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“Fides et Ratio”

Physics of Information Technology II
Physics of Molecular Bionics II
2014 Autumn

Lecture 5
Matrix Representation of kets, bras and operators
Quantum Mechanics in Dirac notation
Transition between discrete levels
induced by a time-dependent perturbation
Perturbation theory

P.A.M. Dirac's „bra" and „ket" Notation

Information we can know about a state

In quantum physics a ***physical state*** is represented by a ***state vector i***n a complex vector space, called ***Hilbert space***.

We call the state vector a ***„ket",*** and denote it by $\left|\psi\right\rangle$

(This state ket is postulated to contain complete information about the physical state. Everything we are allowed to ask about the state is contained in the ket.)

Two kets can be added, and can be multiplied by a complex number, and the result is also a ket

$$\left|\alpha\right\rangle + \left|\beta\right\rangle = \left|\gamma\right\rangle \qquad \lambda\left|\alpha\right\rangle = \left|\alpha\right\rangle\lambda$$

Null ket $\quad \lambda\left|\alpha\right\rangle \text{ if } \lambda = 0$

$|\alpha\rangle$ and $\lambda|\alpha\rangle$, with $\lambda \neq 0$, represent the same physical state.

(Only the „direction" in vector space is of significance. We are dealing with rays rather than vectors .)

The state space of quantum physics is the Hilbert space

$$|a\rangle, |b\rangle \in \mathcal{H} \quad |a\rangle + |b\rangle = |c\rangle \in \mathcal{H}; \quad \lambda|a\rangle \in \mathcal{H} \quad \lambda \text{ complex number}$$

The dimension of the vector space depends on the physical system (Spin : 2; Finite dim.: *n*; Bounded: countable infinite; Free: continuously infinite)

Observable is represented by a linear operator

The operator acts on the ket from left, and maps a ket on a ket.

$$\hat{\mathbf{A}} \cdot \left(|a\rangle\right) = \hat{\mathbf{A}}|a\rangle \in \mathcal{H}$$

In general $\hat{\mathbf{A}}\left|a\right\rangle \neq c\cdot\left|a\right\rangle$, but there are such kets

$$\hat{\mathbf{A}}\left|a^{(n)}\right\rangle = a^{(n)}\cdot\left|a^{(n)}\right\rangle \quad \rightarrow \quad \hat{\mathbf{A}}\left|n\right\rangle = a_n\cdot\left|n\right\rangle$$

$$\left|a^{(1)}\right\rangle,\left|a^{(2)}\right\rangle,\ldots,\left|a^{(\mathrm{n})}\right\rangle,\ldots \rightarrow \left|1\right\rangle,\left|2\right\rangle,\ldots,\left|n\right\rangle \quad \text{"eigen-kets"}$$

$$a^{(1)},a^{(2)},\ldots,a^{(\mathrm{n})},\ldots \rightarrow a_1,a_2,\ldots,a_n \quad \text{eigenvalues of operaot } \hat{\mathbf{A}}$$

In an N-dimensional vector space every ket can be expressed as

$$\left|a\right\rangle = \sum_n c_n\left|n\right\rangle$$

Dirac’s „bra”-space and „ket”-space

Ket $\left|a\right\rangle$ Bra $\left\langle a\right|$ $\forall\left|a\right\rangle \Leftrightarrow \left\langle a\right|$

$\psi(\mathbf{r},t)$ $\psi^*(r,t)$ $\psi \Leftrightarrow \psi^*$

The „bra”-space is the „dual vector space” of the ket-space

Eigen-kets and their dual eigen-bras

$$\left\{\left|n\right\rangle\right\} \Leftrightarrow \left\{\left\langle n\right|\right\}$$

The Hilbert space is a linear vector space over the complex numbers, in which the scalar product of the elements exist.

