

INTRODUCTION TO QUANTUM MECHANICS

PART-III THE HAMILTONIAN EQUATIONS and the SCHRODINGER EQUATION

CHAPTER-8

FROM THE HAMILTONIAN EQUATIONS TO THE SCHRODINGER EQUATION.

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References:

Feynman lectures Vol. III, Chapters 13 and 16.

CHAPTER-8

FROM THE HAMILTONIAN EQUATIONS TO THE SCHRÖDINGER EQUATION.

One of the purposes of this chapter is to show that the correct fundamental quantum mechanics equation (the Schrödinger equation) has the same form that one obtains for the limiting case when $b \rightarrow 0$ of an electron moving along a line of atoms separated by a distance b from each other.

Starting from a problem where an electron moves along a set of discretely separated atoms along a line, an equation is obtained for the case in which the separation distance tends to zero. This procedure can help us understand better the interpretation of the wavefunction solutions of the Schrödinger equation.

8.1 Hamiltonian for an electron propagating in a crystal lattice¹

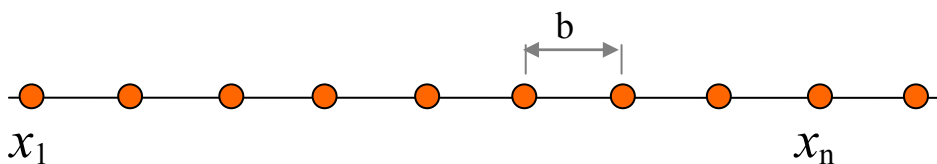
In our study of a two-state system, we learned that there is an amplitude probability for the system to jump back and forth to the other energy state.

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 is perfect, the electrons are able to travel through the crystal smoothly and easily, almost as if they were in vacuum.

8.1.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. However many of them are quite bounded that to affect their state of motion a lot of energy (in excess of 10 eV) is needed. We will assume that the motion of an extra electron (weakly bounded to the atom, the depth of the 'well' is much smaller than 10 eV.) It is the dynamics of this weekly bounded electron that we are interest in.
- b) What would be a reasonable set of base states?

We could try:

$$\begin{aligned} |1\rangle & \text{ crystal state in which the atom is in the atom 1.} \\ |2\rangle & \text{ crystal state in which the atom is in the atom 2.} \\ \dots & \\ |n\rangle & \text{ crystal state in which the atom is in the atom } n. \\ \dots & \end{aligned} \quad (1)$$

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

$$|\phi(t)\rangle = \sum_n |n\rangle A_n(t) = \sum_n |n\rangle \langle n | \phi(t) \rangle \quad (2)$$

where the scalars $A_n(t) = \langle n | \phi(t) \rangle$ are the amplitude probabilities of finding the state $|\phi(t)\rangle$ in the base states $|n\rangle$, respectively, at the time t .

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

$$i\hbar \frac{dA_n(t)}{dt} = \sum_j H_{nj}(t) A_j(t) \quad (3)$$

So we need to find the coefficients H_{nj} first.

- c) How is the Hamiltonian going to look like? That is, how to find the coefficients H_{nj} ?

We 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

$$H_{nn} = E_o, \quad n = 1, 2, 3, \quad (4)$$

On the other hand, an electron can move from one atom to any other atom, thus transferring the negative ion to another place. 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 ,

$$H_{n(n+1)} \equiv -W, \quad H_{n(n-1)} \equiv -W \quad (4)'$$

and

$$H_{nj} = 0 \quad \text{for } j \neq n \pm 1.$$

The equation of motion (3) takes the form

$$\begin{aligned} & \dots \\ i\hbar \frac{dA_{n-1}}{dt} &= -W A_{n-2} + E_o A_{n-1} - W A_n \\ i\hbar \frac{dA_n}{dt} &= -W A_{n-1} + E_o A_n - W A_{n+1} \\ i\hbar \frac{dA_{n+1}}{dt} &= -W A_n + E_o A_{n+1} - W A_{n+2} \\ & \dots \end{aligned} \quad (5)$$

