1

The Old Quantum Theory

1.1 Introduction

The *Old Quantum Theory* refers to the early developments, largely during the years 1900 to 1925, which became precursors to modern quantum mechanics. While it lasted, the OQT produced many significant advances in theoretical chemistry, including an understanding of the periodic structure of the elements.

Physics around 1900 was regarded by many scientists as a completed theory, needing only some refinements "to a few decimal places." The foundations of *classical physics*, as this is now known, are based on Isaac Newton's laws of mechanics, James Clerk Maxwell's theory of electromagnetism, and statistical mechanics as developed principally by Ludwig Boltzmann, J. Willard Gibbs, and J. C. Maxwell. From our modern viewpoint, we can identify three failures of classical physics: its inadequacy to explain blackbody radiation, the photoelectric effect, and the origin of line spectra. (Sometimes, the heat capacity of crystals at low temperatures is cited.) As it turns out, these seemingly minor flaws were ultimately responsible for the demolition of the entire foundation of classical physics.

1.2 Blackbody Radiation

It is a matter of common experience that a hot object can emit radiation. A piece of metal stuck into a flame can become "red hot." Josiah Wedgwood, the famous pottery designer, invented a pyrometer (ca 1782) based on his observation that different materials become red hot at the same temperature. The radiation given off by material bodies when they are heated is called *blackbody radiation*, a blackbody being an idealized perfect absorber and emitter of all possible wavelengths λ of radiation. Figure 1.1 shows experimental wavelength distributions of thermal radiation $\rho(\lambda)$ at several temperatures. The maximum in the distribution, which determines the predominant color, increases with temperature in accordance with Wien's displacement law

$$\lambda_{\max} T = 2.898 \times 10^6 \text{ nm K}.$$

where the wavelength is expressed in nanometers (nm). Integration of a distribution for a given temperature over all wavelengths gives the total radiation energy density per unit volume, known as the Stefan-Boltzmann law:

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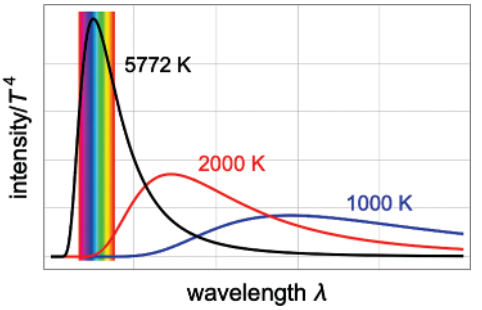

Figure 1.1 Intensity distributions of blackbody radiation at three different temperatures. The total radiation intensity varies as T^4 (Stefan-Boltzmann law) so the total radiation at 2000 K is actually $2^4 = 16$ times that at 1000 K. The visible region of wavelengths is shown.

$$\mathcal{E} = \int_0^\infty \rho(\lambda)\, d\lambda = 5.670 \times 10^{-8}\, T^4.$$

At room temperature (300 K), the maximum occurs around 9700 nm, in the infrared region. In Figure 1.1, the approximate values of $\lambda_{\max}$ are 2900 nm at 1000 K, 1450 nm at 2000 K, and 500 nm at 5772 K, the approximate surface temperature of the Sun. The Sun's $\lambda_{\max}$ is near the middle of the visible range (380-750 nm) and is perceived by our eyes as white light.

The origin of blackbody radiation was a major challenge to nineteenth century physics. Lord Rayleigh proposed that the electromagnetic field could be represented by a collection of oscillators of all possible frequencies. We need first to calculate the number of oscillators per unit volume for each wavelength λ. The reciprocal of the wavelength, $k = 1/\lambda$, is known as the *wavenumber*, equal to the number of wave oscillations per unit length. The wavenumber actually represents the magnitude of the *wavevector* $\mathbf{k}$, which also gives the direction in which a wave is propagating. Now, all the vectors $\mathbf{k}$ of constant magnitude k in a 3-dimensional space can be considered to sweep out a spherical shell of radius k and infinitesimal thickness dk. The volume (in $\mathbf{k}$-space) of this shell is equal to $4\pi k^2 dk$ and can be identified with the number of modes of oscillation per unit volume (in real space). Expressed in terms of λ, the number of modes per unit volume thereby equals $(4\pi/\lambda^4)d\lambda$. Sir James Jeans recognized that this must be multiplied by 2 to take account of the two possible polarizations of each mode of the electromagnetic field.

Rayleigh assumed that every oscillator contributed equally to the radiation, in accordance with the *equipartition principle*. Assuming equipartition of energy, each oscillator has the energy kT, where k here is Boltzmann's constant $R/N_A = 1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}$. We obtain thereby the energy per unit volume per unit wavelength range:

$$\rho(\lambda) = \frac{8\pi kT}{\lambda^4}, \tag{1.1}$$

which is known as the Rayleigh-Jeans law. This agrees fairly well with experiments at lower frequencies (higher wavelengths), in the infrared region and beyond. But the formula implies that $\rho(\lambda)$ increases without limit as $\lambda \to 0$. Indeed, if ultraviolet rays and higher frequencies were really produced in increasing numbers, we might get roasted like marshmallows by sitting in front of a fireplace! Fortunately, this doesn't happen. A theory with such disagreements with observation, which classical physics could not reconcile, is said to suffer from an "ultraviolet catastrophe."

Max Planck in 1900 derived the correct form of the blackbody radiation law by introducing a bold postulate. He proposed that energies involved in absorption and emission of electromagnetic radiation did not belong to a continuum, as implied by classical theory, but were actually made up of discrete bundles, which he called "quanta." On this basis, Planck is traditionally regarded as the father of quantum theory. A quantum associated with radiation of frequency ν is proposed to carry an energy

$$E = h\,\nu, \tag{1.2}$$

where the proportionality factor $h = 6.626 \times 10^{-34}$ J sec is known as *Planck's constant*. Using the relation between frequency and wavelength

$$\lambda\,\nu = c, \tag{1.3}$$

where $c = 2.9979 \times 10^8$ m/sec, the speed of light, we can alternatively express Planck's formula in terms of wavelength:

$$E = \frac{hc}{\lambda}. \tag{1.4}$$

Our development of the quantum theory of atoms and molecules will make extensive use of Planck's iconic formula.

