Lecture 4

Question 1. Consider the Gaussian probability distribution, the probability density is given by

$$\rho(x) = Ae^{-\lambda(x-a)^2}$$

where A, a, and λ are positive real-valued constants.
(1) The total probability should be equal to 1. What is the value of A?
(2) Find the expectation values of x, x^2, and the standard deviation.
(3) Sketch the graph of $\rho(x)$.
Useful integrals:

$$\int_{-\infty}^{+\infty} e^{-\lambda x^2} dx = \sqrt{\frac{\pi}{\lambda}}$$

$$\int_{-\infty}^{+\infty} x^2 e^{-\lambda x^2} dx = \frac{1}{2\lambda}\sqrt{\frac{\pi}{\lambda}}$$

Question 2.[1] The wavefunction of a particle circling around a center (i.e., a particle on a ring with a fixed radius) is

$$\psi(\phi) = Ae^{im\phi}$$

where ϕ is an angle that characterizes the position of the particle on the ring, and m is a real number.
(1) Determine the normalization constant A. Note that ϕ ranges from 0 to 2π for this particle traveling a whole circle.
(2) What is the boundary condition? Based on the boundary condition on a ring, determine the possible values of m. Is m quantized?
(3) What is the probability of finding the particle between $\phi = \pi/2$ to $\phi = 3\pi/2$?
(4) Where is the particle "on average"? (Determine the expectation value of ϕ.)

Question 3.[2] The ground-state wavefunction of the electron in a hydrogen atom is

$$\psi(r) = Ae^{-r/a_0}$$

where a_0 is a constant – the first Bohr radius (a_0 = 53 pm).
(1) Determine the normalization constant A (a real number). Note that this is a 3D problem, and based on the spherical symmetry of an atom, the volume element is

$$d\tau = r^2 \sin\theta dr d\theta d\phi$$

where $r \geq 0$, $0 \leq \theta \leq \pi$, and $0 \leq \phi \leq 2\pi$ are the three spherical coordinates. Please review spherical coordinates and how to perform integration in spherical coordinates by reading McQuarrie, Chapter 8, section 8.4.
Useful integral:

$$\int_{0}^{+\infty} x^n e^{-x/a} dx = n!\, a^{n+1}$$

(2) Based on the normalized wavefunction, calculate the probability that the electron will be found somewhere within a small sphere of radius 1.0 pm centered on the nucleus.

[1] Adapted from Atkins, 9th ed., Chapter 7 – Exercises & Problems.
[2] Adapted from Atkins, 9th ed., Chapter 7 – Examples & Problems.

Hint: It is safe to treat the wavefunction as a constant within this very thin sphere (1.0 pm << a_0!).
(3) Now suppose that the same sphere is located at $r = a_0$. What is the probability that the electron is inside it?
(4) What is the expectation value of r? This is the "averaged" orbital radius in the ground state.

Lecture 5

Question 4. (1) Start from the time-dependent Schrödinger equation in 1D, prove that the following integral is time-independent:

$$\frac{\partial}{\partial t}\int_{-\infty}^{+\infty} \Psi_1^*(x,t)\Psi_2(x,t)dx = 0$$

where Ψ_1 and Ψ_2 are two well-behaved solutions (not necessarily stationary eigenstates) to the time-dependent Schrödinger equation.
Hint: Do integration by parts. At $x = \pm\infty$, a well-behaved wavefunction goes to zero because it is square-integrable (normalizable).
(2) Consequently, please show that once your time-dependent wavefunction $\Psi(x,t)$ is normalized, it stays as normalized.
Note: Physically, the above mathematical result tells us that the number of particles (e.g., electrons) in the system is always conserved – the total probability of finding the particles does not evolve with respect to time. It also implies that the time-dependent Schrödinger equation cannot be used to describe the annihilation or creation of particles (e.g., generation of new photons).

Question 5. Let us consider a free particle in 1D space with the following wavefunction

$$\psi(\vec{x}) = e^{-i\vec{k}\vec{x}}$$

where $\vec{k}$ is the 1D wavevector pointing towards to the positive direction of the x-axis.
(1) Please show that if the time-dependence is given by

$$h(t) = e^{iEt/\hbar}$$

then the time evolution of the wave $\Psi(x,t) = \psi(\vec{x})h(t)$ is unphysical.
(2) Please show that if the time-dependence is given by

$$g(t) = e^{-iEt/\hbar}$$

then the time evolution of the wave $\Psi(x,t) = \psi(\vec{x})g(t)$ makes sense.

Question 6. Stationary states are the states of which the <u>probability density</u> distribution $\Psi^*(x,t)\Psi(x,t)$ does not evolve with respect to time. The observables computed from a stationary state are time-independent.
(1) Please prove that any wavefunction in the following form is stationary

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

in which $\psi(x)$ is an eigenstate with energy E as given by the time-independent Schrödinger equation.
(2) Suppose a particle starts out in a linear combination of just two stationary states

$$\Psi(x,t=0) = c_1\psi_1(x) + c_2\psi_2(x)$$

To keep things simple, let us consider the constants c_n and the eigenstates $\psi_n(x)$ are all real. The energy of the eigenstate $\psi_n(x)$ is E_n. What is the wavefunction $\Psi(x,t)$ at subsequent times? Find the probability density and describe its motion. Is $\Psi(x,t)$ a stationary state in general?

