Physics 362k, Spring 2015

Notes 3

I. Hydrogen spectroscopy, electron spin and interactions with fields, fine structure, and Zeeman effect

References 1, 2, 3, 4, 5, and 6 are sources for the historical material in this section of notes.

A. Spectrum of the hydrogen atom

Early history

Hydrogen was first isolated and identified as a distinct substance by Henry Cavendish in 1776. Hydrogen was given it name ("water forming") by Antoine Lavoisier in about 1783.

The *prism spectrometer*, shown in Figure I-1(a), was developed in the early to mid-1800s. In the device, light is first passed through a narrow slit, then through a collimating lens, and then through a prism. Following the prism, the light rays for different wavelengths (or colors) are bent through different angles. This effect is called *dispersion*, and was first described by Isaac Newton in his work *Opticks* (1730). In early spectrometers, the dispersed light would be sent through a telescope and viewed by eye. The typical appearance of the view through the telescope eyepiece, for the case of a gas discharge light source, is shown in Figure I-1(b). It consists of series of images of the slit of different colors. This occurs because the light source contains only a limited set of discrete wavelengths. These are called *spectral lines*. The term "lines" originates from the appearance of the slit images in the spectrometer. The spectrometer incorporates a scale that allows deflection angles to precisely determined. From that the wavelengths of the spectral lines can be precisely determined.

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1. Dan Kleppner, "Experiments with Atomic Hydrogen," in *Atomic Physics and Astrophysics,* Vol. I, eds. M Chrétien and E. Lipworth (Gordon and Breach, 1971).

2. *Quantum Mechanics of One and Two Electron Atoms,* Bethe and Salpeter (Springer-Verlag, 1957).

3. Hindmarsh, Atomic Spectra (Contains English translations of some of the original papers by Balmer, Bohr, Rydberg, and others.)

4. H. A. Boorse, L. Motz, and J. H. Weaver, *The Atomic Scientist* (Wiley, New York, 1989).

5. J. C. Slater, *Quantum Theory of Atomic Structure,* Vols. I, II (McGraw-Hill, New York, 1960).

6. Wolfgang Pauli, 1945 Nobel Prize lecture, available at
http://nobelprize.org/nobel_prizes/physics/laureates/1945/pauli-lecture.html
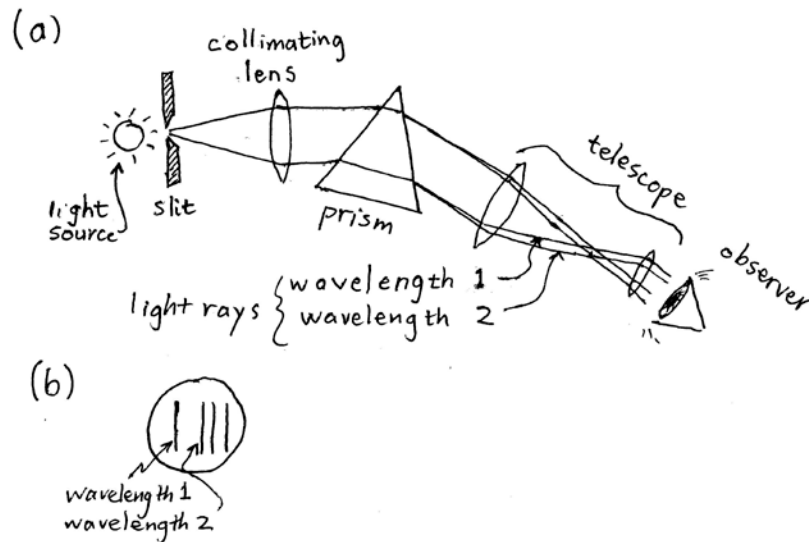
Figure I-1. (a) Prism spectrometer. (b) Appearance of the image seen by the observer for a gas discharge source. It consist of a series of images of the slit, each a different color.
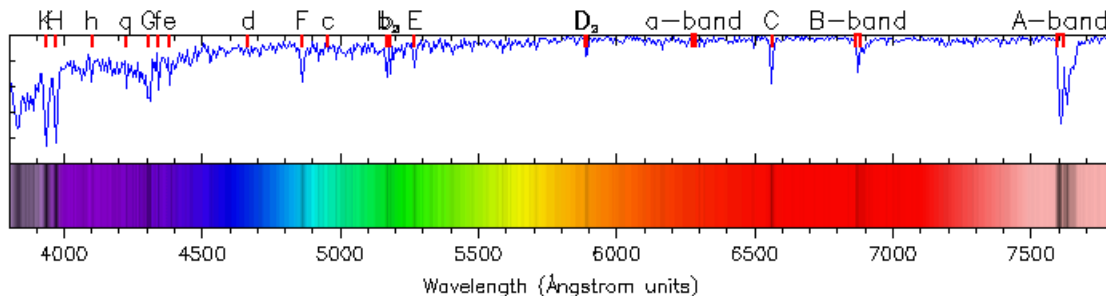

Figure I-2. Solar spectrum as it appears in a spectrometer, along with Fraunhofer's labelling of the dark lines.[7]

The *spectrum* of a light source is its intensity as a function of wavelength, as observed in a spectrometer. A *line spectrum* is one that contains only discrete lines like those illustrated in Figure I-1(b). Gaseous sources like a gas discharge tube usually produce line spectra. Other sources may produce spectra with a continuous band of colors. For instance, the filament of a light bulb produces a continuous spectrum.

In 1802, William Wollaston viewed the light from the sun through a spectrometer. It was known since Newton's time that sunlight has a continuous spectrum. But Wollaston noticed for the first time that the continuous band of colors is crossed by dark lines. You can see these lines in the spectrum shown in Figure I-2. In 1817, Fraunhofer measured the wavelengths of more than 500 of these dark lines, and labelled the strongest lines with a series of letters. The "C line," at

7. This image is from the website http://media.radiosai.org/journals/Vol_05/01JAN07/04-musings.htm

6562 Å and the "F line," at 4861 Å were among the most prominent $\left(1\,\text{Å} = 10^{-10}\,\text{m}\right)$. In Fraunhofer's time, the origin of these lines was a complete mystery.

In 1809, Joseph Gay-Lussac carried out experiments on chemically reacting gases, and proved the result now known as *Gay-Lussac's law of combining volumes*: *the ratio between the combining volumes of gases and their reaction products, if gaseous, can be expressed in small whole numbers.* For example, if one volume of nitrogen reacts with three of hydrogen, two volumes of ammonia are produced.

Amedeo Avogadro quickly realized the significance of these results, and in 1811 put forward *Avogadro's law: equal volumes of different gases at the same temperature and pressure contain the same number of molecules.* With such a law, Gay-Lussac's law could be explained (following John Dalton) as a simple rearrangement of the atoms into different states of molecular binding. The number of atoms of each element in a molecule would then be determined by the volume ratios in the experiments. In this way, Avogadro first determined the correct chemical formula for water, ammonia, nitrous oxide, and nitrogen dioxide.