8.1.B Stationary States

From our experience studying the ammonia molecule, let's recall that after identifying two "localized" states $|1\rangle$ and $|2\rangle$, (none of which having a prescribed fixed energy) we were able to find peculiar states $|S_I\rangle$ and $|S_{II}\rangle$,

$$|S_I\rangle \equiv \frac{1}{\sqrt{2}} (|1\rangle + |2\rangle) \quad \text{and} \quad |S_{II}\rangle \equiv \frac{1}{\sqrt{2}} (|1\rangle - |2\rangle) \quad (6)$$

which had the following dependence on time (see Chapter 7, expression (51)),

$$|S_I(t)\rangle = e^{-(i/\hbar)E_I t} |S_I(0)\rangle, \text{ where } E_I = E_0 - W$$

$$|S_{II}(t)\rangle = e^{-(i/\hbar)E_{II} t} |S_{II}(0)\rangle \text{ where } E_{II} = E_0 + W$$

That is, $|S_I\rangle$ and $|S_{II}\rangle$, are states of definite energy.

Expression (6) could be re-written as

$$|S_I(t)\rangle \equiv \underbrace{\frac{1}{\sqrt{2}} e^{-(i/\hbar)E_I t}}_{\swarrow} |1\rangle + \underbrace{e^{-(i/\hbar)E_I t} \frac{1}{\sqrt{2}}}_{\nearrow} |2\rangle$$

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

The other solution gives a similar outlook, except for a 180 degrees phase difference between the amplitudes

$$|S_{II}(t)\rangle \equiv \underbrace{\frac{1}{\sqrt{2}} e^{-(i/\hbar)E_{II} t}}_{\swarrow} |1\rangle - \underbrace{e^{-(i/\hbar)E_{II} t} \frac{1}{\sqrt{2}}}_{\nearrow} |2\rangle$$

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

Let's look for a solution in which all the amplitudes A_n vary with time at the same frequency; that is, a state of single energy E (whose value is still to be determined.)

$$A_n^{(E)}(t) = a_n e^{-(i/\hbar)(E) t} \quad (7)$$

$$| \phi^{(E)}(t) \rangle = \sum_n | n \rangle \underbrace{A_n^{(E)}(t)}_{\text{amplitude}} = \sum_n | n \rangle \underbrace{a_n e^{-(i/\hbar)(E)t}}_{\text{oscillating at frequency } (E/\hbar)}$$

All the amplitude-probabilities oscillating at the same frequency (E/\hbar) , but with potentially different phase between each other

Replacing (7) in (6)

$$E a_n = -W a_{n-1} + E_o a_n - W a_{n+1} \quad (8)$$

If we label the atoms by their positions,

$$x_n = n b$$

where b is the spacing between contiguous atoms in the crystal

equation (8) takes the form,

$$E a(x_n) = -W a(x_{n-1}) + E_o a(x_n) - W a(x_{n+1}) \quad (9)$$

Trial solution,

$$a(x_n) = e^{ikx_n} \quad (10)$$

Replacing (10) in (9) one obtains,

$$E e^{ikx_n} = -W e^{ikx_{n-1}} + E_o e^{ikx_n} - W e^{ikx_{n+1}}$$

$$E = -W e^{-ikb} + E_o - W e^{ikb}$$

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

$$E(k) = E_o - 2W \cos(kb) \quad (11)$$

For any choice of k there is a solution $a(x_n) = e^{ikx_n}$. It would appear that there is an infinite number of solutions (one for each value of k that can occur to us.) We will see later that this is not completely true.

We have found that for a given k ,

- There exists a stationary solution

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

of energy

$$E(k) = E_o - 2W\cos(kb)$$

- Notice the amplitude probabilities vary 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 (independent of n). Only the phase is different for different atom location, changing in the amount (kb) from atom to atom.

