Chapter 9

Overview

The atom can be viewed in a variety of ways. From a macroscopic point of view, the atom is the smallest entity of significance and the building blocks of matter. From a microscopic point of view, the atom is a perplexing composite of more basic particles of which only the electron appears to be fundamental or elementary; the proton and neutron are composed of more bizarre constituents. Our focus will not be at the subatomic level where the strong and weak forces must be considered along with the electromagnetic force nor the macroscopic and mesoscopic level involving clusters of particles but in between where the Coulomb interaction between the electrons and the nucleus as well as between electrons and between nuclei dominant interparticle forces of concern. We will assume the nucleus (composed of protons and neutrons) and the electron to be the basic constituents of concern. Our primary goal is to model atoms and molecules both in the absence and presence of weak and strong external electromagnetic fields.

We will confine our discussion to three specific types of systems – one-electron atoms, two-electron atoms and diatomic molecules. As their name implies, the one- and two-electron atoms will involve atoms that have one or two active electrons that spend most of their time outside a positively charged core. We will look in some detail at the structure of these atoms as well as the structure of diatomic and linear triatomic molecules. We will also look at bound-bound radiative transitions and bound-free transitions responsible for ionization, dissociation and dissociative-ionization processes.

Since there are numerous texts that cover details of the information presented in this part, we will take the approach of giving key results without detail derivation, for the most part, and direct the reader to salient references. The goal is to present enough information for the reader to un-

derstand the important concepts. The reader will necessarily have to read additional material to become an expert.

In our discussion, we will treated the motion of the electrons and nuclei quantum mechanically and the external field classically. Consequently, we will seek solutions to Schrödinger's equation,

$$i\hbar\frac{\partial}{\partial t}\Psi\left(\vec{r},t\right)=\widehat{H}\Psi\left(\vec{r},t\right),\tag{9.1}$$

for specific Hamiltonians, $\widehat{H}$.

We begin our discussion by considering a hydrogen-like, one-electron atom, in the absence of an external field. This atom will be described by a family of stationary states of well defined energies, that can be ascertained from the time-independent Schrödinger equation

$$\widehat{H}\psi\left(\vec{r}\right)=E\psi\left(\vec{r}\right).\tag{9.2}$$

Equation 9.2 is obtained from Eq. 9.1 by letting $\Psi\left(\vec{r},t\right)\rightarrow\mathrm{e}^{-iEt/\hbar}\psi\left(\vec{r}\right)$. The Hamiltonian is taken as the quantum mechanical analog of the classical Hamiltonian given by $T+V$ where $T=p^2/2m_e$ and the potential, $V\left(r\right)$, is just the Coulomb potential, $-Ze^2/4\pi\varepsilon_o r$, with Z being the charge on the nucleus ($Z=1$ for neutral atoms). Since $p\rightarrow-i\hbar\nabla$ (see Appendix B.8), the quantum mechanical Hamiltonian for this single-particle non-relativistic case takes the simple form

$$\widehat{H}=-\frac{\hbar^2}{2m_e}\nabla^2-\frac{Ze^2}{4\pi\varepsilon_o r},\tag{9.3}$$

where m_e is the mass of the electron, e is the elementary charge, $\hbar$, is Planck's constant divided by 2π and ε_o is the vacuum permittivity.

9.1 The Bohr Atom

Before solving Eq. 9.2 with the Hamiltonian given in Eq. 9.3, it is interesting to see that it is possible to determine the energy spectrum classically by assuming the existence of stationary states – Bohr's hypothesis that the electron does not radiate when circling the nucleus. For stationary states to exist, the Coulomb force ($-Ze^2/4\pi\varepsilon_o r^2$) must equal the centripetal force ($-m_e v^2/r$, where v is the tangential velocity). This leads to a kinetic energy of

$$T=\frac{1}{2}m_e v^2=\frac{1}{2}\left(\frac{Ze^2}{4\pi\varepsilon_o r}\right),\tag{9.4}$$

and a total energy

$$E = T + V = -\frac{1}{2}\left(\frac{Ze^2}{4\pi\varepsilon_o r}\right). \tag{9.5}$$

