CHAPTER 9
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to the SCHRODINGER EQUATION
The case of an electron propagating in a crystal lattice

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References:
Feynman lectures Vol. III, Chapters 13 and 16.
CHAPTER-9
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This chapter addresses the problem of an electron moving along a set of atoms discretely separated by a distance $b$ along a line. It turns out, when taking the limiting case $b \to 0$ one obtains the correct fundamental quantum mechanics equation, the Schrödinger equation. This procedure can help us understand better the interpretation of the wavefunction solutions of the Schrödinger equation.

9.1 Hamiltonian for an electron propagating in a crystal lattice

In our study of a two-state system, we learned that there is an amplitude probability for the system to jump back and forth to the other energy state.

Similarly in a crystal,

One can imagine an electron in a ‘well’ at one particular atom and with some particular energy.
Suppose there is an amplitude probability that the electron move into another ‘well’ at one of the nearby atom.
From its new position it can further move to another atom or return to its initial ‘well’.

This study will allow understanding an ubiquitous phenomenon in nature that if the lattice were perfect (i.e. no defects), the electrons would able to travel through the crystal smoothly and easily, almost as if they were in vacuum.

9.1.A Defining the base states and the Hamiltonian matrix

We would like to analyze quantum mechanically the dynamics of an extra electron put in a lattice (as if to produce one slightly bound negative ion).

Some considerations first:

a) An atom has many electrons. Many of them are quite bounded that to affect their state of motion a lot of energy (in excess of 10 eV) is needed, but others are much weakly bounded. In this section, we will assume that the atom has one electron weakly bounded to the atom (i.e. the depth of the ‘well’ is much smaller than 10 eV.) It is the dynamics of this weakly bounded electron that we are interested in.
b) What would be a reasonable set of base states for the lattice of atoms?

We could try the following:

\[ |1\rangle \text{ crystal state in which the } e^- \text{ is in the atom 1.} \]
\[ |2\rangle \text{ crystal state in which the } e^- \text{ is in the atom 2.} \]
\[ \cdots \]
\[ |n\rangle \text{ crystal state in which the } e^- \text{ is in the atom } n. \]

(1)

Any lattice state \( |\phi(t)\rangle \) of the one-dimensional crystal can then be expressed as,

\[ |\phi(t)\rangle = \sum_n |n\rangle A_n(t) = \sum_n \langle n | \phi(t) \rangle \]

(2)

where the scalar \( A_n(t) = \langle n | \phi(t) \rangle \) is the amplitude probability of finding the state \( |\phi(t)\rangle \) in the base state \( |n\rangle \), at the time \( t \).

The evolution of \( A_n(t) \) as a function of time is determined by,

\[ i\hbar \frac{dA_n(t)}{dt} = \sum_j H_{nj}(t) A_j(t) \]

(3)

So we need to find the components \( H_{nj} \) of the Hamiltonian matrix first.

c) How does the Hamiltonian look like?

That is, how to find the components \( H_{nj} \)?

We will proceed similarly to the case of the ammonia molecule (treated in the previous chapter.) Since all the atoms sites in the crystal are energetically equivalent, we can assume

\[ H_{nn} = E_o, \quad n = 1, 2, 3, \ldots \]

(4)

On the other hand, an electron can move from one atom to any other atom. We will assume however that the electron will jump only from one atom to the neighbor of either side. That is, for a given \( n \),

\[ H_{n(n+1)} = -W. \]
\[ H_{n(n-1)} = -W. \]

and \( H_{nj} = 0 \) for \( j \neq n \pm 1 \).

Replacing these values in the equation of motion (3) on obtains,
\[ i\hbar \frac{dA_{n-1}}{dt} = -WA_{n-2} + E_o A_{n-1} - WA_n \]

\[ i\hbar \frac{dA_n}{dt} = -WA_{n-1} + E_o A_n - WA_{n+1} \]  \hspace{1cm} (6)

\[ i\hbar \frac{dA_{n+1}}{dt} = -WA_n + E_o A_{n+1} - WA_{n+2} \]

\...

### 9.1.B Stationary States

Before attempting to solve (6), let’s draw the attention first to a peculiar characteristic of the stationary states found for the case of the ammonia molecule.

Recall that after identifying two “localized” states \(|1\rangle\) and \(|2\rangle\), we were able to find two stationary states (see Chapter 8, expression (45)),

\[ |S_I(t)\rangle = e^{-(i/\hbar)E_I t} |S_I\rangle, \quad \text{where} \quad E_I = E_0 - W, \quad |S_I\rangle \equiv \frac{1}{\sqrt{2}} \left( |1\rangle + |2\rangle \right) \]

\[ |S_{II}(t)\rangle = e^{-(i/\hbar)E_{II} t} |S_{II}\rangle, \quad \text{where} \quad E_{II} = E_0 + W, \quad |S_{II}\rangle \equiv \frac{1}{\sqrt{2}} \left( |1\rangle - |2\rangle \right) \]

We want to highlight the peculiar phase with which the states \(|1\rangle\) and \(|2\rangle\) participate in \(|S_I\rangle\) and \(|S_{II}\rangle\).

- Notice, state \(|S_I(t)\rangle\) can be re-written as,

\[ |S_I(t)\rangle = \frac{1}{\sqrt{2}} e^{-(i/\hbar)E_I t} |1\rangle + e^{-(i/\hbar)E_I t} \frac{1}{\sqrt{2}} |2\rangle \]

*Notice, both amplitude vary with the same frequency \(E_I / \hbar\), and are in phase.*

- State \(|S_{II}(t)\rangle\) looks similar, except for a 180 degrees phase difference between the amplitudes,

\[ |S_{II}(t)\rangle = \frac{1}{\sqrt{2}} e^{-(i/\hbar)E_{II} t} |1\rangle - e^{-(i/\hbar)E_{II} t} \frac{1}{\sqrt{2}} |2\rangle \]

*Notice, both amplitude vary with the same frequency \(E_{II} / \hbar\), but are 180 degrees out of phase.*

- That is, \(|S_I\rangle\) and \(|S_{II}\rangle\) have the following general form,
\[ |S(t)\rangle \equiv a_1 |1\rangle + a_2 |2\rangle \]

where \( a_1 \) and \( a_2 \) are complex numbers that determine the eventual phase difference with which the states \( |1\rangle \) and \( |2\rangle \) participate in the wavefunction \( |S(t)\rangle \).

