

Part IB — Quantum Mechanics

Theorems with proof

Based on lectures by J. M. Evans

Notes taken by Dexter Chua

Michaelmas 2015

These notes are not endorsed by the lecturers, and I have modified them (often significantly) after lectures. They are nowhere near accurate representations of what was actually lectured, and in particular, all errors are almost surely mine.

Physical background

Photoelectric effect. Electrons in atoms and line spectra. Particle diffraction. [1]

Schrödinger equation and solutions

De Broglie waves. Schrödinger equation. Superposition principle. Probability interpretation, density and current. [2]

Stationary states. Free particle, Gaussian wave packet. Motion in 1-dimensional potentials, parity. Potential step, square well and barrier. Harmonic oscillator. [4]

Observables and expectation values

Position and momentum operators and expectation values. Canonical commutation relations. Uncertainty principle. [2]

Observables and Hermitian operators. Eigenvalues and eigenfunctions. Formula for expectation value. [2]

Hydrogen atom

Spherically symmetric wave functions for spherical well and hydrogen atom.

Orbital angular momentum operators. General solution of hydrogen atom. [5]

Contents

0	Introduction	3
0.1	Light quanta	3
0.2	Bohr model of the atom	3
0.3	Matter waves	3
1	Wavefunctions and the Schrödinger equation	4
1.1	Particle state and probability	4
1.2	Operators	4
1.3	Time evolution of wavefunctions	4
2	Some examples in one dimension	5
2.1	Introduction	5
2.2	Infinite well — particle in a box	5
2.3	Parity	5
2.4	Potential well	5
2.5	The harmonic oscillator	5
3	Expectation and uncertainty	6
3.1	Inner products and expectation values	6
3.2	Ehrenfest’s theorem	7
3.3	Heisenberg’s uncertainty principle	7
4	More results in one dimensions	9
4.1	Gaussian wavepackets	9
4.2	Scattering	9
4.3	Potential step	9
4.4	Potential barrier	9
4.5	General features of stationary states	9
5	Axioms for quantum mechanics	10
5.1	States and observables	10
5.2	Measurements	10
5.3	Evolution in time	11
5.4	Discrete and continuous spectra	11
5.5	Degeneracy and simultaneous measurements	11
6	Quantum mechanics in three dimensions	12
6.1	Introduction	12
6.2	Separable eigenstate solutions	12
6.3	Angular momentum	12
6.4	Joint eigenstates for a spherically symmetric potential	13
7	The hydrogen atom	14
7.1	Introduction	14
7.2	General solution	14
7.3	Comments	14

0 Introduction

0.1 Light quanta

0.2 Bohr model of the atom

0.3 Matter waves

1 Wavefunctions and the Schrödinger equation

1.1 Particle state and probability

1.2 Operators

1.3 Time evolution of wavefunctions

Proposition. The probability density

$$P(x, t) = |\Psi(x, t)|^2$$

obeys a conservation equation

$$\frac{\partial P}{\partial t} = -\frac{\partial j}{\partial x},$$

where

$$j(x, t) = -\frac{i\hbar}{2m} \left(\Psi^* \frac{d\Psi}{dx} - \frac{d\Psi^*}{dx} \Psi \right)$$

is the *probability current*.

Proof. This is straightforward from the Schrödinger equation and its complex conjugate. We have

$$\begin{aligned} \frac{\partial P}{\partial t} &= \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi \\ &= \Psi^* \frac{i\hbar}{2m} \Psi'' - \frac{i\hbar}{2m} \Psi''^* \Psi \end{aligned}$$

where the two V terms cancel each other out, assuming V is real

$$= -\frac{\partial j}{\partial x}. \quad \square$$

2 Some examples in one dimension

2.1 Introduction

2.2 Infinite well — particle in a box

2.3 Parity

2.4 Potential well

2.5 The harmonic oscillator

3 Expectation and uncertainty

3.1 Inner products and expectation values

Proposition. The operators \hat{x} , \hat{p} and H are all Hermitian (for real potentials).

