Physics 461: Quantum Mechanics II

Review

The Postulates of Quantum Mechanics are

1) The set of all possible states of a physical system stand in 1-1 correspondence with the vector directions (rays) in a Hilbert space $\mathcal{H}$. Since the state is described by the entire ray, we have that $|\psi\rangle$ and $\lambda|\psi\rangle$ with $\lambda \in \mathbb{C}$ describe the same state.

2) The physical observables of a system stand in a 1-1 correspondence with the set of Hermitian operators on the state space $\mathcal{H}$. That is, to each measurable quantity Ω, there corresponds a Hermitian operator A acting on $\mathcal{H}$. Out of the set of all Hermitian operators, there is a subset which consists of mutually commuting operators and they are assumed to be complete (they form a CSCO).

3) Spectral Decomposition

a) The only possible result of the measurement of a physical observable $\mathcal{A}$ is one of the (real) eigenvalues of the corresponding Hermitian operator A.

b) Let $\{|\phi_k\rangle\}$ be the simultaneous eigenstates of a CSCO so that

$$A|\phi_k\rangle = a_k|\phi_k\rangle \text{ etc.}$$

These states form an orthonormal basis for the state space $\mathcal{H}$.

For a system in state $|\psi\rangle$ (with $\langle\psi|\psi\rangle = 1$), the probability of measuring the value a_k for the physical observable $\mathcal{A}$ is

$$P_k = |\langle\phi_k|\psi\rangle|^2 .$$

Immediately following the measurement, the system is in the state $|\phi_k\rangle$.

4) The time evolution of the physical states is given by the Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t)\, |\psi(t)\rangle ,$$

where $H = H(t)$ is the Hermitian Hamiltonian operator. $H(t)$ is the total energy of the system. (In general the observables may also have explicit time dependence, $A = A(t)$.)

For an isolated system, the observables including the Hamiltonian are independent of time $\frac{dA}{dt} = 0$ and H is a constant operator.

<u>Comments</u>: 1) We extend the Hilbert space of states to include generalized kets with infinite (continuum) norms but whose scalar product with every ket of $\mathcal{H}$ is finite. So doing, to every bra-vector $\langle\psi|$ there corresponds a ket-vector and vice-versa in the extended Hilbert space and its dual.

2) Then in postulate 3 we can have discrete as well as continuous (or even mixed) sets of basis vectors. That is, if the orthonormal basis is a discrete basis, then the simultaneous eigenvectors, $|\phi_{ab\ldots}\rangle$, of the CSCO $\{A, B, \ldots\}$ obey

$$\langle\phi_{a'b'\ldots}|\phi_{ab\ldots}\rangle = \delta_{a'a}\,\delta_{b'b}\cdots$$

$$\mathbb{1} = \sum_{a,b,\ldots} |\phi_{ab\ldots}\rangle\langle\phi_{ab\ldots}|$$

where

$$A|\phi_{ab\ldots}\rangle = a|\phi_{ab\ldots}\rangle$$

$$B|\phi_{ab\ldots}\rangle = b|\phi_{ab\ldots}\rangle, \text{ etc.},$$

with the eigenvalues $\{a, b, \ldots\}$ taking discrete values (in 1-1 correspondence with the integers).

An arbitrary state vector $|\psi\rangle$ has the expansion in terms of the $|\phi_{ab\ldots}\rangle$ basis

$$|\psi\rangle = \sum_{a,b,\ldots} \psi_{ab\ldots}|\phi_{ab\ldots}\rangle$$

with

$$\psi_{ab\ldots} = \langle \phi_{ab\ldots} | \psi \rangle .$$

This implies

$$A|\psi\rangle = \sum_{a,b,\ldots}{}' a\, \psi_{ab\ldots} |\phi_{ab\ldots}\rangle$$

$$B|\psi\rangle = \sum_{a,b,\ldots}{}' b\, \psi_{ab\ldots} |\phi_{ab\ldots}\rangle, \text{ etc.}$$

The probability of finding the values $a, b, \ldots$ when $A, B, \ldots$ are measured when the system is in state $|\psi\rangle$ is

$$P_{ab\ldots} = |\langle \phi_{ab\ldots} |\psi\rangle|^2 .$$

Note that

$$\sum_{a,b,\ldots}{}' P_{ab\ldots} = \sum_{a,b,\ldots}{}' |\langle \phi_{ab\ldots} |\psi\rangle|^2$$

$$= \sum_{a,b,\ldots}{}' \langle \psi | \phi_{ab\ldots} \rangle \langle \phi_{ab\ldots} | \psi \rangle$$

$$= \langle \psi | \psi \rangle = 1$$ as required of a probability.

