PH 253 / LeClair   Fall 2010

Problem Set 7: Solutions

1. **(a)** How many different photons can be emitted by hydrogen atoms that undergo transitions from the ground state from the $n=4$ state? **(b)** Enumerate their energies, in electron volts.

Solution: One can brute-force this quickly enough to find that there are 6 transitions. One may also solve the problem for an arbitrary n. The number of possible transitions is just equal to the number of ways one can choose 2 numbers from a set of n without worrying about their order (i.e., the number of combinations choosing 2 elements from a set of n):

$$\text{(number of different photons)} = \binom{n}{2} = \frac{n!}{2!\,(n-2)!} = \frac{n\,(n-1)}{2} \tag{1}$$

Note that this is also the sum of the first $n-1$ integers. This works because the order does not matter: if we have $n=4$ and pick the pair $(4,3)$ or $(3,4)$ we need only count the first ordering, not the second, since we only want downward transitions. Hence, we use a combination rather than a permutation. Further, you can easily convince yourself that this includes all possible intermediate states, accounting for multi-step transitions such as $4 \to 3 \to 1$. Given $n=4$, we readily find 6 different transitions from the formula above.

Of course, since we want the energies, we'll need to enumerate all the possibilities anyway, but now we at least know how many there should be. All states from $n=4$ to $n=1$ have different energies, and their spacing is not equal. Thus, we have the following possible paths from $n=4$ to the ground state:

$$4 \to 1$$
$$4 \to 2, 2 \to 1$$
$$4 \to 3, 3 \to 1$$
$$4 \to 3, 3 \to 2, 2 \to 1$$

The different photons that can be emitted correspond to the unique level transitions above:

$$4 \to 1$$
$$4 \to 2$$
$$4 \to 3$$
$$3 \to 2$$
$$3 \to 1$$
$$2 \to 1$$

Thus, there are 6 possible transitions, just as we calculated above, and the energy differences are calculated according to the Bohr model

$$\Delta E_{nn'} = -13.6\,\text{eV}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) \tag{2}$$

where $n=4$ and $n'=\{3, 2, 1\}$ are the numbers of the initial and final states, respectively.

2. The wave function for the 3s state of hydrogen $(n=3, l=0, m_l=0)$ is

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}a_o^{3/2}}\left(27 - 18\frac{r}{a_o} + 2\frac{r^2}{a_o^2}\right)e^{-r/3a_o} \tag{3}$$

where a_o is the Bohr radius.

(a) What is the *most probable* value of r?
(b) What is $\langle r \rangle$?
(c) What is the total probability of finding the electron at a distance greater than this radius?

Solution: The probability density is easy enough to write down:

$$P = 4\pi r^2 |\psi|^2 = \frac{4r^2}{19683a_o^3}\left(27 - 18\frac{r}{a_o} + 2\frac{r^2}{a_o^2}\right)^2 e^{-2r/3a_o} \tag{4}$$

The most probable radius is when $dP/dr=0$. The probability density is messy, and the derivative will only be worse. Perhaps we should employ a computing device of some sort. Go to Wolfram Alpha

http://www.wolframalpha.com

and type in the probability density above, with $x=r/a_o$ and ignoring all the irrelevant multiplying constants:

$$(d/dx)(x^2(27 - 18x + 2x^2)^2 * e \wedge (-2x/3))$$

Presto, it calculates the derivatives *and* tells you the roots. A quick plot verifies that the global maximum is at the largest root, $r \approx 13.07a_o$. The expected value of r is found from

$$\langle r \rangle = \int_0^\infty r|\psi^2| \, 4\pi r^2 \, dr = \int_0^\infty \frac{4r^3}{19683a_o^3} \left(27 - 18\frac{r}{a_o} + 2\frac{r^2}{a_o^2}\right)^2 e^{-2r/3a_o} \, dr \qquad (5)$$

Again, let $x = r/a_o$, and let Wolfram do the work, just enter

integral of $(4x^3/(19683)) * (27 - 18x + 2x^2)^2 * e \wedge (-2x/3)$ from 0 to infinity

into Wolfram Alpha, and you'll find $\langle r \rangle = 27/2$. The general result is

$$\langle r \rangle = a_o n^2 \left(\frac{3}{2} - \frac{l(l+1)}{n^2}\right) \qquad (6)$$

for what it's worth. Abuse Wolfram once more to find the probability that the electron is outside this radius, since we just need to integrate P from $\langle r \rangle$ to ∞. Given the form of P above, this amounts to typing this into Wolfram:

integral of $(4r^2/(19683)) * (27 - 18r + 2r^2)^2 * e \wedge (-2r/3)$ from 13.5 to infinity

which yields ≈ 0.512.

