Chapter 2

Quantum Mechanics

The formalism underpinning the scaling laws of materials with size tunable properties is couched in the physics language of “quantum size effects”


2.1 Background

2.1.1 Review of classical mechanics

*Objective: describe physics needed from m to μm to nm scale.*

The motion of a particle is described by Newton’s laws. The second law is a second-order linear partial differential equation. In 1D,

\[ F = ma \quad \text{or} \quad m \frac{d^2x}{dt^2} = F. \]

The solution \( x = x(t) \) is known as the equation of motion and gives the position of the particle at a time \( t \) given initial conditions (two needed since second order differential equation).

Newtonian mechanics is believed to be valid down to micron size objects though motion can look very different. Thus, a large object (e.g., an apple) under free fall will keep accelerating downwards, while a dense micron size particle will likely achieve a terminal velocity due to viscous forces that can be described (for smooth flow) via Stoke’s law

\[ F = 6\pi \eta R v, \]

where \( R \) is the Reynolds number. However, a nanosize particle like an \( O_2 \) molecule will move erratically due to impact from other molecules.
Light

The classical theory of light is that it is a wave. This was deduced on the basis of phenomena such as diffraction and interference.

2.1.2 Why quantum mechanics?

There exists phenomena that occur on a microscopic length scale ($< 1 \mu m$) which cannot be explained using classical physics. Resolution of these problems require the following considerations:

- particle nature of radiation
- wave properties of matter
- position and momentum cannot be simultaneously specified exactly.

2.2 Wave Mechanics

2.2.1 Particle nature of radiation

- Blackbody radiation (Planck, 1900)
  Classical theory gave rise to ultraviolet catastrophe: emission intensity diverges at short wavelengths. Planck obtained the experimental curve with assumption

Figure 2.1: Black-body radiation.
2.2. WAVE MECHANICS

\[ E = hf = \hbar \omega = \frac{\hbar c}{\lambda}, \]  
\[(2.1)\]

since \( \omega = 2\pi f, c = f\lambda \) and where \( \hbar = 6.626 \times 10^{-34} \text{ Js}, \hbar \equiv \hbar/(2\pi). \)

- Photoelectric effect (Einstein, 1905)
  
  Classical theory: light incident on metal ejects electrons with a kinetic energy proportional to incident intensity. Experiment differs.

Einstein’s solution:

\[ \frac{hc}{\lambda} = \phi + eV_s. \]

- Compton effect (Compton, 1922)

\[ \Delta \lambda = \frac{h}{mc}(1 - \cos \theta) \]

requires

\[ E = pc \]  
\[(2.2)\]

for photons.

Note: combining Eqs. (2.1) and (2.2) gives

\[ p = \frac{h}{\lambda}. \]
\[(2.3)\]

This equation summarizes the particle nature of the wave.
2.2.2 Wave nature of matter

de Broglie’s hypothesis (1924):

\[ \lambda = \frac{h}{p}. \quad (2.4) \]

This is, mathematically, the same equation as Eq. (2.3); however, it now gives the wave nature of matter. Recall that, for a free particle, the energy is the kinetic energy:

\[ E = \frac{1}{2} mv^2 = \frac{p^2}{2m}. \quad (2.5) \]

Why is it difficult to demonstrate wave nature of matter? For example, diffraction requires ‘aperture size’ to be comparable to wavelength.

- optics: \( \lambda \sim 5000 \text{ Å} \)
- macroscopic particle:
  \[ m \sim 1 \text{ g}, v \sim 1 \text{ m/s}, \]
  \[ \lambda \sim 10^{-31} \text{ m}. \]
- microscopic particle (e.g., electron):
  \[ m \sim 9.1 \times 10^{-31} \text{ kg}, v \sim 0.01c, \]
  \[ \lambda \sim 10^{-10} \text{ m}. \]

Was observed with diffraction of electrons from nickel. Original paper by Davisson is available.[5]

Figure 2.3: Electron diffraction off nickel.
2.2.3 Classical wave

Consider a string of length $L$ tied at both ends and we pluck it in order to set up a transverse wave.

Mathematical problem: the wave is described by a second-order linear differential equation (wave equation), here subject to the boundary conditions that the string does not move at the ends:

$$\frac{\partial^2 y(x,t)}{\partial x^2} - \frac{1}{v^2} \frac{\partial^2 y(x,t)}{\partial t^2} = 0,$$

(2.6)

$$y(0,t) = y(L,t) = 0 \forall t.$$  

(2.7)

$y(x,t)$ is known as the transverse wave displacement or the wave function. The lowest natural modes of vibration (standing waves) have wavelengths given by

\[
\lambda_n = \frac{2L}{n}, \quad n \in \mathbb{Z}_+, \tag{2.8}
\]

\[
f_n = \frac{v}{\lambda_n} = \frac{n}{2L}, \tag{2.9}
\]

where $L$ is the length of the string and $v$ is the speed of the wave.

