

CHEM 3541 Physical Chemistry  
Answers for Assignment 3

Atkins' Physical Chemistry, 10th Edition

December 1, 2018

## Discussion questions

### 8B.2

If the quantum number  $\nu$  is large enough, the most probable location shifts to the outside of the well. The probability density will look just like the classical probability. The exponential tails into the classically forbidden region decreases with increasing  $\nu$ , so the quantum oscillator looks more and more like the classical one.

You can refer to [this website](#) for more details.

### 8B.3

The physical reason is the uncertainty principle. If a particle is at least partly localized, its position is not completely uncertain, and therefore its momentum, and hence its kinetic energy, cannot be exactly zero. The potential energy of the harmonic oscillator at least partially localizes the oscillator in the neighbourhood of the equilibrium position, so zero momentum (and therefore zero kinetic energy) is precluded. Furthermore, the confinement is not perfect, which makes the particle's potential energy also differ from zero.

### 8C.1

In quantum mechanics, particles are said to have wave characteristics. The fact of the existence of the particle then requires that the wavelengths of the waves representing it be such that the wave does not experience destructive interference in its motion around a closed loop. This means that a whole number of wavelengths must fit on the circumference of the ring:  $n\lambda = 2\pi r$  making the wavelength quantized. This in turn requires the angular momentum and energy to be quantized. Mathematically, this comes out in the cyclic boundary condition discussed in Section 8C.1(b), which restricts the constant  $m_l$  in the wavefunction  $\psi(\phi) = e^{im_l\phi}$  to be an integer. That way, the wavefunction has the same value at  $\phi$  and at  $\phi + 2\pi$  - as it must since these two 'different' angles represent the same angular position. The constant  $m_l$  must be an integer because that ensures  $e^{2\pi im_l} = 1$ .

### 8C.3

A vector can be used to represent angular momentum. The vector's length represents the magnitude of the angular momentum, and its direction is along the axis of rotation. In classical mechanics, both the length and direction are well defined and continuously variable. In quantum mechanics, however, the length is quantized. The orientation of the vector is both restricted and indefinite in that one component of the vector (call it the  $z$  component) is quantized, while the other two components are indefinite. The result is that the classical mechanical vector is replaced by a set of cones that represent vectors allowed by quantum constraints. Each cone is the set of vectors of a given (quantized) length and definite  $z$  component; the cone is generated by taking one such vector and 'sweeping' it through all possible directions in the  $xy$  plane. (The 'sweeping' does not correspond to any sort of motion. At this stage, the model describes time-independent rotational states.)

## Exercises

### 8B.2(a)

The difference in adjacent energy level is

$$\Delta E = E_{\nu+1} - E_{\nu} = \hbar\omega = \hbar \left( \frac{k_f}{m} \right)^{1/2}$$

Hence

$$k_f = m \left( \frac{\Delta E}{\hbar} \right)^2 = 278 \text{ N} \cdot \text{m}^{-1}$$

### 8B.3(a)

The requirement for a transition to occur is that  $\Delta E(\text{system}) = E(\text{photon})$ , so  $\Delta E(\text{system}) = \hbar\omega = E(\text{photon}) = h\nu = \frac{hc}{\lambda}$

Therefore,  $\frac{hc}{\lambda} = \frac{h\omega}{2\pi} = \frac{h}{2\pi} \sqrt{\frac{k_f}{m}}$

$$\lambda = 2\pi c \sqrt{\frac{m}{k_f}} = 2.64 \text{ } \mu\text{m}$$

**8B.5(a)**

(i) From introductory physics, we have

$$\begin{aligned}\omega &= \sqrt{\frac{g}{l}} \\ \Delta E &= \hbar\omega \\ &= 3.3 \times 10^{-34} \text{ J}\end{aligned}$$

(ii)  $\Delta E = h\nu = 3.3 \times 10^{-33} \text{ J}$

**8B.6(a)**

The zero-point energy is  $E_0 = \frac{1}{2}\hbar\omega = \frac{\hbar}{2}\sqrt{\frac{k}{\mu}}$

$$\mu = 2.9033 \times 10^{-26} \text{ kg}$$

so  $E_0 = 5.61 \times 10^{-21} \text{ J}$

**8B.8(a)**

The most probable displacements are the values of  $x$  that maximize  $\psi^2$ . Maxima in  $\psi^2$  correspond to maxima and minima in  $\psi$  itself, so one can solve this exercise by finding all points where  $\frac{d\psi}{dx} = 0$ . The wavefunction is

$$\begin{aligned}\psi_1 &= 2N_1 y \exp(-y^2/2) \text{ with } y = x/\alpha \text{ and } \alpha = \left(\frac{\hbar^2}{mk_f}\right)^{1/4} \\ \frac{d\psi}{dx} &= \frac{dy}{dx} \frac{d\psi}{dy} = \frac{2N_1}{\alpha} [\exp(-y^2/2) - y^2 \exp(-y^2/2)] = 0\end{aligned}$$

Dividing through by constants and the exponential functions yields

$$1 - y^2 = 0 \text{ so } y = \pm 1 \text{ and } x = \pm\alpha$$

**8C.1(a)**

The magnitude of angular momentum is

$$\langle l^2 \rangle^{1/2} = \sqrt{l(l+1)}\hbar = \sqrt{2}\hbar$$

Possible projections on to an arbitrary axis are

$$\langle l_z \rangle = m_l \hbar$$

where  $m_l = 0$  or  $\pm 1$ . So possible projections include  $0, \pm\hbar$ .

