ELEMENTARY QUANTUM CHEMISTRY

F.L.Pilar

elementary quantum chemistry

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To the students of my first bona fide class in quantum chemistry: ***John Festa, Ed Hach, Don Land, Jim Quirk, Jack Sabin, Bart Solomon, and Irene Tyminski***

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Preface

The word *elementary* and the term *quantum chemistry* mean different things to different people. This text is *elementary* in the sense that an attempt is made to present certain selected topics of quantum theory on the lowest possible level at which triviality and misrepresentation can be avoided more often than not. The decision marking such a level depends, of course, upon the judgment of the author and cannot be expected to satisfy a diversity of critics. As to quantum chemistry, the coverage is obviously limited in scope and sometimes even in depth. If this text may be said to have a single aim, that aim is to provide a guide to the computer-age quantum theory of atomic and molecular electronic structure. By computer age is meant (with some exceptions) the post-1950 activity in quantum chemistry.

To the average chemistry student, the area known as quantum chemistry often appears to consist of an almost inpenetrable jungle of partial differential equations, matrix theory, operator algebra, and other esoteric mathematics. One of the purposes of this text is to blaze a rough trail into the interior of this apparent jungle. It is the task of the reader to go back and broaden the path, smooth out the bumps and corners, strengthen the bridges, and (above all) build new avenues. This can be accomplished only by studying more mathematics and physics and, especially, by intimate study of the literature of quantum chemistry.

In at least some respects, quantum mechanics is mathematically easier than, say, thermodynamics. Yet it is a common experience that exposure to a first course in quantum mechanics leaves the average student with a far weaker grasp of a useful tool than exposure to a first course in thermodynamics. This regrettable circumstance has at least two explanations: first, the subject matter of thermodynamics is closer to the previous training of a chemist than the subject matter of quantum mechanics and, second, thermodynamics can be taught relatively thoroughly and rigorously on the basis of the minimum mathematics required for an ACS-accredited B.S. degree in chemistry. In teaching an elementary course in quantum chemistry one has two extreme alternatives to consider. The first is to build upon the actual mathematical background possessed by most chemistry students and thereby run the very real risk of gross oversimplification. Certainly this approach has virtually no chance of exposing the essential structure of quantum chemistry, since this structure has been deliberately suppressed. Such an approach leads to physical insights which are too often trivial or downright false. Even more serious, such an approach imparts a vanishingly small ability to analyze even simple problems of a quantum-theoretical nature. Furthermore, the student is not given a useful foundation for improving his level of competence by self-study: he will likely find the research literature incomprehensible (and distasteful). The second extreme is to teach quantum chemistry in an intellectually honest manner along with the concomitant mathematical background. This has several obvious disadvantages. One certainly cannot teach very much rigorous mathematics and yet have time to cover much rigorous quantum chemistry (including extensive applications!). Furthermore, the student is forced to cope with two extremely difficult problems at the same time, viz., he is forced to struggle with the formal mathematical structure and the conceptual structure of quantum mechanics simultaneously. Either problem alone is battle enough for most people! The present text represent's one man's attempt to follow some middle trail. If the reader obtains the impression that the formal mathematical structure generally tends to overshadow the conceptual structure, he may very well be correct. The author feels that the converse would place the student at an even greater disadvantage when he attempts to deepen his knowledge of quantum chemistry by self-study, e.g., by studying the research literature. The author does not make the claim that mastery of this text will transform the workbench chemist into a theoretician capable of carrying out and appreciating high-level analyses and calculations. Instead, the aim is to impart a modicum of proficiency in enough fundamental areas, so that the dedicated student is likely to feel competent to continue his own education in quantum chemistry should the need or desire exist.

The writer has taught the material in this text to both beginning and advanced graduate students representing all areas of chemistry. There appears to be no reason why the material should not be suitable for advanced undergraduate classes as well. It is assumed that the student has had mathematics through the calculus and at least one year of undergraduate physics taught on the basis of the calculus. A background in differential equations, linear algebra, and modern (or atomic) physics is very helpful but not absolutely essential at the outset. Mathematical and physical material not necessarily assumed as part of the students' background, e.g., vectors, matrices, electromagnetic theory, and some restricted aspects of classical mechanics, is incorporated into the text, usually in a condensed fashion. The device of introducing much of the strictly mathematical material with or before those topics for which such a background is seriously needed for the first time (as opposed to collecting such material in appendixes) appears to the author as the most natural and effective approach for those having little mathematical background. Admittedly, this device imparts neither sophistication nor depth, but at least it does permit the student to continue without acquiring the hopeless feeling that first he needs to master an entire specialized text or take a full course in some specialized auxiliary area. Those who have a sophisticated knowledge of such topics may use the material for a quick review or may ignore it altogether.

