GEORG KARAGOUNIS

INTRODUCTORY ORGANIC QUANTUM CHEMISTRY

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PREFACE

Organic chemists have often shied away from the quantum-mechanical approach to their discipline. This short introduction is aimed at giving a rapid and exact survey both to the young chemist in his formative years as well as to the older, established chemist who has never been exposed to quantum mechanics.

The lack of rigorous treatment will hopefully allay the inherent fears of the timid reader and overcome any trauma he may have acquired previously. At the same time it will perhaps show him the beauty and elegance of this method of looking at organic chemistry and stimulate him into the use of more advanced books on this subject.

It was a great pleasure and satisfaction to learn that an American publishing house was interested in bringing out an English translation of my German text "Einführung in die Elektronentheorie Organischer Verbindungen."

The author is much indebted to Dr. Frederick C. Nachod for his careful translation and for many valuable suggestions. The publishers have been most cooperative in the preparation of this edition for which his gratitude is recorded.

GEORG KARAGOUNIS

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Historical Introduction.
The Quantum of Action

The manner in which great new concepts arise and gain acceptance can be likened to the germination of seeds. There are long periods of latency in darkness when hardly any change takes place. Then, after a critical measure of energy is fulfilled, there follow periods which have no relationship to the long previous time span. New facts or connections of unrelated phenomena appear which then mark a turning point in the historical development of mankind. This is followed by times of rest and perfection, until germination of new ideas produces new impulses for development. This stepwise process is found not only at the beginning of big epochs but also, to a lesser degree, in most scientific disciplines, characterized by the fact that the rhythm between change and rest is becoming more rapid in recent times. Presently we are experiencing a penetration of physical concepts which are based on quantum mechanics and which have a pronounced effect on the structure of organic chemistry. This impact serves to create order and provide means of explanation. Before we deal with it in detail we must review some physical concepts and theories.

The discovery of the universal quantum of action by Max Planck in 1900 is a turning point in the history of natural sciences. It is the discovery of the discontinuous structure of matter which can be likened to the intuitive discovery of atoms by Democritus and Leucippus (480 and 540 B.C.), even though this explanation of existence only makes an oblique statement about the indivisible nature of energy. The property which is universally indivisible is action, viz., the product of time and energy—a concept which cannot be easily visualized. The elementary quantum $h = 6.625 \times 10^{-27}$ erg sec followed as a necessary and inescapable assumption in order to describe the laws of radiation in such a way that theory and experience would coincide.

If one had previously assumed that in any radiation process absorption or emission of energy, respectively, takes place in arbitrarily small portions—an assumption based on macroscopic experience—this concept of continuity had to be abandoned after Planck's discovery. A minimum action had to be postulated which could not be reduced further. The quantum of action cannot be partitioned and the action of any process hence must be composed of multiples of this quantity. If the frequency of a vibrational process v is known, there result whole energy quanta hv which are not further divisible as far as this process is concerned. The energy of a linear harmonic oscillator, for example, is expressed by $E = nhv$ where n takes the values of the whole integers, 0, 1, 2, 3, etc. With a known frequency v, discrete energy quanta hv are absorbed or emitted, but never energy values which lie between these quanta. The magnitude of energy quanta, however, is not universally constant but is proportional to the vibrational frequency v. Hence one can find another oscillator which vibrates with a different frequency v' and absorbs or emits energy quanta hv' of somewhat different magnitude. For the total field of all vibrational processes there must therefore exist a continuous series of energy values. The only property which is discontinuous and equal for all processes universally is action. Numerically it is expressed by the quantum h.

