QM(2017) Lecture Notes

Part-II Wave Mechanics

A One Semester Course of Lectures for M.Sc. Students

A. K. Kapoor
http://0space.org/users/kapoor
akkapoor@iitbbs.ac.in; akkhcu@gmail.com

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§1 Conservation of probability

We shall discuss some aspects of the Schrodinger equation using the coordinate representation for a particle in a potential $V(\vec{r})$. The classical Hamiltonian, H_{cl}, is

$$H_{cl} = \frac{\vec{p}^{\,2}}{2M} + V(\vec{r}) \tag{1}$$

The corresponding quantum mechanical operator, $\hat{H}$, in the coordinate representation is obtained by replacement $\vec{p} \to -i\hbar\nabla$ in the classical Hamiltonian. So we have

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^{\,2} + V(\vec{r}). \tag{2}$$

The Schrodinger equation assumes the form

$$-i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \hat{H}\psi(\vec{r},t) \tag{3}$$

or

$$-i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \frac{1}{2M}\nabla^{\,2}\psi(\vec{r},t) + V(\vec{r},t)\psi(t). \tag{4}$$

Consider motion of a particle in a potential well $V(\vec{r})$. The time dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\vec{r})\psi(\vec{r},t) \tag{5}$$

Taking complex conjugate we get (assuming the potential to be real $V(\vec{r})^* = V(\vec{r})$

$$-i\hbar\frac{\partial\psi^*(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi^*(\vec{r},t) + V(\vec{r})\psi^*(\vec{r},t) \tag{6}$$

If we multiply Eq.(5) by $\psi^*(\vec{r},t)$ and Eq.(6) by $\psi(\vec{r},t)$ and subtract, the potential terms cancel, and we get

$$i\hbar\psi^*(\vec{r},t)\frac{\partial}{\partial t}(\vec{r},t) + i\hbar\psi(\vec{r},t)\frac{\partial}{\partial t}\psi^*(\vec{r},t) = -\frac{\hbar^2}{2m}[\psi^*(\vec{r},t)\vec{\nabla}^2\psi(\vec{r},t) - \psi(\vec{r},t)\vec{\nabla}^2\psi^*(\vec{r},t)] \tag{7}$$

Eq.(7) can be written as

$$i\hbar\frac{\partial}{\partial t}\{\psi^*(\vec{r},t)\psi(\vec{r},t)\} = -\frac{\hbar^2}{2m}\vec{\nabla}[\psi^*(\vec{r},t)\vec{\nabla}\psi(\vec{r},t) - \psi(\vec{r},t)\vec{\nabla}\psi^*(\vec{r},t)] \tag{8}$$

To see this expand, the right hand side of Eq.(8). It will give four terms, two of which cancel giving the right hand side of Eq.(7). We define

$$\rho = \psi^*(\vec{r},t)\psi(\vec{r},t) = |\psi(\vec{r},t)|^2 \tag{9}$$

$$\vec{j} = -\frac{i\hbar}{2m}\left(\psi^*(\vec{r},t)\vec{\nabla}\psi(\vec{r},t) - \psi^*(\vec{r},t)\vec{\nabla}\psi(\vec{r},t)\right) \tag{10}$$

With ρ and $\vec{j}$ defined as in (9) and (10), Eq.(8) can be written as

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla}.\vec{j} \tag{11}$$

or

$$\frac{\partial \rho}{\partial t} + \vec{\nabla}.\vec{j} = 0 \tag{12}$$

This equation is called the equation of continuity. In electrodynamics a similar relation holds between *charge density* (ρ) and *current density* ($\vec{j}$) and it represents conservation of total charge. Here, in quantum mechanics, $\rho = |\psi|^2$ represents probability density and therefore $\vec{j}$ is called probability current density. As a consequence of Eq.(12), the total probability $\int_{-\infty}^{\infty} |\psi|^2 d\vec{r}$ is independent of time. To see this we integrate (12) over a volume V enclosed by a surface S to get

$$\begin{aligned} \frac{\partial}{\partial t}\int_V \rho d^3x &= -\int_V \vec{\nabla}.\vec{j}\, dV \\ &= -\int_S (\vec{j}.\hat{n})\, dS \end{aligned} \tag{13}$$

where $\hat{n}$ is the unit vector perpendicular to the surface. If V represents volume of a sphere of radius R, S will be the surface of the sphere. The surface area increases as R^2 when R becomes very large. If $\vec{j}$ decreases faster than $1/R^2$, as $R \to \infty$, the right hand side of (13) becomes zero when $R \to \infty$. The left side becomes integral over all space and we get

$$\frac{\partial}{\partial t}\iiint_{-\infty}^{\infty} \rho\, d^3x = 0 \tag{14}$$

Therefore the norm

$$\iiint_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)\, d^3x = (\psi,\psi) = \|\psi\|^2 \tag{15}$$

is independent of time and (12) represents conservation of total "norm" and is a consequence of the fact $\hat{H}$ is a hermitian operator. While Eq.(14) representing the conservation of total probability follows from (12), (12) is, in fact, a stronger equation, it represents a local conservation law.

$$\frac{\partial \rho}{\partial t} + \vec{\nabla}.\vec{j} = 0$$

Electrodynamics	Quantum Mechanics
ρ = charge density	Probability density
$\vec{j}$ = (charge) current density	Probability current density
$\int_V \rho d\vec{r}$ = charge in volume V	Probability of finding particle in volume V.
$\int_S \vec{j}.\hat{n}dS$ current through S; charge flowing out of S per unit time	Probability that the particle crosses the surface in unit time.