Throughout the course the writer has found it both desirable and convenient to refer the student to several auxiliary texts in quantum chemistry and related areas. Foremost of these are Pauling and Wilson, "Introduction to Quantum Mechanics," Eyring, Walter, and Kimball, "Quantum Chemistry," Slater, "Quantum Theory of Atomic Structure," vols. 1 and 2, and "Quantum Theory of Molecules and Solids," vol. 1, Herzberg's four volumes on atomic and molecular spectroscopy, and Bethe and Salpeter, "The Quantum Mechanics of One- and Two-Electron Atoms." Many areas which the present text deals with rather summarily are amplified in the above texts and reference works.

It would be impossible to acknowledge adequately all the sources of the material appearing in this text: the numerous books, journal publications, and technical reports—and, perhaps most important—teachers I have studied under. Nevertheless, certain persons have influenced and inspired me to a special degree and deserve at least my explicit thanks: Professor Hans H. Jaffé (University of Cincinnati), my first teacher in quantum chemistry; Professor Per-Olov Löwdin (Uppsala University and University of Florida), Professor Ruben Pauncz (Technion, Israel Institute of Technology), and Professor J. de Heer (University of Colorado), whose lectures I attended at the University of Florida Institute in Quantum Chemistry; and Professor C. A. Coulson (Oxford University), who was my gracious host during a pleasant year's stay at the Mathematical Institute. Especial thanks are due to my wife, Anita Pilar, who consistently encouraged and counseled me in my efforts, often turned despair into renewed hope, and more than once rescued portions of the manuscript from certain members of the next generation.

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chapter 1

Origins of the Quantum Theory

1-1 *Pre-1900 Physics.* Toward the close of the nineteenth century it appeared as if the penultimate chapter in physics had been written. There were indications that the final chapter would be little more than the working out of details of fundamental theories and their applications to problems in physics, chemistry, engineering, and, hopefully, in *all* fields of human endeavor. In fact, a well-known physicist was led to make the remark that all that remained to be done in physics was the calculation of the next decimal point. Nevertheless, for those who could read them, the signs of a coming cataclysm in classical ideas were already manifest. In 1887 Hertz quite accidentally discovered the photoelectric effect. Even earlier, the phenomenon of blackbody radiation had been well known and quite well studied both by experimentalists and by theoreticians. It was true that neither of these phenomena could be successfully explained by the most powerful methods of nineteenth-century theoretical physics, but such failures were commonly regarded as no more than temporary obstructions to the eventual, complete triumph of the basic structure of physical theory as it then existed. Only the most progressive and daring of scientists could have predicted that physics was on the brink of a new era, an era marked by the abandonment of some long-cherished concepts of scientist, philosopher, and layman.