Planck realized that the fatal flaw was equipartition, which is based on the assumption that the possible energies of each oscillator belong to a continuum ($0 \le E < \infty$). If, instead, the energies of an oscillator of wavelength λ come in discrete bundles $h\nu = hc/\lambda$, then the possible energies are given by

$$E_{\lambda,n} = nh\nu = nhc/\lambda, \qquad \text{where } n = 0, 1, 2 \ldots \tag{1.5}$$

By the Boltzmann distribution in statistical mechanics, the average energy of an oscillator at temperature T is given by

$$\langle E_\lambda \rangle_{\text{av}} = \frac{\sum_n E_{\lambda,n}\, e^{-E_{\lambda,n}/kT}}{\sum_n e^{-E_{\lambda,n}/kT}}. \tag{1.6}$$

More explicitly,

$$\langle E_\lambda \rangle_{\text{av}} = \sum_{n=0}^{\infty} (nhc/\lambda)\, e^{-nhc/\lambda kT} \Big/ \sum_{n=0}^{\infty} e^{-nhc/\lambda kT}. \tag{1.7}$$

Mathematica can evaluate this:

```
In[1]:= Sum[(n h c)/λ e^(-(n h c)/(λ k T)), {n, 0, ∞}] / Sum[e^(-(n h c)/(λ k T)), {n, 0, ∞}]

Out[1]= (c h)/((-1 + e^(c h)/(k T λ)) λ)
```

Therefore

$$\langle E_\lambda \rangle_{\text{av}} = \frac{hc/\lambda}{e^{hc/\lambda kT} - 1}. \tag{1.8}$$

This implies that the higher-energy modes are less populated than what is implied by the equipartition principle. Substituting this value, rather than kT, into the Rayleigh-Jeans formula (1.1), we obtain the Planck distribution law

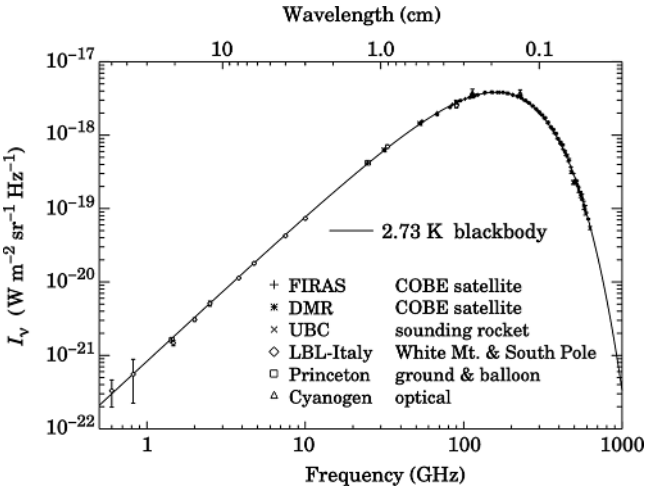

Figure 1.2 Cosmic Microwave Background. Adapted from G. F. Smoot and D. Scott.

$$\rho(\lambda) = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}. \tag{1.9}$$

Note that, for large values of λ and/or T, the average energy (1.8) is approximated by $\langle E_\lambda \rangle_{\text{av}} \approx kT$ and the Planck formula reduces to the Rayleigh-Jeans approximation. The Planck distribution law accurately accounts for the experimental data on thermal radiation shown in Figure 1.1. Remarkably, measurements by the Cosmic Microwave Background Explorer satellite (COBE) give a perfect fit for a blackbody distribution at temperature 2.73K, as shown in Figure 1.2. The cosmic microwave background radiation, which was discovered by Penzias and Wilson in 1965, is a relic of the Big Bang 13.8 billion years ago.

From the Planck distribution law one can calculate the wavelength at which $\rho(\lambda)$ is a maximum at a given T. This is somewhat tricky since it involves a transcendental equation. We first find the derivative of $\rho(\lambda)$ and find the value of λ for which this is equal to 0:

```
In[1]:= Simplify[∂λ (8 π h c / λ^5  1 / (e^(ch/kTλ) - 1))]

Out[1]= (8 c h π (c e^(ch/kTλ) h - 5 (-1 + e^(ch/kTλ)) k T λ)) / ((-1 + e^(ch/kTλ))^2 k T λ^7)

In[2]:= Solve[N[c e^(ch/kTλ) h - 5 (-1 + e^(ch/kTλ)) k T λ] == 0, λ]

··· Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for
    complete solution information.

Out[2]= {{λ → 0.201405 c h / k T}}
```

The result agrees with the Wien displacement law:

$$\lambda_{\max} T = 0.2014 \frac{hc}{k} = 2.898 \times 10^6 \text{ nm K}. \tag{1.10}$$

By integration of Eq (1.26) over all wavelengths λ, we obtain the total radiation energy density per unit volume:

```
In[1]:= Integrate[8 π h c / λ^5 * 1 / (e^(c h / (k T λ)) - 1), {λ, 0, ∞}]

Out[1]= 8 k^4 π^5 T^4 / (15 c^3 h^3)  if Re[c h / (k T)] > 0
```

Therefore

$$\mathcal{E} = \int_0^\infty \rho(\lambda)\, d\lambda = \frac{8\pi^5 k^4}{15 c^3 h^3} T^4, \tag{1.11}$$

in accord with the Stefan-Boltzmann law.

