Chem 440
Spring 2020

Hour Exam 1

Useful numbers and formulas you may need are given at the end.
You must turn in (or upload PDF or JPEG on Moodle if remote) your answer by 10:55 to get full credit.

1. (10 pts) Let's do some Bayesian statistics. Hunter and Lauda have been racing 6 times, and Hunter lost 4 times. It rained 3 times, both times when Hunter won, and once when Hunter lost. We still suspect Hunter drives better in the rain than when it's dry compared to Lauda.

a. (2) **What is** the overall probability P(A) that it rained during the series of 6 races?

Solution: Event A = it rained during the race. The frequency of event A is 3, so

$$P(A) = \frac{3}{6} = \frac{1}{2}$$

b. (2) **What is** the overall probability P(B) that Hunter won in those 6 races?

Solution: Event B = Hunter won the race. The frequency of even B is 2, so the probability is

$$P(B) = \frac{2}{6} = \frac{1}{3}$$

c. (2) **What is** the probability P(A|B) that it rains when Hunter wins?

Solution: In both of the two races that Hunter won it rained, so the probability is

$$P(A|B) = 1$$

d. (1+2+1) **Write down** a formula for the probability that Hunter wins when it rains. Calculate the probability. **Would yo**u bet on Hunter or Lauda if we know it will rain in the next race?

Solution: We can use Bayes' formula to calculate it, or

$$P(B|A) = P(A|B)\frac{P(B)}{P(A)} = 1 \cdot \frac{1/3}{1/2} = \frac{2}{3}$$

We would still bet on Hunter the next time it rains because past experience suggests he has a 2/3 chance of winning in the rain.

2. (10 pts) Let's apply an operator to a wavefunction and see what happens.

a. (4) **Apply** the 'frequency operator' $\hat{\nu} = \frac{i}{2\pi}\frac{\partial}{\partial t}$ to the function $\Psi = \mathrm{e}^{-\frac{i}{\hbar}Et}$.

Solution:

$$\hat{\nu}\Psi = \frac{i}{2\pi}\frac{\partial}{\partial t}\left(\mathrm{e}^{-\frac{i}{\hbar}Et}\right) = \frac{i}{2\pi} \times \left(-\frac{i}{\hbar}E\right)\mathrm{e}^{-\frac{i}{\hbar}Et} = \frac{E}{2\pi\hbar}\mathrm{e}^{-\frac{i}{\hbar}Et} = \frac{E}{2\pi\hbar}\Psi$$

b. (2+1) **Is Ψ** an eigenfunction of the frequency operator? If yes, **what is** its eigenvalue?

Solution: Yes, Ψ is an eigenfunction of the frequency operator with eigenvalue $\frac{E}{2\pi\hbar}$.

c. (2+1) Since the eigenvalue of the frequency operator is the frequency ν, **write down** a formula for ν in terms of i, $h=2\pi\hbar$ and E, and solve for E. Looks like you just derived a 'law'! **What is** the name of this 'law'?

Solution: $\nu = \frac{E}{2\pi\hbar} = \frac{E}{h}$,
so we have the Planck's energy–frequency relation $E = h\nu$.

3. (10 pts) When a quantum spring oscillates, the kinetic energy can go negative when the spring stretches beyond 'x_{max}' or compresses beyond 'x_{min}', the classically allowed range!

a. (4) For the n=1 excited state of a spring with energy $E_1 = \frac{3h\nu}{2}$, **at what two values** of x is $E_1=V(x)=kx^2/2$? Call them x_{max} and x_{min}=- x_{max} and write them down in terms of k, h, and ν.

Solution: $E_1 = \frac{3h\nu}{2}$

$$V(x) = E_1 \Rightarrow \frac{1}{2}kx^2 = \frac{3h\nu}{2} \Rightarrow x^2 = \frac{3h\nu}{k} \Rightarrow x_{max} = +\sqrt{\frac{3h\nu}{k}} \text{ and } x_{min} = -\sqrt{\frac{3h\nu}{k}}$$

b. (6) **Calculate** the probability of being in the "forbidden region" where kinetic energy is negative (where $E_1>V(x)$). For simplicity, let's pick ν and k so x_{max}=1, in which case the normalized n=1 wavefunction becomes $\Psi(x) \approx 2.422xe^{-3x^2/2}$.