The twentieth century opened on a scientific world in which all physics appeared to be encompassed within the mechanics of Newton and the electromagnetic theory of Maxwell. The labors of many mathematicians and physicists had extended newtonian mechanics to an elegance that appeared to lack little, if anything, in perfection. By the use of Newton's laws and certain of their generalizations, one could carry out very precise calculations concerning the motions of astronomical bodies and the behavior of machines. Indeed, by purely theoretical calculations, Leverrier and Adams in 1846 used the known perturbations of the motion of Uranus to predict the existence of the then unknown planet Neptune. Young's double-slit diffraction experiment and Fresnel's interference experiment appeared to furnish conclusive proofs of the wave nature of light and thereby to demolish the rival corpuscular theory of Newton. Maxwell, motivated largely by Faraday's brilliant experiments, developed a general mathematical theory of electromagnetic radiation which encompassed the discoveries of Coulomb, Ampere, Gauss, Volta, and Faraday and united them with the laws of optics. The atomic theory of Dalton had been fully vindicated, and even though atoms were known to consist of charged particles, these were believed to occupy the atom in a dense, compact fashion and to obey ordinary laws of physics. Curiously enough (especially with the advantage of hindsight), although matter was known to be discontinuous, energy was regarded as continuous. The laws of chemical binding were as yet undiscovered, but scientists such as Gibbs, van't Hoff, Arrhenius, and Ostwald had just begun to enjoy a modicum of success in the interpretation and formulation of certain chemical facts in terms of mathematical physics. Many felt that this approach would soon lay bare the fundamentals of chemistry, which would undoubtedly have their bases in newtonian mechanics and maxwellian electrodynamics, with, perhaps, a tempering of Maxwell-Boltzmann statistics. Even organic chemists of that time were often thoroughly grounded in mathematics and physics, perhaps in the expectation that they, too, would find order in chaos. Certainly there appeared little reason why the prevailing structure of physics would not be adequate for the description of nature on the atomic and subatomic scale of size. After all, an electron was thought to be a particle—even if ever so tiny—and therefore should be expected to obey Newton's and Maxwell's laws. Small wonder, then, that the climax of physical theory appeared to be just over the horizon. The few remaining discrepancies between theory and fact hardly seemed capable, at first sight, of spawning the upheaval which produced the theories of relativity and quanta.

In the remainder of this chapter we shall discuss some of the more important experiments and ideas which ultimately led to the quantum theory of today. We begin with the events leading up to Planck's reluctantly tendered hypothesis and eventually reach the speculations of de Broglie at the dawn of modern wave mechanics. Hardly a generation is spanned by this story.

1-2 The Spectral Shape of Blackbody Radiation.[1] Before the end of the nineteenth century, it was a well-known fact that any heated solid was capable of emitting radiation and that this radiation consisted of a spread of different wavelengths at different intensities. Similarly, it had been observed that such bodies were also capable of absorbing radiation and that radiations of certain wavelengths were absorbed more strongly than others. One of the tasks of the physicist was to account for the details of such absorption and emission.

The theoretical study of these phenomena is most conveniently approached by means of a model known as the *blackbody*. In physics and chemistry, as well as in other closely related sciences, actual systems of interest are often far too complex to study directly, and so one replaces them with a hypothetical model which is considerably simpler to handle and whose behavior approaches that of the actual system under some set of well-defined limiting conditions. Such a model should be relatively easy to visualize and should lend itself to rigorous mathematical interpretations which, at worst, are at least first approximations to the behavior of the actual system which the model represents. Such a model, if successful, may later be refined, leading ultimately to rather sophisticated understanding of the actual complex system. For example, the physical chemist's concept of the ideal gas concerns an imaginary model which is not, in general, a good approximation to the behavior of real gases, but under conditions of high temperatures or low pressures (or both) all real gases approach the behavior predicted by Boyle's and Charles' laws.

A blackbody is much the same sort of an idealization of a substance which can absorb and emit radiant energy. It is defined as a body whose surface absorbs 100 percent of all the radiation incident upon it; i.e., the absorptivity is unity for all wavelengths. No real substance behaves in this idealized fashion (as handbook tables of absorptivities of metals and other solids will testify). However, certain substances such as lampblack and black velvet reflect but a small portion of incident radiation and thus approach the behavior of blackbodies.

For experimental purposes, an acceptable blackbody may be obtained by using a cavity with a small hole in its side and whose walls are maintained at some temperature T. Such an enclosure is often called a *hohlraum* or an *isothermal enclosure*. The radiant energy enclosed in such a cavity is called *blackbody radiation*. The amount of energy associated with each wavelength differs with the wavelength, and, furthermore, the distribution varies as the temperature of the walls changes. The blackbody problem in terms of this model is this: if the cavity is filled with radiation at a given temperature T, what is the spectral distribution of the radiant energy? Alternatively: what is the specific heat of a vacuum?