The physical interpretation of the probability current density can be seen by evaluating it for plane waves

$$\begin{aligned} \psi(\vec{r}) &= N\exp(ipx/\hbar) \\ \rho = |N|^2 \qquad \vec{j} &= |N|^2\vec{p}/m = |\bar{N}|^2\vec{v} = \rho\vec{v} \end{aligned} \tag{16}$$

The expression (11) for $\vec{j}$ is similar to that for the current density ($\vec{j} = \rho\vec{v}$) in the electromagnetic theory. This expression for $\vec{j}$ can be understood in classical terms if we interpret ρ as number density of particles, then the flux of the beam can be expressed in terms of $\vec{j}$. To see this let us consider a beam of particles incident on a small surface of area ΔS, see Fig.4 below. The number of particles crossing ΔS in time Δt equals the number of particles in a cylinder of height $|\vec{v}|\Delta t$, base ΔS, and having its axis parallel to the velocity $\vec{v}$ of the particles. The volume of the cylinder is given by $\Delta S\cdot\cos\theta(|\vec{v}|\Delta t)$, where θ is the angle between the velocity $\vec{v}$ and the normal to the surface ΔS. If the number density of the particles is $\rho = |N|^2$,the number of particles in cylinder $= |N|^2\Delta S(\cos\theta)|\vec{v}|\Delta t = \vec{j}\cdot\vec{n}\Delta S\Delta t$. This is the number of particles crossing the surface ΔS in time Δt. Thus the flux of particles, defined as the number of particles of the incident crossing a surface per unit area per unit time can be written as $\vec{j}\cdot\vec{n}$

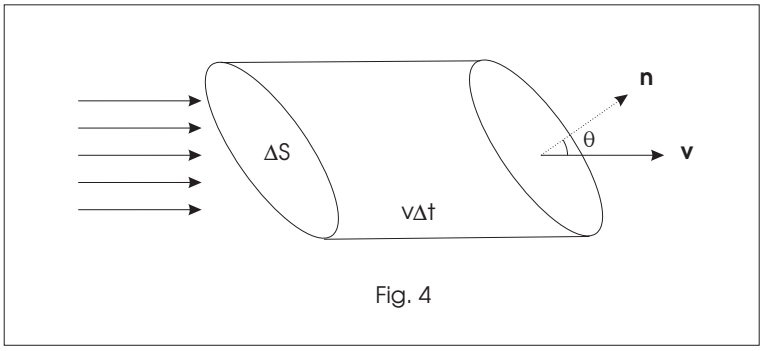

Fig. 4

In the above we interpreted ρ as the number density of particles in the beam and concluded that $\vec{j}.\vec{n}$ gives the number of particles crossing a unit area in unit time. For a single particle, ρ has the interpretation of being probability density, and hence $\vec{j}$ will called the probability current density.

§2 Schrödinger equation for a charged particle

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The Lagrangian for a particle, having charge q, and moving in electric and magnetic field described by vector potential $\vec{A}(\vec{r},t)$ and scalar potential $\phi(\vec{r},t)$ is given by

$$L = \frac{1}{2}m\vec{v}^2 + \frac{q}{c}\,\vec{v}\cdot\vec{A}(\vec{r},t) - q\phi(\vec{r},t), \tag{17}$$

where $\vec{v} = \frac{d\vec{r}}{dt}$ is the velocity of the particle. You must verify that this is the correct Lagrangian by showing that it gives correct equations of motion. The classical Hamiltonian for a charged particle in electromagnetic field is easily obtained by first computing the canonical momentum $\vec{p}$ defined by

$$\vec{p} = \frac{dL}{d\vec{v}} = m\vec{v} + \frac{q}{c}\vec{A}(\vec{r},t), \tag{18}$$

$$\therefore \quad \vec{v} = \frac{1}{m}\Big[\vec{p} - \frac{q}{c}\vec{A}(\vec{r},t)\Big]. \tag{19}$$

The Hamiltonian is seen to be

$$H_{\rm cl} = \vec{p}\cdot\frac{d\vec{r}}{dt} - L \tag{20}$$

$$= \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}(\vec{r},t)\right)^2 + q\phi(\vec{r},t) \tag{21}$$

Comparing this with the free particle Hamiltonian $\frac{\vec{p}^2}{2m}$, we see that the Hamiltonian in presence of electromagnetic field is obtained from the free particle Hamiltonian by making replacements

$$\vec{p} \to \vec{p} - \frac{q}{c}\vec{A}, \qquad H \to H + q\phi. \tag{22}$$

The Hamiltonian operator is obtained from (22) using the quantisation rule $\vec{p} \to -i\hbar\nabla$. This gives the time dependent Schrödinger equation

$$i\hbar\frac{d\psi}{dt} = \frac{1}{2m}\left(-i\hbar\nabla - \frac{q}{c}\vec{A}\right)^2\psi + q\phi(\vec{r},t)\psi. \tag{23}$$

Gauge invariance

The electric and magnetic fields remain unchanged under gauge transformation of the potentials

$$\vec{A} \to \vec{A}' = \vec{A} - \nabla\Lambda(\vec{r},t), \tag{24}$$

$$\phi \to \phi' = \phi - \frac{1}{c}\frac{\partial\Lambda(\vec{r},t)}{\partial t}. \tag{25}$$

Under a gauge transformation the change in Lagrangian (17) is a total time derivative and hence the equations of motion remain unchanged. In quantum mechanics the Schrödinger equation does not remain invariant under a gauge transformation. The observable quantities remain unchanged if the wave function transforms as

$$\psi(\vec{r},t) \to \psi'(\vec{r},t) = \exp\left(\frac{iq}{c}\Lambda(\vec{r},t)\right)\psi(\vec{r},t). \tag{26}$$

It should be noted that the wave function, and the vector and scalar potentials are not physical quantities and are not measurable. The measurable quatities are average values of gauage invariant dynamical variables. The averages of gauge invariant quantities computed using the potentials $\vec{A},\phi$ and the wave function ψ will be the same as those computed using the transformed potentials $\vec{A}',\phi'$ and transformed wave function ψ'.

§3 Time reversal symmetry

Consider classical motion of a particle under influence of a force field. If at some instant t_0 the direction of velocity is reversed, the particle will retrace its path. For a charged particle in magnetic field, the path will be retraced if the magnetic field is also reversed.

To see the time reversal symmetry of the classical equations in another way consider a thought experiment of motion of a particle thrown up in a gravitational field. Let the motion of the particle be captured on a film while going up and on a second film while going down. Now let one of the films be run backwards, what you see cannot be distinguished from what you see in the second film running forward. Assuming that the effect of air friction to be negligible, no measurement on the motions seen in the two films, one running backwards and the other film running forward, will be able to distinguish between them.

