

Notes of Quantum Mechanics

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Preface

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Chapter 1

Mathematical Formalism

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1.1 Eigenvalue equations. Observables

1.1.1 Eigenket and eigenbra equations

$|\psi\rangle$ is said to be an **eigenvector** (or eigenket) of the linear operator A if

$$\text{Eigenket equation of } A \quad A|\psi\rangle = \lambda|\psi\rangle, \quad \lambda \in \mathbb{C}. \quad (1.1)$$

This eigenket equation possesses solutions only when λ takes on certain values, called **eigenvalues** of A . The set of the eigenvalues is called **spectrum** of A .

Collinear of an eigenvector is also an eigenvector

If $|\psi\rangle$ is an eigenvector of A with eigenvalue λ , then $\alpha|\psi\rangle$, $\alpha \in \mathbb{C}$ is also an eigenvector of A .

The eigenvalue λ is called *non-degenerate* (or simple) when its corresponding eigenvector is **unique** to within a constant factor (collinear). On the other hand, if there exists at least two linearly independent eigenkets with the **same** eigenvalue, the eigenvalue is said to be *degenerate*. Its *degree of degeneracy* g is then the number of linearly independent eigenvectors $|\psi^i\rangle$, $i = \{1, 2, \dots, g\}$ associated with it.

The set of eigenkets associated with a degenerate eigenvalue constitutes a g -dimensional vector space called **eigensubspace** of λ .

Taking the adjoint of the eigenket equation yields its corresponding form to eigenbra equation

$$\text{Eigenbra equation of } A^\dagger \quad \langle\psi|A^\dagger = \lambda^*\langle\psi|. \quad (1.2)$$

If $|\psi\rangle$ is an eigenket of A with λ , it can also be said that $\langle\psi|$ is an eigenbra of A^\dagger with λ^* .

Finding the eigenvalues and eigenvector in an operator

Assuming the state space is of finite dimension N , granting the generalization to an infinite-dimensional state space.

Choosing $\{|u_i\rangle\}$, lets us project the vector (1.1) onto the various orthonormal basis vectors $|u_i\rangle$:

$$\langle u_i|A|\psi\rangle = \lambda\langle u_i|\psi\rangle. \quad (1.3)$$

Inserting the closure relation between A and $|\psi\rangle$:

$$\langle u_i|A\mathbb{1}|\psi\rangle = \sum_j \underbrace{\langle u_i|A|u_j\rangle}_{A_{ij}} \underbrace{\langle u_j|\psi\rangle}_{c_j} = \lambda \underbrace{\langle u_i|\psi\rangle}_{c_i} \longrightarrow \sum_j [A_{ij} - \lambda\delta_{ij}]c_j = 0. \quad (1.4)$$

Equation (1.4) is a system of equations with N equations and N unknowns c_j . It has non-trivial solution iff its characteristic equation is zero:

$$\text{Characteristic equation of the eigenket equation} \quad P(\lambda) = \det[A - \lambda I] = 0. \quad (1.5)$$

This expression enable us to determine the spectrum of A . The characteristic equation is **independent** of the representation chosen. Then,

The eigenvalues of an operator are the roots λ of its N th order characteristic equation $P(\lambda)$.

Determination of eigenvectors

Given a transformation $T(v) = Mv : V \in \mathbb{C}^N \longrightarrow W \in \mathbb{C}^N$, the theorem says:

$$\dim(V) = \text{rank}(T) + \text{null}(T), \quad (1.6)$$

where

$\dim(V)$ = Number of columns of V

$\text{rank}(T)$ = Number of independent equations (non zero rows)

$\text{null}(T) = \dim[\ker(T)]$ = Number of free variables, degree of freedom (dof).

In our case, $T(v) = Mv = (A - \lambda I)v$ and $\dim(V) = N$.

Based on the nature of the eigenvalue, we can have different eigenvalues but also repeated. Therefore, we define the following useful quantities:

- **Algebraic multiplicity (AM)** Number of repetition of the eigenvalue (degree of degeneracy g).
- **Geometric multiplicity (GM)** Dimension of the subspace that the eigenvalues generate (how many linearly independent eigenvectors exist for that eigenvalue).

