

This note¹ deals with approximate treatments of two real-life systems; atoms and periodic solids. The focus will be on finding their ground states. These systems will both be treated in the simplest approximation where the electron-electron interactions will be neglected, and the lowest energy state is built up by filling electrons into low-energy single-particle states one at a time.

Atoms

An atom(ion) with Z protons and N electrons is described by the Hamiltonian

$$H = \sum_{i=1}^N \left(\frac{\vec{P}_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_i|} \right) + \sum_{i,j,i \neq j} \frac{1}{2} \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|}.$$

The first sum describes N electrons, each feeling a Coulomb-potential of the nucleus which has charge Ze . The second (double) sum describes the electron-electron repulsion. Note that we have not included relativistic corrections, nor interactions between electron spins/nuclear spins. $\vec{r}_i$ and $\vec{P}_i$ are the position and momentum operators respectively acting on electron i .

This Hamiltonian cannot be solved exactly, so we will use approximations. First, we will simply omit the electron-electron term. Then the Hamiltonian separates into N hydrogen-like problems with a nuclear charge Ze . Remembering that each electron also has a spin-1/2 degree of freedom we can write a general energy eigenstate of the simplified Hamiltonian as

$$|\psi\rangle = |n_1 l_1 m_1\rangle \otimes |n_2 l_2 m_2\rangle \otimes \dots \otimes |n_N, l_N, m_N\rangle \otimes |m_{s1}\rangle \otimes |m_{s2}\rangle \otimes \dots \otimes |m_{sN}\rangle$$

where the N first factors are the spatial parts of the hydrogen-like energy eigenstates of electron number 1 to N , and the last N factors are spin-1/2 S_z eigenstates for electrons 1 to N . Possible values for the quantum numbers are $n_i \in \{1, 2, \dots\}$, $l_i \in \{0, 1, \dots, n-1\}$, $m_i \in \{-l_i, -l_i + 1, \dots, l_i\}$, and $m_{si} \in \{-1/2, +1/2\}$. We have neglected spin-interactions in the Hamiltonian, so all states that differ by their spin arrangements are degenerate. The energy of this state is found by applying the Hamiltonian to the state.

$$H|\psi_N\rangle = E_{1z} \left(\sum_{i=1}^N \frac{1}{n_i^2} \right) |\psi_N\rangle$$

where $E_{1z} = -13.6\text{eV} * Z^2$. Thus the energy is just the sum of the single-particle energies of the N electrons. Although it is an energy eigenstate of the simplified Hamiltonian, the state $|\psi\rangle$ is not a proper fermionic state as is required for a system of identical fermions. It should be antisymmetric with respect to the interchange of any two particle labels. In order to construct a proper fermionic state, we will have to add other states with the same set of quantum numbers $\{n_i, l_i, m_i, m_{si}\}$, but distributed such that when interchanging particle labels the state is antisymmetric. Here is an example of a fermionic (unnormalized) state with two electrons:

$$|\psi_2\rangle = |n_1, l_1, m_1\rangle \otimes |n_2, l_2, m_2\rangle \otimes |m_{s1}\rangle \otimes |m_{s2}\rangle - |n_2, l_2, m_2\rangle \otimes |n_1, l_1, m_1\rangle \otimes |m_{s2}\rangle \otimes |m_{s1}\rangle$$

¹Adapted from Griffiths "Introduction to quantum mechanics", Cambridge Univ. Press.

