5.10: Problems

1. Consider the data given in the table for lines found in the pure rotational spectrum of $^{12}C^{16}O$. Determine an approximate value for B and assign the spectrum (the lower $\rightarrow$ upper state rotational quantum numbers for each line.) Make a graph of $\frac{\tilde{v}_J}{(J+1)}$ vs. $(J+1)^2$ and determine

line	$\tilde{v}\left(\mathrm{cm}^{-1}\right)$
1	3.84503319
2	7.68991907
3	11.5345096
4	15.378662
5	19.222223
6	23.065043

the best fit line. Use these results to determine B and D for the molecule. Compare your results to those found in the NIST Webbook of Chemistry for the ground electronic state of CO.

2. Consider the following data for the rotation-vibration spectrum of $H^{35}Cl$.
   a. Using the differences in frequency, assign the location of the band origin and assign the P - and R-branches accordingly.
   b. Using combination differences, fir the data to find B', D', B" and D'.
   c. Use your results to find B_e, α_e and De_e.
   d. Based on your value of B_e, find a value for r_e for the molecule.
   e. Compare your results to those found in the NIST Webbook of Chemistry.

line	Freq. $\left(\mathbf{cm}^{-1}\right)$	$\Delta\tilde{v}$
1	3085.62	
2	3072.76	
3	3059.07	
4	3044.88	
5	3029.96	
6	3014.29	
7	2997.78	
8	2980.90	
9	2963.24	
10	2944.89	
11	2925.78	
12	2906.25	
13	2865.09	
14	2843.65	
15	2821.49	
16	2798.78	
17	2775.79	

line	Freq. $\left(\mathbf{cm}^{-1}\right)$	$\Delta\tilde{v}$
18	2752.03	
19	2727.75	
20	2703.06	
21	2677.73	
22	2651.97	
23	2625.74	
24	2599.00	

3. A recursion formula for the Legendre Polynomials is given by

$$(l+1)P_{l+1}(x) = (2l+1)xP_l(x) - lP_{l-1}(x)$$

Based on $P_0(x) = 1$ and $P_1(x) = x$ find expressions for $P_2(x)$ and $P_3(x)$.

4. The function describing the $l = 1,\ \mathrm{m}_l = 0$ spherical harmonic is $Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}}\cos(\theta)$
   a. Show that this function is normalized. To do this, you must use the limits on θ and ϕ of $0 \leq \theta \leq \pi$, and $0 \leq \phi \leq 2\pi$. Also, for the angular part of the Laplacian, $d\tau = \sin(\theta)d\theta d\phi$
   b. Using plane polar graph paper (or a suitable graphing program) plot the square of the function from problem 2 in the yz plane (which gives a cross-section of the probability function for the particular spherical harmonic.) Does the shape look familiar?

5. Based on the given bond-length data, calculate values for the rotational constants for the following molecules:

Molecule	Bond Length $(\mathring{\mathrm{A}})$
$\mathrm{H}^{35}\mathrm{Cl}$	1.2746
$\mathrm{H}^{79}\mathrm{Br}$	1.4144
$\mathrm{H}^{127}\mathrm{I}$	1.6092

6. The spacing between lines in the pure rotational spectrum of BN is $3.31\ \mathrm{cm}^{-1}$. From this, find B and calculate the bond length (r_{BN}) in the BN molecule.
7. From your result in problem 6, calculate the frequencies of the first 4 lines in the pure rotational spectrum of BN.