5.61 Fall 2017 Problem Set #1 Solutions

1. Transfer of momentum between a photon and a particle

A. Compute the momentum of one 500nm photon using $p_{\text{photon}} = E_{\text{photon}}/c$ where c is the speed of light, $c = 3 \times 10^8 \ m/s$, and $\nu = c/\lambda$.

Solution:

The Concept: Explore Particle-Wave Duality

$$p_{\text{proton}} = E_{\text{proton}}/c$$

$$p = \text{Momentum}$$

$$E = \text{Energy} = h\nu$$

$$c = \text{Speed of light, } 3 \times 10^8 m/s$$

$$p_{\rm PH} = \frac{h\nu}{c} \quad \nu = c/\lambda$$

$$p_{\rm PH} = h/\lambda \ (\lambda \text{ in meters}), \ 500nm = 500 \times 10^{-9}m$$

$$p_{\rm PH} = h/500 \times 10^{-9} = 6.626 \times 10^{-34}/500 \times 10^{-9} = 1.325 \times 10^{-27} \text{kg m/s}$$

B. You are going to use a photon to observe one point on the trajectory of a Na atom between a source and a target. Suppose the photon hits the Na atom and is permanently absorbed by the Na atom. What is the change in velocity of the Na atom?

Solution:

Na ATOMS $\rightarrow 22.99 \text{ g/mol}$ $\frac{0.02299 \text{ }kg}{\text{mol}} \cdot \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{Atoms}}$ AVERAGE MASS OF ONE Na ATOM = $\boxed{3.818 \times 10^{-26} \text{ kg/atom}}$

$$\begin{split} \Delta p &= m \Delta \nu = 3.818 \times 10^{-26} kg \quad \Delta \nu = \Delta p = h/\lambda \text{(in meters)} \\ \Delta v &= \frac{h}{\lambda (3.818 \times 10^{-26} kg)} \quad \text{IF IT'S THE PHOTON (from Part A) } \Delta v = 0.0347 m/s \end{split}$$

C. Answer the same question for the photon hitting and being absorbed by an electron.

Solution

MASS $e^- = 9.109 \times 10^{-31}$ kg BY SAME ALGEBRA

$$\Delta v = \frac{h}{\lambda(9.109 \times 10^{-31} kg)} \quad \text{Photon from Part } \mathbf{A}, \, \Delta v = 1450 m/s$$

D. A photon of $\lambda = 500$ nm can determine the position of an atom to $\Delta x \approx 500$ nm. Compute $\Delta x \Delta p$ for detection of a Na atom by a 500 nm photon.

Solution

$$\Delta x \Delta p \approx 500 nm \cdot 1.325 \times 10^{-27} kg \ m/s \ (\text{See Part } \mathbf{A})$$
$$= 500 \times 10^{-9} \cdot 1.325 \times 10^{-27} = 6.63 \times 10^{-34} kg \ m^2/s$$

E. Suppose instead you use a 1 nm photon. Will $\Delta x \Delta p$ be smaller, larger, or the same as for a 500 nm photon?

Solution

LET'S TRY MORE SYMBOLICALLY THIS TIME

$$\begin{split} \Delta x \Delta p &\approx \lambda \Delta p \\ \Delta p &= h/\lambda \\ \Delta x \Delta p &= \lambda h/\lambda = h = \boxed{6.63 \times 10^{-34} \ kg \ m^2/s} \end{split}$$

2.

A. A baseball has diameter = 7.4 cm. and a mass of 145g. Suppose the baseball is moving at v = 1nm/second. What is its de Broglie wavelength

$$\lambda = \frac{h}{p} = \frac{h}{m\nu}$$

and will such a slow moving baseball diffract off of the stationary bat of a player attempting to bunt the ball?