1.3 The Photoelectric Effect

A common device in modern technology is the photocell or "electric eye," which runs a variety of useful gadgets, including automatic door openers. The principle involved in these devices is the photoelectric effect, which was first observed by Heinrich Hertz in the same laboratory in which he discovered electromagnetic waves. Visible or ultraviolet radiation impinging on clean metal surfaces can cause electrons to be ejected from the metal; see Figure 1.3. Such an effect is not, in itself, inconsistent with classical theory since electromagnetic waves are allowed to carry energy and momentum. But the detailed behavior as a function of radiation frequency and intensity can *not* be explained classically.

The energy required to eject an electron from a metal is determined by its *work function* Φ. For example, sodium has $\Phi = 1.82$ eV. The electron-volt is a convenient unit of energy on the atomic scale: 1 eV $= 1.602 \times 10^{-19}$ J, corresponding to the energy which an electron picks up when accelerated across a potential difference of 1 volt. The classical expectation would be that radiation of sufficient intensity should cause ejection of electrons from a metal surface, with their kinetic energies increasing with the radiation intensity. Moreover, a time

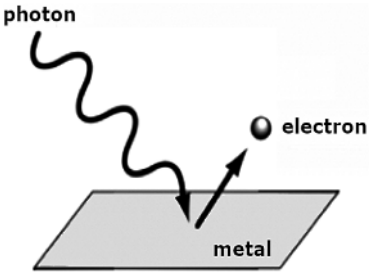

Figure 1.3 Photoelectric effect.

delay would be expected between the absorption of radiation and the ejection of electrons. The experimental facts are quite different. It is found that no electrons are ejected, no matter how high the radiation intensity, unless the radiation *frequency* exceeds some threshold value ν_0 for each metal. For sodium $\nu_0 = 4.39 \times 10^{14}$ Hz (corresponding to a wavelength of 683 nm). It is found that, for frequencies ν above the threshold, the ejected electrons acquire a kinetic energy given by

$$\tfrac{1}{2}mv^2 = h(\nu - \nu_0) = h\nu - \Phi. \tag{1.12}$$

Evidently, the work function Φ can be identified with $h\nu_0$, equal to 3.65×10^{-19} J = 1.82 eV for sodium. The kinetic energy increases *linearly* with frequency above the threshold but is independent of the radiation intensity. Increased intensity does, however, increase the *number* of photoelectrons.

In 1905, Albert Einstein proposed an explanation of the photoelectric effect (for which he received the Nobel Prize in 1921). Einstein's argument appears completely obvious once stated. He accepted Planck's hypothesis that a quantum of radiation carries an energy $h\nu$. Thus, if an electron is bound in a metal with an energy Φ, a quantum of energy $h\nu_0 = \Phi$ will be sufficient to dislodge it. The photon will instantaneously transfer its energy to a single electron. And any excess energy $h(\nu - \nu_0)$ will appear as kinetic energy of the ejected electron. Einstein believed that the radiation field actually did consist of quantized particles, which he named *photons*. Einstein's explanation of the photoelectric effect was a significant advance in the concept of energy quantization.

1.4 Line Spectra

A sample of matter, when heated to incandescence or excited by a high-voltage electrical discharge, can emit electromagnetic radiation over a range of wavelengths in the visible region. The resulting emission spectrum can be displayed using a spectrometer or, even simpler, a glass prism. The two principal types are continuous spectra and line spectra, as shown in Figure 1.4. A continuous spectrum extends over a band of wavelengths, like a rainbow. It can be produced by excitation of a solid or a high-pressure gas. Blackbody radiation is such a continuum. By contrast, a line spectrum consists of a discrete set of wavelengths. It can appear as an emission spectrum, with colored lines against a black background, when a low-pressure gas is excited. Each chemical element produces a characteristic set of spectral lines, with some examples shown in Figure 1.5.

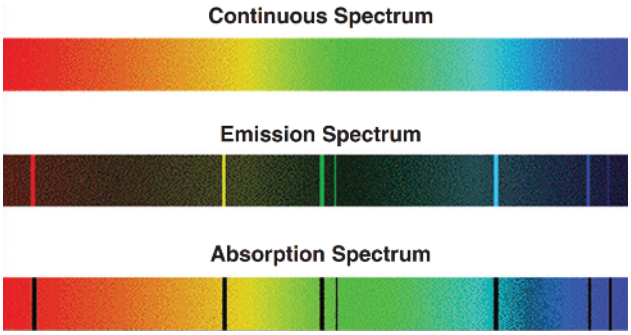

Figure 1.4 Continuous spectrum and two types of line spectra.

An absorption line spectrum can be produced when light from a continuous source, such as the interior of the Sun, passes through the photosphere, the outer layer of the Sun. Frauenhofer, between 1814 and 1823, discovered nearly 600 dark lines in the solar spectrum viewed at high resolution. These are absorption lines, narrow regions of decreased intensity, that are the result of photons being absorbed as light passes through the photosphere. Chemical elements in the photosphere can be identified by comparing wavelengths of lines in the emission spectra.

Classical electrodynamics does predict that motions of electrical charges within atoms can be associated with the absorption and emission of radiation. What is completely mysterious is how such radiation can occur for discrete frequencies, rather than as a continuum. The breakthrough that explained line spectra is credited to Neils Bohr in 1913. Building on the ideas of Planck and Einstein, Bohr postulated that the energy levels of atoms belong to a discrete set of values E_n, rather than a continuum as in classical mechanics. As illustrated schematically in Figure 1.6, when an atom makes a downward transition from a higher energy level E_m to a lower energy level E_n, this is associated with the emission of a photon with

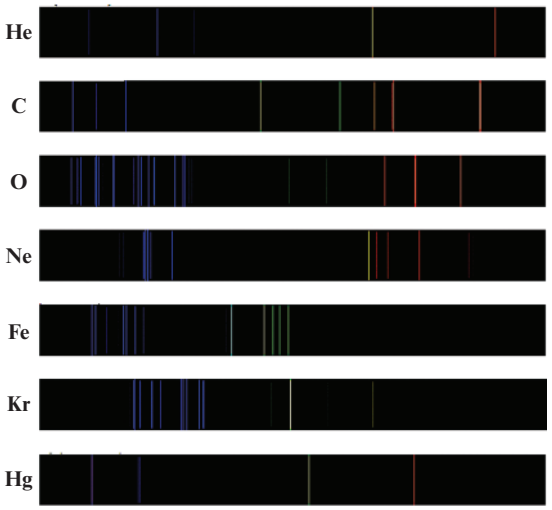

Figure 1.5 Emission spectra of several elements.

