Problem Set 1 Solutions

1. The first 4 lines in the visible region of atomic line spectrum of hydrogen atom occur at wavelengths of 656.2, 486.1, 434.0, and 410.2 nm (this is known as the Balmer series). Using Bohr’s theory, show that these correspond to transitions in which the smaller integer in the equation is always n=2.

Bohr’s theory gives the following formula for the wavelengths in the atomic line spectrum of hydrogen,

\[
\frac{1}{\lambda} = \left( \frac{m e^4}{8 e^2 h^3 c} \right) \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)
\]

or

\[
\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right),
\]

where \(R\) is the Rydberg constant, 109737.3 cm\(^{-1}\). Note that in this equation \(n_1\) is always smaller than \(n_2\) (so that the wavelength is positive). Therefore, we would set \(n_1=2\) and try various integers greater than 2 for the value of \(n_2\).

Substituting \(n_1=2\) and \(n_2=3\), for example, leads to the result

\[
\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{3^2} \right)
\]

\[
= \left( 109737.3 \text{ cm}^{-1} \right) \left( \frac{1}{4} - \frac{1}{9} \right)
\]

\[
\frac{1}{\lambda} = 15241.3 \text{ cm}^{-1}.
\]

Converting to wavelength by taking the inverse of both sides and converting to nm, we get

\[
\lambda = \frac{1}{15241.3 \text{ cm}^{-1}}
\]

\[
= \left( 6.5611 \times 10^{-5} \text{ cm} \right) \left( \frac{10^7 \text{ nm}}{1 \text{ cm}} \right)
\]

\[
\lambda = 656.1 \text{ nm}.
\]

Note that this value closely matches the first wavelength listed in the problem.
1. Continued

We can now carry out similar calculations for \( n_1 = 2 \) and \( n_2 = 3, 4, 5, \) and \( 6 \) to see if these transitions match the other wavelengths listed in the problem. The results are summarized in the table below.

<table>
<thead>
<tr>
<th>( n_1 )</th>
<th>( n_2 )</th>
<th>Calculated wavelength (nm)</th>
<th>Experimental wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3</td>
<td>656.1</td>
<td>656.2</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>486.0</td>
<td>486.1</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>433.9</td>
<td>434.0</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>410.1</td>
<td>410.2</td>
</tr>
</tbody>
</table>

As can be seen from the table, the calculated wavelengths are in good agreement with the experimental wavelengths for \( n_1 = 2 \) and \( n_2 = 3, 4, 5, \) and \( 6. \)

2. The ionization potential of an atom is defined as the energy required to completely remove an electron.

Using Bohr's theory, calculate the ionization potential of the hydrogen atom.

The ionization potential \( (IP) \) is the energy required to remove an electron from the first orbit \( (n=1) \) to infinite separation \( (n=\infty) \).

\[
IP = E_{n=\infty} - E_{n=1}.
\]

From the Bohr theory, the energy levels of the hydrogen atom are

\[
E_n = -\frac{m e^4}{8\varepsilon_o n^2 \hbar^2}.
\]

Substituting the expression for the Bohr energies into the equation for the ionization potential yields

\[
IP = -\frac{m e^4}{8\varepsilon_o \hbar^2} \left( \frac{1}{\infty^2} - \frac{1}{1^2} \right)
\]

\[
IP = \frac{m e^4}{8\varepsilon_o \hbar^2}.
\]

Substituting for the constants and converting from Joules to Electron Volts gives

\[
IP = \frac{\left( 9.10938 \times 10^{-31} \text{ kg} \right) \left( 1.60218 \times 10^{-19} \text{ C} \right)^4}{8 \left( 8.85418 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \right)^2 \left( 6.62607 \times 10^{-34} \text{ J} \text{ s} \right)^2} \times \left( \frac{1 \text{ eV}}{1.60218 \times 10^{-19} \text{ J}} \right)
\]

\[
IP = 13.6 \text{ eV}.
\]
3. Determine the absorption frequency in wavenumbers \((\text{cm}^{-1})\) for an electron in the hydrogen atom undergoing a transition from the \(n=2\) level to the \(n=5\) level.

From the Bohr theory, the energy levels of the hydrogen atom are

\[
E_n = -\frac{m e^4}{8\epsilon_o n^2 h^2}.
\]

The energy difference between the \(n=2\) and \(n=5\) levels is

\[
\Delta E = E_5 - E_2
\]

\[
= -\frac{m e^4}{8\epsilon_o 5^2 h^2} - \left( -\frac{m e^4}{8\epsilon_o 2^2 h^2} \right)
\]

\[
= \frac{m e^4}{8\epsilon_o h^2} \left( \frac{1}{2^2} - \frac{1}{5^2} \right)
\]

\[
= \frac{\left( 9.10938 \times 10^{-31} \text{ kg} \right) \left( 1.60218 \times 10^{-19} \text{ C} \right) \left( 8.85418 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \right) \left( 6.62607 \times 10^{-34} \text{ J} \text{ s} \right) \left( \frac{1}{4} - \frac{1}{25} \right)}{8 \left( 8.85418 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \right) ^2 \left( 6.62607 \times 10^{-34} \text{ J} \text{ s} \right) ^2}
\]

\[
\Delta E = 4.57778 \times 10^{-19} \text{ J}.
\]

