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PH 102-2 / LeClair

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Problem Set 11: SOLUTIONS

1. 15 points. The typical operating voltage for an electron microscope is $\Delta V = 50 \text{ kV}$. **(a)** What is the smallest feature one could hope to resolve? **(b)** What is the equivalent resolution if neutrons are used? **(c)** Explain in words why electrons are used, and not protons or neutrons.

The smallest feature one could hope to resolve would be of the order of the wavelength of the electron, as we discussed in more detail in relation to light waves. For massive objects, de Broglie first related an object's wavelength λ to its momentum $|\vec{p}|$:

$$\lambda = \frac{h}{|\vec{p}|}$$

where h is Planck's constant as usual. If we can find the particle's momentum, we can find its wavelength, and hence estimate the microscope's resolution. If the electron is accelerated by a $\Delta V = 50 \text{ kV}$ electric potential, we know that it starts with a relative potential energy $e\Delta V$ which is wholly converted into kinetic energy. From the accelerating voltage, we can get kinetic energy, from which we can get velocity, which gives us momentum and finally wavelength.

Somewhat shorter is to use an alternative formula for kinetic energy, which you can readily verify is correct, and add conservation of energy as described above:

$$KE = \frac{|\vec{p}|^2}{2m} = e\Delta V$$

Solving this equation for momentum ...

$$\begin{aligned} |\vec{p}|^2 &= 2me\Delta V \\ |\vec{p}| &= \sqrt{2me\Delta V} \end{aligned}$$

Now plugging that into the de Broglie relationship, and using the requisite constants and electron mass:

$$\begin{aligned} \lambda &= \frac{h}{|\vec{p}|} = \frac{h}{\sqrt{2me\Delta V}} \\ &= \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2 \cdot 9.11 \times 10^{-31} \text{ kg} \cdot 1.60 \times 10^{-19} \text{ C} \cdot 50.0 \times 10^3 \text{ V}}} \\ &= 5.49 \times 10^{-12} \frac{[\text{kg} \cdot \frac{\text{m}^2}{\text{s}^2} \cdot \text{s}]}{\sqrt{[\text{kg} \cdot \text{C} \cdot \text{V}]}} \\ &= 5.49 \times 10^{-12} \frac{[\text{kg} \cdot \text{m}^2]}{[\text{s} \sqrt{\text{kg} \cdot \text{C} \cdot (\text{N}/\text{C}) \cdot \text{m}}]} \\ &= 5.49 \times 10^{-12} \frac{[\text{kg} \cdot \text{m}^2]}{[\text{s} \sqrt{\text{kg} \cdot (\text{kg} \cdot \text{m}/\text{s}^2) \cdot \text{m}}]} \\ &= 5.49 \times 10^{-12} \frac{[\text{kg} \cdot \text{m}^2]}{[\text{s} \cdot \text{kg} \cdot \text{m}/\text{s}]} \\ &= 5.49 \times 10^{-12} \text{ m} = 5.49 \text{ pm} \end{aligned}$$

So the units are a bit ugly here ... for the units to come out right, it is easiest to remember that the entire bit under the radical above must have units of momentum, or $\text{kg} \cdot \text{m/s}$ (which avoids much of the manipulation above), or at least to remember that $1 \text{ N/C} = 1 \text{ V/m}$ to do it the hard way (line 5 above). Anyway: this is a decent estimate of the *fundamental* resolution of an electron microscope operating at 50 kV accelerating potential. In reality, the resolution limit is a few orders larger most of the time - the electromagnetic lenses aren't perfect, and we have thermal motion to worry about besides.

What about if we use neutrons? The answer is far simpler in this case: since neutrons have no charge, they can't be accelerated by electric potentials like electrons. The microscope simply won't work like this, there is no resolution! Why not protons, though, since they can be accelerated by potentials? Electrons, we found, are bound to their atomic nuclei with energies on the order of a few or a dozen electron volts - they are easy enough to remove from atoms for acceleration and focusing. Protons, being bound within the nucleus, are much, much harder to separate from their constituent atoms - their binding energy is more like a million electron volts (MeV). We use electrons because they are relatively easily isolated and pushed around.