As Avogadro deduced, the correct chemical formula for hydrogen is H_2, a fact that Dalton had missed. That is, each fundamental unit of hydrogen consists of two atoms bound together, not one. It took some time for chemists to accept this hypothesis. For one thing, "chemical combining" data – *i.e.* data on the relative number of grams of reactants to products – was in very poor shape at this time. But chemists also suffered from a conceptual problem: if one hydrogen atom interacts with another so strongly that they always bind together, why does the binding stop at two atoms? Why doesn't a third atom want to stick to the first two, and then a fourth to the first three? This was a quite reasonable objection to Avogadro's theory, and it took until the 1920s for this question to be fully answered. It cannot be explained without reference to quantum mechanics.

In the following sections, we'll be discussing the spectrum of individual hydrogen atoms, not hydrogen H_2 molecules. This can be done experimentally by passing an electric current through a hydrogen gas. Sometimes, the electrons that make up the current will strike the molecules hard enough to knock them apart, so that the gas does contain some individual hydrogen atoms. Alternatively, the H_2 molecular bond can be broken at temperatures above about 2,000 Kelvin.

In 1861, Anders Ångström measured the spectrum of atomic hydrogen in the laboratory, probably for the first time. He made precise measurements of the wavelengths of four of the strongest lines corresponding, giving the results shown in Table 1. He found that they had the same wavelengths as some of the strong lines in the solar spectrum measured by Fraunhofer, thus establishing that the sun contains hydrogen. (The solar atmosphere contains atomic rather than molecular hydrogen due to its high temperature.)

Line	Wavelength measured by Ångström (Å)	Wavelength from Balmer's formula (Å)	Difference (Å)
H_α (C line)	6562.10	6562.08	−0.02
H_β (F line)	4860.74	4860.80	+ 0.06
H_γ (before G)	4340.1	4340.0	−0.1
H_δ (h line)	4101.2	4101.3	+0.1

Table 1. Comparison of Ångström's measurements with wavelengths given by Balmer's formula.

In 1884, Johann Balmer discovered his formula for the wavelengths of the four lines measured by Ångström. He found that these wavelengths could be written as $(9/5)\,\lambda_0$, $(4/3)\,\lambda_0$, $(25/21)\,\lambda_0$, and $(9/8)\,\lambda_0$, with $\lambda_0 = 3645.6$ Å. The accuracy of the comparison with Ångström's measurements, shown in Table 1, is impressive.

Rydberg first wrote Balmer's formula in the standard form:

$$\frac{1}{\lambda_{n,n'}} = R_H \left(\frac{1}{n^2} - \frac{1}{n'^2} \right) \tag{1.1}$$

where $R_H \approx 1.097 \times 10^7$ m^{-1} is the *Rydberg constant* for hydrogen, and $n' = 1, 2, 3, ...,$ with $n' > n$. The Balmer series corresponds to $n = 2$, $n' = 3, 4, 5, ...$.

Rydberg-Ritz combination principle

Balmer's formula (1.1) shows that the inverse wavelength of hydrogen's spectral lines $1/\lambda_{nn'}$ can be written as differences of quantities with dimensions of 1/length. In the first decade of the 1900s, Walter Ritz noticed that this is true for other atomic spectra. That is, *the inverse wavelengths of the spectral lines of an atom can be expressed as differences of a smaller number of "terms"*. A *term* T_n is a fixed quantity with dimensions of inverse length. This statement is now called the *Rydberg-Ritz combination principle*. Mathematically it can be written as

$$\frac{1}{\lambda_{nn'}} = T_n - T_{n'} \tag{1.2}$$

This is an extension of Balmer's formula to other atoms, although it is generally not possible to specify a simple functional form for T_n as Balmer did for hydrogen. This discovery was important because it showed that there is an underlying simplifying regularity in all atomic spectra. Even a complex spectrum with hundreds of lines can often be accounted for with a few dozen terms.

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Bohr model

In 1913, Bohr formulated his model for the hydrogen atom. I'll assume you're familiar with the details of this model, and just remind you that according to this model, the electron can only exist in discrete orbits labelled by a quantum number $n = 1, 2, 3, ...$, and that the energy of the electron in the nth orbit is

$$E_n = -\frac{1}{2}\left(\frac{m_e}{\hbar^2}\right)\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\left(\frac{m_p}{m_p + m_e}\right)\frac{1}{n^2} \tag{1.3}$$

where m_e is the mass of the electron, and m_p is the mass of the proton. Furthermore, Bohr postulated that a photon may be given off only in a *Bohr transition* between these energy states, with the photon wavelength given by

$$\frac{hc}{\lambda_{n,n'}} = E_n - E_{n'} \tag{1.4}$$

Since hc / λ is the energy of a photon, this is just a statement of conservation of energy for a Bohr transition. Comparing with Balmers' formula, we obtain

$$R_H = R_\infty\left(\frac{m_p}{m_p + m_e}\right) \tag{1.5}$$

with

$$R_\infty = \left(\frac{1}{4\pi}\right)\frac{m}{\hbar^3 c}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \tag{1.6}$$

The last factor in eq. (1.5) is the reduced mass correction, and R_∞ is the Rydberg constant for infinite mass nucleus. The difference between R_∞ and R_H is very small since the proton is very heavy compared to the electron. It is customary in atomic physics to simply refer to R_∞ as "the" Rydberg constant R (sometimes also written Ry), *i.e.* the convention is that if the reduced mass correction is important, it will be specifically indicated as in eq. (1.5). The Rydberg is presently known to about 12 digit accuracy:

$$R_\infty = 1.0973731568539(55) \times 10^5 \text{ cm}^{-1} \tag{1.7}$$

In this notation, the numbers in parentheses give the uncertainty in the last digits. In a more familiar notation, equation (1.7) can be written as

$$R_\infty = (1.0973731568539 \pm 0.0000000000055) \times 10^5 \text{ cm}^{-1} \tag{1.8}$$

