

Lecture Notes: Quantum Mechanics

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Chapter 1

General principles of quantum theory

1.1 Classical-Mechanical Quantities Are Represented by Linear Operators in Quantum Mechanics

In quantum mechanics, operators play a fundamental role in describing physical observables and the dynamics of quantum systems. In quantum mechanics, physical quantities such as position, momentum, energy, and angular momentum are represented by mathematical operators. These operators act on the wave function of a quantum system and yield the observable values of these quantities when applied to a wave function.

Postulate 2 To every observable in classical mechanics there corresponds a linear operator in quantum mechanics.

An operator \hat{A} is a mathematical entity that transforms a function $f(x)$ into another function $g(x)$

$$\hat{A}f(x) = g(x). \quad (1.1.1)$$

We usually denote an operator by a capital letter with a carat over it (e.g., \hat{A}). The operator \hat{A} operates on $f(x)$ to give a new function $g(x)$.

An operator is a symbol that tells you to do something to whatever follows the symbol. For example, we can consider $\frac{df}{dx}$ to be the $\frac{d}{dx}$ operator operating on the function $f(x)$.

Classical-Mechanical Observables and Their Corresponding Quantum-Mechanical Operators

Observable		Operator	
Name	Symbol	Symbol	Operation
Position	x	\hat{X}	Multiply by x
	\mathbf{r}	$\hat{\mathbf{R}}$	Multiply by \mathbf{r}
Momentum	p_x	\hat{P}_x	$-i\hbar \frac{\partial}{\partial x}$
	\mathbf{p}	$\hat{\mathbf{P}}$	$-i\hbar(\mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z})$
Kinetic energy	T_x	\hat{T}_x	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
	T	\hat{T}	$-\frac{\hbar^2}{2m} (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$
			$= -\frac{\hbar^2}{2m} \nabla^2$
Potential energy	$V(x)$	$\hat{V}(\hat{x})$	Multiply by $V(x)$
	$V(x, y, z)$	$\hat{V}(\hat{x}, \hat{y}, \hat{z})$	Multiply by $V(x, y, z)$
Total energy	E	\hat{H}	$-\frac{\hbar^2}{2m} (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) + V(x, y, z)$
			$= -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$
	$l_x = yp_z - zp_y$	\hat{l}_x	$-i\hbar(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y})$
$l_y = zp_x - xp_z$	\hat{l}_y		$-i\hbar(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z})$
	$l_z = xp_y - yp_x$	\hat{l}_z	$-i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$

Some other examples are SQR (square what follows), $\int_0^1 dx$ (integrate what follows from 0 to 1), 3 (multiply by 3).

HW1: Perform the following operations

- (a) $\hat{A}(2x)$, $\hat{A} = \frac{d^2}{dx^2}$
- (b) $\hat{A}(x^2)$, $\hat{A} = \frac{d^2}{dx^2} + 2\frac{d}{dx} + 3$
- (c) $\hat{A}(xy^3)$, $\hat{A} = \frac{\partial}{\partial y}$
- (d) $\hat{A}(e^{ikx})$, $\hat{A} = -i\hbar \frac{d}{dx}$

In quantum mechanics, we deal only with **linear operators**. The operator \hat{A} is linear if it satisfies the following criteria

$$\hat{A}[c_1f_1(x) + c_2f_2(x)] = c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x) \quad (1.1.2)$$

where c_1 and c_2 are (possibly complex) constants. Clearly, the "differentiate" and "integrate" operators are linear because

$$\frac{d}{dx}[c_1f_1(x) + c_2f_2(x)] = c_1\frac{df_1}{dx} + c_2\frac{df_2}{dx}$$

and

$$\int [c_1f_1(x) + c_2f_2(x)] dx = c_1 \int f_1(x) dx + c_2 \int f_2(x) dx.$$

The "square" operator, SQR, on the other hand, is nonlinear because

$$\begin{aligned} \text{SQR}[c_1f_1(x) + c_2f_2(x)] &= c_1^2f_1^2(x) + c_2^2f_2^2(x) + 2c_1c_2f_1(x)f_2(x) \\ &\neq c_1f_1^2(x) + c_2f_2^2(x) \end{aligned}$$

and therefore it does not satisfy the definition given by Equation 1.1.2.

HW2: Determine whether the following operators are linear or nonlinear:

(a) $\hat{A}f(x) = \text{SQRT } f(x)$ (**take the square root**)

(b) $\hat{A}f(x) = x^2f(x)$

1.2 Many operators do not commute

The operator \hat{C} is the *sum* of the operators \hat{A} and \hat{B} if

$$\begin{aligned}\hat{C}\psi &= (\hat{A} + \hat{B})\psi \\ &= \hat{A}\psi + \hat{B}\psi\end{aligned}$$

Example: Suppose $\hat{A} = \frac{d^2}{dx^2}$, $\hat{B} = \frac{d}{dx}$ and $\hat{C} = \hat{x} + \frac{d}{dx}$,

$$\begin{aligned}\hat{C}\psi(x) &= (\hat{A} + \hat{B})\psi(x) \\ &= \left(\frac{d^2}{dx^2} + x\right)\psi(x) \\ &= \frac{d^2}{dx^2}\psi(x) + x\psi(x) \\ &= \hat{A}\psi(x) + \hat{B}\psi(x)\end{aligned}$$

The operator \hat{C} is the *product* of the operators \hat{A} and \hat{B} if

$$\begin{aligned}\hat{C}\psi &= \hat{A}\hat{B}\psi \\ &= \hat{A}(\hat{B}\psi)\end{aligned}$$

where first \hat{B} operates on ψ and then \hat{A} operates on the resulting function. In multiplication, the order of \hat{A} and \hat{B} is important because $\hat{A}\hat{B}\psi$ is not necessarily equal to $\hat{B}\hat{A}\psi$.

