QUANTUM MECHANICS NOTES

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Contents

1. Introduction

1.1. Schrödinger Equation.

Note 1.1. *In the introduction, we keep position general with $x \in \mathbb{R}^n$ given by $x = (x_1, \cdots, x_n)$, the usual math notation. The notation in cartesian coordinates changes in three dimensions to $r = (x, y, z)$, the usual physics notation.*

Definition 1.2. *A particle with potential energy $V(x,t)$ is completely decribed 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 1.3. *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 1.4. *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*

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

and

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

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

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

If the partical 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 1.5. *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 1.6. *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 1.7. *Let* A *be an operator, then*

    (1) for each Ψ_1, Ψ_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

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

(2) For each Ψ_1, Ψ_2, we have that

$$\langle A\Psi_1|\Psi_2\rangle = \langle \Psi_1|A^\dagger\Psi_2\rangle$$
$$= \langle (A^\dagger)^\dagger\Psi_1|\Psi_2\rangle$$

This implies that for each Ψ_1, Ψ_2,

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

Therefore for each Ψ_1,

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

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

$\square$

Definition 1.8. *An linear operator Q is **self-adjoint** if*

$$Q = Q^\dagger$$

Interpretation 1.9. *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 1.10. *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

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

Finally

$$\langle\Psi_1|H\Psi_2\rangle - \langle H\Psi_1|\Psi_2\rangle = \int_{\mathbb{R}^n} \Psi_1^*\left(-\frac{\hbar^2}{2m}\Delta\Psi_2 + V\Psi_2\right)dx - \int_{\mathbb{R}^n}\left(-\frac{\hbar^2}{2m}\Delta\Psi_1 + V\Psi_1\right)^*\Psi_2 dx$$

$$= \frac{\hbar^2}{2m}\int_{\mathbb{R}^n}(\Delta\Psi_1^*)\Psi_2 - \Psi_1^*(\Delta\Psi_2)dx$$

$$= 0 \qquad \text{(Green's second identity)}$$

$$\square$$

Exercise 1.11. *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

$$\lambda\langle\Psi|\Psi\rangle = \langle\Psi|Q\Psi\rangle$$
$$= \langle Q\Psi|\Psi\rangle$$
$$= \lambda^*\langle\Psi|\Psi\rangle$$

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

$$\lambda_2\langle\Psi_1|\Psi_2\rangle = \langle\Psi_1|Q\Psi_2\rangle$$
$$= \langle Q\Psi_1|\Psi_2\rangle$$
$$= \lambda_1\langle\Psi_1|\Psi_2\rangle$$

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

$$\square$$

Definition 1.12. *Let A and B be operators. The **commutator** of A and B, $[A, B]$, is defined by*

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

Exercise 1.13. *We have $[X_i, P_j] = \delta_{i,j}i\hbar$.*

Proof. For a position wave function Ψ,

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

$$= (-i\hbar)\left[x_j\frac{\partial}{\partial x_j}\Psi(x,t) - \frac{\partial}{\partial x_j}x_j\Psi(x,t)\right]$$

$$= (-i\hbar)\left[x_j\frac{\partial}{\partial x_j}\Psi(x,t) - \Psi(x,t) - x_j\frac{\partial}{\partial x_j}\Psi(x,t)\right]$$

$$= i\hbar\Psi(x,t)$$

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

For $i \neq j$,

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

So

$$[X_i, P_j] = 0$$

$\square$

Exercise 1.14. *Let A, B and C be operators, then $[AB, C] = A[B,C] + [A,C]B$*

Proof. We have

$$[AB, C] = ABC - CAB$$
$$= ABC - ACB + ACB - CAB$$
$$= A(BC - CB) + (AC - CA)B$$
$$= A[B,C] + [A,C]B$$

$\square$

1.3. Continuity Equation.

Exercise 1.15. *If V is real and Ψ satisfies the Schrödinger equation, then*

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

Proof. We have that

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

$\square$

Exercise 1.16. *We have that*

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

Proof.

$$\frac{\partial}{\partial t}(\Psi^*\Psi) = \left(\frac{\partial}{\partial t}\Psi^*\right)\Psi + \Psi^*\left(\frac{\partial}{\partial t}\Psi\right)$$

$$= \left(\frac{\hbar}{2mi}(\Delta\Psi^*)\Psi - \frac{1}{i\hbar}V\Psi^*\Psi\right) + \left(-\frac{\hbar}{2mi}\Psi^*(\Delta\Psi) + \frac{1}{i\hbar}V\Psi^*\Psi\right)$$