<u>Solution</u>

$$D_{\text{ball}} = 0.074m$$
$$m_{\text{ball}} = 0.145 \ kg$$
$$v_{\text{ball}} = 1 \ nm/s = 1 \times 10^{-9} m/s$$

Using de Broglie:

$$\lambda_{\text{ball}} = \frac{h}{p} = \frac{h}{m\nu} = \frac{6.626 \times 10^{-34} m^2 kg/s}{0.145 \ kg \cdot 1 \times 10^{-9} \ m/s} = \boxed{4.6 \times 10^{-24} m = \lambda_{\text{ball}}}$$

NOTE: At first glance, you might notice how slow the ball is moving and think it will have a small momentum, resulting in a relatively large λ . However, the large mass of the baseball (it is on the macroscopic scale, not atomic) means that the ball has an *extremely* large momentum in terms of quantum mechanical problems, leading to an extremely small de Broglie wavelength.

The ball will <u>NOT</u> diffract off the bat because the λ_{ball} is ~ 23 orders of magnitude smaller than the bat.

B. How might you measure the velocity of a baseball moving at $v \approx 1$ nm/sec?

Solution:

Because the ball is moving so slowly, traditional techniques (doppler radar, high speed cameras with length scales) will be unable to measure the speed of the ball (even modern equipment can't measure such minute differences). Multiple possible schemes exist, but here is one possible setup:

- use coherent nm x-ray source monochromatic, in-phase x-rays
- when light path from baseball→detector and mirror→detector differ by an integer number of wavelengths, we see constructive interference.
- when these paths differ by $\frac{1}{2}$ (integer wave-length) we see destructive interference.
- We see alternating bright and dark regions on the detector.



3. A pulsed Nd:YAG laser is found in many physical chemistry laboratories.

A. For a 2.00mJ pulse of laser light, how many photons are there at 1.06μ m (the Nd:YAG fundamental), 537nm (the 2nd harmonic), and 266nm (the 4th harmonic)?

Solution:

The concept: Practice using the concepts of photons and their energy. Given the total energy, use the energy per photon to determine the number of photons.

For 1.06 μm Light Energy of one photon = $E_p = h\nu; \nu = c/\lambda; E_p = hc/\lambda$ $\lambda = 1.06 \mu m = 1.06 \times 10^{-6} m$ $c = 3 \times 10^8 m/s$ $h = \text{Planck's constant} = 6.626 \times 10^{-34} kg m^2/s$

 $E_p = 1.88 \times 10^{-19} J$ 1.88×10^{-19} J/photon, we want photons/pulse.

$$\frac{1}{1.88 \times 10^{19} \text{J/photon}} \times \frac{2.00 \times 10^{-3}}{\text{pulse}} = \boxed{1.07 \times 10^{16} \text{photons/pulse}}$$

For 537nm Light

2 possible strategies — 1 is the same as above. Note that $\lambda_{ii} = \frac{1}{2}i$; thus each photon has 2× the energy Each pulse has 1/2 the photons = 5.35 × 10¹⁵ photons/pulse

For 266 nm Light

Same 2 strategies as part ii) $\rightarrow 2.68 \times 10^{15}$ photons/pulse

B. The duration of a typical Nd:YAG laser pulse is 6 nanoseconds. During the laser pulse, (2 mJ at 1.06 μ m) what are:

i) the number of photons/second?

Solution:

From A. we know how many photons per pulse

$$1.07 \times 10^{16}$$
 photons/pulse $\cdot \frac{1}{6 \cdot 10^{-9} \ s/pulse} = 1.8 \times 10^{24} \text{ photons/sec}$

and *ii*) the power in Watts (Joules/second)?

Solution:

We know from above that each pulse has $E = 2 \times 10^{-3} J$

Power =
$$\frac{2 \times 10^{-3} J}{6 \times 10^{-9} s} = \boxed{3 \times 10^5 W}$$

4. from McQuarrie, page 38, #19

A. Given that the work function of chromium is 4.40 eV, calculate the kinetic energy of electrons emitted from a clean chromium surface that is irradiated with ultraviolet radiation of wavelength 200 nm.