Atoms and solids

Note that if the spatial states are identical, for instance $|n_1 = 1, l_1 = 0, m_1 = 0\rangle$ and $|n_2 = 1, l_2 = 0, m_2 = 0\rangle$, this state reduces to

$$|\psi_2\rangle = |1, 0, 0\rangle \otimes |1, 0, 0\rangle \otimes (|m_{s1}\rangle \otimes |m_{s2}\rangle - |m_{s2}\rangle \otimes |m_{s1}\rangle)$$

and we see that m_{s1} must be different from m_{s2} , otherwise the state is just the null state which is not physical. Thus two particles cannot share the same set of quantum numbers in a fermionic state. This is the Pauli principle. In this simplified treatment of the Hamiltonian where we have omitted the e-e-repulsion we note that the lowest energy state of the atom(ion) is the one which has the lowest sum of single-particle energies. Thus to find the ground state of the atom(ion) we want to construct the fermionic state with as many low single-electron parts as possible. If we for instance take all the spatial parts to be $|1, 0, 0\rangle$ then we have the lowest possible energy. While possible for $N = 2$ as seen above, this is not possible for $N > 2$. This can be seen from

$$|\psi_3\rangle = |1, 0, 0\rangle \otimes |1, 0, 0\rangle \otimes |1, 0, 0\rangle \otimes |\chi_3\rangle$$

where the spin part $|\chi_3\rangle$ is

$$\begin{aligned} |\chi_3\rangle = & |m_{s1}\rangle \otimes |m_{s2}\rangle \otimes |m_{s3}\rangle - |m_{s2}\rangle \otimes |m_{s1}\rangle \otimes |m_{s3}\rangle + |m_{s2}\rangle \otimes |m_{s3}\rangle \otimes |m_{s1}\rangle \\ & - |m_{s2}\rangle \otimes |m_{s1}\rangle \otimes |m_{s3}\rangle + |m_{s3}\rangle \otimes |m_{s1}\rangle \otimes |m_{s2}\rangle - |m_{s3}\rangle \otimes |m_{s2}\rangle \otimes |m_{s1}\rangle \end{aligned}$$

Now the only possibilities for $m_s = \pm 1/2$, thus it is unavoidable that at least two of the three single-spin states $|m_{s1}\rangle, |m_{s2}\rangle, |m_{s3}\rangle$ are equal, and therefore $|\chi_3\rangle = |null\rangle$, and $|\psi_3\rangle$ is therefore an unphysical state. So at most two electrons can have the same spatial state. To write down the lowest energy state for an atom(ion) with three electrons we need to also include, in addition to two $|1, 0, 0\rangle$'s, one state with $n = 2$, that is any one of $|2, 1, \pm 1\rangle$ or $|2, 1, 0\rangle$. They all have the same single-particle energy as the energy depends on n alone. The different choices of l, m and m_s means that the ground state is degenerate. For an atom(ion) with four electrons one needs another $n = 2$ state. There can be at most

$$2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$$

level- n single-particle states in a fermionic state. The 2 is for spin-up and down, the sum over l are over all allowed l values, and the factor $(2l+1)$ signifies the number of m values for each l . To find how the ground state is built up from single-particle states for a given number of electrons N , one fills the shell with $n = 1$ first, then the one with $n = 2$ and so on until one has filled in N electrons. Every time a shell is filled the energy per particle makes a jump since the next particle must be in a shell which is higher in energy. These atoms with filled shells are thus expected to be particularly stable. If we define the inert elements as those where a shell is filled, we get predictions for the inert elements as follows from the table 1. This prediction for the inert elements, except for He and Ne, does not match very well the inert elements (noble gases) of periodic table. Thus we need to improve our approximation and take better into account the electron-electron repulsion that we have so far neglected.

Atoms and solids

n	#	Predicted inert elements and names
1	2	2 (He)
2	8	10 (Ne)
3	18	28 (Ni)
4	32	60 (Nd)

Table 1: The maximum number (#) of single-particle states with a certain principal quantum number n in a fermionic state.

