Chapter 1 Review of Quantum Mechanics

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Basic Questions

- **A.** How do we describe motion of a quantum system, say, a particle moving inside a box, or an electron in Hydrogen atom?
- **B.** What is $a^{\dagger}|10\rangle$ for a harmonic oscillator?
- **C.** Where do Pauli matrices come from?

1.1 State and operator

In **Classical Mechanics**, a state of a particle's motion is specified by its position \mathbf{r} and momentum \mathbf{p} at a given time t, $(\mathbf{r}(t), \mathbf{p}(t))$, where the momentum is defined as 1st order time derivative,

$$\mathbf{p} \equiv m\mathbf{v} = m\frac{d\mathbf{r}}{dt}$$

with *m* as its mass. Notice that both the position and momentum can be measured experimentally. The equation of motion which determines $(\mathbf{r}(t), \mathbf{p}(t))$ is given by Newton's 2nd law of motion involving 2nd order time derivative

$$\frac{d\mathbf{p}}{dt} = m\frac{d^2\mathbf{r}}{dt^2} = \mathbf{f}$$

where **f** is the total force acting on the particle. If the initial condition $(\mathbf{r}(0), \mathbf{p}(0))$ is given, one can from the above equation determine completely the particle's motion $(\mathbf{r}(t), \mathbf{p}(t))$ at any later time.

An equivalent description is provided by Hamiltonian formalism. Hamiltonian of a particle is defined as the sum of its kinetic and potential energy

$$H \equiv T + V$$

$$T \equiv \frac{1}{2}mv^{2} = \frac{p^{2}}{2m} = \frac{1}{2m}\left(p_{x}^{2} + p_{y}^{2} + p_{z}^{2}\right)$$

$$\mathbf{f} = -\nabla V, \text{ or } V_{2} - V_{1} = -\int_{1}^{2} \mathbf{f} \cdot d\mathbf{r}.$$

The equation of motion in this formalism is given by

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad i = x, y, z \longrightarrow v_x = \frac{dx}{dt}$$
 etc.
 $\dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad i = x, y, z \longrightarrow m\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x} = f_x$ etc.

with notation $(q_x, q_y, q_z) = (x, y, z) = \mathbf{r}$, and $\dot{q}_i \equiv dq_i/dt$ etc..

In **Quantum Mechanics**, the state of motion for a particle is NOT specified by its position and momentum. In fact, the position and momentum can not be precisely determined simultaneously. Instead, the state of motion for a quantum particle is described by a **wavefunction** (or **state function**) which extends to a large region of space, and can be a complex function. Typically, a (time independent) wavefunction of a stationary state for a quantum particle is written as

$$\Phi_{k}\left(\mathbf{r}\right)$$

where k represents one set of so-called **quantum numbers**, usually discrete. Examples of quantum numbers are linear momentum, angular momentum, etc. Different set of quantum numbers, say, k_1, k_2, \dots , represent different wavefunction

$$\Phi_{k_{1}}\left(\mathbf{r}
ight),\Phi_{k_{2}}\left(\mathbf{r}
ight),\cdots$$

which correspond to different states of the particle's motion. Therefore, people sometime use these discrete set of quantum numbers to characterize state of the particle's motion.

A state function such as $\Phi_k(\mathbf{r})$ can not be measured directly. It has a meaning of probability : its modular $|\Phi_k(\mathbf{r})|^2$ gives the spatial distribution of the particle's position with quantum number k. Hence, in this representation of a quantum state, the quantum number (e.g., momentum) is known precisely, but particle's position is unknown (known by a distribution).

Note:

(a) Normalization: Since $|\Phi_k(\mathbf{r})|^2$ has the meaning of distribution, it must be normalizable

$$\int d^3r \, \left| \Phi_k \left(\mathbf{r} \right) \right|^2 = \int \left| \Phi_k \left(\mathbf{r} \right) \right|^2 \, d^3r = 1 \; .$$

(b) Linear Superposition: If $\Phi_{k_1}(\mathbf{r})$, $\Phi_{k_2}(\mathbf{r})$ are two possible states of a particle, their linear summation

$$\Psi\left(\mathbf{r}\right) = C_{1}\Phi_{k_{1}}\left(\mathbf{r}\right) + C_{2}\Phi_{k_{2}}\left(\mathbf{r}\right)$$

is also a state of the particle. In the above eq. C_1 and C_2 are any two complex numbers. There are also other properties we will discuss them later.

A general time-dependent wavefunction can be written as $\Psi(\mathbf{r}, t)$, which can usually expand in terms $\Phi_k(\mathbf{r})$ as

$$\Phi\left(\mathbf{r},t\right) = \sum_{k} C_{k} \Phi_{k}\left(\mathbf{r}\right) f_{k}\left(t\right)$$

where C_k is a constant and $f_k(t)$ depends only on t.

Example: Plane wave is given by a state function

$$\Phi_{p}(\mathbf{r},t) = e^{i(\mathbf{p}\cdot\mathbf{r}-E_{p}t)/\hbar}, \quad E_{p} = \frac{p^{2}}{2m}, \quad \omega = \frac{E}{\hbar} = \frac{\hbar k^{2}}{2m}$$
$$= \sum_{k} C_{k} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{k}t)}, \quad C_{k} = \begin{cases} 1, & \mathbf{k} = \frac{\mathbf{p}}{\hbar}\\ 0, & \text{otherwise} \end{cases}$$

The state $\Phi_k(\mathbf{r})$ with a definite quantum number is usually referred as **pure state** and state $\Psi(\mathbf{r}, t)$ which is a linear combination of pure state is referred to as **mixed** state.