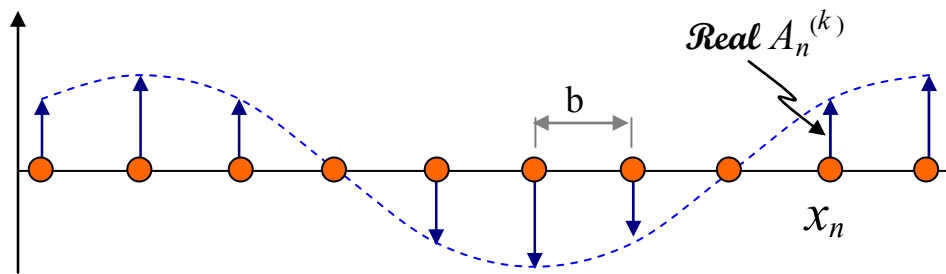


Fig 8.1 Real part of the amplitude probability A_n for finding the atom location of the extra electron in the crystal, at a given time.

The energy E as a function of k is shown in the figure below.

- 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 values in this band.
(This allows understanding the energy bands formation in a crystal, which explains the working principle of electrical conductivity in metals and semiconductors.)

- The smallest energies $E \sim (E_o - 2W)$ 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 $|k|$ **larger than π/b** the energy would start to decrease, but **there is no need to consider such values**, because they do not give new states.

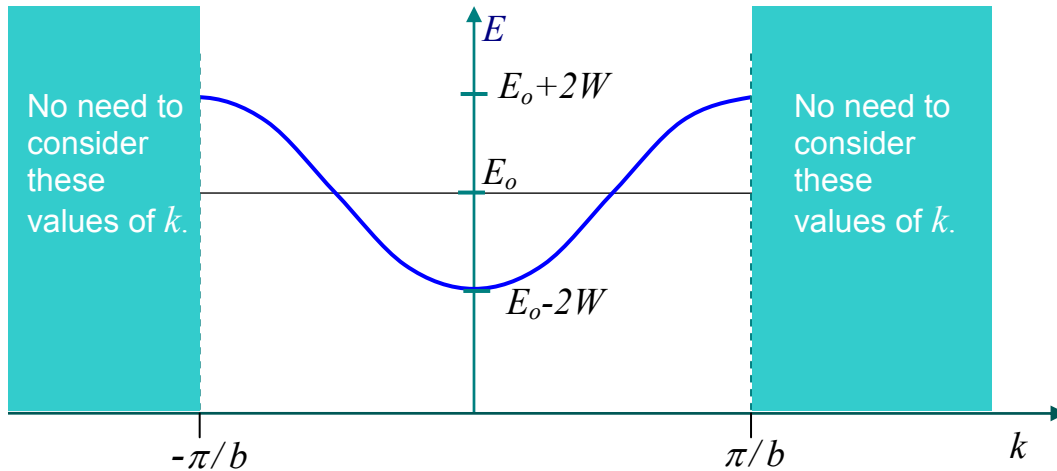


Fig 8.2 Energy of the stationary states as a function of k , where k is the wavevector of the state $|\phi^{(k)}\rangle = \sum_n |n\rangle A_n^{(k)} = \sum_n |n\rangle e^{ikx_n} e^{-(i/\hbar)[E(k)]t}$

In effect, while a wavevector $k_2 = k_1 + 2\pi/b$ has a profile of higher spatial and thus is indeed different than that the profile corresponding to the wavevector k_1 , it turns out that both profiles have the same value at each atom location (see Fig. 8.3 below). Hence, as far as the evaluation of the probability-amplitude at the atoms-site is concerned, **both wave-vectors describe the same quantum state.**