To take into account the e-e-repulsion in an approximate way we propose that it merely changes the Coulomb potential so that if the electron is close to the nucleus, it sees the full nuclear charge Ze due to the Z protons, while if it is far outside the other electrons it sees only the charge $(Z - (N - 1))e$ since the $N - 1$ other electrons screen the interaction. This modified potential far from the nucleus is still rotationally symmetric, but does no longer decay as $1/r$. This means that the single-particle energies become dependent on both n and l . A set of single-particle quantum numbers (n, l) is known as a subshell, and takes at most $2(2l + 1)$ electrons. It is standard notation to name such a subshell as "n char _{l} ", where char _{l} is a lower case coding character: $\{s, p, d, f, g, h, i, k, \dots\}$ corresponding to $l = \{0, 1, 2, 3, 4, 5, 6, 7, \dots\}$, respectively. For instance, $4f$ means $(n, l) = (4, 3)$. With

(n,l)	name	#
(1,0)	1s	2
(2,0)	2s	2
(2,1)	2p	6
(3,0)	3s	2
(3,1)	3p	6
(3,2)	3d	10

Table 2: All subshells with $n \leq 3$, their names and max number of electrons in each.

this subshell encoding one can specify which single-particle states (or at least their values of (n, l)) that occur in a given state by a string such as

$$(1s)^2(2s)^2(2p)^5$$

which means two electrons in $1s$, two in $2s$ and five in $2p$. Such a string is termed an electron configuration. It does not uniquely specify the lowest energy state of the atom as values of m and m_s are not specified. However, it contains the main ingredients to identify its energy. Sometimes the electron configuration alone is enough to uniquely specify the state. For instance $(1s)^2$ is the state $|\psi_2\rangle$ above as both $m_1 = m_2 = 0$ and the spin state must be antisymmetric since the spatial state is symmetric.

In order to construct the electron configuration appropriate for the ground state of atoms we need to know the energies of the different single-particle subshells. These must be determined from numerical or approximate calculations considering the e-e-repulsion treated in an average way known as the Thomas-Fermi approximation. The result from such calculations is that in general a lower n value has lower energy. A higher l value has higher energy, because it is farther from the nucleus and so is less bound because of the

Atoms and solids

screening of the nucleus by the other electrons. There is a rule of thumb for the energy sequence of the subshells, known as the Madelung rule or aufbau principle, which says that the energy sequence goes as $n + l$, and for same values of $n + l$ the largest n has the largest energy. From the Madelung rule one can make Table 3 where the energy is increasing towards the right and downwards with approximately same energies on the same line. The Madelung rule applies only to neutral atoms ($N = Z$) in their ground states. Large gaps

	$n + l$			
1s	1			
2s 2p	2	3		
3s 3p	3	4		
4s 3d 4p	4	5	5	
5s 4d 5p	5	6	6	
6s 4f 5d 6p	6	7	7	7
7s 5f 6d 7p	7	8	8	8

Table 3: Sequence of energies for different subshells following the Madelung rule. The lowest energy is at the top left. Going right, the subshell energies increase slightly. Moving a line down the energy increases a bigger amount. The right part of the diagram shows the corresponding values of $n + l$.

in energies are encountered when the p -shells are filled, and we identify these with the inert elements (noble gases). There are exceptions to the Madelung rule: Copper which has 29 electrons is $[Ar](4s)^2(3d)^9$ after the Madelung rule where $[Ar]$ means the electron configuration of Argon, but is actually closer to $[Ar](4s)^1(3d)^{10}$. There are also exceptions for some other atoms with partially filled d and f subshells. Note how Table 3 is similar to the periodic table. Atoms with same electron-structure in the outer shell are chemically equivalent.

Atoms: Ground state multiplets

As mentioned in the previous section the electron configuration does not completely specify the ground state of the atom because of the remaining m and m_s degeneracies. However, the atom is rotationally invariant which means that the ground state can be labelled by the quantum numbers of the total angular momentum J , the total orbital angular momentum L and the total spin S . Thus it is possible to specify the degeneracy further by determining the angular momentum multiplet structure of the ground state.

