量子化学作业　（2017-2018 学期）

1. The $J=0$ to $J=1$ transition for carbon monoxide ($^{12}C^{16}O$) occurs at $1.153\times 10^{5}\,\text{MHz}$. Calculate the value of the bond length in carbon monoxide.

2. This problem involves the calculation of the moment of inertia of a linear triatomic molecule such as $H^{12}C^{14}N$. The moment of inertia of any set of point masses is

$$I=\sum_{j} m_j l_j^2$$

where l_j is the distance of the j th mass from the center of mass. Thus, the moment of inertia of $H^{12}C^{14}N$ is

$$I=m_H l_H^2+m_C l_C^2+m_N l_N^2$$

Show that equation above can be written as

$$I=\frac{m_H m_C r_{CH}^2+m_H m_N r_{NH}^2+m_C m_N r_{CN}^2}{m_H+m_C+m_N}$$

where the r's are the various inter-nuclear distances. Given that $r_{CH}=106.8\,pm$ and $r_{CN}=115.6\,pm$, calculate the value of *I*.

3. Given that $l = 156\,pm$ and $k = 250 N \cdot m^{-1}$ for ^{6}LiF, use the rigid rotator-harmonic oscillator approximation to construct to scale an energy-level diagram for the first five rotational levels in the $v = 0$ and $v = 1$ vibrational states. Indicate the allowed transitions in an absorption experiment, and calculate the frequencies of the first few lines in the *R* and *P* branches of the rotation-vibration spectrum of ^{6}LiF.

4. The following spectroscopic constants were determined for pure samples of ^{74}Ge^{32}S and ^{72}Ge^{32}S:

Molecule	B_e/MHz	α_e/MHz	D/kHz	$l(v=0)$/pm
^{74}Ge^{32}S	5593.08	22.44	2.349	0.20120
^{72}Ge^{32}S	5640.06	22.74	2.388	0.20120

Determine the frequency of the $J = 0$ to $J = 1$ transition for ^{74}Ge^{32}S and ^{72}Ge^{32}S in their ground vibrational state. The width of a microwave absorption line is on the order of 1 KHz. Could you distinguish a pure sample of ^{74}Ge^{32}S from a 50/50 mixture of ^{74}Ge^{32}S and ^{72}Ge^{32}S using microwave spectroscopy?

5. Using the parameters given in Table 6.1, calculate the frequencies (in cm^{-1}) of the $0 \rightarrow 1, 1 \rightarrow 2, 2 \rightarrow 3,$ and $3 \rightarrow 4$ rotational transitions in the ground vibrational state of $H^{35}CI$ in the nonrigid-rotator approximation

6. Use the data in Table 6.1 to calculate the ratio of centrifugal distortion energy to the total rotational energy of $H^{35}Cl$ and $^{35}Cl^{35}Cl$ in the $J = 10$ state.

7. In terms of the variable θ, Legendre's equation is

$$\sin\theta \frac{d}{d\theta}\left[\sin\theta \frac{d\Theta(\theta)}{d\theta}\right] + (\beta^2 \sin^2\theta - m^2)\Theta(\theta) = 0$$

Let $x = \cos\theta$ and $P(x) = \Theta(\theta)$ and show that

$$(1-x^2)\frac{d^2P(x)}{dx^2} - 2x\frac{dP(x)}{dx} + (\beta^2 - \frac{m^2}{1-x^2})P(x) = 0$$

8. Show that the first 3 spherical harmonics in Table 6.5 satisfy the orthonormal condition (Equation 6.57).

9. Using explicit expressions for $Y_l^m(\theta,\phi)$, show that

$$\left|Y_1^1(\theta,\phi)\right|^2 + \left|Y_1^0(\theta,\phi)\right|^2 + \left|Y_1^{-1}(\theta,\phi)\right|^2 = \text{constant}$$

This is a special case of the general theorem

$$\sum_{m=-l}^{+l} \left|Y_l^m(\theta,\phi)\right|^2 = \text{constant}$$

known as Unsöld's theorem. What is the physical significance of this result?

10. In Cartesian coordinates,

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Convert this equation to spherical coordinates, showing that

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial \phi}$$

11. Convert $\hat{L}_x$ and $\hat{L}_y$ from Cartesian coordinates to spherical coordinates.

12. Compute the value of $\hat{L}^2 Y(\theta,\phi)$ for the following functions:

(a) $1/(4\pi)^{1/2}$ (b) $(3/4\pi)^{1/2}\cos\theta$

(c) $(3/8\pi)^{1/2}\sin\theta e^{i\phi}$ (d) $(3/8\pi)^{1/2}\sin\theta e^{-i\phi}$

Do you find anything interesting about the results?

13. Prove that $\hat{L}^2$ commutes with $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ but that

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z \qquad \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x \qquad \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$

(Hint: Use Cartesian coordinates.) Do you see a pattern in these formulas?

Mathematics

1. Find the values of x that satisfy the following determinant equation:

$$\begin{vmatrix} x & 1 & 1 & 1 \\ 1 & x & 0 & 0 \\ 1 & 0 & x & 0 \\ 1 & 0 & 0 & x \end{vmatrix} = 0$$

2. Show that

$$\begin{vmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{vmatrix} = 0$$

3. Solve the following set of equations using Cramer's rule:

$$
\begin{aligned}
x + 2y + 3z &= -5 \\
-x - 3y + z &= -14 \\
2x + y + z &= 1
\end{aligned}
$$