Chapter 3

Exact Results from Quantum Mechanics

3.1 Introduction

In this chapter we summarize a few exactly solved problems of quantum mechanics\(^1\). The set of exactly solved problems is important, because they form the basis on which most analysis of deviations is based.

3.2 States of definite energy

As discussed in Chapter 2, all possible information about the quantum states of the electron are buried in the wavefunction \(|\psi\rangle\). In this chapter, we want to identify this wavefunction projected to the real space, i.e., \(\psi(x) = \langle x | \psi \rangle\) for certain cases. We then want to extract the information that interests us from \(\psi(x)\) by applying corresponding operators on them. To do that, we have to first solve the time-independent Schrodinger equation for an electron in various potentials \(V(x)\):

\[
\frac{-\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) + V(x) \psi(x) = E \psi(x). \tag{3.1}
\]

The set of solutions \(\langle x | n \rangle = \psi(n, x)\) will then be the eigenfunctions corresponding to states of definite energy with corresponding eigenvalues \(E_n\). As discussed in Chapter 2, the states of definite energy are also stationary states. They form the most convenient basis for describing the situations when the potential deviates from the ideal, i.e., if

\(^1\)Exactly solvable within the assumptions made, that is!
\( V(x) \to V(x) + W(x, t) \). Thus, the states of definite energy form the basis to uncover what happens when we perturb the quantum system. We begin with the simplest of potentials: when \( V(x) = 0 \).

### 3.3 The free electron

For \( V(x) = 0 \), the Schrödinger equation reads

\[
- \frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) = E\psi(x) .
\]

The equation has the most general solution of the form

\[
\psi(x) = A e^{ikx} + B e^{-ikx},
\]

where

\[
k = \sqrt{\frac{2m_e E}{\hbar^2}} = \frac{2\pi}{\lambda} .
\]

The energy can be expressed as

\[
E = \frac{\hbar^2 k^2}{2m_e} .
\]

We note that the general solution in Eq. 3.3 represents a superposition of two waves: one going to the right (\( \psi_+(x) = A e^{ikx} \)) and the other to the left (\( \psi_-(x) = B e^{-ikx} \)). Since it is a ‘mixed’ state, clearly it is not a state of a definite momentum. We verify this by operating upon the wavefunction by the momentum operator:

\[
\hat{p}_x \psi(x) = -i\hbar \frac{d}{dx} \psi(x) = -i\hbar (ik A e^{ikx} - ik B e^{-ikx}) = \hbar k (A e^{ikx} - B e^{-ikx}) \neq p\psi(x) \quad (3.6)
\]

but... for just the right going state we get

\[
\hat{p}_x \psi_+(x) = -i\hbar \frac{d}{dx} \psi_+(x) = -i\hbar (ik A e^{ikx}) = \hbar k \psi_+(x) = p\psi_+(x) \quad (3.7)
\]
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and it is a state of definite momentum. The free electron wavefunction cannot be normalized, because it extends over all space from \(-\infty \leq x \leq +\infty\). To normalize it, we wrap the infinitely long line and join the infinities to form a circle.

\[
\psi(x + L) = \psi(x) \rightarrow e^{ik(x+L)} = e^{ikx} \rightarrow e^{ikL} = 1 \rightarrow kL = 2n\pi \quad (3.8)
\]

\[
k_n = \frac{2\pi}{L} n = 0, \pm 1, \pm 2, \ldots \quad (3.9)
\]

\[
\psi(n, x) = Ae^{ik_n x}.
\]

\[
\int_0^L dx|\psi(n, x)|^2 = 1 \rightarrow |A|^2 \times L = 1 \rightarrow A = \frac{1}{\sqrt{L}} \rightarrow \psi(n, x) = \frac{1}{\sqrt{L}} e^{ik_n x} \quad (3.10)
\]

Note that \(n = 0\) is allowed as a result of the periodic boundary condition.

\[
E_n = \frac{\hbar^2 k_n^2}{2m_e} = \frac{n^2 (2\pi\hbar)^2}{2m_e L^2} = n^2 \frac{\hbar^2}{2m_e L^2} \quad (3.11)
\]

\[
L = p \times r = \hbar k_n \times \frac{L}{2\pi} = \frac{2\pi\hbar}{L} n \times \frac{L}{2\pi} = n\hbar \quad (3.12)
\]
3.5 The particle in a box

\[ V(x) = 0, \quad 0 \leq x \leq L \]  
\[ V(x) = \infty, \quad x < 0, x > L \]  

(3.13)  
(3.14)

The major change is that \( \psi(x) = 0 \) in regions where \( V(x) = \infty \).

\[ \psi(x) = A e^{ikx} + B e^{-ikx} \rightarrow \psi(0) = 0 = A + B, \psi(L) = A e^{ikL} + B e^{-ikL} = 0 \]  
(3.15)

\[ \frac{A}{B} = -e^{-2ikL} = -1 \rightarrow 2kL = 2n\pi \rightarrow k_n = \frac{n\pi}{L}, n = \pm 1, \pm 2, \pm 3, \ldots \]  
(3.16)

Note that \( n = 0 \) is not allowed, because then \( \psi(x) = 0 \) and there is no particle. The wavefunction after normalization over the length \( L \) is

\[ \psi(n, x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) = \sqrt{\frac{2}{L}} \sin(k_n x) \]  
(3.17)

\[ E_n = n^2 \frac{(\pi\hbar)^2}{2m_eL^2} = n^2 \frac{\hbar^2}{8m_eL^2} \]  
(3.18)

3.6 The harmonic oscillator

\[ V(x) = \frac{1}{2}m_\omega^2 x^2 \]  
(3.19)

\[ E_n = (n + \frac{1}{2})\hbar\omega \]  
(3.20)

\[ a = \sqrt{\frac{m_\omega}{2\hbar}} \left( \hat{x} + i \frac{\hat{p}}{m_\omega} \right) \]  
(3.21)

\[ a^\dagger = \sqrt{\frac{m_\omega}{2\hbar}} \left( \hat{x} - i \frac{\hat{p}}{m_\omega} \right) \]  
(3.22)
\[ \hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (a^\dagger + a) \quad (3.23) \]
\[ \hat{p} = i \sqrt{\frac{m\omega\hbar}{2}} (a^\dagger - a) \quad (3.24) \]
\[ [a, a^\dagger] = 1 \quad (3.25) \]
\[ a|n\rangle = \sqrt{n}|n - 1\rangle \quad (3.26) \]
\[ a^\dagger |n\rangle = \sqrt{n + 1}|n + 1\rangle \quad (3.27) \]

**Figure 3.2:** XX.

### 3.7 The Hydrogen atom

\[ V(r) = -\frac{q^2}{4\pi\varepsilon_0 r} \quad (3.28) \]

### 3.8 Electrons in a periodic potential: Bloch Theorem

We finally consider an electron in a periodic potential,

\[ -\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E\psi(x), \quad (3.29) \]
where \( V(x + a) = V(x) \). In the absence of the potential \( V(x) \), the wavefunctions were of the form \( \psi_0(x) = Ae^{ikx} \), where \( k \) was allowed to take all values. If we considered a ring of length \( L \), then \( k_n = \frac{2\pi}{L} n \), and \( \psi(n, x) = \frac{1}{\sqrt{L}} e^{ik_n x} \). Imagine the ring has a periodic lattice, such that \( L = Na \). Then, \( k_n = \frac{2\pi}{a} \frac{n}{N} \), where \( n = 0, 1, ..., N - 1 \).