We say that the classical Newton's laws retain their form under time reversal $t \to t' = -t$. This means that one cannot distinguish the motion of a particle in a force field with time reversed motion. What about quantum mechanics? In quantum mechanics the time evolution is described by the Schrödinger equation.

$$i\hbar \frac{d\psi(\vec{r},t)}{dt} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r})\psi(\vec{r},t). \tag{27}$$

It is easy to see that the form of the Schrödinger equation does not change if we take take complex conjugate of the Schrodinger equation and then make a replacement $t \to -t \equiv t'$, we would successively get

$$-i\hbar \frac{d\psi^*(\vec{r},t)}{dt} = -\frac{\hbar^2}{2m}\nabla^2\psi^*(\vec{r},t) + V(\vec{r})\psi^*(\vec{r},t), \tag{28}$$

$$i\hbar \frac{d\psi^*(\vec{r},t')}{dt'} = -\frac{\hbar^2}{2m}\nabla^2\psi^*(\vec{r},t') + V(\vec{r})\psi^*(\vec{r},t') \tag{29}$$

The wave function $\psi^*(\vec{r},t')$ describes the time reversed motion. The Schrodinger equation for a charged particle in presence of magnetic field has time reversal symmetry, if the sign of the magnetic field is also reversed. As a simple example, $\exp(ikx)$ represents a (free) particle moving to the right on x axis, and the complex conjugate wave function, $\exp(-ikx)$, represents a particle moving to the left.

§4 Solution of time dependent Schrödinger equation

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We assume that the Hamiltonian of the particle is independent of time and that it can be written in the form

$$H = \frac{p^2}{2m} + V(\vec{r}) \tag{30}$$

The Schrodinger equation for the particle moving in potential $V(\vec{r})$ can be written as

$$-i\hbar \frac{\partial\psi(t)}{\partial t} = \frac{1}{2M}\nabla^2\psi(t) + V(\vec{r})\psi(t). \tag{31}$$

The possible states of the particle at a time t will be represented by square integrable wave function wave function $\psi(\vec{r},t)$.

When time does not appear in the hamiltonian of a system, the equation of motion can be solved by the method of separation of variables. Thus by substituting

$$\psi(\vec{r},t) = u(\vec{r})T(t) \tag{32}$$

in Eq.(31) we get

$$i\hbar\frac{1}{T(t)}\frac{dT(t)}{dt} = \hat{H}u(\vec{r}) \tag{33}$$

Equating each side to a constant, say E we get two equations for $u(\vec{r})$, and for $T(t)$, as follows.

$$i\hbar\frac{d}{dt}T(t) = ET(t) \tag{34}$$

$$\hat{H}u(\vec{r}) = Eu(\vec{r}) \tag{35}$$

Let $u_1(\vec{r}), u_2(\vec{r}), ...$ denote the eigenvectors of the Hamiltonian $\hat{H}$ with the eigenvalues $E_1, E_2, ...$, respectively.

$$\hat{H}u_k(\vec{r}) = E_k u_k(\vec{r}); \qquad k = 1, 2, 3, ... \tag{36}$$

Eq.(34) and Eq.(35) have solutions given by

$$T_k(t) = \text{const} \times \exp(-iE_k t/\hbar), \qquad Hu_k(\vec{r}) = E_k u_k(\vec{r}) \tag{37}$$

and (31) has *an infinite number of solutions*, one for each real k, given by

$$\phi_k(\vec{r},t) = u_k(\vec{r},t)\exp(-iE_k t/\hbar) \tag{38}$$

and the most general solution is a linear combination of solutions $\phi_k(\vec{r},t)$ in Eq.(38) and is given by

$$\psi(\vec{r},t) = \sum_{k=1}^{\infty} c_k u_k(\vec{r})\exp(-iE_k t)/\hbar). \tag{39}$$

If the wave function at time t_0, is $\psi(\vec{r},t_0) \equiv \psi_o(\vec{r})$, the expression (39) evaluated at $t = t_0$ gives

$$\psi_0(\vec{r}) = \sum_{k=1}^{\infty} c_k u_k(\vec{r})\exp(-iE_k t_0)/\hbar) \tag{40}$$

Using the orthogonality of energy eigenfunctions we can find the coefficients α_k and are given by.

$$(u_k, \psi_0) = c_k \exp(-iE_k t_0)/\hbar) \tag{41}$$

and the knowledge of the coefficients c_k allows us to compute the wave function at time t from (39). The final answer for the wave function at time t is given by

$$\psi(\vec{r},t) = \sum_{k=1}^{\infty} c_k u_k(\vec{r})\exp(-iE_k t)/\hbar)\psi(\vec{r},t) = \sum_{k=1}^{\infty}(u_k,\psi_0)\exp(-iE_k(t-t_0)/\hbar)\,u_k(\vec{r}) \tag{42}$$

ψ_0 is the wave function of the system at time t_0.

Flagged for adding a section on stationary states

§5 Propagator

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The propagator, $K(x,t;x_0,t_0)$, for time dependent Schrödinger equation

$$i\hbar\frac{d\psi(x,t)}{dt} = H\psi(x,t). \tag{43}$$

is defined as the solution of

$$i\hbar\frac{d}{dt}K(x,t;x_0,t_0) = HK(x,t;x_0,t_0). \tag{44}$$

obeying the initial condition

$$\lim_{t\to t_0} K(x,t;x_0,t_0) = \delta(x-x_0). \tag{45}$$

To describe in words, the propagator $K(x,t;x_0,t_0)$ is seen to coincide with the wave function of a particle at time t evolving from the state having precise position x_0 at time t_0.

If the wave function at time t_0 the wave function is known to be $\psi_0(x)$, the wave function at time t, $\psi(x,t)$ can be written in terms of propagator as

$$\psi(x,t) = \int K(x,t;x_0,t_0)\psi_0(x_0)dx_0. \tag{46}$$

That $\psi(x,t)$ satisfies initial condition

$$\lim_{t\to t_0} \psi(x,t) = \psi_0(x) \tag{47}$$

is obvious from Eq. (45). Also it follows from (44) and that $\psi(x,t)$ is a solution of the time dependent Schrödinger equation (43).

To obtain an expression for propagator, we recall that the most general solution of the Schrödinger equation is given by

$$\sum c_n e^{-iE_nt/\hbar}u_n(x). \tag{48}$$

in terms of the energy eigenvalues E_n and the energy eigenfunctions $u_n(x)$. Writing the propagator, $K(x,t;x_0,t_0)$, equal to the above expression (48) and setting $t = t_0$ gives

$$\delta(x-x_0) = \sum c_n u_n(x). \tag{49}$$

Multiplying by $u_k^*(x)$, integrating over x and using orthogonality property of the energy eigenfunctions we get

$$c_k = u_k^*(x)e^{iE_kt/\hbar}. \tag{50}$$

Substituting for the coefficients c_n in (48), the propagator takes the form

$$K(x,t;x_0,t_0) = \sum_n c_n e^{-iE_nt/\hbar}u_n(x) = \sum_n e^{-iE_n(t-t_0)/\hbar}u_n(x_0)u_n(x). \tag{51}$$

If we substitute Eq.(**??**) in Eq.(**??**), the resulting equation coincides with (42).

