frac{4\pi}{3} r_s^3, \quad r_s = \left(\frac{3}{8\pi} \right)^{1/3} a = 2.8027 \text{ \AA}.$$

Bohr radius:

$$a_B = 0.52917721067 \text{ \AA}.$$

$$\frac{r_s}{a_B} = 3.92505.$$

The nearest neighbor distance between Na atoms:

$$d = \frac{\sqrt{3}}{2} a = 3.65896 \text{ \AA}.$$

The Fermi wave number:

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

Fermi energy:

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{2}{a^3}\right)^{2/3} = 3.2427 \text{ eV}.$$

The average kinetic energy per electron

$$\langle E \rangle = \frac{3}{5} E_F = 1.9456 \text{ eV}.$$

5. Perturbation theory

We start with the Schrödinger equation for the Bloch function, $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$

$$\left[\frac{1}{2m} \mathbf{p}^2 + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + U(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = \left(E_{\mathbf{k}} - \frac{\hbar^2 \mathbf{k}^2}{2m} \right) u_{\mathbf{k}}(\mathbf{r}),$$

$$\left[\frac{1}{2m} \mathbf{p}^2 + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + U(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = \left(E_{\mathbf{k}} - \frac{\hbar^2 \mathbf{k}^2}{2m} \right) u_{\mathbf{k}}(\mathbf{r}),$$

or

$$-\frac{\hbar^2}{2m} (\nabla^2 + 2i\mathbf{k} \cdot \nabla) u_{\mathbf{k}}(\mathbf{r}) + U(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) = \left(E_{\mathbf{k}} - \frac{\hbar^2 \mathbf{k}^2}{2m} \right) u_{\mathbf{k}}(\mathbf{r})$$

We assume that

$$u_k(\mathbf{r}) = u_0(\mathbf{r}) + u_1^k(\mathbf{r}) + \dots$$

$$E_k = E_0 + \frac{\hbar^2 \mathbf{k}^2}{2m} + \dots$$

Thus we have

$$-\frac{\hbar^2}{2m}(\nabla^2 + 2i\mathbf{k} \cdot \nabla)[u_0(\mathbf{r}) + u_1^k(\mathbf{r})] + U(\mathbf{r})[u_0(\mathbf{r}) + u_1^k(\mathbf{r})] = E_0[u_0(\mathbf{r}) + u_1^k(\mathbf{r})]$$

or

$$-\frac{\hbar^2}{2m}(\nabla^2 + 2i\mathbf{k} \cdot \nabla)[u_0(\mathbf{r}) + u_1^k(\mathbf{r})] + U(\mathbf{r})[u_0(\mathbf{r}) + u_1^k(\mathbf{r})] \approx E_0[u_0(\mathbf{r}) + u_1^k(\mathbf{r})]$$

with

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) - E_0\right]u_1^k(\mathbf{r}) = \frac{i\hbar^2}{m}\mathbf{k} \cdot \nabla u_0(\mathbf{r})$$

where

$$-\frac{\hbar^2}{2m}\nabla^2 u_0(\mathbf{r}) + U(\mathbf{r})u_0(\mathbf{r}) = E_0 u_0(\mathbf{r})$$

We show that a particular solution for $u_1^k(\mathbf{r})$ is given by

$$u_1^{(a)}(\mathbf{r}) = (-i\mathbf{k} \cdot \mathbf{r})u_0(\mathbf{r}).$$

Noting that

$$\nabla^2 [(i\mathbf{k} \cdot \mathbf{r})u_0(\mathbf{r})] = (i\mathbf{k} \cdot \mathbf{r})\nabla^2 u_0(\mathbf{r}) + (2i\mathbf{k}) \cdot \nabla u_0(\mathbf{r}),$$

we have

$$\begin{aligned}
\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) - E_0\right)u_1^a(\mathbf{r}) &= -\frac{\hbar^2}{2m}\nabla^2 u_1^a(\mathbf{r}) + [U(\mathbf{r}) - E_0]u_1^a(\mathbf{r}) \\
&= -\frac{\hbar^2}{2m}\left[(-i\mathbf{k}\cdot\mathbf{r})\nabla^2 u_0(\mathbf{r}) + (-2i\mathbf{k})\cdot\nabla u_0(\mathbf{r})\right] + [U(\mathbf{r}) - E_0](-i\mathbf{k}\cdot\mathbf{r})u_0(\mathbf{r}) \\
&= (-i\mathbf{k}\cdot\mathbf{r})\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) - E_0\right]u_0(\mathbf{r}) + \frac{i\hbar^2}{m}\mathbf{k}\cdot\nabla u_0(\mathbf{r}) \\
&= \frac{i\hbar^2}{m}\mathbf{k}\cdot\nabla u_0(\mathbf{r})
\end{aligned}$$

where

$$-\frac{\hbar^2}{2m}\nabla^2 u_0(\mathbf{r}) + U(\mathbf{r})u_0(\mathbf{r}) = E_0 u_0(\mathbf{r}).$$

6. Effective mass (P.W. Anderson)

Using the perturbation theory, we have

$$E_n = E_n^{(0)} + \sum_{m \neq n} \frac{\left| \langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}.$$

Perturbation for the non-degenerate case

$$\begin{aligned}
E_n &= E_0 + \frac{\hbar^2}{2m}k^2 + \sum_n \frac{\left| \langle n | \hat{H}' | 0 \rangle \right|^2}{E_0 - E_n} \\
&= E_0 + \frac{\hbar^2}{2m^*}k^2
\end{aligned}$$

where Perturbation for the non-degenerate case

$$\begin{aligned}
E &= E_0 + \frac{\hbar^2}{2m}k^2 + \sum_n \frac{\left| \langle n | \hat{H}' | 0 \rangle \right|^2}{E_0 - E_n} \\
&= E_0 + \frac{\hbar^2}{2m^*}k^2
\end{aligned}$$

where m is the effective mass of electron

$$H' = \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p}$$

$$\frac{\hbar^2}{2m^*} k^2 = \frac{\hbar^2}{2m} k^2 + \sum_n \frac{|\langle n | \hat{H}' | 0 \rangle|^2}{E_0 - E_n},$$

or

$$\frac{1}{m^*} = \frac{1}{m} + \frac{2m}{\hbar^2 k^2} \sum_n \frac{|\langle n | \hat{H}' | 0 \rangle|^2}{\varepsilon_0 - \varepsilon_n},$$

$$E = E_0 + \frac{3}{5} \frac{\hbar^2}{2m^*} \left(3\pi^2 \frac{N}{V} \right)^{2/3},$$

where m^* is the effective mass of electron.

7. Cohesive energy

The stability of the simple metals with respect to free atoms is caused by the lowering of the energy of the Bloch orbital with $\mathbf{k} = 0$ in the crystal compared to the ground valence orbital of the free atom. The effect is illustrated in **Fig.7** for sodium and in **Fig.9** for a linear periodic potential of attractive square wells. The ground orbital energy is much lower (because of lower kinetic energy) at the actual spacing in the metal than for isolated atoms.

A decrease in ground orbital energy will increase the binding. The decrease in ground orbital energy is a consequence of the change in the boundary condition on the wavefunction. The Schrödinger boundary condition for the free atom is $\psi(r) \rightarrow 0$ as $r \rightarrow \infty$. In the crystal the $\mathbf{k} = 0$ wavefunction $u_0(\mathbf{r})$ has the symmetry of the lattice and is symmetric about $\mathbf{r} = 0$. To have this, the normal derivative of ψ must vanish across every plane midway between adjacent atoms.

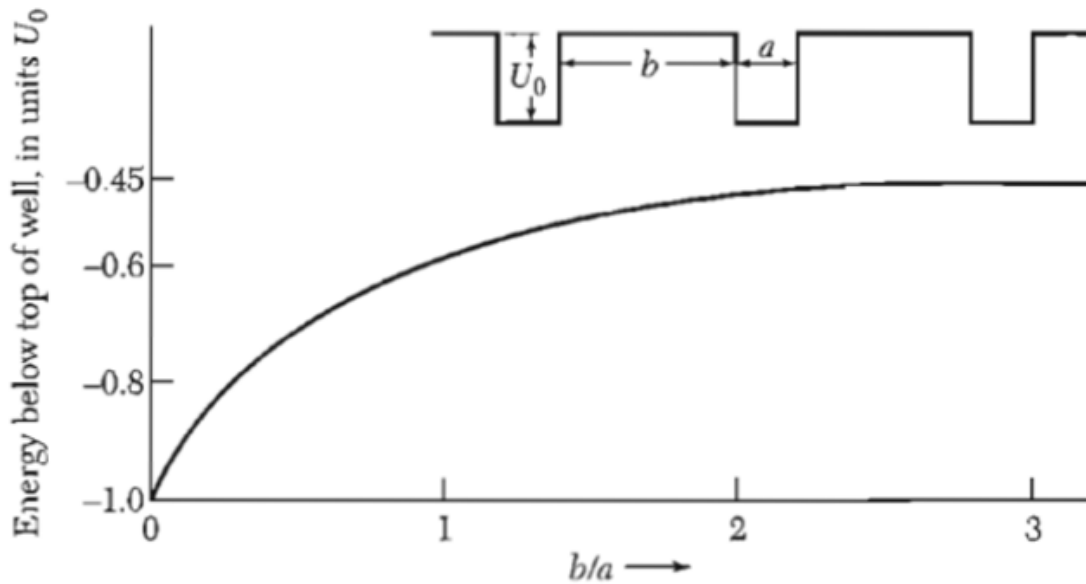


Fig.9 Ground orbital ($k = 0$) energy for an electron in a periodic square well potential of the depth $|U_0| = \frac{2\hbar^2}{ma^2}$. This figure is the same as **Fig.1**. The energy is lowered as the well come close together. Here a is held constant and b is varied. The large ratio $s = b/a$ correspond to separated atoms (C.Y. Fong).

In a spherical approximation to the shape of the smallest Wigner-Seitz cell we use the Wigner-Seitz boundary condition

$$\left(\frac{d\psi}{dr} \right)_{r=r_s} = 0,$$

where r_s is the radius of a sphere equal to volume to a primitive cell of the lattice. In sodium, $r_s = 3.95 r_B$, or 2.08 \AA . The spherical approximation is not bad for fcc and bcc structures. The boundary condition allows the ground orbital wavefunction to have much less curvature than free atom boundary condition. Much less curvature means much less kinetic energy. In sodium the other filled orbitals in the conduction band can be represented in a rough approximation by wavefunction of the form with

$$\psi_k = e^{ik \cdot r} u_0(\mathbf{r}),$$

with

$$E_k = E_0 + \frac{\hbar^2 k^2}{2m}.$$

Here we show our result for the energy eigenvalue of electron in the 1D periodic square well potential. The detail of this calculation will be later). The result for the $k = 0$ state is the same as that obtained by C.V. Fong.

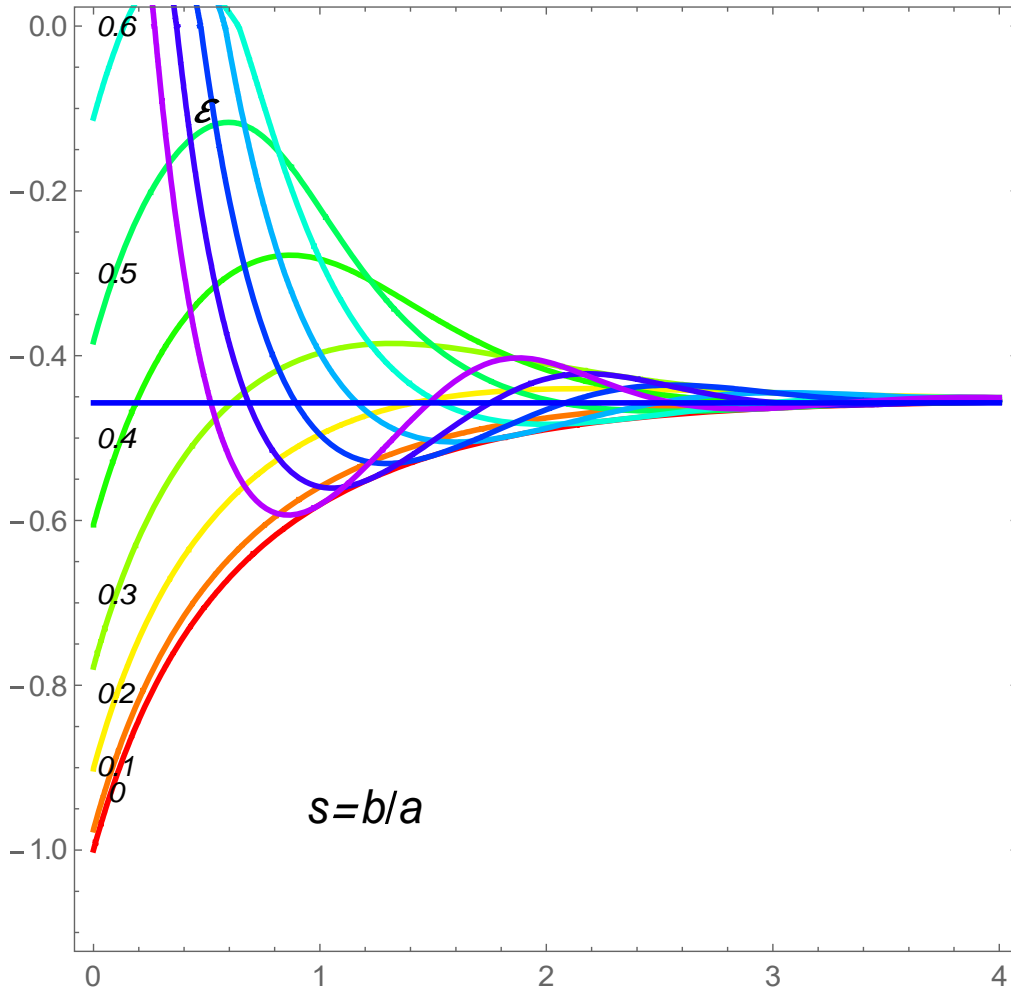


Fig.10 The energy eigenvalue $\epsilon = \epsilon^{(0)}$ for $\beta = U/U_0$ ($=1$) [$\epsilon^{(0)} = E/U_0$, $\epsilon = E/U$] for an electron in a periodic square well potential of the depth $|U_0| = \frac{2\hbar^2}{ma^2}$, as a function of the ratio $s = b/a$. $ka = \pi x$ with $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$, and 0.6 . Here the width a is held constant and the separation b is varied. The energy is lowered as the well come close together. The large ratio $s = b/a$ correspond to separated atoms. $\epsilon = -0.454453$.

The curve with $ka = 0$ is in good agreement with the result obtained by C.V. Fong (C. Kittel, Introduction to Solid State Physics).

Part II Kronig-Penney model for the 1D periodic well potential with the use of Mathematica

1. One dimensional bound state

As a simple example of the calculation of discrete energy levels of a particle (with mass m) in quantum mechanics, we consider the one-dimensional (1D) motion of a particle in the presence of a square-well potential barrier (width a and a depth U) as shown below.

$$U(x) = 0 \text{ for } |x| > \frac{a}{2}, \text{ and } -U \text{ for } -\frac{a}{2} < x < \frac{a}{2}.$$

where $a > 0$ and $U > 0$. If the energy of the particle E is negative, the particle is confined and in a bound state. Here we discuss the energy eigenvalues and the eigenfunctions for the bound states from the solution of the Schrödinger equation.

