

Answers

1. The operation of conventional fluorescent lights involves transitions of electrons in mercury atoms. The most prominent line of the Hg spectrum is at 253.652 nm. Other lines are at 365.015, 435.833 and 1013.975 nm.

- a. Which line represents the most “energetic line”?

As per Planck: $E = h\nu = \frac{hc}{\lambda}$

$\therefore$ small λ associated w/ large E.

Therefore the 253.652 nm line is the most “energetic”.

- b. What is the frequency, ν , and energy, E, for this line.

$$\nu = \frac{c}{\lambda} = \frac{2.997925 \times 10^8 \text{ m/s}}{253.652 \times 10^{-9} \text{ m}} = \underline{1.18190 \times 10^{15} \text{ s}^{-1}}$$

$$E = h\nu = 6.626076 \times 10^{-34} \text{ Js} \times 1.18190 \times 10^{15} \text{ s}^{-1} = \underline{7.83136 \times 10^{-19} \text{ J/photon}}$$

- c. In what region of the general EMR spectrum are each of the above lines found?

Look up regions in Petrucci Fig 8.3, CDS #6 or, better yet, know by heart:

253 nm	UV
365 nm	just in UV
405 nm	violet
435 nm	blue
1014 nm	IR

2. An electron moves at a speed of 6.00×10^6 m/s with an uncertainty of 1%. What is the uncertainty in its location?

As per Heisenberg, $(\Delta x)(\Delta mv) \geq \frac{h}{4\pi}$

In our case, mass of an electron $m = 9.109 \times 10^{-31} \text{ kg}$
uncertainty in speed $\Delta v = 6.00 \times 10^6 \text{ m/s} \times 0.01 = 6 \times 10^4 \text{ m/s}$

$$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-34} \text{ Js} \left(= \frac{\text{kg m}^2}{\text{s}} \right)}{4\pi \times 9.109 \times 10^{-31} \text{ kg} \times 6 \times 10^4 \text{ m/s}}$$

$$= \underline{9.6 \times 10^{-10} \text{ m}} \approx 1 \times 10^{-9} \text{ m} = 1 \text{ nm} = \underline{1000 \text{ pm}}$$

$\therefore$ The uncertainty in position is larger than the typical size of an atom (100 - 200 pm). Therefore we are quite uncertain where the electron is located in the atomic context; the best we can do is to find the probability of finding the electron at a certain location.

3. The yellow color of the sodium flame test is due to emission of photons at $\lambda = 589 \text{ nm}$. What is the apparent mass of these photons? (Hint: Planck & Einstein)

Comment: The line at 589 nm is the most prominent one; others are present in the visible and other parts of the spectrum.

$$E = mc^2, E = h\nu = \frac{hc}{\lambda}$$

$$\therefore mc^2 = \frac{hc}{\lambda}$$

$$m = \frac{h}{c\lambda} = \frac{6.626 \times 10^{-34} \text{ Js} \left(= \frac{\text{kg m}^2}{\text{s}} \right)}{3.00 \times 10^8 \text{ m/s} \times 589 \times 10^{-9} \text{ m}} = \underline{3.75 \times 10^{-36} \text{ kg per photon}}$$

This is about 6 orders of magnitude lower than the mass of an electron (10^{-36} vs 10^{-30}).

4. Give all possible m_ℓ values for orbitals with the following quantum numbers:

a.) $\ell = 2$ b.) $n = 1$ c.) $n = 4, \ell = 3$

The quantum number m_ℓ can have values from $-\ell, \dots, +\ell$

a.) $\ell = 2$: $m_\ell = -2, -1, 0, +1, +2$ (five different values)

b.) $n = 1$: ℓ can only be 0, therefore m_ℓ can only be 0 (one value only)

c.) $n = 4, \ell = 3$: $m_\ell = -3, -2, -1, 0, +1, +2, +3$ (seven different values)

5. Explain briefly why each of the following is not a possible set of quantum numbers

a.) $n = 2, \ell = 2, m_\ell = 0$; b.) $n = 3, \ell = 0, m_\ell = 1$; c.) $n = 3, \ell = 0, m_\ell = -2$

a.) ℓ values can only go from 0 to $n-1$; in this case up to 1; therefore $\ell = 2$ is impossible

b.) if $\ell = 0$, m_ℓ can only be 0; 1 is impossible

c.) same argument as under b.)