### 8C.3(a)

The energy levels of a particle on a ring are given by

$$E = \frac{m_l^2 \hbar^2}{2mr^2}, m_l = 0, \pm 1, \pm 2, \dots$$

The minimum excitation energy is the energy difference between the ground state and the first excited level. So the minimum excitation energy is

$$\Delta E = \frac{(1^2 - 0^2)\hbar^2}{2mr^2} = 3.32 \times 10^{-22} \text{ J.}$$

### 8C.4(a)

The energy levels are

$$E = \frac{l(l+1)\hbar^2}{2I}, l = 0, 1, 2, \dots$$

The minimum energy to start it rotating is the minimum excitation energy, the energy to take it from the motionless  $l = 0$  to the rotating  $l = 1$  state:

$$\Delta E = E_1 = 2.11 \times 10^{-22} \text{ J}$$

### 8C.6(a)

The minimum energy allowed for this system is zero - but that corresponds to rest, not rotation. So the minimum energy of rotation occurs for the state that has  $l = 1$ . The angular momentum in that state is

$$\sqrt{l(l+1)}\hbar = \sqrt{2}\hbar = 1.49 \times 10^{-34} \text{ J} \cdot \text{s}$$

### 8C.8(a)

The rotational energy depends only on the quantum number  $l$ , but there are distinct states for every allowed value of  $m_l$ , which can range from  $-l$  to  $l$  in integer steps. For  $l = 3$ , possible values of  $m_l = 0, \pm 1, \pm 2, \pm 3$ . There are 7 such values, so the degeneracy is 7.

## Problems

### 8B.1

$\omega = \sqrt{\frac{k_f}{\mu}}$ . Also,  $\omega = 2\pi\nu = 2\pi c\tilde{\nu}$ . Therefore  $k_f = \omega^2\mu = 4\pi^2c^2\tilde{\nu}^2\mu = \frac{4\pi^2c^2\tilde{\nu}^2m_1m_2}{m_1+m_2}$

Therefore we can calculate all the  $k_f$  for these five species with unit  $\text{N} \cdot \text{m}^{-1}$  as 516,412,314,1902,1595.

Therefore, the order of stiffness is  $\text{HI} < \text{HBr} < \text{HCl} < \text{NO} < \text{CO}$ .

### 8B.5

$$\langle E_k \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{E}_k \psi dx$$

$$\hat{E}_k = -\frac{\hbar\omega}{2} \frac{d^2}{dx^2} = -\frac{\hbar^2}{2m\alpha^2} \frac{d^2}{dy^2} = -\frac{\hbar\omega}{2} \frac{d^2}{dy^2}, \left[ x = \alpha y, \alpha^2 = \frac{\hbar}{m\omega} \right]$$

which implies that

$$\hat{E}_k \psi = -\frac{\hbar\omega}{2} \frac{d^2\psi}{dy^2}$$

We then use  $\psi = NH \exp(-y^2/2)$ , and obtain

$$\frac{d^2\psi}{dy^2} = N \frac{d^2}{dy^2} [H \exp(-y^2/2)] = N(H'' - 2yH' - H + y^2H) \exp(-y^2/2)$$

From Table 8B.1

$$\frac{d^2\psi}{dy^2} = N \left[ \frac{1}{4}H_{\nu+2} + \nu(\nu-1)H_{\nu-2} - \left(\nu + \frac{1}{2}\right)H_{\nu} \right] \exp(-y^2/2)$$

Therefore,

$$\begin{aligned} \langle E_k \rangle &= N_{\nu}^2 \left( -\frac{\hbar\omega}{2} \right) \int_{-\infty}^{+\infty} H_{\nu} \left[ \frac{1}{4}H_{\nu+2} + \nu(\nu-1)H_{\nu-2} - \left(\nu + \frac{1}{2}\right)H_{\nu} \right] \exp(-y^2) dx \\ &= \alpha N_{\nu}^2 \left( -\frac{\hbar\omega}{2} \right) \left[ -\left(\nu + \frac{1}{2}\right) \sqrt{\pi} 2^{\nu} \nu! \right] \\ &= \frac{1}{2} \left(\nu + \frac{1}{2}\right) \hbar\omega \end{aligned}$$

