Contents

Preface xi
List of physical constants and useful interrelations xiii

1 Introduction 1
   1.1 Atomic physics is more than quantum mechanics 1
   1.2 Trajectories versus probabilities 2
   1.3 Semiempirical parametrization 5

2 Semiclassical conceptual models 6
   2.1 Classical position probability densities for periodic systems 6
   2.2 Quantum mechanical oscillation of the localizability 7
   2.3 Einstein–Brillouin–Keller quantization 8
   2.4 The Kepler problem 11
   2.5 Semiclassical formulation of the decay meanlife 37

3 Semiempirical parametrization of energy-level data 42
   3.1 Historical development 42
   3.2 Description of complex atoms by two-body collective modes 44
   3.3 The Rydberg formula and the Ritz parametrization 47
   3.4 The core polarization model 54
   3.5 Screening parametrizations 58
   3.6 Screening parametrization of the fine structure 61
   3.7 Screening parametrization of transition rates 67

4 The vector model of angular momentum 72
   4.1 The Schrödinger approximation 72
   4.2 The intrinsic angular momentum and magnetic moment of the electron 73
   4.3 The Pauli spin matrices 74
   4.4 Internal magnetic fields 76
   4.5 Coupling approximations 77
   4.6 Quantum mechanical vector coupling of angular momenta 79
   4.7 The connection between spin and statistics 80
Contents

4.8 The Landé interval rule 81
4.9 External magnetic fields 82

5 The intermediate coupling model 90
5.1 Spectroscopic notation 90
5.2 Two-valence-electron systems 92
5.3 Screening parametrizations of Slater parameters 107
5.4 Systems with three or more valence electrons 109
5.5 Antisymmetrization of a multielectron system 112

6 Electric dipole radiation 113
6.1 Hierarchies in transition arrays 114
6.2 Ab initio calculations 120
6.3 Commutation relations involving the E1 transition moment 123
6.4 Quadratic Stark effect and atomic polarizability 125
6.5 Core polarization contributions to the E1 transition moment 129
6.6 Cancellation 131

7 Line strengths in two-valence-electron systems 138
7.1 Relativistic E1 transitions 138
7.2 jj-based reformulation 155
7.3 Gyromagnetic ratios in intermediate coupling 161

8 Magnetic dipole transitions 164
8.1 M1 transitions 164
8.2 M1 line strengths 165

9 Absorption of radiation 179
9.1 Driven damped harmonic oscillator 180
9.2 Doppler broadening 182
9.3 Comparison of the Lorentzian and Gaussian functions 183
9.4 Convolutions of lineshape functions 184
9.5 Equivalent width 187
9.6 Atomic derivation of the Planck radiation law 191

10 Time-resolved measurements 194
10.1 Time dependence of measured decay curves 195
10.2 Adjusted normalization of decay curve (ANDC) method 200
10.3 Differential lifetime measurements 202
10.4 Hanle effect 205

11 Hyperfine structure 207
11.1 The origins of hyperfine structure observations 207
11.2 Magnetic dipole moment of the nucleus 208
11.3 Electric quadrupole moment of the nucleus 213
11.4 Example: hyperfine splitting of the 4p term in $^{23}\text{Na}$ 215
Contents

11.5 Isotope shifts 215
11.6 Hyperfine quenching 218

12 Electrostatic polarizabilities and long-range interactions 220
12.1 Rayleigh–Schrödinger perturbation theory 220
12.2 The Dalgarno–Lewis operator 222
12.3 Application: ground-state polarizabilities 223
12.4 Nonadiabatic correlations 228
12.5 Casimir–Polder retardation corrections 229
12.6 Quadratic Stark effect 230
12.7 Indices of refraction for inert gases 231

13 Coherence and anisotropic excitation 234
13.1 Density matrix representation 234
13.2 Stokes parameters 238
13.3 Application to a measurement of elliptic polarization 243
13.4 Alignment and orientation 246
13.5 Quantum-beat spectroscopy 248
13.6 Level crossing and optical double resonance spectroscopy 251

References 252
Index 261
If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would convey the most information in the fewest words? I believe it is the atomic hypothesis (or the atomic fact) that all things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.

