

Fourier Series Solution

1. Introduction

We now try the method of putting the approximations off until the end (rather than at the beginning: as in approximating the solutions as those of free electrons subject to a slight perturbation, or approximating the potential as a square well and then solving the Schrodinger Equation as we did in the previous two sections). We will work mainly in 1-D (x) since we assume that Schrodinger's Equation can be separated as we did before: $\psi(x,t) = X(x)*Y(y)*Z(z)*T(t)$.

We do *not* try to put in potential energy in closed form, but rather we put the **potential energy in the form of a Fourier Series** since the potential energy as a function of distance repeats over the distance, a (the interatomic distance):

$$PE(x) = \sum_{n=-\infty}^{+\infty} U_n \exp[ik_n x], \quad \text{where } k_n = n(2\pi/a) = nG.$$

Recall that $(2\pi/a)$ was what we labelled as G_x , the x component of the reciprocal lattice vector. Since we are only working in 1-D, we'll use G for G_x in the work below.

Even though it looks like $PE(x)$ as expressed above is a complex function, due to the symmetry of the lattice, for any particular value of n , such as s : $U_{-s} = U_s$; and $k_{-s} = -s(2\pi/a) = -k_{+s}$; therefore

$$U_{-s} e^{-is(2\pi/a)x} + U_{+s} e^{+is(2\pi/a)x} = 2U_s \cos([2\pi s/a]x) = 2U_s \cos(k_s x)$$

which is real - as the potential energy function should be!

2. Schrodinger's Equation

Using the above expression for the potential energy, Schrodinger's Equation in 1-D becomes:

$$(-\hbar^2/2m) \partial^2 \psi(x,t) / \partial x^2 + [\sum_n U_n e^{inGx}] \psi(x,t) = i\hbar \partial \psi(x,t) / \partial t.$$

If we try the method of separation of variables as we did before for the free electron case:

$\psi(x,t) = X(x)T(t)$, we get the following two equations for $X(x)$ and $T(t)$:

$$i\hbar dT(t)/dt = \epsilon T(t) \quad \text{and} \quad (-\hbar^2/2m) d^2X(x)/dx^2 + [\sum_n U_n e^{inGx}] X(x) = \epsilon X(x).$$

The first equation gives us: $T(t) = T_0 e^{-i(\epsilon/\hbar)t}$.

This is simply a phase factor that changes over time, but does not affect the probability at all. [Recall that the Probability depends on $\psi^* \psi$.]

3. The differential equation for $X(x)$

The second equation is what we are really concerned with. This is a harder equation to solve, but we can try to solve it by **assuming** a solution in series form:

$$X(x) = \sum_k C_k e^{ikx}.$$

Our assumption is true if this function does indeed satisfy the differential equation. So we simply substitute our trial solution in and see what we get:

$$(-\hbar^2/2m) d^2 [\sum_k C_k e^{ikx}] / dx^2 + [\sum_n U_n e^{inGx}] [\sum_k C_k e^{ikx}] = \epsilon [\sum_k C_k e^{ikx}], \quad \text{or}$$

$$k \sum (\hbar^2 k^2 / 2m) C_k e^{ikx} + \sum_n \sum_k U_n C_k e^{i(k+nG)x} = \sum_k \epsilon C_k e^{ikx}.$$

4. An aside: how to solve such equations

Now before we consider this more fully, consider the following: is there any way that the following equation can be true for all values of x :

$$Ax^2 + Bx + C = 0 \quad ?$$

If we have any particular values of A , B , and C , we can find two values of x that work. The question here is different. Are there values of A , B , and C that will work for **all values of x** ? The only way that this can be true for all values of x is for: $A=0$, $B=0$, and $C=0$. Otherwise there are only two values of x that can make this equation true. Now consider this equation:

$$A \sin(kx) + Bx^{1/2} = 0.$$

The only way this equation can be true for **all values of x** is for $A=0$ and $B=0$. In exactly the same way, our equation at the top of the page can be true only if the coefficients of each of the different functions of x [that is, each of the e^{ikx} terms] are zero.