3. Schrödinger's equation for a simple harmonic oscillator reads

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi \qquad (7)$$

The ground state wave function has the form

$$\psi_o = ae^{-\alpha^2 x^2} \qquad (8)$$

(a) Determine the value of the constant α and the energy of the state.
(b) Find $\langle r \rangle$, $\langle r^2 \rangle$, and Δr.

Solution: We really just need to substitute into Schrödinger's equation. First, we will need $\frac{\partial^2 \psi}{\partial x^2}$:

$$\frac{\partial \psi}{\partial x} = -2\alpha^2 x a e^{-\alpha^2 x} \tag{9}$$

$$\frac{\partial^2 \psi}{\partial x^2} = -2\alpha^2 a e^{-\alpha^2 x} + 4\alpha^4 x^2 a e^{-\alpha^2 x} = \psi_o \left(4\alpha^4 x^2 - 2\alpha^2\right) \tag{10}$$

Next, we substitute in to Schrödinger's equation:

$$-\frac{\hbar^2}{2m} \left(4\alpha^4 x^2 - 2\alpha^2\right) \psi_o + \frac{1}{2} m\omega^2 x^2 \psi_o = E\psi_o \tag{11}$$

If this equation is to have a general solution, the coefficients of the x^2 terms on either side must be the same, and the constant terms on either side must be equal in sum. The quadratic terms give:

$$\frac{4\hbar^2 \alpha^4}{2m} = \frac{1}{2} m\omega^2 \qquad \Longrightarrow \qquad \alpha = \sqrt{\frac{m\omega}{2\hbar}} \tag{12}$$

Equating the constant terms:

$$E = \frac{\alpha^2 \hbar^2}{m} = \frac{\hbar^2}{m} \left(\frac{m\omega}{2\hbar}\right) = \frac{1}{2}\hbar\omega \tag{13}$$

4. By considering the visible spectrum of hydrogen and He$^+$, show how you could determine spectroscopically if a sample of hydrogen was contaminated with helium. (Hint: look for differences in the visible emission lines, $\lambda \approx 390 \sim 750$ nm. A difference of 10 nm is easily measured.)

Solution: We know the energies in a hydrogen atom are just $E_n = -13.6$ eV$/n^2$ for a given level n. For the He$^+$ ion, the only real difference is the extra positive charge in the nucleus. If we have Z positive charges in the nucleus, the energies become $E_n = -13.6$ eVZ^2/n^2. For $Z = 2$, we just end up multiplying all the energies by a factor 4. The questions are: does this lead to any new radiative transitions, are they in the visible range, and are they well-separated enough? We can just list the energy levels for the two systems and see what we come up with.

We already know that the visible transitions in Hydrogen occur when excited states relax to the $n = 2$ level, and that for large n the transitions will probably have an energy too high to be in the visible range. Thus, we can probably find a new transition for He$^+$ by just considering the first several levels alone.

We see a couple of things already. The $n = 2$ state for He$^+$ happens to accidentally have the same energy as the $n = 1$ state for H, likewise for the $n = 4$ state for He$^+$ and the $n = 2$ state for H. That means that we can't just pick transitions at random, some of them will accidentally have the same

	H	He$^+$
n	E_n (eV)	E_n (eV)
1	-13.6	$-13.6 \cdot 4$
2	$-13.6 \cdot \frac{1}{4}$	-13.6
3	$-13.6 \cdot \frac{1}{9}$	$-13.6 \cdot \frac{4}{9}$
4	$-13.6 \cdot \frac{1}{16}$	$-13.6 \cdot \frac{1}{4}$
5	$-13.6 \cdot \frac{1}{25}$	$-13.6 \cdot \frac{4}{25}$

energy.