– Richard P. Feynman [97]

1.1 Atomic physics is more than quantum mechanics

With the stirring testimonial above [97] from one of the foremost scientific minds of our time, why is it that the subject of atomic structure is relegated to a chapter near the end of most elementary physics textbooks? Introductory physics texts tend to discuss gravitational interactions extensively, yet most of the examples treated are atomic in nature. Since “weightlessness” occurs when there is no floor to provide atomic charge polarizations to oppose a gravitational attraction, weight must be considered an atomic phenomenon. Barring the remote possibility of experiencing the huge gravitational gradients predicted near a black hole, no one is ever directly injured by a gravitational force, but rather by the atomic polarization that ultimately opposes it. Why is so important a topic as atomic physics not given an early and thorough conceptual presentation?

Part of the answer to this question lies in discovery-oriented pedagogic tendencies. Scientific facts are deemed inextricable from scientific inquiry. The facts are taught in the order that they were discovered, in the context of those experiments that sorted out the valid concepts from among the misconceptions (which, unfortunately, requires programmatic obfuscation to make the misconceptions seem initially plausible). Thus, the first course in physics deals with 18th-century mechanics, and the second course deals with 19th-century electromagnetics. If time permits there is an addendum describing how the gross mistakes that were made in the 18th and 19th centuries were corrected at the beginning of the 20th century. Unfortunately, the accidents of history have trapped subjects such as the relativistic origin of the magnetic field, the nature of continuum thermal radiation, photovoltaics, and atomic physics firmly in the back of the book.
However, an even larger part of the problem lies in the widely held perception that these “modern” topics require a quantitative knowledge of quantum mechanics, and this is thought to exceed the mathematical prerequisites for an elementary course. These pedagogic practices are now being questioned, and many physics educators are asking their colleagues “Is physics just an application of mathematics, or is there more to it?” Since Newton studied physics first, and this later motivated him to invent calculus, perhaps an early detailed conceptual study of atomic physics could provide the motivation for a subsequent rigorous mathematical study of quantum theory.

Because the study of atomic spectroscopy provided much of the impetus for the development of quantum mechanics, most textbooks on quantum mechanics include extensive examples drawn from the field of atomic physics. However, this does not imply that a textbook on atomic structure should contain within it a course in quantum mechanics. Many of the examples drawn from atomic physics that are most suitable for a quantum mechanics course involve the hydrogen atom, which is a special case not particularly well-suited for illustrating the structure of complex atoms. While quantum mechanical theory is an essential part of the study of atomic structure, there are many other important aspects of this subject that can be concealed by an overemphasis on the details of the quantum mechanical formulation.

Historically, one of the most appealing models for the formulation of mechanics was the motion of the planets as observed through their illumination by light from the Sun. Since the energy of optical photons is very small compared to the mass energy of a planet, these observations are very nearly passive. Thus the positions, speeds, and accelerations of the planets can be followed instantaneously, without being altered by the act of observation. The convenience of this characterization is in sharp contrast to examples (such as an electron illuminated by an x-ray photon) in which the energy of the probe is much greater than the mass energy of the object observed, and the act of observation removes that particular object from further consideration.

Thus, one of the strongest motivations for embedding the study of atomic physics inside a rigorous quantum mechanical presentation has little to do with quantization, but has everything to do with its formulation in terms of position probability densities rather than forces. Since planets can be observed passively with photons and electrons cannot, we pedagogically isolate the electrons in the 20th century instead of updating the archaic 17th-century formulation of the planetary Kepler problem to one of position probability densities. Overcoming this historical bias is one of the goals of this book.