This observation (that in a given stationary state of a two-state system, there are different phases associated to each of the two localized-state participating in the wavefunction) will be extrapolated to the case in which the number of localized states participating in the system is infinite. In effect, for solving Eq. (5), let’s look for a wavefunction

\[ |\phi(t)\rangle = \sum_n |n\rangle A_n(t) \]

with the following characteristics:

- To be a stationary solution. That is, a solution in which all the amplitudes \( A_n \) vary with time at the same frequency \( e^{-(i\hbar/E)t} \); with the single energy \( E \) still to be determined.

- The different amplitudes \( A_n \) are required to have correspondingly different phase \( a_n \). Such phases still to be determined.

These two requirements are summarized in the following expression,

\[ A_n^{(E)}(t) = a_n e^{-(i\hbar/E)t} \]  

(7)

Accordingly let’s look for a stationary solution \( |\phi^{(E)}(t)\rangle \) of the form,

\[ |\phi^{(E)}(t)\rangle = \sum_n |n\rangle A_n^{(E)}(t) \]

\[ = \sum_n |n\rangle a_n e^{-(i\hbar/E)t} \]  

(8)

The amplitudes will eventually have different phase between each other; that is, the \( a_n \) are complex numbers. All the amplitude-probabilities oscillate at the same frequency \( (E/\hbar) \).

We have to find values for \( E \) and the different \( a_n \) compatible with Eq. (6).

Replacing (8) in (6) one obtains,

\[ Ea_n = -W a_{n-1} + E_0 a_n - W a_{n+1} \]  

(9a)

Alternative notation:

If we label the atoms by their positions,
\[ x_n = n \, b, \text{ where } b \text{ is the spacing between contiguous atoms in the crystal,} \]

then equation (8) takes the form,

\[ E_a(x_n) = -W_a(x_{n-1}) + E_o \, a(x_n) - W_a(x_{n+1}) \]  \hspace{1cm} (9b)

Trial solution for Eq. (9b),

\[ a(x_n) = e^{ikx_n} \quad \text{(Proposed solution about how the phase changes from site to site)} \]  \hspace{1cm} (10)

where the value of \( k \) is still to be determined.

Replacing (10) in (9b) one obtains,

\[ E \, e^{ikx_n} = -W \, e^{ikx_{n-1}} + E_o \, e^{ikx_n} - W \, e^{ikx_{n+1}} \]

\[ E = -W \, e^{-ikb} + E_o - W \, e^{ikb} \]

\[ = E_o - W \left[ e^{-ikb} + e^{ikb} \right] \]

\[ E(k) = E_o - 2W \cos(kb) \quad \text{Energy of the stationary states} \]  \hspace{1cm} (11)

We realize, for any real value of \( k \),

there is an energy \( E(k) = E_o - 2W\cos(kb) \), and

an infinite-set of values \( a(x_n) = e^{ikx_n}, \, n=1,2,3, \ldots \)

which, when entered in (8), constitute a stationary solution of Eq. (6).

Comment: It would appear that there are an infinite number of solutions (one for each arbitrarily selected real value of \( k \).) We will see later that this is not completely true.
Summary.
We have found that for any given real value of \( k \),

- There exists a corresponding **stationary solution** (from expression (8))
  \[
  | \phi^{(k)}(t) \rangle = \sum_n | n \rangle A_n^{(k)}(t) = \sum_n | n \rangle e^{ikx_n} e^{-i\hbar/E(k)t}
  \]
  (12)
  where the energy is given by (see expression (11))
  \[
  E(k) = E_0 - 2W \cos(kb)
  \]
- Notice the amplitude probability at the site \( n \) varies with time as,
  \[
  A_n^{(k)}(t) = e^{ikx_n} e^{-i\hbar/[E(k)]t}
  \]
- The expression above indicates the electron is equally likely to be found at every atom, since all the quantities \( |A_n^{(k)}(t)|^2 \) are equal (and independent of \( n \)). Only the phase is different for different atom location, changing in the amount \((kb)\) from atom to atom.

![Fig 9.1](image)

**Fig 9.1** Real part of the amplitude probability \( A_n \) for finding the atom location of the extra electron in the crystal, at a given time.

**Crystal lattice’s energy bands diagram**
The energy \( E \) as a function of \( k \) is shown in the Fig. 9.2.

![Fig 9.2](image)

**Fig 9.2** Energy of the stationary states as a function of \( k \), according to expression (11). Notice, the formation of an “energy band” whose width is proportional to \( W \). The different stationary states (one state for each value of \( k \) selected within the continuum interval \(-\pi/b, \pi/b\)) are given by expression (12),

\[
|\phi^{(k)}\rangle = \sum_i |n\rangle A_n^{(k)} = \sum_i |n\rangle e^{ikx_n} e^{-i\hbar/[E(k)]t}
\]
Only energies in the range from \( E - 2W \) to \( E + 2W \) are allowed. If an electron in a crystal is in a stationary state, it can have no energy other than the values in this band. Notice the width of the band scales with \( W \).

The above illustrates the working principle of the **energy bands formation** in a crystal, which is used to explain the electrical conductivity in metals and semiconductors (See Fig. 9.3).

**Example of energy bands diagram**

![Energy bands diagram](image)

**Fig. 9.3** Formation of energy bands by bringing together initially isolated carbon atoms.

When isolated (carbon) atoms are brought together to form a solid (diamond), various interactions occur between neighboring atoms. In the process, important changes occur in the electron energy configurations. When the solid is formed, the forces of attraction and repulsion between atoms find a balance at the proper interatomic spacing. The split energy levels display essentially continuum bands of energy.