Question: If we know a particle is in a state $\Psi(\mathbf{r}, t)$ (a pure state or a mixed state), what are its observables, i.e., its position, momentum, energy?

In QM, all observables become operator, represented by headed notation, e.g., \hat{A} . An operator is meant to act on right side, as

$$\Phi' = \hat{A}\Phi$$

with Φ' as a new state function. The experimentally measurable quantity is the so-called expectation value of \hat{A} is a state

$$\left\langle \hat{A} \right\rangle = \int d^3 r \, \Psi^* \hat{A} \Psi$$

which in general is a function of time.

Transposed operator is defined as, for any two state function Φ and Ψ

$$\int d^3r \,\Phi\left(\hat{A}\Psi\right) = \int d^3r \,\Psi\left(\tilde{A}\Phi\right) = \int d^3r \,\left(\tilde{A}\Phi\right)\Psi$$

where \tilde{A} is the transposed operator of \hat{A} . It is left-acting. Example, operator $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$ has its transposed counter part

$$\tilde{\nabla} = -\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

Hermitian conjugate operator is defined as complex conjugate of its transposed operator

$$\hat{A}^{\dagger} = \tilde{A}^*$$

and if $\hat{A} = \hat{A}^{\dagger}$ it is said that \hat{A} is a **Hermitian operator**. Observables such as momentum or energy are real numbers. Hence their corresponding operators must be Hermitian operators.

Correspondence principle. The relation between classical quantities and corresponding quantum mechanical operators are given as

$$\begin{array}{ll} \mathbf{r} & \rightarrow & \hat{\mathbf{r}} = \mathbf{r} \\ \mathbf{p} & \rightarrow & \hat{\mathbf{p}} = -i\hbar\nabla \quad (\text{gradient}) \end{array}$$

and in general

$$F(\mathbf{r},\mathbf{p}) \to \hat{F} = \hat{F}(\mathbf{r},-i\hbar\nabla)$$

For example, the expectation value of position and momentum of a particle at in state $\Psi(\mathbf{r}, t)$ are

$$\begin{aligned} \langle \hat{\mathbf{r}} \rangle &= \int d^3 r \, \Psi^* \hat{\mathbf{r}} \Psi = \int \mathbf{r} d^3 r \, |\Psi|^2 \\ \langle \hat{\mathbf{p}} \rangle &= \int d^3 r \, \Psi^* \hat{\mathbf{p}} \Psi = -i\hbar \int d^3 r \, \Psi^* \nabla \Psi \end{aligned}$$

Hamiltonian operator. According the Corresponding Principle, the Hamiltonian operator of a quantum particle is given by

$$\hat{H} = \frac{1}{2m}\hat{\mathbf{p}}^2 + V(\hat{\mathbf{r}})$$
$$= -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

with

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and the energy expectation value of a particle in a state $\Psi(\mathbf{r}, t)$.

Product of two operators. If A and B are two operators of a quantum system, their product

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

is also an operator of the system. Note that in general

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$
.

Commutation of two operator is defined as

$$\left[\hat{A},\hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \; .$$

If $\begin{bmatrix} \hat{A}, \hat{B} \end{bmatrix} = 0$, \hat{A} and \hat{B} are said commute with one another. **Prove**

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

1.2 Schrödinger Equation

We have learned in the previous section that a quantum state of a particle is specified by a wavefunction. How do we determine this wavefunction? First, we discuss eigenstate and equation in general.

Eigenequation. For a given operator \hat{A} , if we can find a wavefunction Φ and a number *a* such that

$$\hat{A}\Phi = a\Phi$$

then, Φ is an **eigenstate** of \hat{A} and a is the corresponding **eigenvalue**, and the above equation is called eigenequation. Usually, there are more than one eigenstate for a given operator. Suppose there are N of them. We can label them by an index $n = 1, 2, \dots, N$ (quantum number as mentioned before) and write the eigenequation as

$$A\Phi_n = a_n \Phi_n, \quad n = 1, 2, ..., N$$
.

Example: Prove two eigen states of a Hermitian operator are always orthogonal to each other if the corresponding eigenvalues are different.

Proof: The eigenequation are

$$A\Phi_n = a_n\Phi_n, \quad n = 1, 2, \quad a_1 \neq a_2$$

we have

$$\int d^3r \, \Phi_1^* \hat{A} \Phi_2 = a_2 \int d^3r \, \Phi_1^* \Phi_2$$
$$= \int d^3r \, \left(\hat{A} \Phi_1\right)^* \Phi_2$$
$$= a_1 \int d^3r \, \Phi_1^* \Phi_2$$

where we have applied the property of Hermitian operator on the 2nd eq. Hence we have

$$(a_2 - a_1) \int d^3r \, \Phi_1^* \Phi_2 = 0 \to \int d^3r \, \Phi_1^* \Phi_2 = 0$$

since $a_1 \neq a_2$.

Example. Eigenstates of linear momentum in a box of size L.

