Subject: Chemistry (Hons.)
Semester: 4
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Topic: Foundation of Quantum Mechanics – 2

[Based on the class-lectures, here is the 2nd installment of home-assignments. The students must go through all the assignments. The students are advised to remain in contact for any type of academic discussion.]

1. The wavefunction corresponding to a freely moving particle can be represented as: $\psi = N.e^{ikx}$. Check whether the wavefunction is an eigenfunction of linear momentum. Using the wavefunction find out the value of the commutator: $[x, p_x]$. For a particular value of k comment on the position of the particle.
Hints:
Eigenvalue equation: $\hat{A}\psi = a\psi$
Linear momentum operator: $\frac{\hbar}{i}\frac{\partial}{\partial x}$
Keep in mind 'uncertainty' While commenting.

2. Using any arbitrary function (of x) check whether $\frac{d}{dx}$ is a linear operator. Is 'taking a square root' a linear operation?
Ans.: $\frac{d}{dx}cf(x) = c\frac{d}{dx}f(x)$, where c is a constant.
Thus, $\frac{d}{dx}$ is a linear operator. 'Taking square root' is nonlinear.

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Operators in quantum mechanics correspond to respective observables in classical mechanics. If eigenvalue equation ($\hat{A}\psi = a\psi$) is satisfied, the 'eigenvalue' (a) corresponds to the value of the observable defined by the operator (Take a reference of problem #1). It is not necessary that eigenvalue equation would always be satisfied (see problem #3).

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3. The wavefunction corresponding to a particle moving within (otherwise free – no potential energy) 1-dimentional box can be represented as: $\psi = N\sin(kx)$ where N and k are independent of x. Find out whether the function is an eigenfunction of linear momentum.

Hints: The answer is no. Thus, there is no 'specific' linear momentum ! (but a distribution). If not specific, can we have any estimate of average linear momentum within a certain length of the box? The answer is yes. It is called the 'expectation value'.

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Expectation value:
When large number of measurements are carried out to evaluate an observable corresponding to the operator $\hat{A}$ on a system (of corresponding wavefunction ψ), the expectation value (average outcome) would be:

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

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Hermitian operator:

A hermitian operator (say $\hat{A}$) is such that $\int \psi_1^* \hat{A} \psi_2 d\tau = \int (\hat{A}\psi_1)^* \psi_2 d\tau$

- Hermitian operators obey eigenvalue equation.

- The eigenvalues of a hermitian operator are real.

Proof:

$\hat{A}\psi = a\psi$ (eigenvalue equation)

$\Rightarrow \psi^* \hat{A}\psi = \psi^* a\psi$ (multiplying both sides by ψ^*)

$\Rightarrow \int \psi^* \hat{A}\psi \, d\tau = a \int \psi^* \psi \, d\tau$ ________________ (i)

Again, $(\hat{A}\psi)^* = a^* \psi^*$ (taking complex conjugate of both sides of the eigenvalue equation)

$\Rightarrow (\hat{A}\psi)^* \psi = a^* \psi^* \psi$ (multiplying both sides by ψ)

$\Rightarrow \int (\hat{A}\psi)^* \psi \, d\tau = a^* \int \psi^* \psi \, d\tau$ ________________ (ii)

Now, from the definition of hermiticity, the left hand sides of equations (i) and (ii) are equal.

Thus, $a \int \psi^* \psi \, d\tau = a^* \int \psi^* \psi \, d\tau$

$\Rightarrow a = a^*$ as $\int \psi^* \psi \, d\tau \neq 0$

- Eigenfunctions with different eigenvalues of a hermitian operator are orthogonal.

Proof:

$\hat{A}\psi_1 = a_1 \psi_1$ ________________ (iii)

$\hat{A}\psi_2 = a_2 \psi_2$ ________________ (iv)

From equation (iii), $(\hat{A}\psi_1)^* = a_1^* \psi_1^*$

$\Rightarrow \psi_2 (\hat{A}\psi_1)^* = \psi_2 a_1^* \psi_1^*$ (multiplying both sides by $\hat{A}\psi_2 = a_2\psi_2$)

$\Rightarrow \int (\hat{A}\psi_1)^* \psi_2 d\tau = a_1^* \int \psi_1^* \psi_2 d\tau = a_1 \int \psi_1^* \psi_2 d\tau$ (as $a_1 = a_1^*$) ________________ (v)

Again, $\psi_1^* \hat{A}\psi_2 = \psi_1^* a_2 \psi_2$ (multiplying both sides of equation (iv) by ψ_1^*)

$\Rightarrow \int \psi_1^* \hat{A}\psi_2 d\tau = a_2 \int \psi_1^* \psi_2 d\tau$ ________________ (vi)

From the definition of hermitian operator, the left hand sides of equations (v) and (vi) are equal.

Thus, $a_1 \int \psi_1^* \psi_2 d\tau = a_2 \int \psi_1^* \psi_2 d\tau$

$\Rightarrow (a_1 - a_2) \int \psi_1^* \psi_2 d\tau = 0$

$\Rightarrow \int \psi_1^* \psi_2 d\tau = 0$ as $a_1 \neq a_2$

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Complete set of eigenfunctions:

Any arbitrary function (say Ψ) can be expanded as a linear combination of all the eigenfunctions (ψ_i) of an operator. All the eigenfunctions taken together constitute complete set of eigenfunctions.

$\Psi = \sum_i c_i \psi_i$, c_i are the coefficients.