This fundamental assumption resulted from the functional relationship between emitted energy $E_{\lambda T}$, the wavelength λ, and the temperature T of a black body radiator, formerly considered continuously. In the classical picture this correlation is expressed by

$$E_{\lambda T} = \frac{c}{\lambda^4} \cdot kT \qquad (1)$$

(c = light velocity, k = Boltzmann's constant), where for a given wavelength λ and temperature T, the emitted energy $E_{\lambda T}$ is proportional to the temperature and inversely proportional to the fourth power of the wavelength. After the introduction of Planck's quantum theory, this relationship became much more complicated as is shown by Planck's radiation equation:

$$E_{\lambda T} = \frac{c}{\lambda^4} \cdot \frac{hv}{e^{hv/kT} - 1}. \qquad (2)$$

In Eq. (1) the energy increases towards infinity for smaller and smaller wavelengths (Fig. 1, dotted curve) which is contradictory to experience. On the other hand, the curves of the Planck equation (2) go through a maximum which has a different position for different temperatures, chang-

ing towards shorter wavelengths with increasing temperature. This indeed is the behavior of the black body under the influence of heat.

The comparison and discussion of Eqs. (1) and (2) clearly points up the difference between the classical and the quantum theoretical concept of the mechanism of the radiation process. Equation (1) describes the so-called equipartition principle according to which the energy introduced into a system of oscillators is distributed among them according to its

Wavelength λ (μ)
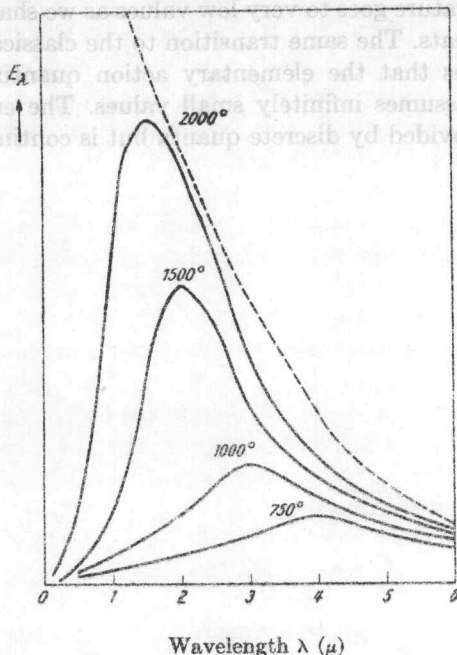
Fig. 1. Radiation of a black body.

degrees of freedom in the same manner, i.e., one calorie per degree of freedom. In contrast to this, in the quantum theoretical picture [Eq. (2)], the energy distribution among the oscillators is determined by the values of the frequency ν and thereby the values of the particular energy $h\nu$ of the oscillator. An oscillator with a higher frequency ν absorbs more energy than an oscillator with a smaller frequency since it can only absorb such energy quanta as correspond to its own $h\nu$.

If the frequency becomes very small or, conversely, the temperature becomes very large, the expression $h\nu/(e^{h\nu/kT} - 1)$ approaches kT, i.e.,

Eq. (2) becomes Eq. (1). This shows how the classical picture can be considered a limiting case of the quantum mechanical one, a fact which we shall encounter repeatedly. In our everyday experience we do not notice the quantized exchange of energy in macroscopic processes because the steps of energy exchange are very small owing to the smallness of Planck's constant h. Hence they are of no consequence because of the large supply of quanta in matter even at normal temperatures. This, however, is different when the temperature goes to very low values as we shall see in the discussion of specific heats. The same transition to the classical Eq. (1) takes place if one assumes that the elementary action quantum h converges towards zero, i.e., assumes infinitely small values. The energy exchange then is no longer provided by discrete quanta but is continuous.
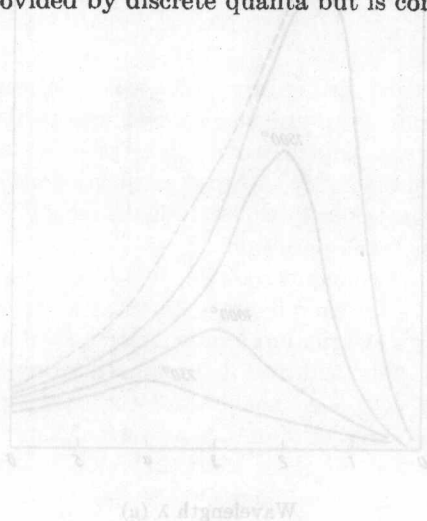
Wavelength λ (μ)

Fig. 1. Radiation of a black body

CHAPTER 2

Some Applications of the Elementary Action Quantum. The Specific Heat

Inasmuch as each elementary process is determined and regulated by the action quantum there are no physical processes which are not quantized. A phenomenon which can no longer be explained by the classical continuous concept of energy exchange and which necessitates the introduction of quanta is particularly well demonstrated by the decrease of specific heat with decreasing temperature.