Spectral Series in hydrogen

(Wavelengths in Ångströms)

```
  .
  .
  .
  5
  4
  3        H_α 6563  H_β 4861  H_γ 4340  H_δ 4102   18750  12100  10940   26300  40500
  2
                                                                    Pfund
                                                                    (1924)

           L_α 1216  L_β 1026  L_γ 973
n = 1
           Lyman              Balmer          Paschen    Brackett
           (1916)             (1884)          (1908)     (1922)
```
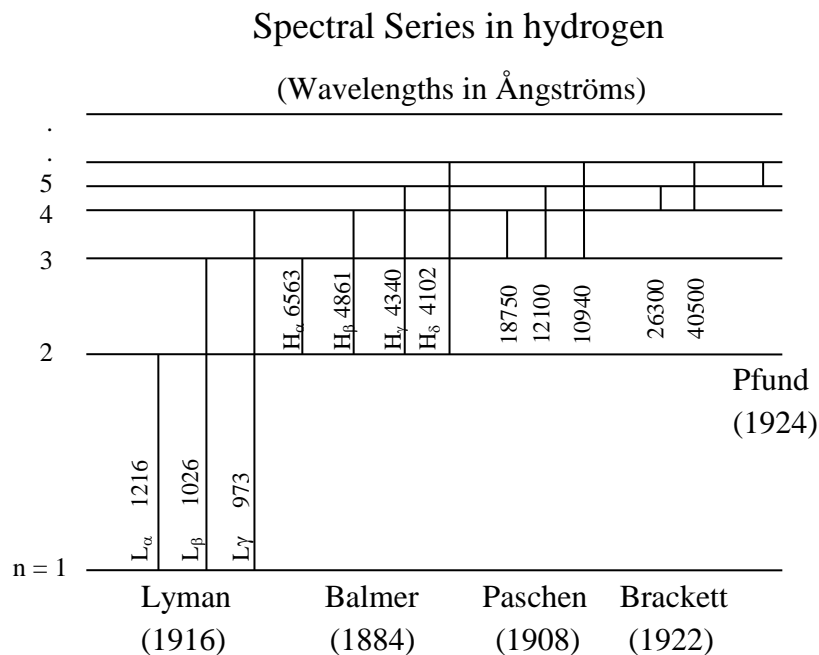
Figure I-3. Spectral series of the hydrogen atom.

After Ryberg's, Balmer's and Bohr's work, other series of lines were observed in hydrogen, as indicated in Figure I-3. The observed wavelengths agree with the Bohr theory at the level of one part in 10,000. The transitions ending in the $n = 1$ level are called the Lyman series. The first transition, from $n' = 2$ to $n = 1$, is in the deep ultraviolet with a wavelength of 121.6 nm, and is called the Lyman-α transition. The next transition is called the Lyman-β transition, the next the Lyman-γ transition, and so on. The series ending in $n = 2$ is called the Balmer series, and include the prominent red Balmer-α with a wavelength of 656.3 nm. The higher series (Paschen, Brackett…) are in the infrared part of the spectrum.

The levels with very high values of n (>20 or so) are referred to as Rydberg levels. An interesting observation of these levels comes from astronomy: in the late 1960s, microwave lines corresponding to transitions between states with quantum numbers of n ~ 100 were observed in interstellar clouds of hydrogen. Rydberg states with principal quantum numbers greater than 1000 have been produced in laboratory experiments with combinations of laser, radio frequency, and microwave excitation.

Wavenumber or inverse centimeter units

The basic features of the Bohr model extend to all atoms. Each atom has discrete energy levels with energies E_n. (In general it is not possible to give a simple formula for E_n as Bohr did for hydrogen.) Also, photons are emitted by Bohr transitions, with wavelengths $\lambda_{n,n'}$ given by equation (1.4). This explains the Rydberg-Ritz combination principle, since

$$\frac{1}{\lambda_{nn'}} = T_n - T_{n'} = \frac{E_n}{hc} - \frac{E_{n'}}{hc} \tag{1.9}$$

We see that a term is just a level energy divided by *hc*.

When working with atomic spectra, one has to add and subtract inverses of wavelengths so frequently that it has become common practice to use units of inverse wavelength, called *wavenumbers* or *inverse centimeters* – an inverse wavelength in cm units - to measure "energies". It is also common practice to redefine the zero of energy for an atom as the energy of the ground state. So, for example the "energy" of the $n = 1$ level of hydrogen may be listed as 0 cm^{-1}, and the "energy" of the $n = 2$ level listed as $82,259 \text{ cm}^{-1}$. This is the value E_2 / hc, where E_2 is measured relative to the energy E_1.

Note that this use of the term "wavenumber" is different than its use in wave physics, where it means the magnitude *k* of the wavevector, and has the value $2\pi / \lambda$.

Transition energies can also be measured in wavenumbers, *i.e.* by

$$\bar{\nu} = \frac{1}{wavelength} = \frac{1}{\lambda} \tag{1.10}$$

According to equation (1.9) wavenumbers of transitions are sums and differences of each other. For instance, the $n = 2$ to $n = 1$ (Lyman-α) transition of hydrogen has an energy of $82,259 \text{ cm}^{-1}$, and the $n = 3$ to $n = 2$ (Balmer-α) transition of hydrogen has an energy of $15,233 \text{ cm}^{-1}$. It follows that the transition energy of the $n = 3$ to $n = 1$ (Lyman-β) transition is $82,259 + 15,233 = 97492 \text{ cm}^{-1}$. The wavelength of a photon emitted on this transition is $1/97492 = 1.0257 \times 10^{-5}$ cm.

Here are some useful unit conversions:

$$1 \text{ cm}^{-1} \leftrightarrow 29.979 \text{ GHz} \tag{1.11}$$

$$8066 \text{ cm}^{-1} \leftrightarrow 1 \text{ eV} \tag{1.12}$$

Solution of the Schrödinger equation for the hydrogen atom

In 1926, Schrödinger wrote down his equation and solved it for hydrogen. The energy levels are identical to those obtained by Bohr. However, it was understood all along that the Bohr model was an incomplete theory, because it could not account for other properties of the hydrogen atom, and it could not be extended at all to other atoms. By contrast, the Schrödinger equation approach allows you to accurately calculate all other properties of hydrogen. Furthermore, as we'll see later the Schrödinger equation can be extended to all atoms.

Since I'm assuming everyone is already familiar with the solution of the Schrödinger equation for hydrogen, I'll give only a brief summary here. I'll actually do that for the *hydrogenic atom,* which is an atom with one electron bound to a nucleus of charge Ze. For instance, hydrogen has $Z = 1$. A He^+ ion is a hydrogenic atom with one electron bound to a helium nucleus $(Z = 2)$, and a Li^{++} ion is a hydrogenic atom with one electron bound to a lithium nucleus $(Z = 3)$. I'll assume that the center of mass degree-of-freedom has already been separated out, and denote the vector from the nucleus to the electron as $\vec{r}$, as shown in Figure I-4(a). Due to the spherical symmetry of the atom, we'll normally express $\vec{r}$ in spherical coordinates (r, θ, ϕ) as shown in Figure I-4(b).
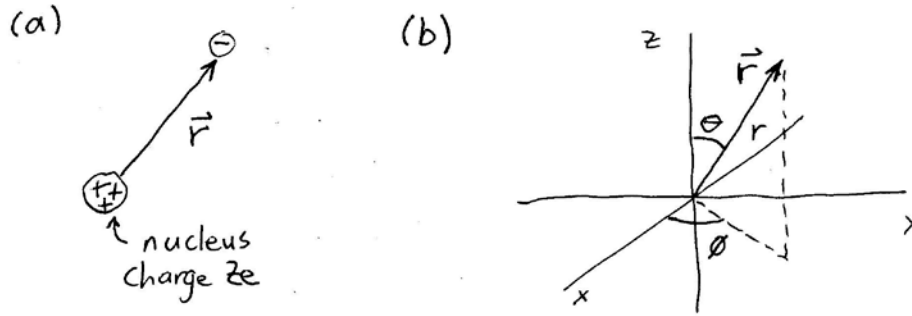

Figure I-4. (a) Hydrogenic atom. (b) Vector $\vec{r}$ in spherical coordinates.