We then can have the following three cases:

- $AM = GM = 1$ Only one eigenvector corresponds to the eigenvalue (within a constant factor). At the moment of substituting an eigenvalue λ_0 into equation (1.4) there will be $\text{rank}(M) = N - 1$ independent equations so one equation is redundant. When this happens, $\text{null}(M) = 1$ free variable (or degree of freedom, dof) c_1 is available which can be defined arbitrarily and from which all other variables can be expressed.

If we fix c_1 , then all c_j are proportional to it:

$$c_j = \alpha_j^0 c_1 \quad (\alpha_1^0 = 1). \quad (1.7)$$

the $N - 1$ coefficients α_j^0 , $j \neq 1$ are determined from the matrix elements A_{ij} and λ_0 . The eigenvectors associated with λ_0 differ only by the value chosen for c_1 . They are therefore all given by

$$|\psi_0(c_1)\rangle = \sum_j \alpha_j^0 c_1 |u_j\rangle = c_1 |\psi_0\rangle, \quad \text{with} \quad |\psi_0\rangle = \sum_j \alpha_j^0 |u_j\rangle. \quad (1.8)$$

When λ_0 is simple, only one eigenvector corresponds to it.

Ejemplo 1.1

In the matrix

$$A = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 2 & 1 \\ 0 & 0 & 3 \end{bmatrix}$$

Simple eigenvalues

the eigenvalues are $\lambda \in \{1, 2, 3\}$. Lets make $\lambda_0 = 1$ and replace it into the eigenvalue problem:

$$(A - \lambda I)v = (A - I)v = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 1 & 1 \\ 0 & 0 & 2 \end{bmatrix} v = 0$$

We see that there is no value in the first column, meaning that x_1 is free whereas $x_2 = x_3 = 0$. Therefore, the eigenvector is $v_1 = (1 \ 0 \ 0)$.

- $AM = GM > 1$ When evaluating λ_0 , the system will have $\text{rank}(M) = N - p$ independent equations ($1 < p < q$). To the eigenvalue λ_0 there corresponds an eigensubspace of dimension $\text{null}(M) = p$, and λ_0 is a p -fold degenerate eigenvalue.

Assuming that for $\lambda = \lambda_0$ is composed of $N - 2$ linearly independent equations. These equations enable us to calculate the coefficients c_j in terms of any of them, for example c_1 and c_2 :

$$c_j = \beta_j^0 c_1 + \gamma_j^0 c_2.$$

All the eigenvectors associated with λ_0 are then of the form

$$|\psi_0(c_1, c_2)\rangle = c_1|\psi_0^1\rangle + c_2|\psi_0^2\rangle, \quad \text{with} \quad |\psi_0^1\rangle = \sum_j \beta_j^0 |u_j\rangle, \quad |\psi_0^2\rangle = \sum_j \gamma_j^0 |u_j\rangle. \quad (1.9)$$

The vectors $|\psi_0(c_1, c_2)\rangle$ do indeed constitute a two-dimensional vector space, this being characteristic of a two-fold degenerate eigenvalue.

- $AM > GM > 1$ In this case, the subspace is less than the degree of degeneracy and therefore not all degenerate eigenvectors are linearly independent. This means that there is not enough information to create a basis. However, techniques such as Jordan canonical form helps to create generalized eigenvector and to span the whole space.

When an operator is Hermitian, it can be shown that the degree of degeneracy p of an eigenvalue λ is always equal to the multiplicity of the corresponding root in the characteristic equations. In a space of finite dimension N , a Hermitian operator always has N linearly independent eigenvectors: this operator can therefore be diagonalized.

1.1.2 Observables

Properties of the eigenvalues and eigenvectors of a Hermitian operator

- The eigenvalues of a Hermitian operator are real.
- Two eigenvectors of a Hermitian operator corresponding to two different eigenvalues are orthogonal.