Solution: The eigenequation is

$$-i\hbar\nabla\Phi\left(\mathbf{r}\right)=\mathbf{p}\Phi\left(\mathbf{r}\right)$$

where we denoted the eigenvalue as \mathbf{p} . It is easy to prove that the normalized eigenfunction is

$$\Phi\left(\mathbf{r}\right) = \frac{1}{\sqrt{V}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$$

where $V = L^3$ is volume of the box. If we impose a periodical boundary condition (pbc)

$$\Phi(\mathbf{r}) = \Phi(\mathbf{r} + L\hat{\alpha}), \quad \hat{\alpha} = \hat{i}, \hat{j}, \hat{k}$$

with \hat{i},\hat{j},\hat{k} as unit vector in x,y,z directions, we see that the eigenvalue **p** must be discrete and satisfy

$$\mathbf{p} = \frac{2\pi\hbar}{L} \left(n_x, n_y, n_z \right), \quad n_x, n_y, n_z = 0, \pm 1, \pm 2, \cdots$$

We can now specify the eigenstates by these integers (or quantum numbers)

$$\Phi_{n_x,n_y,n_z}\left(\mathbf{r}\right) = \Phi_{\mathbf{n}}\left(\mathbf{r}\right) \; .$$

Separation of Variables. If an operator \hat{C} can be written as sum of two

$$\hat{C} = \hat{A} + \hat{B}$$

with \hat{A} and \hat{B} independent to one another, i.e., $\hat{A} = \hat{A}(\hat{\mathbf{r}}_a, \hat{\mathbf{p}}_a)$ and $\hat{B} = \hat{B}(\hat{\mathbf{r}}_b, \hat{\mathbf{p}}_b)$, and with their eigenfunctions and eigenvalues

$$\hat{A}\Phi_{\alpha}\left(\mathbf{\hat{r}}_{a}\right) = E_{\alpha}\Phi_{\alpha}\left(\mathbf{\hat{r}}_{a}\right), \quad \hat{B}\Phi_{\beta}\left(\mathbf{\hat{r}}_{b}\right) = E_{\beta}\Phi_{\beta}\left(\mathbf{\hat{r}}_{b}\right)$$

it is easy to prove that operator \hat{C} 's eigenfunction is the product, and its eigen value is the sum

$$\hat{C}\Psi_{k}\left(\hat{\mathbf{r}}_{a},\hat{\mathbf{r}}_{b}\right) = E_{k}\Psi_{k}\left(\hat{\mathbf{r}}_{a},\hat{\mathbf{r}}_{b}\right)
\Psi_{k}\left(\hat{\mathbf{r}}_{a},\hat{\mathbf{r}}_{b}\right) = \Phi_{\alpha}\left(\hat{\mathbf{r}}_{a}\right)\Phi_{\beta}\left(\hat{\mathbf{r}}_{b}\right), \quad E_{k} = E_{\alpha} + E_{\beta}$$

with its quantum number $k = (\alpha, \beta)$.

Schrödinger Equation. In CM, the time evolution of state $(\mathbf{r}(t), \mathbf{p}(t))$ is determined by the Newton's 2nd law involving 2nd order time derivative. In QM, the time evolution of state of a particle's motion is determine by the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi\left(\mathbf{r},t\right)=\hat{H}\Psi\left(\mathbf{r},t\right)$$

with \hat{H} the Hamiltonian of the particle. It involves only 1st order time derivative.

If operator \hat{H} is time-independent, e.g.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

the solution is in a form

$$\Psi\left(\mathbf{r},t\right) = \Phi\left(r\right)e^{iEt/\hbar}$$

and Schrödinger eq. reduces to an eigenequation, time-independent Schrödinger eq.

$$\hat{H}\Phi\left(\mathbf{r}\right) = E\Phi\left(\mathbf{r}\right)$$

with $\Phi(r)$ as the eigenstate and E the corresponding eigenvalue.

Many-particle system. Consider two particle system. The Hamiltonian in general is given by

$$\hat{H} = \hat{H}_{1} + \hat{H}_{2} + \hat{V}_{12} \hat{H}_{i} = -\frac{\hbar^{2}}{2m} \nabla_{i}^{2} + V(\mathbf{r}_{i}), \quad \hat{V}_{12} = V(\mathbf{r}_{1}, \mathbf{r}_{2})$$

its eigenequation can be written as

$$\hat{H}\Psi_{k}\left(\mathbf{r}_{1},\mathbf{r}_{2}\right)=E_{k}\Psi_{k}\left(\mathbf{r}_{1},\mathbf{r}_{2}\right)$$
.

If the interaction can be ignored, $V(\mathbf{r}_1, \mathbf{r}_2) = 0$, with $\hat{H} = \hat{H}_1 + \hat{H}_2$, then by the Principle of Separation of Variables, we have

$$\Psi_k(\mathbf{r}_1, \mathbf{r}_2) = \Phi_{n_1}(\mathbf{r}_1) \Phi_{n_2}(\mathbf{r}_2), \quad E_k = e_{n_1} + e_{n_2}$$

with

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Phi_n(\mathbf{r}) = e_n\Phi_n(\mathbf{r}) \ .$$

Summary

(a) In QM, state of a particle's motion is specified by a state function and observables now becomes Hermitian operators. Their expectation values with respect to a wavefunction gives measurable physical values in a given state.

(b) State functions of an hermitian operator are determined by its eigenequation. (c) Eigen state functions $\Phi_k(\mathbf{r})$ has following properties:

• Normalization

$$\int \left| \Phi_k \left(\mathbf{r} \right) \right|^2 d^3 r = 1$$

• Linear Superposition

If $\Phi_{k_1}(\mathbf{r})$, $\Phi_{k_2}(\mathbf{r})$ are two possible states of a particle, their linear summation

$$\Psi\left(\mathbf{r}\right) = C_{1}\Phi_{k_{1}}\left(\mathbf{r}\right) + C_{2}\Phi_{k_{2}}\left(\mathbf{r}\right)$$

is also a state of the particle. In the above eq. C_1 and C_2 are any two complex numbers

• Orthogonality

Two states with different quantum numbers must be orthogonal to each other

$$\int \Phi_{k_1}^*\left(\mathbf{r}\right) \Phi_{k_2}\left(\mathbf{r}\right) d^3r = 0.$$

• Completeness

Any state Ψ of a particle's motion can always be written as a linear summation of all eigenstates Φ_k of one of its Hermitian operator

$$\Psi = \sum_{k} C_k \Phi_k$$

where C_k are complex number.