Here, we adopt the usual convention that negative energy means the system is bound. Prior to the development of quantum mechanics, it was known that atoms emitted light at specific wavelengths. In the late 19th century it was determined that the energy of the light, in wavenumbers (see Eq. A.4 and Appendix A), associated with a transition between energy levels n and n' was found to obeyed[12]

$$\tilde{\nu}_{n'n} = \mathcal{C}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right), \tag{9.6}$$

where $\mathcal{C}$ is a constant that is related to the Rydberg constant. If one further postulates that the energy levels are quantized such that $r \to n^2 r_1$, where r_1 is the minimum stable radius, Eq. 9.5 becomes

$$E_n = -\frac{1}{2}\left(\frac{Ze^2}{4\pi\varepsilon_o n^2 r_1}\right). \tag{9.7}$$

It follows that

$$hc\tilde{\nu}_{n'n} = E_{n'} - E_n = \frac{1}{2}\left(\frac{Ze^2}{4\pi\varepsilon_o r_1}\right)\left(\frac{1}{n^2} - \frac{1}{n'^2}\right). \tag{9.8}$$

If we identify the constant as

$$\mathcal{C} = \frac{1}{2hc}\left(\frac{Ze^2}{4\pi\varepsilon_o r_1}\right), \tag{9.9}$$

the energy spectrum for hydrogen and hydrogen-like ions [3] takes this simple form:

$$E_n = -hc\mathcal{C}\frac{1}{n^2}. \tag{9.10}$$

Since the potential is not harmonic, the energy levels are not equally spaced. Figure 9.1 shows that the second level, the first excited state, is three-quarters of the way to the ionization limit while subsequent levels are more and more closely spaced.

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[1]This general formula was proposed by Rydberg in 1889. Prior to this date, Balmer used the empirial formula, $(4/B)\left(1/2^2 - 1/n^2\right)$ to fit the visible hydrogen spectral lines he observed. With $n = 3, 4, 5, 6, ...$, he extracted a value of 3645.6 Å for B.

[2]Find the reference to the Rydberg and Balmer footnote.

[3]Hydrogen-like ions are ions with a single electron plus the nucleus. These include H, He^+, as well as all multiply-charged ions that have all but one electron removed; Ca^{19+} would be an example.
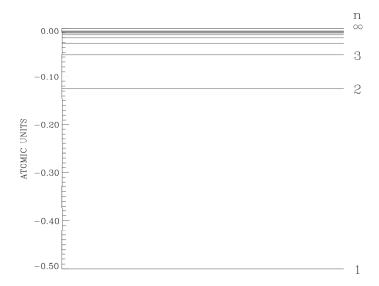
Figure 9.1: Bound energy levels of the traditional Bohr hydrogen atom. *Redraw this in Autocad to include the continuum states. See "bohrlevels.eps" (Bill's attempt, I think) and Fig. 18-1 in Cowan.*

It is possible to determine $\mathcal{C}$ by fitting the spectrum to Eq. 9.6 from which we can estimate r_1. Furthermore, it is possible to predict $\mathcal{C}$, and r_1 theoretically from the Correspondence Principle.[4] When the radius of the electron orbit gets large, n gets large and the circulating electron will radiate, as any charged particle must classically, with a frequency given by

$$\frac{v}{2\pi n^2 r_1}. \tag{9.11}$$

When a classical particle radiates, it looses energy. Quantum mechanically, radiation is accompanied by transitions between quantum levels, as implied by Eq. 9.6. To remain classical, radiation must be between levels with large n. Consider a transition between two adjacent levels where $n' = n + 1$. Equation 9.6 then becomes

$$\tilde{\nu}_{n'n} = \mathcal{C}\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right) \simeq \frac{2\mathcal{C}}{n^3}. \tag{9.12}$$

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[4]The Correspondence Principle states that in the limit of large sizes the quantum description must approach the classical description

Multiplying Eq. 9.12 by c, the speed of light, and equating it with Eq. 9.11, using Eq. 9.4 to express v and Eq. 9.5 to express $\mathcal{C}$, we can show that

$$r_1 = \left(\frac{4\pi\varepsilon_o}{e^2} \right) \frac{\hbar^2}{Zm_e} \tag{9.13}$$

from which we identify the minimum radius for $Z = 1$

$$a_o = \left(\frac{4\pi\varepsilon_o}{e^2} \right) \frac{\hbar^2}{m_e}, \tag{9.14}$$

called the Bohr radius.[5] The Rydberg constant, for an infinitely massive nucleus,[6] is then defined as

$$\mathcal{R}_\infty \equiv \frac{1}{4\pi} \left(\frac{e^2}{4\pi\varepsilon_o} \right) \frac{1}{\hbar c a_o} = \frac{\mathcal{C}}{Z^2}. \tag{9.15}$$