Definition of a observable

Consider a Hermitian operator A with discrete spectrum. The degree of degeneracy of the eigenvalue a_n is denoted by g_n . We shall denote by $|\psi_n^i\rangle$ g_n linearly independent vectors chosen in the eigensubspace \mathcal{E}_n of a_n :

$$A|\psi_n^i\rangle = a_n|\psi_n^i\rangle, \quad i = 1, 2, \dots, g_n. \quad (1.10)$$

Every vector of \mathcal{E}_n is orthogonal to every vector of another subspace $\mathcal{E}_{n'}$: $\langle \psi_n^i | \psi_{n'}^j \rangle = 0$, $n \neq n'$.

Inside the subspace \mathcal{E}_n , the $|\psi_n^i\rangle$ can always be chosen orthonormal, such that

$$\langle \psi_n^i | \psi_n^j \rangle = \delta_{ij}. \quad (1.11)$$

If such a choice is made, the result is an orthonormal system of eigenvectors of A : the $|\psi_n^i\rangle$ satisfying the relations:

$$\langle \psi_n^i | \psi_{n'}^{i'} \rangle = \delta_{nn'} \delta_{ii'}. \quad (1.12)$$

Observable

The Hermitian operator A is an **observable** if its eigenvectors **form a basis** in the state space:

$$\text{Closure relation of an observable} \quad \sum_{n=1}^{\infty} \sum_{i=1}^{g_n} |\psi_n^i\rangle \langle \psi_n^i| = \mathbb{1}. \quad (1.13)$$

The projector onto the subspace \mathcal{E}_n is written as:

$$P_n = \sum_{i=1}^{g_n} |\psi_n^i\rangle \langle \psi_n^i|. \quad (1.14)$$

The observable A is the given by:

$$A = \sum_n a_n P_n. \quad (1.15)$$

Equation (1.13) can be generalized to include cases of continuous spectrum using the previous table of the first section.

If A has a mixed spectrum, then it is an observable if this system form a basis, that is, if

$$\sum_n \sum_{i=1}^{g_n} |\psi_n^i\rangle \langle \psi_n^i| + \int_{\nu_1}^{\nu_2} d\nu |\psi_\nu\rangle \langle \psi_\nu| = \mathbb{1}. \quad (1.16)$$

The projector P_ψ is an observable

The projector $P_\psi = |\psi\rangle \langle \psi|$ is an observable. We know that it is Hermitian, and that its eigenvalues are 1 and 0, the first one is simple and the other infinitely degenerate. It can be shown that any ket $|\psi\rangle$ can be expanded on these eigenkets, therefore P_ψ is an observable.

1.1.3 Sets of commuting observables

Important theorems

Theorem I

If two operators A and B commute, and if $|\psi\rangle$ is an eigenvector of A , $B|\psi\rangle$ is also an eigenvector of A , with the same eigenvalue.

Another form:

If two operators A and B commute, every eigensubspace of A is globally invariant under the action of B ($B|\psi\rangle$ belongs to the eigensubspace \mathcal{E}_a of A , corresponding to the eigenvalue a).

Theorem II (consequence of theorem I)

If two observables A and B commute, and if $|\psi_1\rangle$ and $|\psi_2\rangle$ are two eigenvectors of A with different eigenvalues, the matrix element $\langle\psi_1|B|\psi_2\rangle$ is zero.

Theorem III

If two observables A and B commute, one can construct an orthonormal basis of the state space with eigenvectors common to A and B .

Lets prove the theorem III. Consider two commuting observables A and B , with discrete spectrum. Since A is observable, there exists at least one orthonormal system of eigenvectors $|u_n^i\rangle$ which forms a basis in the state space:

$$A|u_n^i\rangle = a_n|u_n^i\rangle, \quad \begin{matrix} n = 1, 2, \dots \\ i = 1, 2, \dots, g_n \end{matrix} \quad (1.17)$$