Solution:

The chromium surface is irradiated with 200 nm UV light. These photons have energy

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{34} J \cdot s)(3 \times 10^8 m \cdot s^{-1})}{200 \times 10^{-9} m}$$

= 9.94 × 10⁻¹⁹ J
= 6.20 eV

The photo–ejected electron has kinetic energy

$$KE = E_{\text{photon}} - \phi_o = 6.20eV - 4.40eV = 1.80eV = 2.88 \times 10^{-19} J$$

B. What are the speed and the de Broglie wavelength of the ejected electron from question 4A?

Solution:

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

 $\rightarrow v + \sqrt{2KE/m} = \sqrt{2 \cdot 1.80eV/(9.11 \times 10^{-31}kg)} = 7.96 \times 10^5 m/s$
 $\rightarrow \lambda_{\text{deBroglie}} = h/p = h/\sqrt{2}mKE = 9.14 \times 10^{-10}m = 9.14$

5. From McQuarrie, page 38, #21

Some data for the kinetic energy of ejected electrons as a function of the wavelength of the incident radiation for the photoelectron effect for sodium metal are shown below:

| λ/nm | 100 | 200 | 300 | 400 | 500 |
|--------------|------|------|------|-------|-------|
| KE/eV | 10.1 | 3.94 | 1.88 | 0.842 | 0.222 |

Use some sort of plot of these data to determine values for h and ϕ .

Solution:

First, let's remind ourselves of the relationship between the electron's max KE and the incident photon wavelingth

$$KE = h\nu - \phi = \frac{hc}{\lambda} - \phi.$$

Plotting KE vs. $1/\lambda$ will yield a straight line, with slope hc and intercept $-\phi$. Below is an example plot (note the units). 12



The fit yielded the following results:

$$KE = a\left(\frac{1}{\lambda}\right) + b$$
$$a = hc = 1234 \pm 3eV \cdot nm$$
$$b = -\phi = -2.24 \pm 0.02eV$$

First, solving for ϕ , we get

$$\phi = 2.24 \pm 0.02 \ eV$$

Solving for Planck's constant, we find

$$h = \frac{a}{c} = \frac{(1234 \pm 3)eV \cdot nm}{3 \times 10^8 m \cdot s^{-1}}$$

= (4.113 ± 10) × 10⁻¹⁸ eV · s
= (6.589 ± 0.016) × 10⁻³⁴ J · s

compared to $6.626 \times 10^{-34} J \cdot s$.

6. From McQuarrie, page 39, #32

A. Derive the Bohr formula for $\tilde{\nu}$ (a modified form of Eq. 1.29) for one electron bound to a nucleus of atomic number Z.

Solution:

This problem asks us to find the difference in energy (in wavenumbers, $\tilde{\nu}$), between different levels of a Bohr atom with nuclear charge +Ze. The first step is to setup the kinematics of circular motion in a Coulomb potential. Then we will apply quantization of angular momentum by units of \hbar . This will allow us to determine the energies of each quantized level, from which we can determine the Bohr formula.

Circular motion of electron in Coulomb potential:

The electron experiences an inward electrostatic force with magnitude:

$$f_{\rm Coulomb} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

which must equal the centripetal force maintaining the circular orbit, so

$$\frac{Ze^2}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r}.$$

We will want to find the angular momentum of the electron, so it's necessary to solve the above equation for v,

$$v = \sqrt{\frac{Ze^2}{4\pi\varepsilon_0 r m_e}}$$

The angular momentum, $L = p \times r = mvr$ is then,

$$L = mvr = \sqrt{\frac{Ze^2m_er}{4\pi\varepsilon_0}}$$

Applying Bohr's postulate, we force the angular momentum to be quantized in units of \hbar ,

$$L_n = \sqrt{\frac{Ze^2m_er_n}{4\pi\varepsilon_0}} = n\hbar.$$

Below we will need the value of r_n . Solving for that now gives

$$r_n = \frac{n^2 \hbar^2 4\pi\varepsilon_0}{Z e^2 m_e}$$

Now that we've quantized the angular momentum, we can determine the total energy of each discrete state. The total energy will be the orbital kinetic energy and the electrostatic potential energy,

$$E_n = \frac{L_n^2}{2I} + V(r_n)$$
$$= \frac{n^2\hbar^2}{2m_e r_n^2} + \frac{-Ze^2}{4\pi\varepsilon_0 r_n}.$$

