

QUANTUM MECHANICS NOTES

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1. INTRODUCTION

1.1. Schrödinger Equation.

Definition 1.1. A particle with potential energy $V(x, t)$ is completely described by its **position wavefunction** $\Psi(x, t)$, which satisfies the **Schrödinger equation**:

$$i\hbar \frac{\partial}{\partial t} \Psi = -\frac{\hbar^2}{2m} \Delta \Psi + V \Psi$$

Interpretation 1.2. We interpret $|\Psi(x, t)|^2$ to be the **probability density** for the position, x , of the particle at time t . Therefore, we require that for each $t \in \mathbb{R}$,

$$\int_{\mathbb{R}^n} \Psi(x, t)^* \Psi(x, t) dx = 1$$

1.2. Operators.

Definition 1.3. We define the j^{th} **position** and **momentum coordinate operators** X_j, P_j , (in position space) by

$$X_j \Psi(x, t) = x_j \Psi(x, t)$$

and

$$P_j \Psi(x, t) = -i\hbar \frac{\partial}{\partial x_j} \Psi(x, t)$$

We define the **position** and **momentum** operators, X and P , by

$$X = (X_1, X_2, \dots, X_n)$$

and

$$P = (P_1, P_2, \dots, P_n)$$

We denote $P \cdot P$ by P^2 . Note that

$$P^2 = -\hbar^2 \Delta$$

If the particle has potential energy $V(x, t)$, we define the **Hamiltonian** operator, H , by

$$H = \frac{P^2}{2m} + V$$

Thus the Schrödinger equation reads

$$i\hbar \frac{\partial}{\partial t} \Psi = H \Psi$$

Note 1.4. If the potential energy doesn't depend on time, we may write

$$H = \frac{P^2}{2m} + V(X)$$

meaning Hamiltonian only depends on the position and momentum operators, X and P . For the rest of these notes, we assume that the potential energy V does not depend on time.

Definition 1.5. Let A and B be operators. Then B is said to be the **adjoint** of A if for each Ψ_1, Ψ_2 ,

$$\langle \Psi_1 | A \Psi_2 \rangle = \langle B \Psi_1 | \Psi_2 \rangle$$

i.e.

$$\int_{\mathbb{R}^n} \Psi_1^* (A \Psi_2) dx = \int_{\mathbb{R}^n} (B \Psi_1)^* \Psi_2 dx$$

If B is the adjoint of A , we write

$$B = A^\dagger$$

Exercise 1.6. Let A be an operator, then

$$(1) \text{ for each } \Psi_1, \Psi_2, \langle A \Psi_1 | \Psi_2 \rangle = \langle \Psi_1 | A^\dagger \Psi_2 \rangle$$

$$(2) (A^\dagger)^\dagger = A$$

Proof. (1) For wavefunctions Ψ_1, Ψ_2 , we have

$$\begin{aligned} \langle A \Psi_1 | \Psi_2 \rangle &= \langle \Psi_2 | A \Psi_1 \rangle^* \\ &= \langle A^\dagger \Psi_2 | \Psi_1 \rangle^* \quad (\text{by definition}) \\ &= \langle \Psi_1 | A^\dagger \Psi_2 \rangle \end{aligned}$$

(2) For each Ψ_1, Ψ_2 , we have that

$$\begin{aligned} \langle A \Psi_1 | \Psi_2 \rangle &= \langle \Psi_1 | A^\dagger \Psi_2 \rangle \\ &= \langle (A^\dagger)^\dagger \Psi_1 | \Psi_2 \rangle \end{aligned}$$

This implies that for each Ψ_1, Ψ_2 ,

$$\langle [A - (A^\dagger)^\dagger] \Psi_1, \Psi_2 \rangle = 0$$

Therefore for each Ψ_1 ,

$$[A - (A^\dagger)^\dagger] \Psi_1 = 0$$

Hence $\langle A - (A^\dagger)^\dagger = 0$ and $A = (A^\dagger)^\dagger$.

□

Definition 1.7. An linear operator Q is **self-adjoint** if

$$Q = Q^\dagger$$

Interpretation 1.8. For each measurable, observable quantity \hat{Q} , there is a self-adjoint operator Q whose eigenvalues are the possible measurment values and whose eigenfunctions are the possible states of the system at measurment.

Exercise 1.9. The operators X_j, P_j and H are self adjoint.

Hint: for H , use Green's second identity.

