Homework H9 Solution

1. **(Turn in)** Use postulate (4) of quantum mechanics to prove very explicitly that the energy of a quantum particle with wavefunction $\Psi_n(x)e^{-\frac{iE_nt}{\hbar}}$ is simply $E_n$ with 100% probability.

Remember what postulate (4) says in GENERAL: if an observable A is measured, its value can’t be just anything. It MUST BE one of the solutions of the equation $\hat{A}\varphi_n(x) = a_n\varphi_n(x)$. In this equation, $A_n$ is called an “eigenvalue” of the operator $\hat{A}$ for the observable $A$, and $\varphi_n(x)$ is called an “eigenfunction.” The probability of measuring that “nth” eigenvalue as the actual value of $A$ is $P(A=a_n) = |\int dx \ \varphi^*_n(x)\psi(x, t)|^2$.

a. For the SPECIFIC case where $A$ is the energy, write down the operator for $A$, the eigenvalue equation, and the probability $P(E=E_n)$; call the eigenvalues $E_n$ and the eigenfunctions $\Psi_n(x)$ in this specific case.

b. Now assume that the wavefunction $\psi(x, t)$ in your probability is not just any function, but the stationary state $\psi(x, t) = \Psi_n(x)e^{-iE_nt/\hbar}$, and write down the probability formula.

c. Now remember that $e^{-iE_nt/\hbar}$ does not depend on $x$ and can be pulled out of the integral, and that $e^a e^{+a} = 1$, and simplify the formula. Also remember that $\int dx |\Psi(x)|^2 = \int dx P(x) = 1$ to finally prove that $P(E=E_n)=1$.

When the quantum particle has wavefunction $\Psi_n(x)e^{-\frac{iE_nt}{\hbar}}$, it is 100% guaranteed to have energy $E_n$!

**Solution:**

**a.** When the observable is energy (E), the corresponding quantum mechanical operator is the Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$.

When an operator acting on a certain function, returns the same function multiplied by a constant, we call the function to be the “eigenfunction” of the operator, and the constant to be the “eigenvalue”. Thus the equation that all eigenvalues of $\hat{H}$ must satisfy is,

$$\hat{H}\Psi_n(x) = E_n\Psi_n(x).$$

Postulate (4) says that individual measurement of the energy of a quantum particle can only yield one of the eigenvalues $E_n$, no other value!

By postulate 4, $P(E=E_n) = |\int dx \ \Psi^*_n(x)\psi(x, t)|^2$

**b.** Now, the particle has the wavefunction $\psi(x, t) = \Psi_n(x)e^{-iE_nt/\hbar}$.
Therefore \( P(E = E_n) = \left| \int dx \, \Psi_n^*(x) \Psi_n(x) e^{-\frac{i}{\hbar}E_n t} \right|^2 \) according to postulate (4).

c. We can simplify this special case by realizing that \( e^{-\frac{i}{\hbar}E_n t} \) is independent of \( x \), so we can pull it out of the integral. Also \( |a|^2 \) is just \( a^*a \), so \( |e^{-\frac{i}{\hbar}E_n t} e^{\frac{i}{\hbar}E_n t}|^2 \) is just \( e^{-\frac{i}{\hbar}E_n t} e^{\frac{i}{\hbar}E_n t} \).

Therefore

\[
P(E = E_n) = \left| \int dx \, \Psi_n^*(x) \Psi_n(x) e^{-\frac{i}{\hbar}E_n t} \right|^2
= e^{-\frac{i}{\hbar}E_n t} e^{\frac{i}{\hbar}E_n t} | \int dx \, \Psi_n^*(x) \Psi_n(x) |^2
= 1
\]

The third line is obtained because \( e^{-a}e^a = 1 \) for any number, and because \( \Psi_n^*(x) \) is normalized. Thus, the stationary state is guaranteed (100% probable) to have energy \( E_n \).

