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PH3520 Quantum Physics

Handout 1

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# 1 Quantum Mechanics (a brief tour)

## 1.1 Wave-Particle Duality

We have seen that Compton scattering is one of the key phenomenon that helps establish the quantum nature of (electromagnetic) radiation. Other such phenomena are the photoelectric effect, blackbody radiation, and so on. Thus, corresponding to ‘wavelike’ properties such as frequency and wavelength, we have particle-like properties such as energy and momentum. The connecting links are the Einstein-de Broglie relationships

$$\varepsilon = h\nu, \quad p = h/\lambda \tag{1}$$

It turns out that the links work both ways. Just as radiation has particle-like characteristics, so do material particles display wave characteristics as has been demonstrated. e.g., by electron diffraction from crystals.

This wave particle duality has its underlying explanation in quantum mechanics. We don’t go into QM in detail here, but a few key results of QM will be noted and commented upon.

## 1.2 The Uncertainty Principle

- It is impossible to specify with arbitrarily high precision, **even in principle**, the simultaneous values of certain physical variables – e.g., for a single particle, the  $x$ -components of the position and momentum; or the  $y$ -components; or the  $z$ -components.
- What **can** be specified in such cases are the probabilities that the variables can take different values, and hence average values, variances. etc. We will use the symbol  $(\Delta x)^2$  for the variance of  $x$ , i.e,  $\Delta x$  is the standard deviation is  $x$ . Its value depends on the state of the particle, and will change from state to state.
- In any state of the particle, we can calculate  $\Delta x, \Delta p_x, \Delta y, \Delta p_y, \Delta z, \Delta p_z$ , etc. The usual form of the uncertainty principle says that in any state of the particle; the product

$$\begin{aligned} (\Delta x)(\Delta p_x) & \text{ cannot be less than } \hbar/2 \\ (\Delta y)(\Delta p_y) & \text{ cannot be less than } \hbar/2 \\ (\Delta z)(\Delta p_z) & \text{ cannot be less than } \hbar/2. \end{aligned}$$

- The general rule is as follows. Classically, if the **Poisson bracket** of any two dynamical variables (or functions of these) is zero, i.e., if  $\{A, B\} = 0$ , then, quantum mechanically, it is possible to specify the values of  $A$  and  $B$  simultaneously with arbitrarily high precision. In other words, one can put the system in a state such that  $(\Delta A)(\Delta B) = 0$  in that state – in fact, such that, both  $(\Delta A)$  and  $(\Delta B)$  vanish.
- On the other hand, if classically  $\{A, B\} \neq 0$ , then in general in any quantum state  $(\Delta A)(\Delta B)$  is non-zero. Precisely what the least possible value of  $(\Delta A)(\Delta B)$  is, depends on the actual value of  $\{A, B\}$ .
- In the case of a pair of **canonically conjugate** dynamical variables (e.g.,  $q_i$  and  $p_i$ , its conjugate momentum), we know that  $\{q_i, p_i\} = 1$  classically. Quantum mechanically, this leads to

$$(\Delta q_i)(\Delta p_i) \geq \hbar/2. \quad (2)$$

This is the usual form of the uncertainty principle.

**Exercise:** What would the uncertainty principle say in the following cases, for the least value of the product  $(\Delta A)(\Delta B)$  ?

1.  $A = x, B = p_y$  ( $\mathbf{r}, \mathbf{p}$  being the position and momentum of a particle.)
  2.  $A = x, B = y$
  3.  $A = p_x, B = p_z$
  4.  $A = x_1, B = p_{x_2}$  ( $(\mathbf{r}_1, \mathbf{p}_1$  and  $\mathbf{r}_2, \mathbf{p}_2$  being the positions and momenta of two particles)
  5.  $A = z_1, B = p_{z_1}$
  6.  $A = \varphi, B = p_\varphi$  ( $\mathbf{r} = (r, \theta, \varphi)$  and  $\mathbf{p} = (p_r, p_\theta, p_\varphi)$  being the position and momentum of a particle)
- It must be emphasized that the uncertainty principle **has nothing to do with limitations of accuracy in experimental measurements. It expresses fundamental limitations in our description of nature.** You **cannot** ever put a particle in such a state that both  $x$  and  $p_x$  can be simultaneously specified exactly, i.e., such that  $\Delta x$  and  $\Delta p_x$  are simultaneously zero. The limitation  $(\Delta x)(\Delta p_x) \geq \hbar/2$  means that you may be able to find a state in which  $\Delta x$  can be made arbitrarily small, but then  $\Delta p$  would (in that state) automatically be sufficiently large so as to ensure that  $(\Delta x)(\Delta p_x)$  does not fall below  $\hbar/2$ .
  - A state of a system in which the physical observables  $A$  and  $B$  have the least possible value of the uncertainty product  $(\Delta A)(\Delta B)$  is a **minimum uncertainty state** for that pair of quantities. Usually the term is reversed for a state of a particle in which  $(\Delta q_i)(\Delta p_i)$  is **equal** to  $\hbar/2$ ,  $q_i$  and  $p_i$  being a canonically conjugate pair of dynamical variables. We will give examples of such states later on.

### 1.3 The state of a quantum mechanical system

We have kept mentioning the “state” of a particle, a system, etc. What is meant by this?