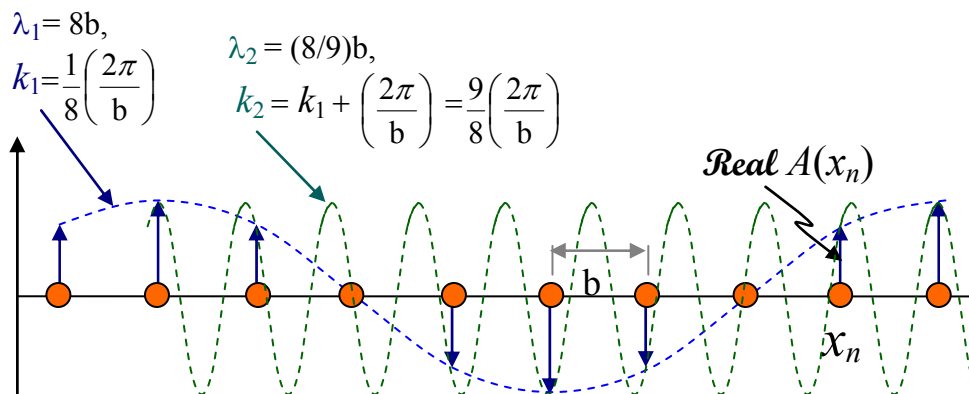


Fig 8.3 Real part of $A(x_n) = e^{ikx_n} e^{-(i/\hbar)[E(k)]t}$ for two different values of k , with k_1 and k_2 separated by $2\pi/b$. Although both profiles are in general different, both have the same value at the atom-sites. Thus, both describe the same quantum state (the value of A at the atom's site is what matter.).

Formally, this is a consequence of the fact that.

$$\begin{aligned}
 e^{i[k+(2\pi/b)]x_n} &= e^{ikx_n} e^{i[2\pi/b]x_n} \\
 &\quad \text{since } x_n = nb \\
 &= e^{ikx_n} e^{in2\pi} \\
 e^{i[k+(2\pi/b)]x_n} &= e^{ikx_n} \quad (11)
 \end{aligned}$$

Accordingly, only the values within the range $-\pi/b < k < \pi/b$ are considered in the description of the quantum states.

In this range,

- The higher $|k|$ the higher the energy of the stationary state.
- **For small values of k** , the following approximation holds,
 $E(k) = E_o - 2W \cos(kb) = E_o - 2W [1 - (1/2)(kb)^2]$;

$$E(k) = (E_o - 2W) + W b^2 k^2 \quad (\text{Case for small } k) \quad (12)$$

8.1.C Time-dependent States

In a stationary state, an electron is equally likely to be found in any atom in the crystal.

In contrast, how to represent a situation in which an electron of a certain energy is located in a certain region? That is, a situation in which an electron is more likely to be found in one region than at some other place?

Electron wavepacket

An alternative is to make a wavepacket, out of a proper linear combination of the stationary states $|\phi^{(k)}(t)\rangle$ found in the previous section,

$|\phi^{(k)}(t)\rangle = \sum_n |n\rangle A_n^{(k)}(t) = \sum_n |n\rangle e^{ikx_n} e^{-(i/\hbar)[E(k)]t}$. (Each stationary state identified by the value of k .)

For example, we can make a wavepacket that peaks around a given atom at x_{n_0} . That is, in the expansion

$$|\Psi(t)\rangle = \sum_n |x_n\rangle A_n(t) = \sum_n |x_n\rangle A(x_n, t)$$

the amplitude $A(x_n, t)$ peaks around the n_0 -th atom (at a given time t .)

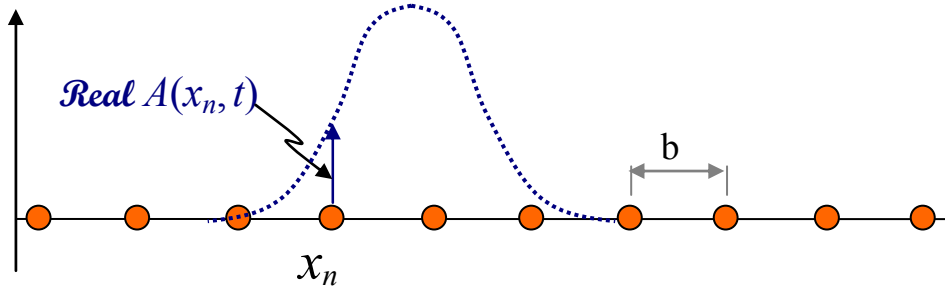


Fig. 8.4 Profile (dashed blue line) of the real part of the wavepacket at a given time t .