§2 Free Particle

§1 Free particle in one dimension

The classical Hamiltonian for a free particle in one dimension is

$$H_{\text{cl}} = \frac{p^2}{2m}. \tag{52}$$

The corresponding operator $\hat{H}$ in coordinate representation is given by

$$\hat{H} = \frac{1}{2m}\frac{d^2}{dx^2} \tag{53}$$

and the energy eigenvalue equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x). \tag{54}$$

For $E > 0$, we define k by $k^2 = 2mE/\hbar^2$ and write the eigenvalue equation as

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \tag{55}$$

and its most general solution is given by

$$\psi_k(x) = Ae^{ikx} + Be^{-ikx}, \qquad k = \sqrt{\frac{2mE}{\hbar^2}} \tag{56}$$

Here A, B are complex constants. There is no restriction on k and hence all positive energies are allowed. For each value of energy there are two solutions

$$\psi_k(x) = e^{ikx}, e^{-ikx} \tag{57}$$

which correspond to momentum eignevalues $\hbar k, -\hbar k$ and represent the particle moving to the right and left, respectively.

It must be noted that two linearly independent eigenvectors of energy can be written in several ways. A particularly interesting form of solutions is

$$\psi(x) = \sin kx, \cos kx. \tag{58}$$

In contrast with solutions in (57) , the above solutions are not eigenfunctions of momentum.

No solution exists for $E < 0$. We shall now show that the energy eigenvalue problem has no solution for $E < 0$. For $E < 0$, we define $\alpha^2 = -\frac{2mE}{\hbar^2} = \frac{2m|E|}{\hbar^2}$ and rewrite the differential equation (54) in the form

$$\frac{d^2\psi}{dx^2} - \alpha^2\psi(x) = 0, \tag{59}$$

which has most general solution

$$\psi(x) = Ae^{\alpha x} + Be^{-\alpha x}, \qquad \alpha = \sqrt{\frac{2m|E|}{\hbar^2}} \tag{60}$$

In order that the eigenfunction does not blow up for $x \to \infty$, we must demand $A = 0$. Similarly, demanding that the solution remains finite as $x \to -\infty$ gives $B = 0$. These values together imply that the free particle wave function vanishes everywhere. This does not represent a physical state and is therefore unacceptable. Thus we arrive at the conclusion that $E < 0$ is not possible.

Normalisation For $E > 0$ the eigenfunctions are not square integrable and hence cannot be normalized. For solutions of eigenvalue problem for continuous eigenvalue one generally uses delta function normalization which for the present case reads

$$\int_{-\infty}^{\infty} \psi^*_{E_1}(x)\psi_{E_2}(x)\, dx = \delta(E_1 - E_2), \tag{61}$$

Free particle in two and three dimensions The free particle solution in three dimensions corresponding to energy eigenvalue E are given by

$$u_E(x, y) = N \exp(ik_1 x + ik_2 y + ik_3 z) \tag{62}$$

where

$$E = \frac{\hbar^2 k^2}{2m}, \qquad k^2 = k_i^2 + k_2^2 + k_3^2 \tag{63}$$

and k_1, k_2, k_3 are otherwise arbitrary. If we write $\hat{k} = k\hat{n}$, where $\hat{n}$ is aunit vector, the solution $u_E(x, y, z)$ can be written as

$$u_E(x, y, z) = N \exp(i\vec{k} \cdot \vec{r}) = N \exp(ik\hat{n} \cdot \vec{r}). \tag{64}$$

These energy eigenfunctions are also eigenfunctions of momentum operator with eigenvalue $\hbar\vec{k}$. For a fixed energy there are infinite number of solutions, one corresponding to each direction of momentum.

One can impose a delta function normalisation or periodic boundary conditions with box normalisation on the free particle eigenfunctions. Similar results hold for a free particle in two dimensions.

§2 Periodic boundary condition and box normalization

is

§3 Free particle in two and three dimensions

A rigid rectangular box is represented by zero potential inside the box and infinite potential outside the box. Taking one of the corners of the box as the origin, a rigid box in three dimensions and of sides a, b, c corresponds to the potential

$$V(x,y,z) = \begin{cases} 0, & \text{if } 0 < x < a,\ 0 < y < b, \text{ and } 0 < z, c \\ \infty & \text{otherwise} \end{cases}. \tag{65}$$

Since the potential is infinity outside the box, the wave function must be taken to be zero. The boundary conditions to be satisfied are

$$\psi(0,y,z) = \psi(a,y,z) = 0, \qquad \text{for all } y, z, \tag{66}$$
$$\psi(x,0,z) = \psi(x,b,z) = 0, \qquad \text{for all } z, x, \tag{67}$$
$$\psi(x,y,0) = \psi(x,y,c) = 0, \qquad \text{for all } x, y. \tag{68}$$

Recall that *there is no condition on the partial derivatives of the wave function when the potential jumps by an infinite amount across a boundary.* Inside the box, the Schrödinger equation is free particle equation. Thus, for $0 < x < a$, $0 < y < b$, $0 < z < c$ we have

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(\vec{r})}{\partial x^2} + \frac{\partial^2\psi(\vec{r})}{\partial y^2} + \frac{\partial^2\psi(\vec{r})}{\partial z^2}\right) = E\psi(\vec{r}). \tag{69}$$

This solution is separable in several coordinate systems,

$$-\frac{\hbar^2}{2m}\frac{d^2X(x)}{dx^2} = E_1X(x), \tag{70}$$
$$-\frac{\hbar^2}{2m}\frac{d^2Y(y)}{dx^2} = E_2Y(y), \tag{71}$$
$$-\frac{\hbar^2}{2m}\frac{d^2X(z)}{dz^2} = E_3X(z). \tag{72}$$

where $E_1 + E_2 + E_3 = E$. The boundary condition (66) gives

$$X(0)Y(y)Z(z) = X(a)Y(y)Z(z) = 0, \forall y, z. \tag{73}$$

This condition can be satisfied by a nontrivial solution if and only if $X(0) = X(a) = 0$. Similarly, $Y(0) = Y(b) = 0$ and $Z(0) = Z(c) = 0$. Thus the solution of the three dimensional box problem can be down in terms of solutions of the particle in one dimensional box. A little thinking shows that we must have