Example: Suppose $\hat{A} = \hat{x}$, $\hat{B} = \frac{d}{dx}$ and $\hat{C} = \hat{x} + \frac{d}{dx}$,

$$\begin{aligned}\hat{C}\psi(x) &= \hat{A}\hat{B}\psi(x) \\ &= \hat{A}(\hat{B}\psi(x)) \\ &= \hat{x}\left(\frac{d}{dx}\psi(x)\right) \\ &= x\psi'(x)\end{aligned}$$

In multiplication, the order of \hat{A} and \hat{B} is important because $\hat{A}\hat{B}\psi$ is not necessarily equal to $\hat{B}\hat{A}\psi$.

Example: Suppose $\hat{A} = \hat{x}$, $\hat{B} = \frac{d}{dx}$ and $\hat{C} = \hat{x} + \frac{d}{dx}$,

$$\begin{aligned}\hat{A}\hat{B}\psi(x) &= \hat{A}(\hat{B}\psi(x)) \\ &= \hat{x}\left(\frac{d}{dx}\psi(x)\right) \\ &= x\psi'(x)\end{aligned}$$

$$\begin{aligned}\hat{B}\hat{A}\psi(x) &= \hat{B}(\hat{A}\psi(x)) \\ &= \frac{d}{dx}\hat{x}\psi(x) \\ &= \frac{d}{dx}x\psi(x) \\ &= x\psi'(x) + \psi(x)\end{aligned}$$

$$\hat{A}\hat{B}\psi(x) \neq \hat{B}\hat{A}\psi(x)$$

Operators obey the *associative law of multiplication*, namely

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$$

Operators may be combined. Thus, the square \hat{A}^2 of an operator \hat{A} is just the product $\hat{A}\hat{A}$

$$\hat{A}^2\psi = \hat{A}\hat{A}\psi = \hat{A}(\hat{A}\psi)$$

The **commutator** of \hat{A} and \hat{B} , written as $[\hat{A}, \hat{B}]$, is an operator defined as

$$\begin{aligned}[\hat{A}, \hat{B}] &= \hat{A}\hat{B} - \hat{B}\hat{A} \\ &= -[\hat{B}, \hat{A}]\end{aligned}$$

If $\hat{A}\hat{B}\psi = \hat{B}\hat{A}\psi$, then we have and $\hat{A}\hat{B} = \hat{B}\hat{A}$ and $[\hat{A}, \hat{B}] = \hat{0}$; in this case we say that \hat{A} and \hat{B} commute.

Question: Let $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x^2$. Evaluate the commutator $[\hat{A}, \hat{B}]$.

We let \hat{A} and \hat{B} act upon an arbitrary function $f(x)$:

$$\begin{aligned}\hat{A}\hat{B}f(x) &= \frac{d}{dx}[x^2 f(x)] \\ &= 2xf(x) + x^2 \frac{df(x)}{dx}\end{aligned}$$

$$\begin{aligned}\hat{B}\hat{A}f(x) &= x^2 \frac{d}{dx}f(x) \\ &= x^2 \frac{df(x)}{dx}\end{aligned}$$

$$\begin{aligned}[\hat{A}, \hat{B}]f(x) &= (\hat{A}\hat{B} - \hat{B}\hat{A})f(x) \\ &= \hat{A}\hat{B}f(x) - \hat{B}\hat{A}f(x) \\ &= 2xf(x) + \cancel{x^2 \frac{df(x)}{dx}} - \cancel{x^2 \frac{df(x)}{dx}} \\ &= 2xf(x)\end{aligned}$$

Because, and only because, $f(x)$ is arbitrary, we write

$$[\hat{A}, \hat{B}] = 2x\hat{I}$$

\hat{I} is the unit operator (the multiply-by-one operator).

Note: When evaluating a commutator, it is essential to include a function $f(x)$ as we have done; otherwise, we can obtain a spurious result. To this end, note well that

$$\begin{aligned}[\hat{A}, \hat{B}] &= \hat{A}\hat{B} - \hat{B}\hat{A} \\ &= \frac{d}{dx}x^2 - x^2 \frac{d}{dx} \\ &\neq 2x - x^2 \frac{d}{dx}\end{aligned}$$

a result that is obtained by forgetting to include the function $f(x)$. Such errors will not occur if an arbitrary function $f(x)$ is included from the outset.

For a one-dimensional system, the momentum operator is $\hat{P}_x = -i\hbar \frac{d}{dx}$ and the position operator

is \hat{X} (multiply by x). Evaluate $[\hat{P}_x, \hat{X}] = i\hbar\hat{I}$, \hat{I} is the unit operator (the multiply-by-one operator).

Theorem: If two operators do not commute, then their corresponding observable quantities do not have simultaneously well-defined values.

HW: Prove the relationships

(a) Let $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x^2$. Evaluate the commutator $[\hat{A}, \hat{B}]$.