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

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

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

Therefore

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

$\square$

Definition 1.17. *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 1.18. *We define the **momemtum wavefunction**, Φ, of the particle to be the Fourier transform of the position wavefunction:*

$$\Phi(p,t) = F[\Psi](p,t)$$

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

Note 1.19. *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 1.20. *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 1.21. *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

$$i\hbar\frac{\partial}{\partial t}\Psi = \left[\frac{P^2}{2m} + V(X)\right]\Psi$$

$$= \left[\frac{-\hbar^2}{2m}\Delta + V(x)\right]\Psi \qquad \text{(position space)}$$

Taking Fourier transforms of both sides, we see that

$$i\hbar\frac{\partial}{\partial t}\Phi = \left[\frac{P^2}{2m} + V(X)\right]\Phi$$

$$= \left[\frac{p^2}{2m} + V(i\hbar\nabla)\right]\Phi \qquad \text{(position space)}$$

$\square$

Interpretation 1.22. *We interpret $|\Phi(p, t)|^2$ to be the probability density for the momentum, p, of the particle at time t.*

Note 1.23. *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 1.24. *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 discreet $(E_n)_{n\in\mathbb{N}}$ 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 1.25. *An energy eiganvalue E_n of H is said to have a **degeneracy of degree** k if it corresponds to k orthonomal stationary states.*

Note 1.26. *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 1.27. *If the set of eigenvalues (spectrum) of the Hamiltonian is discreet, 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

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

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 $x \to -\infty$, $B = 0$. Since e^{lx} blows up as $x \to \infty$, $F = 0$.

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 $\alpha \to \infty$. As $\alpha \to \infty$, we have that $l \to \infty$. Hence $\psi_1 \to 0$ and $\psi_3 \to 0$. 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 imples 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

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

$\square$

2.2. The Harmonic Oscillator.

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

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

*We define the **lowering operator**, a_-, by*

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

*and we define the **raising operator**, a_+, by*

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

Exercise 2.4. *The adjoint of the lowering operator is the raising operator:*

$$(a_-)^\dagger = a_+$$

Proof. Let Ψ_1, Ψ_2 be wavefunctions. Since X, P are self-adjoint, we have that

$$\begin{aligned}
\langle \Psi_1 | a_- \Psi_2 \rangle &= \frac{1}{\sqrt{2\hbar m\omega}}\langle \Psi_1 | (m\omega X + iP)\Psi_2 \rangle \\
&= \frac{1}{\sqrt{2\hbar m\omega}}\Big[m\omega\langle \Psi_1 | X\Psi_2 \rangle + i\langle \Psi_1 | P\Psi_2 \rangle\Big] \\
&= \frac{1}{\sqrt{2\hbar m\omega}}\Big[\langle m\omega X\Psi_1 | \Psi_2 \rangle + \langle -iP\Psi_1 | \Psi_2 \rangle\Big] \\
&= \frac{1}{\sqrt{2\hbar m\omega}}\langle (m\omega X - iP)\Psi_1 | \Psi_2 \rangle \\
&= \langle a_+ \Psi_1 | \Psi_2 \rangle
\end{aligned}$$

$\square$

Exercise 2.5. *We have that*
  (1) $a_- a_+ = \frac{1}{\hbar\omega}H + \frac{1}{2}$
  (2) $a_+ a_- = \frac{1}{\hbar\omega}H - \frac{1}{2}$
  (3) $[a_-, a_+] = 1$

Proof.   (1)

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

  (2) Similar
  (3) Trivial

$\square$

Exercise 2.6. *If $H\psi = E\psi$, then*
(1) $Ha_-\psi = (E - \hbar\omega)a_-\psi$
(2) $Ha_+\psi = (E + \hbar\omega)a_+\psi$

Proof.
(1)

$$Ha_-\psi = \hbar\omega\left(a_-a_+ - \frac{1}{2}\right)a\psi$$

$$= \hbar\omega\left(a_-a_+a_- - \frac{1}{2}a_-\right)\psi$$

$$= \hbar\omega a_-\left(a_+a_- - \frac{1}{2}\right)\psi$$

$$= \hbar\omega a_-\left(a_+a_- + \frac{1}{2} - 1\right)\psi$$

$$= \hbar\omega a_-\left(\frac{1}{\hbar\omega}H - 1\right)\psi$$

$$= a_-H\psi - \hbar\omega a_-\psi$$

$$= (E - \hbar\omega)a_-\psi$$

(2) Similar

$\square$

Interpretation 2.7. *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 $a_+\psi$ with energy $E + \hbar\omega$.*

Definition 2.8. *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 rasing operator n times and then normalizing.*

Exercise 2.9. *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)
$$\psi_n = c_n(a_+)^n\psi_0 \quad \text{(for some constant } c_n\text{)}$$

(4)
$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

Proof.

