POSTULATES OF QUANTUM MECHANICS: SCHRÖDINGER EQUATION AND PROPAGATORS

Link to: physicspages home page.

To leave a comment or report an error, please use the auxiliary blog.

References: Shankar, R. (1994), *Principles of Quantum Mechanics*, Plenum Press. Section 4.3.

The first three postulates of quantum mechanics concern the properties of a quantum state. The fourth postulate concerns how states evolve with time. The postulate simply states that in non-relativistic quantum mechanics, a state satisfies the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = H |\psi\rangle \tag{1}$$

where H is the Hamiltonian, which is obtained from the classical Hamiltonian by means of the other postulates of quantum mechanics, namely that we replace all references to the position x by the quantum position operator X with matrix elements (in the x basis) of

$$\langle x' | X | x \rangle = \delta \left(x - x' \right) \tag{2}$$

and all references to classical momentum p by the momentum operator P with matrix elements

$$\langle x' | P | x \rangle = -i\hbar \delta' \left(x - x' \right) \tag{3}$$

Although we've posted many articles based on Griffiths's book in which we solved the Schrödinger equation, the approach taken by Shankar is a bit different and, in some ways, a lot more elegant. We begin with a Hamiltonian that does not depend explicitly on time, and then by observing that, since the Schrödinger equation contains only the first derivative with respect to time, The time evolution of a state can be uniquely determined if we specify only the initial state $|\psi(0)\rangle$. [A differential equation that is second order in time, such as the wave equation, requires both the initial position and initial velocity to be specified.]

The solution of the Schrödinger equation is then found in analogy to the approach we used in solving the coupled masses problem earlier. We find the eigenvalues and eigenvectors of the Hamiltonian in some basis and use these to construct the propagator $U(t)$. We can then write the solution as

$$|\psi(t)\rangle = U(t) |\psi(0)\rangle \tag{4}$$

For the case of a time-independent Hamiltonian, we can actually construct $U(t)$ in terms of the eigenvectors of H. The eigenvalue equation is

$$H|E\rangle = E|E\rangle \tag{5}$$

where E is an eigenvalue of H and $|E\rangle$ is its corresponding eigenvector. Since the eigenvectors form a vector space, we can expand the wave function in terms of them in the usual way

$$\begin{align}
|\psi(t)\rangle &= \sum |E\rangle \langle E|\psi(t)\rangle \tag{6}\\
&\equiv \sum a_E(t)|E\rangle \tag{7}
\end{align}$$

The coefficient $a_E(t)$ is the component of $|\psi(t)\rangle$ along the $|E\rangle$ vector as a function of time. We can now apply the Schrödinger equation 1 to get (a dot over a symbol indicates a time derivative):

$$\begin{align}
i\hbar \frac{\partial}{\partial t}|\psi(t)\rangle &= i\hbar \sum \dot{a}_E(t)|E\rangle \tag{8}\\
&= H|\psi(t)\rangle \tag{9}\\
&= \sum a_E(t)H|E\rangle \tag{10}\\
&= \sum a_E(t)E|E\rangle \tag{11}
\end{align}$$

Since the eigenvectors $|E\rangle$ are linearly independent (as they form a basis for the vector space), each term in the sum in the first line must be equal to the corresponding term in the sum in the last line, so we have

$$i\hbar \dot{a}_E(t) = a_E(t)E \tag{12}$$

The solution is

$$\begin{align}
a_E(t) &= a_E(0)e^{-iEt/\hbar} \tag{13}\\
&= e^{-iEt/\hbar}\langle E|\psi(0)\rangle \tag{14}
\end{align}$$