Note: When evaluating a commutator, it is essential to include a function $f(x)$; otherwise, we can obtain a spurious result.

$$(a) [\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$$

$$(b) [\hat{A}\hat{B}, \hat{C}] = [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}]$$

Solutions:

(a) Using property of commutator and *associative law of multiplication*, we obtain

$$\begin{aligned} [\hat{A}, \hat{B}\hat{C}] &= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} \\ &= \hat{A}\hat{B}\hat{C} - \underbrace{\hat{B}\hat{A}\hat{C}}_{\hat{B}\hat{A}\hat{C}} + \underbrace{\hat{B}\hat{A}\hat{C}}_{\hat{B}\hat{A}\hat{C}} - \hat{B}\hat{C}\hat{A} \\ &= (\hat{A}\hat{B} - \hat{B}\hat{A})\hat{C} + \hat{B}(\hat{A}\hat{C} - \hat{C}\hat{A}) \\ &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \end{aligned}$$

(b) Using property of commutator and *associative law of multiplication*, we obtain

$$\begin{aligned} [\hat{A}\hat{B}, \hat{C}] &= \hat{A}\hat{B}\hat{C} - \hat{C}\hat{A}\hat{B} \\ &= \hat{A}\hat{B}\hat{C} - \hat{C}\hat{A}\hat{B} \\ &= \underbrace{\hat{A}\hat{C}\hat{B}}_{\hat{A}\hat{C}\hat{B}} - \hat{C}\hat{A}\hat{B} + \hat{A}\hat{B}\hat{C} - \underbrace{\hat{A}\hat{C}\hat{B}}_{\hat{A}\hat{C}\hat{B}} \\ &= [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}] \end{aligned}$$

HW: Quantum mechanical operator $\hat{A} = (\hat{x} + \frac{d}{dx})$, $f(x) = x^2$. Evaluate the operator \hat{A}^2 .

Note: When evaluating a operator, it is essential to include a function $f(x)$; otherwise, we can obtain a spurious result.

Solutions: Let's start by applying the operator \hat{A} to $f(x)$:

$$\begin{aligned}\hat{A}f(x) &= \hat{A}(x^2) \\ &= (\hat{x} + \frac{d}{dx})(x^2) \\ &= \hat{x}(x^2) + \frac{d(x^2)}{dx} \\ &= x^3 + 2x\end{aligned}$$

$$\begin{aligned}\hat{A}^2 f(x) &= \hat{A}(\hat{A}f(x)) \\ &= \hat{A}(x^3 + 2x) \\ &= (\hat{x} + \frac{d}{dx})(x^3 + 2x) \\ &= \hat{x}(x^3 + 2x) + \frac{d(x^3 + 2x)}{dx} \\ &= (x^4 + 2x^2) + \frac{dx^3}{dx} + \frac{d2x}{dx} \\ &= x^4 + 2x^2 + 3x^2 + 2 \\ &= x^4 + 5x^2 + 2\end{aligned}$$

So, \hat{A}^2 acting on the function $f(x) = x^2$ results in the function $x^4 + 5x^2 + 2$.

1.3 Eigenfunctions and eigenvalues

In general, the function $\phi(x)$ is obtained by the application of the operator \hat{A} on an arbitrary function $\psi(x)$. The function $\phi(x)$ is linearly independent of $\psi(x)$. However, for some particular function $\psi_1(x)$, it is possible that

$$\hat{A}\psi_1(x) = \alpha_1\psi_1(x)$$

where α_1 is a complex number. In such a case $\psi_1(x)$ is said to be an **eigenfunction** of \hat{A} and α_1 is the corresponding **eigenvalue**. The problem of determining $\psi_1(x)$ and α_1 for a given \hat{A} is called an **eigenvalue problem**.

HW3: (a) Show that $e^{\alpha x}$ is an eigenfunction of the operator $\frac{d^n}{dx^n}$. What is the eigenvalue?

(b) Show that e^{ikx} is an eigen function of the operator $\hat{P}_x = -i\hbar\frac{\partial}{\partial x}$. What is the eigenvalue?

For a given operator \hat{A} , many eigenfunctions may exist, so that

$$\hat{A}\psi_i(x) = \alpha_i\psi_i(x)$$

where $\psi_i(x)$ are the eigenfunctions, which may even be infinite in number, and α_i are the corresponding eigenvalues. Each eigenfunction of \hat{A} is unique, that is to say, is **linearly independent** of the other eigenfunctions.

If $f(x) \neq cg(x)$ for any real number $c \neq 0$, we say $f(x)$ and $g(x)$ are linearly independent functions. Suppose $f(x) = 2x$ and $g(x) = 3x$, then both the functions are said to be called linearly dependent because $f(x) = \frac{2}{3}g(x)$. The functions $f(x) = 2x$ and $g(x) = 3x^2$ are linearly independent as $f(x) \neq cg(x)$. **Moreover, wavefunctions of a particle confined in a one-dimensional box are linearly independent.**

Sometimes two or more eigenfunctions have the same eigenvalue. In that situation the eigenvalue is said to be **degenerate**. When two, three, ..., n eigenfunctions have the same eigenvalue, the

eigenvalue is doubly, triply, . . . , n -fold degenerate. When an eigenvalue corresponds only to a single eigenfunction, the eigenvalue is non-degenerate.

1.4 Hermitian operators

The linear operator \hat{A} is **hermitian** if it possesses the property that

$$\int_{-\infty}^{\infty} dx f_m^*(x) \hat{A} f_n(x) = \int_{-\infty}^{\infty} dx f_n(x) [\hat{A}^* f_m^*(x)] \quad (1.4.1)$$

where $f_m(x)$ and $f_n(x)$ are any two well-behaved functions.