Classically<sup>1</sup>, we know what specifies that state of a system: the complete set of values of generalized coordinates  $(q_1, \dots, q_n)$  and the corresponding momenta  $(p_1, \dots, p_n)$ : i.e., the specification of the coordinates of a point in the  $(2n$ -dimensional) phase space, for a system with  $n$  degrees of freedom. Quantum mechanically, this is not possible – as we can see from the uncertainty principle.

- The object that replaces the phase space point  $(q_1, \dots, q_n, p_1, \dots, p_n)$  as the description of the state of a system is called the **wavefunction**, denoted by  $\psi(q_1, \dots, q_n, t)$ . We shall restrict our attention to systems consisting of particles, with some number  $n$  of degrees of freedom, the corresponding generalized coordinates being  $(q_1, \dots, q_n)$ ; their conjugate momenta being  $(p_1, \dots, p_n)$ ; and the Hamiltonian of the system being

$$H(q_1, \dots, q_n, p_1, \dots, p_n) \text{ or } H(q, p) \text{ for short.} \quad (3)$$

- The physical requirements on  $\psi$  are:
  - (i) It should be a **continuous** function of its arguments.
  - (ii) It should be **twice differentiable** w.r.t. its arguments, in general, but there may be points where this is not satisfied, in some instances.
  - (iii) It should be **single-valued**, i.e., if its arguments are given, it must have a unique value for each given  $(q_1, \dots, q_n)$ .
  - (iv) It should be **square-integrable**, i.e.,

$$\int \dots \int dq_1 \dots dq_n |\psi(q_1, \dots, q_n, t)|^2 < \infty \quad (4)$$

where the  $q_i$ 's run over the full range of relevant values in any given situation. We shall see, shortly, the physical reason for these requirements on  $\psi$ . Note that  $\psi$  can, in general, be a **complex-valued function**. For convenience, let us write  $dq_1 \dots dq_n$  as simply  $dq$  and  $\psi(q_1, \dots, q_n, t)$  as simply  $\psi(q, t)$ , henceforth.

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<sup>1</sup>The term “classically” is a standard short form for “in classical mechanics”.

## 1.4 The physical interpretation of $\psi$

$\psi$  is also called a **probability amplitude**. It is the “probability amplitude” that, at time  $t$ , the coordinates of the system have values  $q_1, \dots, q_n$ . Its modulus squared,  $|\psi(q_1, \dots, q_n, t)|^2$ , is the probability that the coordinates have these values. More precisely, since  $(q_1, \dots, q_n)$  are continuous variables,  $|\psi|^2$  is the **probability density**. Thus

$$|\psi(q_1, \dots, q_n, t)|^2 dq_1 \cdots dq_n$$

is the probability that, at time  $t$ , the generalized coordinates have values between  $q_1$  and  $q_1 + dq_1, \dots, q_n$  and  $q_n + dq_n$ .

With this interpretation, it is possible to see why we require  $\psi$  to satisfy the foregoing requirements. In particular, we impose the condition

$$\int \cdots \int |\psi(q_1, \dots, q_n, t)|^2 dq_1 \cdots dq_n = 1 \quad (5)$$

at all values of  $t$ , so that the total probability (of the system existing) is set equal to unity, i.e.,  $\psi$  is properly normalized.

## 1.5 The average (mean, or expectation) value of observables

Once we have appropriate probability density, it is easy to calculate average values.

- The average value of any function  $F(q_1, \dots, q_n)$  of generalized coordinates is, at time  $t$  denoted by  $\langle F(t) \rangle$ . It is given by

$$\langle F(t) \rangle = \int dq \psi^*(q, t) F(q_1, \dots, q_n, t) \psi(q, t) . \quad (6)$$

To be precise we must divide the RHS by the total probability  $\int |\psi(q, t)|^2 dq$ , but we have assumed that  $\psi$  has been “normalized to unity”.

- The expectation value of a function of **momenta** is not so straightforward. When the coordinates are specified precisely, the momenta have arbitrarily large uncertainties (and vice versa). It turns out that the expectation value of  $p_i$  (which is conjugate to  $q_i$ ) is given by the formula

$$\langle p_i(t) \rangle = \int dq \psi^*(q, t) (-i\hbar) \frac{\partial}{\partial q_i} \psi(q, t) \quad (7)$$

In other words, the effect of measuring the momentum  $p_i$  when the system is in the state described by the wavefunction  $\psi$ , is to put the system in a new state described by the wavefunction  $(-i\hbar) \frac{\partial}{\partial q_i} \psi$ . We say: “the momentum **operator** is represented by the **differential operator**  $-i\hbar \frac{\partial}{\partial q_i}$ .”

- The expectation value of the square of the momentum  $p_i$  is given by

$$\begin{aligned}\langle p_i^2(t) \rangle &= \int dq \psi^*(q, t) (-i\hbar) \frac{\partial}{\partial q_i} (-i\hbar) \frac{\partial}{\partial q_i} \psi(q, t) \\ &= -\hbar^2 \int dq \psi^*(q, t) \frac{\partial^2}{\partial q_i^2} \psi(q, t) .\end{aligned}\quad (8)$$

Similarly the expectation value of a smooth function  $f(p_i)$  is given by

$$\langle f \rangle = \int dq \psi^*(q, t) f\left(-i\hbar \frac{\partial}{\partial q_i}\right) \psi(q, t) ,\quad (9)$$

where  $p_i \rightarrow -i\hbar \frac{\partial}{\partial q_i}$ ,  $p_i^2 \rightarrow (-i\hbar)^2 \frac{\partial^2}{\partial q_i^2}, \dots$  in the power series expansion of  $f(p_i)$ . Similarly, if there are two momenta  $p_1, p_2$  in the problem,

$$\langle p_1 p_2 \rangle = \int dq \psi^*(q, t) (-i\hbar)^2 \frac{\partial^2}{\partial q_1 \partial q_2} \psi(q, t) ,\quad (10)$$

and so on.

