

Cuántica-Griffiths

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La Ecuación de Onda

Imaginamos una masa de masa m que se mueve en el eje x con fuerza $F(x, t)$.

Dado esto, en mecánica clásica podemos obtener $x(t)$ usando la segunda ley. Sin embargo, en mecánica cuántica lo único que podemos encontrar es la **función de onda** $\Psi(x, t)$ que se consigue como solución a la **ecuación de Schrodinger**:

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

Donde $\hbar = \frac{h}{2\pi} = 1,05457 \times 10^{-34} Js$.

Motivación: Empezamos con que la energía se conserva $K + V = E$. Multiplicamos ambos lados por la función $\Psi \sim e^{i(kx-\omega t)}$ (le proponemos con esta forma para que parezca una onda).

Entonces tenemos que: $K\Psi + V\Psi = E\Psi$. Recordamos que $K = \frac{p^2}{2m}$ y que $p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda} = \hbar k$ (k es la frecuencia angular espacial).

Por otro lado, la energía de una onda es $E = h\nu = \hbar 2\pi\nu = \hbar\omega$.

Además, notamos que se tiene que $\partial_x \Psi = ik\Psi = i\frac{p}{\hbar}\Psi$

Y que $\partial_t \Psi = -i\omega\Psi$.

Metemos todo esto en la ecuación de Energía:

$$\begin{aligned} K\Psi + V\Psi &= E\Psi \\ \Rightarrow \frac{p^2}{2m}\Psi + V\Psi &= \hbar\omega\Psi \\ \Rightarrow \frac{1}{2m}(-i\hbar\partial_x)^2\Psi + V\Psi &= \hbar(i\partial_t)\Psi \\ \Rightarrow \frac{-\hbar^2}{2m}\partial_x^2\Psi + V(x)\Psi &= i\hbar\partial_t\Psi \end{aligned}$$

Y es más, desde aquí nos damos cuenta que como Ψ tiene la forma $e^{i(kx-\omega t)}$, entonces aplicar ∂_x nos da $\partial_x \Psi = ik\Psi = i\frac{p}{\hbar}\Psi$.

Además, podemos ver que $\partial_t \Psi = -i\omega \Psi$, por lo que tenemos que $\hbar\omega = -i\hbar\partial_t$. Por lo que definimos:

- $p = -i\hbar\partial_x$
- $E = i\hbar\partial_t$

La interpretación estadística

Según la interpretación de Born, tenemos que:

$|\Psi(x, t)|^2 dx$ es la probabilidad de encontrar la part. entre $x, x+dx$ en tiempo t

Supongamos que medimos una partícula y la encontramos en un punto C, nos preguntamos ahora dónde estaba la partícula antes de estar en C. Resulta que hay varias interpretaciones:

- **Realista:** La partícula estaba en C, pero la teoría está incompleta por falta de conocimiento de variables ocultas.
- **Ortodoxa (Copenhagen):** La partícula no estaba en ningún lado en particular, la probabilidad es algo real y el acto de medición es lo que produce una determinación de la posición.
- **Agnóstica:** Oponerse a contestar y solamente preocuparse por lo que se puede medir y por lo que conocemos.

En 1964 Bell demostró que hay una diferencia observable entre si la partícula tiene una posición precisa o no antes de la medida. Por lo que se elimina el agnosticismo como una posición razonable y hay una forma experimental de determinar cuál es la interpretación correcta, eso lo veremos después.

Probabilidad

Distribución Continua: Digamos que tenemos una densidad de probabilidad $\rho(x)$, lo que significa que la probabilidad de que x tome un valor entre x y $x + dx$ es de $\rho(x)dx$. Entonces tenemos las siguientes definiciones:

- **Probabilidad entre a y b :** $P_{ab} = \int_a^b \rho(x)dx$
- **Promedio:** $\langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)dx$
- **Valor esperado de una función:** $\langle f(x) \rangle = \int_{\mathbb{R}} f(x)\rho(x)dx$
- **Varianza:** $\sigma^2 := \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$

Normalización

Regresando a la interpretación estadística de la función de onda, se debe de cumplir la condición de normalización:

$$\int_{\mathbb{R}} |\Psi(x, t)|^2 dx = 1$$

El problema es que aunque la función esté normalizada al principio, eso no nos asegura que vaya a permanecer normalizada con el tiempo. Para ello, hay que probar que $\frac{d}{dt} \int_{\mathbb{R}} |\Psi(x, t)|^2 dx = 0$. Entonces lo probamos:

$$\begin{aligned} \frac{d}{dt} \int_{\mathbb{R}} |\Psi(x, t)|^2 dx &= \int_{\mathbb{R}} \frac{\partial}{\partial t} |\Psi(x, t)|^2 dx = \int_{\mathbb{R}} \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi dx \\ &= \int_{\mathbb{R}} \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) dx \quad \text{usamos la ec. de Schro y que V es real} \\ &= \int_{\mathbb{R}} \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \\ &= \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \Big|_{-\infty}^{\infty} \\ &= 0 \end{aligned}$$

Momentum

Para una partícula en el estado Ψ , el valor esperado de x es:

$$\langle x \rangle = \int_{\mathbb{R}} x |\Psi(x, t)|^2 dx$$

Claro que este promedio se refiere a hacer varias medidas a sistemas Ψ iguales, no a hacer varias medidas a una misma partícula en sistema Ψ (pues la primera medida colapsa el sistema y las repeticiones dan el mismo valor y listo).

Ahora buscamos cómo cambia $\langle x \rangle$ con el tiempo. Es decir, calculamos:

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= \int x \frac{\partial}{\partial t} |\Psi|^2 dx = \int x \left(\Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi \right) dx \\ &= \frac{i\hbar}{2m} \int x \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \quad \text{por ecuación de Schrodinger} \end{aligned}$$

Esta expresión se puede simplificar usando integración por partes, con lo que llegamos a que:

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= -\frac{i\hbar}{2m} \int \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \\ &= -\frac{i\hbar}{m} \int \Psi^* \frac{\partial \Psi}{\partial x} dx \end{aligned}$$

Donde usamos $\partial x / \partial x = 1$, integración por partes y que Ψ va a cero en infinito.

Luego veremos cómo calcular la densidad de probabilidad de v , pero por ahora sólo podemos calcular el valor esperado como:

$$\langle v \rangle = \frac{d\langle x \rangle}{dt} = -\frac{i\hbar}{m} \int \Psi^* \frac{\partial \Psi}{\partial x} dx$$

Con lo que llegamos a que el valor esperado del momento es:

$$\langle p \rangle = -i\hbar \int \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) dx$$

Con ello, hemos demostrado que:

- $\langle x \rangle = \int \Psi^* x \Psi dx$
- $\langle p \rangle = \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx$

Decimos que el **operador** x representa a la posición y que el operador $(\hbar/i)\partial/\partial x$ representa al momento.

Para calcular el valor esperado hay que meter este operador entre Ψ^* y Ψ e integrar.

En cualquier caso, si Q es una cantidad física, en general depende de x, p , es decir $Q = Q(x, p)$ y luego podemos encontrar su valor esperado como:

$$\langle Q(x, p) \rangle = \int \Psi^* Q(x, \frac{\hbar}{i} \partial_x) \Psi dx$$

For example, we can find the expected value of T as:

$$\langle T \rangle = \frac{-\hbar^2}{2m} \int \Psi^* \frac{\partial^2 \Psi}{\partial x^2} dx$$

The Uncertainty Principle

The wavelength of Ψ is related to the momentum of the particle by the **de Broglie formula** (which we will prove later):

$$p = \frac{\hbar}{\lambda} = \frac{2\pi\hbar}{\lambda}$$

Thus, a spread in wavelength corresponds to a spread in momentum. But we observe that for a given wave, there is a trade off between the wavelength (momentum) and the position of the wave. Therefore:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

where σ_x is the standard deviation in x and σ_p is the standard deviation in p . This is Heisenberg's **uncertainty principle** (we will prove it later).

Meaning: You can prepare a system such that repeated position measurements will be very close together, but then, the principle implies that momentum measurements are widely scattered (and vice versa).

Time - Independent Schrodinger Equation

Estados Estacionarios

We want to solve Schrodinger's equation, given by:

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

To solve it, we begin by proposing a separation of variables in form of a product:

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

Putting this in the equation, we get: $i\hbar\psi \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}f + V\psi f$. We propose a separation constant E and we get the following ODEs:

$$\frac{df}{dt} = -\frac{iE}{\hbar}f \Rightarrow f(t) = e^{-iEt/\hbar}$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

This equation is called the **time-independent Schrodinger equation**.

The rest of this chapter will be devoted to solving the time-independent Schrodinger equation for simple potentials. The solutions satisfy the following properties:

- 1 They are **stationary states**. The wave function itself is:

$$\boxed{\Psi(x, t) = \psi(x)e^{-iEt/\hbar}}$$

It obviously depend on t , but the probability density is given by:

$$|\Psi(x, t)|^2 = \Psi^*\Psi = \psi^*e^{iEt/\hbar}\psi e^{-iEt/\hbar} = |\psi(x)|^2$$

So the probability density does not depend on time.

The same thing happens when calculating the expected value of a physical quantity in a stationary state, the expected value of this variable is time independent and given by:

$$\langle Q(x, p) \rangle = \int \psi^*Q(x, \frac{\hbar}{i} \frac{d}{dx})\psi dx$$

Every expectation value in a stationary state is constant in time.

- 2 This states have a **definite total energy**. In classical mechanics the total energy is called the **hamiltonian** and given by $H(x, p) = \frac{p^2}{2m} + V(x)$. The corresponding Hamiltonian operator is:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

Then, the time independent equation is written simply as an eigenvalue problem:

$$\hat{H}\psi = E\psi$$

And the expectation value of the total energy is:

$$\langle H \rangle = \int \psi^* \hat{H} \psi dx = E \int |\psi|^2 dx = E$$

Moreover:

$$\hat{H}^2\psi = \hat{H}(\hat{H}) = \hat{H}(E\psi) = E^2\psi$$

and hence:

$$\langle H^2 \rangle = \int \psi^* \hat{H}^2 \psi dx = E^2 \int |\psi|^2 = E^2$$

So the standard deviation in H is $\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0$.

Conclusion: A separable solution has the property that every measurement of the total energy is certain to result the value E.

- The general solution is a **linear combination** of separable solutions. The time independent Schrodinger equation yields an infinite collection of solutions $\psi_1(x), \psi_2(x), \dots$, each with its associated value of separation constant E_1, E_2, \dots . Thus, there is a different wave function for each **allowed energy**:

$$\Psi_1(x, t) = \psi_1(x)e^{-iE_1 t/\hbar}$$

$$\Psi_2(x, t) = \psi_2(x)e^{-iE_2 t/\hbar}$$

⋮

And the most general solution is:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}$$

Every solution to the time-dependent Schrodinger equation can be written in this form, simply by finding the right constants for the initial condition

Infinite Square Well (box)

Suppose:

$$V(x) = \begin{cases} 0 & , 0 \leq x \leq a \\ \infty & , cc \end{cases}$$

A particle in this potential is completely free, except at $x = 0, a$ where an infinite force prevents it from scaping.

Outside the well, we have $\psi(x) = 0$. Inside the well, we have $V = 0$, so the time independent equation reads:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= E\psi \\ \Rightarrow \psi(x) &= A \sin kx + B \cos kx , \quad k := \frac{\sqrt{2mE}}{\hbar} \end{aligned}$$

Now we take into account the boundary conditions. ψ has to be continuous (and so has to be $\frac{d\psi}{dx}$, unless $V = \infty$ as is the case here).

Continuity of ψ implies $\psi(0) = \psi(a) = 0$.

Which implies that:

$$\psi_n(x) = A \sin k_n x , \quad k_n = \frac{n\pi}{a} , \quad n = 1, 2, 3, \dots$$

This condition hence implies the values of E_n , by definition $E = \frac{\hbar^2 k^2}{2m}$. Therefore:

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

We can get the value of A by integrating and setting to 1, $A = \sqrt{2/a}$. Then:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

The **ground state** is $n = 1$, which has energy $E_1 = \frac{\hbar^2 \pi^2}{2ma^2}$. The other energies are given by: $E_n = E_1 n^2$.

The functions $\psi_n(x)$ have the following properties:

- 1 They are alternately odd and even with respect to the center of the well.
- 2 As you go up in energy each successive state has one more node.
- 3 They are mutually orthogonal:

$$\int \psi_m(x)^* \psi_n(x) dx = \delta_{mn}$$

- 4 They are **complete**, in the sense that any other function, $f(x)$ can be expressed as:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right)$$

To find the numbers c_n we use the Fourier Trick.

The stationary states are:

$$\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}$$

The general solution is:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}$$

And we want it to fit the initial condition, $\Psi(x, 0) = \sum c_n \psi_n(x)$, for which we use the completeness of ψ .

Calculate expected values for some ψ_n :

- $\langle x \rangle = \int_{\mathbb{R}} |\psi_n|^2 x dx = \dots = \frac{a}{2}$
- $\langle x^2 \rangle = \int_{\mathbb{R}} |\psi_n|^2 x^2 dx = a^2 \left(\frac{1}{3} - \frac{1}{2(n\pi)^2} \right)$
- $\langle p \rangle = m \frac{d\langle x \rangle}{dt} = 0$
- $\langle p^2 \rangle = \int \psi_n^* \left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 \psi_n dx = \dots = \left(\frac{n\pi\hbar}{a} \right)^2$
- $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2 = \dots = \frac{a^2}{4} \left(\frac{1}{3} - \frac{2}{(n\pi)^2} \right)$
- $\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2 = \left(\frac{n\pi\hbar}{a} \right)^2$
- We see that $\sigma_x \sigma_p = \frac{\hbar}{2} \sqrt{\frac{(n\pi)^2}{3} - 2}$, and this clearly fulfills the uncertainty $\sigma_x \sigma_p \geq \hbar/2$

Problem 2.6: A particle in the infinite square well has as its initial wave function the mixture:

$$\Psi(x, 0) = A\psi_1(x) + A\psi_2(x)$$

a) **Normalize $\Psi(x, 0)$:**

$$\text{We can use } 1 = \int |\Psi|^2 dx = |A|^2 \int [|\psi_1|^2 + \psi_1^* \psi_2 + \psi_2^* \psi_1 + |\psi_2|^2] dx = 2|A|^2 \Rightarrow A = \frac{1}{\sqrt{2}}$$

b) **Find $\Psi(x, t)$, $|\Psi(x, t)|^2$ and define $\omega := \pi^2\hbar/2ma^2$**

$$\Psi(x, t) = \frac{1}{\sqrt{2}} [\psi_1 e^{-iE_1 t/\hbar} + \psi_2 e^{-iE_2 t/\hbar}] \quad \text{but } \frac{E_n}{\hbar} = n^2\omega, \text{ so we have:}$$

$$\Psi(x, t) = \frac{1}{\sqrt{a}} e^{-i\omega t} \left[\sin\left(\frac{\pi}{a}x\right) + \sin\left(\frac{2\pi}{a}x\right) e^{-3i\omega t} \right]$$

$$\Rightarrow |\Psi(x, t)|^2 = \dots = \frac{1}{a} \left[\sin^2\left(\frac{\pi}{a}x\right) + \sin^2\left(\frac{2\pi}{a}x\right) + 2 \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) \cos(3\omega t) \right]$$

c) **Compute** $\langle x \rangle$:

$$\langle x \rangle = \int x |\Psi(x, t)|^2 dx = \dots = \frac{a}{2} \left[1 - \frac{32}{9\pi^2} \cos(3\omega t) \right]$$

It has an amplitude $\frac{32}{9\pi^2} \frac{a}{2}$ around $\frac{a}{2}$, and an angular frequency $3\omega = \frac{3\pi^2 \hbar}{2ma^2}$

d) **Calculate** $\langle p \rangle$

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = \dots = \frac{8\hbar}{3a} \sin(3\omega t)$$

e) **Find the expectation value of H:** We could either get $E_1 = \pi^2 \hbar^2 / 2ma^2$, $E_2 = 2\pi^2 \hbar^2 / ma^2$, each with equal probability $P_1 = P_2 = 1/2$ (we will see why later). Then, the expected value for total energy is $\frac{1}{2}(E_1 + E_2) = \frac{5\pi^2 \hbar^2}{4ma^2}$. Though we can only get one of the values of E.

Problem 2.8: A particle in the infinite square well has the initial wave function $\Psi(x, 0) = \begin{cases} Ax & , x \in [0, a/2] \\ A(a-x) & , x \in [a/2, a] \end{cases}$

a) **Calculate A:**

We have to make sure $\Psi(x, 0)$ is normalized in $t = 0$, so $1 = A^2 \int_0^{a/2} x^2 dx + A^2 \int_{a/2}^a (a-x)^2 dx = \dots \Rightarrow ; \dots \Rightarrow A = \frac{2\sqrt{3}}{\sqrt{a^3}}$

b) **Find $\Psi(x, t)$ given this initial condition.:**

We have to write $\Psi(x, 0) = \sum c_n \psi_n(x, 0) = \sum c_n \frac{2}{a} \sin\left(\frac{n\pi}{a}x\right)$. To find the c_n , we use the Fourier trick and we get:

$$c_n = \sqrt{\frac{2}{a}} \frac{2\sqrt{3}}{\sqrt{a}} \int_R \psi_n(x) dx.$$

We finally get $c_n = (-1)^{(n-1)/2} \frac{4\sqrt{6}}{(n\pi)^2}$, n odd

So:

$$\Psi(x, t) = \frac{4\sqrt{6}}{\pi^2} \sqrt{\frac{2}{a}} \sum_{n=1,3,5,\dots} (-1)^{(n-1)/2} \frac{1}{n^2} \sin\left(\frac{n\pi}{a}x\right) e^{-E_n t \hbar}, \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

The probability of getting each value of energy is $P_n = |c_n|^2 = \frac{96}{n^4 \pi^4}$. We see that $\sum |c_n|^2 = 1$ as it should.

c) **Average Hamiltonian**

$$\text{We get it as } \langle H \rangle = \sum |c_n|^2 E_n = \sum \frac{96}{n^4 \pi^4} \frac{n^2 \pi^2 \hbar^2}{2ma^2} = \dots = \frac{6\hbar^2}{ma^2}$$

Harmonic Oscillator

We have a potential given by $V(x) = \frac{1}{2}m\omega^2x^2$, so the t-i Schrodinger equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi$$

We have two approaches to solve this problem:

Algebraic Method

We write the equation in a more suggestive form: $\frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right]\psi = E\psi$. We then define the operators:

$$a_{\pm} := \frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{d}{dx} \pm im\omega x\right)$$

We can operate them to find:

$$\begin{aligned} a_-a_+ &= \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right] + \frac{1}{2}\hbar\omega \\ a_+a_- &= \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right] - \frac{1}{2}\hbar\omega \end{aligned}$$

Therefore, we find the commutator:

$$a_-a_+ - a_+a_- = \hbar\omega$$

And Schrodinger's equation is given by:

$$\begin{aligned} (a_-a_+ - \frac{1}{2}\hbar\omega)\psi &= E\psi \\ (a_+a_- + \frac{1}{2}\hbar\omega)\psi &= E\psi \end{aligned}$$

Theorem: If ψ satisfies Schrodinger's equation with energy E , then $a_+\psi$ satisfies it with energy $E + \hbar\omega$:

$$\begin{aligned} \bullet (a_+a_- + \frac{1}{2}\hbar\omega)(a_+\psi) &= (a_+a_-a_+ + \frac{1}{2}\hbar\omega a_+)\psi \\ &= a_+(a_-a_+ + \frac{1}{2}\hbar\omega)\psi = a_+[(a_-a_+ - \frac{1}{2}\hbar\omega)\psi + \hbar\omega\psi] \\ &= a_+(E\psi + \hbar\omega\psi) = (E + \hbar\omega)(a_+\psi) \quad \text{QED} \end{aligned}$$

Theorem: Similarly, $a_-\psi$ is a solution with energy $(E - \hbar\omega)$.

We call a_{\pm} **ladder operators** because they allow us to climb up and down energy levels. If I apply the lowering operator repeatedly, eventually I'm going to reach a state with energy

less than zero, which doesn't exist. Therefore, there must be a minimum solution that when lowered gives the solution zero.

$$a_- \psi_0 = 0$$

That is to say, this first solution has the property:

$$\begin{aligned} \frac{1}{\sqrt{2m}} \left(\frac{\hbar}{i} \frac{d\psi_0}{dx} - im\omega x\psi_0 \right) &= 0 \\ \Rightarrow \frac{d\psi_0}{dx} &= -\frac{m\omega}{\hbar} x\psi_0 \\ \Rightarrow \psi_0(x) &= A_0 e^{-\frac{m\omega}{2\hbar} x^2} \end{aligned}$$

To determine the energy of this state, we plug it into the Schrodinger equation, and use the fact that $a_- \psi_0 = 0$. Evidently then:

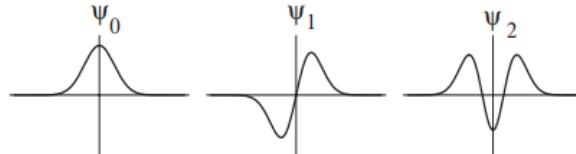
$$E_0 = \frac{1}{2} \hbar\omega$$

Knowing the solution for the smallest energy, we can go up from here to the excited states:

$$\psi_n(x) = A_n (a_+)^n e^{-\frac{m\omega}{2\hbar} x^2}, \quad E_n = (n + \frac{1}{2}) \hbar\omega$$

After getting a solution, we still need to get the normalization constant A_n

Algunas soluciones:



Analytic Method

We return now to the Schrodinger equation for the harmonic oscillator:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi = E\psi$$

Then we define $\xi := \sqrt{\frac{m\omega}{\hbar}} x$. Then, the schrodinger equation is:

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi$$

Where $K := \frac{2E}{\hbar\omega}$.

To solve this, we first notice that for large ξ , the equation looks like $\frac{d^2\psi}{d\xi^2} \sim \xi^2\psi$.

Which has the normalizable solution $\psi(\xi) \sim Ae^{-\xi^2/2}$. Then, we propose a solution of the form:

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}$$

Plugging this function on the Schrodinger equation, we get:

$$\frac{d^2h}{d\xi^2} - 2\xi \frac{dh}{d\xi} + (K - 1)h = 0$$

We propose a solution as a power series $h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \dots$. Plugging this into the equation for h , we get the recursion formula

$$a_{j+2} = \frac{(2j + 1 - K)}{(j + 1)(j + 2)}a_j$$

This polynomials are called Hermite polynomials. And we find the solutions to be:

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}$$

Table 2.1: The first few Hermite polynomials, $H_n(x)$.

$H_0 = 1,$
$H_1 = 2x,$
$H_2 = 4x^2 - 2,$
$H_3 = 8x^3 - 12x,$
$H_4 = 16x^4 - 48x^2 + 12,$
$H_5 = 32x^5 - 160x^3 + 120x.$

And they are given by the **Rodrigues Formula**:

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2}$$

Free Particle

Now we see the case $V(x) = 0$ everywhere. The Schrodinger equation is then:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= E\psi \\ \Rightarrow \frac{d^2\psi}{dx^2} &= -k^2\psi \quad , \quad k := \frac{\sqrt{2mE}}{\hbar} \end{aligned}$$

Then, the solution is given by:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

There are no boundary conditions, which allows the free particle to carry any positive energy. Tacking the standard time dependence:

$$\Psi(x, t) = Ae^{ik(x - \frac{\hbar k}{2m}t)} + Be^{ik(x + \frac{\hbar k}{2m}t)}$$

We see these equations are waves moving to the right and to the left. We might as well write the equation as:

$$\Psi_k(x, t) = Ae^{i(kx - \frac{\hbar k^2}{2m}t)}$$

With $k = \pm \frac{\sqrt{2mE}}{\hbar}$ and the choice of the sign gives the direction the wave travels. The speed of this waves are given by using $x \pm vt$, therefor:

$$v_{quantum} = \sqrt{\frac{E}{2m}}$$

This is twice the classical speed that we would get by $v_{class} = \sqrt{\frac{2E}{m}} = 2v_{quantum}$

Evidently, this wave equation is not normalizable, since $\int_{\mathbb{R}} |\Psi_k(x)|^2 dx = |A|^2(\infty)$
This means that the separable equations do not represent physically realizable states. A free particle can not exist in a stationary state, there is no such thing as a free particle with a definite energy.

That doesn't mean the separable solutions are of no use to us. The general solution can still be achieved as a combination of the separable solutions with coefficients $\phi(k)$ such as:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} dk$$

Which is a **Fourier Transform**.

The factor $\sqrt{2\pi}$ is taken out for convenience. The role of c_n in this solution is given by $(1/\sqrt{2\pi})\phi(k)dk$.

Now this wave function can be normalized but it necessarily carries a range of k's, we call it a **wave packet**.

In a generic quantum problem we are given $\Psi(x, 0)$ and we have to find $\Psi(x, t)$. To do that, the only thing we need to get is $\phi(k)$. When $t = 0$ we get:

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{ikx} dk$$

To get $\phi(k)$ we use the inversion theorem for the Fourier Transform:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \Psi(x, 0) e^{-ikx} dx$$

As we said earlier, the phase velocity of a single wave was $v = \sqrt{\frac{E}{2m}}$. But we want to know the group velocity as well. The **dispersion relation** is a formula $\omega(k)$.

Let $\phi(k)$ be a wave packet narrowly peaked about a value k_0 . Then, in first approximation we have:

$$\omega(k) \simeq \omega_0 + \omega'_0(k - k_0)$$

Where ω'_0 is the derivative of ω with respect to k at the point k_0 .

Changing variables from k to $s := k - k_0$, we have:

$$\Psi(x, t) \simeq \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k_0 + s) e^{i[(k_0 + s)x - (\omega_0 + \omega'_0 s)t]} ds$$

At $t = 0$ we have:

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k_0 + s) e^{i(k_0 + s)x} ds$$

Thus, the packet moves with a speed given by:

$$v_{group} = \frac{d\omega}{dk}$$

and a phase speed of:

$$v_{phase} = \frac{\omega}{k}$$

We find that:

$$v_{class} = v_{group} = 2v_{phase}$$

Problem 2.22: A free particle has the initial wave function $\Psi(x, 0) = Ae^{-ax^2}$ where A, a are constants.

a) **Normalize** $\Psi(x, 0)$

$$1 = |A|^2 \int_{\mathbb{R}} e^{-2ax^2} dx = |A|^2 \sqrt{\frac{\pi}{2a}} \Rightarrow A = \left(\frac{2a}{\pi}\right)^{1/4}$$

b) **Find** $\Psi(x, t)$:

We know that in general $\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} dk$ and when $t = 0$ we get

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{ikx} dk$$

Then, using the inverse transform, we have that:

$$\begin{aligned}\phi(k) &= \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \Psi(x, 0) e^{-ikx} dx \\ &= \frac{1}{\sqrt{2\pi}} \left(\frac{2a}{\pi} \right)^{1/4} \int_{\mathbb{R}} e^{-ax^2 - ikx} dx \\ &= \dots = \frac{1}{(2\pi a)^{1/4}} e^{-k^2/4a}\end{aligned}$$

■ **Find** $|\Psi(x, t)|^2$, express it in terms of $\omega^2 = a/[1 + (2\hbar\hat{a}/m)^2]$.

We have $\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} dk$ so that:

$$\Psi(x, t) = \dots = \left(\frac{2a}{\pi} \right)^{1/4} \frac{e^{-ax^2/(1+2i\hbar\hat{a}/m)}}{\sqrt{1 + 2i\hbar\hat{a}/m}}$$

So that:

$$|\Psi|^2 = \sqrt{\frac{2a}{\pi}} \frac{e^{-2ax^2/(1+\theta^2)}}{\sqrt{1 + \theta^2}}$$

Donde $\theta := 2\hbar\hat{a}/m$.

As t increases, the graph of $|\Psi|^2$ flattens out and broadens.

d) **find** $\langle x \rangle, \langle x^2 \rangle, \langle p \rangle, \langle p^2 \rangle :$

- $\langle x \rangle = \int_{\mathbb{R}} x |\Psi|^2 dx = 0$
- $\langle x^2 \rangle = \int_{\mathbb{R}} x^2 |\Psi|^2 = \dots = \frac{1}{4\omega^2}$
- $\langle p \rangle = m \frac{d\langle x \rangle}{dt} = 0$
- $\langle p^2 \rangle = \int_{\mathbb{R}} \Psi^* (-i\hbar \frac{d}{dx})^2 \Psi dx = \dots = \hbar^2 a$
- $\sigma_x = \frac{1}{2\omega}$
- $\sigma_p = \hbar\sqrt{a}$
- **Uncertainty:** $\sigma_x \sigma_p = \frac{\hbar}{2} \sqrt{1 + (s\hbar\hat{a}/m)^2} \geq \frac{\hbar}{2}$

Professor:

We study the free particle $-\frac{\hbar^2}{2m}\partial_x^2\psi(x) = E\psi(x)$

The solutions can be written in terms of $p = \pm\sqrt{2mE}$, so that:

$$\psi_p(x) = A_p e^{ip/\hbar x}$$

Then, the full solution is:

$$\Psi(x, t) = \int \phi(p)(A_p e^{ip/\hbar x})e^{-iE_p/\hbar t} dp$$

We still need to fixate the initial condition $\psi_{t0}(x)$, that is $\Psi(x, 0) = \psi_{t0}(x)$, therefore:

$$\int \psi(p)(A_p e^{ip/\hbar x})dp = \psi_{t0}(x)$$

The solutions are Dirac orthogonal if we use $A_p = \frac{1}{\sqrt{2\pi\hbar}}$, that is, we have:

$$\int \psi_{p_1}^*(x)\psi_{p_2}(x)dx = \delta(p_1 - p_2)$$

Then, the coefficients $\phi(p)$ of the solution with initial conditions $\psi_{t0}(x)$ is:

$$\phi(p) = \int \psi_p^*(x)\psi_{t0}(x)dx$$

Delta Function Potential

Bound State: When the particle is bounded in space due to the energy limit.

Scattering State: States in which the particle are not bounded, it can go to infinity.

A potential can have only bound states, scattering states or both. Because of tunneling, the particles can leak through any finite potential barrier, so the only thing that matters is the potential at infinite:

$$\begin{cases} E < V(-\infty), V(\infty) & \text{bound state} \\ E > V(-\infty), V(\infty) & \text{scattering state} \end{cases}$$

As many potentials go to zero at infinity, it simplifies to:

$$\begin{cases} E < 0 & \Rightarrow \text{bound state} \\ E > 0 & \Rightarrow \text{scattering state} \end{cases}$$

Let's consider a potential of the form:

$$V(x) = -\alpha\delta(x)$$

In this case, the Schrodinger equation is:

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

Bound States ($E < 0$):

In the region $x < 0$ or the region $x > 0$, $V(x) = 0$, so:

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= -\frac{2mE}{\hbar^2}\psi = k^2\psi \\ k &:= \frac{\sqrt{-2mE}}{\hbar} \end{aligned}$$

The general solution is then:

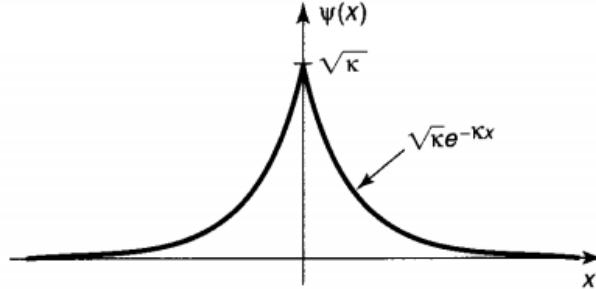
$$\begin{aligned} (x < 0) &\Rightarrow \psi(x) = Be^{kx} \\ (x > 0) &\Rightarrow \psi(x) = Fe^{-kx} \end{aligned}$$

We know that ψ has to be continuous and $\frac{d\psi}{dx}$ is continuous except at point where the potential is infinite.

1. ψ is always continuous, and
 2. $d\psi/dx$ is continuous except at points where the potential is infinite.

The first boundary condition means that $F = B$

$$\psi(x) = \begin{cases} Be^{\kappa x}, & (x \leq 0), \\ Be^{-\kappa x}, & (x \geq 0). \end{cases}$$



Now we have the idea to integrate the equation from $-\epsilon$ to ϵ and take a limit:

$$-\frac{\hbar^2}{2m} \int_{-\epsilon}^{\epsilon} \frac{d^2\psi}{dx^2} dx + \int_{-\epsilon}^{\epsilon} V(x)\psi(x) dx = E \int_{-\epsilon}^{\epsilon} \psi(x) dx$$

The first integral is $d\psi/dx$ evaluated in the endpoints. The last integral is 0 because ψ is continuous. So:

$$\Delta \left(\frac{d\psi}{dx} \right) = \frac{2m}{\hbar^2} \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} V(x)\psi(x) dx$$

Ordinarily, the limit on the right is zero, and hence $d\psi/dx$ is **continuous**.

But when $V(X)$ is infinite, $d\psi/dx$ might not be continuous. In this case $V(x) = -\alpha\delta(x)$ so:

$$\Delta \left(\frac{d\psi}{dx} \right) = -\frac{2m\alpha}{\hbar^2} \psi(0)$$

For the case in hand:

for the case at hand (Equation 2.104),

$$\begin{cases} d\psi/dx = -B\kappa e^{-\kappa x}, & \text{for } (x > 0), \\ d\psi/dx = +B\kappa e^{+\kappa x}, & \text{for } (x < 0), \end{cases} \quad \text{so } \left. \frac{d\psi}{dx} \right|_+ = -B\kappa, \quad \left. \frac{d\psi}{dx} \right|_- = +B\kappa,$$

and hence $\Delta(d\psi/dx) = -2B\kappa$. And $\psi(0) = B$. So Equation 2.107 says

$$\kappa = \frac{m\alpha}{\hbar^2}, \quad [2.108]$$

and the allowed energy (Equation 2.99) is

$$E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{m\alpha^2}{2\hbar^2}. \quad [2.109]$$

Finally, we normalize ψ :

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 2|B|^2 \int_0^{\infty} e^{-2\kappa x} dx = \frac{|B|^2}{\kappa} = 1,$$

so (choosing, for convenience, the positive real root):

$$B = \sqrt{\kappa} = \frac{\sqrt{m\alpha}}{\hbar}. \quad [2.110]$$

Evidently the delta-function well, regardless of its "strength" α , has exactly one bound state:

$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}; \quad E = -\frac{m\alpha^2}{2\hbar^2}.$

[2.111]

Scattering States:

States with $E > 0$, The equation reads:

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi \quad , \quad k := \frac{\sqrt{2mE}}{\hbar}$$

The general solution is:

$$\begin{aligned} (x < 0) \Rightarrow \psi(x) &= Ae^{ikx} + Be^{-ikx} \\ (x > 0) \Rightarrow \psi(x) &= Fe^{ikx} + Ge^{-ikx} \end{aligned}$$

The continuity of $\psi(x)$ at $x = 0$ gives $F + G = A + B$

Finally, the other condition is $\delta\left(\frac{d\psi}{dx}\right) = -\frac{2m\alpha}{\hbar^2}\psi(0)$

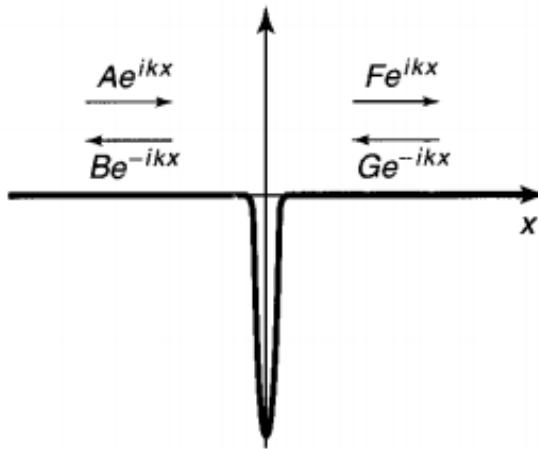
This means that:

$$\begin{aligned} ik(F - G - A + B) &= -\frac{2m\alpha}{\hbar^2}(A + B) \\ \Rightarrow F - G &= A(1 + 2i\beta) - B(1 - 2i\beta) \quad , \quad \beta := \frac{m\alpha}{\hbar^2 k} \end{aligned}$$

We are still left with 5 unknowns A,B,F,G and k.

Recall that when coupled with the time-dependent factor $e^{-iEt/\hbar}$, an exponent e^{-ikx} is a wave propagating to the right and otherwise it goes to the left.

So A is the amplitude of a wave coming to the left to the right and B is a wave going to the left. F is a wave at the right that goes to the right and G is a wave at the right that goes to the left.



A is the amplitude of the **incident wave**, B is the amplitude of the **reflected wave** and F is the amplitude of the **transmitted wave**.

Solving the equations, we have that:

$$B = \frac{i\beta}{1 - i\beta}A \quad , \quad F = \frac{1}{1 - i\beta}A$$

Now, the probability of finding a particle at a location is $|\Psi|^2$, so the relative probability or **reflection coefficient** is:

$$R := \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2} = \frac{1}{1 + (2\hbar^2 E / m\alpha^2)}$$

And the **transmission coefficient** is:

$$T := \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2} = \frac{1}{1 + (m\alpha^2 / 2\hbar^2 E)}$$

of course, we should also have:

$$R + T = 1$$

Finite Square Well

We have a potential given by:

$$V(x) = \begin{cases} -V_0 & , -a < x < a \\ 0 & , |x| > a \end{cases}$$

This potential admits both bound states ($E < 0$) and scattering states ($E > 0$).

We have to solve it by sections:

- ($x < -a$): The potential here is 0, so the equation reads:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \Rightarrow \frac{d^2\psi}{dx^2} = k^2\psi$$

$$k := \frac{\sqrt{-2mE}}{\hbar}$$

The general solution finite in $x \rightarrow -\infty$ is:

$$\psi(x) = Be^{kx}$$

- ($-a < x < a$): Here $V(x) = -V_0$ and the equation is:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - V_0\psi = E\psi \Rightarrow \frac{d^2\psi}{dx^2} = -l^2\psi$$

$$l := \frac{\sqrt{2m(E + V_0)}}{\hbar}$$

The general solution is:

$$\psi(x) = C \sin(lx) + D \cos(lx)$$

- ($x > a$): Here $V = 0$ so the solution is:

$$\psi(x) = Fe^{-kx}$$

Boundary conditions: ψ and $d\psi/dx$ are continuous. We will work only with even solutions $D \cos(lx)$ for the section $[-a, a]$.

So the solution is:

$$\psi(x) = \begin{cases} Fe^{-kx} & , x > a \\ D \cos(lx) & , 0 < x < a \\ \psi(-x) & , a < 0 \end{cases}$$

We apply continuity of ψ and of the derivative.

Using this we get to $k = l \tan(la)$. We now define $z := la$ and $z_0 := \frac{a}{\hbar} \sqrt{2mV_0}$. This takes us to:

$$\tan z = \sqrt{(z_0/z)^2 - 1}$$

which is a transcendental equation for z .

-
- **Wide, deep well:** If z_0 is very large, the intersections $\tan z = \sqrt{(z_0/z)^2 - 1}$ are close to $z_n = n\pi/2$ for n odd, so:

$$E_n + V_0 \simeq \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2}$$

- **Shallow, narrow well:**

Move on to the scattering states ($E > 0$). To the left, where $V(x) = 0$, we have:

$$\psi(x) = A e^{ikx} + B e^{-ikx} , \quad k := \frac{\sqrt{2mE}}{\hbar}$$

Inside the well, where $V(x) = -V_0$ we have:

$$\psi(x) = C \sin(lx) + D \cos(lx) , \quad l := \frac{\sqrt{2m(E + V_0)}}{\hbar}$$

To the right, we have:

$$\psi(x) = F e^{ikx}$$

Then we have to use the boundary conditions, the transmission coefficient is $T = |F|^2/|A|^2$ which comes to be:

$$T^{-1} = 1 + \frac{V_0^2}{4E(E + V_0)} \sin^2 \left(\frac{2a}{\hbar} \sqrt{2m(E + V_0)} \right)$$

Problem 2.33: Consider the step function potential $V(x) = \begin{cases} 0 & , x \leq 0 \\ V_0 & , x > 0 \end{cases}$

- **Calculate the reflection coefficient, for the case $E < V_0$:**

For $x < 0$, the equation and solution is:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= E\psi \Rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi , \quad k := \frac{\sqrt{2mE}}{\hbar} \\ \Rightarrow \psi(x) &= A e^{ikx} + B e^{-ikx} \end{aligned}$$

For $x > 0$ we have:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - V_0\psi &= E\psi \\ \Rightarrow \psi(x) &= F e^{-lx} , \quad l := \frac{\sqrt{2m(V_0 - E)}}{\hbar} \end{aligned}$$

Now we use the boundary conditions:

- Continuity of ψ : $A + B = F$

-
- Continuity of ψ' : $ik(A - B) = -lF$

Then, $A + B = -\frac{ik}{l}(A - B)$ and we can find that:

$$R = \left| \frac{B}{A} \right|^2 = \frac{|(i + ik/l)|^2}{|(1 - ik/l)|^2} = \frac{1 + (k/l)^2}{1 + (k/l)^2} = 1$$

So although the wave function penetrates into the barrier (because of the F term), it is eventually all reflected.

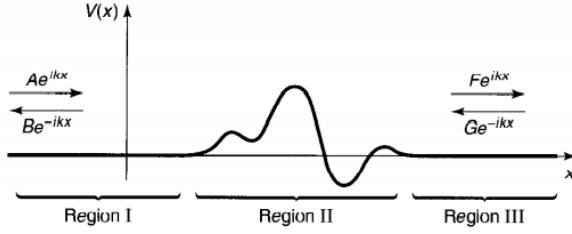
- b) **Calculate the reflection coefficient for the case $E > V_0$:**

In this case we get:

$$R = \frac{(\sqrt{E} - \sqrt{E - V_0})^4}{V_0^2}$$

Scattering Matrix

The theory of scattering generalizes in a pretty obvious way to arbitrary localized potentials.



- **Region 1:** We have $V=0$ so:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad k := \frac{\sqrt{2mE}}{\hbar}$$

- **Region III:** We have $V = 0$, so:

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}, \quad k := \frac{\sqrt{2mE}}{\hbar}$$

- **Region II:** we have:

$$\psi(x) = Cf(x) + Dg(x)$$

Where f, g are two independent solutions to the Region II potential. There are four boundary conditions. Two of these eliminate C and F and the other two can be solved for B and G in terms of A and G:

$$\begin{aligned} B &= S_{11}A + S_{12}G \\ F &= S_{21}A + S_{22}G \end{aligned}$$

These coefficients which depend on k give us a matrix:

$$S = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}$$

called the **scattering matrix**. And it works for:

$$\begin{pmatrix} B \\ F \end{pmatrix} = S \begin{pmatrix} A \\ G \end{pmatrix}$$

When scattering comes from the left, $G=0$, the coefficients are:

$$R_l = \left| \frac{B}{A} \right|_{G=0}^2 = |S_{11}|^2, \quad T_l = \left| \frac{F}{A} \right|_{G=0}^2 = |S_{21}|^2$$

When scattering comes from the right, $A=0$, the coefficients are:

$$R_r = \left| \frac{F}{G} \right|_{A=0}^2 = |S_{22}|^2, \quad T_r = \left| \frac{B}{G} \right|_{A=0}^2 = |S_{12}|^2$$

Further Problems Chapter 2

Problem 2.36: A particle in the infinite square well has the initial wave function

$$\Psi(x, 0) = A \sin^3(\pi x/a)$$

Find $\langle x \rangle$ as a function of time

First of all, the stationary solutions are $\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$, so the general solution is $\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-iE_nt/\hbar}$. Then, using the initial condition, we have $A \sin^3(\pi x/a) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$.

To find the coefficients, we could use the Fourier Trick or we could use the fact that $\sin^3\left(\frac{\pi x}{a}\right) = \frac{3}{4} \sin\left(\frac{\pi x}{a}\right) - \frac{1}{4} \sin\left(\frac{3\pi x}{a}\right)$.

So we find $c_1 = \sqrt{\frac{a}{24}}$ and $c_3 = -\sqrt{\frac{a}{24}}$. So the complete solution is:

$$\Psi(x, 0) = A \sqrt{\frac{a}{24}} \psi_1(x) - A \sqrt{\frac{a}{24}} \psi_3(x)$$

Using normalization, we have that $A = \frac{4}{\sqrt{5a}}$. So, the complete solution is:

$$\Psi(x, t) = \frac{1}{\sqrt{10}} [3\psi_1(x)e^{-iE_1t/\hbar} - \psi_3(x)e^{-iE_3t/\hbar}]$$

So:

$$|\Psi(x, t)|^2 = \frac{1}{10} \left[p\psi_1^2 + \psi_3^2 - 6\psi_1\psi_3 \cos\left(\frac{E_3 - E_1}{\hbar}t\right) \right]$$

Then, we can find the expected value of x by multiplying by x and integrating:

$$\langle x \rangle = \frac{9}{10} \int_0^a x\psi_1^2 dx + \frac{1}{10} \int_0^a x\psi_3^2 dx - \frac{6}{10} \cos\left(\frac{E_3 - E_1}{\hbar}t\right) \int_0^a x\psi_1\psi_3 dx$$

The first two integrals are expected values of the first and third states, and as such their value is $a/2$. The last integral is 0. Therefore:

$$\langle x \rangle = \frac{9}{10} \frac{a}{2} + \frac{1}{10} \frac{a}{2} = \frac{a}{2}$$

Problem 2.38: A particle of mass m is in the ground state of the infinite square well. Suddenly the well expands as the wall at a goes to $2a$ - leaving the wave function momentarily undisturbed. What is the most probable value of the energy?

The new allowed energies are $E_n = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}$, the wave function is still: $\Psi(x, 0) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right)$.

But the stationary states are $\psi_n(x) = \sqrt{\frac{2}{2a}} \sin\left(\frac{n\pi}{2a}x\right)$. Then, we have to write the wave function in terms of the stationary states $\Psi(x, 0) = \sum c_n \psi_n(x)$. We find c_n with the fourier trick:

$$c_n = \int_0^a \Psi(x, 0) \psi_n(x) dx = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right) \sqrt{\frac{2}{2a}} \sin\left(\frac{n\pi}{2a}x\right) dx = \dots$$

$$= \begin{cases} 0 & , n \text{ par} \\ \pm \frac{4\sqrt{2}}{\pi(n^2 - 4)} & , n \text{ impar} \end{cases}$$

Un caso a parte es c_2 that has a value of $c_2 = \frac{1}{\sqrt{2}}$.

Then, the probabilities are $P_n = |c_n|^2 = \begin{cases} \frac{1}{2}, & n = 2 \\ \frac{32}{\pi^2(n^2 - 4)^2}, & n \text{ odd} \\ 0, & cc \end{cases}$

The most probable energy is $E_2 = \frac{\pi^2\hbar^2}{2ma^2}$ with a probability of $P_2 = 1/2$.

The next most probable is $E_1 = \frac{\pi^2\hbar^2}{8ma^2}$ with proba $P_1 = \frac{32}{9\pi^2} = 0,36$.

The expected hamiltonian can be found as $\langle H \rangle = \int \Psi^* H \Psi dx = \frac{2}{a} \int_0^a \sin\left(\frac{\pi}{a}x\right) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\right) \sin\left(\frac{\pi}{a}x\right) dx = \frac{\pi^2\hbar^2}{2ma^2}$

Problem 2.43: In problem 2.22 you analyzed the stationary gaussian free particle
Now solve the same problem for the traveling one, with initial wave function:

$$\Psi(x, 0) = A e^{-ax^2} e^{ilx}$$

With l a real constant

The normalization constant can be found to be $A = \left(\frac{2a}{\pi}\right)^{1/4}$

As we saw before, the case of a free particle has stationary states given by $\Psi_k(x, t) = A e^{i(kx - \frac{\hbar k^2}{2m}t)}$. where $k = \pm \frac{\sqrt{2mE}}{\hbar}$.

So that the general solution is $\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} dk$.

At initial condition, we have $\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{ikx} dk$.

Then, by inverse theorem:

$$\begin{aligned}\phi(k) &= \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \Psi(x, 0) e^{-ikx} dx = \frac{1}{\sqrt{2\pi}} \left(\frac{2a}{\pi} \right)^{1/4} \int_{\mathbb{R}} e^{-ax^2} e^{ilx} e^{-ikx} dx = \\ &= \frac{1}{(2\pi a)^{1/4}} e^{-(k-l)^2/4a}\end{aligned}$$

Then, we use the formula to find Ψ :

$$\begin{aligned}\Psi(x, t) &= \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} dk \\ &= \dots = \left(\frac{2a}{\pi} \right)^{1/4} \frac{1}{\sqrt{1 + 2i\hbar at/m}} e^{-l^2/4a} e^{a(ix + l/2a)^2/(1 + 2ia\hbar t/m)}\end{aligned}$$

Now we can find $|\Psi|^2$. First we define $\theta = 2\hbar at/m$. Simplifying a little bit, we get:

$$|\Psi(x, t)|^2 = \sqrt{\frac{2}{\pi}} \omega e^{-2\omega^2(x - \theta l/2a)^2}$$

Where $\omega := \sqrt{a/(1 + \theta^2)}$

Now the expected value is:

$$\langle x \rangle = \int_{\mathbb{R}} x |\Psi(x, t)|^2 dx = \dots = \hbar l$$

And also:

$$\langle x^2 \rangle = \int_{\mathbb{R}} x^2 |\Psi(x, t)|^2 dx = \dots = \frac{1}{4\omega^2} + \left(\frac{\hbar lt}{m} \right)^2$$

So that $\sigma_x = \frac{1}{2\omega}$

Formalism

Hilbert Space

Espacios Finitos:

In a finite dimensional space, every vector can be written as:

$$|\alpha\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}$$

And we write the **inner product** as:

$$\langle \alpha | \beta \rangle = \sum a_i^* b_i$$

Linear transformations T, are represented by **matrices** and:

$$|\beta\rangle = T|\alpha\rangle \Rightarrow \vec{b} = \vec{T}\vec{a} = \begin{pmatrix} t_{11} & t_{12} & \cdots & t_{1N} \\ t_{21} & t_{22} & \cdots & t_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ t_{N1} & t_{N2} & \cdots & t_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}$$

In QM we change finite dimensional vectors by infinite dimensional ones

Hilbert Space: We define the set of all **square integrable functions**:

$$f(x) \mid \int_a^b |f(x)|^2 dx < \infty$$

Mathematicians call it $L_2(a, b)$ and physicists call it **Hilbert Space**

In this space we define the **inner product of two functions** as:

$$\langle f | g \rangle = \int_a^b f(x)^* g(x) dx$$

If f, g are square integrable, this integral is guaranteed to existed due to the **Schwarz inequality**:

$$\left| \int_a^b f(x)^* g(x) dx \right| \leq \sqrt{\int_a^b |f(x)|^2 dx \int_a^b |g(x)|^2 dx}$$

The inner product satisfies the following properties:

- $\langle g | f \rangle = \langle f | g \rangle^*$

-
- $\langle f|(a|g\rangle + |h\rangle) = a\langle f|g\rangle + \langle f|h\rangle$
 - $\langle f|f\rangle = 0$ sii $f(x) = 0$ almost always.

A function is **normalized** if $\langle f|\rangle = 1$

Two functions are **orthogonal** if $\langle f|g\rangle$

A set $\{f_n\}$ is **orthonormal** if:

$$\langle f_m|f_n\rangle = \delta_{mn}$$

A set of functions is **complete** if any other function of the Hilbert space can be written as:

$$f(x) = \sum_{n=1}^{\infty} c_n f_n(x)$$

If the functions f_n are orthonormal, then the coefficients are given by:

$$c_n = \langle f_n|f\rangle$$

Observables

Hermitian Operators

As we saw before, the expectation value of an observable $Q(x, p)$ can be expressed as:

$$\langle Q \rangle = \int \Psi^* \hat{Q} \Psi = \langle \Psi | \hat{Q} \Psi \rangle$$

There operator \hat{Q} are linear, because \hat{x} and \hat{p} are.