$$X(x) = \sqrt{\frac{2}{a}} \sin k_1 x, \qquad k_1 = \frac{n_1 \hbar \pi}{a}, \qquad E_1 = \frac{\hbar^2 k_1^2}{2m} = \frac{\hbar^2 n_1^2 \pi^2}{2ma^2} \tag{74}$$

$$Y(y) = \sqrt{\frac{2}{b}} \sin k_2 y, \qquad k_2 = \frac{n_2 \hbar \pi}{b}, \qquad E_2 = \frac{\hbar^2 k_2^2}{2m} = \frac{\hbar^2 n_2^2 \pi^2}{2mb^2} \tag{75}$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin k_3 z, \qquad k_3 = \frac{n_3 \hbar \pi}{c}, \qquad E_3 = \frac{\hbar^2 k_3^2}{2m} = \frac{\hbar^2 n_3^2 \pi^2}{2mc^2} \tag{76}$$

$$\tag{77}$$

and the energy total wave function $\psi(x, y, z)$ and E are given by

$$E = \frac{\hbar^2}{2m}\Big(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\Big), \qquad \psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin k_1 x \, \sin k_2 y \, \sin k_3 z. \tag{78}$$

For a cubical box of side L we have

$$E = \frac{\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2). \tag{79}$$

The ground state corresponds to $n_1 = n_2 = n_3 = 1$ and is nondegenerate. For a cubical box The next energy level corresponds to the values $(n_1, n_2, n_3) = (2, 1, 1), (1, 2, 1), (1, 1, 2)$. and has energy equal to $4(\hbar^2\pi^2/2mL^2)$ and is threefold degenerate. For energy $E = 14E_0$, $(E_0 = \hbar^2\pi^2/2mL^2)$, there are six permutations of 1,2,3 for n_1, n_2 and n_3, giving six wave functions for the which correspond to the same energy $E = 14E_0$.

§3 Wave packets

§1 Wave packets

A classical particle has precise value of position and can have a very precise value of momentum. On the other hand a wave is not localized in space, it can have very precise value of wavelength.

A quantum particle, due its dual nature cannot have 100% precise values of position and momentum simultaneously. Any attempt to make position well defined results in large uncertainty in momentum and vice-versa. It is therefore natural to ask, "How are then particles represented in quantum mechanics?"

Consider a particle with a definite value of momentum p. It will be described by a plane wave:

$$\psi(x) = e^{ipx/\hbar} \tag{80}$$

and the probability density is $|\psi(x)|^2 = 1$ for all positions. Such a quantum particle has equal probability of being anywhere in space and is therefore not localised. However, if we

form a superposition of states corresponding to a range of momenta values and consider the state given by the wave function

$$\Psi(x) = \int_{-\infty}^{\infty} \phi(p) e^{ipx/\hbar}\, dp, \tag{81}$$

it is possible to describe a localised particle.

A suitable choice of the function $\phi(p)$ is the one which has a maximum at some momentum value p_0 and has small value for momentum outside a range Δp around p_0. A few such functions are shown in figure below. The Fourier transform $\psi(x)$ will be a function peaked around some point x_0 and will be appreciable within a range Δx around x_0, schematically shown in see Figs (1) and (2). Note that $|\psi(x)|^2, |\phi(p)|^2$ give the probability densities for position and momenta of the quantum particle. Such a superposition represents a quantum particle localised in space around position x_0 and having uncertainty in position equal to Δx. The value p_0 gives approximately the value of average momentum of the particle. The spreads in the position and momentum will be constrained by the uncertainty relation $\Delta x \Delta p \geq \frac{\hbar}{2}$. Such a superposition of plane wave is called a **wave packet**. A wave packet is a close representation of classical particle having definite position and momentum values.

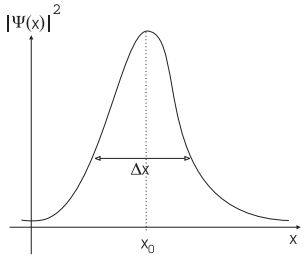

Fig. **1**

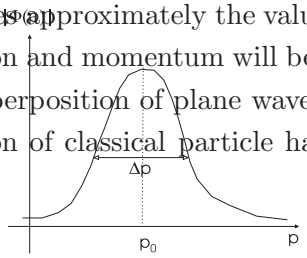

Fig. **2**

Several questions need to be answered at this stage. How can we locate the position of the peak ? What happens as time passes? Does the time evolution of a wave packet in any way resemble the motion of a free particle? To answer these questions we take up a very special case of wave packet known as *gaussian wave packet*.

§2 Time evolution of a Gaussian wave packet

Gaussian wave packet is described by the following wave function.

$$\psi(x) = (2\pi\Delta^2)^{-\frac{1}{4}} \exp\Big(-(x-x_0)^2/4\Delta^2 + ip_0 x/\hbar \Big). \tag{82}$$

For such a wave function we have

$$\langle x\rangle = \int_{-\infty}^{\infty} \psi^*(x) x \psi(x)\, dx = x_0 \tag{83}$$

$$\langle p\rangle = \int_{-\infty}^{\infty} \psi^*(x)\Big(-i\hbar\frac{d}{dx}\Big)\psi(x)\, dx \tag{84}$$

$$(\Delta x)^2 = \langle x\rangle^2 - x_0^2 = \left(\int_{-\infty}^{\infty} \psi^*(x) x^2 \psi(x)\, dx\right) - x_0^2 = \Delta^2 \tag{85}$$

$$(\Delta p)^2 = \langle p\rangle^2 - p_0^2 = \left(\int_{-\infty}^{\infty} \psi^*(x)\Big(-\hbar^2\frac{d^2}{dx^2}\Big)\psi(x)\, dx\right) - p_0^2 = \hbar^2\Delta^2. \tag{86}$$

The above wave packet represents a particle localised around x_0 and having average momentum p_0. We will now obtain the time evolution of a Gaussian wave packet and demonstrate explicitly that the time development of the wave packet closely follows the motion of a classical particle.

§3 Motion of a free particle wave packet

Given the wave packet (82) as wave function at time $t = 0$, and taking the Hamiltonian as the free particle Hamiltonian, how does the wave packet move? The can be answered by finding its wave function at time t following the steps given below.