## 1.6 The commutator of $q_i$ with $p_i$

In classical mechanics, we know that  $\{q_i, p_i\} = 1$ . What happens in quantum mechanics?

In QM, we can only speak of the expectation value of the observables. If  $q_i$  and  $p_i$  are a canonically conjugate pair, then a state described by  $\psi$ , we have

$$\langle q_i p_i \rangle = \int dq \psi^*(q, t) q_i (-i\hbar) \frac{\partial}{\partial q_i} \psi(q, t),\quad (11)$$

On the other hand,

$$\langle p_i q_i \rangle = \int dq \psi^*(q, t) (-i\hbar) \frac{\partial}{\partial q_i} q_i \psi(q, t),\quad (12)$$

The operator  $\frac{\partial}{\partial q_i}$  acts on everything to its right. Therefore,

$$\begin{aligned}\langle p_i q_i \rangle &= -i\hbar \int dq \psi^*(q, t) \psi(q, t) - i\hbar \int dq \psi^*(q, t) q_i \frac{\partial}{\partial q_i} \psi(q, t), \\ &= -i\hbar - i\hbar \int dq \psi^*(q, t) q_i \frac{\partial}{\partial q_i} \psi(q, t),\end{aligned}\quad (13)$$

since  $\int dq \psi^*(q, t) \psi(q, t) = 1$ . Subtracting Eq. (13) from Eq. (11), we get

$$\langle q_i p_i - p_i q_i \rangle = -i\hbar.\quad (14)$$

Since this has been established for an arbitrary state  $\psi$ , we have the **operator** relation

$$\boxed{q_i p_i - p_i q_i \equiv [q_i, p_i] = i\hbar \mathbf{1}} \quad (15)$$

where we have written  $\mathbf{1}$  on the RHS for the unit operator, to remind ourselves that the quantities on the LHS ( $q_i, p_i, q_i p_i, p_i q_i$ ) are all operators that act on  $\psi$ .

The generalization of the above is

$$[q_i, p_j] = i\hbar \delta_{ij} \mathbf{1} \quad (16)$$

Even more generally, the classical-quantum connection is

Classical		Quantum Commutator	
Poisson bracket	$\longrightarrow$	$[A, B]$	
$\{A, B\}$		divided by $i\hbar$	(17)

All the algebraic identities associated with Poisson brackets translate into identities for commutators: e.g.,

$$\begin{aligned} [A, B] &= -[B, A] \\ [A, BC] &= B[A, C] + [A, B]C . \end{aligned} \quad (18)$$

Note that the **order** in which operators appear in a product is very crucial in QM. One has to take great care to see that this is maintained properly, because  $AB$  and  $BA$  can be very different from each other.

## 1.7 The Fundamental Equation of QM: The Schrödinger Equation

So far, we haven't said anything about how the wavefunction  $\psi(q, t)$  **itself** is determined. We now address this question.

For simplicity, consider first the case of a particle of mass  $m$  moving in one dimension with coordinate  $q$  and momentum  $p$ . We have  $[q, p] = i\hbar \mathbf{1}$ . Let the Hamiltonian of the particle be

$$H(q, p) = \frac{p^2}{2m} + V(q) \quad (V = \text{potential}) \quad (19)$$

Then, according to a basic postulate of QM,  $\psi$  obeys the Schrödinger equation

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi(q, t) &= H(q, p)\psi(q, t) \\ &= \left[ \frac{p^2}{2m} + V(q) \right] \psi(q, t) \end{aligned} \quad (20)$$

Remembering that  $q$  and  $p$  are operators, this becomes

$$\boxed{i\hbar \frac{\partial}{\partial t} \psi(q, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(q, t)}{\partial q^2} + V(q) \psi(q, t) .} \quad (21)$$

This is called the time-dependent Schrödinger equation for the particle. To find its solution, we need to specify its initial state  $\psi(q, 0)$ , and also impose suitable boundary conditions on  $\psi(q, t)$ , so that the normalization condition  $\int dq |\psi(q, t)|^2 = 1$  is maintained at all times.

The generalization to the case of a particle moving in more than one dimension is straight forward. The kinetic energy is  $p^2/2m = |\mathbf{p}|^2/2m$ . Since each Cartesian component of the momentum is represented by the corresponding derivative operator according to  $p_i = -i\hbar \frac{\partial}{\partial q_i}$ , we have  $\mathbf{p} = -i\hbar \nabla$  and so  $p^2 = (-i\hbar)^2 \nabla \cdot \nabla = -\hbar^2 \nabla^2$ . The Schrödinger equation for a particle moving in a potential  $V(\mathbf{r})$  is then (since  $\mathbf{r} = (q_1, q_2, q_3)$ )

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}, t) + V(\mathbf{r}) \psi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) .} \quad (22)$$

For a collection of particles with coordinates  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ , the above equation is readily generalized to

$$\begin{aligned} \sum_{i=1}^N \left( \frac{-\hbar^2}{2m_i} \right) \nabla_i^2 \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) + V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \\ = i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) . \end{aligned} \quad (23)$$