*Only discrete values of wavelength are allowed.*

![Figure 2.4: Lowest modes of a vibrating string.](image_url)
2.2.4 Bohr’s atom (1912)

Experiment:
- atoms are stable
- hydrogen line spectrum can be fitted using the electron energies as (Rydberg formula)

\[ E_n \approx -\frac{13.6}{n^2} \text{ eV}. \]  

(2.10)

Assume:
- electrons exist in discrete, ‘stationary’ (i.e., time-independent) states or orbits
- the states are defined to be such that there is an integral number of wavelengths

\[ \frac{2\pi r}{\lambda} = \frac{2\pi r}{h/p} = \frac{rp}{h} = \frac{L}{\hbar} \equiv n, \]

where \( L \) is the angular momentum. Thus,

\[ L = nh, \]

i.e., the wave picture has led to the quantization of angular momentum. \( n \) is known as the principal quantum number.
2.2.5 Energy quantization

One can now use the Bohr atom to demonstrate energy quantization. Simpler is to consider a one-dimensional problem, that of an electron confined to a box. When we study quantum mechanics proper (i.e., by solving the so-called Schrödinger’s equation), we will find that the electron in a box problem is mathematically equivalent to the wave on a string problem. In the wave picture, the correspondence is obvious since the electron is the wave and the box is the boundary condition. Then, the (nonrelativistic) energy of the electron is given by its kinetic energy:

\[
E = \frac{p^2}{2m} = \frac{\hbar^2}{2m\lambda^2} = \frac{\hbar^2 n^2}{8mL^2},
\]

using the wave-particle duality and Eq. (2.9). Thus, the energy of the electron is quantized. The quantization is a direct consequence of the imposition of the boundary conditions. Similar arguments applied to a spherical atom leads to the Rydberg formula.

2.2.6 Heisenberg uncertainty relations

Cannot measure position and momentum, or energy and time, simultaneously with infinite accuracy.

\[
\Delta x \Delta p \geq \frac{\hbar}{2}, \tag{2.12}
\]

\[
\Delta E \Delta t \geq \frac{\hbar}{2}. \tag{2.13}
\]

2.2.7 Pauli exclusion principle

There exists a class of particles known as fermions (e.g., electrons) of which no two can have the same set of quantum numbers (e.g., \(n, l, m_l, m_s\)). The other type of particle is known as bosons (e.g., photons).

2.3 Quantum Mechanics

2.3.1 Schrödinger’s equation

What is the wave equation for matter waves:

\[
E = \hbar \omega, \quad p = \hbar k,
\]

\[
E = K + V = \frac{p^2}{2m} + V.
\]
CHAPTER 2. QUANTUM MECHANICS

Compare light waves: 
\[ E = pc, \text{ or } E^2 - p^2 c^2 = 0, \]

has the wave equation 
\[ \left[ \frac{\partial^2}{\partial t^2} - c^2 \frac{\partial^2}{\partial x^2} \right] y(x, t) = 0. \]

For example, 
\[ E \rightarrow i\hbar \frac{\partial}{\partial t}, p \rightarrow -i\hbar \frac{\partial}{\partial x}. \]

So 
\[ E = \frac{p^2}{2m} + V, \]
becomes 
\[ i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi \tag{2.14} \]
: time-dependent Schrödinger’s equation.

If \( \Psi(x, t) = \psi(x)e^{-i\omega t} \), then 
\[ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{2.15} \]
: time-independent Schrödinger’s equation (TISE).

2.3.2 Properties of the wave function

- All the knowledge of a system is contained in the state or wave function \( \Psi(r, t) \).
- Born postulate: The probability density of finding a particle at a point \( r \) is \( |\Psi(r, t)|^2 \).
- Normalization: Since \( \Psi(r, t) \) is a measure of the probability of finding a particle, then if we have a system consisting of a single particle in all of space, then the net probability is one: 
\[ \int_{-\infty}^{\infty} d^3 r \ |\Psi(r, t)|^2 = 1. \]
- Can \( \Psi(x) \forall x \) be zero? 
  No; otherwise the particle does not exist anywhere.
- Can \( \Psi \rightarrow \infty? \) 
  No; otherwise the wave function is not normalizable.
- Can \( \Psi \) be discontinuous? 
  No; otherwise at the point of discontinuity, the probability of finding the particle is multivalued.
- Can \( \Psi' \) be discontinuous?
2.3. QUANTUM MECHANICS

2.3.3 Solving the TISE

Assume \( V(x) \) given. \( E \) is the total energy of the particle — unknown. Indeed, the basic problem in quantum mechanics is to find the allowed \( E \). As a second-order differential equation, two boundary conditions are needed for a special solution.