We also have $\langle u_n^i | u_{n'}^{i'} \rangle = \delta_{nn'} \delta_{ii'}$. What does the matrix look like which represent B in the $\{|u_n^i\rangle\}$ basis? We know that the matrix elements $\langle u_n^i | B | u_{n'}^{i'} \rangle$ are zero when $n \neq n'$ (theorem II). Let us arrange the basis vectors $|u_n^i\rangle$ in the order:

$$|u_1^1\rangle, |u_1^2\rangle, \dots, |u_1^{g_1}\rangle; |u_2^1\rangle, \dots, |u_2^{g_2}\rangle; |u_3^1\rangle, \dots$$

Whe then obtain for B a block-diagonal matrix of the form:

$$\begin{bmatrix} \mathcal{E}_1 & & & \\ \mathcal{E}_1 & \ddots & \ddots & \\ & \ddots & \ddots & \\ \mathcal{E}_2 & & & \\ & 0 & \ddots & \ddots & \ddots \\ & & \ddots & \ddots & \ddots \\ \mathcal{E}_3 & 0 & & 0 & \ddots & 0 \\ \vdots & 0 & & 0 & 0 & \ddots & \ddots \end{bmatrix} \quad (1.18)$$

Then the degeneracy of the eigenvalue is 1, then the block reduces to a 1×1 matrix. In the column associated with $|u_n\rangle$ all the other matrix elements are zero, this expresses the fact that $|u_n\rangle$ is an eigenvector common to A and B . When a_n is a g_n -degenerate eigenvalue of A , the block which represents B in \mathcal{E}_n is not, in general, diagonal: the $|u_n^i\rangle$ are not, in general, eigenvector of B . The action of A in the g_n eigenvectors $|u_n^i\rangle$ reduces to $a_n|u_n^i\rangle$, the matrix representing the restriction of A to within \mathcal{E}_n is equal to $a_n I_{g_n \times g_n}$. The matrix representing the operator A in \mathcal{E}_n is always diagonal and equal to $a_n I_{g_n \times g_n}$.

We use this property to obtain a basis of \mathcal{E}_n composed of vectors that are also eigenvectors of B . The matrix representing B in \mathcal{E}_n when the basis is chosen is

$$\{|u_n^i\rangle, \quad i = 1, 2, \dots, g_n\}, \quad (1.19)$$

has for its elements:

$$\beta_{ij}^{(n)} = \langle u_n^i | B | u_n^j \rangle. \quad (1.20)$$

This matrix is Hermitian, since B is a Hermitian operator. It is therefore diagonalizable: one can find a new basis $\{|v_n^i\rangle; i = 1, 2, \dots, g_n\}$ in which B is represented by a diagonal matrix:

$$\langle v_n^i | B | v_n^j \rangle = \beta_i^n \delta_{ij}. \quad (1.21)$$

This means that the new basis vectors in \mathcal{E}_n are eigenvectors of B :

$$B | v_n^i \rangle = \beta_i^{(n)} | v_n^i \rangle. \quad (1.22)$$

These vectors are automatically eigenvectors of A with an eigenvalue a_n since they belong to \mathcal{E}_n .

Eigenvectors of A associated with degenerate eigenvalues are not necessarily eigenvectors of B . It is always possible to choose, in every eigensubspace of A , a basis of eigenvectors common to A and B .

If we perform this operation in all the subspaces \mathcal{E}_n , we obtain a basis of \mathcal{E} , formed by eigenvectors common to A and B .

We shall denote by $|u_{n,p}^i\rangle$ the eigenvectors common to A and B :

$$A | u_{n,p}^i \rangle = a_n | u_{n,p}^i \rangle, \quad \text{and} \quad B | u_{n,p}^i \rangle = b_p | u_{n,p}^i \rangle. \quad (1.23)$$

The index i will be used to distinguish between different basis vectors which correspond to the same eigenvalues a_n and b_p .

Complete sets of commuting observables (C.S.C.O.)

Consider an observable A and a basis \mathcal{E} composed of eigenvectors $|u_n^i\rangle$ of A .