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Substituting r_n with the expression we found above yields

$$E_n = \frac{n^2 \hbar^2 Z^2 e^4 m_e^2}{2m_e n^4 \hbar^4 (4\pi\varepsilon_0)^2} = \frac{Z^2 e^4 m_e}{n^2 \hbar^2 (4\pi\varepsilon_0)^2}$$
$$= -\frac{1}{2} \left(\frac{Z^2 e^4 m_e}{n^2 \hbar^2 (4\pi\varepsilon_0)^2} \right)$$
$$= -\frac{1}{8} \left(\frac{Z^2 e^4 m_e}{h^2 \varepsilon_0^2} \right) \frac{1}{n^2}.$$

The Bohr formula can now be obtained:

$$\begin{split} \tilde{\nu} &= \frac{1}{\lambda} = \frac{v}{c} = \frac{E_{m_2} - E_{m_1}}{hc} \\ &= -\frac{Z^2 e^4 m_e}{8h^3 c \varepsilon_0^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \\ &= Z^2 R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \end{split}$$

Note that this formula assumes an infinitely heavy nucleus (which isn't such a bad approximation). A further refinement is to replace the Rydberg constant, R_{∞} , as

$$R_{\infty} \to R_M = R_{\infty} \frac{1}{1 + m_e/M},$$

where M is the nuclear mass. This is identical with replacing the electron mass, m_e , with the reduced mass of the electron-nucleus system, $\mu = \frac{m_e M}{m_e + M}$.

B. Use the Bohr Theory to predict the wavelength (in Å) of the $n = 2 \leftarrow n = 1$ "Lyman α " transition of a U⁺⁹¹ atomic ion.

Solution:

The Lyman α transition of U⁺⁹¹ corresponds to $n = 2 \rightarrow n = 1$. This transition occurs at

$$\tilde{\nu} = Z^2 R_{\infty} \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$
$$= \frac{3}{4} Z^2 R_{\infty}.$$

The wavelength of this transition is

$$\begin{split} \lambda &= \frac{1}{\tilde{\nu}} = \frac{4}{3Z^2 R_{\infty}} \\ &= \frac{4}{3(92^2)(1.09737 \times 10^{-3} \text{\AA}^{-1})} \\ &= 0.14 \text{ \AA}. \end{split}$$

C. For the U⁺⁹¹ n = 1 Bohr orbit, what are the radius and the electron speed? Is there anything impossible about this result?

Solution:

The radius of the n = 1 Bohr orbit can be obtained from part **A**, where we determined

$$r_n = \frac{n^2 \hbar^2 4\pi \varepsilon_0}{Z e^2 m_e}.$$

Substituting n = 1 and Z = 92 gives

$$r_{1} = \frac{1^{2}(1.0545 \times 10^{-34} J \cdot s)^{2} 4\pi (8.8542 \times 10^{-12} F \cdot m^{-1})}{92(1.602 \times 10^{-19} C)^{2} (9.11 \times 10^{-31} kg)}$$

= $a_{0}/92$
= 5.75×10^{-3} Å.

The electron speed can be found by using any one of the many relations we have for v. The simplest is the angular momentum quantization condition $m_e v r_n = n\hbar$,

$$v = \frac{n\hbar}{m_e r_1} = \frac{(1)(1.0545 \times 10^{-34} J \cdot s)}{(9.11 \times 10^{-31} kg)(5.75 \times 10^{-3} \text{ \AA})}$$
$$= 2.01 \times 10^8 m \cdot s^{-1}.$$

This velocity is a significant fraction of the speed of light. Therefore, we expect that relativistic effects will be non-negligible in U^{91+} .

D. For U^{+91} n = 1000, what are the orbit-radius and speed?

Solution:

We are asked to do the same as part **C**, but with n = 1000. This is a good chance to use scaling laws, which are both extremely useful and insightful. In this case, we are interested in how certain quantities, namely radius and velocity, scale with the principle quantum number, n. Examining our expressions for r_n and v_n , we obtain

$$r \propto n^2$$

 $v \propto n^{-1}$.

