Quantum Mechanics - Formalism

Dirac Notation

Matrix notation will be used throughout this course to represent quantum mechanical states. This choice is made partly for its notational simplicity and partly because it is widely used in research in atomic, nuclear and particle physics.

Recall the usual notation. For a unit vector with components $\vec{i}, \vec{j}, \vec{k}, \ldots$, an arbitrary vector can be written as

$$\vec{a} = a_i \vec{i} + a_j \vec{j} + a_k \vec{k} \ldots$$

Where

$$\vec{i} \cdot \vec{j} = \delta_{ij}$$

form an orthonormal set.

[The scalar product is defined by

$$\vec{a} \cdot \vec{b} = a_i b_i + a_j b_j + a_k b_k \ldots]$$

Of course, from the orthonormality condition one can write down ~~to~~ an expression for the coefficients a_i:

$$a_i = \vec{a} \cdot \vec{i} .$$

Now, it is often convenient to write out $\vec{a}$ as a column or row vector:

$$\vec{a} = \begin{pmatrix} a_i \\ a_j \\ a_k \\ \vdots \end{pmatrix} .$$

The basis vectors are then

$$\vec{i} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} \quad \vec{j} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} \quad \vec{k} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \end{pmatrix} \text{ etc.}$$

To do the inner product, we take the <u>adjoint</u> of the column vector

$$\vec{b} = (b_i, b_j, b_k \cdots).$$

$$\Rightarrow \vec{b} \cdot \vec{a} = (b_i, b_j, b_k \cdots) \begin{pmatrix} a_i \\ a_j \\ a_k \\ \vdots \end{pmatrix} \text{ etc.}$$

In quantum mechanics, we solve for a series of states (which may be discrete) $\psi_1, \psi_2, \cdots$

Dirac introduced an abbreviation for the components of a solution ψ_a expressed in these states.

$$|a\rangle = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix}$$

<u>ket vector</u>

Now, the solutions are in general complex, and so are the coefficients. Thus, in forming the adjoint, we take the <u>complex</u> <u>transpose</u>

$$\langle a| = (a_1^*, a_2^* \cdots)$$

<u>bra vector</u>

i.e. $|a\rangle^\dagger = \langle a|$ $\quad \langle a|^\dagger = |a\rangle$.

The scalar [complex!] product is then represented by

$$\langle b|a\rangle = (b_1^*, b_2^*, b_3^* \ldots)\begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix}$$

Note $\langle b|a\rangle^\dagger = \langle a|b\rangle = (\langle b|a\rangle)^*$

(i.e., the order in the product counts).

Operators

An operator $\hat{A}$ in an N-dimensional space is defined by its action on the vectors of that space

$$|b\rangle = \hat{A}|a\rangle \quad \text{, where } |b\rangle \text{ may be } c|a\rangle.$$

The operators of interest here are

1. Linear $\quad \hat{A}[c|a\rangle + d|b\rangle] = c\hat{A}|a\rangle + d\hat{A}|b\rangle$.
2. Associative law: $\quad (\hat{A}\hat{B})\hat{C} = \hat{A}(\hat{B}\hat{C})$
3. Distributive law $\quad \hat{A}(\hat{B}+\hat{C}) = \hat{A}\hat{B} + \hat{A}\hat{C}$.

But they may not commute $\quad \hat{A}\hat{B} \neq \hat{B}\hat{A}$.

The operator can be expressed in matrix form: $\hat{A} = \begin{pmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & \cdots & \\ & \ddots & A \ldots \end{pmatrix}$

The adjoint of the operator $\hat{A}^{+}$ is defined by

$$\langle b| = \langle a|\hat{A}^{+} \quad \text{if} \quad |b\rangle = \hat{A}|a\rangle .$$

so that $A^{+} = (A^{*})^{T}$

$$\Rightarrow \langle \alpha_i|\hat{A}|\alpha_j\rangle = (\langle \alpha_j|\hat{A}^{+}|\alpha_i\rangle)^{*}$$ where α form some set of basis states

take trans. $= (\langle \alpha_j|)^{*}\hat{A}^{T}(|\alpha_i\rangle)^{*}$

If $\hat{A}$ is Hermitian, $\hat{A}^{+} = \hat{A}$, then

$$\langle \alpha_i|\hat{A}|\alpha_j\rangle = \langle \alpha_j|\hat{A}|\alpha_i\rangle^{*}$$

