


ELEMENTARY QUANTUM



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FRANK L. PILAR



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ELEMENTARY QUANTUM CHEMISTRY

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Frank L. Pilar

*Professor of Chemistry
University of New Hampshire*

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ABOUT THE AUTHOR

Frank L. Pilar received B.S. and M.S. degrees from the University of Nebraska (Lincoln) in 1951 and 1953, respectively, and a Ph.D. from the University of Cincinnati in 1957. Between 1953 and 1955 he was a research chemist at the Standard Oil Company (Indiana), where he worked on Ziegler-Natta olefin polymerization. Since 1957 he has taught at the University of New Hampshire and has been chairman of the chemistry department since 1982.

Dedicated to those former undergraduate and graduate students at the University of New Hampshire who shared my interests in quantum chemistry: M. Donald Jordan, Jr., John R. Morris, III, Larry Siegel, James J. Eberhardt, Mark Springgate, James D. Quirk, Donald R. Land, John R. Sabin, Robert H. Carrier, Frank Block, and Shu-jun Su.

PREFACE

“Elementary” is often used to denote a level at which one is exposed superficially to a body of knowledge which will probably never be used again. The term, as used here, implies the lowest level of completeness and sophistication necessary in order for the chemist to acquire the competence needed to begin a serious, nontrivial understanding of the research literature of the late twentieth century—a research literature in which quantum concepts are playing an ever-increasing role.

Experimental chemists have progressed well beyond the point of studying the “average” behavior of reacting species described by the Arrhenius rate equation and are beginning to probe the step-by-step behavior of individual atoms and molecules as they collide, form “transition states,” and ultimately form products. Such experiments are generally assisted by sophisticated quantum mechanical calculations of potential-energy surfaces—computations which help to fill gaps in observation and which assist in the interpretation of what is observed. Similarly, organic and inorganic chemists are studying increasingly sophisticated aspects of molecular behavior (e.g., photodissociation), the understanding of which requires a much deeper insight into quantum theory than provided by the “hand-waving” treatments of the past. As Fritz Schaefer has pointed out, theory has become accepted by organic, inorganic, and physical chemists as a legitimate tool for the study of legitimate chemical problems. Although this text stops far short of describing the level of computations and concepts needed in all such studies, it does attempt to provide a suitable foundation upon which expertise in such endeavors can be built.

The author has taught the material in this text to advanced undergraduate students and to beginning graduate students. At the undergraduate level it is sometimes necessary (particularly in a one-semester course) to limit oneself to only the simpler aspects of a topic and to spend less time on details of mathematical formalism, molecular symmetry, and molecular orbital calculations. It is assumed that the student has had mathematics through calculus and at least one year of undergraduate physics taught on the basis of calculus. A

background in differential equations, linear algebra, and modern (or atomic) physics is very helpful but not absolutely essential. Mathematical and physical material not necessarily assumed to be part of the students' background—and which may be useful to some as a review—is supplied in a number of appendixes. The first edition worked most of these right into the text material itself; I hope the change won't tempt some students to forgo these topics entirely.

The present edition differs from the first in two very important aspects: first, rather than being derived entirely from the published works of others, many features of atomic and molecular structure are illustrated by calculations carried out specifically for this text; second, there are a number of computer-generated diagrams (e.g., so-called three-dimensional, or surface, orbital plots) which I have also constructed personally. Furthermore, all these computations and graphics can be reproduced by students using relatively modest computational facilities and readily available programs and software, e.g., GAMESS, Gaussian 88 (and previous versions), and RS/1. Some calculations can even be done on microcomputers such as the IBM PC (or compatibles) and the Macintosh series—or even on an Apple II, II+, IIe, IIfx, IIGS, or various other popular micros.

I am constantly aware of what a huge debt I owe to the sources of much of my material: the numerous books, journals, and technical reports I have read—and perhaps most important of all, the very inspiring teachers and colleagues I have had. Those who have influenced me to a special degree deserve at least my explicit thanks: Prof. Hans H. Jaffé (University of Cincinnati), my first teacher in quantum chemistry; Prof. Per-Olov Löwdin (Uppsala University and University of Florida), who influenced my philosophical approach to quantum chemistry; Prof. Ruben Pauncz (Technion, Israel Institute of Technology), who gave the clearest, most beautiful lectures I have ever heard in quantum chemistry; Prof. J. de Heer (University of Colorado), whose trenchant wit enlivened some otherwise mundane topics; and the late Charles A. Coulson (Oxford University), who was my gracious host during a pleasant year's stay at the Mathematical Institute. Also, in a very special and personal way, I thank my wife, Anita, for her years of loyal support of a project which has benefited her very little in a material way. I also thank my five children for outgrowing the crayon years; this means that the backsides of manuscript pages of the second edition escaped becoming "artwork," a fate befalling some of the pages of the first edition.