If none of the eigenvalues of A is degenerate, the various basis vectors of \mathcal{E} can be labelled by the eigenvalue a_n (index i is not necessary). Therefore, specifying the eigenvalue determines in a unique way the corresponding eigenvector. In other words, there exists only one basis of \mathcal{E} formed by the eigenvectors of A . It is said that the observable A constitutes, by itself, a C.S.C.O.

On the other hand, if at least one eigenvalue of A is degenerate, specifying a_n is no longer always sufficient to characterize a basis vector: the basis of eigenvectors of A is not unique. One can choose any basis inside each of the degenerate eigensubspaces \mathcal{E}_n . We can choose another observable B which commutes with A to construct an orthonormal basis of eigenvectors common to A and B . A and B form a C.S.C.O. if this basis is unique, that is, if to each of the possible pairs of eigenvalues $\{a_n, b_p\}$ there corresponds only one basis vector. For A and B to constitute a C.S.C.O., it is necessary and sufficient that, inside each of these subspaces, all the g_n eigenvalues of B be distinct. We can add indefinitely observables until we reach the C.S.C.O.

A set of observables A, B, C, \dots is called a complete set of commuting observables if:

- (i) all the observables commute by pairs.
- (ii) specifying the eigenvalue of all the operators determines a unique common eigenvector. The ket then is denoted as $|a_n, b_p, c_r, \dots\rangle$.

This means that they are C.S.C.O. if there exists a unique orthonormal basis of common eigenvectors.

Identification of CSCOs is necessary in order to construct physically meaningful bases for \mathcal{E} . Knowing the CSCOs that are available tells the experimenter the possible sets of measurements that can be made to achieve this goal.

We list some CSCOs for specific problems. (table 31 anerson)

1.2 More about operators

1.2.1 Trace of an operator

The trace of an operator A , $\text{Tr}[A]$, is the sum of its diagonal matrix elements:

$$\text{Tr}[A] = \sum_i \langle u_i | A | u_i \rangle, \quad \text{and} \quad \text{Tr}[A] = \int d\alpha \langle \omega_\alpha | A | \omega_\alpha \rangle.$$

The trace is **invariant of the basis**, meaning that a change of representation will not affect the final result.

For a discrete basis, for instance, we have

$$\sum_i \langle u_i | A | u_i \rangle = \sum_i \langle u_i | \left[\sum_k |t_k\rangle \langle t_k| \right] A | u_i \rangle = \sum_{i,j} \langle t_k | A | u_i \rangle \langle u_i | t_k \rangle = \sum_k \langle t_k | A | \mathbb{1} | t_k \rangle = \sum_k \langle t_k | A | t_k \rangle.$$

If A is an observable, then $\text{Tr}[A]$ can be calculated in a basis of eigenvectors of A . The diagonal matrix elements are then the eigenvalues a_n of A and the trace can be written

$$\text{Tr}[A] = \sum_n g_n a_n, \quad g_n = \text{degree of degeneracy of } a_n. \quad (1.24)$$

We list some properties:

$$\text{Tr}[AB] = \text{Tr}[BA] \quad | \quad \text{Tr}[ABC] = \text{Tr}[BCA] = \text{Tr}[CAB] \quad (\text{cyclic permutation})$$

1.2.2 Function of an operator

To express a function of an operator A , $F(A)$, we use Taylor expansion:

$$F(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!} (x-a)^n = \sum_{n=0}^{\infty} f_n (x-a)^n \implies F(A) = \sum_{n=0}^{\infty} f_n (A-a)^n. \quad (1.25)$$

For example, the e^A operator around $a = 0$ is:

$$e^A = \sum_{n=0}^{\infty} \frac{A^n}{n!} = \mathbb{1} + A + \frac{A^2}{2!} + \frac{A^3}{3!} + \dots$$

Let $|\varphi_k\rangle$ be an eigenvector of A with eigenvalue λ_k , then (assuming $a = 0$):

$$A|\varphi_k\rangle = \lambda_k|\varphi_k\rangle \implies F(A)|\varphi_k\rangle = \sum_{n=0}^{\infty} f_n A^n \lambda_k |\varphi_k\rangle = \sum_{n=0}^{\infty} f_n \lambda_k^n |\varphi_k\rangle = F(\lambda_k)|\varphi_k\rangle.$$

If the operator A has an eigenpar (λ_k, φ_k) , then $(F(\lambda_k), \varphi_k)$ is the eigenpar of $F(A)$.