Solution:

$\Psi(x) \approx 2.422xe^{-\frac{3x^2}{2}}$; forbidden region (Kinetic energy<0): ($x<x_{min}$) and ($x>x_{max}$)

$$P_{forbidden} = 2\int_{x_{max}}^{\infty} dx\, |\Psi(x)|^2 = 2(2.422)^2 \int_{1}^{\infty} dx\, x^2 e^{-3x^2}$$
$$= 11.7\left[\frac{\sqrt{3\pi}}{36}\operatorname{erf}(\sqrt{3}x) - \frac{x}{6}e^{-3x^2}\right]_1^\infty$$

$$\boldsymbol{P_{forbidden} = 0.111}$$

⇨ 11% chance to find the oscillator in the forbidden region

4. (10 pts) Let's talk about the wavefunction for two electrons.

a. (4) Prove that if $\hat{H}_1\Psi_1(x_1) = E_1\Psi_1(x_1)$ for the 1st electron, and $\hat{H}_2\Psi_2(x_2) = E_2\Psi_2(x_2)$ for the 2nd electron, then $\Psi(x_1, x_2) = \Psi_1(x_1)\Psi_2(x_2)$ is an eigenfunction of $\hat{H} = \hat{H}_1 + \hat{H}_2$.

Solution: $(\hat{H}_1 + \hat{H}_2)\Psi_1(x_1)\Psi_2(x_2) = \hat{H}_1\Psi_1(x_1)\Psi_2(x_2) + \hat{H}_2\Psi_1(x_1)\Psi_2(x_2)$
$$= \Psi_2(x_2)\hat{H}_1\Psi_1(x_1) + \Psi_1(x_1)\hat{H}_2\Psi_2(x_2)$$
$$= \Psi_2(x_2)E_1\Psi_1(x_1) + \Psi_1(x_1)E_2\Psi_2(x_2)$$
$$= E_1\Psi_1(x_1)\Psi_2(x_2) + E_2\Psi_1(x_1)\Psi_2(x_2)$$

$$= (E_1 + E_2)\Psi_1(x_1)\Psi_2(x_2)$$

b. (2) What is the eigenvalue (total energy of both electrons)?

Solution: from the above equation, $E_1 + E_2$

c. (4) The wavefunction is not quite right: it violates postulate #4 because $\Psi(x_1, x_2) \neq -\Psi(x_2, x_1)$ if we swap the two electrons. Prove that $\Psi(x_1, x_2) = \Psi_1(x_1)\Psi_2(x_2) - \Psi_1(x_2)\Psi_2(x_1)$ does satisfy postulate 4.

Solution: $\Psi(x_2, x_1) = \Psi_1(x_2)\Psi_2(x_1) - \Psi_1(x_1)\Psi_2(x_2)$
$= -\Psi_1(x_1)\Psi_2(x_2) + \Psi_1(x_2)\Psi_2(x_1)$
$= -\Psi(x_1, x_2)$
This wavefunction changes to (-) itself when electrons are swapped.

Useful information:
1 atomic mass unit = 1.66×10^{-27} kg; mass of electron $m_e = 9.109 \times 10^{-31}$ kg

Planck's constant $h = 6.626 \times 10^{-34}$ J·s; note that $\hbar = h/2\pi$ is about 6.28 times smaller.

1 Å = 0.1 nm = 100 pm; $c \approx 3 \cdot 10^8$ m/s

$\partial/\partial x\, e^{ax} = a e^{ax}$

$\int e^{-x/a}\, dx = -a\, e^{-x/a}$

$(1/a)\cdot\int x \cdot e^{-x/a}\, dx = -(a+x)e^{-x/a}$

$\int x^2 \cdot e^{-3x^2}\, dx = \frac{\sqrt{3\pi}}{36}\operatorname{erf}(\sqrt{3}x) - \frac{x}{6}e^{-3x^2}$ where "erf" is the error function

$\operatorname{erf}(\sqrt{3}) \approx 0.986$; $\operatorname{erf}(-\sqrt{3}) \approx -0.986$; $\operatorname{erf}(\infty) \approx 1$; $\operatorname{erf}(-\infty) = -1$

$\lim_{x\to\infty} x e^{-x/a} = 0$ and $\lim_{x\to\infty} x e^{-bx^2} = 0$ for a or b.

Color and wavelength, and complementary color wheel