Proof. We do \hat{x} first: we want to show $(\phi, \hat{x}\psi) = (\hat{x}\phi, \psi)$. This statement is equivalent to

$$\int_{-\infty}^{\infty} \phi(x)^* x\psi(x) dx = \int_{-\infty}^{\infty} (x\phi(x))^* \psi(x) dx.$$

Since position is real, this is true.

To show that \hat{p} is Hermitian, we want to show $(\phi, \hat{p}\psi) = (\hat{p}\phi, \psi)$. This is equivalent to saying

$$\int_{-\infty}^{\infty} \phi^* (-i\hbar\psi') dx = \int_{-\infty}^{\infty} (i\hbar\phi')^* \psi dx.$$

This works by integrating by parts: the difference of the two terms is

$$-i\hbar[\phi^*\psi]_{-\infty}^{\infty} = 0$$

since ϕ, ψ are normalizable.

To show that H is Hermitian, we want to show $(\phi, H\psi) = (H\phi, \psi)$, where

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x).$$

To show this, it suffices to consider the kinetic and potential terms separately. For the kinetic energy, we just need to show that $(\phi, \psi'') = (\phi'', \psi)$. This is true since we can integrate by parts twice to obtain

$$(\phi, \psi'') = -(\phi', \psi') = (\phi'', \psi).$$

For the potential term, we have

$$(\phi, V(\hat{x})\psi) = (\phi, V(x)\psi) = (V(x)\phi, \psi) = (V(\hat{x})\phi, \psi).$$

So H is Hermitian, as claimed. \square

Proposition (Cauchy-Schwarz inequality). If ψ and ϕ are any normalizable states, then

$$\|\psi\| \|\phi\| \geq |(\psi, \phi)|.$$

Proof. Consider

$$\begin{aligned} \|\psi + \lambda\phi\|^2 &= (\psi + \lambda\phi, \psi + \lambda\phi) \\ &= (\psi, \psi) + \lambda(\psi, \phi) + \lambda^*(\phi, \psi) + |\lambda|^2(\phi, \phi) \geq 0. \end{aligned}$$

This is true for any complex λ . The $\phi = 0$ case is trivial. Otherwise, set

$$\lambda = -\frac{(\phi, \psi)}{\|\phi\|^2}.$$

Then the above equation becomes

$$\|\psi\|^2 - \frac{|(\psi, \phi)|^2}{\|\phi\|^2} \geq 0.$$

So done. \square

3.2 Ehrenfest's theorem

Theorem (Ehrenfest's theorem).

$$\begin{aligned}\frac{d}{dt}\langle\hat{x}\rangle_{\Psi} &= \frac{1}{m}\langle\hat{p}\rangle_{\Psi} \\ \frac{d}{dt}\langle\hat{p}\rangle_{\Psi} &= -\langle V'(\hat{x})\rangle_{\Psi}.\end{aligned}$$

Proof. We have

$$\begin{aligned}\frac{d}{dt}\langle\hat{x}\rangle_{\Psi} &= (\dot{\Psi}, \hat{x}\Psi) + (\Psi, \hat{x}\dot{\Psi}) \\ &= \left(\frac{1}{i\hbar}H\Psi, \hat{x}\Psi\right) + \left(\Psi, \hat{x}\left(\frac{1}{i\hbar}H\right)\Psi\right)\end{aligned}$$

Since H is Hermitian, we can move it around and get

$$\begin{aligned}&= -\frac{1}{i\hbar}(\Psi, H(\hat{x}\Psi)) + \frac{1}{i\hbar}(\Psi, \hat{x}(H\Psi)) \\ &= \frac{1}{i\hbar}(\Psi, (\hat{x}H - H\hat{x})\Psi).\end{aligned}$$

But we know

$$\hat{x}H - H\hat{x}\Psi = -\frac{\hbar^2}{2m}(x\Psi'' - (x\Psi)') + (xV\Psi - Vx\Psi) = -\frac{\hbar^2}{m}\Psi' = \frac{i\hbar}{m}\hat{p}\Psi.$$

So done.