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

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

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 2.10.
(1) $\psi_{n+1} = \frac{1}{\sqrt{n+1}} a_+ \psi_n$
(2) $\psi_{n-1} = \frac{1}{\sqrt{n}} a_- \psi_n$
Hint: use the adjoint-ness of a_- and a_+

Proof.
(1)

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

Since $\psi_{n+1} = c a_+ \psi_n$, we have that

$$1 = \langle \psi_{n+1} | \psi_{n+1} \rangle$$
$$= \langle c a_+ \psi_n | c a_+ \psi_n \rangle$$
$$= |c|^2 \langle a_+ \psi_n | a_+ \psi_n \rangle$$
$$= |c|^2 \langle a_- a_+ \psi_n | \psi_n \rangle$$
$$= |c|^2 \langle (n+1) \psi_n | \psi_n \rangle$$
$$= |c|^2 (n+1) \langle \psi_n | \psi_n \rangle$$
$$= |c|^2 (n+1)$$

So $c = \frac{1}{\sqrt{n+1}}$
(2) Similar to (1).

□

Exercise 2.11. *The nth stationary state is given by $\psi_n = \frac{1}{\sqrt{n!}} (a_+)^n \psi_0$*

Proof. Clear by induction. □

Exercise 2.12. *Show that*

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

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

Proof. Straightforward. □

Exercise 2.13. *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. □

3. SPHERICAL COORDINATES AND ORBITAL ANGULAR MOMENTUM

Note 3.1. *In the rest of the notes we will be working in three dimensions. In this section, we develop a method to solve the time independent Schrödinger equation when the potential energy us spherically symmetric. We also develop a theory of orbital angular momentum and see how it relates to the time independent Schrödinger equation.*

3.1. **The Time Independent Schrödinger Equation in Spherical Coordinates.**

Definition 3.2. *We will now 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 3.3. *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 3.4. *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*

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

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

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

Definition 3.5. *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*

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

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

*This equation is called the **azimuthal equation** and 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 lth **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

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

where

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

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

Exercise 3.6. *Compute some spherical harmonics.*

Definition 3.7. *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. **Orbital Angular Momentum.**

Definition 3.8. *Extrapolating from the classical formula for angular momentum, we define the* **orbital angular momentum operator** *L, of a particle by*

$$L = R \times P$$

so that

$$L_x = YP_z - ZP_y$$
$$L_y = ZP_x - XP_z$$
$$L_z = XP_y - YP_x$$

and

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

Exercise 3.9. *We have that*
  (1) $[L_x, L_y] = i\hbar L_z$
  (2) $[L_y, L_z] = i\hbar L_x$
  (3) $[L_z, L_x] = i\hbar L_y$

Proof.
  (1)

$$\begin{aligned}
[L_x, L_y] &= (YP_z - ZP_y)(ZP_x - XP_z) - (ZP_x - XP_z)(YP_z - ZP_y) \\
&= YP_x(P_zZ - ZP_z) + XP_y(ZP_z - P_zZ) \\
&= (XP_y - YP_x)[Z.P_z] \\
&= i\hbar L_z
\end{aligned}$$

  (2) Similar
  (3) Similar

$\square$

Exercise 3.10.
  (1) $[L^2, L_x] = 0$
  (2) $[L^2, L_y] = 0$
  (3) $[L^2, L_z] = 0$

Proof.
  (1)

$$\begin{aligned}
[L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\
&= \big(L_y[L_y, L_x] + [L_y, L_x]L_y\big) + \big(L_z[L_z, L_x] + [L_z, L_x]L_z\big) \\
&= -i\hbar\big(L_yL_z + L_zL_y\big) + i\hbar\big(L_zL_y + L_yL_z\big) \\
&= 0
\end{aligned}$$

  (2) Similar.
  (3) Similar.