**Whenever a quantum particle is in a state \( \Psi_n \) that solves the stationary Schrödinger equation \( \hat{H}\Psi_n=E_n\Psi_n \), its energy is \( E_n \).**

2. a. Calculate the normalization integral of the Gaussian wavefunction \( \Psi_0(x) = \exp(-ax^2) \) from \( x = -\infty \) to \( \infty \). This integral is not equal to 1. Note \( \Psi^*\Psi = \exp(-2ax^2) \)

b. To normalize the Gaussian, it needs to be divided by the square root of the integral you got in a. Why the square root?

c. Write down the normalized Gaussian wavefunction.

d. Insert the function from c. into the time-independent Schrödinger equation \( \hat{H}\Psi(x) = E_0 \Psi(x) \) for the vibrating molecule with mass \( m=1 \) and force constant \( k=1 \) we discussed in class and show that \( \Psi_0(x) \) is only a solution if \( a=1/(2\hbar) \) and \( E_0 = \hbar/2 \).

**Solution:**

a. This integral is generally solved by relating to polar co-ordinates, where \( r \) is the polar vector, and \( \theta \) is the angle its projection on the x-y plane makes with the x axis.

So, \( r^2 = x^2 + y^2 \).

Now, \( \iint_{-\infty}^{\infty} dx \, dy \, e^{-2a(x^2+y^2)} = \left[ \int_{-\infty}^{\infty} dx \, e^{-2ax^2} \right]^2 = \int_0^{2\pi} d\theta \int_0^{\infty} e^{-2ar^2} \, r \, dr \)

\[
= 2\pi \int_0^{\infty} dr \, r \, e^{-2ar^2}
= 2\pi \left( \frac{-1}{4a} \right) e^{-2ar^2} \bigg|_0^{\infty}
= -\frac{\pi}{2a} [0 - 1] = \frac{\pi}{2a}
\]

\[
\therefore \int_{-\infty}^{\infty} dx \, e^{-2ax^2} = \left( \frac{\pi}{2a} \right)^{1/2}
\]
b. To normalize it, it should be divided by \( \left( \frac{\pi}{2a} \right)^{1/4} \). This is done so as to ensure that the total probability of finding the particle over all space is 1, i.e., \( |\Psi_0(x)|^2 = 1 \).

c. Thus the normalized Gaussian function is \( \Psi_0(x) = \left( \frac{2a}{\pi} \right)^{1/4} e^{-ax^2} \).

d. For a vibrating molecule (considering it to be a harmonic oscillator), the Hamiltonian can be written as \( \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2 = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial x^2} + \frac{1}{2} x^2 \) since \( k=m=1 \).

Plugging into the time-independent Schrödinger equation,

\[
\left[-\frac{\hbar^2}{2} \frac{\partial^2}{\partial x^2} + \frac{1}{2} x^2 \right]^{1/4} e^{-ax^2} = \left[\frac{2a}{\pi} \right]^{1/4} \left[ \hbar^2 a \left(-2a^2 e^{-ax^2} + e^{-ax^2} \right) + \frac{1}{2} x^2 e^{-ax^2} \right]
\]

For this to be an eigenvalue equation, that is, so that, the Hamiltonian operator remains the wavefunction unchanged,

\[
\frac{1}{2} - 2a^2 \hbar^2 = 0
\]

or, \( a^2 = \frac{1}{4\hbar^2} \). therefore \( a = \frac{1}{2\hbar} \)

Plugging the value of \( a \) in the Schrödinger equation,

\[
\hat{H} \left[ \frac{1}{\pi \hbar} \right]^{1/4} e^{-\frac{x^2}{2\hbar}} = \frac{\hbar}{2} \left[ \frac{1}{\pi \hbar} \right]^{1/4} e^{-\frac{x^2}{2\hbar}}.
\]

Thus, comparing with \( \hat{H}\Psi_0(x) = E_0\Psi_0(x) \), we get \( E_0 = \frac{\hbar}{2} \).

NOTE: if we had set \( m \neq 1 \) and \( k \neq 1 \) in our Schrödinger equation, and plugged in \( e^{-ax^2} \), we would have gotten that \( E_0 = \hbar \omega/2 \), where \( \omega = \sqrt{k/m} \) is the vibrational frequency of the spring.