## ATOMIC SPECTRA

**Objectives:**

In this experiment we will measure the optical emission spectra of atomic hydrogen and atomic mercury. We will use the spectra to understand the energy levels and electronic structure of these atoms.

**Background:**

1) Use your modern physics book (Physics 211-212) and the Background Information in this chapter of the lab manual to review

    i) the quantum mechanical solution of the hydrogen atom, including energy levels and quantum numbers, and

    ii) the quantum numbers, configurations, and energy levels of multielectron atoms. In particular, make sure you know what notation such as $6^3S_1$ means.

2) Sections 3.7 - 3.9 in Taylor.

3) Sections 1.4-1.6 in Melissinos.

**Theory and Apparatus:**

We will be using an optical grating spectrometer, with hydrogen and mercury discharge tubes as the light sources. When collimated light of wavelength $\lambda$ passes through a diffraction grating that has line spacing $d$, as shown in Fig. 1, the light diffracts at angle $\theta$ according to the grating equation

$$n\,\lambda = d\,\sin\theta \qquad\qquad (1)$$

where $n$ is the diffraction order. The diffraction is to both sides of $\theta = 0°$. We will observe diffraction only in first order, so $n = 1$.
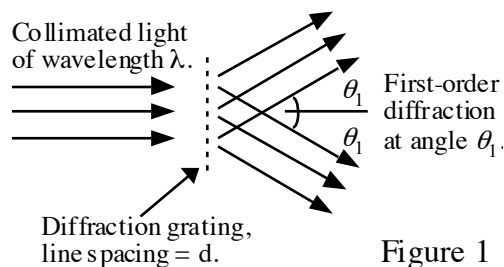


Figure 1

The grating spectrometer is a turntable for measuring angles *very* accurately. With care, you can use it to measure wavelengths to at least 3, maybe 4, significant figures. The critical part of the procedure, in order to obtain accurate results, is the alignment of the spectrometer.
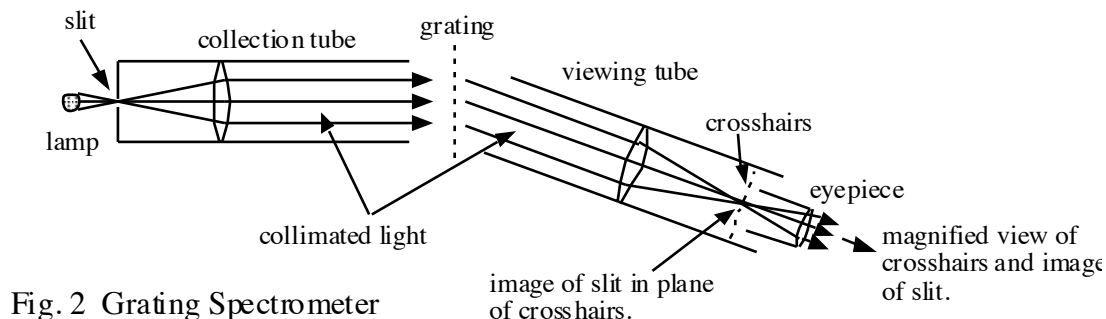


Fig. 2  Grating Spectrometer

**Procedure:**

1.  Note and record the actual number of lines per unit length for your the grating (it will be either ~700 lines/mm or ~300 lines/mm).

2.  You will need to align the spectrometer.  The essentials of this process are to adjust the focus, ensure the alignment of the collection and viewing tubes, and place the grating perpendicular to the light path.

3.  To align the spectrometer *follow the procedures that accompany the apparatus*. (Even though this is a multistep process, in your report it will be "we aligned the spectrometer.")

4.  **Caution:**  The spectral tubes are fragile so handle with care.  Be sure the power is off when installing/removing tubes.  When removing the tubes remember that they may have gotten quite hot.