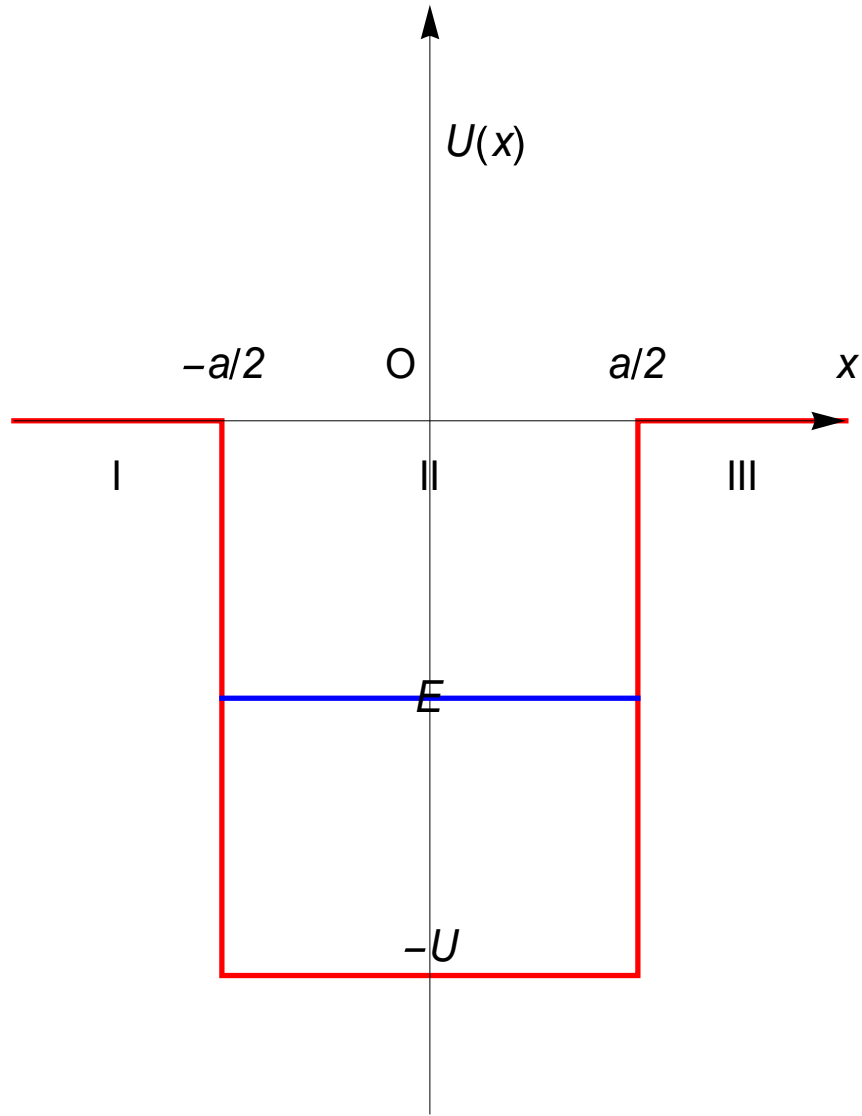


Fig.11 One dimensional square well potential of width (a) and depth U . For convenience, we use the symmetric potential with respect to the origin. $E = -|E|$ (<0). $U > 0$. The energy $-U$ is the bottom of the 1D square well potential.

(a) The parity of the wave function

When potential is an even function (symmetric with respect to x), the wave function should have even parity or odd parity.

((Proof)) Quantum mechanics

$$[\hat{\pi}, \hat{H}] = 0.$$

$\hat{\pi}$ is the parity operator.

$$\hat{\pi}^2 = 1 \quad \hat{\pi}^+ = \hat{\pi} = \hat{\pi}^{-1}.$$

$$\hat{\pi}\hat{x}\hat{\pi} = -\hat{x}. \quad \hat{\pi}\hat{p}\hat{\pi} = -\hat{p}.$$

\hat{H} is the Hamiltonian.

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(\hat{x}),$$

and

$$\begin{aligned} \hat{\pi}\hat{H}\hat{\pi} &= \hat{\pi}\left[\frac{\hat{p}^2}{2m} + U(\hat{x})\right]\hat{\pi} \\ &= \frac{1}{2m}(\hat{\pi}\hat{p}\hat{\pi})^2 + U(\hat{\pi}\hat{x}\hat{\pi}) \\ &= \frac{1}{2m}(-\hat{p})^2 + U(-\hat{x}) \\ &= \frac{1}{2m}\hat{p}^2 + U(\hat{x}) \end{aligned}$$

since $U(-\hat{x}) = U(\hat{x})$. Then we have a simultaneous eigenket:

$$\hat{H}|\psi\rangle = E|\psi\rangle, \text{ and } \hat{\pi}|\psi\rangle = \lambda|\psi\rangle.$$

Since $\hat{\pi}^2 = 1$,

$$\hat{\pi}^2|\psi\rangle = \lambda\hat{\pi}|\psi\rangle = \lambda^2|\psi\rangle = |\psi\rangle.$$

Thus we have $\lambda = \pm 1$.

or

$$\hat{\pi}|\psi\rangle = \pm|\psi\rangle,$$

$$\langle x|\hat{\pi}|\psi\rangle = \pm\langle x|\psi\rangle.$$

Since

$$\hat{\pi}|x\rangle = |-x\rangle, \text{ or } \langle x|\hat{\pi}^+ = \langle x|\hat{\pi} = \langle -x|$$

we have

$$\langle -x|\psi\rangle = \pm\langle x|\psi\rangle,$$

or

$$\psi(-x) = \pm\psi(x).$$

(b) Wavefunctions

In the Regions I, II, and III, the Schrödinger equation takes the form

$$\frac{d^2}{dx^2}\psi(x) - \kappa^2\psi(x) = 0 \quad \text{outside the well.}$$

$$\frac{d^2}{dx^2}\psi(x) + k^2\psi(x) = 0 \quad \text{inside the well.}$$

Here we define

$$\kappa^2 = \frac{2m}{\hbar^2}|E|, \quad k^2 = \frac{2m}{\hbar^2}(U - |E|).$$

Here we introduce parameters (β and ε) for convenience,

$$\kappa^2 = \frac{2m}{\hbar^2}|E| = \frac{2mU}{\hbar^2} \frac{|E|}{U} = \frac{4\beta^2}{a^2} \varepsilon,$$

or

$$\kappa^2 = \frac{4\beta^2}{a^2} \varepsilon,$$

and

$$k^2 = \frac{2m}{\hbar^2}(U - |E|) = \frac{2mU}{\hbar^2} \left(1 - \frac{|E|}{U}\right) = \frac{4\beta^2}{a^2} (1 - \varepsilon),$$

where

$$\varepsilon = \frac{|E|}{U}, \quad \text{and} \quad \beta = \sqrt{\frac{mUa^2}{2\hbar^2}}$$

$$\frac{2mU}{\hbar^2} = \frac{4\beta^2}{a^2}$$

We note that

$$k^2 + \kappa^2 = \frac{4\beta^2}{a^2},$$

or

$$\xi^2 + \eta^2 = \beta^2,$$

where $\xi = \frac{ka}{2}$ and $\eta = \frac{\kappa a}{2}$. The energy ε is given by

$$\varepsilon = \frac{\eta^2}{\beta^2} = 1 - \frac{\xi^2}{\beta^2}.$$

The stationary solution of the three regions are given by

$$\varphi_I(x) = Ae^{\kappa x},$$

$$\varphi_{II}(x) = B_1 e^{ikx} + B_2 e^{-ikx},$$

$$\varphi_{III}(x) = Ce^{-\kappa x}.$$

(i) The wave function with even parity

$$A = C, \quad B_1 = B_2 \equiv \frac{B}{2}.$$

The wavefunctions can be described by

$$\varphi_I(x) = Ae^{\kappa x},$$

$$\varphi_{II}(x) = B \cos(kx),$$

$$\varphi_{III}(x) = Ae^{-\kappa x}.$$

The derivatives are obtained by

$$\frac{d\varphi_I(x)}{dx} = A\kappa e^{\kappa x},$$

$$\frac{d\varphi_{II}(x)}{dx} = -Bk \sin(kx),$$

$$\frac{d\varphi_{III}(x)}{dx} = -A\kappa e^{-\kappa x}.$$

At $x = a/2$, $\varphi(x)$ and $\frac{d\varphi(x)}{dx}$ are continuous. Then we have

$$Ae^{-\kappa a/2} - B \cos\left(\frac{ka}{2}\right) = 0,$$

$$-A\kappa e^{-\kappa a/2} + Bk \sin\left(\frac{ka}{2}\right) = 0,$$

or

$$MX=0,$$

where

$$M = \begin{pmatrix} e^{-\kappa a/2} & -\cos\left(\frac{ka}{2}\right) \\ -\kappa e^{-\kappa a/2} & k \sin\left(\frac{ka}{2}\right) \end{pmatrix}, \quad X = \begin{pmatrix} A \\ B \end{pmatrix}.$$

The condition $\det M=0$ leads to

$$k \sin\left(k \frac{a}{2}\right) e^{-\kappa a/2} = \kappa e^{-\kappa a/2} \cos\left(\frac{ka}{2}\right),$$

or

$$\tan\left(\frac{ka}{2}\right) = \frac{\kappa}{k} \text{ for the even parity,}$$

or

$$\kappa a = ka \tan\left(\frac{ka}{2}\right) \quad \text{for the even parity.}$$

or

$$\eta = \xi \tan \xi .$$

with

$$\xi = \frac{ka}{2} \quad \text{and} \quad \eta = \frac{\kappa a}{2}$$

The constants A , B , and C are given by

$$A = C = B e^{\kappa a/2} \cos\left(\frac{ka}{2}\right).$$

The condition of the normalization leads to the value of B .

(ii) The wave function with odd parity

$$A = -C,$$

$$B_1 = -B_2 \equiv \frac{B}{2i}.$$

The wavefunctions are given by

$$\varphi_I(x) = -A e^{\kappa x},$$

$$\varphi_{II}(x) = B \sin(kx),$$

$$\varphi_{III}(x) = A e^{-\kappa x}.$$

The derivatives are obtained as

$$\frac{d\varphi_I(x)}{dx} = -A \kappa e^{\kappa x},$$

$$\frac{d\varphi_{II}(x)}{dx} = Bk \cos(kx),$$

$$\frac{d\varphi_{III}(x)}{dx} = -A \kappa e^{-\kappa x}.$$

At $x = a/2$, $\varphi(x)$ and $\frac{d\varphi(x)}{dx}$ are continuous. Then we have

$$-Ae^{-\kappa a/2} + B \sin\left(\frac{ka}{2}\right) = 0,$$

$$-A\kappa e^{-\kappa a/2} - Bk \cos\left(\frac{ka}{2}\right) = 0,$$

or

$$MX=0,$$

where

$$M = \begin{pmatrix} -e^{-\kappa a/2} & \sin(ka) \\ -\kappa e^{-\kappa a/2} & -k \cos\left(\frac{ka}{2}\right) \end{pmatrix}, \quad X = \begin{pmatrix} A \\ B \end{pmatrix}.$$

The condition $\det M=0$ leads to

$$k \cos\left(\frac{ka}{2}\right) e^{-\kappa a/2} = -\kappa e^{-\kappa a/2} \sin\left(\frac{ka}{2}\right),$$

or

$$\kappa \frac{a}{2} = -k \frac{a}{2} \cot\left(\frac{ka}{2}\right) \quad \text{for the odd parity,}$$

or

$$\eta = -\xi \cot \xi .$$

We solve this eigenvalue problem using the Mathematica. The result is as follows.

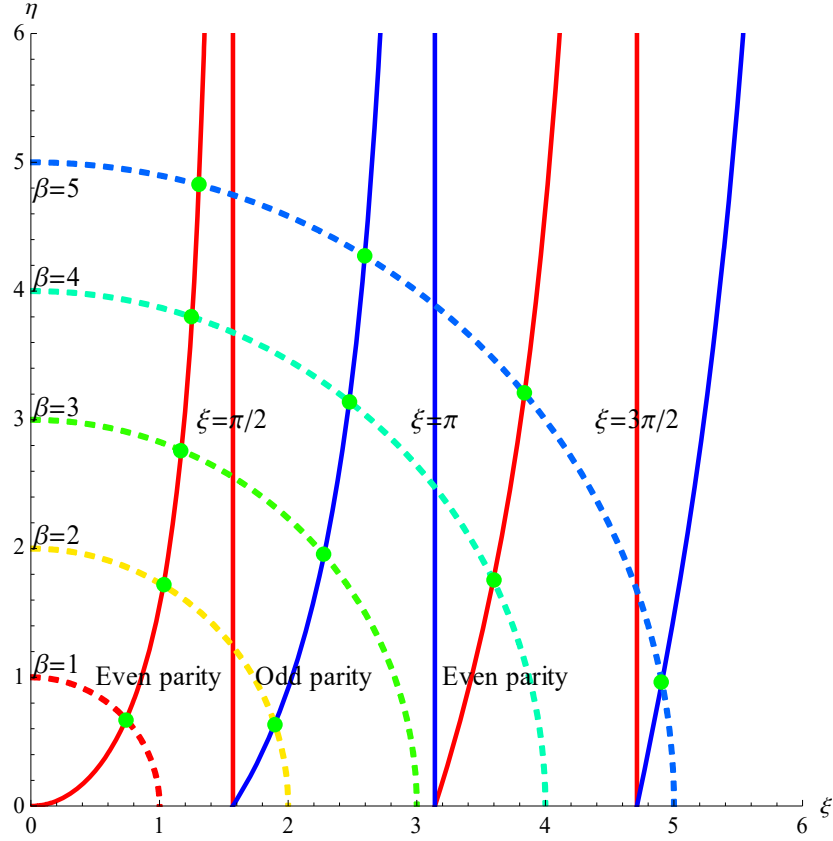


Fig.12 Graphical solution. One solution with even parity for $0 < \beta < \pi/2$. One solution with even parity and one solution with odd parity for $\pi/2 < \beta < \pi$. Two solutions with even parity and one solution with odd parity for $\pi < \beta < 3\pi/2$. Two solutions with even parity and two solutions with odd parity for $3\pi/2 < \beta < 2\pi$. $\eta = \xi \tan \xi$ for the even parity (red lines). $\eta = -\xi \cot \xi$ for the odd parity (blue lines). The circles are denoted by $\xi^2 + \eta^2 = \beta^2$. The parameter β is changed as $\beta = 1, 2, 3, 4,$ and 5 . $\varepsilon = \frac{|E|}{U} = \frac{\eta^2}{\beta^2} = 1 - \frac{\xi^2}{\beta^2}$. $\xi = \frac{ka}{2}$ and $\eta = \frac{\kappa a}{2}$.