2. 15 points. An accelerating charge loses electromagnetic energy at a rate of

$$\mathcal{P} = \frac{\Delta E}{\Delta t} = -\frac{2k_e q^2 a^2}{3c^3}$$

where k_e is Coulomb's constant, q is the charge of the particle, c is the speed of light, and a is the acceleration of the charge. Assume that an electron is one Bohr radius ($a_0 = 0.053 \text{ nm}$) from the center of a Hydrogen atom. **(a)** Find the acceleration of the electron (hint: circular path). **(b)** Calculate the kinetic energy of the electron and determine within an order of magnitude how long it will take the electron to lose all of its energy, assuming a constant acceleration as found in part (a).

If the electron is traveling in a circular path (a naive, but occasionally useful picture), all of the forces acting on it must provide the centripetal acceleration:

$$a_{\text{centr}} = \frac{v^2}{r}$$

The only force acting on the electron is the electric force due to the presence of the proton a distance r away, so the centripetal and electric forces must be equal:

$$\begin{aligned} F_{\text{centr}} + F_e &= 0 \\ \frac{mv^2}{r} + \frac{-k_e e^2}{r^2} &= 0 \\ mv^2 &= \frac{k_e e^2}{r} \\ \Rightarrow v &= \sqrt{\frac{k_e e^2}{mr}} = \sqrt{\frac{(9 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \cdot (1.6 \times 10^{-19} \text{ C})^2}{(9.11 \times 10^{-31} \text{ kg}) \cdot (0.053 \times 10^{-9} \text{ m})}} \\ &\approx 2.18 \times 10^6 \text{ m/s} \end{aligned}$$

In this case, the units work out fairly easily if you remember that $1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^2$. Armed with the electron's velocity, we can easily find its acceleration:

$$a_{\text{centr}} = \frac{v^2}{r} = \frac{(2.18 \times 10^6 \text{ m/s})^2}{0.053 \times 10^{-9} \text{ m}} \approx 9.00 \times 10^{22} \text{ m/s}^2$$

Truly, a fearsome number, about ten thousand billion billion "g's." Of course, electrons are terribly light, so the overall *force* is still not so large. Incidentally, we could have done this a bit more directly, by just calculating the electric force directly to get acceleration: $a = F_e/m$. However, since we will need both velocity (for kinetic energy) and acceleration (for power) in the end, this is just as easy.

With the electron's velocity, we can calculate its kinetic energy from its mass and velocity. Since the velocity we found is still a relatively small fraction of the speed of light, there is no compelling reason to invoke special relativity.

$$KE = \frac{1}{2}mv^2 = \frac{1}{2} (9.11 \times 10^{-31} \text{ kg}) (2.18 \times 10^6 \text{ m/s})^2 \approx 2.17 \times 10^{-18} \text{ J} \approx 13.6 \text{ eV}$$

Basically, we have just reproduced our original calculation of the lowest energy level of the hydrogen atom - also known as the ionization energy.

How long is this classical atom stable? We should remember at this point that power is energy per unit time. The power in this case means how much energy we are losing per unit time, hence the negative sign. What we want to find is how long it will take for the electron to lose *all* of its energy, the whole kinetic energy we just calculated. Thus:

$$\mathcal{P} = \frac{\Delta E}{\Delta t} = \frac{K}{\Delta t}$$

$$\implies \Delta t = \frac{K}{\mathcal{P}}$$

Thus, if we can calculate the power - the rate of energy loss - using the (now) known acceleration a and various fundamental constants, we can use the kinetic energy to find out how long it takes the electron to lose all of its energy.

