Part IB — Quantum Mechanics

Theorems with proof

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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

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

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

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

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

□

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

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

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

$$\int_{-\infty}^{\infty} \phi^*(-i\hbar\psi')\;\mathrm{d}x = \int_{-\infty}^{\infty} (i\hbar\phi')^*\psi\;\mathrm{d}x.$$

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

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

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. □

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. Set

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

which is always well-defined since ϕ is normalizable, and then the above equation becomes

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

So done. □

3.2 Ehrenfest's theorem

Theorem (Ehrenfest's theorem)**.**

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{x}\rangle_\Psi &= \frac{1}{m}\langle\hat{p}\rangle_\Psi\\ \frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{p}\rangle_\Psi &= -\langle V'(\hat{x})\rangle_\Psi.\end{aligned}$$

Proof. We have

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

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

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

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

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

Then we have

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

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. $\square$

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

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

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

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

where

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

is the commutator.

Proof. If Q does not have time dependence, then

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

□

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) $[\mathbf{L}^2, L_i] = 0$.

(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

$$\begin{aligned} L_1L_2 &= (-i\hbar)^2\left(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}\right)\left(x_3\frac{\partial}{\partial x_1} - x_1\frac{\partial}{\partial x_3}\right)\\ &= -\hbar^2\left(x_2\frac{\partial}{\partial x_3}x_3\frac{\partial}{\partial x_1} - x_1x_2\frac{\partial^2}{\partial x_3^2} - x_3^2\frac{\partial^2}{\partial x_2\partial x_1} + x_3x_1\frac{\partial^2}{\partial x_2\partial x_3}\right) \end{aligned}$$

Now note that

$$x_2\frac{\partial}{\partial x_3}x_3\frac{\partial}{\partial x_1} = x_2x_3\frac{\partial^2}{\partial x_3 x_1} + x_2\frac{\partial}{\partial x_1}.$$

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

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

□

6.4 Joint eigenstates for a spherically symmetric potential

7 The hydrogen atom

7.1 Introduction

7.2 General solution

7.3 Comments