5.  Now that everything is aligned, bring the hydrogen source up closer to the collection tube - about 1 cm. Note that the hydrogen discharge is blue at the ends and red in the center. Adjust the lamp vertically, if needed, to make sure you're observing the red part of the discharge (the blue part is the emission from molecular hydrogen $H_2$). Make very small adjustments in the position of the light source while looking through the eyepiece until you have maximum intensity. Unlock the position locking screw, then slowly rotate the viewing tube in the direction that gives positive angles $\approx 25°$ rather than angles $\approx 335°$. Sight through the tube while rotating until you find the violet, blue, and red lines of the hydrogen spectrum.

If needed, adjust the slit width to be as narrow as possible while still providing enough intensity to see the cross hair.

7.  Starting with the red line, which is brightest, center the cross hair on the slit and then record the angle in degrees and minutes. Before going further determine the wavelength and see if it matches the accepted 656 nm.  Repeat for the blue and violet lines. Then rotate the tube to the other side of the axis and record the angles *as you read them*, meaning ≈335°.

8. Repeat the procedure of step 7 two more times, alternating from one side of the axis to the other. When done, you'll have six angle measurements for each wavelength - three at an angle ≈25° and three at an angle ≈335°.

9.  Repeat steps 6 - 8 for the mercury discharge tube, but only make one repeat of the measurements in step 8. If your spectrometer is well focused, you should see <u>two</u> closely spaced yellow lines, a green line, a violet line, a dim blue line about halfway between green and violet, and (if you're lucky!) perhaps a dim extreme violet line and a dim red line. Measure the two yellows, the green, the dim blue, and the bright violet lines. You can skip the dim red and dim violet.

**Analysis**:

**Note**: You have data to four significant figures, so you need to use fundamental constants to <u>five</u> significant figures to avoid introducing new uncertainties.

$$h = 6.6261 \times 10^{-34} \text{ J s} \qquad e = 1.6022 \times 10^{-19} \text{ C} \qquad c = 2.9979 \times 10^{8} \text{ m/s}$$

1.  The following procedure applies to each spectral line.
NOTE:  To do arithmetic/add/subtract/find the mean etc. it will be easiest to convert all angles to decimal form, e.g. $25^{\circ} 15' = 25.25^{\circ}$.
i) Find the mean of the three (for hydrogen) or two (for mercury) angles at ≈25°. Keep 3 decimal places to avoid round-off error.
ii) Subtract your three angles at ≈335° from $360^{\circ} = 359^{\circ} 60'$ to get the actual diffraction angles. Average these angles.
iii) Your averages in i) and ii) may differ slightly if your grating was rotated slightly from 0°. To compensate for any slight rotation of the grating, average the two values you found in i)

and ii). This is now your best estimate of the diffraction angle θ for that wavelength. Repeat i) - iii) for each wavelength.

2.  You need an uncertainty δθ for each wavelength. For hydrogen, find the standard deviation $\sigma_\theta$ of the three measurements at ≈25°, then divide by $\sqrt{3}$ to find the standard deviation of the mean. Repeat this for the three angles measured at ≈335°. (Note that you cannot combine these six measurements because of possible systematic offsets if the grating is slightly rotated.) You now have two different standard deviations of the mean, so it's reasonable to average them. This is your value of δθ. Repeat for the other wavelengths in hydrogen.

You don't have enough data on mercury to use this same procedure, but your mercury measurements should be the same precision as your hydrogen measurements. Consequently, you can use the hydrogen δθ that is closest to each mercury wavelength.

3.  Now use the grating equation to find the wavelength of each line in the spectra. You'll need to do **and show explicitly** the error analysis to find δλ (see Section 3.7 in Taylor). *Think carefully* about the units of δθ. Make a table (one each for hydrogen and mercury) showing the final values of θ, δθ, λ, and δλ. In spectroscopy, it is customary to express λ and δλ in nanometers (nm).

4.  The accepted values of the wavelengths in hydrogen are 656.3 nm, 486.1 nm, and 434.0 nm. Are your measurements in agreement? Recall that "agreement" means "are the measurements within two standard deviations of the accepted values?"