$$\mathcal{P} = -\frac{2k_e q^2 a^2}{3c^3}$$

$$= -\frac{2 (9 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \cdot (1.6 \times 10^{-19} \text{ C})^2 (9.00 \times 10^{22} \text{ m/s}^2)^2}{3 \cdot (3 \times 10^8 \text{ m/s})^3}$$

$$\approx -4.62 \times 10^{-8} \text{ J/s} = -4.62 \times 10^{-8} \text{ W}$$

Remember that $1 \text{ N} \cdot \text{m} = 1 \text{ J}$, and $1 \text{ W} = 1 \text{ J/s}$ and the units should work out just fine. Given the power, finding the time is easy. We don't need to worry about the negative sign for power here - all it signifies is that the system is *losing* energy, not gaining. Our time should of course be positive, it makes no sense that the atom collapsed some time in the past already.

$$\Delta t = \frac{K}{\mathcal{P}}$$

$$= \frac{2.17 \times 10^{-18} \text{ J}}{4.62 \times 10^{-8} \text{ W}}$$

$$\approx 4.7 \times 10^{-11} \text{ s} = 47 \text{ ps}$$

Of course, there are many *many* problems with this analysis. First, the whole Bohr model is a kludge of sorts, we know it to be deeply flawed (though still useful). Second, it is perhaps silly to think that the electron loses energy at a constant rate as it continues on its death spiral. Finally, we now know better - atoms are indeed stable, and the answer lies in the wave-like nature of matter and the uncertainty principle.

3. 15 points. A hydrogen atom has a radius of $\sim 0.05 \text{ nm}$. **(a)** Assuming we know the position of an electron in a hydrogen atom to an accuracy of 1% of this radius, estimate the uncertainty in the velocity of the electron. How does this value compare to c ? **(b)** Compare this value to the uncertainty in the velocity of a ball of mass 0.2 kg and radius 0.05 m whose position is known within 1% of its radius.

This is one of those problems I give very rarely, where one simply has to plug the right stuff into the right formula. Don't get used to it.

The uncertainty in the position of the electron is 1% of the radius of its orbit, or 1% of 0.05 nm . Thus, $\Delta x = (0.01)(0.05 \text{ nm})$. We just plug this into the uncertainty principle, noting that momentum is mass times velocity, with mass being an invariant constant:

$$\begin{aligned}
\Delta x \Delta p = m \Delta x \Delta v &\geq \frac{\hbar}{2} \\
\Rightarrow \Delta v &\geq \frac{\hbar}{2m\Delta x} \\
\Delta v &\geq \frac{1.05 \times 10^{-34} \text{ J} \cdot \text{s}}{2(9.11 \times 10^{-31} \text{ kg})(0.01)(0.05 \times 10^{-9} \text{ m})} \\
\Rightarrow \Delta v &\gtrsim 1 \times 10^8 \text{ m/s} \sim 0.3c
\end{aligned}$$

Recall from the last problem that we actually calculated the electron's velocity to be $\sim 0.007c$. In other words, *the uncertainty in the electron's velocity would be larger than its actual velocity* - we have essentially no idea how fast the electron is going if we localize its position too well. Similarly, if we knew the velocity to 1% or better, we would have no idea of *where* the electron is.

How about the 0.2 kg ball? Same formulas, different mass and position.

$$\begin{aligned}
\Delta v &\geq \frac{\hbar}{2m\Delta x} \\
&\geq \frac{1.05 \times 10^{-34} \text{ J} \cdot \text{s}}{2(0.2 \text{ kg})(0.01)(0.05 \text{ m})} \\
&\gtrsim 3 \times 10^{31} \text{ m/s}
\end{aligned}$$

Basically: quantum uncertainty is utterly irrelevant for everyday objects.

4. 10 points. A molecule is known to exist in an unstable higher energy configuration for $\Delta t = 10$ nsec, after which it relaxes to its lower energy stable state by emitting a photon. **(a)** What uncertainty in the frequency Δf of the emitted photon is implied? **(b)** If this state is being probed with Nuclear Magnetic Resonance (NMR) at a frequency of $f \approx 500$ MHz, what is the relative uncertainty in the measurement, $\Delta f/f$?

The idea here is that our molecule has a stable ground state, whose energy we will call zero, and an excited state which has an energy E_0 higher. Thus, we can think of the molecule itself as being excited from an energy level zero to one E_0 higher. After excitation, the molecule can relax back to its lower energy state by emitting a photon of energy $E_0 = hf$ - if a photon carries away exactly this energy, the molecule is back to its lower state.