The second part is similar. We have

$$\begin{aligned}\frac{d}{dt}\langle\hat{p}\rangle_{\Psi} &= (\dot{\Psi}, \hat{p}\Psi) + (\Psi, \hat{p}\dot{\Psi}) \\ &= \left(\frac{1}{\hbar}H\Psi, \hat{p}\Psi\right) + \left(\Psi, \hat{p}\left(\frac{1}{i\hbar}H\right)\Psi\right)\end{aligned}$$

Since H is Hermitian, we can move it around and get

$$\begin{aligned}&= -\frac{1}{i\hbar}(\Psi, H(\hat{p}\Psi)) + \frac{1}{i\hbar}(\Psi, \hat{p}(H\Psi)) \\ &= \frac{1}{i\hbar}(\Psi, (\hat{p}H - H\hat{p})\Psi).\end{aligned}$$

Again, we can compute

$$\begin{aligned}(\hat{p}H - H\hat{p})\Psi &= -i\hbar\left(\frac{-\hbar^2}{2m}\right)((\Psi'')' - (\Psi')'') - i\hbar((V(x)\Psi)' - V(x)\Psi') \\ &= -i\hbar V'(x)\Psi.\end{aligned}$$

So done. □

3.3 Heisenberg's uncertainty principle

Theorem (Heisenberg's uncertainty principle). If ψ is any normalized state (at any fixed time), then

$$(\Delta x)_{\psi}(\Delta p)_{\psi} \geq \frac{\hbar}{2}.$$

Proof of uncertainty principle. Choose $\alpha = \langle \hat{x} \rangle_\psi$ and $\beta = \langle \hat{p} \rangle_\psi$, and define

$$X = \hat{x} - \alpha, \quad P = \hat{p} - \beta.$$

Then we have

$$\begin{aligned} (\Delta x)_\psi^2 &= (\psi, X^2\psi) = (X\psi, X\psi) = \|X\psi\|^2 \\ (\Delta p)_\psi^2 &= (\psi, P^2\psi) = (P\psi, P\psi) = \|P\psi\|^2 \end{aligned}$$

Then we have

$$\begin{aligned} (\Delta x)_\psi(\Delta p)_\psi &= \|X\psi\| \|P\psi\| \\ &\geq |(X\psi, P\psi)| \\ &\geq |\operatorname{im}(X\psi, P\psi)| \\ &\geq \left| \frac{1}{2i} [(X\psi, P\psi) - (P\psi, X\psi)] \right| \\ &= \left| \frac{1}{2i} [(\psi, XP\psi) - (\psi, PX\psi)] \right| \\ &= \left| \frac{1}{2i} (\psi, [X, P]\psi) \right| \\ &= \left| \frac{\hbar}{2} (\psi, \psi) \right| \\ &= \frac{\hbar}{2}. \end{aligned}$$

So done. □

4 More results in one dimensions

4.1 Gaussian wavepackets

4.2 Scattering

4.3 Potential step

4.4 Potential barrier

4.5 General features of stationary states

5 Axioms for quantum mechanics

5.1 States and observables

5.2 Measurements

Proposition. Let Q be Hermitian (an observable), i.e. $Q^\dagger = Q$. Then

- (i) Eigenvalues of Q are real.
- (ii) Eigenstates of Q with different eigenvalues are orthogonal (with respect to the complex inner product).
- (iii) Any state can be written as a (possibly infinite) linear combination of eigenstates of Q , i.e. eigenstates of Q provide a basis for V . Alternatively, the set of eigenstates is *complete*.

Proof.

- (i) Since Q is Hermitian, we have, by definition,

$$(\chi, Q\chi) = (Q\chi, \chi).$$

Let χ be an eigenvector with eigenvalue λ , i.e. $Q\chi = \lambda\chi$. Then we have

$$(\chi, \lambda\chi) = (\lambda\chi, \chi).$$

So we get

$$\lambda(\chi, \chi) = \lambda^*(\chi, \chi).$$

Since $(\chi, \chi) \neq 0$, we must have $\lambda = \lambda^*$. So λ is real.