In this section we will describe how to determine this. Let us begin with a simple example; that of an atom with electron configuration $(1s)^2$. For this example the two electrons have orbital angular momentum $l = 0$ and spin $s = 1/2$ each. The total orbital angular momentum is therefore $L = 0$ and the total spin is $S = 0$ or $S = 1$ since two spin-1/2 either combine into a spin singlet ($S = 0$) or a spin triplet ($S = 1$). With $l = 0$ for each electron, the spatial state is necessarily symmetric as the l_1, l_2, m_1 and m_2 are all 0. Thus the spin state must be antisymmetric. Only the $S = 0$ state is antisymmetric under the interchange of the two electrons, so it is the only one allowed. Combining the total orbital angular momentum with the total spin, we find that the total angular momentum must be $J = 0$. We denote the resulting atomic state: $^1S_0$ where we have used the

Atoms and solids

notation $^{2S+1}L_J$ where the code character $L = \{S, P, D, F, G, H, I, K\}$ corresponds to the total orbital angular momentum being $L = \{0, 1, 2, 3, 4, 5, 6, 7, \dots\}$, respectively. In general a filled subshell has $L = 0$ and $S = 0$.

A more involved example is that of carbon which has six electrons. Carbon has electron configuration $(1s)^2(2s)^2(2p)^2$. Thus there are two filled subshells, each with $L = 0$ and $S = 0$. The two p electrons have $l = 1$ and $s = 1/2$ each. Therefore the possible values of L and S are

$$L = \{0, 1, 2\}, \quad S = \{0, 1\}.$$

Using the Clebsch-Gordan tables we can infer the symmetry under the interchange of the two particle labels. For the combination of the two $l = 1$ s we inspect the Clebsch-Gordan table 1×1 and get the result in Table 4. Combining the two spin- $1/2$ s we use the $1/2 \times 1/2$

L	symmetry
0	+
1	-
2	+

Table 4: Symmetry under the interchange of particle label for combining two $l = 1$. + means symmetric and - means antisymmetric.

table and get the spin singlet and the spin triplet which has symmetry properties shown in Table 5 Interchanging particle labels means interchanging both the spin and orbital part.

L	symmetry
0	-
1	+

Table 5: Symmetry under the interchange of particle label for combining two $s = 1/2$.

Taking the product of the signs we thus find the symmetry under interchange of labels in Table ?? So only the (L, S) combinations $(0, 0)$, $(1, 1)$ and $(2, 0)$ satisfy the fermionic

(L,S)	symmetry
(0,0)	-
(0,1)	+
(1,0)	+
(1,1)	-
(2,0)	-
(2,1)	+

Table 6: Symmetry under the interchange of particle label for combining two $s = 1/2$. The symmetry is the product of the signs found in Tables 4 and 5.

symmetry requirement. $(0, 0)$ is denoted $^1S_0$ while $(1, 1)$ can be $^3P_0$, $^3P_1$ or $^3P_2$ dependent on the value of J and $(2, 0)$ is $^1D_2$. These possible ground state spin and angular momentum multiplets for carbon allowed by the fermionic symmetry are shown in Table 7. Which one these has the lowest energy is determined by the effects of the e-e-interaction that we

(L, S)	J	$^{2S+1}L_J$
(0,0)	0	$^1S_0$
(1,1)	0,1,2	$^3P_0, ^3P_1, ^3P_2$
(2,0)	2	$^1D_2$

Table 7: Symmetry-allowed ground state multiplets for carbon.

have so far neglected. That is we need to go beyond the approximation where the e-e-repulsion is only considered to modify the Coulomb interaction between the electron and the nucleus. Treating the e-e-repulsion in a more accurate way one arrives at a set of rules for determining the lowest energy multiplet known as Hund's rules. Hund's rules are to be applied in sequence, until there is only one multiplet left. They are:

1. Highest S has lowest energy.
2. Highest L has lowest energy.
3. If subshell more than half-filled, then $J = L + S$ has lowest energy, otherwise $J = |L - S|$ has lowest energy.

Applying Hund's first rule to the symmetry-allowed multiplets of carbon, we find that the highest S states are $^3P_0, ^3P_1, ^3P_2$. Then we apply Hund's second rule to these. They all have $L = 1$, thus the second rule does not constrain the choice further. We therefore need to apply Hund's third rule. The p shell takes six electrons. It has only two in its p -shell, thus the subshell is less than half-filled, which by Hund's third rule implies that $J = 0$ has the lowest energy. This means that $^3P_0$ is the ground state multiplet of carbon.