The outcome of a measurement must be real to make sense, that is:

$$\langle Q \rangle = \langle Q \rangle^*$$

So $\langle \Psi | \hat{Q} \Psi \rangle = \langle Q \rangle = \langle Q \rangle^* = \langle \Psi | \hat{Q} \Psi \rangle^* = \langle \hat{Q} \Psi | \Psi \rangle$. That means:

$$\langle \Psi | \hat{Q} \Psi \rangle = \langle \hat{Q} \Psi | \Psi \rangle$$

This must be true for any wave function Ψ , thus operators representing **observables** have the **hermitian** property:

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q} g | f \rangle$$

Hermitian Conjugate

If \hat{Q} is an operator, we define its adjoint as \hat{Q}^T such that:

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q}^T f | g \rangle$$

Determinate States

Ordinarily, when you measure an observable Q on an ensemble of identically prepared systems, all in the state Ψ , you do not get the same result each time.

Would it be possible to prepare a state such that every measurement of Q is certain to return the same value (let's say q)?

This would be a **determinate state** for the observable Q .

We already know one example: Stationary states (solutions to the time independent wave equation) are determinate states of the Hamiltonian. A measurement of the total energy on a particle in a stationary state Ψ_n is certain to yield the corresponding allowed energy E_n .

Theorem: Ψ is a determined state of \hat{Q} with value q if and only if $\hat{Q}\Psi = q\Psi$

- If q is a determined state of \hat{Q} , then the standard deviation should be 0, that means:

$$\begin{aligned} 0 &= \langle (\hat{Q} - \langle Q \rangle)^2 \rangle = \langle \Psi | (\hat{Q} - q)^2 \Psi \rangle \\ &= \langle (\hat{Q} - q)\Psi | (\hat{Q} - q)\Psi \rangle \\ &\Rightarrow (\hat{Q} - q)\Psi = 0 \\ &\Rightarrow \hat{Q}\Psi = q\Psi \end{aligned}$$

Where we used that $\hat{Q} - q$ is hermitian.

- The argument above can be reversed. Still, we could prove the return in a different way:
 $\langle Q \rangle = \langle \Psi | \hat{Q}\Psi \rangle = \langle \Psi | q\Psi \rangle = q\langle \Psi | \Psi \rangle = q$.
And $\langle Q^2 \rangle = \langle \Psi | \hat{Q}^2\Psi \rangle = \langle \Psi | q^2\Psi \rangle = q^2\langle \Psi | \Psi \rangle = q^2$.
So that $\sigma_Q = \langle Q^2 \rangle - \langle Q \rangle^2 = 0$. Which means that Ψ is a determined state of \hat{Q}

So:

Determinate States of \hat{Q} are eigenfunctions of \hat{Q}

Spectrum: The collection of all eigenvalues of an operator.

Eigenfunctions of A Hermitian Operator

If we have an hermitian operator, its spectra fall into two categories:

Discrete: Eigenvalues are separated from one another. Then the eigenfunctions lie in Hilbert space and constitute physically realizable states.

Continuous: Eigenvalues fill out an entire range. Then the eigenfunctions are not normalizable and don't represent wave functions. Still, we can have linear combinations of the.

Discrete Spectrum

Mathematically, the normalizable eigenfunctions of a hermitian operator have two properties:

- **Theorem 1:** Their eigenvalues are real:
 - Suppose $\hat{Q}f = qf$, then $\langle f | \hat{Q}f \rangle = \langle \hat{Q}f | f \rangle \Rightarrow q\langle f | f \rangle = q^*\langle f | f \rangle$
- **Theorem 2:** Eigenfunctions belonging to different eigenvalues are orthogonal.
 - Suppose $\hat{Q}f = qf$, $\hat{Q}g = q'g \Rightarrow \langle f | \hat{Q}g \rangle = \langle \hat{Q}f | g \rangle \Rightarrow q'\langle f | g \rangle = q^*\langle f | g \rangle$.

This holds for determinate states of any observable.

Theorem 2 says nothing about degenerate states. However, if two or more eigenfunctions have the same eigenvalue, we can use the **Gram - Schmidt** procedure to find a set of eigenfunctions with the same dimension that generates the same space but such that this basis is orthonormal (here it is important to use that the sum of degenerate eigenfunctions is still an eigenfunction with the same eigenvalue).

So even in the presence of degeneracy, the eigenfunctions can be chosen to be orthogonal.

In finite dimensional vector space, the eigenvectors of a Hermitian operator span the space. This property does not expand to infinite dimensional, but we will take it as an axiom.

Continuous Spectra

If the spectrum of a hermitian operator is continuous, the eigenfunctions are not normalizable and the proofs of theorems 1 and 2 fail.

In continuous spectrum, linear combinations are replaced by integrals.

Examples:

- **Eigenfunctions of momentum operator:**
Let $f_p(x)$ be the eigenfunction and p the eigenvalue:

$$\frac{\hbar}{i} \frac{d}{dx} f_p(x) = p f_p(x)$$

Then the general solution is:

$$f_p(x) = A e^{ipx/\hbar}$$

This is not square integrable for any p , so the momentum operator has no eigenfunctions inside the Hilbert space. And yet, if we restrict ourselves to real eigenvalues, we

recover a kind of orthonormality:

$$\int_{\mathbb{R}} f_{p'}^* f_p(x) dx = |A|^2 \int_{-\infty}^{\infty} e^{i(p-p')x/\hbar} dx = |A|^2 2\pi\hbar \delta(p - p')$$

So that we prefer to choose $A = 1/\sqrt{2\pi\hbar}$ so that:

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

$$\Rightarrow \langle f_{p'} | f_p \rangle = \delta(p - p')$$

Functions with this property are called **Dirac orthonormality**. Most important, this eigenfunctions are complete, with the sum replaced by integral. Any square-integrable function $f(x)$ can be written as:

$$f(x) = \int_{\mathbb{R}} c(p) f_p(x) dp = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} c(p) e^{ipx/\hbar} dp$$

The coefficients can be obtained by Fourier inversion or by Fourier's trick as:

$$\int_{\mathbb{R}} f(x) f_{p'}(x)^* dx = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} f(x) e^{-ip'x/\hbar} dx$$

$$= \langle f_{p'} | f \rangle = \int_{\mathbb{R}} c(p) \langle f_{p'} | f_p \rangle dp = \int_{\mathbb{R}} c(p) \delta(p - p') dp = c(p')$$

That means:

$$c(p') = \langle f_{p'} | f \rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} f(x) e^{-ip'x/\hbar} dx$$

The eigenfunctions of momentum are sinusoidal with wavelength:

$$\lambda = \frac{2\pi\hbar}{p}$$

It is a little bit more subtle than it seems, there is no such thing as a particle with determinate momentum (because the spectrum is continuous), we need a wave packet in order for this to make sense.

- **Position:** Find the eigenfunctions of the position operator. Let $g_y(x)$ be an eigenfunction of this operator with eigenvalue y :

$$x g_y(x) = y g_y(x)$$

Here y is a fixed number but x is a continuous variable. The eigenfunction has got to be zero outside $x = y$. Actually, the function is dirac delta:

$$g_y(x) = A \delta(x - y)$$

The eigenvalue has to be real. And we see the condition for dirac orthonormality:

$$\langle g_{y'} | g_y \rangle = \int_{\mathbb{R}} g_{y'}^*(x) g_y(x) dx = |A|^2 \int_{\mathbb{R}} \delta(x - y') \delta(x - y) dx = |A|^2 \delta(y - y')$$

We pick $A = 1$ so that the eigenfunctions are:

$$g_y(x) = \delta(x - y)$$

then:

$$\langle g_{y'} | g_Y \rangle = \delta(y - y')$$

These eigenfunctions are complete:

$$f(x) = \int_{\mathbb{R}} c(y) g_y(x) dy = \int_{\mathbb{R}} c(y) \delta(x - y) dy$$

So:

$$c(y) = f(y)$$

Generalized Statistical Interpretation

If you measure an observable $Q(x, p)$ on a particle in state $\Psi(x, t)$, you are certain to get one of the eigenvalues of $\widehat{Q}(x, -i\hbar d/dx)$.

If the spectrum of \widehat{Q} is discrete, the probability of getting a particular eigenvalue q_n associated with the orthonormalized eigenfunction $f_n(x)$ is:

$$|c_n|^2 \quad , \quad c_n = \langle f_n | \Psi \rangle$$

If the spectrum is continuous, with real eigenvalues $q(z)$ and associated Dirac-orthonormalized eigenfunctions $f_z(x)$, the probability of getting a result in the range dz is:

$$|c(z)|^2 dx \quad , \quad c(z) = \langle f_z | \Psi \rangle$$

Upon measurement, the wave function collapses to the corresponding eigenstate (or to a narrow range in the case of the continuous spectrum).

This interpretation is radically different from anything we now.

To support it, we observe that the eigenfunctions of an observable operator are complete, so the wave function can be written as:

$$\Psi(x, t) = \sum_n c_n f_n(x)$$

Because of orthonormality, the coefficients are obtained as:

$$c_n = \langle f_n | \Psi \rangle = \int f_n(x)^* \Psi(x, t) dx$$

c_n tell you how much f_n is in Ψ . Given that a measurement has to return one of the eigenvalues of \widehat{Q} , it is reasonable that the probability of getting a particular q_n eigenvalue is $|c_n|^2$ (because probabilities are obtained as absolute squares).

Theorem: the total probability has got to be 1:

- $1 = \langle \Psi | \Psi \rangle = \left\langle \sum_{n'} c_{n'} f_{n'} \right| \sum_n c_n f_n \rangle = \sum_{n'} \sum_n c_{n'}^* c_n \langle f_{n'} | f_n \rangle$

$$= \sum_{n'} \sum_n c_{n'}^* c_n \delta_{n'n} = \sum_n c_n^* c_n = \sum_n |c_n|^2$$

Similarly, the expectation value of Q should be the pondered average of eigenvalues, that is:

$$\langle Q \rangle = \sum_n q_n |c_n|^2$$

Indeed this is true, $\langle Q \rangle = \langle \Psi | \widehat{Q} \Psi \rangle = \langle \sum_{n'} c_{n'} f_{n'} | \widehat{Q} \sum_n c_n f_n \rangle = \langle \sum_{n'} c_{n'} f_{n'} | \sum_n c_n q_n \rangle$
 $= \sum_{n'} \sum_n c_{n'}^* c_n \langle f_{n'} | f_n \rangle = \sum_{n'} \sum_n c_{n'}^* c_n q_n \delta_{n'n} = \sum_n q_n |c_n|^2$

Position Measurements: A measurement of x of a particle in state Ψ will return one of the eigenvalues of position operator (any real number). We saw that the eigenfunctions are $g_y(x) = \delta(x - y)$. So:

$$c(y) = \langle g_y | \Psi \rangle = \int_{\mathbb{R}} \delta(x - y) \Psi(x, t) dx = \Psi(y, t)$$

So the probability of a result in a range dy is $|\Psi(y, t)|^2 dy$, as expected.

Momentum: The eigenfunctions are $f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$, so:

$$c(p) = \langle f_p | \Psi \rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} e^{-ipx/\hbar} \Psi(x, t) dx$$

We call this quantity the **momentum space wave function**. It is the Fourier transform of the position state:

$$\begin{aligned} \Phi(p, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} e^{-ipx/\hbar} \Psi(x, t) dx \\ \Psi(x, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} e^{ipx/\hbar} \Phi(p, t) dp \end{aligned}$$

And the probability of getting a momentum is $|\Phi(p, t)|^2 dp$

Uncertainty principle

Proof

For any observable A , we have:

$$\sigma_A^2 = \langle (\hat{A} - \langle A \rangle) |\Psi| (\hat{A} - \langle A \rangle) \Psi \rangle = \langle f | f \rangle$$

Where $f := (\hat{A} - \langle A \rangle) \Psi$. Likewise, for any other observable B :

$$\sigma_B^2 = \langle g | g \rangle , \quad g := (\hat{B} - \langle B \rangle) \Psi$$

Therefore, the Schwarz inequality gives:

$$\sigma_A^2 \sigma_B^2 = \langle f | f \rangle \langle g | g \rangle \geq |\langle f | g \rangle|^2$$

For any complex number: $|z|^2 \geq [Im(z)]^2 = \left(\frac{1}{2i}(z - z^*) \right)^2$. Therefore, setting $z = \langle f | g \rangle$ we get:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} [\langle f | g \rangle - \langle g | f \rangle] \right)^2$$

But:

$$\begin{aligned} \langle f | g \rangle &= \langle (\hat{A} - \langle A \rangle) \Psi | (\hat{B} - \langle B \rangle) \Psi \rangle = \langle \Psi | (\hat{A} - \langle A \rangle)(\hat{B} - \langle B \rangle) \Psi \rangle \\ &= \langle \Psi | (\hat{A}\hat{B} - \hat{A}\langle B \rangle - \hat{B}\langle A \rangle + \langle A \rangle \langle B \rangle) \Psi \rangle \\ &= \langle \Psi | \hat{A}\hat{B} \Psi \rangle - \langle B \rangle \langle \Psi | \hat{A} \Psi \rangle - \langle A \rangle \langle \Psi | \hat{B} \Psi \rangle + \langle A \rangle \langle B \rangle \langle \Psi | \Psi \rangle \\ &= \langle \hat{A}\hat{B} \rangle - \langle B \rangle \langle A \rangle - \langle A \rangle \langle B \rangle + \langle A \rangle \langle B \rangle \\ &= \langle \hat{A}\hat{B} \rangle - \langle A \rangle \langle B \rangle \end{aligned}$$

Similarly, $\langle g | f \rangle = \langle \hat{B}\hat{A} \rangle - \langle A \rangle \langle B \rangle$

So $\langle f | g \rangle - \langle g | f \rangle = \langle \hat{A}\hat{B} \rangle - \langle \hat{B}\hat{A} \rangle = \langle [\hat{A}, \hat{B}] \rangle$

Where, $[\hat{A}, \hat{B}] := \hat{A}\hat{B} - \hat{B}\hat{A}$

SO our conclusion is the **generalized uncertainty principle**:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2$$

The i inside the parenthesis cancels out because the difference $\hat{A}\hat{B} - \hat{B}\hat{A}$ of hermitian operators is antihermitian $\hat{Q}^T = \hat{Q}$, and its expected value is purely imaginary.

Example: Suppose $\hat{A} = x$ and $\hat{B} = \frac{\hbar}{i} \frac{d}{dx}$. The commutator is found to be:

$$[\hat{x}, \hat{p}] = i\hbar$$

So:

$$\sigma_x^2 \sigma_p^2 \geq \left(\frac{1}{2i} i\hbar \right)^2 = \left(\frac{\hbar}{2} \right)^2$$

So:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

Incompatible observables: When two observables do not commute, and so they have an uncertainty principle.

Incompatible observables don't admit a complete set of common eigenfunctions.

Compatible observables: Their commutators commute and they accept complete set of common eigenfunctions.

Theorem: If $AB = BA$ and x is an eigenvector of A with eigenvalue of multiplicity 1, then x is an eigenvector of B :

- $ABx = BAx = B\lambda x = \lambda Bx$

So x and Bx are both eigenvectors of A with eigenvalue λ , but if the eigenspace of λ in A is 1-D then $B(x)$ is a multiple of x and so x is an eigenvector of B

This fact is what tells us that commuting operators have a complete mutual family of eigenvectors.

You can certainly measure the position of a particle, but the act of measurement collapses the wave function to a narrow spike, which necessarily has a broad length of wavelengths (momenta) and vice versa.

Energy - time:

$$\Delta t \Delta E \geq \frac{\hbar}{2}$$

If we have some observable A , we can compute its derivative as:

$$\frac{d}{dt} \langle Q \rangle = \frac{d}{dt} \langle \Psi | \hat{Q} \Psi \rangle = \langle \partial_t \Psi | \hat{Q} \Psi \rangle + \langle \Psi | \partial_t \hat{Q} \Psi \rangle + \langle \Psi | \hat{Q} \partial_t \Psi \rangle$$

But Schrodinger says that $i\hbar \partial_t \Psi = \hat{H} \Psi$. So:

$$\frac{d}{dt} \langle Q \rangle = -\frac{1}{i\hbar} \langle \hat{H} \Psi | \hat{Q} \Psi \rangle + \frac{1}{i\hbar} \langle \Psi | \hat{Q} \hat{H} \Psi \rangle + \langle \partial_t \hat{Q} \rangle$$

But \hat{H} is hermitian, so we get:

$$\frac{d}{dt} \langle Q \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \langle \partial_t \hat{Q} \rangle$$

Dirac notation

Imagine a vector \vec{A} in two dimensions, how would you describe it to someone?, you could write it as $A_x \hat{i} + A_y \hat{j}$ where $A_x = \hat{i} \cdot \vec{A}$.

But you could do the same for other coordinates system and get a different set of coordinates, even though a vector itself lives out there in space and has no coordinates.

The same is true for a state in QM. It is represented by a vector $|S(t)\rangle$ that lives out there in Hilbert Space. But we can express it with respect to a wide number of different bases. This $|S(t)\rangle$ represents the particle.

The wave function $\Psi(x, t)$ is just the coefficient of the expansion of $|S(t)\rangle$ in the basis of position eigenfunctions:

$$\Psi(x, t) = \langle x | S(t) \rangle$$

Where $|x\rangle$ stands for the eigenfunction of \hat{x} with eigenvalue x ($\delta(y - x)$).

Whereas the momentum space wave function $\Phi(p, t)$ is the expansion of $|S(t)\rangle$ in the basis of momentum eigenfunctions:

$$\Phi(p, t) = \langle p | S(t) \rangle$$

with $|p\rangle$ standing for the eigenfunction of \hat{p} with eigenvalue p , $\frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$.

Or we can expand $|S\rangle$ in the basis of energy eigenfunctions (suppose it is discrete):

$$c_n(t) = \langle n | S(t) \rangle$$

Where $|n\rangle$ stands for the nth eigenfunction of \hat{H} .

But it's all the same state, they all contain the same information.

$$\begin{aligned} \Psi(x, t) &= \int \Psi(y, t) \delta(x - y) dy = \int \Phi(p, t) \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} dp \\ &= \sum c_n e^{-iE_nt/\hbar} \psi_n(x). \end{aligned}$$

Operators (representing observables) are linear transformations, they transform one vector into another:

$$|\beta\rangle \hat{Q} |\alpha\rangle$$

Just as vectors are represented in a basis $\{|e_n\rangle\}$ by their components $|\alpha\rangle = \sum a_n |e_n\rangle$ with $a_n = \langle e_n | \alpha \rangle$.

Operators are represented (respect to a basis) by their **matrix elements**:

$$\langle e_m | \hat{Q} | e_n \rangle := Q_{mn}$$

In this notation, we can find that:

$$b_m = \sum_n Q_{mn} a_n$$

Example: Imagine a system in which there are just two linearly independent states:

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The equals here means “is represented by”.

Then, the most general state is:

$$|D\rangle = a|1\rangle + b|2\rangle = \begin{pmatrix} a \\ b \end{pmatrix}, \text{ with } |a|^2 + |b|^2 = 1$$

$|a|^2$ is the probability of finding it in state $|1\rangle$ and similarly for $|b|^2$ for $|2\rangle$.

The hamiltonian can be expressed as a hermitian matrix, suppose it has the form:

$$H = \begin{pmatrix} h & g \\ g & h \end{pmatrix}$$

If the system starts out at $t = 0$ in state $|1\rangle$, what's the state at time t .

Sol: The time dependent Schrodinger equation says:

$$i\hbar \frac{d}{dt} |D\rangle = H|D\rangle$$

As always, we first solve the time-independent equation:

$$H|d\rangle = E|d\rangle$$

That is, we look for eigenvectors and eigenvalues of H .

In this cases, given the matrix form of H , the eigenvalues are $E_{\pm} = h \pm g$.
So these are the allowed energies.

We can calculate the eigenvectors as usual for matrices and find:

$$|d_{\pm}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$$

Where we normalized. Next, we expand the initial state in terms of the eigenvectors:

$$|D(0)\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}(|d_+\rangle + |d_-\rangle)$$

And we tack on the typical time dependence $e^{-iE_n t/\hbar}$:

$$\begin{aligned} |D(t)\rangle &= \frac{1}{\sqrt{2}}[e^{-i(h+g)t/\hbar}|d_+\rangle + e^{-i(h-g)t/\hbar}|d_-\rangle] \\ &= \frac{1}{2}e^{-iht/\hbar} \begin{pmatrix} e^{-igt/\hbar} + e^{igt/\hbar} \\ e^{-igt/\hbar} - e^{igt/\hbar} \end{pmatrix} = e^{-iht/\hbar} \begin{pmatrix} \cos(gt/\hbar) \\ -i \sin(gt/\hbar) \end{pmatrix} \end{aligned}$$

Dirac proposed to chop the braket notation $\langle \alpha | \beta \rangle$ into two pieces, the **bra** $\langle \alpha |$ and the **ket** $|\beta\rangle$. The latter is a vector.

And the former is a linear function of vectors, that when hits a vector produces a complex number. It can be thought of as an instruction:

$$\langle f | = \int f^*[\dots]dx$$

The kets are represented by columns (in a finite dimensional):

$$|\alpha\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$$

And the bra is a row:

$$\langle \alpha | = (a_1^*, a_2^*, \dots, a_n^*)$$

The collection of all bras is the **dual space**

Projection operator: If we have a vector $|\alpha\rangle$, we define:

$$\hat{P} := |\alpha\rangle\langle\alpha|$$

that operates as:

$$\hat{P}|\beta\rangle = \langle\alpha|\beta\rangle|\alpha\rangle$$

We call it the projection operator because it picks out the portion of any vector that lies along $|\alpha\rangle$.

If $\{|e_n\rangle\}$ is a discrete orthonormal basis:

$$\langle e_m | e_n \rangle = \delta_{nm}$$

And :

$$\sum_n |e_n\rangle\langle e_n| \alpha\rangle = |\alpha\rangle$$

Resumen Interpretación

- 1) Schrodinger's equation comes from taking a wave equations and asking it to have $\lambda = h/p$ and $E = \hbar\omega$. The equation is:

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

- 2) To solve it, we use separation of variables $\Psi(x, t) = \psi(x)f(t)$. We find that the temporal part has an easy solution $f(t) = e^{-iEt/\hbar}$. And the spacial equation has the form:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

Where E is a constant. When imposing the boundary conditions, we find that we can only choose some values E_n with eigen functions $\psi_n(x)$. Then, the general solution is $\Psi(x, t) = \sum c_n \psi_n(x) f_n(t)$.

To find the constants c_n , we impose the initial conditions $\Psi(x, 0) = \sum c_n \psi_n(x)$ and use Fourier's trick.

- 3) $|\Psi|^2$ is interpreted as the probability density of finding the particle. It has to be normalized, meaning that $\int_{\mathbb{R}} |\Psi|^2 dx = 1$.

It can be proved that once normalized, the normalization doesn't change with time.

- 4) Once we find the state Ψ the particle is in, we can find the expected value of x as:

$$\langle x \rangle = \int x |\Psi|^2 dx$$

Now we can find the expected value of v as $\langle v \rangle = \frac{d}{dt} \langle x \rangle$. Then, it can be proven that:

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} = \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx$$

This takes us to define the **momentum operator** as:

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

- 5) If we have any physical quantity $Q(x, p)$, then the associated operator is $Q(x, \frac{\hbar}{i} \frac{\partial}{\partial x}) \Psi dx$. Then the expected value of Q is:

$$\langle Q \rangle = \int \Psi^* Q(x, \frac{\hbar}{i} \frac{\partial}{\partial x}) \Psi dx$$

6) This allows us to define many operators:

- $\hat{x} = x$
- $\hat{V}(x) = V(x)$
- $\hat{p} = -i\hbar \frac{\partial}{\partial x}$
- $\hat{E} = i\hbar \frac{\partial}{\partial t}$

Then, Schrodinger's equation is given by:

$$\hat{H} := \frac{\hat{p}^2}{2m} + \hat{V} = \hat{E}$$

7) The operators \hat{Q} are hermitian. Which means that:

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$$

Where:

$$\langle f | g \rangle = \int_{\mathbb{R}} f^* g dx$$

This property is equivalent to asking Q to have a real expected value, that is $\langle Q \rangle = \langle Q \rangle^*$.

So **Observables are represented by hermitian operators.**

8) We can find the expected value of any operator, but we don't know the possible values the variable can take and the probability of each one.

Ordinarily, when you measure an observable Q on an ensemble of identically prepared systems, all in state Ψ , you do not get the same result each time.

A **determinate state of Q** is a state Ψ such that every measurement of Q is certain to return the value q .

Theorem: Ψ is a determined state of \hat{Q} with value q if and only if $\hat{Q}\Psi = q\Psi$

- If q is a determined state of \hat{Q} , then the standard deviation should be 0, that means:

$$\begin{aligned} 0 &= \langle (\hat{Q} - \langle Q \rangle)^2 \rangle = \langle \Psi | (\hat{Q} - q)^2 \Psi \rangle \\ &= \langle (\hat{Q} - q)\Psi | (\hat{Q} - q)\Psi \rangle \\ &\Rightarrow (\hat{Q} - q)\Psi = 0 \Rightarrow \hat{Q}\Psi = q\Psi \end{aligned}$$

So **determinate states of \hat{Q} (states with variance 0)** are eigenfunctions of \hat{Q}

Spectrum: The collection of all eigenvalues of an operator.

We have already seen an example of determined states, those for hamiltonian. The determined states of hamiltonian are $\hat{H}\Psi = E\Psi$.

Which is the time-independent equation. This means that this states have determined total energy. The complete solution can then be found as a sum of this determined states.

Theorem: The eigenvalues of an hermitian operator \hat{Q} are real, their eigenfunctions are orthonormal and complete.

9) If \hat{Q} is an operator, then its **eigenfunctions** are functions e_i such that:

$$\hat{Q}|e_i\rangle = \lambda_i|e_i\rangle$$

This eigenfunctions e_i are a complete and orthonormal basis.

For it to be orthonormal, we ask it to:

$$\langle e_i | e_j \rangle = \int_{\mathbb{R}} e_i^* e_j dx = \delta_{ij}$$

If the spectrum is continuous instead of discrete, we ask $\langle e_\lambda | e_\mu \rangle = \delta(\lambda - \mu)$

Now, if Ψ is the state of the particle, we can write it in terms of the eigenfunctions:

$$|\Psi\rangle = \sum c_n |e_n\rangle$$

Where:

$$c_n = \langle e_n | \Psi \rangle$$

This wave function might not be a determined state of Q . When we measure \hat{Q} , we are bound to get a determined state $|e_n\rangle$ with value $Q = \lambda_n$.

And the expected value of \hat{Q} is:

$$\begin{aligned} \langle Q \rangle &= \int \Psi^* \hat{Q} \Psi dx \\ &= \int (c_1^* |e_1\rangle^* + c_2^* |e_2\rangle^* + \dots) \hat{Q} (c_1 |e_1\rangle + c_2 |e_2\rangle + \dots) dx \\ &= \int (c_1^* |e_1\rangle^* + c_2^* |e_2\rangle^* + \dots) (\lambda_1 c_1 |e_1\rangle + \lambda_2 c_2 |e_2\rangle + \dots) dx \\ &= \lambda_1 |c_1|^2 + \lambda_2 |c_2|^2 + \dots \end{aligned}$$

As we said earlier, when we measure Q , it gives us a determined state, so it can only take the values $\lambda_1, \lambda_2, \dots$. And seeing the sum that gives us $\langle Q \rangle$, we conclude:

The probability of getting λ_i when measuring \hat{Q} is $|c_i|^2 = |\langle e_i | \Psi \rangle|^2 = \left| \int_{\mathbb{R}} e_i^* \Psi dx \right|^2$

And it can be proved that $\sum |c_n|^2 = 1$, as expected.

10) Ejemplos

- **Energy:** Let's say we have the solution Ψ of a problem. Then, we can calculate the mean energy as $\int \Psi^* \hat{H} \Psi dx$. The possible values of energy are the eigenvalues of \hat{H} and the possible definite states are the eigenvectors of \hat{H} . That is, we look for functions ψ_n such that:

$$\begin{aligned}\hat{H}\psi_n &= E_n\psi_n \\ -\frac{\hbar^2}{2m}\frac{\partial^2\psi_n}{\partial x^2} + V\psi_n &= E_n\psi_n\end{aligned}$$

We notice that this is actually the time independent Schrodinger equation, which we might have already solved before.

These states ψ_n have determined energy E_n .

Now we have $\Psi_n = \psi_n f(t)$, and we have to write $\Psi = \sum c_n \Psi_n$.

Then, the probability of getting an eigenvalue E_n is:

$$|c_n|^2 = |\langle \Psi_n | \Psi \rangle|^2 = |\langle \psi_n | \psi \rangle|^2$$

- **Position:** This is kind of overkill, but it is only a consistency check. Lets say the wave equation is Ψ . Now we look for the eigenvectors g_λ of \hat{x} , they have to fulfill:

$$\begin{aligned}xg_\lambda(x) &= \lambda g_\lambda(x) \\ \Rightarrow g_\lambda(x) &= \delta(x - \lambda)\end{aligned}$$

To check they are dirac normalized, we see that $\int_{\mathbb{R}} g_\lambda(x) g_\mu(x) dx = \delta(\lambda - \mu)$.

Then, any real number is an eigenvalue, so we have a continuous spectrum.

We are supposed to write Ψ as a combination of this eigenfunctions with coefficients $c(\lambda)$, so:

$$\Psi(x, t) = \int c(\lambda) \delta(\lambda - x)$$

Where:

$$c(\lambda) = \langle g_\lambda(x) | \Psi \rangle = \int_{\mathbb{R}} \delta(x - \lambda) \Psi dx = \Psi(\lambda, t)$$

So the probability of finding the particle in the range $d\lambda$ is:

$$|c(\lambda)|^2 d\lambda = |\Psi(\lambda, t)|^2 d\lambda$$

-
- **Momentum:** Let's say Ψ is the wave equation. Now we look for the eigenvectors of $\hat{p} = -i\hbar\partial_x$. That is, solve $\hat{p}|e_p(x)\rangle = pe_p(x)$. The solutions are:

$$e_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

Where p is the eigenvalue and it can be any real, so we have a continuous spectrum. These eigenvectors are already normalized, in the sense that $\langle e_p(x)|e_q(x)\rangle = \int e_p(x)e_q(x)dx = \delta(p-q)$

Then, the p-component of $|\Psi\rangle$ is given by:

$$c(p) = \langle e_p|\Psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} e^{-ipx/\hbar} \Psi(x, t) dx := \Phi(p, t)$$

Then, Φ is the probability density of momentum. And the probability of having a momentum in a range dp is:

$$|c_p|^2 = |\Phi(p, t)|^2 dp$$

Then, the **moment space wave function** is (ignoring the \hbar) the Fourier transform of Ψ .

The fact that $\int |\Phi(p, t)|^2 dp = 1$ is due to Plancherel's theorem.

We see that the determined states of momentum $\frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$ are not normalizable and are impossible to find on their own.

Nevertheless, when we measure momentum, we get a small range dp of these states that together form a possible wave function.

Each individual determined state is a wave with wavelength $\lambda = \frac{2\pi\hbar}{p}$, but these states are impossible on their own, we need a combination of them.

And Ψ can be obtained back with these components as:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \Phi(p, t) dp$$

Other way: Let's say we begin knowing that momentum of a function is $p = \frac{\hbar}{\lambda}$. Then, we need to calculate the spectrum of λ in Ψ .

For that, we use the Fourier transform with variable λ (instead of the typical angular freq α or freq ξ). So the spectrum is $\int_{\mathbb{R}} \Psi e^{-2\pi i x/\lambda} dx$

Then, the transform is $\int_{\mathbb{R}} \Psi e^{-2\pi i x p/\hbar} dx = \int_{\mathbb{R}} \Psi e^{-ipx/\hbar} dx$

If we put on a conversion factor, we get $\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} e^{-ipx/\hbar} \Psi(x, t) dx$.

- **Two States:** Let's say we have a variable (like spin) with only two possible states represented by:

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The matrix are just representations of the states.

Then, the most general state is:

$$|D\rangle = a|1\rangle + b|2\rangle = \begin{pmatrix} a \\ b \end{pmatrix}, \quad |a|^2 + |b|^2 = 1$$

$|a|^2$ is the probability of finding it in state $|1\rangle$ and probability $|b|^2$ of state $|2\rangle$

- The Hamiltonian H is a Hermitian operator (between vectors, that can be really vectors if we have a finite set of stationary states or functions otherwise). Because the Hamiltonian H is Hermitian, it has a complete set of orthonormal eigenfunctions $|u_i\rangle$ with real eigenvalues λ_i such that:

$$I = |u_i\rangle\langle u_i|$$

Therefore, the operator itself is:

$$H = \lambda_i |u_i\rangle\langle u_i|$$

The limits of the sums depends on the type of Hamiltonian (finite space, discrete, indiscrete [change by an integral])

Such that:

$$f(H) = f(\lambda_i) |u_i\rangle\langle u_i|$$

Then, say we have an initial state $|\Psi(0)\rangle$, then the solution of Schrodinger's equation is:

$$\begin{aligned} H|\Psi(t)\rangle &= i\hbar \frac{d}{dt} |\Psi(t)\rangle \\ \Rightarrow \frac{d}{dt} |\Psi(t)\rangle &= -\frac{i}{\hbar} H |\Psi(t)\rangle \\ \Rightarrow |\Psi(t)\rangle &= e^{-i/\hbar t H} |\Psi(0)\rangle \\ \Rightarrow &= e^{i/\hbar t \lambda_i} |u_i\rangle\langle u_i| |\Psi(0)\rangle \\ \Rightarrow &= \sum e^{i/\hbar t \lambda_i} c_i |u_i\rangle \end{aligned}$$

Where $c_i = \langle u_i | \Psi(0) \rangle$

Problems

Ejemplo

Resolver la partícula en una caja con condición inicial $\Psi(x, 0) = \sqrt{\frac{8}{3L}} \sin^2(\pi x/L)$ (notar que esto está normalizado, pues $\int_{\mathbb{R}} |\Psi(x, 0)|^2 dx = 1$.

Tenemos que el problema es:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t}$$

Para $x \in [0, L]$ y con condiciones $\Psi(0, t) = \Psi(L, t) = 0$ y que $\Psi(x, 0) = \sqrt{\frac{8}{3L}} \sin^2(\pi x/L)$

Ya sabemos que para la ecuación indep. del tiempo, cambiamos el operador \hat{E} por E y nos queda:

$$-\frac{\hbar^2}{2m} \partial_x^2 \psi = E \psi$$

Lo que nos da por solución $\psi(x) = A \cos(\frac{\sqrt{2mE}}{\hbar}x) + B \sin(\frac{\sqrt{2mE}}{\hbar}x)$. Por otro lado, sabemos que la solución temporal es $f(t) = e^{-iEt/\hbar}$

Por tanto, la solución general es:

$$\Psi_n(x) = \cos(\frac{\sqrt{2mE}}{\hbar}x) + B \sin(\frac{\sqrt{2mE}}{\hbar}x) e^{-iEt/\hbar}$$

Al imponer las primeras dos condiciones de frontera nos queda que $A = 0$ y que $\frac{\sqrt{2mE}}{\hbar} = \frac{\pi n}{L}$. Lo que implica que las energías accesibles (autovalores) son $E_n = \frac{\pi^2 \hbar^2 n^2}{2mL^2}$.

Entonces las soluciones estacionarias (eigenfunciones) son de la forma $\sin(\frac{\sqrt{2mE}}{\hbar}x) = \sin(\frac{\pi n}{L}x)$.

Para hacerlas de norma 1, hay que agregar un factor $\sqrt{\frac{2}{L}} \sin(\frac{\pi n}{L}x)$. Para que la integral $\int_{\mathbb{R}} \psi_n^2 dx$ sea 0 (conste que la función vale 0 fuera de $[0, L]$).

Luego, la solución general es de la forma:

$$\Psi_n(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{L}} \sin(\frac{\pi n}{L}x) e^{-iE_n t/\hbar}$$

Luego, cuando $t = 0$ buscamos escribir $\sqrt{\frac{8}{3L}} \sin^2(\pi x/L)$ como una combinación lineal de estas soluciones, para lo que usamos una serie de Fourier de senos en el intervalo $[0, L]$. Habiendo determinado los c_n como $\int_{\mathbb{R}} \sqrt{\frac{2}{L}} \sin(\frac{\pi n}{L}x) \sqrt{\frac{8}{3L}} \sin^2(\pi x/L) dx$ (claro que las funciones

se hacen 0 fuera de $[0, L]$), nos va a quedar al final que:

$$\Psi(x, t) = \sum_{n \text{ impar}} -\frac{16}{\sqrt{3}\pi(n^3 - 4n)} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n}{L}x\right) e^{-iE_n t/\hbar}$$

La energía: Los eigenvalores de \hat{H} son $E_n = \frac{\pi^2 \hbar^2 n^2}{2mL^2}$. Pero no estamos en ninguno de los estados estacionarios correspondientes a las eigenfunciones de \hat{H} (que las eigenfunciones son nuestras soluciones $\Psi_n(x, t)$). Si nos quedaramos en sólo uno de esos estados, estaríamos 100 % seguros de que la energía es el valor correspondiente. Pero nel, estamos en una combinación lineal de todos, con coeficientes $-\frac{16}{\sqrt{3}\pi(n^3 - 4n)}$ para n impar (y 0 para n par).

Tenemos que encontrar los eigenvectores de \hat{H} . Como vimos antes, los encontramos como parte del proceso de encontrar Ψ . Obtuvimos que los eigenvectores son $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n}{L}x\right)$.

El facto de $\sqrt{\frac{2}{L}}$ es lo que nos permite que $\int \psi_n(x)^2 dx = 1$ y por tanto son una base orto-normal.

Y como vimos antes, los eigenvalores es̄an dados por $E_n = \frac{\pi^2 \hbar^2 n^2}{2mL^2}$.

Luego, para obtener la probabilidad de obtener un eigenvalor en específico, calculamos el coeficiente de Ψ en la dirección del eigenvector, que se obtiene como:

$$|c_n|^2 = |\langle \psi_n | \Psi \rangle|^2 = \left| -\frac{16}{\sqrt{3}\pi(n^3 - 4n)} \right|^2$$

$$P_{E_n \text{ (impar)}} = \frac{256}{3\pi^2(n^3 - 4n)^2}$$

Podemos comprobar que esto suma 1 sobre los impares, por lo que sí es una proba. Y de hecho, hay un casi 96 % de proba de que se enceunte en el primer estado.

E incluso podemos calcular el valor esperado de E como:

$$\begin{aligned} \langle E \rangle &= \sum P_{E_n} E_n \\ &= \sum_{n \text{ impar}} \frac{256}{3\pi^2(n^3 - 4n)^2} \frac{\pi^2 \hbar^2 n^2}{2mL^2} \\ &= \frac{6,57973 \hbar^2}{L^2 m} \end{aligned}$$

Que pudimos haber calculado igual usando la otra reglita:

$$\begin{aligned} \langle E \rangle &= \int \Psi^* \hat{E} \Psi dx \\ &= \int \Psi^* \left(-\frac{\hbar^2}{2m} \frac{\partial}{\partial x} \right) \Psi dx \end{aligned}$$

y da lo mismo.

Example 3.4

A particle of mass m is bound in the delta function well $V(x) = -\alpha\delta(x)$. What is the probability that a measurement of its momentum would yield a value greater than $p_0 = m\alpha/\hbar$

Solution: The position space wave function was found earlier and it is $\Psi(x, t) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2} e^{-iEt/\hbar}$
Where $E = -m\alpha^2/2\hbar^2$. Then, the momentum space wave function is:

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \frac{\sqrt{m\alpha}}{\hbar} e^{-iEt/\hbar} \int_{\mathbb{R}} e^{ipx/\hbar} e^{-m\alpha|x|/\hbar^2} dx = \dots = \sqrt{\frac{2}{\pi}} \frac{p_0^{3/2} e^{-iEt/\hbar}}{p^2 + p_0^2}$$

So the probability is then:

$$\frac{2}{\pi} p_0^3 \int_{p_0}^{\infty} \frac{1}{(p^2 + p_0^2)^2} dp = \frac{1}{\pi} \left[\frac{pp_0}{p^2 + p_0^2} + \tan^{-1} \left(\frac{p}{p_0} \right) \right]_{p_0}^{\infty} = \dots = 0,091$$

Problem 3.11

Find the momentum space wave function $\Phi(p, t)$ for a particle in the ground state of the harmonic oscillator. What is the probability that a measurement of p on a particle in this state would yield a value outside the classical range

The wave function in this case is $\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} e^{-i\omega t/2}$
Then, the momentum wave function is:

$$\begin{aligned} \Phi(p, t) &= \frac{1}{\sqrt{2\pi\hbar}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-i\omega t/2} \int_{\mathbb{R}} e^{-ipx/\hbar} e^{-\frac{m\omega}{2\hbar}x^2} dx \\ &= \frac{1}{(\pi m\omega\hbar)^{1/4}} e^{-p^2/2m\omega\hbar} e^{-i\omega t/2} \end{aligned}$$

So that:

$$|\Phi(p, t)|^2 = \frac{1}{\sqrt{\pi m\omega\hbar}} e^{-p^2/m\omega\hbar}$$

The maximum classical momentum is $\frac{p^2}{2m} = E = \frac{1}{2}\hbar\omega \Rightarrow p = \sqrt{m\omega\hbar}$.
So the probability of being outside the range is:

$$P = \int_{-\infty}^{-\sqrt{m\omega\hbar}} |\Phi|^2 dp + \int_{\sqrt{m\omega\hbar}}^{\infty} |\Phi|^2 dp = \dots = 0,157$$

Problem 3.12

It can be proven that in the momentum space, the position operator is:

$$\hat{x} = -i\hbar \frac{\partial}{\partial p}$$

Problem 3.13

We can prove that for the commutators:

$$\begin{aligned}[AB, C] &= A[B, C] + [A, C]B \\ [x^n, p] &= i\hbar n x^{n-1} \\ [f(x), p] &= i\hbar \frac{df}{dx}\end{aligned}$$

Problem 3.27

An operator \hat{A} has two normalized eigenstates ψ_1, ψ_2 with eigenvalues a_1, a_2 . Operator \hat{B} has two normalized eigenstates ϕ_1, ϕ_2 with eigenvalues b_1, b_2 . The states are related by:

$$\psi_1 = \frac{3}{5}\phi_1 + \frac{4}{5}\phi_2 \quad , \quad \psi_2 = \frac{4}{5}\phi_1 - \frac{3}{5}\phi_2$$

A is measured and the value a_1 is obtained, what state are we in after the measurement?

We are in state ψ_1

If B is now measured what are the possible results

We could get state ϕ_1 ($B = b_1$) with probability 9/25 or state ϕ_2 ($B = b_2$) with proba 16/25

Let's say we got b_1 . Now A is measured again, what is the proba of getting a_1 ?

We are in state $\phi_1 = \frac{3}{5}\psi_1 + \frac{4}{5}\psi_2$, so the proba of getting a_1 is 9/25.

Problem 3.28

**Problem 3.28 Find the momentum-space wave function $\Phi_n(p, t)$ for the n th stationary state of the infinite square well. Graph $|\Phi_1(p, t)|^2$ and $|\Phi_2(p, t)|^2$, as functions of p (pay particular attention to the points $p = \pm n\pi\hbar/a$). Use $\Phi_n(p, t)$ to calculate the expectation value of p^2 . Compare your answer to Problem 2.4.

Problem 3.28

$$\Psi_n(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-iE_n t/\hbar}, \quad \text{with } E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

$$\begin{aligned}\Phi_n(p, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi_n(x, t) dx = \frac{1}{\sqrt{2\pi\hbar}} \sqrt{\frac{2}{a}} e^{-iE_n t/\hbar} \int_0^a e^{-ipx/\hbar} \sin\left(\frac{n\pi}{a}x\right) dx \\ &\quad - \frac{1}{\sqrt{\pi\hbar a}} e^{-iE_n t/\hbar} \frac{1}{2i} \int_0^a [e^{i(n\pi/a-p/\hbar)x} - e^{i(-n\pi/a-p/\hbar)x}] dx \\ &= \frac{1}{\sqrt{\pi\hbar a}} e^{-iE_n t/\hbar} \frac{1}{2i} \left[\frac{e^{i(n\pi/a-p/\hbar)x}}{i(n\pi/a-p/\hbar)} - \frac{e^{i(-n\pi/a-p/\hbar)x}}{i(-n\pi/a-p/\hbar)} \right]_0^a \\ &= \frac{-1}{2\sqrt{\pi\hbar a}} e^{-iE_n t/\hbar} \left[\frac{e^{i(n\pi-pa/\hbar)} - 1}{(n\pi/a-p/\hbar)} + \frac{e^{-i(n\pi+pa/\hbar)} - 1}{(n\pi/a+pa/\hbar)} \right] \\ &= \frac{-1}{2\sqrt{\pi\hbar a}} e^{-iE_n t/\hbar} \left[\frac{(-1)^n e^{-ipa/\hbar} - 1}{(n\pi-ap/\hbar)} + \frac{(-1)^n e^{-ipa/\hbar} - 1}{(n\pi+ap/\hbar)} \right] \\ &= -\frac{1}{2} \sqrt{\frac{a}{\hbar}} e^{-iE_n t/\hbar} \frac{2n\pi}{(n\pi)^2 - (ap/\hbar)^2} \left[(-1)^n e^{-ipa/\hbar} - 1 \right] \\ &= \boxed{\sqrt{\frac{a\pi}{\hbar}} \frac{ne^{-iE_n t/\hbar}}{(n\pi)^2 - (ap/\hbar)^2} [1 - (-1)^n e^{-ipa/\hbar}].}\end{aligned}$$

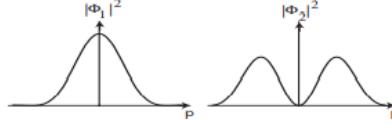
Noting that

$$1 - (-1)^n e^{-ipa/\hbar} = e^{-ipa/2\hbar} [e^{ipa/2\hbar} - (-1)^n e^{-ipa/2\hbar}] = 2e^{-ipa/2\hbar} \begin{cases} \cos(pa/2\hbar) & (n \text{ odd}), \\ i \sin(pa/2\hbar) & (n \text{ even}), \end{cases}$$

we have

$$|\Phi_1(p, t)|^2 = \frac{4\pi a}{\hbar} \frac{\cos^2(pa/2\hbar)}{[\pi^2 - (pa/\hbar)^2]^2}, \quad |\Phi_2(p, t)|^2 = \frac{16\pi a}{\hbar} \frac{\sin^2(pa/2\hbar)}{[(2\pi)^2 - (pa/\hbar)^2]^2}.$$

Mathematica has no trouble with the points $p = \pm n\pi\hbar/a$, where the denominator vanishes. The reason is that the numerator is also zero there, and the function as a whole is finite—in fact, the graphs show no interesting behavior at these points.



$$\begin{aligned}\langle p^2 \rangle &= \int_{-\infty}^{\infty} p^2 |\Phi_n(p, t)|^2 dp = \frac{4n^2\pi a}{\hbar} \int_{-\infty}^{\infty} \frac{p^2}{[(n\pi)^2 - (ap/\hbar)^2]^2} \left\{ \frac{\cos^2(pa/2\hbar)}{\sin^2(pa/2\hbar)} \right\} dp \quad [\text{let } x \equiv \frac{ap}{n\pi\hbar}] \\ &= \frac{4n\hbar^2}{a^2} \int_{-\infty}^{\infty} \frac{x^2}{(1-x^2)^2} T_n(x) dx = \frac{4n\hbar^2}{a^2} I_n,\end{aligned}$$

where

$$T_n(x) \equiv \begin{cases} \cos^2(n\pi x/2), & \text{if } n \text{ is odd,} \\ \sin^2(n\pi x/2), & \text{if } n \text{ is even.} \end{cases}$$

The integral can be evaluated by partial fractions:

$$\begin{aligned}\frac{x^2}{(x^2-1)^2} &= \frac{1}{4} \left[\frac{1}{(x-1)^2} + \frac{1}{(x+1)^2} + \frac{1}{(x-1)} - \frac{1}{(x+1)} \right] \Rightarrow \\ I_n &= \frac{1}{4} \left[\int_{-\infty}^{\infty} \frac{1}{(x-1)^2} T_n(x) dx + \int_{-\infty}^{\infty} \frac{1}{(x+1)^2} T_n(x) dx + \int_{-\infty}^{\infty} \frac{1}{(x-1)} T_n(x) dx - \int_{-\infty}^{\infty} \frac{1}{(x+1)} T_n(x) dx \right].\end{aligned}$$

For odd n :

$$\int_{-\infty}^{\infty} \frac{1}{(x \pm 1)^k} \cos^2\left(\frac{n\pi x}{2}\right) dx = \int_{-\infty}^{\infty} \frac{1}{y^k} \cos^2\left[\frac{n\pi}{2}(y \mp 1)\right] dy = \int_{-\infty}^{\infty} \frac{1}{y^k} \sin^2\left(\frac{n\pi y}{2}\right) dy.$$

For even n :

$$\int_{-\infty}^{\infty} \frac{1}{(x \pm 1)^k} \sin^2\left(\frac{n\pi x}{2}\right) dx = \int_{-\infty}^{\infty} \frac{1}{y^k} \sin^2\left[\frac{n\pi}{2}(y \mp 1)\right] dy = \int_{-\infty}^{\infty} \frac{1}{y^k} \sin^2\left(\frac{n\pi y}{2}\right) dy.$$

In either case, then,

$$I_n = \frac{1}{2} \int_{-\infty}^{\infty} \frac{1}{y^2} \sin^2\left(\frac{n\pi y}{2}\right) dy = \frac{n\pi}{4} \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2} du = \frac{n\pi^2}{4}.$$

Therefore

$$\langle p^2 \rangle = \frac{4n\hbar^2}{a^2} I_n = \frac{4n\hbar^2}{a^2} \frac{n\pi^2}{4} = \left(\frac{n\pi\hbar}{a}\right)^2 \quad (\text{same as Problem 2.4}).$$

Problem 3.29

Problem 3.29 Consider the wave function

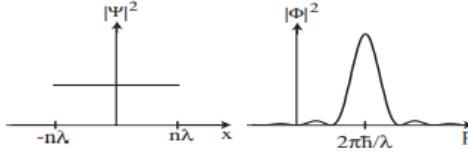
$$\Psi(x, 0) = \begin{cases} \frac{1}{\sqrt{2n\lambda}} e^{i2\pi x/\lambda}, & -n\lambda < x < n\lambda, \\ 0, & \text{otherwise,} \end{cases}$$

where n is some positive integer. This function is purely sinusoidal (with wavelength λ) on the interval $-n\lambda < x < n\lambda$, but it still carries a *range* of momenta, because the oscillations do not continue out to infinity. Find the momentum space wave function $\Phi(p, 0)$. Sketch the graphs of $|\Psi(x, 0)|^2$ and $|\Phi(p, 0)|^2$, and determine their widths, w_x and w_p (the distance between zeros on either side of the main peak). Note what happens to each width as $n \rightarrow \infty$. Using w_x and w_p as estimates of Δx and Δp , check that the uncertainty principle is satisfied. *Warning:* If you try calculating σ_p , you're in for a rude surprise. Can you diagnose the problem?