1. Find the eigenfunctions of the Hamiltonian, and for a free particle these are given by plane waves

$$\psi_p(x) = e^{ipx/\hbar}. \tag{87}$$

2. Write the wave function at time $t = 0$ as superposition of the energy eigenfunctions:

$$\psi(x) = \int_{-\infty}^{\infty} \phi(p) e^{ipx/\hbar}\, dp \tag{88}$$

where the superposition coefficients $\phi(p)$ are given by

$$\phi(p) = \left(\frac{1}{2\pi\hbar}\right)\int_{-\infty}^{\infty} \psi(x) e^{-ipx/\hbar}. \tag{89}$$

3. The wave function $\Psi(x,t)$, at time t, is obtained by supplying a factor $\exp(-iEt/\hbar)$ with the plane wave inside the integral in Eq.(88).

$$\Psi(x,t) = \int_{-\infty}^{\infty} \phi(p) e^{ipx/\hbar} e^{-iE_p t/\hbar}\, dp. \tag{90}$$

In the present case of free particle, $E_p = \frac{p^2}{2m}$.

4. Computing $\phi(p)$ from Eq.(89) and substituting in Eq.(90) and doing the p integral gives the wave function at time t.

$$\Psi(x,t) = (2\pi\Delta^2)^{-1/4}\left(1+\frac{i\hbar t}{2\Delta^2 m}\right) \exp\left[-\frac{1}{1+i\hbar t/2\Delta^2 m}\left\{-\frac{x^2}{4\Delta^2}+\frac{ip_0x}{\hbar}-\frac{ip_0^2t}{2m\hbar}\right\}\right]. \tag{91}$$

The position probability density is given by

$$|\Psi(x,t)|^2 = (2\pi\Delta^2)^{-1/4}\left(1+\frac{i\hbar^2t^2}{2\Delta^2 m}\right)\exp\left[-\frac{x^2}{4\Delta^2(1+\frac{\hbar^2t^2}{(1+4m^2\Delta^2)}}\right]. \tag{92}$$

The average position at time t, and the uncertainty in position at time t are given by

$$\begin{aligned}
\langle x\rangle_t &= \int_{-\infty}^{\infty}\Psi^*(x,t)x\Psi(x,t)dx, &(93)\\
&= x_0+\frac{p_0t}{m} = x_0+vt &(94)\\
(\Delta x)_t &= (\Delta x)_0\left(1+\frac{\hbar^2t^2}{4\Delta^2m^2}\right)^{1/2}. &(95)
\end{aligned}$$

The average position changes with time as expected according to the classical free particle motion. Also remembering that the spread in position at time t is Δ, we see that the uncertainty in position increases with time. Thus there is a spreading of of the wave packet with time. The spreading takes place because the wave packet is a superposition of plane waves and different waves have different velocities.

§4 Free Particle Propagator

The propagator, being solution of the time dependent free particle Schrodinger equation, has the form given by superposition of free particle solutions. The solutions of time dependent free particle Schrödinger equation are given by

$$\psi_p(x,t) = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}e^{-iEt/\hbar}, \qquad E=\frac{p^2}{2m}. \tag{96}$$

Writing the propagator $K(x,t;x_0,t_0)$ as superposition of the above solutions we get

$$K(x,t;x_0,t_0) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}C(p)e^{ipx/\hbar}e^{-iE_pt/\hbar}, \tag{97}$$

where $C(p)$ are coefficients to be fixed and are determined by setting $t = t_0$. This gives

$$\delta(x,t;x_0,t_0) = (\sqrt{2\pi\hbar})^{-1/2}\int_{-\infty}^{\infty} C(p)e^{ipx/\hbar}e^{-iE_pt_0/\hbar},\, dp. \tag{98}$$

where $E_p = \frac{p^2}{2m}$. The function $C(p)$ is determined by taking inverse Fourier transform of the above equation. Thus we have

$$C(p) = (\sqrt{2\pi\hbar})^{-1/2}\int_{-\infty}^{\infty} \delta(x-x_0)e^{ipx/\hbar}e^{-iE_pt_0/\hbar},\, dx. \tag{99}$$

$$= (\sqrt{2\pi\hbar})^{-1/2}e^{ipx_0/\hbar}e^{-iE_pt_0/\hbar}. \tag{100}$$

Therefore the expression for the propagator becomes

$$K(x,t;x_0,t_0) = \left(\frac{1}{2\pi\hbar}\right)\int_{-\infty}^{\infty} e^{-ip(x-x_0)/\hbar}e^{iE_p(t-t_0)}dp. \tag{101}$$

Substituting $E_p = p^2/2m$ and doing a Gaussian integral over p gives the final answer for the free particle propagator

$$K(x,t;x_0,t_0) = \left(\frac{m}{2\pi\hbar(t-t_0)}\right)^{1/2}\exp\left(-\frac{m(x-x_0)^2}{2i\hbar(t-t_0)}\right) \tag{102}$$

§4 Spin as a dynamical variable

§1 Schrodinger description of a particle with spin

For a classical particle the angular momentum, given by $\vec{r}\times\vec{p}$, is zero when the particle is at rest.In order to explain anomalous Zeeman effect it was suggested by Goudsmidt and Uhlenbeck that electron possesses angular momentum at rest whose component in any fixed direction can take one of the two values $\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$). Associated with spin there is a magnetic moment, of one negative Bohr magneton, given by

$$\vec{\mu} = -\frac{e}{mc}\vec{S}$$

Many elementary particles are found to have angular momentum at rest. This angular momentum is called *spin*.

In order to explain the Zeeman splitting of atomic spectra in presence of magnetic fields it became necessary to assign additional angular momentum to the electron which is named spin. More precisely spin of a particle is the angular momentum of the particle at rest.

Spin is an observable associated with all the fundamental particles, having the same properties as the angular momentum. We associate three operators S_x, S_y, and S_z with spin angular momentum and assume that they satisfy angular momentum algebra.]

$$[S_x, S_y] = i\hbar S_z \tag{103}$$

$$[S_y, S_z] = i\hbar S_x \tag{104}$$

$$[S_z, S_x] = i\hbar S_y \tag{105}$$

This algebra implies that the operator $\vec{S}^2 = S_x^2 + S_y^2 + S_z^2$ commutes with all the three components of spin. Since different components of spin do not commute, a commuting set of operators has $\vec{S}^2$ and components of the spin along any one direction; most choice being $\vec{S}^2$ and S_z. The results on angular momentum apply to the spin also and we have

- The eigenvalues of $\vec{S}^2$ are given by $s(s+1)\hbar^2$ where s is a positive integer of half integer.
- For a given value of s, the eigenvalues of S_z are $s, s-1, s-2, \ldots, -s$.
- A particle will be said to have spin s if the the maximum allowed value of S_z is $s\hbar$, which is same as $\vec{S}^2$ having value $s(s+1)\hbar^2$.