5. Getting the Central Equation

The first and third terms have simple e^{ikx} terms and so can be added together. The second term, however, involves a double sum rather than a single sum; and the function of x is also a little different: $e^{i(k+nG)x}$. Hence, if we choose to look at some particular e^{ikx} term, then we must choose $k=K$ (where K is one of the k 's in the sum over k) in the first and third terms, but we must have a different k for each value of n in the second sum in the second term such that: $(k+nG)=K$. Hence in looking at this particular function e^{iKx} we get:

$$\{(\hbar^2 K^2/2m) - \epsilon\} C_K e^{iKx} + \sum_n U_n C_{k=K-nG} e^{iKx} = 0.$$

Or, factoring out the e^{iKx} from each term, we get the condition that:

$$\{(\hbar^2 K^2/2m) - \epsilon\} C_K + \sum_n U_n C_{k=K-nG} = 0.$$

We call the equation above the **Central Equation**. This equation holds for each of the different (essentially infinite) values of K . Hence we have changed our problem from one of solving a tough differential equation (Schrodinger's Equation) to one of solving a set of essentially infinite algebraic equations of the form above.

But what are we solving for? Answer: the C_k 's. If we can find all the C_k 's, then we know $X(x)$ and hence $\psi(x,t)$ and hence the probability of finding the electron in the material. (This is the complete solution of Schrodinger's equation, and by knowing this we can find out anything else we need to know!)

Therefore, what we presently have is an essentially infinite number of these Central Equations (one for each of the different values of K), and each of these equations has an essentially infinite number of C_k 's in them. In principle, then, we should be able to solve an infinite number of equations for an infinite number of unknowns. But of course being able to do this in principle does not mean being able to do it in practice. It should be obvious that we cannot deal with an essentially infinite number. **This is where we start to employ approximations.** Note that up to this point, we have not assumed anything (other than the existence of the solution in series form).

6. Seeing the set of Central Equations for the C_k 's

Let's see what the Central Equation looks like for $k=K$:

$$\dots + U_{-2G}C_{K(-2G)} + U_{-G}C_{K(-G)} + \{(\hbar^2K^2/2m) - \varepsilon + U_0\}C_K + U_G C_{K+G} + U_{+2G}C_{K+2G} + \dots$$

Let's now see what the Central Equation looks like for $k=K+G$:

$$\dots + U_{-2G}C_{(K+G)(-2G)} + U_{-G}C_{(K+G)(-G)} + \{(\hbar^2[K+G]^2/2m) - \varepsilon + U_0\}C_{K+G} + U_G C_{(K+G)+G} + U_{+2G}C_{(K+G)+2G} + \dots$$

And finally let's see what the Central Equation looks like for $k=K-G$:

$$\dots + U_{-2G}C_{(K-G)(-2G)} + U_{-G}C_{(K-G)(-G)} + \{(\hbar^2[K-G]^2/2m) - \varepsilon + U_0\}C_{K-G} + U_G C_{(K-G)+G} + U_{+2G}C_{(K-G)+2G} + \dots$$

Let's now simplify these three equations and choose $U_0=0$ (setting $U_0=0$ is equivalent to setting $h=0$ at ground level for $PE_{\text{gravity}}=mgh$):

$$k=K+G: \quad \dots + U_{-2G}C_{K+3G} + U_{-G}C_{K+2G} + \{(\hbar^2[K+G]^2/2m) - \varepsilon\}C_{K+G} + U_G C_K + U_{+2G}C_{K-G} + \dots$$

$$k=K: \quad \dots + U_{-2G}C_{K+2G} + U_{-G}C_{K+G} + \{(\hbar^2K^2/2m) - \varepsilon\}C_K + U_G C_{K-G} + U_{+2G}C_{K-2G} + \dots$$

$$k=K-G: \quad \dots + U_{-2G}C_{K+G} + U_{-G}C_K + \{(\hbar^2[K-G]^2/2m) - \varepsilon\}C_{K-G} + U_G C_{K-2G} + U_{+2G}C_{K-3G} + \dots$$

7. Determining whether a solution to this set of equations exists

From algebra theory we know (and you are to *demonstrate this in homework problem 30*) that for a set of simultaneous equations of the following form to have a non-trivial solution (that is, there is always the trivial solution $x=0, y=0, z=0$), the determinate of the coefficients must be zero:

$$\begin{aligned} ax + by + cz &= 0 \\ dx + ey + fz &= 0 \\ gx + hy + jz &= 0 \end{aligned} \quad \text{has a non-trivial solution only if} \quad \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & j \end{vmatrix} = 0$$

What this means in our case, is that for our solution of Schrodinger's equation to work, the following (essentially infinite) determinate must be zero:

