

Contents

2	Atoms: Some Basics	1
2.1	Spectroscopic Notation	1
2.2	One-Electron Atoms	2
2.2.1	The Bohr Atom	2
2.2.2	Radial Schrödinger equation for central potentials	3
2.2.3	Radial equation for hydrogen	5
2.3	One Electron Atoms with Cores: The Quantum Defect	7
2.3.1	Phenomenology	7
2.3.2	Explanation	7
2.3.3	Quantum defects for a model atom	9
2.4	Metrology and Precision Measurement and Units	10
2.4.1	Dimensions and Dimensional Analysis	11
2.4.2	SI units	12
2.4.3	Metrology	13
2.5	Universal Units and Fundamental Constants	14
2.6	Atomic Units	15
2.7	The Fine Structure Constant	16

Chapter 2

Atoms: Some Basics

This chapter comprises some miscellaneous topics in basic atomic physics. They do not form a unified exposition and the discussions are in some cases very informal. The topics are intended to provide helpful reviews and to introduce a number of useful concepts.

2.1 Spectroscopic Notation

Neutral atoms consist of a heavy nucleus with charge Z surrounded by Z electrons. Positively charged atomic ions generally have structure similar to the atom with the same number of electrons except for a scale factor; negative ions lack the attractive Coulomb interaction at large electron-core separation and hence have few if any bound levels. Thus the essential feature of an atom is its number of electrons, and their mutual arrangement as expressed in the quantum numbers.

An isolated atom has two good angular momentum quantum numbers, J and M_J . (This is strictly true only for atoms whose nuclei have spin $I = 0$. However, J is never significantly destroyed by coupling to I in ground state atoms.) In zero external field the atomic Hamiltonian possesses rotational invariance which implies that each J level is degenerate with respect to the $2J + 1$ states with specific M_J (traditional atomic spectroscopists call these states “sublevels”). For each J, M_J an atom will typically have a large number of discrete energy levels (plus a continuum) which may be labeled by other quantum numbers.

If Russel-Saunders coupling ($L - S$ coupling) is a good description of the atom, then L and S , where

$$\mathbf{L} = \sum_{i=1}^N \ell_i \quad (2.1)$$

$$\mathbf{S} = \sum_{i=1}^N \mathbf{s}_i \quad (2.2)$$

are nearly good quantum numbers and may be used to distinguish the levels. In this case the level is designated by a *Term* symbolized $^{2S+1}L_J$ where $2S + 1$ and J are written numerically and L is designated with this letter code:

$L:$	O	1	2	3	4	...
Letter:	S	P	D	F	G	

The Letters stand for Sharp, Principal, Diffuse, and Fundamental - adjectives applying to the spectral lines of one electron atoms. The term symbol is frequently preceded by the n value of the outermost electron, e.g.. the $3^2S_{1/2}$ ground state of Na.

This discussion of the term symbol has been based on an external view of the atom. Alternatively one may have or assume knowledge of the internal structure - the quantum numbers of each electron. These are specified as the *configuration*, e.g..

$$1s^22s^22p^2, \quad (2.3)$$

a product of symbols of the form $n\ell^k$ which represents k electrons in the orbital n, ℓ . n is the principal quantum number, which characterizes the radial motion and has the largest influence on the energy. n and m are written numerically, but the *spdf* ... coding is used for ℓ . An example of the configuration for Ca is $1s^22s^22p^63s3d$ which is frequently abbreviated $3d$. In general each configuration leads to several terms which may be split apart by several eV. The above Ca configuration gives rise to 1D_2 and $^3D_{1,2,3}$ for example.

In classifying levels, the term is generally more important than the configuration because it determines the behavior of an atom when it interacts with E or B fields. Selection rules, for instance, generally deal with $\Delta J, \Delta L, \Delta S$. Furthermore the configuration may not be pure - if two configurations give rise to the same term (and have the same parity) then intra-atomic electrostatic interactions can mix them together. This process, called configuration interaction, results in shifts in the level positions and intensities of spectral lines involving them as well as in correlations in the motions of the electrons within the atoms.

2.2 One-Electron Atoms

In trying to understand some new phenomenon for the first time it is common sense (and good science) to study it in the simplest situation where it is manifest. With atoms it is evident that hydrogen is of paramount simplicity and, much of the “fundamental” physics which has been discovered in atoms has been discovered in hydrogen (but Na and other alkalis have taken over since tunable lasers arrived). In this chapter we shall use the phrase “one electron atom” to include not only atoms which are isoelectronic with H (e.g. $\text{He}^+, \text{Li}^{++}$... etc.) but also atoms with one electron which is far less weakly bound than all the others so that the inner electrons may be considered collectively as a core whose interaction with the active electron may be adequately described by parameters such as a scattering length for low energy electrons, polarizability, etc.

2.2.1 The Bohr Atom

We briefly review the Bohr atom— a model that was soon obsolete, but which nevertheless provided the major impetus for developing quantum mechanics. Balmer’s empirical formula of 1885 had reproduced Angstrom’s observations of spectral lines in hydrogen to 0.1 Å accuracy, but it was not until 1913 that Bohr gave an explanation for this based on a quantized mechanical model of the atom. This model involved the postulates of the Bohr Atom:

- Electron and proton are point charges whose interaction is coulombic at all distances.
- Electron moves in circular orbit about the center of mass in *stationary states* with orbital angular momentum $L = n\hbar$.