**The Brillouin zone** \(-\pi/b < k < \pi/b\) (Region of \(k\)-values that generate independent stationary wavefunctions)

In expression (12) and in Fig. 9.2, the parameter \( k \) specifies the corresponding stationary state. The smallest values of energies \( \sim (E_o - 2W) \) are obtained for the smallest values of \( k \approx 0 \).
As \(|k|\) increases, the energy increases as well, until it reaches a maximum at \(|k| = \pi /b\). For values of \(|k|\) larger than \(\pi / b\) the energy would start to decrease, but, as we show below, there is no need to consider such values, because they do not give new states. To illustrate this statement, consider two stationary wavefunctions with corresponding different wavevectors \(k_2\) and \(k_3\) that differ from each other by \(2\pi /b\),

\[
|\phi^{(k_2)}(t)\rangle = \sum_n |n\rangle A_n^{(k_2)}(t) = \sum_n |n\rangle e^{ik_2 x_n} e^{-(i\hbar)[E(k_2)]t}
\]

\[
|\phi^{(k_1)}(t)\rangle = \sum_n |n\rangle A_n^{(k_1)}(t) = \sum_n |n\rangle e^{ik_1 x_n} e^{-(i\hbar)[E(k_1)]t}
\]

(13)

Notice, since \(E(k)\) has a period of \(2\pi /b\) then both states have the same energy; that is, \(E(k_1) = E(k_2)\). Their spatial profile is basically defined by their corresponding factors \(e^{ik_2 x_n}\) and \(e^{ik_1 x_n}\).

![Fig. 9.4 Wave-vectors \(k\) that differ from each other by \(2\pi /b\) define the same state (as demonstrated in the text.)](image)

Even though the wavefunction with wave-vector \(k_2\) clearly displays a profile of higher spatial frequency than the profile corresponding to the wave-vector \(k_1\), it turns out that both profiles \(\phi^{(k_2)}\) and \(\phi^{(k_1)}\) have the same value at each atom location. A specific example is displayed in Fig. 9.5 below. Hence, as far as the evaluation of the probability-amplitude at the atoms’ site is concerned, both wave-vectors \(k_2\) and \(k_1\) describe the same quantum state.

Analytical justification. The graphical justification given above that \(|\phi^{(k_2)}\rangle\) and \(|\phi^{(k_1)}\rangle\) given in (13) define the same state, is a consequence of the fact that, for a given \(k\), one obtains,

\[
e^{i[k+(2\pi/b)]x_n} = e^{ik x_n} e^{i(2\pi/b)x_n}
\]

since \(x_n = nb\) one obtains,

\[
e^{i[k+(2\pi/b)]x_n} = e^{i k x_n} e^{in2\pi}
\]

(14)

That is, two stationary wavefunctions whose wavevectors differ by a multiple of \(2\pi /b\) define the same state.
In short, the values of $k$ within the range $-\pi/b < k < \pi/b$ are sufficient to describe the quantum states. This range is called the Brillouin zone.

The values of $k$ within the Brillouin zone are sufficient to define all the stationary states of the crystal. Values outside this zone are redundant.

\[ \lambda_1 = 8b, \quad k_1 = \frac{1}{8} \left( \frac{2\pi}{b} \right) \]
\[ \lambda_2 = (8/9)b, \quad k_2 = k_1 + \left( \frac{2\pi}{b} \right) = \frac{9}{8} \left( \frac{2\pi}{b} \right) \]

**Fig 9.5** Real part of $A(x_n) = e^{ikx_n} e^{-(i\hbar)[E(k)]t}$ (at fixed time $t$) for two different values of $k$, with $k_1$ and $k_2$ separated by $2\pi/b$. Although both profiles are in general different, both have the same value at the atoms’ sites. Thus, both describe the same quantum state (the value of the amplitude $A$ at the atom’s site is what matters).

**E(k) depends on k quadratically for small values of k**

\[ E(k) \approx (E_o - 2W) + W b^2 k^2 \quad \text{Energy of stationary states with small values of k.} \] (15)

In this Brillouin zone:

- The higher $|k|$ the higher the energy of the stationary state.
- For small values of $k$, the following approximation holds,

\[ E(k) = E_o - 2W \cos(kb) \approx E_o - 2W \left[ 1 - \left( \frac{1}{2} \right) (kb)^2 \right]; \]

\[ E(k) \sim (E_o - 2W) + W b^2 k^2 \]
9.1. C Bloch theorem
Here we show that the periodicity “b” of the crystal is reflected in the analytical form of a given stationary state.

For a given \( k \) in the Brillouin zone, let’s consider a set of harmonic functions whose wavevectors differ from each other by an integer number of \( G = 2\pi/b \).

\[
\{ |\phi(k)(t)\rangle, |\phi(k \pm G)(t)\rangle, |\phi(k \pm 2G)(t)\rangle, |\phi(k \pm 3G)(t)\rangle, \ldots \} \tag{16}
\]

where

\[
|\phi(k)(t)\rangle = \sum_n |n\rangle e^{ikx_n} e^{-i/h[E(k)]t}.
\]

According to (14), each of functions in the set (16) describes an eigenfunctions of energy \( E(k) \).

Notice, similar to a Fourier expansion procedure, we can form then a wavefunction of any arbitrary spatial profile (which will be associated to a given wavevector \( k \) in the Brillouin zone),

\[
|\Psi^k(t)\rangle = \sum_{n} C_{k \pm mG} |n\rangle e^{i(k \pm mG)x_n} e^{-i/h[E(k)]t}, \quad \text{with fixed } k \text{ in the Brillouin zone} \tag{17}
\]

|\Psi^k(t)\rangle is then an arbitrary wavefunction of energy \( E(k) \).