(d) If Hamiltonian of a particle is time-independent, its wavefunction can be written as

$$\Psi_k(r,t) = \Phi_k(r) e^{iE_k t/\hbar}$$

where $\Phi_k(r)$ and E_k are the eigenstates and eigenvalues of Hamiltonian operator, obeying the time-independent Schrödinger eq.

$$H\Phi_k = E_k\Phi_k$$
.

1.3 Harmonic Oscillator and Dirac notation

A harmonic oscillator is system consisting of a particle attached to a spring. Classically, if we choose the equilibrium position as origin, the equation of motion is

$$m\frac{d^2x}{dt^2} = -kx, \quad k = \text{const}$$

which leads to a harmonic (periodical) motion of angular frequency $\omega = \sqrt{\frac{k}{m}}$

$$x(t) = x_0 \sin(\omega t + \theta_0), \quad p(t) = x_0 \cos(\omega t + \theta_0)$$

This periodical motion can be visualized if we plot its potential

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

as shown. Depending on the initial condition, the particle just swings between two extreme position with conserved total energy and this energy can be any number.

Quantum mechanically, we will see the particle's motion is quite different: it must be in one of discrete energy levels. The time-independent Schrödinger eq. is given by

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right)\psi(x) = E\psi(x)$$

It is easy to prove that a Gaussian type of function

$$\psi_0(x) = Ae^{-\alpha x^2}, \ \alpha = m\omega/2\hbar, \quad A = \text{const.} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

is a solution with eigenvalue $E_0 = \hbar \omega/2$. In fact, all its eigenvalues can be simply written as

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, 3, \cdots$$

with n = 0 corresponding to the ground state, the state with lowest energy.

In the following, we will apply algebraic technique to find all state functions and corresponding eigenvalues.

1.3.1 Dirac Notation

Some times it is very convenient to use Dirac notation in QM. The state functions mention above are quite similar to vectors, with similar summation, inner product properties. Using Dirac notation, a state function $\Phi(\mathbf{r})$ corresponds to a vector in **Hilbert space** (infinite dimension), denoted as $|\Phi\rangle$,

$$\Phi(\mathbf{r}) \rightarrow |\Phi\rangle$$

and the complex conjugate of $\Phi(\mathbf{r})$ is denoted as

$$\Phi^*(\mathbf{r}) \to \langle \Phi |$$

A scalar in \mathcal{H} is just a complex number. In \mathcal{H} scalar multiplication and vector addition are defined as the usual complex operations, *e.g.*

$$\Phi = c_1 \Phi_1 + c_2 \Phi_2$$

or

$$\left|\Phi\right\rangle = c_1 \left|\Phi_1\right\rangle + c_2 \left|\Phi_2\right\rangle$$

The dot product (inner product) between two state vectors is defined as the following definite integral

$$\langle \Phi_1 | \Phi_2 \rangle \equiv \int \Phi_1^*(\mathbf{r}) \Phi_2(\mathbf{r}) \, d^3 r \; .$$

There are several properties of state vector dot product:

Two state functions are orthogonal is similarly expressed as their inner product is zero

$$\langle \Phi_1 | \Phi_2 \rangle = 0$$
.

A complete orthonormal set of \mathcal{H} state-vectors $\{|\Phi_n\rangle, n = 1, 2, ..., \infty\}$ is defined as (a) any state vector in \mathcal{H} can be written as a linear combination of $\{|\Phi_n\rangle\}$; (b) $\langle \Phi_n | \Phi_m \rangle = \delta_{nm}$.

A vector $|\Psi\rangle$ in \mathcal{H} can be written in a component form as

$$|\Psi\rangle = \sum_{n=1}^{\infty} C_n |\Phi_n\rangle = \sum_{n=1}^{\infty} \langle \Phi_n | \Psi \rangle |\Phi_n\rangle, \quad C_n = \langle \Phi_n | \Psi \rangle.$$

where C_n is $|\Psi\rangle$'s component in $|\Phi_n\rangle$.

Operators in \mathcal{H} . $\Psi(\mathbf{r}) = \widehat{O} \Phi(\mathbf{r})$ in Dirac notation, we write

$$|\Psi\rangle = \hat{O} |\Phi\rangle = \left|\hat{O}\Phi\right\rangle \ .$$

Hermitian conjugate. Let $\Psi = \hat{O}\Phi$, then

$$\Psi^* = \left(\widehat{O}\Phi\right)^* = \Phi^*\widehat{O}^\dagger$$

where \hat{O}^{\dagger} is called the Hermitian conjugate of \hat{O} . It is left-acting. In Dirac notation,

 $|\Psi\rangle = \hat{O} |\Phi\rangle = |\hat{O}\Phi\rangle$ Hermitian conjugate $\langle \Psi| = \langle \Phi|\hat{O}^{\dagger} = \langle \hat{O}\Phi|$

or

$$\left(\left\langle \Phi_1 \right| \hat{A} \left| \Phi_2 \right\rangle \right)^* = \left\langle \Phi_2 \right| \hat{A}^{\dagger} \left| \Phi_1 \right\rangle \ .$$

Therefore, any operator \hat{A} can be right-acting or left-acting and the relation between the two is the Hermitian conjugate to one another. e.g.

$$\int \Phi^* \hat{A} \Psi \, d^3 r = \langle \Phi | \, \hat{A} \, | \Psi \rangle = \langle \Phi | \, \hat{A} \Psi \rangle, \quad \hat{A} \equiv \hat{B}^{\dagger}$$
$$= \langle \Phi | \, \hat{B}^{\dagger} \, \Psi \rangle = \left\langle \hat{B} \Phi \right| \, \Psi \rangle = \left\langle \hat{A}^{\dagger} \Phi \right| \, \Psi \rangle$$

Example: The following 1D operator, with x_0, p_0 as constants,

$$\hat{A} = \frac{\hat{x}}{x_0} + i\frac{\hat{p}}{p_0}$$

has its hermitian conjugate

$$\hat{A}^{\dagger} = \frac{\hat{x}}{x_0} - i\frac{\hat{p}}{p_0}$$

since both \hat{x} and \hat{p} are Hermitian operators, i.e. $\hat{x}^{\dagger} = \hat{x}, \hat{p}^{\dagger} = \hat{p}$.