These two postulates give the energy levels:

$$-E_n = \frac{1}{2} \left(\frac{m(e^2/4\pi\epsilon_0)^2}{\hbar^2} \frac{M}{M+m} \right) / n^2 = hcR_H/n^2 \quad (2.4)$$

where $m(e^2/4\pi\epsilon_0)^2/\hbar^2$ is the hartree¹, $M/(M+m)$ is the reduced mass factor, and hcR_H is the Rydberg in H: ($hcR_H = 1.09677576 \times 10^5 \text{ cm}^{-1}$).

- One quantum of radiation is emitted when the system changes between these energy levels.
- The wave number of the radiation is given by the Bohr frequency criterion:

$$\sigma_{n \rightarrow m} = (E_n - E_m)/(hc)$$

(Note that the wave number is a spectroscopic unit defined as the number of wavelengths per cm, $\sigma = 1/\lambda$. It is important not to confuse the wave number with the magnitude of the *wave vector* \mathbf{k} which defines a traveling wave of the form $\exp i(\mathbf{k} \cdot \mathbf{r} - \omega t)$. The magnitude of the wave vector is 2π times the wave number.

The mechanical spirit of the Bohr atom was extended by Sommerfeld in 1916 using the Wilson-Sommerfeld quantization rule,

$$\oint p_i dq_i = n_i h \quad (2.5)$$

where q_i and p_i are conjugate coordinate and momentum pairs for each degree of freedom of the system. This extension yielded elliptical orbits which were found to have an energy nearly degenerate with respect to the orbital angular momentum for a particular principal quantum number n . The dependency was lifted by a relativistic correction whose splitting was in agreement with the observed fine structure of hydrogen. (This was a great cruel coincidence in physics. The mechanical description ultimately had to be completely abandoned, in spite of the excellent agreement of theory and experiment.) Although triumphant in hydrogen, simple mechanical models of helium or other two-electron atoms failed, and real progress in understanding atoms had to await the development of quantum mechanics.

2.2.2 Radial Schrödinger equation for central potentials

Stationary solutions of the time dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = H(\mathbf{r}) \psi(\mathbf{r}, t) \quad (2.6)$$

(H is the Hamiltonian operator) can be represented as

$$\psi(\mathbf{r}, t) = e^{-iE_n t/\hbar} \psi_n(\mathbf{r}), \quad (2.7)$$

where n stands for all quantum numbers necessary to label the state. This leads to the time-independent Schrödinger equation

¹There is often confusion about the capitalization of units named after people. The rule is that the unit is spelled lower case, but the abbreviation is upper case. Thus, 2.4 newton, or 2.4 N.

$$[H(\mathbf{r}) - E_n]\psi_n(\mathbf{r}) = \mathbf{0} \quad (2.8)$$

A pervasive application of this equation in atomic physics is for the case of a spherically symmetric one-particle system of mass μ . In this case the Hamiltonian is

$$\begin{aligned} H &\equiv \text{Kinetic Energy} + \text{Potential Energy} \\ &= p^2/2\mu + V(r) = \frac{-\hbar^2 \nabla^2}{2\mu} + V(r) \\ &= -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] + V(r) \end{aligned} \quad (2.9)$$

where the kinetic energy operator ∇^2 has been written in spherical coordinates. Because V is spherically symmetric, the angular dependence of the solution is characteristic of spherically symmetric systems in general and may be factored out:

$$\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi) \quad (2.10)$$

$Y_{\ell m}$ are the *spherical harmonics* and ℓ is the eigenvalue of the operator for the orbital angular momentum, \mathbf{L} ,

$$L^2 Y_{\ell m} = \ell(\ell + 1)\hbar^2 Y_{\ell m} \quad (2.11)$$

and m is the eigenvalue of the projection of L on the quantization axis (which may be chosen at will)

$$L_z Y_{\ell m} = m\hbar Y_{\ell m} \quad (2.12)$$

With this substitution Eq. 2.10 the time independent radial Schrödinger equation becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR_{n\ell}}{dr} \right) + \left[\frac{2\mu}{\hbar^2} [E_{n\ell} - V(r)] - \frac{\ell(\ell + 1)}{r^2} \right] R_{n\ell} = 0 \quad (2.13)$$

This is the equation which is customarily solved for the hydrogen atom's radial wave functions. For most applications (atoms, scattering by a central potential, diatomic molecules) it is more convenient to make a further substitution.

$$R_{n\ell}(r) = y_{n\ell}(r)/r \quad (2.14)$$

which leads to

$$\frac{d^2 y_{n\ell}(r)}{dr^2} + \left[\frac{2\mu}{\hbar^2} [E_{n\ell} - V(r)] - \frac{\ell(\ell + 1)}{r^2} \right] y_{n\ell}(r) = 0 \quad (2.15)$$

with the boundary condition $y_{n\ell}(0) = 0$. This equation is identical with the time independent Schrödinger equation for a particle of mass μ in an effective one dimensional potential,

$$V^{\text{eff}}(r) = V(r) + L^2/(2\mu r^2) = V(r) + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} \quad (2.16)$$

The term $\hbar^2 \ell(\ell + 1)/2\mu r^2$ is called the *centrifugal potential*, and adds to the actual potential the kinetic energy of the circular motion that must be present to conserve angular momentum.