$\square$

Exercise 3.11. *The operators L_x, L_y and L_z are self-adjoint.*

Proof. Let Ψ_1, Ψ_2 be wave functions. Since X_i and P_j are self-adjoint and commute for $i \neq j$, we have that

$$\begin{aligned}
\langle \Psi_1 | L_x \Psi_2 \rangle &= \langle \Psi_1 | Y P_z \Psi_2 \rangle - \langle \Psi_1 | Z P_y \Psi_2 \rangle \\
&= \langle P_z Y \Psi_1 | \Psi_2 \rangle - \langle P_y Z \Psi_1 | \Psi_2 \rangle \\
&= \langle Y P_z \Psi_1 | \Psi_2 \rangle - \langle Z P_y \Psi_1 | \Psi_2 \rangle \\
&= \langle L_x \Psi_1 | \Psi_2 \rangle
\end{aligned}$$

So L_x is self-adjoint. The case is similar for L_y and L_z $\qquad\square$

Definition 3.12. *We define the **raising operator** L_+ and **lowering operator** L_- by*

$$L_+ = L_x + iL_y \quad and \quad L_- = L_x - iL_y$$

Exercise 3.13.

$$[L^2, L_+] = [L^2, L_-] = 0$$

Proof. Trivial. $\qquad\square$

Exercise 3.14. *The lowering operator is the adjoint of the raising operator:*

$$L_- = (L_+)^\dagger$$

Proof. Let Ψ_1, Ψ_2 be wavefunctions. Then

$$\begin{aligned}
\langle \Psi_1 | L_+ \Psi_2 \rangle &= \langle \Psi_1 | L_x \Psi_2 \rangle + i \langle \Psi_1 | L_y \Psi_2 \rangle \\
&= \langle L_x \Psi_1 | \Psi_2 \rangle + i \langle L_y \Psi_1 | \Psi_2 \rangle \\
&= \langle L_x \Psi_1 | \Psi_2 \rangle + \langle -i L_y \Psi_1 | \Psi_2 \rangle \\
&= \langle (L_x - i L_y) \Psi_1 | \Psi_2 \rangle \\
&= \langle L_- \Psi_1 | \Psi_2 \rangle
\end{aligned}$$

Hence $L_- = (L_+)^\dagger$. $\qquad\square$

Exercise 3.15. *We have*
  (1) $[L_z, L_+] = \hbar L_+$
  (2) $[L_z, L_-] = -\hbar L_-$

Proof.
  (1)

$$\begin{aligned}
[L_z, L_+] &= [L_z, L_x] + i[L_z, L_y] \\
&= i\hbar L_y + \hbar L_x \\
&= \hbar L_+
\end{aligned}$$

  (2) Similar.

$\qquad\square$

Exercise 3.16. *We have*
  (1) $L^2 = L_+ L_- + L_z^2 - \hbar L_z$
  (2) $L^2 = L_- L_+ + L_z^2 + \hbar L_z$

Proof.

(1)

$$L_+L_- = (L_x + iL_y)(L_x - iL_y)$$
$$= L_x^2 - i(L_xL_y - L_yL_x) + L_y^2$$
$$= L_x^2 + L_y^2 - i[L_x, L_y]$$
$$= L^2 - L_z^2 + \hbar L_z$$

Therefore

$$L^2 = L_+L_- + L_z^2 - \hbar L_z$$

(2) Similar

$\square$

Exercise 3.17. *Suppose that f is simultaneously an eigenfunction of L^2 with eigenvalue λ and an eigenfunction of L_z with eigenvalue μ. Then*

(1) *L_+f is simultaneously an eigenfunction of L^2 with eigenvalue λ and an eigenfunction of L_z with eigenvalue $\mu + \hbar$*

(2) *L_-f is simultaneously an eigenfunction of L^2 with eigenvalue λ and an eigenfunction of L_z with eigenvalue $\mu - \hbar$*

Proof.

(1) First we have

$$L^2 L_+f = L_+L^2f$$
$$= L_+\lambda f$$
$$= \lambda L_+f$$

Second we see that

$$L_zL_+f = \left[L_+L_z + \left(L_zL_+ - L_+L_z\right)\right]f$$
$$= \left(L_+L_z + [L_z, L_+]\right)f$$
$$= (\mu L_+ + \hbar L_+)f$$
$$= (\mu + \hbar)L_+f$$

(2) Similar.