((Note-1))

$$\eta^2 = \frac{\kappa^2 a^2}{4} = \frac{1}{4} \frac{2ma^2}{\hbar^2} |E| = \frac{ma^2 U}{2\hbar^2} \frac{|E|}{U} = \beta^2 \varepsilon$$

and

$$\eta^2 = \frac{\kappa^2 a^2}{4} = \frac{1}{4} \frac{2ma^2}{\hbar^2} |E| = \frac{ma^2 U_0}{2\hbar^2} \frac{|E|}{U_0} = \frac{|E|}{U_0} = \varepsilon^{(0)}$$

or

$$\varepsilon^{(0)} = \beta^2 \varepsilon$$

with

$$\varepsilon_0 = \frac{|E|}{U_0}, \quad \varepsilon = \frac{|E|}{U},$$

$$U_0 = \frac{2\hbar^2}{ma^2} \quad \beta = \sqrt{\frac{mUa^2}{2\hbar^2}} = \sqrt{\frac{U}{U_0}}$$

The normalized wavefunction for the even parity and odd parity are given by

$$\psi_{eI} = \frac{e^{\eta+x\eta} \cos[\xi]}{\sqrt{1 + \frac{\cos[\xi]^2}{\eta} + \frac{\sin[2\xi]}{2\xi}}}; \quad \psi_{eII} = \frac{\cos[x\xi]}{\sqrt{1 + \frac{\cos[\xi]^2}{\eta} + \frac{\sin[2\xi]}{2\xi}}};$$

$$\psi_{eIII} = \frac{e^{\eta-x\eta} \cos[\xi]}{\sqrt{1 + \frac{\cos[\xi]^2}{\eta} + \frac{\sin[2\xi]}{2\xi}}};$$

$$\psi_{oI} = -\frac{e^{\eta+x\eta} \sin[\xi]}{\sqrt{1 + \frac{\sin[\xi]^2}{\eta} - \frac{\sin[2\xi]}{2\xi}}}; \quad \psi_{oII} = \frac{\sin[x\xi]}{\sqrt{1 + \frac{\sin[\xi]^2}{\eta} - \frac{\sin[2\xi]}{2\xi}}};$$

$$\psi_{oIII} = \frac{e^{\eta-x\eta} \sin[\xi]}{\sqrt{1 + \frac{\sin[\xi]^2}{\eta} - \frac{\sin[2\xi]}{2\xi}}};$$

for the regions I, II, and III, where ψ_e is the wavefunction with the even parity and ψ_o is the wavefunction with the odd parity.

$$\beta = 1$$

$$\xi_{11} = 0.739085$$

$$\eta_{11} = 0.673612$$

$$\varepsilon_{11} = 0.453753$$

even

$$\beta^2 \varepsilon_{21} = \varepsilon_{21}^{(0)} = 1 \times 0.453753 = 0.453753 \quad \text{even}$$

$\beta = 2$

$$\begin{array}{llll} \xi_{21} = 1.02987 & \eta_{21} = 1.71446 & \varepsilon_{21} = 0.734844 & \text{even} \\ \xi_{22} = 1.89549 & \eta_{22} = 0.638045 & \varepsilon_{22} = 0.101775 & \text{odd} \end{array}$$

$$\beta^2 \varepsilon_{21} = \varepsilon_{21}^{(0)} = 4 \times 0.734844 = 2.9394 \quad \text{even}$$

$$\beta^2 \varepsilon_{22} = \varepsilon_{22}^{(0)} = 4 \times 0.101775 = 0.4071 \quad \text{odd}$$

$\beta = 3$

$$\begin{array}{llll} \xi_{31} = 1.17012 & \eta_{31} = 2.76239 & \varepsilon_{31} = 0.847869 & \text{even} \\ \xi_{32} = 2.27886 & \eta_{32} = 1.9511 & \varepsilon_{32} = 0.422976 & \text{odd} \end{array}$$

$$\beta^2 \varepsilon_{31} = \varepsilon_{31}^{(0)} = 9 \times 0.847869 = 7.63082 \quad \text{even}$$

$$\beta^2 \varepsilon_{32} = \varepsilon_{32}^{(0)} = 9 \times 0.422976 = 3.806784 \quad \text{odd}$$

$\beta = 4$

$$\begin{array}{llll} \xi_{41} = 1.25235 & \eta_{41} = 3.7989 & \varepsilon_{41} = 0.901976 & \text{even} \\ \xi_{42} = 2.47458 & \eta_{42} = 3.14269 & \varepsilon_{42} = 0.617279 & \text{odd} \\ \xi_{43} = 3.5953 & \eta_{43} = 1.75322 & \varepsilon_{43} = 0.192111 & \text{even} \end{array}$$

$$\beta^2 \varepsilon_{41} = \varepsilon_{41}^{(0)} = 16 \times 0.901976 = 14.4316 \quad \text{even}$$

$$\beta^2 \varepsilon_{42} = \varepsilon_{42}^{(0)} = 16 \times 0.617279 = 9.908464 \quad \text{odd}$$

$$\beta^2 \varepsilon_{43} = \varepsilon_{43}^{(0)} = 16 \times 0.192111 = 3.073776$$

$\beta = 5$

$$\begin{array}{llll} \xi_{51} = 1.30644 & \eta_{51} = 4.8263, & \varepsilon_{51} = 0.931729 & \text{even} \\ \xi_{52} = 2.59574 & \eta_{52} = 4.27342, & \varepsilon_{52} = 0.730486 & \text{odd} \\ \xi_{53} = 3.83747 & \eta_{53} = 3.20528, & \varepsilon_{53} = 0.410954 & \text{even} \\ \xi_{54} = 4.9063 & \eta_{54} = 0.963467, & \varepsilon_{54} = 0.0371307 & \text{odd} \end{array}$$

$$\beta^2 \varepsilon_{51} = \varepsilon_{51}^{(0)} = 25 \times 0.931729 = 23.293225 \quad \text{even}$$

$$\begin{aligned} \beta^2 \varepsilon_{52} = \varepsilon_{52}^{(0)} &= 25 \times 0.730486 = 18.26215 && \text{odd} \\ \beta^2 \varepsilon_{53} = \varepsilon_{53}^{(0)} &= 25 \times 0.410954 = 10.27385 && \text{even} \\ \beta^2 \varepsilon_{54} = \varepsilon_{54}^{(0)} &= 25 \times 0.0371307 = 0.9282675 && \text{odd} \end{aligned}$$

Wavefunctions and energy eigenvalues.

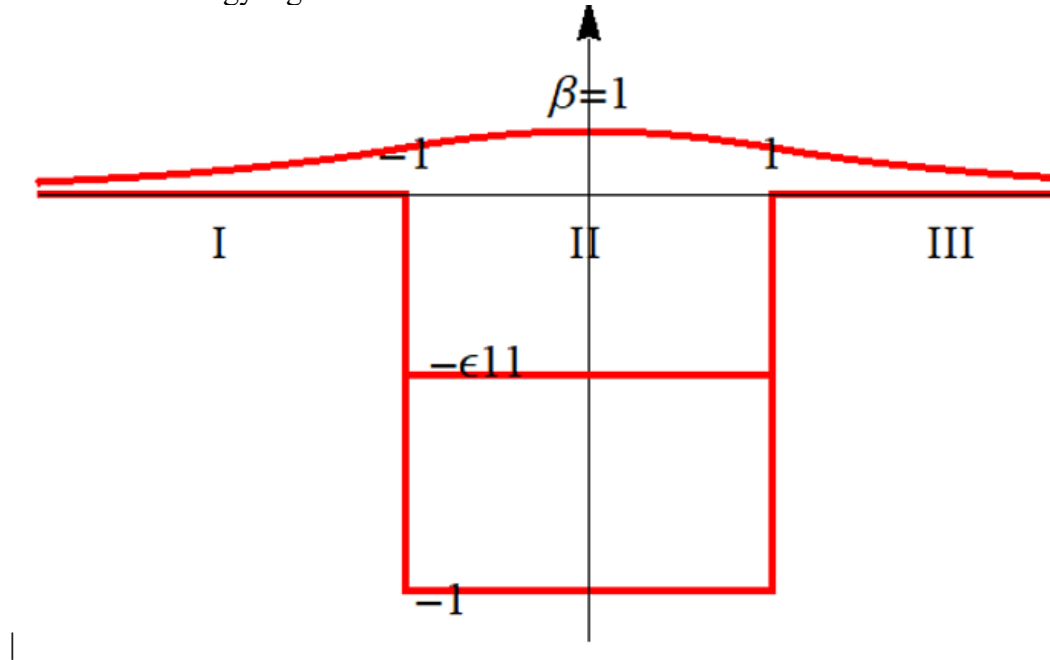


Fig.13 $[U(x)/U, \psi(x)]$ vs x/a . $\beta=1$. Square well potential $U(x)$ of width $2a$ and depth U , and the corresponding wavefunction $\psi(x)$ which is normalized. There is one bound state (even parity) ($-\epsilon_{11} = -0.45735$), where $\epsilon = |E|/U$. The horizontal axis is $x/(a/2)$.

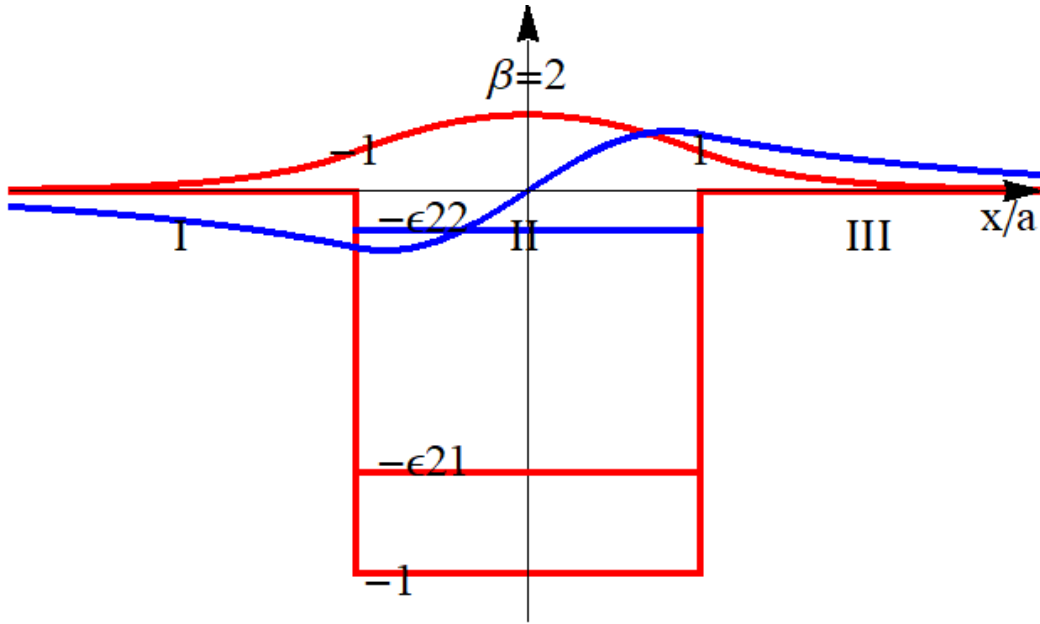


Fig.14 $[U(x)/U, \psi(x)]$ vs x/a . $\beta = 2$. There are two bound states. (i) The bound state (denoted by red) with even parity ($-\epsilon_{21} = -0.734844$). (ii) The bound state (denoted by blue) with odd parity ($-\epsilon_{22} = -0.101775$).

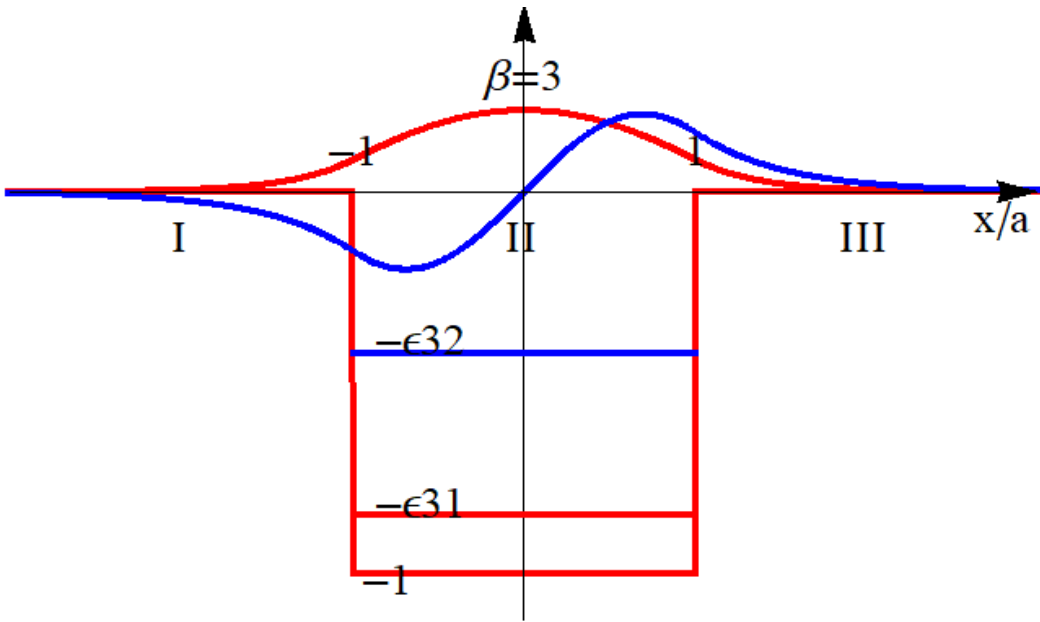


Fig.15 $[U(x)/U, \psi(x)]$ vs x/a . $\beta = 3$. There are two bound states. (i) The bound state (denoted by red) with even parity ($-\epsilon_{31} = -0.847869$). (ii) The bound state (denoted by blue) with odd parity ($-\epsilon_{32} = -0.422976$).

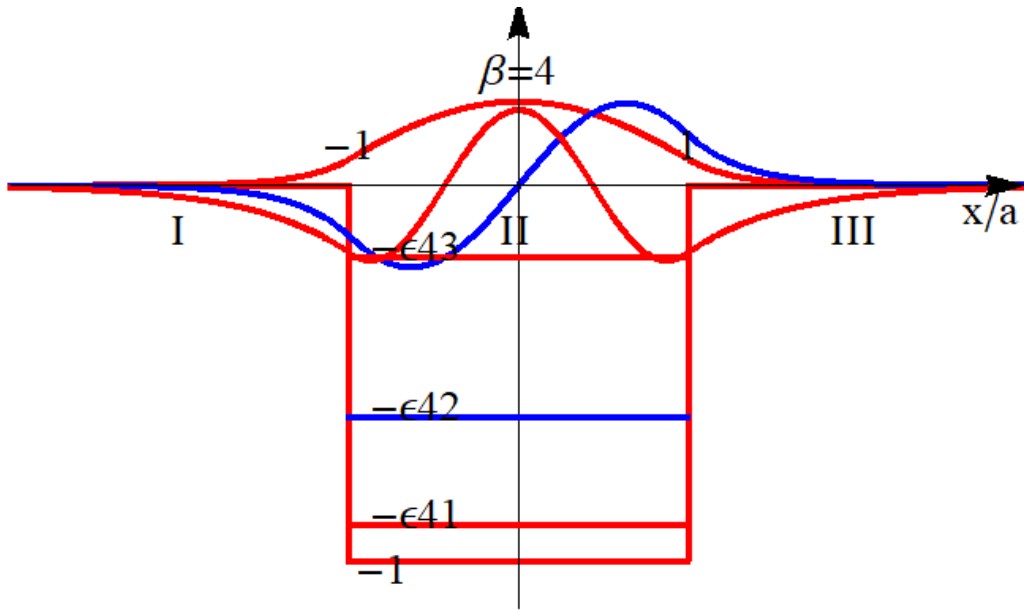


Fig.16 $[U(x)/U, \psi(x)]$ vs x/a . $\beta = 4$. There are three bound states. (i) The bound state (denoted by red) with even parity ($-\epsilon_{41} = -0.901976$). (ii) The bound state (denoted by blue) with odd parity ($-\epsilon_{42} = -0.617279$). (iii) The bound state (denoted by red) with even parity ($-\epsilon_{43} = -0.192111$).