Interchanging the summations

\[
= \sum_n \{ e^{i(k \pm mG)x_n} \sum_{n} C_{k \pm mG} e^{imGx_n} \} e^{-i/h[E(k)]t}
\]

\[
= \underbrace{U(x_n)}_{\text{Definition of the function } U} \quad \text{Notice } U(x_n + b) = U(x_n)
\]

\[
|\Psi^k(t)\rangle = \sum_{n} |n\rangle \{ e^{i(k \pm mG)x_n} U(x_n) \} e^{-i/h[E(k)]t} \quad \text{Wavepacket of energy } E(k) \tag{17'}
\]

We have obtained the very important result:

For a given \( k \) in the Brillouin zone, the corresponding stationary state \( |\Psi^k(t)\rangle \) of energy \( E(k) \) for the crystal lattice has the form of a plane wave \( e^{ikx_n} \) times a function \( U(x_n) \) that has a periodicity equal to the lattice space \( b \).

This is known as the Bloch theorem.
9.1.D Time-evolution of States *(How a solid conducts electricity)*

In a stationary state (see expression (12) above), an electron is equally likely to be found in any atom in the crystal. This raises the question,

how to represent a situation in which an electron is located in a certain region?

We are referring to a situation in which an electron is more likely to be found in one region than at some other place.

**Electron wave-packet**

One way to address the question above is to construct a wave-packet using a proper linear combination of the stationary states $|\phi^{(k)}(t)\rangle$ found in the previous section (see expression (12)); each stationary state identified by the value of $k$.

\[
|\Psi(t)\rangle = \int dk \, F(k) \, |\phi^{(k)}(t)\rangle
\]

Wavepacket built out of stationary states

\[
= \int dk \, F(k) \sum_n |n\rangle A^{(k)}(t)
\]

\[
= \int dk \, F(k) \sum_n |n\rangle e^{i\hat{k} \cdot \hat{x}_n} e^{-\frac{i}{\hbar}(E(k))t}
\]

\[
= \sum_n |n\rangle \left[ \int dk \, F(k) e^{i\hat{k} \cdot \hat{x}_n} e^{-\frac{i}{\hbar}(E(k))t} \right]
\]

\[
= \sum_n |n\rangle A(x_n, t)
\]

Given the base \{ |n\rangle \}, the state $|\Psi(t)\rangle$ is represented by the (infinite) set of amplitudes \{ $A(x_n, t)$, where $n = 1, 2, 3, \ldots$ \}.

\[
A(x_n, t) = \int dk \, F(k) e^{i\hat{k} \cdot \hat{x}_n} e^{-\frac{i}{\hbar}(E(k))t}
\]

(18b)

For convenience, let’s picture a wavepacket $|\Psi'(t)\rangle$ of spatial width $\Delta X$ (see Fig. below) that has a maximum at around the atom located at $x_{no}$. That is, the set \{ $A(x_n, t)$ \} has, by definition, a maximum at around the $n_o$-th atom (at a given time $t$), as schematically shown in Fig. 9.7.
For a pulse $A(x_n, t)$ localized (in space) with a width $\Delta X$, there will be an associated Fourier transform $F(k)$ with a predominant wavenumber $k_0$, and all the other wavenumbers $k$ within a range $\Delta K$; that is, the integral in (18b) expands predominantly over a width $\Delta K$,

$$A(x_n, t) = \frac{1}{\sqrt{2\pi}} \int \frac{(dk) F(k) e^{i[k x_n - (E(k)/\hbar) t]}}{\Delta K}$$

Using $\omega(k) \equiv \frac{E(k)}{\hbar}$,

$$A(x_n, t) = \frac{1}{\sqrt{2\pi}} \int \frac{F(k) e^{i[k x_n - \omega(k) t]}}{\Delta K} dk$$

**Group velocity**

We learned in Chapter-5 that, even though wave components $e^{i[k x_n - \omega(k) t]}$ of different $k$ wavevector travel at different phase velocity respectively, still we can define a velocity for the wave-packet called the group velocity,

$$V_{\text{wavefunction's group-velocity}} = V_g = \frac{d\omega(k)}{dk} \bigg|_{k_0} = \frac{1}{\hbar} \frac{dE(k)}{dk} \bigg|_{k_0}$$

**Particular case: Wave-packet with small values of $k$**

In the particular case that $k_0$ is in the low-value range, we can use the expression (15) derived above $E(k) \sim (E_o - 2W) + W b^2 k^2$, which leads to,

$$V_{\text{wavefunction's group-velocity}} = V_g = \frac{2W b^2}{\hbar} k_0 \quad \text{(valid for small values of $k_0$)}$$

Velocity of a low-energy wave-packet having a predominant wavenumber $k=k_0$,
Effective mass (case of low energy electrons)

For small values of \( k \) we have \( E(k) = (E_o - 2W) + W b^2 k^2 \) and \( v_g = \frac{2Wb^2}{\hbar} k \). From these two expressions we realize that low-energy electrons move with energy proportional to the square of its velocity, like a classical particle. Such a resemblance with a classical particle can be made more transparent through the definition of an effective mass. For that purpose, in the expression \( E(k) = (E_o - 2W) + W b^2 k^2 \) let’s first move our zero energy reference to the level \((E_o - 2W)\); thus,

\[
E(k) = W b^2 k^2 \quad \text{Energy of stationary states with small values of } k
\]

![Energy of stationary states with small values of k](image)

Fig. 9.8 Compared to Fig. 9.2 the minimum energy is used as the zero energy reference. In this new reference \( E_o = 2W \). Accordingly, expression (11) becomes \( E(k) = 2W - 2W \cos(kb) \).