Hermitian conjugate of a product. Let $\hat{O} = \hat{A}\hat{B}$, the Hermitian conjugate of \hat{O} is given by $\hat{O}^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger}$ since

$$\left\langle \Psi \right| \hat{A} \hat{B} \left| \Phi \right\rangle = \left\langle \hat{A}^{\dagger} \Psi \right| \hat{B} \left| \Phi \right\rangle = \left\langle \hat{B}^{\dagger} \hat{A}^{\dagger} \Psi \right| \Phi \rangle$$

If \hat{A} and \hat{B} are Hermitian operators, \hat{O} is not necessarily Hermitian. This is because \hat{A} and \hat{B} in general do not commute, namely $\hat{A}\hat{B} \neq \hat{B}\hat{A}$.

Eigenvector, eigenvalue, and eigenoperator. If

$$\widehat{O}\Phi = c\Phi, \quad \operatorname{or}\widehat{O} |\Phi\rangle = c |\Phi\rangle$$

 \hat{O} is eigenoperator, c is its eigenvalue, $|\Phi\rangle$ is its eigenvector.

The expectation value of an operator \hat{O} with respect to a state vector $|\psi\rangle$ is given by

$$\overline{O} = \left\langle \widehat{O} \right\rangle \equiv \frac{\left\langle \Phi \right| \widehat{O} \left| \Phi \right\rangle}{\left\langle \Phi \right| \left| \Phi \right\rangle}$$

where $\langle \Phi | \Phi \rangle$ is the normalization factor.

1.3.2 Creation and Destruction Operators

Now we are ready to apply algebraic technique to solve quantum harmonic problem.

First we define creation (or raising) and destruction (or annihilation or lowering) operators as

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}, \quad \hat{a}^{\dagger} \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}.$$

It is easy to prove their commutation is

$$[\hat{a}, \ \hat{a}^{\dagger}] = \hat{a}\hat{a}^{\dagger} - \hat{a}^{\dagger}\hat{a} = 1$$
.

Since

$$\hat{a}^{\dagger}\hat{a} = \left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}\right) \cdot \left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}\right)$$
$$= \frac{m\omega}{2\hbar}\hat{x}^{2} + \frac{1}{2m\hbar\omega}\hat{p}^{2} + \frac{i}{2\hbar}\left(\hat{x}\hat{p} - \hat{p}\hat{x}\right) = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2},$$

we can write the harmonic oscillator Hamiltonian as

$$\hat{H} = \hbar \omega \left(\hat{a}^{\dagger} \hat{a} + \frac{1}{2} \right) \; .$$

Therefore, to find the eigenstates and eigenvalues of \hat{H} is to find the eigenstates and eigenvalues of operator $\hat{a}^{\dagger}\hat{a}$.

It is quite easy to find the eigenstates and eigenvalues of operator $a^{\dagger}a$. First let us assume there is state $|0\rangle$ such that

$$\hat{a}\left|0\right\rangle = 0$$
.

Hence state $|0\rangle$ is an eigenstate of $\hat{a}^{\dagger}\hat{a}$ with eigenvalue equal to zero

$$\hat{a}^{\dagger}\hat{a}\left|0\right\rangle = 0\left|0\right\rangle$$
.

It is not difficult to find this state $|0\rangle$ from the equation

$$\begin{aligned} a \left| 0 \right\rangle &= 0 \rightarrow \\ \left(\sqrt{\frac{m\omega}{2\hbar}} \, \hat{x} + \frac{i\hat{p}}{\sqrt{2m\hbar\omega}} \right) \psi_0(x) &= \left(\sqrt{\frac{m\omega}{2\hbar}} \, x + \frac{\hbar}{\sqrt{2m\hbar\omega}} \frac{\partial}{\partial x} \right) \psi_0(x) = 0. \end{aligned}$$

or

$$-\frac{m\omega x}{\hbar}\psi_0(x) = \psi'_0(x)$$
$$-\frac{m\omega x}{\hbar}dx = \frac{d\psi_0}{\psi_0}$$
$$\psi_0 = A\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

as we have seen before.