A simultaneous eigenvector of $\vec{S}^2$ and S_z will be denoted by $|sm\rangle$ which will have the properties

$$\vec{S}^2|sm\rangle = s(s+1)\hbar^2|sm\rangle \tag{106}$$

$$\vec{S}_z|sm\rangle = m\hbar|sm\rangle \tag{107}$$

In all there are $(2s+1)$ values of m ranging from $-s$ to s and therefore $(2s+1)$ eigenvectors $|sm\rangle$. The vector space needed to descrbe spin is linear span of all the vectors $|sm\rangle$ and is $(2s+1)$ dimensional.

§2 Spin wave function and spin operators

Representation of Spin Wave Function

In order to describe the spin degrees of freedom, it is convenient to introduce a representation. For this we need to select a complete commuting set of hermitian operators and construct an orthonormal basis from their simultaneous eigenvectors. a suitable set consists of $\vec{S}^2$ and S_z. In order to proceed further, we want to work with an explicit representation of the spin. We arrange the eigenvectors $|s,m\rangle$ in *descending order* in m to get a basis $\big\{|s,m\rangle\big|m = s, s-1, \cdots, -s+1, -s\big\}$. An arbitrary state vector $|x\rangle$ is then a linear combination of the basis elements

$$|x\rangle = \sum_{m=-s}^{s} \alpha_m |sm\rangle \tag{108}$$

The interpretation of the numbers α_m is that square of its modulus, $|\alpha_k|^2$, gives the probability that S_z will have the corresponding value $m\hbar$. Following the convention of arranging the basis vectors in the order of decreasing values for the spin projection S_z, the $|x\rangle$ will be represented by a column vector

$$\chi = \begin{pmatrix} \alpha_s \\ \alpha_{s-1} \\ \vdots \\ \alpha_{-s} \end{pmatrix} \tag{109}$$

with $(2s+1)$ components.

Representation of Spin Operators

The spin operators $\vec{S}$ will be represented by matrices with $(2s+1)$ rows and $(2s+1)$ columns. First of all, the matrix for S_z will be diagonal matrix with eigenvalues of S_z appearing along the main diagonal.

$$S_z = \hbar \begin{pmatrix} s & 0 & 0 & \cdots & \cdots & 0 \\ 0 & s-1 & 0 & \cdots & \cdots & 0 \\ 0 & 0 & s-2 & \cdots & \cdots & 0 \\ 0 & 0 & 0 & \cdots & \cdots & \\ \cdots & \cdots & \cdots & \cdots & \cdots & 0 \\ 0 & 0 & 0 & \cdots & \cdots & -s \end{pmatrix} \tag{110}$$

The matrices for S_x and S_y are found by first obtaining the matrices for $S_\pm$ and using $S_x = \frac{1}{2}(S_+ + S_-)$ and $\frac{-i}{2}(S_+ - S_-)$. To construct these matrices one needs to know the matrix elements $\langle s, m'|S_\pm|s, m\rangle$ which can be computed by making use of the result

$$S_\pm|s, m\rangle = \sqrt{s(s+1) - m(m \pm 1)}\,\hbar\,|s, m \pm 1\rangle \tag{111}$$

We shall give the answer for spin $\frac{1}{2}$ and spin 1 matrices. The spin half matrices are related to the Pauli matrices $\sigma_x, \sigma_y, \sigma_z$ and are given by

$$\vec{S} = \frac{\hbar}{2}\,\vec{\sigma} \tag{112}$$

This result is derived in the solved problem below. The corresponding result for the spin one matrices is

$$S_x = \tfrac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \quad S_y = \tfrac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}; \quad S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

and is left as en exercise for the reader.

§3 Pauli matrices

We summarize some important properties of Pauli Matrices.

1. The three Pauli matrices are given by

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{113}$$

2. The Pauli matrices satisfy the commutation relations.

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k \tag{114}$$

3. The square of each Pauli matrix is unity. So is the square of $\hat{n} \cdot \vec{\sigma}$ where $\hat{n}$ is a unit vector.

$$\sigma_1^2 = \sigma_2^2 = \sigma_3^2 = \hat{I}; \qquad \hat{n} \cdot \vec{\sigma}^2 = \hat{I} \tag{115}$$

4. Every Pauli matrix anticommutes with the other two Pauli matrices. There does not exist a nonzero 2×2 matrix which *anticommutes* with

   all the three Pauli matrices.

5. The above relations can be written in various different forms.

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k \tag{116}$$

$$\sigma_j\sigma_k + \sigma_k\sigma_j = 2\delta_{jk} \tag{117}$$

6. The above two relations imply that

$$\sigma_j\sigma_k = \delta_{jk} + i\epsilon_{jk\ell}\sigma_\ell \tag{118}$$

7. The above statements are can be rewritten as

   (a) $[\vec{a} \cdot \vec{\sigma}, \vec{b} \cdot \vec{\sigma}] = 2i(\vec{a} \times \vec{b}) \cdot \vec{\sigma}$

   (b) $(\vec{a} \cdot \vec{\sigma})^2 = |\vec{a}|^2$

   (c) $(\vec{a} \cdot \vec{\sigma})(\vec{b} \cdot \vec{\sigma}) + (\vec{b} \cdot \vec{\sigma})(\vec{a} \cdot \vec{\sigma}) = 2(\vec{a} \cdot \vec{b})\hat{I}$

   (d) $(\vec{a} \cdot \vec{\sigma})(\vec{b} \cdot \vec{\sigma}) = (\vec{a} \cdot \vec{b})\hat{I} + i(\vec{a} \times \vec{b}) \cdot \vec{\sigma}$

   where $\vec{a}, \vec{b}$ are two arbitrary numerical vectors.

8. The trace of each of the three matrices is zero. If we use the notation $\sigma_0 = \hat{I}$ we have the relation, we can write

$$Tr(\sigma_\mu\sigma_\nu) = 2\delta_{\mu\nu} \tag{119}$$

9. The above identity can be used to prove linear independence of Pauli matrices. The four matrices $\sigma_\mu, \mu = 0, .., 3$ form a basis in the complex vector space of all 2×2 matrices.

