

DISCRETE SPECTRA

H

$n = \infty$	0
$n = 3$	-1.5 eV
$n = 2$	-3.4 eV
$n = 1$	-13.6 eV

He⁺

$n = \infty$	0
$n = 3$	-6.0 eV
$n = 2$	-13.6 eV
$n = 1$	-54.4 eV

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by

Paul M. Parker and William C. Lane

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Author: Paul M. Parker and William C. Lane, Michigan State University

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Input Skills:

1. Vocabulary: atom, photon, electron (MISN-0-212), wavelength of light (MISN-0-212), frequency of light (MISN-0-212), photon energy (MISN-0-212).
2. Given the wavelength light coming from an object, state the light's perceived color (MISN-0-212).

Output Skills (Knowledge):

- K1. Vocabulary: quantization, energy level, energy level diagram, ground state, excited state, ionization, hydrogen-like ion, quantum jump, principle quantum number, atomic one-electron system, atomic number, spectrometer.
- K2. State the energy level formula for atomic one-electron systems.

Output Skills (Rule Application):

- R1. Given the atomic number Z for an atom, state the symbol for its corresponding hydrogen-like ion.

Output Skills (Problem Solving):

- S1. Construct an energy-level diagram for any atomic one-electron system, showing energy and quantum number values for each level.
- S2. Calculate the wavelength and frequency of the photon emitted when any given atomic one-electron system makes a transition from one specified energy level to another. State the perceived color of light made up of those photons.
- S3. Given a distribution of emitted energy over a discrete set of wavelengths, use linear interpolation on a table of tri-stimulus values, plus a Chromaticity Diagram, to determine the light's chromaticity coordinates and perceived color.

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A. A. Strassenburg	S. U. N. Y., Stony Brook

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1. Overview

In certain circumstances, light coming from atoms and molecules consists of photons at various individual isolated wavelengths that are typical of the particular species of atom or molecule. The discrete nature of such photon emission/absorption spectra leads us to conclude that the energy states of atoms and molecules exhibit “quantization,” that the atom or molecule can only exist in certain “allowed” energy states. The possible energy states of a system are expressed in terms of “energy levels” and are illustrated by means of an “energy level diagram” for the system (atom or molecule) being studied. The photon spectra originate from transitions between the energy levels in the system.

In this module we examine the operation of the simplest atomic/molecular system, one-electron atoms. Discrete spectra in other atoms and molecules are due to similar mechanisms but there are no simple equations for those cases. In fact, large complex computer programs and algorithms that took decades to develop are necessary for even slightly more complicated systems.

2. Atomic One-Electron Systems

2a. Atomic Hydrogen. The simplest example of an atomic one-electron system is atomic hydrogen, which consists of an electron and a single proton bound together by electrostatic attraction. Since the electron and proton have equal but opposite charges, they form a neutral-charge system properly called an atom.

2b. Hydrogen-like Ions. A hydrogen-like ion is obtained by starting with a neutral (zero total electric charge) atom and stripping it of all but one of its electrons. For example, suppose we start with a neutral nitrogen atom, ${}_{7}\text{N}^0$, which consists of the nucleus with charge $+7e$ and seven orbiting electrons, each with charge $-e$. After six of these electrons have been sequentially removed, we are left with only the nitrogen nucleus ($+7e$) and one electron ($-e$). This is a hydrogen-like ion of net charge $+6e$, denoted by ${}_{7}\text{N}^{6+}$. The subscript is called the “atomic number” of

the system and denotes the number of protons in the nucleus.

Starting with hydrogen itself and proceeding up the periodic table, we obtain this sequence of atomic one-electron systems: ${}_{1}\text{H}^0$, ${}_{2}\text{He}^+$, ${}_{3}\text{Li}^{++}$, ${}_{4}\text{Be}^{+++}$, ${}_{5}\text{B}^{4+}$, ${}_{6}\text{C}^{5+}$, ${}_{7}\text{N}^{6+}$, \dots

3. Energy Levels

3a. The Energy Level Formula. The energy levels of one-electron atoms are given by:

$$E_n = (-13.6\text{eV})Z^2n^{-2}, \quad (1)$$

where Z is the atomic number of the system and n is the “principal quantum number,” a positive integer, i.e. $n = 1, 2, 3, \dots$. No simple formula like Eq. (1) exists for atoms which have more than one electron. For multiple-electron atoms, energy levels and other atomic properties must usually be calculated approximately using sophisticated numerical techniques on computers. The more electrons, the more elaborate the techniques that are needed and the less accurate the answers.