The excited state is unstable, and exists for only 10 ns. The energy-time uncertainty principle tells us is that states which exist for only a short time cannot have a definite energy - the shorter the lifetime of the excited state (or time an object spends in an energy level), the less well-defined the energy of that state is. In spectroscopy, this usually means that excited states with finite lifetime do not have definite energies, and what one would expect to be a narrow spectroscopic feature (a resonance line in this case) is actually broadened. For our molecule, if the lifetime of the excited state Δt is short, the energy of the excited state E_0 is actually not definite, but has a "spread" or uncertainty of ΔE . If this is the case, then the emitted photon must share the same uncertainty in *frequency*¹: $\Delta E = h\Delta f$. Thus:

$$\begin{aligned}
\Delta E \Delta t = h \Delta f \Delta t &\geq \frac{\hbar}{2} \\
\Rightarrow \Delta f &\geq \frac{\hbar}{2h\Delta t} \\
&\geq \frac{1}{4\pi\Delta t} = \frac{1}{4 \cdot \pi \cdot 10^{-8} \text{ s}} \\
&\gtrsim 8 \text{ MHz}
\end{aligned}$$

In the second line, remember that $\hbar = h/2\pi$. Thus, our resonance line will have an intrinsic width of 8 MHz due purely to the uncertainty principle. If all extrinsic linewidths are minimized as far as possible, this sort of "lifetime broadening" is indeed observable for excited states that are sufficiently short-lived.

¹Since Planck's constant is ... well ... *constant* the uncertainty must be in frequency, or equivalently, wavelength.

The relative uncertainty, if we were measuring a NMR resonance line at 500 MHzⁱⁱ is just the linewidth divided by the base frequency:

$$\frac{\Delta f}{f} = \frac{8 \text{ MHz}}{500 \text{ MHz}} \approx 1.6\%$$

A small effect, perhaps, but not at all unmeasurable.

5. 10 points. In a coordination compound, the so-called “crystal field” gives rise to a difference in energy levels for some of the electrons in a transition metal ion. That is, electrons can occupy one of two states, separated by the crystal field splitting energy Δ .

The octahedral complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$ has a crystal field splitting of $\Delta_o \sim 2.16 \text{ eV}$, while $[\text{Co}(\text{NH}_3)_6]^{3+}$ has $\Delta_o \sim 2.84 \text{ eV}$. What color are these compounds? Make use of the table below. If a compound absorbs a certain color of light, it exhibits the color *complementary* to the color of absorbed light.

Table 1: Absorbed wavelength λ and observed color

λ (nm)	absorbed color	observed color
400	violet	greenish-yellow
450	blue	yellow
490	blue-green	red
570	yellow-green	violet
580	yellow	dark blue
600	orange	blue
650	red	green

This problem has a long setup for what is a very simple problem. Our coordination compounds have two distinct energy levels. Presumably, under normal conditions, only the lowest level is occupied. Incident photons can be absorbed by electrons, exciting them into the higher level, but only if the photons’ energy is equal to the splitting between the energy levels. The key is that for the electron to make a transition between the two energy levels, it must acquire more energy, in an amount equal to the difference between the lower and higher levels.

Thus, exactly one energy of incident photon is absorbed, photons that satisfy $\Delta_o = hf = \frac{hc}{\lambda}$. When only a single color is absorbed by the compound, this color is *removed* from the spectrum, and we see the complementary color as detailed in the table above. All we need to do is find the wavelength such that the photon energy matches the crystal field splitting and use the table to find the complementary color.

$$\begin{aligned} \Delta_o &= \frac{hc}{\lambda} \\ \implies \lambda &= \frac{hc}{\Delta_o} \\ &= \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}) (3 \times 10^8 \text{ m/s})}{\Delta_o [\text{J}] \cdot \frac{1 \text{ eV}}{1.60 \times 10^{-19} \text{ J}}} \\ &= \frac{1.24 \times 10^{-6} [\text{eV} \cdot \text{m}]}{\Delta_o [\text{eV}]} \end{aligned}$$