Eigenvalues and Eigenvectors

For some sets of vectors and operators, the operation

$$\hat{A}|a_i\rangle$$

only changes the magnitude of $|a_i\rangle$:

$$\hat{A}|a_i\rangle = a_i|a_i\rangle$$

Here, $|a_i\rangle$ is said to be an eigenvector with a_i its eigenvalue. You're used to examples of this from linear algebra, so we won't pursue them here. Instead, let's just summarize and review what we need:

I The eigenvalues of a Hermitian operator are all real.

$$\hat{A}|a_i\rangle = a_i|a_i\rangle \Rightarrow \langle a_i|\hat{A}|a_i\rangle = a_i\langle a_i|a_i\rangle$$

$$\langle a_i|\hat{A}^\dagger = \langle a_i|a_i^* \Rightarrow \langle a_i|\hat{A}^\dagger|a_i\rangle = a_i^*\langle a_i|a_i\rangle$$

But l.h.s.'s are equal since $\hat{A} = \hat{A}^\dagger \Rightarrow a_i = a_i^*$
$\therefore$ real.

(2) The eigenvectors of any non-degenerate Hermitian operator [ie. all eigenvalues of the operator are distinct] are mutually orthogonal.

Proof: $\langle a_k|\hat{A}|a_j\rangle = a_j\langle a_k|a_j\rangle$

$\qquad \parallel$

$\langle a_k|\hat{A}^\dagger|a_j\rangle = a_k^*\langle a_k|a_j\rangle$

Hermitian

$\therefore (a_j - a_k)\langle a_k|a_j\rangle = 0$ $\quad a_k = a_k^*$ by (1)

or

$\langle a_k|a_j\rangle = \delta_{jk}$

[assuming $|a\rangle$ normalized]

2a) The eigenvectors corresponding to the equal eigenvalues of a degenerate Hermitian operator are not unique. [ie. linear combinations are OK]

2b) Not all eigenvectors associated with equal eigenvalues need be orthogonal.

2c) But there exists at least one set of (N) orthogonal eigenvectors for any degenerate Hermitian operator.

(3) Every Hermitian operator has at least one set of orthonormal eigenvectors. The nondegenerate part of the set is unique.

(4) If two operators have a common set of eigenvectors, then they commute.

Say: $\hat{A}\,|a_i, b_i\rangle = a_i\,|a_i, b_i\rangle$

$\hat{B}\,|a_i, b_i\rangle = b_i\,|a_i, b_i\rangle$

$$\therefore \hat{B}\left(\hat{A}\,|a_i, b_i\rangle\right) = a_i b_i\,|a_i, b_i\rangle = \hat{A}\left(\hat{B}\,|a_i, b_i\rangle\right)$$

$$\Rightarrow \hat{A}\hat{B} - \hat{B}\hat{A} \equiv [\hat{A}, \hat{B}] = 0.$$

Further, if two operators do not commute, they cannot have a common set of eigenvectors.

(5) (Inverse of 4) If two nondegenerate operators commute, then their eigenvectors must be common to both operators.

(6) Any two commuting operators have at least one common set of orthonormal eigenvectors, even if they are degenerate.

Projection operators

We can define an operator which projects out the components of an arbitrary vector $|a\rangle$ onto a complete set of basis vectors $|\alpha_i\rangle$. From our discussion of the dot product on 3.1, the coefficient of $|\alpha_i\rangle$ is

$\langle\alpha_i|a\rangle$ i.e. $$|a\rangle = \sum_i \left(\langle\alpha_i|a\rangle\right)|\alpha_i\rangle = \sum_i |\alpha_i\rangle\langle\alpha_i|a\rangle = \sum_i \hat{P}_i\,|a\rangle$$

Where $\hat{P}_i$ is the projection operator. Since this result is valid for any $|\alpha\rangle$, then

$$\sum_i |a_i\rangle\langle a_i| = 1 \quad \Rightarrow \sum_i \hat{P}_i = 1$$

(up to page 60, Weider).