**Method 1**

1. Choose a value for \( E \).

2. Solve the differential equation by traditional methods to obtain \( \psi(x) \).

3. Does the \( \psi(x) \) satisfy the boundary conditions?
   - If yes, then the chosen \( E \) is allowed.
   - If no, repeat the above steps.

**Method 2**

Rewrite the TISE as

\[
\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right] \psi(x) = E \psi(x).
\]  

Has the form

\[
\hat{H} \psi(x) = E \psi(x),
\]

an eigenvalue problem. \( \hat{H} \) is known as a (differential) operator.

Example: \( V = 0 \)

Try as solution \( \psi(x) = \sin kx \).

Then

\[
\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\right] \psi(x) = \frac{\hbar^2 k^2}{2m} \sin kx \equiv E \sin kx,
\]

and the solution is valid if

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

\( E \) is known as the (energy) eigenvalue. A general solution to Schrödinger’s equation is a linear combination of the eigenstates.
**2.3.4 Application: Quantum well**

Infinite barrier

\[
\begin{align*}
\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \psi(x) &= E\psi(x), \\
\text{For } x < 0 \text{ and } x > L : \psi(x) &= 0. \\
\text{For } 0 < x < L: \\
-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= E\psi, \\
\text{or} \\
\frac{d^2\psi}{dx^2} &= -\frac{2m}{\hbar^2} E\psi = -k^2\psi.
\end{align*}
\]

Since \(E = T + V = T > 0\), then \(k^2 > 0\) and

\[
\psi(x) = Ae^{ikx} + Be^{-ikx},
\]

where

\[
k = \sqrt{\frac{2mE}{\hbar^2}}.
\]

Boundary conditions:

\[
\psi(0) = \psi(L) = 0.
\]

Then,

\[
\psi(0) = A + B = 0, \text{ or } A = -B,
\]

i.e.,

\[
\psi(x) = C \sin kx.
\]

Also,

\[
\psi(L) = 0, \text{ implies } k = \frac{n\pi}{L}, n \in \mathbb{Z}_+.
\]
Therefore,
\[
\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{k_n x}{L} \quad (0 \leq x \leq L),
\]
(2.22)
\[
E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2}.
\]
(2.23)

\(\psi_1\) is known as the ground state or lowest level and \(E_1\) is the energy of the ground state; it is also the confinement energy. It can also be readily shown from Eq. (2.18) that
\[
E \propto \frac{1}{L^2}.
\]
(2.24)

The physics of (length) scaling is very useful.

**Finite barrier**

For \(|x| \leq L/2 : V(x) = 0,\)
\[
\psi_{II}(x) = Ae^{ikx} + Be^{-ikx}.
\]
(2.25)

For \(|x| \geq L/2 : V(x) = V_0,\)
\[
\frac{d^2 \psi}{dx^2} = \frac{2m}{\hbar^2} (V_0 - E) \psi.
\]

If \(E > V_0\), the wave function is oscillatory; i.e., it does not go to zero at infinity. Thus the wave function will not be normalized in the sense we have discussed. Such a state is a scattering state. Here we are interested in bound states. Thus \(E < V_0\) and
\[
\psi(x) = Ce^{kx} + De^{-kx},
\]
(2.26)

where
\[
k = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} > 0.
\]
(2.27)
Thus,

\[
\psi_I(x) = Ce^{\kappa x}, \\
\psi_{II}(x) = Ae^{ikx} + Be^{-ikx}, \\
\psi_{III}(x) = De^{-\kappa x}.
\] (2.28, 2.29, 2.30)

Boundary condition: \( \psi \) and \( d\psi/dx \) continuous at \( x = \pm L/2 \).

Exercise: sketch lowest 2 modes.

N.B:

- \( \psi_{I,III} \neq 0 \): the particle can exist in barrier.
- If \( E > V \), then the wave function is oscillatory.
- If \( E < V \), then the wave function is exponentially decaying.