Potential operator

The potential operator is a function $V(\cdot)$ with the position operator X as the argument, $V(X)$.

The eigenequation associated to this function is

$$V(\mathbf{R})|\mathbf{r}\rangle = V(\mathbf{r})|\mathbf{r}\rangle. \quad (1.26)$$

The matrix elements in $\{|\mathbf{r}\rangle\}$ are:

$$\langle \mathbf{r}|V(\mathbf{R})|\mathbf{r}'\rangle = V(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}'). \quad (1.27)$$

Finally, using the eigenequation above and the fact that $V(\mathbf{R})$ is Hermitian (the function $V(\mathbf{r})$ is real), we obtain:

$$\langle \mathbf{r}|V(\mathbf{R})|\psi\rangle = V(\mathbf{r})\psi(\mathbf{r}). \quad (1.28)$$

This shows that the action of $V(\mathbf{R})$ is simply multiplication by $V(\mathbf{r})$.

1.2.3 Commutator algebra

We have seen that the commutator of two operators is

$$[A, B] = AB - BA. \quad (1.29)$$

We then present some properties:

$[A, B] = -[B, A]$ $[A, B]^\dagger = [B^\dagger, A^\dagger]$ $[F(A), A] = 0$ $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$ $e^A e^B = e^{A+B} e^{\frac{1}{2}[A, B]} \quad ([A, [A, B]] = [B, [A, B]] = 0)$ $[X, P] = i\hbar$	$[A + B, C + D] = [A, C] + [A, D] + [B, C] + [B, D]$ $[A, BC] = [A, B]C + B[A, C]$ $[A, B] = 0 \implies [F(A), B] = [A, F(B)] = [F(A), F(B)] = 0$ $[A, [A, B]] = [B, [A, B]] = 0 \implies [A, F(B)] = [A, B] \frac{dF(B)}{dB}$ $[A, [A, B]] = [B, [A, B]] = 0 \implies [F(A), B] = [A, B] \frac{dF(A)}{dA}$
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1.2.4 Derivative of an operator

Let $A(t)$ be a time-dependent operator, whose derivative is dA/dt . In a time-independent basis $\{|u_n\rangle\}$, the matrix elements of A and dA/dt are:

$$A_{ij}(t) = \langle u_i | A | u_j \rangle, \quad \text{and} \quad \left(\frac{dA}{dt} \right)_{ij} = \langle u_i | \frac{dA}{dt} | u_j \rangle = \frac{d}{dt} \langle u_i | A | u_j \rangle = \frac{dA_{ij}}{dt}. \quad (1.30)$$

The last equation corresponds to the matrix elements of dA/dt . We see that,

To obtain the matrix elements of dA/dt , we compute the derivative of each element of A .

Properties of differentiation also apply here. For instance, for product rule we have

$$\begin{aligned} \langle u_i | FG | u_j \rangle &= \sum_k \langle u_i | F | u_k \rangle \langle u_k | G | u_j \rangle \implies \langle u_i | \frac{d(FG)}{dt} | u_j \rangle = \sum_k \left[\langle u_i | \frac{dF}{dt} | u_k \rangle \langle u_k | G | u_j \rangle + \langle u_i | F | u_k \rangle \langle u_k | \frac{dG}{dt} | u_j \rangle \right] \\ &= \langle u_i | \frac{dF}{dt} G + F \frac{dG}{dt} | u_j \rangle. \end{aligned}$$

Other two examples are

$$\frac{d(e^{At})}{dt} = A e^{At} \text{ they commute } \stackrel{=}{=} e^{At} A, \quad \text{and} \quad \frac{d(e^{At} e^{Bt})}{dt} = A e^{At} e^{Bt} + e^{At} B e^{Bt}.$$

1.2.5 Unitary operators

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