Postulates of Quantum Mechanics

Postulate #1. One can associate a linear Hermitian operator (in a complex space) with every dynamical observable.

e.g. $r \rightarrow \hat{r} = \hat{r}^{\dagger}$ $\qquad p \rightarrow \hat{p} = \hat{p}^{\dagger}$

Note: $e^{\hat{x}} \equiv \sum_{n=0}^{\infty} \frac{1}{n!} \hat{x}^n$

Postulate #2 The commutation relations between operators associated with two classical observables is deduced from the Poisson bracket of these observables using the correspondence:

$$\{A, B\} \longleftrightarrow \frac{[\hat{A}, \hat{B}]}{i\hbar}$$

e.g. $[\hat{x}_i, \hat{x}_j] = 0 \qquad [\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}\, \underline{\hat{1}}$ unit operator

$[\hat{L}_i, \hat{L}_j] = i\hbar \hat{L}_k$ (cyclic)

$[\hat{L}_i, \hat{L}^2] = 0$

This is not to imply that all of these relations are independent; they can be derived from one central equation in QM. in the same way as they were in classical mechanics.

Postulate #3 The quantum values allowed to any observable are determined by the eigenvalues of the corresponding operator. Any measurement of the system yields one of these values.

Postulate #4 The state of any physical system is characterized by a state vector of unit length. If the system is characterized by a vector $|\beta\rangle$ and a measurement is made of an observable $\hat{A}$ [with eigenvectors $|a_i\rangle$] then the probability of observing the system with a value a_i is

$$\mathcal{P}_\beta(a_i) = \left| \langle a_i | \beta \rangle \right|^2 \leq 1$$

That is, take the projection operator of a_i on β.

$$\langle \beta | a_i \rangle \langle a_i | \beta \rangle = |\langle a_i | \beta \rangle|^2 .$$

The expectation value of $\hat{A}$ is defined in the same way as it is classically:

$$\langle A \rangle_\beta \equiv \frac{\sum_i \mathcal{P}_\beta(a_i) \cdot a_i}{\sum_i \mathcal{P}_\beta(a_i)} .$$

The numerator is:

$$\sum_i \mathcal{P}_\beta(a_i)\, a_i = \sum_i \langle \beta | a_i \rangle \langle a_i | \beta \rangle a_i$$
$$= \sum_i \langle \beta | a_i | a_i \rangle \langle a_i | \beta \rangle$$
$$= \sum_i \langle \beta | \hat{A} | a_i \rangle \langle a_i | \beta \rangle$$
$$= \langle \beta | \hat{A}\, \hat{1} | \beta \rangle$$

(assuming the $|a_i\rangle$ form a complete set)

The denominator is

$$\sum_i \mathcal{P}_\beta(a_i) = \sum_i \langle \beta | a_i \rangle \langle a_i | \beta \rangle = \langle \beta | \beta \rangle$$

$$\Rightarrow \quad \langle \hat{A} \rangle_\beta \equiv \frac{\langle \beta | \hat{A} | \beta \rangle}{\langle \beta | \beta \rangle}.$$

Since the states are usually normalized, $\langle \beta | \beta \rangle = 1$, then

$$\langle \hat{A} \rangle_\beta = \langle \beta | \hat{A} | \beta \rangle.$$

The uncertainty, or r.m.s. deviation, of a measurement of $\hat{A}$ is

$$\Delta A_\beta = \left[\langle \beta | (\hat{A} - \langle A \rangle_\beta)^2 | \beta \rangle \right]^{1/2}.$$
$$= \left[\langle \beta | \hat{A}\hat{A} | \beta \rangle - 2 \langle A \rangle_\beta \langle \beta | \hat{A} | \beta \rangle + \langle A \rangle_\beta^2 \langle \beta | \beta \rangle \right]^{1/2}$$
$$= \left[\langle \hat{A}^2 \rangle_\beta - 2 \langle \hat{A} \rangle_\beta^2 + \langle \hat{A} \rangle_\beta^2 \right]^{1/2}$$
$$= \left[\langle \hat{A}^2 \rangle_\beta - \langle \hat{A} \rangle_\beta^2 \right]^{1/2}.$$

Note that for an eigenvector, $|\beta\rangle = |a_i\rangle$,

$$\Delta A_{a_i} = \left[\langle a_i|\hat{A}^2|a_i\rangle - \langle a_i|\hat{A}|a_i\rangle^2 \right]^{1/2}$$
$$= \left[a_i^2 - a_i^2 \right]^{1/2} = 0.$$

That is, the observable is well-defined.

