Chem. 1410: Solutions for Hand-In Problems.

1)**(2 points)** Consider $\hat{x}\hat{p}F(x) = x\frac{\hbar}{i}\frac{\partial F(x)}{\partial x}$ (i)

Now consider:

$$\hat{p}xF(x) = \frac{\hbar}{i}\frac{\partial[xF(x)]}{\partial x} = \frac{\hbar}{i}\left[x\frac{\partial F(x)}{\partial x} + F(x)\right] \quad \text{(ii)}$$

Subtraction (i)-(ii), we obtain: $[\hat{x}\hat{p} - \hat{p}\hat{x}]F(x) = i\hbar F(x)$, QED.

2) a)**(2 points)** The Gaussian $f(x)$ is an even function (symmetric about *x=0*); *sin(jx*) is an odd function (antisymmetric about *x=0*). The product of an even and an odd function is an odd function. That is, *f(x)sin(jx*) is an odd function. [Plot it if you have doubts!] The integral of an odd function over any interval positioned symmetrically about *x=0* is *0*. That is the case with the integral which defines b_j. Hence $b_j = 0$.

b)**(2 points)**If $\sigma << \pi$, then the Gaussian function f(x) has decayed for all practical purposes to 0 by the time $x = \pm\pi$. Thus, the integrand f(x) is identically 0 from $[\pi, \infty]$ and from $[-\infty, -\pi]$, and hence extending $\int_{-\pi}^{\pi}$ to $\int_{-\infty}^{\infty}$ does not change the result. [Note: these arguments are also valid when *f(x)* is replaced with *f(x)cos(jx),* since $|\cos(jx)| \leq 1$.]

c)**(2 points)**i) Using the integral identity with parameter $\gamma = 0$, we see that

$\int_{-\infty}^{\infty} dx f(x) = 1$, and hence $a_0 = \frac{1}{2\pi}$.

ii) Using the integral identity with parameter $\gamma = j$, we see that

$\int_{-\infty}^{\infty} dx f(x)\cos(jx) = \exp(-j^2\sigma^2/2)$, and hence $c_j = \frac{1}{\pi}\exp(-j^2\sigma^2/2)$.

d)**(2 points)** Results for $f_2(x)$, $f_6(x)$ (showing the periodicity of the Fourier expansion on an interval of 2π) are compared to $f(x)$ (on the interval $[-\pi, \pi]$) in Fig. A1 for the case that $\sigma = 0.5$. Note that $f_2(x)$ (i.e., N=2 in the Fourier expansion) is not fully converged w.r.t. $f(x)$, but $f_6(x)$ is. (Plots of $f_N(x)$, N>6 [not shown] are indistinguishable from the N=6 case.)

e) **(2 points)** Results for $f_2(x)$, $f_6(x)$ (showing the periodicity of the Fourier expansion on an interval of 2π) are compared to $f(x)$ (on the interval $[-\pi,\pi]$) for the case that $\sigma = 0.25$ Note that neither $f_2(x)$ nor $f_6(x)$ is fully converged, but by N=10-15 the Fourier series does converge (cf. Fig. A3). This behavior is expected: as the Gaussian $f(x)$ becomes more narrowly localized in space, it takes a wider range of wavevectors in the sine/cosine expansion to build up the Gaussian near x=0, and to sum to zero (by destructive interference) for $|x| \gg \sigma$.

[Note: This is an allegory for the Heisenberg Uncertainty Principle, since the eigenfunction of the momentum operator $\hat{p}$ corresponding to momentum value p is the plane wave $\exp(ipx/\hbar)$, i.e., a cos/sin wave corresponding to wavevector $p/\hbar$.]