2.2.3 Radial equation for hydrogen

The quantum treatment of hydrogenic atoms or ions appears in many textbooks and we present only a summary². For hydrogen Eq. 2.15 becomes

$$\frac{d^2 y_{n\ell}(r)}{dr^2} + \left[\frac{2\mu}{\hbar^2} \left[E_n + \frac{e^2}{r} \right] - \frac{\ell(\ell+1)}{r^2} \right] y_{n\ell}(r) = 0 \quad (2.17)$$

First look at this as $r \rightarrow 0$, the dominant terms are

$$\frac{d^2 y}{dr^2} - \frac{\ell(\ell+1)}{r^2} y = 0 \quad (2.18)$$

for any value of E . It is easily verified that the two independent solutions are

$$y \sim r^{\ell+1} \text{ and } y \sim r^{-\ell} \quad (2.19)$$

For $\ell \geq 1$ the only normalizable solution is $y \sim r^{\ell+1}$.

Question: What happens to these arguments for $\ell = 0$? What implications does this have for the final solution? Messiah has a good discussion of this.

We look next at the solution for $r \rightarrow \infty$ where we may investigate a simpler equation if $\lim_{r \rightarrow \infty} rV(r) = 0$. For large r :

$$\frac{d^2 y}{dr^2} + \frac{2\mu E}{\hbar^2} y = 0 \quad (2.20)$$

If $E > 0$, this equation has oscillating solutions corresponding to a free particle. For $E < 0$ the equation has exponential solutions, but only the decaying exponential is physically acceptable (i.e.. normalizable)

$$R(r) = y(r)/r = \frac{1}{r} e^{(-2\mu E/\hbar^2)^{\frac{1}{2}} r} \quad (2.21)$$

When $E < 0$, it is possible to obtain physically reasonable solutions to Eq. 2.15 (or indeed *any* bound state problem) only for certain discrete values of E , its eigenvalues. This situation arises from the requirement that the radial solution be normalizable, which requires that $\int_0^\infty y^2(r) dr = 1$, or alternatively, that $y(r)$ vanishes sufficiently rapidly at large r .

Eq. 2.17 is a prescription for generating a function $y(r)$ for arbitrary $E < 0$ given y and dy/dr at any point. This can be solved exactly as hydrogen. For other central potentials, one can find the eigenvalues and eigenstates by computation. One proceeds as follows: Select a trial eigenvalue, $E < 0$. Starting at large r a “solution” of the form of Eq. 2.21 is selected and extended in to some intermediate value of r , r_m . At the origin one must select the solution of the form $y_\ell \sim r^{\ell+1}$ Eq. (2.19); this “solution” is then extended out to r_m . The two “solutions” may be made to have the same value at r_m by multiplying one by a constant; however, the resulting function is a valid solution only if the first derivative is continuous at r_m , and this occurs only for a discrete set of $E_{n\ell}$. The procedure described here is, in fact, the standard Numerov-Cooley algorithm for finding bound states. Its most elegant feature is a procedure for adjusting the trial eigenvalue using the discontinuity in

²The most comprehensive treatment of hydrogen is the classic text of Bethe and Salpeter, *The Quantum Mechanics of One- and Two-Electron Atoms*, H. A. Bethe and E. E. Salpeter, Academic Press (1957). Messiah is also excellent.

the derivative that converges to the correct energy very rapidly.

For the hydrogen atom, the eigenvalues can be determined analytically. The substitution

$$y_\ell(r) = r^{\ell+1} e^{-(2\mu E/\hbar^2)^{1/2} r} v_\ell(r) \quad (2.22)$$

leads to a particularly simple equation. To make it dimensionless, one changes the variable from r to x

$$x = [2(-2\mu E)^{1/2}/\hbar]r \quad (2.23)$$

so the exponential in Eq. 2.22 becomes $e^{-1/2x}$, and defines

$$v = \frac{\hbar}{(-2\mu E)^{1/2} a_o} \quad (2.24)$$

where a_o is the Bohr radius:

$$\left[x \frac{d^2}{dx^2} + (2\ell + 2 - x) \frac{d}{dx} - (\ell + 1 - v) \right] v_\ell = 0 \quad (2.25)$$

This is a Laplace equation and its solution is a confluent hypergeometric series. To find the eigenvalues one now tries a Taylor series

$$v_\ell(x) = 1 + a_1 x + a_2 x^2 + \dots \quad (2.26)$$

for v_ℓ . This satisfies the equation only if the coefficients of each power of x are satisfied, i.e..

$$\begin{aligned} x^0 : & \quad (2\ell + 2)a_1 - (\ell + 1 - v) = 0 \\ x^1 : & \quad 2(2\ell + 3)a_2 - (\ell + 2 - v)a_1 = 0 \\ x^{p-1} : & \quad p(2\ell + 1 + p)a_p - (\ell + p - v)a_{p-1} = 0 \end{aligned} \quad (2.27)$$

The first line fixes a_1 , the second then determines a_2 , and in general

$$a_p = \frac{(\ell + p - v)}{p(2\ell + 1 + p)} a_{p-1} \quad (2.28)$$

In general Eq. 2.27 will give a p^{th} coefficient on the order of $1/p!$ so

$$v_\ell(x) \sim \sum_{p=0} x^p/p! = e^x \quad (2.29)$$

this spells disaster because it means $y = r^{\ell+1} e^{-x/2} v_\ell(r)$ diverges. The only way in which this can be avoided is if the series truncates, i.e. if v is an integer:

$$v = n = n' + \ell + 1 \quad n = 0, 1, 2, \dots \quad (2.30)$$

so that a_n , will be zero and v_ℓ will have n' nodes. Since $n' \geq 0$, it is clear that you must look at energy level $n \geq \ell + 1$ to find a state with angular momentum ℓ (e.g.. the $2d$ configuration does not exist). This gives the eigenvalues of hydrogen (from Eq. 2.24)

$$E_n = -\frac{1}{2} \alpha^2 \mu c^2 / (n' + \ell + 1)^2 = -\frac{1}{2} \frac{\mu (e^2/4\pi\epsilon_o)^2}{\hbar^2} \frac{1}{n^2} = -\frac{hcR_H}{n^2}, \quad (2.31)$$

which agrees with the Bohr formula.