Here we worked out all the constants and unit conversions - since Planck’s constant is usually given in Joules times seconds, we would have to first convert Δ_o to Joules. We did this before plugging in any numbers, because it gives us a nice equation

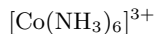
ⁱⁱThis would require a magnetic field of about 11.75 T, which is accessible. NMR spectrometers running at 500 MHz are not uncommon.

for quickly relating wavelength and energy in electron volts. With the numbers we are given:



$$\lambda = \frac{1.24 \times 10^{-6} \text{ eV} \cdot \text{m}}{2.16 \text{ eV}} = 5.74 \times 10^{-7} \text{ m} = 574 \times 10^{-9} \text{ m} = 574 \text{ nm}$$

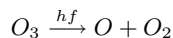
Since $[\text{Cr}(\text{NH}_3)_6]^{3+}$ absorbs light in the $\sim 570 \text{ nm}$ range, *i.e.*, yellow-green, it will appear to be violet. Being nearly halfway in between two entries in the table, one could argue that the absorption is slightly greenish-yellow, and the compound appears as a dark blue with hints of violet.



$$\lambda = \frac{1.24 \times 10^{-6} \text{ eV} \cdot \text{m}}{2.84 \text{ eV}} = 4.37 \times 10^{-7} \text{ m} = 437 \times 10^{-9} \text{ m} = 437 \text{ nm}$$

$[\text{Co}(\text{NH}_3)_6]^{3+}$ on the other hand absorbs closest to 450 nm in the table, *i.e.*, bluish, so it should appear to be yellow. Possibly a little on the green side of yellow, but mostly yellow.

6. 10 points. The energy required to break one O=O bond in ozone (O_3 , $\text{O}=\text{O}=\text{O}$) is about 500 kJ/mol . What is the maximum wavelength of the photon that has enough energy to photodissociate ozone by breaking one of the O=O bonds?



Note Avagadro's number is $N_A = 6.02 \times 10^{23}$ things/mol.

If we are to break the double oxygen bond in ozone, we need to supply a photon with an energy greater or equal to the bond energy. Two adjacent oxygens are ultimately bonded together because they gain $\Delta E = 500 \text{ kJ/mol}$ worth of energy between them to stay that way - if we want to coax them apart and break the bond, we need to supply that much energy with an incident photon. If we can convert 500 kJ/mol to an energy per bond in, say, electron volts, we can find out what sort of photon has enough energy to break the bond. To do this, we must create an unholy alliance of chemistry and physics units:

$$\begin{aligned} \Delta E &= 500 \times 10^3 \frac{\text{J}}{\text{mol}} \cdot \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ bonds}} \\ &= 8.30 \times 10^{-19} \frac{\text{J}}{\text{bond}} \cdot \frac{1 \text{ eV}}{1.60 \times 10^{-19} \text{ J}} \\ &= 5.18 \frac{\text{eV}}{\text{bond}} \end{aligned}$$

Now we are getting somewhere! It takes just over 5 electron volts per bond to break an oxygen double bond in an ozone molecule. An incident photon with at least this much energy can be absorbed by one of the oxygen atoms, which will then have enough energy to leave its bound state and break the bond. Thus, to break a single bond:

$$\begin{aligned} E_{\text{photon}} &= \frac{hc}{\lambda} = 5.18 \text{ eV} \\ \implies \lambda &= \frac{hc}{5.18 \text{ eV}} \\ &= \frac{1.24 \times 10^{-6} \text{ eV} \cdot \text{m}}{5.18 \text{ eV}} \\ &= 2.39 \times 10^{-7} = 239 \text{ nm} \end{aligned}$$

Here we used our handy relationship from the last problem - $hc = 1.24 \times 10^{-6} \text{ eV} \cdot \text{m}$. A photon of wavelength 239 nm or lower will break up an ozone molecule, which is well into the ultraviolet (UV). This is one way the ozone layer protects us - it absorbs harmful UV radiation and prevents it from reaching the earth's surface.