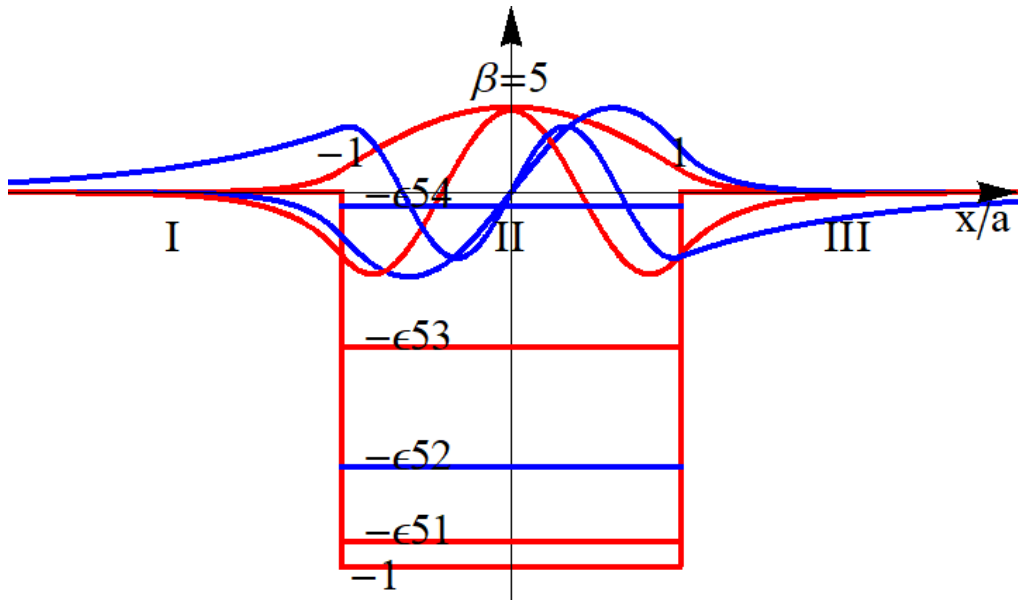


Fig.17 $[U(x)/U, \psi(x)]$ vs x/a . $\beta = 5$. There are four bound states. (i) The bound state (denoted by red) with even parity ($-\epsilon_{51} = -0.931729$). (ii) The bound state (denoted by blue) with odd parity ($-\epsilon_{52} = -0.730486$). (iii) The bound state (denoted by red) with

even parity ($-\varepsilon_{53} = -0.410954$). (iv) The bound state (denoted by blue) with odd parity ($-\varepsilon_{54} = -0.0371307$).

2. Kronig-Penney model for the 1D square well potential

The essential features of the behavior of electrons in a periodic potential may be explained by a relatively simple 1D model which was first discussed by Kronig and Penney. We assume that the potential energy of an electron has the form of a periodic array of square wells.

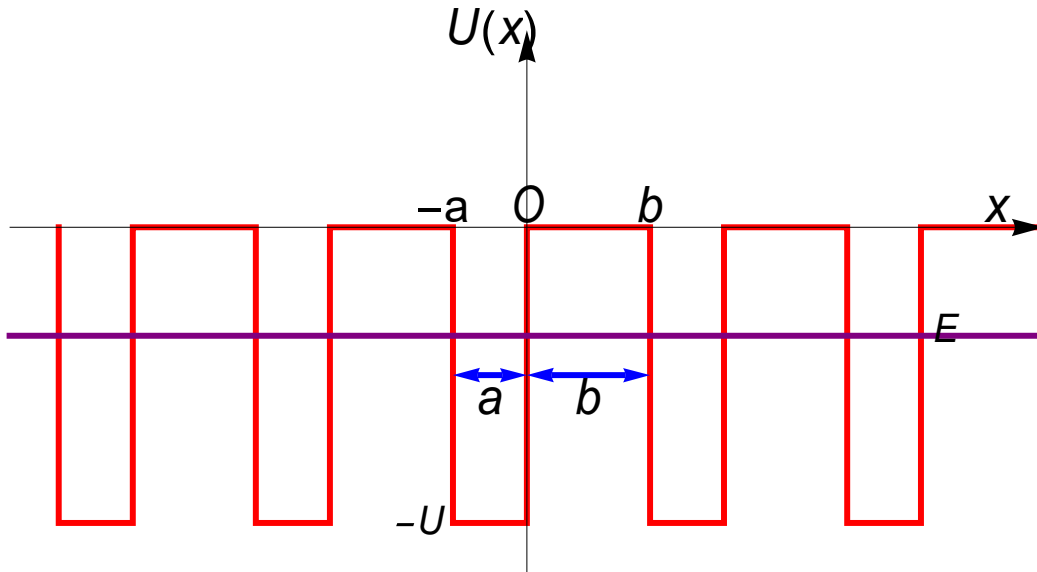


Fig.18 Periodic potential in the Kronig-Penney model with the periodicity $(a + b)$ and depth U . $E < 0$. $-U$ is the bottom of the 1D periodic square well potential.

We now consider a Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + U(x)\psi(x) = E\psi(x),$$

where E is the energy eigenvalue ($E = -|E|$) with $0 < |E| < U$.

(i) $U(x) = 0$ for $0 \leq x \leq b$

$$\psi_1(x) = Ae^{Kx} + Be^{-Kx}, \quad d\psi_1(x)/dx = K(Ae^{Kx} - Be^{-Kx}),$$

with $|E| = \frac{\hbar^2 K^2}{2m}, \quad E = -\frac{\hbar^2 K^2}{2m}$

(ii) $U(x) = -U$ for $-a \leq x \leq 0$

$$\psi_2(x) = Ce^{iQx} + De^{-iQx}, \quad d\psi_2(x)/dx = iQ(Ce^{iQx} - De^{-iQx}),$$

with

$$U + E = U - |E| = \frac{\hbar^2}{2m} Q^2.$$

We note that for simplicity we use

$$U_0 = \frac{2\hbar^2}{ma^2}.$$

The Bloch theorem can be applied to the wave function

$$\psi(x+a+b) = e^{ik(a+b)}\psi(x),$$

where k is the wave number. The constants A , B , C , and D are chosen so that ψ and $d\psi/dx$ are continuous at $x = 0$ and $x = a$.

(a) At $x = 0$,

$$A + B = C + D,$$

$$K(A - B) = iQ(C - D).$$

Thanks to the Bloch theorem, the boundary condition of the wave function at $x = b$ is related to that at $x = -a$. In other words, we have only to know the knowledge of the wave function in a unit cell (the period is $a + b$).

(b) At $x = -a$,

$$\psi_1(b) = e^{ik(a+b)}\psi_2(-a),$$

$$\psi_1'(b) = e^{ik(a+b)}\psi_2'(-a),$$

or

$$Ae^{Kb} + Be^{-Kb} = e^{ik(a+b)}(Ce^{-iQa} + De^{iQa}),$$

$$K(Ae^{Kb} - Be^{-Kb}) = iQe^{ik(a+b)}(Ce^{-iQa} - De^{iQa}).$$

The above four equations for A , B , C , and D have a solution only if $\det[M]=0$, where the matrix M is given by

$$M = \begin{pmatrix} 1 & 1 & -1 & -1 \\ K & -K & -iQ & iQ \\ e^{Kb} & e^{-Kb} & -e^{-iQa+ik(a+b)} & -e^{iQa+ik(a+b)} \\ Ke^{Kb} & -Ke^{-Kb} & -iQe^{-iQa+ik(a+b)} & iQe^{iQa+ik(a+b)} \end{pmatrix}.$$

The condition of $\det[M] = 0$ leads to

$$\cos[k(a+b)] = \cos(Qa) \cosh(Kb) + \frac{(K^2 - Q^2)}{2KQ} \sin(Qa) \sinh(Kb).$$

The general case of β with $\beta_0 = 1$

$$\beta = \sqrt{\frac{mUa^2}{2\hbar^2}}, \quad U = \frac{2\beta^2\hbar^2}{ma^2} = \beta^2 U_0,$$

where

$$\beta_0 = \sqrt{\frac{mU_0 a^2}{2\hbar^2}} = 1, \quad U_0 = \frac{2\hbar^2}{ma^2},$$

$$U + E = \frac{\hbar^2 Q^2}{2m}, \quad E = -\frac{\hbar^2 K^2}{2m}.$$

Note that

$$U = \frac{\hbar^2}{2m}(K^2 + Q^2) = \frac{2\beta^2 \hbar^2}{ma^2}, \quad \text{or} \quad K^2 + Q^2 = \frac{4\beta^2}{a^2}$$

Suppose that

$$Ka = 2\sqrt{-\varepsilon}, \quad Qa = 2\sqrt{\varepsilon + \beta^2}$$

The ratio is given by

$$\frac{E}{U_0} = \varepsilon^{(0)} = -\frac{\hbar^2 K^2}{2m} \frac{ma^2}{2\hbar^2} = -\frac{1}{4}(Ka)^2$$

where $\varepsilon^{(0)} < 0$.

$$\cos(k_1) = \cos(2\sqrt{\beta^2 + \varepsilon^{(0)}}) \cosh(2s\sqrt{-\varepsilon^{(0)}}) - \frac{(2\varepsilon^{(0)} + \beta^2)}{2\sqrt{-\varepsilon^{(0)}}\sqrt{\beta^2 + \varepsilon^{(0)}}} \sin(2\sqrt{\beta^2 + \varepsilon^{(0)}}) \sinh(2s\sqrt{-\varepsilon^{(0)}})$$

where

$$k_1 = k(a+b), \quad s = \frac{b}{a}, \quad Kb = Ka \frac{b}{a} = sKa$$

When $\varepsilon^{(0)} = x$

$$\cos(k_1) = \cos(2\sqrt{\beta^2 + x}) \cosh(2s\sqrt{-x}) - \frac{(2x + \beta^2)}{2\sqrt{-x}\sqrt{\beta^2 + x}} \sin(2\sqrt{\beta^2 + x}) \sinh(2s\sqrt{-x})$$

((Note)) Evaluation of U_0

$$U_0 = \frac{2\hbar^2}{ma^2} = 15.2399 [a(\text{\AA})]^2 \text{ (eV)}$$

where m is the mass of free electron.

3. The case of $E > 0$

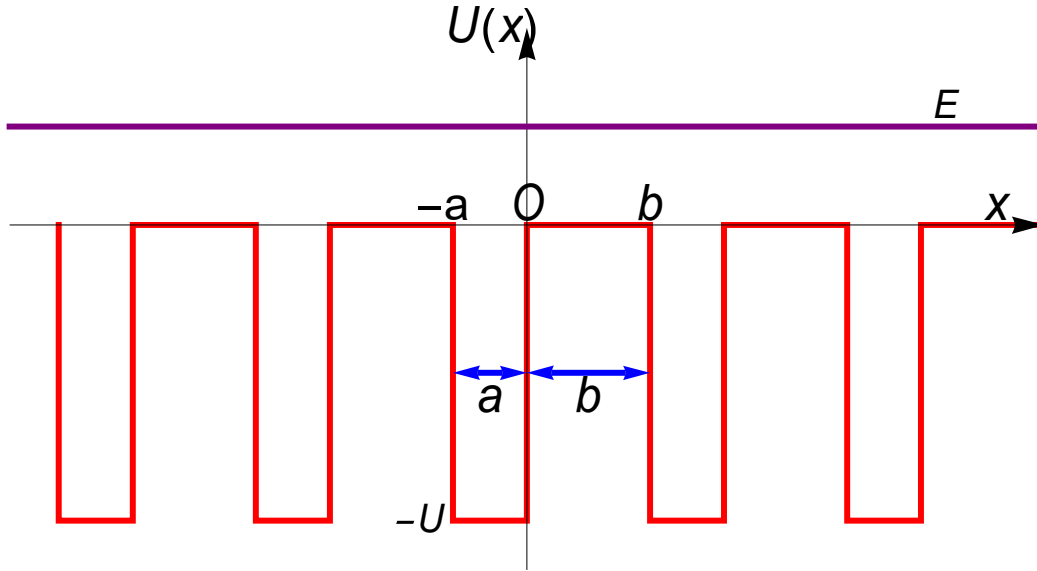


Fig.19 Periodic potential in the Kronig-Penney model with the periodicity $(a + b)$ and depth U . $E > 0$. $-U$ is the bottom of the 1D periodic square well potential.

We now consider a Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + U(x)\psi(x) = E\psi(x),$$

where E is the energy eigenvalue ($E > 0$).

(i) $U(x) = 0$ for $0 \leq x \leq b$

$$\psi_1(x) = Ae^{iKx} + Be^{-iKx}, \quad d\psi_1(x)/dx = iK(Ae^{iKx} - Be^{-iKx}),$$

with $E = \frac{\hbar^2 K^2}{2m}$.

(ii) $U(x) = -U$ for $-a \leq x \leq 0$

$$\psi_2(x) = Ce^{iQx} + De^{-iQx}, \quad d\psi_2(x)/dx = iQ(Ce^{iQx} - De^{-iQx}),$$

with

$$U + E = \frac{\hbar^2}{2m} Q^2.$$

We note that for simplicity we use

$$U_0 = \frac{2\hbar^2}{ma^2}.$$

The Bloch theorem can be applied to the wave function

$$\psi(x+a+b) = e^{ik(a+b)}\psi(x),$$

where k is the wave number. The constants A , B , C , and D are chosen so that ψ and $d\psi/dx$ are continuous at $x = 0$ and $x = a$.

(a) At $x = 0$,

$$A + B = C + D,$$

$$K(A - B) = iQ(C - D).$$

Thanks to the Bloch theorem, the boundary condition of the wave function at $x = b$ is related to that at $x = -a$. In other words, we have only to know the knowledge of the wave function in a unit cell (the period is $a + b$).

(b) At $x = -a$,

$$\psi_1(b) = e^{ik(a+b)}\psi_2(-a),$$

$$\psi_1'(b) = e^{ik(a+b)}\psi_2'(-a),$$

or

$$Ae^{iKb} + Be^{-iKb} = e^{ik(a+b)}(Ce^{-iQa} + De^{iQa}),$$

$$iK(Ae^{iKb} - Be^{-iKb}) = iQe^{ik(a+b)}(Ce^{-iQa} - De^{iQa}).$$

The above four equations for A , B , C , and D have a solution only if $\det[M]=0$, where the matrix M is given by

$$M = \begin{pmatrix} 1 & 1 & -1 & -1 \\ iK & -iK & -iQ & iQ \\ e^{Kb} & e^{-Kb} & -e^{-iQa+ik(a+b)} & -e^{iQa+ik(a+b)} \\ iKe^{iKb} & -iKe^{-iKb} & -iQe^{-iQa+ik(a+b)} & iQe^{iQa+ik(a+b)} \end{pmatrix}.$$

The condition of $\det[M] = 0$ leads to

$$\begin{aligned} \cos[k(a+b)] &= \cos(Qa) \cosh(iKb) + \frac{(-K^2 - Q^2)}{2iKQ} \sin(Qa) \sinh(iKb) \\ &= \cos(Qa) \cos(Kb) - \frac{(K^2 + Q^2)}{2KQ} \sin(Qa) \sin(Kb) \end{aligned}$$

where

$$\cosh(ix) = \cos x, \quad \sinh(ix) = i \sin x$$

$$U + E = \frac{\hbar^2 Q^2}{2m}, \quad E = \frac{\hbar^2 K^2}{2m}$$

We note that for simplicity we use

$$U_0 = \frac{2\hbar^2}{ma^2}, \quad U = \beta^2 U_0$$

$$\frac{E}{U_0} = \varepsilon^{(0)} = \frac{\hbar^2 K^2}{2m} \frac{ma^2}{2\hbar^2} = \frac{1}{4} (Ka)^2$$

$$Ka = 2\sqrt{\varepsilon_0}, \quad Qa = 2\sqrt{\beta^2 + \varepsilon^{(0)}}$$

When $x = \varepsilon^{(0)}$

$$\cos k_1 = \cos(2s\sqrt{x}) \cos(2\sqrt{\beta^2 + x}) - \frac{(\beta^2 + 2x) \sin(2s\sqrt{x}) \sin(2\sqrt{\beta^2 + x})}{2\sqrt{x}\sqrt{\beta^2 + x}}$$

We solve this equation by using the Mathematica (ContourPlot, FindRoot programs).

