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Introduction

The great end of life is not knowledge but action.

– T. H. Huxley

1.1 Different Is Usually Controversial

Perhaps all breakthroughs in science are initially clouded with controversies. Consider the discovery of gravity. Isaac Newton invoked the concept of “action at a distance” when he developed his theory of gravity. Action at distance couples the motion of objects; yet, the objects possess no clear physical connection. Newton argued that the motion of an apple falling from a tree was similar to the motion of the moon falling toward (and fortunately missing) the earth. The source of the motion of both objects is consistent with an “action at a distance” caused by the presence of the earth and its gravitational field.

We can contrast the trajectory of the moon with a simpler object such as a golf ball. It is easy to understand that a golfer can make the ball move by striking it. A ball struck just right will carry hundreds of yards (or meters). Residents of Newton’s time would be comfortable with this idea. The golf club directly contacts the ball, albeit for a very short time. The physical connection to the ball is the club swung by the golfer. But how can the earth change the moon’s trajectory? The earth does not carry a big golf club to strike the moon. While the action at a distance theory may not be apparent to a lay person, or even a good scientist in Newton’s time, the laws of gravity predicted the behavior of astronomical bodies such as the moon’s orbit incredibly well. Hardly anyone would argue that we ignore the practical application of Newton’s theory until someone resolved this action at distance business. For years, scientists argued the meaning of “action at distance” and the nature of space itself. Eventually, scientists agreed that the concept of Newtonian space was problematic. It was left to Einstein to straighten out issues of space, time, and gravity. In some sense, it hardly mattered if you wanted to predict planetary motion. A practical application of Newton’s theory accomplished that really well, save some relatively minor fixes from Einstein. (We are not going to worry about issues such as worm holes or gravity waves.)

Perhaps one should view the theory of quantum mechanics in the same manner. The theory remains “mysterious” in some ways. Oddly, some of the central components of the theory are understandable only because we can think about them in classical terms. Still, quantum theory can be used to predict properties of matter with unprecedented accuracy. Upon the invention of quantum mechanics, the famous physicist Dirac wrote the following [1]:

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems with out much computation ...

Dirac’s quote of nearly a century ago is correct and appropriate. In principle, the underlying physical laws (of quantum mechanics) should allow one to predict “much of physics” (condensed matter physics as an example) and “the whole of chemistry.” What stands in our way is a practical machinery to accomplish this task. Computational physicists often refer to this task as addressing *Dirac’s Challenge*.

Dirac’s warning about avoiding “too much computation” is an anachronism. Dirac’s world of 1929 did not envision a computer capable of carrying out billions or trillions of mathematical operations within a second. When we contemplate the use of a modest computer, such as a laptop, for the work outlined in this book, it is indeed “without too much computation.”

1.2 The Plan: Addressing Dirac’s Challenge

Dirac’s challenge for us is to develop “approximate practical methods of applying quantum mechanics.” The goal of this book is to address, or better start to address, *the* challenge.

The book is roughly divided into three parts. The first part will focus on the theory. We will use a minimum of theory to get to the “good part.” Our intent is not to write a quantum mechanics textbook. Rather, our intent in this part of the book is to review essential features. For example, we will consider the simplest of all atoms, hydrogen, and we will start with the simplest of theories from Bohr. We will then introduce the Schrödinger equation and briefly sketch out how to solve the hydrogen atom problem analytically.

The hydrogen atom is one of the rarest of quantum systems – one where we can do an analytical solution of the Schrödinger equation. The next several chapters will involve introducing the *real* problem, one with more than a single electron. A clear example of such a system is helium, where we have two electrons. Our study of the helium atom will lead us to consider the Hartree and Hartree–Fock

approximations. Our next objective will be to consider a practical method for more than one or two electrons. A practical theory for this is based on “density functional theory,” which focuses on how electrons are distributed in space.