[below, for space considerations, we let $\varepsilon_k = (\hbar^2k^2/2m)$] and only write out the central parts of three lines of the determinate

$$\begin{array}{cccccc} & C_{K+3G} & C_{K+2G} & C_{K+G} & C_K & C_{K-G} & C_{K-2G} & C_{K-3G} \\ \dots & U_{-2G} & U_{-G} & \{\varepsilon_{K+G} - \varepsilon\} & U_G & U_{2G} & U_{3G} & U_{4G} & \dots \\ \dots & U_{-3G} & U_{-2G} & U_{-G} & \{\varepsilon_K - \varepsilon\} & U_G & U_{2G} & U_{3G} & \dots \\ \dots & U_{-4G} & U_{-3G} & U_{-2G} & U_{-G} & \{\varepsilon_{K-G} - \varepsilon\} & U_G & U_{2G} & \dots \end{array} = 0$$

Note that this determinate will give us **a relation between the energy, ε , and the wavevector, k** (k is in the ε_k). **This relation alone will give us our most useful information concerning semiconductors.** This is the real reason we have performed all this work.

8. First check: potential energy is zero

As a check, let's see if we get the free electron case when we let all the $U_{nG}'s=0$ (that is, we set the potential energy = 0).

In this case, each Central Equation reduces to:

$$\{(\hbar^2k^2/2m) - \varepsilon\} C_k = 0$$

which is true as long as $\varepsilon = \varepsilon_k = \hbar^2k^2/2m$. But this is the result we got for the free electron energy!

9. Look at an approximate solution for k at the zone boundary: $K = \frac{1}{2}G$

If we neglect all the terms in the huge determinate except for the four middle terms, we get:

$$\begin{vmatrix} \{\varepsilon_K - \varepsilon\} & U_G \\ U_{-G} & \{\varepsilon_{K-G} - \varepsilon\} \end{vmatrix} = \begin{vmatrix} \{\varepsilon_{\frac{1}{2}G} - \varepsilon\} & U_G \\ U_{-G} & \{\varepsilon_{-\frac{1}{2}G} - \varepsilon\} \end{vmatrix} = 0$$

or, recalling that $U_{-G} = U_G$ (see previous section, part 1) and $\varepsilon_K = \varepsilon_{\frac{1}{2}G} = \frac{\hbar^2 K^2}{2m} = \varepsilon_{-\frac{1}{2}G}$:

$$\{\varepsilon_{\frac{1}{2}G} - \varepsilon\}^2 - U_G^2 = 0 \quad ,$$

or: $\{\varepsilon_{\frac{1}{2}G} - \varepsilon\} = \pm U_G \quad ,$

or: $\varepsilon = \varepsilon_{\frac{1}{2}G} \pm U_G \quad , \quad \text{or} \quad \varepsilon = (\frac{\hbar^2 K^2}{2m}) \pm U_G \quad .$

This indicates that **at the zone boundary ($K = \frac{1}{2}G$) there is an energy gap of $2U_G$.**

If we now use this knowledge, we can go back to the Central Equation and solve for C_K and C_{K-G} (again keeping the only those terms we had kept before):

$$\{\varepsilon_K - \varepsilon\} C_K + U_G C_{K-G} = 0 \quad ;$$

with $\varepsilon = \varepsilon_{\frac{1}{2}G} \pm U_G$ and $\varepsilon_K = \varepsilon_{\frac{1}{2}G}$, this becomes:

$$\mp C_K + C_{K-G} = 0. \quad \text{or} \quad C_K = \pm C_{K-G} \quad .$$

Therefore, we can write $X(x)$ as:

$$X(x) = C_K e^{iKx} + C_{K-G} e^{i(K-G)x} = C_{\frac{1}{2}G} e^{i\frac{1}{2}Gx} \pm C_{\frac{1}{2}G} e^{-i\frac{1}{2}Gx} \quad ;$$

or if we simply let $C_K = A$ and $\frac{1}{2}G = K$:

$$X(x) = A e^{iKx} \pm A e^{-iKx} \quad .$$

Thus, $X^+(x) = 2A \cos(Kx)$ with $\varepsilon = (\frac{\hbar^2 K^2}{2m}) + U_G$; and

$$X^-(x) = 2iA \sin(Kx) \quad \text{with} \quad \varepsilon = (\frac{\hbar^2 K^2}{2m}) - U_G \quad .$$

Recall that ion cores attract electrons and hence the potential energy (here the U_G) should be negative (that is, it gets more negative as you approach the ion core). Hence the + solution has the lower energy. This agrees with our semi-quantitative approach we considered previously using the Bragg reflection argument: the electrons nearer the ion cores [$X^+(x) = \cos(Kx)$ indicates this] have the lower energy.

So far this has just confirmed our previous analyses. However, we are now in a position to see how ε depends on k **near** the zone boundary. We do this next.