Now we apply the algebra to find the excited states. Consider state $a^\dagger \left| 0 \right\rangle$ and call it $\left| 1 \right\rangle$

$$|1\rangle = \hat{a}^{\dagger} |0\rangle$$

we can prove it is an eigenstate of $\hat{a}^{\dagger}\hat{a}$ with eigenvalue equal to 1. Prove:

$$\begin{aligned} \hat{a}^{\dagger}\hat{a}\left|1\right\rangle &= \hat{a}^{\dagger}\hat{a}\hat{a}^{\dagger}\left|0\right\rangle = \hat{a}^{\dagger}\left(\hat{a}\hat{a}^{\dagger}\right)\left|0\right\rangle \\ &= \hat{a}^{\dagger}\left(\hat{a}^{\dagger}\hat{a}+1\right)\left|0\right\rangle \quad \text{use} \quad \left[\hat{a}, \ \hat{a}^{\dagger}\right] = 1 \\ &= \hat{a}^{\dagger}\hat{a}^{\dagger}\hat{a}\left|0\right\rangle + a^{\dagger}\left|0\right\rangle \quad \text{use} \quad a\left|0\right\rangle = 0 \\ &= \hat{a}^{\dagger}\left|0\right\rangle = \left|1\right\rangle \;. \end{aligned}$$

QED In fact, the state $|1\rangle$ has the state function as

$$|1\rangle = a^{\dagger} |0\rangle \rightarrow \left(\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}\right)\psi_0(x) = Bx\psi_0(x) = \psi_1(x) .$$

In general, the nth state $|n\rangle$ is given by a^{\dagger} acting on the ground state $|0\rangle$ n times, namely

$$|n\rangle = \frac{1}{\sqrt{n!}} \left(a^{\dagger}\right)^n |0\rangle$$

Using the commutation relation $[a, a^{\dagger}] = 1$, we can proof $|n\rangle$ is an eigenstate of $a^{\dagger}a$

$$a^{\dagger}a \left| n \right\rangle \left| n \right\rangle,$$

therefore

$$H |n\rangle = \hbar\omega \left(a^{\dagger}a + \frac{1}{2}\right) |n\rangle = \left(n + \frac{1}{2}\right) \hbar\omega |n\rangle, \quad n = 0, 1, 2, 3, \dots$$

Proof:

We use deduction for the proof. Since $|n\rangle = \frac{1}{\sqrt{n!}} \left(a^{\dagger}\right)^{n} |0\rangle$,

$$\begin{array}{rcl} a^{\dagger}a \left| 0 \right\rangle &=& 0 \left| 0 \right\rangle, \\ a^{\dagger}a \left| 1 \right\rangle &=& a^{\dagger}a \, a^{\dagger} \left| 0 \right\rangle \\ &=& a^{\dagger} \left(a^{\dagger}a + 1 \right) \left| 0 \right\rangle \\ &=& a^{\dagger} \left| 0 \right\rangle = 1 \cdot \left| 1 \right\rangle. \end{array}$$

Assuming for n > 1,

$$a^{\dagger}a \left| n-1 \right\rangle = \left(n-1 \right) \left| n-1 \right\rangle,$$

we have

$$\begin{aligned} a^{\dagger}a \left| n \right\rangle &= a^{\dagger}a \left(\frac{a^{\dagger}}{\sqrt{n}} \right) \left| n - 1 \right\rangle \\ &= \frac{1}{\sqrt{n}} a^{\dagger} \left(a^{\dagger}a + 1 \right) \left| n - 1 \right\rangle \\ &= \frac{1}{\sqrt{n}} a^{\dagger} \left(n - 1 + 1 \right) \left| n - 1 \right\rangle \\ &= n \left(\frac{a^{\dagger}}{\sqrt{n}} \left| n - 1 \right\rangle \right) \\ &= n \left| n \right\rangle. \quad \text{QED} \end{aligned}$$

Notice that the equation $a |0\rangle = 0$ can also be written as

$$\langle 0 | a^{\dagger} = 0.$$

It is now straightforward to derive the orthogonal relation between the states

$$\langle n | n' \rangle = \delta_{nn'}.$$

Therefore, the Hamiltonian of a harmonic oscillator has eigenstates and eigenvalues as

$$\hat{H} |n\rangle = E_n |n\rangle$$

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \cdots$$

$$|n\rangle \rightarrow \frac{1}{\sqrt{n!}} \left(\sqrt{\frac{m\omega}{2\hbar}}x - \frac{\hbar}{\sqrt{2m\hbar\omega}}\frac{\partial}{\partial x}\right)^n \psi_0(x)$$

where

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

is the ground state. As given earlier, the first excited state is $|1\rangle = a^{\dagger}|0\rangle$, or in real space, $\psi_1(x) = Bx\psi_0(x)$ with constant *B* determined by normalization condition. The shapes of first four eigenfunctions are shown in Fig. 1.



Fig. 1 The shapes of the first 4 eigenfunctions of Harmonic oscillator.

1.4 Matrix representation of QM

We have seen operators in QM behave just like matrices, such as transposed, Hermitian, and eigenvalue problems, etc. In fact, we can formulate a QM problem completely in terms of matrix analysis: a state becomes a column matrix and an operator becomes a square matrix. This is particularly useful if we can solve the eigenequation of a particular operator of a system rather easily and we can then use the solution as basis to solve the eigenequation of other operator.

1.4.1 Basis set

For, example, if we have a simple Hermitian operator \hat{A} of a quantum system which has *m* eigenstate functions with corresponding eigenvalues as A_k , $k = 1, 2, \dots, M$

$$\hat{A}\Phi_k = A_k\Phi_k, \quad k = 1, 2, \cdots, M$$

where Φ_k are a set of normalized orthogonal wavefunctions. Note that M could be infinite. We can write

$$\Phi_1 \rightarrow |1\rangle = \begin{pmatrix} 1\\0\\\dots\\0 \end{pmatrix}, \quad \Phi_1^* \rightarrow \langle 1| = (1, 0, \dots, 0)$$
$$\Phi_2 \rightarrow |2\rangle = \begin{pmatrix} 0\\1\\\dots\\0 \end{pmatrix}, \quad \Phi_2^* \rightarrow \langle 2| = (0, 1, \dots, 0)$$

etc. The orthonormal relationship (inner product between any pair) is

$$\int d^3r \, \Phi_{k'}^* \Phi_k = \langle k' | k \rangle = \delta_{k'k} \; .$$

In this fashion, operator \hat{A} becomes diagonal matrix

$$\hat{A} = \begin{pmatrix} A_1 & 0 & 0 & 0 \\ 0 & A_2 & 0 & 0 \\ \dots & & & \\ & & & A_M \end{pmatrix}$$

The eigenequation becomes a simple matrix equation

$$\hat{A} \left| k \right\rangle = A_k \left| k \right\rangle$$

Notice that all calculations become matrix algebra. And the complete orthonormal set of states $\{|k\rangle, k = 1, 2, \dots, M\}$ is referred to as **basis set**.