Problem 3.29

$$\begin{aligned} \Phi(p, 0) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x, 0) dx = \frac{1}{2\sqrt{n\pi\hbar\lambda}} \int_{-n\lambda}^{n\lambda} e^{i(2\pi/\lambda-p/\hbar)x} dx \\ &= \frac{1}{2\sqrt{n\pi\hbar\lambda}} \frac{e^{i(2\pi/\lambda-p/\hbar)x}}{i(2\pi/\lambda-p/\hbar)} \Big|_{-n\lambda}^{n\lambda} = \frac{1}{2\sqrt{n\pi\hbar\lambda}} \frac{e^{i2\pi n} e^{-ipn\lambda/\hbar} - e^{-i2\pi n} e^{ipn\lambda/\hbar}}{i(2\pi/\lambda-p/\hbar)} \\ &= \boxed{\sqrt{\frac{\hbar\lambda}{n\pi}} \frac{\sin(np\lambda/\hbar)}{(p\lambda - 2\pi\hbar)}}. \end{aligned}$$

$$|\Psi(x, 0)|^2 = \frac{1}{2n\lambda} \quad (-n\lambda < x < n\lambda); \quad |\Phi(p, 0)|^2 = \frac{\lambda\hbar}{n\pi} \frac{\sin^2(np\lambda/\hbar)}{(p\lambda - 2\pi\hbar)^2}.$$



The width of the $|\Psi|^2$ graph is $w_x = 2n\lambda$. The $|\Phi|^2$ graph is a maximum at $2\pi\hbar/\lambda$, and goes to zero on either side at $\frac{2\pi\hbar}{\lambda} \left(1 \pm \frac{1}{2n}\right)$, so $w_p = \frac{2\pi\hbar}{n\lambda}$. As $n \rightarrow \infty$, $w_x \rightarrow \infty$ and $w_p \rightarrow 0$; in this limit the particle has a well-defined momentum, but a completely indeterminate position. In general,

$$w_x w_p = (2n\lambda) \frac{2\pi\hbar}{n\lambda} = 4\pi\hbar > \hbar/2,$$

so the uncertainty principle is satisfied (using the widths as a measure of uncertainty). If we try to check the uncertainty principle more rigorously, using standard deviation as the measure, we get an uninformative result, because

$$\langle p^2 \rangle = \frac{\lambda\hbar}{n\pi} \int_{-\infty}^{\infty} p^2 \frac{\sin^2(np\lambda/\hbar)}{(p\lambda - 2\pi\hbar)^2} dp = \infty.$$

(At large $|p|$ the integrand is approximately $(1/\lambda^2) \sin^2(np\lambda/\hbar)$, so the integral blows up.) Meanwhile $\langle p \rangle$ is zero, so $\sigma_p = \infty$, and the uncertainty principle tells us nothing. The source of the problem is the discontinuity in Ψ at the end points; here $\hat{p}\Psi = -i\hbar d\Psi/dx$ picks up a delta function, and $\langle \Psi | \hat{p}^2 \Psi \rangle = \langle \hat{p}\Psi | \hat{p}\Psi \rangle \rightarrow \infty$ because the integral of the square of the delta function blows up. In general, if you want σ_p to be finite, you cannot allow discontinuities in Ψ .

Problem 3.30

Suppose:

$$\Psi(x, 0) = \frac{A}{x^2 + a^2}$$

a) Determine A to normalize Ψ :

$$1 = \int_{\mathbb{R}} |\Psi(x, 0)|^2 dx = \int_{\mathbb{R}} \frac{|A|^2}{(x^2 + a^2)^2} = \dots = |A|^2 \frac{\pi}{2a^3} \Rightarrow A = a\sqrt{\frac{2a}{\pi}}$$

Find $\langle x \rangle, \langle x^2 \rangle$ and σ_x

$$\begin{aligned}\langle x \rangle &= A^2 \int_{\mathbb{R}} \frac{x}{(a^2 + x^2)^2} dx = 0 \\ \langle x^2 \rangle &= 2A^2 \int_{\mathbb{R}} \frac{x^2}{(a^2 + x^2)^2} dx = a^2 \\ \sigma_x &= \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = a\end{aligned}$$

Find $\Phi(p, 0)$

$$\Phi(p, 0) = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} e^{-ipx/\hbar} \Psi dx = \frac{A}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} e^{-ipx/\hbar} \frac{1}{x^2 + a^2} dx = \dots = \sqrt{\frac{a}{\hbar}} e^{-|p|a/\hbar}$$

We can check that this result is normalized.

Calculate $\langle p \rangle, \langle p^2 \rangle$

$$\begin{aligned}\langle p \rangle &= \int_{\mathbb{R}} p |\Phi(p, 0)|^2 dp = \frac{a}{\hbar} \int_{\mathbb{R}} p e^{-2|p|a/\hbar} dp = 0 \\ \langle p^2 \rangle &= 2 \frac{a}{\hbar} \int_0^\infty p^2 e^{-2pa/\hbar} dp = \frac{\hbar}{\sqrt{2a}}\end{aligned}$$

Problem 3.31

Virial theorem: Use eq. 3.71 to show:

$$\frac{d}{dt} \langle xp \rangle = 2\langle T \rangle - \langle x \frac{dV}{dx} \rangle$$

Where T is the kinetic energy. In a stationary state, the left side is zero, so

$$2\langle T \rangle = \langle x \frac{dV}{dx} \rangle$$

Problem 3.31

Equation 3.71 $\Rightarrow \frac{d}{dt} \langle xp \rangle = \frac{i}{\hbar} \langle [H, xp] \rangle$; Eq. 3.64 $\Rightarrow [H, xp] = [H, x]p + x[H, p]$; Problem 3.14 $\Rightarrow [H, x] = -\frac{i\hbar p}{m}$; Problem 3.17(d) $\Rightarrow [H, p] = i\hbar \frac{dV}{dx}$. So

$$\frac{d}{dt} \langle xp \rangle = \frac{i}{\hbar} \left[-\frac{i\hbar}{m} \langle p^2 \rangle + i\hbar \langle x \frac{dV}{dx} \rangle \right] = 2\left(\frac{p^2}{2m}\right) - \langle x \frac{dV}{dx} \rangle = 2\langle T \rangle - \langle x \frac{dV}{dx} \rangle. \quad \text{QED}$$

In a stationary state all expectation values (at least, for operators that do not depend explicitly on t) are time-independent (see item 1 on p. 26), so $d\langle xp \rangle/dt = 0$, and we are left with Eq. 3.97.

For the harmonic oscillator:

$$V = \frac{1}{2}m\omega^2 x^2 \Rightarrow \frac{dV}{dx} = m\omega^2 x \Rightarrow x \frac{dV}{dx} = m\omega^2 x^2 = 2V \Rightarrow 2\langle T \rangle = 2\langle V \rangle \Rightarrow \langle T \rangle = \langle V \rangle. \quad \text{QED}$$

In Problem 2.11(c) we found that $\langle T \rangle = \langle V \rangle = \frac{1}{4}\hbar\omega$ (for $n = 0$); $\langle T \rangle = \langle V \rangle = \frac{3}{4}\hbar\omega$ (for $n = 1$). ✓
In Problem 2.12 we found that $\langle T \rangle = \frac{1}{2}(n+\frac{1}{2})\hbar\omega$, while $\langle x^2 \rangle = (n+\frac{1}{2})\hbar/m\omega$, so $\langle V \rangle = \frac{1}{2}m\omega^2 \langle x^2 \rangle = \frac{1}{2}(n+\frac{1}{2})\hbar\omega$, and hence $\langle T \rangle = \langle V \rangle$ for all stationary states. ✓

Problem 3.33

Problem 3.37 The Hamiltonian for a certain three-level system is represented by the matrix

$$\mathbf{H} = \begin{pmatrix} a & 0 & b \\ 0 & c & 0 \\ b & 0 & a \end{pmatrix},$$

where a , b , and c are real numbers (assume $a - c \neq \pm b$).

(a) If the system starts out in the state

$$|\mathcal{S}(0)\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix},$$

what is $|\mathcal{S}(t)\rangle$?

(b) If the system starts out in the state

$$|\mathcal{S}(0)\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$

what is $|\mathcal{S}(t)\rangle$?

Conclusion: The (normalized) eigenvectors of \mathbf{H} are

$$|s_1\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |s_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}, \quad |s_3\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}.$$

(a) Here $|\mathcal{S}(0)\rangle = |s_1\rangle$, so

$$|\mathcal{S}(t)\rangle = e^{-iE_1 t/\hbar} |s_1\rangle = \boxed{e^{-iet/\hbar} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}}.$$

(b)

$$\begin{aligned} |\mathcal{S}(0)\rangle &= \frac{1}{\sqrt{2}} (|s_2\rangle + |s_3\rangle). \\ |\mathcal{S}(t)\rangle &= \frac{1}{\sqrt{2}} \left(e^{-iE_2 t/\hbar} |s_2\rangle + e^{-iE_3 t/\hbar} |s_3\rangle \right) = \frac{1}{\sqrt{2}} \left[e^{-i(a+b)t/\hbar} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} + e^{-i(a-b)t/\hbar} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \right] \\ &= \frac{1}{2} e^{-iat/\hbar} \begin{pmatrix} e^{-ibt/\hbar} + e^{ibt/\hbar} \\ 0 \\ e^{-ibt/\hbar} - e^{ibt/\hbar} \end{pmatrix} = \boxed{e^{-iat/\hbar} \begin{pmatrix} \cos(bt/\hbar) \\ 0 \\ -i \sin(bt/\hbar) \end{pmatrix}}. \end{aligned}$$

Problem 3.38

Conclusion: The (normalized) eigenvectors of \mathbf{H} are

$$|s_1\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |s_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}, \quad |s_3\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}.$$

(a) Here $|\mathcal{S}(0)\rangle = |s_1\rangle$, so

$$|\mathcal{S}(t)\rangle = e^{-iE_1 t/\hbar} |s_1\rangle = \boxed{e^{-iet/\hbar} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}}.$$

(b)

$$\begin{aligned} |\mathcal{S}(0)\rangle &= \frac{1}{\sqrt{2}} (|s_2\rangle + |s_3\rangle). \\ |\mathcal{S}(t)\rangle &= \frac{1}{\sqrt{2}} \left(e^{-iE_2 t/\hbar} |s_2\rangle + e^{-iE_3 t/\hbar} |s_3\rangle \right) = \frac{1}{\sqrt{2}} \left[e^{-i(a+b)t/\hbar} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} + e^{-i(a-b)t/\hbar} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \right] \\ &= \frac{1}{2} e^{-iat/\hbar} \begin{pmatrix} e^{-ibt/\hbar} + e^{ibt/\hbar} \\ 0 \\ e^{-ibt/\hbar} - e^{ibt/\hbar} \end{pmatrix} = \boxed{e^{-iat/\hbar} \begin{pmatrix} \cos(bt/\hbar) \\ 0 \\ -i \sin(bt/\hbar) \end{pmatrix}}. \end{aligned}$$

Problem 3.38 The Hamiltonian for a certain three-level system is represented by the matrix

$$\mathbf{H} = \hbar\omega \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}.$$

Two other observables, A and B , are represented by the matrices

$$\mathbf{A} = \lambda \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad \mathbf{B} = \mu \begin{pmatrix} 2 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

where ω , λ , and μ are positive real numbers.

(a) Find the eigenvalues and (normalized) eigenvectors of \mathbf{H} , \mathbf{A} , and \mathbf{B} .

(b) Suppose the system starts out in the generic state

$$|\delta(0)\rangle = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix},$$

with $|c_1|^2 + |c_2|^2 + |c_3|^2 = 1$. Find the expectation values (at $t = 0$) of H , A , and B .

(c) What is $|\delta(t)\rangle$? If you measured the energy of this state (at time t), what values might you get, and what is the probability of each? Answer the same questions for A and for B .

(a) \mathbb{H} :

$$E_1 = \hbar\omega, E_2 = E_3 = 2\hbar\omega; |h_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, |h_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, |h_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

A:

$$\begin{vmatrix} -a & \lambda & 0 \\ \lambda & -a & 0 \\ 0 & 0 & (2\lambda - a) \end{vmatrix} = a^2(2\lambda - a) - (2\lambda - a)\lambda^2 = 0 \Rightarrow [a_1 = 2\lambda, a_2 = \lambda, a_3 = -\lambda.]$$

$$\lambda \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = a \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \Rightarrow \begin{cases} \lambda\beta = a\alpha \\ \lambda\alpha = a\beta \\ 2\lambda\gamma = a\gamma \end{cases}$$

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(1)

$$\begin{aligned} \lambda\beta = 2\lambda\alpha &\Rightarrow \beta = 2\alpha, \\ \lambda\alpha = 2\lambda\beta &\Rightarrow \alpha = 2\beta, \\ 2\lambda\gamma = 2\lambda\gamma; & \end{aligned} \quad \left. \begin{array}{l} \alpha = \beta = 0; \\ |a_1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \end{array} \right\}$$

(2)

$$\begin{aligned} \lambda\beta = \lambda\alpha &\Rightarrow \beta = \alpha, \\ \lambda\alpha = \lambda\beta &\Rightarrow \alpha = \beta, \\ 2\lambda\gamma = \lambda\gamma; &\Rightarrow \gamma = 0. \end{aligned} \quad \left. \begin{array}{l} |a_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}. \end{array} \right\}$$

(3)

$$\left. \begin{array}{l} \lambda\beta = -\lambda\alpha \Rightarrow \beta = -\alpha, \\ \lambda\alpha = -\lambda\beta \Rightarrow \alpha = -\beta, \\ 2\lambda\gamma = -\lambda\gamma; \Rightarrow \gamma = 0. \end{array} \right\} \quad \boxed{|a_3\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}.}$$

B:

$$\begin{vmatrix} (2\mu - b) & 0 & 0 \\ 0 & -b & \mu \\ 0 & \mu & -b \end{vmatrix} = b^2(2\mu - b) - (2\mu - b)\mu^2 = 0 \Rightarrow \boxed{b_1 = 2\mu, b_2 = \mu, b_3 = -\mu.}$$

$$\mu \begin{pmatrix} 2 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = b \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} \Rightarrow \begin{cases} 2\mu\alpha = b\alpha \\ \mu\gamma = b\beta \\ \mu\beta = b\gamma \end{cases}$$

(1)

$$\left. \begin{array}{l} 2\mu\alpha = 2\mu\alpha, \\ \mu\gamma = 2\mu\beta \Rightarrow \gamma = 2\beta, \\ \mu\beta = 2\mu\gamma \Rightarrow \beta = 2\gamma; \end{array} \right\} \quad \beta = \gamma = 0; \quad \boxed{|b_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.}$$

(2)

$$\left. \begin{array}{l} 2\mu\alpha = \mu\alpha \Rightarrow \alpha = 0, \\ \mu\gamma = \mu\beta \Rightarrow \gamma = \beta, \\ \mu\beta = \mu\gamma; \Rightarrow \beta = \gamma. \end{array} \right\} \quad \boxed{|b_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}.}$$

(3)

$$\left. \begin{array}{l} 2\mu\alpha = -\mu\alpha \Rightarrow \alpha = 0, \\ \mu\gamma = -\mu\beta \Rightarrow \gamma = -\beta, \\ \mu\beta = -\mu\gamma; \Rightarrow \beta = -\gamma. \end{array} \right\} \quad \boxed{|b_3\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}.}$$

(b)

$$\begin{aligned}\langle H \rangle &= \langle S(0) | H | S(0) \rangle - \hbar\omega (c_1^* c_2^* c_3^*) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \boxed{\hbar\omega (|c_1|^2 + 2|c_2|^2 + 2|c_3|^2)} . \\ \langle A \rangle &= \langle S(0) | A | S(0) \rangle = \lambda (c_1^* c_2^* c_3^*) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \boxed{\lambda (c_1^* c_2 + c_2^* c_1 + 2|c_3|^2)} . \\ \langle B \rangle &= \langle S(0) | B | S(0) \rangle = \mu (c_1^* c_2^* c_3^*) \begin{pmatrix} 2 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \boxed{\mu (2|c_1|^2 + c_2^* c_3 + c_3^* c_2)} .\end{aligned}$$

(c)

$$\begin{aligned}\langle S(0) \rangle &= c_1 |h_1\rangle + c_2 |h_2\rangle + c_3 |h_3\rangle \Rightarrow \\ \langle S(t) \rangle &= c_1 e^{-iE_1 t/\hbar} |h_1\rangle + c_2 e^{-iE_2 t/\hbar} |h_2\rangle + c_3 e^{-iE_3 t/\hbar} |h_3\rangle = c_1 e^{-i\omega t} |h_1\rangle + c_2 e^{-2i\omega t} |h_2\rangle + c_3 e^{-2i\omega t} |h_3\rangle \\ &= e^{-2i\omega t} \left[c_1 e^{i\omega t} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + c_2 \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + c_3 \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \right] = \boxed{e^{-2i\omega t} \begin{pmatrix} c_1 e^{i\omega t} \\ c_2 \\ c_3 \end{pmatrix}} .\end{aligned}$$

H: $h_1 = \hbar\omega$, probability $|c_1|^2$; $h_2 = h_3 = 2\hbar\omega$, probability $(|c_2|^2 + |c_3|^2)$.

$$A: \boxed{a_1 = 2\lambda}, \quad \langle a_1 | S(t) \rangle = e^{-2i\omega t} (0 \ 0 \ 1) \begin{pmatrix} c_1 e^{i\omega t} \\ c_2 \\ c_3 \end{pmatrix} = e^{-2i\omega t} c_3 \Rightarrow \boxed{\text{probability } |c_3|^2} .$$

$$\boxed{a_2 = \lambda}, \quad \langle a_2 | S(t) \rangle = e^{-2i\omega t} \frac{1}{\sqrt{2}} (1 \ 1 \ 0) \begin{pmatrix} c_1 e^{i\omega t} \\ c_2 \\ c_3 \end{pmatrix} = \frac{1}{\sqrt{2}} e^{-2i\omega t} (c_1 e^{i\omega t} + c_2) \Rightarrow$$

$$\text{probability} = \frac{1}{2} (c_1^* e^{-i\omega t} + c_2^*) (c_1 e^{i\omega t} + c_2) = \boxed{\frac{1}{2} (|c_1|^2 + |c_2|^2 + c_1^* c_2 e^{-i\omega t} + c_2^* c_1 e^{i\omega t})} .$$

$$\boxed{a_3 = -\lambda}, \quad \langle a_3 | S(t) \rangle = e^{-2i\omega t} \frac{1}{\sqrt{2}} (1 \ -1 \ 0) \begin{pmatrix} c_1 e^{i\omega t} \\ c_2 \\ c_3 \end{pmatrix} = \frac{1}{\sqrt{2}} e^{-2i\omega t} (c_1 e^{i\omega t} - c_2) \Rightarrow$$

$$\text{probability} = \frac{1}{2} (c_1^* e^{-i\omega t} - c_2^*) (c_1 e^{i\omega t} - c_2) = \boxed{\frac{1}{2} (|c_1|^2 + |c_2|^2 - c_1^* c_2 e^{-i\omega t} - c_2^* c_1 e^{i\omega t})} .$$

Note that the sum of the probabilities is 1.

$$B: \boxed{b_1 = 2\mu}, \quad \langle b_1 | S(t) \rangle = e^{-2i\omega t} (1 \ 0 \ 0) \begin{pmatrix} c_1 e^{i\omega t} \\ c_2 \\ c_3 \end{pmatrix} = e^{-2i\omega t} c_1 \Rightarrow \boxed{\text{probability } |c_1|^2} .$$

$$\boxed{b_2 = \mu}, \quad \langle b_2 | S(t) \rangle = e^{-2i\omega t} \frac{1}{\sqrt{2}} (0 \ 1 \ 1) \begin{pmatrix} c_1 e^{i\omega t} \\ c_2 \\ c_3 \end{pmatrix} = \frac{1}{\sqrt{2}} e^{-2i\omega t} (c_2 + c_3) \Rightarrow$$

$$\text{probability} = \frac{1}{2} (c_1^* + c_2^*) (c_1 + c_2) = \boxed{\frac{1}{2} (|c_1|^2 + |c_2|^2 + c_1^* c_2 + c_2^* c_1)} .$$

$$\boxed{b_3 = -\mu}, \quad \langle b_3 | S(t) \rangle = e^{-2i\omega t} \frac{1}{\sqrt{2}} (0 \ 1 \ -1) \begin{pmatrix} c_1 e^{i\omega t} \\ c_2 \\ c_3 \end{pmatrix} = \frac{1}{\sqrt{2}} e^{-2i\omega t} (c_2 - c_3) \Rightarrow$$

$$\text{probability} = \frac{1}{2} (c_2^* - c_3^*) (c_2 - c_3) = \boxed{\frac{1}{2} (|c_2|^2 + |c_3|^2 - c_2^* c_3 - c_3^* c_2)} .$$

Again, the sum of the probabilities is 1.

Quantum Mechanics in Three Dimensions

The moment operators in 3D are given by:

$$p_x = \frac{\hbar}{i} \partial_x \quad , \quad p_y = \frac{\hbar}{i} \partial_y \quad , \quad p_z = \frac{\hbar}{i} \partial_z$$

Then, the general momentum operator is:

$$\vec{p} = \frac{\hbar}{i} \nabla$$

Thus, Schrodinger's equation is:

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

The probability of finding the particle in the infinitesimal volume $d^3\vec{r} = dx dy dz$ is $|\Psi(\vec{r}, t)|^2 d^3\vec{r}$, and the normalization condition is:

$$\int |\Psi|^2 d^3\vec{r} = 1$$

If we use separation of variables, we find that the time independent equation is:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

And the temporal solution is as always:

$$f(t) = e^{-iE_n t/\hbar}$$

Then, the complete solution is:

$$\Psi_n(\vec{r}, t) = \psi_n(\vec{r}) e^{-iE_n t/\hbar}$$

And the most general solution is:

$$\Psi(\vec{r}, t) = \sum c_n \psi_n(\vec{r}) e^{-iE_n t/\hbar}$$

The solutions to the independent equation are the energy definite states. When we sum them as $\sum c_n \psi_n(\vec{r}) e^{-iE_n t/\hbar}$ we get the general solution. To which we might apply initial or boundary conditions.

Problema

a) Work out all of the canonical commutation relations $[x, y], [x, p_y], \text{etc}$

- $[r_i, r_j] = r_i r_j - r_j r_i = 0$
- $[p_i, p_j] = -\hbar i \partial_i (-\hbar i \partial_j) - -\hbar i \partial_j (-\hbar i \partial_i) = 0$
- $[r_i, p_j] = i \hbar \delta_{ij}$

Ehrenfest's theorem:

$$\frac{d}{dt} \langle \vec{r} \rangle = \frac{1}{m} \langle \vec{p} \rangle \quad , \quad \frac{d}{dt} \langle \vec{p} \rangle = \langle -\nabla V \rangle$$

Heisenberg's principle:

$$\sigma_j \sigma_{p_i} \geq \hbar/2$$

Para $i = j$. Para $\sigma_j \sigma_{p_i}$ con $i \neq j$, no hay restricción.

Schrodinger Equation in Spherical Coordinates

Separation of Variables

We begin with Schrodinger's time independent equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi$$

We adopt spherical coordinates, in which the Laplacian takes the form:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right)$$

So we plug this in the Schrodinger equation.

We begin by proposing a separation of variables:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

The resulting equations with separation of variables turn out to be:

$$\begin{aligned} \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} &= -m^2 \\ \frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta &= m^2 \\ \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E]R &= l(l+1)R \end{aligned}$$

Where we must have $m \in \mathbb{Z}$ for the first equation to be univalued.

And $l = 0, 1, 2, \dots$ for the second equation (Lagrange equation) to be finite at the ends $\theta = -\pi/2, \pi/2$.

Also, $|m| < l$ for Legendre's associated equation to make sense too:

$$l = 0, 1, 2, \dots, m \in \mathbb{Z}, |m| < l$$

▪ **Azimuthal:**

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \Phi(\phi) = e^{im\phi}$$

Actually there are two solutions $\pm m$ but we cover them all by letting m be negative too.

▪ **Polar Angle**

The equation is:

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + [l(l+1) \sin^2 \theta - m^2] \Theta = 0$$

The equation is not so simple, but Legendre can solve it, its solution is:

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

Where P_l^m is the **associated Legendre function**, defined by:

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

Where $P_l(x)$ is the **lth Legendre pynomial**, defined by the **Rodrigues Formula**:

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

And:

$$l = 0, 1, 2, \dots, m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l$$

The other solutions to the Legendre equation exist but they blow up at the edges.

So in general we have the **Spherical Armonics**:

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta)$$

Where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$.

This solutions are already orthonormalized (they are naturally orthogonal and the first term is a normalization):

$$\int_0^{2\pi} \int_0^\pi [Y_l^m(\theta, \phi)]^* [Y_{l'}^{m'}(\theta, \phi)] \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'}$$

■ Radial Equation

The equation is:

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] R = l(l+1)R$$

This equation is usually simplified by replacing $u(r) = rR(r)$ so that the equation is now:

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

It is identical to the one dimensional schrodinger but with **effective potential** $V_{eff} = V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$

The extra term $\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$ is the **centrifugal term**.

Problem

Example 4.1: Consider the infinite spherical well

$$V(r) = \begin{cases} 0 & , \quad r \leq a \\ \infty & , \quad r > a \end{cases}$$

Find the solutions ant energies.

Solution: Outside the wave equation is 0. Inside the well, the wave equation is:

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

Where $k := \frac{\sqrt{2mE}}{\hbar}$. And we have the boundary condition $u(a) = 0$.

The case $l = 0$ is easy:

$$\frac{d^2u}{dr^2} = -k^2u \quad \Rightarrow \quad u(r) = A \sin(kr) + B \cos(kr)$$

But the actual solution is $R(r) = u(r)/r$, so $[\cos(kr)]/r$ blows up and we are left with $\sin(kr)/r$. And the initial condition implies $\sin(ka) = 0$ son $ka = n\pi$. That is:

$$u_{l=0}(r) = \frac{\sin(\frac{n\pi}{a}r)}{r}$$

And the allowed energies are then (knowing $ka = n\pi$):

$$E_{n,l=0} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

We can normalize it with a $A = \sqrt{2/a}$ factor. If we tack on the angular part $Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$, we conclude that:

$$\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}$$

Notice that the stationary states are labeled by n,l,m while the energy depends only on n,l.

For arbitrary l , the equation $\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2 \right] u$ is a type of Bessel equation with solution:

$$u(r) = A r j_l(kr) + B r n_l(kr)$$

Where $j_l(x)$ is the **spherical Bessel function** given by $j_l(x) := (-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\sin x}{x}$ and

n_l is the **spherical Neumann function** of order l given by $n_l(x) = -(-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\cos x}{x}$.

But the Neumann functions blow up at the origin so the solution must be:

$$R(r) = A j_l(kr)$$

There remains the boundary condition $R(a) = 0$, that is $j_l(ka) = 0$. Which means that ka is a zero of j_l . This leaves us with a discrete selection of k s but that can not be written in a general form. In any case:

$$k = \frac{1}{a} \beta_{nl}$$

Where β_{nl} is the nth zero of the lth spherical Bessel function. The allowed energies are then:

$$E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2$$

And the complete wavefunctions are:

$$\psi_{nlm}(r, \theta, \phi) = A_{nl} j_l(\beta_{nl} r/a) Y_l^m(\theta, \phi)$$

Where A_{nl} is a normalization constant.

Hydrogen Atom

The hydrogen atom consists of an electron with charge $-e$ around a nucleus of charge e , so the potential energy is:

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

So the radial equation becomes:

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2m r^2} \right] u = Eu$$

Where as always $R(r) = u(r)/r$.

The radial wave function

First, we define $k := \frac{\sqrt{-2mE}}{\hbar}$. So the equation becomes:

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

So we introduce the change of variables:

$$\rho := kr \quad , \quad \rho_0 := \frac{me^2}{2\pi\epsilon_0\hbar^2 k}$$

So that:

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

The asymptotic form of the equation as $\rho \rightarrow \infty$ is $\frac{d^2u}{d\rho^2} = u$, whose solution is $u(\rho) = Ae^{-\rho}$ (the other part e^ρ blows up).

On the other hand, as $\rho \rightarrow 0$, the equation is approx. $\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u$. The general solution is $u(\rho) = C\rho^{l+1} + D\rho^l$ but the last part blows up, so $u(\rho) = C\rho^{l+1}$ for small ρ .

So we propose the solution to have the form $u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$ and get a differential equation for v .

We solve this equation by series proposing $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$. And the solution is:

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

Where:

$$c_{j+1} = \left(\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right) c_j$$

We need this series to terminate somewhere, so we propose:

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

We define $n := j_{max} + l + 1$ the **principal quantum number**. We have then that:

$$\rho_0 = 2n$$

And ρ determines k and k determines E , so:

$$E = -\frac{\hbar^2 k^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}$$

And the allowed energies are:

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2} \quad , \quad n = 1, 2, 3, \dots$$

This is the famous **Bohr formula**. Combining this equations, we have:

$$k = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2} \right) \frac{1}{n} = \frac{1}{an}$$

Where:

$$a := \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0,529 \times 10^{-10} m$$

The **Bohr radius**. It follows that:

$$\rho = \frac{r}{an}$$

Blah-Blah.

General solution: After all, the general solution is:

$$\sqrt{\left(\frac{2}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na} \right)^l [L_{n-l-1}^{2l+1}(2r/na)] Y_l^m(\theta, \phi)$$

Where:

- $L_q(x) := e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q)$

-
- $L_{q-p}^p := (-1)^p \left(\frac{d}{dx} \right)^p L_q(x)$
 - $Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta)$
 - $a := \frac{4\pi\epsilon_0\hbar^2}{me^2}$

The functions are orthonormal:

$$\int \psi_{nlm}^* \psi_{n'l'm'} r^2 \sin \theta dr d\theta d\phi = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

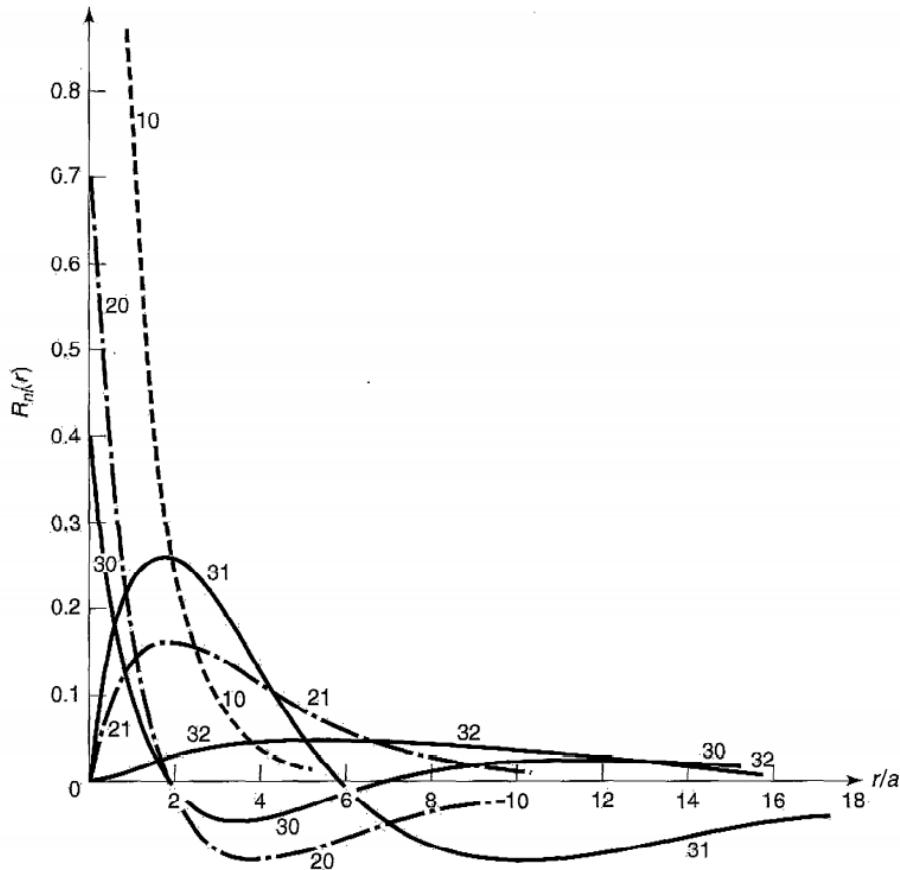


FIGURE 4.4: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

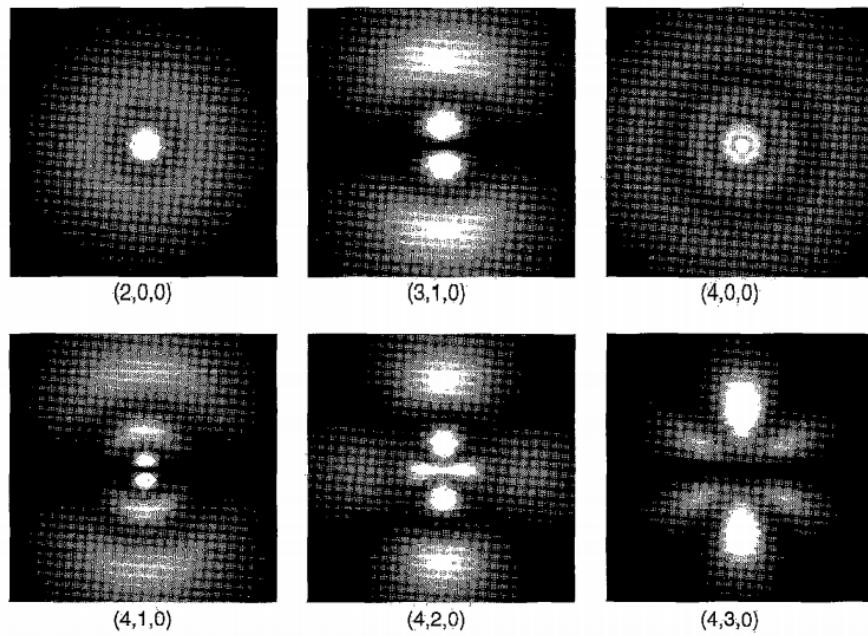


FIGURE 4.5: Density plots for the hydrogen wave functions (n, l, m) . Imagine each plot to be rotated about the (vertical) z axis. Printed by permission using “Atom in a Box,” v1.0.8, by Dauger Research. You can make your own plots by going to the Web site <http://dauger.com>.

6. Resolver la ecuación de Schrodinger estacionaria en coordenadas esféricas

:

$$-\frac{\hbar^2}{2M} \nabla^2 \Psi(r, \theta, \phi) + V(r) \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

para el caso particular del potencial $V(r) = -e^2/r$ (átomo de hidrógeno), donde e es la carga del electrón. Expresar las autofunciones en términos de armónicos esféricos y polinomios ortogonales de Laguerre. Visualizar las órbitas de la función de ondas del átomo de hidrógeno (más información en el problema 7.22 del Capítulo 13 del Boas)

Primero, reescribimos la ecuación desarrollando el Laplaciano en coordenadas esféricas:

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

(Usé M para la masa en la ecuación para poder usar m más adelante como una de las constantes de separación, como es la convención usual).

Luego, proponemos una solución separable como $\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$.

Sustituimos esto en la ecuación (y multiplicamos toda la ecuación por $-\frac{2M}{\hbar^2}$):

$$\begin{aligned} \frac{1}{r^2} Y(\theta, \phi) \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) + \frac{1}{r^2 \sin \theta} R(r) \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y(\theta, \phi) \\ + \frac{1}{r^2 \sin^2 \theta} R(r) \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) - \frac{2M}{\hbar^2} [V(r) - E] R(r) Y(\theta, \phi) = 0 \end{aligned}$$

Ahora dividimos entre $R(r)Y(\theta, \phi)$ y multiplicamos por r^2 para obtener:

$$\begin{aligned} \frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) + \frac{1}{\sin \theta} \frac{1}{Y(\theta, \phi)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y(\theta, \phi) \\ + \frac{1}{\sin^2 \theta} \frac{1}{Y(\theta, \phi)} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) - \frac{2M}{\hbar^2} [V(r) - E] r^2 = 0 \\ \Rightarrow \frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) - \frac{2Mr^2}{\hbar^2} [V(r) - E] \\ = -\frac{1}{\sin \theta} \frac{1}{Y(\theta, \phi)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{1}{Y(\theta, \phi)} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) \end{aligned}$$

En la última ecuación, el lado izquierdo es función de únicamente r y el derecho de θ, ϕ . Para que se cumpla la igualdad, ambos lados deben de ser constantes.

Por tanto, agregamos una constante de separación k .

Obtenemos así, la **ecuación radial**:

$$\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) - \frac{2Mr^2}{\hbar^2} [V(r) - E] = k$$

Y la **ecuación angular**:

$$\frac{1}{Y(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{Y(\theta, \phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) = -k$$

Ahora separamos la ecuación angular en la parte polar y la azimutal.

Para ello, proponemos que la solución $Y(\theta, \phi)$ se ve como $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$.

Sustituimos esto en la ecuación angular:

$$\begin{aligned} & \frac{1}{\Theta(\theta)\Phi(\phi) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)\Phi(\phi)}{\partial \theta} \right) + \frac{1}{\Theta(\theta)\Phi(\phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \Theta(\theta)\Phi(\phi) = -k \\ & \Rightarrow \frac{1}{\Theta(\theta) \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \frac{1}{\Phi(\phi) \sin^2 \theta} \frac{d^2}{d\phi^2} \Phi(\phi) = -k \\ & \Rightarrow \frac{1}{\Theta(\theta) \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + k = -\frac{1}{\Phi(\phi) \sin^2 \theta} \frac{d^2}{d\phi^2} \Phi(\phi) \\ & \Rightarrow \frac{\sin \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + k \sin^2 \theta = -\frac{1}{\Phi(\phi)} \frac{d^2}{d\phi^2} \Phi(\phi) \end{aligned}$$

El lado izquierdo es función de solamente θ , mientras que el lado derecho es función de solamente ϕ . Para que ambos lados sean iguales, deben de ser igual a una constante. Elegimos como constante de separación a m^2 .

Por tanto, nos queda la **ecuación polar**:

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

Y tenemos la **ecuación azimutal**:

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

Resolver las ecuaciones:

■ **Ecuación Azimutal:**

La ecuación azimutal es la más fácil de resolver. Tenemos que:

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

Que es la ecuación de oscilador armónico y tiene por solución:

$$\Phi(\phi) = \begin{cases} \cos m\phi \\ \sin m\phi \end{cases}$$

Sin embargo, $\Phi(\phi)$ tiene que ser de periodo 2π (porque la variable angular ϕ indica el mismo punto que $\phi + 2\pi$ y por tanto, la función $\Phi(\phi)$ debe de valer lo mismo en ϕ que en $\phi + 2\pi$).

Para que $\cos m\phi, \sin m\phi$ tenga este periodo, m debe de ser un entero.

■ **Ecuación Polar:**

Tenemos la ecuación:

$$\begin{aligned} & \frac{\sin \theta}{\Theta(\theta)} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + k \sin^2 \theta = m^2 \\ & \Rightarrow \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + k \sin^2 \theta \Theta(\theta) - m^2 \Theta(\theta) = 0 \\ & \Rightarrow \sin^2 \theta \frac{d^2}{d\theta^2} \Theta(\theta) + \sin \theta \cos \theta \frac{d}{d\theta} \Theta(\theta) + k \sin^2 \theta \Theta(\theta) - m^2 \Theta(\theta) = 0 \end{aligned}$$

Y como vimos en clase, conviene hacer el cambio de variable $x = \cos \theta$ (entonces x varía en $[-1, 1]$ conforme θ varía en $[0, \pi]$). Primero vemos cómo se transforman las derivadas:

$$\frac{d\Theta(\theta)}{d\theta} = \frac{d\Theta(x)}{dx} \frac{dx}{d\theta} = (-\sin \theta) \frac{d\Theta(x)}{dx}$$

$$\begin{aligned} \frac{d^2\Theta(\theta)}{d\theta^2} &= \frac{d}{d\theta} \left(\frac{d}{d\theta} \Theta(\theta) \right) = \frac{d}{d\theta} \left(-\sin \theta \frac{d\Theta(x)}{dx} \right) = -\cos \theta \frac{d\Theta(x)}{dx} - \sin \theta \frac{d}{d\theta} \frac{d\Theta(x)}{dx} \\ &= -\cos \theta \frac{d\Theta(x)}{dx} - \sin \theta \frac{d}{dx} \frac{dx}{d\theta} \frac{d\Theta(x)}{dx} = -\cos \theta \frac{d\Theta(x)}{dx} - \sin \theta \frac{d}{dx} (-\sin \theta) \frac{d\Theta(x)}{dx} \\ &= -\cos \theta \frac{d\Theta(x)}{dx} + \sin^2 \theta \frac{d^2\Theta(x)}{dx^2} \end{aligned}$$

Ahora ya sustituimos esto en la ecuación polar para hacer el cambio de variables:

$$\sin^2 \theta \left(-\cos \theta \frac{d\Theta(x)}{dx} + \sin^2 \theta \frac{d^2\Theta(x)}{dx^2} \right) + \sin \theta \cos \theta \left((-\sin \theta) \frac{d\Theta(x)}{dx} \right) + k \sin^2 \theta \Theta(x) - m^2 \Theta(x) = 0$$

Dividimos por $\sin^2 \theta$

$$\begin{aligned} & \Rightarrow -\cos \theta \frac{d\Theta(x)}{dx} + \sin^2 \theta \frac{d^2\Theta(x)}{dx^2} - \cos \theta \frac{d\Theta(x)}{dx} + k\Theta(x) - m^2 \frac{\Theta(x)}{\sin^2(\theta)} = 0 \\ & \Rightarrow -2 \cos \theta \frac{d\Theta(x)}{dx} + \sin^2 \theta \frac{d^2\Theta(x)}{dx^2} + k\Theta(x) - m^2 \frac{\Theta(x)}{\sin^2(\theta)} = 0 \end{aligned}$$

Ahora terminamos de sustituir $x = \cos \theta$ y $\sin^2 \theta = 1 - \cos^2 \theta = 1 - x^2$ para terminar la sustitución:

$$\begin{aligned} & -2x \frac{d\Theta(x)}{dx} + (1 - x^2) \frac{d^2\Theta(x)}{dx^2} + k\Theta(x) - m^2 \frac{\Theta(x)}{1 - x^2} = 0 \\ & \Rightarrow (1 - x^2) \frac{d^2\Theta(x)}{dx^2} - 2x \frac{d\Theta(x)}{dx} + k\Theta(x) - \frac{m^2}{1 - x^2} \Theta(x) = 0 \end{aligned}$$

Esta es una ecuación que ya vimos en clase, es la ecuación asociada de Legendre. Vimos en clase que esta ecuación era finita en $x = \pm 1$ sólo si k era el producto de dos enteros consecutivos.

Es decir, si $k = l(l+1)$ con l un entero (y en realidad, basta con fijarnos en l un entero

≥ 0 porque las soluciones para $l < 0$ se pueden escribir en términos de las soluciones a la ecuación asociada de Legendre para $l \geq 0$ y no nos dan información nueva).

Entonces, la solución es la función asociada de Legendre $\Theta(x) = P_l^m(x)$.

Además, ya habíamos encontrado en la ecuación anterior que m es un entero pero para que la ecuación de Legendre sea válida, hemos visto en clase que debemos de tener también que $|m| \leq l$. Con el cambio de variable $x = \cos \theta$, nos queda:

$$\Rightarrow \boxed{\Theta(\theta) = P_l^m(\cos \theta)}$$

Y obtuvimos las condiciones que $k = l(l + 1)$ con $l \geq 0$ un entero y m un entero con $0 \leq |m| \leq l$

■ Ecuación Radial:

La ecuación radial a la que habíamos llegado es (poniendo $k = l(l + 1)$):

$$\begin{aligned} \frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) - \frac{2Mr^2}{\hbar^2} [V(r) - E] &= l(l + 1) \\ \Rightarrow \frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) - \frac{2Mr^2}{\hbar^2} \left[-\frac{e^2}{r} - E \right] &= l(l + 1) \\ \Rightarrow \frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{2Me^2r}{\hbar^2} + \frac{2Mr^2}{\hbar^2} E &= l(l + 1) \\ \Rightarrow \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \left[\frac{2Me^2r}{\hbar^2} + \frac{2Mr^2}{\hbar^2} E - l(l + 1) \right] R(r) &= 0 \end{aligned}$$

Hacemos un cambio de variable propuesto por el problema 22 del capítulo 13 del Boas. El cambio de variable $y(r) = rR(r) \Rightarrow R(r) = \frac{y(r)}{r}$. Con esta sustitución, la derivada se transforma como:

$$\begin{aligned} \frac{d}{dr} \left(r^2 \frac{d}{dr} R(r) \right) &= \frac{d}{dr} \left(r^2 \frac{d}{dr} \frac{y(r)}{r} \right) \\ &= \frac{d}{dr} \left(r^2 (-r^{-2}y(r) + r^{-1}y'(r)) \right) \\ &= \frac{d}{dr} (-y(r) + ry'(r)) \\ &= -y'(r) + y'(r) + ry''(r) \\ &= ry''(r) \end{aligned}$$

Al sustituir en la ecuación a la que habíamos llegado, tenemos:

$$\begin{aligned} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \left[\frac{2Me^2r}{\hbar^2} + \frac{2Mr^2}{\hbar^2} E - l(l + 1) \right] R(r) &= 0 \\ \Rightarrow r \frac{d^2y(r)}{dr^2} + \left[\frac{2Me^2r}{\hbar^2} + \frac{2Mr^2}{\hbar^2} E - l(l + 1) \right] \frac{y(r)}{r} &= 0 \end{aligned}$$

Luego definimos $\alpha^2 = -\hbar^2/(2ME)$ (que es positivo porque la energía E es negativa en el estado ligado del átomo).

Por lo que nos queda:

$$r \frac{d^2y(r)}{dr^2} + \left[\frac{2Me^2r}{\hbar^2} - \frac{1}{\alpha^2} r^2 - l(l+1) \right] \frac{y(r)}{r} = 0$$

Y hacemos el cambio de variable $x = 2r/\alpha$, $r = \alpha x/2$. Para hacer el cambio, vemos cómo se transforman las derivadas:

$$\begin{aligned} \frac{dy}{dr} &= \frac{dy}{dx} \frac{dx}{dr} = \frac{dy}{dx}(2/\alpha) = \frac{2}{\alpha} \frac{dy}{dx} \\ \frac{d^2y}{dr^2} &= \frac{d}{dr} \left(\frac{dy}{dr} \right) = \frac{d}{dr} \left(\frac{2}{\alpha} \frac{dy}{dx} \right) = \frac{2}{\alpha} \frac{d}{dr} \frac{dy}{dx} = \frac{2}{\alpha} \frac{2}{\alpha} \frac{d}{dx} \frac{dy}{dx} = \frac{4}{\alpha^2} \frac{d^2y}{dx^2} \end{aligned}$$

Por tanto, la ecuación diferencial queda como:

$$\begin{aligned} r \frac{d^2y(r)}{dr^2} + \left[\frac{2Me^2r}{\hbar^2} - \frac{1}{\alpha^2} r^2 - l(l+1) \right] \frac{y(r)}{r} &= 0 \\ \Rightarrow \frac{\alpha x}{2} \left(\frac{4}{\alpha^2} \frac{d^2y}{dx^2} \right) + \left[\frac{2Me^2 \alpha x}{\hbar^2} \frac{x}{2} - \frac{1}{\alpha^2} \frac{\alpha^2 x^2}{4} - l(l+1) \right] \frac{y(x)}{(\alpha x)/2} &= 0 \\ \Rightarrow \frac{2x}{\alpha} \frac{d^2y}{dx^2} + \left[\frac{Me^2 \alpha x}{\hbar^2} - \frac{x^2}{4} - l(l+1) \right] \frac{2y(x)}{\alpha x} &= 0 \\ \Rightarrow \frac{d^2y}{dx^2} + \left[\frac{Me^2 \alpha x}{\hbar^2} - \frac{x^2}{4} - l(l+1) \right] \frac{y(x)}{x^2} &= 0 \\ \Rightarrow \frac{d^2y}{dx^2} + \left[-\frac{1}{4} + \frac{Me^2 \alpha}{\hbar^2 x} - \frac{l(l+1)}{x^2} \right] y(x) &= 0 \end{aligned}$$

Ahora definimos $\lambda = Me^2 \alpha / \hbar^2$. Con lo que la ecuación queda como:

$$\boxed{\frac{d^2y}{dx^2} + \left[-\frac{1}{4} + \frac{\lambda}{x} - \frac{l(l+1)}{x^2} \right] y = 0}$$

Para resolver esta ecuación diferencial, proponemos una solución de la forma $y = x^{l+1} e^{-x/2} v(x)$, con $v(x)$ una función desconocida.

Sustituimos esta posible solución en la ecuación diferencial para ver qué debe de cumplir $v(x)$

$$\begin{aligned} (x^{l+1} e^{-x/2} v)'' + \left[-\frac{1}{4} + \frac{\lambda}{x} - \frac{l(l+1)}{x^2} \right] x^{l+1} e^{-x/2} v &= 0 \\ \Rightarrow \left((l+1)e^{-x/2} x^l v - \frac{1}{2} e^{-x/2} x^{l+1} v + e^{-x/2} x^{l+1} v' \right)' - \frac{1}{4} x^{l+1} e^{-x/2} v + \lambda x^l e^{-x/2} v - l(l+1)x^{l-1} e^{-x/2} v &= 0 \\ \Rightarrow l(l+1)e^{-x/2} x^{l-1} v - (l+1)x^l e^{-x/2} v + \frac{1}{4} x^{l+1} e^{-x/2} v + 2(l+1)x^l e^{-x/2} v' - x^{l+1} e^{-x/2} v' + x^{l+1} e^{-x/2} v'' \\ - \frac{1}{4} x^{l+1} e^{-x/2} v + \lambda x^l e^{-x/2} v - l(l+1)x^{l-1} e^{-x/2} v &= 0 \end{aligned}$$

Dividimos por $x^l e^{-x/2}$

$$l(l+1)x^{-1}v - (l+1)v + \frac{1}{4}xv + 2(l+1)v' - xv' + xv'' - \frac{1}{4}xv + \lambda v - l(l+1)x^{-1}v = 0$$

$$\Rightarrow \boxed{xv'' + (2l+2-x)v' + (\lambda - l - 1)v = 0}$$

$v(x)$ debe de cumplir con esta ecuación.

Esta ecuación se parece mucho a la ecuación de Laguerre asociada. La **ecuación de Laguerre asociada** es $xy'' + (p+1-x)y' + sy = 0$ donde s y p son números naturales. Y tiene como solución al polinomio de Laguerre asociado L_s^p . Definido a partir de los polinomios de Laguerre como $L_s^p(x) = (-1)^p \frac{d^p}{dx^p} L_{s+p}(x)$

Por lo que la ecuación que tenemos para v es igual a la de Laguerre asociada pero con $p = 2l+1$ y $\lambda - l - 1 = s$.

Como $s = \lambda - l - 1$ tiene que ser un natural para la ecuación de Laguerre y ya vimos que l es un natural, eso obliga a λ a ser un número natural, por lo que denotaremos $n := \lambda$. Con lo que nos aseguramos que s sea un entero, pero para que sea un natural, debemos de tener también que $s = n - l - 1 \geq 0$, es decir $n > l$.

Y entonces, se tendrá la solución para v como:

$$v(x) = L_{n-l-1}^{2l+1}(x)$$

Y por tanto, la solución $y(x)$ es:

$$y(x) = x^{l+1} e^{-x/2} L_{n-l-1}^{2l+1}(x)$$

Ahora deshacemos las sustituciones para poder regresar a $R(r)$. Empezamos cambiando la x por r usando $x = \frac{2r}{\alpha}$.

Con lo que nos queda $y(r) = \left(\frac{2r}{\alpha}\right)^{l+1} e^{-r/\alpha} L_{n-l-1}^{2l+1}\left(\frac{2r}{\alpha}\right)$

Y por último, usamos que $R(r) = y(r)/r$ y omitimos las constantes que están multiplicando y seguiremos teniendo una solución:

$$\boxed{R(r) = r^l e^{-r/\alpha} L_{n-l-1}^{2l+1}\left(\frac{2r}{\alpha}\right)}$$

Donde $\alpha^2 = -\hbar^2/2ME$ y $n = Me^2\alpha/\hbar^2$ (con n obligado a ser un entero)

Ya que tenemos las soluciones $\Theta(\theta)$, $\Phi(\phi)$, $R(r)$, las podemos juntar para obtener una solución a la ecuación original:

$$\begin{aligned} \Psi(r, \theta, \phi) &= R(r)\Theta(\theta)\Phi(\phi) \\ &= r^l e^{-r/\alpha} L_{n-l-1}^{2l+1}\left(\frac{2r}{\alpha}\right) P_l^m(\cos \theta) \begin{cases} \cos m\phi \\ \sin m\phi \end{cases} \end{aligned}$$

Donde $P_l^m(\cos \theta) \begin{cases} \cos m\phi \\ \sin m\phi \end{cases}$ son los armónicos esféricos.