In 1884 Boltzmann derived a theoretical relationship for the variation of the total emissive power of a blackbody as a function of the absolute temperature. This rela-

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[1] An unusually interesting historical account of this and following topics is given by E. U. Condon, 60 Years of Quantum Physics, *Phys. Today*, October, 1962, p. 37. A more complete and sophisticated discussion is given in Ref. 7. (Numbered references appear at the end of the chapter.)

tionship, which arose from the consideration of a Carnot engine operated with radiation as the working substance, is now known as the Stefan-Boltzmann law and is given by

$$\mathcal{E} = \sigma T^4 \tag{1-1}$$

where $\mathcal{E}$, the total emissive power at the absolute temperature T, is the energy emitted per unit area per unit time by any blackbody surface[1] and σ is a constant (the Stefan-Boltzmann constant) having the value 0.56697×10^{-4} erg sec^{-1} cm^{-2} deg^{-4}. This equation may also be written in terms of the energy density (energy per unit volume) as

$$\rho = aT^4 = \frac{4\mathcal{E}}{c} \tag{1-2}$$

where a is known as Stefan's constant and c is the speed of light. Equation (1-1) is a consequence of the second law of thermodynamics and therefore compatible with that area of classical physics.[2] It is of interest to note that there is a rather close analogy between radiation in a hohlraum and an ideal gas in a flask. Whereas the gas density is a function of volume and temperature, the radiation density is a function of temperature alone. Furthermore, the distribution of velocities in a gas is analogous to the distribution of frequencies in the radiation.

Unfortunately, the Stefan-Boltzmann law did not lead to an explanation of the distribution of the radiation with respect to the wavelengths of the emitted radiation; nor did the law provide any means of deducing the value of the Stefan-Boltzmann constant in a purely theoretical manner. According to the classical principle of the equipartition of energy, the total energy of a hohlraum should be equal to fkT, where k is the Boltzmann constant and f is the number of degrees of freedom. For, say, a crystal of N atoms, $f = 3N$ and is finite since N is finite. However, for an "empty" cavity, one is talking not about the oscillation of material particles but rather about the oscillation of the so-called *ether*, which is taken to be a continuum. Thus, f is infinite for a vacuum, and so the total energy must be infinite. This implies that the cavity will absorb energy endlessly from the walls in an attempt to reach thermal equilibrium. Thus, thermal energy would be endlessly converted to radiation of smaller and smaller wavelengths, the so-called *ultraviolet catastrophe*. All this, however, contradicts Stefan's law, which states that the energy density is finite.

In Fig. 1-1 is shown the experimentally determined distribution of the radiation density as a function of wavelength. The distribution is described by a curve which passes through a maximum at some intermediate wavelength and drops off rapidly at both higher and lower wavelengths. At lower temperatures the height and sharp-

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[1] For actual bodies, i.e., nonblackbodies, the temperature enters in approximately as T^5.

[2] By *classical physics* we shall henceforth mean pre-1900 physics.

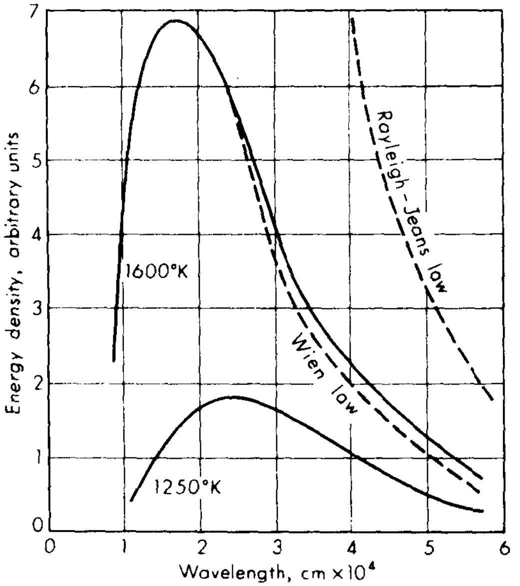

***Fig. 1-1.** The spectral shape of blackbody radiation at two different temperatures. Wien's law fits the experimental curve (solid line) almost perfectly to the left of the maxima.*

ness of the maximum decreases, and its position shifts to a higher wavelength. By the use of classical mechanics, Wien[1] was able to show that the position of the maximum obeyed the relationship

$$\lambda_{\max} T = 0.290 \text{ cm deg approx} \tag{1-3}$$

This relationship, called the *Wien displacement law*, was verified experimentally by Lummer and Pringsheim. This law makes it possible to obtain correct blackbody spectra at any given temperature T, provided a complete spectrum is known at some particular temperature. Using some rather special assumptions concerning the process of absorption and emission, Wien was able to derive the spectral-distribution formula

$$\rho(\nu)\,d\nu = \frac{8\pi k\beta}{c^3} e^{-\beta\nu/T}\nu^3\,d\nu \tag{1-4}$$

where $\rho(\nu)$ is defined by

$$\rho = \int_0^\infty \rho(\nu)\,d\nu \tag{1-5}$$

and where β is an empirical constant. As shown in Fig. 1-1, the Wien equation fits the experimental curve very well at low wavelengths. In general, the discrepancies become noticeable only when ν/T is greater than about 10^{11} sec^{-1} deg^{-1}.

