Physics 143a – Workshop 5

On Quantum Mechanics in One Dimension

Week Summary

- **Canonical Commutation Relation:** For $\hat{X}$ representing the position operator and $\hat{P}$ representing the momentum operator, we have the *canonical commutation relation*

$$[\hat{X}, \hat{P}] = i\hbar. \tag{1}$$

Eq.(1), together with the generalized uncertainty principle, yields what is known as the *Heisenberg uncertainty principle*:[1]

$$\Delta_\phi \hat{X} \Delta_\phi \hat{P} \geq \frac{\hbar}{2}. \tag{2}$$

- **Time-Independent Schrödinger Equation (position space, in one-dimension):** The eigenspectrum problem for a Hamiltonian $\hat{H}$ is

$$\hat{H}|E_j\rangle = E_j|E_j\rangle, \tag{3}$$

where E_j is the energy eigenvalue associated with the energy eigenket $|E_j\rangle$. When we consider Eq.(3) for a particle of mass m moving in one-dimension along the real axis, we obtain

$$-\frac{\hbar^2}{2m}\frac{d^2\phi_j(x)}{dx^2} + V(x)\phi_j(x) = E_j\phi_j(x), \tag{4}$$

where $\phi_j(x) = \langle x|E_j\rangle$ is the energy-eigenket *wave function* (i.e., the energy eigenket in the position basis) and $V(x)$ is the potential energy of the particle. After solving Eq.(4) for $\phi_j(x)$, we find that the general solution to the time-dependent Schrödinger equation is

$$\Psi(x,t) = \sum_j c_j e^{-iE_jt/\hbar}\phi_j(x). \tag{5}$$

The coefficients c_j are determined from the initial condition $\Psi(x,0)$ and the completeness of $\phi_j(x)$:

$$c_\ell = \int dx\, \Psi(x,0)\phi_\ell(x). \tag{6}$$

- **Free Particle Quantum Mechanics:** For a free particle there is a continuous spectrum of energy eigenkets (given by $\phi_k(x) = e^{ikx}$) and energy eigenvalues (given by $E_k = \hbar^2k^2/2m$) labeled by k, the wave number of the wave function. Thus, the discrete sum in Eq.(5) is replaced with the continuous integral

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\, c(k)\, e^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}. \tag{7}$$

The coefficient[2] $c(k)$ is related to the initial wave function $\Psi(x,0)$ through a Fourier Transform:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\, c(k)\, e^{ikx} \quad\longleftrightarrow\quad c(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dx\, \Psi(x,0)\, e^{-ikx}. \tag{8}$$

[1] We note$(\Delta_\phi\hat{A})^2 = \langle\phi|\hat{A}^2|\phi\rangle - \langle\phi|\hat{A}|\phi\rangle^2$ and $|\phi\rangle$ is an arbitrary state.

[2] The factor of $1/\sqrt{2\pi}$ is a standard normalization which leads to symmetrical Fourier Transforms.

1 Problems

1. **Fun with Gaussians**
In the following problems, take the following integral as given:

$$\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}. \tag{9}$$

   (a) Derive

$$\int_{-\infty}^{\infty} dx\, e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}} e^{b^2/4a}. \tag{10}$$

   You can take a and b to be real, but this result is also valid for imaginary a and b.

   (b) Differentiate (twice) both sides of Eq.(10) with respect to b and then set $b = 0$ to find $\int_{-\infty}^{\infty} dx\, x^2 e^{-ax^2} \sqrt{a/\pi}$. Check this result by differentiating both sides of Eq.(10) with respect to a and setting $b = 0$.

   (c) The teacher writes down the wave function

$$\Psi(x,t) = \frac{1}{(\pi\alpha(t))^{1/4}} \left(\frac{\text{Re}\,\alpha(t)}{\alpha(t)}\right)^{1/4} e^{-x^2/2\alpha(t)}, \tag{11}$$

   with $\alpha(t)$ a complex number with a monotonically increasing imaginary part and decreasing real part. Billy does a quick calculation and concludes that this wave function does not conserve probability. Here is his calculation:

$$\begin{aligned} |\Psi(x,t)|^2 &= \frac{1}{(\pi\alpha(t))^{1/4}} \left(\frac{\text{Re}\,\alpha(t)}{\alpha(t)}\right)^{1/4} e^{-x^2/2\alpha(t)} \frac{1}{(\pi\alpha^*(t))^{1/4}} \left(\frac{\text{Re}\,\alpha(t)}{\alpha^*(t)}\right)^{1/4} e^{-x^2/2\alpha^*(t)} \\ &= \frac{1}{(\pi|\alpha(t)|)^{1/2}} \left(\frac{\text{Re}\,\alpha(t)}{|\alpha(t)|}\right)^{1/2} e^{-x^2/|\alpha(t)|^2} \\ \int_{-\infty}^{\infty} dx\, |\Psi(x,t)|^2 &= \frac{1}{(\pi|\alpha(t)|)^{1/2}} \left(\frac{\text{Re}\,\alpha(t)}{|\alpha(t)|}\right)^{1/2} \int_{-\infty}^{\infty} dx\, e^{-x^2/|\alpha(t)|^2} \\ &= \frac{1}{(\pi|\alpha(t)|)^{1/2}} \left(\frac{\text{Re}\,\alpha(t)}{|\alpha(t)|}\right)^{1/2} (\pi|\alpha(t)|)^{1/2} = \left(\frac{\text{Re}\,\alpha(t)}{|\alpha(t)|}\right)^{1/2}. \end{aligned} \tag{12}$$

   Billy's argument is that since $\int_{-\infty}^{\infty} dx\, |\Psi(x,t)|^2$ is time dependent, the total probability to be anywhere in the system changes with time. Is Billy right?