2.3 One Electron Atoms with Cores: The Quantum Defect

2.3.1 Phenomenology

It is observed that the eigenvalues of atoms which have one valence electron have the same density (in energy space) as those of hydrogen, but not the same positions. If one defines an effective quantum number

$$n^* = (R/E_n)^{1/2} \quad (2.32)$$

such that

$$T_n = -\frac{const}{n^{*2}} \quad (2.33)$$

then the formula can naturally reproduce the energy levels of a particular term (e.g. D). However, it was found that the n^* values for adjacent levels differ by almost exactly 1.000, especially after the first few terms. Thus the term energy can be written

$$T_n = -\frac{const}{n^2 - \delta_\ell^2} \quad (2.34)$$

where the *quantum defect* δ_ℓ is defined by

$$\delta_\ell \equiv n - n^*. \quad (2.35)$$

Here, n is the principal quantum number of the valence electron for that term (if one does not know n , using the closest larger integer than n^* still leads to useful results), remains very constant with respect to n , but decreases rapidly with respect to L . A more accurate empirical formula for the term values of a series is the Balmer-Ritz formula

$$T_n = \frac{Z^2 R}{(n - \delta_\ell - \beta_\ell/n^2)^2} \quad (2.36)$$

A somewhat related concept in the study of x-ray lines was proposed by Moseley. When comparing spectra of isoelectronic ions, he found that a useful empirical formula was

$$T_n = \frac{(Z - \Delta Z)^2 R}{n^2} \quad (2.37)$$

in which the charge is adjusted, rather than n . ΔZ may be regarded as the amount of nuclear charge shielded by the core electrons, and an effective nuclear charge, $Z_e = Z - \Delta Z$ can be introduced.

2.3.2 Explanation

It must always be kept in mind that the quantum defect is a phenomenological result. To explain how such a simple result arises is obviously an interesting challenge, but it is not to be expected that the solution of this problem will lead to great new physical insight. The only new results obtained from understanding quantum defects in one electron systems are the connection between the quantum defect and the electron scattering length for the same system (Mott and Massey section III 6.2) which may be used to predict low energy electron scattering cross sections (ibid. XVII 9&10), and the simple expressions relating δ_L to the polarizability of the core for larger δ_L [1]. The principal use of the quantum defect is to predict the positions of higher terms in a series for which δ_L is known.

Explanations of the quantum defect range from the elaborate fully quantal explanation of Seaton [2] to the extremely simple treatment of Parsons and Weisskopf [3], who assume that the electron can not penetrate inside the core at all, but use the boundary condition $R(r_c) = 0$ which requires relabeling the lowest ns state $1s$ since it has no nodes outside the core. This viewpoint has a lot of merit because the exclusion principle and the large kinetic energy of the electron inside the core combine to reduce the amount of time it spends in the core. This is reflected in the true wave function which has n nodes in the core and therefore never has a chance to reach a large amplitude in this region.

To show the physics without much math (or rigor) we turn to the JWKB solution to the radial Schrödinger Equation (see Messiah Ch. VI). Defining the wave number

$$k_\ell(r) = \sqrt{2m[E - V_{\text{eff}}(r)]/\hbar} \quad (\text{remember } V_{\text{eff}} \text{ depends on } \ell) \quad (2.38)$$

then the phase accumulated in the classically allowed region is

$$\phi_\ell(E) = \int_{r_i}^{r_o} k_\ell(r) dr \quad (2.39)$$

where r_i and r_o are the inner and outer turning points. Bound state eigenvalues are found by setting

$$[\phi_\ell(E) - \pi/2] = n\pi \quad (2.40)$$

(The $\pi/2$ comes from the connection formulae and would be $1/4$ for $\ell = 0$ state where $r_i = 0$. Fortunately it cancels out.)

To evaluate $\phi(E)$ for hydrogen use the Bohr formula for $n(E)$,

$$\phi_H(E) = \pi(hcR_H/E)^{1/2} + \pi/2 \quad (\text{independent of } \ell) \quad (2.41)$$

In the spirit of the JWKB approximation, we regard the phase as a continuous function of E . Now consider a one-electron atom with a core of inner shell electrons that lies entirely within r_c . Since it has a hydrogenic potential outside of r_c , its phase can be written (where r_{oH}, r_{iH} are the outer and inner turning points for hydrogen at energy E):

$$\begin{aligned} \phi_\ell(E) &= \int_{r_i}^{r_{oH}} k_\ell(r) dr = \int_{r_i}^{r_c} k_\ell(r) dr + \int_{r_c}^{r_{oH}} k_H(r) dr \\ &= \int_{r_i}^{r_c} k(r) dr - \int_{r_{iH}}^{r_c} k_H(r) dr + \int_{r_{iH}}^{r_{oH}} k_H(r) dr \end{aligned}$$

The final integral is the phase for hydrogen at some energy E , and can be written as $\phi_H(E) = (n^* + 1/2)\pi$. Designating the sum of the first two integrals by the phase $\delta\phi$, then we have

$$\delta\phi + (n^* + 1/2)\pi = (n + 1/2)\pi \quad (2.42)$$

or

$$n^* = n - \delta\phi/\pi \quad (2.43)$$

Hence, we can relate the quantum defect to a phase:

$$\delta_\ell = \left[\int_{r_i}^{r_c} k(r) dr - \int_{r_{iH}}^{r_c} k_H(r) dr \right] \frac{1}{\pi} \quad (2.44)$$

since it is clear from Eq. 2.38 and the fact that the turning point is determined by $E + V_{\text{eff}}(r_i) = 0$ that δ_ℓ approaches a constant as $E \rightarrow 0$.