5.  The hydrogen lines you observed are part of the Balmer series $n \rightarrow 2$ in hydrogen, where $n$ is an **integer**. The photon energies $E_{ph}$ correspond to $\Delta E_{atom} = E_n - E_2$. Using the hydrogen energy levels, these should be

$$E_{ph} = hf = \frac{hc}{\lambda} = \Delta E_{atom} = E_R \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$

(2)

where $E_R$ is the Rydberg energy with a *theoretical* value of 13.60 eV. Rearranging,

$$\lambda = \frac{hc/E_R}{1/4 - 1/n^2} = \frac{hc}{E_R} q$$

(3)

where $q = (1/4 - 1/n^2)^{-1}$. A graph of λ-versus-$q$ should be a straight line passing through the origin and having a *slope* of $hc/E_R$ and a y-intercept of 0.

Determine the values of *n* and *q* for each of your lines. (**Note:** The values of *n* are the *exact integers* that define the Balmer serier. They are <u>not</u> computed with Equation 3.) Then use Matlab to make a graph of *λ*-versus-*q* and fit a straight line to your data. The equation of the line gives you the slope and intercept. You will need to think carefully about the *units* and the appropriate number of *significant figures*.

**Note**: In Excel, to change the number of significant figures shown for the slope and intercept, click on the equation to highlight it, then go the the **Format/TrendlineLabel**. Choose **Number** and then select "Scientific" with the appropriate number of decimal places.

Use the slope of your graph to determine an *experimental* value for $E_R$. Use MATLAB's one-sigma confidence intervals as an estimate of your uncertainty. These commands should be helpful:

```
params = coeffvalues(fittedmodel)
ranges = confint(fittedmodel,0.6827)
```

Also, determine whether your *experimental y*-intercept is very close to zero.

6. IF you've finished the Fundamental Unit of Charge (Millikan oil drop) experiment, proceed with this part. If not, record your value of $E_R$ in your lab book and do this calculation then. Then go to Step 7.

From quantum mechanics, $E_R$ – in joules! – is defined as

$$E_R = \frac{me^4}{(4\pi\varepsilon_0)^2 \cdot 2\hbar^2},$$

where *m* is the electron mass. In experiments Charge to Mass Ratio and Fundamental Unit of Charge (Millikan) you determined experimental values for *e* and *m*, along with uncertainties δ*e* and δ*m*. Combine these with your experimental value of $E_R$ to find an experimental value of Planck's constant *h* and its uncertainty δ*h*. *Show your error analysis*. Compare your value for *h* with the accepted value. Remember that "to compare" means determine whether or not your error bars overlap the accepted value.

7. For the mercury spectrum, use your data to calculate the energy (in eV) of each emission line you observed. Make sure the number of significant figures you show is consistent with the significant figures of your data. Then use the information found at the end of this experiment to identify the atomic transition that corresponds to each line. For example, a transition might be identified as 6s8s $^1P_1 \rightarrow$ 6s$^2$ $^1S_0$. Use this notation to identify each transition. (You will find it useful to use the energy level diagram to pick out transitions that

have roughly the right energy, then go to the table of energy levels to narrow the choices.)
Make sure your proposed identifications obey the selection rules given in the Background
Information. Note that for mercury a few transitions have $\Delta S$=1.

**Additional Questions:**

1. You observed the hydrogen spectrum in the first order. How many orders of the red
Balmer line can be observed with this grating? At what angle would the line appear in each
order?

2. What is the limit (the shortest possible wavelength) of the Balmer series? Why didn't you
observe this limit?

3. Why are some lines brighter than others?

4. Consider a 6s6d configuration in the mercury atom.
a. What are the possible values of $L$?
b. What are the possible values of $S$?
c. List all the possible terms that arise from this configuration.

5. The mercury atoms are excited by collisions with electrons in the discharge tube. For a
mercury atom at rest, what is the minimum electron speed that can cause the emission of a
photon at the green wavelength that you observed in the mercury spectrum? (Caution: This
question is more subtle than it may appear. You must think carefully about how atoms are
excited and de-excited.)