- (ii) Let $Q\chi = \lambda\chi$ and $Q\phi = \mu\phi$. Then we have

$$(\phi, Q\chi) = (Q\phi, \chi).$$

So we have

$$(\phi, \lambda\chi) = (\mu\phi, \chi).$$

In other words,

$$\lambda(\phi, \chi) = \mu^*(\phi, \chi) = \mu(\phi, \chi).$$

Since $\lambda \neq \mu$ by assumption, we know that $(\phi, \chi) = 0$.

- (iii) We will not attempt to justify this, or discuss issues of convergence. □

Proposition.

- (i) The expectation value of Q in state ψ is

$$\langle Q \rangle_\psi = (\psi, Q\psi) = \sum \lambda_n P_n,$$

with notation as in the previous part.

- (ii) The uncertainty $(\delta Q)_\psi$ is given by

$$(\Delta Q)_\psi^2 = \langle (Q - \langle Q \rangle_\psi)^2 \rangle_\psi = \langle Q^2 \rangle_\psi - \langle Q \rangle_\psi^2 = \sum_n (\lambda_n - \langle Q \rangle_\psi)^2 P_n.$$

Proof.

(i) Let $\psi = \sum \alpha_n \chi_n$. Then

$$Q\psi = \sum \alpha_n \lambda_n \chi_n.$$

So we have

$$(\psi, Q\psi) = \sum_{n,m} (\alpha_m, \chi_n, \alpha_n \lambda_n \chi_n) = \sum_n \alpha_n^* \alpha_n \lambda_n = \sum \lambda_n P_n.$$

(ii) This is a direct check using the first expression. □

5.3 Evolution in time

Theorem (Ehrenfest's theorem). If Q is any operator with no explicit time dependence, then

$$i\hbar \frac{d}{dt} \langle Q \rangle_\Psi = \langle [Q, H] \rangle_\Psi,$$

where

$$[Q, H] = QH - HQ$$

is the commutator.

Proof. If Q does not have time dependence, then

$$\begin{aligned} i\hbar \frac{d}{dt} (\Psi, Q\Psi) &= (-i\hbar \dot{\Psi}, Q\Psi) + (\Psi, Q i\hbar \dot{\Psi}) \\ &= (-H\Psi, Q\Psi) + (\Psi, QH\Psi) \\ &= (\Psi, (QH - HQ)\Psi) \\ &= (\Psi, [Q, H]\Psi). \end{aligned} \quad \square$$

5.4 Discrete and continuous spectra

5.5 Degeneracy and simultaneous measurements

6 Quantum mechanics in three dimensions

6.1 Introduction

6.2 Separable eigenstate solutions

6.3 Angular momentum

Proposition.

- (i) $[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k$.
- (ii) $[L^2, L_i] = 0$.
- (iii) $[L_i, \hat{x}_j] = i\hbar\varepsilon_{ijk}\hat{x}_k$ and $[L_i, \hat{p}_j] = i\hbar\varepsilon_{ijk}\hat{p}_k$

Proof.

- (i) We first do a direct approach, and look at specific indices instead of general i and j . We have

$$\begin{aligned} L_1L_2 &= (-i\hbar)^2 \left(x_2 \frac{\partial}{\partial x_3} - x_3 \frac{\partial}{\partial x_2} \right) \left(x_3 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_3} \right) \\ &= -\hbar^2 \left(x_2 \frac{\partial}{\partial x_3} x_3 \frac{\partial}{\partial x_1} - x_1 x_2 \frac{\partial^2}{\partial x_3^2} - x_3^2 \frac{\partial^2}{\partial x_2 \partial x_1} + x_3 x_1 \frac{\partial^2}{\partial x_2 \partial x_3} \right) \end{aligned}$$

Now note that

$$x_2 \frac{\partial}{\partial x_3} x_3 \frac{\partial}{\partial x_1} = x_2 x_3 \frac{\partial^2}{\partial x_3 x_1} + x_2 \frac{\partial}{\partial x_1}.$$

Similarly, we can compute L_2L_1 and find

$$[L_1, L_2] = -\hbar^2 \left(x_2 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial x_2} \right) = i\hbar L_3,$$

where all the double derivatives cancel. So done.