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[1] Cf. Ref. 11 for a full discussion of the reasoning.

Rayleigh made the assumption, based on the classical principle of the equipartition of energy, that each possible vibration within the isothermal enclosure contributed equally to the energy.[1] In this manner, he was led to the alternative spectral-distribution formula

$$\rho(\nu)\,d\nu = \frac{8\pi kT}{c^3}\nu^2\,d\nu \tag{1-6}$$

which did not contain any undetermined constant but which also was not generally valid, agreement with experiment being limited to small values of ν/T, that is, large wavelengths. Unfortunately, the Rayleigh equation leads to the ultraviolet catastrophe, that is,

$$\lim_{\nu\to\infty}\rho(\nu) = \lim_{\lambda\to 0}\rho(\lambda) = \infty \tag{1-7}$$

Apparently, some unknown factor was responsible for decreasing the radiation density as the wavelength decreased toward the ultraviolet.

If one lets $x = \nu/T$, both the Wien and Rayleigh formulas can be written in the general form

$$\rho(\nu)\,d\nu = \frac{8\pi}{c^3}F(x)\nu^3\,d\nu \tag{1-8}$$

where

$$F(x) = \begin{cases} k\beta e^{-\beta x} & \text{Wien} \\ \dfrac{k}{x} & \text{Rayleigh} \end{cases} \tag{1-9}$$

The difference between Eqs. (1-4) and (1-6) is thus simply due to different guesses at $F(x)$.

In 1900, Planck obtained an empirical formula for the spectral distribution which satisfied the entire spectrum. He simply found a function $F(x)$ which would reduce to the Wien function for high values of x and to the Rayleigh function for low values of x, or

$$F(x) = k\beta(e^{\beta x} - 1)^{-1} \tag{1-10}$$

He then set himself the task of deriving the entire equation from some simple set of assumptions. Using the thermodynamic requirement that the entropy and the energy must be related by the relationship

$$dS = \frac{dE}{T} \tag{1-11}$$

where (by the second law of thermodynamics) T must be the same for all radiation frequencies, Planck showed that at thermodynamic equilibrium between radiation

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[1] See Ref. 10 and also J. Rice, *Trans. Faraday Soc.*, **11**, 1 (1915).

and absorbers the average energy of an oscillator must be given by the Maxwell-Boltzmann statistical relationship

$$\bar{\epsilon} = \frac{\sum_{n=0}^{\infty} \epsilon_n e^{-\epsilon_n/kT}}{\sum_{n=0}^{\infty} e^{-\epsilon_n/kT}} = \nu F(x) \tag{1-12}$$

where ϵ_n is the energy associated with the nth oscillator. According to classical physics, the energy should vary continuously from zero to infinity, so that the summations in Eq. (1-12) may be replaced by integration. It was evident from the experimental shape of the spectral-distribution curve that ϵ_n had to be such that as the frequency became higher and higher, its contribution to the total energy density became smaller and smaller. Planck[1] now abandoned the classical concept of the continuity of energy in favor of an entirely novel and nonclassical supposition. He assumed that a blackbody could be viewed as a collection of isotropic oscillators capable of interacting with radiation but with the restriction that such oscillators could exist only in certain allowed energy states and could radiate energy only in certain exact integral multiples of a basic energy unit, i.e., a *quantum,* or *bundle,* of energy. In order to introduce the desired effect of reducing the contributions of higher frequencies to the total energy, it is necessary to set the oscillator energies ϵ_n proportional to the frequency. Thus Planck postulated the now-famous relationship

$$\epsilon_n = nh\nu \qquad n = 0, 1, 2, \ldots \tag{1-13}$$

where h is a constant independent of the composition of the blackbody. It is not hard to see that the Boltzmann factor $\exp(-\epsilon_n/kT) = \exp(-nh\nu/kT)$ becomes smaller as ν increases. Thus, the *probability* of an oscillator emitting energy of a given frequency drops off at very high frequencies, going through a maximum at some lower frequency.