The Schrödinger equation for the hydrogenic atom is

$$H\psi(\vec{r}) = \left[-\frac{\hbar^2}{2m_e}\vec{\nabla}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{1.13}$$

(For precise work, the electron mass m_e should be replaced by the reduced mass $m_e\left(\dfrac{m_N}{m_N + m_e}\right)$, where m_N is the mass of the nucleus.) Expressing the Laplacian $\vec{\nabla}^2$ in spherical coordinates, we find that equation (1.13) can be rewritten as

$$H\psi(\vec{r}) = \left[-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\vec{L}^2}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r} \right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{1.14}$$

where $\vec{L} = \vec{r} \times \vec{p}$ is the angular momentum operator. The Hamiltonian H, $\vec{L}^2$, and L_z mutually commute, so we expect that the solutions of equation (1.14) can be expressed as simultaneous eigenfunctions of H, $\vec{L}^2$, and L_z. This turns out to be a complete set of commuting observables, *i.e.* the quantum numbers of these three observables are sufficient to completely determine a given quantum state. The eigenfunctions of $\vec{L}^2$, and L_z are spherical harmonics $Y_{\ell m_\ell}(\theta, \phi)$, which obey the eigenvalue equations

$$\vec{L}^2 Y_{\ell m_\ell}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{\ell m_\ell}(\theta,\phi) \tag{1.15}$$

$$\vec{L}_z Y_{\ell m_\ell}(\theta,\phi) = m_\ell \hbar Y_{\ell m_\ell}(\theta,\phi) \tag{1.16}$$

where $\ell = 0,1,2,...$ and for each ℓ, $m_\ell = -\ell, -\ell+1,..., \ell$.

We can continue the solution of equation (1.14) with the method of separation of variables by taking $\psi(\vec{r}) = R(r)Y_{\ell m_\ell}(\theta,\phi)$. $R(r)$ is called the *radial wavefunction.* Substituting this into equation (1.14) gives

$$\left[-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r} \right]R(r) = ER(r) \tag{1.17}$$

Thus, we have an equation for R for the case $\ell = 0$, another for the case $\ell = 1$, another for the case $\ell = 2$, and so on. It is sometimes helpful to define another function $u(r)$ by $u(r) = rR(r)$. Substituting for $R(r) = u(r)/r$ in equation (1.17) gives

$$\left[-\frac{\hbar^2}{2m_e}\frac{d^2}{dr^2} + V_{eff}(r) \right]u(r) = Eu(r) \tag{1.18}$$

where

$$V_{eff}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2} \tag{1.19}$$

is the *effective radial potential.* It is the sum of the Coulomb potential of the nucleus $-\dfrac{Ze^2}{4\pi\varepsilon_0 r}$

and the centrifugal potential $\dfrac{\ell(\ell+1)\hbar^2}{2m_e r^2}$. It is different for each value of ℓ, as illustrated in

Figure I-5.

Equation (1.18) has the simple form of an eigenvalue problem for a particle moving in the 1-dimensional potential $V_{eff}(r)$. Thus, we expect that there will be a set of bound state solutions for the effective potential with $\ell = 0$, another set for $\ell = 1$, and so on. We label these bound state energies as $E_{n\ell}$, where ℓ tells us which effective potential (*i.e.* the value of ℓ), and n tells us which eigenvalue in that potential. By convention, we start the counting at $n = 1$ for $\ell = 0$, at $n = 2$ for $\ell = 1$, *etc.* That is, we have states $\ell = 0$, $n = 1,2,3,...$; $\ell = 1$, $n = 2,3,4,...$; $\ell = 2$, $n = 3,4,5,...$; *etc.* Another way to say the same thing is that $n = 1,2,3,...$ and $\ell = 0,1,2,...,n-1$.
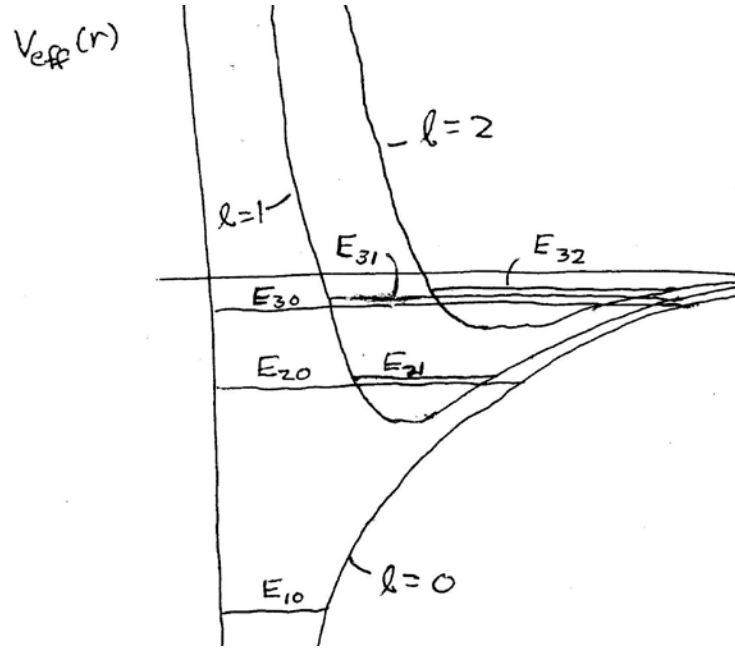
Figure I-5. Effective potentials for an electron in a hydrogenic atom. A few of the energy levels with energies $E_{n\ell}$ are also shown.