Proof. Since x_j is real, clearly

$$\langle \Psi_1 | X_j \Psi_2 \rangle = \langle X_j \Psi_1 | \Psi_2 \rangle$$

Similarly, we have that

$$\begin{aligned} \langle \Psi_1 | P_j \Psi_2 \rangle &= \int_{\mathbb{R}^n} \Psi_1^* \left(-i\hbar \frac{\partial}{\partial x_j} \Psi_2 \right) dx \\ &= -i\hbar \int_{\mathbb{R}^n} \Psi_1^* \left(\frac{\partial}{\partial x_j} \Psi_2 \right) dx \\ &= i\hbar \int_{\mathbb{R}^n} \left(\frac{\partial}{\partial x_j} \Psi_1^* \right) \Psi_2 dx \quad (\text{integration by parts}) \\ &= \int_{\mathbb{R}^n} \left(-i\hbar \frac{\partial}{\partial x_j} \Psi_1 \right)^* \Psi_2 dx \\ &= \langle P \Psi_1 | \Psi_2 \rangle \end{aligned}$$

Finally

$$\begin{aligned} \langle \Psi_1 | H \Psi_2 \rangle - \langle H \Psi_1 | \Psi_2 \rangle &= \int_{\mathbb{R}^n} \Psi_1^* \left(-\frac{\hbar^2}{2m} \Delta \Psi_2 + V \Psi_2 \right) dx - \int_{\mathbb{R}^n} \left(-\frac{\hbar^2}{2m} \Delta \Psi_1 + V \Psi_1 \right)^* \Psi_2 dx \\ &= \frac{\hbar^2}{2m} \int_{\mathbb{R}^n} (\Delta \Psi_1^*) \Psi_2 - \Psi_1^* (\Delta \Psi_2) dx \\ &= 0 \quad (\text{Green's second identity}) \end{aligned}$$

□

Exercise 1.10. Let Q be a self-adjoint operator. Then

- (1) the eigenvalues of Q are real.
- (2) the eigenfunctions of Q corresponding to distinct eigenvalues are orthogonal.

Proof.

(1) Let λ be an eigenvalue of Q with corresponding eigenfunction Ψ . Then

$$\begin{aligned}\lambda\langle\Psi|\Psi\rangle &= \langle\Psi|Q\Psi\rangle \\ &= \langle Q\Psi|\Psi\rangle \\ &= \lambda^*\langle\Psi|\Psi\rangle\end{aligned}$$

Thus $\lambda = \lambda^*$ and is real

(2) Let λ_1 and λ_2 be eigenvalues of Q with corresponding eigenfunctions Ψ_1 and Ψ_2 . Suppose that $\lambda_1 \neq \lambda_2$. Then

$$\begin{aligned}\lambda_2\langle\Psi_1|\Psi_2\rangle &= \langle\Psi_1|Q\Psi_2\rangle \\ &= \langle Q\Psi_1|\Psi_2\rangle \\ &= \lambda_1\langle\Psi_1|\Psi_2\rangle\end{aligned}$$

So $(\lambda_2 - \lambda_1)\langle\Psi_1|\Psi_2\rangle = 0$. Which implies that $\langle\Psi_1|\Psi_2\rangle = 0$

□

Definition 1.11. Let A and B be operators. The **commutator** of A and B , $[A, B]$, is defined by

$$[A, B] = AB - BA$$

Exercise 1.12. We have $[X_j, P_j] = i\hbar$.

Proof. For a position wave function Ψ ,

$$\begin{aligned}[X_j, P_j]\Psi(x, t) &= [x_j, -i\hbar\frac{\partial}{\partial x_j}]\Psi(x, t) \\ &= (-i\hbar)\left[x_j\frac{\partial}{\partial x_j}\Psi(x, t) - \frac{\partial}{\partial x_j}x_j\Psi(x, t)\right] \\ &= (-i\hbar)\left[x_j\frac{\partial}{\partial x_j}\Psi(x, t) - \Psi(x, t) - x_j\frac{\partial}{\partial x_j}\Psi(x, t)\right] \\ &= i\hbar\Psi(x, t)\end{aligned}$$

Hence $[X_j, P_j] = i\hbar$

□

1.3. Continuity Equation.

Exercise 1.13. If V is real and Ψ satisfies the Schrödinger equation, then

$$i\hbar\frac{\partial}{\partial t}\Psi^* = -H\Psi^*$$

Proof. We have that

$$\begin{aligned}i\hbar\frac{\partial}{\partial t}\Psi^* &= \left(-i\hbar\frac{\partial}{\partial t}\Psi\right)^* \\ &= \left(-\left[-\frac{\hbar^2}{2m}\Delta\Psi + V\Psi\right]\right)^* \\ &= -\left[-\frac{\hbar^2}{2m}\Delta\Psi^* + V\Psi^*\right] \\ &= -H\Psi^*\end{aligned}$$

□

Exercise 1.14. *We have that*

$$\frac{\partial}{\partial t}(\Psi^*\Psi) + \frac{\hbar}{2mi}\nabla \cdot \left[\Psi^*(\nabla\Psi) - (\nabla\Psi^*)\Psi \right] = 0$$

Proof.