Solids

Solids consists of many atoms in a periodic arrangement. They are thus naturally more complex than a single atom studied in the previous section. We will study two simple models of a solid.

Free fermions in an empty box

We begin by the very simplest model, where we totally ignore the positively charged periodic ion lattice and the electron-electron interactions. Thus we take the N electrons to be simply uncharged fermions inside a cubic box of volume $V = L^3$. The Hamiltonian of this simplest of models for a solid is

$$H = \sum_{i=1}^N \left(\frac{\vec{P}_i^2}{2m} + V_{pot}(\vec{r}_i) \right)$$

where $V_{pot}(\vec{r}) = 0$ inside the box and ∞ outside. The Hamiltonian does not couple the different particles, and so separates into N independent particle-in-a-box problems. The particle-in-a-box problem has unnormalized energy eigenfunctions characterized by quantum numbers (k_x, k_y, k_z)

$$\psi_{\vec{k}}(\vec{r}) = \sin(k_x x) \sin(k_y y) \sin(k_z z).$$

Atoms and solids

The potential outside the box is infinity, so the wave function must vanish at the box boundaries. This means that $\psi_{\vec{k}}(L, y, z) = \psi_{\vec{k}}(x, L, z) = \psi_{\vec{k}}(x, y, L) = \psi_{\vec{k}}(0, y, z) = \psi_{\vec{k}}(x, 0, z) = \psi_{\vec{k}}(x, y, 0) = 0$ which implies that $k_x = \frac{\pi}{L}n_x$, $k_y = \frac{\pi}{L}n_y$, $k_z = \frac{\pi}{L}n_z$, where $n_x, n_y, n_z \in \{1, 2, 3, \dots\}$. States with either of the n 's zero are identically zero and therefore not allowed, while states with negative n 's differ by a sign from states with positive n 's thus describe the same state, and so should not be counted twice. The associated energy of these single-particle energy eigenfunctions are

$$E_{\vec{k}} = \frac{\hbar^2}{2m} \vec{k}^2 = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2).$$

Thus we can visualize the allowed one-particle quantum numbers as points in $\vec{k}$ -space where all the components of $\vec{k}$ are positive and where there is a spacing π/L between nearby points in all three directions. Thus each single-particle eigenstate can be considered to take up a volume $(\frac{\pi}{L})^3$ in $\vec{k}$ -space. The energy is proportional to $\vec{k}^2$ so the states closest to the origin are lowest in energy, and the energy increases the further away from the origin $\vec{k}$ is. In order to find the ground state of the solid with N electrons, we will construct a fermionic state involving as many as the low-lying one-particle states as possible. This means that we will build the ground state of the solid in the same way as we built the atom in the previous section, by filling in single-particle states with successively higher energies, one at a time. The lowest energy state is the state $|1, 1, 1\rangle$. Antisymmetrizing in the two electron spins we can fill in 2 electrons in this state. The next states are $|2, 1, 1\rangle, |1, 2, 1\rangle, |1, 1, 2\rangle$. Each of these takes two electrons, and so we can fill in six electrons here. Going further, we want figure out how many electrons can be filled into states which have $|\vec{k}| < k_f$, where k_f is a certain length in $\vec{k}$ -space. We do this by taking the volume of one-eighth (the positive octant) of a sphere of radius k_f and divide by the volume each $\vec{k}$ -state takes up. This gives

$$\text{\#single-particle states with } |\vec{k}| < k_f = \frac{1}{8} \frac{4\pi k_f^3}{3} \frac{L^3}{\pi^3} = \frac{1}{6\pi^2} (k_f L)^3$$