To determine the absorption frequency, the photon energy, \(E_{\text{photon}} = h \nu\), must be set equal to the energy spacing between the levels,

\[
E_{\text{photon}} = h \nu = \Delta E.
\]

Solving for the frequency and substituting yields,

\[
\nu = \frac{\Delta E}{h}
\]

\[
= \frac{4.57778 \times 10^{-19} \text{ J}}{6.62607 \times 10^{-34} \text{ J} \text{ s}}
\]

\[
\nu = 6.90874 \times 10^{14} \text{ s}^{-1}.
\]

This result gives the frequency in \(s^{-1}\). To get the "frequency" in units of \(\text{cm}^{-1}\), the conversion is the speed of light,

\[
\tilde{\nu} \left( \text{cm}^{-1} \right) = \frac{\nu \left( s^{-1} \right)}{c \left( \text{cm/s} \right)}
\]

\[
= \frac{6.90874 \times 10^{14} \text{ s}^{-1}}{2.99793 \times 10^{10} \text{ cm/s}}
\]

\[
\tilde{\nu} = 23045 \text{ cm}^{-1}.
\]
4. Show that Bohr's condition for the quantization of angular momentum in the hydrogen atom, \( nh = mv r \), can be obtained by requiring an integer number of standing waves around an electron orbit of radius \( r \). (Hint: you also need to use the expression for the deBroglie wavelength.)

To start, note that the circumference of an orbit of radius \( r \) is \( 2 \pi r \).

If we require an integer number of waves with wavelength \( \lambda \) to fit around the circumference of the orbit, this leads to the condition:

\[
2 \pi r = n \lambda .
\]

For matter, the deBroglie wavelength is \( \lambda = \frac{h}{p} = \frac{h}{mv} \). If we substitute this expression into the equation above, we get

\[
2 \pi r = \frac{nh}{mv} .
\]

This equation can be rearranged to yield

\[
mvr = \frac{nh}{2\pi} ,
\]

which is the condition for quantization of angular momentum.
5. Data for the photoelectric effect experiment on sodium metal is given below. Use this data to determine a value for Planck's constant, \( h \), and the work function \( \phi \) for sodium metal. Report your result for \( h \) in units of Joule-seconds, and your value of \( \phi \) in electron volts (eV).

<table>
<thead>
<tr>
<th>Photon Frequency (s(^{-1}))</th>
<th>Electron Kinetic Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.993\times10^{14}</td>
<td>1.848</td>
</tr>
<tr>
<td>8.817\times10^{14}</td>
<td>1.309</td>
</tr>
<tr>
<td>7.889\times10^{14}</td>
<td>0.972</td>
</tr>
<tr>
<td>7.138\times10^{14}</td>
<td>0.695</td>
</tr>
<tr>
<td>6.517\times10^{14}</td>
<td>0.408</td>
</tr>
<tr>
<td>5.996\times10^{14}</td>
<td>0.182</td>
</tr>
<tr>
<td>5.552\times10^{14}</td>
<td>0.0085</td>
</tr>
</tbody>
</table>

From the equation \( KE = h\nu - \phi \), it is easy to see that a plot of \( KE \) on the y-axis vs. frequency on the x-axis should yield a straight line with slope \( h \) and intercept \(-\phi \). The graph is shown in the figure below.
5. Continued

From the fit of a linear trendline, the graph has a slope of $4.0973 \times 10^{-15} \text{ eV} \cdot \text{s}$ and an intercept of $-2.263 \text{ eV}$. Therefore, using the conversion factor $1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$, we get Planck’s constant $h$ from the slope:

$$h = 6.656 \times 10^{-34} \text{ J s} \text{ (close to the literature value of } 6.626 \times 10^{-34} \text{ J s).}$$

From the intercept (which is $-\phi$), we get the work function:

$$\phi = 2.263 \text{ eV}.$$

Note that, if you did not plot the points, you could use any two of the points and solve two equations for two unknowns to get $h$ and $\phi$. Your numerical values will be slightly different in that case.

6. The threshold wavelength for the ejection of photoelectrons from sodium metal is $5420 \text{ Å}$. Calculate the velocity of photoelectrons ejected by light of wavelength $4000 \text{ Å}$.

The threshold frequency $\nu_0$ is the frequency at which the ejected electrons have zero kinetic energy:

$$KE = 0 = h\nu_0 - \phi,$$

or

$$\nu_0 = \frac{\phi}{h}.$$

We can use this equation to determine the work function of sodium metal. However, we are given the threshold wavelength and the equation above contains the threshold frequency.