$$\begin{aligned} \frac{\partial}{\partial t}(\Psi^*\Psi) &= \left(\frac{\partial}{\partial t}\Psi^* \right)\Psi + \Psi^*\left(\frac{\partial}{\partial t}\Psi \right) \\ &= \left(\frac{\hbar}{2mi}(\Delta\Psi^*)\Psi - \frac{1}{i\hbar}V\Psi^*\Psi \right) + \left(-\frac{\hbar}{2mi}\Psi^*(\Delta\Psi) + \frac{1}{i\hbar}V\Psi^*\Psi \right) \\ &= \frac{\hbar}{2mi} \left[(\Delta\Psi^*)\Psi - \Psi^*(\Delta\Psi) \right] \\ &= -\frac{\hbar}{2mi} \left[\Psi^*(\Delta\Psi) - (\Delta\Psi^*)\Psi \right] \\ &= -\frac{\hbar}{2mi}\nabla \cdot \left[\Psi^*(\nabla\Psi) - (\nabla\Psi^*)\Psi \right] \end{aligned}$$

Therefore

$$\frac{\partial}{\partial t}(\Psi^*\Psi) + \frac{\hbar}{2mi}\nabla \cdot \left[\Psi^*(\nabla\Psi) - (\nabla\Psi^*)\Psi \right] = 0$$

□

Definition 1.15. *We define the **probability current density**, j , of the particle to be*

$$j = \frac{\hbar}{2mi} \left[\Psi^*(\nabla\Psi) - (\nabla\Psi^*)\Psi \right]$$

1.4. Position and Momentum Space.

Definition 1.16. *We define the **momentum wavefunction**, Φ , of the particle to be the Fourier transform of the position wavefunction:*

$$\begin{aligned} \Phi(p, t) &= F[\Psi](p, t) \\ &= \frac{1}{(2\pi\hbar)^{n/2}} \int_{\mathbb{R}^n} \Psi(x, t) e^{-i\frac{p \cdot x}{\hbar}} dx \end{aligned}$$

Note 1.17. *We recall the following facts about Fourier transforms:*

(1)

$$\Phi(p, t) = \frac{1}{(2\pi\hbar)^{n/2}} \int_{\mathbb{R}^n} \Psi(x, t) e^{-i\frac{p \cdot x}{\hbar}} dx$$

and

$$\Psi(x, t) = \frac{1}{(2\pi\hbar)^{n/2}} \int_{\mathbb{R}^n} \Phi(p, t) e^{i\frac{p \cdot x}{\hbar}} dp$$

(2)

$$F \left[\frac{\partial}{\partial x_j} \Psi \right] = \frac{ip_j}{\hbar} F[\Psi]$$

and

$$F^{-1} \left[\frac{\partial}{\partial p_j} \Phi \right] = -\frac{ix_j}{\hbar} F[\Psi]$$

(3)

$$\int_{\mathbb{R}^n} \Psi_1^* \Psi_2 dx = \int_{\mathbb{R}^n} F[\Psi_1]^* F[\Psi_2] dx$$

Note 1.18. Let $Q(X, P)$ be a self-adjoint operator. Then the properties of the Fourier transform imply that:

$$Q(X, P) = \begin{cases} Q(x, -i\hbar\nabla) & (\text{position space}) \\ Q(i\hbar\nabla, p) & (\text{momentum space}) \end{cases}$$

Exercise 1.19. If Ψ satisfies the Schrödinger equation, then Φ satisfies

$$i\hbar \frac{\partial}{\partial t} \Phi = \frac{p^2}{2m} \Phi + V(i\hbar\nabla) \Phi$$

Proof. Starting with the Schrödinger equation, we have

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Psi &= \left[\frac{P^2}{2m} + V(X) \right] \Psi \\ &= \left[\frac{-\hbar^2}{2m} \Delta + V(x) \right] \Psi \quad (\text{position space}) \end{aligned}$$

Taking Fourier transforms of both sides, we see that

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Phi &= \left[\frac{P^2}{2m} + V(X) \right] \Phi \\ &= \left[\frac{p^2}{2m} + V(i\hbar\nabla) \right] \Phi \quad (\text{position space}) \end{aligned}$$

□

Interpretation 1.20. We interpret $|\Phi(p, t)|^2$ to be the probability density for the momentum, p , of the particle at time t .