Finally, my special thanks to four colleagues who reviewed portions of the final manuscript: Ernest Davidson, Indiana University; Mark Gordon, North Dakota State University; Hans Jaffé, the University of Cincinnati; and George Petersson, Wesleyan University.

Frank L. Pilar

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CHAPTER 1

ORIGINS OF THE QUANTUM THEORY

Toward the close of the nineteenth century, many scientists thought that physics was virtually a closed book. As Sir William Cecil Dampier wrote in *A History of Science*: "It seemed as though the main framework had been put together once and for all, and that little remained to be done but to measure physical constants to the increased accuracy represented by another decimal point."¹ Yet, the beginnings of a profound revolution were already brewing—a revolution which would change drastically how scientists and philosophers would view the structure of the universe. In just one short generation the theories of relativity and quanta changed physics and its dependent sciences more comprehensively than had ever occurred before. The present chapter summarizes some of the early work which led to modern quantum mechanics and some of its more important applications to chemistry.

¹ Quoted by O. W. Greenberg, *American Scientist*, July–August 1988, p. 361. See also comments in *Phys. Today*, April 1968, p. 56; August 1968, pp. 9, 11; and January 1969, p. 9.

1-1 THE SPECTRAL SHAPE OF BLACKBODY RADIATION

When a solid is heated to some temperature T , it emits radiation (of which visible light is one specific example). Experiments show that the radiation consists of a spread of different wavelengths, each wavelength generally appearing with a different intensity. Normally, each temperature is characterized by a given radiation wavelength whose energy density is higher than that of radiation of either higher or lower wavelengths; i.e., the energy of the radiation exhibits a maximum value for some particular frequency, and such maxima occur at different frequencies for different temperatures. Figure 1-1 shows how the energy density varies with wavelength for several different temperatures. This figure represents the radiation emitted by an idealized material known as a *blackbody*—a hypothetical material which absorbs all incident radiation and is also a perfect emitter of this radiation. For experimental purposes, an acceptable blackbody may be approximated by an enclosed cavity, the walls of which are kept at some temperature T and which have a small hole in one side. The blackbody radiation shown at 5700°C is very close to that emitted by our sun; most of the emitted radiation falls within that portion of the electromagnetic spectrum known as *visible light* [approximately 400 to 700 nanometers (nm)].

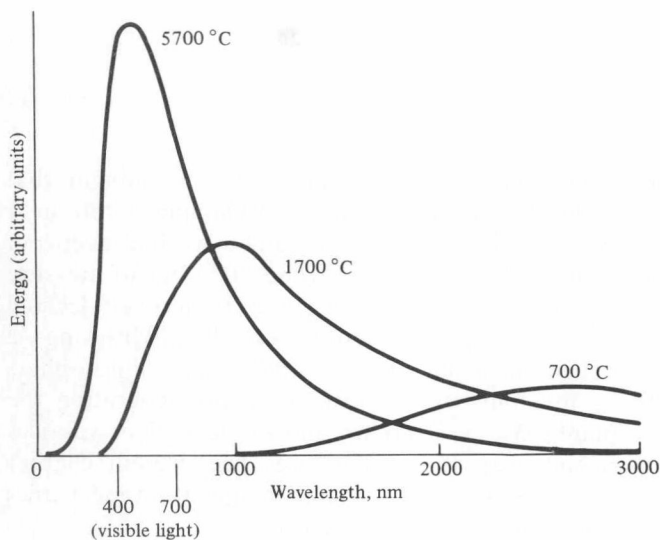


FIGURE 1-1

The spectral shape of blackbody radiation at three different temperatures. The curve at 5700°C closely resembles the emissive behavior of the sun. The 1700°C curve represents a body that emits primarily infrared radiation.