3b. Corrections to the Formula. Even in atomic one-electron systems Eq. (1) is not precisely correct. Relativistic corrections to Eq. (1) change the answer in the fifth digit. More exotic effects, like polarization of the vacuum, give corrections beginning in the sixth digit. Those tiny effects have been calculated from theory and confirmed by experiment. Such tiny effects will not concern us here.

3c. Energy Level Diagrams. A very powerful tool used to visualize and classify the energy levels of an atomic or molecular system is the “en-

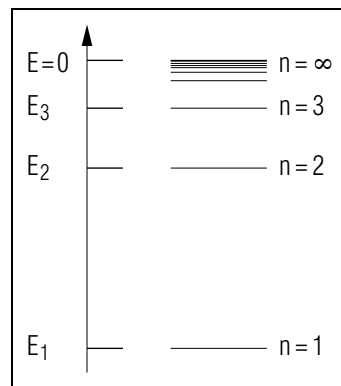


Figure 1. Energy level diagram for an atomic one-electron system (roughly to scale). Also shown are the principal quantum numbers, n .

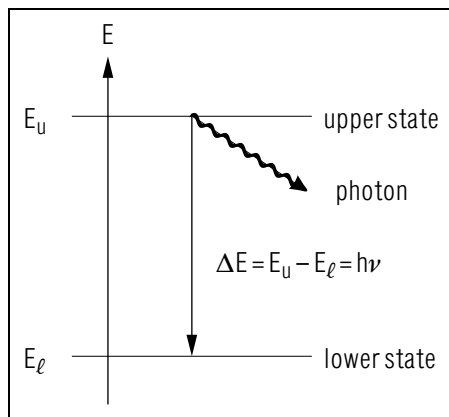


Figure 2. A quantum jump from an upper state E_u to a lower state E_l resulting in the emission of a photon of energy $h\nu$.

ergy level diagram.” As illustrated in Fig. 1, the energy levels of an atomic one-electron system are represented by horizontal lines on a vertical scale denoting the total energy of the system. The lowest possible (most negative) energy level of any quantized system is called the “ground state,” and higher levels are called “excited states.” For the system illustrated in Fig. 1, E_1 is the ground state, E_2 is the first excited state, E_3 is the second excited state, etc. When n is ∞ the energy of the system is zero. This corresponds to complete separation of the electron from the nucleus, i.e. the system is completely “ionized.” Energy states above $E = 0$ form a “continuum” since any energy state is possible for a free electron.

4. Optical Spectra

4a. Atoms May Reach Excited States By Collisions. The bombardment of a low-pressure gas of atoms or molecules with electron beams results in the collisional excitation of the atoms or molecules of the gas from the ground state, where each normally resides, into one of its excited states. The lifetime of an atom in an excited state is ordinarily quite short, of the order of 10^{-8} seconds, after which the atom reverts very quickly to its ground state in either a single “quantum jump” or a sequential series of jumps through intermediate levels. Every time such a downward (in energy) jump takes place, the energy lost by the atom is carried away by a photon created at the time of the jump, as illustrated in Fig. 2. The photon’s energy must equal the energy lost by the atom, ΔE :

$$\Delta E = h\nu \quad (2)$$

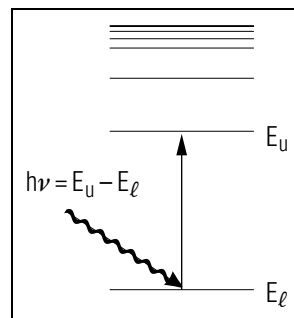


Figure 3. Absorption of a photon by an atomic or molecular system.

where ν is the frequency of the photon and h is Planck’s constant. Equation (2) is the basic equation for all of radiation spectroscopy.

