量子化学作业 第五章（2017-2018 学期）

1. The general solution for the classical harmonic oscillator is $x(t)=C\sin(\omega t+\phi)$. Show that the displacement oscillates between $+C$ and $-C$ with a frequency of ω radian·s^{-1} or $\nu=\omega/2\pi$ cycle· s^{-1}. What is the period of the oscillations?

2. Carry out the Maclaurin expansion of the Morse potential $V(x)=D(1-e^{-\beta x})^2$ through terms in x^4. Express γ_3 in Equation 5.30 of the textbook in terms of D and β.

3. In the infrared spectrum of $H^{127}I$, there is an intense line at 2309 cm^{-1}. Calculate the force constant of $H^{127}I$ and the period of vibration of $H^{127}I$.

4. The fundamental line in the infrared spectrum of $^{12}C^{16}O$ occurs at 2143.0cm^{-1}, and the first overtone occurs at 4260.0cm^{-1}. Calculate the values of $\tilde{\omega}_e$ and $\tilde{x}_e\tilde{\omega}_e$ for $^{12}C^{16}O$.

5. Verify that $\psi_1(x)$ and $\psi_2(x)$ given in Table 5.4 of the textbook satisfy the Schrodinger equation for a harmonic oscillator.

6. To normalize the harmonic-oscillator wave functions and calculate various expectation values, we must be able to evaluate integrals of the form:

$$I_v(a) = \int_{-\infty}^{\infty} x^{2v} e^{-ax^2} dx \qquad v = 0, 1, 2, ...$$

We can simply either look them up in a table of integrals or continue this problem. First, show that

$$I_v(a) = 2\int_0^{\infty} x^{2v} e^{-ax^2} dx$$

The case $v = 0$ can be handled by the following trick. Show that the square of $I_0(a)$ can be written in the form:

$$I_v^2(a) = 4\int_0^{\infty}\int_0^{\infty} dxdy\, e^{-a(x^2+y^2)}$$

Now convert to plane polar coordinates, letting

$$r^2 = x^2 + y^2 \qquad \text{and} \qquad dxdy = rdrd\theta$$

Show that the appropriate limits of integration are $0 \le r < +\infty$ and $0 \le \theta \le \pi/2$ and that

$$I_0^2(a) = 4\int_0^{\pi/2} d\theta \int_0^{\infty} dr\, re^{-ar^2}$$

which is elementary and gives

$$I_0^2(a) = 4 \cdot \frac{\pi}{2} \cdot \frac{1}{2a} = \frac{\pi}{a}$$

or

$$I_0(a) = (\frac{\pi}{a})^{1/2}$$

Now prove that $I_v(a)$ may be obtained by repeated differentiation of $I_0(a)$ with respect to a and, in particular, that

$$\frac{d^v I_0(a)}{da^v} = (-1)^v I_v(a)$$

Use this result and the fact that $I_0(a) = (\pi / a)^{1/2}$ to generate $I_1(a)$, $I_2(a)$.

7. The three-dimensional harmonic oscillator has the potential-energy function:

$$V = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2$$

where the k_x, k_y, k_z are three force constants. (a) Find the energy eigenvalues of its Schrödinger equation. (b) If $k_x = k_y = k_z$, find the degree of degeneracy of each of the four lowest energy levels.

8. Show that $<p>=0$ and that

$$<p^2>=\int_{-\infty}^{+\infty}\psi_2(x)\hat{P}^2\psi_2(x)dx=\frac{5}{2}\hbar(\mu k)^{1/2}$$

for a harmonic oscillator, where $\psi_2(x)$ can be found in Table 5.4 of the textbook.

9. There are a number of general relations between the Hermite polynomials and their derivatives (which we will not derive). Some of these are

$$\frac{dH_v(\xi)}{d\xi}=2\xi H_v(\xi)-H_{v+1}(\xi)$$

$$H_{v+1}(\xi)-2\xi H_v(\xi)+2vH_{v-1}(\xi)=0$$

and

$$\frac{dH_v(\xi)}{d\xi}=2vH_{v-1}(\xi)$$

Such connecting relations are called recursion formulas. Verify these formulas explicitly using the first few Hermite polynomials given in Table 5.3.

10. Use the recursion formulas for the Hermite polynomials given in Problem 9 to show that $<\mathbf{p}>=\mathbf{0}$ and $<p^2>=\hbar(\mu k)^{1/2}(v+1/2)$.

11. Show the probability of finding the ground state harmonic oscillator in the region forbidden by classical mechanics. (Hint: Ending with an integral expression is totally fine.)

12. Determine the number of translational, rotational, and vibrational degrees of freedom in (a) CH_3Cl (b)OCS (c) C_6H_6 (d) H_2CO

13. Use the fact that

$$\hat{a}^{+}\psi_v = \frac{1}{\sqrt{2}}[(\frac{\mu\omega}{\hbar})^{1/2}\hat{x} - (\frac{\hbar}{\mu\omega})^{1/2}\frac{d}{dx}]\psi_v \propto \psi_{v+1}$$

and that $\psi_0(x) = (\alpha/\pi)^{1/4} e^{-\alpha x^2/2}$ to generate $\psi_1(x)$ and $\psi_2(x)$. (Hint: The normalized constants can be found in Equation 5.46 in the textbook.)

Mathematics:

1. Describe the graphs of the following equations:

(a) $r = 5$ (b) $\theta = \pi/4$ (c) $\phi = \pi/2$

2. Show that the two functions $f_1(\mathbf{r}) = e^{-r}\cos\theta$ and $f_2(\mathbf{r}) = (2-r)e^{-r/2}\cos\theta$ are orthogonal.

3. Express the gradient of a function $f(x, y, z)$ in spherical coordinates.

4. Verify the formula below, which is called *Gaussian product rule*:

$$e^{-a(x-A)^2} \cdot e^{-b(x-B)^2} = e^{-\mu X_{AB}^2} \cdot e^{-p(x-M)^2}$$

Where $p = a + b, \mu = \dfrac{ab}{a+b}, M = \dfrac{aA + bB}{p}, X_{AB} = A - B$