6. What is the max. number of orbitals that can be identified by each of the following sets of quantum numbers?

a.) $n = 4, \ell = 3$; b.) $n = 5, \ell = 1$; c.) $n = 7, \ell = 5$; d.) $n = 4, \ell = 2, m_\ell = -2$

a.) m_ℓ values can range from -3 to $+3$; therefore 7 orbitals possible

b.) m_ℓ values can be from $-1, 0$ to $+1$; therefore 3 orbitals

c.) m_ℓ values can range from -5 to $+5$; therefore 11 orbitals

d.) if an m_ℓ value is specified (that is allowed), then only 1 orbital is possible

7. What is the shortest wavelength photon that an excited H atom can emit?
Calculate & Explain.

“Shortest wavelength” corresponds to largest energy difference; i.e., transition from outside the atom ($n = \infty$) to the shell closest to the nucleus ($n=1$). Acc. to Bohr:

$$\Delta E_{\text{sys}} = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -R_H \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = -R_H = \underline{-2.179 \times 10^{-18} \text{ J/photon emitted}}$$

(comment: the minus sign indicates that the system, nucleus and electron, loses energy)

Therefore, each emitted photon has $\underline{E = 2.179 \times 10^{-18} \text{ J}}$

Acc. to Planck (see earlier):

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.00 \times 10^8 \text{ m/s}}{2.179 \times 10^{-18} \text{ J}} = 9.12 \times 10^{-8} \text{ m} = \underline{91.2 \text{ nm}} \text{ (UV range)}$$

8. How many orbitals can have the following quantum number or letter designation?

a.) 3p b.) 4p c.) 4p_x d.) n=5 e.) 6d f.) 5d g.) 7s

a.) 3 b.) 3 c.) 1 d.) 25 e.) 5 f.) 5 g.) 1

Note re d.) $n = 5$

l	0	1	2	3	4
m _l	0	-1 ... +1	-2 ... +2	-3 ... +3	-4 ... +4
orbitals	1	3	5	7	9
for a total of	25				

9. The following are hypothetical situations.

- a.) What is the “point probability” of finding a 1s electron at a distance $y = d$ if the probability at $x=d$ is 1×10^{-4} ?

What is the probability of finding the electron at $z = 0.5d$, greater or smaller?

- s orbitals have spherical symmetry
therefore probability at $y = d$ is the same as at $x = d$; i.e., 1×10^{-4}
- “point” probability increases for 1s electrons as we move closer to the nucleus;
therefore the probability at $z = 0.5d$ is greater

- b.) Assume that the probability of finding a 2p_x electron at $x = d$ is 1×10^{-3} . What is the probability of finding this electron at $y=d$?, at $z=d$?

2p_x orbitals have a nodal plane in the yz plane;
therefore, the probability at $y = d$ and $z = d$ are both 0

10. A ground state H atom absorbs a photon of wavelength 94.91 nm to reach a higher energy level (excited state). Subsequently, the excited atom returns to ground state in a 2-step process by emitting 2 photons in sequence. First, an intermediate level is reached by emission of a “1281 nm” photon. The second photon is emitted when the electron returns from the intermediate level to the ground state.

Problem can be solved by repeated application of Bohr & Planck equations

$$\text{Bohr: } \Delta E_{\text{sys}} = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{Planck: } E_{\text{ph}} = \frac{hc}{\lambda}$$

Note that for **absorption**, system energy increases by E_{ph} ; i.e., $\Delta E_{\text{sys}} = +E_{\text{ph}}$
for **emission**, system energy decreases by E_{ph} ; i.e., $\Delta E_{\text{sys}} = -E_{\text{ph}}$

- a.) What higher level did the atom reach? ($n = ?$)

The first step is absorption; therefore

$$\Delta E_{\text{sys}} = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = E_{\text{ph}} \left(= \frac{hc}{\lambda} \right)$$

Solve for n_f (given $n_i = 1$)

$$\begin{aligned} n_f &= \sqrt{\frac{1}{-\frac{E_{\text{ph}}}{R_H} + \frac{1}{n_i^2}}} = \sqrt{\frac{1}{-\frac{hc}{\lambda R_H} + \frac{1}{1^2}}} \\ &= \sqrt{\frac{1}{-\frac{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ m/s}}{9.491 \times 10^{-8} \text{ m} \times 2.179 \times 10^{-18} \text{ J}} + 1}} \\ &= 5.06 \approx 5 \end{aligned}$$

During absorption of the exciting photon, the electron reaches level $n = 5$.

10 b.) What intermediate level was attained? ($n_f = ?$)

the second step is emission, therefore

$$\Delta E_{\text{sys}} = - R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = - E_{\text{ph}} \left(= - \frac{hc}{\lambda} \right) \text{ or}$$

$$R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = E_{\text{ph}}$$

now with $\lambda = 1281 \text{ nm} = 1.281 \times 10^{-6} \text{ m}$ and $n_i = 5$, we obtain for n_f

$$n_f = \sqrt{\frac{1}{\frac{E_{\text{ph}}}{R_H} + \frac{1}{n_i^2}}} = \sqrt{\frac{1}{\frac{hc}{\lambda R_H} + \frac{1}{5^2}}}$$

$$= \sqrt{\frac{1}{\frac{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ m/s}}{1.281 \times 10^{-6} \text{ m} \times 2.179 \times 10^{-18} \text{ J}} + \frac{1}{5^2}}} = 2.999 \approx \underline{3}$$

10 c.) What is the wavelength of the second photon emitted?