For a localized (in space) pulse $A(x_n, t)$, there will be an associated Fourier transform $F(k)$ with a predominant wavenumber k_0 and all the other wavenumbers k within a range Δk : that is,

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

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

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

Group velocity

We learned in Chapter-4 that, even though the k -components travel at different phase velocities, still we can define a velocity for the wavepacket called the group velocity

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

If k_o is in the low-energy range, then we can use expression (12) for the energy, which gives

$$V_{\text{wavefunction's group-velocity}} = V_g = \frac{2Wb^2}{\hbar} k_o \quad (\text{for small values of } k) \quad (13)$$

*Velocity of a low-energy wavepacket
having a predominant wavenumber $k=k_o$,*

Effective mass (case of low energy electrons)

Since $E(k) = (E_o - 2W) + Wb^2 k^2$ (for small values of k), we realize that low-energy electrons move with energy proportional to the square of its velocity, like a classical particle. Indeed, this resemblance with a classical particle can be made more transparent through the definition of an effective mass. For that purpose, first let's move our zero energy reference to $(E_o - 2W)$, as to obtain,

$$E = Wb^2 k^2.$$

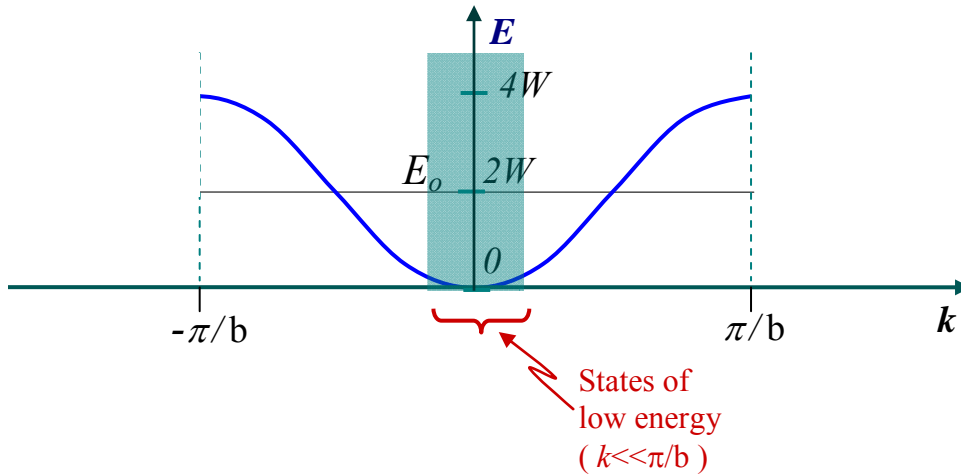


Fig. 8.5 Relative to Fig. 8.2 the minimum energy has been moved to the zero energy level. Accordingly, $E_o = 2W$ and $E(k) = 2W - 2W \cos(kb)$. (Here $E_o = H_{nm}$ is the energy of the electron when located in an isolated atom.)

A wavepacket of predominant wavevector $k=k_o$ will have an energy equal to $E= W b^2 k_o^2$. In terms of the associated group velocity, given in (13) above), the energy can be expressed as

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

Thus, for a wavepacket whose predominant wave-vector k is relatively small compared to π/b , one obtains,

$$E = \frac{1}{2} \left[\frac{\hbar^2}{2Wb^2} \right] v_g^2 \quad (14)$$

This expression can be written as

$$E = \frac{1}{2} m_{\text{eff}} v_g^2 \quad (15)$$

for, thus, resembling the motion of the quantum packet with the classical description of the motion of an electron. That is, amplitude-probability waves behave like a particle.

The constant m_{eff} is called the “effective mass”.

$$m_{\text{eff}} \equiv \frac{\hbar^2}{2Wb^2} \quad (\text{for small values of } k) \quad (16)$$

- m_{eff} has nothing to do with the electron’s mass. It has been defined as to resemble the motion of a classical particle. In a real crystal it turns out to have a magnitude of about 2 to 20 times the free-space mass of an electron.
- Notice however the appealing to interpret m_{eff} as a real mass: For example, the smaller W the greater the m_{eff} ; that is, a smaller amplitude probability (W) for an electron to move from one position to another is translated into an equivalent heavier mass inertia.