According to the concepts valid until 1907, the atomic specific heat at constant volume C_v for each degree of freedom was set equal to $\frac{1}{2}R$, corresponding to nearly a calorie. For a monoatomic solid body with its 6 degrees of freedom (3 for potential and 3 for kinetic energy) the atomic specific heat must be $6 \times R/2$, i.e., 6 cal/atom at all temperatures. This indeed is observed in a large number of metals at normal temperature (Dulong-Petit law). The requirement, however, that the value 6.0 should remain constant for all temperatures is not fulfilled. On the contrary, one observes a decrease of atomic heat with falling temperature which takes place at different temperatures for different solids (Fig. 2). The atomic specific heat of silver at room temperature is 5.8 cal and a marked decrease takes place only below 150°K, whereas the atomic specific heat of diamond at the same point is approximately 0.3 cal and at room temperature only reaches approximately 1.5 cal.

The explanation of this behavior was furnished by Einstein in 1907 by the application of the Planck equation to specific heats. In order to arrive at atomic specific heats in the case of an oscillator with three degrees of freedom and average energy content according to the quantum theory, one must differentiate Eq. (3) with respect to temperature

$$\bar{E} = \frac{3h\nu}{e^{h\nu/kT} - 1} \tag{3}$$

which yields

$$C_v \equiv \frac{\partial \bar{E}}{\partial T} = 3R \left(\frac{h\nu}{kT}\right)^2 \cdot \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}. \tag{4}$$

Thus it becomes apparent that specific heat is a function of temperature in such a fashion that with diminishing temperature the function decreases. The magnitude of this decrease depends on the magnitude of the energy quantum $E = h\nu$, which is proportional to the frequency of the vibrating
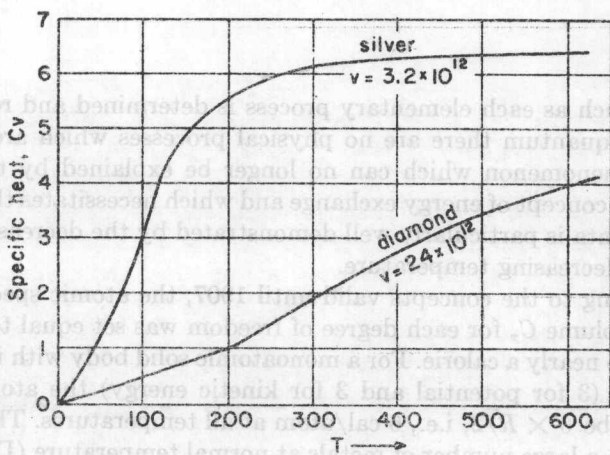
FIG. 2. Decrease of specific heats with decreasing temperature.

atoms. The carbon atoms in the diamond lattice vibrate with frequency $\nu = 24 \times 10^{12}$ whereas the atomic frequency of silver is 3.2×10^{12}. Consequently, the specific heat of diamond indicates that the quantized decrease of vibrational states takes place at a higher temperature than is found for silver. Furthermore, one can see that when T approaches infinity, the specific heat C_v approaches the classical value $3R$. Thus, both mechanisms of energy exchange—the classical and the quantum mechanical—approach each other and finally coincide.

The Photoelectric Effect and the Dual Nature of Light

In this section we plan to explain the photoelectric effect by introducing the elementary action quantum, since it forms a transition between the necessary dualistic concept of the nature of light and hence forms a transition to the concept of corpuscles as waves.