Y donde m, l, n son números enteros.

Con $l \geq 0$, $0 \leq |m| \leq l$, $l < n$
y con $n = Me^2\alpha/\hbar^2 \cdot \alpha^2 = -\hbar^2/(2ME)$.

Despejando la expresión de n , tenemos que $\alpha = \frac{\hbar^2}{me^2}n := an$, con $a = \frac{\hbar^2}{me^2}$.

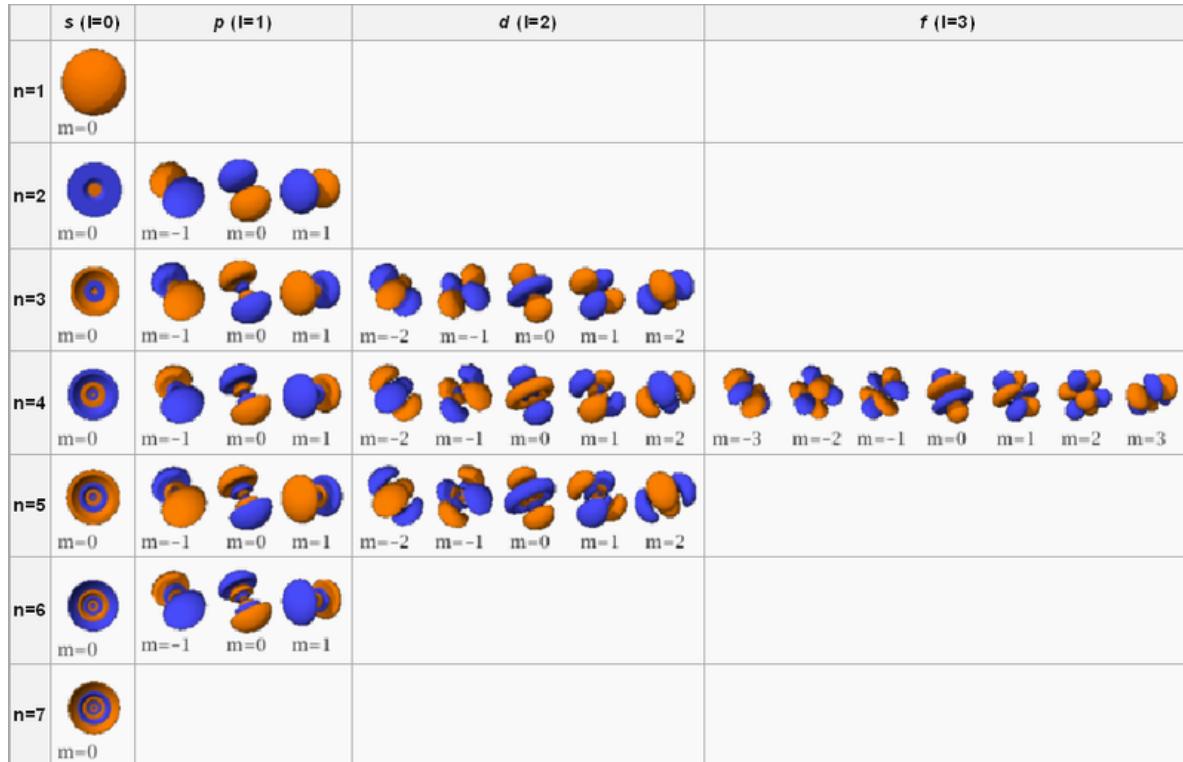
Con lo que podemos reescribir la solución haciendo más explícitos los lugares en los que aparece n :

$$\Psi(r, \theta, \phi) = r^l e^{-r/(an)} L_{n-l-1}^{2l+1} \left(\frac{2r}{an} \right) P_l^m(\cos \theta) \begin{cases} \cos m\phi \\ \sin m\phi \end{cases}$$

Nuevamente, con las condiciones que m, l, n son enteros con $l \geq 0$, $0 \leq |m| \leq l$, $l < n$

Además, por la definición de $\alpha^2 = \hbar^2/(2ME)$ y de que $\alpha = an$, podemos despejar E en función de n como $E = -\frac{Me^4}{2\hbar^2 n^2}$. Por lo que obtenemos que la energía del átomo está cuantizada por n .

En la siguiente imagen se visualizan algunos de los orbitales posibles.



A lo largo de los renglones se va cambiando el valor de n desde 1 hasta 7. Las columnas indican el valor de l , tomando en cuenta que $l < n$.

Y en cada celda se muestran las gráficas para distintos valores de m , tomando en cuenta que $0 \leq |m| \leq l$.

Las figuras muestran en 3d la probabilidad de encontrar el electrón en el espacio en cada uno de los casos. La diferencia de colores se usa para distinguir los lugares del espacio en el que la función de onde Ψ tiene fase positiva o negativa.

Problems

- **Problem 4.13: Find $\langle r \rangle$ and $\langle r^2 \rangle$ for an electron in the ground state of H.**

We have $\psi = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$, so:

- $\langle r^n \rangle = \frac{1}{\pi a^3} \int r^n e^{-2r/a} (r^2 \sin \theta dr d\theta d\phi) = \frac{4\pi}{\pi a^3} \int_0^\infty r^{n+2} e^{-2r/a} dr$
- $\langle r \rangle = \frac{4\pi}{\pi a^3} \int_0^\infty r^{n+2} e^{-2r/a} dr = \frac{3}{2}a$
- $\langle r^2 \rangle = \frac{4}{a^3} \int_0^\infty r^4 e^{-2r/a} dr = 3a^2$

- **Find $\langle x \rangle$**

$$\langle x \rangle = 0 \text{ for simmetry, } \langle x^2 \rangle = \frac{1}{3} \langle r^2 \rangle = a^2$$

- **Find $\langle x^2 \rangle$ in the state $n = 2, l = 1, m = 1$**

This state is not symmetric, so we need to integrate. First of all, $\psi_{211} = R_{21}Y_1^1 = -\frac{1}{\sqrt{\pi a}} \frac{1}{8a^2} r e^{-r/2a} \sin \theta e^{i\phi}$

- $\langle x^2 \rangle = \frac{1}{\pi a} \frac{1}{(8a^2)^2} \int (r^2 e^{-r/a} \sin^2 \theta) (r^2 \sin^2 \theta \cos^2 \phi) r^2 \sin \theta dr d\theta d\phi = \dots = 12a^2$

- **Find the most probable value of r for the ground state (not the expected value)**

$\psi = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$. First of all, $P = |\psi|^2 4\pi r^2 dr = \frac{4}{a^3} e^{-2r/a} r^2 dr = p(r)dr$.

So $p(r) = \frac{4}{a^3} r^2 e^{-2r/a}$.

So the most probable r is found as $\frac{dp}{dr} = 0 \Rightarrow \dots \Rightarrow r = a$

- **4.15 A hydrogen atom starts out in the following linear combination of the stationary states $n = 2, l = 1, m = 1$ and $n = 2, l = 1, m = -1$**

$$\Psi(\vec{r}, 0) = \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1})$$

a) Construct $\Psi(\vec{r}, t)$ and simplify it

$$\Psi(\vec{r}, t) = \frac{1}{\sqrt{2}} (\psi_{211} e^{-iE_2 t/\hbar} + \psi_{21-1} e^{-iE_2 t/\hbar}) = \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1}) e^{-iE_2 t/\hbar} , \quad E_2 = \frac{E_1}{4} = -\frac{\hbar^2}{8ma^2}$$

Where $\psi_{211} + \psi_{21-1} = -\frac{1}{\sqrt{\pi a}} \frac{1}{8a^2} rr^{-r/2a} \sin \theta (e^{i\phi} - e^{-i\phi}) = -\frac{i}{\sqrt{\pi a} 4a^2} r e^{-r/2a} \sin \theta \sin \phi$
So, in total:

$$\Psi(\vec{r}, t) = -\frac{i}{\sqrt{2\pi a} 4a^2} r e^{-r/2a} \sin \theta \sin \phi e^{-iE_2 t/\hbar}$$

b) Find $\langle V \rangle$:

$$\langle V \rangle = \int |\Psi|^2 \left(-\frac{e^2}{4\pi\epsilon t} \right) r^2 \sin \theta dr d\theta d\phi = \dots = -\frac{\hbar^2}{4ma^2} = \frac{1}{2} E_1 = -6.8 \text{ eV}$$

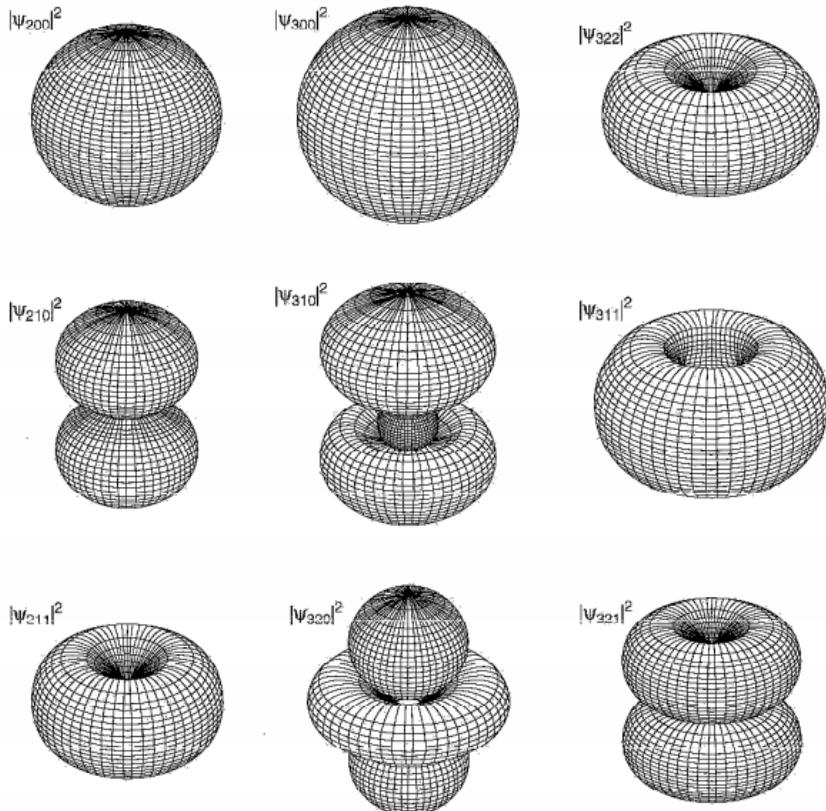


FIGURE 4.6: Surfaces of constant $|\psi|^2$ for the first few hydrogen wave functions.
Reprinted by permission from Siegmund Brandt and Hans Dieter Dahmen, *The Picture Book of Quantum Mechanics*, 3rd ed., Springer, New York (2001).

The Spectrum of Hydrogen

transition: When we put a hydrogen atom in a state Ψ_{nlm} and tickle it slightly, it can transition into another state.

Either by absorbing energy and moving to a higher energy level or by giving off energy and moving down.

Transitions are constantly happening and the energy needed or created is:

$$E_\gamma = E_i - E_f = -13,6\text{eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

Now, if this is the energy of a photon, the Planck formula says $E_\gamma = h\nu = h\frac{c}{\lambda}$.

So the wavelength of the photon is:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Where:

$$R := \frac{m}{4\pi c \hbar^3} \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 = 1,097 \times 10^7 \text{m}^{-1}$$

Is known as **Rydberg constant**

There are various series of spectrum, the **Lyman series** when $n_f = 1$, the **Balmer series** when $n_f = 2$ and etc.

Problems

- **4.16** if we have an ionized atom with one electron but Z protons, calculate the energy

The energies are:

$$E_n(Z) = Z^2 E_n$$

And the radius are:

$$a(Z) = a/Z$$

Angular Momentum

As we have seen, the stationary states of a hydrogen atom are labeled by n,l,m. We've seen that the number n determines the energy of the state.

It turns out that l, m are related to the orbital quantum momentum.

In classical theory, angular momentum is $\vec{L} = \vec{r} \times \vec{p}$, so:

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x$$

So the corresponding quantum operators are obtained as always by doing $p_x = -i\hbar\partial_x$, $p_y = -i\hbar\partial_y$, $p_z = -i\hbar\partial_z$.

Eigenvalues

The operators L_x, L_y do not commute, in fact:

$$\begin{aligned} [L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] = [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \\ &= yp_x[p_z, z] + xp_y[z, p_z] = i\hbar(xp_y - yp_x) = i\hbar L_z \end{aligned}$$

The middle elements in the penultimate expression disappear because they commute. So, in general:

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y$$

So L_x, L_y, L_z are incompatible observables, we cannot determine them both at the same time:

$$\begin{aligned} \sigma_{L_x}^2 \sigma_{L_y}^2 &\geq \left(\frac{1}{2i} \langle i\hbar L_z \rangle \right)^2 = \frac{\hbar^2}{4} \langle L_z \rangle^2 \\ \Rightarrow \quad \sigma_{L_x} \sigma_{L_y} &\geq \frac{\hbar}{2} |\langle L_z \rangle| \end{aligned}$$

Thus, it would be futile to look for states that are simultaneously eigenfunctions of L_x and L_y .

Now we consider the **square of the total angular momentum** which is:

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

This does commute with L_x :

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

In general:

$$[L^2, L_z] = [L^2, L_y] = [L^2, L_z] = 0$$

Or compactly:

$$[L^2, \vec{L}] = 0$$

So, we are allowed to now L^2 and a component of \vec{L} simultaneously.

Now we can hope to find simultaneous eigenstates of L^2 and (say) L_z :

$$L^2 f = \lambda f \quad , \quad L_z f = \mu f$$

We want f so that L^2 and L_z are determined simultaneously.

We now define an operator:

$$L_{\pm} := L_x \pm iL_y$$

The commutator with L_z is:

$$[L_z, L_{\pm}] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm i(-i\hbar L_x) = \pm\hbar(L_x \pm iL_y)$$

So:

$$[L_z, L_{\pm}] = \pm\hbar L_{\pm}$$

And of course:

$$[L^2, L_{\pm}] = 0$$

Theorem: If f is an eigenfunction of L^2 and L_z , so also is $L_{\pm}f$ with the same eigenvalue:

$$L^2(L_{\pm}f) = L_{\pm}(L^2f) = L_{\pm}(\lambda f) = \lambda(L_{\pm}f)$$

Theorem: If f is an eigenfunction of L_z with eigenvalue μ , then $L_{\pm}f$ is an eigenfunction of L_z with eigenvalue $\mu \pm \hbar$:

$$\begin{aligned} L_z(L_{\pm}f) &= (L_z L_{\pm} - L_{\pm} L_z)f + L_{\pm} L_z f = \pm\hbar L_{\pm} f + L_{\pm}(\mu f) \\ &= (\mu \pm \hbar)(L_{\pm}f) \end{aligned}$$

So L_+ is the **raising operator** because it increases the eigenvalue for L_z by \hbar and L_- is the **lowering operator** because it lowers the eigenvalue by \hbar .

For a given value of λ , we can obtain a ladder of states, with each rung separated by \hbar in the eigenvalue of L_z . To ascend, you simply apply the raising operator, and to descend you apply the lowering.

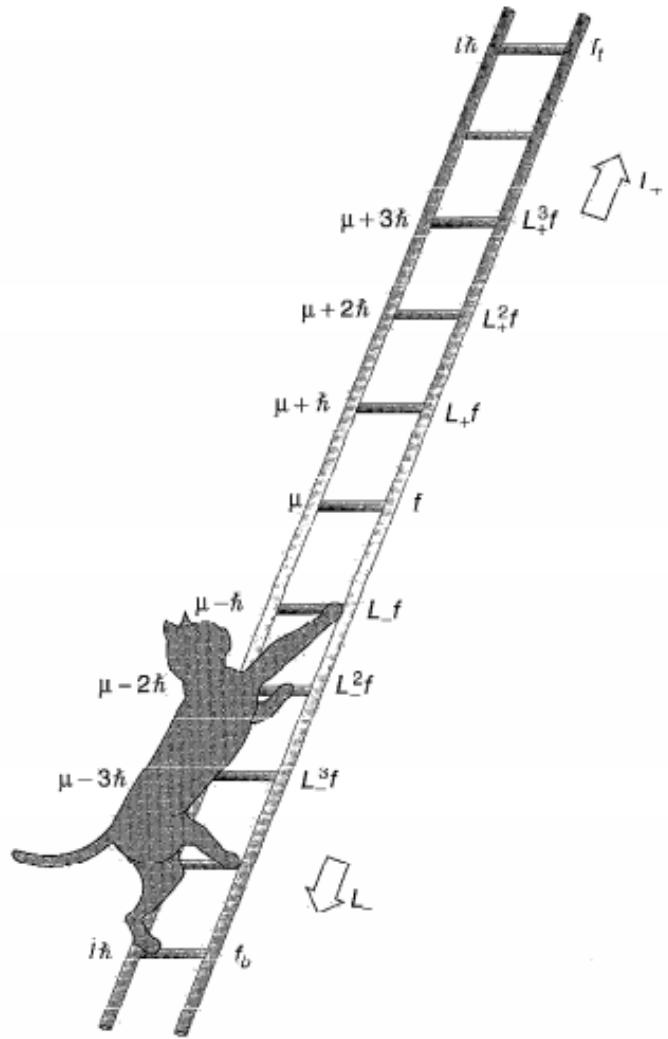


FIGURE 4.8: The “ladder” of angular momentum states.

This process cannot go forever, we can not reach an eigenfunction in which the eigenvalue of L_z exceeds the total angular momentum (the eigenvalue of L^2). So there must be a top rung, f_t , such that:

$$L_+ f = 0$$

Let $\hbar l$ be the eigenvalue of L_z at this top rung:

$$L_z f_t = \hbar l f_t , \quad L^2 f_t = \lambda f_t , \quad L_+ f_t = 0$$

Now, it can be proven by simple algebra that:

$$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$$

It follows that:

$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t = (0 + \hbar^2 l^2 + \hbar^2 l) f_t = \hbar^2 l(l+1) f_t$$

and hence:

$$\lambda = \hbar^2 l(l+1)$$

This tells us the eigenvalue of L^2 in terms of the **maximum** eigenvalue of L_z

Meanwhile, there is also (for the same reason) a bottom rung f_b such that $L_- f_b = 0$. Let $\hbar \bar{l}$ be the eigenvalue of L_z at the bottom rung, so:

$$L_z f_b = \hbar \bar{l} f_b , \quad L^2 f_b = \lambda f_b$$

Using the expression for L^2 , we find:

$$L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b = (0 + \hbar^2 \bar{l}^2 - \hbar^2 \bar{l}) f_b = \hbar^2 \bar{l}(\bar{l} - 1) f_b$$

And therefore:

$$\lambda = \hbar^2 \bar{l}(\bar{l} - 1)$$

This gives a comparison between the eigenvalue of L^2 and the lowest eigenvalue of L_z .

We can see that $l(l+1) = \bar{l}(\bar{l}-1)$ which implies that $\bar{l} = -l$

Evidently, the eigenvalues of L_z are $m\hbar$ where m goes from $-l$ to $+l$ in N integer steps. In particular, it follows that $l = -l + N$ and hence $l = N/2$. So l must be an integer or a half integer.

The eigenfunctions are characterized by l, m :

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m , \quad L_z f_l^m = \hbar m f_l^m$$

Where:

$$l = 0, 1/2, 1, 3/2, \dots ; \quad m = -l, -l+1, \dots, l-1, l$$

For a given l , there are $2l+1$ values of m .

We can represent this result for the different diagram:

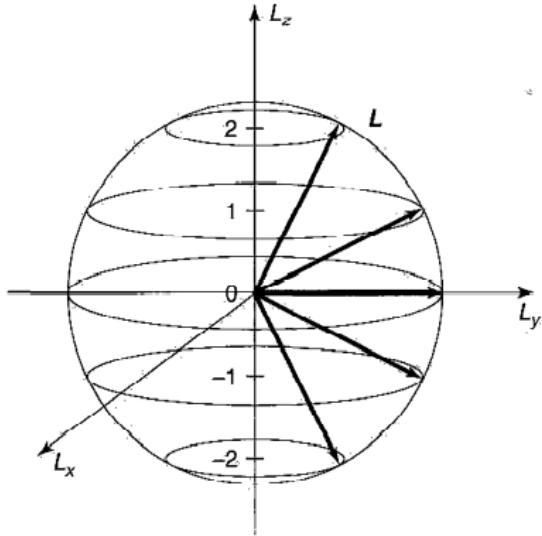


FIGURE 4.9: Angular momentum states (for $l = 2$).

The arrows represent the possible angular momenta. They have the length $\sqrt{l(l+1)}$ (for l a half integer) and their allowed z componentes are $m\hbar$ for $m = -l, -l+1, \dots, l-1, l$. In general, $\sqrt{l(l+1)} > l$ (except if $l = 0$) so you can't have the angular momentum pointing directly in the z direction. This is because you can not know the three componentes of L simultaneously. A particle just cannot have a determinate angular momentum vector, any more than it can simultaneously have a determinate position and momentum. If L_z is determined, then the other two are not.

Eigenfunctions

We already have the eigenvalues of L^2 and L_z (the possible values this things can take). Now let's see which are the eigenfunctions.

Now, we have that $\vec{L} = (\hbar/i)(\vec{r} \times \nabla)$. Where:

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \partial_{\theta} + \hat{\phi} \frac{1}{r \sin \theta} \partial_{\phi}$$

Meanwhile $\vec{r} = r\hat{r}$ so, with a little work, we get:

$$\vec{L} = \frac{\hbar}{i} \left(\hat{\phi} \frac{\partial}{\partial \theta} - \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right)$$

The unit vectors can be resolved in cartesian coordinates, so we can get:

$$L_x = \frac{\hbar}{i} (-\sin \phi \partial_{\theta} - \cos \phi \cot \theta \partial_{\phi})$$

$$L_y = \frac{\hbar}{i} (+\cos \phi \partial_{\theta} - \sin \phi \cos \theta \partial_{\phi})$$

$$L_z = \frac{\hbar}{i} \partial_{\phi}$$

So, defining L_{\pm} , we have:

$$\begin{aligned} L_{\pm} &= L_x \pm iL_y = \frac{\hbar}{i} [(-\sin \phi \pm i \cos \phi) \partial_{\theta} - (\cos \phi \pm i \sin \phi) \cos \theta \partial_{\phi}] \\ &= \pm \hbar e^{\pm i\phi} (\partial_{\theta} \pm i \cot \theta \partial_{\phi}) \end{aligned}$$

Also:

$$L_+ L_- = -\hbar^2 (\partial_{\theta}^2 + \cot \theta \partial_{\theta} + \cot^2 \theta \partial_{\phi}^2 + i \partial_{\phi})$$

Hence:

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

We can now determine the $f_l^m(\theta, \phi)$ eigenfunctions of L^2 with eigenvalue $\hbar^2 l(l+1)$:

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

But this is precisely the angular equation we had for the hydrogen atom.
And it is also an eigenfunction of L_z with eigenvalue $\hbar m$ as:

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

Which is equivalent to the azimuthal equation for Hydrogen.
The result, as before is $Y_l^m(\theta, \phi)$.

Conclusion: Spherical harmonics are eigenfunctions of L^2 and L_z .

When we solved the Schrodinger equation for Hydrogen, we were inadvertently solving the system for operators H, L^2, L_z :

$$H\psi = E\psi , \quad L^2\psi = \hbar^2 l(l+1)\psi , \quad L_z\psi = \hbar m\psi$$

So when we measure \vec{L} , we are sure to get that $L^2 = \hbar^2 l(l+1)$ for some l and $L_z = \hbar m$ for some m with $|m| < l$.

But what if we just happen to aim my z-axis along the direction of \vec{L} ?

No! It is not merely that we do not know the components of \vec{L} , there simply aren't three components, a particle just cannot have a determinate angular momentum vector, because we can not simultaneously know all the components of the vector.

***Problem 4.18** The raising and lowering operators change the value of m by one unit:

$$L_{\pm} f_l^m = (A_l^m) f_l^{m \pm 1}, \quad [4.120]$$

where A_l^m is some constant. *Question:* What is A_l^m , if the eigenfunctions are to be *normalized*? *Hint:* First show that L_{\mp} is the hermitian conjugate of L_{\pm} (since L_x and L_y are *observables*, you may assume they are hermitian ... but *prove* it if you like); then use Equation 4.112. *Answer:*

$$A_l^m = \hbar \sqrt{l(l+1) - m(m \pm 1)} = \hbar \sqrt{(l \mp m)(l \pm m + 1)}. \quad [4.121]$$

Note what happens at the top and bottom of the ladder (i.e., when you apply L_+ to f_l^l or L_- to f_l^{-l}).

Problem 4.18

$$\langle f | L_{\pm} g \rangle = \langle f | L_x g \rangle \pm i \langle f | L_y g \rangle = \langle L_x f | g \rangle \pm i \langle L_y f | g \rangle = \langle (L_x \mp i L_y) f | g \rangle = \langle L_{\mp} f | g \rangle, \text{ so } (L_{\pm})^\dagger = L_{\mp}.$$

Now, using Eq. 4.112, in the form $L_{\mp} L_{\pm} = L^2 - L_z^2 \mp \hbar L_z$:

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

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Conclusion: $A_l^m = \hbar \sqrt{l(l+1) - m(m \pm 1)}$.

Spin

In classical mechanics, a rigid object admits two kinds of angular momentum, **orbital** $\vec{L} = \vec{r} \times \vec{p}$ and a momentum of **spin**.

An analogous thing happens in quantum mechanics. In addition to angular momentum, the electron also carries another form of angular momentum, which is **intrinsic** to the elementary particle itself.

The algebraic theory of spin is a copy to the theory of orbital angular momentum. The spin is a vector \vec{S} and the operators follow the following relations:

$$[S_x, S_y] = i\hbar S_z \quad , \quad [S_y, S_z] = i\hbar S_x \quad , \quad [S_z, S_x] = i\hbar S_y$$

It follows as before, that the simultaneous eigenvectors of S^2 and S_z satisfy:

$$S^2|sm\rangle = \hbar^2 s(s+1)|sm\rangle \quad , \quad S_z|sm\rangle = \hbar m|sm\rangle$$

And

$$S_{\pm}|sm\rangle = \hbar \sqrt{s(s+1) - m(m \pm 1)}|s(m \pm 1)\rangle$$

where: $S_{\pm} := S_x \pm iS_y$

Where $|sm\rangle$ means a particle in state with quantum numbers s, m .

Where the values of s, m are:

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \quad , \quad m = -s, -s+1, \dots, s-1, s$$

It so happens that every elementary particle has a specific and immutable value of s , which we call **the spin**.

Pi mesons have spin 0, electrons 1/2, photons 1, deltas 3/2, etc.

By contrast, the orbital angular momentum quantum number l can take any integer value and will change if the system is perturbed, buy s is fixed.

Spin 1/2

By far the most important case is $s = 1/2$, for this is the spin of ordinary matter.

There are two eigenstates, depending on the value of m , the states are **spin up** $|\frac{1}{2}, \frac{1}{2}\rangle$ and **spin down** $|\frac{1}{2}, -\frac{1}{2}\rangle$.

To represent a specific spin state, we use an ordered pair:

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

And a general **spinor** is of the form:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-$$

Spin Operator:

Now the spin operators become 2×2 matrices. The operator S^2 has as its eigenstates χ_+ and χ_- , both with eigenvalue $s(s+1)\hbar^2$:

$$S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+ \quad , \quad S^2\chi_- = \frac{3}{4}\hbar^2\chi_-$$

We propose S^2 to have the form $S^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix}$. After using the relations seen before, we get that the matrix representing the operator is:

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

Similarly for S_z , the eigenstates are the same and the eigenvalues are $m\hbar$ with $m = -1/2$ for χ_- and $m = 1/2$ for χ_+ . We have the relations:

$$S_z\chi_+ = \frac{\hbar}{2}\chi_+ \quad , \quad S_z\chi_- = -\frac{\hbar}{2}\chi_-$$

It follows that:

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

Similarly, by the definition of S_{\pm} , we have:

$$S_+\chi_- = \hbar\chi_+ \quad , \quad S_-\chi_+ = \hbar\chi_- \quad , \quad S_+\chi_+ = S_-\chi_- = 0$$

So:

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad , \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Now $S_{\pm} = S_x \pm iS_y$, so $S_x = \frac{1}{2}(S_+ + S_-)$ and $S_y = \frac{1}{2i}(S_+ - S_-)$. Hence:

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad , \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Since these matrices carry a factor $\hbar/2$, it is tidier to define **Pauli spin matrices** without this factor:

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

We see they are all hermitian (as they should be to represent observables). On the other hand, S_+, S_- are not hermitian, they are not observable.

The eigenspinors of S_z are: $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ with e.val $\hbar/2$ and $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ with e.val $-\hbar/2$

If you measure S_z on a particle in the general state $\chi = \begin{pmatrix} a \\ b \end{pmatrix}$, then you could get $\hbar/2$ with probability $|a|^2$ or a $-\hbar/2$ with probability $|b|^2$. And $|a|^2 + |b|^2 = 1$

But what if instead you choose to measure S_x ?

We need to know the eigenspinors of $S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$.

We can find that the eigenvalues are $\pm \frac{\hbar}{2}$ (obviously it should be the same as S_z).

The eigenspinors of S_x are obtained as usually and we get the states:

$$\chi_+^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \quad \text{e.val} = \frac{\hbar}{2}, \quad \chi_-^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}, \quad \text{e.val} = -\frac{\hbar}{2}$$

Where we are still in the "base" of eigenvectors of S_z .

The generic spinor $\begin{pmatrix} a \\ b \end{pmatrix}$ in the z-base can be written on this base as:

$$\chi = \left(\frac{a+b}{\sqrt{2}} \right) \chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}} \right) \chi_-^{(x)}$$

If you measure S_x , the probability of getting $\hbar/2$ is $(1/2)|a+b|^2$ and the probability of getting $-\hbar/2$ is $(1/2)|a-b|^2$

Example: Suppose a sin $-1/2$ is in the state $\chi = \frac{1}{\sqrt{6}} \begin{pmatrix} 1+i \\ 2 \end{pmatrix}$, what are the prob. of getting $\hbar/2$ or $-\hbar/2$ if you measure S_z or S_x

Hera $a = \frac{1+i}{\sqrt{6}}$ and $b = \frac{2}{\sqrt{6}}$. For S_z the probability of getting $+\hbar/2$ is $|(1+i)/\sqrt{6}|^2 = 1/3$ and the probability of getting $-\hbar/2$ is $2/3$

For S_x , the probability of getting $\hbar/2$ is $(1/2)|(3+i)/\sqrt{6}|^2 = 5/6$ and the proba of $-\hbar/2$ is $1/6$.

The expected value of S_x is $\frac{5}{6} \left(\frac{\hbar}{2} \right) + \frac{1}{6} \left(-\frac{\hbar}{2} \right) = \frac{\hbar}{3}$.

Or we could obtain it directly by: $\langle S_x \rangle = \chi^T S_x \chi = \begin{pmatrix} 1-i & 2 \\ \sqrt{6} & \sqrt{6} \end{pmatrix} \begin{pmatrix} 0 & \hbar/2 \\ \hbar/2 & 0 \end{pmatrix} \begin{pmatrix} (1+i)/\sqrt{6} \\ 2/\sqrt{6} \end{pmatrix} = \frac{\hbar}{3}$

Let's say we begin with a particle in state χ_+ . The z-component of the spin S_z is unambiguously $\hbar/2$.

Now we want the S_x measure, there is a 50-50 chance of getting either $\hbar/2$ or $-\hbar/2$.

We know precisely the state of spin of the particle, but it simply does not have a particular x -component of spin.

Now we measure the x-component of spin and we get $\hbar/2$, so now it does have a particular value of S_x . The problem is that now the particle is in the state $\chi_+^{(x)}$ and we no longer know S_z and it could take any of the two values.

***Problem 4.27** An electron is in the spin state:

$$\chi = A \begin{pmatrix} 3i \\ 4 \end{pmatrix}.$$

- (a) Determine the normalization constant A .
- (b) Find the expectation values of S_x , S_y , and S_z .
- (c) Find the "uncertainties" σ_{S_x} , σ_{S_y} , and σ_{S_z} . (Note: These sigmas are standard deviations, not Pauli matrices!)
- (d) Confirm that your results are consistent with all three uncertainty principles (Equation 4.100 and its cyclic permutations—only with S in place of L , of course).

Problem 4.27

(a)

$$\chi^\dagger \chi = |A|^2(9 + 16) = 25|A|^2 = 1 \Rightarrow A = 1/5.$$

(b)

$$\langle S_x \rangle = \chi^\dagger \mathbf{S}_x \chi = \frac{1}{25} \frac{\hbar}{2} (-3i \ 4) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 3i \\ 4 \end{pmatrix} = \frac{\hbar}{50} (-3i \ 4) \begin{pmatrix} 4 \\ 3i \end{pmatrix} = \frac{\hbar}{50} (12i + 12i) = \boxed{0}$$

$$\langle S_y \rangle = \chi^\dagger \mathbf{S}_y \chi = \frac{1}{25} \frac{\hbar}{2} (-3i \ 4) \begin{pmatrix} 0 & -i \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 3i \\ 4 \end{pmatrix} = \frac{\hbar}{50} (-3i \ 4) \begin{pmatrix} -4i \\ -3 \end{pmatrix} = \frac{\hbar}{50} (-12 - 12) = \boxed{-\frac{12}{25}\hbar}$$

$$\langle S_z \rangle = \chi^\dagger \mathbf{S}_z \chi = \frac{1}{25} \frac{\hbar}{2} (-3i \ 4) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 3i \\ 4 \end{pmatrix} = \frac{\hbar}{50} (-3i \ 4) \begin{pmatrix} 3i \\ -4 \end{pmatrix} = \frac{\hbar}{50} (9 - 16) = \boxed{-\frac{7}{50}\hbar}$$

(c)

$$\langle S_x^2 \rangle = \langle S_y^2 \rangle = \langle S_z^2 \rangle = \frac{\hbar^2}{4} \text{ (always, for spin 1/2), so } \sigma_{S_x}^2 = \langle S_x^2 \rangle - \langle S_x \rangle^2 = \frac{\hbar^2}{4} - 0, \boxed{\sigma_{S_x} = \frac{\hbar}{2}}.$$

$$\sigma_{S_y}^2 = \langle S_y^2 \rangle - \langle S_y \rangle^2 = \frac{\hbar^2}{4} - \left(\frac{12}{25}\right)^2 \hbar^2 = \frac{\hbar^2}{2500} (625 - 576) = \frac{49}{2500} \hbar^2, \boxed{\sigma_{S_y} = \frac{7}{50}\hbar}$$

$$\sigma_{S_z}^2 = \langle S_z^2 \rangle - \langle S_z \rangle^2 = \frac{\hbar^2}{4} - \left(\frac{7}{50}\right)^2 \hbar^2 = \frac{\hbar^2}{2500} (625 - 49) = \frac{576}{2500} \hbar^2, \boxed{\sigma_{S_z} = \frac{12}{25}\hbar}$$

(d)

$$\sigma_{S_x} \sigma_{S_y} = \frac{\hbar}{2} \cdot \frac{7}{50}\hbar \stackrel{?}{\geq} \frac{\hbar}{2} |\langle S_z \rangle| = \frac{\hbar}{2} \cdot \frac{7}{50}\hbar \quad (\text{right at the uncertainty limit}). \checkmark$$

$$\sigma_{S_y} \sigma_{S_z} = \frac{7}{50}\hbar \cdot \frac{12}{25}\hbar \stackrel{?}{\geq} \frac{\hbar}{2} |\langle S_x \rangle| = 0 \quad (\text{trivial}). \checkmark$$

$$\sigma_{S_z} \sigma_{S_x} = \frac{12}{25}\hbar \cdot \frac{\hbar}{2} \stackrel{?}{\geq} \frac{\hbar}{2} |\langle S_y \rangle| = \frac{\hbar}{2} \cdot \frac{12}{25}\hbar \quad (\text{right at the uncertainty limit}). \checkmark$$

***Problem 4.28** For the most general normalized spinor χ (Equation 4.139), compute $\langle S_x \rangle$, $\langle S_y \rangle$, $\langle S_z \rangle$, $\langle S_x^2 \rangle$, $\langle S_y^2 \rangle$, and $\langle S_z^2 \rangle$. Check that $\langle S_x^2 \rangle + \langle S_y^2 \rangle + \langle S_z^2 \rangle = \langle S^2 \rangle$.

Problem 4.28

$$\langle S_x \rangle = \frac{\hbar}{2} (a^* b^*) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \frac{\hbar}{2} (a^* b^*) \begin{pmatrix} b \\ a \end{pmatrix} = \boxed{\frac{\hbar}{2}(a^*b + b^*a)} = \hbar \operatorname{Re}(ab^*).$$

$$\begin{aligned} \langle S_y \rangle &= \frac{\hbar}{2} (a^* b^*) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \frac{\hbar}{2} (a^* b^*) \begin{pmatrix} -ib \\ ia \end{pmatrix} \\ &= \frac{\hbar}{2} (-ia^*b + iab^*) = \boxed{\frac{\hbar}{2}i(ab^* - a^*b)} = -\hbar \operatorname{Im}(ab^*). \end{aligned}$$

$$\langle S_z \rangle = \frac{\hbar}{2} (a^* b^*) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \frac{\hbar}{2} (a^* b^*) \begin{pmatrix} a \\ -b \end{pmatrix} = \frac{\hbar}{2}(a^*a - b^*b) = \boxed{\frac{\hbar}{2}(|a|^2 - |b|^2)}.$$

$$S_x^2 = \frac{\hbar^2}{4} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{\hbar^2}{4}; \quad S_y^2 = \frac{\hbar^2}{4} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{\hbar^2}{4};$$

$$S_z^2 = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar^2}{4}; \quad \text{so } \boxed{\langle S_x^2 \rangle = \langle S_y^2 \rangle = \langle S_z^2 \rangle = \frac{\hbar^2}{4}}.$$

$$\langle S_x^2 \rangle + \langle S_y^2 \rangle + \langle S_z^2 \rangle = \frac{3}{4}\hbar^2 \stackrel{?}{=} s(s+1)\hbar^2 = \frac{1}{2}(\frac{1}{2}+1)\hbar^2 = \frac{3}{4}\hbar^2 = \langle S^2 \rangle. \checkmark$$

Problem 4.31 Construct the spin matrices (\mathbf{S}_x , \mathbf{S}_y , and \mathbf{S}_z) for a particle of spin 1. Hint: How many eigenstates of S_z are there? Determine the action of S_z , S_+ , and S_- on each of these states. Follow the procedure used in the text for spin 1/2.

Problem 4.31

There are three states: $\chi_+ = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$, $\chi_0 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$, $\chi_- = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$.

$$S_z \chi_+ = \hbar \chi_+, \quad S_z \chi_0 = 0, \quad S_z \chi_- = -\hbar \chi_-, \quad \Rightarrow \quad \boxed{S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}}. \quad \text{From Eq. 4.136:}$$

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CHAPTER 4. QUANTUM MECHANICS IN THREE DIMENSIONS

$$\left. \begin{array}{l} S_+ \chi_+ = 0, \quad S_+ \chi_0 = \hbar \sqrt{2} \chi_+, \quad S_+ \chi_- = \hbar \sqrt{2} \chi_0 \\ S_- \chi_+ = \hbar \sqrt{2} \chi_0, \quad S_- \chi_0 = \hbar \sqrt{2} \chi_-, \quad S_- \chi_- = 0 \end{array} \right\} \Rightarrow S_+ = \sqrt{2} \hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \quad S_- = \sqrt{2} \hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}.$$

$$S_x = \frac{1}{2}(S_+ + S_-) = \boxed{\frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}}, \quad S_y = \frac{1}{2i}(S_+ - S_-) = \boxed{\frac{i\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}}.$$

Electron in Magnetic Field

A spinning particle constitutes a magnetic dipole. Its **magnetic dipole moment** $\vec{\mu}$ is proportional to its spin angular momentum \vec{S} :

$$\vec{\mu} = \gamma \vec{S}$$

Where γ is called the **gyromagnetic ratio**.

When a magnetic dipole is placed in a magnetic field \vec{B} , it experiences a torque $\vec{\mu} \times \vec{B}$ which tends to line it up parallel to the field. The energy associated with this torque is:

$$\vec{H} = -\vec{\mu} \cdot \vec{B}$$

So the hamiltonian of a spinning charged particle at rest at a field \vec{B} is:

$$H = -\gamma \vec{B} \cdot \vec{S}$$

Larmor Precession

Imagine a particle of spin 1/2 at rest in a uniform magnetic field $\vec{B} = B_0 \hat{k}$. The hamiltonian is:

$$\mathbf{H} = -\gamma B_0 \mathbf{S}_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The eigenstates of H are the same than those of S_z :

$$\begin{aligned} \chi_+, &\quad \text{with energy } E_+ = -(\gamma B_0 \hbar)/2 \\ \chi_-, &\quad \text{with energy } E_- = (\gamma B_0 \hbar)/2 \end{aligned}$$

Since the hamiltonian is time independent, the general solution to the time dependent Schrödinger equation $i\hbar \frac{\partial \chi}{\partial t} = H\chi$

Can be written in terms of the stationary states:

$$\chi(t) = a\chi_+ e^{iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar} = \begin{pmatrix} ae^{i\gamma B_0 t/2} \\ be^{-i\gamma B_0 t/2} \end{pmatrix}$$

The constants a, b are obtained by the initial conditions:

$$\chi(0) = \begin{pmatrix} a \\ b \end{pmatrix}$$

Of course $|a|^2 + |b|^2 = 1$. In general I'll write $a = \cos(\alpha/2)$, $b = \sin(\alpha/2)$. Thus:

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2) e^{i\gamma B_0 t/2} \\ \sin(\alpha/2) e^{-i\gamma B_0 t/2} \end{pmatrix}$$

We can calculate the expectation value for S_x, S_y, S_z :

-
- $\langle S_x \rangle = \chi(t)^T S_x \chi(t) = (\cos(\alpha/2)e^{-i\gamma B_0 t/2} \quad \sin(\alpha/2)e^{i\gamma B_0 t/2}) \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix}$
 $= \frac{\hbar}{2} \sin \alpha \cos(\gamma B_0 t)$
 - $\langle S_y \rangle = \chi(t) S_y \chi(t) = -\frac{\hbar}{2} \sin \alpha \sin(\gamma B_0 t)$
 - $\langle S_z \rangle = \chi(t) S_z \chi(t) = -\frac{\hbar}{2} \cos \alpha$

Evidently $\langle \vec{S} \rangle$ is tilted at a constant angle α to the z axis, and processes about the field at the **larmor frequency**:

$$\omega = \gamma B_0$$

just as it would classically.

No surprise here, Ehrenfest's theorem guarantees that $\langle \vec{S} \rangle$ evolves according to the classical laws.

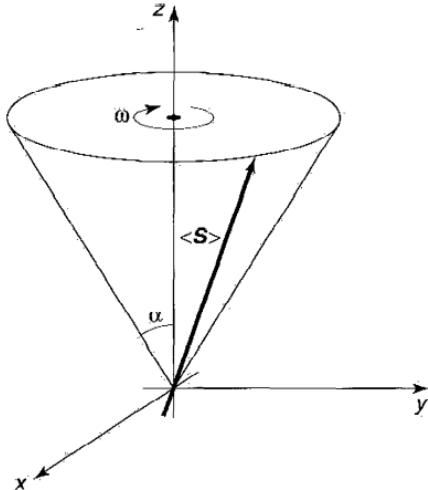


FIGURE 4.10: Precession of $\langle \vec{S} \rangle$ in a uniform magnetic field.

Stern Gerlach Experiment

In an inhomogeneous magnetic field, there is not only torque, but also a force, on a magnetic dipole:

$$\vec{F} = \nabla(\vec{\mu} \cdot \vec{B})$$

This force can be used to separate out particles with a particular spin orientation. Imagine a beam of relatively heavy neutral atoms, traveling in the y direction, which passes through an inhomogeneous field, say:

$$\vec{B}(x, y, z) = -\alpha x \hat{i} + (B_0 + \alpha z) \hat{k}$$

Where B_0 is a strong uniform field and α is a small deviation from homogeneity. The force on the atoms is then:

$$\vec{F} = \gamma\alpha(-S_x\hat{i} + S_z\hat{k})$$

But because the Larmor precession about B_0 , S_x oscillates rapidly, and averages to 0, the net force is in the z direction:

$$F_z = \gamma\alpha S_z$$

And the field is deflected up or down, in proportion to S_z . Classically, we would expect a smear, but in fact the beam splits into $2s + 1$ separate streams, demonstrating the quantization of spin. In the case $s = 1/2$, the beam splits in two.

Addition of Angular Momentum

Suppose now we have two spin 1/2 particles. For example, an electron and a proton. Then we have four possibilities for the spin:

$$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$$

Where the first is the electron and the second the proton. What is the total angular momentum of the atom?

$$\vec{S} = \vec{S}^{(1)} + \vec{S}^{(2)}$$

Each of these composite states is an eigenstate of S_z - the z components simply add:

$$\begin{aligned} S_z\chi_1\chi_2 &= (S_z^{(1)} + S_z^{(2)})\chi_1\chi_2 = (S_z^{(1)}\chi_1)\chi_2 + \chi_1(S_z^{(2)}\chi_2) \\ &= *(\hbar m_1\chi_1)\chi_2 + \chi_1(\hbar m_2\chi_2) = \hbar(m_1 + m_2)\chi_1\chi_2 \end{aligned}$$

Note that S^i only acts on χ_i . So m (the quantum number of the hole system is $m = m_1 + m_2$) and it can be 1,0,0,-1:

$$\begin{aligned} \uparrow\uparrow &: m = 1 \\ \uparrow\downarrow &: m = 0 \\ \downarrow\uparrow &: m = 0 \\ \downarrow\downarrow &: m = -1 \end{aligned}$$

m is supposed to advance in integer steps from $-s$ to s so it appears that $s = 1$. But there is an extra state with $m = 0$.

One way to untangle this problem is to apply the lowering operator $S_- = S_-^{(1)} + S_-^{(2)}$ to the state $\uparrow\uparrow$, using that $S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$, we have:

$$\begin{aligned} S_-(\uparrow\uparrow) &= (S_-^{(1)}\uparrow)\uparrow + \uparrow(S_-^{(2)}\uparrow) \\ &= (\hbar\downarrow)\uparrow + \uparrow(\hbar\downarrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow) \end{aligned}$$

Evidently, there are three states with $s = 1$

$$\left\{ \begin{array}{l} |11\rangle = \uparrow\uparrow \\ |10\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1-1\rangle = \downarrow\downarrow \end{array} \right\} \quad s = 1 \text{ (triplet).}$$

This is called the **triplet combination**. Meanwhile the orthogonal state with $m = 0$ carries $s = 0$:

$$\left\{ |00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \right\} \quad s = 0 \text{ (singlet).}$$

if you apply the raising or lowering operator to this state, you'll get zero.

We then claim that the combination of two spin-1/2 particles can carry a total spin of 1 or 0, depending on whether they occupy the triplet or the singlet.

To confirm this, we need to prove that the triplet states are eigenvectors of S^2 with eigenvalue $s(s+1)\hbar^2 = 2\hbar^2$, and the singlet is an eigenvector of S^2 with eigenvalue 0. Now:

$$S^2 = (\vec{S}^{(1)} + \vec{S}^{(2)}) \cdot (\vec{S}^{(1)} + \vec{S}^{(2)}) = (S^{(1)})^2 + (S^{(2)})^2 + 2\vec{S}^{(1)} \cdot \vec{S}^{(2)}$$

We have:

$$\begin{aligned}
\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} (\uparrow\downarrow) &= (S_x^{(1)} \uparrow)(S_x^{(2)} \downarrow) + (S_y^{(1)} \uparrow)(S_y^{(2)} \downarrow) + (S_z^{(1)} \uparrow)(S_z^{(2)} \downarrow) \\
&= \left(\frac{\hbar}{2} \downarrow\right) \left(\frac{\hbar}{2} \uparrow\right) + \left(\frac{i\hbar}{2} \downarrow\right) \left(\frac{-i\hbar}{2} \uparrow\right) + \left(\frac{\hbar}{2} \uparrow\right) \left(\frac{-\hbar}{2} \downarrow\right) \\
&= \frac{\hbar^2}{4} (2 \downarrow\uparrow - \uparrow\downarrow).
\end{aligned}$$

Similarly,

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} (\downarrow\uparrow) = \frac{\hbar^2}{4} (2 \uparrow\downarrow - \downarrow\uparrow).$$

It follows that

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} |10\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}} (2 \downarrow\uparrow - \uparrow\downarrow + 2 \uparrow\downarrow - \downarrow\uparrow) = \frac{\hbar^2}{4} |10\rangle, \quad [4.180]$$

and

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)} |00\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}} (2 \downarrow\uparrow - \uparrow\downarrow - 2 \uparrow\downarrow + \downarrow\uparrow) = -\frac{3\hbar^2}{4} |00\rangle. \quad [4.181]$$

Returning to Equation 4.179 (and using Equation 4.142), we conclude that

$$S^2 |10\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2 \frac{\hbar^2}{4} \right) |10\rangle = 2\hbar^2 |10\rangle, \quad [4.182]$$

so $|10\rangle$ is indeed an eigenstate of S^2 with eigenvalue $2\hbar^2$; and

$$S^2 |00\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} - 2 \frac{3\hbar^2}{4} \right) |00\rangle = 0, \quad [4.183]$$

so $|00\rangle$ is an eigenstate of S^2 with eigenvalue 0. (I will leave it for you to confirm that $|11\rangle$ and $|1-1\rangle$ are eigenstates of S^2 , with the appropriate eigenvalue—see Problem 4.34(c).)

What we have just done (combining spin $1/2$ and $1/2$ to get spin 1 or spin 0) is the simplest example of a larger problem: If you combine spin s_1 with spin s_2 , what total spins s do you get? You get every spin from $(s_1 + s_2)$ to $(s_1 - s_2)$ or $(s_2 - s_1)$ if $s_2 > s_1$ - in integer steps:

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \dots, |s_1 - s_2|$$

Roughly speaking, the highest total spin occurs when the individual spins are aligned parallel to one another.

For example, if a hydrogen atom is in state ψ_{nlm} the net angular momentum of the electron is $l+1/2$ or $l-1/2$. If you throw in the spin of the proton, the atom's **total** angular momentum quantum number is $l+1, l, l-1$.

The combined stat $|sm\rangle$ with total spin s and z -component m will be some linear combination of the composite states $|s_1 m_1\rangle |s_2 m_2\rangle$:

$$|sm\rangle = \sum_{m_1+m_2=m} C_{m_1 m_2 m}^{s_1 s_2 s} |s_1 m_1\rangle |s_2 m_2\rangle$$

Because the z components add, the only composite states that contribute are those for which $m_1 + m_2 = m$. The constants C are called the **Clebsch-Gordan coefficients**

TABLE 4.8: Clebsch-Gordan coefficients. (A square root sign is understood for every entry; the minus sign, if present, goes *outside* the radical.)