Notice also, from (13) and (16),

$$m_{eff} v_g = \hbar k_o \quad (17)$$

where k_o is the predominant wavenumber of the wavepacket

We understand now how an electron can ride through the crystal, flowing perfectly free (with $v = v_{group}$) despite having all the atom to hit against. It does by having its amplitude probability flying 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 conduct electricity.

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

In the previous section we realized that

“an amplitude-probability (wavepacket)” propagate in a crystal as if it were a particle. For example, it was found that its energy is equal to $\frac{1}{2} m_{eff} v_g^2$, its de Broglie momentum $\hbar k_o$ is equal to $m_{eff} v_g$. That is, the Hamiltonian description of amplitude-probability waves in a lattice-crystal resembles the mechanistic description of a particle.

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 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 Schrodinger equation. The latter is precisely the objective to be pursued in this section.

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

8.2.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, 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.)

$$\begin{array}{ccc} \text{Discrete case} & & \text{Continuum case} \\ |x_n\rangle & \xrightarrow{b \rightarrow 0} & |x\rangle \end{array} \quad (18)$$

$|x\rangle$ stands for a state in which a particle is located at a spatial coordinate x .

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

will be also written as

$$|\phi\rangle = \sum_n |x_n\rangle [A_\phi(x_n)]$$

We use A_ϕ instead of simply A , as to make more explicit that the amplitude probabilities corresponds to the state ϕ .

We know that $\langle x_n | \phi \rangle = [A_\phi(x_n)]$

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

$\langle x_n | \phi \rangle$ gives the *amplitude probability of the general state $|\phi\rangle$ to be found at $|x_n\rangle$* . Alternatively the following notation is also used,

$$\langle x_n | \phi \rangle = [A_\phi(x_n)] \equiv \phi(x_n) \xrightarrow{b \rightarrow 0} \langle x | \phi \rangle = A_\phi(x) \equiv \phi(x)$$

amplitude probability to find the state $|\phi\rangle$ at the state $|x\rangle$.

(19)

Note: Pay attention to the potential confusion that may occur when writing $\langle x | \phi \rangle \equiv \phi(x)$. The same symbol ϕ is being used for, *i*) labeling a particular physical state $|\phi\rangle$ of an electron; and *ii*) defining a mathematical function of x , $\phi(x)$, which gives the amplitude probability that an electron in the state $|\phi\rangle$ be found at the state $|x\rangle$.

8.2.B From a general reference of the states $|\Psi\rangle$, to a detailed account of the amplitude-probability on position $\Psi(x)$

If we can work out the equations that relate the amplitude probabilities at one point to the amplitude-probability at neighboring points, then we would have the quantum mechanical description of an electron's motion in the continuum space.

Discrete case. Let's review the results we have for the discrete case. For a lattice the Hamiltonian equations are,

$$i\hbar \frac{dA(x_n)}{dt} = -W A(x_{n-1}) + E_o A(x_n) - W A(x_{n+1}) \quad (20)$$

These equations determines the amplitude-probabilities $A_n \equiv A(x_n)$ of the general solution

$$|\phi\rangle = \sum_n |x_n\rangle [A_n] = \sum_n |x_n\rangle [A(x_n)]$$

or, just to be more specific,

$$|\phi\rangle = \sum_n |x_n\rangle [A_\phi(x_n, t)] \quad (21)$$

A different state ϕ generates a different set of amplitude probabilities. Hence the notation A_ϕ in order to reflect the dependence of A on ϕ .) The amplitudes vary also from atom to atom, hence its dependence on x_n . Finally, these amplitudes depend also on time.