The solution for the radial wavefunctions is a bit of work. As for the energies, we'll have solutions labeled by both n and ℓ. Along with some equations from above, the answer turns out to be

$$\psi_{n\ell m_\ell}(\vec{r}) = R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\phi) \tag{1.20}$$

where the normalized radial wavefunction is

$$R_{n\ell}(r) = -\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3}\right]^{\frac{1}{2}} e^{-\frac{Zr}{na_0}}\left(\frac{2Z}{na_0}r\right)^\ell L_{n+\ell}^{2\ell+1}\left(\frac{2Z}{na_0}r\right) \tag{1.21}$$

where

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 0.5292 \times 10^{-10}\ \text{m} \tag{1.22}$$

is the Bohr radius, $L_{n+\ell}^{2\ell+1}(x)$ is the associated Laguerre polynomial, and where $n = 1, 2, 3, ...$ is the *principal quantum number*, $\ell = 0, 1, ..., n-1$ is the *orbital angular momentum quantum number*, $m_\ell = -\ell, -\ell+1, ..., \ell$ is the *magnetic or azimuthal quantum number*. Tables of the first few radial wavefunctions and spherical harmonics are given in the class formula sheet. Plots of the first few radial wavefunctions are shown in Figure I-6.
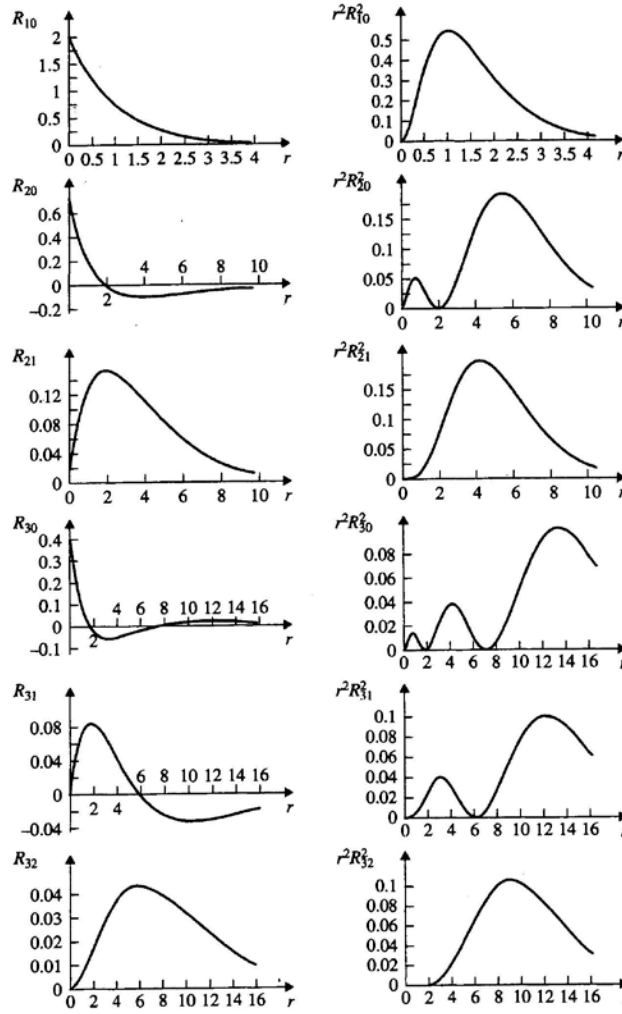
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Figure 7.9 Radial functions $R_{nl}(r)$ and radial distribution functions $r^2 R_{nl}^2(r)$ for atomic hydrogen. The unit of length is $a_\mu = (m/\mu)a_0$, where a_0 is the first Bohr radius (1.66).

Figure I-6. Hydrogenic atom radial wavefunctions and radial probability densities. (Reproduced from Bransden and Joachain, Quantum Mechanics, 2nd ed.)

Note that the wavefunction is normalized in three dimensions,

$$\int \left|\psi\left(\vec{r}\right)\right|^2 d^3r = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \left|\psi\left(\vec{r}\right)\right|^2 r^2 \sin\theta dr d\theta d\phi = 1 .$$

The spherical harmonics are normalized so that they are "orthonormal on the unit sphere", which means that

$$\int Y_{\ell m_\ell}{}^*\left(\theta,\phi\right)Y_{\ell'm_\ell'}\left(\theta,\phi\right)d\Omega = \int_0^{2\pi}\int_0^{\pi}Y_{\ell m_\ell}{}^*\left(\theta,\phi\right)Y_{\ell'm_\ell'}\left(\theta,\phi\right)\sin\theta d\theta d\phi = \delta_{\ell\ell'}\delta_{m_\ell m_\ell'} \tag{1.23}$$

The radial functions are normalized so that

$$\int_0^\infty |R_{n\ell}|^2 r^2 dr = 1 \tag{1.24}$$

Note that $r^2 |R_{n\ell}(r)|^2$ is the *radial probability density, i.e.* $r^2 |R_{n\ell}(r)|^2 dr$ is the probability to find the electron with radius between r and $r + dr$. This function is shown in the right-hand column of Figure I-6.

Neglecting the reduced mass corrections, the energies of these states are

$$E_{n\ell} = -\frac{1}{2}\left(\frac{m_e}{\hbar^2}\right)\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{Z^2}{n^2} \tag{1.25}$$

which are exactly the same as those of the Bohr model. The energies turn out to depend only on n, not on ℓ, so we usually just write the energies as E_n. Some useful alternative ways to write E_n include

$$E_n = -\frac{hcR_\infty Z^2}{n^2} = -\frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0 a_0}\right)\frac{Z^2}{n^2} = -\frac{1}{2}\alpha^2 m_e c^2 \frac{Z^2}{n^2} = -13.60 \text{ eV}\frac{Z^2}{n^2} \tag{1.26}$$

where

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 c} \approx \frac{1}{137.04} \tag{1.27}$$

is the fine-structure constant.

Other properties of the hydrogen atom quantum states

a) <u>Small-r dependence of the radial wavefunctions</u>:

$$R_{n\ell}(r) \sim r^\ell \tag{1.28}$$

This relation is important because it shows that only states with $\ell = 0$ have non-zero amplitude at the atomic nucleus. This is due to the fact that states with nonzero ℓ are blocked from the origin by the centrifugal potential (see Figure I-5). Also, we can show that

$$\langle \delta^3(\vec{r})\rangle = \begin{cases} \dfrac{1}{\pi n^3 a_0^3}, & \text{if } \ell = 0 \\ 0, & \text{if } \ell \neq 0 \end{cases} \tag{1.29}$$

b) <u>degeneracy of nth energy level</u>: $\ell = 0, 1, \ldots, n-1, \quad m_\ell = -\ell, \ldots, \ell$

Total degeneracy (not including spin) $= \sum_{\ell=1}^{n-1}(2\ell+1) = n^2 \tag{1.30}$

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c) <u>number of radial nodes</u> $= n - \ell - 1$ (spheres) $\hspace{3cm}$ (1.31)

d) <u>number of angular nodes</u> $= \ell - |m|$ (cones) $\hspace{3cm}$ (1.32)

e) <u>mean values of r^n</u>: $\hspace{2cm}$ $\langle r^n \rangle = \int r^n |\psi(r,\theta,\phi)|^2 \, d^3r$

$$\langle r \rangle = \frac{a_0}{2}\left[3n^2 - \ell(\ell+1)\right] \hspace{4cm} (1.33)$$

$$\langle r^2 \rangle = \frac{n^2 a_0^2}{3}\left[5n^2 + 1 - 3\ell(\ell+1)\right] \hspace{3cm} (1.34)$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0 n^2} \hspace{6cm} (1.35)$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{a_0^2\left(\ell + \dfrac{1}{2}\right)n^3} \hspace{4cm} (1.36)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a_0^3\,\ell(\ell+1)\left(\ell + \dfrac{1}{2}\right)n^3} \hspace{3cm} (1.37)$$

Note that the size of the atom is $\sim n^2 a_0$.