**Background Information: Atomic Physics**

This information is a brief *review* of material from Physics 211-212. Refer to your Modern Physics textbook for more information.

**1. Hydrogen atoms**

Each state in the hydrogen atom is characterized by a unique set of five quantum numbers: $n$, $l$, $s$, $m_l$, $m_s$ .

1. Principal quantum number $n$ ($n$ = 1, 2, 3...)

2. Orbital angular momentum quantum number $l$, which must be less than n:
$$(l = 0, 1, 2, 3, ..., n\text{-}1.)$$
The $l$-value of the state is usually designated by a letter, with s meaning $l$ = 0, p meaning $l$ = 1, and d meaning $l$ = 2. Note that each letter represents a unique and well-defined value of $l$.

3. Spin angular momentum quantum number $s$ = 1/2

4. $z$-component of the orbital angular momentum $m_l$
$$(m_l = \text{-}l \text{ to } +l \text{ in integer steps; } 2l+1 \text{ values})$$

5. $z$-component of the spin angular momentum $m_s$
$$(m_s = \text{-}1/2, +1/2)$$

Since $s$=1/2 for all electron states, only the four quantum numbers ($n$, $l$, $m_l$, $m_s$) are needed to uniquely specify each state.

The **energy** of the hydrogen-atom state with quantum numbers ($n$, $l$, $m_l$, $m_s$) is

$$E(n, l, m_l, m_s) = -13.6 \,(1/n^2) \text{ eV,} \tag{4}$$

where zero energy corresponds to the electron at infinity ($r \rightarrow \infty$ as $n \rightarrow \infty$). This is called the **ionization limit**, and 13.6 eV is the **ionization energy** for hydrogen. The quantity 13.6 eV is also called $E_R$, the **Rydberg energy**. Its value is predicted by quantum theory and confirmed by experiment.

Note that Eq. 4 applies <u>only</u> to hydrogen, not to any other element. It is an interesting fact that the energy depends only on the principal quantum number $n$ and not on the angular momentum $l$. This situation is unique to hydrogen. For multi-electron atoms, the energy will depend on both $n$ and $l$.

The electron in the hydrogen atom can make **transitions** between the quantum states by absorbing or emitting photons. The photon energy is just the difference in energy between the two states involved. For a transition from state $n$ to a lower energy state $m$, the photon energy and wavelength are

$$E_{\text{photon}} = hf = hc/\lambda = 13.6 \; [1/m^2 - 1/n^2] \; \text{eV}. \qquad\qquad (5)$$

**2. Multi-electron atoms:**

Multi-electron atoms are complicated due to the fact that electrons interact not only with the nucleus (attractive forces) but also with each other (repulsive forces). The Schrodinger equation cannot be solved exactly for any multi-electron atom, but there are many approximation techniques and numerical methods that give good results.

In the **independent particle approximation**, we can imagine that each electron occupies a hydrogen-like one-electron state. However the Pauli exclusion principle requires each electron to have a unique set of one-electron quantum numbers ($n, l, m_l, m_s$). Starting with $n=1$, $l=0$, $m_l=0$, $m_s= \pm 1/2$, imagine the electrons of a particular atom filling the available states. But because of electron-electron repulsion, the energies of the one electron states depend on l as well as n. In general, states with lower values of $l$ for a given $n$ fill first - that is, states are filled in the order 1s, 2s, 2p, 3s, 3p, etc. For higher values of $n$, this rule gets modified so that, for example, 4s fills before 3d.

When all the available states with the same value of n are filled, we say the electrons form a **closed shell**.

The list of one-electron states occupied in an atom is known as its **electron configuration**. When the lowest possible one-electron states are filled, we say the atom is in its **ground electronic state**. For example, the ground state of oxygen, with 8 electrons, is written $1s^2 2s^2 2p^4$, where the superscripts indicate the number of electrons in each state. In this

example, the 1s shell is closed and the 2s **subshell** is also closed. The four electrons in the open 2p subshell are the valence electrons for oxygen.