The use of the energy expression (1-13) led to

$$\bar{\epsilon} = \nu F(x) = h\nu(e^{h\nu/kT} - 1)^{-1} \tag{1-14}$$

This, in turn, led to the correct spectral-distribution law

$$\rho(\nu)\,d\nu = \frac{8\pi h}{c^3}(e^{h\nu/kT} - 1)^{-1}\nu^3\,d\nu \tag{1-15}$$

in which Wien's constant β turns out to be h/k. Integrating Eq. (1-15) over the entire frequency range gives Stefan's law

$$\rho = \int_0^\infty \rho(\nu)\,d\nu = \left(\frac{8\pi k^4}{c^3h^3}\int_0^\infty \frac{x^3}{e^x - 1}\,dx\right)T^4 \tag{1-16}$$

in which the quantity in parentheses represents a theoretical expression for Stefan's constant a. The integral may be evaluated graphically to give the value of 6.494· · ·.

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[1] M. Planck, *Ann. Physik,* **4,** 553 (1901). A very good account of just how Planck probably reasoned is given in Ref. 7.

Using the experimental value of Stefan's constant, one can then obtain an estimate of the constant h.

The constant h, which has the dimensions of *action*, i.e., energy × time, is now known as the *quantum of action* or as *Planck's constant*. The smallness of this quantity (about 6×10^{-27} erg sec) compared to the gross energies usually measured in macroscopic systems precluded any earlier suspicion that energy could be quantized. We now know that h is a fundamental constant related to all dynamical discontinuities in nature, especially evident on the atomic and subatomic scale. Planck's own feeling, which persisted for many years, was that the quantum hypothesis itself could have no basic significance but rather was an artificiality which would eventually be replaced with a more reasonable alternative.

One should note that Planck's work did not suggest anything concerning the nature of the electromagnetic radiation with which the material oscillators interacted. In the following section we shall show how Einstein was led to extend Planck's hypothesis to the radiation itself, an extension which Planck regarded at first as a feat of reckless abandon.

Exercises

1-1. Verify Eq. (1-14). *Hint:* It is useful to note that $(1 - e^{-x})^{-1} = 1 + e^{-x} + e^{-2x} + \cdots$ and that $(e^{x} - 1)^{-1} = e^{-x} + e^{-2x} + e^{-3x} + \cdots$.

1-2. Show that the constant in the Wien displacement law (1-3) is given approximately by $hc/5k$. *Hint:* Use the limiting form of Planck's equation when ν/T is very large.

1-3 The Photoelectric Effect. In 1887 Hertz[1] set out to demonstrate the existence of electromagnetic waves in order to provide experimental support for Maxwell's equations. During the course of these experiments (which were successful) Hertz accidentally discovered the photoelectric effect. The discovery attracted early attention, and soon the salient experimental facts emerged.

The photoelectric effect occurs most readily when light of a suitable frequency (usually the visible or ultraviolet regions) illuminates the surface of an electropositive metal such as cesium or potassium. If the electropositive metal is made to serve as a cathode (with a negative potential relative to a plate), there is a flow of current from the cathode to the plate as long as the cathode is illuminated. In 1890 Stoletow[2] was able to produce a continuous photocurrent by means of the arrangement shown schematically in Fig. 1-2. In 1889 Elster and Geitel[3] demonstrated that the more electropositive the metal, the longer wavelength one could use to produce the effect, the alkali metals responding quite well to visible light. In 1900, the brilliant researches of Lenard[4] showed that the absorption of light by the metal is followed (virtually instantaneously) by the emission of cathode rays (electrons)

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[1] H. Hertz, *Ann. Physik*, **31**, 983 (1887). Cf. also P. Lenard, *ibid.*, **8**, 149 (1902).

[2] A. G. Stoletow, *J. Phys.*, **9**, 486 (1890).

[3] J. Elster and H. Geitel, *Ann. Physik*, **38**, 40 (1889).

[4] P. Lenard, *Ann. Physik*, **2**, 359 (1900).