Alternatively, we can do this in an abstract way. We have

$$\begin{aligned} L_iL_j &= \varepsilon_{iar}\hat{x}_a\hat{p}_r\varepsilon_{jbs}\hat{x}_b\hat{p}_s \\ &= \varepsilon_{iar}\varepsilon_{jbs}(\hat{x}_a\hat{p}_r\hat{x}_b\hat{p}_s) \\ &= \varepsilon_{iar}\varepsilon_{jbs}(\hat{x}_a(\hat{x}_b\hat{p}_r - [\hat{p}_r, \hat{x}_b])\hat{p}_s) \\ &= \varepsilon_{iar}\varepsilon_{jbs}(\hat{x}_a\hat{x}_b\hat{p}_r\hat{p}_s - i\hbar\delta_{br}\hat{x}_a\hat{p}_s) \end{aligned}$$

Similarly, we have

$$L_jL_i = \varepsilon_{iar}\varepsilon_{jbs}(\hat{x}_b\hat{x}_a\hat{p}_s\hat{p}_r - i\hbar\delta_{as}\hat{x}_b\hat{p}_r)$$

Then the commutator is

$$\begin{aligned} L_iL_j - L_jL_i &= -i\hbar\varepsilon_{iar}\varepsilon_{jbs}(\delta_{br}\hat{x}_a\hat{p}_s - \delta_{as}\hat{x}_b\hat{p}_r) \\ &= -i\hbar(\varepsilon_{iab}\varepsilon_{jbs}\hat{x}_a\hat{p}_s - \varepsilon_{iar}\varepsilon_{jba}\hat{x}_b\hat{p}_r) \\ &= -i\hbar((\delta_{is}\delta_{ja} - \delta_{ij}\delta_{as})\hat{x}_a\hat{p}_s - (\delta_{ib}\delta_{rj} - \delta_{ij}\delta_{rb})\hat{x}_b\hat{p}_r) \\ &= i\hbar(\hat{x}_i\hat{p}_j - \hat{x}_j\hat{p}_i) \\ &= i\hbar\varepsilon_{ijk}L_k. \end{aligned}$$

So done.

(ii) This follows from (i) using the *Leibnitz property*:

$$[A, BC] = [A, B]C + B[A, C].$$

This property can be proved by directly expanding both sides, and the proof is uninteresting.

Using this, we get

$$\begin{aligned} [L_i, \mathbf{L}^2] &= [L_i, L_j L_j] \\ &= [L_i, L_j]L_j + L_j[L_i, L_j] \\ &= i\hbar\varepsilon_{ijk}(L_k L_j + L_j L_k) \\ &= 0 \end{aligned}$$

where we get 0 since we are contracting the antisymmetric tensor ε_{ijk} with the symmetric tensor $L_k L_j + L_j L_k$.

(iii) We will use the Leibnitz property again, but this time we have it the other way round:

$$[AB, C] = [A, C]B + A[B, C].$$

This follows immediately from the previous version since $[A, B] = -[B, A]$. Then we can compute

$$\begin{aligned} [L_i, \hat{x}_j] &= \varepsilon_{iab}[\hat{x}_a \hat{p}_b, \hat{x}_j] \\ &= \varepsilon_{iab}([\hat{x}_a, \hat{x}_j]\hat{p}_b + \hat{x}_a[\hat{p}_b, \hat{x}_j]) \\ &= \varepsilon_{iab}\hat{x}_a(-i\hbar\delta_{bj}) \\ &= i\hbar\varepsilon_{ija}\hat{x}_a \end{aligned}$$

as claimed.

We also have

$$\begin{aligned} [L_i, \hat{p}_j] &= \varepsilon_{iab}[\hat{x}_a \hat{p}_b, \hat{p}_j] \\ &= \varepsilon_{iab}([\hat{x}_a, \hat{p}_j]\hat{p}_b + \hat{x}_a[\hat{p}_b, \hat{p}_j]) \\ &= \varepsilon_{iab}(i\hbar\delta_{aj}\hat{p}_b) \\ &= i\hbar\varepsilon_{ijb}\hat{p}_b. \end{aligned} \quad \square$$

6.4 Joint eigenstates for a spherically symmetric potential

7 The hydrogen atom

7.1 Introduction

7.2 General solution

7.3 Comments