With n = 1000, we can simply scale our answers to part C yielding

$$r_{1000} = r_1 \cdot 1000^2 = 5.75 \times 10^3 \text{ Å}$$

 $v_{1000} = v_1/1000 = 2.01 \times 10^5 m \cdot s^{-1}.$

OPTIONAL PROBLEMS (7-10 BELOW)

Questions about complex numbers and complex functions of a real variable.

7. From McQuarrie, page 49, #A-2

If z = x + 2i y, then find

A. $\operatorname{Re}(z^*)$

Solution: Re(x+2iy) = x

B. $\operatorname{Re}(z^2)$

Solution: $Re((x+2iy)^2) = Re(x^2 + 4ixy - 4y^2) = x^2 - 4y^2$

C. $Im(z^2)$

Solution: $Im(x^2 + 4ixy - 4y^2) = 4xy$

D. $\operatorname{Re}(zz^*)$

Solution: $Re(x - 2iy)(x + 2iy)) = Re(x^2 + 4y^2) = x^2 + 4y^2$

E. $\operatorname{Im}(zz^*)$

Solution: $Im(x^2 + 4y^2) = 0.$

8. From McQuarrie, page 49, #A-3 and #A-4

A. Express the following complex numbers in the form $re^{i\theta}$:

i) 6iii) $4 - \sqrt{2}i$ iii) -1 - 2iiv) $\pi + ei$

Solution:



B. Express the following complex numbers in the form x + iy:

i) $e^{i\pi/4}$ ii) $6e^{2\pi i/3}$ iii) $e^{-(\pi/4)/i+\ln 2}$ iv) $e^{-2\pi i} + e^{4\pi i}$

Solution:

 $z = re^{i\theta} = r\cos\theta + ir\sin\theta$

i)
$$z = \cos\left(\frac{\pi}{4}\right) + i\sin\left(\frac{\pi}{4}\right) = \left\lfloor\frac{\sqrt{2}}{2} + i\frac{\sqrt{2}}{2}\right\rfloor$$

ii) $z = 6\cos\left(\frac{2\pi}{3}\right) + 6i\sin\left(\frac{2\pi}{3}\right) = \left[-3 + i3\sqrt{3}\right]$
iii) $z = e^{\ln 2}e^{-\left(\frac{\pi}{4}\right)i} = 2\cos\left(\frac{-\pi}{4}\right) + 2i\sin\left(\frac{-\pi}{4}\right) = \left[\sqrt{2} - i\sqrt{2}\right]$
iv) $z = (\cos(-2\pi) + i\sin(-2\pi) + \cos(4\pi) + i\sin(4\pi)) = \left[2\right]$

9. From McQuarrie, page 49,50 #A-6 – A-8 and A-10

A. Show that

and

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$
$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$$

Solution:

This is a simple application of Euler's relation $e^{i\theta} = \cos\theta + i\sin\theta$:

$$\frac{e^{i\theta} + e^{-i\theta}}{2} = \frac{\cos\theta + i\sin\theta + \cos(-\theta) + i\sin(-\theta)}{2}$$
$$= \frac{2\cos(\theta)}{2} = \cos(\theta),$$

and

$$\frac{e^{i\theta} - e^{-i\theta}}{2i} = \frac{\cos\theta + i\sin\theta - \cos(-\theta) - i\sin(-\theta)}{2i}$$
$$= \frac{2i\sin\theta}{2i} = \sin\theta.$$

B. Use McQuarrie A.6 Equation to derive

$$z^{n} = r^{n}(\cos\theta + i\sin\theta)^{n} = r^{n}(\cos n\theta + i\sin n\theta)$$

and from this, the formula of de moivre:

$$(\cos\theta + i\sin\theta)^n = \cos n\theta + i\sin n\theta.$$

Solution:

$$z^{n} = (re^{i\theta})^{n}$$

= $r^{n}(e^{i\theta})^{n} = r^{n}(e^{in\theta})$
= $r^{n}(\cos\theta + i\sin\theta)^{n} = r^{n}(\cos n\theta + i\sin\theta)$
 $\rightarrow (\cos\theta + i\sin\theta)^{n} = \cos n\theta + i\sin n\theta$