The energy spectrum can then be expressed as

$$E_n = -\frac{1}{2} \left(\frac{e^2}{4\pi\varepsilon_o} \right) \frac{Z^2}{n^2 a_o} = -hc\mathcal{R}_\infty \frac{Z^2}{n^2} = -\frac{1}{2} \left(\frac{e^2}{4\pi\varepsilon_o} \right)^2 \frac{Z^2 m_e}{n^2 \hbar^2}, \tag{9.16}$$

which depends only on integers, Z and n, and fundamental constants.

For an infinite nuclear mass, we identify $n^2 a_o$ as the radius of the orbit of the nth state for hydrogen. This is not exact because the nucleus has finite mass m_N. To account for this, we can let $m_e \to \mu$, the reduced mass mass. The nth radius then becomes

$$r_n = \frac{m_e}{\mu} \frac{n^2 a_o}{Z} \simeq \frac{n^2 a_o}{Z}, \tag{9.17}$$

assuming the nucleus has charge Z, where the reduced mass is given by

$$\mu \equiv (1/m_e + 1/m_N)^{-1}. \tag{9.18}$$

If we let $m_e \to \mu$ in Eq. 9.16, however, we shift the energy levels requiring the *finite mass* Rydberg constant to be defined as

$$\mathcal{R}_M = \mathcal{R}_\infty \left(1 + \frac{m_e}{M_N} \right)^{-1}. \tag{9.19}$$

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[5]We note that $r_1 = a_o/Z$.

[6]An atom with an infinite nuclear mass is sometimes called the *fixed nucleus* or *stationary nucleus* atom.

A.4 Atomic Energy Unit (Hartree)

The atomic energy (au), also know as a hartree, is e times the electric potential associated with two elementary charges (e) separated by the Bohr radius (a_o),

$$1 \text{ au} = e \left(\frac{e}{4\pi\varepsilon_o a_o} \right) = \frac{\alpha\hbar c}{a_o} = 4.35974381(34) \times 10^{-18} \text{ J}. \qquad (A.6)$$

In Eq. A.6, α $\left(\equiv e^2/4\pi\varepsilon_o\hbar c \sim \frac{1}{137} \right)$ is the fine structure constant, $\hbar$ is Planck's Constant and c is the speed of light. These units are equivalent to setting $e = \hbar = m_e = 1$, where m_e is the electron rest mass.

A.5 Rydberg Energy Unit

The Rydberg energy units is given by

$$1 \text{ Ry} = \frac{1}{2} \text{ Hartree} = 13.60569172(53) \text{ } eV, \qquad (A.7)$$

and is the binding energy of the hydrogen atom with an infinitely massive nucleus. This unit is equivalent to setting $\hbar = e^2/2 = 2m_e = 1$. The atomic energy unit (a.u.) and Rydberg energy unit (cm^{-1}) are alos related:

$$1 \text{ au} = 4\pi\hbar c \mathcal{R}_\infty, \qquad (A.8)$$

where $\mathcal{R}_\infty$ is the Rydberg constant

$$\mathcal{R}_\infty \equiv \frac{1}{2} \frac{e^2}{4\pi\varepsilon_o a_o hc} = \frac{\alpha}{4\pi a_o} = 109737.31568549(83) \text{ cm}^{-1}. \qquad (A.9)$$

A.6 eV Energy Unit

Since the quantity in parentheses in Eq. A.6 has units of volts, we can also define a new energy unit called an electron volt, eV. An atomic unit of enery is related to the eV through:

$$1 \text{ au} = 1 \text{ Hartree} = 27.2113834(11) \text{ } eV. \qquad (A.10)$$

The conversion between Rydberg energy unit and electron-Volt units (eV) is:

$$1 \text{ } eV = 8065.54477(32) \text{ cm}^{-1}. \qquad (A.11)$$

It is helpful to know that the NIST web site also offers a conversion factor applet that was used here to convert from au to eV.