## 1.8 Stationary States: the time-independent Schrödinger Equation.

Of the different kinds of states a system can have, the most important class is the class of **stationary states**. A stationary state is defined as **a state in which the Hamiltonian of the system has definite sharp value, called the energy eigenvalue of the state concerned**. In general, in a stationary state, while the Hamiltonian has zero uncertainty, neither the position nor the momentum can be specified with arbitrary precision: in other words, in a stationary state we have in general,

$$\Delta H = 0, \text{ but } \Delta q_i \neq 0, \Delta p_i \neq 0 \quad (i = 1, \dots, n) \quad (24)$$

Let  $\phi(q, t)$  be a stationary state of a system with energy eigenvalue  $E$ . This means that

$$\boxed{H(q, p) \phi(q, t) = E \phi(q, t) .} \quad (25)$$

Here  $H$  is an operator (the Hamiltonian operator) that acts on  $\phi(q, t)$  to produce constant ( $E$ ) times the same state  $\phi(q, t)$ . Such an equation is called an eigenvalue equation-

$$(\text{operator}) (\text{eigenstate}) = (\text{eigenvalue}) (\text{eigenstate}). \quad (26)$$

But we know from Schrödinger equation that, for **any** state of the system,

$$H \psi(q, t) = i\hbar \frac{\partial}{\partial t} \psi(q, t). \quad (27)$$

Therefore, for a **stationary state**  $\phi$ , we have

$$i\hbar \frac{\partial}{\partial t} \phi(q, t) = E \phi(q, t) \quad (28)$$

This is a trivial equation to solve, because  $E$  is just a number. The solution is

$$\phi(q, t) = e^{-iEt/\hbar} \phi(q, 0). \quad (29)$$

Substituting in the original time-dependent Schrödinger equation, we get (for a particle moving in one dimension in a potential  $V(q)$ )

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} \phi(q, 0) + V(q) \phi(q, 0) = E \phi(q, 0). \quad (30)$$

Now  $\phi(q, 0)$  is a function of  $q$  alone, and so we may write (denoting  $\phi(q, 0)$  by just  $\phi(q)$ ).

$$\boxed{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} \phi(q) + V(q) \phi(q) = E \phi(q)}. \quad (31)$$

This is the **time-independent** Schrödinger equation for a particle of mass  $m$  moving in one dimensional potential  $V(q)$ . In three dimensions, we get

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \phi(\mathbf{r}) + V(\mathbf{r}) \phi(\mathbf{r}) = E \phi(\mathbf{r})}. \quad (32)$$

The set of eigenvalues  $\{E\}$  satisfying this equation is the set of allowed values of the total energy of the particle. (It is called the **spectrum** of the Hamiltonian,  $H$ . The corresponding solutions  $\{\phi(\mathbf{r})\}$  are the energy eigenstates of the system. The complete wavefunction corresponding to the eigenvalue  $E$  is of course

$$\phi(\mathbf{r}, t) = e^{-iEt/\hbar} \phi(\mathbf{r}, 0). \quad (33)$$

Therefore  $|\phi(\mathbf{r}, t)|^2 = |\phi(\mathbf{r})|^2 = |\phi(\mathbf{r}, 0)|^2$  for a stationary state – i.e., the probability **density** itself remains constant in a stationary state. This is **not true** for a general state, although the **total** probability

$$\int dV |\psi(\mathbf{r}, t)|^2 = \int dV |\psi(\mathbf{r}, 0)|^2 = 1 \quad (34)$$

is constant in time, in general. The lowest allowed value of  $E$  is called the **ground state energy**.



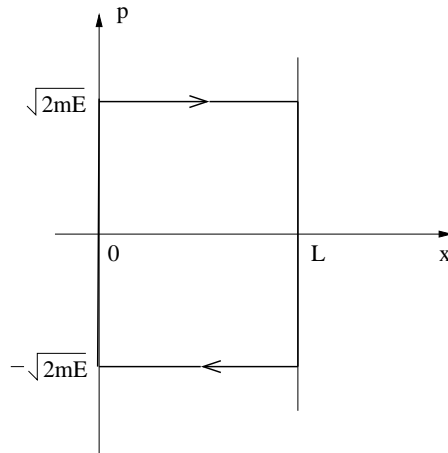


Figure 1: Classical phase trajectory (Particle in a box)

## 1.9 Energy levels and stationary states of a free particle in a box: one-dimensional case

The simplest problem we can consider is that of a particle of mass  $m$  confined to move along the  $x$ -axis inside a ‘box’ of length  $L$ , i.e.,  $0 \leq x \leq L$ . The particle can’t escape from this ‘box’ (the potential is infinite outside it), but it can move freely within the region  $0 \leq x \leq L$ .