A logical pathway to take us from Hartree–Fock theory to density functional theory arises from a “free electron” model. We introduce this model using concepts removed from the physics of an isolated atom. We will “backtrack” in our discussions to consider some solid-state physics concepts. Theories based on electron density will provide some key approximations. In particular, we will begin with the Thomas–Fermi approximation, which can lead to contemporary density functional theories. This approach will allow us to consider a “one-electron” Schrödinger equation to solve a many-electron problem.

The last chapter of this section will center on the “pseudopotential approximation.” This key approximation will allow us to fix the length and energy scales of the many-electron problem by considering only the chemically relevant electronic states. The pseudopotential approximation treats an element such as lead on an equal footing with an element such as carbon. Both lead and carbon have the same configuration for the outermost, or valence, electrons. These chemically active states provide the chemical bond or “electronic glue” that holds atoms, clusters, molecules, and nanocrystals together.

The next part of the book illustrates numerical methods. Numerical methods are important as there are few atomic systems that can be solved *analytically*, save the aforementioned hydrogen atom. This is also true for classical systems where analytically only the two-body system is solvable.

We initially consider an isolated, spherically symmetric atom. We introduce the variational method and show how approximate wave functions can be used to obtain accurate estimates for the exact solution. We also solve the problem by integrating a one-dimensional equation.

We will consider solutions for many-electron atoms and molecules, using a numerical basis. This is the standard method for most quantum chemistry approaches to molecules and atoms, although it may not be the best method for these systems, especially for pedagogical purposes. An alternate is to solve the problem in real space on a grid. This approach is easy to implement and understand. With either a basis or a grid approach, we solve an “eigenvalue problem.” Iterative methods can solve such problems and we will illustrate this.

The last part of the book demonstrates the application of quantum theory to atoms, molecules, and clusters using a common numerical method. Physical concepts such as pseudopotentials, density functional theory, and a real-space grid form the underpinnings for computing a solution of the electronic structure problem. The pseudopotential model of solids is widely used as the *standard model* for describing atomistic systems. The model divides electronic states into those that are valence states (chemically active) and those that are core states (chemically inert). For example, systems made up of silicon atoms have valence states derived from the atomic $3s^23p^2$ configuration. The valence states form bonds by promoting a $3s$ electron to form sp^3 bond. One can omit the core states $1s^22s^22p^6$ altogether in pseudopotential theory. As such, the energy and length scales for determining a basis are set by the valence state.

Density functional theory is perhaps the weakest approximation made in our toolbox, but it is indispensable. Density functional theory allows us to consider one electron at a time as it maps the difficult many-body problem to a one-electron problem.

Our use of a real-space grid reflects the bias of the author. The use of a grid to solve difficult differential equations is well known in the engineering community. There are good reasons for its popularity. Grids are easy to implement and possess a number of advantages for running on high-performance computers; e.g. they can reduce the number of global communications.

Many of the numerical solutions in our book are based on computer codes using MATLAB. The inventors of MATLAB claim: *MATLAB is a high-level language and interactive environment that enables you to perform computationally intensive tasks faster than with traditional programming languages such as C, C++, and Fortran.* There is merit to this claim; MATLAB is easy to use and implement. A transcription of a “state of the art” research program forms the basis of the codes in this book.

The application to atoms will focus on ionization energies, electron affinities, and polarizabilities. We will examine some diatomic molecules along with some organics such as methane and benzene. We will also examine solutions for chemical trends, ionicities, energy levels, bond energies, vibrational levels, and bond lengths. Clusters of atoms represent a “new” form of matter, i.e. a combination of atoms that is stable only in isolation. Systems in isolation represent a serious challenge for experiment. The systems must be probed without any material interactions. We can examine properties in clusters as for molecules, but we can also examine other seminal properties such as the evolution of properties from atoms to crystals. We will look at nanoscale structures such as nanocrystals. In these systems, quantum confinement can play an important role in altering physical properties. An appendix at the end will give the reader access to the essential codes.

Reference

- 1 Dirac, P.A.M. (1929). *Proceedings of the Royal Society of London Series A* 123: 714.