2. **Constructing Hamiltonians**
   A benzene molecule is composed of six carbons arranged in a hexagonal ring:

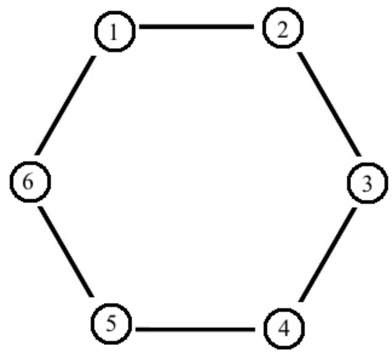

Figure 1: Schematic of benzene molecule with carbon atoms labeled

Suppose we have a single electron which can be localized at any one of the six carbon atom positions. The carbon atoms are identical, so the electron has the same interaction energy across all the carbon atoms. There is also a constant non-zero transition probability for the electron to move to any other adjacent carbon atom.

   (a) In the basis of $\{|\phi_j\rangle\}$ where $|\phi_j\rangle$ denotes the state of an electron localized at carbon atom j, write the Hamiltonian of this system? (Make sure to define any parameters you introduce)

   (b) Do the eigenstates of this Hamiltonian have the electron localized at single carbon atoms?

3. **Free Particle Wave Function**
   A free particle has the initial wave function

$$\Psi(x, 0) = A\delta(x - x_0), \tag{13}$$

where A and x_0 are positive real constants with dimensions of $1/\sqrt{\text{length}}$ and length respectively.

Write down five (sufficiently different) questions we can ask about this system. Answer three of these questions, and outline how you would answer the remaining two.

2 Solutions

1. (a) In order to derive the provided identity we make the change of variables $u = (x - b/2a)^2$. We then find $au^2 = ax^2 - bx + b^2/4a$, and the integral becomes

$$\int_{-\infty}^{\infty} dx\, e^{-ax^2+bx} = \int_{-\infty}^{\infty} du\, e^{-au^2+b^2/4a} = \sqrt{\frac{\pi}{a}} e^{b^2/4a}. \tag{14}$$

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(b) Differentiating the LHS and RHS of Eq.(14) with respect to b twice, we find

$$\int_{-\infty}^{\infty} dx\, x^2\, e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}} e^{b^2/4a} \left(\frac{b^2}{4a^2} + \frac{1}{2a} \right). \tag{15}$$

Alternatively differentiating the LHS and RHS of Eq.(14) with respect to a, we have

$$-\int_{-\infty}^{\infty} dx\, x^2\, e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}} e^{b^2/4a} \left(-\frac{b^2}{4a^2} - \frac{1}{2a} \right). \tag{16}$$

Setting $b = 0$ on both sides of Eq.(15) and on both sides of Eq.(16) yields

$$\int_{-\infty}^{\infty} dx\, x^2\, e^{-ax^2} = \frac{1}{2a}\sqrt{\frac{\pi}{a}}. \tag{17}$$

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(c) If $\int_{-\infty}^{\infty} dx\, |\Psi(x,t)|^2$ were time dependent, we would indeed find that this system does not conserve probability. However, Billy's calculation is incorrect. One error is incorrectly evaluating the integral in going from the third line of Eq.(12) to the fourth line (It should be $\sqrt{\pi|\alpha(t)|^2}$), but there is another error which supersedes this one. In going from the first to the second line, Billy incorrectly wrote

$$\frac{1}{2\alpha(t)} + \frac{1}{2\alpha^*(t)} = \frac{1}{|\alpha(t)|^2}. \qquad \text{[Incorrect Equation]} \tag{18}$$

If he had performed the calculation correctly, he would have found that the $\Psi(x,t)$ was properly normalized.