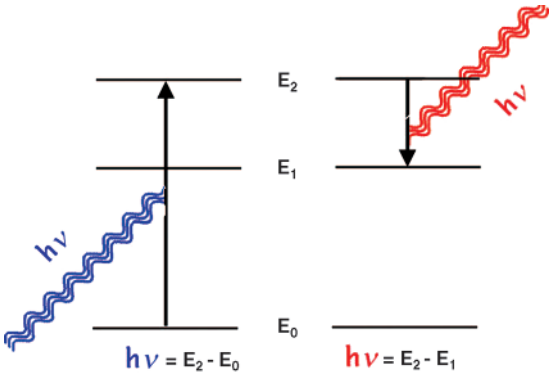

Figure 1.6 Origin of line spectra. Absorption of the photon shown in blue causes atomic transition from E_0 to E_2. Transition from E_2 to E_1 causes emission of the photon shown in red.

Figure 1.7 Emission spectrum of atomic hydrogen in visible region.

frequency $\nu = (E_m - E_n)/h$. The quantization of atomic energy levels is what accounts for the discreteness of the emission frequencies. Conversely, a photon with the same energy can cause an excitation, or upward transition, from E_n to E_m. Absorption and emission processes occur at the same set of frequencies, as is shown by the two types of line spectra in Figure 1.4.

The emission spectrum of atomic hydrogen contains four lines in the visible region, shown in Figure 1.7: a red line at 656.21 nm (15239 cm^{-1}), a blue-green line at 486.07 nm (20573 cm^{-1}) and two violet lines at 434.01 nm (23041 cm^{-1}) and 410.12 nm (24383 cm^{-1}). The spectrum is obtained in the laboratory by passing a 5000-volt electrical discharge through gaseous molecular hydrogen. The wavenumber $\tilde{\nu}$ (in cm^{-1}) is a unit favored by spectroscopists, equal to the reciprocal of the wavelength expressed in centimeters:

$$\tilde{\nu} = \frac{1}{\lambda} \text{ cm}^{-1}.$$

Johann Balmer, a Swiss mathematician, found that the wavenumbers of the four spectral lines could be fitted to a simple formula:

$$\frac{1}{\lambda} = \text{const}\left(1 - \frac{4}{m^2}\right) \quad \text{with} \quad m = 3, 4, 5, 6.$$

After more lines in the infrared and ultraviolet spectrum of hydrogen were found, the Swedish physicist Johannes Rydberg found a generalization of Balmer's formula:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ with } n_1 = 1, 2, 3, \ldots \text{ and } n_2 = n_1 + 1, n_1 + 2, \ldots \tag{1.13}$$

Here, $R = 109678\,\text{cm}^{-1}$, known as the Rydberg constant. The series of lines beginning with $n_1 = 2$ reduces to Balmer's formula. This is now known as the Balmer series. The more intense series of lines with $n_1 = 1$, discovered in 1906, lie in the ultraviolet and are known as the Lyman series. Other atomic species produce characteristic line spectra, which can serve as "fingerprints" to identify elements, particularly in distant stars. But no atom other than hydrogen has a simple relationship for its spectral frequencies, nothing analogous to Rydberg's formula.

1.5 Bohr Theory of the Hydrogen Atom

J. J. Thomson discovered in 1897 that electrons were a component of all atoms. For several years thereafter, the prevalent picture of the atom was the "plum pudding model," in which the negatively charged electrons were pictured as plums embedded throughout a positive sphere—the pudding. If the plum-pudding model were correct, alpha particles scattered through a metallic foil should be deflected by, at most, small angles. Scattering cross-sections would then be about the magnitude of the square of the atomic diameter, of the order of 10^{-16} cm^2. Experiments in Ernest Rutherford's laboratory in 1909 directed a beam of 6 MeV alpha particles, produced by radioactive disintegration, at a very thin gold foil, just the thickness of several atoms. The surprising result was that a small fraction of the alpha particles was scattered at large angles. Rutherford concluded that the scattering centers were very small. It is now known that these nuclear radii are of typically of the order of several times 10^{-13} cm.

The unit 10^{-13} cm is known as 1 fermi (fm), which can also be interpreted as 1 femtometer (10^{-15} m). Rutherford in 1911 proposed the "nuclear model of the atom." As we now understand it, a neutral atom of atomic number Z consists of a compact, nearly pointlike, positively charged nucleus $+Ze$ surrounded by a cloud of Z negatively charged electrons, each with charge -e.

Neils Bohr spent a postdoctoral year in Rutherford's laboratory in Manchester. No doubt influenced by Rutherford's nuclear model, he adapted the quantum concepts introduced by Planck and Einstein to propose a planetary model of the atom: a miniature version of the Solar System with electrons orbiting the nucleus. We have modified Bohr's original argument, to take advantage of a century of pedagogical experience, as well as the availability of Mathematica's capabilities. The Rydberg formula for hydrogen, Eq (1.13), suggests that the discrete—we can now call them quantized—energy levels of a hydrogen atom have the form

$$E_n = -\frac{Rhc}{n^2}. \tag{1.14}$$

These have negative values since they correspond to bound states of the atom. The integers labeling the energy states: $n = 1, 2, 3, \ldots$ are called *quantum numbers*.