Note 1.21. For a self-adjoint operator $Q(X, P)$, the expected value of Q , is given by

$$\langle Q \rangle = \begin{cases} \langle \Psi(x, t) | Q(x, -i\hbar\nabla) \Psi(x, t) \rangle & (\text{position space}) \\ \langle \Phi(p, t) | Q(i\hbar\nabla, p) \Phi(p, t) \rangle & (\text{momentum space}) \end{cases}$$

1.5. Stationary States.

Definition 1.22. When the potential energy V doesn't depend on time, we look for solutions to the Schrödinger equation of the form

$$\Psi(x, t) = \psi(x) \varphi(t)$$

With a closer look, we find that

- (1) $H\psi = E\psi$
- (2) $\varphi(t) = e^{-i\frac{E}{\hbar}t}$

Statement (1) is referred to as the **time-independent Schrödinger equation**. Eigenfunctions of the Hamiltonian operator are called **stationary states**. If the possible eigenvalues

for the Hamiltonian operator are discrete $(E_n)_{n \in \mathbb{N}}$ with stationary states $(\psi_n)_{n \in \mathbb{N}}$, then the general solution to the Schrödinger equation is

$$\Psi(x, t) = \sum_{n \in \mathbb{N}} c_n \psi_n(x) e^{-i \frac{E_n}{\hbar} t}$$

where

$$c_n = \int_{\mathbb{R}^n} \psi_n^*(x) \Psi(x, 0) dx$$

Definition 1.23. An energy eigenvalue E_n of H is said to have a **degeneracy of degree** k if it corresponds to k orthonormal stationary states.

Note 1.24. If the energy eigenvalues $(E_n)_{n \in \mathbb{N}}$ have degeneracies of degrees $(k_n)_{n \in \mathbb{N}}$ with corresponding orthonormal stationary states $(\psi_{n,j})_{j=1}^{k_n}$ and

$$\Psi(x, t) = \sum_{n \in \mathbb{N}} \sum_{j=1}^{k_n} c_{n,j} \psi_{n,j}(x) e^{-i \frac{E_n}{\hbar} t}$$

Then the probability of measuring the energy E_n is

$$\mathbb{P}(E_n) = \sum_{j=1}^{k_n} |c_{n,j}|^2$$

Definition 1.25. If the spectrum of the Hamiltonian is discrete, the stationary state with the least energy is called the **ground state**. The stationary states that are not the ground state are called **excited states**.

2. FUNDAMENTAL EXAMPLES IN ONE DIMENSION

2.1. The Infinite Square Well.

Definition 2.1. The infinite square well is defined by the potential

$$V(x) = \begin{cases} \infty & x \in I_1 = (-\infty, a] \\ 0 & x \in I_2 = (0, a) \\ \infty & x \in I_3 = [a, \infty) \end{cases}$$

Exercise 2.2. By starting with a finite potential well and letting the height of the well go to infinity, show that the stationary states and their energies are given by

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) & x \in (0, a) \\ 0 & x \notin (0, a) \end{cases}$$

and

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

Proof. Define

$$V_\alpha(x) = \begin{cases} \alpha & x \in I_1 \\ 0 & x \in I_2 \\ \alpha & x \in I_3 \end{cases}$$

For the potential energy V_α , in sections I_1, I_3 the Schrödinger equation may be written as

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(\alpha - E)\psi$$

Assuming $\alpha > E$, we may write $l = \frac{\sqrt{2m(\alpha-E)}}{\hbar}$ and substitute to get

$$\frac{d^2\psi}{dx^2} = l^2\psi$$

Thus in region I_1 , $\psi_1(x) = Ae^{lx} + Be^{-lx}$ and in region I_3 , $\psi_3(x) = Fe^{lx} + Ge^{-lx}$. Since e^{-lx} blows up as $x \rightarrow -\infty$, $B = 0$. Since e^{lx} blows up as $x \rightarrow \infty$, $F = 0$.

In section I_2 , the Schrödinger equation may be written as

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi$$

We write $k = \frac{\sqrt{2mE}}{\hbar}$ and substitute to get

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

Hence in region I_2 , $\psi_2(x) = C \sin(kx) + D \cos(kx)$.

So far we have

$$\psi_\alpha(x) = \begin{cases} Ae^{lx} & x \in I_1 \\ C \sin(kx) + D \cos(kx) & x \in I_2 \\ Ge^{-lx} & x \in I_3 \end{cases}$$

To find possible wavefunctions ψ for the infinite potential, we let $\alpha \rightarrow \infty$. As $\alpha \rightarrow \infty$, we have that $l \rightarrow \infty$. Hence $\psi_1 \rightarrow 0$ and $\psi_3 \rightarrow 0$. So for the infinite potential,

$$\psi(x) = \begin{cases} C \sin(kx) + D \cos(kx) & x \in (0, a) \\ 0 & x \notin (0, a) \end{cases}$$

By continuity at the points $x = 0$ and $x = a$, we see that $0 = C \sin(0) + D \cos(0)$ which implies that $D = 0$ and $0 = C \sin(ka)$ which yields various solutions

$$k_n = \frac{n\pi}{a} \quad n \in \mathbb{Z}$$

To avoid non-normalizable solutions or linearly dependent solutions, we restrict $n \in \mathbb{N}$. Our energies are then

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2ma^2} \quad n \in \mathbb{N}$$

and (after normalizing) our stationary states are

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) & x \in (0, a) \\ 0 & x \notin (0, a) \end{cases}$$

