CHEM 482, sec 0102. Exam #3, answers Apr 19, 2004

Problem 1.

1. For each of the operators listed in the left column find an eigenfunction (if any) from the list of functions in the column on the right and calculate the corresponding eigenvalues. Keep in mind that for some of the operators you might not find an eigenfunction from this list.

	Operators
1	$-i\hbar\frac{\partial}{\partial\phi}$
2	p_x^2
3	$kx^2/2$
4	$p_x^2 + x^2$

Functions
A/x^2
$\cos(7\pi x/a)e^{-i5\phi}$
e^{-ax^2}, where $a = \frac{1}{2\hbar}$
$\log(x)\, e^{-iby}$

Answers:

	Operators	Eigenfunction	Eigenvalue
1	$-i\hbar\frac{\partial}{\partial\phi}$	$\cos(7\pi x/a)e^{-i5\phi}$	$-5\hbar$
2	p_x^2	$\cos(7\pi x/a)e^{-i5\phi}$	$(7\pi\hbar/a)^2$
3	$kx^2/2$	none	--
4	$p_x^2 + x^2$	e^{-ax^2}, where $a = \frac{1}{2\hbar}$	$2a\hbar^2$

Problem 2. The temperature of the Sun's surface is 6000 K.

(1) Assuming that the human eye evolved to be most sensitive at the wavelength of light corresponding to the Sun's radiant energy distribution, determine the wavelength of light to which the eye is most sensitive.

Answer: From Wien displacement law, $\lambda_{max} * T = 2898\ \mu m*K$, we get λ_{max}= 483 nm (close to the upper edge of the blue part of visible spectrum, 450 to 490 nm).

(2) This sensitivity should be supported by the proper chemistry, right? Assume that the light is absorbed in the eye by linear, polyene-type molecules in which π-electrons behave like particles in a one-dimensional box. (In fact, the oxidation of β-carotene results in retinal (vitamin A) that is a precursor to the pigment in the retina responsible for vision). Assuming for simplicity that when the light is absorbed by π-electron, a transition occurs between the energy levels with n = 3 and n = 4, estimate the length of this linear molecule.

Answer: For a particle in a 1-D box:

$\Delta E = E_4 - E_3 = \frac{h^2}{8ma^2}\left(4^2 - 3^2\right)$. Equating it to the energy of the absorbed photon, $h\nu = hc/\lambda_{max}$, we get $a = \sqrt{\frac{h\lambda_{max}}{8mc}\left(4^2 - 3^2\right)}$ =1.01 nm = 10.1 Å

Problem 3. The rate of a chemical reaction increased by 2 fold when the temperature increased from 25°C to 35°C. What is the activation energy for such a reaction? (assume Arrhenius kinetics) Adding an enzyme at 25 °C caused a 1000-fold increase in the reaction rate. Calculate the change in the activation energy introduced by the enzyme.
How will this enzyme affect the rate of the reverse reaction?

Answers:
The activation energy is $E_a = R \ln(2) /(1/T_1-1/T_2)$ = 52.868 kJ/mol, where T_1 = 298K, T_2 = 308K. (For those of you who solved the problem for a 20-fold (instead of 2-fold) increase in the reaction rate, the answer is 228.49 kJ/mol).
The change in the activation energy is $\Delta E_a = - RT \ln(1000)$ = -17.106 kJ/mol (minus means a decrease in E_a).
The rate of the reverse reaction will also increase by a factor of 1000.

Bonus Problem. The wavefunction (not normalized) of a quantum mechanical system is $\Psi = 3e^{-i2x} + 2e^{i2x} + 5e^{i3x} + 4e^{-i3x}$. What is the probability that a single measument of the linear momentum will give a value of $3\hbar$?

Answer:
According to the expression for the wavefunction Ψ, it is a superposition of 4 wavefunctions each being an eigenfunction of the linear momentum operator: $\Psi = \sum c_k \psi_k$ (recall that $\psi_k = e^{ikx}$ is an eigenfunction of $\hat{p}_x$ corresponding to an eigenvalue $p_x = \hbar k$). This means that the probability that the system will be found in the state with $p_x = 3\hbar$ is proportional to the square (by absolute value) of the coefficient at e^{i3x}, i.e. to $|c_3|^2 = 5^2$ (I used "proportional" instead of "equal" because this number is not normalized here) To get the exact value of the probability, we have to divide this number by the sum of the probabilities to find the system in all available states, i.e. by $3^2+2^2+5^2+4^2 = 54$. This gives the probability = 25/54 = 0.463.

The same result can be obtained by first normalizing the wavefunction: Ψ → NΨ, where

$$N^2 = \frac{1}{\int |\Psi|^2 dx} = \frac{1}{\left(3^2+2^2+5^2+4^2\right)\int dx} = \frac{n^2}{\left(3^2+2^2+5^2+4^2\right)} \text{ and } n^2 = \frac{1}{\int \left|e^{ikx}\right|^2 dx} = \frac{1}{\int dx} \text{ is the}$$

squared normalization factor for e^{ikx}, i.e. $\psi_k = ne^{ikx}$ (this normalization factor does not depend on k). Note that functions e^{ikx} and $e^{ik'x}$ with $k \neq k'$ are orthogonal. Presenting Ψ (now normalized) as a superposition of (normalized) eigenfunctions ψ_k, we obtain

$$\Psi = \frac{1}{\sqrt{\left(3^2+2^2+5^2+4^2\right)}}\left(3\psi_{-2} + 2\psi_2 + 5\psi_3 + 4\psi_{-3}\right)$$, and from here the probability (normalized) that this system will be found in the state with $p_x = 3\hbar$ is $|c_3|^2 = 5^2/(3^2+2^2+5^2+4^2) = 0.463$.