Bohr considered the specific case of the hydrogen atom, consisting of a single electron in interaction with a single proton. The attractive Coulomb force between the two particles, varying as the inverse square of their separation, is analogous to the gravitational attraction between a planet and the Sun. Bohr exploited this analogy with the Kepler problem, concluding that the electron should orbit the proton in an elliptical trajectory, with the proton at one focus. Bohr considered the simplest case of a circular orbit with the proton at the center. The attractive force between a proton of charge $+e$ and electron of charge $-e$, separated by a distance r, is given by

$$F = -\frac{e^2}{r^2}. \tag{1.15}$$

We use Gaussian electromagnetic units, as in the original work (no factors $4\pi\epsilon_0$), The Coulomb attraction provides a *centripetal* force to keep the electron in a circular orbit. Thus

$$F = -\frac{mv^2}{r} = -\frac{e^2}{r^2}. \tag{1.16}$$

The potential energy of the orbiting electron is given by

$$V = -\frac{e^2}{r}, \tag{1.17}$$

while the kinetic energy is

$$T = \tfrac{1}{2}mv^2. \tag{1.18}$$

Since the electron's motion is circular, it is convenient to introduce the orbital angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times m\mathbf{v}$. Since the velocity $\mathbf{v}$ is perpendicular to the radial vector $\mathbf{r}$, the angular momentum simplifies to the scalar relation $L = rmv$. Thus the kinetic energy can be written

$$T = \frac{L^2}{2mr^2}. \tag{1.19}$$

The energy of the orbiting electron is the sum of its kinetic and potential energies:

$$E = T + V = \frac{L^2}{2mr^2} - \frac{e^2}{r}. \tag{1.20}$$

By virtue of Eq (1.16), we find that the kinetic and potential energies are related by

$$T = -\tfrac{1}{2}V. \tag{1.21}$$

This is *virial theorem* for an inverse-square force law. The total energy of the electron E, using Eq (1.14), can thereby be written alternatively as

$$-\frac{Rhc}{n^2} = \tfrac{1}{2}V = -\frac{e^2}{2r} \quad \text{and} \quad -\frac{Rhc}{n^2} = -T = -\frac{L^2}{2mr^2}. \tag{1.22}$$

To obtain a solution giving the values of R, L, and r we need a third relation. This can be provided by Bohr's *correspondence principle*, which states that in the limit of large values of the quantum numbers, a quantum system will approach classical behavior. In this application, Bohr reasoned that, for large values of n, the frequency associated with a transition $n \to n+1$ will approach the classical frequency of the radiation emitted by an electron in a circular orbit. Using Eq (1.13), the wavenumber for this transition is given by

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right) \approx \frac{2R}{n^3} \quad \text{for large } n. \tag{1.23}$$

(Note also that $\frac{d}{dn}\left(-\frac{R}{n^2}\right) = \frac{2R}{n^3}$.) It is convenient to introduce the radian frequency of the orbit

$$\omega = 2\pi\nu = \frac{2\pi c}{\lambda} \approx 2\pi c \times \frac{2R}{n^3}. \tag{1.24}$$

The radian frequency is related to the angular momentum by

$$\omega = \frac{L}{mr^2}, \tag{1.25}$$

where $I = mr^2$ is the moment of inertia of the orbiting electron. We now have a third relation:

$$\frac{4\pi cR}{n^3} = \frac{L}{mr^2}. \tag{1.26}$$

At this point we turn to Mathematica's equation solver to determine R, L, and r in terms of fundamental constants and quantum numbers.

```
In[1]:= Solve[{Rhc/n^2 == e^2/2r, Rhc/n^2 == L^2/2mr^2, 4πcR/n^3 == L/mr^2}, {R, L, r}]
Out[1]= {{R → 2e^4 mπ^2/ch^3, L → hn/2π, r → h^2 n^2/4e^2 mπ^2}}
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The predicted value of the Rydberg constant gives $R = 2\pi^2 me^4/ch^3 = 109737\,\text{cm}^{-1}$. The slight discrepancy with the experimental value for hydrogen ($109678\,\text{cm}^{-1}$) can be corrected by replacing $m = m_e$ by the reduced mass of the electron in hydrogen: $\mu_\text{H} = \frac{m_e M_p}{m_e + M_p}$. The value found above pertains to infinite nuclear mass $M_p \to \infty$ and is designated R_∞.

The result determining L actually introduces the profound concept of angular-momentum quantization. Dirac later wrote the constant $h/2\pi$, which occurs frequently in quantum-theory formulas, as a single symbol $\hbar$ (pronounced "h-bar"). The quantum condition for the

component of orbital angular momentum in any direction can then be written

$$L = n\hbar, \tag{1.27}$$

where n is an integer.

The third output of the Solve command above gives the radius of the electron's orbit around the proton. For $n = 1$, we have the radius of the lowest energy state (the ground state) which is known as the Bohr radius and designated a_0:

$$a_0 = \frac{\hbar^2}{me^2} = 0.529177 \times 10^{-10}\,\text{m} = 52.9177\,\text{pm} = 0.529177\,\text{Å}. \tag{1.28}$$

Picometers (1 pm $= 10^{-12}$ m) are a popular unit for atomic dimensions. Still in use is the angstrom unit Å, equal to 10^{-10} m or .01 pm. This actually can be considered the first theoretical determination of the magnitude of atomic dimensions. More generally the electron orbital radius is given by

$$r_n = n^2 a_0, \quad n = 1, 2, 3, \ldots \tag{1.29}$$

The energy can then be written most compactly as

$$E_n = -\frac{e^2}{2r_n} = -\frac{e^2}{2n^2 a_0}, \quad n = 1, 2, 3, \ldots \tag{1.30}$$

Figure 1.8 is a diagram showing the first few orbits. The proton is represented by a blue point, the electron by a red point. The radius of the innermost circle equals a_0. Also shown is a "quantum jump" of an electron to a lower orbit, accompanied by an emission of a photon.

Figure 1.9 shows an energy level diagram for the hydrogen atom. The energies $E_n = -e^2/2n^2a_0$ are negative for bound states and approach 0 as $n \to \infty$. Energies in the continuum with $E > 0$ represent ionized states of a proton plus an electron, which are interacting but no longer bound into an atom. The series of transitions in an emission spectrum from levels $n = 2, 3, \ldots$ to the $n = 1$ ground state is known as the *Lyman series*. The transition $n = 2 \to n = 1$ is called the *Lyman alpha* line. It lies in the ultraviolet with $\lambda = 121.567$ nm. It is especially significant in astronomical spectroscopy, in the spectra of distant galaxies and quasars. The transitions in the *Balmer series*, terminating at $n = 2$, are responsible for the visible spectrum of hydrogen in Figure 1.7.

The Bohr model applies more generally to one-electron ions, with a nucleus of atomic number Z, where $Z = 1$ for H, $Z = 2$ for He^+, $Z = 3$ for Li^{2+}, and so on. With the nuclear charge $+Ze$, the potential energy generalizes to $V = -Ze^2/r$, the orbital radius to

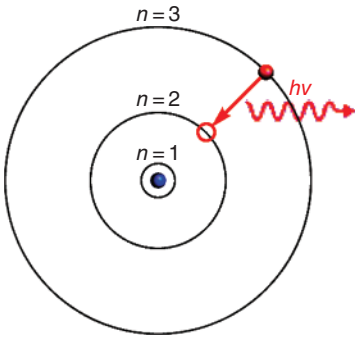

Figure 1.8 Bohr orbits for $n = 1, 2, 3$. The transition from $n = 3$ to $n = 2$ creates a photon of frequency $\nu = (E_3 - E_2)/h$.

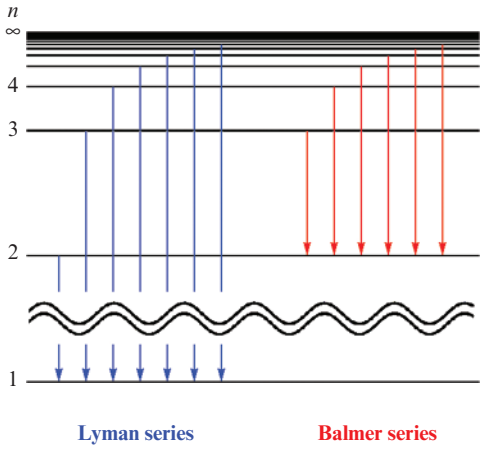

Figure 1.9 Energy level diagram for hydrogen atom showing the Lyman and Balmer series of transitions.

$$r_n = n^2 a_0/Z, \tag{1.31}$$

and the energy to

$$E_n = -\frac{Z^2 e^2}{2n^2 a_0}, \quad n = 1, 2, 3, \ldots \tag{1.32}$$

The Bohr atom represent a spectacular departure from classical theories of mechanics and electrodynamics. Since an electron in a circular orbit is undergoing centripetal acceleration, it ought to radiate. In fact, it should radiate away its energy in about 10^{-11} seconds and experience a death spiral into the nucleus. I like to call this the "atomic Hindenberg disaster." (The Hindenberg, a hydrogen-filled dirigible, crashed and burned in a famous disaster in 1937.) Nonetheless, the extraordinary agreement with the spectrum of atomic hydrogen amply must somehow justify this exemption from classical physics.

1.6 Bohr-Sommerfeld Orbits

Sommerfeld and Wilson in 1916 generalized Bohr's formula for the allowed orbits to a set of quantum conditions on action integrals, of the form