When light falls on a metal plate, electrons are emitted (Hertz,[1] Hallwachs,[2] and Lenard[3]). Their velocity does not depend on the intensity but on the color, in other words, the frequency of the incident light. By increasing the intensity of the light one only increases the number of emitted electrons. The connection between energy and frequency cannot be explained through the wavelike propagation of the light since, as a measure of energy of the wave train, it would assume the square of the amplitude and thus would not establish a connective relationship between energy and wavelength. However, if one assumes that light consists of corpuscles, that is, a stream of fine particles, namely photons, which have an impulse of $h\nu/c$, the energy content of the photon according to the quantum concept is the product $h\nu$, and one arrives at the Einstein[4] relationship (1905)

$$\tfrac{1}{2}mv^2 + P = h\nu. \tag{5}$$

The kinetic energy of the emitted electron, $\tfrac{1}{2}mv^2$, plus the work P which it must expend in order to leave the metal surface is equal to the energy content of the photon, $h\nu$. When photons collide with the metal, they give off their total energy content to the electrons and are destroyed in the

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[1] H. Hertz, *Ann. Physik* [3] **31**, 983 (1887).

[2] W. Hallwachs, *Ann. Physik* [3] **33**, 301 (1888).

[3] P. Lenard, *Wien. Ber.* **108**, 1649 (1898); *Ann. Physik* [4] **2**, 359 (1900); [4] **8**, 149 (1902); cf. J. J. Thomson, *Phil. Mag.* [5] **48**, 547 (1899).

[4] A. Einstein, *Ann. Physik* [4] **17**, 132 (1905); [4] **20**, 199 (1906).

process. Now, the above-mentioned connection between velocity of emitted electrons and the color of the incident light is established.

For each corpuscular photon which falls on the metal surface, one electron is liberated immediately. If one would like to explain the photoelectric electron emission by the incidence of a wave train, one would have to stipulate accumulation of energy in the case of low light intensity, until such a level is reached that a quantum has been accumulated. For example, in the case of x-rays, one would have to wait a century for the electron to leave the metal surface. Experience shows, however, that the electron is emitted for all wavelengths instantaneously.

The marked success of the assumption of the corpuscular nature of light in the case of the photoelectric effect has not solved the problem in general. There are, on the other hand, a group of phenomena, such as diffraction and interference, which can better be explained with the wave nature of light. Hence one has had to accept a compromise of corpuscular properties on the one side, and wavelike properties on the other, depending on the experimental method employed. Or, as one likes to express it nowadays, if one draws the utmost consequence, light has no nature *per se*, but only coupled with the instrumental techniques with which it interacts; it behaves either as a corpuscle or as a wave.

The Bohr Atomic Model.
Its Success and Shortcomings

In the atomic model of Rutherford[1a] (1911) the mass of the H atom is concentrated in a small positively charged space of 10^{-13} cm diameter and the negative electron moves around it in an orbit. The resulting centrifugal force is compensated by Coulomb attraction of the two particles. Such an atom is unstable. An accelerated charge radiates energy and hence the electron should continuously shorten its internuclear distance until it finally, after a very short period of time, falls into the nucleus. Other difficulties in the use of this model were also encountered. For example, there was no connection between the angular velocity of the radiating electron and the spectral lines of the atoms.

Bohr[1b] introduced into the atomic model of Rutherford the elementary action quantum h (1913), in postulating that the action $qd\varphi$ of the angular momentum $q = m[r \cdot v]$ of a rotating electron in a closed circular orbital must be a multiple integer of h as expressed by:

$$\int_0^{2\pi} qd\varphi = nh. \tag{6}$$

If an electron moves in such orbitals where n may be integers of 1, 2, 3, etc., it would not emit energy. Therefore radius and velocity remain constant in time. These stationary states were considered "permitted" in contrast to the in-between states which were considered "forbidden." Instability was then associated with the "forbidden" in-between states.