4b. The Optical Emission Spectrum. As the collisional excitations and photon emission processes continuously take place in a sample of excited gas, the characteristic spectrum of the particular gas present is observed.

When analyzed, all emitted light should contain only frequencies ν that satisfy Eq. (2). For hydrogen these frequencies are given by:

$$h\nu = E_u - E_l = 13.6 \text{ eV} \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right), \quad (3)$$

where n_l and n_u are the values of the principal quantum number n for the lower and upper energy states, respectively.

4c. The Optical Absorption Spectrum. If a beam of photons with a continuous range of energies is incident on a collection of atoms or molecules, certain photons are absorbed, yielding an “optical absorption spectrum.” If the energy of the photon corresponds to a possible quantum jump upward for the atom or molecule in its present energy state, then the photon may be absorbed, as illustrated in Fig. 3, with the atom or molecule now at a higher energy level. After a short period of time ($\approx 10^{-8}$ s) the atom or molecule may make a downward quantum jump from E_u to E_l with the emission of a photon of energy $h\nu = E_u - E_l$, but whose direction is random. Consequently the original beam of photons will be depleted of those photons whose energies correspond to possible quantum jumps in the atom or molecule. The effect is *as though* those particular photons were scattered out of the beam (actually, they were absorbed and re-emitted).

4d. Accuracy of the Predicted Frequencies. The observed frequencies of hydrogen and the hydrogen-like ions agree with those predicted by Eqs. (1) and (2) to four significant digits in all known cases.

▷ A hydrogen atom jumps from $n_u = 5$ to $n_\ell = 2$. Show that the energy of the emitted photon is, by Eq. (3), 2.86 eV. *Help: [S-1]*

Show that the frequency ν and wavelength λ of this radiation are 6.91×10^{14} Hz and 434 nm, respectively. *Help: [S-2]*

This wavelength is indeed found to be present in the spectrum of hydrogen. Use the Table in Appendix A and the Chromaticity Diagram in Appendix B to show that this wavelength lies in the blue-violet visible region of the electromagnetic spectrum. *Help: [S-3]*

▷ Show that the same “5 to 2 jump” in ${}_3\text{Li}^{++}$ produces a photon with energy, frequency, and wavelength given by 25.7 eV, 6.22×10^{15} Hz, and 48.2 nm, respectively. *Help: [S-4]*

Show that the wavelength of this photon lies below the visible spectrum, in the ultraviolet. *Help: [S-5]*

The eye cannot see it, but it can be detected in UV (ultraviolet) spectrometers.

Acknowledgments

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Glossary

- **atomic number:** the number of protons (particles with charge $+e$) in the nucleus of the atomic one-electron system, denoted by the symbol Z . Z is usually indicated by a left subscript on the chemical symbol of the system, i.e. ${}_4\text{Be}$.
- **atomic one-electron system:** a two-particle system bound together by electrostatic attraction, consisting of a nucleus with charge $+Ze$ and a single electron with charge $-e$ where Z is the atomic number of the system.
- **energy level:** a possible value for the total energy of a real system.

- **energy-level diagram:** a one-dimensional graph of the energy levels of a system, with the levels indicated by horizontal lines at the appropriate places on a vertical energy scale. Bound states of the systems are represented by negative energy levels.
- **excited state:** an energy level of a system higher on the energy scale (more positive) than the system’s lowest (most negative) energy level.
- **ground state:** a system’s lowest (most negative) energy level, whether the system is currently in that state or not.
- **hydrogen-like ion:** an ion produced by stripping away all but one electron from an initially neutral atom, leaving a system consisting of a nucleus of charge $+Ze$ and a single electron.
- **ionization:** the process of adding electrons to, or removing electrons from, an initially neutral atom to form a charged particle called an “ion.” By removing all the electrons, the atom is “completely ionized.”
- **principal quantum number:** the quantum number (commonly denoted n , an integer greater than zero) that fixes the energy of single-electron atoms; in quantum mechanics it is one more than the number of radial nodes in the wave function (not counting a possible node at the origin or one at infinity).
- **quantization:** the property of atomic and molecular systems wherein certain quantities, such as total energy, may only take on discrete “allowed” values.
- **quantum jump:** a transition between quantized energy states.
- **spectrometer:** a device for determining the spectrum of light in any particular beam, resulting in photograph, a plot, or a table of intensity versus wavelength.