Example: The momentum operator $\hat{p}_x = -i\hbar \frac{d}{dx}$ is hermitian since

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_j^*(x) \hat{p}_x \psi_i(x) dx &= \int_{-\infty}^{\infty} \psi_j^*(x) \left(-i\hbar \frac{d\psi_i(x)}{dx} \right) dx \\ &= -i\hbar \left[\int_{-\infty}^{\infty} \psi_j^*(x) \frac{d\psi_i(x)}{dx} dx \right] \end{aligned}$$

Applying integration by parts

$$\begin{aligned} \int u(x)v(x) dx &= u(x) \int v(x) dx - \int \left(\frac{du(x)}{dx} \int v(x) dx \right) dx \\ &= -i\hbar \left[\int_{-\infty}^{\infty} \underbrace{\psi_j^*(x)}_{u(x)} \underbrace{\frac{d\psi_i(x)}{dx}}_{v(x)} dx \right] \\ &= -i\hbar \left[\psi_j^*(x) \int_{-\infty}^{\infty} \frac{d\psi_i(x)}{dx} dx - \int_{-\infty}^{\infty} \left(\frac{d\psi_j^*(x)}{dx} \int_{-\infty}^{\infty} \frac{d\psi_i(x)}{dx} dx \right) dx \right] \\ &= -i\hbar \left[\psi_j^*(x) \psi_i(x) \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{d\psi_j^*(x)}{dx} \psi_i(x) dx \right] \\ &= -i\hbar \cancel{\psi_j^*(x) \psi_i(x)} \Big|_{-\infty}^{\infty} + i\hbar \int_{-\infty}^{\infty} \psi_i(x) \left(\frac{d\psi_j^*(x)}{dx} \right) dx \\ &= \int_{-\infty}^{\infty} \psi_i(x) \left(i\hbar \frac{d\psi_j^*(x)}{dx} \right) dx \\ &= \int_{-\infty}^{\infty} \psi_i(x) (\hat{p}_x^* \psi_j^*(x)) dx \end{aligned}$$

The integrated part $\psi_j^*(x) \psi_i(x) \Big|_{-\infty}^{\infty}$ is zero if the functions $\psi_i(x)$ vanish at ∞ , which they must

in order to be well-behaved. The remaining integral is $\int_{-\infty}^{\infty} \psi_i(x) (\hat{p}_x^* \psi_j^*(x)) dx$, so that we have

$$\begin{aligned}\int_{-\infty}^{\infty} \psi_j^*(x) \hat{p}_x \psi_i(x) dx &= \int_{-\infty}^{\infty} \psi_i(x) (\hat{p}_x^* \psi_j^*(x)) dx \\ &= \int_{-\infty}^{\infty} \psi_i(x) (\hat{p}_x \psi_j(x))^* dx\end{aligned}$$

The operator $\frac{d}{dx}$ is not hermitian because

$$\int_{-\infty}^{\infty} \psi_j^*(x) \frac{d\psi_i(x)}{dx} dx = - \int_{-\infty}^{\infty} \psi_i(x) \frac{d\psi_j^*(x)}{dx} dx$$

The operator $\frac{d^2}{dx^2}$, however, is hermitian.

Note: The hermitian character of an operator depends not only on the operator itself, but also on the functions on which it acts and on the range of integration. An operator may be hermitian with respect to one set of functions, but not with respect to another set. It may be hermitian with respect to a set of functions defined over one range of variables, but not with respect to the same set over a different range. For example, the hermiticity of the momentum operator \hat{p}_x is dependent on the vanishing of the functions ψ_i at ∞ .

Theorem 1. *The eigenvalues of a hermitian operator are real.*

Another one is

Theorem 2. *If ψ_m and ψ_n are eigenfunctions of a hermitian operator \hat{A} with different eigenvalues a_m and a_n , then ψ_m and ψ_n are orthogonal.*

Consider the two eigenvalue equations

$$\begin{aligned}\hat{A}\psi_n &= a_n \psi_n \\ \hat{A}\psi_m &= a_m \psi_m\end{aligned}\tag{1.4.2}$$

We multiply the first of eqs. (1.4.2) by ψ_m^* and integrate; then we take the complex conjugate of the second, multiply by ψ_n and integrate to obtain

$$\begin{aligned}\hat{A}\psi_n &= a_n\psi_n \\ \int_{-\infty}^{\infty} \psi_m^* \hat{A}\psi_n dx &= a_n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx\end{aligned}\tag{1.4.3}$$

$$\begin{aligned}\hat{A}\psi_m &= a_m\psi_m \\ (\hat{A}\psi_m)^* &= a_m^*\psi_m^* \\ \int_{-\infty}^{\infty} \psi_n (\hat{A}\psi_m)^* dx &= \int_{-\infty}^{\infty} \psi_n \hat{A}^* \psi_m^* dx \\ &= \left[\int_{-\infty}^{\infty} \psi_n^* \hat{A}\psi_m dx \right]^* \\ &= \left[\int_{-\infty}^{\infty} \psi_n^* a_m \psi_m dx \right]^* \\ &= \left[a_m \int_{-\infty}^{\infty} \psi_n^* \psi_m dx \right]^* \\ &= a_m^* \int_{-\infty}^{\infty} \psi_n \psi_m^* dx \\ &= a_m^* \int_{-\infty}^{\infty} \psi_m^* \psi_n dx\end{aligned}\tag{1.4.4}$$

From eqs. (1.4.3) and (1.4.4), we obtain

$$\int_{-\infty}^{\infty} \psi_m^* \hat{A}\psi_n dx - \int_{-\infty}^{\infty} \psi_n \hat{A}^* \psi_m^* dx = (a_n - a_m^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx\tag{1.4.5}$$