Now we can find the bound state energies for the atom with a core; starting with Eq. 2.40,

$$\begin{aligned} n\pi &= \phi(E) - \pi/2 \\ &= \pi\delta_L(E) + \pi(hcR_H/E)^{1/2} \\ \Rightarrow E &= hcR_H/[n - \delta_L(E)]^2 \equiv \frac{hcR_H}{[n - \delta_\ell^{(0)} + \delta_\ell^{(1)}hcR_H/n^2]^2} \end{aligned} \quad (2.45)$$

thus we have explained the Balmer-Ritz formula (Eq. 2.36).

If we look at the radial Schrödinger equation for the electron ion core system in the region where $E > 0$ we are dealing with the scattering of an electron by a modified Coulomb potential (Mott & Massey Chapter 3). Intuitively one would expect that there would be an intimate connection between the bound state eigenvalue problem described earlier in this chapter and this scattering problem, especially in the limit $E \rightarrow 0$ (from above and below). Since the quantum defects characterize the bound state problem accurately in this limit one would expect that they should be directly related to the scattering phase shifts $\sigma_\ell(k)$ (k is the momentum of the *free* particle) which obey

$$\lim_{k \rightarrow 0} \cot[\sigma_\ell(k)] = \pi\delta_\ell^o \quad (2.46)$$

This has great intuitive appeal: $\pi\delta_\ell^o$ as discussed above is precisely the phase shift of the wave function with the core present relative to the one with $V = e^2/r$. On second thought Eq. 2.46 might appear puzzling since the scattering phase shift is customarily defined as the shift relative to the one with $V = 0$. The resolution of this paradox lies in the long range nature of the Coulomb interaction; it forces one to redefine the scattering phase shift, $\sigma_\ell(k)$, to be the shift relative to a pure Coulomb potential.

2.3.3 Quantum defects for a model atom

Now we give a calculation of a quantum defect for a potential $V(r)$ which is not physically realistic, but has only the virtue that it is easily solvable. The idea is to put an extra term in the potential which goes as $1/r^2$ so that the radial Schrödinger equation (Eq. 2.15) can be solved simply by adjusting ℓ . The electrostatic potential corresponds to having all the core electrons in a small cloud of size r_n (which is a nuclear size) which decays as an inverse power of r .

$$\begin{aligned} \phi_\ell(r) &= \frac{e}{r} + \frac{(Z-1)er_n}{2r^2} \\ \Rightarrow E(r) &= \frac{e}{r^2} + \frac{(Z-1)er_n}{r^3} \\ \Rightarrow Q_{\text{inside}}(r) &= e + \frac{(Z-1)er_n}{r} \\ \Rightarrow \rho(r) &= \frac{dQ/dr}{4\pi r^2} = -(Z-1)er_n/4\pi r^4 \end{aligned} \quad (2.47)$$

At $r = r_n$, $Q_{\text{inside}}(r_n) = Ze$. We presume r_n is the nuclear size and pretend that it is so small we don't have to worry about what happens inside it.

When the potential $V(r) = -e\phi(r)$ is substituted in Eq. 2.17, one has

$$\frac{d^2y}{dr^2} + \left[\frac{2\mu}{\hbar^2} \left[E_n + \frac{e^2}{r} \right] - \frac{\ell(\ell+1) - A}{r^2} \right] y = 0 \quad (2.48)$$

$$\text{where } A = \frac{2\mu(Z-1)e^2r_n}{\hbar^2} \quad (2.49)$$

If one now defines

$$\ell'(\ell'+1) = \ell(\ell+1) - A \quad (2.50)$$

then $\ell' < \ell$ since $A > 0$, and one can write

$$\ell' = \ell - \delta_\ell \quad (2.51)$$

Substituting Eq. 2.50 in Eq. 2.48 gives the radial Schrödinger equation for hydrogen, (Eq.2.15), except that ℓ' replaces ℓ ; eigenvalues occur when (see Eq. 2.30)

$$v = n' + \ell' + 1 = n^* \quad n' = 0, 1, 2, \dots \quad (2.52)$$

where n' is an integer. Using $n = n' + \ell + 1$ as before, we obtain the corresponding eigenvalues as

$$E_n = hcR_H/n^{*2} = hcR_H/(n - \delta_\ell)^2 \quad (2.53)$$

The quantum defect is independent of E

$$\delta_\ell = \ell - \ell' = n - n^* \quad (2.54)$$

Eq. 2.50 may be solved for δ_ℓ using the standard quadratic form. Retaining the solution which $\rightarrow 0$ as $Z \rightarrow 1$, gives

$$\delta_\ell = (\ell + 1/2) - \sqrt{(\ell + 1/2)^2 - A} \approx \frac{A}{2\ell + 1} \text{ for } A \ll \ell + 1/2 \quad (2.55)$$

This shows that $\delta_\ell \rightarrow 0$ as $\ell \rightarrow \infty$.