Definition of the scalar product of a bra and a ket

$$\langle b|a\rangle = \text{number (in general complex), for which } \langle b|a\rangle = \langle a|b\rangle^*$$

Scalar product is a „**bra**c**ket**"

$$\langle a|a\rangle = \text{real number}; \quad \langle a|a\rangle \geq 0; \quad \text{If } \langle a|a\rangle = 0 \rightarrow \langle a| \text{ null ket}$$

To kets are orthogonal

$$|a\rangle \perp |b\rangle \quad \text{if} \quad \langle a|b\rangle = 0$$

Normalized ket:

$$|\bar{a}\rangle = \frac{1}{\sqrt{\langle a|a\rangle}}|a\rangle \quad \rightarrow \langle \bar{a}|\bar{a}\rangle = 1$$

Bra Ket Bra-ket Operator

$\langle b|$ $|a\rangle$ $\langle b|a\rangle$ $\hat{\mathrm{A}}$

State vectors of a physical system

Scalar product

Hamiltonian Observables

$\psi^*(r,t)$ $\psi(\mathbf{r},t)$

$$\int_V \psi^* \cdot \psi \mathrm{dV}$$

Linear Operators

$$\hat{\mathbf{X}}\left(c_a|a\rangle + c_b|b\rangle\right) = c_a\hat{\mathbf{X}}|a\rangle + c_b\hat{\mathbf{X}}|b\rangle$$

If $\hat{\mathbf{X}} = \hat{\mathbf{X}}^\dagger$ then they are self-adjoint (Hermitian)

$\hat{\mathbf{X}}|a\rangle$ és $\langle a|\hat{\mathbf{X}}$ in general are not dual

$\hat{\mathbf{X}}^{\dagger}$ is the adjoint of $\hat{\mathrm{X}}$ if $\hat{\mathbf{X}}|a\rangle$ and $\langle a|\hat{\mathbf{X}}^{\dagger}$ are dual

If $\hat{\mathbf{X}} = \hat{\mathbf{X}}^{\dagger}$ then they are self-adjoint (Hermitian)

Products of Operators In general $\hat{\mathbf{X}}\hat{\mathbf{Y}} \neq \hat{\mathbf{Y}}\hat{\mathbf{X}};$

$$\left(\hat{\mathbf{X}}\hat{\mathbf{Y}}\right)^{\dagger} = \hat{\mathbf{Y}}^{\dagger}\hat{\mathbf{X}}^{\dagger};$$

‚Outer' product $|a\rangle\langle b|$

Matrix representation of kets bras and operators

In quantum physics the mathematical representation of observables are linear self-adjoint operators

Lemma 1. Eigenvalues of self-adjoint operators are real numbers. The eigen-kets belonging to different eigenvalues are orthogonal.

$$\hat{\mathbf{A}}\left|n\right\rangle = a^{(n)} \cdot \left|n\right\rangle \qquad a^{(1)}, a^{(2)}, ..., a^{(\mathrm{n})}, ...\text{eigenvalues of } \hat{\mathbf{A}}$$

$$\left|1\right\rangle, \left|2\right\rangle, ..., \left|n\right\rangle, ...\text{"eigen} - \text{kets"}$$

$$\left\langle n \middle| m \right\rangle = \delta_{nm}$$

Lemma 2. Eigen-kets constitute a complete orthonormal basis.

$$|a\rangle = \sum_n c_n |n\rangle \qquad c^{(n)} = \langle n|a\rangle$$

$$|a\rangle = \sum_n |n\rangle\langle n|a\rangle \qquad \sum_n |n\rangle\langle n| = \mathbf{1}$$

$$\langle a|a\rangle = \left\langle a \middle| \sum_n |n\rangle\langle n| \right\rangle |a\rangle \qquad = \sum_n \left|\langle n|a\rangle\right|^2$$

If $|a\rangle$ is normalized, then $\sum_n |c_n|^2 = \sum_n \left|\langle n|a\rangle\right|^2 = 1$

Projection operator $\hat{\Lambda}_{a^{(n)}} = |n\rangle\langle n|$

$$\hat{\Lambda}_{a^{(n)}} |a\rangle = |n\rangle\langle n|a\rangle = c_{a^{(n)}} |n\rangle \qquad \sum_n \hat{\Lambda}_{a^{(n)}} = \hat{1} \quad \text{(Completeness)}$$

If N is the dimension of the space of kets,
the representation of operator **X**

$$\hat{\mathbf{X}} = \hat{\mathbf{X}} \to \hat{\mathbf{X}} = \left(\sum_{n=1}^{N} |n\rangle\langle n| \right) \hat{\mathbf{X}} \left(\sum_{m=1}^{N} |m\rangle\langle m| \right) =$$

$$= \sum_{m=1}^{N} \sum_{n=1}^{N} |m\rangle\langle m|\mathbf{X}|n\rangle\langle n|$$