Filling in two electrons in each of these means that the lowest energy is found by filling up states to k_f such that

$$N = 2 \frac{1}{6\pi^2} (k_f L)^3 \implies k_f L = (3\pi^2 N)^{1/3} \implies k_f = (3\pi^2 N/V)^{1/3}$$

where we have used $V = L^3$. The distance k_f from the origin in $\vec{k}$ -space marks the boundary between occupied and unoccupied single-particle states. It is called the Fermi wave vector. The corresponding energy $E_f = \frac{\hbar^2 k_f^2}{2m}$ is known as the Fermi energy. While the Fermi wave vector and energy as introduced here strictly hold for the free particle model, these concepts hold more generally and the Fermi wave vector is defined more generally as the boundary between occupied and unoccupied single-particle states.

The total energy of the solid in this approximation can be calculated easily by summing over all single-particle energies of occupied states. We find

$$\begin{aligned} E &= \sum_{|\vec{k}| < k_f} \epsilon_{\vec{k}} \approx \frac{2}{8} \frac{L^3}{\pi^3} \int_0^{k_f} dk k^2 4\pi \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 L^3}{2\pi^2 m} \int_0^{k_f} dk k^4 = \frac{\hbar^2 L^3}{10\pi m} k_f^5 = \frac{\hbar^2 V}{10\pi^2 m} (3\pi^2 N/V)^{5/3} \\ &= aN \left(\frac{N}{V} \right)^{2/3} \end{aligned}$$

where a is a constant. With this result we can calculate the internal pressure of the solid (which would be what determines its the compressibility of the solid) in this approximation as a Fermi gas of non-interacting particles

$$P = -\frac{\partial E}{\partial V} = -a \frac{2}{3} N \left(\frac{N}{V} \right)^{-1/3} \left(-\frac{N}{V^2} \right) = \frac{2}{3} \frac{E}{V}. \quad (1)$$

Periodic potential

The next and more realistic model for a solid consists of letting the electrons move in an underlying periodic potential due to the periodic crystal arrangement of the nuclei, While this periodic arrangement is really in three dimensions, we will here consider a simpler one-dimensional example. It still contains many of the essential features of the more realistic three dimensional model. We thus have a Hamiltonian which is

$$H = \sum_{i=1}^N \left(\frac{P_i^2}{2m} + V(x_i) \right) \quad (2)$$

where $V(x_i)$ now is a periodic potential with period a . That is $V(x+a) = V(x)$. We will also make this one-dimensional material a ring, so that periodic boundary conditions can be used. The reasons for doing this is to eliminate boundary/surface effects to focus on the bulk behavior of the solid.

Energy eigenfunctions of a single particle moving in a periodic potential is of a certain form. They follow what is known as Bloch's theorem. Let us consider one particle moving in the periodic potential. The periodic potential is invariant under translation by a . Thus the Hamiltonian possesses a symmetry and its energy eigenstates can also be labelled by the energy eigenvalues of the translation operator T_a . The translation operator by the period a is

$$T_a = e^{a \frac{\partial}{\partial x}} = e^{\frac{i}{\hbar} a P},$$

and is a unitary operator. Its inverse corresponds to a translation by $-a$, that is $T_a^{-1} = T_a^\dagger$. Now an eigenfunction of T_a satisfies

$$T_a \psi(x) = \lambda(a) \psi(x) \implies \psi(x+a) = \lambda(a) \psi(x),$$

where we have explicitly made it clear that the eigenvalue depends on the amount of translation a . Taking the norm of both sides we find that $|\lambda(a)|^2 = 1$ which means that $\lambda(a)$ must be a phase factor $\lambda(a) = e^{i\theta(a)}$ Now a translation by $2a$ should correspond to applying T_a twice. That is $\lambda(2a) = (\lambda(a))^2$ or equivalently

$$e^{i\theta(2a)} = e^{i2\theta(a)} \implies \theta(2a) = 2\theta(a) \implies \theta(a) = \bar{K}a,$$

where $\bar{K}$ is a real constant independent of x and a . Thus the eigenvalue of the translation operator is $e^{i\bar{K}a}$, and we have the relation

$$\psi(x+a) = e^{i\bar{K}a} \psi(x) \quad (3)$$

which holds for the energy eigenfunctions. This is known as Bloch's theorem after Felix Bloch who worked out this in his PhD-thesis under the supervision of Werner Heisenberg. This was also the first application of mathematical group theory in physics.