If one connects the equation which equates centrifugal force and Coulomb attraction between nucleus and electron

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[1a] E. Rutherford, *Phil. Mag.* [6] 21, 669 (1911).
[1b] N. Bohr, *Phil. Mag.* [6] 26, (1913).

$$\frac{e^2}{r^2} = \frac{mv^2}{r} \tag{7}$$

with Eq. (6), one arrives, as a sequel of the quantization of action, at the quantization of the radii of the orbitals:

$$r_n = \frac{1}{m}\left(\frac{nh}{2\pi e}\right)^2. \tag{8}$$

Here m stands for the mass and e for the charge of the electron. The various discrete radii represent the distances of the electron from the nucleus for the various quantum numbers n. They increase with the square of these integers. The above-mentioned relationship between mechanical rotatory frequency of the electron and the frequency of the emitted light does not exist here either, since the electron is not permitted to radiate in the stationary orbital. Bohr postulated that the difference in the energies of two stationary states would be emitted or absorbed, i.e.,

$$E_{n=2} - E_{n=1} = h\nu = 2m\left(\frac{\pi \cdot e^2}{h}\right)^2 \cdot \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right). \tag{9}$$

This equation was the greatest success of the Bohr atom model because it agreed excellently with experience. In this manner the empirical relationships of the Balmer series of the hydrogen spectrum can be written (9a), where ν is the emitted frequency,

$$\nu = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right). \tag{9a}$$

They are interpreted as an electron jump from an orbital with $n = 2$ to orbitals with $n = 3, 4, 5$, etc. Analogously, the other series spectra of Lyman with a transition from $n = 1$ to $n = 2, 3, 4$, etc., and of Paschen with $n = 3$ to $n = 4, 5, 6$, etc., could be derived. The constant R, the Rydberg constant, which had been determined previously empirically, could be related to mass and charge of the electron and to the elementary action quantum. This numerical coincidence left nothing to be desired, particularly since Sommerfeld[1c] later (1916) took into consideration the relativistic mass changes of the electron in noncircular, i.e., elliptical, orbitals and the motion of the

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[1c] Cf. A. Sommerfeld, "Atombau und Spektrallinien," 5th ed., p. 699. Vieweg, Braunschweig, 1916.

nucleus. One should note the difference between the quantum theoretical and the classical concept of the mechanism of light emission. According to the latter, the atom contains oscillators which may assume arbitrary energy states and whose mechanical frequency is emitted as light frequency. According to the quantum concept of Bohr which uses a special atom model, only certain discrete states are permitted, the energy of the emitted light being the energy difference between two such permitted states. This strong contrast is modified in a certain way by the Bohr correspondence principle to which only passing reference can be made here.[1c]

For the fundamental assumption of Bohr, that on certain closed orbitals the electron does not emit energy in spite of its acceleration, a physical justification was lacking. This was an *ad hoc* hypothesis, which was only accepted because of its success in explaining the hydrogen spectrum. Difficulties first arose in the case of the spectrum of helium. It proved impossible to calculate the ionization energy of helium based on a model fashioned after the Bohr H model. However, the value calculated with wave mechanical methods of $198,310.67$ cm^{-1} is in excellent agreement with the experimental value of $198,310.82$ cm^{-1} [2] It soon became apparent that for certain phenomena, such as the pure rotational spectrum of certain hydrogen halides, not whole numbers but half-quantum numbers had to be introduced $(1/2, 3/2, 5/2)$ if correspondence with experience was to be maintained. While the Bohr theory was successful in the calculation of the frequency of spectral lines, it ran into difficulties in the calculation of intensities of these lines. The reasons for its failure are deeper than had been first suspected, in believing that one only dealt with mathematical difficulties in a multiple-body problem. Heisenberg demonstrated in 1925 that any atomic model irrespective of its special design was a much too detailed representation of reality and that no direct or even indirect access to such models had any meaning. They were *de facto* macroscopic pictures which had been extended to atomic dimensions without justification. This then resulted in the uncertainty principle of Heisenberg, a fundamental building block in the modern concept of quantum mechanics.[3]

Heisenberg, who restricted himself to directly observable quantities such as frequencies and intensities of spectral lines, arrived at a new system of quantum mechanics which, owing to its use of matrices, became known as matrix mechanics.

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[2] E. A. Hylleraas and J. Midtdal, *Phys. Rev.* **103**, 829 (1956); C. L. Pekeris, *ibid.* **112**, 1649 (1958).

[3] W. Heisenberg, *Z. Physik* **43**, 172 (1927).