4. Fourier transform of the 1D square well potential energy

Because of the periodicity in $U(x)$ as

$$U(x+a+b) = U(x)$$

$U(x)$ can be expressed by

$$U(x) = \sum_G U_G e^{iGx}$$

where G is the reciprocal lattice, $G = \left(\frac{2\pi}{a+b}\right)n$ (n : integer). The coefficient U_G can be calculated as

$$\begin{aligned} U_G &= \frac{1}{a+b} \int_0^{a+b} dx U(x) e^{-iGx} \\ &= -\frac{U_0}{a+b} \int_0^a dx e^{-iGx} \\ &= \frac{U_0}{(a+b)iG} [e^{-iGa} - 1] \end{aligned}$$

or

$$\begin{aligned} U_G^* U_G &= \frac{U_0^2}{(a+b)^2} \left[\frac{e^{-iGa} - 1}{iG} \right] \left[\frac{e^{iGa} - 1}{-iG} \right]^* \\ &= U_0^2 \frac{4 \sin^2 \left(\frac{Ga}{2} \right)}{G^2 (a+b)^2} \end{aligned}$$

or

$$|U_G| = U_0 \frac{2 \left| \sin \left(\frac{Ga}{2} \right) \right|}{G(a+b)}$$

At $G = \left(\frac{2\pi}{a+b}\right)n$, we have

$$\frac{|U_G|}{U_0} = \frac{U_n}{U_0} = \frac{\left| \sin\left(\frac{\pi n}{1+s}\right) \right|}{\pi n}$$

At $G = 0$,

$$\frac{|U_G|}{U_0} = \frac{1}{1+s}$$

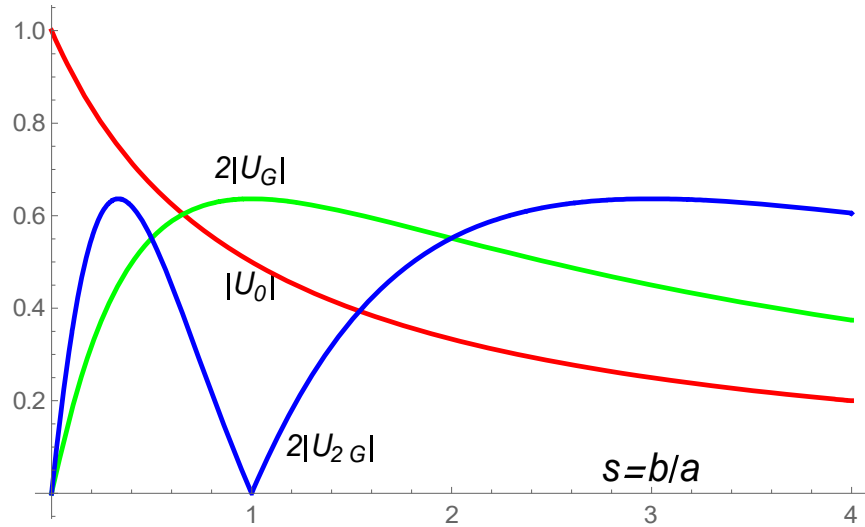


Fig.20 Fourier transform co-efficient of $U(x)$ as a function of $s = b/a$.

The energy gap is given as

$$2|U_G| = 2|U_1|, \quad 2|U_{2G}| = 2|U_2|.$$

and the base of the energy band is $|U_0|$,

5. Energy band structure for the 1D periodic potential with the lattice constant a .

The above results on the energy dispersion relation are summarized as follows. Three different zone schemes are useful. (a) The extended zone scheme where different bands are drawn in different zones in wavevector space. (b) The reduced zone scheme where all bands are drawn in the first Brillouin zone. (c) The periodic zone scheme where every band is drawn in every zone.

The formation of energy bands and gaps are generated. The main effects are at the zone boundary of the Brillouin zone.

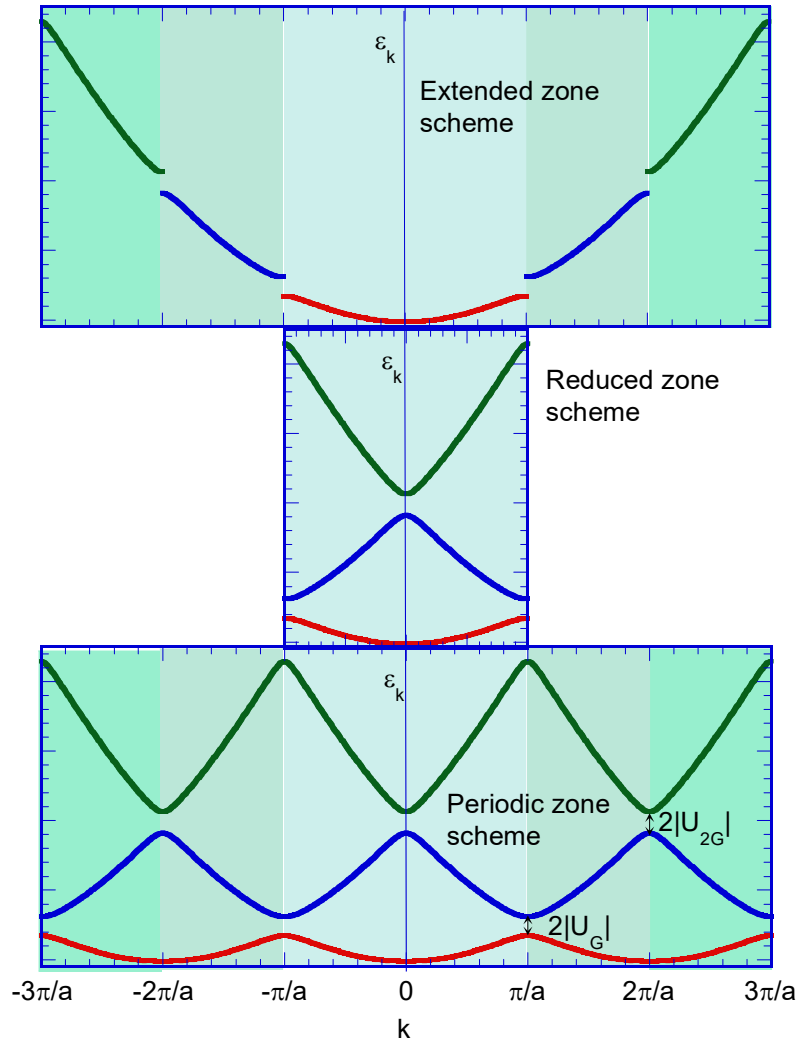


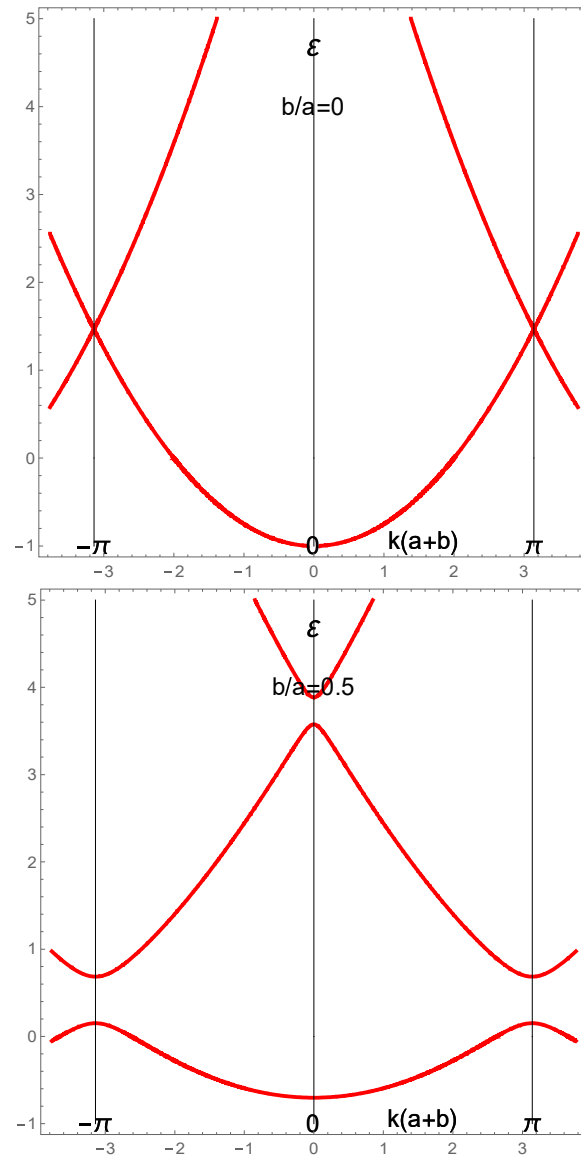
Fig.21 Three zone schemes for the 1D system with the lattice constant a . Extended zone scheme. Reduced zone scheme. Periodic zone scheme. Note that the period of the system is a in this case.

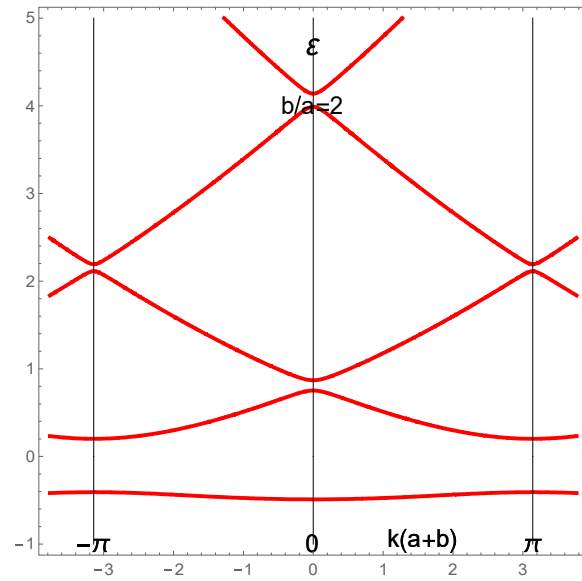
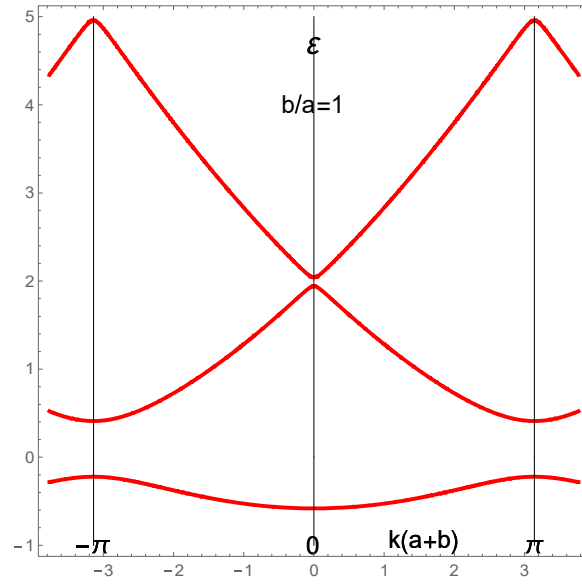
6. The energy dispersion for $\beta = 1$

We calculate the energy dispersion $\epsilon^{(0)} = E/U_0$ as a function of $k(a+b)$, where $s = b/a$ is changed as a parameter. Note that a is kept constant. Hereafter we use ϵ instead of $\epsilon^{(0)}$, for convenience.

$$\varepsilon = \frac{E}{U_0}$$

To this end, we use the ContourPlot of Mathematica 12.0, for the energy dispersion for $\beta = 1$ (Kronig-Penney model).





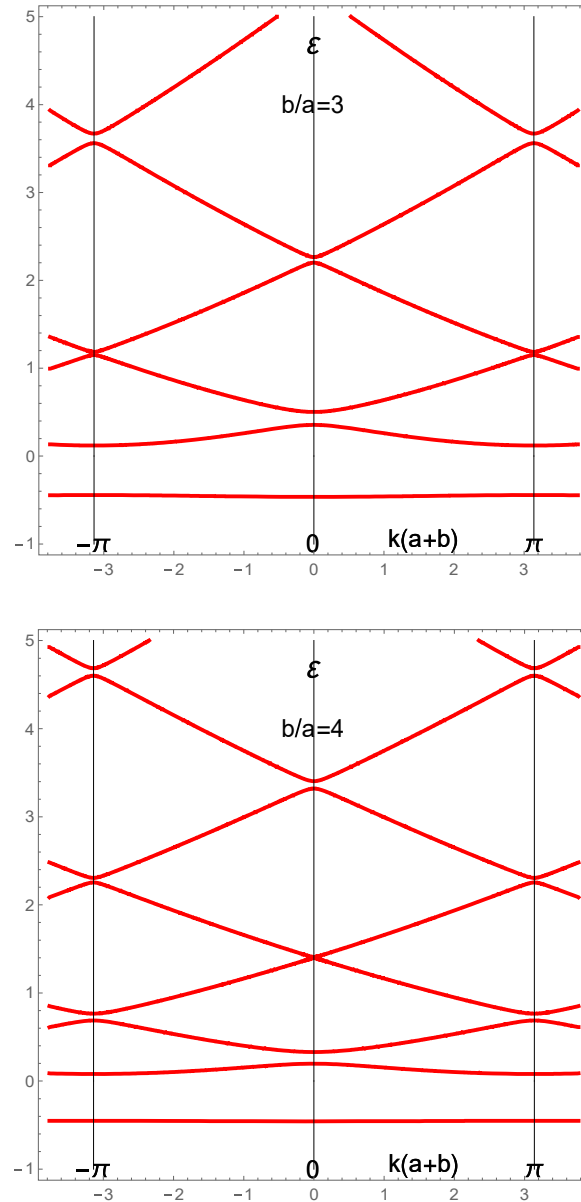


Fig.22 Energy dispersion curve [ϵ vs $k(a+b)$], where the ratio $s = b/a$ is changed as a parameter. $\beta = 1$. $k = \pm\pi/(a+b)$ is the zone boundary of the Brillouin zone.