Because \hat{A} is Hermitian,

$$\begin{aligned}\int_{-\infty}^{\infty} \psi_m^* \hat{A}\psi_n dx &= \int_{-\infty}^{\infty} \psi_n \hat{A}^* \psi_m^* dx \\ &= \int_{-\infty}^{\infty} \psi_n (\hat{A}\psi_m)^* dx \\ \int_{-\infty}^{\infty} \psi_m^* \hat{A}\psi_n dx - \int_{-\infty}^{\infty} \psi_n \hat{A}^* \psi_m^* dx &= 0 \\ \int_{-\infty}^{\infty} \psi_m^* \hat{A}\psi_n dx - \int_{-\infty}^{\infty} \psi_n (\hat{A}\psi_m)^* dx &= 0\end{aligned}\tag{1.4.6}$$

Applying the hermiticity condition expressed in eq.(1.4.6) in eq. (1.4.5), we get

$$(a_n - a_m^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad (1.4.7)$$

There are two possibilities to consider in eq. (1.4.7), $n = m$ and $n \neq m$.

When $n = m$, the integral is unity by normalization and so we have

$$\begin{aligned} (a_n - a_n^*) \int_{-\infty}^{\infty} \psi_n^* \psi_n dx &= 0 \\ (a_n - a_n^*) \underbrace{\int_{-\infty}^{\infty} \psi_n^* \psi_n dx}_1 &= 0 \\ (a_n - a_n^*) &= 0 \\ a_n &= a_n^* \end{aligned}$$

which is just another proof that the **eigenvalues are real**.

When $n \neq m$, we have

$$(a_n - a_m) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad \text{Eigenvalues of a hermitian operator is real.}$$

Now if the system is nondegenerate, $a_n \neq a_m$, and

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad (1.4.8)$$

A set of eigenfunctions that satisfies the condition in eq. (1.4.8) is said to be orthogonal. We have just proved that the **eigenfunctions of a Hermitian operator are orthogonal, at least for a nondegenerate system**.

1.5 The Schrodinger Equation and a Particle in a Box

Let us consider a particle of mass m confined to a box along the x axis between $x = 0$ and $x = a$. This case is called the problem of **a particle in a one-dimensional box**. This simple model has at least a crude application to the re electrons in a linear conjugated hydrocarbon.

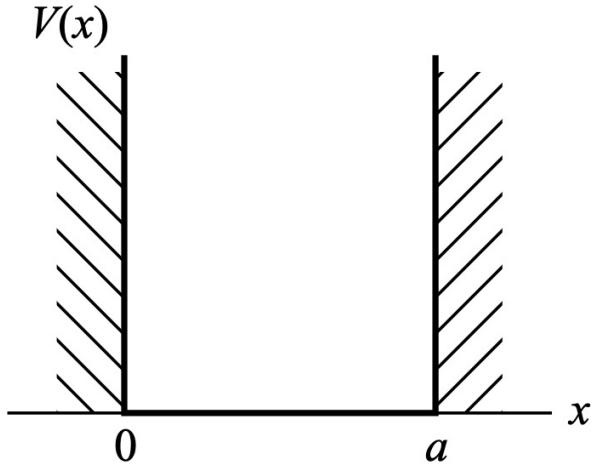


Figure 1.5.1: The potential energy $V(x)$ for a particle in a one-dimensional box of length a .

The potential energy for such a particle is given by $V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq a \\ \infty, & \text{if } x < 0, x > a \end{cases}$

The momentum operator is

$$\begin{aligned}\hat{p}_x &= -i\hbar \frac{d}{dx} \\ \hat{p}_x^2 &= \left(-i\hbar \frac{d}{dx}\right) \cdot \left(-i\hbar \frac{d}{dx}\right) \\ &= -\hbar^2 \frac{d^2}{dx^2}\end{aligned}$$

and the Hamiltonian operator is

$$\begin{aligned}\hat{H} &= \frac{\hat{p}_x^2}{2m} + \hat{V}(\hat{x}) \\ &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\end{aligned}$$

Our aim is finding the acceptable **wavefunction** and **energy** of the confined particle solving the **Time-Independent Schrödinger Equation (TISE)**

$$\hat{H}\psi(x) = E\psi(x)$$

Outside the potential well, the **TISE** is given by

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

for which the solution is simply $\psi(x) = 0$; the probability is zero for finding the particle outside the box where the potential is infinite.

Inside the box, the **TISE** is

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} &= E\psi(x) \\ \frac{d^2\psi(x)}{dx^2} &= -\frac{2mE}{\hbar^2}\psi(x) \\ \frac{d^2\psi(x)}{dx^2} + \frac{2mE}{\hbar^2}\psi(x) &= 0 \\ \frac{d^2\psi(x)}{dx^2} + k^2\psi(x) &= 0 \end{aligned} \quad (1.5.1)$$

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad (1.5.2)$$

The general solution of the homogeneous second order linear differential equation with constant coefficients (eq. 1.5.1) is

$$\psi(x) = A \cos(kx) + B \sin(kx) \quad (1.5.3)$$

where A and B are arbitrary constants (real or complex) of integration.