$$\oint \mathbf{p} \cdot d\mathbf{r} = nh \quad n = 1, 2, 3, \ldots \tag{1.33}$$

The Sommerfeld-Wilson quantum conditions reduce to Bohr's results in the case of circular orbits, but now elliptical Kepler orbits are allowed as well, with the nucleus at one focus. In elliptical orbits, the momentum $\mathbf{p}$ can vary as a function of position.

For the hydrogen atom treated as a 3-dimensional problem in spherical polar coordinates r, θ, ϕ, there is actually a set of three quantum conditions:

$$\oint p_r dr = \left(n + \tfrac{1}{2}\right) h, \quad \oint p_\theta d\theta = \left(\ell + \tfrac{1}{2}\right) h, \quad \oint p_\phi d\phi = mh, \tag{1.34}$$

where n, ℓ, m are integers with the ranges $n = 1, 2, 3, \ldots$, $\ell = 0, 1, \ldots, n-1$, $m = -\ell, -\ell + 1, \ldots, +\ell$, ($2\ell + 1$ possible values). The extra terms $\frac{1}{2}$ for the r and θ integrals are due to the corresponding motions being *librations*, while the ϕ motion is a true rotation. The energy E_n

is completely determined by n, which is called the principal quantum number. The value of ℓ, known as the azimuthal quantum number, determines the orbital angular momentum. The different values of m, called the magnetic quantum number, exhibit the phenomenon of space quantization, in which an elliptical orbit can be oriented in $2\ell+1$ possible directions in 3-dimensional space. The full details about ℓ and m require the quantum-mechanical theory (Chapters 6 and 8).

The $n = 1$ ground state is still a circular orbit, but the $n = 2$ level allows an elliptical orbit in addition to the circular one, with possible values $\ell = 0, 1$. The $n = 3$ level has three allowed orbits, with $\ell = 0, 1, 2$, and so on. The semimajor axis of the ellipse has the same value as the Bohr orbit, $a = n^2 a_0$. The semiminor axis is then given by $b = (n^2 - \ell n)a_0$. The orbits for $n = 1, 2$, and 3 are shown in Figure 1.10. For a given n, the multiplicity of values of ℓ and m imply that there is are, in total, n^2 allowed orbits. The energy level E_n is said to be n-fold degenerate.

Circulating electric charges give rise to magnetic moments. The general relation is

$$\mu = \frac{e}{2mc} L.$$

Thus an orbiting electron with one unit of angular momentum ($L = \hbar$) has a magnetic moment equal to

$$\mu_B = \frac{e\hbar}{2mc},$$

known as a *Bohr magneton*. Its value is 9.274×10^{-21} ergs/gauss (or 9.274×10^{-24} J/T).

Many atomic spectral lines appear, under sufficiently high resolution, to be closely spaced doublets, a prime example being the yellow sodium D-lines. Uhlenbeck and Goudsmit proposed in 1925 that this was due to an intrinsic angular momentum possessed by the electron (in addition to its orbital angular momentum) which could have two possible orientations. This property, known as spin, occurs as well in other elementary particles. Spin and orbital angular momenta are roughly analogous to the daily and annual motions, respectively, of the Earth around the Sun. To distinguish spin from orbital angular momentum, we designate the corresponding quantum numbers as s and m_s, instead of ℓ and m. For electrons, s always has the value $\frac{1}{2}$, meaning that its intrinsic angular momentum equals $\frac{1}{2}\hbar$. Correspondingly, m_s has two possible values, $\pm\frac{1}{2}$. The electron is said to be a "spin-$\frac{1}{2}$ particle." Particles with spin equal to an odd half-integer are known as fermions. By contrast, particles with integer values of spin, such as the photon with spin 1, are called bosons.

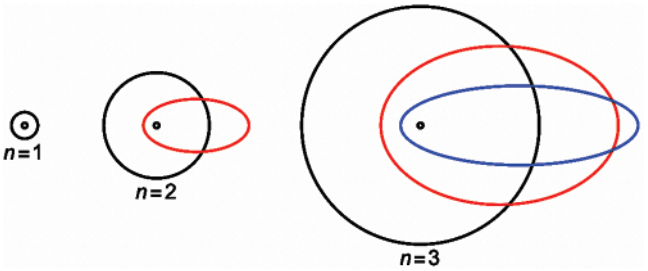

Figure 1.10 Bohr-Sommerfeld orbits for $n = 1, 2, 3$.

A charged particle with spin also exhibits a magnetic moment, given by the slightly generalized relation

$$\mu = \frac{ge}{2mc} S,$$

where S here means the intrinsic angular momentum, equal to $\frac{1}{2}\hbar$ for the electron. It turns out that the g-factor for electron spin is equal to 2, so that the spin magnetic moment is also equal to 1 Bohr magneton, μ_B. (More accurately, the g-factor equals 2.0023..., due to effects of quantum electrodynamics.) Interactions between the orbital and spin angular momenta give rise to fine structure splittings of spectral lines, which are smaller in magnitude than the energies of orbiting electrons by a factor of the order of $\alpha \approx 1/137$, known as the *fine structure constant*.

Wolfgang Pauli proposed his *exclusion principle* in 1925. For fermions in a quantum system, such as the electrons in an atom or molecule, all the individual quantum states can be, at most, singly occupied. No such restriction applies to bosons, any number can occupy each quantum state. An example is a Bose-Einstein condensate, in which almost all the particles in a system occupy the ground state.