In contrast to the predictions of the above simple model, quantum defects for realistic core potentials decrease much more rapidly with increasing ℓ [for example as $(\ell + 1/2)^{-3}$] and generally exhibit $\delta_\ell^{(0)}$ close to zero for all ℓ greater than the largest ℓ value occupied by electrons in the core.

2.4 Metrology and Precision Measurement and Units

As scientists we take the normal human desire to understand the world to quantitative extremes. We demand agreement of theory and experiment to the greatest accuracy possible. We measure quantities way beyond the current level of theoretical understanding in the hope that this measurement will be valuable as a reference point or that the difference between our value and some other nearly equal or simply related quantity will be important. The science of measurement, called metrology, is indispensable to this endeavor because the accuracy of measurement limits the accuracy of experiments and their inter-comparison. In fact, the construction, intercomparison, and maintenance of a system of units is really an art (with some, a passion), often dependent on the latest advances in the

art of physics (e.g.. quantized Hall effect, cold atoms, trapped particle frequency standards).

As a result of this passion, metrological precision typically marches forward a good fraction of an order of magnitude per decade. Importantly, measurements of the same quantity (e.g. α or e/h) in different fields of physics (e.g.. atomic structure, QED, and solid state) provide one of the few cross-disciplinary checks available in a world of increasing specialization. Precise null experiments frequently rule out alternative theories, or set limits on present ones. Examples include tests of local Lorentz invariance, and the equivalence principle, searches for atomic lines forbidden by the exclusion principle, searches for electric dipole moments (which violate time reversal invariance), and the recent searches for a “fifth [gravitational] force”.

A big payoff, often involving new physics, sometimes comes from attempts to achieve routine progress. In the past, activities like further splitting of the line, increased precision and trying to understand residual noise have lead to the fine and hyperfine structure of H , anomalous Zeeman effect, Lamb shift, and the discovery of the 3K background radiation. One hopes that the future will bring similar surprises. Thus, we see that precision experiments, especially involving fundamental constants or metrology not only solidify the foundations of physical measurement and theories, but occasionally open new frontiers.

This chapter deals briefly with SI units (and its ancestor, the mks system), then systems of units which might appear more natural to a physicist, and then introduces atomic units, which will be used in this course.

2.4.1 Dimensions and Dimensional Analysis

Oldtimers were brought up on the mks system - meter, kilogram, and second. This simple designation emphasized an important fact: three dimensionally independent units are sufficient to span the space of all physical quantities. The dimensions are respectively ℓ - length, m -mass, and t -time. These three dimensions suffice because when a new physical quantity is discovered (e.g.. charge, force) it always obeys an equation which permits its definition in terms of m,k, and s. Some might argue that fewer dimensions are necessary (e.g.. that time and distance are the same physical quantity since they transform into each other in moving reference frames); we’ll keep them both, noting that the definition of length is now based on the speed of light. Practical systems of units have additional units beyond those for the three dimensions, and often additional “as defined” units for the same dimensional quantity in special regimes (e.g.. x-ray wavelengths or atomic masses).

Dimensional analysis consists simply in determining for each quantity its dimension along the three dimensions (seven if you use the SI system rigorously) of the form

$$\text{Dimension } (G) = [G] = m^{-1}l^3t^{-2}, \text{ where } [x] \equiv \text{dimensions of } x.$$

Dimensional analysis yields an estimate for a given unknown quantity by combining the known quantities so that the dimension of the combination equals the dimension of the desired unknown. The art of dimensional analysis consists in knowing whether the wavelength or height of the water wave (both with dimension l) is the length to be combined with

the density of water and the local gravitational acceleration to predict the speed of the wave.

2.4.2 SI units

A single measurement of a physical quantity, by itself, never provides information about the physical world, but only about the size of the apparatus or the units used. In order for a single measurement to be significant, some other experiment or experiments must have been done to measure these “calibration” quantities. Often these have been done at an accuracy far exceeding our single measurement so we don’t have to think twice about them. For example, if we measure the frequency of a rotational transition in a molecule to six digits, we have hardly to worry about the calibration of the frequency generator if it is a high accuracy model that is good to nine digits. And if we are concerned we can calibrate it with an accuracy of several more orders of magnitude against station WWV or GPS satellites which give time valid to 20 ns or so.

Time/frequency is currently the most accurately measurable physical quantity and it is relatively easy to measure to 10^{-12} . In the SI (System International, the agreed-upon systems of weights and measures) the second is defined as 9,192,631,770 periods of the Cs hyperfine oscillation in zero magnetic field. Superb Cs beam machines at places like NIST-Boulder provide a realization of this definition at about 10^{-14} . Frequency standards based on laser-cooled atoms and ions have the potential to do several orders of magnitude better owing to the longer possible measurement times and the reduction of Doppler frequency shifts. To give you an idea of the challenges inherent in reaching this level of precision, if you connect a 10 meter coaxial cable to a frequency source good at the 10^{-16} level, the frequency coming out the far end in a typical lab will be an order of magnitude less stable - can you figure out why?

The meter was defined at the first General Conference on Weights and Measures in 1889 as the distance between two scratches on a platinum-iridium bar when it was at a particular temperature (and pressure). Later it was defined more democratically, reliably, and reproducibly in terms of the wavelength of a certain orange krypton line. Most recently it has been defined as the distance light travels in $1/299,792,458$ of a second. This effectively defines the speed of light, but highlights the distinction between defining and realizing a particular unit. Must you set up a speed of light experiment any time you want to measure length? No: just measure it in terms of the wavelength of a He-Ne laser stabilized on a particular hfs component of a particular methane line within its tuning range; the frequency of this line has been measured to about a part in 10^{-11} and it may seem that your problem is solved. Unfortunately the reproducibility of the locked frequency and problems with diffraction in your measurement both limit length measurements at about 10^{-11} .