7. 10 points. An FM radio transmitter has a power output of 130 kW and operates at a frequency of 98.3 MHz. How many photons per second does the transmitter emit?

We need for this only two things: the definition of power, and the fact that the energy emitted must come in the form of single photons. Since the frequency of the photons is fixed at $f = 98.3$ MHz, then their energy is also fixed by $E = hf$. If the energy comes only in discrete bundles, one photon at a time, then the total energy is just the number of photons N , times the energy per photon hf . Power, you may recall, is just energy per unit time, and thus:

$$\mathcal{P} = \frac{\Delta E}{\Delta t} = \frac{(\text{number of photons})(\text{energy per photon})}{\Delta t} = \frac{Nhf}{\Delta t}$$

Now what we want is the number of photons per second, or $N/\Delta t$:

$$\frac{N}{\Delta t} = \frac{\mathcal{P}}{hf} = \frac{130 \times 10^3 \text{ W}}{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(98.3 \times 10^6 \text{ 1/s})} \approx 2 \times 10^{30} \text{ 1/sec}$$

Recall that $1 \text{ Hz} = 1 \text{ s}^{-1}$, and $1 \text{ W} = 1 \text{ J/s}$ to make the units come out properly. The units should just be “per second” since we want just the number of photons, which is dimensionless, per second.

8. 10 points. A pulsed ruby laser emits light at 694.3 nm. For a 13.6 ps pulse containing 3.40 J of energy, how many photons are in the pulse? 1 ps is 10^{-12} s.

The time duration of the pulse is actually irrelevant here - if we know the wavelength, we know the energy per photon. Since all of the photons have the same wavelength, if we also know the total energy of the pulse we know how many photons must make it up. The time would only be relevant if we were given the *power* of the pulse - *then* we would multiply power and time duration to get total energy. Since we already have energy, there is not much to do. Let N be the number of photons, and $\lambda = 694.3 \text{ nm}$ their wavelength.

$$E = (\text{number of photons})(\text{energy per photon}) = N \frac{hc}{\lambda} = 3.40 \text{ J}$$

$$\implies N = \frac{E\lambda}{hc} = \frac{(3.4 \text{ J})(694.3 \times 10^{-9} \text{ m})}{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3 \times 10^8 \text{ m/s})} \approx 1 \times 10^{19}$$

Note that all the units cancel, and we end up with just a number, like we expect.

9. 5 points. A light-emitting diode (LED) emits blue photons of wavelength 480 nm. What would be the minimum voltage you would expect to apply to the LED before it emits light? (Hint: we assume all of the potential energy of one electron is converted into light.)

In a light emitting diode, the electrical potential energy of electrons is converted into light energy. How this happens in detail we covered in lecture, but no matter what the mechanism, we can apply conservation of energy. We know that when the LED is glowing, which happens when the voltage is greater than the LED’s threshold voltage, only one single color of light is emitted. This means that all photons emitted have the same wavelength, and therefore the same energy energy, since $E = hc/\lambda$. If all of the photons have essentially the same energy, then the increase in brightness of the LED can only come from the LED emitting more and more photons as voltage is increased, it cannot be due to the photons simply having more and more energy.ⁱⁱⁱ

If photons of only a specific frequency and energy are emitted, then we should expect nothing to happen until the electrical potential energy supplied to the LED is equal to the energy of the photons emitted. In other words, we imagine that the potential energy of each electron injected into the LED is converted completely to light energy. Right at the threshold voltage V_{th} , the electrical energy eV_{th} is just equal to the photon energy:

$$e\Delta V_{th} = \frac{hc}{\lambda}$$

ⁱⁱⁱIf this were true, the color would shift toward the blue as voltage increases.

Above the threshold voltage, the excess electrical energy is just used to create more photons. Using the energy-wavelength relationship we developed above:

$$e\Delta V = \frac{hc}{\lambda}$$
$$\Delta V = \frac{hc}{e\lambda}$$
$$\Rightarrow \Delta V = 2.6 \text{ V}$$

If you plug in all of the constants in with consistent units and put the wavelength in meters, the answer will come out in Volts as expected.