$1/2 \times 1/2$	$2 \times 1/2$	$3/2 \times 1/2$
$\begin{array}{ c c c } \hline & 1 & 0 \\ \hline +1/2 & 1 & 0 \\ \hline -1/2 & 1/2 & 1/2 \\ \hline -1/2 & 1/2 & -1/2 \\ \hline -1/2 & -1/2 & 1 \\ \hline \end{array}$	$\begin{array}{ c c c } \hline & 5/2 & 5/2 \\ \hline +2 & 1/2 & 1/2 \\ \hline +1 & 1/2 & 4/5 \\ \hline +1/2 & 1/2 & -1/5 \\ \hline +1/2 & 1/2 & 1/2 \\ \hline \end{array}$	$\begin{array}{ c c c } \hline & 5/2 & 3/2 \\ \hline +1 & -1/2 & 2/5 \\ \hline 0 & +1/2 & 3/5 \\ \hline -2 & 1/2 & -2/5 \\ \hline 0 & -1/2 & 5/2 \\ \hline -1 & +1/2 & 2/5 \\ \hline -1 & +1/2 & -3/5 \\ \hline -2 & -1/2 & 5/2 \\ \hline \end{array}$
$1 \times 1/2$	$3/2 \times 1/2$	$3/2 \times 1/2$
$\begin{array}{ c c c } \hline & 3/2 & 1/2 \\ \hline +1 & 1/2 & 1 \\ \hline -1/2 & 1/2 & -1/2 \\ \hline 1/2 & 1/2 & 1/2 \\ \hline -1/2 & 1/2 & -1/2 \\ \hline 1/2 & -1/2 & 1/2 \\ \hline 0 & +1/2 & 2/3 \\ \hline 2/3 & -1/2 & 1/3 \\ \hline -1/2 & 2/3 & -2/3 \\ \hline -1/2 & -1/2 & 3/2 \\ \hline \end{array}$	$\begin{array}{ c c c } \hline & 2 & 1 \\ \hline +3/2 & 1/2 & 1 \\ \hline +1 & +1 & +1 \\ \hline +1/2 & +1/2 & 3/4 \\ \hline +1/2 & -1/2 & 1/4 \\ \hline -3/2 & +1/2 & 3/4 \\ \hline -3/2 & -1/2 & 1/4 \\ \hline -1/2 & +1/2 & 1/2 \\ \hline -1/2 & -1/2 & 1/2 \\ \hline -1 & -1/2 & 1/2 \\ \hline -1 & +1/2 & 1/2 \\ \hline -2 & -1/2 & 1 \\ \hline \end{array}$	$\begin{array}{ c c c } \hline & 2 & 1 \\ \hline +3/2 & 1/2 & 1 \\ \hline +1 & +1 & +1 \\ \hline +1/2 & +1/2 & 3/4 \\ \hline +1/2 & -1/2 & 1/4 \\ \hline -3/2 & +1/2 & 3/4 \\ \hline -3/2 & -1/2 & 1/4 \\ \hline -1/2 & +1/2 & 1/2 \\ \hline -1/2 & -1/2 & 1/2 \\ \hline -1 & -1/2 & 1/2 \\ \hline -1 & +1/2 & 1/2 \\ \hline -2 & -1/2 & 1 \\ \hline \end{array}$
2×1	$3/2 \times 1$	$3/2 \times 1$
$\begin{array}{ c c c } \hline & 3 & 2 \\ \hline +2 & 0 & 2/3 \\ \hline +1 & 1/2 & -1/3 \\ \hline -1/2 & 1/3 & 1 \\ \hline 1/2 & -1/3 & 1 \\ \hline 1/2 & 1/3 & 1 \\ \hline -1/2 & -1/3 & 1 \\ \hline \end{array}$	$\begin{array}{ c c c } \hline & 5/2 & 3/2 \\ \hline +3/2 & 1 & 1 \\ \hline +1/2 & +1 & +3/2 \\ \hline +1/2 & 0 & 2/5 \\ \hline +1/2 & 3/5 & 1/2 \\ \hline -3/2 & +1/2 & 1/2 \\ \hline -3/2 & -1/2 & 1/2 \\ \hline -1/2 & +1/2 & 1/2 \\ \hline -1/2 & -1/2 & 1/2 \\ \hline -1 & -1/2 & 1/2 \\ \hline -1 & +1/2 & 1/2 \\ \hline -2 & -1/2 & 1 \\ \hline \end{array}$	$\begin{array}{ c c c } \hline & 2 & 1 \\ \hline +3/2 & -1 & 1/10 \\ \hline +1 & 0 & 8/15 \\ \hline 0 & +1 & 6/15 \\ \hline 0 & 0 & -1/2 \\ \hline 0 & -1/2 & 1/10 \\ \hline 1/2 & 0 & 1/3 \\ \hline 1/2 & 1/3 & 1/3 \\ \hline -1/2 & 1/3 & -1/3 \\ \hline -1/2 & -1/2 & 1/3 \\ \hline 1/2 & -1/2 & -1/3 \\ \hline 1/2 & 1/2 & 1/6 \\ \hline -1/2 & 1/2 & -1/6 \\ \hline -1/2 & -1/2 & -1/6 \\ \hline -1 & -1/2 & -1/6 \\ \hline -1 & 1/2 & 1/6 \\ \hline -2 & -1/2 & -1/6 \\ \hline -2 & 1/2 & 1/6 \\ \hline -3/2 & -1/2 & -1/6 \\ \hline -3/2 & 1/2 & 1/6 \\ \hline -1/2 & -1/2 & -1/2 \\ \hline -1/2 & 1/2 & -1/2 \\ \hline -1 & -1/2 & -1/2 \\ \hline -1 & 1/2 & -1/2 \\ \hline -2 & -1/2 & -1/2 \\ \hline -2 & 1/2 & -1/2 \\ \hline -3/2 & -1/2 & -1/2 \\ \hline -3/2 & 1/2 & -1/2 \\ \hline -1/2 & -1/2 & 1/2 \\ \hline -1/2 & 1/2 & 1/2 \\ \hline -1 & -1/2 & 1/2 \\ \hline -1 & 1/2 & 1/2 \\ \hline -2 & -1/2 & 1 \\ \hline \end{array}$
1×1	$3/2 \times 1$	$3/2 \times 1$
$\begin{array}{ c c c } \hline & 2 & 1 \\ \hline +1 & 1 & 1 \\ \hline -1 & 1 & 1 \\ \hline 0 & 0 & 1 \\ \hline 0 & 1 & -1 \\ \hline 0 & -1 & 1 \\ \hline \end{array}$	$\begin{array}{ c c c } \hline & 2 & 1 \\ \hline +1 & -1 & 1/2 \\ \hline 0 & 0 & 0 \\ \hline 0 & 0 & -2/5 \\ \hline 0 & -2/5 & 1/2 \\ \hline -1 & 1/2 & 3/10 \\ \hline -1 & -1 & -1 \\ \hline \end{array}$	$\begin{array}{ c c c } \hline & 2 & 1 \\ \hline +1/2 & -1 & 6/15 \\ \hline 0 & 0 & 1/2 \\ \hline 0 & 1/2 & 1/6 \\ \hline 0 & -1/2 & -3/10 \\ \hline -1 & 1/2 & -1/6 \\ \hline -1 & -1 & 3/5 \\ \hline -2 & -1 & -2 \\ \hline -2 & 1 & -2 \\ \hline -3/2 & -1 & -3 \\ \hline -3/2 & 1 & -3 \\ \hline -1/2 & -1 & -1 \\ \hline -1/2 & 1 & -1 \\ \hline -1 & -1 & -1 \\ \hline -1 & 1 & -1 \\ \hline -2 & -1 & -1 \\ \hline -2 & 1 & -1 \\ \hline -3/2 & -1 & -1 \\ \hline -3/2 & 1 & -1 \\ \hline -1/2 & -1 & 1/2 \\ \hline -1/2 & 1 & 1/2 \\ \hline -1 & -1 & 1/2 \\ \hline -1 & 1 & 1/2 \\ \hline -2 & -1 & 1 \\ \hline \end{array}$

For example, the shaded column of the 2×1 table tells us that:

$$|30\rangle = \frac{1}{\sqrt{5}}|21\rangle|1-1\rangle + \sqrt{\frac{3}{5}}|20\rangle|10\rangle + \frac{1}{\sqrt{5}}|2-1\rangle|11\rangle$$

This equations also work the other way around:

$$|s_1 m_1\rangle |s_2 m_2\rangle = \sum_s C_{m_1 m_2 m}^{s_1 s_2 s} |sm\rangle$$

for example, the shaded row in the $3/2 \times 1$ table tells us that:

$$\left| \frac{3}{2} \frac{1}{2} \right\rangle |10\rangle = \sqrt{\frac{3}{5}} \left| \frac{5}{2} \frac{1}{2} \right\rangle + \sqrt{\frac{1}{15}} \left| \frac{3}{2} \frac{1}{2} \right\rangle - \sqrt{\frac{1}{3}} \left| \frac{1}{2} \frac{1}{2} \right\rangle$$

Further Problems

Problem 4.42

The Momentum space wave function function in 3D is:

$$\phi(\vec{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int e^{-i(\vec{p}\cdot\vec{r})/\hbar} \phi(\vec{r}) d^3\vec{r}$$

- Find the momentum space wave function of the ground state of H

We have $\psi = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \Rightarrow \phi(\vec{p}) = \frac{1}{(2\pi\hbar)^{2/3}} \frac{1}{\sqrt{\pi a^3}} \int e^{-1\vec{p}\cdot\vec{r}/\hbar} e^{-r/a} r^2 \sin\theta dr d\theta d\phi$

We select the polar axis through \vec{p} , so: $\vec{p} \cdot \vec{r} = pr \cos\theta$. So we make the integral:

$$\begin{aligned} \phi(\vec{p}) &= \frac{2\pi}{(2\pi a\hbar)^{3/2}} \frac{1}{\sqrt{\pi}} \int_0^\infty r^2 e^{-r/a} \left(\int_0^\pi e^{-ipr \cos\theta/\hbar} \sin\theta d\theta \right) dr \\ &= \dots = \frac{1}{\pi} \left(\frac{2a}{\hbar} \right)^{3/2} \frac{1}{[1 + (ap/\hbar)^2]^2} \end{aligned}$$

- Check that $\phi(\vec{p})$ is normalized

it is

- Calculate $\langle p \rangle$

$$\langle p^2 \rangle = \int p^2 |\phi|^2 d^3\vec{p} = \frac{1}{\pi^2} \left(\frac{2a}{\hbar} \right)^3 4\pi \int_0^\infty \frac{p^4}{[1 + (ap/\hbar)^2]^4} dp = \frac{\hbar^2}{a^2}$$

- Calculate the value of $\langle T \rangle$

The value is: $\frac{1}{2m} \langle p^2 \rangle = \frac{1}{2m} \frac{\hbar^2}{a^2} = \frac{\hbar^2}{2m} \frac{m^2}{\hbar^4} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = -E_1$

This is consistent with the virial theorem $2\langle T \rangle = \langle V \rangle$

Problem 4.44

- Construct the wave function for hydrogen in the state $n = 4, l = 3, m = 3$
Express your answer as a function of the spherical coordinates r, θ , and ϕ .
- Find the expectation value of r in this state. (As always, look up any nontrivial integrals.)
- If you could somehow measure the observable $L_x^2 + L_y^2$ on an atom in this state, what value (or values) could you get, and what is the probability of each?

Problem 4.44

- (a) From Tables 4.3 and 4.7,

$$\psi_{433} = R_{43}Y_3^3 = \frac{1}{768\sqrt{35}} \frac{1}{a^{3/2}} \left(\frac{r}{a}\right)^3 e^{-r/4a} \left(-\sqrt{\frac{35}{64\pi}} \sin^3 \theta \cos \theta e^{3i\phi}\right) = \boxed{-\frac{1}{6144\sqrt{\pi}a^{9/2}} r^3 e^{-r/4a} \sin^3 \theta e^{3i\phi}}.$$

(b)

$$\begin{aligned} \langle r \rangle &= \int r |\psi|^2 d^3r = \frac{1}{(6144)^2 \pi a^9} \int r \left(r^6 e^{-r/2a} \sin^6 \theta\right) r^2 \sin \theta dr d\theta d\phi \\ &= \frac{1}{(6144)^2 \pi a^9} \int_0^\infty r^9 e^{-r/2a} dr \int_0^\pi \sin^7 \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{(6144)^2 \pi a^9} [9!(2a)^{10}] \left(\frac{2 \cdot 4 \cdot 6}{3 \cdot 5 \cdot 7}\right) (2\pi) = \boxed{18a}. \end{aligned}$$

- (c) Using Eq. 4.133: $L_x^2 + L_y^2 = L^2 - L_z^2 = 4(5)\hbar^2 - (3\hbar)^2 = 11\hbar^2$, with probability 1.

Problem 4.49 An electron is in the spin state

$$\chi = A \begin{pmatrix} 1 - 2i \\ 2 \end{pmatrix}.$$

- (a) Determine the constant A by normalizing χ .
- (b) If you measured S_z on this electron, what values could you get, and what is the probability of each? What is the expectation value of S_z ?
- (c) If you measured S_x on this electron, what values could you get, and what is the probability of each? What is the expectation value of S_x ?
- (d) If you measured S_y on this electron, what values could you get, and what is the probability of each? What is the expectation value of S_y ?
-

Problem 4.49

- (a) $1 = |A|^2(1 + 4 + 4) = 9|A|^2$; $\boxed{A = 1/3}$.

(b) $\boxed{\frac{\hbar}{2}, \text{ with probability } \frac{5}{9}; -\frac{\hbar}{2}, \text{ with probability } \frac{4}{9}}$. $\langle S_z \rangle = \frac{5}{9} \frac{\hbar}{2} + \frac{4}{9} \left(-\frac{\hbar}{2}\right) = \boxed{\frac{\hbar}{18}}$.

- (c) From Eq. 4.151,

$$\begin{aligned} c_+^{(x)} &= \left(\chi_+^{(x)}\right)^\dagger \chi = \frac{1}{3} \frac{1}{\sqrt{2}} (1 \ 1) \begin{pmatrix} 1 - 2i \\ 2 \end{pmatrix} = \frac{1}{3\sqrt{2}} (1 - 2i + 2) = \frac{3 - 2i}{3\sqrt{2}}; \quad |c_+^{(x)}|^2 = \frac{9 + 4}{9 \cdot 2} = \frac{13}{18}. \\ c_-^{(x)} &= \left(\chi_-^{(x)}\right)^\dagger \chi = \frac{1}{3} \frac{1}{\sqrt{2}} (1 \ -1) \begin{pmatrix} 1 - 2i \\ 2 \end{pmatrix} = \frac{1}{3\sqrt{2}} (1 - 2i - 2) = -\frac{1 + 2i}{3\sqrt{2}}; \quad |c_-^{(x)}|^2 = \frac{1 + 4}{9 \cdot 2} = \frac{5}{18}. \end{aligned}$$

$$\boxed{\frac{\hbar}{2}, \text{ with probability } \frac{13}{18}; -\frac{\hbar}{2}, \text{ with probability } \frac{5}{18}}. \quad \langle S_x \rangle = \frac{13}{18} \frac{\hbar}{2} + \frac{5}{18} \left(-\frac{\hbar}{2}\right) = \boxed{\frac{2\hbar}{9}}.$$

- (d) From Problem 4.29(a),

$$\begin{aligned} c_+^{(y)} &= \left(\chi_+^{(y)}\right)^\dagger \chi = \frac{1}{3} \frac{1}{\sqrt{2}} (1 \ -i) \begin{pmatrix} 1 - 2i \\ 2 \end{pmatrix} = \frac{1}{3\sqrt{2}} (1 - 2i - 2i) = \frac{1 - 4i}{3\sqrt{2}}; \quad |c_+^{(y)}|^2 = \frac{1 + 16}{9 \cdot 2} = \frac{17}{18}. \\ c_-^{(y)} &= \left(\chi_-^{(y)}\right)^\dagger \chi = \frac{1}{3} \frac{1}{\sqrt{2}} (1 \ i) \begin{pmatrix} 1 - 2i \\ 2 \end{pmatrix} = \frac{1}{3\sqrt{2}} (1 - 2i + 2i) = \frac{1}{3\sqrt{2}}; \quad |c_-^{(y)}|^2 = \frac{1}{9 \cdot 2} = \frac{1}{18}. \end{aligned}$$

$$\boxed{\frac{\hbar}{2}, \text{ with probability } \frac{17}{18}; -\frac{\hbar}{2}, \text{ with probability } \frac{1}{18}}. \quad \langle S_y \rangle = \frac{17}{18} \frac{\hbar}{2} + \frac{1}{18} \left(-\frac{\hbar}{2}\right) = \boxed{\frac{4\hbar}{9}}.$$

Problem 4.55 The electron in a hydrogen atom occupies the combined spin and position state

$$R_{21} \left(\sqrt{1/3} Y_1^0 \chi_+ + \sqrt{2/3} Y_1^1 \chi_- \right).$$

- (a) If you measured the orbital angular momentum squared (L^2), what values might you get, and what is the probability of each?
- (b) Same for the z component of orbital angular momentum (L_z).
- (c) Same for the spin angular momentum squared (S^2).
- (d) Same for the z component of spin angular momentum (S_z).

Let $\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$ be the *total* angular momentum.

- (e) If you measured J^2 , what values might you get, and what is the probability of each?
 - (f) Same for J_z .
 - (g) If you measured the *position* of the particle, what is the probability density for finding it at r, θ, ϕ ?
 - (h) If you measured both the z component of the spin *and* the distance from the origin (note that these are compatible observables), what is the probability density for finding the particle with spin up and at radius r ?
-

Problem 4.55

(a) For both terms, $l = 1$, so $\hbar^2(1)(2) = \boxed{2\hbar^2, P = 1}$.

(b) $\boxed{0, P = \frac{1}{3}}$ or $\boxed{\hbar, P = \frac{2}{3}}$.

(c) $\boxed{\frac{3}{4}\hbar^2, P = 1}$.

(d) $\boxed{\frac{\hbar}{2}, P = \frac{1}{3}}$ or $\boxed{-\frac{\hbar}{2}, P = \frac{2}{3}}$.

(e) From the $1 \times \frac{1}{2}$ Clebsch-Gordan table (or Problem 4.51):

$$\begin{aligned} \frac{1}{\sqrt{3}}|\frac{1}{2} \frac{1}{2}\rangle|1 0\rangle + \sqrt{\frac{2}{3}}|\frac{1}{2} -\frac{1}{2}\rangle|1 1\rangle &= \frac{1}{\sqrt{3}} \left[\sqrt{\frac{2}{3}}|\frac{3}{2} \frac{1}{2}\rangle - \frac{1}{\sqrt{3}}|\frac{1}{2} \frac{1}{2}\rangle \right] + \sqrt{\frac{2}{3}} \left[\frac{1}{\sqrt{3}}|\frac{3}{2} \frac{1}{2}\rangle + \sqrt{\frac{2}{3}}|\frac{1}{2} \frac{1}{2}\rangle \right] \\ &= \left(2\frac{\sqrt{2}}{3} \right) |\frac{3}{2} \frac{1}{2}\rangle + \left(\frac{4}{3} \right) |\frac{1}{2} \frac{1}{2}\rangle. \quad \text{So } s = \frac{3}{2} \text{ or } \frac{1}{2} \quad \boxed{\frac{15}{4}\hbar^2, P = \frac{8}{9}} \text{ or } \boxed{\frac{3}{4}\hbar^2, P = \frac{1}{9}} \end{aligned}$$

(f) $\boxed{\frac{1}{2}\hbar, P = 1}$.

(g)

$$\begin{aligned} |\psi|^2 &= |R_{21}|^2 \left\{ \underbrace{\frac{1}{3}|Y_1^0|^2}_{1} (\chi_+^\dagger \chi_+) + \underbrace{\frac{\sqrt{2}}{3} \left[Y_1^{0*} Y_1^1 (\chi_+^\dagger \chi_-) + Y_1^{1*} Y_1^0 (\chi_-^\dagger \chi_+) \right]}_{0} + \underbrace{\frac{2}{3}|Y_1^1|^2}_{1} (\chi_-^\dagger \chi_-) \right\} \\ &= \frac{1}{3}|R_{21}|^2 (|Y_1^0|^2 + 2|Y_1^1|^2) = \frac{1}{3} \cdot \frac{1}{24} \cdot \frac{1}{a^3} \cdot \frac{r^2}{a^2} e^{-r/a} \left[\frac{3}{4\pi} \cos^2 \theta + 2 \frac{3}{8\pi} \sin^2 \theta \right] \quad [\text{Tables 4.3, 4.7}] \\ &= \frac{1}{3 \cdot 24 \cdot a^5} r^2 e^{-r/a} \cdot \frac{3}{4\pi} (\cos^2 \theta + \sin^2 \theta) = \boxed{\frac{1}{96\pi a^5} r^2 e^{-r/a}}. \end{aligned}$$

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(h)

$$\frac{1}{3}|R_{21}|^2 \int |Y_1^0|^2 \sin^2 \theta d\theta d\phi = \frac{1}{3}|R_{21}|^2 = \frac{1}{3} \cdot \frac{1}{24a^3} r^2 e^{-r/a} = \boxed{\frac{1}{72a^5} r^2 e^{-r/a}}.$$

Identical Particles

Two Particle System

For a single particle, $\Psi(\vec{r}, t)$ is a function of the spacial coordinates \vec{r} and time t . The state of a two-particle system is a function of the coordinates of particle one \vec{r}_1 and of particle two \vec{r}_2 and time:

$$\Psi(\vec{r}_1, \vec{r}_2, t)$$

The time evolution of this equation is determined by Schrodinger as:

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

Where H is the Hamiltonian for the whole system:

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t)$$

The statistical interpretation is:

$$|\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d^3\vec{r}_1 d^3\vec{r}_2$$

is the probability of finding particle 1 in $d^3\vec{r}_1$ and particle 2 in $d^3\vec{r}_2$.

Ψ must be normalized as to:

$$\int |\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d^3\vec{r}_1 d^3\vec{r}_2 = 1$$

For time-independent potentials, we obtain a complete set of solutions by separation of variables:

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2)e^{-iE_t/\hbar}$$

Where the spacial wave function ψ satisfies the time-independent Schrodinger:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V\psi = E\psi$$

Bosons and Fermions

Suppose particle 1 is in the (one particle) state $\psi_a(\vec{r})$ and particle 2 is in the state $\psi_b(\vec{r})$. In that case, $\psi(\vec{r}_1, \vec{r}_2)$ is a simple product.

(It is not true that every two-particle wave function is a product of two one-particle wave functions. If particle 1 is in state a and particle 2 is in state b then we use the product for probability's product rule, but if we have particles in a two-particle state, there exist entangled states that can't be decomposed this way).

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$

Of course, this assumes that we can tell the particles apart, otherwise it wouldn't make sense to claim that number 1 is in state ψ_a and 2 in state ψ_b . All we could say is that there is one particle in ψ_a and one in ψ_b but we wouldn't know which is which.

In quantum mechanics, all electrons are identical, there is no way of differentiating them.

There is a way to accommodate the existence of indistinguishable particles. If we have two indistinguishable particles in states ψ_a, ψ_b , the complete wave function can be:

$$\psi_{\pm}(\vec{r}_1, \vec{r}_2) = A[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)]$$

That way there is no commitment to which particle is in which state. Thus, the theory admits two kinds of identical particles:

- **Boson:** We use the plus sign
- **Fermions:** We use the minus sign.

It so happens that:

$$\begin{aligned} \text{All particles with integer spin are bosons} \\ \text{All particles with half integer spin are fermions} \end{aligned}$$

It follows the **Pauli Exclusion Principle**, that says that two identical fermions cannot occupy the same state. For if $\psi_a = \psi_b$, then:

$$\psi_{-}(\vec{r}_1, \vec{r}_2) = A[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)] = 0$$

There is a more general and sophisticated formulation. We define the **exchange operator** P that interchanges two particles as:

$$Pf(\vec{r}_1, \vec{r}_2) = f(\vec{r}_2, \vec{r}_1)$$

Clearly $P^2 = 1$ (identity), so the eigenvalues of P are ± 1 .

Now, if the two particles are identical, the Hamiltonian must treat them the same: $m_1 = m_2$ and $V(\vec{r}_1, \vec{r}_2) = V(\vec{r}_2, \vec{r}_1)$. It follows that P and H are compatible observables:

$$[P, H] = 0$$

And hence, we can find a complete set of functions that are simultaneous eigenstates of both. That is to say, we can find solutions to the Schrodinger equation that are symmetric (eigenvalue 1 for P) or antisymmetric (eigenvalue -1 for P). That is, the solutions are:

$\psi(\vec{r}_1, \vec{r}_2) = \pm\psi(\vec{r}_2, \vec{r}_1)$

5,14

Moreover, if a system starts out in such a state of symmetry or antisymmetry, it will remain in such state.

Symmetrization requirement: For identical particles the wave function is required to satisfy the equation 5.14.

Example 5.1: Suppose we have two noninteracting particles, both of mass m , in the infinite square well. The one-particle states are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) , \quad E_n = n^2 K$$

(Where $K = \pi^2 \hbar^2 / 2ma^2$).

If the particles are **distinguishable**, with #1 in state n_1 and #2 in state n_2 , the composite wave function is a simple product:

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2) , \quad E_{n_1 n_2} = (n_1^2 + n_2^2)K$$

For example, the ground state is:

$$\psi_{11} = \frac{2}{a} \sin(\pi x_1/a) \sin(\pi x_2/a) , \quad E_{11} = 2K$$

And the first excited state is doubly degenerate:

$$\begin{aligned} \psi_{12} &= \frac{2}{a} \sin(\pi x_1/a) \sin(2\pi x_2/a) , \quad E_{12} = 5K \\ \psi_{21} &= \frac{2}{a} \sin(2\pi x_1/a) \sin(\pi x_2/a) , \quad E_{21} = 5K \end{aligned}$$

and so on.

If the particles are **identical bosons**, the states are:

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2) + \psi_{n_1}(x_2)\psi_{n_2}(x_1)$$

So, the ground state is now:

$$\psi_{11}(x_1, x_2) = \frac{2}{a} \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{\pi}{a}x_2\right) + \frac{2}{a} \sin\left(\frac{\pi}{a}x_2\right) \sin\left(\frac{\pi}{a}x_1\right) = \frac{4}{a} \sin\left(\frac{\pi}{a}x_1\right) \sin\left(\frac{\pi}{a}x_2\right)$$

So it is the same state, we just need to normalize it.

The first excited state is nondegenerate:

$$\psi_{12}(x_1, x_2) = \frac{\sqrt{2}}{a} [\sin(\pi x_1/a) \sin(2\pi x_2/a) + \sin(2\pi x_1/a) \sin(\pi x_2/a)]$$

Where we still need to normalize.

If the particles are **fermions**, there is no state with energy $2K$, the ground state is:

$$\frac{\sqrt{2}}{a} [\sin(\pi x_1/a) \sin(2\pi x_2/a) - \sin(2\pi x_1/a) \sin(\pi x_2/a)]$$

Exchange Forces

We will work out a 1D example to see what the symmetrization requirement really does. Suppose one particle is in state $\psi_a(x)$ and the other is in state $\psi_b(x)$, and these two states are orthogonal and normalized.

If the two particles are distinguishable, the combined wave equation is:

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$$

If they are identical bosons, the composite wave function is:

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)]$$

If they are identical fermions, it is:

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)]$$

Let's calculate the expectation value of the square of the separation distance between two particles.

$$\langle(x_1 - x_2)^2\rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$$

- **Case 1: Distinguishable particles:** For the wavefunction, we have:

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_a$$

(the expectation value of x^2 in the one-particle state ψ_a)

$$\langle x_2^2 \rangle = \int |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b$$

and:

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b$$

and:

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b$$

In this case, then:

$$\langle(x_1 - x_2)^2\rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$$

-
- **Case 2: Identical particles:** For the wave functions $\psi_{\pm}(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2)]$, we have:

$$\begin{aligned}\langle x_1^2 \rangle &= \frac{1}{2} \left[\int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \right. \\ &\quad \left. \pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^* \psi_a(x_2) dx_2 \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0) = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b)\end{aligned}$$

Similarly:

$$\langle x_2^2 \rangle = \frac{1}{2} (\langle x^2 \rangle_b + \langle x^2 \rangle_a)$$

Naturally, $\langle x_2^2 \rangle = \langle x_1^2 \rangle$, since you can't tell them apart. But:

$$\begin{aligned}\langle x_1 x_2 \rangle &= \frac{1}{2} \left[\int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \right. \\ &\quad \left. \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \right. \\ &\quad \left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} (\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}) \\ &= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2\end{aligned}$$

Where:

$$\langle x \rangle_{ab} := \int x \psi_a(x)^* \psi_b(x) dx$$

So:

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2$$

So, we can see the difference in the expected distance between the particles in each case:

$$\langle (\delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2$$

Identical bosons tend to be somewhat close together, and identical fermions somewhat farther apart than distinguishable particles in the same two states.

Notice that $\langle x \rangle_{ab}$ vanishes unless the two wave functions actually overlap.

So if ψ_a represent an electron in Chicago and ψ_b in Seattle, it's not going to make any difference whether you antisymmetrize. So it's ok to pretend that electrons with nonoverlapping wave functions are distinguishable.

Were there is some overlap of the wave functions, the systems acts as if there were a ' force of attraction ' between identical bosons and a ' repulsion ' between identical fermions (remember we are ignoring spin). We call it **exchange force**, although it is not a force, buy a consequence of the symmetrization requirement with no classical counterpart.

If we had a H_2 molecule, if electrons were bosons, they would concentrate near the middle. But as they are fermions, they separate to the edges and tear the molecule apart. But wait, the complete state of an electron also needs spin:

$$\psi(\vec{r})\chi(\vec{s})$$

So, when we put two electrons, it is the hole state (with spin) that has to be antisymmetric to exchange.

The singlet combination is antisymmetric (and hence would have to be joined with a symmetric spatial function, which would lead to bonding), whereas the three triplet states are symmetric (and require antisymmetric spatial function, which would lead to antibonding). So electrons must be oppositely spinned and in the singlet state, with total spin 0.

Problem 5.6

***Problem 5.6** Imagine two noninteracting particles, each of mass m , in the infinite square well. If one is in the state ψ_n (Equation 2.28), and the other in state ψ_l ($l \neq n$), calculate $\langle(x_1 - x_2)^2\rangle$, assuming (a) they are distinguishable particles, (b) they are identical bosons, and (c) they are identical fermions.

Problem 5.6

(a) Use Eq. 5.19 and Problem 2.4, with $\langle x \rangle_n = a/2$ and $\langle x^2 \rangle_n = a^2 \left(\frac{1}{3} - \frac{1}{2(n\pi)^2} \right)$.

$$\langle(x_1 - x_2)^2\rangle = a^2 \left(\frac{1}{3} - \frac{1}{2(n\pi)^2} \right) + a^2 \left(\frac{1}{3} - \frac{1}{2(m\pi)^2} \right) - 2 \cdot \frac{a}{2} \cdot \frac{a}{2} = a^2 \left[\frac{1}{6} - \frac{1}{2\pi^2} \left(\frac{1}{n^2} + \frac{1}{m^2} \right) \right].$$

(b) $\langle x \rangle_{mn} = \frac{2}{a} \int_0^a x \sin\left(\frac{m\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x\right) dx = \frac{1}{a} \int_0^a x \left[\cos\left(\frac{(m-n)\pi}{a}x\right) - \cos\left(\frac{(m+n)\pi}{a}x\right) \right] dx$

$$= \frac{1}{a} \left[\left(\frac{a}{(m-n)\pi} \right)^2 \cos\left(\frac{(m-n)\pi}{a}x\right) + \left(\frac{a}{(m-n)\pi} \right) \sin\left(\frac{(m-n)\pi}{a}x\right) \right. \\ \left. - \left(\frac{a}{(m+n)\pi} \right)^2 \cos\left(\frac{(m+n)\pi}{a}x\right) - \left(\frac{a}{(m+n)\pi} \right) \sin\left(\frac{(m+n)\pi}{a}x\right) \right]_0^a$$

$$= \frac{1}{a} \left[\left(\frac{a}{(m-n)\pi} \right)^2 (\cos[(m-n)\pi] - 1) - \left(\frac{a}{(m+n)\pi} \right)^2 (\cos[(m+n)\pi] - 1) \right].$$

But $\cos[(m \pm n)\pi] = (-1)^{m+n}$, so

$$\langle x \rangle_{mn} = \frac{a}{\pi^2} [(-1)^{m+n} - 1] \left(\frac{1}{(m-n)^2} - \frac{1}{(m+n)^2} \right) = \begin{cases} \frac{a(-8mn)}{\pi^2(m^2-n^2)^2}, & \text{if } m \text{ and } n \text{ have opposite parity,} \\ 0, & \text{if } m \text{ and } n \text{ have same parity.} \end{cases}$$

$$\text{So Eq. 5.21} \Rightarrow \langle(x_1 - x_2)^2\rangle = a^2 \left[\frac{1}{6} - \frac{1}{2\pi^2} \left(\frac{1}{n^2} + \frac{1}{m^2} \right) \right] - \frac{128a^2m^2n^2}{\pi^4(m^2-n^2)^4}.$$

(The last term is present only when m, n have opposite parity.)

Problem 5.7

Problem 5.7 Suppose you had *three* particles, one in state $\psi_a(x)$, one in state $\psi_b(x)$, and one in state $\psi_c(x)$. Assuming ψ_a , ψ_b , and ψ_c are orthonormal, construct the three-particle states (analogous to Equations 5.15, 5.16, and 5.17) representing (a) distinguishable particles, (b) identical bosons, and (c) identical fermions. Keep in mind that (b) must be completely symmetric, under interchange of *any* pair of particles, and (c) must be completely *antisymmetric*, in the same sense. *Comment:* There's a cute trick for constructing completely antisymmetric wave functions: Form the **Slater determinant**, whose first row is $\psi_a(x_1)$, $\psi_b(x_1)$, $\psi_c(x_1)$, etc., whose second row is $\psi_a(x_2)$, $\psi_b(x_2)$, $\psi_c(x_2)$, etc., and so on (this device works for any number of particles).

Problem 5.7

(a)
$$\boxed{\psi(x_1, x_2, x_3) = \psi_a(x_1)\psi_b(x_2)\psi_c(x_3).}$$

(b)
$$\boxed{\psi(x_1, x_2, x_3) = \frac{1}{\sqrt{6}}[\psi_a(x_1)\psi_b(x_2)\psi_c(x_3) + \psi_a(x_1)\psi_c(x_2)\psi_b(x_3) + \psi_b(x_1)\psi_a(x_2)\psi_c(x_3) + \psi_b(x_1)\psi_c(x_2)\psi_a(x_3) + \psi_c(x_1)\psi_b(x_2)\psi_a(x_3) + \psi_c(x_1)\psi_a(x_2)\psi_b(x_3)].}$$

(c)
$$\boxed{\psi(x_1, x_2, x_3) = \frac{1}{\sqrt{6}}[\psi_a(x_1)\psi_b(x_2)\psi_c(x_3) - \psi_a(x_1)\psi_c(x_2)\psi_b(x_3) - \psi_b(x_1)\psi_a(x_2)\psi_c(x_3) - \psi_b(x_1)\psi_c(x_2)\psi_a(x_3) - \psi_c(x_1)\psi_b(x_2)\psi_a(x_3) + \psi_c(x_1)\psi_a(x_2)\psi_b(x_3)].}$$

Atoms

A neutral atom of number Z , consists of a heavy nucleus of charge Ze and Z electrons of charge $-e$. The hamiltonian of the system is (*assuming the nucleus is stationary)

$$H = \sum_{j=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right] + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

The problem is to solve:

$$H\psi = E\psi$$

for the wave function $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z)$. Because electrons are fermions, only solutions for which the complete state:

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z)\chi(\vec{s}_1, \vec{s}_2, \dots, \vec{s}_Z)$$

is antisymmetric with respect to changes in electrons are allowed.

The equation cannot be solved exactly and one must resort to elaborate approximations. We will see some solutions neglecting repulsion of electrons:

Helium

The hamiltonian is:

$$H = \left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right) + \left(-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right) + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

If we simply ignore the electron repulsion, the Hamiltonian consists of two hydrogenic Hamiltonians. So the solution is the product of hydrogen wave functions:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{nlm}(\vec{r}_1)\psi_{n'l'm'}(\vec{r}_2)$$

Only with half the Bohr radius and four times the Bohr energies (because of the nucleus). The complete energy would be:

$$E = 4(E_n + E_{n'})$$

Where $E_n = -13,6/n^2$ eV. In particular, the ground state would be:

$$\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$$

And the energy would be:

$$E_0 = 8(-13,6eV) = -109eV$$

Because ψ_0 is symmetric, the spin has to be antisymmetric, so it requires to be a singlet configuration, with the spins oppositely aligned.

Experimentally, the energy is actually $-78,975\text{eV}$, the difference is accounted by the electron interaction.

The excited states of helium consist of one electron in the hydrogenic ground state, and the other in an excited:

$$\psi_{nlm}\psi_{100}$$

The Periodic Table

To first approximation, the individual electrons occupy one-particle hydrogenic states (n, l, m) called **orbitals** in the Coulomb potential of a nucleus of charge Ze .

Only two electrons can occupy a given orbitals (and with different spin).

Shell: Each value of n determines a **shell** which has room for n^2 orbitals, or $2n^2$ electrons, corresponding to the horizontal rows of the periodic table.

With Helium, the $n = 1$ shell is filled.

With Lithium ($Z=3$), we need to put an electron in the $n = 2$ shell. But we have the possibilities $l = 0, 1$. But it always favors the lower number of l , because that is the closest position to the nucleus, so the less shielded by the inner electrons, and therefore, the must tightly bound.

Continuing in this way, we reach ($Z = 10$), were $n = 2$ shell is filled, so we need to populate the $n = 3$ shell.

We can take $l = 0, 1, 2$, etc.

Solids

In the solid state, a few of loosely bound outermost **valence** electrons in each atom detach and roam around throughout the material.

The Free Electron Gas

We suppose the object in question is a rectangular solid with dimensions l_x, l_y, l_z and imagine the electrons to experience no force at all, except the impenetrable walls:

$$V(x, y, z) = \begin{cases} 0 & , \quad 0 < x < l_x , \quad 0 < y < l_y , \quad 0 < z < l_z \\ \infty & , \quad cc \end{cases}$$

The Schrodinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi$$

separates into:

$$-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X \quad , \quad -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_y Y \quad , \quad -\frac{\hbar^2}{2m} \frac{d^2 Z}{dz^2} = E_z Z$$

and $E = E_x + E_y + E_z$. Letting:

$$k_x := \frac{\sqrt{2mE_x}}{\hbar} \quad , \quad k_y := \frac{\sqrt{2mE_y}}{\hbar} \quad , \quad k_z := \frac{\sqrt{2mE_z}}{\hbar}$$

We obtain the solutions for X, Y, Z . And applying boundary conditions we get $k_x l_x = n_x \pi$. so the normalized wave functions are:

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right)$$

And the allowed energies are:

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m}$$

Where k is the magnitude of the **wave vector** $k = (k_x, k_y, k_z)$.

If you imagine a 3D space with planes in $k_x = n\pi/l_x$, $k_y = n\pi/l_y$, $k_z = n\pi/l_z$, each intersection point simbolizes a distinct one particle stationary state. Each block in this state, and hence also each state, occupies a volume:

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$$

of k-space, where $V = l_x l_y l_z$ is the volume of the electron gas itself. Suppose our sample contains N atoms each with q free electrons. As electrons are fermions, only two of them can

occupy any given state. They will fill up one octant of a sphere in k-space, whose radius k_F is determined by the fact that each pair of electrons requires a volume π^3/V :

$$\frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right) = \frac{Nq}{2} \left(\frac{\pi^3}{V} \right)$$

Thus:

$$k_F = (3\rho\pi^2)^{1/3}$$

Where:

$$\rho := \frac{Nq}{V}$$

is the free electron density.

The boundary separating occupied and unoccupied states, in k -space is called the **Fermi surface**, the corresponding energy is the **Fermi Energy** E_F . For a free electron gas, the energy of electrons at this state is:

$$E_F = \frac{\hbar^2}{2m} k_F = \frac{\hbar^2}{2m} (3\rho\pi^2)^{2/3}$$

Total Energy: The total energy is calculated as follows: A shell of thickness dk contains a volume $\frac{1}{8}4\pi k^2 dk = \frac{1}{2}\pi k^2 dk$, so the number of electron states in the shell is the volume of this shell divided by the volume of one electron in k-space multiplied by 2 (spin):

$$\frac{2[(1/2)\pi k^2 dk]}{\pi^3/V} = \frac{V}{\pi^2} k^2 dk$$

Each of these states carries an energy $\hbar^2 k^2 / 2m$, so the energy of the shell is:

$$dE = \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk$$

And hence the total energy is:

$$E_{tot} = \frac{\hbar^2 V}{2\pi^2 m} \int_0^{k_F} k^4 dk = \frac{\hbar^2 k_F^5 V}{10\pi^2 m} = \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m} V^{-2/3}$$

This quantum energy plays an analogous role to the internal energy U of thermodynamics. In particular, it exerts a pressure on the walls, for if the box expands by an amount dV , the energy decreases:

$$dE_{Tot} = -\frac{2}{3} \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m} V^{-5/3} dV = -\frac{2}{3} E_{tot} \frac{dV}{V}$$

Band Structure

We now improve on the free electron model by including the forces exerted on the electrons by regularly spaced positively charged nuclei. This potential should be periodic if we suppose the nuclei are:

$$V(x+a) = V(x)$$

Bloch's theorem tells us that for such a potential, the solutions of the Schrodinger equation $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$ can be taken to satisfy the condition:

$$\psi(x+a) = e^{iKa}\psi(x)$$

for some constant K

No solid is infinite and we have problems at the edges. Still, if the object is N atoms long (N is the order of Avogadro's number), then we will impose to wrap the wave function around and make it periodic :

$$\psi(x+Na) = \psi(x)$$

It follows that:

$$e^{iNka}\psi(x) = \psi(x)$$

So that:

$$K = \frac{2\pi n}{Na} \quad , \quad n \in \mathbb{Z}$$

The simplest possible model for the potential caused by the nuclei is the **Dirac Comb** consisting of evenly spaced delta functions.

That is:

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja)$$

In the region $0 < x < a$ the potential is 0, so:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= E\psi \\ \Rightarrow \frac{d^2\psi}{dx^2} &= -k^2\psi \quad , \quad k = \frac{\sqrt{2mE}}{\hbar} \\ \Rightarrow \psi(x) &= A \sin(kx) + B \cos(kx) \quad , \quad 0 < x < a \end{aligned}$$

According to Bloch's theorem, the wave function in the cell immediately to the left is:

$$\psi(x) = e^{-iKa}[A \sin k(x+a) + B \cos k(x+a)] \quad , \quad -a < x < 0$$

but at $x = 0$, ψ must be continuous, so:

$$B = e^{-iKa} [A \sin(ka) + B \cos(ka)] \quad 5.61$$

Its derivative suffers a discontinuity proportional to the strength of the delta function as we saw in chapter 2:

$$kA - e^{iKa} k[A \cos(ka) - B \sin(ka)] = \frac{2m\alpha}{\hbar^2} B$$

Solving 5.61 for A gives: $A \sin(ka) = [e^{iKa} - \cos(ka)]B$, substituting in 5.62 and cancelling kB , we find:

$$[e^{iKa} - \cos(ka)][1 - e^{-iKa} \cos(ka)] + e^{-iKa} \sin^2(ka) = \frac{2m\alpha}{\hbar^2 k} \sin(ka)$$

Which simplifies to:

$$\cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k} \sin(ka) \quad 5.64$$

Equation 5.64 determines the possible values of k , and hence the allowed energies. Let:

$$z := ka \quad , \quad \beta = \frac{m\alpha a}{\hbar^2}$$

So equation 5.64 can be written as:

$$\cos(Ka) = f(z) := \cos(z) + \beta \frac{\sin(z)}{z}$$

The graph of $f(z)$:

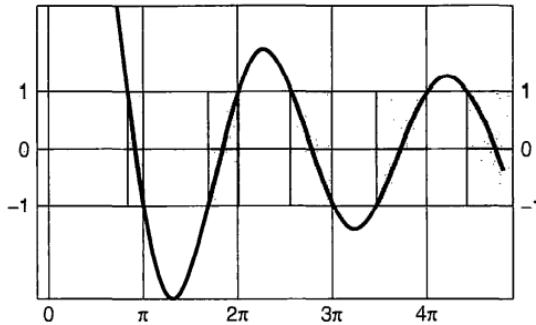


FIGURE 5.6: Graph of $f(z)$ (Equation 5.66) for $\beta = 10$, showing allowed bands (shaded) separated by forbidden gaps (where $|f(z)| > 1$).

The important thing to notice is that there are some points in which $f(z)$ strays outside the range $(-1, 1)$, so there is no hope of solving 5.64. These **gaps** represent forbidden energies and are separated by **bands** of allowed energies.

Within a given band, virtually any energy is allowed, since $Ka = 2\pi n/N$, where N is huge. So any band has N spaces.

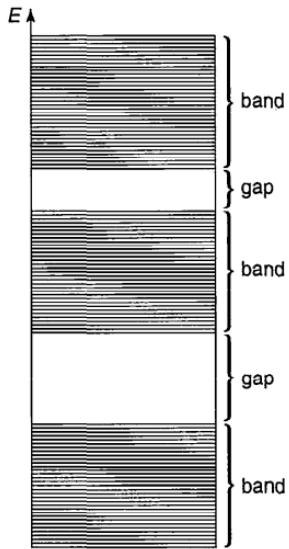


FIGURE 5.7: The allowed energies for a periodic potential form essentially continuous bands.

We have Nq electrons that can only occupy and no two can occupy the same state. If $q = 1$, they will half fill the first band (spin), if $q = 2$, they will completely fill the first band, if $q = 3$ they will half fill the second band and so on.

If a band is perfectly filled, it takes a large energy to excite an electron, as it has to make a big jump across the forbidden zone. Such materials are **insulators**.

If the band is partly filled, it takes little energy to excite an electron. Such materials are **conductors**.

If you **dope** an insulator with a few atoms of larger or smaller q , this puts some extra electrons into the next higher band or creates some **holes** in the previously filled one, allowing in either case for weak electric currents to flow. Such materials are **semiconductors**.

Quantum Statistical Mechanics

The **fundamental assumption of statistical mechanics** is that in **thermal equilibrium** every distinct state with the same total energy E is equally probable.

Random thermal motions constantly shift energy from one particle to another but the total energy is conserved.

The assumption is that this continual redistribution of energy does not favor any particular state.

The **temperature T** is simply a measure of the total energy of a system in thermal equilibrium. The problem is with how we count the distinct states for a given energy, and this depends on the type of particle (distinguishable, fermion, boson).

An Example

Suppose we have just three noninteracting particles of mass m in the one-dimensional infinite square well. The total energy is:

$$E = E_A + E_B + E_C = \frac{\pi^2 \hbar^2}{2ma^2} (n_A^2 + n_B^2 + n_C^2)$$

where n_A, n_B, n_C are positive integers. Now suppose for the sake of argument that:

$$n_A^2 + n_B^2 + n_C^2 = 363$$

There are, as it happens, 13 combinations of three positive integers whose squares sum 363:

$$\begin{aligned} & (11, 11, 11) \\ & (13, 13, 5), (13, 5, 13), (5, 13, 13) \\ & (1, 1, 19), (1, 19, 1), (19, 1, 1) \\ & (5, 7, 17), (5, 17, 7), (7, 5, 17), (7, 17, 5), (17, 5, 7), (17, 7, 5), \end{aligned}$$

If the particles are **distinguishable**, all these states are possible and distinct, and the fundamental assumption says that in thermal equilibrium, they are equally likely.

But I'm only interested in the total number of particles in each state, the **occupation number N_n** for the state ψ_n . The collection of all occupation numbers for a given 3-particle state we will call the **configuration**.

If all three are in ψ_{11} , the configuration is:

$$(0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 3, 0, 0, 0, 0, \dots)$$

i.e $N_{11} = 3$. If two are in ψ_{13} and one in ψ_5 , the configuration is:

$$(0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 2, 0, 0, 0, 0, \dots)$$

i.e $N_5 = 1$, $N_{13} = 2$.

If there is one particle in ψ_1 , one in ψ_{19} , the configuration is:

i.e. $N_1 = 2, N_{19} = 1$

And if there is one particle in ψ_5 , one in ψ_7 and one in ψ_{17} , the configuration is:

$$(0, 0, 0, 0, 1, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, \dots)$$

i.e. $N_5 = N_7 = N_{17} = 1$

Of these, the last is the most probable configuration, because it can be achieved in 6 different ways. The middle two configurations occur in three ways and the first one only once.

If we selected one of these three particles, what is the probability P_n of getting an specific allowed energy E_n ?

The only way to get E_1 is if it's in the third configuration, so $3/13$ chances of being in that configuration, and the probability of getting E_1 is $2/3$, so $P_1 = (3/13)(2/3) = 2/13$

You could get E_5 either from configuration 2 (chances 3/13 with prob 1/3) or from config 4 (chances 6/13 with prob 1/3), so $P_5 = (3/13)(1/3) + (6/13)(1/3) = 3/13$.

Similarly, $P_7 = (6/13)(1/3) = 2/13$

$$P_{11} = 1/13$$

$$P_{13} = (3/13)(2/3) = 2/13$$

$$P_{17} = (6/13)(1/3) = 2/13$$

$P_{19} = (3/13)(1/3) = 1/13$. Note that:

$$P_1 + P_5 + P_7 + \cdots + P_{19} = 1$$

If the particles are **identical fermions**, that excludes the first three configurations, and the only state is the fourth configuration.

So $P_5 = P_7 = P_{17} = 1/3$.

If they are **identical bosons**, the symmetrization requirement allows for one state in each configuration:

$$P_1 = (1/4)(2/3) = 1/6$$

$$P_5 = (1/4)(1/3) + (1/4)(1/3) = 1/6$$

$$P_7 = (1/4)(1/3) = 1/12$$

$$P_{11} = (1/4)(1) = 1/4$$

$$P_{13} = (1/4)(2/3) = 1/6$$

$$P_{17} = (1/4)(1/3) = 1/12$$

$$P_{19} = (1/4)(1/3) = 1/12$$

The general case

Now consider an arbitrary potential, with allowed energies of E_1, E_2, \dots with degeneracies d_1, d_2, d_3, \dots (i.e there are d_n distinct one-particle states with energy E_n).

Suppose we put N particles into this potential, we are interested in the configuration (N_1, N_2, \dots) for which there are N_1 particles in E_1 , N_2 in E_2 , etc.

How many different ways can this be achieved? The answer $Q(N_1, N_2, N_3, \dots)$ of distinct states with a particular configuration depends on the type of particle (distinguishable, identical fermion, boson).

- **Distinguishable:**

From the N particles, there is $\binom{N}{N_1}$ ways to choose the N_1 particles in the first bin.

Now, within the first bin, there are d_1 states (multiplicity), so we can reorder the particles in the bin in $d_1^{N_1}$ ways. For a total of $\frac{N!d_1^{N_1}}{N_1!(N-N_1)!}$

ways of selecting and arranging N_1 distinct particles out of N in the first bin (which has d_1 possible states).

The same goes for the bin 2 (E_2), but now with $N - N_1$ total particles, so:

$$\frac{(N - N_1)!d_2^{N_2}}{N_2!(N - N_1 - N_2)!}$$

And so, it follows that the total number of ways of putting N_1 particles in energy E_1 , N_2 in E_2 , etc is:

$$\begin{aligned} Q(N_1, N_2, N_3, \dots) &= \frac{N!d_1^{N_1}}{N_1!(N - N_1)!} \frac{(N - N_1)!d_2^{N_2}}{N_2!(N - N_1 - N_2)!} \frac{(N - N_1 - N_2)!d_3^{N_3}}{N_3!(N - N_1 - N_2 - N_3)!} \\ &= N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!} \end{aligned}$$

- **Identical Fermions:** Because they are indistinguishable, it doesn't matter which particles are in which states. The antisymmetrization says that there is just one N -particle state in which a specific set of one-particle states are occupied. Moreover, only one particle can occupy any given state. There are:

$$\binom{d_n}{N_n}$$

ways to choose the N_n occupied states in the n th bin, so:

$$Q(N_1, N_2, N_3, \dots) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}$$

Which is zero in any case that $N_n > d_n$ (considering negative factorials as infinite).

■ Identical bosons

The symmetrization requirement means that there is just one N -particle state in which a specific set of one-particle states are occupied, but this time there is no restriction on the number of particles that can share the same one-particle state.

For the n th bin, the question becomes: How many different ways can we assign N_n identical particles to d_n different slots? The result is (bars and stars) $\frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$

And then we conclude that:

$$Q(N_1, N_2, \dots) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$$

The most probable configuration

In thermal equilibrium, every state of N particles in total energy E is equally likely. So the most probable configuration (N_1, N_2, \dots) is the one with maximum $Q(N_1, N_2, \dots)$ subject to the constraints:

$$\begin{aligned} \sum_{n=1}^{\infty} N_n &= N \\ \sum_{n=1}^{\infty} N_n E_n &= E \end{aligned}$$

We solve this problem by lagrange multipliers. The problem of maximizing $F(x_1, x_2, \dots)$ with constraints $f(x_1, x_2, \dots) = 0$, $g(x_1, x_2, \dots) = 0$ can be solved by defining $G(x_1, x_2, \dots) = F + \lambda_1 f_1 + \lambda_2 f_2 + \dots$.