- (i) First, look at it classically. Given an energy  $E \geq 0$ , the momentum of the particle is found from  $E = p^2/2m$ , i.e.,  $p = \pm(2mE)^{1/2}$ . The phase trajectory of the particle looks like this : at the ‘walls’  $x = 0$  and  $x = L$  the momentum of the particle is abruptly reversed in sign (but no change occurs in its magnitude as the walls are assumed to be perfectly rigid reflectors).
- (ii) **Semi-classical approximation:** If we use the Bohr-Sommerfeld quantization rule for this periodic motion, we get

$$\int_{\text{closed traj.}} p \, dx = nh \quad (n = \text{positive integer}) \quad (35)$$

But the LHS is just the area enclosed by the trajectory, and is therefore equal to  $2L(2mE)^{1/2}$ . therefore the allowed ‘orbits’ have energies  $E_n$  given by

$$2L(2mE)^{1/2} = nh \quad (n = 1, 2, \dots) \quad (36)$$

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (n = 1, 2, \dots) \quad (37)$$

The ground state energy is thus  $E_1 = h^2/8mL^2$ .<sup>2</sup> This means that the lowest

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<sup>2</sup>This happens to be the answer even in quantum mechanics. The semi-classical approximation is expected to hold only for large quantum numbers. In this problem, it is interesting that it gives the correct energy eigenvalue even for the ground state.

allowed value of the total energy of the particle inside the box is  $E_1$ , rather than 0 as someone would expect classically. This is a direct consequence of the uncertainty principle.  $\Delta x$  is not infinite in this problem as we know that the particle is somewhere in the box.  $\therefore \Delta x$  is finite (and of the order of  $L$ ). This implies that  $\Delta p \neq 0$ . But  $\langle p \rangle = 0$  as the particle has no net momentum. Thus,  $2mE = \langle p^2 \rangle = \Delta p^2 \neq 0$ .

(iii) Now consider the exact **quantum mechanical** problem. The stationary states of the particle are given by

$$\phi(x, t) = e^{-iEt/\hbar} \phi(x) , \quad (38)$$

where both  $E$  and  $\phi(x)$  are to be determined from the time-dependent Schrödinger equation

$$H \phi(x) = E \phi(x) . \quad (39)$$

But  $H = \frac{p^2}{2m} + V(x)$ , where  $V(x)$  is zero for  $0 \leq x \leq L$ , and  $\infty$  otherwise. Therefore we must have

$$\left. \begin{array}{l} \frac{d^2}{dx^2} \phi(x) = \frac{-2mE}{\hbar^2} \phi(x) \quad : \text{ for } 0 < x < L, \\ \text{and } \phi(x) \equiv 0, \quad : \text{ otherwise} \end{array} \right\} \quad (40)$$

Since  $E \geq 0$  in this case, put  $2mE/\hbar^2 \equiv k^2$ . Then  $\phi(x)$  has the general solution

$$\phi(x) = A \sin kx + B \cos kx \quad (41)$$

Imposing the boundary condition  $\phi(0) = 0$  gives  $B = 0$ . Imposing the other boundary condition  $\phi(L) = 0$  gives

$$\sin kL = 0, \text{ i.e., } kL = n\pi \quad (n = \text{integer}). \quad (42)$$

Therefore the stationary state wavefunctions are of the form,

$$\phi_n(x) = A_n \sin \left( \frac{n\pi x}{L} \right), \quad (n = \text{integer}). \quad (43)$$

Since  $\sin(-\theta) = -\sin \theta$ , negative values of  $n$  don't lead to new solutions. Further, since we must have  $\phi_n(x) \neq 0$  (so that  $\int dx |\phi^2(x)| = 1$  can be maintained),  $n$  can't be zero. Finally, we obtain the stationary state wavefunctions

$$\phi_n(x, t) = A_n e^{-iE_n t/\hbar} \sin \left( \frac{n\pi x}{L} \right) \quad (n = 1, 2, \dots) . \quad (44)$$

Correspondingly, the allowed energy eigenvalues are found from the condition  $k = n\pi/L$ , i.e.,

$$\boxed{E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 \hbar^2}{8mL^2} \quad (n = 1, 2, \dots) .} \quad (45)$$

This is exactly the same as the result found semi-classically; this coincidence obtains only in the case of the free particle.

The normalized eigenstates corresponding to the above values of  $E_n$  are

$$\boxed{\phi_n(x, t) = \sqrt{\frac{2}{L}} e^{-iE_n t/\hbar} \sin\left(\frac{n\pi x}{L}\right)} \quad (46)$$

as can be verified easily. It is instructive to sketch the form of  $\phi_n(x)$  as a function of  $x$  for the first few values of  $n$ .

### 1.10 Particle in a three-dimensional cuboidal box:

This case is easily solved, using the solutions obtained above in the one-dimensional case. Let the box be given by  $0 < x < L_1$ ,  $0 < y < L_2$ ,  $0 < z < L_3$ . Then the time-dependent Schrödinger equation is

$$\begin{aligned} -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \phi(x, y, z) &= E\phi(x, y, z) \quad (\text{inside box}) \\ \phi(x, y, z) &\equiv 0 \quad (\text{outside box}) \end{aligned} \quad (47)$$

The normalized stationary states are easily found to be given by

$$\phi_{n_1 n_2 n_3}(\mathbf{r}, t) = e^{-\frac{iE_{n_1 n_2 n_3} t}{\hbar}} \left( \frac{8}{L_1 L_2 L_3} \right)^{1/2} \sin\left(\frac{n_1 \pi x}{L_1}\right) \sin\left(\frac{n_2 \pi y}{L_2}\right) \sin\left(\frac{n_3 \pi z}{L_3}\right) \quad (48)$$

The corresponding energy eigenvalues are given by

$$E_{n_1 n_2 n_3} = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right), \quad (49)$$

where  $n_1$ ,  $n_2$  and  $n_3$  (called **quantum numbers**) run over the values 1, 2, ..., ad infinitum. Note that, in contrast to the one-dimensional case, the energy eigenvalues and corresponding wavefunctions now depend on three distinct quantum numbers instead of just one. **In general, there are as many quantum numbers as degrees of freedom in a system.**