Valence electrons can be excited to higher one-electron states. For example, one of the 2p electrons in oxygen could be excited to a vacant 3d state, creating the configuration $1s^2 2s^2 2p^3 3d$. It is customary to list just the electrons outside of closed shells and closed subshells, so this excitation would be called $2p^4 \rightarrow 2p^3 3d$. The excited atom can return to a lower energy state by the emission of a photon.

Unlike hydrogen, the energies of the various possible states in a multielectron atom depend on the principal quantum numbers $n_1$, $n_2$, $n_3$, ... <u>and</u> on their angular momentum quantum numbers $l_1$, $l_2$, $l_3$, ... It is useful to define a **total orbital angular momentum**

$$\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 + \mathbf{l}_3 + ...$$

that is the vector sum of the individual electron orbital angular momentum vectors $\mathbf{l}_1$, $\mathbf{l}_2$, $\mathbf{l}_3$, ... This total angular momentum $\mathbf{L}$ is also quantized, and the atom as-a-whole is characterized by its total angular momentum quantum number $L$. Quantum number $L$ can have integer values

$$L = 0, 1, 2, 3, \dots = S, P, D, F, ...$$

and it is represented by a letter just like the individual electrons - S for $L$=0, P for $L$=1, D for $L$=2 - except that we use upper-case letters for $L$. There are rules for how the possible values for L depend on the values for $l_1$, $l_2$, $l_3$, ..., but we needn't worry about them here.

Similarly, define the **total spin angular momentum S** is defined as

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + ...$$

where $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{s}_3$, ... are the spins of electrons in unfilled shells. For electrons in closed shells, $\mathbf{S} = 0$. The total spin angular momentum must also be quantized, giving quantum number $S$. For a single electron outside of closed shells, such as in sodium, $S = 1/2$. With two valence electrons, their individual spins can be either parallel or anti-parallel, so the total spin quantum number $S$ must be either $S = 0$ or $S = 1$.

Finally, we can define the atom's **total angular momentum J**

$$\mathbf{J} = \mathbf{L} + \mathbf{S}.$$

The total angular momentum is also quantized and is characterized by quantum number $J$, which must have one of the values in the range

$$|L - S|, \ |L - S| + 1, \ |L - S| + 2, \ \dots \text{ up to } L + S.$$

For example, the excited state of sodium that emits the characteristic yellow light of sodium has total orbital angular momentum $L = 1$ (a P-state) and total spin angular momentum $S = 1/2$. The total angular momentum quantum number $J$ must range from $1 - 1/2$ to $1 + 1/2$, giving the two possible values $J = 1/2$ or $J = 3/2$. As another example, the $L = 1$, $S = 0$ combination in the mercury atom can produce total angular momentum only with $J = 1$. But the $L = 1$, $S = 1$ combination can produce $J = 0$, $J = 1$, or $J = 2$.

Each **state** of a multielectron atom is designated by the four quantum numbers $L, S, J, M_J$, where $M_J$ must be in the range $-J, -J+1, -J+2, ..., J-1, J$. In the absence of a magnetic field, the energy is independent of $M_J$. Thus the $2J+1$ states with the same value of $J$ are **degenerate** – they have the same energy.

The $2J+1$ states of a multielectron atom that share the same values of $L, S,$ and $J$ are collectively called a **term** and are designated by the term symbol

$$^{2S+1}L_J.$$

Numerical values are used for $2S+1$ and for $J$, but $L$ is represented by its letter equivalent. For example, an atom with a 3s and a 3p electron outside of the closed $n = 2$ shell gives rise to the four terms having $(L,S,J) = (1,0,1)$, $(1,1,0)$, $(1,1,1)$, and $(1,1,2)$. These terms would be designated $^1P_1$, $^3P_0$, $^3P_1$, and $^3P_2$.