However, the $n = 3$ state for He$^+$ has the curious fraction $4/9$ in it, which can't possibly occur for H. Transitions into the $n = 3$ state should yield unique energies. Let's compute the visible transitions in hydrogen H, since there are only a few, and see if some He$^+$ transitions stick out in the in-between wavelengths:

H transition	λ_H (nm)	He$^+$ transition	λ_{He^+} (nm)
$3 \rightarrow 2$	656	$4 \rightarrow 3$	469
$4 \rightarrow 2$	486	$3 \rightarrow 2$	164
$5 \rightarrow 2$	434		
$6 \rightarrow 2$	410		

Already with just the $4 \rightarrow 3$ transition in He$^+$, we have an expected emission (or absorption) at 469 nm, a full 17 nm from the nearest H line, and well in the visible range to boot (a nice pretty blue). Should be easy to pick out!

5. Show that whenever a solution $\Psi(x, t)$ of the time-dependent Schrödinger equation separates into a product $\Psi(x, t) = F(x) \cdot G(t)$ then $F(x)$ *must* satisfy the corresponding time-independent Schrödinger equation and $G(t)$ *must* be proportional to $e^{-iEt/\hbar}$.

Solution: The time-dependent Schrödinger equation reads

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \tag{14}$$

Where $\hat{H}$ represents the kinetic plus potential energy,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{15}$$

Substituting our separated solution, and noting that any spatial derivative of $G(t)$ is zero,

$$\left(\frac{-\hbar^2}{2m}\frac{\partial^2 F(x)}{\partial x^2} + V(x)F(x) \right) G(t) = i\hbar F(x)\frac{\partial G(t)}{\partial t} \tag{16}$$

Separate everything that depends on x to the left, and everything that depends on t to the right:

$$\frac{\frac{-\hbar^2}{2m}\frac{\partial^2 F(x)}{\partial x^2} + V(x)F(x)}{F(x)} = \frac{i\hbar\frac{\partial G(t)}{\partial t}}{G(t)} \tag{17}$$

If both sides are equal, then they must both be equal to the same constant value, which we will denote as E. Thus,

$$\frac{-\hbar^2}{2m}\frac{\partial^2 F(x)}{\partial x^2} + V(x)F(x) = EF(x) \tag{18}$$

Thus, $F(x)$ obeys the time-independent Schrödinger equation. Further,

$$i\hbar\frac{\partial G(t)}{\partial t} = EG(t) \tag{19}$$

The latter equation can be re-written

$$\frac{\partial G(t)}{\partial t} = \frac{E}{i\hbar}G(t) = -\frac{iE}{\hbar}G(t) \tag{20}$$

which has the general solution[i]

$$G(t) = Ce^{-iEt/\hbar} \tag{21}$$

NB: this is probably not something I would ask on the exam, as it is more math than physics.

6. An experimenter asks for funds from a foundation to observe visually through a microscope the quantum behavior of a small harmonic oscillator. According to his proposal, the oscillator consists of an object 10^{-6} m in diameter and estimated mass of 10^{-15} kg. It vibrates on the end of a thin fiber with a maximum amplitude of 10^{-5} m and frequency 1000 Hz. You are the referee for the proposal.

(a) What is the approximate quantum number for the system in the state described?
(b) What would its energy be in electron volts if it were in its lowest energy state? Compare with the average thermal energy at room temperature, $\sim 1/40$ eV.
(c) What would its classical amplitude of vibration be if it were in its lowest energy state? Compare with the wavelength of visible light, about 500 nm, with which it is presumably observed.
(d) Would you, as a referee of this proposal, recommend award of a grant to carry out this research?

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[i]Recall that if $-a\frac{dy}{dx} = y$, the general solution is $y = Ce^{-t/a}$, where C is a constant.