C. Use the formula of de Moivre, which is given in part **B**, to derive the following very useful trigonometric identities:

$$\cos 2\theta = \cos^2 \theta - \sin^2 \theta$$
$$\sin 2\theta = 2 \sin \theta \cos \theta$$
$$\cos 3\theta = \cos^3 \theta - 3 \cos \theta \sin^2 \theta$$
$$= 4 \cos^3 \theta - 3 \cos \theta$$
$$\sin 3\theta = 3 \cos^2 \theta \sin \theta - \sin^3 \theta$$
$$= 3 \sin \theta - 4 \sin^3 \theta.$$

Solution:

$$(\cos \theta + i \sin \theta)^{2} = (\cos 2\theta) + i(\sin 2\theta) \quad (\text{by part } \mathbf{B})$$
$$(\cos^{2} \theta - \sin^{2} \theta) + i(2 \sin \theta \cos \theta) = (\cos 2\theta) + i(\sin 2\theta)$$
$$\rightarrow \cos 2\theta = \cos^{2} \theta - \sin^{2} \theta$$
$$\rightarrow \sin 2\theta = 2 \sin \theta \cos \theta$$
$$(\cos \theta + i \sin \theta)^{3} = (\cos 3\theta) + i(\sin 3\theta)$$
$$(\cos^{3} \theta - 3 \cos \theta \sin^{2} \theta) + i(3 \cos^{2} \theta \sin \theta - \sin^{3} \theta) = (\cos 3\theta) + i(\sin 3\theta)$$
$$\rightarrow \cos 3\theta = \cos^{3} \theta - 3 \cos \theta \sin^{2} \theta$$
$$= 4 \cos^{3} \theta - 3 \cos \theta$$
$$\rightarrow \sin \theta = 3 \cos^{2} \theta \sin \theta - \sin^{3} \theta$$
$$= 3 \sin \theta - 4 \sin^{3} \theta.$$

10. From McQuarrie, page 50, #A-9

Consider the set of functions

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad \begin{cases} m = 0, \pm 1, \pm 2, \dots \\ 0 \le \phi \le 2\pi \end{cases}$$

First show that

$$\int_0^{2\pi} d\phi \Phi_m(\phi) = \begin{cases} 0 & \text{for all values of } m \neq 0 \\ \sqrt{2\pi} & m = 0. \end{cases}$$

Next show that

$$\int_0^{2\pi} d\phi \Phi_m^*(\phi) \Phi_n(\phi) = \begin{cases} 0 & m \neq n \\ 1 & m = n. \end{cases}$$

Solution:

Our set of functions is defined as

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi},$$

where $m = 0, \pm 1, \pm 2, \ldots$ We must first evaluate the integral of each function over the range $[0, 2\pi]$.

$$\int_0^{2\pi} \Phi_m(\phi) d\phi = \frac{1}{\sqrt{2\pi}} \int_0^{2\pi} e^{im\phi} d\phi$$
$$= \frac{1}{\sqrt{2\pi}} \int_0^{2\pi} (\cos m\phi + i\sin m\phi) d\phi.$$

For $m \neq 0$, the integral over each trigonometric function is zero because they each have a period that is a multiple of 2π . For m = 0, the sin $m\phi$ term is zero, and the cos $m\phi$ term is 1, leaving

$$\frac{1}{\sqrt{2\pi}} \int_0^{2\pi} d\phi = \frac{2\pi}{\sqrt{2\pi}} = \sqrt{2\pi}.$$

In summary,

$$\int_0^{2\pi} \Phi_m(\phi) d\phi = \begin{cases} 0 & m \neq 0\\ \sqrt{2\pi} & m = 0. \end{cases}$$

Now we must evaluate the integrals $\int_0^{2\pi} \Phi_m^*(\phi) \Phi_n(\phi) d\phi$ for all m and n.

$$\int_{0}^{2\pi} \Phi_{m}^{*}(\phi) \Phi_{n}(\phi) d\phi = \frac{1}{2\pi} \int_{0}^{2\pi} e^{-im\phi} e^{in\phi} d\phi$$
$$= \frac{1}{2\pi} \int_{0}^{2\pi} e^{i(n-m)\phi} d\phi$$

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5.61 Physical Chemistry Fall 2017

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