Kronig-Penney potential

We will now use Bloch's theorem to study a particular periodic potential; the Kronig-Penney potential which consists of a periodic arrangement of M delta-functions spaced by a . The Hamiltonian is

$$H = -\frac{\hbar^2 \partial^2}{2m \partial^2 x} + \alpha \sum_{j=0}^{M-1} \delta(x - ja) \quad (4)$$

where the strength of each delta-function potential is α . We will use periodic boundary conditions where we require that

$$\psi(x + Ma) = \psi(x)$$

Using Bloch's theorem M times this implies

$$e^{i\bar{K}Ma} = 1 \implies \bar{K} = \frac{2\pi n}{Ma}$$

where n is an integer.

In-between the delta-function peaks the potential is zero, thus the eigenfunctions there are like free particles. This means that

$$\psi(x) = A \sin kx + B \cos kx, \quad 0 < x < a \quad (5)$$

where the energy is $E = \hbar^2 k^2 / 2m$. For $a < x + a < 2a$ we use Bloch's theorem and find

$$\psi(x + a) = e^{i\bar{K}a} (A \sin kx + B \cos kx), \quad 0 < x < a$$

which can also be written

$$\psi(x) = e^{i\bar{K}a} (A \sin k(x - a) + B \cos k(x - a)), \quad a < x < 2a \quad (6)$$

Continuity of the wave function at a gives the equation

$$A \sin ka + B \cos ka = e^{i\bar{K}a} B \implies A = B \frac{e^{i\bar{K}a} - \cos ka}{\sin ka} \quad (7)$$

The delta-function potential means that the wave function has a discontinuity in the derivative at a . This can be seen by integrating the Schrödinger equation in a narrow interval around a :

$$\int_{a-\epsilon}^{a+\epsilon} dx \left(-\frac{\hbar^2}{2m} \psi''(x) + \alpha \delta(x - a) \psi(x) \right) = \int_{a-\epsilon}^{a+\epsilon} dx E \psi(x)$$

where ϵ is a small positive number much smaller than a . Performing the integral over the very small interval from $a - \epsilon$ to $a + \epsilon$, we get

$$-\frac{\hbar^2}{2m} [\psi'(a + \epsilon) - \psi'(a - \epsilon)] + \alpha \psi(a) = E \psi(a) 2\epsilon$$

where we have approximated the right hand side by treating $\psi(x)$ as a constant over the small interval. Now taking the limit $\epsilon \rightarrow 0$ we find

$$\psi'(a_+) - \psi'(a_-) = \frac{2m\alpha}{\hbar^2} \psi(a) \quad (8)$$

where a_+ (a_-) means that the function should be evaluated as the $x \rightarrow a$ limit of the expression valid for $x > a$ ($x < a$). Evaluating Eq. (8) by differentiating and inserting the wave function forms in Eqs. (5) and (6), we find

$$e^{i\bar{K}a}Ak - (Ak \cos ka - Bk \sin ka) = \frac{2m\alpha}{\hbar^2}Be^{i\bar{K}a}$$

which can be reorganized into

$$e^{i\bar{K}a}k \left[A \left(1 - e^{-i\bar{K}a} \cos ka \right) + Be^{-i\bar{K}a} \sin ka \right] = \frac{2m\alpha}{\hbar^2}Be^{i\bar{K}a}.$$

Multiplying by $e^{-i\bar{K}a}$ on both sides and inserting the expression for A , we get when multiplying by $\sin(ka)$

$$B \left(e^{i\bar{K}a} - \cos ka \right) \left(1 - e^{-i\bar{K}a} \cos ka \right) + Be^{-i\bar{K}a} \sin^2 ka = \frac{2m\alpha}{\hbar^2 k} B \sin ka$$