In the special case of a cubical box,  $L_1 = L_2 = L_3 = L$ . We then have

$$E_{n_1 n_2 n_3} = \frac{\pi^2 \hbar^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2), \quad (50)$$

A common feature of systems with more than one degree of freedom (with certain amount of symmetry) is evident from this last expression, namely, **degeneracy**: while the ground state energy  $E_{111} = 3\pi^2 \hbar^2 / (2mL^2)$  corresponds to the unique state (or wavefunction)

$$\psi_{111}(\mathbf{r}, t) = (8/L^3)^{1/2} \exp^{-iE_{111}t/\hbar} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right), \quad (51)$$

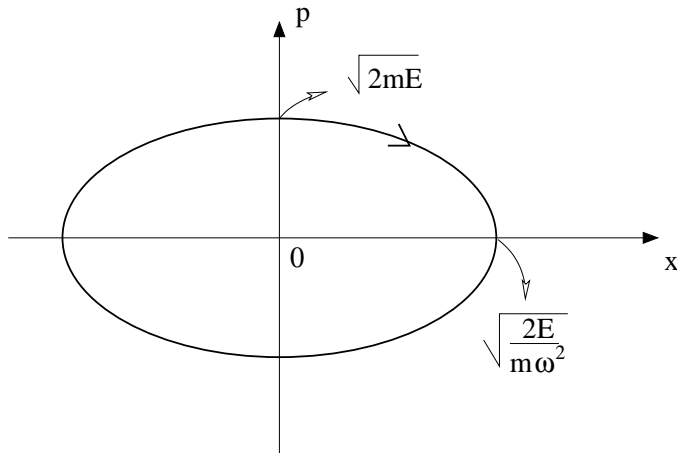


Figure 2: Classical phase trajectory (simple harmonic oscillator)

there are three different states  $\psi_{112}$ ,  $\psi_{121}$  and  $\psi_{211}$  corresponding to the first excited energy level  $6\pi^2\hbar^2/2mL^2 = 3\pi^2\hbar^2/mL^2$ . Similarly, the higher energy levels have in general more than one state associated with them. As the quantum numbers become larger and larger, the levels become practically continuous, and the degeneracy increases. We have already seen that for very large values of  $E$ , we may speak of a density of states rather than a degeneracy factor. In the case of a particle in a cubical box, it follows from the expression for  $E_{n_1n_2n_3}$  that the **density** of states is proportional to  $E^{1/2}$ , a result we have already used in our study of the ideal gas.

## 1.11 The quantum mechanical simple harmonic oscillator

(i) **Semi-classical Quantization:** Consider the linear harmonic with Hamiltonian

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2. \quad (52)$$

The phase trajectories are ellipses in the  $xp$ -plane. For a given energy  $E > 0$ , the integral

$$\oint_{\text{closed traj.}} p \, dx = nh \quad (53)$$

is just the area enclosed by the ellipse whose equation is

$$\frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 = E. \quad (54)$$

Therefore the allowed energy values  $E_n$  are given by

$$\begin{aligned} \pi(2mE_n)^{1/2} \left( \frac{2E_n}{m\omega^2} \right)^{1/2} &= nh, \\ \text{or } E_n &= n\hbar\omega. \end{aligned} \quad (55)$$

Actually, this semi-classical quantization is only valid for large values of the quantum numbers. We will see shortly that the exact quantum mechanical answer is  $E_n = (n + 1/2)\hbar\omega$  where  $n = 0, 1, \dots$  ad infinitum.

(ii) **Quantum mechanically**, we must find the energy eigenvalues by solving the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \phi(x) + \frac{1}{2} m \omega^2 x^2 \phi(x) = E \phi(x) \quad (56)$$

together with the boundary conditions  $\phi \rightarrow 0$  as  $x \rightarrow \pm\infty$ , to ensure that the normalization condition  $\int_{-\infty}^{\infty} dx |\phi(x)|^2 = 1$  is satisfied. This is a standard differential equation, but the solutions are a bit involved. Here we merely quote the result for the energy eigenvalues as already mentioned, they are given by

$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega, \quad (57)$$

where  $n = 0, 1, \dots$  ad infinitum. The corresponding wavefunctions are of the form

$$\phi_n(x) = A_n \exp\left(\frac{-m\omega x^2}{2\hbar}\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right) \quad (58)$$

where  $A_n$  is an  $n$ -dependent normalization constant, and  $H_n$  is a polynomial of degree  $n$  called the **Hermite** polynomial. Note that  $(m\omega/\hbar)^{1/2}$  has the physical dimensions  $L^{-1}$ .  $H_n(\xi)$  is an even/odd function of  $\xi$  according as  $n$  is even/odd. Further,  $H_0(\xi) = 1$ ;  $H_1(\xi) = 2\xi$ , etc. The ground state of the oscillator has an energy  $E_0 = \hbar\omega/2$ , rather than zero (as would be expected on classical grounds). This is called the **zero-point energy** of the oscillator, and arises because the uncertainty principle forbids a state of zero-energy: this would imply that both  $x$  and  $p$  are exactly zero in the ground state, which is impossible.