PROBLEM SUPPLEMENT

$$h = 0.4135 \times 10^{-14} \text{ eV s}; \quad hc = 1.2397 \text{ KeV nm}; \quad c = 3.00 \times 10^8 \text{ m/s}$$

Problem 4 also occurs in this module's *Model Exam*.

▷ **FIRST DO** problems 1-2 which are in-text problems in Sect. 4d.

3. The energy levels of a certain atomic one-electron system have been determined to be:

$n = \infty$		$E = 0$
$n = 4$		$E = -3.4 \text{ eV}$
$n = 3$		$E = -6.0 \text{ eV}$
$n = 2$		$E = -13.6 \text{ eV}$
$n = 1$		$E = -54.4 \text{ eV}$

- a. Assuming the atom is initially in the ground state (a good assumption), is it possible for a 27.0 nm photon to be absorbed? Why or why not?
 - b. Answer the same question for a 25.6 nm photon.
 - c. Assuming the atom is a hydrogenlike ion, what is the charge of the nucleus?
4. A singly ionized helium atom in the ground state absorbs a photon and is excited to the $n = 4$ energy level. The system can de-excite by emitting other photons. Assuming all quantum jumps to lower energy levels are allowed, calculate all possible wavelengths of emitted photons and identify the region of the spectrum they belong to. If in the visible region, state the perceived color of light made up of such photons. *Help: [S-8]*

5. Construct an energy-level diagram for an N^{6+} hydrogen-like ion, showing the energy and quantum number values for several of the lowest lying energy levels. Your diagram should be roughly to scale.
6. Calculate the wavelength of the photon emitted when a C^{5+} hydrogen-like ion makes a transition from the state with $n = 4$ to the state with $n = 3$. Sketch the energy levels and mark this transition on it as an arrow. Note: The ground state energy of hydrogen is (-13.6 eV) . Is this a visible photon?
7. (only for those interested and who have studied "Specification of Color: Chromaticity," MISN-0-227) Determine the chromaticity coordinates, to two significant digits, and hence the color, of a commercial clear mercury lamp whose emitted energy in the visible region is almost completely in these four spectral lines as quoted by the lamp's manufacturer: *Help: [S-7]*

$\lambda(\text{nm})$	Energy
404.7	250
435.8	520
546.1	625
578.0	840

Note: this is a regular fluorescent lamp without the usual phosphor coating on the inside of the glass.

Brief Answers:

3. a. No. The energy of the photon is 45.9 eV. In absorbing such a photon, the atom would be raised to an energy level of -8.5 eV , where no allowed state exists (this is between the allowed $n = 2$ and $n = 3$ levels).
 - b. Yes. The energy of this photon is 48.4 eV, which would excite the atom from the $n = 1$ state at -54.4 eV to the $n = 3$ state at -6.0 eV .
 - c. $3.2 \times 10^{-19} \text{ C}$.
4. Incoming photon: $hc/\lambda = E_4 - E_1$

Outgoing photons:

$$n = 4 \rightarrow n = 3: \lambda = 468.8 \text{ nm (visible)}$$

$$n = 4 \rightarrow n = 2: \lambda = 121.5 \text{ nm (ultraviolet)}$$

$$n = 4 \rightarrow n = 1: \lambda = 24.3 \text{ nm (ultraviolet)}$$

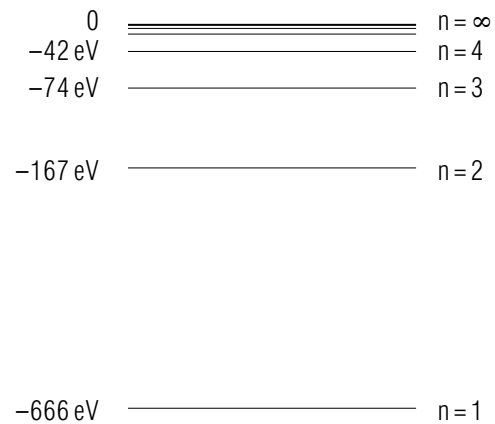
$$n = 3 \rightarrow n = 2: \lambda = 164.1 \text{ nm (ultraviolet)}$$