And setting $\frac{\partial G}{\partial x_n} = 0$, $\frac{\partial G}{\partial \lambda_n} = 0$.

Before we proceed with Q , we take the log (the maximum won't change place), and let:

$$G := \log(Q) + \alpha \left(N - \sum_{n=1}^{\infty} N_n \right) + \beta \left(E - \sum_{n=1}^{\infty} N_n E_n \right)$$

We have different cases:

■ Distinguishable particles:

For the Q found earlier:

$$G = \log(N!) + \sum_{n=1}^{\infty} [N_n \log(d_n) - \log(N_n!)] + \alpha \left(N - \sum_{n=1}^{\infty} N_n \right) + \beta \left(E - \sum_{n=1}^{\infty} N_n E_n \right)$$

We use **Stirling** $\log(z!) \sim z \log(z) - z$ to write:

$$G \sim \sum_{n=1}^{\infty} [N_n \log(d_n) - N_n \log(N_n) + N_n - \alpha N_n - \beta E_n N_n] + \log(N!) + \alpha N + \beta E$$

it follows that $\frac{\partial G}{\partial N_n} = \log(d_n) - \log(N_n) - \alpha - \beta E_n$

Setting this equal to zero and solving for N_n , we conclude that the most probable occupation numbers are:

$$N_n = d_n e^{-(\alpha + \beta E_n)}$$

- **Identical Fermions:** with the given Q and defining G as earlier:

$$G = \sum_{n=1}^{\infty} [\log(d_n!) - \log(N_n!) - \log((d_n - N_n)!) + \alpha \left(N - \sum_{n=1}^{\infty} N_n \right) + \beta \left(E - \sum_{n=1}^{\infty} N_n E_n \right)]$$

This time we assume N_n is large but also $d_n \geq N_n$ as we saw, so:

$$\begin{aligned} G \simeq & \sum_{n=1}^{\infty} [\log(d_n!) - N_n \log(N_n) + N_n - (d_n - N_n) \log(d_n - N_n) \\ & + (d_n - N_n) - \alpha N_n - \beta E_n N_n] + \alpha N + \beta E \end{aligned}$$

So $\frac{\partial G}{\partial N_n} = -\log(N_n) + \log(d_n - N_n) - \alpha - \beta E_n$. Setting this equal to 0 and solving for N_n we find the most probable occupation numbers:

$$N_n = \frac{d_n}{e^{\alpha + \beta E_n} + 1}$$

- **Identical Bosons:** We solve it just as before with lagrange multipliers and some algebra:

$$N_n = \frac{d_n - 1}{e^{\alpha + \beta E_n} - 1}$$

Example ideal gas, significance of α, β

For the case of a quantum gas (large number of noninteracting particles of same mass in a 3D infinite square well.

We found the allowed energies to be:

$$E_k = \frac{\hbar^2}{2m} k^2$$

where:

$$\vec{k} = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z} \right)$$

We treat \vec{k} as a continuous variable with one state (or $2s + 1$ states for spin s) per volume π^3/V of k-space.

Taking our bins the spherical shells in the first octant and degeneracy is:

$$d_k = \frac{1}{8} \frac{4\pi k^2 dk}{(\pi^3/V)} = \frac{V}{2\pi^2} k^2 dk$$

For distinguishable particles, the first constraint $\sum_{n=1}^{\infty} N_n = N$ with $N_n = d_n e^{-(\alpha + \beta E_n)}$ becomes :

$$N = \frac{V}{2\pi^2} e^{-\alpha} \int_0^{\infty} e^{-\beta \hbar^2 k^2 / 2m} k^2 dk = V e^{-\alpha} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2}$$

So:

$$e^{-\alpha} = \frac{N}{V} \left(\frac{2\pi\beta\hbar^2}{m} \right)^{3/2}$$

The second constraint $E = \sum N_n E_n$ says:

$$E = \frac{V}{2\pi^2} e^{-\alpha} \frac{\hbar^2}{2m} \int_0^{\infty} e^{-\beta \hbar^2 k^2 / 2m} k^4 dk = \frac{3V}{2\beta} e^{-\alpha} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2}$$

Or putting what we found for $e^{-\alpha}$ earlier:

$$E = \frac{3N}{2\beta}$$

This is reminiscent of the classical formula for the average kinetic energy of an atom at temperature T :

$$\frac{E}{N} = \frac{3}{2} k_B T$$

This suggest that β is related to the temperature:

$$\frac{1}{k_B T}$$

It is customary to replace α (that is clearly a function of T) by the **chemical potential**:

$$\mu(T) := -\alpha k_B T$$

And we may now rewrite the formulas for the most probable number of particles in a particular one particle state with energy ϵ (to go from the number of particles in a given energy to the number of particles in a given state with that energy, we divide by the degeneracy of the state):

$$n(\epsilon) = \begin{cases} e^{(-\epsilon-\mu)/k_B T} & \text{Maxwell Boltzmann, distinguishable} \\ \frac{1}{e^{(\epsilon-\mu)/k_B T} - 1} & \text{Fermi Dirac, identical Fermions} \\ \frac{1}{e^{(\epsilon-\mu)/k_B T} - 1} & \text{Bose-Einstein, identical Bosons} \end{cases}$$

The fermi-dirac has a particularly simple behavior as $T \rightarrow 0$:

$$n(\epsilon) \rightarrow \begin{cases} 1 & , \epsilon < \mu(0) \\ 0 & , \epsilon > \mu(0) \end{cases}$$

All states are filled, up to an energy $\mu(0)$ and none are occupied for energies above this.

Blackbody spectrum

Photons are identical bosons with spin 1. They follow the quantum- relativistic assertions:

- The energy of a photon is $h\nu = \hbar\omega$
- The wave number k is related to the frequency as $k = 2\pi/\lambda = \omega/c$
- Only two spin states occur (the quantum number m can be -1 or 1 but no 0)
- The number of photons is not conserved, when temperature rises, the number of photons increases.

So the first constraint doesn't apply, and we set $\alpha \rightarrow 0$. Thus, the most probable occupation number is:

$$N_\omega = \frac{d_k}{e^{\hbar\omega/k_B T} - 1}$$

For free photons in a box of volume V , d_k is given as in the quantum gas by $\frac{1}{8} \frac{4\pi k^2 dk}{\pi^3/V} = \frac{V}{2\pi^2} k^2 dk$ multiplied by 2 for spin and expressed in terms of ω :

$$d_k = \frac{V}{\pi^2 c^3} \omega^2 d\omega$$

So the energy density, $N_\omega \hbar\omega / V$, in the frequency range $d\omega$ is $\rho(\omega)d\omega$ where:

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_B T} - 1)}$$

Resumen Completo

- 1) Schrodinger's equation comes from taking a wave equation and asking it to have $\lambda = h/p$ and $E = \hbar\omega$. The equation is:

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

- 2) To solve it, we use separation of variables $\Psi(x, t) = \psi(x)f(t)$. The temporal part turns out to be $f(t) = e^{-iEt/\hbar}$. And the spatial equation is the **time-independent Schrodinger equation**:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

Where E is a constant. When imposing the boundary conditions, we find that we can only choose some values E_n with eigenfunctions $\psi_n(x)$. Then, the general solution is $\Psi(x, t) = \sum c_n \psi_n(x) f_n(t) = \sum c_n \psi_n(x) e^{-iE_n t/\hbar}$

To find the constants c_n , we impose the initial conditions $\Psi(x, 0) = \sum c_n \psi_n(x)$ and use Fourier's trick (the ψ_n are orthogonal and can be made orthonormal and are complete). Therefore $c_n = \langle \psi_n | \Psi(x, 0) \rangle = \int_{\mathbb{R}} \psi_n(x) \Psi(x, 0) dx$

Therefore, if $\psi_n(x)$ are the normalized solutions to the independent equation with energy eigenvalues E_n , then:

$$\Psi(x, t) = \sum \langle \psi_n | \Psi(x, 0) \rangle | \psi_n(x) \rangle e^{-iE_n t/\hbar}$$

- 3) $|\Psi|^2$ is interpreted as the probability density of finding the particle. It has to be normalized $\int_{\mathbb{R}} |\Psi|^2 = 1$.

It can be proven that once normalized, the normalization doesn't change with time.

- 4) Once we find the state Ψ the particle is in, we can find the expected value of x as:

$$\langle x \rangle = \int x |\Psi|^2 dx$$

We define $\langle v \rangle = \frac{d}{dt} \langle x \rangle$, and it can be proven that:

$$\langle p \rangle = m \frac{d \langle x \rangle}{dt} = \int \Psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi dx$$

This takes us to define **the momentum operator**:

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}$$

-
- 5) If we have any physical quantity $Q(x, p)$, then the associated operator is $Q(x, \frac{\hbar}{i} \frac{\partial}{\partial x})$. Then, the expected value of Q is:

$$\langle Q \rangle = \int \Psi^* Q(x, \frac{\hbar}{i} \frac{\partial}{\partial x}) \Psi dx$$

That is, the operator associated to a quantity is an operator that transforms functions into other functions and such that when sandwiched between the state Ψ of a particle, it returns the expected value.

- 6) This allows us to define many operators:

- $\hat{x} = x$
- $\hat{V}(x) = V(x)$
- $\hat{p} = -i\hbar \frac{\partial}{\partial x}$
- $\hat{E} = i\hbar \frac{\partial}{\partial t}$

Then, Schrodinger's equation is given by:

$$\hat{H} := \frac{\hat{p}^2}{2m} + \hat{V} = \hat{E}$$

An operator is called an observable if it has the property that $\langle Q \rangle$ is real, that is $\langle Q \rangle = \langle Q \rangle^*$.

Theorem: An operator is an observable if and only if \hat{Q} is Hermitian, that is:

$$\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$$

- 7) Ordinarily, when you measure an observable Q on an ensemble of identically prepared systems, all in state Ψ , you get a variety of results, with average $\langle Q \rangle$.

A **determinate state of Q** is a state Ψ of a particle such that every measurement of Q is certain to return the value q .

Theorem: Ψ is a determined state of \hat{Q} with value q iff $\hat{Q}\Psi = q\Psi$:

- If q is a determined state of \hat{Q} , then the standard deviation should be 0, that means:

$$\begin{aligned} 0 &= \langle (\hat{Q} - \langle Q \rangle)^2 \rangle = \langle \Psi | (\hat{Q} - q)^2 \Psi \rangle \\ &= \langle (\hat{Q} - q)\Psi | (\hat{Q} - q)\Psi \rangle \\ &\Rightarrow (\hat{Q} - q)\Psi = 0 \Rightarrow \hat{Q}\Psi = q\Psi \end{aligned}$$

So **determinate states of \hat{Q} (states with variance 0)** are eigenfunctions of \hat{Q}

Spectrum: The collection of all eigenvalues of an operator.

Theorem: The eigenvalues of a hermitian operator \hat{Q} are real, their eigenfunctions are orthonormal and complete.

- 8) If \hat{Q} is an operator, then its **eigenfunctions** are functions e_i such that:

$$\hat{Q}|e_i\rangle = \lambda_i|e_i\rangle$$

This eigenfunctions e_i are a complete and orthonormal basis. For it to be orthonormal, we ask it to:

$$\langle e_i | e_j \rangle = \int_{\mathbb{R}} e_i^* e_j dx = \delta_{ij}$$

If the spectrum is continuous instead of discrete, we ask $\langle e_\lambda | e_\mu \rangle = \delta(\lambda - \mu)$

Now, if Ψ is the state of the particle, we can write it in terms of eigenfunctions:

$$|\Psi\rangle = \sum c_n |e_n\rangle$$

Where:

$$c_n = \langle e_n | \Psi \rangle = \int_{\mathbb{R}} e_n^* \Psi dx$$

This wave function might not be a determined state of \hat{Q} . When we measure \hat{Q} , we are bound to get a determined state $|e_n\rangle$ with value $Q = \lambda_n$.

And then, the expected value of \hat{Q} is:

$$\begin{aligned} \langle Q \rangle &= \int \Psi^* \hat{Q} \Psi dx \\ &= \int (c_1^* |e_1\rangle^* + c_2^* |e_2\rangle^* + \dots) \hat{Q} (c_1 |e_1\rangle + c_2 |e_2\rangle + \dots) dx \\ &= \int (c_1^* |e_1\rangle^* + c_2^* |e_2\rangle^* + \dots) (\lambda_1 c_1 |e_1\rangle + \lambda_2 c_2 |e_2\rangle + \dots) dx \\ &= \lambda_1 |c_1|^2 + \lambda_2 |c_2|^2 + \dots \end{aligned}$$

Just after measuring \hat{Q} , if we get a result q (that has to be an eigenvalue of \hat{Q}), the particle has changed state, now we are sure it is in the state with value q (that is, the state given by the eigen function e_q corrsponding to eigenvalue q).

So, the possible results of measuring \hat{Q} must be the eigenvalues of \hat{Q} which are $\lambda_1, \lambda_2, \dots$

And seeing the sum that gives $\langle Q \rangle$, we conclude:

The probability of getting λ_i when measuring \hat{Q} is $|c_i|^2 = |\langle e_n | \Psi \rangle|^2 = |\int_{\mathbb{R}} e_i^* \Psi dx|^2$

And it can be proved, as expected, that $\sum |c_n|^2 = 1$.

9) Cases:

- **Energy:** Let's say we have the state Ψ of a particle in a given problem. Then, we can calculate the mean energy as $\int \Psi^* \hat{H} \Psi dx$. The possible values of energy are the eigenvalues of \hat{H} and the possible definite state are the eigenvectors of \hat{H} . That is, we look for functions ψ_n such that:

$$\begin{aligned}\hat{H}\psi_n &= E_n \psi_n \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_n}{\partial x^2} + V\psi_n &= E_n \psi_n\end{aligned}$$

We notice that this is actually the time independent Schrodinger equation, which we might have already solved before.

These states ψ_n have determined energy E_n .

Now we have $\Psi_n = \psi_n f(t)$, and we have to write $\Psi = \sum c_n \Psi_n$.

Then, the probability of getting an eigenvalue E_n is:

$$|c_n|^2 = |\langle \Psi_n | \Psi \rangle|^2 = |\langle \psi_n | \psi \rangle|^2$$

- **Position:** This is just a consistency check. Lets say the wave equation is Ψ . now we look for the eigenvectors g_λ of \hat{x} , they have to fulfill:

$$\begin{aligned}x g_\lambda(x) &= \langle g_\lambda(x) | \hat{x} | g_\lambda(x) \rangle \\ \Rightarrow g_\lambda(x) &= \delta(x - \lambda)\end{aligned}$$

To check they are dirac-normalize, we see that $\int_{\mathbb{R}} g_\lambda(x)^* g_\mu(x) dx = \delta(\lambda - \mu)$.

Then, any real number is an eigenvalue, so we have a continuous spectrum.

We are supposed to write Ψ as a combination of this eigenfunctions with coefficients $c(\lambda)$, so:

$$\Psi(x, t) = \int c(\lambda) \delta(x - \lambda) d\lambda$$

Where:

$$c(\lambda) = \langle g_\lambda(x) | \Psi \rangle = \int_{\mathbb{R}} \delta(x - \lambda) \Psi dx = \Psi(\lambda, t)$$

So the probability of finding the particle in the range $d\lambda$ is:

$$|c(\lambda)|^2 d\lambda = |\Psi(\lambda, t)|^2 d\lambda$$

-
- **Momentum:** Let's say Ψ is the wave functions. Now we look for the eigenvectors (determined states) of $\hat{p} = -i\hbar\partial_x$. That is, we look to solve $\hat{p}\psi_p(x) = p\psi_p(x)$. The solutions are:

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

Where p is the eigenvalue and it can be any real. So we have a continuous spectrum. The eigen vectors are already normalized $\langle \psi_p(x) | \psi_q(x) \rangle = \int \psi_p^*(x) \psi_q(x) dx = \delta(p - q)$.

Then, the p-component of $|\Psi\rangle$ is given by:

$$c(p) = \langle \psi_p | \Psi \rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} e^{-ipx/\hbar} \Psi(x, t) dx := \Phi(p, t)$$

Then, Φ is the probability density of momentum. And the probability of having a momentum in the range dp is:

$$|c_p|^2 = |\Phi(p, t)|^2 dp$$

Then, the **moment space wave function** is the Fourier transform of Ψ . The fact that $\int |\Phi(p, t)|^2 dp = 1$ is due to Plancherel.

We see that the determined states of momentum $\frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$ are not normalizable and impossible to find on their own.

Nevertheless, when we measure momentum, we get a small range dp of these states that together form a possible wave function.

Each individual state is a wave with wavelength $\lambda = \frac{2\pi\hbar}{p}$, but these states are impossible on their own, we need a combination of them.

And Ψ can be obtained back with these components as:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{ipx/\hbar} \Phi(p, t) dp$$

10) Solutions to different potentials

- **Infinite Square Well:**

$$V(x) = \begin{cases} 0 & , \quad 0 \leq x \leq a \\ \infty & , \quad cc \end{cases}$$

The time independent equation is $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$. And has solutions given by

$$\psi(x) = A \sin kx + B \cos kx , \quad k := \frac{\sqrt{2mE}}{\hbar}$$

Using continuity at the edges, we obtain the determined states solutions:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

Which have energy:

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2} = E_1 n^2$$

The must general solution is:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-iE\hbar t} = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}$$

And we want it to fit the initial condition $\Psi(x, 0) = \sum c_n \psi_n(x)$, for which we use the completeness of ψ .

- **Harmonic Oscillator:**

$$\begin{aligned} V(x) &= \frac{1}{2} m \omega^2 x^2 \\ \Rightarrow -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} m \omega^2 x^2 \psi &= E\psi \end{aligned}$$

We can solve it by the algebraic method, we define:

$$a_{\pm} := \frac{1}{\sqrt{2m}} \left(\frac{\hbar}{i} \frac{d}{dx} \pm im\omega x \right)$$

We find that:

$$a_- a_+ - a_+ a_- = \hbar\omega$$

And Schrodinger's equation is given by:

$$\begin{aligned} (a_- a_+ - \frac{1}{2}\hbar\omega)\psi &= E\psi \\ (a_+ a_- + \frac{1}{2}\hbar\omega)\psi &= E\psi \end{aligned}$$

Theorem: If ψ satisfies Schrodinger's independent equation with energy E then $a_+ \psi$ satisfies it with energy $E + \hbar\omega$ and $a_- \psi$ satisfies it with energy $E - \hbar\omega$.

We call a_{\pm} **ladder operators**.

There must be a minimum solution with $a_- \psi_0 = 0$, we find to be:

$$\begin{aligned} \psi_0(x) &= A_0 e^{-\frac{m\omega}{2\hbar}x^2} \\ E_0 &= \frac{1}{2}\hbar\omega \end{aligned}$$

Knowing the solution of smallest energy, we can go up the ladder to the excited states:

$$\psi_n(x) = A_n (a_+)^n e^{-\frac{m\omega}{2\hbar}x^2}, \quad E_n = (n + \frac{1}{2})\hbar\omega$$

Using the analytical method, we find this turns out to be:

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\chi) e^{-x^2/2}$$

Where:

$$\begin{aligned} \chi &:= \sqrt{\frac{m\omega}{\hbar}} x \\ H_n(\chi) &= (-1)^n e^{\chi^2} \left(\frac{d}{d\chi}\right)^n e^{-\chi^2} \end{aligned}$$

• free Particle

$$V(x) = 0$$

The equation is then:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= E\psi \\ \Rightarrow \frac{d^2\psi}{dx^2} &= -k^2\psi \quad , \quad k := \frac{\sqrt{2mE}}{\hbar} \end{aligned}$$

The general solution is given by:

$$\begin{aligned} \Psi_k(x, t) &= A e^{i(kx - \frac{\hbar k^2}{2m} t)} \\ k &:= \pm \frac{\sqrt{2mE}}{\hbar} \end{aligned}$$

Evidently any of these solutions are not normalizable. A free particle cannot exist in a stationary state, there is no such thing as a free particle with definite energy. That doesn't mean the separable solutions are of no use. The general solution can still be achieved as a combination of the separable solutions with coefficients $\phi(k)$ such as:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{ikx - \frac{\hbar k^2}{2m} t} dk$$

Which is a **Fourier Transform**. The factor $\sqrt{2\pi}$ is taken for convenience. The function necessarily carries a range of ks, a **wave packet**.

In a generic quantum problem, we are given $\Psi(x, 0)$ and we have to find $\Psi(x, t)$. To do that, the only thing we need to get is $\phi(k)$. When $t = 0$ we get:

$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \phi(k) e^{ikx} dk$$

To get $\phi(k)$ we use the inversion theorem:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \Psi(x, 0) e^{-ikx} dx$$

• Delta Function

$$V(x) = -\alpha\delta(x)$$

The equation is:

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

We find:

$$\begin{aligned} (x < 0) &\Rightarrow \psi(x) = Be^{kx} \\ (x > 0) &\Rightarrow \psi(x) = Fe^{-kx} \end{aligned}$$

Ψ has to be continuous and $\frac{d\psi}{dx}$ has to be continuous except when V is infinite, if that is in 0, we have:

$$\Delta \left(\frac{d\psi}{dx} \right) = -\frac{2m\alpha}{\hbar^2} \psi(0)$$

For the case in hand, when putting these two conditions, we get:

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}, \quad E = -\frac{m\alpha^2}{2\hbar^2}$$

• Finite Square Well

$$V(x) = \begin{cases} -V_0 & , -a < x < a \\ 0 & , |x| > a \end{cases}$$

We can solve it in each interval:

- $(x < -a) \Rightarrow \psi(x) = Be^{kx}, k := \frac{\sqrt{-2mE}}{\hbar}$
- $(x > a) \Rightarrow \psi(x) = Fe^{-kx}, k := \frac{\sqrt{-2mE}}{\hbar}$
- $(-a < x < a) \Rightarrow \psi(x) = C \sin(lx) + D \cos(lx), l := \frac{\sqrt{2m(E + V_0)}}{\hbar}$

When we apply the boundary conditions, we get the solution:

$$\psi(x) = \begin{cases} Fe^{-lx} & , x > a \\ D \cos(lx) & , 0 < x < a \\ \psi(-x) & , a < 0 \end{cases}$$

Using boundary, we get $k = l \tan(la)$. We now define $z := la$ and $z_0 := \frac{a}{\hbar} \sqrt{2mV_0}$, and it takes us to the condition:

$$\tan z = \sqrt{(z_0/z)^2 - 1}$$

11) Uncertainty principle

For any observable A , we have:

- $\langle A \rangle = \langle \Psi | A \Psi \rangle$
- $\langle A^2 \rangle = \langle \Psi | A^2 \Psi \rangle$
- $\sigma_A^2 = \langle A^2 \rangle - \langle A \rangle^2$

Or it can be found as:

$$\sigma_A^2 = \langle \Psi | (\hat{A} - \langle A \rangle)^2 \Psi \rangle = \langle (\hat{A} - \langle A \rangle) | \Psi | (\hat{A} - \langle A \rangle) \Psi \rangle$$

Likewise, with any other observable B .

It can be found that:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2$$

Where:

$$[\hat{A}, \hat{B}] := \hat{A}\hat{B} - \hat{B}\hat{A}$$

The i inside the parenthesis cancels out because the difference $\hat{A}\hat{B} - \hat{B}\hat{A}$ is antihermitian and has imaginary expected value.

For example: $[\hat{x}, \hat{p}] = i\hbar$, so $\sigma_a \sigma_p \geq \frac{\hbar}{2}$.

Incompatible observables: When two observables do not commute, they have an uncertainty principle. Incompatible observables don't admit a complete set of common eigenfunctions, because we would have definite states for both observables and then we violate the uncertainty principle.

Compatible observables: They commute, so they accept complete set of common eigenfunctions.

Theorem: If $AB = BA$ and x is an eigenvector of A with eigenvalue of multiplicity 1, then x is an eigenvector of B :

- $ABx = BAx = B\lambda x = \lambda Bx$

So x and Bx are both eigenvectors of A with eigenvalue λ , but if the eigenspace of λ in A is 1-D then $B(x)$ is a multiple of x and so x is an eigenvector of B

This fact is what tells us that commuting operators have a complete mutual family of eigenvectors.

Energy Time:

$$\Delta t \Delta E \geq \frac{\hbar}{2}$$

derivative of an observable:

$$\frac{d}{dt} \langle Q \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \langle \partial_t \hat{Q} \rangle$$

11) Dirac Notation

Operator: An operator \hat{A} is a mathematical rule that transforms a ket $|\psi\rangle$ into another ket $|\phi\rangle$ like:

$$\hat{A}|\psi\rangle = |\phi\rangle$$

Ket: A ket is a vector representing the state of a system. In the case of spin 1/2 for example, it is a 2 term vector, in other cases it might be a function.

Bra: A bra is the conjugate transpose of the ket.

Inner product: The inner product of two vectors $|u\rangle$ and $|v\rangle$ is written as:

$$\langle u|v \rangle$$

And it satisfies:

- $\langle u|v \rangle^* = \langle v|u \rangle$
- $\langle u|u \rangle \geq 0$
- $\langle u|av + bw \rangle = \alpha\langle u|v \rangle + \beta\langle u|w \rangle$

For finite dimension vectors, the inner product is simply a matrix product of $\langle u|$ and $|v\rangle$.

For functions, the inner product is $\langle f|g \rangle = \int_{\mathbb{R}} f^* g dx$

Orthonormality: A group of vector $\{|u_i\rangle\}$ are orthonormal if:

$$\langle u_i|u_j \rangle = \delta_{ij}$$

Any spanning set of vectors can be orthogonalized with Gram Schmidt.

Outer Product: The product of a ket $|\psi\rangle$ and a bra $\langle\phi|$, written as $|\psi\rangle\langle\phi|$ is called the outer product. When applied to a ket $|X\rangle$, it gives:

$$(|\psi\rangle\langle\phi|)|X\rangle = \langle\phi|X\rangle \ |\psi\rangle$$

Projection:

If we have a normalized vector $|u_i\rangle$, then the operator given by:

$$P_i = |u_i\rangle\langle u_i|$$

gives the projection of a vector in the direction $|u_i\rangle$. That is:

$$P_i(|\psi\rangle) = |u_i\rangle\langle u_i|\psi\rangle = \langle u_i|\psi\rangle |u_i\rangle$$

Closure Relation: Given an orthonormal basis set $\{|u_i\rangle\}$ in n dimensions, we have:

$$I = \sum_{i=1}^n |u_i\rangle\langle u_i|$$

This is simply saying that the basis is complete:

$$|\psi\rangle = \hat{I}|\psi\rangle = \left(\sum_{i=1}^n |u_i\rangle\langle u_i| \right) |\psi\rangle = \sum_{i=1}^n \langle u_i|\psi\rangle |u_i\rangle$$

Representation of an Operator using a matrix

Given an operator \hat{A} on a orthonormal basis $|u_i\rangle$, we can define the representation matrix as:

$$\hat{A} = \begin{pmatrix} \langle u_1|\hat{A}|u_1\rangle & \langle u_1|\hat{A}|u_2\rangle & \cdots & \langle u_1|\hat{A}|u_n\rangle \\ \langle u_2|\hat{A}|u_1\rangle & \langle u_2|\hat{A}|u_2\rangle & \cdots & \langle u_2|\hat{A}|u_n\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle u_n|\hat{A}|u_1\rangle & \langle u_n|\hat{A}|u_2\rangle & \cdots & \langle u_n|\hat{A}|u_n\rangle \end{pmatrix}$$

Types of operators:

Hermitian Conjugate: The hermitian A^T of an operator A is the operator such that:

$$\langle a|A^T|b\rangle = \langle b|A|a\rangle^*$$

Its matrix is obtained by transposing and conjugating.

- **Normal:** It is an operator such that:

$$AA^T = A^TA$$

The operator has the following properties:

- $|A(|\psi\rangle)| = |A^T(|\psi\rangle)|$
- If λ is an e.val of A then $\bar{\lambda}$ is an eigenvalue of A^T

-
- If λ_1, λ_2 are different eigenvalues of A , then their eigenvectors are orthogonal.
 - A is normal in a finite dimensional space iff there is an orthonormal basis of eigenvectors of A
 - **Self Adjoint:** An operator with $A = A^T$.
It has the properties:
 - The eigenvalues are real.
 - It is normal, so it has the other properties.
 - Its matrix representation is the same when we transpose and conjugate.
 - **Unitary:** An operator with $AA^T = I$
Properties:
 - The eigenvalues are complex numbers of norm 1.
 - It is normal, so it has all those properties.
 - The columns of its matrix representation are a orthonormal set, that way $AA^T = I$

Spectral Decomposition: For every normal operator A , we can find a basis of the space formed of eigenvectors $\{|u_i\rangle\}$. Therefore, the operator can be written as:

$$\begin{aligned} A &= \sum_{i=1}^n \lambda_i |u_i\rangle\langle u_i| \\ &= \sum_{i=1}^n \lambda_i P_i \end{aligned}$$

Where the eigenvectors are $A|u_i\rangle = \lambda_i|u_i\rangle$.

So the normal operator A acts only on n orthonormal directions and it 'enlarges' each one by a factor λ_i .

If A is hermitian, the enlargement is real.

If A is unitary, the 'enlargement' is actually a rotation with a complex number of norm 1.

And we have $\sum_i P_i = I$

Observables: In QM, dynamical variables are represented by a Hermitian operator.

Expectation Value of an Operator: Given an operator A and a particle in state $|\Psi\rangle$, the expectation value of A is:

$$\langle A \rangle = \langle \Psi | A | \Psi \rangle$$

And $\langle A^2 \rangle = \langle \Psi | A^2 | \Psi \rangle$.

The variance is $\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$

After measuring a variable with operator A , the particle will take a state such that the variance of A is 0 (because we already know A).

This determinate states are the eigenvectors of A , so the particle must transform into a state that is an eigenvector $|u_i\rangle$ of A .

And the value of the variable is the corresponding eigenvalue because the expectation value is now $\langle A \rangle = \langle u_i | A | u_i \rangle = \langle u_i | \lambda_i u_i \rangle = \lambda_i$.

Function of Operators: Given an operator written as $A = \sum_i \lambda_i |u_i\rangle\langle u_i|$ (where $|u_i\rangle$ are the eigenvectors of A).

Then we have that:

$$A^n = \sum_i \lambda_i^n |u_i\rangle\langle u_i|$$

Which can be proved by induction.

If we define a function f on an operator by its Taylor series, then:

$$f(A) = \sum_i f(\lambda_i) |u_i\rangle\langle u_i|$$

In particular, if H is a Hermitian operator, then:

$$U = e^{iaH}$$

for any real a is a unitary operator, because:

$$U = e^{iaH} = \sum_i e^{ia\lambda_i} |u_i\rangle\langle u_i|$$

So, we see that taking the conjugate is the same as taking the inverse, then $U^* = U^{-1}$, so U is unitary.

Measurement: When we measure an operator $A = \sum_n \lambda_n |u_n\rangle\langle u_n|$, then we are bound to get an eigenvalue of λ_n upon measurement.

The probability of getting this value is:

$$Pr(\lambda_n) = |\langle u_n | \Psi \rangle|^2$$

Time evolution of the system:

We can write Schrodinger's equation as:

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

Where H is the Hamiltonian operator. Then, given the initial state $|\Psi(0)\rangle$ of the particle, the time evolution of the state is given by solving the equation:

$$|\Psi(t)\rangle = e^{-iHt/\hbar} |\Psi(0)\rangle$$

If the eigenvalues of H are h_i and eigenvectors are $|u_i\rangle$, then $H = h_i|u_i\rangle\langle u_i|$, and $e^{-iHt/\hbar} = \sum_i e^{-ih_i t/\hbar}|u_i\rangle\langle u_i|$

So the time evolution is:

$$\begin{aligned} |\Psi(t)\rangle &= \sum_i e^{-ih_i t/\hbar}|u_i\rangle\langle u_i| |\Psi(0)\rangle \\ &= \sum_i e^{-ih_i t/\hbar}\langle u_i|\Psi(0)\rangle |u_i\rangle \end{aligned}$$

11) Quantum in 3D

The momentum operator is:

$$\vec{p} = \frac{\hbar}{i}\nabla$$

So the Schrodinger equation is:

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

The probability of finding a particle in $d^3\vec{r} = dx dy dz$ is $|\Psi(\vec{r}, t)|^2 d^3\vec{r}$.

We use separation of variables $\Psi = \psi f$ and find that:

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi &= E_n \psi \\ f(t) &= e^{-iE_n t/\hbar} \end{aligned}$$

So the nth solution is:

$$\Psi_n(\vec{r}, t) = \psi_n(\vec{r})e^{-iE_n t/\hbar}$$

And the complete solution is:

$$\Psi(\vec{r}, t) = \sum c_n \psi_n(\vec{r}) e^{-iE_n t/\hbar}$$

12) Using separations of variables to Schrodinger's equation in Spherical coordinates gives the functions:

$$\begin{aligned} \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} &= -m^2 \\ \frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta &= m^2 \\ \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] R &= l(l+1)R \end{aligned}$$

Where $m \in \mathbb{Z}$, $l = 0, 1, 2, \dots$ for the lagrange equation and $|m| < l$.

- **Azimuthal:**

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

- **Polar:**

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

The **Spherical Harmonics:**

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta)$$

Where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. These solutions are orthonormalized.

- **Radial equation:** We need the form of $V(r)$ to solve it.

12) **Hydrogen Atom:** The potential is $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$.

The angular solution is Y_l^m as before.

The radial equation can be solved too and we find: (normalized):

$$R(r) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}(2r/na)$$

So the **General time independent solution is:**

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}(2r/na) Y_l^m(\theta, \phi)$$

Where:

- $L_q(x) := e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$
- $L_{q-p}^p := (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$
- $Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta)$
- $a := \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0,529 \times 10^{-10} m$
- $E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}$

For $n = 1, 2, 3, \dots$

The solutions are orthonormal. These solutions are the stationary states of a hydrogen electron.

Spectrum: Hydrogen gives out light with an energy of:

$$E_i - E_f = -13,6eV \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

13) Angular Momentum

Angular momentum is defined as $\vec{L} = \vec{r} \times \vec{p}$, so:

$$L_x = yp_z - zp_y , \quad L_y = zp_x - xp_z , \quad L_z = xp_y - yp_x$$

Square of Total Angular Momentum:

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

Commutators:

$$\begin{aligned} [L_x, L_y] &= i\hbar L_z , \quad [L_y, L_z] = i\hbar L_x , \quad [L_z, L_x] = i\hbar L_y \\ [L^2, L_x] &= [L^2, L_y] = [L^2, L_z] = 0 \end{aligned}$$

So L_x, L_y, L_z are incompatible, the angular momentum is never fully determined, at most we can determine one of its coordinates.

But we can find states with determined simultaneous values of L^2 and (say) L_z . That is, a function f such that:

$$L^2 f = \lambda f , \quad L_z f = \mu f$$

We now define an operator:

$$L_{\pm} := L_x \pm iL_y$$

The commutators are:

$$[L_z, L_{\pm}] = \pm L_{\pm} , \quad [L^2, L_{\pm}] = 0$$

Theorem: If f is an eigenfunction of L^2 and L_z , so is also $L_{\pm}f$. $L_{\pm}f$ has the same eigenvalue λ for L^2 and has eigenvalue $\mu \pm \hbar$ for L_z .

So L_{\pm} are raising or lowering operators.

It can be proven that:

$$L^2 = L_{\pm}L_{\mp} + L_z^2 \mp \hbar L_z$$

There must be a lowest rung f_T such that:

$$L_z f_T = \hbar l f_T , \quad L^2 f_T = \lambda f_T , \quad L_+ f_T = 0$$

Solving this, we find $L^2 f_T = (L_- L_+ + L_z^2 + \hbar L_z) f_T = (0 + \hbar^2 l^2 + \hbar^2 l) f_T = \hbar^2 l(l+1) f_T$. Hence, the maximum eigenvalue of L^2 in terms of the maximum eigenvalue of L_Z is:

$$\lambda = \hbar^2 l(l+1)$$

Meanwhile, there is also a bottom rung f_b such that:

$$L_- f_b = 0 , \quad L_z f_b = \hbar \bar{l} f_b , \quad L^2 f_b = \lambda f_b$$

And we find the relation between the lowest rung's L_z eigenvalue \bar{l} and the eigenvalue of L^2 :

$$\lambda = \hbar^2 \bar{l}(\bar{l}-1)$$

This implies that $l(l+1) = \bar{l}(\bar{l}-1) \Rightarrow \bar{l} = -l$.

So, the eigenvalues of L_z are $m\hbar$ where m goes from $-l$ to l in N integer steps. It follows that $l = N/2$ is a half integer. So, the eigenfunctions are characterized by l, m :

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m , \quad L_z f_l^m = \hbar m f_l^m$$

Where:

$$l = 0, 1/2, 1, 3/2, \dots , \quad m = -l, -l+1, \dots , l-1, l$$

Eigenfunctions: We have $\vec{L} = \frac{\hbar}{i} \vec{r} \times \nabla$. So $\vec{L} = \frac{\hbar}{i} \left(\hat{\phi} \partial_\theta - \hat{\theta} \frac{1}{\sin \theta} \partial_\phi \right)$. We can resolve in cartesian coordinates, to get:

$$\begin{aligned} L_x &= \frac{\hbar}{i} (-\sin \phi \partial_\theta - \cos \phi \cot \theta \partial_\phi) \\ L_y &= \frac{\hbar}{i} (\cos \phi \partial_\theta - \sin \phi \cos \theta \partial_\phi) \\ L_z &= \frac{\hbar}{i} \partial_\phi \end{aligned}$$

With some work, we can get L^2 , and the eigenfunctions f_l^m should fulfill:

$$\begin{aligned} L^2 f_l^m &= \hbar^2 l(l+1) f_l^m \\ L_z f_l^m &= \hbar m f_l^m \end{aligned}$$

And it results that:

$$f_l^m = Y_l^m(\theta, \phi)$$

Finally, if $L_{\pm} f_l^m = (A_l^m) f_l^{m\pm 1}$ and we want it normalized, then we must have specific values of A :

$$L_{\pm} f_l^m = \hbar \sqrt{(l \mp m)(l \pm m + 1)} f_l^m$$

When we measure a particle and get an specific L_z and L^2 , we get specific values, and this makes the particle to change into the state f_l^m .

- 14) **Spin:** Spin is a intrinsic angular momentum of particles. The algebraic theory is a copy to that of \vec{L} .

We represent by \vec{S} the spin vector, and as before, it has the properties:

$$\begin{aligned} [S_x, S_y] &= i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y \\ [S^2, S_x] &= [S^2, S_y] = [S^2, S_z] = 0 \\ S_{\pm} &:= S_x \pm iS_y \\ [S_z, S_{\pm}] &= \pm S_{\pm}, \quad [S^2, S_{\pm}] = 0 \end{aligned}$$

We will get the same results as with angular momentum. So we define $|sm\rangle$ as the state of a particle with quantum numbers s, m .

Where the values of s, m are:

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots, \quad m = -s, -s+1, \dots, s-1, s$$

The theory leads as before to:

$$\begin{aligned} S^2 |sm\rangle &= \hbar^2 s(s+1) |sm\rangle, \quad S_z |sm\rangle = \hbar m |sm\rangle \\ S_{\pm} |sm\rangle &= \hbar \sqrt{s(s+1) - m(m \pm 1)} |s(m \pm 1)\rangle \end{aligned}$$

The value of s is immutable for each type of particle and is called the **spin**.

15) Spin 1/2

This is the spin of ordinary matter. We have two options: **spin up**: $|sm\rangle = |\frac{1}{2}, \frac{1}{2}\rangle$ which we represent with χ_+ and **spin down** $|sm\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle$ which we represent with χ_- . To represent a specific spin state, we use an ordered pair:

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} , \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

A general **spinor** is of the form:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-$$

These coordinates are in the 'z-space'.

All we need for the spin state of a 1/2 spin particle are the numbers a and b.

Spin Operators: The spin operators in this case are 2x2 matrices. As before, given a state $|sm\rangle$, the operator helps us find the expected value.

- **S^2 operator:** By definition, it has eigenstates χ_+ , χ_- with eigenvalue $s(s+1)\hbar^2$:

$$S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+ , \quad S^2\chi_- = \frac{3}{4}\hbar^2\chi_-$$

So we find that in the coordinates used earlier:

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

- **S_z operator:** The eigenstates are the same but with eigenvalues $m\hbar$ for $m = -1/2$ and $m = 1/2$:

$$S_z\chi_+ = \frac{\hbar}{2}\chi_+ , \quad S_z\chi_- = -\frac{\hbar}{2}\chi_-$$

So:

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

- **Operators S_+ , S_- :**

$$S_+\chi_- = \hbar\chi_+ , \quad S_-\chi_+ = \hbar\chi_- , \quad S_+\chi_+ = S_-\chi_- = 0$$

So:

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} , \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

- **Operators** S_x, S_y :

We know $S_{\pm} = S_x \pm iS_y$, so we can write $S_x = \frac{1}{2}(S_+ + S_-)$, $S_y = \frac{1}{2i}(S_+ - S_-)$. So:

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

The eigenspinors of S_x turn out to be:

$$\chi_+^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \quad \text{e. val} = \frac{\hbar}{2}, \quad \chi_-^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}, \quad \text{e. val} = -\frac{\hbar}{2}$$

- So we define the **Pauli matrices** without the factor $\hbar/2$:

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

The generic spinor is $\begin{pmatrix} a \\ b \end{pmatrix}$ that can be written as:

$$\chi = a\chi_+ + b\chi_- = \left(\frac{a+b}{\sqrt{2}}\right) \chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}}\right) \chi_-^{(x)}$$

So if we measure S_x , the probability of getting $\hbar/2$ is $(1/2)|a+b|^2$ and the probability of $-\hbar/2$ is $(1/2)|a-b|^2$.

If a particle is in state $\chi = \begin{pmatrix} a \\ b \end{pmatrix}$, then the expected value of S_x, S^2, S_y, S_z are:

- $\langle S_x \rangle = \chi^T S_x \chi$
- $\langle S_y \rangle = \chi^T S_y \chi$
- $\langle S_z \rangle = \chi^T S_z \chi$
- $\langle S^2 \rangle = \chi^T S^2 \chi$

when we measure a quantity like S_z or S^2 , we are bound to get an eigenvalue of it, and the particle takes now the eigenstate. The probability of getting this response is given by the square of the component of this state in the original state of the particle.

After the measurement, the particle takes the new state (say spin up or spin down in this case) and we are free to measure something else starting from this new state.

16) Electron in Magnetic Field

A spinning particle constitutes a magnetic dipole with **moment**:

$$\vec{\mu} = \gamma \vec{S}$$

And when put in a magnetic field \vec{B} , it has an energy:

$$H = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{B} \cdot \vec{S}$$

Larmor Precession:

If we have a particle of spin 1/2 at rest in a uniform electric field $\vec{B} = B_0 \hat{k}$, the Hamiltonian is:

$$\hat{H} = -\gamma B_0 \hat{S}_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The eigenstates are the same than those of S_z :

$$\begin{aligned} \chi_+, \text{ with energy } E_+ &= -(\gamma B_0 \hbar)/2 \\ \chi_- \text{ with energy } E_- &= (\gamma B_0 \hbar)/2 \end{aligned}$$

The general solution is still $i\hbar \frac{\partial \chi}{\partial t} = \hat{H}\chi$ and can be written as:

$$\chi(t) = a\chi_+ e^{iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar} = \begin{pmatrix} ae^{i\gamma B_0 t/2} \\ be^{-i\gamma B_0 t/2} \end{pmatrix}$$

Where the constants a, b are found with the initial conditions: $\chi(0) = \begin{pmatrix} a \\ b \end{pmatrix}$, of course $|a|^2 + |b|^2 = 1$. In general we can write $a = \cos(\alpha/2)$, $b = \sin(\alpha/2)$. Thus:

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix}$$

We can calculate the expectation values:

- $\langle S_x \rangle = \chi(t)^T S_x \chi(t) = \dots = \frac{\hbar}{2} \sin \alpha \cos(\gamma B_0 t)$
- $\langle S_y \rangle = \chi(t)^T S_y \chi(t) = \dots = -\frac{\hbar}{2} \sin \alpha \sin(\gamma B_0 t)$
- $\langle S_z \rangle = \chi(t)^T S_z \chi(t) = \dots = -\frac{\hbar}{2} \cos \alpha$

Evidently, $\langle \vec{S} \rangle$ is tilted at a constant angle α from the z axis and precesses about the field at the **Larmor Freq**:

$$\omega = \gamma B_0$$

- 17) Suppose now we have two spin 1/2 particles. Then we have four possibilities for the spin:

$$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$$

Where the first is the electron and the second the proton. The total angular momentum is:

$$\vec{S} = \vec{S}^{(1)} + \vec{S}^{(2)}$$

Suppose we want to measure the total z component of the pair, where the first particle is in state χ_1 and the second in χ_2 . Then, the complete state of the pair is $\chi_1\chi_2$.

The S_z component for each particle can be $m_1 = -\frac{1}{2}\hbar, \frac{1}{2}\hbar$ and $m_2 = -\frac{1}{2}\hbar, \frac{1}{2}\hbar$. And the complete S_z component is $m\hbar = (m_1 + m_2)\hbar$

There are four possible eigen states for the complete pair:

- $\uparrow\uparrow: m = 1$
- $\uparrow\downarrow: m = 0$
- $\downarrow\uparrow: m = 0$
- $\downarrow\downarrow: m = -1$

For the complete pair, treating it as a single thing, m is supposed to go from $-s$ to s so it appears that $s = 1$ (s is the total spin). But there is an extra state with $m = 0$. But if we apply the S_- operator to $\uparrow\uparrow$, we get $\hbar(\downarrow\uparrow + \uparrow\downarrow)$.

- $s = 1$ (triplet):

We have three possibilities for $m = 0, -1, 1$:

- $|11\rangle = \uparrow\uparrow$
- $|10\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$
- $|1-1\rangle = \downarrow\downarrow$

We propose these three states because of the earlier discovery that $S_-(\uparrow\uparrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow)$

- $s = 0$ (singlet):

We have just one possibility for $m = 0$:

- $|00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

We write this one because applying the raising or lowering operator gives 0.

So the combination of two spin-1/2 particles $|s_1 m_1\rangle$ and $|s_2 m_2\rangle$ can carry a total spin of $s = 1, 0$ depending on whether they occupy the triplet or the singlet.

To confirm this, it can be proven that the triplet states are eigenvectors of $S^2 = (\vec{S}^{(1)} + \vec{S}^{(2)}) \cdot (\vec{S}^{(1)} + \vec{S}^{(2)})$ with eigenvalue 0.

Similarly, we can prove that $|00\rangle$ is a eigenstate of S^2 with eigenvalue 0.

In general, to combine a particle of spin s_1 and one with s_2 , we can get total spins $(s_1 + s_2)$ to $(s_1 - s_2)$ (if $s_1 > s_2$).

The highest total spin happens when the individual spins are aligned.

The combined state $|sm\rangle$ with total spin s and z -component m will be a linear combination of the composite states $|s_1m_1\rangle|s_2m_2\rangle$:

$$|sm\rangle = \sum_{m_1+m_2=m} C_{m_1m_2m}^{s_1s_2s} |s_1m_1\rangle|s_2m_2\rangle$$

Or the other way around:

$$|s_1m_1\rangle|s_2m_2\rangle = \sum_s C_{m_1m_2m}^{s_1s_2s} |sm\rangle$$

18) Two Particle System

the complete wave function is $\Psi(\vec{r}_1, \vec{r}_2, t)$ and $|\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d^3\vec{r}_1 d^3\vec{r}_2$ gives the probability of finding the particle 1 in $d^3\vec{r}_1$ and particle 2 in $d^3\vec{r}_2$.

The Schrodinger equation is:

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

Where:

$$H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t)$$

We can use separation of variables $\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2)f(t)$, we fine $f(t)$ easily. For a stationary state:

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2)e^{-iEt/\hbar}$$

Where the spatial wave function is obtained from the time independent Schrodinger:

$$-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi$$

If particle 1 is in the (one-particle) state $\psi_a(\vec{r})$ and particle 2 in the one particle state $\psi_b(\vec{r})$. In that case, $\psi(\vec{r}_1, \vec{r}_2)$ is a simple product:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$

Of course, this assumes that we can tell the particles apart.

Types of particles:

- **Distinguishable:**

We have a particle 1 in state $\psi_a(\vec{r}_1)$ and particle 2 in state $\psi_b(\vec{r}_2)$, then the complete state for both particles is:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$

- **Indistinguishable:**

One particle is in state ψ_a and the other in state ψ_b , but they are indistinguishable, meaning the result shouldn't change if we interchange the particles. ψ should at most change sign in the interchange. So:

$$\psi_{\pm}(\vec{r}_1, \vec{r}_2) = [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)]$$

- **Boson:** We use the plus sign, so:

$$\psi_+(\vec{r}_1, \vec{r}_2) = \psi_+(\vec{r}_2, \vec{r}_1)$$

All particles with integer spin are bosons

- **Fermion:** We use the minus sign:

$$\psi_-(\vec{r}_1, \vec{r}_2) = -\psi_-(\vec{r}_2, \vec{r}_1)$$

All particles with half integer spin are fermions.

Pauli Exclusion: Two identical fermions cannot occupy the same state. For if $\psi_a = \psi_b \Rightarrow \psi_- = 0$

Simmetrization Requirement: For identical particles, the complete wave function is required to satisfy:

$$\psi(\vec{r}_1, \vec{r}_2) = \pm\psi(\vec{r}_2, \vec{r}_1)$$

With + for boson and - for fermion.

19) Exchange Forces

Suppose one particle is in state ψ_a and the other in state ψ_b , they are normalized and orthogonal. So, the complete normalized wave function is:

- **Distinguishable:**

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$$

- **Boson:**

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)]$$

- **Fermions:**

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)]$$

We can calculate $\langle(x_1 - x_2)^2\rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$ the expected square distance between the particles. We get:

- **Distinguishable particles:**

$$\langle(x_1 - x_2)^2\rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$$

- **Bosons:**

$$\langle(x_1 - x_2)^2\rangle_+ = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b - 2|\langle x \rangle_{ab}|^2$$

- **Fermions:**

$$\langle(x_1 - x_2)^2\rangle_- = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b + 2|\langle x \rangle_{ab}|^2$$

Where $\langle x \rangle_{ab} = \int x \psi_a(x)^* \psi_b(x) dx$.

So:

$$\langle(\Delta x)^2\rangle_{\pm} = \langle(\Delta x)^2\rangle_d \mp 2|\langle x \rangle_{ab}|^2$$

So, bosons tend to be closer together than distinguishable and fermions tend to be farther apart.

Notice that $\langle x \rangle_{ab}$ vanishes unless the two wave functions actually overlap.

So if the two particles are far away, it won't make any difference.

If the particles are close, the system acts as if there were some attraction between bosons and repulsion for fermions.

Actually, the complete state is $\psi(\vec{r})\chi(\vec{s})$. So, the evenness or oddness of the wave function depends on both parts.

The singlet combination for spin is antisymmetric, so if ψ is antisymmetric too, the product is symmetric.

- 20) **Atoms:** A neutral atom of number Z, consists of a heavy nucleus of charge Ze and Z electrons. The hamiltonian is:

$$\hat{H} = \sum_{j=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right] + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

The problem to solve is:

$$\hat{H}\psi = E\psi$$

Only solutions in which the complete state:

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z)\chi(\vec{s}_1, \vec{s}_2, \dots, \vec{s}_Z)$$

are antisymmetric are allowed.

21) Solids

The Free Electron Gas:

It is a rectangular object of dimensions l_x, l_y, l_z where the potential is 0 inside and ∞ outside.