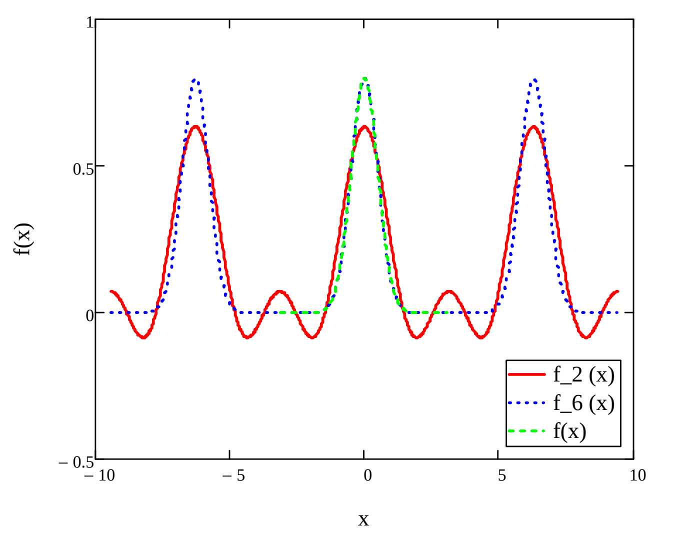

Fig. A1: Plots of $f_2(x), f_6(x), f(x)$ for $\sigma = 0.5$

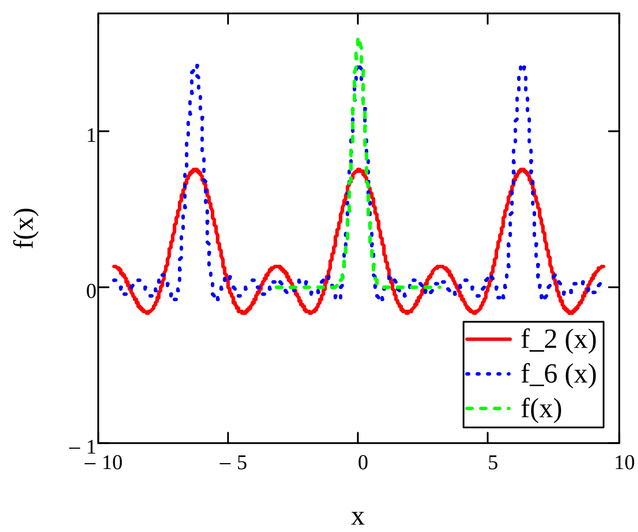

Fig. A2. Plots of $f_2(x), f_6(x), f(x)$ for $\sigma = 0.25$

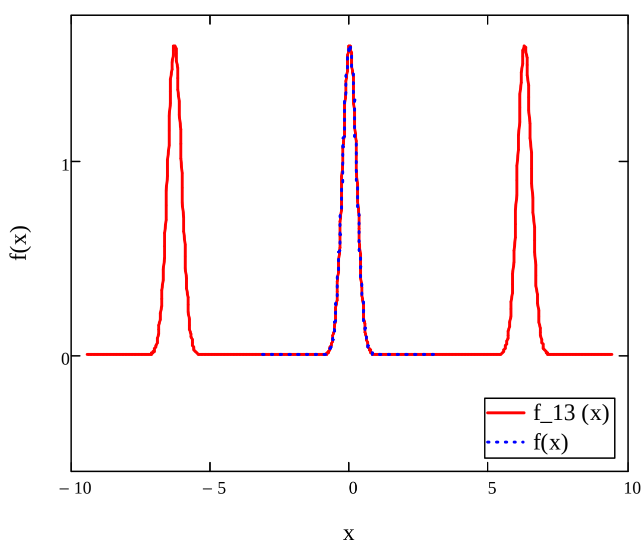

Fig. A3. Plots of $f_{13}(x), f(x)$ for $\sigma = 0.25$.

2.5) [redacted]) Show that $\dfrac{a+ib}{c+id} = \dfrac{ac+bd+i(bc-ad)}{c^2+d^2}$

$$\frac{a+ib}{c+id} = \left(\frac{a+ib}{c+id}\right)\left(\frac{c-id}{c-id}\right) = \frac{ac+bd+ibc-iad}{c^2+d^2} = \frac{ac+bd+i(bc-ad)}{c^2+d^2}$$

P2.10) [redacted]) Determine in each of the following cases if the function in the first column is an eigenfunction of the operator in the second column. If so, what is the eigenvalue?

a) $\sin\theta\cos\phi$ $\qquad \dfrac{\partial}{\partial\phi}$

b) $e^{-x^2/2}$ $\qquad \dfrac{1}{x}\dfrac{d}{dx}$

c) $\sin\theta$ $\qquad \dfrac{\sin\theta}{\cos\theta}\dfrac{d}{d\theta}$

a) $\sin\theta\cos\phi$ $\qquad \dfrac{\partial}{\partial\phi}$

$\dfrac{\partial}{\partial\phi}\sin\theta\cos\phi = -\sin\theta\sin\phi.$ Not an eigenfunction

b) $e^{-\frac{1}{2}x^2}$ $\qquad \dfrac{1}{x}\dfrac{d}{dx}$

$\dfrac{1}{x}\dfrac{d}{dx}e^{-\frac{1}{2}x^2} = -e^{-\frac{1}{2}x^2}$ Eigenfunction with eigenvalue -1

c) $\sin\theta$ $\qquad \dfrac{\sin\theta}{\cos\theta}\dfrac{d}{d\theta}$

$\dfrac{\sin\theta}{\cos\theta}\dfrac{d}{d\theta}\sin\theta = \sin\theta$ Eigenfunction with eigenvalue $+1$