The expectation values of  $x$ ,  $x^2$ ,  $p$ ,  $p^2$  etc. in any of the stationary states can be easily calculated. We find, for instance,

$$\langle x \rangle_n = \int_{-\infty}^{\infty} \phi_n^*(x) x \phi_n(x) dx = 0 \quad (59)$$

because  $H_n(x)$  is an even function of  $x$  for even values of  $n$ , and an odd function of  $x$  for odd values of  $n$ . Therefore  $\phi_n^* \phi_n$  is always an even function of  $x$ . Similarly,

$$\langle p \rangle_n = \int_{-\infty}^{\infty} \phi_n^*(x) \left( -i\hbar \frac{d}{dx} \right) \phi_n(x) dx = 0 \quad (60)$$

because if  $\phi_n$  is even,  $\frac{d\phi_n}{dx}$  is odd, and vice versa. However, the variances of  $x$  and  $p$  are non-zero in any stationary state. In the state  $\phi_n$ , we find the result

$$(\Delta x)_n (\Delta p)_n = \left( n + \frac{1}{2} \right) \hbar \quad (61)$$

Therefore in the ground state of the harmonic oscillator, we have,

$$\boxed{(\Delta x)_0(\Delta p)_0 = \frac{\hbar}{2}} \quad (62)$$

But we have already said that the least possible value of  $(\Delta x)(\Delta p)$  for a pair of conjugate coordinate-momentum variables is  $\hbar/2$ . Therefore **the ground state of the linear harmonic oscillator is a minimum uncertainty state**. The corresponding wavefunction is (using the fact that the Hermite polynomial  $H_0 = 1$  identically)

$$\begin{aligned} \phi_0(x, t) &= \exp(-iE_0t/\hbar)\phi_0(x) \\ &= A_0 \exp(-i\omega t/2) \exp(-m\omega x^2/2\hbar) \end{aligned} \quad (63)$$

where  $A_0$  is the normalization constant. The noteworthy feature of this expression is that the wavefunction is a **Gaussian** centered at  $x = 0$ . This is an illustration of a more general feature: Gaussian wavepackets are minimum uncertainty wavepackets. Note that the wave functions corresponding to the excited states of the oscillator are not minimum uncertainty states.

Minimum uncertainty wavepackets have interesting practical uses, for instance, in quantum optics.

## 1.12 The probability density: some simple examples

The explicit solutions obtained for the wavefunctions of the stationary states of a particle in a box and the linear harmonic oscillator help us understand several principles of a quantum mechanics in a simple way. An example is the behaviour of the probability density  $|\phi_n(x, t)|^2 = |\phi_n(x)|^2$  in the two cases. For the particle in a box, we have

$$|\phi_n(x)|^2 = \begin{cases} \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) & , \quad 0 < x < L \\ 0, & , \quad \text{otherwise} \end{cases} \quad (64)$$

where  $n = 0, 1, \dots$  ad infinitum. For the harmonic oscillator, we have

$$|\phi_n(x)|^2 = |A|^2 \exp\left(\frac{-m\omega x^2}{2\hbar}\right) H_n^2\left(x\sqrt{\frac{m\omega}{\hbar}}\right), \quad (n = 0, 1, \dots) \quad (65)$$

The first two densities are sketched in figure 3 in each of the two cases. The following points are noteworthy. As the potential is effectively infinite outside the box in the former case,  $|\phi_n(x)|^2$  vanishes identically for  $x \leq 0$  and  $x \geq L$  in that case. On the other hand, the quantum mechanical oscillator has a non-zero probability of being anywhere in  $-\infty < x < \infty$  even in its ground state. If it were a classical oscillator, a total energy equal to  $\hbar\omega/2$  implies that it has an amplitude given by

$$\frac{1}{2}m\omega^2 x^2 = \frac{\hbar\omega}{2} \quad (66)$$

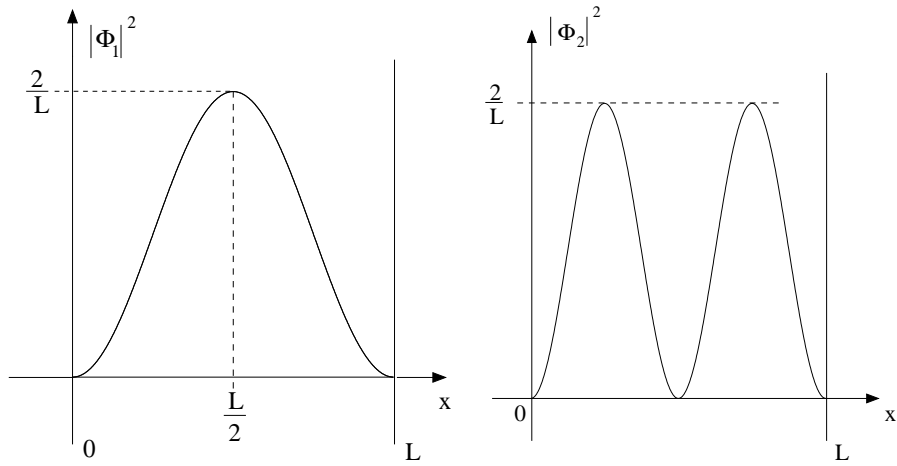


Figure 3:  $|\phi|^2$  for the first two energy eigenstates (particle in a box)