The final step is from level $n = 3$ to level $n = 1$, obviously emission; therefore

$$\text{photon energy, } E_{\text{ph}} = -\Delta E_{\text{sys}} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = 2.179 \times 10^{-18} \text{ J} \left(\frac{1}{1^2} - \frac{1}{3^2} \right)$$

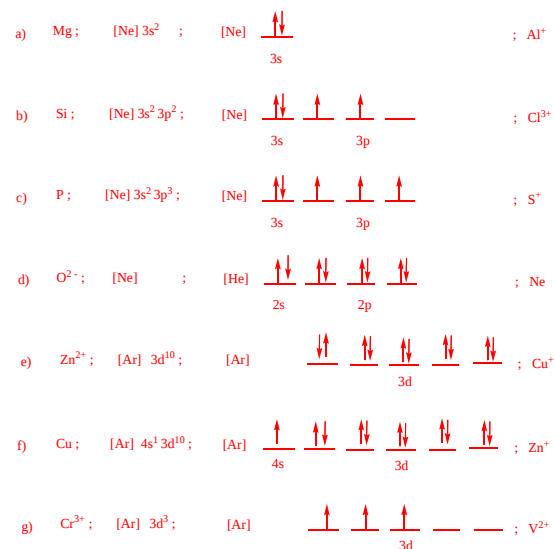
$$= 1.937 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{hc}{E_{\text{ph}}} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.00 \times 10^8 \text{ m/s}}{1.937 \times 10^{-18} \text{ J}} = 1.026 \times 10^{-7} \text{ m} = \underline{102.6 \text{ nm}}$$

11. Write “standard” and “orbital filling” notations for each of the following:

a.) Mg, b.) Si, c.) P d.) O^{2-} , e.) Zn^{2+} , f.) Cu, g.) Cr^{3+}

Use the “core” notation. Also write an isoelectronic species for each of the 7 cases.



12. How many unpaired electrons are present in

a.) Ti^{2+} b.) Fe^{3+} c.) Co^{2+} d.) Fe^{2+} , e.) Cu^+

a) Ti^{2+} ;  ; 2 unpaired electrons

b) Fe^{3+} ;  ; 5 unpaired electrons

c) Co^{2+} ;  ; 3 unpaired electrons

d) Cu^+ ;  ; 0 unpaired electrons

13. Arrange the following atoms in order of a.) increasing size, b.) first ionization energy

Al, B, C, K, Na

a.) size: $\text{C} < \text{B} < \text{Al} < \text{Na} < \text{K}$ (K is largest)

b.) IE_1 : $\text{K} < \text{Na} < \text{Al} < \text{B} < \text{C}$ (C requires the most energy for ionization)

14. a.) Which has the largest (absolute) electron affinity: Se, Cl or Br?

“absolute” means the amount of energy released if an electron is captured

This generally increases left $\rightarrow$ right, bottom $\rightarrow$ top (with noble gases as the most important exception)

$\therefore$ Cl has the largest absolute EA, has the strongest tendency to capture an electron

b.) Which has the largest size: O^{2-} , F^- , F

anions are larger than the corresponding neutral atoms;

nuclear charge decreases $\text{F}^- \rightarrow \text{O}^{2-}$

$\therefore \text{O}^{2-}$ has the largest size

c.) Place the following in order of increasing radius: Na^+ , O^{2-} , N^{3-} , F^-

the four species are isoelectronic; less nuclear charge will cause larger size

$\therefore \text{Na}^+ < \text{F}^- < \text{O}^{2-} < \text{N}^{3-}$

15. A particular metal surface has a “work function” (binding energy for electrons) = $3.69 \times 10^{-19} \text{ J}$. The material is subjected to an experiment to test the photoelectric effect. What will be the speed of the emitted electrons if the wavelength of the light used is a.) 300 nm b.) 600 nm?

$\lambda \rightarrow \text{energy of photon} \rightarrow \text{KE of } e^- \rightarrow \text{speed of } e^-$

$$\begin{aligned} \text{a.) } \text{KE} &= h\nu - \Phi = \frac{hc}{\lambda} - \Phi = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.00 \times 10^8 \text{ m/s}}{300 \times 10^{-9} \text{ m}} - 3.69 \times 10^{-19} \text{ J} \\ &= 6.62 \times 10^{-19} \text{ J} - 3.69 \times 10^{-19} \text{ J} = 2.93 \times 10^{-19} \text{ J} \end{aligned}$$

$$\text{KE} = \frac{1}{2} m_e v^2 \rightarrow v = \sqrt{\frac{2 \text{ KE}}{m_e}} \quad 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}, m_e = 9.109 \times 10^{-31} \text{ kg}$$

$$v = \sqrt{\frac{2 (2.93 \times 10^{-19} \text{ kg m}^2 \text{ s}^{-2})}{9.109 \times 10^{-31} \text{ kg}}} = \underline{8.02 \times 10^5 \text{ m/s}}$$

$$\text{b.) photon energy} = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.00 \times 10^8 \text{ m/s}}{600 \times 10^{-9} \text{ m}} = 3.31 \times 10^{-19} \text{ J}$$

This energy is less than the binding energy Φ ; therefore no electrons are emitted.