A wave-packet of predominant wave-vector \( k = k_o \) will have an energy equal to the energy of the component of wave-vector \( k = k_o \); that is \( E = W b^2 k_o^2 \). In terms of the associated group velocity \( v_g = \frac{2Wb^2}{\hbar} k_o \), given in (20) above, the energy of the wave-packet can be expressed as,

\[
E = W b^2 k_o^2 = W b^2 \left( \frac{\hbar v_g}{2Wb^2} \right)^2 = \frac{1}{4Wb^2} \hbar^2 v_g^2 .
\]

Thus, for a wave-packet whose predominant wave-vector \( k \) is relatively small compared to \( \pi/b \), one obtains,

\[
E = \frac{1}{2} \left( \frac{\hbar^2}{2Wb^2} \right) v_g^2
\]

This expression can be written as

\[
E = \frac{1}{2} \left( \frac{\hbar^2}{2Wb^2} \right) v_g^2
\]
which makes the motion of the quantum packet to resemble the classical description of the electron’s motion. That is, amplitude-probability waves resemble the motion of a classical free particle. The constant \( m_{\text{eff}} \) is called the “effective mass”.\(^1\)

\[
E = \frac{1}{2} m_{\text{eff}} v_g^2
\]  

\[(22)\]

\[
m_{\text{eff}} \equiv \frac{\hbar^2}{2 W b^2}
\]

\[(23)\]

\( m_{\text{eff}} \) has nothing to do with the electron’s mass. It has been arbitrarily defined just to make the amplitude probability motion to resemble the motion of a classical particle. In a real crystal \( m_{\text{eff}} \) turns out to have a magnitude of about 2 to 20 times the free-space mass of an electron.

• Notice, however, the expression for \( m_{\text{eff}} \) is appealing to interpret it as a real mass. For example, expression (23) indicates that: the smaller \( W \) the greater the \( m_{\text{eff}} \); that is, a smaller amplitude probability \( (W) \) for an electron to move from one position to another can be interpreted as an equivalent heavier mass inertia.

Notice also, from (20) \( v_g = \frac{2 W b^2}{\hbar} k_o \) and (23) \( m_{\text{eff}} \equiv \frac{\hbar^2}{2 W b^2} \),

\[
m_{\text{eff}} v_g = \hbar k_o
\]

\[(24)\]

The representative de Broglie momentum of the wavepacket, \( \hbar k_o \), ends up being expressed as a classical momentum “mass \( \times \) velocity”.

Summary: We understand now how an electron can ride through the crystal, flowing perfectly free, unperturbed, with a velocity equal to \( v_g \), despite having all the atom to hit against. It does by having its amplitude probability to fly from one atom to the next, with \( W \) providing the quantum probability to move from one atom to the next. That is how a solid conducts electricity.

The picture above would lead to an infinite conductivity, since it predicts that an electron, once acquiring a velocity \( v_g \) it would drift forever. Indeed, it is currently accepted that the finite conductivity of a crystal is not due to the collision of electrons with the atoms; instead the finite conductivity is caused by the presence of defects in the lattice, which cause scattering of the electrons’ motion.

9.2 Hamiltonian equations in the limit when the lattice space tends to zero

In the previous section we realized that

\(^1\) The effective mass can be defined also for a general value of \( k \); no only for small values of \( k \). This is addressed in the homework assignment.
“an amplitude-probability (wavepacket)” propagates in a crystal as if it were a particle. For example, it was found that its energy is equal to $\frac{1}{2} m_{\text{eff}} v_g^2$, and that its de Broglie momentum $\hbar k_o$ is equal to $m_{\text{eff}} v_g$. That is, the Hamiltonian description of amplitude-probability waves in a lattice-crystal resembles the mechanistic description of a particle (under proper identification of the quantities involved).

One would expect then that, the Hamiltonian description of amplitude probability waves in a discrete lattice would inherently have in it (or be nothing but a mirror reflection of) a more general quantum mechanical description for the motion of a particle. Maybe by taking the limiting case of the lattice distance “$b$” equal to zero, the resulting continuum equation would resemble the more formal Schrödinger equation.

The latter is precisely the **objective that we will pursue in this section**: To obtain the Schrödinger equation as a limit case of the Hamiltonian equations (describing the motion of a particle along an array the atoms) when the lattice constant $b$ tends to zero.

Incidentally, this chapter offers also an opportunity to illustrate the transition from $a$) the, until now, somewhat loose general description of a quantum state $|\Psi\rangle$, to $b$) a much more **detailed** description of the wavefunction, i.e. giving an account on how the amplitude-probability’s $\Psi(x)$ depends on the position coordinates.

### 9.2.A From a discrete basis to a continuum basis

Let’s first formalize the definition of a continuum spatial basis

Let’s take a linear lattice of atoms, and imagine that the lattice spacing “$b$” were to be taken smaller and smaller. In the limit, we would have the case in which the electron could be anywhere along the line.

In other words, assume the possibility of labeling the space with infinity of points (in a continuous fashion.)

<table>
<thead>
<tr>
<th>Discrete case</th>
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<tbody>
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$b \rightarrow 0$  

<table>
<thead>
<tr>
<th>Continuum case</th>
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$|x\rangle$ stands for a state in which a particle is located at the spatial coordinate $x$.

The expression for a wavefunction

$$|\phi\rangle = \sum_n |x_n\rangle A(x_n)$$

may also be preferably written as

$$|\phi\rangle = \int_{-\infty}^{\infty} |x\rangle A(x) \, dx$$

$$|\phi\rangle = \sum_n |x_n\rangle A^*(x_n)$$

$$|\phi\rangle = \int_{-\infty}^{\infty} |x\rangle A^*(x) \, dx$$
The last notation uses \( A^\phi \) instead of simply \( A \), as to make more explicit that the amplitude probabilities corresponds to the state \( \phi \).

In (26), multiplying on the left by \( \langle x_k | \) , one obtains:

\[
\langle x_k | \phi \rangle = A^\phi (x_k)
\]

(Notice the expression on the left side constitutes a better notation, emphasizing that there is no need to include the character \( A \).)

\( \langle x_k | \phi \rangle \) gives the \textit{amplitude probability that the state} \( |\phi \rangle \) \textit{be found at} \( |x_k \rangle \).