□

2.2. The Harmonic Oscillator.

Definition 2.3. The **harmonic oscillator** in one dimension is defined by the potential energy:

$$V(x) = \frac{1}{2}m\omega^2x^2$$

We define the **lowering operator**, a , by

$$a = \frac{1}{\sqrt{2\hbar m\omega}}(m\omega X + iP)$$

Exercise 2.4. The adjoint of the lowering operator is

$$a^\dagger = \frac{1}{\sqrt{2\hbar m\omega}}(m\omega X - iP)$$

Proof. For a wave functions Ψ_1, Ψ_2 ,

$$\begin{aligned} \int_{\mathbb{R}} \left[\frac{1}{\sqrt{2\hbar m\omega}}(m\omega X - iP)\Psi_1 \right]^* \Psi_2 dx &= \frac{1}{\sqrt{2\hbar m\omega}} \int_{\mathbb{R}} (m\omega x \Psi_1(x, t)^* \Psi_2(x, t) - \hbar \left(\frac{\partial}{\partial x} \Psi_1(x, t)^* \right) \Psi_2(x, t) dx \\ &= \frac{1}{\sqrt{2\hbar m\omega}} \int_{\mathbb{R}} (m\omega x \Psi_1(x, t)^* \Psi_2(x, t) + \hbar \Psi_1(x, t)^* \left(\frac{\partial}{\partial x} \Psi_2(x, t) \right) dx \\ &= \int_{\mathbb{R}} \Psi_1^* \left[\frac{1}{\sqrt{2\hbar m\omega}}(m\omega X + iP)\Psi_2 \right] dx \end{aligned}$$

□

Definition 2.5. We call a^\dagger the **raising operator** and together, a and a^\dagger are called the **ladder operators**.

Exercise 2.6. We have that

- (1) $aa^\dagger = \frac{1}{\hbar\omega}H + \frac{1}{2}$
- (2) $a^\dagger a = \frac{1}{\hbar\omega}H - \frac{1}{2}$
- (3) $[a, a^\dagger] = 1$

Proof. (1)

$$\begin{aligned} aa^\dagger &= \frac{1}{2\hbar m\omega}(m\omega X + iP)(m\omega X - iP) \\ &= \frac{1}{2\hbar m\omega} \left[(m^2\omega^2 X^2 + P^2) - m\omega i(XP - PX) \right] \\ &= \frac{1}{\hbar\omega} \left(\frac{1}{2m}P^2 + \frac{1}{2}m\omega^2 X^2 \right) - \frac{i}{2\hbar}[X, P] \\ &= \frac{1}{\hbar\omega}H + \frac{1}{2} \end{aligned}$$

(2) Similar

(3) Trivial

□

Exercise 2.7. If $H\psi = E\psi$, then

- (1) $Ha\psi = (E - \hbar\omega)a\psi$
- (2) $Ha^\dagger\psi = (E + \hbar\omega)a^\dagger\psi$

Proof.

(1)

$$\begin{aligned}
 Ha\psi &= \hbar\omega \left(aa^\dagger - \frac{1}{2} \right) a\psi \\
 &= \hbar\omega \left(aa^\dagger a - \frac{1}{2}a \right) \psi \\
 &= \hbar\omega a \left(a^\dagger a - \frac{1}{2} \right) \psi \\
 &= \hbar\omega a \left(a^\dagger a + \frac{1}{2} - 1 \right) \psi \\
 &= \hbar\omega a \left(\frac{1}{\hbar\omega} H - 1 \right) \psi \\
 &= aH\psi - \hbar\omega a\psi \\
 &= (E - \hbar\omega)a\psi
 \end{aligned}$$

(2) Similar

□

Interpretation 2.8. *The lowering operator “lowers” a stationary state ψ with energy E to a stationary state $a\psi$ with energy $E - \hbar\omega$ and the raising operator “raises” a stationary state ψ with energy E to a stationary state $a^\dagger\psi$ with energy $E + \hbar\omega$.*

Definition 2.9. *Since the zero function is a solution to the time-independent Schrödinger equation, we define the ground state, ψ_0 of the harmonic oscillator to be the stationary state that satisfies $a\psi_0 = 0$. The excited states ψ_n , for $n \geq 1$, are obtained by applying the raising operator n times and then normalizing.*

Exercise 2.10. *We have that*

(1)

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}$$

(2)

$$E_0 = \frac{1}{2}\hbar\omega$$

(3)

$$\psi_n = c_n(a^\dagger)^n\psi_0 \quad (\text{for some constant } c_n)$$

(4)

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

Proof.