$\square$

Interpretation 3.18. *The rasing/lowering operators change the state of a particle from simultaneous eigenstate to simultaneous eigenstate and increase/decrease the z-component of the orbital angular momentum of a particle by $\hbar$, but does not change the total orbitle angular momentum of the particle.*

Note 3.19. *If we repeatedly applied the increasing/decreasing operator to a simultaneous eigenstate of a particle, we would arrive at a top/bottom eigenstate since there is a finite amount of total angular momentum.*

Definition 3.20. *We define the **top state** f_t to be the simultaneous eigenstate of L^2 and L_z such that*

$$L_+f_t = 0$$

and we define the **bottom state** f_b to be the simultaneous eigenstate of L^2 and L_z such that
$$L_- f_b = 0$$

Exercise 3.21. Let $\hbar l$ and $\hbar l'$ be the eigenvalues of L_z for f_t and f_b respectively. Then
  (1) $\hbar^2 l(l+1)$ and $\hbar^2 l'(l'-1)$ are the eigenvalue of L^2 for f_t and f_b respectively
  (2) $l' = -l$
  (3) $l \in \frac{1}{2}\mathbb{N}_0$

Proof.
  (1)
$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t$$
$$= \hbar^2 l^2 f_t + \hbar^2 l f_t$$
$$= \hbar^2 l(l+1)$$

The case is similar for l'.
  (2) For some $N \in \mathbb{N}_0$ and constant C, we have $f_b = C L_-^N f_t$. Thus
$$\hbar^2 l'(l'-1) f_b = L^2 f_b$$
$$= L^2 C L_-^N f_t$$
$$= C L_-^N L^2 f_t$$
$$= C L_-^N \hbar^2 l(l+1) f_t$$
$$= \hbar^2 l(l+1) f_b$$

So $l'(l'-1) = l(l+1)$. By completing the square, we see that the only two ways that this equation is satisfied is if $l' = l+1$ or $l' = -l$. The first case is not possible since it would imply that the orbital angular momentum for a particle is greater in the state f_b than in the state f_t. So $l' = -l$.
  (3) Since for some $N \in \mathbb{N}_0$ and constant C, $L_b = C L_-^N f_t$, a previous exercise implies that
$$-\hbar l f_b = L_z f_b$$
$$= L_z C L_-^N f_t$$
$$= \hbar(l - N) C L_-^N f_t$$
$$= \hbar(l - N) f_b$$

So $-l = l - N$ and $l = \frac{N}{2}$. Thus $l \in \frac{1}{2}\mathbb{N}_0$.
$\square$

Definition 3.22. For $m = -l, -l+1, \cdots l-1, l$ define f_l^m to be the simultaneous eigenstate of L^2 and L_z given by
$$f_l^m = \langle L_-^{l-m} f_t | L_-^{l-m} f_t \rangle^{-\frac{1}{2}} L_-^{l-m} f_t$$

Exercise 3.23. We have that
  (1) the eigenvalue of L^2 corresponding to f_l^m is $\hbar^2 l(l+1)$
  (2) the eigenvalue of L_z corresponding to f_l^m is $\hbar m$.

Proof. Straightforward (and kind of already did it in the last exercise). $\square$

Exercise 3.24. For $l \in \mathbb{N}_0$ and $m \in \{-l, -l+1, \cdots, l\}$ we have that

(1) $L_+ f_l^m = \hbar\sqrt{l(l+1) - m(m+1)}\, f_l^{m+1}$
(2) $L_- f_l^m = \hbar\sqrt{l(l+1) - m(m-1)}\, f_l^{m-1}$

Proof.   (1) By definition, there exists $c \in \mathbb{C}$ such that $L^+ f_l^m = c f_l^{m+1}$. Since $L_- = (L_+)^\dagger$ and $L_- L_+ = L^2 - L_z^2 - \hbar L_z$, we have that

$$
\begin{aligned}
|c|^2 &= \langle L^+ f_l^m | L^+ f_l^m \rangle \\
&= \langle f_l^m | L_- L^+ f_l^m \rangle \\
&= \langle f_l^m | (L^2 - L_z^2 - \hbar L_z) f_l^m \rangle \\
&= [\hbar^2 l(l+1) - \hbar^2 m^2 - \hbar^2 m]\langle f_l^m | f_l^m \rangle \\
&= \hbar^2 [l(l+1) - m(m+1)]
\end{aligned}
$$

So $c = \hbar\sqrt{l(l+1) - m(m+1)}$.
(2) Similar to (1).