Since $\lambda \nu = c$, we can solve to get the threshold wavelength as $\lambda_0 = \frac{c}{\nu_0}$.

Substituting the expression for the threshold frequency, the equation becomes $\lambda_0 = \frac{hc}{\phi}$.

Solving for the work function $\phi$ gives

$$\phi = \frac{hc}{\lambda_0} = \frac{6.62607 \times 10^{-34} \text{ J s} \cdot 2.99793 \times 10^8 \text{ ms}^{-1}}{5420 \times 10^{-10} \text{ m}}$$

$$\phi = 3.6651 \times 10^{-19} \text{ J}.$$
Now, to get the velocity of ejected photoelectrons at frequencies other than the threshold, we use the equation $KE = hν − φ$. Substituting $ν = c / λ$ for the frequency and $KE = \frac{1}{2}mv^2$ for the kinetic energy, we get

\[ KE = hν − φ \]
\[ \frac{1}{2}mv^2 = \frac{hc}{λ} − φ. \]

This equation can be solved for the velocity to yield

\[ v = \left[ \frac{2}{m} \left( \frac{hc}{λ} − φ \right) \right]^{1/2}. \]

Substituting $λ = 4000 \text{Å}$ (or $4.0 \times 10^{-7} \text{ m}$) and $φ$ from above, and using the electron mass of $m = 9.10938 \times 10^{-31} \text{ kg}$, the photoelectron velocity is

\[ v = \left[ \frac{2}{9.10938 \times 10^{-31} \text{ kg}} \left( \frac{6.62607 \times 10^{-34} \text{ Js}}{2.99793 \times 10^8 \text{ m/s}} \right) \left( \frac{2.99793 \times 10^8 \text{ m/s}}{4.0 \times 10^{-7} \text{ m}} \right) − 3.6651 \times 10^{-19} \text{ J} \right]^{1/2} \]
\[ v = 5.35 \times 10^5 \text{ m/s}. \]
7. **Using Bragg's Law**, \( n\lambda = 2d \sin \theta \), determine the distance in Å between crystal planes in an atomic solid if electromagnetic radiation of frequency \( 3.32 \times 10^{17} \text{ s}^{-1} \) incident at a 40º angle creates constructive interference fringes (assume \( n=1 \)).

Setting \( n=1 \) and solving for the distance \( d \) yields

\[
d = \frac{\lambda}{2\sin \theta}.
\]

Converting wavelength into frequency of light using the relation \( \lambda = \frac{c}{\nu} \) leads to the expression

\[
d = \frac{c}{2\nu \sin \theta}.
\]

Substituting,

\[
d = \frac{c}{2\nu \sin \theta} = \left( \frac{2.99793 \times 10^8 \text{ ms}^{-1}}{2 \left( 3.32 \times 10^{17} \text{ s}^{-1} \right) \sin(40^\circ)} \right)
\]

\[
d = 7.02 \times 10^{-10} \text{ m} \text{ or } 7.02 \text{ Å}.
\]
8. Calculate the deBroglie wavelength of an electron in the first Bohr orbit in the hydrogen atom. Does quantum or classical mechanics apply to this electron?

The deBroglie wavelength is defined as

\[ \lambda = \frac{h}{p} = \frac{h}{mv} \]

The Bohr quantization condition for angular momentum is

\[ m \cdot v \cdot r = n \cdot \frac{h}{2\pi} \]

Solving the second equation for \( m \cdot v \) gives

\[ m \cdot v = \frac{nh}{2\pi r} \]

Substituting this into the deBroglie wavelength expression leads to the relation

\[ \lambda = \frac{2\pi hr}{nh} = \frac{2\pi r}{n} \]

To get a numerical value for the deBroglie wavelength, we use the expression from class for the quantized orbit,

\[ r = \frac{\varepsilon_o n^2 h^2}{\pi me^2} \]

Substituting this into the deBroglie expression and using \( n=1 \) for the lowest Bohr orbit leads to

\[ \lambda = \frac{2\pi \cdot \varepsilon_o n^2 h^2}{nh} = \frac{2\varepsilon_o n h^2}{me^2} = \frac{2 \left( 8.85418 \times 10^{-12} \text{ C}^2 \text{J}^{-1} \text{m}^{-1} \right) \left( 6.62607 \times 10^{-34} \text{ J} \cdot \text{s} \right)^2}{\left( 9.10938 \times 10^{-31} \text{ kg} \right) \left( 1.60218 \times 10^{-19} \text{ C} \right)^2} \]

\[ \lambda = 3.32 \times 10^{-10} \text{ m} \quad \text{or} \quad 3.32 \text{ Å} \]

Since the deBroglie wavelength is the same order of magnitude as the path that the electron travels (in this case, it equals the circumference of the orbit, \( 2\pi r \)), quantum mechanics should be applied to the electron.