1.4.2 Matrix representation of a state

Now we intend to use these eigenstate of \hat{A} as a **basis** to discuss any eigenstates of other operators. Consider an arbitrary state $|\Psi\rangle$, by the completeness of the basic set $|i\rangle$, we can always write $|\Psi\rangle$ as a linear combination of $|k\rangle$

$$|\Psi\rangle = \sum_{k=1}^{M} c_k |k\rangle$$

where $\{C_k\}$ are constant. In matrix notation it becomes

$$|\Psi\rangle = \sum_{k=1}^{M} c_k |k\rangle = \begin{pmatrix} c_1 \\ c_2 \\ \dots \\ c_M \end{pmatrix} = C$$

$$\langle \Psi | = \sum_{k=1}^{M} c_k^* \langle k | = (c_1^*, c_2^*, \cdots, c_M^*) = C^{\dagger}$$

so C_k is the component of the state vector $|\Psi\rangle$ in the k-direction. The inner product

$$\langle \Psi | \Psi \rangle = \sum_{k=1}^{M} |c_k|^2 \to C^{\dagger} \cdot C .$$

1.4.3 Matrix representation of an operator

Consider an arbitrary operator \hat{B} of the same system. We wish to find the matrix representation of \hat{B} in the above basic set (eigenstates of \hat{A}). Let \hat{B} act on an arbitrary state $|\Psi\rangle$ and resulting new state is denoted as $|\Omega\rangle$

$$\hat{B} |\Psi\rangle = |\Omega\rangle$$
.

Both $|\Psi\rangle$ and $|\Omega\rangle$ can be written as linear combination of the basic set

$$\begin{split} |\Psi\rangle &= \sum_{k=1}^{M} c_k \, |k\rangle = \begin{pmatrix} c_1 \\ c_2 \\ \cdots \\ c_M \end{pmatrix} \to C \\ |\Omega\rangle &= \sum_{k=1}^{M} d_k \, |k\rangle = \begin{pmatrix} d_1 \\ d_2 \\ \cdots \\ d_M \end{pmatrix} \to D \end{split}$$

and the original eq. becomes

$$\sum_{k'=1}^{M} c_{k'} \hat{B} |k'\rangle = \sum_{k'=1}^{M} d_{k'} |k'\rangle$$

taking inner product with states $\langle k |$ on both sides

$$\sum_{k'=1}^{M} B_{kk'}c_{k'} = \sum_{k'=1}^{M} d_{k'}\delta_{kk'} = d_k, \quad k = 1, 2, \cdots, M$$
$$B_{kk'} \equiv \langle k | \hat{B} | k' \rangle = \int d^3r \, \Phi_k^* \Phi_{k'}$$

or in a matrix notation

$$B \cdot C = D$$

where B is a $(M \times M)$ square matrix with element $B_{kk'} \equiv \langle k | \hat{B} | k' \rangle = \int d^3r \, \Phi_k^* \Phi_{k'}$

$$B = \begin{pmatrix} B_{11} & B_{12} & \dots & B_{1M} \\ B_{21} & B_{22} & \dots & B_{2M} \\ \dots & & & & \\ B_{M1} & B_{M2} & \dots & B_{MM} \end{pmatrix}$$

Note that the matrix representation of operator $\hat{B} \to B$ is independent of state $|\Psi\rangle$, it only involves the basic set $\{|k\rangle, k = 1, 2, \dots, M\}$. Once the basic set is choose, the matrix representation of any operator \hat{B} is determined. Therefore $\hat{B} \to B$ is totally equivalent and we can write, directly

$$\hat{B} = \begin{pmatrix} B_{11} & B_{12} & \dots & B_{1M} \\ B_{21} & B_{22} & \dots & B_{2M} \\ \dots & & & & \\ B_{M1} & B_{M2} & \dots & B_{MM} \end{pmatrix}$$

without causing any problem.

1.4.4 Eigen value problem

To find the eigenstates and eigenvalues of \hat{B} is to diagonalize this matrix. We write an eigenstate $|\lambda\rangle$ of \hat{B} in terms of $|k\rangle$ as, with eigenvalue λ

$$|\lambda\rangle = \sum_{k=1}^{m} b_k |k\rangle = \begin{pmatrix} b_1 \\ b_2 \\ \dots \\ b_M \end{pmatrix}$$

The eigenequation

$$\hat{B} \ket{\lambda} = \lambda \ket{\lambda}$$

or

or

$$\begin{pmatrix} B_{11} & B_{12} & \dots & B_{1M} \\ B_{21} & B_{22} & \dots & B_{2M} \\ \dots & & & & \\ B_{M1} & B_{M2} & \dots & B_{MM} \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ \dots \\ b_M \end{pmatrix} = \lambda \begin{pmatrix} b_1 \\ b_2 \\ \dots \\ b_M \end{pmatrix}$$
$$\begin{pmatrix} B_1 - \lambda & B_{12} & \dots & B_{1M} \\ B_{21} & B_{22} - \lambda & \dots & B_{2M} \\ \dots & & & & \\ B_{M1} & B_{M2} & \dots & B_{MM} \lambda \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ \dots \\ b_M \end{pmatrix} = 0$$

and corresponding secular equation is

$$\det \begin{vmatrix} B_{11} - \lambda & B_{12} & \dots & B_{1M} \\ B_{21} & B_{22} - \lambda & \dots & B_{2M} \\ \dots & & & & \\ B_{M1} & B_{M2} & \dots & B_{MM} - \lambda \end{vmatrix} = 0 .$$

If the dimension M is a very large number, it becomes difficult to manage the $(M \times M)$ matrix. We can introduce a truncation, and consider only $k = 1, 2, \dots, N$ with N < M, and consider smaller $(N \times N)$ matrix as an approximation.