$\langle m|\mathbf{X}|n\rangle$ N^2 number; $\langle m|$ is a row vector;

$|n\rangle$ is a column vector

$$\hat{\mathbf{X}} = \begin{bmatrix} \langle 1|\hat{\mathbf{X}}|1\rangle & \langle 1|\hat{\mathbf{X}}|2\rangle & \dots & \langle 1|\hat{\mathbf{X}}|N\rangle \\ \langle 2|\hat{\mathbf{X}}|1\rangle & \langle 2|\hat{\mathbf{X}}|2\rangle & \dots & \langle 2|\hat{\mathbf{X}}|N\rangle \\ \dots & \dots & & \dots \\ \langle N|\hat{\mathbf{X}}|1\rangle & \langle N|\hat{\mathbf{X}}|2\rangle & \dots & \langle N|\hat{\mathbf{X}}|N\rangle \end{bmatrix}$$

$$|b\rangle = \hat{\mathbf{X}}|a\rangle$$

$$|a\rangle = \sum_n |n\rangle\langle n|a\rangle$$

$$|b\rangle = \sum_n |n\rangle\langle n|b\rangle$$

$$|a\rangle = \begin{bmatrix} \langle 1|a\rangle \\ \langle 2|a\rangle \\ \dots \\ \langle N|a\rangle \end{bmatrix}; \quad |b\rangle = \begin{bmatrix} \langle 1|b\rangle \\ \langle 2|b\rangle \\ \dots \\ \langle N|b\rangle \end{bmatrix};$$

Bra Ket Bra-ket Operator

$$\langle b| \qquad |a\rangle \qquad \langle b|a\rangle \qquad \hat{\mathrm{A}}$$

State vectors of a physical system

$$\psi^*(r,t) \qquad \psi(\mathbf{r},t)$$

Scalar product

$$\int_V \psi^* \cdot \psi \,\mathrm{d}V$$

Hamiltonian

Observables

$$\langle b| = \begin{bmatrix} \langle 1|b\rangle^* & \langle 2|b\rangle^* & \dots & \langle N|b\rangle^* \end{bmatrix} \qquad |a\rangle = \begin{bmatrix} \langle 1|a\rangle \\ \langle 2|a\rangle \\ \dots \\ \langle N|a\rangle \end{bmatrix}$$

$$\hat{\mathbf{A}} = \begin{bmatrix} \langle 1|\hat{\mathbf{A}}|1\rangle & \langle 1|\hat{\mathbf{A}}|2\rangle & \dots & \langle 1|\hat{\mathbf{A}}|N\rangle \\ \langle 2|\hat{\mathbf{A}}|1\rangle & \langle 2|\hat{\mathbf{A}}|2\rangle & \dots & \langle 2|\hat{\mathbf{A}}|N\rangle \\ \dots & \dots & & \dots \\ \langle N|\hat{\mathbf{A}}|1\rangle & \langle N|\hat{\mathbf{A}}|2\rangle & \dots & \langle N|\hat{\mathbf{A}}|N\rangle \end{bmatrix}$$

$$\langle b|a\rangle =$$

$$= \begin{bmatrix} \langle 1|b\rangle^* & \langle 2|b\rangle^* & \dots & \langle N|b\rangle^* \end{bmatrix} \begin{bmatrix} \langle 1|a\rangle \\ \langle 2|a\rangle \\ \dots \\ \langle N|a\rangle \end{bmatrix}$$

Observables – physical quantities which can be measured

A „strong" measurement always causes the system to jump into an eigen-state of the dynamical variable that is being measured.

Before the measurement $$|a\rangle = \sum |n\rangle\langle n|a\rangle$$

After the measurement $$|a\rangle \quad \Longrightarrow \quad |n\rangle$$

For example, a silver atom spin orientation will change into either $|S_z +\rangle$ or $|S_z -\rangle$ when subjected to a Stern-Gerlach apparatus of type SGz

Measurement, in general, changes the state. The only exception is when the state is already in one of the eigen-states of the observable being measured.

$$|n\rangle \quad \Longrightarrow \quad |n\rangle$$

$$\left|a\right\rangle = \sum_n c_n \left|n\right\rangle$$

Probability that $\left|a\right\rangle$ goes into state $\left|n\right\rangle$

$$\left|c_n\right|^2 = \left|\left\langle n\middle|a\right\rangle\right|^2$$

Expectation value of a measurement

$$\left\langle \hat{\mathbf{A}} \right\rangle = \left\langle a\middle|\hat{\mathbf{A}}\middle|a\right\rangle$$

Quantum Mechanics in Dirac Notation

Introduction

Let us consider a quantum system described by a Hamiltonian $\hat{\mathbf{H}}_0$ independent of time.

