

PQM Supplementary Notes: Quantum Mechanics with Wavefunctions

(material from Part IB Quantum Mechanics, based on notes by Dr J.M. Evans)

1 Wavefunctions and Stationary States

The quantum mechanics of a single particle, or beam of particles, is described by a complex wavefunction $\Psi(\mathbf{x}, t)$. Physical quantities become operators acting on the wavefunction; in particular

$$\text{Momentum : } \mathbf{p} \rightarrow -i\hbar\nabla, \quad \text{Energy or Hamiltonian : } H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}) \rightarrow -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x})$$

Dynamics (evolution in time) is governed by the **time-dependent Schrödinger equation**

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{x})\Psi$$

Physical predictions and interpretations involve the probability density and probability current

$$\rho(\mathbf{x}, t) = |\Psi(\mathbf{x}, t)|^2 \quad \text{and} \quad \mathbf{j} = -\frac{i\hbar}{2m}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)$$

and also the concepts of eigenvalue λ and eigenstate χ for an operator Q , defined by

$$Q\chi = \lambda\chi.$$

Stationary states are solutions of the Schrödinger equation of the form

$$\Psi(\mathbf{x}, t) = \psi(\mathbf{x})e^{-iEt/\hbar} \quad \text{with} \quad H\psi(\mathbf{x}) = E\psi(\mathbf{x}),$$

the **time-independent Schrödinger equation**, and it follows that $\rho = |\Psi|^2 = |\psi|^2$ is independent of time. Both Ψ and ψ are eigenstates of H and the eigenvalues E are the allowed energy levels of the system. For a potential with $V(\mathbf{x}) \rightarrow 0$ as $|\mathbf{x}| \rightarrow \infty$ there are two kinds of stationary state solutions.

(i) **Bound states:** $E < 0$ and discrete, or quantized, energy levels. The wave function is normalisable so we can choose

$$\int d^3\mathbf{x} |\Psi|^2 = 1$$

and interpret $\rho = |\Psi|^2$ as the probability density for the position of a single particle, corresponding to a bounded classical orbit.

(ii) **Scattering states:** $E > 0$ and continuous energy levels. The wave function is not normalisable, but the solution can be interpreted in terms of beams of particles with flux (the number crossing unit area per unit time) given by \mathbf{j} .

2 Observables and Measurements in General

A complex inner-product on wave functions is defined by

$$(\Phi, \Psi) = \int d^3\mathbf{x} \Phi(\mathbf{x}, t)^*\Psi(\mathbf{x}, t)$$

It is (anti)linear in its arguments, hermitian, and positive definite:

$$(\Phi, \alpha_1\Psi_1 + \alpha_2\Psi_2) = \alpha_1(\Phi, \Psi_1) + \alpha_2(\Phi, \Psi_2), \quad (\beta_1\Phi_1 + \beta_2\Phi_2, \Psi) = \beta_1^*(\Phi_1, \Psi) + \beta_2^*(\Phi_2, \Psi)$$

$$(\Phi, \Psi) = (\Psi, \Phi)^*, \quad (\Psi, \Psi) \geq 0 \quad \text{and} \quad = 0 \iff \Psi = 0.$$

Given any linear operator Q , its hermitian conjugate, or adjoint, is an operator Q^\dagger defined by

$$(\Phi, Q^\dagger\Psi) = (Q\Phi, \Psi) = (\Psi, Q\Phi)^* \quad \text{for all } \Psi, \Phi.$$

Measurable physical quantities or **observables** correspond to operators which are **hermitian**, meaning that $Q = Q^\dagger$ (e.g. position, momentum, energy, angular momentum). Q hermitian implies

- The eigenvalues of Q are real.
- Eigenstates of Q corresponding to distinct eigenvalues are orthogonal.

Any wavefunction can be expanded as a sum of eigenstates of Q . These results ensure the consistency of the following postulates for physical measurements. Assume, for simplicity, that each eigenvalue λ of Q has a normalized eigenstate χ which is unique (up to a phase). Then:

- The outcome of a measurement of Q is some eigenvalue λ .
- The result λ is obtained with probability $|(\chi, \Psi)|^2$, where Ψ is the normalized state of the system immediately before the measurement is made.
- The effect of the measurement is to force the system into the eigenstate χ : this is the new state immediately after the measurement is made.