Spectroscopic notation and selection rules

In atomic physics, spectroscopic notation is widely used. This consists of replacing the number ℓ with a letter according the following rule:

$$\ell = \ 0, \ 1, \ 2, \ 3, \ 4, \ 5,...$$
is denoted by $\quad s, \ p, \ d, \ f, \ g, \ h,...$ $\hspace{4cm}$ (1.38)

For example, a state with $n = 5, \ell = 2$ would be called a "5d state". Note that these states are still degenerate, since each has $2\ell + 1$ eigenfunctions with different values of m_ℓ. An energy level diagram of hydrogen using this notation is given in Figure I-6.
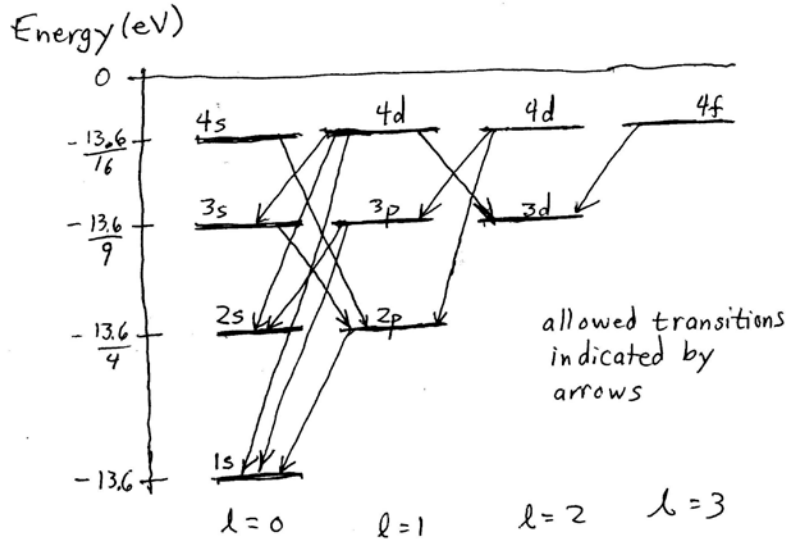
Figure I-7. Hydrogen atom levels indicated by spectroscopic notation, with allowed transitions indicated by arrows.

We shall see later in this course that there is a selection rule for so-called "electric dipole transitions", which give by far the largest intensity for the spectral lines. That rule is that the value of ℓ must change by 1. For instance, p-states can only make transitions to s-states or d-states. The allowed transitions of the hydrogen atom are also shown in Figure I-6.

B. Hamiltonian of an electron interacting with an electromagnetic field

Next, we will study relativistic effects and magnetic effects in the hydrogen atom. In order to do this, we'll need to first review two bits of physics - the general expression for the Hamiltonian of a charged particle in an electromagnetic field (this section), and electron spin (the next section).

You are probably used to seeing the Hamiltonian for a particle with charge q and mass m written as

$$H = \frac{\vec{p}^2}{2m} + V(\vec{r}) \tag{1.39}$$

$$V(\vec{r}) = q\Phi(\vec{r}) \tag{1.40}$$

where $\Phi(\vec{r})$ is the electrostatic potential. For instance, for the hydrogen atom we take Φ to be

the electrostatic potential of the proton, and write $V(r) = \dfrac{-e^2}{4\pi\varepsilon_0 r}$. However, equations (1.40) and

(1.41) are not correct if a magnetic field is present. In the more general case, we must use the correct classical Hamiltonian for a charged particle interacting with an electromagnetic field.

In classical physics, we describe the electromagnetic quantities in terms of

sources: discrete charges q_i are positions $\vec{r}_i(t)$, and/or

continuous charge density $\rho(\vec{r},t)$, and current density $\vec{J}(\vec{r},t)$

potentials: scalar potential $\Phi(r,t)$, vector potential $\vec{A}(\vec{r},t)$

fields: electric field $\vec{\mathcal{E}}(\vec{r},t)$, magnetic field $\vec{B}(\vec{r},t)$.

In general complete knowledge of any one of these sets of quantities enables you to calculate the other two sets. For example, in statics (nothing depends on time) with continuous charge distributions, if you know the charge and current density you can calculate the potentials from the relations

$$\Phi(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \tag{1.41}$$

$$\vec{A}(\vec{r}) = \frac{\mu_0}{4\pi} \int \frac{\vec{J}(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \tag{1.42}$$

If you know the potentials (in the general time-dependent case), you can calculate the fields from the relations

$$\vec{\mathcal{E}}(\vec{r},t) = -\vec{\nabla}\Phi(\vec{r},t) - \frac{\partial\vec{A}(\vec{r},t)}{\partial t} \tag{1.43}$$

$$\vec{B}(\vec{r},t) = \vec{\nabla} \times \vec{A}(\vec{r},t) \tag{1.44}$$

where $\vec{\nabla} = \hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z}$ is the gradient operator. In Phys. 352k, you spend a large part of the semester learning to transform back and forth between these sets of quantities.

Equations (1.44) and (1.45) will always give you the correct fields from the potentials, but it turns out that there is more than one set of potentials that will give rise to the same fields. Since, in classical physics, everything can be described in terms of fields only, this means that there is no one "correct" set of potentials. Any set which gives the same fields according to equations (1.44) and (1.45) is as valid as any other.

You can see that this is true mathematically if you transform the potentials with the equations

$$\vec{A}_{new} = \vec{A}_{old} + \vec{\nabla}\chi \tag{1.45}$$

$$\Phi_{new} = \Phi_{old} - \frac{\partial \chi}{\partial t} \tag{1.46}$$

where $\chi(\vec{r},t)$ is *any* continuous function. It is possible to show that these two sets of potentials $\left(\Phi_{old}, \vec{A}_{old} \right)$ and $\left(\Phi_{new}, \vec{A}_{new} \right)$, when substituted into equations (1.44) and (1.45), *give exactly the same fields* $\vec{\mathcal{E}}(\vec{r},t)$ *and* $\vec{B}(\vec{r},t)$.

The freedom to adjust the potentials Φ and $\vec{A}$ in this way is called *gauge freedom.* A *particular* choice for how to set the potentials within this freedom is called a *gauge*. This corresponds to the choice of a particular value of χ in equations (1.46) and (1.47). Any formula that leads to definite values of Φ and $\vec{A}$ carries with it an implicit choice of gauge. For instance, equations (1.42) and (1.43) are written in the so-called "Coulomb gauge". With some other choice of gauge, these equations would be different. We won't concern ourselves in this course with the exact condition that defines any particular gauge.