Finally, the expectation value of $A, B, \ldots$ in state $|\psi\rangle$ is

$$\langle\psi|A|\psi\rangle = \sum_{a,b,\ldots}' a \underbrace{\psi_{ab\ldots}}_{=\langle\phi_{ab\ldots}|\psi\rangle} \langle\psi|\phi_{ab\ldots}\rangle$$

$$= \sum_{a,b,\ldots}' a \, |\langle\phi_{ab\ldots}|\psi\rangle|^2$$

$$= \sum_{a,b,\ldots}' a \, P_{ab\ldots}$$, etc., again as expected for $P_{ab\ldots}$ a probability.

On the other hand, if the orthonormal basis is continuous, then

$$\langle\phi_{\alpha'\beta'\ldots}|\phi_{\alpha\beta\ldots}\rangle = \delta(\alpha'-\alpha)\,\delta(\beta'-\beta)\cdots$$

$$\mathbb{1} = \int d\alpha\, d\beta \cdots |\phi_{\alpha\beta\ldots}\rangle\langle\phi_{\alpha\beta\ldots}|$$

where

$$A|\phi_{\alpha\beta\ldots}\rangle = \alpha\,|\phi_{\alpha\beta\ldots}\rangle$$

$$B|\phi_{\alpha\beta\ldots}\rangle = \beta\,|\phi_{\alpha\beta\ldots}\rangle, \text{ etc.,}$$

with the eigenvalues $\{\alpha, \beta, \ldots\}$ taking on a continuum of values.

An arbitrary state vector $|\psi\rangle$ has the expansion in terms of the continuous basis $\{|\phi_{\alpha\beta\ldots}\rangle\}$ given by

$$|\psi\rangle = \int d\alpha\, d\beta \cdots \psi(\alpha,\beta,\ldots)\, |\phi_{\alpha\beta\ldots}\rangle$$

with

$$\psi(\alpha,\beta,\ldots) = \langle \phi_{\alpha\beta\ldots} | \psi \rangle .$$

This implies

$$A|\psi\rangle = \int d\alpha\, d\beta \cdots \alpha\, \psi(\alpha,\beta,\ldots)\, |\phi_{\alpha\beta\ldots}\rangle$$

$$B|\psi\rangle = \int d\alpha\, d\beta \cdots \beta\, \psi(\alpha,\beta,\ldots)\, |\phi_{\alpha\beta\ldots}\rangle \text{, etc.}$$

For the system in state $|\psi\rangle$, the probability of measuring A in the range α to $\alpha + d\alpha$, B in the range β to $\beta + d\beta$, etc. is

$$dP(\alpha,\beta,\ldots) = |\langle \phi_{\alpha\beta\ldots}|\psi\rangle|^2\, d\alpha\, d\beta \cdots .$$

Note, as required of a probability density

$$\int dP(\alpha,\beta,\ldots) = \int d\alpha\, d\beta \cdots |\langle \phi_{\alpha\beta\ldots}|\psi\rangle|^2$$

$$= \langle \psi | \int d\alpha\, d\beta \cdots |\phi_{\alpha\beta\ldots}\rangle\langle\phi_{\alpha\beta\ldots}|\psi\rangle$$

$$= \langle \psi | \psi \rangle = 1.$$

And finally the expectation value of $A, B, \ldots D$ in state $|\psi\rangle$ is

$$\langle \psi | A | \psi \rangle = \int d\alpha\, d\beta \cdots \alpha\, \underbrace{\psi(\alpha, \beta, \ldots)}_{= \langle \phi_{\alpha\beta\ldots} | \psi \rangle} \langle \psi | \phi_{\alpha\beta\ldots} \rangle$$

$$= \int d\alpha\, d\beta \cdots \alpha\, |\langle \phi_{\alpha\beta\ldots} | \psi \rangle|^2$$