(3) For a superposition state $\Psi(x,t)$ in general $(-\infty < x < +\infty)$, the time-independent part of which is not necessarily an eigenfunction of the Hamiltonian, please prove that

$$\frac{d\langle p_x\rangle}{dt} = \langle -\frac{\partial V}{\partial x}\rangle$$

Note: This relation tells us that, in quantum mechanics, the change of the expectation value of the momentum $\langle p_x\rangle$ with respect to time is the expectation value of the negative gradient of the potential *V*. In classical mechanics, dp_x/dt is the force F_x on a particle (Newton's 2nd law), which is equal to the negative gradient of the potential as well! Expectation values obey classical laws! This shows a natural connection between classical mechanics and quantum mechanics.

(4) Prove the following statement: The time-independent wavefunction $\psi(x)$ that obeys the time-independent Schrödinger equation can always be taken to be a real function (unlike $\Psi(x,t)$, which is necessarily a complex function).

Note: This does NOT mean that every solution to the time-independent Schrödinger equation is real; what it says is that if you've got one that is not, it can always be expressed as a linear combination of solutions (with the same energy) that are. So, you might as well stick to the time-independent wavefunctions that are real. (Chemists love real functions! Easy to plot and visualize!)

Hint: If $\psi(x)$ has an energy E from the time-independent Schrödinger equation, how about its complex conjugate $\psi^*(x)$? How about the combinations $\psi(x)+\psi^*(x)$ and $i[\psi(x)-\psi^*(x)]$? Are these combinations real-valued functions?

Lecture 6

Question 7. Eigenfunctions and eigenvalues.[3]

(1) Identify which of the following functions are eigenfunctions of the operator $\hat{D} = \partial/\partial x$. Give the corresponding eigenvalue where appropriate.

(a) e^{ikx} (b) $\cos(kx)$ (c) k (d) kx (e) e^{-ax^2}

(2) Which of the functions in **(1)** are also eigenfunctions of $\hat{D}^2 = \partial^2/\partial x^2$? Give the corresponding eigenvalue where appropriate.

(3) Which of the functions in **(1)** are only eigenfunctions of $\hat{D}^2 = \partial^2/\partial x^2$, but not of $\hat{D}$? Give the corresponding eigenvalue where appropriate.

(4) Determine which of the following functions are eigenfunctions of the inversion operator $\hat{C}$? State the eigenvalue of $\hat{C}$ when relevant.

(a) $x^3 - kx$ (b) $\cos(kx)$ (c) $x^2 + kx - 1$

Note: An inversion operator has the effect of making the replacement $x \to -x$, i.e., performing an inversion operation.

(5) Construct the quantum mechanical operators for the following observables from the momentum operator and position operator:

(a) kinetic energy in 1D and in 3D
(b) the inverse separation $1/x$ in 1D and $1/r$ in 3D (where r is the norm of the position vector $\vec{r}$)
(c) electric dipole moment in 1D and in 3D for a set of charges $\{q_i\}$
(d) the standard deviations of the position Δx and momentum Δp_x of a particle in 1D from the mean values

(6) Prove that the standard deviation ΔE (i.e., the uncertainty of the physical observable *E*) of the normalized eigenfunctions of the Hamiltonian operator $\hat{H}$ must be zero.

[3] Adapted from Atkins, 9th ed., Chapter 7 – Problems.

Question 8. Commutators and uncertainty principle.

(1) In the derivation of the uncertainty principle, we have $\langle \Delta F \rangle^2 \langle \Delta G \rangle^2 \geq \left(\frac{i}{2} \langle [\hat{F}, \hat{G}] \rangle \right)^2$.

Please use Dirac notation to prove that the term $\frac{i}{2} \langle [\hat{F}, \hat{G}] \rangle$ is always a real number.

Hint: Show that the commutator $\hat{A} = [\hat{F}, \hat{G}]$ itself is an anti-Hermitian operator (i.e., $\hat{A}^\dagger = -\hat{A}$), and its expectation value is purely imaginary.

(2) From the time-dependent Schrödinger equation, prove the following result

$$\frac{d\langle \hat{Q} \rangle}{dt} = -\frac{i}{\hbar} \langle [\hat{Q}, \hat{H}] \rangle$$

Q is any physical observable, the corresponding operator $\hat{Q}$ of which does not explicitly depend on time (that is $\partial \hat{Q} / \partial t = 0$; Please distinguish total derivative *d*/*dt* from partial derivative). $\hat{H}$ is the Hamiltonian operator.