When applied to the electrons in an atom, the exclusion principle requires that every electron be described by a unique set of quantum numbers: n, ℓ, m, and m_s. No two electrons can have the same set. The values of ℓ are usually designated by a code (originating in the classification of spectral lines, but no longer relevant): $\ell = 0$ is designated s (not to be confused with the spin angular momentum), $\ell = 1$ is designated p, $\ell = 2$ is d, $\ell = 3$ is f (this continues alphabetically for higher angular momenta, but we will not need them).

1.7 The Periodic Structure of the Elements

Based on the contributions of Rutherford and Bohr, the structure of a complex atom can be represented as a central nucleus of charge $+Ze$ surrounded by Z electrons moving in Bohr-Sommerfeld orbits. The logos of the International Atomic Energy Agency and the former U. S. Atomic Energy Commission are both idealized versions of such pictures, as shown in Figure 1.11.

The structure of the periodic system of the elements could be rationally explained for the first time on the basis of the Old Quantum Theory. In accordance with the *Aufbau principle*, as the atomic number is increased, electrons successively occupy the lowest available Sommerfeld-Bohr orbits, taking account of the Pauli exclusion principle, which restricts each set of quantum numbers n, ℓ, m, m_s to, at most, a single electron. This produces the familiar

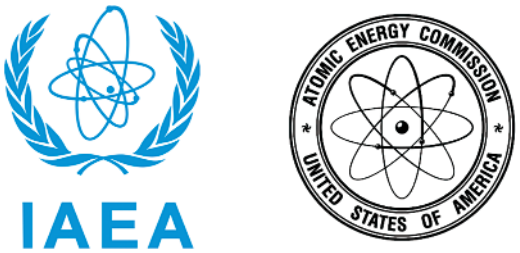

Figure 1.11 Logos showing Bohr-Sommerfeld orbits.

shell structure of atoms. Complete shells, containing all values of the quantum numbers up to certain combinations of n and ℓ are occupied, appear to confer an enhanced stability to a set of atoms with the "magic numbers" $Z = 2, 10, 18, 36, 54, 86$, and 118. These are the so-called *noble gases*: helium, neon, argon, krypton, xenon, radon, and the synthetic transuranium element 118, oganesson, discovered in 2006.

A Bohr-Rutherford diagram gives a compact representation of the electronic structure of an atom. Figure 1.12 shows diagrams for the first 20 elements in the periodic table as they are filled, in accord with the Aufbau principle. Only the outermost (valence) shell electrons are shown as red dots. The filled inner shells are represented by red circles. The first three shells are filled by 2, 8, and 8 electrons, respectively.

Figure 1.13 shows a "staircase form" of the periodic table proposed by Bohr in 1921. Bohr supported Mendeleev's original prediction that there was a missing element with $Z = 72$. It was first isolated in 1923 as an impurity in zircon by Danish chemists in Copenhagen. This led to the element being named hafnium (Hf), which was the Latin name for Copenhagen.

The picture of the atom based on the Sommerfeld-Wilson quantum conditions and Bohr-Sommerfeld orbits of electrons according to the Old Quantum Theory has thereby had a number of successful applications. However, the theory suffers from some serious flaws. To cite one, angular momenta are usually too large by one unit of $\hbar$. For example, the hydrogen atom ground state is known to be zero rather than $\hbar$. Zero angular momentum might be accomplished with a "pendulum orbit," in which the electron oscillates linearly through the nucleus. This is, however, usually ruled out in the OQT because it involves collisions of the electron with the nucleus. Also the theory is inconsistent with known behavior of atoms as nearly spherical particles. Although the Bohr model might have been able to sidestep the "Hindenberg disaster," it can not avoid what might be called the "Heisenberg disaster." By this we mean that the presumption of well-defined orbits is completely contrary to modern quantum theory, in particular the Heisenberg uncertainty principle, which states that the position and momentum of a particle cannot simultaneously be known exactly.

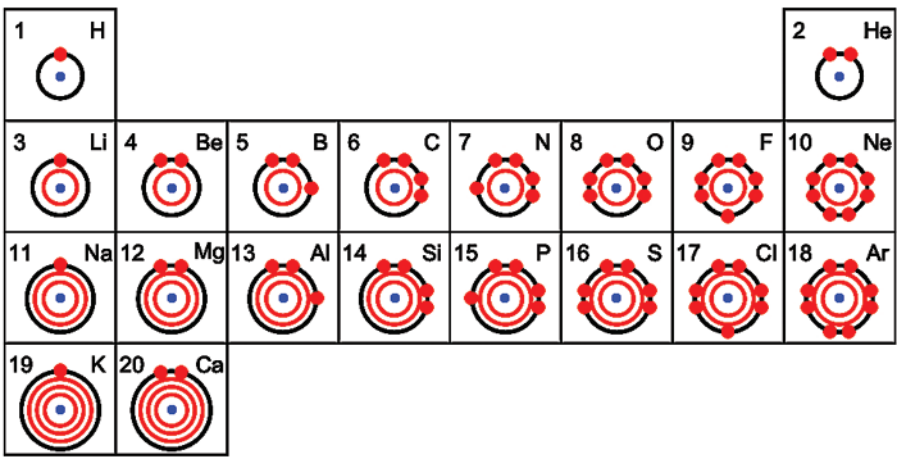

Figure 1.12 Bohr-Rutherford diagrams for first 20 elements.

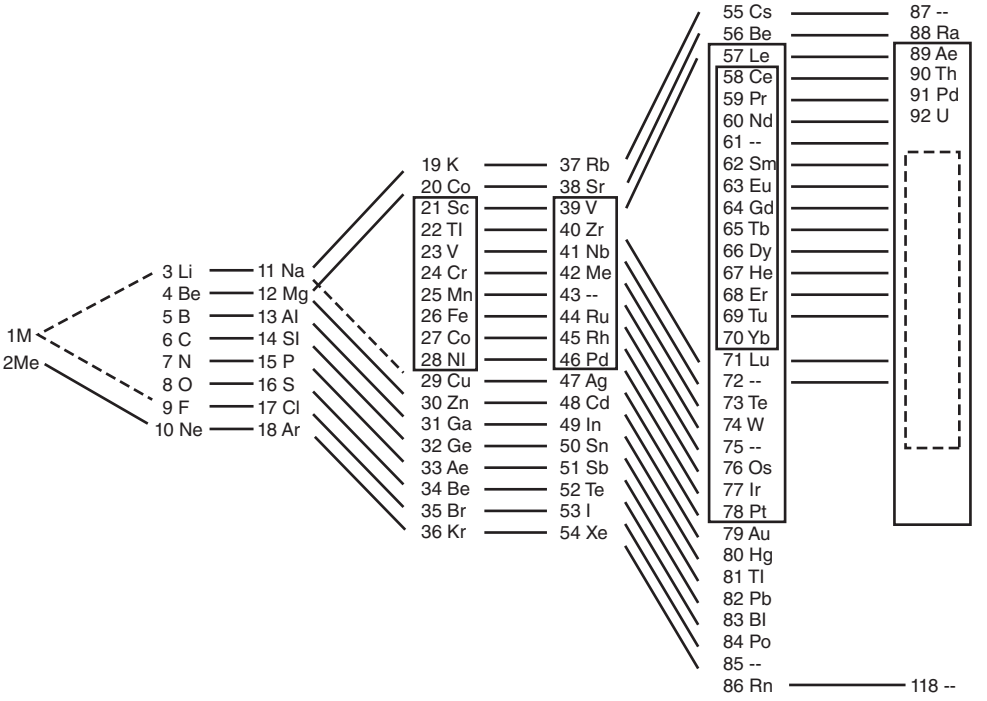

Figure 1.13 Bohr's staircase model for the periodic table.

In addition, the Bohr theory was unable to produce any quantitatively valid results for atoms and ions containing more than one electron, most notably the helium atom. And it was a complete disaster in attempted applications to molecules. Despite its failings, the Old Quantum Theory was an important transitional step in the development of the modern picture of the atom. The reigning theory is now quantum mechanics, which emerged, beginning in 1925–1926, with major contributions from Werner Heisenberg, Erwin Schrödinger and P. A. M. Dirac.