Alternatively the following notation is also used,

\[
\langle x_k | \phi \rangle \equiv \phi (x_k)
\]

\[\text{amplitude probability to find the state} \quad |\phi \rangle \quad \text{at the state} \quad |x \rangle.\]  

\textbf{Note:} When writing \( \langle x | \phi \rangle \equiv \phi (x) \), the same symbol \( \phi \) is being used, for \textit{i}) labeling a particular physical state \( |\phi \rangle \) for an electron; and for \textit{ii}) defining a mathematical function of \( x \), \( \phi (x) \). In both cases the expression gives the amplitude probability that an electron in the state \( |\phi \rangle \) be found at the state \( |x \rangle \).

If in the expression \( |\phi \rangle = \sum \limits_n |x_n \rangle A^\phi (x_n) \) we wanted to emphasize the time dependence, we would write,

\[
|\phi (t) \rangle = \sum \limits_n |x_n \rangle A^\phi (x_n, t)
\]

\[A^\phi (x, t) = \int \limits_{-\infty}^{\infty} |x \rangle A^\phi (x, t) \, dx\]

where the amplitudes are expressed in different alternative forms

\[
A^\phi (x_k , t) = \langle x_k | \phi (t) \rangle = \phi (x_k , t)
\]

\[A^\phi (x , t) = \langle x | \phi (t) \rangle = \phi (x , t)\]  

\[9.2.B \quad \text{From a general description of the state} \quad |\phi \rangle \quad \text{to a more detailed account of its dependence with the position: How does} \quad \phi (x) \quad \text{look like?}\]
Starting from the solution corresponding to the case of an electron moving across a discrete lattice, we want to work out the equations that relate the value of the amplitude-probability at one point $x$ to the amplitude-probability at points arbitrarily close to it. This will be done by making $b \to 0$. That way we would obtain a quantum mechanical description of an electron’s motion in the continuum space.

Let’s start with the most general solution $|\phi\rangle$ of the Hamiltonian describing the motion of an electron in a discrete lattice,

$$|\phi(t)\rangle = \sum_n |x_n\rangle A^\phi(x_n, t)$$  \hspace{1cm} (30)

the amplitudes $A^\phi(x_n, t)$ have to satisfy the Hamiltonian equations,

$$i\hbar \frac{dA^\phi(x_n)}{dt} = -W A^\phi(x_{n-1}) + E_0 A^\phi(x_n) - W A^\phi(x_{n+1})$$  \hspace{1cm} (31)

(here we are using $A^\phi(x_n)$ instead of $A^\phi(x_n, t)$ just to simplify the notation).

Let’s analyze now the continuum case, by taking the limit $b \to 0$.

First, let’s choose the origin of the energy scale at the minimum (see Figs. 9.6 and 9.8). That makes $E_0 = 2W$. Thus we rewrite (31) as,

$$i\hbar \frac{dA^\phi(x_n)}{dt} = -W A^\phi(x_{n-1}) + 2W A^\phi(x_n) - W A^\phi(x_{n+1})$$  \hspace{1cm} (32)

Rearranging terms,

$$i\hbar \frac{dA^\phi(x_n)}{dt} = W \left[ A^\phi(x_n) - A^\phi(x_{n-1}) \right] - W \left[ A^\phi(x_{n+1}) - A^\phi(x_n) \right]$$

$$= Wb \frac{A^\phi(x_n) - A^\phi(x_{n-1})}{x_n - x_{n-1}} - Wb \frac{A^\phi(x_{n+1}) - A^\phi(x_n)}{x_{n+1} - x_n}$$

where we have used $b = x_{n+1} - x_n$

Now we take $b \to 0$

$$i\hbar \frac{dA^\phi(x_n)}{dt} = Wb \frac{dA^\phi}{dx}(x_n) - Wb \frac{dA^\phi}{dx}(x_{n+1})$$

$$= -Wb^2 \frac{d^2A^\phi}{dx^2}(x_{n+1})$$

$$i\hbar \frac{dA^\phi(x_n)}{dt} = -Wb^2 \frac{d^2A^\phi}{dx^2}(x_n + b)$$  \hspace{1cm} (33)
If we blindly took $b \to 0$, then expression (33) would give $i\hbar \frac{dA^\phi}{dt}(x_n) = 0$, which would reveal no useful information. Recall, however, that $W$ gives the likelihood the electron jumps to the neighbor atom and, thus, it is plausibly to think that as the spacing “$b$” decreases the value of $W$ simultaneously increases. Thus, we could conveniently consider that as “$b$” decreases, the product $Wb^2$ remains constant. Using expression (23) we can take this factor to be equal to $Wb^2 = \frac{\hbar^2}{2m_{\text{eff}}}$. So we will consider that as $b \to 0$, the value of $W$ increases such that the product $Wb^2$ remains constant and equal to $\frac{\hbar^2}{(2m_{\text{eff}})}$.

\[
Wb^2 \quad \frac{b \to 0}{\quad \frac{\hbar^2}{2m_{\text{eff}}}} \quad (34)
\]

Consequently, as $b \to 0$, Eq. 33 becomes,

\[
i\hbar \frac{dA^\phi(x,t)}{dt} = -\frac{\hbar^2}{2m_{\text{eff}}} \frac{d^2 A^\phi(x,t)}{dx^2} \quad (35)
\]

In summary,

When the crystal lattice $b$ tend to zero, the Hamiltonian equations take the form:

\[
i\hbar \frac{\partial A^\phi(x,t)}{\partial t} = -\frac{\hbar^2}{2m_{\text{eff}}} \frac{\partial^2 A^\phi(x,t)}{\partial x^2} \quad (36)
\]

where $m_{\text{eff}}$ is defined through the expression $Wb^2 = \frac{\hbar^2}{2m_{\text{eff}}}$

and with the requirements that the quantity $Wb^2$ remains constant as $b \to 0$.

The solutions of this equation determine the amplitude probabilities $A^\phi(x,t)$ that define the state

\[
| \phi(t) \rangle = \int | x \rangle A^\phi(x,t) \, dx
\]

where we have extrapolated the discrete expansion given in expression (26) above.