1.4.5 Examples

A spin-1/2 system. Our task is find spin operators in a matrix form. We know there are only two spin states in this case, spin-up $|\uparrow\rangle$ and spin-down $|\downarrow\rangle$. They are eigenstates of \hat{S}_z . So the dimension of our basis set is two. We write

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

using

$$\hat{S}_{z}\left|\uparrow\right\rangle = \frac{\hbar}{2}\left|\uparrow\right\rangle, \quad \hat{S}_{z}\left|\downarrow\right\rangle = \frac{\hbar}{2}\left|\downarrow\right\rangle$$

so the matrix form for \hat{S}_z is

$$\hat{S}_{z} = \begin{pmatrix} \langle 1 | \hat{S}_{z} | 1 \rangle & \langle 1 | \hat{S}_{z} | 2 \rangle \\ \langle 2 | \hat{S}_{z} | 1 \rangle & \langle 2 | \hat{S}_{z} | 2 \rangle \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

it is diagonal as expected.

According to the general formula

$$\hat{L}^{\pm} \left| l, m \right\rangle = \hbar \sqrt{l \left(l + 1 \right) - m \left(m \pm 1 \right)} \left| l, m \pm 1 \right\rangle$$

we have, with $l = S = 1/2, m = \pm 1/2$

$$\begin{array}{rcl} \hat{S}^{+}\left|\uparrow\right\rangle &=& \hat{S}^{-}\left|\downarrow\right\rangle = 0\\ \hat{S}^{+}\left|\downarrow\right\rangle &=& \hbar\left|\uparrow\right\rangle, \quad \hat{S}^{-}\left|\uparrow\right\rangle = \hbar\left|\downarrow\right\rangle \end{array}$$

hence, their matrix forms are given

$$\hat{S}^{+} = \begin{pmatrix} \langle 1 | \hat{S}^{+} | 1 \rangle & \langle 1 | \hat{S}^{+} | 2 \rangle \\ \langle 2 | \hat{S}^{+} | 1 \rangle & \langle 2 | \hat{S}^{+} | 2 \rangle \end{pmatrix} = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$\hat{S}^{-} = \begin{pmatrix} \langle 1 | \hat{S}^{-} | 1 \rangle & \langle 1 | \hat{S}^{-} | 2 \rangle \\ \langle 2 | \hat{S}^{-} | 1 \rangle & \langle 2 | \hat{S}^{-} | 2 \rangle \end{pmatrix} = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

and using

$$\hat{S}^{\pm} = \hat{S}_x \pm i\hat{S}_y \quad \to \quad \hat{S}_x = \frac{1}{2}\left(\hat{S}^+ + \hat{S}^-\right), \quad \hat{S}_y = \frac{1}{2}\left(\hat{S}^+ - \hat{S}^-\right)$$

we have matrix forms for \hat{S}_x and \hat{S}_y

$$\hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1\\ 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \frac{\hbar}{2i} \begin{pmatrix} 0 & 1\\ -1 & 0 \end{pmatrix}$$

Note also operator $\hat{S}^2 = \frac{\hbar^2}{2} \left(\frac{1}{2} + 1\right) = \frac{3}{4}$ becomes an identity matrix multiplying a number,

$$\hat{S}^2 = \frac{3\hbar^2}{4} \left(\begin{array}{cc} 1 & 0\\ 0 & 1 \end{array} \right) \; .$$

Note: in some text book, spin operator is defined as dimensionless, $\hat{\mathbf{S}} \to \hat{\mathbf{S}}/\hbar$.

Electron in a magnetic field. Suppose the field makes an angle θ with the z axis and given by

$$\mathbf{B} = (B\sin\theta, 0, B\cos\theta)$$

and the magnetic energy potential is, using magnetic moment $\mu_s = -e\hat{\mathbf{S}}/m$

$$\hat{H}_m = -\mu_s \cdot \mathbf{B} = \frac{e}{m} \mathbf{\hat{S}} \cdot \mathbf{B} = \frac{e}{m} \left(\sin \theta \hat{S}_x + \cos \theta \hat{S}_z \right) = \frac{e\hbar}{2m} \left(\begin{array}{c} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{array} \right)$$

The secular eq.

$$0 = \det \begin{vmatrix} \cos \theta - \lambda & \sin \theta \\ \sin \theta & -\cos \theta - \lambda \end{vmatrix} = \lambda^2 - \cos^2 \theta - \sin^2 \theta = \lambda^2 - 1$$

with two solutions $\lambda = \pm 1$. Hence the eigenvalues of \hat{H}_m are $\pm \frac{e\hbar}{2m}$ with the corresponding normalized eigenstates

$$|+\rangle = \begin{pmatrix} \cos\frac{\theta}{2}\\ \sin\frac{\theta}{2} \end{pmatrix}, \quad |-\rangle = \begin{pmatrix} -\sin\frac{\theta}{2}\\ \cos\frac{\theta}{2} \end{pmatrix}.$$