Assignment 1 Solutions

1.1 Here are the answers with some intermediate steps shown. Let me know if you are having trouble following these steps or getting these answers.

(a)

$$\frac{d^2}{dx^2} e^{-ax^2} = \frac{d}{dx}\left(\frac{d\, e^{-ax^2}}{dx}\right) = \frac{d}{dx}\left(-2ax e^{-ax^2}\right) = \left(4a^2x^2 - 2a\right) e^{-ax^2}$$

(b)

$$\frac{d^2}{dx^2} e^{-iax} = (ia)^2 e^{-iax} = -a^2 e^{-iax}$$

(c)

$$\frac{\partial^2}{\partial\theta\,\partial\phi} \sin\phi\, \cos^2\theta = \frac{\partial}{\partial\theta}\left(\frac{\partial}{\partial\phi} \sin\phi\, \cos^2\theta\right) = \frac{\partial}{\partial\theta}\left(\cos\phi\, \cos^2\theta\right) = -2\cos\phi\, \cos\theta\, \sin\theta$$

Integrals: (a) A trig identity substitution does the trick here:

$$\int_0^\pi \sin^2 x\ dx = \int_0^\pi \frac{1-\cos 2x}{2}\ dx = \frac{1}{2}\int_0^\pi dx - \frac{1}{2}\int_0^\pi \cos 2x\ dx = \frac{\pi}{2} - \frac{1}{2}\left.\frac{\sin 2x}{2}\right|_0^\pi = \frac{\pi}{2}$$

(b) Again, the same trig identity will help here, too,:

$$\int_0^\pi x \sin^2 x\ dx = \int_0^\pi \frac{x - x\cos 2x}{2}\ dx = \frac{1}{2}\int_0^\pi x\ dx - \frac{1}{2}\int_0^\pi x\cos 2x\ dx = \frac{\pi^2}{4}$$

(c)

$$\int_0^a \sin\left(\frac{\pi x}{a}\right)\ dx = -\frac{a}{\pi}\cos\left.\frac{\pi x}{a}\right|_0^a = \frac{2a}{\pi}$$

Other things: (a) We use the identity for a complex argument exponential:

$$e^{i\pi} = \cos\pi + i\sin\pi = -1$$

(b) We write the summation out term by term:

$$\sum_{m=-J}^{J} 1 \qquad = 1 + 1 + \ldots + 1 \qquad = 2J + 1$$

total of $2J + 1$ terms in the sum
as m goes in unit steps from $-J$ to J

(c) Straightforward summation:

$$\sum_{m=0}^{4} (2m+1) = (2\cdot 0 + 1) + (2\cdot 1 + 1) + (2\cdot 2 + 1) + (2\cdot 3 + 1) + (2\cdot 4 + 1) = 25$$

1.2 The spectrum must fall in the 2000–8000 Å range to be seen; so, if we convert these wavelengths into wavenumbers (the units in which the energy levels are given): 2000 Å → 50,000 cm^{-1} and 8000 Å → 12,500 cm^{-1}, then we can form a table of all possible energy level differences and see at a glance which transitions fall in our observation window. The table below, from Excel, does that, and the transitions in bold are the seven we can observe.

	0	21850	21870	21911	35051
0	0	**21850**	**21870**	**21911**	**35051**
21850		0	20	61	**13201**
21870			0	41	**13181**
21911				0	**13140**
35051					0

1.3 We exploit the meaning of *normalized* and *orthogonal* functions here: ψ_1 and ψ_2 are orthonormal. If ψ and ψ' are orthogonal, then

$$\int \psi\,\psi'\,dx = 0$$

where the integral is assumed to be over all space and all coordinates of ψ (which I've assumed are just x here). If $\gamma = 60° = \pi/3$, then $\sin\gamma = \sqrt{3}/2$ and $\cos\gamma = 1/2$. Thus, we can write the orthogonal integral as

$$\int \psi\,\psi'\,dx = \frac{1}{2}\int \left(\psi_1 + \sqrt{3}\,\psi_2\right)\left(\cos\gamma'\psi_1 + \sin\gamma'\psi_2\right)dx = 0\ .$$

Expanding gives

$$\int \left(\psi_1 + \sqrt{3}\,\psi_2\right)\left(\cos\gamma'\,\psi_1 + \sin\gamma'\,\psi_2\right)dx =$$

$$\cos\gamma'\int \psi_1\psi_1\,dx + \sin\gamma'\int \psi_1\psi_2\,dx + \sqrt{3}\cos\gamma'\int \psi_2\psi_1\,dx + \sqrt{3}\sin\gamma'\int \psi_2\psi_2\,dx = 0\ ,$$

and now we can invoke the power of orthonormality. The first and fourth integrals are 1 by normality, and the second and third are zero by orthogonality. We're left with

$$\int \left(\psi_1 + \sqrt{3}\,\psi_2\right)\left(\cos\gamma'\,\psi_1 + \sin\gamma'\,\psi_2\right)dx = \cos\gamma' + \sqrt{3}\,\sin\gamma' = 0\ .$$

Thus, we want to pick γ' such that $\cos \gamma' = -\sqrt{3}\,\sin \gamma'$. A little thought (or a look at a graph of $\cos \gamma'$ and $-\sqrt{3}\,\sin \gamma'$, such as shown below) tells us that $\gamma' = 5\pi/6$ (150°) or $11\pi/6$ (330°, equivalent to –30° or $-\pi/6$). This should not be a surprise; things that are orthogonal in geometry are at 90° to each other, and our orthogonal functions have mixing angles γ' that are 90° from $\gamma = 60°$ for either of the two choices, $\gamma' = 150°$ or $\gamma' = -30°$.