P2.15 [redacted]) Which of the following wave functions are eigenfunctions of the operator d^2/dx^2? If they are eigenfunctions, what is the eigenvalue?

a) $ae^{-3x} + be^{-3ix}$ b) $\sin^2 x$ c) e^{-ix} d) $\cos ax$ e) e^{-ix^2}

a) $\dfrac{d^2\left(ae^{-3x}+be^{-3ix}\right)}{dx^2} = 9ae^{-3x} - 9be^{-3ix}$ Not an eigenfunction

b) $\dfrac{d^2\sin^2 x}{dx^2} = -2\sin^2 x + 2\cos^2 x$ Not an eigenfunction

c) $\dfrac{d^2 e^{-ix}}{dx^2} = -e^{-ix}$ Eigenfunction with eigenvalue -1

d) $\dfrac{d^2\cos ax}{dx^2} = -a^2\cos ax$ Eigenfunction with eigenvalue $-a^2$

e) $\dfrac{d^2 e^{-ix^2}}{dx^2} = -2ie^{-ix^2} - 4x^2e^{-ix^2}$ Not an eigenfunction

P2.18)

[redacted]) Find the result of operating with $\frac{d^2}{dx^2} - 4x^2$ on the function e^{-ax^2}. What must the value of a be to make this function an eigenfunction of the operator?

$$\frac{d^2 e^{-ax^2}}{dx^2} - 4x^2 e^{-ax^2} = -2ae^{-ax^2} - 4x^2 e^{-ax^2} + 4a^2 x^2 e^{-ax^2} = -2ae^{-ax^2} + 4\left(a^2 - 1\right) x^2 e^{-ax^2}$$

For the function to be an eigenfunction of the operator, the terms containing $x^2 e^{-ax^2}$ must vanish. This is the case if $a = \pm 1$.

P2.23)

[redacted]) Normalize the set of functions $\phi_n(\theta) = e^{in\theta}$, $0 \le \theta \le 2\pi$. To do so, you need to multiply the functions by a so-called normalization constant N so that the integral

$$N N^* \int_0^{2\pi} \phi_m^*(\theta)\phi_n(\theta)d\theta = 1 \quad \text{for} \quad m = n$$

$N N^* \int_0^{2\pi} e^{-in\theta} e^{in\theta} d\theta = N N^* \int_0^{2\pi} d\theta = 2\pi N N^* = 1$ This is satisfied for $N = \frac{1}{\sqrt{2\pi}}$ and the normalized functions are $\phi_n(\theta) = \frac{1}{\sqrt{2\pi}} e^{in\theta}$, $0 \le \theta \le 2\pi$.

P2.30)

[redacted]) Let $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ represent the unit vectors along the x and y directions, respectively. The operator $\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$ effects a rotation in the x-y plane. Show that the length of an arbitrary vector $\begin{pmatrix} a \\ b \end{pmatrix} = a\begin{pmatrix} 1 \\ 0 \end{pmatrix} + b\begin{pmatrix} 0 \\ 1 \end{pmatrix}$, which is defined as $\sqrt{a^2 + b^2}$, is unchanged by this rotation. See the Math Supplement for a discussion of matrices.

$$\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a\cos\theta - b\sin\theta \\ a\sin\theta + b\cos\theta \end{pmatrix}$$

The length of the vector is given by

$$\sqrt{(a\cos\theta - b\sin\theta)^2 + (a\sin\theta + b\cos\theta)^2} = (a^2\cos^2\theta + b^2\sin^2\theta - 2ab\sin\theta\cos\theta$$
$$+ a^2\sin^2\theta + b^2\cos^2\theta + 2ab\sin\theta\cos\theta)^{1/2}$$
$$= \sqrt{a^2\left(\cos^2\theta + \sin^2\theta\right) + b^2\left(\cos^2\theta + \sin^2\theta\right)} = \sqrt{a^2 + b^2}$$

This result shows that the length of the vector is not changed.