Heisenberg's Uncertainty Principle

7) ~~If~~ Three observables satisfy the commutation relation

$$[\hat{A}, \hat{B}] = i\hat{C}$$

Then, regardless of the state of the system, $|\beta\rangle$, the results of measurements of these observables must conform to Heisenberg's inequality.

$$\Delta A_\beta^2 \cdot \Delta B_\beta^2 \geq \left(\tfrac{1}{2} \langle C\rangle_\beta \right)^2$$

Starting back with our definitions of ΔA_β etc. on the previous page.

$$\Delta A_\beta^2 = \underbrace{\langle\beta|(\hat{A} - \langle A\rangle_\beta)}_{\equiv \langle\gamma|}\underbrace{(\hat{A} - \langle A\rangle_\beta)|\beta\rangle}_{|\gamma\rangle} = \langle\gamma|\gamma\rangle.$$

Similarly ΔB_β^2 is in the form $\langle\delta|\delta\rangle$.

$$\therefore \Delta A_\beta^2 \cdot \Delta B_\beta^2 = \langle\gamma|\gamma\rangle \cdot \langle\delta|\delta\rangle$$
$$\geq |\langle\gamma|\delta\rangle|^2$$ by Schwarz's inequality.

[This is obviously true for real vectors
$$a^2 \cdot b^2 \geq (\vec{a} \cdot \vec{b})^2$$
$$= a^2 b^2 \cos^2\theta$$]

But $\langle \gamma | \delta \rangle = \langle \beta | \underbrace{(\hat{A} - \langle A \rangle_\beta)(\hat{B} - \langle B \rangle_\beta)}_{\equiv \hat{G}} | \beta \rangle$.

not necessarily Hermitian unless $[\hat{A}, \hat{B}] = 0$.
$(\hat{A}\hat{B})^\dagger = (\hat{B}^\dagger \hat{A}^\dagger)$
$= \hat{B}\hat{A} \neq (\hat{A}\hat{B})$
since $\hat{A}, \hat{B}$ hermitian

Decompose $\hat{G}$ into

$\hat{G} = \hat{D} + \frac{i}{2}\hat{C}$ where $\hat{C}$ and $\hat{D}$ are both Hermitian. Symmetric and antisymmetric combinations of $\hat{A}\hat{B}$

$$\hat{D} = \frac{(\hat{A} - \langle A \rangle_\beta)(\hat{B} - \langle B \rangle_\beta) + (\hat{B} - \langle B \rangle_\beta)(\hat{A} - \langle A \rangle_\beta)}{2}$$

$$\hat{C} = \frac{(\hat{A} - \langle A \rangle_\beta)(\hat{B} - \langle B \rangle_\beta) - (\hat{B} - \langle \hat{B} \rangle_\beta)(\hat{A} - \langle A \rangle_\beta)}{2i} = \frac{[\hat{A}, \hat{B}]}{i}.$$

$$\text{So } |\langle G \rangle_\beta|^2 = \langle \hat{D} + \tfrac{i}{2}\hat{C} \rangle_\beta \cdot \langle \hat{D} - \tfrac{i}{2}\hat{C} \rangle_\beta$$
$$= \langle D \rangle_\beta^2 + \frac{1}{4}\langle C \rangle_\beta^2 \geq \frac{1}{4}\langle C \rangle_\beta^2.$$

$$\text{So} \quad \Delta A_\beta^2 \cdot \Delta B_\beta^2 \geq \left(\frac{1}{2}\langle C \rangle_\beta\right)^2 \quad \text{where } \hat{C} = -i[\hat{A}, \hat{B}]$$

Taking a few cases in point:

$[\hat{x}_i, \hat{x}_j] = 0 \quad \Rightarrow \quad \Delta x_i \cdot \Delta x_j \geq 0$

Same with $\quad \Delta p_i \cdot \Delta p_j \geq 0$

<u>But</u> $\quad \Delta x_i \cdot \Delta p_j \geq \frac{1}{2}\hbar\,\delta_{ij} \quad$ since $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$.