A list of spectral lines whose frequency is known to better than 10^{-9} is given in Appendix II of the NIST special publication #330, available on the www at³ - see both publications and reference data. The latest revision of the fundamental constant CODATA98 published as a NIST publication by Cohen and Taylor in 2000⁴ or in Rev. Mod. Phys. Vol. 72, No. 2 2000.

³<http://physics.nist.gov/Pubs/SP330/cover.html>

⁴<http://physics.nist.gov/cuu/Constants/index.html>

The third basic unit of the SI system is kilogram, the only fundamental SI base unit still defined in terms of an artifact - in this case a platinum-iridium cylinder kept in clean air at the Bureau de Poids et Mesures in Sevres, France. The dangers of mass change due to cleaning, contamination, handling, or accident are so perilous that this cylinder has been compared with the dozen secondary standards that reside in the various national measurement laboratories only two times in the last century. Clearly one of the major challenges for metrology is replacement of the artifact kilogram with an atomic definition. This could be done analogously with the definition of length by defining Avogadro's number. While atomic mass can be measured to 10^{-11} , there is currently no sufficiently accurate method of realizing this definition, however. (The unit of atomic mass, designated by μ is 1/12 the mass of a ^{12}C atom.)

There are four more base units in the SI system - the ampere, kelvin, mole, and the candela - for a total of seven. While three are sufficient (or more than sufficient) to do physics, the other four reflect the current situation that electrical quantities, atomic mass, temperature, and luminous intensity can be and are regularly measured with respect to auxiliary standards at levels of accuracy greater than that with which can be expressed in terms of the above three base units. Thus measurements of Avogadro's constant, the Boltzmann constant, or the mechanical equivalents of electrical units play a role of inter-relating the base units of mole (number of atoms of ^{12}C in 0.012 kg of ^{12}C), kelvin, or the new de facto volt and ohm (defined in terms of Josephson and quantized Hall effects respectively). In fact independent measurement systems exist for other quantities such as x-ray wavelength (using diffraction from calcite or other standard crystals), but these other de facto measurement scales are not formally sanctified by the SI system.

2.4.3 Metrology

The preceding discussion gives a rough idea of the definitions and realizations of SI units, and some of the problems that arise in trying to define a unit for some physics quantity (e.g., mass) that will work across many orders of magnitudes. However, it sidesteps questions of the border between metrology and precision measurements. (Here we have used the phrase "precision measurement" colloquially to indicate an accurate absolute measurement; if we were verbally precise, precision would imply only excellent relative accuracy.)

It is clear that if we perform an experiment to measure Boltzmann's constant we are not learning any fundamental physics; we are just measuring the ratio of energy scales defined by our arbitrary definitions of the first three base units on the one hand and the thermal energy of the triple point of water on the other. This is clearly a metrological experiment. Similarly, measuring the hfs frequency of Cs would be a metrological experiment in that it would only determine the length of the second.

If we measure the hfs frequency of H with high accuracy, this might seem like a physics experiment since this frequency can be predicted theoretically. Unfortunately theory runs out of gas at about 10^{-6} due to lack of accurate knowledge about the structure of the proton (which causes a 42 ppm shift). Any digits past this are just data collection until one gets to the 14th, at which point one becomes able to use a H maser as a secondary time standard. This has stability advantages over Cs beams for time periods ranging from seconds to days

and so might be metrologically useful – in fact, it is widely used in very long baseline radio astronomy.

One might ask “Why use arbitrarily defined base units when Nature has given us quantized quantities already?” Angular momentum and charge are quantized in simple multiples of \hbar and e , and mass is quantized also although not so simply. We then might define these as the three main base units - who says we have to use mass, length and time? Unfortunately the measurements of e , \hbar , and N_A^{-1} (which may be thought of as the mass quantum in grams) are only accurate at about the 10^{-8} level, well below the accuracy of the realization of the current base units of SI.

The preceding discussion seems to imply that measurements of fundamental constants like e , \hbar , and N_A^{-1} are merely determinations of the size of SI units in terms of the quanta of Nature. In reality, the actual state of affairs in the field of fundamental constants is much more complicated. The complication arises because there are not single accurate experiments that determine these quantities - real experiments generally determine some combination of these, perhaps with some other calibration type variables thrown in (e.g., the lattice spacing of Si crystals).

To illustrate this, consider measurement of the Rydberg constant,

$$Ry_\infty = \frac{m_e e^4}{(4\pi)^3 \epsilon_0^2 \hbar^3 c} \quad (2.56)$$

a quantity which is an inverse length (an energy divided by $\hbar c$), closely related to the number of wavelengths per cm of light emitted by a H atom (the units are often given in spectroscopists' units, cm^{-1} , to the dismay of SI purists). Clearly such a measurement determines a linear combination of the desired fundamental quantities. Too bad, because it has recently been measured by several labs with results that agree to 10^{-11} . (In fact, the quantity that is measured is the Rydberg *frequency* for hydrogen, cRy_H , since there is no way to measure wavelength to such precision.) This example illustrates a fact of life of precision experiments: with care you can trust the latest adjustment of the fundamental constants and the metrological realizations of physical quantities at accuracies to 10^{-7} ; beyond that the limit on your measurement may well be partly metrological. In that case, what you measure is not in general clearly related to one single fundamental constant or metrological quantity. The results of your experiment will then be incorporated into the least squares adjustment of the fundamental constants, and the importance of your experiment is determined by the size of its error bar relative to the uncertainty of all other knowledge about the particular linear combination of fundamental and metrological variables that you have measured.