Equation (20) admits stationary solutions $|\phi^{(k)}\rangle$ (one for each value of k within the range $-\pi/b < k < \pi/b$)

$$|\phi^{(k)}\rangle = \sum_n |x_n\rangle [A_\phi^{(k)}(x_n, t)] \quad (22)$$

where $A_\phi^{(k)}(x_n, t) = e^{ikx_n} e^{-(i/\hbar)[E(k)]t}$
and $E(k) = E_o - 2W \cos(kb)$

For convenience, let's move the origin of the energy scale (see Fig. 8.2 above) to the minimum energy of the band (see Fig. 8.5 below).

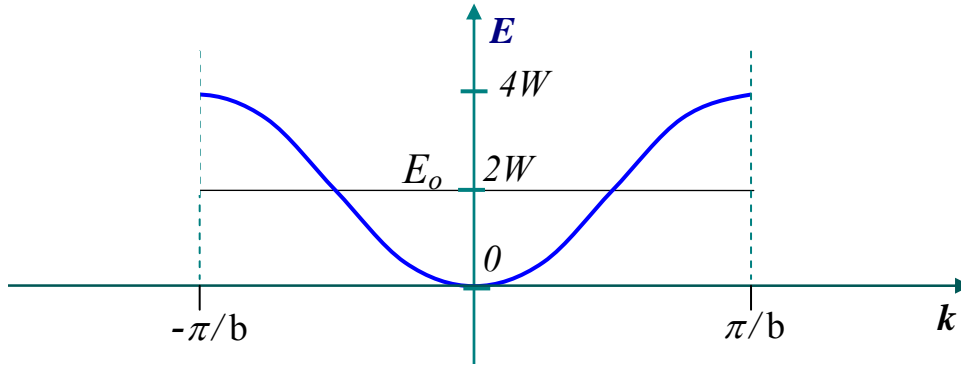


Fig. 8.5 Relative to Fig. 8.2 the minimum energy has been moved to the zero energy level. Accordingly, $E_o = 2W$ and $E(k) = 2W - 2W \cos(kb)$. (Here $E_o = H_{nn}$ is the energy of the electron when located in an isolated atom.)

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

We start from the discrete case, Eq. (20), which governs the behavior of the amplitude probabilities $A_\phi(x_n, t)$. These components make up the state

$$|\phi\rangle = \sum_n |x_n\rangle [A_\phi(x_n, t)]$$

In the new energy scale, indicated in Fig. 8.3), the equations become

$$i\hbar \frac{dA(x_n)}{dt} = -W A(x_{n-1}) + 2W A(x_n) - W A(x_{n+1}) \quad (23)$$

Rearranging terms,

$$\begin{aligned}
i\hbar \frac{dA(x_n)}{dt} &= W [A(x_n) - A(x_{n-1})] - W [A(x_{n+1}) - A(x_n)] \\
&= Wb \frac{A(x_n) - A(x_{n-1})}{x_n - x_{n-1}} - Wb \frac{A(x_{n+1}) - A(x_n)}{x_{n+1} - x_n}
\end{aligned}$$

(Notice above that for simplicity we are using $A(x_n)$ but we should be using $A_\phi(x_n, t)$)

Now we evaluate what happens when $b \rightarrow 0$

$$\begin{aligned}
&= Wb \frac{dA}{dx}(x_n) - Wb \frac{dA}{dx}(x_{n+1}) \\
&= -Wb \left[\frac{dA}{dx}(x_{n+1}) - \frac{dA}{dx}(x_n) \right] \\
&= -Wb^2 \frac{d^2 A}{dx^2}(x_{n+1}) \\
i\hbar \frac{dA(x_n)}{dt} &= -Wb^2 \frac{d^2 A}{dx^2}(x_n + b) \tag{24}
\end{aligned}$$

If we blindly took $b \rightarrow 0$, expression (24) would give $i\hbar \frac{dA}{dt}(x_n) = 0$,

and we get nothing. Recall however that W gives the likelihood the electron jumps to the neighbor atom and, thus, it is plausible to think that as the spacing “b” decreases the value of W simultaneously increases. We could conveniently consider then that as “b” decreases, the product Wb^2 remains constant. Similar to expression

(16) we can call this factor $Wb^2 = \frac{\hbar^2}{2m_{eff}}$.