With these preliminaries, the classical Hamiltonian for a particle with charge q in an electromagnetic field is

$$H = \frac{1}{2m} \left(\vec{p} - q\vec{A} \right)^2 + q\Phi \tag{1.47}$$

A derivation of this formula can be found [here]. We can also prove that this leads to the correct equation of motion for a charged particle in an electromagnetic field as follows. In Hamiltonian mechanics, the momentum conjugate to position x turns out to be $\mathcal{P}_x = p_x + qA_x$, where $p_x = mv_x$ is the ordinary or "kinetic" momentum, and you can think of qA_x as related to the momentum carried by the electromagnetic field. Hamilton's equations give the equation of motion for x and $\mathcal{P}_x$:

$$\frac{dx}{dt} = \frac{\partial H}{\partial \mathcal{P}_x} \qquad\qquad \frac{d\mathcal{P}_x}{dt} = -\frac{\partial H}{\partial x} \tag{1.48}$$

and similarly for the y and z components. If we solve equations (1.49) with Hamiltonian (1.48), we find that the equation of motion for the particle's position is

$$m\frac{d^2\vec{r}}{dt^2} = q\left(\vec{\mathcal{E}} + \vec{v} \times \vec{B} \right) \tag{1.49}$$

where $\vec{v} = d\vec{r}/dt$. This is just the combination of Newton's second law and the Lorentz force law, exactly as it should be. This shows that eq. (1.48) must be the correct classical Hamiltonian. Note that the Hamiltonian itself will have a different form in different gauges, because it contains the potentials. But the equation of motion (1.50) will be the same no matter the gauge, because it contains only the fields.

When we carry this Hamiltonian over to quantum mechanics, we run into a problem that we haven't encountered yet. As before $\vec{p} \to -i\hbar\vec{\nabla}$. When we expand the square in equation (1.48), we end up with a term that we would write in classical physics as $-q\vec{p}\cdot\vec{A}/m$. But in quantum mechanics the operators $\vec{p}$ and $\vec{r}$ don't commute. And, since $\vec{A}$ depends on $\vec{r}$, which is an operator, $\vec{A}(\vec{r})$ is also an operator, and does not commute with $\vec{p}$. Therefore in quantum mechanics it matters whether we write $\vec{p}\cdot\vec{A}$, or $\vec{A}\cdot\vec{p}$, or some other combination of $\vec{p}\cdot\vec{A}$ and $\vec{A}\cdot\vec{p}$.

So, what order do we choose? The answer is that you have to accept another ad-hoc postulate of quantum mechanics:

When a classical Hamiltonian contains a product AB of non-commuting operators A and B, you must use the symmetric combination $\dfrac{AB+BA}{2}$ of those operators.

The justification for this postulate is that the predictions of the resulting theory agree with experiment.

Thus, to be careful, the Hamiltonian of a charged particle that we should use in quantum mechanics is

$$H = \frac{1}{2m}\left(\vec{p}^2 - q\vec{A}\cdot\vec{p} - q\vec{p}\cdot\vec{A} + q^2\left|\vec{A}\right|^2\right) + q\Phi \tag{1.50}$$

Sometimes we will write this Hamiltonian as in equation (1.48) for brevity, but it should be kept in mind that equation (1.51) is the accurate one. This Hamiltonian reduces to the simpler form of

$$H = \frac{\vec{p}^2}{2m} + V(\vec{r}) \text{ with } V(\vec{r}) = q\Phi(\vec{r}) \text{ only if } \vec{A} = 0.$$

C.   Electron spin

There is an important property of the electron which is missing from classical theory: *electron spin*. We'll see later that this is a relativistic property. For now, we'll just review the basics.

The spin operator $\vec{s}$ is given by

$$\vec{s} = \frac{\hbar}{2}\vec{\sigma} \tag{1.51}$$

where $\vec{\sigma}$ is a dimensionless vector operator in the two-state spin space whose three Cartesian components are given by the Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{1.52}$$

The ordered basis implicit these matrices is $\{|\text{spin up}\rangle, |\text{spin down}\rangle\}$. The structure of these operators follows directly from the extension of the theory of orbital (integer) quantum angular momentum to the case of half-integer angular momentum. Note that in this definition $\vec{s}$ has the dimensions of angular momentum, *i.e.* we are not defining the spin operator in dimensionless form, as is sometimes done.

Some important properties of the Pauli matrices are

$$\sigma_x^{\,2} = \sigma_y^{\,2} = \sigma_z^{\,2} = 1 \tag{1.53}$$

$$\sigma_x\sigma_y = -\sigma_y\sigma_x = i\sigma_z \qquad \sigma_y\sigma_z = -\sigma_z\sigma_y = i\sigma_x \qquad \sigma_z\sigma_x = -\sigma_x\sigma_z = i\sigma_y \tag{1.54}$$

The eigenstates of the spin operator can be written as $|s, m_s\rangle$, where $s = 1/2$, and $m_s = \pm 1/2$. In matrix form

$$\left| s = \frac{1}{2}, m_s + \frac{1}{2} \right\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad\qquad \left| s = \frac{1}{2}, m_s - \frac{1}{2} \right\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{1.55}$$

The corresponding eigenvalue equations are

$$\left|\vec{s}\right|^2 |s, m_s\rangle = s(s+1)\hbar^2 |s, m_s\rangle = \frac{3}{4}\hbar^2 |s, m_s\rangle \tag{1.56}$$

$$s_z |s, m_s\rangle = m_s\hbar |s, m_s\rangle = \pm\frac{\hbar}{2} |s, m_s\rangle \tag{1.57}$$

It is found experimentally that the electron has a spin magnetic moment, which is given by

$$\vec{\mu}_s = -g_e\mu_B \frac{\vec{s}}{\hbar} \tag{1.58}$$

where g_e is the *electron g-factor*, and

$$\mu_B = \frac{e\hbar}{2m_e} \approx 9.273\times10^{-24} \text{ J/T} \tag{1.59}$$

is the *Bohr magneton*.

Experimentally, the electron g-factor is measured to be very close to the value $g_e = 2$.

A natural classical model for an electron would be a classical spinning ball with a radius r_e, uniform mass density $\rho_m = \dfrac{m_e}{(4/3)\pi r_e^{\,3}}$ and charge density $\rho_e = \dfrac{-e}{(4/3)\pi r_e^{\,3}}$. If we adopt such a model, then the angular momentum of the ball is

$$\vec{s} = \int \left(\vec{r}\times\rho_m\vec{v}\right) d^3r \tag{1.60}$$

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and its magnetic moment is

$$\vec{\mu} = \frac{1}{2}\int (\vec{r} \times \rho_e \vec{v}) d^3r \qquad (1.61)$$

The factor of ½ is there to make this definition reduce to the usual definition current × area in the case of a simple current loop. We can rewrite this as

$$\vec{\mu} = \frac{\rho_e}{2\rho_m}\int (\vec{r} \times \rho_m \vec{v}) d^3r = \frac{\rho_e}{2\rho_m}\vec{s} = -\frac{e}{2m}\vec{s} = -\mu_B \frac{\vec{s}}{\hbar} \qquad (1.62)$$

Comparison of equations (1.59) and (1.63) shows that *if the "classical spinning ball" model is correct, we expect to find* $g_e = 1$. The experimental value of $g_e \neq 1$ tells us that the electron is *not* a classical, spinning charged ball. This seemed somewhat mysterious at first, but Dirac was able to explain the result $g_e \approx 2$ as a relativistic effect in 1928.