### 1.2 Trajectories versus probabilities

The various pedagogic formulations of physics are often characterized as either “classical” or “quantum mechanical.” Most of the differences between these presentations arise not from quantum mechanical or correspondence limit requirements, but rather from a nonessential heuristic tendency to treat macroscopic systems by instantaneous quantities and microscopic systems by time-averaged expectation values. In many cases modern theoretical developments now indicate that the historical assumptions that led to these characterizations may
have been ill-founded, and they sometimes unnecessarily fragment physical concepts. A mathematically simple, pedagogically transparent approach will be presented here that uses position probability densities to describe both macroscopic and microscopic systems. This approach will be applied to a number of familiar examples, sometimes with surprising results.

This observational bias led to many misconceptions that required centuries to correct. For example, classical probabilistic formulations were inhibited by the doctrine of Laplacian determinism. In 1776 Pierre Simon Laplace asserted [105] that “The present state of the system of nature is evidently a consequence of the preceding moment, and if we conceive an intelligence that at a given instant comprehends all the relations of the entities of this universe, it could state the respective positions, motions and general effects at any time in the past or future. . . . So it is that we owe to the weakness of the human mind one of the most delicate and ingenious of mathematical theories, the science of chance or probability.” The inherent fallacy of this view was emphasized in 1903 by Henri Poincaré in his statement [165] that “It may happen that small differences in the initial conditions produce very great ones in the final phenomena – prediction then becomes impossible.” In 1887 Poincaré had entered a contest sponsored by the King of Sweden that contained a challenge to show rigorously that the solar system is dynamically stable. It at first appeared that Poincaré had succeeded, but an error was found. Poincaré’s correction of that error is generally regarded as the birth of chaos theory. This indicates the limitations of the linearized approximations that were considered by Laplace. The development of quantum mechanics in 1924 with its inherent Heisenberg uncertainty principle showed clearly that there is a fundamental limitation on the accuracy to which position and velocity can be measured simultaneously. Even when applied to macroscopic systems, modern considerations of quantum gravity indicate that space and time themselves break down for very short distances.

Laplace himself did not seem completely comfortable with Laplacian determinism. A recurring theme of Laplace’s work was his lifelong tendency to couple the sciences of probability and astronomy. Consistent with the spirit of Laplacian determinism, probability was viewed by him as a means of repairing the defects in knowledge. However, there are tantalizing passages scattered throughout his writings [105] that suggest that he may have had an inkling (or perhaps a repressed belief) that there are inherently random processes in nature that are not merely the result of our ignorance.

One aspect of his work in which Laplace may have “pried open the first chink in the armor of deterministic physics” was his application of probability to demography and actuarial determination. This inspired his Belgian pupil Adolphe Quetelet to formulate the study of “Staatswissenschaft,” which was the forerunner of the modern statistical social sciences. Quetelet’s work [166] was heralded as a cure for societal ills, and was championed by the social reformer Florence Nightingale. This subsequently led James Clerk Maxwell, through his reading of an 1850 essay on Quetelet’s work written [120] by John Herschel, to adopt a strategy using Laplace’s law of errors as a basis for his kinetic theory of gases. Maxwell’s formulation of statistical mechanics marked a turning point in physics, since it presupposed the operation of chance in nature [105]. Thus, contrary to popular belief, the “exact sciences” here borrowed from the methods of the “social sciences” and not vice versa.
Fig. 1.1. Lorentzian scatter for a hypothetical doublet transition. The line spacing is twenty times the natural line width, and statistical sample sizes are chosen to be characteristic of various fields of inquiry.