The general solution 7 is therefore

$$|\psi(t)\rangle = \sum e^{-iEt/\hbar}|E\rangle \langle E|\psi(0)\rangle \tag{15}$$

from which we can read off the propagator:

$$U(t) = \sum e^{-iEt/\hbar}|E\rangle \langle E| \tag{16}$$

Thus if we can determine the eigenvalues and eigenvectors of H, we can write the propagator in terms of them and get the general solution. We can see from this that $U(t)$ is unitary:

$$U^\dagger U = \sum_{E'}\sum_{E} e^{-i(E-E')t/\hbar} |E\rangle \langle E|E'\rangle \langle E'| \tag{17}$$

$$= \sum_{E'}\sum_{E} e^{-i(E-E')t/\hbar} |E\rangle \delta_{EE'} \langle E'| \tag{18}$$

$$= \sum_{E} |E\rangle \langle E| \tag{19}$$

$$= 1 \tag{20}$$

This derivation uses the fact that the eigenvectors are orthonormal and form a complete set, so that $\langle E|E'\rangle = \delta_{EE'}$ and $\sum_{E}|E\rangle\langle E| = 1$. Since a unitary operator doesn't change the norm of a vector, we see from 4 that if $|\psi(0)\rangle$ is normalized, then so is $|\psi(t)\rangle$ for all times t. Further, the probability that the state will be measured to be in eigenstate $|E\rangle$ is constant over time, since this probability is given by

$$|a_E(t)|^2 = \left| e^{-iEt/\hbar} \langle E|\psi(0)\rangle \right|^2 = |\langle E|\psi(0)\rangle|^2 \tag{21}$$

This derivation assumed that the spectrum of H was discrete and non-degenerate. If the possible eigenvalues E are continuous, then the sum is replaced by an integral

$$U(t) = \int e^{-iEt/\hbar} |E\rangle \langle E| \, dE \tag{22}$$

If the spectrum is discrete and degenerate, then we need to find an orthonormal set of eigenvectors that spans each degenerate subspace, and sum over these sets. For example, if E_1 is degenerate, then we find a set of eigenvectors $|E_1, \alpha\rangle$ that spans the subspace for which E_1 is the eigenvalue. The index α runs from 1 up to the degree of degeneracy of E_1, and the propagator is then

$$U(t) = \sum_{\alpha}\sum_{E_i} e^{-iE_i t/\hbar} |E_i, \alpha\rangle \langle E_i, \alpha| \tag{23}$$

The sum over E_i runs over all the distinct eigenvalues, and the sum over α runs over the eigenvectors for each different E_i.

Another form of the propagator can be written directly in terms of the time-independent Hamiltonian as

$$U(t) = e^{-iHt/\hbar} \tag{24}$$

This relies on the concept of the function of an operator, so that $e^{-iHt/\hbar}$ is a matrix whose elements are power series of the exponent $-\frac{iHt}{\hbar}$. The power series must, of course, converge for this solution to be valid. Since

H is Hermitian, $U(t)$ is unitary. We can verify that the solution using this form of $U(t)$ satisfies the Schrödinger equation:

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle \tag{25}$$

$$= e^{-iHt/\hbar}|\psi(0)\rangle \tag{26}$$

$$i\hbar|\dot{\psi}(t)\rangle = i\hbar\frac{d}{dt}\left(e^{-iHt/\hbar}\right)|\psi(0)\rangle \tag{27}$$

$$= i\hbar\left(-\frac{i}{\hbar}\right)He^{-iHt/\hbar}|\psi(0)\rangle \tag{28}$$

$$= He^{-iHt/\hbar}|\psi(0)\rangle \tag{29}$$

$$= H|\psi(t)\rangle \tag{30}$$

The derivative of $U(t)$ can be calculated from the derivatives of its matrix elements, which are all power series.

PINGBACKS

Pingback: Time-dependent propagators
Pingback: Free particle revisited: solution in terms of a propagator
Pingback: Propagator for a Gaussian wave packet for the free particle
Pingback: Path integral formulation of quantum mechanics: free particle propagator
Pingback: Harmonic oscillator energies and eigenfunctions derived from the propagator
Pingback: Invariance of symmetric and antisymmetric states; exchange operators
Pingback: Translational invariance and conservation of momentum
Pingback: Time translation and conservation of energy
Pingback: Time reversal, antiunitary operators and Wigner's theorem
Pingback: Spinor in oscillating magnetic field - part 2