The electron *g*-factor is the most precisely measured fundamental constant in physics. A relatively recent result (Phys. Rev. Lett. **100**, 12081 (2008)) has determined its value to be

$$g_e = 2 \times (1.00115965218073(28)) \qquad (1.63)$$

It deviates very slightly from the integer value 2. As we'll discuss later, the small difference of g_e and 2 is an effect of quantum electrodynamics.

D.   Electron in a uniform magnetic field

Before moving on to the problem of a hydrogen atom in a magnetic field, let's look at the more basic problem of a single electron in a uniform magnetic field $\vec{B} = B\hat{z}$, with no electric field present; $\vec{\mathcal{E}} = 0$. The electron experiences no *z*-component of force. Therefore, motion in the *z*-direction is a free particle, constant-velocity motion that is uncoupled from motion in the *x-y* plane. For this discussion, we'll assume that particle has no component of velocity in the *z*-direction, and focus our attention on the more complex motion in the *x-y* plane.
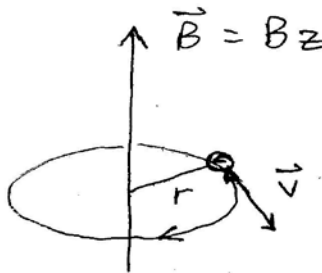

Figure I-8. Electron cyclotron orbit.

In classical physics, the electron exhibits a circular *cyclotron orbit* in the *x-y* plane, as shown in Figure I-7. The Lorentz force on the particle points towards the center of the orbit, and has magnitude $\left| e\vec{v} \times \vec{B} \right| = evB$. From Newton's second law we then find

$$evB = \frac{m_e v^2}{r} \tag{1.64}$$

where $v = \omega_c r$ is the velocity of the electron, with ω_c the orbital frequency and *r* the orbit radius. Solving for the frequency we find that

$$\omega_c = \frac{eB}{m_e} \tag{1.65}$$

independent of the orbit radius. This frequency is called the *cyclotron frequency.*

Quantum mechanically, this is a tricky problem is spite of its apparent simplicity. Part of the complication stems from the fact that there is no natural center for the orbit, so the wavefunctions can be expressed in a number of different ways, as linear combinations of functions that extend over the *x-y* plane. But I'll give an abbreviated version of the problem here.

We first choose a specific gauge (the Coulomb gauge) in which the potentials can be written as

$$\Phi = 0 \qquad \qquad \vec{A} = \frac{1}{2}\left(\vec{B} \times \vec{r} \right) \tag{1.66}$$

where the electron position $\vec{r}$ is measured with respect to a completely arbitrary origin of coordinates. Including the effect of the spin magnetic moment, the Hamiltonian of the electron is then

$$H = \frac{\left(\vec{p} + e\vec{A} \right)^2}{2m_e} - \vec{\mu}_s \cdot \vec{B} \tag{1.67}$$

It consists of the sum of the classical Hamiltonian (1.48), with $\Phi = 0$, and the interaction $-\vec{\mu}_s \cdot \vec{B}$ between the spin magnetic moment and the magnetic field.

With some vector algebra, it is possible to show that equation (1.68) can be rewritten as

$$H = \frac{\vec{p}^2}{2m_e} - \vec{\mu} \cdot \vec{B} + \frac{e^2}{8m_e}\left(x^2 + y^2 \right) \tag{1.68}$$

where

$$\vec{\mu} = \vec{\mu}_\ell + \vec{\mu}_s = -\mu_B \left(\frac{\vec{\ell} + g_e \vec{s}}{\hbar} \right) \tag{1.69}$$

with $\vec{\mu}_\ell = -\mu_B \dfrac{\vec{\ell}}{\hbar}$ the *orbital magnetic moment* of the electron, and where $\vec{\ell} = \vec{r} \times \vec{p}$ is the orbital angular momentum operator. Thus, the total magnetic moment of the electron (neglecting its diamagnetic moment) is the sum of its spin magnetic moment $\vec{\mu}_s$ and its orbital magnetic moment $\vec{\mu}_\ell$.
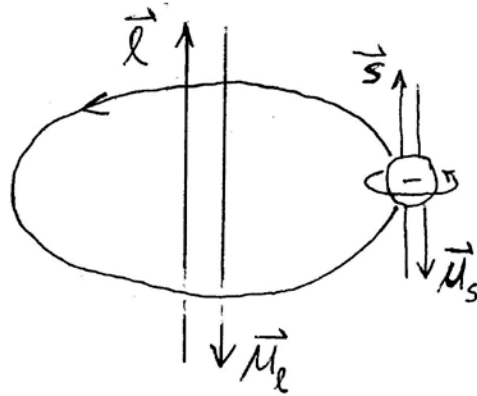

Figure I-9. Two main sources of an electron magnetic moment. The electron spins about its own axis with angular momentum $\vec{s}$, and may also have an orbital motion with an angular momentum $\vec{\ell}$. The electric currents associated with these motions give rise to a spin magnetic moment $\vec{\mu}_s$, and an orbital magnetic moment $\vec{\mu}_\ell$.

The first term in equation (1.69) is the kinetic energy of the electron. The second term is the interaction of the electron's spin and orbital magnetic moment with the magnetic field. The third term in equation (1.69) is called the *diamagnetic term*. The physics of this term is similar to Lenz's law in elementary E&M. The vacuum with a free electron is a little like an electrically conducting material. If you slowly turn on a magnetic field in the presence of this "material", it will respond by producing a reaction current that opposes the applied magnetic field. But, unlike an ordinary current, there is no electrical resistance, so that current lasts indefinitely, like a superconducting current. The magnetic dipole moment associated with this current is called the *diamagnetic moment*. The last term can be thought of as the interaction between the diamagnetic moment of the free electron and the magnetic field.

Diamagnetism is a weak effect, but it can be experimentally significant. For a particularly dramatic example, see this video of the "Dutch flying frog." In this video, the gradient of an applied magnetic field interacts with the induced diamagnetic moment of the frog. The resulting force is strong enough to lift the frog against the force of gravity. In fact, in this particular arrangement the sum of the diamagnetic and gravitational potentials has a local minimum in space, so that the frog is stably suspended in space for as long as the magnet is left on.

I'll leave the remaining details of working out the energy levels of the electron in a magnetic field as a homework problem.