Stripped of the mantle of Laplacian determinism, the differences between the “hard” physical sciences and the “softer” social sciences are largely reduced to a question of available statistical sample sizes. This is illustrated metaphorically in Fig. 1.1. Here a simulation is made of a hypothetical doublet transition, in which the line spacing is set at twenty times the natural line width, and the number of photon counts is chosen to match the sample size available in various fields of scientific inquiry. The spread of points was generated using an inverse Lorentzian function of a probability obtained from a random number generator. The plot labeled “Experimental Physics” includes 10,000 counts which is typical of many experiments at the forefront of a field. The plot labeled “Social Sciences” includes 1,000 counts, which is the standard sample size used to obtain 3% statistical accuracy in survey research studies. The plot labeled “Observational Astronomy” includes 100 points, and is modeled on a field such as stellar atmospheres. Since the number of known stars is only about 1% of the number of atoms in a gram molecular weight, when a sample of stars is selected that exhibits a desired feature and otherwise has more likenesses than differences, the sample size is often quite small. In the plot labeled “Quantum Theory,” only the positions of the two line centers are indicated. The Schrödinger equation yields the energies of the time-independent stationary states, but their radiative decay and their Lorentzian spread require the invocation of the Weisskopf–Wigner approximation. It seems clear that the probabilistic formulation provides a universally applicable technique, which a conceptual reliance on instantaneous motions only tends to fragment.

Even during the time of Laplace, position probability densities were actually (albeit unconsciously) favored over instantaneous positions and velocities in the specification of planetary interactions. Laplace, Gauss, and others calculated the perturbations of the planets by considering the time-averaged loci of their orbits smeared as rings around the Sun, as one automatically assumes when representing them in a Legendre polynomial expansion.
1.3 Semiempirical parametrization

Atomic physics has many different facets. It can be used to test fundamental theory to levels of accuracy that exceed those attainable in virtually any other field. It is also an enabling science, that provides measured structural constants that are essential to, e.g., the interpretation of observations, the design of new types of devices, and the modeling of physical processes. Without dismissing the importance of fundamental quantum mechanical theory, it is not the optimal starting point for all processes that it ultimately governs. The construction of a building is also governed by the laws of quantum mechanics, but the architect must be more concerned with the measured values for Young’s modulus than with any theoretical predictions for that quantity that can be obtained from \textit{ab initio} solution of the Schrödinger equation. Similarly, in many applications involving complex atoms, either direct measurements or semiempirical determinations are essential to obtaining the required precision.

While the development of quantum mechanics provided a thorough understanding of the underlying basis of atomic physics, with a few exceptions the accuracy of \textit{ab initio} quantum mechanical methods lag far behind experimental capabilities for atoms more complex than hydrogen and helium. Spectroscopic accuracies are often of the order of parts in $10^8$ or better, and theoretical calculations can at best provide a planning guide to definitive experimental measurements. Needed values for energy levels, transition wavelengths, ionization potentials, polarizabilities, fine and hyperfine structure splittings, transition probabilities, level lifetimes, etc., can be determined experimentally for complex atoms more precisely than they can be specified using the best currently available theoretical methods.

Thus, as the experimental methods have continued to improve, many of the semiempirical techniques used prior to the development of quantum mechanics are still in active use. Methods such as the quantum defect formulation of Rydberg series, the fine structure screening parametrization of Sommerfeld, etc., have been greatly refined, and their application can be understood in terms of simple conceptual models. While it is sometimes asserted that quantum mechanics has made conceptual models obsolete, the rejection of a simpler model because a more fundamental approach exists can be extended to a \textit{reductio ad absurdum}. One can reject conceptual models and adopt the Schrödinger approach, but the nonrelativistic scalar nature of this formulation separates spin from space. This leads to a radial wave function that is independent of the total angular momentum, which is of course physically wrong. One could reject the Schrödinger model and adopt the Dirac approach, but this is a single-electron theory that includes the electron’s own spin, but relegates spin–spin and spin–other-orbit to perturbative inclusion, and does not include second quantization. Nonetheless, just as the Dirac equation offers some conceptual insights over a “sea” of Feynman diagrams and the Schrödinger picture provides advantages over the Dirac equation in the inclusion of configuration interaction and correlation, the Einstein–Brillouin–Keller semiclassical quantization can provide some very useful insights into various aspects of the quantum mechanical structure of the atom.