Eigen-values and eigen-states of $\hat{\mathbf{H}}_0$ are denoted by

$$E_1, E_2, \dots, E_n, \dots$$

$$|1\rangle, |2\rangle, \dots, |n\rangle, \dots$$

Suppose at $t = 0$ the system is in its most general state

$$|\psi(0)\rangle = \sum_n c_n |n\rangle$$

According to the Schrödinger equation the system at a later time is in the state

$$|\psi(t)\rangle = \sum_n c_n e^{-\mathrm{j}\frac{E_n}{\hbar}t} |n\rangle$$

The probability of finding the system in state $|\varphi\rangle$

$$P_\varphi(t) = \left|\langle \varphi | \psi(t) \rangle\right|^2$$

Thus the probability that the system has made a transition from the state $|\psi(0)\rangle$ to the state $|\varphi\rangle$ between times 0 and *t*

$$P_{\psi(0)\to\varphi}(t) = \left|\langle\varphi|\psi(t)\rangle\right|^2$$

In particular, if the system is initially prepared in the eigenstate $|n\rangle$, it is given in any later time t by the state vector

$$|\psi(t)\rangle = e^{-\mathrm{j}\frac{E_n}{\hbar}t}|n\rangle$$

The probability of finding it later in a state $|m\rangle, m \neq n$, is then zero

$$P_{n\to m}(t) = \left|\langle m|\psi(t)\rangle\right|^2 = \left|\langle m|n\rangle\right|^2 = 0$$

E.g. the electron of a hydrogen atom initially in state $|n.l.m\rangle$ would remain indefinitely in this state if the atom were not coupled to the exterior environment.

Exterior interactions of various origins:

-- Interaction of an atom with external oscillating electromagnetic field (classical) (sinusoidal time-dependent external effect)

-- Collisions of an atom with ions, atoms, electrons (impulsive time-dependent external effect)

-- Coupling to quantized electromagnetic field (photon absorption, spontaneous and stimulated photon emission)

In general, the future of the state vector describing the system cannot be calculated exactly for all time.

Exact expressions can be given for the transition probabilities

Transition between discrete levels induced by a time-dependent perturbation

We consider a system described by a Hamiltonian

$$\hat{H} = \hat{H}_0 + H_I(t)$$

$\hat{H}_0$ is independent of time, its eigenvalues and eigenstates

being denoted by E_n and $|n\rangle$

$$\hat{H}_0 |n\rangle = E_n |n\rangle$$

$H_I(t)$ is an interaction term. and it is assumed that

$$\langle n | H_I | m \rangle << |E_n - E_m|$$

The coupling $H_I(t)$ will be capable of inducing transitions between different eigenstates of $\hat{H}_0$

$$P_{n\to m}(t) = ?$$

Supposing, for simplicity, that the energy levels are non-degenerate.

Two simple $H_I(t)$ examples

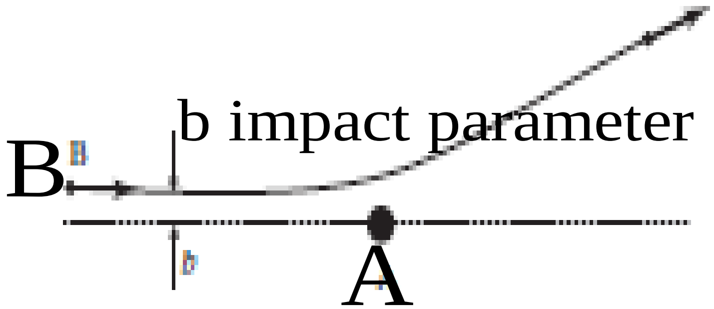
1. An atom of $\hat{H}_0$ interacts with an incident classical electromagnetic wave of which the electric field at the position of the stationary atom is

$$\mathbf{E}(t) = \mathbf{E}\cos(\omega t + \varphi)$$

To a good approximation, the interaction of the atom and the field can be given in terms of electric dipole coupling $\hat{H}_I(t) = -\hat{\mathbf{D}} \cdot \mathbf{E}(t)$; where the electric dipole of the atom is $\hat{\mathbf{D}} = q\hat{\mathbf{r}}$ (Here q is the electric charge, and $\mathbf{r}$ the radius vector between the nucleus and its valence electron).