(1) The simple differential equation $a\psi_0 = 0$ has the solution

$$\psi_0 = Ae^{-\frac{m\omega}{2\hbar}x^2}$$

Thus

$$|\psi_0|^2 = |A|^2 e^{-\frac{m\omega}{\hbar}x^2}$$

If we normalize this function, we obtain

$$\psi_0 = \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}$$

(2) It is tedious but straightforward to show that

$$H\psi_0 = \frac{1}{2}\hbar\omega\psi_0$$

(3) Clear by definition.

(4) Clear by previous exercise.

□

Exercise 2.11.

(1) $\psi_{n+1} = \frac{1}{\sqrt{n+1}}a^\dagger\psi_n$

(2) $\psi_{n-1} = \frac{1}{\sqrt{n}}a\psi_n$

Hint: use the adjoint-ness of a and a^\dagger

Proof.

(1)

$$\begin{aligned} aa^\dagger\psi_n &= \left(\frac{1}{\hbar\omega}H + \frac{1}{2} \right)\psi_n \\ &= \frac{1}{\hbar\omega}E_n\psi_n + \frac{1}{2}\psi_n \\ &= (n+1)\psi_n \end{aligned}$$

Since $\psi_{n+1} = ca^\dagger\psi_n$, we have that

$$\begin{aligned} 1 &= \langle\psi_{n+1}|\psi_{n+1}\rangle \\ &= \langle ca^\dagger\psi_n|ca^\dagger\psi_n\rangle \\ &= |c|^2\langle a^\dagger\psi_n|a^\dagger\psi_n\rangle \\ &= |c|^2\langle aa^\dagger\psi_n|\psi_n\rangle \\ &= |c|^2\langle (n+1)\psi_n|\psi_n\rangle \\ &= |c|^2(n+1)\langle\psi_n|\psi_n\rangle \\ &= |c|^2(n+1) \end{aligned}$$

So $c = \frac{1}{\sqrt{n+1}}$

(2) Similar to (1).

□

Exercise 2.12. The n^{th} stationary state is given by $\psi_n = \frac{1}{\sqrt{n!}}(a^\dagger)^n\psi_0$

Proof. Clear by induction.

□

Exercise 2.13. Show that

(1) $\psi_1(x) = \left(\frac{4m^3\omega^3}{\hbar^3\pi} \right) x e^{-\frac{m\omega}{2\hbar}x^2}$

$$(2) E_1 = \frac{3}{2} \hbar \omega$$

Proof. Straightforward. \square

Exercise 2.14. If particle one is in state ψ_0 at time $t = 0$, then the momentum wave function is

$$\Phi(p, t) = \left(\frac{1}{m\omega\pi\hbar} \right)^{\frac{1}{4}} e^{-\frac{1}{2m\omega\hbar} p^2} e^{-i\frac{\omega}{2} t}$$

Proof. By assumption

$$\Psi(x, t) = \psi_0(x) e^{-i\frac{\omega}{2} t}$$

Thus

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} \Psi(x, t) e^{-i\frac{px}{\hbar}} dx$$

The rest is straightforward. \square

3. FUNDAMENTAL EXAMPLES IN THREE DIMENSIONS

3.1. Spherical Coordinates.

Definition 3.1. We now set $n = 3$, and work with spherical coordinates (r, θ, ϕ) where r is the distance in from the origin, $0 \leq \theta \leq \pi$ is the angle with initial side on the positive z -axis, and $0 \leq \phi < 2\pi$ is the angle in the x - y plane with initial side on the positive x -axis going towards the positive y -axis.

Proposition 3.2. In spherical coordinates, the time independent Schrödinger equation becomes

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi + V\psi = E\psi$$

Definition 3.3. If the potential energy V only depends on r , then we can solve for stationary solutions of the form $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$. It results that there is some constant l such that

$$(1) \quad \frac{1}{R} \frac{d}{dr} r^2 \frac{dR}{dr} - \frac{2m}{\hbar^2} r^2 (V - E) = l(l+1)$$

$$(2) \quad \frac{1}{Y} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] = -l(l+1)$$

The number l is called the **azimuthal quantum number**, equation (1) is called the **radial equation** and equation (2) is called the **angular equation**.

Definition 3.4. We can look for solutions to the angular equation of the form $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$. It results that there is some constant m such that

$$(1) \quad \frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta = m^2$$

$$(2) \quad \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2$$

Equation (2) has the solution

$$\Phi(\phi) = e^{im\phi}$$

Since (r, θ, ϕ) is the same point in space as $(r, \theta, \phi + 2\pi)$, we require that $\Phi(\phi) = \Phi(\phi + 2\pi)$. This implies that $m \in \mathbb{Z}$. The integer m is called the **magnetic quantum number**.