10. Let S be complex 2×2 matrix which is expanded in terms of the matrices σ_μ

$$S = \sum_{\mu=0}^{3} C_\mu\sigma_\mu \tag{120}$$

    The expansion coefficients are given by

$$C_\mu = \frac{1}{2}Tr(S\sigma_\mu) \tag{121}$$

11. The completeness relation for the Pauli matrices is contained in the identity

$$\sum_a (\sigma^a)_{ij}(\sigma^a)_{kl} = 2\delta_{il}\delta_{jk} - \delta_{ij}\delta kl. \tag{122}$$

12. An important identity satisfied by the Pauli matrices is

$$\exp(i\vec{\alpha}\cdot\vec{\sigma}) = \cos|\vec{\alpha}| + i\vec{\alpha}\cdot\sigma\sin|\vec{\alpha}| \tag{123}$$

where $\vec{\alpha}$ is a vector and

$$(\alpha_1, \alpha_2, \alpha_3), \qquad |\vec{\alpha}| = \sqrt{\alpha_1^2 + \alpha 2^2 + \alpha_2^2} \tag{124}$$

§4 Total wave function of a particle with spin

We have so far discussed a quantum description of the spin degrees of freedom of a particle. The other dynamical variables of a particle are the usual coordinates, momenta, etc. It is assumed that the spin and position are independent of each other and hence can be measured simultaneously. Similarly spin and momentum can be measured simultaneously. Thus the spin operators $\vec{S}$ commute with position operators and also with the momentum operators.In such a space a representation could be chosen in which the basis vectors are simultaneous eigenvectors of $\vec{S}^2, S_z$, and $\vec{r}$ operators. Denoting a basis vector as $|\vec{r}\rangle|sm\rangle$, an arbitrary vector will have an expansion

$$|\psi\rangle = \sum_m \int dx C_{m\vec{r}}|\vec{r}\rangle|sm\rangle \tag{125}$$

The coefficients $C_{m\vec{r}}$ give the probability amplitude of position begin $\vec{r}$ and S_z having a value m, and just the $(2s+1)$ component functions. By a change in notation we write the $(2s+1)$ component wave function as

$$\Psi(\vec{r}) = \begin{pmatrix} \psi_1(\vec{r}) \\ \psi_1(\vec{r}) \\ \vdots \end{pmatrix} \tag{126}$$

In this representation the state of a particle with spin is described by a vector in the vector space which is tensor product of a complex vector space of dimension $(2s+1)$ and the space of square integrable functions. So a particle with spin $\frac{1}{2}$, such as an electron, is described by a two component wave function

$$\Psi(\vec{r}) = \begin{pmatrix} \psi_1(\vec{r}) \\ \psi_1(\vec{r}) \end{pmatrix} \tag{127}$$

The interpretation of the different components of Ψ is, that $|\psi_1(\vec{r})|^2 d^3r$ gives the probability of spin being *up* and position being between $\vec{r}$ and $\vec{r} + d\vec{r}$. Similarly, $|\psi_2(\vec{r})|^2 d^3r$

gives the probability of spin being *down* and position being between $\vec{r}$ and $\vec{r}+d\vec{r}$. The normalization condition now reads

$$\int \Psi^\dagger(\vec{r})\,\Psi(\vec{r})d^3\vec{r} = \int \left(|\psi_1(\vec{r})|^2 + |\psi_2(\vec{r})|^2\right) d^3\vec{r} = 1 \tag{128}$$

Frequently, the total wave function factorizes and assumes the form

$$\Psi(\vec{r}) = \psi(\vec{r}) \times \chi \tag{129}$$

where χ is a column vector with $(2s+1)$ components, so for an electron we will have

$$\chi = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \tag{130}$$

We shall then refer to $\psi(\vec{r})$ as the *space part* of the wave function and the column vector χ as the *spin part* of the wave function. The function $\psi(\vec{r})$ describes the translational degrees of freedom, as usual, and the spin degrees of freedom are described by the column vector χ.

Short Examples 1 *The following examples are about a spin half particle.*

(1a) The allowed values of all three spin operators S_x, S_y, S_z are $\pm\frac{\hbar}{2}$. This is most easily seen by computing the eigenvalues of the corresponding spin operators, $\frac{\hbar}{2}\vec{\sigma}$, for a spin $\frac{1}{2}$ particle. For the general case of $\hat{a}\cdot\vec{S}$ the computation of the eigenvalues is left as an exercise.

(1b) For a spin $\frac{1}{2}$ particle the spin wave function corresponding to S_z obviously are

$$\frac{\hbar}{2}, \quad \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \qquad -\frac{\hbar}{2}, \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \tag{131}$$

(1c) For a spin $\frac{1}{2}$ particle, the spin wave functions corresponding to values $\pm\frac{\hbar}{2}$ for S_x can be easily seen to be

$$\frac{\hbar}{2}, \quad \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}; \qquad -\frac{\hbar}{2}, \quad \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}; \tag{132}$$

(1d) For a spin $\frac{1}{2}$ particle, the spin wave functions corresponding to values $\pm\frac{\hbar}{2}$ for S_y can be easily seen to be

$$\frac{\hbar}{2}, \quad \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}; \qquad -\frac{\hbar}{2}, \quad \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}; \tag{133}$$

(1e) For the general case of $\hat{n}\cdot\vec{S}$, where $\hat{n}$ is a unit vector, the eigenvectors can be written as

$$\frac{\hbar}{2}, \quad \frac{1}{\sqrt{2}}\begin{pmatrix} 1+n_3 \\ n_1+in_2 \end{pmatrix}; \qquad -\frac{\hbar}{2}, \quad \frac{1}{\sqrt{2}}\begin{pmatrix} n_1-in_2 \\ -1-n_3 \end{pmatrix}; \tag{134}$$

Short Examples 2 *Using the results outlined in the previous 'Short Example List' and remembering the postulates, it is now easy to see that*

(2a) the spin wave function of spin $\frac{1}{2}$ particle

(i) is given by $\chi_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$, if the spin points along positive x axis and

(ii) is given by $\chi_2 = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$, *if the spin points along negative* x *axis.*

(iii) is given by $\chi_3 = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\i\end{pmatrix}$, *if the spin points along positive* y *axis*

(iv) is given by $\chi_4 = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-i\end{pmatrix}$, *if the spin points along negative* y *axis.*

(2b) If the spin component along the unit vector $\hat{n}$ *is* $\hbar/2$, *the spin wave function can be written as* $\chi_1 = \begin{pmatrix}1+n_3\\n_1+in_2\end{pmatrix}$ *(apart from an overall normalisation constant) If the spin component along the unit vector* $\hat{n}$ *is* $-\hbar/2$ *the (un-normalized) spin wave function can be written as* $\chi_2 = \begin{pmatrix}n_1-in_2\\-1-n_3\end{pmatrix}$.