2. We consider a stationary atom "A", of which is described the hamiltonian $\hat{H}_0$, and we suppose that another particle

"A".



The interaction potential depends on the distance between A and B: $\hat{V}\left[R(t)\right], thus$ it depends on time.

Before the collision the state of atom A is $|n\rangle$

If the energies before and after the collision are the same: ELASTIC COLLISION

There is a possibility that after the collision the state changes to $|m\rangle$

Otherwise: INELASTIC COLLISION

Perturbation Theory

$$\hat{H} = \hat{H}_0 + H_I(t) \qquad \hat{H}|n\rangle = E_n|n\rangle$$

Weak interaction: $\langle n|H_I|m\rangle << |E_n - E_m|$

$$\hat{H}_I(t) = \lambda H_I^{'}(t);$$

$$\lambda << 1$$

λ is a real, diemnsionless parameter, much smaller than unity, which characterizes the relative strenghts of the interaction $\hat{H}_I(t)$

(In the two examples, λ is proportional (i) to the amplitude of the incident electric field, (ii) λ is a function of the impact parameter b)

$\lambda << 1$ is valid if the electric field is weak,
or the impact parameter is large.

Schrödinger equation: $$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle=\left(\hat{H}_0+\lambda H_I^{'}(t)\right)|\psi(t)\rangle$$

Expanding $|\psi(t)\rangle$ in the basis of eigen-states of $\hat{H}_0$ we get

$$|\psi(t)\rangle=\sum_n c_n(t)e^{-\mathrm{j}\frac{E_n}{\hbar}t}|n\rangle$$

We project on the eigen-state $|k\rangle$ of $\hat{H}_0$, and use the identity $$\sum_n|n\rangle\langle n|=1$$

$$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle k|\psi(t)\rangle=\langle k|\hat{H}_0|\psi(t)\rangle+\lambda\langle k|H_I^{'}(t)|\psi(t)\rangle=$$

$$=E_k\langle k|\psi(t)\rangle+\lambda\sum_n\langle k|H_I^{'}(t)|n\rangle c_n(t)e^{-\mathrm{j}\frac{E_n}{\hbar}t}$$

$$\left[E_k c_k(t)+\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_k(t)\right]e^{-\mathrm{j}\frac{E_k}{\hbar}t}=E_k c_k(t)e^{-\mathrm{j}\frac{E_k}{\hbar}t}+\lambda\sum_n\langle k|H_I^{'}(t)|n\rangle c_n(t)e^{-\mathrm{j}\frac{E_n}{\hbar}t}$$

$$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_k(t)=\lambda\sum_n\langle k|H_I^{'}(t)|n\rangle e^{\mathrm{j}\frac{(E_k-E_n)}{\hbar}t}c_n(t)$$

No approximation having been made this far!

Possibly infinite system of ordinary differential equations

The coefficients $c_n(t)$ depend on λ

Perturbation theory consists of developing $c_n(t)$ as a power series of λ

$$c_k(t)=c_k^0(t)+\lambda c_k^1(t)+\lambda^2 c_k^2(t)+\ldots$$

Substituting this series we can collect together the same order in λ

Oder 0 $$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_k^0(t)=0$$

Oder 1 $$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_k^1(t)=\lambda\sum_n\langle k|H_I^{'}(t)|n\rangle e^{\mathrm{j}\frac{(E_k-E_n)}{\hbar}t}c_n^0(t)$$

Oder *r* $$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_k^r(t)=\lambda\sum_n\langle k|H_I^{'}(t)|n\rangle e^{\mathrm{j}\frac{(E_k-E_n)}{\hbar}t}c_n^{r-1}(t)$$

This system of equations can be solved iteratively. The zeroes order terms are already known: they are the constants determined by the initial state of the system . On substituting these terms, the first order solutions for $c_k^1(t);\, k=1,2,3,\ldots$ can be found. And so on.