The constants A and B are determined by the *boundary conditions* placed on the solution $\psi(x)$. Since $\psi(x)$ must be continuous, the boundary conditions require that $\psi(x)$ vanish at each end of the box so as to match the value of $\psi(x)$ outside the box, i.e., $\psi(0) = \psi(a) = 0$. At $x = 0$, the function $\psi(0)$ from eq. (1.5.3) is

$$\psi(0) = A \cos(0) + B \sin(0) = A$$

so that $A = 0$ and $\psi(x)$ is now

$$\psi(x) = B \sin(kx)$$

At $x = a$, $\psi(a)$ is

$$\psi(a) = B \sin(ka) = 0$$

The constant B cannot be zero, for then $\psi(x)$ would vanish everywhere and there would be no particle. Consequently, we have $\sin(ka) = 0$ or

$$ka = n\pi \quad n = 0, \pm 1, \pm 2, \pm 3, \dots \quad (1.5.4)$$

Important to note that the value of n is restricted to any positive integer greater than zero. The solution $n = 0$ would cause to vanish everywhere and is therefore not acceptable. Negative values of n give redundant solutions because $\sin(-\theta)$ equals $-\sin(\theta)$.

By using eq. (1.5.2) and (1.5.4), we find that

$$\begin{aligned} E_n &= \frac{k^2 \hbar^2}{2m} \\ &= \frac{\hbar^2}{2m} \frac{n^2 \pi^2}{a^2} \\ &= \frac{n^2 \pi^2 \hbar^2}{2ma^2} \\ &= \frac{n^2 \pi^2 h^2}{2ma^2 4\pi^2} \\ &= \frac{n^2 h^2}{8ma^2} \end{aligned} \quad (1.5.5)$$

The energy of the particle is said to be quantized and the integer n is called a quantum number. Note that the quantization arises naturally from the boundary conditions. The lowest allowed energy level is called the zero-point energy and is given by $E_1 = \frac{\hbar^2}{8ma^2}$.

The wave function corresponding to E_n is (using eq. (1.5.4))

$$\begin{aligned} \psi_n(x) &= B \sin(ka) \\ &= B \sin\left(\frac{n\pi x}{a}\right) \quad n = 1, 2, 3, \dots \end{aligned} \quad (1.5.6)$$

We will determine the constant B shortly.

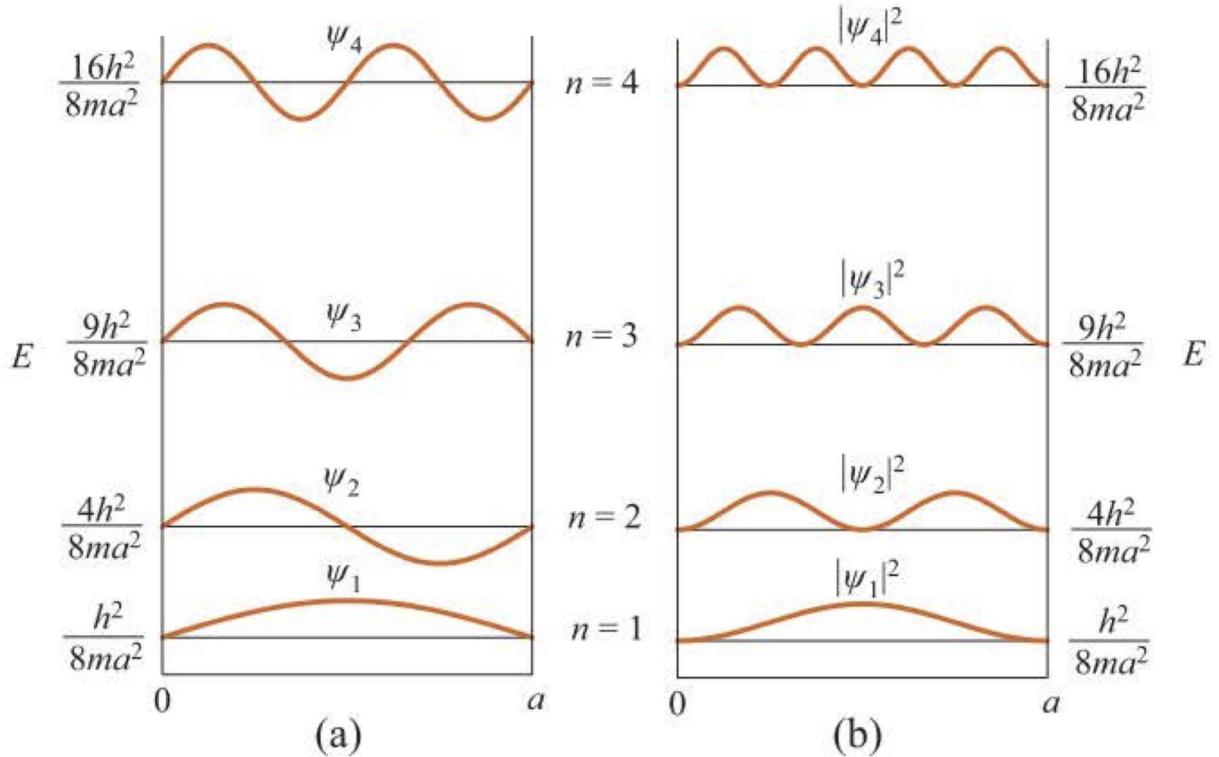


Figure 1.5.2: The energy levels, wave functions (a), and probability densities (b) for the particle in a box. Note that the energy increases with the number of nodes.