### 8B.11

As expressed in the problem, the potential energy function assumes that is defined as we would expect; that is,  $\phi = 0$  corresponds to an eclipsed conformation. Thus,  $\phi = 0$  is not a stable equilibrium point, and small displacements from this point are not harmonic; in fact,  $\phi = 0$  is a position of unstable equilibrium, and small displacements from it would grow larger. We must express the potential energy in terms of displacements from a stable equilibrium position. One such equilibrium position is the staggered conformation directly opposite  $\phi = 0$ , namely  $\phi = \pi$ . So let the displacement  $x = \phi - \pi$ . So, in terms of  $x$ , the potential energy function

is  $V = -V_0 \cos 3x$ . Conventionally, the potential energy in harmonic motion is measured with respect to that stable equilibrium position. Note that the potential energy at the stable equilibrium position is  $V = -V_0$ . We can redefine the potential energy function to measure energy relative to the stable equilibrium by letting

$$V' = V_0 + V = V_0 - V_0 \cos 3x = V_0(1 - \cos 3x).$$

Use the first two terms of the Taylor series expansion of cosine:

$$V' = V_0(1 - \cos 3x) \approx \frac{9V_0}{2}x^2$$

The Schrödinger equation becomes

$$-\frac{\hbar^2}{2I} \frac{\partial^2 \psi}{\partial x^2} + \frac{9V_0}{2} x^2 \psi = E \psi$$

This has the form of the Schrödinger equation for the harmonic oscillator wavefunction. The difference in adjacent energy levels is:

$$E_1 - E_0 = \hbar\omega \text{ where } \omega = \sqrt{\frac{9V_0}{I}}$$

If the displacements are sufficiently large, the potential energy does not rise as rapidly with the angle as would a harmonic potential (i.e. The cosine potential energy is not well approximated by the first few terms of its expansion). Each successive energy level would become lower than that of a harmonic oscillator, so the energy levels would become progressively closer together.

### 8C.1

The angular momentum states are defined by the quantum number  $m_l = 0, \pm 1, \pm 2$ , etc. The energy of state  $m_l$  is  $E_{m_l} = \frac{m_l^2 \hbar^2}{2I}$  and the angular momentum is  $J_z = m_l \hbar$ .

(a) If there are 22 electrons, two in each of the lowest 11 states, then the highest occupied states are  $m_l = \pm 5$ , so,  $J_z = \pm 5.275 \times 10^{-34} \text{ J} \cdot \text{s}$  and  $E_{\pm 5} = \frac{25\hbar^2}{2I}$ .

The moment of inertia of an electron on a ring of radius 440 pm is  $I = mr^2 = 1.76 \times 10^{-49} \text{ kg} \cdot \text{m}^2$ . Hence  $E_{\pm 5} = 7.89 \times 10^{-19} \text{ J}$ .

(b) The lowest unoccupied energy level is  $m_l = \pm 6$ , which has energy  $E_{\pm 6} = 1.14 \times 10^{-18} \text{ J}$ . Radiation that would induce a transition between these levels must have a frequency such that  $\nu = \Delta E/h = 5.2 \times 10^{14} \text{ Hz}$ . This corresponds to a wavelength of about 570 nm, a wave of visible light.

### 8C.3

In each case, if the function is an eigenfunction of the operator, the eigenvalue is also the expectation value; if it is not an eigenfunction we form  $\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi d\tau$ .

For the  $z$ -component of the angular momentum: (a)  $\hbar$  (b)  $-2\hbar$  (c) 0 (d)  $\hbar \cos 2\chi$

For the kinetic energy: (a)  $\hbar^2/2I$  (b)  $2\hbar^2/I$  (c)  $\hbar^2/2I$  (d)  $\hbar^2/2I$

### 8C.5

$$E = \frac{l(l+1)\hbar^2}{2I} = \frac{l(l+1)\hbar^2}{2\mu R^2} = l(l+1) \times (1.31 \times 10^{-22} \text{ J})$$

Hence, the energies are (in  $10^{22}$  J) 0, 2.62, 7.86, 15.72.

### 8C.7

Call the integral  $I$ :

$$I = \int_0^\pi \int_0^{2\pi} Y_{3,3}^* Y_{3,3} \sin \theta d\theta d\phi = \frac{1}{64} \frac{35}{\pi} \int_0^\pi \sin^7 \theta d\theta \int_0^{2\pi} d\phi$$

Integration over  $d\phi$  yields a factor of  $2\pi$ . Noting that  $\sin \theta d\theta = d \cos \theta$ , and that  $\sin^2 \theta = 1 - \cos^2 \theta$ , the integral becomes

$$I = \frac{35}{32} \int_{-1}^1 (1 - \cos^2 \theta)^3 d \cos \theta$$

Letting  $x = \cos \theta$  and expanding the integrand, we have

$$I = \frac{35}{32} \int_{-1}^1 (1 - 3x^2 + 3x^4 - x^6) dx = 1$$

### 8C.8

$$\begin{aligned} \nabla^2 f &= \frac{d^2 \cos ax}{dx^2} \cos by \cos cz + \cos ax \frac{d^2 \cos by}{dy^2} \cos cz + \cos ax \cos by \frac{d^2 \cos cz}{dz^2} \\ &= -(a^2 + b^2 + c^2) \cos ax \cos by \cos cz \\ &= -(a^2 + b^2 + c^2) f \end{aligned}$$

Thus  $f$  is indeed the eigenfunction of  $\nabla^2$  with eigenvalue  $-(a^2 + b^2 + c^2)$ .

### 8C.9

Please refer to the slides for week 12.