Terms with $S = 0$ ($2S+1 = 1$) are called **singlets**. Similarly, terms with $S = 1/2$ ($2S+1 = 2$) are called **doublets** and terms with $S = 1$ ($2S+1 = 3$) are called **triplets**.

Each of the terms has a different energy, and these are the **energy levels** shown in the energy-level diagram of a multielectron atom. There are many handbooks that list the energy levels, or terms, for multielectron atoms. These are determined experimentally rather than by calculation because the calculations, other than for hydrogen, are far too difficult. Notice that one configuration - such as 3s3p - can give rise to <u>several</u> different terms, each with a different energy. Each term represents a different way that the locations and angular momenta of the individual valence electrons can be arranged inside the atom.

Rather than letting $E = 0$ represent the ionization limit, it is customary to call the ground state energy $E = 0$. Then the listed energy of each term (now a positive value) is its energy <u>above</u> the ground state.

The emission or absorption of electromagnetic radiation in multi-electron atoms corresponds to transitions between different terms. A transition between a term of energy $E_1$ and a term of energy $E_2$ causes the emission or absorption of a photon of frequency $f$ and wavelength $\lambda$ given by

$$hf = hc/\lambda = |E_1 - E_2|.$$

Not all possible transitions actually occur. Quantum mechanics dictates that the **allowed transitions** should obey the **selection rules**:

$\Delta J = 0, \pm 1$ (but $J{=}0$ to $J{=}0$ is excluded)
$\Delta L = 0, \pm 1$
$\Delta S = 0$
and $\Delta l = \pm 1$

The first two rules are based on conservation of angular momentum, recalling that a photon has spin = 1. The other rules concern the fact that emission of radiation depends on an oscillating electric dipole in the atom; these rules ensure that the electric dipole is not zero.

**Note:** The $\Delta J$ and the $\Delta l$ selection rules are rigorously obeyed. The $\Delta L$ and $\Delta S$ rules begin to break down for heavy elements. A couple of the transitions you observe in mercury do, in fact, have $\Delta S = 1$.

For example, $^3P_1 \rightarrow {}^3S_1$ is an allowed transition with $\Delta S = 0$, $\Delta J = 0$, and $\Delta L = 1$. But $^3P_1 \rightarrow {}^3D_3$ would not be seen because $\Delta J = 2$ violates the selection rule.

**Some energy levels of the mercury atom:**

Ground state configuration: $[1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10}] 6s^2$

All excited state configurations are [closed shells] $6snl$, with one of the 6s valence electrons being excited to a higher level having single-electron quantum numbers $nl$. To fully specify an energy level, you show its term symbol preceded by the n-value of the excited electron. Thus the 6s6p excited configuration has several terms, one of which has $S=1$, $L=1$, and $J=0$. This term is listed as the energy level 6s6p $6^3P_0$.

| Term | | Energy (eV) |
|---|---|---|
| $6s^2$ | $6^1S_0$ | 0.0000 |
| 6s6p | $6^3P_0$ | 4.6658 |
| 6s6p | $6^3P_1$ | 4.8848 |
| 6s6p | $6^3P_2$ | 5.4588 |
| 6s6p | $6^1P_1$ | 6.7014 |
| 6s7s | $7^3S_1$ | 7.7278 |
| 6s7s | $7^1S_0$ | 7.9234 |
| 6s7p | $7^3P_0$ | 8.6160 |
| 6s7p | $7^3P_1$ | 8.6340 |
| 6s7p | $7^3P_2$ | 8.8256 |
| 6s7p | $7^1P_1$ | 8.8364 |
| 6s6d | $6^1D_2$ | 8.8412 |
| 6s6d | $6^3D_1$ | 8.8415 |
| 6s6d | $6^3D_2$ | 8.8490 |
| 6s6d | $6^3D_3$ | 8.8533 |
| 6s8s | $8^3S_1$ | 9.1669 |
| 6s8s | $8^1S_0$ | 9.2218 |
| 6s8p | $8^3P_0$ | 9.4750 |
| 6s8p | $8^3P_1$ | 9.4775 |
| 6s8p | $8^3P_2$ | 9.5216 |
| 6s8p | $8^1P_1$ | 9.5266 |