$$= \int dP(\alpha, \beta, \ldots)\, \alpha \;, \quad \text{etc.}\,.$$

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3) Further, immediately following the measurement of A, the state of the system is reduced to that part of $|\psi\rangle$ which is precisely that eigenvector of A. So if A is measured to yield a, the system immediately afterwards is in state

$$|\psi\rangle \longrightarrow \frac{\sum\limits_{b,c,\ldots} \psi_{a,b,c\ldots} |\phi_{abc\ldots}\rangle}{\left(\sum\limits_{b,c,\ldots} |\psi_{a,b,c\ldots}|^2\right)^{1/2}}$$

normalizes new state to 1.

In the case of continuous eigenvalues the state of the system reduces to the state

$$|\psi\rangle \longrightarrow \frac{\int_{\alpha-\frac{\Delta\alpha}{2}}^{\alpha+\frac{\Delta\alpha}{2}} d\alpha \int d\beta\, d\gamma \cdots \psi(\alpha,\beta,\gamma,\ldots)\, |\phi_{\alpha,\beta,\gamma,\ldots}\rangle}{\left(\int_{\alpha-\frac{\Delta\alpha}{2}}^{\alpha+\frac{\Delta\alpha}{2}} d\alpha \int d\beta\, d\gamma \cdots |\psi(\alpha,\beta,\gamma,\ldots)|^2\right)^{1/2}}$$

immediately after the measurement of A which yields α to within $\Delta\alpha$.

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4) The Hilbert space is completely characterized by giving all algebraic relations (commutation relations) among the elements of any irreducible set of linear operators. An irreducible set of operators is one such that the only operator to commute with all the members of the set is the identity. For the case of a single particle with no other internal degrees of freedom (ex., no spin) we had that the position operator $\underline{X}$ adits

canonically conjugate momentum operator $\vec{P}$ formed an irreducible set. Their CCR are

$$[X_i, P_j] = i\hbar\delta_{ij}$$

$$[X_i, X_j] = 0 = [P_i, P_j].$$

So if an operator commutes with $\vec{X}$, it cannot be a function of $\vec{P}$ since they do not commute. If it also commutes with $\vec{P}$ likewise, it cannot be a function of $\vec{X}$. Hence, the operator is independent of $\vec{X}$ and $\vec{P}$, since there are not other degrees of freedom for the operator to act on, it must be a multiple of the identity. From the irreducible set we can extract a CSCO whose eigenvectors form a basis for the Hilbert space. Thus we are led to consider the coordinate basis and the momentum basis.

<u>Coordinate Representation</u>: Given a Cartesian coordinate system with the particle position denoted by vector $\vec{r}$ we have

$$X_i|\vec{r}\rangle = x_i|\vec{r}\rangle \quad ; \quad (x_1, x_2, x_3) \in \mathbb{R}^3$$

The states are continuum normalized

1) $$\langle \vec{r}'|\vec{r}\rangle = \delta^3(\vec{r}' - \vec{r})$$

and complete

2) $$\mathbb{1} = \int d^3r \, |\vec{r}\rangle\langle\vec{r}| .$$

Hence any state $|\psi\rangle$ has the expansion

$$|\psi\rangle = \int d^3r \, \psi(\vec{r}) \, |\vec{r}\rangle$$

with wavefunction $\psi(\vec{r}) = \langle\vec{r}|\psi\rangle$.

Any function of X_i has expectation value

$$\langle\psi|F(\vec{R})|\psi\rangle = \int d^3r \, \psi^*(\vec{r}) F(\vec{r}) \psi(\vec{r})$$

since $$F(\vec{R})|\vec{r}\rangle = F(\vec{r})|\vec{r}\rangle .$$

Consider the unitary operator (translation operator)

$$\mathcal{U}(\vec{a}) \equiv e^{-\frac{i}{\hbar}\vec{P}\cdot\vec{a}}$$

$$\mathcal{U}^{\dagger}(\vec{a}) = \mathcal{U}(-\vec{a}) = \mathcal{U}^{-1}(\vec{a}) \quad \text{since } \vec{P}^{\dagger} = \vec{P}.$$

Since $[X_i, P_j] = i\hbar\delta_{ij}$ we have that

$$[X_i, \mathcal{U}(\vec{a})] = -\frac{i}{\hbar}(i\hbar a_i)\,\mathcal{U}(\vec{a})$$

$$= a_i\,\mathcal{U}(\vec{a})$$

Thus $\vec{R}\,\mathcal{U}(\vec{a}) = \mathcal{U}(\vec{a})(\vec{R} + \vec{a})$.