The **expectation value** (mean) and **uncertainty** (variance) when measuring Q are

$$\langle Q \rangle_\Psi = (\Psi, Q\Psi), \quad (\Delta Q)_\Psi^2 = \langle (Q - \langle Q \rangle)^2 \rangle_\Psi = \langle Q^2 \rangle_\Psi - \langle Q \rangle_\Psi^2$$

When interpreting probabilities in terms of many, repeated measurements of Q , it is important to realize that the system must be prepared in the same state Ψ before each measurement.

Observables A and B can be simultaneously measured if and only if their commutator $[A, B] = AB - BA$ vanishes. A related result, valid in any state Ψ , is

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|$$

In particular, the basic commutation relation for position and momentum operators in one dimension

$$[x, p] = i\hbar \quad \Rightarrow \quad \Delta x \Delta p \geq \hbar/2$$

which is a mathematically precise formulation of the **Uncertainty Principle**.

3 The Harmonic Oscillator

The harmonic oscillator in one dimension is a particle with Hamiltonian

$$H = \frac{1}{2m}p^2 + \frac{m\omega^2}{2}x^2$$

Apart from piecewise flat potentials (steps, wells, barriers, δ -functions, etc.) this is the simplest problem which can be solved exactly. Introducing a dimensionless variable $y = (m\omega/\hbar)^{1/2}x$, the time-independent Schrödinger equation can be written

$$f'' - 2yf' + (2\mathcal{E} - 1)f = 0 \quad \text{where} \quad \psi(x) = e^{-y^2/2}f(y) \quad \text{and} \quad E = \hbar\omega\mathcal{E} .$$

The exponential factor is motivated by the large y behaviour of the equation and there is, indeed, a normalizable solution with f constant and $\mathcal{E} = 1/2$. More general solutions are obtained by expanding $f(y)$ as a power series: the resulting recurrence relation for the coefficients reveals that $f(y)$ will grow like e^{y^2} for large y , rendering the solution non-normalizable, unless the series terminates, which restricts the values of \mathcal{E} . The resulting normalizable solutions are of the form

$$f(y) = c_n H_n(y) , \quad \mathcal{E} = n + 1/2 , \quad n = 0, 1, 2, \dots$$

where H_n are polynomials of degree n , the **Hermite polynomials**, and c_n are normalization constants. The energy levels of the oscillator are $E = \hbar\omega(n + 1/2)$.

Angular Momentum and Spherically Symmetric Potentials

(more material from Part IB Quantum Mechanics)

4 Angular Momentum and Spherical Harmonics

The **orbital angular momentum** operators are defined by

$$\mathbf{L} = \mathbf{x} \times \mathbf{p} = -i\hbar\mathbf{x} \times \nabla \quad \text{or} \quad L_i = \varepsilon_{ijk}x_j p_k = -i\hbar\varepsilon_{ijk}x_j \frac{\partial}{\partial x_k} \quad \text{and} \quad \mathbf{L}^2 = L^2 = L_i L_i .$$

These operators are hermitian and obey

$$[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k \quad \text{and} \quad [L^2, L_i] = 0 .$$

Different components of angular momentum cannot be measured simultaneously, but a given component, L_3 say, and the total angular momentum, L^2 , can.

In spherical polars (r, θ, ϕ) the angular momentum operators do not involve r :

$$L_3 = -i\hbar \frac{\partial}{\partial \phi} , \quad L_{\pm} = L_1 \pm iL_2 = \pm\hbar e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \phi} \right) , \quad L^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) .$$

Simultaneous eigenfunctions of L_3 and L^2 can be constructed by solving the differential equations

$$L^2 Y_{\ell m} = \hbar^2 \ell(\ell + 1) Y_{\ell m} , \quad L_3 Y_{\ell m} = \hbar m Y_{\ell m} ,$$

to obtain the **spherical harmonic** functions:

$$Y_{\ell m}(\theta, \phi) = c_{\ell m} e^{im\phi} P_{\ell}^m(\cos \theta) \quad \text{with} \quad P_{\ell}^m(u) = (1-u^2)^{|m|/2} \frac{d^{|m|}}{du^{|m|}} P_{\ell}(u)$$

where $P_{\ell}(u)$ are **Legendre polynomials** of degree ℓ , which obey $P_{\ell}(-u) = (-1)^{\ell} P_{\ell}(u)$, and $P_{\ell}^m(u)$ are called **associated Legendre functions**. The allowed eigenvalues are given by

$$\ell = 0, 1, 2, \dots \quad \text{and} \quad m = 0, \pm 1, \pm 2, \dots, \pm \ell .$$

Note that m must be an integer to ensure the solution is periodic in ϕ with period 2π . Other conditions on the eigenvalues arise from the termination of power series solutions to prevent divergences at $\theta = 0, \pi$ or $u = \pm 1$.