$\square$

Proposition 3.25. *In spherical coordinates, we may write*

$$
L^2 = \hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]
$$

and

$$
L_z = -i\hbar\frac{\partial}{\partial\phi}
$$

Note 3.26. *Using the relations given above we see that simultaneous eigenstates f_l^m of L^2 and L_z satisfy*

$$
\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] f_l^m = L^2 f_l^m
$$
$$
= \hbar^2 l(l+1) f_l^m
$$

and

$$
-i\hbar\frac{\partial}{\partial\phi} f_l^m = L_z f_l^m
$$
$$
= \hbar m f_l^m
$$

which implies that

$$
-\hbar^2\frac{\partial^2}{\partial\phi^2} f_l^m = \hbar^2 m^2 f_l^m
$$

If we recall from earlier, these are just the angular and azimuthal equations respectively. Thus the simultaneous eigenstates of L^2 and L_z are $f_l^m = Y_l^m$. Therefore, if $R(r)$ solves the radial equation and is normalized, then the states $R(r)Y_l^m(\theta, \phi)$ are simultaneous eigenstates of H, L^2 and L_z.

Note 3.27. *the quantum number m is is dependent on the quantum number l. Later we will write m_l to emphasize this, as well as to avoid confusion with mass or other quantum numbers.*

4. Fundamental Examples in Three Dimensions

Note 4.1. *In this section we will introduce discuss the 3D harmonic oscillator and the hydrogen atom.*

4.1. Spherical Harmonic Oscillator (Cartesian Coordinates).

Definition 4.2. *The spherical harmonic oscillator (in cartesian coordinates) is defined by the potential energy*

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

Exercise 4.3. *In cartesian coordinates, the 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

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

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

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_x}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\psi_x = E_x\psi_x$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_y}{\partial y^2} + \frac{1}{2}m\omega^2 y^2\psi_y = E_y\psi_y$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_z}{\partial z^2} + \frac{1}{2}m\omega^2 z^2\psi_z = E_z\psi_z$$

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

$$\psi_x = \psi_{n_x} = \frac{1}{\sqrt{n_x!}}(a_+)^{n_x}\psi_0 \text{ and } E_x = E_{n_x} = \hbar\omega\left(n_x + \frac{1}{2}\right)$$

$$\psi_y = \psi_{n_y} = \frac{1}{\sqrt{n_y!}}(a_+)^{n_y}\psi_0 \text{ and } E_y = E_{n_y} = \hbar\omega\left(n_y + \frac{1}{2}\right)$$

$$\psi_z = \psi_{n_z} = \frac{1}{\sqrt{n_z!}}(a_+)^{n_z}\psi_0 \text{ and } E_z = E_{n_z} = \hbar\omega\left(n_z + \frac{1}{2}\right)$$

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 4.4. *Show that the degree of degeneracy of E_n is*

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

Proof. Stars and bars   □

Interpretation 4.5. *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.*

4.2. **The Hydrogen Atom.**

Definition 4.6. *We will consider a hydrogen atom consisting of one proton and one electron. We will fix the proton at the origin and investigate the electron. This model is defined by the potential energy of the electron given by*

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

Note 4.7. *We will walk through the solution to the radial equation. The goal will be to find the asymptotic behavior of $R(r)$ as $r \to 0$ and $r \to \infty$ and then glue this behavior together. This is a clever and useful technique that can be utilized in various situations.*

Exercise 4.8. *Since $\sup\limits_{r\in\mathbb{R}} V(r) = 0$, we know that for the bound states of the electron, the energy must satisfy $E < 0$. Making the substitution*

$$\kappa = \frac{\sqrt{-2mE}}{\hbar}$$

we can rewrite the radial equation as

$$\frac{1}{\kappa^2}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{l(l+1)}{(\kappa r)^2}\right]u$$

Then making the substitutions

$$\rho = \kappa r \text{ and } \rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$$

, we can further simplify the radial equation as

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

Proof. Straightforward using chain rule.   □

Exercise 4.9. *As $\rho \to \infty$, $u \approx e^{-\rho}$.*

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

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

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

$$\frac{d^2u}{d\rho^2} = e^{-\rho}$$
$$= u$$

$\square$

Exercise 4.10. *As $\rho \to 0$, $u \approx \rho^{l+1}$.*

Proof. As $\rho \to 0$,

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

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

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

$\square$

Note 4.11. *We can now, "glue" these functions together with a third unknown function $v(\rho)$ to obtain the prototype solution*