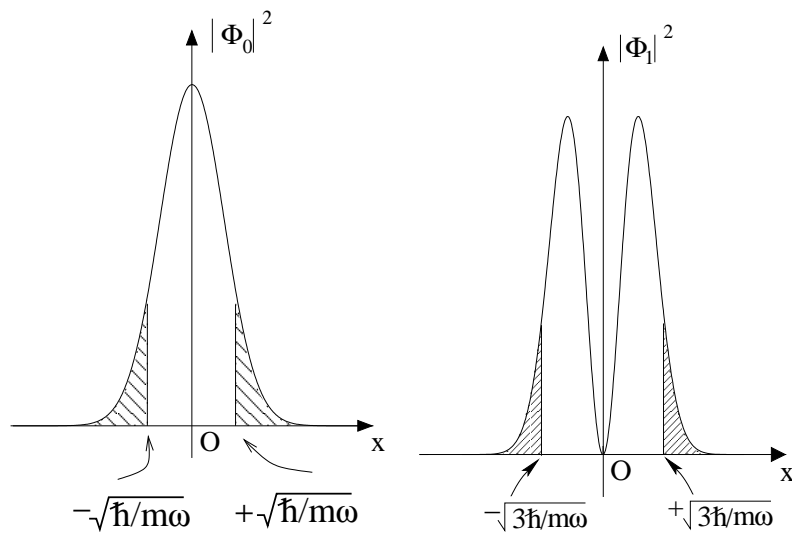


Figure 4:  $|\phi|^2$  for the first two energy eigenstates (SHO)

i.e.,  $|x|$  must be less than or equal to  $(\hbar/m\omega)^{1/2}$ .

An inspection of figure 4 shows, however, that the quantum oscillator has finite probability of being found in the ‘non-classical region’  $|x| > (\hbar/m\omega)^{1/2}$ . This probability is the area that is shaded in the figure on the left. Similarly, in each of the higher stationary states, the oscillator has a finite, non-zero probability of being in the region that is forbidden to it according to classical mechanics. It is very important to remember that this is a direct consequence of quantum mechanics: **in a stationary state, the total energy of the oscillator has a definite value; neither the kinetic energy nor the potential energy, taken by itself, has a definite value in such a state.** Each of them has an **average** value that happens to equal one half of the total energy, in this particular case.

For large values of the quantum number  $n$  where we expect the semi-classical approximation to be valid, it is interesting to ask what classical quantity should  $|\phi_n|^2$  compared with? It turns out that there is a natural probability density that one associates with a classical SHO – it is the probability density that is proportional to the time  $\Delta t$  spent by the oscillator in the interval  $(x, x + \Delta x)$ . We thus write

$$p(x)\Delta x \propto \Delta t = \frac{\Delta t}{\Delta x} \Delta x = \frac{\Delta x}{\dot{x}} . \quad (67)$$

Thus, one finds that the classical probability density is given by

$$p_n(x) \propto \frac{1}{\dot{x}} \propto \frac{1}{x_{max}^2(n) - x^2} \quad (68)$$

where  $x_{max}(n) = \sqrt{2E/m\omega^2} = \sqrt{(2n+1)\hbar/m\omega}$  is the amplitude of the oscillator (for energy  $E$  equal to the energy level  $n$ ). The normalised probability density is thus

$$p_n(x) = \begin{cases} \frac{1}{2\pi\sqrt{x_{max}^2(n)-x^2}} & |x| \leq x_{max}(n) \\ 0 & \text{otherwise} \end{cases} \quad (69)$$

The student is encouraged to check that  $p_n(x)$  is an **smoothened** version of  $|\phi_n|^2$  (in the classically accessible region) for large value of  $n$  by plotting both functions on the same graph. The plot for the case  $n = 24$  is plotted below. One can also see that the quantum probability has 24 nodes.



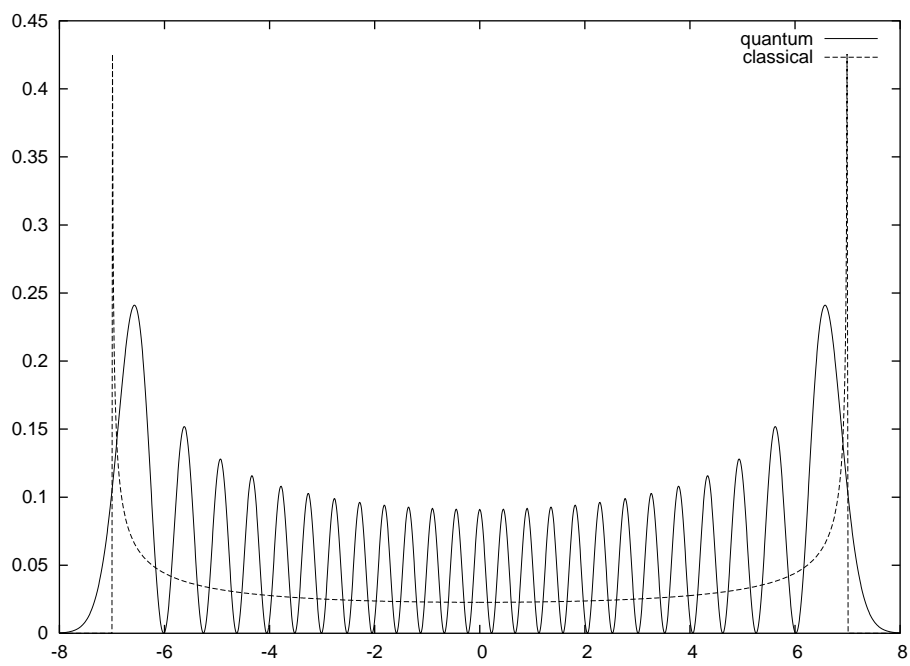


Figure 5: The classical and quantum probabilities for the SHO corresponding to the energy level with quantum number  $n = 24$