We are to solve the Schrodinger independent equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi$$

Which has solutions:

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right)$$

And the allowed energies are:

$$E_{n_x n_y n_z} = \frac{\hbar^2 k^2}{2m}$$

Where k is the magnitude of $\vec{k} = (k_x, k_y, k_z)$.

Where $k_x = n\pi/l_x$, $k_y = n\pi/l_y$, $k_z = n\pi/l_z$.

In the k-space, if we put planes at $k_x = n\pi/l_x$, $k_y = n\pi/l_y$, $k_z = n\pi/l_z$, then each intersection point symbolizes a stationary state. Each state then occupies a volume:

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$$

Where $V = l_x l_y l_z$

Total Energy: Suppose we have N atoms in the gas with q electrons each. The total energy is calculated as follows: in the k-space, an octant shell of thickness dk has a volume $\frac{1}{8}4\pi k^2 dk = \frac{1}{2}\pi k^2 dk$. So the number of electron state in the shell is the volume of the shell divided by the volume of each state times 2 (each state has 2 electrons because of spin):

$$\text{number of states in shell} = \frac{2[(1/2)\pi k^2 dk]}{\pi^3/V} = \frac{V}{\pi^2} k^2 dk$$

Each of these states has an energy $\hbar^2 k^2 / 2m$, so the energy of the shell is:

$$dE = \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk$$

The total energy is obtained by integrating this from $k = 0$ to $k = k_f$. As each pair of electrons requires a volume π^3/V (they are fermions, so we cannot have more than two in this volume), the total volume of the octant sphere is $\frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right)$, which should

be equal to the volume of $Nq/2$ states, that is $\frac{Nq}{2} \left(\frac{\pi^3}{V} \right)$. Then we get $k_f = (3\rho\pi^2)^{1/3}$, where $\rho = Nq/V$.

So, the total energy is:

$$E = \frac{\hbar^2(3\pi^2Nq)^{5/3}}{10\pi^2m} V^{-2/3}$$

22) Quantum Statistical mechanics

Fundamental assumption of statistical mechanics: In thermal equilibrium, every distinct state with same total energy E is equally probable.

Consider an arbitrary potential, with allowed energies E_1, E_2, \dots , each one with degeneracies d_1, d_2, \dots (i.e d_n one-particle states with energy E_n).

Suppose we put N particles into this potential, we are interested in the configuration (N_1, N_2, \dots) for which there are N_1 particles in E_1 , N_2 in E_2 , etc.

How many different ways can we achieve this? The answer is $Q(N_1, N_2, \dots)$.

- **Distinguishable:**

There are $\frac{N!d_1^{N_1}}{N_1!(N-N_1)!}$ ways of arranging N_1 distinct particles out of N in the first energy. The same goes for bin 2 (E_2), but now with $N - N_1$ total particles, so $\frac{(N - N_1)!d_2^{N_2}}{N_2!(N - N_1 - N_2)!}$. And so, it results:

$$Q(N_1, N_2, \dots) = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}$$

- **Identical Fermions:**

Because they are identical, it doesn't matter which particles are in which states. There is just one N -particle-state in which a specific set of one-particle-states are occupied. There are $\binom{d_n}{N_n}$ ways to choose the N_n occupied states in the n th bin for identical particles, (where $N_n < d_n$ because fermions), so:

$$Q(N_1, N_2, \dots) = \pi_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}$$

- **Identical Bosons:** There are $\frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$ ways of assigning N_n identical particles in d_n slots with possible repetition. So:

$$Q(N_1, N_2, \dots) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$$

The most probable configuration:

Given N particles with total energy E , all states are equally likely, so the most probable configuration (N_1, N_2, \dots) is the one with maximum ways to get it, maximum $Q(N_1, N_2, \dots)$, subject to the constraints:

$$\sum_{n_1}^{\infty} N_n = N$$

$$\sum_{n=1}^{\infty} N_n E_n = E$$

We can solve the problem of finding said configuration with lagrange multipliers for the function Q (better $\log Q$). And we find that:

- **Distinguishable:**

The most probable configuration is:

$$N_n = d_n e^{-(\alpha + \beta E_n)}$$

Where we can find α, β by using the constraints again.

- **Indistinguishable Fermions:**

The most probable configuration is:

$$N_n = \frac{d_n}{e^{\alpha + \beta E_n} + 1}$$

Where we can find α, β by using the constraints again.

-

- **Indistinguishable Bosons:**

The most probable configuration is:

$$N_n = \frac{d_n - 1}{e^{\alpha + \beta E_n} - 1}$$

Where we can find α, β by using the constraints again.

For a particle gas as the one we saw before, we can get α, β by using the constraints and we find, that $N(\epsilon)$, the number of particles with energy ϵ is

- MB (distinguishable): $N(\epsilon) = d_n e^{(-\epsilon - \mu)/k_B T}$
- FD (Fermions): $N(\epsilon) = \frac{d_n}{e^{(\epsilon - \mu)/k_B T} + 1}$
- MB (Bosons): $N(\epsilon) = \frac{d_n}{e^{(\epsilon - \mu)/k_B T} - 1}$

Nondegenerate Perturbation Theory

General formulation Suppose we have solved the time independent Schrodinger equation for some potential:

$$H^0\psi_n^0 = E_n^0\psi_n^0$$

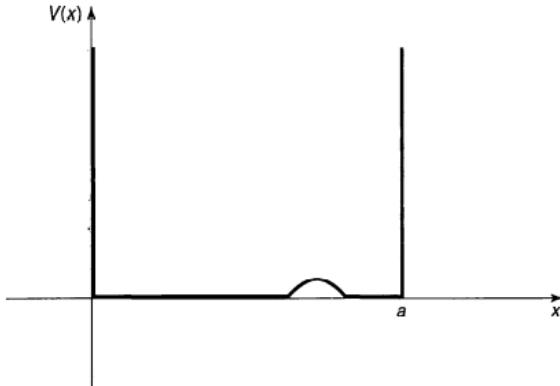
Obtaining a complete set of orthonormal eigenfunctions ψ_n^0 :

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm}$$

And the corresponding eigenvalues E_n^0 .

Now we perturb the potential slightly and we'd like to find the new eigenfunctions and eigenvalues:

$$H\psi_n = E_n\psi_n$$



Perturbation theory is a systematic procedure for obtaining approximate solutions to the perturbed problem by building on the known exact solutions of the unperturbed case.

To begin with, we write the perturbed Hamiltonian as a perturbation from the original:

$$H = H^0 + \lambda H'$$

Where H' is the perturbation. (The superscript 0 always means unperturbed quantity). And H is the true hamiltonian (with the small perturbation added).

The real hamiltonian is $H^0 + H'$, we will solve the problem for small λ and try to crank it up to $\lambda = 1$.

Next, the ψ and E will correct to new perturbed values ψ_n and E_n , we write ψ_n and E_n as a power series in λ :

$$\begin{aligned} \psi_n &= \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots \\ E_n &= E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \end{aligned}$$

Where E_n^1 is the **first order correction** to the nth eigenvalue, and ψ_n^1 is the first order correction to the nth eigenfunction. E_n^2 and ψ_n^2 are the **second order corrections** (not

anything squared).

We plug this into the equation with the perturbed hamiltonian:

$$(H^0 + \lambda H')[\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)[\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots]$$

collecting like powers of λ :

$$\begin{aligned} & H^0\psi_n^0 + \lambda(H^0\psi_n^1 + H'\psi_n^0) + \lambda^2(H^0\psi_n^2 + H'\psi_n^1) + \dots \\ &= E_n^0\psi_n^0 + \lambda(E_n^0\psi_n^1 + E_n^1\psi_n^0) + \lambda^2(E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0) + \dots \end{aligned}$$

To lowest order, this is simply the original $H^0\psi_n^0 = E_n^0\psi_n^0$.

To first order, this is simply:

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

To second order, this is:

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$$

We are done with λ now, it was just a device to keep track of the different orders, so let's crank it up to 1.

First Order Theory

The first order equation is $H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$.

We take the inner product with ψ_n^0 (that is, multiply by $(\psi_n^0)^*$ and integrate), to get:

$$\langle\psi_n^0|H^0\psi_n^1\rangle + \langle\psi_n^0|H'\psi_n^0\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle + E_n^1\langle\psi_n^0|\psi_n^0\rangle$$

But H^0 is hermitian, so:

$$\langle\psi_n^0|H^0\psi_n^1\rangle = \langle H^0\psi_n^0|\psi_n^1\rangle = \langle E_n^0\psi_n^0|\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle$$

And also $\langle\psi_n^0|\psi_n^0\rangle$, so:

$$E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle$$

This is a very important equation.

It says that the first order correction to the energy is the expectation value of the perturbation in the unperturbed state.

Now we try to find the correction to the **wave function**.

We rewrite a equation we had found earlier $(H_0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$, we do some calculations (Griffiths 253) and we actually find:

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{(E_n^0 - E_m^0)} \psi_m^0$$

This is not undefined because $E_n^0 \neq E_m^0$ because the spectrum is **nondegenerate...**

Example 6.1: The unperturbed wave functions of an infinite square well are:

$$\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

Suppose we perturb the system by simply raising the floor of the well by a constant amount V_0 , what is the new energy?

In this case $H' = V_0$, and the first order correction for the energy of the nth state is:

$$E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0$$

So the new energies are approx $E_n \simeq E_n^0 + V_0$ (in this case, this is obvious and actually this new solution is completely right).

Now consider a constant perturbation V_0 but only in the segment $[0, a/2]$ of the square well

So H' is V_0 in $[0, a/2]$ and 0 in $[a/2, a]$

In this case, the correction for the energy is:

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \int_0^a \psi_n^{0*} H' \psi_n^0 = \int_0^{a/2} \psi_n^{0*} \psi_n^0 = \frac{2V_0}{a} \int_0^{a/2} \sin^2\left(\frac{n\pi}{a}x\right) dx = \frac{V_0}{2}$$

So the energy is $E_n \simeq E_n^0 + E_n^1 = E_n^0 + V_0/2$.

This is not the actual exact solution, but it is a reasonable first order approx.

***Problem 6.1** Suppose we put a delta-function bump in the center of the infinite square well:

$$H' = \alpha \delta(x - a/2),$$

where α is a constant.

- (a) Find the first-order correction to the allowed energies. Explain why the energies are not perturbed for even n .
- (b) Find the first three nonzero terms in the expansion (Equation 6.13) of the correction to the ground state, ψ_1^1 .

Problem 6.1

(a)

$$\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), \text{ so } E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \frac{2}{a}\alpha \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) \delta\left(x - \frac{a}{2}\right) dx.$$

$$E_n^1 = \frac{2\alpha}{a} \sin^2\left(\frac{n\pi}{a}\frac{a}{2}\right) = \frac{2\alpha}{a} \sin^2\left(\frac{n\pi}{2}\right) = \begin{cases} 0, & \text{if } n \text{ is even,} \\ 2\alpha/a, & \text{if } n \text{ is odd.} \end{cases}$$

For even n the wave function is zero at the location of the perturbation ($x = a/2$), so it never “feels” H' .

(b) Here $n = 1$, so we need

$$\langle \psi_m^0 | H' | \psi_1^0 \rangle = \frac{2\alpha}{a} \int \sin\left(\frac{m\pi}{a}x\right) \delta\left(x - \frac{a}{2}\right) \sin\left(\frac{\pi}{a}x\right) dx = \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{\pi}{2}\right) = \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right).$$

This is zero for even m , so the first three nonzero terms will be $m = 3$, $m = 5$, and $m = 7$. Meanwhile,

$$E_1^0 - E_m^0 = \frac{\pi^2 \hbar^2}{2ma^2}(1 - m^2), \text{ so}$$

$$\begin{aligned} \psi_1^1 &= \sum_{m=3,5,7,\dots} \frac{(2\alpha/a)\sin(m\pi/2)}{E_1^0 - E_m^0} \psi_m^0 = \frac{2\alpha}{a} \frac{2ma^2}{\pi^2 \hbar^2} \left[\frac{-1}{1-9} \psi_3^0 + \frac{1}{1-25} \psi_5^0 + \frac{-1}{1-49} \psi_7^0 + \dots \right] \\ &= \frac{4m\alpha}{\pi^2 \hbar^2} \sqrt{\frac{2}{a}} \left[\frac{1}{8} \sin\left(\frac{3\pi}{a}x\right) - \frac{1}{24} \sin\left(\frac{5\pi}{a}x\right) + \frac{1}{48} \sin\left(\frac{7\pi}{a}x\right) + \dots \right] \\ &= \frac{m\alpha}{\pi^2 \hbar^2} \sqrt{\frac{a}{2}} \left[\sin\left(\frac{3\pi}{a}x\right) - \frac{1}{3} \sin\left(\frac{5\pi}{a}x\right) + \frac{1}{6} \sin\left(\frac{7\pi}{a}x\right) + \dots \right]. \end{aligned}$$

***Problem 6.2** For the harmonic oscillator [$V(x) = (1/2)kx^2$], the allowed energies are

$$E_n = (n + 1/2)\hbar\omega, \quad (n = 0, 1, 2, \dots),$$

where $\omega = \sqrt{k/m}$ is the classical frequency. Now suppose the spring constant increases slightly: $k \rightarrow (1 + \epsilon)k$. (Perhaps we cool the spring, so it becomes less flexible.)

- (a) Find the *exact* new energies (trivial, in this case). Expand your formula as a power series in ϵ , up to second order.
- (b) Now calculate the first-order perturbation in the energy, using Equation 6.9. What is H' here? Compare your result with part (a). *Hint:* It is not necessary—in fact, it is not *permitted*—to calculate a single integral in doing this problem.

Problem 6.2

(a) $E_n = (n + \frac{1}{2})\hbar\omega'$, where $\omega' \equiv \sqrt{k(1+\epsilon)/m} = \omega\sqrt{1+\epsilon} = \omega(1 + \frac{1}{2}\epsilon - \frac{1}{8}\epsilon^2 + \frac{1}{16}\epsilon^3 \dots)$, so

$$E_n = (n + \frac{1}{2})\hbar\omega\sqrt{1+\epsilon} = (n + \frac{1}{2})\hbar\omega(1 + \frac{1}{2}\epsilon - \frac{1}{8}\epsilon^2 + \dots).$$

(b) $H' = \frac{1}{2}k'x^2 - \frac{1}{2}kx^2 = \frac{1}{2}kx^2(1 + \epsilon - 1) = \epsilon(\frac{1}{2}kx^2) = \epsilon V$, where V is the unperturbed potential energy. So $E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \epsilon \langle n | V | n \rangle$, with $\langle n | V | n \rangle$ the expectation value of the (unperturbed) potential energy in the n^{th} unperturbed state. This is most easily obtained from the virial theorem (Problem 3.31), but it can also be derived algebraically. In this case the virial theorem says $\langle T \rangle = \langle V \rangle$. But $\langle T \rangle + \langle V \rangle = E_n$. So $\langle V \rangle = \frac{1}{2}E_n^0 = \frac{1}{2}(n + \frac{1}{2})\hbar\omega$; $E_n^1 = \frac{\epsilon}{2}(n + \frac{1}{2})\hbar\omega$, which is precisely the ϵ^1 term in the power series from part (a).

In a similar manner, we could get the second order correction to the total energy:

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$$

Degenerate Perturbation Theory

Let's suppose the unperturbed states are degenerate, that is, there are two or more distinct states ψ_a^0, ψ_b^0 that share the same energy. Then, on the equation for $\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0$, the denominator is 0 and it blows up, except if the numerator is also 0.

Two fold degeneracy

Suppose that:

$$H^0 \psi_a^0 = E^0 \psi_a^0, \quad H^0 \psi_b^0 = E^0 \psi_b^0, \quad \langle \psi_a^0 | \psi_b^0 \rangle = 0$$

With ψ_a^0, ψ_b^0 normalized.

Note that any linear combination of these states $\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$ is still an eigenstate of H with value E^0 , $H^0 \psi^0 = E^0 \psi^0$

Typically, the perturbation H' will break the degeneracy.

We want to solve Schrodinger's independent equation:

$$H\psi = E\psi$$

With $H = H^0 + \lambda H'$ and

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \dots, \quad \psi = \psi^0 + \lambda \psi^1 + \lambda^2 \psi^2 + \dots$$

We plug these equations into Schrodinger and take the first order in λ to get:

$$H^0 \psi^1 + H' \psi^0 = E^0 \psi^1 + E^1 \psi^0$$

We take the inner product with ψ_a^0

$$\langle \psi_a^0 | H^0 \psi^1 \rangle + \langle \psi_a^0 | H' \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle$$

Because H^0 is hermitian, the first term on the left cancels the first on the right, and using orthonormality $\langle \psi_a^0 | \psi_b^0 \rangle$, we get:

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1$$

Or more compactly:

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1$$

Where:

$$W_{ij} := \langle \psi_i^0 | H' | \psi_j^0 \rangle \quad (i, j = a, b)$$

Similarly, had we done the inner product with ψ_b^0 , we would have gotten:

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1$$

Notice that the W elements are known, they are the matrix elements of H' with respect to the unperturbed wave functions.

If we play around with both equations, and noting that $W_{ba} = W_{ab}^*$, we get that:

$$E'_\pm = \frac{1}{2} \left(W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right)$$

Theorem: Let A be a hermitian operator that commutes with H^0 and H' . If ψ_a^0, ψ_b^0 (the degenerate eigenfunctions of H^0) are also eigenfunctions of A , with distinct eigenvalues:

$$A\psi_a^0 = \mu\psi_a^0 \quad , \quad A\psi_b^0 = \nu\psi_b^0 \quad (\mu \neq \nu)$$

Then $W_{ab} = 0$.

And therefore, the correction to the energies are:

$$\begin{aligned} E_+^1 &= W_{aa} = \langle \psi_a^0 | H' | \psi_a^0 \rangle \\ E_-^1 &= W_{bb} = \langle \psi_b^0 | H' | \psi_b^0 \rangle \end{aligned}$$

Moral: If you're faced with degenerate states, look for a hermitian operator A that commutes with H^0 and H' ; pick as your unperturbed states ones that are simultaneously eigenfunctions of H^0 and A .

The use **ordinary** first order perturbation theory to get the corrections of the energy.

Higher Order Degeneracy

Realize that we can rewrite the equations we had for two fold as:

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

So E^1 is nothing but the eigenvalues of the W matrix, where $W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle$

Example 6.2: Consider the 3D infinite cubical well

$$V(x, y, z) = \begin{cases} 0 & , \text{ si } 0 < x < a, 0 < y < a, 0 < z < a \\ \infty & \text{cc} \end{cases}$$

The stationary states are:

$$\psi_{n_x n_y n_z}^0(x, y, z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a}x\right) \sin\left(\frac{n_y \pi}{a}y\right) \sin\left(\frac{n_z \pi}{a}z\right)$$

The corresponding allowed energies, are:

$$E_{n_x n_y n_z}^0 = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$

Notice that the ground state ψ_{111} is nondegenerate, its energy is $E_0^0 := 3 \frac{\pi^2 \hbar^2}{2ma^2}$

But for example, the first excited state is (triply) degenerate:

$$\psi_a = \psi_{112}, \psi_b = \psi_{121}, \psi_c = \psi_{211}$$

All share the same energy $E_1^0 := \frac{3\pi^2 \hbar^2}{ma^2}$

Now we introduce the perturbation:

$$H' = \begin{cases} V_0 & , 0 < x < a/2 \ y \ 0 < y < a/2 \\ 0 & , \text{cc} \end{cases}$$

These raises the potential by an amount V_0 in one quarter of the box. The first order correction to the ground state energy is simply (non degenerate):

$$\begin{aligned} E_0^1 &= \langle \psi_{111} | H' | \psi_{111} \rangle \\ &= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx \int_0^{a/2} \sin^2\left(\frac{\pi}{a}y\right) dy \int_0^a \sin^2\left(\frac{\pi}{a}z\right) dz \\ &= \frac{1}{4} V_0 \end{aligned}$$

So the total corrected energy is the original energy plus $\frac{1}{4}V_0$.

For the first excited state (three degeneracy), we need the full machinery of the matrix W .

You can check for yourself that: $W_{aa} = \langle \psi_a^0 | H' | \psi_a^0 \rangle = \dots = \frac{1}{4}V_0$

And similarly:

$$W_{aa} = W_{bb} = W_{cc} = \frac{1}{4}V_0$$

The off diagonal elements are more interesting:

$$W_{ab} = \langle \psi_a^0 | H' | \psi_b^0 \rangle = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx \int_0^{a/2} \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}y\right) dy \int_0^a \sin\left(\frac{2\pi}{a}z\right) \sin\left(\frac{\pi}{a}z\right) dz = 0$$

So $W_{ab} = W_{ac} = 0$

But the other terms aren't 0, in general, we get:

$$W = \frac{V_0}{4} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & k \\ 0 & k & 1 \end{pmatrix}$$

Where $k = (8/3\pi)^2$

The eigenvalues of W can be found to be:

$$w_1 = 1; \quad w_2 = 1 + k; \quad w_3 = 1 - k$$

Then, to first order in λ , the new energies are:

$$E_1(\lambda) = \begin{cases} E_1^0 + \lambda V_0 / 4 \\ E_1^0 + \lambda(1+k) V_0 / 4 \\ E_1^0 + \lambda(1-k) V_0 / 4 \end{cases}$$

Meanwhile, the good unperturbed states are linear combinations of the form:

$$\psi^0 = \alpha \psi_a + \beta \psi_b + \gamma \psi_c$$

Where the coefficients from the eigenvectors of the matrix W :

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & k \\ 0 & k & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

For $w = 1$ we get $\alpha = 1, \beta = \gamma = 0$

For $w = 1 \pm k$ we get $\alpha = 0, \beta = \pm \gamma = 1/\sqrt{2}$.

Thus, the 'good' states are:

$$\psi^0 = \begin{cases} \psi_a \\ (\psi_b + \psi_c)/\sqrt{2} \\ (\psi_b - \psi_c)/\sqrt{2} \end{cases}$$

Fine structure of Hydrogen

The hamiltonian is:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \frac{1}{r}$$

As a first correction, we can replace the mass m by the reduce mass to account for the motion of the nucleus.

Another correction is the **fine structure**, which is actually due to a relativistic correction and a spin orbit coupling.

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137,036}$$

Is the **fine structure constant**. This is a correction to the energy, which is much less than the Bohr energy.

We can also make a further correction, of smaller order called the lamb shift and then the Hyperfine structure.

The relativistic correction

The first term in the hamiltonian is supposed to represent kinetic energy:

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$$

But this is the classical kinetic energy, if we take a relativistic one, we find:

$$T = (\gamma - 1)mc^2 = \frac{mc^2}{\sqrt{1 - (v/c)^2}} - mc^2$$

The first term γmc^2 is the total relativistic (non potential) energy and we substract the mc^2 rest energy to get only the kinetic energy.

We can also use that $E^2 = p^2c^2 + m^2c^4$, square root and then take away the rest energy, so that we find an expression of T in terms of p :

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

We can expand it using taylor:

$$T = mc^2 \left(\sqrt{1 + \left(\frac{p}{mc} \right)^2} - 1 \right) = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots$$

So, the lowest order correction to the hamiltonian is $H'_r = -\frac{p^4}{8m^3c^2}$

In first order perturbation theory, the correction to E_n is the expectation value of H in the unperturbed state:

$$E_r^1 = \langle H'_r \rangle = \langle \psi_n | H'_r \psi \rangle = -\frac{1}{8m^3c^2} \langle \psi | p^4 \psi \rangle = -\frac{1}{8m^3c^2} \langle p^2 \psi | p^2 \psi \rangle$$

Now, the Schrodinger equation for the unperturbed state says:

$$p^2 \psi = 2m(E - V)\psi$$

And hence:

$$E_r^1 = -\frac{1}{2mc^2} \langle (E - V)^2 \rangle = -\frac{1}{2mc^2} [E^2 - E\langle V \rangle + \langle V^2 \rangle]$$

We are interested in hydrogen, for which $V(r) = -(1/4\pi\epsilon_0)e^2/r$:

$$E_r^1 = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \langle \frac{1}{r} \rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \langle \frac{1}{r^2} \rangle \right]$$

Where E_n is the unperturbed energy. To complete the job, we need the expectation values of $1/r$, $1/r^2$ for state ψ_{nlm} . The first is easy:

$$\langle \frac{1}{r} \rangle = \frac{1}{n^2 a}$$

Where a is the Bohr radius, and the second one can be found to be:

$$\langle \frac{1}{r^2} \rangle = \frac{1}{(l+1/2)n^3 a^2}$$

It then follows that:

$$E_r^1 = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a} + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{(l+1/2)n^3 a^2} \right]$$

Or eliminating a using the expression in terms of E_n , we get:

$$E_r^1 = -\frac{(E_n)^2}{2mc^2} \left[\frac{4n}{l+1/2} - 3 \right]$$

Evidently the relativistic correction is smaller than E_n , by a factor of about $E_n/mc^2 = 2 \times 10^{-5}$.

You might have noticed that I used *nondegenerate* perturbation theory in this calculation (Equation 6.51), in spite of the fact that the hydrogen atom is highly degenerate. But the perturbation is spherically symmetrical, so it commutes with L^2 and L_z . Moreover, the eigenfunctions of these operators (taken together) have distinct eigenvalues for the n^2 states with a given E_n . Luckily, then, the wave functions ψ_{nlm} are the “good” states for this problem (or, as we say, n , l , and m are the **good quantum numbers**), so as it happens the use of nondegenerate perturbation theory was legitimate (see the “Moral” to Section 6.2.1).

Spin Orbit Coupling

From the point of view of the electron, it sees the nucleus going around it and that creates a field \vec{B} . This field \vec{B} tends to align the moment $\vec{\mu}$ along the direction of the field. The hamiltonian of this is:

$$H = -\vec{\mu} \cdot \vec{B}$$

The magnetic field of the proton is $B = \frac{\mu_0 I}{2r}$ with an effective current $I = e/T$ with T the period of the orbit.

On the other hand, the orbital angular momentum of the electron (in the rest frame of the nucleus) is $L = rmv = 2\pi mr^2 T$.

Moreover, \vec{B}, \vec{L} point in the same direction, so:

$$\vec{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \vec{L}$$

Magnetic dipole moment of the electron: The magnetic dipole moment of a spinning charge is related to its spin angular momentum. The proportionality factor is the **gyromagnetic ratio**.

Lets derive it.

Consider first a charge q smeared out around a ring of radius r , which rotates about the axis at period T . The magnetic moment of the ring is defined as Ia :

$$\mu = \frac{q\pi r^2}{T}$$

If the mass of the ring is m , the angular momentum is the moment of inertia mr^2 times the angular velocity $2\pi/T$:

$$S = \frac{2\pi mr^2}{T}$$

Therefore, the **gyromagnetic ratio** is $\mu/S = q/2m$

It is independent of r, T , so for a more complicated object, we can divide it in rings and sum them up, using that the ratio is the same in each of them.

$$\vec{\mu} = \frac{q}{2m} \vec{S}$$

That was purely classical.

However, it turns out that the ratio is twice this one, that is, actually:

$$\vec{\mu}_e = -\frac{e}{m} \vec{S}$$

The extra factor of 2 was explained by Dirac in his relativistic theory.

Putting all of this together, we have that:

$$H = \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

But this isn't actually right, we need to add the following:

$$H'_{SO} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

The total angular momentum is:

$$\vec{J} := \vec{L} + \vec{S}$$

And therefore:

$$J^2 = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S}) = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$$

$$\text{So } \vec{L} \cdot \vec{S} = \frac{1}{2}(J^2 - L^2 - S^2)$$

And therefore, the eigenvalues of $\vec{L} \cdot \vec{S}$ are:

$$\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]$$

In this case of course, $s = 1/2$. Meanwhile, the expectation value of $1/r^3$ is:

$$\langle \frac{1}{r^3} \rangle = \frac{1}{l(l+1/2)(l+1)n^3 a^3}$$

And we conclude that:

$$E_{SO}^1 = \langle H'_{SO} \rangle = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c^2} \frac{(\hbar^2/2)[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)n^3 a^3}$$

And so:

$$E_{SO}^1 = \frac{(E_n)^2}{mc^2} \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)}$$

We can also add the relativistic correction to this spin-orbit one, so we get the complete fine structure formula:

$$E_{fs}^1 = \frac{(E_n)^2}{2mc^2} \left(3 - \frac{4n}{j+1/2} \right)$$

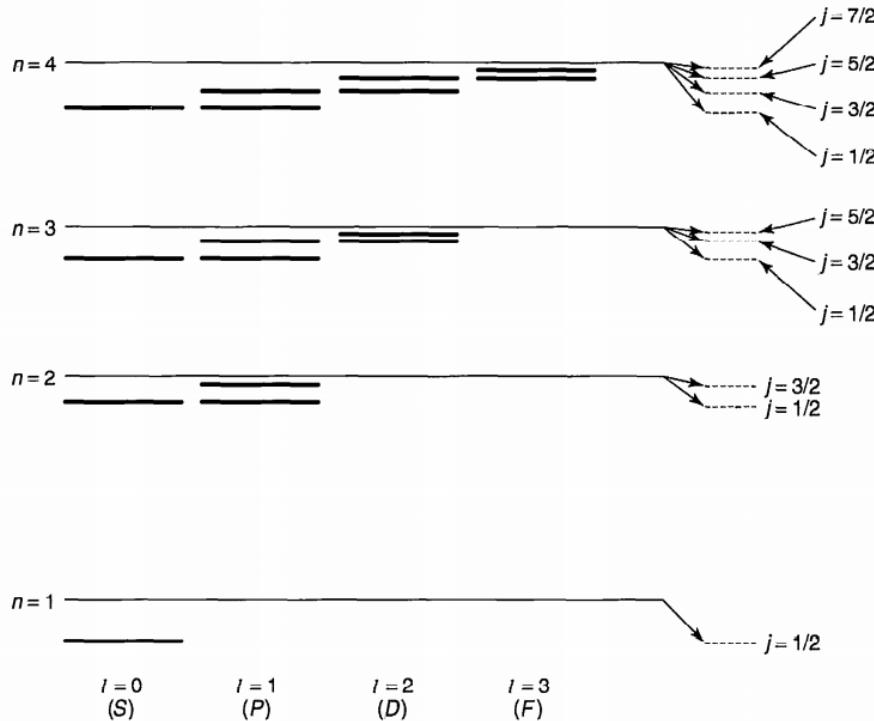


FIGURE 6.9: Energy levels of hydrogen, including fine structure (not to scale).

Combining this with Bohr's formula, we get the grand result for levels of energy of hydrogen:

$$E_{nj} = -\frac{13,6 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right]$$

Zeeman Effect

When an atom is placed in a uniform magnetic field \vec{B}_{ext} , the energy levels are shifted. This is the **zeeman effect**.

For a single electron, the perturbation is a new hamiltonian:

$$H'_Z = -(\vec{\mu}_l + \vec{\mu}_S) \cdot \vec{B}_{ext}$$

Where:

$$\vec{\mu}_S = -\frac{e}{m} \vec{S}$$

Is the magnetic dipole moment due to electron spin, and

$$\vec{\mu}_l = -\frac{e}{2m} \vec{L}$$

Is the dipole thus to orbital motion. Thus:

$$H'_Z = \frac{e}{2m} (\vec{L} + 2\vec{S}) \cdot \vec{B}_{ext}$$

The effect of Zeeman depends on the strength of the external field in comparison with the internal field that gives rise to the spin orbit coupling.

If $B_{ext} \ll B_{int}$, then fine structure dominates, and H'_Z can be treated as a small perturbation.

While if $B_{ext} \gg B_{int}$, then the Zeeman effect dominates, and the fine structure becomes the perturbation.

Weak Field Zeeman

If $B_{ext} \ll B_{int}$, fine structure dominates.

The zeeman correction to the energy is:

$$E_Z^1 = \langle nljm_l | H'_Z | nljm_j \rangle = \frac{e}{2m} \vec{B}_{ext} \cdot \langle \vec{L} + 2\vec{S} \rangle$$

It turns out that the energy levels are now:

$$-13,6eV(1 + \alpha^2/4) \pm \mu_B B_{ext}$$

Strong Zeeman Effect

If $B_{ext} \gg B_{int}$, the Zeeman effect dominates; with B_{ext} in the z direction. The Zeeman Hamiltonian is:

$$H'_Z = \frac{e}{2m} B_{ext} (L_z + 2S_z)$$

And the 'unperturbed' energies are:

$$E_{nm_lm_s} = -\frac{13,6eV}{n^2} + \mu_B B_{ext} (m_l + 2m_s)$$

The Variational Principle

Theory

Suppose you want to calculate the ground state energy E_{gs} for a system with Hamiltonian H , but we can't solve the time independent Schrodinger equation.

The **Variational principle** will get you an upper bound for E_{gs} .

Pick any normalized function ψ whatsoever, I claim that:

$$E_{gs} \leq \langle \psi | H | \psi \rangle := \langle H \rangle$$

That is, the expectation value of H in the (presumably incorrect) state ψ is certain to overestimate the ground state energy.

Of course, if ψ just happens to be one of the excited states, then obviously $\langle H \rangle$ exceeds E_{gs} , the point is that this holds for any ψ whatsoever.

- **Proof:** Since the (unknown) eigenfunctions of H form a complete set, we can express ψ as a linear combination of them:

$$\psi = \sum c_n \psi_n$$

With $H\psi_n = E_n \psi_n$

Since ψ is normalized, we have that:

$$1 = \langle \psi | \psi \rangle = \left\langle \sum c_m \psi_m \middle| \sum c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2$$

(Assuming the eigenfunctions themselves have been normalized $\langle \psi_m | \psi_n \rangle = \delta_{mn}$.
Meanwhile:

$$\langle H \rangle = \left\langle \sum c_m \psi_m \middle| H \sum c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2$$

But the ground state energy is, by definition, the smallest eigenvalue, so $E_{gs} \leq E_n$ and hence:

$$\langle H \rangle = \sum_n E_n |c_n|^2 \geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$

Example 7.1: Suppose we want to find the ground state energy for the one dimensional harmonic oscillator :

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2$$

We know that the exact answer is $E_{gs} = \frac{1}{2}\hbar\omega$.

We will pick as our 'trial' function the Gaussian:

$$\psi(x) = Ae^{-bx^2}$$

Where b is a constant and A is determined by normalization:

$$1 = |A|^2 \int_{\mathbb{R}} e^{-2bx^2} dx = |A|^2 \sqrt{\frac{\pi}{2b}} \Rightarrow A = \left(\frac{2b}{\pi}\right)^{1/4}$$

Now, $\langle H \rangle = \langle T \rangle + \langle V \rangle$

Where, in this case:

$$\langle T \rangle = -\frac{\hbar^2}{2m}|A|^2 \int_{\mathbb{R}} e^{-bx^2} \frac{d^2}{dx^2}(e^{-bx^2}) dx = \frac{\hbar^2 b}{2m}$$

And:

$$\langle V \rangle = \frac{1}{2}m\omega^2|A|^2 \int_{\mathbb{R}} e^{-2bx^2} x^2 dx = \frac{m\omega^2}{8b}$$

So that:

$$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

According to the theorem, this exceeds E_{gs} for any b . To get the tightest bound, let's minimize $\langle H \rangle$, we find:

$$\frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \Rightarrow b = \frac{m\omega}{2\hbar}$$

Putting this back into H , we find that:

$$\langle H \rangle_{min} = \frac{1}{2}\hbar\omega$$

So we hit the ground state right on the nose, this is a coincidence.

Using the Gaussian as trial is easy even when the real function doesn't have this form.

Example 7.2: Suppose we're looking for the ground state energy of the delta function potential:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - \alpha\delta(x)$$

We already know that the exact answer is: $E_{gs} = -m\alpha^2/2\hbar^2$.

We try again with a normalized Gaussian $\psi(x) = \left(\frac{2b}{\pi}\right)^{1/4} e^{-bx^2}$.

We've already calculated $\langle T \rangle$ before and it is the same now:

$$\langle T \rangle = \frac{\hbar^2 b}{2m}$$

And we need $\langle V \rangle$:

$$\langle V \rangle = -\alpha|A|^2 \int_{\mathbb{R}} e^{-2bx^2} \delta(x) dx = -\alpha \sqrt{\frac{2b}{\pi}}$$

Evidently then:

$$\langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha \sqrt{\frac{2b}{\pi}}$$

We know that this exceeds E_{gs} for all b . Minimizing it,

$$\frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \Rightarrow b = \frac{2m^2\alpha^2}{\pi\hbar^4}$$

So, using Gaussians:

$$\langle H \rangle_{min} = -\frac{m\alpha^2}{\pi\hbar^2}$$

This is indeed less than the somewhat higher $E_{gs} = \frac{-m\alpha^2}{2\hbar^2}$

Discontinuous functions need some care to handle:

Example 7.3: Find an upper bound on the ground state energy of the one dimensional square well, using the 'triangular' trial wave function:

$$\psi(x) = \begin{cases} Ax & , 0 \leq x \leq a/2 \\ A(a-x) & , a/2 \leq x \leq a \\ 0 & cc \end{cases}$$

Where A is determined by normalization to be:

$$A = \frac{2}{a} \sqrt{\frac{3}{a}}$$

The derivative of the triangular trial function is:

$$\frac{d\psi}{dx} = \begin{cases} A & , 0 < x < a/2 \\ -A & , a/2 < x < a \\ 0 & , cc. \end{cases}$$

And the second derivative is:

$$\frac{d^2\psi}{dx^2} = A\delta(x) - 2A\delta(x - a/2) + A\delta(x - a)$$

And hence:

$$\begin{aligned} \langle H \rangle &= \frac{\hbar^2 A}{2m} \int [\delta(x) - 2\delta(x - a/2) + \delta(x - a)]\psi(x)dx \\ &= -\frac{\hbar^2 A}{2m} [\psi(0) - 2\psi(a/2) + \psi(a)] = \frac{\hbar^2 A^2 a}{2m} = \frac{12\hbar^2}{2ma^2} \end{aligned}$$

The exact ground state energy is $E_{gs} = \pi^2 \hbar^2 / 2ma^2$, so the theorem works.

The Ground State of Helium

The Helium atom consists of two electrons in orbit around a proton with two protons. The Hamiltonian is:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)$$

We want the ground state energy E_{gs} .

We can measure experimentally the ionization energy required to remove a single electron, which turns out to be experimentally $-78,975\text{eV}$.

The problem comes from the electron-electron repulsion.

If we ignore this term, H splits into two independent Hamiltonians like Hydrogen each with $2e$, so the wave function for ground state ignoring e-e interaction is:

$$\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$$

But the energy here would be $8E_1 = -109\text{eV}$ which is very different to -79eV .

to get a better approximation, we apply the variational principle using ψ_0 as the trial wave function. This is a good choice because ψ_0 is an eigenfunction of most of the Hamiltonian (all but the $e - e$ potential):

$$H\psi_0 = (KE + 2V_{pe} + V_{ee})\psi_0 = (8E_1 + V_{ee})\psi_0$$

Thus:

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle$$

In this state. Where, in this state:

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a^3} \right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2$$

We do the \vec{r}_2 integral first, letting \vec{r}_1 fixed. By the law of cosines:

$$|\vec{r}_1 - \vec{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}$$

Hence:

$$\begin{aligned} I_2 &:= \int \frac{e^{-4r_2/a}}{|\vec{r}_1 - \vec{r}_2|} d^3r_2 = \int \frac{e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}} r_2^2 \cos \theta_2 dr_2 d\theta_2 d\phi_2 \\ &= \frac{\pi a^3}{8r_1} \left[1 - \left(1 + \frac{2r_1}{a} \right) e^{-4r_1/a} \right] \end{aligned}$$

It follows that $\langle V_{ee} \rangle$ with this state is:

$$\begin{aligned} \langle V_{ee} \rangle &= \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a^3} \right) \int \left[1 - \left(1 + \frac{2r_1}{a} \right) e^{-4r_1/a} \right] e^{4r_1/a} r_1 \sin \theta_1 dr_1 d\theta_1 d\phi_1 \\ &= \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a^3} \right) \frac{5a^2}{128} \\ &= \frac{5}{4a} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5}{2} E_1 = 34eV \end{aligned}$$

And therefore:

$$\langle H \rangle = -109eV + 34eV = -75eV$$

Not bad, considering the good one is $-79eV$

to get a better approximation, we suppose the electron causes a shield of the nucleus. So that the other electron sees an effective nuclear charge Z that is somewhat less than 2. So we use a trial of the form:

$$\psi_1(\vec{r}_1, \vec{r}_2) := \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$$

We will treat Z as the variational parameter, picking the value that minimizes H .

This wave function is an eigenstate of the 'unperturbed' Hamiltonian (the one neglecting e-e interaction), only with Z instead of 2. With this in mind, we rewrite H as follows (H is still the same, but written different):

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)$$

The expectation value of H is evidently:

$$\langle H \rangle = 2Z^2 E_1 + 2(Z - 2) \left(\frac{e^2}{4\pi\epsilon_0} \right) \langle \frac{1}{r} \rangle + \langle V_{ee} \rangle$$

Here $\langle 1/r \rangle$ is the expectation value of $1/r$ in the (one particle) hydrogenic ground state ψ_{100} (but with nuclear charge Z):

$$\langle \frac{1}{r} \rangle = \frac{Z}{a}$$

The expectation value of V_{ee} is the same as before, except that Z is arbitrary instead of 2, so we multiply by $2/Z$:

$$\langle V_{ee} \rangle = \frac{5Z}{8a} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5Z}{4} E_1$$

Putting all this together, we find:

$$\langle H \rangle = [2Z^2 - 4Z(Z - 2) - (5/4)Z]E_1 = [-2Z^2 + (27/4)Z]E_1$$

According to the variational principle, this quantity exceeds E_{gs} for any value of Z . The lowest upper bound occurs when $\langle H \rangle$ is minimized:

$$\frac{d}{dZ} \langle H \rangle = [-4Z + (27/4)]E_1 = 0$$

So that:

$$Z = \frac{27}{16} = 1,69$$

So the effective nuclear charge, taking into account shielding is $Z = 1,69$ instead of 2. Then:

$$\langle H \rangle = \frac{1}{2} \left(\frac{3}{2} \right)^6 E_1 = -77,5 eV$$

Adiabatic Approximation

An adiabatic process is one that happens very slowly. This is the **Adiabatic Approximation**

Adiabatic Theorem: A particle is initially within a Hamiltonian H^i and at the nth eigenstate of this Hamiltonian. If the Hamiltonian is changed adiabatically to H^f , then the particle will be carried into the nth eigenstate of H^f .

(We assume that the spectrum of all the Hamiltonians in the transition are nondegenerate and discrete spectrum).

For example, if we have a system in a infinite square well (distance a) in ground state at state

$$\psi^i(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right)$$

Then we move the wall out to $2a$, then the particle will be still in the ground state:

$$\psi^f(x) = \sqrt{\frac{1}{a}} \sin\left(\frac{\pi}{2a}x\right)$$

This is different of what would happen if we suddenly moved the wall, in which case the system would still be in $\psi^i(x)$, but now this state is a linear combination of the eigenstates of H^f .

Example 10.1: Imagine an electron at rest at the origin in the presence of a magnetic field whose magnitude B_0 is constant but whose direction sweeps out a cone of opening angle α at constant velocity ω :

$$\vec{B}(t) = B_0[\sin \alpha \cos(\omega t)\hat{i} + \sin \alpha \sin(\omega t)\hat{j} + \cos \alpha \hat{k}]$$

The Hamiltonian is:

$$\begin{aligned} H(t) &= \frac{e}{m} \vec{B} \cdot \vec{S} = \frac{e\hbar B_0}{2m} [\sin \alpha \cos(\omega t) \sigma_x + \sin \alpha \sin(\omega t) \sigma_y + \cos \alpha \sigma_z] \\ &= \frac{\hbar \omega_1}{2} \begin{pmatrix} \cos \alpha & e^{-i\omega t} \sin \alpha \\ e^{i\omega t} \sin \alpha & -\cos \alpha \end{pmatrix} \end{aligned}$$

Where $\omega_1 := \frac{eB_0}{m}$

Then, the normalized eigenspinors of $H(t)$ are:

$$\chi_+(t) = \begin{pmatrix} \cos(\alpha/2) \\ e^{i\omega t} \sin(\alpha/2) \end{pmatrix}$$

And

$$\chi_-(t) = \begin{pmatrix} e^{-i\omega t} \sin(\alpha/2) \\ -\cos(\alpha/2) \end{pmatrix}$$

They represent spin up and spin down along the instantaneous direction of $\vec{B}(t)$. The corresponding eigenvalues are:

$$E_{\pm} = \pm \frac{\hbar\omega_1}{2}$$

Suppose the electron starts out with spin up, along $\vec{B}(0)$:

$$\chi(0) = \begin{pmatrix} \cos(\alpha/2) \\ \sin(\alpha/2) \end{pmatrix}$$

The exact solution to the time dependent Schrodinger equation is:

$$\chi(t) = \begin{pmatrix} [\cos(\lambda t/2) - i \frac{(\omega_1 - \omega)}{\lambda} \sin(\lambda t/2)] \cos(\alpha/2) e^{-i\omega t/2} \\ [\cos(\lambda t/2) - i \frac{(\omega_1 + \omega)}{\lambda} \sin(\lambda t/2)] \cos(\alpha/2) e^{+i\omega t/2} \end{pmatrix}$$

Where $\lambda := \sqrt{\omega^2 + \omega_1^2 - 2\omega\omega_1 \cos \alpha}$

Or, expressing it as a linear combination of χ_+ and χ_- :

$$\begin{aligned} \chi(t) &= \left[\cos\left(\frac{\lambda t}{2}\right) - i \frac{(\omega_1 - \omega \cos \alpha)}{\lambda} \sin\left(\frac{\lambda t}{2}\right) \right] e^{-i\omega t/2} \chi_+(t) \\ &\quad + i \left[\frac{\omega}{\lambda} \sin \alpha \sin\left(\frac{\lambda t}{2}\right) \right] e^{+i\omega t/2} \chi_-(t). \end{aligned} \quad [10.33]$$

Evidently the (exact) probability of a transition to spin down (along the current direction of \mathbf{B}) is

$$|\langle \chi(t) | \chi_-(t) \rangle|^2 = \left[\frac{\omega}{\lambda} \sin \alpha \sin\left(\frac{\lambda t}{2}\right) \right]^2. \quad [10.34]$$

The adiabatic theorem says that this transition probability should vanish in the limit $T_e \gg T_i$, where T_e is the characteristic time for changes in the Hamiltonian (in this case, $1/\omega$) and T_i is the characteristic time for changes in the wave function (in this case, $\hbar/(E_+ - E_-) = 1/\omega_1$). Thus the adiabatic approximation means $\omega \ll \omega_1$: The field rotates slowly, in comparison with the phase of the (unperturbed) wave functions. In the adiabatic regime $\lambda \approx \omega_1$, and therefore

$$|\langle \chi(t) | \chi_-(t) \rangle|^2 \cong \left[\frac{\omega}{\omega_1} \sin \alpha \sin\left(\frac{\lambda t}{2}\right) \right]^2 \rightarrow 0, \quad [10.35]$$

as advertised. The magnetic field leads the electron around by its nose, with the spin always pointing in the direction of \mathbf{B} . By contrast, if $\omega \gg \omega_1$ then $\lambda \approx \omega$, and the system bounces back and forth between spin up and spin down (Figure 10.4).

Nonholonomic

A **nonholonomic process** is one that occurs around a closed loop but such that after ending a loop, the system doesn't return to its original state (like a thermodynamic cycle that isn't reversible or transporting a vector around a loop in curved space).

The question is this: What happens to the state of a quantum system after the Hamiltonian is carried adiabatically around a closed cycle?

The Adiabatic theorem says that if a particle starts in the nth eigenstate of $H(0)$, it remains in the nth state of $H(t)$ (carried adiabatically), picking up only a phase factor. Specifically, when proving the theorem, it is seen that:

$$\Psi_n(t) = e^{i[\theta_n(t)+\gamma_n(t)]} \psi_n(t)$$

Where:

$$\theta_n(t) := -\frac{1}{\hbar} \int_0^t E_n(t') dt'$$

Is called the **dynamic phase** (generalizing the usual factor $e^{-iE_n t/\hbar}$ to the case where E_n is a function of time, and:

$$\gamma_n(t) := i \int_0^t \langle \psi_n(t') | \frac{\partial}{\partial t'} \psi_n(t') \rangle dt'$$

is called the **Geometric phase**

Now, $\psi_n(t)$ depends on t because the Hamiltonian has some parameter R that depends on t , $R(t)$ (for example, the width of a the expanding square well). Thus:

$$\frac{\partial \psi_n}{\partial t} = \frac{\partial \psi_n}{\partial R} \frac{dR}{dt}$$

So that:

$$\gamma_n(t) = i \int_0^t \langle \psi_n | \frac{\partial \psi_n}{\partial R} \rangle \frac{dR}{dt} dt' = i \int_{R_i}^{R_f} \langle \psi_n | \frac{\partial \psi_n}{\partial R} \rangle dR$$

Where R_i, R_f are the initial and final values of R .

We can see that if the route is a cycle of period T , then $R_i = R_f$ and the integral is 0, $\gamma(T) = 0$.

However, if there are many parameters changing, $R_1(t), R_2(t), \dots, R_N(t)$, then:

$$\frac{\partial \psi_n}{\partial t} = \sum \frac{\partial \psi_n}{\partial R_i} \frac{dR_i}{dt} = (\nabla_R \psi_n) \cdot \frac{d\vec{R}}{dt}$$

Where $\vec{R} := (R_1, \dots, R_n)$

This time we have:

$$\gamma_n(t) = i \int_{\vec{R}_i}^{\vec{R}_f} \langle \psi_n | \nabla_R \psi_n \rangle \cdot d\vec{R}$$

And if the Hamiltonian returns to its original state after a time T , the net geometric phase change is:

$$\boxed{\gamma_n(T) = i \oint \langle \psi_n | \nabla_R \psi_n \rangle \cdot d\vec{R}}$$

This is a line integral around a closed loop in parameter space, and is not generally 0. This is called the **Berry Phase**

Notice that $\gamma_n(T)$ depends only on the path taken but not on the speed (as long as it is slowly enough to be adiabatic)

We tend to assume that the only important thing is $|\Psi|^2$, so that the phase cancels out and is not important and the initial phase of $\psi_n(t)$ is actually arbitrary.

However Berry discovered that the difference in phase at the beginning and end of a cycle is not arbitrary, and can actually be measured.

for example, suppose we take a beam of particles (all in state Ψ) and split it in two. One beam passes through an adiabatically changing potential while the other does not. When the two beams are recombined, the total wave function has the form:

$$\Psi = \frac{1}{2} \Psi_0 + \frac{1}{2} \Psi_0 e^{i\Gamma}$$

Where Ψ_0 is the direct beam wave function and Γ is the extra phase acquired by a beam going through a varying H . Then:

$$\begin{aligned} |\Psi|^2 &= \frac{1}{4} |\Psi_0|^2 (1 + e^{i\Gamma})(1 + e^{-i\Gamma}) \\ &= \frac{1}{2} |\Psi_0|^2 (1 + \cos \Gamma) = |\Psi_0|^2 \cos^2(\Gamma/2) \end{aligned}$$

So, by looking at the points of constructive and destructive interference (where Γ is an even or odd multiple of π), one can easily measure Γ

An alternate expression for $\gamma_n(\Gamma)$ for dimensions (3 dimensions of \vec{R}) is:

$$\gamma_n(T) = i \int [\nabla_R \times \langle \psi_n | \nabla \psi_n \rangle] \cdot d\vec{a}$$

.