7. The energy of the ground state as a function of $s = b/a$ where $\beta = 1$ and 2, and a is kept constant

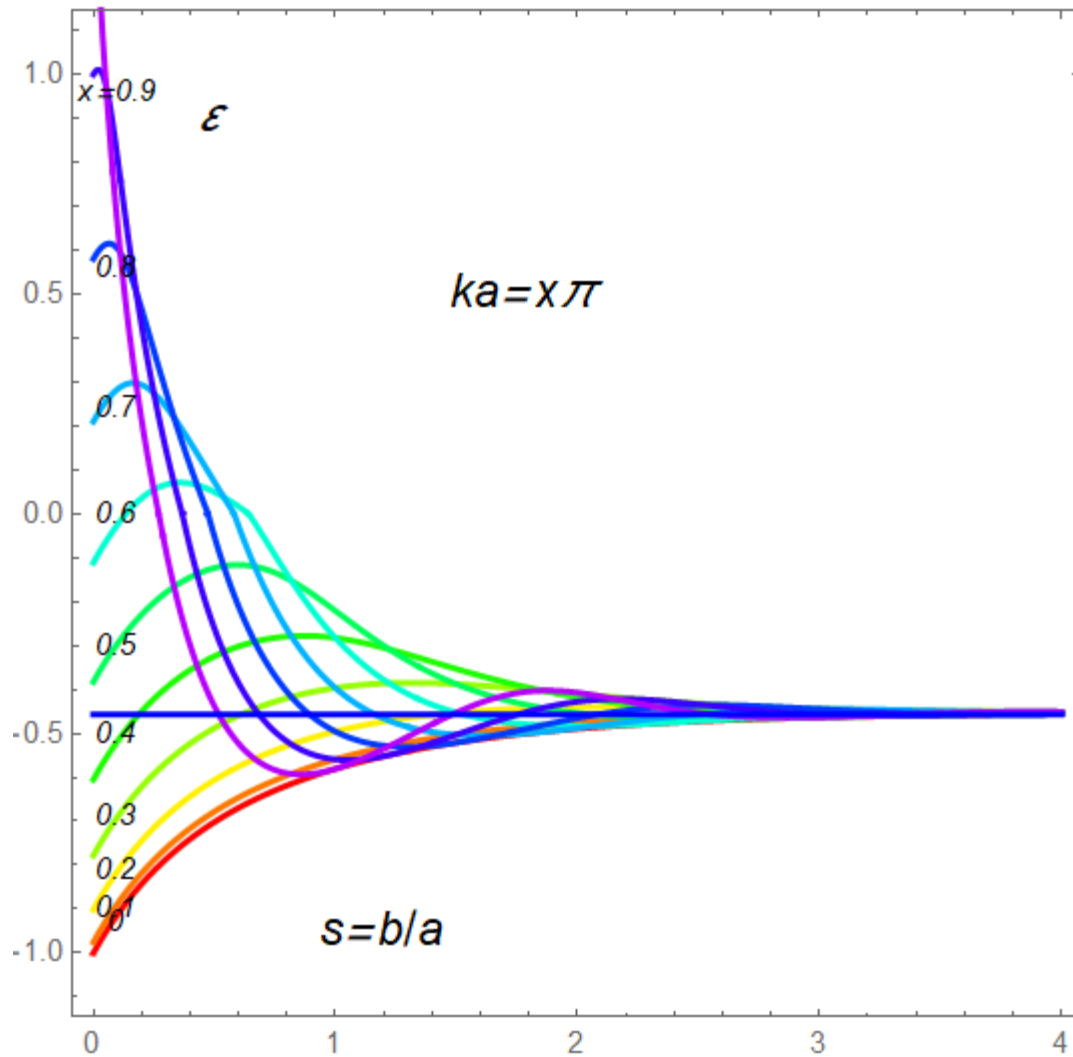


Fig.23 The energy of the ground state for $\beta = 1$ (wavefunction with even parity) as a function of $s = b/a$, where $ka = \pi x$ is changed as a parameter. $x = 0 - 0.9$. $x = 0$ for red. $x = 1$ for purple.

The above result of ϵ vs $s = b/a$ for $\beta = 1$ is the same as that reported in the Kittel's book (C.Y. Fong). The energy eigenvalue ϵ is equal to -1 for $s = 0$ and -0.453753 for $s = \infty$ corresponding to the ground state energy for the isolated atom. This indicates that the ground state energy is much lower for atoms at the actual spacing in the metal than for isolated atoms. At the fixed small value of ka , the lowest state energy increases with increasing ka .

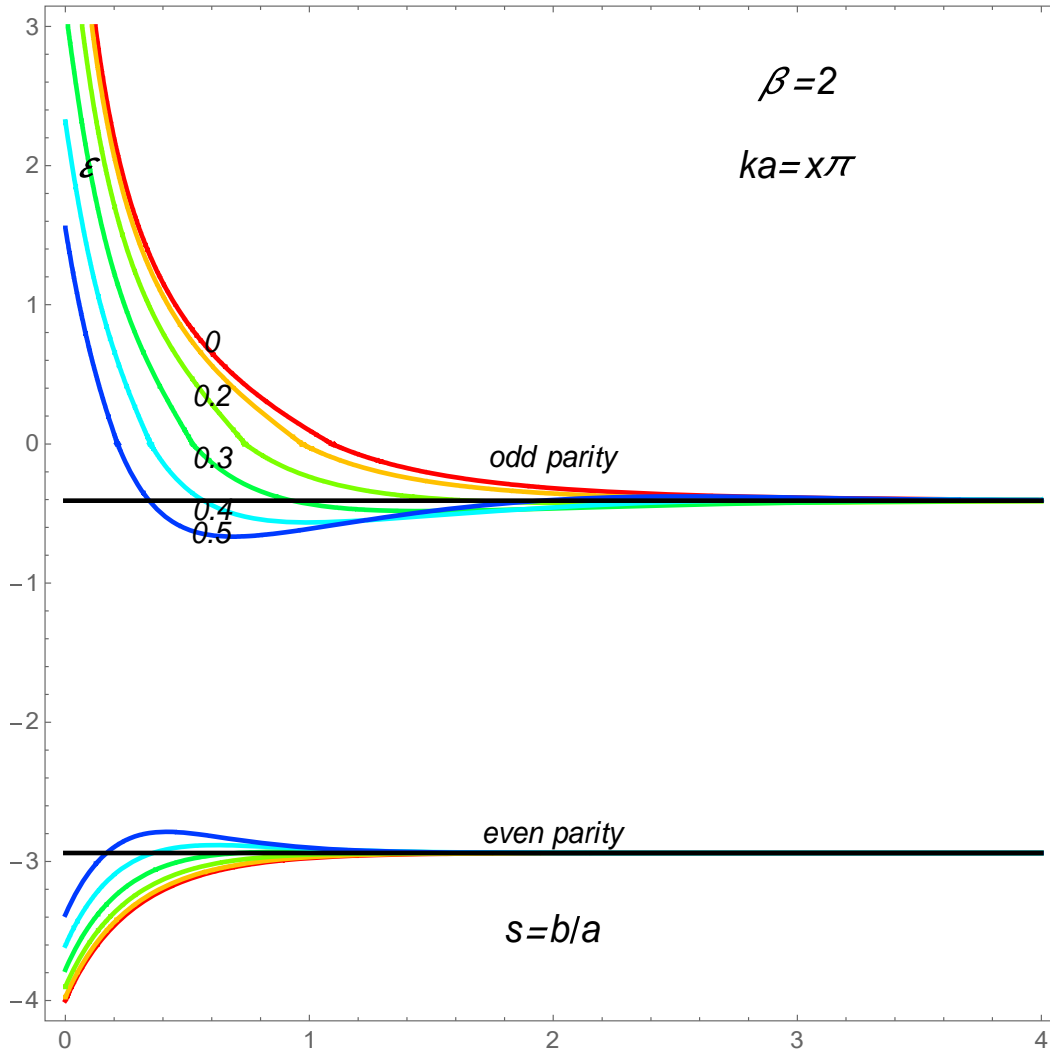
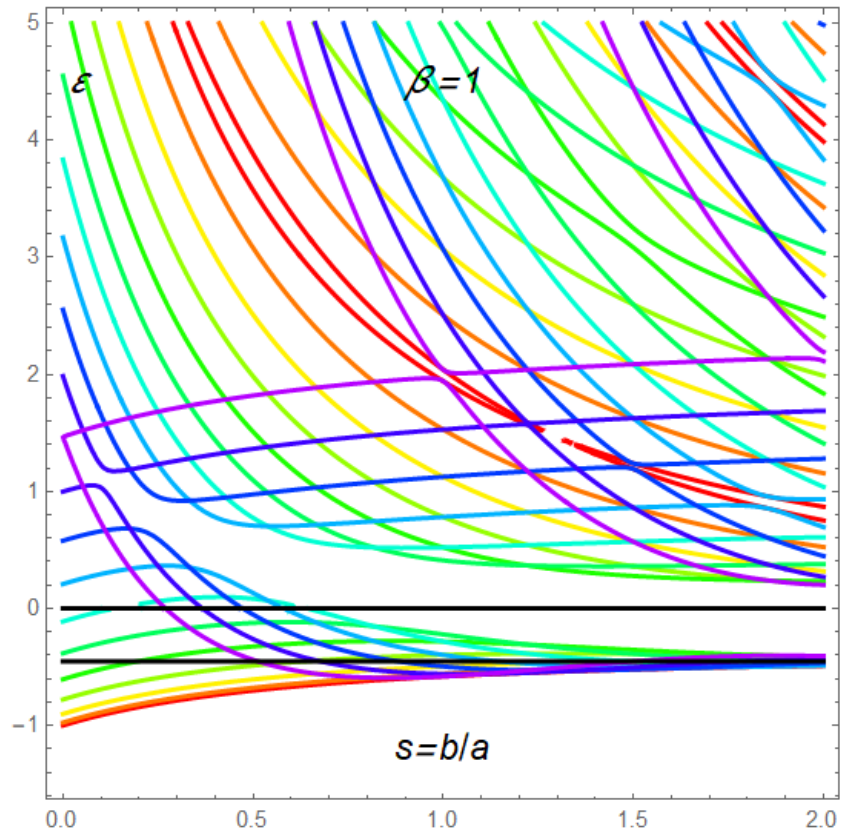


Fig.24 The energy of the ground state for $\beta = 2$ as a function of $s = b/a$, where $ka = \pi x$ is changed as a parameter. $x = 0 - 0.5$.

The ground state energy eigenvalue \mathcal{E} (even parity) for $\beta = 2$ is equal to -4 for $s = 0$ and -2.9394 for $s = \infty$. The first excited energy eigenvalue (odd parity) for $\beta = 2$ is equal to 5.8696 for $s = 0$ and -0.4071 for $s = \infty$. Note that the ground state energy is much lower for atoms at the actual spacing in the metal than for isolated atoms. At the fixed small value of ka , the lowest state energy increases with increasing ka . On the other hand, that the first excited state energy is much higher for atoms at the actual spacing in the metal than for isolated atoms. At the fixed small value of ka , the first excited state energy decreases with increasing ka .

8. The energy of the ground state as a function of $s = b/a$ at various $\beta = 1$



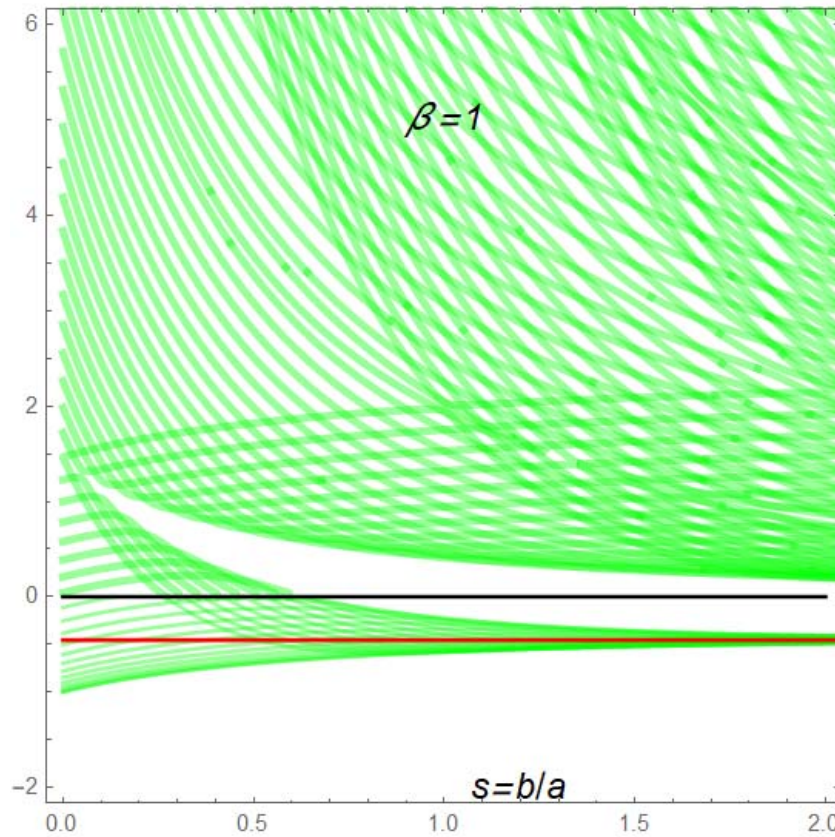
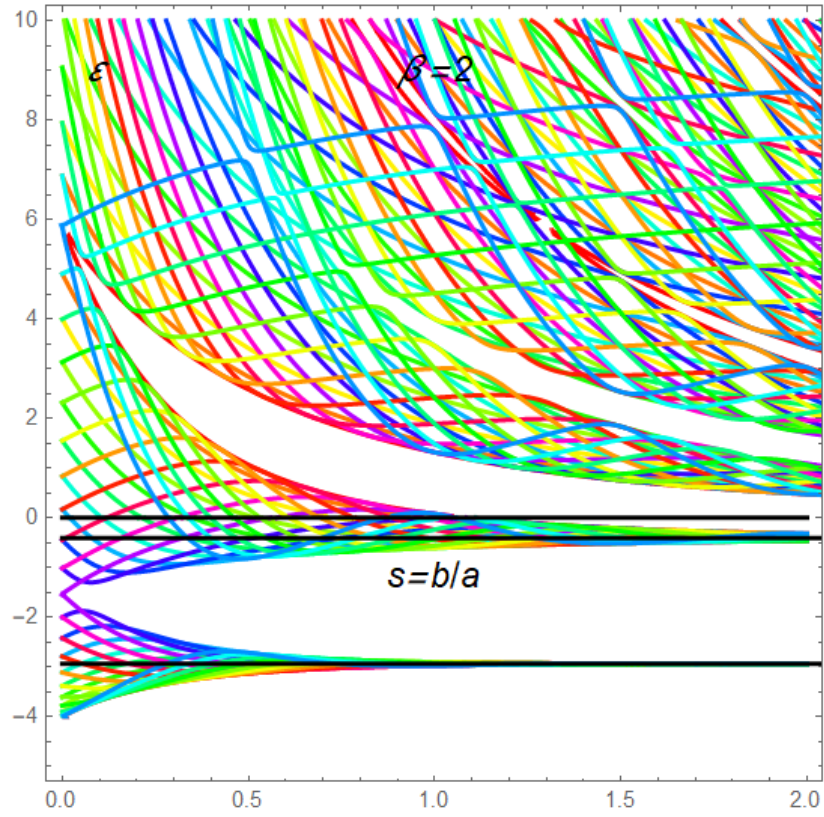


Fig.25 $\beta = 1$. Energy vs $s = b/a$, where a is kept constant. The parameter x of $ka = \pi x$ is changed between 0 and 1. $x = 0$ for color red, and $x = 1$ for color purple (see **Fig.23**). The red lines denote the bound state in the limit of $s \rightarrow \infty$. There is one bound state.