Note: This very interesting result indicates the equation of motion of the expectation value of an observable. In particular, if the corresponding operator commutes with the Hamiltonian, you immediately know that the expectation value does not evolve with respect to time without solving the equation. Importantly, this has nothing to do with whether one has a stationary state at hand. One immediate consequence, for instance, is that the energy is conserved since $[\hat{H}, \hat{H}] = 0$.

Hint: Use Dirac notation. Write the time-dependent Schrödinger equation in the ket notation, and its complex-conjugate form in the bra notation. Recall that the complex conjugate of a ket is a bra. Apply the chain rule to do the time derivative of $\langle \hat{Q} \rangle$ in the bra-ket form.

(3) Define $\Delta E = \Delta H$ and $\Delta t = \frac{\Delta Q}{|d\langle Q \rangle / dt|}$ (in which Q is any physical observable, and its corresponding operator does not explicitly depend on time), please prove the energy-time uncertainty principle: $\Delta E \Delta t \geq \hbar/2$. Δt characterizes the amount of time it takes that expectation value of Q to change by one standard deviation.

Note: The energy-time uncertainty principle is of central importance in the interpretation of the line width in the observed spectra (along with other factors). It is particularly useful in understanding the lifetime of an unstable excited state in, e.g., photochemistry.

Hint: Try to evaluate $\Delta \hat{H} \Delta \hat{Q}$ first, which requires $[\hat{H}, \hat{Q}]$. The result derived in **(2)** links $[\hat{H}, \hat{Q}]$ with $d\langle \hat{Q} \rangle / dt$.

(4) Compute $\Delta x \Delta p_x$ for the wave function $\psi(x) = \frac{1}{x^2 + a^2}$ ($-\infty < x < +\infty$), and validate the uncertainty principle in this case. Remember to normalize the wave function first.

Useful integrals: $\int_0^{+\infty} \frac{1}{(x^2+a^2)^3} dx = \frac{3\pi}{16a^5}$ $\qquad$ $\int_0^{+\infty} \frac{1}{(x^2+a^2)^2} dx = \frac{\pi}{4a^3}$

$\int_0^{+\infty} \frac{x^2}{(x^2+a^2)^4} dx = \frac{\pi}{32a^5}$ $\qquad$ $\int_0^{+\infty} \frac{x^2}{(x^2+a^2)^2} dx = \frac{\pi}{4a}$

Question 9. More practice on operators and Dirac notation. (Practice makes perfect!)

(1) Given a complete orthonormal basis set $\{|1\rangle,\cdots,|i\rangle,\cdots,|N\rangle\}$ in Hilbert space, please prove the resolution of identity (which is also called the closure relation): $\hat{I}=\sum_{i=1}^{N}|i\rangle\langle i|$

Note: The identity operator is like number 1 in algebra – You multiply any operator with the identity operator result in the same operator. The resolution of identity is very useful in simplifying the derivations in, e.g., linear variation for computing molecular orbitals.

(2) The classical angular momentum ***L*** (a vector that describes rotational motion) is defined as:

$$\boldsymbol{L}=\boldsymbol{r}\times\boldsymbol{p}=\begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

where ***r*** is the position of the particle (with *x*, *y*, *z* being the three components), ***p*** is the linear momentum (with p_x, p_y, p_z being the three components). The three unit vectors along the *x*, *y*, and *z* axis are ***i***, ***j***, and ***k***.

Note: If you have never worked with determinants and cross product of vectors before, please review the mathematical background presented in McQuarrie, Chapter 9, section 9.1, and Chapter 5, section 5.3. If you don't know angular momentum in classical mechanics, please review the physics background by reading Atkins, 9th ed, Further information, section (c).

(2.1) Write down the quantum mechanical operators for L_x, L_y, and L_z in terms of the position and linear momentum operators.

(2.2) Are these angular-momentum operators Hermitian operators? Prove your statement using $\hat{L}_x$ as an example.

Hint: You only need to show that the combinations of position and linear momentum operators (which are themselves Hermitian) yield Hermitian operators.

(2.3) Show that the operator $\hat{L}_x$ does not commute with $\hat{L}_y$, and the corresponding commutator $[\hat{L}_x,\hat{L}_y]$ is, in fact, proportional to $\hat{L}_z$. What is the proportionality coefficient?

Hint: Try to reduce the commutator $[\hat{L}_x,\hat{L}_y]$ to the position-momentum commutators of which you know the results. You could use the following easy-to-prove algebraic relations to simplify your task: (a) $[\hat{A},\hat{B}]=-[\hat{B},\hat{A}]$; (b) $[\hat{A}\hat{B},\hat{C}]=\hat{A}[\hat{B},\hat{C}]+[\hat{A},\hat{C}]\hat{B}$

(2.4) Show that the operator $\hat{L}_x$ commutes with $\hat{L}^2$. The square of the total angular momentum is equal to the summation of squares of the three components: $\hat{L}^2=\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2$.

(2.5) Based on what you have learned in **(2.3)** and **(2.4)**, can you precisely measure the total angular momentum as a vector? Keep in mind that one has to determine all components simultaneously in order to determine a vector (norm *and* direction).