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

Exercise 4.12. *Suppose that for some nice function $v(\rho)$,*

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

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

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

Proof. Very tedious but straightforward. $\square$

Exercise 4.13. *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 relation

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

Proof. Tedious but straightforward. $\square$

Exercise 4.14. *If for each $j \geq 0$, $c_j \neq 0$, then v behaves asymptotically like e^ρ. Thus $u(\rho)$ behaves asymptotically like $\rho^{l+1}e^\rho$. This implies that $R(r)$ is not normalizable. Therefore there exists $j_{max} \geq 0$ such that $c_{j_{max}+1} = 0$ and $v(\rho)$ is a polynomial of degree j_{max}.*

Proof. Suppose that for each $j \geq 0$, $c_j \neq 0$. Then as $j \to \infty$,

$$c_{j+1} \approx \frac{2}{j+1} c_j$$

Thus asymptotically,

$$v(\rho) \approx c_0 \sum_{j=0}^{\infty} \frac{(2\rho)^j}{j!}$$
$$= c_0 e^{2\rho}$$

This implies that asymptotically,

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

Therefore asymptotically,

$$R(r) = \frac{1}{r}(r\kappa)^{l=1} e^{r\kappa}$$

which blows up as $r \to \infty$.   □

Exercise 4.15. *The allowed energies of the electron are given by*

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n \in \mathbb{N}$$

Proof. Starting with the relation

$$0 = \left[\frac{2(j_{max} + l + 1) - \rho_0}{(j_{max} + 1)(j_{max} + 2l + 2)} \right] c_{j_{max}}$$

we can see that

$$\rho_0 = 2(j_{max} + l + 1)$$

Since j_{max} and l may be any nonnegative integers, we introduce a postitive integer $n = j_{max} + l + 1$. If we know n and l, then we know j_{max} and l and vice versa, so it is the same information, but it will help us more neatly index the energies. So we put $\rho_0 = 2n$ and using the fact that

$$\kappa^2 = -\frac{2mE}{\hbar^2} \text{ and } \rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$$

we solve for E to get that

$$E_n = -\frac{me^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}$$
$$= -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2}$$

□

Note 4.16. *Since $n = j_{max} + l + 1$, $j_{max} \geq 0$ and $n \geq 1$ we know that $l = n - j_{max} - 1 \leq n - 1$. Thus the simultaneous eigenstates of H, L^2, L_z are $\psi_{n,l,m}(r, \theta, \phi) R_n(r) Y_l^m$ with $1 \leq n$, $0 \leq l \leq n - 1$ and $-l \leq m \leq l$.*

4.3. **Spherical Harmonic Oscillator (Spherical Coordinates).**

Definition 4.17. *The spherical harmonic oscillator (in spherical coordinates) is defined by the potential energy*

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

Exercise 4.18. *Making the substitution $\kappa = \frac{\sqrt{2mE}}{\hbar}$, we can rewrite the radial equation for the harmonic oscillator as*

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

Proof. Straightforward □

Exercise 4.19. *Making the substitution $\rho = \kappa r$ and $\rho_0 = \frac{\hbar\omega}{2E}$, we can rewrite the radial equation as*

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

Proof. Straightforward. □

Exercise 4.20. *We have*

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

and thus we may rewrite the radial equation as

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

Proof. Straightforward by chain-rule. □

Exercise 4.21. *As $\rho \to \infty$, $u \approx e^{-\frac{\rho_0}{2}\rho^2}$*

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

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

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

$$\frac{d^2u}{d\rho^2} = (\rho_0^2\rho^2 - \rho_0)e^{-\frac{\rho_0}{2}\rho^2}$$
$$\approx \rho_0^2\rho^2 e^{-\frac{\rho_0}{2}\rho^2} \quad (\text{as } \rho \to \infty)$$
$$= \rho_0^2\rho^2 u$$

□

Exercise 4.22. *As $\rho \to 0$, $u \approx \rho^{l+1}$*

Proof. Same as in the case of the hydrogen atom. □

Note 4.23. *Just like in the case of the hydrogen atom, we can "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 4.24. *Suppose that for some nice function $v(\rho)$,*

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

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

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

Proof. Very tedious but straightforward. □

Exercise 4.25. *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 4.26. *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 $c_{j_{max}+2} = 0$ and $v(\rho)$ is a polynomial of degree j_{max} and consists of only even powers of ρ.*