5 Spherically Symmetric Potentials

The kinetic energy of a particle can be written

$$\frac{1}{2m} \mathbf{p}^2 = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{2mr^2} L^2 .$$

The L^2 term is the rotational kinetic energy and involves the angular part of ∇^2 . If the particle moves in a spherically symmetric potential $V(r)$ then

$$H = \frac{1}{2m} \mathbf{p}^2 + V(r) \quad \Rightarrow \quad [L_i, H] = [L^2, H] = 0 .$$

Joint eigenstates $\psi_{\ell m}(\mathbf{x})$ with

$$H\psi_{\ell m} = E\psi_{\ell m} , \quad L^2\psi_{\ell m} = \hbar^2 \ell(\ell+1)\psi_{\ell m} , \quad L_3\psi_{\ell m} = \hbar m\psi_{\ell m}$$

can be found as separable wavefunctions

$$\psi_{\ell m}(\mathbf{x}) = R(r)Y_{\ell m}(\theta, \phi) \quad \text{with} \quad -\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} (rR) + \left(\frac{\hbar^2}{2mr^2} \ell(\ell+1) + V(r) \right) R = ER$$

($rR(r)$ satisfies the **radial Schrödinger equation**). The energies E will depend on ℓ , in general, but will be independent of m as a consequence of the rotational invariance of H . Under spatial reflection

$$\mathbf{x} \mapsto -\mathbf{x} \quad \text{or} \quad r \mapsto r , \quad \theta \mapsto \pi - \theta , \quad \phi \mapsto \phi + \pi .$$

It follows from the definitions and properties above that

$$Y_{\ell m}(\pi - \theta, \phi + \pi) = (-1)^{\ell} Y_{\ell m}(\theta, \phi) \quad \text{and} \quad \psi_{\ell m}(-\mathbf{x}) = (-1)^{\ell} \psi_{\ell m}(\mathbf{x}) .$$

6 The Hydrogen(ic) Atom

The **Coulomb potential** for an electron of charge $-e$ due to a nucleus of charge $+Ze$ (at the origin) is

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} = Z\alpha \frac{\hbar c}{r} , \quad \alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137} .$$

This is a **hydrogenic**, or hydrogen-like atom—for hydrogen itself, $Z = 1$. Following the general approach to spherically symmetric potentials, we look for energy eigenstates with definite values of ℓ and m . The solutions for the radial part of the wavefunction and the corresponding energies are

$$R_{n\ell}(r) = C_{n\ell} \exp(-Zr/na) r^\ell L_{n-\ell-1}^{(2\ell+1)}(2Zr/na) , \quad E_n = -\frac{Z^2}{2n^2} \frac{e^2}{4\pi\epsilon_0 a} = -\frac{Z^2\alpha^2}{2n^2} mc^2 .$$

where $L_q^{(p)}$ are **associated Laguerre polynomials** of degree q , $C_{n\ell}$ are normalization constants,

$$a = \frac{1}{\alpha} \frac{\hbar}{mc} , \text{ the } \mathbf{Bohr \ radius} , \quad n = \ell+1, \ell+2, \ell+3, \dots , \text{ the } \mathbf{principal \ quantum \ number} .$$

Note that \hbar/mc is the **Compton wavelength** of the electron, and mc^2 is the famous energy formula from $E = mc^2$. The solutions can be found using power series which, once again, must terminate in order to give a physically sensible, normalizable wavefunction. It is a very special property of the Coulomb potential that the energy E_n corresponding to $R_{n\ell}$ is independent of ℓ .

In summary: the Hydrogenic wave functions and energies are

$$\psi_{n\ell m}(\mathbf{x}) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) , \quad E_n = -\frac{Z^2\alpha^2}{2n^2} mc^2 , \quad \begin{array}{l} n = 1, 2, \dots ; \\ \ell = 0, 1, \dots, n-1 ; \\ m = 0, \pm 1, \pm 2, \dots, \pm \ell . \end{array}$$

The degeneracy of the energy level E_n is therefore

$$1 + 3 + \dots + (2n-1) = n^2 ,$$

or double this if electron spin is taken into account.