So we will consider that as $b \rightarrow 0$, the value of W increases such that the product Wb^2 remains constant and equal to $\hbar^2/(2m_{eff})$.

$$Wb^2 \xrightarrow{b \rightarrow 0} \frac{\hbar^2}{2m_{eff}}$$

Consequently, as $b \rightarrow 0$, Eq. 24 becomes,

$$i\hbar \frac{dA(x,t)}{dt} = -\frac{\hbar^2}{2m_{eff}} \frac{d^2 A(x,t)}{dx^2} \quad (25)$$

In summary,

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

$$\boxed{i\hbar \frac{\partial A_\phi(x,t)}{\partial t} = -\frac{\hbar^2}{2m_{eff}} \frac{\partial^2 A_\phi(x,t)}{\partial x^2}} \quad (26)$$

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

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

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

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

where we have extrapolated the discrete expansion given in expression (2)

Given the equivalent notations $\langle x | \phi \rangle = A_\phi(x) = \phi(x)$, the equation above is also written as

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

Motion of an electron
along a continuum line
space (27)

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

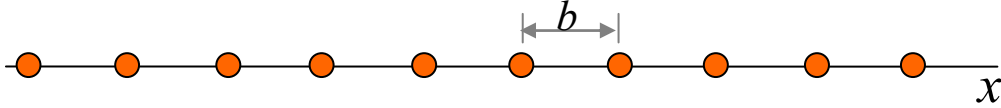


Fig. 8.6 Electron in a discrete linear lattice. In the limit, when the spacing b tends to zero, the problem resembles one in which the electron moves in a continuum line space.

8.2.C Particle in a potential $V=V(x,t)$

What would be the limiting case $b \rightarrow 0$ 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,

$$\begin{aligned} \dots \\ i\hbar \frac{dA_{n-1}}{dt} &= -W A_{n-2} + E_o A_{n-1} - W A_n \\ i\hbar \frac{dA_n}{dt} &= -W A_{n-1} + E_o A_n - W A_{n+1} \\ i\hbar \frac{dA_{n+1}}{dt} &= -W A_n + E_o A_{n+1} - W A_{n+2} \\ \dots \end{aligned} \quad (28)$$

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 $E_o = H_{nn}$ ($n=1, 2, 3, \dots$)

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 $V_n = -Ex_n$ 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 $V_n \equiv V(x_n)$

$$i\hbar \frac{dA_n}{dt} = -W A_{n-1} + (E_o + V_n) A_n - W A_{n+1} \quad (29)$$

This is practically the same Eq. (20); only the elements along the diagonal become modified. The application of taking the limiting process $b \rightarrow 0$ becomes, then, very similar. We should obtain,

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

Or, equivalently

$$i\hbar \frac{\partial \phi(x,t)}{\partial t} = -\frac{\hbar^2}{2m_{eff}} \frac{\partial^2 \phi(x,t)}{\partial x^2} + V(x,t) \phi(x,t) \quad (30)$$

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

8.3 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.

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} \quad \begin{array}{l} \text{Schrodinger equation} \\ \text{(free particle)} \end{array} \quad (31)$$

Notice that the Schrodinger equation is very similar to the equation (26) 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 section was to show that:

- *the correct fundamental quantum mechanics equation (31), has the same form than,*
- *the equation (27) obtained when considering the limiting case of an electron moving along a line of atoms."*

*"This means that we can think of Eq. (31) 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 Schrodinger equation (31) 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

Schrodinger equation $-i \frac{\partial \psi}{\partial t} = \frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial x^2}$:

- while the diffusion equation leads to exponentially decaying solutions (as ρ tends to a uniform distribution of molecules),
- the Schrodinger 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 Schrodinger is,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x,t)\psi \quad \begin{array}{l} \text{Schrodinger} \\ \text{Equation} \end{array} \quad (32)$$

*“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 Schrodinger 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

Although the result (24) is kind of a postulate, we do have some clues about how to interpret it, based on the particular case of the dynamics of an electron in a crystal lattice, studied the sections above.

¹ The Feynman Lectures, Vol III, Chapter 13