If $l \in \mathbb{N}_0$ and $m \leq l$, then equation (1) has the solution

$$\Theta(\theta) = AP_l^m(\cos \theta)$$

where P_l^m is the **associated Legendre function** given by

$$P_l^m(x) = (1 - x^2)^{\frac{|m|}{2}} \left(\frac{d}{dx} \right)^{|m|} P_l(x)$$

and $P_l(x)$ is the l^{th} **Legendre polynomial** defined by

$$P_l(x) = \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l$$

The angular function $Y_l^m(\theta, \phi) = A_l^m P_l^m(\cos \theta) e^{im\phi}$ may be normalized by setting

$$A_l^m = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}}$$

where

$$\epsilon = \begin{cases} (-1)^m & m \geq 0 \\ 1 & m < 0 \end{cases}$$

The normalized angular functions are called **spherical harmonics**.

Exercise 3.5. Compute some spherical harmonics.

Definition 3.6. If we make the substitution $u(r) = rR(r)$, we may rewrite the radial equation as

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu$$

which looks like the one dimensional Schrödinger equation. The function

$$V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$$

is called the **effective potential**.

3.2. Spherical Harmonic Oscillator (Cartesian Coordinates).

Definition 3.7. The spherical harmonic oscillator (in cartesian coordinates) is defined by the potential energy

$$V(x, y, z) = x^2 + y^2 + z^2$$

Exercise 3.8. In cartesian coordinates, the stationary states of the harmonic oscillator are given by

$$\psi_{n_x, n_y, n_z}(x, y, z) = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z)$$

with energies

$$E_{n_x, n_y, n_z} = \hbar\omega \left(n_x + n_y + n_z + \frac{3}{2} \right)$$

where $\psi_{n_x}, \psi_{n_y}, \psi_{n_z}$ are stationary states for the one dimensional harmonic oscillator.

Proof. We look for solutions of the form $\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z)$. Plugging this into the time-independent Schrödinger equation, we get

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2 \psi_x}{\partial x^2} \psi_y \psi_z + \psi_x \frac{\partial^2 \psi_y}{\partial y^2} \psi_z + \psi_x \psi_y \frac{\partial^2 \psi_z}{\partial z^2} \right] + \frac{1}{2} m \omega^2 (x^2 + y^2 + z^2) \psi = E \psi$$

Dividing both sides by ψ and rearranging, we obtain

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_x}{\partial x^2} \frac{1}{\psi_x} + \frac{1}{2} m \omega^2 x^2 \right) + \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_y}{\partial y^2} \frac{1}{\psi_y} + \frac{1}{2} m \omega^2 y^2 \right) + \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_z}{\partial z^2} \frac{1}{\psi_z} + \frac{1}{2} m \omega^2 z^2 \right) = E$$

Thus each part is constant and we may write

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_x}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \psi_x &= E_x \psi_x \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_y}{\partial y^2} + \frac{1}{2} m \omega^2 y^2 \psi_y &= E_y \psi_y \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_z}{\partial z^2} + \frac{1}{2} m \omega^2 z^2 \psi_z &= E_z \psi_z \end{aligned}$$

So we have three one-dimensional harmonic oscillators and we have

$$\begin{aligned} \psi_x &= \psi_{n_x} = \frac{1}{\sqrt{n_x!}} (a^\dagger)^{n_x} \psi_0 \text{ and } E_x = E_{n_x} = \hbar \omega \left(n_x + \frac{1}{2} \right) \\ \psi_y &= \psi_{n_y} = \frac{1}{\sqrt{n_y!}} (a^\dagger)^{n_y} \psi_0 \text{ and } E_y = E_{n_y} = \hbar \omega \left(n_y + \frac{1}{2} \right) \\ \psi_z &= \psi_{n_z} = \frac{1}{\sqrt{n_z!}} (a^\dagger)^{n_z} \psi_0 \text{ and } E_z = E_{n_z} = \hbar \omega \left(n_z + \frac{1}{2} \right) \end{aligned}$$

Thus

$$\psi = \psi_{n_x, n_y, n_z}(x, y, z) = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z)$$

with energy

$$E = E_{n_x, n_y, n_z} = \hbar \omega \left(n_x + n_y + n_z + \frac{3}{2} \right)$$

□

Exercise 3.9. Show that the degeneracy of E_n is

$$\deg(E_n) = \binom{n+2}{2}$$

Proof. Stars and bars

□

Interpretation 3.10. The energies of the three-dimensional harmonic oscillator are given by $E_n = \hbar \omega \left(n + \frac{3}{2} \right)$ which correspond to $\binom{n+2}{2}$ stationary states.