9. The energy of the ground state as a function of $s = b/a$ at $\beta = 2$

$\beta = 2$



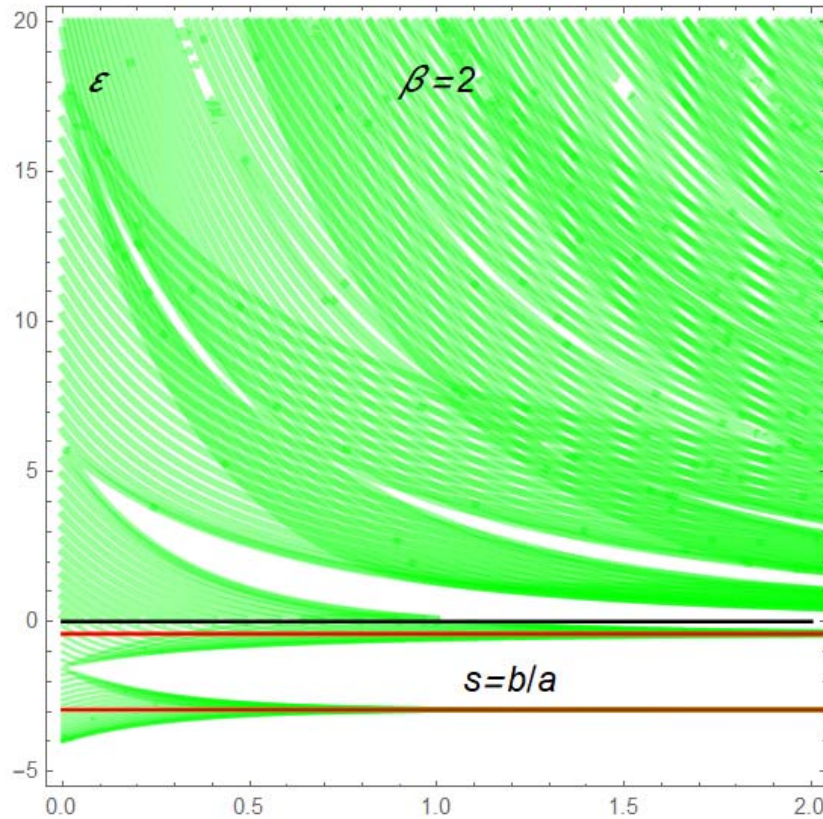


Fig.26 $\beta = 2$. Energy vs $s = b/a$. The parameter x of $ka = \pi x$ is changed between 0 and 1. The red lines denotes the bound state in the limit of $s \rightarrow \infty$. There are two bound states.

10. The energy of the ground state as a function of $s = b/a$ at $\beta = 3$
 $\beta = 3$

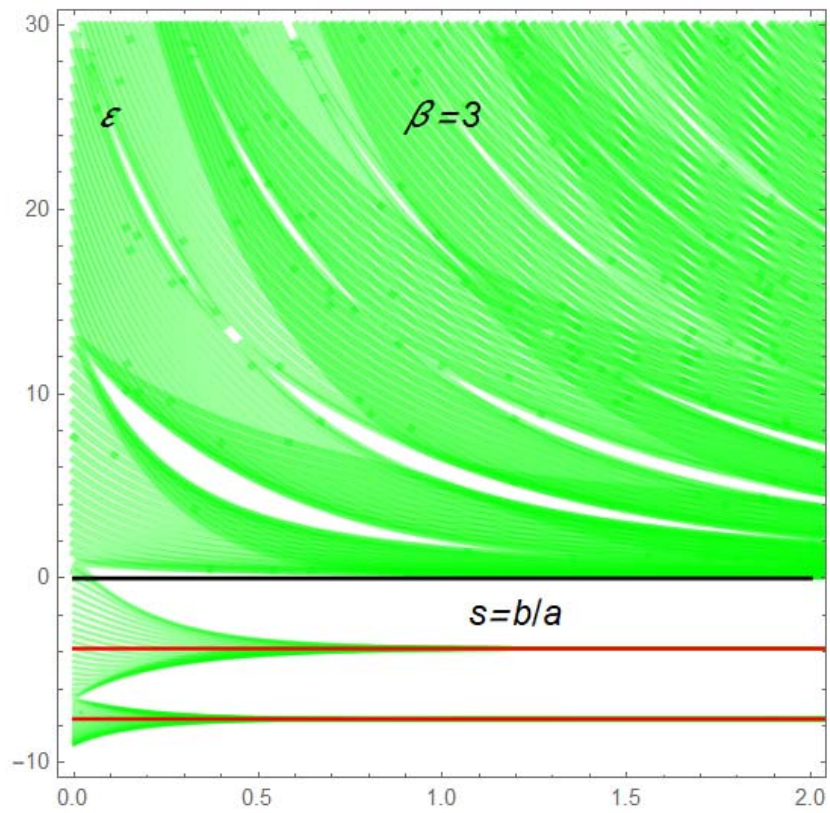
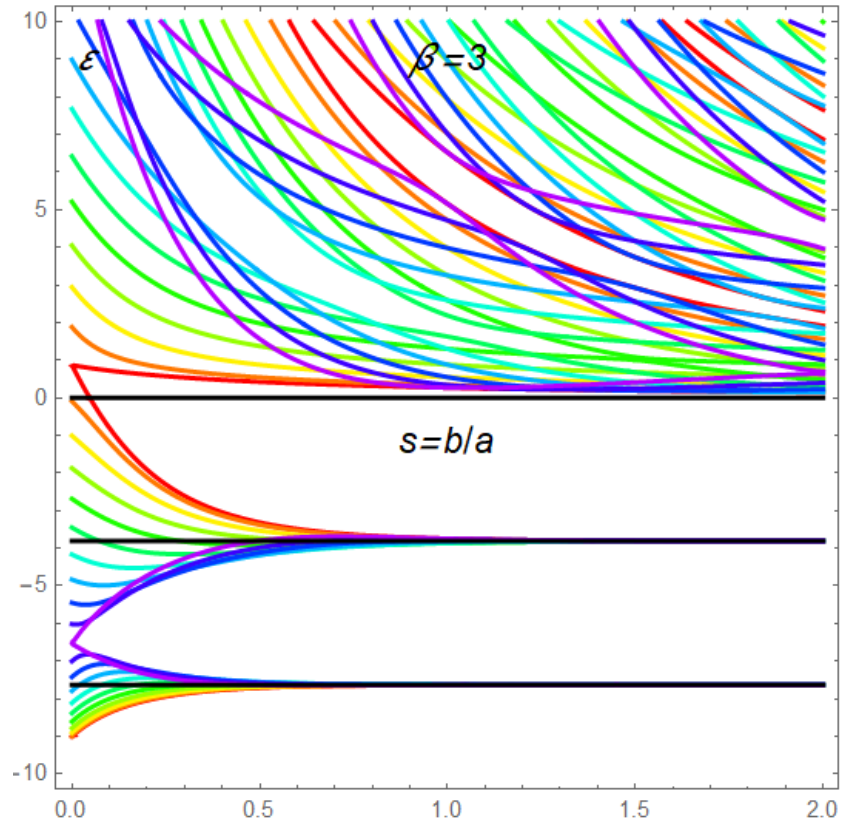
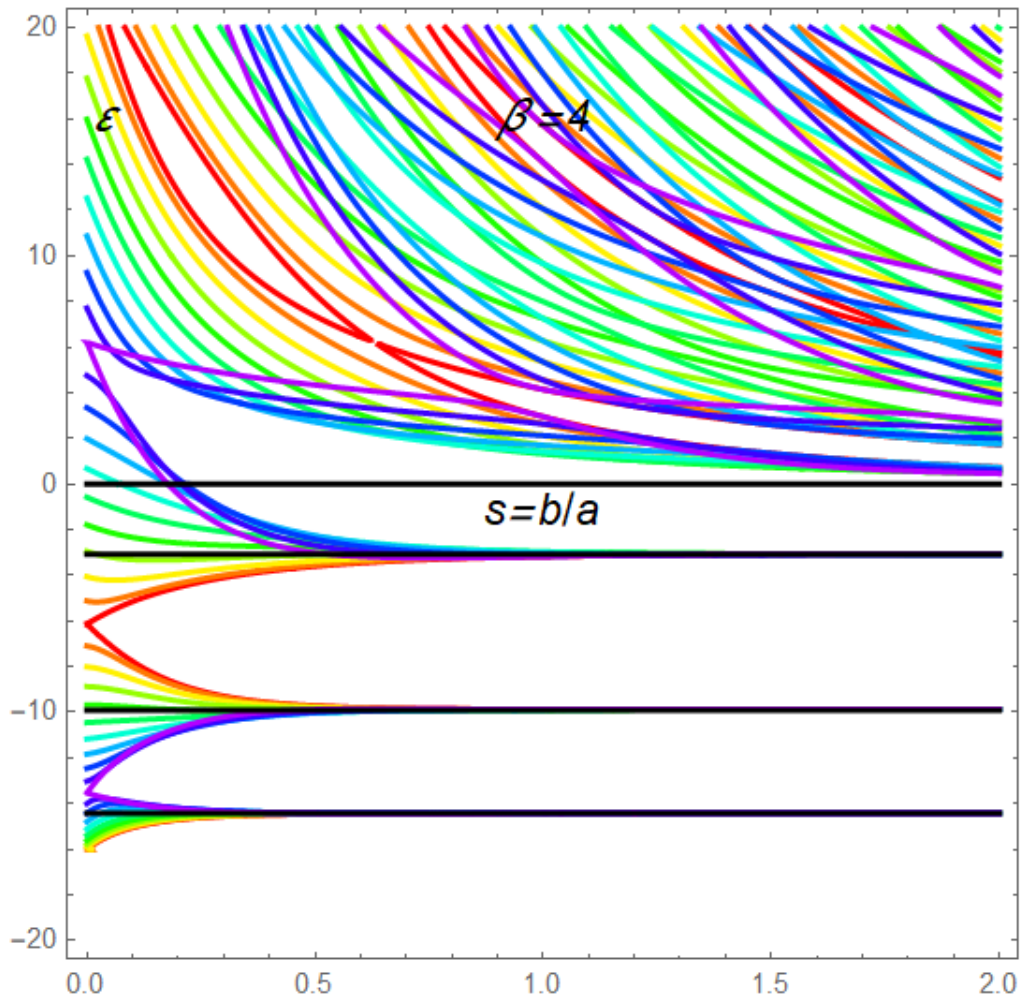


Fig.27 $\beta=3$. Energy vs $s = b/a$. The parameter x of $ka = \pi x$ is changed between 0 and 1. The red lines denotes the bound state in the limit of $s \rightarrow \infty$. There are two bound states.

11. The energy of the ground state as a function of $s = b/a$ at $\beta = 4$

$\beta = 4$



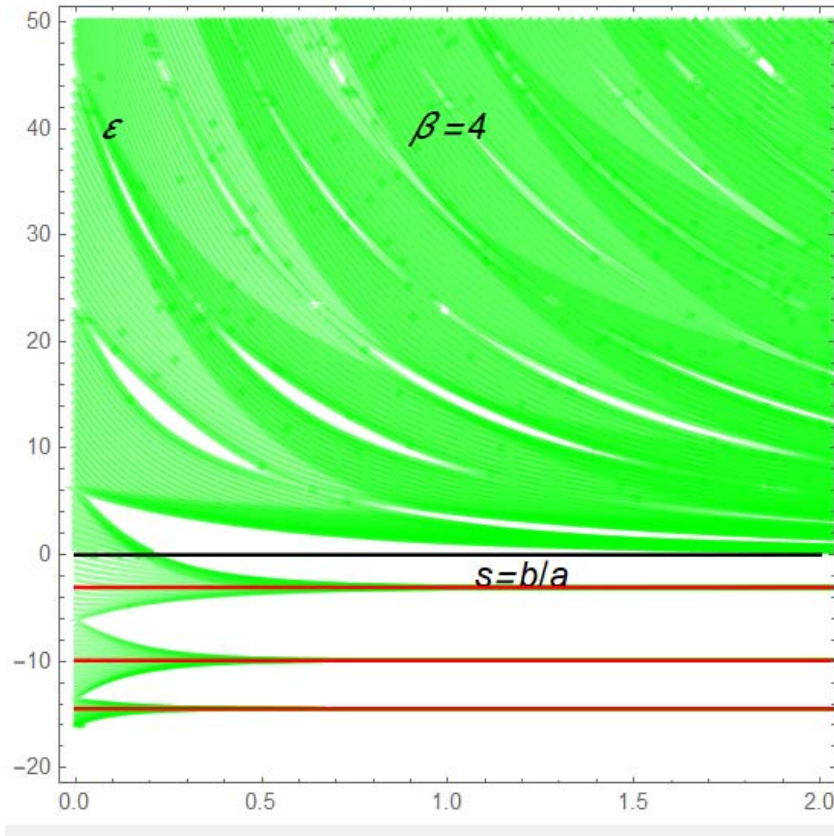


Fig.28 $\beta = 4$. Energy vs $s = b/a$. The parameter x of $ka = \pi x$ is changed between 0 and 1. The red lines denotes the bound state in the limit of $s \rightarrow \infty$. There are three bound states.

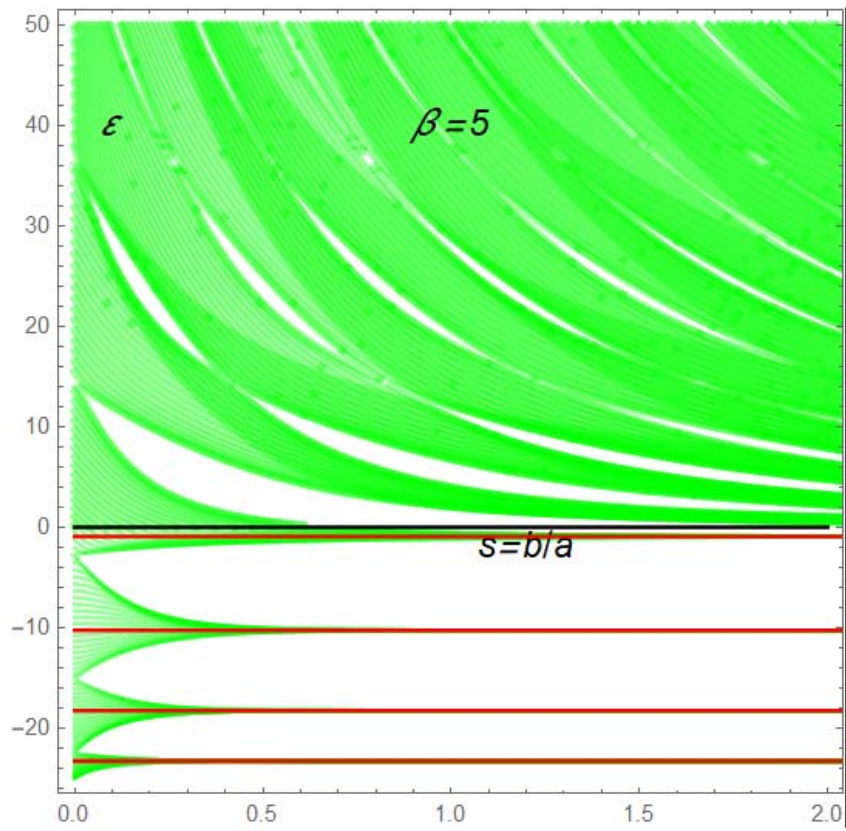
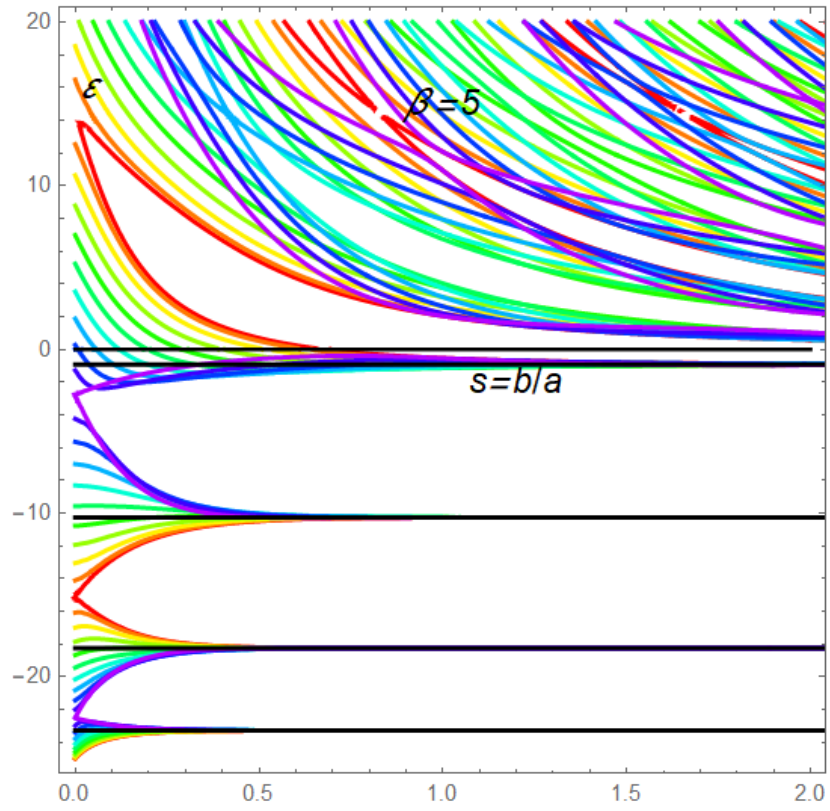


Fig.29 $\beta = 5$. Energy vs $s = b/a$. The parameter x of $ka = \pi x$ is changed between 0 and 1. The red lines denotes the bound state in the limit of $s \rightarrow \infty$. There are four bound states.