Given the equivalent notations $A^\phi(x,t) = \langle x | \phi(t) \rangle = \phi(x,t)$, as given in (29) above, the equation above is also written as,
Motion of an electron along a continuum line space

\[ i\hbar \frac{\partial \phi(x,t)}{\partial t} = -\frac{\hbar^2}{2m_{\text{eff}}} \frac{\partial^2 \phi(x,t)}{\partial x^2} \]

\[ |\phi\rangle = \int |x\rangle \langle x| \phi \rangle \, dx = \int |x\rangle \phi(x,t) \, dx \]

Fig. 9.7 Electron in a discrete linear lattice. In the limit, when the spacing \( b \) tends to zero, the problem resembles one in which the electron moves along a continuum line space.

9.2.C Particle in a potential \( V = V(x,t) \)

What would be the limiting case \( b \to 0 \) of the Hamiltonian equations if the atoms were subjected to an external potential?

For comparison, let’s take a look to the Hamiltonian equations corresponding to the case \( V(x) = 0 \), which was given in the expression (6) and reproduced below,

\[ \begin{align*}
  i\hbar \frac{dA_{n-1}}{dt} & = -W A_{n-2} + E_o A_{n-1} - W A_n \\
  i\hbar \frac{dA_n}{dt} & = -W A_{n-1} + E_o A_n - W A_{n+1} \\
  i\hbar \frac{dA_{n+1}}{dt} & = -W A_n + E_o A_{n+1} - W A_{n+2}
\end{align*} \]

(38)

First, let’s recall that \( E_o \) is the energy of the electron when located in an isolated atom.) When no external voltage is applied, all the atoms are equivalent; accordingly \( E_o = H_{nn} \) ( \( n = 1, 2, 3, \ldots \))

However when an external voltage is applied, the electron potential energy varies from atom to atom (for example if an uniform electric field \( E \) were applied, then a potential \( V_n = -e E x_n \) would be established.) Thus, in the case of a general voltage \( V = V(x) \) were applied, the energy \( E_o \) of an electron will be shifted to \( E_o + V_n \) where \( V_n \equiv V(x_n) \)
\[ i \hbar \frac{dA_n}{dt} = -W A_{n-1} + (E_0 + V_n)A_n - W A_{n+1} \]  

(39)

This is practically the same Eq. (27); only the elements along the diagonal become modified. The application of taking the limiting process \( b \to 0 \) becomes, then, very similar. We should obtain,

\[ i \hbar \frac{\partial A^\phi(x,t)}{\partial t} = -\frac{\hbar^2}{2m_{\text{eff}}} \frac{\partial^2 A^\phi(x,t)}{\partial x^2} + V(x,t)A^\phi(x,t) \]

Or, equivalently

\[ i \hbar \frac{\partial \phi(x,t)}{\partial t} = -\frac{\hbar^2}{2m_{\text{eff}}} \frac{\partial^2 \phi(x,t)}{\partial x^2} + V(x,t)\phi(x,t) \]  

(40)

\[ |\phi\rangle = \int |x\rangle \langle x|\phi\rangle \, dx = \int |x\rangle \phi(x,t) \, dx \]

9.3 The Postulated Schrodinger Equation (Non-relativistic particle motion)

The correct quantum mechanical equation for the motion of an electron in free space was first discovered by Schrodinger.

\[ i \hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} \]

Schrodinger equation (free particle)  

(41)

Notice that the Schrodinger equation is very similar to the equation (28) above.

“**We do not intend to have you think we have derived the Schrodinger equation but only wish to show you one way of thinking about it. When Schrodinger first wrote it down, he gave a kind of derivation based on some heuristic arguments and some brilliant intuitive guesses. Some of the arguments he used were even false, but that does not matter; the only important thing is that the ultimate equation gives a correct description of nature.**”

“The purpose of the discussion in the previous sections was to show that:

- the correct fundamental quantum mechanics equation (37),
  has the same form as,
- the equation (35) obtained when considering the limiting case of an electron moving along a line of atoms spaced at discrete steps."

“This means that we can think of Eq. (37) as describing the diffusion of a probability amplitude \( \Psi(x,t) \) from one point to the next along the line.”
“That is, if an electron has a certain amplitude probability to be at one point, it will, a little time later, have some amplitude to be at neighboring points.”

*Taken from The Feynman Lecture on Physics, Vol III, page 16-4.*

The diffusion argument given above springs from the fact that the Schrödinger equation (41) looks very similar to the diffusion equation \( \frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} \), (the latter governing, for example, the time evolution of a gas spreading along a tube.) But, there is a substantial difference between these two equations due to the complex number in front of the time derivative of the Schrödinger equation \( \frac{\partial \psi}{\partial t} = i \frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} \):

- while the diffusion equation leads to exponentially decaying solutions (i.e. the density \( \rho \) tends to a uniform distribution of molecules),
- in contrast, in the Schrödinger equation the imaginary coefficient in front of the time derivative makes the behavior completely different. Its solutions are complex-variable propagating waves.

For a particle moving inside a potential \( V(x,t) \) the Schrödinger is,

\[
\frac{i\hbar}{\partial t} \psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x,t) \psi \quad \text{(Schrödinger Equation)}
\]

“This equation marked a historic moment constituting the birth of the quantum mechanical description of matter. The great historical moment marking the birth of the quantum mechanical description of matter occurred when Schrödinger first wrote down his equation in 1926.

For many years the internal atomic structure of the matter had been a great mystery. No one had been able to understand what held matter together, why there was chemical binding, and especially how it could be that atoms could be stable. (Although Bohr had been able to give a description of the internal motion of an electron in a hydrogen atom which seemed to explain the observed spectrum of light emitted by this atom, the reason that electrons moved this way remained a mystery.)