Although many renowned physicists tried to provide a theoretical explanation of the details of blackbody radiation, none of the attempts based on classical mechanics succeeded. Nevertheless, it was known that the emitted energy obeyed a relationship of the general form

$$\rho_\nu d\nu = \frac{8\pi}{c^3} \nu^3 F(x) d\nu \quad (1-1)$$

where $\rho_\nu d\nu$ = energy density of radiation having a frequency between ν and $\nu + d\nu$

c = velocity of light (in a vacuum)

$F(x)$ = some unknown function of $x = \nu/T$

The appearance of the variable x originates in the *Wien displacement law*

$$\lambda_{\max} T = 2.90 \times 10^6 \text{ nm} \cdot \text{K} \text{ (approx)} \quad (1-2)$$

an expression which the German physicist Wilhelm Wien managed to derive using classical methods. Here λ_{\max} represents that predominant wavelength for which the energy density of the blackbody emission is a maximum. However, all attempts by Wien and his contemporaries to obtain an explicit mathematical form for the function $F(x)$ by the use of classical mechanics failed. In particular, all classical attempts to account for the spectral shape of blackbody radiation predicted what is often called the *ultraviolet catastrophe*; i.e.,

$$\lim_{\nu \rightarrow \infty} \rho(\nu) = \lim_{\lambda \rightarrow 0} \rho(\lambda) = \infty$$

This means that classical theory could not account for the appearance of a maximum in the spectral distribution.

In 1900 the German thermodynamicist Max Planck obtained an empirical form for $F(x)$:

$$F(x) = k\beta(e^{\beta x} - 1)^{-1} \quad (1-3)$$

where k is Boltzmann's constant (the ideal gas constant R divided by Avogadro's number) and β is an empirical constant (of unknown significance at this point). Planck then proceeded to derive Eq. (1-3) by making some unconventional assumptions about the nature of the blackbody emitter. Since Planck's original approach remains somewhat unclear even to this day, and since Planck himself subsequently modified his assumptions several times, only those ideas which have remained essentially unmodified to this day are given here. Basically, Planck treated the blackbody as a collection of isotropic oscillators capable of interacting with electromagnetic radiation, each oscillator having a vibrational frequency ν . Planck then proposed two new nonclassical ideas:

1. Each of the oscillators has a discrete set of possible energy values given by

$$\epsilon_n = nh\nu \quad (1-4)$$

where $n = 0, 1, 2, \dots$, and h is a constant independent of blackbody

composition.² Unlike in classical mechanics (which would allow ϵ_n to have a continuum of values) Planck's formula implies that the energy of a black-body oscillator is *quantized*, i.e., exists as packets, bundles, or *quanta* of size $h\nu$.

2. The emission and absorption of radiation are associated with transitions, or jumps, between two different energy "levels." Each emission or absorption involves loss or gain of a quantum of radiant energy of magnitude $h\nu$, ν being the frequency of the radiation absorbed or emitted.

Planck also imposed the requirement that the entropy and the energy must be related by the relationship $dS = dE/T$, where (by the second law of thermodynamics) T must be the same for all radiation frequencies. He then calculated the average energy of an oscillator, using Eq. (1-4) and classical Maxwell-Boltzmann statistics, to show that the constant β in $F(x)$ was simply h/k so that

$$F(x) = h(e^{h\nu/kT} - 1)^{-1} \quad (1-5)$$

The constant h (now called *Planck's constant*) has the dimensions of *action* (energy \times time) and is sometimes called the *quantum of action*. It also has the dimensions of angular momentum. The modern numerical value of Planck's constant is 6.626196×10^{-34} J \cdot s. Although Planck spent most of his life believing that the assumption of Eq. (1-4) was fundamentally incorrect and only fortuitously led to a successful blackbody equation, we now know that the constant h is a fundamental constant related to all dynamic discontinuities in nature, especially evident on the atomic and subatomic scale.

EXERCISES

- 1-1. Verify Eq. (1-5) using the following information: the average energy of an oscillator is given by Maxwell-Boltzmann statistics as

$$\bar{\epsilon} = \nu F(x) = \frac{\sum_{n=0}^{\infty} \epsilon_n e^{-\epsilon_n/kT}}{\sum_{n=0}^{\infty} e^{-\epsilon_n/kT}}$$

You will also need the relationships $(1-y)^{-1} = 1 + y + y^2 + y^3 + \cdots$ and $(1-y)^{-2} = 1 + 2y + 3y^2 + 4y^3 + \cdots$.

² In actuality, Planck did not quantize the individual oscillators but assumed that the *total* energy possessed at equilibrium by *all* oscillators in the frequency range ν to $\nu + d\nu$ equals a multiple of $h\nu$. See T. S. Kuhn, *Black-Body Radiation and the Quantum Discontinuity*, Oxford University Press, New York, 1978. It is now known that the correct formula is $\epsilon_n = (n + \frac{1}{2})h\nu$, but this is of no consequence in the present context.