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2. (a) If we were to define E_0 as the interaction energy between an electron and a single carbon atom at a vertex on the hexagon ring, and define a as proportional to the transition probability to move from one carbon atom to an adjacent carbon atom, then we would have the Hamiltonian matrix element

$$\langle \phi_j | \hat{H} | \phi_k \rangle = \begin{cases} E_0 & \text{if } j = k \\ -a & \text{if } j = k-1 \text{ or } j = k+1 \end{cases} \tag{19}$$

or, with a single line,

$$\langle \phi_j | \hat{H} | \phi_k \rangle = E_0 \delta_{jk} - a(\delta_{j,k+1} + \delta_{j,k-1}), \tag{20}$$

where $j = 1, 2, \cdots, 6$ and $j = 7 \to 1$ and $j = 0 \to 6$, and k is similarly defined. Writing these results as a matrix yields

$$\hat{H} = \begin{pmatrix} E_0 & -a & 0 & 0 & 0 & -a \\ -a & E_0 & -a & 0 & 0 & 0 \\ 0 & -a & E_0 & -a & 0 & 0 \\ 0 & 0 & -a & E_0 & -a & 0 \\ 0 & 0 & 0 & -a & E_0 & -a \\ -a & 0 & 0 & 0 & -a & E_0 \end{pmatrix}. \tag{21}$$

We chose $-a$ by convention, but given the constraints of the problem, these off diagonal elements could be a modulo a phase such that $\hat{H}$ is still Hermitian.

(b) We know the states which define the electron as being localized at a single carbon atom are defined by $|\phi_j\rangle$. But since the Hamiltonian $\hat{H}$ is not diagonal in this basis, we know that the eigenstates of $\hat{H}$ are not $|\phi_j\rangle$. Thus, the eigenstates of $\hat{H}$ must be linear combinations of various $|\phi_j\rangle$ which implies the electron is not localized at a single carbon atom.

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3. The purpose of this question is to get you to practice asking questions about physical systems. In most problems in this class you're given a physical system and are tasked with answering questions about said system, but the purpose of this question is to get you to practice *asking* questions about physical systems. Whenever you study a physical system using quantum mechanics, or anything else you've learned, it will be your ability to clearly formulate many possible questions—as much if not more than your ability to answer them—which will determine how much information you can obtain from the system.

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We can ask a number of questions about the system defined by the given wave function.

(i) Is this system consistent with quantum mechanics?
(ii) What is A such that the state is normalized?
(iii) What is the wave function $\Psi(x,t)$?
(iv) What are $\langle x\rangle$ and $\langle p\rangle$ for this state?
(v) What is the expression of this state in the momentum basis?

(i) This is arguably the most important question, and the answer is yes, but we must be careful. Although the given $\Psi(x,0)$ is fun to play around with, it is not the most physical state given that it precisely specifies the position of the particle and consequently has an infinite uncertainty in momentum. It would appear that the fact that $\Psi(x,0)$ precisely specifies the position would lead to a violation of the Heisenberg uncertainty principle, but in fact if we were to take appropriate limiting expressions (by taking $\Psi(x,0) = \lim_{a\to 0} Ae^{-x^2/2a^2}/\sqrt{2\pi a^2}$) then we would find that although the momentum uncertainty of $\Psi(x,0)$ diverges the product of the momentum and position uncertainty is finite.

(ii) To normalize the state we use the fact that $\delta(x)\cdot\delta(x) = \delta(x)$ to find

$$\int_{-\infty}^{\infty} dx\,|\Psi(x,t)|^2 = |A|^2 \int_{-\infty}^{\infty} dx\,\delta(x-x_0) = |A|^2 = 1. \tag{22}$$

Therefore in order for the state to be normalized A must be a complex phase, i.e., $A = e^{i\phi}$.

(iii) We can compute the wave function at later times t, by Eq.(8) and Eq.(7). Computing $c(k)$ first we find

$$c(k) = \frac{A}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\,\delta(x-x_0)\,e^{-ikx} = \frac{A}{\sqrt{2\pi}} e^{-ikx_0}. \tag{23}$$

And then computing the time-dependent wave function we have

$$\Psi(x,t) = \frac{A}{2\pi}\int_{-\infty}^{\infty} dk\ e^{ik(x-x_0)}e^{-i\hbar k^2 t/2m} = A\sqrt{\frac{m}{2\pi i\hbar t}}\exp\left[\frac{m}{2i\hbar t}(x-x_0)^2\right]. \tag{24}$$

We note that Eq.(24) would not be normalized, for any A, if we take the x domain of the particle to be the entire real axis. This is reflection of the fact that this

(iv) The average of x is simply x_0 by the definition of the Dirac delta function. We note this average is only defined for $t=0$. The average of p is 0 as we can see from the following calculation:

$$\langle p\rangle = |A|^2\int_{-\infty}^{\infty} dx\,\delta(x-x_0)\frac{\hbar}{i}\frac{d}{dx}\delta(x-x_0) = -|A|^2\int_{-\infty}^{\infty} dx\,\frac{\hbar}{i}\frac{d}{dx}\big[\delta(x-x_0)\big]\delta(x-x_0). \tag{25}$$

Since a quantity is found to be equal to its negative the quantity itself must be zero.

(v) In (iii), we already partly answered this question. In the momentum basis the particle wave function, at $t=0$, is

$$\Phi(p,0) = \int_{-\infty}^{\infty}\frac{dx}{\sqrt{2\pi\hbar}}\,e^{-ipx_0/\hbar}\Psi(x,0) = \frac{1}{\sqrt{2\pi\hbar}}e^{-ipx_0}. \tag{26}$$

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