| quantum number $l$ | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| label | $s$ | $p$ | $d$ | $f$ |
| magnitude of $L$ | 0 | $\sqrt{2}\,\hbar$ | $\sqrt{6}\,\hbar$ | $\sqrt{12}\,\hbar$ |

| $n$ | $E = 0$ eV | ionization limit | | | |
|---|---|---|---|---|---|
| 4 | −0.85 eV | $4s$ | $4p$ | $4d$ | $4f$ |
| 3 | −1.51 eV | $3s$ | $3p$ | $3d$ | |
| 2 | −3.40 eV | $2s$ | $2p$ | | |
| 1 | −13.60 eV | $1s$ | ⟵ ground state | | |

Energy level diagram for the hydrogen atom.
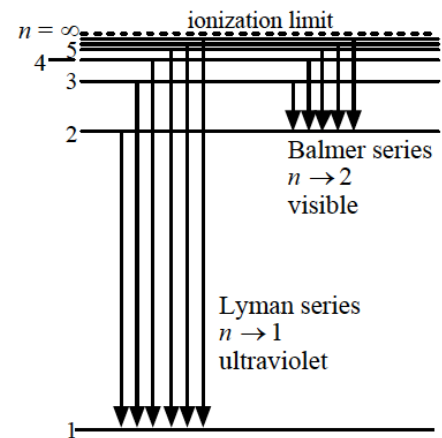
Emission spectrum of hydrogen.
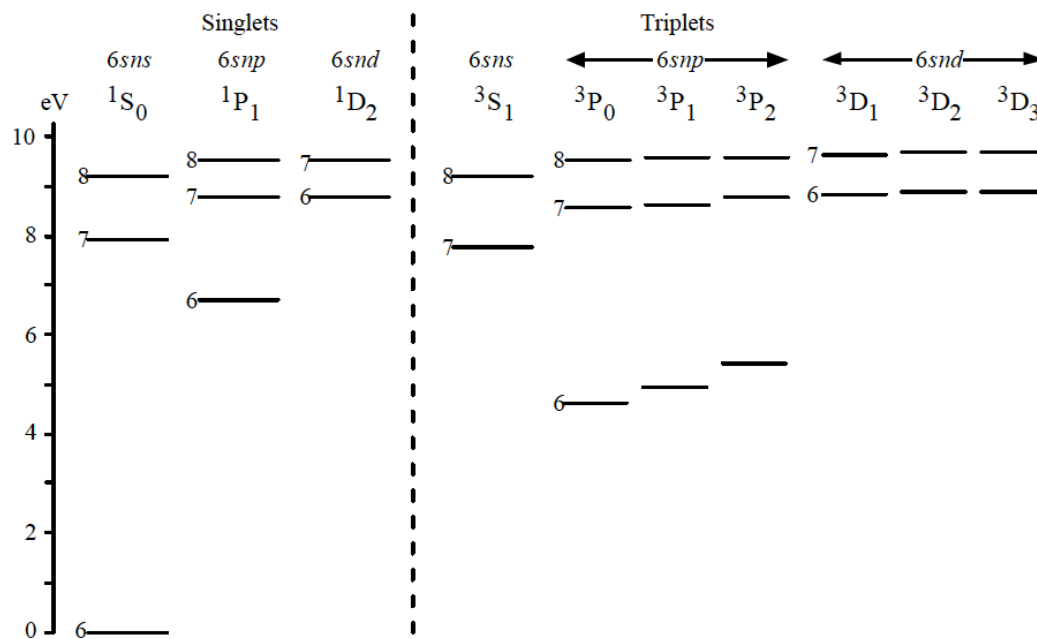
Energy level diagram for the mercury atom.