Example:

Example 10.2 The classic example of Berry's phase is an electron at the origin, subjected to a magnetic field of constant magnitude but changing direction. Consider first the special case (analyzed in Example 10.1) in which $\mathbf{B}(t)$ precesses around at a constant angular velocity ω , making a fixed angle α with the z axis. The *exact* solution (for an electron that starts out with “spin up” along \mathbf{B}) is given by Equation 10.33. In the adiabatic regime, $\omega \ll \omega_1$,

$$\lambda = \omega_1 \sqrt{1 - 2 \frac{\omega}{\omega_1} \cos \alpha + \left(\frac{\omega}{\omega_1} \right)^2} \cong \omega_1 \left(1 - \frac{\omega}{\omega_1} \cos \alpha \right) = \omega_1 - \omega \cos \alpha, \quad [10.52]$$

and Equation 10.33 becomes

$$\begin{aligned} \chi(t) &\cong e^{-i\omega_1 t/2} e^{i(\omega \cos \alpha)t/2} e^{-i\omega t/2} \chi_+(t) \\ &+ i \left[\frac{\omega}{\omega_1} \sin \alpha \sin \left(\frac{\omega_1 t}{2} \right) \right] e^{+i\omega t/2} \chi_-(t). \end{aligned} \quad [10.53]$$

As $\omega/\omega_1 \rightarrow 0$ the second term drops out completely, and the result matches the expected adiabatic form (Equation 10.23). The dynamic phase is

$$\theta_+(t) = -\frac{1}{\hbar} \int_0^t E_+(t') dt' = -\frac{\omega_1 t}{2}. \quad [10.54]$$

(where $E_+ = \hbar\omega_1/2$, from Equation 10.29), so the geometric phase is

$$\gamma_+(t) = (\cos \alpha - 1) \frac{\omega t}{2}. \quad [10.55]$$

For a complete cycle $T = 2\pi/\omega$, and therefore Berry's phase is

$$\gamma_+(T) = \pi(\cos \alpha - 1). \quad [10.56]$$

Now consider the more general case, in which the tip of the magnetic field vector sweeps out an *arbitrary* closed curve on the surface of a sphere of radius $r = B_0$ (Figure 10.9). The eigenstate representing spin up along $\mathbf{B}(t)$ has the form (see Problem 4.30):

$$\chi_+ = \begin{pmatrix} \cos(\theta/2) \\ e^{i\phi} \sin(\theta/2) \end{pmatrix}, \quad [10.57]$$

where θ and ϕ (the spherical coordinates of \mathbf{B}) are now *both* functions of time. Looking up the gradient in spherical coordinates, we find

$$\begin{aligned} \nabla \chi_+ &= \frac{\partial \chi_+}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial \chi_+}{\partial \theta} \hat{\theta} + \frac{1}{r \sin \theta} \frac{\partial \chi_+}{\partial \phi} \hat{\phi} \\ &= \frac{1}{r} \begin{pmatrix} -(1/2) \sin(\theta/2) \\ (1/2) e^{i\phi} \cos(\theta/2) \end{pmatrix} \hat{\theta} + \frac{1}{r \sin \theta} \begin{pmatrix} 0 \\ i e^{i\phi} \sin(\theta/2) \end{pmatrix} \hat{\phi}. \end{aligned} \quad [10.58]$$

Hence

$$\begin{aligned} \langle \chi_+ | \nabla \chi_+ \rangle &= \frac{1}{2r} \left[-\sin(\theta/2) \cos(\theta/2) \hat{\theta} + \sin(\theta/2) \cos(\theta/2) \hat{\theta} + 2i \frac{\sin^2(\theta/2)}{\sin \theta} \hat{\phi} \right] \\ &= i \frac{\sin^2(\theta/2)}{r \sin \theta} \hat{\phi}. \end{aligned} \quad [10.59]$$

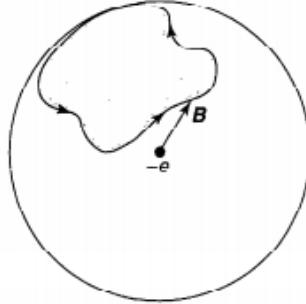


FIGURE 10.9: Magnetic field of constant magnitude but changing direction sweeps out a closed loop.

For Equation 10.51 we need the *curl* of this quantity:

$$\nabla \times (\chi_+ | \nabla \chi_+) = \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \left(\frac{i \sin^2(\theta/2)}{r \sin \theta} \right) \right] \hat{r} = \frac{i}{2r^2} \hat{r}. \quad [10.60]$$

According to Equation 10.51, then,

$$\gamma_+(T) = -\frac{1}{2} \int \frac{1}{r^2} \hat{r} \cdot d\mathbf{a}. \quad [10.61]$$

The integral is over the area on the sphere swept out by \mathbf{B} in the course of the cycle, so $d\mathbf{a} = r^2 d\Omega \hat{r}$, and we conclude that

$$\gamma_+(T) = -\frac{1}{2} \int d\Omega = -\frac{1}{2} \Omega. \quad [10.62]$$

where Ω is the solid angle subtended at the origin. This is a delightfully simple result, and tantalizingly reminiscent of the classical problem with which we began the discussion (transport of a frictionless pendulum around a closed path on the surface of the earth). It says that if you take a magnet, and lead the electron's spin around adiabatically in an arbitrary closed path, the net (geometric) phase change will be minus one-half the solid angle swept out by the magnetic field vector. In view of Equation 10.37, this general result is consistent with the special case (Equation 10.56), as of course it *had* to be.

The Aharonov Bohm Effect

In classical electrodynamics, the potentials ψ, \vec{A} are not directly measured, but they define the fields:

$$\begin{aligned} \vec{E} &= -\nabla \psi - \frac{\partial \vec{A}}{\partial t} \\ \vec{B} &= \nabla \times \vec{A} \end{aligned}$$

The potentials are not references in the fundamental laws of EM and actually, we can change the potentials with impunity without changing the field:

$$\begin{aligned} \psi &\rightarrow \psi' = \psi - \frac{\partial \lambda}{\partial t} \\ \vec{A} &\rightarrow \vec{A}' = \vec{A} + \nabla \lambda \end{aligned}$$

And the fields are still the same. These are called **Gauge transformations**.

However, in QM, the potentials have a more fundamental role, since now H is written in terms of them:

$$H = \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - q \vec{A} \right)^2 + q\psi$$

Nevertheless, it can be proven that the QM theory is still invariant under Gauge transformations.

Aharonov Bohm proved that a particle can fell the effect of potentials even if there is no field.

Example: Imagine a particle is constrained to move in a circle of radius b . Along the axis runs a solenoid of radius $a < b$ carrying a current I .

The magnetic field inside is uniform and outside is zero. But \vec{A} outside is not zero. In fact (adopting the Coulomb gauge $\nabla \cdot \vec{A} = 0$), we get:

$$\vec{A} = \frac{\Phi}{2\pi r} \hat{\phi} \quad (r > a)$$

Where $\Phi = \pi a^2 B$ is the **Magnetic Flux** through the solenoid.

Meanwhile, the solenoid itself is uncharged, so the scalar potential ψ is 0. In this case, the Hamiltonian becomes:

$$H = \frac{1}{2m} \left[-\hbar^2 \nabla^2 + q^2 A^2 + 2i\hbar q \vec{A} \cdot \nabla \right]$$

But the wave function depends only on the azimuthal angle ϕ ($\theta = \pi/2, r = b$), So $\nabla \rightarrow (\hat{\phi}/b)(d/d\phi)$, and the Schrodinger equation reads:

$$\frac{1}{2m} \left[-\frac{\hbar^2}{b^2} \frac{d^2}{d\phi^2} + \left(\frac{q\Phi}{2\pi b} \right)^2 + i\frac{\hbar q\Phi}{\pi b^2} \frac{d}{d\phi} \right] \psi(\phi) = E\psi(\phi)$$

This is a linear equation with constant coefficients:

$$\frac{d^2\psi}{d\phi^2} - 2i\beta \frac{d\psi}{d\phi} + \epsilon\psi = 0$$

Where $\beta := \frac{q\Phi}{2\pi\hbar}$ and $\epsilon := \frac{2mb^2E}{\hbar^2} - \beta^2$.

Solutions are:

$$\psi = Ae^{i\lambda\phi}$$

Where $\lambda = \beta \pm \sqrt{\beta^2 + \epsilon} = \beta \pm \frac{b}{\hbar} \sqrt{2mE}$

Continuity of $\Psi(\phi)$ at $\phi = 2\pi$, requires λ to be an *integer*:

$$\beta \pm \frac{b}{\hbar} \sqrt{2mE} = n$$

And it follows that:

$$E_n = \frac{\hbar^2}{2mb^2} \left(n - \frac{q\Phi}{2\pi\hbar} \right)^2 \quad n = 0, \pm 1, \pm 2, \dots$$

The solenoid lifts the two fold degeneracy of the bead on a ring (problem 2.46):

Positive n : Representing a particle traveling in the same direction as the current in the solenoid, has a somewhat lower energy (assuming q is positive)

Negative n : Describing a particle traveling in the opposite direction.

More importantly, the allowed energies depend on the field inside the solenoid, even though the field at the location of the particle is 0.

Generally

If a particle moves in a region where \vec{B} is zero ($\nabla \times \vec{A} = 0$) but \vec{A} is not zero. The Schrodinger equation is:

$$\left[\frac{1}{2m} \left(\frac{\hbar}{i} \nabla - q\vec{A} \right)^2 + V \right] \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

With the potential V (which may or may not include the electrical contribution $q\phi$)
It can be simplified by writing:

$$\Psi = e^{ig}\Psi'$$

Where:

$$g(\vec{r}) := \frac{q}{\hbar} \int_O^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}'$$

And O is some arbitrary chosen reference point.

This definition makes sense only when $\nabla \times \vec{A} = 0$ throughout the region in question, otherwise the line integral would depend on the path taken from O to \vec{r} , and hence would not define a function of \vec{r} .

In terms of Ψ' , the gradient Ψ is:

$$\nabla\Psi = e^{ig}(i\nabla g)\Psi' + e^{ig}(\nabla\Psi');$$

But $\nabla g = (q/\hbar)\vec{A}$ so that:

$$\left(\frac{\hbar}{i} \nabla - q\vec{A} \right) = \frac{\hbar}{i} e^{ig} \nabla \Psi'$$

And it follows that:

$$\left(\frac{\hbar}{i} \nabla - q\vec{A} \right)^2 \Psi = -\hbar^2 e^{ig} \nabla^2 \Psi'$$

Putting this into the equation , and cancelling the common factor e^{ig} , we are left with:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi' + V \Psi' = i\hbar \frac{\partial \Psi'}{\partial t}$$

Evidently, Ψ' satisfies the Schrodinger equation without \vec{A}

Aharonov and Bohm proposed an experiment in which a beam of electrons is split in two, and passed either side of a long solenoid, before being recombined (Figure 10.11). The beams are kept well away from the solenoid itself, so they encounter only regions where $\mathbf{B} = 0$. But \mathbf{A} , which is given by Equation 10.66, is *not* zero, and (assuming V is the same on both sides), the two beams arrive with *different phases*:

$$g = \frac{q}{\hbar} \int \mathbf{A} \cdot d\mathbf{r} = \frac{q\Phi}{2\pi\hbar} \int \left(\frac{1}{r} \dot{\phi} \right) \cdot (r\dot{\phi} d\phi) = \pm \frac{q\Phi}{2\hbar}. \quad [10.81]$$

The plus sign applies to the electrons traveling in the same direction as \mathbf{A} —which is to say, in the same direction as the current in the solenoid. The beams arrive out

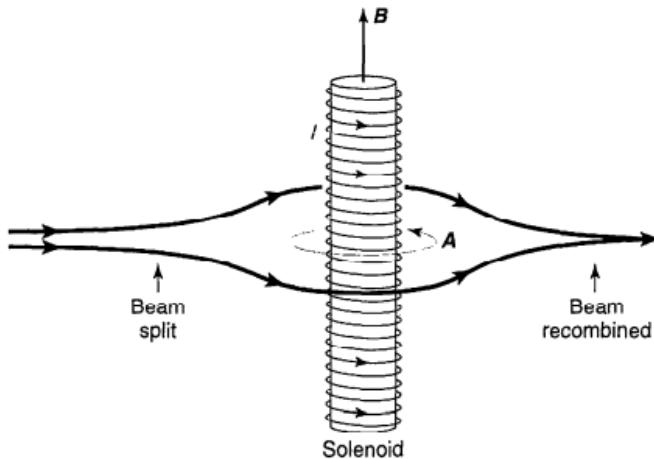


FIGURE 10.11: The Aharonov-Bohm effect: The electron beam splits, with half passing either side of a long solenoid.

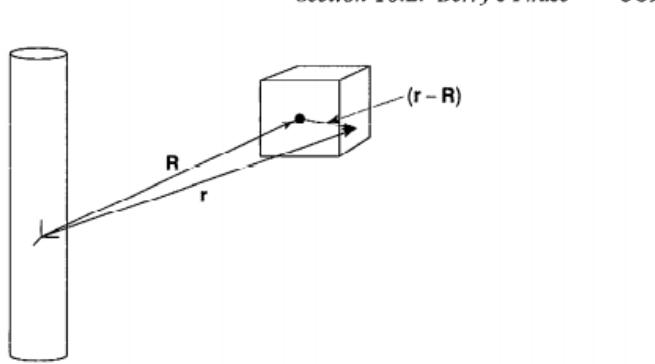


FIGURE 10.12: Particle confined to a box, by a potential $V(\mathbf{r} - \mathbf{R})$.

of phase by an amount proportional to the magnetic flux their paths encircle:

$$\text{phase difference} = \frac{q\Phi}{\hbar}. \quad [10.82]$$

This phase shift leads to measurable interference (Equation 10.47), which has been confirmed experimentally by Chambers and others.¹⁶

As Berry pointed out in his first paper on the subject, the Aharonov-Bohm effect can be regarded as an example of geometric phase. Suppose the charged particle is confined to a box (which is centered at point \mathbf{R} outside the solenoid) by a potential $V(\mathbf{r} - \mathbf{R})$ —see Figure 10.12. (In a moment we’re going to transport the box around the solenoid, so \mathbf{R} will become a function of time, but for now it is just some fixed vector.) The eigenfunctions of the Hamiltonian are determined by

$$\left\{ \frac{1}{2m} \left[\frac{\hbar}{i} \nabla - q \mathbf{A}(\mathbf{r}) \right]^2 + V(\mathbf{r} - \mathbf{R}) \right\} \psi_n = E_n \psi_n. \quad [10.83]$$

We have already learned how to solve equations of this form: Let

$$\psi_n = e^{ig} \psi'_n. \quad [10.84]$$

where¹⁷

$$g \equiv \frac{q}{\hbar} \int_{\mathbf{R}}^{\mathbf{r}} \mathbf{A}(\mathbf{r}') \cdot d\mathbf{r}'. \quad [10.85]$$

and ψ' satisfies the same eigenvalue equation, only with $\mathbf{A} \rightarrow 0$:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r} - \mathbf{R}) \right] \psi'_n = E_n \psi'_n. \quad [10.86]$$

Notice that ψ'_n is a function only of the displacement $(\mathbf{r} - \mathbf{R})$, not (like ψ_n) of \mathbf{r} and \mathbf{R} separately.

Now let's carry the box around the solenoid (in this application the process doesn't even have to be adiabatic). To determine Berry's phase we must first evaluate the quantity $\langle \psi_n | \nabla_R \psi_n \rangle$. Noting that

$$\nabla_R \psi_n = \nabla_R \left[e^{ig} \psi'_n(\mathbf{r} - \mathbf{R}) \right] = -i \frac{q}{\hbar} \mathbf{A}(\mathbf{R}) e^{ig} \psi'_n(\mathbf{r} - \mathbf{R}) + e^{ig} \nabla_R \psi'_n(\mathbf{r} - \mathbf{R}),$$

we find

$$\begin{aligned} \langle \psi_n | \nabla_R \psi_n \rangle &= \int e^{-ig} [\psi'_n(\mathbf{r} - \mathbf{R})]^* e^{ig} \left[-i \frac{q}{\hbar} \mathbf{A}(\mathbf{R}) \psi'_n(\mathbf{r} - \mathbf{R}) + \nabla_R \psi'_n(\mathbf{r} - \mathbf{R}) \right] d^3 \mathbf{r} \\ &= -i \frac{q}{\hbar} \mathbf{A}(\mathbf{R}) - \int [\psi'_n(\mathbf{r} - \mathbf{R})]^* \nabla \psi'_n(\mathbf{r} - \mathbf{R}) d^3 \mathbf{r}. \end{aligned} \quad [10.87]$$

The ∇ with no subscript denotes the gradient with respect to \mathbf{r} , and I used the fact that $\nabla_R = -\nabla$, when acting on a function of $(\mathbf{r} - \mathbf{R})$. But the last integral is i/\hbar times the expectation value of momentum, in an eigenstate of the Hamiltonian $-(\hbar^2/2m)\nabla^2 + V$, which we know from Section 2.1 is zero. So

$$\langle \psi_n | \nabla_R \psi_n \rangle = -i \frac{q}{\hbar} \mathbf{A}(\mathbf{R}). \quad [10.88]$$

Putting this into Berry's formula (Equation 10.45), we conclude that

$$\gamma_n(T) = \frac{q}{\hbar} \oint \mathbf{A}(\mathbf{R}) \cdot d\mathbf{R} = \frac{q}{\hbar} \int (\nabla \times \mathbf{A}) \cdot d\mathbf{a} = \frac{q\Phi}{\hbar}, \quad [10.89]$$

which neatly confirms the Aharonov-Bohm result (Equation 10.82), and reveals that the Aharonov-Bohm effect is a particular instance of geometric phase.¹⁸

What are we to make of the Aharonov-Bohm effect? Evidently our classical preconceptions are simply *mistaken*: There *can* be electromagnetic effects in regions where the fields are zero. Note however that this does not make \mathbf{A} itself

AfterWord

We will try to see what QM means.

The quantum state does not uniquely determine the outcome of an experiment, but just a statistical distribution of possible results.

This gives various interpretations:

- **Realist:** The system actually had the attribute well defined previous to measurement
- **Orthodox:** The measurement itself created the property, limited only to the statistical constraint of the wave function.
- **Agnostic:** Doesn't matter.

According to the realist, QM is incomplete

According to the Orthodox, strange things happen. The act of measurement **collapses** the wave function.

EPR paradox

Einstein, Podolsky and Rosen published the EPR paradox, which aimed to prove that the realist view is the only sustainable one.

Consider the decay of a neutral pi meson into an electron and positron:

$$\pi^0 \rightarrow e^- + e^+$$

Assuming the pion was at rest, the e^- and e^+ travel in opposite directions.

The Pion has spin zero, so conservation of spin requires that the electron and positron are in the singlet configuration:

$$\frac{1}{\sqrt{2}}(\uparrow_{-}\downarrow_{+} - \downarrow_{-}\uparrow_{+})$$

If the electron has spin up, the positron must have spin down and vice versa.

That is, the measurements will be correlated.

Suppose we let the electron fly away a big distance and we measure then its spin. Then, immediately we will know the state of the positron that is far away.

To the realist, this is not surprising, both particles already had their spins defined the moment they were created and its just that QM is incomplete.

To the orthodox, neither particle had either spin until measuring. And the act of measuring the spin of electron instantaneously produced the spin of the positron far away 'spooky action at a distance'

so the orthodox view makes no sense, right?

The fundamental assumption of EPR is that no influence can propagate FTL. This is the **principle of locality**.

Problem 12.1 Entangled states. The singlet spin configuration (Equation 12.1) is the classic example of an *entangled state*—a two-particle state that cannot be expressed as the product of two one-particle states, and for which, therefore, one cannot really speak of “the state” of either particle separately. You might wonder whether this is somehow an artifact of bad notation—maybe some linear combination of the one-particle states would disentangle the system. Prove the following theorem:

Consider a two-level system, $|\phi_a\rangle$ and $|\phi_b\rangle$, with $\langle\phi_i|\phi_j\rangle = \delta_{ij}$. (For example, $|\phi_a\rangle$ might represent spin up and $|\phi_b\rangle$ spin down.) The two-particle state

$$\alpha|\phi_a(1)\rangle|\phi_b(2)\rangle + \beta|\phi_b(1)\rangle|\phi_a(2)\rangle$$

(with $\alpha \neq 0$ and $\beta \neq 0$) *cannot* be expressed as a product

$$|\psi_r(1)\rangle|\psi_s(2)\rangle,$$

for *any* one-particle states $|\psi_r\rangle$ and $|\psi_s\rangle$.

Problem 12.1

Suppose, on the contrary, that

$$\alpha|\phi_a(1)\rangle|\phi_b(2)\rangle + \beta|\phi_b(1)\rangle|\phi_a(2)\rangle = |\psi_r(1)\rangle|\psi_s(2)\rangle,$$

for some one-particle states $|\psi_r\rangle$ and $|\psi_s\rangle$. Because $|\phi_a\rangle$ and $|\phi_b\rangle$ constitute a complete set of one-particle states (this is a two-level system), any other one-particle state can be expressed as a linear combination of them. In particular,

$$|\psi_r\rangle = A|\phi_a\rangle + B|\phi_b\rangle, \quad \text{and} \quad |\psi_s\rangle = C|\phi_a\rangle + D|\phi_b\rangle,$$

for some complex numbers A, B, C , and D . Thus

$$\begin{aligned} \alpha|\phi_a(1)\rangle|\phi_b(2)\rangle + \beta|\phi_b(1)\rangle|\phi_a(2)\rangle &= [A|\phi_a(1)\rangle + B|\phi_b(1)\rangle][C|\phi_a(2)\rangle + D|\phi_b(2)\rangle] \\ &= AC|\phi_a(1)\rangle|\phi_a(2)\rangle + AD|\phi_a(1)\rangle|\phi_b(2)\rangle + BC|\phi_b(1)\rangle|\phi_a(2)\rangle + BD|\phi_b(1)\rangle|\phi_b(2)\rangle. \end{aligned}$$

- (i) Take the inner product with $\langle\phi_a(1)|\langle\phi_b(2)|$: $\alpha = AD$.
- (ii) Take the inner product with $\langle\phi_a(1)|\langle\phi_a(2)|$: $0 = AC$.
- (iii) Take the inner product with $\langle\phi_b(1)|\langle\phi_a(2)|$: $\beta = BC$.
- (iv) Take the inner product with $\langle\phi_b(1)|\langle\phi_b(2)|$: $0 = BD$.

(ii) \Rightarrow either $A = 0$ or $C = 0$. But if $A = 0$, then (i) $\Rightarrow \alpha = 0$, which is excluded by assumption, whereas if $C = 0$, then (iii) $\Rightarrow \beta = 0$, which is likewise excluded. *Conclusion:* It is impossible to express this state as a product of one-particle states. QED

Bell's Theorem

EPR did not doubt QM is correct, they just said it is incomplete, there must be some **hidden variable**

However, Bell proved that any local hidden variable theory is incompatible with QM

Bell suggested a generalization of the EPR experiment: Instead of orienting the electron and positron detectors along the same direction, he allowed for them to be rotated independently. The first measures the component of the electron spin in the direction of unit vector \vec{a} , and the second measures the spin of the positron along the direction \vec{b}

Each detector registers the value $+1$ (spin up) or -1 (spin down) along the direction in question.

For example:

electron	positron	product
+1	-1	-1
+1	+1	+1
-1	+1	-1
+1	-1	-1
-1	-1	+1
:	:	:

Bell proposed to calculate the average value of the product of the spins, for a given set of detector orientations.

Call this average $P(\vec{a}, \vec{b})$.

If the detectors are parallel, we recover the original EPR configuration and the product must be always -1 , and hence:

$$P(\vec{a}, \vec{a}) = -1$$

By the same token, if they are anti parallel, ($\vec{b} = -\vec{a}$), then every product is $+1$, so:

$$P(\vec{a}, -\vec{a}) = +1$$

For arbitrary orientations, QM predicts:

$$P(\vec{a}, \vec{b}) = -\vec{a} \cdot \vec{b}$$

*****Problem 4.50** Suppose two spin-1/2 particles are known to be in the singlet configuration (Equation 4.178). Let $S_a^{(1)}$ be the component of the spin angular momentum of particle number 1 in the direction defined by the unit vector \hat{a} . Similarly, let $S_b^{(2)}$ be the component of 2's angular momentum in the direction \hat{b} . Show that

$$\langle S_a^{(1)} S_b^{(2)} \rangle = -\frac{\hbar^2}{4} \cos \theta, \quad [4.198]$$

where θ is the angle between \hat{a} and \hat{b} .

Problem 4.50

We may as well choose axes so that \hat{a} lies along the z axis and \hat{b} is in the xz plane. Then $S_a^{(1)} = S_z^{(1)}$, and $S_b^{(2)} = \cos \theta S_z^{(2)} + \sin \theta S_x^{(2)}$. $\langle 0\ 0 | S_a^{(1)} S_b^{(2)} | 0\ 0 \rangle$ is to be calculated.

$$S_a^{(1)} S_b^{(2)} | 0\ 0 \rangle = \frac{1}{\sqrt{2}} [S_z^{(1)} (\cos \theta S_z^{(2)} + \sin \theta S_x^{(2)})] (\uparrow\downarrow - \downarrow\uparrow)$$

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$$\begin{aligned} &= \frac{1}{\sqrt{2}} [(S_z \uparrow)(\cos \theta S_z \downarrow + \sin \theta S_x \downarrow) - (S_z \downarrow)(\cos \theta S_z \uparrow + \sin \theta S_x \uparrow)] \\ &= \frac{1}{\sqrt{2}} \left\{ \left(\frac{\hbar}{2} \uparrow \right) \left[\cos \theta \left(-\frac{\hbar}{2} \downarrow \right) + \sin \theta \left(\frac{\hbar}{2} \uparrow \right) \right] - \left(-\frac{\hbar}{2} \downarrow \right) \left[\cos \theta \left(\frac{\hbar}{2} \uparrow \right) + \sin \theta \left(\frac{\hbar}{2} \downarrow \right) \right] \right\} \text{ (using Eq. 4.145)} \\ &= \frac{\hbar^2}{4} \left[\cos \theta \frac{1}{\sqrt{2}} (-\uparrow\downarrow + \downarrow\uparrow) + \sin \theta \frac{1}{\sqrt{2}} (\uparrow\uparrow + \downarrow\downarrow) \right] = \frac{\hbar^2}{4} \left[-\cos \theta | 0\ 0 \rangle + \sin \theta \frac{1}{\sqrt{2}} (| 1\ 1 \rangle + | 1\ -1 \rangle) \right]. \end{aligned}$$

$$\text{so } \langle S_a^{(1)} S_b^{(2)} \rangle = \langle 0\ 0 | S_a^{(1)} S_b^{(2)} | 0\ 0 \rangle = \frac{\hbar^2}{4} \langle 0\ 0 | \left[-\cos \theta | 0\ 0 \rangle + \sin \theta \frac{1}{\sqrt{2}} (| 1\ 1 \rangle + | 1\ -1 \rangle) \right] = -\frac{\hbar^2}{4} \cos \theta \langle 0\ 0 | 0\ 0 \rangle$$

Theorem: This result is incompatible with any local hidden variable theory:

Suppose that the 'complete' state of the electron positron system is characterized by the hidden variable λ (λ varies, in some way that we neither understand nor control, from one pion decay to the next).

Suppose further that the outcome of the electron measurement is independent of the orientation \vec{b} of the positron detector (which may in any case be changed by the experimenter in the positron side just before the measurement, too far from the electron experimenter to get the news -this is the locality assumption-).

then, there exists some function $A(\vec{a}, \lambda)$ which gives the result of an electron measurement, and some other $B(\vec{b}, \lambda)$ for the positron.

These functions can only take the values ± 1 :

$$\begin{aligned} A(\vec{a}, \lambda) &= \pm 1 \\ B(\vec{b}, \lambda) &= \pm 1 \end{aligned}$$

When the detectors are aligned, the results are perfectly anticorrelated $A(\vec{a}, \lambda) = -B(\vec{a}, \lambda)$ 12.6) for all λ .

Now, the average of the product of the measurements is:

$$P(\vec{a}, \vec{b}) = \int \rho(\lambda) A(\vec{a}, \lambda) B(\vec{b}, \lambda) d\lambda$$

Where $\rho(\lambda)$ is the probability density for the hidden variable (it fulfills $\int \rho = 1$ and is nonnegative, but we make no further assumptions).

Then, we can eliminate B in view of 12.6:

$$P(\vec{a}, \vec{b}) = - \int \rho(\lambda) A(\vec{a}, \lambda) A(\vec{b}, \lambda) d\lambda$$

If \vec{c} is any other unit vector:

$$P(\vec{a}, \vec{b}) - P(\vec{a}, \vec{c}) = - \int \rho(\lambda) [A(\vec{a}, \lambda) A(\vec{b}, \lambda) - A(\vec{a}, \lambda) A(\vec{c}, \lambda)] d\lambda$$

Or, since $[A(\vec{b}, \lambda)]^2 = 1$:

$$P(\vec{a}, \vec{b}) - P(\vec{a}, \vec{c}) = - \int \rho(\lambda) [1 - A(\vec{b}, \lambda) A(\vec{c}, \lambda)] A(\vec{a}, \lambda) A(\vec{b}, \lambda) d\lambda$$

But it because A can only take the values ± 1 , we have $-1 \leq [A(\vec{a}, \lambda) A(\vec{b}, \lambda)] \leq +1$. More over, $\rho(\lambda)[1 - A(\vec{b}, \lambda) A(\vec{c}, \lambda)] \geq 0$, so:

$$|P(\vec{a}, \vec{b}) - P(\vec{a}, \vec{c})| \leq \int \rho(\lambda) [1 - A(\vec{b}, \lambda) A(\vec{c}, \lambda)] d\lambda$$

Or:

$$|P(\vec{a}, \vec{b}) - P(\vec{a}, \vec{c})| \leq 1 + P(\vec{b}, \vec{c})$$

This is **Bell inequality**.

It holds for any local hidden variable theory.

But it is easy to show that the QM prediction is incompatible with Bell's inequality.

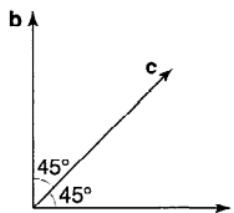


FIGURE 12.3: An orientation of the detectors that demonstrates quantum violations of Bell's inequality.

a plane, and c makes a 45° angle with a and b (Figure 12.3); in this case quantum mechanics says

$$P(a, b) = 0, \quad P(a, c) = P(b, c) = -0.707,$$

which is patently inconsistent with Bell's inequality:

$$0.707 \not\leq 1 - 0.707 = 0.293.$$

So if EPR were right, QM is wrong. On the other hand, if QM is right, there is no hidden variable local theory (maybe a non local one).

This has been tested, and results are compatible with QM (incompatible with Bells inequality)

this spelled the demise of realism (but there still remains the possibility of non local hidden variable)

to which Bell's theorem does not apply⁹). The real shock was the demonstration that *nature itself is fundamentally nonlocal*. Nonlocality, in the form of the instantaneous collapse of the wave function (and for that matter also in the symmetrization requirement for identical particles) had always been a feature of the orthodox interpretation, but before Aspect's experiment it was possible to hope that quantum nonlocality was somehow a nonphysical artifact of the formalism, with no detectable consequences. That hope can no longer be sustained, and we are obliged to reexamine our objection to instantaneous action-at-a-distance.

Why are physicists so squeamish about superluminal influences? After all, there are many things that travel faster than light. If a bug flies across the beam of a movie projector, the speed of its shadow is proportional to the distance to the screen; in principle, that distance can be as large as you like, and hence the shadow can move at arbitrarily high velocity (Figure 12.4). However, the shadow does not carry any *energy*; nor can it transmit a *message* from one point to another on the screen. A person at point *X* cannot *cause anything to happen* at point *Y* by manipulating the passing shadow.

On the other hand, a *causal* influence that propagated faster than light would carry unacceptable implications. For according to special relativity there exist inertial frames in which such a signal propagates *backward in time*—the effect preceding the cause—and this leads to inescapable logical anomalies. (You could, for example, arrange to kill your infant grandfather. Not a good idea!) The question is, are the superluminal influences predicted by quantum mechanics and detected by

Aspect *causal*, in this sense, or are they somehow ethereal enough (like the motion of the shadow) to escape the philosophical objection?

Well, let's consider Bell's experiment. Does the measurement of the electron *influence* the outcome of the positron measurement? Assuredly it *does*—otherwise we cannot account for the correlation of the data. But does the measurement of the electron *cause* a particular outcome for the positron? Not in any ordinary sense of the word. There is no way the person manning the electron detector could use his measurement to send a signal to the person at the positron detector, since he does not control the outcome of his own measurement (he cannot *make* a given electron come out spin up, any more than the person at *X* can affect the passing shadow of the bug). It is true that he can decide *whether to make a measurement at all*, but the positron monitor, having immediate access only to data at his end of the line, cannot tell whether the electron was measured or not, for the lists of data compiled at the two ends, considered separately, are completely random. It is only when we *compare* the two lists later that we discover the remarkable correlations. In another reference frame the positron measurements occur *before* the electron measurements, and yet this leads to no logical paradox—the observed correlation is entirely symmetrical in its treatment, and it is a matter of indifference whether we say the observation of the electron influenced the measurement of the positron, or the other way around. This is a wonderfully delicate kind of influence whose only manifestation is a subtle correlation between two lists of otherwise random data.

We are led, then, to distinguish two types of influence: the “causal” variety, which produce actual changes in some physical property of the receiver, detectable by measurements on that subsystem alone, and an “ethereal” kind, which do not transmit energy or information, and for which the only evidence is a correlation in the data taken on the two separate subsystems—a correlation which by its nature cannot be detected by examining either list alone. Causal influences *cannot* propagate faster than light, but there is no compelling reason why ethereal ones should not. The influences associated with the collapse of the wave function are of the latter type, and the fact that they “travel” faster than light may be surprising, but it is not, after all, catastrophic.¹⁰

The No clone theorem

Quantum measurements are **destructive**, they alter the state of the system measured. This is how the uncertainty principle is enforced in laboratory.

You might wonder why we don't take a bunch of **clones** of the original state and measure them, leaving the original system unchanged.

Because it can't be done

unscathed. It can't be done. Indeed, if you could build a cloning device (a "quantum Xerox machine"), quantum mechanics would be out the window.

For example, it would then be possible to send superluminal messages using the EPRB experiment. Say the message to be transmitted, from the operator of the positron detector to the operator of the electron detector, is either "yes" or "no." If the message is "yes," the sender measures S_z (of the positron). Never mind what result she gets—all that matters is that she makes the measurement, for this means that the electron is now in the definite state \uparrow or \downarrow (never mind which). The receiver immediately makes a million clones of the electron, and measures S_z on each of them. If they all yield the same answer (never mind *which* answer), we can be pretty sure that the electron *was* in fact measured, so the message is "yes." If half of them are spin up, and half spin down, then the electron was definitely *not* measured, and the message is "no."

But you *can't* make a quantum Xerox machine, as Wootters, Zurek, and Dieks proved in 1982.¹¹ Schematically, we want the machine to take as input a particle in state $|\psi\rangle$ (the one to be copied), plus a second particle in state $|X\rangle$ (the "blank sheet of paper"), and spit out *two* particles in the state $|\psi\rangle$ (original plus copy):

$$|\psi\rangle|X\rangle \rightarrow |\psi\rangle|\psi\rangle. \quad [12.13]$$

Suppose we have made a device that successfully clones the state $|\psi_1\rangle$:

$$|\psi_1\rangle|X\rangle \rightarrow |\psi_1\rangle|\psi_1\rangle. \quad [12.14]$$

and also works for state $|\psi_2\rangle$:

$$|\psi_2\rangle|X\rangle \rightarrow |\psi_2\rangle|\psi_2\rangle \quad [12.15]$$

($|\psi_1\rangle$ and $|\psi_2\rangle$ might be spin up and spin down, for example, if the particle is an electron). So far, so good. But what happens when we feed in a linear combination $|\psi\rangle = \alpha|\psi_1\rangle + \beta|\psi_2\rangle$? Evidently we get¹²

$$|\psi\rangle|X\rangle \rightarrow \alpha|\psi_1\rangle|\psi_1\rangle + \beta|\psi_2\rangle|\psi_2\rangle. \quad [12.16]$$

which is not at all what we wanted—what we *wanted* was

$$\begin{aligned} |\psi\rangle|X\rangle &\rightarrow |\psi\rangle|\psi\rangle = [\alpha|\psi_1\rangle + \beta|\psi_2\rangle][\alpha|\psi_1\rangle + \beta|\psi_2\rangle] \\ &= \alpha^2|\psi_1\rangle|\psi_1\rangle + \beta^2|\psi_2\rangle|\psi_2\rangle + \alpha\beta[|\psi_1\rangle|\psi_2\rangle + |\psi_2\rangle|\psi_1\rangle]. \end{aligned} \quad [12.17]$$

You can make a machine to clone spin-up electrons and spin-down electrons, but it's going to fail for any nontrivial linear combinations. It's as though you bought a Xerox machine that copies vertical lines perfectly, and also horizontal lines, but completely distorts diagonals.

Schrodinger Cat

The measurement process plays a mischievous role in quantum mechanics: It is here that indeterminacy, nonlocality, the collapse of the wave function, and all the attendant conceptual difficulties arise. Absent measurement, the wave function evolves in a leisurely and deterministic way, according to the Schrödinger equation, and quantum mechanics looks like a rather ordinary field theory (much simpler than classical electrodynamics, for example, since there is only *one* field (Ψ), instead of *two* (\mathbf{E} and \mathbf{B}), and it's a *scalar*). It is the bizarre role of the measurement process that gives quantum mechanics its extraordinary richness and subtlety. But what, exactly, *is* a measurement? What makes it so different from other physical processes?¹³ And how can we tell when a measurement has occurred?

Schrödinger posed the essential question most starkly, in his famous **cat paradox**:¹⁴

A cat is placed in a steel chamber, together with the following hellish contraption.... In a Geiger counter there is a tiny amount of radioactive substance, so tiny that maybe within an hour one of the atoms decays, but equally probably none of them decays. If one decays then the counter triggers and via a relay activates a little hammer which breaks a container of cyanide. If one has left this entire system for an hour, then one would say the cat is living if no atom has decayed. The first decay would have poisoned it. The wave function of the entire system would express this by containing equal parts of the living and dead cat.

At the end of the hour, the wave function of the cat has the schematic form

$$\psi = \frac{1}{\sqrt{2}}(\psi_{\text{alive}} + \psi_{\text{dead}}). \quad [12.18]$$

The cat is neither alive nor dead, but rather a linear combination of the two, until a measurement occurs—until, say, you peek in the window to check. At that moment your observation forces the cat to “take a stand”: dead or alive. And if you find him to be dead, then it’s really *you* who killed him, by looking in the window.

Schrödinger regarded this as patent nonsense, and I think most physicists would agree with him. There is something absurd about the very idea of a *macroscopic* object being in a linear combination of two palpably different states. An electron can be in a linear combination of spin up and spin down, but a cat simply cannot *be* in a linear combination of alive and dead. How are we to reconcile this with the orthodox interpretation of quantum mechanics?

The most widely accepted answer is that the triggering of the Geiger counter constitutes the “measurement,” in the sense of the statistical interpretation, not the intervention of a human observer. It is the essence of a measurement that some *macroscopic* system is affected (the Geiger counter, in this instance). The measurement occurs at the moment when the microscopic system (described by the laws of quantum mechanics) interacts with the macroscopic system (described by the laws of classical mechanics) in such a way as to leave a permanent record. The macroscopic system itself is not permitted to occupy a linear combination of distinct states.¹⁵

I would not pretend that this is an entirely satisfactory resolution, but at least it avoids the stultifying solipsism of Wigner and others, who persuaded themselves that it is the involvement of human consciousness that constitutes a measurement in quantum mechanics. Part of the problem is the word “measurement” itself, which certainly carries a suggestion of human participation. Heisenberg proposed the word “event,” which might be preferable. But I’m afraid “measurement” is so ingrained by now that we’re stuck with it. And, in the end, no manipulation of the terminology can completely exorcise this mysterious ghost.

Quantum Zeno

The collapse of the wave function is undoubtedly the *most* peculiar feature of this whole bizarre story. It was introduced on purely theoretical grounds, to account for the fact that an immediately repeated measurement reproduces the same value. But surely such a radical postulate must carry directly observable consequences. In

1977 Misra and Sudarshan¹⁶ proposed what they called the **quantum Zeno effect** as a dramatic experimental demonstration of the collapse of the wave function. Their idea was to take an unstable system (an atom in an excited state, say), and subject it to repeated measurements. Each observation collapses the wave function, resetting the clock, and it is possible by this means to delay indefinitely the expected transition to the lower state.¹⁷

Specifically, suppose a system starts out in the excited state ψ_2 , which has a natural lifetime τ for transition to the ground state ψ_1 . Ordinarily, for times substantially less than τ , the probability of a transition is proportional to t (see Equation 9.42); in fact, since the transition rate is $1/\tau$,

$$P_{2 \rightarrow 1} = \frac{t}{\tau}. \quad [12.19]$$

If we make a measurement after a time t , then, the probability that the system is still in the *upper* state is

$$P_2(t) = 1 - \frac{t}{\tau}. \quad [12.20]$$

Suppose we *do* find it to be in the upper state. In that case the wave function collapses back to ψ_2 , and the process starts all over again. If we make a *second* measurement, at $2t$, the probability that the system is *still* in the upper state is evidently

$$\left(1 - \frac{t}{\tau}\right)^2 \approx 1 - \frac{2t}{\tau}. \quad [12.21]$$

which is the same as it would have been had we never made the first measurement at t . This is what one would naively expect; if it were the whole story there would be nothing gained by repeatedly observing the system, and there would be no quantum Zeno effect.

However, for *extremely* short times, the probability of a transition is *not* proportional to t , but rather to t^2 (see Equation 9.39).¹⁸

$$P_{2 \rightarrow 1} = \alpha t^2. \quad [12.22]$$

In this case the probability that the system is still in the upper state after the two measurements is

$$\left(1 - \alpha t^2\right)^2 \approx 1 - 2\alpha t^2. \quad [12.23]$$

whereas if we had never made the first measurement it would have been

$$1 - \alpha(2t)^2 \approx 1 - 4\alpha t^2. \quad [12.24]$$

Evidently our observation of the system after time t decreased the net probability of a transition to the lower state!

Indeed, if we examine the system at n regular intervals, from $t = 0$ out to $t = T$ (that is, we make measurements at $T/n, 2T/n, 3T/n, \dots, T$), the probability that the system is still in the upper state at the end is

$$\left(1 - \alpha(T/n)^2\right)^n \approx 1 - \frac{\alpha}{n} T^2. \quad [12.25]$$

which goes to 1 in the limit $n \rightarrow \infty$: A *continuously* observed unstable system never decays at all! Some authors regard this as an absurd conclusion, and a proof that the collapse of the wave function is fallacious. However, their argument hinges on a rather loose interpretation of what constitutes “observation.” If the track of a particle in a bubble chamber amounts to “continuous observation,” then the case is closed, for such particles certainly do decay (in fact, their lifetime is not measurably extended by the presence of the detector). But such a particle is only intermittently interacting with the atoms in the chamber, and for the quantum Zeno effect to occur the successive measurements must be made *extremely* rapidly, in order to catch the system in the t^2 regime.

As it turns out, the experiment is impractical for spontaneous transitions, but it can be done using *induced* transitions, and the results are in excellent agreement with the theoretical predictions.¹⁹ Unfortunately, this experiment is not as compelling a confirmation of the collapse of the wave function as its designers hoped; the observed effect can be accounted for in other ways.²⁰

In this book I have tried to tell a consistent and coherent story: The wave function (Ψ) represents the state of a particle (or system); particles do not in general possess specific dynamical properties (position, momentum, energy, angular momentum, etc.) until an act of measurement intervenes; the probability of getting a particular value in any given experiment is determined by the statistical interpretation of Ψ ; upon measurement the wave function collapses, so that an immediately repeated measurement is certain to yield the same result. There are other possible interpretations—nonlocal hidden variable theories, the “many worlds” picture, “consistent histories,” ensemble models, and others—but I believe this one

¹⁹W. M. Itano, D. J. Heinzen, J. J. Bollinger, and D. J. Wineland. *Phys. Rev. A* **41**, 2295 (1990).

²⁰L. E. Ballentine. *Found. Phys.* **20**, 1329 (1990); T. Petrosky, S. Tasaki, and I. Prigogine. *Phys. Lett. A* **151**, 109 (1990).

Chapter 12 Afterword

is conceptually the *simplest*, and certainly it is the one shared by most physicists today.²¹ It has stood the test of time, and emerged unscathed from every experimental challenge. But I cannot believe this is the end of the story; at the very least, we have much to learn about the nature of measurement and the mechanism of collapse. And it is entirely possible that future generations will look back, from the vantage point of a more sophisticated theory, and wonder how we could have been so gullible.

Apéndices

Apéndice de Hilbert y espacios de Funciones

Antes de continuar, un resumen de espacios de Hilbert.

Como dijimos antes, el producto interno toma dos vectores es una operación que cumple: 1) $(x, y) = (y, x)^*$, 2) $(\lambda x, y) = \lambda(x, y)$, 3) $(x + y, z) = (x, z) + (y, z)$, 4) $(x, x) > 0$ cuando $x \neq 0$.

Y tienen una norma definida por $\|x\|^2 = (x, x)$.

En el espacio \mathbb{C}^n podemos definir el producto interno como $(a, b) = a_1^*b_1 + \cdots + a_n^*b_n$

En el espacio de funciones cuadrado integrables, tenemos que $(f, g) = \int f^*g dx$. Le llamamos espacio L^2 o bien $L^2(a, b)$ si integramos en este intervalo.

Espacio de Hilbert

Es un espacio con producto interior tal que toda secuencia de Cauchy converge a un límite dentro del espacio.

Propiedad del Producto más cercano

Sea A un subconjunto cerrado y convexo de H un espacio de Hilbert. Entonces para todo $x \in H$ existe un único $y \in A$ tal que:

$$\|x - y\| = \int_{a \in A} \|x - a\|$$

Expansiones Ortogonales

Decimos que dos vectores $x, y \in V$ son **ortogonales** si $(x, y) = 0$

Sistema Ortogonal: Es un conjunto de elementos $(e_a)_{a \in A} \in V/\{0\}$ tales que $e_a \perp e_b$ y es **ortonormal** si $(e_a, e_b) = \delta_{a,b}$

Coeficiente de Fourier: Si (e_n) es una secuencia ortonormal en un espacio de Hilbert H , entonces para todo $x \in H$ definimos el **n-ésimo coeficiente de Fourier** de x respecto a la secuencia ortonormal como:

$$a_n = (x, e_n)$$

Serie de Fourier: Dado un $x \in H$, definimos su serie de Fourier como:

$$\sum_n (x, e_n) e_n$$

No sabemos aún si este resultado será igual a x .

Teorema:

Si e_1, \dots, e_n es un sistema ortonormal en un espacio de Hilbert H . Y sea $x \in H$. Entonces el punto $y \in \text{lin}\{e_1, \dots, e_n\}$ más cercano a x tiene la forma dada por:

$$y = \sum_{j=1}^n (x, e_j) e_j$$

Y la distancia $d = \|x - y\|$ está dada por $d^2 = \|x\|^2 - \sum_{j=1}^n |(x, e_j)|^2$.

Desigualdad de Bessel:

Sea (e_n) una secuencia ortonormal en el espacio de Hilbert H , entonces para todo $x \in H$ tenemos que:

$$\sum_{n=1}^{\infty} |(x, e_n)|^2 \leq \|x\|^2$$

Nota sobre convergencia: La convergencia en L^2 es respecto al producto interno, pero no necesariamente es puntual.

Secuencias Ortonormales Completas

Dado un espacio de Hilbert, nos gustaría escribir $x = \sum_{n=1}^{\infty} (x, e_n) e_n$.

Secuencia Ortonormal Completa (base ortonormal): Es una secuencia (e_n) en un espacio de Hilbert que cumple que si $y \in H$ es ortogonal a todo e_n , entonces $y = 0$.

Equivalencias de Secuencias ortonotmales:

Dado un espacio de Hilbert H , siempre podemos encontrar una base ortonormal (e_n) .

Se cumplen las siguientes equivalencias para bases ortonormales:

- (e_n) es completo (un elemento ortogonal a todo e_n tiene que ser 0)
- Para todo x se cumple que:

$$x = \sum_{n=1}^{\infty} (x, e_n) e_n$$

- $\text{cl}_H\{e_n \mid n \in \mathbb{N}\} = H$

- Parseval:

$$\|x\|^2 = \sum_{n=1}^{\infty} |(x, e_n)|^2$$

Donde $\|x\|^2$ es la norma cuadrada del vector x (que puede ser una función). Y el lado derecho es la suma de los coeficientes de fourier de x al cuadrado-norma.

Conste que e_n es una base ortonormal en el espacio H con el producto interno adecuado.

Series de Fourier

Teorema: Sea $e_n(x) = \sqrt{\frac{1}{2\pi}} e^{inx}$ en $-\pi < x < \pi$. Entonces (e_n) es una base ortonormal en $L^2(-\pi, \pi)$.

Sistemas de Sturm Liouville

Def: Un sistema regular de SL regular (RSL) es una ecuación diferencial en $[a, b]$ junto con condiciones de frontera como sigue:

$$\frac{d}{dx} \left(p \frac{df}{dx} \right) + qf = -\lambda \rho f \quad , \quad a \leq x \leq b$$
$$\begin{cases} \alpha f(a) + \alpha' f'(a) = 0 \\ \beta f(b) + \beta' f'(b) = 0 \end{cases}$$

Donde:

- p, q, ρ son funciones continuas y reales en $[a, b]$
- p, ρ son positivas en $[a, b]$

-
- p' existe y es continua en $[a, b]$
 - $\alpha, \beta, \alpha', \beta'$ son reales constantes.

La ecuación de SL se puede escribir usando el operador L dado por:

$$Lf = \frac{d}{dx} \left(p \frac{df}{dx} \right) + qf$$

Y entonces la ecuación de un RSL es:

$$Lf = -\lambda \rho f$$

Propiedad de Autoadjunto: Se cumple que:

$$(Lf, g) = (f, Lg)$$

Expansión en Eigenfunciones

Teorema de Ortogonalidad: Sean f, g eigenfunciones de un problema de SL con distintos eigenvalores. Entonces $\rho^{1/2}f$, $\rho^{1/2}g$ son ortogonales. Es decir:

$$\int \rho(x)f(x)g(x)dx = 0$$

Lo que significa que son ortogonales respecto al peso f, g .

Luego, si queremos una solución particular a la ecuación diferencial, escribimos combinaciones lineales de estas soluciones.

Muchas ec. diferenciables se pueden conseguir para distintos ρ, p, q y se pueden resolver con métodos de series u otros.

Cosas de Fourier

Si tenemos una función f no muy fea (cantidad finita de discontinuidades, número finito de max y mins) en un intervalo $[a, b]$, entonces tenemos bases dadas por:

$$\cos\left(\frac{2\pi nx}{L}\right), \quad \sin\left(\frac{2\pi nx}{L}\right)$$
$$e^{i2\pi nx/L}$$

Y entonces $f(x)$ se puede escribir como $f(x) = \frac{a_0}{2} + \sum_{k=1}^{\infty} a_k \cos kx + b_k \sin kx$ donde:

$$a_n = \frac{2}{L} \int_a^b f(x) \cos\left(\frac{2\pi nx}{L}\right) dx$$
$$b_n = \frac{2}{L} \int_a^b f(x) \sin\left(\frac{2\pi nx}{L}\right) dx$$

O bien, se puede escribir como $f(x) = \sum_{n \in \mathbb{Z}} c_n e^{inx}$ donde:

$$c_n = \frac{1}{L} \int_a^b f(x) e^{-2\pi inx/L} dx$$

Teorema de Parseval:

Sea $f \in L^2(a, b)$, donde el producto punto está definido como $(f, g) = \frac{1}{L} \int_a^b f(x)g(x)^* dx$.

Entonces, podemos calcular los coeficientes de Fourier de f llamados $\hat{f}(n)$ y tendremos que:

$$\|f\|^2 = \sum_{n \in \mathbb{Z}} |\hat{f}(n)|^2$$

Transformada de Fourier

Definimos la transformada de Fourier de f como:

$$\hat{f}(\alpha) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} f(x) e^{-i\alpha x} dx$$

y entonces, se cumple la inversa:

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} \hat{f}(\alpha) e^{i\alpha x} dx$$

Identidad de Plancherel:

Definimos el producto punto como:

$$(f, g) = \int_{\mathbb{R}} f(x)g(x)^* dx$$

Y entonces se va a cumplir que:

$$\|f\|^2 = \|\hat{f}\|^2$$