The normalization constant B in eq. (1.5.6) is determined by using the normalization condition of the wavefunction as

$$\int_0^a \psi_n^*(x) \psi_n(x) dx = 1 \quad (1.5.7)$$

$$|B|^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1 \quad (1.5.8)$$

Let $\frac{n\pi x}{a} = z$, then $\frac{n\pi}{a} dx = dz$, $dx = \frac{a}{n\pi} dz$. The limits: when $x = 0, z = 0$ but when $x = a, z = n\pi$

$$\begin{aligned} \frac{a}{n\pi} \int_0^{n\pi} \sin^2 z dz &= \frac{a}{2n\pi} \int_0^{n\pi} 2 \sin^2(z) dz \\ &= \frac{a}{2n\pi} \int_0^{n\pi} (1 - \cos(2z)) dz \\ &= \frac{a}{2n\pi} \left[\int_0^{n\pi} dz + \int_0^{n\pi} \cos(2z) dz \right] \\ &= \frac{a}{2n\pi} \left[n\pi + \frac{\sin(2z)}{2} \Big|_0^{n\pi} \right] \\ &= \frac{a}{2n\pi} [n\pi + \sin(2n\pi) - \sin(0)] \end{aligned}$$

$$\begin{aligned}
&= \frac{a}{2n\pi} [n\pi + \cancel{\sin(2n\pi)}^0 - \sin(0)] \quad n = 1, 2, 3, \dots \\
&= \frac{a}{2}
\end{aligned} \tag{1.5.9}$$

From eqs. (1.5.8) and (1.5.9), we obtain

$$\begin{aligned}
|B|^2 \frac{a}{2} &= 1 \\
B &= \sqrt{\frac{2}{a}}
\end{aligned} \tag{1.5.10}$$

Inserting eq. (1.5.10) in eq.(1.5.6), we get

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad n = 1, 2, 3, \dots \tag{1.5.11}$$

1.6 The Hydrogen Atom

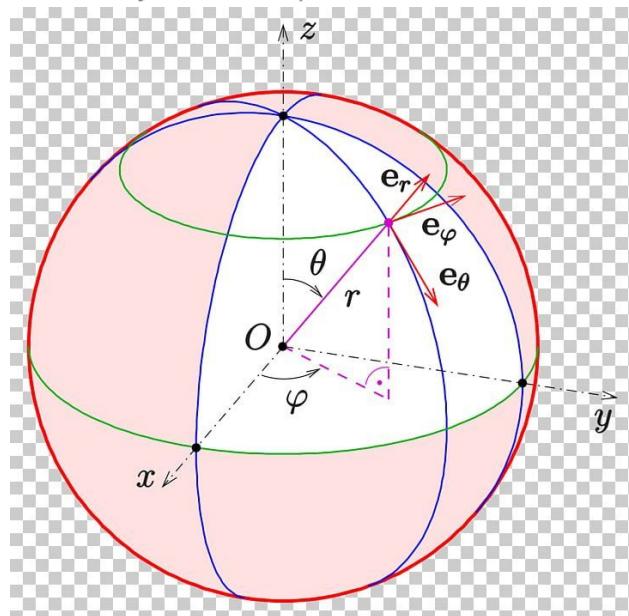
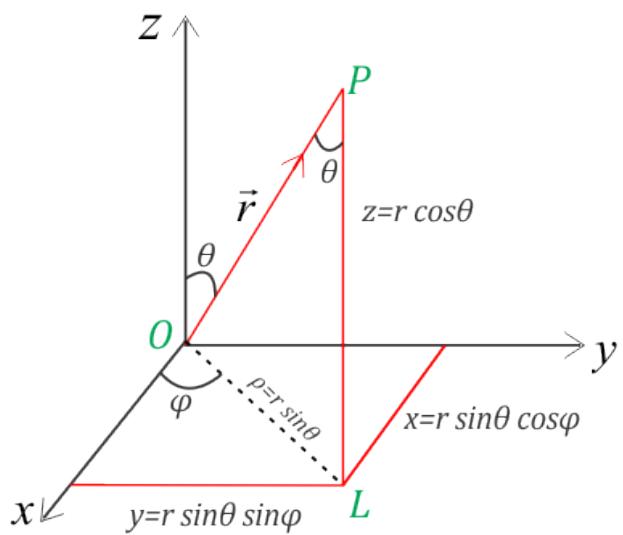
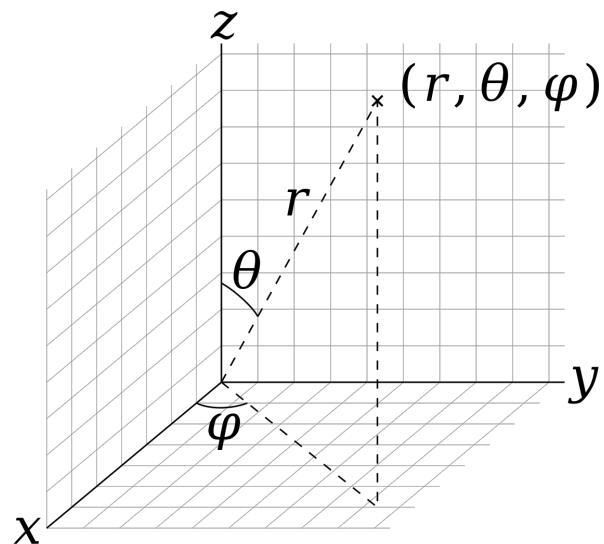
Spherical coordinate system