Applying this to the position eigenstates we'll find

$$\vec{R}(\mathcal{U}(\vec{a})\,|\vec{r}\rangle) = (\vec{r} + \vec{a})(\mathcal{U}(\vec{a})|\vec{r}\rangle)$$

thus $\mathcal{U}(\vec{a})|\vec{r}\rangle = |\vec{r} + \vec{a}\rangle$.

Now

$$\langle\vec{r}|\,\mathcal{U}^{\dagger}(\vec{a})\,|\psi\rangle = \langle\vec{r}|\,\mathcal{U}(-\vec{a})\,|\psi\rangle$$

$$\langle\mathcal{U}(\vec{a})\vec{r}|\psi\rangle = \langle\vec{r}+\vec{a}|\psi\rangle = \psi(\vec{r}+\vec{a})$$

but for infinitesimal $\vec{a} = \vec{\epsilon}$ we have

$$U^\dagger(\vec{\epsilon}) = 1 + \frac{i}{\hbar}\vec{P}\cdot\vec{\epsilon} + O(|\vec{\epsilon}|^2)$$

So

$$\langle \vec{r}|U^\dagger(\vec{\epsilon})|\psi\rangle = \langle \vec{r}|\psi\rangle + \frac{i}{\hbar}\langle \vec{r}|\vec{P}\cdot\vec{\epsilon}|\psi\rangle$$

$$= \psi(\vec{r}) + \frac{i}{\hbar}\langle \vec{r}|\vec{P}\cdot\vec{\epsilon}|\psi\rangle$$

but this $= \psi(\vec{r}+\vec{\epsilon}) = \psi(\vec{r}) + \vec{\epsilon}\cdot\vec{\nabla}\psi(\vec{r})$

$\Rightarrow$

$$\langle \vec{r}|\vec{P}|\psi\rangle = -i\hbar\vec{\nabla}\psi(\vec{r})$$

$$= -i\hbar\vec{\nabla}\langle \vec{r}|\psi\rangle$$

Since $|\psi\rangle$ was arbitrary $\Rightarrow$

$\langle \vec{r}|\vec{P} = -i\hbar\vec{\nabla}_{\vec{r}}\langle \vec{r}|$, that is

$\vec{P}$ is represented by $\frac{\hbar}{i}\vec{\nabla}_{\vec{r}}$ in the $\{|\vec{r}\rangle\}$ basis.

Suppose $|\psi\rangle$ is a momentum eigenstate $|\vec{p}\rangle$

$$\vec{P}|\vec{p}\rangle = \vec{p}\,|\vec{p}\rangle \quad ; \quad \vec{p} \in \mathbb{R}^3$$

with continuum normalization

1) $$\langle \vec{p}\,' | \vec{p}\rangle = (2\pi\hbar)^3 \delta^3(\vec{p}\,' - \vec{p})$$

Then
$$\langle \vec{r}|\vec{P}|\vec{p}\rangle = -i\hbar \vec{\nabla}_{\vec{r}} \langle \vec{r}|\vec{p}\rangle$$

$$= \vec{p}\,\langle \vec{r}|\vec{p}\rangle$$

$$\Rightarrow \boxed{\langle \vec{r}|\vec{p}\rangle = N e^{+\frac{i}{\hbar}\vec{p}\cdot\vec{r}}}$$