This is the fundamental statement of Heisenberg's Uncertainty principal.

Time evolution of states — Quantum dynamics

Thus far we have concentrated on the definition of what a state is and how to obtain some properties of operators, such as momentum, quantum mechanically. Here, we wish to go a step further and find the operator equation which defines the time evolution. What we want to be able to do is relate the motion as seen at the quantum mechanical level, to what is observed classically. That is, for a state vector $|\beta, t\rangle$, we need to be able to go:

$$\langle \beta, t | \hat{A} | \beta, t \rangle \longleftrightarrow A_{classical}(t)$$

(i.e. take $\hat{A} = \hat{r}$ and find motion of centroid). This requirement is known as Ehrenfest's Theorem [can be done in reverse, too: i.e. postulate $\mathcal{H}\psi = i\hbar \frac{\partial}{\partial t}\psi$ and find equations of motion].

What we want to satisfy is

$$\frac{d}{dt} A = \{A, \mathcal{H}\} + \frac{\partial A}{\partial t}$$

$$\downarrow$$

$$\frac{d}{dt} \langle \beta, t | A | \beta, t \rangle = \langle \beta, t | \frac{[\hat{A}, \hat{\mathcal{H}}]}{i\hbar} | \beta, t \rangle + \langle \beta, t | \frac{\partial \hat{A}}{\partial t} | \beta, t \rangle$$

This can be satisfied with the following representation of $\mathcal{H}$:

$$\hat{\mathcal{H}} |\beta, t\rangle = i\hbar \frac{d}{dt} |\beta, t\rangle$$

$$\langle \beta, t | \hat{\mathcal{H}} = -i\hbar \frac{d}{dt} \langle \beta, t | \qquad \left[\text{since } \hat{\mathcal{H}} = \hat{\mathcal{H}}^{+}\right]$$

Proof:

$$\frac{d}{dt}\langle\beta,t|\hat{A}|\beta,t\rangle = \langle\beta,t|\hat{A}\left\{\frac{d}{dt}|\beta,t\rangle\right\} + \left\{\frac{d}{dt}\langle\beta,t|\right\}\hat{A}|\beta,t\rangle + \langle\beta,t|\frac{\partial\hat{A}}{\partial t}|\beta,t\rangle$$

$$= \langle\beta,t|\hat{A}\frac{1}{i\hbar}\hat{\mathcal{H}}|\beta,t\rangle - \frac{1}{i\hbar}\langle\beta,t|\hat{\mathcal{H}}\hat{A}|\beta,t\rangle + \langle\beta,t|\frac{\partial\hat{A}}{\partial t}|\beta,t\rangle$$

$$\Rightarrow \quad \frac{d}{dt}\langle A\rangle_\beta = \left\langle\frac{[\hat{A},\hat{\mathcal{H}}]}{i\hbar}\right\rangle_\beta + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle_\beta .$$

Hence, we have the replacement $\mathcal{H} \to i\hbar\frac{d}{dt}$ required by Ehrenfest's Theorem + Postulate #2.

Note that we can formally write down the time evolution for a system governed by a time independent $\hat{\mathcal{H}}$:

$$|\beta,t\rangle = \underbrace{\exp\left(-\frac{i}{\hbar}\hat{\mathcal{H}}(t-t_0)\right)}_{\text{often defined as an evolution operator } U(t,t_0)}|\beta,t_0\rangle .$$

Now, if $|\beta,t\rangle$ is an eigenstate of $\hat{\mathcal{H}}$ with energy ϵ_β:

$$|\beta,t_2\rangle = \exp\left(-\frac{i}{\hbar}\hat{\mathcal{H}}(t_2-t_1)\right)|\beta,t_1\rangle = \underline{\underline{\exp\left(-\frac{i\epsilon_\beta}{\hbar}t_2-t_1\right)}}|\beta,t_1\rangle$$

This is just a phase factor.

$\therefore$ this is a <u>STATIONARY STATE</u>.