Schrodinger’s discovery of the proper equations of motion for electrons on an atomic scale provided a theory from which atomic phenomena could be calculated quantitatively, accurately and in detail.” Feynman’s Lectures, Vol III, page 16-13
APPENDIX

[Note: It turns out that $\hbar k$ gives the linear momentum of the electron described by the wavefunction]

$$|\Psi^{(k)}\rangle = \sum_n |x_n\rangle e^{i k x_n} e^{-i/h}[E(k)] t$$

Or equivalently

$$\Psi^{(k)}(x_n) = e^{i k x_n} e^{-i/h}[E(k)] t$$

Using: $\langle x | \phi_p \rangle \equiv \phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{i (p/\hbar) x}$

$$\frac{1}{\sqrt{2\pi\hbar}} \Psi^{(k)}(x_n) = \frac{1}{\sqrt{2\pi\hbar}} e^{i k x_n} e^{-i/h}[E(k)] t$$

$$= \frac{1}{\sqrt{2\pi\hbar}} e^{i (p/\hbar) x_n} e^{-i/h}[E(k)] t$$

where $k = p/\hbar$

$$\frac{1}{\sqrt{2\pi\hbar}} |\Psi^{(p)}\rangle = \phi_p(x_n) e^{-i/h}[E(p/\hbar)] t$$
Equivalently,

\[ \frac{1}{\sqrt{2\pi\hbar}} |\Psi^{(p)}\rangle = |\phi_p\rangle e^{-(i/\hbar)[E(p/\hbar)]t} \]

\[ \tilde{P} \frac{1}{\sqrt{2\pi\hbar}} |\Psi^{(p)}\rangle = \tilde{P} |\phi_p\rangle e^{-(i/\hbar)[E(p/\hbar)]t} \]

\[ \frac{1}{\sqrt{2\pi\hbar}} \tilde{P} |\Psi^{(p)}\rangle = p|\phi_p\rangle e^{-(i/\hbar)[E(p/\hbar)]t} \]

In the \{ |x_n\rangle \} basis,

\[ \frac{1}{\sqrt{2\pi\hbar}} \tilde{P} |\Psi^{(p)}\rangle = \sum_n |x_n\rangle p \langle x_n |\phi_p\rangle e^{-(i/\hbar)[E(p/\hbar)]t} \]

\[ = \sum_n |x_n\rangle p \frac{1}{\sqrt{2\pi\hbar}} e^{i(p/\hbar)x_n} e^{-(i/\hbar)[E(p/\hbar)]t} \]

Going back to the variable where \( k = p/\hbar \)

\[ \frac{1}{\sqrt{2\pi\hbar}} \tilde{P} |\Psi^{(k)}\rangle = \sum_n |x_n\rangle \hbar k \frac{1}{\sqrt{2\pi\hbar}} e^{ikx_n} e^{-(i/\hbar)[E(k)]t} \]

\[ \tilde{P} |\Psi^{(k)}\rangle = \sum_n |x_n\rangle \hbar k e^{ikx_n} e^{-(i/\hbar)[E(k)]t} \]

\[ = \hbar k \sum_n |x_n\rangle e^{ikx_n} e^{-(i/\hbar)[E(k)]t} \]

\[ \tilde{P} |\Psi^{(k)}\rangle = \hbar k |\Psi^{(k)}\rangle \]

Simplified version (but less rigorous) is the following

\[ \tilde{P} |\phi^{(k)}\rangle = \tilde{P} \{ \sum_n |x_n\rangle [ A^{(k)}(x_n, t)] \} \]

\[ = \tilde{P} \{ \sum_n |x_n\rangle e^{ikx_n} e^{-(i/\hbar)[E(k)]t} \} = \]

\[ = \frac{\hbar}{i} \frac{\partial}{\partial x} \{ \sum_n |x_n\rangle e^{ikx_n} e^{-(i/\hbar)[E(k)]t} \} \]
\[\begin{align*}
&= \frac{i}{\hbar} \left\{ \sum_n \left| x_n \right\rangle \frac{\partial}{\partial x} e^{ikx_n} e^{-(i/\hbar)[E(k)]t} \right\} \\
&= \frac{\hbar}{i} \left\{ \sum_n \left| x_n \right\rangle i \hbar \right. e^{ikx_n} e^{-(i/\hbar)[E(k)]t} \\
&= \hbar k \left\{ \sum_n \left| x_n \right\rangle \right. e^{ikx_n} e^{-(i/\hbar)[E(k)]t} \\
&= \hbar k \left| \phi^{(k)} \right\rangle \\
\text{Thus,} \quad \widetilde{P} \left| \phi^{(k)} \right\rangle = \hbar k \left| \phi^{(k)} \right\rangle
\end{align*}\]

However, \(\Psi^{(k)} = \sum_n \left| x_n \right\rangle \right. e^{ikx_n} e^{-(i/\hbar)[E(k)]t}\) is not the most general wavefunction describing an electron. When a periodic potential is considered (as opposed to the constant zero potential above), the wavefunction are given by the Bloch functions

\[\begin{align*}
\Psi^{(k)}_{\text{Bloch}} &= \sum_n \left| x_n \right\rangle \right. e^{ikx_n} u(x_n) e^{-(i/\hbar)[E(k)]t} \\
\text{Notice} \quad \widetilde{P} \Psi^{(k)}_{\text{Bloch}} &= \hbar k \Psi^{(k)}_{\text{Bloch}} + \frac{\hbar}{i} \sum_n \left| x_n \right\rangle \right. e^{ikx_n} \frac{\partial u(x_n)}{\partial x} e^{-(i/\hbar)[E(k)]t}
\end{align*}\]

So \(\hbar k \Psi^{(k)}_{\text{Bloch}}\) is not an eigenstate of \(\widetilde{P}\)

But, \(\hbar k\) is still the crystal momentum of the electron, when this is in the stationary state \(\Psi^{(k)}_{\text{Bloch}}\)

\(^1\) The Feynman Lectures, Vol III, Chapter 13