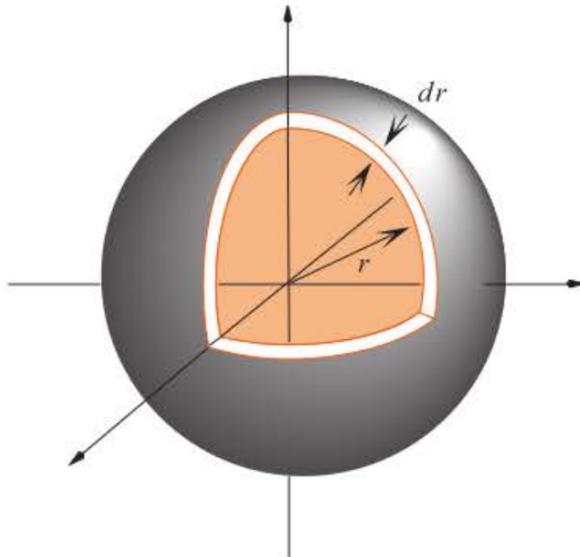
Energy of the hydrogen atom is

$$\begin{aligned}
E_n &= -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} \\
&= -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} \quad n = 1, 2, 3, \dots
\end{aligned} \tag{1.6.1}$$

Bohr radius is

$$\begin{aligned}
a_0 &= \frac{\epsilon_0 h^2}{\pi m_e e^2} \\
&= \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}
\end{aligned} \tag{1.6.2}$$





Introducing eq. (1.6.2) in eq. (1.6.1), we get

$$\begin{aligned}
 E_n &= -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} \\
 &= -\frac{e^2}{8\pi \epsilon_0 n^2} \frac{m_e e^2}{4\pi \epsilon_0 \hbar^2} \\
 &= -\frac{e^2}{8\pi \epsilon_0 n^2} \frac{1}{a_0} \\
 &= -\frac{e^2}{8\pi \epsilon_0 a_0 n^2} \quad n = 1, 2, 3, \dots
 \end{aligned} \tag{1.6.3}$$

It is surely remarkable that these are the same energies obtained from the Bohr model of the hydrogen atom. Of course, the electron now is not restricted to the sharply defined orbits of Bohr, but is described by its wavefunction, $\psi(r, \theta, \phi)$.

The radial wavefunctions, depend on two quantum numbers n and l and are given by

1.7 Important Theorems of Quantum Mechanics

1.7.1 Virial Theorem

Theorem. When the potential energy, $V(r)$, due to interaction of any two particles is proportional to r^n , then: $2 \langle T \rangle = n \langle V \rangle$.

For Coulomb energy, $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$, $n = -1$, therefore $2\langle T \rangle = -\langle V \rangle$ for all atoms and molecules, the motions of the planets, etc.

$$\begin{aligned}\hat{H} &= \hat{K} + \hat{V} \\ E_n &= \langle T \rangle + \langle V \rangle \\ &= \langle T \rangle - 2\langle T \rangle \\ &= -\langle T \rangle\end{aligned}$$

$$\begin{aligned}E_n &= \langle T \rangle + \langle V \rangle \\ &= -\frac{1}{2}\langle V \rangle + \langle V \rangle \\ &= \frac{1}{2}\langle V \rangle \\ \langle V \rangle &= 2E_n\end{aligned}$$

For a harmonic oscillator, $V(x) = \frac{1}{2}kx^2$, $n = 2$ so that $\langle T \rangle = \langle V \rangle$, again in either classical or quantum mechanics.

1.7.2 Hellmann-Feynman theorem

Theorem. *In quantum mechanics, the Hellmann-Feynman theorem relates the derivative of the total energy with respect to a parameter to the expectation value of the derivative of the Hamiltonian with respect to that same parameter.*

The theorem states

$$\frac{dE_\lambda}{d\lambda} = \langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \rangle,$$

- where \hat{H}_λ is a Hermitian operator depending upon a continuous parameter λ ,
- $|\psi_\lambda\rangle$, is an eigenstate (eigenfunction) of the Hamiltonian, depending implicitly upon λ ,

- E_λ is the energy (eigenvalue) of the state $|\psi_\lambda\rangle$, i.e., $\hat{H}_\lambda |\psi_\lambda\rangle = E_\lambda |\psi_\lambda\rangle$.

Using Dirac's bra-ket notation these two conditions are written as

$$\begin{aligned}\hat{H}_\lambda |\psi_\lambda\rangle &= E_\lambda |\psi_\lambda\rangle \\ \langle \psi_\lambda | \psi_\lambda \rangle &= 1 \\ \frac{d \langle \psi_\lambda | \psi_\lambda \rangle}{d\lambda} &= 0\end{aligned}$$

The proof then follows through an application of the derivative product rule to the expectation value of the Hamiltonian viewed as a function of λ :

$$\begin{aligned}\frac{dE_\lambda}{d\lambda} &= \frac{d}{d\lambda} \langle \psi_\lambda | \hat{H} | \psi_\lambda \rangle \\ &= \left\langle \frac{d\psi_\lambda}{d\lambda} \middle| \hat{H} \middle| \psi_\lambda \right\rangle + \langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \rangle + \left\langle \psi_\lambda \middle| \hat{H} \middle| \frac{d\psi_\lambda}{d\lambda} \right\rangle \\ &= E_\lambda \left\langle \frac{d\psi_\lambda}{d\lambda} \middle| \psi_\lambda \right\rangle + \langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \rangle + \underbrace{\left\langle \hat{H}\psi_\lambda \middle| \frac{d\psi_\lambda}{d\lambda} \right\rangle}_{\text{property of hermitian op is applied}} \\ &= \overbrace{E_\lambda \left\langle \frac{d\psi_\lambda}{d\lambda} \middle| \psi_\lambda \right\rangle + E_\lambda \left\langle \psi_\lambda \middle| \frac{d\psi_\lambda}{d\lambda} \right\rangle}^0 + \langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \rangle \\ &= E_\lambda \cancel{\frac{d \langle \psi_\lambda | \psi_\lambda \rangle}{d\lambda}}^0 + \langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \rangle \\ &= \langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \rangle\end{aligned}$$