Since $\{|\vec{r}\rangle\}$ is complete we have

$$\langle \vec{p}\,'|\vec{p}\rangle = (2\pi\hbar)^3 \delta^3(\vec{p}\,' - \vec{p})$$

$$= \int d^3r \, \langle \vec{p}\,'|\vec{r}\rangle\langle \vec{r}|\vec{p}\rangle$$

$$= \int d^3r \; e^{\frac{i}{\hbar}(\vec{p} - \vec{p}\,')\cdot\vec{r}} \, |N|^2$$

$$= |N|^2 (2\pi\hbar)^3 \delta^3(\vec{p}\,' - \vec{p}),$$

Thus we take $\boxed{N = 1.}$

Likewise the completeness relation for the momentum basis $\{|\vec{p}\rangle\}$ is

$$1 = \int \frac{d^3p}{(2\pi\hbar)^3} |\vec{p}\rangle\langle\vec{p}| .$$

Any state $|\psi\rangle$ has the expansion in terms of momentum eigenstates

$$|\psi\rangle = \int \frac{d^3p}{(2\pi\hbar)^3} \tilde{\psi}(\vec{p}) |\vec{p}\rangle$$

with $\tilde{\psi}(\vec{p}) = \langle\vec{p}|\psi\rangle$.

Thus

$$\psi(\vec{r}) = \int \frac{d^3p}{(2\pi\hbar)^3} e^{\frac{i\vec{p}\cdot\vec{r}}{\hbar}} \tilde{\psi}(\vec{p})$$

and

$$\tilde{\psi}(\vec{p}) = \int d^3r\, e^{-\frac{i\vec{p}\cdot\vec{r}}{\hbar}} \psi(\vec{r}) .$$

Finally for $H = \frac{1}{2m}\vec{P}^2 + V(\vec{R})$, the Schrödinger equation in the $\{|\vec{r}\rangle\}$-basis takes the form of the Schrödinger wave equation

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 + V(\vec{r})\right]\psi(\vec{r},t)$$

with $\psi(\vec{r},t) = \langle\vec{r}|\psi(t)\rangle$.

In addition to single particles moving in a potential, we also consider many particle systems with inter-particle as well as external potentials. In such cases the wave equation had the form

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; t) = H \psi(\vec{r}_1 \ldots \vec{r}_N; t)$$

$$= \sum_{i=1}^{N} \frac{-\hbar^2}{2m_i} \nabla_{r_i}^2 \psi(\vec{r}_1, \ldots, \vec{r}_N; t)$$

$$+ V(\vec{r}_1, \ldots, \vec{r}_N; t) \psi(\vec{r}_1, \ldots, \vec{r}_N; t) .$$

In the case of the two body central potential $V(\vec{r}_1, \vec{r}_2; t) = V(|\vec{r}_1 - \vec{r}_2|)$ this reduces to

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}_1, \vec{r}_2, t) = -\frac{\hbar^2}{2m_1} \nabla_{r_1}^2 \psi - \frac{\hbar^2}{2m_2} \nabla_{r_2}^2 \psi$$

$$+ V(|\vec{r}_1 - \vec{r}_2|) \psi$$

and we were able to separate the variables to CM & relative coordinates in order to have 2 - "single" particle problems.

<u>Ex.</u> Hydrogen atom: $V = \frac{-e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}$

Important to ~~these~~ central potential problems is the translational and rotational symmetries of the Hamiltonian.

In particular the rotational invariance of the central potential implied that the orbital angular momentum $\vec{L}$ commuted with H. Since

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$$

we found that $\{H, \vec{L}^2, L_z\}$ were a ~~set of~~ CSCO and we used the eigenfunctions of $\vec{L}^2$ & L_z, the $Y_\ell^m(\theta,\varphi)$ to expand our stationary states of the Hydrogen atom,

$$\psi_{n\ell m} = R_{n\ell}(r)\, Y_\ell^m(\theta,\varphi)$$

with

$$H\psi_{n\ell m} = E_n \psi_{n\ell m}$$

$$\vec{L}^2\psi_{n\ell m} = \ell(\ell+1)\hbar^2 \psi_{n\ell m}$$

$$L_z\psi_{n\ell m} = m\hbar\, \psi_{n\ell m}$$

&

$$E_n = -\left[\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2}\right]\frac{1}{n^2}$$

$n = 1, 2, 3, \ldots,\ \ell = 0, 1, \ldots, n-1;\ m = -\ell, \ldots, +\ell$

As we see symmetries of the Hamiltonian are important, since the symmetry implies an operator related to it will commute with the H, and hence will be part of a CSCO along with H. Hence, we will like to undertake a more systematic discussion of ~~sy~~ transformations, symmetries and conservation laws in Q.M.