13. Effective mass

Ground state ($k = 0$) energy for an electron in a periodic square well (attractive) potential of depth $U_0 = \frac{2\hbar^2}{ma^2}$. The energy is lowered as the wells come closer together. Here a is held constant and b is varied. The large b/a corresponds to separated atoms. The ground energy is much lower for atoms at the actual spacing in the metal than for isolated atoms.

(a) The energy $\frac{E}{U_0} = \varepsilon$ vs ka , where $s = b/a$ is changed as a parameter.

$$E = E_{k=0} + \frac{\hbar^2}{2m^*} k^2, \quad (\text{energy dispersion relation})$$

$$\frac{E}{U_0} = \varepsilon = -\frac{\hbar^2 K^2}{2m} \frac{ma^2}{2\hbar^2} = -\frac{1}{4}(Ka)^2,$$

$$\varepsilon = \frac{E}{|U_0|} = \frac{E_{k=0}}{|U_0|} + \frac{\hbar^2}{2m^*} k^2 \frac{ma^2}{2\hbar^2} = \frac{E_{k=0}}{|U_0|} + \frac{m}{4m^*} (ka)^2.$$

When $m^* = m$, we have $m/(4m^*) = 0.25$. The following figure show the wave number dependence of the energy eigenvalue for $\beta = 1$, where the ratio b/a is changed as a parameter. It can be well

described by $\varepsilon = \frac{E}{|U_0|} = \frac{E_{k=0}}{|U_0|} + \frac{m}{4m^*} (ka)^2$ The least squares fit of the data (ε vs ka) to this

quadratic equation yields the relation of the mass ratio $m/(4m^*)$ as a function of the ratio b/a .

We find that the mass ratio $m/(4m^*)$ decreases with increasing the ratio b/a .

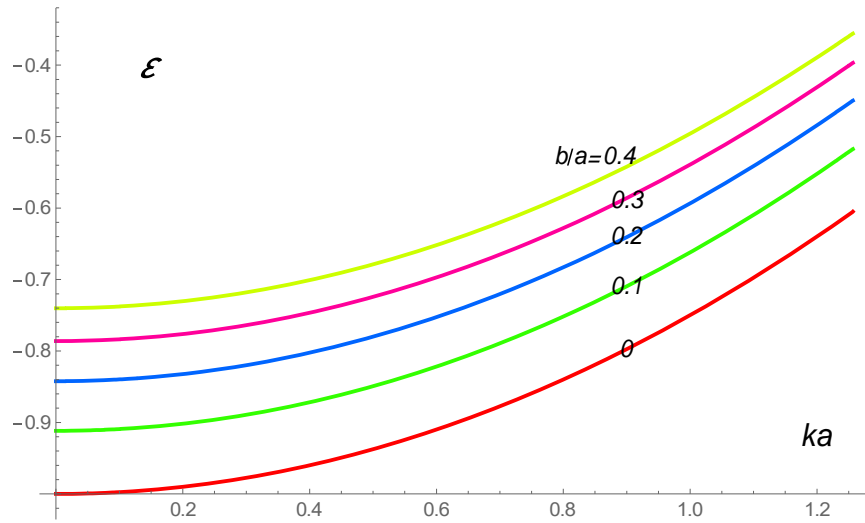


Fig.30 Energy ϵ vs ka as the parameter $s = b/a$ is changed. $\beta = 1$. The maximum value of ka , $(ka)_{\max} = \frac{\pi}{1+s}$. $(ka)_{\max} = \pi$ at $s = 0$. $(ka)_{\max} = 2.244$ at $s = 0.4$.

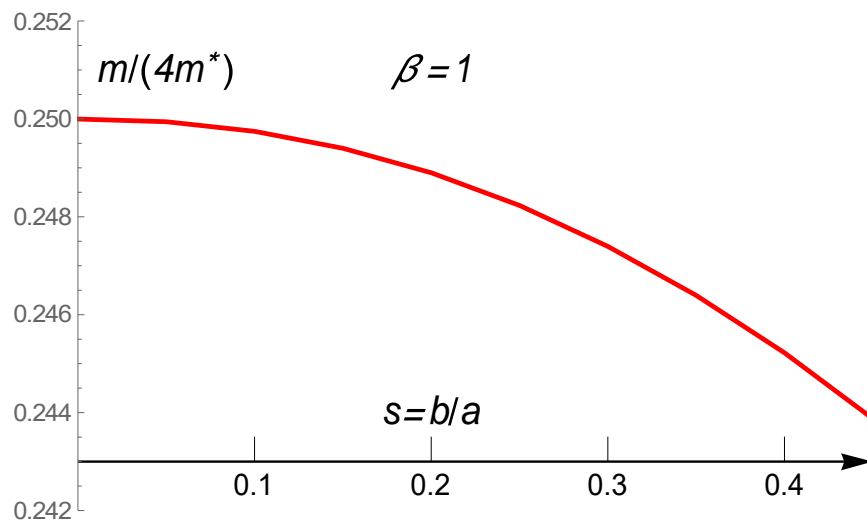


Fig.31 Effective mass ratio $m/(4m^*)$ vs $s = b/a$ for the ground state with $\beta = 1$. At $b/a = 0$, $m^* = m$

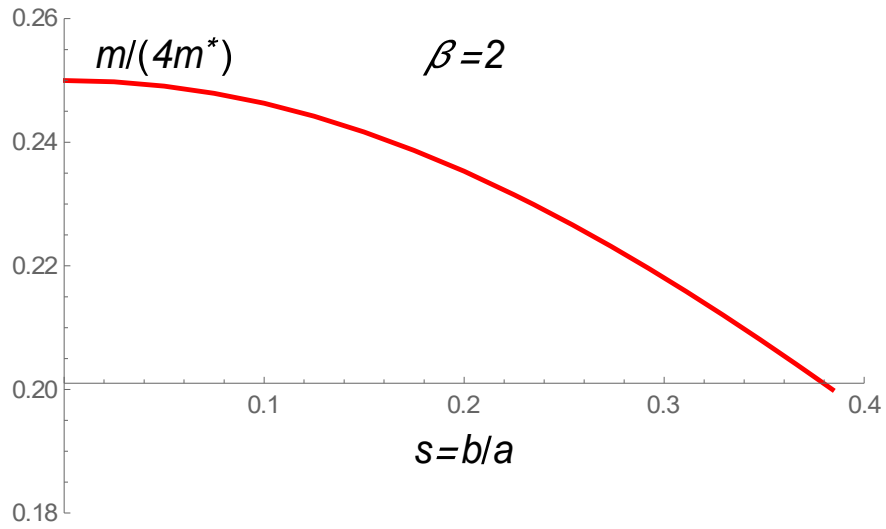


Fig.32 Effective mass ratio $m/(4m^*)$ vs $s = b/a$ for the ground state with $\beta = 2$. At $b/a = 0$, $m^* = m$

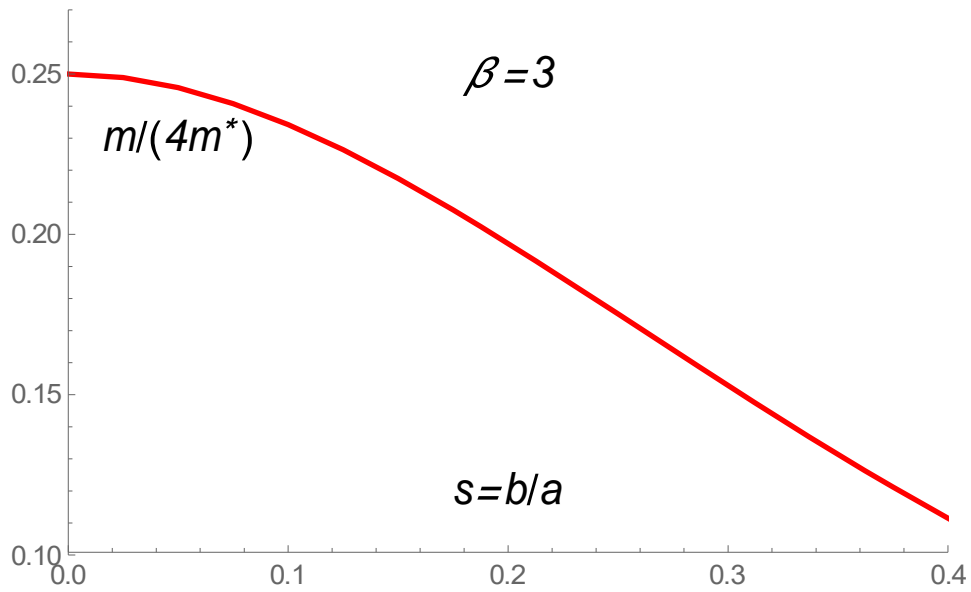


Fig.33 Effective mass ratio $m/(4m^*)$ vs $s = b/a$ for the ground state with $\beta = 3$. At $b/a = 0$, $m^* = m$.

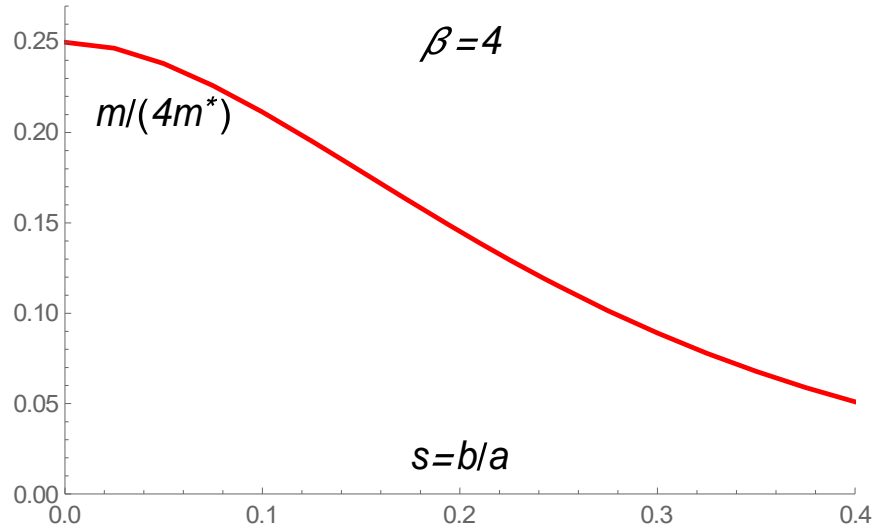


Fig.34 Effective mass ratio $m/(4m^*)$ vs $s = b/a$ for the ground state with $\beta = 4$. At $b/a = 0$, $m^* = m$.

14. Conclusion

Using the 1D Kronig-Penney model on an electron in a periodic (attractive) square well potential with the width a and the separation b , we have determined exactly the energy eigenvalue of electron, as a function of ka , the ratio $s = b/a$, and the potential depth ($\beta = U/U_0$). We use the Mathematica 12.0 for the calculation of the energy eigenvalue. In this system, the wavefunction of ground state has an even parity. For $ka = 0$, the energy eigenvalue $\varepsilon = E/U_0$ for the ground state increases with increasing the ratio b/a and reaches the ground-state energy of the isolated system (in the limit of $s \rightarrow \infty$), which is the origin of the cohesive energy of metals. For fixed ratio $s = b/a$, the energy-eigenvalue increases with increasing ka in the small value of ka . The effective mass ratio defined by $m/(4m^*)$ is equal to 0.25 at $s = b/a$, and decreases with increasing the ratio s . This result is in good agreement with that predicted from the perturbation theory.

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APPENDIX ((Mathematica)) Derivation of Fig.27

```

Clear["Global`*"];
EN1[x_, β_] := Module[{s1, x1, h1, h2, β1}, x1 = x;
  β1 = β;
  h1 = -√(-y) √(β1² + y) Cos[x1 (1 + s1)] +
    √(-y) √(β1² + y) Cos[2 √(β1² + y)] Cosh[2 s1 √(-y)] -
    (β1² + 2 y) / 2 Sin[2 √(β1² + y)] Sinh[2 s1 √(-y)];
  ContourPlot[Evaluate[h1 == 0], {s1, 0, 2}, {y, -10, 0},
    ContourStyle → {Hue[0.25 x1], Thick}, PlotPoints → 60];
EN2[x_, β_] := Module[{s1, x1, p1, p2, β1}, x1 = x;
  β1 = β;
  p1 = -√y √(β1² + y) Cos[x1 (1 + s1)] +
    √y √(β1² + y) Cos[2 √(β1² + y)] Cos[2 s1 √y] -
    (β1² + 2 y) / 2 Sin[2 √(β1² + y)] Sin[2 s1 √y];
  ContourPlot[Evaluate[p1 == 0], {s1, 0, 2}, {y, 0, 10}, PlotPoints → 60,
    ContourStyle → {Hue[0.25 x1], Thick}];
U11 = Show[Table[{EN1[a π, 3], EN2[a π, 3]}, {a, 0, 1.0, 0.1}], PlotRange → All];
U12 = Graphics[{Text[Style["s=b/a", Black, 15, Italic], {1.0, -1.2}],
  Text[Style["ε", Black, 15, Italic], {0.05, 9}],
  Text[Style["β=3", Black, 15, Italic], {1, 9}], Black, Thick,
  Line[{{0, 0}, {2, 0}}]};

```

```

a1 = -7.63082;
a2 = -3.806784;
U13 = Graphics[{Black, Thick, Line[{{0, a1}, {2, a1}}],
  Line[{{0, a2}, {2, a2}}]}}];
Show[U11, U12, U13, PlotRange -> {{0, 2}, {-10, 10}}]

```