Solution: The energy of a quantum simple harmonic oscillator can be written in terms of its frequency f, its principle quantum number n, and Planck's constant h:

$$E = \left(n + \frac{1}{2} \right) hf \tag{22}$$

If the object is a mechanical oscillator, then its vibrational energy must also be related to its amplitude of vibration A:

$$E = \frac{1}{2} kA^2 \qquad \text{with} \qquad 2\pi f = \sqrt{\frac{k}{m}} \tag{23}$$

here k is the effective spring constant and m the mass of the oscillator. Combining the last two expressions, and using the quantities given, we have

$$\left(n + \frac{1}{2} \right) hf = 2\pi^2 m f^2 A^2 \tag{24}$$

$$n = \frac{2\pi^2 m}{h} fA^2 - \frac{1}{2} \approx \frac{2\pi^2 m}{h} fA^2 \approx 3 \times 10^{12} \tag{25}$$

The system is in a *very* high quantum state, far too high to expect to observe any discretization of vibrational modes – this would require a precision of ~1 part in 10^{12} in frequency measurement. Its energy in electron volts for the lowest state, $n=0$, may then be calculated from either expression:

$$E_0 = \left(0 + \frac{1}{2} \right) hf \approx 3 \times 10^{-31}\,\text{J} \approx 2 \times 10^{-12}\,\text{eV} \tag{26}$$

Clearly, the thermal energy at room temperature will induce an overwhelming random vibration. The amplitude of vibration can be determined by inverting the expression for energy above:

$$A = \frac{1}{\pi f} \sqrt{\frac{E}{2m}} \approx 4 \times 10^{-12}\,\text{m} = 4 \times 10^{-3}\,\text{nm} \tag{27}$$

This is roughly five orders of magnitude smaller than the wavelength of light, definitively precluding any optical observation. Very hard X-rays would be required, and at a wavelength of $10^{-12}\,\text{m}$, the photon energy would be about $1\,\text{MeV}$, more than sufficient to disturb the oscillator. We cannot recommend funding of this project!

7. The molecular bonding in the compound NaCl is predominantly ionic, and to a good approximation we can consider a sodium chloride molecule as consisting of two units – an Na^+ ion and a Cl^- ion – bound together. Assuming an electrostatic attraction and a power-law repulsion between

the ions, their potential energy as a function of ion spacing has the form

$$V(r) = -\frac{ke^2}{r} + \frac{A}{r^n} \tag{28}$$

(a) Find the equilibrium spacing r_o.
(b) Find the potential energy at this separation, V_{min}.
(c) Find the effective "spring constant" for the molecule, assuming small deviations from r_o. One way to do this is to find the second derivative of $V(r)$ at $r=r_o$.

Solution: Equilibrium spacing occurs when $dV/dr=0$:

$$\left.\frac{dV}{dr}\right|_{r_o} = \frac{ke^2}{r_o^2} - \frac{nA}{r_o^{n+1}} = 0 \tag{29}$$

$$ke^2 = \frac{nA}{r_o^{n-1}} \tag{30}$$

$$r_o = \left(\frac{nA}{ke^2}\right)^{1/(n-1)} \tag{31}$$

At this separation, we have

$$V(r_o) = -\frac{ke^2 \left(ke^2\right)^{1/(n-1)}}{(nA)^{1/(n-1)}} + \frac{A \left(ke^2\right)^{n/(n-1)}}{(nA)^{n/(n-1)}} = -\frac{\left(ke^2\right)^{n/(n-1)}}{(nA)^{1/(n-1)}} + A\left(\frac{ke^2}{nA}\right)^{n/(n-1)} \tag{32}$$

$$= \left(ke^2\right)^{n/(n-1)} \left(\frac{1}{(nA)^{1/(n-1)}} + \frac{A}{(nA)^{n/(n-1)}}\right) \tag{33}$$

$$= \left(ke^2\right)^{n/(n-1)} \left(\frac{1}{(nA)^{1/(n-1)}} + \frac{1}{n\,(nA)^{1/(n-1)}}\right) = \left(\frac{k^n e^{2n}}{nA}\right)^{1/(n-1)} \left(1 + \frac{1}{n}\right) \tag{34}$$

The spring constant can be found by approximating d^2V/dr^2 as constant near r_o:

$$\left.\frac{d^2V}{dr^2}\right|_{r_o} = -\frac{2ke^2}{r_o^3} + \frac{n\,(n+1)\,A}{r_o^{n+2}} = -2ke^2 \left(\frac{ke^2}{nA}\right)^{3/(n-1)} + n\,(n+1)\,A \left(\frac{ke^2}{nA}\right)^{(n+2)/(n-1)} \tag{35}$$