Canceling B on both sides, multiplying out the parentheses and using $\sin^2(ka) + \cos^2(ka) = 1$, we get

$$e^{i\bar{K}a} - 2 \cos(ka) + e^{-i\bar{K}a} = \frac{2m\alpha a \sin(ka)}{\hbar^2 ka}$$

which also can be written

$$\cos(\bar{K}a) = \cos(ka) + \frac{m\alpha a \sin(ka)}{\hbar^2 ka}. \quad (9)$$

Finally introducing the variable $z \equiv ka$, and $\beta = m\alpha a/\hbar^2$, the energy becomes $E = \hbar^2 z^2/2ma^2$ and the allowed values of z is determined from Eq. (9) which becomes

$$\cos(\bar{K}a) = \cos(z) + \beta \frac{\sin(z)}{z}. \quad (10)$$

We solve this equation graphically. Plotting the right hand side of the equation as a function of z we see, Fig. 1, that it is a function that oscillates with a gradually diminishing amplitude until it becomes a pure cosine-function. The $\cos \bar{K}a$ -function takes values in the interval $[-1, 1]$, thus only values of z which gives values for the right hand side in this interval can solve the equation. When the number of delta-functions M is large the allowed values of $\bar{K}$ approaches a continuum in the interval $[-1, 1]$. It follows that in the same limit the allowed values for z approaches continua shown as blue shaded regions in the figure. When converting z to energy, these regions are known as energy bands. The energy bands are separated by energy gaps where no states exists. The number of states in an energy band depends on the number of $\bar{K}$ values in one period of the cosine-function. Since $\bar{K}a = 2\pi n/M$ we see that there are M values of $\bar{K}a$ in-between 0 and 2π . Thus each energy band contains M states, and can therefore accommodate $2M$ electrons.

For a system with N electrons, the bands will be filled up filling the lowest energy states first. If the number of electrons per nuclei is even, that is $N = mM$ where M is the number of nuclei and m is an even integer, the last band to be filled will be completely filled up. Thus the highest lying filled single-particle energy states will be separated by

the energy gap to the next higher-energy unoccupied states. This means that the system will be difficult to excite, and will not react to a small electric field. Thus the solid is an insulator. On the contrary if m is an odd integer, the last band to be filled will be half-filled. Then the highest occupied states are then only infinitesimally far away from the lowest unoccupied states (for large M) and so even a small perturbing electric field will cause the electrons to move. Thus in this case the solid is a metal. Although our periodic model for a solid is exceedingly simple, it does explain the basic difference between an insulator and a metal.

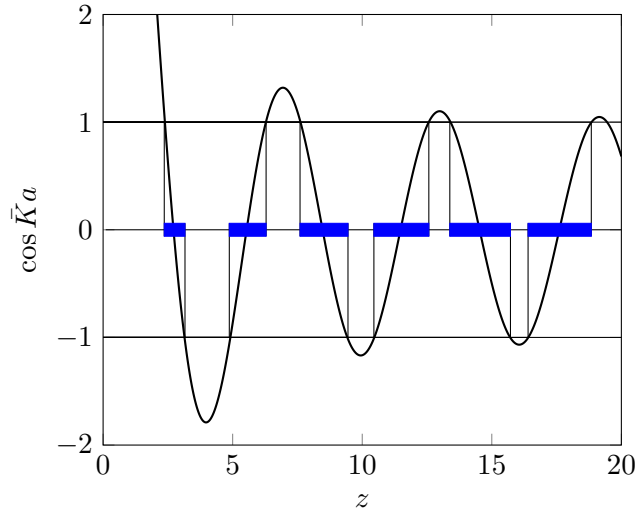


Figure 1: Graphical solution of Eq. (10) that determines allowed values of $z \equiv ka$. The allowed values of z are lying in the blue shaded regions, and implies that the single-particle energies consists of energy bands separated by gaps.