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

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

$$= e^{(\sqrt{\rho_0}\rho)^2}$$

$$= e^{\rho_0 \rho^2}$$

□

Exercise 4.27. *The energies allowed for this system are*

$$E_n = \hbar\omega\left(n + \frac{3}{2}\right) \quad n \in \mathbb{N}_0$$

Proof. Using the recursion relation found earlier, we have that

$$0 = \left[\frac{\rho_0(2j_{max} + 2l + 3) - 1}{(j_{max} + 2)(j_{max} + 2l + 3)}\right] c_{j_{max}}$$

This implies that

$$0 = \rho_0(2j_{max} + 2l + 3) - 1$$

and so

$$\frac{1}{\rho_0} = 2j_{max} + 2l + 3$$

Using the fact that $\rho_0 = \frac{\hbar\omega}{2E}$, we solve for E to obtain

$$E = \hbar\omega\left(j_{max} + l + \frac{3}{2}\right)$$

Since j_{max} and l may be any non-negative integers, we introduce a non-negative integer $n = j_{max} + l$ and index the allowed energies as

$$E_n = \hbar\omega\left(n + \frac{3}{2}\right) \qquad n \in \mathbb{N}_0$$

$\square$

5. Spin

5.1. **Introduction.**

Definition 5.1. *It turns out that there is another inherent quality which all things have which was revealed by experiment. We call this inherent quality* **spin**. *In these notes we take as given that the spin of a particle in the x, y and z directions is a measurable quantity which corresponds to self adjoint operators S_x, S_y, S_z that satisfy the commutation relations:*

(1) $[S_x, S_y] = i\hbar S_z$
(2) $[S_y, S_z] = i\hbar S_x$
(3) $[S_z, S_x] = i\hbar S_y$

With this assumption we can follow the exact same procedure as we did with the orbital angular momentum to obtain for each $s \geq 0$, a set of simultaneous eigenstates of S^2 and S_z called **spin states** *given by $(|s, m\rangle)_{m=-s}^{s}$ such that*

(1) $S^2|s, m\rangle = \hbar^2 s(s + 1)|s, m\rangle$
(2) $S_z|s, m\rangle = \hbar m|s, m\rangle$
(3) $S_{\pm}|s, m\rangle = \hbar\sqrt{s(s + 1) - m(m \pm 1)}|s, m \pm 1\rangle$

The nonnegative integer s is called the **spin quantum number**. *The difference between the simultaneous eigenstates in the spin case and in the orbital case is that in the spin case, the eigenstates are not functions of position, they are simply a basis of a $2s+1$ dimensional vector space. The quantum number s is inherent to the type of particle. For example, electrons have spin $s = \frac{1}{2}$, photons have spin $s = 1$.*

Definition 5.2. *Consider a particle with spin eigenstates $(|s, m_s\rangle)_{m_s=-s}^{s}$ and energy eigenstate $|\psi_n\rangle_{n=1}^{\infty}$ can be fully described by the tensor product of these two spaces. That*

5.2. **Spin $\frac{1}{2}$ Particles.**

Definition 5.3. *In the case $s = \frac{1}{2}$, it is easier on the eyes to denote the states $|\frac{1}{2}, \frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$ as $|\uparrow\rangle$ and $|\downarrow\rangle$ respectively. We now fix the ordered basis $(|\uparrow\rangle, |\downarrow\rangle)$ and define*

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Exercise 5.4. *If we identify the operators in definition 5.1, then we have that*

(1) $S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

(2) $S_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

(3) $S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$

(4) $S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$

(5) $S_x = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

(6) $S_y = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

Proof. Parts (1) through (4) are straight forward using the properties given in definition 5.1. For parts (5) and (6), we observe that $S_x = \frac{1}{2}(S_+ + S_-)$ and $S_y = -\frac{i}{2}(S_+ - S_-)$ $\qquad\square$

Definition 5.5. *We define the **Pauli spin matrices** to be*

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

So that $S_x = \frac{1}{2}\hbar\sigma_x$, $S_y = \frac{1}{2}\hbar\sigma_y$ and $S_z = \frac{1}{2}\hbar\sigma_z$

6. PERTURBATION THEORY

7. MULTIPLE PARTICLES

7.1. Schrodinger Equation.

Definition 7.1. *Suppose we have a system consisting of two particles.*

7.2. Exchange Operator.