3.3. Spherical Harmonic Oscillator (Spherical Coordinates).

Definition 3.11. *The spherical harmonic oscillator (in spherical coordinates) is defined by the potential energy*

$$V(r) = r^2$$

Exercise 3.12. *Making the substitution $\kappa = \frac{\sqrt{2mE}}{\hbar}$, we can rewrite the radial equation for the harmonic oscillator as*

$$\frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = \left[\frac{\hbar^2 \omega^2 (\kappa r)^2}{2^2 E^2} + \frac{l(l+1)}{(\kappa r)^2} - 1 \right] u$$

Proof. Straightforward □

Exercise 3.13. *Making the substitution $\rho = \kappa r$ and $\rho_0 = \frac{\hbar \omega}{2E}$, we can rewrite the radial equation as*

$$\frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = \left[\rho_0^2 \rho^2 + \frac{l(l+1)}{\rho^2} - 1 \right] u$$

Proof. Straightforward. □

Exercise 3.14. *We have*

$$\frac{d^2 u}{d\rho^2} = \frac{1}{\kappa^2} \frac{d^2 u}{dr^2}$$

and thus we may rewrite the radial equation as

$$\frac{d^2 u}{d\rho^2} = \left[\rho_0^2 \rho^2 + \frac{l(l+1)}{\rho^2} - 1 \right] u$$

Proof. Straightforward by chain-rule. □

Exercise 3.15. *As $\rho \rightarrow \infty$, $u \approx e^{-\frac{\rho_0}{2}\rho^2}$*

Proof. As $\rho \rightarrow \infty$,

$$\frac{d^2 u}{d\rho^2} \approx \rho_0^2 \rho^2 u$$

Trying the function $u(\rho) = e^{-\frac{\rho_0}{2}\rho^2}$, we see that

$$\begin{aligned} \frac{d^2 u}{d\rho^2} &= (\rho_0^2 \rho^2 - \rho_0) e^{-\frac{\rho_0}{2}\rho^2} \\ &\approx \rho_0^2 \rho^2 e^{-\frac{\rho_0}{2}\rho^2} \quad (\text{as } \rho \rightarrow \infty) \\ &= \rho_0^2 \rho^2 u \end{aligned}$$

□

Exercise 3.16. *As $\rho \rightarrow 0$, $u \approx \rho^{l+1}$*

Proof. As $\rho \rightarrow 0$,

$$\frac{d^2 u}{d\rho^2} \approx \frac{l(l+1)}{\rho^2} u$$

Trying the function $u(\rho) = \rho^{l+1}$, we see that

$$\begin{aligned}\frac{d^2u}{d\rho^2} &= l(l+1)\rho^{l-1} \\ &= \frac{l(l+1)}{\rho^2}u\end{aligned}$$

□

Note 3.17. We can now, “glue” these functions together with a third unknown function $v(\rho)$ to obtain the prototype solution

$$u(\rho) = \rho^{l+1}e^{-\frac{\rho_0}{2}\rho^2}v(\rho)$$

Exercise 3.18. Suppose that for some nice function $v(\rho)$,

$$u(\rho) = \rho^{l+1}e^{-\frac{\rho_0}{2}\rho^2}v(\rho)$$

Then computing $\frac{d^2u}{d\rho^2}$ and plugging into the radial equation and simplifying, we obtain the relation

$$\rho \frac{d^2v}{d\rho^2} + 2(l+1-\rho_0\rho^2) \frac{dv}{d\rho} + \rho(1-\rho_0(2l+3))v = 0$$

Proof. Very tedious but straightforward. □

Exercise 3.19. If $v(\rho)$ can be represented by a power series

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

then plugging in $v(\rho)$ into the previous relation combining like terms and solving for the coefficients yields the relations

$$c_1 = 0$$

and

$$c_{j+2} = \left[\frac{\rho_0(2j+2l+3)-1}{(j+2)(j+2l+3)} \right] c_j \quad j \geq 0$$

This implies that for each odd j , $c_j = 0$.

Proof. Tedious but straightforward. □

Exercise 3.20. If for each $j \geq 0$, $c_{2j} \neq 0$, then v behaves asymptotically like $e^{\rho_0\rho^2}$. Thus $u(\rho)$ behaves asymptotically like $\rho^{l+1}e^{\frac{\rho_0}{2}\rho^2}$. This implies that $R(r)$ is not normalizable. Therefore there exists $j_{\max} \geq 0$ such that $c_{2j+2} = 0$ and $v(\rho)$ is a polynomial of degree $2j_{\max}$ and consists of only even powers of ρ .

Proof. As $j \rightarrow \infty$, $c_{j+2} \approx \frac{2\rho_0}{j}c_j$. Hence $v(\rho)$ behaves asymptotically like

$$\begin{aligned}\sum_{j=0}^{\infty} \frac{2^j \rho_0^j}{\prod_{k=1}^j 2k} \rho^{2j} &= \sum_{j=0}^{\infty} \frac{(\sqrt{\rho_0}\rho)^{2j}}{j!} \\ &= e^{(\sqrt{\rho_0}\rho)^2} \\ &= e^{\rho_0\rho^2}\end{aligned}$$

**Exercise 3.21.**

3.4. **The Infinite Spherical Box.**

3.5. **The Hydrogen Atom.**

3.6. **Orbital Angular Momentum.**