2.5 Universal Units and Fundamental Constants

The sizes of the meter, kilogram and second were originally selected for convenience. They bear no relationship to things which most physicists would regard as universal or fundamental. Given the arbitrary nature of SI units, physicists generally prefer to use systems of units that are natural for the problem at hand. We will now discuss Planck units, which seem most universal, and Atomic units fulfill this role when discussing atoms and their

interactions with light. But let us start at the beginning by considering “are some of the 42 fundamental constants listed by Ref. [4] more fundamental or universal?”

To begin, we assert that the three most universal constants are:

- c - the speed of light
- \hbar - the quantum of action
- G - the gravitational constant

These quantities involve light, the quantum and gravitation. Since \hbar can be found from measurements on light, these constants do not depend on the existence of quantized matter (only quantized radiation).

Next, we come to the atomic constants, whose magnitude is determined by the size of the quantized matter which we find all around us. Clearly, the most fundamental of these is:

e - the quantum of charge.

because it is the same (except for the sign) for all particles.

Even though the existence of quantized charge seems independent of the physics which underlies the construction of universal units, this is probably not the case because charge does not have independent units. In fact, the fine structure constant

$$\alpha \equiv \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} = (137.036 \dots)^{-1} \quad (2.57)$$

is arguably the only fundamental constant truly worthy of that name in atomic physics. High energy physicists regard α as the not so fundamental coupling strength of the electromagnetic interaction – At higher energies and correspondingly smaller distances, it gets larger as we approach the “bare charge” more closely. When we really understand E&M, QED, and the origins of quantized matter, we should be able to predict it. The fact that we have to measure it is a sign of our ignorance, but the good agreement of the many seemingly independent ways of measuring it in different subfields of physics shows that we begin to understand some things.

Other atomic constants like masses (m_e, m_p, m_n, \dots) and magnetic moments (u_e, u_p, u_n) seem to be rather arbitrary at our current level of physical knowledge except that certain relationships are given by QED ($\mu_e = g_e e \hbar / (2m)$ with g_e a little more than 2) and quark models of the nucleons.

2.6 Atomic Units

Formulae in these notes will be displayed with the factors of \hbar, e, m (m is the electron mass) etc., factored into atomic units to facilitate interpretation; numerical evaluations may be done using either atomic units or Gaussian-esu units. The system of atomic units (a.u.) is defined by setting $\hbar = m = e = 1$. Units for other physical quantities are formed by dimensionally suitable combinations of these units. When their use is frequent, they are given names (analogous to erg, dyne, etc., in cgs). In atomic units, the units of length and energy are the most important - they are called the Bohr (a_0) and Hartree (H) respectively.

Quantity	Symbol	Value	Name
*charge	e	$1.6 \times 10^{-19} C$	
*angular Momentum	\hbar	$1.05 \times 10^{-34} J s$	
*mass	m	$0.910 \times 10^{-31} kg$	
length	a_o	$\hbar^2/m(e^2/4\pi\epsilon_o)^2 = 0.53 \times 10^{-11} m$	bohr
energy	H	$m(e^2/4\pi\epsilon_o)^2/\hbar^2 = 4.36 \times 10^{-18} J$ $\Rightarrow 27.2 eV \Rightarrow 2 Ry = 2.2 \times 10^7 m^{-1}$	hartree
time	-	$\hbar^3/m(e^2/4\pi\epsilon_o)^2 = 2.42 \times 10^{-17} s$	
velocity	-	$(e^2/4\pi\epsilon_o)/\hbar = \alpha_c = 2.2 \times 10^6 m/s$	
magnetic moment	μ_B	$e\hbar/2m = 1.4 \times 10^4 MHz T^{-1}$	Bohr magneton
electric field	-	$e/a_o^2 = 5.14 \times 10^{11} V/m$	

*Charge, Angular Momentum and Mass are the *Basic Units*

expressions for energy and length can generally be expressed in terms of H or a_o and powers of the dimensionless constant α

2.7 The Fine Structure Constant

$$\alpha = \frac{e^2}{4\pi\epsilon_o\hbar c} = (137.0606 \dots)^{-1} \quad (2.58)$$

is ubiquitous in atomic physics. The name, fine structure, reflects the appearance of this quantity (squared) in the ratio of the hydrogenic fine structure splitting to the Rydberg:

$$\frac{\Delta(\text{fine structure})}{\text{Rydberg}} = \alpha^2 \frac{Z^4}{n^3 \ell(\ell + 1)} \quad (2.59)$$

The fine structure constant will often crop up as the ratio between different physical quantities having the same dimensions. An impressive example of this is length: the “hydrogen wavelength” (1/Rydberg), Bohr radius, Compton wavelength, and classical radius of the electron are all related by powers of α .

References for Chapter 2

- [1] R.R. Freeman and D. Kleppner, Phys. Rev. A. (1967).
- [2] M.J. Seaton, Proc. Phys. Soc. **88**, 801 (1966).
- [3] R.G. Parsons and V.F. Weisskopf, Z. Phys. **202**, 492 (1967).
- [4] E.R. Cohen and B.N. Taylor, Rev. Mod. Phys. **72**, No. 2 (2000).