### 2.3.5 Application: Semiconductor nanowires

![Image](image.jpg)

Figure 2.6: Square cross-section ZnS nanowires.

The electrons in the free-standing nanowires shown in Fig. 2.6 have energy levels that can be modelled using a 2D infinite-barrier quantum-wire model. The 2D Schrödinger equation is separable and one can show that the wave function is given by a product of 1D solutions:

\[
\psi(x, y) = \sin(k_x x) \sin(k_y y),
\] (2.31)

and the energy is given by the sum of the 1D solutions:

\[
E(n_x, n_y) = \frac{\hbar^2 \pi^2 n_x^2}{2m_e L_x^2} + \frac{\hbar^2 \pi^2 n_y^2}{2m_e L_y^2},
\] (2.32)
where $L_x$ and $L_y$ are the cross-sectional sides. Positive values of the two quantum numbers $n_x$ and $n_y$ are required for uniqueness and for the wave function not to be identically vanishing. Thus, one can label a given state as $(n_x, n_y)$. Note that, for a square nanowire, the state $(m, n)$ has the same energy as the state $(n, m)$; these states are known as degenerate. Again, for a square nanowire, the lowest (ground) state is (1,1) and the next lowest state (i.e., with the next smallest energy) is (1,2) and (2,1) [since they are degenerate].

One aspect of nanowire energy levels that is of interest to nanopeople is how the ground state (i.e., the confinement energy) scales with cross-sectional dimensions. It was already mentioned that a simple model would predict an inverse-length-squared scaling. Actual experimental data for InP nanowires [6] are shown in Fig. 2.7 together with fitted results.

Figure 2.7: InP nanowires. Photoluminescence data [6] and fitted confinement energies as a function of diameter.

### 2.4 Quantum Computation

#### 2.4.1 Qubit

A qubit is any quantum object possessing two distinguishable (orthogonal) states that can be used to encode information. Examples are given in Table 2.1. Why would these be different from classical switches? A general qubit state is given by

$$
\psi = a.0 + b.1 \quad \Rightarrow \quad a^2 + b^2 = 1.
$$

(2.33)
Table 2.1: Examples of qubits.

<table>
<thead>
<tr>
<th></th>
<th>off</th>
<th>on</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generic</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Photon</td>
<td>H-polarized</td>
<td>V-polarized</td>
</tr>
<tr>
<td>atom/ion</td>
<td>excited</td>
<td>ground state</td>
</tr>
<tr>
<td>spin-1/2</td>
<td>up</td>
<td>down</td>
</tr>
</tbody>
</table>

This is known as a superposition state. Upon measurement, one gets either 0 or 1; this is known as the collapse or decoherence of a qubit:

$$\psi = a.0 + b.1 \rightarrow 0 \text{ or } 1. \quad (2.34)$$

The probability of getting an off state is $|a|^2$, while the probability of getting an on state is $|b|^2$. Thus, a qubit can be in a superposition state, i.e., neither on nor off.

Why are qubits useful? A 2-qubit state is given by

$$\psi = a.00 + b.01 + c.10 + d.11 \quad \Rightarrow \quad a^2 + b^2 + c^2 + d^2 = 1. \quad (2.35)$$

An N-qubit state involves $2^N$ base states. Classically, a system is only in one state at any time. A qubit can be in all base states at once. Put another way, given $N$ classical bits, a classical computer will represent one number (between 0 and $2^N - 1$. On the other hand, a quantum computer, given $N$ qubits, will represent all $2^N$ numbers simultaneously.

## 2.5 Quantum Cryptography

Quantum cryptography is based on two premises: 1) the secret encryption key is a result of quantum entanglement, and 2) one can always tell whether someone is eavesdropping or not.

Quantum entanglement refers to the fact that two quantities, spatially distinct, can still have a “connection,” even one that might appear to violate Einstein’s special theory of relativity. Thus, under certain conditions, atoms and quantum dots can emit two photons which would travel in opposite directions. The polarization state of those two photons are entangled: if one is observed with up, the other will certainly be observed with down, and vice versa.

The connection to nanostructures is due to the fact that one of the most promising source of entangled photons is a quantum dot.

### 2.5.1 Summary

- Wave-particle duality.
• Quantization is the condition resulting from the imposition of vanishing boundary conditions on waves.

• The quantum dynamics (i.e., time dependence) of a particle is deterministic and depends only upon one initial condition. However, the solution is only a probability function.

• Quantum mechanics allows barrier penetration by particles (tunneling).