$$n = 3 \rightarrow n = 1: \lambda = 25.6 \text{ nm (ultraviolet)}$$

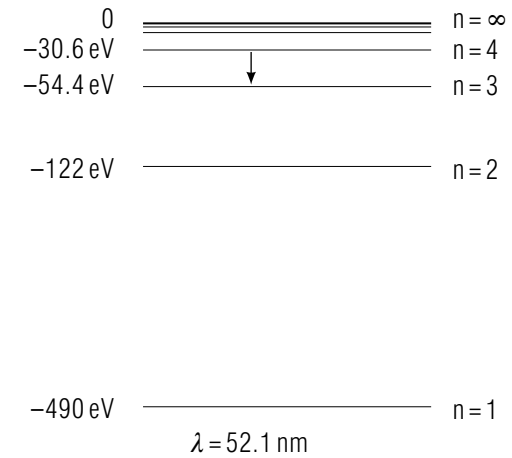
$$n = 2 \rightarrow n = 1: \lambda = 30.4 \text{ nm (ultraviolet)}$$

(These answers use $hc = 1.2397 \text{ KeV nm}$ and $E = -13.6 \text{ eV } Z^2/n^2$)

5. Energy levels of N^{6+} :



6. C^{5+}



No

7. $x = 0.34, y = 0.40$; a shade of white.

SPECIAL ASSISTANCE SUPPLEMENT

S-1 (from TX-4d)

$$h\nu = \left(\frac{-13.6 \text{ eV}}{5^2} \right) - \left(\frac{-13.6 \text{ eV}}{2^2} \right) = 13.6 \text{ eV} \left(\frac{1}{4} - \frac{1}{25} \right)$$

S-2 (from TX-4d)

$$\nu = \frac{E}{h} = \frac{2.86 \text{ eV}}{0.414 \times 10^{-14} \text{ eV s}}$$

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ m/s}}{6.91 \times 10^{-14} / \text{s}}$$

S-3 (from TX-4d)

Interpolation in the Table of Appendix A gives:

$$x = 0.1689 + 0.4(0.1644 - 0.1689)$$

$$y = 0.0069 + 0.4(0.0109 - 0.0069)$$

Help: [S-6]

S-4 (from TX-4d)

Notice that the energy of this photon is 3^2 times the energy of the photon from the hydrogen transition. Notice also that Li has $Z = 3$ and H has $Z = 1$.

S-5 (from TX-4d)

The lower limit for the spectrum of visible light is 400 nm.

The number 48.2 is smaller than the number 400.

S-6 (from [S-3])

434 nm is 0.4 of the way from 430 nm to 440 nm

S-7 (from PS, problem 7)

Interpolate, just as you did in the problem in the text, Sect. 4d. For a check, we get for the 435.8 nm line: $x_\lambda = 0.321$, $y_\lambda = 0.018$, $z_\lambda = 1.595$. If you do not know what to do with these numbers, you did not acquire the prerequisite skills listed in this module's *ID Sheet*.

S-8 (from PS, problem 4)

See "Characteristics of Photons" (MISN-0-212), Figure 1.

MODEL EXAM

$$h = 0.4135 \times 10^{-14} \text{ eV s}; \quad hc = 1.2397 \text{ KeV nm}; \quad c = 3.00 \times 10^8 \text{ m/s}$$

The ground state energy of hydrogen is (-13.6 eV).

Note: the actual exam will have an attached table of chromaticity coordinates for a series of wavelengths and a Chromaticity Diagram.

1. See Output Skills K1-K2 in this module's *ID Sheet*.
2. A singly ionized helium atom in the ground state absorbs a photon and is excited to the $n = 4$ energy level. The system can de-excite by emitting other photons. Assuming all quantum jumps to lower energy levels are allowed, calculate all possible wavelengths of emitted photons and identify the region of the spectrum they belong to. If in the visible region, state the perceived color of light made up of such photons.

Brief Answers:

1. See this module's *text*.
2. See problem 4 in this module's *Problem Supplement*.

